

Supporting Information

Reduction and Cycloaddition of Heteroalkenes at Ga(I) Bisamide Center

Vladimir A. Dodonov, Olga A. Kushnerova, Evgeny V. Baranov and Igor L. Fedushkin *

G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Tropinina Str. 49, 603137 Nizhny Novgorod, Russia; dodonov@iomc.ras.ru (V.A.D.); kushnerova@iomc.ras.ru (O.A.K.); bar@iomc.ras.ru (E.V.B.)

* Correspondence: igorfed@iomc.ras.ru

Experimental Section

All compounds are air- and moisture-sensitive, the manipulations were carried out in vacuum or under argon using standard Schlenk technique or under argon atmosphere in a drybox. Solvents (diethyl ether, 1,2-dimethoxyethane, pyridine, tetrahydrofuran) were dried using appropriate methods and were distilled under argon or condensed in vacuum prior to use. C₆D₆, THF-d₈ and pyridine-d₅ were dried over Na/K alloy. [(dpp-bian)GaNa(DME)₂] (**1**), [88] was prepared according to literature procedures. Other chemicals were purchased from commercial sources and used without further purification. The IR spectra were recorded on FSM-1201 spectrometer in Nujol, the NMR spectra – on Bruker AvanceNEO300 (300 MHz) or Avance III (400 MHz) spectrometers and were referenced to the residual ¹H or ¹³C signals of deuterated solvents. Chemical shifts are given in ppm. Abbreviations used: Ph – phenyl, Napht – naphthalene, d – doublet, m – multiplet, t – triplet, pst – pseudotriplet, s – singlet, br – broad, hept – heptet. Elemental analyses were carried out on Elementar VarioEL III instrument.

Synthesis of 2.

0.119 g (1 mmol) of phenyl isocyanate was added to a yellow-green solution of **1** in 10 ml of DME at 25 °C. The solution color changed to green within 5 min. The vessel was sealed and stored two days at -20 °C. That gave green needles of compound **2**. Yield 0.220 g, 18%. IR (nujol, cm⁻¹) 1640 s, 1592 s, 1515 s, 1490 w, 1429 w, 1341 s, 1319 s, 1283 w, 1255 m, 1211 m, 1189 m, 1178 m, 1112 s, 1081 s, 1032 w, 999 m, 982 w, 956 w, 935 s, 927 s, 877 m, 858 m, 844 m, 819 w, 808 s, 783 w, 761 s, 742 m, 692 m, 684 w, 667 w, 662 w, 645 w, 623 m, 590 w, 571 w, 548 w, 540 w, 518 m. ¹H NMR (400 MHz, THF-d₈): δ 7.53 (d, 2H, CH Ph, J = 7.5 Hz), 7.23 (t, 2H, CH Ph, J = 7.6 Hz), 7.04 (t, 1H, CH Ph, J = 7.8 Hz), 6.99 (d, 4H, CH Ph, J = 7.5 Hz), 6.97 (d, 4H, CH Ph, J = 9.2 Hz), 6.94 (t, 2H, CH Ph, J = 4.5 Hz), 6.81 (d, 2H, CH Napht, J = 8.0 Hz), 6.76 (t, 4H, CH Ph, J = 7.6 Hz), 6.64 (pst, 2H, CH Napht, J = 8.3 Hz, J = 7.3 Hz), 6.55 (t, 2H, CH Ph, J = 7.3 Hz), 5.73 (d, 2H, CH Napht, J = 6.8 Hz), 3.74 (sept, 4H, CH₃iPr, J = 6.8 Hz), 0.89 (d, 12H, CH₃iPr, J = 6.8 Hz), 0.75 (d, 12H, CH₃iPr, J = 6.8 Hz). ¹³C NMR (75 MHz, THF-d₈): δ 152.8 (C=N), 146.2 (C Ph), 145.4 (C Ph), 140.3 (C Ph), 137.3 (C Napht), 136.9 (C Ph), 135.1 (C Napht), 128.7 (C Napht), 128.3 (C-N), 127.9 (CH Ph), 127.8 (CH Ph), 126.7 (CH Ph), 126.1 (CH Napht), 124.1 (CH Ph), 122.5 (CH Ph), 122.4 (CH Ph), 121.9 (CH Napht), 121.4 (CH Ph), 120.8 (CH Ph), 115.7 (CH Napht), 27.4 (CH iPr), 24.5 (CH₃iPr), 24.1 (CH₃iPr). Elemental analysis C₇₂H₉₅GaN₅NaO₇ (1235.23), calc. C 70.00, H 7.75, N 5.66 %; found C 69.93, H 8.01, N 5.73 %. A further concentration of mother liquor gave a mixture of **2** and [(dpp-bian)GaO]₂[Na(DME)₂]₂ (**6**) as a minor product.

Synthesis of 3 and 4.

0.125 g (1 mmol) of cyclohexyl isocyanate was added to a yellow-green solution of **1** in 10 ml of DME at 25 °C. The solution color changed to green within 5 min. All volatiles were removed in a vacuum. The residue was dissolved in 5 ml of THF. Layering

the solution with 20 ml of Et₂O gave a mixture of green crystals of compounds **3** and **4**. Yield 0.168 g. IR (nujol, cm⁻¹) 1628 m, 1602 m, 1517 s, 1352 w, 1316 w, 1258 m, 1178 m, 1153 m, 1106 w, 1078 w, 1045 m, 963 w, 924 m, 894 m, 805 m, 758 s, 617 m, 548 s.

Synthesis of 5.

0.250 g (2 mmol) of cyclohexyl isocyanate was added to a yellow-green solution of **1** in 10 ml of THF at 25 °C. The solution color changed to blue within 5 min. All volatiles were removed in a vacuum. The residue was dissolved in 5 ml of pyridine. Slow concentration gave blue crystals of compound **5**. Yield 0.150 g, 11%. IR (nujol, cm⁻¹) 1711 m, 1661 m, 1581 s, 1517 w, 1256 m, 1214 w, 1108 w, 1069 w, 1029 m, 990 m, 926 w, 892 w, 800 w, 766 w, 747 m, 701 s, 601 w. ¹H NMR (400 MHz, C₆D₆): δ 7.35 – 7.23 (m, 6H Ph), 7.12 (d, 2H, CH Napht, *J* = 8.2 Hz), 6.86 (dd, 2H, CH Napht, *J* = 8.3, *J* = 6.9 Hz), 6.29 (d, 2H, CH Napht, *J* = 6.9 Hz), 4.82 (br. s, 1H, CH Cy), 4.31 (sept, 2H, CH iPr, *J* = 6.9 Hz), 4.05 (sept, 2H, CH iPr, *J* = 6.9 Hz), 3.54 (br. s, 1H, CH Cy), 2.79 (br. s, 2H, CH₂ Cy), 1.89 (m, 2H, CH₂ Cy), 1.70 (br. s, 4H, CH₂ Cy), 1.57 (m, 4H, CH₂ Cy), 1.45 (d, 6H, CH₃ iPr, *J* = 6.9 Hz), 1.37 (m, 4H, CH₂ Cy), 1.32 (d, 6H, CH₃ iPr, *J* = 6.8 Hz), 1.26 (d, 6H, CH₃ iPr, *J* = 6.8 Hz), 1.18 (m, 4H, CH₂ Cy), 1.07 (d, 6H, CH₃ iPr, *J* = 6.9 Hz). ¹³C NMR (75 MHz, C₆D₆): δ 164.1 (C=O), 163.7 (C=N), 147.8 (C Ph), 145.9 (C Ph), 144.6 (C Ph), 137.3 (C Napht), 134.5 (C Napht), 127.8 (CH Napht), 127.5 (C Napht), 126.1 (C–N), 125.2 (CH Ph), 125.1 (CH Ph), 123.5 (CH Napht), 123.4 (CH Ph), 117.9 (CH Napht), 67.4 (CH Cy), 55.4 (CH Cy), 35.9 (CH₂ Cy), 30.2 (CH₂ Cy), 28.9 (CH iPr), 28.3 (CH iPr), 27.4 (CH₂ Cy), 26.5 (CH₂ Cy), 26.5 (CH₃ iPr), 25.7 (CH₃ iPr), 25.3 (CH₂ Cy), 25.3 (CH₃ iPr), 24.9 (CH₃ iPr), 23.2 (CH₂ Cy). Elemental analysis C_{82.5}H_{94.5}GaN_{10.5}NaO₂ (1357.89), calc. C 72.97, H 7.01, N 10.83 %; found C 72.67, H 6.73, N 11.01 %.

