Electronic supplementary materials *Mendeleev Commun.*, 2021, **31**, 201–203

Nucleophilic addition of amino acid esters to nitrilium derivatives of *closo*-decaborate anion

**Alexey V. Nelyubin, Ilya N. Klyukin, Alexander S. Novikov, Andrey P. Zhdanov,
Mikhail S. Grigoriev, Konstantin Yu. Zhizhin and Nikolay T. Kuznetsov**

Contents

1 General Information

Reagents and solvents: The started compound $(NBu_4)[B_{10}H_9NCMe]$ **1** was synthesized by a modified method [S1]. Amino acids (Aldrich, Acros organics, 99%) were used without additional purification. All solvents were purified according to the literature method [S2].

Elemental analysis for carbon, nitrogen, and hydrogen was carried out using a Carlo Erba CHNS3 FA 1108 Elemental Analyzer. The boron content was analyzed by using ICP MS on an iCAP 6300 Duo inductively coupled plasma–atomic emission spectrometer at the Shared Knowledge Center "Scientific Research Analytical Center FSUE IREA National Research Center Kurchatov Institute."

IR spectra (4000−500 cm^{-1}) of prepared compounds were recorded on an Infralyum FT 08 Fourier transform spectrometer (Lumex Instruments Research and Production Company) in the region of 4000–500 cm^{-1} with the resolution of 1 cm^{-1}. Samples were prepared in KBr pellets.

^{1}H, ^{11}B and ^{13}C NMR studies were performed within the framework of the State Assignment of the Kurnakov Institute (IGIC RAS) in the field of fundamental scientific research. Spectra were recorded in CD_3CN on a Bruker Avance II 300 spectrometer operating at 300.3, 96.32 and 75.49 MHz, respectively, using internal deuterium lock. Tetramethylsilane and boron trifluoride etherate were used as external references.

2 General Procedures

Synthesis of amino acid ethyl esters

Amino acid ethyl esters were obtained as hydrochlorides according to the literature procedure [S6]. The corresponding amino acid (100 mmol) was dissolved in ethanol (100 ml). The resulting solution was cooled to 0 °C, and $SOCl_2$ (150 mmol, 10.9 ml) was added dropwise. After the addition, the reaction mass was heated and was kept on stirring for 2 hours under reflux. The evolved gas was bubbled through a NaOH solution. After cooling, the precipitate was filtered off, the mother liquor was evaporated on a rotary evaporator, and the residue was added to the previously obtained precipitate. The crude product was recrystallized from a mixture of ethanol and diethyl ether, then dried over P_2O_5.

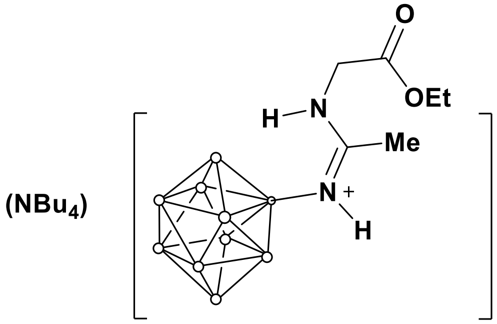
The general procedure of obtaining of borylated amidines

Triethylamine (1.1 mmol; 0.150 ml) was added to a 10 ml aqueous solution of the corresponding ethyl ester hydrochloride (2.0 mmol), and the resulting mixture was stirred for 15 min, then CH_2Cl_2 (15 ml) was added. The organic phase was separated, dried over $CaCl_2$, and poured into a solution of $(NBu_4)[B_{10}H_9NCMe]$ (0.4 g; 1.0 mmol) in CH_2Cl_2 (5 ml). The mixture was kept on stirring for 2 hours under reflux in a dry argon atmosphere. After cooling to room temperature, the solution was concentrated on a rotary evaporator, aqueous HCl (30 ml of 0.1 N) was added and placed in an ultrasonic bath for 10 minutes. The target product was extracted with CH_2Cl_2; the organic phase was dried over anhydrous Na_2SO_4 and evaporated on a rotary evaporator. The product was recrystallized from acetonitrile/ethyl alcohol.

Tetraphenylphosphonium salt (2'a) for X-ray experiment was obtained by successive cation metathesis reaction with sodium tetraphenylborate and tetraphenylphosphonium chloride

3 Product characterization

Tetra-*n*-butylammonium 2-[(*Z*)-{1-[(2-ethoxy-2-oxoethyl)amino]ethylidene}ammonio]-nonahydro-*closo*-decaborate (1-) (2a)



$(NBu_4)[2\text{-}B_{10}H_9(NHC(Me)HNCH_2COOEt]$

Yield 0.472 g (93.4%).

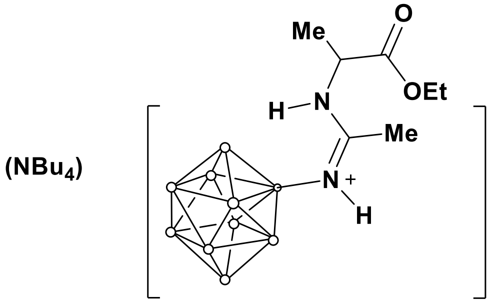
Anal. found: B, 21.8; C, 52.22; H, 11.36; N, 8.31. Calcd for $C_{22}H_{57}B_{10}N_3O_2$: B, 21.5; C 52.45; H, 11.40; N, 8.34. IR spectrum in KBr, selected bands, cm^{-1}: 3417, 3296, 3242 (ν N-H), 2470 (ν B-H), 1746 (ν C=O), 1641 (ν C=N), 1055 (δ B-B-H);

^{11}B NMR (CD_3CN, ppm), δ: 2.9 (d, 1B, B^{10}, $J^{\text{B-H}}$ = 146 Hz), –4.2 (d, 1B, B^{1}, $J^{\text{B-H}}$ = 139 Hz), –15.0 (s, 1B, B^{2}), –23.7 (d, 3B, B^{4,7,8}, $J^{\text{B-H}}$ = 127 Hz), –26.8 (d, 4B, B^{3,5,6,9}, $J^{\text{B-H}}$ = 126 Hz);

