Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information for

Computational and experimental investigations of CO_2 and N_2O fixation by sterically demanding *N*-heterocyclic carbenes (NHC) and NHC/borane FLP systems

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Contents:

1. **X-ray structure of 6**
2. **Selected NMR spectra**
3. **Computational Details**

1. X ray structure of 6

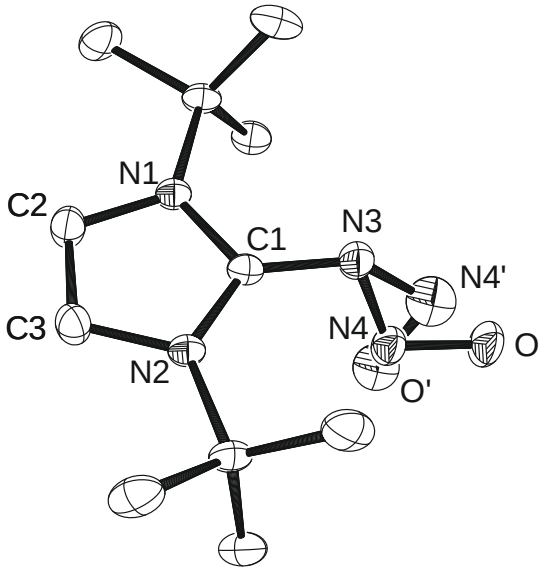


Figure S1. ORTEP diagram of **6** (ca. 10% disorder around N4 and O) with thermal displacement parameters drawn at 50% probability. Selected bond lengths (Å) and angles (°) for the main *trans*-C,O isomer: C1-N3 1.3720(13), N3-N4 1.3350(15), N4-O 1.2574(14), C1-N3-N4 109.35(9), N3-N4-O 113.24(12).

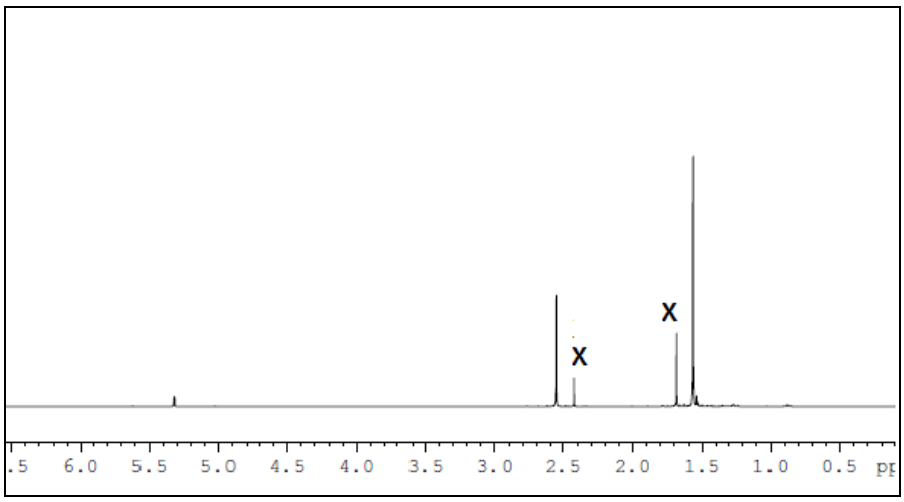
Crystal data: $C_{11}H_{20}N_4O$, monoclinic, space group $P2_1/n$, a = 9.2956, b = 11.7049(2), c = 11.2144(2) Å, β = 99.208(2)°, Z = 4, D_x = 1.237 Mg m^{-3}, μ(Cu $K\alpha$) = 0.66 mm^{-1}. *Data collection*: A yellow plate 0.10 × 0.05 × 0.04 mm was used to register 19755 intensities on an Oxford Diffraction Nova A diffractometer using Cu $K\alpha$ radiation (λ = 1.54184 Å). Absorption corrections were based on multi-scans. *Structure refinement*: The structure was refined anisotropically on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttiongen, Germany). Methyl groups were idealized and allowed to rotate but not tip; other hydrogens were included using a riding model starting from calculated positions.

Two significant residual electron density peaks (0.76, 0.67 e Å^{-3}; all other peaks < 0.25 e Å^{-3}) were interpreted as representing a minor disorder component of N4 and O, but it proved impossible to refine these atoms with convincing bond lengths and angles despite the use of restraints. For this reason the structure should be interpreted with caution, although we are convinced that the main component (over 90% occupied) is at least qualitatively correct.

The final *wR*2 for all reflections was 0.093, with a corresponding *R*1 of 0.036 ($I > 2\sigma(I)$); S = 1.05, max. Δρ 0.25 e Å^{-3}. Data have been deposited under CCDC-964196.

