

Supplementary Information for:

Cycloaddition Reactions of $(\text{C}_6\text{F}_5)_2\text{BN}_3$ with Dialkyl Acetylenedicarboxylates

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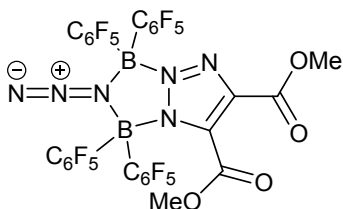
1. Experimental

1.1 General Experimental

With the exception of the synthesis of starting materials, all reactions and manipulations were carried out under an atmosphere of dry, O₂-free nitrogen using standard double-manifold techniques with a rotary oil pump. A nitrogen-filled glove box (MBRAUN) was used to manipulate solids including storage starting materials, room temperature reactions, product recovery and sample preparation for analysis. Molecular sieves (4 Å) were dried at 120 °C for 24 h prior to use. All solvents (toluene, DCM, THF, pentane, hexane) were dried by employing a Grubbs-type column system (Innovative Technology), degassed and stored over molecular sieves under a nitrogen atmosphere. Deuterated solvents were dried over molecular sieves before use. Chemicals were purchased from commercial suppliers and used as received. ¹H, ¹³C ¹¹B and ¹⁹F NMR spectra were recorded on a Bruker Avance III or a Bruker Avance 500 spectrometer. $(\text{C}_6\text{F}_5)_2\text{BN}_3$ ¹ was synthesised according to literature methods from $(\text{C}_6\text{F}_5)_2\text{BCl}$.² Chemical shifts are expressed as parts per million (ppm, δ) downfield of tetramethylsilane (TMS) and are referenced to *d*₈-toluene, *d*₆-benzene, *d*₈-THF, CDCl₃ and CD₂Cl₂ as internal standards. NMR spectra were referenced to CFCl₃ (¹⁹F) and BF₃·Et₂O/CDCl₃ (¹¹B). The description of signals include: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br. = broad. All coupling constants are absolute values and *J* values are expressed in Hertz (Hz). All spectra were analysed assuming a first order approximation. A Perkin-Elmer Analyser was used for carbon, hydrogen and nitrogen elemental analyses. High resolution mass spectrometry was performed in house employing DART or electrospray ionisation techniques in positive ion mode. Mass spectral data were recorded on an AB/Sciex QStarXL mass spectrometer (ESI) or a JEOL AccuTOF model JMS-T1000LC mass spectrometer (DART).

Caution: Covalent azides are potentially explosive and safety precautions should be taken during work with azides.

1.2 Experimental Details: Synthesis of 5



(C₆F₅)₂BN₃ (0.2 mmol) was dissolved in toluene (5 ml) and dimethyl but-2-ynedioate (28 mg, 0.2 mmol) was added. The reaction was stirred for 48 h to give a green solution. The solvent was removed *in vacuo* and the remaining oil was heated to *ca.* 50 °C for a few minutes in a concentrated pentane/toluene mixture until a clear solution resulted. Layering of this solution with pentane afforded large colourless crystals of the product. The remaining solution was removed and the crystals washed with pentane (3 x 2 ml) to afford the pure product (65 mg, 0.07 mmol, 14%).

¹H NMR (400 MHz, CD₂Cl₂, 298 K): 4.01 (s, 3H, CH₃), 3.78 (s, 3H, CH₃).

¹¹B NMR (128 MHz, CD₂Cl₂, 298 K): 0.7.

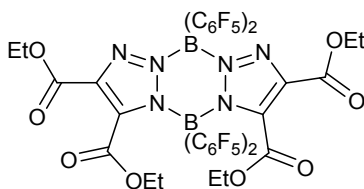
¹⁹F NMR (377 MHz, CD₂Cl₂, 298 K): -133.9 (m, 2F, *o*-F), -134.6 (m, 2F, *o*-F), -151.0 (t, 1F, ³J_{FF} = 19.5 Hz, *p*-F), -151.5 (t, 1F, ³J_{FF} = 20.0 Hz, *p*-F), -161.7 (m, 4F, *m*-F).

