Electronic Supplementary Material (ESI) for ChemComm.

TOC of the Supporting Information

Section S1: Computational details

Geometry optimizations were performed without symmetry constraints using the Gaussian09[1] suite of programs at the BP86[2]/def2-TZVPP[3] level of theory using the D3 dispersion correction suggested by Grimme et al.[4] This level is denoted BP86-D3/def2-TZVPP. All species were also characterized by frequency calculations, and have positive definite Hessian matrices thus confirming that the computed structures are minima on the potential energy surface. Transition states (TS's) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.[5]

The interaction between the transition metal fragment and pro-ligand **L1** in the complexes has been investigated with the EDA-NOCV method,[6] which combines the energy decomposition analysis (EDA)[7] with the natural orbitals for chemical valence (NOCV)[8] methods. Within this approach, the interaction energy can be decomposed into the following physically meaningful terms:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} + \Delta E_{disp}$$

The term ΔE_{elstat} corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the deformed reactants and is usually attractive. The Pauli repulsion ΔE_{Pauli} comprises the destabilizing interactions between occupied orbitals and is responsible for any steric repulsion. The orbital interaction ΔE_{orb} accounts for charge transfer (interaction between occupied orbitals on one moiety with unoccupied orbitals on the other, including HOMO–LUMO interactions) and polarization (empty-occupied orbital mixing on one fragment due to the presence of another fragment). Finally, the ΔE_{disp} term takes into account the interactions which are due to dispersion forces. The EDA-NOCV method makes it possible to further partition the total orbital interactions into pairwise contributions of the orbital interactions.

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[1] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[2] (a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098; (b) J. P. Perdew, *Phys. Rev. B* 1986, **33**, 8822.

[3] F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys*., 2005, **7**, 3297.

[4] S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys*., 2010, **132**, 154104.

[5] C. González and H. B. Schlegel, *J. Phys. Chem*., 1990, **94**, 5523.

[6] M. P. Mitoraj, A. Michalak and T. Ziegler, *J. Chem. Theory Comput*., 2009, **5**, 962.

[7] For reviews on the EDA method, see: a) F. M. Bickelhaupt, E. J. Baerends, in *Reviews in Computational Chemistry*, (Eds. K. B. Lipkowitz, D. B. Boyd), Wiley-VCH: New York, 2000, Vol. 15, pp. 1-86; b) M. von Hopffgarten and G. Frenking, *WIREs Comput. Mol. Sci*. 2012, **2**, 43; c) I. Fernández, in *Applied Theoretical Organic Chemistry*, (Ed. D. J. Tantillo), World Scientific, New Jersey, 2018, pp. 191-226.

[8] M. P. Mitoraj, A. Michalak and T. Ziegler, *J. Chem. Theory Comput*., 2009, **5**, 962.

The EDA-NOCV calculations were carried out using the BP86-D3/def2-TZVPP optimized geometries with the program package AMS 2020.101[9] using the same functional (BP86-D3) in conjunction with a triple-ζ-quality basis set using uncontracted Slater-type orbitals (STOs) augmented by two sets of polarization function with a frozen-core approximation for the core electrons.[10] An auxiliary set of s, p, d, f, and g STOs were used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.[11] Scalar relativistic effects were incorporated by applying the zeroth-order regular approximation (ZORA).[12] This level of theory is denoted ZORA-BP86-D3/TZ2P//BP86-D3/def2-TZVPP.

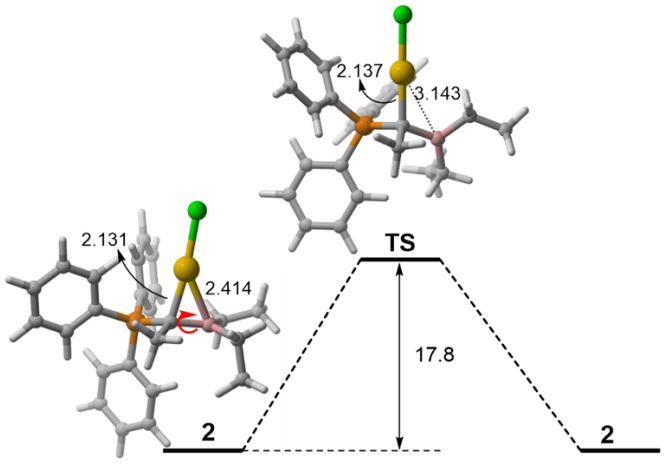

*Figure S1. Computed (BP86-D3/def2-TZVPP level) reaction profile associated with the rotation around the C_{ylide}–B bond in **2**. Activation barrier is given in kcal mol^{-1}, whereas bond distances are given in angstroms.*

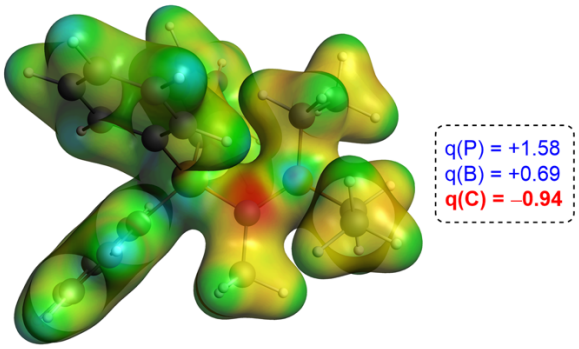

*Figure S2. Computed (BP86-D3/def2-TZVPP level) molecular electrostatic potential and corresponding NBO-charges for pro-ligand **L1**. See also Table S1.*

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[9] a) G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders and T. Ziegler, *J. Comput. Chem*., 2001, **22**, 931; b) ADF2020, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.

[10] J. G. Snijders, P. Vernooijs and E. J. Baerends, *At. Data Nucl. Data Tables,* 1981, **26**, 483.

[11] J. Krijn and E. J. Baerends, *Fit Functions in the HFS-Method*, Internal Report (in Dutch), Vrije Universiteit Amsterdam, The Netherlands, 1984

[12] a) E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys*., 1993, **99**, 4597; b) E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys*., 1994, **101**, 9783; c) E. van Lenthe, A. Ehlers and E. J. Baerends, *J. Chem. Phys*., 1999, **110**, 8943

Table S1. Comparison of the charges and Wiberg Bond Indices of related species

	L1	$[H_2C{=}BEt_2]^-$	$Ph_3P{=}CMe_2$	$[Ph_3P\text{-}CH(Me)\text{-}BEt_2]^+$
q(C)	-0.94	-0.98	-0.63	-0.91
q(B)	0.69	0.38		1.00
q(P)	1.58		1.50	1.60
WBI(C-B)	1.24	1.71		0.80
WBI(C-P)	1.11		1.27	0.91

Section S2: Further informations

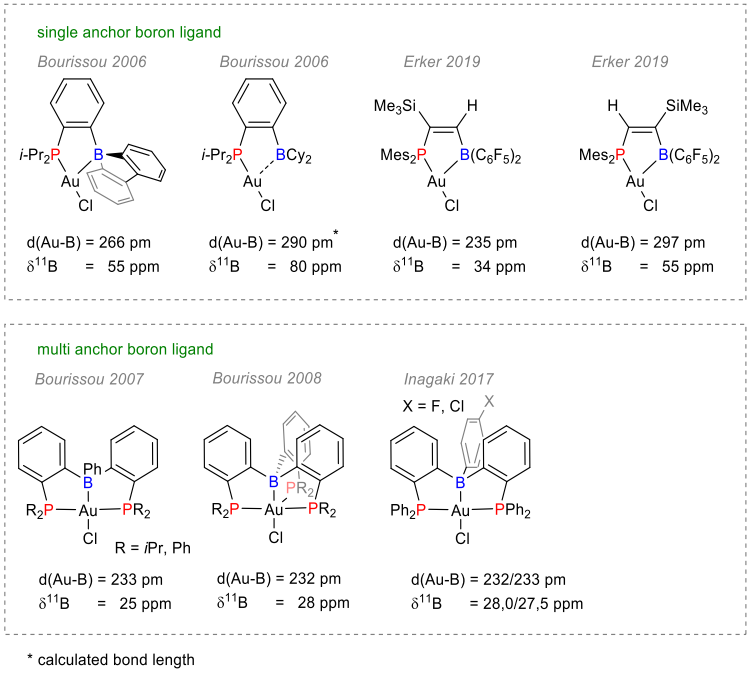

Chart S1. Known Au complexes with Au→B interaction.[13] *Omitted are some of the complexes from Inagaki et al. that were synthesized by chloride abstraction of known complexes.*[13d] *The complexes of compounds, which coordinate via an electron-rich boron atom are left out; we hereby refer to the literature.*[14]

[13] a) S. Bontemps, G. Bouhadir, K. Miqueu, D. Bourissou, *J. Am. Chem. Soc.*, 2006, **128**, 12056-12057; b) M. Sircoglou, S. Bontemps, M. Mercy, N. Saffon, M. Takahashi, G. Bouhadir, L. Maron, D. Bourissou, *Angew. Chem. Int. Ed.,* 2007, **46**, 8583-8586; c) M. Sircoglou, S. Bontemps, G. Bouhadir, N. Saffon, K. Miqueu, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov, D. Bourissou, *J. Am. Chem. Soc.*, 2008, **130**, 16729-16738; d) F. Inagaki, C. Matsumoto, Y. Okada, N. Maruyama, C. Mukai, *Angew. Chem. Int. Ed.*, 2015, **54**, 818-822; e) F. Inagaki, K. Nakazawa, K. Maeda, T. Koseki, C. Mukai, *Organometallics*, 2017, **36**, 3005-3008; f) A. Ueno, K. Watanabe, C. G. Daniliuc, G. Kehr, G. Erker, *Chem. Commun.*, 2019, **55**, 4367-4370.

[14] a) D. A. Ruiz, G. Ung, M. Melaimi, G. Bertrand, *Angew. Chem. Int. Ed.*, 2013, **52**, 7590-7592; b) M. Arrowsmith, D. Auerhammer, R. Bertermann, H. Braunschweig, M. A. Celik, J. Erdmannsdörfer, I. Krummenacher, T. Kupfer, *Angew. Chem. Int. Ed.*, 2017, **56**, 11263-11267; c) R. Shang, S. Saito, J. O. C. Jimenez-Halla, Y. Yamamoto, *Dalton Trans.*, 2018, **47**, 5181-5188; d) L. Kong, R. Ganguly, Y. Li, R. Kinjo, *Chem. Sci.*, 2015, **6**, 2893-2902; e) W. Lu, H. Hu, Y. Li, R. Ganguly, R. Kinjo, *J. Am. Chem. Soc.*, 2016, **138**, 6650-6661; f) H. Niu, R. J. Mangan, A. V. Protchenko, N. Phillips, W. Unkrig, C. Friedmann, E. L. Kolychev, R. Tirfoin, J. Hicks, S. Aldridge, *Dalton Trans.*, 2018, **47**, 7445-7455; g) H. Braunschweig, K. Radacki, R. Shang, *Chem. Commun.*, 2013, **49**, 9905-9907.

Section S3: Experimental Section

All operations were conducted under a dry argon atmosphere using standard Schlenk and glovebox techniques. For the {$AgN(SO_2CF_3)_2$} and {$AuN(SO_2CF_3)_2$} complexes exposure to light was avoided. Solvents were dried rigorously and degassed before use. [AuCl(dms)] and $AgN(SO_2CF_3)_2$ was purchased from Sigma-Aldrich and used without further purification. $Ph_3PC(Me)BEt_2$ (**L1**) was synthesized according to a previously reported procedure.[15] [$CuN(SO_2CF_3)_2$·MesH]: MesCu and $AgN(SO_2CF_3)_2$ were stirred in CH_2Cl_2 overnight. Evaporation of the solvent and drying in high vacuum yielded $Cu(I)N(SO_2CF_3)_2$·MesH as colorless powder. The chemical shifts are expressed in parts per millions and ^1H and ^{13}C signals are given relative to TMS. Coupling constants J are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as s, d, q, sept or m for singlets, doublets, quartets, septets or multiplets, respectively. The assignments were confirmed as necessary with the use of 2D NMR correlation experiments. IR spectra were measured with a Bruker Alpha spectrometer using the attenuated total reflection (ATR) technique on powdered samples, and the data are quoted in wavenumbers (cm^{-1}). The intensity of the absorption band is indicated as vw (very weak), w (weak), m (medium), s (strong) and vs. (very strong). The melting points were measured with a Thermo Fischer melting point apparatus and is not corrected. Elemental analyses were carried out in the institutional technical laboratories of the Karlsruhe Institute of Technology (KIT).

[$CuCl\{\eta^2$-$Ph_3PC(Me)BEt_2\}$] (**1**): A schlenk tube was charged with **L1** (200 mg, 0.56 mmol), CuCl (55 mg, 0.56 mmol) and CH_2Cl_2 (5 ml). After stirring for one hour at 40 °C the mixture became colorless. After reducing to 1 ml pentane (5 ml) were added. Evaporation of all volatiles yielded **1** (190 mg, 42 mmol, 74 %) as colorless solid.

M. p.: 79 °C

^1H NMR (300 MHz, C_6D_6, 293 K, ppm): δ = 7.82 – 7.72 (m, H_{aryl}, 6H), 7.02 – 6.92 (m, H_{aryl}, 9H), 1.74 (d, $^3J_{PH}$ = 18.5 Hz, H_{Me}, 3H), 1.86 – 1.44 (m, H_{BCH2}, 2H), 1.35 (t, $^3J_{HH}$ = 7.9 Hz, H_{BCH3}, 3H), 1.02 (t, $^3J_{HH}$ = 7.7 Hz, H_{BCH3}, 3H), 0.82 – 0.52 (m, H_{BCH2}, 2H).

^{11}B NMR (96 MHz, C_6D_6, ppm): δ = 53.5 (bs).

$^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 293 K, ppm): δ = 134.4 (d, $^2J_{PC}$ = 9.1 Hz, C_{ortho}), 132.6 (d, $^4J_{PC}$ = 2.8 Hz, C_{para}), 129.1 (d, $^3J_{PC}$ = 11.4 Hz, C_{meta}), 125.9 (d, $^1J_{PC}$ = 82.3 Hz, C_{ipso}), 17.1 (d, $^2J_{PC}$ = 6.3 Hz, C_{Me}), 15.1 (m, C_{BCH2}), 14.3 (bs, C_{BCH2}), 11.5 (s, C_{BCH3}), 11.0 (s, C_{BCH3}).

$^{31}P\{^1H\}$ NMR (121 MHz, 293 K, C_6D_6, ppm): δ = 28.9 (s).

IR (ATR, cm^{-1}): ũ = 3056 (vw), 2944 (vw), 2862 (vw), 2147 (vw), 2015 (vw), 1980 (vw), 1962 (vw), 1588 (vw), 1482 (vw), 1457 (vw), 1435 (m), 1370 (vw), 1300 (w), 1235 (w), 1190 (w), 1159 (vw), 1098 (s), 1027 (vw), 997 (w), 982 (w), 919 (m), 846 (vw), 804 (vw), 747 (m), 712 (vs), 689 (vs), 590 (w), 551 (w), 528 (vs), 496 (m), 433 (vw), 420 (vw), 389 (vw).

Elemental analysis: (%): $C_{24}H_{28}CuBClP$·0.25 CH_2Cl_2 calc. C, 60.87, H 6.00; found C, 60.55, H, 5.60.

[15] M. Radius, F. Breher, *Chem. Eur. J.*, 2018, **24**, 15744-15749

[AuCl{η^2-$Ph_3PC(Me)BEt_2$}] (**2**) A mixture of [AuCl(dms)] (180 mg, 0,611 mmol) and **L1** was placed in a Schlenk flask, dissolved in CH_2Cl_2 (5 mL) and stirred at room temperature for five minutes. During this period the initially yellow coloured solution turned colourless. Evaporation of the solvent and volatiles in high vacuum yielded **2** as a colorless powder (330 mg, 91 % yield). For X-ray diffraction, suitable crystals were obtained by slow solvent evaporation of a solution of **2** in a small amount of CH_2Cl_2.

M. p.: 132 °C (decomposition)

^{1}H NMR (300 MHz, toluene-d_8, 293 K, ppm): δ = 7.79 – 7.66 (m, H_{aryl}, 6H), 7.07 – 7.00 (m, H_{aryl}, 3H), 6.99 – 6.91 (m, H_{aryl}, 6H), 1.73 (d, $^3J_{PH}$ = 18.6 Hz, H_{Me}. 3H), 1.62 – 1.29 (m, H_{BCH2}, 2H), 1.21 (t, $^3J_{HH}$ = 7.3 Hz, H_{BCH3}. 3H), 1.00 (t, $^3J_{HH}$ = 7.7 Hz, H_{BCH3}. 3H), 0.77 – 0.43 (m, H_{BCH2}, 2H).

^{11}B NMR (96 MHz, toluene-d_8, 293 K, ppm): δ = 53.3 (bs).

^{13}C{^{1}H} NMR (75 MHz, toluene-d_8, 293 K, ppm): δ = 134.6 (d, $^2J_{PC}$ = 8.9 Hz, C_{ortho}), 132.8 (d, $^4J_{PC}$ = 2.9 Hz, C_{para}), 129.2 (d, $^3J_{PC}$ = 10.9 Hz, overlapped with tol-d8 C_{meta}), 124.5 (d, $^1J_{PC}$ = 81.8 Hz, C_{ipso}), 19.3 (d, $^2J_{PC}$ = 6.3 Hz, C_{Me}), 14.7 (bs, C_{BCH2}), 13.7 (bs, C_{BCH2}), 112.0 (s, C_{BCH3}), 10.9 (s, C_{BCH3})

^{31}P{^{1}H} NMR (121 MHz, toluene-d_8, 293 K, ppm): δ = 27.8 (s).

IR (ATR, cm-1): ũ = 2954 (vw), 2861 (vw), 1482 (vw), 1456 (vw), 1435 (m), 1300 (vw), 1261 (vw), 1184 (w), 1095 (m), 1057 (vw), 997 (w), 915 (w), 799 (vw), 749 (m), 732 (m), 709 (vs), 688 (vs), 607 (vw), 564 (w), 531 (vs), 492 (s), 432 (vw), 412 (w), 393 (w).

Elemental analysis (%): $C_{24}H_{28}AuBClP$ calc. C, 48.80, H 4.78; found C, 48.52, H, 4.50.

[$CuN(SO_2CF_3)_2${η^2-$Ph_3PC(Me)BEt_2$}] (**3**): A schlenk tube was charged with **L1** (100 mg, 0.28 mmol), $CuN(SO_2CF_3)_2$·MesH (130 mg, 0.28 mmol) and CH_2Cl_2 (5 ml). After stirring for five minutes at RT the mixture became colorless. After evaporation of all volatiles the grey residue was treated with pentane (5 ml) at 50 °C. The pentane layer was removed via syringe. The residue was extracted with a mixture of CH_2Cl_2 (2 ml) and pentane (5 ml) and filtered. Evaporation of all volatiles and drying in high vacuum yielded **3** as colorless high viscous oil.

