Direct Iodination of Electron-Deficient Benzothiazoles: Rapid Access to Two-Photon Absorbing Fluorophores with Quadrupolar D-π-A-π-D Architecture and Tunable Heteroaromatic Core

*Jela Nociarová,[a] Patrik Osuský,[a] Erik Rakovský,[a] Dimitris Georgiou,[b] Ioannis Polyzos,[b] Mihalis Fakis,[b] Peter Hrobárik [a,c]**

[a] Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University, Ilkovičova 6, SK-84215 Bratislava, Slovakia

[b] Department of Physics, University of Patras, GR-26504 Patras, Greece

[c] Laboratory for Advanced Materials, Comenius University Science Park, Ilkovičova 8, SK-84215 Bratislava, Slovakia

peter.hrobarik@uniba.sk

Supporting Information

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1 General Experimental Details

All chemicals were used as received from commercial suppliers without purification (benzothiazole, 2-chlorobenzothiazole, benzothiazol-2(3*H*)-one, trimethylsilyl acetylene, aniline, $Pd(PPh_3)_2Cl_2$, $Pd(PPh_3)_4$, and CuI were purchased from TCI Chemicals, *N*-iodosuccinimide, 4-bromotriphenylamine and 4-iodoanisole from Fluorochem Ltd., 2-methylbenzothiazole, I_2, ICl, $POCl_3$ and all organic solvents from Acros Organics). Solvents for Pd-catalysed cross-coupling reactions were purified prior to the synthesis: tetrahydrofuran was distilled from Na/benzophenone, triethylamine from CaH_2.

NMR spectra were recorded with Varian NMR System^{TM} 300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) and Varian NMR System 600 (600 MHz for ^{1}H and 151 MHz for ^{13}C) instruments. Chemical shifts (δ) are given relative to tetramethylsilane, samples were prepared in $CDCl_3$ (^{1}H δ 7.26, ^{13}C δ 77.0 ppm) and DMSO-*d*$_6$ (^{1}H δ 2.50, ^{13}C δ 39.5 ppm).

UV-vis spectra were measured on Hewlett Packard 8452A Diode Array spectrophotometer and fluorescence spectra were measured on Shimadzu RF 6000 Spectrofluorophotometer.

IR spectra were measured on Agilent Technologies Cary 630 FTIR. Melting points were measured on Büchi Melting Point M-565.

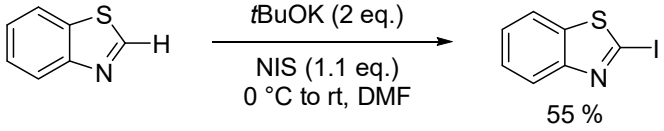
High-resolution mass spectrometry (HRMS) was performed on Thermo Scientifc Orbitrap Fusion Tribrid® mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) equipped with Dionex Ultimate 3000RS HPLC pump and Dionex Ultimate 3000RS autosampler.

Column chromatography was performed with Merck Silica Gel 60 (0.040−0.063 mm) and Merck Alumina 90 (neutral), respectively. Thin layer chromatography (TLC) was performed with Merck plates (Silica Gel 60, F-254). Compounds were detected at 254 nm and 365 nm, respectively.

2 Synthesis of Iodinated Benzothiazoles

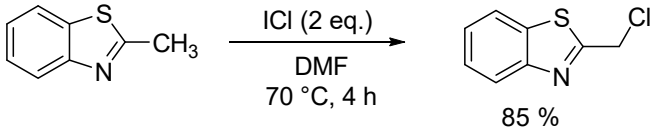
General safety warning: The reaction of potassium permanganate with concd. sulfuric acid is strongly exothermic and generates highly reactive Mn_2O_7, as a dark green oil, besides other unstable manganese(VII) species.[1,2] Using reported amounts of H_2SO_4 and finely grinded $KMnO_4$ allows to avoid potentially dangerous "sparkling flashes" during the preparation of the iodination mixture. Do not reduce the reported amounts of H_2SO_4 with respect to $KMnO_4$, otherwise very viscous mixture, difficulties with stirring and more vigorous reaction can occur.

2.1 Synthesis of 2-iodobenzothiazole from benzothiazole



Benzothiazole (4.00 g, 29.6 mmol) was dissolved in DMF (50 mL). Subsequently, *N*-iodosuccinimide (7.32 g, 32.5 mmol) was added, the flask was closed with a stopper and the reaction mixture was cooled to –10 °C in an ice-salt bath. Potassium *tert*-butoxide (6.64 g, 59.2 mmol) was added at –10 °C in small portions and the reaction mixture was stirred at rt overnight. After pouring to water (450 mL), the product was isolated by filtration to obtain 2-iodobenzothiazole as a white solid (4.25 g, 55 %). $\boldsymbol{R_f}$ 0.66 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 78 - 79 °C (lit.[3] mp 77 – 78 °C); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 154.3 139.2, 126.4, 125.6, 122.6, 120.4, 105.6.

2.2 Attempt for iodination of 2-methylbenzothiazole with ICl – an efficient synthesis of 2-(chloromethyl)benzothiazole

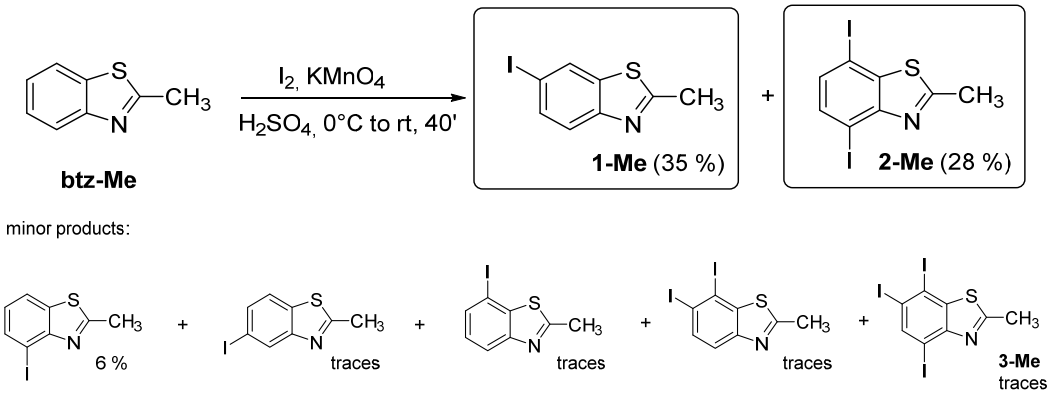


2-Methylbenzothiazole (1.00 g, 6.70 mmol) and iodine monochloride (2.18 g, 13.40 mmol) were dissolved in DMF (10 mL) and the reaction mixture was heated to 70 °C for 4 h in an oil bath. After cooling to rt, the mixture was poured to 5 % aqueous solution of $Na_2S_2O_5$ (50 mL) and extracted by ethylacetate (5×25 mL). Combined organic layers were washed with 5 % aqueous solution of $Na_2S_2O_5$, water and brine and dried over Na_2SO_4. The crude product was purified by column chromatography (eluent: hexanes/EtOAc = 10/1) to obtain 2-(chloromethyl)benzothiazole as an yellow oil (1.08 g, 85 %). $\boldsymbol{R_f}$ 0.45 (SiO_2, hexanes/EtOAc = 6:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.51

(t, J = 7.7 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 4.95 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.8, 152.8, 135.8, 126.4, 125.7, 123.4, 121.8, 42.0. **HRMS** calcd for C_8H_7ClNS $[M+H]^+$, 183.9988; found, 183.9986. Both ^{1}H and ^{13}C NMR shifts match those reported previously for 2-(chloromethyl)benzothiazole in ref. 4.

2.3 Iodination of 2-methylbenzothiazole

2.3.1 One-pot synthesis of 6-iodo-2-methylbenzothiazole (1-Me) and 4,7-diiodo-2-methylbenzothiazole (2-Me) using I_2/$KMnO_4$



Finely grinded iodine (5.53 g, 21.8 mmol) was added into vigorously stirred concentrated sulfuric acid (75 mL) at 0 °C. Subsequently, finely grinded potassium permanganate (2.70 g, 17.1 mmol) was added portionwise over 5 min and the mixture was stirred for 5 min at 0 °C and 30 min at rt to obtain a homogenous dark-brown solution. The iodination mixture was transferred into a dropping funnel and added dropwise over 30 min to the solution of 2-methylbenzothiazole (5.00 g, 33.5 mmol), dissolved in concentrated sulfuric acid (35 mL) cooled in an ice bath. The dark-brown reaction mixture was stirred at rt for additional 40 min, then poured onto 300 g of ice and left standing for 30 min. The precipitated solid ("acidic fraction") containing mainly 4,7-diiodo-2-methylbenzothiazole (**2-Me**) was filtered off and the crude product (2.42 g, 28 %)[†] containing up to 5 % of 4,6,7-triiodo-2-methylbenzothiazole was obtained. The crude **2-Me** may be used in further reactions as obtained or purified by column chromatography using dioxane/hexanes (5:95). $\boldsymbol{R_f}$ 0.63 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 159 – 161 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.58 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 2.86 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.1, 151.9, 142.4, 136.6, 134.9, 89.3, 83.4, 20.5; **FTIR** (ATR): 2919 (w), 1517 (m), 1325 (m), 1291 (m), 1165 (m), 1078 (s), 890 (s), 794 (s), 736 (m), 647 (m), 518 (m) cm^{-1}. **HRMS** calcd for $C_8H_6I_2NS$ $[M+H]^+$, 401.8305; found, 401.8310.

[†] Yield was calculated considering I_2 as a stoichiometry limiting reactant.

6-Iodo-2-methylbenzothiazole (1-Me)[5] was isolated from the filtrate (obtained after isolation of 4,7-diiodo-2-methylbenzothiazole, **2-Me**) by its neutralization with 10 % aqueous NaOH solution. The precipitate obtained after neutralization was filtered off, suspended in chloroform (100 mL) and insoluble solid residue was removed. The organic ($CHCl_3$) layer was transferred into separatory funnel and washed with 5 % aqueous solution of $Na_2S_2O_5$ (25 mL), saturated $NaHCO_3$ solution (25 mL) and brine, then dried over Na_2SO_4 and concentrated in vacuo. 6-Iodo-2-methylbenzothiazole (**1-Me**) was isolated from the crude mixture as a white solid by column chromatography using hexanes/EtOAc 6/1 (3.22 g, 35 %) or by crystallisation from cyclohexane (approx. 40 mL) (2.82 g, 30 %). $\boldsymbol{R_f}$ 0.43 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 140 - 141 °C (lit.[5] mp 140 – 142 °C); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 1.4 Hz, 1H), 7.72 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 2.82 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.5, 152.8, 137.8, 135.0, 129.9, 123.9, 88.9, 20.0.

Characterization of minor byproducts:

4-Iodo-2-methylbenzothiazole was isolated from the "neutral fraction" by column chromatography using hexanes/EtOAc 6/1 as a white solid (590 mg, 6 %). $\boldsymbol{R_f}$ 0.60 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 45-47 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.07 – 7.04 (m, 1H), 2.87 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.1, 154.2, 135.7, 134.5, 126.0, 121.4, 89.3, 20.2; **FTIR** (ATR): 3049 (w), 1518 (m), 1392 (s), 1366 (m), 1304 (m), 1250 (m), 1210 (m), 1154 (s), 1077 (s), 989 (m), 858 (s), 752 (s), 732 (s) cm^{-1}; **HRMS** calcd for C_8H_7INS $[M+H]^+$, 275.9338; found, 275.9335.

5-Iodo-2-methylbenzothiazole was isolated in trace amounts from the "neutral fraction" by column chromatography using hexanes/EtOAc = 6/1 as the eluent. $\boldsymbol{R_f}$ 0.53 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 79 – 82 °C (lit.[6] mp. 84-85 °C); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.30 (d, *J* = 1.5 Hz, 1H), 7.63 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 2.83 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.2, 154.8, 135.2, 133.3, 131.4, 122.7, 90.1, 20.1; **FTIR** (ATR): 3039 (w), 2920 (w), 1509 (m), 1433 (m), 1399 (m), 1378 (m), 1292 (m), 1167 (s), 1148 (s), 1065 (s), 1043 (m), 992 (m), 901 (m), 881 (s), 792 (s) cm^{-1}; **HRMS** calcd for C_8H_7INS $[M+H]^+$, 275.9338; found, 275.9336.

7-Iodo-2-methylbenzothiazole was identified in the mother liquor after crystallization of 6-iodo-2-methylbenzothiazole in trace amounts (together with unreacted 2-methyl-benzothiazole and 6,7-diiodo-2-methylbenzothiazole). Due to similar R_f values, this compound was not isolated in pure form from the crude mixture. The efficient procedure for preparation

of pure 7-iodo-2-methylbenzothiazole along with its detailed spectroscopic characterization is reported in Section 2.3.2. R_f 0.43 (SiO_2, hexanes/EtOAc = 6:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.17 (t, *J* = 7.9 Hz, 1H), 2.82 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.9, 151.2, 143.6, 133.9, 127.3, 122.0, 83.5, 20.3.

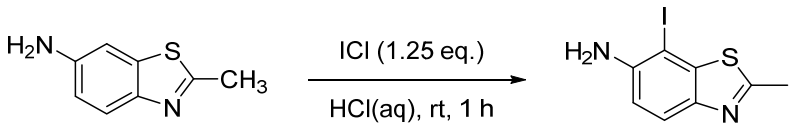
6,7-Diiodo-2-methylbenzothiazole was isolated from the "neutral fraction" by column chromatography using hexanes/EtOAc 6/1 in trace amounts. R_f 0.43 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 180 – 183 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 2.79 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.4, 149.5, 145.6, 136.1, 123.1, 103.5, 97.3, 20.1; **FTIR** (ATR): 2918 (w), 2836 (w), 1568 (m), 1509 (m), 1401 (s), 1358 (s), 1262 (s), 1173 (m), 1063 (m), 897 (m), 809 (s), 755 (m) cm^{-1}; **HRMS** calcd for $C_8H_6I_2NS$ $[M+H]^+$, 401.8305; found, 401.8305.

4,6,7-Triiodo-2-methylbenzothiazole (3-Me) was isolated from the "acidic fraction" by column chromatography in dioxane/hexane (5/95) in trace amounts. R_f 0.64 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 208-210 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.29 (s, 1H), 2.82 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.4, 150.7, 143.9, 143.8, 104.0, 97.3, 89.9, 20.3; **FTIR** (ATR): 3063 (w), 1498 (m), 1387 (m), 1302 (m), 1260 (m), 1170 (s), 1134 (m), 1084 (s), 894 (s), 863 (s), 731 (m), 701 (m) cm^{-1}; **HRMS** calcd for $C_8H_5I_3NS$ $[M+H]^+$, 527.7271; found, 527.7277.

2.3.2 Efficient synthesis of 7-iodo-2-methylbenzothiazole

7-Iodo-2-methylbenzothiazole can be obtained efficiently by hydrodeamination of 7-iodo-2-methylbenzothiazol-6-amine,[7] the latter being prepared by direct iodination of 2-methyl-benzothiazol-6-amine with ICl.[8] 2-Methylbenzothiazol-6-amine was prepared by nitration of 2-methylbenzothiazole and subsequent reduction, as reported in ref. 5.

Iodination of 2-methylbenzothiazol-6-amine

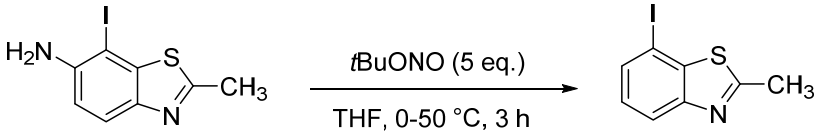


63 %

Iodine monochloride (3.71 g, 22.8 mmol) was dissolved in diluted HCl (4.5 mL of concentrated HCl and 15 mL of water) and the resulting mixture was added to the solution of 2-methylbenzothiazol-6-amine (3.00 g, 18.3 mmol) in diluted HCl (2.25 mL of concd. HCl and 30 mL of water). The reaction mixture was stirred at rt for 1 h and subsequently neutralized

with saturated $NaHCO_3$ solution. The solid was filtered off and washed thoroughly with 5 % aqueous solution of $Na_2S_2O_5$ and water. The product was obtained after flash chromatography (eluent: hexanes/EtOAc = 4/1) as a white solid (3.34 g, 63 %). $\boldsymbol{R_f}$ 0.08 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 118 - 120 °C (lit.[8] mp 119 – 121 °C); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.6 Hz, 1H), 6.83 (d, *J* = 8.6 Hz, 1H), 4.12 (s, 2H), 2.74 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.6, 144.9, 144.8, 143.7, 122.7, 113.8, 71.1, 19.9.

Hydrodeamination of 7-iodo-2-methylbenzothiazol-6-amine

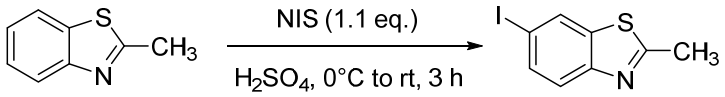


75 %

A solution of 7-iodo-2-methylbenzothiazol-6-amine (0.38 g, 1.16 mmol) in THF (15 ml) under argon atmosphere, placed in a two-neck flask equipped with a condenser and septum, was cooled to 0 °C. *Tert*-butyl nitrite (0.7 mL, 5.80 mmol) was added dropwise at 0 °C and the reaction mixture was subsequently stirred 30 min at rt and 3 h at 50 °C in an oil bath. After cooling to rt, the mixture was diluted with water and extracted with ethyl-acetate (3x 40 ml). The combined organic fractions were washed with water, brine and dried over Na_2SO_4. The crude product was purified by column chromatography (eluent: hexanes/EtOAc = 8/1) to obtain 7-iodo-2-methylbenzothiazole as a white solid (0.24 g, 75 %). $\boldsymbol{R_f}$ 0.43 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 113 – 115 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.17 (t, *J* = 7.9 Hz, 1H), 2.82 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.9, 151.2, 143.6, 133.9, 127.3, 122.0, 83.5, 20.3. **FTIR** (ATR) 2919 (w), 1515 (m), 1385 (m), 1176 (m), 1040 (m), 774 (s), 716 (m) cm^{-1}; **HRMS** calcd for C_8H_7INS $[M+H]^+$, 275.9338; found, 275.9334.

2.3.3 Direct iodination of 2-methylbenzothiazole with NIS/H_2SO_4

Although **1-Me** can be prepared by direct iodination of 2-methylbenzothiazole using I_2/$KMnO_4$/H_2SO_4 (section 2.3.1), the following procedure using *N*-iodosuccinimide (NIS)/H_2SO_4 provides somewhat higher yield (43 % vs. 35 %):



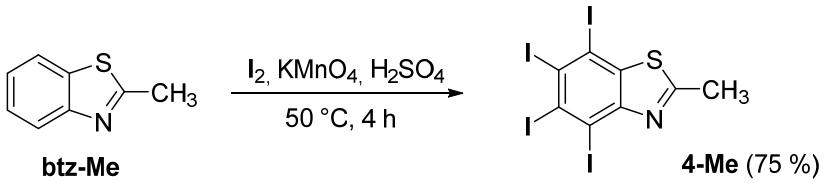
btz-Me **1-Me** (43 %)

2-methylbenzothiazole (5.00 g, 33.5 mmol) was dissolved in the mixture prepared from concentrated sulfuric acid (100 mL) and water (5 mL) cooled in an ice-bath. *N*-iodosuccinimide (8.29 g, 37 mmol) was added portionwise over 3 min at 0 °C. The dark-brown reaction mixture was stirred at rt for 3 h, then poured onto ice (250 g) and left standing for 30 min. The solid (containing mainly diiodo- and triiodo-derivatives of 2-methylbenzothiazole) was filtered off and the filtrate was neutralized with 10 % aqueous NaOH solution. The precipitate was isolated by filtration, dissolved in chloroform (100 mL) and washed with 5 % aqueous solution of $Na_2S_2O_5$ (25 mL), saturated $NaHCO_3$ solution (25 mL) and brine, dried over Na_2SO_4 and concentrated in vacuo. Recrystallisation from cyclohexane (40 mL) yielded 6-iodo-2-methylbenzothiazole (**1-Me**) as a white solid (3.97 g, 43 %).

2.3.4 4,5,6,7-Tetraiodo-2-methylbenzothiazole (4-Me)

2-Methylbenzothiazole was periodinated using $I_2/KMnO_4/H_2SO_4$ (**Method A**), $I_2/H_5IO_6/H_2SO_4$ (**Method B**) and NIS/H_2SO_4 (**Method C**). No further purification of the crude product is required when using **Method A**. In other cases, minor quantities of intermediate (4,6,7-triiodo-2-methylbenzothiazole) may be removed by crystallization from dioxane.

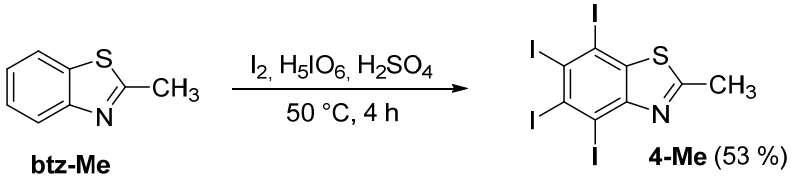
Method A: Periodination with $I_2/KMnO_4$ in H_2SO_4



btz-Me **4-Me** (75 %)

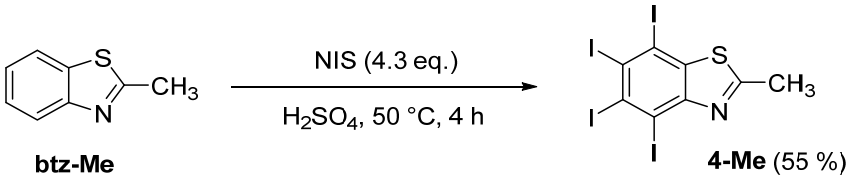
Finely grinded iodine (3.75 g, 14.7 mmol) was added into vigorously stirred concentrated sulfuric acid (50 mL) at 0 °C. Subsequently, finely grinded potassium permanganate (1.82 g, 11.5 mmol) was added portionwise over 5 min and the mixture was stirred for 5 min at 0 °C and 30 min at rt to obtain a homogenous dark-brown solution. The iodination mixture was then slowly poured into an ice-bath cooled solution of 2-methylbenzothiazole (1.00 g, 6.7 mmol) in concentrated sulfuric acid (10 mL). The dark-brown reaction mixture was subsequently heated to 50 °C for 4 h in an oil bath, then poured onto ice and left standing for 30 min. The solid was filtered off and washed with water, 5 % aqueous solution of $Na_2S_2O_5$, saturated $NaHCO_3$ and deionized water. After drying *in vacuo* the product was obtained as a yellow solid (3.28 g, 75 %). R_f 0.53 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 243-245 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 2.72 (s, 3H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 167.3, 151.7, 141.9, 119.9, 118.1, 105.0, 98.9, 20.3; **FTIR** (ATR): 1502 (m), 1420 (m), 1324 (m), 1299 (s), 1161 (s), 1077 (s), 902 (m), 665 (s) cm^{-1}; **HRMS** calcd for $C_8H_4I_4NS$ $[M+H]^+$, 653.6238; found, 653.6232.

Method B: Periodination with I_2/H_5IO_6 in H_2SO_4



Finely grinded iodine (3.75 g, 14.7 mmol) was added to vigorously stirred concentrated sulfuric acid (50 mL) at 0 °C. Subsequently, periodic acid (0. g, 11.5 mmol) was added portionwise over 5 min and the mixture was stirred for 30 min at rt to obtain a homogenous dark-brown solution. The iodination mixture was slowly poured into an ice-bath cooled solution of 2-methylbenzothiazole (1.00 g, 6.7 mmol) in concentrated sulfuric acid (10 mL). The dark-brown reaction mixture was subsequently heated to 50 °C for 4 h in an oil bath, then poured onto ice and left standing for 30 min. The solid was filtered off and washed with water, 5 % aqueous solution of $Na_2S_2O_5$, saturated $NaHCO_3$ and deionized water. The crude product was recrystallized using dioxane (60 mL) to obtain the product as a yellow crystalline solid (2.31 g, 53 %).

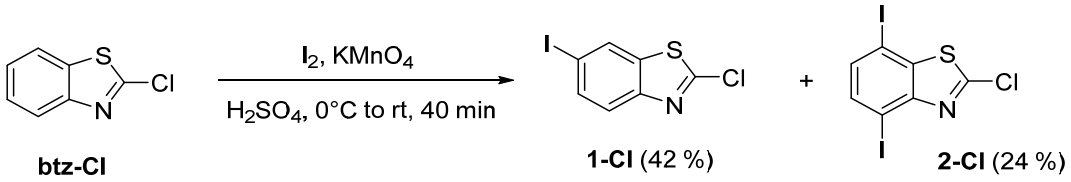
Method C: Periodination with *N*-iodosuccinimide in H_2SO_4



N-iodosuccinimide (3.32 g, 14.7 mmol) was added portionwise to the stirred solution of 2-methylbenzothiazole (0.50 g, 3.4 mmol) in the mixture of concentrated sulfuric acid (40 mL) and water (2 mL) cooled in an ice bath. The dark-brown reaction mixture was subsequently heated to 50 °C for 4 h in an oil bath, then poured onto ice and left standing for 30 min. The solid was filtered off and washed with water, 5 % aqueous solution of $Na_2S_2O_5$, saturated $NaHCO_3$ and deionized water. The crude product was recrystallized using dioxane (30 mL) to obtain the product as a yellow crystalline solid (1.21 g, 55 %).

2.4 Iodination of 2-chlorobenzothiazole with $I_2/KMnO_4$

2.4.1 One-pot synthesis of 2-chloro-6-iodobenzothiazole (1-Cl) and 2-chloro-4,7-diiodobenzothiazole (2-Cl) using $I_2/KMnO_4$



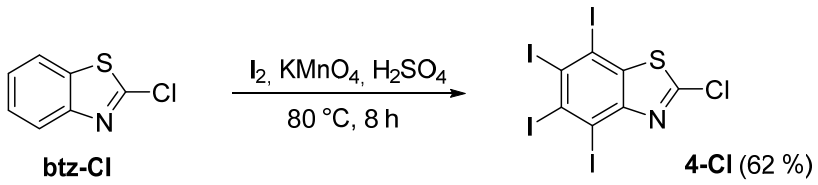
Finely grinded iodine (9.73 g, 38.3 mmol) was added into vigorously stirred concentrated sulfuric acid (100 mL) at 0 °C. Subsequently, finely grinded potassium permanganate (4.75 g, 30.1 mmol) was added portionwise over 10 min and the mixture was stirred for 5 min at 0 °C and then 30 min at rt to obtain a homogenous dark-brown solution. The iodination mixture was transferred into a dropping funnel and added dropwise over 30 min into an ice-bath cooled solution of 2-chlorobenzothiazole (10.00 g, 59.0 mmol) in concentrated sulfuric acid (50 mL). The dark-brown reaction mixture was stirred at rt for additional 40 min, then poured onto ice (65 g) and the resulting mixture was cooled in the ice bath. To the stirred mixture, 35 mL of water was added dropwise and the mixture was left standing at rt for 30 min. The precipitated solid ("acidic fraction"), containing mainly 2-chloro-4,7-diiodobenzothiazole (**2-Cl**), was filtered off through the glass frit S3 (without any washing), suspended in water and extracted to chloroform (150 mL). Organic layer was washed with 5 % aqueous solution of $Na_2S_2O_5$ (25 mL), saturated $NaHCO_3$ solution (25 mL) and brine, dried over Na_2SO_4 and concentrated in vacuo. The crude product (3.87 g, 24 %)[†] containing traces of 2-chloro-6-iodobenzothiazole may be used in further reactions as obtained or purified by crystallization from dioxane/hexanes mixture (8 mL/40 mL) to afford **2-Cl** as a white solid (crystallization of the product is facilitated by scraping the walls of the beaker with a glass rod). R_f 0.73 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 134 – 135 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.64 (d, J = 8.1 Hz, 1H), 7.40 (d, J = 8.1 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.0, 150.3, 142.9, 137.5, 135.7, 89.4, 82.6; **FTIR** (ATR): 3076 (w), 1467 (s), 1438 (m), 1318 (s), 1290 (m), 1025 (s), 813 (s), 777 (m) cm^{-1}; **HRMS** calcd for $C_7H_3ClI_2NS$ $[M+H]^+$, 421.7759; found, 421.7766.

2-Chloro-6-iodobenzothiazole (**1-Cl)** may be isolated from the filtrate obtained after isolation of 2-chloro-4,7-diiodobenzothiazole (**2-Cl**): the filtrate was diluted with ice to 800 mL and left standing for 30 min. The precipitate was collected by filtration and dried in vacuo to obtain

[†] Yield was calculated considering I_2 as a stoichiometry limiting reactant.

14.07 g of the crude product ("neutral fraction"), which was recrystallized from cyclohexane (100 mL per 10 g of the crude product) to obtain 7.31 g of 2-chloro-6-iodobenzothiazole (42 %). $\boldsymbol{R_f}$ 0.71 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 134 – 136 °C (lit.[5] mp 135 – 137 °C); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 1.4 Hz, 1H), 7.77 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.8, 150.3, 137.9, 135.9, 129.5, 124.3, 90.1; **HRMS** calcd for C_7H_4ClINS $[M+H]^+$, 295.8792; found, 295.8790.

2.4.2 2-Chloro-4,5,6,7-tetraiodobenzothiazole (4-Cl) using I_2/$KMnO_4$

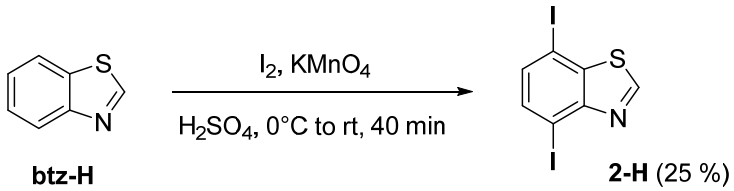


btz-Cl **4-Cl** (62 %)

Finely grinded iodine (2.25 g, 8.8 mmol) was added into vigorously stirred concentrated sulfuric acid (50 mL) at 0 °C. Subsequently, finely grinded potassium permanganate (1.12 g, 7.1 mmol) was added portionwise over 5 min and the mixture was stirred for 5 min at 0 °C and 30 min at rt to obtain a homogenous dark-brown solution. The iodination mixture was then slowly poured into an ice-bath cooled solution of 2-chlorobenzothiazole (0.50 g, 2.9 mmol) in concentrated sulfuric acid (10 mL). The dark-brown reaction mixture was subsequently heated to 80 °C for 8 hours (in an oil bath), then poured onto ice and left standing for 30 min. The solid was filtered off and washed with water, 5 % aqueous solution of $Na_2S_2O_5$, saturated $NaHCO_3$ and deionized water. After recrystallisation from dioxane (30 ml) the product was obtained as a yellowish solid (1.22 g, 62 %). $\boldsymbol{R_f}$ 0.63 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 231-234 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) - no signals due to absence of hydrogen atoms in **4-Cl**; **^{13}C NMR** (151 MHz, DMSO-d_6) δ 152.2, 149.7, 141.9, 121.5, 120.0, 105.5, 98.7; **FTIR** (ATR): 2852 (m), 1464 (m), 1292 (m), 1254 (m), 1116 (m), 1019 (m), 865 (s), 614 (m) cm^{-1}; **HRMS** calcd for C_7HClI_4NS $[M+H]^+$, 673.5691; found, 673.5694.

2.5 Iodination of benzothiazole with I_2/$KMnO_4$

2.5.1 One-pot synthesis of 4,7-diiodobenzothiazole (2-H) using I_2/$KMnO_4$



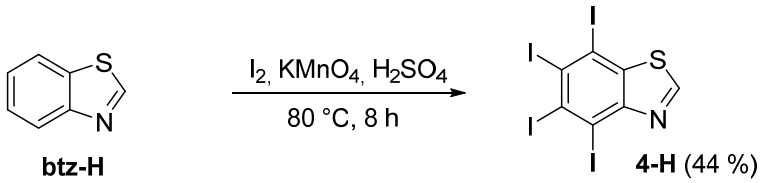
btz-H **2-H** (25 %)

Finely grinded iodine (6.10 g, 24.0 mmol) was added into vigorously stirred concentrated sulfuric acid (75 mL) at 0 °C. Subsequently, finely grinded potassium permanganate (2.98 g, 18.9 mmol) was added portionwise over 5 min and the mixture was stirred for 5 min at 0 °C and then 30 min at rt to obtain a homogenous dark-brown solution. The iodination mixture was transferred into a dropping funnel and added dropwise over 30 min into an ice-bath cooled solution of benzothiazole (5.00 g, 37.0 mmol) in concentrated sulfuric acid (35 mL). The dark-brown reaction mixture was stirred at rt for additional 40 min, then poured onto ice (300 g) and left standing for 30 min. The solid "acidic fraction", containing mainly 4,7-diiodo-benzothiazole (**2-H**), was filtered off. The crude product (2.33 g, 25 %)[†] may be used in further reactions as obtained or purified by column chromatography using dioxane/hexane (5/95) as the eluent to yield **2-H** as a white solid. The purification can be alternatively performed by crystallization from dioxane/hexanes mixture (10 mL/40 mL). $\boldsymbol{R_f}$ 0.51 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 144 – 146 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.17 (s, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.6, 151.9, 141.1, 137.0, 135.9, 90.9; 84.0; **FTIR** (ATR): 3025 (w), 1457 (w), 1437 (m), 1320 (m), 1291 (w), 1099 (m), 1070 (s), 897 (s), 833 (s), 803 (s), 771 (m) cm^{-1}; **HRMS** calcd for $C_7H_4I_2NS$ $[M+H]^+$, 387.8148; found, 387.8151.

On the contrary to iodinations of **btz-Me** and **btz-Cl**, work-up of the filtrate by neutralization with aqueous NaOH and extraction with chloroform, followed by washing the combined organic layers with $Na_2S_2O_5$ solution, water and brine, drying over sodium sulphate and concentration in vacuo led to complex mixture of unreacted benzothiazole, 6-iodobenzothiazole and other monoiodinated benzothiazole species, which was difficult to separate. Therefore we developed alternative, simple and highly efficient procedures for multigram synthesis of 6-iodobenzothiazole from 6-iodobenzothiazol-2(3*H*)-one and 2-chloro-6-iodobenzothiazole, respectively (see Section 2.6 below).

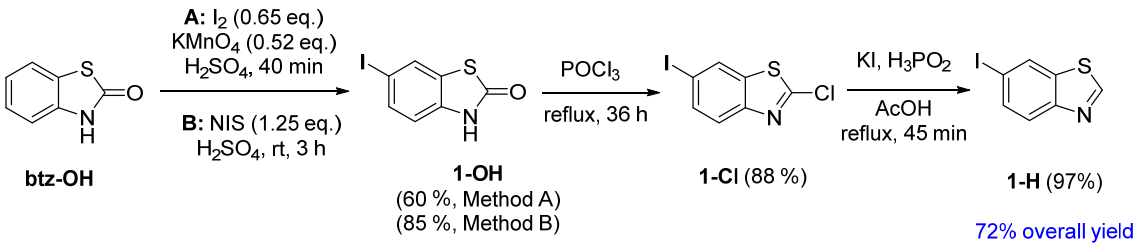
[†] Yield was calculated considering I_2 as a stoichiometry limiting reactant.

2.5.2 4,5,6,7-Tetraiodobenzothiazole (4-H) using $I_2/KMnO_4$



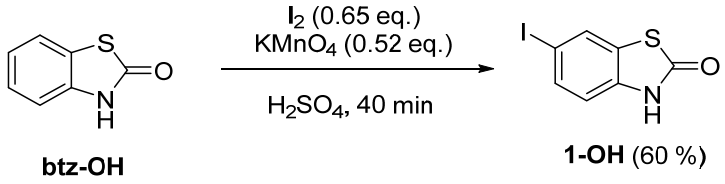
Finely grinded iodine (2.82 g, 11.1 mmol) was added into vigorously stirred concentrated sulfuric acid (50 mL) at 0 °C. Subsequently, finely grinded potassium permanganate (1.40 g, 8.9 mmol) was added portionwise over 5 min and the mixture was stirred for 5 min at 0 °C and 30 min at rt to obtain a homogenous dark-brown solution. The iodination mixture was then slowly poured into an ice-bath cooled solution of benzothiazole (0.50 g, 3.7 mmol) in concentrated sulfuric acid (10 mL). The dark-brown reaction mixture was subsequently heated to 80 °C for 8 h (in an oil bath), then poured onto ice and left standing for 30 min. The solid was filtered off and washed with water, 5 % aqueous solution of $Na_2S_2O_5$, saturated $NaHCO_3$ and deionized water. After recrystallisation from dioxane (40 ml) the product was obtained as a yellowish solid (1.05 g, 44 %). $\boldsymbol{R_f}$ 0.34 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 281-284 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 9.46 (s, 1H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 156.2, 152.0, 141.1, 120.3, 119.6, 106.7, 99.7; **FTIR** (ATR): 3058 (w), 1447 (m), 1328 (m), 1296 (s), 1268 (m), 1229 (m), 1069 (m), 905 (m), 836 (s), 787 (m) cm^{-1}; **HRMS** calcd for $C_7H_2I_4NS$ $[M+H]^+$, 639.6081; found, 639.6079.

2.6 Synthesis of 6-iodobenzothiazole (1-H) from benzothiazol-2(3*H*)-one



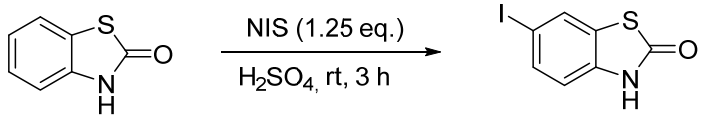
2.6.1 6-Iodobenzothiazol-2(3*H*)-one (1-OH) from benzothiazol-2(3*H*)-one

Method A: Iodination using $I_2/KMnO_4$



Finely grinded iodine (10.92 g, 43 mmol) was added into vigorously stirred concentrated sulfuric acid (100 mL) at 0 °C. Subsequently, finely grinded potassium permanganate (5.33g, 34 mmol) was added portionwise over 10 min and the mixture was stirred for 5 min at 0 °C and 30 min at rt to obtain a homogenous dark-brown solution. The iodination mixture was transferred into a dropping funnel and added dropwise over 30 min to the solution of benzothiazol-2(*3H*)-one (10.0 g, 66 mmol), dissolved in concentrated sulfuric acid (50 mL) at 0 °C. The dark-brown reaction mixture was stirred at rt for additional 40 min and then poured onto 600 g of ice. The precipitated solid was filtered off, washed with water, 5 % aqueous solution of $Na_2S_2O_5$ and dried in vacuo to obtain the desired product (10.95 g; 60 %) as a brownish solid. R_f 0.13 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 222 – 223 °C (lit.[9] mp 225 – 226 °C); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.18 (s, 1H), 7.71 (d, *J* = 1.2 Hz, 1H), 7.58 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.1, 135.3, 134.4, 130.8, 126.1, 113.0, 85.3. **FTIR** (ATR): 3133 (w) 3004 (m), 2877 (m), 1665 (s), 1459 (m), 1211 (m), 808 (m), 711 (m), 644 (m) cm^{-1}; **HRMS** calcd for C_7H_3INOS $[M-H]^-$ (negative ion mode), 275.8986; found, 275.8984.

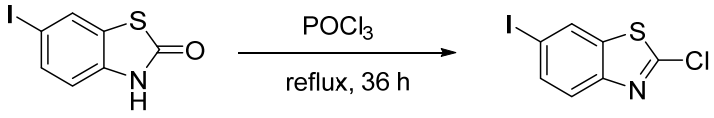
Method B: Iodination using *N*-iodosuccinimide



btz-OH **1-OH** (85 %)

Benzothiazol-2(3*H*)-one (10.0 g, 66 mmol) was dissolved in the sulfuric acid (200 mL) diluted with 10.0 mL of deionized water. *N*-Iodosuccinimide (18.6 g, 83 mmol) was added portionwise over 5 min at 0 °C. The reaction mixture was stirred at rt for 3 hours and then poured onto ice (600 g). The solid was filtered off, washed with water until neutral reaction of the filtrate, then with 5 % aqueous solution of $Na_2S_2O_5$, saturated $NaHCO_3$ solution and deionized water. The solid was dried in vacuo to obtain 6-iodobenzothiazol-2(*3H*)-one as a brownish solid (15.6 g, 85 %). See full spectroscopic characterization of the product in Method A.

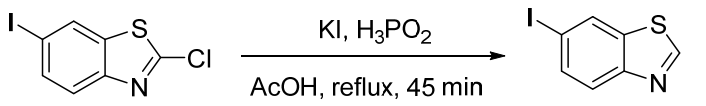
2.6.2 2-Chloro-6-iodobenzothiazole (1-Cl) from 6-iodobenzothiazol-2(3*H*)-one



1-OH **1-Cl** (88 %)

$POCl_3$ (80 mL) was added via syringe into an argon-flushed round-bottom flask equipped with a condenser and containing 6-iodobenzothiazol-2(*3H*)-one (10.0 g, 36 mmol). The reaction mixture was heated to reflux for 36 h in an oil bath. After consumption of the starting material (monitored by TLC), the mixture was cooled to rt and then added into 500 mL of vigorously stirred water in small portions over 30 min (the temperature throughout the addition was maintained under 40°C). The precipitate formed was collected by filtration, dissolved in chloroform (250 mL), dried over Na_2SO_4 and concentrated in vacuo to obtain **1-Cl** as a white solid (9.33 g, 88 %). R_f 0.71 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 134 – 136 °C (lit.[5] mp 135 – 137 °C); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 1.4 Hz, 1H), 7.77 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.8, 150.3, 137.9, 135.9, 129.5, 124.3, 90.1; **HRMS** calcd for C_7H_4ClINS $[M+H]^+$, 295.8792; found, 295.8789.

2.6.3 **6-Iodobenzothiazole (1-H)** from 2-chloro-6-iodobenzothiazole

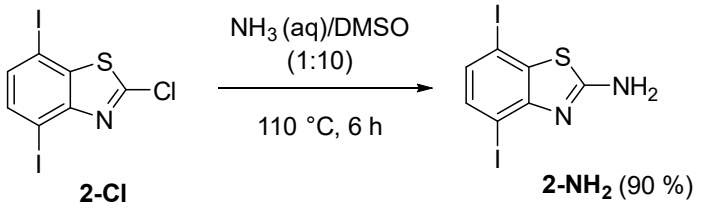


1-Cl **1-H** (97 %)

2-Chloro-6-iodobenzothiazole (9.315 g, 31.5 mmol) was dissolved in acetic acid (150 mL) and KI (15.7 g, 95 mmol) and H_3PO_2 (20 mL) were added. The mixture was heated to 80 °C for 45 min in an oil bath. After cooling to rt, the mixture was poured onto ice, neutralized with aqueous NaOH (20 %) and extracted with DCM (3×100 mL). Combined organic layers were washed with 5 % aqueous solution of $Na_2S_2O_5$, water, brine and dried over Na_2SO_4 to afford **1-H** as a white solid (7.94 g, 97 %). $\boldsymbol{R_f}$ 0.37 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 77 – 79 °C (lit.[3] mp 78 – 80 °C); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.30 (d, J = 1.2 Hz, 1H), 7.87 (d, J = 8.6 Hz, 1H), 7.79 (dd, J = 8.6, 1.5 Hz, 1H)); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 154.3, 152.7, 135.9, 135.3, 130.4, 125.1, 90.1.

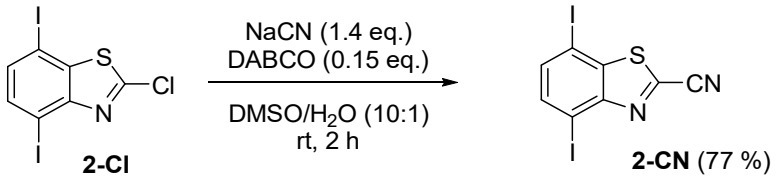
3 Functionalizations of Iodinated Benzothiazoles

3.1 4,7-Diiodobenzothiazol-2-amine (2-NH_2) from 2-Cl



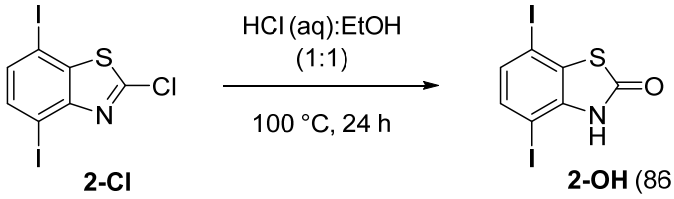
To the suspension of 2-chloro-4,7-diiodobenzothiazole (2.00 g, 4,7 mmol) in dimethylsulfoxide (40 mL) aqueous ammonia (w = 0.26, 4.0 mL) was added. The flask was closed with septum pierced with a needle equipped with a nitrogen balloon and carefully heated (in an oil bath) to 110 °C for 6 hours. After consumption of the starting material (monitored by TLC), the reaction mixture was cooled to rt and poured into water (150 mL). The product was isolated by filtration and dried in vacuo to obtain a white solid (1.72 g, 90 %). $\boldsymbol{R_f}$ 0.10 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 257 – 258 °C); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43 (d, J = 8.2 Hz, 1H), 7.12 (d, J = 8.2 Hz, 1H), 5.44 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.8, 151.3, 137.9, 136.5, 132.3, 85.2, 82.9; **FTIR** (ATR): 3445 (s), 3264 (s), 3066 (s), 1629 (s), 1518 (s), 1350 (s), 1070 (s), 906 (s), 781 (m) cm^{-1}; **HRMS** calcd for $C_7H_5I_2N_2S$ $[M+H]^+$, 402.8257; found, 402.8263.

3.2 4,7-Diiodobenzothiazol-2-carbonitrile (2-CN) from 2-Cl



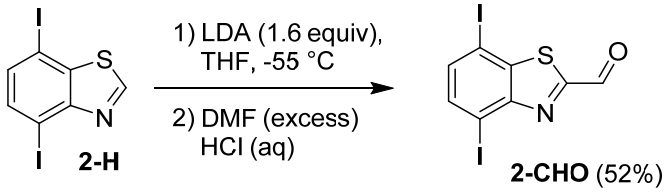
Sodium cyanide (185 mg, 3.8 mmol) dissolved in 6 mL of distilled water was slowly added to the stirred solution of 2-chloro-4,7-diiodobenzothiazole (1.15 g, 2.7 mmol) and DABCO (46 mg, 0.4 mmol) in DMSO (60 mL). Resulting solution was stirred at rt for 2 hours and subsequently diluted with water (200 mL). The crude product was isolated by filtration and purified by column chromatography in hexanes/EtOAc (7/1) to obtain 0.87 g (77 %) of white solid. $\boldsymbol{R_f}$ 0.58 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 198 – 200 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 151.1, 142.6, 138.8, 138.3, 134.8, 112.4, 92.4, 82.9; **FTIR** (ATR): 3071 (w), 2920 (w), 2850 (w), 2233 (m), 1440 (m), 1293 (s), 1108 (s), 1062 (s), 908 (s), 824 (s), 786 (m) cm^{-1}; **HRMS**, calcd for $C_9H_7I_2N_2OS$ $[M + CH_3OH + H]^+$, 444.8363; found, 444.8362.

3.3 4,7-Diiodobenzothiazol-2(3*H*)-one (2-OH) from 2-Cl



2-Chloro-4,7-diiodobenzothiazole (200 mg, 0.5 mmol) was suspended in the mixture of ethanol (w = 0.96, 5 mL) and hydrochloric acid (w = 0.37, 5 mL) and the resulting mixture was heated to 100 °C for 24 hours. The reaction was monitored by TLC. After consumption of the starting material, the reaction mixture was cooled to rt and poured into water (75 mL). The product was isolated by filtration as a white solid (165 mg, 86 %). $\boldsymbol{R_f}$ 0.32 (SiO_2, hexanes/EtOAc = 6:1); **Mp** 248 – 249 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.22 (d, J = 8.4 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.3, 136.8, 136.1, 133.3, 130.6, 87.2, 74.7; **FTIR** (ATR): 3094 (m), 3020 (m), 1668 (s), 1565 (s), 1456 (m), 1387 (m), 1283 (m), 1216 (m), 1113 (m), 1071 (s), 918 (m), 785 (s), 706 (m) cm^{-1}; **HRMS**, calcd for $C_7H_2I_2NOS$ $[M-H]^-$ (negative ion mode), 401.7952; found, 401.7947.

3.4 4,7-Diiodobenzothiazole-2-carbaldehyde (2-CHO) from 2-H



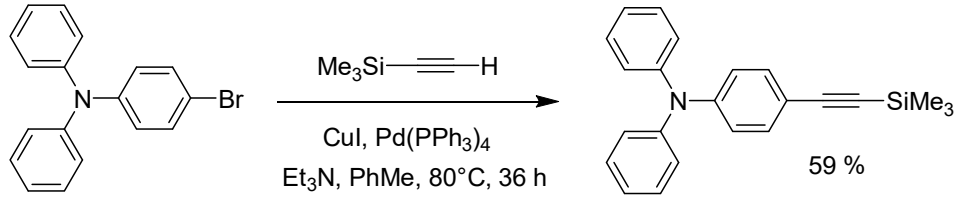
4,7-Diiodobenzothiazole (0.5 g, 1.29 mmol) was dissolved in freshly distilled THF under argon atmosphere. Reaction mixture was cooled to -55 °C and lithium diisopropylamide (LDA) (2 M in THF, 1.6 eq, 1 mL, 2.07 mmol) was added dropwise. The reaction mixture was stirred at -55 °C for 60 minutes, then dry DMF (0.4 mL, 5.17 mmol) was added dropwise and the mixture was stirred 2 hours at room temperature. Subsequently, 3.6 % solution of HCl (10 mL) was added and the mixture was extracted using ethylacetate (3×25 mL). Organic phase was washed with brine (10 mL) and dried over Na_2SO_4. The product was purified using column chromatography on silica to obtain 4,7-diiodobenzothiazole-2-carbaldehyde (**2-CHO**) as a yellow solid (277 mg, 52 %). $\boldsymbol{R_f}$ 0.31 (SiO_2, hexanes/EtOAc = 5:1); **Mp** 182 - 184 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.16 (s, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 185.20, 152.14, 143.74, 138.22, 138.17, 93.33, 84.73. **FTIR** (ATR): 1683 (s), 1476 (m), 1437 (m), 1298 (m), 1105 (m), 870 (s), 642 (s) cm^{-1}. **HRMS** calcd for $C_8H_4I_2NOS$ $[M+CH_3OH+H]^+$, 447.8360 ; found, 447.8363.

4 Synthesis of Target Fluorophores via Sonogashira Cross-Coupling

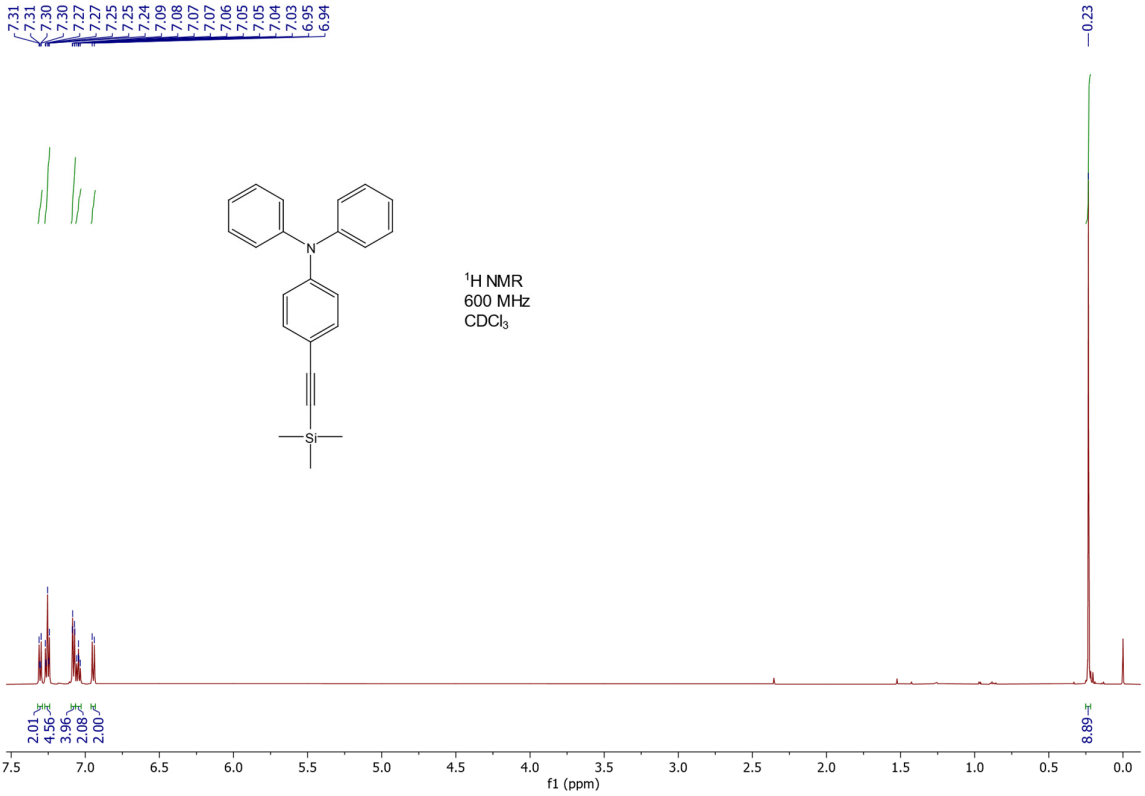
4.1 Synthesis of starting arylacetylenes

4.1.1 4-(*N*,*N*-Diphenylamino)phenylacetylene

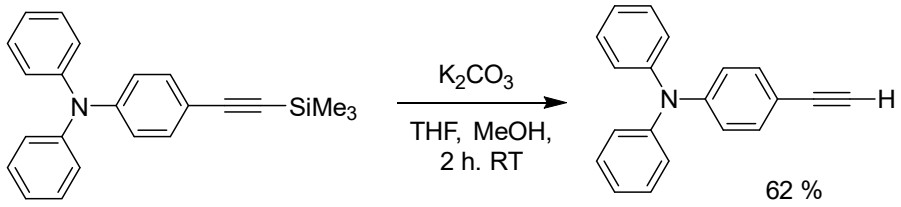
Synthesis of *N*,*N*-diphenyl-4-[(trimethylsilyl)ethynyl]aniline



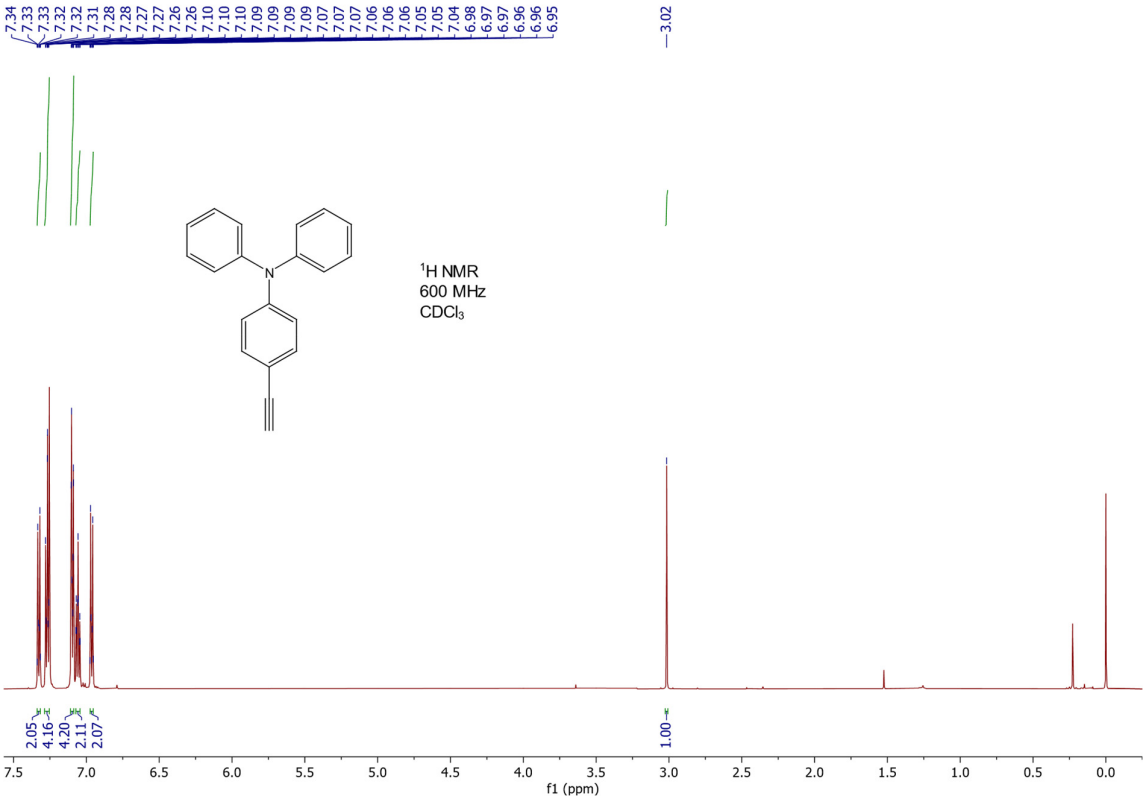
4-Bromotriphenylamine (10 g, 30.8 mmol), CuI (295 mg, 1.54 mmol) and $Pd(PPh_3)_4$ (1.424 g, 1.232 mmol) were dissolved in dry toluene (50 mL) and dry triethylamine (52 mL) was added. Then trimethylsilylacetylene (6.6 mL, 46.2 mmol) was added and the mixture was heated to 80°C (in an oil bath) under inert atmosphere for 36 hours. Subsequently, the reaction mixture was cooled to rt and concentrated under reduced pressure. The crude solid was purified by column chromatography on silica gel (eluent: hexanes), which afforded the product as an orange solid (6.17 g) in 59 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 2H), 7.26 (t, *J* = 7.9 Hz, 4H), 7.10 – 7.07 (m, 4H), 7.06 – 7.03 (m, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 0.23 (s, 9H). ^{1}H NMR shifts match those reported for this compound in ref. 10.



Synthesis of 4-(*N*,*N*-diphenylamino)phenylacetylene

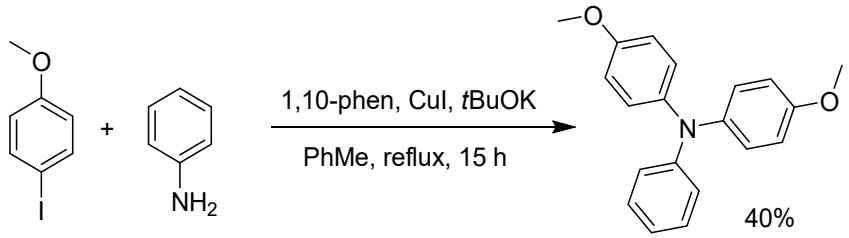


N,N-Diphenyl-4-((trimethylsilyl)ethynyl)aniline (6.17 g, 18.1 mmol) and potassium carbonate (24.96 g, 18.1 mmol) were dissolved in MeOH (100 mL) and THF (100 mL) and the mixture was stirred at room temperature for 2 hours. Then insoluble K_2CO_3 was filtered off and organic solvents evaporated under reduced pressure. Purification by column chromatography on silica gel (eluent: hexanes / EtOAc 9:1) afforded the desired arylacetylene as a yellow solid (3.02 g) in 62 % yield. **Mp** 80-82 °C (lit.[5] 80-82 °C) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 – 7.32 (m, 2H), 7.29 – 7.25 (m, 4H), 7.11 – 7.09 (m, 4H), 7.07 – 7.04 (m, 2H), 6.97 – 6.95 (m, 2H), 3.02 (s, 1H). ^{1}H NMR shifts match those reported previously in ref. 5.

