Electronic supplementary materials *Mendeleev Commun.*, 2021, **31**, 350–351

Cyclobutadiene cobalt complexes as catalysts for insertion of diazo compounds into X–H bonds

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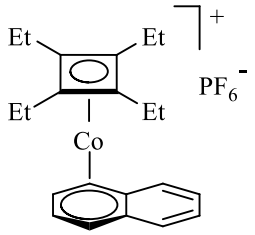
Experimental part

General remarks. All reactions were carried out under argon in anhydrous solvents which were purified and dried using standard procedures. The isolation of products was conducted in air unless otherwise stated. Column chromatography was performed on silica gel or neutral Al_2O_3. 3-Hexyne, ethyl diazoacetate and other organic reagents were purchased from commercial sources (Sigma-Aldrich) and were used without further purification. High-quality granulated anhydrous aluminum chloride (Sigma-Aldrich) was grounded before use. NMR spectra were measured with a Bruker Avance 400 spectrometer at 20 °C. Chemical shifts are given in ppm relative to residual signal of solvents ($CDCl_3$, CD_3NO_2, *etc.*).

Synthesis of [(C₄Et₄)Co(C₁₀H₈)]PF₆ 3



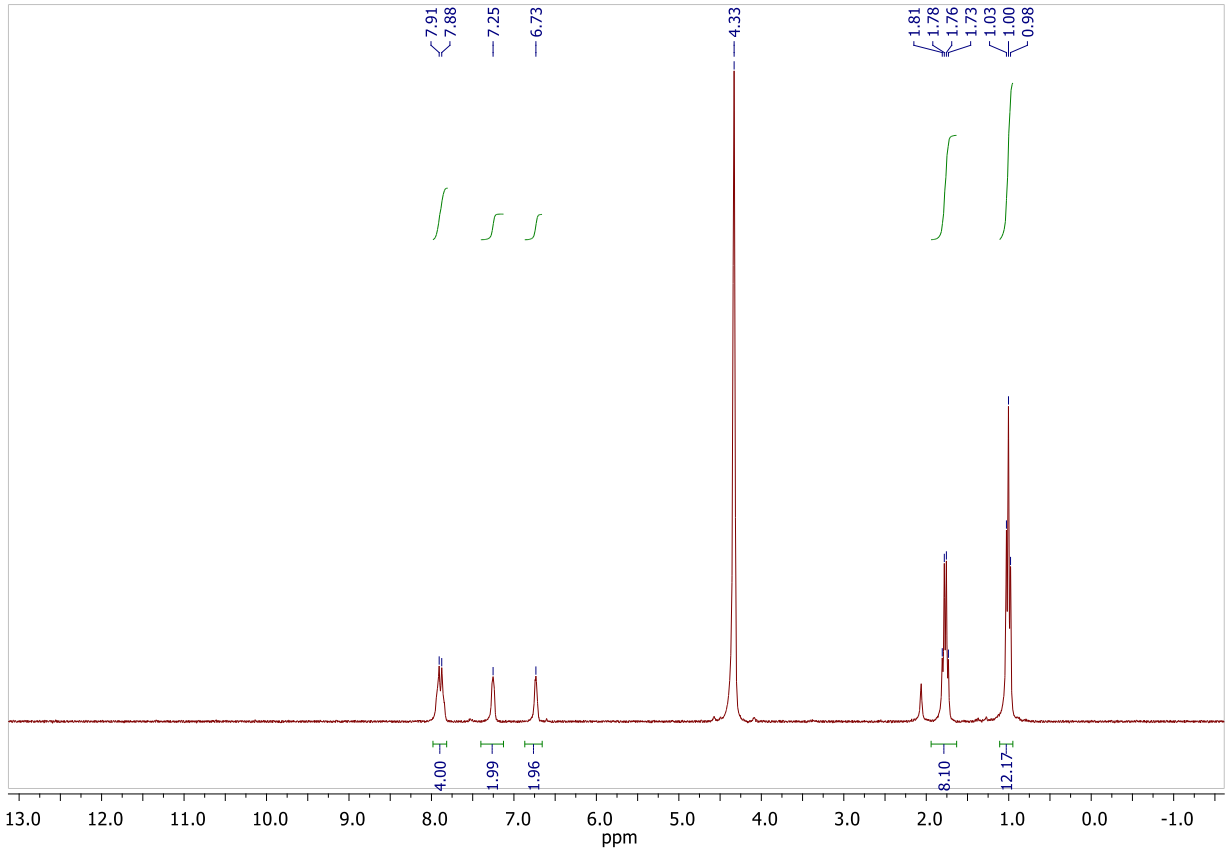
Complex $[(C_4Et_4)Co(C_{10}H_8)]PF_6$ was synthesized analogously to $[(C_4Me_4)Co(C_{10}H_8)]PF_6$. (E. V. Mutseneck, D. A. Loginov, A. A. Pronin, P. V. Petrovskii, A. R. Kudinov, *Russ. Chem. Bull., Int. Ed.*, 2007, **56**, 1927−1929).

