Supporting Information

https://doi.org/10.24959/ophcj.24.316200

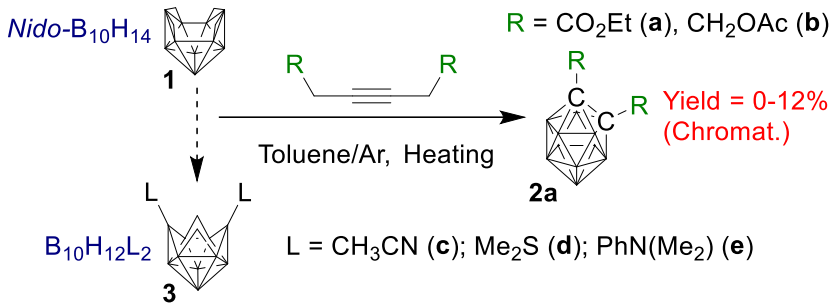
Freely available online on
http://ophcj.nuph.edu.ua

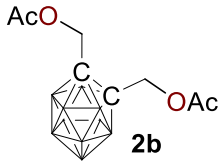
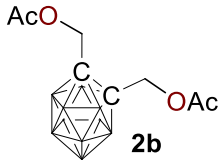
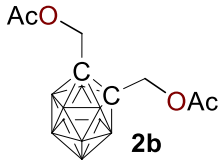
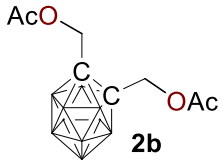
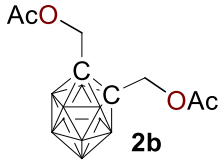
J. Org. Pharm. Chem. **2024**, *22* (3)

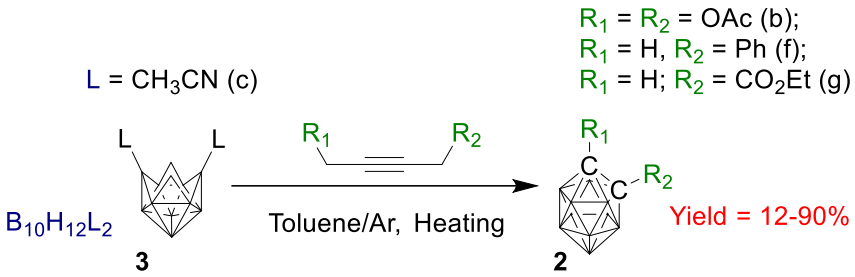
Reevaluation of the *ortho*-Carborane Synthesis: Success with Mono-Substituted Acetylenes in the Presence of Silver Salts

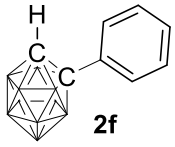
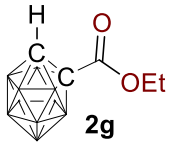
O. V. Svaliavyn[1,2], A. M. Mishchenko[2], Yu. L. Lishchenko[2], A. P. Mityuk[2,3], A. S. Cherednichenko[1], N. A. Shtil[1,2], V. V. Turcheniuk[2], R. V. Smaliy[2,4], Yu. V. Rassukana[1], O. Ye. Pashenko[1,2,3]

[1] Institute of Organic Chemistry of the National Academy of Sciences of Ukraine, 5, Akademik Kuhar str., 02660 Kyiv, Ukraine
[2] Enamine Ltd, 78, Winston Churchill str., 02094 Kyiv, Ukraine
[3] Taras Shevchenko National University of Kyiv, 60, Volodymyrska str., 01033 Kyiv, Ukraine
[4] National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", 37, Peremohy ave., 03056 Kyiv, Ukraine



Expected Product	Conditions	Analysis by LCMS	NMR spectrum
 **2b**	Substrate: **1**; L = $PhN(CH_3)_2$ (**e**, 10 eq., *in situ*); Acetylene: **R = b** 110°C, 12h	LCMS, negative mode, rt, m/z (rel.int.): 1.477; 292.2 (19), 290.2 (19) $[M]^-$, 280.0 (52). Yield: 11%.	^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.0 (s, CH_2, 4H), 2.9 – 1.2 (m), 2.1 (s, CH_3, 6H)
 **2b**	Acetylene: **R = b**; 120°C, 12h	LCMS, negative mode, rt, m/z (rel.int.): 1.396; 279.2 (52), 278.2 (100), 277.2 (98), 276 (57). Yield: 7%.	
 **2b**	1) *Substrate: **1** + $PhN(CH_3)_2$ (**e**, 10 eq., *in situ*); 80°C, 2h 2) Acetylene: **R = b**; 120°C, 48h	LCMS, negative mode, rt, m/z (rel.int.): 1.428; 279.2 (5), 278.2 (21), 276.2 (20), 274.4 (12) $[M\text{-}CH_3]^-$. Yield: 8%.	
 **2b**	Substrate: **3d**; Acetylene: **R = b**; 110°C, 12h	LCMS, positive mode, rt, m/z (rel.int.): 1.661; 290.2 (5), 288.2 (6) $[M]^+$, 287 (3). Yield: 12%.	
 **2b**	Substrate: **3c**; Acetylene: **R = b**; 110°C, 12h	LCMS, negative mode, rt, m/z (rel.int.): 1.497; 292.2 (41), 291.2 (28), 290.2 (20) $[M]^-$, 280.0 (52). Yield: 10%.	^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.21 (q, J = 7.3 Hz, 4H), 2.47 – 1.97 (m), 2.1 (s, 6H).