¹³C NMR (100 MHz, CD₂Cl₂, 298 K): 158.5 (s), 156.5 (s), 149.0 (m, ¹J_{C-F} = 245 Hz), 148.6 (m, ¹J_{C-F} = 245 Hz), 144.3 (s), 142.0 (m, ¹J_{C-F} = 255 Hz), 138.0 (m, ¹J_{C-F} = 248 Hz), 127.9 (m, ¹J_{C-F} = 255 Hz), 136.3 (s), 54.7 (s), 54.2 (s), signals for boron-bound carbon atoms were not observed.

Elem. Anal. calcd (%) for C₃₀H₆N₆O₄B₂F₂₀: C 39.34; H 0.66; N 9.17; Found: C 39.35, H 0.91; N 9.07.

ESI+ MS, *m/z*: 186.1 (calcd for [C₆H₇N₃O₄+H]⁺: 186.1), no peak was observed due to the molecular ion.

Synthesis of 6



(C₆F₅)₂BN₃ (1 mmol) was dissolved in toluene (10 ml) and diethyl but-2-ynedioate (170 mg, 1 mmol) was added. The reaction was stirred for 48 h and the solvent removed to give a red oil. Hexane (5 ml) was added to the oil in a little DCM and, over a period of 7 months, large colourless crystals were formed from slow

recrystallisation. The remaining solution was removed and the crystals washed with pentane (3 x 2 ml) to afford the pure product (123 mg, 0.11 mmol, 22%).

^1H NMR (400 MHz, d_8 -thf, 298 K): 4.38 (q, 2H, $^3J_{\text{CH}} = 7.13$ Hz, -CH₂), 4.09 (q, 2H, $^3J_{\text{CH}} = 7.30$ Hz, -CH₂), 1.31 (t, 3H, $^3J_{\text{CH}} = 7.13$ Hz, -CH₃), 1.24 (t, 3H, $^3J_{\text{CH}} = 7.30$ Hz, -CH₃).

^{11}B NMR (128 MHz, d_8 -thf, 298 K): 0.2.

^{19}F NMR (377 MHz, d_8 -thf, 298 K): -131.0 (d, 2F, $^3J_{\text{FF}} = 19.2$ Hz, *o*-F), -134.0 (d, 2F, $^3J_{\text{FF}} = 20.1$ Hz, *o*-F), -150.6 (t, 1F, $^3J_{\text{FF}} = 19.9$ Hz, *p*-F), -152.2 (t, 1F, $^3J_{\text{FF}} = 20.4$ Hz, *p*-F), -162.2 (m, 2F, *m*-F), -162.9 (m, 2F, *m*-F).

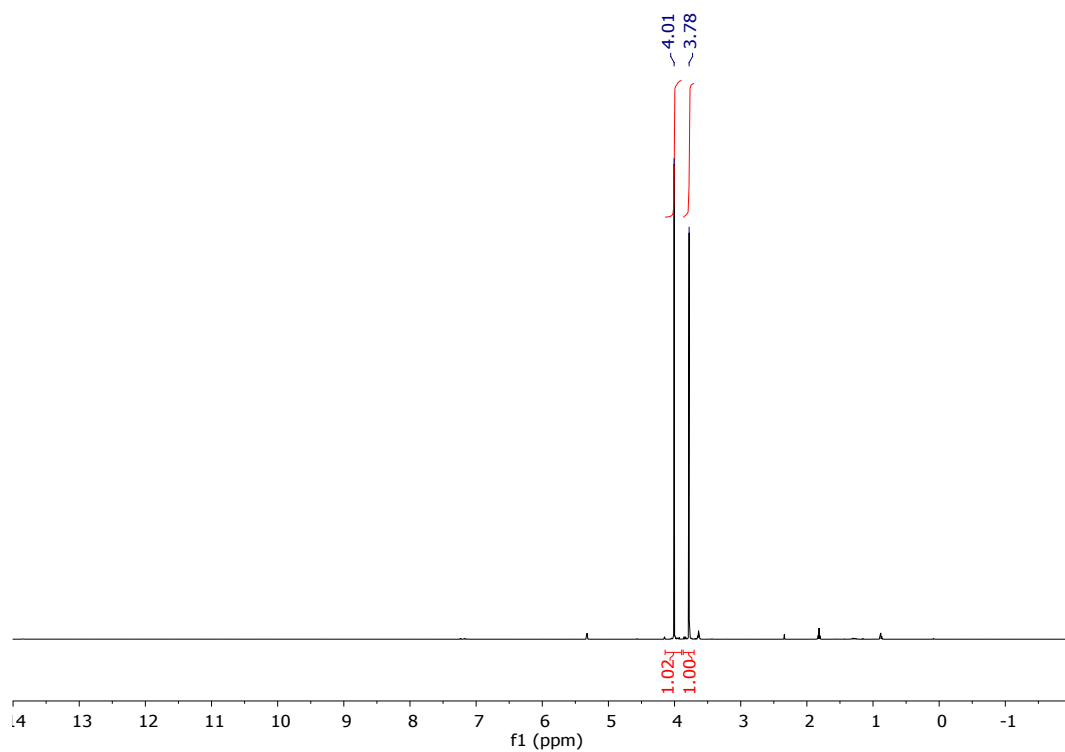
^{13}C NMR (100 MHz, CD₂Cl₂, 298 K) partial: 157.8 (s), 157.6 (s), 142.1 (s), 65.4 (s), 63.9 (s), 14.4 (s), 13.8 (s), signals for boron- and fluorine-bound carbon atoms were not observed.

