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Reactions of ytterbium and magnesium gallylene complexes with carbon dioxide and diphenylketene

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Experimental Section

All manipulations were carried out in vacuum or under argon (nitrogen) using standard Schlenk technique or under argon (nitrogen) atmosphere in a drybox. The solvents were dried using appropriate methods and were distilled in vacuum prior to use. Digallane [(dpp-bian)Ga−Ga(dpp-bian)][S1] (dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene).[S2] All other chemicals were purchased and used without further purification. IR spectra were recorded on FSM-1201 spectrometers in Nujol. Elemental analyses were carried out on an Elementar Vario mirco cube. NMR spectra were recorded on Bruker Advance NEO (300 MHz) or Advance III (400 MHz) spectrometers and were referenced to the residual signals of deuterated solvents. Abbreviations used: Ar - aromatic, d - doublet, m - multiplet, t - triplet, s - singlet, br - broad, sept - septet.

Synthesis of 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene gallium methanide 1,2-dimethoxyethanate (3). A solution of $[(dpp\text{-}bian)Ga]_2$ (0.607 g, 0.5 mmol) in 1,2-dimethoxyethane (30 ml) was added to an excess of freshly activated ytterbium metal. The mixture was heated and stirred vigorously at 60 °C for 4 h. The color of the solution changed to green. The excess of metal was filtered off. Carbon dioxide (1 mmol, 25 °C, 25 ml, 1 atm) was added to the obtained solution at -35 °C. The color of the solution became blue-green within 10 min. Slow concentration and keeping the solution at -35 °C gave light-blue crystals of the compound **3**. Yield 0.190 g, 26%. IR (cm^{-1}) 465 VW, 509 VW, 542 W, 625 W, 685 W, 752 S, 758 S, 770 M, 787 M, 795 M, 818 M, 835 W, 860 M, 885 VW, 918 M, 926 M, 938 W, 978 VW, 1001 W, 1051 S, 1109 M, 1159 W, 1188 M, 1208 W, 1252 S, 1302 S, 1362 M, 1431 S, 1518 W, 1586 M, 1611 W, 1642 W, 1653 W, 1671 M. Elemental analysis for $C_{43}H_{58}GaN_2O_3$ (824.76), calc. C 71.67, H 8.11, N 3.89 %; found C 71.41, H 8.27, N 3.67 %.

Synthesis of gallium 1-((2*E*)-1-((2,6-di(propan-2-yl)phenyl)amido)-2-((2,6-di(propan-2-yl)phenyl)imino)-1,2-dihydroacenaphthylen-1-yl)-2,2-diphenylethenolate methanide (4). A solution of $[(dpp\text{-}bian)Ga]_2$ (0.607 mg, 0.5 mmol) in 1,2-dimethoxyethane (30 ml) was added to an excess of freshly activated magnesium metal. The mixture was heated and stirred vigorously

