Supporting information to the article

1,3-C–H Bond Activation on a Transient Gallium(I)/isocyanate adduct

by

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Content:

Synthetic Methods

General:
All manipulations were performed using standard inert atmosphere (N_2 gas) glovebox and Schlenk techniques. Toluene was dried using a Grubbs-type solvent purification system. Benzene-d_6 was pre-dried and distilled from K/Na alloy and stored in a glass vessel in the glovebox. NMR spectra were obtained with a Bruker AVANCE III HD 400 and 600 MHz spectrometers (^{1}H, 400 and 600 MHz; ^{13}C, 101 and 151 MHz; ^{11}B, 128 MHz, ^{31}P 162 and 243 MHz) at room temperature, unless stated otherwise, then processed and analyzed with MestReNova software (v10.0.2-15465). ^{11}B NMR spectra were processed with the broadening of 30 Hz and with backward linear prediction using built in Topspin processing parameters. All reagents were purchased from Sigma Aldridge and Alfa Aesar and used as received. Compound NacNacGa was prepared according to a literature procedure.[1]

Preparation of NacNacGa(py-O)(OCNHPh) (6). A mixture of pyridine oxide (0.019 g, 0.19 mmol) and PhNCO (0.021 mL, 0.19 mmol) in toluene was treated with one equivalent of NacNacGa (0.095 g, 0.19 mmol) at room temperature. The solvent was removed by reduced pressure, and the residue was redissolved in diethyl ether. Crystallization at -30℃ afforded **6** in the form of yellow crystals ((yield 43%).

^{1}H NMR (400 MHz, C_6D_6) δ 10.59 (s, 1H, $C_6H_5N\mathit{H}$), 8.08 (d, 2H, $C_6\mathit{H}_5NH$, $^{3}J_{H\text{-}H}$ = 7.5), 7.39 (d, 1H, C_5H_4N, $^{3}J_{H\text{-}H}$ = 5.5 Hz), 7.13 (m, 2H, $C_6\mathit{H}_5NH$), 7.12 (m, 1H, C_6H_3), 7.11 (m, 2H, C_6H_3), 7.03 (dd, 2H, C_6H_3, $^{3}J_{H\text{-}H}$ = 5.9 Hz, $^{3}J_{H\text{-}H}$ =2.3 Hz), 6.85 (t, 1H, $C_6\mathit{H}_5NH$, $^{3}J_{H\text{-}H}$ = 7.3Hz), 6.25 (b, 1H, C_5H_4N), 6.14 (t, 1H, C_5H_4N, $^{3}J_{H\text{-}H}$ =7.3 Hz), 5.95(b, 1H, C_5H_4N), 3.92 (hept, 2H, $C\mathit{H}(CH_3)_2$, $^{3}J_{H\text{-}H}$ = 7.0 Hz), 3.33 (hept, 2H, $C\mathit{H}(CH_3)_2$, $^{3}J_{H\text{-}H}$ = 6.8 Hz), 1.68 (s, 6H, $NCCH_3$), 1.34 (d, 6H, $CH(C\mathit{H}_3)_2$, $^{3}J_{H\text{-}H}$ = 6.8 Hz), 1.20 (d, 6H, $CH(C\mathit{H}_3)_2$, $^{3}J_{H\text{-}H}$ = 6.8 Hz), 1.11 (d, 6H, $CH(C\mathit{H}_3)_2$, $^{3}J_{H\text{-}H}$ = 6.8 Hz), 0.96 (d, 6H, $CH(C\mathit{H}_3)_2$, $^{3}J_{H\text{-}H}$ = 6.8 Hz).

^{13}C {^{1}H} NMR (101 MHz, C_6D_6) δ 170.3 (N*C*CH$_3$), 163.1 (GaC=O),146.3, 142.6, 142.5, 126.9, 124.9, 123.2 (C_6H_3), 136.3, 134.8, 125.5, 122.4 (C_5H_4N), 98.8 (CH), 28.5, 27.9 (CH*(CH$_3$)$_2$*), 25.7, 24.6, 24.3, 23.8 (CH(CH$_3$)$_2$), 23.5 (NC*C*H$_3$).

Elemental Analysis: Calculated for $C_{41}H_{51}GaN_4O_2$: C, 70.19; H, 7.33; N, 7.99. Found: C, 70.47; H, 7.42; N, 8.09.