Elem. Anal. calcd (%) for C₂₀H₁₀N₃O₄BF₁₀: C 43.12; H 1.81; N 7.54; Found: C 43.08, H 2.05; N 7.44.

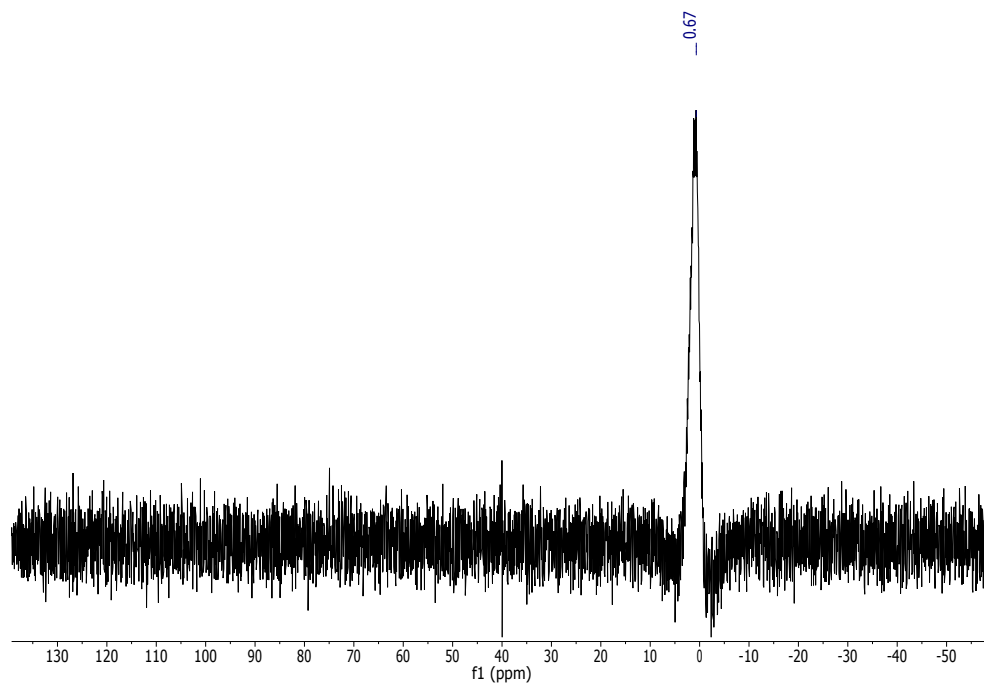
DART MS, m/z : 1115.1 (calcd for [M₂ (dimer)]⁺: 1115.1), 575.1 (calcd for [M+NH₄]⁺: 575.1), 557.1 (calcd for [M (monomer)]⁺: 557.1), 214.1 (calcd for [M-B(C₆F₅)₃ + H]⁺: 214.1).