A solution of $[(C_4Et_4)Co(C_6H_6)]PF_6$ **2** (160 mg, 0.36 mmol) in MeCN (5 ml) was refluxed for 7 h. The solvent was evaporated directly from the reaction flask in vacuum. The residue was thoroughly dried in vacuum at 40 ºC for 2 h to give bright red powder of tris-acetonitrile cyclobutadiene cobalt complex (note: the formed $[(C_4Et_4)Co(MeCN)_3]PF_6$ complex is air sensitive and rapidly decomposes in solution without inert atmosphere). The same reaction flask was charged with naphthalene (1 g, 7.8 mmol) and $MeNO_2$ (2 ml), and the mixture was stirred overnight. The solvent was removed in vacuum and the residue was washed with ether (2×10 ml). The solid was then dissolved in CH_2Cl_2 and filtered through a short pad of silica (2 cm). The solvent was evaporated, the yellow residue was re-dissolved in CH_2Cl_2, and the solution was centrifuged to remove insoluble impurities. The separated clear solution was concentrated, and the yellow product **3** was re-precipitated several times with ether from the minimal volume of CH_2Cl_2. The yield of **3**: 103 mg (58%).

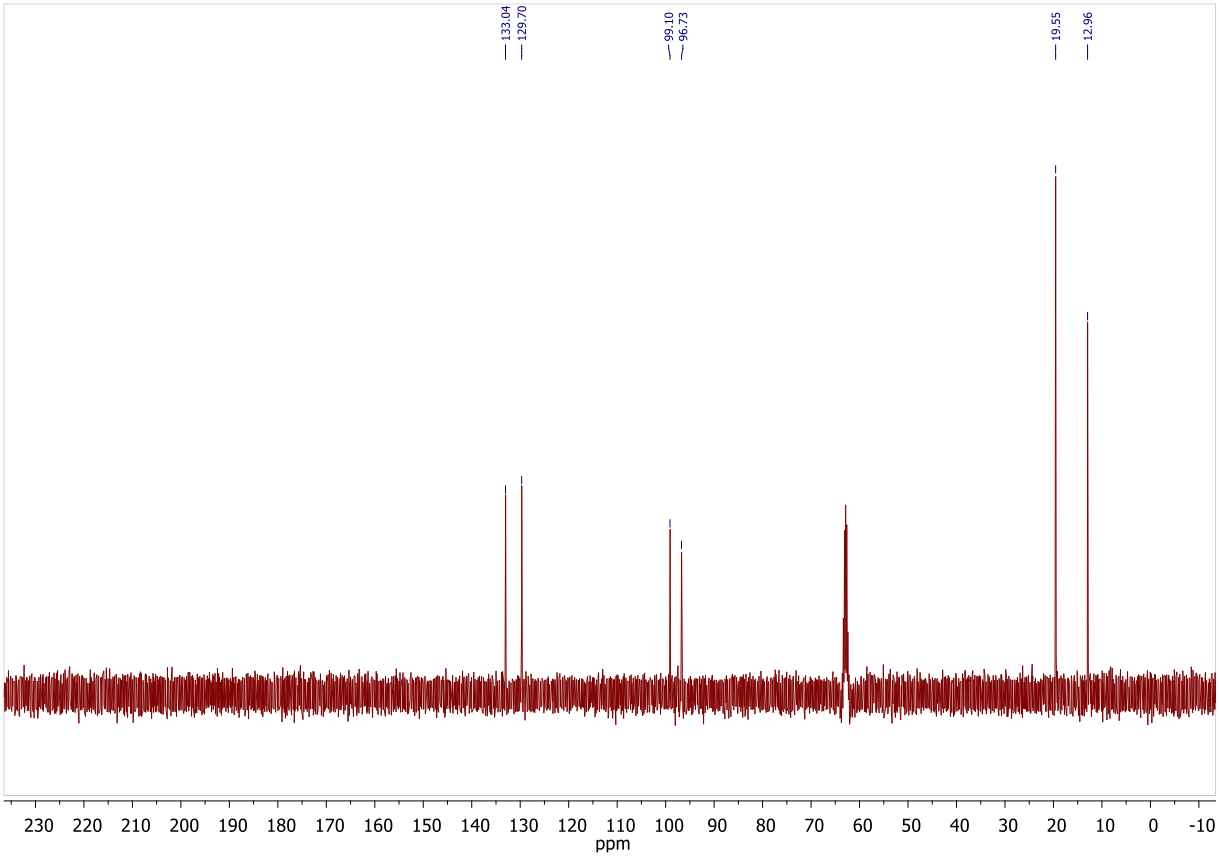
^{1}H NMR (300 MHz, CD_3NO_2) δ, 1.00 (t, J = 7.4 Hz, 12H, CH_3), 1.77 (q, J = 7.4 Hz, 8H, CH_2), 6.73 (s, 2H, Ar), 7.25 (s, 2H, Ar), 7.89 (d, J = 9.4 Hz, 4H, Ar).