Synthesis of 6.

25 ml (25 °C, 1 atm, 1 mmol) of dinitrogen monoxide was added to a yellow-green solution of **1** in 10 ml of DME at 25 °C. The solution color changed to green within 5 min. The solution was stirred for 10 minutes. All volatiles were removed in a vacuum. The residue was dissolved in 5 ml of THF. Slow concentration gave green crystals of compound **6**. Yield 0.950 g, 66%. IR (nujol, cm⁻¹) 1589 m, 1519 s, 1428 s, 1347 w, 1255 s, 1208 m, 1208 m, 1192 m, 1178 m, 1116 m, 1084 m, 1028 m, 996 m, 981 m, 926 s, 898 m, 881 w, 885 m, 808 s, 765 s, 681 m, 624 s, 589 w, 550 s, 519 w, 499 w. ¹H NMR (400 MHz, THF-*d*₈): δ 7.08 – 6.90 (m, 12H, CH Ph), 6.74 (d, 4H, CH Napht, *J* = 8.3 Hz), 6.58 (dd, 4H, CH Napht, *J* = 7.0 Hz, *J* = 6.8 Hz), 5.55 (d, 4H, CH Napht, *J* = 6.8 Hz), 3.77 (sept, 8H, CH iPr, *J* = 7.0 Hz, *J* = 6.8 Hz), 0.96 (d, 24H, CH₃ iPr, *J* = 6.8 Hz), 0.86 (d, 24H, CH₃ iPr, *J* = 6.5 Hz). ¹³C NMR (75 MHz, THF-*d*₈): δ 144.1 (C Ph), 135.4 (C Napht), 130.4 (C Napht), 126.1 (C Napht), 125.7 (C Napht), 124.4 (CH Napht), 123.9 (C Ph), 121.4 (CH Ph), 120.6 (CH Ph), 120.4 (CH Ph), 119.3 (CH Napht), 113.6 (CH Napht), 25.5 (CH iPr), 22.2 (CH₃ iPr), 21.9 (CH₃ iPr). Elemental analysis C₈₂H₁₀₅Ga₂N₄Na₂O_{6.9} (1442.51), calc. C 68.21, H 7.27, N 3.88 %; found C 67.94, H 7.01, N 4.07 %.

Synthesis of 7.

25 ml (25 °C, 1 atm, 1 mmol) of carbonyl sulfide was added to a solution of **1** mmol of **1** in DME (10 ml). The reaction mixture color was changed from yellow-green to greenish brown. Green crystals of complex **7** were obtained from THF. Yield 0.35 g, 35 %. IR (nujol, cm⁻¹): 1761 w, 1664 w, 1645 w, 1590 s, 1540 w, 1512 m, 1344 w, 1258 s, 1208 w, 1190 w, 1175 m, 1109 w, 1079 w, 1057 w, 999 m, 924 m, 894 w, 855 m, 836 m, 822 m, 805 s, 761 s, 681 s, 645 s, 623 s, 587 m, 548 m, 515 m. Elemental analysis C₁₁₂H₁₆₄Ga₂N₄Na₂O₁₂S₂ (2008.00), calc: C 66.98, H 8.23, N 2.79, S 3.19 %. found: C 67.28, H 8.41, N 3.06, S 3.33%.

Synthesis of 8.

0.125 g (1 mmol) of cyclohexyl isocyanate was added to a yellow-green solution of **1** mmol of **1** in 10 ml of THF at 25 °C. The solution color changed to greenish-blue within 5 min. All volatiles were removed in a vacuum. The residue was dissolved in 5 ml of DME.

Slow concentration gave green crystals of compound **8**. Crystals suitable for XRD were obtained from C₆D₆. Yield 0.075 g, 9%. IR (nujol, cm⁻¹) 3364 m (N–H), 1622 m, 1591 s, 1522 s, 1334 s, 1246 m, 1211 w, 1192 w, 1180 w, 1131 w, 1114 m, 1088 s, 1064 w, 1033 m, 976 w, 923 m, 894 w, 861 w, 851 w, 804 m, 763 s. ¹H NMR (400 MHz, THF-*d*₅): δ 6.92 (m, 4H, CH Ph), 6.83 (m, 4H, CH Napht), 6.72 (t, 4H, CH Ph, *J* = 7.5 Hz), 6.63 (t, 4H, CH Napht, *J* = 6.6 Hz), 6.50 (m, 4H, CH Ph), 5.79 (d, 1H, N–H), 5.46 (dd, 4H, CH Napht, *J* = 6.9, *J* = 2.3 Hz), 3.84 (m, 4H, CH *i*Pr), 3.48 (m, 4H, CH *i*Pr), 3.07 (m, 1H, CH Cy), 2.20 (d, 4H, CH₂ Cy, *J* = 11.5 Hz), 1.99 (br. s, 4H, CH₂ Cy), 1.20 (d, 12H, CH₃ *i*Pr, *J* = 5.8 Hz), 1.12 (m, 2H, CH₂ Cy), 1.03 (d, 12H, CH₃ *i*Pr, *J* = 4.6 Hz), 0.74 (d, 12H, CH₃ *i*Pr, *J* = 5.5 Hz), 0.71 (d, 12H, CH₃ *i*Pr, *J* = 9.1 Hz). Elemental analysis C₉₄H₁₂₂D₃Ga₂N₅NaO₉ (1634.43), calc. C 69.07, H 7.89, N 4.28 %; found C 68.61, H 8.26, N 4.01 %.

Synthesis of 9.

0.364 g (2 mmol) of benzophenone was added to a yellow-green solution of **1** in 10 ml of THF at 25 °C. The solution color changed to green within 5 min. All volatiles were removed in a vacuum. The residue was dissolved in 5 ml of pyridine. Slow concentration gave green crystals of compound **9**. Yield 0.591 g, 53 %. IR (nujol, cm⁻¹) 1592 s, 1515 s, 1338 s, 1255 s, 1181 m, 1106 m, 1051 s, 999 s, 924 s, 902 m, 852 m, 805 s, 767 s, 750 s, 706 s, 617 s, 518 m, 460 s. ¹H NMR (400 MHz, Py-*d*₅): δ 7.76 (d, 8H, CH Ph, *J* = 7.3 Hz), 7.38 (br. s, 6H, CH Ph), 6.95 (d, 2H, CH Napht, *J* = 8.3 Hz), 6.84 (d, 2H, CH Napht), 6.82 (m, 12H, CH Ph), 6.13 (d, 2H, CH Napht, *J* = 8.3 Hz), 4.48 (sept, 4H, CH *i*Pr, *J* = 6.8 Hz), 1.35 (d, 12H, CH₃ *i*Pr, *J* = 6.8 Hz), 1.26 (d, 12H, CH₃ *i*Pr, *J* = 6.8 Hz). ¹³C NMR (75 MHz, Py-*d*₅): δ 152.8 (C=N), 150.9 (C Napht), 147.8 (C Ph), 147.1 (C Ph), 137.9 (C Napht), 135.8 (C Ph), 132.8 (C Napht), 130.3 (CH Ph), 128.3 (C–N), 127.2 (CH Napht), 125.9 (CH Ph), 124.2 (CH Ph), 123.6 (CH Ph), 123.0 (CH Ph), 121.7 (CH Napht), 116.5 (CH Napht), 88.6 (C–O), 28.2 (CH *i*Pr), 25.0 (CH₃ *i*Pr), 23.9 (CH₃ *i*Pr). Elemental analysis C₇₇H₇₀Ga₄NaO₂ (1116.06), calc. C 78.63, H 5.99, N 4.76 %; found C 78.88, H 6.27, N 4.96 %.