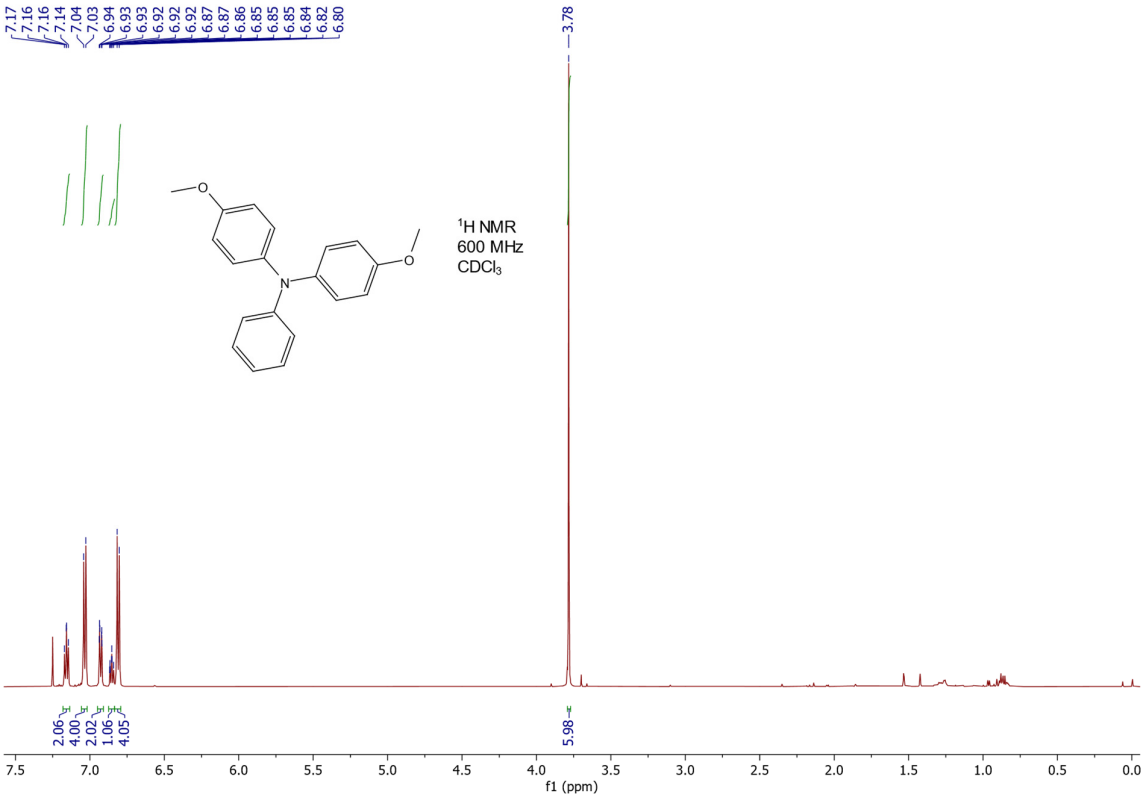


4.1.2 4-[*N*,*N*-bis(4-methoxyphenyl)amino]phenylacetylene

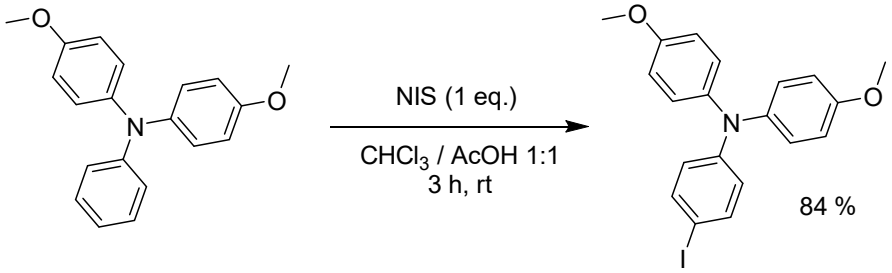
Synthesis of *N*,*N*-bis(4-methoxyphenyl)aniline



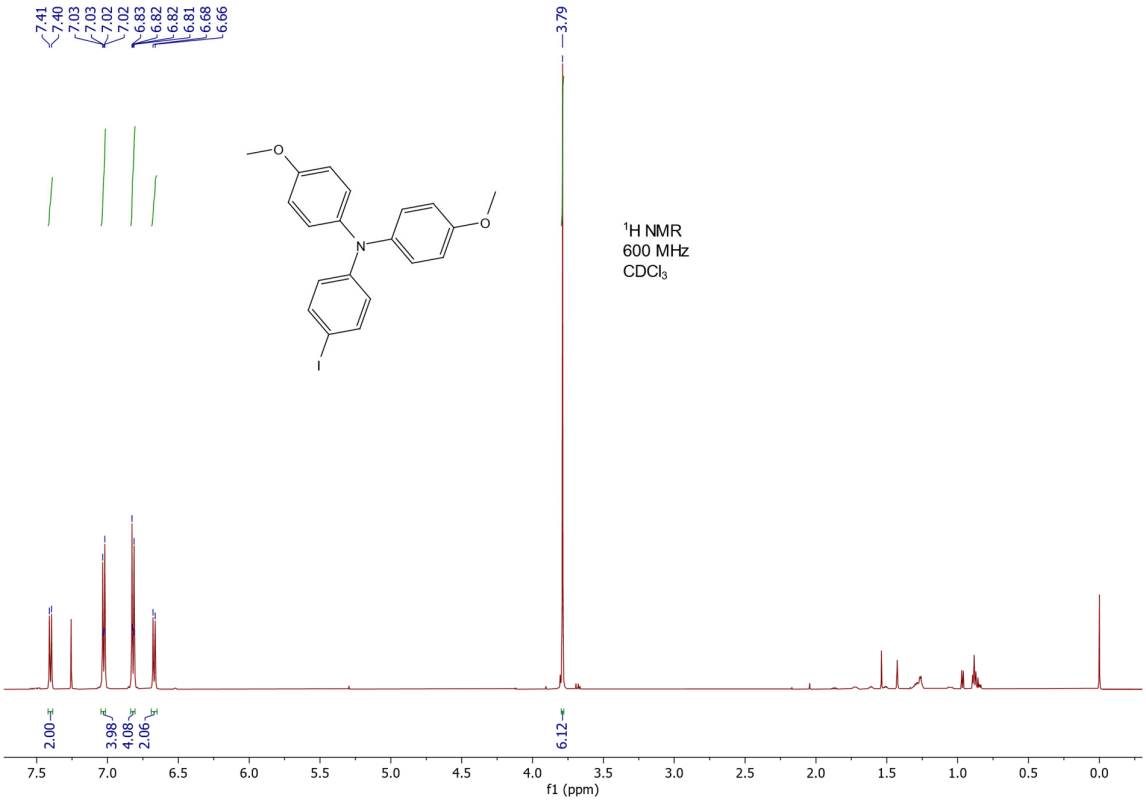
1-Iodo-4-methoxybenzene (20 g, 85.46 mmol), aniline (3.8 mL, 40.7 mmol), CuI (1.55 g, 8.14 mmol), 1,10-phenantroline (1.47 g, 8.14 mmol) and *tert*-BuOK (36.5 g, 325.6 mmol) were dissolved in dry toluene (250 mL) under argon atmosphere. Reaction mixture was heated to reflux in an oil bath for 16 hours. After cooling to rt, the reaction mixture was quenched with water (250 mL) and extracted with dichloromethane (3×250 mL). Organic phase was washed with brine (200 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude solid was purified by column chromatography on silica gel (eluent: hexanes / dichloromethane 1:1) affording the product as a yellow solid (4.9 g) in 40 % yield. **Mp** 105-106 °C (lit.[11] 104-106 °C). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 8.6, 7.3 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 4H), 6.95 – 6.91 (m, 2H), 6.87 – 6.83 (m, 1H), 6.81 (d, *J* = 8.9 Hz, 4H), 3.78 (s, 6H).



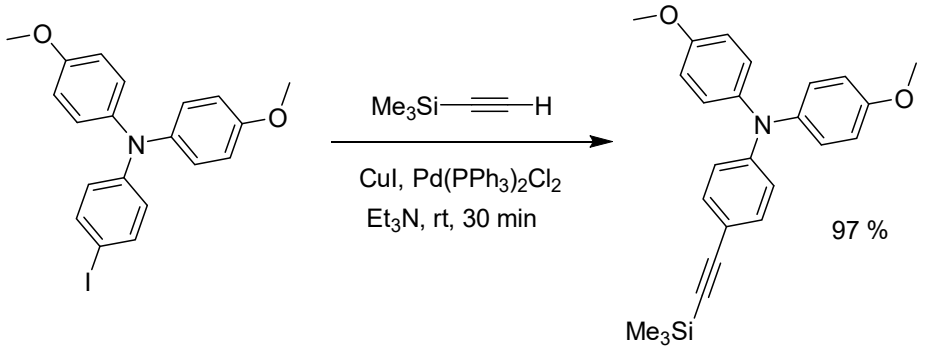
Synthesis of 4-iodo-*N*,*N*-bis(4-methoxyphenyl)aniline



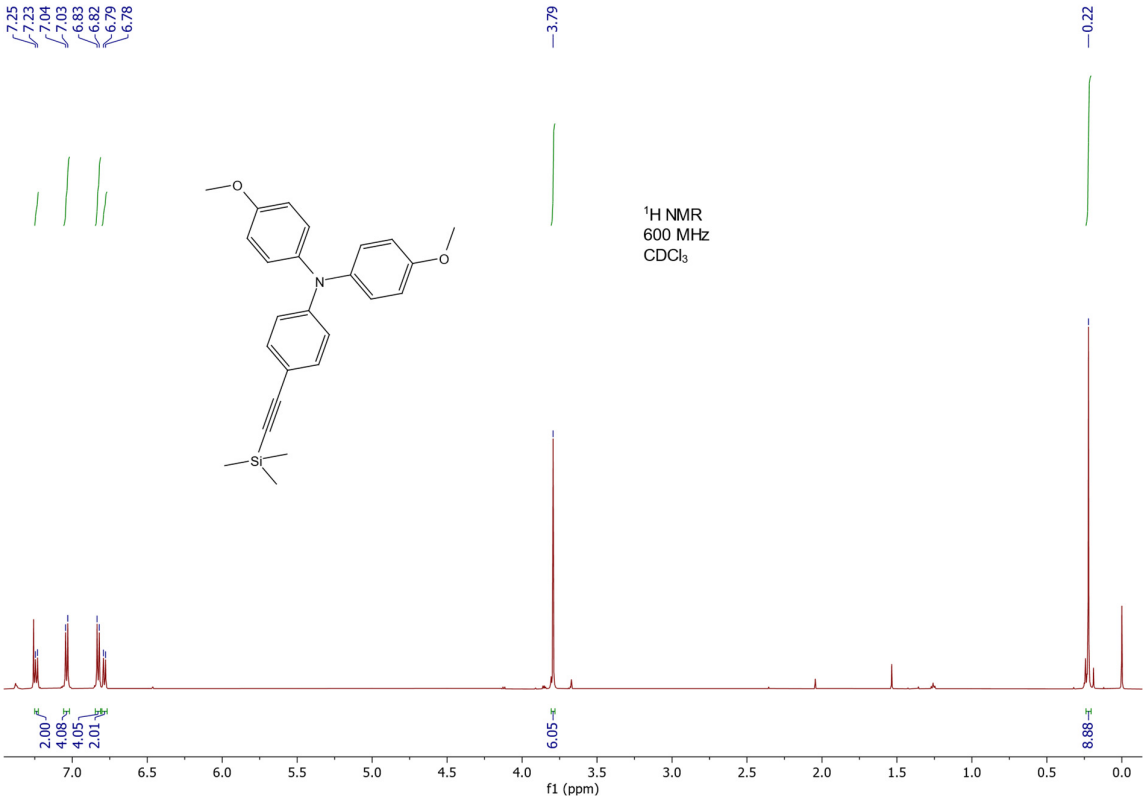
N,*N*-Bis(4-methoxyphenyl)aniline (6.40 g, 20.96 mmol) was dissolved in a mixture of chloroform (25 mL) and acetic acid (25 mL). Then *N*-iodosuccinimide (4.72 g, 20.96 mmol) was added portionwise to reaction mixture. The reaction mixture was stirred at room temperature for 3 hours, then quenched with water (50 mL) and extracted using chloroform (3×30 mL). Organic phase was dried over Na_2SO_4 and solvents removed under reduced pressure. The solid residue was purified by column chromatography on silica gel (eluent: hexanes / dichloromethane 1:1) affording the product as a yellow solid (7.60 g) in 84 % yield. **Mp** 113-115 °C (lit.[12] 114-116 °C) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.8 Hz, 2H), 7.05 – 7.01 (m, 4H), 6.84 – 6.81 (m, 4H), 6.67 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 6H).



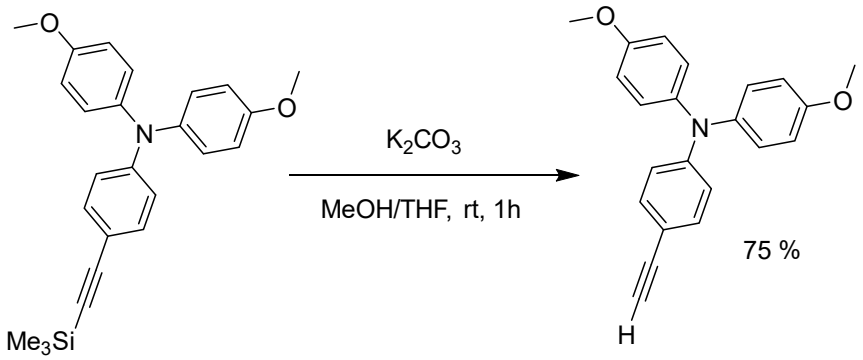
Synthesis of *N,N*-bis(4-methoxyphenyl)-4-[(trimethylsilyl)ethynyl]aniline



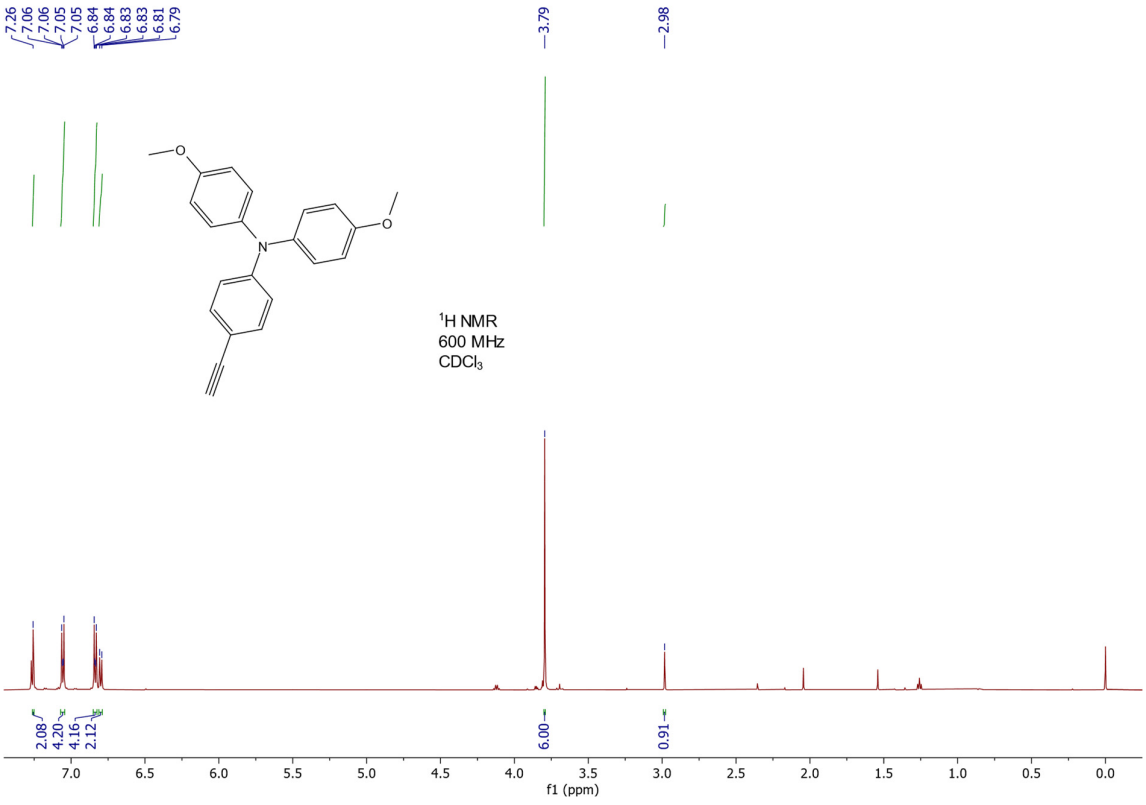
4-Iodo-*N*,*N*-bis(4-methoxyphenyl)aniline (0.5 g, 1.16 mmol), CuI (11 mg, 0.058 mmol) and $Pd(PPh_3)_2Cl_2$ (41 mg, 0.058 mmol) were dissolved in dry triethylamine (7 mL). Then trimethylsylilacetylene (0.25 mL, 1.74 mmol) was added dropwise. The reaction mixture was stirred under argon for 30 minutes. After this time, the mixture was concentrated under reduced pressure, the solid residue suspended in chloroform (10 mL) and filtered through a short pad of silica. The desired product was obtained upon evaporation of chloroform under reduced pressure as a yellow solid (451 mg) in 97 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.9 Hz, 2H), 7.04 (d, *J* = 9.0 Hz, 4H), 6.83 (d, *J* = 9.0 Hz, 4H), 6.79 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 6H), 0.22 (s, 9H). ^{1}H NMR shifts match those reported for this compound in ref. 13.



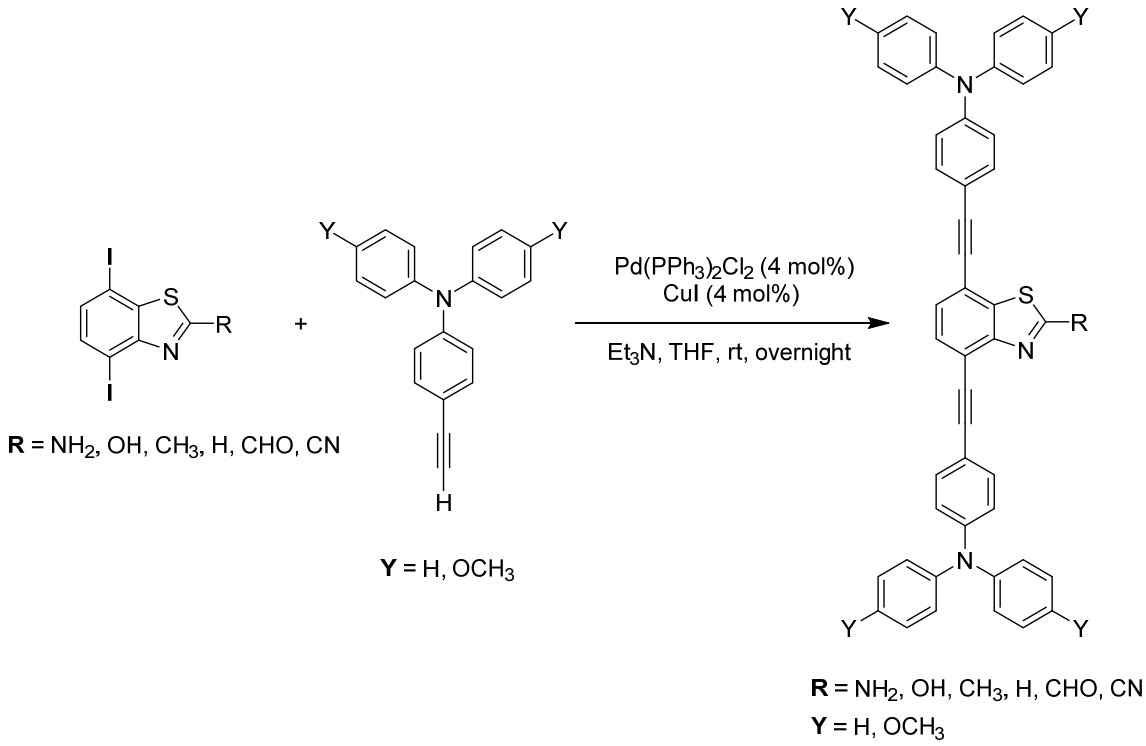
Synthesis of 4-[*N*,*N*-bis(4-methoxyphenyl)amino]phenylacetylene



N,N-bis(4-methoxyphenyl)-4-[(trimethylsilyl)ethynyl]aniline (451 mg, 1.123 mmol) and potassium carbonate (233 mg, 1.686 mmol) were dissolved in a mixture of methanol (10 mL) and tetrahydrofuran (5 mL). The reaction mixture was stirred at room temperature for 1 hour, then filtered and concentrated under reduced pressure. The solid residue was purified by column chromatography on silica gel (eluent: hexanes / dichloromethane 1:1) affording the desired arylacetylene as a yellow solid (278 mg) in 75 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.26 (s, 2H), 7.07 – 7.04 (m, 4H), 6.85 – 6.82 (m, 4H), 6.80 (d, J = 8.7 Hz, 2H), 3.79 (s, 6H), 2.98 (s, 1H). ^{1}H NMR shifts match those reported for this compound in ref. 13.

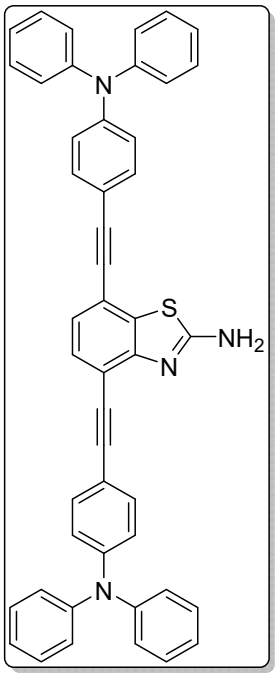


4.2 General procedure for Sonogashira cross-coupling reactions



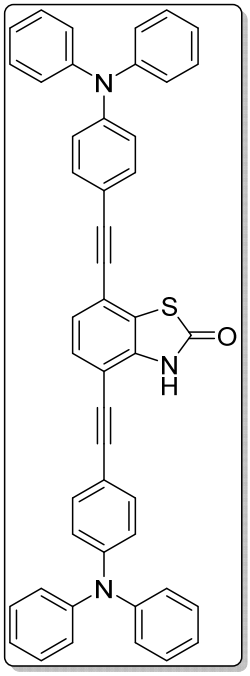
A mixture of C-2 substituted 4,7-diiodobenzothiazole (0.75 mmol), copper(I) iodide (4 mol%) and $Pd(PPh_3)_2Cl_2$ (4 mol%) was dissolved under argon atmosphere in a dry (freshly distilled) THF (8 mL) and triethylamine (30 equivalents, freshly distilled from CaH_2) was added. Corresponding arylacetylene (2.05 equivalents) was dissolved in a dry THF (5 mL) and then added dropwise via syringe to the reaction mixture under inert atmosphere over the course of 60 min. Then the reaction mixture was stirred overnight at room temperature, organic solvents were evaporated under reduced pressure and the solid residue was purified using column chromatography (on silica or alumina) or crystalized to afford the desired product.

4,7-Bis[(4-(*N*,*N*-diphenylamino)phenylethynyl]benzothiazol-2-amine (Qbtz-NH_2)



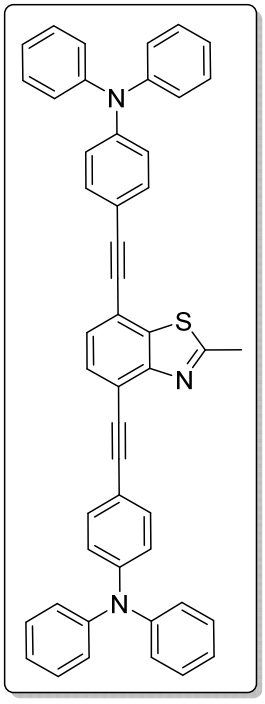
Crude product was purified using column chromatography on alumina (eluent: hexanes / DCM = 1:1 + 1% Et_3N) to afford **Qbtz-NH_2** as a yellow solid in 45 % yield. **R_f** = 0.2. **Mp** 252 – 254 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 10.8, 8.3 Hz, 3H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.31 – 7.26 (m, 8H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.15 – 7.10 (m, 8H), 7.08 (t, *J* = 7.9 Hz, 2H), 7.06 – 6.99 (m, 6H), 5.88 (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.6, 152.2, 148.4, 148.0, 147.2, 147.0, 134.7, 132.8, 132.6, 129.7, 129.4, 129.4, 125.1, 125.0, 124.6, 123.7, 123.5, 122.2, 122.0, 116.5, 116.0, 115.2, 113.8, 95.2, 94.6, 91.0, 90.9, 86.6, 86.5. **HRMS** calcd. for $C_{47}H_{32}N_4S$ $[M+H]^+$: 685.2420 found 685.2427. **FTIR** (ATR): 3464 (m), 3029 (w), 1586 (s), 1511 (s), 1488 (s), 1316 (s), 1281 (s), 750 (s) cm^{-1}.

4,7-Bis[4-*N*,*N*-diphenylamino)phenylethynyl]benzothiazol-2(3H)-one (Qbtz-OH)



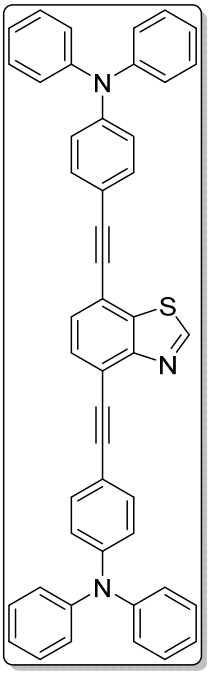
Crude product was filtered through a short pad of Al_2O_3 (eluent: dichloromethane) and crystalized from the mixture dichloromethane / hexanes to afford **Qbtz-OH** as a yellow solid in 51 % yield. **Mp** 266 – 268 °C. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.46 (s, 1H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.39 – 7.35 (m, 8H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.13 (dt, *J* = 28.6, 8.2 Hz, 12H), 6.92 (dd, *J* = 11.5, 8.7 Hz, 4H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 169.9, 148.8, 148.4, 146.9, 146.7, 133.5, 133.2, 130.3, 130.2, 129.7, 125.7, 125.5, 124.8, 124.6, 121.4, 121.2, 116.8, 114.9, 113.6, 106.9, 97.1, 96.9, 85.7, 85.6. **HRMS** calcd. for $C_{47}H_{31}N_3OS$ $[M+Na]^+$: 708.2085 found 708.2082. **FTIR** (ATR): 3034 (w), 2202 (m), 1675 (s), 1585 (s), 1512 (s), 1486 (s), 1328 (s), 1284 (s) cm^{-1}.

4,7-Bis[(4-(*N*,*N*-diphenylamino)phenylethynyl]-2-methylbenzothiazole (Qbtz-Me)



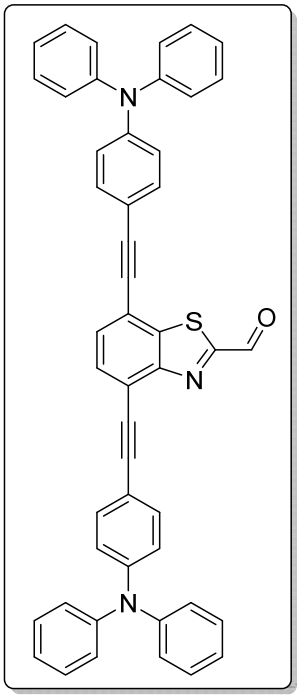
Crude product was purified using column chromatography on silica (eluent: hexanes/DCM = 7:3) to afford **Qbtz-Me** as a yellow powder in 89% yield. $\mathbf{R_f}$ = 0.23. **Mp** 101 – 103 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.31 – 7.26 (m, 8H), 7.13 (dd, *J* = 7.4, 5.1 Hz, 8H), 7.10 – 7.05 (m, 4H), 7.02 (dd, *J* = 8.8, 5.0 Hz, 4H), 2.90 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.2, 152.9, 148.5, 148.1, 147.1, 147.0, 138.9, 132.9, 132.6, 129.8, 129.4, 129.4, 127.0, 125.2, 125.0, 123.8, 123.6, 122.0, 121.9, 117.5, 116.9, 115.89, 115.0, 95.9, 95.6, 86.4, 86.1, 20.5. **HRMS** calcd. for $C_{48}H_{33}N_3S$ $[M+H]^+$: 684.2468 found 684.2466. **FTIR** (ATR): 1585 (s), 1508 (s), 1485 (s), 1313 (s), 1270 (s), 824 (s), 751 (s) cm^{-1}.

4,7-Bis[(4-(*N*,*N*-diphenylamino)phenylethynyl]benzothiazole (Qbtz-H)



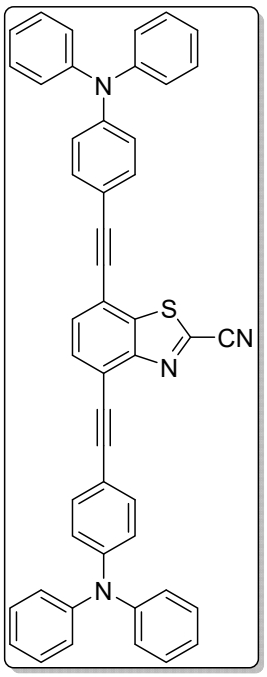
Crude product was purified using column chromatography on silica (eluent: hexanes/ EtOAc = 9:1) to provide **Qbtz-H** as a yellow powder in 64% yield. $\mathbf{R_f}$ = 0.2. **Mp** 200 – 201 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.10 (s, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.29 (dd, *J* = 15.0, 7.3 Hz, 8H), 7.13 (t, *J* = 7.3 Hz, 8H), 7.08 (dd, *J* = 17.9, 7.4 Hz, 4H), 7.02 (t, *J* = 8.3 Hz, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 154.9, 152.8, 148.6, 148.2, 147.1, 146.9, 137.1, 132.9, 132.7, 130.0, 129.5, 129.4, 127.9, 125.2, 125.1, 123.8, 123.6, 121.9, 121.9, 118.8, 117.6, 115.6, 114.8, 96.5, 96.1, 86.2, 85.8. **HRMS** calcd. for $C_{47}H_{31}N_3S$ $[M+H]^+$: 670.2311 found 670.2299. **FTIR** (ATR): 1586 (s), 1509 (s), 1487 (s), 1314 (s), 1276 (s), 826 (s) cm^{-1}.

4,7-Bis[(4-(*N*,*N*-diphenylamino)phenylethynyl]benzothiazole-2-carbaldehyde (Qbtz-CHO)



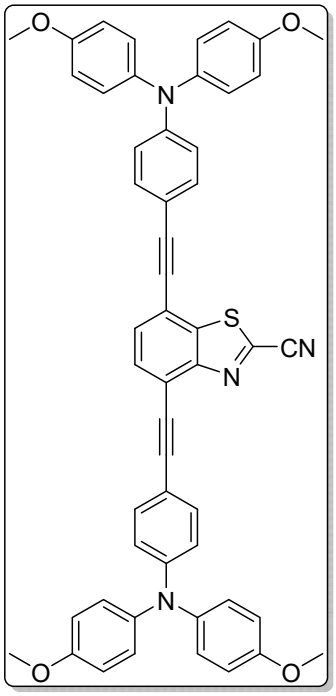
Crude product was purified using column chromatography on silica (eluent: hexanes / EtOAc 15:1) to afford **Qbtz-CHO** as a red solid in 62 % yield. $\mathbf{R_f}$ = 0.25. **Mp** 118 – 119 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.23 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.30 (td, *J* = 8.0, 3.7 Hz, 8H), 7.16 – 7.12 (m, 8H), 7.12 – 7.07 (m, 4H), 7.03 (dd, *J* = 8.7, 2.4 Hz, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 185.6, 165.7, 153.0, 148.8, 148.6, 146.9, 146.9, 139.8, 132.9, 132.8, 130.9, 130.2, 129.5, 129.4, 125.3, 125.2, 123.9, 123.8, 121.8, 121.7, 120.9, 118.2, 115.1, 114.3, 98.2, 97.2, 85.4, 85.4. **HRMS** calcd. for $C_{48}H_{31}N_3OS$ $[M+MeOH+Na]^+$; 752.2342 found 752.2340. **FTIR** (ATR): 2360 (m), 2197 (w), 1693 (s), 1584 (s), 1508 (s), 1485 (s), 1270 (s) cm^{-1}.

4,7-Bis[(4-(*N*,*N*-diphenylamino)phenylethynyl]benzothiazol-2-carbonitrile (Qbtz-CN)



Crude product was purified using column chromatography on silica (eluent: hexanes/$CHCl_3$ 1:1) to afford **Qbtz-CN** as a red solid in 55 % yield. $\mathbf{R_f}$ = 0.21. **Mp** 117 – 119 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.30 (q, *J* = 7.4 Hz, 8H), 7.15 – 7.07 (m, 12H), 7.03 (d, *J* = 8.8 Hz, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 151.8, 148.9, 148.7, 146.9, 146.8, 138.7, 137.1, 133.0, 132.7, 131.2, 130.3, 129.5, 129.4, 125.4, 125.2, 124.0, 123.8, 121.7, 121.6, 120.5, 117.4, 114.8, 113.9, 112.9, 98.7, 97.7, 85.1, 84.9. **HRMS** calcd. for $C_{48}H_{30}N_4S$ $[M+H]^+$ 695.2264, found 695.2257. **FTIR** (ATR): 2150 (m), 1585 (s), 1509 (s), 1486 (s), 1314 (s), 1271 (s), 752 (s) cm^{-1}.

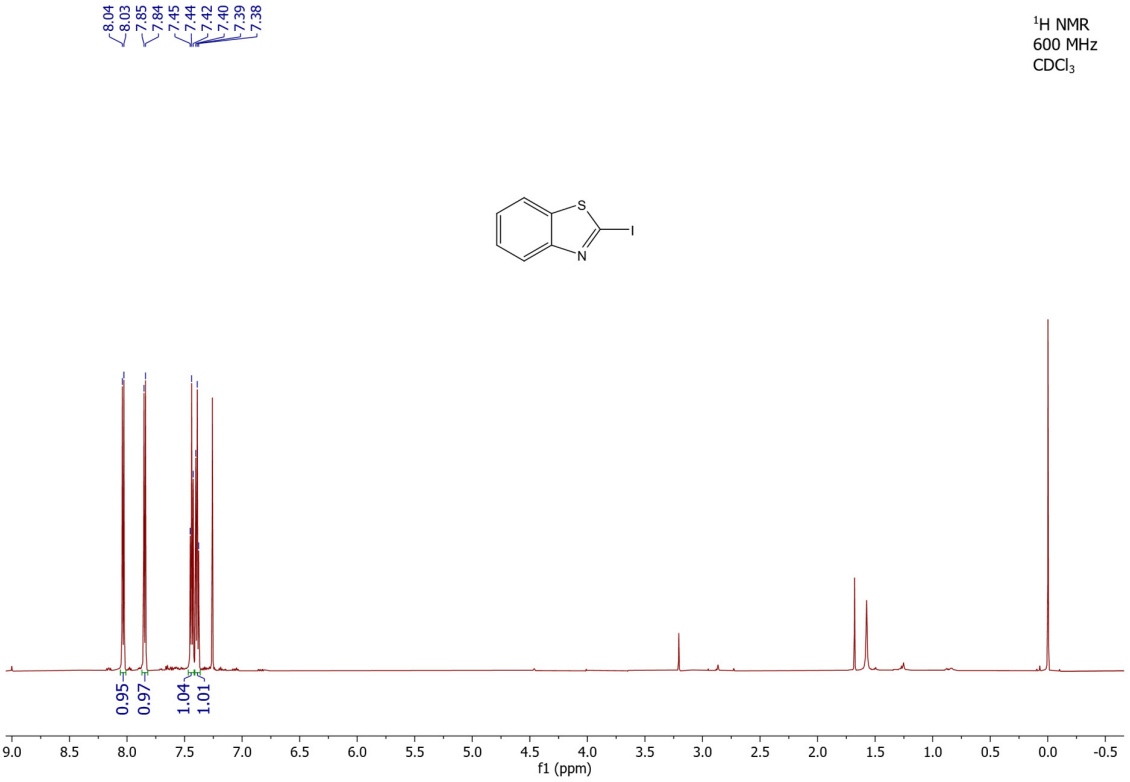
4,7-Bis{4-[*N*,*N*-bis(4-methoxyphenyl)amino]phenylethynyl}benzothiazol-2-carbonitrile (Qbtz'-2-CN)

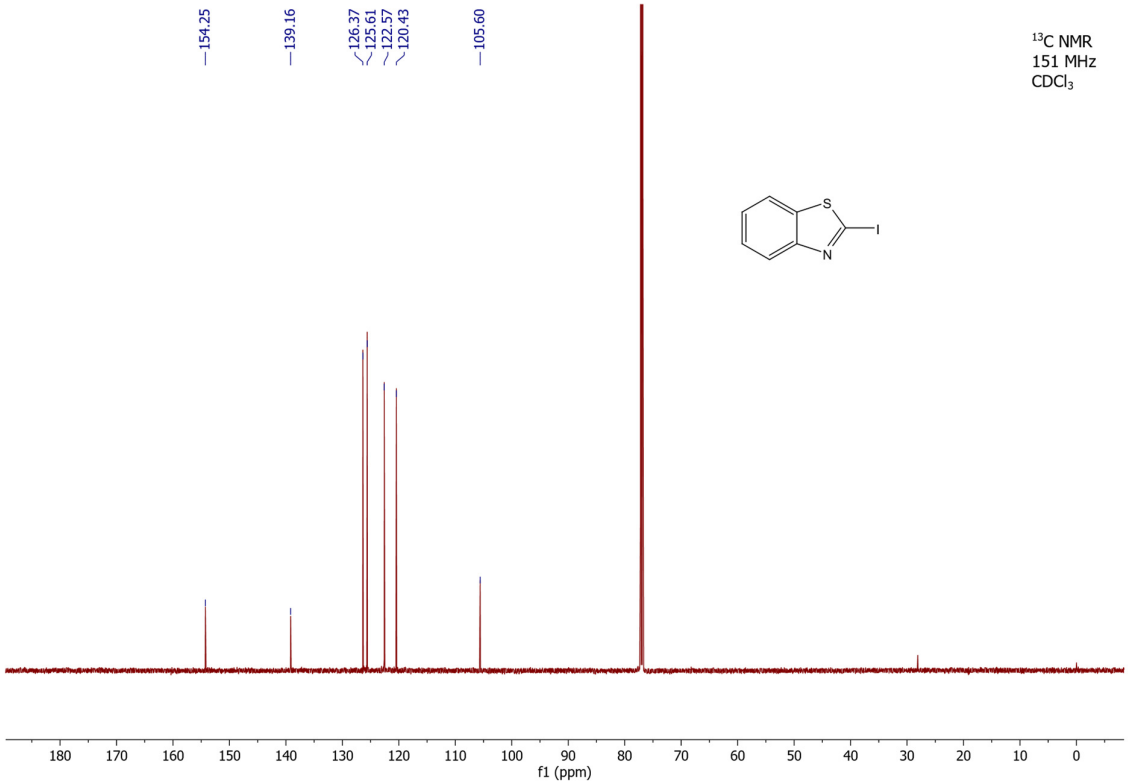


Crude product was purified using column chromatography on silica (eluent: hexanes/$CHCl_3$ 1:1) to afford **Qbtz'-CN** as a red solid in 50 % yield. $\mathbf{R_f}$ = 0.22. **Mp** 108 – 110 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.10 (dd, *J* = 8.9, 3.4 Hz, 8H), 6.86 (dd, *J* = 8.8, 4.0 Hz, 12H), 3.81 (s, 12H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.6, 156.5, 151.7, 149.8, 149.5, 146.1, 139.9, 139.7, 136.9, 132.9, 132.7, 131.1, 130.2, 127.4, 127.3, 120.5, 118.7, 118.6, 117.4, 114.9, 114.8, 112.9, 112.7, 111.8, 99.1, 98.2, 84.8, 84.6, 55.5. **HRMS** calcd. for $C_{52}H_{38}N_4O_4S$ $[M+H]^+$; 815.2692 found 815.2691. **FTIR** (ATR): 2832 (w), 2196 (m), 1596 (s), 1500 (s), 1317 (s), 1286 (s), 1237 (s) cm^{-1}.

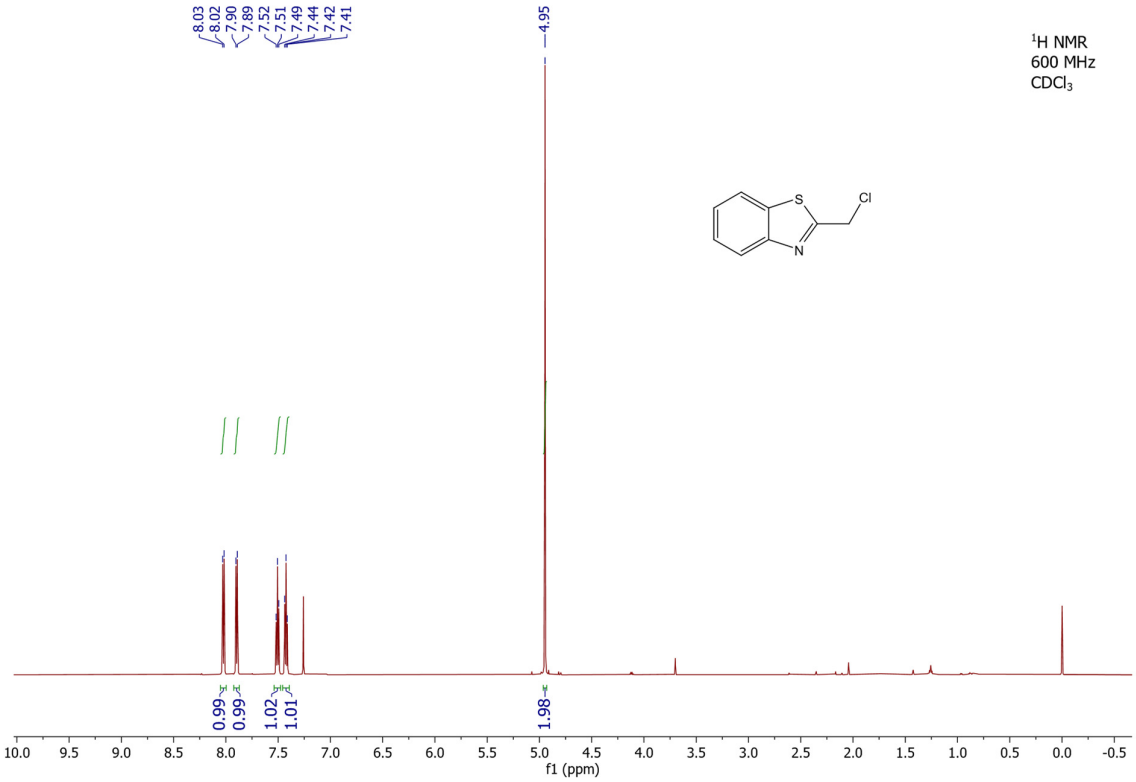
5 NMR Spectra of Halogenated Benzothiazoles and Target Fluorophores

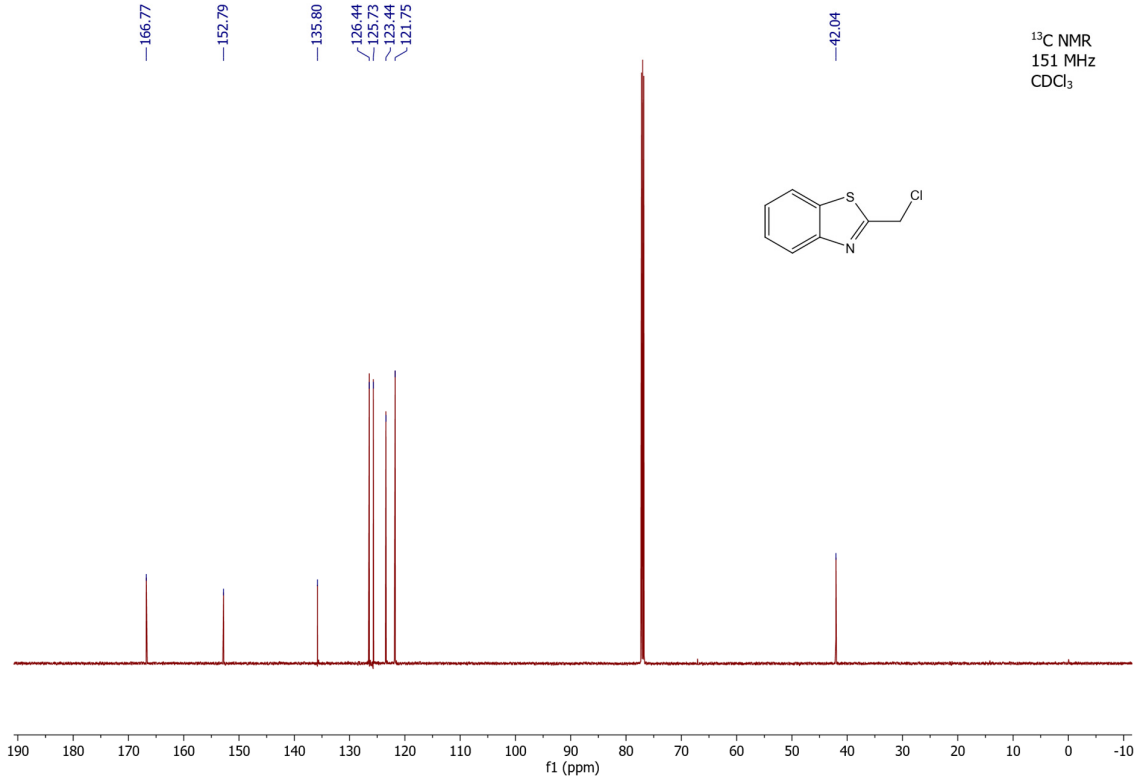
2-Iodobenzothiazole



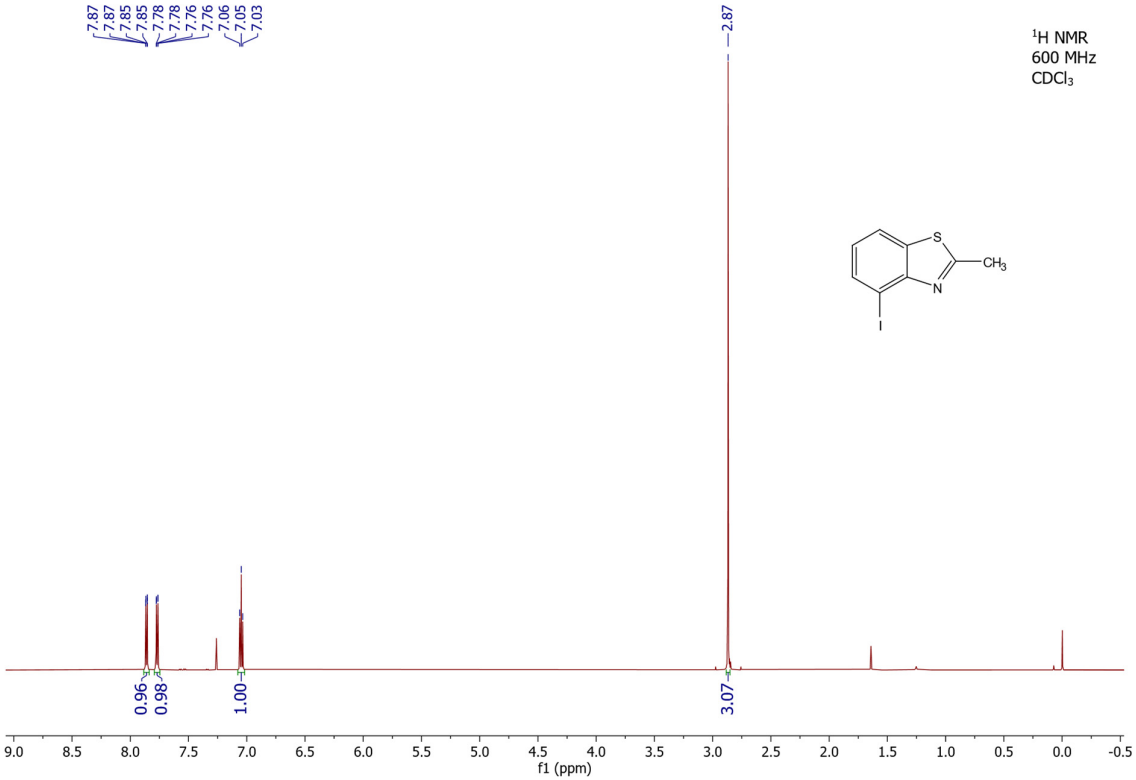


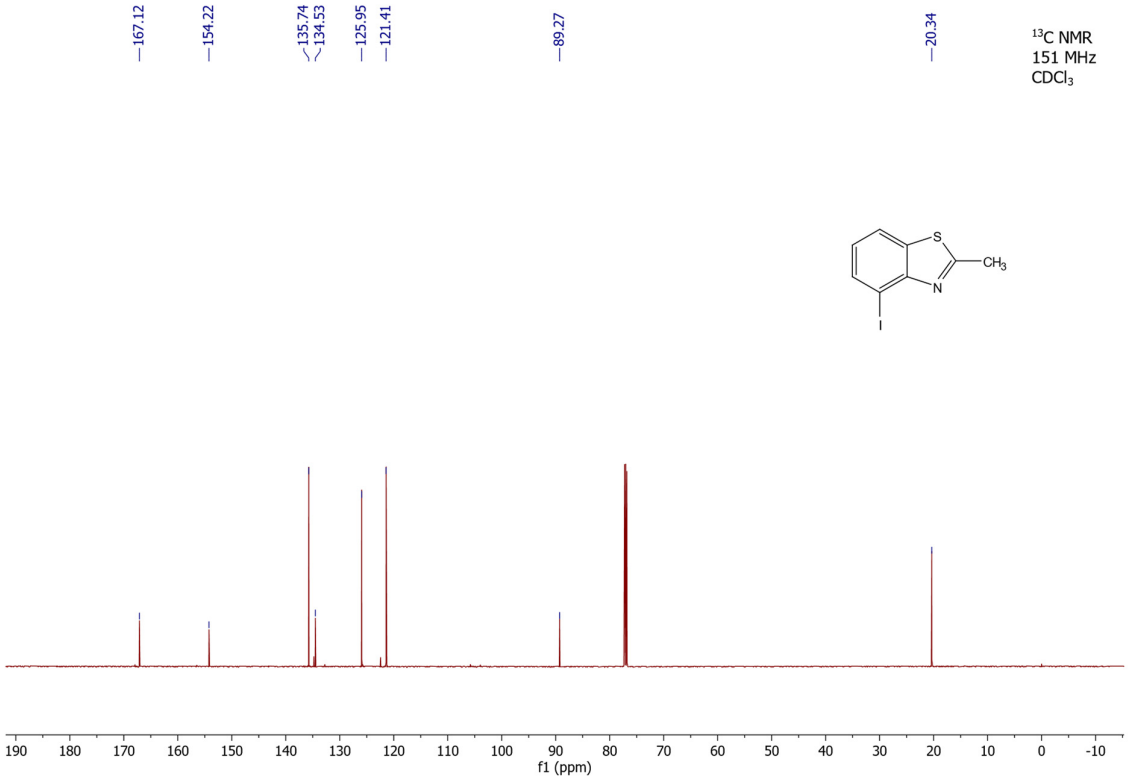
2-(Chloromethyl)benzothiazole



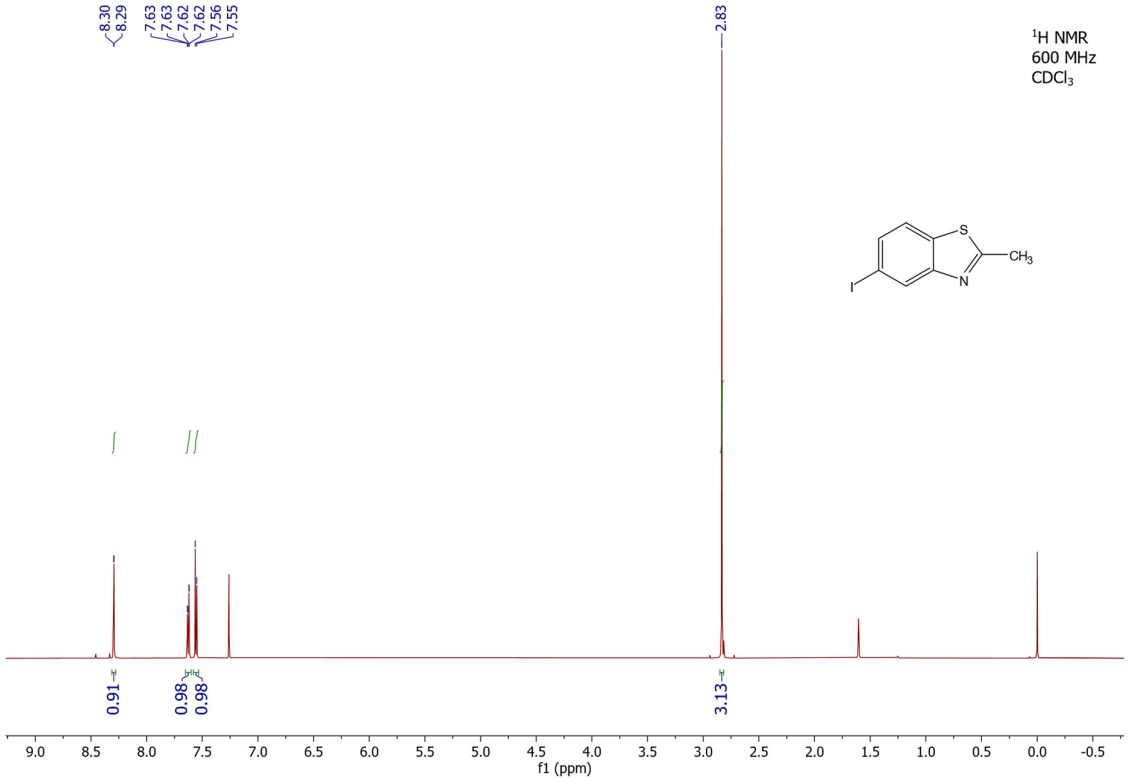


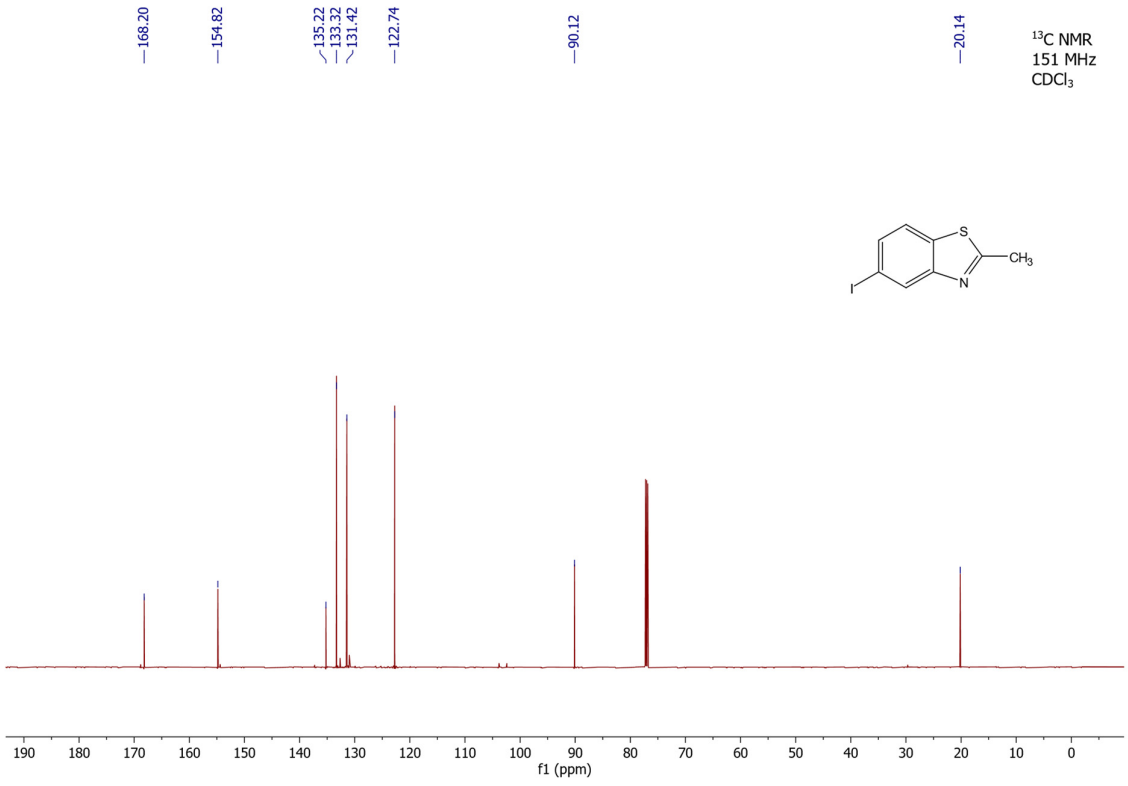
4-Iodo-2-methylbenzothiazole



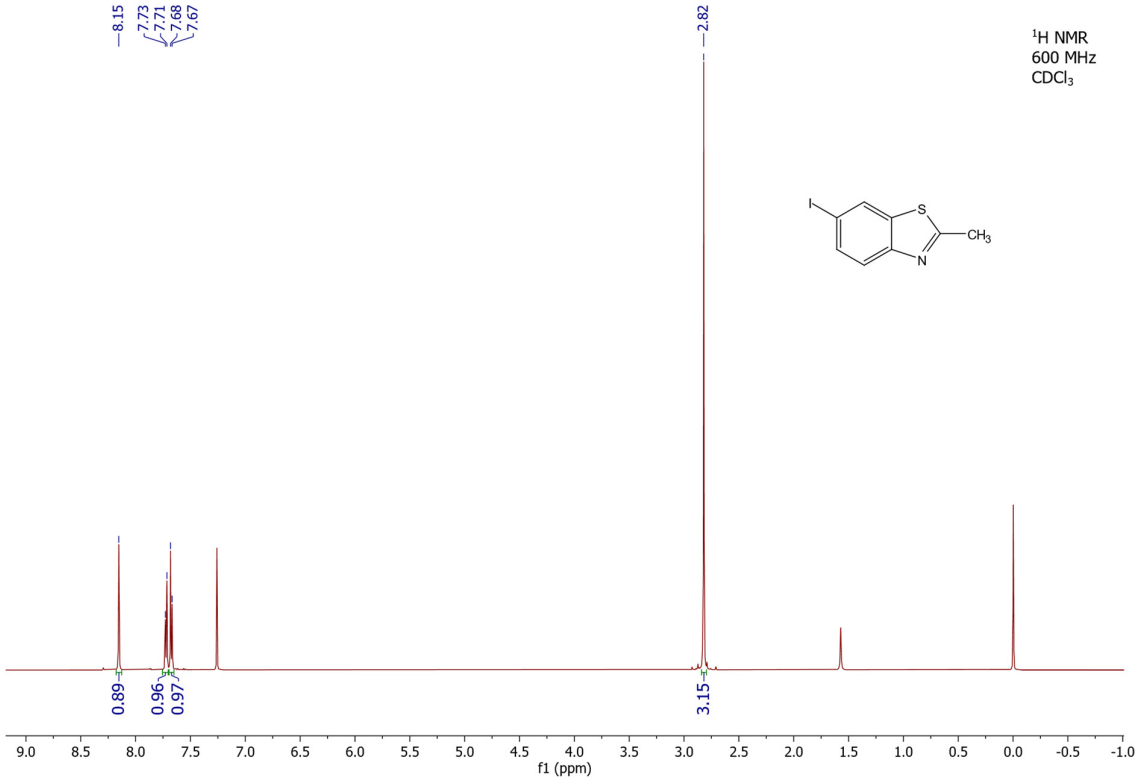


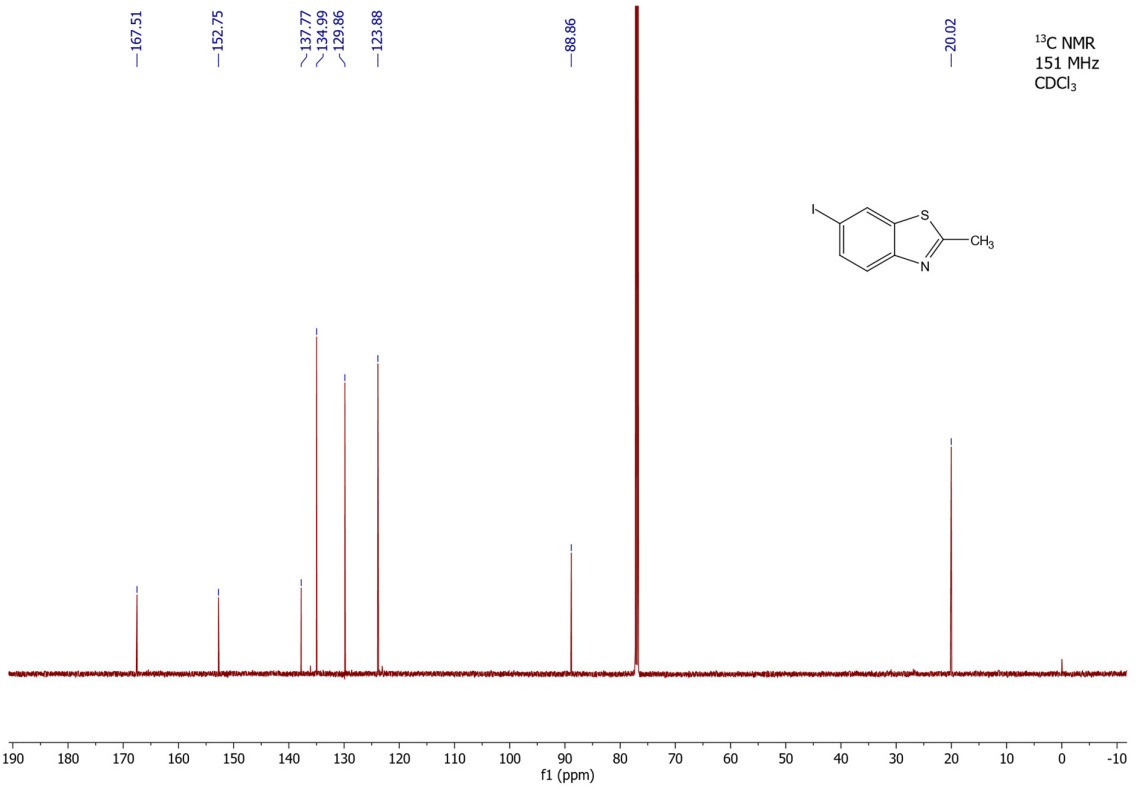
5-Iodo-2-methylbenzothiazole



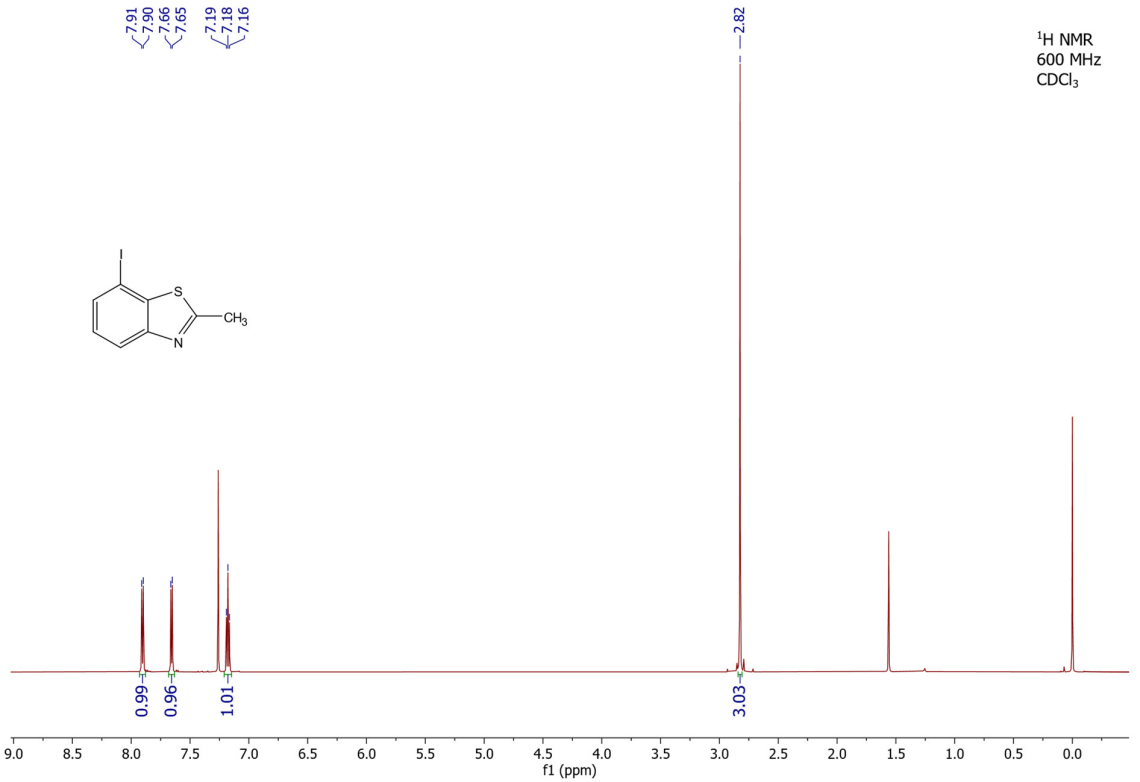


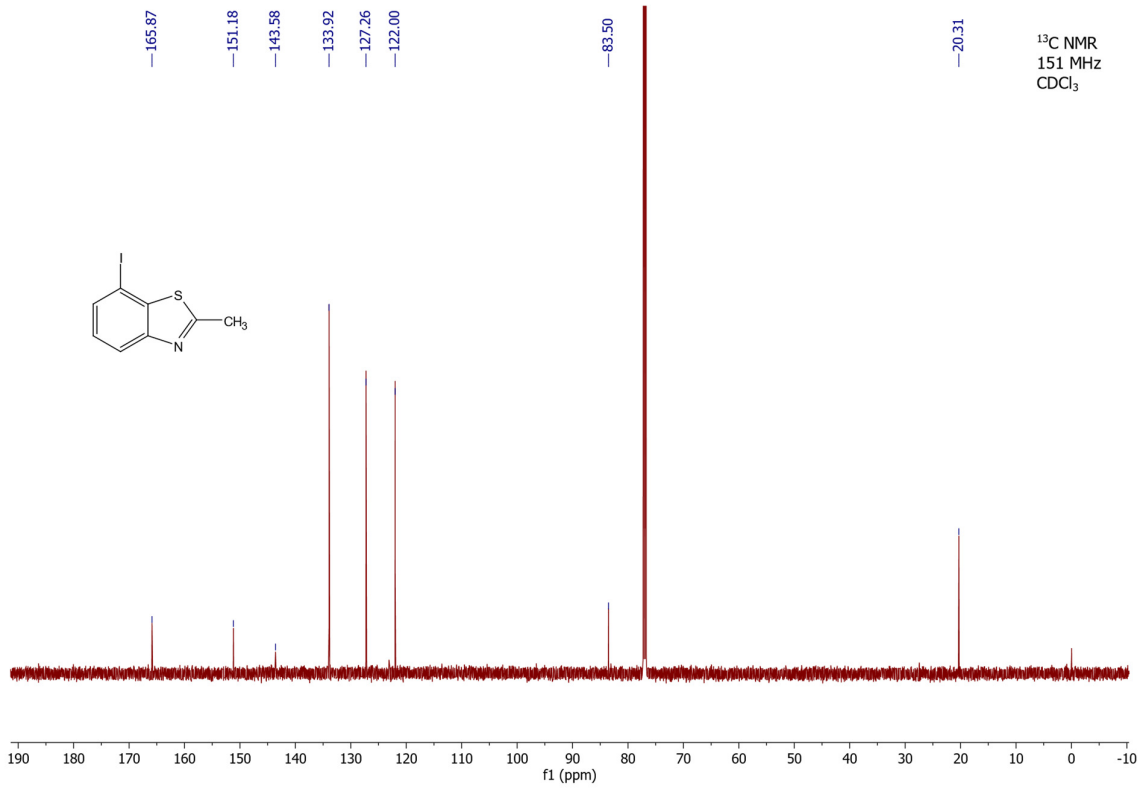
6-Iodo-2-methylbenzothiazole (**1-Me**)



