Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

Silica Gel-Induced Aryne Generation from *o*-Triazenylarylboronic Acids as Stable Solid Precursors

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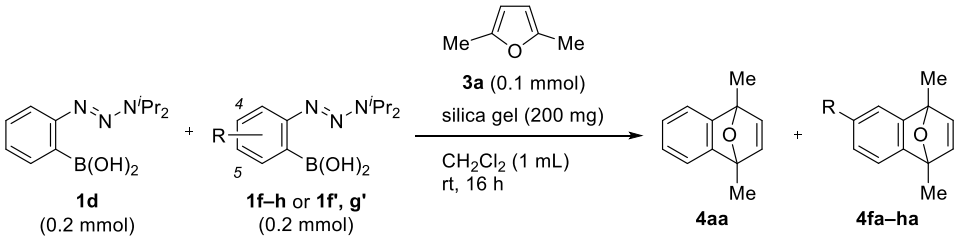
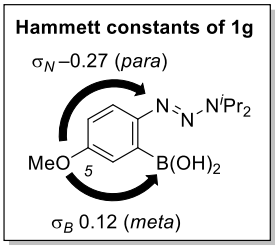
Experimental Section

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}). ^1H NMR spectra were recorded on JEOL JNM-AL 300 (300 MHz) spectrometer or JEOL JNM-ECA 400 (400 MHz) spectrometer or JEOL JNM-ECZ 500 (500 MHz) spectrometer. Chemical shifts are reported relative to internal standard (tetramethylsilane at δ_H 0.00, $CDCl_3$ at δ_H 7.26, C_6D_6 at δ_H 7.15). 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 or JEOL JNM-ECZ 500 (125 MHz) spectrometer. Chemical shifts are reported relative to internal standard ($CDCl_3$ at δ 77.00, C_6D_6 at δ 128.62). 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. Spherical silica gel (neutral, 40–50 μm) was purchased from Kanto Chemical and used after heating under vacuum to driness. *o*-Triazenylphenylboronic acid **1a**,[1] and arynophiles **3d**,[2] **3h'**,[3] **3j**,[2] and **3k**[4] were synthesized according to the literature procedures. *o*-Iodoarylamines including 2-iodo-3-methylaniline, 2-iodo-4-methoxyaniline, and 2-iodo-5-methoxyaniline were synthesized by reduction of corresponding nitrobenzenes using $FeCl_3$•$6H_2O$ and N_2H_4•$6H_2O$.[5] 3-Amino-2-iodonaphthalene,[6] 3-amino-4-iodopyridine,[7] 6-amino-5-iodoquinoline,[8] and 5-amino-4-iodo-*N*-tosylindole[9] were synthesized according to the literature procedures.

1. Analyses of the reaction of 1 and 3a using Hammett constants.





substituent	σ_N	σ_B	k_R/k_H*
5-Cl (**1f**)	0.23	0.37	1.30
4-Cl (**1f'**)	0.37	0.23	0.153
5-OMe (**1g**)	–0.27	0.12	12.7
4-OMe (**1g'**)	0.12	–0.27	0.170
5-CF_3 (**1h**)	0.53	0.49	0.180

* determined by ^{1}H NMR.

To a solution of **1d** (0.200 mmol), **1f–h** or **1f'**, **g'** (0.200 mmol), and 2,5-dimethylfuran (**3a**, 0.100 mmol) in CH_2Cl_2 (1.0 mL) was added silica gel (200 mg). After stirring at room temperature for 16 h, the organic components were eluted with THF, and filtrate was concentrated in vacuo to furnish the crude product. The ratio of products **4aa** and **4fa**–**ha** were determined by analyses of the crude products on ^{1}H NMR spectroscopy to estimate k_R/k_H value.

Obtained k_R/k_H values were then analyzed using Hammett constants of each substituent based on triazenyl group (σ_N) and that based on borono group (σ_B). The results of Hammett plot analyses based on σ_N and σ_B are shown in Figure S1a and S1b, respectively. As a result, plot of $\log(k_R/k_H)$ displayed linear relationship neither against σ_N nor against σ_B. Thus, the electronic perturbation does not occur at just one of triazenyl and borono groups.

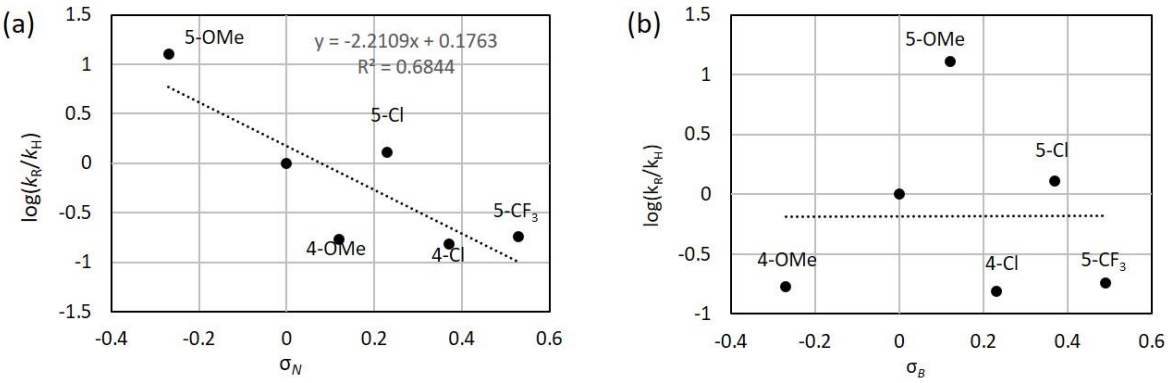


Figure S1

On the other hand, it is known that the relationship between $\log(k_R/k_H)$ and Hammett

constants in the reactions involving electronic perturbation at two sites are represented by Hammett equation (1), and linear analysis of the equation is undertaken by Jaffé's equation (2) and (3).

$$\log(k_{\mathrm{R}}/k_{\mathrm{H}}) = \rho_N\sigma_N + \rho_B\sigma_B \qquad (1)$$

$$\log(k_{\mathrm{R}}/k_{\mathrm{H}})/\sigma_N = \rho_N + \rho_B(\sigma_B/\sigma_N) \qquad (2)$$

$$\log(k_{\mathrm{R}}/k_{\mathrm{H}})/\sigma_B = \rho_N(\sigma_N/\sigma_B) + \rho_B \qquad (3)$$

The results of Jaffé's plot based on equations (2) and (3) are shown in Figure S2a and S2b, respectively. Both analyses displayed linear relationship in good R^2 value, and the each provided negative ρ_N value and positive ρ_B value. These values suggested build-up of positive and negative charge on the nitrogen atom and the boron atom, respectively, in the rate-determining step.[10)]

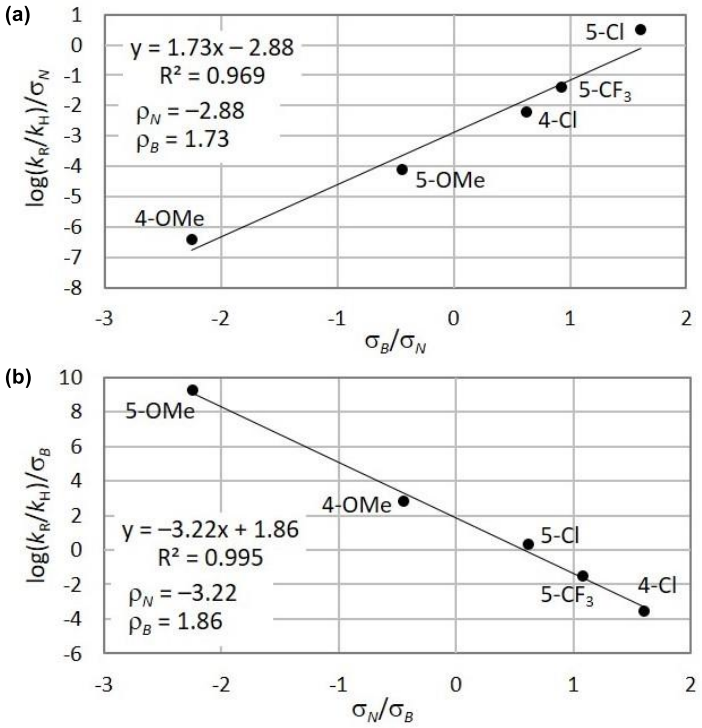
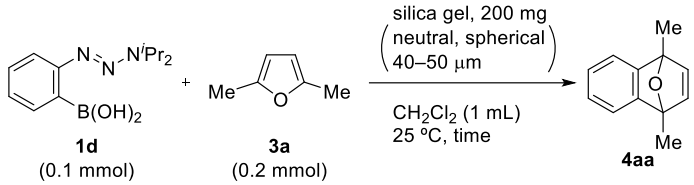


Figure S2

2. Time course study of the reaction of 1d and 3a.



To suspension of 2,5-dimethylfuran (**3a**, 0.100 mmol) and silica gel in CH_2Cl_2 (1.0 mL) was added aryne precursor **1d** (0.200 mmol) at 25 ºC. After stirring at the same temperature for indicated time, silica gel was filtered off, and the eluent was concentrated in vacuo to furnish the crude product. Recovery of **1d** and yield of **4aa** were estimated by ^{1}H NMR analysis of the crude product using 1,1,2,2-tetrachloroethane as an internal standard (Figure S3).

Rate of N_2 evolution was measured using an eudiometer apparatus.[11] The reaction was performed at 25 ºC with the use of **1d** (0.800 mmol), **3a** (0.400 mmol), silica gel (800 mg), and CH_2Cl_2 (4.0 mL).

time (min)	**1d** (mmol)	**4aa** (mmol)
0	0.200	0.000
5	0.052	0.016
15	0.040	0.031
30	0.038	0.049
60	0.036	0.062
90	0.027	0.073
120	0.019	0.085
180	0.011	0.089
240	0.014	0.095

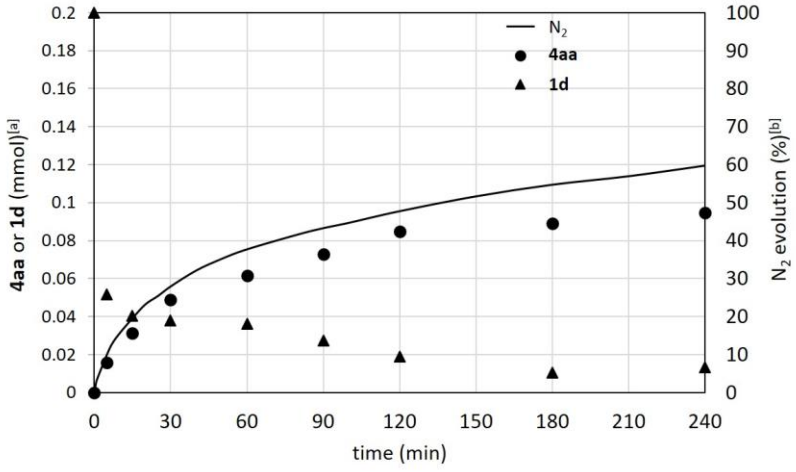


Figure S3

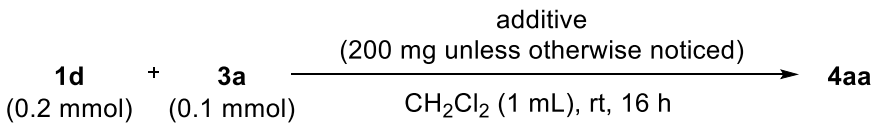
[a] Determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. [b] Based on **1d** (0.8 mmol).

3. Influence of silica gel and other additives on the reaction of 1d and 3a.

In order to elucidate factors responsible for activation of precursors **1**, we investigated the influence of additives on reaction of **1d** and **3a** (Table S1). Comparing with spherical silica gel (entry 1), crushed shape silica gel (purchased from Kanto Chemical or Merck) displayed lower activity (entries 2 and 3). It seems likely that the activity of silica gel

depend on magnitude of their specific surface area. In addition, recycling use of spherical silica gel led to a slight loss of activity (entry 4). Analysis of the recovered silica gel on IR spectroscopy indicated that both borate and diisopropylamine remained adsorbed on silica gel surface after the reaction (Figure S4). Thus, we considered the observed loss of activity attributed to denaturation of silica gel surface. Next, we performed the reaction in the dark, and no loss of activity was observed (entry 5). Hence, silica gel did not played a role as the photo-catalyst.[11] No reaction was observed with the use of other adsorbent such as alumina (neutral or basic), and MS 4A (entry 6). Aside from silica gel, Brønsted acids induced the generation of aryne from **1d**. (±)-Camphorsulfonic acid [(±)-CSA] led a smooth conversion of **1d** in less than 4 h to provide **4aa** in 97% yield (entry 7). On the other hand, the use excess amount of acetic acid displayed lower activity than that of silica gel (entry 8). Thus, we consider that silica gel did not play a role as a simple Brønsted acid.

Table S1



specific surface aria of silica gel (neutral)
spherical (40-50 μm, Kanto Chemical) : 630-730 m^2/g
crashed shape (40-63 μm, Kanto Chemical) : 470-530 m^2/g
crashed shape (40-63 μm, Merck) : 480-540 m^2/g

Entry	Additive [Variation from standard conditions]	NMR Yield (%)
1	Spherical silica gel	Quant.
2	Crushed shape silica gel (Kanto Chemical)	73
3	Crushed shape silica gel (Merck)	73
4	Spherical silica gel (recycled)	84
5	Spherical silica gel [in the dark]	Quant.
6	Neutral alumina or Basic alumina or MS 4A	NR
7	(±)-CSA (0.2 mmol) [reaction time: 4 h]	97
8	AcOH/CH_2Cl_2 (1:2, 1 mL) [reaction time: 6 h]	47

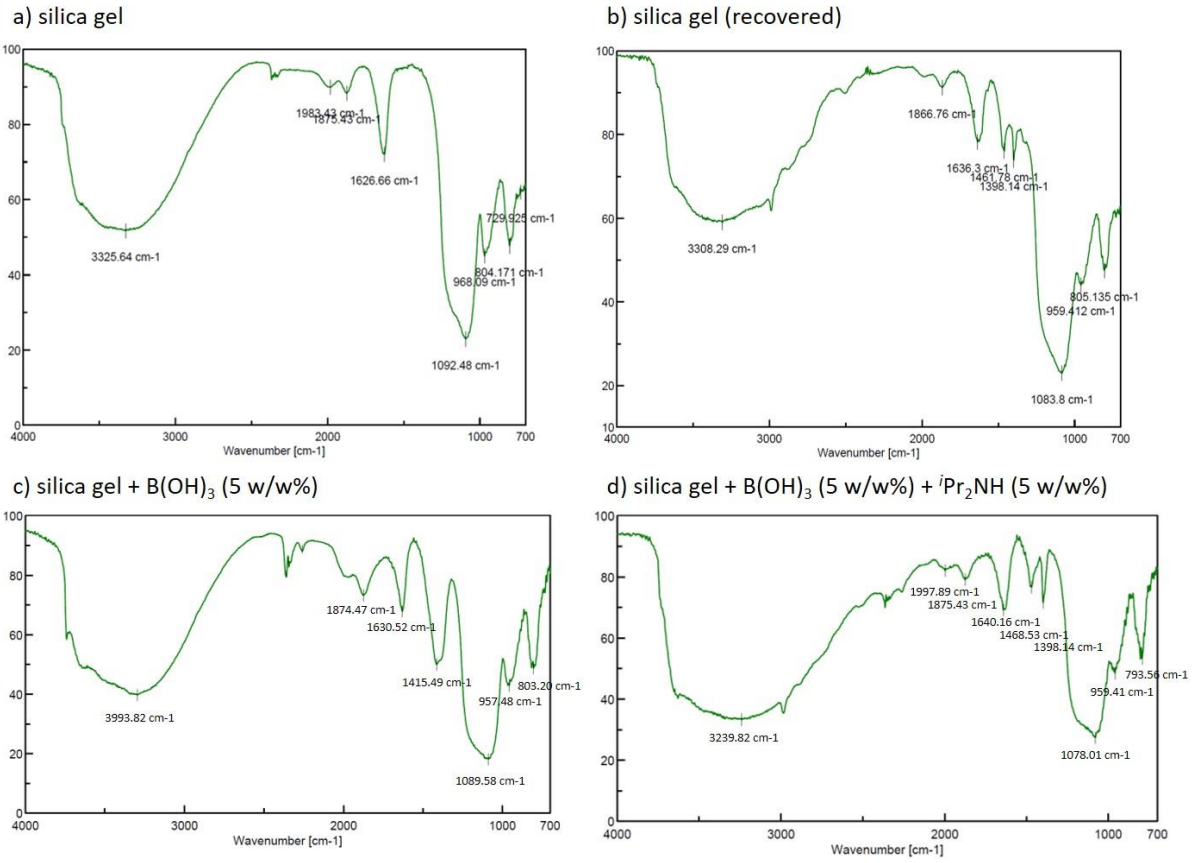
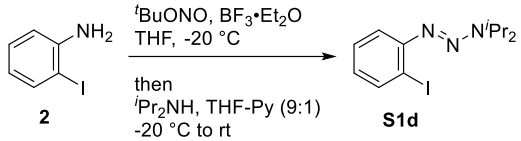


Figure S4

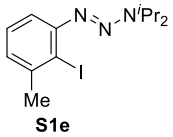
4. Typical procedure for the synthesis of *o*-iodoaryltriazenes: Preparation of 1-(2-iodophenyl)-3,3-diisopropyltriaz-1-ene.[13)]



To a solution of 2-iodoaniline **2** (6.57 g, 30.0 mmol) in THF (45 mL) was added BF_3•Et_2O (5.70 mL, 45.0 mmol) and ^{t}BuONO (5.40 mL, 45.0 mmol) at –20 °C. After stirring at the same temperature for 1 h, the formed precipitates were collected by suction and washed with Et_2O to give crude diazonium salt. The crude diazonium salt was added to a solution of ^{i}Pr$_2$NH (13.0 mL, 90.0 mmol) in THF–pyridine (9:1, 40 mL) at –20 °C, and the mixture was allowed to warm to room temperature. After stirring overnight, the reaction was quenched with saturated aqueous NH_4Cl, and the whole mixture was extracted with AcOEt. The combined organic layers were successively washed with brine, 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 *n*-hexane/AcOEt) to give 1-(2-iodophenyl)-3,3-diisopropyltriaz-1-ene **S1d** (8.26 g, 83%,) as a yellow solid: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34 (broad doublet, 6H, CH(C*H*$_3$)$_2$), 1.37 (broad doublet, 6H, CH(C*H*$_3$)$_2$), 4.04 (broad septet, 1H, C*H*(CH$_3$)$_2$), 5.19 (broad septet, 1H, C*H*(CH$_3$)$_2$), 6.81 (ddd, *J* = 8.1, 7.2, 1.5 Hz, 1H, Ar*H*), 7.26 (ddd, *J* = 8.1, 7.2, 1.5 Hz, 1H, Ar*H*), 7.35 (dd, *J* = 8.1, 1.5 Hz, 1H, Ar*H*), 7.83 (dd, *J* = 8.1, 1.5 Hz, 1H, Ar*H*).

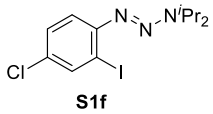
1-(2-Iodo-3-methylphenyl)-3,3-diisopropyltriaz-1-ene (S1e)



S1e

Yield 88% (1.22 g); purified by column chromatography (silica gel, 20:1 *n*-hexane/AcOEt); a yellow oil; IR (KBr) *v* 2968, 1578, 1403, 1243, 1152, 1009, 945 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (broad doublet, 6H, CH(C*H*$_3$)$_2$), 1.38 (broad doublet, 6H, CH(C*H*$_3$)$_2$), 2.51 (s, 3H, ArC*H*$_3$), 4.03 (broad septet, 1H, C*H*(CH$_3$)$_2$), 5.21 (broad septet, 1H, C*H*(CH$_3$)$_2$), 6.99 (dd, *J* = 6.0, 2.8 Hz, 1H, Ar*H*), 7.12–7.16 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1 (CH_3), 23.8 (CH_3), 29.0 (CH_3), 47.5 (CH), 49.7 (CH), 103.9 (C), 114.5 (CH), 125.8 (CH), 127.9 (CH), 142.4 (C), 151.2 (C); HRMS (EI) calcd for $C_{13}H_{20}IN_3$ $[M]^+$ 345.0702, found 345.0705.

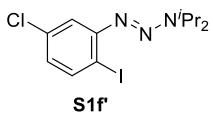
1-(4-Chloro-2-iodophenyl)-3,3-diisopropyltriaz-1-ene (S1f)



S1f

Yield 85% (3.11 g); purified by column chromatography (silica gel, 20:1 *n*-hexane/AcOEt); an orange oil; IR (KBr) *v* 2976, 1550, 1407, 1252, 1157, 1028, 817 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (d, 6H, *J* = 6.4 Hz CH(C*H*$_3$)$_2$), 1.38 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 4.04 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 5.16 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 7.23 (dd, *J* = 8.4, 2.0 Hz, 1H, Ar*H*), 7.28 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.81 (d, *J* = 2.0 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0 (CH_3), 23.8 (CH_3), 47.9 (CH), 50.0 (CH), 96.3 (C), 117.5 (CH), 128.7 (CH), 130.1 (C), 138.0 (CH), 149.6 (C); HRMS (EI) calcd for $C_{12}H_{17}ClIN_3$ $[M]^+$ 365.0156, found 365.0155.

1-(5-Chloro-2-iodophenyl)-3,3-diisopropyltriaz-1-ene (S1f')

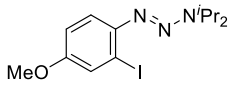


S1f'

Yield 73% (798 mg); purified by column chromatography (silica gel, 20:1 *n*-hexane/AcOEt); a yellow oil; IR (KBr) *v* 2968, 1563, 1403, 1228, 1080, 1013, 929, 802 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 1.40 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 4.06 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 5.16 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 6.80 (dd, *J* = 8.4, 2.4 Hz, 1H, Ar*H*), 7.32 (d, *J* = 2.4 Hz, 1H, Ar*H*), 7.72 (d, *J* = 8.4 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0 (CH_3), 23.7

(CH_3), 48.1 (CH), 50.3 (CH), 93.7 (C), 117.2 (CH), 125.9 (CH), 134.8 (C), 139.6 (CH), 151.7 (C); HRMS (EI) calcd for $C_{12}H_{17}ClIN_3$ $[M]^+$ 365.0156, found 365.0154.

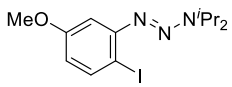
1-(2-Iodo-4-methoxyphenyl)-3,3-diisopropyltriaz-1-ene (S1g)



S1g

Yield 73% (1.06 g); purified by column chromatography (silica gel, 10:1 *n*-hexane/ AcOEt); a yellow oil; IR (KBr) *v* 2976, 2359, 2060, 1590, 1423, 1208, 1017, 809 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.34 (broad doublet, 12H, CH(C*H*$_3$)$_2$), 3.79 (s, 3H, OC*H*$_3$), 4.00 (broad septet, 1H, C*H*(CH_3)$_2$), 5.13 (broad septet, 1H, C*H*(CH_3)$_2$), 6.87 (dd, *J* = 9.2, 2.8 Hz, 1H, Ar*H*), 7.29 (d, *J* = 9.2 Hz, 1H, Ar*H*), 7.38 (d, *J* = 2.8 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2 (CH_3), 23.8 (CH_3), 47.3 (CH), 49.5 (CH), 55.7 (CH_3), 96.7 (C), 115.3 (CH), 117.4 (CH), 123.1 (CH), 144.9 (C), 157.3 (C); HRMS (EI) calcd for $C_{13}H_{20}IN_3O$ $[M]^+$ 361.0651, found 361.0655.

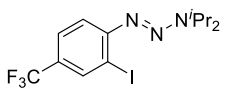
1-(2-Iodo-5-methoxyphenyl)-3,3-diisopropyltriaz-1-ene (S1g')



S1g'

Yield 70% (1.62g); purified by column chromatography (silica gel, 20:1 *n*-hexane/AcOEt); a yellow oil; IR (KBr) *v* 2972, 1579, 1401, 1265, 1159, 1127, 1032, 865 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.33 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 1.39 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 3.80 (s, 3H, OC*H*$_3$), 4.04 (septet, *J* = 6.4 Hz, 1H, C*H*(CH_3)$_2$), 5.17 (septet, *J* = 6.4 Hz, 1H, C*H*(CH_3)$_2$), 6.48 (dd, *J* = 8.8, 2.8 Hz, 1H, Ar*H*), 6.97 (d, *J* = 2.8 Hz, 1H, Ar*H*), 7.68 (d, *J* = 8.8 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0 (CH_3), 23.7 (CH_3), 47.7 (CH), 50.0 (CH), 55.3 (CH_3), 85.9 (C), 102.8 (CH), 112.7 (CH), 139.0 (CH), 151.6 (C), 160.4 (C); HRMS (EI) calcd for $C_{13}H_{20}IN_3O$ $[M]^+$ 361.0651, found 361.0655.

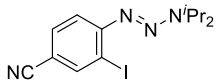
1-[2-Iodo-4-(trifluoromethyl)phenyl]-3,3-diisopropyltriaz-1-ene (S1h)



S1h

Yield 84% (1.69 g); purified by column chromatography (silica gel, 20:1 *n*-hexane/AcOEt); a yellow oil; IR (KBr) *v* 2976, 1598, 1407, 1256, 1069, 889 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.34 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 1.41 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 4.09 (septet, *J* = 6.4 Hz, 1H, C*H*(CH_3)$_2$), 5.21 (septet, *J* = 6.4 Hz, 1H, C*H*(CH_3)$_2$), 7.40 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.51 (d, *J* = 8.4 Hz, 1H, Ar*H*), 8.07 (s, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0 (CH_3), 23.7 (CH_3), 48.3 (CH), 50.4 (CH), 95.7 (C), 116.8 (CH), 123.4 (q, J_{CF} = 271 Hz, CF_3), 125.6 (q, J_{CF} = 3.9 Hz, CH), 127.4 (q, J_{CF} = 32.4 Hz, C), 136.1 (q, J_{CF} = 3.8 Hz, CH), 153.5 (C); HRMS (EI) calcd for $C_{13}H_{17}F_3IN_3$ $[M]^+$ 399.0419, found 399.0421.

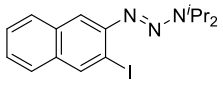
1-(4-Cyano-2-iodophenyl)-3,3-diisopropyltriaz-1-ene (S1i)



S1i

Yield 86% (1.23 g); purified by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt); a yellow solid; mp 86–87 °C; IR (KBr) *ν* 2974, 2223, 1586, 1466, 1404, 1360, 1261, 1229, 1130, 1026, 831 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.41 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 4.11 (septet, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 5.21 (septet, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 7.40 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.53 (dd, *J* = 8.4, 2.0 Hz, 1H, Ar*H*), 8.09 (d, *J* = 2.0 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.9 (CH_3), 23.7 (CH_3), 48.8 (CH), 50.8 (CH), 95.8 (C), 108.5 (C), 116.8 (CH), 118.2 (C), 132.3 (CH), 142.6 (CH), 154.2 (C); HRMS (EI) calcd for $C_{13}H_{17}IN_4$ $[M]^+$ 356.0498, found 356.0500.

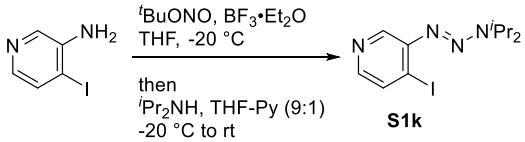
1-(3-Iodonaphthalen-2-yl)-3,3-diisopropyltriaz-1-ene (S1j)



S1j

Yield 72% (247 mg); purified by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt); an orange solid; mp 72–74 °C; IR (KBr) *ν* 3044, 2972, 1570, 1399, 1271, 1160, 985, 886, 809, 746 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 1.45 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 4.08 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 5.24 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 7.34 (dt, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 7.41 (dt, *J* =7.6, 1.2 Hz, 1H, Ar*H*), 7.65 (s, 1H, Ar*H*), 7.66 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.76 (d, *J* = 7.6 Hz, 1H, Ar*H*), 8.39 (s, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2 (CH_3), 23.8 (CH_3), 47.7 (CH), 49.9 (CH), 96.9 (C), 113.0 (CH), 125.0 (CH), 126.3 (CH), 126.5 (CH), 128.0 (CH), 133.0 (C), 133.9 (C), 138.2 (CH), 147.7 (C); HRMS (EI) calcd for $C_{16}H_{20}IN_3$ $[M]^+$ 381.0702, found 381.0702.