Synthesis of 10.

0.388 g (2 mmol) of diphenylketene was added to a yellow-green solution of **1** in 10 ml of DME at 25 °C. The solution color changed to green within 5 min. Storage a solution at -20 °C gave green crystals of compound **10**. Yield 0.257 g, 22%. IR (nujol, cm⁻¹) 1606 w, 1551 m, 1520 m, 1493 w, 1343 w, 1258 s, 1181 m, 1123 w, 1082 m, 1057 m, 1003 w, 986 w, 924 s, 903 s, 856 s, 808 s, 766 s, 700 s, 673 s, 648 m, 623 w, 549 m. ¹H NMR (400 MHz, THF-*d*₅): δ 7.76 (d, 2H, CH Ph, *J* = 7.5 Hz), 7.36 (d, 2H, CH Ph, *J* = 7.3 Hz), 7.15 – 7.09 (m, 4H, CH Ph), 7.08 – 7.01 (m, 8H, CH Ph), 6.91 (d, 2H, CH Ph, *J* = 7.5 Hz), 6.87 (d, 2H, CH Napht, *J* = 8.3 Hz), 6.81 (d, 2H, CH Ph, *J* = 7.0 Hz), 6.77 – 6.65 (d, 2H, CH Napht, 6H, CH Ph), 5.72 (d, 2H, CH napht, *J* = 6.8 Hz), 3.97 (sept, 2H, CH *i*Pr, *J* = 6.7 Hz), 3.86 (sept, 2H, CH *i*Pr, *J* = 6.4 Hz), 1.25 (d, 6H, CH₃ *i*Pr, *J* = 6.8 Hz), 0.96 (d, 12H, CH₃ *i*Pr, *J* = 6.8 Hz), 0.93 (d, 6H, CH₃ *i*Pr, *J* = 6.8 Hz). ¹³C NMR (75 MHz, THF-*d*₅): δ 161.1 (O=C=O), 158.1 (O=C–Ga), 149.9 (C Ph), 148.7 (C Ph), 146.9 (C Ph), 145.5 (C Ph), 144.0 (C Ph), 143.9 (C Ph), 143.8 (C Ph), 138.9 (C Napht), 135.2 (C Napht), 132.4 (CH Ph), 132.3 (CH Ph), 131.0 (C–N), 130.9 (CH Ph), 129.9 (C Napht), 129.3 (CH Ph), 129.2 (CH Ph), 128.4 (CH Ph), 128.3 (CH Napht), 127.6 (Ph₂C=COGa), 127.4 (CH Ph), 126.7 (CH Ph), 125.9 (CH Ph), 125.8 (CH Ph), 125.3 (CH Ph), 124.7 (CH Ph), 123.6 (CH Ph), 123.3 (CH Ph), 123.2 (CH Ph), 122.4 (CH Napht), 117.8 (CH Napht), 88.6 (Ph₂C=CO₂), 29.5 (CH *i*Pr), 29.4 (CH *i*Pr), 27.3 (CH₃ *i*Pr), 26.4 (CH₃ *i*Pr), 25.6 (CH₃ *i*Pr), 25.3 (CH₃ *i*Pr). Elemental analysis C₇₈H₉₅Ga₄N₂NaO₉ (1297.26), calc. C 72.31, H 7.38, N 2.15 %; found C 71.95, H 7.52, N 1.96 %.

Synthesis of 11.

0.416 g (2 mmol) of 1,2-dibenzylidenetrihydrazine was added to a yellow-green solution of **1** in 10 ml of Et₂O at 25 °C. The solution color changed to green within 5 min. All volatiles were removed in a vacuum. The residue was dissolved in 5 ml of DME. Storage a solution at 20 °C two days gave green crystals of compound **11**. Yield 0.493 g, 39%. IR (nujol, cm⁻¹) 1661 m, 1598 m, 1581 m, 1545 w, 1512 w, 1341 w, 1247 w, 1192 w,

1117 w, 1068 w, 1029 w, 999 m, 924 m, 899 w, 858 m, 808 s, 756 s, 698 s, 637 m, 615 m, 582 w. ^1H NMR (400 MHz, THF-*d*₈): δ 7.37 (br. s, 2H, N=CH(Ph)), 7.18 (d, 4H, CH Ph, J = 7.9 Hz), 7.14 (s, 4H, CH Ph), 7.01 (t, 4H, CH Ph, J = 7.4 Hz), 6.75 (t, 8H, 2 \times CH Napht, 6 \times CH Ph, J = 6.9 Hz), 6.65 (m, 8H, 2 \times CH Napht, 6 \times CH Ph), 5.69 (d, 1H, CH Napht, J = 6.6 Hz), 5.56 (d, 1H, CH Napht, J = 6.6 Hz), 5.08 (s, 2H, N-CH(Ph)), 4.18 (sept, 2H, CH iPr, J = 7.2 Hz), 4.12 (sept, 2H, CH iPr, J = 7.2 Hz), 1.2 (d, 6H, CH₃ iPr, J = 6.5 Hz), 1.07 (d, 6H, CH₃ iPr, J = 6.5 Hz), 1.04 (d, 6H, CH₃ iPr, J = 6.6 Hz), 0.87 (d, 6H, CH₃ iPr, J = 6.5 Hz). ^{13}C NMR (75 MHz, THF-*d*₈): δ 148.0 (C Ph), 147.6 (C Ph), 146.6 (C Ph), 146.1 (C Ph), 145.3 (C Napht), 140.0 (C Ph), 137.7 (C Napht), 132.4 (C Napht), 132.3 (C Napht), 131.2 (H-C=N), 129.0 (CH Ph), 128.3 (C Napht), 128.1 (CH Ph), 128.0 (CH Ph), 127.6 (CH Ph), 126.9 (CH Ph), 126.2 (CH Napht), 126.2 (CH Ph), 126.1 (CH Napht), 125.5 (CH Ph), 125.4 (CH Ph), 124.6 (CH Ph), 124.5 (CH Ph), 123.5 (CH Ph), 123.4 (CH Ph), 122.4 (CH Ph), 122.3 (CH Ph), 121.1 (CH Napht), 120.8 (CH Napht), 116.1 (CH Napht), 115.8 (CH Napht), 68.8 (H-C-N), 27.7 (CH iPr), 27.2 (CH iPr), 24.8 (CH₃ iPr), 24.6 (CH₃ iPr), 23.9 (CH₃ iPr), 23.7 (CH₃ iPr). Elemental analysis C₇₆H₉₄GaN₆NaO₆ (1280.28), calc. C 71.29, H 7.40, N 6.56 %; found C 70.90, H 7.62, N 6.42 %.

Synthesis of 12.

