Supporting Information

Activation and modification of carbon dioxide by redox-active low-valent gallium species

Vladimir A. Dodonov,[a] Olga A. Kushnerova,[a] Evgeny V. Baranov,[a] Alexander S. Novikov,[b] Igor L. Fedushkin*[a]

[a] G.A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Tropinina str. 49, N. Novgorod, Russia. Email: igorfed@iomc.ras.ru.

[b] Institute of Chemistry, Saint Petersburg State University, Universitetskaya Nab., 7/9, Saint Petersburg 199034, Russia; a.s.novikov@spbu.ru.

All manipulations were carried out under standard Schlenk or glovebox techniques. Solvents were dried according appropriate methods and distilled right prior use. Diphenylketene was prepared according literature procedure[1], all other chemicals were purchased and used without further purification. The IR spectra of solid compounds were recorded on FSM-1201 spectrometer in Nujol, of gases – in cuvette of 100 mm light path and ⌀ 40 mm CaF_2 cell windows. The NMR spectra were registered on Bruker Advance III (400 MHz) or Bruker AvanceNEO300 (300 MHz) spectrometer and were referenced to the residual signals of deuterated solvents at 298 K unless otherwise stated. Ar=aromatic, d=doublet, m=multiplet, t=triplet, pst=pseudotriplet, s=singlet, br.s=broad singlet, hept=heptet. Chemical shifts are given in ppm. Impurities of diamine (dpp-bian)H_2[2] that might be generated during NMR sample preparation and of common solvents[3] are not indicated in spectra for simplicity. Elemental analyses were performed with an Elementar Vario micro cube instrument. Solutions of [(dpp-bian)GaNa(DME)$_3$] (**1**)[4] were prepared by stirring of digallane [(dpp-bian)GaGa(dpp-bian)][5] with an equivalent of sodium metal in dimethoxyethane (DME) until the latter complete dissolution.

Synthesis of [(dpp-bian)Ga(CO_2)$_2$Ga(dpp-bian)][Na(DME)$_2$]$_2$ (2). A solution of 1 mmol [(dpp-bian)GaNa(DME)$_2$] in 10 ml of DME was treated with 25 ml (298 K, 1 atm) of carbon dioxide. The solution color changed from yellow-green to emerald-green. The solution was stirred for 10 minutes. Vacuum was applied briefly to remove excess of the gas. Layering the solution with 40 ml of pentane gave green crystals of complex **2**. Yield 0.78 g, 93 %. Elemental analysis $C_{92}H_{125}Ga_2N_4Na_2O_{13}$ (1680.42): calc. C 65.77, H 7.50, N 3.33 %; found: C 66.01, H 7.58, N 3.34 %. ^{1}H NMR (400 MHz, THF-d8) 7.04 – 6.87 (m, 6H), 6.74 (d, J = 8.2 Hz, 2H), 6.58 (dd, J = 8.2, 6.9 Hz, 2H), 5.59 (d, J = 6.8 Hz, 2H), 3.90 (hept, J = 6.7 Hz, 2H), 3.52 (hept, J = 6.8 Hz, 2H), 1.09 (d, J = 7.1 Hz, 6H), 0.82 (d, J = 6.9 Hz, 6H), 0.77 (d, J = 6.9 Hz, 6H), 0.73 (d, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, THF-d8) 164.8 (OCO), 147.7, 145.3, 144.8, 137.0, 132.3, 127.6, 126.1, 125.5, 123.2, 123.0, 121.4, 121.2, 115.8, 27.4 (CH-iPr), 26.9 (CH-iPr), 24.7 (CH3-iPr), 24.6 (CH3-iPr), 23.8 (CH3-iPr), 23.7 (CH3-iPr). IR (Nujol, ν/cm^{-1}): 517 W, 542 W, 625 W, 646 W, 669 W, 762 S, 797 S, 808 S, 858 M, 880 M, 899 M, 926 S, 936 M, 961 M, 980 M, 999 M, 1030 M, 1084 S, 1113 S, 1125 S, 1177 S, 1190 S, 1210 M, 1262 S, 1310 S, 1323 S, 1350 S, 1431 S, 1493 S, 1512 S, 1590 M, 1613 W, 1671 W.

Synthesis of {[(dpp-bian)Ga(CO_2)$_2$Ga(dpp-bian)][Na(DME)(CH_3OCH_2–)]$_2$}$_n$ (3). The same procedure as for **2**, followed by slow concentration (to approx. volume of 1.5 ml) of the solution instead of layering with pentane. Item by item examination of XRD parameters of obtained crystals gave compound **3** among crystals of **2**.

Synthesis of [(dpp-bian)Ga(CO_2)$_2$Ga(dpp-bian)][Na(18-crown-6)]$_2$ (4). A solution of 1 mmol [(dpp-bian)GaNa(DME)$_2$] in 10 ml of DME was treated with 25 ml (298 K, 1 atm) of carbon dioxide. The solution color changed from yellow-green to emerlad-green. The solution was stirred for 10 minutes. Vacuum was applied briefly to remove excess of the gas. A solution of 0.264 g of 18-crown-6 in 5 ml of DME was added. The mixture was left unshaken for 2 days. That resulted in formation of yellow-green crystals of **4**. Yield 0.58 g, 64 %. Elemental analysis $C_{108}H_{153}Ga_2N_4Na_2O_{21}$ (2028.81), calc. C 63.94, H 7.60, N 2.76 %; found C 63.76, H 7.77, N 2.59 %. ^{1}H NMR (400 MHz, THF-d8, 328 K) 7.18 – 7.06 (m, 8H), 6.90 – 6.85 (m, 4H), 6.63 (d, *J* = 8.3 Hz, 4H), 6.54 (t, *J* = 7.5 Hz, 4H), 5.63 (d, *J* = 6.8 Hz, 4H), 4.01 (hept, *J* = 6.7 Hz, 4H), 3.95 (hept, *J* = 6.7 Hz, 4H), 1.28 (d, *J* = 6.7 Hz, 12H), 0.97 (d, *J* = 6.8 Hz, 12H), 0.92 (d, *J* = 6.8 Hz, 12H), 0.46 (d, *J* = 6.8 Hz, 12H). ^{13}C NMR (101 MHz, THF-d8, 328 K, indirect observation) 147.89, 146.7, 137.9, 129.6, 129.5, 126.0, 122.1, 120.3, 115.3, 27.3 (CH-iPr), 26.3 (CH-iPr), 25.3 (CH3-iPr), 24.8 (CH3-iPr), 24.1 (CH3-iPr), 23.9 (CH3-iPr). IR (Nujol, ν/cm^{-1}): 403 W, 424 M, 444 W, 503 W, 521 M, 548 W, 586 W, 625 M, 646 W, 679 W, 760 S, 806 S, 826 M, 847 W, 899 M, 928 S, 935 S, 995 W, 1063 S, 1101 S, 1173 M, 1188 W, 1236 S, 1258 S, 1352 S, 1429 S, 1510 S, 1582 S, 1611 S.

Thermal decomposition of 2. A sealed evacuated ampule containing a solution **2** in 10 ml of DME prepared from 1 mmol of [(dpp-bian)GaNa(DME)$_2$] and 1 mmol of CO_2 was heated overnight at 120°C. Solution color changed to blue-green. Concentration of the solution (to approx. volume of 4 ml) gave 0.192 g (34%) of blue crystals, which NMR- and IR- spectra matched with ones of digallane [(dpp-bian)GaGa(dpp-bian)].[5]

Synthesis of [(dpp-bian)Ga(CO_3)(O)Ga(dpp-bian)][Na_2(THF)$_5$] (5). A solution of **2** in 10 ml of DME was prepared from 1 mmol of [(dpp-bian)GaNa(DME)$_2$] and 1 mmol of CO_2. All volatiles and the solvent were removed in vacuum. The residue was dissolved in hot THF (60°C) and placed in a sealed evacuated vessel. Heating continued for 1h. The evacuation – dissolution – heating cycle was repeated two more times. Final solution color of the was blue-green. Concentration of the obtained solution (to approx. volume of 2 ml) gave 0.076 g of blue crystals of **5**. Layering the mother liquor with 20 ml of hexanes gave additional 0.428 g of **5**. Total yield 0.504 g, 59 %. Elemental analysis $C_{97}H_{130}Ga_2N_4Na_2O_{10}$ (1697.46), calc. C 68.63, H 7.72, N 3.30 %; found C 68.37, H 7.86, N 3.54 %. ^{1}H NMR (400 MHz, THF-d8) 7.02 (d, J = 4.5 Hz, 8H), 6.92 (d, J = 4.5 Hz, 4H), 6.80 (d, J = 8.2 Hz, 4H), 6.64 (dd, J = 8.2, 7.0 Hz, 4H), 5.73 (d, J = 6.9 Hz, 4H), 3.96 – 3.77 (m, 8H, CH-iPr), 1.32 (d, J = 6.8 Hz, 12H, CH3-iPr), 0.99 (d, J = 6.9 Hz, 12H, CH3-iPr), 0.90 (d, J = 6.8 Hz, 12H, CH3-iPr), 0.54 (d, J = 6.9 Hz, 12H, CH3-iPr). ^{13}C NMR (101 MHz, THF-d8) 198.0 (CO3), 147.3, 145.8, 144.7, 137.1, 133.8, 128.3, 128.1, 126.2, 123.2, 123.0, 122.0, 121.4, 115.9, 27.5 (CH-iPr), 26.8 (CH-iPr), 25.5 (CH3-iPr), 24.6 (CH3-iPr), 24.1 (CH3-iPr), 23.8 (CH3-iPr). IR (Nujol, ν/cm^{-1}): 465 VW, 498 VW, 517 W, 540 W, 550 W, 590 VW, 623 M, 644 W, 669 W, 683 W, 706 W, 760 VS, 779 W, 808 VS, 839 M, 899 VS, 924 VS, 936 S, 999 W, 1049 VS, 1071 S, 1105 M, 1136 M, 1179 S, 1190 M, 1210 M, 1258 S, 1323 VS, 1346 VS, 1431 VS, 1518 VS, 1590 M, 1613 W.

Synthesis of [(dpp-bian)GaOC(O)C(Ph)$_2$C(CPh$_2$)O][Na(DME)$_2$] (6). 0.389 g (2 mmol) of diphenylketene was added to a solution of 1 mmol of **2** in 10 ml of DME. Color of the solution changed to yellow-green with concomitant extrusion of gas within 10 min. All volatiles and the solvent were removed in vacuum. The residue was dissolved in 10 ml of Et_2O. Slow concentration (to approx. volume of 2 ml) gave blue crystals of **6**. Yield 0.353 g, 30 %. Elemental analysis $C_{72}H_{80}GaN_2NaO_7$ (1178.09): C 73.40, H 6.84, N 2.38 %; found C 73.84, H 6.89, N 2.35 %. ^{1}H NMR (400 MHz, THF-d8) 7.52 (d, J = 8.0 Hz, 2H), 7.33 – 7.13 (m, 10H), 7.12 – 6.99 (m, 8H), 6.90 – 6.76 (m, 5H), 6.71 – 6.57 (m, 7H), 6.49 (t, J = 7.5 Hz, 2H), 6.18 (d, J = 7.8 Hz, 2H), 5.58 (s, 2H), 4.12 (s, 2H), 1.24 (d, J = 6.8 Hz, 6H), 1.08 (d, J = 6.8 Hz, 6H), 0.88 (d, J = 6.7 Hz, 6H), 0.83 (d, J = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, THF-d8) 204.2 (O_2C), 147.5, 147.2, 144.7, 144.5, 143.0, 142.7, 138.7, 132.0, 130.3, 129.8, 129.1, 128.2, 126.8, 126.4, 126.0, 125.0, 124.2, 123.5, 123.2, 122.8, 122.5, 121.8, 117.6, 116.2, 71.5 (C=*C*Ph2), 63.5 (O*C*=CPh2), 27.9 (CH-iPr), 27.4 (CH-iPr), 24.5 (CH3-iPr), 23.6 (CH3-iPr), 23.0 (CH3-iPr). IR (Nujol, ν/cm^{-1}): 544 W, 588 M, 612 W, 696 S, 762 M, 781 M, 801 M, 851 M, 911 M, 924 M, 936 M, 966 M, 1001 W, 1013 M, 1034 M, 1071 M, 1086 M, 1113 M, 1156 M, 1192 M, 1211 M, 1254 M, 1283 M, 1302 M, 1325 S, 1339 S, 1366 S, 1489 M, 1518 W, 1576 W, 1597 W, 1659 M.

Synthesis of [(dpp-bian)GaN(Cy)C(O)N(Cy)C(O)O]$_2$[Na(DME)$_2$]$_2$ (7). 0.250 g (2 mmol) of cyclohexyl isocyanate was added to a solution of 1 mmol of **2** in 10 ml of DME. Color of the solution changed to blue-green with concomitant extrusion of gas within 10 min. Vacuum was applied briefly to remove gaseous products. The solution was layered with 30 ml of Et_2O, what gave blue crystals of **7**. Yield 0.362 g, 35 %. Elemental analysis $C_{118}H_{169}Ga_2N_8Na_2O_{12.7}$ (2088.3), calc. C 67.81, H 8.09, N 5.36 %; found C 68.02, H 8.28, N 5.57 %. ^{1}H NMR (300 MHz, THF-d8) 7.22 – 7.11 (m, 5H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.75 (t, *J* = 8.1 Hz, 2H), 5.80 (d, *J* = 7.6 Hz, 2H), 3.84 (br. s, 4H), 3.06 (br. s, 1H), 2.14 (s, 1H), 1.98 – 1.84 (m, 4H), 1.80 – 1.62 (m, 9H), 1.57 – 1.30 (m, 14H), 1.25 (d, *J* = 6.6 Hz, 6H), 1.07 (d, *J* = 6.6 Hz, 6H), 0.78 (br. s, 12H). 13C NMR (75 MHz, THF-d8) 167.8 (O*C*O), 158.0(N*C*O), 146.6, 143.7, 136.0, 131.8, 128.7, 128.0, 126.3, 126.2, 125.1, 124.5, 122.8, 122.3, 116.6, 53.2 (CH-Cy), 52.8 (CH-Cy), 34.7 (CH2-Cy), 33.9 (CH2-Cy), 27.8 (CH-iPr), 27.7 (CH-iPr), 26.1 (CH2-Cy), 25.6 (CH2-Cy), 25.4 (CH2-Cy), 25.2 (CH2-Cy), 24.5 (CH3-iPr), 23.9 (CH3-iPr), 23.7 (CH2-Cy). IR (Nujol, ν/cm^{-1}): 463 VW, 500 VW, 519 W, 538 VW, 550 VW, 588 W, 608 VW, 623 W, 648 W, 683 W, 760 S, 777 W, 799 M, 810 M, 839 M, 860 M, 901 M, 926 M, 936 M, 955 VW, 997 W, 1005 W, 1028 M, 1057 M, 1080 S, 1105 M, 1121 M, 1132 M, 1179 M, 1188 M, 1210 M, 1246 S, 1264 S, 1341 S, 1435 S, 1514 S, 1557 M, 1593 M, 1622 M.

Synthesis of [(dpp-bian)GaN(Ph)C(O)O]$_2$[Na(DME)$_2$]$_2$ (8). 0.119 g (1 mmol) of phenylisocyanate was added to a solution of 1 mmol of **2** in 10 ml of DME. Color of the solution changed to blue-green with concomitant extrusion of gas within 10 min. Vacuum was applied briefly to remove gaseous products. The solution was layered with 40 ml of pentane, what gave blue crystals of **8**. Yield 0.510 g, 28 %. Elemental analysis $C_{102}H_{130}Ga_2N_6Na_2O_{12}$ (1817.58), calc. C 67.40, H 7.21, N 4.62 %; found C 67.01, H 7.02, N 4.46 %. ^{1}H NMR (400 MHz, THF-d8) 7.48 – 7.39 (m, 5H), 7.18 – 7.04 (m, 10H), 6.96 (d, J = 8.3 Hz, 2H), 6.76 (t, J = 7.5 Hz, 2H), 6.70 (d, J = 7.2 Hz, 2H), 5.73 (d, J = 6.9 Hz, 2H), 3.98 – 3.89 (hept, J = 6.7 Hz, 4H), 1.05 (d, J = 7.1 Hz, 12H), 0.96 (d, J = 6.7 Hz, 12H). ^{13}C NMR (75 MHz, THF-d8) 165.7 (N*C*O), 146.9, 146.2, 144.1, 136.4, 132.3, 128.8, 128.5, 127.8, 126.3, 124.3, 122.8, 119.6, 118.5, 116.7, 27.9 (CH-iPr), 24.2 (CH3-iPr), 24.1 (CH3-iPr). IR (Nujol, ν/cm^{-1}): 465 W, 517 W, 550 W, 573 W, 590 M, 621 W, 648 W, 669 W, 693 M, 754 S, 808 M, 837 W, 858 M, 907 W, 924 M, 936 W, 961 W, 995 W, 1028 W, 1080 M, 1111 W, 1179 W, 1188 W, 1210 W, 1246 W, 1277 VW, 1314 W, 1333 W, 1514 M, 1593 M, 1624 M, 1638 M, 1655 M, 1711 M.

Synthesis of [(dpp-bian)Ga(O)(CO$_3$)Ga(dpp-bian)]$_2$[Na(DME)]$_2$[Na(DME)$_3$]$_2$ (9). 0.091 g (0.5 mmol) of azobenzene was added to a solution of 1 mmol of **2** in 10 ml of DME. Color of the solution changed to blue-green within 10 min. The solution was cooled to –20°C and was layered with 50 ml of cold (–20 °C) mixture of 1:1 C_6H_6:pentane, what gave blue crystals of **9**. Yield 0.150 g, 9 %. The compound is susceptible to decomposition at room temperature in vacuum (~10 min), THF, benzene or hexane solvents. No reasonable NMR spectra were collected due to decomposition during sample preparation. Elemental analysis $C_{195.44}H_{261.37}Ga_4N_8Na_4O_{24}$ (3477.57), calc. C 67.44, H 7.52, N 3.23 %; found C 67.97, H 7.91, N 3.52 %. IR (Nujol, ν/cm^{-1}): 465 VW, 513 M, 536 W, 550 W, 573 W, 585 W, 625 W, 646 W, 669 W, 693 M, 741 S, 760 VS, 787 M, 808 S, 841 S, 862 S, 878 M, 899 M, 926 S, 938 M, 986 M, 999 W, 1032 S, 1063 M, 1088 VS, 1113 S, 1127 S, 1161 M, 1177 M, 1194 S, 1210 M, 1260 S, 1283 S, 1323 S, 1354 VS, 1364 VS, 1431 VS, 1485 S, 1516 S, 1549 S, 1591 S, 1601 S, 1674 M.

Synthesis of [(dpp-bian)Ga(OTMS)(N$_3$)][Na(DME)$_3$] (10). 0.115 g (1 mmol) of $TMSN_3$ was added to a solution of 1 mmol of **2** in 10 ml of DME. No change in solution color and evolution of gas were observed. The solution was cooled to –20°C and was layered with 40 ml of cold (–20 °C) pentane, what gave blue crystals of **10**. Yield 0.412 g, 41 %. NMR was registered in protio-DME due to decomposition in THF-d8. Elemental analysis $C_{51}H_{79}GaN_5NaO_7Si$ (995.00), calc. C 61.56, H 8.00, N 7.04 %; found C 61.80, H 8.23, N 6.89 %. ^{1}H NMR (400 MHz, protio-DME, no lock) 7.85 – 7.59 (m, 7H), 7.51 (t, J = 7.3 Hz, 1H), 7.41 (d, J = 8.6 Hz, 1H), 7.26 (t, J = 8.0 Hz, 1H), 4.69 (br. s, 2H, CH-iPr), 4.34 (br. s, 2H, CH-iPr), 1.91 (d, J = 6.5 Hz, 6H, CH3-iPr), 1.79 (d, J = 6.8 Hz, 6H, CH3-iPr), 1.73 (d, J = 6.8 Hz, 6H, CH3-iPr), 1.48 (d, J = 6.3 Hz, 6H, CH3-iPr), 0.33 (s, 9H, CH3-TMS). ^{13}C NMR (101 MHz, protio-DME, no lock) 147.7, 144.6, 137.0, 132.9, 126.9, 126.5, 124.8, 124.1, 123.3, 122.7, 122.3, 116.6, 28.2 (CH-iPr), 28.0(CH-iPr), 25.2 (CH3-iPr), 24.8 (CH3-iPr), 24.7 (CH3-iPr),

23.6 (CH3-iPr), 3.0 (TMS). ^{29}Si NMR (79.5 MHz, protio-DME, indirect observation) 1.0. IR (Nujol, ν/cm^{-1}): 467 VW, 521 W, 536 VW, 550 W, 569 VW, 600 W, 623 M, 654 M, 669 W, 681 W, 721 M, 764 S, 783 M, 808 S, 837 M, 860 S, 905 M, 924 S, 936 M, 968 M, 997 M, 1019 M, 1030 M, 1086 S, 1105 M, 1123 M, 1159 W, 1179 M, 1190 M, 1210 M, 1244 M, 1254 M, 1264 M, 1321 M, 1343 M, 1491 M, 1510 S, 2101 S.

Synthesis of [(dpp-bian)Ga(OTMS)(Cl)][Na(THF)$_2$(Et$_2$O)] (11). A 0.109 g (1 mmol) of TMSCl was added to a solution of 1 mmol of **2** in 10 ml of DME. Evolution of gas and no change in solution color was observed. The solution was cooled to –20°C and was layered with 40 ml of cold (–20 °C) mixture of 1:1 THF:Et$_2$O, what gave green crystals of **11**. Yield 0.328 g, 35 %. NMR was registered in protio-DME due to decomposition in THF-d8. Elemental analysis $C_{51}H_{75}ClGaN_2NaO_4Si$ (936.40), calc. C 65.41, H 8.07, N 2.99 %; found C 61.8, H 8.23, N 6.89 %. ^{1}H NMR (400 MHz, protio-DME, no lock) 7.38 – 6.76 (m, 5H), 6.65 (t, J = 7.3 Hz, 1H), 4.15 (br. s, 4H, CH-iPr), 4.34 (br. s, 2H, CH-iPr), 1.23 (br. s, 12H, CH3-iPr), 1.07 (br. s, 6H, CH3-iPr), 1.01 (br. s, 6H, CH3-iPr), -0.15 (s, 9H, CH3-iPr). ^{29}Si NMR (79.5 MHz, THF-d8, indirect observation) 5.1. IR (Nujol, ν/cm^{-1}): 469 W, 498 VW, 521 W, 550 VW, 621 W, 648 W, 669 W, 683 W, 721 M, 747 M, 764 S, 783 W, 806 M, 816 M, 835 S, 857 M, 909 W, 922 S, 936 M, 1001 S, 1034 W, 1057 W, 1111 M, 1136 W, 1184 W, 1210 M, 1252 S, 1316 S, 1331 S, 1343 S, 1364 M, 1443 VS, 1510 S, 1537 W, 1590 M, 1615 W

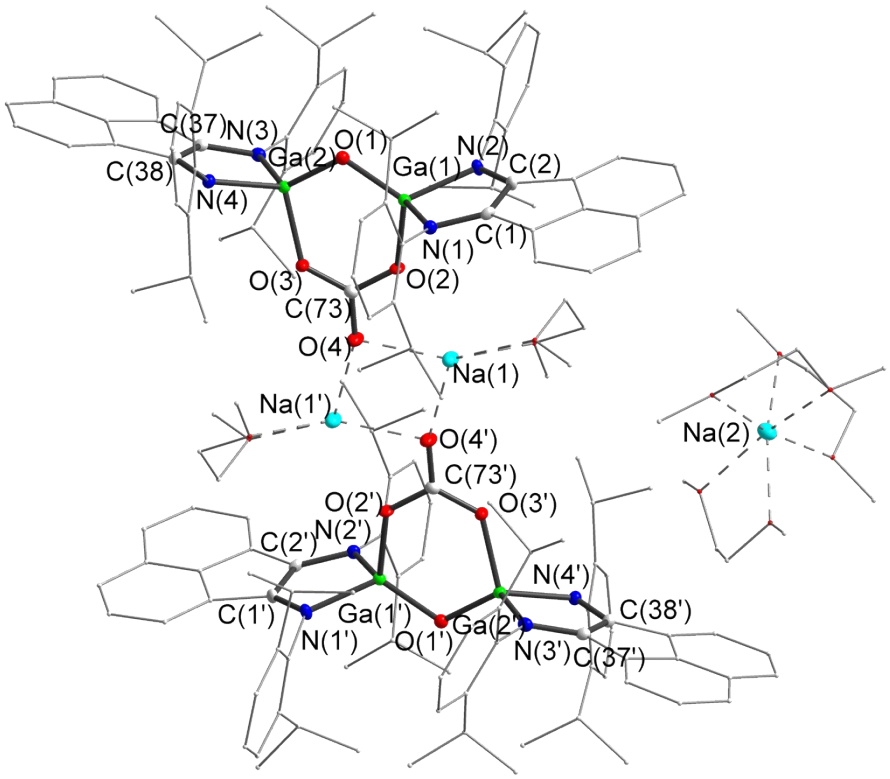


Figure S1. Molecular structure of **9**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms and Na(2') cation are omitted. Selected bond lengths (Å) and angles (°): Ga(1)-N(1) 1.912(4), Ga(1)-N(2) 1.913(4), Ga(1)-O(2) 1.920(3), N(1)-C(1) 1.391(6), N(2)-C(2) 1.392(6), O(2)-C(73) 1.315(6), O(3)-C(73) 1.299(6), O(4)-C(73) 1.241(6), C(1)-C(2) 1.366(6), Ga(1)-O(1) 1.775(3), O(1)-Ga(1)-N(1) 125.58(16), O(1)-Ga(1)-N(2) 118.92(16), N(1)-Ga(1)-N(2) 90.37(16), O(1)-Ga(1)-O(2) 107.58(14), N(1)-Ga(1)-O(2) 104.28(16), N(2)-Ga(1)-O(2) 108.07(16), C(1)-N(1)-Ga(1) 105.9(3), C(2)-N(2)-Ga(1) 105.6(3), C(73)-O(2)-Ga(1) 129.1(3), C(2)-C(1)-N(1) 118.7(4), C(1)-C(2)-N(2) 119.2(4), O(4)-C(73)-O(3) 121.0(4), O(4)-C(73)-O(2) 118.3(4), O(3)-C(73)-O(2) 120.6(4), O(1)-Ga(1)-N(1) 125.58(16).