3-(3,3-Diisopropyltriaz-1-en-1-yl)-4-iodopyridine (S1k)

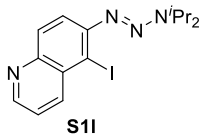


S1k

[Caution! Diazonium tetrafluoroborates derived from 3-aminopyridines spontaneously detonate when dry. Never collect them by suction, and avoid preparing them in large scale.][14] To a solution of 3-amino-4-iodopyridine[7] (880 mg, 4.00 mmol) in THF (16 mL) was added BF_3•Et_2O (2.01 mL, 16.0 mmol) and ^{t}BuONO (1.66 mL, 14.0 mmol) at –20 °C.[15] After stirring at the same temperature for 1 h, the precipitates were formed and supernatant solvent was removed by decantation using syringe as temperature was kept at –20 °C. The precipitate was washed with Et_2O by repeating decantation twice. The crude diazonium salt was dissolved

in THF (1 mL), and a solution of $^{i}Pr_2NH$ (1.68 mL, 12.0 mmol) in THF–pyridine (9:1, 4 mL) was added at –20 °C. The mixture was allowed to warm to room temperature and stirred overnight. After completion, the reaction was quenched with saturated aqueous NH_4Cl, and the whole mixture was extracted with AcOEt. The combined organic layers were successively washed with brine, were dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 6:1 *n*-hexane/AcOEt) to give triazene **S1k** (1.03 g, 78%,) as a beige solid: mp 85 °C (decomp.); IR (KBr) *v* 2972, 1535, 1403, 1275, 1148, 1021, 817 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.33 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 1.41 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 4.07 (septet, *J* = 6.4 H, 1H, C*H*(CH$_3$)$_2$), 5.19 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 7.75 (d, *J* = 5.2 Hz, 1H, Ar*H*), 7.90 (d, *J* = 5.2 Hz, 1H, Ar*H*), 8.44 (s, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0 (CH_3), 23.6 (CH_3), 47.8 (CH), 50.3 (CH), 106.1 (C), 133.8 (CH), 139.2 (CH), 145.3 (CH), 147.2 (C); HRMS (EI) calcd for $C_{11}H_{17}IN_4$ $[M]^+$ 332.0498, found 332.0499.

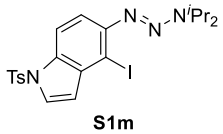
6-(3,3-Diisopropyltriaz-1-en-1-yl)-5-iodoquinoline (S1l)



S1l

The reaction was performed using 6-amino-5-iodoquinoline[8] (675 mg, 2.50 mmol), BF_3•Et_2O (1.26 mL, 10.0 mmol) and ^{t}BuONO (1.04 mL, 8.75 mmol).[15] Yield 90% (860 mg); purified by column chromatography (silica gel, 4:1 *n*-hexane/AcOEt); a colorless solid; mp 108–110 °C; IR (KBr) *v* 2972, 1550, 1395, 1236, 1157, 1028, 969, 837 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.39 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 1.45 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 4.12 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 5.32 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 7.42 (dd, *J* = 8.8, 4.4 Hz, 1H, Ar*H*), 7.92 (d, *J* = 9.2 Hz, 1H, Ar*H*), 7.97 (dd, *J* = 9.2, 0.8 Hz, 1H, Ar*H*), 8.60 (ddd, *J* = 8.8, 1.2, 0.8 Hz, 1H, Ar*H*), 8.75 (dd, *J* = 4.4, 1.2 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1 (CH_3), 23.8 (CH_3), 48.3 (CH), 50.2 (CH), 98.7 (C), 120.9 (CH), 122.4 (CH), 130.2 (CH), 131.4 (C), 140.1 (CH), 147.6 (C), 149.2 (CH), 149.4 (C); HRMS (EI) calcd for $C_{15}H_{19}IN_4$ $[M]^+$ 382.0654, found 382.0655.

5-(3,3-Diisopropyltriaz-1-en-1-yl)-4-iodo-1-tosyl-1*H*-indole (S1m)

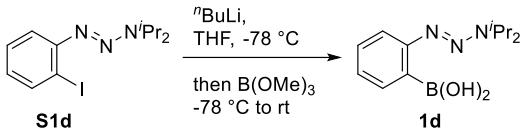


S1m

The reaction was performed using 5-amino-4-iodo-*N*-tosylindole[9] (412 mg, 1.00 mmol), BF_3•Et_2O (188 μL, 1.50 mmol) and ^{t}BuONO (178 μL, 1.50 mmol). Yield 85% (444 mg); purified by column chromatography (silica gel, 3:1 *n*-hexane/CH_2Cl_2); a colorless amorphous; IR (KBr) *v* 3141, 2973, 1403, 1241, 1190, 999, 811, 754 cm^{-1}; ^1H NMR (400 MHz, C_6D_6): δ 1.04 (doublet, *J* =

4.8 Hz, 6H, CH(CH_3)$_2$), 1.11 (doublet, J = 4.8 Hz, 6H, CH(CH_3)$_2$), 1.64 (s, 3H, CH_3), 3.50 (septet, J = 4.8 Hz, 1H, CH(CH$_3$)$_2$), 5.14 (septet, J = 4.8 Hz, 1H, CH(CH$_3$)$_2$), 6.45 (d, J = 6.4 Hz, 2H, ArH), 6.65 (d, J = 3.2 Hz, 1H, ArH), 7.41 (d, J = 3.2 Hz, 1H, ArH), 7.57 (d, J = 7.2 Hz, 2H, ArH), 7.58 (d, J = 7.2 Hz, 1H, ArH), 8.15 (d, J = 7.2 Hz, 1H, ArH); ^{13}C NMR (100 MHz, C_6D_6): δ 18.9 (CH$_3$), 21.0 (CH$_3$), 23.6 (CH$_3$), 47.6 (CH), 49.7 (CH), 90.0 (C), 113.5 (CH), 114.2 (CH), 115.0 (CH), 126.8 (CH), 127.0 (CH), 128.3 (CH), 128.5 (CH), 129.8 (CH), 132.3 (C), 135.9 (C), 136.7 (C), 144.5 (C), 147.8 (C); HRMS (EI) calcd for $C_{21}H_{25}IN_4O_2S$ $[M]^+$ 524.0743, found 524.0746.

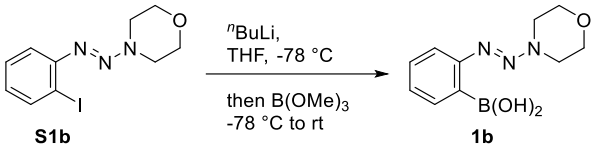
5. Typical procedure for the synthesis of *o*-triazenylarylboronic acid 1:[1] **Preparation of 2-(3,3-diisopropyltriaz-1-en-1-yl)phenylboronic acid (1d)**.



S1d **1d**

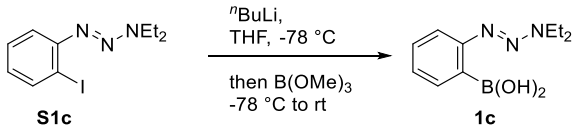
To a solution of **S1d** (6.62 g, 20.0 mmol) in THF (100 mL) was added ^{n}BuLi (1.6 M in *n*-hexane, 25.0 mL, 40.0 mmol) at –78 °C. After stirring at the same temperature for 30 min, a solution of B(OMe)$_3$ (4.50 mL, 40.0 mmol) in THF (20 mL) was added, and the mixture was allowed to warm to room temperature. After stirring overnight, the reaction was quenched with water, and the whole mixture was extracted with AcOEt. The combined organic layers were successively washed with saturated aqueous NH_4Cl, were dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude mixture, and Et_2O–*n*-hexane was added to the mixture. The formed precipitates were collected by suction and washed with Et_2O–*n*-hexane and dried in vacuo to give **1d** (4.33 g, 87%,) as a beige solid: mp 130 °C (decomp.); IR (KBr) ν 3382, 2980, 1587, 1395, 1240, 1101, 1017, 785 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.32 (broad doublet, 6H, CH(CH_3)$_2$), 1.42 (broad doublet, 6H, CH(CH_3)$_2$), 4.08 (broad septet, 1H, CH(CH$_3$)$_2$), 4.97 (broad septet, 1H, CH(CH$_3$)$_2$), 7.18 (t, J = 7.5 Hz, 1H, ArH), 7.40 (dt, J = 7.5, 1.2 Hz, 1H, ArH), 7.61 (d, J = 7.5 Hz, 1H, ArH), 7.62 (brs, 2H, B(OH)$_2$), 7.92 (d, J = 7.5 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2 (CH$_3$), 24.0 (CH$_3$), 47.5 (CH), 49.5 (CH), 115.2 (CH), 124.9 (CH), 131.6 (CH), 135.7 (CH), 156.1 (C) (*C*–B was not detected.); HRMS (EI) calcd for $C_{12}H_{20}BN_3O_2$ $[M]^+$ 249.1649, found 249.1651.

2-(Morpholinodiazenyl)phenylboronic acid (1b)



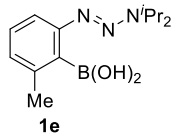
Starting material **S1b** was prepared according to the literature procedure.[16] Yield 67% (236 mg); purified by precipitation from Et_2O–*n*-hexane followed by washing with the same solvent; a beige solid; mp 89 °C (decomp.); IR (KBr) *v* 3354, 2853, 1590, 1348, 1108, 1013, 770 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.80–3.93 (m, 8H, -N(CH_2)$_2$O-), 7.05 (brs, 2H, B(O*H*)$_2$), 7.27 (dt, *J* = 7.2, 1.2 Hz, 1H, Ar*H*), 7.43 (dt, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 7.60 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.94 (dd, *J* = 7.2, 1.2 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 66.0 (CH_2 × 2), 115.76 (CH), 126.5 (CH), 131.8 (CH), 135.9 (CH), 154.5 (C) (*C*–B was not detected.); MS (EI) *m*/*z* 121 ([M-(Mor-N=N)]$^+$, 64), 149 ([M-(Mor)]$^+$, 13), 235 ([M]$^+$, 6), 327 ([boroxine+2H]$^{2+}$, 6).

2-(3,3-Diethyltriaz-1-en-1-yl)phenylboronic acid (1c)



Starting material **S1c** was prepared according to the literature procedure.[16] Yield 63% (139 mg); purified by precipitation from Et_2O–*n*-hexane followed by washing with the same solvent; a beige solid; mp 105 °C (decomp.); IR (KBr) *v* 3335, 2968, 1598, 1383, 1116, 1013, 774 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.31 (broad triplet, 3H, CH_2CH_3), 1.36 (broad triplet, 3H, CH_2CH_3), 3.75 (broad quartet, 2H, CH_2CH_3), 3.84 (broad quartet, 2H, CH_2CH_3), 7.18 (dt, *J* = 7.2, 1.2 Hz, 1H, Ar*H*), 7.41 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H, Ar*H*), 7.46 (brs, 2H, B(O*H*)$_2$), 7.64 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.92 (dd, *J* = 7.2, 1.6 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.6 (CH_3), 14.5 (CH_3), 42.0 (CH_2), 49.8 (CH_2), 115.1 (CH), 125.2 (CH), 131.6 (CH), 135.7 (CH), 155.4 (C) (*C*–B was not detected.); HRMS (EI) calcd for $C_{10}H_{16}BN_3O_2$ [M]$^+$ 221.1336, found 221.1336.

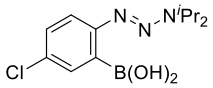
2-(3,3-Diisopropyltriaz-1-en-1-yl)-6-methylphenylboronic acid (1e)



Yield 57% (298 mg); purified by precipitation from Et_2O–*n*-hexane followed by washing with the same solvent; a pale yellow solid; mp 120–122 °C ; IR (KBr) *v* 3303, 2976, 1590, 1411, 1224, 1028, 813 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.31 (broad doublet, 6H, CH(CH_3)$_2$), 1.40 (broad doublet, 6H,

CH(C*H*$_3$)$_2$), 2.62 (s, 3H, ArC*H*$_3$), 4.06 (broad septet, 1H, C*H*(CH$_3$)$_2$), 4.95 (broad septet, 1H, C*H*(CH$_3$)$_2$), 7.01 (d, *J* = 7.2 Hz, 1H, Ar*H*), 7.26 (t, *J* = 7.2 Hz, 1H, Ar*H*), 7.41 (d, *J* = 7.2 Hz, 1H, Ar*H*), 7.45 (brs, 2H, B(O*H*)$_2$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 19.2 (CH$_3$), 23.7 (CH$_3$), 24.0 (CH$_3$), 47.4 (CH), 49.3 (CH), 113.7 (CH), 127.9 (CH), 130.4 (CH), 146.1 (C), 156.5 (C) (*C*–B was not detected.); HRMS (EI) calcd for $C_{13}H_{22}BN_3O_2$ $[M]^+$ 263.1805, found 263.1802.

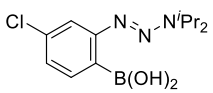
5-Chloro-2-(3,3-diisopropyltriaz-1-en-1-yl) phenylboronic acid (1f)



1f

Yield 79% (890 mg); purified by precipitation from Et$_2$O–*n*-hexane followed by washing with the same solvent; a beige solid; mp 130 °C (decomp.); IR (KBr) *v* 3350, 2980, 1587, 1407, 1028, 909, 826 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.32 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 1.42 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 4.10 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 4.93 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 7.33 (dd, *J* = 8.8, 2.4 Hz, 1H, Ar*H*), 7.54 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.86 (brs, 2H, B(O*H*)$_2$), 7.87 (d, *J* = 2.4 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, CDCl$_3$): δ 19.1 (CH$_3$), 24.0 (CH$_3$), 47.8 (CH), 49.7 (CH), 116.7 (CH), 130.4 (C), 131.5 (CH), 135.2 (CH), 154.5 (C) (*C*–B was not detected.); HRMS (EI) calcd for $C_{12}H_{19}ClN_3O_2B$ $[M]^+$ 283.1259, found 283.1260.

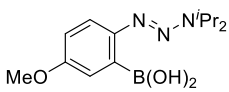
4-Chloro-2-(3,3-diisopropyltriaz-1-en-1-yl)phenylboronic acid (1f')



1f'

Yield 71% (282 mg); purified by precipitation from Et$_2$O–*n*-hexane followed by washing with the same solvent; a beige solid; mp 141–144 °C; IR (KBr) *v* 3350, 2980, 1587, 1399, 1021, 869 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.32 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 1.44 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 4.11 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 4.94 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 7.14 (dd, *J* = 8.0, 2.0 Hz, 1H, Ar*H*), 7.56 (d, *J* = 2.0 Hz, 1H, Ar*H*), 7.70 (brs, 2H, B(O*H*)$_2$), 7.85 (d, *J* = 8.0 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, CDCl$_3$): δ 19.1 (CH$_3$), 24.0 (CH$_3$), 47.9 (CH), 50.0 (CH), 115.4 (CH), 124.8 (CH), 137.0 (CH), 137.7 (C), 157.1 (C) (*C*–B was not detected.); HRMS (EI) calcd for $C_{12}H_{19}BClN_3O_2$ $[M]^+$ 283.1259, found 283.1263.

2-(3,3-Diisopropyltriaz-1-en-1-yl)-5-methoxyphenylboronic acid (1g)

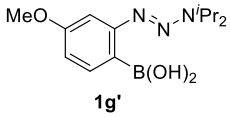


1g

Yield 73% (390 mg); purified by precipitation from Et$_2$O–*n*-hexane followed by washing with the same solvent; a pale brown solid; mp 88–90 °C; IR (KBr) *v* 3367, 2976, 1594, 1399, 1212, 1024, 822 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.33 (broad doublet, 6H, CH(C*H*$_3$)$_2$), 1.39 (broad doublet, 6H, CH(C*H*$_3$)$_2$), 3.85 (s, 3H, OC*H*$_3$), 4.03 (broad septet, 1H, C*H*(CH$_3$)$_2$), 4.91 (broad septet, 1H,

C*H*(CH_3)$_2$), 6.97 (dd, *J* = 8.8, 2.8 Hz, 1H, Ar*H*), 7.42 (d, *J* = 2.8 Hz, 1H, Ar*H*), 7.58 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.72 (brs, 2H, B(O*H*)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2 (CH_3), 24.0 (CH_3), 47.1 (CH), 49.2 (CH), 55.5 (CH_3), 116.6 (CH), 118.1 (CH), 118.9 (CH), 150.2 (C), 157.0 (C) (*C*–B was not detected.); HRMS (EI) calcd for $C_{13}H_{22}N_3O_3B$ $[M]^+$ 279.1754, found 279.1748.

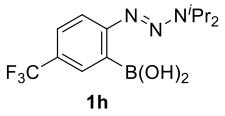
2-(3,3-Diisopropyltriaz-1-en-1-yl)-4-methoxyphenylboronic acid (1g')



1g'

Yield 76% (212 mg); purified by precipitation from Et_2O–*n*-hexane followed by washing with the same solvent; a pale yellow solid; mp 135–138 °C; IR (KBr) *v* 3362, 2976, 1597, 1407, 1223, 1124, 808 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.43 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 3.85 (s, 3H, OC*H*$_3$), 4.09 (septet, *J* = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 4.96 (septet, *J* = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 6.76 (dd, *J* = 8.0, 2.4 Hz, 1H, Ar*H*), 7.17 (d, *J* = 2.4 Hz, 1H, Ar*H*), 7.29 (brs, 2H, B(O*H*)$_2$), 7.85 (d, *J* = 8.0 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1 (CH_3), 24.0 (CH_3), 47.6 (CH), 49.6 (CH), 55.1 (CH_3), 100.4 (CH), 110.8 (CH), 137.1 (CH), 157.8 (C), 162.4 (C) (*C*–B was not detected.); HRMS (EI) calcd for $C_{13}H_{22}BN_3O_3$ $[M]^+$ 279.1754, found 279.1753.

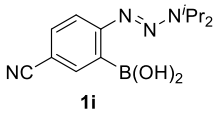
2-(3,3-Diisopropyltriaz-1-en-1-yl)-5-(trifluoromethyl)phenylboronic acid (1h)



1h

Yield 77% (490 mg); purified by precipitation from Et_2O–*n*-hexane followed by washing with the same solvent; a colorless solid; mp 93–96 °C; IR (KBr) *v* 3363, 2984, 1610, 1411, 1112, 925, 837 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.44 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 4.14 (septet, *J* = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 4.99 (septet, *J* = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 7.61 (dd, *J* = 8.8, 2.0 Hz, 1H, Ar*H*), 7.67 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.73 (brs, 2H, B(O*H*)$_2$), 8.20 (d, *J* = 2.0 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1 (CH_3), 24.0 (CH_3), 48.2 (CH), 50.1 (CH), 115.5 (CH), 124.5 (q, J_{CF} = 271 Hz, CF_3), 126.4 (q, J_{CF} = 31.5 Hz, C), 128.3 (q, J_{CF} = 3.8 Hz, CH), 132.9 (q, J_{CF} = 3.8 Hz, CH), 158.6 (C) (*C*–B was not detected.); HRMS (EI) calcd for $C_{13}H_{19}BF_3N_3O_2$ $[M]^+$ 317.1522, found 317.1524.

5-Cyano-2-(3,3-diisopropyltriaz-1-en-1-yl)phenylboronic acid (1i)

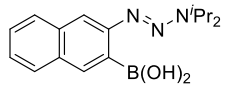


1i

Yield 64% (351 mg); purified by precipitation from Et_2O–*n*-hexane followed by washing with the same solvent; a yellow solid; mp 146–149 °C; IR (KBr) *v* 3363, 2980, 2219, 1594, 1407, 1028, 914, 738 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.45 (d, *J* = 6.8 Hz, 6H,

CH(C*H*$_3$)$_2$), 4.17 (septet, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 4.98 (septet, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 7.61 (brs, 2H, B(O*H*)$_2$), 7.63 (dd, *J* = 8.8, 1.6 Hz, 1H, Ar*H*), 7.66 (dd, *J* = 8.8, 0.4 Hz, 1H, Ar*H*), 8.23 (d, *J* = 1.6 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, CDCl$_3$): δ 19.0 (CH$_3$), 24.0 (CH$_3$), 48.6 (CH), 50.4 (CH), 107.7 (C), 115.9 (CH), 119.6 (C), 134.8 (CH), 140.5 (CH), 159.0 (C) (*C*–B was not detected.); HRMS (ESI) calcd for $C_{13}H_{20}BN_4O_2$ $[M+H]^+$ 275.1674, found 275.1679.

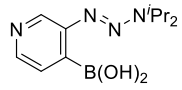
[3-(3,3-Diisopropyltriaz-1-en-1-yl)naphthalen-2-yl]boronic acid (1j)



1j

Yield 75% (182 mg); purified by precipitation from Et$_2$O–*n*-hexane followed by washing with the same solvent; a pale red solid; mp 125 °C (decomp.); IR (KBr) *v* 3374, 2980, 1733, 1594, 1372, 1152, 886, 746 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.37 (broad doublet, 6H, CH(C*H*$_3$)$_2$), 1.48 (broad doublet, 6H, CH(C*H*$_3$)$_2$), 4.13 (broad septet, 1H, C*H*(CH$_3$)$_2$), 5.05 (broad septet, 1H, C*H*(CH$_3$)$_2$), 7.38 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H, Ar*H*), 7.46 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H, Ar*H*), 7.53 (brs, 2H, B(O*H*)$_2$), 7.81 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.86 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.89 (s, 1H, Ar*H*), 8.49 (s, 1H, Ar*H*); ^{13}C NMR (100 MHz, CDCl$_3$): δ 19.3 (CH$_3$), 24.1 (CH$_3$), 47.6 (CH), 49.6 (CH), 111.5 (CH), 124.7 (CH), 127.2 (CH), 127.9 (CH), 128.6 (CH), 131.4 (C), 135.5 (C), 137.4 (CH), 152.5 (C) (*C*–B was not detected.); HRMS (EI) calcd for $C_{16}H_{22}BN_3O_2$ $[M]^+$ 299.1805, found 299.1806.

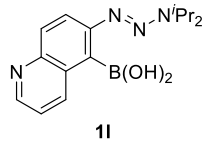
[3-(3,3-Diisopropyltriaz-1-en-1-yl)pyridin-4-yl]boronic acid (1k)



1k

Yield 41% (207 mg); purified by precipitation from Et$_2$O–*n*-hexane followed by washing with the same solvent; a pale yellow solid; mp 164 °C (decomp.); IR (KBr) *v* 3231, 2976, 1830, 1407, 1236, 1056, 909, 854, 778 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.33 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 1.45 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 4.12 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 5.00 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 7.30 (s, 2H, B(O*H*)$_2$), 7.72 (d, *J* = 4.8 Hz, 1H, Ar*H*), 8.41 (d, *J* = 4.8 Hz, 1H, Ar*H*), 8.86 (s, 1H, Ar*H*); ^{13}C NMR (100 MHz, CDCl$_3$): δ 19.1 (CH$_3$), 23.9 (CH$_3$), 47.5 (CH), 50.0 (CH), 128.7 (CH), 138.5 (CH), 145.4 (CH), 150.7 (C) (*C*–B was not detected.); HRMS (EI) calcd for $C_{11}H_{19}BN_4O_2$ $[M]^+$ 250.1601, found 250.1600.

[6-(3,3-Diisopropyltriaz-1-en-1-yl)quinolin-5-yl]boronic acid (1l)

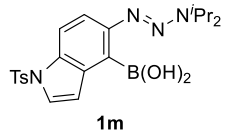


1l

Yield 55% (246 mg); purified by precipitation from Et$_2$O–*n*-hexane followed by washing with the same solvent; a beige solid; mp 131 °C (decomp.); IR (KBr) *v* 2980, 1587, 1367, 1236, 1092, 822 cm^{-1}; ^{1}H NMR

(400 MHz, $CDCl_3$): δ 1.37 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 1.48 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 4.16 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 5.01 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 7.40 (dd, *J* = 8.8, 3.6 Hz, 1H, Ar*H*), 7.71 (brs, 2H, B(O*H*)$_2$), 8.12 (d, *J* = 9.2 Hz, 1H, Ar*H*), 8.14 (d, *J* = 9.2 Hz, 1H, Ar*H*), 8.79 (d, *J* = 3.6 Hz, 1H, Ar*H*), 9.56 (d, *J* = 8.8 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2 (CH_3), 24.0 (CH_3), 48.2 (CH), 50.0 (CH), 119.8 (CH), 121.4 (CH), 133.3 (C), 133.4 (CH), 137.6 (CH), 147.1 (C), 148.6 (CH), 155.8 (C) (*C*–B was not detected.); HRMS (ESI) calcd for $C_{17}H_{26}BN_4O_2$ $[M+H]^+$ 329.2143, found 329.2146 [Molecular ion peak was detected as dimethyl boronate (Ar-B(OMe)$_2$), because MeOH was used as a solvent for ionization.].

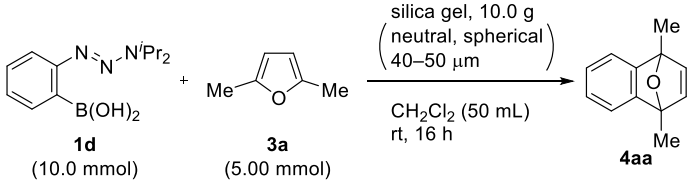
[5-(3,3-Diisopropyltriaz-1-en-1-yl)-1-tosyl-1*H*-indol-4-yl]boronic acid (1m)



1m

Yield 63% (227 mg); purified by precipitation from Et_2O–*n*-hexane followed by washing with the same solvent; a pale gray solid; mp 148 °C (decomp.); IR (KBr) *ν* 3352, 2976, 1577, 1409, 1167, 814, 762 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (broad doublet, 6H, CH(C*H*$_3$)$_2$), 1.42 (broad doublet, 6H, CH(C*H*$_3$)$_2$), 2.31 (s, 3H, ArC*H*$_3$), 4.08 (broad septet, 1H, C*H*(CH$_3$)$_2$), 4.92 (broad septet, 1H, C*H*(CH$_3$)$_2$), 7.17 (d, *J* = 6.0 Hz, 2H, Ar*H*), 7.47 (d, *J* = 2.8 Hz, 1H, Ar*H*), 7.55 (d, *J* = 2.8 Hz, 1H, Ar*H*), 7.65 (d, *J* = 7.2 Hz, 1H, Ar*H*), 7.72 (d, *J* = 6.0 Hz, 2H, Ar*H*), 7.96 (brs, 2H, B(O*H*)$_2$), 8.03 (d, *J* = 7.2 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1 (CH_3), 21.5 (CH_3), 24.0 (CH_3), 47.6 (CH), 49.5 (CH), 112.6 (CH), 112.9 (CH), 116.5 (CH), 126.6 (CH), 126.7 (CH), 129.7 (CH), 132.6 (C), 135.4 (C), 136.7 (C), 144.7 (C), 153.2 (C) (*C*–B was not detected.); HRMS (ESI) calcd for $C_{23}H_{32}BN_4O_4S$ $[M+H]^+$ 470.2232, found 470.2230 [Molecular ion peak was detected as dimethyl boronate (Ar-B(OMe)$_2$), because MeOH was used as a solvent for ionization.].

6. Procedure for the large scale reaction of *o*-triazenylarylboronic acid 1d and 2,5-dimethylfuran (3a) induced by silica gel.

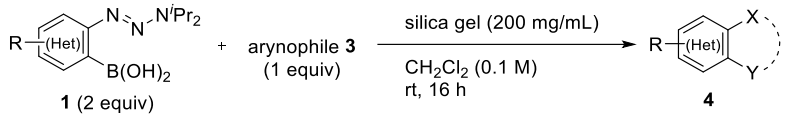


1d (10.0 mmol) **3a** (5.00 mmol) **4aa**

To a suspension of 2,5-dimethylfuran (**3a**, 0.534 mL, 5.00 mmol) and silica gel (neutral, spherical, 40–50 μm, 10.0 g, used after heating under vacuum to dryness) in CH_2Cl_2

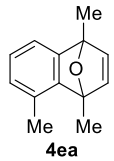
(50 mL) was added aryne precursor **1d** (2.49 g, 10.0 mmol). After stirring at room temperature for 16 h, silica gel was filtered off using CH_2Cl_2 as the eluent, and the eluent was concentrated in vacuo to furnish the crude product, which was purified by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt) to give cycloadduct **4aa** (810 mg, 94%) as 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*).[2)]

7. Typical procedure for the silica gel induced reactions of *o*-triazenylarylboronic acid 1 and arynophiles.



To a suspension of arynophile **3** (0.100 mmol) and silica gel (neutral, spherical, 40–50 μm, 200 mg, used after heating under vacuum to dryness prior to use) in CH_2Cl_2 (1.0 mL) was added aryne precursor **1** (0.200 mmol). After stirring at room temperature for 16 h, silica gel was filtered off, and the eluent was concentrated in vacuo to furnish the crude product. ^{1}H NMR yield was estimated by analysis of the crude product using 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified by column chromatography to give adduct **4**.

