Supporting Information

Transformation of carbodiimides to guanidine derivatives facilitated by gallylenes

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All manipulations were carried out under standard Schlenk or glovebox techniques. 1,2-dimethoxymethane (DME), Et_2O, tetrahydrofuran (THF), toluene-d_8 and THF-d_8 were dried, stored over sodium-benzophenone and distilled right prior use. All other chemicals were purchased and used without further purification. For compounds **3**, **4a** and **4e** the IR spectra were recorded on FSM-1201 spectrometer in Nujol. The NMR spectra were registered on Bruker Advance III (400 MHz) spectrometer and were referenced to the residual ^{1}H or ^{13}C signals of deuterated solvents. Ar=aromatic, d=doublet, m=multiplet, t=triplet, pst=pseudotriplet, s=singlet, br.s=broad singlet, sept=septet. The Uv/Vis spectra were recorded on a Perkin–Elmer Lambda 25 spectrometer in a 10 mm Quartz cuvette. For compounds **4b**, **4c**, **4d** and **5**, NMR spectra were recorded on a Mercury Plus-400 spectrometer. Elemental analyses were performed with an Elementar VarioEL III instrument. IR spectra were recorded using a Nicolet AVATAR 360 FT-IR spectrometer. UV/Vis spectra were done on Agilent Cary-100. The [(dpp-bian)GaNa(DME)$_3$] **1**,[1] [(dpp-dad)GaNa(THF)$_4$] **2a** and [(dpp-dad)GaK(THF)$_4$(dpp-dad)][K(THF)$_6$] **2b**[2] were prepared according literature procedures. Elemental analyses were carried out by Pregl method.

Synthesis of [(dpp-bian)Ga(NCy)$_2$C=NCy][Na(DME)$_2$] (3). 0.413 g (2.0 mmol) of N,N'-Dicyclohexylcarbodiimide was added to a solution of 1 mmol of **1** in 10 ml of DME. After 10 minutes the solution color changed from yellow-green to emerald-green. The mixture was heated at 90 °C within 1h. All volatiles were removed in vacuum. The residue was dissolved in 5 ml benzene. Slow concentration gives green crystals of complex **3**. Yield 0.48 g, 40 %. Elemental analysis C72H102GaN5NaO4 (1194.29): C 72.41, H 8.61, N 5.86 %; found: C 72.18, H 8.52, N 5.84 %. ^{1}H NMR (400 MHz, toluene-d_8, 333 K, δ/ppm): 7.26 (d, *J* = 7.0 Hz, 4H, CH-Ar), 7.21 (d, *J* = 6.5 Hz, 2H, CH-Ar), 6.81 (pst, *J* = 7.3 Hz, 2H, CH-Ar), 6.13 (d, *J* = 7.0 Hz, 2H, CH-Ar), 4.17 (br. s, 4H, C*H*(CH)$_3$), 3.70 (br. s, 1H, CH-Cy), 3.12 (br. s, 1H, CH-Cy), 1.87 (d, *J* = 12.5 Hz, 2H, CH$_2$-Cy), 1.78 (d, *J* = 14.5 Hz, 2H, CH$_2$-Cy), 1.65 (d, *J* = 10.0 Hz, 4H, CH$_2$-Cy), 1.53 (d, *J* = 11.0 Hz, 2H, CH$_2$-Cy), 1.42 (d, *J* = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.31 (d, *J* = 6.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.18 (d, *J* = 12.5 Hz, 4H, CH$_2$-Cy), 1.05 (d, *J* = 11.8 Hz, 2H, CH$_2$-Cy). UV-Vis (Toluene) λ_{max} = 327, 650 nm. IR (Nujol, ν/cm^{-1}): 498 W, 519 W, 554 W, 625 W, 646 W, 675 S, 752 M, 760 M, 779 W, 804 M, 812 M, 839 W, 860 M, 889 W, 899 M, 924 M, 934 M, 984 W, 1034 M, 1088 S, 1125 M, 1181 W, 1192 W, 1210 W, 1256 M, 1285 M, 1298 M, 1321 M, 1337 S, 1518 S, 1590 W, 1651 M.

Synthesis of [(dpp-bian)GaN(*i*Pr)C(*i*PrN)N*(i*Pr)C(*i*PrN)][Na(DME)$_2$] (4a). 0.252 g (2.0 mmol) of N,N'-Diisopropylcarbodiimide was added to a solution of 1 mmol of **1** in 10 ml of DME. After 10 minutes the solution color changed from yellow-green to emerald-green. All volatiles were removed in vacuum. The residue was dissolved in 5 ml benzene. The solution was layered with 15 ml of pentane, what gives green crystals of complex **4a**. Crystals for XRD-measurement were obtained by recrystallization from Et$_2$O. Yield 0.74 g, 65 %. Elemental analysis for $C_{64}H_{94}GaN_6NaO_4$ (1104.18): C 69.62, H 8.58, N 7.61 %; found C 69.42, H 8.36, N 7.35 %. ^{1}H NMR (400 MHz, THF-d$_8$, 323 K, δ/ppm): 7.01-6.93 (m, 4H, CH-Ar), 6.84 (pst, J = 7.2 Hz, 2H, CH-Ar), 6.78 (d, J = 8.1 Hz, 2H, CH-Ar), 6.64 (pst, J = 7.2 Hz, 2H, CH-Ar), 5.87 (d, J = 6.0 Hz, 2H, CH-Ar), 4.09 (br. s, 4H, C*H*(CH)$_3$), 3.99 (br. s, 2H, C*H*(CH)$_3$), 3.81 (br. s, 2H, C*H*(CH)$_3$), 1.42 (d, J = 6.1 Hz, 6H, CH(C*H*)$_3$), 1.13 (d, J = 6.4 Hz, 12H, CH(C*H*)$_3$), 1.10-0.93 (m, 24H, CH(C*H*)$_3$), 0.71 (br. s, 6H, CH(C*H*)$_3$). UV-Vis (Toluene) λ_{max} = 326, 642 nm. IR (Nujol, ν/cm^{-1}): 461 W, 494 W, 517 W, 548 W, 573 W, 583 W, 623 W, 637 W, 648 W, 677 S, 762 S, 779 W, 799 M, 812 M, 839 W, 858 M, 874 W, 893 M, 924 M, 936 M, 999 W, 1007 W, 1030 M, 1047 M, 1059 M, 1080 S, 1113 M, 1123 S, 1159 M, 1179 M, 1190 M, 1206 M, 1256 M, 1277 M, 1318 S, 1339 S, 1356 M, 1433 S, 1514 S, 1553 M, 1568 M, 1601 M, 1630 M, 1659 M.

Synthesis of [(dpp-dad)GaN(*i*Pr)C(*i*PrN)N(*i*Pr)C(*i*PrN)][Na(THF)$_3$] (4b). 0.252 g (2.0 mmol) N,N'-Diisopropylcarbodiimide was added to a solution of 1 mmol of **2a** in 30 ml of THF. The solution color changed from brownish-grey to orange. The resultant orange solution was stirred at ambient temperature for 3 days. The mixture was filtered, and the brownish red filtrate was concentrated. Yellow crystals were grown from a toluene-THF solution at −20 °C for 1 week (0.685 g, 71 %). Elemental analysis for $C_{54}H_{92}GaN_6NaO_3$ (966.04): C 67.14, H 9.60, N 8.70 %; found C 67.20, H 9.23, N 9.05 %.^{1}H NMR (400 MHz, THF-d$_8$, 293 K, *δ*/ppm): 6.84 (dd, *J* = 7.5 Hz, 2H, m-C$_6$H$_3$), 6.81 (dd, *J* = 7.5 Hz, 2H, m-C$_6$H$_3$), 6.62 (t, *J* = 7.5 Hz, 2H, p-C$_6$H$_3$), 4.22 (sept, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 3.99 (sept, *J* = 6.0 Hz, 1H, C*H*(CH$_3$)$_2$), 3.92 (sept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.80 (sept, *J* = 6.4 Hz 2H, C*H*(CH$_3$)$_2$), 3.66 (br.s, 1H, C*H*(CH$_3$)$_2$, this one being superimposed with the THF signals), 3.62 (THF), 3.50 (br.s, 1H, C*H*(CH$_3$)$_2$), 1.78 (THF), 1.60 (s, 6H, CC*H*$_3$), 1.41 (d, *J* = 6.8 Hz, 6H, (CH(C*H*$_3$)$_2$), 1.25 (d, *J* = 6.8 Hz, 6H, (CH(C*H*$_3$)$_2$) 1.08 (dd, *J* = 6.8 Hz, 12H, (CH(C*H*$_3$)$_2$), 1.03 (d, *J* = 6.8 Hz, 6H, (CH(C*H*$_3$)$_2$), 1.00 (d, *J* = 6.8 Hz, 6H, (CH(C*H*$_3$)$_2$), 0.94 (d, *J* = 6.0 Hz, 6H, (CH(C*H*$_3$)$_2$), 0.76 (d, *J* = 6.4 Hz, 6H, (CH(C*H*$_3$)$_2$). ^{13}C NMR (100.6 MHz, THF-*d*$_8$, 298 K, δ/ppm): 148.9 ((N−*C*CH$_3$)), 145.7 (*i*PrN=C), 145.1 (*i*PrN=C), 123.4, 123.0, 122.6, 119.7 (Ar), 68.0 (THF), 45.5 (N*C*H(CH$_3$)$_2$), 45.9 (N*C*H(CH$_3$)$_2$), 25.1 (THF), 27.6 (*C*H(CH$_3$)$_2$), 27.5 (*C*H(CH$_3$)$_2$), 27.2 (*C*H(CH$_3$)$_2$), 26.9 (*C*H(CH$_3$)$_2$), 26.4 (CH(*C*H$_3$)$_2$), 26.2 (CH(*C*H$_3$)$_2$), 26.1 (CH(*C*H$_3$)$_2$), 25.8 (CH(*C*H$_3$)$_2$), 24.4(CH(*C*H$_3$)$_2$), 16.1 (NC*C*H$_3$). UV-Vis (THF) λ_{max} = 266, 325 nm. IR (Nujol, ν/cm^{-1}): 468 M, 649 W, 923 W, 951 M, 1231 M, 1167 M, 1308 M, 1369 S, 1476 S, 1506 M, 1609 M.