^{1}H NMR (CD_3CN, ppm), δ: -1.01-1.55 (m, 9H, $B_{10}H_9$), 8.62 (br.s, 1H, N$\underline{H}$-C=NH), 6.47 (br.s, 1H, NH-C=N$\underline{H}$), 4.28 (q, 2H, COO-C$\underline{H_2}$-CH_3 J= 7.15 Hz), 4.15 (d, 2H, NH-C$\underline{H_2}$-COO J= 6.24 Hz), 3.15 (m, 16H, NBu_4), 2.02 (s, 3H, NH=C-C$\underline{H_3}$), 1.64 (m, 16H, NBu_4), 1.40 (m, 16H, NBu_4), 1.33(t, 3H, COO-CH_2-C$\underline{H_3}$ J= 7.15 Hz), 1.00 (m, 24H, NBu_4);

^{13}C NMR (CD_3CN, ppm), δ: 168.8 ($\underline{C}$OO), 166.2 ($\underline{C}$=NH), 61.2 (COO-$\underline{C}H_2$-CH_3), 58.7 (NBu_4), 46.2 ($\underline{C}H_2$-COO), 23.7 (NBu_4), 19.7 (NBu_4), 18.6 (NH=C-$\underline{C}H_3$), 13.8 (COO-CH_2-$\underline{C}H_3$), 13.2 (NBu_4).

Tetra-*n*-butylammonium 2-[(*Z*)-{1-[(1-ethoxy-1-oxoprop-2-yl)amino]ethylidene}-ammonio]nonahydro-*closo*-decaborate (1-) (2b)



$(NBu_4)[2\text{-}B_{10}H_9NHC(Me)HNCH(Me)COOEt]$

Yield 0.457 g (88.9%).

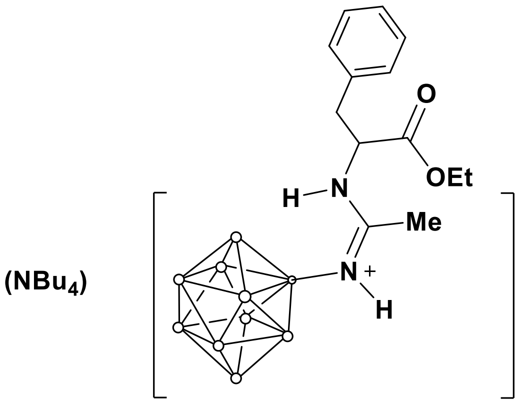
Anal. found: B, 21.0; C, 52.99; H, 11.48; N, 8.15. Calcd for $C_{23}H_{59}B_{10}N_3O_2$: B, 21.2; C 53.12; H, 11.44; N, 8.08. IR spectrum in KBr, selected bands, cm^{-1}: 3398, 3335, 3296, 3241 (ν N-H), 2468 (ν B-H), 1742 (ν C=O), 1640 (ν C=N), 1062 (δ B-B-H);

^{11}B NMR (CD_3CN, ppm): 3.1 (d, 1B, B(10), $J^{B\text{-}H}$ = 145 Hz), –4.0 (d, 1B, B(1), $J^{B\text{-}H}$ = 141 Hz), –15.0 (s, 1B, B(2)), –23.6 (d, 3B, B(4,7,8), $J^{B\text{-}H}$ = 122 Hz), –26.7 (d, 4B, B(3,5,6,9), $J^{B\text{-}H}$ = 127 Hz);

^{1}H NMR (CD_3CN, ppm), δ: -0.95-1.80 (m, 9H, $B_{10}H_9$), 8.60 (br.s, 1H, $N\underline{H}$-C=NH), 6.39 (br.s, 1H, NH-C=$N\underline{H}$), 4.28 (m, 1H, NH-$C\underline{H}$-COO), 4.24 (q, 2H, COO-$C\underline{H_2}$-CH_3 J=7.06 Hz), 3.15 (m, 16H, NBu_4), 2.00 (s, 3H, NH=C-$C\underline{H_3}$), 1.65 (m, 16H, NBu_4), 1.57 (d, 3H NH-CH($C\underline{H_3}$)-COO J=7.34 Hz), 1.40 (m, 16H, NBu_4), 1.31 (t, 3H COO-CH_2-$C\underline{H_3}$ J=7.15 Hz), 1.00 (m, 24H, NBu_4);

^{13}C NMR (CD_3CN, ppm), δ: 171.3 ($\underline{C}$OO), 164.8 ($\underline{C}$=NH), 61.7 (COO-$\underline{C}H_2$-CH_3), 58.7 (NBu_4), 51.9 ($\underline{C}$H-COO), 23.7 (NBu_4), 19.7 (NBu_4), 18.1 (NH=C-$\underline{C}H_3$), 18.0 (CH-($\underline{C}H_3$)-COO), 13.6 (COO-CH_2-$\underline{C}H_3$), 13.2 (NBu_4);

Tetra-*n*-butylammonium 2-[(*Z*)-{1-[(1-ethoxy-1-oxo-3-phenylprop-2-yl)amino]ethylidene}-ammonio]nonahydro-*closo*-decaborate (1-) (2c)



$(NBu_4)[2\text{-}B_{10}H_9(NHC(Me)HNCH(Bn)COOEt]$

Yield 0.542 g (91.3%).