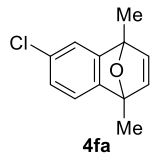
1,4,5-Trimethyl-1,4-dihydro-1,4-epoxynaphthalene (4ea)[17]



4ea

Yield 84% (15.7 mg); purified by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt); a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.86 (s, 3H, C*H*$_3$), 2.01 (s, 3H, C*H*$_3$), 2.36 (s, 3H, ArC*H*$_3$), 6.72 (d, *J* = 7.6 Hz, 1H, Ar*H*), 6.75 (d, *J* = 5.2 Hz, 1H, C*H*=CH), 6.80 (d, *J* = 5.2 Hz, 1H, C*H*=CH), 6.86 (t, *J* = 7.6 Hz, 1H, Ar*H*), 6.95 (d, *J* = 7.6 Hz, 1H, Ar*H*).

6-Chloro-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene (4fa)

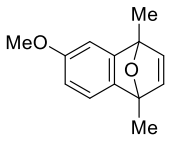


4fa

Yield 98% (from **1f**, 20.2 mg); purified by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt); a yellow oil; IR (KBr) *ν* 3075, 2976, 1590, 1379, 1303, 1140, 862 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.86 (s, 3H, C*H*$_3$), 1.87 (s, 3H, C*H*$_3$), 6.75 (d, *J* = 5.2 Hz, 1H, C*H*=CH), 6.77 (d, *J* = 5.2 Hz, 1H, C*H*=CH), 6.94 (dd, *J* = 7.6, 2.0 Hz, 1H, Ar*H*), 7.01 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.09 (d, *J* = 2.0 Hz, 1H, Ar*H*);

^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1 (CH_3), 15.2 (CH_3), 88.4 (C × 2), 119.1 (CH), 119.4 (CH), 124.2 (CH), 130.5 (C), 146.3 (CH), 146.9 (CH), 151.1 (C), 155.1 (C); HRMS (EI) calcd for $C_{12}H_{11}ClO$ $[M]^+$ 206.0498, found 206.0496.

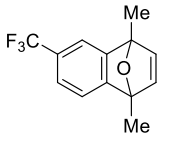
6-Methoxy-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene (4ga)[17)]



4ga

Yield 98% (from **1g**, 19.9 mg); purified by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt); a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.85 (s, 3H, C*H*$_3$), 1.86 (s, 3H, C*H*$_3$), 3.76 (s, 3H, OC*H*$_3$), 6.40 (dd, *J* = 7.5, 2.1 Hz, 1H, Ar*H*), 6.73 (d, *J* = 5.1 Hz, 1H, C*H*=CH), 6.76 (s, 1H, Ar*H*), 6.77 (d, *J* = 5.1 Hz, 1H, C*H*=CH), 6.99 (d, *J* = 7.5 Hz, 1H, Ar*H*).

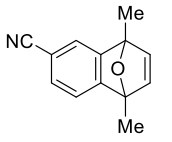
1,4-Dimethyl-6-(trifluoromethyl)-1,4-dihydro-1,4-epoxynaphthalene (4ha)[16)]



4ha

Yield 68% (16.2 mg); purified by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt); a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.90 (s, 3H, C*H*$_3$), 1.91 (s, 3H, C*H*$_3$), 6.77 (d, *J* = 5.4 Hz, 1H, C*H*=CH), 6.79 (d, *J* = 5.4 Hz, 1H, C*H*=CH), 7.18 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.28 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.31 (s, 1H, Ar*H*).

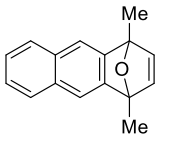
6-Cyano-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene (4ia)[18)]



4ia

Yield 96% (18.9 mg); purified by column chromatography (silica gel, 4:1 *n*-hexane/AcOEt); a brown oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.89 (s, 3H, C*H*$_3$), 1.90 (s, 3H, C*H*$_3$), 6.76 (d, *J* = 5.4 Hz, 1H, C*H*=CH), 6.79 (d, *J* = 5.4 Hz, 1H, C*H*=CH), 7.19 (dd, *J* = 7.2, 1.2 Hz, 1H, Ar*H*), 7.33 (s, 1H, Ar*H*), 7.36 (dd, *J* = 7.2, 1.2 Hz, 1H, Ar*H*).

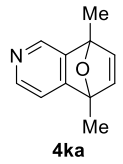
1,4-Dimethyl-1,4-dihydro-1,4-epoxyanthracene (4ja)[19)]



4ja

Yield 93% (20.7 mg); purified by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt); a purple solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.96 (s, 6H, C*H*$_3$), 6.70 (s, 2H, C*H*=C*H*), 7.41 (dd, *J* = 6.0, 3.3 Hz, 2H, Ar*H*), 7.43 (s, 2H, Ar*H*), 7.70 (dd, *J* = 6.0, 3.3 Hz, 2H, Ar*H*).

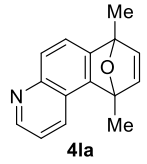
5,8-Dimethyl-5,8-dihydro-5,8-epoxyisoquinoline (4ka)[20)]



4ka

The reaction was performed using **1k** (25.0 mg, 0.100 mmol), **3a** (53.4 μL, 0.500 mmol), silica gel (200 mg), and CH_2Cl_2 (1.0 mL). Yield 62% (10.8 mg); purified by column chromatography (silica gel, AcOEt only); a colorless solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.88 (s, 3H, C*H*$_3$), 1.94 (s, 3H, C*H*$_3$), 6.74 (d, *J* = 5.4 Hz, 1H, C*H*=CH), 6.80 (d, *J* = 5.4 Hz, 1H, C*H*=CH) , 7.10 (d, *J* = 4.8 Hz, 1H, Ar*H*), 8.30 (d, *J* = 4.8 Hz, 1H, Ar*H*), 8.33 (s, 1H, Ar*H*).

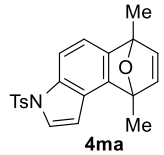
7,10-Dimethyl-7,10-dihydro-7,10-epoxybenzo[*f*]quinoline (4la)



4la

The reaction was performed using **1l** (29.9 mg, 0.100 mmol), **3a** (21.4 μL, 0.200 mmol), silica gel (200 mg), and CH_2Cl_2 (1.0 mL). Yield 63% (14.0 mg); purified by column chromatography (silica gel, 3:2 *n*-hexane/AcOEt); a colorless oil; IR (KBr) *v* 3049, 2976, 1512, 1381, 1296, 1149, 885, 728 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01 (s, 3H, C*H*$_3$), 2.27 (s, 3H, C*H*$_3$), 6.94 (d, *J* = 5.2 Hz, 1H, C*H*=CH), 7.00 (d, *J* = 5.2 Hz, 1H, C*H*=CH), 7.34 (dd, *J* = 8.0, 4.0 Hz, 1H, Ar*H*), 7.62 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.87 (d, *J* = 8.0 Hz, 1H, Ar*H*), 8.35 (d, *J* = 8.0 Hz, 1H, Ar*H*), 8.81 (dd, *J* = 4.0, 1.6 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.3 (CH_3), 18.5 (CH_3), 89.1 (C), 90.5 (C), 120.5 (CH), 121.0 (CH), 122.7 (C), 127.2 (CH), 130.7 (CH), 146.3 (C), 148.1 (CH), 148.4 (CH), 149.7 (CH), 150.0 (C), 153.0 (C); HRMS (EI) calcd for $C_{15}H_{13}NO$ $[M]^+$ 223.0997, found 223.0998.

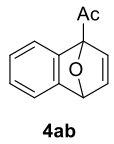
6,9-Dimethyl-3-tosyl-6,9-dihydro-3*H*-6,9-epoxybenzo[*e*]indole (4ma)



4ma

Yield 96% (35.0 mg); purified by column chromatography (silica gel, 4:1 *n*-hexane/AcOEt); a pale yellow solid; mp 167–169 °C; IR (KBr) *v* 3369, 2972, 2243, 1594, 1372, 1144, 997, 850, 734 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.91 (s, 3H, C*H*$_3$), 2.04 (s, 3H, C*H*$_3$), 2.34 (s, 3H, ArC*H*$_3$), 6.65 (dd, *J* = 4.0, 0.8 Hz, 1H, Ar*H*), 6.83 (d, *J* = 5.2 Hz, 1H, C*H*=CH), 6.85 (d, *J* = 5.2 Hz, 1H, C*H*=CH), 7.12 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.20 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.58 (d, *J* = 4.0 Hz, 1H, Ar*H*), 7.60 (dd, *J* = 8.0, 0.8 Hz, 1H, Ar*H*), 7.72 (d, *J* = 8.0 Hz, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.5 (CH_3), 16.6 (CH_3), 21.5 (CH_3), 89.2 (C), 89.3 (C), 105.6 (CH), 108.9 (CH), 115.1 (CH), 124.5 (C), 126.8 (CH), 128.2 (CH), 129.8 (CH), 133.6 (C), 134.9 (C), 144.9 (C), 145.4 (C), 146.9 (CH), 147.9 (CH), 148.5 (C); HRMS (EI) calcd for $C_{21}H_{19}NO_3S$ $[M]^+$ 365.1086, found 365.1082.

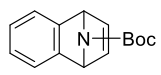
1-Acetyl-1,4-dihydro-1,4-epoxynaphthalene (4ab)[2)]



4ab

Yield 91% (17.0 mg); purified by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt); a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H, $COCH_3$), 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*).

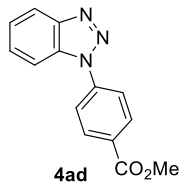
9-(*tert*-Butoxycarbonyl)-1,4-dihydro-1,4-epiminonaphthalene (4ac)[21)]



4ac

Yield 82% (19.9 mg); purified by column chromatography (silica gel, 4:1 *n*-hexane/AcOEt); a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.37 (s, 9H, *t*-Bu), 5.48 (brs, 2H, NC*H*), 6.92–6.98 (m, 4H, C*H*=C*H* and Ar*H*), 7.25 (brs, 2H, Ar*H*).

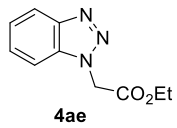
1-(4-Methoxycarbonylphenyl)-1,2,3-benzotriazol (4ad)[2)]



4ad

Yield 68% (17.1 mg); purified by column chromatography (silica gel, 3:1 *n*-hexane/AcOEt); a colorless solid; ^{1}H 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*).

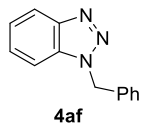
1-Ethoxycarbonylmethyl-1,2,3-benzotriazol (4ae)[2)]



4ae

Yield 81% (16.6 mg); purified by column chromatography (silica gel, 2:1 *n*-hexane/AcOEt); a colorless solid; ^{1}H 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 = 8.4, 6.3, 1.5 Hz, 1H, Ar*H*), 7.46–7.56 (m, 2H, Ar*H*), 8.10 (dt, J = 8.4, 0.9 Hz, 1H, Ar*H*).

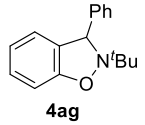
1-Phenylmethyl-1,2,3-benzotriazol (4af)[2)]



4af

Yield 75% (15.7 mg); purified by column chromatography (silica gel, 3:1 *n*-hexane/AcOEt); a colorless solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.85 (s, 2H, NCH_2Ph), 7.26–7.43 (m, 8H, Ar*H*), 8.07 (dd, J = 8.7, 1.2 Hz, 1H, Ar*H*).

2-*tert*-Butyl-3-phenyl-2,3-dihydrobenzo[*d*]isoxazole (4ag)[21)]

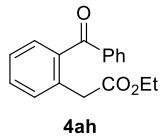


4ag

Yield 96% (24.2 mg); purified by column chromatography (silica gel, 20:1 *n*-hexane/AcOEt); a brown solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17 (s, 9H, *t*-Bu), 5.58 (s, 1H, Ar_2CH), 6.76–6.81 (m, 2H, Ar*H*), 6.87 (d, J = 6.6 Hz, 1H,

Ar*H*), 7.13 (t, *J* = 7.8 Hz, 1H, Ar*H*), 7.21–7.26 (m, 1H, Ar*H*), 7.31 (t, *J* = 7.8 Hz, 2H, Ar*H*), 7.39 (d, *J* = 7.8 Hz, 2H, Ar*H*).

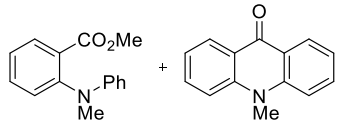
Ethyl (2-benzoylphenyl)acetate (4ah)[22)]



4ah

Yield 51% (13.7 mg); purified by column chromatography (silica gel, 4:1 *n*-hexane/AcOEt, then CH_2Cl_2); a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.11 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3), 3.88 (s, 2H, $ArCH_2$), 4.01 (q, *J* = 7.2 Hz, 2H, OCH_2CH_3), 7.30–7.49 (m, 6H, Ar*H*), 7.57 (t, *J* = 7.8 Hz, 1H, Ar*H*), 7.81 (dd, *J* = 7.8 Hz, 2H, Ar*H*).

Methyl 2-[Methyl(phenyl)amino]benzoate (4ai)[23)] **and *N*-methylacridone (4ai')**[24)]

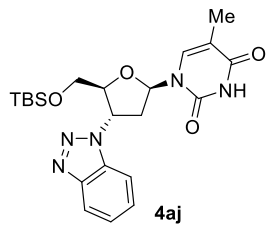


4ai **4ai'**

4ai: Yield 75% (18.2 mg); purified by column chromatography (silica gel, 20:1 to 3:2 *n*-hexane/AcOEt); a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.28 (s, 3H, NCH_3), 3.58 (s, 3H, OCH_3), 6.63 (d, *J* = 8.1 Hz, 2H, Ar*H*), 6.73 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.15 (dd, *J* = 8.1, 1.5 Hz, 2H, Ar*H*), 7.22–7.29 (m, 2H, Ar*H*), 7.52 (dt, *J* = 7.5, 1.5 Hz, 1H, Ar*H*), 7.79 (dd, *J* = 7.5, 1.5 Hz, 1H, Ar*H*).

4ai': Yield 22% (4.7 mg); a colorless solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.91 (s, 3H, NCH_3), 7.31 (t, *J* = 7.5 Hz, 2H, Ar*H*), 7.54 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.74 (ddd, *J* = 8.4, 7.5, 1.8 Hz, 2H, Ar*H*), 8.57 (dd, *J* = 7.5, 1.8 Hz, 2H, Ar*H*).

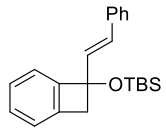
3'-(1*H*-Benzotriazol-1-yl)-5'-*O*-*tert*-butyldimethylsilyl-3'-deoxythymidine (4aj)[2)]



4aj

Yield 87% (40.0 mg); purified by column chromatography (silica gel, 1:2 *n*-hexane/CH_2Cl_2); a colorless amorphous; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.11 (s, 3H, $SiCH_3$), 0.14 (s, 3H, $SiCH_3$), 0.96 (s, 9H, ^{t}Bu), 2.00 (s, 3H, $ArCH_3$), 2.72 (ddd, *J* = 14.0, 8.4, 6.0 Hz, 1H, H-2'a), 3.22 (dt, *J* = 14.0, 6.0 Hz, 1H, H-2'b), 3.79 (dd, *J* = 11.6, 2.0 Hz, 1H, H-5'a), 4.07 (dd, *J* = 11.6, 2.0 Hz, 1H, H-5'b), 4.63–4.64 (m, 1H, H-4'), 5.58 (dt, *J* = 8.8, 5.2 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, Ar*H* × 2 and N-C*H*=C), 8.13 (d, *J* = 8.4 Hz, 1H, Ar*H*), 8.34 (s, 1H, N*H*).

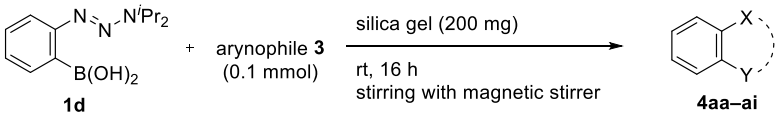
1-(*tert*-Butyldimethylsilyloxy)-1-(*E*)-styrylbenzocyclobutane (4ak)



4ak

Yield 58% (19.4 mg); purified by column chromatography (silica gel, 10:1 *n*-hexane/CH_2Cl_2 + 1% Et_3N); a colorless oil; IR (KBr) *v* 2928, 1459, 1254, 1223, 1069, 966, 835 cm^{-1}; ^1H NMR (400 MHz, C_6D_6): δ –0.18 (s, 3H, SiC*H*$_3$), –0.06 (s, 3H, SiC*H*$_3$), 0.86 (s, 9H, ^{t}Bu), 3.18 (d, *J* = 14.0 Hz, 1H, PhC*H*H), 3.25 (d, *J* = 14.0 Hz, 1H, PhCH*H*), 6.34 (d, *J* = 15.6 Hz, 1H, Ph-CH=C*H*-), 6.73 (d, *J* = 15.6 Hz, 1H, Ph-C*H*=CH-), 6.84 (t, *J* = 7.2 Hz, 2H, Ar*H*), 6.88–6.98 (m, 5H, Ar*H*), 7.04 (d, *J* = 7.2 Hz, 2H, Ar*H*); ^{13}C NMR (100 MHz, C_6D_6): δ –3.0 (CH_3), –2.8 (CH_3), 18.4 (C), 26.0 (CH_3), 49.1 (CH_2), 81.5 (C), 122.8 (CH), 124.4 (CH), 126.9 (CH), 127.5 (CH), 127.6 (CH), 128.2 (CH, overlapping with C_6D_6), 128.8 (CH), 129.7 (CH), 134.3 (CH), 137.4 (C), 141.9 (C), 149.8 (C); HRMS (FAB) calcd for $C_{22}H_{28}OSi$ $[M]^+$ 336.1909, found 336.1905.

8. Typical procedure for the solid-state reactions of *o*-triazenylarylboronic acid 1 and arynophiles.



The mixture of aryne precursor **1d** (0.200 mmol), arynophile **3** (0.100 mmol), and silica gel (neutral, spherical, 40–50 μm, 200 mg, heated under vacuum to dryness prior to use) was stirred at room temperature. After 16 h, filtration with THF and evaporation in vacuo furnished the crude product, which was analyzed on ^1H NMR using 1,1,2,2-tetrachloroethane as an internal standard to estimate the yield of **4**.

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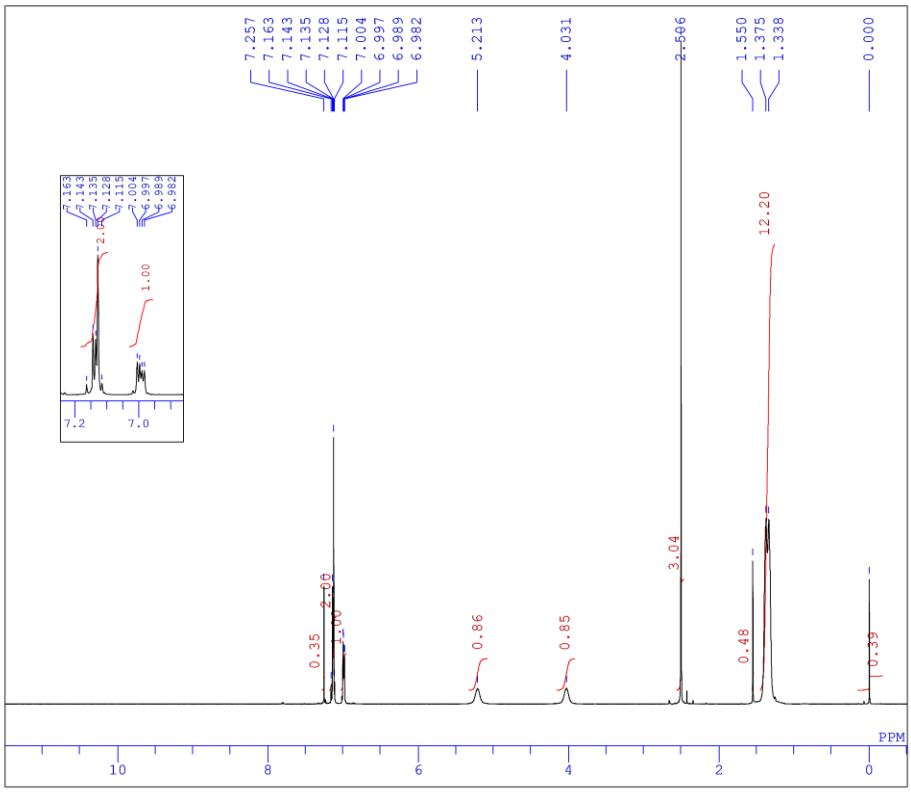
1-(2-Iodo-3-methylphenyl)-3,3-diisopropyltriaz-1-ene (S1e)

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PD            5.0000 sec
PW1              3.35 usec
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CTEMP          19.3 c
SLVNT  CDCL3
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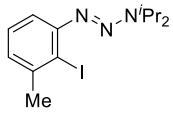
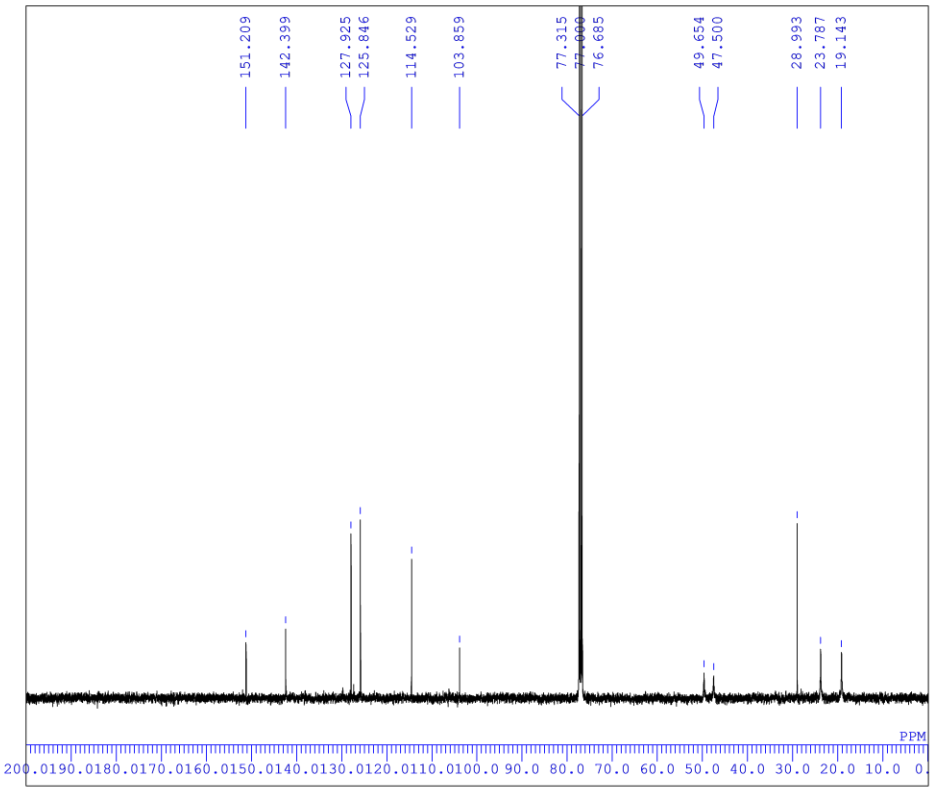


S1e

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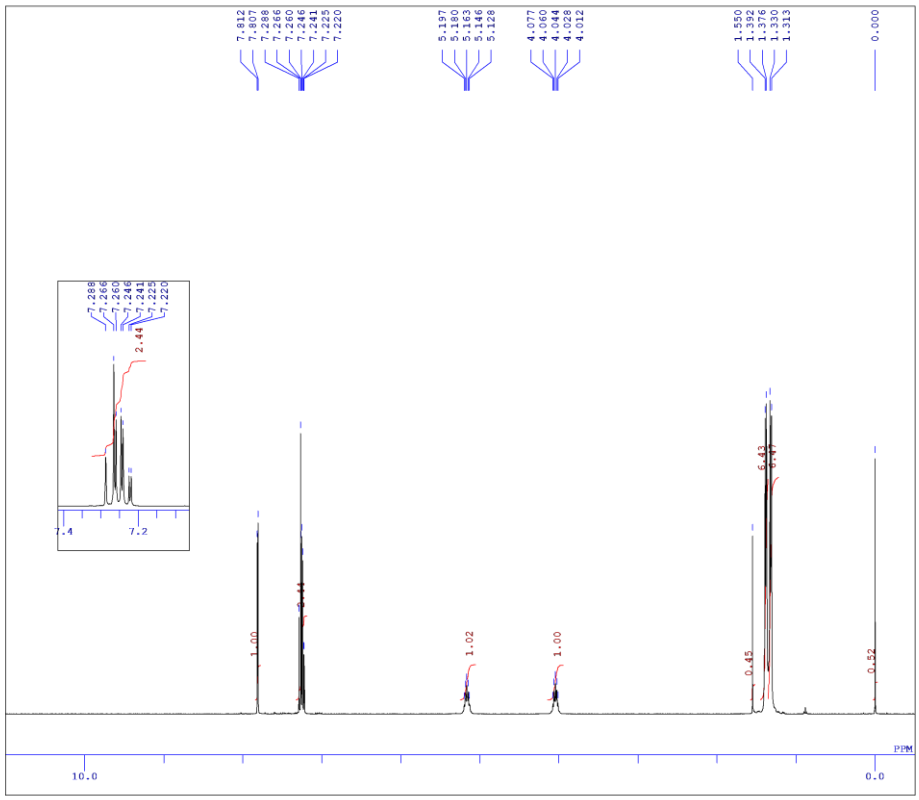
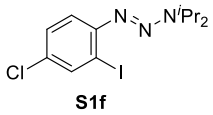
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            60
```

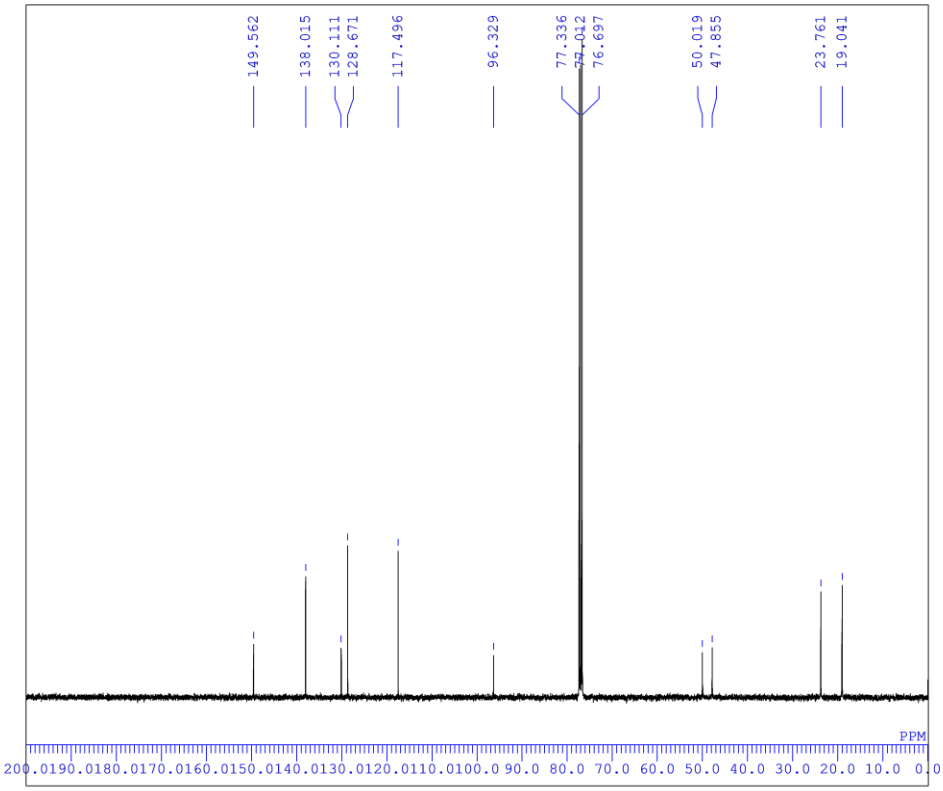
1-(4-Chloro-2-iodophenyl)-3,3-diisopropyltriaz-1-ene (S1f)