^{13}C NMR (400 MHz, CD_3NO_2) δ, 12.96, 19.55, 96.73, 99.10, 129.70, 133.04.

Calc. for $C_{22}H_{28}CoF_6P$: %C = 53.24, %H = 5.69; found: %C = 52.98, %H = 5.90.



^{1}H NMR spectrum of [(C_4Et_4)Co($C_{10}H_8$)]PF_6.



^{13}C NMR spectrum of [(C_4Et_4)Co($C_{10}H_8$)]PF_6.

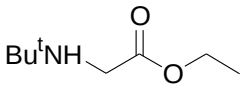
Synthesis of [(C4Et4)Co(C6H6)]PF6 2

A mixture of $(C_4Et_4)Co(CO)_2I$ (600 mg, 1.48 mmol), (P. O'Donohue, S. A. Brusey, C. M. Seward, Y. Ortin, B. C. Molloy, H. Muller-Bunz, A. R. Manning, M. J. McGlinchey, *J. Organomet. Chem.*, 2009, **694**, 2536–2547), anhydrous aluminum chloride (2.0 g, 15 mmol), and benzene (16 ml) was vigorously stirred under reflux for 7 h. After cooling, the mixture was carefully hydrolyzed with cold water. The aqueous phase was separated, filtered, and stirred with $Me_3NO{\cdot}2H_2O$ (ca. 60 mg, 0.36 mmol) and $NaI{\cdot}2H_2O$ (ca. 120 mg, 0.6 mmol) overnight. The brown precipitate of $(C_4Et_4)Co(CO)_2I$ was removed by filtration. Addition of an aqueous solution of KPF_6 (300 mg, 1.6 mmol) to the product afforded a yellow precipitate of **2**, which was collected by filtration, washed with water, and dried in vacuum. The product was further purified by re-precipitation with ether from acetone solution to give a yellow solid $[(C_4Et_4)Co(C_6H_6)]PF_6$. The yield of **2**: 220 mg (30%; non-optimized). The product **2** was sometimes contaminated by small amount of $[(C_4Et_4)Co(CO)_3]PF_6$. However, it can be used for further reaction without additional purification. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ, 1.11 (t, *J* = 7.5 Hz, 12H, CH_3), 2.19 (q, *J* = 7.5 Hz, 8H, CH_2), 6.77 (s, 6H, Ar).

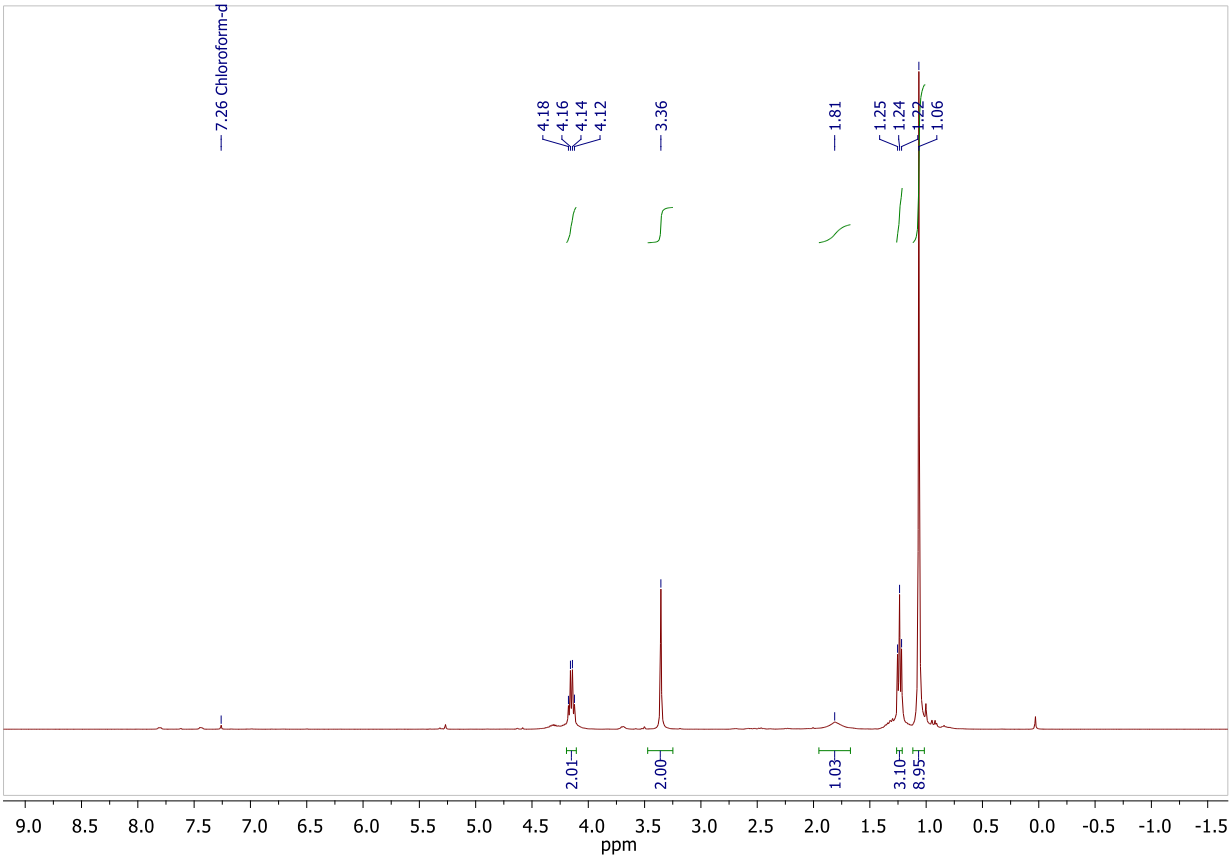
General procedure for catalytic reactions.