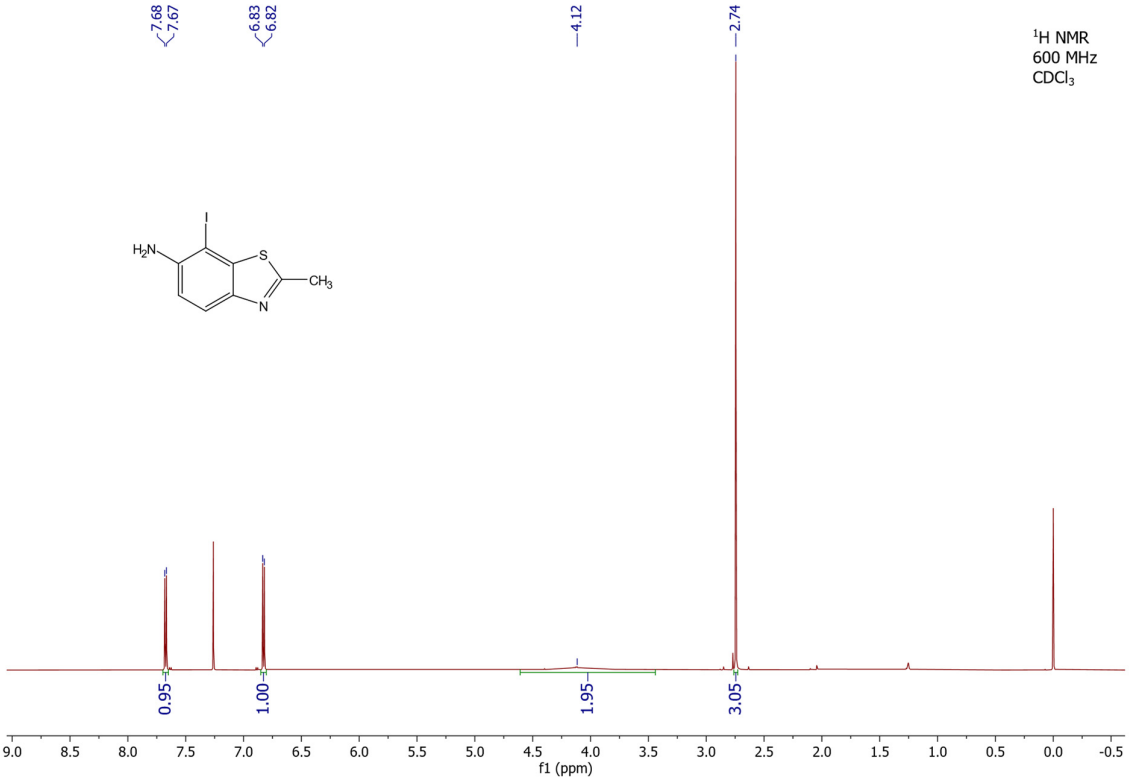


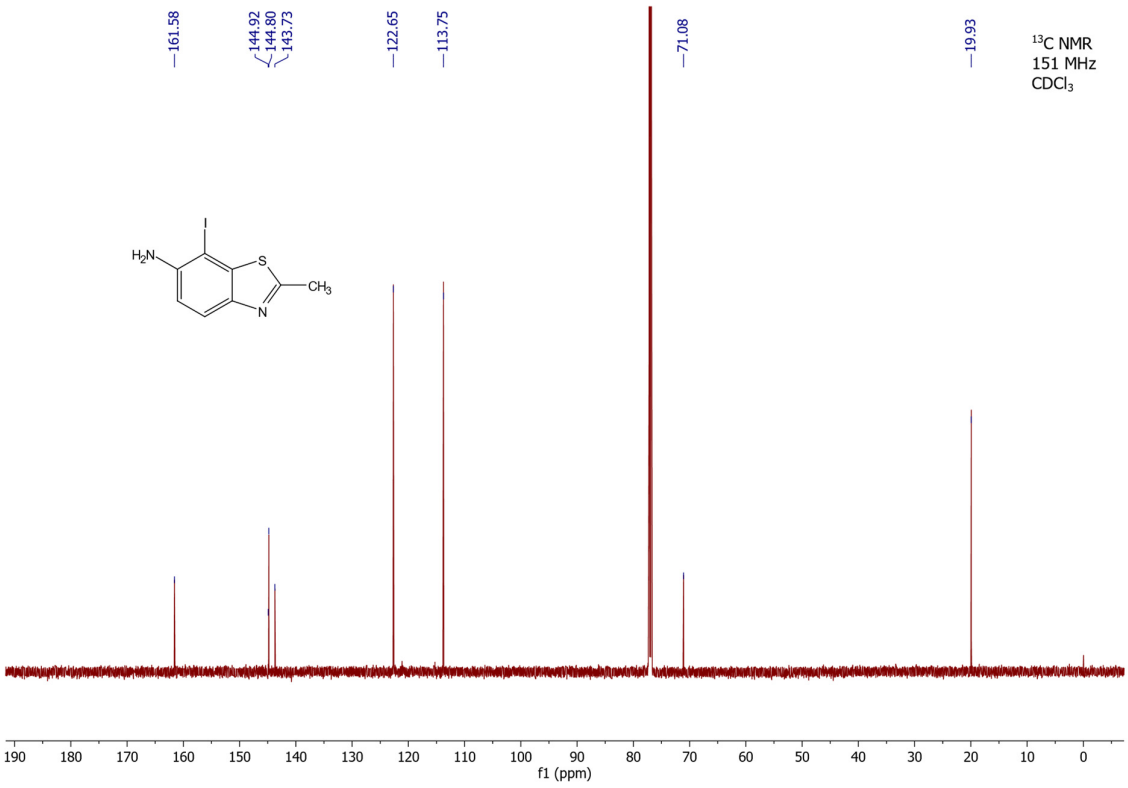
7-Iodo-2-methylbenzothiazole



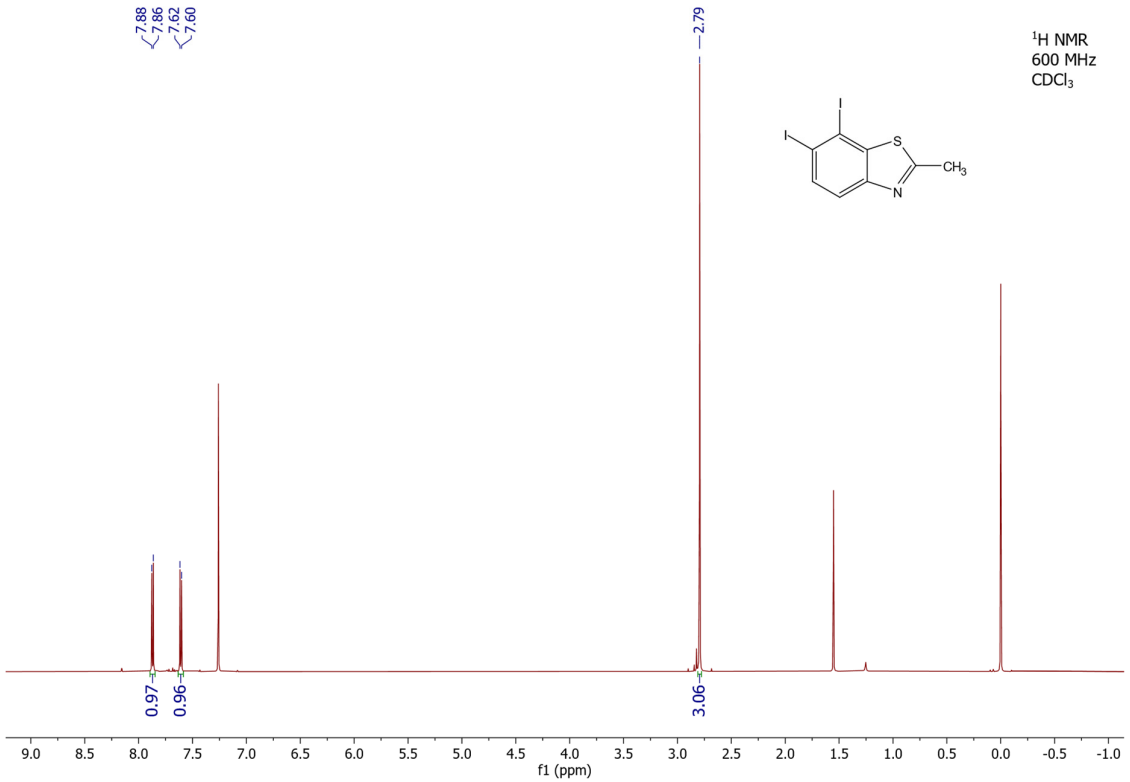


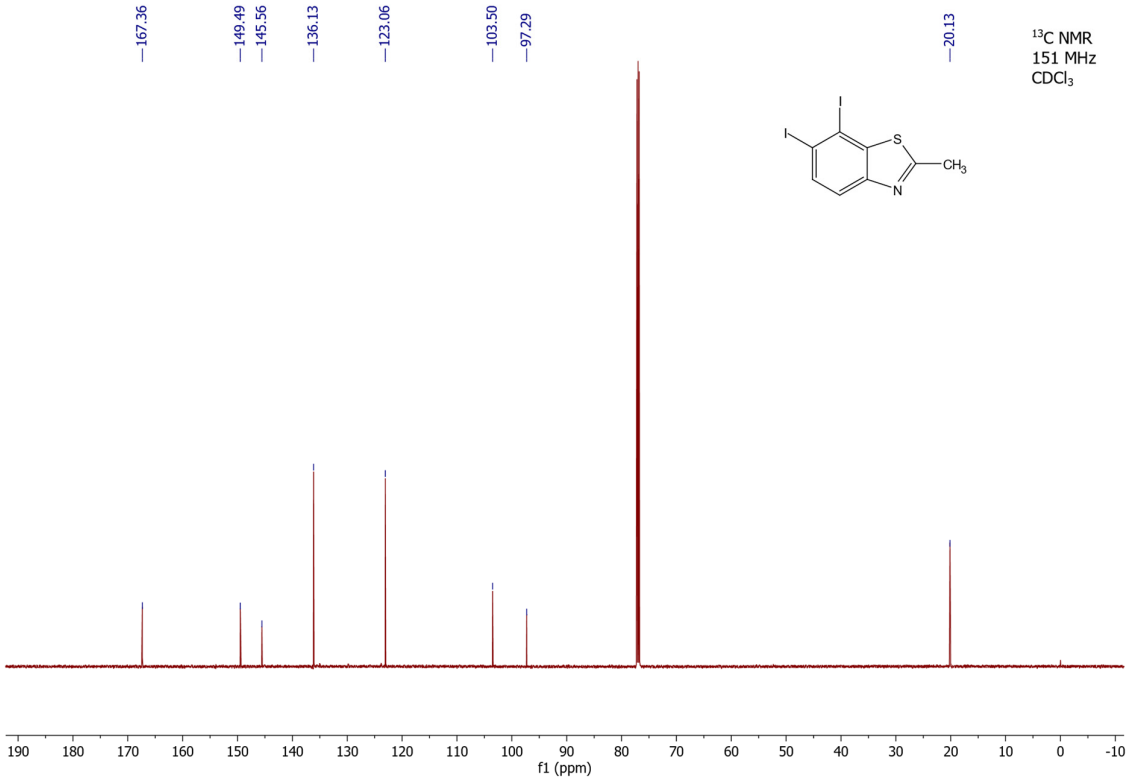
7-Iodo-2-methylbenzothiazol-6-amine



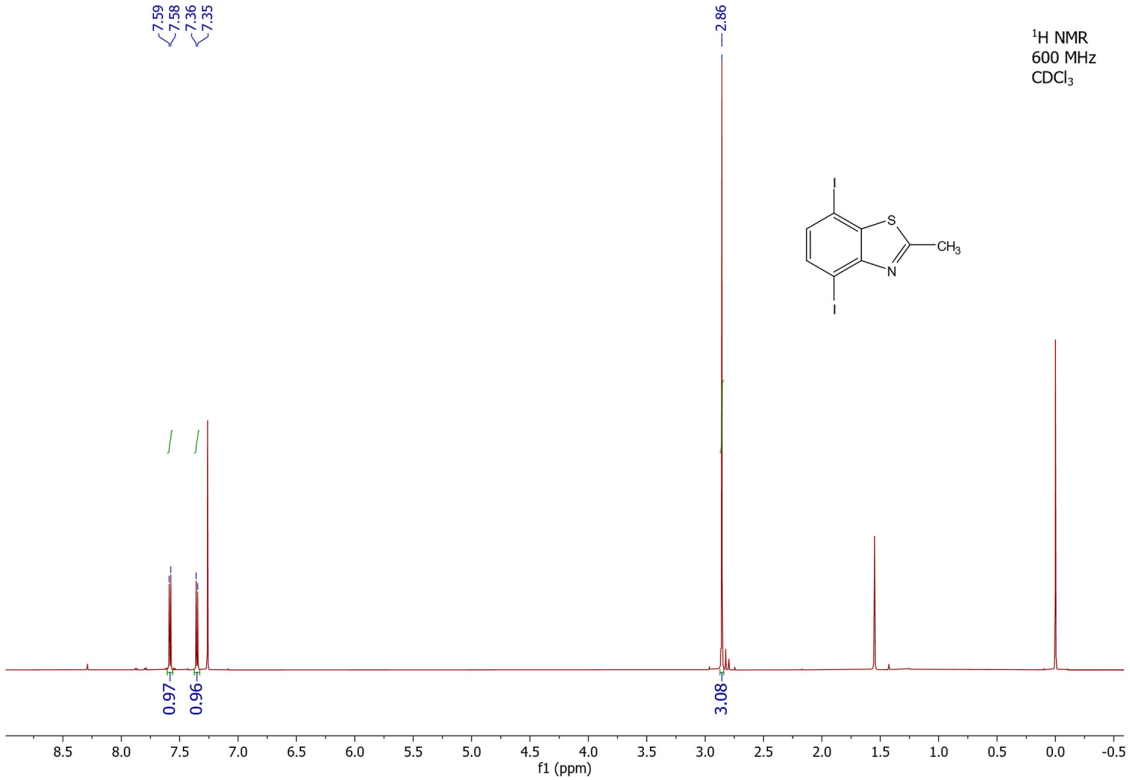


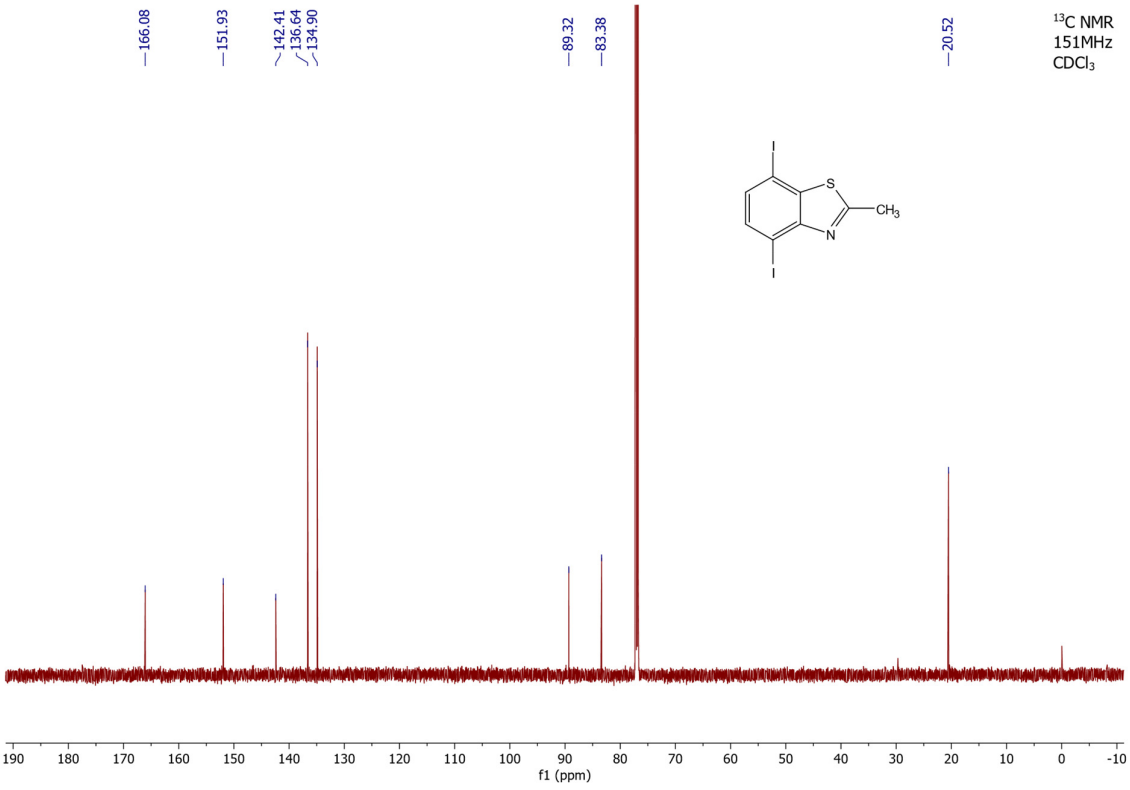
6,7-Diiodo-2-methylbenzothiazole



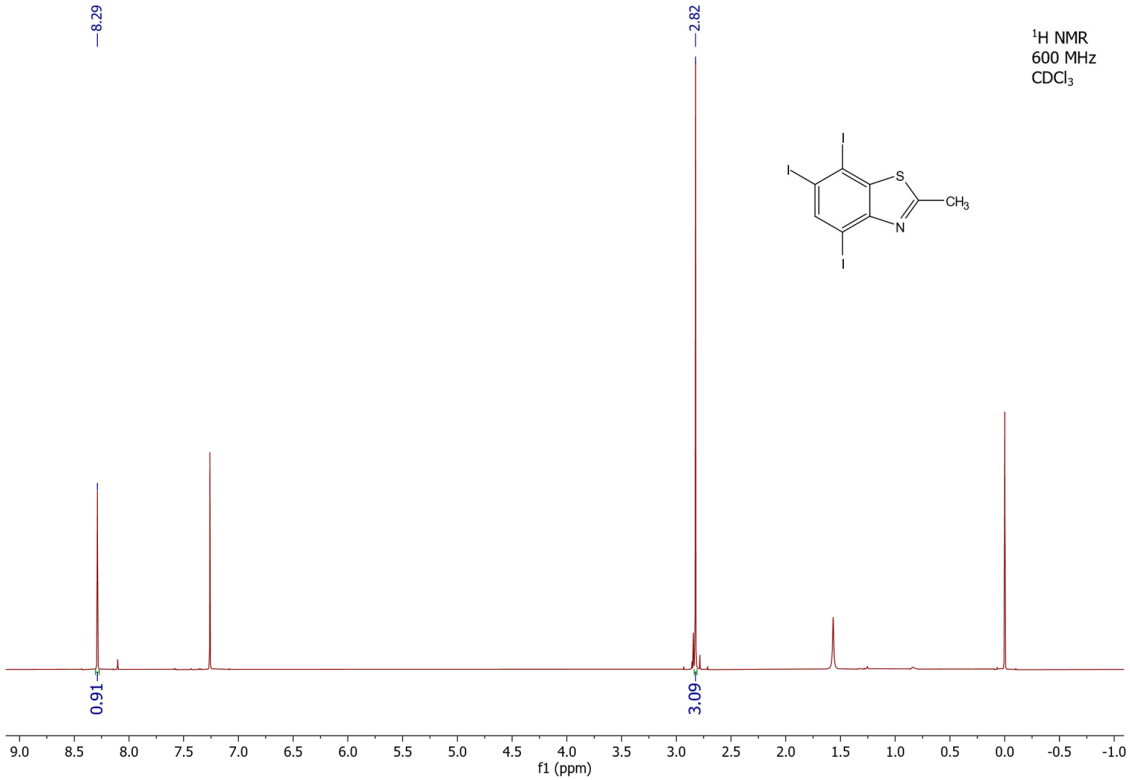


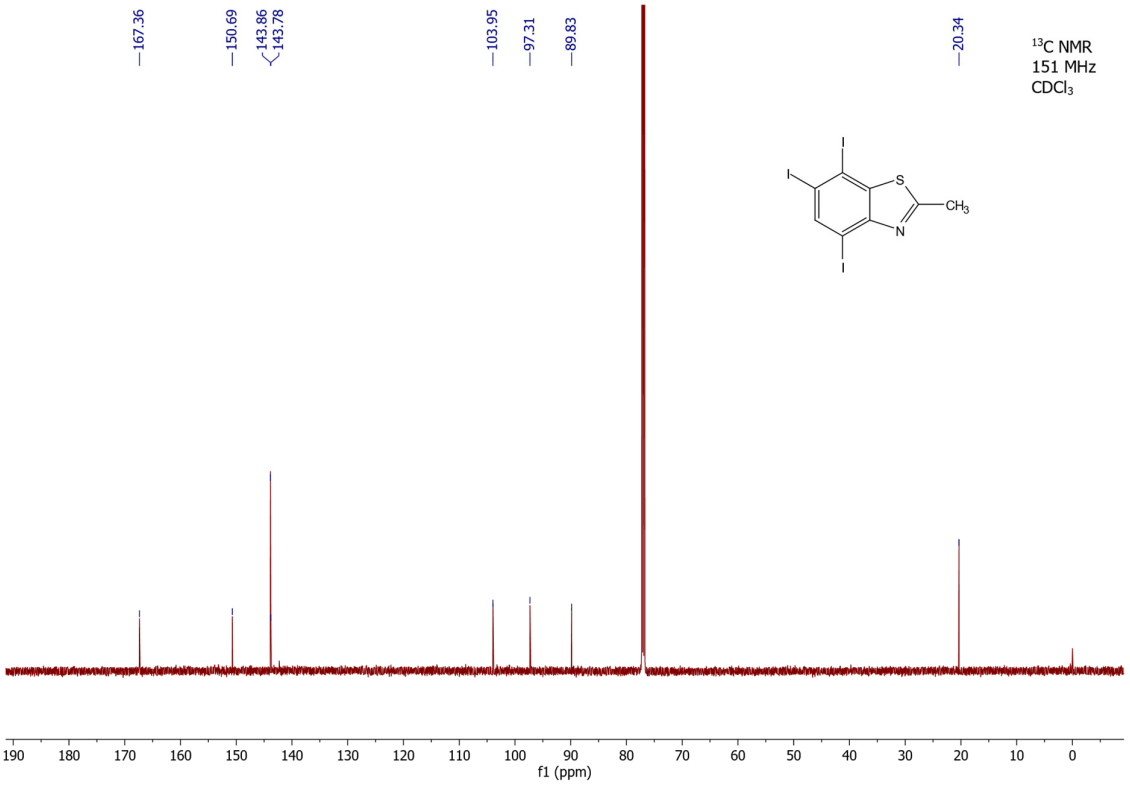
4,7-Diiodo-2-methylbenzothiazole (**2-Me**)



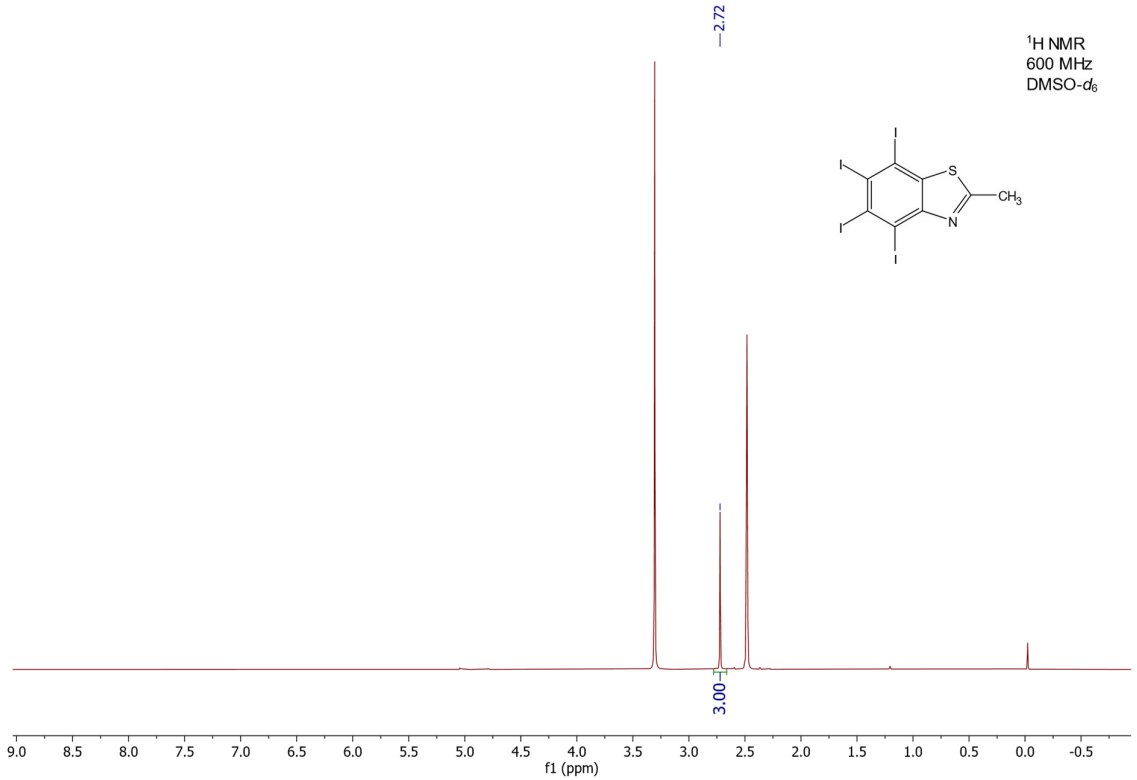


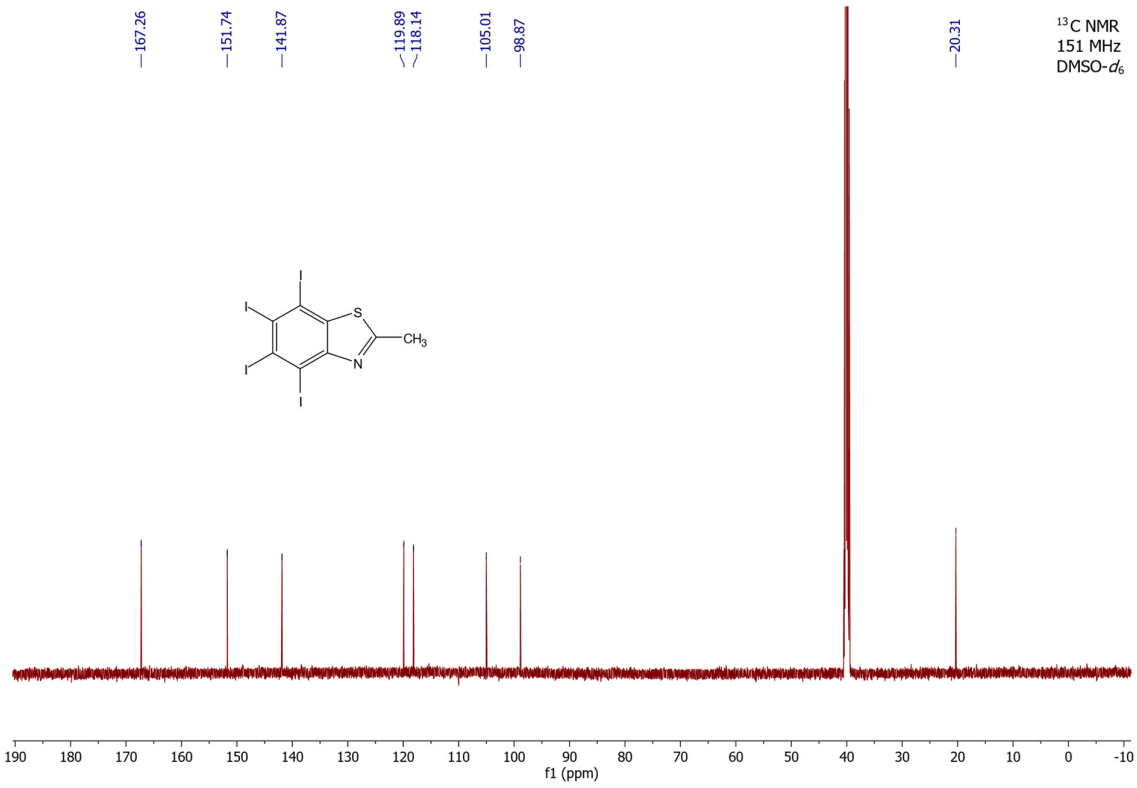
4,6,7-Triiodo-2-methylbenzothiazole (**3-Me**)



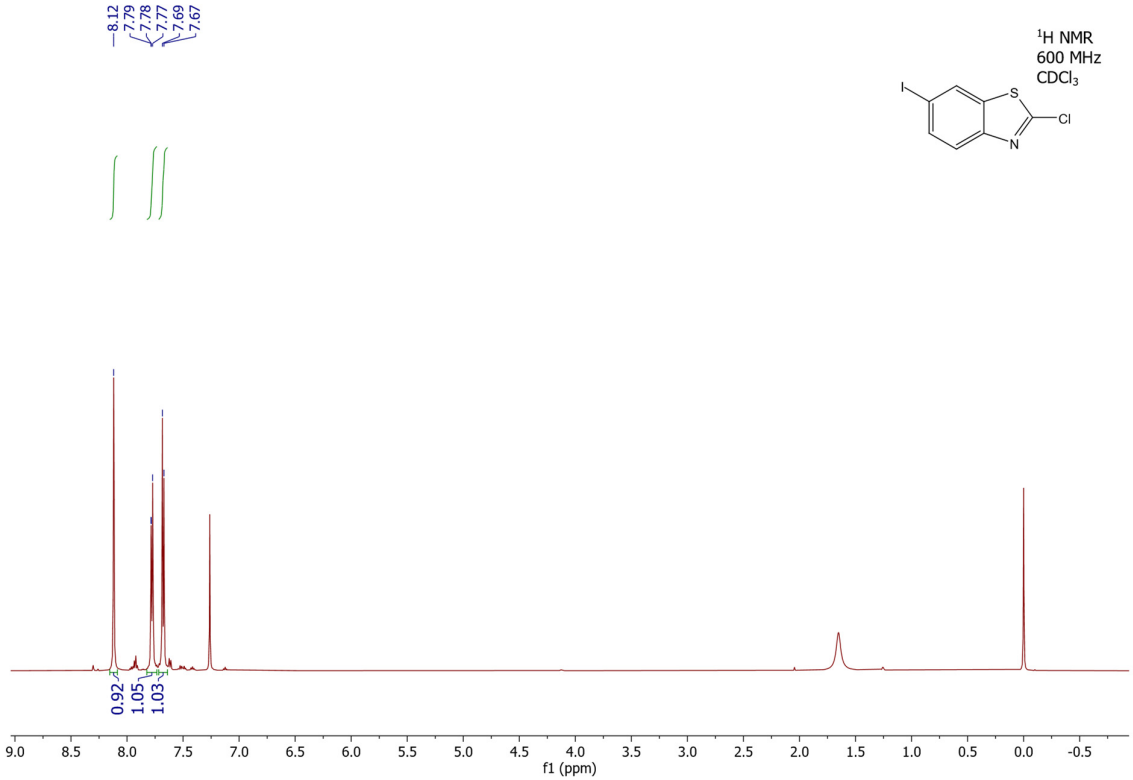


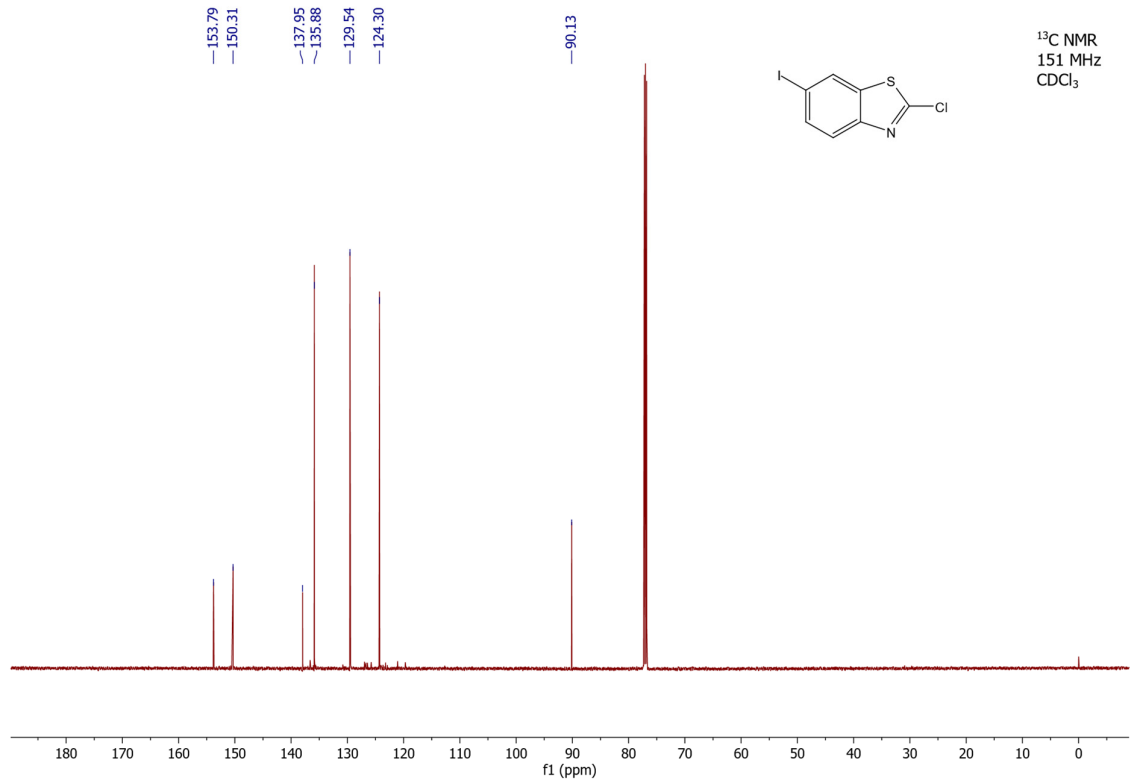
4,5,6,7-Tetraiodo-2-methylbenzothiazole (**4-Me**)



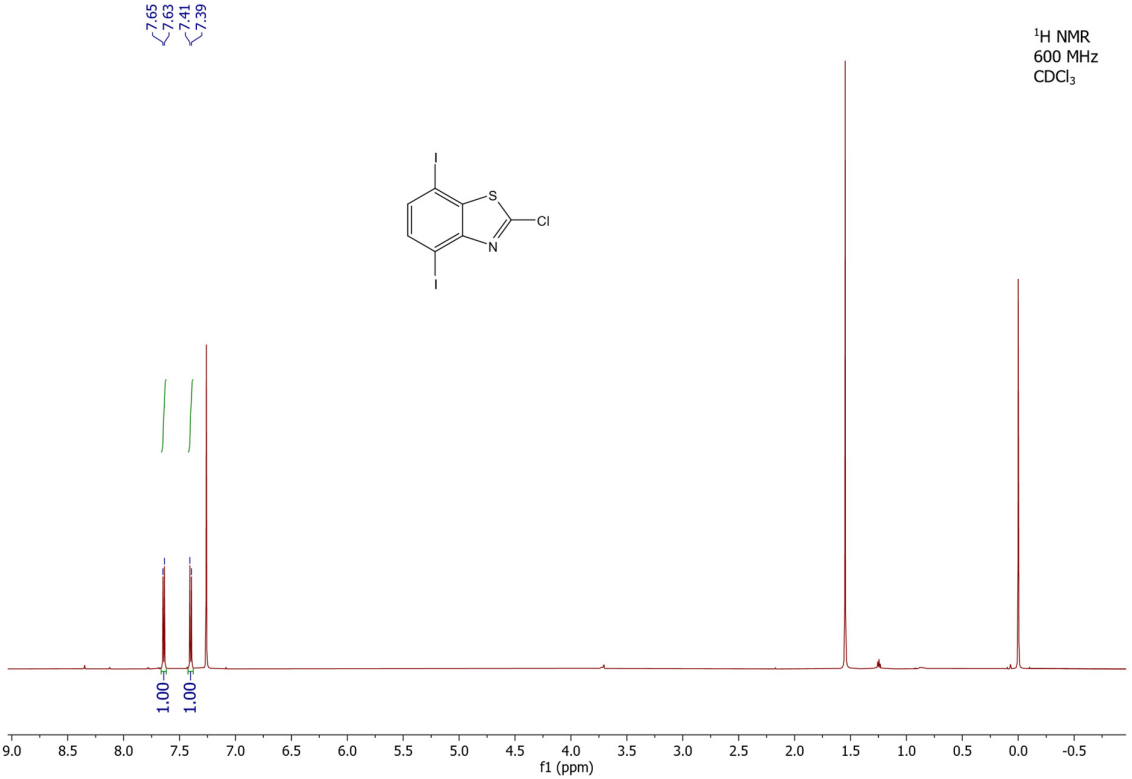


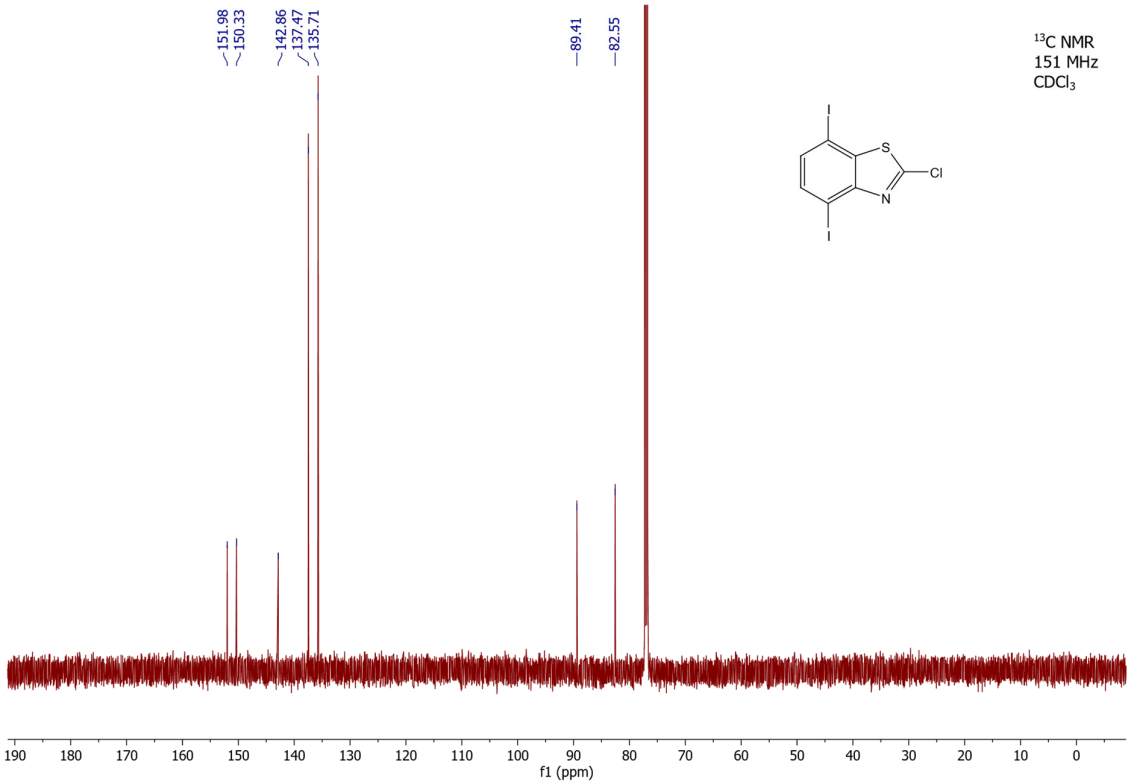
2-Chloro-6-iodobenzothiazole (**1-Cl**)



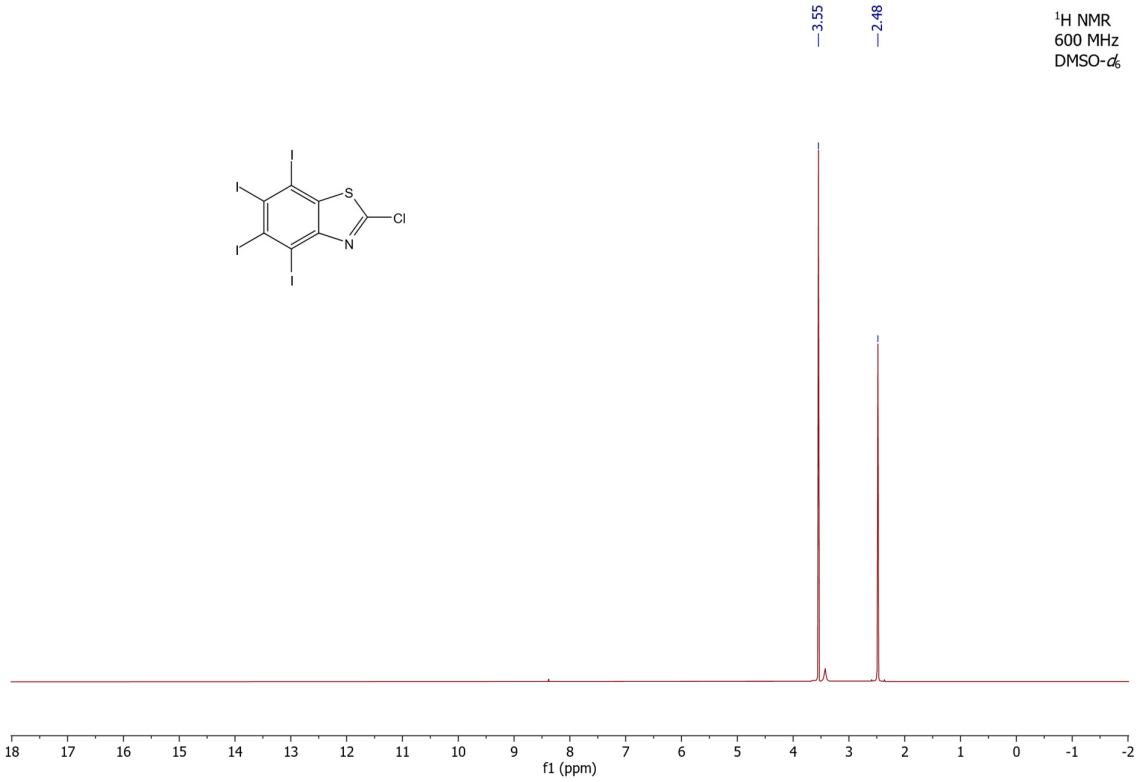


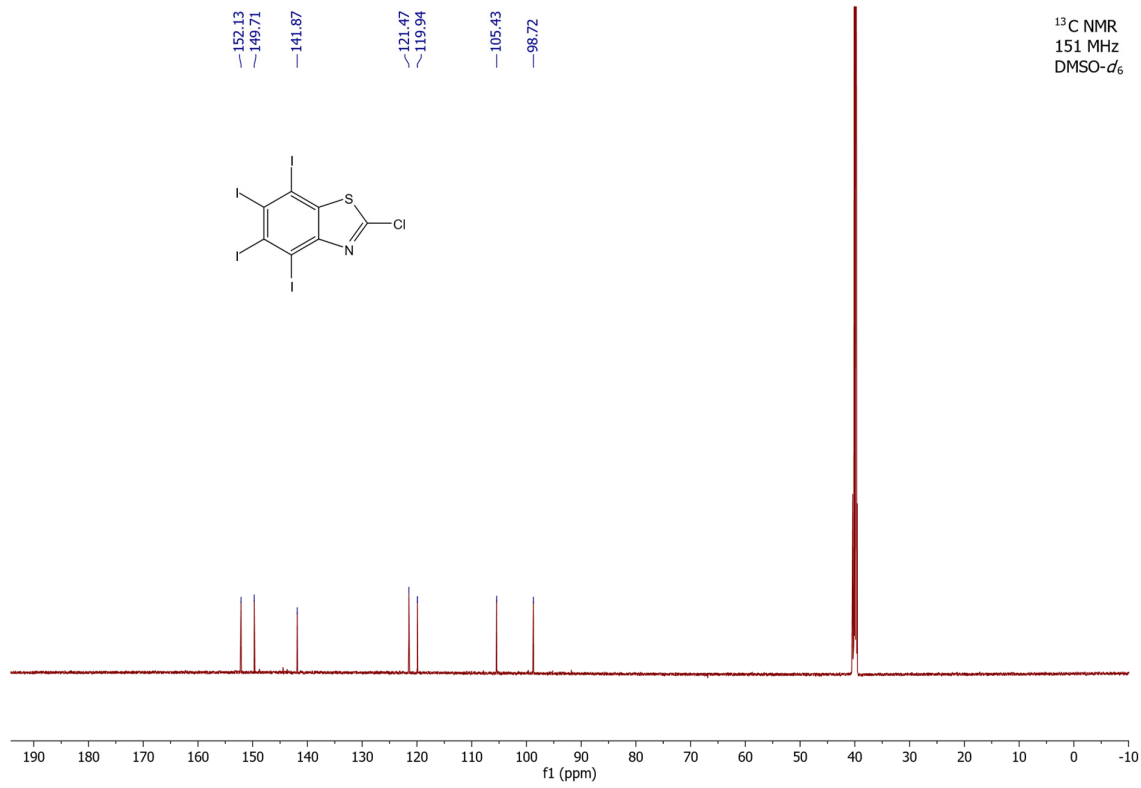
2-Chloro-4,7-diiodobenzothiazole (**2-Cl**)



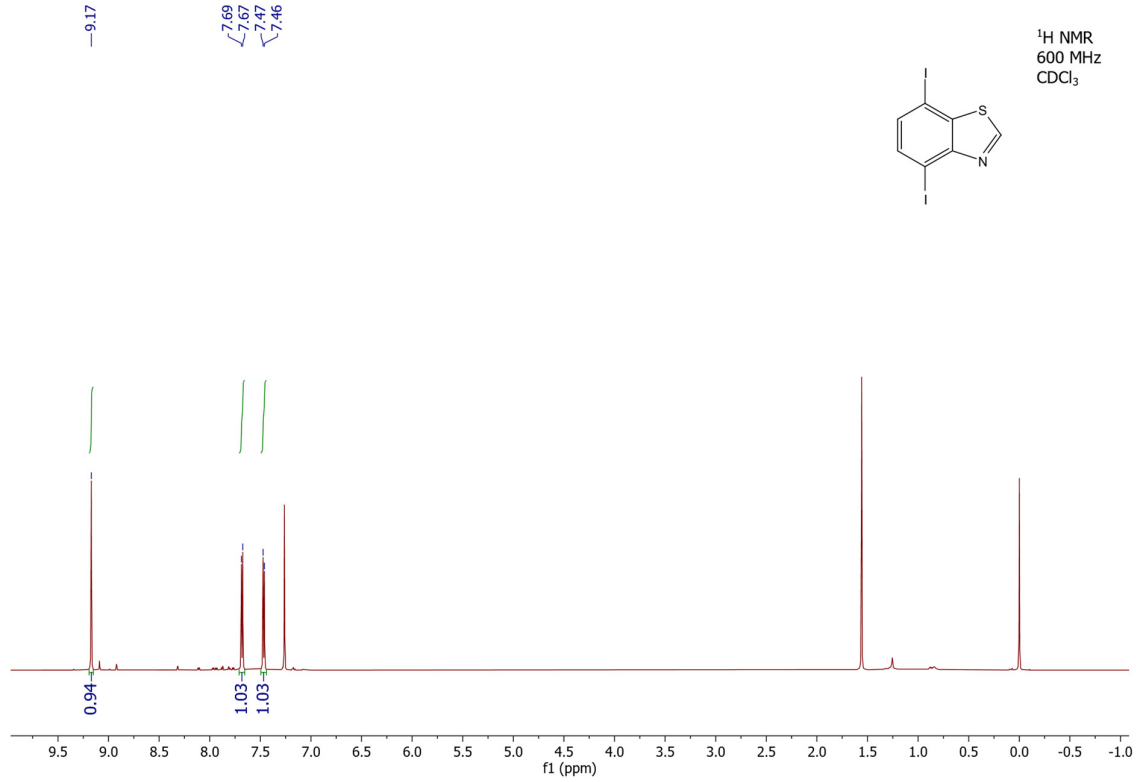


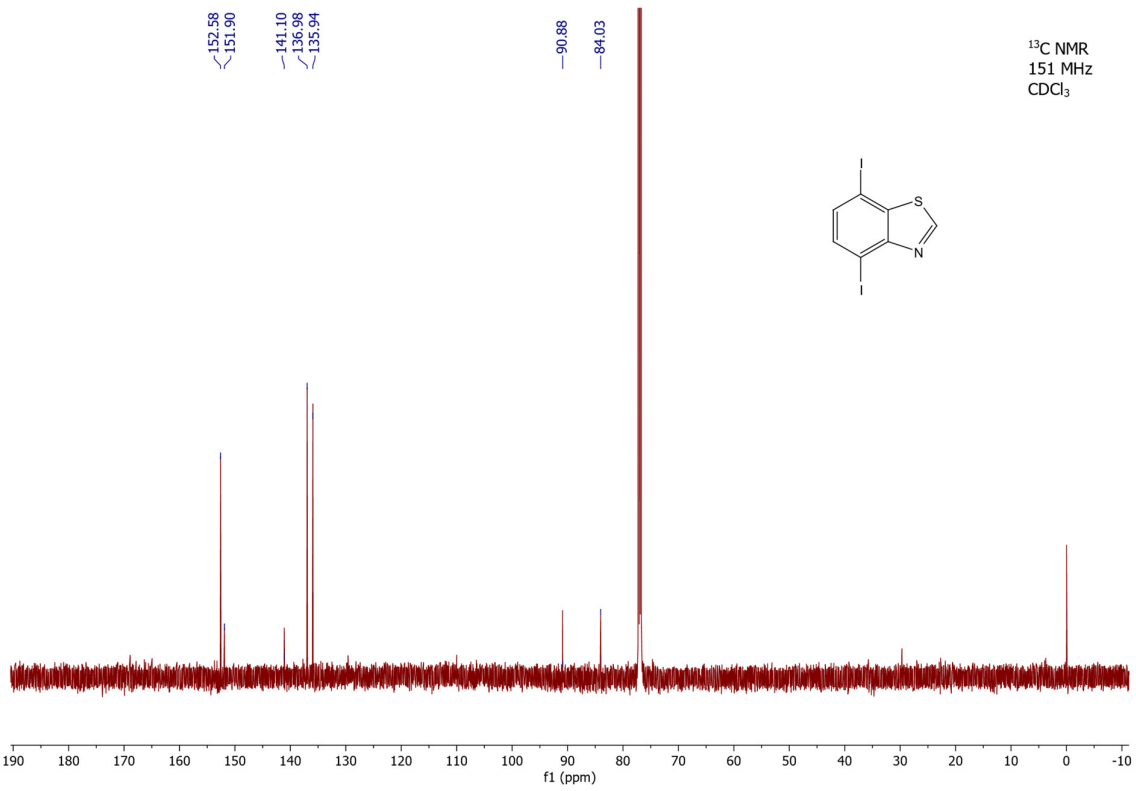
2-Chloro-4,5,6,7-tetraiodobenzothiazole (**4-Cl**)



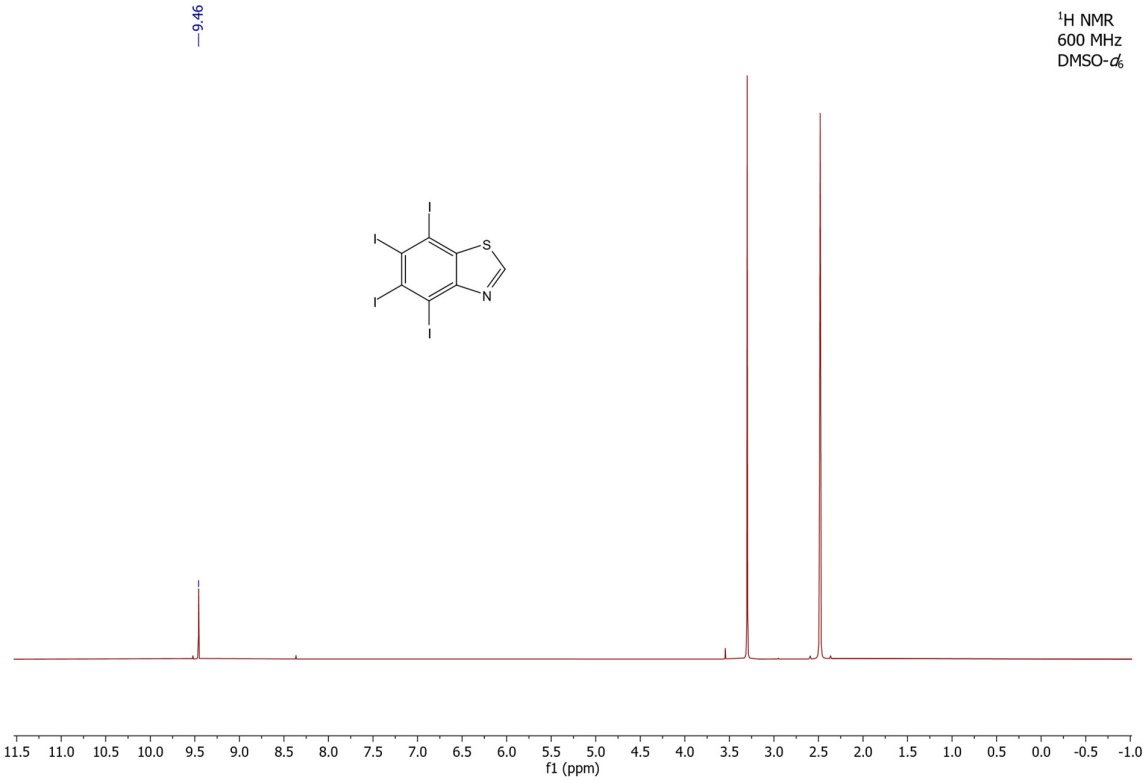


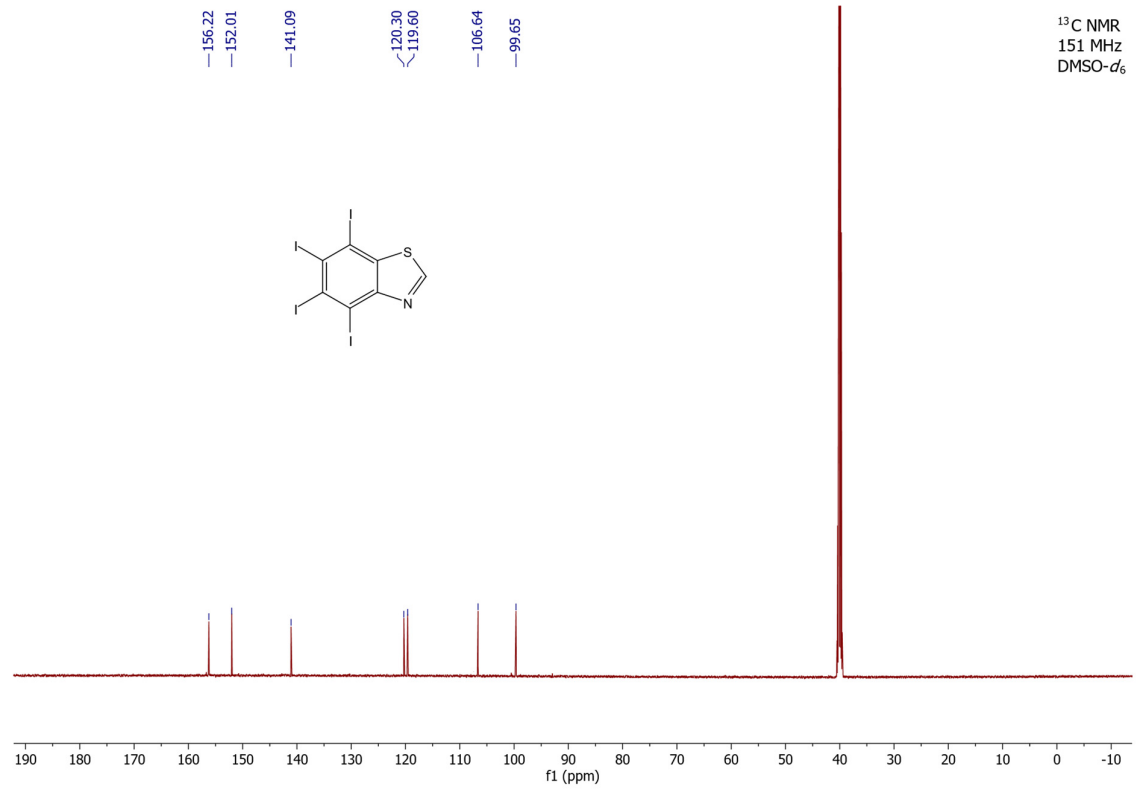
4,7-Diiodobenzothiazole (**2-H**)