```
DFILE YY306_1H-normal-1-1 I
COMNT single_pulse
DATIM 2020-10-09 11:41:48
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         19.7 c
SLVNT CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           40
```

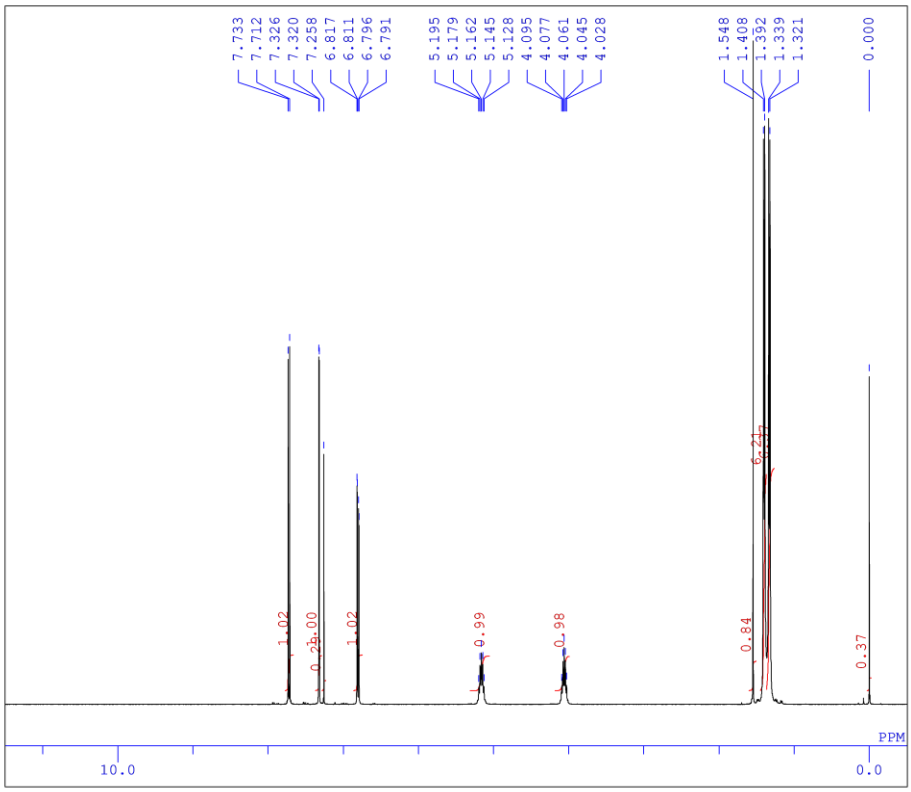


S1f



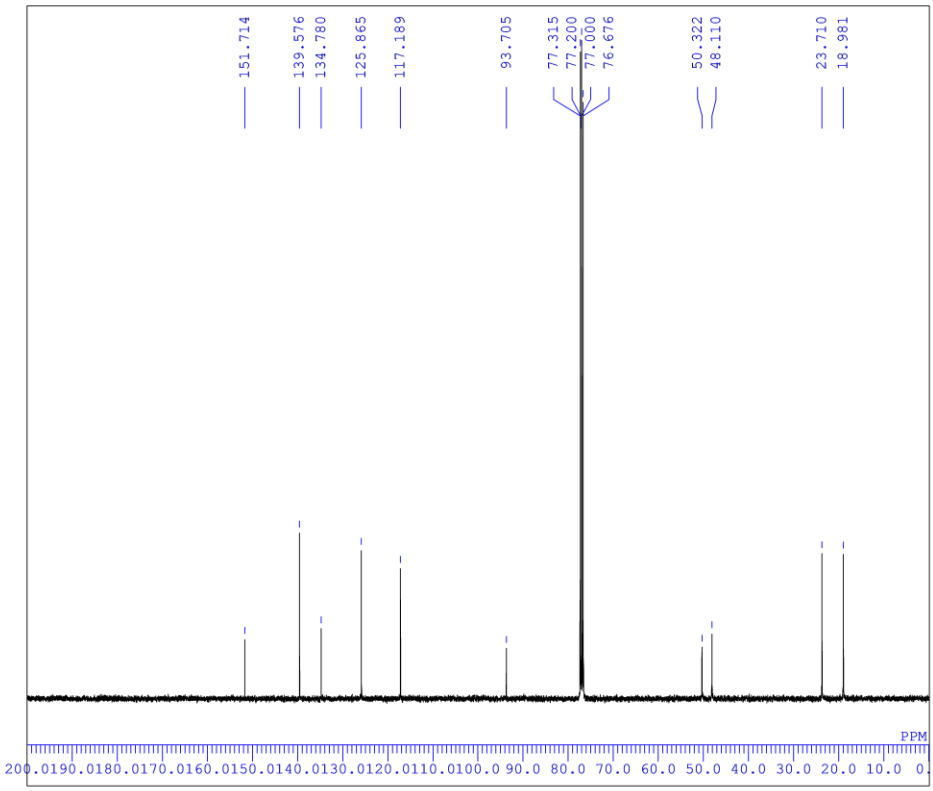

```
DFILE  YY306_E13C-1-1 Ï.al
COMNT  single pulse decoup
DATIM  2020-10-09 11:44:48
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ       100.53 MHz
OBSET         5.35 KHz
OBFIN         5.86 Hz
POINT        26214
FREQU      25125.63 Hz
SCANS          1300
ACQTM       1.0433 sec
PD          2.0000 sec
PW1            3.60 usec
IRNUC  1H
CTEMP         19.5 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            1.20 Hz
RGAIN           60
```

1-(5-Chloro-2-iodophenyl)-3,3-diisopropyltriaz-1-ene (S1f')



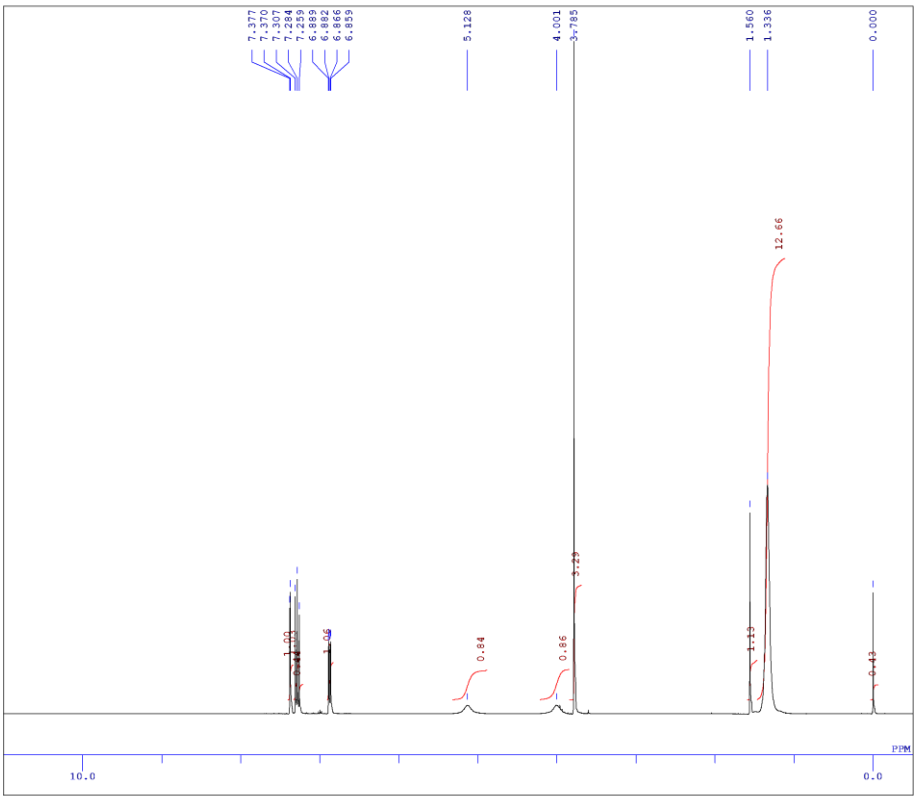

```
DFILE  YY297__1H-normal-1-
COMNT  single_pulse
DATIM  2020-08-20 11:49:24
OBNUC  1H
EXMOD  single_pulse.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         26214
FREQU       6002.40 Hz
SCANS            16
ACQTM         4.3673 sec
PD            5.0000 sec
PW1             3.35 usec
IRNUC  1H
CTEMP          24.5 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            38
```

S1f'



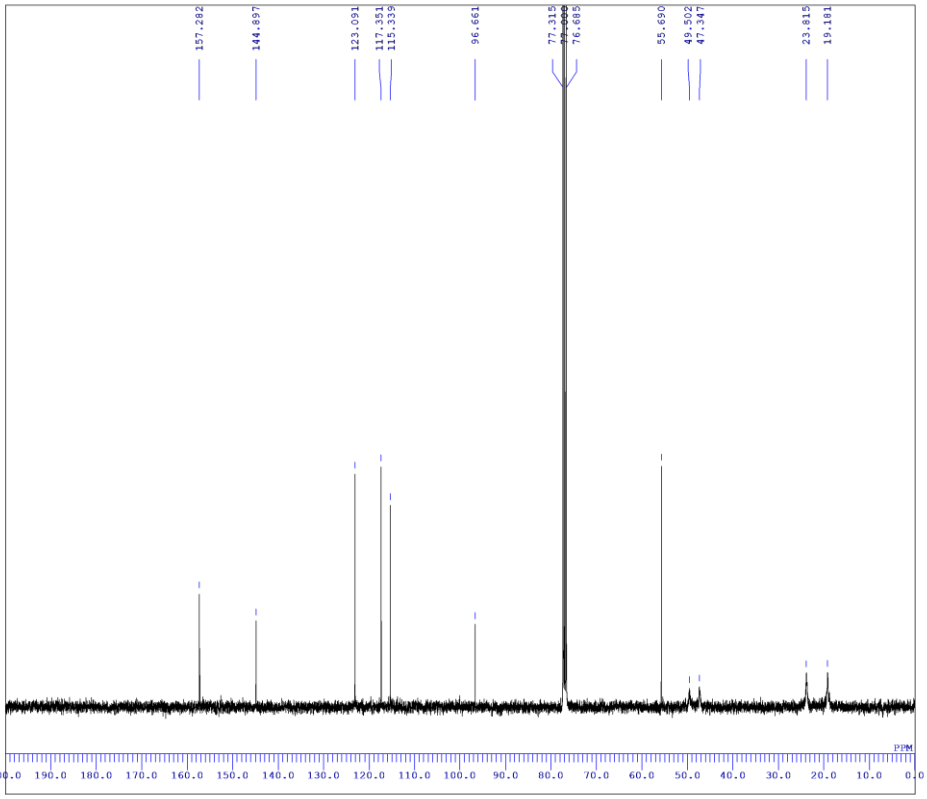

```
DFILE  YY297_E13C-1-1 Ï.al
COMNT  single pulse decoup
DATIM  2020-08-20 11:52:24
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26214
FREQU      25125.63 Hz
SCANS          1500
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.60 usec
IRNUC  1H
CTEMP          24.7 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            60
```

1-(2-Iodo-4-methoxyphenyl)-3,3-diisopropyltriaz-1-ene (S1g)



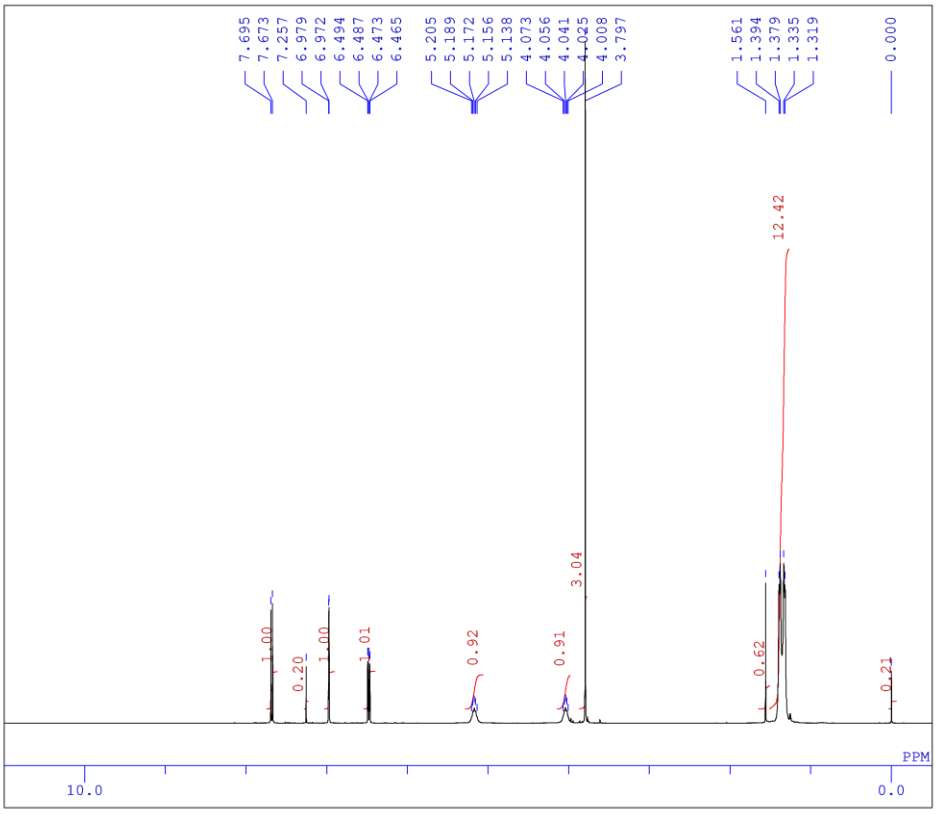
DFILE OMe_1H-normal-1-1.als
COMNT single_pulse
DATIM 2020-09-08 11:29:32
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 26214
FREQU 6002.40 Hz
SCANS 16
ACQTM 4.3673 sec
PD 5.0000 sec
PW1 3.35 usec
IRNUC 1H
CTEMP 23.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40

S1g

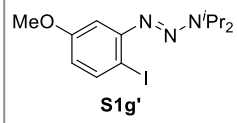


DFILE OMe_E13C-1-1 I.als
COMNT single pulse decoupled
DATIM 2020-09-08 11:32:33
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1500
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.60 usec
IRNUC 1H
CTEMP 23.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60

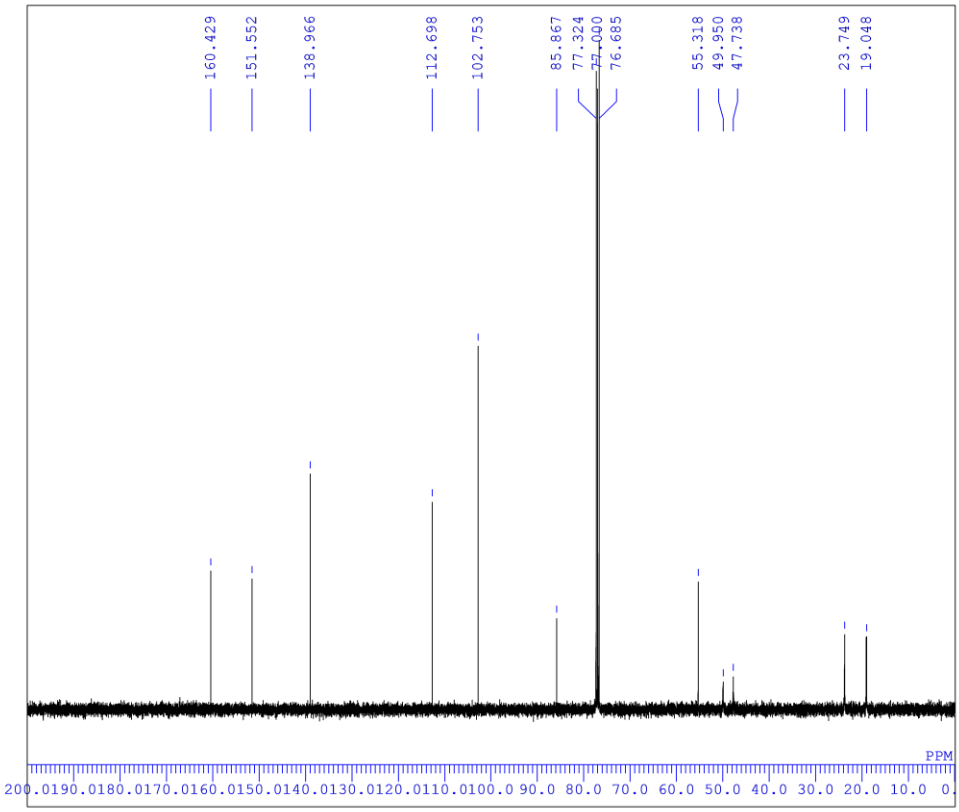
1-(2-Iodo-5-methoxyphenyl)-3,3-diisopropyltriaz-1-ene (S1g')




```
DFILE  5-MeO-2-iodoC6H3N=N
COMNT  single_pulse
DATIM  2020-06-08 16:55:01
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          0.00 ppm
BF             0.17 Hz
RGAIN            36
```

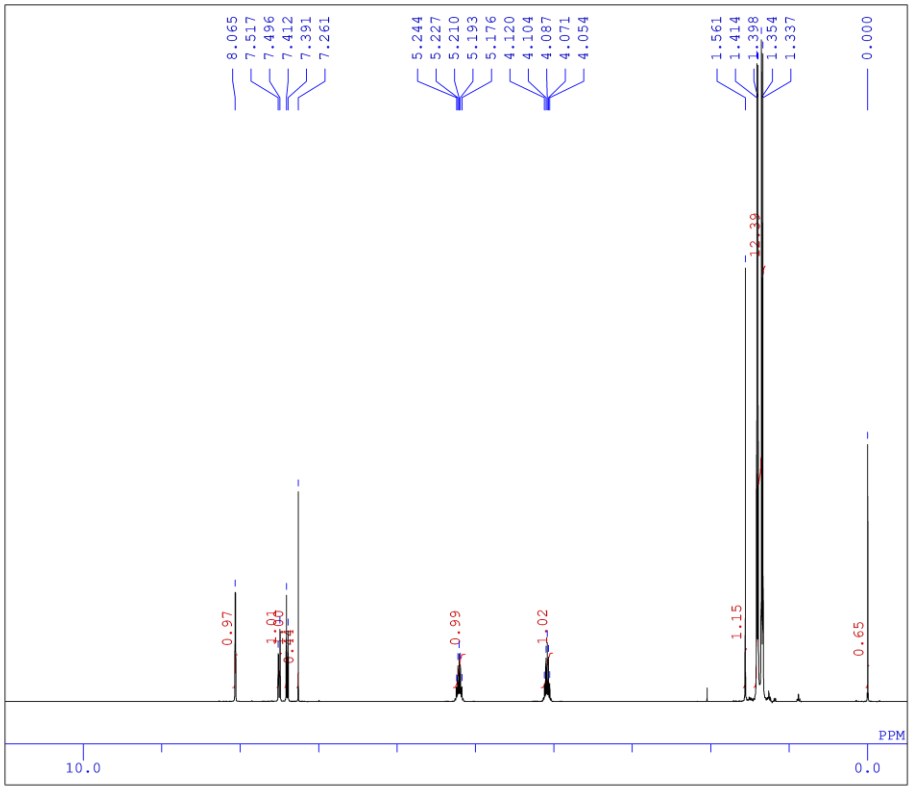


S1g'

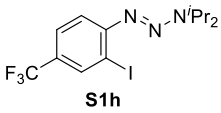



```
DFILE  5-MeO-2-iodoC6H3N=N
COMNT  single pulse decoup
DATIM  2020-06-08 16:58:00
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26214
FREQU      25125.63 Hz
SCANS            512
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.60 usec
IRNUC  1H
CTEMP          22.6 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.17 Hz
RGAIN            60
```

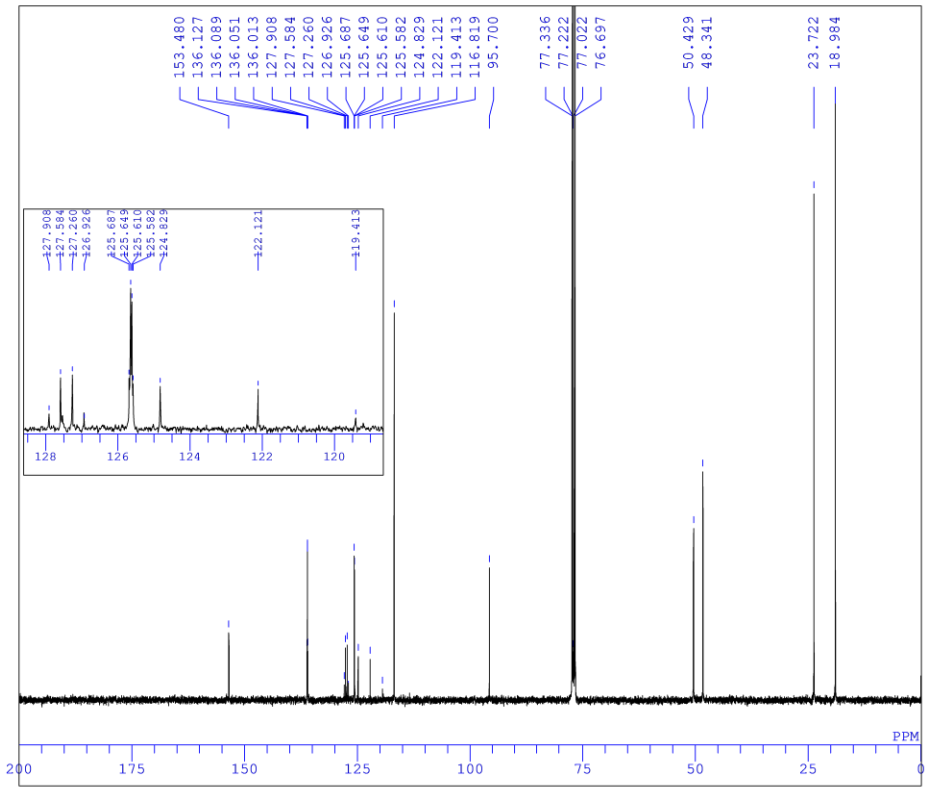
1-[2-Iodo-4-(trifluoromethyl)phenyl]-3,3-diisopropyltriaz-1-ene (S1h)




```
DFILE  4CF3-2iodoC6H3N=N-N
COMNT  single_pulse
DATIM  2020-10-27 11:28:59
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          19.8 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            42
```

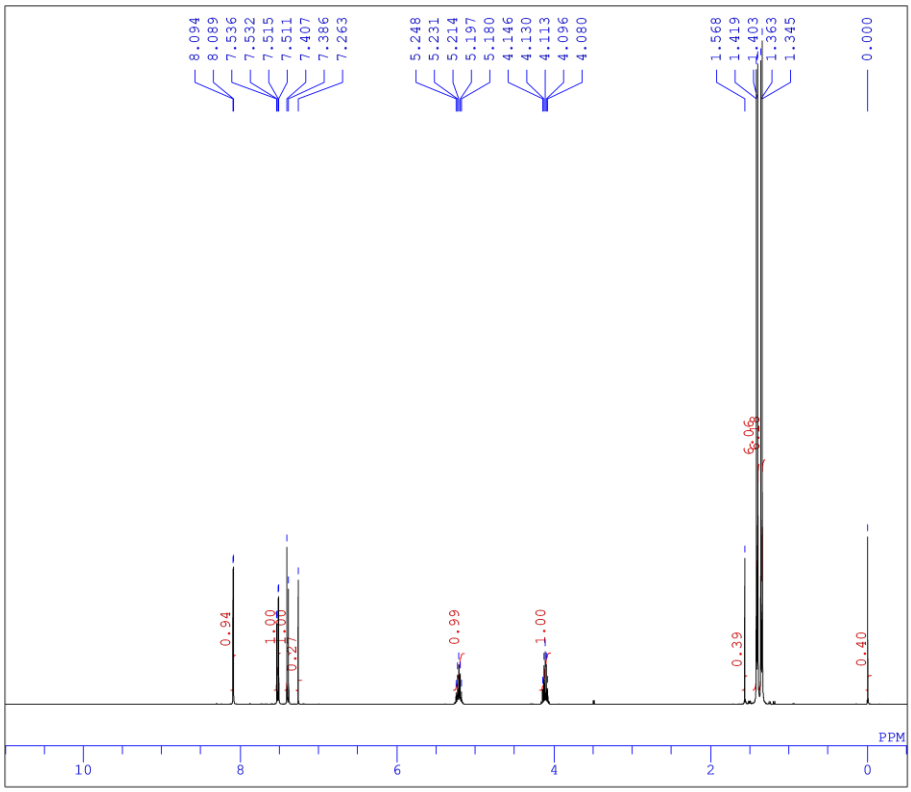


S1h

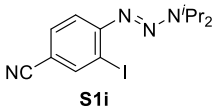



```
DFILE  4CF3-2iodoC6H3N=N-N
COMNT  single pulse decoup
DATIM  2020-10-28 11:21:06
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26214
FREQU      25125.63 Hz
SCANS          2600
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.60 usec
IRNUC  1H
CTEMP          20.7 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             1.20 Hz
RGAIN            60
```

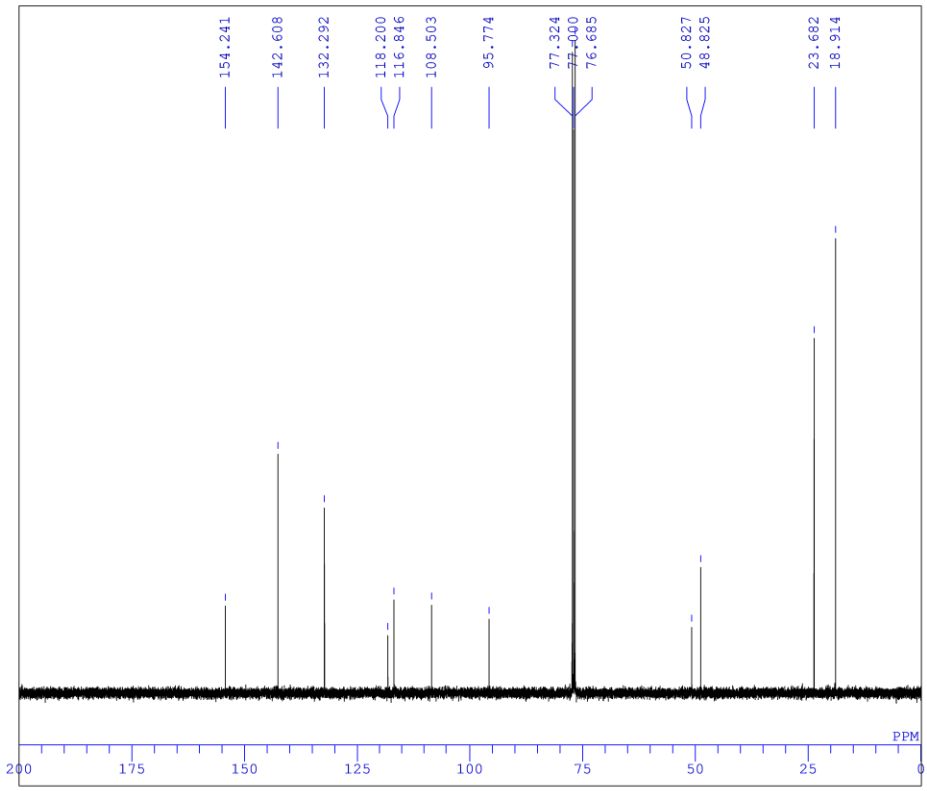
1-(4-Cyano-2-iodophenyl)-3,3-diisopropyltriaz-1-ene (S1i)