Synthesis of [(dpp-dad)GaN(Cy)C(CyN)N(Cy)C(CyN)][Na(THF)$_3$] (4c). 0.413 g (2.0 mmol) N,N'-Dicyclohexylcarbodiimide was added to a solution of 1 mmol of **2a** in 30 ml of THF. The resultant orange solution was stirred at ambient temperature for 3 days. The mixture was filtered, and the brownish red filtrate was concentrated. Yellow crystals were grown from a toluene-THF solution at −20 °C for 1 week (0.718 g, 64 %). Elemental analysis for $C_{66}H_{108}GaN_6NaO_3$ (1126.29): C 70.38, H 9.61, N 7.46 %; found C 70.66, H 9.48, N 7.88 %. ^{1}H NMR (400 MHz, THF-d$_8$, 293 K, *δ*/ppm): 6.84 (dd, *J* = 7.5 Hz, 2H, m-C$_6$*H*$_3$), 6.75 (dd, *J* = 7.5 Hz, 2H, m-C$_6$*H*$_3$), 6.60 (t, *J* = 7.5 Hz, 2H, p-C$_6$*H*$_3$), 3.85 (sept, 2H, C*H*(CH$_3$)$_2$), 3.62 (THF), 3.52 (br.s, 2H, C*H*-Cy), 3.20 (br.s, 2H, C*H*(CH$_3$)$_2$), 3.08 (br.s, 2H, CH-Cy), 1.63-1.67 (m, 10H, CH_2-Cy), 1.63 (s, 6H, CCH_3), 1.41-1.48 (m, 10H, CH_2-Cy), 1.36 (m, 10H, CH_2-Cy), 1.26 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.20 (m, 10H, CH_2-Cy), 1.13 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.03 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 0.96 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (100.6 MHz, THF-d_8, 298 K, δ/ppm): 148.3 ((N−*C*CH$_3$)) 145.7 (CyN=*C*), 144.8 (CyN=*C*), 122.9, 123.3, 122.5, 119.5 (Ar), 68.0 (THF), 55.0 (*C*H-Cy), 38.0 (*C*H$_2$-Cy), 37.0 (*C*H$_2$-Cy), 36.1 (*C*H$_2$-Cy), 28.5 (*C*H-Cy), 27.5(*C*H-Cy), 27.7(*C*H(CH$_3$)$_2$), 27.1 (*C*H(CH$_3$)$_2$), 26.9 (*C*H(CH$_3$)$_2$), 26.1 (THF), 25.5 (CH(*C*H$_3$)$_2$), 25.3 (CH(*C*H$_3$)$_2$), 25.1 (CH(*C*H$_3$)$_2$), 24.9 (CH(*C*H$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 16.4 (NC*C*H$_3$). UV-Vis (THF) λ_{max} = 266, 350 nm. IR (Nujol, ν/cm^{-1}):453 M, 924 w, 951 w, 956 W, 1032 W, 1079 M, 1171 W, 1231 S , 1308 M, 1366 S, 1389 S, 1461 S, 1491 M, 1613 M.

Synthesis of [(dpp-dad)GaN(Cy)C(CyN)N(Cy)C(CyN)][K(THF)$_4$] (4d). 0.413 g (2.0 mmol) N,N'-Dicyclohexylcarbodiimide was added to a solution of 1 mmol of **2b** in 30 ml of THF. The resultant orange solution was stirred at ambient temperature for 3 days. The mixture was filtered, and the brownish red filtrate was concentrated. Yellow crystals were grown from a toluene-THF solution at −20 C for 1 week (0.587 g, 50 %). ^{1}H NMR (400 MHz, THF-d$_8$, 293 K, δ/ppm): 6.88 (dd, *J* = 7.5 Hz, 2H, m-C$_6H_3$), 6.83 (dd, *J* = 7.5 Hz, 2H, m-C$_6H_3$), 6.64 (t, *J* = 7.5 Hz, 2H, p-C$_6H_3$), 3.89 (sept, 2H, C*H*(CH$_3$)$_2$), 3.65 (THF), 3.57 (br.s, 2H, C*H*-Cy), 3.24 (br.s, 2H, C*H*(CH$_3$)$_2$), 3.11 (br.s, 2H, CH-Cy), 1.71 (br, 6H, CH_2-Cy), 1.66 (s, 6H, CCH_3), 1.61-1.48 (m, 10H, CH_2-Cy), 1.41-1.35 (m, 10H, CH_2-Cy), 1.29 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.20-1.27 (m, 10H, CH_2-Cy), 1.17 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.00 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 0.99 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$). 0.85-0.94 (m, 4H, CH_2-Cy); ^{13}C NMR (100.6 MHz, THF-d_8, 298 K, δ/ppm): 148.5 ((N−*C*CH$_3$)) 145.5 (CyN=*C*), 144.8 (CyN=*C*), 123.3, 122.9, 122.5, 119.5 (Ar), 67.2 (THF), 55.0 (*C*H-Cy), 38.0 (*C*H$_2$-Cy), 37.0 (*C*H$_2$-Cy), 36.1 (*C*H$_2$-Cy), 28.6 (*C*H-Cy), 27.8(*C*H-Cy), 27.7(*C*H(CH$_3$)$_2$), 27.6 (*C*H(CH$_3$)$_2$), 27.1 (*C*H(CH$_3$)$_2$), 26.2, (CH(*C*H$_3$)$_2$), 26.0 (CH(*C*H$_3$)$_2$), 25.1 (THF), 16.5 (NC*C*H$_3$). IR (Nujol, ν/cm^{-1}):463 M, 676 M, 729 S, 920 w, 941 w, 956 W, 1026 W, 1068 M, 1132 M, 1185 W , 1301 M, 1376 S, 1397 S, 1450 S, 1514 M, 1610 M.

Synthesis of [(dpp-bian)GaN(Cy)C(CyN)N(Cy)C(CyN)][Na(DME)$_3$] (4e). 0.42 g (2.0 mmol) of N,N'-Dicyclohexylcarbodiimide was added to a solution of [(dpp-bian)GaNa(DME)$_2$] in 10 ml of DME. After 10 minutes the solution color changed from yellow-green to emerlad-green. Solution was layered with pentane. The mixture was left unshaken for two days. Supernatant was decanted and discarded. The residue was washed twice with diethyl ether, dried in vacuum, and then dissolved in 5 ml of DME. Resulting solution was layered with diethyl ether. Two days after, compound **4e** was isolated as green crystals. Yield 0.38 g, 28 %. Elemental analysis for $C_{78}H_{124}GaN_6NaO_{7.51}$ (1358.69): C 69.37, H 9.25, N 6.22 %.; found C 69.65, H 9.46, N 5.94 %. ^{1}H NMR (400 MHz, THF-d$_8$, 298 K, δ/ppm): 6.99-6.92 (m, 4H, CH-Ar), 6.85-6.77 (m, 4H, CH-Ar), 6.66 (dd, 2H, J = 7.0 Hz, J = 6.7 Hz, 2H, CH-Ar), 5.90 (d, J = 6.8 Hz, 2H, CH-Ar), 4.05-3.93 (m, 2H, CH-Ar), 3.99 (sept, J = 6.8 Hz, 2H, C*H*(CH)$_3$), 3.73 (sept, J = 6.8 Hz, 2H, C*H*(CH)$_3$), 3.17-2.95 (m, 3H, CH-Cy), 1.73-1.61 (m, 9H, CH$_2$-Cy), 1.59-1.42 (s, 10H, CH$_2$-Cy), 1.34-1.20 (m, 10H, CH$_2$-Cy), 1.17 (d, J = 6.8 Hz, 6H, CH(C*H*)$_3$), 1.10 (d, J = 6.8 Hz, 6H, CH(C*H*)$_3$), 1.08 (d, J = 6.8 Hz, 6H, CH(C*H*)$_3$), 0.96 (d, J = 6.7 Hz, 6H, CH(C*H*)$_3$), 0.76-0.58 (m, 2H), 0.06-(-0.07) (m, 2H). ^{13}C NMR (100.6 MHz, THF-d$_8$, 298 K) 147.72, 146.03, 145.56, 139.92, 138.29, 129.73, 127.23, 127.17, 127.07, 116.82, 116.75, 38.22, 37.22, 37.14, 30.39, 28.69, 28.48, 27.98, 27.81, 27.61, 27.47, 27.19, 26.31, 26.04. IR (Nujol, ν/cm^{-1}): 517 W, 627 W, 652 VW, 683 W, 762 M, 795 W, 812 W, 839 W, 858 W, 891 W, 924 W, 939 W, 980 W, 1001 W, 1030 W, 1084 S, 1109 W, 1125 M, 1156 VW, 1179 W, 1192 W, 1215 M, 1258 M, 1312 M, 1323 M, 1341 S, 1514 M, 1559 M, 1611 M, 1634 M, 1651 M.

Synthesis of [(dpp-dad)Ga(2,6-*i*Pr$_2$C$_6$H$_3$N)$_2$C][Na(THF)$_2$] (5). 0.362 g (1.0 mmol) of bis(2,6-diisopropylphenyl)carbodiimide was added to a solution of 1 mmol of **2a** in 30 ml of THF. The resultant orange solution was stirred at ambient temperature for 3 days. The mixture was filtered, and the red filtrate was concentrated. Block colorless crystals were grown from a toluene-THF solution at

−20 °C for 1 week (0.459 g, 42 %). Elemental analysis for $C_{68}H_{98}GaN_4NaO_2$ (1096.21): C 74.51, H 9.01, N 5.11 %; found C 74.02, H 9.11, N 5.46 %. ^{1}H NMR (400 MHz, THF-d_8, 293 K, δ/ppm): 7.11-7.19 (6H, Ar-*H*), 6.70-6.83 (6H, Ar-*H*), 3.62 (THF), 3.49 (sept, 4H, C*H*$(CH_3)_2$), 3.33 (sept, 4H, C*H*$(CH_2)_5$), 1.78 (THF), 1.60 (s, 3H, CCH_3), 1.49 (s, 3H, CCH_3), 1.26 (d, *J* = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.15 (d, *J* = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.12 (d, *J* = 6.8 Hz, 12H, $CH(CH_3)_2$), 0.92 (m, 12H, $CH(CH_3)_2$). ^{13}C NMR (100.6 MHz, THF-d_8, 298 K, δ/ppm): 149.9 (ArN*C*NAr), 146.6 (N−*C*CH$_3$) and 143.2 (N−*C*CH$_3$), 133.8, 129.5, 128.7, 125.8, 125.6, 125.0, 123.9, 123.1, 122.1, 121.9, 119.8 (Ar), 68.0 (THF), 27.8 ($CH(CH_3)_2$, 29.8 ($CH(CH_3)_2$, 26.8 ($CH(CH_3)_2$, 26.2 ($CH(CH_3)_2$, 25.1 (THF), 23.4 ($CH(CH_3)_2$, 23.8 ($CH(CH_3)_2$, 15.6 (NCCH_3), 14.5 (NCCH_3). UV-Vis (THF) λ_{max} = 272 nm. IR (Nujol, ν/cm^{-1}): 468 M, 694 M ,850 W, 894 W, 956 W, 1032 W, 1080 M, 1109 W, 1171 W 1308 M, 1384 S, 1466 S, 1613 S.

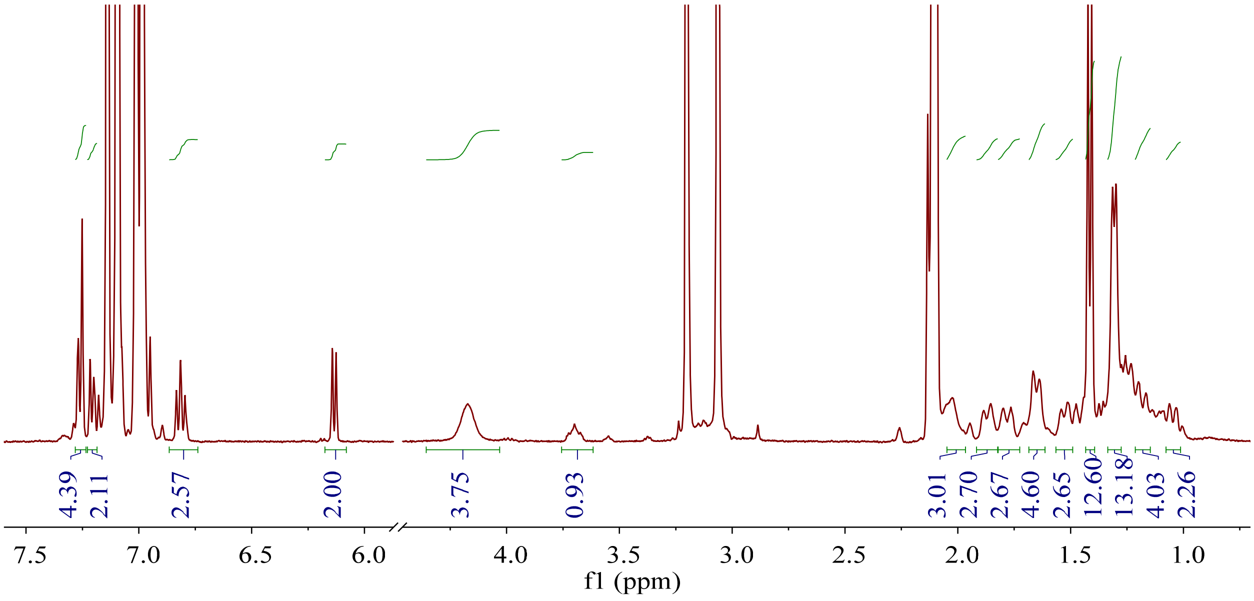


Fig. S1. ^{1}H NMR spectrum of **3** at 333 K in toluene-d_8.