Anal. found: B, 18.0; C, 58.65; H, 10.69; N, 7.07. Calcd for $C_{29}H_{63}B_{10}N_3O_2$: B, 18.5; C 58.43; H, 10.66; N, 7.05. IR spectrum in KBr, selected bands, cm^{-1}: 3422, 3301, 3240 (ν N-H), 2470 (ν B-H), 1750 (ν C=O), 1645 (ν C=N), 1055 (δ B-B-H);
^{11}B NMR (CD_3CN, ppm): 3.1 (d, 1B, B(10), J^{B-H} = 148 Hz), –4.1 (d, 1B, B(1), J^{B-H} = 141 Hz), –15.0 (c, 1B, B(2)), –23.7 (d, 3B, B(4,7,8), J^{B-H} = 124 Hz), –26.8 (d, 4B, B(3,5,6,9), J^{B-H} = 123 Hz);

^{1}H NMR (CD_3CN, ppm), δ: -0.95-1.80 (m, 9H, $B_{10}H_9$), 8.81 (br.s, 1H, N$\underline{H}$-C=NH), 7.45-7.25 (m, 5H, CH_2-$C_6\underline{H_5}$), 6.31 (br.s, 1H, NH-C=N$\underline{H}$), 4.37 (m, 1H, NH-C$\underline{H}$-COO), 4.28 (q, 2H, COO-C$\underline{H_2}$-CH_3 J=7.15 Hz), 3.33 (d, 2H, C$\underline{H_2}$-C_6H_5 J=7.15 Hz), 3.15 (m, 16H, NBu_4), 2.01 (s, 3H, NH=C-C$\underline{H_3}$), 1.65 (m, 16H, NBu_4), 1.62 (s, 2H, NH-CH-C$\underline{H_2}$), 1,40 (m, 16H, NBu_4), 1.32 (t, 3H, COO-CH_2-C$\underline{H_3}$ J=7.15 Hz), 1.00 (m, 24H, NBu_4);

^{13}C NMR (CD_3CN, ppm), δ: 170.2 ($\underline{C}$OO), 165.1 ($\underline{C}$=NH), 136.4, 130.2, 128.9, 127.4 (CH_2-$\underline{C_6}H_5$), 62.0 (COO-$\underline{C}H_2$-CH_3), 58.7 (NBu_4), 56.2 (C$\underline{H}$-COO), 39.4 (CH-$\underline{C}H_2$-C_6H_5), 23.7 (NBu_4), 19.7 (NBu_4), 18.1 (NH=C-$\underline{C}H_3$), 13.8 (COO-CH_2-$\underline{C}H_3$), 13.2 (NBu_4).

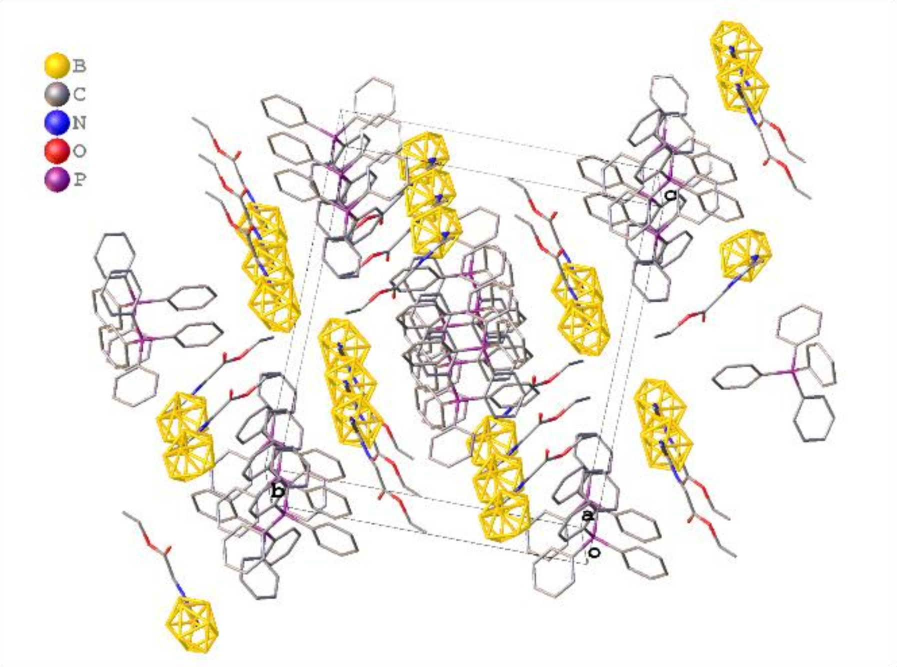


Figure S1 The crystal packing of salt **2'a**.

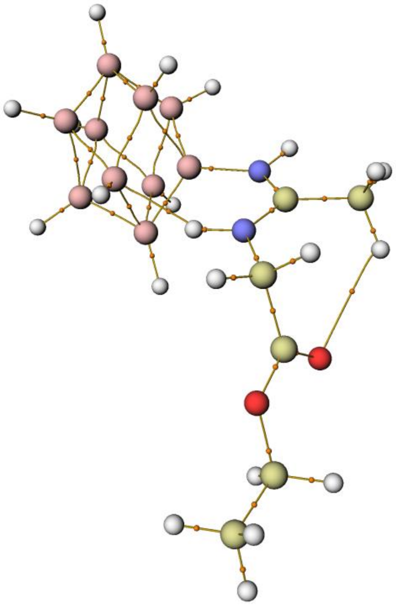


Figure S2 Visualization of the results of QTAIM analysis: molecular graph for optimized equilibrium model structure [2-$B_{10}H_9NH{=}C(Me)NHCH_2COOMe]^-$. Bond critical points are marked as small orange circles

Computational details

The full geometry optimization of model structure [2–$B_{10}H_9NHC(Me)NHCH_2COOEt]^-$ within spin restricted approximation for Kohn–Sham equations was carried out at the ωB97X-D3/6-31++G(d,p) level of theory with the help of the ORCA 4.1.0 program package [S3]. The symmetry operations were not applied during the geometry optimization procedure. The Hessian matrix was calculated numerically for optimized model structure [2–$B_{10}H_9NHC(Me)NHCH_2COOEt]^-$ in order to prove the location of the correct minima on the potential energy surface (no imaginary frequencies). The topological analysis of the electron density distribution with the help of the Quantum Theory of Atoms in Molecules (QTAIM) formalism [S4] has been performed by using the Multiwfn program (version 3.6) [S5].