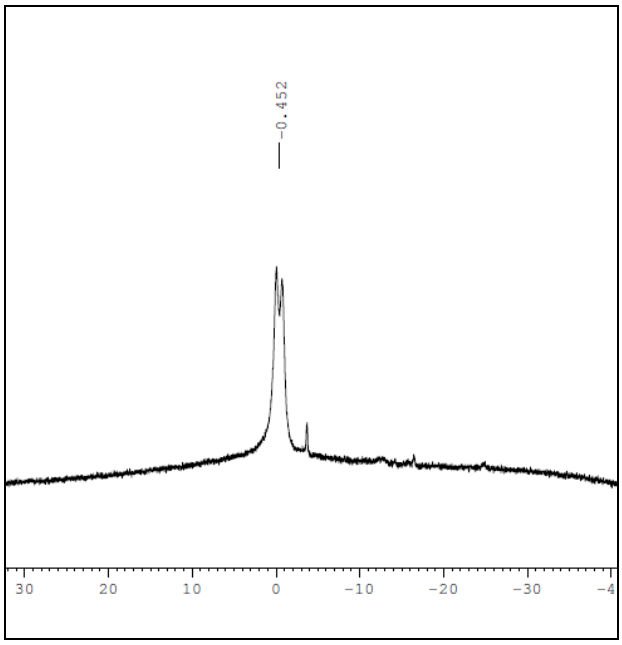
2. Selected NMR spectra

4: ^{1}H NMR in CD_2Cl_2

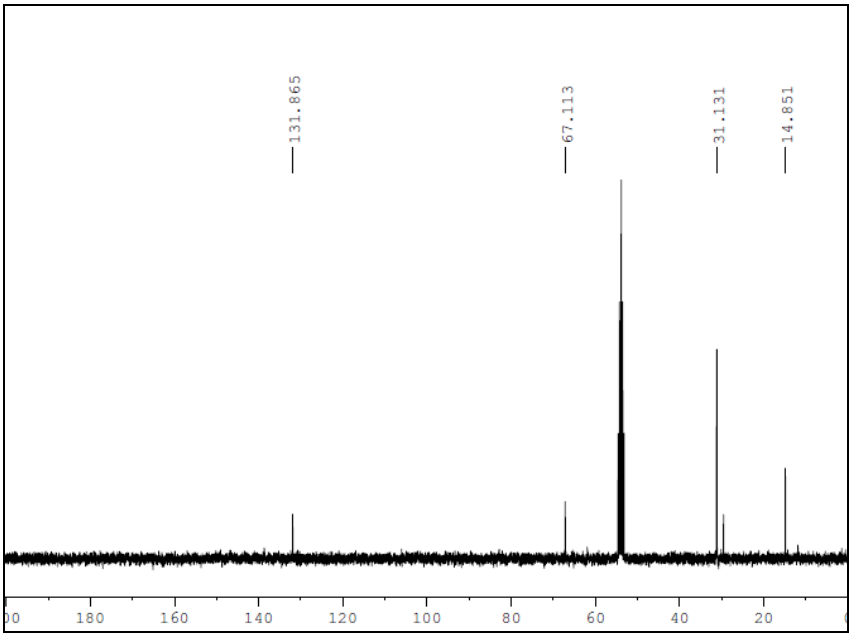


X = impurities (Imidazolium salt)