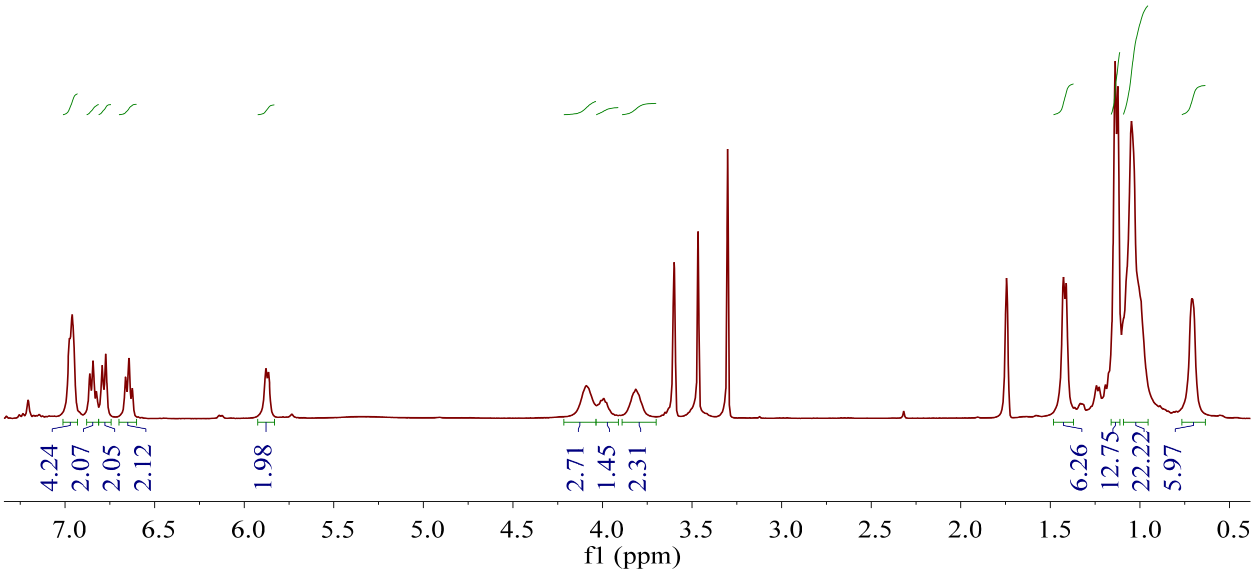


Fig. S2. ^{1}H NMR spectrum of **4a** at 323 K in THF-d_8.

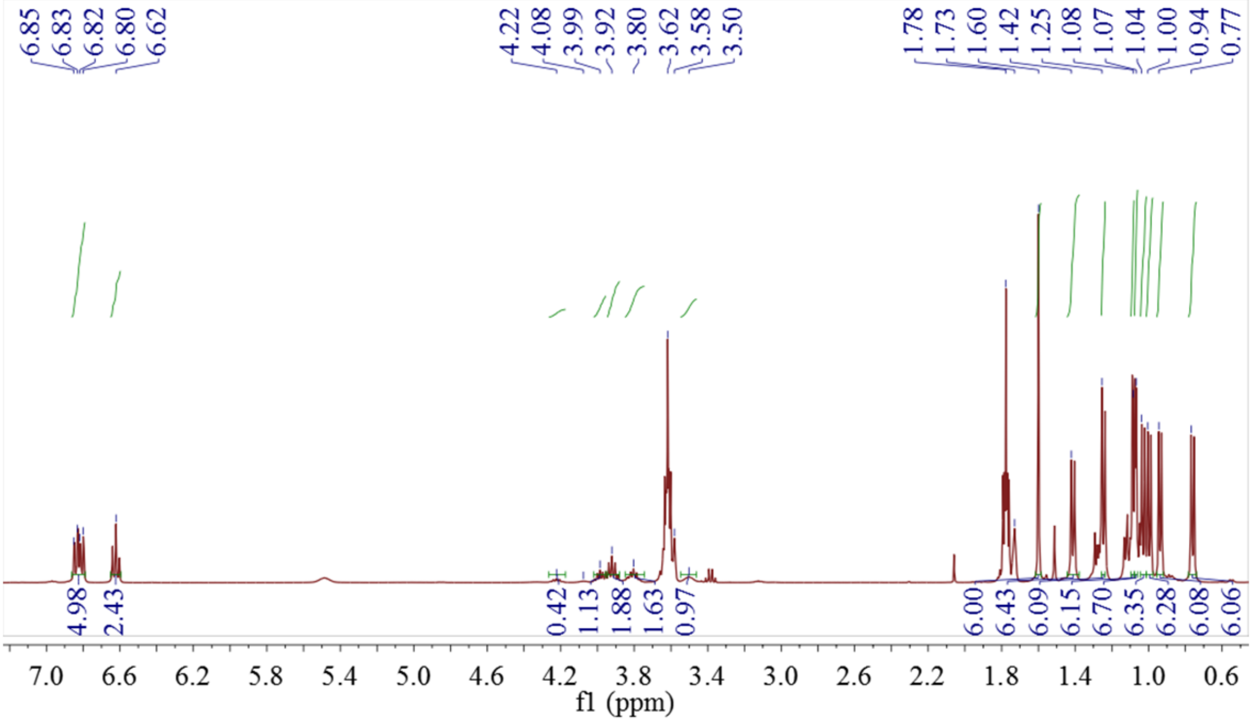


Fig. S3. ^{1}H NMR spectrum of **4b** at 293 K in THF-d_8.

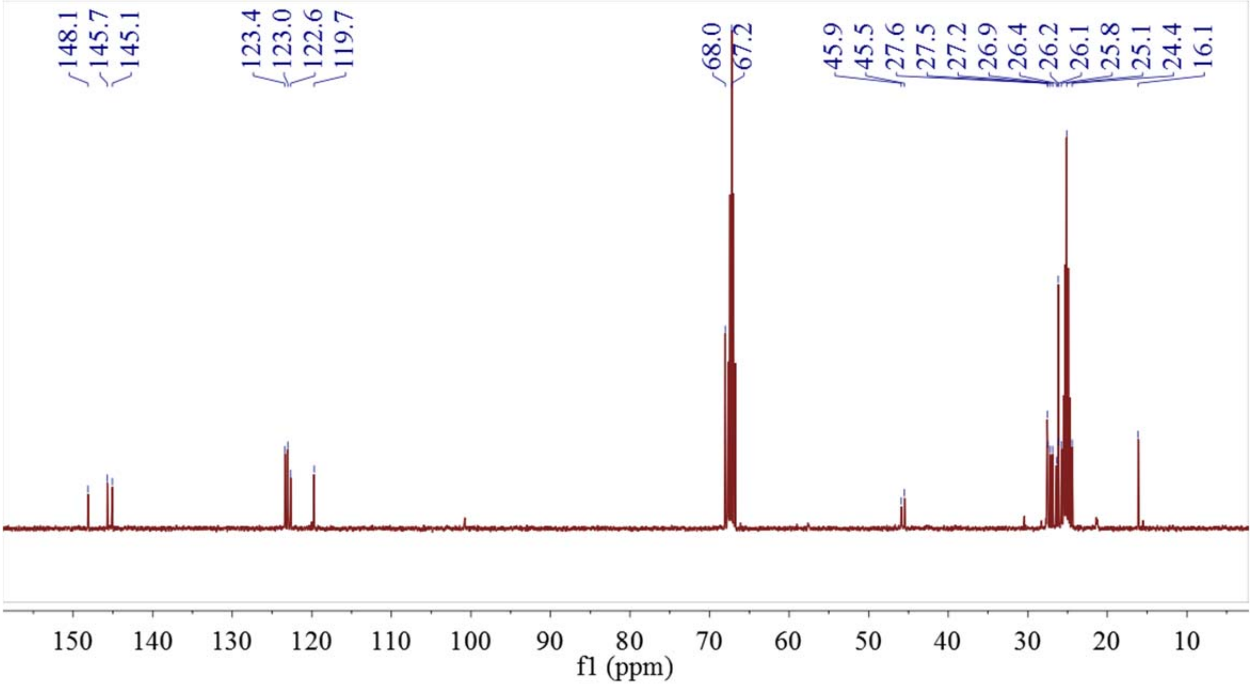


Fig. S4. ^{13}C NMR spectrum of complex **4b** at 293 K in THF-d_8.

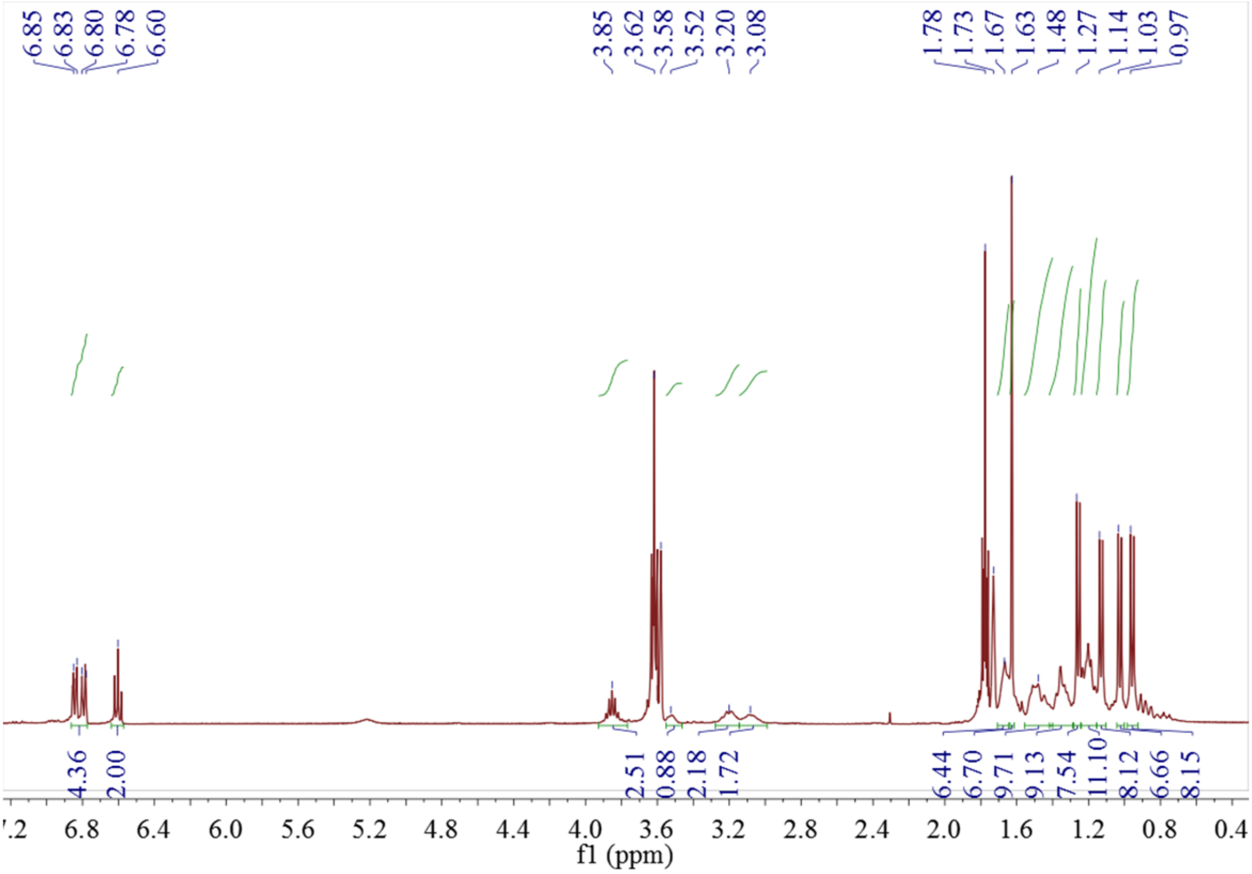


Fig. S5. ^{1}H NMR spectrum of **4c** at 293 K in THF-d$_8$.