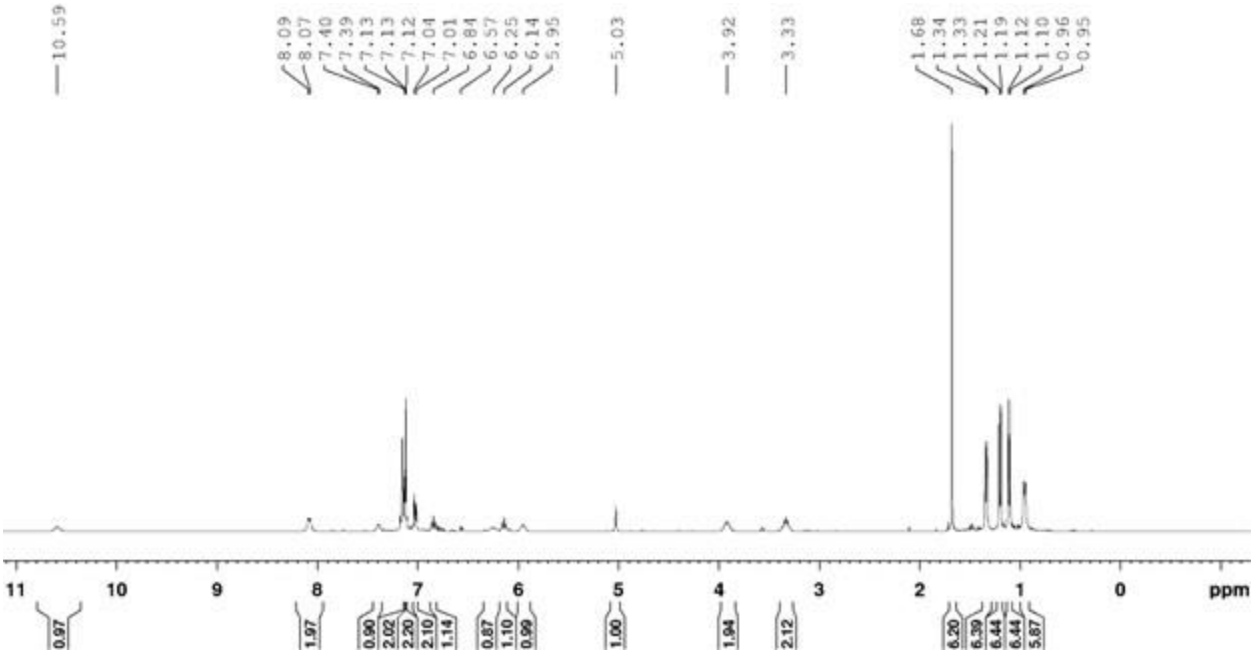

Figure S1: ^{1}H NMR (400 MHz, C_6D_6) spectrum of NacNacGa(py-O)(OCNHPh).

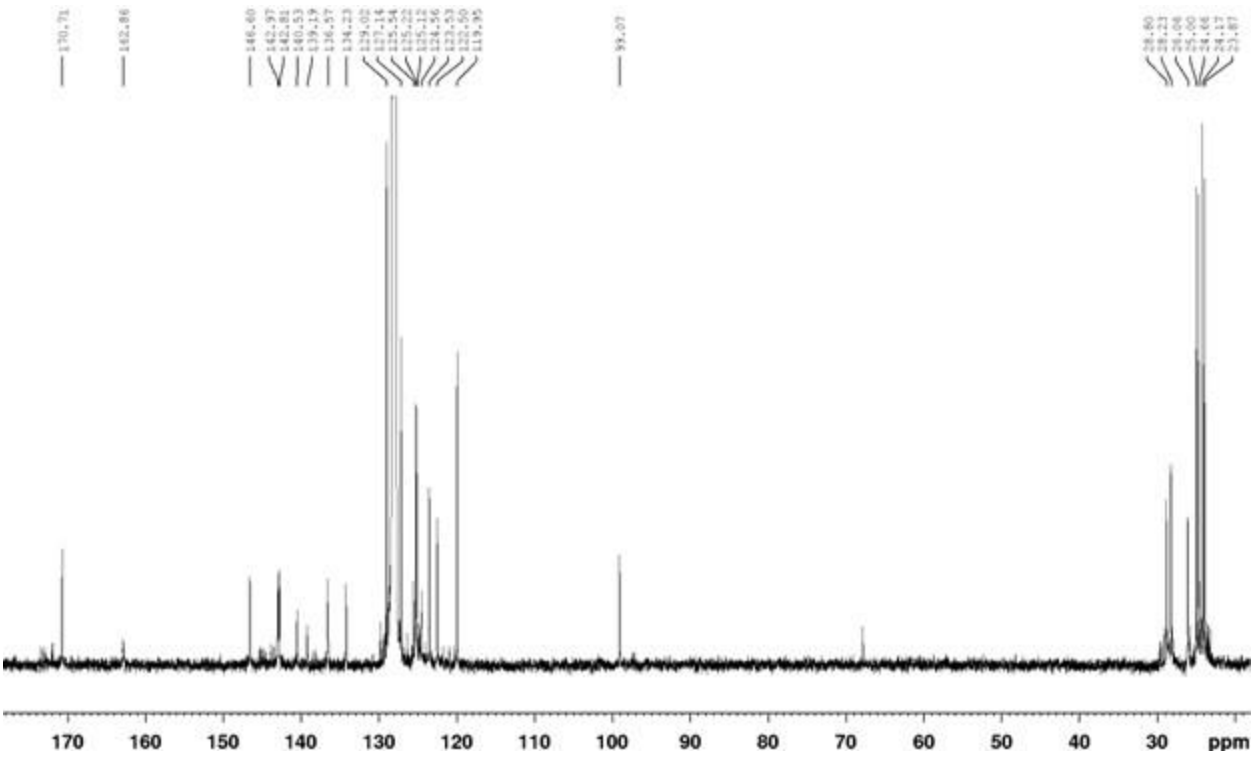

Figure S2: $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) spectrum of NacNacGa(py-O)(OCNHPh).

Preparation of NacNacGa($CH_2S(=O)Me$)(OCNHPh) (7). To a solution of NacNacGa (0.095 g, 0.19 mmol) in toluene was added DMSO (0.014 mL, 0.19 mmol) and the mixture was treated with PhCNO (0.021 mL, 0.19 mmol). The solvent was removed by reduced pressure, and the residue was redissolved in hexanes. Crystallization at -30℃ afforded **7** in the form of colourless crystals (yield 37%).