0.206 g (1 mmol) of 1,2-dibenzylidenehydrazine was added to a yellow-green solution of 1 mmol of **1** in 10 ml of DME at 25 °C. The solution color changed to green within 5 min. All volatiles were removed in a vacuum. The residue was dissolved in 5 ml of pyridine. Solution was heated at 80 °C during 2 hours. All volatiles were removed in a vacuum. The residue was dissolved in 5 ml of DME. Layering the solution with 10 ml of Et₂O gave green crystals of compounds **12**. Yield 0.476 g, 40%. IR (nujol, cm⁻¹) 1661 m, 1605 w, 1581 w, 1548 m, 1341 w, 1319 w, 1255 m, 1208 w, 1192 w, 1123 w, 1087 w, 1032 w, 998 w, 927 s, 899 s, 860 s, 805 s, 764 s, 706 s, 651 m, 590 s, 568 m, 515 m. ^1H NMR (400 MHz, THF-*d*₈): δ 7.73 (s, 1H, N=CH(Ph)), 7.28 (d, 2H, CH Ph, J = 7.5 Hz), 7.09 (m, 10H, CH Ph), 6.85 (m, 2H, CH Napht), 6.74 (m, 4H, CH Ph), 6.62 (d, 1H, C₅H₅(6)N, J = 6.8 Hz), 6.58 (pent, 2H, CH Napht, J = 7.5 Hz), 5.57 (d, 1H, CH Napht, J = 6.8 Hz), 5.79 (d, 1H, CH Napht, J = 6.8 Hz), 5.44 (t, 1H, C₅H₅(4)N, J = 7.0 Hz), 4.58 (d, 1H, N-CH(Ph), J = 9.5 Hz), 4.29 (t, 1H, C₅H₅(5)N, J = 5.6 Hz), 4.23 (d, 1H, C₅H₅(3)N, J = 9.6 Hz), 4.18 (sept, 1H, CH iPr, J = 6.8 Hz), 4.00 (d, 1H, C₅H₅(2)N, J = 6.6 Hz), 3.94 (sept, 1H, CH iPr, J = 6.9 Hz), 3.86 (sept, 1H, CH iPr, J = 6.8 Hz), 3.78 (sept, 1H, CH iPr, J = 6.9 Hz), 1.25 (d, 6H, CH₃ iPr, J = 7.0 Hz), 1.16 (d, 3H, CH₃ iPr, J = 6.8 Hz), 1.10 (d, 3H, CH₃ iPr, J = 6.5 Hz), 1.01 (d, 3H, CH₃ iPr, J = 6.8 Hz), 0.95 (d, 3H, CH₃ iPr, J = 6.5 Hz), 0.90 (d, 3H, CH₃ iPr, J = 6.8 Hz), 0.76 (d, 3H, CH₃ iPr, J = 6.8 Hz). ^{13}C NMR (75 MHz, THF-*d*₈): δ 147.7, 147.4, 147.3, 147.1, 146.5, 146.4, 146.1, 145.9, 145.7, 145.4, 143.8, 143.7 (C₅H₅N), 140.2 (CH Napht), 137.6, 132.9, 132.6, 132.3, 131.5 (H-C=N), 129.0, 128.1, 127.8, 127.5, 127.0, 126.9, 126.7, 126.2, 126.1 (CH Napht), 125.5 (C₅H₅N), 124.3, 124.2, 123.3, 122.9, 122.6, 121.7, 121.1, 119.0, 115.9 (CH Napht), 115.7 (CH Napht), 104.6 (C₅H₅N), 92.5 (C₅H₅N), 73.3 (H-C-N), 62.5 (C₅H₅N), 27.8 (CH iPr), 27.6 (CH iPr), 26.8 (CH iPr), 26.7 (CH iPr), 25.6 (CH₃ iPr), 25.5 (CH₃ iPr), 25.2 (CH₃ iPr), 24.9 (CH₃ iPr), 23.5 (CH₃ iPr), 23.4 (CH₃ iPr), 22.9 (CH₃ iPr), 22.6 (CH₃ iPr). Elemental analysis C₆₉H₉₂GaN₅NaO_{6.5} (1188.18), calc. C 69.68, H 7.74, N 5.89 %; found C 69.31, H 7.52, N 6.1 %.

Synthesis of 12-*d*⁵.

0.206 g (1 mmol) of 1,2-dibenzylidenehydrazine was added to a yellow-green solution of 1 mmol of **1** in 10 ml of DME at 25 °C. The solution color changed to green within 5 min. All volatiles were removed in a vacuum. The residue was dissolved in 5 ml of pyridine-*d*₅. Solution was heated at 80 °C during 2 hours. All volatiles were removed in vacuum. The residue was dissolved in 5 ml of DME. Layering the solution with 10 ml of Et₂O gave green crystals of compounds **12-*d*⁵**. Yield 0.432 g, 36%. IR (nujol, cm⁻¹) 2263 w, 2236 w, 1670 m, 1591 m, 1546 m, 1511 w, 1337 w, 1262 w, 1192 w, 1132 w, 1032 w, 983 w, 923 m, 893 w, 863 m, 808 m, 758 s, 694 s, 660 w, 580 w, 523 m. ^1H NMR (400 MHz, THF-*d*₈): δ 7.73 (s, 1H, N=CH(Ph)), 7.27 (d, 2H, CH Ph, J = 7.8 Hz), 7.09 (m, 10H, CH Ph), 6.86 (t, 2H,

CH Napht, $J = 6.9$ Hz), 6.72 (m, 4H, CH Ph), 6.59 (pent, 2H, CH Napht, $J = 6.9$ Hz), 5.57 (d, 1H, CH Napht, $J = 6.8$ Hz), 5.49 (d, 1H, CH Napht, $J = 7.0$ Hz), 4.57 (s, 1H, N-CH(Ph)), 4.19 (sept, 1H, CH iPr, $J = 6.6$ Hz), 3.94 (sept, 1H, CH iPr, $J = 6.6$ Hz), 3.86 (sept, 1H, CH iPr, $J = 6.9$ Hz), 3.78 (sept, 1H, CH iPr, $J = 6.4$ Hz), 1.25 (d, 6H, CH₃ iPr, $J = 7.0$ Hz), 1.16 (d, 3H, CH₃ iPr, $J = 6.8$ Hz), 1.09 (d, 3H, CH₃ iPr, $J = 5.5$ Hz), 1.01 (d, 3H, CH₃ iPr, $J = 6.5$ Hz), 0.95 (d, 3H, CH₃ iPr, $J = 6.5$ Hz), 0.90 (d, 3H, CH₃ iPr, $J = 6.8$ Hz), 0.75 (d, 3H, CH₃ iPr, $J = 6.8$ Hz). ¹³C NMR (75 MHz, THF-*d*₈): δ 147.7, 147.4, 147.3, 147.1, 146.5, 146.4, 146.1, 145.9, 145.7, 145.4, 143.8, 143.7 (C₅D₅N), 140.2 (CH Napht), 137.6, 132.9, 132.6, 132.3, 131.5 (H-C=N), 129.0, 128.1, 127.8, 127.5, 127.0, 126.9, 126.7, 126.2, 126.1 (CH Napht), 125.5 (C₅D₅N), 124.3, 124.2, 123.3, 122.9, 122.6, 121.7, 121.1, 119.0, 115.9 (CH Napht), 115.7 (CH Napht), 104.6 (C₅D₅N), 92.5 (C₅D₅N), 73.3 (H-C-N), 62.5 (C₅D₅N), 27.8 (CH(CH₃)₂), 27.6 (CH(CH₃)₂), 26.8 (CH(CH₃)₂), 26.7 (CH(CH₃)₂), 25.6 (CH(CH₃)₂), 25.5 (CH(CH₃)₂), 25.2 (CH(CH₃)₂), 24.9 (CH(CH₃)₂), 23.5 (CH(CH₃)₂), 23.4 (CH(CH₃)₂), 22.9 (CH(CH₃)₂), 22.6 (CH(CH₃)₂). Elemental analysis C₆₉H₈₇D₅GaN₅NaO_{6.5} (1193.18), calc. C 69.45, H 8.18, N 5.87 %; found C 69.06, H 7.90, N 6.15 %.

X-ray Crystal Structure Determination.