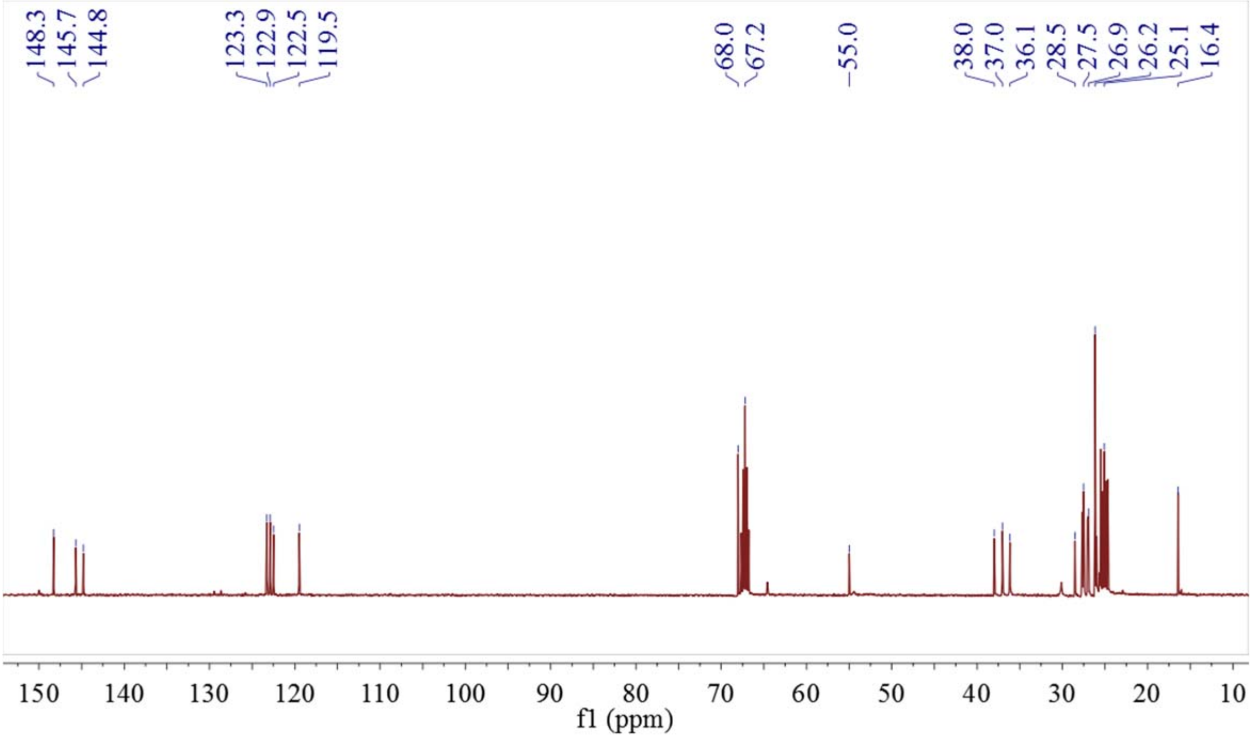


Fig. S6. ^{13}C NMR spectrum of complex **4c** at 293 K in THF-d$_8$.

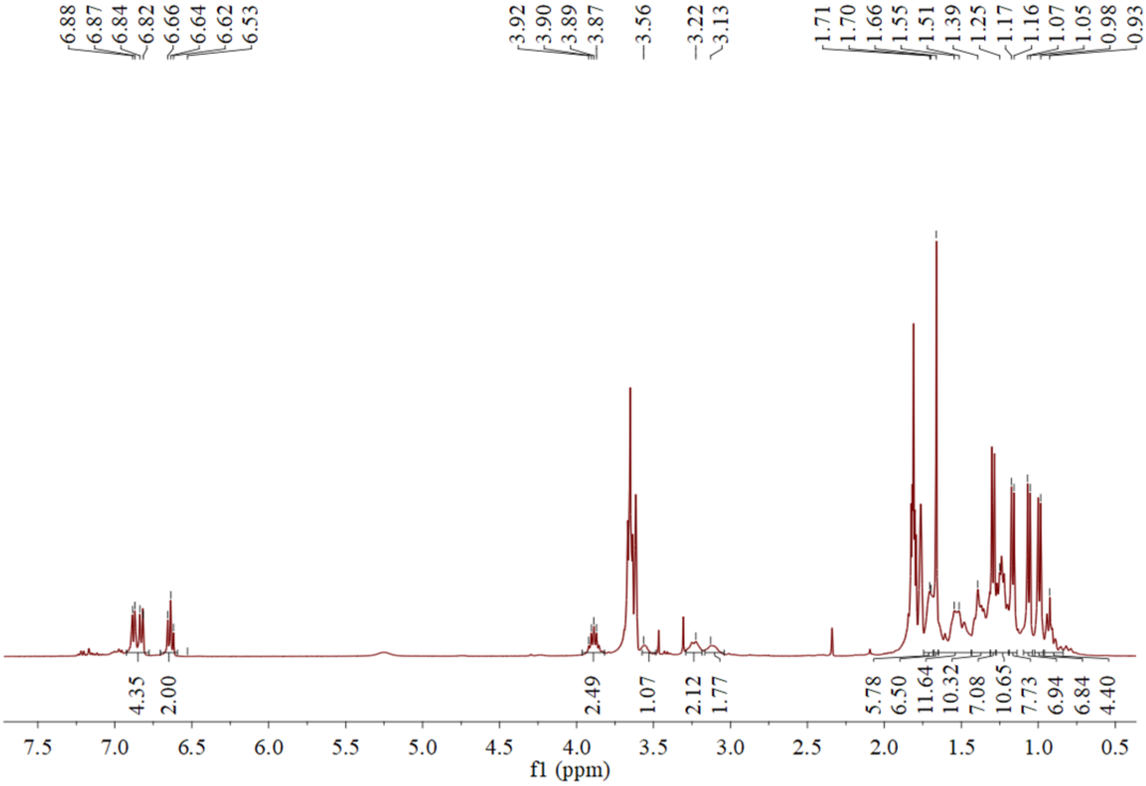


Fig. S7. ^{1}H NMR spectrum of complex **4d** at 298 K in THF-d$_8$.

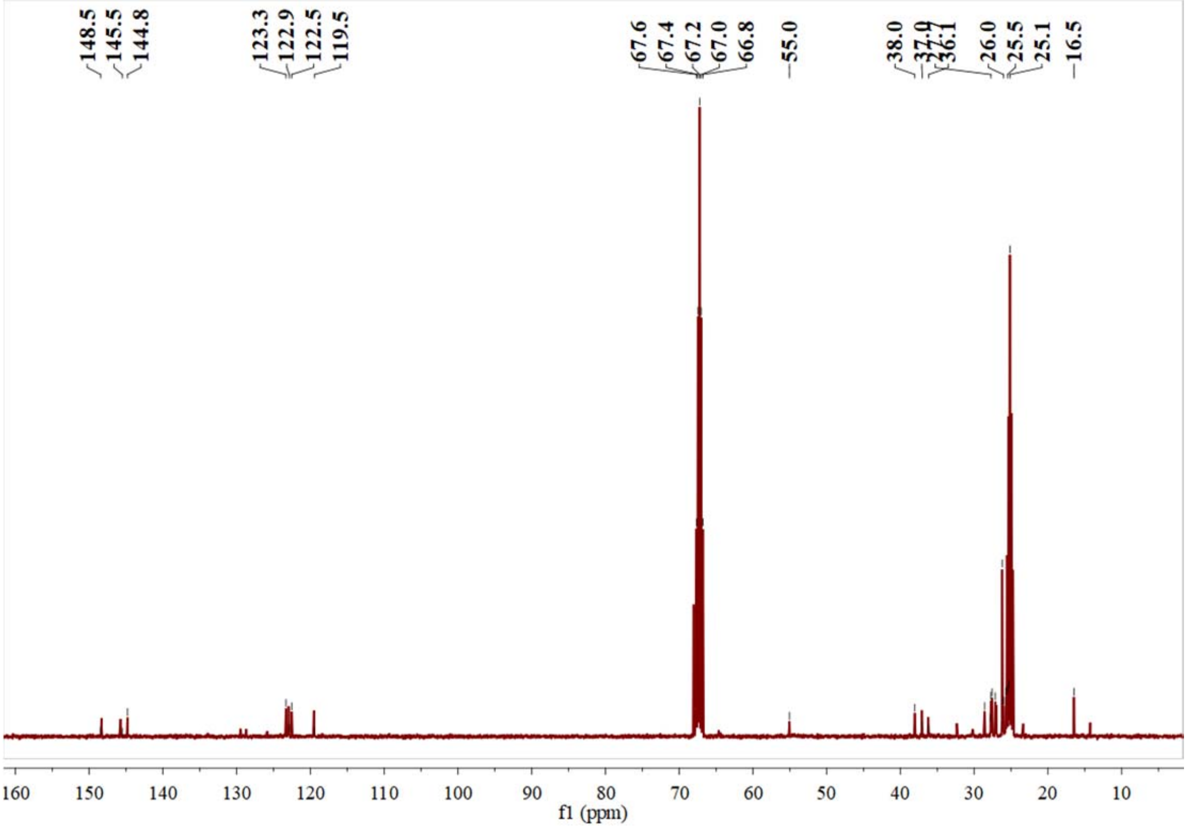


Fig. S8. ^{13}C NMR spectrum of complex **4d** at 293 K in THF-d$_8$.

