Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


# Supporting Information

## One-pot Generation of Benzynes from 2-Aminophenylboronates via Rh(II)-Catalyzed N–H Amination/oxidation/elimination Cascade Process

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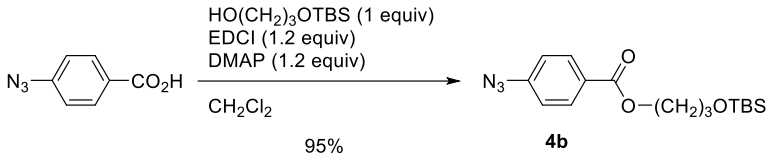
**Experimental Section**

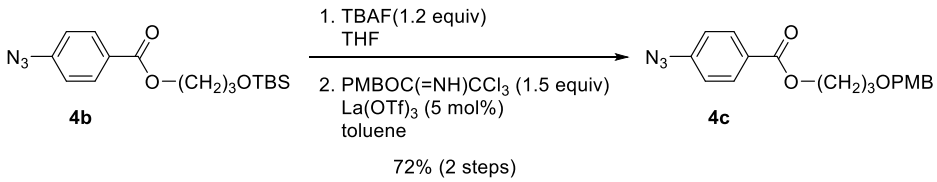
**General.** All melting points were measured on a Yanagimoto micro melting point apparatus. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer and absorbance bands are reported in wavenumber ($cm^{-1}$). $^{1}H$ NMR spectra were recorded on JEOL JNM-AL 300 (300 MHz) spectrometer or JEOL JNM-ECA 400 (400 MHz) spectrometer. Chemical shifts are reported relative to internal standard (tetramethylsilane at $\delta_H$ 0.00, $CDCl_3$ at $\delta_H$ 7.26, DMSO-$d_6$ at $\delta_H$ 2.50, $CD_3OD$ at $\delta_H$ 3.49). Data are presented as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant and integration. $^{13}C$ NMR spectra were recorded on JEOL JNM-ECA 400 (100 MHz) spectrometer. Chemical shifts are reported relative to internal standard ($CDCl_3$ at δ 77.00, $CD_3OD$ at δ 49.86). Mass spectra were recorded on a JEOL JMS 700 instrument with a direct inlet system. Column chromatography was carried out on Kanto silica gel 60 N (40–50 mesh). Analytical thin layer chromatography (TLC) was carried out on Merck Kieselgel 60 $F_{254}$ plates with visualization by ultraviolet, anisaldehyde stain solution or phosphomolybdic acid stain solution. All non-aqueous reactions were carried out in flame-dried glassware under Ar atmosphere unless otherwise noted. Reagents and solvents were used without purification. 4Å MS (powder) from nacalai tesque was used after drying. Dirhodium(II) complex catalysts, $Rh_2(esp)_2$ and $Rh_2(HNCOCF_3)_4$, were prepared according to literatures,[1,2] while $Rh_2(esp)_2$ is commercially available. TsN=IMes was prepared according to a literature.[3] 2-Aminophenylboronates **1b**, **1c** and **1e** were synthesized according to the literature.[4,5] Azides **4a** and **4h** were prepared according to the literature.[6,7]

**1. Procedure for the preparation of 3-(*tert*-butyldimethylsilyloxy)propyl 4-azidobenzoate (4b)**.




To a solution of 4-azidobenzoic acid (856 mg, 5.30 mmol), propylene glycol mono-TBS ether (1.00 g, 5.30 mmol) and DMAP (770 mg, 6.30 mmol) in $CH_2Cl_2$ (53 mL) was added EDCI (1.21 g, 6.30 mmol) at 0 °C. After stirring at room temperature for 12 h, the reaction was quenched with 10 % aqueous HCl, and the mixture was extracted with EtOAc. The organic extract was successively washed with saturated aqueous $NaHCO_3$ and brine, and dried over anhydrous $Na_2SO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 10:1 *n*-hexane/EtOAc) to give 4-azidobenzoate **4b** (1.68 g, 95%) as a light yellow oil: IR (KBr) *v* 2955, 2123, 1721, 1603, 1275, 1100 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 0.06 (s, 6H, SiC*H*$_3$), 0.90 (s, 9H, *t*-Bu), 1.97 (quintet, *J* = 6.0 Hz, 2H, $CH_2CH_2CH_2$), 3.78 (t, *J* = 6.0 Hz, 2H, C*H*$_2$OTBS), 4.41 (t, *J* = 6.0 Hz, 2H, $CO_2CH_2$), 7.06 (d, *J* = 8.4 Hz, 2H, Ar*H*), 8.03 (d, *J* = 8.4 Hz, 2H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ –5.5 ($CH_3$), 18.3 (C), 25.8 ($CH_3$), 31.8 ($CH_2$), 59.4 ($CH_2$), 62.0 ($CH_2$), 118.8 (CH), 126.9 (C), 131.3 (CH), 144.6 (C), 165.7 (C=O); HRMS (FAB) calcd for $C_{16}H_{25}N_3O_3Si$ $[M+H]^+$ 336.1743, found 336.1745.

**2. Procedure for the preparation of 3-(*p*-methoxybenzyloxy)propyl 4-azidobenzoate (4c)**.

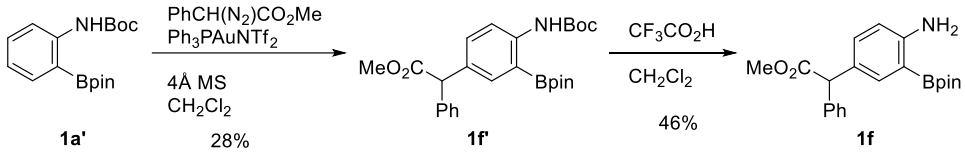



To a solution of **4b** (503 mg, 1.50 mmol) in THF (4.0 mL) was added TBAF (1 M in THF, 2.00 mL, 2.00 mmol) at 0 °C. After stirring at room temperature for 1 h, water was added to the reaction mixture, and the mixture was extracted with EtOAc. The organic extract was successively washed with brine, and dried over anhydrous $Na_2SO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 1:1 *n*-hexane/EtOAc) to give corresponding alcohol (301 mg, 91%) as a colorless oil: IR (KBr) *v* 3410, 2960, 2124, 1716, 1603, 1278 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 2.01 (quintet, *J* = 6.0 Hz, 2H, $CH_2CH_2CH_2$), 2.13 (brs, 1H, O*H*), 3.77 (t, *J* = 6.0 Hz, 2H, C*H*$_2$OH), 4.48 (t, *J* = 6.0 Hz, 2H, $CO_2CH_2$), 7.07 (dd, *J* = 2.0, 8.8 Hz, 2H, Ar*H*),

8.03 (dd, *J* = 2.0, 8.8 Hz, 2H, Ar*H*); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 31.8 ($CH_2$), 59.1 ($CH_2$), 61.8 ($CH_2$), 118.8 (CH), 126.6 (C), 131.4 (CH), 144.9 (C), 166.1 (C=O); HRMS (EI) calcd for $C_{10}H_{11}N_3O_3$ $[M]^+$ 221.0800, found 221.0801.

To a solution of **4b** (301 mg, 1.36 mmol) and $PMBOC(=NH)CCl_3$ (424 μL, 2.04 mmol) in toluene (20 mL) was added $La(OTf)_3$ (39.9 mg, 0.0680 mmol) at room temperature.[8] After stirring at room temperature for 30 min, the whole mixture was evaporated in vacuo to furnish the crude product, which was purified by column chromatography (silica gel, 4:1 *n*-hexane/EtOAc) to give PMB ether **4c** (368 mg, 79%) as a light yellow oil: IR (KBr) *v* 2859, 2122, 1717, 1603, 1512, 1275, 1100 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 2.05 (quintet, *J* = 6.0 Hz, 2H, $CH_2CH_2CH_2$), 3.59 (t, *J* = 6.0 Hz, 2H, $CH_2OPMB$), 3.77 (s, 3H, $OCH_3$), 4.42 (t, *J* = 6.0 Hz, 2H, $CO_2CH_2$), 4.45 (s, 2H, $OCH_2Ar$), 6.85 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.03 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.25 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.97 (d, *J* = 8.8 Hz, 2H, Ar*H*); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 29.1 ($CH_2$), 55.1 ($CH_3$), 62.2 ($CH_2$), 66.1 ($CH_2$), 72.6 ($CH_2$), 113.7 (CH), 118.7 (CH), 126.8 (C), 129.2 (CH), 130.3 (C), 131.3 (CH), 144.5 (C), 159.1 (C), 165.6, (C=O); HRMS (EI) calcd for $C_{18}H_{19}N_3O_4$ $[M]^+$ 341.1376, found 341.1374.

## 3. Procedure for the preparation of 2-amino-5-(2-methoxy-2-oxo-1-phenylethyl)phenylboronic acid pinacol ester (1f).

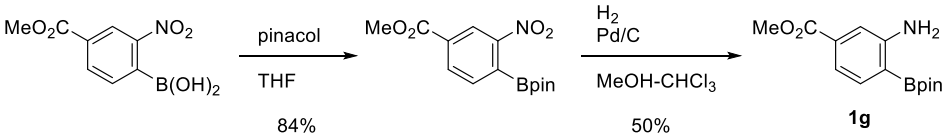



A solution of methyl phenyldiazoacetate [0.25 M in $CH_2Cl_2$, 12.0 mL, pre-dried over 4Å MS (pellets)] was slowly added to a mixture of *N*-Boc-2-aminophenylboronic acid pinacol ester (**1a'**) (1.92 g, 6.00 mmol), $Ph_3PAuNTf_2$ (235 mg, 0.150 mmol, 2.5 mol%), and 4Å MS (powder, 120 mg) in $CH_2Cl_2$ (3.0 mL) at room temperature.[9] After stirring for 1 h at the same temperature, the whole mixture was filtered through a pad of Celite, and the filtrate was evaporated in vacuo to furnish the crude product, which was purified by column chromatography (silica gel, 8:1 *n*-hexane/AcOEt) to give C–H insertion product **1f'** (386 mg, 28%) as a colorless oil: IR (KBr) *v* 3370, 2978, 1733, 1530, 1352, 1157 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 1.34 (s, 12H, $OC(CH_3)_2$), 1.51 (s, 9H, *t*-Bu), 3.72 (s, 3H, $CO_2CH_3$), 4.99 (s, 1H, $Ar_2CHCO_2Me$), 7.23-7.30 (m, 5H, Ar*H*), 7.42 (dd, *J* = 2.4, 8.8 Hz, 1H, Ar*H*), 7.66 (d, *J* = 2.4 Hz, 1H, Ar*H*), 8.15 (d, *J* = 8.8 Hz, 1H, Ar*H*), 8.68 (s, 1H, N*H*); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 24.8 ($CH_3$), 28.3 ($CH_3$), 52.2 ($CH_3$), 56.3 (CH), 79.8 (C), 84.2 (C), 118.0 (CH), 127.0 (CH), 128.4 (CH), 128.5 (CH), 131.3 (C), 132.8 (CH), 136.3 (CH), 138.9 (C), 144.5

(C), 153.0 (C=O), 173.0 (C=O) (*C*-B was not detected.); HRMS (EI) calcd for $C_{26}H_{34}BNO_6$ $[M]^+$ 467.2479, found 467.2481.

*N*-Boc amine **1f'** (105 mg, 0.225 mmol) was dissolved in TFA-$CH_2Cl_2$ (1:3, 2.0 mL) at 0 °C. After stirring for 5 h at the same temperature, the whole mixture was poured into saturated aqueous $NaHCO_3$, and the mixture was extracted with $CH_2Cl_2$. The combined organic extracts were dried over anhydrous $Na_2SO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 3:1 to 2:1 *n*-hexane/AcOEt) to give primary amine **1f** (38.2 mg, 46%) as a colorless oil: IR (KBr) *v* 3286, 3386, 2978, 1736, 1619, 1495, 1432, 1358, 1143 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 12H, $OC(CH_3)_2$), 3.71 (s, 3H, $OCH_3$), 4.74 (brs, 2H, $NH_2$), 4.93 (s, 1H, $Ar_2CHCO_2$), 6.56 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.19–7.29 (m, 6H, Ar*H*), 7.53 (d, *J* = 1.6 Hz, 1H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 24.8 ($CH_3$). 24.9 ($CH_3$), 52.1 ($CH_3$), 56.1 (CH), 83.5 (C), 115.2 (CH), 126.5 (C), 126.9 (CH), 128.3 (CH), 128.4 (CH), 132.8 (CH), 137.0 (CH), 139.5 (C), 153.0 (C), 173.5 (C=O) (*C*-B was not detected.); HRMS (EI) calcd for $C_{21}H_{26}BNO_4$ $[M]^+$ 367.1955, found 367.1956.

## 4. Procedure for the preparation of 2-amino-4-(methoxycarbonyl)phenylboronic acid pinacol ester (1g).[10]

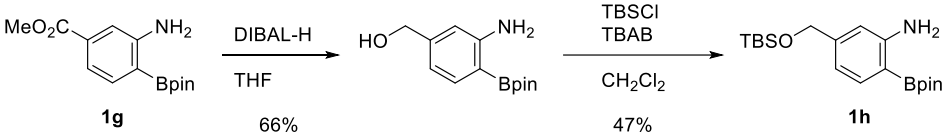



To a solution of 4-methoxycarbonyl-2-nitrophenylboronic acid (900 mg, 4.00 mmol) in THF (20 mL) was added pinacol (472 mg, 4.00 mmol) at room temperature. After stirring overnight at the same temperature, the whole mixture was evaporated in vacuo to furnish the crude product, which was purified by column chromatography (silica gel, 4:1 *n*-hexane/AcOEt) to give corresponding pinacol ester (1.03 g, 84%) as a colorless solid: $^1H$ NMR (300 MHz, $CDCl_3$): δ 1.44 (s, 12H, $OC(CH_3)_2$), 3.99 (s, 3H, $CO_2CH_3$), 6.65 (d, *J* = 7.2 Hz, 1H, Ar*H*), 8.31 (d, *J* = 7.2 Hz, 1H, Ar*H*), 8.79 (s, 1H, Ar*H*).[11]

A solution of pinacol ester (1.02 g, 0.700 mmol) and Pd/C (10%, 102 mg) in MeOH-$CHCl_3$ (2:1, 10 mL) was stirred under hydrogen at an atmospheric pressure at room temperature for overnight. The reaction mixture was then filtered through a pad of Celite, and the Celite filter cake was washed with $CH_2Cl_2$. The filtrate was concentrated in vacuo, and the residue was purified by column chromatography (silica gel, 1:1 *n*-hexane/AcOEt) to give amine **1g** (464 mg, 50%) as a light yellow solid: $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.35 (s, 12H, $OC(CH_3)_2$), 3.88 (s, 3H, $CO_2CH_3$), 4.84 (brs, 2H, $NH_2$), 7.24 (d, *J* = 9.0 Hz, 2H, Ar*H*), 7.66

(d, $J$ = 9.0 Hz, 1H, Ar*H*).[10]

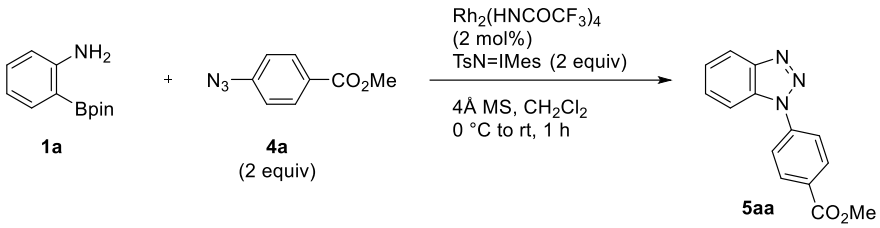
**5. Procedure for the preparation of 2-amino-4-(*tert*-butyldimethylsilyloxymethyl)phenylboronic acid pinacol ester (1h).**




To a solution of **1g** (842 mg, 3.04 mmol) in THF (10 mL) was added DIBAL-H (1.0 M in Hex, 10.6 mL, 10.6 mmol) at –40 ºC. After stirring for 1.5 h at the same temperature, the mixture was allowed to warm to 0 ºC. After stirring overnight, the reaction was quenched with saturated MeOH (5.0 mL) and saturated aqueous solution of Rochelle salt was successively added. The reaction mixture was then filtered through a pad of Celite, and the Celite filter cake was washed with $CH_2Cl_2$. The filtrate was extracted with $CH_2Cl_2$ and the combined organic extracts were dried over anhydrous $Na_2SO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 1:1 *n*-hexane/AcOEt) to give corresponding alcohol (498 mg, 66%) as a colorless oil: IR (KBr) *v* 3385, 2977, 1617, 1434, 1359, 1144, 1056 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.34 (s, 12H, OC(C*H*$_3$)$_2$), 4.58 (s, 2H, OC*H*$_2$Ar), 4.77 (brs, 2H, N*H*$_2$), 6.60 (s, 1H, Ar*H*), 6.64 (d, $J$ = 7.2 Hz, 1H, Ar*H*), 7.59 (d, $J$ = 7.2 Hz, 1H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 24.9 ($CH_3$), 65.2 ($CH_2$), 83.5 (C), 112.7 (CH), 115.2 (CH), 137.1 (CH), 145.8 (C), 153.9 (C) (*C*-B was not detected.); HRMS (FAB) calcd for $C_{13}H_{20}BNO_3$ $[M]^+$ 249.1536, found 249.1540.