A solution of $[(C_4Et_4)Co(C_{10}H_8)]PF_6$ **3** (3 mg, 0.006 mmol) and MeCN (20 µl) in THF (1 ml) was stirred under argon atmosphere at the room temperature for about 15 min. The solution changed its color from yellow to orange indicating the formation of active species $[(C_4Et_4)Co(MeCN)_3]PF_6$. Then the mixture was cooled to 0 °C in an ice bath, and the 5-fold excess of nucleophile (amine, silane or borane) was added followed by addition of ethyl diazoacetate (EDA, 34 mg, 0.3 mmol). The evolution of nitrogen gas began immediately after addition of EDA, and the colour of the solution grew dark. The mixture was stirred at 0 °C for 1 hour and then at room temperature overnight to ensure the complete conversion (the time of the reaction was not optimized). The solvent was evaporated, and the residue was eluted through a short pad of silica gel or neutral alumina (ca. 5 cm) with CH_2Cl_2 containing Et_3N (2 vol.%). The solvent was evaporated *in vacuo*, and the residue was purified by column chromatography on Al_2O_3 (eluent - hexane-EtOAc) or analyzed by ^{1}H NMR spectroscopy (internal standard – dioxane or 1,1,2,2-tetrachloroethane).

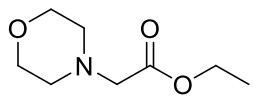
Characterization of products.



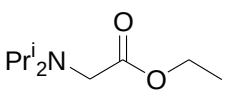
Ethyl 2-(*tert*-butylamino)acetate (**4a**)
Yield = 45% (21 mg). Brown oil. 10-fold excess of *tert*-butylamine relative to the EDA was used. The product was purified by column chromatography on silica gel (eluent – CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ, 1.06 (s, 9H, ^{t}Bu), 1.24 (t, J = 7.1 Hz, 3H, CH_3), 1.81 (bs, 1H, NH), 3.36 (s, 2H, CH_2), 4.15 (q, J = 7.1Hz, 2H, CH_2). *Cf*. N. J. Truax, F. B. Mejia, D. O. Kwansare, M. M. Lafferty, M. H. Kean, E.T. Pelkey, *J. Org. Chem.* **2016**, *81*, 15, 6808–6815.



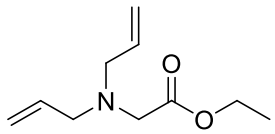
^{1}H NMR spectrum of **4a**



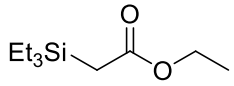
Ethyl 2-Morpholinoacetate (**4b**)
Yield = 78% (NMR). 5-fold excess of morpholine relative to the EDA was used.^{1}H NMR (400 MHz, $CDCl_3$) δ, 1.26 (t, J = 7.2 Hz, 3H, CH_3), 2.56 (m, 4H, CH_2), 3.18 (s, 2H, CH_2), 3.74 (m, 4H, CH_2), 4.17 (q, J = 7.2Hz, 2H,CH_2). *Cf*. W. J. Kerr, M. Middleditch, A. J. B. Watson, *Synlett*, **2011**, *2*, 177-180.