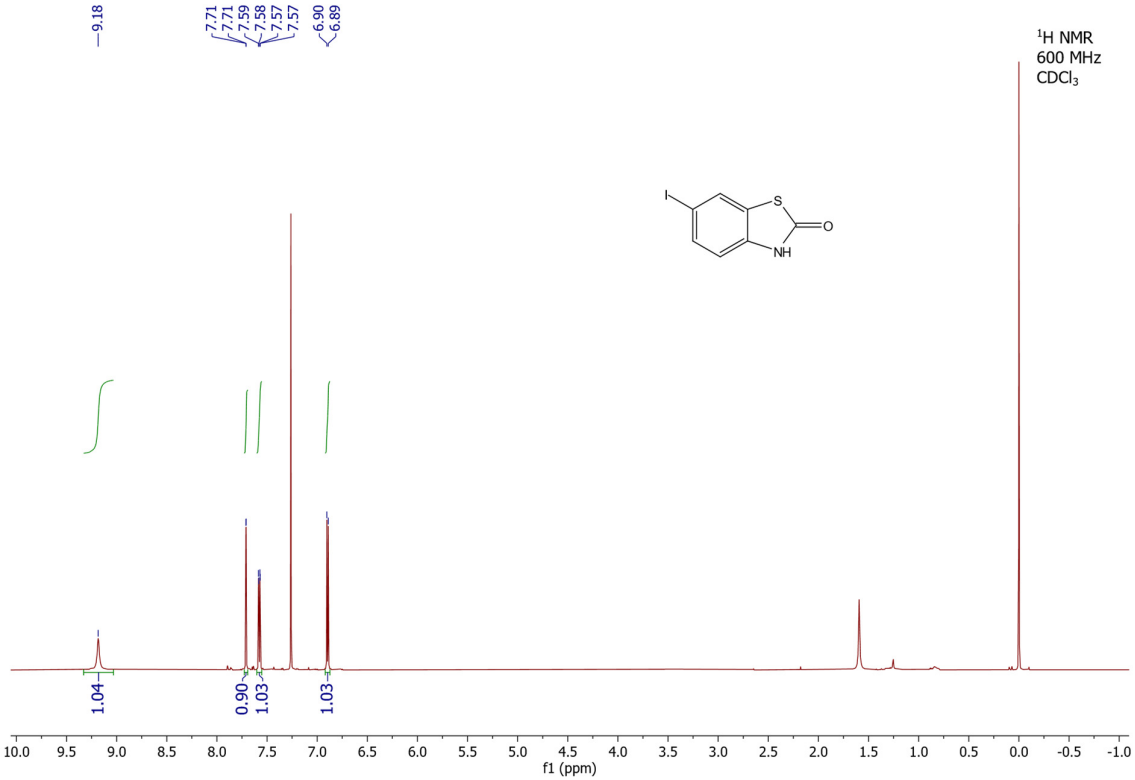


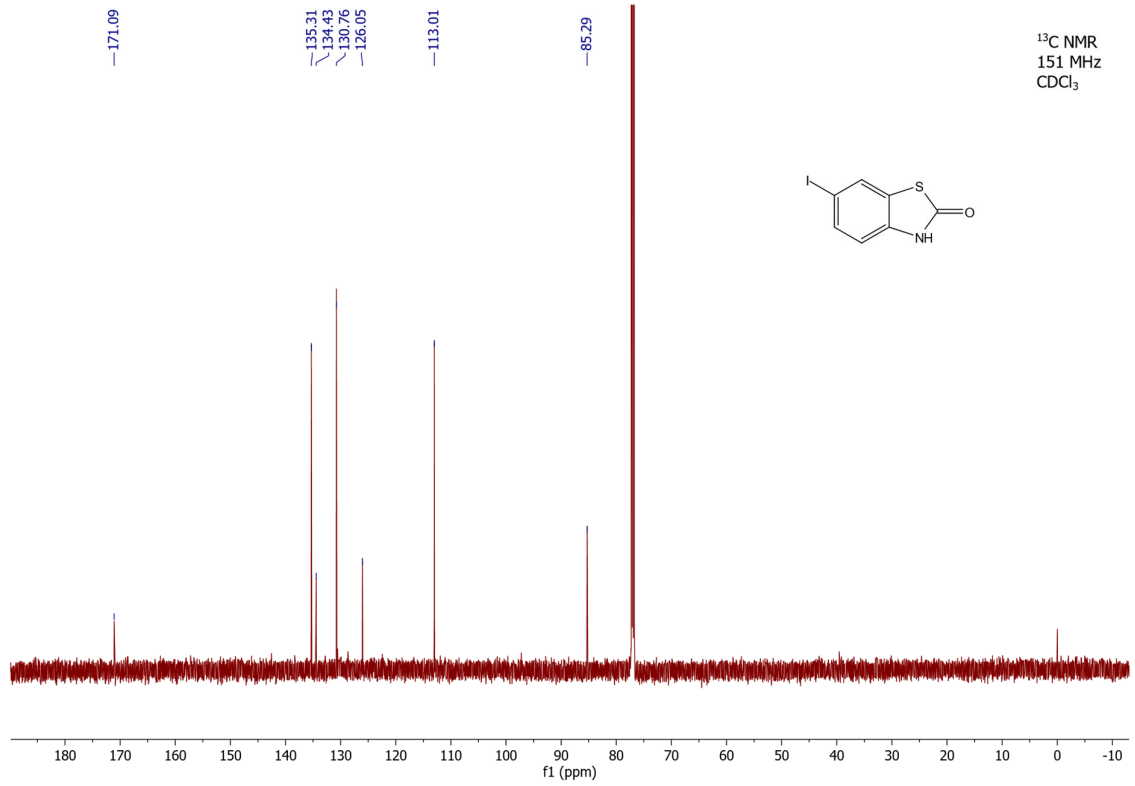
4,5,6,7-Tetraiodobenzothiazole (**4-H**)



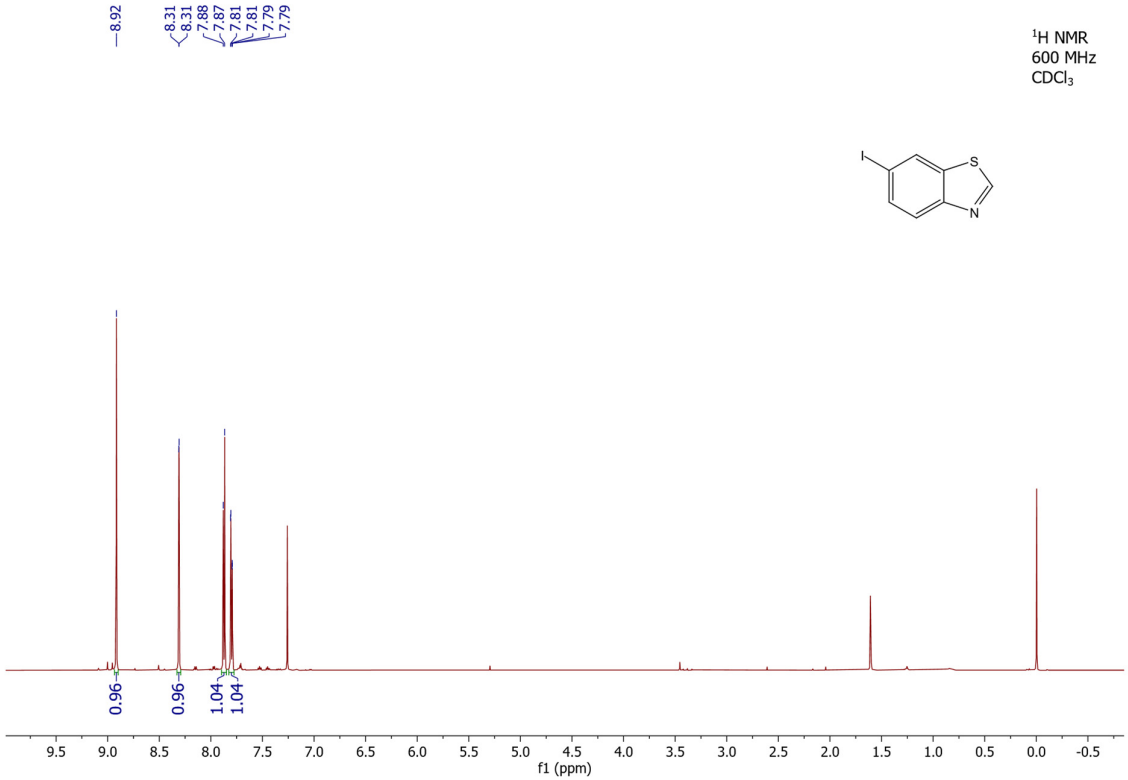


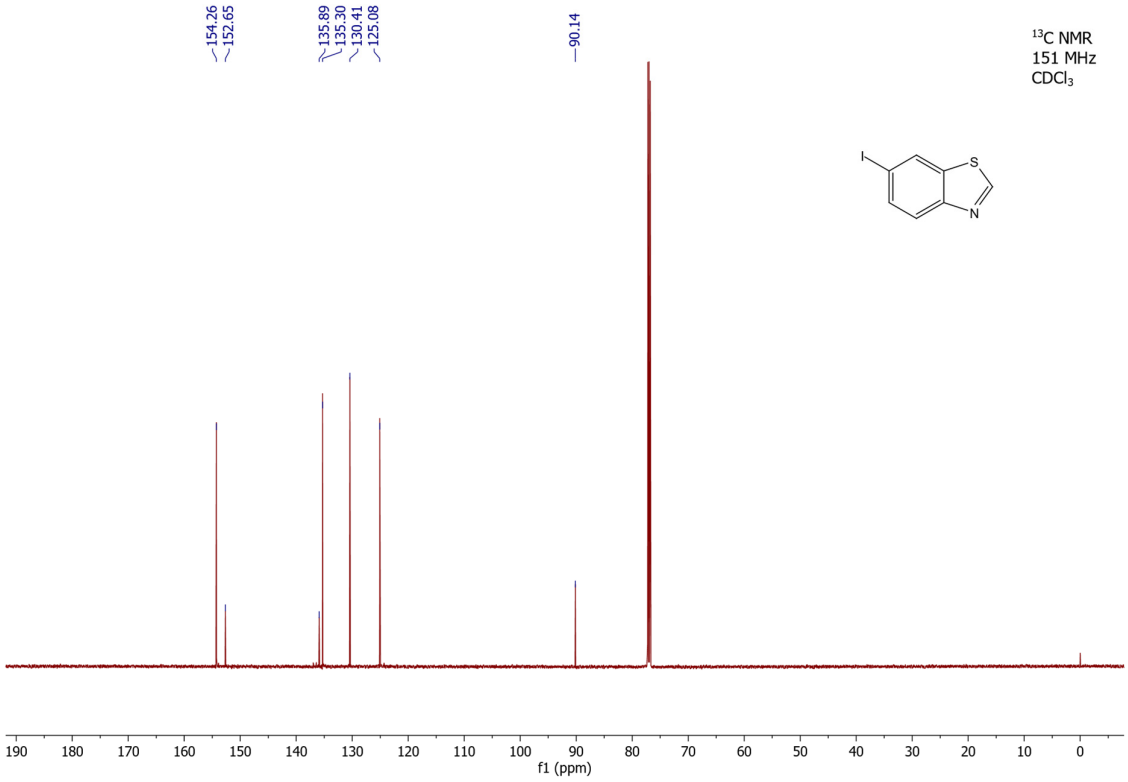
6-Iodobenzothiazol-2(3*H*)-one (**1-OH**)



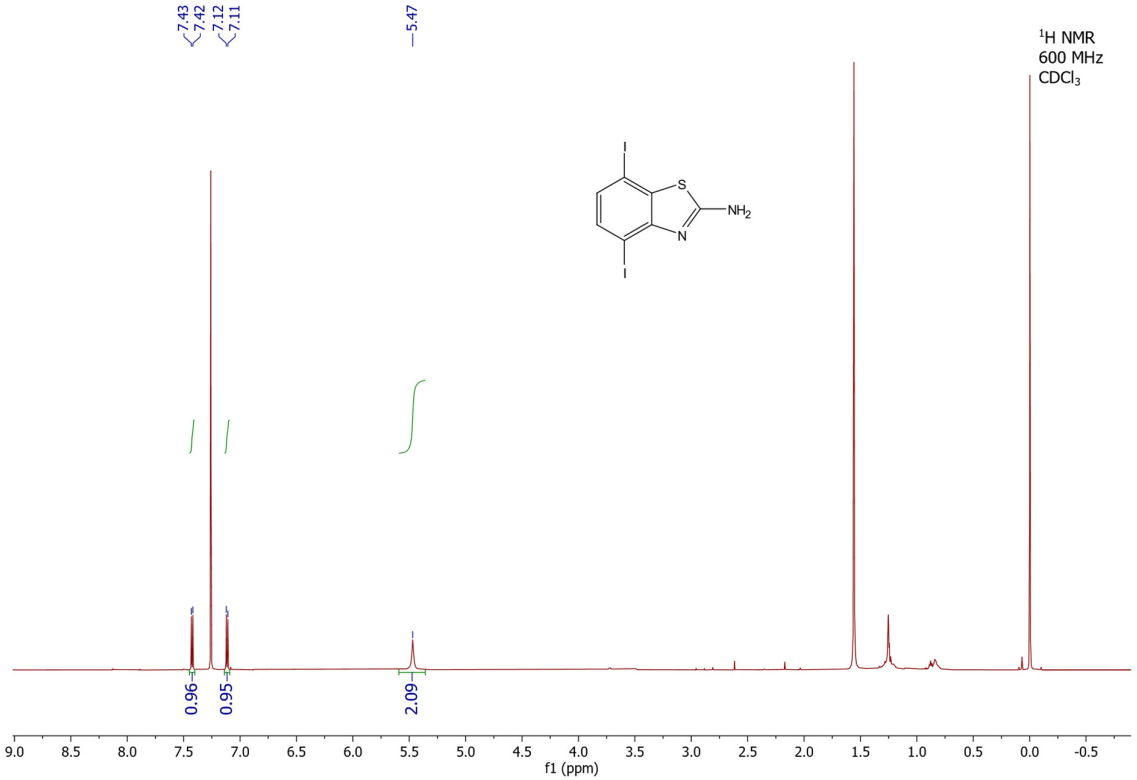


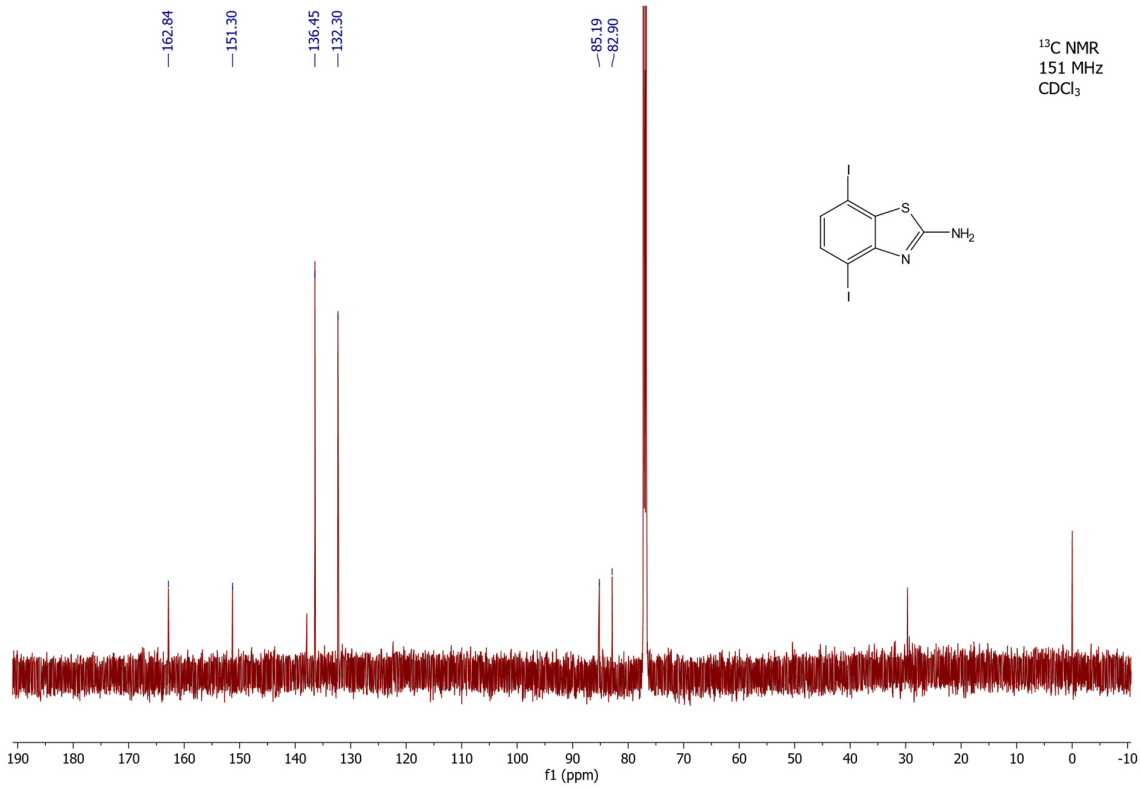
6-Iodobenzothiazole (**1-H**)



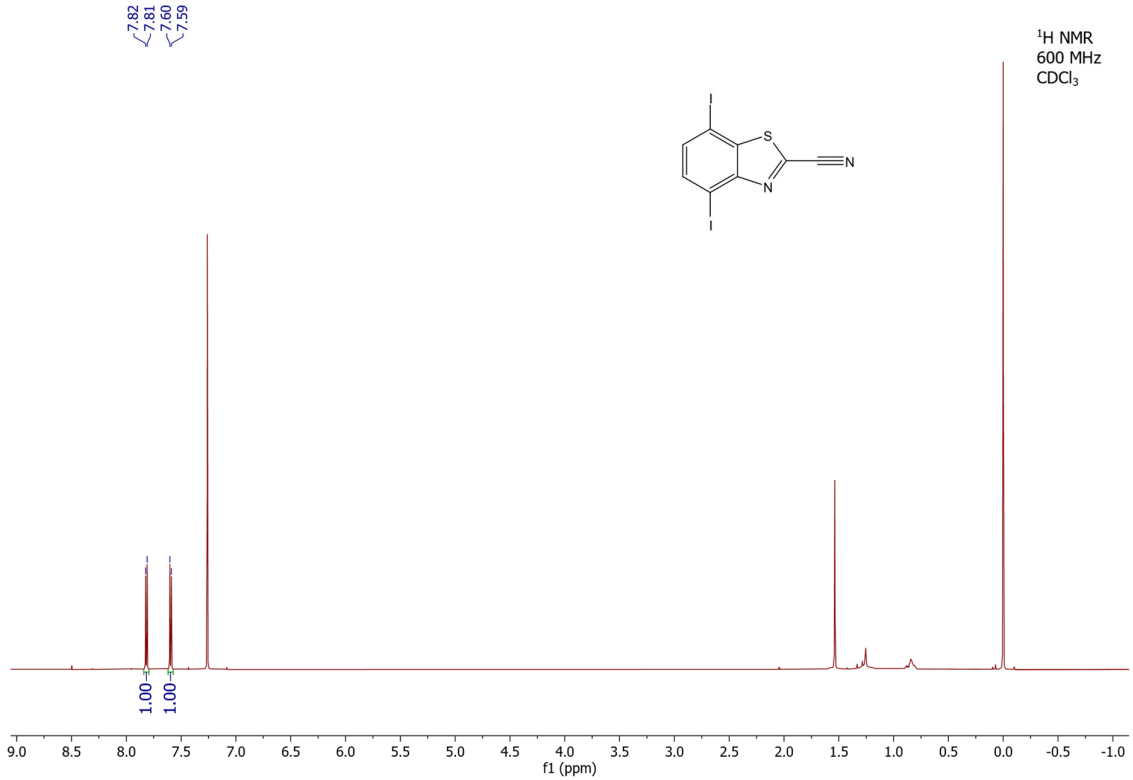


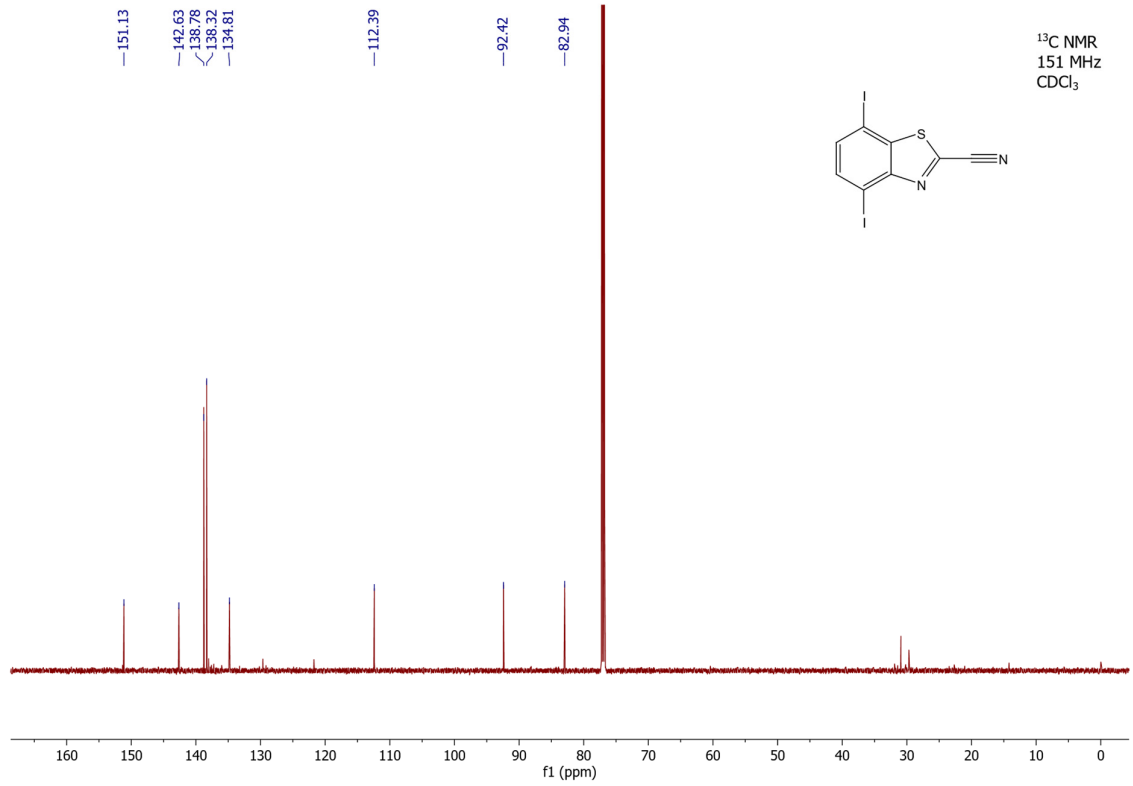
4,7-Diiodobenzothiazol-2-amine (**2-NH$_2$**)



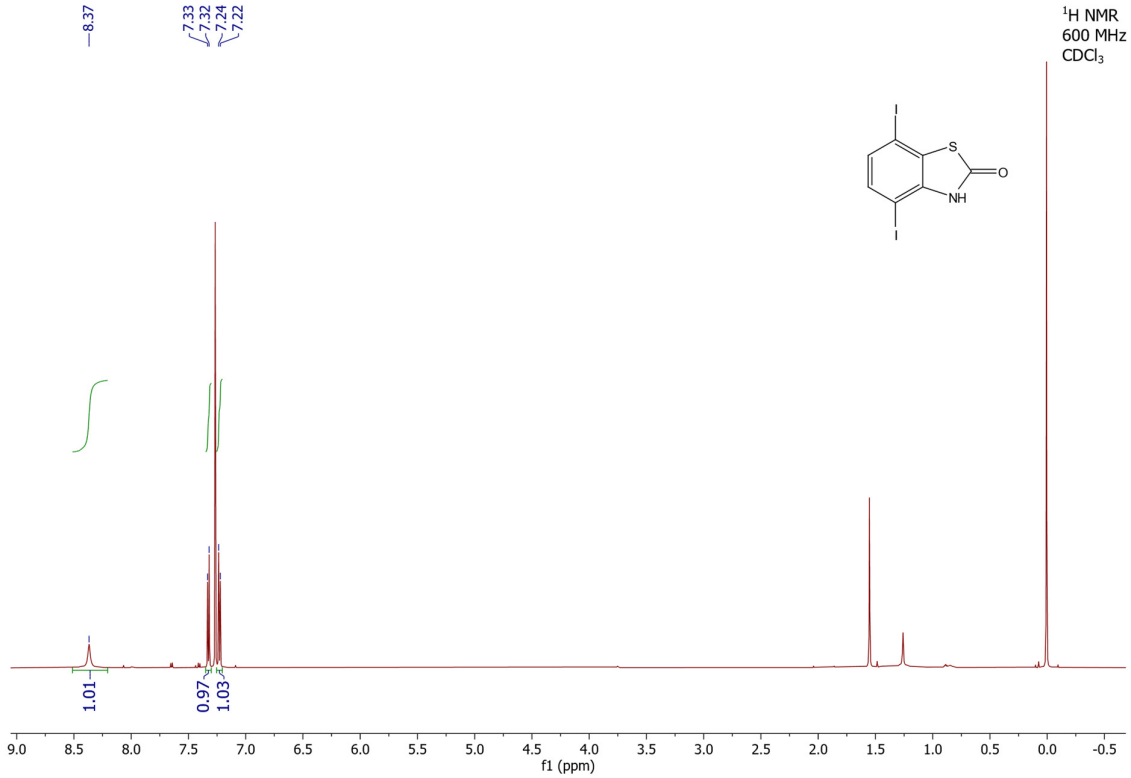


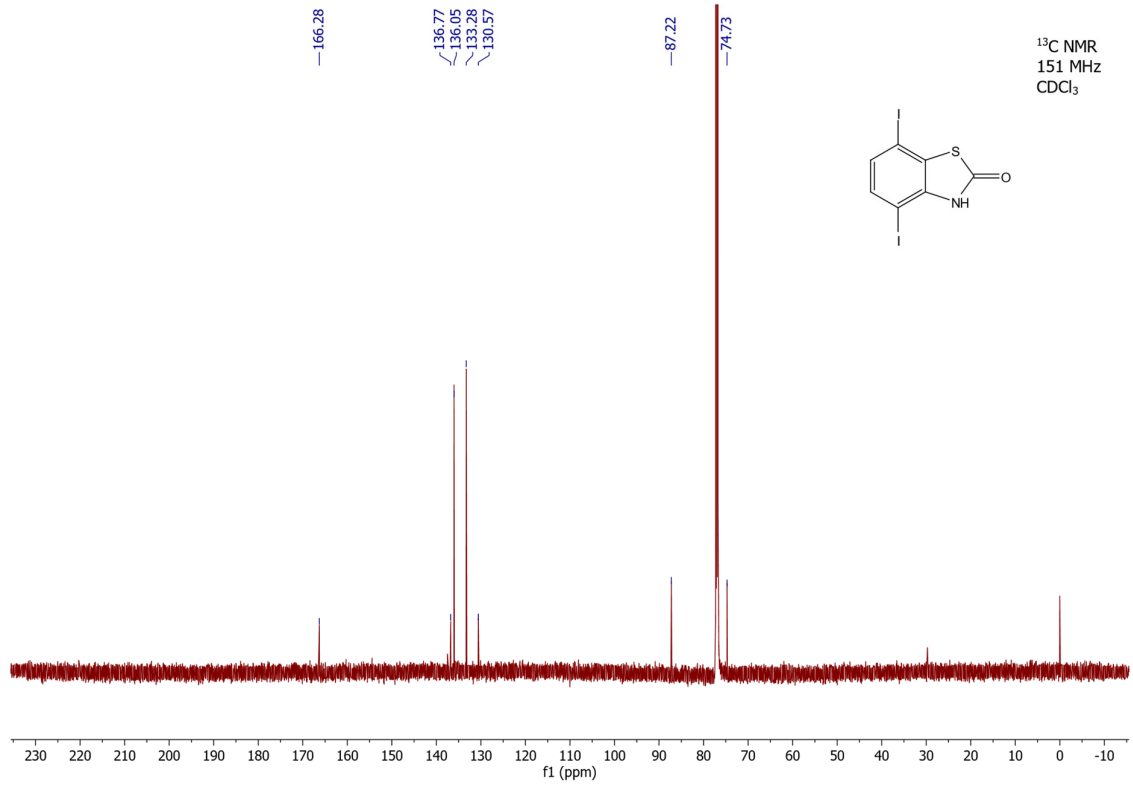
4,7-Diiodobenzothiazole-2-carbonitrile (**2-CN**)



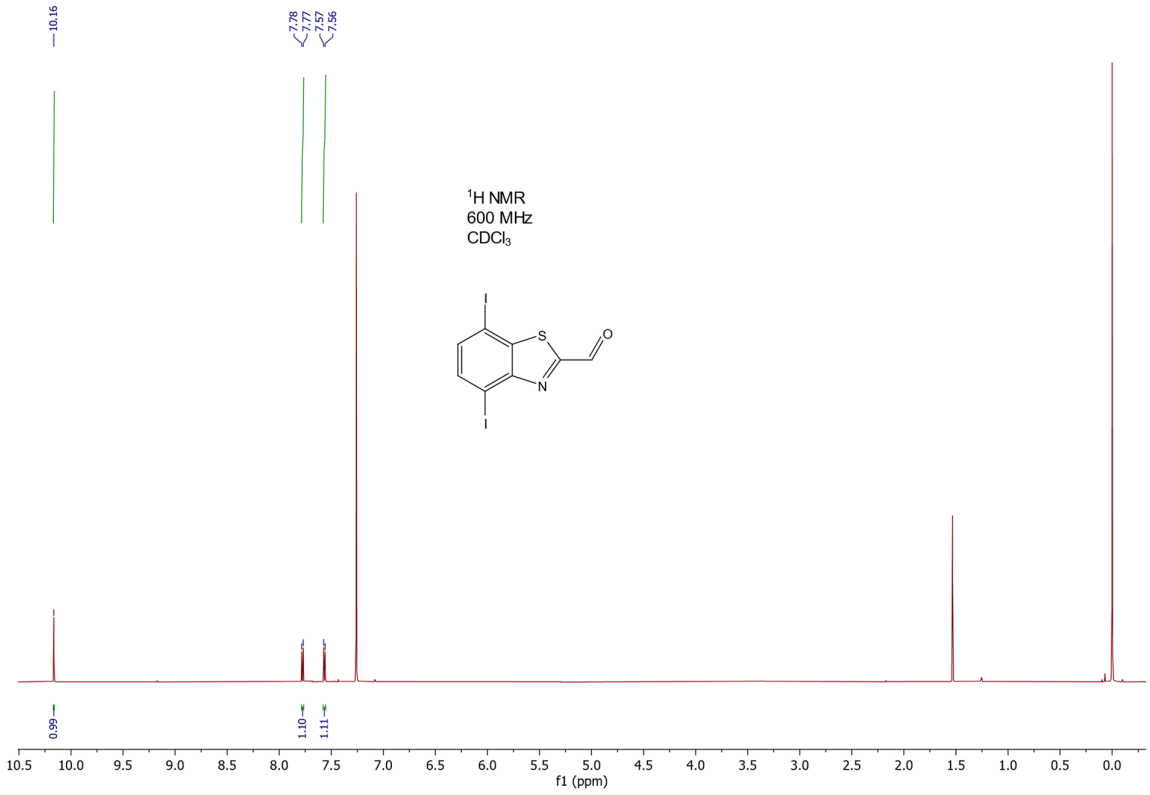


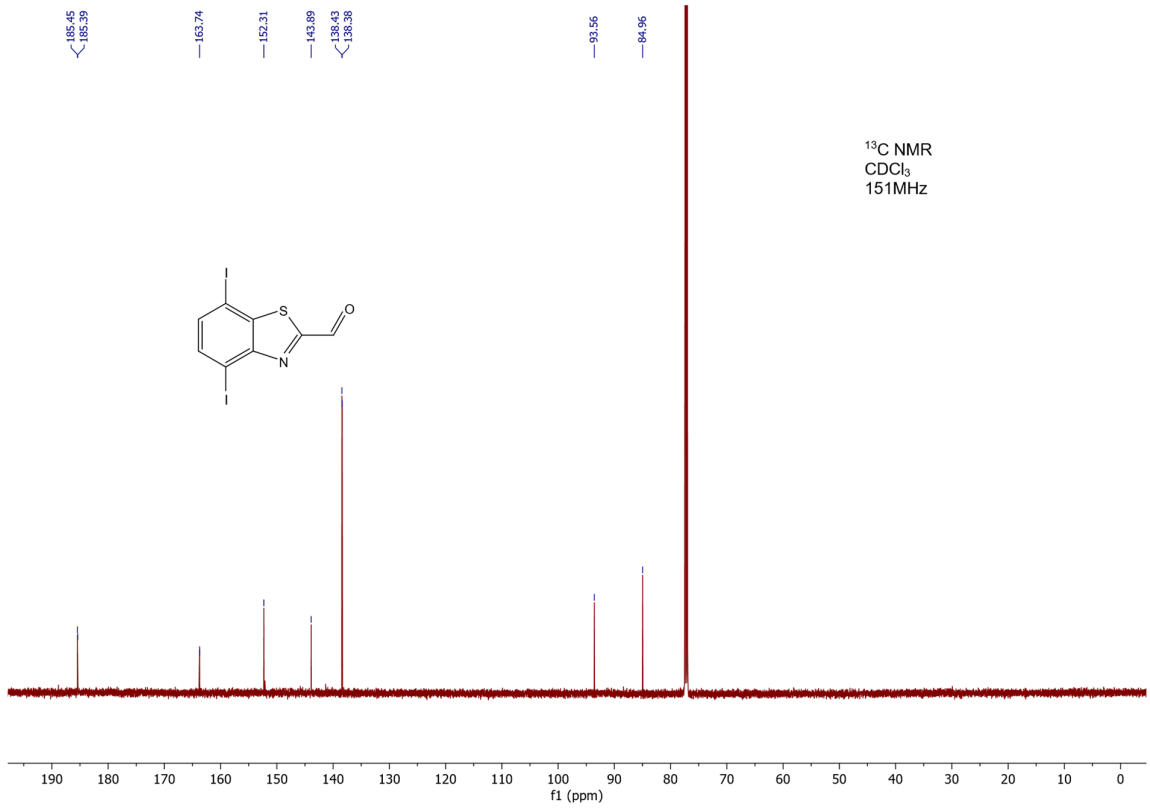
4,7-Diiodobenzothiazol-2(3*H*)-one (**2-OH**)



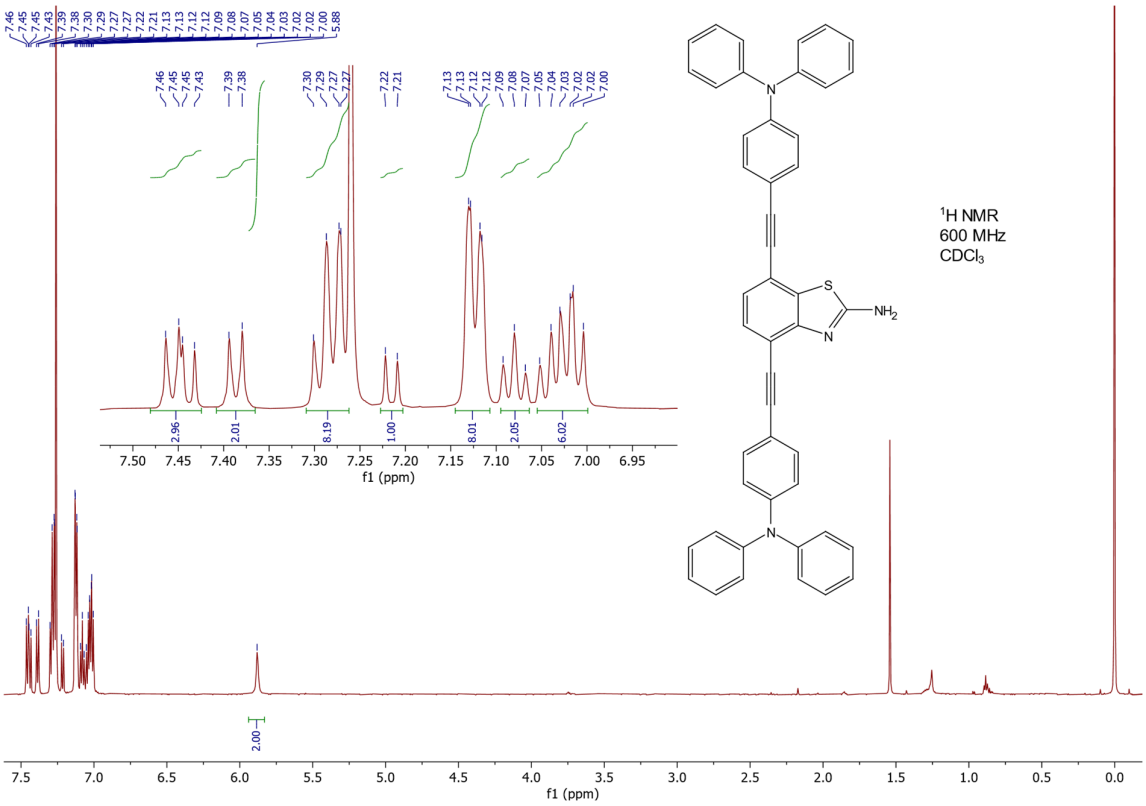


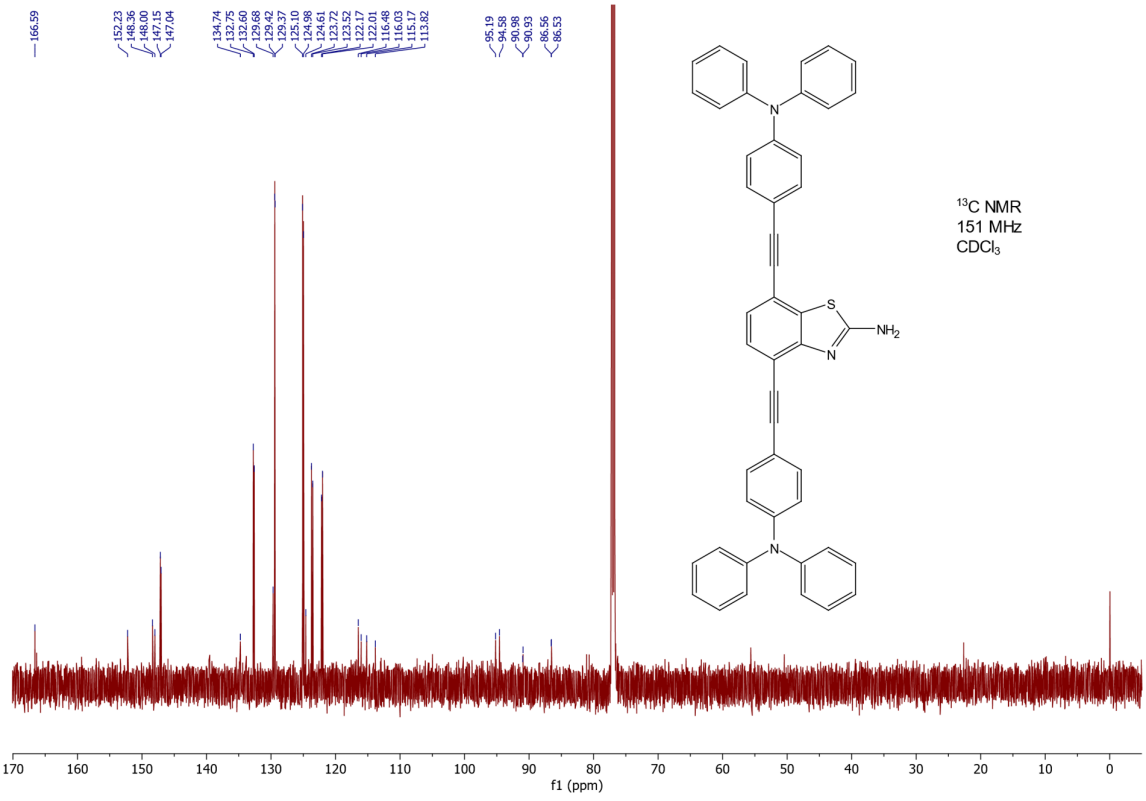
4,7-Diiodobenzothiazole-2-carbaldehyde (**2-CHO**)



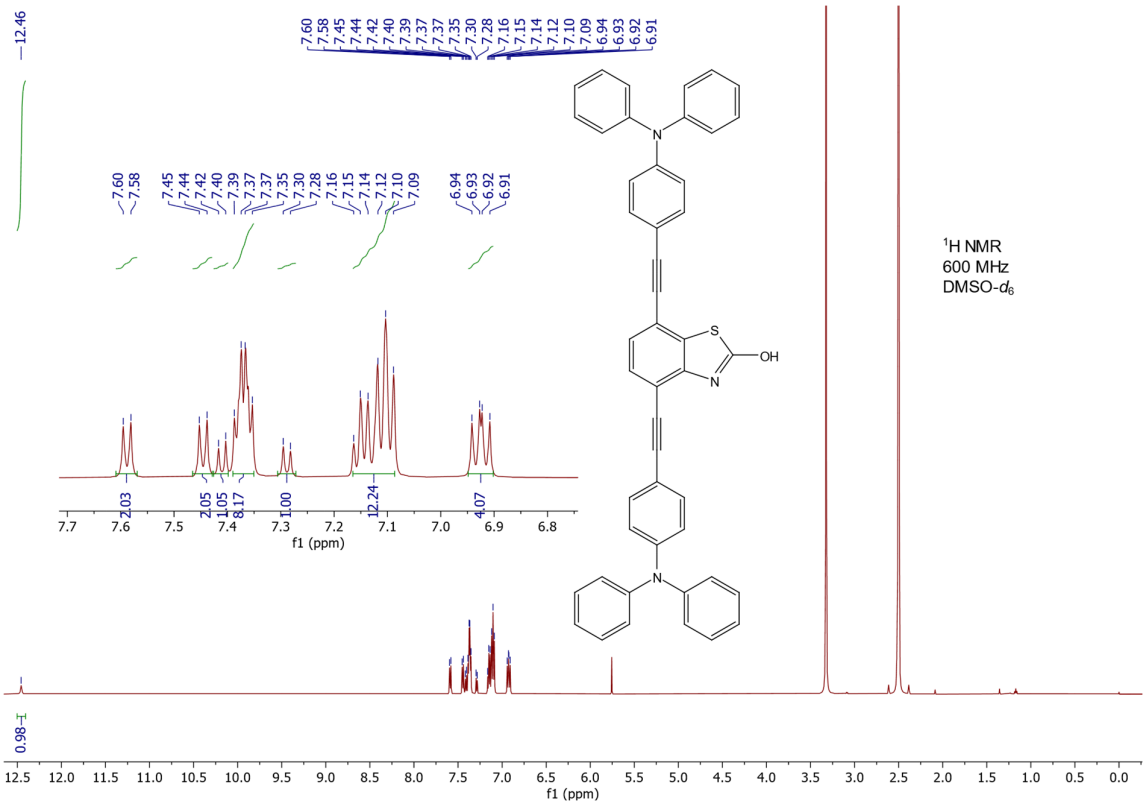


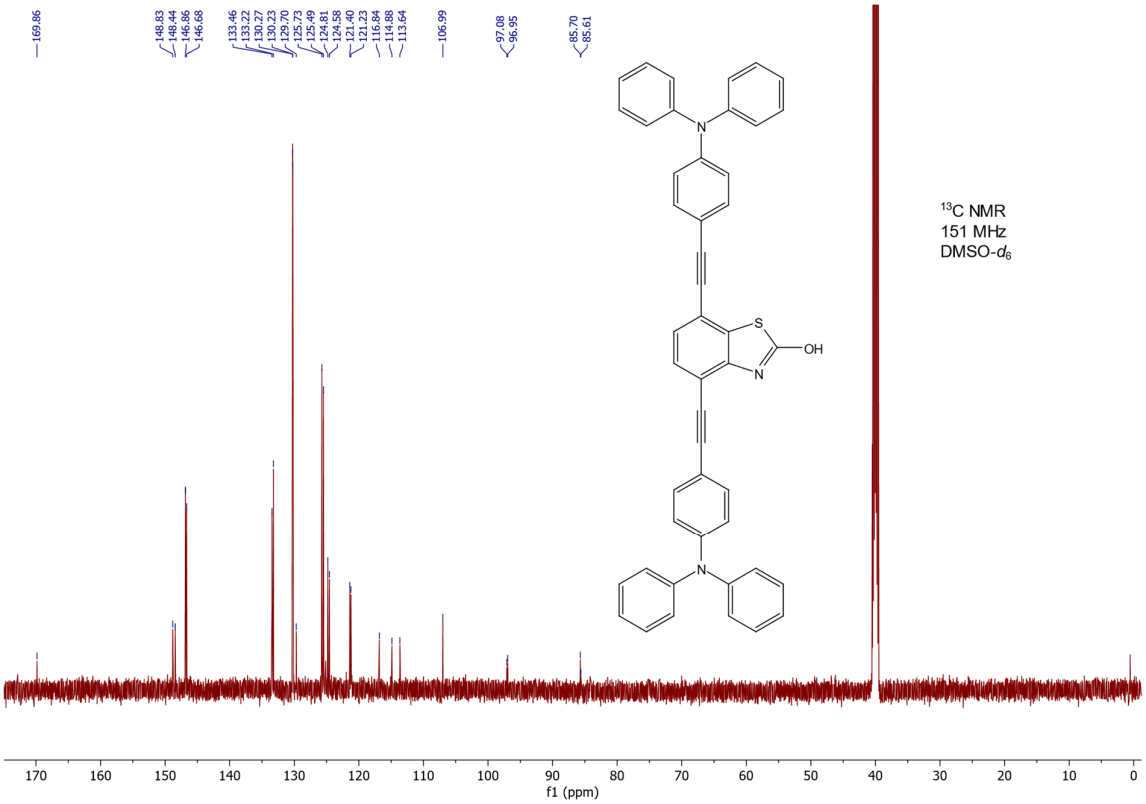
4,7-Bis[(4-(*N*,*N*-diphenylamino)phenylethynyl]benzothiazol-2-amine (**Qbtz-NH$_2$**)



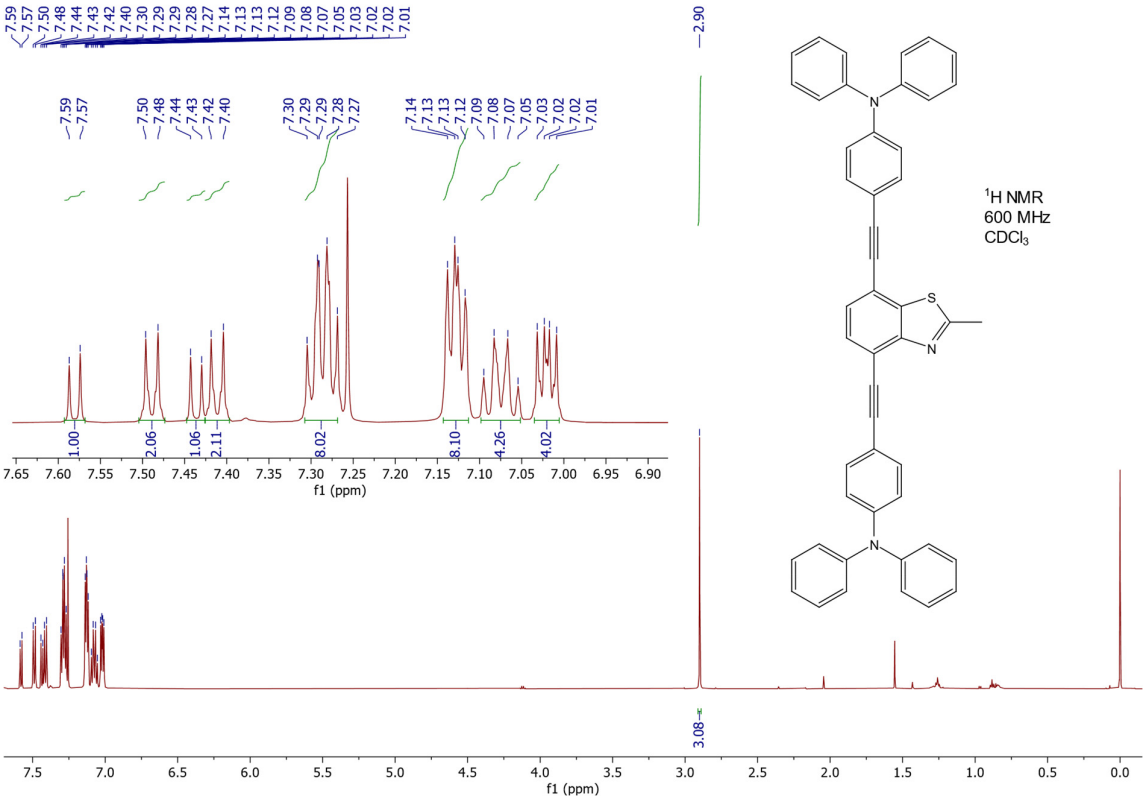


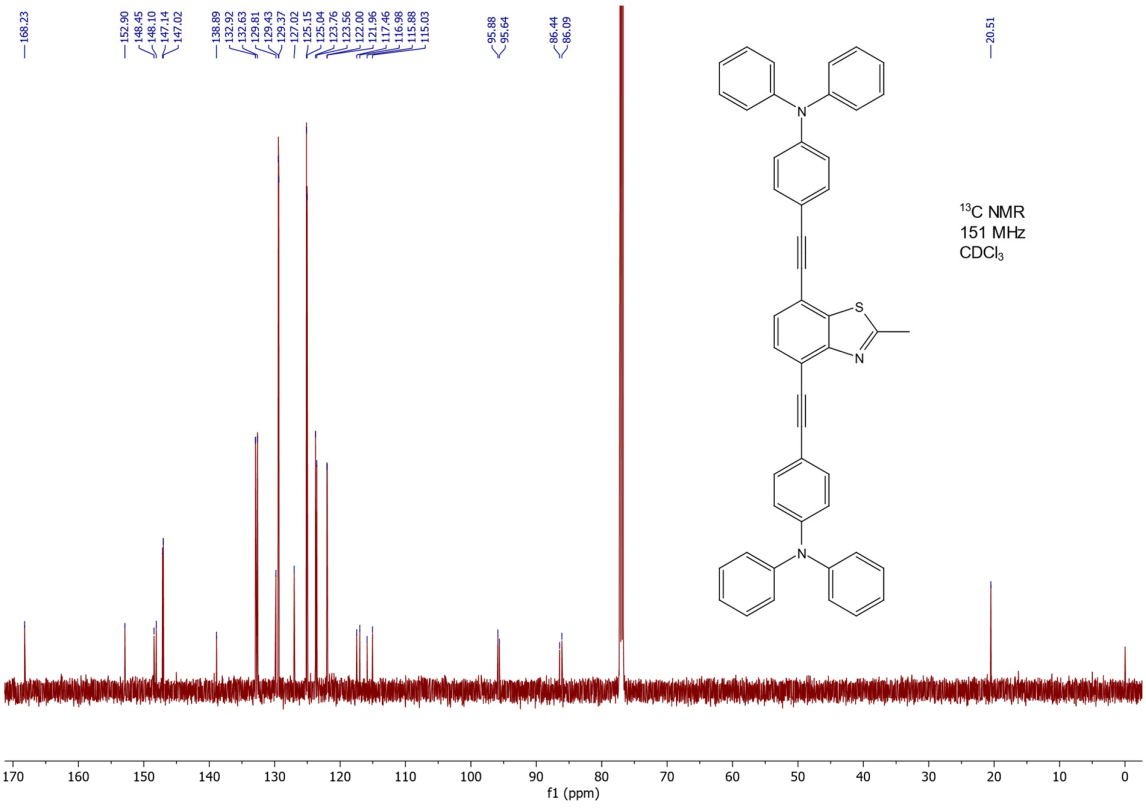
4,7-Bis[4-*N*,*N*-diphenylamino)phenylethynyl]benzothiazol-2(3*H*)-one (**Qbtz-OH**)



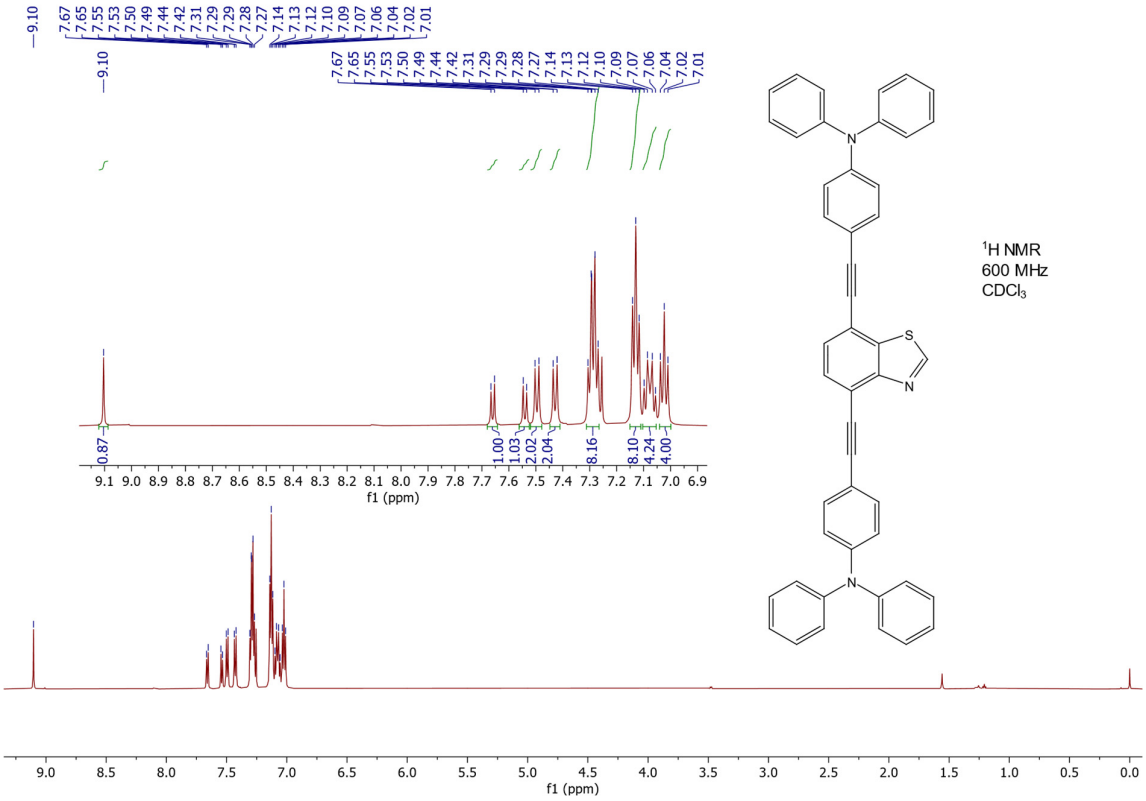


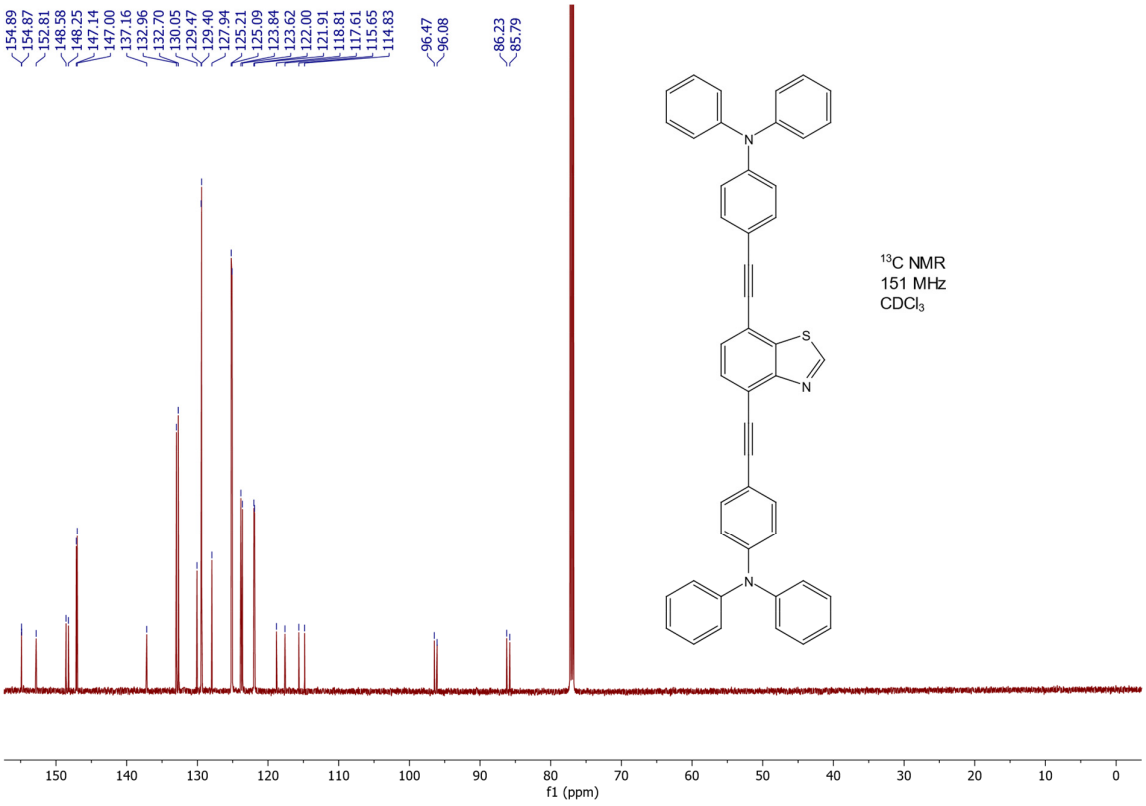
4,7-Bis[(4-(*N*,*N*-diphenylamino)phenylethynyl]-2-methylbenzothiazole (**Qbtz-Me**)