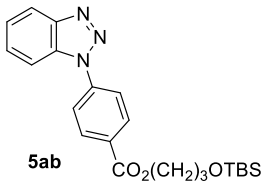
To a solution of alcohol (150 mg, 0.600 mmol) and TBAB (116 mg, 0.360 mmol) in $CH_2Cl_2$ (3.0 mL) was added TBSCl (109 mg, 0.720 mmol) at room temperature under Ar atmosphere.[12] After stirring for overnight, the reaction was quenched with $H_2O$ and saturated aqueous $NaHCO_3$. The mixture was extracted with $CH_2Cl_2$ and the combined organic extracts were dried over anhydrous $Na_2SO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 10:1 to 8:1 *n*-hexane/AcOEt) to give corresponding TBS ether (103 mg, 47%, azeotropically dried with toluene after column chromatography) as a colorless solid; mp 87-89 °C; IR (KBr) *v* 3390, 2930, 1618, 1434, 1357, 1144, 1090 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 0.08 (s, 6H, SiC*H*$_3$), 0.93 (s, 9H, *t*-Bu), 1.33 (s, 12H, OC(C*H*$_3$)$_2$), 4.65 (s, 2H, OC*H*$_2$Ar), 4.73 (brs, 2H, N*H*$_2$), 6.59-6.61 (m, 2H, Ar*H*), 7.56 (d, $J$ = 7.6 Hz, 1H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ -5.26 ($CH_3$), 18.4 (C), 24.9 ($CH_3$), 26.0 ($CH_3$), 64.9 ($CH_2$), 83.4 (C), 112.0 (CH), 114.6 (CH), 136.7 (CH), 146.5 (C), 153.7 (C) (*C*-B was not detected.); HRMS (EI) calcd for $C_{19}H_{34}BNO_3Si$ $[M+H]^+$ 364.2474, found 364.2483.

**6. Typical procedure for the one-pot benzyne generation/cycloaddition with azides: Preparation of 1-(4-methoxycarbonylphenyl)-1,2,3-benzotriazol (5aa).**[4]



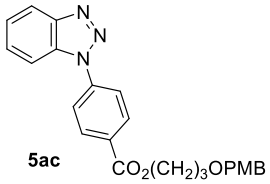

TsN=IMes (83.1 mg, 0.200 mmol) was added to a stirred mixture of 2-aminophenylboronic acid pinacol ester (**1a**) (21.9 mg, 0.100 mmol), methyl 4-azidobenzoate (35.4 mg, 0.200 mmol), $Rh_2(HNCOCF_3)_4$ (1.5 mg, 0.002 mmol, 2 mol %) and 4Å MS (powder, 40 mg) in $CH_2Cl_2$ (1.0 mL) at 0 °C. After stirring at room temperature for 1 h, the whole mixture was filtered through a pad of Celite, and the filtrate was evaporated in vacuo to furnish the crude product, which was purified by column chromatography (silica gel, 3:1 *n*-hexane/AcOEt) to give benzotriazol **5aa** (14.6 mg, 58%) as a colorless solid: mp 154–156 °C; IR (KBr) *v* 1720, 1607, 1290, 1106, 1060, 765 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 3.99 (s, 3H, $CO_2CH_3$), 7.48 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.61 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.82 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.94 (d, *J* = 8.4 Hz, 2H, Ar*H*), 8.18 (d, *J* = 8.4 Hz, 1H, Ar*H*), 8.30 (d, *J* = 8.4 Hz, 2H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 52.4 ($CH_3$), 110.3 (CH), 120.6 (CH), 121.9 (CH), 124.7 (CH), 128.7 (CH), 129.9 (C), 131.4 (CH), 131.9 (C), 140.5 (C), 146.7 (C), 166.0 (C=O); HRMS (FAB) calcd for $C_{14}H_{11}N_3O_2$ $[M]^+$ 253.0851, found 253.0850.

**3-(*tert*-Butyldimethylsilyloxy)propyl 4-(1*H*-Benzotriazol-1-yl)benzoate (5ab)**




Yield 50% (19.7 mg); purified by column chromatography (silica gel, 4:1 *n*-hexane/$CH_2Cl_2$); a colorless solid; mp 88–90 °C; IR (KBr) *v* 2954, 1718, 1274, 1101, 835 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 0.08 (s, 6H, $SiCH_3$), 0.92 (s, 9H, *t*-Bu), 2.03 (quintet, *J* = 6.4 Hz, 2H, $CH_2CH_2CH_2$), 3.82 (t, *J* = 6.4 Hz, 2H, $CH_2OTBS$), 4.50 (t, *J* = 6.4 Hz, 2H, $CO_2CH_2$), 7.49 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.62 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.83 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.94 (d, *J* = 8.8 Hz, 2H, Ar*H*), 8.19 (d, *J* = 8.0 Hz, 1H, Ar*H*), 8.31 (d, *J* = 8.8 Hz, 2H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ –5.4 ($CH_3$), 18.3 (C), 25.9 ($CH_3$), 31.8 ($CH_2$), 59.4 ($CH_2$), 62.4 ($CH_2$), 110.3 (CH), 120.6 (CH), 122.0 (CH), 124.7 (CH), 128.7 (CH), 130.2 (C), 131.3 (CH), 131.9 (C), 140.5 (C), 146.7 (C), 165.5 (C=O); HRMS (FAB) calcd for $C_{22}H_{30}N_3O_3Si$ $[M+H]^+$ 412.2056, found 412.2050.

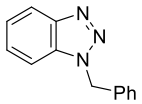
**3-(*p*-Methoxybenzyloxy)propyl 4-(1*H*-Benzotriazol-1-yl)benzoate (5ac)**



**5ac**

Yield 48%; purified by column chromatography (silica gel, 2:1 *n*-hexane/EtOAc); a colorless oil; IR (KBr) *v* 2860, 1718, 1607, 1513, 1274, 1100, 1038 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 2.10 (quintet, *J* = 6.0 Hz, 2H, $CH_2CH_2CH_2$), 3.64 (t, *J* = 6.0 Hz, 2H, $CH_2OPMB$), 3.76 (s, 3H, $OCH_3$), 4.48 (s, 2H, $OCH_2Ar$), 4.50 (t, *J* = 6.0 Hz, 2H, $CO_2CH_2$), 6.86 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.27 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.48 (t, *J* = 8.0 Hz, 1H, Ar*H*), 7.61 (t, *J* = 8.0 Hz, 1H, Ar*H*), 7.82 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.91 (d, *J* = 8.8 Hz, 2H, Ar*H*), 8.18 (d, *J* = 8.0 Hz, 1H, Ar*H*), 8.23 (d, *J* = 8.8 Hz, 2H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 29.1 ($CH_2$), 55.2 ($CH_3$), 62.6 ($CH_2$), 66.1 ($CH_2$), 72.7 ($CH_2$), 110.3 (CH), 113.8 (CH), 120.6 (CH), 121.9 (CH), 124.7 (CH), 128.7 (CH), 129.3 (CH), 130.1 (C), 130.3 (C), 131.3 (CH), 131.9 (C), 140.5 (C), 146.7 (C), 159.2 (C), 165.4 (C=O); HRMS (EI) calcd for $C_{24}H_{23}N_3O_4$ $[M]^+$ 417.1689, found 417,1692.

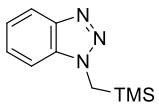
**1-Phenylmethyl-1,2,3-benzotriazol (5ad)**[13]



**5ad**

Yield 56% (11.7 mg); purified by column chromatography (silica gel, 3:1 *n*-hexane/AcOEt); a colorless solid; $^1H$ NMR (300 MHz, $CDCl_3$): δ 5.85 (s, 2H, $NCH_2Ph$), 7.26-7.43 (m, 8H, Ar*H*), 8.07 (dd, *J* = 1.2, 8.7 Hz, 1H, Ar*H*).

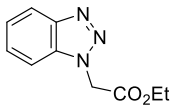
**1-Trimethylsilylmethyl-1,2,3-benzotriazol (5ae)**[14]



**5ae**

Yield 56% (11.6 mg); purified by column chromatography (silica gel, 4:1 *n*-hexane/AcOEt); a colorless solid; $^1H$ NMR (400 MHz, $CDCl_3$): δ 0.21 (s, 9H, $SiCH_3$), 4.04 (s, 2H, $NCH_2TMS$), 7.35 (ddd, *J* = 2.4, 6.0, 8.4 Hz, 1H, Ar*H*), 7.46-7.48 (m, 2H, Ar*H*), 8.04 (d, *J* = 8.4 Hz, 1H, Ar*H*).

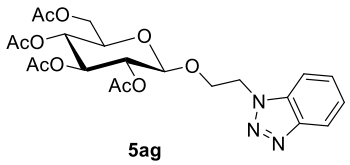
**1-Ethoxycarbonylmethyl-1,2,3-benzotriazol (5af)**[13]



**5af**

Yield 61% (12.5 mg); purified by column chromatography (silica gel, 2:1 *n*-hexane/AcOEt); a colorless solid; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.27 (t, *J* = 7.2 Hz, 3H, $CO_2CH_2CH_3$), 4.26 (q, *J* = 7.2 Hz, 2H, $CO_2CH_2CH_3$), 5.43 (s, 2H, $NCH_2CO_2$), 7.40 (ddd, *J* = 1.5, 6.3, 8.4 Hz, 1H, Ar*H*), 7.46-7.56 (m, 2H, Ar*H*), 8.10 (dt, *J* = 0.9, 8.4 Hz, 1H, Ar*H*).

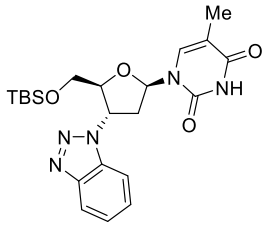
**2-(1*H*-Benzotriazol-1-yl)ethyl 2,3,4,6-Tetra-*O*-acetyl-β-$_D$-glucopyranoside (5ag)**



**5ag**

Yield 58% (28.4 mg); purified by column chromatography (silica gel, 1:1 to 1:2 *n*-hexane/EtOAc); a colorless oil; $[\alpha]_D^{24}$ = −46.8 (*c* 1.01, $CHCl_3$); IR (KBr) *v* 2956, 1753, 1368, 1229, 1041 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.55 (s, 3H, COC*H*$_3$), 1.96 (s, 3H, COC*H*$_3$), 2.01 (s, 3H, COC*H*$_3$), 2.10 (s, 3H, COC*H*$_3$), 3.64-3.68 (m, 1H, H-5), 4.08-4.11 (m, 2H, C*H*$_2$N), 4.22 (dd, *J* = 4.8, 12.4 Hz, 1H, H-6a), 4.38-4.45 (m, 2H, OC*H*H and H-6b), 4.81-4.93 (m, 3H, OCH*H*, H-1 and H-2), 5.04 (t, *J* = 9.2 Hz, 1H, H-3), 5.09 (t, *J* = 9.2 Hz, 1H, H-4), 7.38 (ddd, *J* = 1.2, 6.8, 8.0 Hz, 1H, Ar*H*), 7.50 (ddd, *J* = 1.2, 6.8, 8.0 Hz, 1H, Ar*H*), 7.57 (d, *J* = 8.0 Hz, 1H, Ar*H*), 8.04 (d, *J* = 8.0 Hz, 1H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 20.1 ($CH_3$), 20.4 ($CH_3$), 20.5 ($CH_3$), 20.7 ($CH_3$), 47.9 ($CH_2$), 61.6 ($CH_2$), 68.0 (CH), 68.5 ($CH_2$), 70.7 (CH), 71.9 (CH), 72.6 (CH), 100.5 (CH), 110.1 (CH), 119.6 (CH), 123.9 (CH), 127.6 (CH), 133.9 (C), 145.7 (C), 169.1 (C=O), 169.3 (C=O), 170.1 (C=O), 170.6 (C=O); HRMS (FAB) calcd for $C_{22}H_{27}N_3O_{10}$ $[M]^+$ 493.1696, found 493.1696.

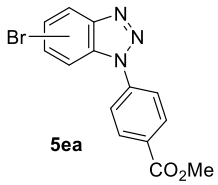
**3'-(1*H*-Benzotriazol-1-yl)-5'-*O*-*tert*-butyldimethylsilyl-3'-deoxythymidine (5ah)**



**5ah**

Yield 58% (26.4 mg); purified by column chromatography (silica gel, 1:2 *n*-hexane/EtOAc); a colorless amorphous; IR (KBr) *v* 2929, 1696, 1470, 1273, 1126 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 0.11 (s, 3H, SiC*H*$_3$), 0.14 (s, 3H, SiC*H*$_3$), 0.96 (s, 9H, *t*-Bu), 2.00 (s, 3H, ArC*H*$_3$), 2.72 (ddd, *J* = 6.0, 8.4, 14.0 Hz, 1H, H-2'a), 3.22 (dt, *J* = 6.0, 14.0 Hz, 1H, H-2'b), 3.79 (dd, *J* = 2.0, 11.6 Hz, 1H, H-5'a), 4.07 (dd, *J* = 2.0, 11.6 Hz, 1H, H-5'b), 4.63-4.64 (m, 1H, H-4'), 5.58 (dt, *J* = 5.2, 8.8 Hz, 1H, H-3'), 6.57 (t, *J* = 6.4 Hz, 1H, H-1'), 7.42 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.53-7.59 (m, 3H, 2×Ar*H* and N-C*H*=C), 8.13 (d, *J* = 8.4 Hz, 1H, Ar*H*), 8.34 (s, 1H, N*H*); $^{13}C$ NMR (400 MHz, $CDCl_3$): δ -5.4 ($CH_3$), -5.3 ($CH_3$), 12.6 ($CH_3$), 18.4 (C), 25.9 ($CH_3$), 38.0 ($CH_2$), 56.9 (CH), 62.3 ($CH_2$), 84.1 (CH), 85.7 (CH), 108.9 (CH), 111.1 (C), 120.4 (CH), 124.4 (CH), 127.8 (CH), 132.7 (C), 135.5 (CH), 146.1 (C), 150.1 (C=O), 163.7 (C=O); HRMS (FAB) calcd for $C_{22}H_{31}N_5O_4Si$ $[M+H]^+$ 458.2218, found 458.2224.

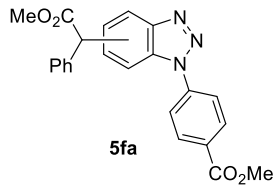
**5-Bromo-1-(4-Methoxycarbonylphenyl)-1,2,3-benzotriazol and 6-Bromo-1-(4-Methoxycarbonylphenyl)-1,2,3-benzotriazol (5ea)**



5ea

Yield 45% (~1:1 mixture of regioisomers, 14.8 mg); purified by column chromatography (silica gel, 6:1 *n*-hexane/EtOAc); a colorless solid; IR (KBr) *v* 1722, 1604, 1514, 1438, 1288, 1112, 1063 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-$d_6$): δ 3.93 (s, 2×3H, $CO_2CH_3$), 7.71 (dd, *J* = 1.6, 8.8 Hz, 1H, Ar*H*), 7.84 (dd, *J* = 1.6, 8.8 Hz, 1H, Ar*H*), 8.03 (d, *J* = 8.8 Hz, 1H, Ar*H*), 8.08-8.12 (m, 4H, Ar*H*), 8.20 (d, *J* = 8.8 Hz, 1H, Ar*H*), 8.23-8.26 (m, 4H, Ar*H*), 8.32 (d, *J* = 1.6 Hz, 1H, Ar*H*), 8.54 (d, *J* = 1.6 Hz, 1H, Ar*H*); HRMS (EI) calcd for $C_{14}H_{10}BrN_3O_2$ $[M]^+$ 330.9956, found 330.9948.

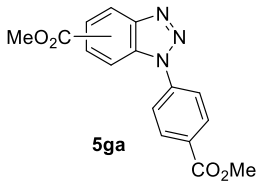
**Methyl 4-[5-(2-Methoxy-2-oxo-1-phenylethyl)-1*H*-benzotriazol-1-yl]benzoate and Methyl 4-[6-(2-Methoxy-2-oxo-1-phenylethyl)-1*H*-benzotriazol-1-yl]benzoate (5fa)**



5fa

Yield 51% (1:0.85 mixture of regioisomers, 19.5 mg); purified by column chromatography (silica gel, 2:1 *n*-hexane/EtOAc and $CH_2Cl_2$ to 10:1 $CH_2Cl_2$/$Et_2O$); a colorless solid; IR (KBr) *v* 1731, 1606, 1516, 1435, 1280, 1162 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 3.78 (s, 3H, $CO_2CH_3$), 3.79 (s, 3H, $CO_2CH_3$), 3.98 (s, 3H, $CO_2CH_3$), 3.99 (s, 3H, $CO_2CH_3$), 5.25 (s, 2×1H, $Ar_2CHCO$) 7.32-7.35 (m, 2×5H, Ar*H*), 7.44 (d, *J* = 8.4 Hz, 1H, Ar*H* for minor product), 7.58 (d, *J* = 8.4 Hz, 1H, Ar*H* for major product), 7.74-7.78 (m, 2×1H, Ar*H*), 7.86-7.91 (m, 2×2H, Ar*H*), 8.09-8.11 (m, 2×1H, Ar*H*), 8.29 (d, *J* = 8.4 Hz, 2×2H, Ar*H*); HRMS (FAB) calcd for $C_{23}H_{19}N_3O_4$ $[M]^+$ 401.1376, found 401.1377.