^{1}H NMR (400 MHz, C_6D_6) δ 11.29 (s, 1H, NH), 8.29 (d, 2H, C_6H_5, $^{3}J_{H-H}$=7.7), 7.20 (t, 2H, C_6H_5, $^{3}J_{H-H}$=7.9), 6.88 (t, 1H, C_6H_5, $^{3}J_{H-H}$=7.5), 7.03 (m, 1H, C_6H_3), 7.02 (m, 1H, C_6H_3), 7.02 (m, 1H, C_6H_3), 4.91 (s, 1H, CH), 3.84 (hept, 1H, C*H*$(CH_3)_2$, $^{3}J_{H-H}$=6.7), 3.68 (hept, 1H, C*H*$(CH_3)_2$, $^{3}J_{H-H}$=6.7), 3.23 (hept, 2H, C*H*$(CH_3)_2$, $^{3}J_{H-H}$=6.7), 1.99 (s, 1H, CH_2S), 1.67 (s, 1H, CH_2S), 1.62 (s, 3H, NCCH3), 1.59 (s, 3H, NCCH3), 1.34 (d, 3H, CH(C*H*$_3)_2$,$^{3}J_{H-H}$=6.7), 1.32 (d, 3H, CH(C*H*$_3)_2$,$^{3}J_{H-H}$=6.7), 1.20 (d, 3H, CH(C*H*$_3)_2$,$^{3}J_{H-H}$=6.7), 1.15(d, 6H, CH(C*H*$_3)_2$,$^{3}J_{H-H}$=6.7), 1.10 (d, 3H, CH(C*H*$_3)_2$,$^{3}J_{H-H}$=6.7), 1.08 (d, 3H, CH(C*H*$_3)_2$,$^{3}J_{H-H}$=6.7), 1.03 (d, 3H, CH(C*H*$_3)_2$,$^{3}J_{H-H}$=6.7).

^{13}C {^{1}H} NMR (101 MHz, C_6D_6) δ 170.3 ((*C*=O)NHPh), 170.0, 169.95 (N*C*CH3), 146.9, 146.6, 142.7, 140.9, 140.7, 125.2, 124.9, 123.4 (C_6H_3), 129.1, 122.7, 119.7 (C_6H_5N), 98.7 (CH), 39.4, 39.3 (Ga*C*H_2S=O), 28.5, 28.4, 27.5, 27.3 (*C*H(CH_3)$_2$), 41.8 (S*C*H_3), 25.75, 24.5, 24.1, 24.0 (CH(*C*H_3)$_2$), 23.4, 23.3 (NC*C*H_3), 25.7, 24.6, 24.6, 24.5, 24.4, 24.1, 23.7, 23.3 (CH(*C*H_3)$_2$).

Elemental Analysis: Calculated for $C_{38}H_{52}GaN_3O_2S$: C, 66.67; H, 7.66; N, 6.14. Found: C, 67.09; H, 7.63; N, 6.32.

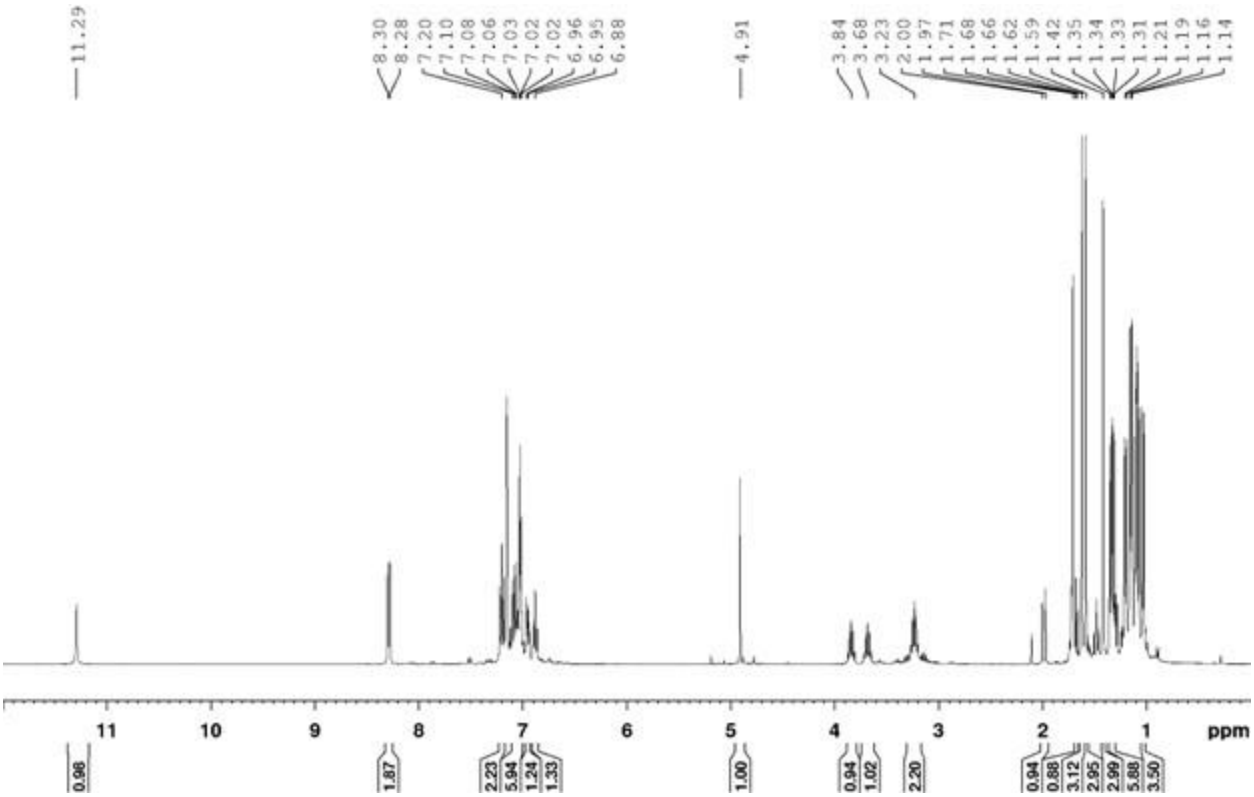

Figure S3: ^{1}H NMR (400 MHz, C_6D_6) spectrum of NacNacGa(CH_2S(=O)Me)(OCNHPh).