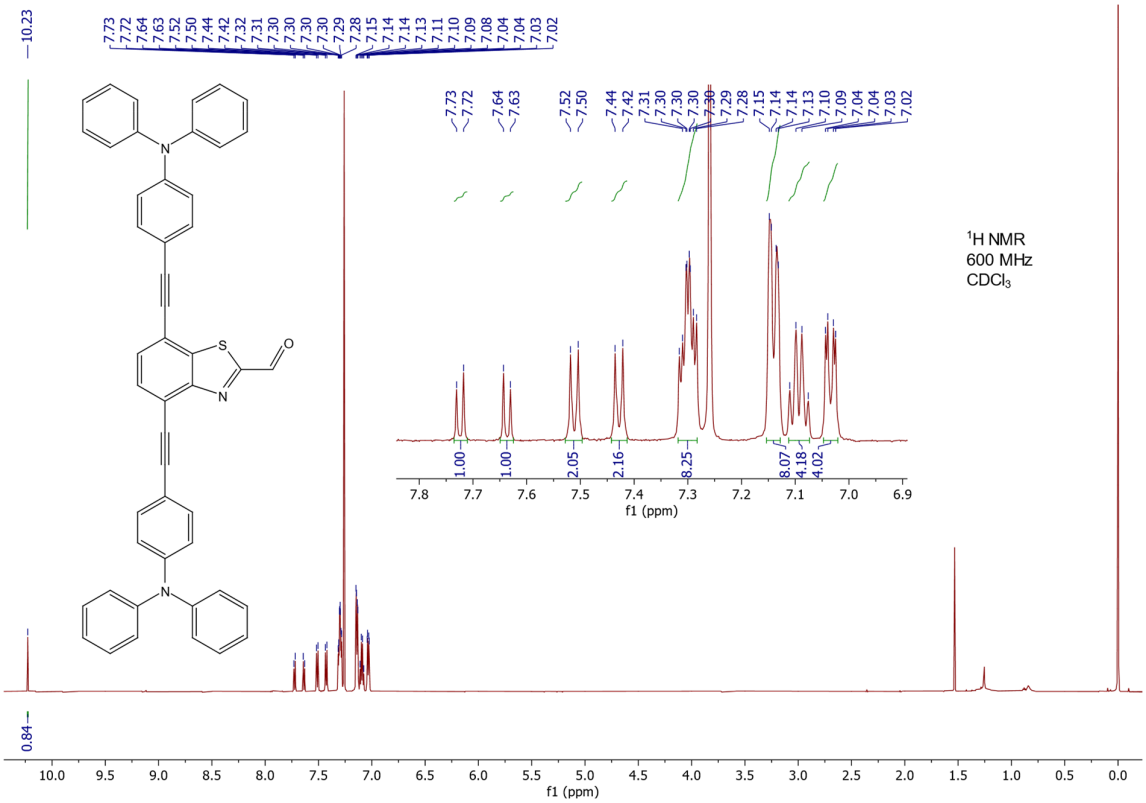


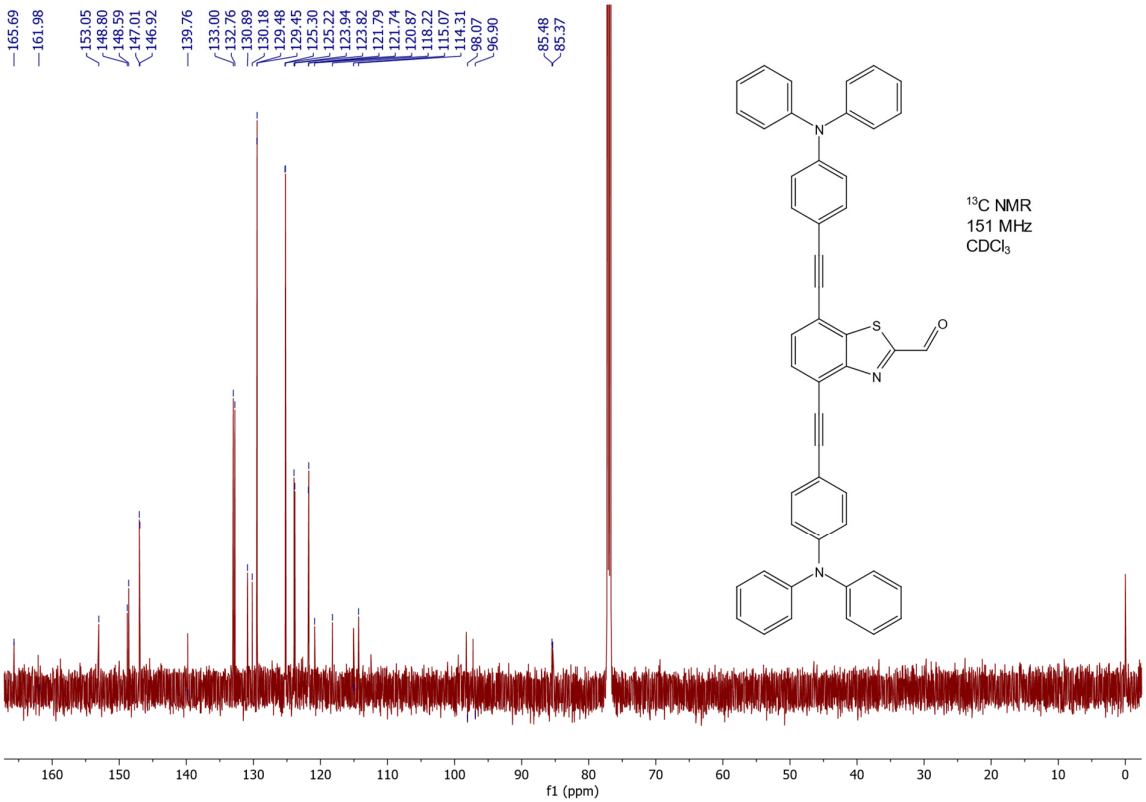
4,7-Bis[(4-(*N*,*N*-diphenylamino)phenylethynyl]benzothiazole (**Qbtz-H**)



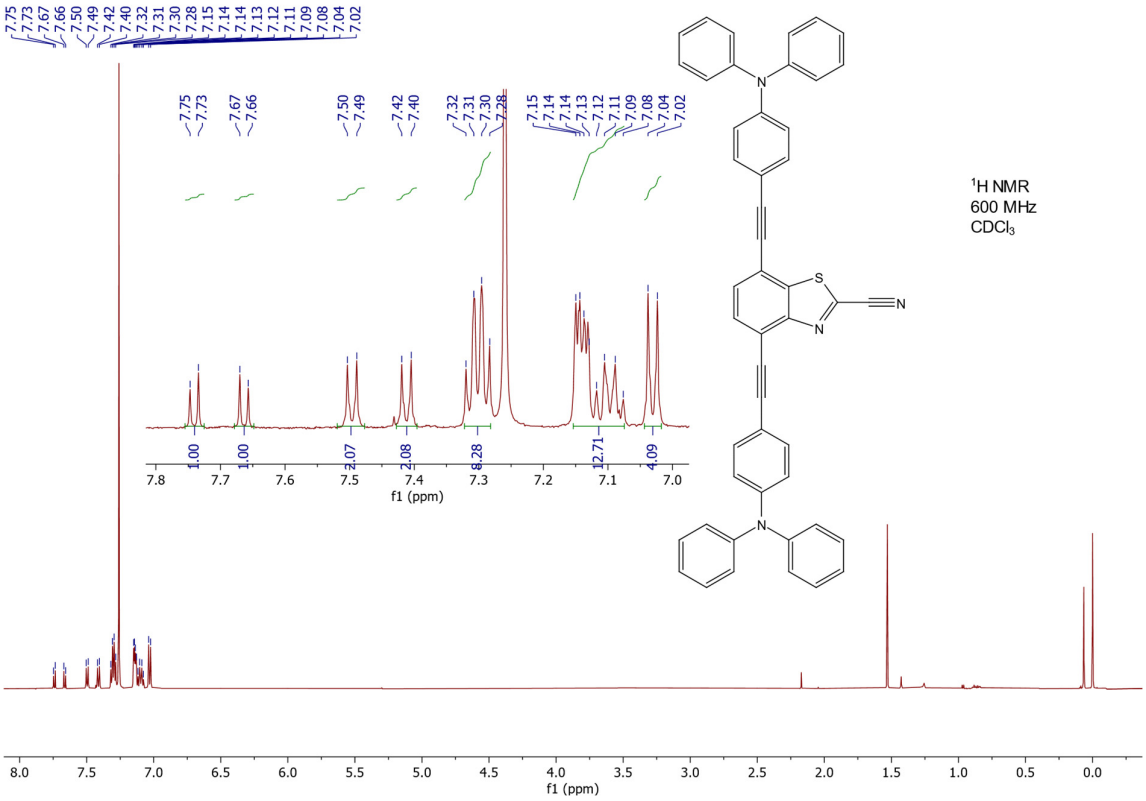


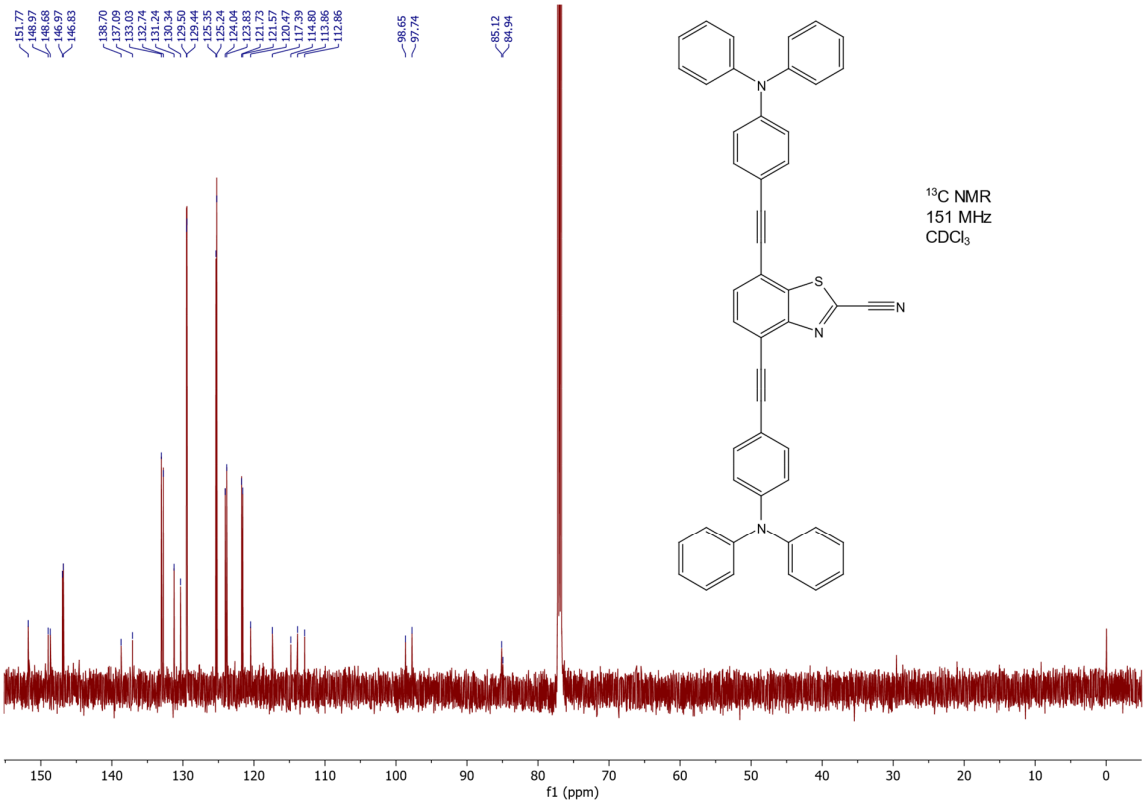
4,7-Bis[(4-(*N*,*N*-diphenylamino)phenylethynyl]benzothiazole-2-carbaldehyde (**Qbtz-CHO**)



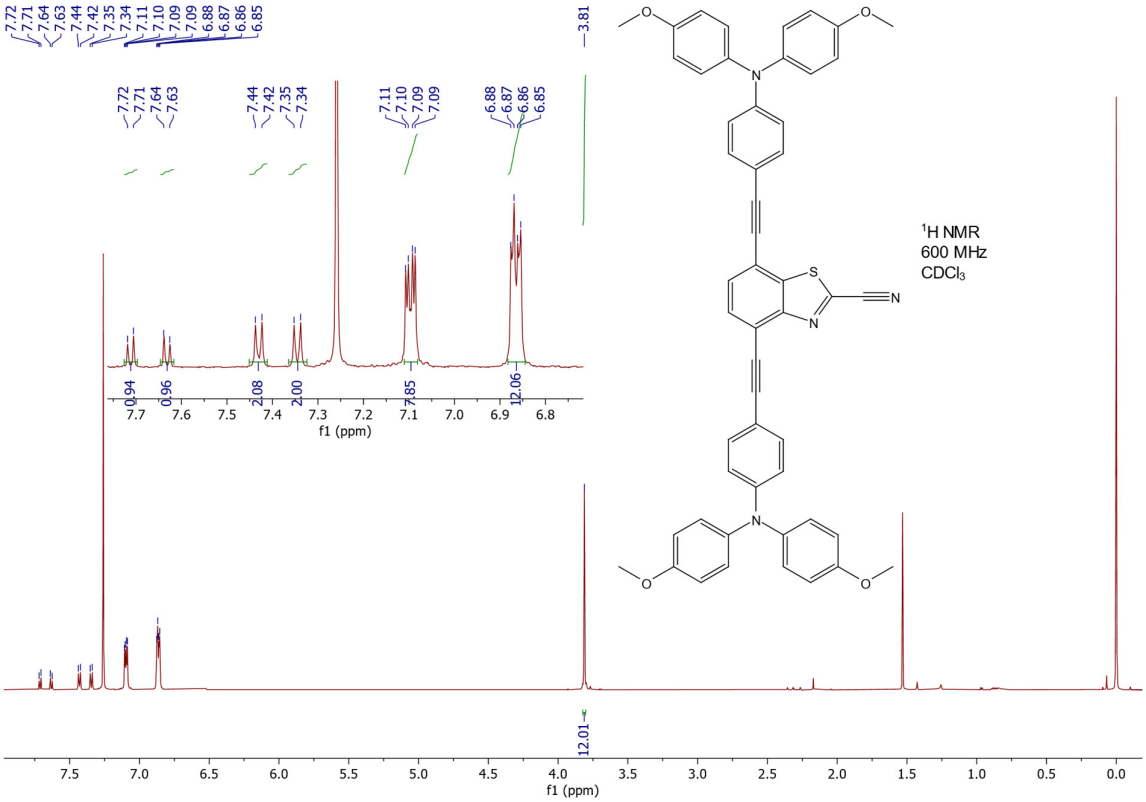


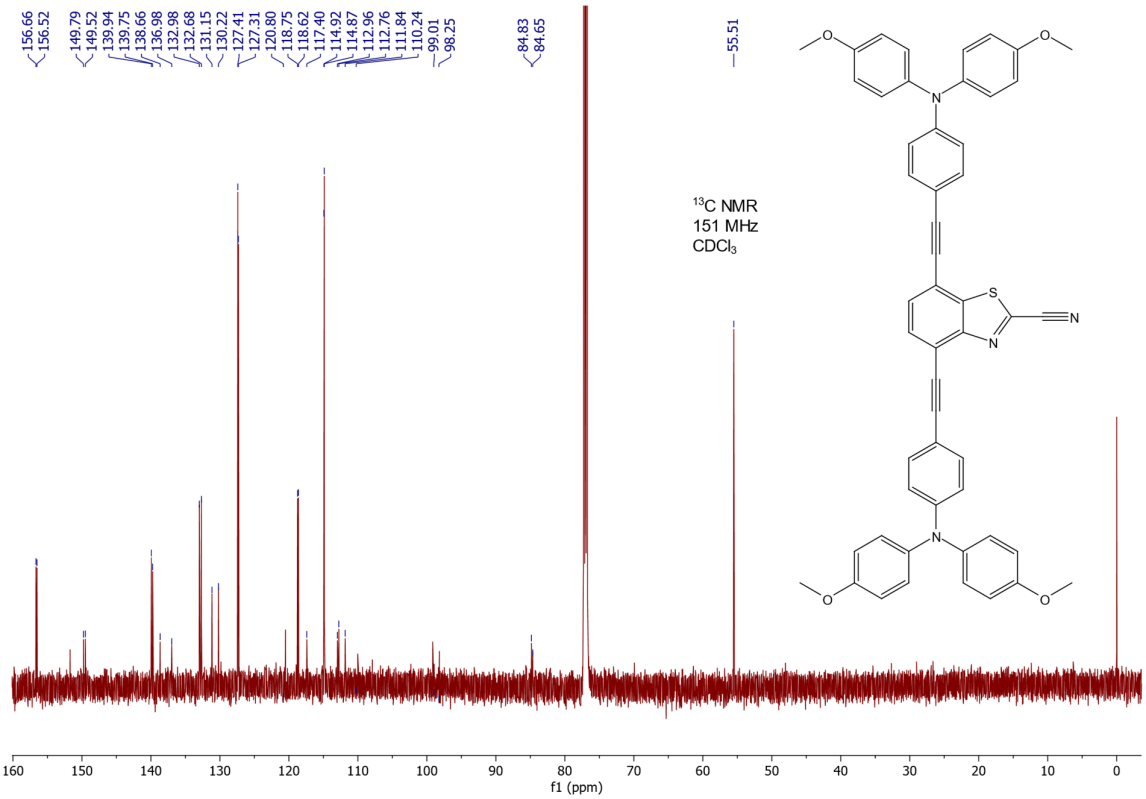
4,7-Bis[(4-(*N*,*N*-diphenylamino)phenylethynyl]benzothiazol-2-carbonitrile (**Qbtz-CN**)





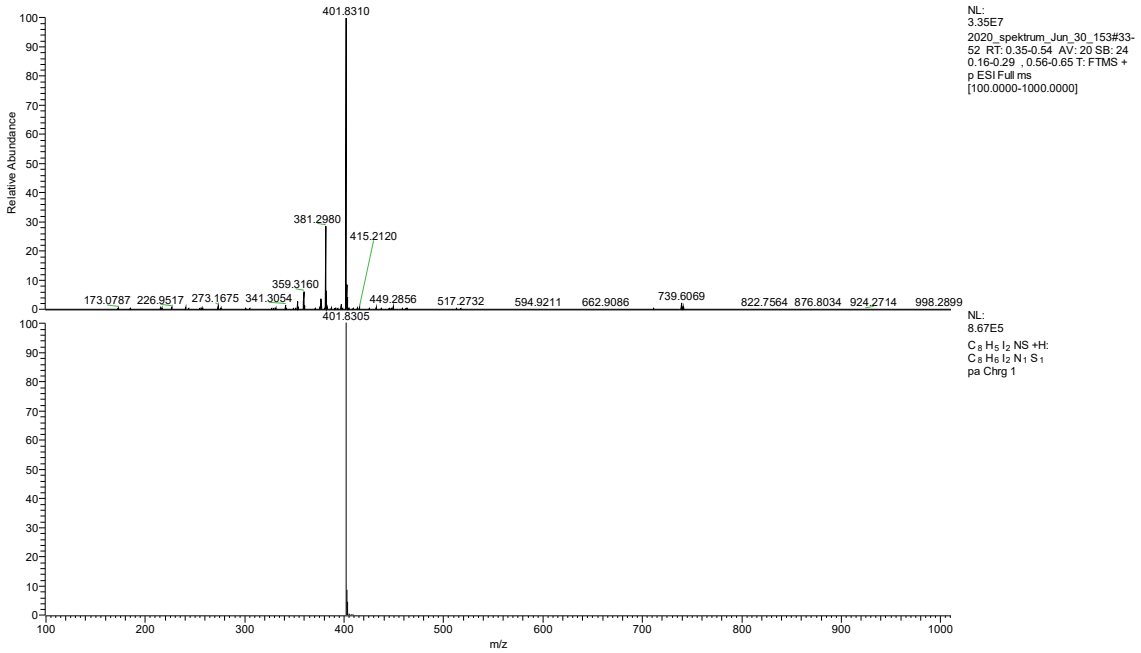
4,7-Bis{4-[*N*,*N*-bis(4-methoxyphenyl)amino]phenylethynyl}benzothiazol-2-carbonitrile (**Qbtz'-2-CN**)



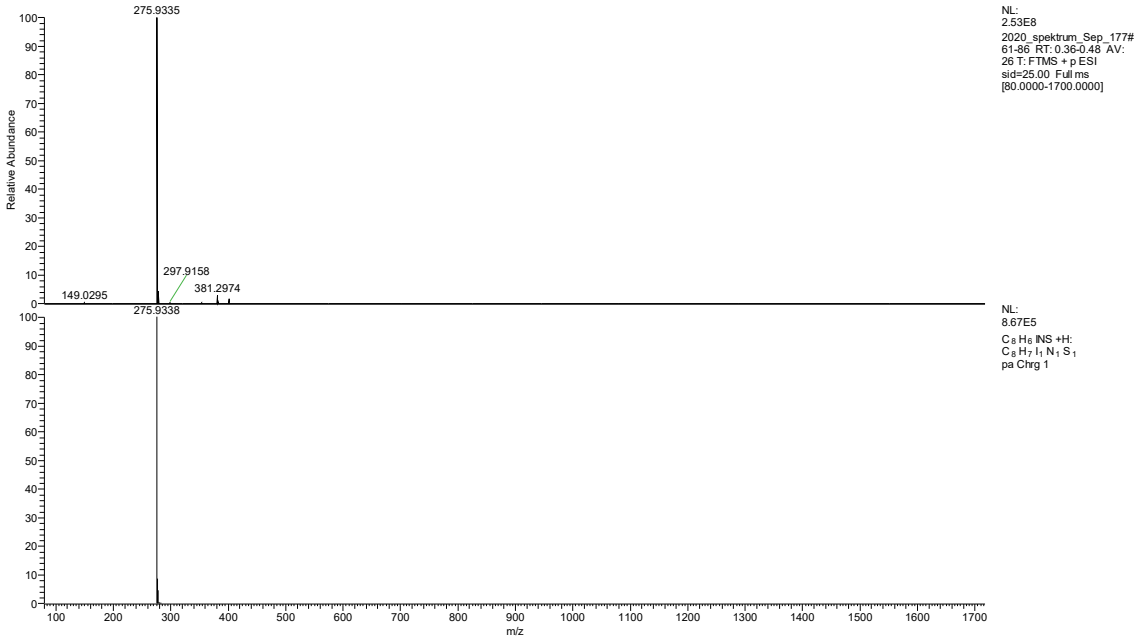


6 HRMS Spectra

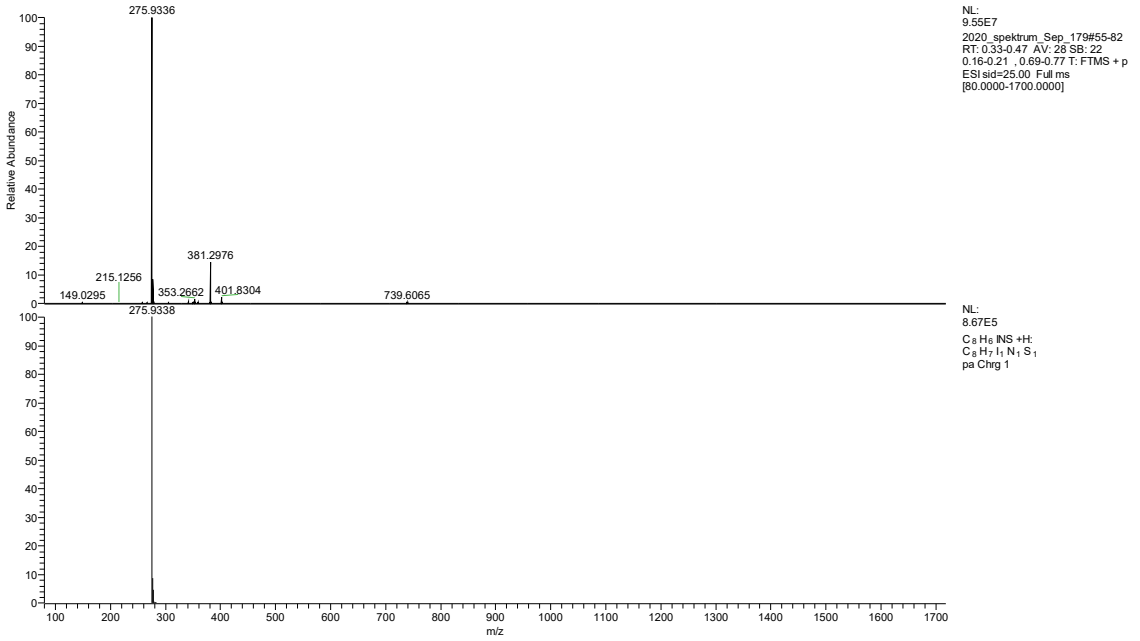
4,7-Diiodo-2-methylbenzothiazole (**2-Me**)



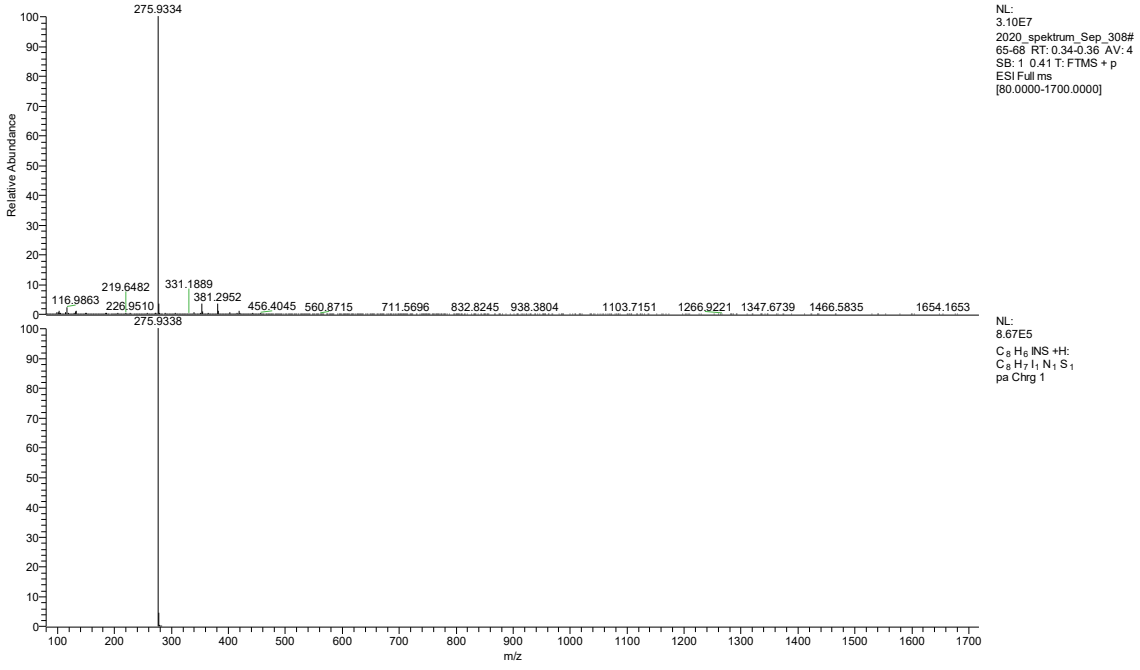
4-Iodo-2-methylbenzothiazole



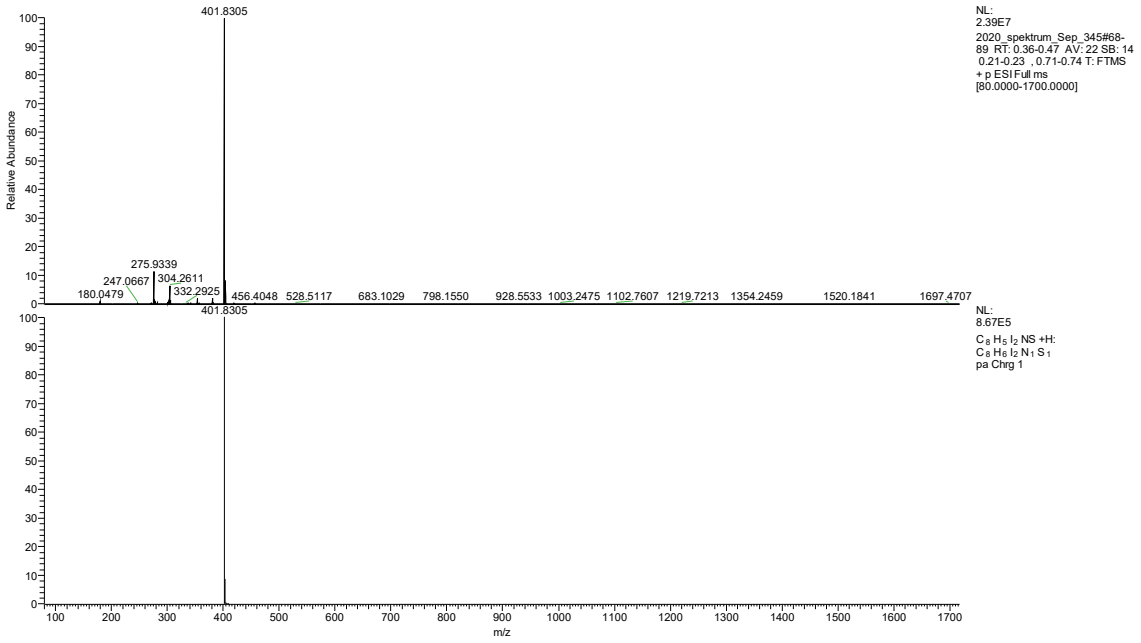
5-Iodo-2-methylbenzothiazole



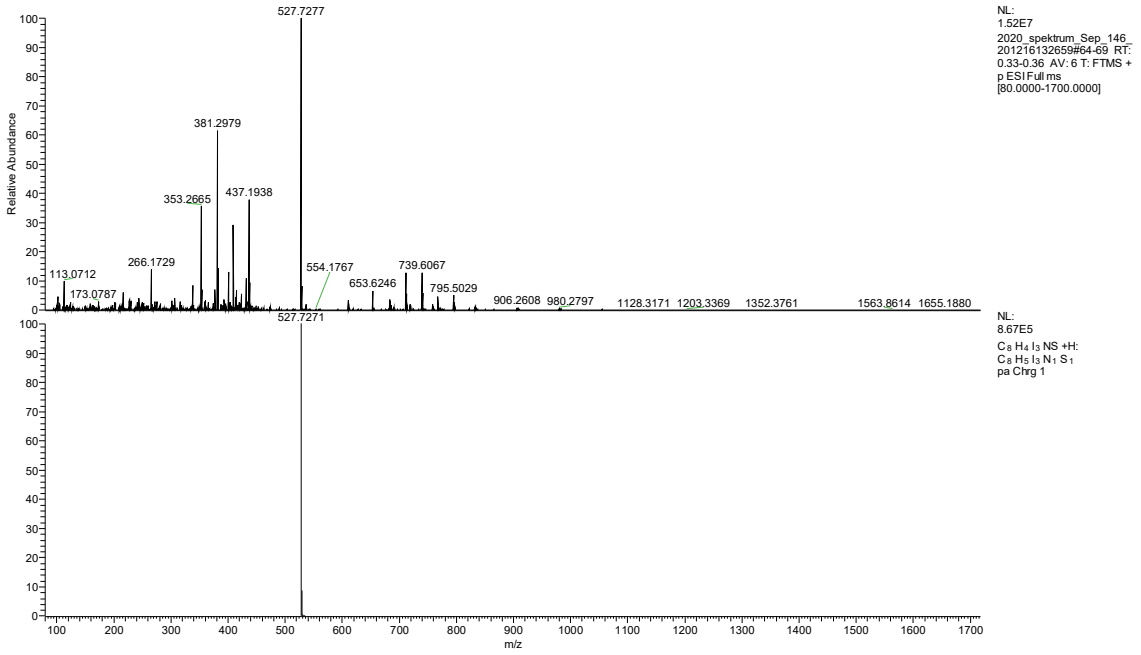
7-Iodo-2-methylbenzothiazole



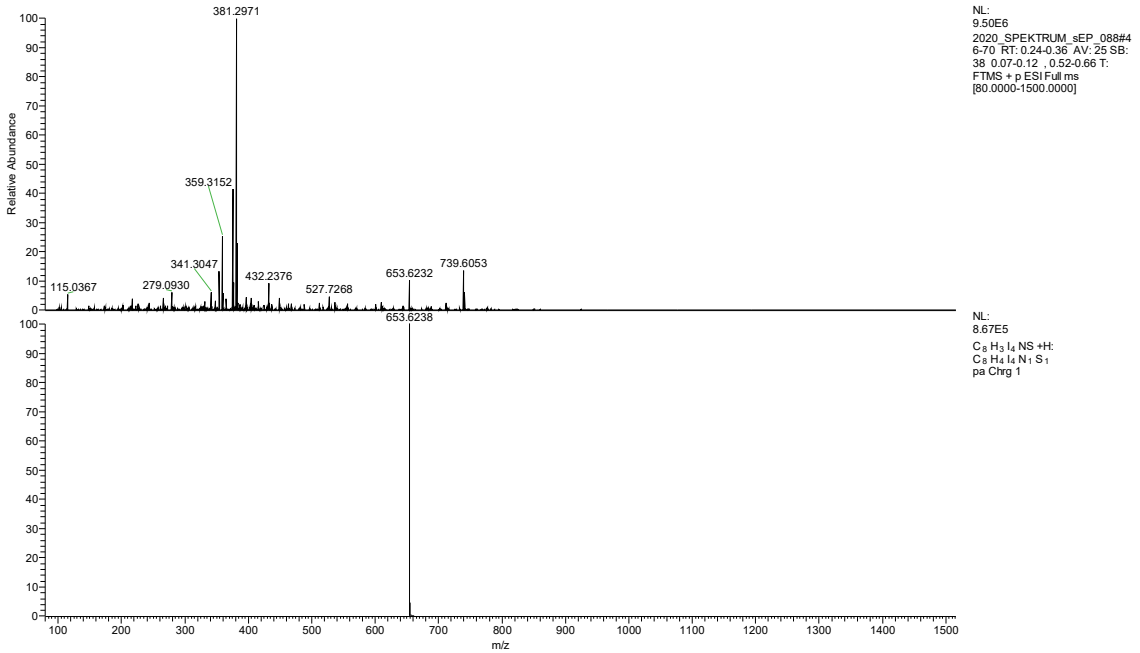
6,7-Diiodo-2-methylbenzothiazole



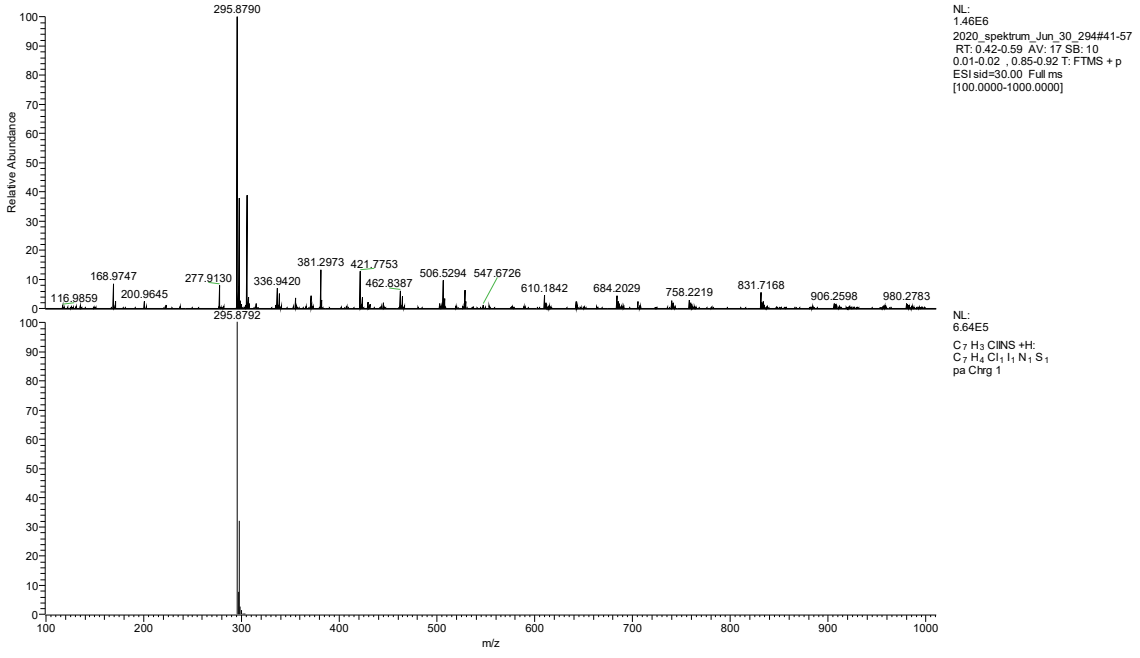
4,6,7-Triiodo-2-methylbenzothiazole (**3-Me**)



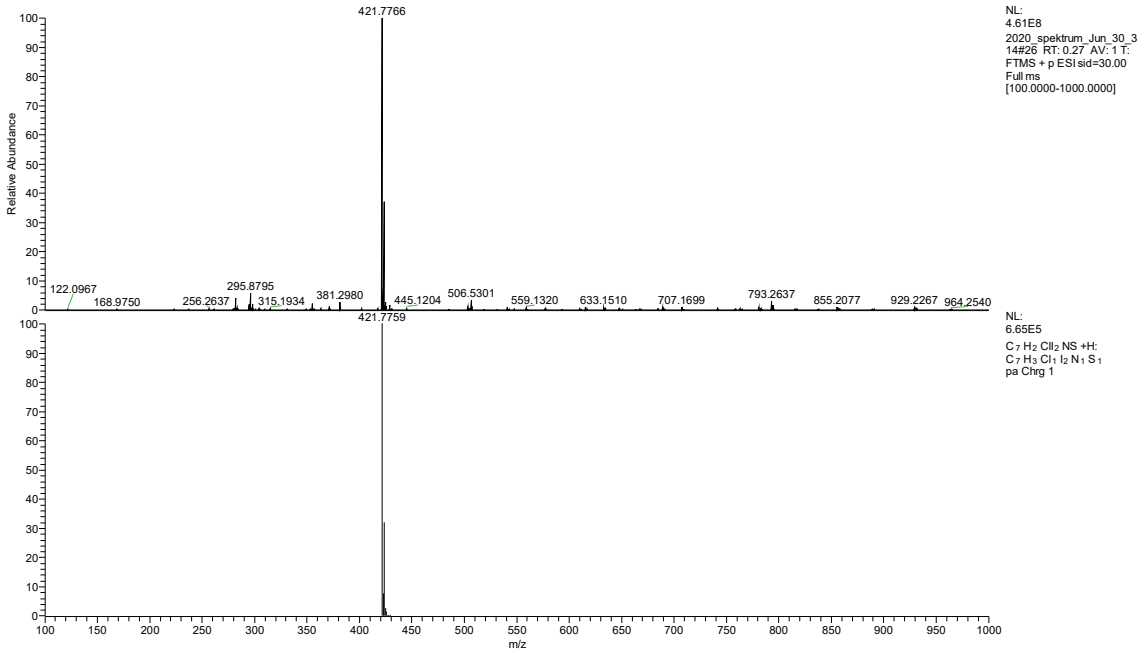
4,5,6,7-Tetraiodo-2-methylbenzothiazole (**4-Me**)



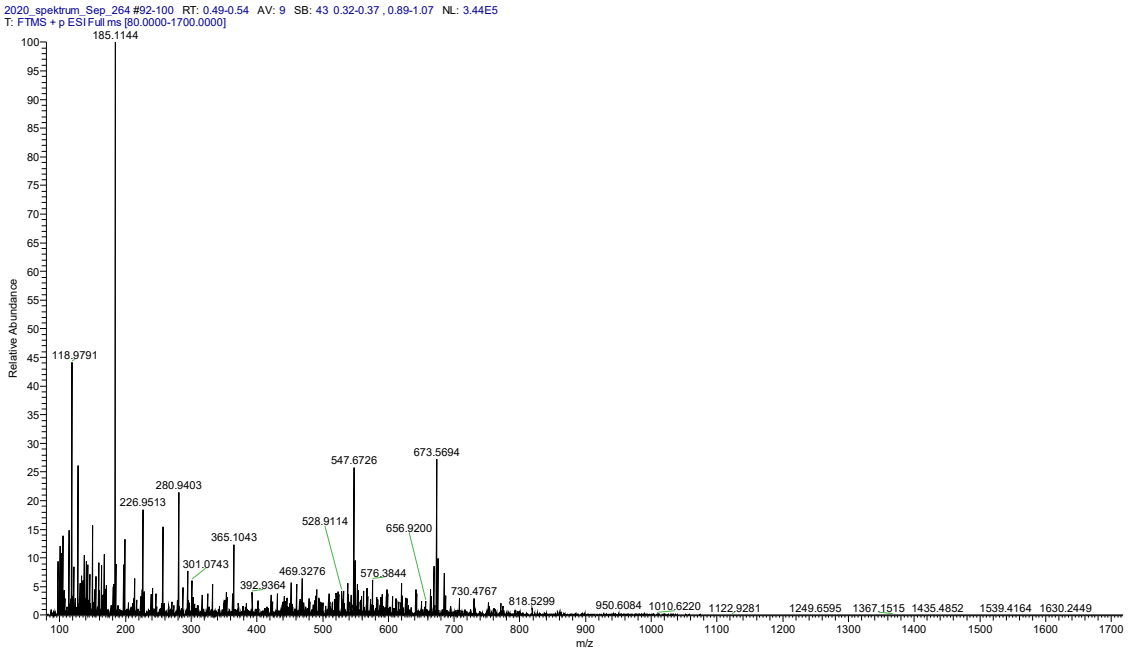
2-Chloro-6-iodobenzothiazole (**1-Cl**)



2-Chloro-4,7-diiodobenzothiazole (**2-Cl**)



2-Chloro-4,5,6,7-tetraiodobenzothiazole (**4-Cl**)



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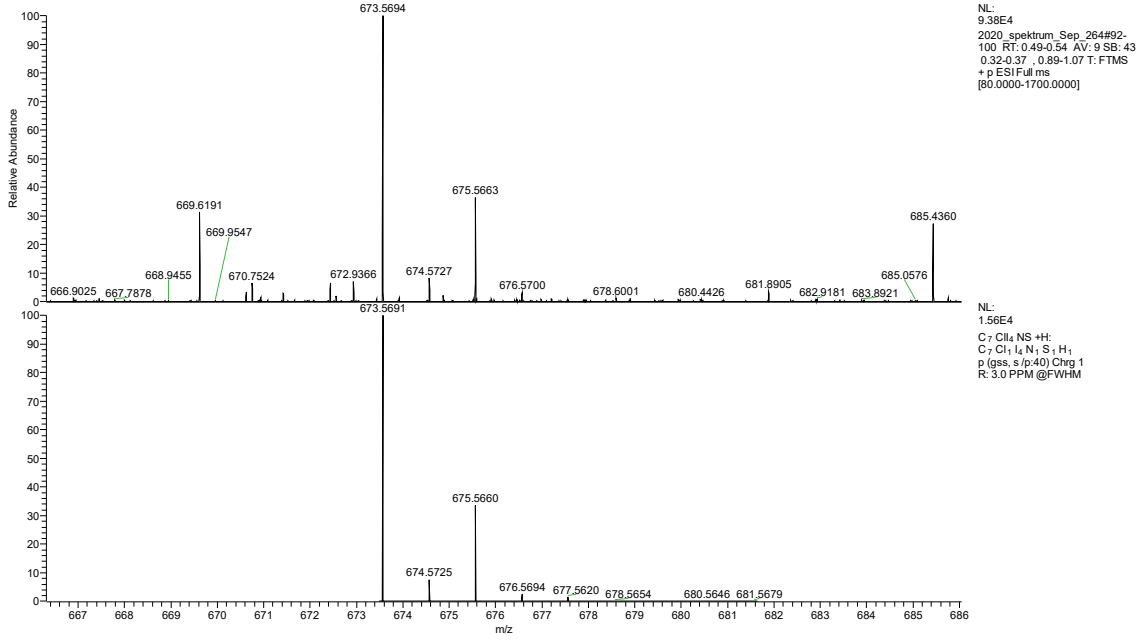
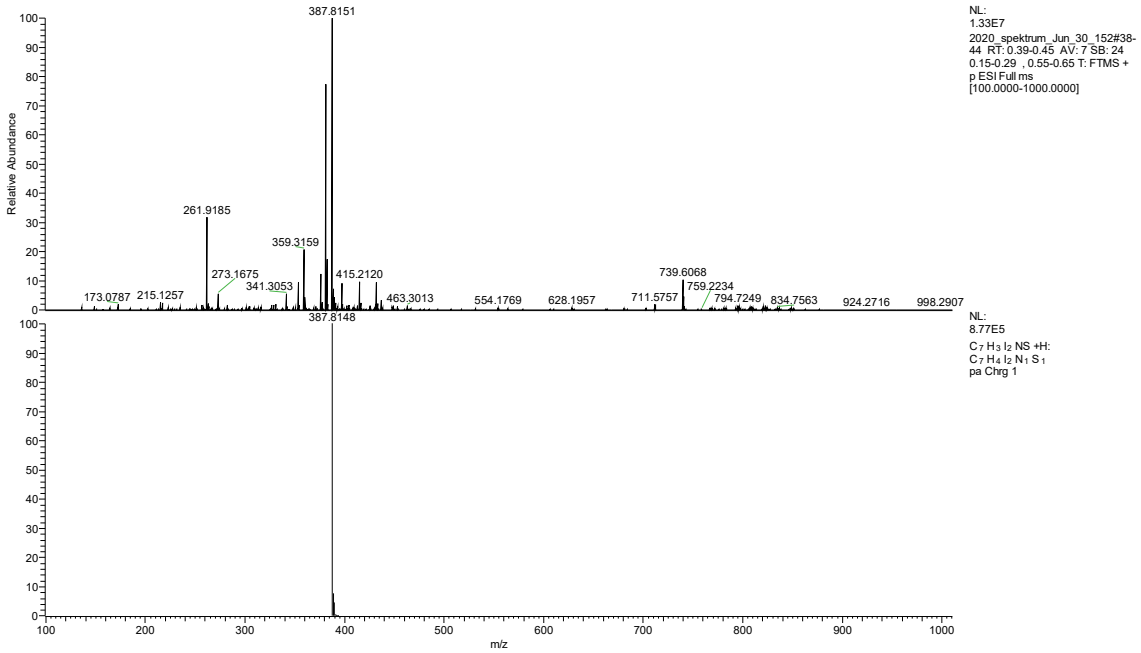
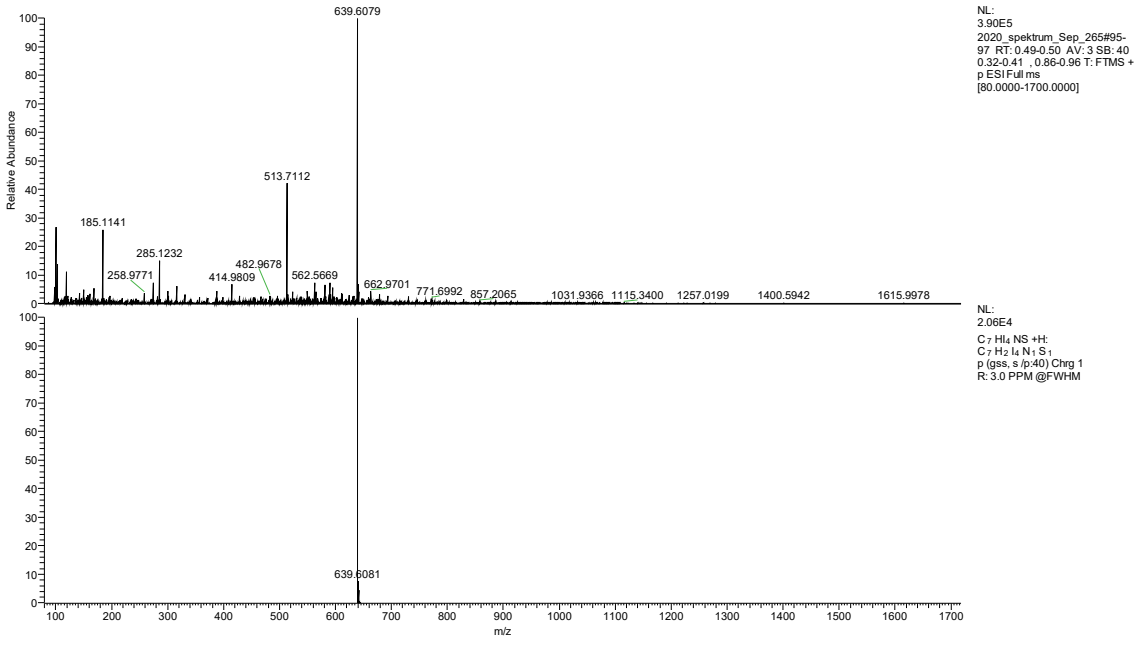


4,7-Diiodobenzothiazole (**2-H**)

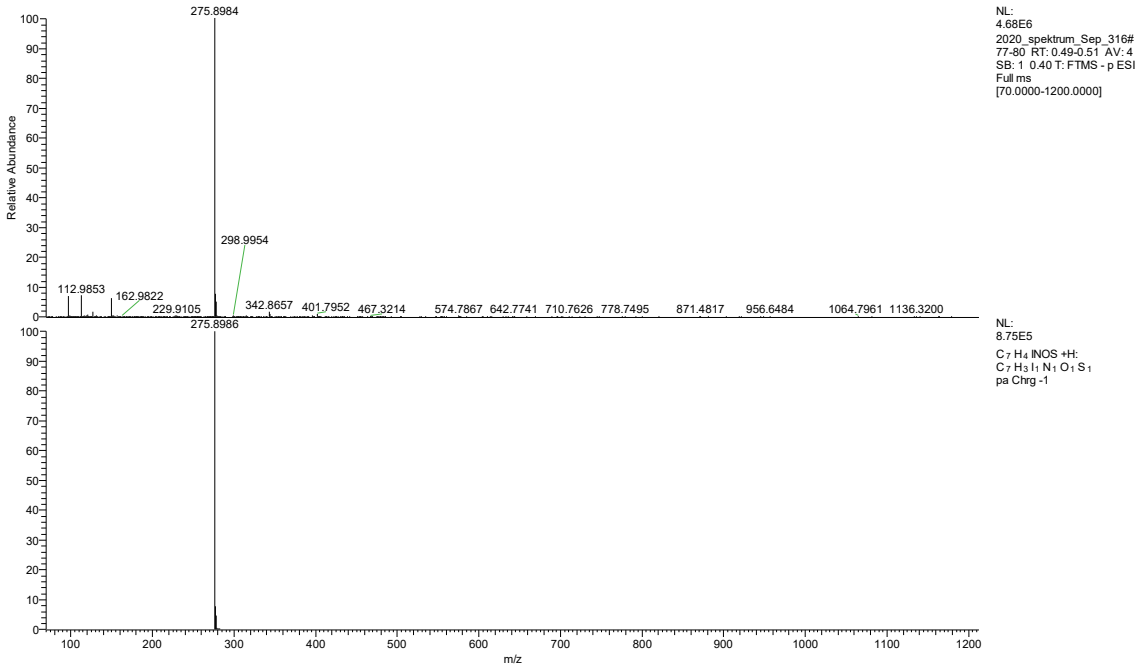


4,5,6,7-Tetraiodobenzothiazole (**4-H**)



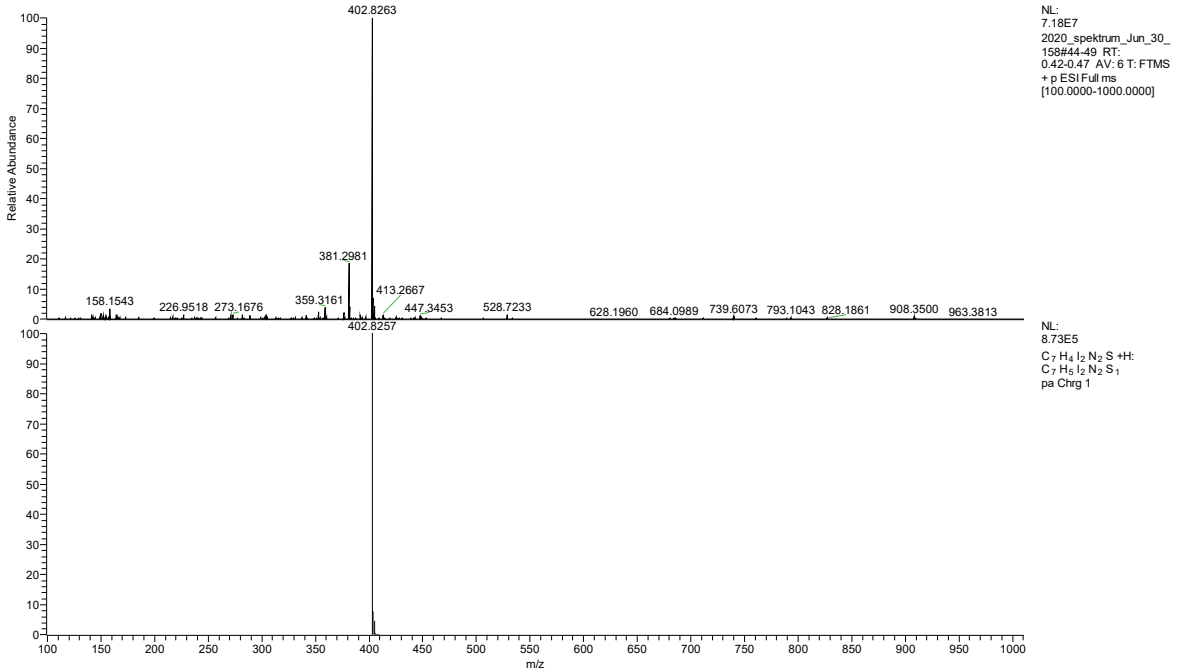
6-Iodobenzothiazol-2(3*H*)-one (**1-OH**)

(negative mode)

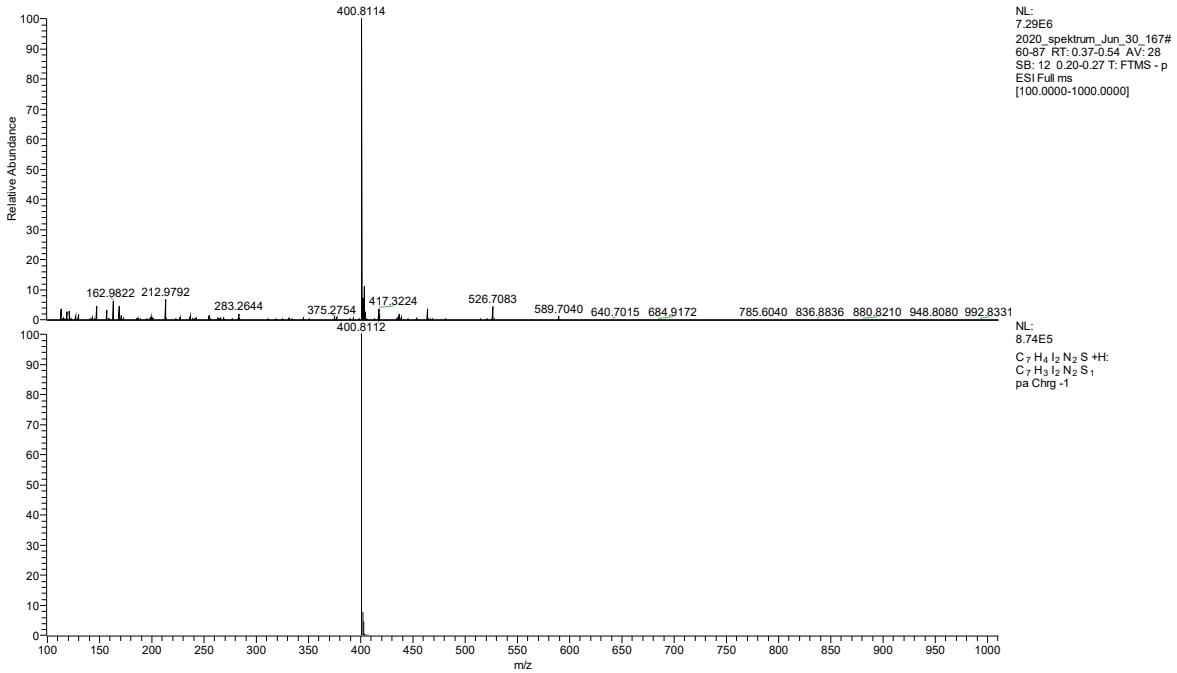


4,7-Diiodobenzothiazol-2-amine (**2-NH_2**)

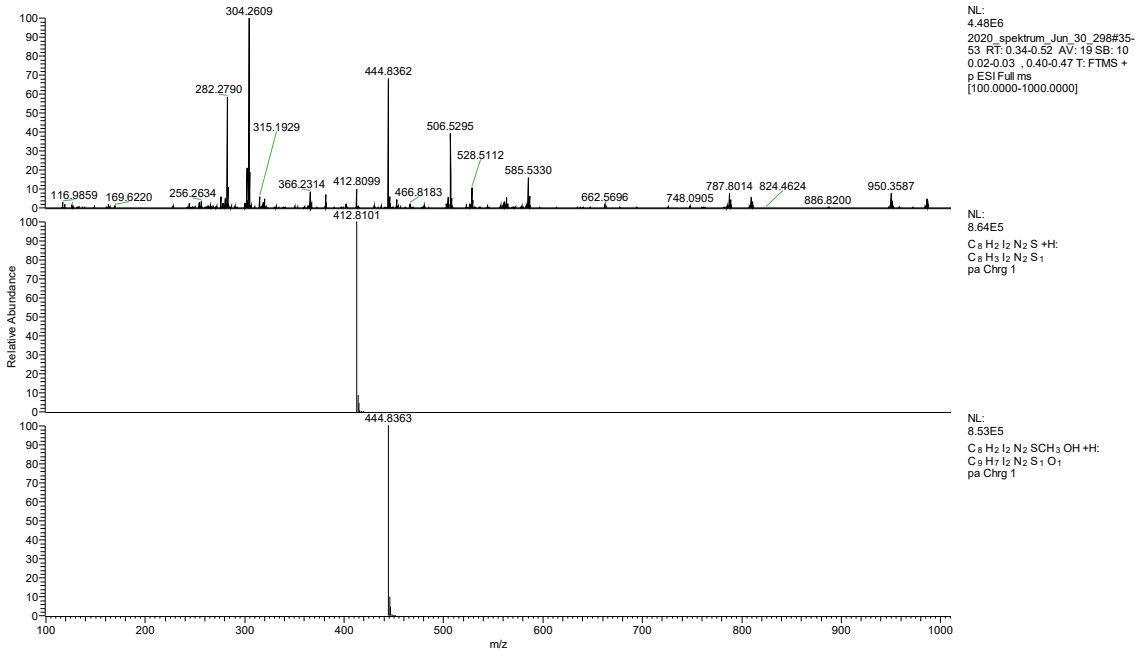
(positive mode)



(negative mode)

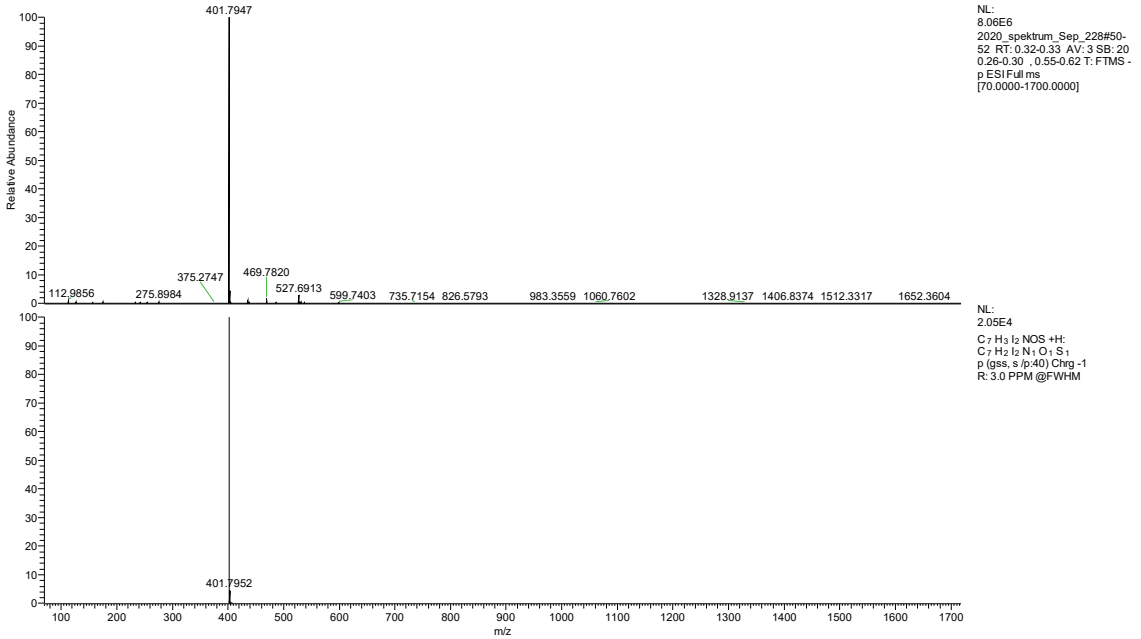


4,7-Diiodobenzothiazol-2-carbonitrile (**2-CN**)