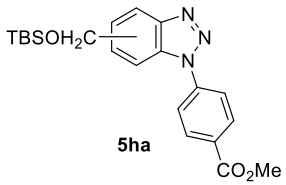
**Methyl 1-(4-Methoxycarbonylphenyl)-1,2,3-benzotriazole-5-carboxylate and Methyl 1-(4-Methoxycarbonylphenyl)-1,2,3-benzotriazole-6-carboxylate (5ga)**



5ga

Yield 58% (1:0.77 mixture of regioisomers, 17.9 mg); purified by column chromatography (silica gel, 3:1 $CH_2Cl_2$ to 20:1 $CH_2Cl_2$/$Et_2O$); a colorless solid; $^1H$ NMR (400 MHz, $CDCl_3$): δ 4.00-4.01 (s, 2 × 3H, $CO_2CH_3$ for major product and s, 2×3H, $CO_2CH_3$ for minor product), 7.84 (d, *J* = 8.8 Hz, 1H, Ar*H* for minor product), 7.92-7.96 (m, 2H, Ar*H* for major product and 2H, Ar*H* for minor product), 8.15 (d, *J* = 8.8 Hz, 1H, Ar*H* for major product), 8.22 (d, *J* = 8.8 Hz, 1H, Ar*H* for major product), 8.29-8.35 (m, 2H, Ar*H* for major product and 3H, Ar*H* for minor product), 8.53 (s, 1H, Ar*H* for major product), 8.90 (s, 1H, Ar*H* for minor product); HRMS (EI) calcd for $C_{16}H_{13}N_3O_4$ $[M]^+$ 311.0906, found 311.0910.

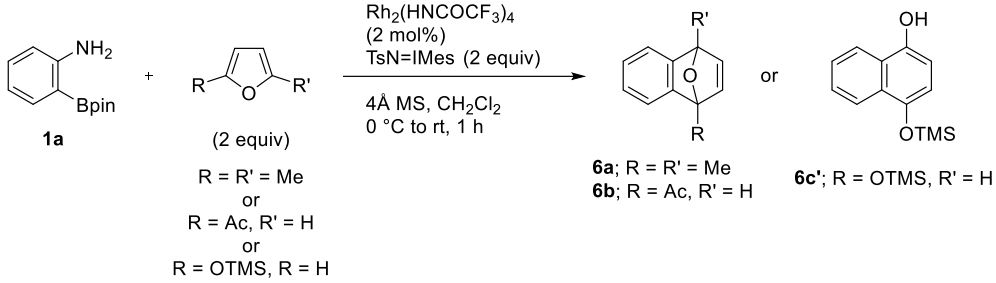
**5-(*tert*-Butyldimethylsilyloxymethyl)-1-(4-methoxycarbonylphenyl)-1,2,3-benzotriazol and 6-(*tert*-Butyldimethylsilyloxymethyl)-1-(4-Methoxycarbonylphenyl)-1,2,3-benzotriazol (5ha)**



**5ha**

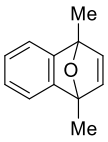
Yield 42% (1:0.80 mixture of regioisomers, 16.8 mg); purified by column chromatography (silica gel, 6:1 *n*-hexane/EtOAc); a colorless oil; IR (KBr) *v* 2953, 1718, 1607, 1515, 1437, 1278, 1103, 851 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 0.14 (s, 6H, SiC*H*$_3$ for major product), 0.15 (s, 6H, SiC*H*$_3$ for minor product), 0.97 (s, 9H, *t*-Bu for minor product), 0.98 (s, 9H, *t*-Bu for major product), 3.99 (s, 3H, $CO_2CH_3$ for minor product and 3H, $CO_2CH_3$ for major product), 4.93 (s, 2H, OC*H*$_2$Ar for minor product), 4.94 (s, 2H, OC*H*$_2$Ar for major product), 7.36 (d, *J* = 8.4 Hz, 1H, Ar*H* for major product), 7.57 (d, *J* = 8.4 Hz, 1H, Ar*H* for minor product), 7.77 (d, *J* = 8.4 Hz, 1H, Ar*H* for minor product), 7.85 (s, 1H, Ar*H* for major product), 7.93-7.96 (m, 2H, Ar*H* for major product and 2H, Ar*H* for minor product), 8.09 (d, *J* = 8.4 Hz, 1H, Ar*H* for major product), 8.13 (s, 1H, Ar*H* for minor product), 8.28-8.30 (m, 2H, Ar*H* for major product and 2H, Ar*H* for minor product); HRMS (FAB) calcd for $C_{21}H_{27}N_3O_3Si$ $[M]^+$ 397.1822, found 397.1826.

**7. Typical procedure for the one-pot benzyne generation/cycloaddition with furans**.




TsN=IMes (83.1 mg, 0.200 mmol) was added to a stirred mixture of 2-aminophenylboronic acid pinacol ester (**1a**) (21.9 mg, 0.100 mmol), furan (0.200 mmol), $Rh_2(HNCOCF_3)_4$ (1.5 mg, 0.002 mmol, 2 mol %) and 4Å MS (powder, 40 mg) in $CH_2Cl_2$ (1.0 mL) at 0 °C. After stirring at room temperature for 1 h, the whole mixture was filtered through a pad of Celite, and the filtrate was evaporated in vacuo to furnish the crude product, which was purified by column chromatography to give cycloadduct **6**.

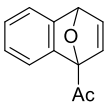
**1,4-Dimethyl-1,4-dihydro-1,4-epoxynaphthalene (6a)**[15]



**6a**

Yield 52% (8.9 mg); purified by column chromatography (silica gel, 10:1 *n*-hexane/EtOAc); a colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): δ 1.89 (s, 6H, C*H*$_3$), 6.77 (s, 2H, C*H*=C*H*), 6.97 (dd, *J* = 3.0, 5.1 Hz, 2H, Ar*H*), 7.13 (dd, *J* = 3.0, 5.1 Hz, 2H, Ar*H*).

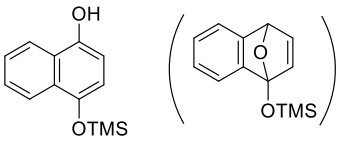
**1-Acetyl-1,4-dihydro-1,4-epoxynaphthalene (6b)**[16]



**6b**

Yield 46% (8.6 mg); purified by column chromatography (silica gel, 10:1 *n*-hexane/EtOAc); a colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H, COC*H*$_3$), 5.80 (d, *J* = 1.8 Hz, 1H, C*H*-CH=CH), 6.98-7.07 (m, 4H, C*H*=C*H*, ArH), 7.24-7.29 (m, 2H, Ar*H*).

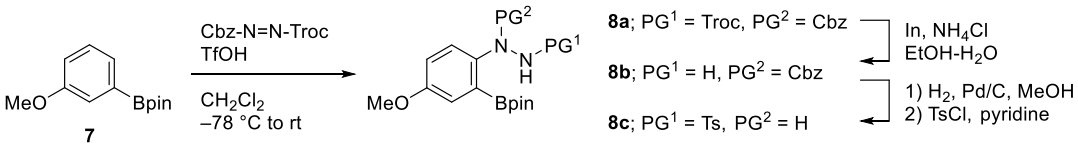
**4-(Trimethylsilyloxy)naphthalene-1-ol (6c')**



**6c'**; 31% **6c**; ND

Yield 31% (7.3 mg); purified by column chromatography (silica gel, 10:1 *n*-hexane/EtOAc); a colorless oil; IR (KBr) *ν* 3385, 2959, 1595, 1471, 1071 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 0.31 (s, 9H, SiC*H*$_3$), 4.95 (brs, 1H, O*H*), 6.91 (dd, *J* = 4.0, 8.8 Hz, 2H, Ar*H*), 7.49 (ddd, *J* = 0.8, 4.0, 8.8 Hz, 2H, Ar*H*), 8.07–8.11 (m, 2H, Ar*H*); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 0.3 ($CH_3$), 108.3 (CH), 112.4 (CH), 121.5 (CH), 122.7 (CH), 125.3 (C), 125.6 (CH), 125.7 (CH), 128.5 (C), 145.2 (C), 145.6 (C); HRMS (EI) calcd for $C_{13}H_{16}O_2Si$ $[M]^+$ 232.0920, found 232.0918.

**8. Procedure for the preparation of 5-methoxy-2-(2-tosylhydrazineyl)phenylboronic acid pinacol ester (8c)**.




To a solution of **7** (375 mg, 1.60 mmol) and 2,2,2-trichloroethyl benzyl azodicarboxylate[17] (652 mg, 1.92 mmol) in $CH_2Cl_2$ (8.0 mL) was added TfOH (14 μL, 0.160 mmol) at –78 °C, and the mixture was allowed to warm to room temperature. After stirring for 6 h, the reaction was quenched with saturated aqueous $NH_4Cl$, and the mixture was extracted with $CH_2Cl_2$. The combined organic extracts were dried over anhydrous $Na_2SO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 4:1 *n*-hexane/EtOAc) to give hydrazine **8a** (1:0.32

mixture of diastereoisomers, 829 mg, 90%,) as a colorless amorphous: IR (KBr) *v* 3386, 2978, 1735, 1344, 1218, 1048 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.27 (s, 12H, OC($CH_3$)$_2$ for minor isomer), 1.29 (s, 12H, OC($CH_3$)$_2$ for major isomer), 3.78 (s, 3H, O$CH_3$), 4.74 (s, 2H, O$CH_2$Ph for major isomer), 4.85 (s, 2H, O$CH_2$Ph for minor isomer), 5.11 (s, 2H, O$CH_2CCl_3$ for minor isomer), 5.15 (s, 2H, O$CH_2CCl_3$ for major isomer), 7.05 (dd, *J* = 2.8, 8.8 Hz, 1H, Ar*H*), 7.16 (d, *J* = 2.8 Hz, 1H, Ar*H*), 7.32-7.38 (m, 6H, Ar*H*), 8.94 (brs, 1H, N*H*); HRMS (EI) calcd for $C_{24}H_{28}BCl_3N_2O_7$ $[M]^+$ 572.1055, found 572.1056.

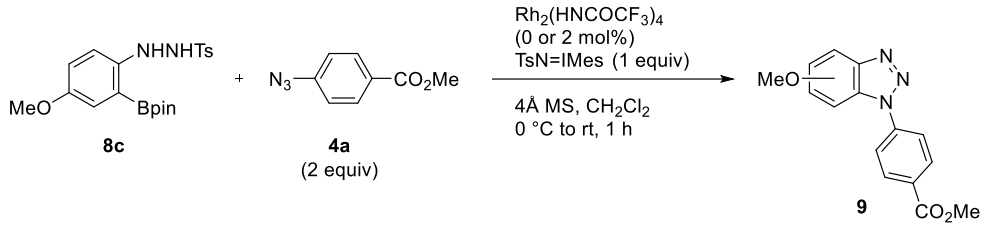
To a solution of **8a** (760 mg, 1.32 mmol) and $NH_4Cl$ (213 mg, 3.97 mmol) in EtOH-$H_2O$ (3:2, 6.7 mL) was added In (powder, 304 mg, 2.65 mmol) at 60 °C. After stirring at the same temperature for 6 h, the whole mixture was filtered through a pad of Celite, and the Celite filter cake was washed with $CH_2Cl_2$. The filtrate was extracted with $CH_2Cl_2$ and the combined organic extracts were dried over anhydrous $Na_2SO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 3:1 *n*-hexane/EtOAc) to hydrazine **8b** (315 mg, 60%) as a brown oil: IR (KBr) *v* 3352, 2978, 1732, 1418, 1349, 1214, 1142, 1058 $cm^{-1}$; $^1H$ NMR (300 MHz, $CD_3OD$, 60 °C): δ 1.34 (s, 12H, OCH(C$H_3$)$_2$), 3.74 (s, 3H, O$CH_3$), 5.11 (s, 2H, O$CH_2$Ph), 6.79 (d, *J* = 9.0 Hz, 1H, Ar*H*), 6.93 (dd, *J* = 3.0, 9.0 Hz, 1H, Ar*H*), 7.17 (d, *J* = 3.0 Hz, 1H, Ar*H*), 7.26-7.36 (m, 5H, Ar*H*); $^{13}C$ NMR (100 MHz, $CD_3OD$, 60 °C): δ 25.1 ($CH_3$), 56.3 ($CH_3$), 68.0 ($CH_2$), 85.4 (C), 114.6 (CH), 120.6 (CH), 121.5 (CH), 128.0 (CH), 128.8 (C), 129.1 (CH), 129.3 (C), 129.42 (C), 129.43 (CH), 154.5 (C=O) (*C*-B was not detected.); HRMS (EI) calcd for $C_{21}H_{27}BN_2O_5$ $[M]^+$ 398.2013, found 398.2019.

A solution of **8b** (84.4 mg, 0.212 mmol) and Pd/C (9.0 mg) in MeOH (2.2 mL) was stirred under hydrogen at an atmospheric pressure at room temperature for 3 h. The reaction mixture was then filtered through a pad of Celite, and the Celite filter cake was washed with $CH_2Cl_2$-MeOH. The filtrate was concentrated in vacuo, and the residue was used witout further purification.

To a solution of the crude product in pyridine (0.50 mL), TsCl (100 mg, 0.530 mmol) was added at 0 °C. After stirring at room temperature for 2 h, the reaction was quenched with water, and the mixture was extracted with $CH_2Cl_2$. The combined organic extracts were dried over anhydrous $Na_2SO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 3:1 to 2:1 *n*-hexane/EtOAc) to *N*-tosylhydrazine **8c** (30.8 mg, 35%) as a baige solid: IR (KBr) *v* 3344, 2978, 1466, 1423, 1308, 1167 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.26 (s, 12H, OC($CH_3$)$_2$), 2.41 (s, 3H, Ar$CH_3$), 3.73 (s, 3H, O$CH_3$), 6.26 (s, 1H, N*H*), 6.82 (dd, *J* = 2.8, 8.8 Hz, 1H, Ar*H*), 6.96 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.0 (d, *J* = 2.8 Hz, 1H, Ar*H*), 7.22 (s, 1H, N*H*), 7.26 (d,

*J* = 8.8 Hz, 2H, Ar*H*), 7.77 (d, *J* = 8.8 Hz, 2H, Ar*H*); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 21.5 ($CH_3$), 24.7 ($CH_3$), 55.8 ($CH_3$), 83.9 (C), 114.5 (CH), 119.6 (CH), 119.9 (CH), 128.2 (CH), 129.5 (CH), 135.1 (C), 144.0 (C), 147.1 (C), 153.0 (C) (*C*-B was not detected.); HRMS (EI) calcd for $C_{20}H_{27}BN_2O_5S$ $[M]^+$ 418.1734, found 418.1743.

**9. Procedure for the cycloaddition of *N*-tosylhydrazine 8c with methyl 4-azidobenzoate (4a)**.




TsN=IMes (30.7 mg, 0.0736 mmol) was added to a stirred mixture of *N*-tosylhydrazine **8c** (30.8 mg, 0.0736 mmol), methyl 4-azidobenzoate (26.2 mg, 0.148 mmol), $Rh_2(HNCOCF_3)_4$ (1.0 mg, 0.0015 mmol, 2 mol %) and 4Å MS (powder, 40 mg) in $CH_2Cl_2$ (1.0 mL) at 0 °C. After stirring at room temperature for 1 h, the whole mixture was filtered through a pad of Celite, and the filtrate was evaporated in vacuo to furnish the crude product, which was purified by column chromatography (silica gel, 2:1 *n*-hexane/AcOEt) to give benzotriazol **9** (1:0.87 mixture of regioisomers, 12.3 mg, 59%) as a colorless solid: IR (KBr) *v* 3422, 2958, 1720, 1607, 1495, 1436, 1280, 1115 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 3.92 (s, 3H, OC*H*$_3$ for minor isomer), 3.94 (s, 3H, OC*H*$_3$ for major isomer), 3.99 (s, 3H, $CO_2CH_3$ for minor isomer), 3.99 (s, 3H, $CO_2CH_3$ for major isomer), 7.07-7.11 (m, Ar*H*, 1H for major isomer and 1H for minor isomer), 7.26 (dd, *J* = 2.4, 8.8 Hz, 1H, Ar*H* for minor isomer), 7.48 (d, *J* = 2.4 Hz, 1H, Ar*H* for major isomer), 7.68 (d, *J* = 8.8 Hz, 1H, Ar*H* for major isomer), 7.88-7.93 (m, 2H, Ar*H*), 8.01 (d, *J* = 8.8 Hz, 1H, Ar*H* for minor isomer), 8.27-8.30 (m, 2H, Ar*H*); HRMS (EI) calcd for $C_{15}H_{13}N_3O_3$ $[M]^+$ 283.0957, found 283.0960.