The X-ray diffraction data were collected on a Bruker D8 Quest (Mo-K α radiation, $\lambda = 0.71073$ Å) (for **2-8** and **11**), an Agilent Xcalibur E (Mo-K α radiation, $\lambda = 0.71073$ Å) (for **9**) and an Agilent SuperNova (Cu-K α radiation, $\lambda = 1.54184$ Å) (for **10** and **12**) diffractometers, equipped with Photon (CMOS), EOS (CCD) and Atlas Sapphire S (CCD) area detectors respectively. Data collection, initial reflection indexing and refinement of the unit cell parameters were carried out with APEX3[113] and CrysAlisPro[114] programs for **2-8**, **11** and **9**, **10**, **12** correspondingly. The crystal of **4** was a non-merohedral 2-component twin with an approximately equal ratio of single-crystal domains (0.47 : 0.53). And the diffraction data for **4**, measured on the Bruker D8 Quest, were eventually treated with the CrysAlisPro software[114]. Collected diffraction data were integrated using the SAINT [115] and CrysAlisPro [114] software respectively for **2**, **3**, **5-8**, **11** and **4**, **9**, **10**, **12**. The SADABS [116,117] (for **2**, **3**, **5-8**, **11**) and SCALE3 ABSPACK algorithm [118] (for **4**, **9**, **10**, **12**) were used for absorption corrections. XABS2 within WINGX v2018.3 software [119] was additionally employed for absorption correction of **12**. All structures were solved by dual-space method using the SHELXT [120] software and refined on F^2_{hkl} with SHELXTL [121,122] (for **1-9**, **11**) and OLEX2 [123] (for **10** and **12**) packages. The structure of twinned crystal **4** was refined for two single-crystal domains with the HKLF5 instruction Non-hydrogen atoms were refined anisotropically. 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 CH₃ groups) of their parent atoms. The H(5) atom of the -NH group of the N-cyclohexylcarbamate ligand in **8** as well as the H atoms of four -CH groups in the 1,2-dibenzylidenehydrazine moieties of **11** were located from the difference Fourier synthesis of the electron density and refined isotropically. Almost all crystals of gallium complexes additionally contain solvate molecules of Et₂O (**2**, **3**, **6**, **12**), pyridine (**5**), DME (**6** and **10**) and deuterated benzene (**8**), disposed either at the common or at the special positions. Most of the solvate molecules, located at the special crystallographic sites, were found to be disordered over two or more positions. Gallium complexes possess disordered molecular fragments: Me-groups in DME ligand (**3**), *cy*-Hex groups in the carbamic moiety (**5**), *i*-Pr groups in BIAN-ligand (**5**, **10**), Ph-group in Ph₂CCO-ligand (**10**), whole THF(**4**), Et₂O (**4**) and DME (**8**) ligands. The main crystallographic data and structure refinement details for **2 - 12** are presented in the Table S1. CCDC 2314238 (**2**), 2314239 (**3**), 2314240 (**4**), 2314241 (**5**), 2314242 (**6**), 2314245 (**7**), 2314246 (**8**), 2314247 (**9**), 2314248 (**10**), 2314249 (**11**) and 2314250 (**12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via ccdc.cam.ac.uk/structures

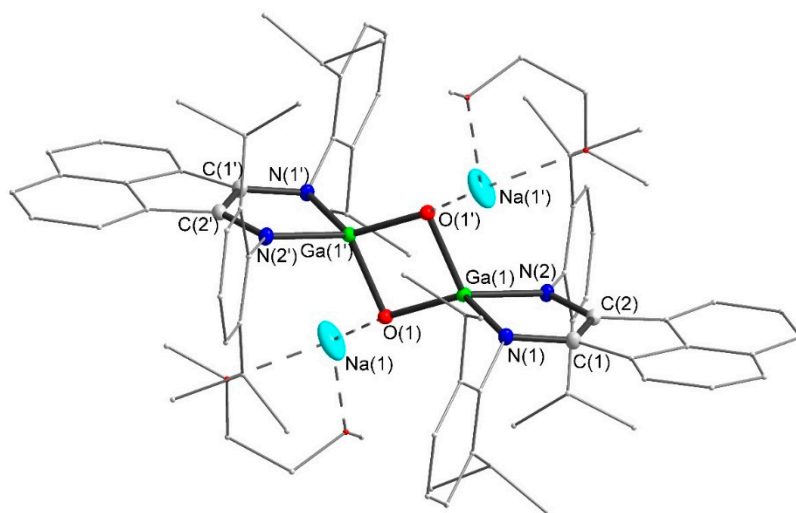


Figure S1. Molecular structure of compound **6**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): Ga(1)–O(1) 1.8322(16), Ga(1)–O(1a) 1.8830(17), Ga(1)···Ga(1a) 2.6336(5), Na(1)–O(1) 2.143(2), N(1)–C(1) 1.406(3), N(2)–C(2) 1.371(3), C(1)–C(2) 1.377(3), O(1)–Ga(1)–O(1a) 89.72(7), O(1)–Ga(1)–N(2) 123.06(8), N(2)–Ga(1)–N(1) 89.99(9), Ga(1)–O(1)–Ga(1a) 90.28(7). (a) -x, 1-y, 1-z.

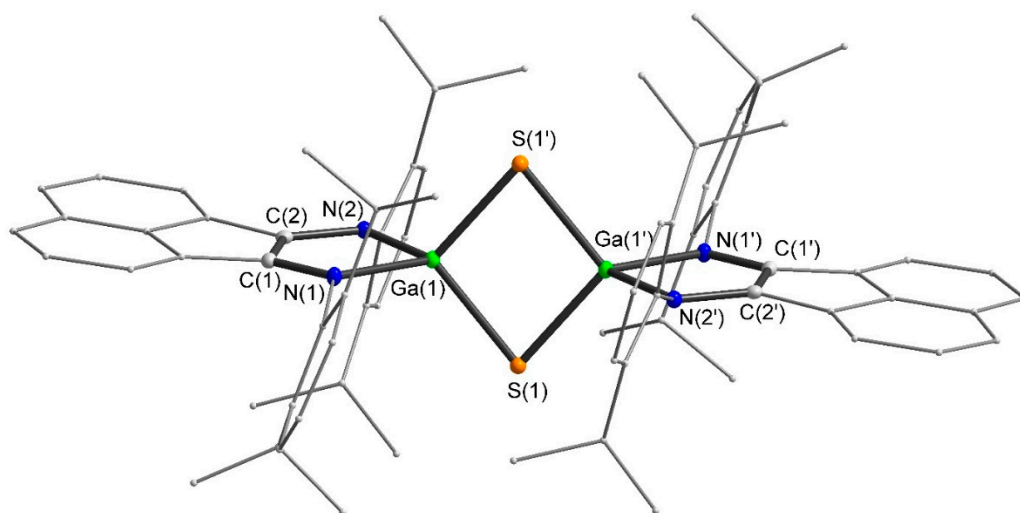


Figure S2. Molecular structure of compound **7**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): Ga(1)–N(2) 1.9446(17), Ga(1)–N(1) 1.9478(16), Ga(1)–S(1) 2.2613(6), Ga(1)–S(1') 2.2630(6), Ga(1)–Ga(1') 2.9151(5), N(1)–C(1) 1.388(3), N(2)–C(2) 1.387(2), C(1)–C(2) 1.382(3), N(2)–Ga(1)–N(1) 88.06(7), N(2)–Ga(1)–S(1) 119.40(5), N(1)–Ga(1)–S(1) 117.23(5), N(2)–Ga(1)–S(1') 116.08(5), N(1)–Ga(1)–S(1') 117.68(5), S(1)–Ga(1)–S(1') 99.771(19), N(2)–Ga(1)–Ga(1') 136.23(5), N(1)–Ga(1)–Ga(1') 135.68(5), S(1)–Ga(1)–Ga(1') 49.910(15), Ga(1)–S(1)–Ga(1') 80.229(19), C(1)–N(1)–Ga(1) 107.40(12), C(2)–N(2)–Ga(1) 107.56(12), C(2)–C(1)–N(1) 118.53(17), N(2)–C(2)–C(1) 118.43(18). (a) 1-x, 1-y, 1-z.

Table S1. Crystallographic data and refinement details for compounds **2–12**.