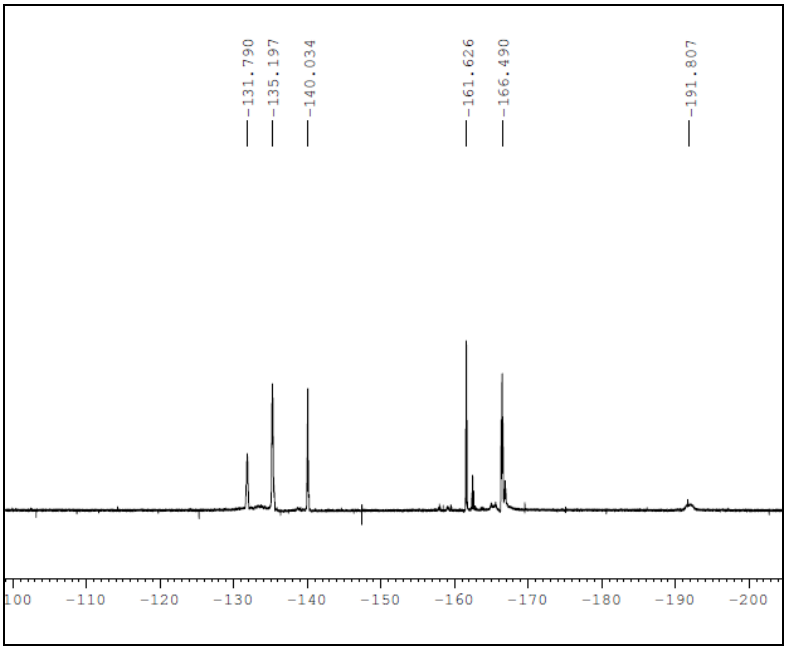
4: ^{11}B NMR in CD_2Cl_2



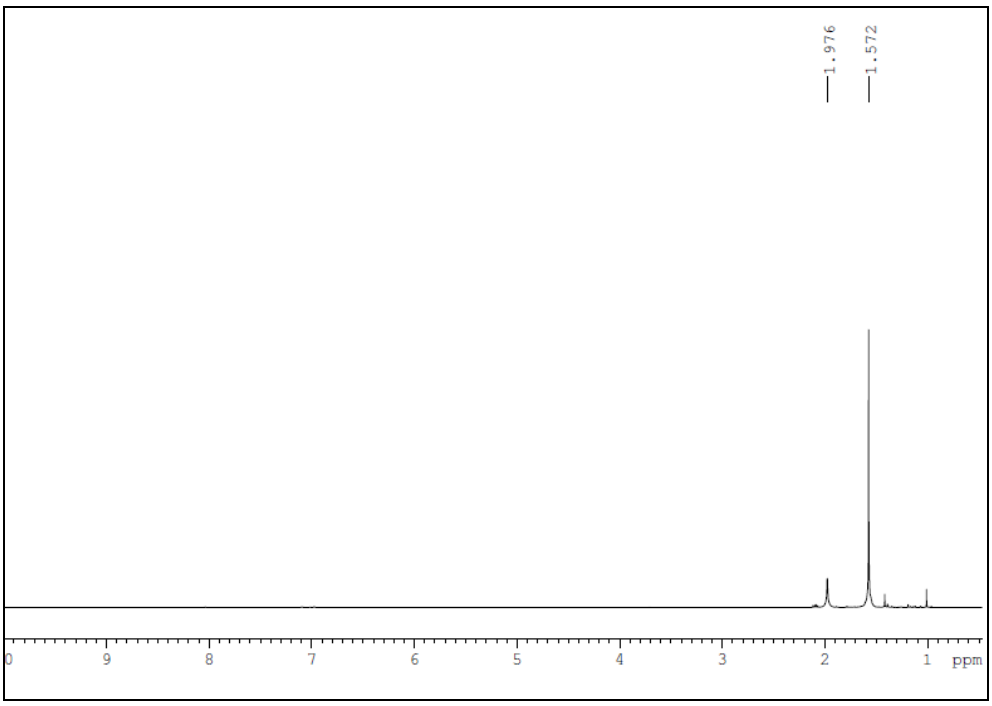
4: ^{13}C NMR in CD_2Cl_2



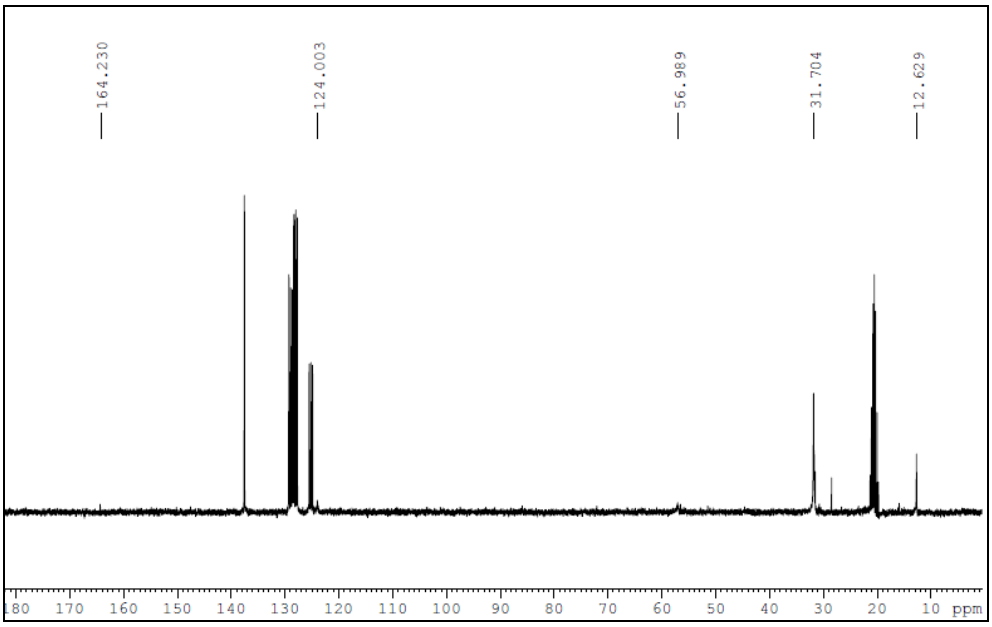
4: ^{19}F NMR in CD_2Cl_2



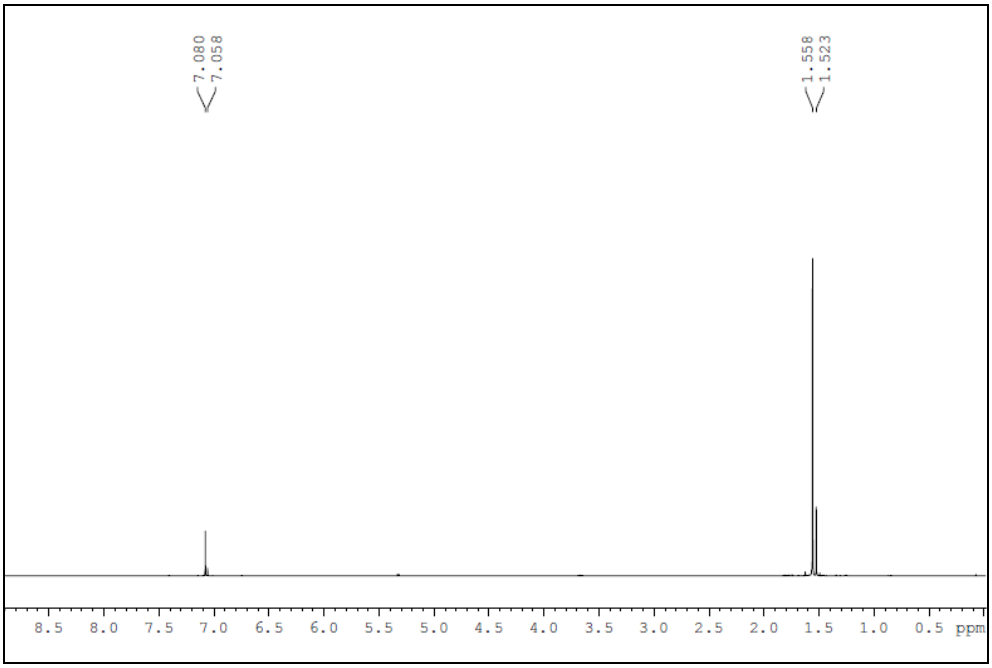