^{1}H NMR (300 MHz, C_6D_6, 293 K, ppm): δ = 7.63 – 7.52 (m, H_{aryl}, 6H), 7.13 – 7.03 (m, H_{aryl}, 9H), 1.75 (d, $^3J_{PH}$ = 17.8 Hz, H_{Me}, 3H), 1.67 – 1.40 (m, H_{BCH2}, 2H), 1.18 (bs, H_{BCH3}, 3H), 0.89 (m, H_{BCH3}, 3H), 0.75 – 0.40 (m, H_{BCH2}, 2H).

^{11}B NMR (96 MHz, C_6D_6, 293 K, ppm): δ = 53.3 (bs).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 293 K, ppm): δ = 134.0 (d, $^2J_{PC}$ = 9.0 Hz, C_{ortho}), 133.2 (d, $^4J_{PC}$ = 3.0 Hz, C_{para}), 129.5 (d, $^3J_{PC}$ = 11.6 Hz, C_{meta}), 124.7 (d, $^1J_{PC}$ = 83.2 Hz, C_{ipso}), 16.3 (d, $^2J_{PC}$ = 5.6 Hz, C_{Me}), 15.6 (m, C_{BCH2}), 10.3 (m, C_{BCH3}).

^{19}F NMR (282 MHz, 293 K, C_6D_6, ppm): δ = -75.8 (s).

^{31}P{^{1}H} NMR (121 MHz, 293 K, C_6D_6, ppm): δ = 31.1 (s).

IR (ATR, cm^{-1}): $\tilde{\upsilon}$ = 2954 (vw), 2870 (vw), 2276 (vw), 2214 (vw), 2121 (vw), 2003 (vw), 1589 (vw), 1484 (vw), 1461 (vw), 1438 (w), 1394 (vs), 1373 (w), 1333 (vw), 1308 (vw), 1196 (vs), 1133 (s), 1103 (w), 1060 (vw), 998 (vw), 974 (vs), 917 (vw), 881 (vw), 829 (w), 750 (w), 717 (w), 693 (m), 656 (vw), 613 (vs), 569 (w), 542 (s), 531 (m), 510 (m), 400 (m).

[$AgN(SO_2CF_3)_2\{\eta^2$-$Ph_3PC(Me)BEt_2\}$] (**4**): A brown glass NMR tube was charged with **L1** (15.0 mg, 42 µmol), $AgN(SO_2CF_3)_2$ (15.6 mg, 42 µmol) and C_6D_6 or toluene-d_8 (0.6 ml). Drying in high vacuum yielded a high viscous colorless oil that is highly light sensitive.

^{1}H NMR (300 MHz, C_6D_6, 293 K, ppm): δ = 7.60 – 7.48 (m, H_{aryl}, 6H), 7.10 – 6.98 (m, H_{aryl}, 9H), 1.65 (dd, $^3J_{PH}$ = 18.1 Hz, $^3J_{AgH}$ = 7.4 Hz, H_{Me}, 3H), 1.57 – 1.31 (m, H_{BCH2}, 2H), 1.23 (bs, H_{BCH3}, 3H), 0.82 (bs, H_{BCH3}, 3H), 0.64 – 0.32 (m, H_{BCH2}, 2H).

^{11}B NMR (96 MHz, C_6D_6, 293 K, ppm): δ = 58.5 (bs).

$^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 293 K, ppm): δ = 133.9 (d, $^2J_{PC}$ = 9.0 Hz, C_{ortho}), 133.3 (d, $^4J_{PC}$ = 2.9 Hz, C_{para}), 129.6 (d, $^3J_{PC}$ = 11.5 Hz, C_{meta}), 124.3 (dd, $^1J_{PC}$ = 83.3 Hz, $^3J_{AgC}$ = 5.1 Hz, C_{ipso}), 122.6 (d, $^1J_{AgC}$ = 322.9 Hz, C_{Ylide}) 18.1 (dd, $^2J_{PC}$ = 5.7 Hz, $^2J_{AgC}$ = 8.6 Hz, C_{Me}), 15.5 (m, C_{BCH2}), 14.2 (bs, C_{BCH2}), 11.6 (s, C_{BCH3}), 10.9 (s, C_{BCH3}).

^{19}F NMR (282 MHz, 293 K, C_6D_6, ppm): δ = -76.3 (s).

$^{31}P\{^1H\}$ NMR (121 MHz, 293 K, C_6D_6, ppm): δ = 31.3 (d, $^2J_{AgP}$ = 27,8 Hz).

IR (ATR, cm^{-1}): $\tilde{\upsilon}$ = 2953 (vw), 2869 (vw), 1589 (vw), 1484 (vw), 1461 (vw), 1438 (w), 1385 (s), 1354 (w), 1307 (vw), 1265 (vw), 1183 (vs), 1131 (vs), 1101 (s), 1059 (w), 991 (vs), 920 (w), 805 (m), 753 (m), 716 (s), 692 (s), 661 (vw), 612 (vs), 596 (m), 569 (m), 531 (m), 511 (s), 424 (vw), 391 (vw)

[$AuN(SO_2CF_3)_2\{\eta^2$-$Ph_3PC(Me)BEt_2\}$] (**5**): A brown glass vial was charged with **2** (15.0 mg, 42 µmol) dissolved in CH_2Cl_2 (2 ml) and $AgN(SO_2CF_3)_2$ (15.6 mg, 42 µmol) dissolved in CH_2Cl_2 (2 ml) was added. After stirring for 5 minutes the reaction mixture was filtered via syringe filter. Drying in high vacuum yielded a sticky colorless solid that is highly light sensitive. For the NMR experiments the residue was extracted with toluene-d_8 (0.6 ml).

^{1}H NMR (400 MHz, toluene-d_8, 293 K, ppm): δ = 7.75 – 7.68 (m, H_{aryl}, 6H), 7.51 – 7.16 (m, H_{aryl}, 9H), 1.72 (d, $^3J_{PH}$ = 18.5 Hz, H_{Me}, 3H), 1.45 – 1.25 (m, H_{BCH2}, 2H), 1.17 (m, H_{BCH3}, 3H), 1.02 (m, H_{BCH3}, 3H), 0.75 – 0.43 (m, H_{BCH2}, 2H).

^{11}B NMR (96 MHz, d_8-thf, 293 K, ppm): δ = 53.8 (bs).

$^{13}C\{^1H\}$ NMR (75 MHz, toluene-d_8, 293 K, ppm): δ = 134.5 (d, $^2J_{PC}$ = 7.7 Hz, C_{ortho}), 133.0 (d, $^4J_{PC}$ = 2.8 Hz, C_{para}), 129.3 (d, $^3J_{PC}$ = 11.6 Hz, C_{meta}) 19.3 (d, $^2J_{PC}$ = 6.2 Hz, C_{Me}), 14.6 (m, C_{BCH2}), 13.9 (m, C_{BCH2}), 12.0 (m, C_{BCH3}), 10.9 (m, C_{BCH3}).

^{19}F NMR (282 MHz, d_8-thf, 293 K, ppm): δ = -73.2 (s).

$^{31}P\{^1H\}$ NMR (121 MHz, toluene-d_8, 293 K, ppm): δ = 28.0 (bs).

IR (ATR, cm^{-1}): $\tilde{\upsilon}$ = 3061 (vw), 2954 (w), 2868 (vw), 1588 (vw), 1484 (vw), 1460 (vw), 1437 (m), 1352 (s), 1334 (w), 1262 (w), 1227 (vw), 1184 (vs), 1136 (w), 1102 (s), 1058 (s), 1014 (w), 999 (w), 913 (w), 799 (w), 751 (w), 735 (m), 717 (s), 692 (s), 653 (vw), 615 (w), 600 (w), 570 (w), 531 (m), 509 (m), 406 (vw).

Section S4: NMR spectra of **1**-**5** including VT NMR spectra

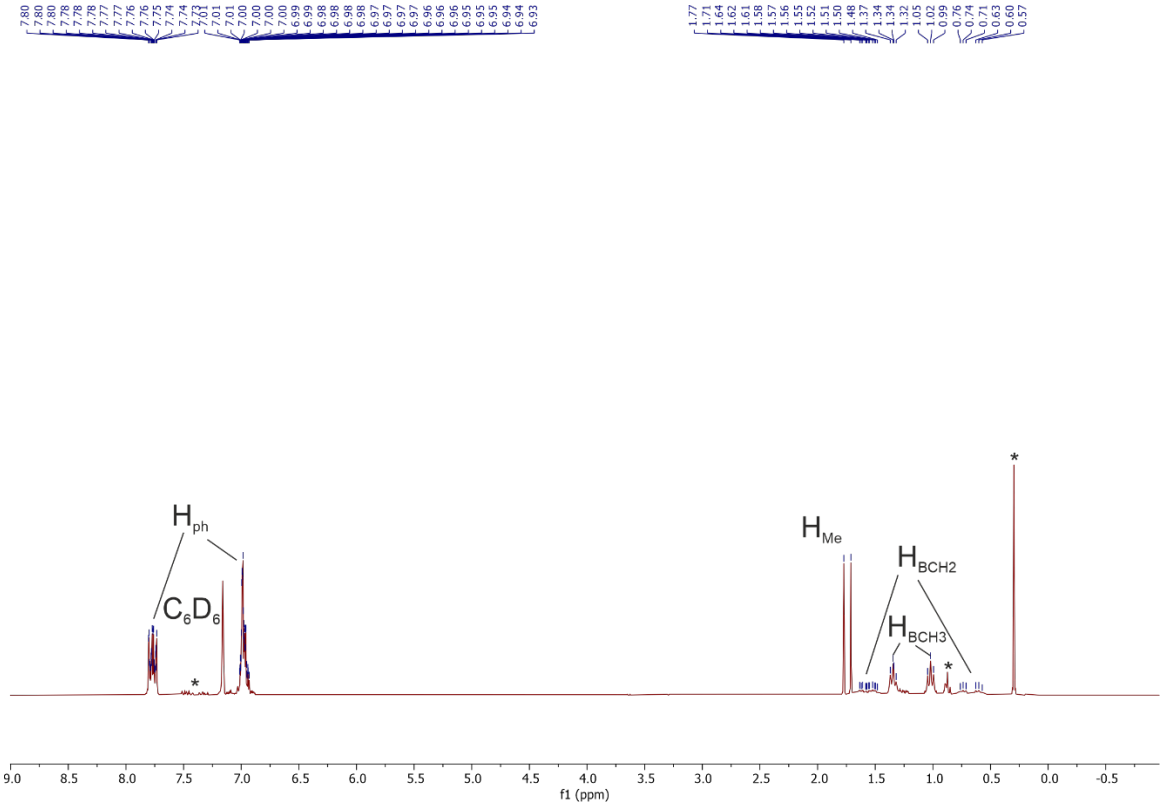

*Figure S1. ^{1}H NMR spectrum of **1** in C_6D_6. Impurities and silicon grease are marked by an asterisk.*

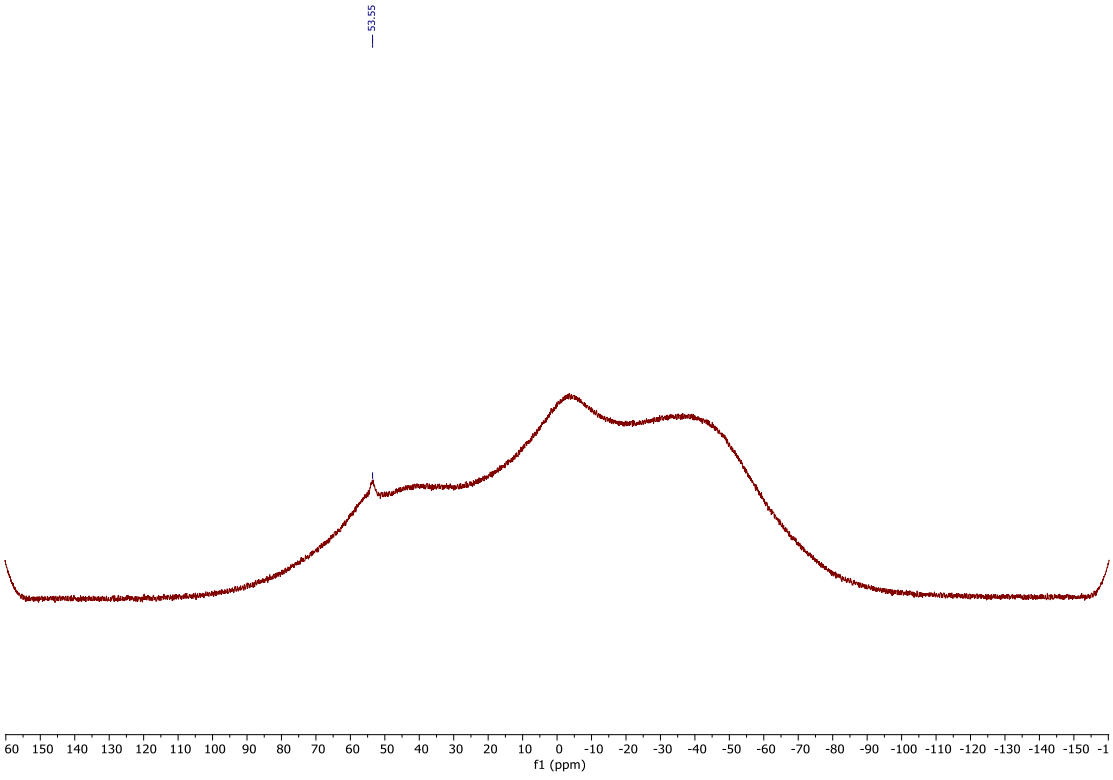

*Figure S2. ^{11}B NMR spectrum of **1** in C_6D_6.*

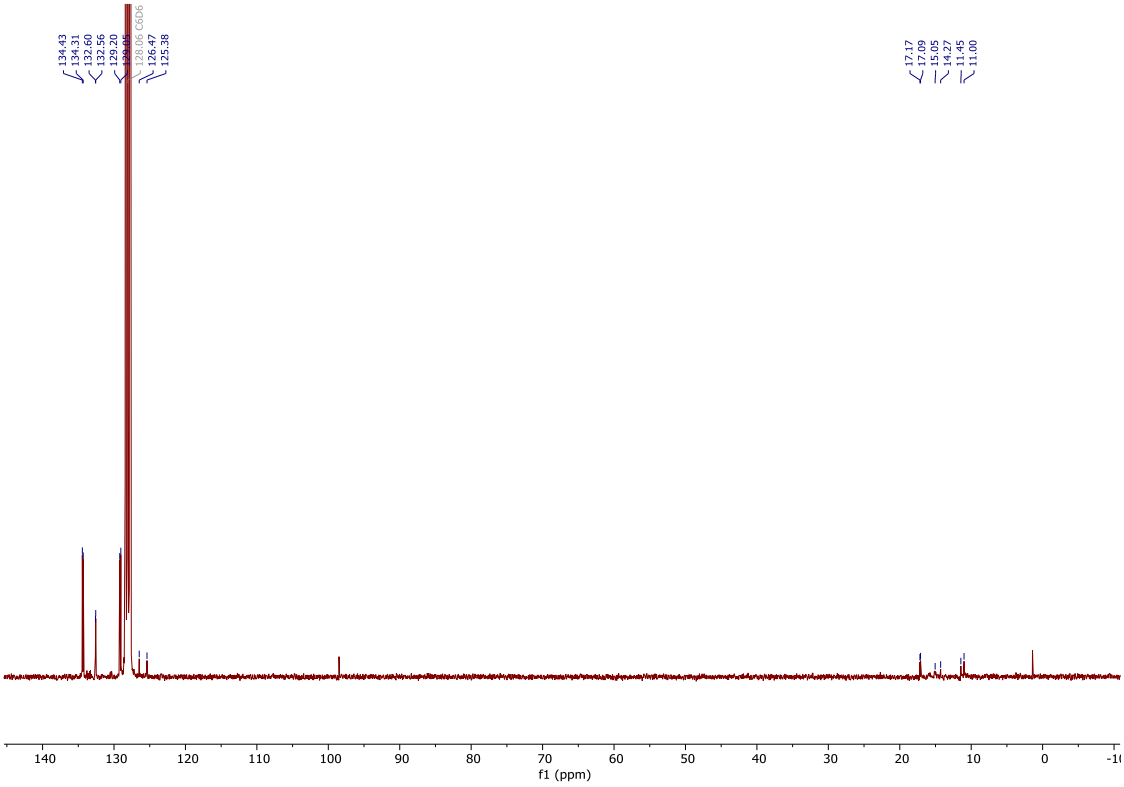

*Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in C_6D_6.*

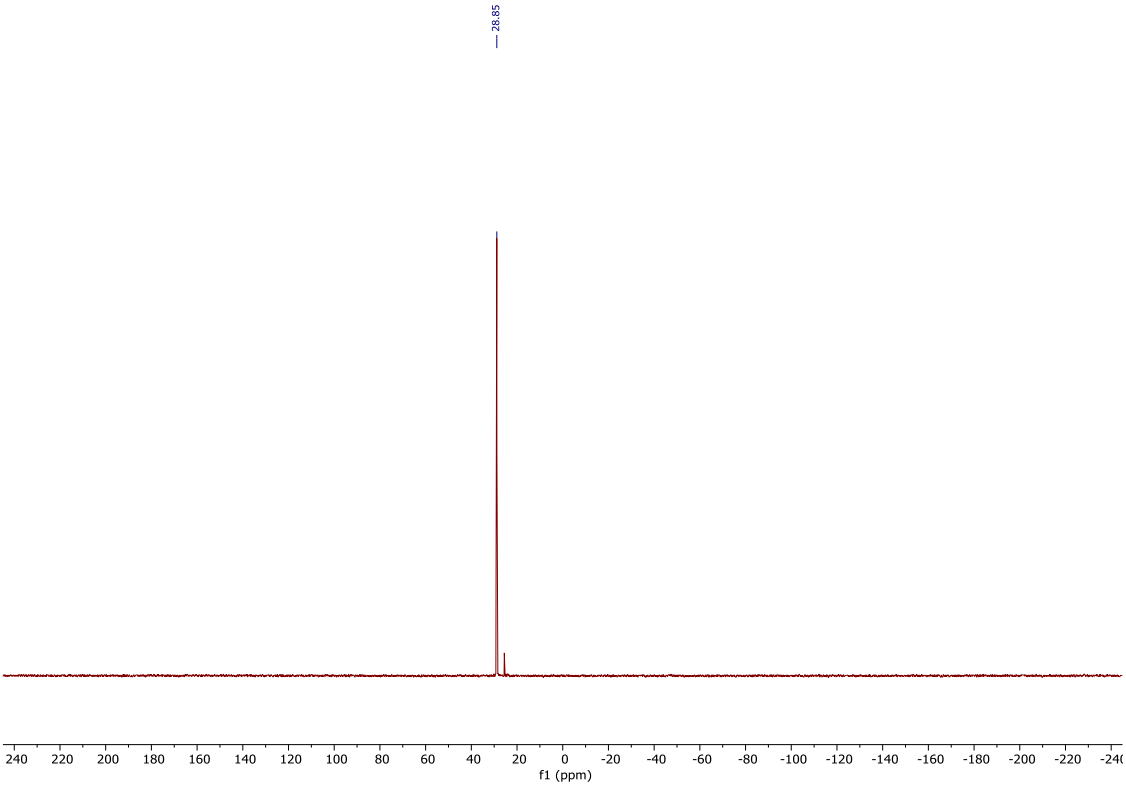

*Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum of **1** in C_6D_6. The signal at 25.5 ppm belongs to $Ph_3PC(Me)BEt_2$.*