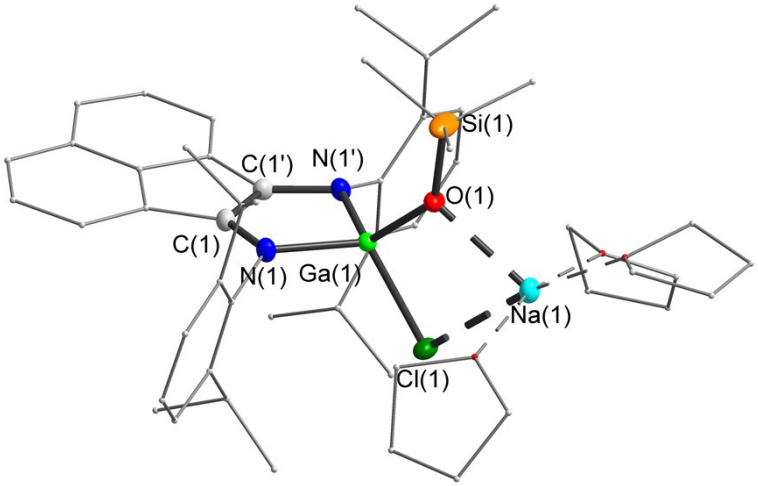


Figure S2. Molecular structure of **11**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): Ga(1)-O(1) 1.824(3), Ga(1)-N(1) 1.904(2), Ga(1)-Cl(1) 2.2238(11), N(1)-C(1) 1.397(4), N(1)-C(8) 1.429(4), C(1)-C(1') 1.383(6), C(1)-C(2) 1.463(4), O(1)-Ga(1)-N(1) 119.21(9), N(1)-Ga(1)-N(1') 91.72(15), O(1)-Ga(1)-Cl(1) 97.35(10), N(1)-Ga(1)-Cl(1) 115.49(8), C(1)-N(1)-Ga(1) 105.06(18).

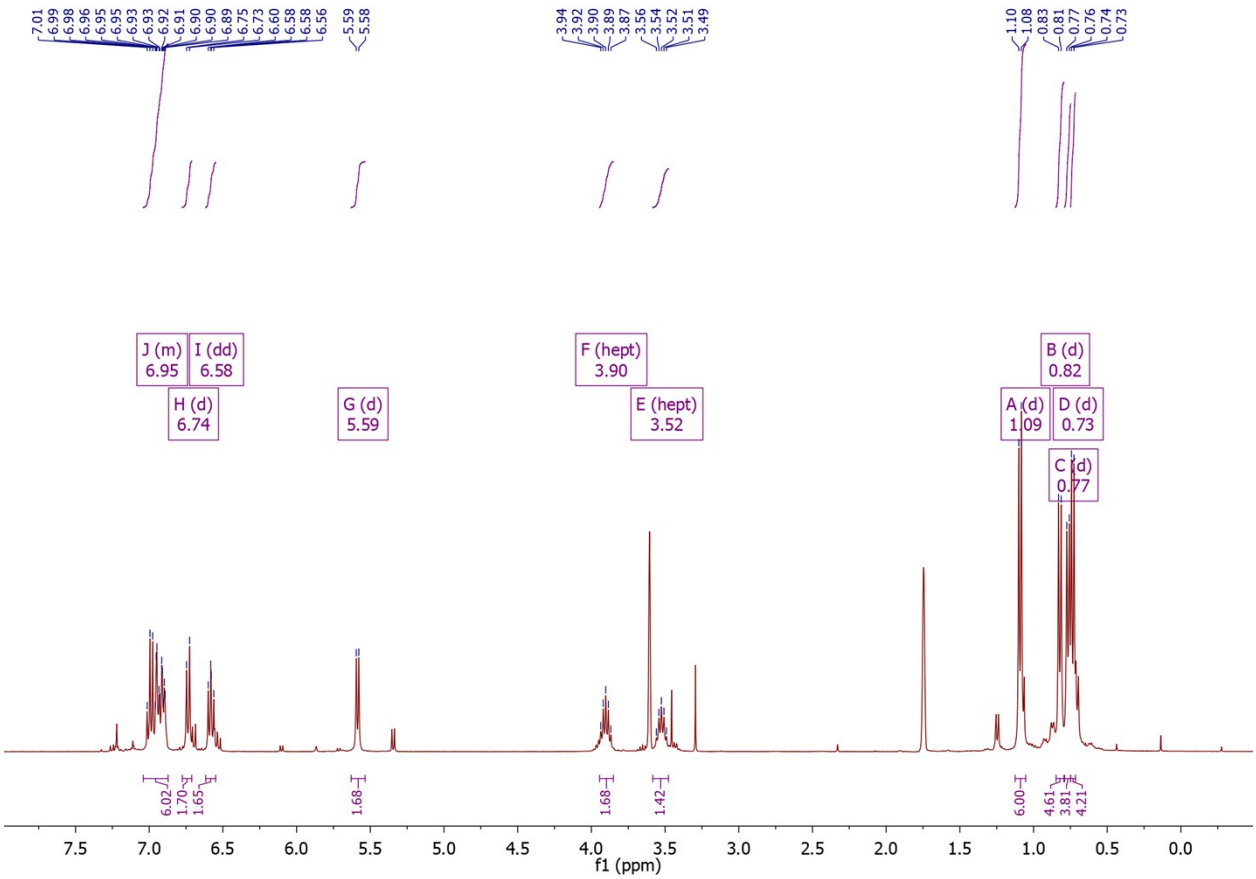


Figure S3. ^{1}H NMR spectrum of **2** at 298 K in thf-d_8.

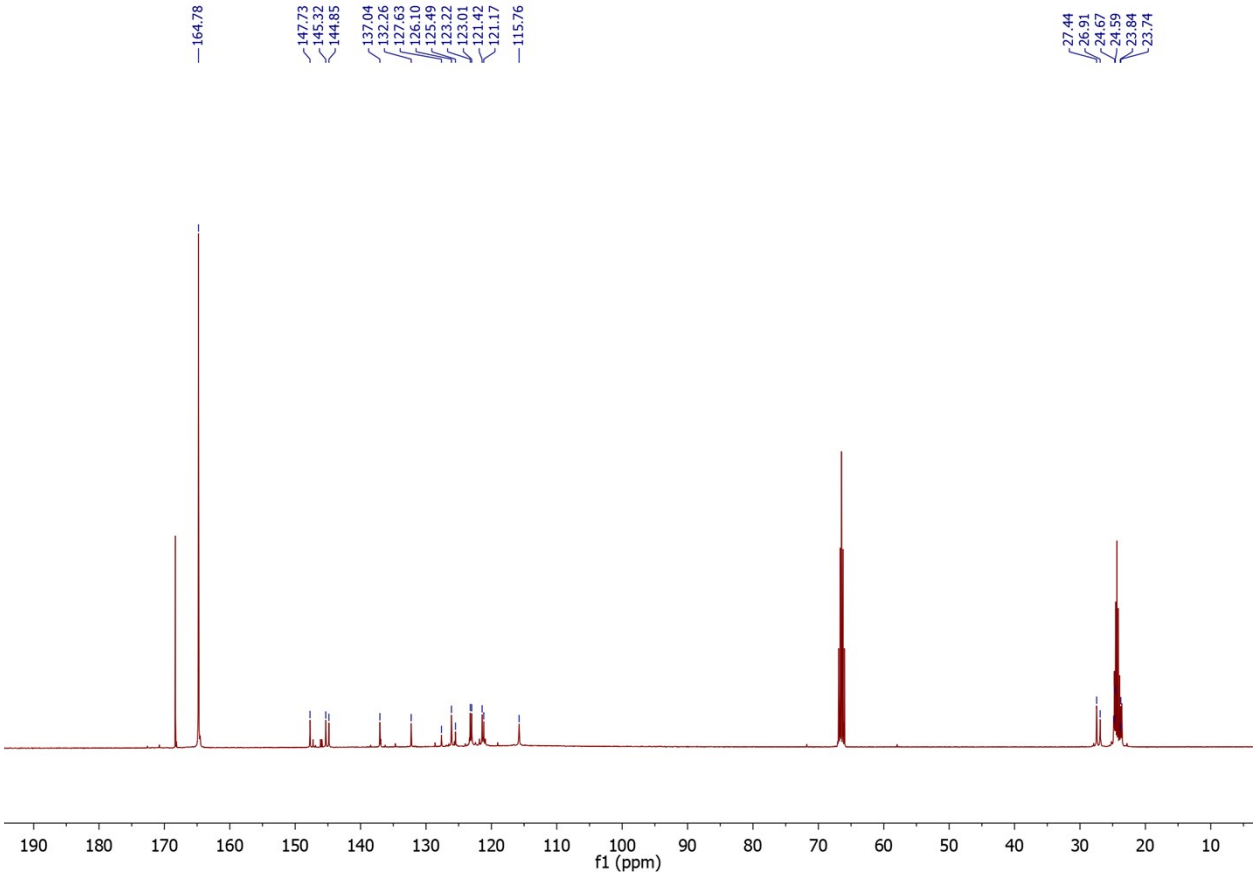


Figure S4. ^{13}C NMR spectrum of **2** (prepared from $^{13}CO_2$) at 298 K in thf-d_8.

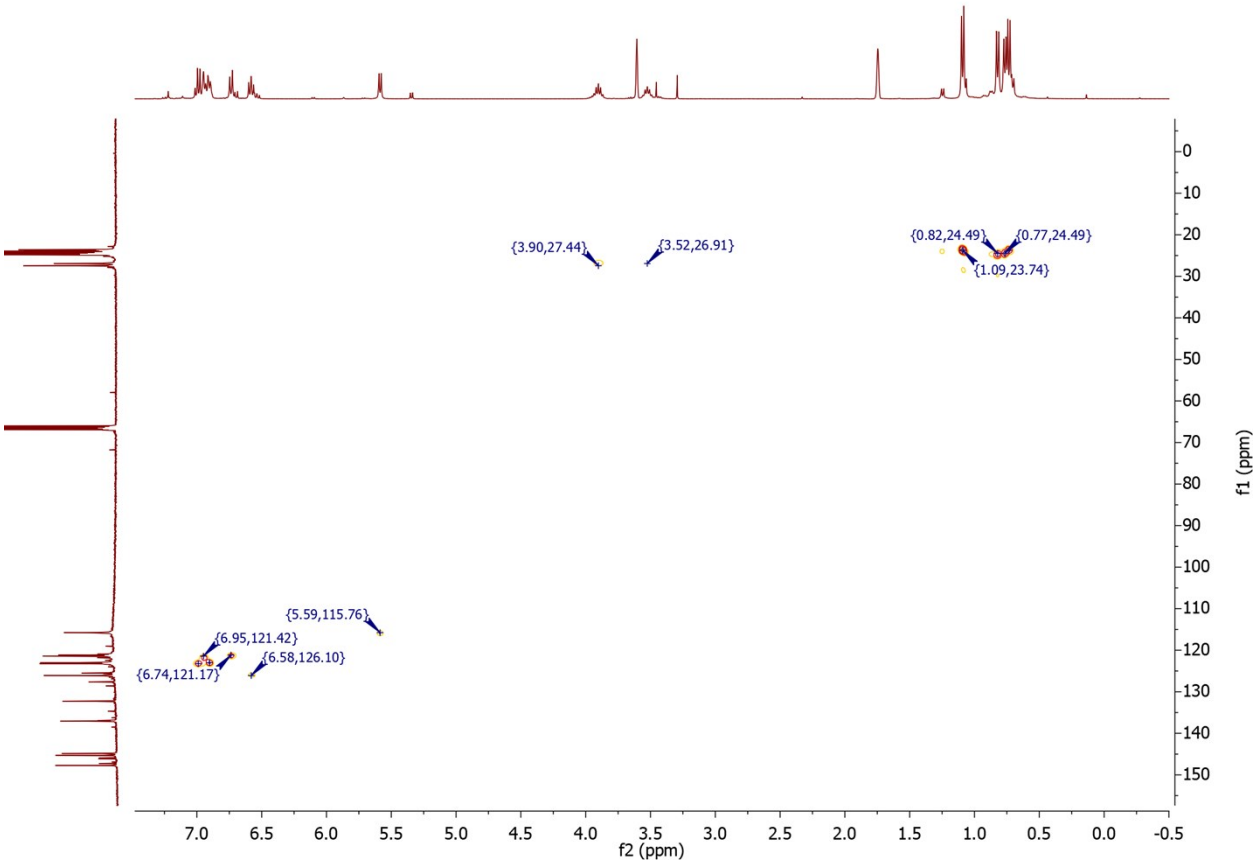


Figure S5. $^{1}H–^{13}C$ HSQC NMR spectrum of **2** at 298 K in thf-d_8.

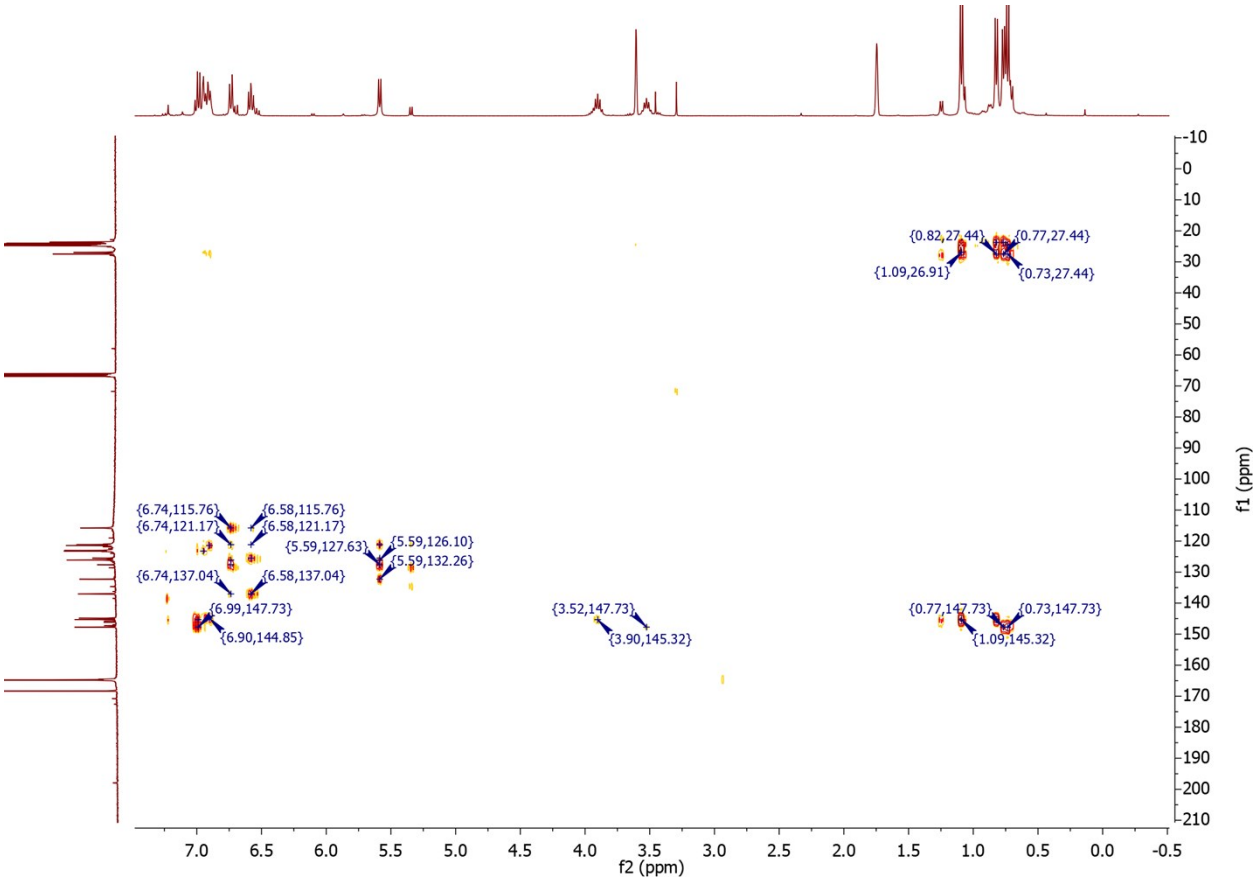


Figure S6. $^{1}H–^{13}C$ HMBC NMR spectrum of **2** at 298 K in thf-d_8.

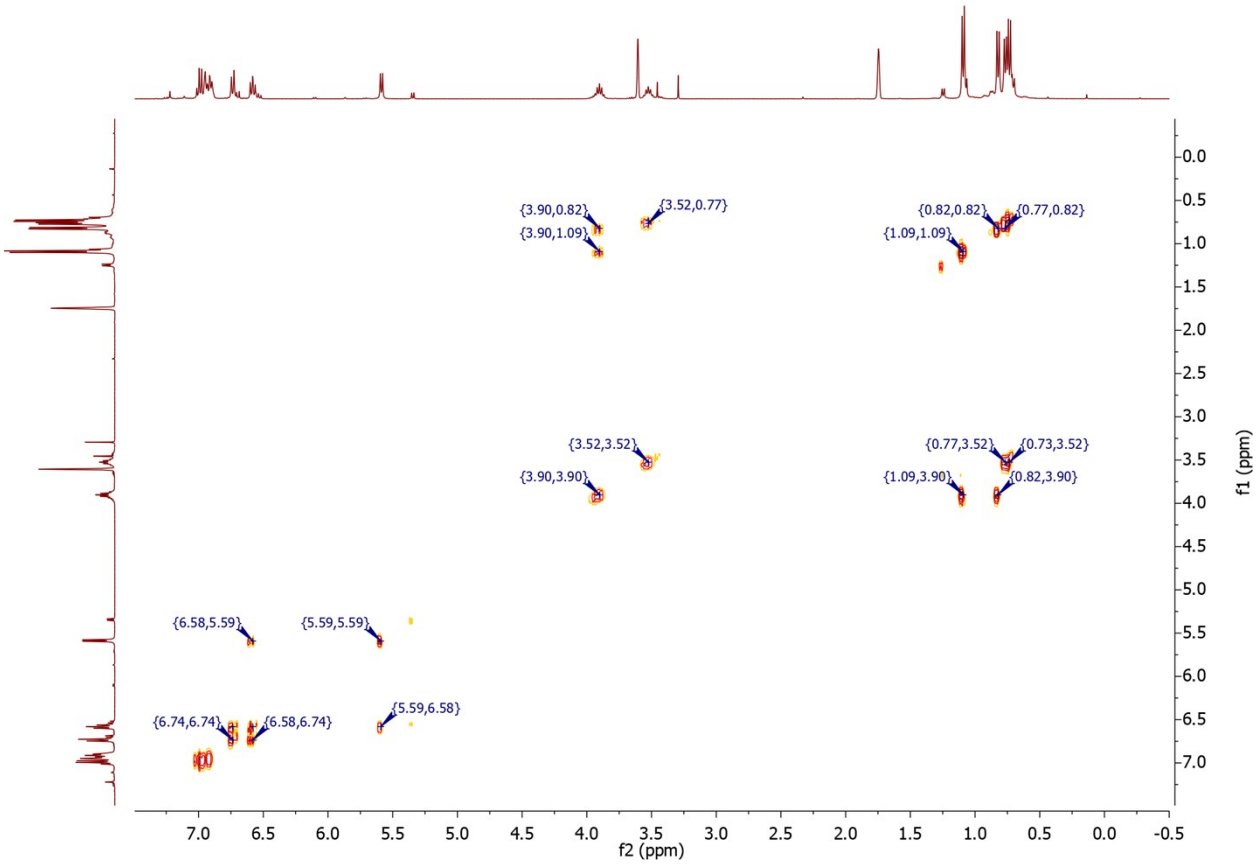


Figure S7. $^{1}H–^{1}H$ COSY NMR spectrum of **2** at 298 K in thf-d_8.

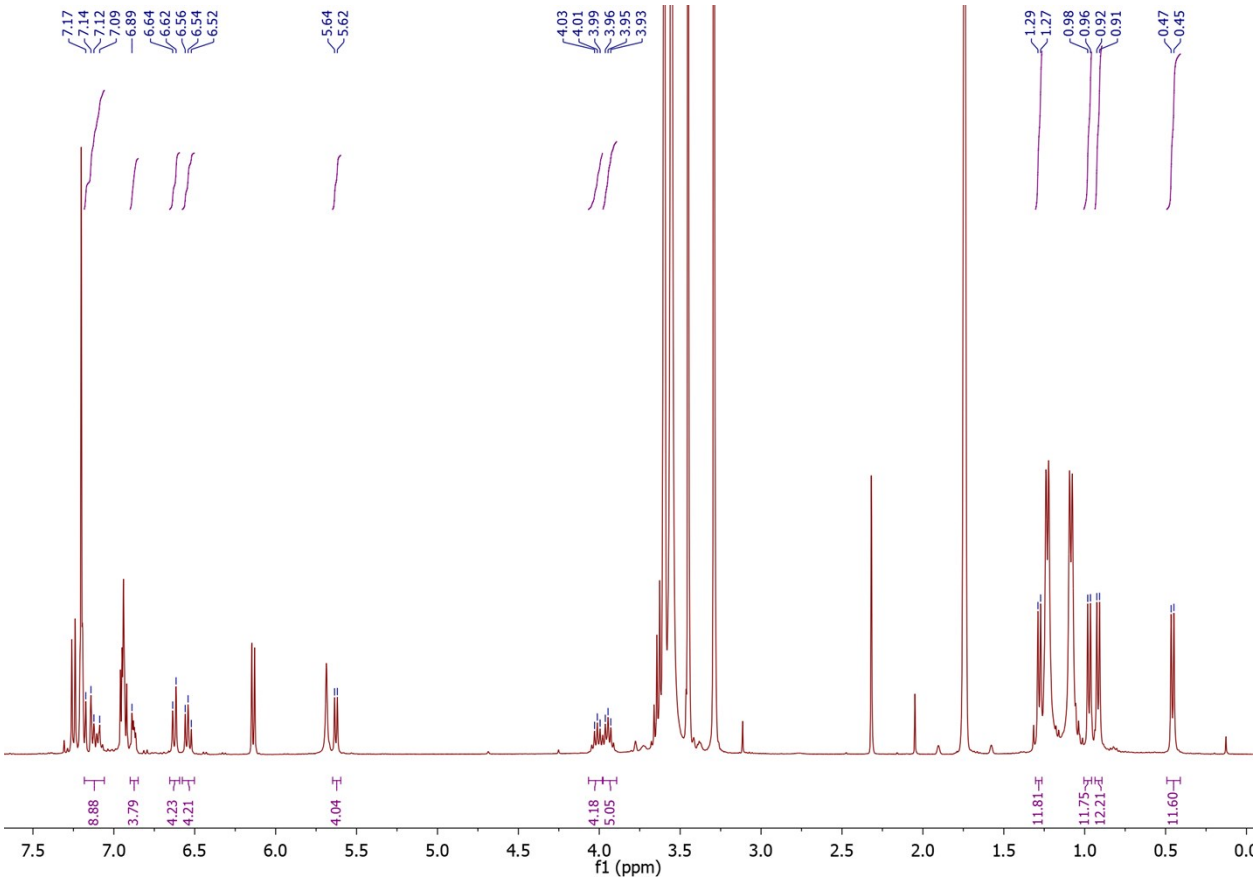


Figure S8. ^{1}H NMR spectrum of **4** at 328 K in thf-d_8.