5a: ^{1}H NMR in toluene d_8



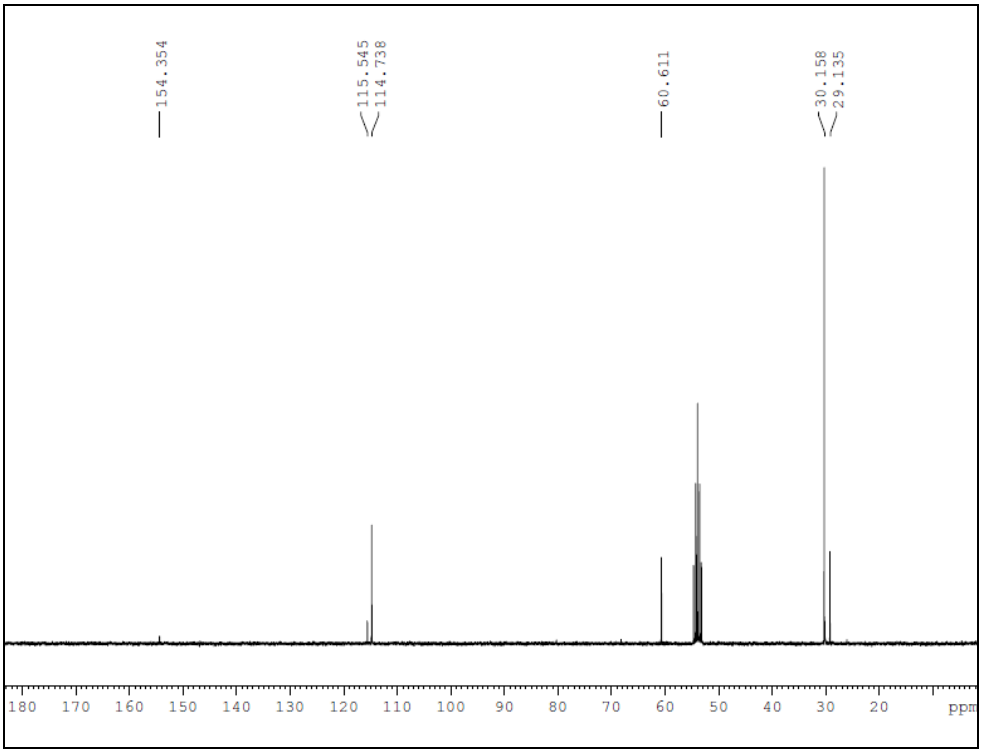
5a: ^{13}C NMR in toluene d_8



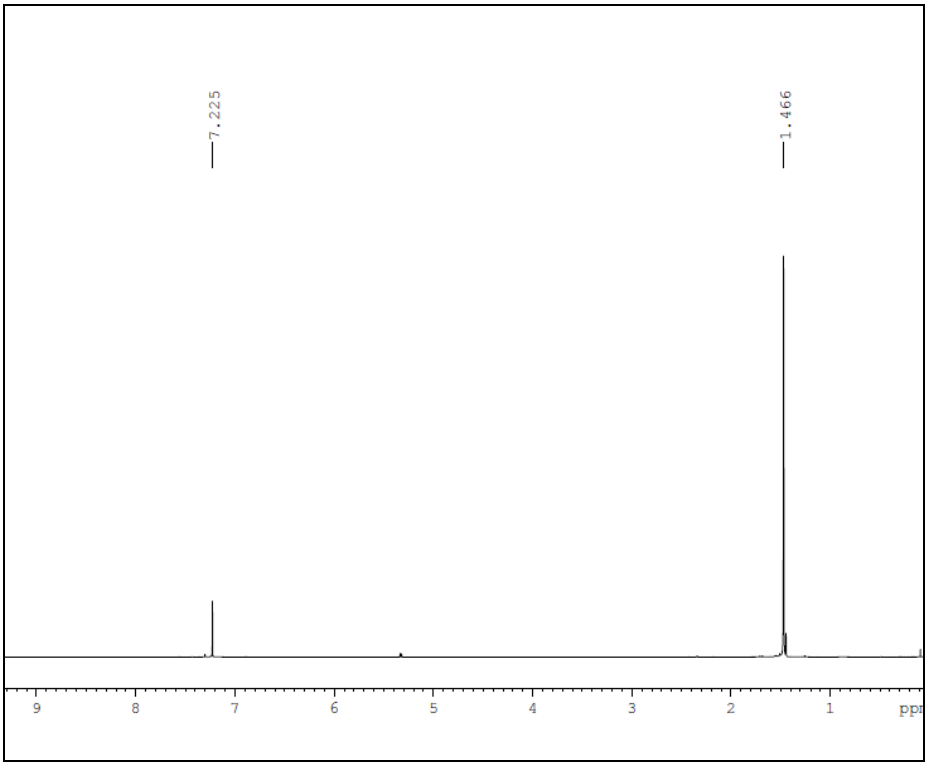
6: ^{1}H NMR in CD_2Cl_2



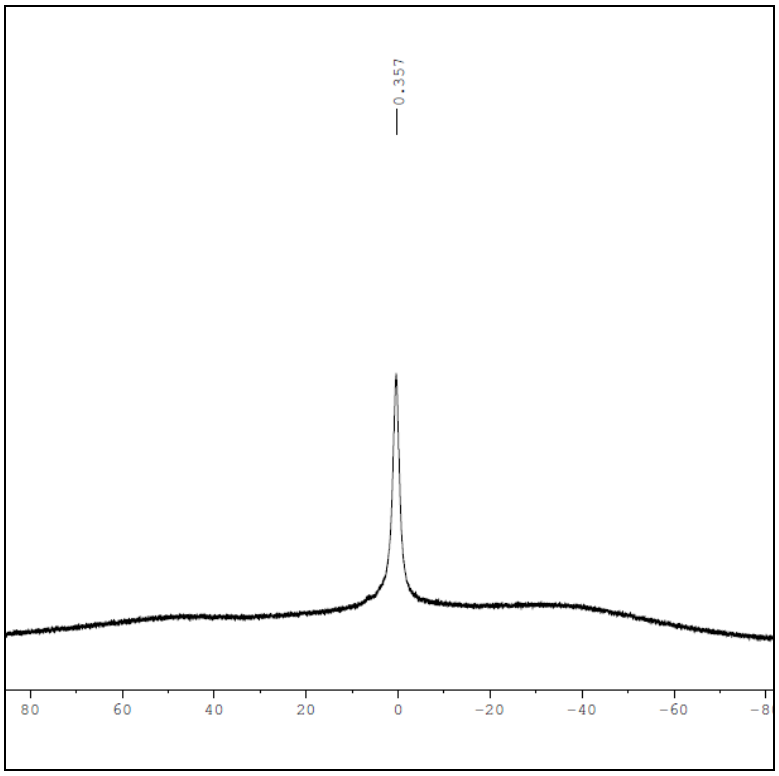
6: ^{13}C NMR in CD_2Cl_2



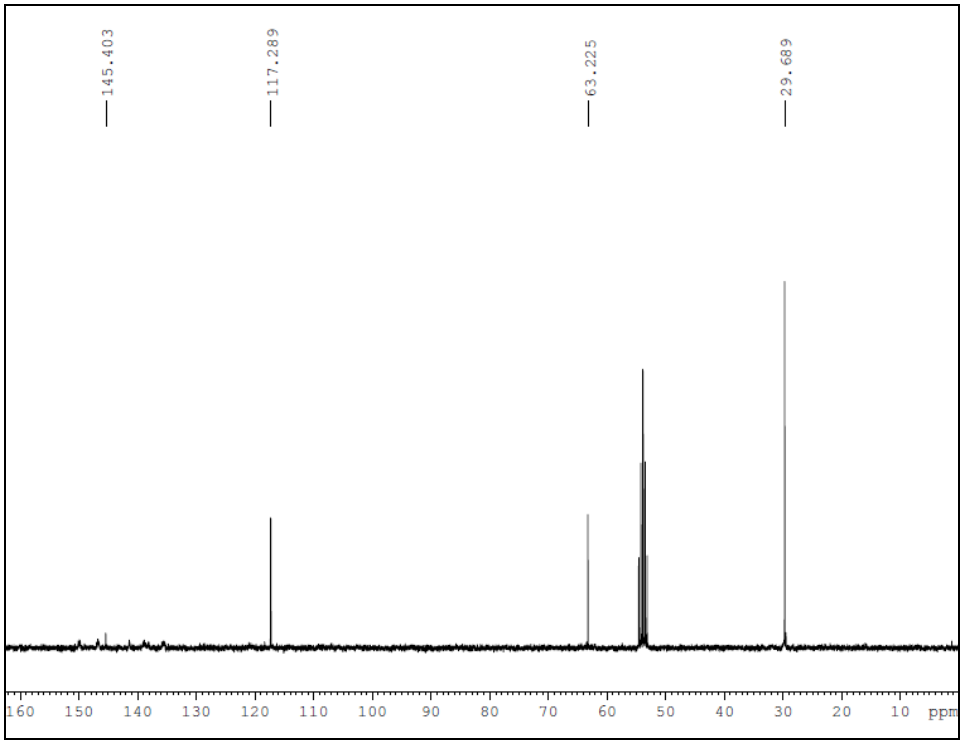