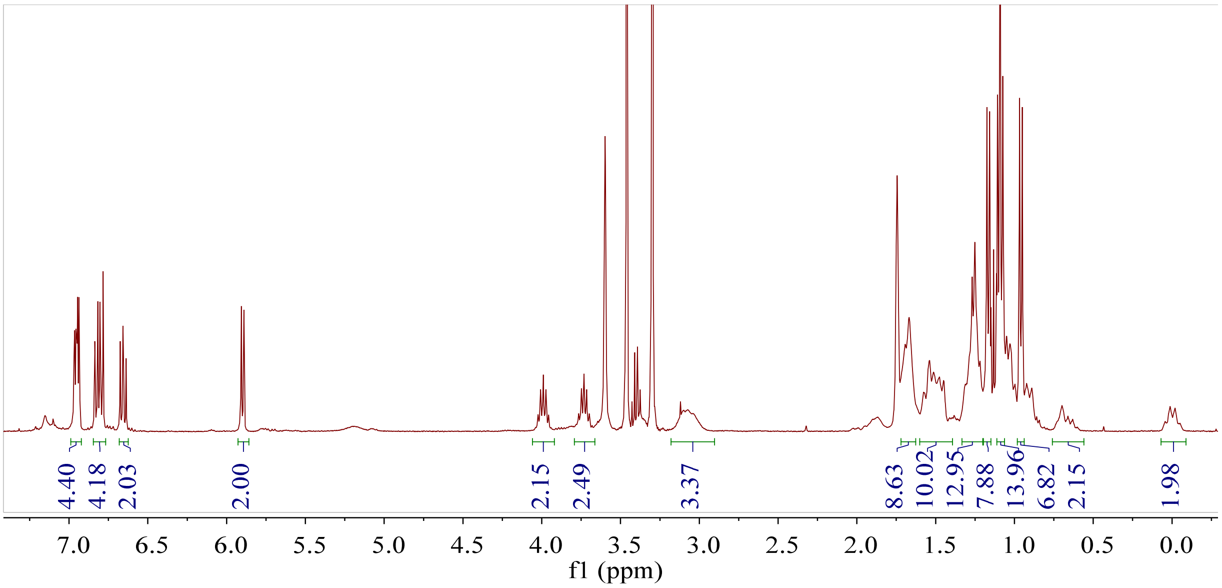


Fig. S9. ^{1}H NMR spectrum of complex **4e** at 298 K in THF-d$_8$.

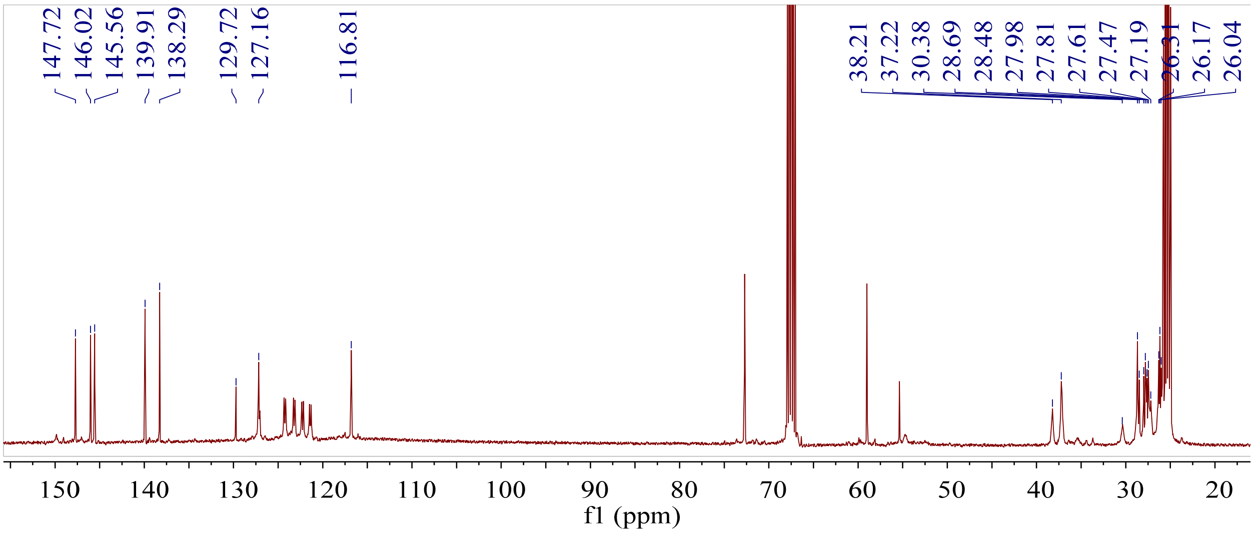


Fig. S10. ^{13}C NMR spectrum of complex **4e** at 298 K in THF-d$_8$.

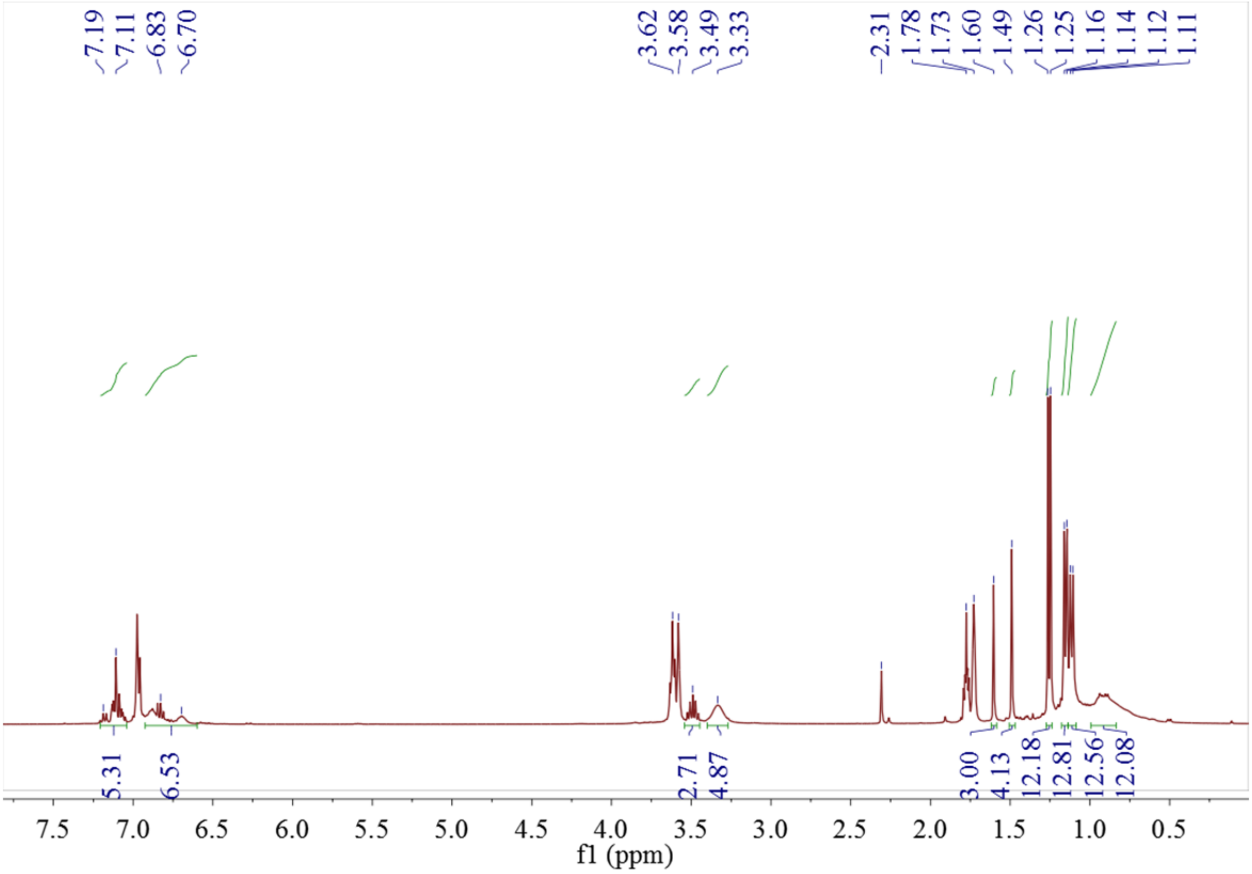


Fig. S11. ^{1}H NMR spectrum of **5** at 293 K in THF-d_8.

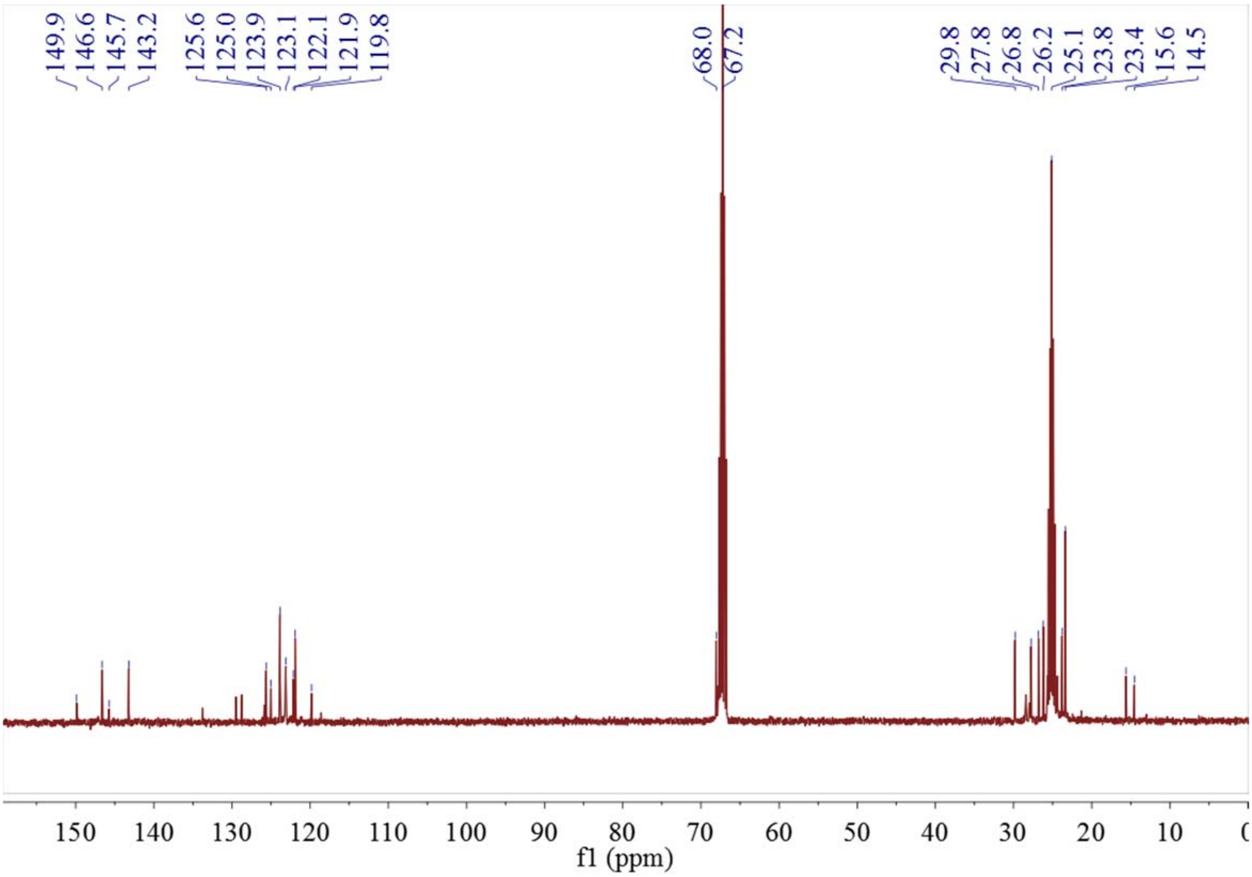


Fig. S12. ^{13}C NMR spectrum of complex **5** at 293 K in THF-d_8.