1.3 NMR spectra of products

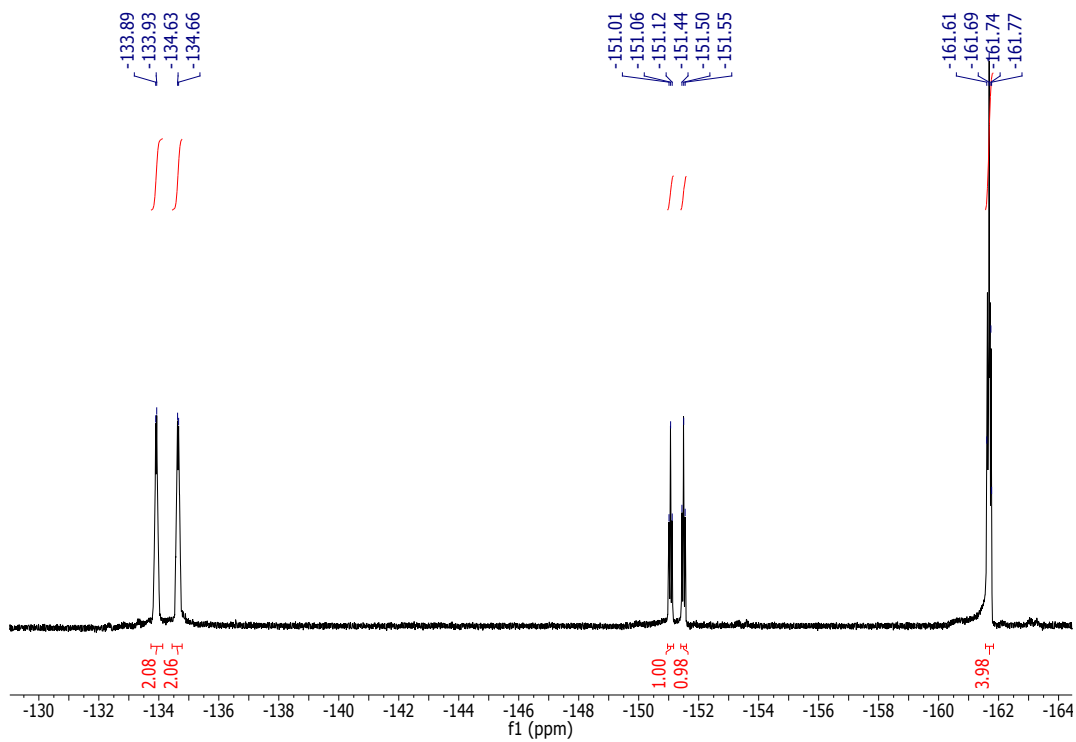
^1H NMR (400 MHz, CD_2Cl_2 , 298K) spectrum of **5**.



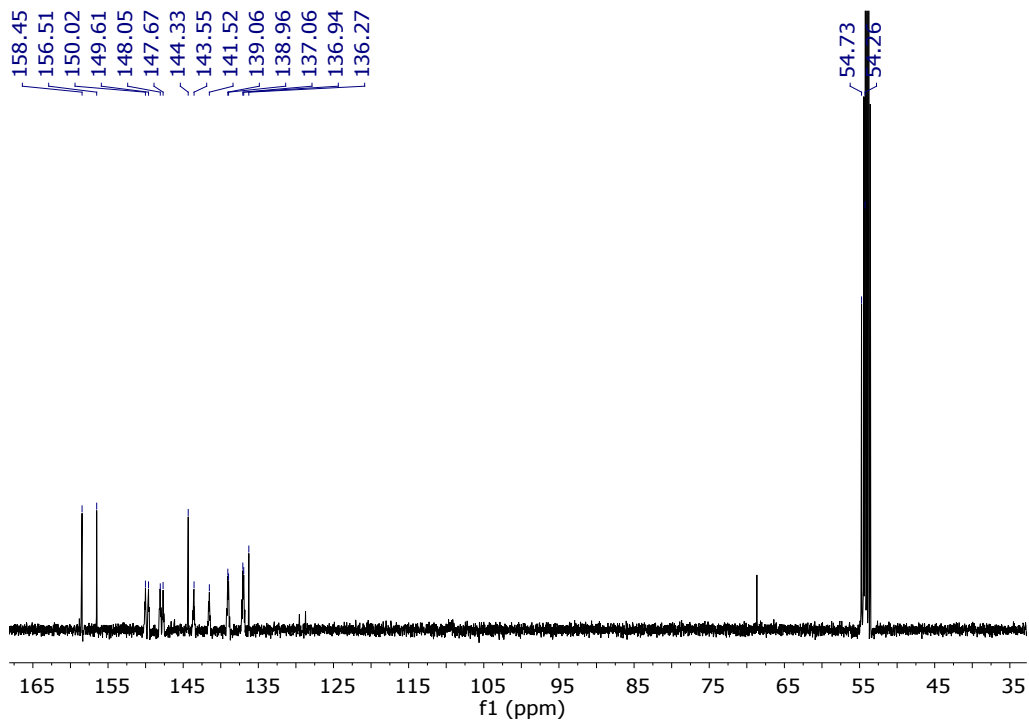
^{11}B NMR (128 MHz, CD_2Cl_2 , 298 K) spectrum of **5**.