```
DFILE  2-iodo-4-CN-C6H3N=N
COMNT  single_pulse
DATIM  2021-02-06 14:23:19
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            5.0000 sec
PW1             3.35 usec
IRNUC  1H
CTEMP          21.3 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.09 Hz
RGAIN            38
```

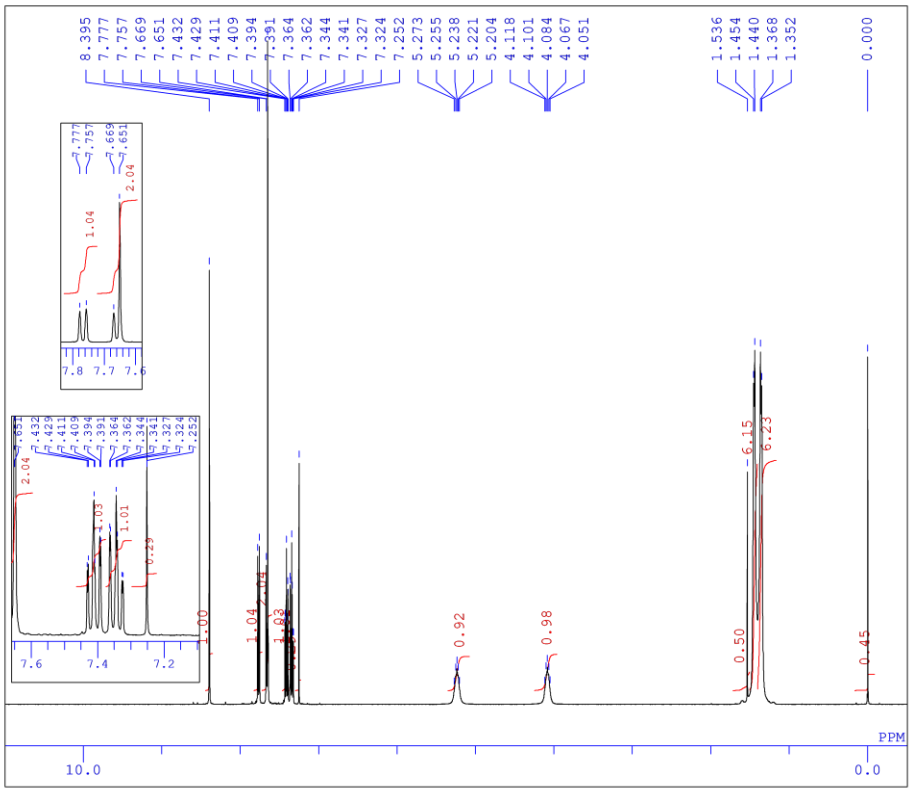


S1i



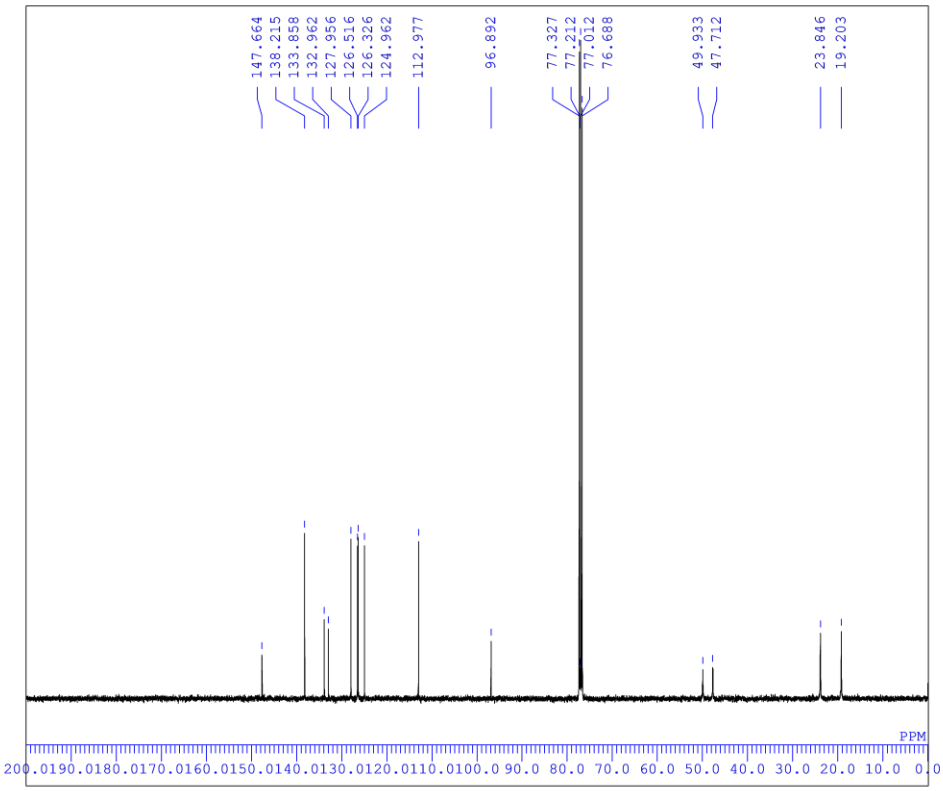

```
DFILE  2-iodo-4-CN-C6H3N=N
COMNT  single pulse decoup
DATIM  2021-02-06 14:25:10
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26214
FREQU      25125.63 Hz
SCANS           840
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.60 usec
IRNUC  1H
CTEMP          21.2 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.09 Hz
RGAIN            60
```

1-(3-Iodonaphthalen-2-yl)-3,3-diisopropyltriaz-1-ene (S1j)



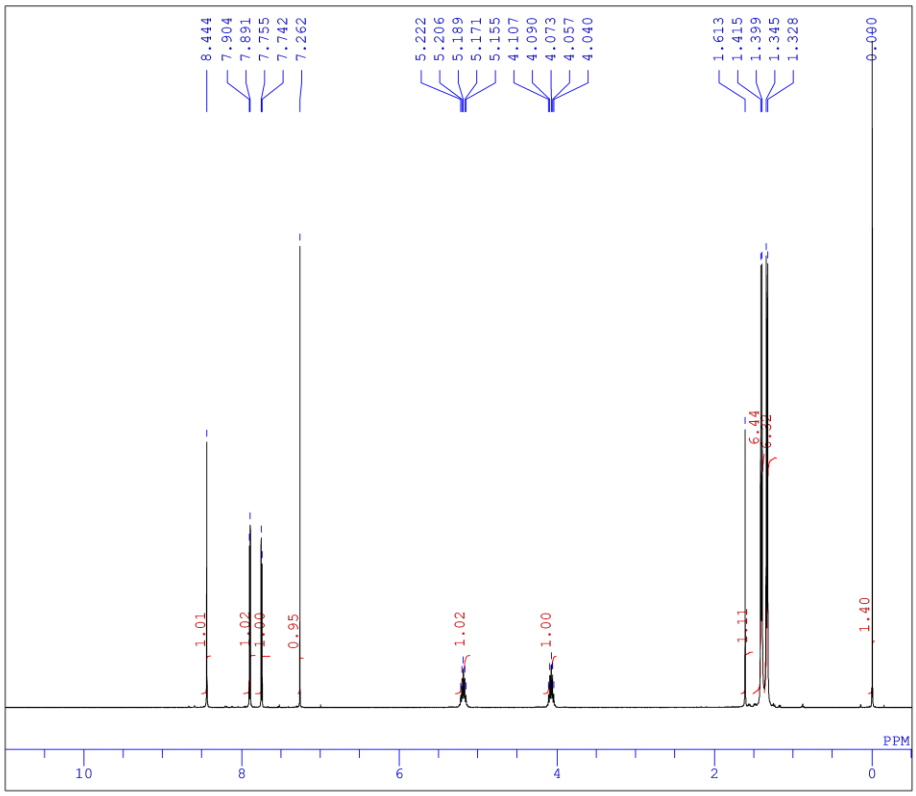
DFILE naphthalene iodonat
COMNT single_pulse
DATIM 2020-09-28 14:31:19
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 26214
FREQU 6002.40 Hz
SCANS 16
ACQTM 4.3673 sec
PD 5.0000 sec
PW1 3.35 usec
IRNUC 1H
CTEMP 20.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 36

S1j

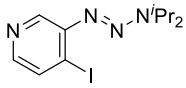


DFILE naphthalene iodonat
COMNT single pulse decoup
DATIM 2020-09-28 14:34:25
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1500
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.60 usec
IRNUC 1H
CTEMP 20.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 60

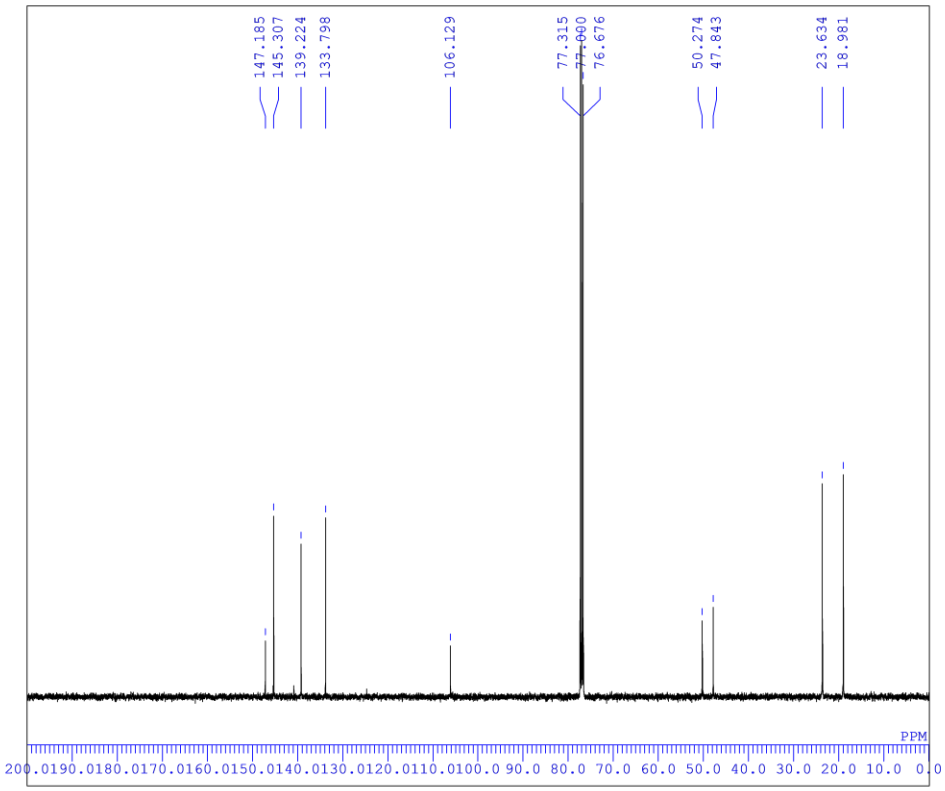
3-(3,3-Diisopropyltriaz-1-en-1-yl)-4-iodopyridine (S1k)




```
DFILE  3-iPr2N-N=N-4-iodoP
COMNT  single_pulse
DATIM  2021-02-15 13:20:17
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          22.9 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            46
```

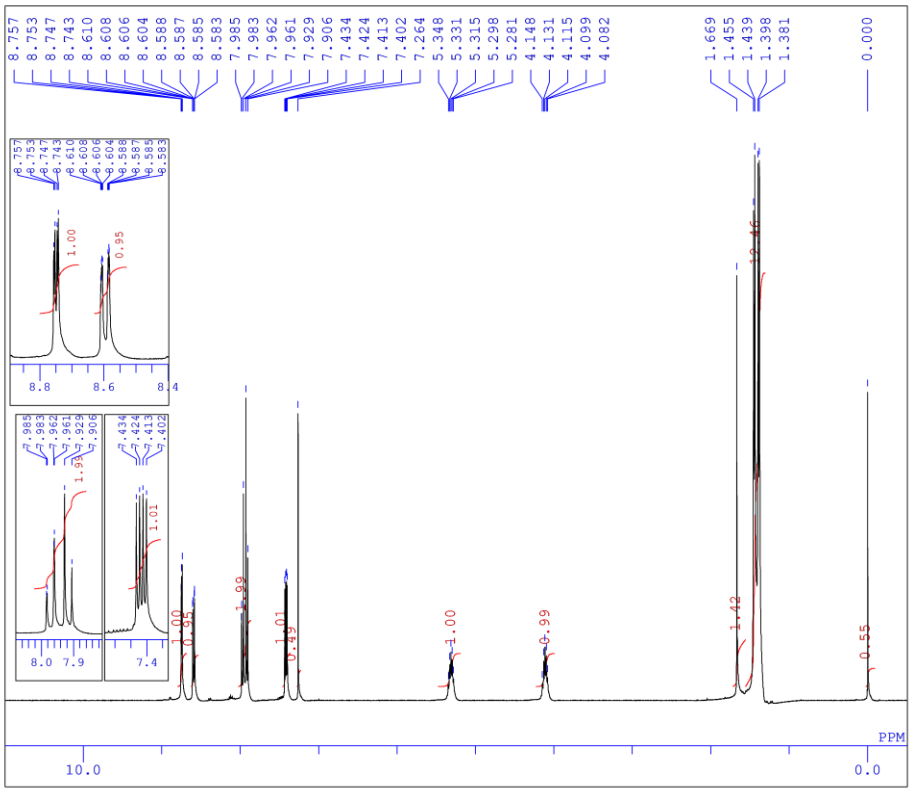


S1k

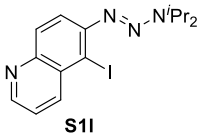



```
DFILE  pyridine iodonation
COMNT  single pulse decoup
DATIM  2020-09-18 11:21:24
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26214
FREQU      25125.63 Hz
SCANS          1500
ACQTM        1.0433 sec
PD           2.0000 sec
PW1            3.60 usec
IRNUC  1H
CTEMP          22.7 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            60
```

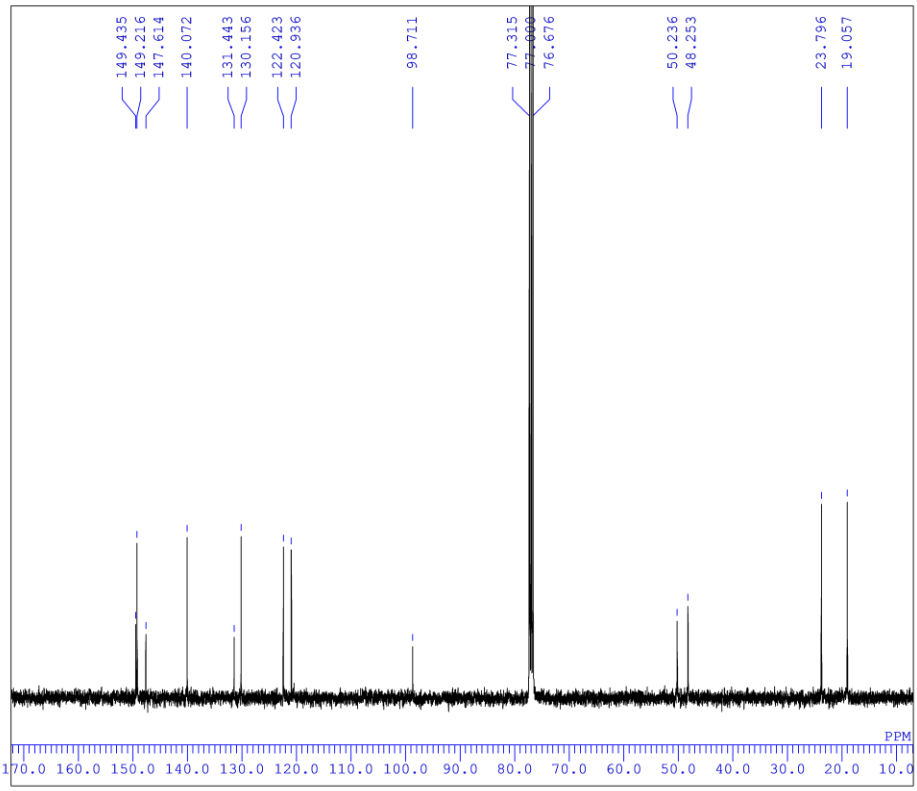
6-(3,3-Diisopropyltriaz-1-en-1-yl)-5-iodoquinoline (S1l)



```
DFILE  quinoline iodonatic
COMNT  single_pulse
DATIM  2020-11-19 11:17:03
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          20.1 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            42
```

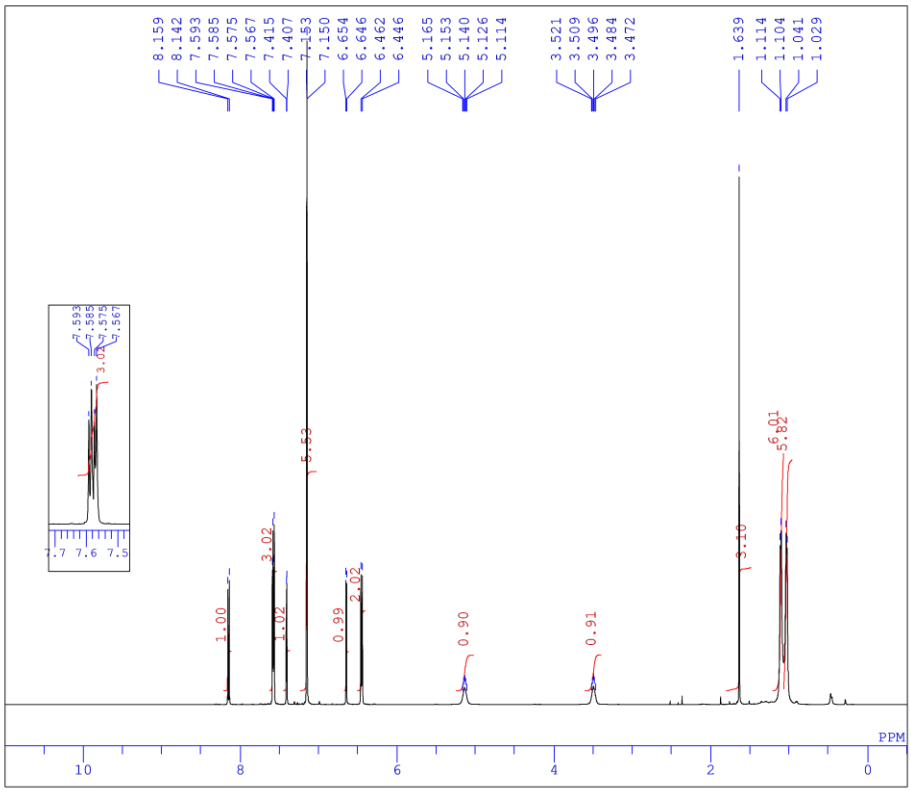


S1l

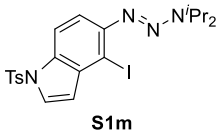


```
DFILE  quinoline iodonatic
COMNT  single pulse decoup
DATIM  2020-11-19 11:20:04
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26214
FREQU      25125.63 Hz
SCANS          2000
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.60 usec
IRNUC  1H
CTEMP          20.6 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            60
```

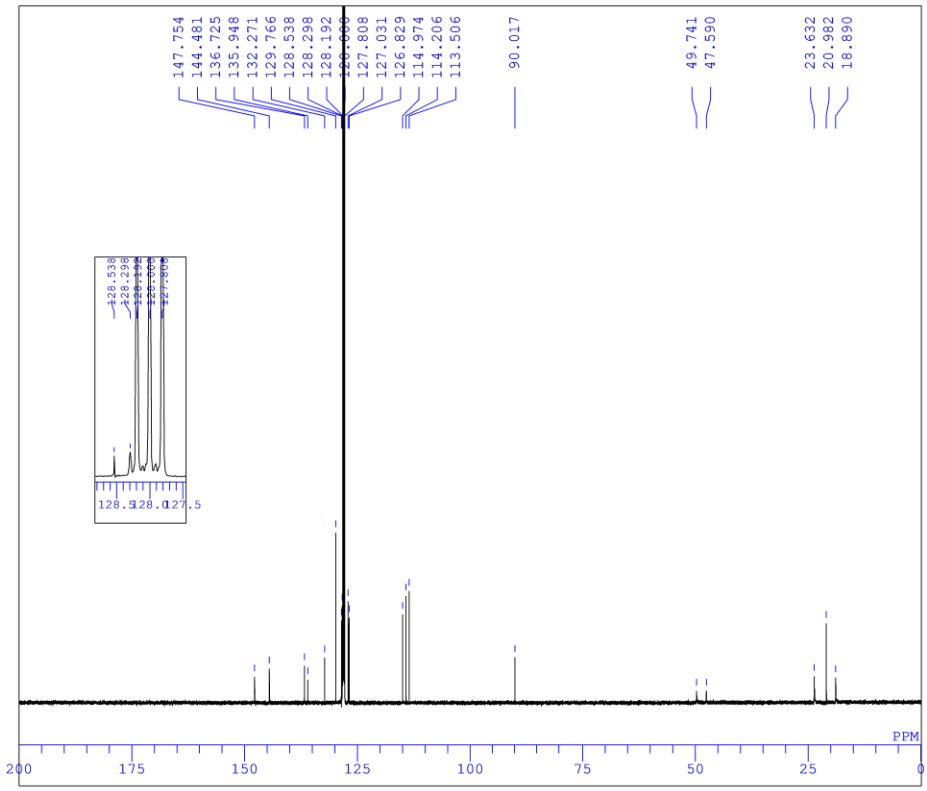
5-(3,3-Diisopropyltriaz-1-en-1-yl)-4-iodo-1-tosyl-1*H*-indole (S1m)




```
DFILE  5-(iPr2N-N=N)-4-iod
COMNT  single_pulse
DATIM  2020-07-31 10:25:20
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         26214
FREQU       7507.51 Hz
SCANS            64
ACQTM         3.4918 sec
PD            5.0000 sec
PW1             3.00 usec
IRNUC  1H
CTEMP          24.0 c
SLVNT  C6D6
EXREF          7.15 ppm
BF             0.22 Hz
RGAIN            46
```

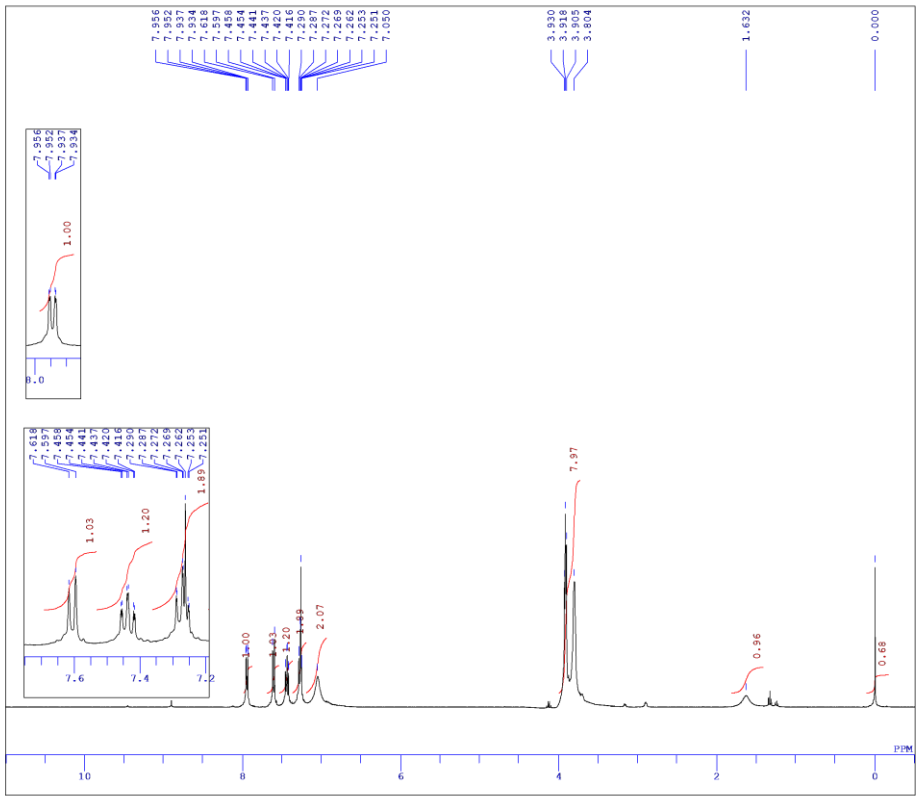


S1m

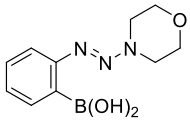



```
DFILE  5-(iPr2N-N=N)-4-iod
COMNT  single pulse decoup
DATIM  2020-07-31 10:35:02
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31645.57 Hz
SCANS          1024
ACQTM         0.8284 sec
PD            2.0000 sec
PW1             3.46 usec
IRNUC  1H
CTEMP          24.0 c
SLVNT  C6D6
EXREF        128.00 ppm
BF             0.22 Hz
RGAIN            36
```

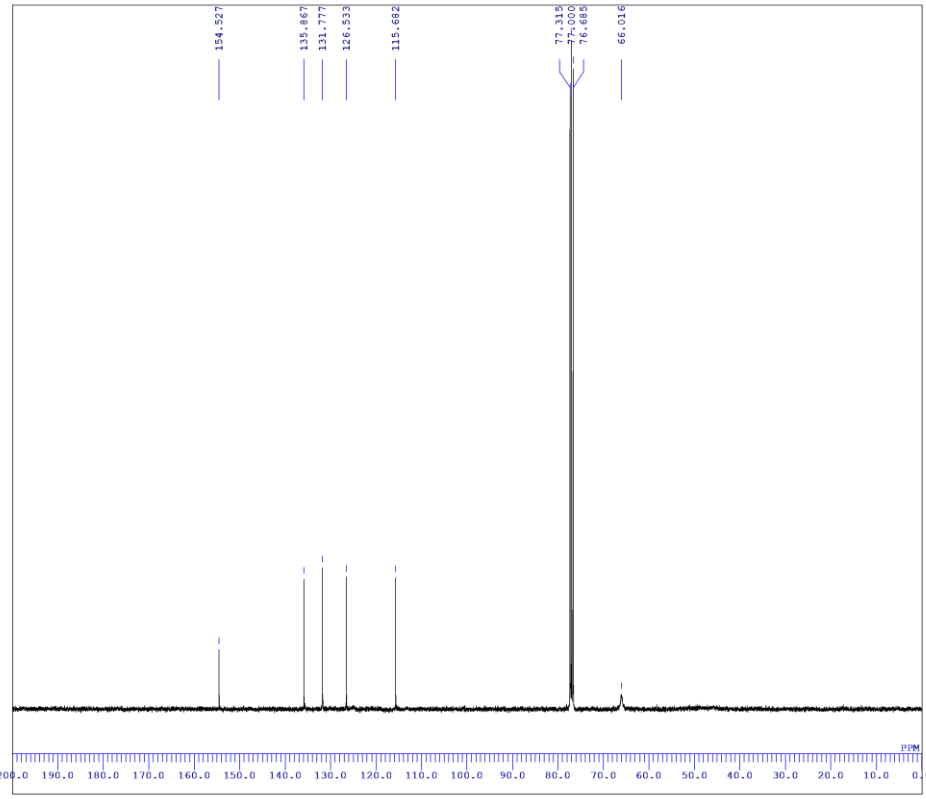
2-(Morpholinodiazenyl)phenylboronic acid (1b)




```
DFILE EK80_1H-normal-1-1 I.
COMNT single_pulse
DATIM 2020-10-29 11:31:54
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         20.3 c
SLVNT CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           42
```

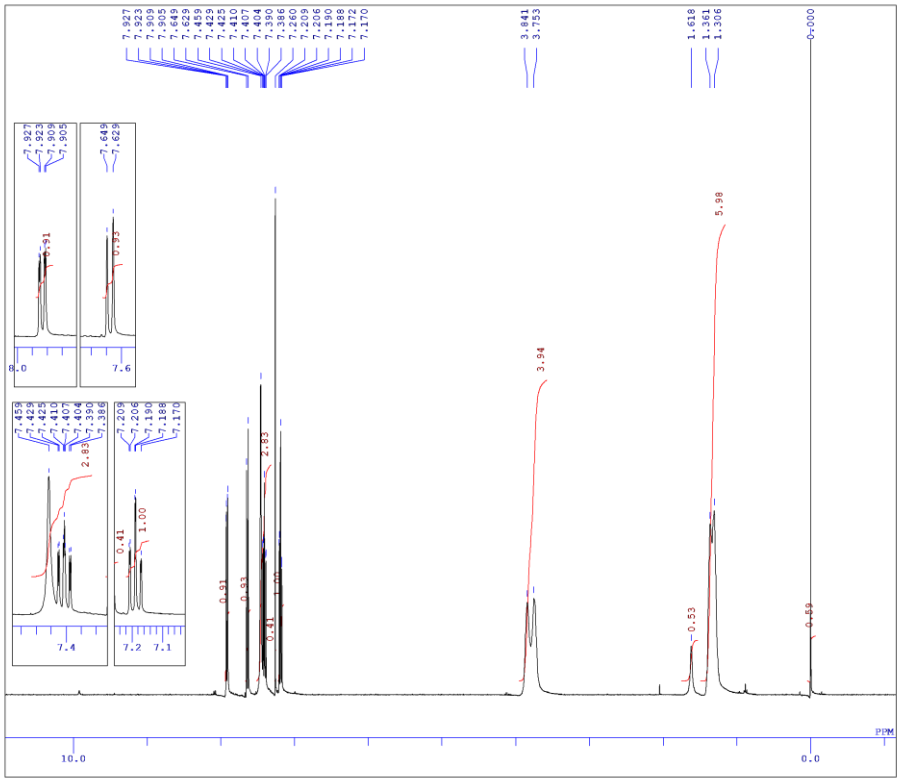


1b

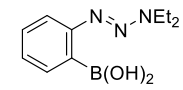