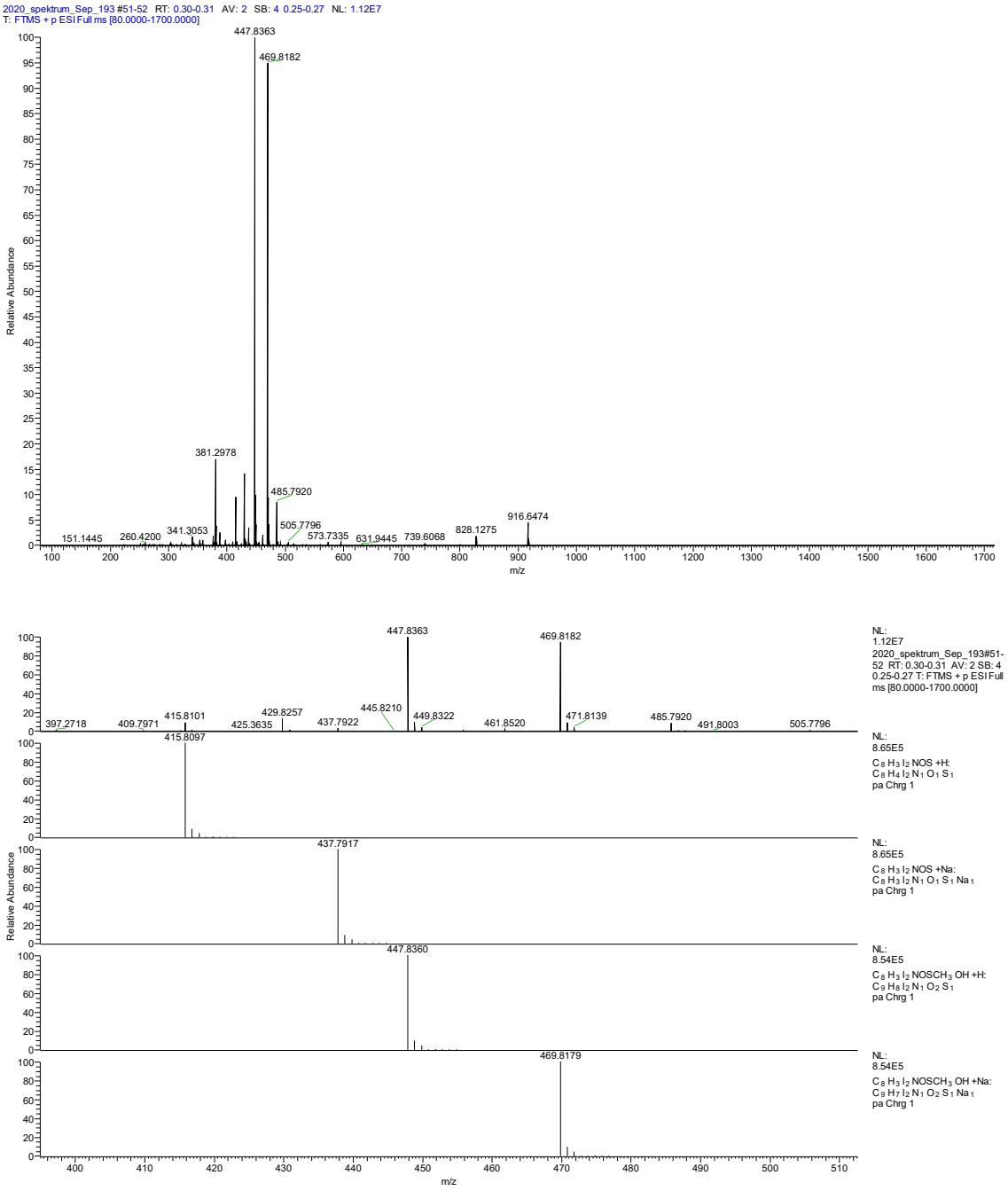


4,7-Diiodobenzothiazol-2(3*H*)-one (**2-OH**)

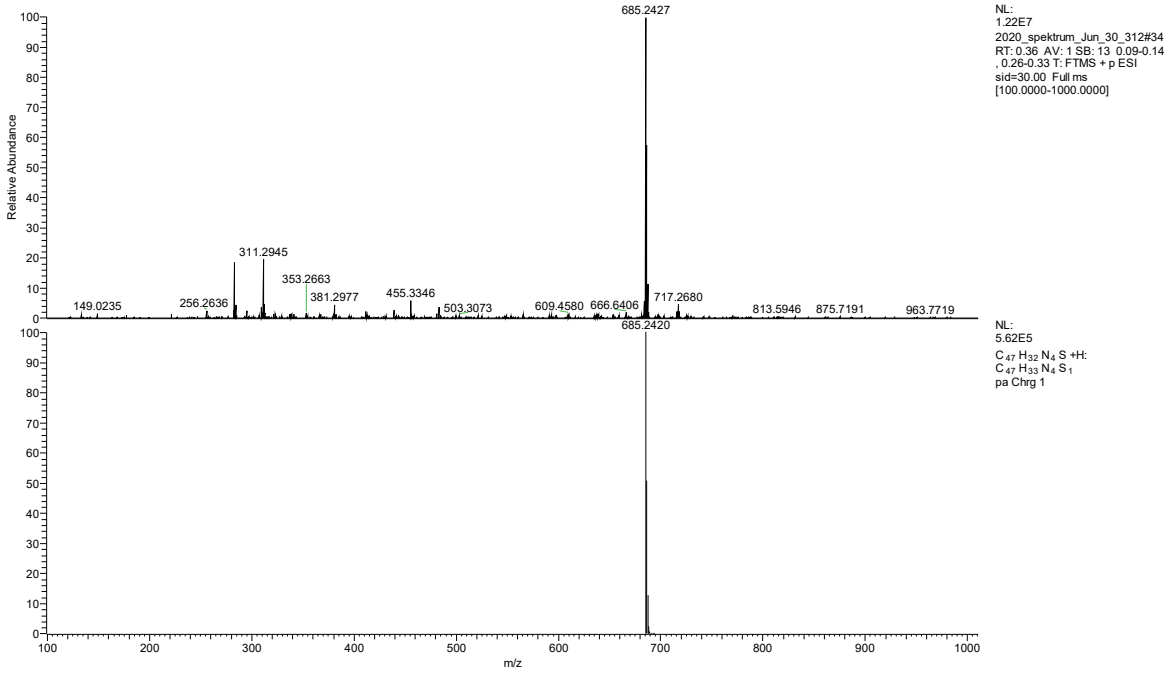
(negative mode)



4,7-Diiodobenzothiazole-2-carbaldehyde (**2-CHO**)



4,7-Bis[(4-(*N*,*N*-diphenylamino)phenylethynyl]benzothiazol-2-amine (**Qbtz-NH$_2$**)



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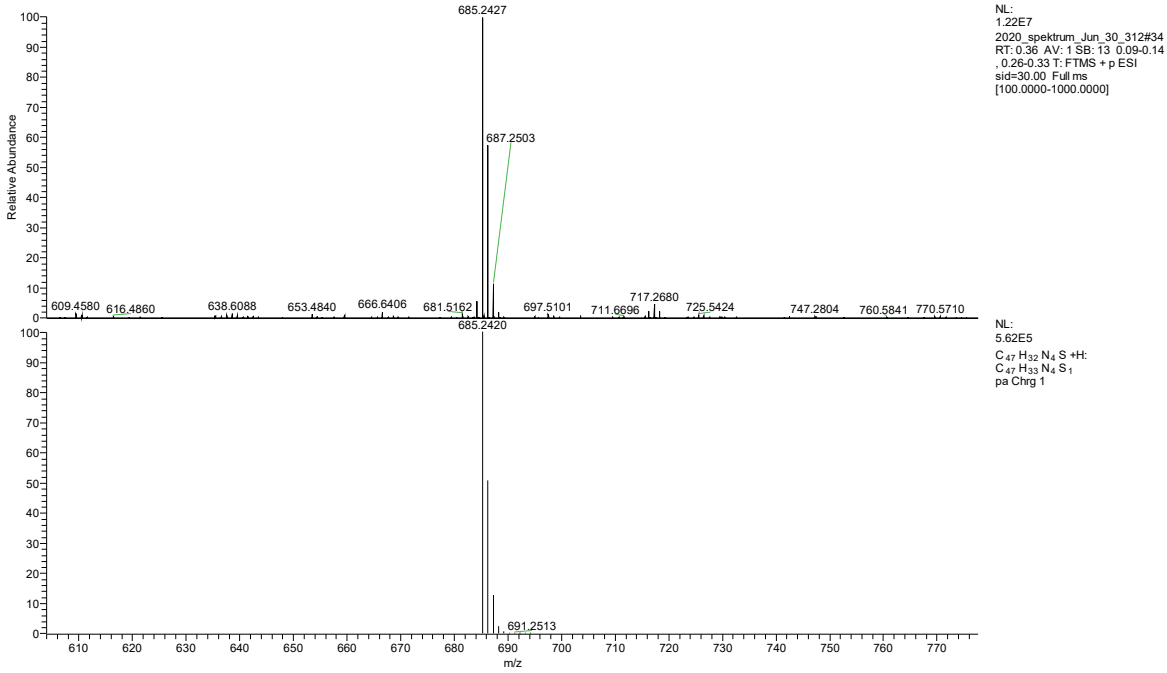
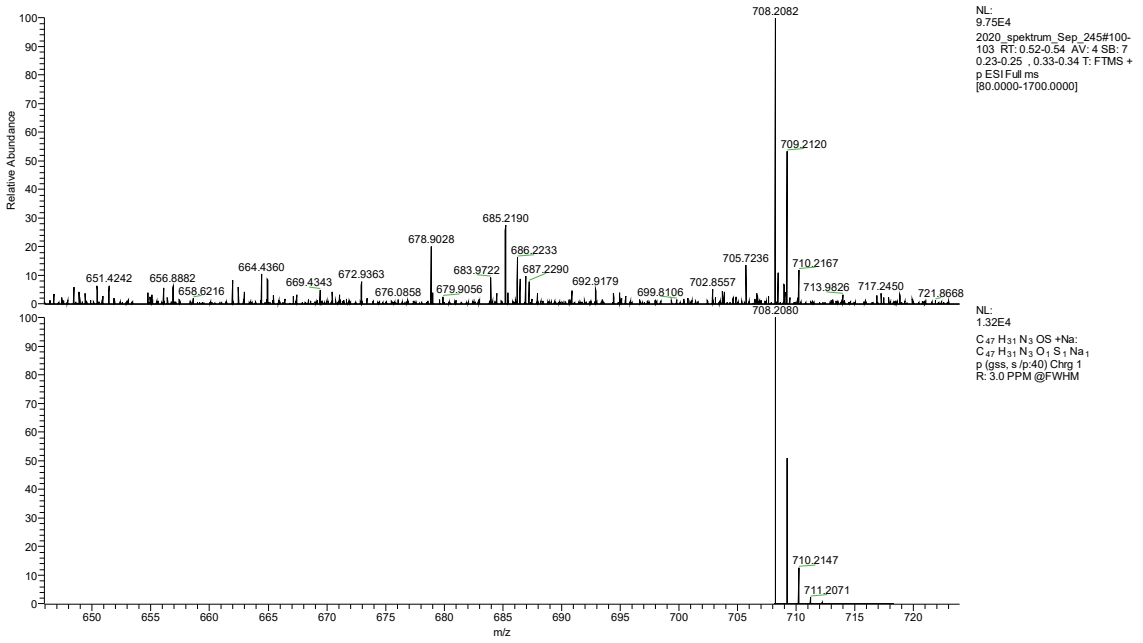
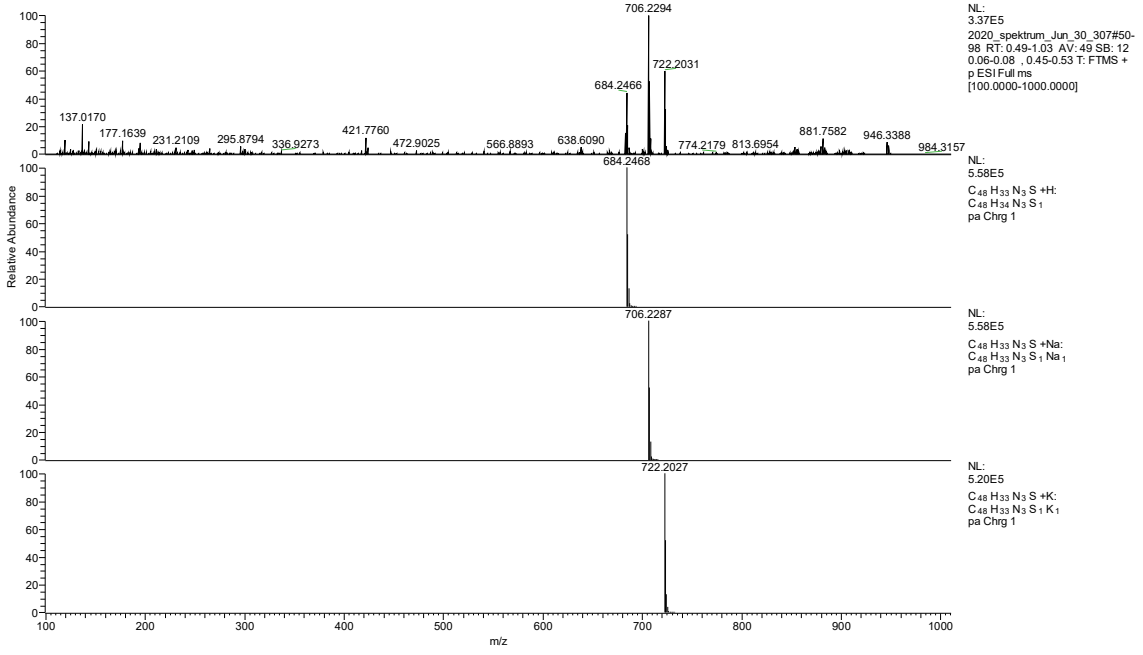


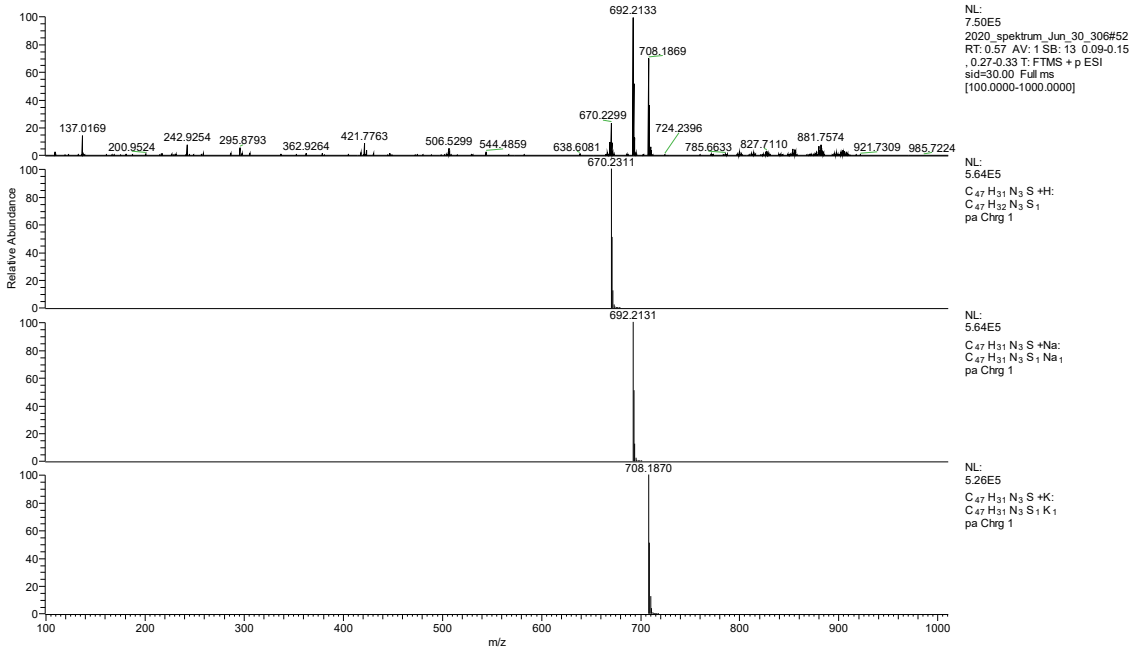
4,7-Bis[4-*N*,*N*-diphenylamino)phenylethynyl]benzothiazol-2(3*H*)-one (**Qbtz-OH**)



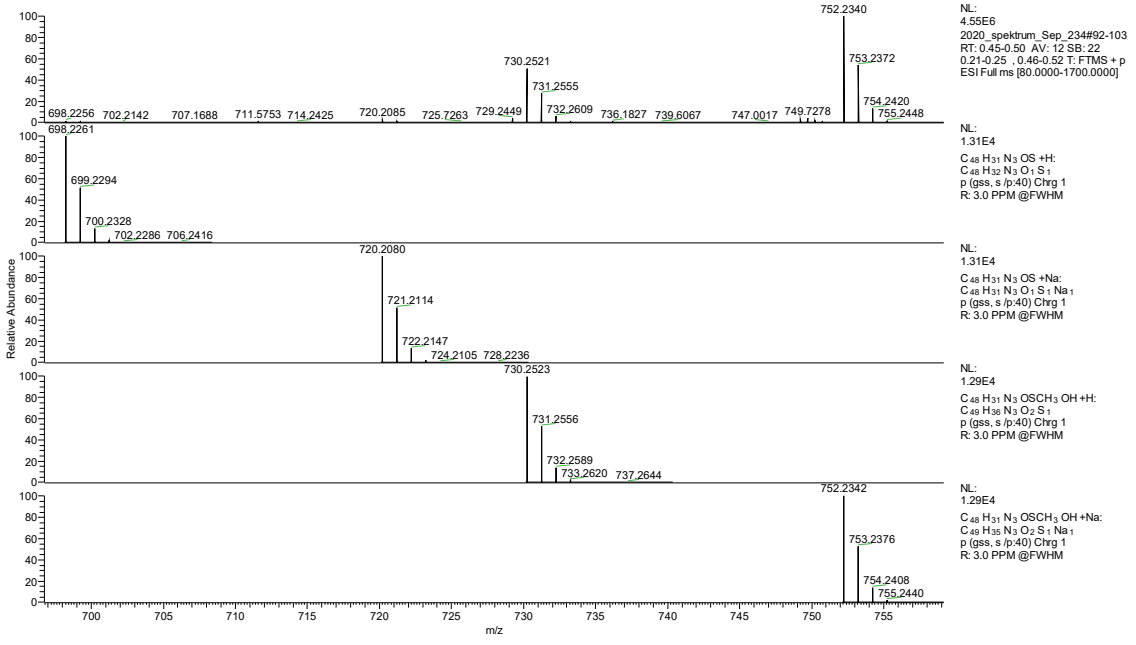
4,7-Bis[(4-(*N*,*N*-diphenylamino)phenylethynyl]-2-methylbenzothiazole (**Qbtz-Me**)



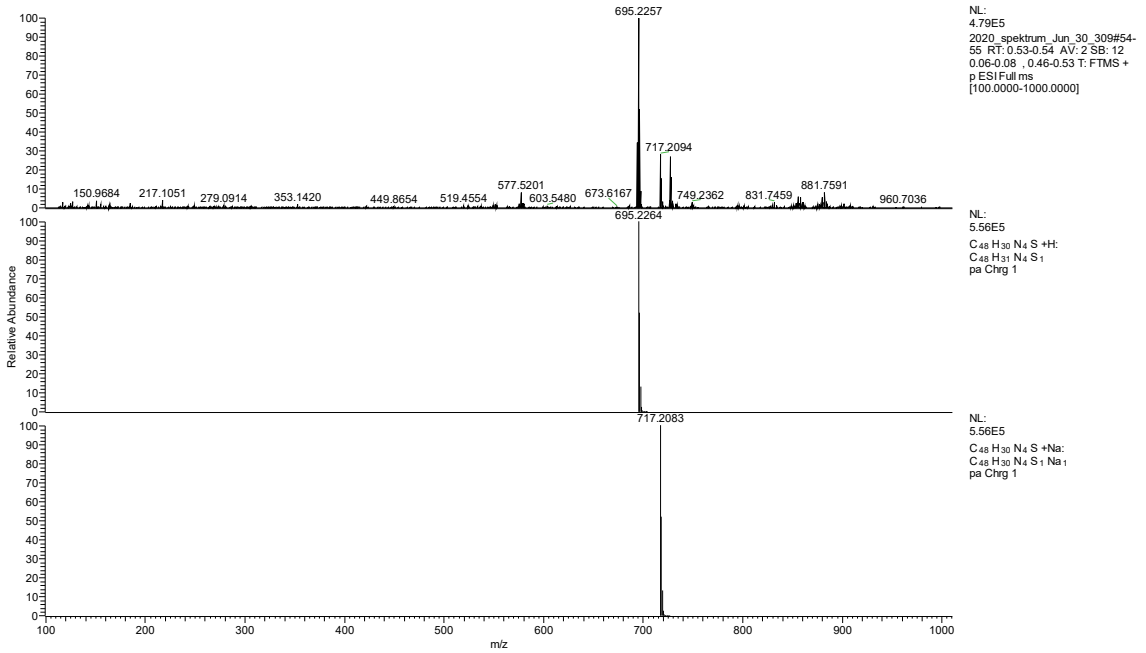
4,7-Bis[(4-(*N*,*N*-diphenylamino)phenylethynyl]benzothiazole (**Qbtz-H**)



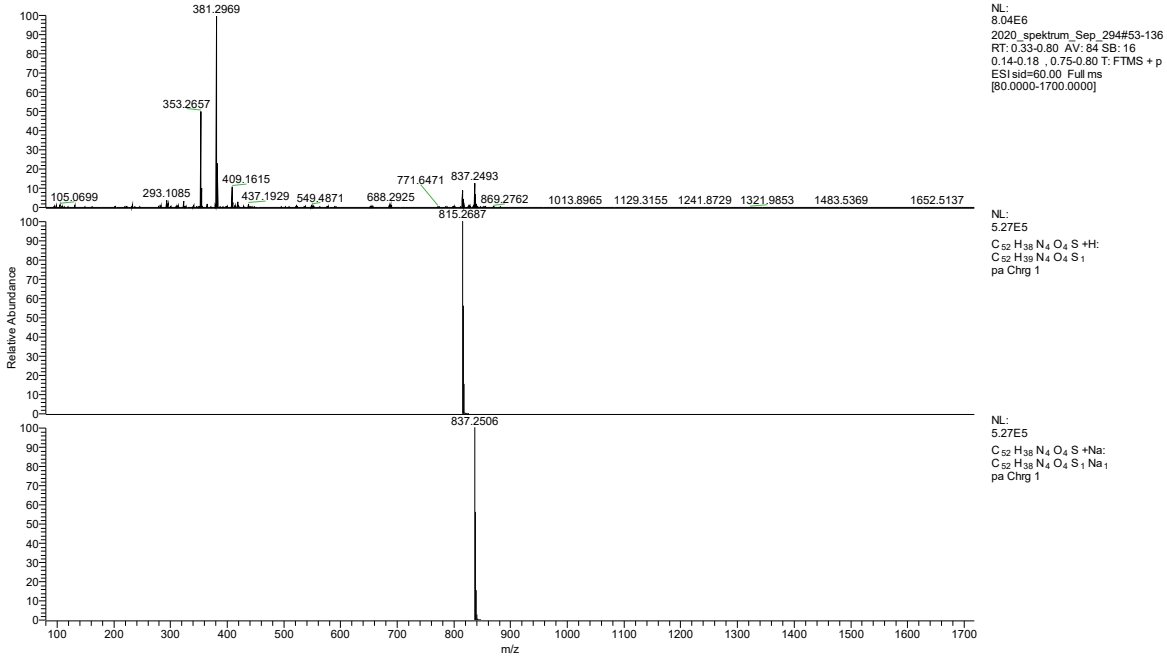
4,7-Bis[(4-(*N*,*N*-diphenylamino)phenylethynyl]benzothiazole-2-carbaldehyde (**Qbtz-CHO**)



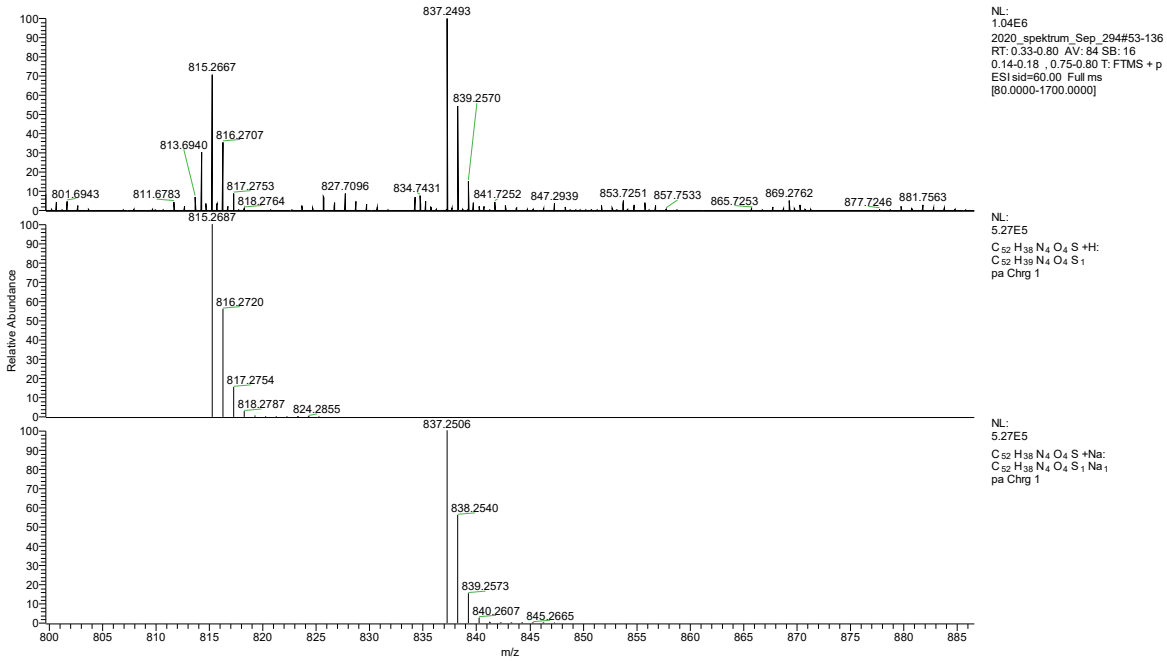
4,7-Bis[(4-(*N*,*N*-diphenylamino)phenylethynyl]benzothiazol-2-carbonitrile (**Qbtz-CN**)



4,7-Bis{4-[*N*,*N*-bis(4-methoxyphenyl)amino]phenylethynyl}benzothiazol-2-carbonitrile (**Qbtz'-2-CN**)



zoomed (top) + simulated



7 UV-vis Absorption and Emission Spectra

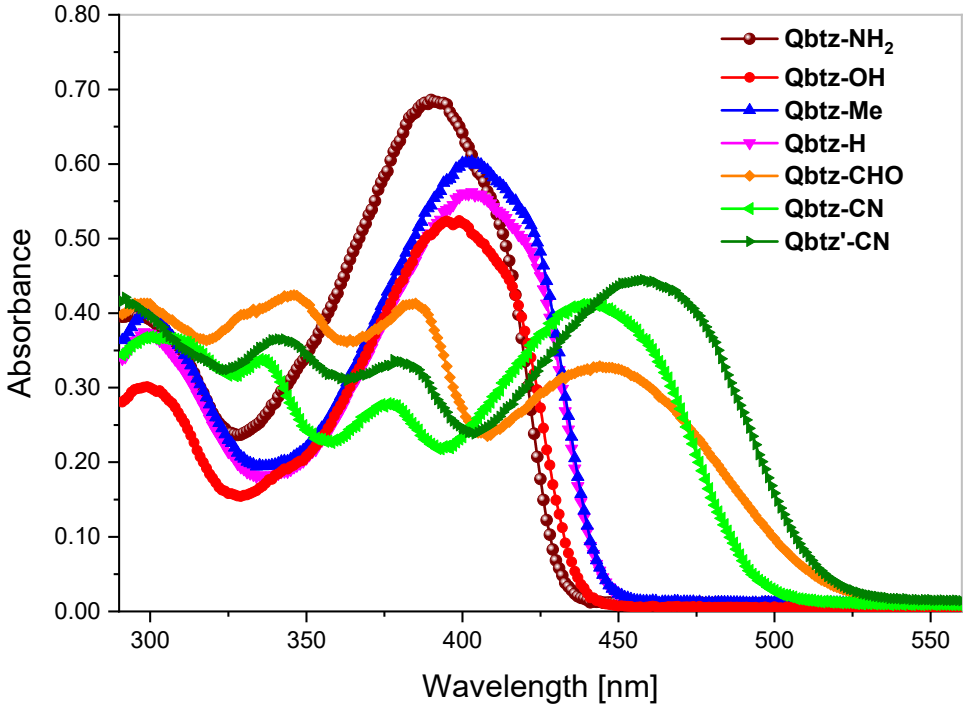


Figure S1. UV-Vis spectra of **Qbtz-R** dyes in toluene (measured at $c = 1\times10^{-5}$ M)

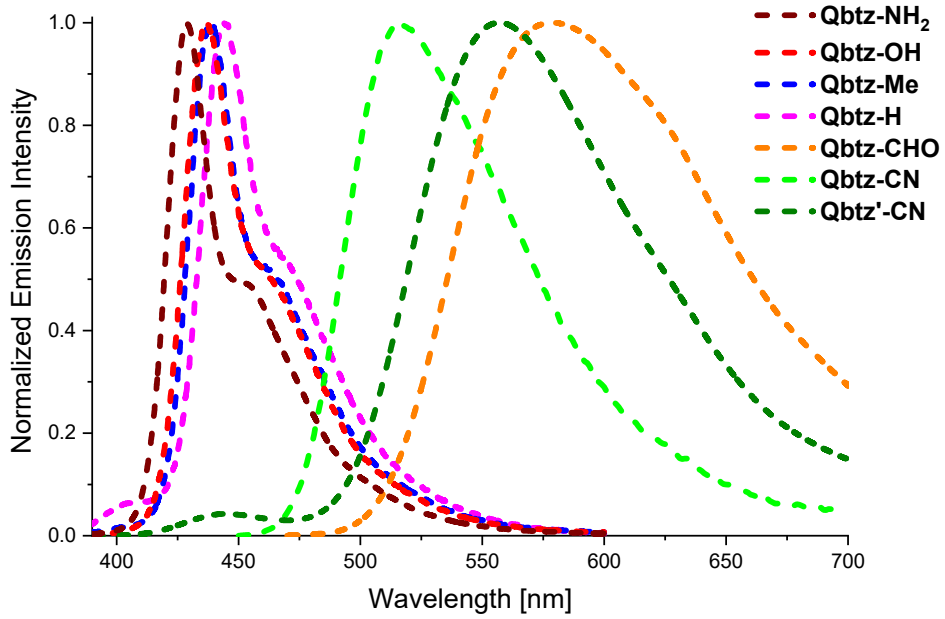


Figure S2. Nomalized emission spectra of **Qbtz-R** dyes in toluene

(measured at concentrations, at which the absorbance at the excitation wavelength < 0.1)

8 Fluorescence Quantum Yields measurements

The fluorescence quantum yields were determined by means of the following model:[14]

$$\Phi_x = \Phi_{ref}\left(\frac{grad_X}{grad_{ref}}\right)\left(\frac{\eta_X^2}{\eta_{ref}^2}\right)$$

where ϕ is the fluorescence quantum yield, *grad* denotes the gradient from the plot of integrated fluorescence intensity (area under the emission curve) *vs.* absorbance, and η is the refractive index of the solvents used in measurement. The subscripts *ref* and *X* stand for the reference and tested dye, respectively.

A series of **Qbtz-R** dye solutions in UV-VIS grade toluene (η = 1.496) was prepared so that the absorbance at excitation wavelength (λ_{exc} = 370 nm) did not exceed 0.1. The standard – quinine sulphate (**QY**, λ_{ex} = 370 nm; Φ_{ref} = 0.546)[15] was dissolved in 0.1 M sulphuric acid (η = 1.3325). Emission intensity (measured as area under emission curve) was plotted against absorbance at λ_{exc} and the slope obtained was used for quantum yield calculation. The results are summarized in the following graph and table.

Table S1. Fluorescence quantum yields of **Qbtz-R** dyes determined in toluene

Sample	Slope	R^2	Quantum Yield
Standard – QY	(3.378±0.213)x10^5	0.99209	0.546 [15]
Qbtz-NH_2	(3.730±0.186)x10^5	0.99753	0.76
Qbtz-OH	(4.416±0.099)x10^5	0.99849	0.95
Qbtz-CH_3	(4.101±0.162)x10^5	0.99536	0.88
Qbtz-H	(4.158±0.186)x10^5	0.99393	0.89
Qbtz-CHO	(1.309±0.040)x10^5	0.99919	0.27
Qbtz-CN	(3.320±0.089)x10^5	0.99928	0.68
Qbtz'-CN	(2.294±0.046)x10^5	0.99963	0.47

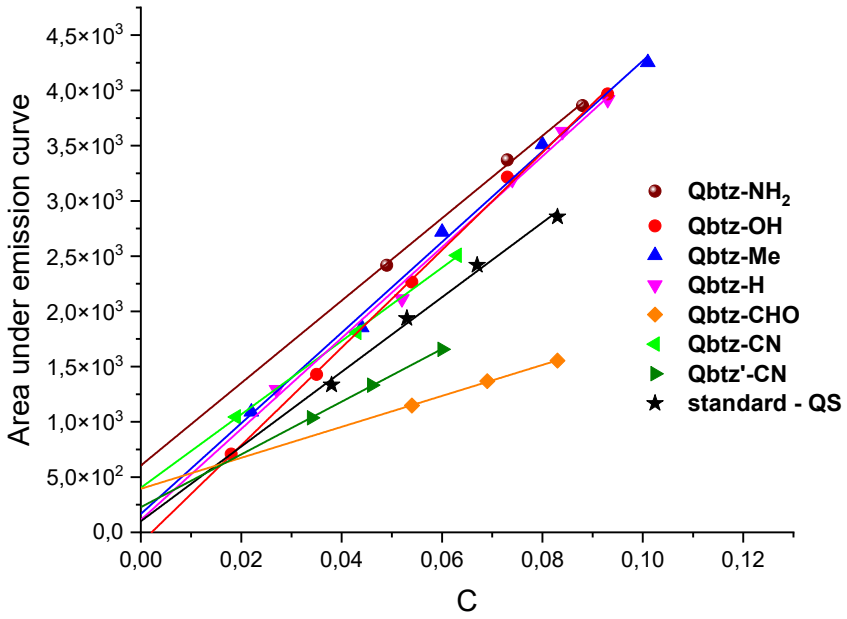


Figure S3. Emission intensity plotted against absorbance for samples in toluene

9 TPEF measurements

The two-photon absorption (TPA) properties of **Qbtz-R** dyes were studied via a two-photon excited fluorescence (TPEF) technique using femtosecond (fs) pulsed excitation.[16-18] A mode-locked Ti:Sapphire fs laser, emitting 80 fs pulses tunable from 730 to 850 nm with 80 MHz repetition frequency, has been used as the excitation source. The laser beam passed through a 5-fold expanding telescope in order to achieve uniform illumination at the back of the microscope objective lens (16-fold), used to focus the fs laser beam in the samples. The samples were measured in quartz cuvettes as 2×10^{-5} M solutions of the dyes in toluene. Three linear motorized stages (Newport) driven by a three-axis controller (Newport) have been utilized to move each sample towards the excitation focal point. The TPA-induced fluorescence has been collected backwards and was separated by the laser beam via a dichroic mirror with a high-pass region (cold mirror) and a set of filters. Finally, a photomultiplier connected to photon-counting electronics (Becker-Hickl) was used to detect the emitted fluorescence. Rhodamine 6G in MeOH (2×10^{-5} M) has been used as the reference sample while the measured scattering intensity from the solvent has been subtracted. The calculations of the TPA cross sections have been made after plotting the TPEF intensity as a function of the excitation intensity in order to confirm the occurrence of the square-law dependence of I_{TPEF} on the excitation power.

The δ_{TPA} values of samples (X) were determined through the equation:

$$\delta_{TPA,X} = \frac{k_{ref}\delta_{ref}\Phi_{ref}n_{ref}C_{ref}P_{ref}^2}{k_X\Phi_X n_X C_X P_X^2}\frac{I_X}{I_{ref}}$$

where k is the fluorescence collection efficiency, Φ is the two-photon fluorescence quantum yield, n the refractive index, C the concentration of the solutions, P the incident power and I is the intensity of two-photon excited fluorescence. Rhodamine 6G, having a well-known TPA spectrum was used as reference.[18] Finally, for the calculation of δ_{TPA}, the fluorescence quantum yield upon two-photon excitation was assumed to be the same as that upon one-photon excitation, following the analysis of Xu et al.[16]

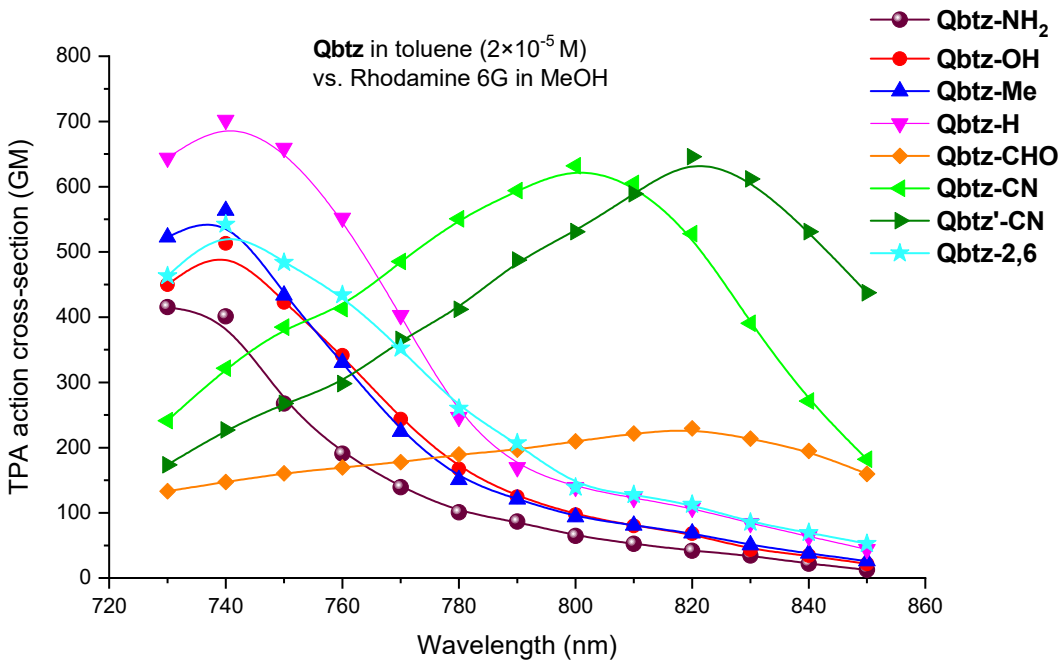


Figure S4. TPA action cross-sections ($\delta_{TPA}\Phi_f$) of **Qbtz-R** dyes in toluene

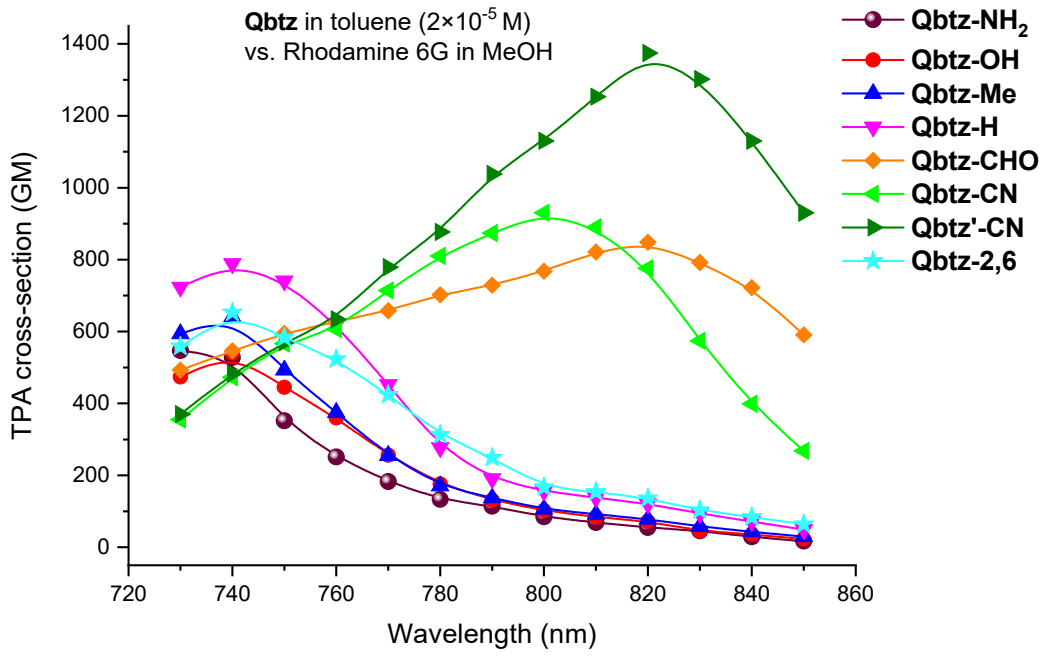


Figure S5. TPA cross-sections (δ_{TPA}) of **Qbtz-R** dyes in toluene

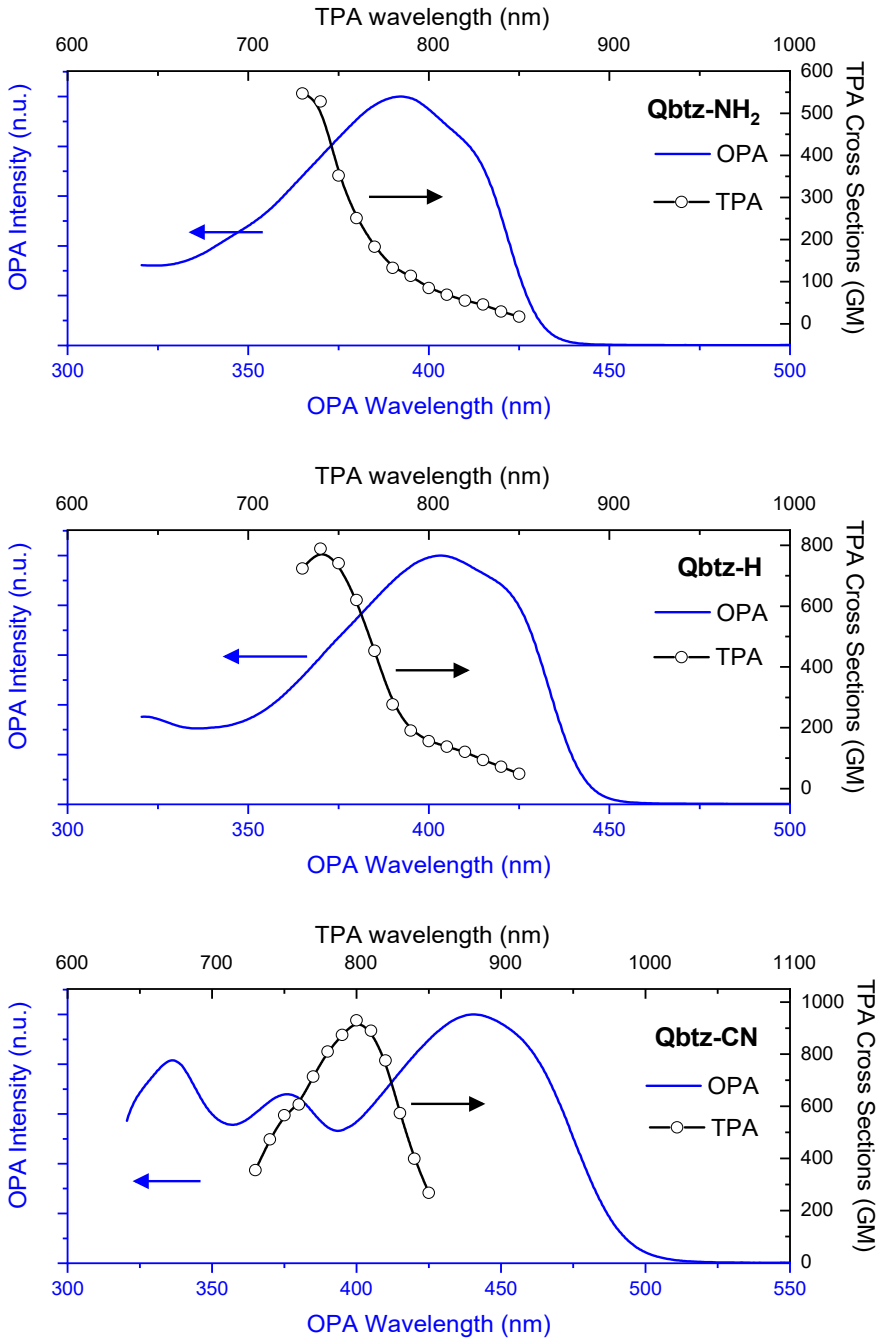


Figure S6. Overlap of one-photon (OPA) and two-photon (TPA) absorption spectra of selected **Qbtz-R** in toluene, confirming the quadrupolar nature of dyes with deeper transitions ($S_0 \rightarrow S_2$ or $S_0 \rightarrow S_3$) as compared to OPA ($S_0 \rightarrow S_1$) process.

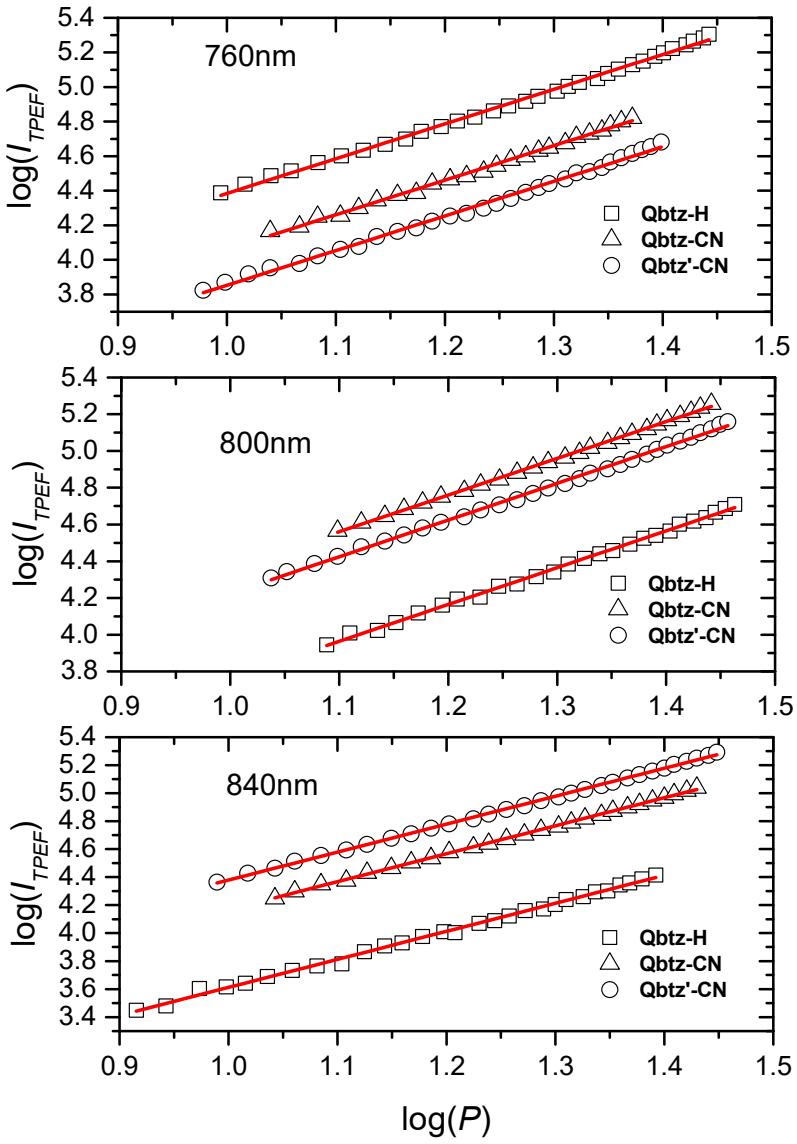


Figure S7. Plot of log(TPEF intensity) vs. log(laser power) for selected **Qbtz-R** dye solutions. The slopes in all cases were exactly 2.00 ($R^2 > 0.99$) confirming the quadratic law dependence and assuring that emission is due to a two-photon induced process.

10 X-ray Structure Analysis

Crystals suitable for X-ray diffraction studies were obtained by dissolving **2-Me**, respectively, **Qbtz-H** in chloroform, layering these $CHCl_3$ solutions with *n*-hexane and by slow evaporation of solvents.

The intensity data for both compounds under study (**2-Me, Qbtz-H**) were collected on a STOE StadiVari partial-χ diffractometer at room temperature using Dectris Pilatus3R 300 K HPAD detector and Incoatec IμS microfocused source with graded multilayer mirror optics (AgKα radiation, λ = 0.56083 Å) for **2-Me** and Xenocs Genix3D Cu HF (CuKα radiation, λ = 1.54186 Å) for **Qbtz-H** by ω-scans. The diffraction intensities were corrected for Lorentz and polarization effects; multi-scan absorption correction was also applied. Data collection, cell refinement, data reduction and finalization including all corrections mentioned above were carried by STOE *X-Area*[19] and *LANA* software.[20]

The structure of **2-Me** was solved by *olex2.solve*[21] using charge flipping method and refined by *SHELXL-2018/3*[22] using high resolution cutoff at 0.78 Å. All non-H atoms were refined with free coordinates. All H atoms were present in a difference map. Aromatic H atoms were placed into idealised positions with riding coordinates and $U_{iso} = 1.2U_{eq}(C_{sp2})$. Methyl group was refined as freely rotating group with $U_{iso}(H) = 1.5U_{eq}(C_{sp3})$.

The structure of **Qbtz-H**.$CHCl_3$ was solved by *SHELXT 2018/2*[23] using dual space „intrinsic phasing“ method and refined by *SHELXL-2018/3*. The initial solution revealed a disorder of the **Qbtz-H** molecule and severely disordered solvent. Benzothiazole moiety has two possible orientations with site occupation factor of major and minor component refined to 0.8059(16) and 0.1941(16), respectively. For all chemically equivalent bonds and angles in the refined part of the disorder and neighboring –C≡C– groups, the distance similarity (SADI) restraints were applied together with FLAT restraint for minor component benzothiazole group to retain correct geometry during component separation. The range of disorder components separation was selected based on the achieved R factor but avoiding too low *S* values to prevent overrefinement. All overlapping atom pairs of the disordered part of the molecule were refined with equivalent ADPs by using the EADP constraint to prevent overlapping atoms from going non-positive definite and to save parameters. Because of the same reason, whole molecule rigid bond (RIGU) restraints for all ADPs were also applied. The ADP shapes of chlorine atoms revealed rotation of the chloroform molecules around C–H bonds and in the case of the major disorder component we were able to separate two positions corresponding to the above-

mentioned rotation movement with site occupations 0.392(7) and 0.374(7). Site occupation factor for minor disorder component was close to the site occupation of main molecule minor disorder component and they were linked together in the final stages of the refinement. Although the sum of site occupations of solvent major disorder component is not equal to the main molecule major disorder component, three of five strongest peaks present in a difference density map correspond to the third possible orientation of CCl_3 group. However, including them in the refinement didn't lead to better-behaved model. All C–Cl bond lengths and Cl–C–Cl angles in chloroform molecules were restrained to be similar by using SADI restraints. In the major component, the chlorine atoms in both orientations of the molecule were retained to be in the same plane by using FLAT restraint. For better behavior of the ADPs, similarity restraint (SIMU) for all chlorine atoms was used. All H atoms were placed geometrically with riding coordinates and $U_{iso}(H) = 1.2U_{eq}(C)$ with site occupancies equal to the occupancies of corresponding parent atoms.

Geometrical analysis was performed using SHELXL-2018/3 and Olex2[24]; Olex2 was also used for structural drawings. Intermolecular contacts were analysed using *CrystalExplorer*[25] and B3LYP/6-311G(d,p) Hirshfeld partitioning with Very High quality setting and X–H distances were normalized to the values obtained from neutron diffraction.[26-28] Electrostatic potential values on Hirshfeld surface are in the interval −0.0674 to 0.0635 au.

Crystal data and conditions of data collection and refinement are reported in Table S2.

Table S2. Experimental and refinement data for X-ray structures of **2-Me** and **Qbtz-H**.$CHCl_3$

Empirical formula	$C_8H_5I_2NS$ (**2-Me**)	$C_{48}H_{32}ClN_3S$ (**Qbtz-H.**$CHCl_3$)
CCDC No.	1901710	2043178
M_r	400.79	789.17
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
Unit cell dimensions	determined from 18233 reflections	determined from 18816 reflections
a [Å], α [°]	13.1690(6), 90	10.5498(8), 114.536(7)
b [Å], β [°]	4.2536(3), 102.592(4)	14.4285(11), 99.447(8)
c [Å], γ [°]	19.0445(9), 90	15.594(2), 101.858(6)
V [Å^3]	1041.13(10)	2028.6(4)
Z, Z'	4, 1	2, 1
μ [mm^{-1}], ρ (calcd.) [g cm^{-3}]	3.274, 2.558	2.814, 1.292
F(000)	728	816
Absorption correction, T_{min}, T_{max}	Multi-scan, 0.1720, 0.8851	Multi-scan, 0.416, 1
Extinction correction	–	0.00102(18) (*SHELXL*)
Crystal size [mm]	0.21 × 0.113 × 0.05	0.1 × 0.14 × 0.2
Crystal habit, color	Block, colourless	Block, orange
θ range for data collection [°]	2.50 – 21.07	3.25 – 71.85
Limiting indices	$h = -16 \rightarrow 16$ $k = -5 \rightarrow 5$ $l = -24 \rightarrow 24$	$h = -12 \rightarrow 12$ $k = -10 \rightarrow 17$ $l = -19 \rightarrow 18$
Reflections collected/unique/observed [$I > 2\sigma(I)$]	10830/2261/1786 [R_{int} = 3.67 %, R_σ = 2.41 %, Friedel opposites merged]	50316/7711/4104 [R_{int} = 4.56 %, R_σ = 3.91 %, Friedel opposites merged]
Completness to θ [°]	98 % to 21.07°	99.2 % to 67.69°
Data/restraints/parameters	2261/9/110	7711/720/608
Final weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0474P)^2 + 0.3003P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0799P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S (goodness-of-fit)	1.019/1.018 (restrained)	0.893/0.899 (restrained)
Final R indices [$I > 2\sigma(I)$]	R = 2.81 %, wR = 7.42 %	R = 4.55 %, wR = 12.33 %
Final R indices (all data)	R = 3.75 %, wR = 8.04 %	R = 8.85 %, wR = 13.84 %
Largest difference peak/hole [e Å^{-3}]	1.067/–0.538	0.206/–0.266

The crystal structure of **2-Me** (Figure S8) has $P2_1/c$ space group symmetry with asymmetric unit consisting of one (Z'=1) molecule of 4,7-diiodo-2-methylbenzothiazole. The intermolecular contacts are based on a weak C10–H10B···N3^{i} interaction (where superscript ^{i} represents symmetry operation $(-x, -y, 1-z)$) thus forming dimers with supramolecular rings with $\mathbf{N_2 = R_2^2(8)}$ graph set (Figure S9a)[29], and C10–H10A…N3^{ii} interaction (where ^{ii} represents symmetry operation $(x, 1+y, z)$) forming supramolecular chains with $\mathbf{N_2 = C(4)}$ graph set (Figure S9b) and complementing parallel-displaced π-stacking interaction (Figure S10a, b) with interplanar distance of 3.648(2) Å. The I···I halogen bonds between neighboring molecules are also present; Figure S11a shows σ-hole on I1 atom in the direction towards I2^{iv} atom and Figure S11b shows σ-hole on I2 atom in the direction of I1^{vii} atom ($^{iv} = (x, -½-y, ½+z)$, $^{vii} = (x, ½-y, -½+z)$). Halogen bonds form zigzag chains in the direction of crystallographic *b* axis (Figure S12). Intermolecular interactions in **2-Me** are listed in **Table 3**.

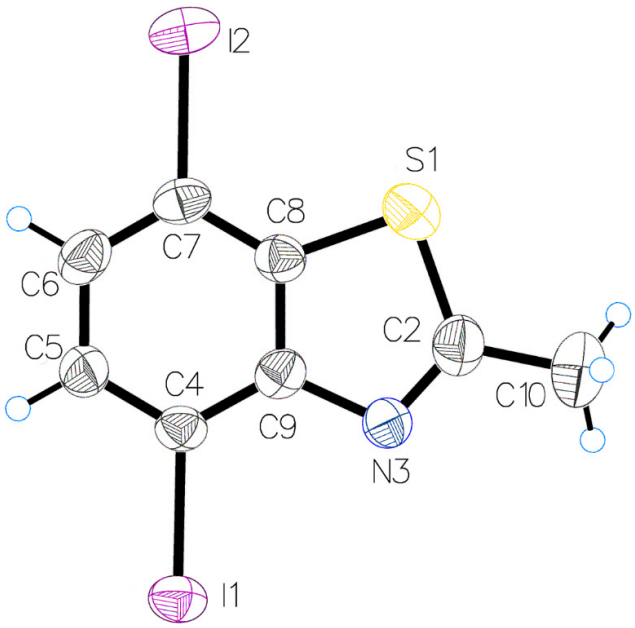


Figure S8. The ADP plot with numbering scheme of the compound **2-Me**. All non-hydrogen atoms are drawn as 50 % probability ellipsoids.

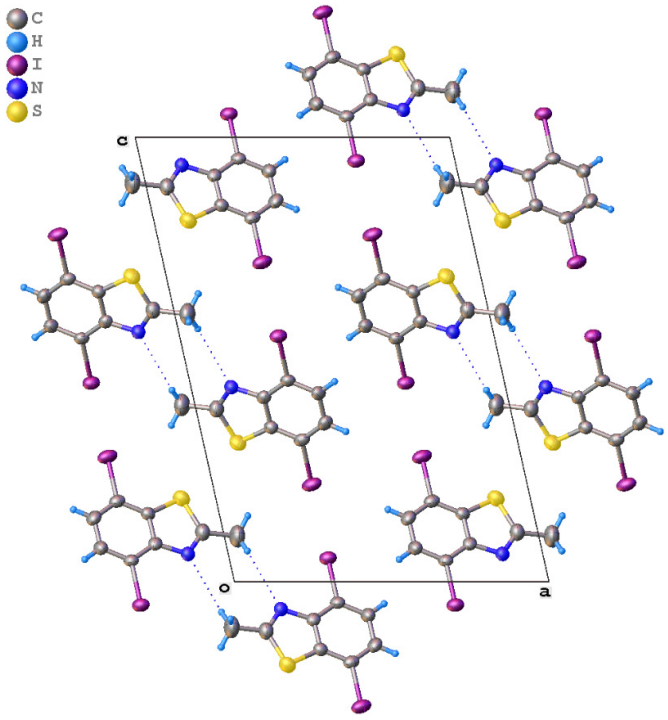


Figure S9a. View of the **2-Me** cell packing along the *b* axis. The dashed lines indicate C10–H10B…N3^{i} (^{i} = (– *x*, – *y*, 1 – *z*)) weak hydrogen bonds forming supramolecular dimers connected via $\mathbf{N_2 = R_2^2(8)}$ rings. The displacement ellipsoids are drawn at the 50 % probability level.

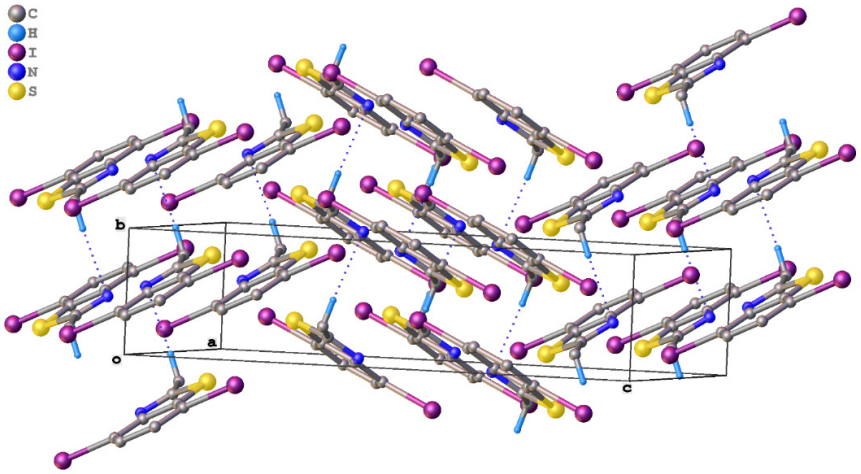


Figure S9b. View of the **2-Me** cell packing. The dashed lines indicate C10–H10A···N3^{ii} (^{ii} = (*x*, 1 + *y*, *z*)) weak hydrogen bonds forming $\mathbf{N_2 = C(4)}$ supramolecular chains complementary to π-stacking interaction. All H atoms except those involved in hydrogen bonding are omitted for clarity.