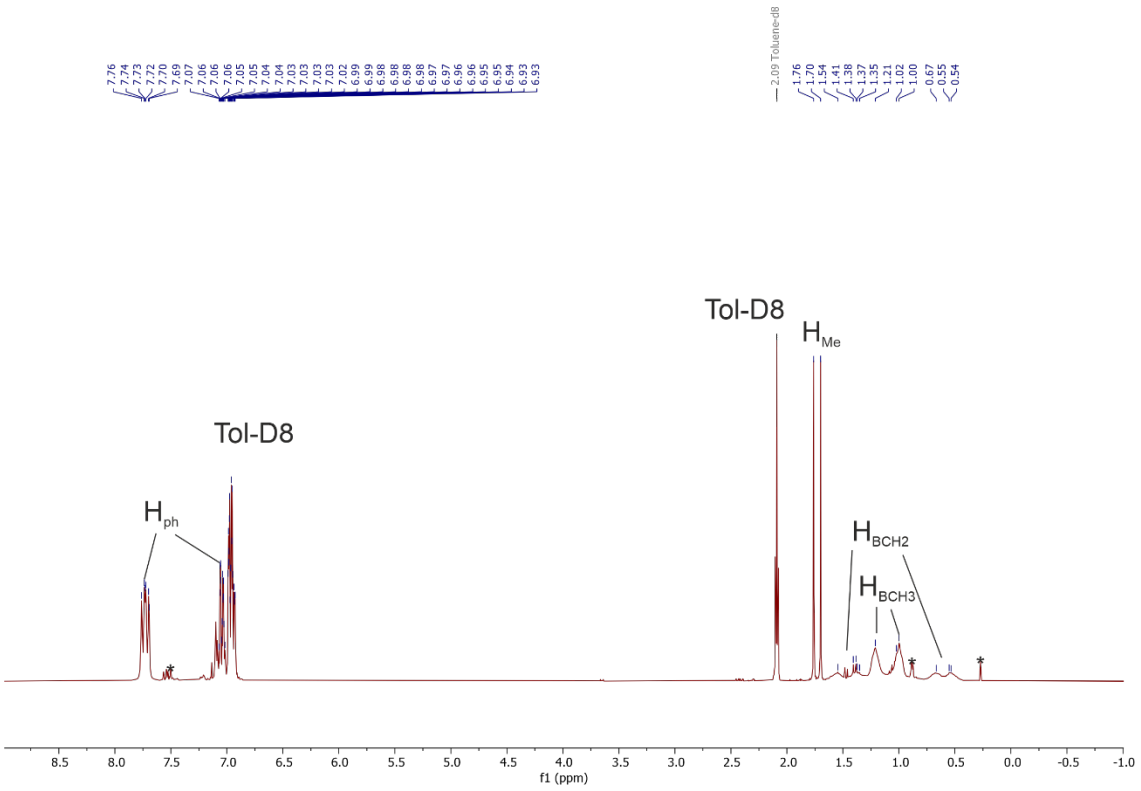

*Figure S5. [1]H NMR spectrum of **2** in toluene-d8. Impurities and silicon grease are marked by an asterisk.*

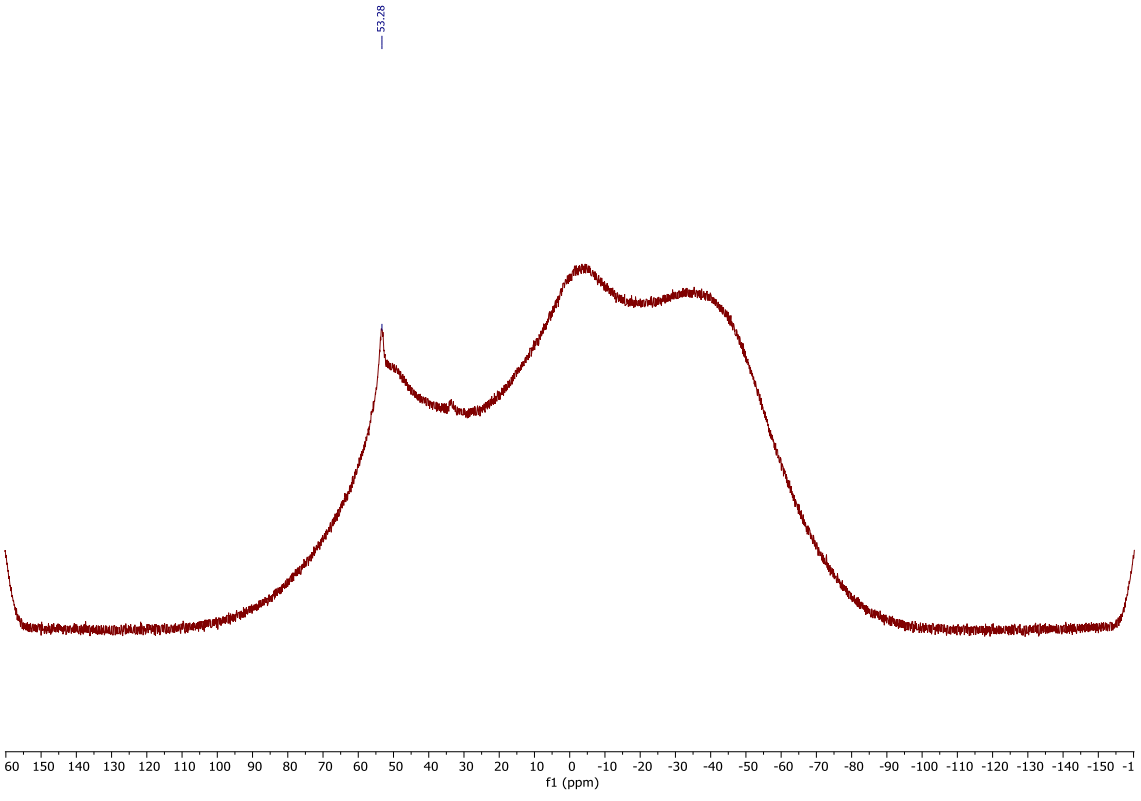

*Figure S6. [11]B NMR spectrum of **2** in toluene-d8.*

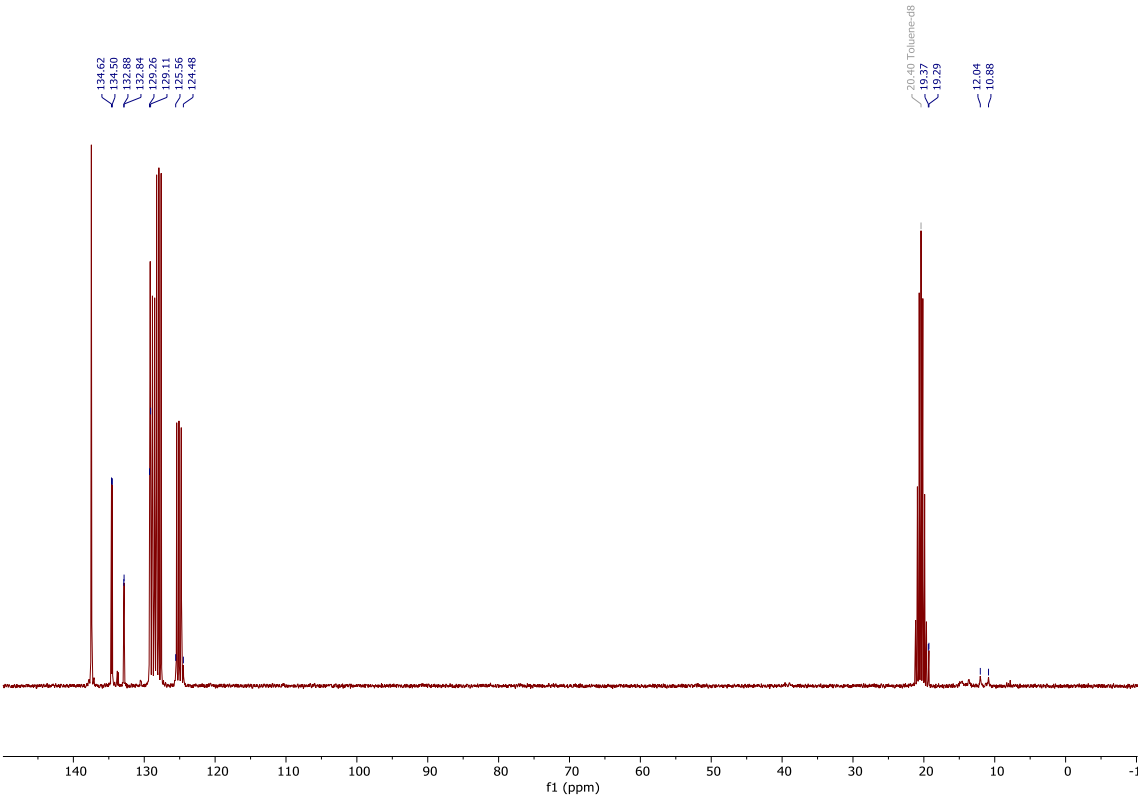

*Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in toluene-d8.*

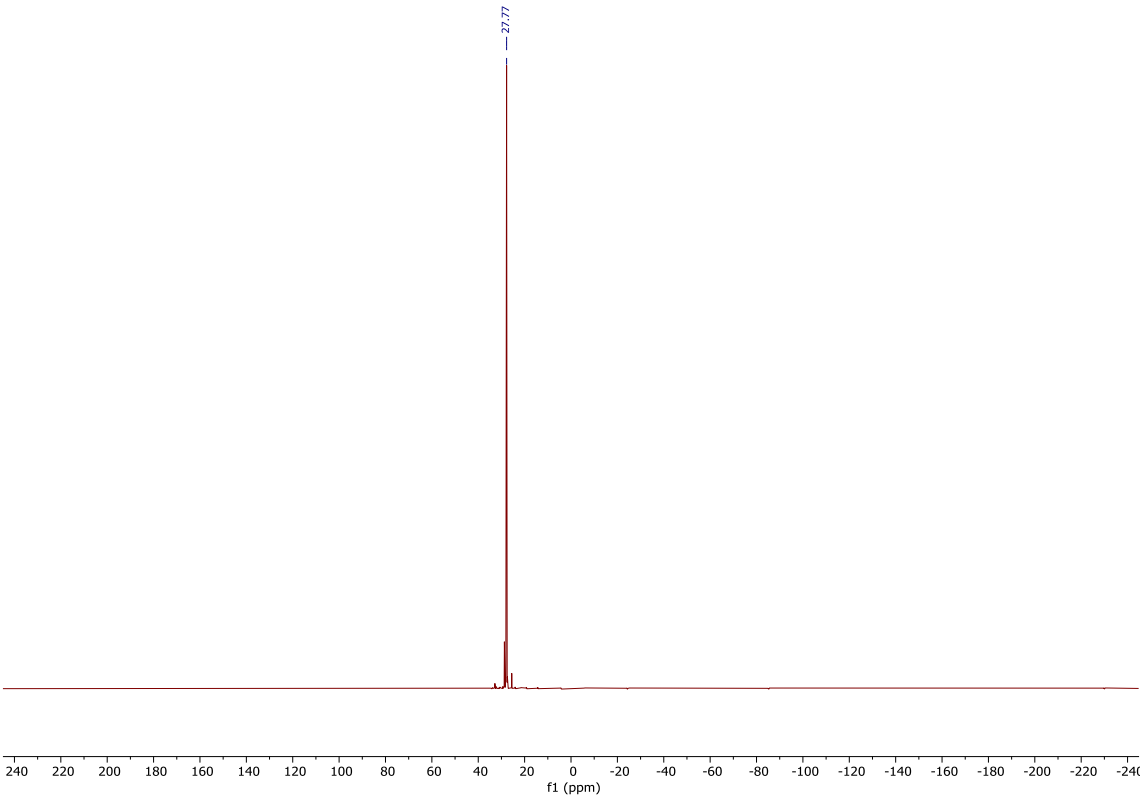

*Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum of **2** in toluene-d8. The signal at 25.5 ppm belongs to $Ph_3PC(Me)BEt_2$.*

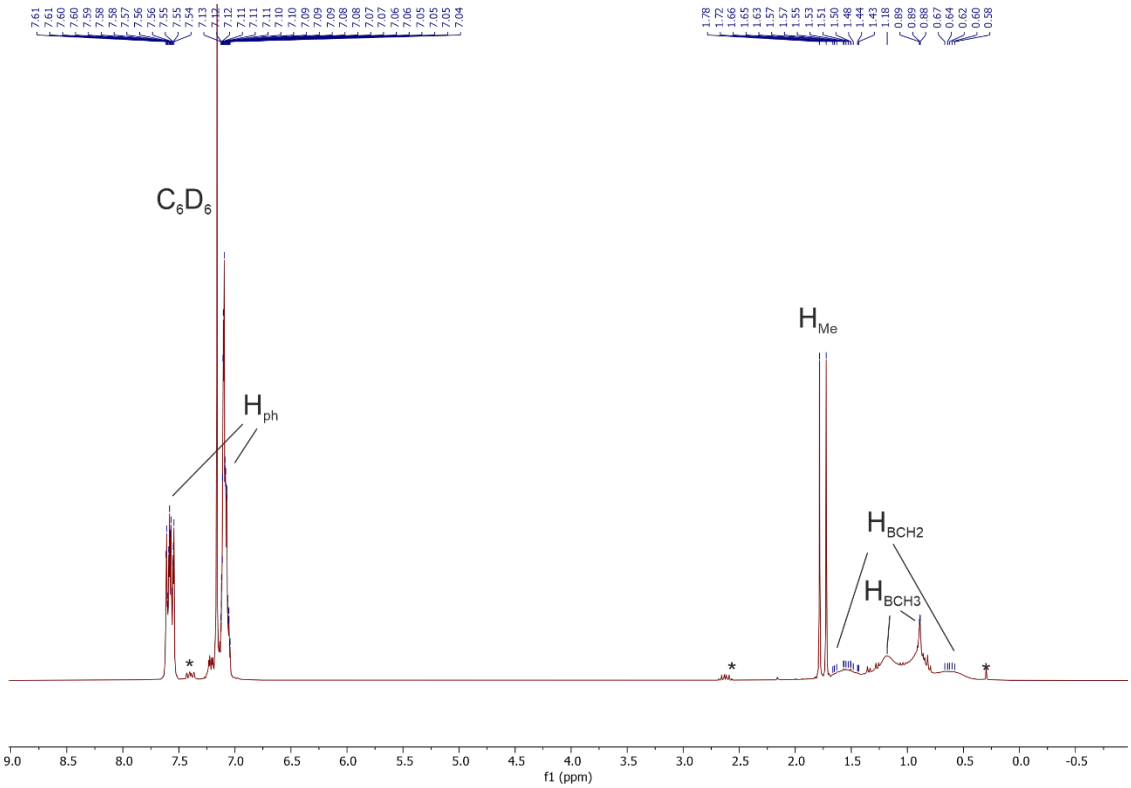

*Figure S9. ^{1}H NMR spectrum of **3** in C_6D_6. Impurities and silicon grease are marked by an asterisk.*