at 60 °C for 4h. The color of the solution changed to green. The excess of metal was filtered off. The obtained solution was treated with Ph_2CCO (0.194 g, 1 mmol). The color of the solution became yellow-green. Slow concentration of the obtained solution gave light-orange crystals of the compound **4**. Yield 0.210 g, 25%. IR (cm^{-1}) 465 VW, 548 VW, 571 W, 600 W, 700 M, 752 M, 779 W, 804 W, 816 VW, 835 W, 938 W, 974 W, 1032 W, 1057 VW, 1073 W, 1115 W, 1154 VW, 1190 W, 1215 W, 1254 W, 1273 VW, 1590 M, 1624 M. ^{1}H NMR (400 MHz, C_6D_6), 7.84 (dd, J = 8.5, 1.3 Hz, 2H), 7.30 (t, J = 7.8, 2H), 6.95 (t, J = 7.8 Hz, 2H), 6.88 (dd, J = 7.8, 5.2 Hz, 2H), 6.79 (t, J = 7.6 Hz, 1H), 6.73 (d, J = 7.1 Hz, 1H), 6.43 (d, J = 7.8 Hz, 1H), 6.11 (d, J = 7.0 Hz, 1H), 5.96 (br. s, 1H), 5.78 (br. s, 1H), 4.71 (sept, J = 6.8 Hz, 1H, C*H*Me$_2$), 3.52 (sept, J = 6.8 Hz, 1H, C*H*Me$_2$), 3.16 (sept, J = 6.8 Hz, 1H, C*H*Me$_2$), 3.01 (sept, J = 6.9 Hz, 1H, C*H*Me$_2$), 1.76 (d, J = 6.8 Hz, 3H, C*H*$_3$CH), 1.53 (d, J = 7.1 Hz, 3H, C*H*$_3$CH), 1.19 (d, J = 7.2 Hz, 3H, C*H*$_3$CH), 1.11 (d, J = 6.8 Hz, 6H, C*H*$_3$CH), 0.89 (d, J = 7.1 Hz, 3H, C*H*$_3$CH), 0.86 (d, J = 6.8 Hz, 3H, C*H*$_3$CH), 0.08 (s, 3H, CH_3-Ga), -0.13 (d, J = 7.0 Hz, 3H, C*H*$_3$CH). 1H NMR (300 MHz, THF-d_8) 7.93 (d, J = 8.1 Hz, 1H), 7.49 – 7.34 (m, 6H), 7.13 – 6.98 (m, 3H), 6.73 (d, J = 8.1 Hz, 3H), 6.67 (d, J = 7.8 Hz, 1H), 6.50 (t, J = 7.6 Hz, 1H), 5.90 (d, J = 7.2 Hz, 1H), 4.44 (sept, J = 6.8 Hz, 1H, C*H*Me$_2$), 3.29 (sept, J = 6.8 Hz, 1H, C*H*Me$_2$), 3.10 (sept, J = 6.8 Hz, 1H, C*H*Me$_2$), 2.86 (sept, J = 6.8 Hz, 1H, C*H*Me$_2$), 1.60 (d, J = 6.8 Hz, 3H, C*H*$_3$CH), 1.36 (d, J = 6.8 Hz, 3H, C*H*$_3$CH), 1.21 (d, J = 6.8 Hz, 3H, C*H*$_3$CH), 1.09 (d, J = 6.8 Hz, 3H, C*H*$_3$CH), 0.92 (d, J = 6.8 Hz, 3H, C*H*$_3$CH), 0.88 (d, J = 7.0 Hz, 3H, C*H*$_3$CH), 0.79 (d, J = 6.8 Hz, 3H, C*H*$_3$CH), 0.23 (s, 3H, CH_3-Ga), -0.32 (d, J = 6.8 Hz, 3H, C*H*$_3$CH). ^{13}C NMR (75 MHz, 298 K, THF-d_8) 185.3 (C=N), 151.0, 150.5, 149.3, 144.7, 144.2, 143.1, 142.6, 141.5, 140.3, 138.9, 136.0, 132.1, 131.1, 129.2, 129.1, 128.2, 127.7, 126.9, 126.4, 126.1, 125.5, 125.0, 124.0, 123.3, 122.5, 122.3, 117.5, 81.2 (C-N), 28.5 (*C*HMe$_2$), 28.1 (*C*HMe$_2$), 28.0 (*C*HMe$_2$), 27.2 (*C*HMe$_2$), 25.9 (CH*C*H$_3$), 24.9 (CH*C*H$_3$), 24.5 (CH*C*H$_3$), 23.7 (CH*C*H$_3$), 23.9 (CH*C*H$_3$), 23.3 (CH*C*H$_3$), 22.8 (CH*C*H$_3$), 20.4 (CH*C*H$_3$), -14.9 (CH_3-Ga). Elemental analysis $C_{53}H_{58}GaN_2O_2$ (824.76), calc. C 77.18, H 7.09, N 3.39 %; found C 77.02, H 6.84, N 3.16 %.

References

[S1] I. L. Fedushkin, A. N. Lukoyanov, A. N. Tishkina, G. K. Fukin, K. A. Lyssenko, M. Hummert, *Chem. Eur. J.* **2010**, *16*, 7563-7571.

[S2] I. L. Fedushkin, V. G. Sokolov, V. M. Makarov, A. V. Cherkasov, G. A. Abakumov, *Russ. Chem. Bull.* **2016**, *65*, 1495-1504.