**References**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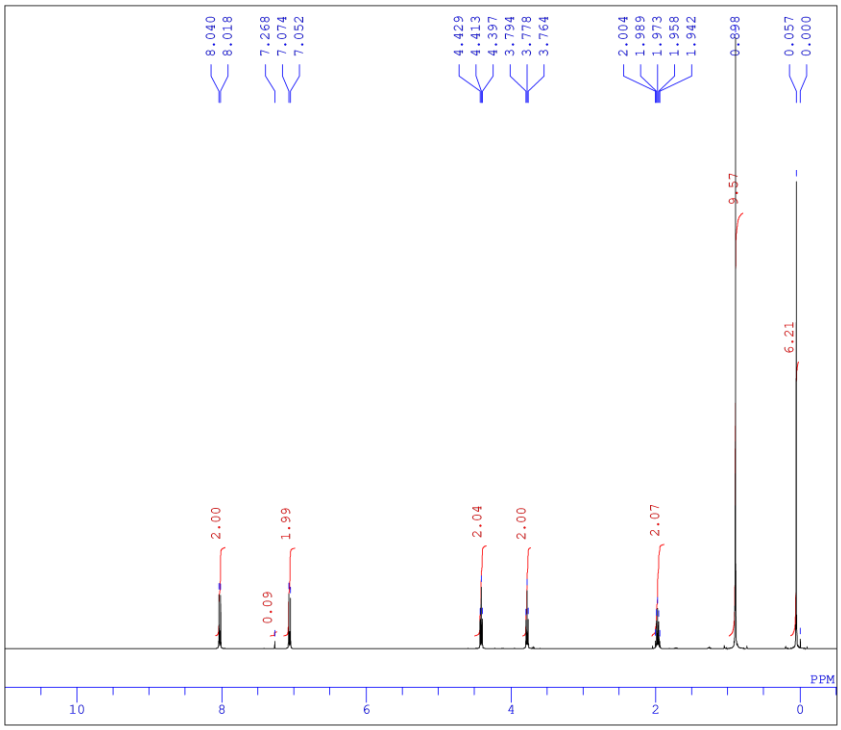
# 3-(*tert*-Butyldimethylsilyloxy)propyl 4-Azidobenzoate (4b)

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OBFIN          7.29 Hz
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PD            5.0000 sec
PW1             3.35 usec
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CTEMP          21.4 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.21 Hz
RGAIN            22
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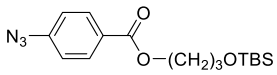
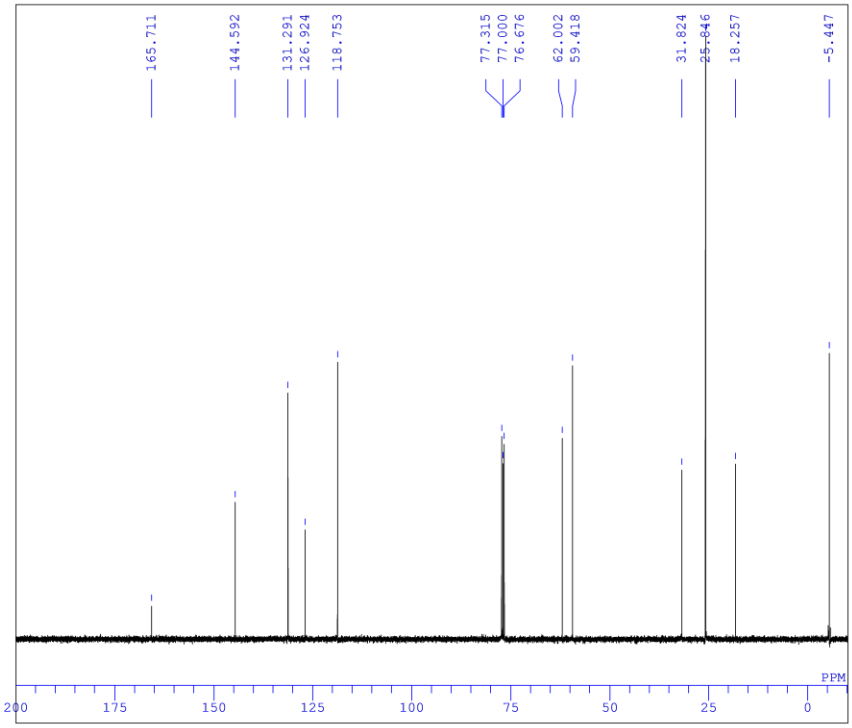



**4b**

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OBFIN          5.86 Hz
POINT         26214
FREQU      25125.63 Hz
SCANS           256
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PD            2.0000 sec
PW1             3.60 usec
IRNUC  1H
CTEMP          21.4 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.21 Hz
RGAIN            60
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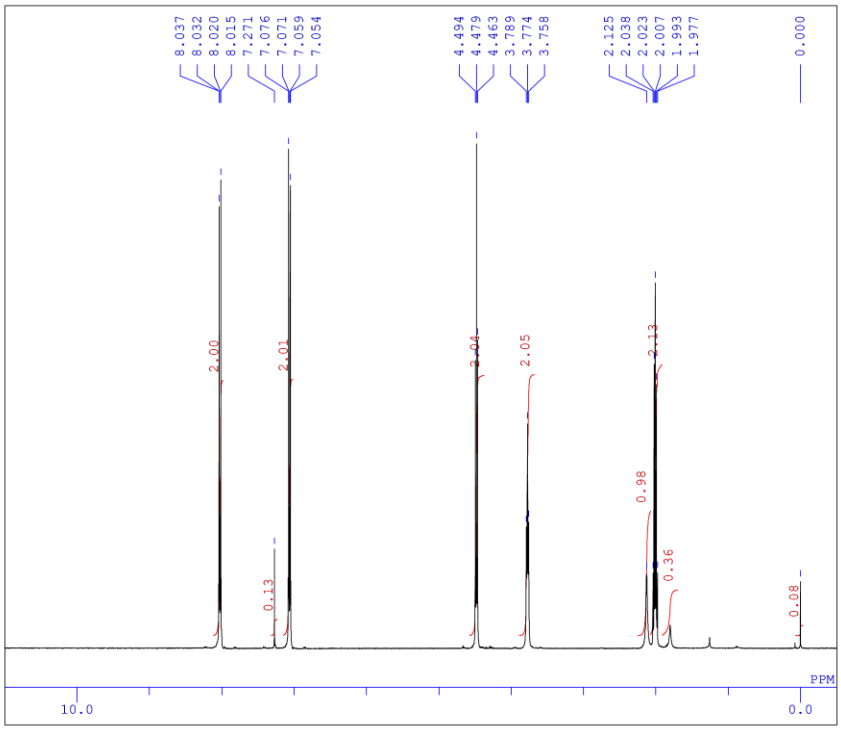
# 3-Hydroxypropyl 4-Azidobenzoate (4c')

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COMNT
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EXMOD  NON
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OBSET        124.00 KHz
OBFIN      10500.00 Hz
POINT        16384
FREQU       7992.01 Hz
SCANS            8
ACQTM        2.0500 sec
PD           4.9500 sec
PW1            5.80 usec
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CTEMP          24.2 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            18
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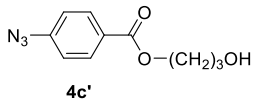
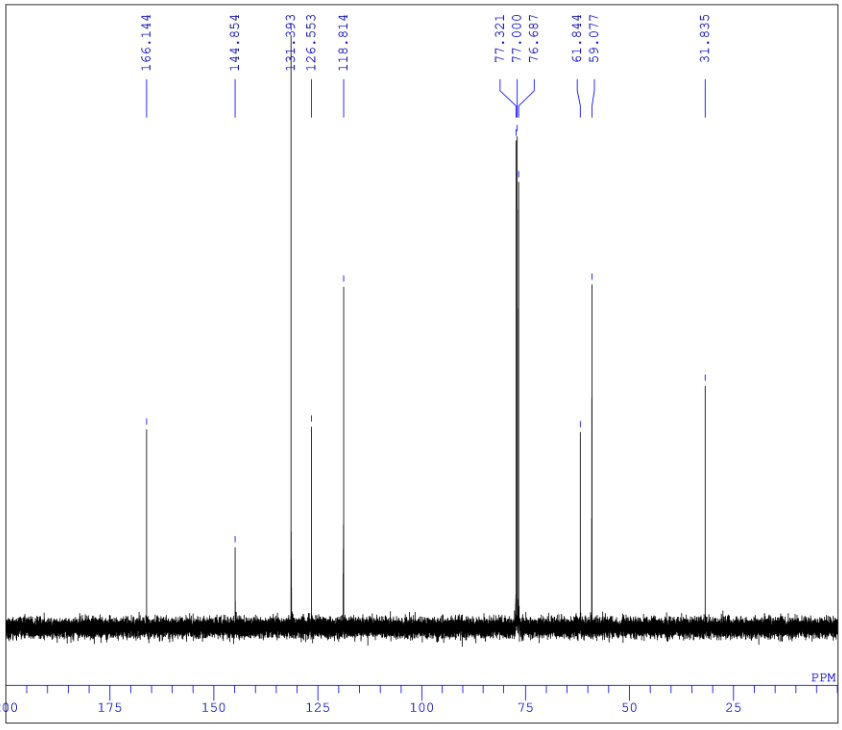



**4c'**

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OBSET        125.00 KHz
OBFIN      10500.00 Hz
POINT        32768
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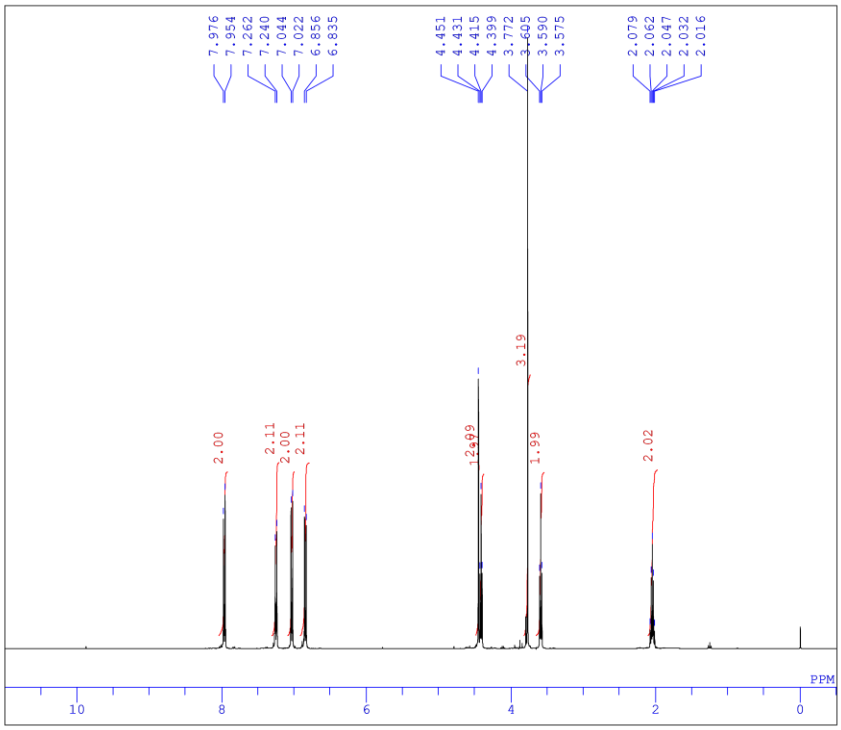
SCANS          256
ACQTM          1.2083 sec
PD             1.7920 sec
PW1            5.80 usec
IRNUC  1H
CTEMP          24.4 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.09 Hz
RGAIN            25
```

# 3-(*p*-Methoxybenzyloxy)propyl 4-Azidobenzoate (4c)

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FREQU       6002.40 Hz
SCANS             8
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PD            5.0000 sec
PW1             3.35 usec
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BF             0.21 Hz
RGAIN            24
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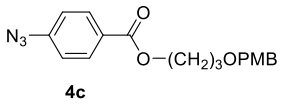
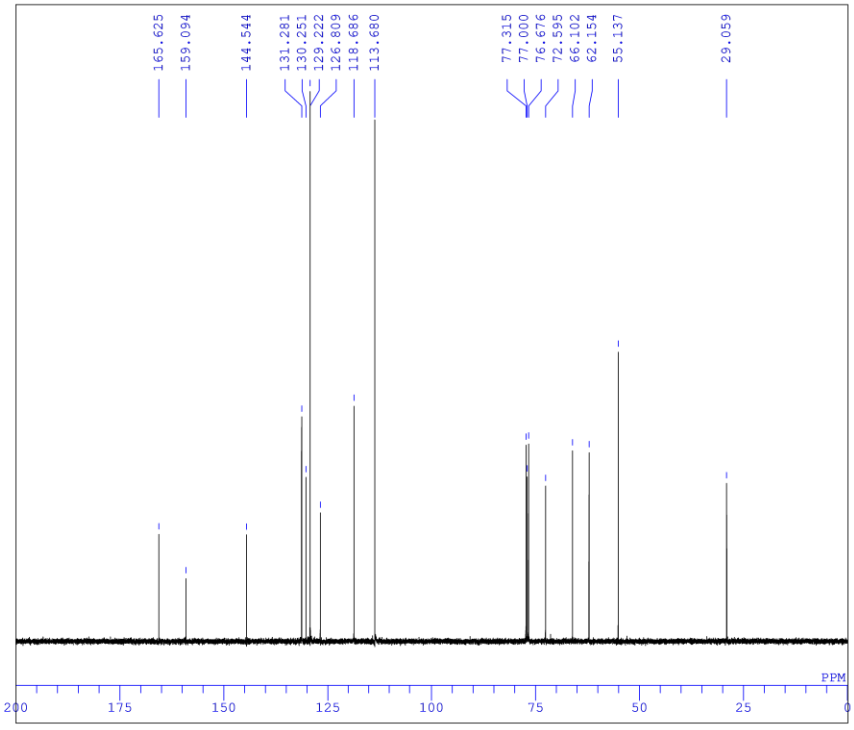



**4c**

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OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26214
FREQU      25125.63 Hz
SCANS           256
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.60 usec
IRNUC  1H
CTEMP          21.7 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.21 Hz
RGAIN            60
```
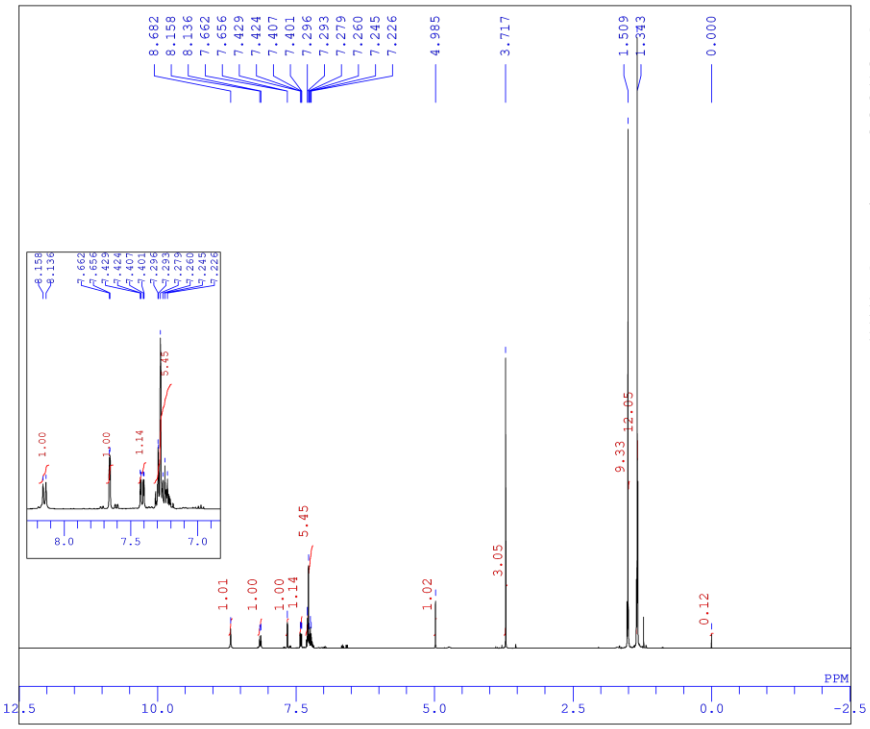

**2-tert-Butoxycarbonylamino-5-(2-methoxy-2-oxo-1-phenylethyl)phenylboronic Acid Pinacol Ester (1f')**

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DATIM 2019-05-23 11:37:28
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OBFIN 7.29 Hz
POINT 26214
FREQU 6002.40 Hz
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PD 5.0000 sec
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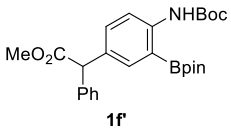
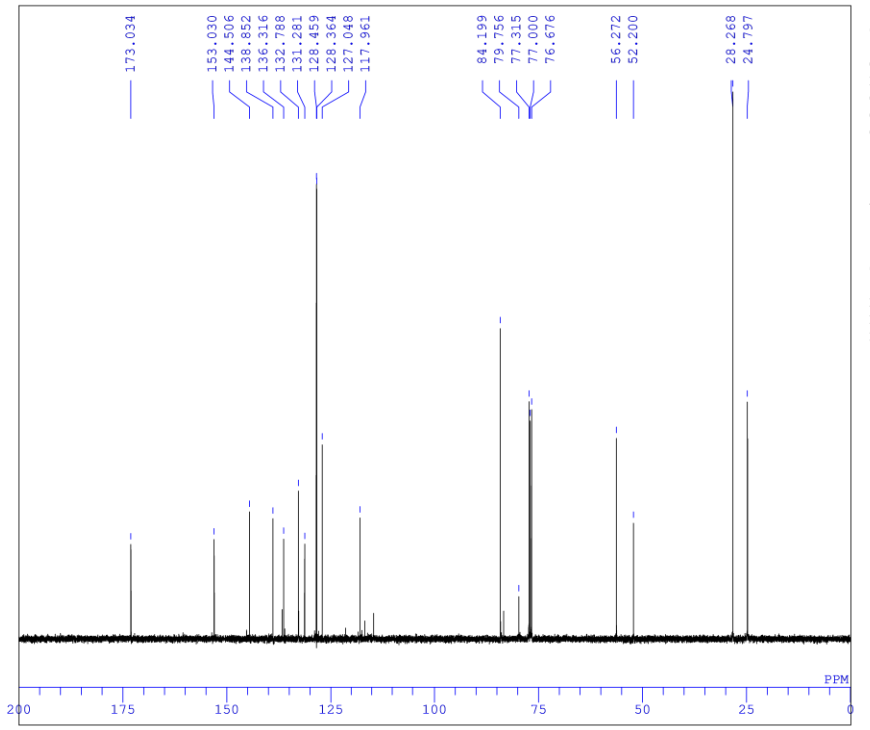
EXREF 0.00 ppm
BF 0.01 Hz
RGAIN 22