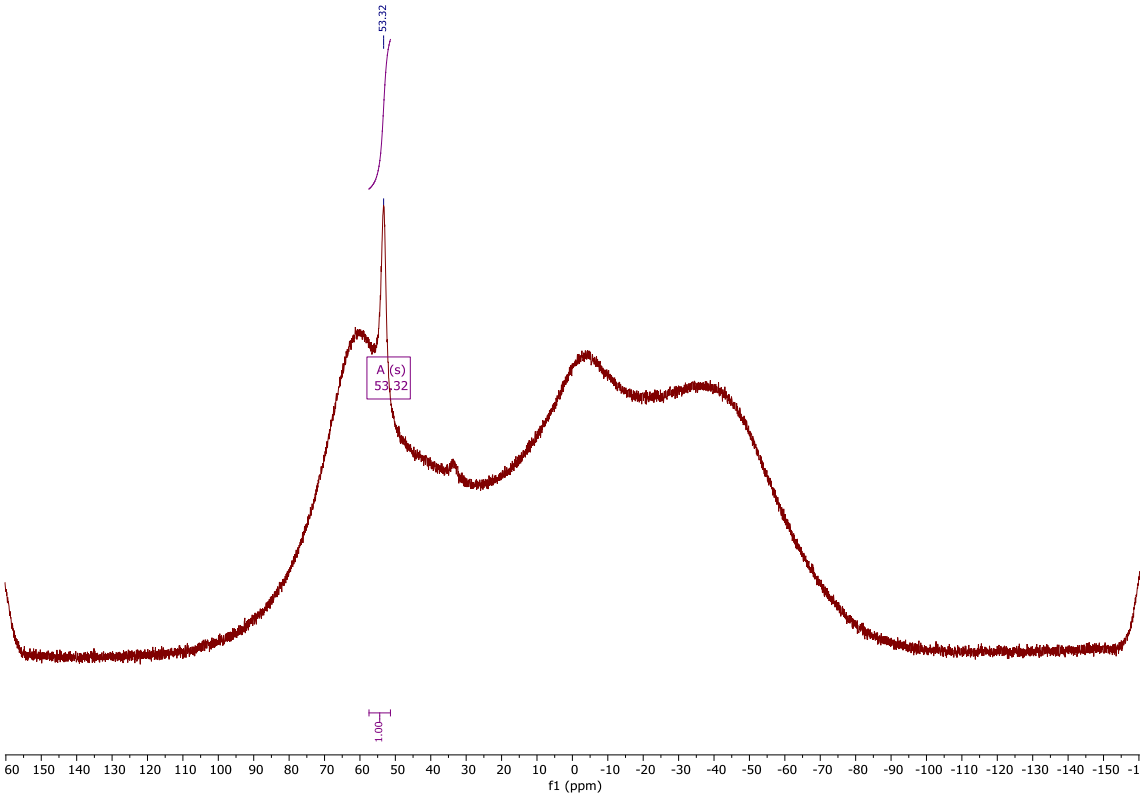

*Figure S10. ^{11}B NMR spectrum of **3** in C_6D_6.*

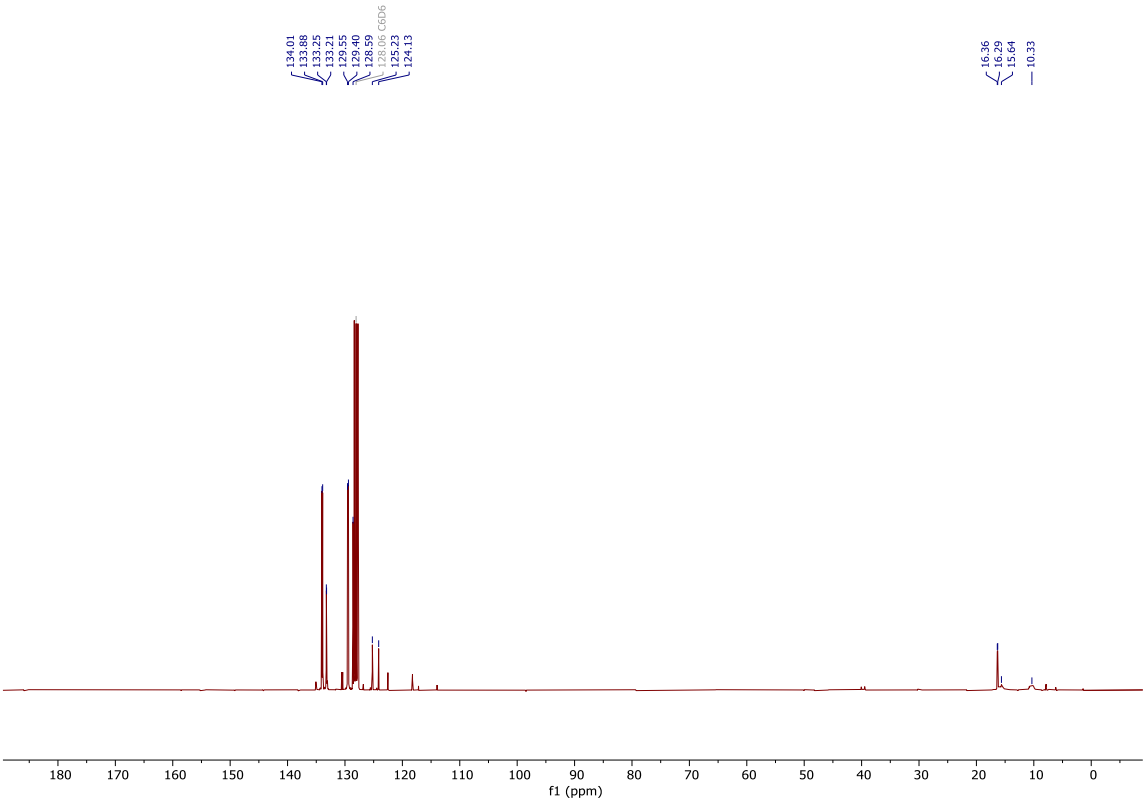

*Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6.*

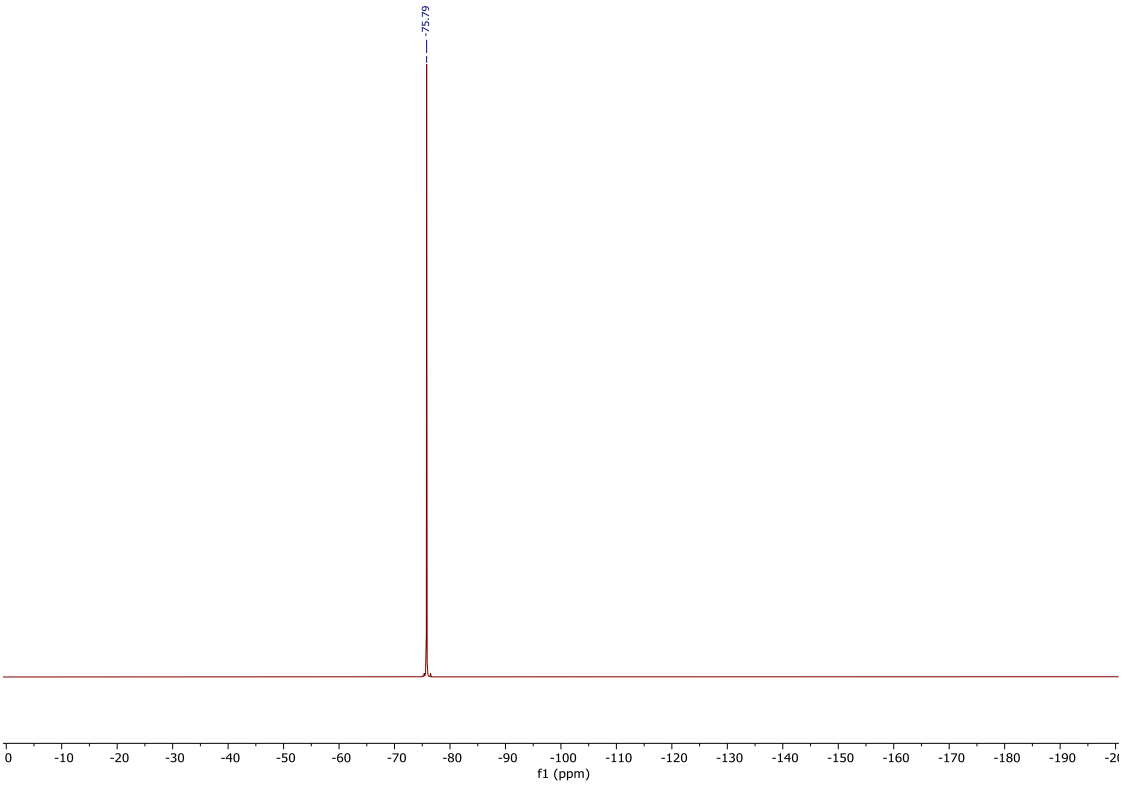

*Figure S12. ^{19}F NMR spectrum of **3** in C_6D_6.*

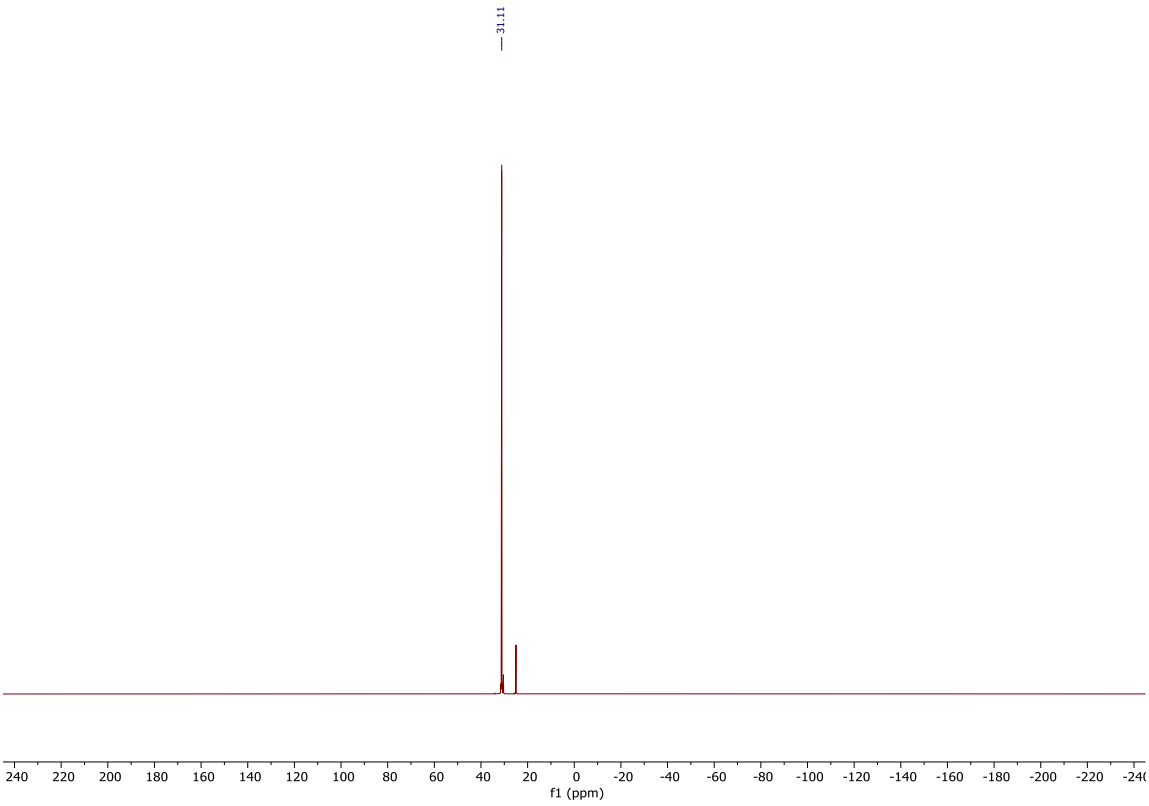

*Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of **3** in C_6D_6. The signal at 25.5 ppm belongs to $Ph_3PC(Me)BEt_2$.*

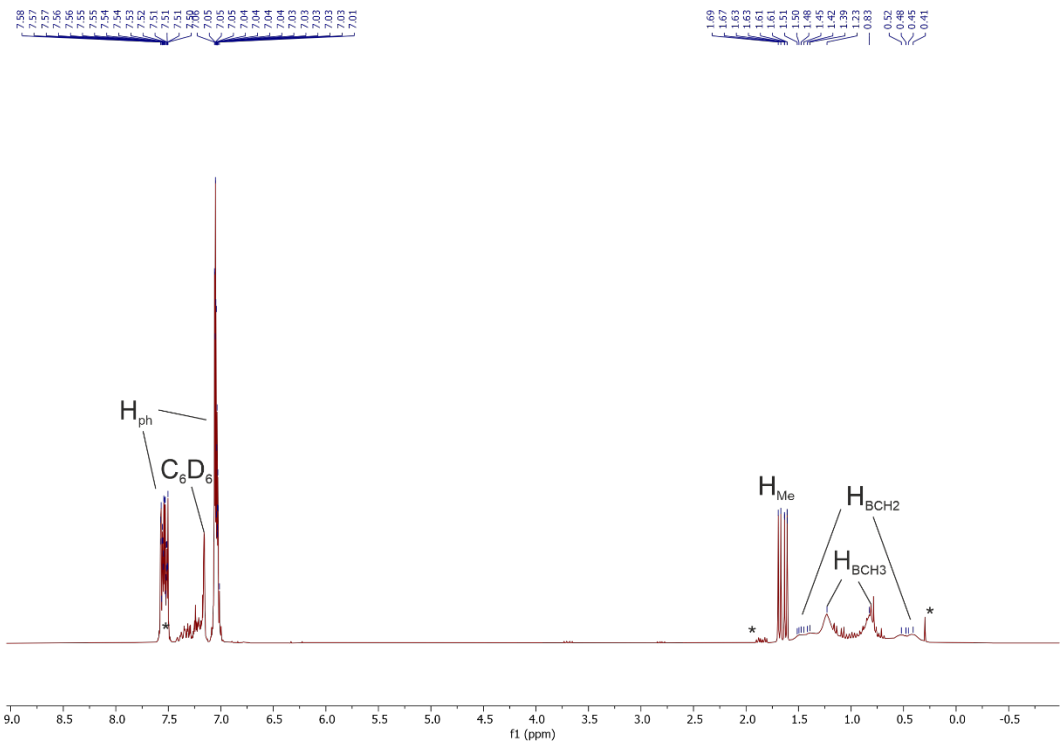

*Figure S14. [1]H NMR spectrum of **4** in C_6D_6. Impurities and silicon grease are marked by an asterisk.*

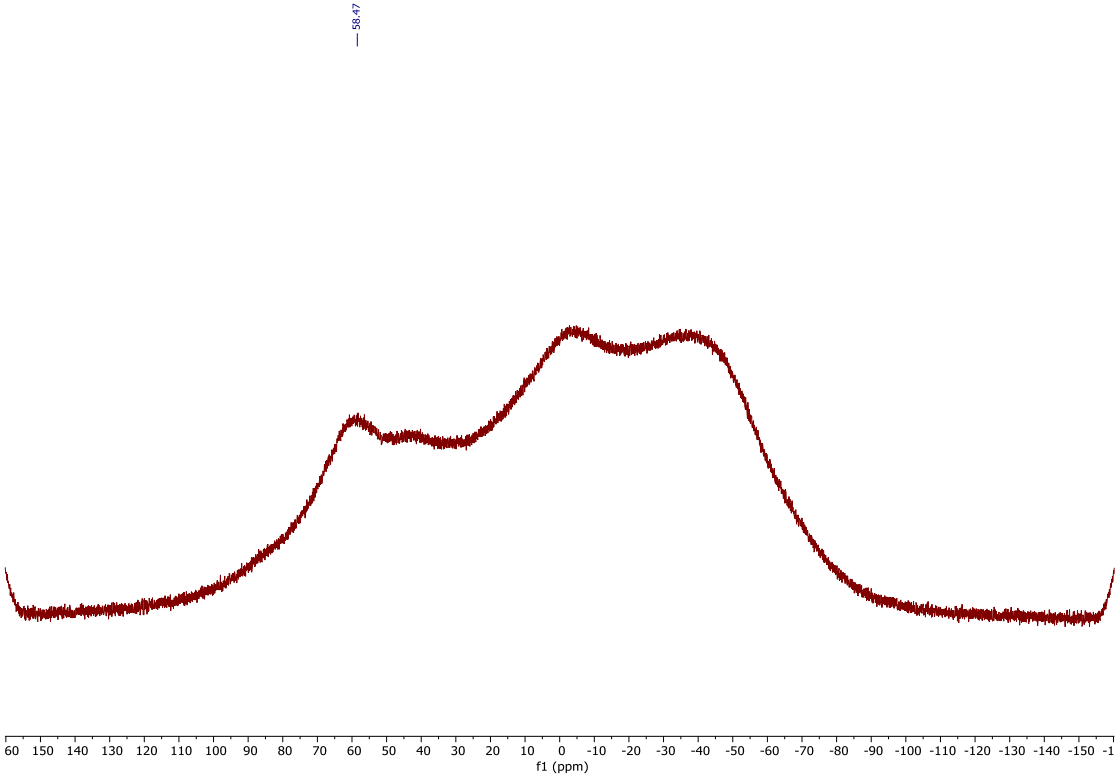

*Figure S15. [11]B NMR spectrum of **4** in C_6D_6.*

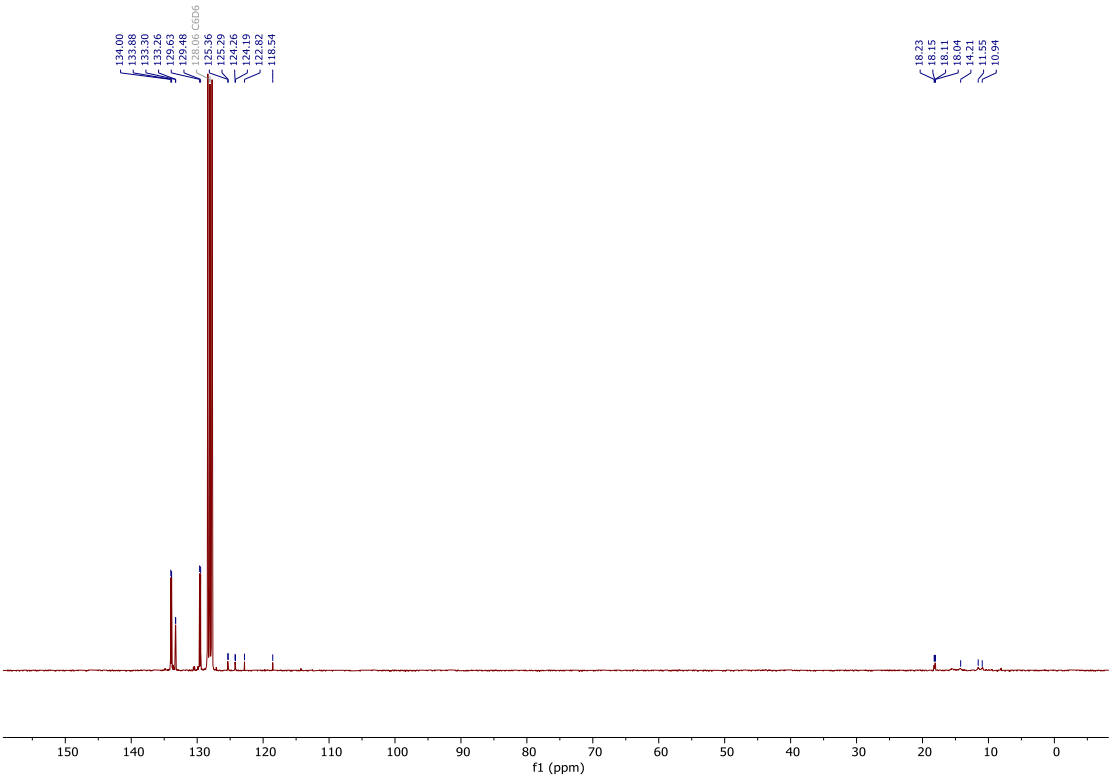

*Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in C_6D_6.*

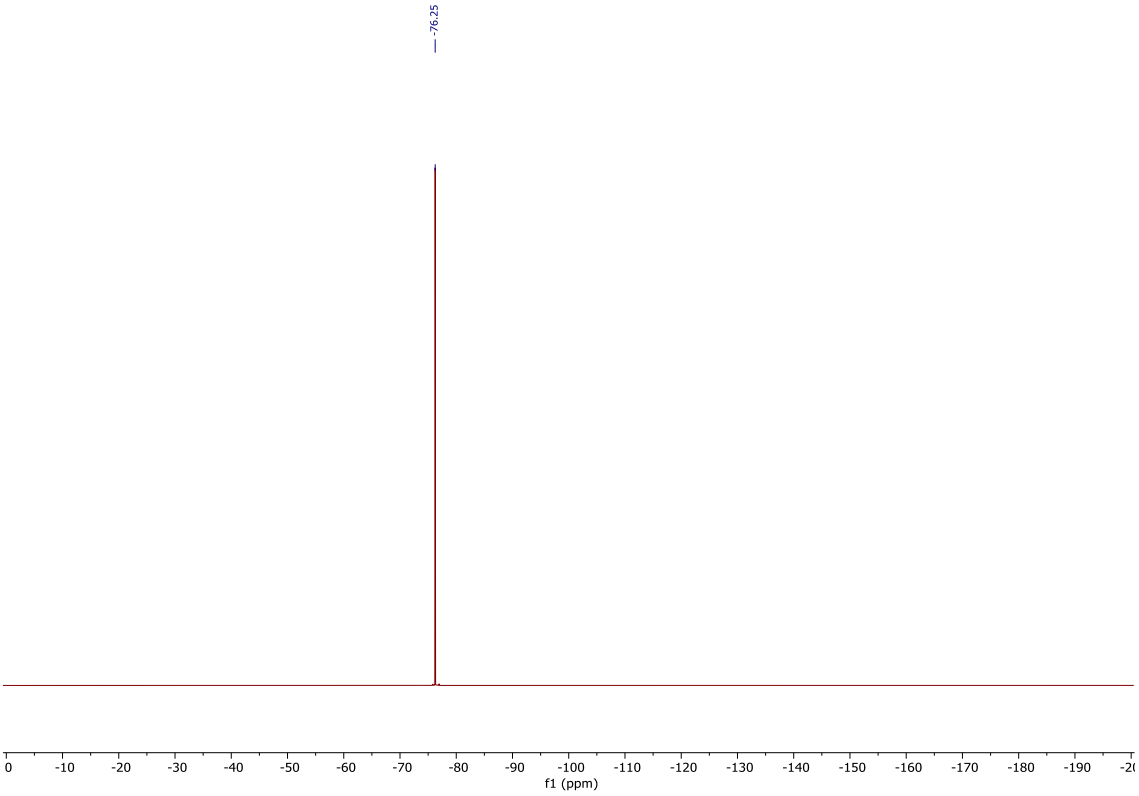

*Figure S17. ^{19}F NMR spectrum of **4** in C_6D_6.*

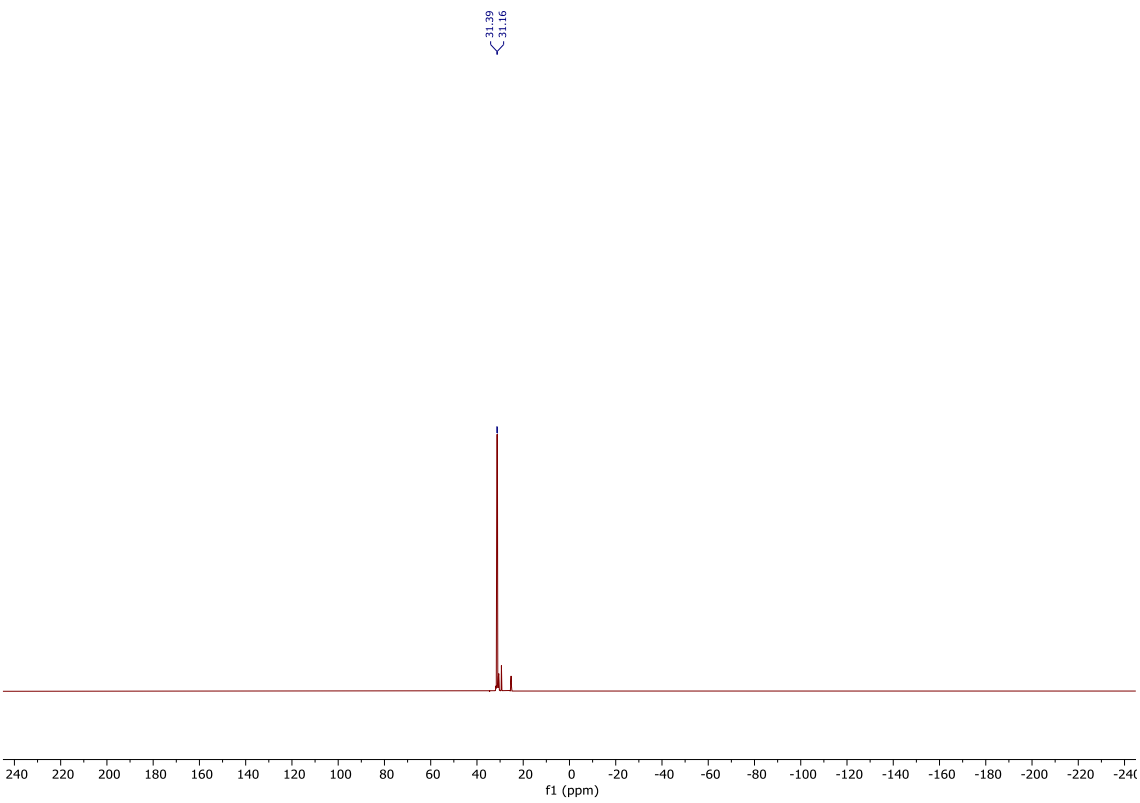

*Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum of **4** in C_6D_6. The signal at 25.5 ppm belongs to $Ph_3PC(Me)BEt_2$.*