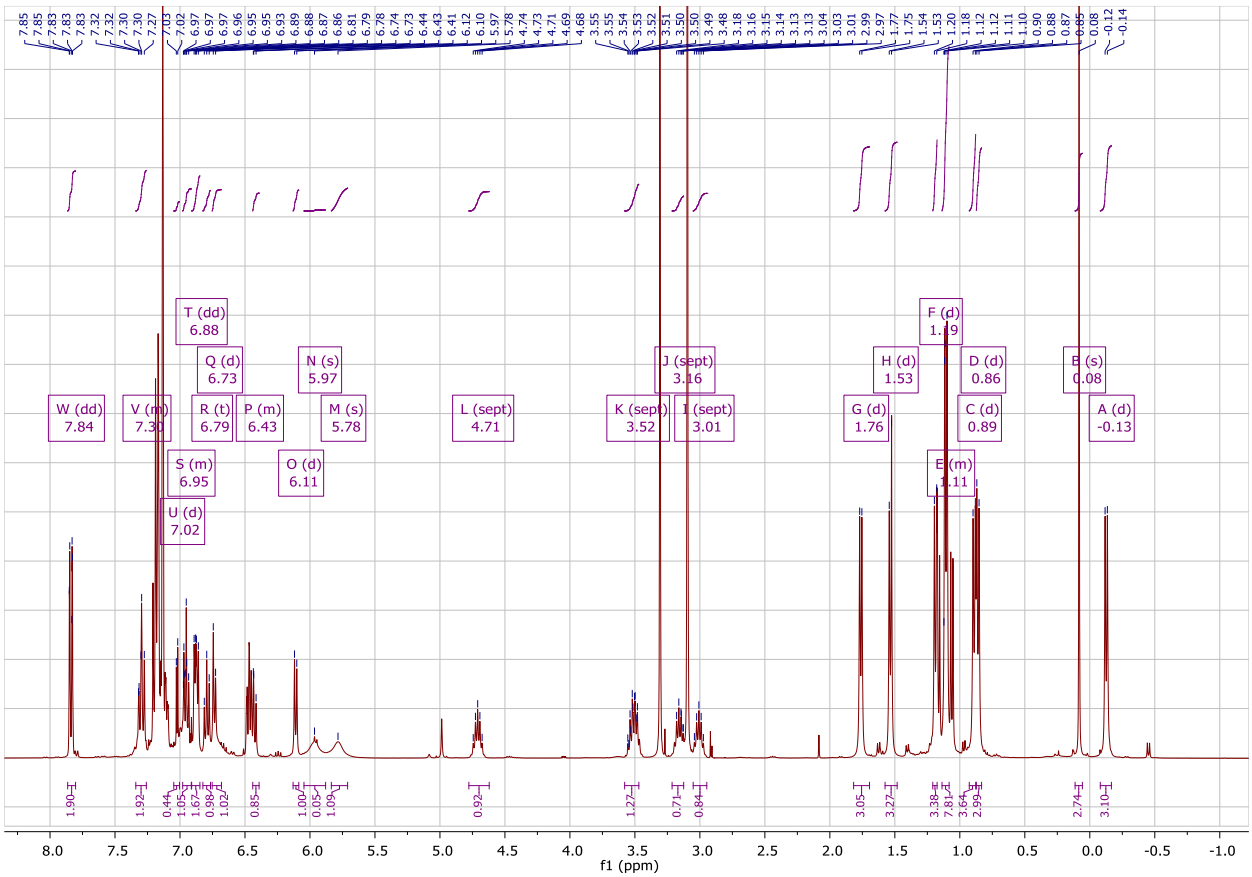

Figure S1. ^{1}H NMR spectrum of **4** at 298 K in C_6D_6.