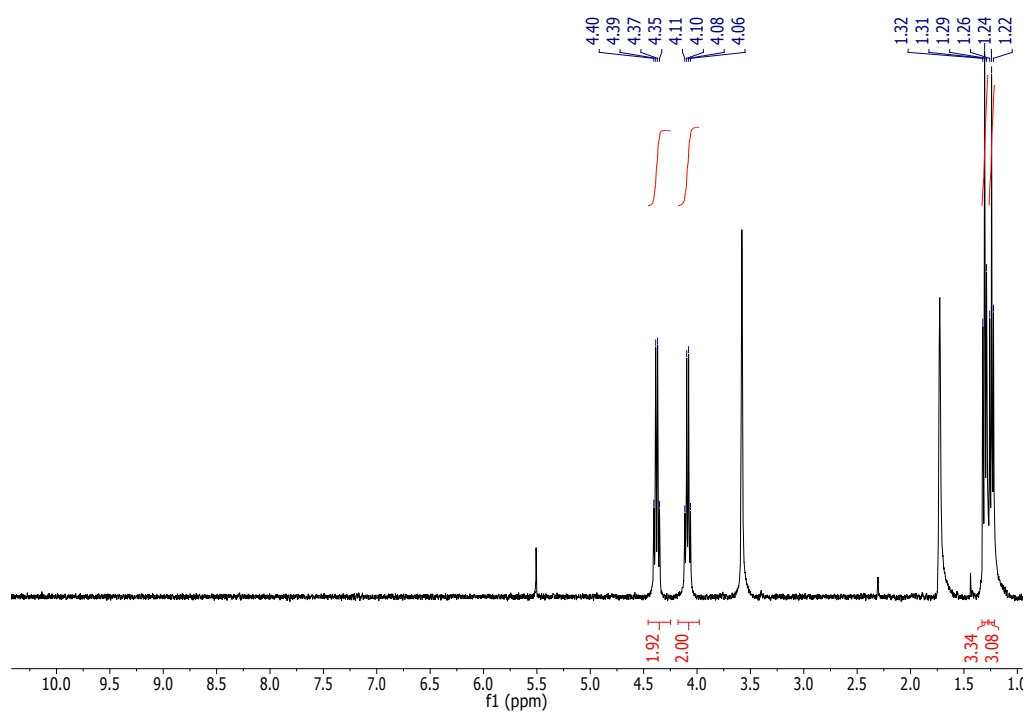
^{19}F NMR (377 MHz, CD_2Cl_2 , 298 K) spectrum of **5**.