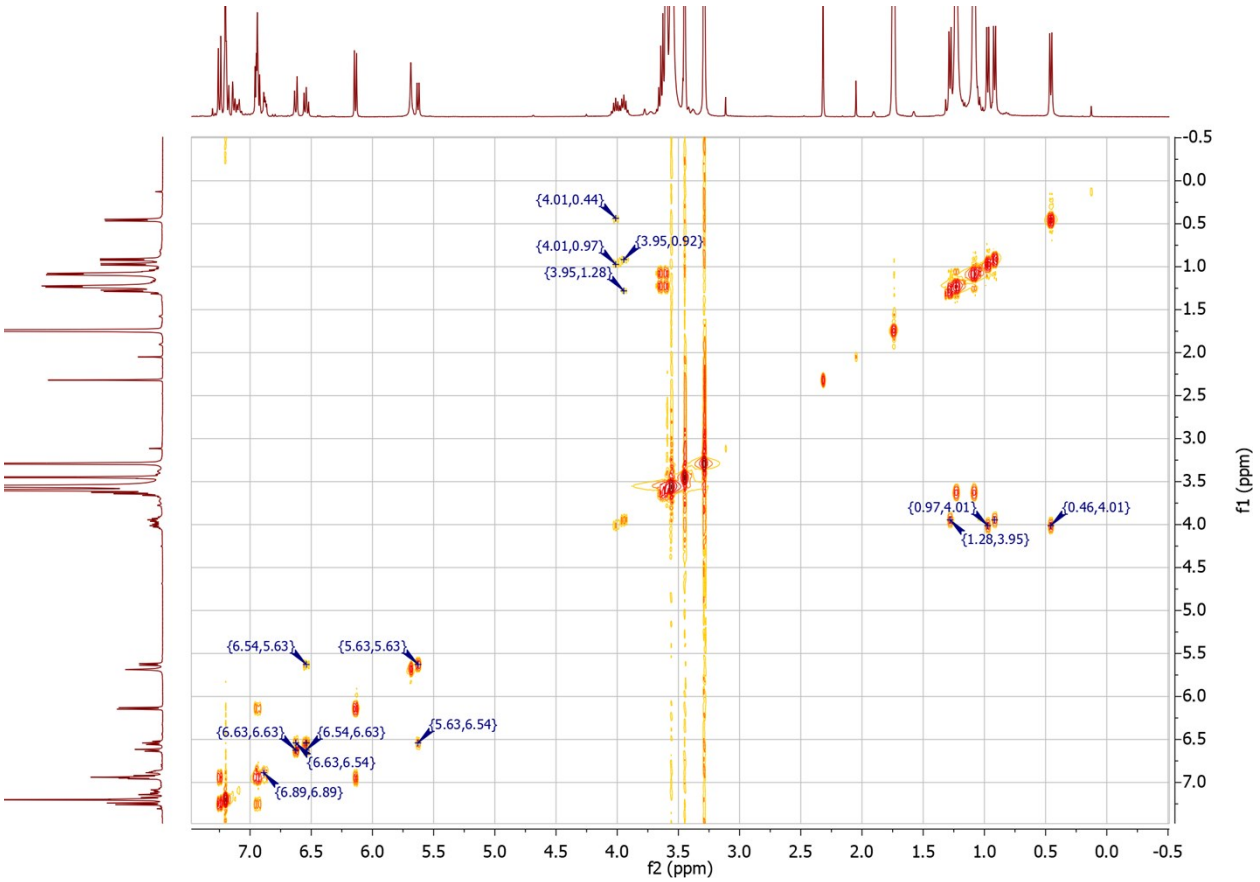


Figure S9. $^{1}H–^{1}H$ COSY NMR spectrum of **4** at 328 K in thf-d_8.

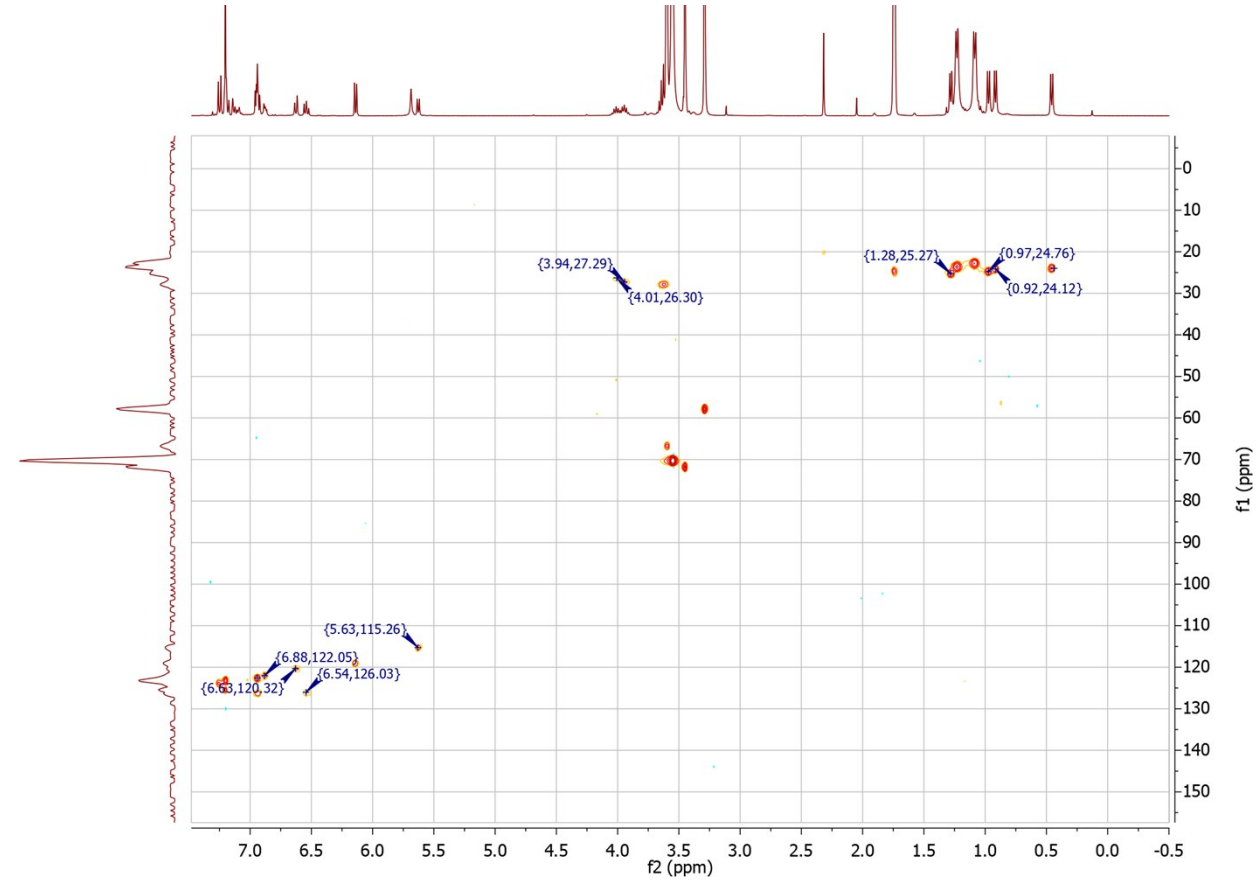


Figure S10. $^{1}H–^{13}C$ HSQC NMR spectrum of **4** at 328 K in thf-d_8.

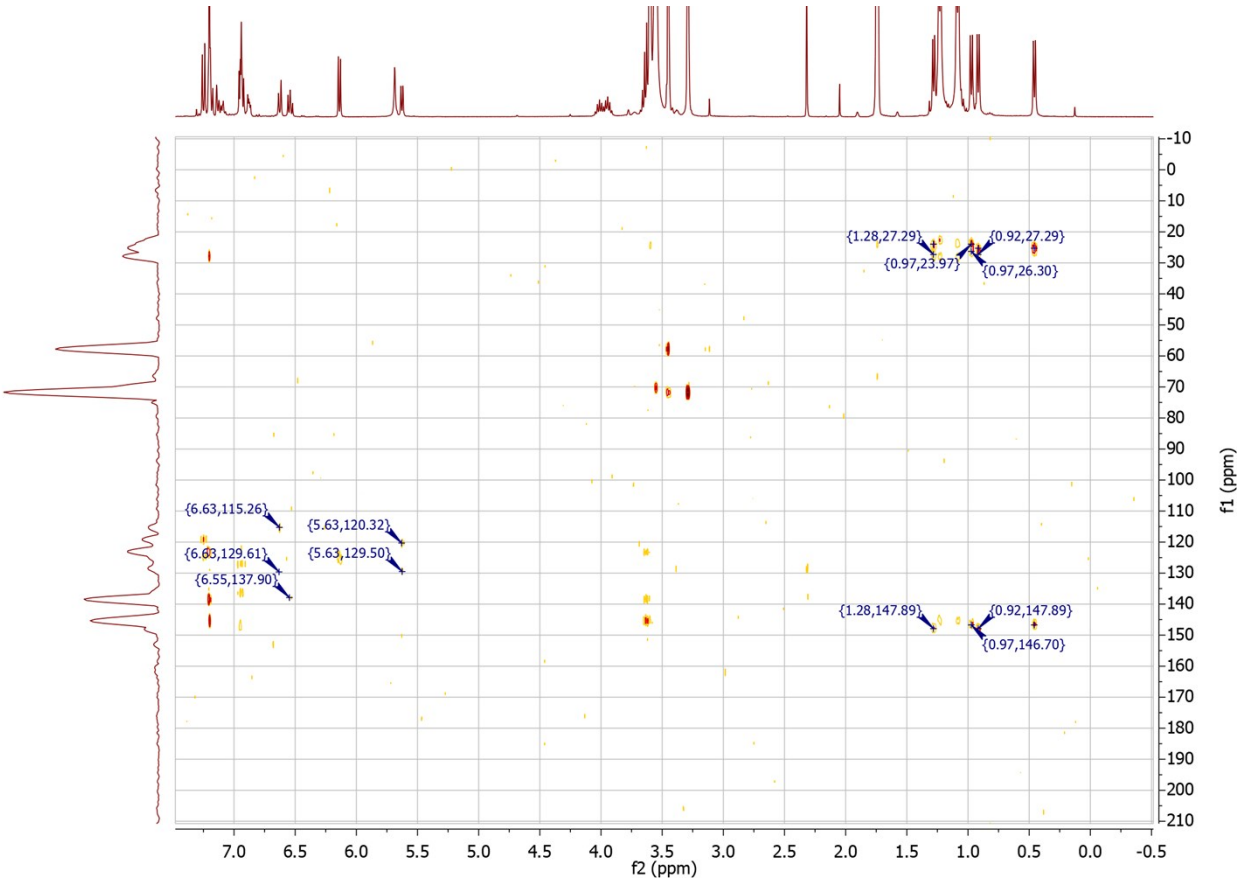


Figure S11. $^{1}H–^{13}C$ HMBC NMR spectrum of **4** at 328 K in thf-d_8.

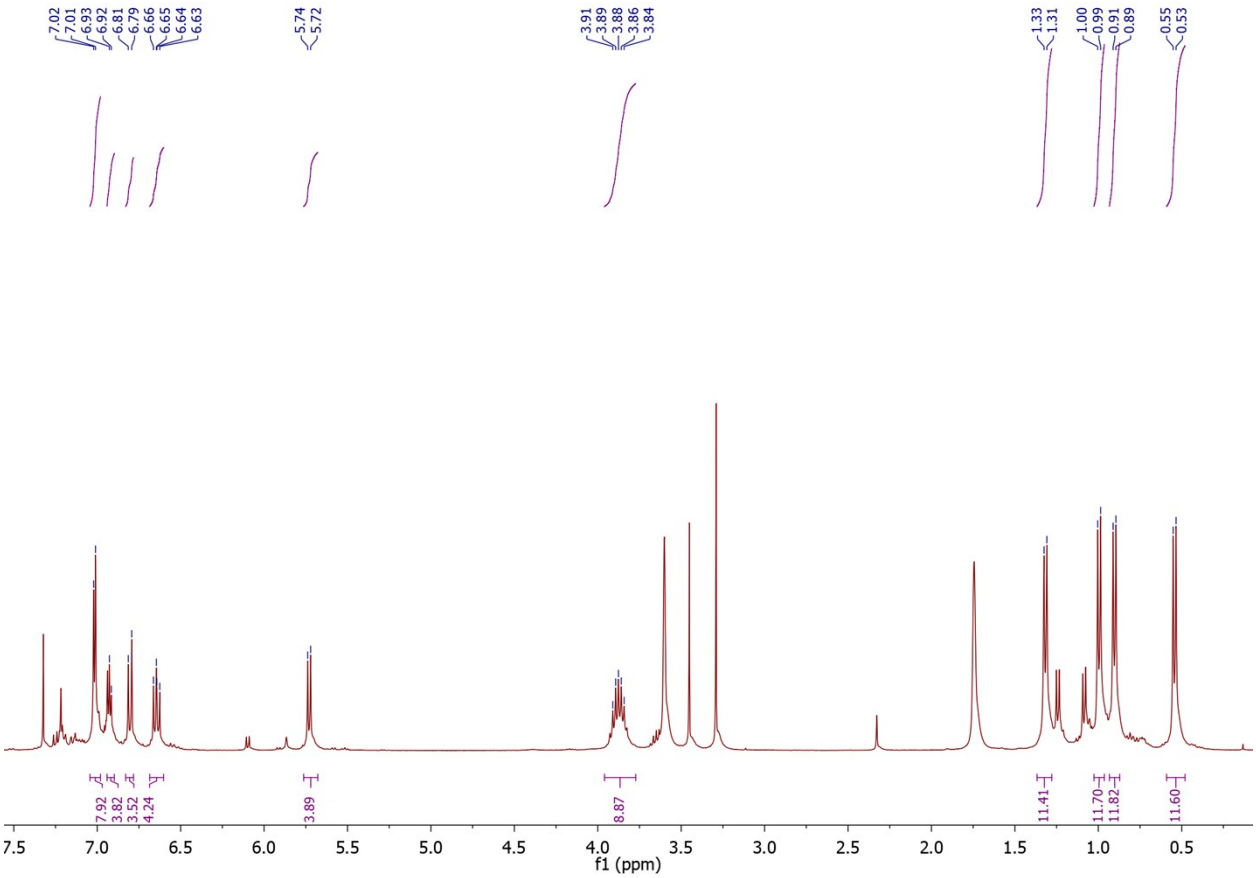


Figure S12. ^{1}H NMR spectrum of **5** at 298 K in thf-d_8.

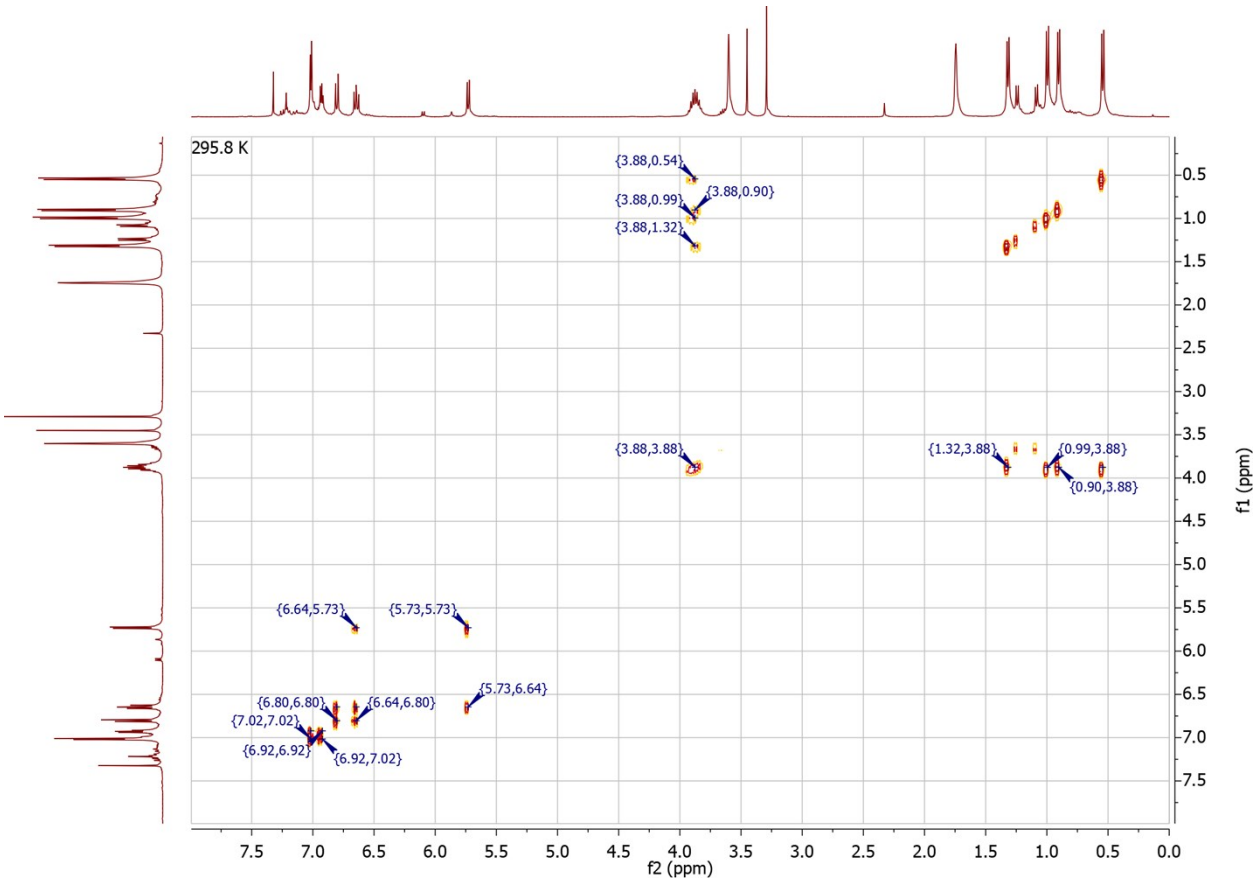


Figure S13. $^{1}H–^{1}H$ COSY NMR spectrum of **5** at 298 K in thf-d_8.

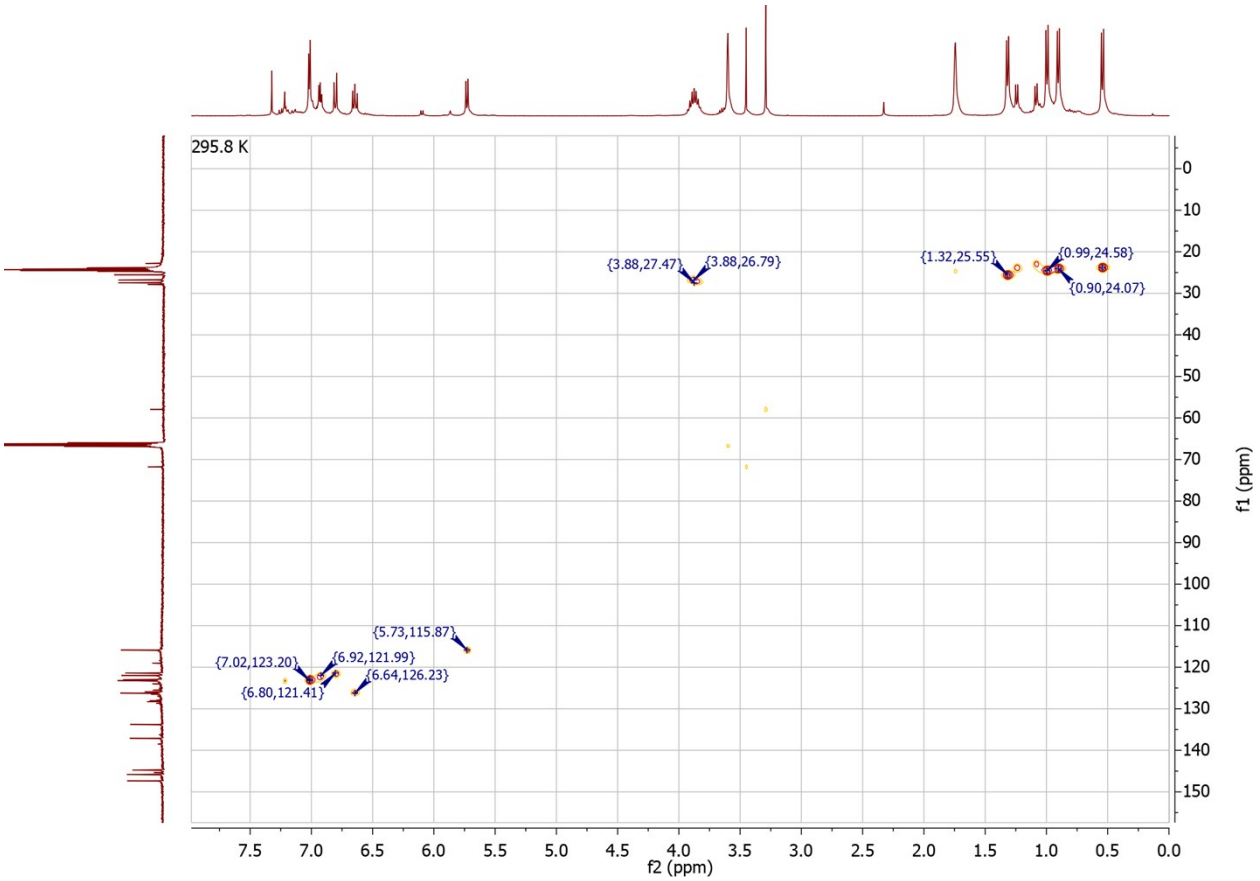


Figure S14. $^{1}H–^{13}C$ HSQC NMR spectrum of **5** at 298 K in thf-d_8.

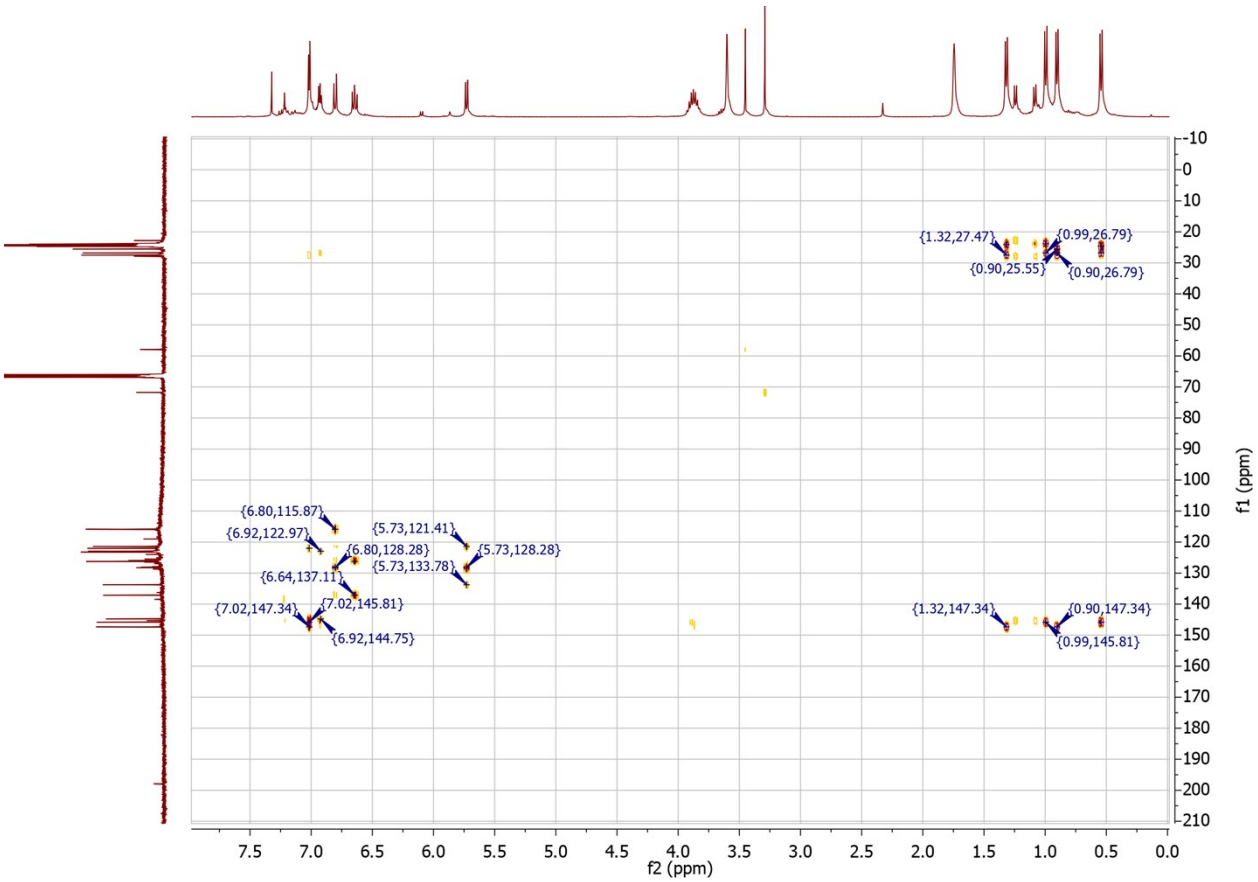


Figure S15. $^{1}H–^{13}C$ HMBC NMR spectrum of **5** at 298 K in thf-d_8.