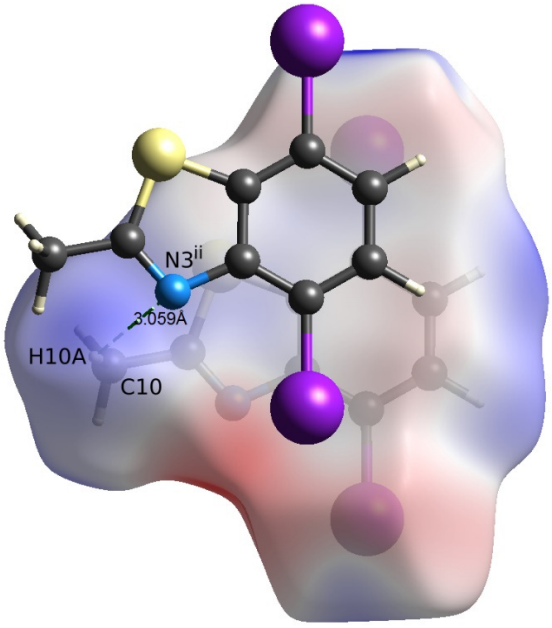


Figure S10a. A view of the π-stacking interaction reinforced by C10–H10A···N3^{ii} (^{ii} = (x, 1 + y, z)) weak hydrogen bond in **2-Me**. Red color indicates negative and blue color indicates positive electrostatic potential on the Hirshfeld surface.

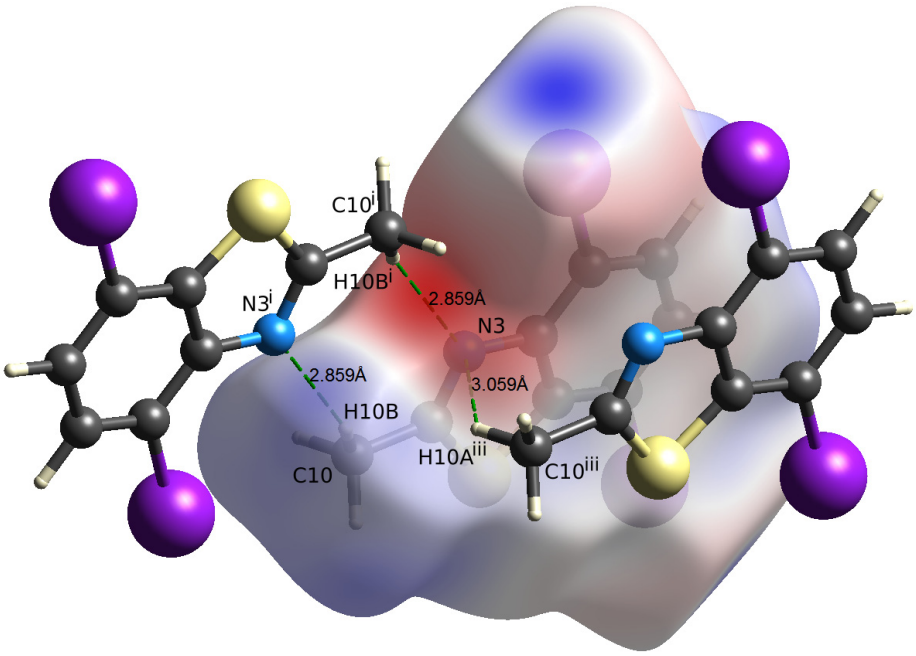


Figure S10b. A view of supramolecular dimers connected via **N_2 = $R_2^2(8)$** rings and the π-stacking interaction reinforced by C10–H10A···N3^{iii} weak hydrogen bond in **2-Me**. Red color indicates negative and blue color indicates positive electrostatic potential on the Hirshfeld surface. Symmetry operations: ^{i} = (x, 1 + y, z), ^{iii} = (x, 1 – y, z).

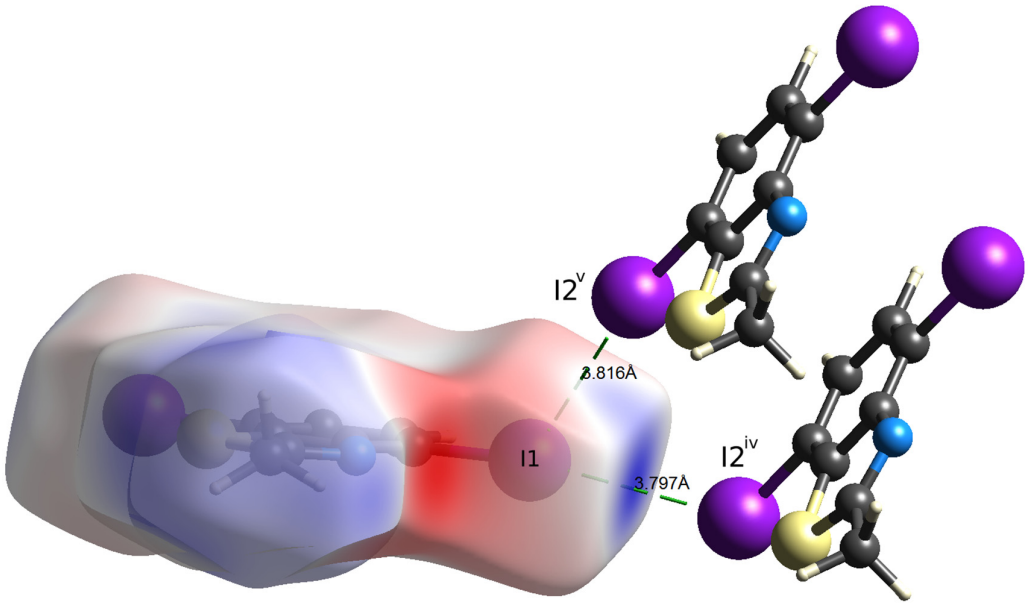


Figure S11a. A view of the I···I interaction (^{iv} = (x, – ½ – y, ½ + z), ^{v} = (x, ½ – y, ½ + z)) in **2-Me**. Red color indicates negative and blue color indicates positive electrostatic potential on the Hirshfeld surface.

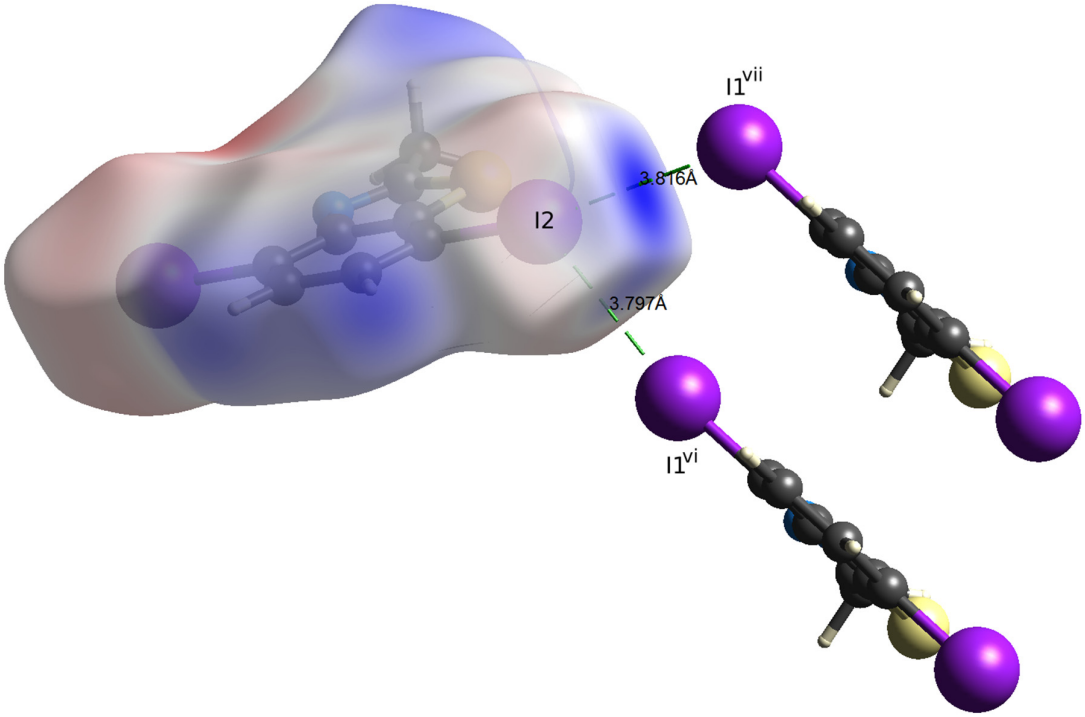


Figure S11b A view of the I···I interaction (^{vi} = (x, – ½ – y, – ½ + z), ^{vii} = (x, ½ – y, – ½ + z)) in **2-Me**. Red color indicates negative and blue color indicates positive electrostatic potential on the Hirshfeld surface.

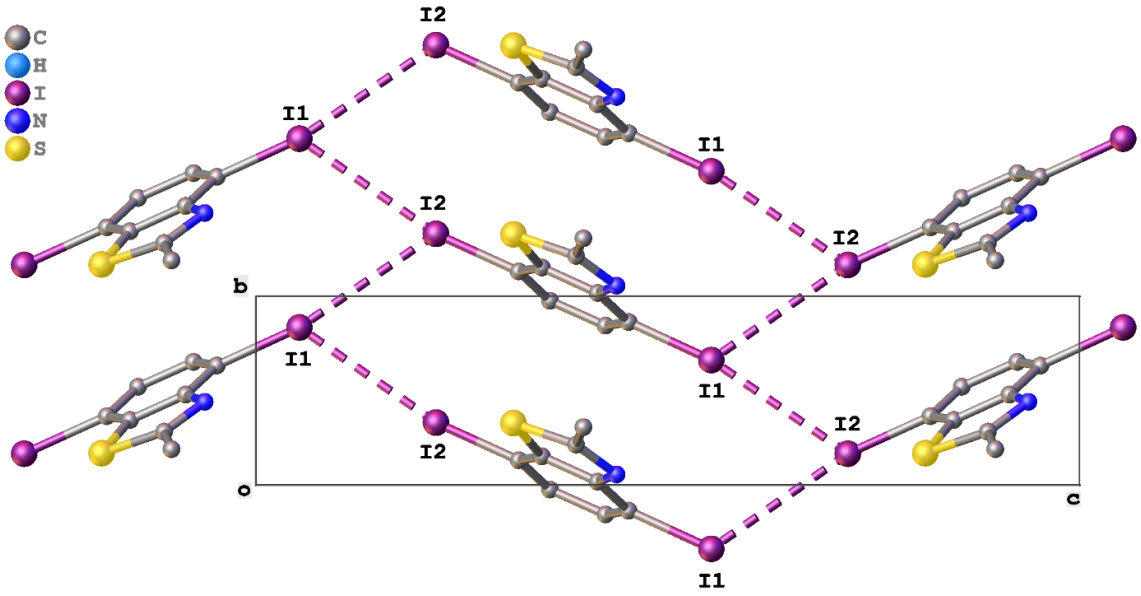


Figure S12. A view of the unit cell of **2-Me** along the *a* axis showing zig-zag chains formed by I···I interactions in the *b* axis direction. All H atoms are omitted for clarity.

Table S3. Intermolecular interactions in the structure of **2-Me**

Weak hydrogen bonds						
D	**H**	**A**	***d*(D–H) [Å]**	***d*(H…A) [Å]**	***d*(D…A) [Å]**	**(D–H…A) [°]**
C10	H10B	N3^{i}	0.96	2.97	3.889(7)	160.0
C10	H10A	N3^{ii}	0.96	3.14	3.869(7)	133.8
I…I bonds						
A	**X1**	**X2**	**B**	***d*(X1…X2) [Å]**	**(A–X1…X2) [°]**	**(X1…X2–B) [°]**
C4	I1	I2^{iv}	C7^{iv}	3.7969(4)	170.44(11)	122.32(11)
C4	I1	I2^{v}	C7^{v}	3.8155(4)	121.61(11)	169.74(11)

Symmetry operations: ^{i} = (– *x*, – *y*, 1 – *z*), ^{ii} = (*x*, 1 + *y*, *z*), ^{iv} = (*x*, – ½ – *y*, ½ + *z*), ^{v} = (*x*, ½ – *y*, ½ + *z*)

The crystal structure of **Qbtz-H** (Figures S13, S14) has *P*–1 space group symmetry with an asymmetric unit containing one molecule of 4,7-bis[4-(*N*,*N*-diphenylamino)phenylethynyl]-benzothiazole and one disordered molecule of chloroform ($Z' = 1$). There are two possible orientations of benzothiazole moiety given by the rotation of the group around the –C≡C– bonds. The solvent molecules are linked to the benzothiazole unit by the formation of a weak C–H···N bond between the molecule of chloroform and benzothiazole ring as indicated by the site occupations and occupy the channels between **Qbtz-H** molecules running in the [110] direction (Figure S15). Non-parallel displaced π-stacking interactions between the molecules are reinforced by weak hydrogen bonds forming supramolecular dimers – C47–H47···N1A for the major disorder component and C25–H25···N1B for the minor disorder component. Otherwise, the major disorder component can form one C25–H25···N1B bond to the neighboring minor disorder component (and similarly, minor disorder component is able to form one C47–H47···N1A bond to the neighbouring major disorder components). This leads to the possibility of forming hydrogen bonded chains of mutually π-stacked alternate major and minor disorder components (Figure S16a), however, as we can infer from the site occupations of both major and minor components, preferred stacking mode are π-stacked major component dimers (Figure S16b). Intermolecular interactions in **Qbtz-H** are listed in **Table S4**.

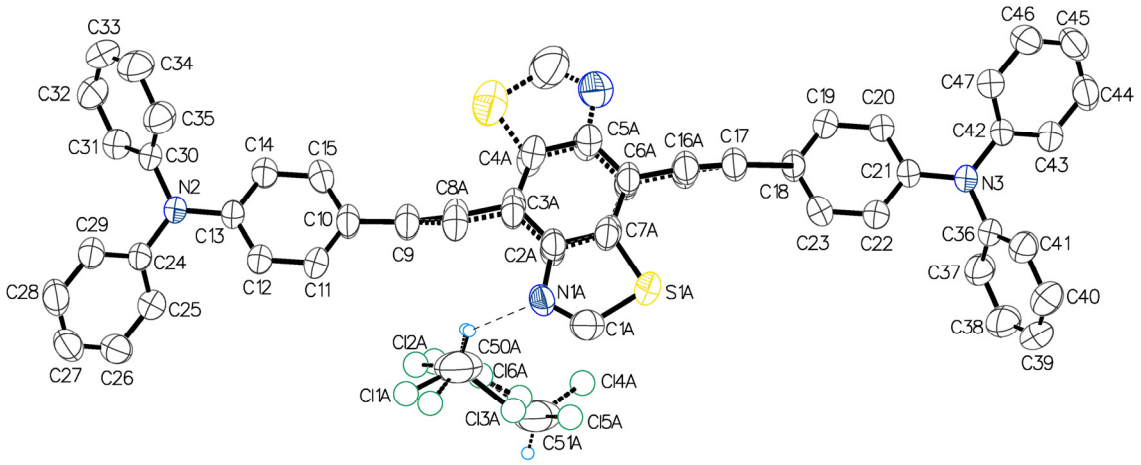


Figure S13. The ADP plot with numbering scheme of the compound **Qbtz-H**. All non-hydrogen atoms are drawn as 50 % probability ellipsoids. All H atoms except those involved in hydrogen bonding are omitted for clarity. In disordered part of the structure, minor disorder component atoms (with B suffix) are not labeled and chlorine atoms are given as a circles with arbitrary radii to prevent overlaps.

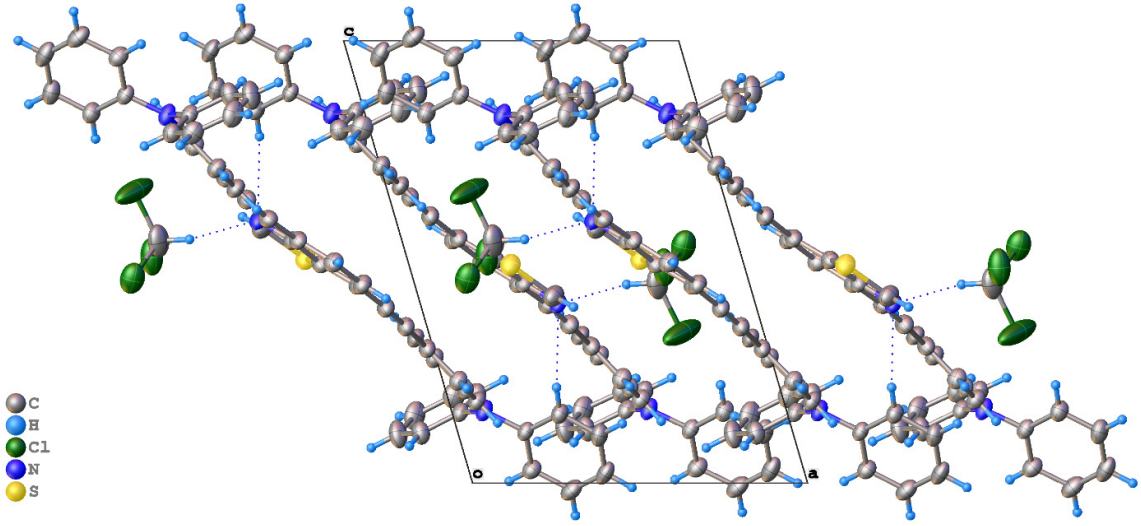


Figure S14. View of the compound **Qbtz-H** cell packing along the *b* axis. The dashed lines indicate C–H···N weak hydrogen bonds. The displacement ellipsoids are drawn at the 30 % probability level. Only major disorder components are displayed.

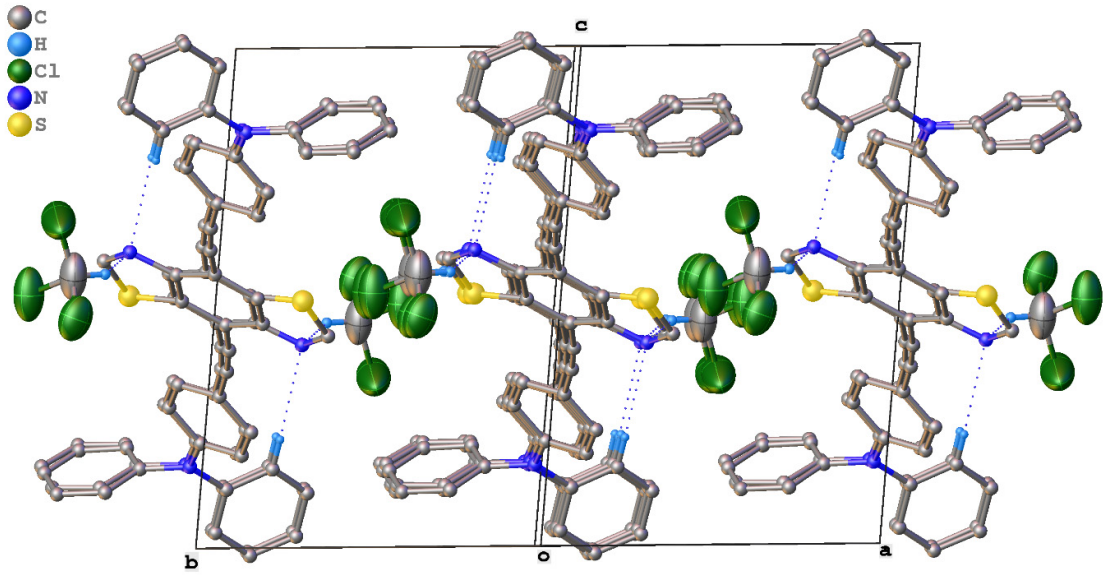


Figure S15. A view of solvent containing channels in the structure of **Qbtz-H** in the [110] direction. The dashed lines indicate C–H···N weak hydrogen bonds. The displacement ellipsoids of $CHCl_3$ molecules are drawn at the 50 % probability level, **Qbtz-H** molecules are displayed as ball and stick model. Only major disorder components are displayed. All hydrogen atoms not involved in hydrogen bonding network are omitted for clarity.

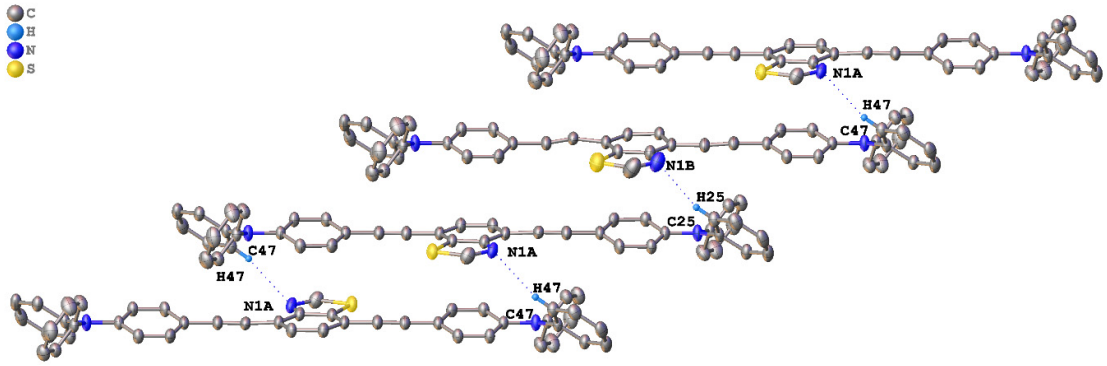


Figure S16a. A possibility of formation hydrogen bonded chain of minor disorder components (top 3 molecules) in the structure of **Qbtz-H** starting from hydrogen bonded dimer formed by major disorder components (bottom two molecules).

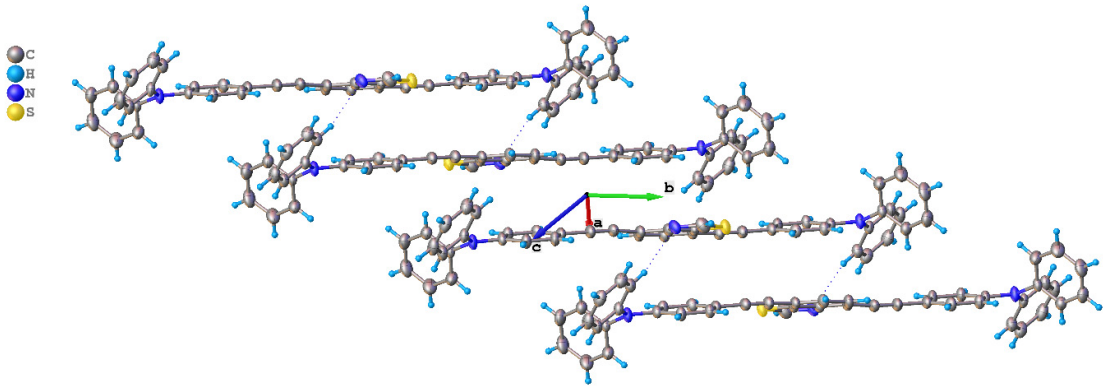


Figure S16b. A view of ordinary π-stacking pattern in the structure of **Qbtz-H** consisting of double C–H···N hydrogen bonded/π-stacked **Qbtz-H** dimers, which are mutually π-stacked. The displacement ellipsoids are drawn at the 30 % probability level. Orientation is given by principal axes.

Table S4. Intermolecular interactions in the structure of **Qbtz-H**.$CHCl_3$

Weak hydrogen bonds						
D	**H**	**A**	***d*(D–H) [Å]**	***d*(H…A) [Å]**	***d*(D…A) [Å]**	**(D–H…A) [°]**
C50A	H50A	N1A	0.98	2.60	3.345(6)	132.4
C50B	H50B	N1A	0.98	2.68	3.345(6)	125.8
C51A	H51A	N1B^{i}	0.98	2.56	3.249(18)	127.7
C25	H25	N1B^{ii}	0.93	2.58	3.487(11)	164.5
C47	H47	N1A^{iii}	0.93	2.73	3.642(3)	167.4
Non-parallel displaced π-π interactions (major component)						
Ring 1	**C18–C19–C20–C21–C22–C23**		**Ring 2**	**S1A^{iii}–C1A^{iii}–N1A^{iii}–C2A^{iii}–C7A^{iii}**		
Centroid (Ring 1) to centroid (Ring 2) distance				3.715(6) Å		
Plane (Ring 1) to centroid (Ring 2) distance				3.688(6) Å		
Plane (Ring 2) to centroid (Ring 1) distance				3.609(12) Å		
Plane (Ring 1) to plane (Ring 2) shift distance				0.447(4) Å		
Plane (Ring 2) to plane (Ring 1) shift distance				0.88(3) Å		
Plane (Ring 1) normal to plane (Ring 2) normal angle				12.3(4)°		
Ring 3	**C10–C11–C12–C13–C14–C15**		**Ring 4**	**C2A^{ii}–C3A^{ii}–C4A^{ii}–C5A^{ii}–C6A^{ii}–C7A^{ii}**		
Centroid (Ring 3) to centroid (Ring 4) distance				3.869(8) Å		
Plane (Ring 3) to centroid (Ring 4) distance				3.380(8) Å		
Plane (Ring 4) to centroid (Ring 3) distance				3.674(9) Å		
Plane (Ring 3) to plane (Ring 4) shift distance				1.882(4) Å		
Plane (Ring 4) to plane (Ring 3) shift distance				1.21(2) Å		
Plane (Ring 3) normal to plane (Ring 4) normal angle				13.6(3)°		

Symmetry operations: $^{i} = (1 + x, y, z)$, $^{ii} = (1 - x, 1 - y, 1 - z)$, $^{iii} = (-x, -y, 1 - z)$

11 Computational Details and Results

The ground-state structures of all systems under investigation were fully optimized at the PBE0[30, 31] level of theory, employing all-electron def2-TZVP basis set[32] an atom-pairwise correction for dispersion forces via Grimme's D3 model[33] with Becke-Johnson (BJ)[34] damping, in the Turbomole program.[35] All structures were characterized as true minima on the harmonic potential energy hypersurface through vibrational analysis (no imaginary frequencies were found).

The same code was used for calculation of free energies for the dissociation of selected protonated *N*-heteroarenes, arylamines and iodinated benzothiazoles and evaluation of pK_a values. These calculations were done at the PBE0-D3(BJ)/def2-TZVP level, using the direct COSMO-RS model for real solvents and considering water as the solvent.[36-38]

The two-component relativistic all-electron DFT calculations of the NMR nuclear shieldings[39, 40] were performed using the Amsterdam Density Functional (ADF) program suite,[41] employing the global hydrid PBE0 (with 25% exact-exchange admixture)[31] exchange-correlation functional, in conjunction with Slater-type orbital basis sets of triple-ζ doubly polarized (TZ2P) quality and an integration accuracy of 5.0. The relativistic zeroth-order regular approximation (ZORA)[39, 40, 42] calculations of NMR shieldings were done by using gauge-including atomic orbitals (GIAOs)[43] and including the terms from the exchange–correlation (XC) response kernel.[44-46] The computed ^{1}H and ^{13}C nuclear shieldings were converted to chemical shifts (δ, in ppm) relative to the shielding of tetramethylsilane (TMS), considering benzene as the secondary standard for aromatic hydrogen and carbon atom resonances.

Time-dependent DFT method using the Coulomb-attenuated CAM-B3LYP[47] exchange-correlation functional, respectively, in conjunction with the 6-311++G** basis set was applied to get vertical excitation energies (E_n), transition dipole moments (μ_{0n}) and adiabatic dipole

moment changes ($\Delta\mu_{0n}$) between the ground-state and the *n*-th excited state. The excited-to-excited transition dipole moments μ_{1n} were obtained from the double-residue of the quadratic response function. All these calculations were carried out with the Dalton program.[48]

The TPA cross-sections δ_{TPA} were evaluated by calculating the two-photon transition moment matrix elements $S_{\alpha\beta}$ in the Dalton program. The matrix elements $S_{\alpha\beta}$ for the two-photon resonant absorption of identical energy can be identified from the sum-over-states formula as:

$$S_{\alpha\beta} = \sum_n \left[\frac{\langle 0|\mu_\alpha|n\rangle\langle n|\mu_\beta|f\rangle}{\omega_n - \frac{\omega_f}{2}} + \frac{\langle 0|\mu_\beta|n\rangle\langle n|\mu_\alpha|f\rangle}{\omega_n - \frac{\omega_f}{2}} \right] \qquad (\alpha, \beta = x, y, z)$$

where ω_n represents the excitation energy from the ground state $|0\rangle$ to the excited state $|n\rangle$, $\omega_f/2$ corresponds to half of the excitation energy associated with the transition from the ground to the final excited state $|f\rangle$, μ_α and μ_β are the Cartesian components of the electronic dipole moment operator. The explicit summation over all excited states of the molecule was avoided through the use of quadratic response theory. Within this formalism, matrix elements $S_{\alpha\beta}$ are extracted as a single residue of the appropriate quadratic response function for the dipole moment operators. This approach is described in detail in refs. [49], [50], [51].

TPA cross-sections of molecules for linearly polarized monochromatic light were calculated (in atomic units) from $S_{\alpha\beta}$ elements as:

$$\delta_{a.u.} = \frac{1}{30} \sum_{\alpha,\beta} (2S_{\alpha\alpha}S^*_{\beta\beta} + 4S_{\alpha\beta}S^*_{\beta\alpha})$$

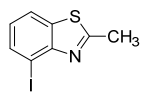
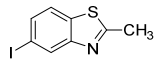
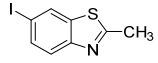
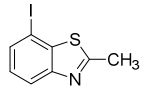
Finally, $\delta_{a.u.}$ values were converted to TPA cross-sections δ_{TPA}, which are directly comparable to experiment, using the following relationship:

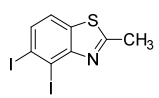
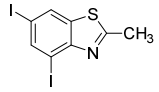
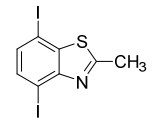
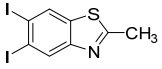
$$\delta_{TPA} = \frac{(2\pi)^3 \alpha a_0^5}{c} \frac{\omega^2}{\pi\Gamma} \delta_{a.u.}$$

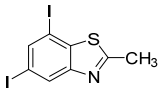
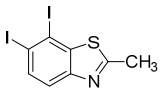
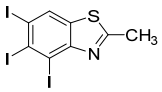
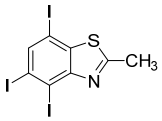
Here, α is the fine structure constant, a_0 the Bohr radius, c the speed of light, ω the energy of the exciting photon (in case of the TPA process, one half of the excitation energy) and $\pi\Gamma$ a

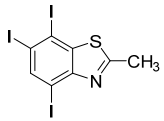
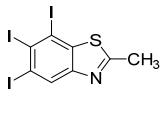
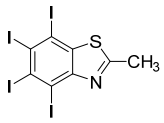
normalization factor due to the Lorentzian line-shape broadening of the excited state (Γ = 0.2 eV was used throughout this work). The units of δ_{TPA} will become GM ($cm^4.s.photon^{-1}$), provided we use centimeter-gram-second units for a_0 and c, and atomic units for ω and Γ. Note that effects on nuclear motion, which may also contribute to δ_{TPA}, are not included in our treatment.

Table S5. Calculated and experimental ^{13}C and ^{1}H NMR shifts (in ppm with respect to TMS) of iodo-substituted 2-methylbenzothiazoles [a]

System		C-2	C-3a	C-4	C-5	C-6	C-7	C-7a	2-CH_3	H-4	H-5	H-6	H-7	2-CH_3
	σ_{calcd}	12.0	27.2	93.5	46.6	59.1	62.4	49.3	170.6	–	23.3	24.2	23.3	28.8
	δ_{calcd}	170.9	155.6	89.3	136.3	123.7	120.4	133.6	22.2	–	7.67	6.85	7.66	2.65
	δ_{expt}	**167.1**	**154.2**	**89.3**	**135.7**	**126.0**	**121.4**	**134.5**	**20.2**	**–**	**7.87**	**7.06**	**7.78**	**2.87**
	σ_{calcd}	9.9	26.5	51.6	93.6	49.6	61.1	48.1	170.4	22.9	–	23.6	23.6	28.9
	δ_{calcd}	173.0	156.4	131.3	89.3	133.2	121.8	134.8	22.3	8.11	–	7.44	7.44	2.64
	δ_{expt}	**168.2**	**154.8**	**131.4**	**90.1**	**133.3**	**122.7**	**135.2**	**20.1**	**8.29**	**–**	**7.63**	**7.56**	**2.83**
	σ_{calcd}	10.6	28.3	60.2	47.8	95.0	52.8	45.5	170.6	23.6	23.5	–	23.0	28.9
	δ_{calcd}	172.3	154.6	122.7	135.0	87.9	130.1	137.4	22.1	7.40	7.51	–	8.01	2.62
	δ_{expt}	**167.5**	**153.3**	**123.9**	**134.5**	**88.5**	**129.9**	**137.8**	**19.3**	**7.68**	**7.72**	**–**	**8.15**	**2.82**
	σ_{calcd}	12.6	29.9	61.9	56.8	48.5	99.9	39.5	170.3	23.4	24.1	23.6	–	28.9
	δ_{calcd}	170.2	153.0	121.0	126.0	134.4	82.9	143.3	22.4	7.62	6.94	7.42	–	2.64
	δ_{expt}	**165.9**	**151.2**	**122.0**	**127.3**	**133.9**	**83.5**	**143.6**	**20.3**	**7.90**	**7.17**	**7.65**	**–**	**2.82**

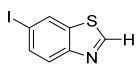
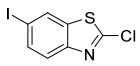
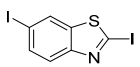
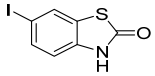
System		C-2	C-3a	C-4	C-5	C-6	C-7	C-7a	2-CH_3	H-4	H-5	H-6	H-7	2-CH_3
	σ_{calcd}	11.4	24.9	77.3	76.1	48.3	62.0	51.2	170.7	–	–	23.5	23.7	28.9
	δ_{calcd}	171.5	157.9	105.6	106.8	134.5	120.9	131.6	22.1	–	–	7.52	7.35	2.63
	σ_{calcd}	11.6	27.3	93.0	38.4	95.5	53.2	47.9	170.8	–	23.1	–	23.1	28.9
	δ_{calcd}	171.3	155.6	89.9	144.4	87.4	129.7	135.0	22.0	–	7.95	–	7.86	2.62
	σ_{calcd}	13.4	29.5	93.2	46.2	48.1	100.4	41.3	170.4	–	23.6	23.8	–	28.8
	δ_{calcd}	169.4	153.4	89.7	136.7	134.8	82.5	141.6	22.3	–	7.39	7.21	–	2.65
		166.1	**151.9**	**89.3**	**136.6**	**134.5**	**83.4**	**142.4**	**20.5**	**–**	**7.58**	**7.35**	**–**	**2.86**
	σ_{calcd}	9.3	27.2	50.7	78.2	79.6	52.1	46.6	170.6	22.8	–	–	22.9	28.9
	δ_{calcd}	173.5	155.7	132.1	104.6	103.2	130.8	136.3	22.2	8.20	–	–	8.13	2.62

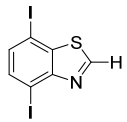
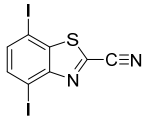
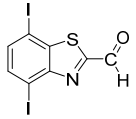
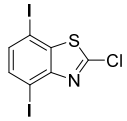
System		C-2	C-3a	C-4	C-5	C-6	C-7	C-7a	2-CH_3	H-4	H-5	H-6	H-7	2-CH_3
	σ_{calcd}	11.3	29.6	52.1	94.3	40.7	100.0	40.1	170.3	23.0	–	23.4	–	28.9
	δ_{calcd}	171.5	153.3	130.7	88.6	142.1	82.8	142.8	22.5	7.97	–	7.61	–	2.62
	σ_{calcd}	12.3	31.9	61.5	46.7	78.4	84.6	37.9	170.6	23.7	23.3	–	–	28.9
	δ_{calcd}	170.5	150.9	121.4	136.1	104.4	98.2	145.0	22.2	7.32	7.70	–	–	2.59
	δ_{expt}	**167.3**	**149.5**	**123.1**	**136.2**	**103.5**	**97.3**	**145.6**	**20.2**	**7.61**	**7.87**	**–**	**–**	**2.79**
	σ_{calcd}	11.0	25.3	78.5	61.7	81.6	52.5	50.6	171.0	–	–	–	22.8	28.9
	δ_{calcd}	171.9	157.6	104.3	121.2	101.3	130.4	132.3	21.8	–	–	–	8.23	2.61
	σ_{calcd}	12.8	28.0	76.6	76.1	39.4	100.4	42.9	170.6	–	–	23.1	–	28.9
	δ_{calcd}	170.1	154.9	106.3	106.8	143.4	82.5	140.0	22.2	–	–	7.91	–	2.62

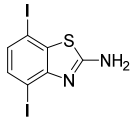
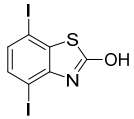
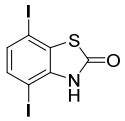
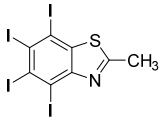
System		C-2	C-3a	C-4	C-5	C-6	C-7	C-7a	2-CH_3	H-4	H-5	H-6	H-7	2-CH_3
	σ_{calcd}	12.3	30.9	93.9	37.8	78.5	85.1	40.4	170.7	–	22.7	–	–	28.9
	δ_{calcd}	170.5	151.9	89.0	145.0	104.3	97.7	142.5	22.0	–	8.26	–	–	2.59
	δ_{expt}	**167.4**	**150.7**	**89.8**	**143.9**	**104.0**	**97.3**	**143.8**	**20.3**	**–**	**8.29**	**–**	**–**	**2.82**
	σ_{calcd}	10.5	32.2	51.0	81.1	63.9	87.6	38.5	170.4	22.8	–	–	–	28.9
	δ_{calcd}	172.4	150.7	131.8	101.8	118.9	95.3	144.4	22.3	8.18	–	–	–	2.55
	σ_{calcd}	14.0	30.2	78.5	63.3	64.8	87.8	42.5	170.9	–	–	–	–	29.0
	δ_{calcd}	168.8	152.6	104.3	119.6	118.0	95.1	140.4	21.9	–	–	–	–	2.52
	δ_{expt}	**167.3**	**151.7**	**105.0**	**119.9**	**118.1**	**98.9**	**141.9**	**20.3**	**–**	**–**	**–**	**–**	**2.74**

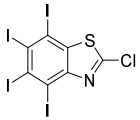
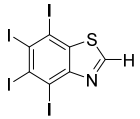
[a] Chemical shielding calculations done at the 2c-ZORA-SO/PBE0-xc/TZ2P level (cf. Computational details). The total shieldings are sum of diamagnetic (σ^{dia}), paramagnetic (σ^{para}) and spin-orbit (σ^{SO}) contributions.

Table S6. Calculated and experimental ^{13}C and ^{1}H NMR shifts (in ppm vs. TMS) of selected mono-, di-, and tetra-iodinated 2-R-benzothiazoles [a]

System		C-2	C-3a	C-4	C-5	C-6	C-7	C-7a	C-R	H-4	H-5	H-6	H-7	H-R (H-3)[b]
 R = **H**	σ_{calcd}	25.3	30.1	58.8	47.5	94.0	51.8	46.5	–	22.3	23.4	–	23.5	22.8
	δ_{calcd}	157.6	152.7	124.1	135.4	88.9	131.0	136.3	–	8.66	7.60	–	7.51	8.24
	δ_{expt}	**154.3**	**152.6**	**125.1**	**135.3**	**90.2**	**130.4**	**135.9**	**–**	**8.93**	**7.89**	**–**	**7.81**	**8.32**
 R = Cl	σ_{calcd}	25.7	32.9	59.7	47.0	93.4	53.0	44.6	–	23.7	23.5	–	23.1	–
	δ_{calcd}	157.2	150.0	123.2	135.9	89.5	129.9	138.3	–	7.35	7.54	–	7.93	–
	δ_{expt}	**153.8**	**150.3**	**124.3**	**135.9**	**90.1**	**129.5**	**137.9**	**–**	**7.67**	**7.77**	**–**	**8.11**	**–**
 R = I	σ_{calcd}	75.2	29.8	60.3	47.4	93.6	53.7	40.7	–	23.6	23.5	–	23.0	–
	δ_{calcd}	107.7	153.1	122.6	135.5	89.2	129.2	142.1	–	7.43	7.49	–	8.05	–
	δ_{expt}	**106.2**	**153.6**	**123.8**	**135.5**	**90.6**	**128.9**	**141.1**	**–**	**7.74**	**7.75**	**–**	**8.20**	**–**
 R = O **H-3**	σ_{calcd}	14.3	48.6	72.2	47.2	99.4	51.8	56.7	–	24.5	23.6	–	23.5	–
	δ_{calcd}	168.5	134.3	110.7	135.7	83.5	131.1	126.1	–	6.53	7.36	–	7.48	–
	δ_{expt}	**171.1**	**134.4**	**113.0**	**135.3**	**85.3**	**130.8**	**126.1**	**–**	**6.89**	**7.58**	**–**	**7.71**	**–**

System		C-2	C-3a	C-4	C-5	C-6	C-7	C-7a	C-R	H-4	H-5	H-6	H-7	H-R (H-3)[b]
 R = H	σ_{calcd}	28.1	30.6	90.9	45.6	47.0	99.1	41.5	–	–	23.6	23.9	–	22.1
	δ_{calcd}	154.7	152.2	92.0	137.3	135.9	83.7	141.4	–	–	7.36	7.13	–	8.90
	δ_{expt}	**151.9**	**152.6**	**90.9**	**137.0**	**135.9**	**84.0**	**141.1**	**–**	**–**	**7.68**	**7.47**	**–**	**9.17**
 R = **C**N	σ_{calcd}	47.3	32.0	88.6	44.1	43.8	100.8	40.0	65.1	–	23.5	23.7	–	–
	δ_{calcd}	135.6	150.8	94.3	138.8	139.1	82.0	142.9	117.7	–	7.52	7.28	–	–
	δ_{expt}	**134.8**	**151.1**	**92.4**	**138.3**	**138.8**	**82.9**	**142.6**	**112.4**	**–**	**7.82**	**7.60**	**–**	**–**
 R = **C**HO	σ_{calcd}	18.6	30.5	87.7	44.6	43.4	98.7	38.9	-5.4	–	23.5	23.8	–	21.2
	δ_{calcd}	164.2	152.3	95.1	138.3	139.4	84.2	143.9	188.3	–	7.50	7.23	–	9.83
	δ_{expt}	**163.7**	**152.3**	**93.6**	**138.4**	**138.4**	**85.0**	**143.9**	**185.4**	**–**	**7.78**	**7.57**	**–**	**10.16**
 R = Cl	σ_{calcd}	27.6	32.9	92.9	45.9	47.2	101.1	40.4	–	–	23.6	23.8	–	–
	δ_{calcd}	155.2	149.9	89.9	136.9	135.7	81.8	142.5	–	–	7.40	7.22	–	–
	δ_{expt}	**152.0**	**150.3**	**89.4**	**137.5**	**135.7**	**82.6**	**142.9**	**–**	**–**	**7.64**	**7.40**	**–**	**–**

System		C-2	C-3a	C-4	C-5	C-6	C-7	C-7a	C-R	H-4	H-5	H-6	H-7	H-R (H-3)[b]
 R = N**H₂**	σ_{calcd}	22.0	30.7	98.6	46.1	51.5	100.9	45.9	–	–	23.8	24.1	–	26.2
	δ_{calcd}	160.8	152.2	84.2	136.8	131.4	82.0	137.0	–	–	7.25	6.89	–	5.30
	δ_{expt}	**162.9**	**151.3**	**85.2**	**136.5**	**132.3**	**82.9**	**137.9**	**–**	**–**	**7.43**	**7.12**	**–**	**5.39**
 R = O**H**	σ_{calcd}	13.1	34.3	96.4	46.1	49.4	99.8	43.9	–	–	23.8	24.1	–	24.8
	δ_{calcd}	169.8	148.5	86.5	136.7	133.4	83.1	138.9	–	–	7.19	6.91	–	6.18
 R = O **H-3**	σ_{calcd}	18.3	45.8	110.1	47.0	49.8	96.4	52.6	–	–	24.0	24.1	–	23.4
	δ_{calcd}	164.5	137.0	72.8	135.8	133.0	86.4	130.3	–	–	7.00	6.92	–	8.09
	δ_{expt}	**166.3**	**136.8**	**74.7**	**136.1**	**133.3**	**87.2**	**130.6**	**–**	**–**	**7.33**	**7.23**	**–**	**8.52**
 R = CH_3	σ_{calcd}	14.0	30.2	78.5	63.3	64.8	87.8	42.5	170.9	–	–	–	–	29.0
	δ_{calcd}	168.8	152.6	104.3	119.6	118.0	95.1	140.4	21.9	–	–	–	–	2.52
	δ_{expt}	**167.3**	**151.7**	**105.0**	**119.9**	**118.1**	**98.9**	**141.9**	**20.3**	**–**	**–**	**–**	**–**	**2.74**

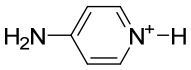
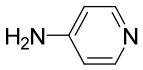
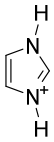
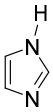
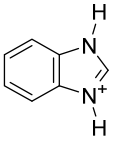
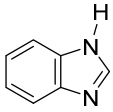
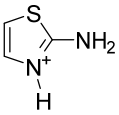
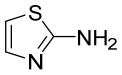
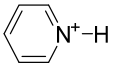
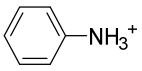
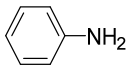
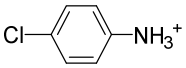
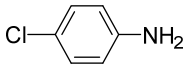
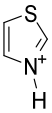
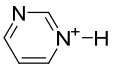
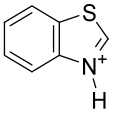
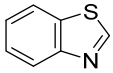
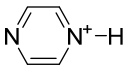
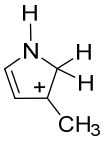
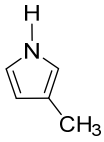
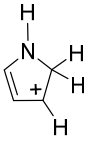
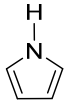
System		C-2	C-3a	C-4	C-5	C-6	C-7	C-7a	C-R	H-4	H-5	H-6	H-7	H-R (H-3)[b]
 R = Cl	σ_{calcd}	27.2	33.3	78.1	61.7	62.8	88.2	41.9	–	–	–	–	–	–
	δ_{calcd}	155.7	149.6	104.7	121.2	120.0	94.6	141.0	–	–	–	–	–	–
	δ_{expt}	**152.2**	**149.7**	**105.5**	**121.5**	**120.0**	**98.7**	**141.9**	**–**	**–**	**–**	**–**	**–**	**–**
 R = H	σ_{calcd}	29.9	31.2	76.6	62.3	62.5	86.8	43.2	–	–	–	–	–	22.3
	δ_{calcd}	153.0	151.7	106.3	120.6	120.4	96.1	139.7	–	–	–	–	–	9.22
	δ_{expt}	**156.2**	**152.0**	**106.7**	**120.3**	**119.6**	**99.7**	**141.1**	**–**	**–**	**–**	**–**	**–**	**9.46**

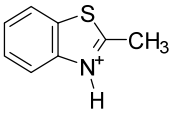
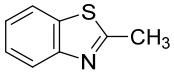
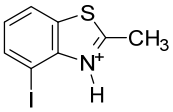
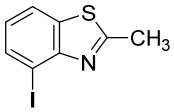
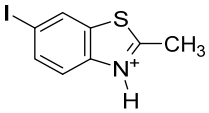
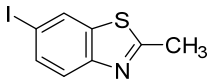
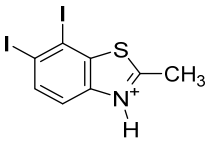
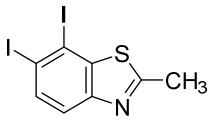
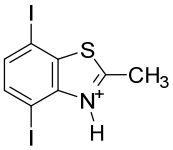
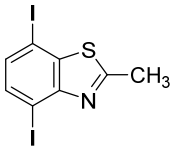
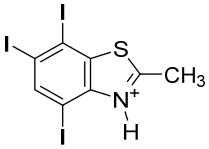
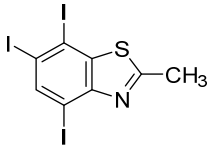
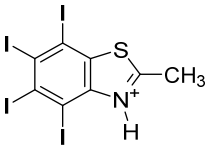
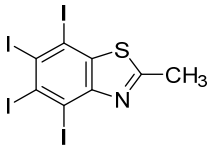
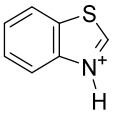
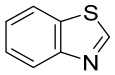
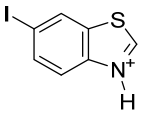
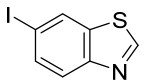
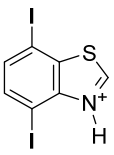
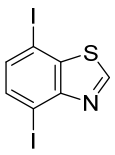
[a] Chemical shielding calculations done at the 2c-ZORA-SO/PBE0-xc/TZ2P level (cf. Computational details). The total shieldings are sum of diamagnetic (σ^{dia}), paramagnetic (σ^{para}) and spin-orbit (σ^{SO}) contributions.

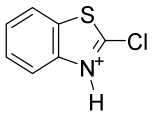
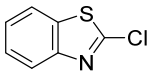
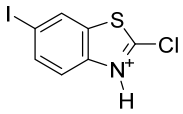
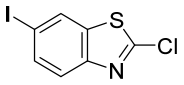
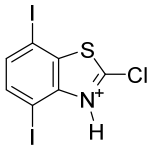
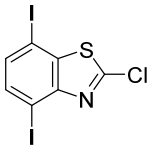
Table S7. Calculated Gibbs free energies and pK_a values for the dissociation of selected protonated *N*-heteroarenes, arylamines and iodinated benzothiazoles [a,b]

$$\mathbf{BH^+ (\mathit{aq}) + H_2O (\mathit{aq}) \rightarrow B (aq) + H_3O^+}$$

$$\Delta G_{diss} = G_{tot}(B) + G_{tot}(H_3O^+) - G_{tot}(BH^+) - G_{tot}(H_2O)$$

acid (BH^+)	base (B)	ΔG_{diss} [a]	pK_a^{calcd} [b]	pK_a^{expt} [c]
		109.0	9.19	9.23
		89.6	6.60	7.0
		79.6	5.28	5.8
		83.2	5.76	5.4
		78.8	5.17	5.14
		76.9	4.91	4.6
		71.0	4.12	4.0
		58.9	2.51	2.8
		53.5	1.79	1.3
		49.0	1.20	1.2
		48.2	1.08	0.7
		30.2	−1.31	−1.0
		10.6	−3.93	−3.8

acid (BH^+)	base (B)	ΔG_{diss} [a]	pK_a^{calcd} [b]	pK_a^{expt} [c]
		52.6	1.67	
		37.2	−0.38	
		47.3	0.97	
		41.7	0.22	
		30.0	−1.35	
		26.1	−1.86	
		23.4	−2.22	
		49.0	1.20	
		43.5	0.46	
		25.7	−1.92	

acid (BH^+)	base (B)	ΔG_{diss} [a]	pK_a^{calcd} [b]	pK_a^{expt} [c]
		19.7	−2.72	
		14.5	−3.41	
		-4.1	−5.90	

[a] PBE0/def2-TZVP/DCOSMO-RS results, H_2O as the solvent (cf. Computational details)

[b] Calculated from a linear free energy relationship given in Figure S17

[c] See ref. 38 for collected experimental pK_a data.

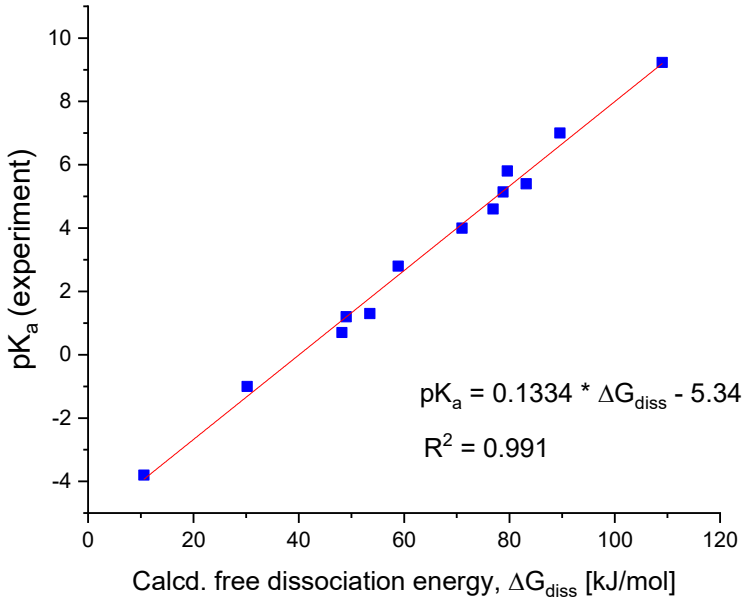
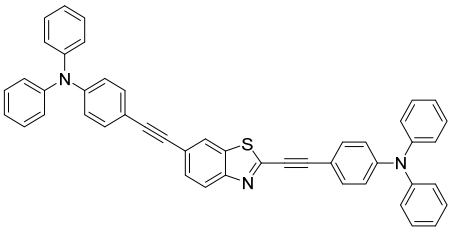


Figure S17. Experimental pK_a values for selected protonated bases vs. calculated free energy of dissociation. Linear regression line showed in red.

Table S8. Calculated one-photon absorption parameters and TPA cross-sections for the first 5 excitations at the CAM-B3LYP/6-311++G** level of theory (see Computational details).