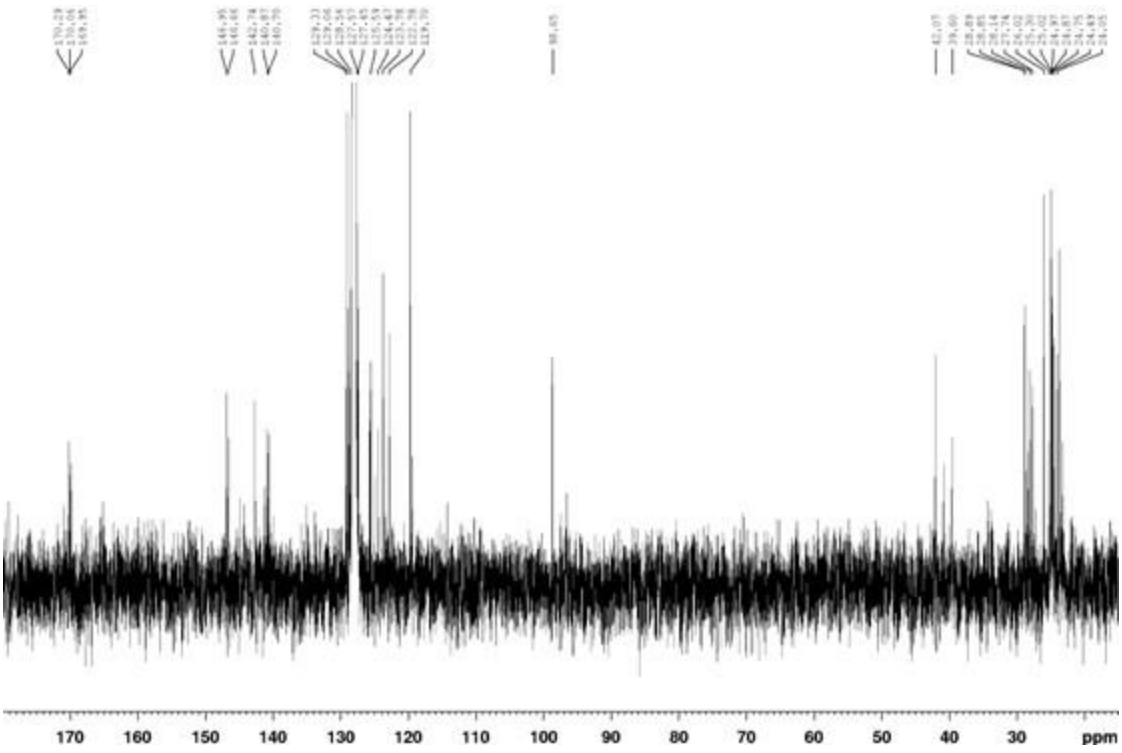

Figure S4: $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) spectrum of NacNacGa($CH_2S(=O)Me$)(OCNHPh).

Preparation of NacNacGa($CH_2C(=O)NMe_2$)(OCNHPh) (8). To a solution of NacNacGa (0.094 g, 0.19 mmol) in toluene, N,N-dimethylacetamide (0.018 mL, 0.19 mmol) was added and the obtained mixture was treated with PhCNO (0.021 mL, 0.19 mmol). The reaction mixture started forming crystals at room temperatures within two hours in the glovebox. It was then placed into the freezer at -30℃ to produce yellow crystals of **8** (yield 52%).

^{1}H NMR (400 MHz, C_6D_6) δ 10.36 (s, 1H, NH), 8.29 (d, 2H, C_6H_5, $^{3}J_{H-H}$=7.7), 7.22 (t, 2H, C_6H_5, $^{3}J_{H-H}$=7.9), 6.89 (t, 1H, C_6H_5, $^{3}J_{H-H}$=7.5), 7.02 (m, 2H, C_6H_3), 7.01 (m, 2H, C_6H_3), 7.00 (m, 2H, C_6H_3), 4.93 (s, 1H, CH), 3.74 (hept, 2H, C*H*(CH_3)$_2$, $^{3}J_{H-H}$=6.9), 3.25 (hept, 2H, C*H*(CH_3)$_2$, $^{3}J_{H-H}$=6.9), 2.52 (s, 3H, CH_3N), 1.66 (s, 3H, CH_3N), 1.60 (s, 2H, CH_2N), 1.58 (s, 6H, NCCH3), 1.25 (d, 6H, CH(C*H*$_3$)$_2$,$^{3}J_{H-H}$=6.7), 1.25 (d, 6H, CH(C*H*$_3$)$_2$,$^{3}J_{H-H}$=6.7), 1.13 (d, 6H, CH(C*H*$_3$)$_2$,$^{3}J_{H-H}$=6.7), 1.08 (d, 6H, CH(C*H*$_3$)$_2$,$^{3}J_{H-H}$=6.7).

^{13}C {^{1}H} NMR (101 MHz, C_6D_6) δ 176.3 ((*C*=O)NMe_2), 171.7((*C*=O)NHPh), 170.0, (N*C*CH_3), 146.0, 142.0, 141.0, 125.2, 124.9, 123.4 (C_6H_3), 128.9, 129.3, 122.4 (C_6H_5N), 98.7 (CH), 28.5, 27.7 (*C*H$(CH_3)_2$), 36.3, 35.1 ((*C*$H_3)_2$N), 25.75, 24.5, 24.1, 24.0 (CH(*C*$H_3)_2$), 23.5(NC*C*H_3), 17.8 (Ga*C*H_2C=O).

Elemental Analysis: Calculated for **8*toluene,** $C_{46}H_{63}GaN_4O_2$: C, 71.84; H, 8.08; N, 7.13. Found: C, 71.84; H, 8.44; N, 7.70.