```
DFILE EK80_E13C-1-1 I.als
COMNT single pulse decoupled
DATIM 2020-10-30 11:18:58
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ       100.53 MHz
OBSET         5.35 KHz
OBFIN         5.86 Hz
POINT        26214
FREQU      25125.63 Hz
SCANS         2200
ACQTM       1.0433 sec
PD          2.0000 sec
PW1            3.60 usec
IRNUC 1H
CTEMP         20.2 c
SLVNT CDCL3
EXREF        77.00 ppm
BF            1.20 Hz
RGAIN           60
```

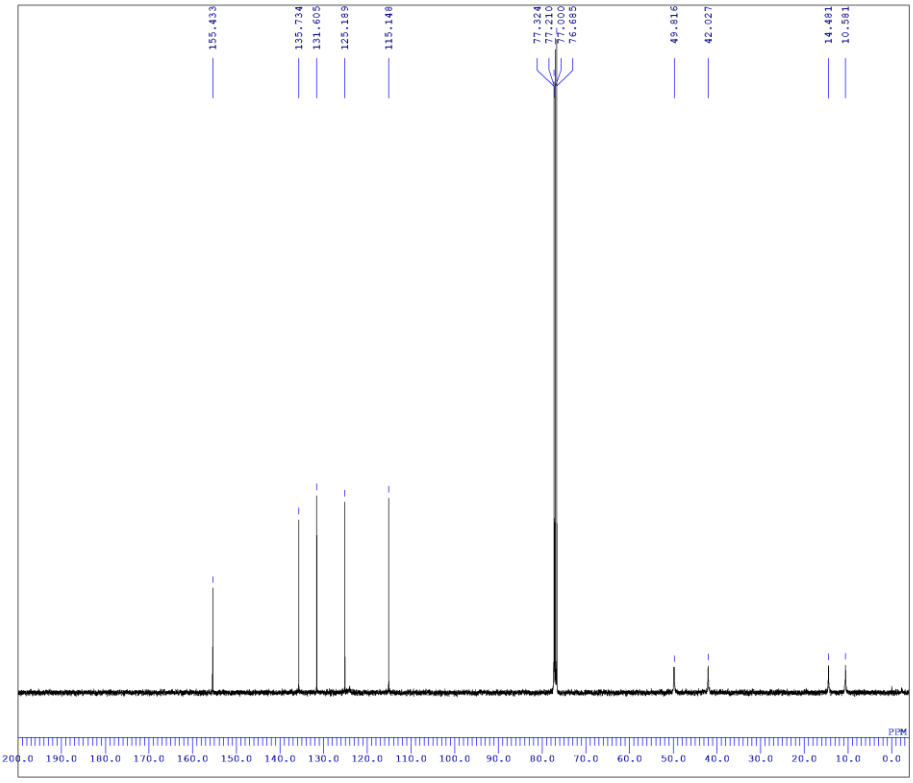
2-(3,3-Diethyltriaz-1-en-1-yl)phenylboronic acid (1c)



```
DFILE YY344__1H-normal-1-1 Ī
COMNT single_pulse
DATIM 2020-10-22 13:48:47
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         20.0 c
SLVNT CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           42
```

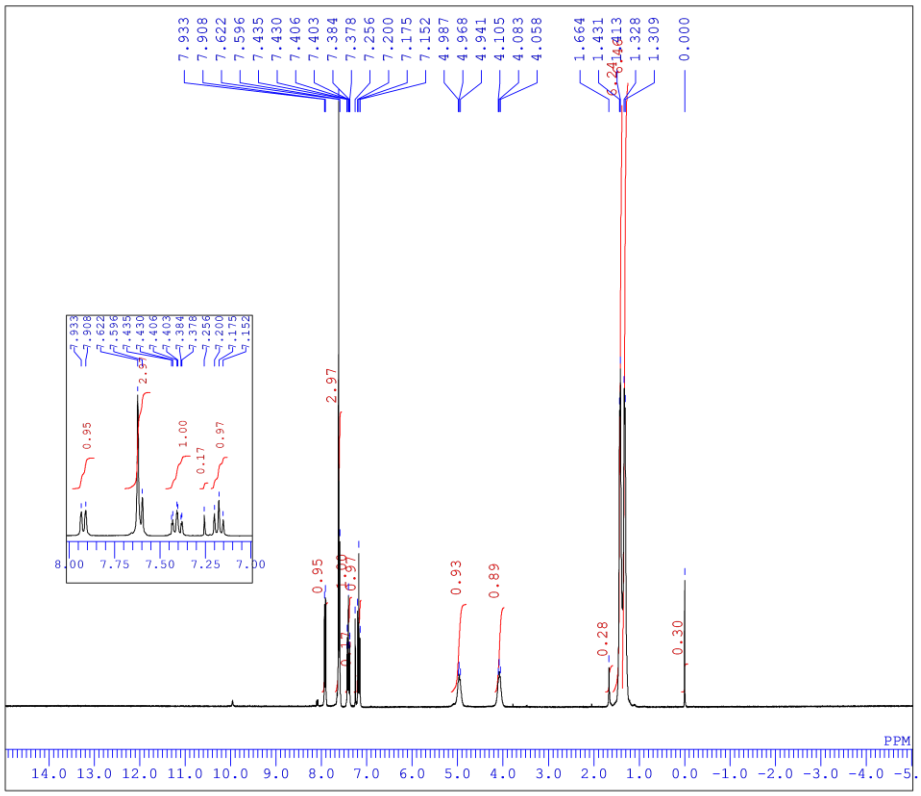


1c

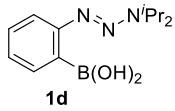


```
DFILE YY344_E13C-1-1 Ī.als
COMNT single pulse decoupled
DATIM 2020-09-25 11:20:21
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ       100.53 MHz
OBSET         5.35 KHz
OBFIN         5.86 Hz
POINT        26214
FREQU     25125.63 Hz
SCANS         1500
ACQTM       1.0433 sec
PD          2.0000 sec
PW1            3.60 usec
IRNUC 1H
CTEMP         20.6 c
SLVNT CDCL3
EXREF        77.00 ppm
BF            1.20 Hz
RGAIN           60
```

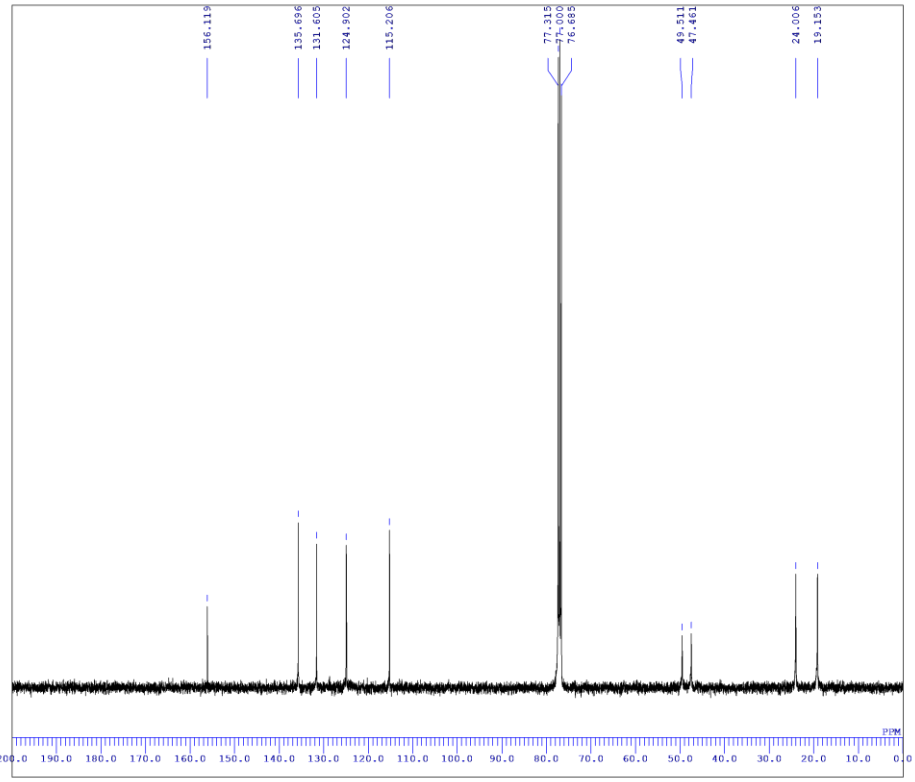
2-(3,3-Diisopropyltriaz-1-en-1-yl)phenylboronic acid (1d)




```
DFILE  1d.als procd.als
COMNT  1d
DATIM  Mon Feb 15 17:44:30
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             5.30 usec
IRNUC  1H
CTEMP           24.2 c
SLVNT  CDCL3
EXREF            0.00 ppm
BF               0.01 Hz
RGAIN              15
```

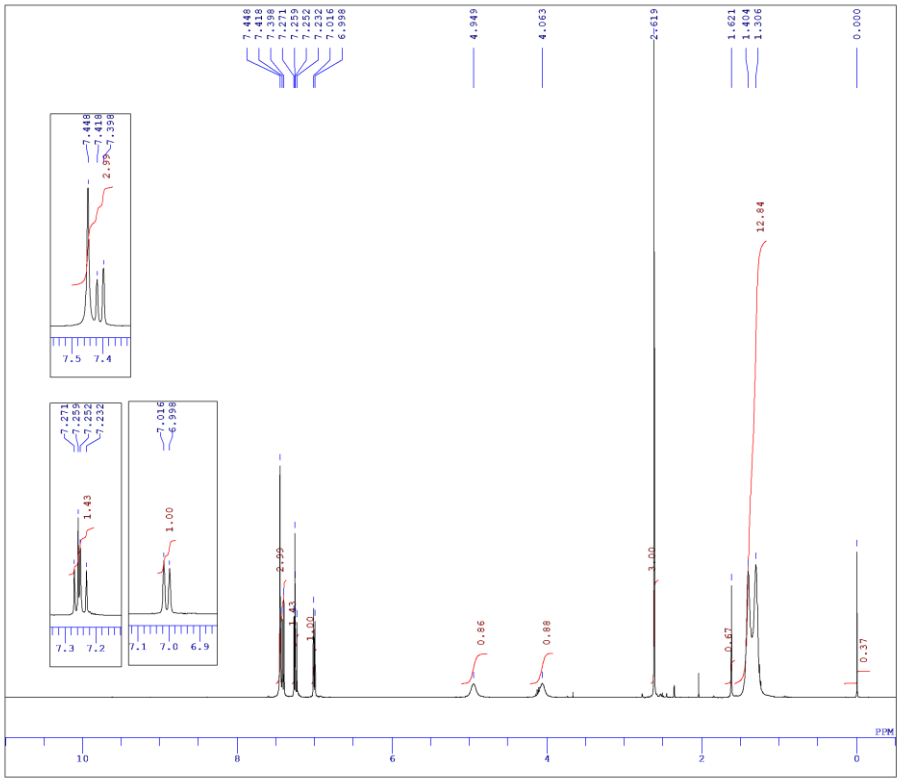


1d

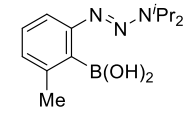



```
DFILE YY334_E13C-1-1 f.als
COMNT single_pulse_decoupled
DATIM 2020-09-14 11:22:22
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26214
FREQU      25125.63 Hz
SCANS          1200
ACQTM        1.0433 sec
PD           2.0000 sec
PW1            3.60 usec
IRNUC 1H
CTEMP          21.3 c
SLVNT CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            60
```

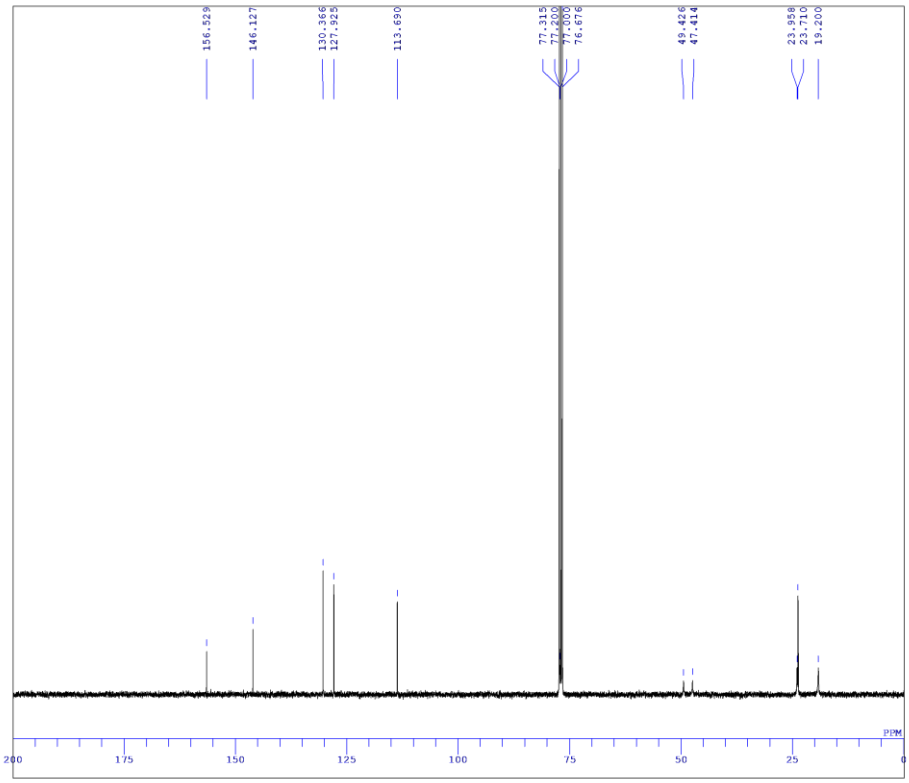
2-(3,3-Diisopropyltriaz-1-en-1-yl)-6-methylphenylboronic acid (1e)




```
DFILE 6-Me-2-(iPr2N3)C6H3B(O
COMNT single pulse
DATIM 2020-11-13 11:20:24
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         19.2 c
SLVNT CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           38
```

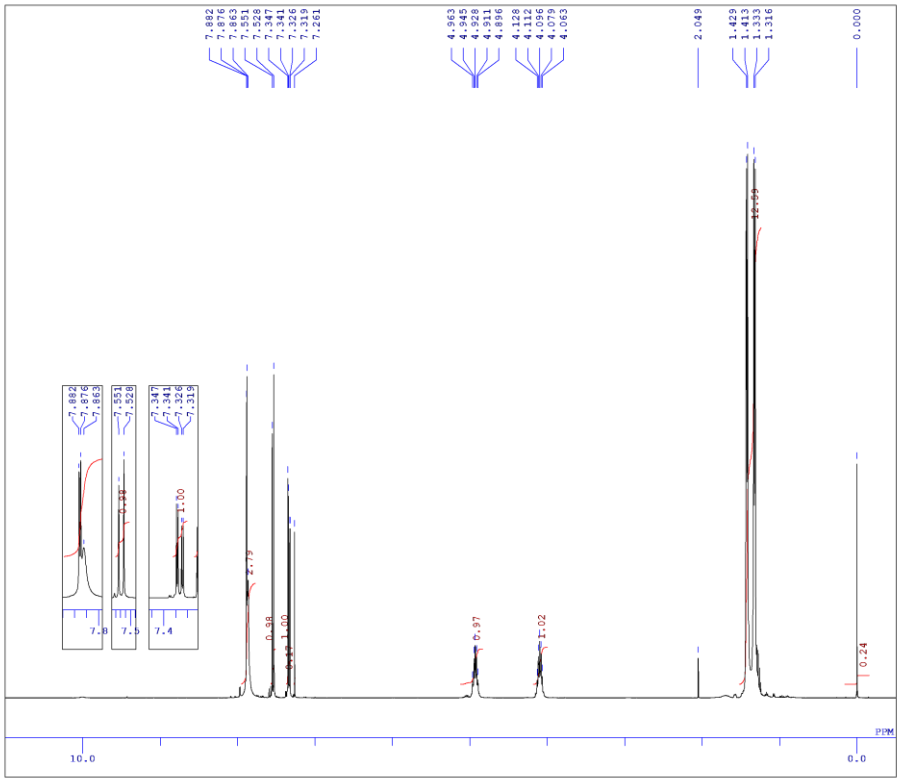


1e

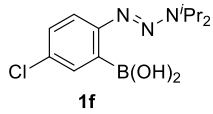



```
DFILE 6-Me-2-(iPr2N3)C6H3B(O
COMNT single pulse decoupled
DATIM 2020-11-13 11:23:24
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ       100.53 MHz
OBSET         5.35 KHz
OBFIN         5.86 Hz
POINT        26214
FREQU      25125.63 Hz
SCANS         1800
ACQTM       1.0433 sec
PD          2.0000 sec
PW1            3.60 usec
IRNUC 1H
CTEMP         19.4 c
SLVNT CDCL3
EXREF        77.00 ppm
BF            1.20 Hz
RGAIN           60
```

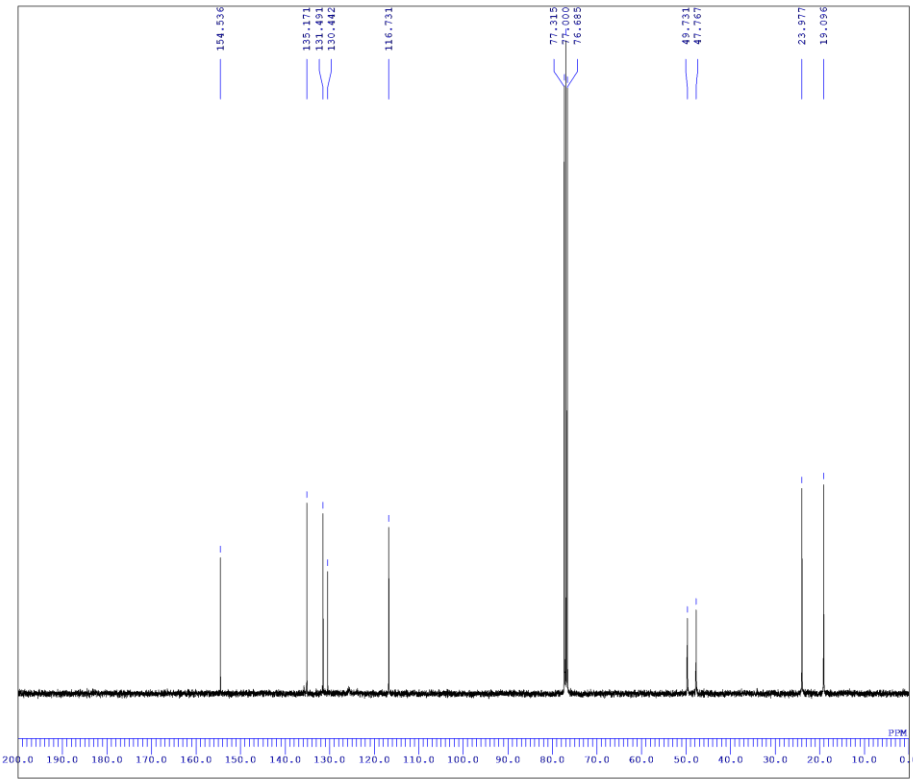
5-Chloro-2-(3,3-diisopropyltriaz-1-en-1-yl) phenylboronic acid (1f)



DFILE c1 B(OH)2__1H-normal-1
COMNT single_pulse
DATIM 2020-10-07 13:22:21
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 20.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 34

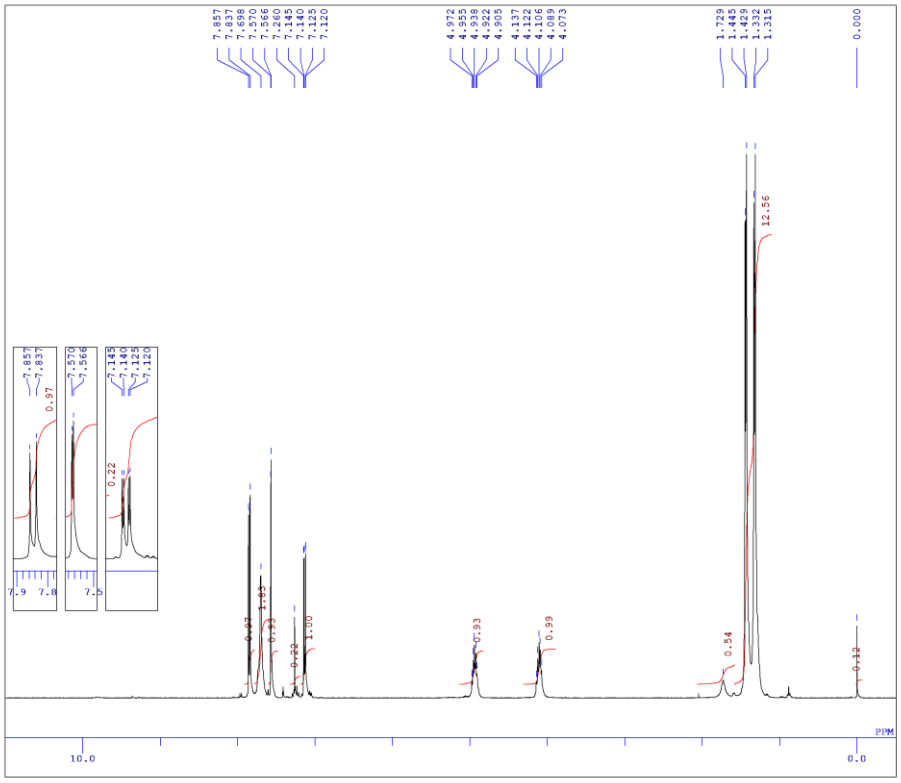


1f

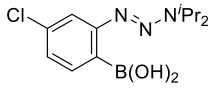


DFILE c1 B(OH)2_E13C-1-1 Ï.a
COMNT single pulse decoupled
DATIM 2020-10-07 13:25:21
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1000
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.60 usec
IRNUC 1H
CTEMP 20.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60

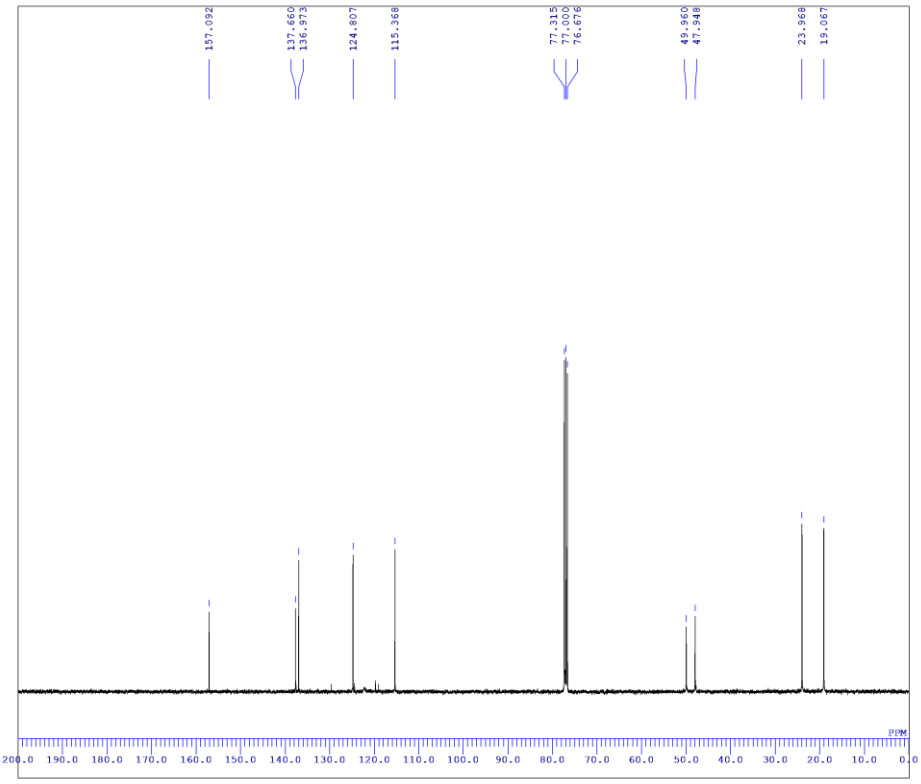
4-Chloro-2-(3,3-diisopropyltriaz-1-en-1-yl)- phenylboronic acid (1f')



DFILE YY299__1H-normal-1-1 Ī
COMNT single_pulse
DATIM 2020-08-21 10:30:56
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 24.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 32

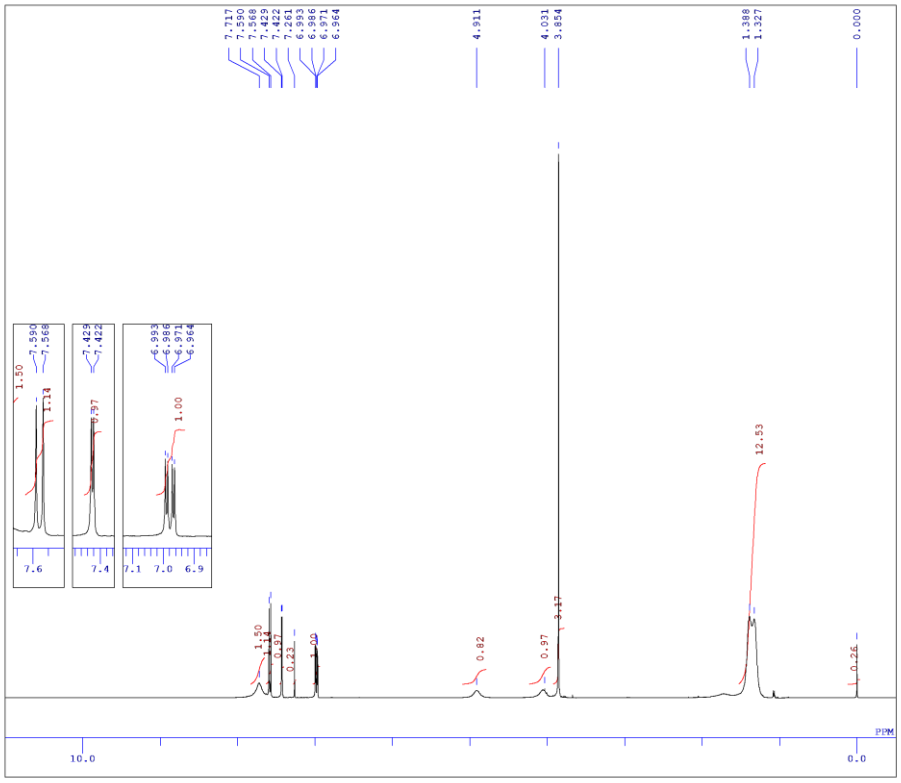


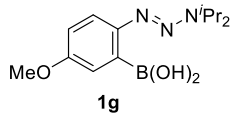
1f'



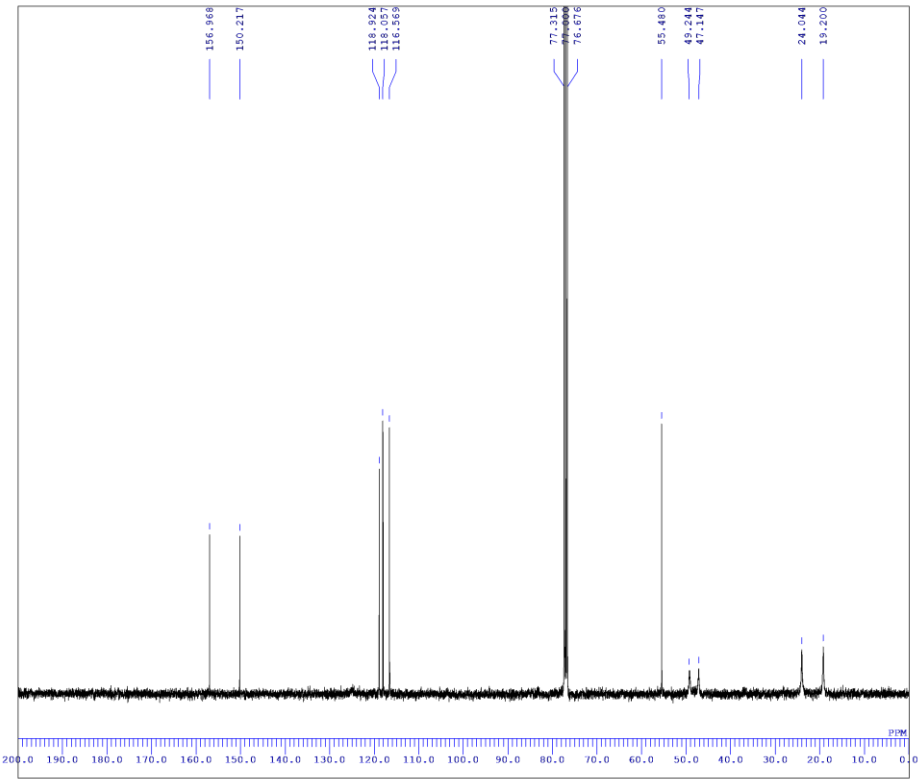
DFILE YY299_E13C-1-1 Ī.als
COMNT single pulse decoupled
DATIM 2020-08-21 10:34:02
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1500
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.60 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60

2-(3,3-Diisopropyltriaz-1-en-1-yl)-5-methoxyphenylboronic acid (1g)

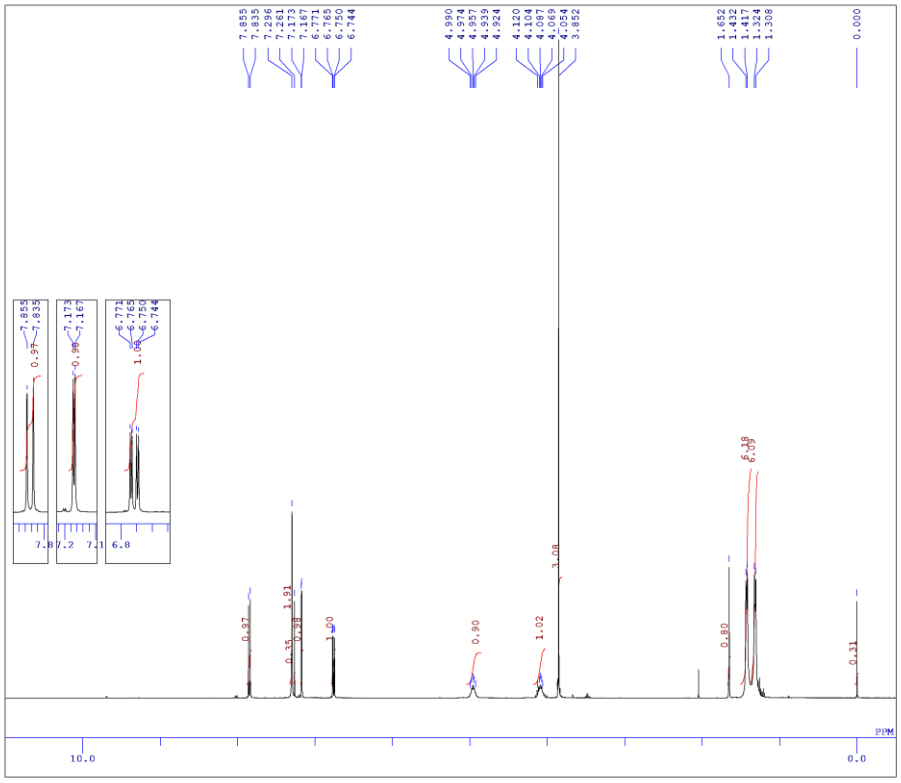




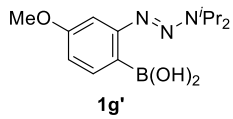
1g



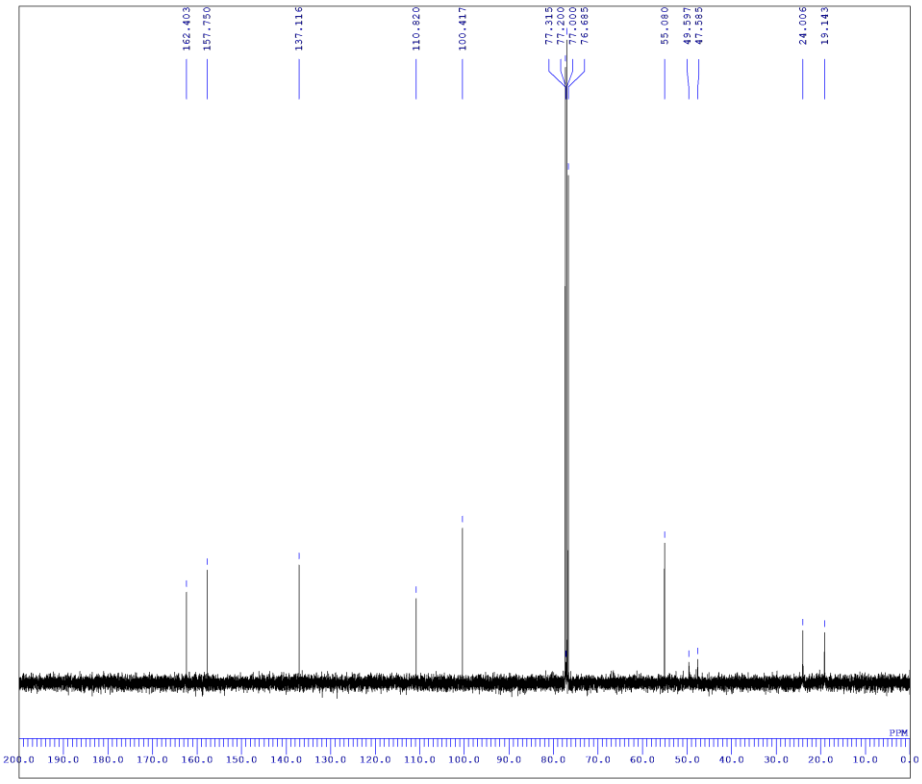
2-(3,3-Diisopropyltriaz-1-en-1-yl)-4-methoxyphenylboronic acid (1g')