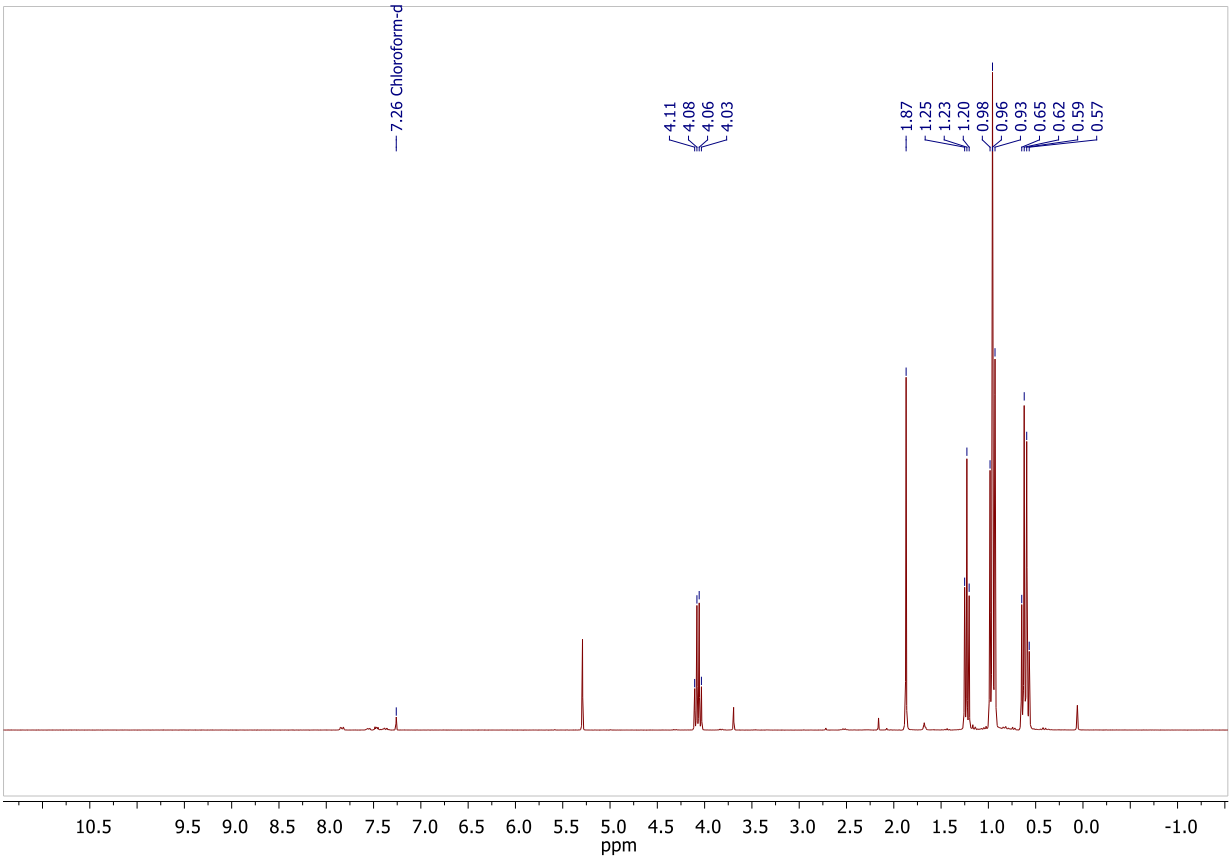
Ethyl 2-(diisopropylamino)acetate (**4c**)
Yield = 54% (NMR). 10-fold excess of diisopropylamine relative to EDA was used. ^{1}H NMR (400 MHz, $CDCl_3$) δ, 1.04 (d, J = 6.8 Hz, 12H, CH_3), 1.27(t, J = 7.1 Hz, 3H, CH_3), 3.03-3.14 (m, 2H, CH), 3.24 (s, 2H, CH_2), 4.17 (q, J = 7.1 Hz, 2H, CH_2). *Cf*. L. Chen, H. Cui, Y. Wang, X. Liang, L. Zhang , C.-Y. Su, *Dalton Trans.*, **2018**, *47*, 3940-3946.



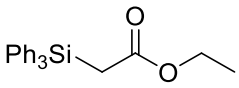
Ethyl 2-(diallylamino)acetate (**4d**)
Yield = 51% (NMR). 3-fold excess of diallylamine relative to EDA was used. ^{1}H NMR (400 MHz, $CDCl_3$) δ, 1.28 (t, J = 7.1 Hz, 3H, CH_3), 3.26 (d, J = 6.6 Hz, 4H, CH_2N), 3.32 (s,2H, CH_2), 4.17 (q, J = 7.1Hz, 2H,CH_2), 5.07-5.26 (m, 4H, CH_2), 5.82-5.93 (m,2H, CH_2). *Cf*. B. J. Anding, L. K. Woo, *Organometallics*, **2013**, *32*, 9, 2599–2607.