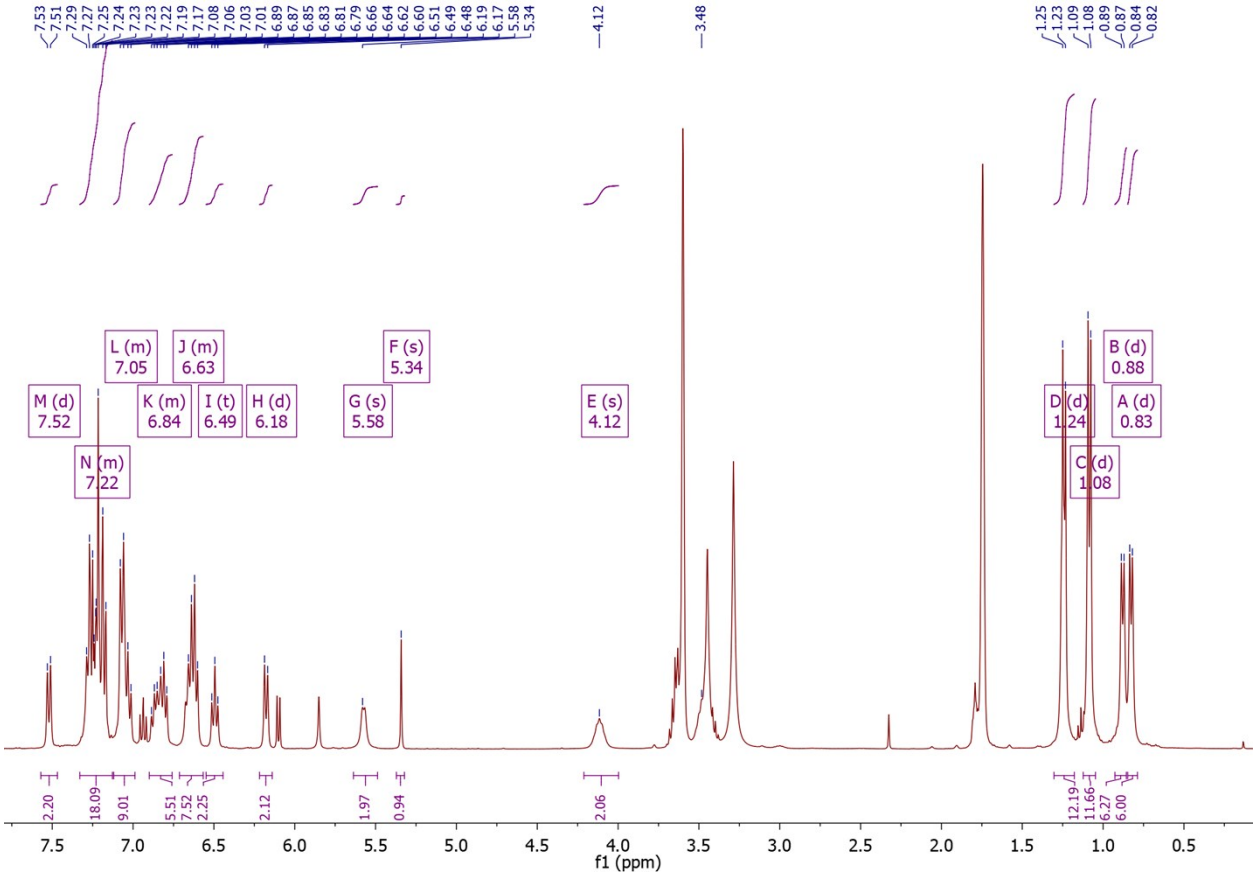


Figure S16. ^{1}H NMR spectrum of **6** at 298 K in thf-d_8.

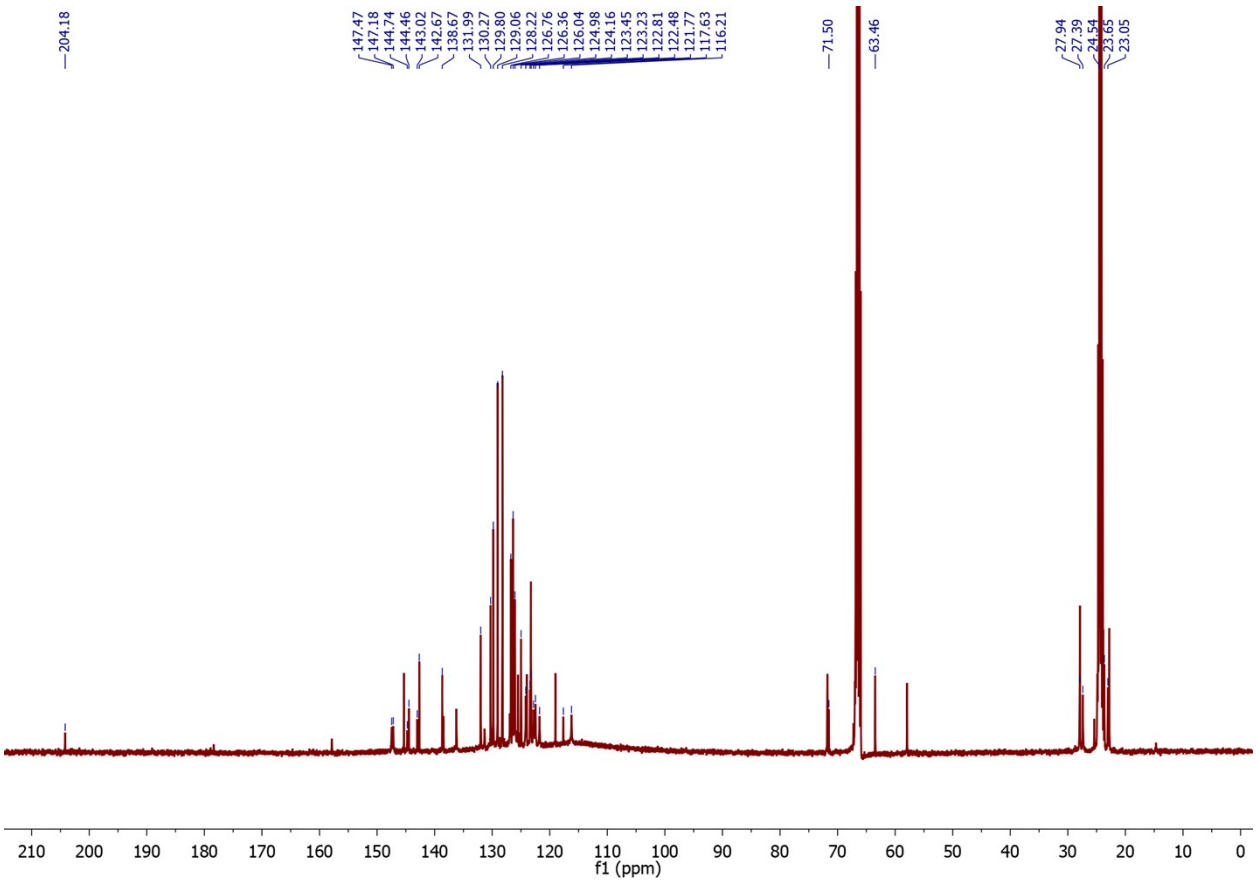


Figure S17. ^{13}C NMR spectrum of **6** at 298 K in thf-d_8.

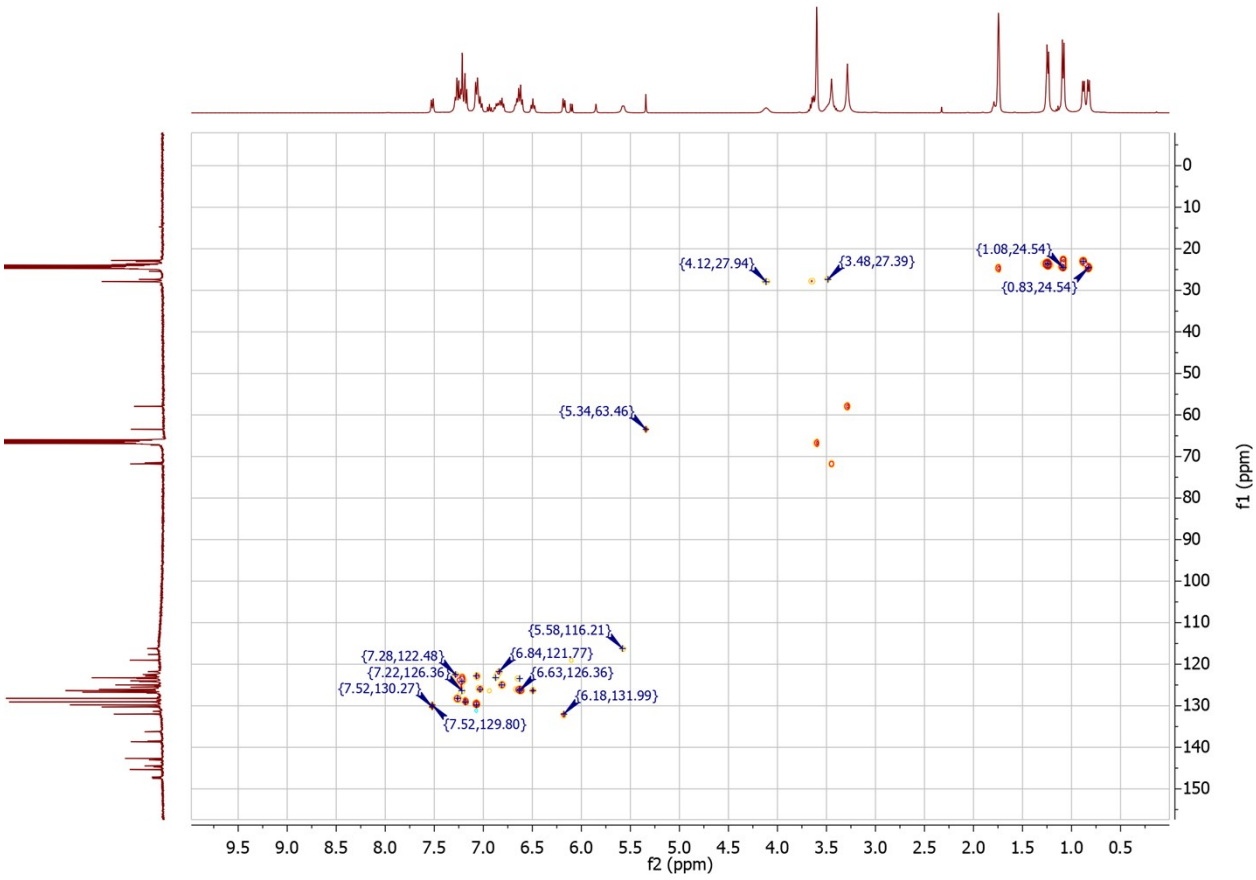


Figure S18. ^{1}H–^{13}C HSQC NMR spectrum of **6** at 298 K in thf-d_8.

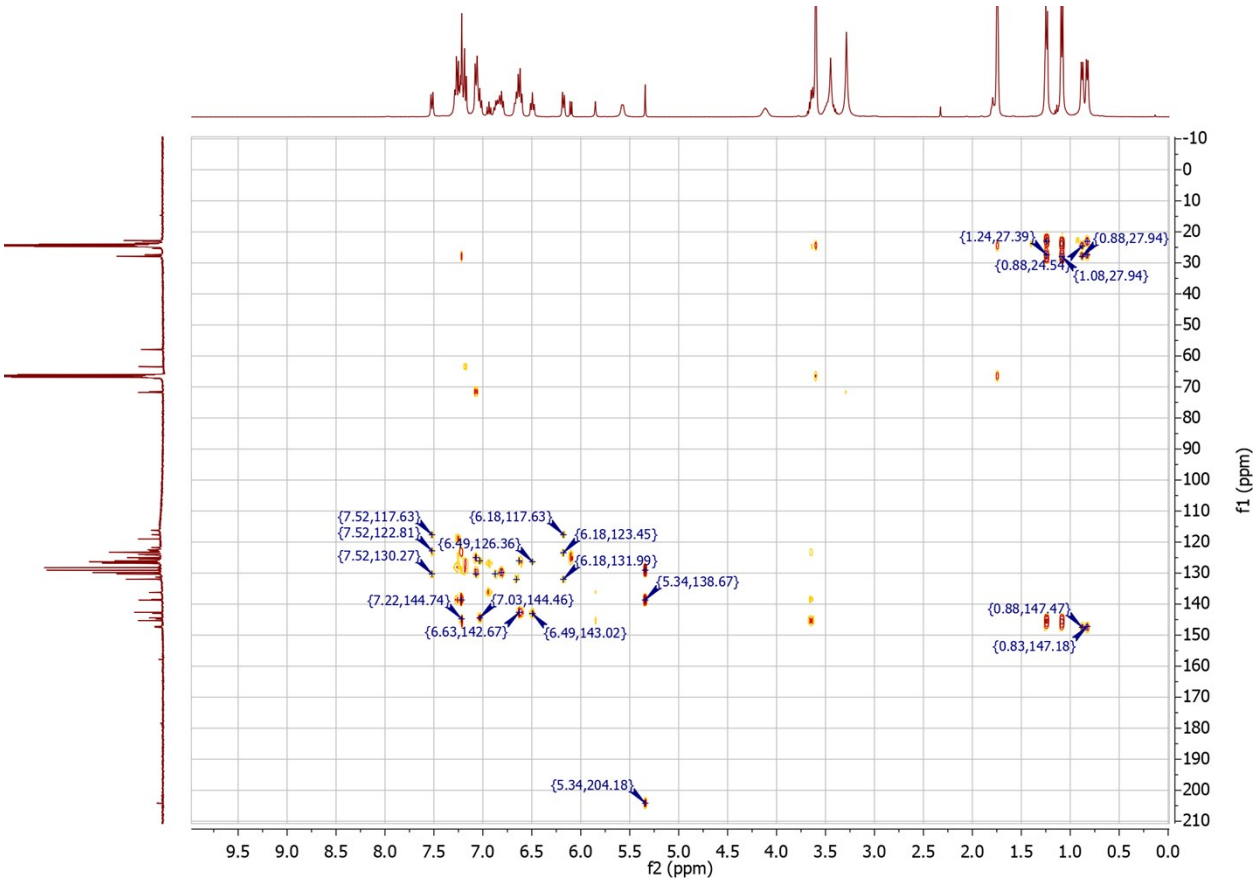


Figure S19. $^{1}H–^{13}C$ HMBC NMR spectrum of **6** at 298 K in thf-d_8.

Figure S20. $^{1}H–^{1}H$ COSY NMR spectrum of **6** at 298 K in thf-d_8.

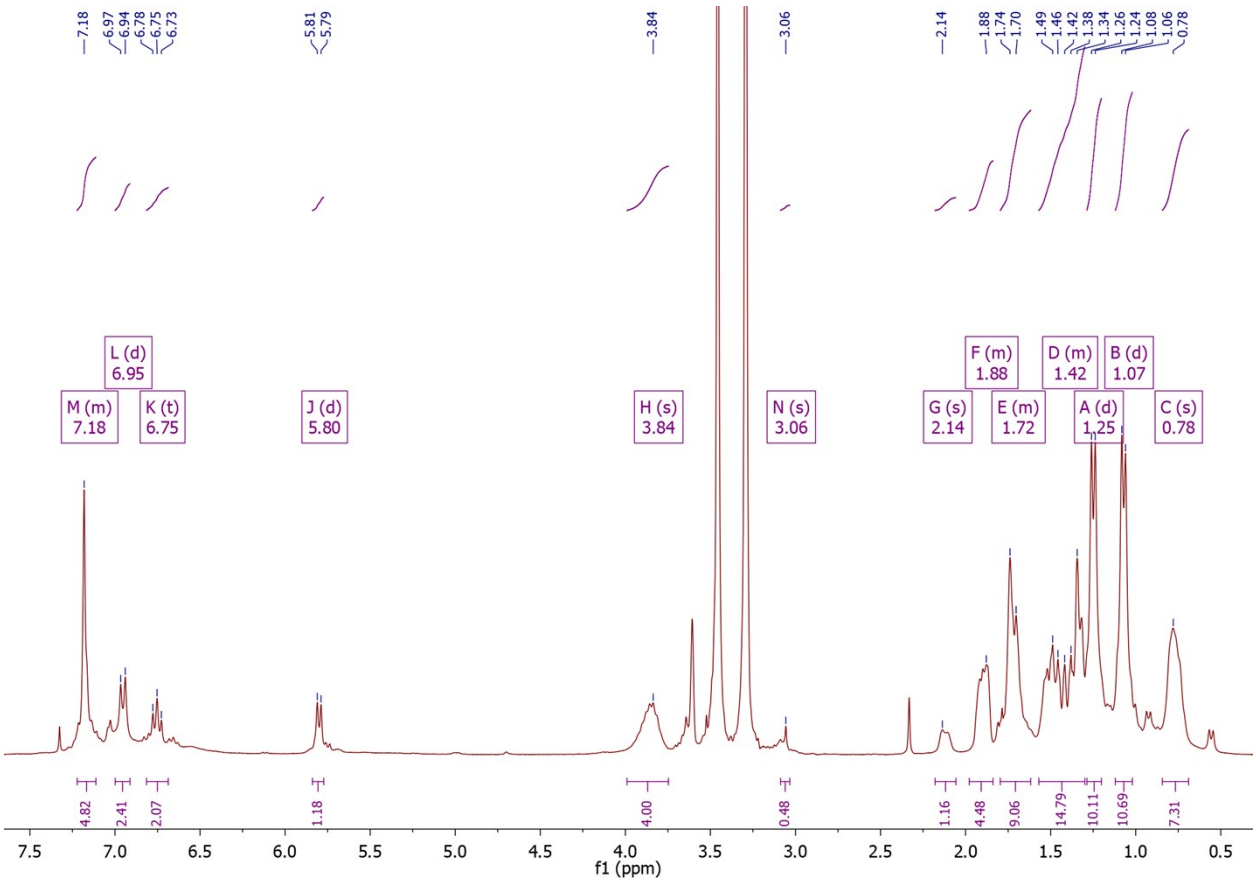


Figure S21. ^{1}H NMR spectrum of **7** at 298 K in thf-d_8.

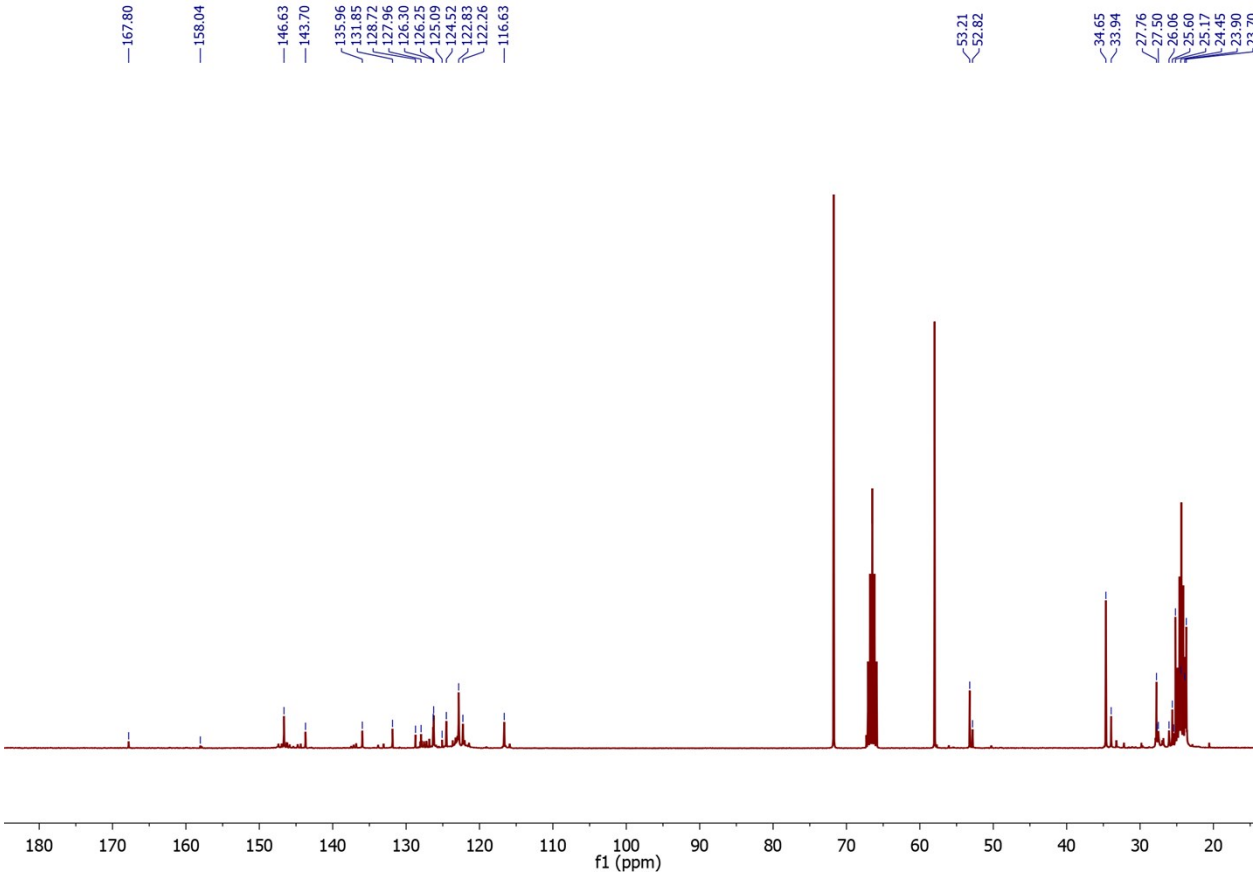


Figure S22. ^{13}C NMR spectrum of **7** at 298 K in thf-d_8.

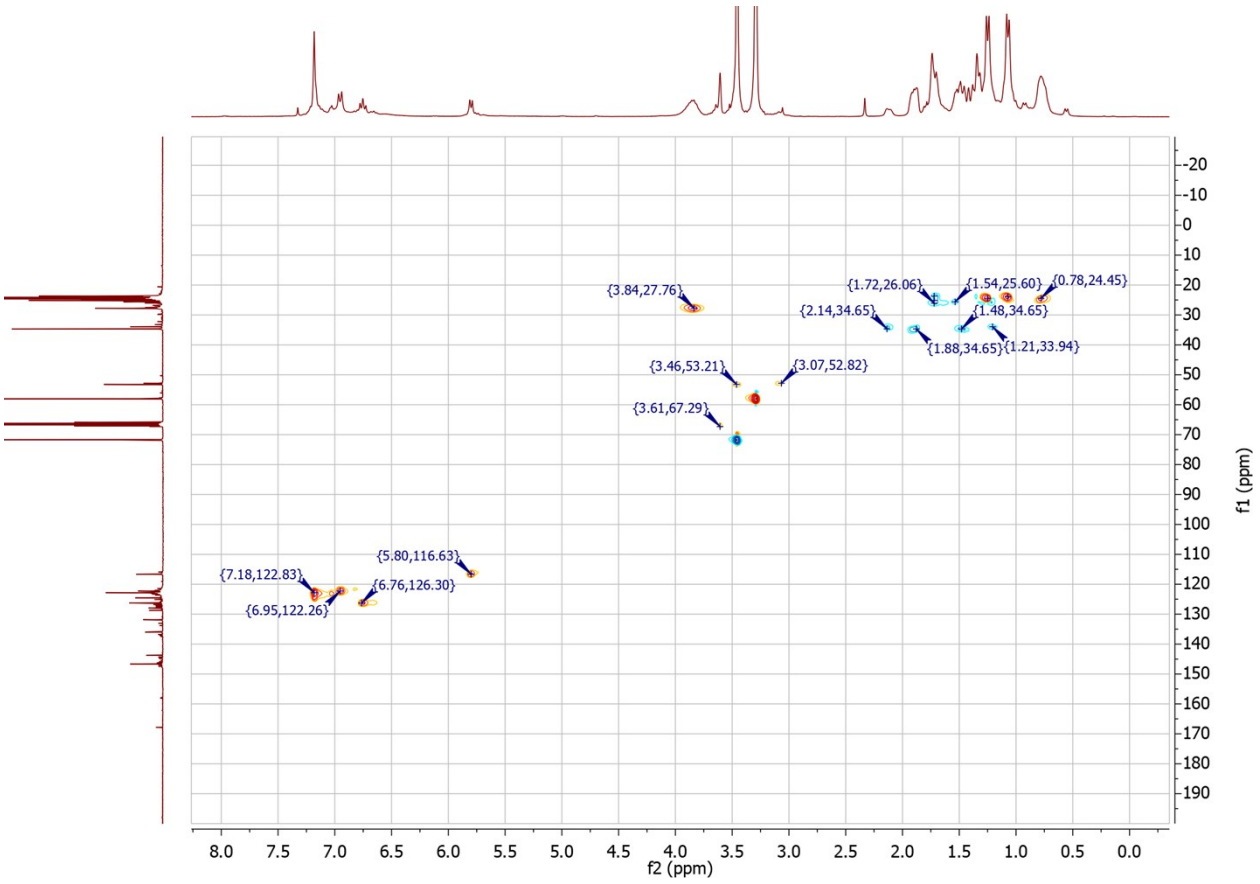


Figure S23. $^{1}H–^{13}C$ HSQC NMR spectrum of **7** at 298 K in thf-d_8.