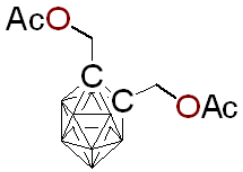


Product	Conditions	NMR spectrum
 **2f** Yield: 69% (pure sample)	Substrate: **3c** Acetylene: **R_1 = H**; **R_2 = Ph** Catalyst: $AgNO_3$	^{1}H NMR (400 MHz, DMSO-*d*) δ 7.49 (d, *J* = 7.4 Hz, 2H), 7.43 – 7.30 (m, 3H), 3.97 (s, 1H), 3.30 – 1.60 (m, 10 H). ^{11}B NMR (192.4 MHz, $CDCl_3$): -2.06 (d, *J* = 144 Hz, 1B), -4.37 (d, *J* = 152 Hz, 1B), -8.94 (d, *J* = 148 Hz, 2B), -8.0 – 14.5 (m, 6B).
 **2g** Yield: 90% (pure sample)	Substrate: **3c** Acetylene: **R_1 = H**; **R_2 = COOEt** Catalyst: $AgNO_3$	^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.3 (qd, *J* = 7.1, 1.0 Hz, 2H), 4.1 (s, 1H), 2.92 – 1.65 (m, 10H), 1.32 (td, *J* = 7.1, 1.0 Hz, 3H).

NMR spectra

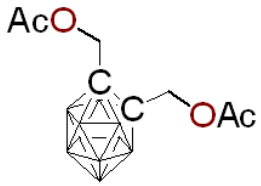
Mixture of products including 2b (7%)

^{1}H NMR (400 MHz, Chloroform-*d*)



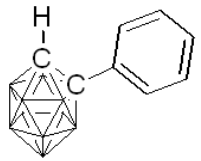
Mixture of products including 2b (10%)

^{1}H NMR (400 MHz, Chloroform-*d*)



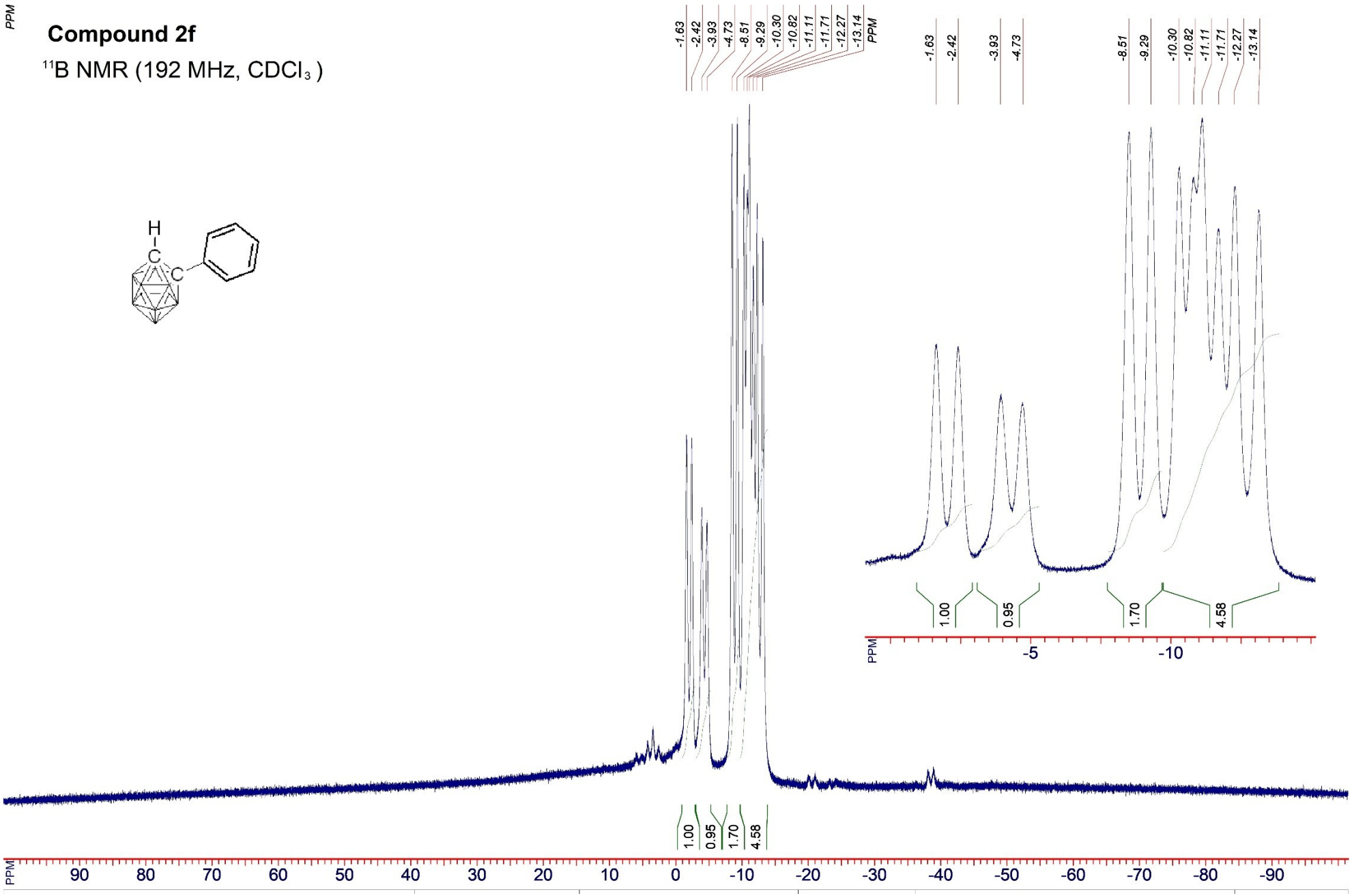
Compound 2f

^{1}H NMR (500 MHz, DMSO-d_6)



Compound 2f

^{11}B NMR (192 MHz, $CDCl_3$)



Compound 2g

1H NMR (400 MHz, Chloroform-*d*)