Ethyl 2-(triethylsilyl)acetate (**6a**)
Yield = 25 mg (41%).Colourless oil. 5-fold excess of triethylsilane relative to EDA was used. The product was purified by column chromatography on neutral alumina (eluent – hexane-EtOAc (20:1)). ^{1}H NMR (400 MHz, $CDCl_3$) δ, 0.61 (q, *J* = 7.9 Hz, 6H, CH_2Si), 0.96 (t, *J* = 7.9 Hz, 9H, CH_3Si), 1.23 (t, *J* = 7.1 Hz, 3H, CH_3), 1.87 (s, 2H, CH_2), 4.07 (q, *J* = 7.1 Hz, 2H, CH_2). *Cf*. M. J. Iglesias, M. C. Nicasio, A. Caballero, P. J. Pérez, *Dalton Trans.*, **2013**, *42*, 1191-1195.

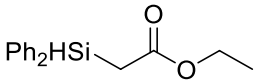


^{1}H NMR spectrum of **6a**



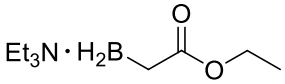
Ethyl 2-(triphenylsilyl)acetate (**6b**)

Yield = 58% (NMR). 5-fold excess of triphenylsilane relative to EDA was used. ^{1}H NMR (400 MHz, $CDCl_3$) δ, 1.03 (t, J = 7.1 Hz, 3H, CH_3), 2.89 (s, 1H, 2H, CH_2), 3.98 (q, J = 7.1 Hz, 2H, CH_2), 7.43-7.52 (m, 9H, Ph), 7.71-7.77 (m, 6H, Ph). *Cf*. M. J. Iglesias, M. C. Nicasio, A. Caballero, P. J. Pérez, *Dalton Trans.*, **2013**, *42*, 1191-1195.



Ethyl 2-(diphenylsilyl)acetate (**6c**)

Yield = 16% (NMR). 5-fold excess of diphenylsilane relative to EDA was used. ^{1}H NMR (400 MHz, $CDCl_3$) δ, 1.12 (t, *J* = 7.1 Hz, 3H, CH_3), 2.59 (d, *J* = 3.6 Hz, 2H, CH_2Si), 4.07 (q, *J* = 7.1 Hz, 2H, CH_2), 5.27 (t, *J* = 3.6 Hz, 1H, SiH), 7.40-7.51 (m, 9H, Ph), 7.69-7.74 (m, 6H, Ph). *Cf*. M. J. Iglesias, M. C. Nicasio, A. Caballero, P. J. Pérez, *Dalton Trans.*, **2013**, *42*, 1191-1195.



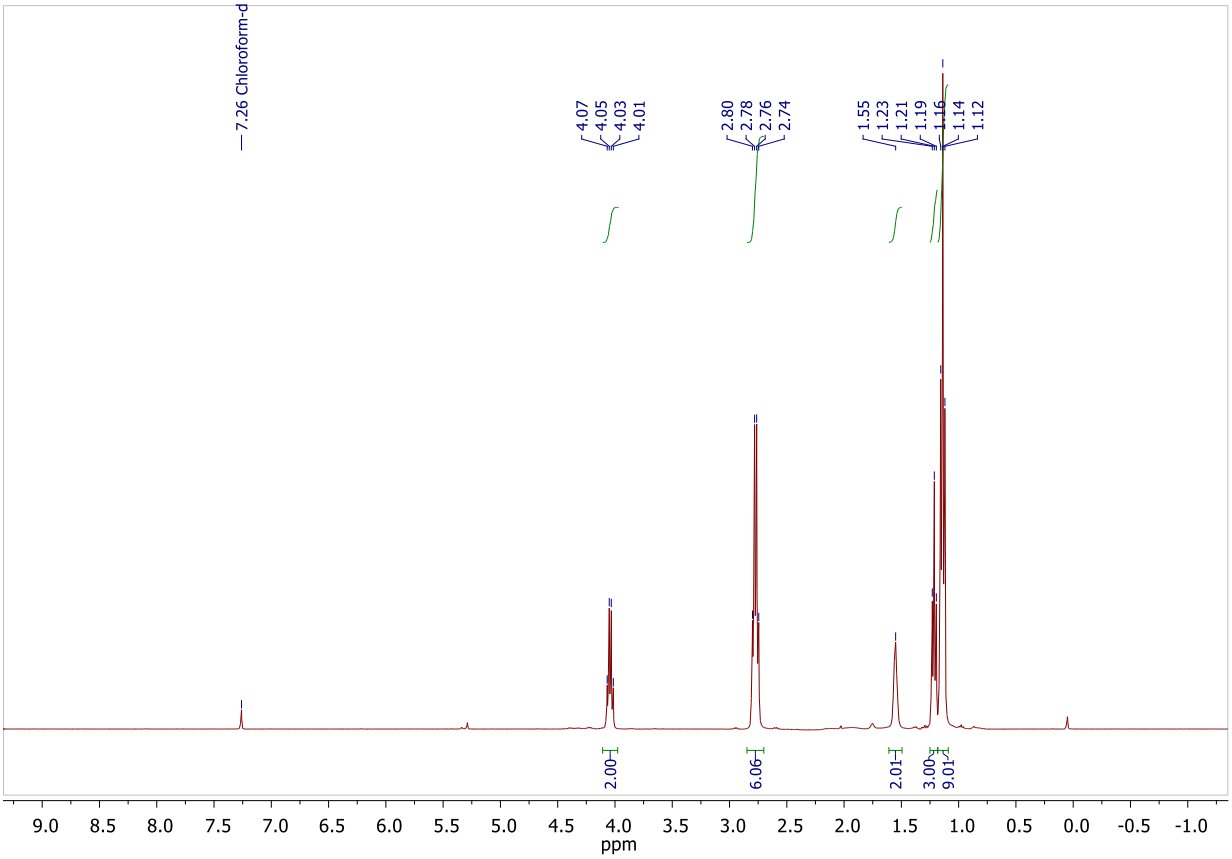
(2-Ethoxy-2-oxoethyl)borane triethylamine complex (**7**)