**1f'**

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OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
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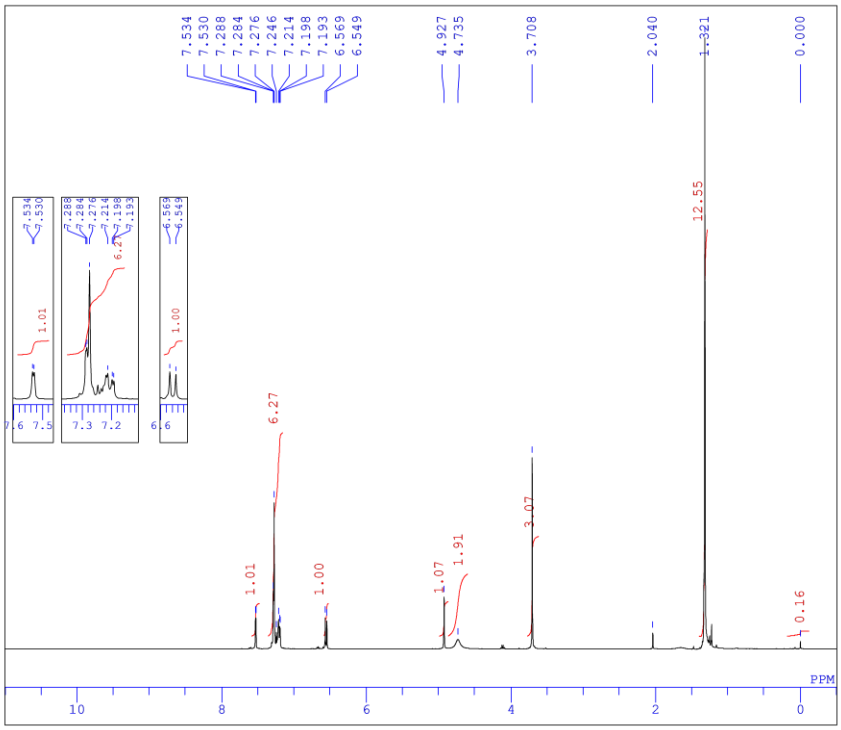
PD 2.0000 sec
PW1 3.60 usec
IRNUC 1H
CTEMP 21.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.21 Hz
RGAIN 60

# 2-Amino-5-(2-methoxy-2-oxo-1-phenylethyl)phenylboronic Acid Pinacol Ester (1f)

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EXMOD  NON
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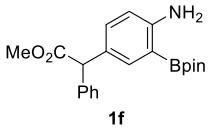
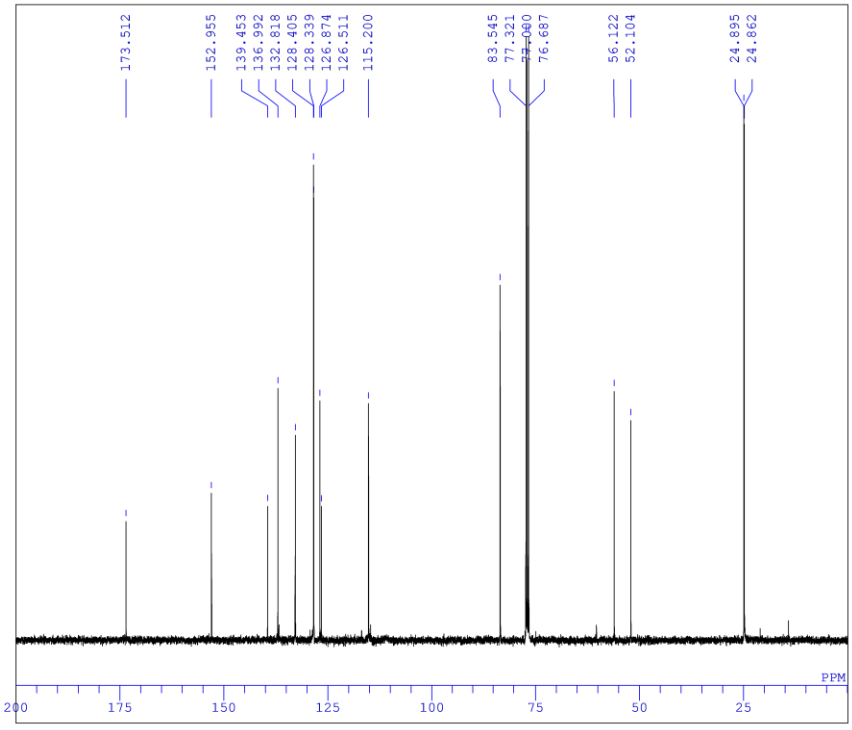
OBFIN      10500.00 Hz
POINT        16384
FREQU       7992.01 Hz
SCANS            8
ACQTM        2.0500 sec
PD           4.9500 sec
PW1            6.20 usec
IRNUC  1H
CTEMP          23.6 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             1.20 Hz
RGAIN            13
```




**1f**

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OBNUC  13C
EXMOD  BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN      10500.00 Hz
POINT        32768
FREQU      27118.64 Hz
SCANS         1024
ACQTM        1.2083 sec
PD           1.7920 sec
PW1            6.20 usec
IRNUC  1H
CTEMP          24.5 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            25
```
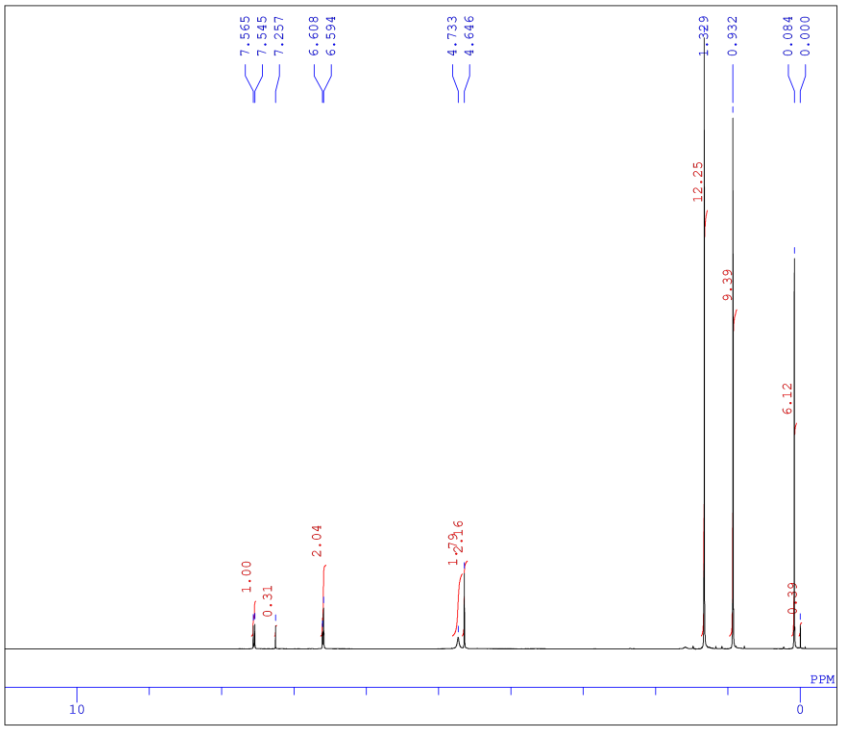

# 2-Amino-4-(*tert*-butyldimethylsilyloxymethyl)phenylboronic Acid Pinacol Ester (1h)

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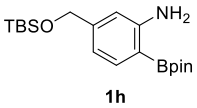
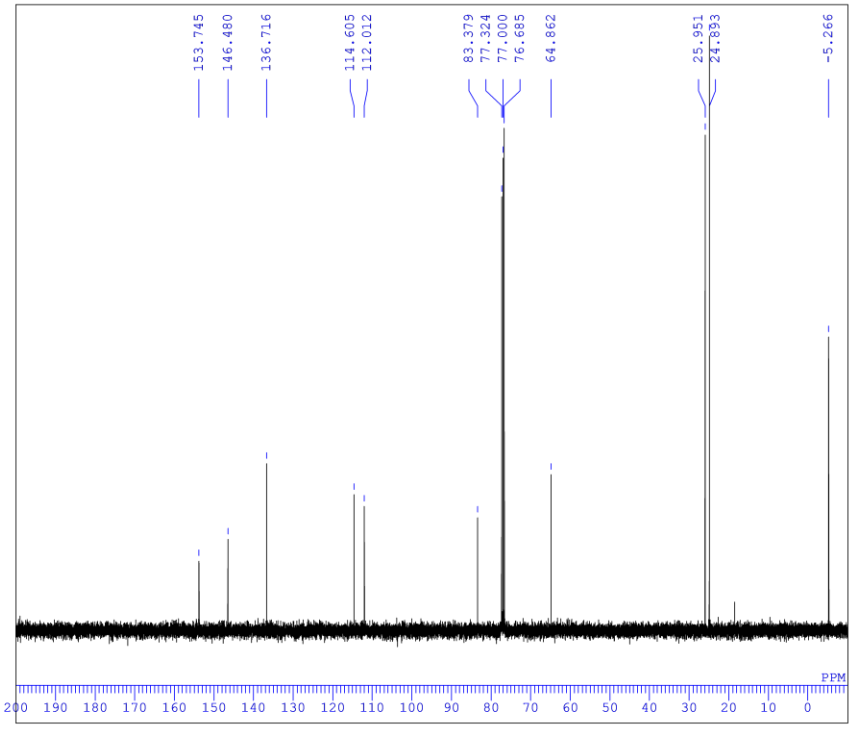
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         26214
FREQU       6002.40 Hz
SCANS             8
ACQTM         4.3673 sec
PD            5.0000 sec
PW1             3.35 usec
IRNUC  1H
CTEMP          20.7 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            30
```




**1h**

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OBNUC  13C
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OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26214
FREQU      25125.63 Hz
SCANS           200
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.60 usec
IRNUC  1H
CTEMP          20.7 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            60
```
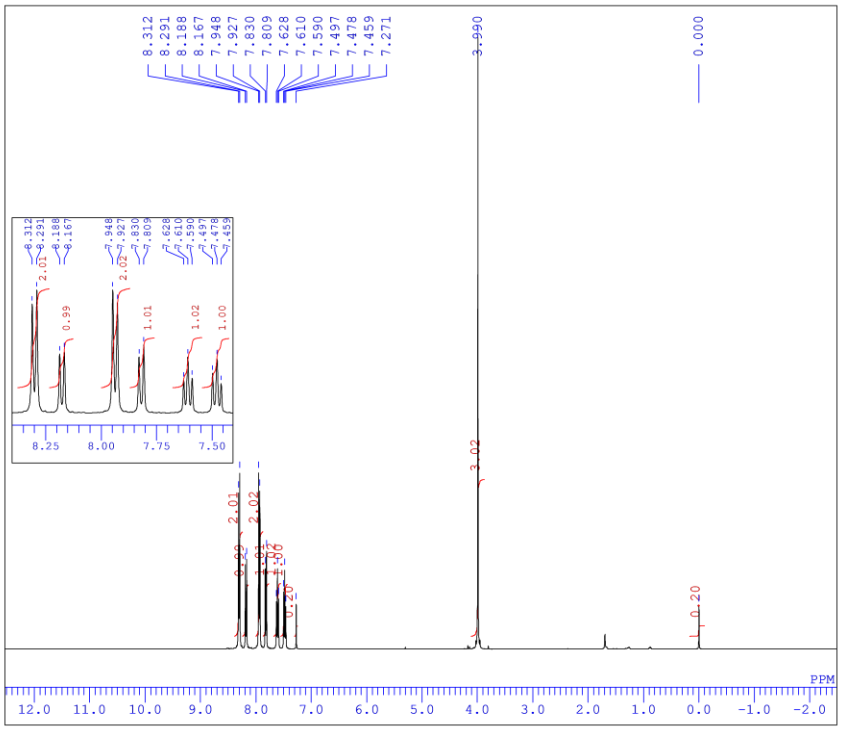

# 1-(4-Methoxycarbonylphenyl)-1,2,3-benzotriazol (5aa)

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EXMOD  single_pulse.jxp
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OBFIN          7.29 Hz
POINT         26214
FREQU       6002.40 Hz
SCANS            16
ACQTM         4.3673 sec
PD            5.0000 sec
PW1           3.35 usec
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CTEMP          20.9 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             1.20 Hz
RGAIN            40
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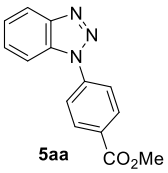


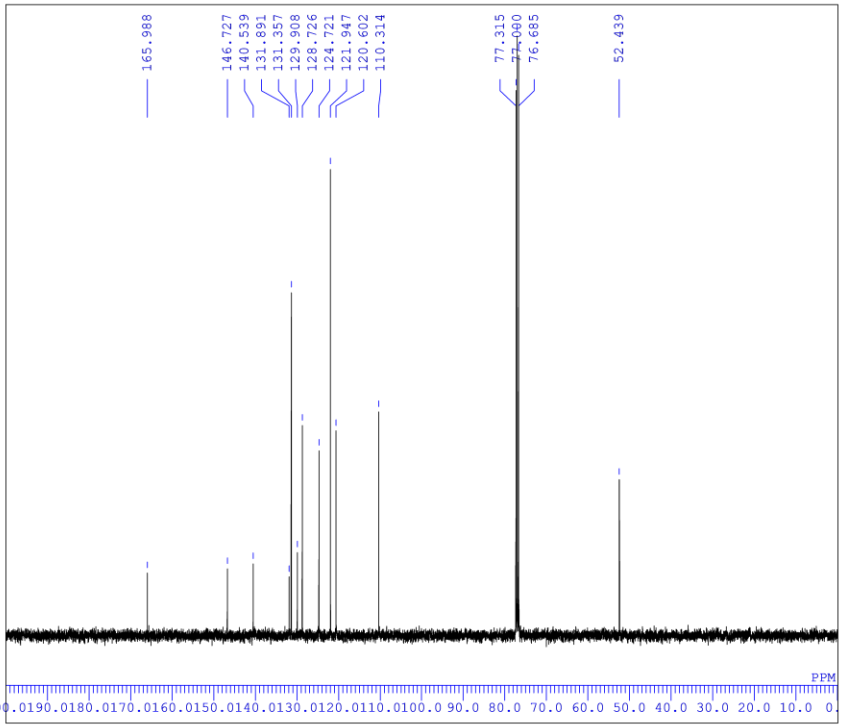


```
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EXMOD  single_pulse_dec
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OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26214
FREQU       25125.63 Hz
SCANS            256
ACQTM         1.0433 sec
PD            2.0000 sec
PW1           3.60 usec
IRNUC  1H
CTEMP          22.2 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            60
```
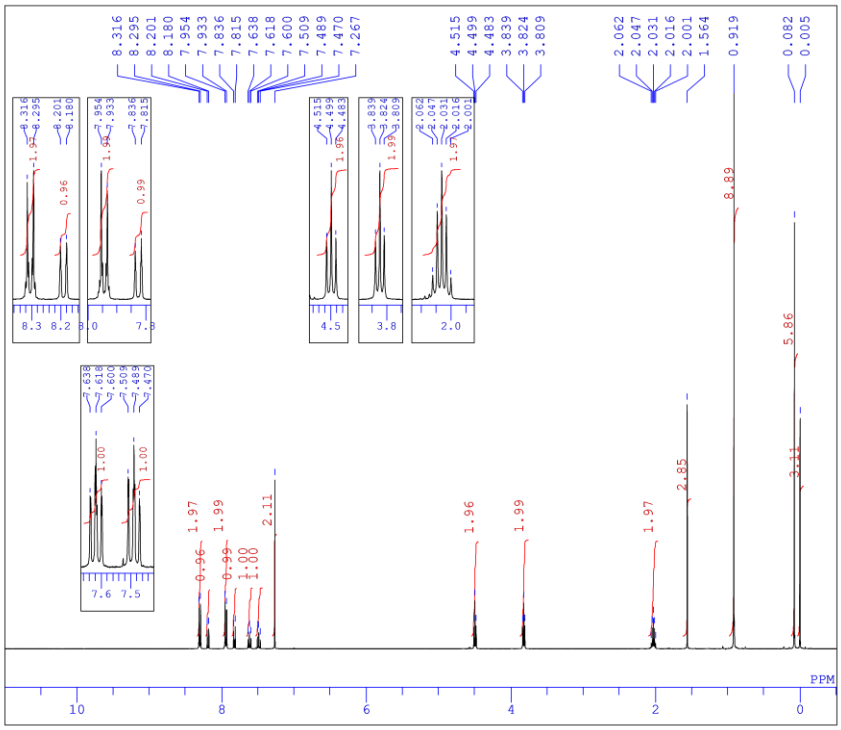
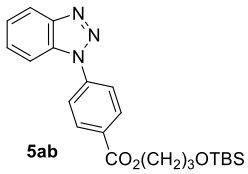
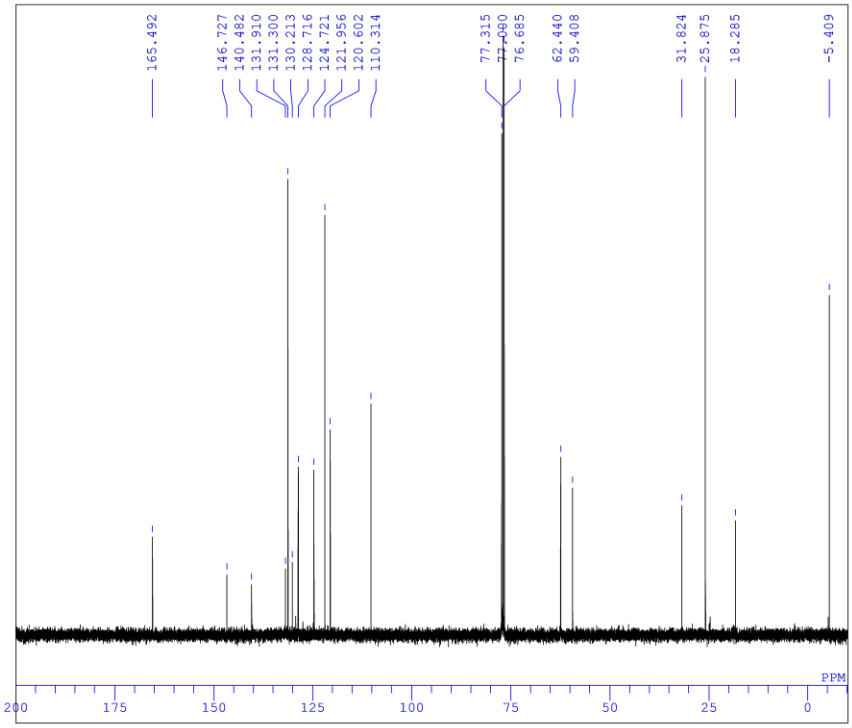