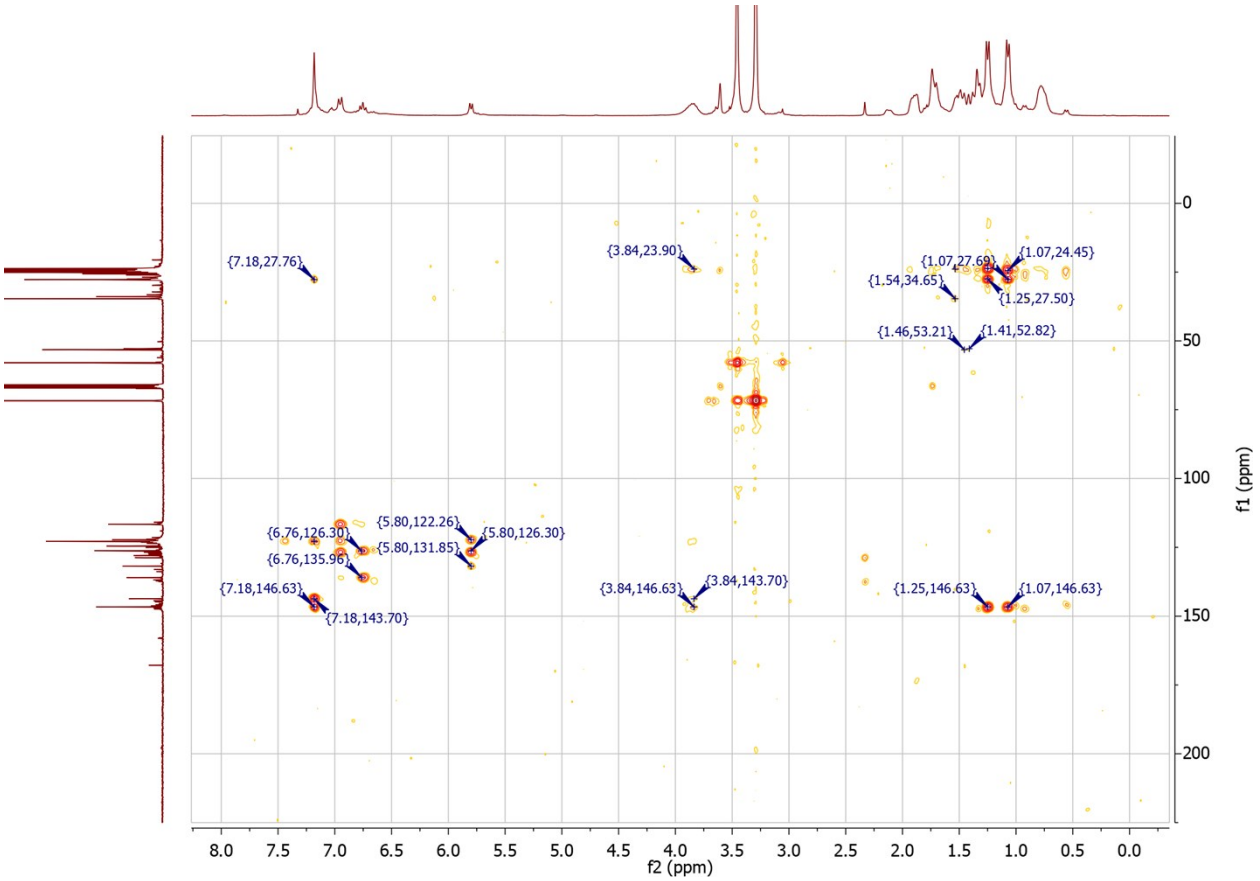


Figure S24. $^{1}H–^{13}C$ HMBC NMR spectrum of **7** at 298 K in thf-d_8.

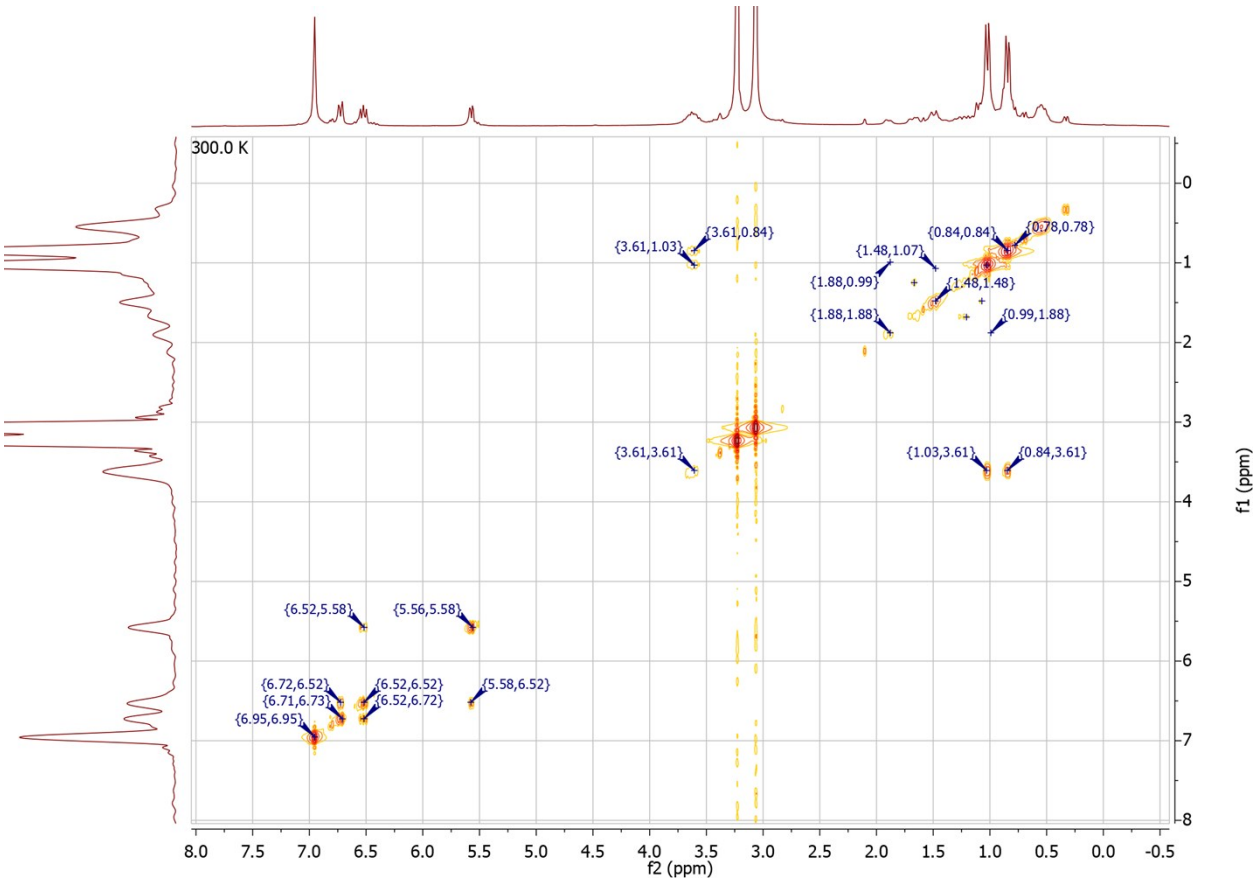


Figure S25. ^{1}H–^{1}H COSY NMR spectrum of **7** at 298 K in thf-d_8.

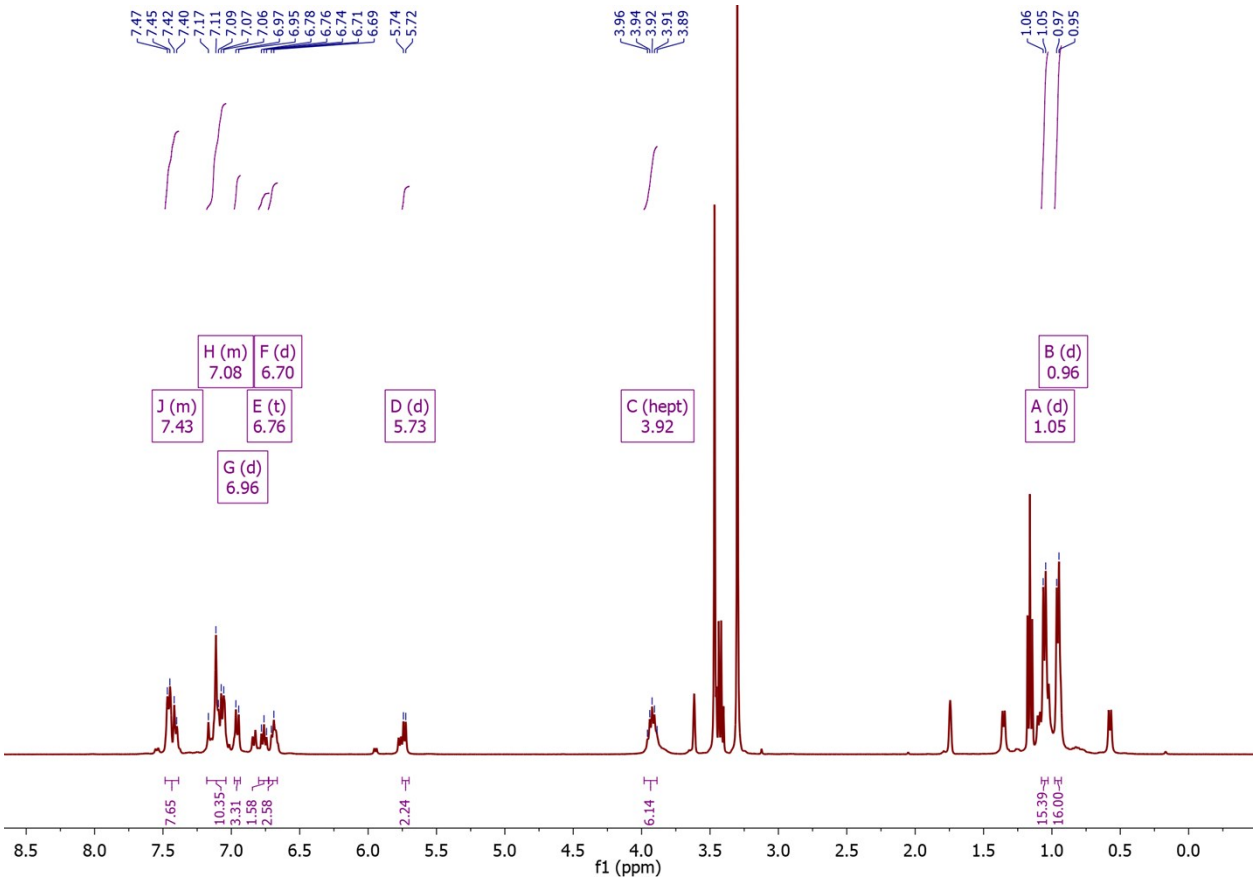


Figure S26. ^{1}H NMR spectrum of **8** at 298 K in thf-d_8.

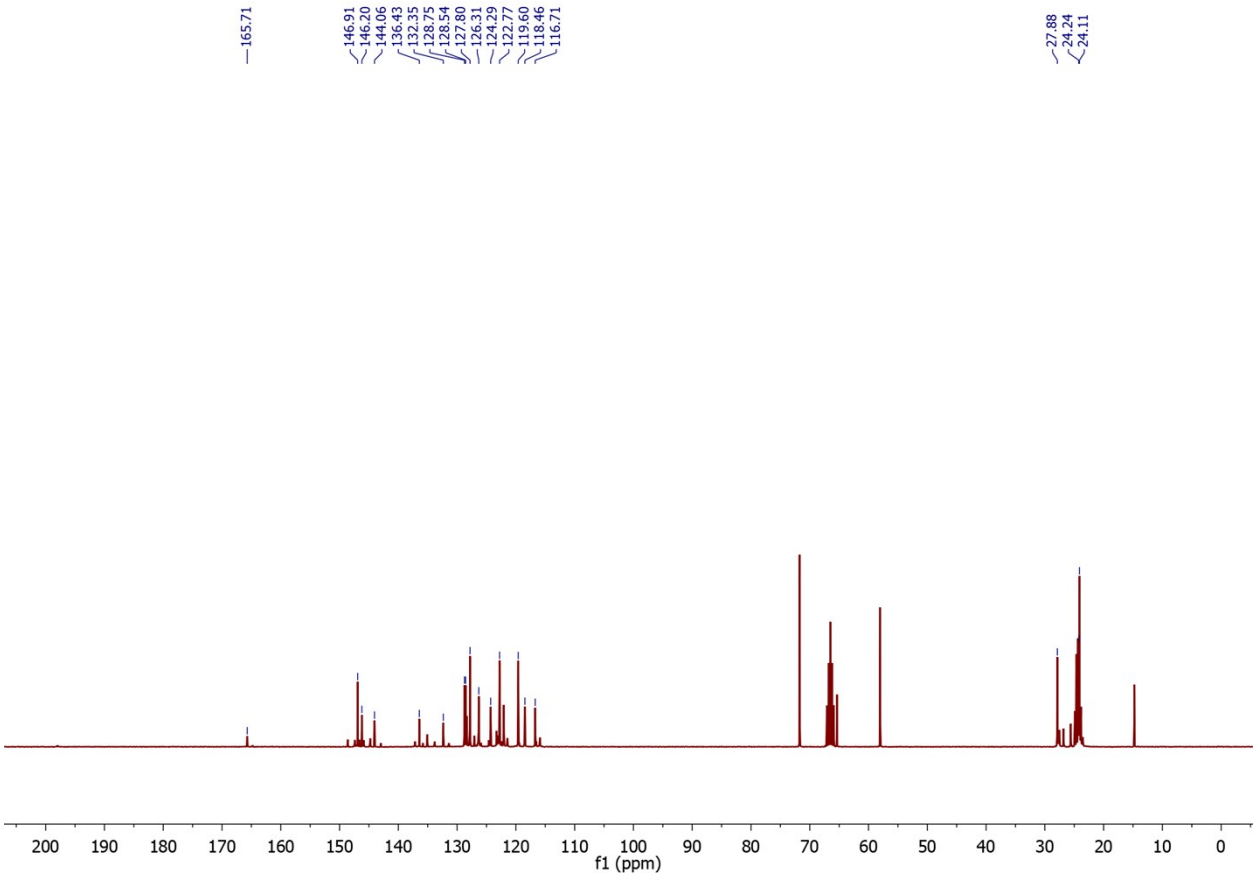


Figure S27. ^{13}C NMR spectrum of **8** at 298 K in thf-d_8.

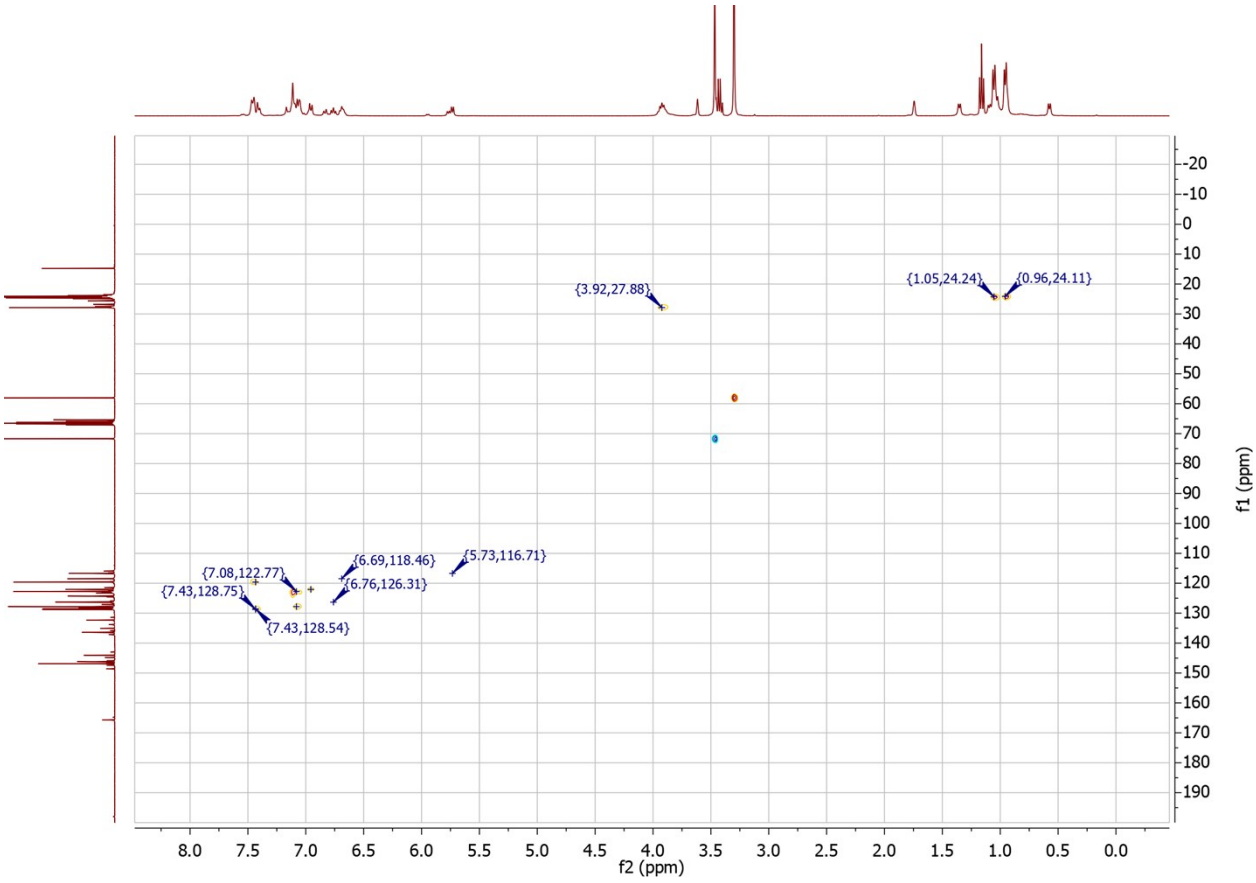


Figure S28. ^{1}H–^{13}C HSQC NMR spectrum of **8** at 298 K in thf-d_8.

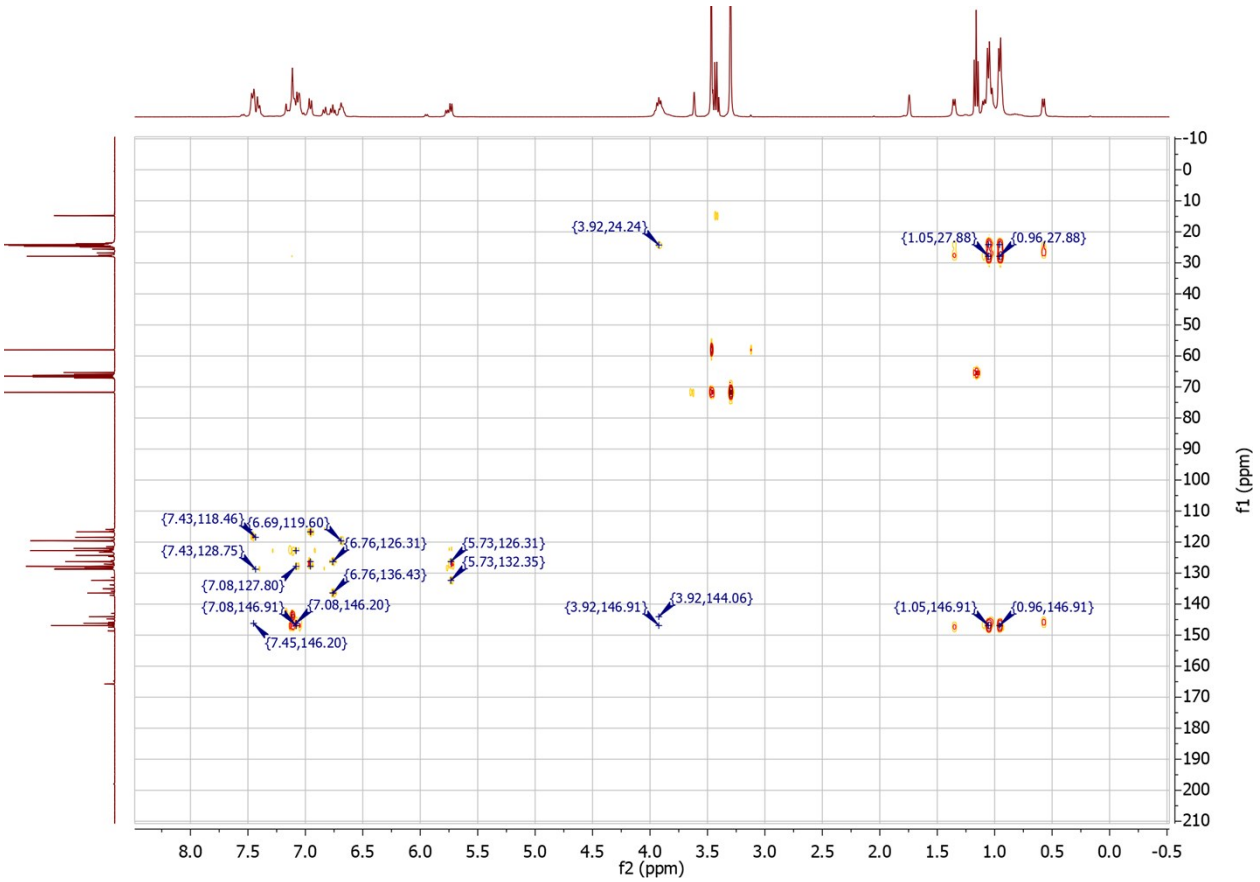


Figure S29. $^{1}H–^{13}C$ HMBC NMR spectrum of **8** at 298 K in thf-d_8.

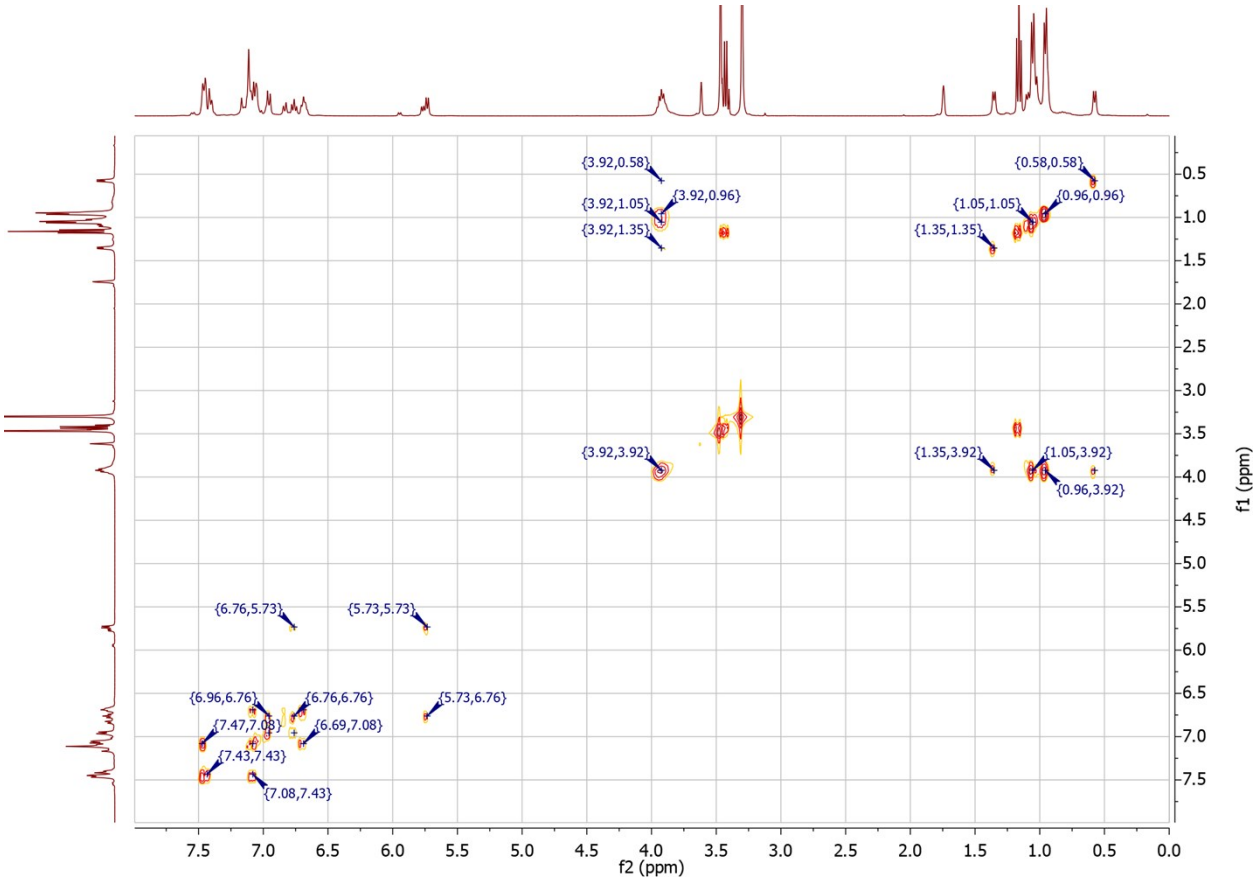


Figure S30. $^{1}H–^{1}H$ COSY NMR spectrum of **8** at 298 K in thf-d_8.