Yield = 46 mg (46%). Colourless oil. 2-fold excess of triethylamine-borane relative to the EDA was used. The product was purified by column chromatography on neutral alumina (eluent – hexane-EtOAc, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ, 1.14 (t, *J* = 7.3 Hz, 9H, CH_3N), 1.21 (t, *J* = 7.1 Hz, 3H, CH_3), 1.55 (bs, 2H, CH_2), 2.77 (q, *J* = 7.3 Hz, 6H, CH_2N), 4.04 (q, *J* = 7.1 Hz, 2H, CH_2).

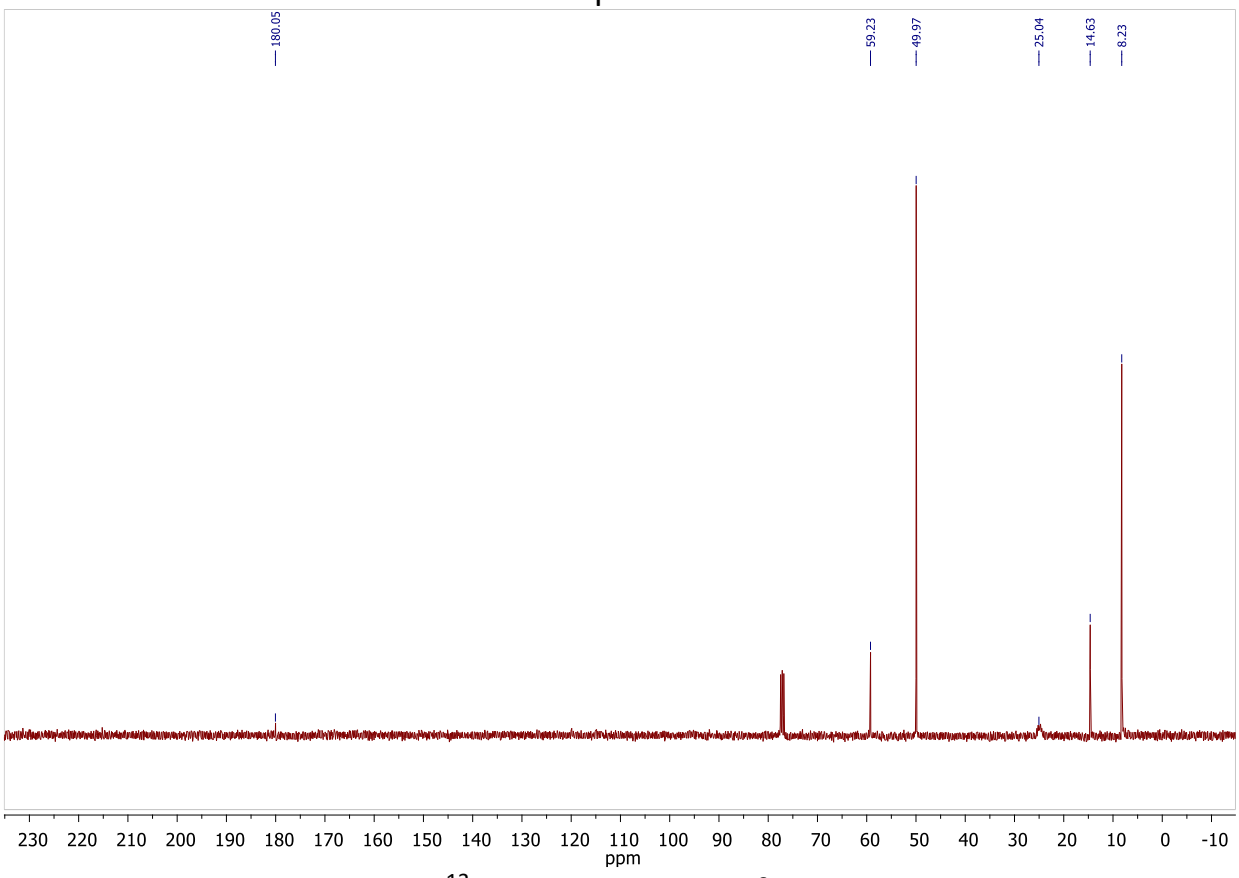
^{13}C NMR(101 MHz, $CDCl_3$) δ, 8.24, 14.64, 25.02(br), 49.97, 59.24, 180.03.