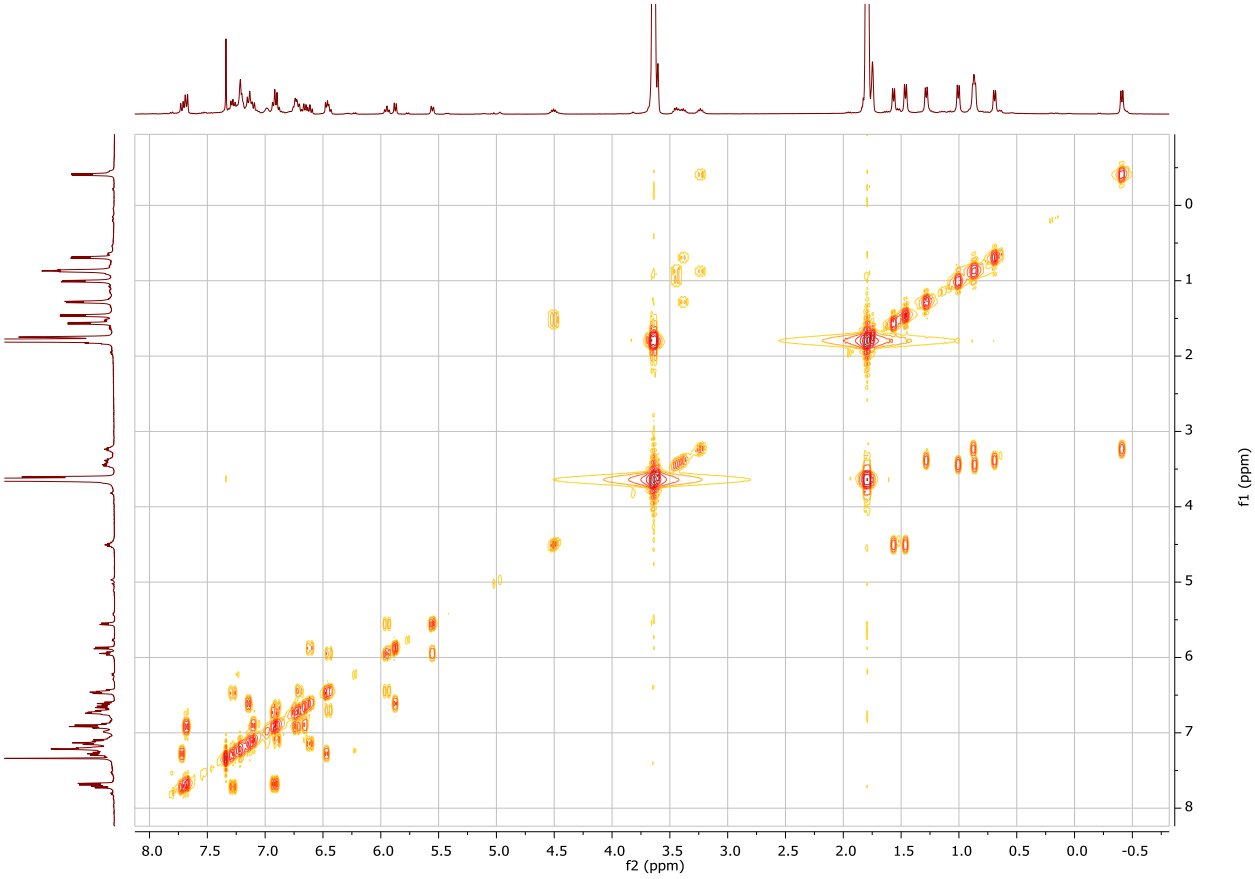

Figure S2. ^{1}H–^{1}H COSY NMR spectrum of **4** at 298 K in C_6D_6.

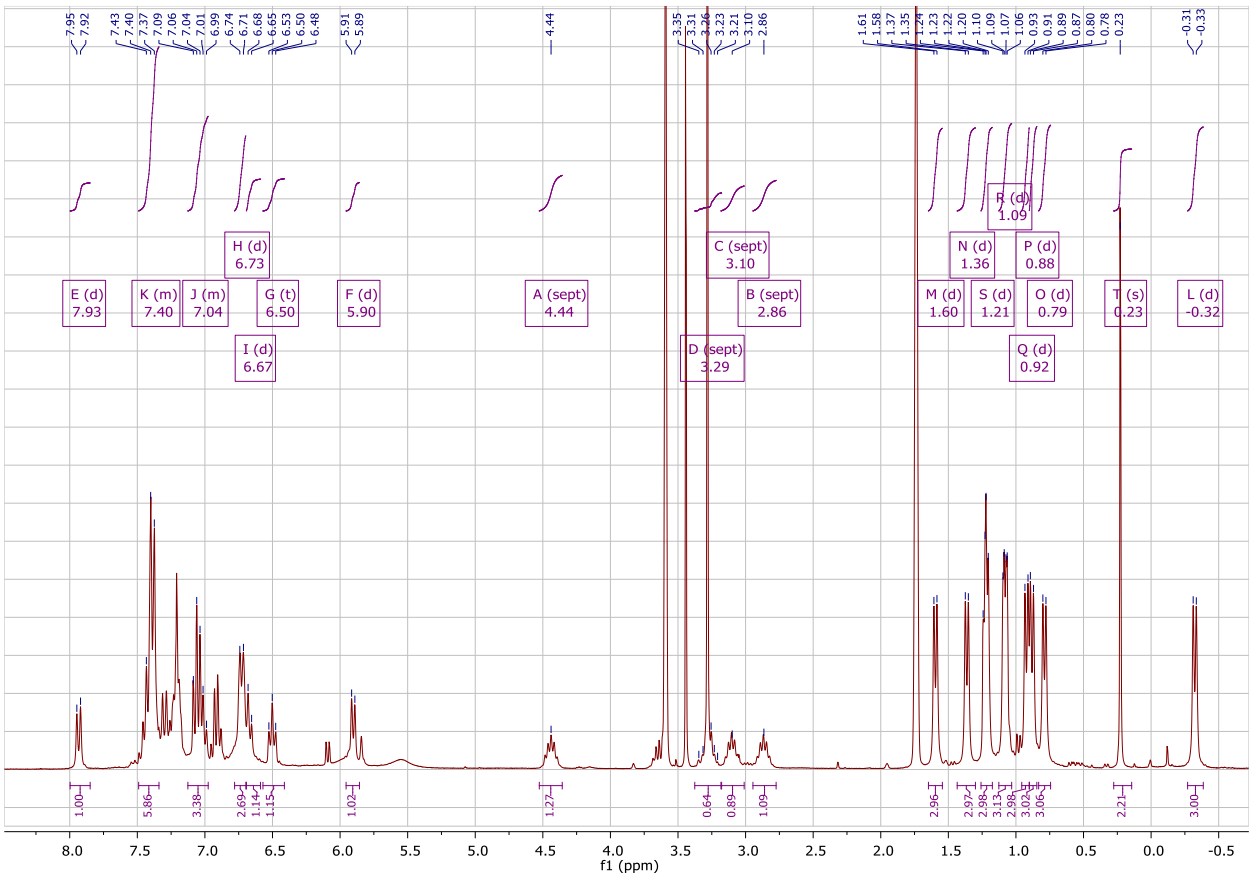

Figure S3. ^{1}H NMR spectrum of **4** at 298 K in THF-d_8.