```
DFILE 4-MeO-2-(iPr2N3)C6H3B(
COMNT single_pulse
DATIM 2020-06-08 16:16:58
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            0.17 Hz
RGAIN           40
```

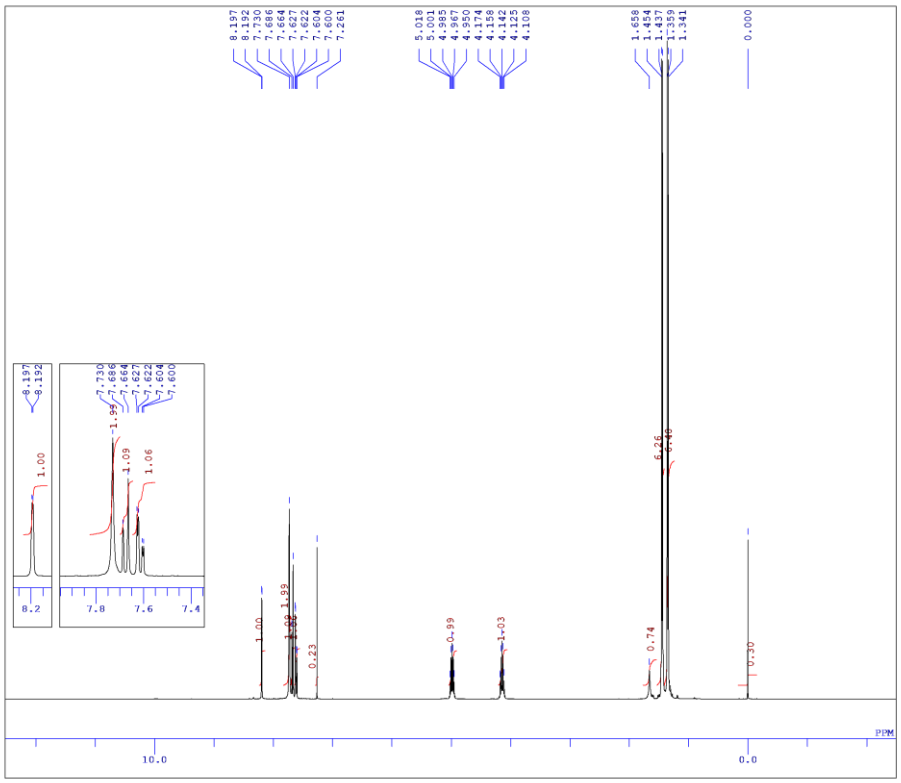


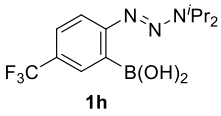
1g'



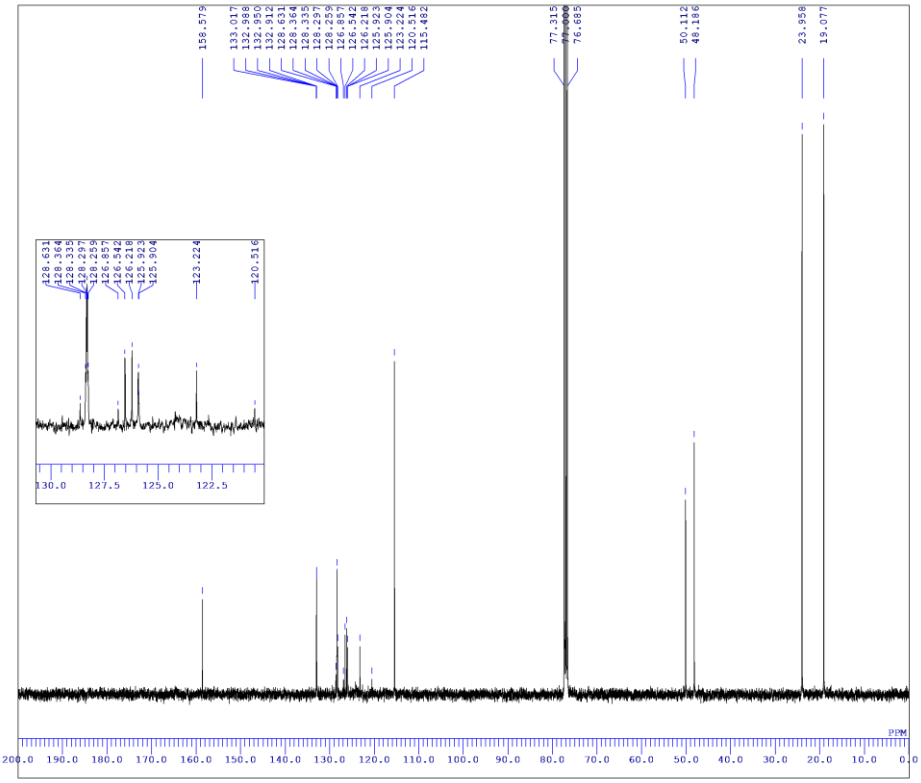

```
DFILE 4-MeO-2-(iPr2N3)C6H3B(
COMNT single pulse decoupled
DATIM 2020-06-08 16:21:04
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ       100.53 MHz
OBSET         5.35 KHz
OBFIN         5.86 Hz
POINT        26214
FREQU     25125.63 Hz
SCANS          281
ACQTM       1.0433 sec
PD          2.0000 sec
PW1            3.60 usec
IRNUC 1H
CTEMP         22.6 c
SLVNT CDCL3
EXREF        77.00 ppm
BF            0.17 Hz
RGAIN           60
```

2-(3,3-Diisopropyltriaz-1-en-1-yl)-5-(trifluoromethyl)phenylboronic acid (1h)

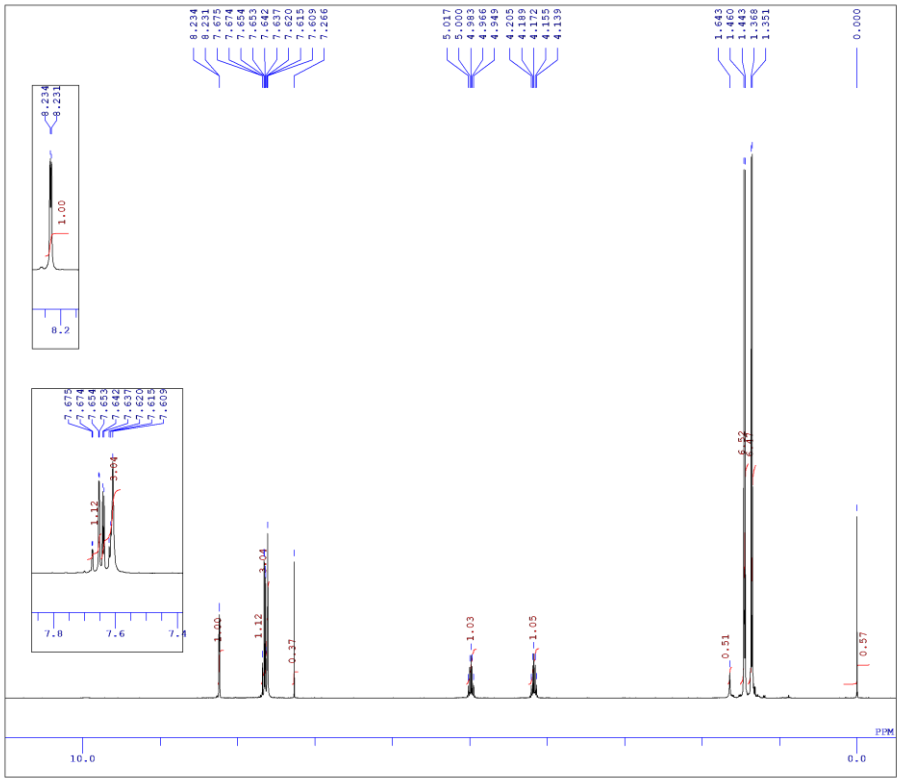




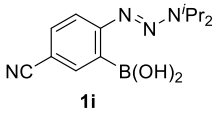
1h



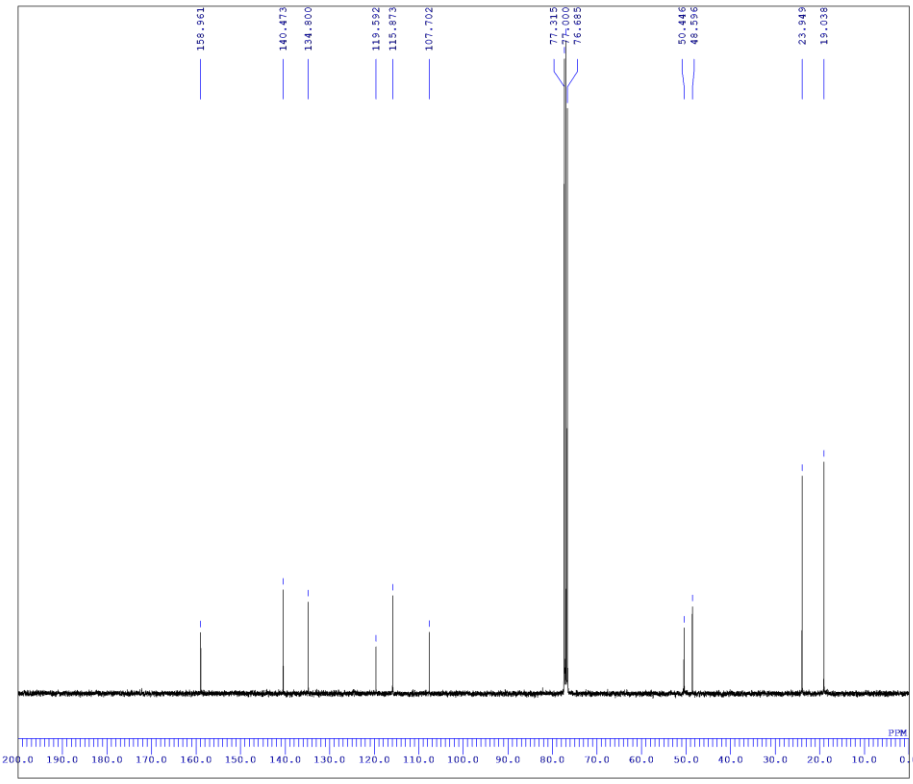
5-Cyano-2-(3,3-diisopropyltriaz-1-en-1-yl)phenylboronic acid (1i)



DFILE CN_B(OH)2__1H-normal-1
COMNT single_pulse
DATIM 2020-10-21 13:47:28
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 19.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40

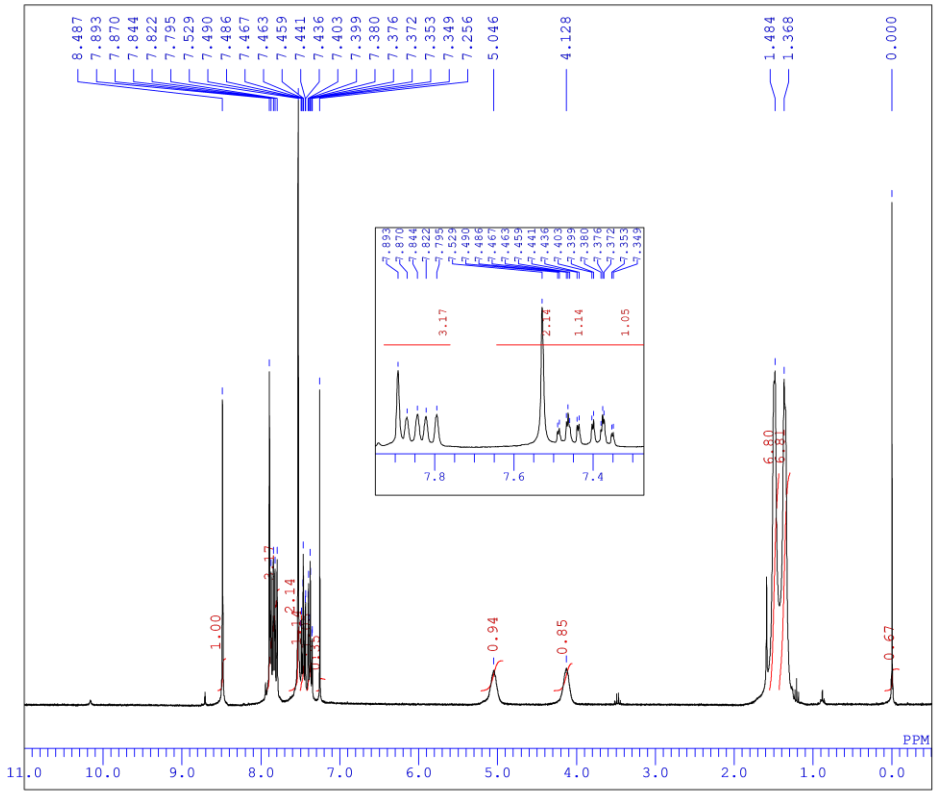


1i

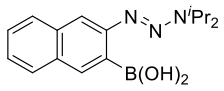


DFILE CN_B(OH)2_E13C-1-10I.a
COMNT single pulse decoupled
DATIM 2020-10-21 13:50:35
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1500
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.60 usec
IRNUC 1H
CTEMP 19.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60

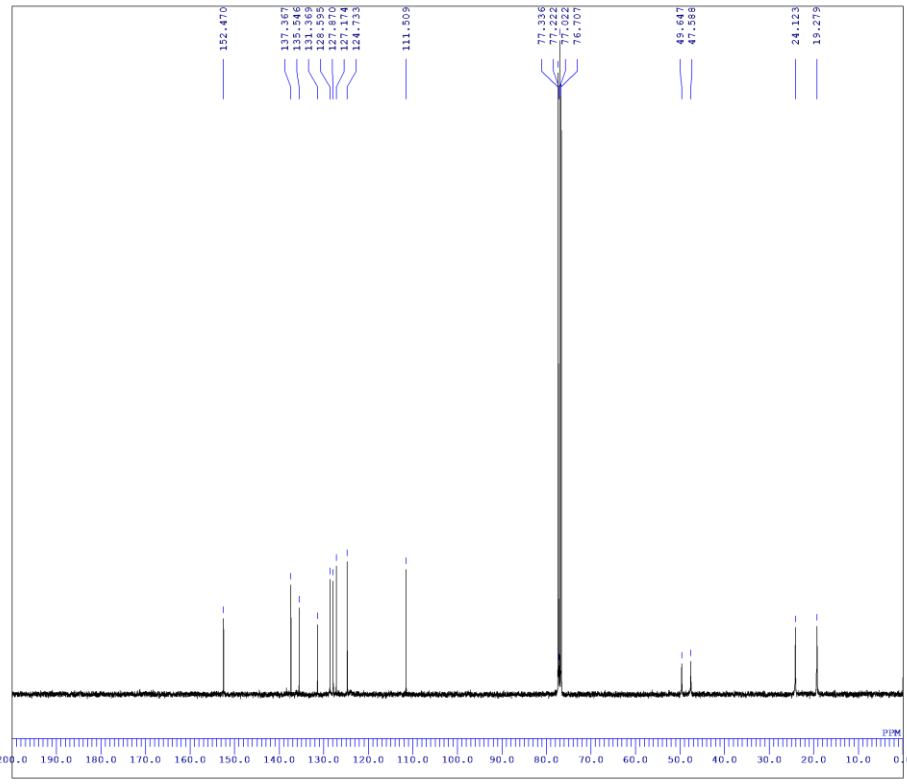
[3-(3,3-Diisopropyltriaz-1-en-1-yl)naphthalen-2-yl]boronic acid (1j)




```
DFILE  naphthalene B(OH)2
COMNT  naphthalene B(OH)2
DATIM  Wed Jan 27 15:39:39
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           24.9 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             17
```

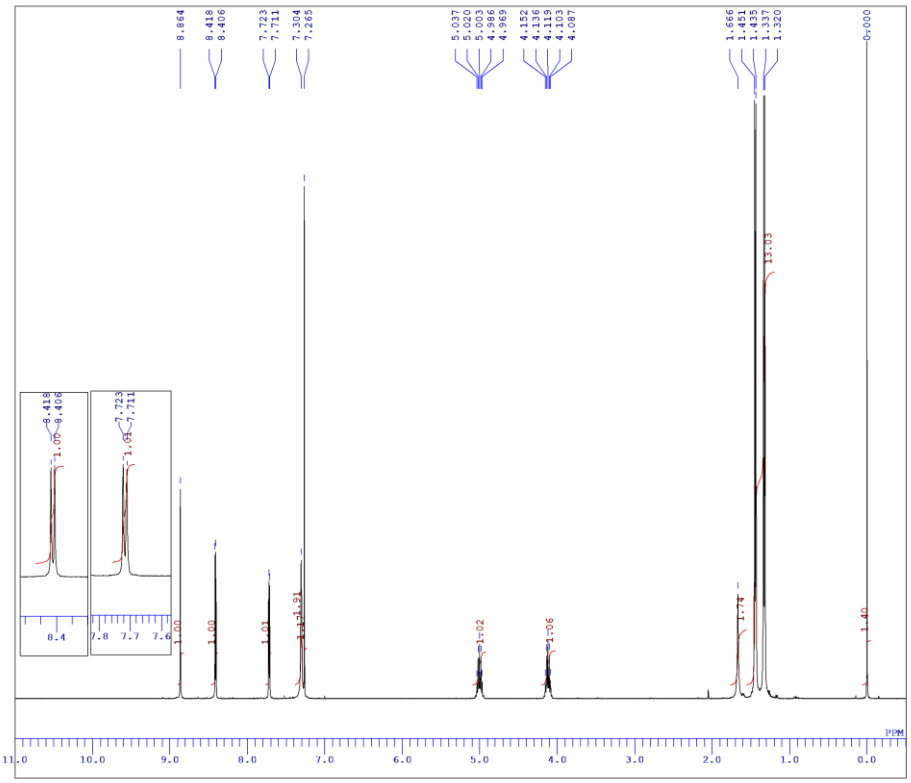


1j

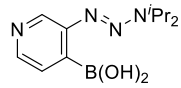



```
DFILE naphthalene B(OH)2_E13
COMNT single pulse decoupled
DATIM 2020-09-29 09:59:60
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ       100.53 MHz
OBSET         5.35 KHz
OBFIN         5.86 Hz
POINT        26214
FREQU     25125.63 Hz
SCANS         1500
ACQTM       1.0433 sec
PD          2.0000 sec
PW1            3.60 usec
IRNUC 1H
CTEMP         20.3 c
SLVNT CDCL3
EXREF         0.00 ppm
BF            1.20 Hz
RGAIN           60
```

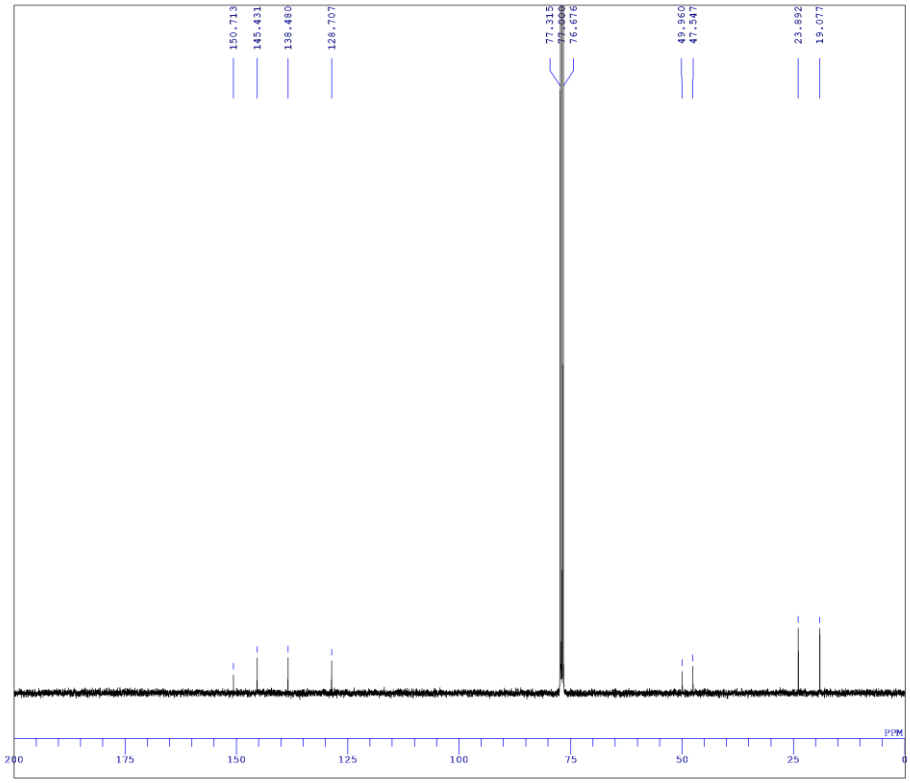
[3-(3,3-Diisopropyltriaz-1-en-1-yl)pyridin-4-yl]boronic acid (1k)



DFILE pyridine B(OH)2__1H-no
COMNT single_pulse
DATIM 2020-11-11 11:57:20
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 19.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 46

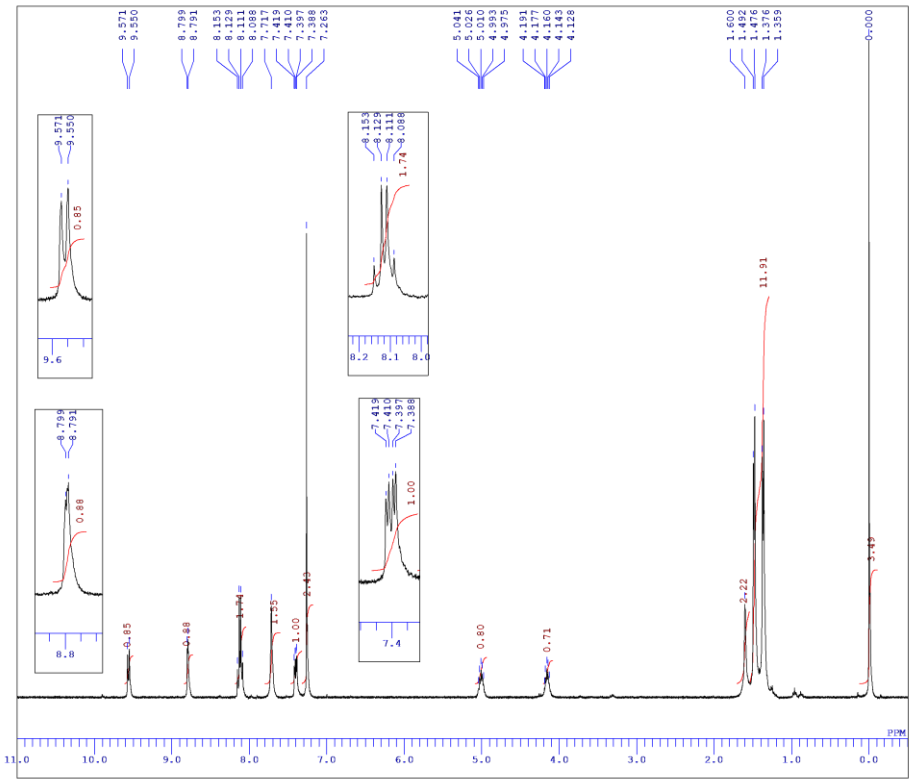


1k

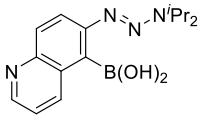


DFILE pyridine B(OH)2_E13C-1
COMNT single pulse decoupled
DATIM 2020-11-11 12:00:20
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1200
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.60 usec
IRNUC 1H
CTEMP 19.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60

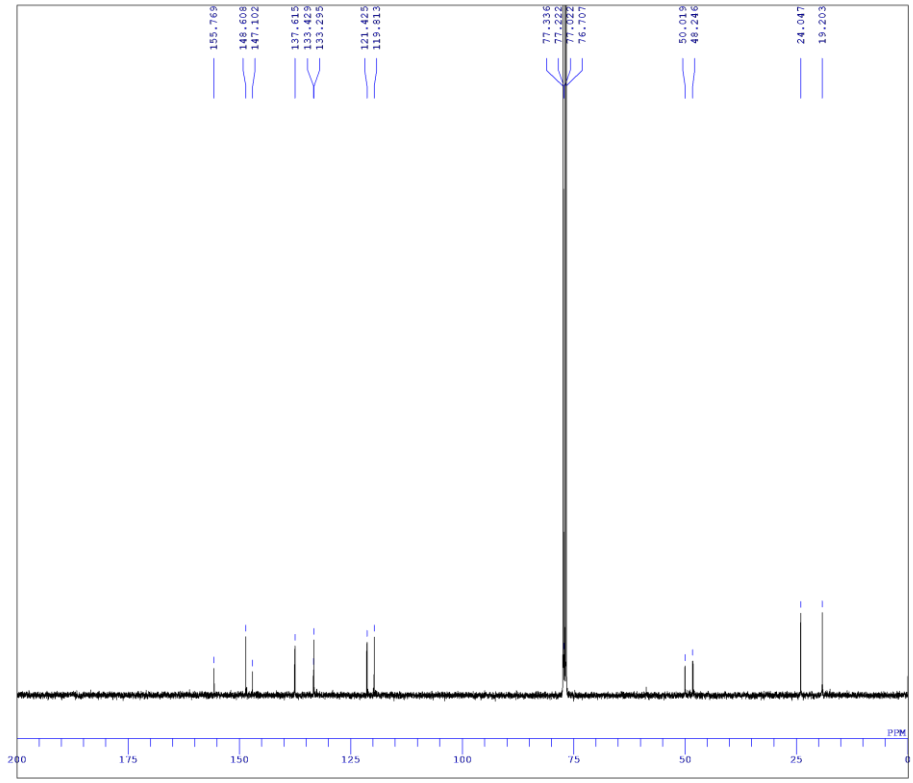
[6-(3,3-Diisopropyltriaz-1-en-1-yl)quinolin-5-yl]boronic acid (1l)