# 3-(*tert*-Butyldimethylsilyloxy)propyl 4-(1*H*-Benzotriazol-1-yl)benzoate (5ab)



```
DFILE  190930 1-[4-TBSO(CH
COMNT  single_pulse
DATIM  2019-09-30 11:15:51
OBNUC  1H
EXMOD  single_pulse.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         26214
FREQU       6002.40 Hz
SCANS            16
ACQTM         4.3673 sec
PD            5.0000 sec
PW1           3.35 usec
IRNUC  1H
CTEMP          22.2 c
SLVNT  CDCL3
EXREF          7.27 ppm
BF             0.12 Hz
RGAIN            48
```

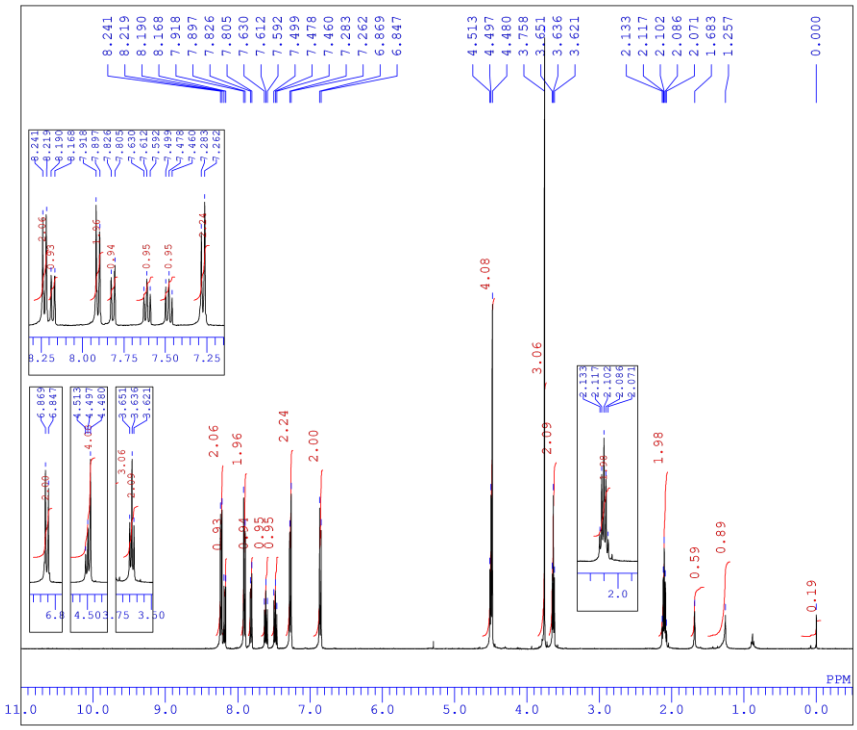


**5ab**

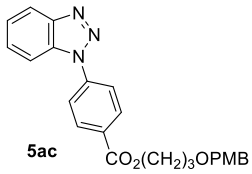


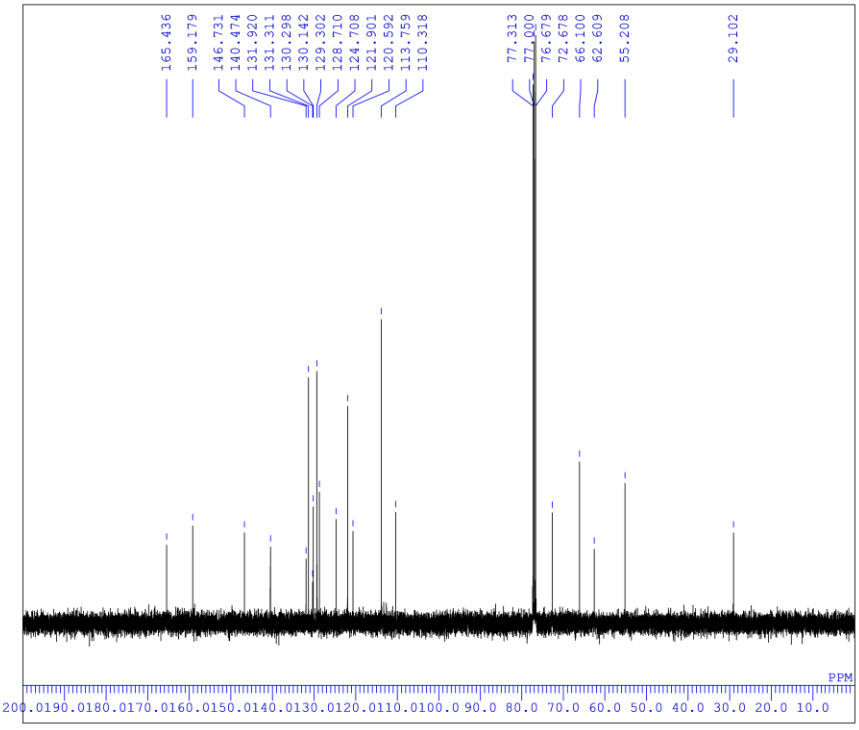
```
DFILE  1-(4-TBSOCH2CH2CH2C
COMNT  single pulse decoup
DATIM  2018-12-26 09:32:40
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26214
FREQU      25125.63 Hz
SCANS            640
ACQTM          1.0433 sec
PD             2.0000 sec
PW1            3.60 usec
IRNUC  1H
CTEMP          21.5 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.09 Hz
RGAIN            60
```

## 3-(*p*-Methoxybenzyloxy)propyl 4-(1*H*-Benzotriazol-1-yl)benzoate (5ac)



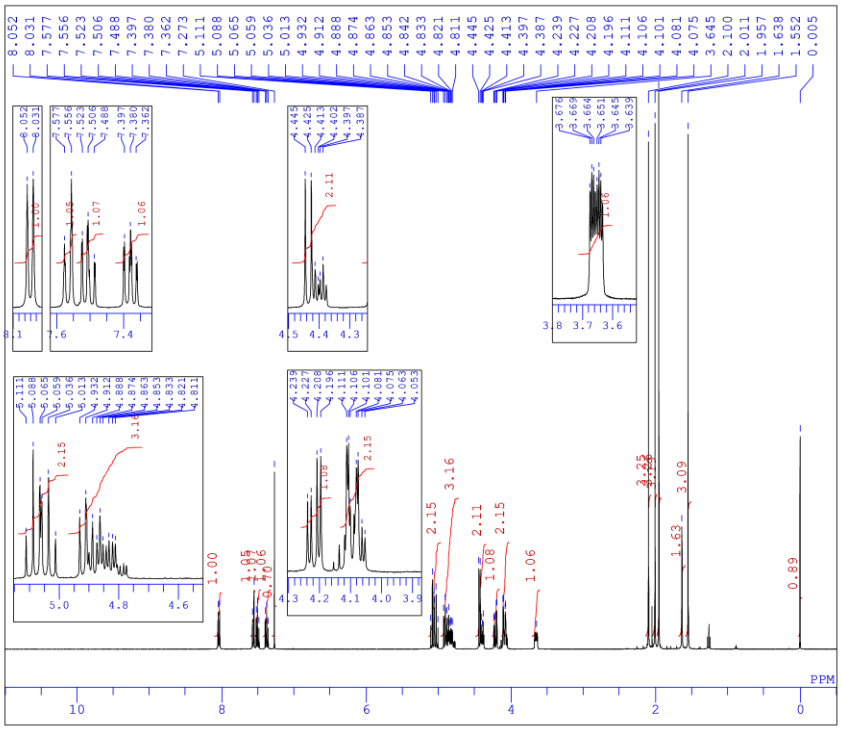
```
DFILE  1-(4-PMBO(CH2)3O2CC
COMNT
DATIM  Thu May 30 11:12:32
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN      10500.00 Hz
POINT        16384
FREQU       7992.01 Hz
SCANS            8
ACQTM        2.0500 sec
PD           4.9500 sec
PW1            5.80 usec
IRNUC  1H
CTEMP          25.0 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            19
```



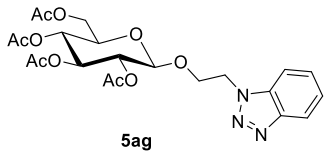



```
DFILE  1-(4-PMBO(CH2)3O2CC
COMNT
DATIM  Thu May 30 11:28:00
OBNUC  13C
EXMOD  BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN      10500.00 Hz
POINT        32768
FREQU      27118.64 Hz
SCANS            256
ACQTM          1.2083 sec
PD             1.7920 sec
PW1            5.80 usec
IRNUC  1H
CTEMP          24.8 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            25
```

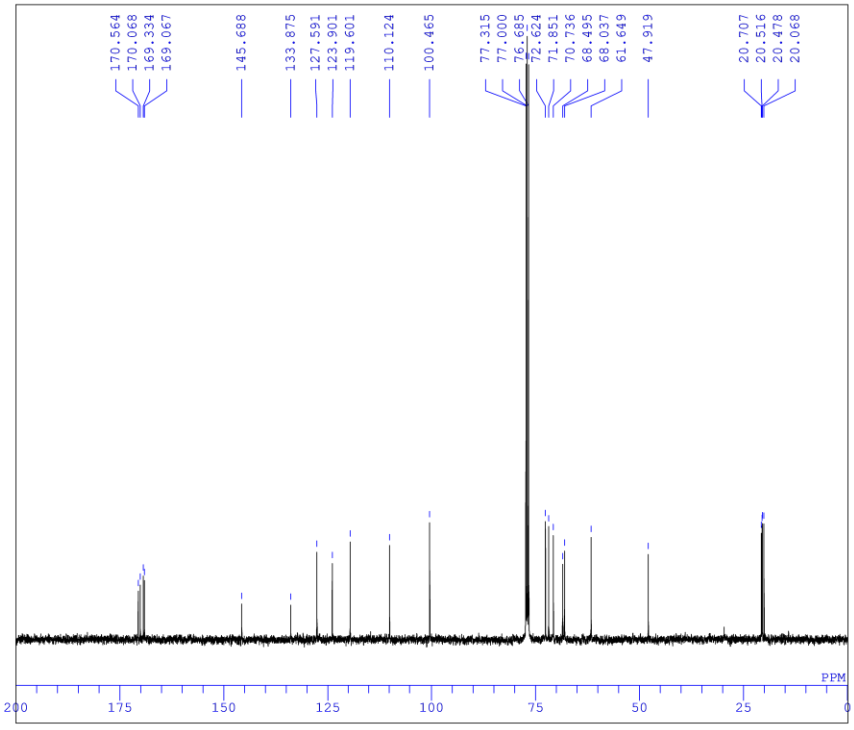
# 2-(1*H*-Benzotriazol-1-yl)ethyl 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranoside (5ag)



```
DFILE  190930Glc+benzyne__
COMNT  single_pulse
DATIM  2019-09-30 11:23:02
OBNUC  1H
EXMOD  single_pulse.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         26214
FREQU       6002.40 Hz
SCANS            16
ACQTM         4.3673 sec
PD            5.0000 sec
PW1              3.35 usec
IRNUC  1H
CTEMP          22.4 c
SLVNT  CDCL3
EXREF          7.27 ppm
BF             0.09 Hz
RGAIN            42
```

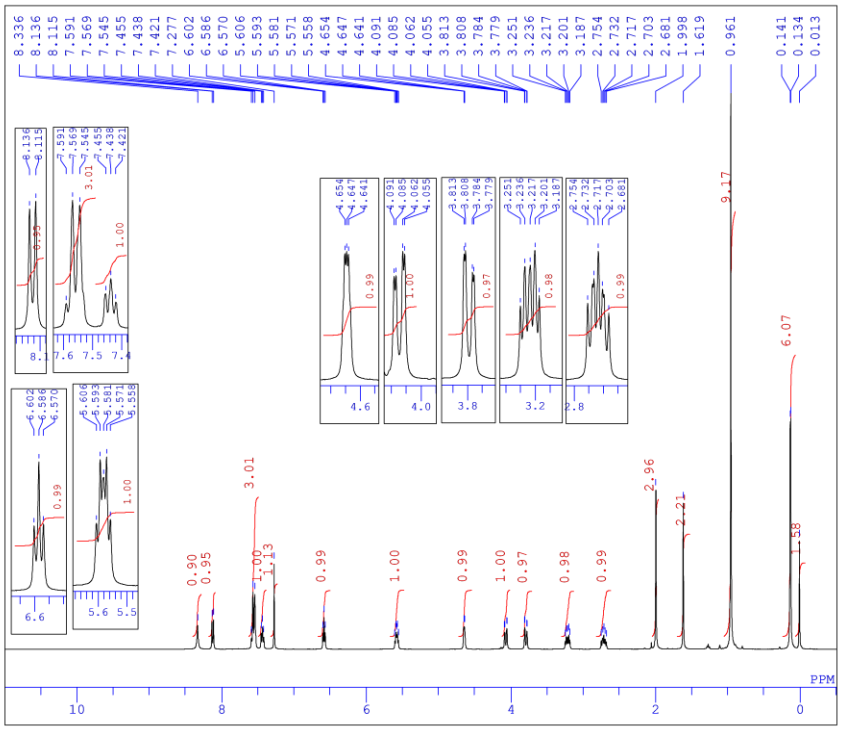


**5ag**

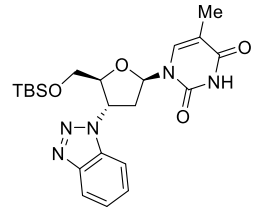


```
DFILE  Glc+benzyne_E13C-1-
COMNT  single pulse decoup
DATIM  2019-02-22 12:21:04
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26214
FREQU      25125.63 Hz
SCANS            512
ACQTM         1.0433 sec
PD            2.0000 sec
PW1              3.60 usec
IRNUC  1H
CTEMP          22.8 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             2.00 Hz
RGAIN            60
```