Table S1. Cartesian atomic coordinates for model structure [2-$B_{10}H_9NHC(Me)NHCH_2COOEt]^-$

Atom	X	Y	Z
Starting experimental XRD geometry			
O	4.383223	14.092397	14.032572
O	2.437307	15.099357	14.504397
N	5.763139	11.772206	17.912256
H	5.762639	11.207075	18.588130
N	4.426980	12.906253	16.449725
H	5.150513	13.114279	15.994781
C	4.572410	12.121199	17.498248
C	3.361022	11.622946	18.206197
H	3.631475	11.041231	18.946852
H	2.801841	11.116943	17.579488
H	2.851597	12.384206	18.556478
C	3.159458	13.454619	15.988662
H	2.776095	14.049854	16.680573
H	2.516364	12.723104	15.815420

C	3.409917	14.227595	14.728914
C	2.606463	15.950208	13.324623
H	2.723575	15.394631	12.513068
H	3.403127	16.528498	13.428864
C	1.370684	16.785375	13.207933
H	1.446113	17.372138	12.426552
H	0.590794	16.202218	13.106014
H	1.267754	17.330677	14.015480
B	7.511279	13.220815	16.153252
H	6.837066	13.828128	15.439817
B	7.153519	12.175459	17.426082
B	8.188854	11.665128	15.995836
H	7.963968	11.035823	15.146509
B	9.205766	13.173946	16.223308
H	9.862474	13.761430	15.536883
B	8.168859	13.671478	17.662838
H	7.857141	14.664558	18.178765
B	9.819110	12.978539	17.900228
H	10.618607	13.662284	18.263170
B	8.382998	12.261265	18.765170
H	7.985463	12.373390	19.797234
B	8.384945	10.839334	17.596791
H	7.925667	9.784784	17.716647
B	9.828886	11.556429	16.749996
H	10.700656	11.061060	16.174142

B	9.777462	11.354712	18.426283
H	10.483127	10.806887	19.162085
Optimized equilibrium geometry (ωB97X-D3/6-31++G(d,p) level of theory)			
O	2.841554	13.145875	14.698264
O	2.732782	15.378800	14.949643
N	5.791260	11.286951	17.158002
H	5.737581	10.296209	17.351009
N	4.699026	13.265227	16.960604
H	5.639159	13.652655	16.821397
C	4.663064	11.934869	17.127487
C	3.349889	11.237323	17.317752
H	3.508612	10.167051	17.458141
H	2.713501	11.392720	16.443056
H	2.838929	11.626551	18.204612
C	3.581077	14.144509	16.782665
H	3.896096	15.155725	17.045236
H	2.752194	13.878552	17.450189
C	3.029602	14.140635	15.360451
C	2.194651	15.492092	13.619379
H	1.266580	14.913919	13.566631
H	2.907987	15.049039	12.918464
C	1.968588	16.963863	13.348832
H	1.555634	17.095118	12.344087
H	1.265787	17.390513	14.070162
H	2.909020	17.517570	13.411121

B	7.615630	12.851161	15.701420
H	6.949606	13.163668	14.750891
B	7.198515	11.901271	17.044506
B	8.588904	11.476830	15.982499
H	8.704598	10.640161	15.125384
B	9.208056	13.193953	16.167288
H	9.900824	13.878631	15.462121
B	7.784234	13.613468	17.225767
H	7.191644	14.643800	17.461302
B	9.402206	13.336175	17.974566
H	9.986903	14.292520	18.410407
B	7.949606	12.424710	18.597609
H	7.213697	12.560236	19.545565
B	8.524575	10.916162	17.718868
H	8.283745	9.747424	17.917706
B	9.974742	11.829548	17.096355
H	11.070615	11.460751	16.766436
B	9.531400	11.822351	18.745004
H	10.146261	11.493873	19.719384

References

S1. A.P. Zhdanov, V.V. Voinova, I.N. Klyukin, A.S. Kubasov, K.Y. Zhizhin and N.T. Kuznetsov, *J. Clust. Sci.*, 2019, **2**,.

S2. D.B.G. Williams and M. Lawton, *J. Org. Chem.*, 2010, **75**, 8351.

S3. F. Neese, *WIREs Comput. Mol. Sci.*, 2012, **2**, 73.

S4. R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, 1994.

S5. T. Lu and F. Chen, *J. Comp. Chem.*, 2011, **33**, 580.

S6. T.J. Rashamuse, Z. Njengele, E.M. Coyanis, Y. Sayed, S. Mosebi and M.L. Bode, *Eur. J. Med. Chem.*, 2020, **190**, 112111.