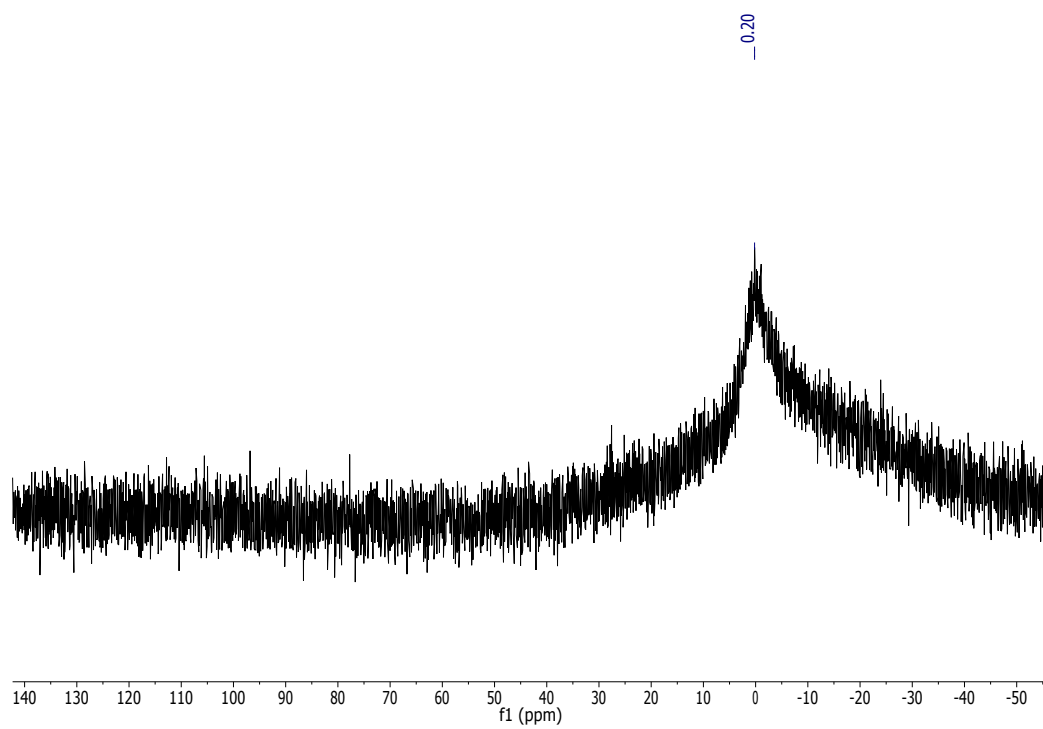
^{13}C NMR (100 MHz, CD_2Cl_2 , 298K) spectrum of **5**.



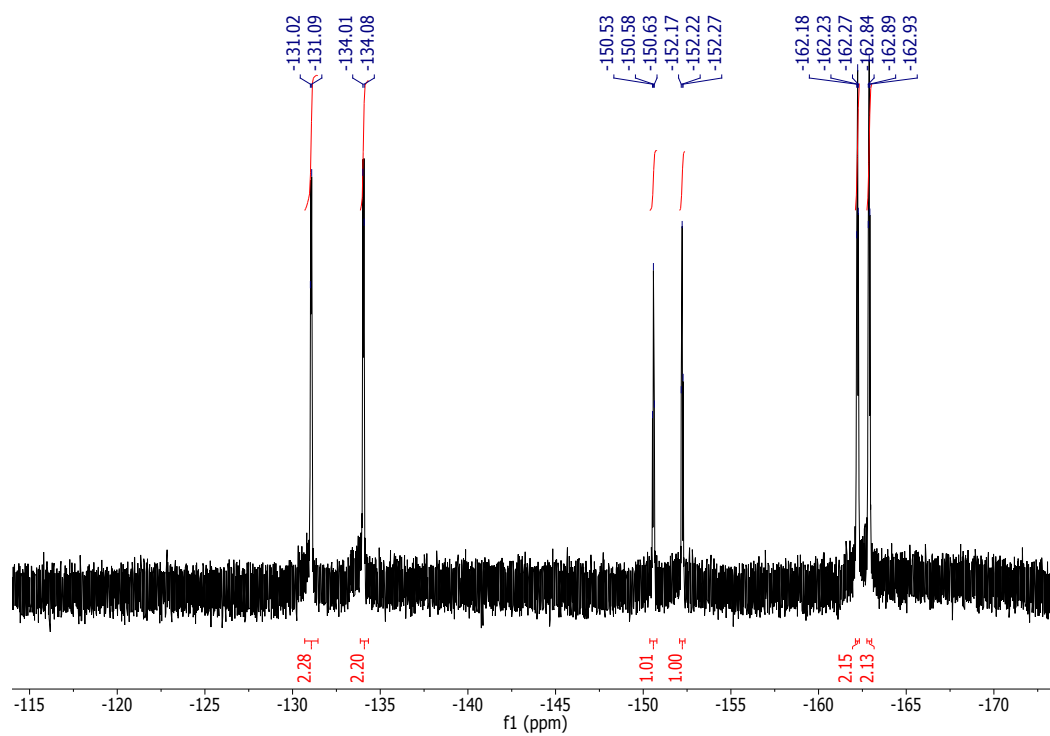
^1H NMR (400 MHz, d_8 -thf, 298K) spectrum of **6**.