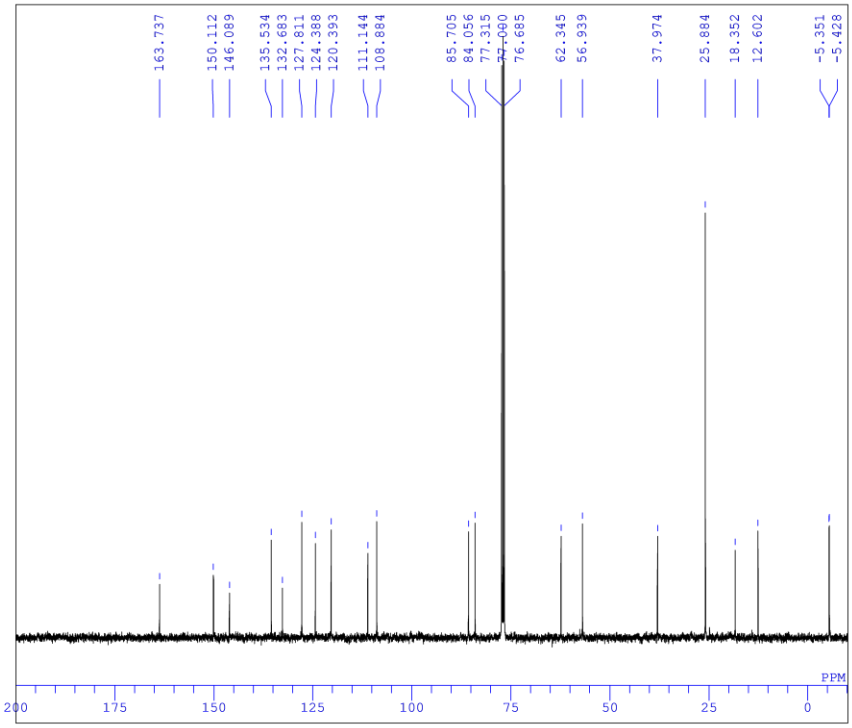
# 3’-(1*H*-Benzotriazol-1-yl)-5’-*O*-*tert*-butyldimethylsilyl-3’-deoxythymidine (5ah)



```
DFILE  190930AZT+benzyne__
COMNT  single_pulse
DATIM  2019-09-30 11:32:23
OBNUC  1H
EXMOD  single_pulse.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         26214
FREQU       6002.40 Hz
SCANS            16
ACQTM         4.3673 sec
PD            5.0000 sec
PW1           3.35 usec
IRNUC  1H
CTEMP          22.5 c
SLVNT  CDCL3
EXREF          7.27 ppm
BF             2.00 Hz
RGAIN            44
```

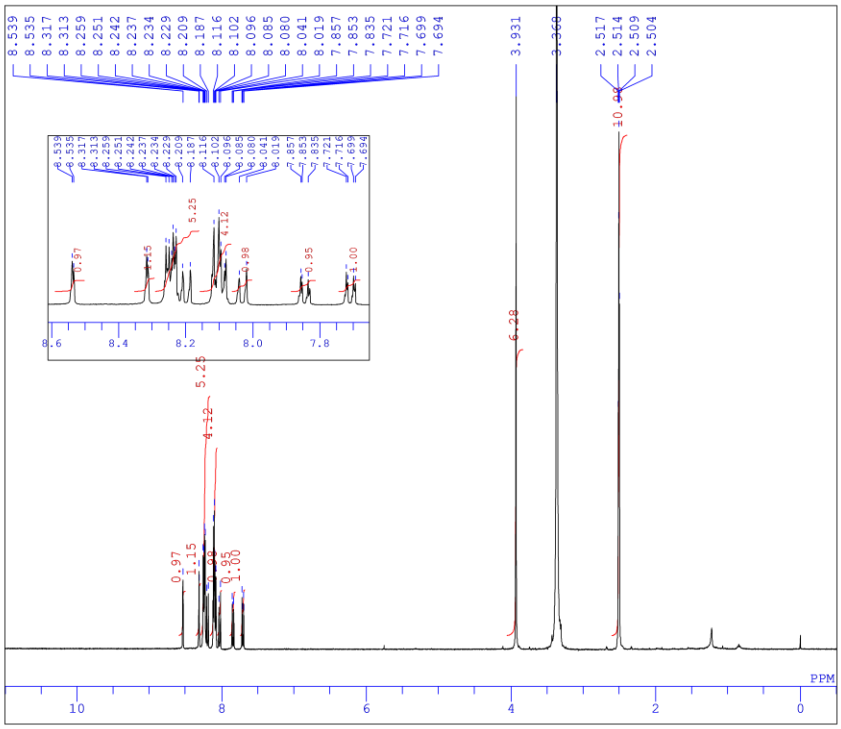



**5ah**

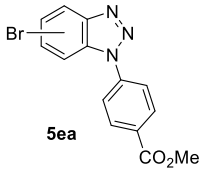


```
DFILE  AZT+benzyne_E13C-1-
COMNT  single pulse decoup
DATIM  2019-02-22 11:19:26
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26214
FREQU       25125.63 Hz
SCANS            512
ACQTM         1.0433 sec
PD            2.0000 sec
PW1           3.60 usec
IRNUC  1H
CTEMP          20.9 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             2.00 Hz
RGAIN            60
```

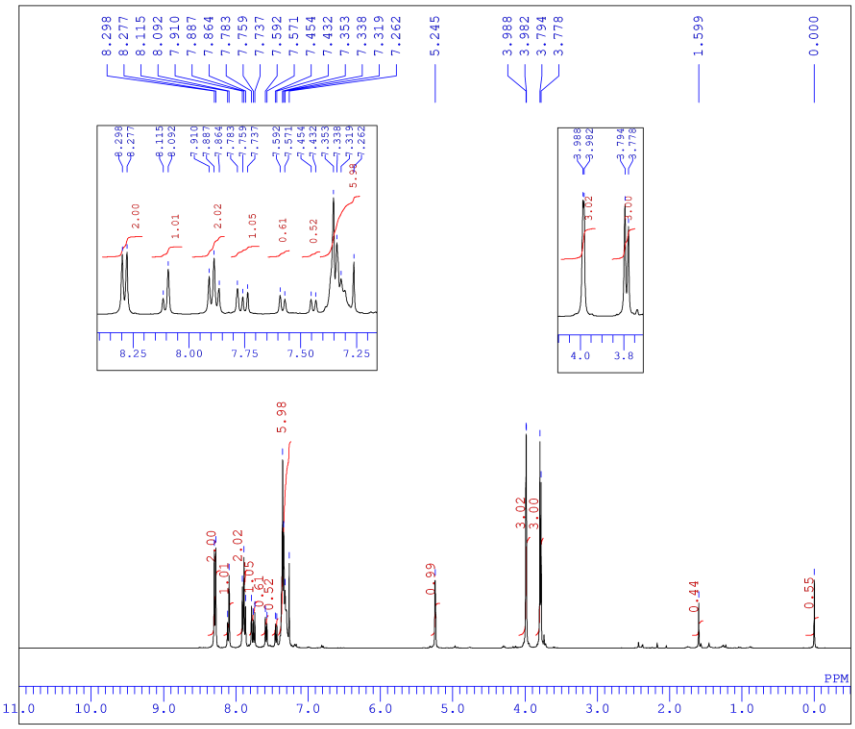
**5-Bromo-1-(4-Methoxycarbonylphenyl)-1,2,3-benzotriazol and 6-Bromo-1-(4-Methoxycarbonylphenyl)-1,2,3-benzotriazol (5ea)**



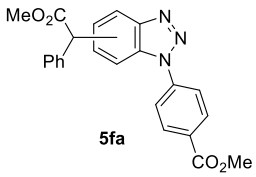

```
DFILE  Br-benzyne+4-MeO2CC
COMNT  auto
DATIM  Tue May 28 16:13:18
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN      10500.00 Hz
POINT        16384
FREQU       7992.01 Hz
SCANS            64
ACQTM        2.0500 sec
PD           4.9500 sec
PW1            5.80 usec
IRNUC  1H
CTEMP          24.2 c
SLVNT  DMSO
EXREF          0.00 ppm
BF             0.01 Hz
RGAIN            18
```



**Methyl 4-[5-(2-Methoxy-2-oxo-1-phenylethyl)-1*H*-benzotriazol-1-yl]benzoate and Methyl 4-[6-(2-Methoxy-2-oxo-1-phenylethyl)-1*H*-benzotriazol-1-yl]benzoate (5fa)**

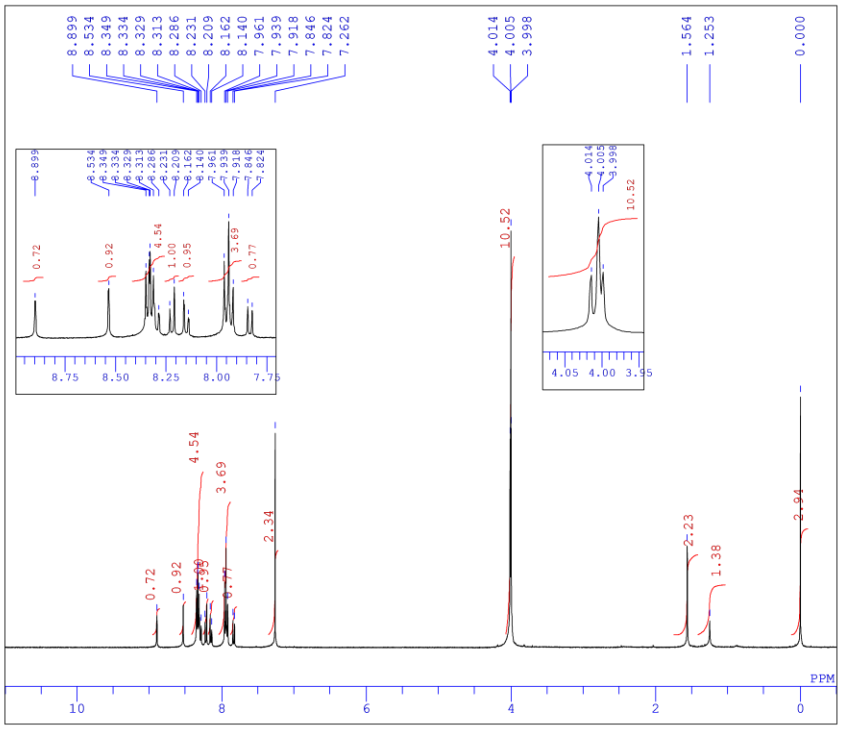



```
DFILE  MeO2CCH(Ph)-benzyne
COMNT  single_pulse
DATIM  2019-02-18 14:39:07
OBNUC  1H
EXMOD  single_pulse.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         26214
FREQU       6002.40 Hz
SCANS            16
ACQTM         4.3673 sec
PD            5.0000 sec
PW1              3.35 usec
IRNUC  1H
CTEMP            21.5 c
SLVNT  CDCL3
EXREF            0.00 ppm
BF               1.20 Hz
RGAIN              44
```

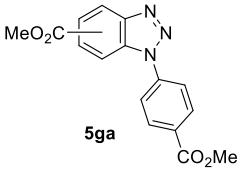



**5fa**

**Methyl 1-(4-Methoxycarbonylphenyl)-1,2,3-benzotriazole-5-carboxylate and Methyl 1-(4-Methoxycarbonylphenyl)-1,2,3-benzotriazole-6-carboxylate (5ga)**

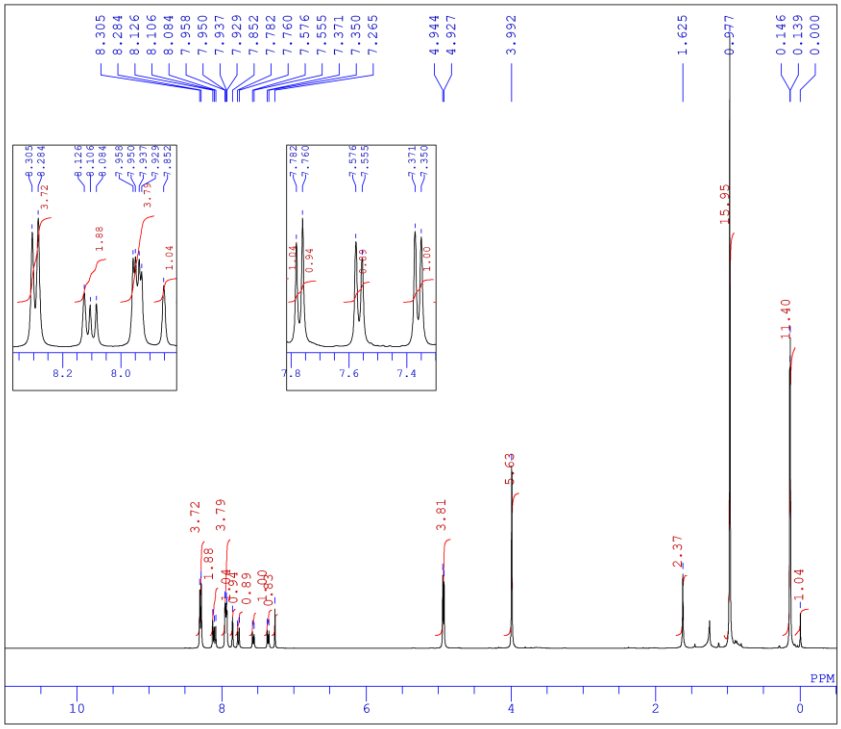



```
DFILE  MeO2C-Benzyne+4-MeC
COMNT  auto
DATIM  Tue May 28 15:57:06
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN      10500.00 Hz
POINT        16384
FREQU       7992.01 Hz
SCANS           64
ACQTM        2.0500 sec
PD           4.9500 sec
PW1            5.80 usec
IRNUC  1H
CTEMP          24.5 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.09 Hz
RGAIN            25
```

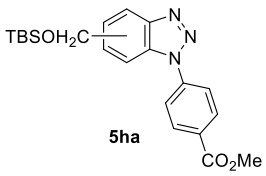



**5ga**

**5-(*tert*-Butyldimethylsilyloxymethyl)-1-(4-methoxycarbonylphenyl)-1,2,3-benzotriazol and 6-(*tert*-Butyldimethylsilyloxymethyl)-1-(4-Methoxycarbonylphenyl)-1,2,3-benzotriazol (5ha)**

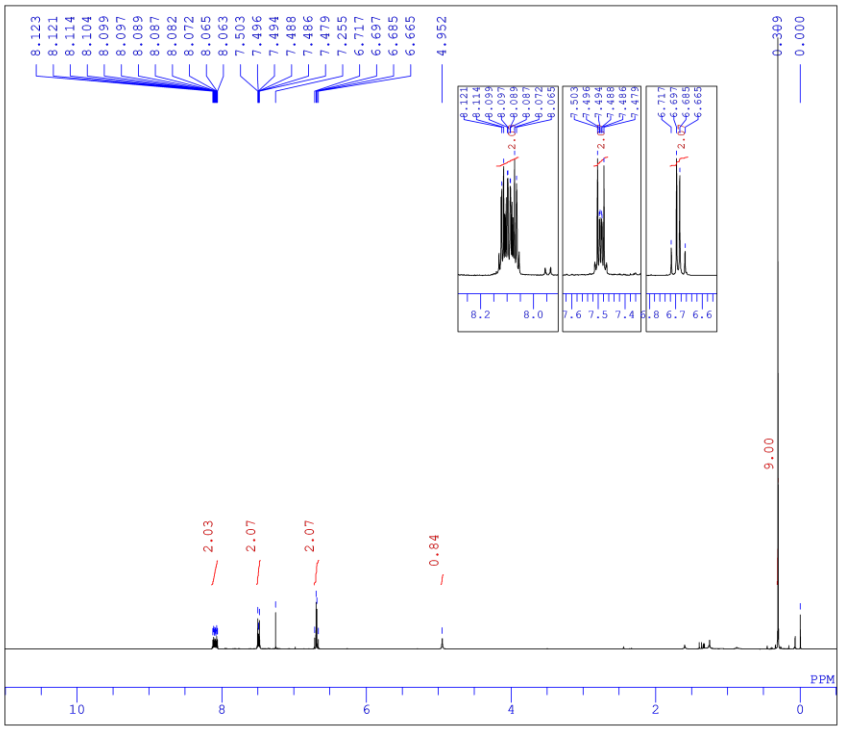



```
DFILE  190930TBSOCH2-benzy
COMNT  single_pulse
DATIM  2019-09-30 12:03:17
OBNUC  1H
EXMOD  single_pulse.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         26214
FREQU       6002.40 Hz
SCANS            16
ACQTM         4.3673 sec
PD            5.0000 sec
PW1              3.35 usec
IRNUC  1H
CTEMP          22.4 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             2.00 Hz
RGAIN            38
```

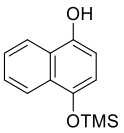



**5ha**

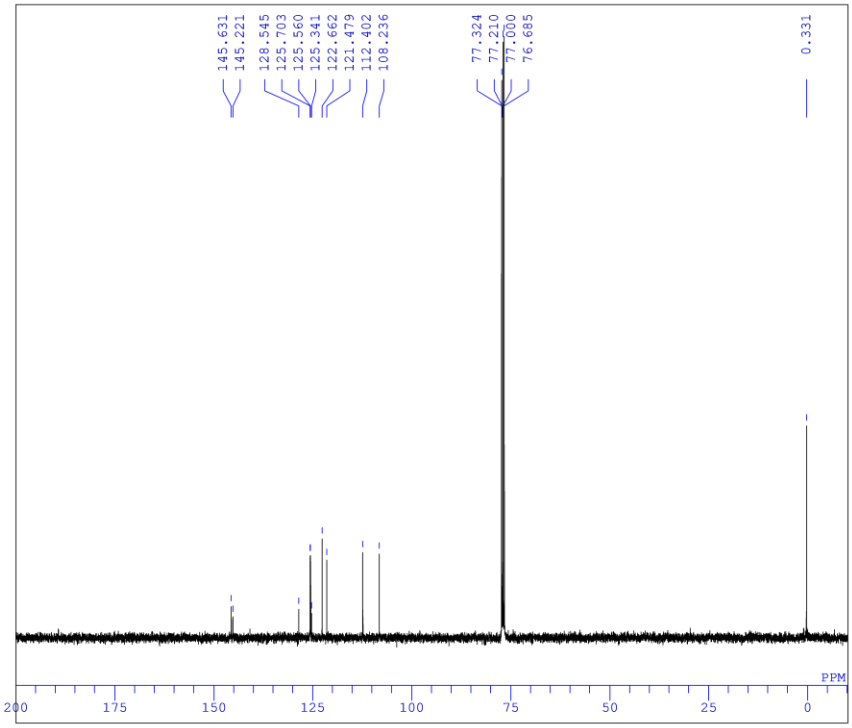
# 4-(Trimethylsilyloxy)naphthalene-1-ol (6c’)




```
DFILE  AT-603_E1H-1-1 FT.a
COMNT  single_pulse
DATIM  2018-01-15 12:08:08
OBNUC  1H
EXMOD  single_pulse.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         26214
FREQU       6002.40 Hz
SCANS             8
ACQTM         4.3673 sec
PD            2.0000 sec
PW1             3.05 usec
IRNUC  1H
CTEMP          22.9 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            40
```