Complex	2×C ₄ H ₁₀ O	3×C ₄ H ₁₀ O	4
Empirical formula	C ₇₂ H ₉₅ Ga ₂ N ₅ NaO ₇	C ₁₂₄ H ₁₇₆ Ga ₂ N ₁₀ Na ₂ O ₁₀	C ₁₀₂ H ₁₃₈ Ga ₂ N ₆ Na ₂ O ₈
Formula weight	1235.23	2152.16	1761.60
Temperature [K]	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P2 ₁ /n	P-1	P2 ₁ /n
Unit cell dimensions			
a[Å]	13.4074(5)	13.2545(5)	14.924(2)
b[Å]	28.9911(10)	15.2235(5)	16.0437(19)
c[Å]	17.5415(6)	15.2965(5)	19.659(2)

α [°]	90	77.6949(12)	90
β [°]	93.397(2)	79.3142(13)	91.627(9)
γ [°]	90	77.5861(13)	90
Volume [Å ³]	6806.3(4)	2913.42(18)	4705.1(10)
Z	4	1	2
Calculated density [Mg/m ³]	1.205	1.227	1.243
Absorption coefficient [mm ⁻¹]	0.466	0.532	0.641
F(000)	2640	1154	1880
Crystal size [mm ³]	0.704 × 0.408 × 0.284	0.380 × 0.140 × 0.050	0.220 × 0.140 × 0.120
θ [°]	2.091 / 28.000	2.251 / 30.507	1.639 / 25.081
Index ranges	-17 ≤ h ≤ 17, -38 ≤ k ≤ 38, -23 ≤ l ≤ 23	-18 ≤ h ≤ 18, -21 ≤ k ≤ 21, -21 ≤ l ≤ 21	-17 ≤ h ≤ 17, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23
Reflections collected / unique	71122 / 16417	49673 / 17765	13959 / 13959
R(int)	0.0431	0.0376	0.1516
Data / restraints / parameters	16417 / 0 / 791	17765 / 6 / 699	13959 / 607 / 580
S	1.029	1.031	1.028
Final R indices [I > 2σ(I)]	0.0419 / 0.0994	0.0439 / 0.0919	0.0767 / 0.1114
R indices (all data)	0.0565 / 0.1045	0.0673 / 0.0996	0.1702 / 0.1271
Largest diff. peak and hole [e/Å ³]	0.865 / -0.391	0.917 / -0.651	2.051 / -1.285

Table S1. *Continued.* Crystallographic data and refinement details for compounds **2–12**.

Complex	5 ×3.5C ₅ H ₅ N	6 ×0.4C ₄ H ₁₀ O ₂ , 0.1C ₄ H ₁₀ O	7
Empirical formula	C _{82.50} H _{94.50} GaN _{10.50} NaO ₂	C ₈₂ H ₁₀₅ Ga ₂ N ₄ Na ₂ O _{6.90}	C ₁₁₂ H ₁₆₄ Ga ₂ N ₄ Na ₂ O ₁₂ S ₂
Formula weight	1357.89	1442.51	2008.00
Temperature [K]	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2 ₁ /n	P2 ₁ /c	P2 ₁ /n
Unit cell dimensions			
a [Å]	12.1435(6)	20.3850(7)	16.8432(9)
b [Å]	23.8032(12)	16.3237(6)	17.154(1)
c [Å]	25.7733(13)	22.9506(8)	19.5039(11)
α [°]	90	90	90
β [°]	98.0683(15)	98.774(2)	107.8082(18)
γ [°]	90	90	90
Volume [Å ³]	7376.1(6)	7547.6(5)	5365.2(5)
Z	4	4	2
Calculated density [Mg/m ³]	1.223	1.269	1.243
Absorption coefficient [mm ⁻¹]	0.434	0.781	0.610
F(000)	2884	3057	2152
Crystal size [mm ³]	0.450 × 0.350 × 0.150	0.714 × 0.666 × 0.432	0.420 × 0.300 × 0.250
θ [°]	2.149 / 26.999	2.187 / 27.999	2.253 / 27.484
Index ranges	-15 ≤ h ≤ 15,	-26 ≤ h ≤ 26,	-21 ≤ h ≤ 21,

	-30 ≤ k ≤ 30, -32 ≤ l ≤ 31	-21 ≤ k ≤ 21, -30 ≤ l ≤ 30	-22 ≤ k ≤ 22, -25 ≤ l ≤ 25
Reflections collected / unique	73577 / 15973	88765 / 18208	77211 / 12304
R(int)	0.0453	0.0615	0.0596
Data / restraints / parameters	15973 / 118 / 969	18208 / 48 / 909	12304 / 0 / 614
S	1.068	1.065	1.012
Final R indices [$I > 2\sigma(I)$]	0.0448 / 0.1179	0.0501 / 0.1272	0.0415 / 0.0816
R indices (all data)	0.0642 / 0.1249	0.0751 / 0.1362	0.0717 / 0.0927
Largest diff. peak and hole [$e/\text{\AA}^3$]	0.571 / -0.500	1.045 / -0.969	0.507 / -0.764

Table S1. *Continued.* Crystallographic data and refinement details for compounds **2–12**.

Complex	8 ×0.5C ₆ D ₆	9	10 ×0.5 C ₄ H ₁₀ O ₂
Empirical formula	C ₉₄ H ₁₂₂ D ₃ Ga ₂ N ₅ NaO ₉	C ₇₂ H ₇₀ GaN ₄ NaO ₂	C ₇₈ H ₉₅ GaN ₂ NaO ₉
Formula weight	1634.43	1116.03	1297.26
Temperature [K]	100(2)	100(2)	150.0(1)
Crystal system	Triclinic	Orthorhombic	Orthorhombic
Space group	P-1	Pbca	P2 ₁ 2 ₁ 2
Unit cell dimensions			
a[Å]	13.0597(3)	21.1085(2)	23.4172(9)
b[Å]	15.7763(4)	19.9958(2)	21.4504(6)
c[Å]	23.4757(5)	27.9009(3)	14.7410(4)
α[°]	90.413(1)	90	90
β[°]	105.982(1)	90	90
γ[°]	110.243(1)	90	90
Volume [Å ³]	4334.38(18)	11776.4(2)	7404.5(4)
Z	2	8	4
Calculated density [Mg/m ³]	1.252	1.259	1.164
Absorption coefficient [mm ⁻¹]	0.686	0.525	0.999
F(000)	1738	4704	2764
Crystal size [mm ³]	0.360 × 0.140 × 0.130	0.480 × 0.370 × 0.270	0.293 × 0.165 × 0.122
θ [°]	2.155 / 28.000	3.076 / 29.999	2.794 / 73.990
Index ranges	-17 ≤ h ≤ 17, -20 ≤ k ≤ 20, -31 ≤ l ≤ 31	-29 ≤ h ≤ 29, -28 ≤ k ≤ 28, -39 ≤ l ≤ 39	-28 ≤ h ≤ 29, -21 ≤ k ≤ 26, -18 ≤ l ≤ 18
Reflections collected / unique	52479 / 20879	222767 / 17157	54530 / 14762
R(int)	0.0251	0.0739	0.0997
Data / restraints / parameters	20879 / 260 / 1176	17157 / 0 / 729	14762 / 99 / 838
S	1.031	1.034	1.032
Final R indices [$I > 2\sigma(I)$]	0.0346 / 0.0836	0.0350 / 0.0818	0.0576 / 0.1185

R indices (all data)	0.0447 / 0.0872	0.0599 / 0.0885	0.0931 / 0.1397
Absolute structure parameter	-	-	-0.015(16)
Largest diff. peak and hole [e/Å ³]	1.084 / -0.793	0.436 / -0.548	0.561 / -0.497

Table S1. *Continued.* Crystallographic data and refinement details for compounds **2–12**.