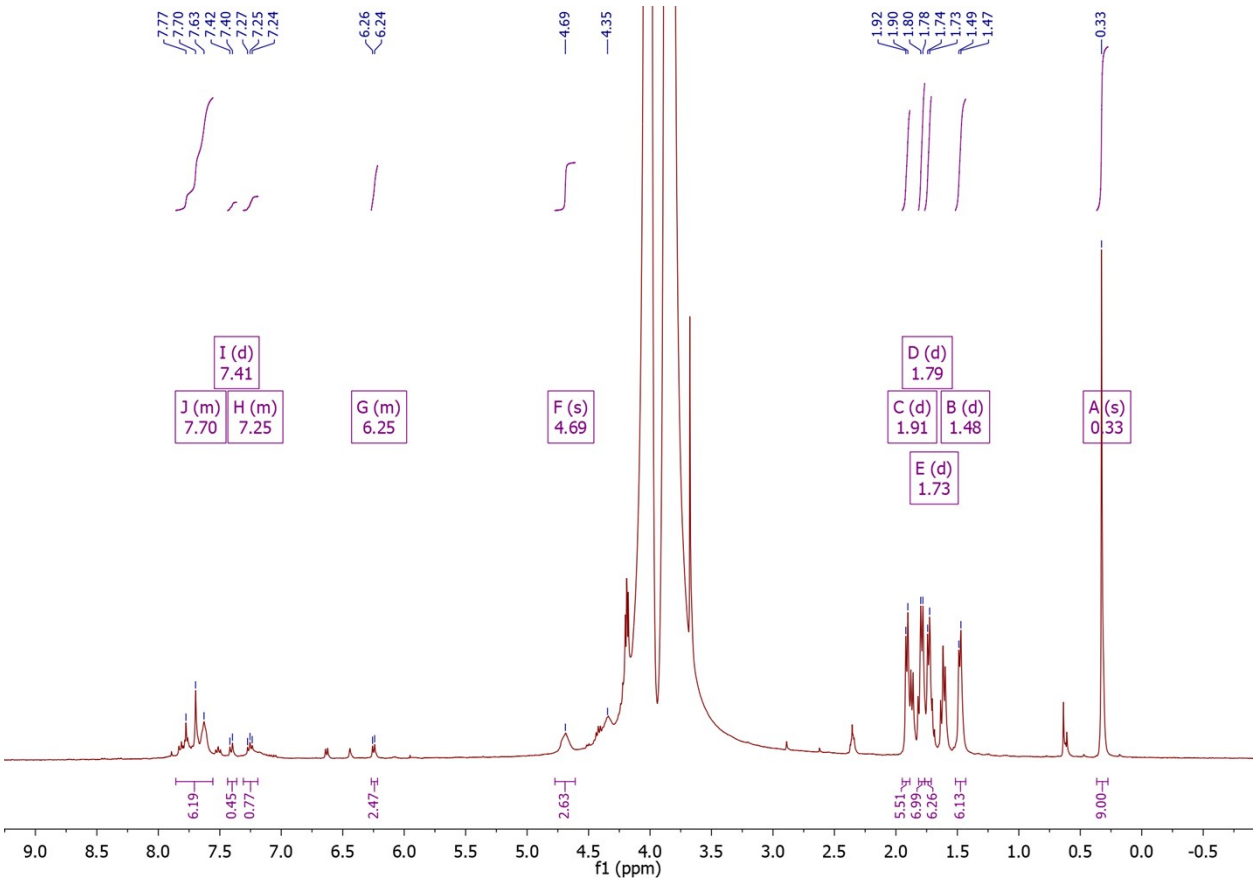


Figure S31. ^{1}H NMR spectrum of **10** at 298 K in protio-DME.

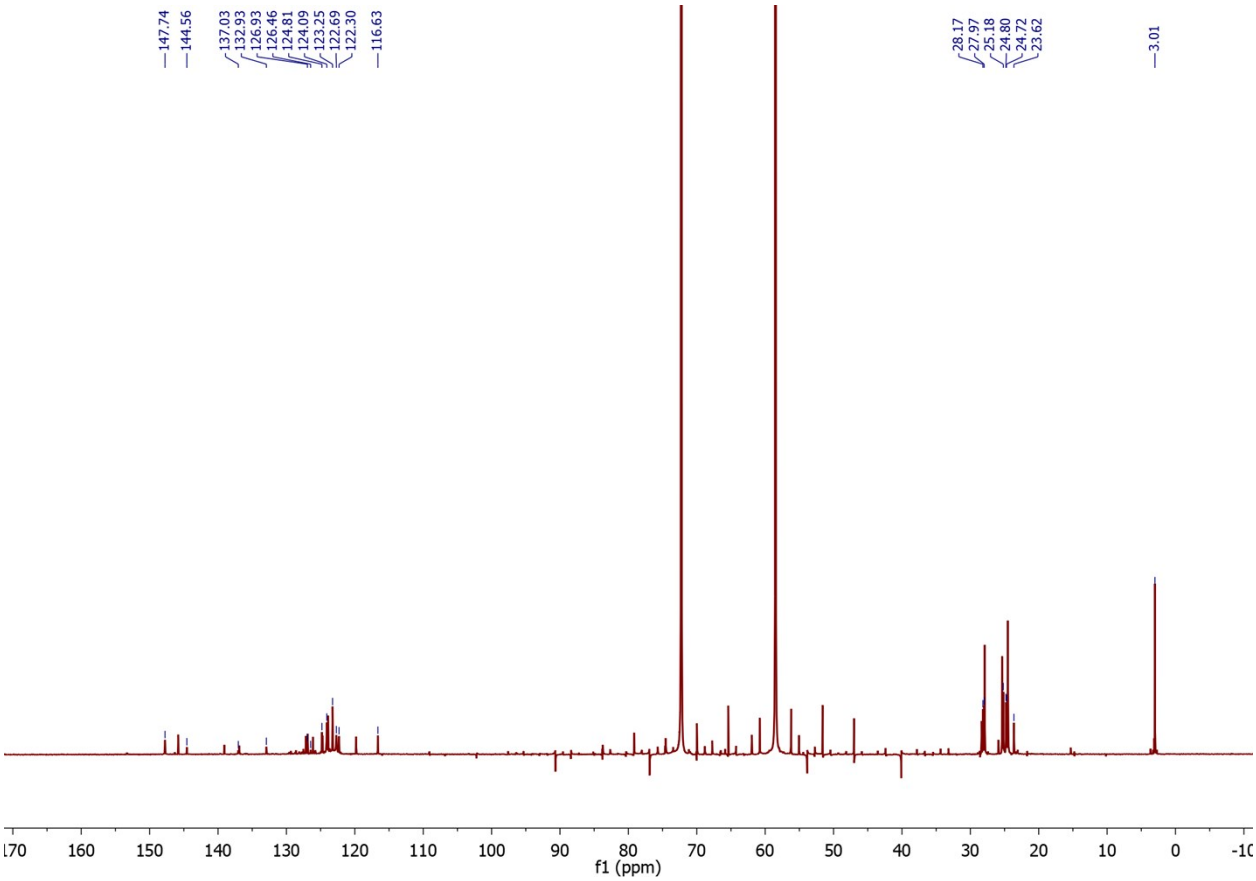


Figure S32. ^{13}C NMR spectrum of **10** at 298 K in protio-DME.

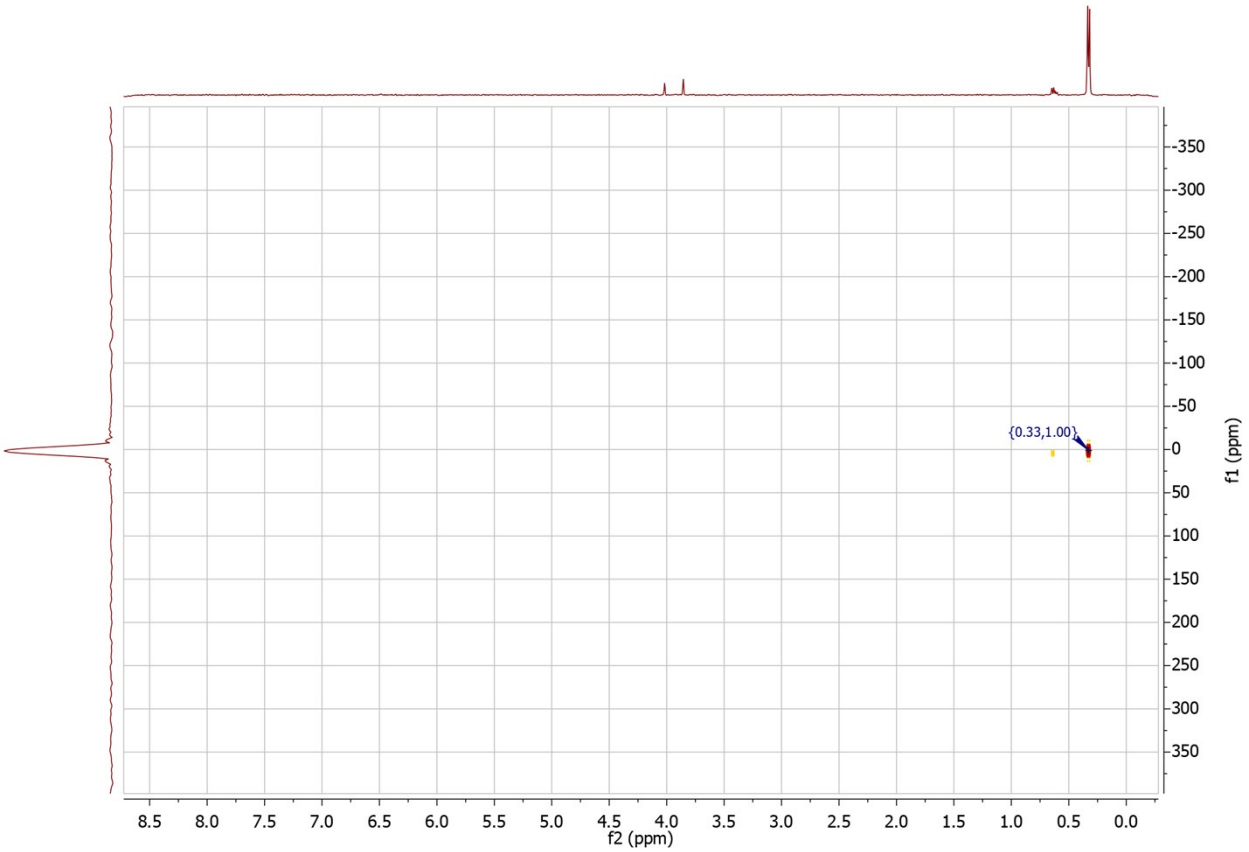


Figure S33. $^{1}H–^{29}Si$ HMBC NMR spectrum of **10** at 298 K in protio-DME.

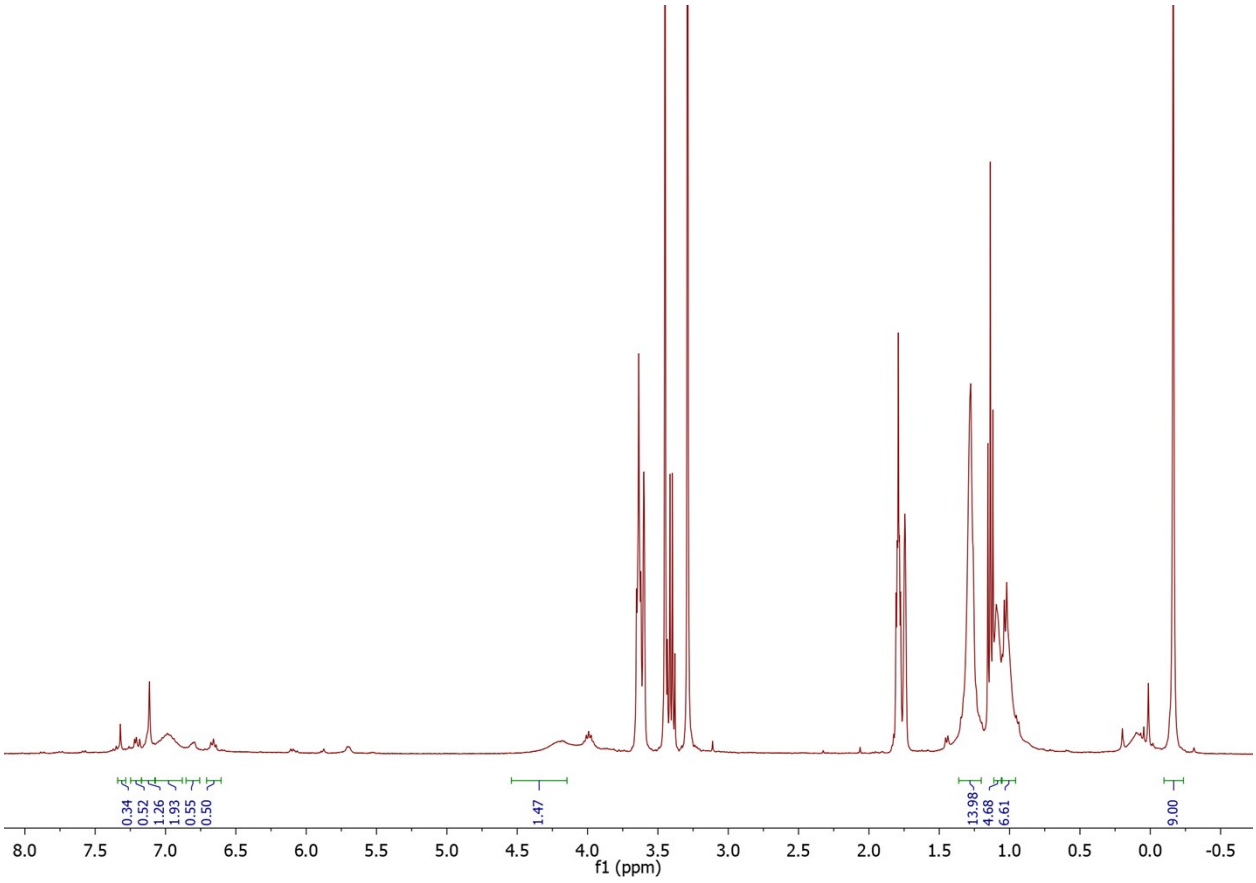


Figure S34. ^{1}H NMR spectrum of **11** at 298 K in protio-DME.

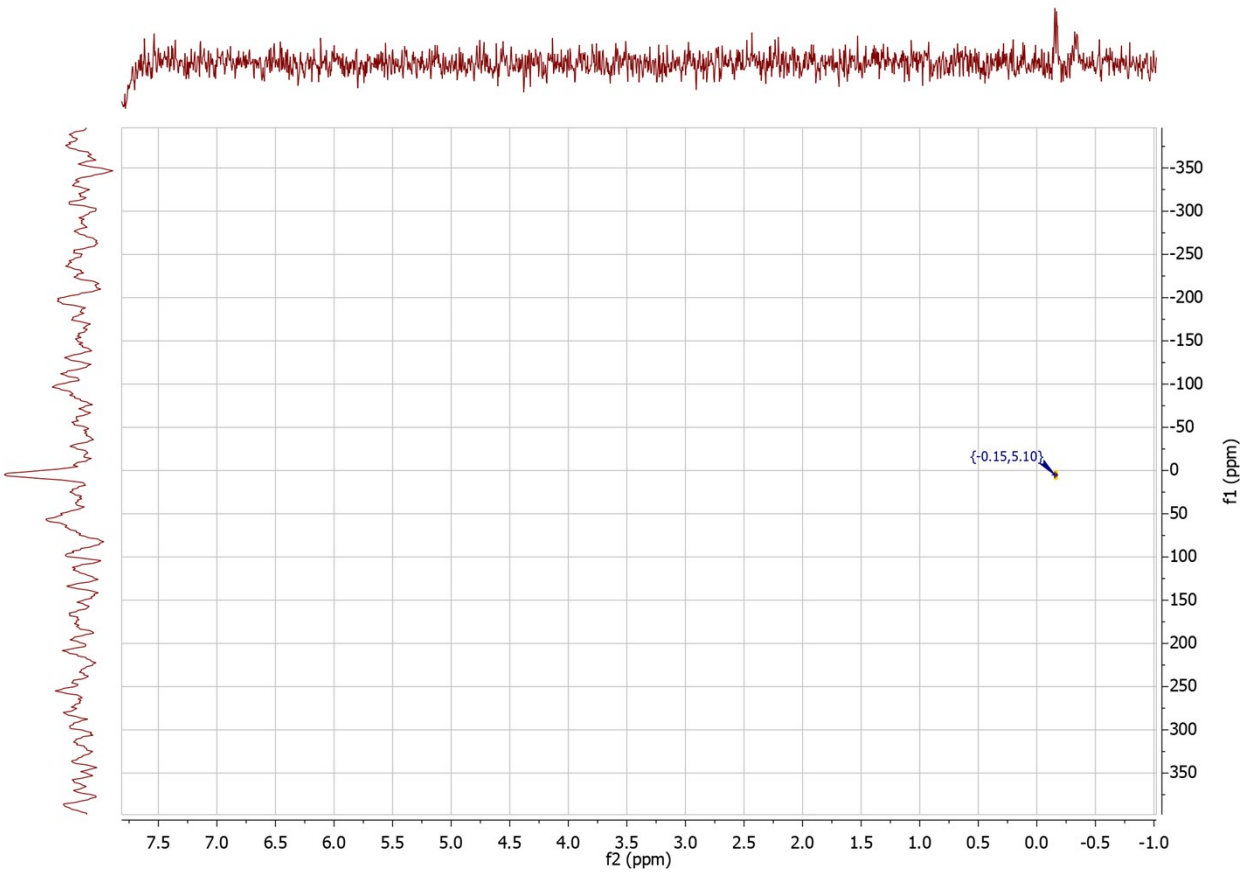


Figure S35. ^{1}H–^{29}Si HMBC NMR spectrum of **11** at 298 K in protio-DME.

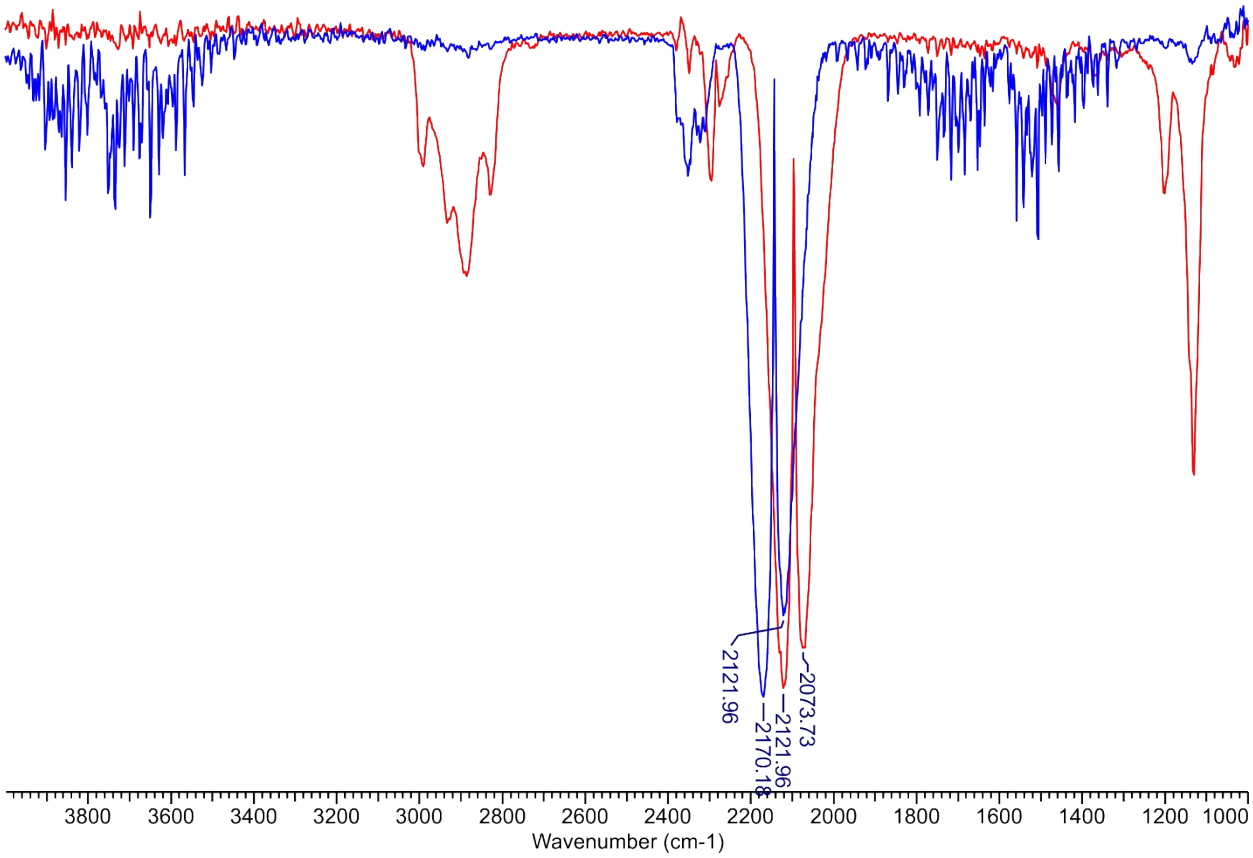


Figure S36. IR spectra of gaseous products of the sequential reaction of **1** with $^{12}CO_2$ and 2 eq. of $Ph_2C^{12}CO$ (blue) and **1** with $^{13}CO_2$ and 2 eq. of $Ph_2C^{12}CO$ (red).

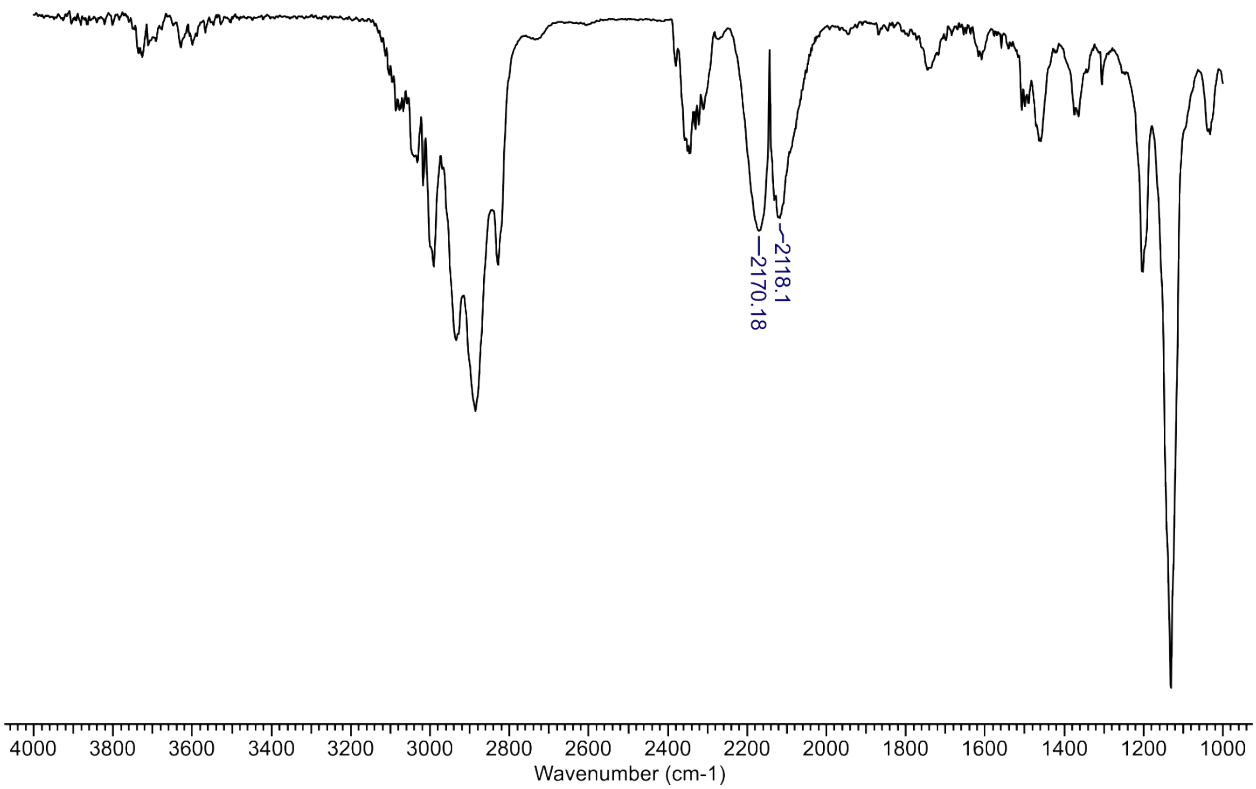


Figure S37. IR spectra of gaseous products of the sequential reaction of **1** with CO_2 and PhNCO.