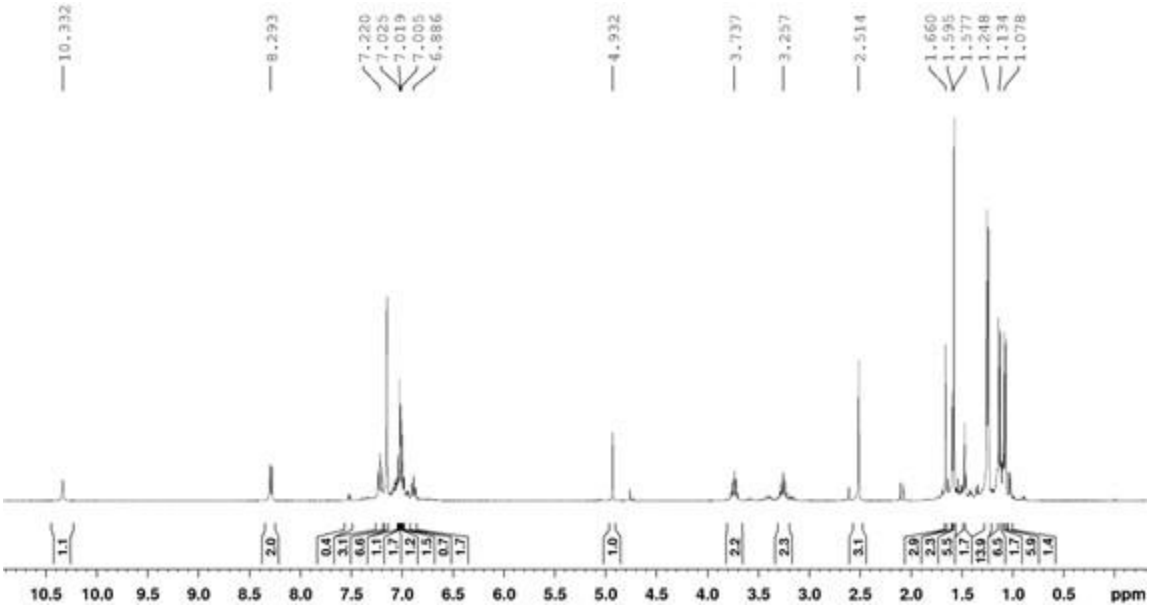

Figure S5: ^{1}H NMR (400 MHz, C_6D_6) spectrum of NacNacGa(CH_2C(=O)NMe_2)(OCNHPh).

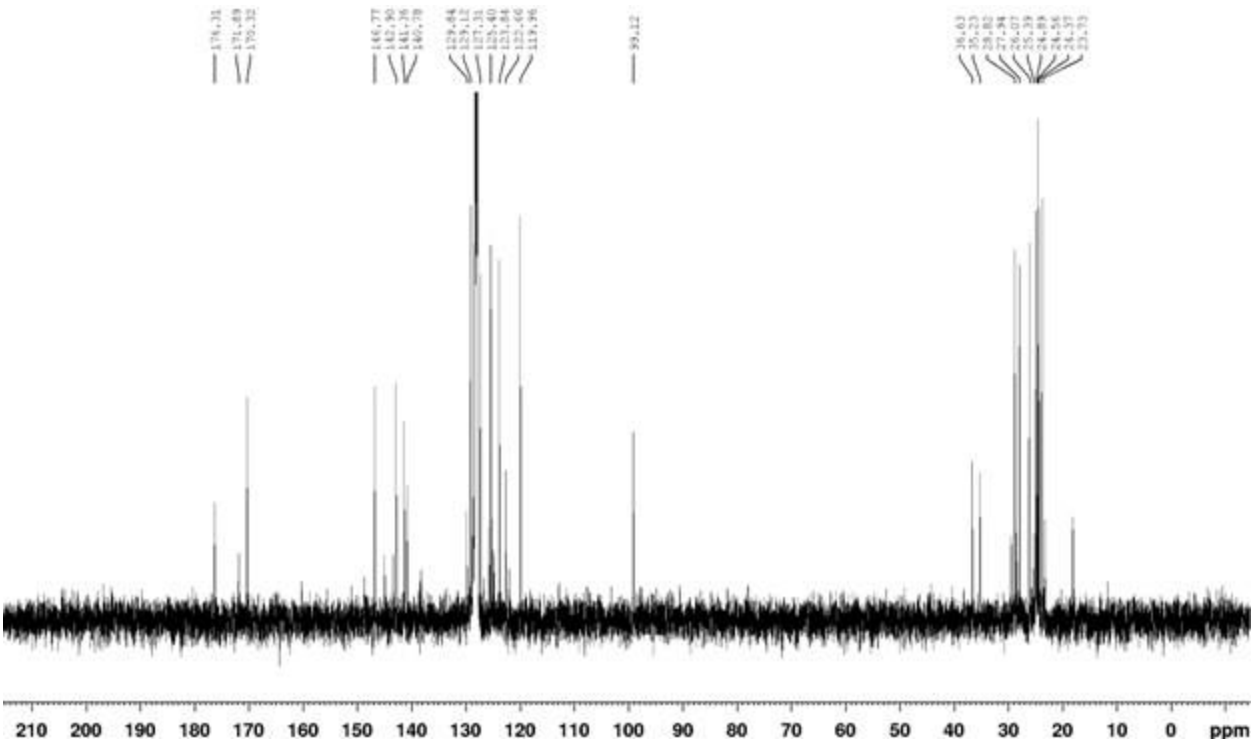

Figure S6: $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) spectrum of NacNacGa($CH_2C(=O)NMe_2$)(OCNHPh).

Preparation of NacNacGa([$C_6H_3NCO]_2$) (9). A mixture of NacNacGa (0.093g, 0.19mmol) and $OPEt_3$ (0.026g, 0.19mmol) was dissolved in toluene and treated with phenyl isocyanate (0.0207 mL, 0.19 mmol). The solution was then concentrated and stored in freezer at (-30℃) to obtain yellow crystals of **9** (yield 49%). After drying, the crystalline product had low solubility in benzene and toluene. Recrystallization was done from diethyl ether.