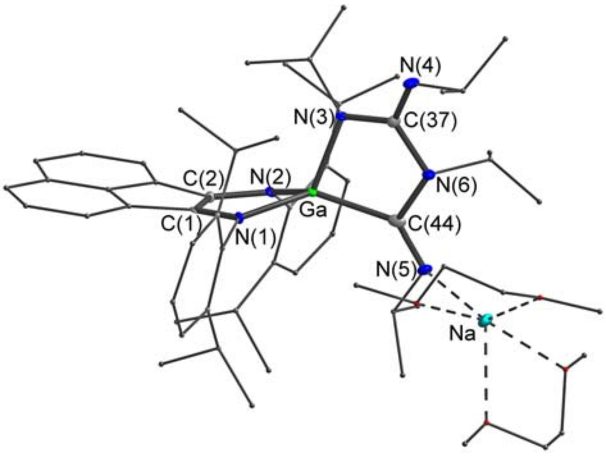


Fig. S13. Molecular structure of **4a**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): C(1)-C(2) 1.362(12), N(1)-C(1) 1.385(10), N(2)-C(2) 1.411(11), Ga(1)-N(1) 1.962(7), Ga(1)-N(2) 1.933(7), N(3)-C(37) 1.374(11), N(4)-C(37) 1.283(12), N(6)-C(37) 1.474(11), N(6)-C(44) 1.414(12), N(5)-C(44) 1.285(11), N(3)-Ga(1)-N(2) 116.7(3), N(3)-Ga(1)-N(1) 114.0(3), N(2)-Ga(1)-N(1) 89.7(3), N(3)-Ga(1)-C(44) 84.7(3), N(3)-C(37)-N(6) 112.9(7), N(5)-C(44)-Ga(1) 133.4(7), N(6)-C(44)-Ga(1) 108.1(6).

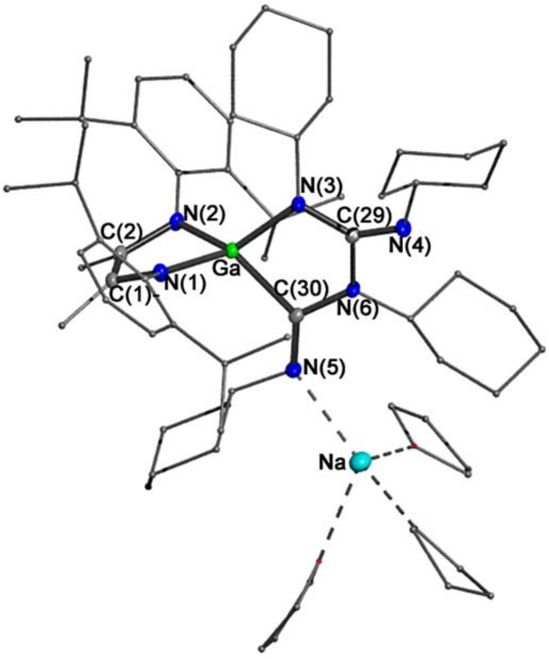


Fig. S14. Molecular structure of **4c**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): C(1)-C(2) 1.322(6), N(1)-C(1) 1.433(5), N(2)-C(2) 1.436(6), Ga(1)-N(1) 1.925(4), Ga(1)-N(2) 1.920(4), Ga(1)-N(3) 1.907(3), Ga(1)-C(30) 2.043(4), N(3)-C(29) 1.362(5), N(4)-C(29) 1.282(5), N(6)-C(29) 1.454(5), N(6)-C(30) 1.396(5), N(5)-C(30) 1.283(5), N(3)-Ga(1)-N(2) 123.09(16), N(3)-Ga(1)-N(1) 124.77(16), N(2)-Ga(1)-N(1) 87.68(16), N(1)-Ga(1)-C(30) 119.79(16), N(2)-Ga(1)-C(30) 119.88(17), N(3)-Ga(1)-C(30) 85.69(16), C(29)-N(3)-Ga(1) 113.9(3), N(3)-C(29)-N(6) 113.0(4), N(3)-C(29)-N(4) 133.9(4), N(4)-C(29)-N(6) 113.0(4), C(30)-N(6)-C(29) 118.2(4), N(5)-C(30)-N(6) 121.0(4), N(5)-C(30)-Ga(1) 133.2(3), N(6)-C(30)-Ga(1) 105.7(3).

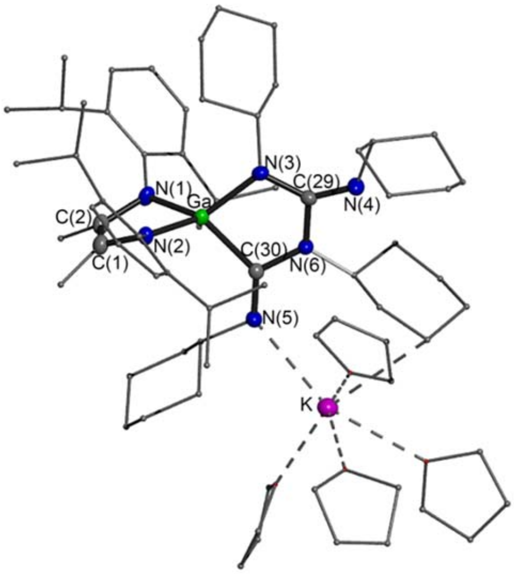


Fig.S15. Molecular structure of **4d**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): C(1)-C(2) 1.347(5), N(1)-C(1) 1.407(5), N(2)-C(2) 1.424(5), Ga(1)-N(1) 1.924(3), Ga(1)-N(2) 1.927(3), Ga(1)-N(3) 1.908(3), Ga(1)-C(30) 2.023(4), N(3)-C(29) 1.376(5), N(4)-C(29) 1.282(4), N(6)-C(29) 1.439(4), N(6)-C(30) 1.396(4), N(5)-C(30) 1.296(4), N(3)-Ga(1)-N(2) 123.58(13), N(3)-Ga(1)-N(1) 123.72(13), N(2)-Ga(1)-N(1) 87.32(12), N(1)-Ga(1)-C(30) 119.79(13), N(2)-Ga(1)-C(30) 120.86(13), N(3)-Ga(1)-C(30) 85.75(13), C(29)-N(3)-Ga(1) 113.8(2), N(3)-C(29)-N(6) 113.2(3), N(3)-C(29)-N(4) 133.8(3), N(4)-C(29)-N(6) 113.0(3), C(30)-N(6)-C(29) 118.6(3), N(5)-C(30)-N(6) 119.1(3), N(5)-C(30)-Ga(1) 134.3(3), N(6)-C(30)-Ga(1) 106.6(2).

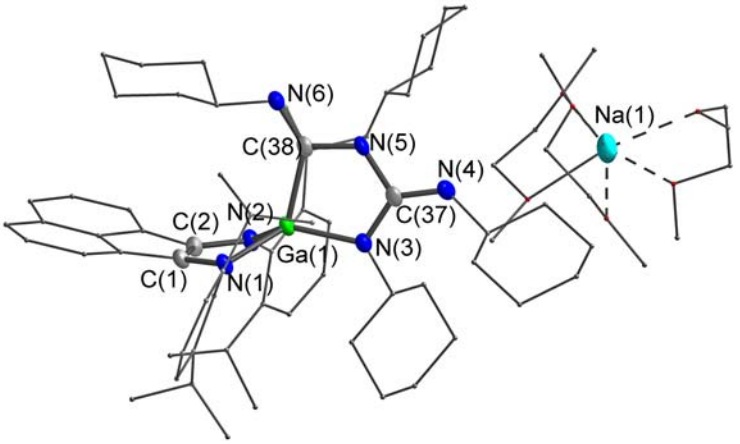


Fig.S16. Molecular structure of **4e**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): Ga(1)-N(3) 1.907(2), Ga(1)-N(1) 1.940(2), Ga(1)-N(2) 1.944(2), Ga(1)-C(38) 1.997(3), N(1)-C(1) 1.393(3), N(2)-C(2) 1.395(4), N(3)-C(37) 1.380(4), N(4)-C(37) 1.290(4), N(5)-C(38) 1.407(3), N(5)-C(37) 1.424(4), N(6)-C(38) 1.279(4), C(1)-C(2) 1.376(4), Ga(1)-N(3) 1.907(2), N(3)-Ga(1)-N(1) 122.15(10), N(3)-Ga(1)-N(2) 124.86(10), N(1)-Ga(1)-N(2) 88.73(9), N(3)-Ga(1)-C(38) 86.95(11), N(1)-Ga(1)-C(38) 119.81(11), N(2)-Ga(1)-C(38) 117.97(11), C(1)-N(1)-Ga(1) 102.98(17), C(2)-N(2)-Ga(1) 102.91(17), C(37)-N(3)-Ga(1) 113.07(19), C(38)-N(5)-C(37) 119.9(2), C(2)-C(1)-N(1) 118.9(2), C(1)-C(2)-N(2) 118.6(2), N(4)-C(37)-N(3) 132.1(3), N(4)-C(37)-N(5) 114.0(3), N(3)-C(37)-N(5) 113.9(2), N(6)-C(38)-N(5) 119.8(3), N(6)-C(38)-Ga(1) 134.1(2), N(5)-C(38)-Ga(1) 106.1(2), N(3)-Ga(1)-N(1) 122.15(10).

X-ray Crystal Structure Determination. For compounds **3**, **4a** and **4e** the X-ray diffraction data were collected on an Agilent Xcalibur E (**3**) and a Bruker D8 Quest (**4a**, **4e**) diffractometers (Mo-Kα radiation, λ = 0.71073 Å) then integrated using the CrysAlisPro[3] and SAINT[4] software respectively. The SCALE3 ABSPACK[5] (**3**) and SADABS[6] (**4a**) were used for absorption corrections. Structures of **3**, **4a** and **4e** were solved by dual-space method using the SHELXT[7] software and refined on F^2_{hkl} using SHELXTL[8] package. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and refined in the «riding model» with U_{iso}(H) = 1.2U_{eq} (U_{iso}(H) = 1.5U_{eq} for the hydrogen atoms in CH_3 groups) of their parent atoms. Crystals of **3** and **4a** contain solvate molecules of benzene disordered at the common and special positions. Ratios between the complex and benzene molecules in **3** and **4a** are 1:1.5 and 1:1 correspondingly. Crystals of **4e** contain disordered solvate molecules of DME and diethyl ether. Ratio between disordered species DME1:DME2:Et_2O in **4e** is 51:29:19.5. Cation in compound **4e** is disordered over two positions in the ratio 56:45. For compounds **4a**, **4b**, **4c**, **4d**, and **5**, Diffraction data were collected on a Bruker SMART APEX II diffractometer at 153 K with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction using SADABS was applied for all data.[6] The structures were solved and refined to convergence on F^2 for all independent reflections by the full-matrix least squares method using the SHELXL−2014 programs[7]. In **5**, about 2.0 molecules of toluene (about 1 toluene molecules per formula, Z = 2) are co-crystallized, with the corresponding electron density (142 electrons) being removed using the SQUEEZE routine implemented within the software program PLATON.[9] The main crystallographic data and structure refinement details for **3** and **4a** are presented in the Table S1. CCDC 1972892 (**3**), 1972891 (**4a**), 1987261 (**4b**), 1987262 (**4c**), 1987263 (**4d**), 1990314 (**4e**) and 1987264 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via ccdc.cam.ac.uk/s.

Table S1. Crystal data and structure refinement details for compounds **3**, **4a** and **4b**.