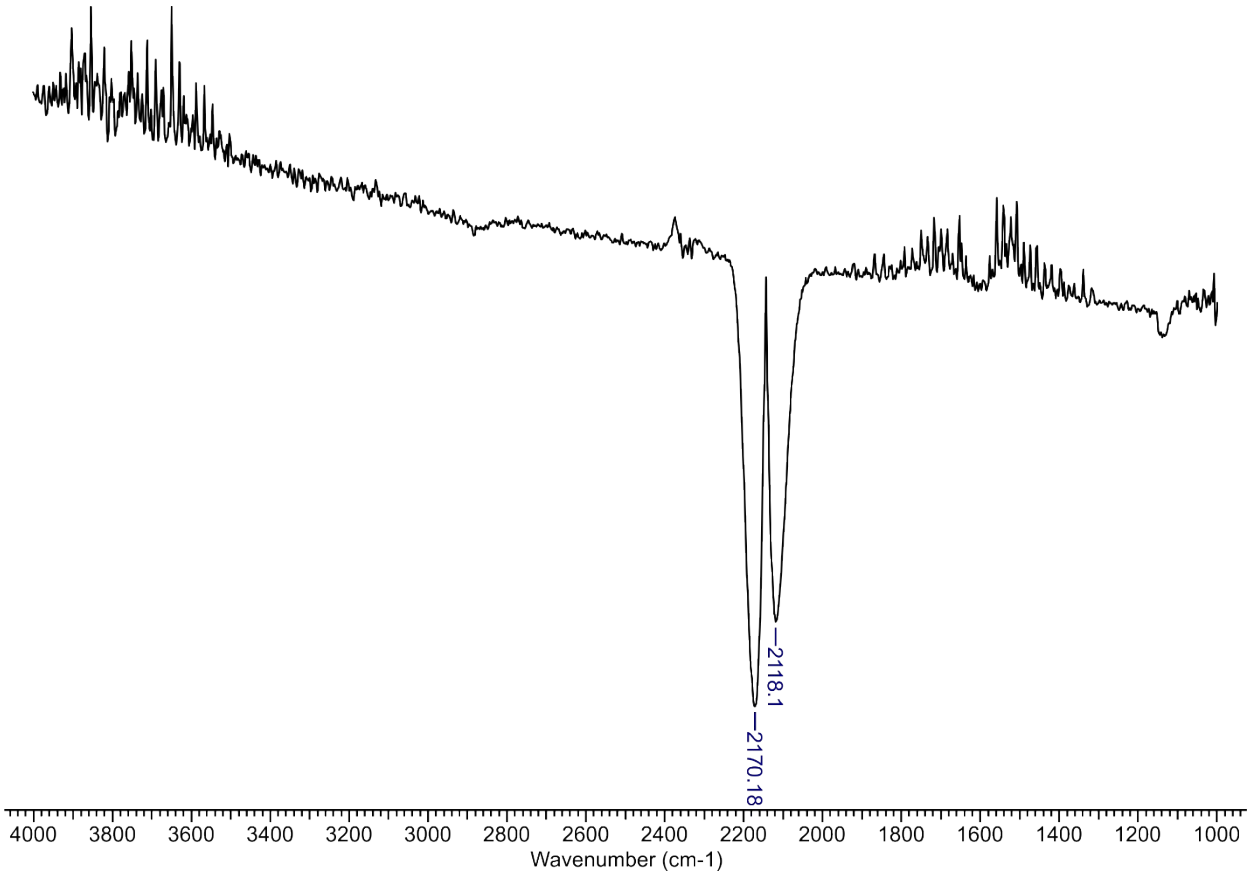


Figure S38. IR spectra of gaseous products of the sequential reaction of **1** with CO_2 and $TMSN_3$.

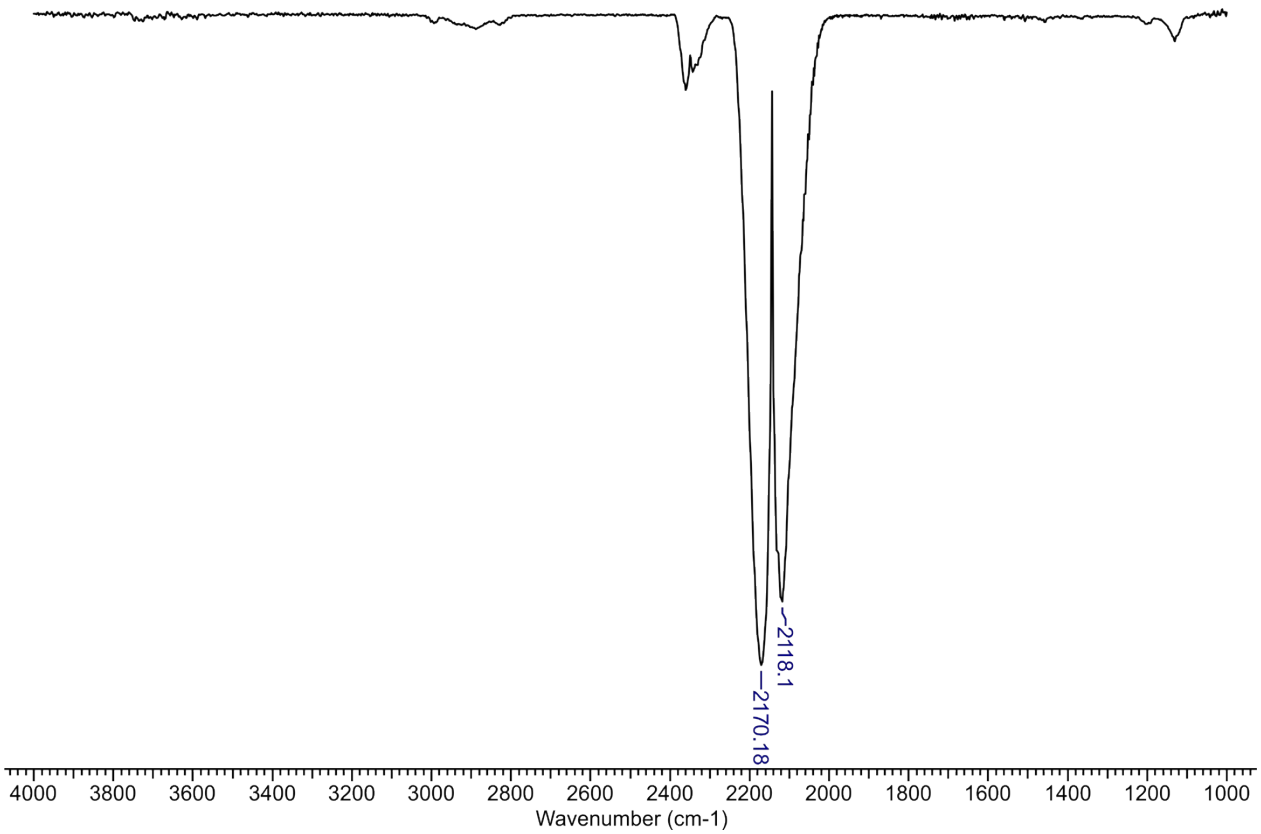


Figure S39. IR spectra of gaseous products of the sequential reaction of **1** with CO_2 and TMSCl.

X-ray Crystal Structure Determination. The X-ray diffraction data were collected on an Agilent Xcalibur E (**2, 3, 5,**) and a Bruker D8 Quest (**4, 6**-**11**) diffractometers (Mo-Kα radiation, λ = 0.71073 Å T = 100 K (**2**-**7**, **9**-**11**) and 150 K (**8**)) then integrated using the CrysAlisPro[6] and SAINT[7] software respectively. Collected diffraction data for **7** at the Bruker D8 Quest were treated with the CrysAlisPro[6] software. The SCALE3 ABSPACK[8] (for **2, 3, 5, 7**) and SADABS[9] (for **4, 6, 8**-**11**) were used for absorption corrections. All structures were solved by dual-space method using the SHELXT[10] software and refined on F^2_{hkl} using SHELXTL[11] 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 **2**, **5**, **7** and **9** contain solvate molecules of DME (**2**, **9**), Et_2O (**5**) and benzene (**9**) respectively, most of them are disordered at the common and special positions (in **5**, **7** and **9**). Solvate molecules of DME in **4**, whose contribution to the final model of **4** was implemented by PLATON/SQUEEZE[12], were revealed at a ratio of 2.5 to one Ga complex. The main crystallographic data and structure refinement details for **2** - **11** are presented in the Table S1. CCDC 2067914 (**2**), CCDC 2067915 (**3**), CCDC 2067916 (**4**), CCDC 2067917 (**5**), CCDC 2067918 (**6**), CCDC 2067919 (**7**), CCDC 2067920 (**8**), CCDC 2067921 (**9**), CCDC 2067922 (**10**) and CCDC 2067923 (**11**) 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 **2–11**.

Compound	**2**	**3**	**4**	**5**	**6**	**7**
formula	$C_{93.2}H_{128}Ga_2N_4Na_2O_{13.6}$	$C_{86}H_{110}Ga_2N_4Na_2O_{10}$	$C_{98}H_{128}Ga_2N_4Na_2O_{16}$	$C_{97}H_{130}Ga_2N_4Na_2O_{10}$	$C_{72}H_{80}GaN_2NaO_7$	$C_{118}H_{169}Ga_2N_8Na_2O_{12.67}$
M_r [g mol^{-1}]	1707.41	1545.19	1803.46	1697.46	1178.09	2087.74
crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	Cc	$C2$	$P\bar{1}$
a [Å]	13.6659(4)	12.9409(5)	13.9328(8)	20.7044(13)	23.891(3)	12.93764(19)
b [Å]	15.7097(4)	13.1598(4)	14.1924(8)	15.9646(10)	13.2144(14)	20.7157(3)
c [Å]	21.6265(6)	14.4219(7)	15.9393(9)	28.8066(13)	21.639(2)	44.2008(9)
α[°]	90	67.419(4)	93.983(2)	90	90	92.1513(15)
β [°]	100.458(3)	86.425(4)	113.353(2)	100.355(5)	110.724(3)	95.3102(15)
γ[°]	90	64.580(3)	113.780(2)	90	90	98.1137(12)
V [Å^3]	4565.8(2)	2032.69(16)	2547.4(3)	9366.6(9)	6389.4(12)	11662.1(4)
Z	2	1	1	4	4	4
ρ_{calc}, [g cm^{-3}]	1.242	1.262	1.176	1.204	1.225	1.189
μ [mm^{-1}]	0.662	0.733	0.598	0.642	0.492	0.530
F(000)	1816	818	956	3616	2496	4473
crystal size, [mm^3]	0.35 × 0.30 × 0.05	0.471 × 0.366 × 0.116	0.195 × 0.181 × 0.073	0.60 × 0.38 × 0.14	0.34 × 0.19 × 0.16	0.417 × 0.290 × 0.230
$\theta_{min}/\theta_{max}$ [°]	3.22 / 27.00	3.07 / 28.00	2.66 / 27.00	2.93 / 25.03	2.19 / 25.00	1.76 / 28.00
index ranges	-17 ≤ h ≤ 17, -20 ≤ k ≤ 20, -20 ≤ l ≤ 27	-17 ≤ h ≤ 17, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19	-17 ≤ h ≤ 17, -18 ≤ k ≤ 18, -20 ≤ l ≤ 20	-24 ≤ h ≤ 24, -18 ≤ k ≤ 12, -24 ≤ l ≤ 34	-28 ≤ h ≤ 28, -15 ≤ k ≤ 15, -25 ≤ l ≤ 25	-17 ≤ h ≤ 17, -27 ≤ k ≤ 27, -58 ≤ l ≤ 58
reflections collected	35462	32646	32214	21670	32140	177556
independent reflections	9946	9789	11014	11721	10631	56234
R_{int}	0.0709	0.0882	0.1138	0.0325	0.0647	0.1291
max/min transmission	1.000/ 0.552	0.933/ 0.781	0.9281/ 0.7248	0.912/ 0.767	0.914/ 0.738	0.917/ 0.871
data/restraints/ parameters	9946 / 0 / 532	9789 / 0 / 480	11014 / 30 / 577	11721 / 1044 / 1174	10631 / 339 / 822	56234 / 259 / 2705
GOF on F^2	1.005	1.027	1.003	1.017	1.042	1.025
final R indices [I>2σ (I)]	0.0570 / 0.1494	0.0596 / 0.0958	0.0830 / 0.1630	0.0671 / 0.1624	0.1050 / 0.1831	0.0953 / 0.2546
R indices (all data)	0.0904 / 0.1686	0.1251 / 0.1095	0.1548 / 0.1811	0.0900 / 0.1814	0.1435 / 0.2037	0.1172 / 0.2805
Absolute structure parameter	-	-	-	0.001(6)	0.10(3)	-
largest diff. peak/hole [e Å^{-3}]	1.206 / -0.848	0.517 / -0.517	1.352 / -1.085	0.642 / -0.398	1.008 / -0.875	1.098 / -0.793

Table S1 (*continued*)**.** Crystal data and structure refinement details for compounds **2**–**11**.

Compound	**8**	**9**	**10**	**11**
formula	$C_{102}H_{130}Ga_2N_6Na_2O_{12}$	$C_{194.96}H_{260.09}Ga_4N_8Na_4O_{25.04}$	$C_{51}H_{79}GaN_5NaO_7Si$	$C_{51}H_{75}ClGaN_2NaO_4Si$
M_r [g mol^{-1}]	1817.53	3487.12	994.99	936.38
crystal system	Tetragonal	Monoclinic	Orthorhombic	Orthorhombic
space group	$P4_12_12$	$C2/c$	$P2_12_12_1$	$Ama2$
a [Å]	15.1442(16)	39.1509(17)	12.7877(7)	19.4444(7)
b [Å]	15.1442(16)	13.2466(6)	18.0210(9)	17.6536(6)
c [Å]	43.794(5)	39.4570(17)	23.4640(13)	14.8679(5)
α[°]	90	90	90	90
β [°]	90	112.069(1)	90	90
γ[°]	90	90	90	90
V [Å^3]	10044(2)	18963.8(14)	5407.2(5)	5103.6(3)
Z	4	4	4	4
ρ_{calc}, [g cm^{-3}]	1.202	1.221	1.222	1.219
μ [mm^{-1}]	0.605	0.638	0.591	0.667
F(000)	3856	7417	2128	2000
crystal size, [mm^3]	0.34 × 0.19 × 0.12	0.49 × 0.34 × 0.19	0.31 × 0.15 × 0.07	0.597 × 0.224 × 0.202
$\theta_{min}/\theta_{max}$ [°]	2.36 / 26.00	2.10 / 27.00	2.07 / 26.02	2.31 / 28.00
index ranges	-18 ≤ h ≤ 16, -17 ≤ k ≤ 18, -53 ≤ l ≤ 54	-49 ≤ h ≤ 50, -16 ≤ k ≤ 16, -50 ≤ l ≤ 50	-15 ≤ h ≤ 14, -21 ≤ k ≤ 22, -28 ≤ l ≤ 26	-25 ≤ h ≤ 25, -23 ≤ k ≤ 23, -19 ≤ l ≤ 19
reflections collected	91251	119240	54438	35057
independent reflections	9887	20501	10644	6304
R_{int}	0.1388	0.0760	0.0858	0.0259
max/min transmission	0.8704/ 0.4475	0.8496/ 0.6470	0.9194/ 0.6593	0.8497/ 0.7687
data/restraints/ parameters	9887 / 864 / 627	20501 / 77 / 1142	10644 / 0 / 612	6304 / 82 / 342
GOF on F^2	1.029	1.075	1.031	1.033
final R indices [I>2σ (I)]	0.0617 / 0.1380	0.0869 / 0.1935	0.0484 / 0.0852	0.0348 / 0.0898
R indices (all data)	0.1046 / 0.1515	0.1147 / 0.2038	0.0780 / 0.0945	0.0382 / 0.0917
Absolute structure parameter	0.07(2)	-	0.004(5)	0.026(3)
largest diff. peak/hole [e Å^{-3}]	0.381 / -0.450	1.241 / -0.900	0.347 / -0.307	0.507 / -0.339

Computational details. The full geometry optimization of all model structures was carried out at the B3LYP/6-31G* level of theory with the help of Gaussian-09 program package.[13] No symmetry restrictions have been applied during the geometry optimization procedure. The Hessian matrices were calculated analytically for all optimized model structures to prove the location of correct minimum on the potential energy surface (no imaginary frequencies were found in all cases) and to estimate the thermodynamic parameters, the latter being calculated at 25 °C (Tables S2 and S3). The Cartesian atomic coordinates for all optimized equilibrium model structures are presented in the attached xyz-files.

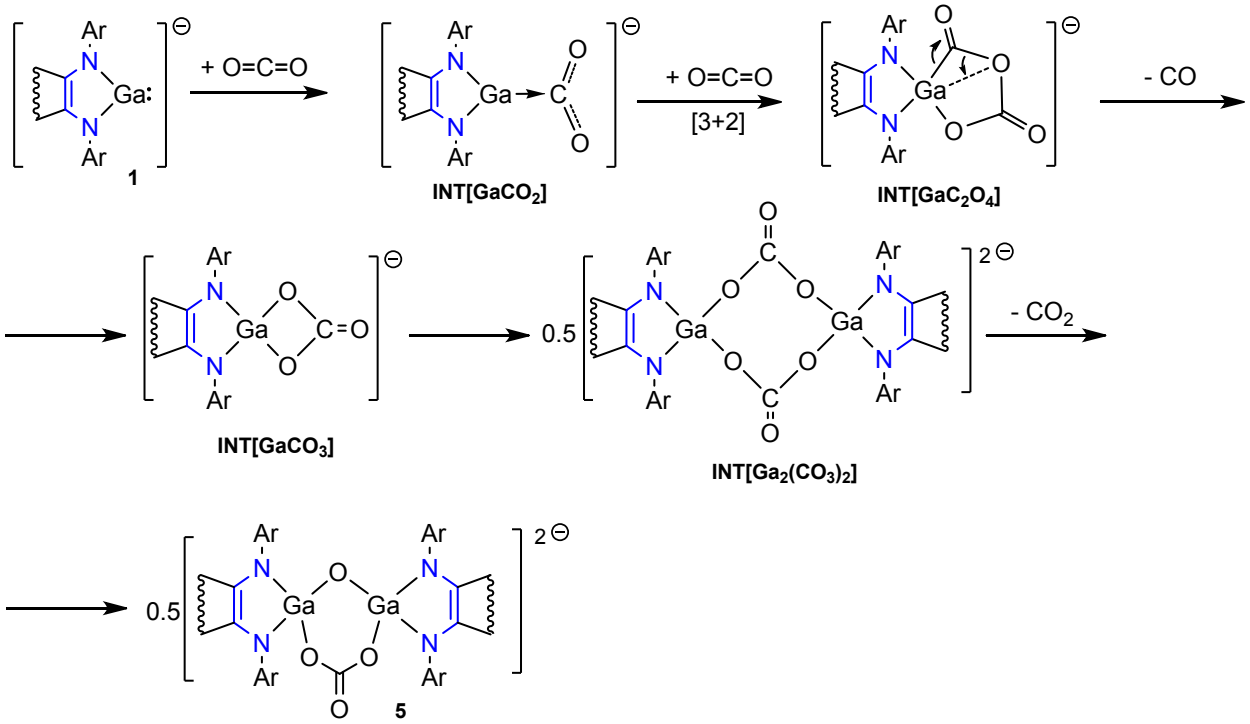
Table S2. Calculated total energies, enthalpies, Gibbs free energies (in Hartree), and entropies (in cal/mol·K) for optimized equilibrium model structures (E, H, G, and S, respectively).

№	Model structure	E	H	G	S
1	**1H**	-2956.735463	-2956.383601	-2956.455627	151.592
2	**2H**	-6290.683779	-6289.945959	-6290.082189	286.720
3	**5H**	-6252.638736	-6251.906467	-6252.040322	281.721
4	**6H**	-4261.522617	-4260.741481	-4260.874103	279.126
5	**7H**	-3448.100138	-3447.623225	-3447.719030	201.638
6	**8H**	-3431.802145	-3431.330191	-3431.422958	195.244
7	**10H**	-3605.580316	-3605.084742	-3605.187835	216.978
8	**11H**	-3901.611232	-3901.129250	-3901.228471	208.828
9	**CO**	-113.309454	-113.301118	-113.323561	47.236
10	**CO_2**	-188.580940	-188.565756	-188.590721	52.543
11	**INT[$Ga_2(CO_3)_2$]**	-6441.239620	-6440.489694	-6440.630831	297.050
12	**INT[Ga_2O_2]**	-6063.995440	-6063.281031	-6063.407271	265.694
13	**INT[GaC_2O_4]**	-3333.945157	-3333.559772	-3333.645843	181.151
14	**INT[$GaCO_2$]**	-3145.317403	-3144.949485	-3145.032892	175.544
15	**INT[$GaCO_2$OCNPh]**	-3545.120092	-3544.636680	-3544.733211	203.166
16	**INT[$GaCO_3$]**	-3220.622057	-3220.247762	-3220.328508	169.943
17	**INT[GaO]**	-3031.957188	-3031.600324	-3031.675081	157.339
18	**MeNCO**	-207.988079	-207.931484	-207.964420	69.320
19	**Ph_2CCO**	-614.708265	-614.499064	-614.551802	110.997
20	**PhNC**	-324.457896	-324.351979	-324.389485	78.938
21	**PhNCO**	-399.732515	-399.620397	-399.660835	85.109
22	**TMSCl**	-869.522591	-869.399510	-869.441657	88.704
23	**$TMSN_3$**	-573.495628	-573.358925	-573.406058	99.200

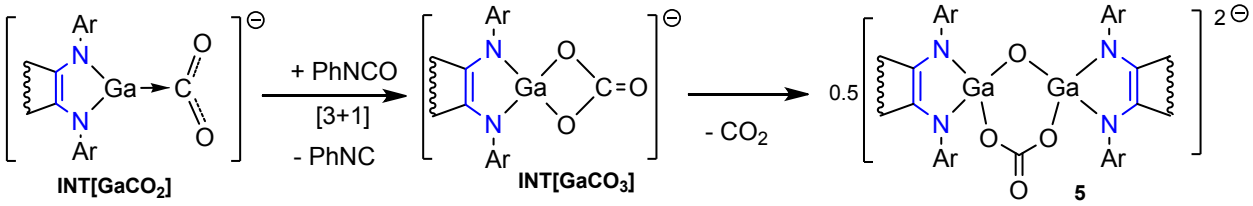
Table S3. Calculated values of total electronic reaction energies (ΔE), enthalpies and Gibbs free energies of reaction (ΔH and ΔG) for various hypothetical transformations (in kcal/mol).