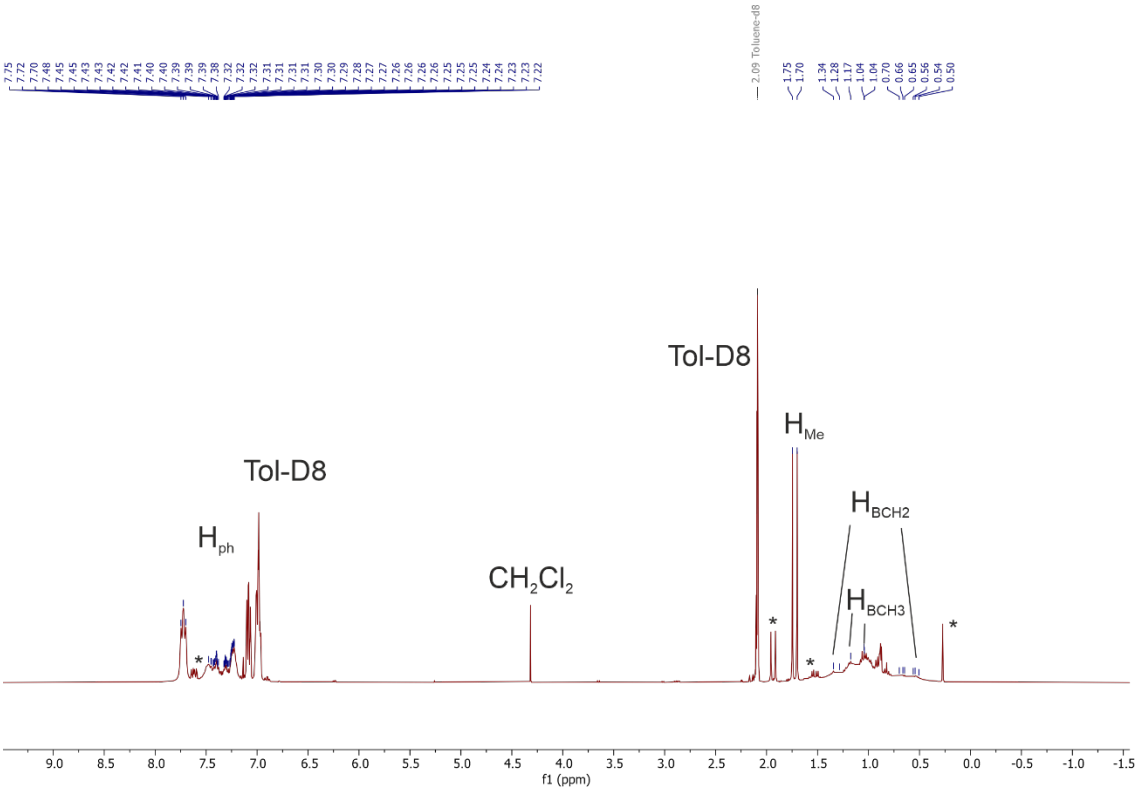

*Figure S19. ^{1}H NMR spectrum of **5** in toluene-d8. Impurities, decomposition products and silicon grease are marked by an asterisk.*

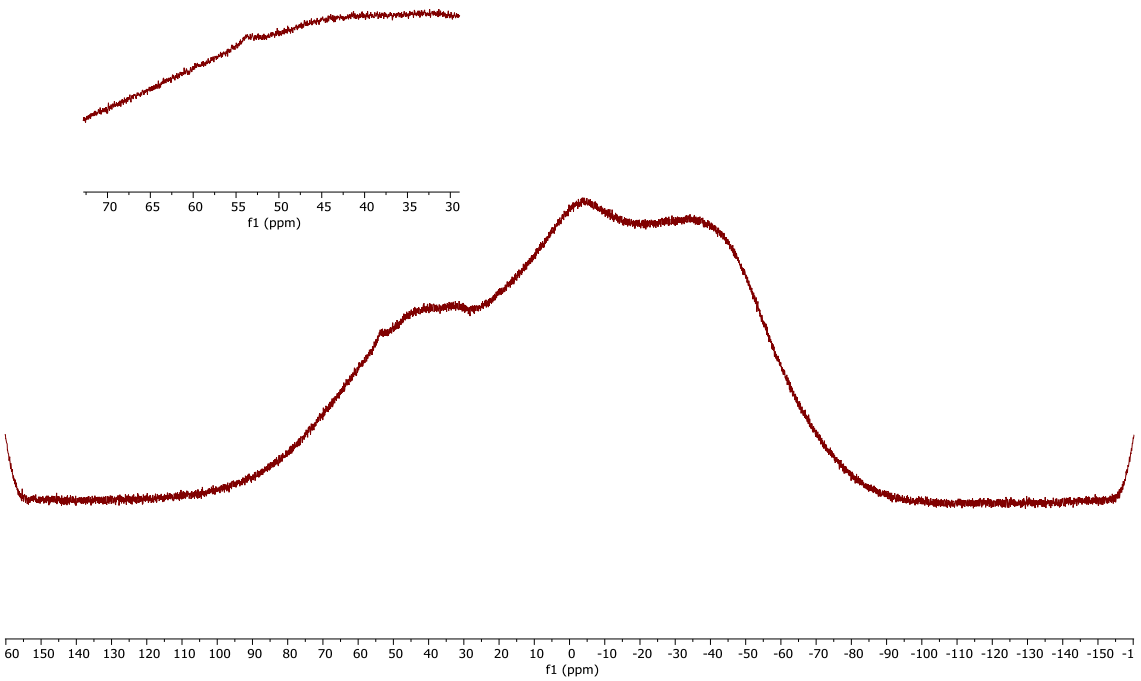

*Figure S20. ^{11}B NMR spectrum of **5** in d8-thf.*

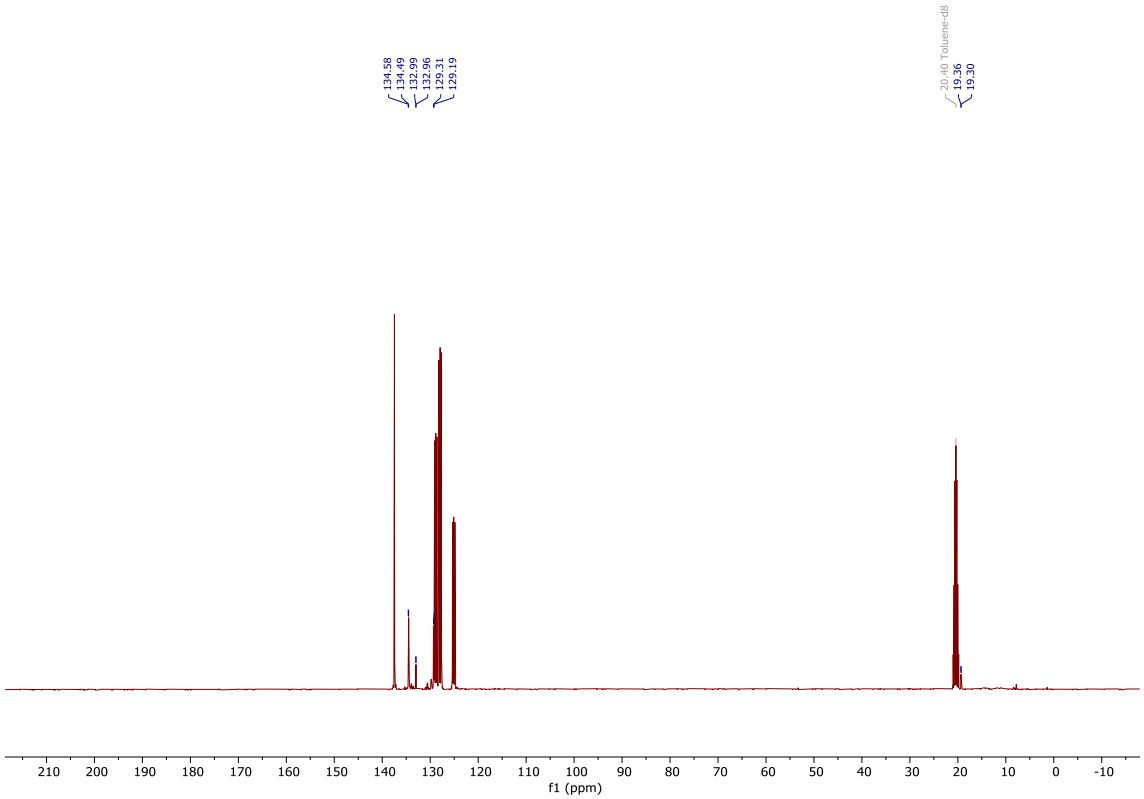

*Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in toluene-d8.*

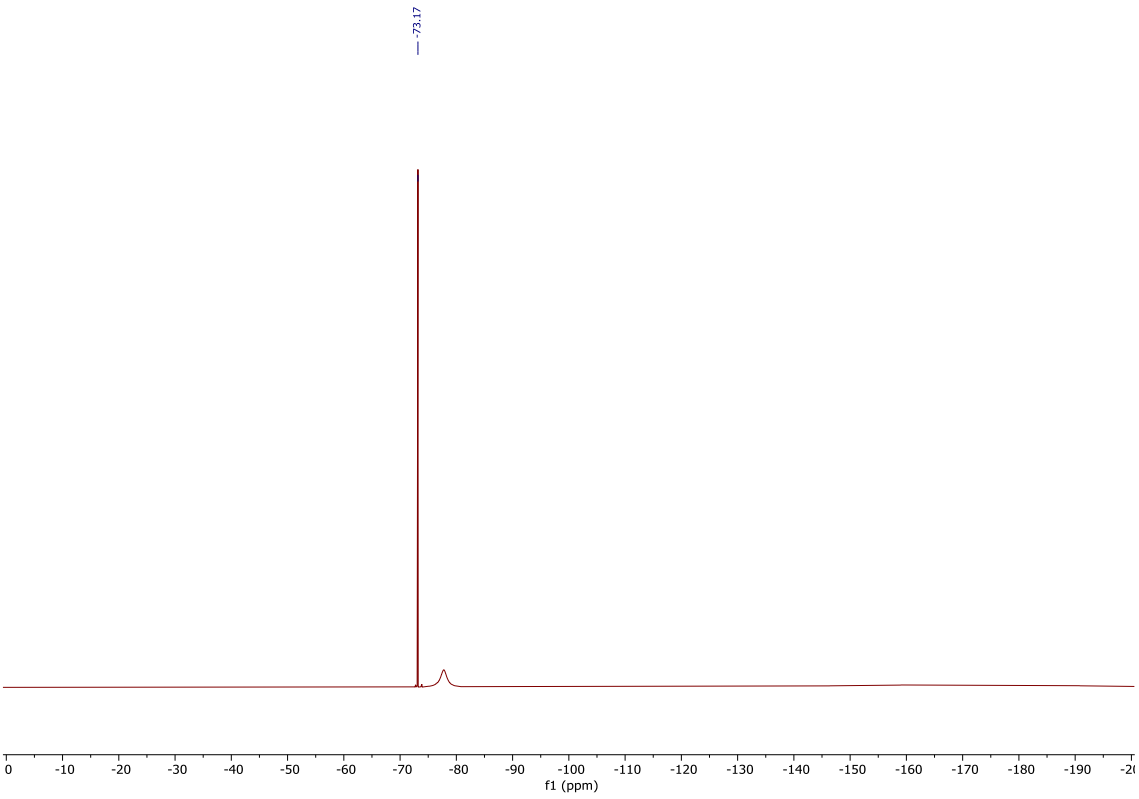

*Figure S22 . ^{19}FNMR spectrum of **5** in d8-thf.*

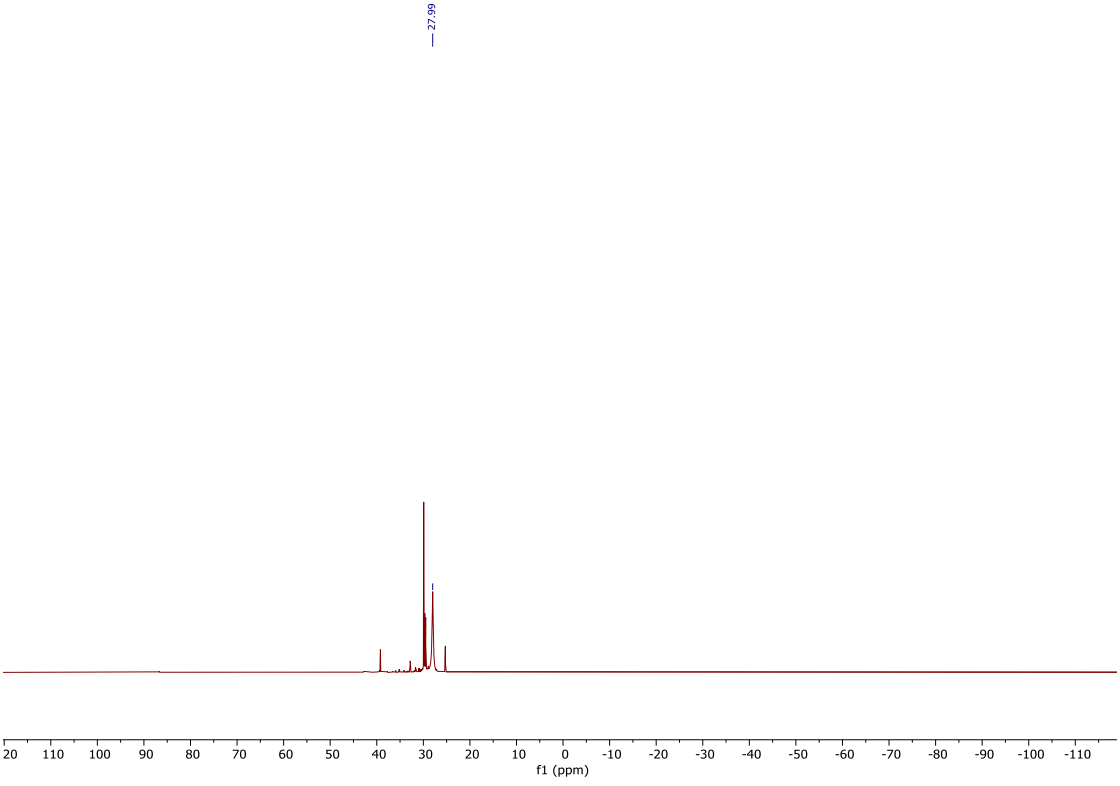

*Figure S23. Figure 24. $^{31}P\{^{1}H\}$ NMR spectrum of **5** in toluene-d8. The signal at 25.5 ppm belongs to $Ph_3PC(Me)BEt_2$. The signals at δ > 29 ppm belong to decomposition products.*