NMR Spectra

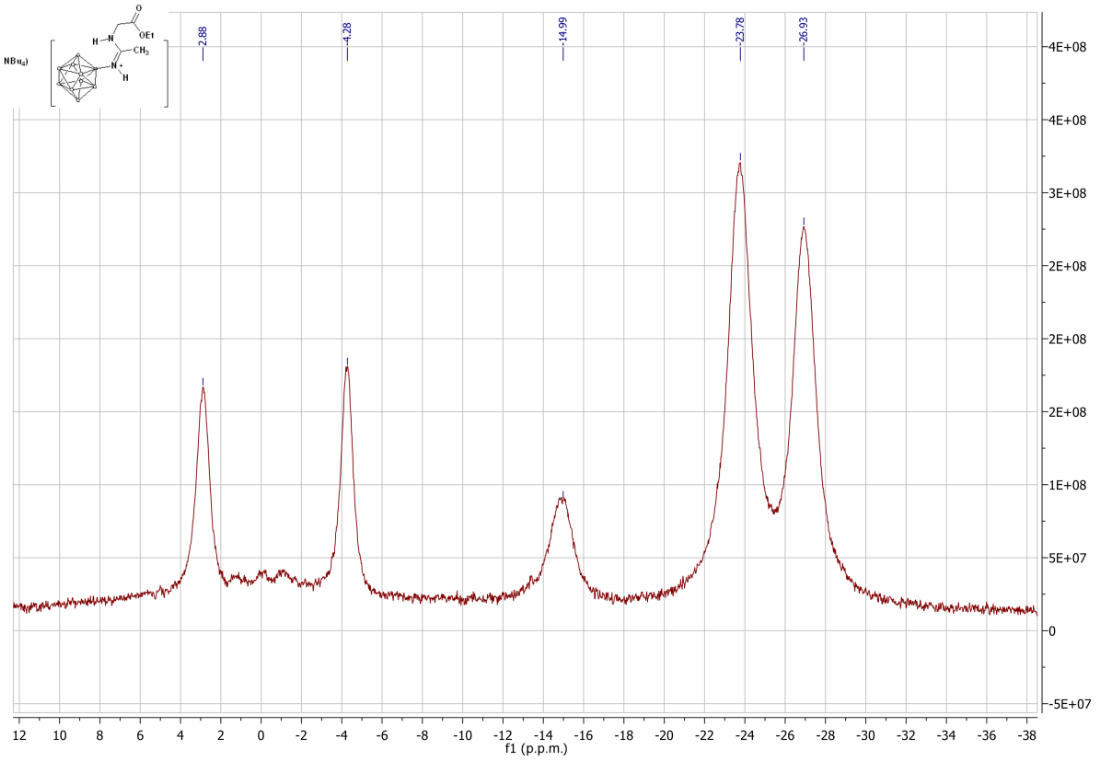


Figure S3 ^{11}B{^{1}H} NMR spectra of 2a

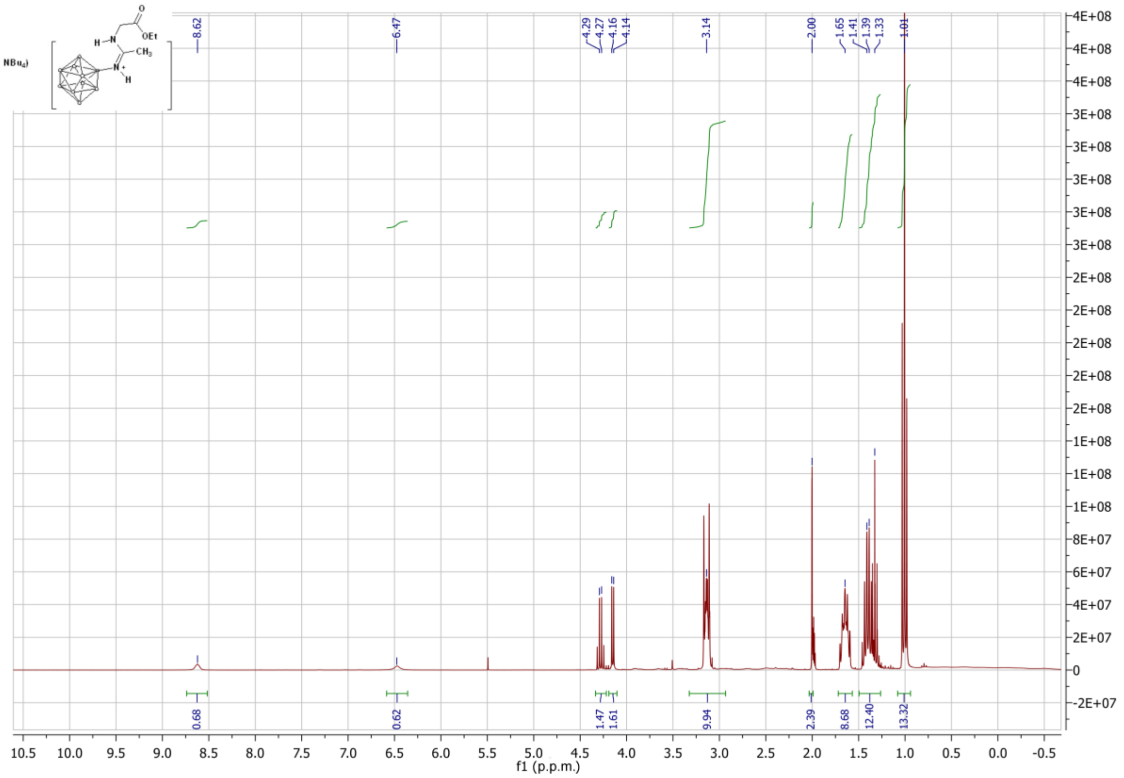


Figure S4 ^{1}**H NMR spectra of 2a**