```
DFILE quinoline B(OH)2__1H-n
COMNT single_pulse
DATIM 2020-11-28 11:34:01
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         19.6 c
SLVNT CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           50
```

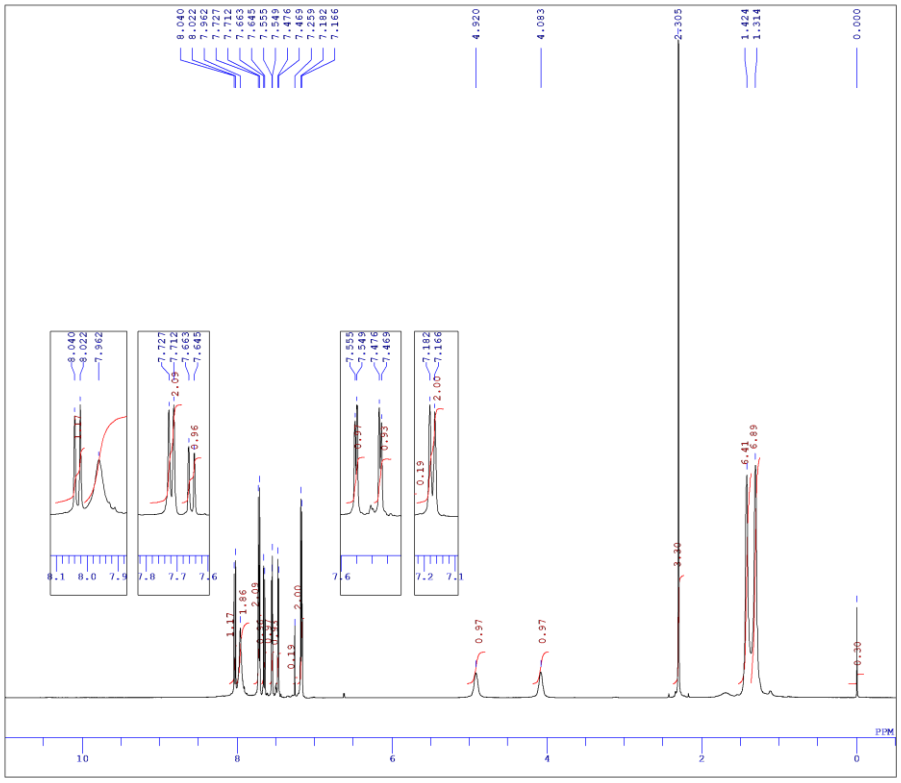


1l

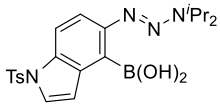


```
DFILE quinoline_E13C-1-1 I.a
COMNT single pulse decoupled
DATIM 2020-12-08 11:22:10
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ       100.53 MHz
OBSET         5.35 KHz
OBFIN         5.86 Hz
POINT        26214
FREQU     25125.63 Hz
SCANS         3000
ACQTM       1.0433 sec
PD          2.0000 sec
PW1            3.60 usec
IRNUC 1H
CTEMP         19.4 c
SLVNT CDCL3
EXREF         0.00 ppm
BF            1.20 Hz
RGAIN           60
```

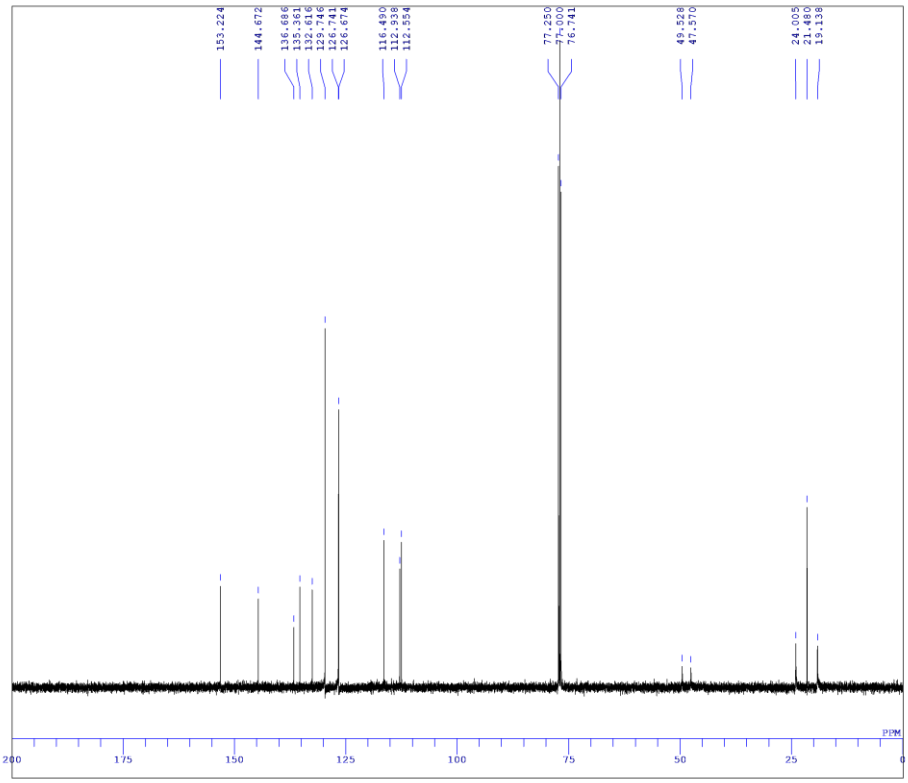
[5-(3,3-Diisopropyltriaz-1-en-1-yl)-1-tosyl-1*H*-indol-4-yl]boronic acid (1m)



```
DFILE 5-(iPr2N-N=N)-N-TsIndo
COMNT single pulse
DATIM 2020-07-31 09:15:37
OBNUC 1H
EXMOD proton.jxp
OBFRQ       500.16 MHz
OBSET         2.41 KHz
OBFIN         6.01 Hz
POINT        26214
FREQU      7507.51 Hz
SCANS            8
ACQTM       3.4918 sec
PD          5.0000 sec
PW1           3.00 usec
IRNUC 1H
CTEMP         23.9 c
SLVNT CDCL3
EXREF         0.00 ppm
BF            0.22 Hz
RGAIN           46
```

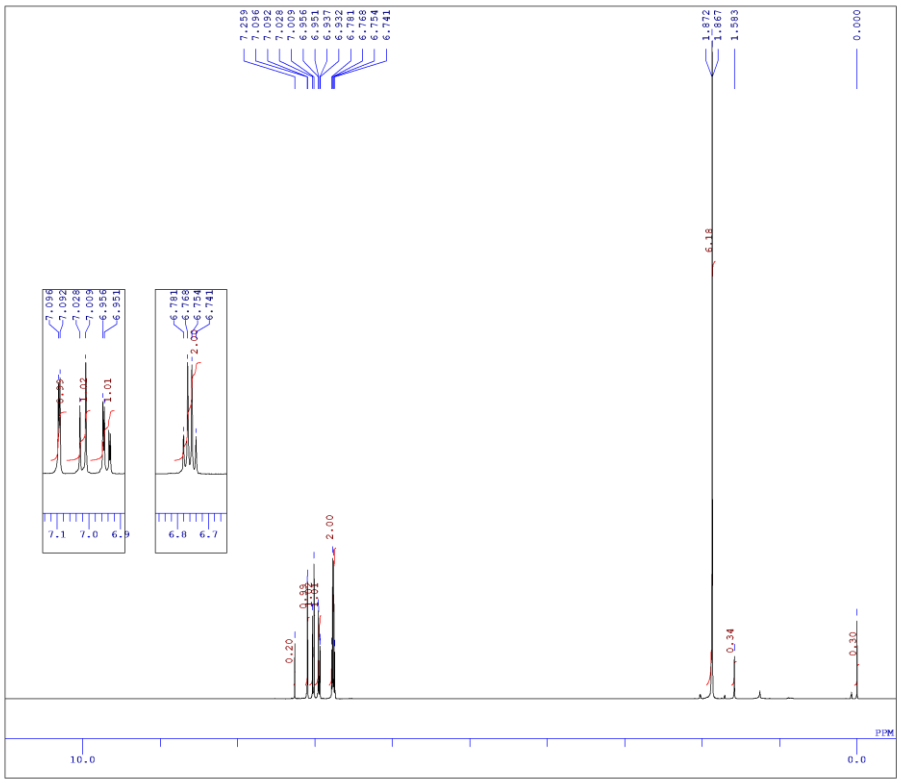


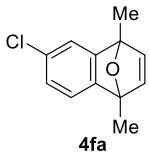
1m



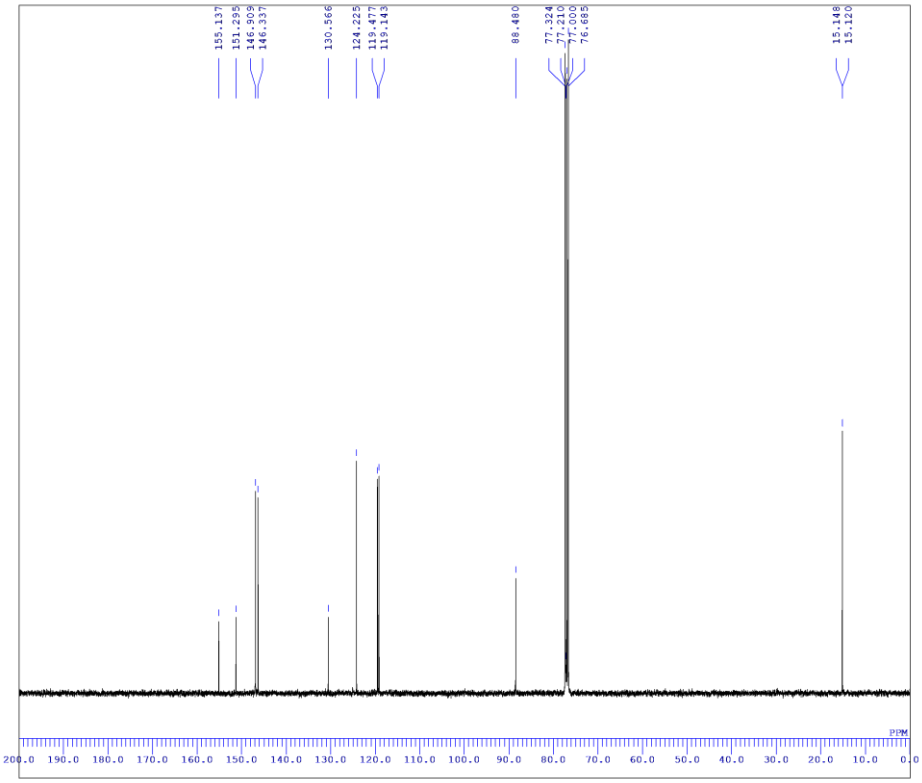
```
DFILE 5-(iPr2N-N=N)-N-TsIndo
COMNT single pulse decoupled
DATIM 2020-07-31 09:17:23
OBNUC 13C
EXMOD carbon.jxp
OBFRQ       125.77 MHz
OBSET         7.87 KHz
OBFIN         4.21 Hz
POINT        26214
FREQU     31645.57 Hz
SCANS          512
ACQTM       0.8284 sec
PD          2.0000 sec
PW1           3.46 usec
IRNUC 1H
CTEMP         24.1 c
SLVNT CDCL3
EXREF        77.00 ppm
BF            0.22 Hz
RGAIN           36
```

6-Chloro-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene (4fa)

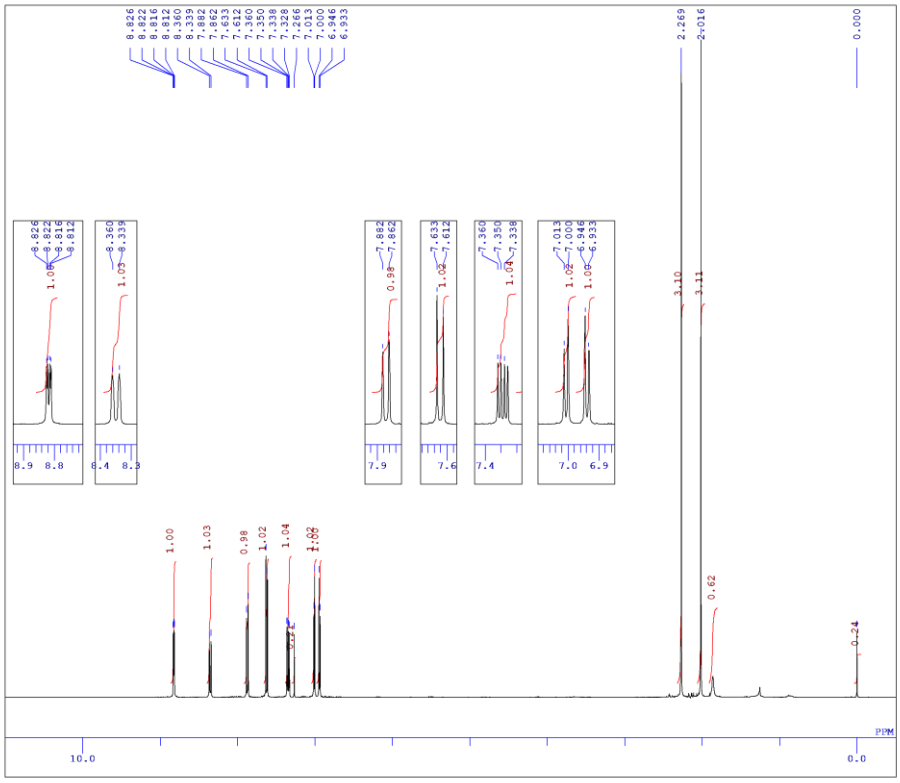


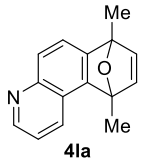


4fa

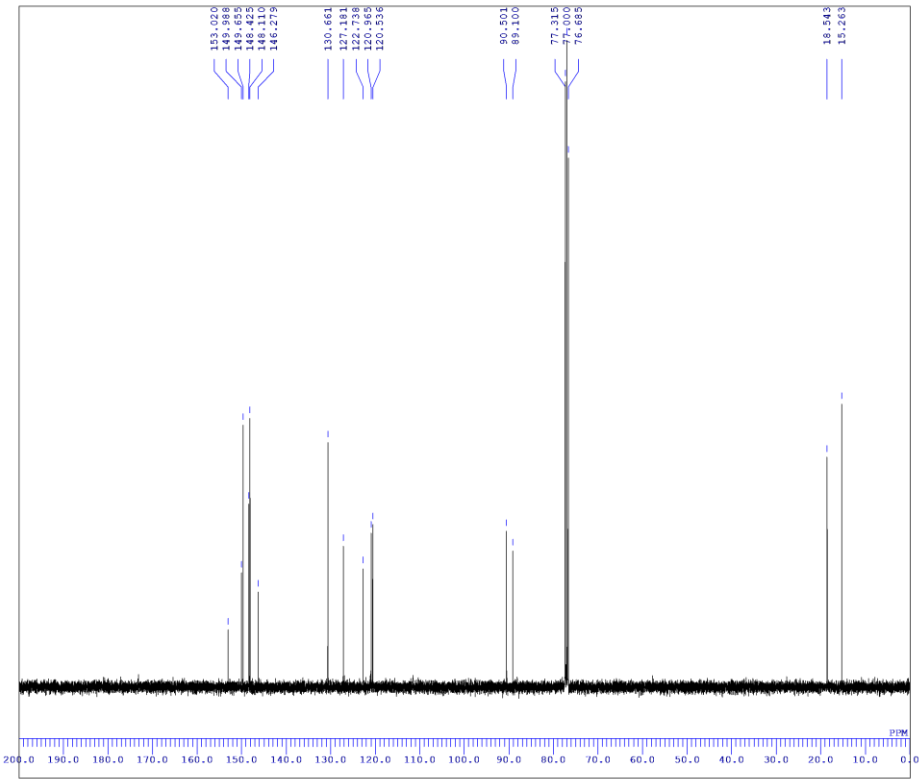


7,10-Dimethyl-7,10-dihydro-7,10-epoxybenzo[*f*]quinoline (4la)

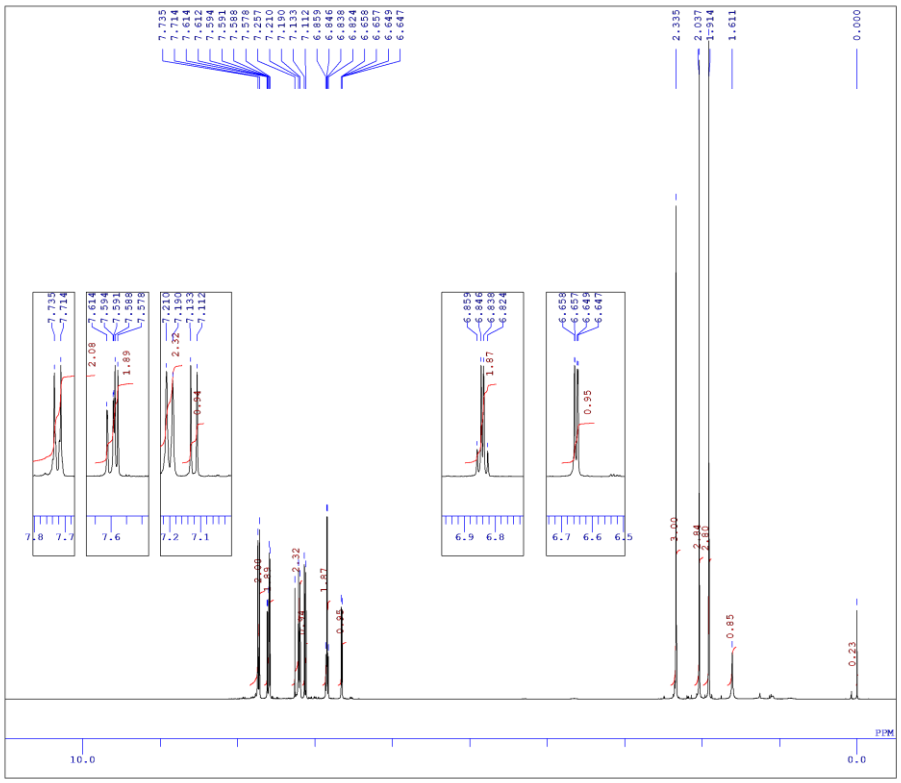


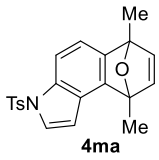


4la

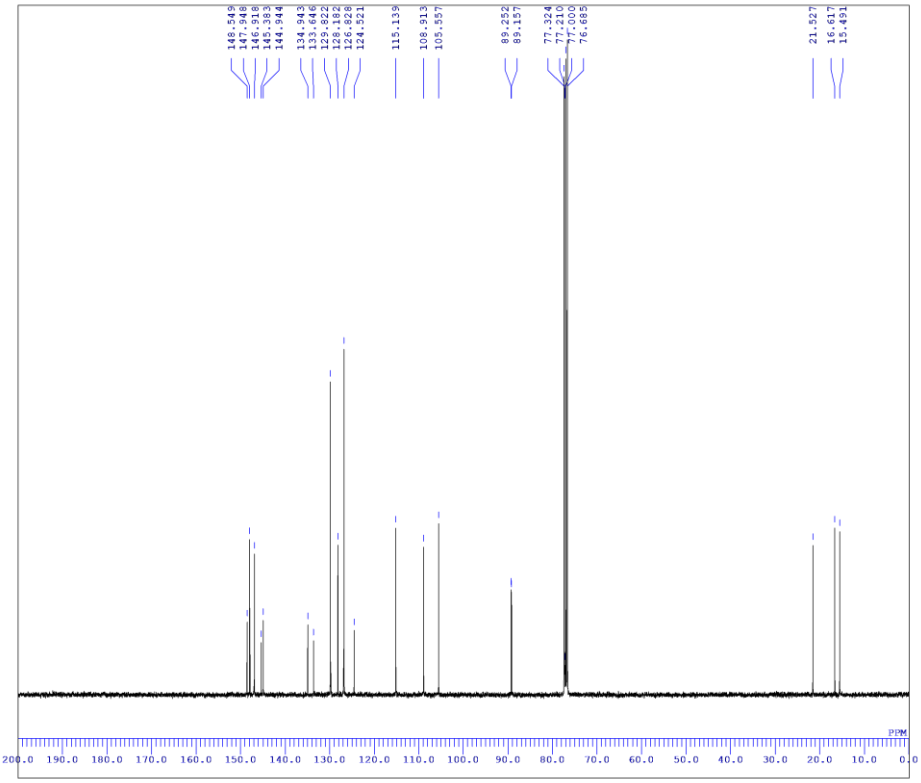


6,9-Dimethyl-3-tosyl-6,9-dihydro-3*H*-6,9-epoxybenzo[*e*]indole (4ma)

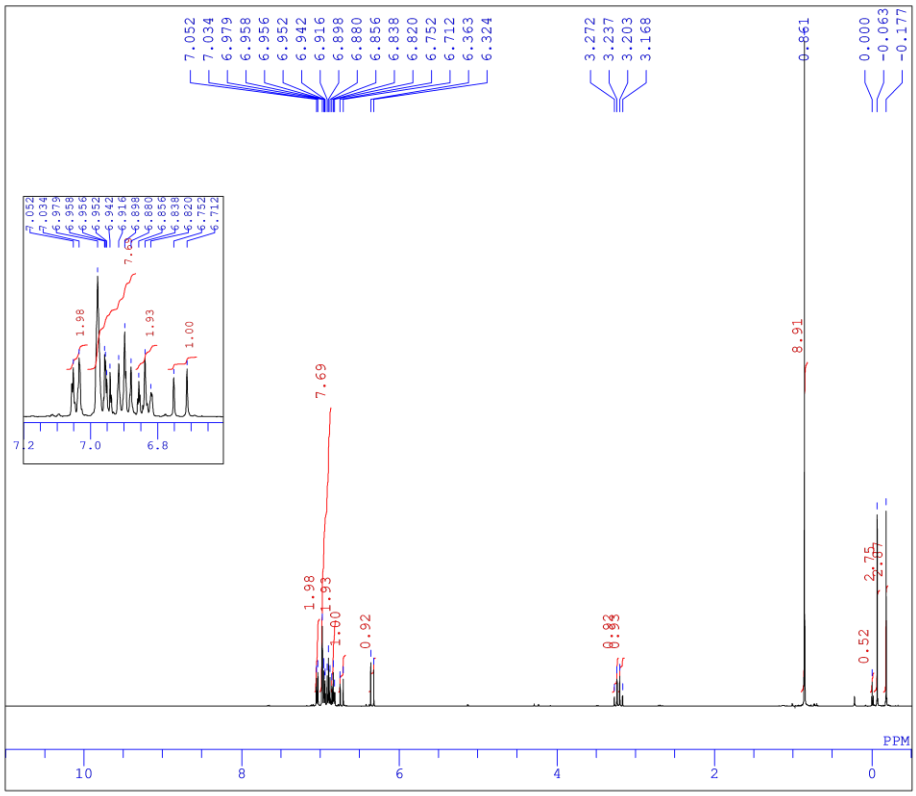




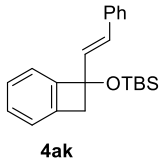
4ma



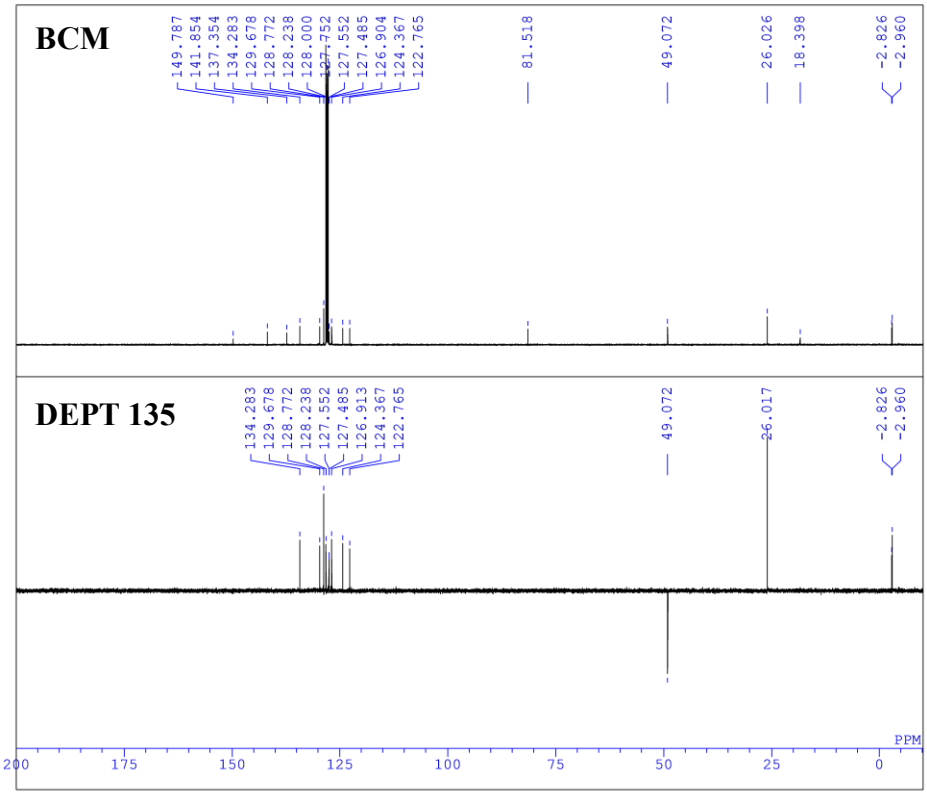
1-(*tert*-Butyldimethylsilyloxy)-1-(*E*)-styrylbenzocyclobutane (4ak)




```
DFILE  1-TBSO-1-stylylBenz
COMNT  single_pulse
DATIM  2021-02-10 11:19:55
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           5.0000 sec
PW1            3.35 usec
IRNUC  1H
CTEMP         21.0 c
SLVNT  C6D6
EXREF         0.00 ppm
BF            0.09 Hz
RGAIN           36
```



4ak




```
DFILE  1-TBSO-1-stylylBenz
COMNT  DEPT with decouplin
DATIM  2021-02-10 12:02:36
OBNUC  13C
EXMOD  dept.jxp
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           10.80 usec
IRNUC  1H
CTEMP         21.1 c
SLVNT  C6D6
EXREF        128.00 ppm
BF            0.09 Hz
RGAIN           50
```