Complex	11	12 ×0.5C ₄ H ₁₀ O
Empirical formula	C ₇₆ H ₉₄ GaN ₆ NaO ₆	C ₆₉ H ₉₂ GaN ₅ NaO _{6.50}
Formula weight	1280.28	1188.18
Temperature [K]	100(2)	150.0(1)
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /n	P2 ₁ /c
Unit cell dimensions		
a[Å]	22.7378(7)	12.7861(8)
b[Å]	13.6552(4)	20.1944(11)
c[Å]	25.4302(8)	25.545(2)
α[°]	90	90
β[°]	115.169(1)	90.030(4)
γ[°]	90	90
Volume [Å ³]	7146.2(4)	6595.9(8)
Z	4	4
Calculated density [Mg/m ³]	1.190	1.197
Absorption coefficient [mm ⁻¹]	0.446	1.057
F(000)	2728	2540
Crystal size [mm ³]	0.481 × 0.264 × 0.171	0.330 × 0.110 × 0.102
θ [°]	2.175 / 27.999	3.460 / 74.138
Index ranges	-30 ≤ h ≤ 30,	-15 ≤ h ≤ 15,
	-18 ≤ k ≤ 18,	0 ≤ k ≤ 24,
	-33 ≤ l ≤ 33	0 ≤ l ≤ 31
Reflections collected / unique	98236 / 17210	12970 / 12970
R(int)	0.0338	0.1165
Data / restraints / parameters	17210 / 0 / 841	12970 / 36 / 780
S	1.041	1.100
Final R indices [I>2σ(I)]	0.0359 / 0.0834	0.0836 / 0.1863
R indices (all data)	0.0478 / 0.0874	0.1473 / 0.2455
Largest diff. peak and hole [e/Å ³]	0.541 / -0.326	0.639 / -0.666

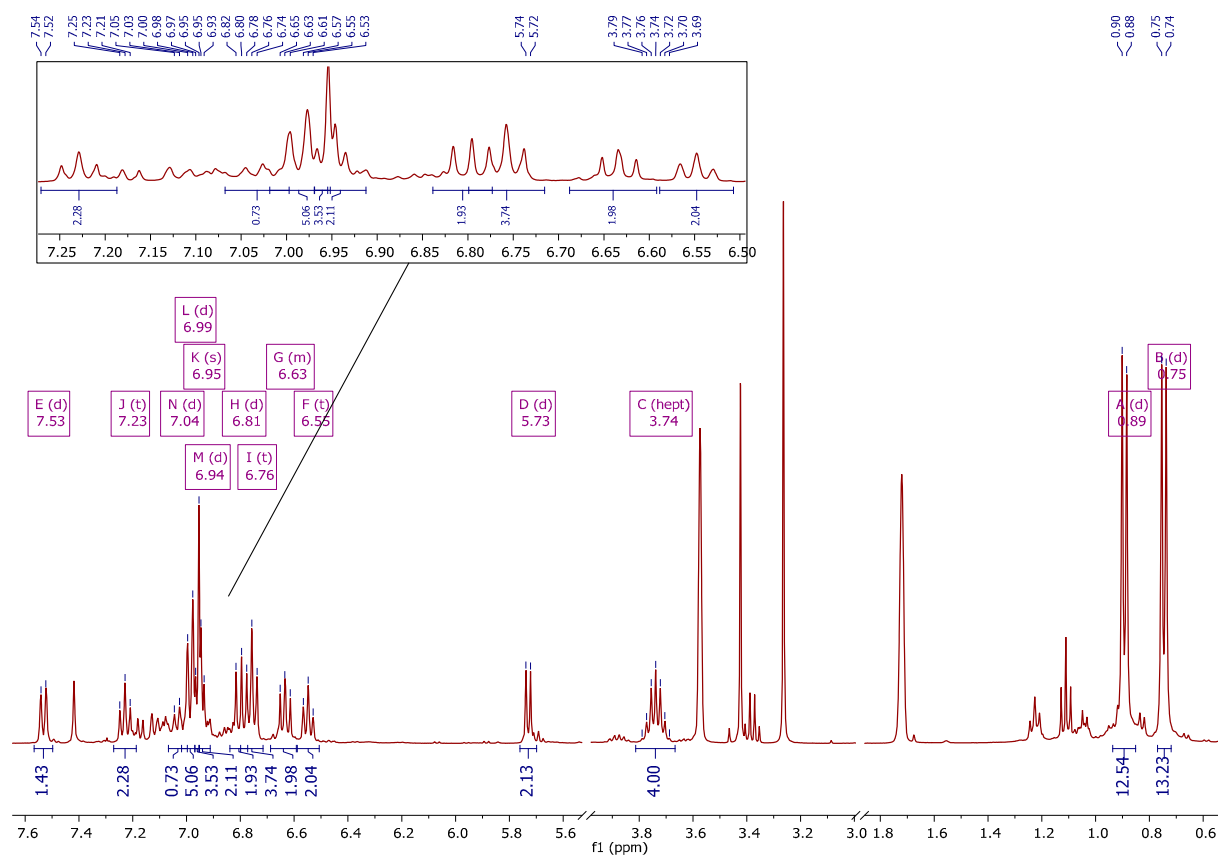


Figure S3. Selected area of ^1H NMR spectrum of compound **2** in $\text{THF-}d_8$.

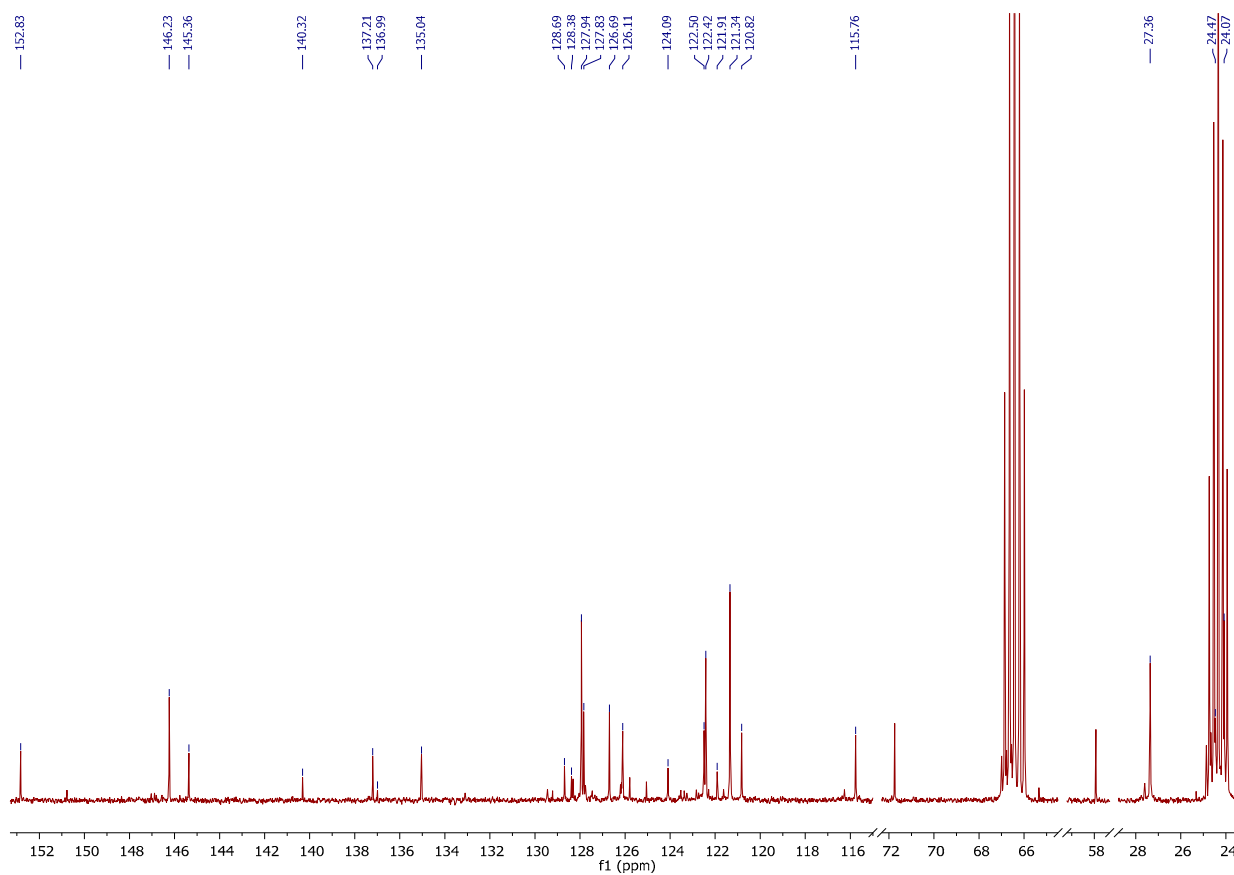


Figure S4. Selected area of ^{13}C NMR spectrum of compound **2** in $\text{THF-}d_8$.