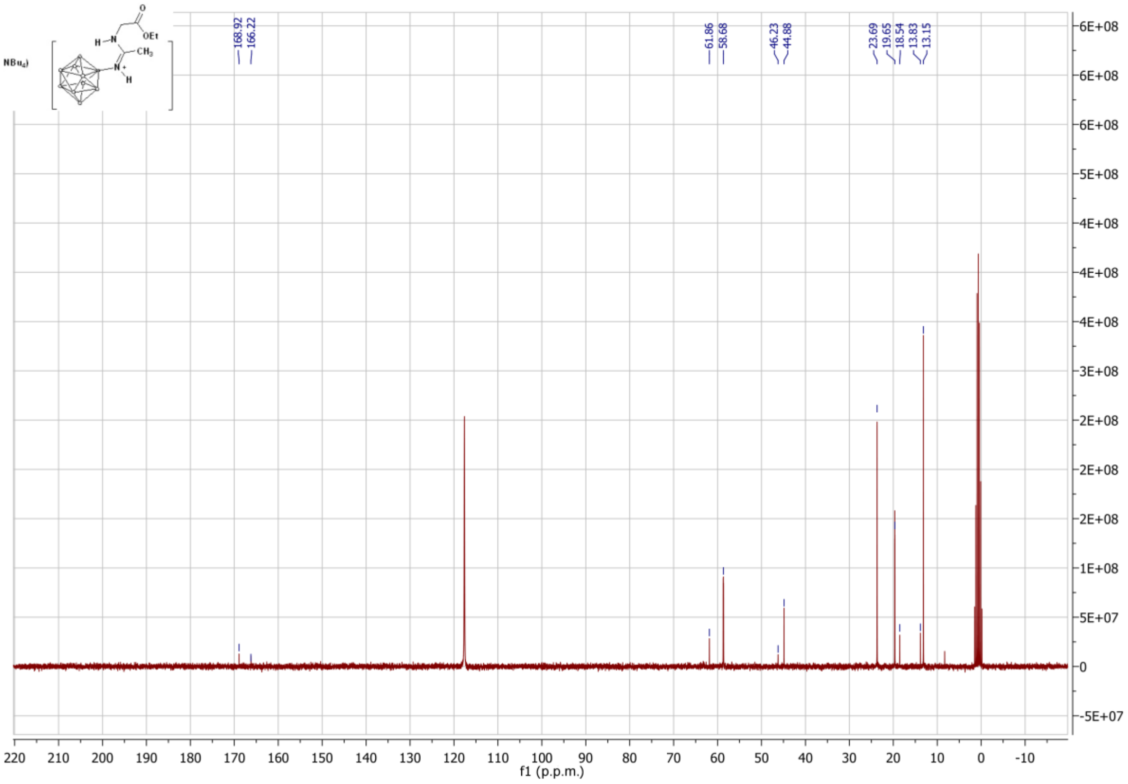


Figure S5 ^{13}**C NMR spectra of 2a**

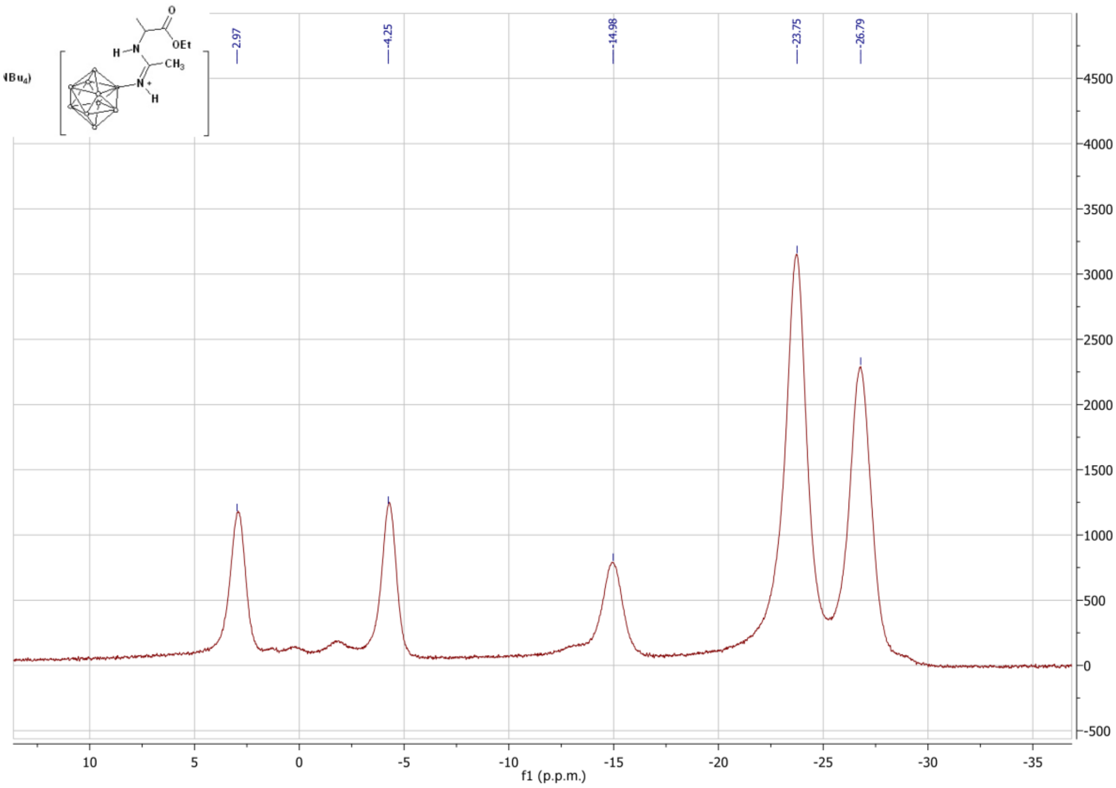


Figure S6 $^{11}B\{^1H\}$ NMR spectra of 2b

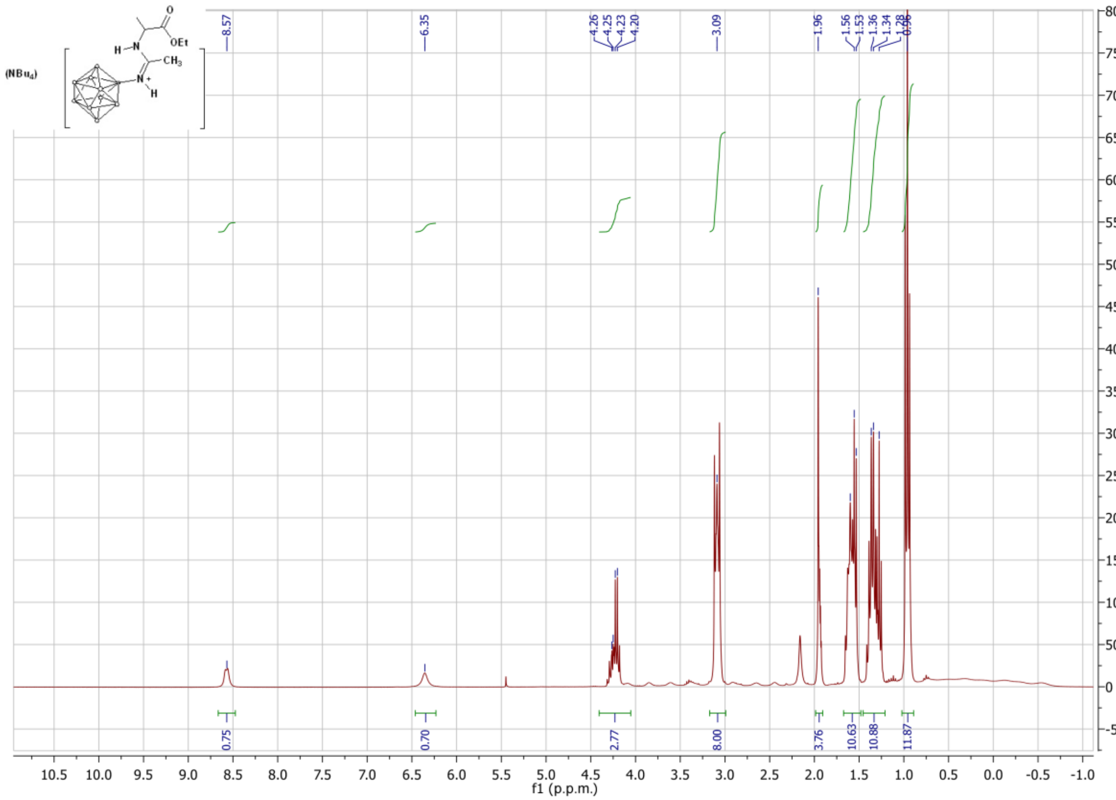