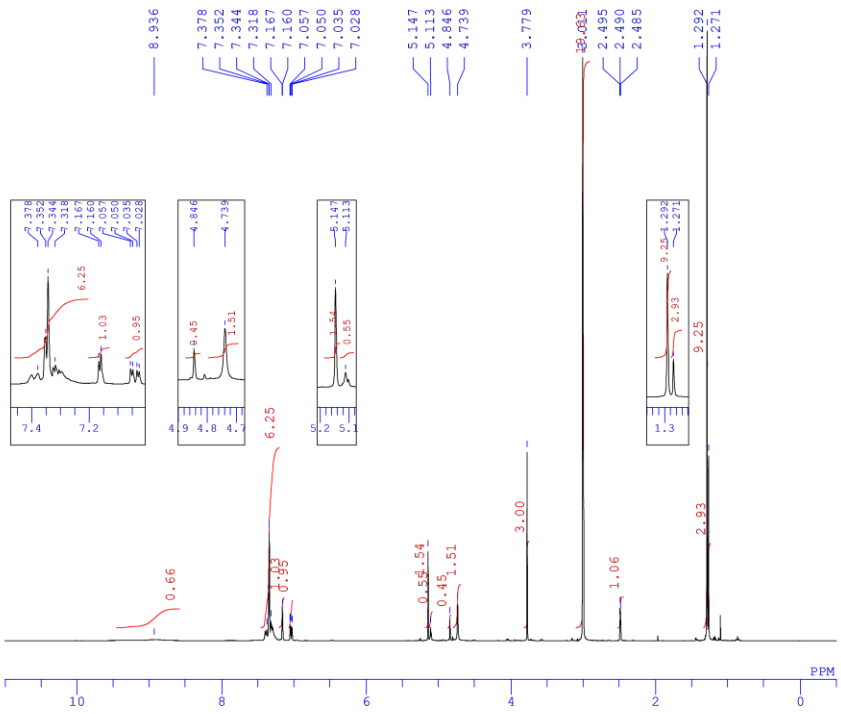



**6c'**

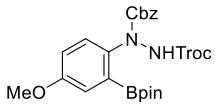



```
DFILE  AT-603_E13C-1-1 FT2
COMNT  single pulse decoup
DATIM  2018-01-15 12:10:01
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26214
FREQU      25125.63 Hz
SCANS           600
ACQTM         1.0433 sec
PD            1.7000 sec
PW1             3.53 usec
IRNUC  1H
CTEMP          23.0 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            60
```

**2-[1-(benzylcarbonyloxy)-2-(2,2,2-trichlorocarbonyloxy)hydrazineyl]-5-methoxyphenylboronic acid pinacol ester (8a)**

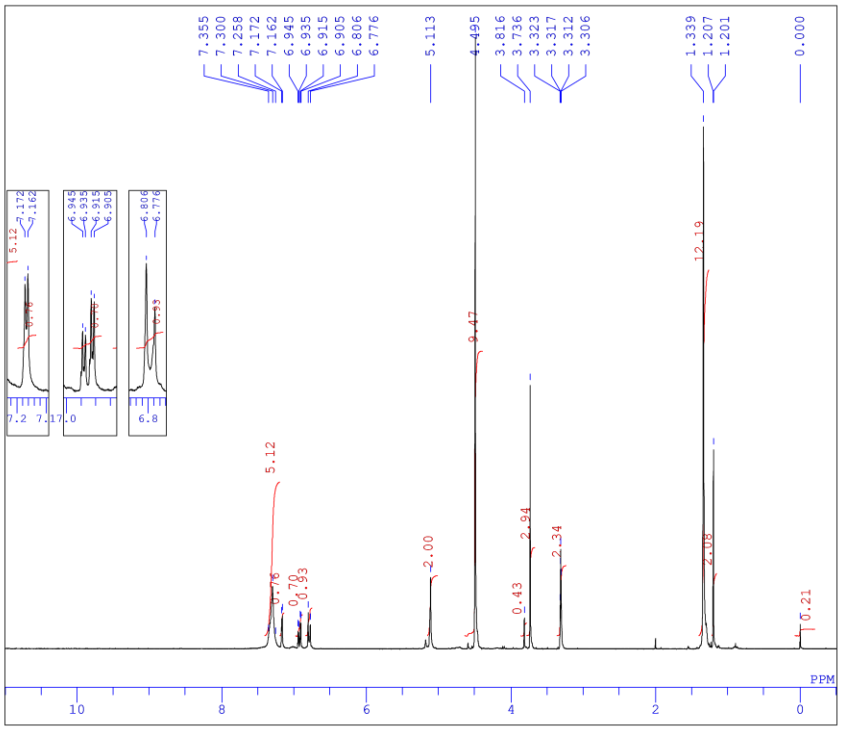



```
DFILE  4-MeO-2-pinBC6H3N(C
COMNT  single_pulse
DATIM  2019-07-17 11:21:48
OBNUC  1H
EXMOD  single_pulse.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         26214
FREQU       6002.40 Hz
SCANS            16
ACQTM         4.3673 sec
PD            5.0000 sec
PW1              3.35 usec
IRNUC  1H
CTEMP         100.0 c
SLVNT  DMSO
EXREF          2.49 ppm
BF             0.01 Hz
RGAIN            34
```

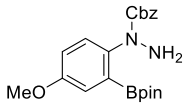



**8a**

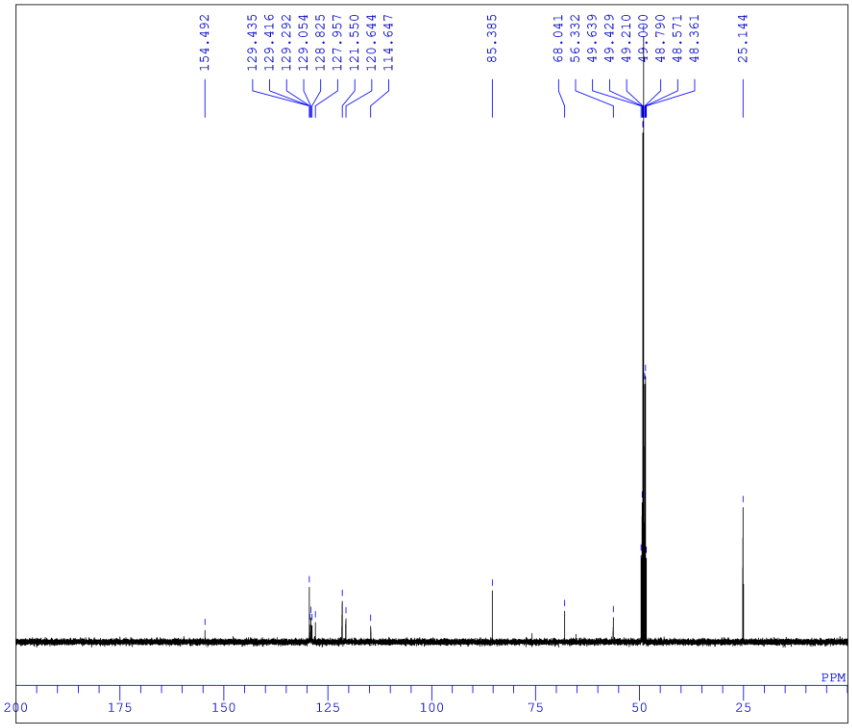
# 2-[1-(benzylcarbonyloxy)hydrazineyl]-5-methoxyphenylboronic acid pinacol ester (8b)




```
DFILE  190718 CD3OD.als pr
COMNT  190718 CD3OD
DATIM  Thu Jul 18 14:56:06
OBNUC  1H
EXMOD  NON
OBFRQ        300.40 MHz
OBSET        130.00 KHz
OBFIN       1150.00 Hz
POINT         32768
FREQU       6006.01 Hz
SCANS            16
ACQTM         5.4559 sec
PD            1.5440 sec
PW1             5.20 usec
IRNUC  1H
CTEMP           60.2 c
SLVNT  CD3OD
EXREF           0.00 ppm
BF              0.09 Hz
RGAIN             17
```

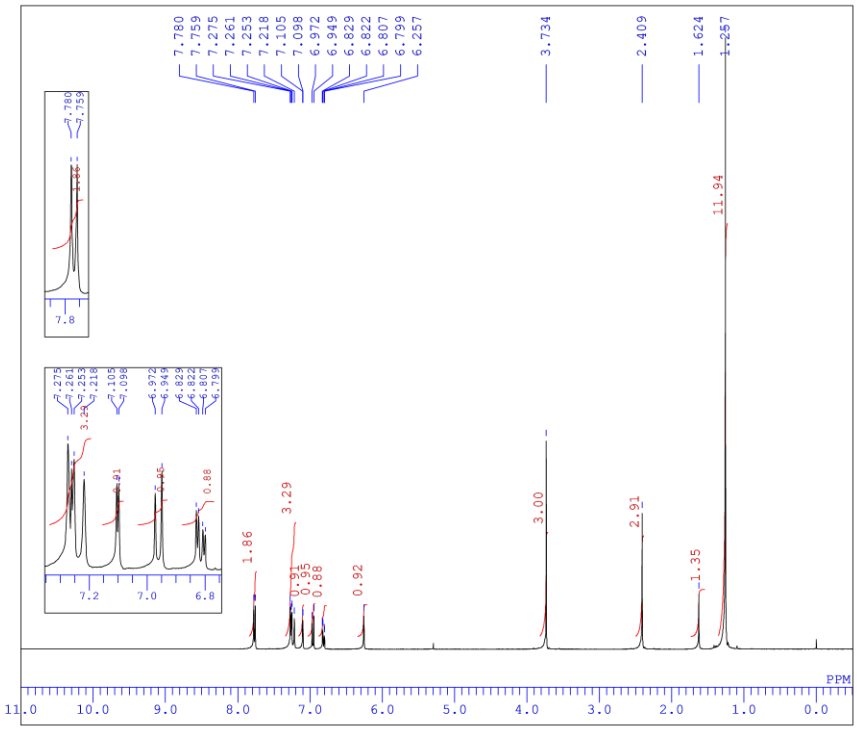



**8b**

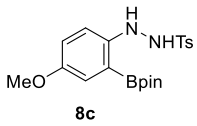



```
DFILE  4-MeO-2-pinBC6H3N_C
COMNT  single pulse decoup
DATIM  2019-07-19 09:51:24
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26214
FREQU      25125.63 Hz
SCANS          1000
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.60 usec
IRNUC  1H
CTEMP           60.0 c
SLVNT  CD3OD
EXREF          49.00 ppm
BF              0.01 Hz
RGAIN             60
```

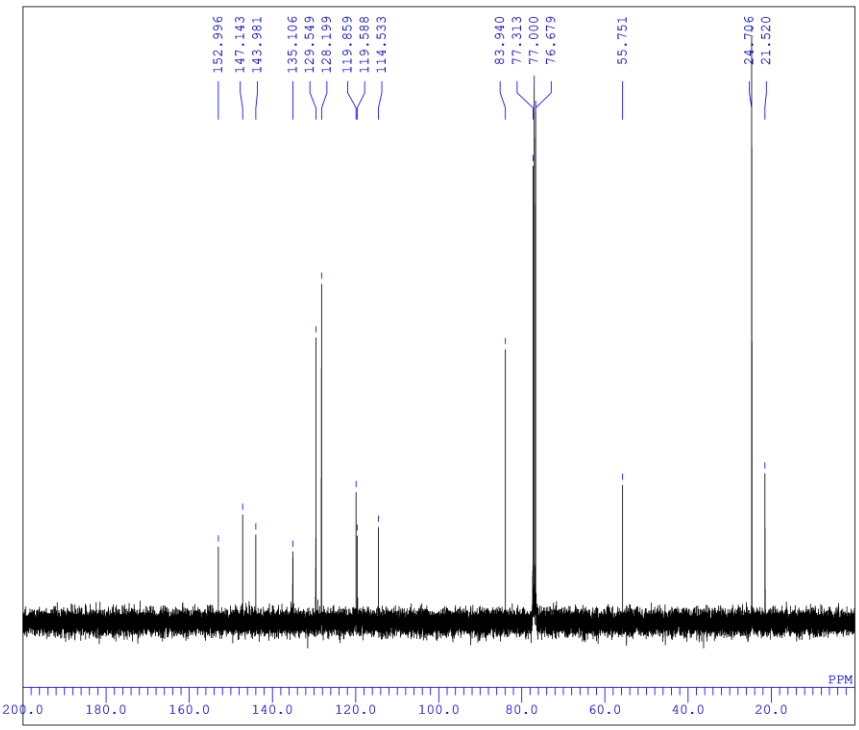
## 2-(2-tosylhydrazineyl)-5-methoxyphenylboronic acid pinacol ester (8c)




```
DFILE  4-MeO-2-pinBC6H3NHN
COMNT  4-MeO-2-pinBC6H3NHN
DATIM  Sat Jul 20 14:35:28
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN      10500.00 Hz
POINT        16384
FREQU       7992.01 Hz
SCANS            8
ACQTM        2.0500 sec
PD           4.9500 sec
PW1            6.20 usec
IRNUC  1H
CTEMP          25.4 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            15
```

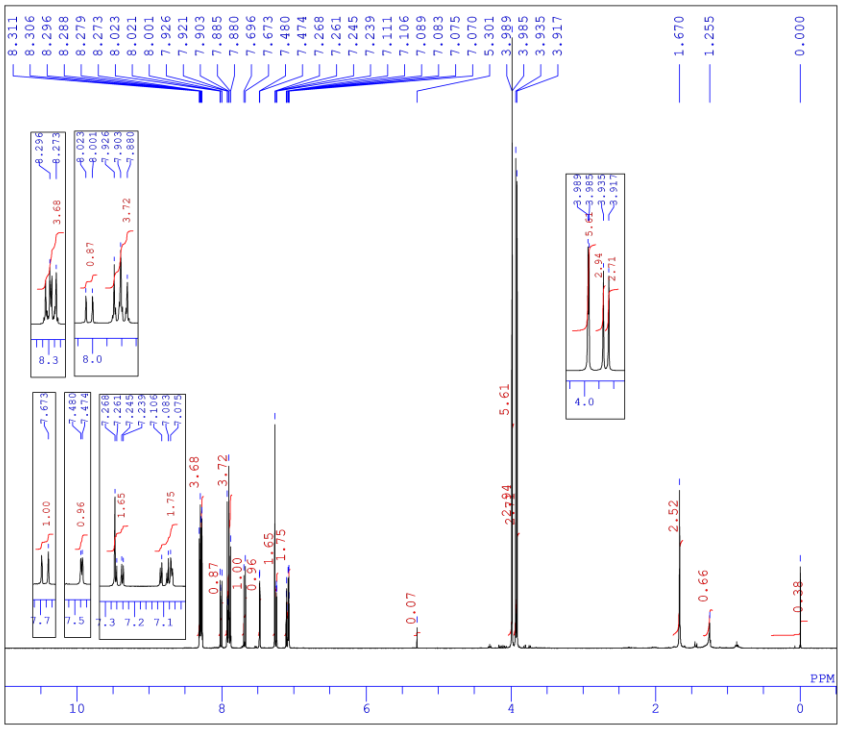



**8c**

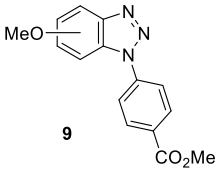



```
DFILE  4-MeO-2-pinBC6H3NHN
COMNT  4-MeO-2-pinBC6H3NHN
DATIM  Sat Jul 20 14:49:29
OBNUC  13C
EXMOD  BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN      10500.00 Hz
POINT        32768
FREQU      27118.64 Hz
SCANS          256
ACQTM        1.2083 sec
PD           1.7920 sec
PW1            6.20 usec
IRNUC  1H
CTEMP          25.4 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            25
```

**5-Methoxy-1-(4-Methoxycarbonylphenyl)-1,2,3-benzotriazol and 6-Methoxy-1-(4-Methoxycarbonylphenyl)-1,2,3-benzotriazol (9)**



```
DFILE  MeO-1-(4-MeO2CC6H4)
COMNT  single_pulse
DATIM  2019-07-17 11:14:16
OBNUC  1H
EXMOD  single_pulse.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         26214
FREQU       6002.40 Hz
SCANS            16
ACQTM         4.3673 sec
PD            5.0000 sec
PW1              3.35 usec
IRNUC  1H
CTEMP            22.7 c
SLVNT  CDCL3
EXREF            0.00 ppm
BF               0.01 Hz
RGAIN              42
```




**9**