8a: ^{1}**H NMR** in CD_2Cl_2



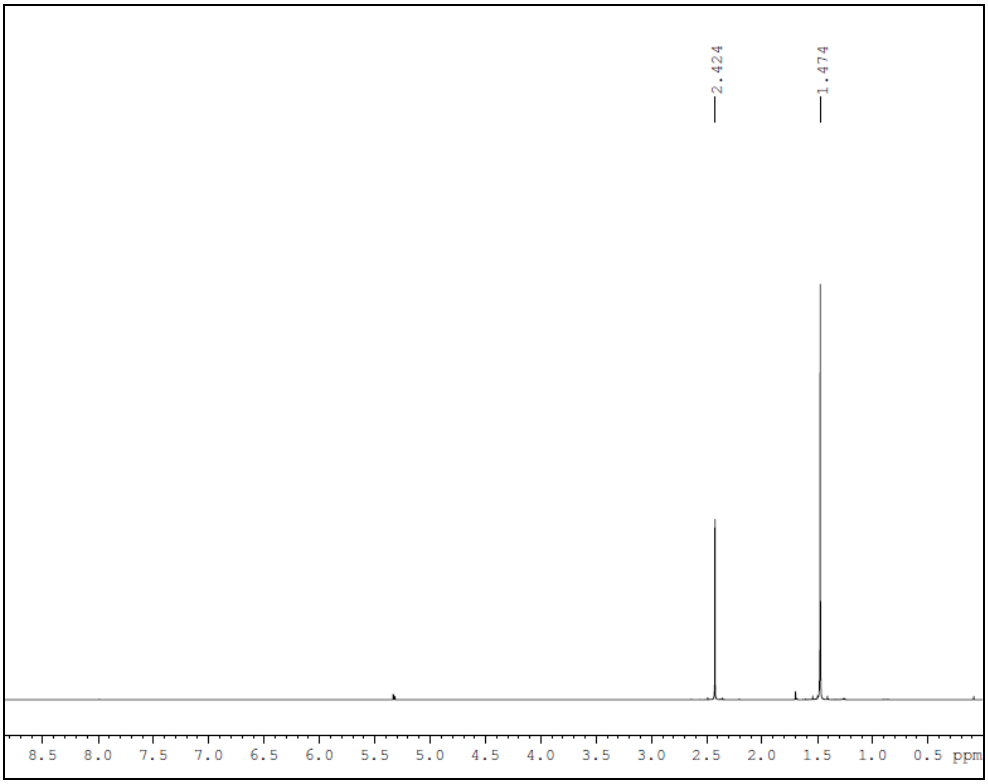
8a: ^{11}**B NMR** in CD_2Cl_2



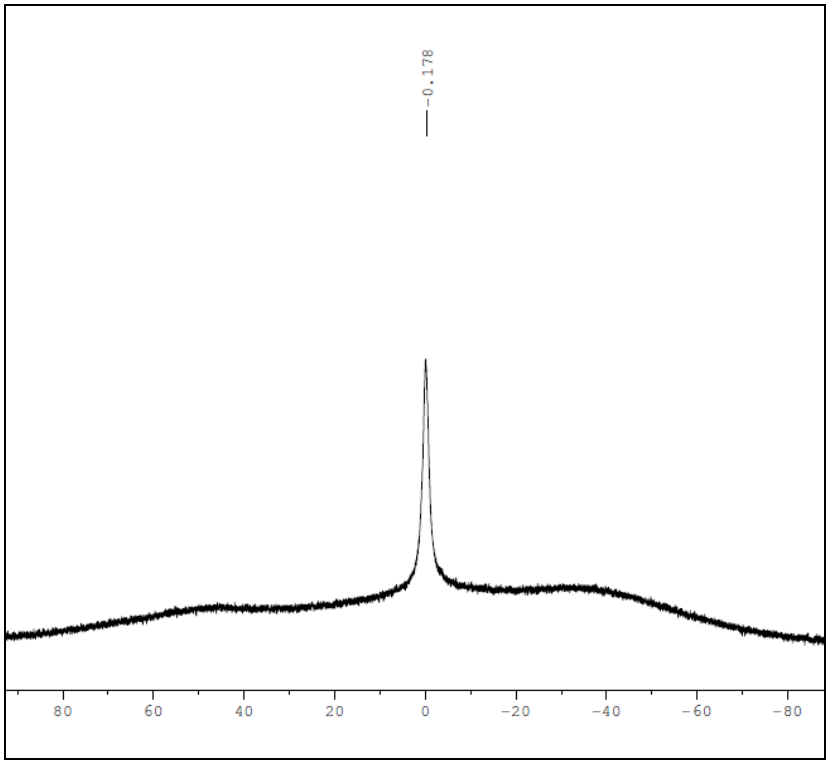
8a: ^{13}**C NMR** in CD_2Cl_2



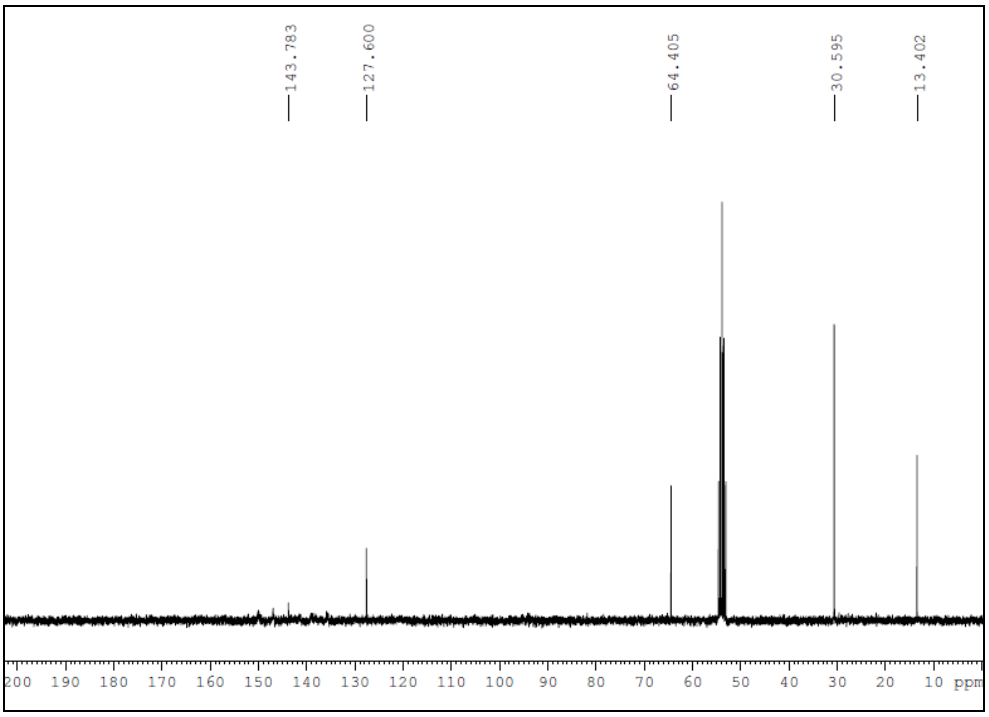
8b: ^{1}**H NMR** in CD_2Cl_2