^{11}B NMR (128 MHz, $CDCl_3$) δ, –9.16.

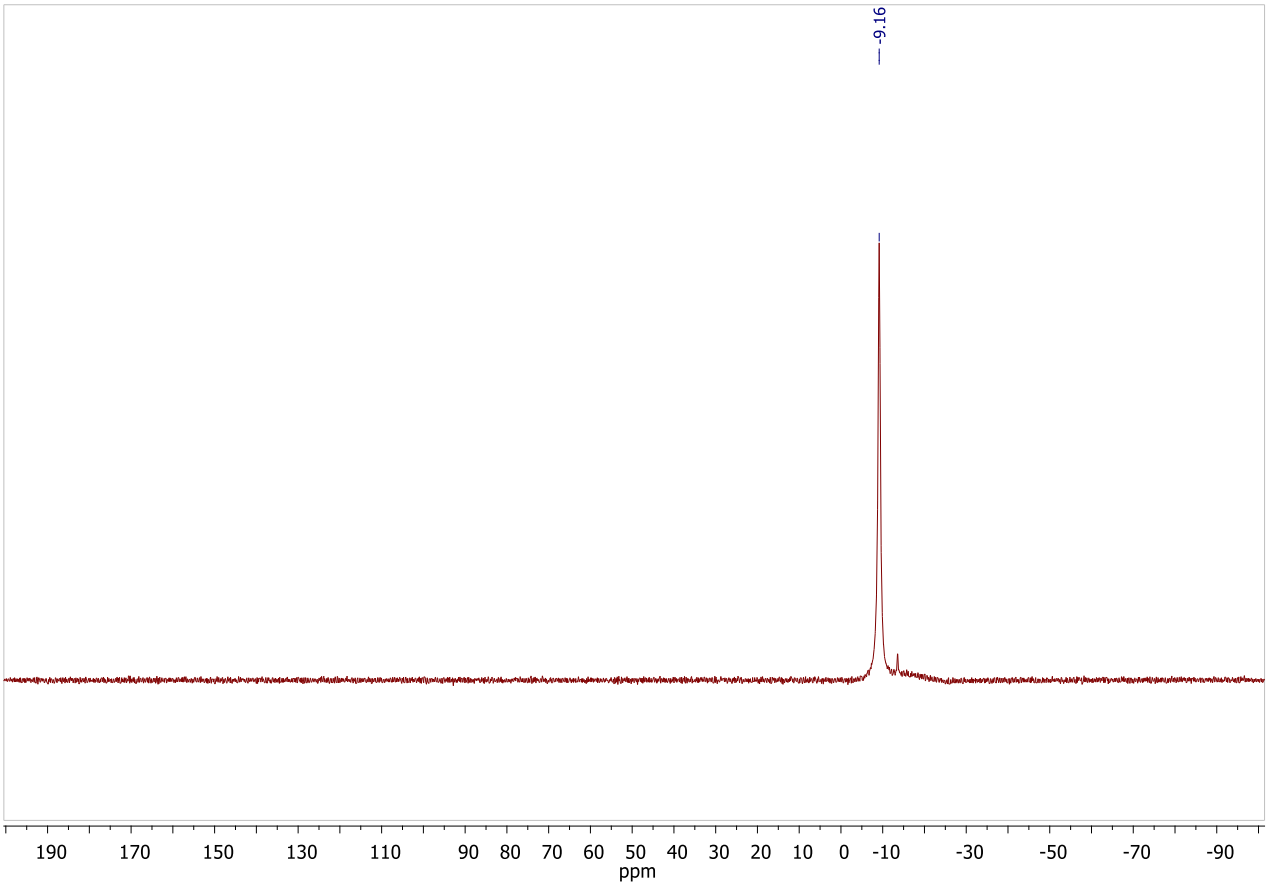
Calc. for $C_{10}H_{24}BNO_2$: %C = 59.72, %H = 12.03, %N = 6.96; found: %C = 59.45, %H = 12.09, %N = 6.86.



^{1}H NMR spectrum of **7**



^{13}C NMR spectrum of **7**



^{11}B NMR spectrum of **7**