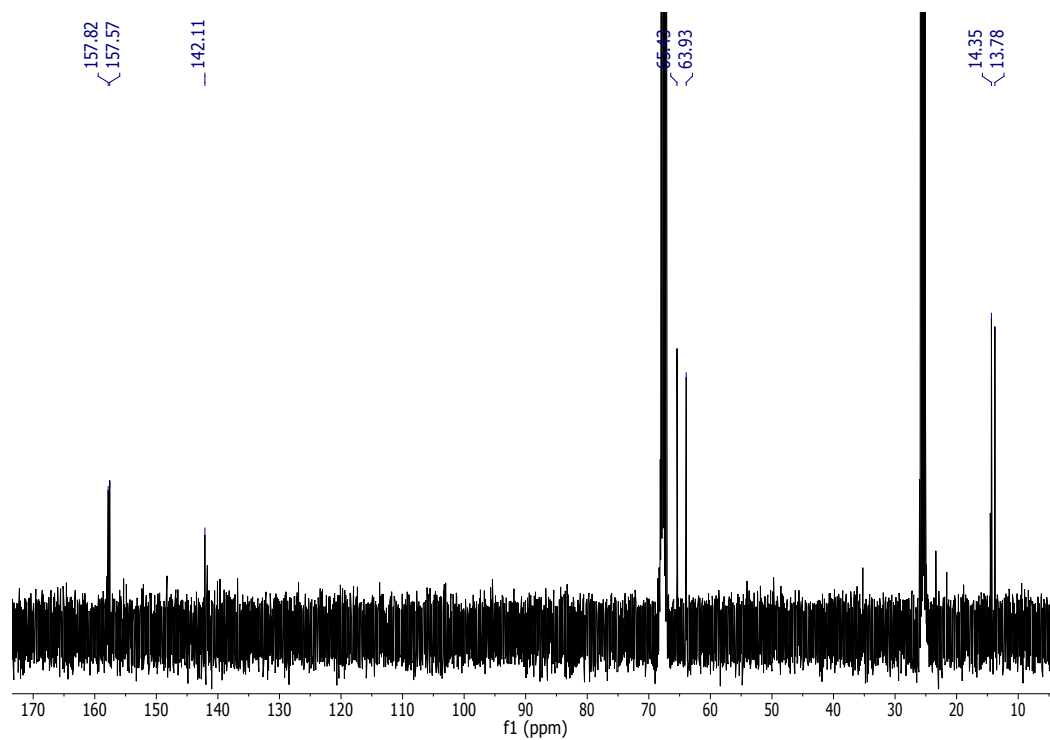
^{11}B NMR (128 MHz, d_8 -thf, 298 K) spectrum of **6**.



^{19}F NMR (377 MHz, d_8 -thf, 298 K) spectrum of **6**.



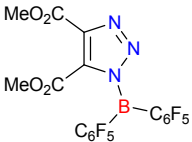
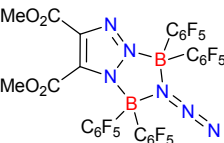
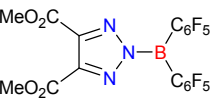
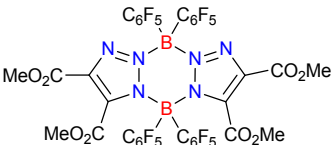
^{13}C NMR (100 MHz, d_8 -thf, 298K) spectrum of **6**.