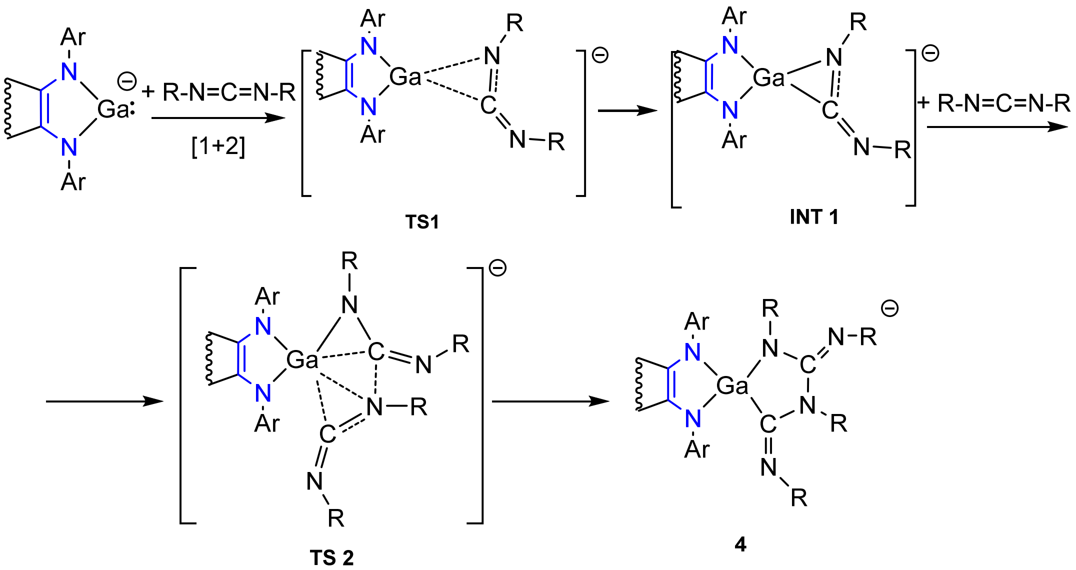
Compound	**3**	**4a**	**4b**
formula	$C_{72}H_{102}GaN_5NaO_4$	$C_{64}H_{94}GaN_6NaO_4$	$C_{54}H_{92}GaN_6NaO_3$
M_r [g mol^{-1}]	1194.29	1104.16	966.04
crystal system	Trigonal	Monoclinic	Monoclinic
space group	$R3c$	$P2_1$/n	$P2_1$/n
a [Å]	37.9555(3)	13.7559(16)	13.499(5)
b [Å]	37.9555(3)	18.926(2)	21.049(8)
c [Å]	26.2830(2)	24.235(3)	19.661(7)
α[°]	90	90	90
β [°]	90	104.957(4)	100.305(5)
γ[°]	120	90	90
V [Å^3]	32791.0(6)	6095.5(13)	5496(4)
Z	18	4	4
ρ_{calc}, [g cm^{-3}]	1.089	1.203	1.167
μ [mm^{-1}]	0.430	0.509	0.554
F(000)	11574	2376	2096
crystal size, [mm^3]	0.44 x 0.38 x 0.34	0.34 × 0.21 × 0.05	0.200 × 0.190 × 0.180
$\theta_{min}/\theta_{max}$ [°]	3.115 / 25.027	2.225 / 24.998	1.430 / 25.229

index ranges	$-45 \le h \le 45$ $-45 \le k \le 45$ $-31 \le l \le 31$	$-16 \le h \le 15$ $-22 \le k \le 19$ $-28 \le l \le 28$	$-16 \le h \le 16$ $-25 \le k \le 23$ $-22 \le l \le 23$
reflections collected	130158	33322	97692
independent reflections	12830	10442	9806
R_{int}	0.0381	0.1315	0.0805
max/min transmission	1.000/ 0.423	0.7453/ 0.2808	0.7452/ 0.1414
data/restraints/ parameters	12830 / 290 / 850	10442/ 116/ 724	9806 / 0 / 610
GOF on F^2	1.053	1.055	1.164
final R indices [$I>2\sigma(I)$]	0.0349 / 0.0947	0.1491 / 0.3109	0.0794 / 0.1980
R indices (all data)	0.0391 / 0.0979	0.2167 / 0.3468	0.0969 / 0.2123
largest diff. peak/hole [e Å^{-3}]	0.396 / –0.295	1.528 / –2.070	1.297 / -0.862

Table S2. Crystal data and structure refinement details for compounds **4c**, **4d**, **4e** and **5**.

Compound	**4c**	**4d**	**4e**	**5**
formula	$C_{66}H_{108}GaN_6NaO_3$	$C_{70}H_{116}GaN_6KO_4$	$C_{78}H_{124}GaN_6NaO_{7.51}$	$C_{68}H_{98}GaN_4NaO_2$
M_r [g mol^{-1}]	1126.29	1214.50	1358.69	1096.21
crystal system	Monoclinic	Monoclinic	Monoclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P\text{-}1$
a [Å]	20.165(5)	20.293(12)	13.7910(5)	13.577(2)
b [Å]	15.683(3)	13.197(8)	36.8339(13)	13.777(2)
c [Å]	22.026(5)	26.694(16)	15.0725(5)	18.806(3)
α[°]	90	90.000	90	83.432(2)
β [°]	109.960(3)	98.225(8)	93.0430(10)	89.491(2)
γ[°]	90	90.000	90	89.466(2)
V [Å^3]	6547(3)	7076(7)	7645.7(5)	3494.3(11)
Z	4	4	4	2
ρ_{calc}, [g cm^{-3}]	1.143	1.140	1.180	1.042
μ [mm^{-1}]	0.474	0.496	0.421	0.441
F(000)	2448	2640	2944	1184
crystal size, [mm^3]	0.350 × 0.200 × 0.200	0.250 × 0.200 × 0.190	0.354 × 0.297 × 0.285	0.250 × 0.250 × 0.200
$\theta_{min}/\theta_{max}$ [°]	1.686 / 24.761	1.542 / 25.140	2.141 / 27.999	1.741 / 25.005
index ranges	$-23 \le h \le 12$ $-18 \le k \le 18$ $-25 \le l \le 25$	$-24 \le h \le 24$ $-15 \le k \le 12$ $-31 \le l \le 31$	$-18 \le h \le 18$ $-48 \le k \le 48$ $-19 \le l \le 19$	$-16 \le h \le 16$ $-16 \le k \le 14$ $-22 \le l \le 22$
reflections collected	28859	43943	108804	21866
independent reflections	11048	12467	18399	11929
R_{int}	0.0906	0.0586	0.0548	0.0352
max/min transmission	0.7452 / 0.2565	0.7452 / 0.4133	0.9011 / 0.7937	0.7452 / 0.4393
data/restraints/ parameters	11048 / 0 / 706	12467 / 0 / 749	18399 / 387 / 1130	11929 / 0 / 631
GOF on F^2	1.066	1.126	1.074	1.170
final R indices [$I>2\sigma(I)$]	0.0645 / 0.1291	0.0597 / 0.1619	0.0709 / 0.1807	0.0662 / 0.1606
R indices (all data)	0.1342 / 0.1525	0.1047 / 0.1903	0.1072 / 0.1990	0.0824 / 0.1658
largest diff. peak/hole [e Å^{-3}]	0.581 / -0.351	0.547 / -0.377	1.045 / -0.563	0.704 / -0.414

DFT computations. The model compounds where the 2,6-diisopropylphenyl groups on the nitrogen atoms were replaced by phenyl groups and the THF or DME molecules by H_2O, were used for the products **3**–**5** in the DFT computations. The structure optimization and NBO bonding analysis for the model compounds **3H**–**5H** were carried out at the DFT (B3LYP) level with the 6-31G* basis sets using the Gaussian 09 program.[10] The B3LYP method is a hybrid of the HF and DFT methods, incorporating Becke's three-parameter exchange functional (B3)[11] with the Lee, Yang, and Parr (LYP) correlation functional. Geometry optimizations gave bond distances that were in good agreement with the X-ray structures. Bonding analyses were performed by means of natural bond orbital (NBO) analysis and natural population analysis (NPA). Wiberg bond indices (WBI) were evaluated with Weinhold's natural bond orbital method.[12,13] The reductive coupling of diisopropylcarbodiimide (DIC) with $[(\text{dpp-dad})\text{Ga}]^-$ (Fig. S17) was chosen as the model reaction. Gaussian 09 software package was utilized for all the gas-phase optimization, harmonic vibrational frequency and solvent calculations. The frequency calculations were performed to ensure that one imaginary frequency for all transition states and no imaginary frequencies for all local minima.



Scheme S1. Possible mechanism for the reaction of gallylenes with carbodiimides.

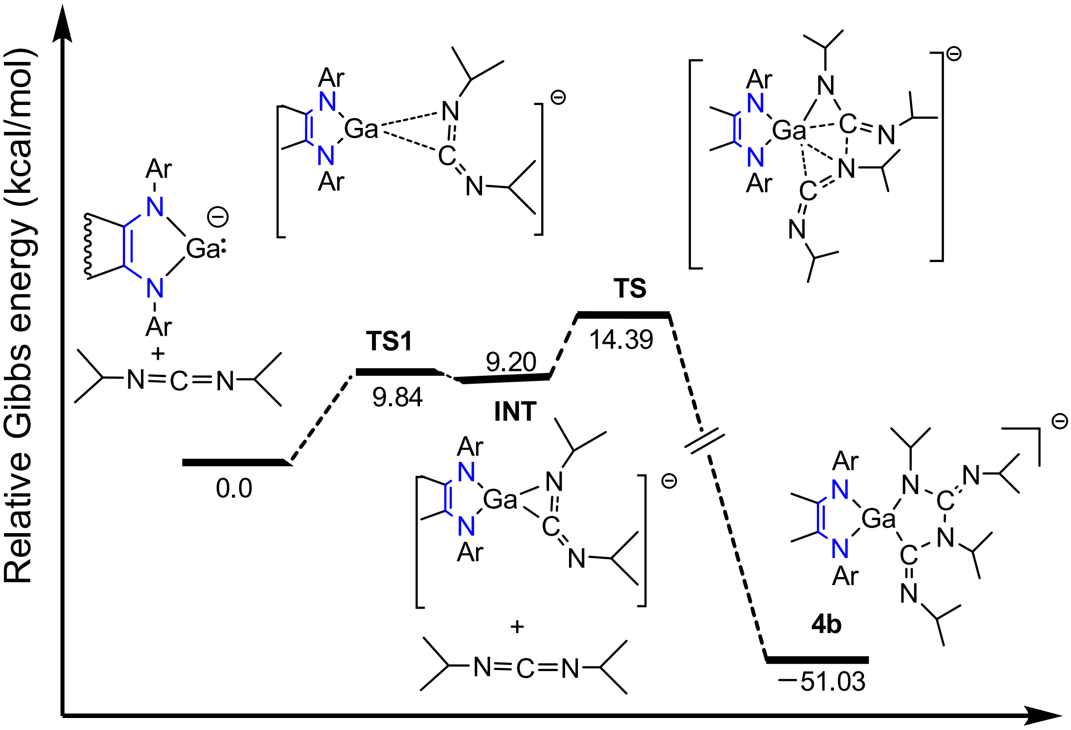
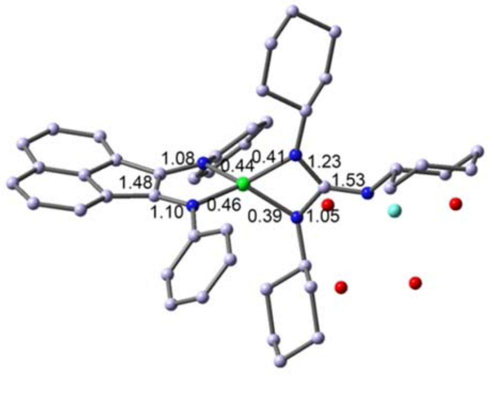
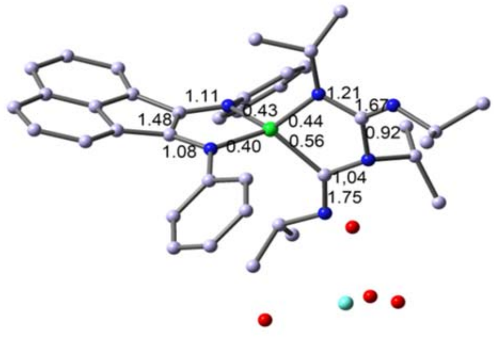