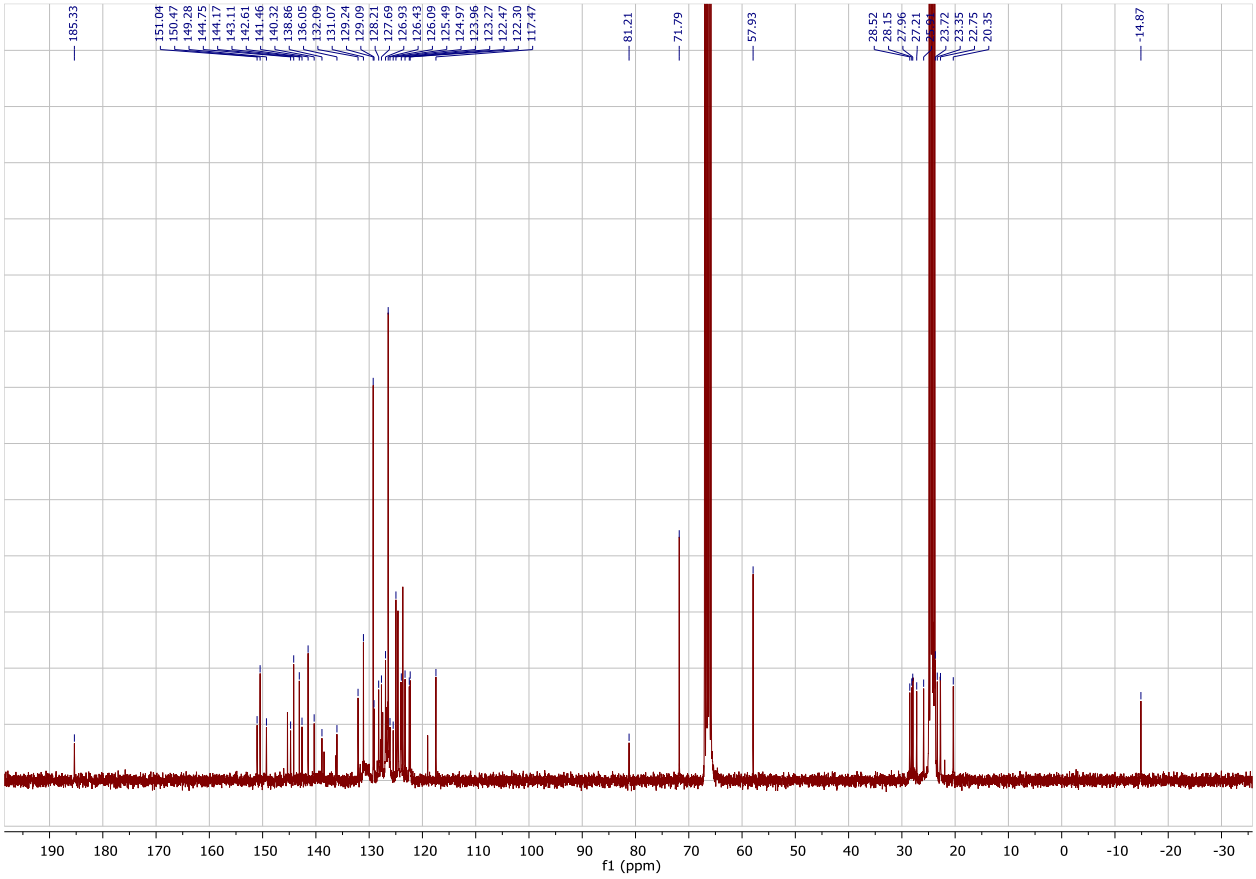

Figure S4. ^{13}C NMR spectrum of **4** at 298 K in THF-d_8.