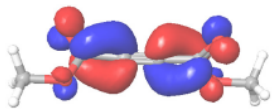


2. Theoretical calculations:

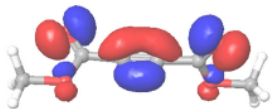
DFT calculations to model the reactivity of **1** with MeO₂CC≡CCO₂Me were undertaken using the B3LYP functional and 6-311G* triple-zeta basis set within Jaguar.³ All structures were geometry-optimised and energies determined (298.15 K) and zero point energy corrected.

Table 1

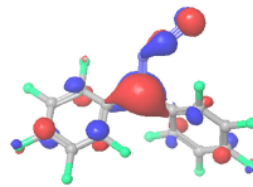
Compound	ΔH Hartree	ΔG Hartree	ΔS Hartree/K
1 (C ₆ F ₅) ₂ BN ₃	-1644.989806	-1645.066339	0.000257
MeO ₂ CC≡CCO ₂ Me	-533.089263	-533.139755	0.000169
I1 	-2178.155303	-2178.254366	0.000332
5 	-3823.175131	-3823.323897	0.000499
I2 	-2178.165968	-2178.268709	0.000345
6' 	-4356.363391	-4356.532995	0.000345



— -0.061160
LUMO

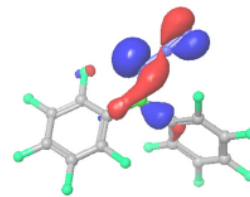


↑↓ -0.297974
HOMO



— -0.110929 LUMO

↑↓ -0.327890 HOMO-4



3. Crystallographic Details:

X-ray diffraction studies to determine the solid-state structure of crystalline materials were undertaken on single crystals grown under an inert atmosphere and protected from atmospheric air and moisture using an inert per-fluorinated polyether oil. Crystals were examined on a Bruker APEX-II diffractometer using monochromatic Mo-K α radiation and a CCD area detector. Data were collected at 150(2) K with temperatures maintained using an Oxford Cryostream cooler. Data were collected and processed using APEX-II software and an absorption correction applied using SAINT. Structure solution and refinement used the SHELXTL suite of programs. Crystallographic data are presented in Table 1, with full structural data available in cif format as ESI.

Table 2: Selected Crystallographic Data for **5** and **6**

Compound	5	6
Empirical Formula	C ₃₀ H ₆ B ₂ F ₂₀ N ₆ O ₄	C ₄₀ H ₂₀ B ₂ F ₂₀ N ₆ O ₈
Crystal System	Monoclinic	Monoclinic
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	12.5226(5)	10.7165(16)
<i>b</i> /Å	13.5536(6)	12.7361(19)
<i>c</i> /Å	19.7868(8)	32.695(5)
α /°	90	90
β /°	90.769(2)	95.618(8)
γ /°	90	90
<i>V</i> /Å ³	3358.0(2)	4440.9(11)
<i>Z</i>	4	4
<i>T</i> /K	150(2)	150(2)
<i>D_c</i> /g.cm ⁻³	1.812	1.666
Crystal size/mm	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.20
Total data	30770	37996
Unique data	10025	9887
R _{int}	0.0520	0.685
R ₁ [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.0443	0.0532
wR ₂ (all data)	0.0789	0.1316
GoF	1.0166	1.0187
ρ_{\min}/ρ_{\max} /eÅ ⁻³	-0.407/0.491	-0.888/1.030

References

1. (a) W. Fraenk, T. M. Klapötke, B. Krumm and P. Mayer, *Chem. Commun.*, 2000, 667; (b) W. Fraenk, T. M. Klapötke, P. M. B. Krumm, H. Nöth, H. Piotrowski and M. Suter, *J. Fluorine Chem.*, 2001, **112**, 73.
2. D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492.
3. A. D. Bochevarov, E. Harder, T. F. Hughes, J. R. Greenwood, D. A. Braden, D. M. Philipp, D. Rinaldo, M. D. Halls, J. Zhang and R. A. Friesner, "Jaguar: A high-performance quantum chemistry software program with strengths in life and materials sciences," *Int. J. Quantum Chem.*, 2013, **113**, 2110.