Transformation	ΔE	ΔH	ΔG
5H → 2 INT[GaO] + CO_2	90.0	87.9	62.4
2H → 2 INT[GaO] + 2 CO	94.4	89.8	53.3
2 INT[GaO] → INT[Ga_2O_2]	-50.9	-50.4	-35.8
INT[GaO] + 2 Ph_2CCO → 6H	-93.4	-89.8	-59.9
INT[GaO] + 2 MeNCO → 7H	-104.7	-100.4	-72.2
INT[GaO] + PhNCO → 8H	-70.6	-68.7	-54.6
2H + 4 Ph2CCO → 2 6H + 2 CO	-92.4	-89.7	-66.5
2H + 4 MeNCO → 2 7H + 2 CO	-114.9	-110.9	-91.2
2H + 2 PhNCO → 2 8H + 2 CO	-46.7	-47.6	-56.0
2H + 2 $TMSN_3$ → 2 10H + 2 CO	-65.6	-67.7	-80.6

2H + 2 TMSCl → 2 11H + 2 CO	-70.5	-72.6	-86.9
2 1H + 2 CO_2 → 2H	-32.0	-29.6	6.6
1H + CO_2 → INT[$GaCO_2$]	-0.6	-0.1	8.4
2H → 2 INT[$GaCO_2$]	30.7	29.5	10.3
INT[$GaCO_2$] + PhNCO → INT[$GaCO_2OCNPh$]	-44.0	-41.9	-24.8
INT[$GaCO_2OCNPh$] → CO + 8H	5.3	3.4	-8.4
2H + CO_2 → 5H + 2 CO	4.4	1.9	-9.1
INT[$GaCO_2$] + CO_2 → INT[GaC_2O_4]	-29.4	-27.9	-13.9
INT[GaC_2O_4] → CO + INT[$GaCO_3$]	8.6	6.8	-3.9
2 INT[$GaCO_3$] → INT[$Ga_2(CO_3)_2$]	2.8	3.7	16.4
INT[$Ga_2(CO_3)_2$] → CO_2 + 5H	12.5	11.0	-0.1
INT[$GaCO_2$] + PhNCO → PhNC + INT[$GaCO_3$]	-18.8	-18.7	-15.2
2 INT[$GaCO_2$] + 2PhNCO → 5H + CO_2 + 2PhNC	-22.4	-22.9	-14.2



Scheme S1. Possible mechanism for formation of **5**.



Scheme S2. Alternate reaction path for the reaction modification of CO_2 with phenylisocyanate.

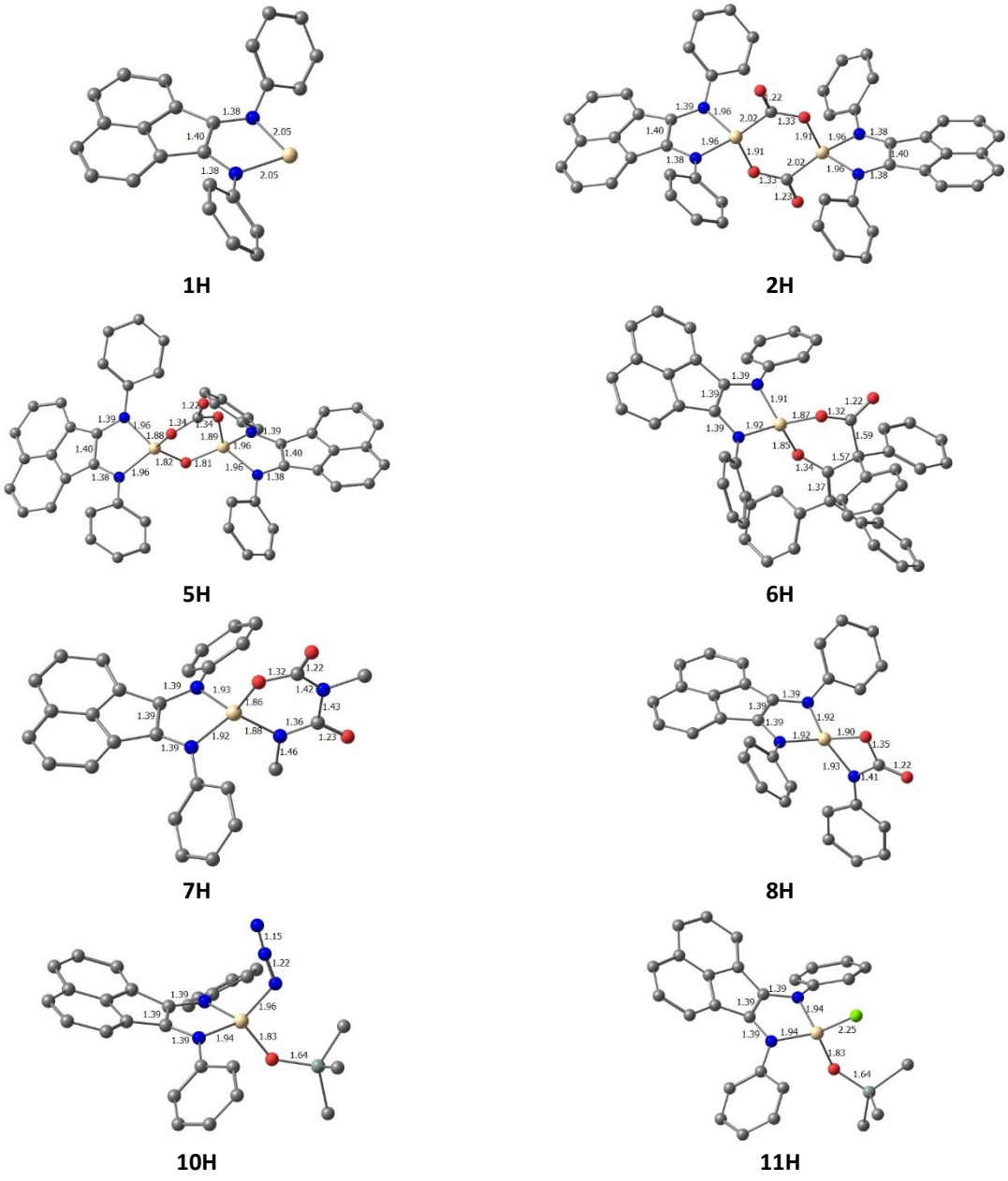
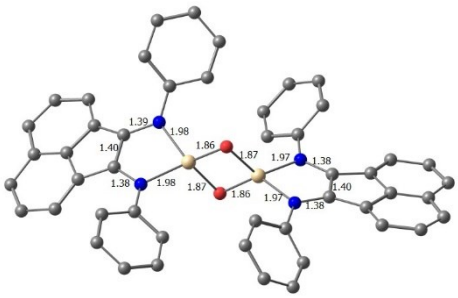
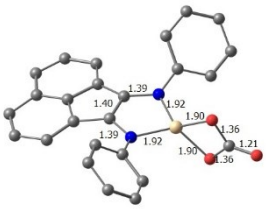


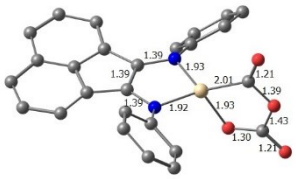
Figure S40. Optimized equilibrium structures of model compounds **1H, 2H, 5H-8H, 10H** and **11H** labelled with selected bond lengths.



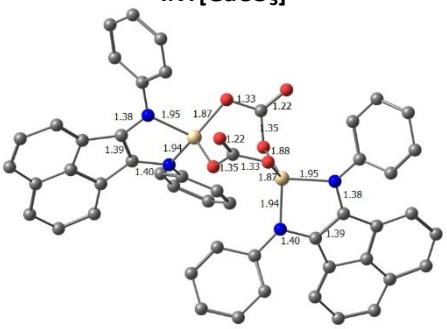
INT[Ga_2O_2]



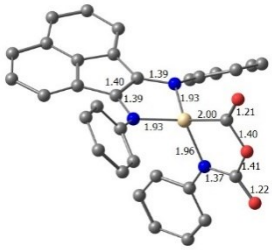
INT[$GaCO_3$]



INT[GaC_2O_4]



INT[$Ga_2(CO_3)_2$]



INT[$GaCO_2OCNPh$]

Figure S41. Optimized equilibrium structures of possible intermediates labelled with selected bond lengths.

Table S4. Distribution of NBO atomic charges in optimized equilibrium structures of model compounds **1H, 2H, 5H-8H, 10H** and **11H**.

Compound	**1H**	**2H**	**5H**	**6H**	**7H**	**8H**	**10H**	**11H**
Ga centers	0.51873	3.03825	3.5748	1.82037	1.79963	1.75526	1.77039	1.67168
L moieties	no	-2.13526	-2.63906	-1.44892	-1.40823	-1.39613	-1.36617	-1.25646
dpp-bian moieties	-1.51876	-2.903	-2.93573	-1.37142	-1.39139	-1.35915	-1.40415	-1.41521

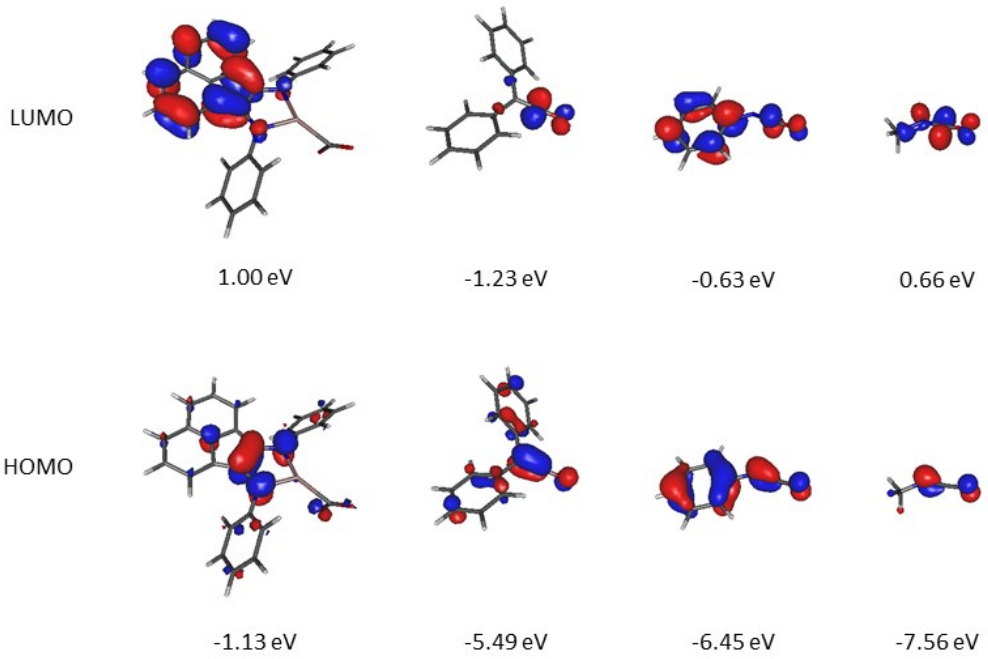


Figure S42. Shape and energies of HOMOs and LUMOs in optimized equilibrium model structures **INT[$GaCO_2$]**, **Ph_2CCO**, **PhNCO** and **MeNCO**.

Table S5. NBO atomic charges in optimized equilibrium structures of model compounds **1H, 2H, 5H** and **6H**.

Atom	**1H**	Atom	**2H**	Atom	**5H**	Atom	**6H**
C 1	-0.23379	C 1	-0.23505	C 1	-0.23483	C 1	-0.22528
C 2	-0.24065	C 2	-0.24044	C 2	-0.24024	C 2	-0.23912
C 3	-0.23106	C 3	-0.23721	C 3	-0.23535	C 3	-0.22295
C 4	-0.07277	C 4	-0.07441	C 4	-0.0738	C 4	-0.07083
C 5	-0.03454	C 5	-0.03226	C 5	-0.03264	C 5	-0.03177
C 6	-0.03628	C 6	-0.02961	C 6	-0.03048	C 6	-0.03968
C 7	-0.23105	C 7	-0.23266	C 7	-0.23292	C 7	-0.22106
C 8	-0.24065	C 8	-0.24235	C 8	-0.24207	C 8	-0.24009
C 9	-0.23379	C 9	-0.23164	C 9	-0.23142	C 9	-0.22368
C 10	-0.03629	C 10	-0.03106	C 10	-0.03224	C 10	-0.04158
C 11	0.12731	C 11	0.12332	C 11	0.12547	C 11	0.12333
C 12	0.12734	C 12	0.1354	C 12	0.13383	C 12	0.13341
N 13	-0.7768	N 13	-0.75233	N 13	-0.75966	N 13	-0.80232
N 14	-0.77683	N 14	-0.75787	N 14	-0.75575	N 14	-0.79373
C 15	0.18268	C 15	0.18933	C 15	0.18967	C 15	0.17611
C 16	-0.26025	C 16	-0.25721	C 16	-0.25323	C 16	-0.26818
Ga 17	0.51873	O 17	-0.83097	O 17	-0.88828	O 17	-0.83787
C 18	-0.23589	Ga 18	1.51631	Ga 18	1.7902	Ga 18	1.82037
C 19	-0.28917	C 19	-0.23332	C 19	-0.23271	C 19	-0.23152
C 20	-0.23669	C 20	-0.29156	C 20	-0.29417	C 20	-0.27072
C 21	-0.28319	C 21	-0.23676	C 21	-0.23749	C 21	-0.23473
C 22	0.18266	C 22	-0.28815	C 22	-0.29487	C 22	-0.25988
C 23	-0.28319	C 23	0.18989	C 23	0.19486	C 23	0.17821

C 24	-0.23668	C 24	-0.29366	C 24	-0.3032	C 24	-0.26796
C 25	-0.28917	C 25	-0.23565	C 25	-0.23449	C 25	-0.2288
C 26	-0.23589	C 26	-0.29439	C 26	-0.2976	C 26	-0.27878
C 27	-0.26027	C 27	-0.22599	C 27	-0.22367	C 27	-0.22975
H 28	0.24115	C 28	-0.25517	C 28	-0.25619	C 28	-0.28295
H 29	0.22122	H 29	0.24354	H 29	0.24398	H 29	0.24359
H 30	0.21755	H 30	0.218	H 30	0.21863	H 30	0.22616
H 31	0.21755	H 31	0.21298	H 31	0.21333	H 31	0.22214
H 32	0.22122	H 32	0.21325	H 32	0.2134	H 32	0.22225
H 33	0.24115	H 33	0.21804	H 33	0.21815	H 33	0.22596
H 34	0.23742	H 34	0.24333	H 34	0.24374	H 34	0.24259
H 35	0.21904	H 35	0.24904	H 35	0.25353	H 35	0.24316
H 36	0.2156	H 36	0.22799	H 36	0.22934	H 36	0.22596
H 37	0.21875	H 37	0.21241	H 37	0.21093	H 37	0.22322
H 38	0.23734	H 38	0.21426	H 38	0.21294	H 38	0.22867
H 39	0.23734	H 39	0.23626	H 39	0.2342	H 39	0.25013
H 40	0.21875	H 40	0.23388	H 40	0.23144	H 40	0.25225
H 41	0.2156	H 41	0.21191	H 41	0.21131	H 41	0.23097
H 42	0.21904	H 42	0.21042	H 42	0.21094	H 42	0.2216
H 43	0.23742	H 43	0.23486	H 43	0.22995	H 43	0.22366
		H 44	0.24024	H 44	0.23774	H 44	0.24057
		C 45	-0.23881	C 45	-0.22794	C 45	-0.1623
		C 46	-0.24053	C 46	-0.24284	O 46	-0.84616
		C 47	-0.23801	C 47	-0.22972	C 47	0.41539
		C 48	-0.07632	C 48	-0.07362	C 48	-0.04196
		C 49	-0.03096	C 49	-0.03241	C 49	-0.19957
		C 50	-0.03179	C 50	-0.03186	C 50	-0.23598
		C 51	-0.23407	C 51	-0.23812	C 51	-0.24818
		C 52	-0.24232	C 52	-0.23966	C 52	-0.24018
		C 53	-0.2358	C 53	-0.23537	C 53	-0.22432
		C 54	-0.03268	C 54	-0.03059	C 54	-0.03381
		C 55	0.12553	C 55	0.14087	C 55	-0.22662
		C 56	0.13771	C 56	0.11752	C 56	-0.24366
		N 57	-0.7603	N 57	-0.76848	C 57	-0.25242
		N 58	-0.75695	N 58	-0.75245	C 58	-0.24004
		C 59	0.18489	C 59	0.19194	C 59	-0.20634
		C 60	-0.26214	C 60	-0.29818	H 60	0.24141
		O 61	-0.83601	O 61	-0.89452	H 61	0.2266
		Ga 62	1.52194	Ga 62	1.7846	H 62	0.22297
		C 63	-0.23343	C 63	-0.23631	H 63	0.2267
		C 64	-0.29197	C 64	-0.29636	H 64	0.24289
		C 65	-0.23597	C 65	-0.2292	H 65	0.23382
		C 66	-0.27946	C 66	-0.24677	H 66	0.22215
		C 67	0.1857	C 67	0.19096	H 67	0.22143
		C 68	-0.26066	C 68	-0.25468	H 68	0.22772
		C 69	-0.23492	C 69	-0.23304	H 69	0.25501

		C 70	-0.2914	C 70	-0.29496	C 70	-0.20834
		C 71	-0.23645	C 71	-0.23688	O 71	-0.61085
		C 72	-0.2855	C 72	-0.29542	C 72	0.8536
		H 73	0.24245	H 73	0.24446	C 73	-0.00906
		H 74	0.21762	H 74	0.2188	C 74	-0.22687
		H 75	0.21278	H 75	0.21375	C 75	-0.2317
		H 76	0.21304	H 76	0.21324	C 76	-0.24656
		H 77	0.21766	H 77	0.21823	C 77	-0.23764
		H 78	0.24176	H 78	0.24352	C 78	-0.20114
		H 79	0.25545	H 79	0.23371	C 79	-0.01669
		H 80	0.22743	H 80	0.21223	C 80	-0.22868
		H 81	0.21615	H 81	0.21095	C 81	-0.23327
		H 82	0.21708	H 82	0.22673	C 82	-0.2428
		H 83	0.23918	H 83	0.24004	C 83	-0.22833
		H 84	0.25113	H 84	0.25111	C 84	-0.22818
		H 85	0.22764	H 85	0.23292	H 85	0.24299
		H 86	0.21253	H 86	0.21299	H 86	0.22502
		H 87	0.21442	H 87	0.2134	H 87	0.22204
		H 88	0.23769	H 88	0.2334	H 88	0.22802
		C 89	0.39581	C 89	1.04985	H 89	0.24322
		O 90	-0.63799	O 90	-0.67185	H 90	0.25358
		C 91	0.4015	O 91	-1.23426	H 91	0.22776
		O 92	-0.6276			H 92	0.22531
						H 93	0.23469
						H 94	0.24828

Table S6. NBO atomic charges in optimized equilibrium structures of model compounds **7H, 8H, 10H** and **11H**.

	7H		**8H**		**10H**		**11H**
C 1	-0.22296	C 1	-0.22248	Ga 1	1.77039	C 1	-0.22595
C 2	-0.23967	C 2	-0.23945	Si 2	2.04867	C 2	-0.24002
C 3	-0.2213	C 3	-0.22081	O 3	-1.25405	C 3	-0.22448
C 4	-0.06984	C 4	-0.06965	N 4	-0.77725	C 4	-0.07096
C 5	-0.03256	C 5	-0.03284	N 5	-0.77723	C 5	-0.03252
C 6	-0.0392	C 6	-0.04018	N 6	-0.68818	C 6	-0.03711
C 7	-0.22165	C 7	-0.22085	N 7	0.21089	C 7	-0.22447
C 8	-0.23947	C 8	-0.23944	N 8	-0.20294	C 8	-0.24003
C 9	-0.22364	C 9	-0.22252	C 9	0.12857	C 9	-0.22595
C 10	-0.03887	C 10	-0.04017	C 10	0.12859	C 10	-0.03711
C 11	0.12844	C 11	0.12717	C 11	-0.03793	C 11	0.12825
C 12	0.1269	C 12	0.12706	C 12	-0.03215	C 12	0.12828
N 13	-0.77875	N 13	-0.7812	C 13	-0.03793	N 13	-0.77681
N 14	-0.78172	N 14	-0.78113	C 14	-0.22473	N 14	-0.77683
C 15	0.18459	C 15	0.18305	H 15	0.24327	C 15	0.18827
C 16	-0.26195	C 16	-0.2889	C 16	-0.23976	C 16	-0.28828
Ga 17	1.79963	O 17	-0.84303	H 17	0.22487	O 17	-1.25846

C 18	-0.22579	Ga 18	1.75526	C 18	-0.22327	Ga 18	1.67168
C 19	-0.28477	C 19	-0.22929	H 19	0.22095	C 19	-0.23057
C 20	-0.22887	C 20	-0.28118	C 20	-0.07051	C 20	-0.28746
C 21	-0.29276	C 21	-0.22553	C 21	-0.22326	C 21	-0.231
C 22	0.18159	C 22	-0.25731	H 22	0.22095	C 22	-0.26333
C 23	-0.2916	C 23	0.18304	C 23	-0.23977	C 23	0.18827
C 24	-0.22949	C 24	-0.28888	H 24	0.22486	C 24	-0.28827
C 25	-0.28354	C 25	-0.22931	C 25	-0.22474	C 25	-0.23057
C 26	-0.22678	C 26	-0.28116	H 26	0.24327	C 26	-0.28746
C 27	-0.26293	C 27	-0.22553	C 27	0.18828	C 27	-0.231
H 28	0.2436	C 28	-0.25728	C 28	-0.28755	C 28	-0.26334
H 29	0.22609	H 29	0.24433	C 29	-0.22993	C 29	-1.21024
H 30	0.22214	H 30	0.22662	H 30	0.22158	Si 30	2.04996
H 31	0.22213	H 31	0.22259	C 31	-0.28624	C 31	-1.22082
H 32	0.22612	H 32	0.22258	H 32	0.21898	C 32	-1.22081
H 33	0.24372	H 33	0.22662	C 33	-0.23037	H 33	0.24326
H 34	0.2387	H 34	0.24432	H 34	0.2243	H 34	0.22439
H 35	0.22727	H 35	0.23865	C 35	-0.2631	H 35	0.22046
H 36	0.22059	H 36	0.22288	C 36	0.18829	H 36	0.22046
H 37	0.22229	H 37	0.22103	C 37	-0.28755	H 37	0.22439
H 38	0.23803	H 38	0.22833	C 38	-0.22993	H 38	0.24327
H 39	0.2388	H 39	0.24338	H 39	0.22158	H 39	0.2386
H 40	0.2228	H 40	0.23864	C 40	-0.28624	H 40	0.22094
H 41	0.22088	H 41	0.22288	H 41	0.21898	H 41	0.21825
H 42	0.22725	H 42	0.22102	C 42	-0.23037	H 42	0.22371
H 43	0.24479	H 43	0.22834	H 43	0.2243	H 43	0.24301
O 44	-0.84565	H 44	0.24341	C 44	-0.26311	H 44	0.2386
N 45	-0.8826	N 45	-0.86359	C 45	-1.2215	H 45	0.22094
C 46	0.83234	C 46	0.93355	H 46	0.24446	H 46	0.21825
O 47	-0.68846	O 47	-0.66427	H 47	0.2294	H 47	0.22371
C 48	-0.46702	C 48	0.18012	H 48	0.25395	H 48	0.243
H 49	0.21837	C 49	-0.2649	C 49	-1.22149	H 49	0.22897
H 50	0.21477	C 50	-0.23439	H 50	0.24448	H 50	0.24372
H 51	0.24478	C 51	-0.2863	H 51	0.25389	H 51	0.24372
N 52	-0.55849	C 52	-0.23145	H 52	0.22941	H 52	0.24553
C 53	0.95855	C 53	-0.27442	C 53	-1.21054	H 53	0.22872
O 54	-0.66308	H 54	0.23042	H 54	0.24374	H 54	0.25268
C 55	-0.4608	H 55	0.22212	H 55	0.22991	H 55	0.22872
H 56	0.24053	H 56	0.21725	H 56	0.24373	H 56	0.24553
H 57	0.23503	H 57	0.22	H 57	0.23899	H 57	0.25268
H 58	0.2135	H 58	0.26276	H 58	0.2396	Cl 58	-0.56636
				H 59	0.23899		
				H 60	0.23957		

References

1. E. C. Taylor, A. McKillop and G. H. Hawks, *Org. Synth.*, 1972, **52**, 36.
2. I. L. Fedushkin, V. A. Chudakova, G. K. Fukin, S. Dechert, M. Hummert and H. Schumann, *Russ. Chem. Bull.*, 2004, **53**, 2744-2750.
3. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.
4. 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.
5. I. L. Fedushkin, A. N. Lukoyanov, S. Y. Ketkov, M. Hummert and H. Schumann, *Chem. Eur. J.*, 2007, **13**, 7050-7056.
6. Data Collection, Reduction and Correction Program, CrysAlisPro 1.171.40.67a - Software Package, Rigaku OD (2019).
7. Bruker (2017) SAINT Data Reduction and Correction Program v. 8.38A, Bruker AXS, Madison, Wisconsin, USA.
8. SCALE3 ABSPACK: Empirical absorption correction, CrysAlisPro 1.171.40.67a - Software Package, Rigaku OD (2019).
9. G.M. Sheldrick (2016). SADABS v.2016/2, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, USA.
10. G.M. Sheldrick (2015). Acta Cryst. A71, 3-8.
11. Sheldrick G.M. SHELXTL. Version 6.14. Structure Determination Software Suite; Madison (WI, USA): Bruker AXS, 2003.
12. A.L. Spek, Acta Cryst., 2015, C71, 9-18.
13. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, 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, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, in Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford, CT, 2010.