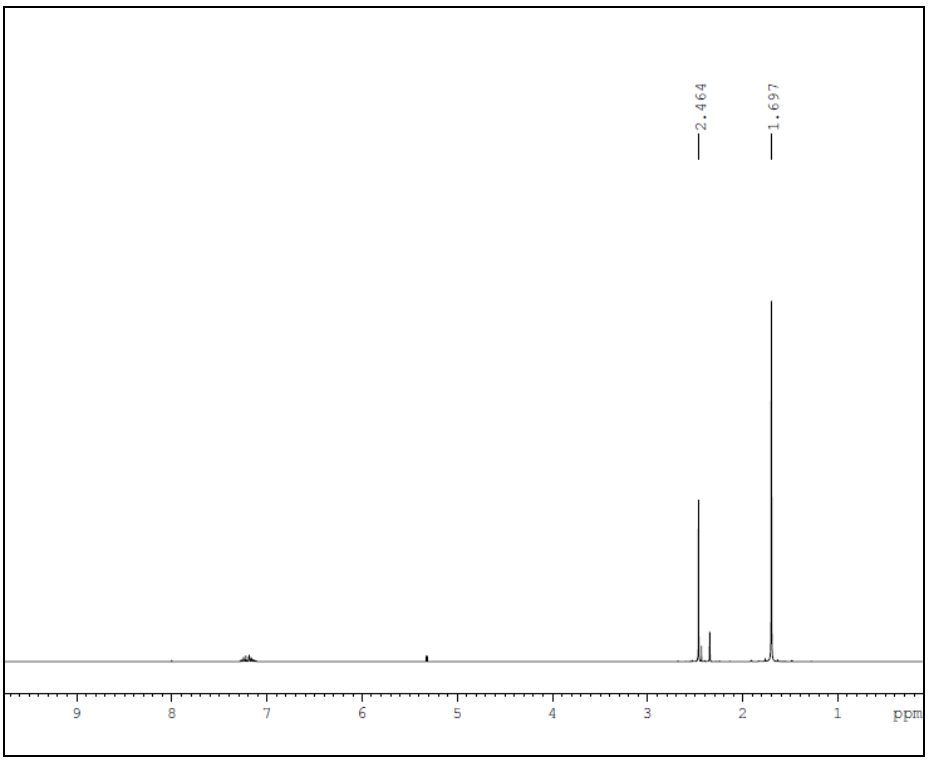
8b: ^{11}**B NMR** in CD_2Cl_2



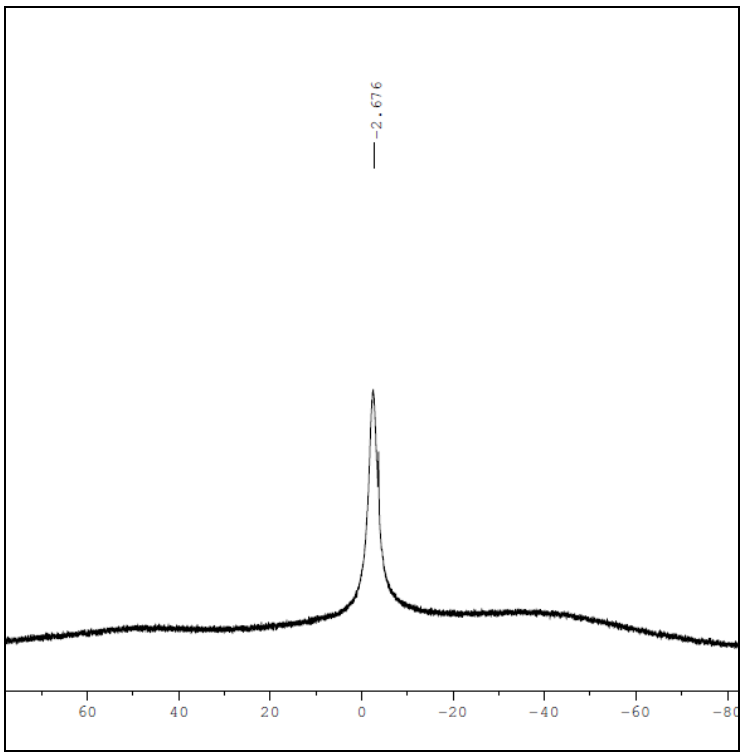
8b: ^{13}**C NMR** in CD_2Cl_2



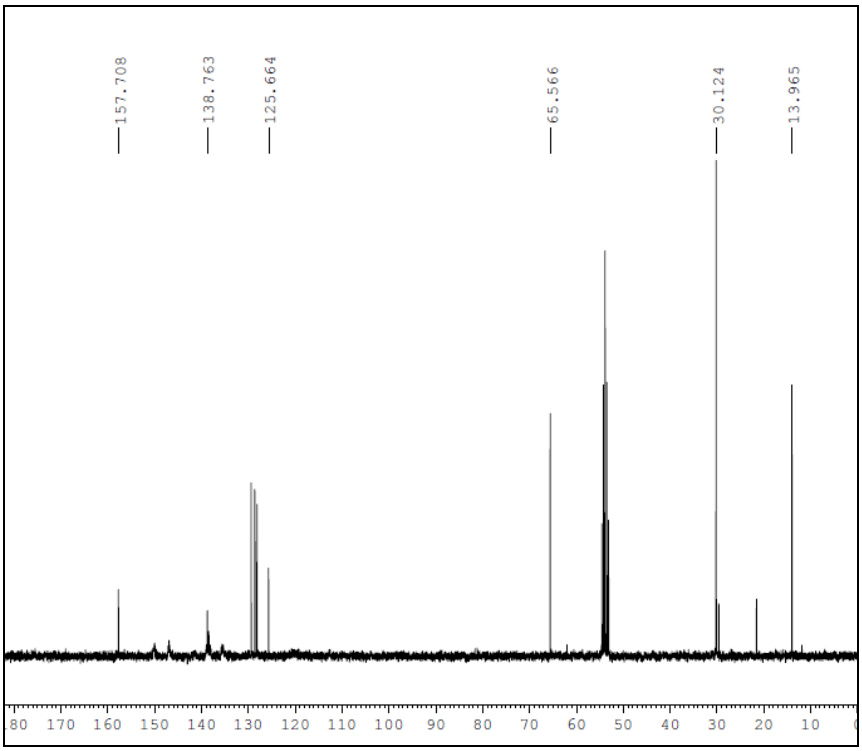
9b: ^{1}H NMR in CD_2Cl_2



9b: ^{11}B NMR in CD_2Cl_2



9b: ^{13}**C NMR** in CD_2Cl_2



3. Computational Details

All computations were performed using the hybrid density functional method M05-2X as implemented in the Gaussian09 program.[1] For all elements (C, H, N, O and F) the all-electron triple-ζ basis set (6-311G**) was used.[2]