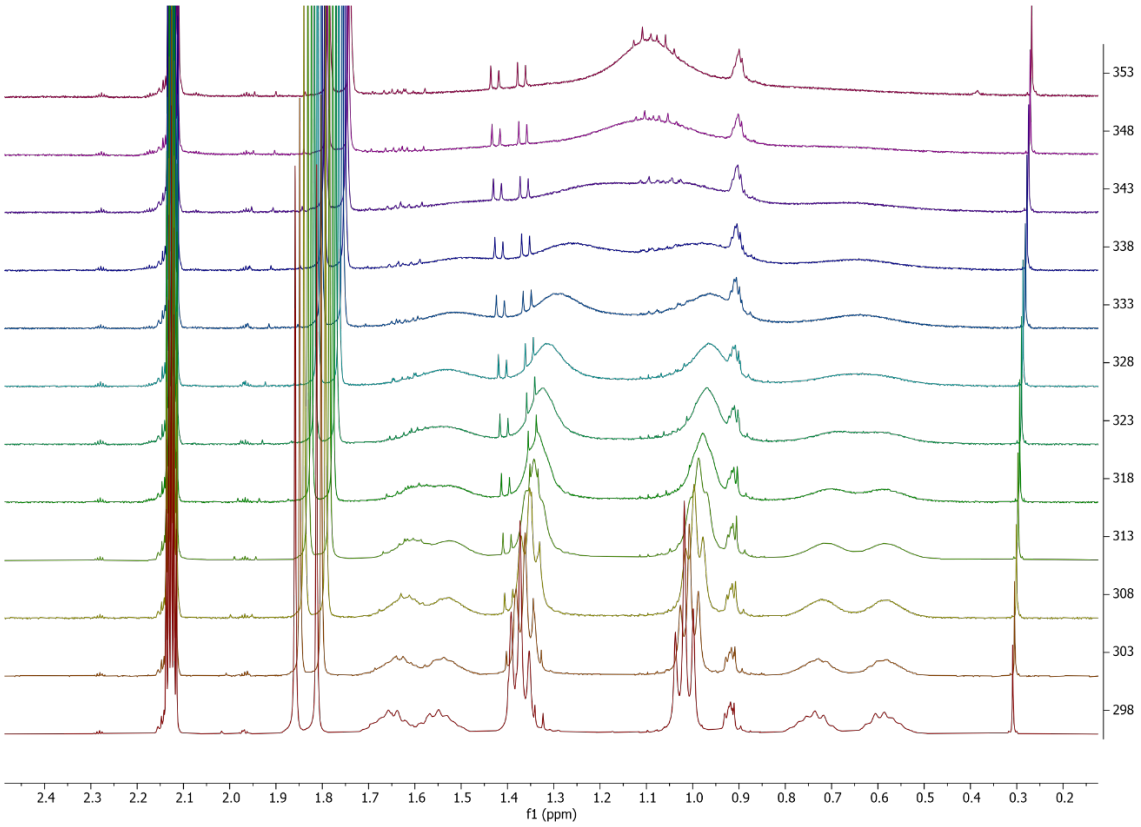

*Figure S25. VT NMR spectra of **1** in toluene-d_8 from 298 – 353 K.*

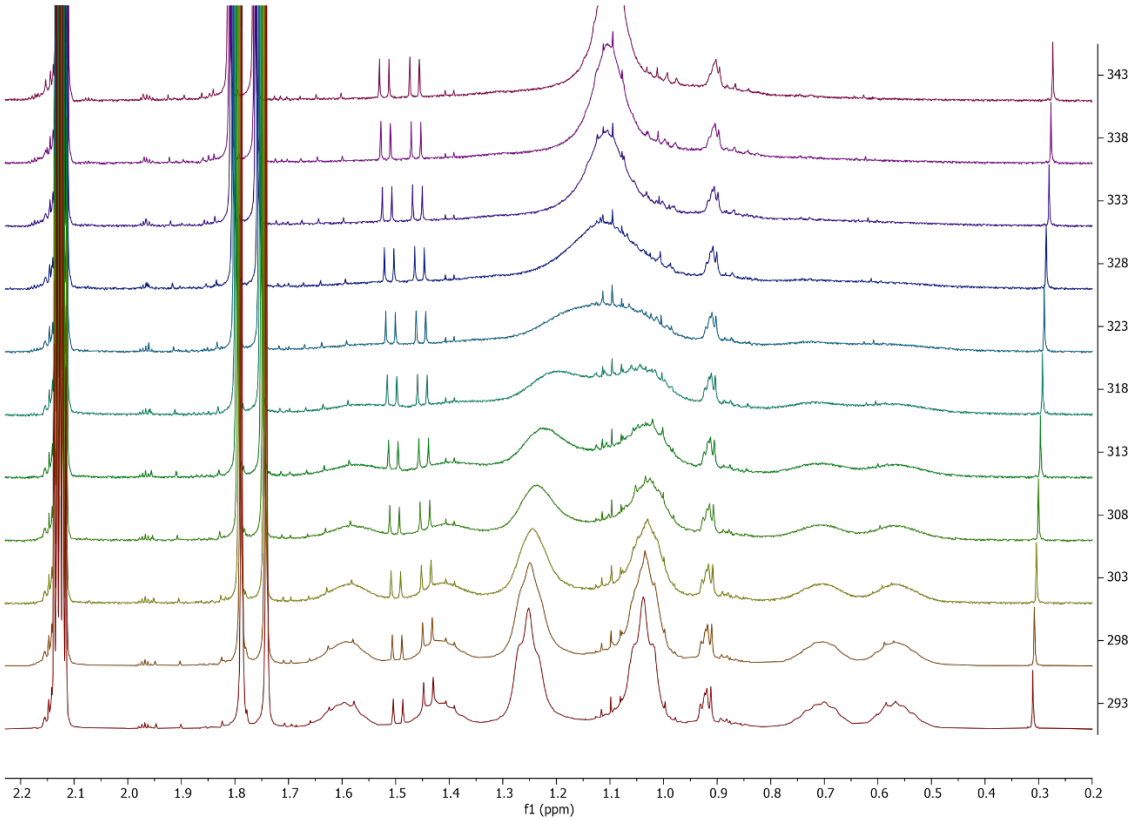

*Figure S26. VT NMR spectra of **2** in toluene-d_8 from 293 – 343 K.*

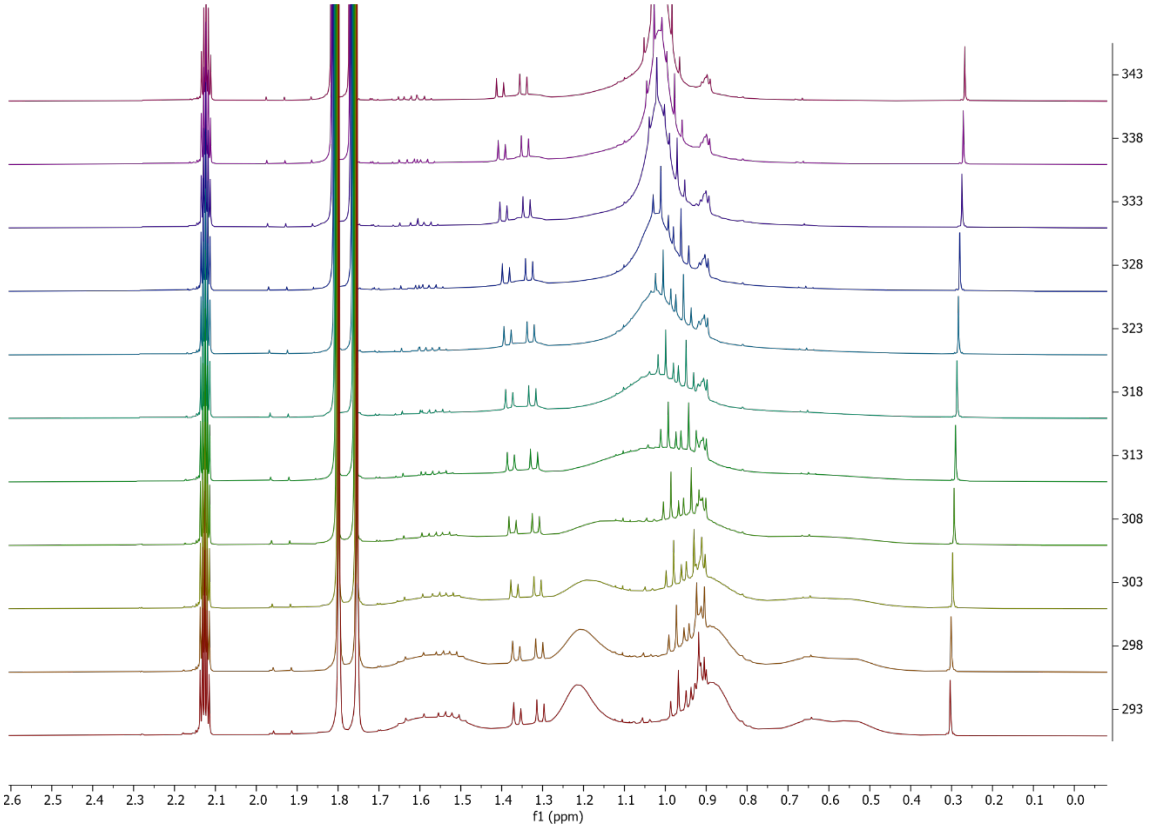

*Figure S27. VT NMR spectra of **3** in toluene-d_8 from 293 – 343 K.*

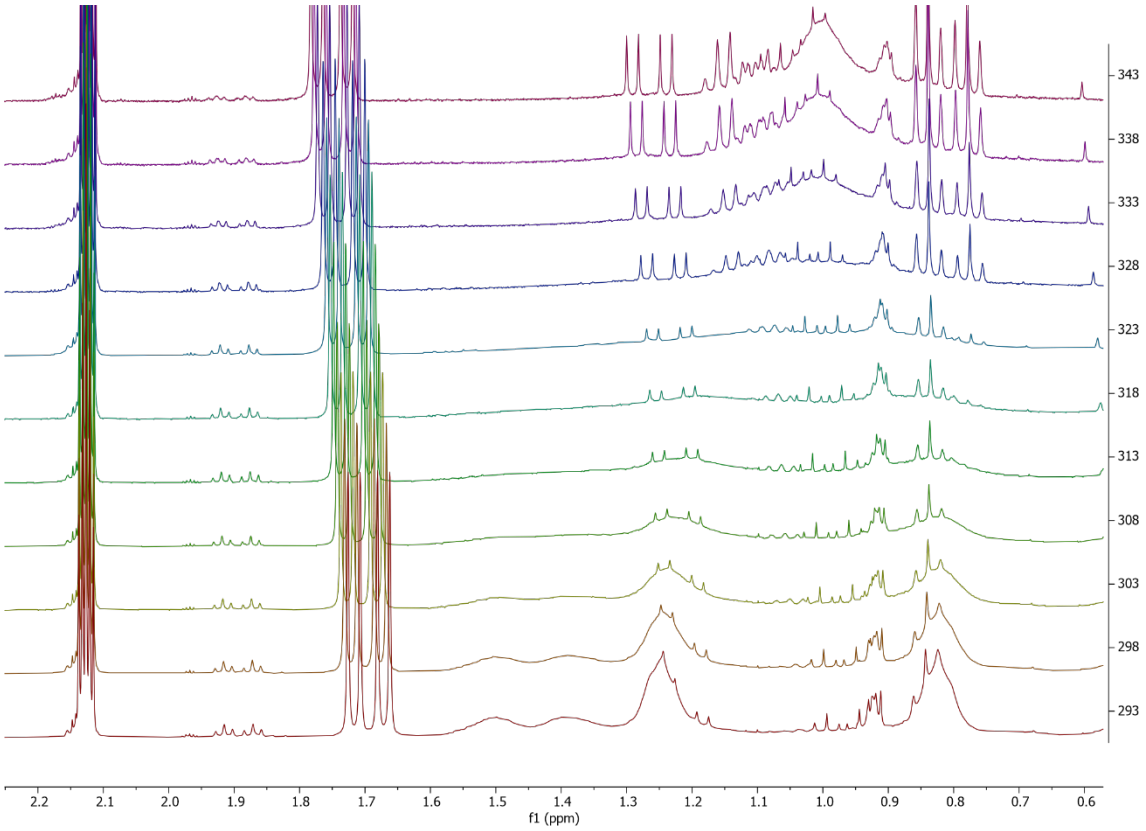

*Figure S28. VT NMR spectra of **4** in toluene-d_8 from 293 – 343 K.*

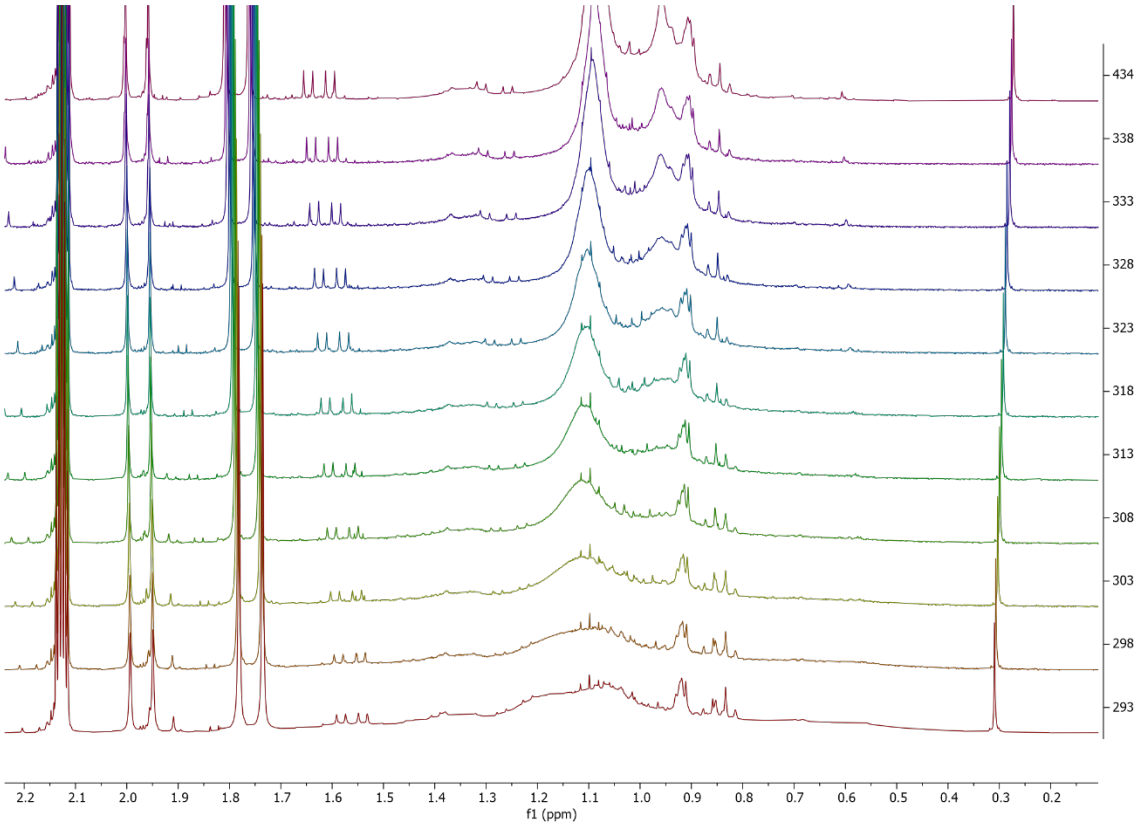

*Figure S29. VT NMR spectra of **5** in toluene-d_8 from 293 – 343 K.*

Section S5: IR spectra of **3**-**5**

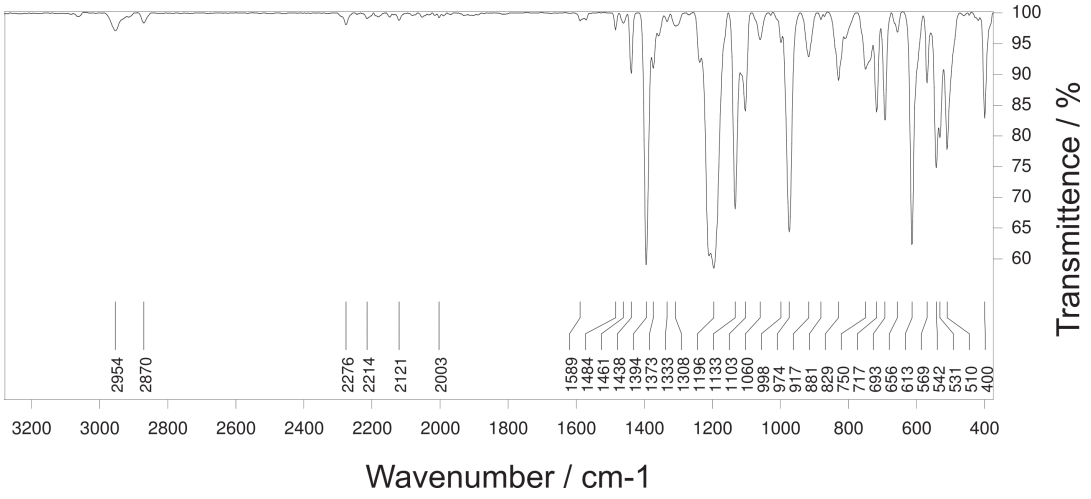

*Figure S32. IR spectrum of **3**.*

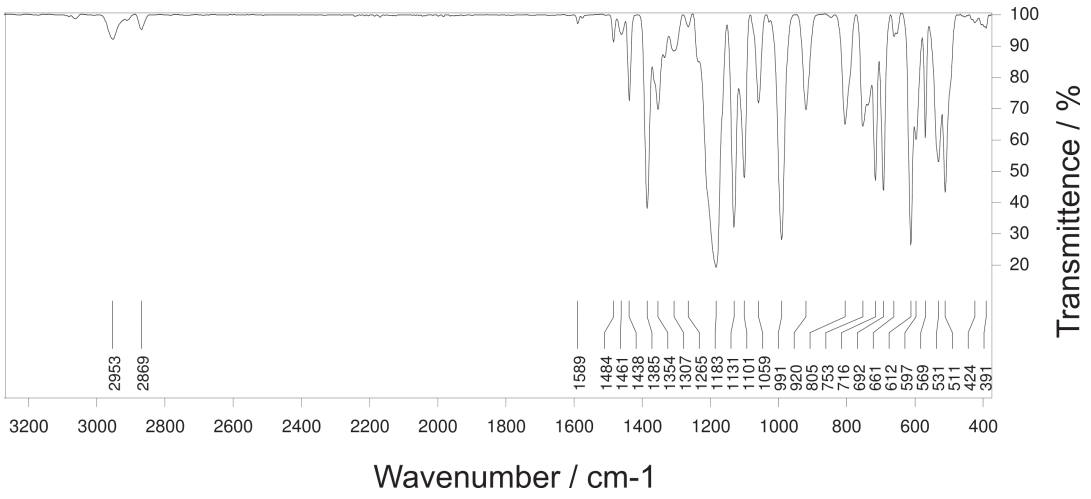

*Figure S33. IR spectrum of **4**.*

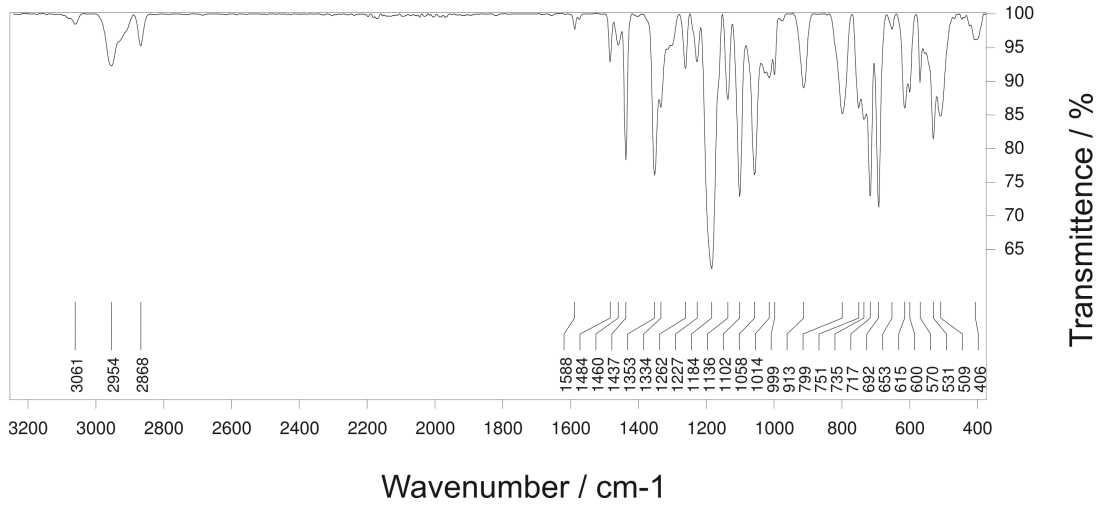

*Figure S34. IR spectrum of **5**.*

Section S6: Estimation of the rotational barriers

With the approximation equation (1) and known coalescence temperature T_c and signal distance δ_V the rotational barriers $\Delta G^{\neq}$ [J mol^{-1}] can be estimated.[16]

$$\Delta G^{\neq} = 19.13\ T_c\ (9.97 + \log \frac{T_c}{\delta_v}) \qquad (1)$$

For the determination of the coalelecence Temperatures with variable temperature NMR (VT NMR) spectroscopy a temperature test for the sample head was performed with glycol in DMSO-d_6. The differences between targeted and actual temperatures are given in Table S2.