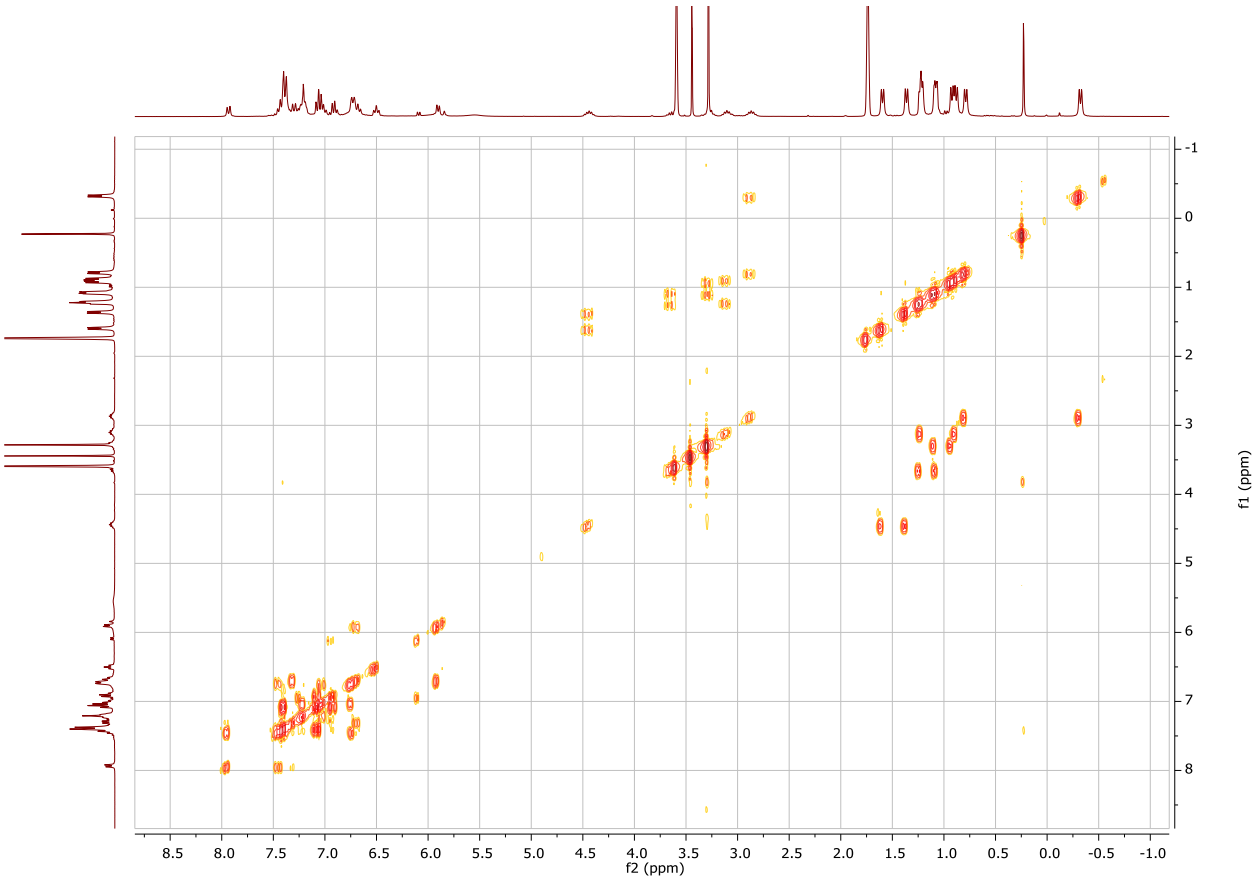

Figure S5. $^{1}H–^{1}H$ COSY NMR spectrum of **4** at 298 K in THF-d_8.