Energies for all optimized structures

Compound	E(0 K)[a]/[Ha]	H(298 K)[b]/[Ha]	G(298 K)[b]/[Ha]
N_2O	-184.669041	-184.665113	-184.685625
CO_2	-188.601386	-188.597845	-188.622059
N_2	-109.539343	-109.536038	-109.557761
$B(C_6F_5)_3$	-2208.548375	-2208.519116	-2208.6088
^{tBu_2}ImC: (**1a**)	-540.453387	-540.437896	-540.494393
$Me_2{}^{tBu_2}$ImC: (**1b**)	-619.028286	-619.009949	-619.071408
^{Xy_2}ImC:	-845.302014	-845,281468	-845,353326
^{Xy_2}ImC-N_2O (**TS1**)	-1029.944786	-1029.921146	-1029.99858
^{Xy_2}ImC-N_2O (**TS2**)	-1029.896058	-1029.872475	-1029.948979
^{Xy_2}ImC-N_2O (*cis*)	-1029.992807	-1029.969604	-1030.045698
^{Xy_2}ImC-N_2O (*trans*)	-1029.995462	-1029.972261	-1030.047682
^{tBu_2}ImC-N_2O (**TS1**)	-725.089625	-725.071444	-725.134895
^{tBu_2}ImC-N_2O (**TS2**)	-725.048633	-725.03037	-725.092252
^{tBu_2}ImC-N_2O (*cis*-**6**)	-725.137226	-725.119357	-725.180433
^{tBu_2}ImC-N_2O (*trans*-**6**)	-725.137115	-725.119104	-725.180372
^{tBu_2}ImC-N_2O (**TS3**)	-725.098059	-725.080495	-725.140186
^{tBu_2}ImC=O (**7**)	-615.751518	-615.735306	-615.792451
^{tBu_2}ImC-N_2O-$B(C_6F_5)_3$ (**INT1**)	-2933.696663	-2933.647321	-2933.781503
^{tBu_2}ImC-N_2O-$B(C_6F_5)_3$ (**INT2**)	-2933.693233	-2933.643613	-2933.780472
^{tBu_2}ImC-N_2O-$B(C_6F_5)_3$ (**INT3**)	-2933.693540	-2933.644048	-2933.779103
^{tBu_2}ImC-N_2O-$B(C_6F_5)_3$ (**TS1'**)	-2933.651098	-2933.60353	-2933.731987
^{tBu_2}ImC-N_2O-$B(C_6F_5)_3$ (**8a**)	-2933.752336	-2933.705153	-2933.833020
$Me_2{}^{tBu_2}$ImC-N_2O (**TS1**)	-803.663461	-803.64237	-803.709643
$Me_2{}^{tBu_2}$ImC-N_2O (**TS2**)	-803.624186	-803.603126	-803.670313
$Me_2{}^{tBu_2}$ImC-N_2O (*cis*)	-803.703237	-803.682311	-803.75051
$Me_2{}^{tBu_2}$ImC-N_2O (*trans*)	-803.704573	-803.683643	-803.75087
$Me_2{}^{tBu_2}$ImC-N_2O (**TS3**)	-803.666913	-803.646816	-803.711227
$Me_2{}^{tBu_2}$ImC=O	-694.318521	-694.299251	-694.364477
$Me_2{}^{tBu_2}$ImC-N_2O-$B(C_6F_5)_3$ (**INT1**)	-3012.272761	-3012.220955	-3012.357794
$Me_2{}^{tBu_2}$ImC-N_2O-$B(C_6F_5)_3$ (**INT2**)	-3012.270271	-3012.217773	-3012.35881
$Me_2{}^{tBu_2}$ImC-N_2O-$B(C_6F_5)_3$ (**INT3**)	-3012.27302	-3012.219966	-3012.360684
$Me_2{}^{tBu_2}$ImC-N_2O-$B(C_6F_5)_3$ (**TS1'**)	-3012.228185	-3012.177324	-3012.313001
$Me_2{}^{tBu_2}$ImC-N_2O-$B(C_6F_5)_3$ (**8b**)	-3012.321805	-3012.271893	-3012.403715
^{tBu_2}ImC-CO_2 (**TS1**)	-729.054329	-729.03607	-729.09991
^{tBu_2}ImC-CO_2 (**5a**)	-729.066592	-729.048808	-729.109302
$Me_2{}^{tBu_2}$ImC-CO_2 (**TS1'**)	-807.62600	-807.605002	-807.674044
$Me_2{}^{tBu_2}$ImC-CO_2 (**5b**)	-807.632758	-807.612204	-807.678631
^{tBu_2}ImC-CO_2-$B(C_6F_5)_3$ (**9a**)	-2937.676137	-2937.629284	-2937.754760
$Me_2{}^{tBu_2}$ImC-CO_2-$B(C_6F_5)_3$ (**9b**)	-3016.248040	-3016.198030	-3016.331069

[a] DFT energy incl. ZPE.
[b] standard conditions T = 298.15 K and p = 1 atm.

[1] Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[2] X. Cao and M. Dolg, *J. Chem. Phys.*, 2001, **115**, 7348.