Figure S7 ^1H NMR spectra of 2b

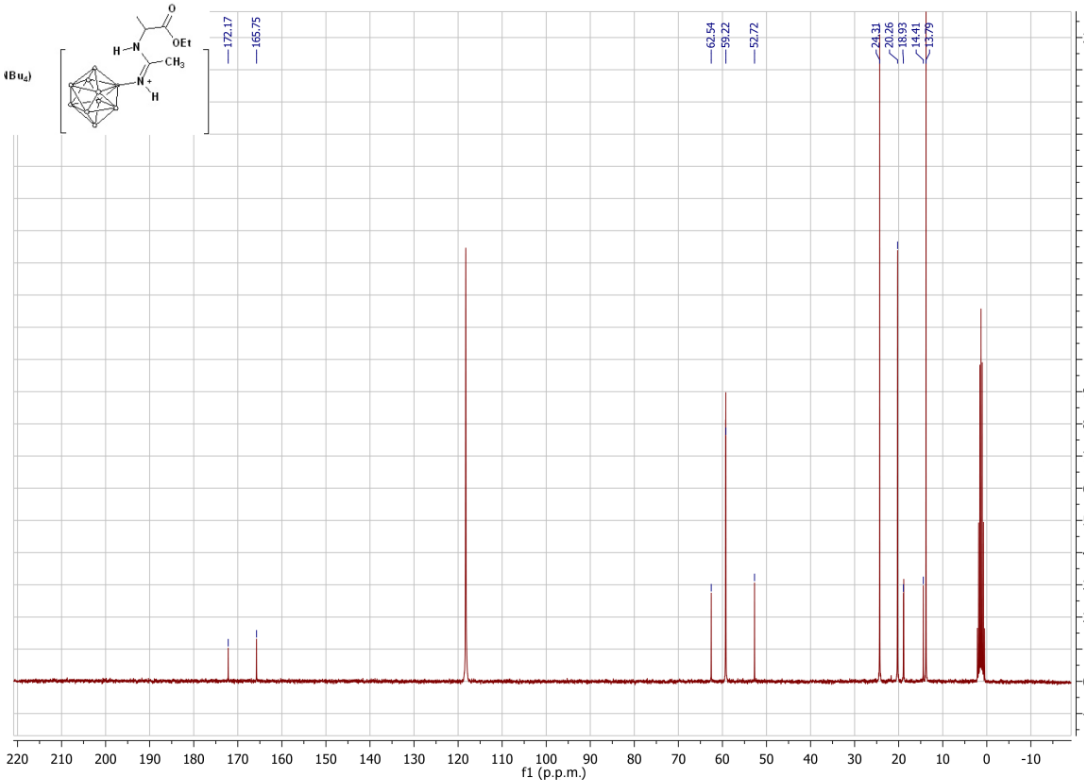


Figure S8 ^{13}C NMR spectra of 2b

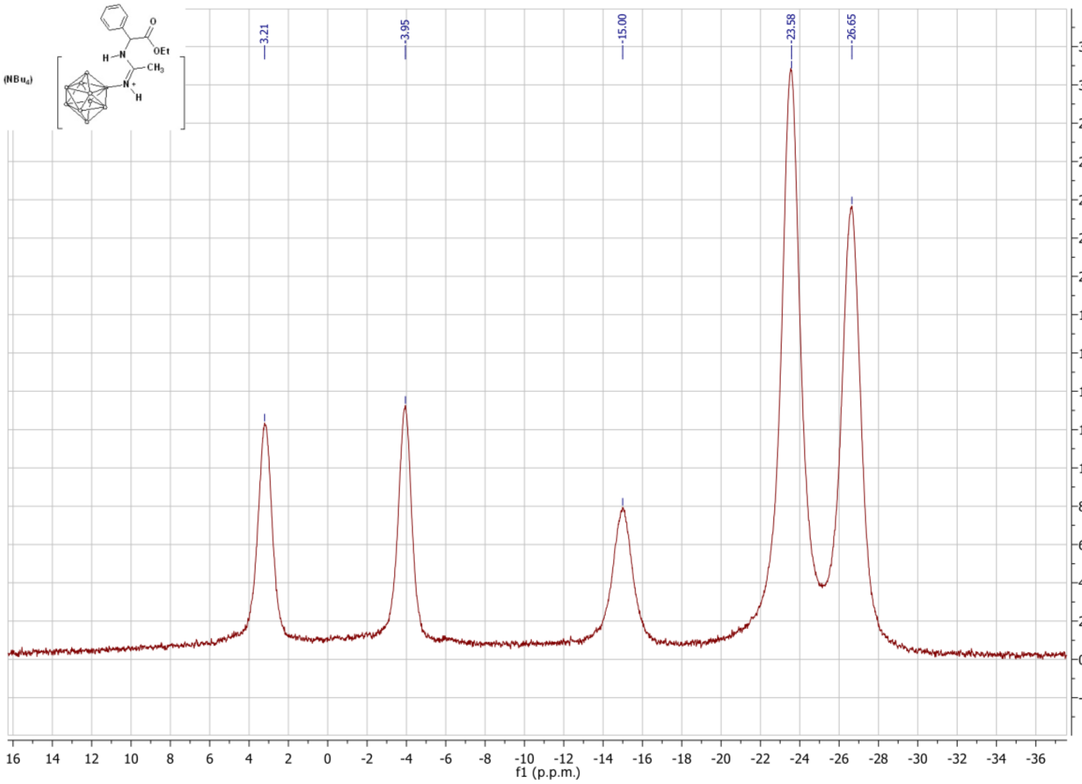