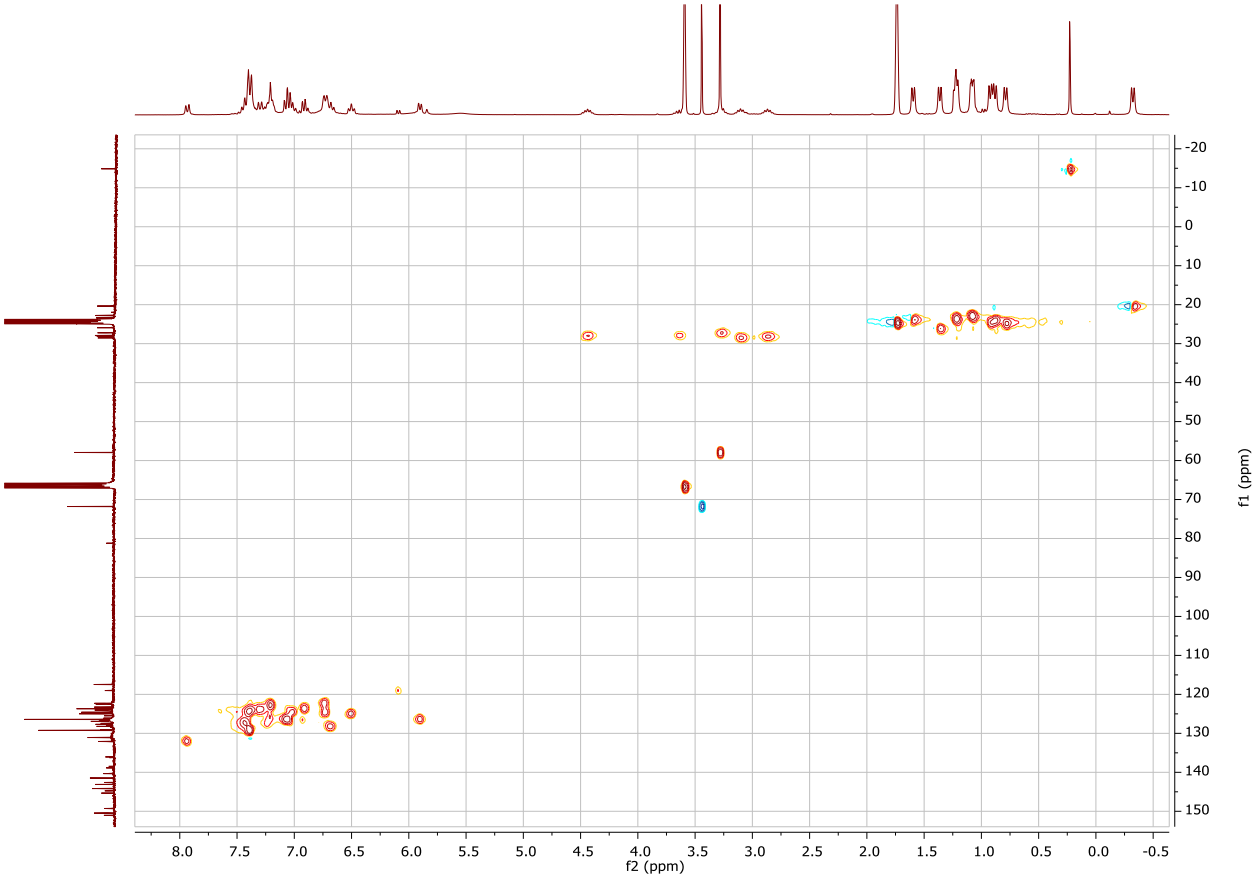

Figure S6. $^{1}H–^{13}C$ HSQC NMR spectrum of **4** at 298 K in THF-d_8.