^{1}H NMR (400 MHz, C_6D_6) δ 8.12 (b, 1H, C_6H_5NGa), 7.32 (m, 2H, C_6H_5NGa), 7.06 (t, 1H, C_6H_3, $^{3}J_{H-H}$=7.4), 7.05 (t, 1H, C_6H_5, $^{3}J_{H-H}$=7.5), 7.00 (m, 1H, C_6H_3), 6.98 (m, 1H, C_6H_3), 6.96 (m, 1H, C_6H_5NGa), 6.89 (m, 2H, C_6H_5N), 6.83 (m, 1H, C_6H_5N), 6.74 (d, 2H, C_6H_5N, $^{3}J_{H-H}$=6.9), 5.05 (s, 1H, CH), 3.33 (hept, 2H, C*H*(CH_3)$_2$, $^{3}J_{H-H}$=6.9), 3.03 (hept, 2H, C*H*(CH_3)$_2$, $^{3}J_{H-H}$=6.9), 2.52 (s, 3H, CH_3N), 1.49 (s, 6H, NCCH3), 1.55 (d, 6H, CH(C*H*$_3$)$_2$,$^{3}J_{H-H}$=6.7), 1.09 (d, 6H, CH(C*H*$_3$)$_2$,$^{3}J_{H-H}$=6.7), 1.01 (d, 6H, CH(C*H*$_3$)$_2$,$^{3}J_{H-H}$=6.7), 0.90 (d, 6H, CH(C*H*$_3$)$_2$,$^{3}J_{H-H}$=6.7).

^{13}C {^{1}H} NMR (101 MHz, C_6D_6) δ 172.1, (N*C*CH$_3$), 145.3, 129.8, 128.2, 124.8, 122.5 (C_6H_5N), 145.1, 143.5, 139.2, 128.6, 124.7, 121.8 (C_6H_3), 136.7, 128.1, 126.9, 125.1 (C_6H_5N), 97.6 (CH), 29.7, 28.0 (*CH(CH$_3$)$_2$*), 25.0, 24.8, 24.3, 24.1 (CH(*C*H$_3$)$_2$), 23.4 (NC*C*H$_3$).

Elemental Analysis: Calculated for $C_{43}H_{51}GaN_4O_2$ C, 71.18; H, 7.08; N, 7.72. Found: C, 71.08; H, 7.24; N, 7.51.

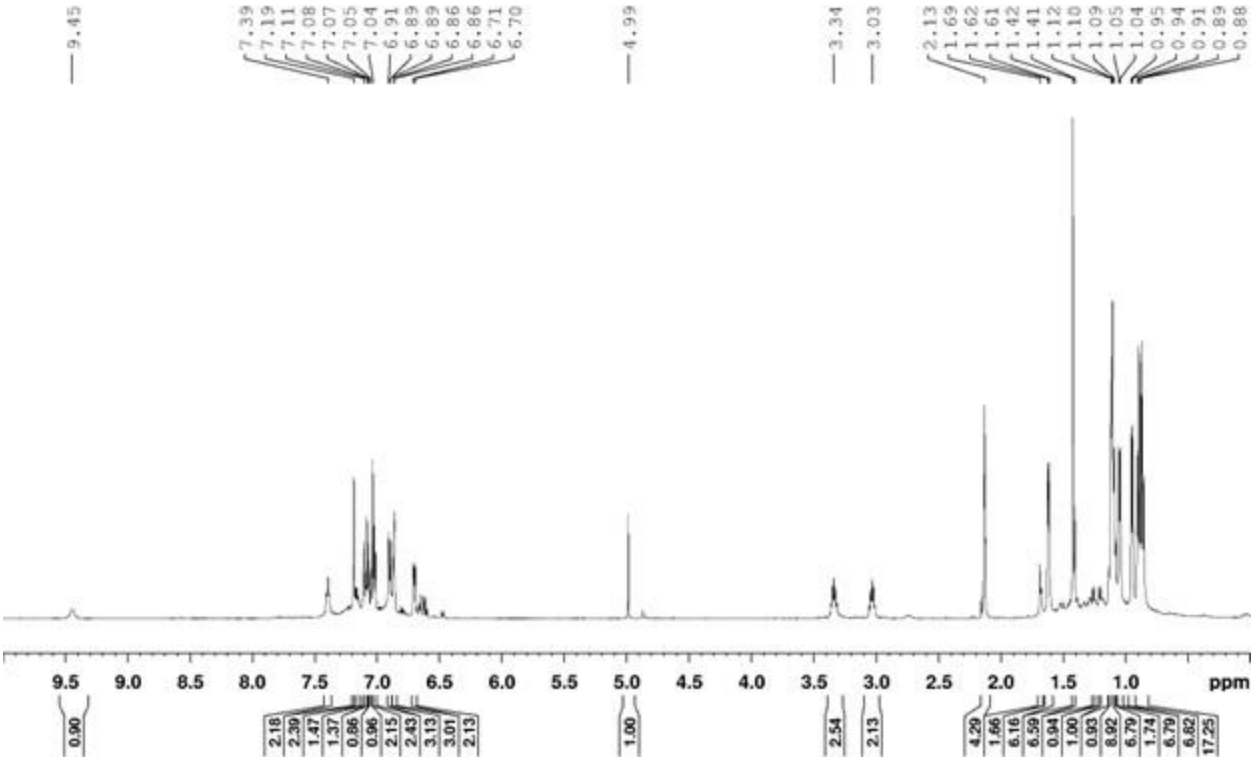

Figure S7: ^{1}H NMR (600 MHz, Toluene-d8) spectrum of NacNacGa([C_6H_3NCO]$_2$).