Table S1. Targeted temperature T_t and actual temperature T_a in K of the probehead.

T_t / K	T_a / K
298	298.38
303	303.23
313	313.09
323	323.07
333	335.11
343	345.78
353	356.47
363	376.23

The coalescence temperatures, signal distances and the estimated rotational barriers of **1**-**5** are listed in Table S3.

*Table S2. Coalescence temperatures in K, signal distances in Hz and the estimated rotational barriers in kcal mol^{-1} of **1**-**5**.*

Comp.	T_c / K	δ_v / Hz	$\Delta G^{\neq}$ / kcal mol^{-1}
1 (CuCl)	345.78	142	16.37
2 (AuCl)	323.07	142	15.25
3 ($CuNTf_2$)	313.09	168	14.66
4 ($AgNTf_2$)	323.07	168	15.15
5 ($AuNTf_2$)	298.38	168	13.94

[16] H. Günther, *NMR spectroscopy: basic principles, concepts and applications in chemistry, Vol. 3*, Wiley-VCH, Weinheim, **2013**.

Section S7: Crystal structure information

Table S4: XRD details for **2**.

Compound	**2**
CCDC #	2131093
Formula	$C_{24}H_{28}AuBClP$
$D_{calc.}$/ g cm^{-3}	1.698
μ/mm^{-1}	6.58
Formula Weight	590.66
Colour	colourless
Shape	fragment
Size/mm^3	0.60×0.38×0.25
T/K	200
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	17.1732(10)
b/Å	13.6458(6)
c/Å	19.7945(11)
α/°	90
β/°	95.133(5)
γ/°	90
V/Å^3	4620.1(4)
Z	8
Z'	2
Wavelength/Å	0.71073
Radiation type	MoK_α
Θ_{min}/°	1.815
Θ_{max}/°	27.000
Measured Refl.	41914
Independent Refl.	10070
Reflections with I > 2(I)	7634
R_{int}	0.0718
Parameters	512
Restraints	0
Largest Peak	1.470
Deepest Hole	-1.793
R_1	0.0529
GooF	1.028
wR_2 (all data)	0.1548
wR_2	0.1448

Crystal data collection and processing parameters are given below. In order to avoid quality degradation, the single crystals were mounted in perfluoropolyalkylether oil on top of an open Mark tube and then brought into the cold nitrogen stream of a low-temperature device (Oxford Cryosystems Cryostream unit) so that the oil solidified. Diffraction data were measured using a Stoe IPDS II diffractometer and graphite-monochromated MoKα (0.71073 Å). Absorption corrections were carried out using the STOE LANA[17] software package by scaling of diffraction intensities. The structures were solved in OLEX2 1.3[18] by dual-space direct methods with SHELXT,[19] followed by full-matrix least-squares refinement using SHELXL-2014/7.[20] All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. A full listing of atomic coordinates, bond lengths, angles and displacement parameters for **2** have been deposited at the Cambridge Crystallographic Data Centre (CCDC 2131093).

[17] J. Koziskova, F. Hahn, J. Richter, J. Kožíšek, *Acta Chimi. Slov.*, 2016, **9**, 136-140

[18] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341

[19] G. Sheldrick, *Acta Crystallogr. Section A,* 2015, **71**, 3-8.

[20] G. Sheldrick, *Acta Crystallographica Section C,* 2015, **71**, 3-8

Section S8: Coordinates of the calculated structures

Cartesian coordinates (in Å) and total energies (in a. u., non corrected zero-point vibrational energies included) of all species discussed in the text (BP86-D3/def2-TZVPP level).

L1: E= –1297.602303

P	–0.199457000	–0.046998000	–0.217456000
C	–1.924618000	0.091162000	–0.813095000
C	0.198143000	1.588913000	0.502258000
C	–0.367101000	–1.208611000	1.200872000
C	0.580303000	–2.229348000	1.347741000
H	1.388574000	–2.306155000	0.617129000
C	0.881144000	–0.522167000	–1.473626000
C	–1.438425000	–1.118708000	2.106697000
H	–2.198290000	–0.345354000	1.977120000
C	0.079814000	1.891381000	1.866584000
H	–0.213642000	1.118614000	2.577362000
C	–2.533280000	1.328067000	–1.068837000
H	–1.998459000	2.254648000	–0.857546000
C	–1.544894000	–2.030274000	3.158982000
H	–2.380457000	–1.958926000	3.857234000
C	0.610902000	2.588268000	–0.394353000
H	0.743998000	2.329935000	–1.446379000
C	0.472674000	–3.139626000	2.403070000
H	1.214760000	–3.931962000	2.512401000
C	0.367271000	3.179672000	2.325003000
H	0.289574000	3.403340000	3.390118000
C	–0.586508000	–3.039520000	3.310210000
H	–0.672766000	–3.753700000	4.130762000
C	0.262196000	–1.085312000	–2.751482000
H	–0.098533000	–2.123673000	–2.643799000
H	1.019099000	–1.098885000	–3.548092000
H	–0.587549000	–0.493553000	–3.127234000

C	-3.830875000	1.378856000	-1.588389000
H	-4.297838000	2.346218000	-1.779670000
C	3.018467000	-0.035254000	0.208413000
H	2.305455000	0.088173000	1.040981000
H	3.683967000	-0.861265000	0.528216000
C	0.759662000	4.176749000	1.426147000
H	0.983406000	5.181280000	1.788593000
C	-2.631706000	-1.093891000	-1.082802000
H	-2.167129000	-2.060904000	-0.882919000
C	3.384086000	-1.055884000	-2.274521000
H	3.113203000	-0.759086000	-3.302355000
H	4.401055000	-0.661947000	-2.104291000
C	0.879683000	3.879319000	0.065330000
H	1.201242000	4.648182000	-0.638728000
C	-4.527334000	0.197807000	-1.857294000
H	-5.539774000	0.239621000	-2.261837000
C	-3.924618000	-1.039602000	-1.603947000
H	-4.463539000	-1.965002000	-1.812590000
C	3.866842000	1.248547000	0.100217000
H	3.233197000	2.119694000	-0.121366000
H	4.610171000	1.171579000	-0.707553000
H	4.411304000	1.466144000	1.032411000
B	2.353399000	-0.488896000	-1.182939000
C	3.434176000	-2.599018000	-2.200200000
H	2.449718000	-3.037097000	-2.425202000
H	3.715527000	-2.937398000	-1.189602000
H	4.162580000	-3.032224000	-2.904501000

1: E= -3398.774304

Cu	-2.252179000	0.144528000	-0.718540000
Cl	-3.940871000	1.271983000	-0.136161000
P	0.647691000	0.269989000	0.015571000
C	2.301518000	-0.503937000	-0.043585000
C	-0.430004000	-0.465471000	-1.190288000

C	2.479165000	-1.648344000	-0.832891000
H	1.637061000	-2.043209000	-1.403221000
C	-1.628684000	-2.639605000	-2.237219000
H	-2.478900000	-3.282543000	-1.962282000
H	-2.006675000	-1.970875000	-3.026741000
C	0.123477000	0.124083000	1.760199000
C	0.884378000	2.042671000	-0.382921000
C	-1.025999000	0.792470000	2.218838000
H	-1.622443000	1.419502000	1.556819000
C	-0.235826000	2.895047000	-0.369081000
H	-1.227948000	2.512696000	-0.120103000
C	3.376098000	-0.014903000	0.722337000
H	3.237575000	0.859779000	1.359924000
C	0.385060000	-0.885218000	3.955096000
H	0.933696000	-1.549682000	4.623936000
C	0.825788000	-0.716376000	2.641301000
H	1.702726000	-1.264640000	2.301084000
C	-0.760490000	-0.222511000	4.403379000
H	-1.109742000	-0.364375000	5.427179000
C	2.123829000	2.551666000	-0.803554000
H	2.994106000	1.900451000	-0.869867000
C	-1.463394000	0.614047000	3.531887000
H	-2.367800000	1.124973000	3.863237000
C	4.614063000	-0.657335000	0.681589000
H	5.442668000	-0.274832000	1.279121000
C	4.788931000	-1.792758000	-0.118945000
H	5.757647000	-2.293704000	-0.148808000
C	3.721371000	-2.288395000	-0.871846000
H	3.850159000	-3.178500000	-1.488874000
C	-0.104210000	4.235814000	-0.731661000
H	-0.984197000	4.879908000	-0.718547000
C	-0.068459000	0.048823000	-2.599446000
H	-0.736520000	-0.412430000	-3.336119000
H	0.965621000	-0.207964000	-2.889524000
H	-0.174151000	1.138607000	-2.697796000

C	-1.082951000	-2.601674000	0.461677000
H	-0.035797000	-2.886573000	0.687647000
H	-1.347606000	-1.904575000	1.271609000
C	-0.501161000	-3.520100000	-2.825127000
H	0.325015000	-2.900770000	-3.209716000
H	-0.854537000	-4.146807000	-3.658344000
H	-0.079452000	-4.193255000	-2.061925000
B	-1.087962000	-1.845160000	-0.956899000
C	1.139240000	4.742731000	-1.122259000
H	1.238503000	5.791148000	-1.407176000
C	2.249150000	3.895728000	-1.165799000
H	3.218375000	4.275805000	-1.491864000
C	-1.977048000	-3.845802000	0.582226000
H	-1.701373000	-4.624051000	-0.145282000
H	-3.031986000	-3.591036000	0.400838000
H	-1.914647000	-4.296026000	1.584649000

1-Ag: E= -1905.067463

Ag	-2.224383000	-0.050058000	-0.657640000
Cl	-4.153613000	0.950601000	0.134030000
P	0.782569000	0.321287000	0.053750000
C	2.545934000	-0.144076000	-0.087260000
C	-0.169119000	-0.570462000	-1.157827000
C	2.873482000	-1.356500000	-0.709868000
H	2.080465000	-1.976940000	-1.130566000
C	-1.033064000	-2.890360000	-2.212978000
H	-1.804005000	-3.632427000	-1.954073000
H	-1.464756000	-2.283359000	-3.024291000
C	0.357705000	0.043850000	1.810898000
C	0.731119000	2.115833000	-0.297365000
C	-0.919673000	0.348386000	2.318390000
H	-1.708972000	0.740956000	1.673333000
C	-0.316473000	2.914641000	0.191953000
H	-1.077053000	2.502464000	0.852479000
C	3.564726000	0.652586000	0.464800000

H	3.313851000	1.594288000	0.955462000
C	0.995976000	-0.793195000	4.002466000
H	1.744740000	-1.250046000	4.650935000
C	1.313134000	-0.529924000	2.668146000
H	2.300455000	-0.796213000	2.294486000
C	-0.273414000	-0.487349000	4.498775000
H	-0.521479000	-0.702114000	5.539264000
C	1.666728000	2.680193000	-1.182859000
H	2.471653000	2.070279000	-1.592839000
C	-1.228455000	0.083240000	3.652489000
H	-2.229621000	0.312564000	4.018655000
C	4.894984000	0.237903000	0.388567000
H	5.681594000	0.859153000	0.818952000
C	5.217430000	-0.972211000	-0.237654000
H	6.258324000	-1.293407000	-0.297926000
C	4.207220000	-1.767572000	-0.785330000
H	4.454634000	-2.710815000	-1.273905000
C	-0.411506000	4.256063000	-0.183571000
H	-1.234104000	4.860121000	0.200279000
C	0.177822000	-0.043003000	-2.565292000
H	-0.404793000	-0.588607000	-3.316955000
H	1.243793000	-0.195669000	-2.811049000
H	-0.036195000	1.027350000	-2.695516000
C	-0.511816000	-2.799160000	0.475409000
H	0.560632000	-3.042753000	0.620571000
H	-0.746203000	-2.139841000	1.322437000
C	0.214587000	-3.629816000	-2.751879000
H	0.981017000	-2.916103000	-3.094137000
H	-0.026194000	-4.284289000	-3.603416000
H	0.675058000	-4.258643000	-1.973364000
B	-0.627325000	-2.027640000	-0.927958000
C	0.530675000	4.814536000	-1.051903000
H	0.451787000	5.862598000	-1.344117000
C	1.567830000	4.022989000	-1.552940000
H	2.300449000	4.446951000	-2.241081000

C	-1.336050000	-4.089288000	0.620622000
H	-1.050099000	-4.847236000	-0.123680000
H	-2.409183000	-3.888056000	0.484086000
H	-1.208947000	-4.542612000	1.615358000

2: E= -1893.858684

Au	-2.019305000	0.075543000	-0.382440000
Cl	-4.015975000	0.957944000	0.312235000
P	1.118978000	0.281656000	0.008140000
C	2.744397000	-0.528221000	-0.169118000
C	-0.083589000	-0.506759000	-1.058729000
C	2.845961000	-1.688418000	-0.949158000
H	1.959372000	-2.084006000	-1.445233000
C	-1.280284000	-2.784948000	-1.913842000
H	-2.147924000	-3.360355000	-1.554354000
H	-1.657714000	-2.180428000	-2.752693000
C	0.786588000	0.268196000	1.804525000
C	1.320819000	2.025826000	-0.514478000
C	-0.204890000	1.099177000	2.353578000
H	-0.774318000	1.781034000	1.725801000
C	0.184007000	2.855799000	-0.543933000
H	-0.795913000	2.453717000	-0.275639000
C	3.879907000	-0.046567000	0.509234000
H	3.801570000	0.834213000	1.148537000
C	1.199780000	-0.665255000	4.008035000
H	1.743583000	-1.362249000	4.646812000
C	1.488063000	-0.615289000	2.643413000
H	2.238117000	-1.287703000	2.229905000
C	0.207431000	0.158232000	4.546967000
H	-0.024400000	0.109906000	5.611895000
C	2.549701000	2.537345000	-0.961040000
H	3.433410000	1.902009000	-0.995852000
C	-0.493284000	1.038285000	3.717410000
H	-1.277929000	1.675550000	4.125804000
C	5.102413000	-0.707320000	0.385002000

H	5.978051000	-0.329493000	0.914470000
C	5.201046000	-1.855906000	-0.409308000
H	6.157615000	-2.371832000	-0.504008000
C	4.072470000	-2.347599000	-1.070183000
H	4.140756000	-3.250359000	-1.678304000
C	0.287292000	4.178855000	-0.972664000
H	-0.605149000	4.805455000	-0.991981000
C	0.181420000	-0.071879000	-2.515231000
H	-0.523272000	-0.584267000	-3.180041000
H	1.199735000	-0.336569000	-2.848818000
H	0.057296000	1.008627000	-2.670469000
C	-0.491869000	-2.635412000	0.699627000
H	0.517340000	-3.096748000	0.697333000
H	-0.462521000	-1.911199000	1.524374000
C	-0.212184000	-3.769009000	-2.444594000
H	0.634065000	-3.229772000	-2.900829000
H	-0.616246000	-4.444513000	-3.213992000
H	0.195211000	-4.395450000	-1.635534000
B	-0.682355000	-1.905861000	-0.716571000
C	1.520523000	4.689548000	-1.389978000
H	1.598793000	5.723811000	-1.728043000
C	2.646890000	3.863476000	-1.391828000
H	3.607918000	4.246009000	-1.738440000
C	-1.537290000	-3.709644000	1.044651000
H	-1.527919000	-4.541802000	0.325480000
H	-2.549970000	-3.279161000	1.034876000
H	-1.367706000	-4.137933000	2.044308000

TS-Cl: E= -3398.745919

Cu	-2.121545000	0.463911000	-0.627599000
Cl	-3.863682000	1.387589000	0.141652000
P	0.567465000	0.174577000	-0.079981000
C	2.388598000	0.101188000	-0.363513000
C	-0.520656000	-0.530930000	-1.273216000

C	2.930475000	-0.847888000	-1.240368000
H	2.272136000	-1.543331000	-1.756935000
C	0.288493000	-3.230894000	-1.463453000
H	-0.142060000	-4.134483000	-1.923111000
H	1.097461000	-2.910344000	-2.142114000
C	0.313057000	-0.608459000	1.553921000
C	0.293964000	1.975249000	0.045816000
C	-0.984668000	-0.889754000	2.019396000
H	-1.856196000	-0.593046000	1.426418000
C	-0.534162000	2.514022000	1.045288000
H	-0.987513000	1.863119000	1.792254000
C	3.252769000	1.004011000	0.285143000
H	2.843629000	1.757859000	0.959221000
C	1.220761000	-1.603605000	3.578606000
H	2.086389000	-1.881719000	4.181437000
C	1.414605000	-0.966637000	2.351445000
H	2.429783000	-0.768972000	2.009094000
C	-0.071364000	-1.889652000	4.028683000
H	-0.219786000	-2.389720000	4.987012000
C	0.843453000	2.822264000	-0.933633000
H	1.511354000	2.418599000	-1.695721000
C	-1.171768000	-1.527798000	3.246758000
H	-2.186074000	-1.734821000	3.590269000
C	4.630269000	0.940814000	0.070403000
H	5.290422000	1.642368000	0.582649000
C	5.161881000	-0.016017000	-0.802352000
H	6.238457000	-0.060651000	-0.973454000
C	4.310140000	-0.907740000	-1.458753000
H	4.717154000	-1.650789000	-2.146035000
C	-0.817974000	3.879161000	1.055120000
H	-1.476581000	4.283507000	1.823761000
C	-0.266902000	-0.031785000	-2.725338000
H	-1.093139000	-0.357773000	-3.373942000
H	0.671795000	-0.412408000	-3.165992000
H	-0.243790000	1.067013000	-2.779467000

C	-2.344716000	-2.515556000	-1.325722000
H	-2.701090000	-2.233951000	-0.312342000
H	-2.899495000	-1.797627000	-1.961115000
C	0.904454000	-3.626593000	-0.098938000
H	1.505046000	-2.813365000	0.327648000
H	1.559158000	-4.504385000	-0.199014000
H	0.126786000	-3.871339000	0.639871000
B	-0.820044000	-2.105657000	-1.325420000
C	-0.290600000	4.714566000	0.064952000
H	-0.529757000	5.778929000	0.065558000
C	0.539137000	4.185846000	-0.927976000
H	0.953754000	4.834725000	-1.700758000
C	-2.754391000	-3.960006000	-1.641998000
H	-2.278830000	-4.674202000	-0.952934000
H	-2.460298000	-4.248365000	-2.662700000
H	-3.842190000	-4.100505000	-1.562070000