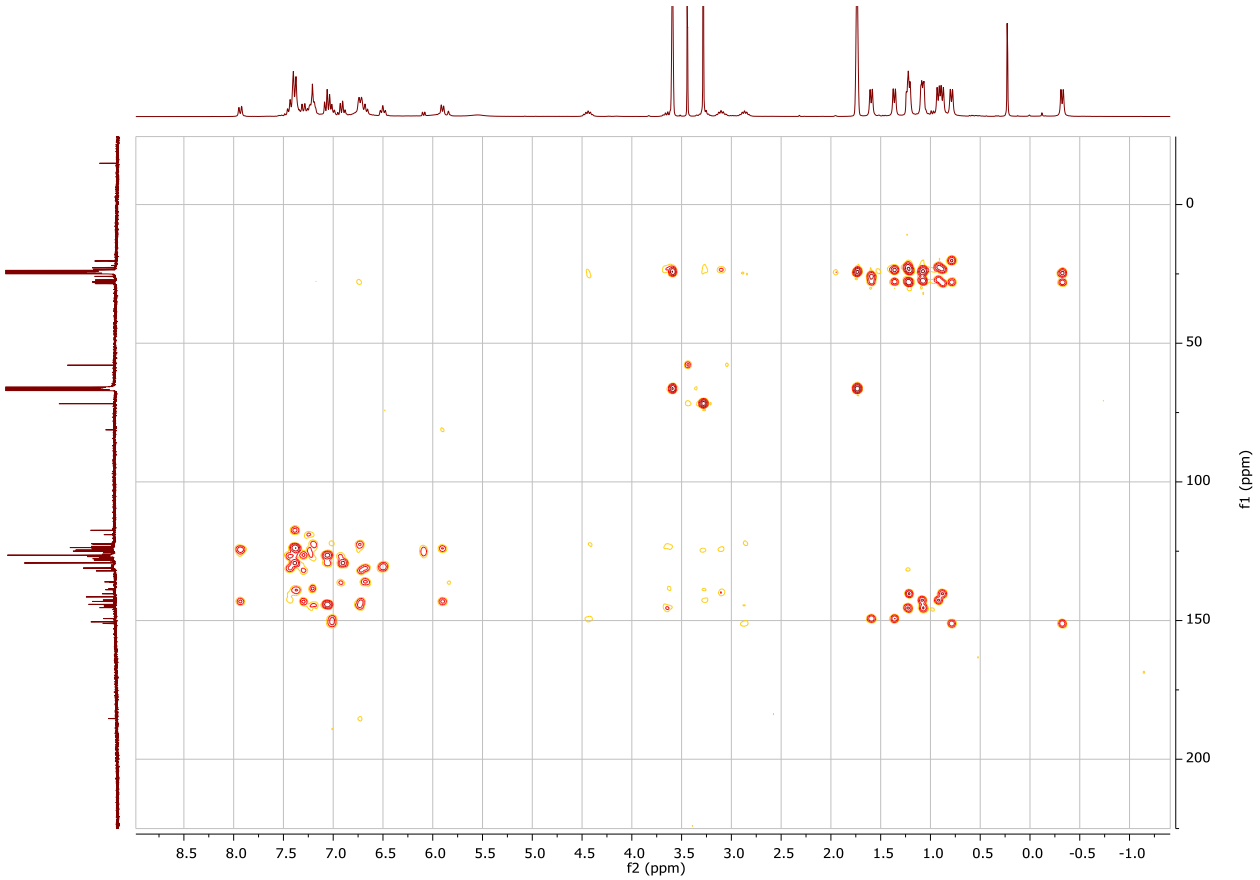

Figure S6. ^{1}H–^{13}C HMBC NMR spectrum of **4** at 298 K in THF-d_8.

X-ray Crystal Structure Determination.

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

Compound	**3**	**4**
formula	$C_{43}H_{58}GaN_2O_3$	$C_{53}H_{58}GaN_2O_2$
M_r [g mol^{-1}]	720.63	824.73
crystal system	Monoclinic	Triclinic
space group	P2(1)/c	P-1
a [Å]	10.3594(2)	10.3097(3)
b [Å]	24.2428(4)	12.3361(4)
c [Å]	15.8450(2)	19.5856(6)
α[°]	90	79.234(3)
β [°]	102.977(2)	85.282(3)
γ[°]	90	65.649(3)
V [Å^3]	3877.70(11)	2229.34(13)
Z	4	2
ρ_{calc}, [g cm^{-3}]	1.234	1.229
μ [mm^{-1}]	1.274	1.161
F(000)	1540	874
crystal size, [mm^3]	0.586 × 0.196 × 0.130	0.268 × 0.196 × 0.042
$\theta_{min}/\theta_{max}$ [°]	3.394 / 73.625	2.296 / 73.707
index ranges	-12 ≤ h ≤ 8, -29 ≤ k ≤ 24, -19 ≤ l ≤ 19	-11 ≤ h ≤ 12, -13 ≤ k ≤ 15, -23 ≤ l ≤ 24
reflections collected	15817	15797
independent reflections	7615	8706
R_{int}	0.0202	0.0277
max/min transmission	1.00000/ 0.65863	1.00000/ 0.65131
data/restraints/ parameters	7615 / 3 / 465	8706 / 0 / 554
GOF on F^2	1.085	1.092
final *R* indices [I>2σ (I)]	0.0366 / 0.0976	0.0381 / 0.0966
R indices (all data)	0.0419 / 0.1016	0.0418 / 0.0995
largest diff. peak/hole [e Å^{-3}]	0.447 / -0.497	0.840 / -0.727

Table S2. Selected bond lengths (Å) and angles (°) in compounds **3** and **4**.

	3	**4**
Ga(1)-N(2)	1.9019(14)	1.8769(15)
Ga(1)-N(1)	1.9000(14)	2.0879(13)
Ga(1)-C(37)	1.9406(18)	1.930(2)
Ga(1)-O(1)	2.1050(13)	1.8969(11)
N(2)-C(2)	1.400(2)	1.473(2)
N(1)-C(1)	1.394(2)	1.285(2)
C(2)-C(1)	1.376(2)	1.555(2)
O(1)-C(38)		1.342(2)
C(39)-C(38)		1.358(2)
C(38)-C(2)		1.577(2)
N(2)-Ga(1)-O(1)	99.79(6)	89.68(5)
N(2)-Ga(1)-C(37)	132.59(8)	139.58(8)
N(1)-Ga(1)-O(1)	101.30(6)	87.36(5)
N(1)-Ga(1)-N(2)	90.82(6)	85.16(6)
N(1)-Ga(1)-C(37)	125.87(8)	118.67(8)
C(37)-Ga(1)-O(1)	100.62(7)	121.28(8)
C(2)-N(2)-Ga(1)	106.00(11)	97.52(10)
C(1)-N(1)-Ga(1)	106.27(11)	102.82(10)
C(1)-C(2)-N(2)	118.42(15)	105.58(12)
C(2)-C(1)-N(1)	118.47(15)	116.78(14)
C(38)-O(1)-Ga(1)		108.94(9)
O(1)-C(38)-C(39)		121.61(15)
O(1)-C(38)-C(2)		110.60(13)
C(39)-C(38)-C(2)		127.09(15)
N(2)-C(2)-C(38)		108.81(13)
C(1)-C(2)-C(38)		99.61(12)