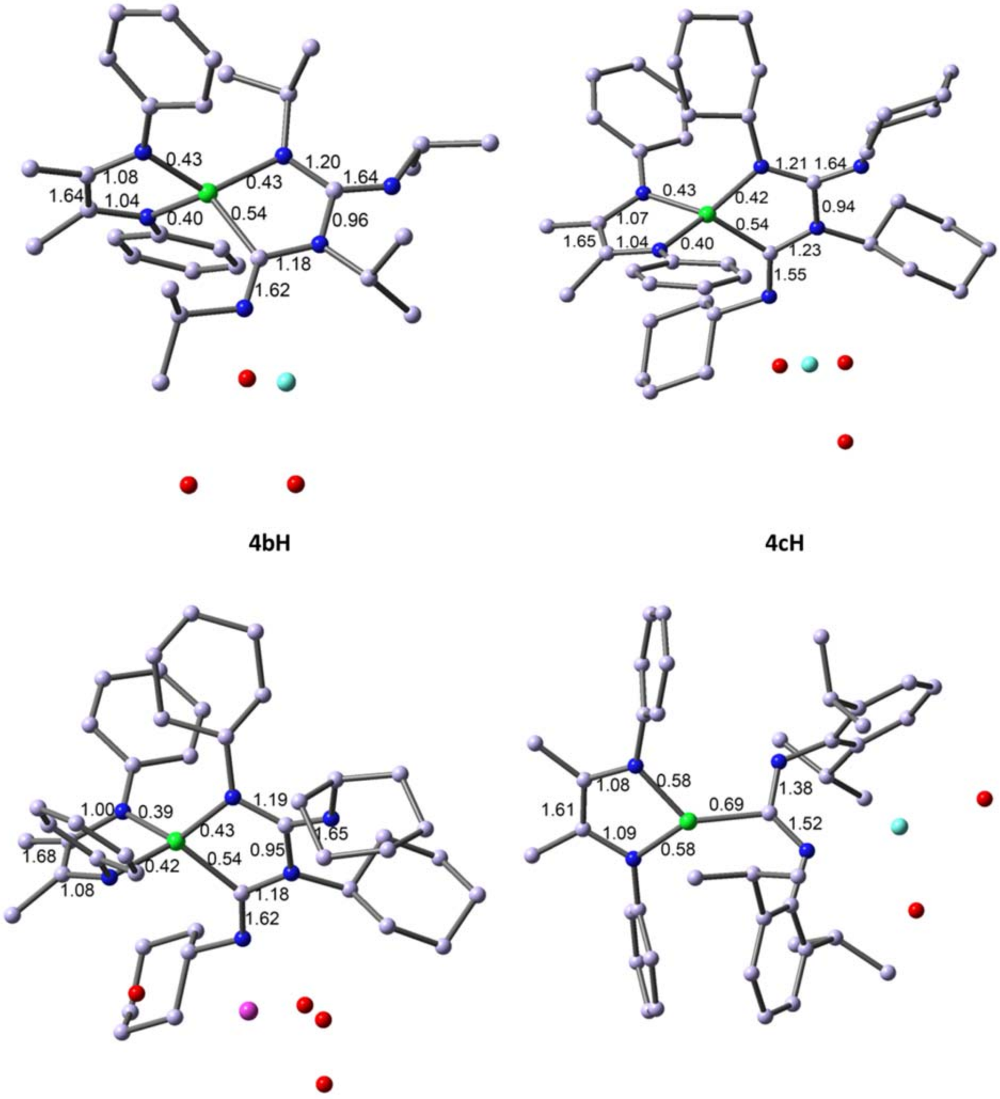
Fig. S17. Energy profile (kcal/mol) for the reaction of **2a** + *i*PrN=C=N*i*Pr + *i*PrN=C=N*i*Pr inclusion of solvent effect and dispersion effects.



3H



4aH



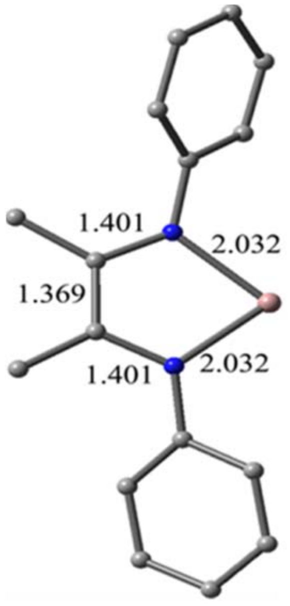
4bH **4cH**

4dH **5H**

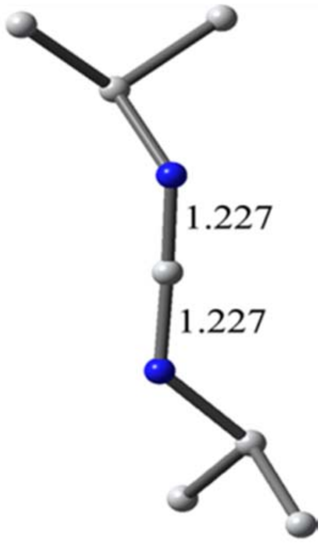
Fig. S18. Optimized structures of **3H**, **4aH**, **4bH**, **4cH**, **4dH** and **5H** labelled with selected bond orders.

Table S3. Natural charges (e) of the model compounds **3**, **4a**, **4b**, **4c**, **4d** and **5**.

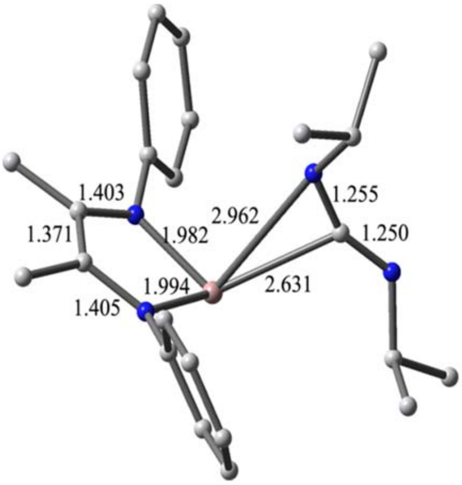
Compound	**3**	**4a**	**4b**	**4c**	**4d**	**5**
Ga	1.7642	1.6428	1.6670	1.6694	1.6763	1.4556
L	−1.3339	−1.3467	−1.3475	−1.3465	−1.3365	−1.1157
(*N*N*C*)$_2$	−1.2925	−1.1360	−1.2260	−1.1762	−1.1946	−1.2617,



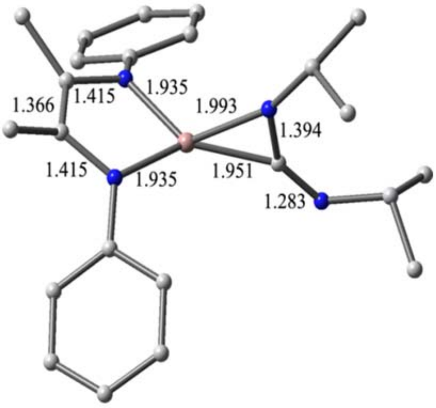
2a



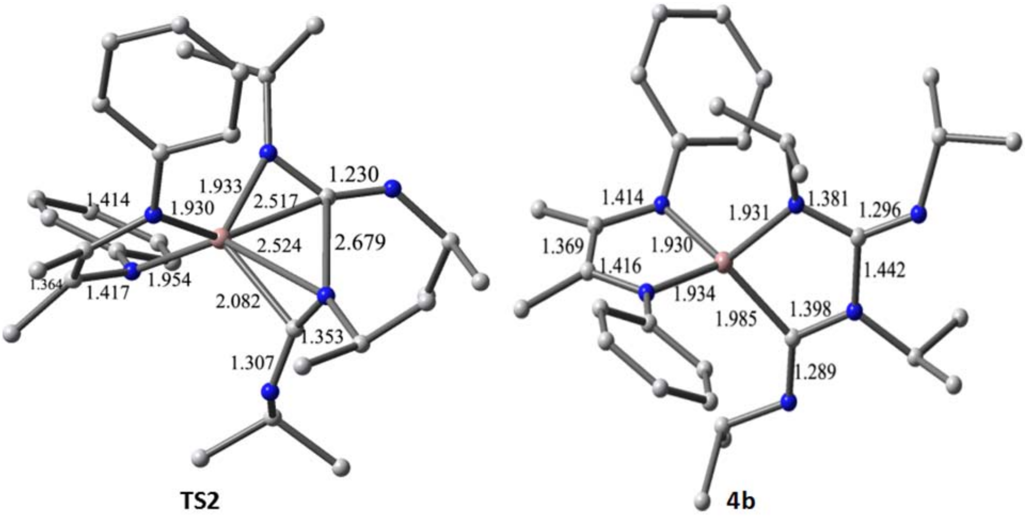
DIC



TS1



INT



TS2 **4b**

Fig. S19. The optimized structures with bond lengths (the hydrogen atoms omitted for clarity) of stationary points for **2a** + (iPrN)$_2$C + (iPrN)$_2$C, obtained with B3LYP/6-31G* method.

Table S4. The energies, enthalpies, free energies, zero-point (vibrational) energy (ZPE) and corresponding relative values (au) for conversion of **2a** to **4b**, obtained with B3LYP/6-31G* method

species	E	H	G	E_{Sol}	ΔG
2a	–2651.558292	–2651.557348	–2651.623011	–2651.92881273	0.232883
DIC	–384.450459	–384.449515	–384.499923	–384.683310166	0.166466
TS1	–3036.005522	–3036.004578	–3036.099002	–3036.61717519	0.420282
INT	–3036.005775	–3036.004831	–3036.099108	–3036.61715353	0.419250
TS2	–3420.457362	–3420.456418	–3420.576058	–3421.31748575	0.611190
4b	–3420.555385	–3420.554441	–3420.671609	–3421.43148327	0.620915

References

1. I. L. Fedushkin, A. N. Lukoyanov, A. N. Tishkina, G. K. Fukin, K. A. Lyssenko and M. Hummert, *Chem. Eur. J.*, 2010, **16**, 7563–7571.

2. Y. Liu, S. Li, X.-J. Yang, Q.-S. Li, Y. Xie, H. F. Schaefer and B. Wu, *J. Organomet. Chem.*, 2011, **696**, 1450–1455.

3. Data Collection, Reduction and Correction Program, CrysAlisPro 1.171.38.46 - Software Package, Rigaku OD, 2015.

4. Bruker (2017) SAINT Data Reduction and Correction Program v. 8.38A, Bruker AXS, Madison, Wisconsin, USA.

5. SCALE3 ABSPACK: Empirical absorption correction, CrysAlisPro 1.171.38.46 - Software Package, Rigaku OD, 2015.

6. G.M. Sheldrick (2016). SADABS v.2016/2, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, USA.

7. G.M. Sheldrick, *Acta Cryst*., 2015, **A71**, 3–8.

8. G.M. Sheldrick, SHELXTL. Version 6.14. Structure Determination Software Suite; Madison (WI, USA): Bruker AXS, 2003.

9. A. L. Spek, *Acta Cryst.*, 2015, **C71**, 9–18.

10. 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, 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., Jr. Montgomery, 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, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

11. A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648–5652.

12. K. B. Wiberg, Tetrahedron, 1968, **24**, 1083–1096.

13. A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.*, 1988, **88**, 899–926.