System	n	E_n [eV]	μ_{0n} [D]	$\Delta\mu_{0n}$ [D]	μ_{1n} [D]	δ_{TPA} [GM]
	1	3.28	15.5	2.6		2
	2	3.77	2.1	3.0	10.0	685
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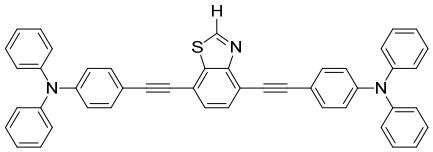
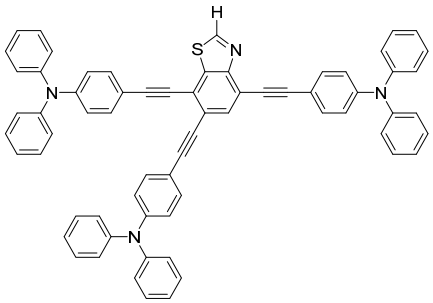
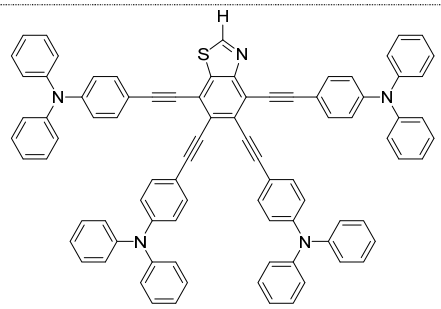
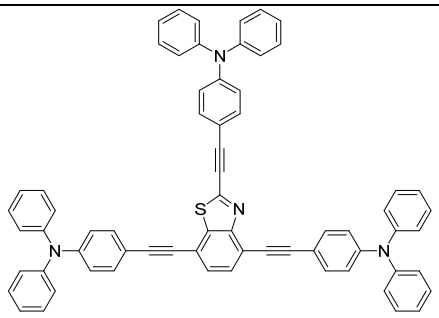
	4	4.13	1.1	1.8	0.2	1
	5	4.33	0.6	3.9	7.2	765
	1	3.21	15.0	0.4		10
	2	3.80	0.9	2.3	10.3	815
	3	4.09	1.1	4.8	0.2	0
	4	4.09	1.1	0.9	0.2	0
	5	4.28	3.4	1.7	1.6	33
	1	3.24	9.7	3.7		27
	2	3.49	11.7	6.2	7.5	121
	3	3.83	4.3	11.1	7.4	431
	4	3.98	4.9	2.9	4.7	93
	5	4.14	1.5	1.5	0.6	3
	1	3.12	9.3	5.7		9
	2	3.38	6.8	11.0	5.8	97
	3	3.55	6.4	6.4	2.5	17
	4	3.60	5.9	7.9	1.1	12
	5	3.95	7.7	8.7	7.9	680
	1	3.13	13.1	2.9		27
	2	3.41	11.5	10.1	4.1	97
	3	3.82	3.2	1.2	8.9	690
	4	3.91	4.2	3.3	7.0	370
	5	4.09	1.0	4.8	0.3	1

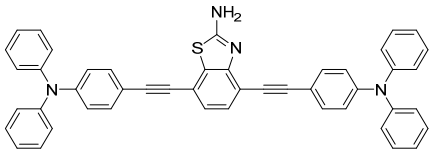
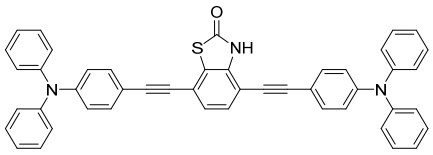
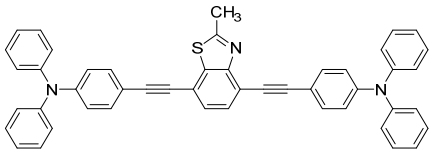
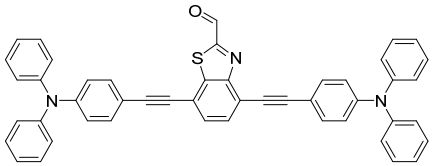
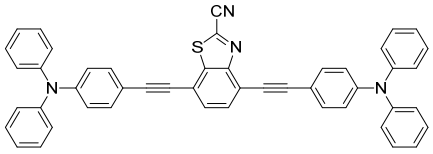
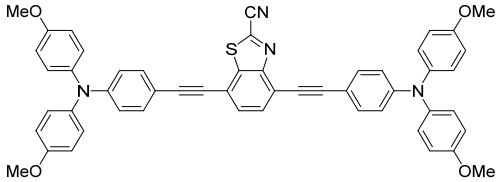
System	n	E_n [eV]	μ_{0n} [D]	$\Delta\mu_{0n}$ [D]	μ_{1n} [D]	δ_{TPA} [GM]
	1	3.29	14.9	2.4		7
	2	3.83	1.3	4.1	7.8	436
	3	4.07	1.1	5.6	0.2	0
	4	4.09	1.1	2.7	0.2	0
	5	4.23	1.6	4.2	0.8	7
	1	3.27	15.0	0.8		4
	2	3.82	0.7	1.3	9.3	625
	3	4.08	1.1	3.6	0.2	0
	4	4.10	1.1	1.9	0.2	0
	5	4.35	3.4	8.5	1.2	25
	1	3.24	15.0	0.6		7
	2	3.82	0.9	2.1	9.5	675
	3	4.09	1.1	4.6	0.2	0
	4	4.09	1.1	1.5	0.2	0
	5	4.30	0.7	1.2	1.3	21
	1	2.95	12.5	7.3		23
	2	3.59	7.5	6.4	9.8	580
	3	3.66	4.5	7.3	13.3	1145
	4	3.70	0.2	0.5	0.5	2
	5	4.10	1.1	4.1	0.9	6
	1	3.02	13.8	7.2		34
	2	3.63	4.5	8.1	13.0	1210
	3	3.79	4.8	9.2	8.1	545
	4	4.11	1.0	4.5	0.2	1
	5	4.11	1.1	6.7	0.5	3
	1	2.95	14.0	8.8		52
	2	3.54	4.4	10.1	16.1	1855
	3	3.71	5.8	10.5	7.9	515
	4	3.92	1.7	7.2	1.8	41
	5	3.92	1.0	6.0	0.3	1

Table S9. Calculated excitation energies (E_n), oscillator strengths (f_{osc}) and dominant transitions between molecular orbitals (MOs) for the first two excitations [a]

Compound	*n*	E_n	f_{osc}		character of transitions (dominant contributions)
Qbtz-NH$_2$	1	3.29	2.76	80%	**HOMO → LUMO**
				9%	HOMO−1 → LUMO +1
	2	3.83	0.02	56%	**HOMO−1 → LUMO**
				26%	HOMO → LUMO +1
Qbtz-H	1	3.21	2.75	80%	**HOMO → LUMO**
				8%	HOMO−1 → LUMO +1
	2	3.80	0.01	59%	**HOMO−1 → LUMO**
				20%	HOMO → LUMO +1
Qbtz-CN	1	3.02	2.18	80%	**HOMO → LUMO**
				9%	HOMO−3 → LUMO
	2	3.63	0.28	50%	**HOMO−1 → LUMO**
				16%	HOMO → LUMO+1
				13%	HOMO−1 → LUMO+1

[a] CAM-B3LYP/6-311++G** results *in vacuo*

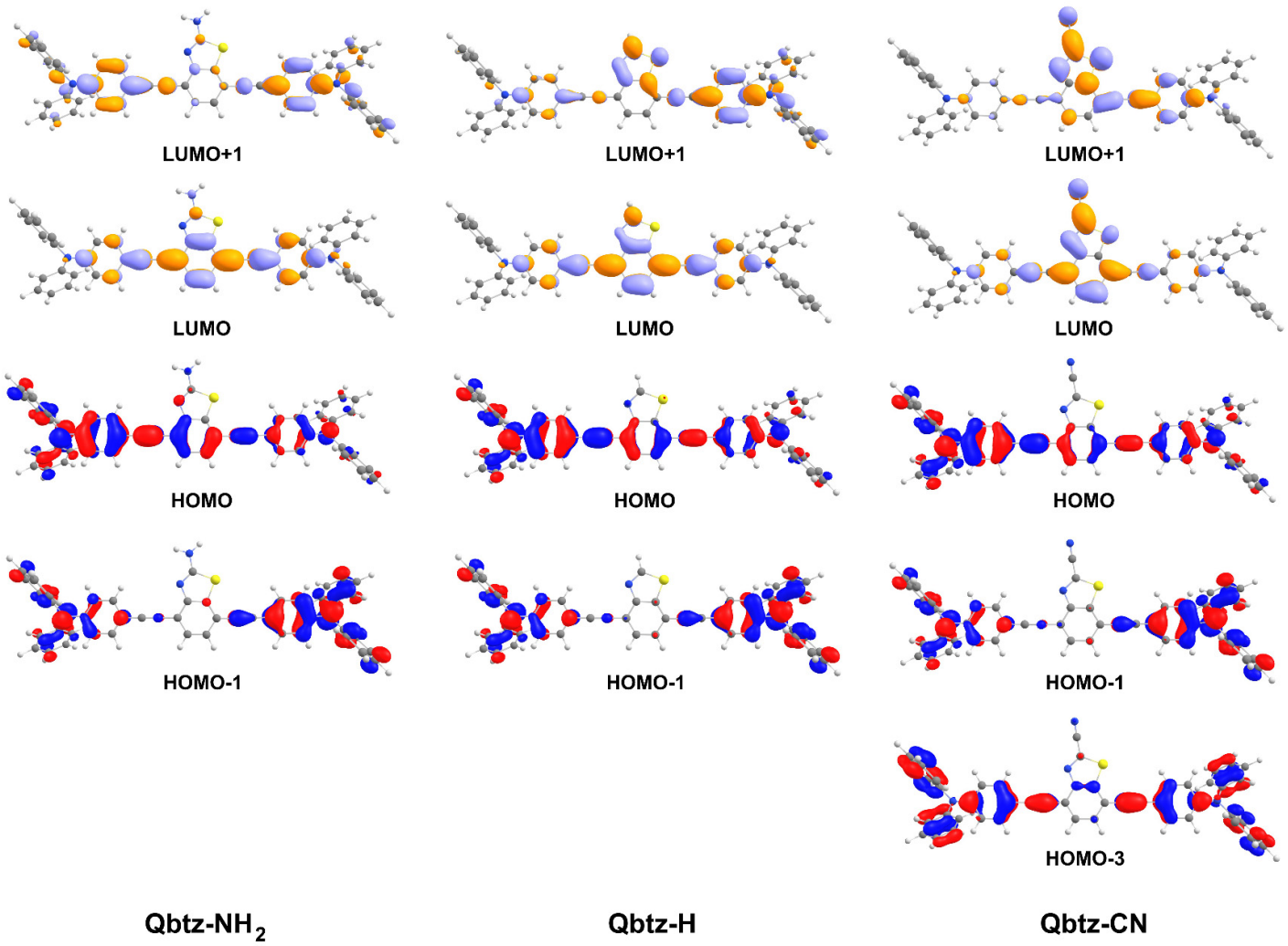


Figure S18. Frontier MOs involved in the first two $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ excitations of **Qbtz-NH$_2$**, **Qbtz-H** and **Qbtz-CN** (cf. Table S9)

12 Cartesian coordinates of pertinent DFT optimized structures

84
Qbtz-NH_2

S	-2.7482150	-0.1417028	0.4293488
C	-2.7245986	-0.1664074	-1.3271346
N	-1.5592350	-0.1382704	-1.8846627
C	-0.5741977	-0.0937836	-0.9329018
C	0.8077043	-0.0547842	-1.1941817
C	1.6786887	-0.0141023	-0.0982705
C	1.2201212	-0.0096342	1.2044754
C	-0.1506979	-0.0459614	1.4906783
C	-1.0181112	-0.0883149	0.3979202
H	2.7437774	0.0160208	-0.2912219
H	1.9216698	0.0237193	2.0281268
N	-3.8808688	-0.2116210	-2.0179440
C	1.2952470	-0.0534354	-2.5170760
C	1.7190912	-0.0474011	-3.6496285
C	2.1857905	-0.0356012	-4.9836797
C	3.5547326	-0.0210652	-5.2758156
C	4.0028244	-0.0115015	-6.5801033
C	3.0975342	-0.0030614	-7.6431538
C	1.7301737	-0.0128649	-7.3590119
C	1.2836824	-0.0349025	-6.0546701
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H	5.0658277	-0.0106098	-6.7873689
H	1.0180293	-0.0015363	-8.1748661
H	0.2211753	-0.0359675	-5.8437116
N	3.5514831	0.0153564	-8.9682592
C	2.8549619	-0.6944065	-9.9645032
C	2.6444749	-0.1245824	-11.2184208
C	1.9672577	-0.8288986	-12.1990066
C	1.4777447	-2.1013614	-11.9424765
C	1.6810112	-2.6673003	-10.6921932
C	2.3706108	-1.9760631	-9.7109959
H	3.0182507	0.8725450	-11.4174097
H	1.8098221	-0.3715757	-13.1692366
H	0.9429252	-2.6473224	-12.7101810
H	1.3117734	-3.6642045	-10.4799073
H	2.5381043	-2.4234221	-8.7385764
C	4.6995801	0.7513998	-9.3155195
C	4.9240984	2.0130908	-8.7682529
C	6.0581745	2.7291596	-9.1102088
C	6.9750201	2.2098171	-10.0127030
C	6.7476764	0.9580913	-10.5658008
C	5.6245483	0.2281779	-10.2169375
H	4.2039785	2.4252136	-8.0718615
H	6.2182709	3.7095287	-8.6760367
H	7.8585500	2.7756767	-10.2824657
H	7.4585578	0.5368682	-11.2675575
H	5.4536429	-0.7532892	-10.6426268
C	-0.6448344	-0.0387354	2.8121192
C	-1.0992511	-0.0306993	3.9334602
C	-1.6249070	-0.0195152	5.2456998
C	-3.0071970	-0.0233704	5.4675594
C	-3.5208872	-0.0160899	6.7469073

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C    -2.6710008    0.0064210    7.8554468
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H    -4.5928751   -0.0298901    6.8995927
H    -0.6202948    0.0372814    8.4904494
H     0.2936597    0.0098138    6.2080652
N    -3.1903096    0.0190331    9.1541032
C    -4.3782521    0.7178589    9.4411640
C    -4.6138562    1.9729221    8.8838110
C    -5.7853287    2.6527309    9.1691241
C    -6.7291617    2.1030824   10.0246892
C    -6.4910900    0.8579697   10.5879838
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H    -7.2223099    0.4138843   11.2537354
H    -5.1489287   -0.8121064   10.7290678
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H    -0.6947102   -2.5358084   13.0447549
H    -0.9530181   -3.5958506   10.8197680
H    -2.1268923   -2.4048496    9.0075818
H    -4.7710972   -0.2385458   -1.5619583
H    -3.8326764   -0.2292004   -3.0201803

83
Qbtz-OH
S    -2.6391478   -0.0736653    0.4693388
C    -2.7059609   -0.0891506   -1.3235266
N    -1.4165701   -0.0781294   -1.7886100
C    -0.4151169   -0.0576109   -0.8514369
C     0.9563540   -0.0418591   -1.1210050
C     1.8214191   -0.0215307   -0.0177505
C     1.3420092   -0.0166930    1.2753183
C    -0.0354423   -0.0315342    1.5455354
C    -0.9026886   -0.0524461    0.4508860
H     2.8885264   -0.0090144   -0.1995269
H     2.0316079   -0.0006166    2.1093242
O    -3.7064016   -0.1060552   -1.9865320
C     1.4072524   -0.0443030   -2.4574698
C     1.7418652   -0.0440044   -3.6211489
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C     3.5176283    0.0081126   -5.3044432
C     3.9270421    0.0154205   -6.6202423
C     2.9919617   -0.0127668   -7.6591244
C     1.6334422   -0.0569677   -7.3331223
C     1.2268204   -0.0738513   -6.0164341
H     4.2547678    0.0247197   -4.5109076
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C	2.4124473	-0.0739230	-11.2080953
C	1.6965888	-0.7502374	-12.1811399
C	1.2124553	-2.0274885	-11.9392613
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C	2.1880259	-1.9643793	-9.7406685
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H	1.0948295	-3.6289648	-10.5144180
H	2.3916278	-2.4381477	-8.7877561
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H    -2.2057888   -2.4009067    9.0212290
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85
Qbtz-Me
S    -2.6753656   -0.1546917    0.4390116
C    -2.6549472   -0.1838372   -1.3093596
N    -1.4849940   -0.1483734   -1.8484735
C    -0.4995046   -0.0949710   -0.8945727
C     0.8833451   -0.0471058   -1.1598181
C     1.7478772    0.0017517   -0.0632673
C     1.2802926    0.0058287    1.2401315
C    -0.0862522   -0.0387661    1.5285458
C    -0.9557943   -0.0898369    0.4308936
H     2.8139688    0.0386729   -0.2486871
H     1.9817473    0.0455788    2.0640065
C    -3.9237811   -0.2467641   -2.0787872
H    -3.6873330   -0.2498756   -3.1417115
H    -4.4873609   -1.1507584   -1.8352998
H    -4.5626568    0.6112547   -1.8565027
C     1.3703826   -0.0459737   -2.4821130
C     1.7911051   -0.0404063   -3.6157818
C     2.2515669   -0.0295733   -4.9515144
C     3.6190758   -0.0118823   -5.2499617
C     4.0606084   -0.0023547   -6.5560976
C     3.1496503    0.0020628   -7.6150672
C     1.7832442   -0.0119141   -7.3238259
C     1.3434829   -0.0331357   -6.0175018
H     4.3361893   -0.0202128   -4.4380525
H     5.1225160    0.0010286   -6.7683295
H     1.0666697   -0.0033231   -8.1356855
H     0.2820653   -0.0368621   -5.8010614
N     3.5969046    0.0207049   -8.9408798
C     2.8871935   -0.6737832   -9.9394850
C     2.6748371   -0.0896772  -11.1862280
C     1.9866420   -0.7788225  -12.1699854
C     1.4885419   -2.0497961  -11.9230270
C     1.6940224   -2.6299325  -10.6796618
C     2.3944560   -1.9538827   -9.6955506
H     3.0557692    0.9063244  -11.3772927
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H     2.5639688   -2.4121520   -8.7285585
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C     7.0463647    2.1685753   -9.9959948
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C     5.6729114    0.2019190  -10.1894998
H     4.2777282    2.4274025   -8.0570383
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82
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H    -5.2173300   -0.7920336   10.5632394
C    -2.5500907   -0.5383372   10.1404334
C    -2.3156388    0.0308774   11.3914448
C    -1.6832162   -0.6874818   12.3829316
C    -1.2525906   -1.9915314   12.1445530
C    -1.4779009   -2.5657587   10.8986122
C    -2.1334146   -1.8415422    9.9131130
H    -2.6426326    1.0462867   11.5816555
H    -1.4984269   -0.2501353   13.3565976
O    -0.6329759   -2.6122496   13.1736220
H    -1.1632138   -3.5785089   10.6857272
H    -2.3176719   -2.2963842    8.9468606
C     0.3204214   -3.9148277  -12.7549682
H    -0.1707950   -4.2268534  -13.6748143
H     1.1445216   -4.6026599  -12.5358087
H    -0.4021462   -3.9470294  -11.9319198
C     9.0942977    2.2512301  -11.2562770
H     9.8866257    2.9837955  -11.3988946
H     9.5076487    1.3652553  -10.7619462
H     8.6916609    1.9613981  -12.2331657
C    -8.8695805    2.3048166   11.2549151
H    -9.6578207    3.0454226   11.3768634
H    -9.2806066    1.4200004   10.7567430
H    -8.4898264    2.0171032   12.2414980
C    -0.1868413   -3.9296816   12.9691990
H     0.2822652   -4.2407897   13.9007905
H    -1.0189771   -4.6050882   12.7420913
H     0.5496568   -3.9831510   12.1596475

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Qbtz-2,6
S     1.4224658   -0.0454696   -0.1049242
C     2.0327920    0.0267108    1.5396541
N     1.1269842    0.0866984    2.4697520
C    -2.5702201    0.0522143    0.5737290
C    -2.5166153    0.1232862    1.9828507
C    -1.3186193    0.1365758    2.6542680
C    -0.1258682    0.0798737    1.9282470
C    -0.1825215    0.0104178    0.5190505
C    -1.3875695   -0.0047327   -0.1630512
H    -1.2772105    0.1902656    3.7350180
H    -3.4490952    0.1665241    2.5312278
H    -1.4284421   -0.0580727   -1.2433682
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C	3.4187121	0.0156375	1.7547898
C	4.6196979	0.0042416	1.8998796
C	6.0171642	-0.0061883	2.0950342
C	6.8986583	0.0269684	1.0078240
C	8.2623792	0.0238674	1.2013147
C	8.7997723	-0.0233996	2.4919467
C	7.9221866	-0.0618614	3.5807044
C	6.5590312	-0.0484410	3.3855548
H	6.4971695	0.0720119	0.0027721
H	8.9277077	0.0634322	0.3483360
N	10.1793278	-0.0297374	2.6905001
H	8.3222081	-0.1062759	4.5855513
H	5.8906286	-0.0856301	4.2369525
C	11.0414419	-0.6217644	1.7445642
C	12.2211394	0.0201014	1.3767183
C	13.0757900	-0.5677387	0.4599036
C	12.7617456	-1.7922815	-0.1109612
C	11.5848480	-2.4306734	0.2527632
C	10.7324743	-1.8570467	1.1804118
C	10.7395561	0.5630043	3.8422702
C	11.7408037	-0.0963832	4.5503187
C	12.3016200	0.4915122	5.6716485
C	11.8648046	1.7340394	6.1074547
C	10.8642050	2.3896951	5.4043619
C	10.3084095	1.8149236	4.2739581
H	12.4632920	0.9795834	1.8176732
H	13.9903408	-0.0569685	0.1812354
H	13.4296644	-2.2467179	-0.8326549
H	11.3323691	-3.3927049	-0.1781578
H	9.8196651	-2.3614549	1.4739674
H	12.0759190	-1.0696635	4.2126670
H	13.0785357	-0.0330659	6.2157118
H	12.3017099	2.1888773	6.9881319
H	10.5210499	3.3652153	5.7291605
H	9.5354715	2.3313890	3.7175912
C	-3.8226638	0.0393929	-0.0853534
C	-4.8970412	0.0294633	-0.6409699
C	-6.1534777	0.0200912	-1.2906685
C	-7.3383498	0.2115671	-0.5701720
C	-8.5630145	0.2107855	-1.2030235
C	-8.6520401	0.0053638	-2.5818843
C	-7.4739650	-0.1932538	-3.3058020
C	-6.2493392	-0.1796141	-2.6727499
H	-7.2840851	0.3786357	0.4987409
H	-9.4674689	0.3722666	-0.6300734
N	-9.8945830	-0.0012592	-3.2241364
H	-7.5283122	-0.3605705	-4.3741946
H	-5.3445857	-0.3413027	-3.2459935
C	-11.0301847	-0.5209367	-2.5725722
C	-12.2547440	0.1371901	-2.6647429
C	-13.3734145	-0.3820416	-2.0357777
C	-13.2864326	-1.5521634	-1.2954771
C	-12.0658131	-2.2046143	-1.1973350
C	-10.9458239	-1.7008903	-1.8363863
C	-10.0246265	0.5131043	-4.5289769
C	-10.8041665	-0.1533209	-5.4718896
C	-10.9426379	0.3606239	-6.7497790
C	-10.2965989	1.5338163	-7.1113547

C	-9.5144941	2.1946944	-6.1750675
C	-9.3836498	1.6961395	-4.8903426
H	-12.3217988	1.0557086	-3.2351507
H	-14.3193581	0.1413986	-2.1154277
H	-14.1624227	-1.9525384	-0.7996155
H	-11.9851397	-3.1243214	-0.6292485
H	-9.9959915	-2.2174670	-1.7688457
H	-11.3024096	-1.0739934	-5.1929869
H	-11.5520347	-0.1693431	-7.4728848
H	-10.4022158	1.9302605	-8.1139402
H	-9.0108457	3.1170336	-6.4413229
H	-8.7818499	2.2193001	-4.1569468

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btz_2,4,7_CCC$_6$H$_4$_*p*-NPh$_2$

S	-0.7570747	-0.1799021	-1.8371943
C	-0.2133179	-0.1122432	-0.1722814
N	-1.1521264	-0.0030724	0.7202593
C	-3.6055598	0.1574297	0.8165986
C	-4.7733543	0.1910390	0.0527885
C	-4.7496476	0.1089410	-1.3303159
C	-3.5509310	-0.0137053	-2.0372901
C	-2.3746773	-0.0480041	-1.2760764
C	-2.3793838	0.0358974	0.1268933
H	-5.7223095	0.2850885	0.5657451
C	-3.5089180	-0.0947259	-3.4446900
C	1.1609226	-0.1677671	0.1062480
C	-3.6352672	0.2447643	2.2217019
H	-5.6776526	0.1395072	-1.8876327
C	2.3515228	-0.2051519	0.3156653
C	3.7345594	-0.2359874	0.5949244
C	4.6786838	-0.3657046	-0.4303121
C	6.0279864	-0.3801096	-0.1523733
C	6.4859512	-0.2729339	1.1645155
C	5.5456473	-0.1515113	2.1925316
C	4.1974525	-0.1295517	1.9122652
H	4.3388451	-0.4390776	-1.4560991
H	6.7442380	-0.4683341	-0.9592854
N	7.8516259	-0.2837744	1.4480020
H	5.8847031	-0.0763791	3.2177407
H	3.4784948	-0.0414104	2.7175203
C	8.7428753	-1.0352279	0.6550323
C	9.9623512	-0.4892346	0.2623847
C	10.8426766	-1.2340781	-0.5038978
C	10.5159757	-2.5230819	-0.8992779
C	9.2990043	-3.0656470	-0.5124548
C	8.4197821	-2.3331657	0.2666024
C	8.3622067	0.4616596	2.5308261
C	9.3153707	-0.0972769	3.3779848
C	9.8250807	0.6397679	4.4334023
C	9.3836241	1.9340111	4.6662270
C	8.4310618	2.4900228	3.8245498
C	7.9279437	1.7653031	2.7579070
H	10.2141583	0.5201804	0.5646140
H	11.7879512	-0.7968706	-0.8043994
H	11.2051586	-3.1011003	-1.5029449
H	9.0351264	-4.0749772	-0.8066943
H	7.4748198	-2.7606962	0.5796463

H	9.6537265	-1.1110393	3.2003491
H	10.5650465	0.1922316	5.0869979
H	9.7792431	2.5054866	5.4971436
H	8.0842353	3.5035924	3.9901188
H	7.1926339	2.2033311	2.0936955
C	-3.6471529	0.3207112	3.4284768
C	-3.6165038	0.4091090	4.8378569
C	-4.7888395	0.5728133	5.5846923
C	-4.7477049	0.6568892	6.9601943
C	-3.5296027	0.5914297	7.6404929
C	-2.3554182	0.4313995	6.9006211
C	-2.3987719	0.3368364	5.5261021
H	-5.7404711	0.6199662	5.0690828
H	-5.6656881	0.7741189	7.5228134
N	-3.4871917	0.6856339	9.0363591
H	-1.4042779	0.3849816	7.4167509
H	-1.4833642	0.2202668	4.9586175
C	-4.3835383	1.5323722	9.7163820
C	-5.0029576	1.1056966	10.8890388
C	-5.8769906	1.9438912	11.5600311
C	-6.1570058	3.2102038	11.0674540
C	-5.5446497	3.6342715	9.8967421
C	-4.6579096	2.8082310	9.2278144
C	-2.5552433	-0.0701147	9.7728849
C	-1.8831341	0.5009008	10.8516710
C	-0.9767419	-0.2475989	11.5829672
C	-0.7155840	-1.5671132	11.2433601
C	-1.3792561	-2.1347120	10.1651080
C	-2.2984791	-1.3981379	9.4379369
H	-4.7913932	0.1136931	11.2695195
H	-6.3533297	1.5970107	12.4699911
H	-6.8462890	3.8612236	11.5915584
H	-5.7472312	4.6246912	9.5053184
H	-4.1712255	3.1443412	8.3200575
H	-2.0791459	1.5341082	11.1118292
H	-0.4601764	0.2109482	12.4184323
H	-0.0010811	-2.1480814	11.8138334
H	-1.1916468	-3.1673134	9.8935229
H	-2.8241219	-1.8458858	8.6032617
C	-3.4397924	-0.1625094	-4.6507578
C	-3.3684572	-0.2351967	-6.0606325
C	-4.4974636	0.0096175	-6.8509883
C	-4.4284741	-0.0496409	-8.2263033
C	-3.2281620	-0.3691897	-8.8664735
C	-2.0993979	-0.6224100	-8.0823334
C	-2.1674958	-0.5501901	-6.7074907
H	-5.4329238	0.2661564	-6.3687296
H	-5.3101952	0.1562833	-8.8201056
N	-3.1587974	-0.4337795	-10.2605351
H	-1.1640712	-0.8789991	-8.5637482
H	-1.2855978	-0.7542003	-6.1122742
C	-4.2721052	-0.8633388	-11.0100756
C	-4.6459979	-0.1797854	-12.1642470
C	-5.7329718	-0.6093020	-12.9059678
C	-6.4686245	-1.7136522	-12.5022213
C	-6.0998008	-2.3922875	-11.3497581
C	-5.0050042	-1.9783232	-10.6109902
C	-1.9838456	-0.0537084	-10.9382149

C	-1.5205842	-0.8101195	-12.0121712
C	-0.3756476	-0.4286215	-12.6899536
C	0.3308068	0.6994777	-12.2997639
C	-0.1261546	1.4499582	-11.2262220
C	-1.2790592	1.0843412	-10.5531000
H	-4.0765344	0.6881742	-12.4746947
H	-6.0141336	-0.0669341	-13.8014801
H	-7.3226290	-2.0435463	-13.0814676
H	-6.6609509	-3.2622031	-11.0279750
H	-4.7097312	-2.5149781	-9.7171189
H	-2.0670608	-1.6964899	-12.3116299
H	-0.0264833	-1.0270530	-13.5237685
H	1.2299482	0.9921715	-12.8284622
H	0.4111186	2.3390465	-10.9162237
H	-1.6420740	1.6779387	-9.7225579

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btz_4,6,7_CCC$_6$H$_4$_*p*-NPh$_2$

S	-4.8610441	0.6786481	-2.3089037
C	-4.7456947	0.7025816	-4.0375572
N	-3.5646178	0.6032368	-4.5413664
C	-2.6313980	0.4956782	-3.5430529
C	-1.2384983	0.3737669	-3.7391125
C	-0.4325924	0.2752625	-2.6110580
C	-0.9543532	0.2924794	-1.3114127
C	-2.3447178	0.4201947	-1.1019062
C	-3.1496520	0.5164798	-2.2400812
H	0.6372428	0.1752224	-2.7381246
C	-0.1078741	0.1629322	-0.1874497
H	-5.6429992	0.7976723	-4.6361807
C	-0.6923855	0.3490384	-5.0387480
C	-0.2308370	0.3256467	-6.1557947
C	0.2783446	0.2999893	-7.4736168
C	1.6529710	0.2088443	-7.7207829
C	2.1415008	0.1801202	-9.0097395
C	1.2727867	0.2517834	-10.1014115
C	-0.1003338	0.3464107	-9.8608948
C	-0.5879888	0.3655044	-8.5717703
H	2.3367224	0.1460050	-6.8828945
H	3.2073453	0.0991141	-9.1831121
H	-0.7838176	0.4080693	-10.6985956
H	-1.6535299	0.4469383	-8.3942523
N	1.7674093	0.2290469	-11.4097935
C	1.0433996	-0.4186240	-12.4299415
C	0.9088032	0.1755937	-13.6825180
C	0.2063644	-0.4684776	-14.6866305
C	-0.3823511	-1.7029458	-14.4541732
C	-0.2540012	-2.2927678	-13.2050256
C	0.4595745	-1.6623679	-12.2002569
H	1.3608692	1.1437679	-13.8615688
H	0.1075965	0.0068123	-15.6559451
H	-0.9366325	-2.2014998	-15.2401139
H	-0.7017901	-3.2610227	-13.0122861
H	0.5694534	-2.1284760	-11.2283948
C	2.9880074	0.8574320	-11.7214217
C	3.3046380	2.0991038	-11.1739611
C	4.5080170	2.7096794	-11.4821307
C	5.4041453	2.1035822	-12.3507197

C	5.0856191	0.8720928	-12.9041112
C	3.8913903	0.2469821	-12.5889212
H	2.6009364	2.5794367	-10.5049165
H	4.7398717	3.6760780	-11.0489775
H	6.3423179	2.5872314	-12.5946189
H	5.7789722	0.3841408	-13.5796455
H	3.6478017	-0.7188670	-13.0149680
C	-2.8732506	0.4411654	0.2038935
C	-3.2347978	0.4351895	1.3575980
C	-3.5528853	0.4086508	2.7359493
C	-4.4716483	-0.5063019	3.2585653
C	-4.6963369	-0.5883116	4.6166747
C	-4.0188112	0.2520239	5.5038008
C	-3.1269376	1.1935801	4.9829555
C	-2.8954903	1.2657487	3.6264946
H	-4.9858685	-1.1816768	2.5857123
H	-5.3912412	-1.3226534	5.0041296
H	-2.6062069	1.8637842	5.6552626
H	-2.1971597	1.9963466	3.2359807
N	-4.2157985	0.1473538	6.8821659
C	-5.4698349	-0.2364391	7.3979245
C	-6.6419102	0.3168357	6.8878055
C	-7.8713403	-0.0672012	7.3950224
C	-7.9492887	-0.9919177	8.4265238
C	-6.7818931	-1.5354578	8.9424171
C	-5.5492492	-1.1683464	8.4299632
H	-6.5797547	1.0479764	6.0907171
H	-8.7754734	0.3722369	6.9891611
H	-8.9124319	-1.2859727	8.8257737
H	-6.8297654	-2.2633444	9.7443318
H	-4.6377932	-1.5988939	8.8271295
C	-3.1518561	0.3937368	7.7738667
C	-3.3755974	1.1113120	8.9457644
C	-2.3337905	1.3445592	9.8275398
C	-1.0559802	0.8866538	9.5435995
C	-0.8287237	0.1775595	8.3729246
C	-1.8704278	-0.0800304	7.4986055
H	-4.3710741	1.4813124	9.1598989
H	-2.5221592	1.9040333	10.7369060
H	-0.2369913	1.0818658	10.2243607
H	0.1690435	-0.1822317	8.1466920
H	-1.6982382	-0.6475390	6.5917110
C	0.5465909	0.0362695	0.8211188
C	1.2603646	-0.1130047	2.0330259
C	2.6468897	-0.2970796	2.0493445
C	3.3279811	-0.4377864	3.2407337
C	2.6466300	-0.4049042	4.4585455
C	1.2620555	-0.2251959	4.4488344
C	0.5818179	-0.0814340	3.2584036
H	3.1888575	-0.3158931	1.1117256
H	4.4024403	-0.5733786	3.2373126
N	3.3433599	-0.5579824	5.6654963
H	0.7207144	-0.1994519	5.3868565
H	-0.4944074	0.0406773	3.2638786
C	4.4244655	-1.4616930	5.7281602
C	5.6260489	-1.0889756	6.3254603
C	6.6801993	-1.9847257	6.3848435
C	6.5573049	-3.2540734	5.8384602

C	5.3631294	-3.6234138	5.2364557
C	4.2991992	-2.7388426	5.1869561
C	3.0233238	0.2232802	6.7872732
C	3.1433190	-0.3085479	8.0716527
C	2.8715855	0.4744895	9.1806918
C	2.4545939	1.7891161	9.0319564
C	2.3110412	2.3122776	7.7552883
C	2.6004858	1.5444746	6.6408432
H	5.7248619	-0.0942377	6.7430097
H	7.6107480	-1.6815004	6.8509090
H	7.3862373	-3.9501286	5.8813783
H	5.2520373	-4.6146058	4.8117871
H	3.3629229	-3.0295824	4.7257555
H	3.4642641	-1.3359436	8.1932319
H	2.9769893	0.0455774	10.1709192
H	2.2404486	2.3995675	9.9008782
H	1.9842082	3.3371832	7.6219966
H	2.5052625	1.9663114	5.6478543

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btz_4,5,6,7-CCC$_6$H$_4$_*p*-NPh$_2$

S	7.9345909	1.0544702	0.4555442
C	8.4398879	-0.6033371	0.4419468
N	7.5120526	-1.4911579	0.3508414
C	6.2825708	-0.8873543	0.2816870
C	5.0558529	-1.5680023	0.1776289
C	3.8786013	-0.8003531	0.1160691
C	3.9194411	0.6154795	0.1633491
C	5.1475451	1.2956242	0.2720396
C	6.3073292	0.5161800	0.3230259
H	9.4930234	-0.8461698	0.5080011
C	4.9406913	-2.9686940	0.1302856
C	4.6328245	-4.1373643	0.0887926
C	4.1096645	-5.4487650	0.0451678
C	4.8517044	-6.5780330	0.4031493
C	4.2723843	-7.8306052	0.4071843
C	2.9352283	-7.9995505	0.0411121
C	2.1972528	-6.8771294	-0.3432426
C	2.7729302	-5.6266556	-0.3375190
H	5.8849908	-6.4593143	0.7059762
H	4.8546468	-8.6929644	0.7069055
N	2.3400842	-9.2659532	0.0619416
H	1.1628440	-6.9948529	-0.6425596
H	2.1958347	-4.7609032	-0.6387181
C	3.0959326	-10.4069919	-0.2727376
C	3.0041674	-11.5646793	0.4962761
C	3.7438497	-12.6850122	0.1576433
C	4.5931723	-12.6637391	-0.9391010
C	4.6895110	-11.5088555	-1.7020783
C	3.9417043	-10.3895715	-1.3793650
C	0.9964402	-9.4163389	0.4542515
C	0.1705032	-10.3266698	-0.2024333
C	-1.1416335	-10.4993687	0.2050218
C	-1.6584436	-9.7526670	1.2532623
C	-0.8431873	-8.8333446	1.8969726
C	0.4758457	-8.6703991	1.5109115
H	2.3482386	-11.5788981	1.3584724
H	3.6647721	-13.5787588	0.7661289

H	5.1753841	-13.5400478	-1.1974491
H	5.3436019	-11.4809084	-2.5661887
H	4.0087730	-9.4908587	-1.9807710
H	0.5689849	-10.9050617	-1.0272220
H	-1.7675657	-11.2177362	-0.3127801
H	-2.6879857	-9.8792067	1.5639085
H	-1.2330007	-8.2468193	2.7213488
H	1.1137855	-7.9634389	2.0272168
C	2.6219773	-1.4341875	0.0105749
C	1.5217731	-1.9258173	-0.0735030
C	0.2094146	-2.4427199	-0.1732266
C	-0.2013506	-3.5498171	0.5768100
C	-1.5008593	-4.0073254	0.5108483
C	-2.4352512	-3.3797585	-0.3159506
C	-2.0221250	-2.2930540	-1.0897508
C	-0.7262210	-1.8311869	-1.0154623
H	0.5080457	-4.0338628	1.2370973
H	-1.8049383	-4.8554714	1.1120625
N	-3.7611244	-3.8219208	-0.3633871
H	-2.7310249	-1.8065834	-1.7480724
H	-0.4179827	-0.9872172	-1.6208958
C	-4.0549274	-5.1947266	-0.2465214
C	-5.1275728	-5.6212067	0.5325824
C	-5.4231957	-6.9704944	0.6306278
C	-4.6447995	-7.9112412	-0.0270943
C	-3.5670998	-7.4891154	-0.7919736
C	-3.2778480	-6.1413145	-0.9114712
C	-4.8089802	-2.8952582	-0.5280012
C	-5.8915864	-3.1967341	-1.3509545
C	-6.9238935	-2.2863872	-1.5052872
C	-6.8824574	-1.0579553	-0.8634356
C	-5.8002397	-0.7508410	-0.0516497
C	-4.7769858	-1.6650545	0.1283732
H	-5.7291863	-4.8871605	1.0549755
H	-6.2632155	-7.2878562	1.2383177
H	-4.8753584	-8.9665651	0.0563937
H	-2.9458428	-8.2147553	-1.3039042
H	-2.4441051	-5.8116330	-1.5198841
H	-5.9184487	-4.1494795	-1.8658310
H	-7.7607286	-2.5367526	-2.1477258
H	-7.6840400	-0.3422146	-0.9953715
H	-5.7566789	0.2093372	0.4502825
H	-3.9397271	-1.4276518	0.7735361
C	2.7060681	1.3321313	0.1100730
C	1.6377925	1.8970294	0.0657503
C	0.3591285	2.5003114	0.0276899
C	-0.7920770	1.7168041	0.1801504
C	-2.0460182	2.2893199	0.1541551
C	-2.1942122	3.6662297	-0.0201567
C	-1.0520577	4.4523348	-0.1751835
C	0.2021415	3.8790411	-0.1555197
H	-0.6878592	0.6499089	0.3358385
H	-2.9259400	1.6686573	0.2739224
N	-3.4711377	4.2465748	-0.0436600
H	-1.1541067	5.5221144	-0.3121636
H	1.0784003	4.4996655	-0.2955210
C	-4.5188191	3.5866955	-0.7148758
C	-5.7889309	3.5113867	-0.1473059

C	-6.8205787	2.8879179	-0.8289156
C	-6.5968616	2.3123901	-2.0710208
C	-5.3280795	2.3684910	-2.6280526
C	-4.2963082	3.0066467	-1.9619367
C	-3.7122903	5.4668417	0.6087274
C	-4.6113285	6.3893648	0.0736961
C	-4.8780832	7.5726988	0.7406657
C	-4.2386362	7.8700794	1.9349103
C	-3.3275113	6.9639693	2.4569453
C	-3.0694925	5.7692328	1.8086711
H	-5.9621945	3.9563356	0.8252164
H	-7.8052360	2.8414073	-0.3768572
H	-7.4028775	1.8194892	-2.6005292
H	-5.1409560	1.9231682	-3.5984940
H	-3.3088383	3.0634302	-2.4043571
H	-5.1084510	6.1660609	-0.8624129
H	-5.5863841	8.2740774	0.3135887
H	-4.4452783	8.7995047	2.4519140
H	-2.8197189	7.1806031	3.3899582
H	-2.3693725	5.0591364	2.2313761
C	5.1393334	2.7018102	0.3410588
C	4.9272540	3.8917773	0.3796971
C	4.4519663	5.2221481	0.4217757
C	3.2140472	5.4556507	1.0340265
C	2.6258972	6.6983542	0.9859498
C	3.2516141	7.7546260	0.3200198
C	4.5103853	7.5422225	-0.2453885
C	5.1023289	6.2959978	-0.1922175
H	2.7172165	4.6356772	1.5377856
H	1.6606647	6.8601438	1.4505828
N	2.5975104	8.9853927	0.2066126
H	5.0094521	8.3578432	-0.7535676
H	6.0617506	6.1338382	-0.6683972
C	1.1988002	8.9909652	0.0104103
C	0.3791092	9.8033273	0.7880841
C	-0.9935663	9.7825775	0.6057848
C	-1.5647584	8.9497792	-0.3453501
C	-0.7471457	8.1472581	-1.1270144
C	0.6271499	8.1680264	-0.9567623
C	3.3005575	10.1976197	0.2865368
C	2.9217319	11.2851669	-0.4994112
C	3.6095187	12.4830963	-0.4085638
C	4.6898675	12.6149775	0.4515922
C	5.0709695	11.5316577	1.2301242
C	4.3802978	10.3345624	1.1583338
H	0.8280444	10.4427298	1.5391748
H	-1.6243100	10.4082068	1.2270513
H	-2.6398008	8.9155580	-0.4672205
H	-1.1834860	7.5039518	-1.8832187
H	1.2685217	7.5427576	-1.5670212
H	2.0852026	11.1840323	-1.1800945
H	3.3031557	13.3184879	-1.0278715
H	5.2287674	13.5524591	0.5153053
H	5.9072005	11.6209873	1.9141889
H	4.6726148	9.4960433	1.7786924

17
4-I-2-Me-btz
S 2.1674461 1.3794289 -0.0001395
C 2.7519453 -0.2643783 -0.0001011
N 1.8395116 -1.1734514 -0.0000736
C 0.5857819 -0.6219708 0.0000283
C -0.6249782 -1.3200272 0.0000237
C -1.8164902 -0.6223078 -0.0000648
C -1.8230531 0.7741575 0.0000090
C -0.6458539 1.4959839 0.0001076
C 0.5486086 0.7878154 0.0001177
C 4.2112603 -0.5477696 -0.0000108
I -0.6202099 -3.3982841 0.0001855
H -2.7540647 -1.1633438 -0.0002331
H -2.7726864 1.2958416 -0.0000086
H -0.6560772 2.5786599 0.0001315
H 4.8013378 0.3682010 -0.0000070
H 4.4728682 -1.1365202 0.8814928
H 4.4729550 -1.1365660 -0.8814576

17
5-I-2-Me-btz
S 2.1841280 1.3753690 -0.0005214
C 2.7617419 -0.2736904 -0.0001621
N 1.8463837 -1.1799925 -0.0000031
C 0.5923121 -0.6191673 -0.0000269
C -0.6040807 -1.3358414 0.0000023
C -1.7888363 -0.6295097 0.0000028
C -1.8165001 0.7683534 0.0001428
C -0.6363706 1.4863599 0.0001343
C 0.5648011 0.7887452 0.0000607
C 4.2208560 -0.5586856 0.0000450
H -0.5786715 -2.4174422 0.0000204
I -3.5999257 -1.6691365 -0.0002956
H -2.7647339 1.2896705 0.0002558
H -0.6585154 2.5692266 0.0000619
H 4.8120024 0.3565895 -0.0000431
H 4.4824921 -1.1472697 0.8817145
H 4.4826700 -1.1475449 -0.8813881

17
6-I-2-Me-btz
S 2.2290415 1.3327354 0.0001704
C 2.8104577 -0.3160942 0.0000392
N 1.8967515 -1.2235145 -0.0000459
C 0.6415264 -0.6664682 -0.0000227
C -0.5589710 -1.3738109 -0.0000040
C -1.7528628 -0.6828134 -0.0000423
C -1.7569511 0.7152285 -0.0000311
C -0.5859818 1.4491879 -0.0000550
C 0.6100536 0.7416654 -0.0000005
C 4.2704060 -0.5973652 -0.0000100
H -0.5393771 -2.4566652 0.0001089
H -2.6910659 -1.2220174 0.0000061
I -3.5862288 1.7212689 0.0000827
H -0.6031640 2.5310027 -0.0001452
H 4.8591681 0.3194210 0.0000685
H 4.5338501 -1.1852749 0.8815435
H 4.5338436 -1.1851268 -0.8816627

17
7-I-2-Me-btz

S	2.1645202	1.3588943	0.0000121
C	2.7475498	-0.2874422	-0.0000699
N	1.8383644	-1.2005798	-0.0001652
C	0.5804095	-0.6489798	-0.0000985
C	-0.6153098	-1.3637266	-0.0000348
C	-1.8074908	-0.6692262	0.0000205
C	-1.8372623	0.7274508	0.0000878
C	-0.6569993	1.4467607	-0.0000302
C	0.5512039	0.7617429	-0.0001122
C	4.2083908	-0.5647545	0.0000438
H	-0.5864137	-2.4459619	-0.0000213
H	-2.7461086	-1.2105308	-0.0000424
H	-2.7855753	1.2493991	0.0002684
I	-0.6841909	3.5291545	-0.0000842
H	4.7949407	0.3535045	0.0000329
H	4.4731957	-1.1519541	0.8817034
H	4.4733159	-1.1520569	-0.8815101

17
4,5-I_2-2-Me-btz

S	2.2230348	1.4705788	-0.0000681
C	2.8086499	-0.1716431	0.0000089
N	1.8962828	-1.0813271	0.0001032
C	0.6415091	-0.5320378	0.0001031
C	-0.5621118	-1.2535655	0.0000357
C	-1.7549807	-0.5466611	-0.0000429
C	-1.7634365	0.8546868	0.0000112
C	-0.5896672	1.5761597	0.0000090
C	0.6079605	0.8750408	0.0000319
C	4.2676587	-0.4550046	-0.0000315
I	-0.4467699	-3.3243206	0.0000599
I	-3.6165539	-1.4843665	-0.0002650
H	-2.7126155	1.3740252	0.0001269
H	-0.6119765	2.6585877	0.0000299
H	4.8578493	0.4608193	-0.0001338
H	4.5289323	-1.0438852	0.8814497
H	4.5288646	-1.0440409	-0.8814282

17
4,6-I_2-2-Me-btz

S	2.2260187	1.4026046	-0.0005739
C	2.8134439	-0.2412644	-0.0001306
N	1.9022024	-1.1517866	0.0001071
C	0.6491253	-0.6023514	0.0000625
C	-0.5613056	-1.3006382	-0.0000090
C	-1.7567316	-0.6089955	0.0001138
C	-1.7544119	0.7883296	-0.0000111
C	-0.5825280	1.5196586	0.0000960
C	0.6090688	0.8068403	-0.0000015
C	4.2730086	-0.5211905	0.0000292
I	-0.5579520	-3.3777236	-0.0003749
H	-2.6940558	-1.1482689	0.0003589
I	-3.5831444	1.7933080	-0.0004142
H	-0.5953076	2.6012164	0.0005276
H	4.8613993	0.3956540	-0.0000643
H	4.5355479	-1.1093953	0.8814950
H	4.5356920	-1.1096701	-0.8812105

17
4,7-I_2-2-Me-btz

S	2.1675349	1.3679261	-0.0007295
C	2.7500058	-0.2760125	-0.0004484
N	1.8395256	-1.1885057	-0.0005069
C	0.5860688	-0.6394282	-0.0005299
C	-0.6225059	-1.3402961	-0.0002776
C	-1.8133800	-0.6410566	0.0001609
C	-1.8297477	0.7543946	0.0002471
C	-0.6472715	1.4688689	-0.0001246
C	0.5539596	0.7724176	-0.0005406
C	4.2093725	-0.5576619	0.0002625
I	-0.6174619	-3.4160387	-0.0003998
H	-2.7530145	-1.1786761	0.0006220
H	-2.7784961	1.2756209	0.0006922
I	-0.6601593	3.5489607	0.0001417
H	4.7987627	0.3586858	0.0002516
H	4.4706356	-1.1460824	0.8820618
H	4.4714853	-1.1466835	-0.8808825

17
5,6-I_2-2-Me-btz

S	2.2869422	1.3682389	0.0001363
C	2.8646464	-0.2828614	0.0000168
N	1.9499669	-1.1896872	0.0000176
C	0.6969546	-0.6282799	0.0001355
C	-0.5010483	-1.3353660	0.0000359
C	-1.7008558	-0.6461006	-0.0000276
C	-1.7167011	0.7587022	-0.0000541
C	-0.5298992	1.4754993	0.0001927
C	0.6680726	0.7783472	0.0003068
C	4.3239023	-0.5661450	-0.0001039
H	-0.4774071	-2.4170771	-0.0000314
I	-3.4461969	-1.7856148	-0.0000378
I	-3.4822715	1.8653980	-0.0004413
H	-0.5492416	2.5572999	0.0002041
H	4.9141858	0.3496060	-0.0003383
H	4.5858197	-1.1545261	0.8815614
H	4.5856492	-1.1548863	-0.8815728

17
5,7-I_2-2-Me-btz

S	2.2337099	1.3326056	-0.0002812
C	2.8073403	-0.3171107	-0.0001137
N	1.8930491	-1.2259505	-0.0000972
C	0.6396568	-0.6660606	-0.0000914
C	-0.5557308	-1.3824122	-0.0000679
C	-1.7401499	-0.6751040	-0.0000018
C	-1.7742777	0.7224107	0.0001530
C	-0.5877049	1.4317244	0.0000028
C	0.6185629	0.7438909	-0.0000546
C	4.2662187	-0.6024390	0.0000685
H	-0.5309134	-2.4637165	0.0000034
I	-3.5523534	-1.7115160	-0.0001852
H	-2.7209461	1.2450061	0.0004977
I	-0.6110298	3.5131003	-0.0001748
H	4.8577073	0.3125591	0.0001016
H	4.5269086	-1.1913675	0.8817169
H	4.5271133	-1.1914330	-0.8814760

17
6,7-I_2-2-Me-btz

S	2.2268170	1.2632076	0.0000156
C	2.8048930	-0.3847696	-0.0000652
N	1.8916101	-1.2945568	-0.0001016
C	0.6384601	-0.7361257	-0.0000161
C	-0.5624184	-1.4409223	-0.0000357
C	-1.7491933	-0.7427785	0.0000358
C	-1.7719642	0.6587859	0.0000109
C	-0.5879548	1.3833542	0.0000173
C	0.6102914	0.6720797	0.0000700
C	4.2644778	-0.6673763	0.0000207
H	-0.5487529	-2.5234732	-0.0001452
H	-2.6889923	-1.2790702	0.0002279
I	-3.6432350	1.5731256	-0.0000436
I	-0.4995369	3.4594146	-0.0001019
H	4.8542309	0.2487660	0.0000985
H	4.5268844	-1.2556139	0.8816328
H	4.5269880	-1.2555251	-0.8816203

17
4,5,6-I_3-2-Me-btz

S	2.1501850	1.3641744	-0.0004433
C	2.7371028	-0.2794031	-0.0000038
N	1.8260255	-1.1900100	-0.0000126
C	0.5711073	-0.6417811	-0.0003790
C	-0.6336178	-1.3562233	-0.0001864
C	-1.8436789	-0.6650899	0.0000597
C	-1.8397403	0.7451708	0.0002059
C	-0.6573376	1.4629907	-0.0001576
C	0.5366070	0.7631174	-0.0003272
C	4.1964343	-0.5599419	0.0002292
I	-0.4820456	-3.4281756	-0.0003410
I	-3.6473858	-1.7042952	0.0001151
I	-3.5860235	1.8883770	0.0009713
H	-0.6751055	2.5443068	-0.0005808
H	4.7852585	0.3567215	0.0002281
H	4.4582628	-1.1485146	0.8817792
H	4.4585008	-1.1486568	-0.8811568

17
4,5,7-I_3-2-Me-btz

S	2.1638464	1.3665173	0.0009745
C	2.7447691	-0.2767539	0.0006502
N	1.8329548	-1.1883879	0.0008427
C	0.5790421	-0.6392992	0.0006463
C	-0.6233818	-1.3613871	0.0002960
C	-1.8155213	-0.6522898	-0.0002155
C	-1.8301327	0.7485870	-0.0002805
C	-0.6500693	1.4620655	0.0000583
C	0.5526533	0.7696162	0.0005714
C	4.2034162	-0.5609695	-0.0003938
I	-0.5107125	-3.4302241	0.0005609
I	-3.6782554	-1.5865458	-0.0009514
H	-2.7778092	1.2692295	-0.0005542
I	-0.6744689	3.5411792	-0.0002142
H	4.7943990	0.3543423	-0.0005530
H	4.4643091	-1.1505096	0.8807741
H	4.4631474	-1.1500560	-0.8822118

17
4,6,7-I_3-2-Me-btz

S	2.1598864	1.3690787	-0.0001428
C	2.7452798	-0.2735539	-0.0000748
N	1.8350463	-1.1870181	-0.0001833
C	0.5836201	-0.6369008	-0.0002518
C	-0.6262939	-1.3346052	-0.0001174
C	-1.8153107	-0.6364135	0.0000275
C	-1.8325728	0.7642567	0.0000125
C	-0.6488596	1.4884823	-0.0001294
C	0.5456917	0.7721351	-0.0002591
C	4.2047770	-0.5534282	0.0001040
I	-0.6311096	-3.4096161	0.0000348
H	-2.7536382	-1.1739452	0.0001788
I	-3.7038240	1.6769282	0.0003352
I	-0.5570274	3.5624486	-0.0000013
H	4.7931368	0.3635719	0.0002211
H	4.4668355	-1.1417781	0.8817373
H	4.4670856	-1.1417233	-0.8814913

17
5,6,7-I_3-2-Me-btz

S	2.1568959	1.3739530	-0.0000289
C	2.7327002	-0.2757768	0.0001569
N	1.8191929	-1.1855941	0.0005538
C	0.5679831	-0.6226129	0.0004795
C	-0.6289003	-1.3279353	0.0003309
C	-1.8244159	-0.6350664	-0.0001036
C	-1.8609371	0.7750321	-0.0000664
C	-0.6603136	1.4850274	0.0001926
C	0.5402972	0.7831520	0.0003177
C	4.1917211	-0.5596234	-0.0002379
H	-0.6079017	-2.4092574	0.0003907
I	-3.5523655	-1.8069236	-0.0009071
I	-3.6772080	1.7889801	-0.0004652
I	-0.5379015	3.5626754	0.0004017
H	4.7826977	0.3556915	-0.0007409
H	4.4531389	-1.1482055	0.8814571
H	4.4525288	-1.1487801	-0.8817309

17
4,5,6,7-I_4-2-Me-btz

S	2.1444741	1.3686024	0.0000951
C	2.7284385	-0.2734899	0.0000744
N	1.8180245	-1.1865323	-0.0000212
C	0.5649153	-0.6361505	-0.0001165
C	-0.6384900	-1.3500662	-0.0001306
C	-1.8441440	-0.6542968	0.0000698
C	-1.8602739	0.7627397	0.0000239
C	-0.6638657	1.4741043	-0.0001040
C	0.5323347	0.7675527	-0.0000886
C	4.1874242	-0.5555068	0.0000922
I	-0.4783222	-3.4207650	-0.0004916
I	-3.6342389	-1.7246716	0.0004928
I	-3.6598930	1.8137168	0.0001458
I	-0.5251727	3.5501346	-0.0003183
H	4.7774470	0.3603768	0.0001347
H	4.4484585	-1.1446105	0.8815175
H	4.4484788	-1.1445384	-0.8813754

13 References

[1] Lux, H. (1963). "Manganese(VII) Oxide". In G. Brauer (ed.). Handbook of Preparative Inorganic Chemistry, 2nd Ed. New York, USA: Academic Press. pp. 1459–1460

[2] Royer, D. J., Evidence for the existence of the permanganyl ion in sulphuric acid solutions of potassium permanganate. *J. Inorg. Nucl. Chem.* **1961,** *17*, 159-167.

[3] Hrobarik, P.; Hrobarikova, V.; Sigmundova, I.; Zahradnik, P.; Fakis, M.; Polyzos, I.; Persephonis, P., Benzothiazoles with Tunable Electron-Withdrawing Strength and Reverse Polarity: A Route to Triphenylamine-Based Chromophores with Enhanced Two-Photon Absorption. *J. Org. Chem.* **2011,** *76*, 8726-8736.

[4] Sharghi, H.; Asemani, O., Methanesulfonic acid/SiO_2 as an efficient combination for the synthesis of 2-substituted aromatic and aliphatic benzothiazoles from carboxylic acids. *Synthetic Commun.* **2009,** *39*, 860-867.

[5] Hrobarikova, V.; Hrobarik, P.; Gajdos, P.; Fitilis, I.; Fakis, M.; Persephonis, P.; Zahradnik, P., Benzothiazole-Based Fluorophores of Donor-pi-Acceptor-pi-Donor Type Displaying High Two-Photon Absorption. *J. Org. Chem.* **2010,** *75*, 3053-3068.

[6] Bassignana, P.; Cogrossi, C.; Gandino, M., Étude des spectres d'absorption dans l'infrarouge de quelques dérivés du cycle thiazolique et oxazolique. Examen de la liaison C=N. *Spectrochimica Acta* **1963,** *19*, 1885-1897.

[7] Homberger, K. R., et al. 7-Aminofuropyridine derivatives. WO2011/100502. August 18, 2011.

[8] Racané, L.; Čičak, H.; Mihalić, Z.; Karminski-Zamola, G.; Tralić-Kulenović, V., New pentacyclic ring systems: intramolecular cyclization of o, o′-disubstituted bibenzothiazoles. *Tetrahedron* **2011,** *67*, 2760-2767.

[9] Hunter, R. F.; Parken, E. R., The unsaturation and tautomeric mobility of heterocyclic compounds. Part VI. The mobility of 5-substituted 1-hydroxybenzthiazoles, and the ultra-violet absorption of mobile and static derivatives of 1-hydroxybenzthiazole. *J. Chem. Soc.* **1935**, 1755-1761.

[10] Xu, F.; Peng, L.; Orita, A.; Otera, J., Dihalo-substituted dibenzopentalenes: their practical synthesis and transformation to dibenzopentalene derivatives. *Org. Lett.* **2012,** *14*, 3970-3973.

[11] Modha, S. G.; Popescu, M. V.; Greaney, M. F., Synthesis of Triarylamines via Sequential C–N Bond Formation. *J. Org. Chem.* **2017,** *82*, 11933-11938.

[12] Lambert, C.; Nöll, G.; Schmälzlin, E.; Meerholz, K.; Bräuchle, C., Synthesis, (Non) Linear Optical and Redox Properties of a Donor-Substituted Truxenone Derivative. *Chem.–Eur. J.* **1998,** *4*, 2129-2135.

[13] Tydlitat, J.; Feckova, M.; Le Poul, P.; Pytela, O.; Klikar, M.; Rodríguez-López, J.; Robin-le Guen, F.; Achelle, S., Influence of Donor-Substituents on Triphenylamine Chromophores Bearing Pyridine Fragments. *Eur. J. Org. Chem.* **2019,** *2019*, 1921-1930.

[14] Williams, A. T. R.; Winfield, S. A.; Miller, J. N., Relative fluorescence quantum yields using a computer-controlled luminescence spectrometer. *Analyst* **1983,** *108*, 1067-1071.

[15] Melhuish, W. H., Quantum efficiencies of fluorescence of organic substances: effect of solvent and concentration of the fluorescent solute. *J. Phys. Chem.* **1961,** *65*, 229-235.

[16] Xu, C.; Webb, W. W., Measurement of two-photon excitation cross sections of molecular fluorophores with data from 690 to 1050 nm. *J. Opt. Soc. Am. B* **1996,** *13*, 481-491.

[17] Fitilis, I.; Fakis, M.; Polyzos, I.; Giannetas, V.; Persephonis, P.; Vellis, P.; Mikroyannidis, J., A two-photon absorption study of fluorene and carbazole derivatives. The role of the central core and the solvent polarity. *Chem. Phys. Lett.* **2007,** *447*, 300-304.

[18] Makarov, N. S.; Drobizhev, M.; Rebane, A., Two-photon absorption standards in the 550–1600 nm excitation wavelength range. *Opt. Express* **2008,** *16*, 4029-4047.

[19] STOE & Cie GmbH (2016). X-Area 1.76, software package for collecting single-crystal data on STOE area-detector diffractometers, for image processing, scaling reflection intensities and for outlier rejection; Darmstadt, Germany
[20] Koziskova, J.; Hahn, F.; Richter, J.; Kožíšek, J., Comparison of different absorption corrections on the model structure of tetrakis(μ_2-acetato)-diaqua-di-copper (II). *Acta Chimica Slovaca* **2016,** *9*, 136-140.
[21] Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A.; Puschmann, H., The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment–Olex2 dissected. *Acta Crystallogr. A* **2015,** *71*, 59-75.
[22] Sheldrick, G. M., Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **2015,** *71*, 3-8.
[23] Sheldrick, G. M., SHELXT–Integrated space-group and crystal-structure determination. *Acta Crystallogr. A* **2015,** *71*, 3-8.
[24] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009,** *42*, 339-341.
[25] CrystalExplorer 17.5; Turner, M. J.; McKinnon, J. J.; Wolff, S. K.; Grimwood, D. J.; Spackman, P. R.; Jayatilaka, D.; Spackman, M. A.; University of Western Australia, **2017**.
[26] Spackman, M. A.; Jayatilaka, D., Hirshfeld surface analysis. *CrystEngComm* **2009,** *11*, 19-32.
[27] Spackman, M. A.; McKinnon, J. J., Fingerprinting intermolecular interactions in molecular crystals. *CrystEngComm* **2002,** *4*, 378-392.
[28] Jayatilaka, D.; Grimwood, D. J. In *Tonto: a Fortran based object-oriented system for quantum chemistry and crystallography*, International Conference on Computational Science 2003, Springer; pp 142-151.
[29] Etter, M. C.; MacDonald, J. C.; Bernstein, J., Graph-set analysis of hydrogen-bond patterns in organic crystals. *Acta Crystallogr. B* **1990,** *46*, 256-262.
[30] Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996,** *77*, 3865–3868.
[31] Adamo, C.; Barone, V., Toward Chemical Accuracy in the Computation of NMR Shieldings: the PBE0 Model. *Chem. Phys. Lett.* **1998,** *298*, 113-119.
[32] Weigend, F.; Ahlrichs, R., Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005,** *7*, 3297-3305.
[33] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010,** *132*.
[34] Grimme, S.; Ehrlich, S.; Goerigk, L., Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011,** *32*, 1456-1465.
[35] TURBOMOLE, version 7.5; TURBOMOLE GmBH, a development of the University of Karlsruhe and Forschungszentrum Karlsruhe, 2020; available from: http://www.turbomole.com.
[36] Sinnecker, S.; Rajendran, A.; Klamt, A.; Diedenhofen, M.; Neese, F., Calculation of solvent shifts on electronic g-tensors with the conductor-like screening model (COSMO) and its self-consistent generalization to real solvents (direct COSMO-RS). *J. Phys. Chem. A* **2006,** *110*, 2235-2245.
[37] Klamt, A.; Jonas, V.; Bürger, T.; Lohrenz, J. C., Refinement and parametrization of COSMO-RS. *J. Phys. Chem. A* **1998,** *102*, 5074-5085.

[38] Eckert, F.; Diedenhofen, M.; Klamt, A., Towards a first principles prediction of pK_a: COSMO-RS and the cluster-continuum approach. *Mol. Phys.* **2010,** *108*, 229-241.
[39] Wolff, S. K.; Ziegler, T., Calculation of DFT-GIAO NMR shifts with the inclusion of spin-orbit coupling. *J. Chem. Phys.* **1998,** *109*, 895-905.
[40] Wolff, S. K.; Ziegler, T.; van Lenthe, E.; Baerends, E. J., Density functional calculations of nuclear magnetic shieldings using the zeroth-order regular approximation (ZORA) for relativistic effects: ZORA nuclear magnetic resonance. *J. Chem. Phys.* **1999,** *110*, 7689-7698.
[41] Amsterdam Density Functional (ADF), version 2017.112, SCM, Theoretical Chemistry, Vrije Univeriteit, Amsterdam, Netherlands, 2018; available from http://www.scm.com.
[42] te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Guerra, C. F.; Van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T., Chemistry with ADF. *J. Comput. Chem.* **2001,** *22*, 931-967.
[43] Hansen, A. E.; Bouman, T. D., Localized orbital/local origin method for calculation and analysis of NMR shieldings. Applications to ^{13}C shielding tensors. *J. Chem. Phys.* **1985,** *82*, 5035-5047.
[44] Autschbach, J., The role of the exchange-correlation response kernel and scaling corrections in relativistic density functional nuclear magnetic shielding calculations with the zeroth-order regular approximation. *Mol. Phys.* **2013,** *111*, 2544-2554.
[45] Greif, A. H.; Hrobarik, P.; Hrobarikova, V.; Arbuznikov, A. V.; Autschbach, J.; Kaupp, M., A relativistic quantum-chemical analysis of the trans influence on ^{1}H NMR hydride shifts in square-planar platinum (II) complexes. *Inorg. Chem.* **2015,** *54*, 7199-7208.
[46] Greif, A. H.; Hrobarik, P.; Autschbach, J.; Kaupp, M., Giant spin–orbit effects on ^{1}H and ^{13}C NMR shifts for uranium(VI) complexes revisited: role of the exchange–correlation response kernel, bonding analyses, and new predictions. *Phys. Chem. Chem. Phys.* **2016,** *18*, 30462-30474.
[47] Yanai, T.; Tew, D. P.; Handy, N. C., A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Lett.* **2004,** *393*, 51-57.
[48] DALTON, a molecular electronic structure program, release Dalton2020, 2020; available from http://daltonprogram.org.
[49] Norman, P.; Ruud, K., Microscopic theory of nonlinear optics. In *Nonlinear optical properties of matter: From molecules to condensed phases*, Springer, Netherlands, 2006; pp 1-49.
[50] Salek, P.; Vahtras, O.; Guo, J. D.; Luo, Y.; Helgaker, T.; Agren, H., Calculations of two-photon absorption cross sections by means of density-functional theory. *Chem. Phys. Lett.* **2003,** *374*, 446-452.
[51] Rudberg, E.; Salek, P.; Helgaker, T.; Agren, H., Calculations of two-photon charge-transfer excitations using Coulomb-attenuated density-functional theory. *J. Chem. Phys.* **2005,** *123*, 184108.