TS-Au: E= -1893.830355

Au	-1.975207000	0.007118000	-0.353551000
Cl	-3.999547000	0.801260000	0.399625000
P	0.935436000	0.266780000	-0.063360000
C	2.671539000	0.573696000	-0.602589000
C	-0.119219000	-0.738635000	-1.106280000
C	3.357978000	-0.342676000	-1.411874000
H	2.860836000	-1.248750000	-1.748420000
C	1.323090000	-3.183156000	-1.214980000
H	1.087208000	-4.191166000	-1.589022000
H	1.968928000	-2.737160000	-1.991261000
C	1.074333000	-0.477307000	1.598340000
C	0.301832000	1.967483000	0.113876000
C	0.011191000	-1.214224000	2.149043000
H	-0.930040000	-1.295799000	1.599532000
C	-0.309199000	2.385072000	1.307449000
H	-0.384544000	1.698117000	2.150333000

C	3.339990000	1.741897000	-0.184930000
H	2.821661000	2.473805000	0.434936000
C	2.391433000	-0.930049000	3.588910000
H	3.322402000	-0.816474000	4.145943000
C	2.264730000	-0.335452000	2.332062000
H	3.104948000	0.221373000	1.917861000
C	1.335999000	-1.673036000	4.125863000
H	1.439030000	-2.140527000	5.106256000
C	0.381067000	2.849693000	-0.977488000
H	0.889818000	2.546764000	-1.893203000
C	0.147229000	-1.810745000	3.403822000
H	-0.686189000	-2.379708000	3.817701000
C	4.664695000	1.973005000	-0.559950000
H	5.169281000	2.880050000	-0.224042000
C	5.338777000	1.050012000	-1.366222000
H	6.371814000	1.234997000	-1.664180000
C	4.681339000	-0.106472000	-1.792832000
H	5.196844000	-0.829605000	-2.426360000
C	-0.866394000	3.660048000	1.393673000
H	-1.358630000	3.970726000	2.315439000
C	-0.000987000	-0.355299000	-2.614692000
H	-0.742996000	-0.925141000	-3.192380000
H	0.994791000	-0.572501000	-3.037263000
H	-0.223685000	0.706813000	-2.788085000
C	-1.391006000	-3.129867000	-1.011108000
H	-1.781071000	-2.929446000	0.008131000
H	-2.129168000	-2.594531000	-1.637311000
C	2.133422000	-3.337184000	0.094402000
H	2.557422000	-2.383731000	0.434508000
H	2.966900000	-4.041839000	-0.039181000
H	1.502717000	-3.714299000	0.912612000
B	-0.019996000	-2.348587000	-1.065887000
C	-0.819271000	4.523682000	0.294790000
H	-1.272930000	5.513457000	0.359554000
C	-0.191844000	4.119249000	-0.887365000

H	-0.147299000	4.793709000	-1.743500000
C	-1.421762000	-4.638586000	-1.291042000
H	-0.771255000	-5.194112000	-0.598566000
H	-1.081026000	-4.867421000	-2.312411000
H	-2.437459000	-5.046965000	-1.186129000

2 (R = CF_3): E= -2411.034373

Au	-1.821617000	0.708565000	-0.174721000
Cl	-3.299946000	2.286069000	0.547740000
P	1.337458000	0.208231000	-0.073480000
C	2.696472000	-0.961863000	-0.368306000
C	-0.136016000	-0.346324000	-0.977131000
C	2.464133000	-2.134686000	-1.100670000
H	1.465151000	-2.357277000	-1.474725000
C	-2.097303000	-2.211504000	-1.450757000
C	1.196041000	0.414912000	1.728363000
C	1.832872000	1.818478000	-0.788869000
C	0.460356000	1.484397000	2.270767000
H	-0.034566000	2.214041000	1.633425000
C	0.918821000	2.889497000	-0.781513000
H	-0.087212000	2.759780000	-0.377984000
C	3.975167000	-0.711902000	0.164505000
H	4.154263000	0.183296000	0.762052000
C	1.678722000	-0.367202000	3.974288000
H	2.147870000	-1.098540000	4.633207000
C	1.806941000	-0.509573000	2.592292000
H	2.356063000	-1.358563000	2.192223000
C	0.938012000	0.689887000	4.507360000
H	0.828458000	0.791333000	5.587922000
C	3.086519000	1.996495000	-1.395913000
H	3.794796000	1.171707000	-1.455578000
C	0.329593000	1.613392000	3.652431000
H	-0.259397000	2.436692000	4.056961000
C	5.011590000	-1.620028000	-0.054039000

H	5.999275000	-1.423927000	0.364867000
C	4.779385000	-2.780930000	-0.800264000
H	5.590344000	-3.490896000	-0.968359000
C	3.507156000	-3.037935000	-1.318008000
H	3.317925000	-3.950115000	-1.884555000
C	1.269141000	4.119033000	-1.338421000
H	0.545807000	4.934976000	-1.327621000
C	0.079996000	-0.038135000	-2.472084000
H	-0.702843000	-0.501498000	-3.075799000
H	1.049423000	-0.433113000	-2.817651000
H	0.080033000	1.040255000	-2.679402000
C	-0.870603000	-2.205878000	0.976490000
B	-1.096536000	-1.413019000	-0.441522000
C	2.530001000	4.297048000	-1.916718000
H	2.801583000	5.259676000	-2.351925000
C	3.432229000	3.231838000	-1.950677000
H	4.410001000	3.354333000	-2.418348000
F	-1.119696000	-1.461277000	2.098909000
F	0.456301000	-2.623015000	1.090571000
F	-1.602854000	-3.343512000	1.111354000
F	-3.246463000	-2.639524000	-0.856687000
F	-2.511299000	-1.506650000	-2.557872000
F	-1.460955000	-3.337625000	-1.943643000

2 (R = OMe): E= -1893.830355

Au	-1.959018000	0.241114000	-0.403753000
Cl	-3.974320000	0.949700000	0.433895000
P	1.130997000	0.203318000	-0.053442000
C	2.717269000	-0.686220000	-0.215595000
C	-0.091260000	-0.377381000	-1.208564000
C	2.863104000	-1.670248000	-1.203334000
H	2.031245000	-1.902287000	-1.869113000
O	-1.133230000	-2.493566000	-2.075504000
C	0.699248000	0.046301000	1.713217000
C	1.473235000	1.966753000	-0.400841000

C	-0.074559000	1.030781000	2.348154000
H	-0.407259000	1.912183000	1.802829000
C	0.391492000	2.861955000	-0.503727000
H	-0.632632000	2.491237000	-0.396119000
C	3.781009000	-0.429170000	0.668896000
H	3.662112000	0.309708000	1.463185000
C	0.732978000	-1.237622000	3.769730000
H	1.045272000	-2.127064000	4.318830000
C	1.104034000	-1.089500000	2.432106000
H	1.677000000	-1.871608000	1.937038000
C	-0.044334000	-0.258605000	4.396996000
H	-0.340683000	-0.381071000	5.439792000
C	2.777348000	2.445192000	-0.606768000
H	3.627951000	1.765837000	-0.568858000
C	-0.446789000	0.873826000	3.683994000
H	-1.063183000	1.635899000	4.161328000
C	4.979439000	-1.133375000	0.549430000
H	5.797981000	-0.930949000	1.241503000
C	5.124573000	-2.103647000	-0.448949000
H	6.060882000	-2.656130000	-0.540028000
C	4.065648000	-2.373407000	-1.319914000
H	4.170323000	-3.138987000	-2.089715000
C	0.616307000	4.211139000	-0.777174000
H	-0.233852000	4.889992000	-0.854576000
C	0.135806000	0.126661000	-2.645990000
H	-0.624841000	-0.328227000	-3.292249000
H	1.124361000	-0.156816000	-3.045520000
H	0.046008000	1.217946000	-2.730976000
O	-0.268875000	-2.500073000	0.217449000
B	-0.557622000	-1.855417000	-0.990185000
C	1.919170000	4.684196000	-0.962633000
H	2.093208000	5.739020000	-1.180254000
C	2.995868000	3.797498000	-0.884271000
H	4.013868000	4.154694000	-1.046033000
C	-1.290363000	-3.070433000	1.042331000

H	-1.408042000	-4.148452000	0.848642000
H	-0.989694000	-2.925414000	2.090165000
H	-2.255876000	-2.562010000	0.889618000
C	-1.581955000	-3.847012000	-2.002023000
H	-2.552257000	-3.911220000	-1.484625000
H	-1.705751000	-4.212009000	-3.030109000
H	-0.853884000	-4.486881000	-1.477894000

3: E= -4766.315052

Cu	-0.436005000	-0.118919000	-0.799106000
P	2.361642000	0.361576000	-0.010146000
C	4.003410000	-0.405214000	0.178539000
C	1.438235000	-0.353653000	-1.363622000
C	4.437529000	-1.336479000	-0.775161000
H	3.779492000	-1.611131000	-1.600544000
C	0.619426000	-2.574710000	-2.673201000
H	-0.133093000	-3.355464000	-2.484583000
H	0.166755000	-1.893421000	-3.410615000
C	1.547498000	0.245962000	1.621733000
C	2.642754000	2.135550000	-0.338049000
C	0.464161000	1.094065000	1.915760000
H	0.158145000	1.872029000	1.217357000
C	1.535987000	2.930946000	-0.687852000
H	0.542545000	2.491518000	-0.792061000
C	4.839365000	-0.073954000	1.260603000
H	4.499507000	0.637752000	2.014683000
C	1.210663000	-0.878907000	3.744429000
H	1.498990000	-1.657845000	4.451135000
C	1.921354000	-0.738377000	2.550889000
H	2.744982000	-1.416790000	2.332573000
C	0.119415000	-0.050411000	4.016639000
H	-0.451965000	-0.183435000	4.935858000
C	3.916415000	2.721465000	-0.271052000
H	4.791276000	2.116612000	-0.034984000

C	-0.251704000	0.938754000	3.102122000
H	-1.116900000	1.575606000	3.284378000
C	6.096778000	-0.667577000	1.379139000
H	6.738894000	-0.412022000	2.223034000
C	6.527607000	-1.592879000	0.421497000
H	7.509304000	-2.058801000	0.518007000
C	5.698159000	-1.926705000	-0.653076000
H	6.027627000	-2.654052000	-1.395935000
C	1.697836000	4.294821000	-0.928796000
H	0.826986000	4.895842000	-1.192504000
C	1.789081000	0.311108000	-2.711365000
H	1.241878000	-0.193227000	-3.516256000
H	2.863906000	0.229889000	-2.946323000
H	1.528819000	1.376390000	-2.756744000
C	1.143701000	-2.751807000	0.012780000
H	2.224630000	-2.901593000	0.210117000
H	0.779053000	-2.194859000	0.887355000
C	1.877500000	-3.228031000	-3.293981000
H	2.621284000	-2.466306000	-3.577991000
H	1.640032000	-3.806766000	-4.199384000
H	2.362944000	-3.912866000	-2.581077000
B	1.022022000	-1.853144000	-1.306571000
C	2.966427000	4.877655000	-0.842713000
H	3.093104000	5.943814000	-1.036098000
C	4.073573000	4.087600000	-0.522433000
H	5.068317000	4.532289000	-0.470155000
C	0.440032000	-4.116939000	-0.006041000
H	0.805957000	-4.760997000	-0.819852000
H	-0.643113000	-3.992352000	-0.142511000
H	0.588699000	-4.660498000	0.938829000
N	-2.167041000	0.131197000	0.046904000
S	-2.635079000	1.706633000	0.129258000
O	-2.884758000	2.195696000	1.467928000
O	-1.716382000	2.416278000	-0.755637000
S	-2.708877000	-1.044020000	1.090870000

O	-1.567329000	-1.796202000	1.574620000
O	-3.753546000	-0.592563000	1.982743000
C	-4.296227000	1.775727000	-0.776844000
F	-4.641559000	3.068870000	-0.927620000
F	-4.178893000	1.207387000	-1.991845000
F	-5.249359000	1.143501000	-0.079019000
C	-3.528791000	-2.205065000	-0.161582000
F	-4.574334000	-1.610029000	-0.761080000
F	-2.639458000	-2.578821000	-1.107233000
F	-3.958735000	-3.301144000	0.489646000

4: E= -3272.612842

Ag	-0.396493000	-0.275302000	-1.007949000
P	2.423266000	0.419632000	0.038170000
C	4.107877000	-0.186375000	0.386816000
C	1.738579000	-0.423132000	-1.393063000
C	4.698750000	-1.112807000	-0.483593000
H	4.140981000	-1.477640000	-1.346651000
C	1.284499000	-2.725096000	-2.739896000
H	0.538466000	-3.529439000	-2.644316000
H	0.933520000	-2.089673000	-3.568120000
C	1.514967000	0.273212000	1.616507000
C	2.554865000	2.205393000	-0.322713000
C	0.416073000	1.109247000	1.887664000
H	0.123574000	1.899133000	1.196899000
C	1.409380000	2.891651000	-0.768597000
H	0.465217000	2.367081000	-0.927337000
C	4.814528000	0.249901000	1.522809000
H	4.350142000	0.950472000	2.218717000
C	1.123821000	-0.882642000	3.714461000
H	1.399129000	-1.666795000	4.420597000
C	1.870083000	-0.718865000	2.546818000
H	2.713998000	-1.379595000	2.352400000
C	0.017320000	-0.066996000	3.962900000
H	-0.582075000	-0.216447000	4.861432000

C	3.761816000	2.906395000	-0.176841000
H	4.667083000	2.388217000	0.137608000
C	-0.332760000	0.931323000	3.050799000
H	-1.208493000	1.557858000	3.214911000
C	6.101709000	-0.228461000	1.771119000
H	6.643179000	0.109613000	2.655574000
C	6.690628000	-1.145910000	0.892955000
H	7.695312000	-1.521654000	1.091704000
C	5.987951000	-1.588731000	-0.230916000
H	6.438315000	-2.313010000	-0.910658000
C	1.466367000	4.260474000	-1.028945000
H	0.565232000	4.774914000	-1.363999000
C	2.216045000	0.251055000	-2.695329000
H	1.847572000	-0.317257000	-3.557389000
H	3.317292000	0.268971000	-2.766116000
H	1.873993000	1.287671000	-2.811457000
C	1.437774000	-2.816251000	-0.009748000
H	2.502752000	-2.988294000	0.250378000
H	1.033452000	-2.248139000	0.838791000
C	2.644773000	-3.350674000	-3.129358000
H	3.396825000	-2.571658000	-3.333912000
H	2.569614000	-3.975178000	-4.032226000
H	3.039081000	-3.984219000	-2.319813000
B	1.433402000	-1.944807000	-1.352617000
C	2.668101000	4.957199000	-0.866149000
H	2.712350000	6.027320000	-1.073459000
C	3.814609000	4.276604000	-0.448397000
H	4.758859000	4.810727000	-0.334121000
C	0.703703000	-4.165789000	-0.060456000
H	1.118794000	-4.836442000	-0.827384000
H	-0.361891000	-4.017347000	-0.288448000
H	0.759415000	-4.691491000	0.904169000
N	-2.306400000	0.092233000	-0.019075000
S	-2.734203000	1.674202000	0.065481000
O	-2.842535000	2.207128000	1.407781000

O	-1.909061000	2.352965000	-0.927063000
S	-2.696335000	-1.038760000	1.126646000
O	-1.494289000	-1.784041000	1.459037000
O	-3.599614000	-0.565705000	2.152804000
C	-4.481777000	1.732386000	-0.656138000
F	-4.843318000	3.022124000	-0.799991000
F	-4.504288000	1.133243000	-1.861911000
F	-5.351911000	1.120140000	0.160648000
C	-3.677669000	-2.238355000	0.040087000
F	-4.790128000	-1.660909000	-0.444723000
F	-2.914603000	-2.653018000	-0.996057000
F	-4.023218000	-3.307462000	0.780765000

5: E= -3261.398891

Au	-0.377697000	-0.200621000	-0.786926000
P	2.479902000	0.435978000	0.085250000
C	4.153555000	-0.236388000	0.333245000
C	1.652040000	-0.430684000	-1.275611000
C	4.635510000	-1.230006000	-0.530207000
H	4.003662000	-1.603446000	-1.335664000
C	1.038928000	-2.770573000	-2.500864000
H	0.289090000	-3.558415000	-2.330133000
H	0.637809000	-2.150967000	-3.317359000
C	1.662567000	0.362123000	1.717493000
C	2.655288000	2.201340000	-0.348818000
C	0.561309000	1.193358000	1.997308000
H	0.234263000	1.952637000	1.288160000
C	1.510061000	2.925091000	-0.732172000
H	0.535713000	2.438423000	-0.803098000
C	4.960084000	0.212997000	1.395300000
H	4.581346000	0.967782000	2.086175000
C	1.356233000	-0.729231000	3.862541000
H	1.666179000	-1.485224000	4.584815000
C	2.063332000	-0.592698000	2.666361000
H	2.907093000	-1.250794000	2.463085000

C	0.241629000	0.073193000	4.116615000
H	-0.328694000	-0.059052000	5.036620000
C	3.901500000	2.847139000	-0.325872000
H	4.804927000	2.296957000	-0.065329000
C	-0.151329000	1.038603000	3.185273000
H	-1.031701000	1.657392000	3.357885000
C	6.236156000	-0.320925000	1.578184000
H	6.854779000	0.028086000	2.405918000
C	6.715451000	-1.306709000	0.707514000
H	7.711788000	-1.725700000	0.855094000
C	5.914234000	-1.761140000	-0.343347000
H	6.278675000	-2.537522000	-1.016949000
C	1.610105000	4.279630000	-1.049109000
H	0.710626000	4.825089000	-1.336174000
C	2.091560000	0.162432000	-2.627873000
H	1.609786000	-0.391881000	-3.441389000
H	3.181780000	0.078202000	-2.772772000
H	1.828585000	1.221151000	-2.746364000
C	1.380264000	-2.783097000	0.214368000
H	2.454372000	-2.999631000	0.389493000
H	1.075541000	-2.168388000	1.071770000
C	2.360499000	-3.426733000	-2.963538000
H	3.110326000	-2.665247000	-3.232607000
H	2.216887000	-4.066420000	-3.847175000
H	2.796342000	-4.052413000	-2.169114000
B	1.289860000	-1.954626000	-1.151175000
C	2.851007000	4.923203000	-1.005316000
H	2.927358000	5.982029000	-1.256648000
C	3.994994000	4.202906000	-0.652445000
H	4.968881000	4.693930000	-0.633242000
C	0.583270000	-4.095978000	0.267734000
H	0.912203000	-4.811017000	-0.500799000
H	-0.486901000	-3.901967000	0.109669000
H	0.685004000	-4.590570000	1.245037000
N	-2.284627000	0.144151000	0.114063000

S	-2.736186000	1.726130000	0.280573000
O	-2.971801000	2.132729000	1.649306000
O	-1.839134000	2.492559000	-0.572173000
S	-2.780579000	-1.046948000	1.175692000
O	-1.617316000	-1.743838000	1.689614000
O	-3.857220000	-0.626474000	2.043990000
C	-4.409509000	1.815238000	-0.600953000
F	-4.782568000	3.108177000	-0.670184000
F	-4.294160000	1.323217000	-1.848597000
F	-5.343211000	1.122650000	0.065408000
C	-3.545983000	-2.246831000	-0.076525000
F	-4.555895000	-1.662368000	-0.743445000
F	-2.620940000	-2.667364000	-0.964607000
F	-4.018516000	-3.312513000	0.596429000