Figure S9 ^{11}B{^{1}H} NMR spectra of 2c

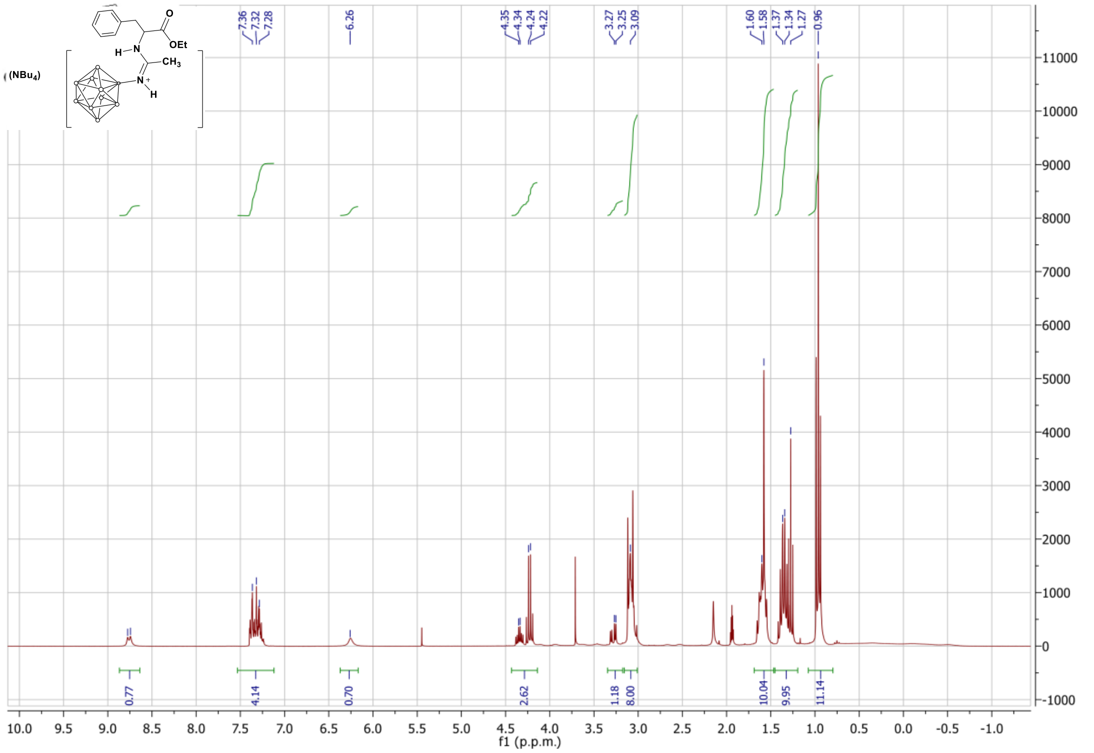


Figure S8 ^{1}H NMR spectra of 2c

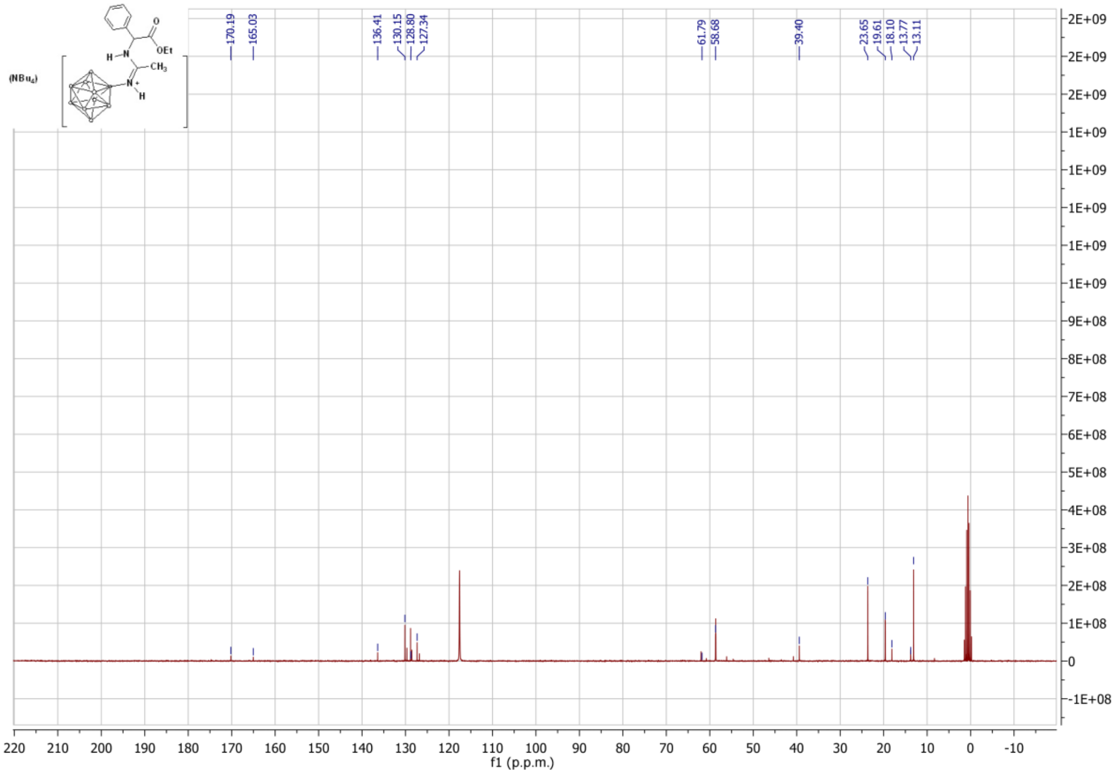


Figure. S9 ^{13}C NMR spectra of 2c