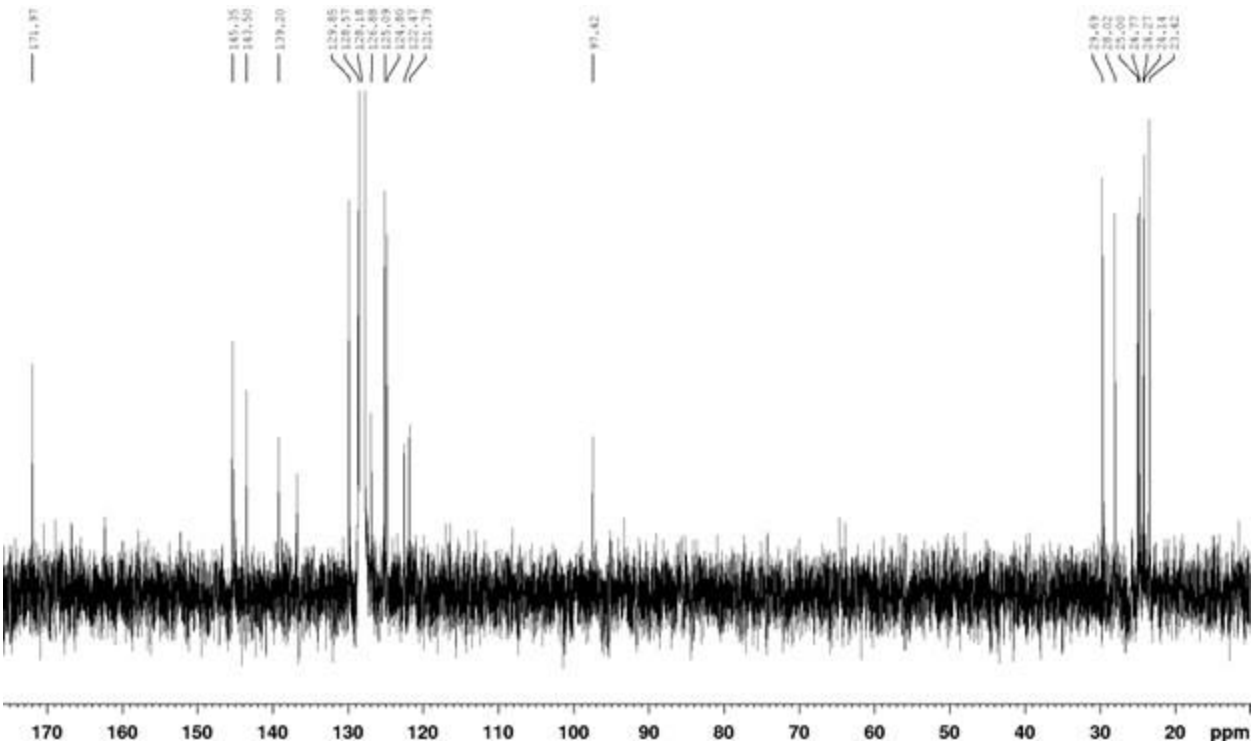

Figure S8: $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) spectrum of NacNacGa($[C_6H_3NCO]_2$).

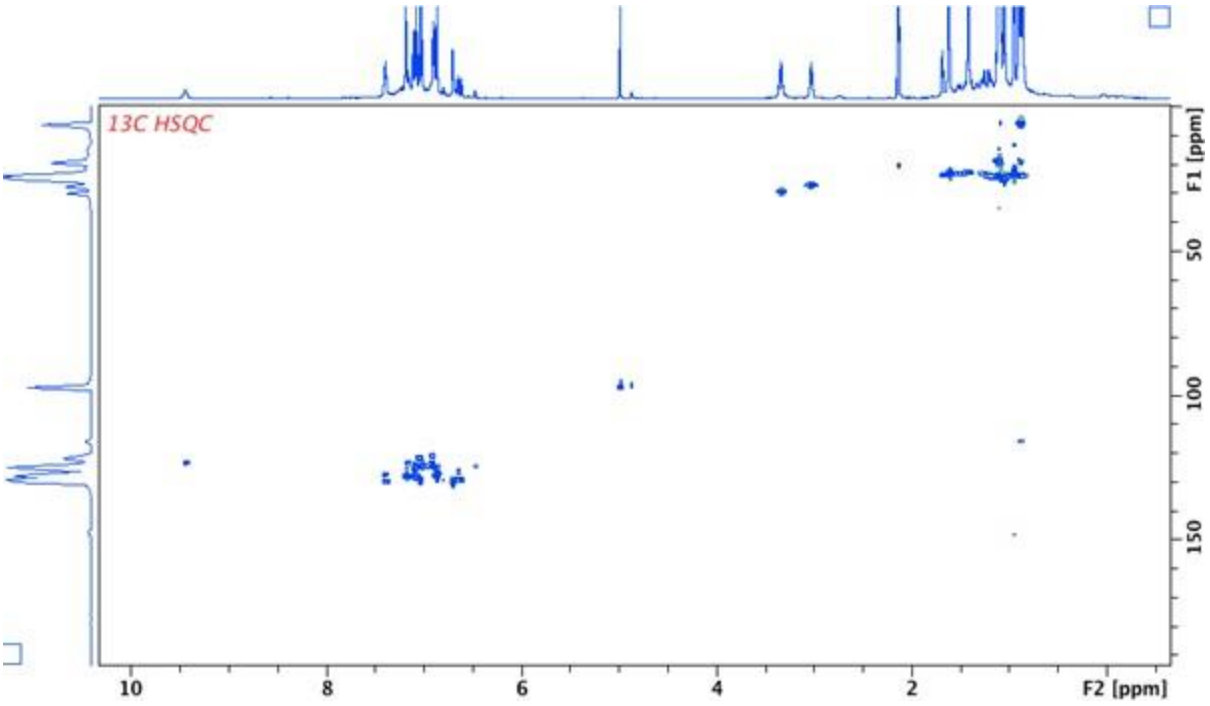

Figure S9: ^{1}H-^{13}C HSQC (101 MHz, toluene-d_8) spectrum of NacNacGa($[C_6H_3NCO]_2$).

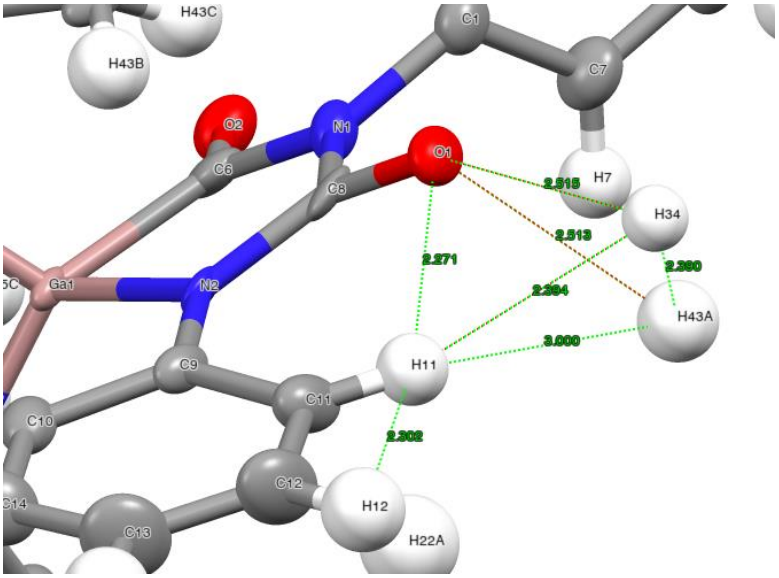

Figure S10: Oxygen-Hydrogen Short Contacts in NacNacGa($[C_6H_3NCO]_2$).

X-ray Crystallographic Studies

Suitable single crystals were mounted on a glass microloop covered with perfluoroether oil (Paratone® N). Crystallographic data were collected on Bruker APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature device operating at 150.0(1) K. Generic phi and omega scans (MoKα, λ = 0.71073 Å) were used for crystal measurements. The diffraction patterns were indexed, and the unit cells refined with SAINT and SADABS software (Bruker, 8.34A after 2013). Data reduction, scaling and absorption correction were performed with SAINT and SADABS software (Bruker, 8.34A after 2013). A multi-scan absorption correction was applied within SADABS-2014/4 (Bruker, 2014/4). Space group determination was based on analysis of systematic absences, *E* statistics, and successful refinement of all structures. The structures were solved by ShelXT (Sheldrick, 2015) structure solution program with Intrinsic phasing algorithm and refined with Least squares method by minimization of Σw(F02-Fc2)2. SHELXL weighting scheme was used under 2018/3 version of ShelXL (Sheldrick, 2015). Structure solution, refinement and CIF compilation was performed within Olex2SyS software

(Dolomanov, 2009). All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were calculated geometrically and refined using the riding model. Neutral atom scattering factors for all atoms were taken from the International Tables for Crystallography.

Table S1. Crystallographic data

Compound	**6**	**7**	**9**
Chemical formula	$C_{48}H_{59}GaN_4O_2$	$C_{38}H_{52}GaN_3O_2S$	$C_{43}H_{51}GaN_4O_2$
M_r (gmol^{-1})	793.61	684.60	725.59
Temperature (K)	150.0(1)	150.0(1)	150.0(1)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1/c$
a (Å)	10.0810(11)	12.1241(7)	13.254(2)
b (Å)	14.5969(16)	19.7684(12)	12.136(2)
c (Å)	29.227(3)	15.2234(9)	24.327(4)
α (°)	90	90	90
β (°)	90	94.397(2)	97.271(6)
γ (°)	90	90	90
V (Å^3)	4300.8(8)	3637.9(4)	3881.5(12)
Z	4	4	4
ρ_{calc} (g cm^{-3})	1.226	1.250	1.242
μ (mm^{-1})	0.682	0.849	0.749
Crystal size (mm^3)	0.24 × 0.23 × 0.22	0.18 × 0.09 × 0.09	0.15 × 0.15 × 0.05
2θ range (°)	3.944 to 56.962	3.382 to 56.922	3.098 to 49.998
Index ranges	-13 ≤ h ≤ 12 -19 ≤ k ≤ 19 -28 ≤ l ≤ 38	-15 ≤ h ≤ 16 -26 ≤ k ≤ 26 -20 ≤ l ≤ 12	-15 ≤ h ≤ 13 -14 ≤ k ≤ 14 -23 ≤ l ≤ 28
Reflections collected	78002	77126	61291
Independent reflections	10728 [R_{int} = 0.0413, R_{sigma} = 0.0333]	9091 [R_{int} = 0.0938, R_{sigma} = 0.0444]	6847 [R_{int} = 0.1256, R_{sigma} = 0.0711]
Data/Restraints/parameters	10728/46/504	9091/0/417	6847/0/420
Goodness of Fit	1.049	1.092	1.182
Final R indexes [I ≥ 2σ]	R_1 = 0.0355, wR_2 = 0.0835	R_1 = 0.0484, wR_2 = 0.0960	R_1 = 0.1087, wR_2 = 0.2423
Final R indexes [all data]	R_1 = 0.0393, wR_2 = 0.0855	R_1 = 0.0651, wR_2 = 0.1038	R_1 = 0.1319, wR_2 = 0.2544
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.84, -0.38	0.52, -0.47	2.11, -1.93
Flack parameter	0.096(10)	n/a	n/a

Computer programs: *SAINT* v8.34A and 8.40B (Bruker, 2013 and 2016) SHELXT 2018/2 (Sheldrick, 2018), *SHELXL* (Sheldrick, 2015), Olex2 1.5 (Dolomanov *et al.*, 2009).

References

1. M. J. Hardman, B. E. Eichler, P. P. Power, *Chem. Commun*. **2000**, 1991−1992.