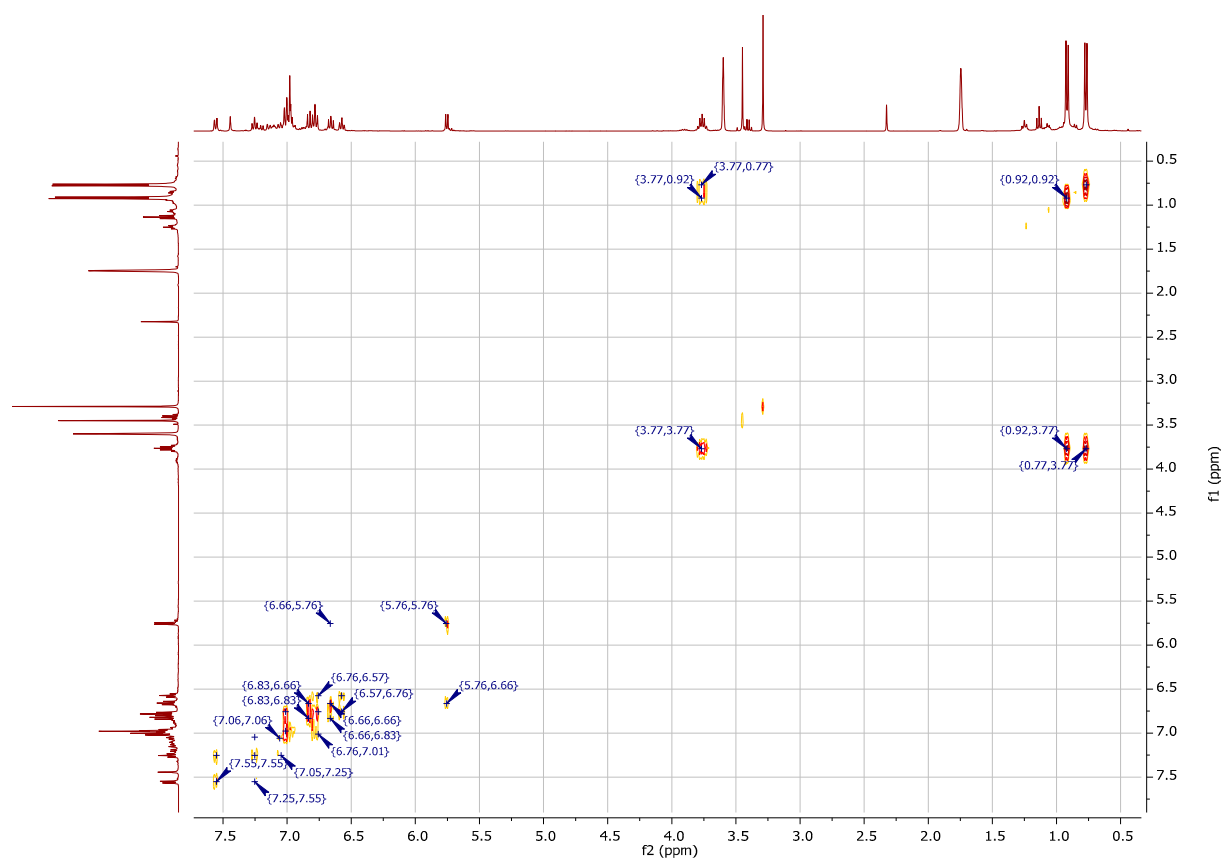


Figure S5. ^1H - ^1H COSY NMR spectrum of compound **2** in $\text{THF-}d_8$.

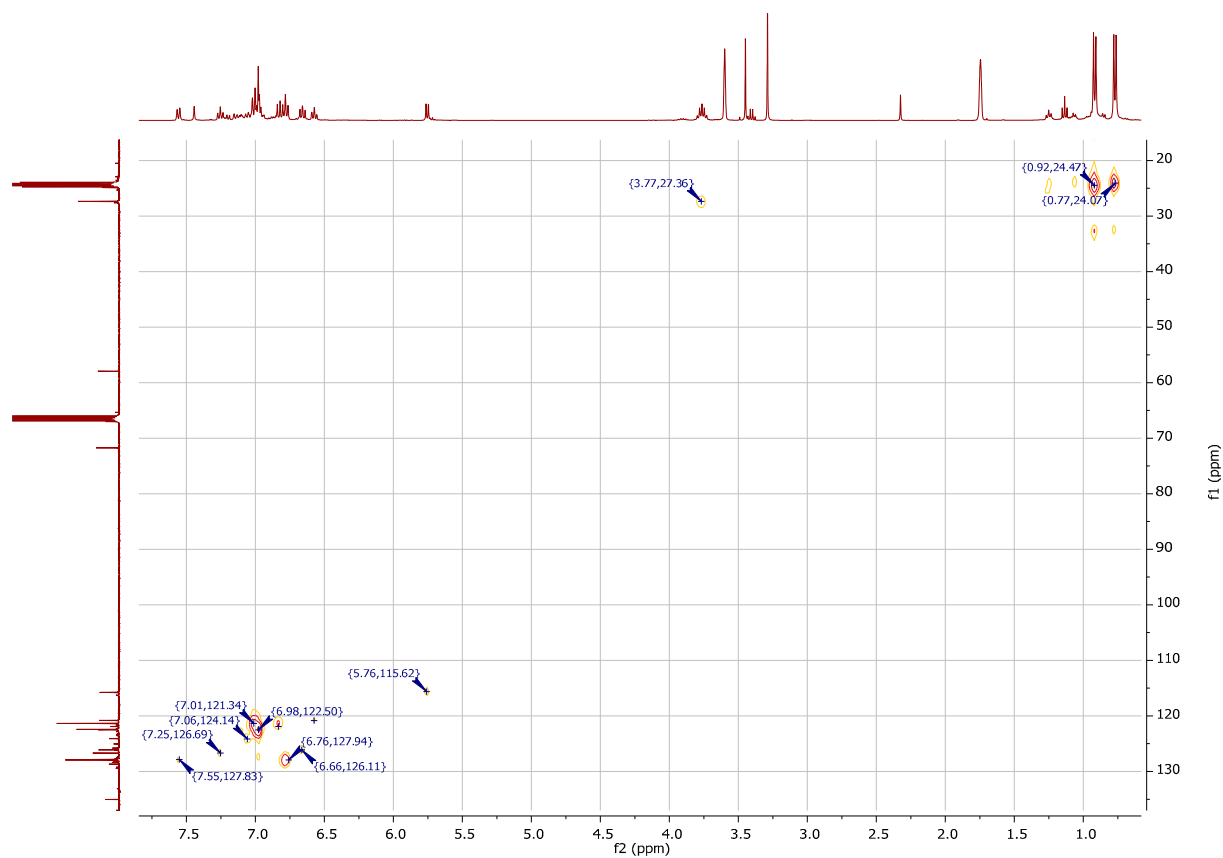


Figure S6. ^1H - ^{13}C HSQC NMR spectrum of compound **2** in $\text{THF-}d_8$.

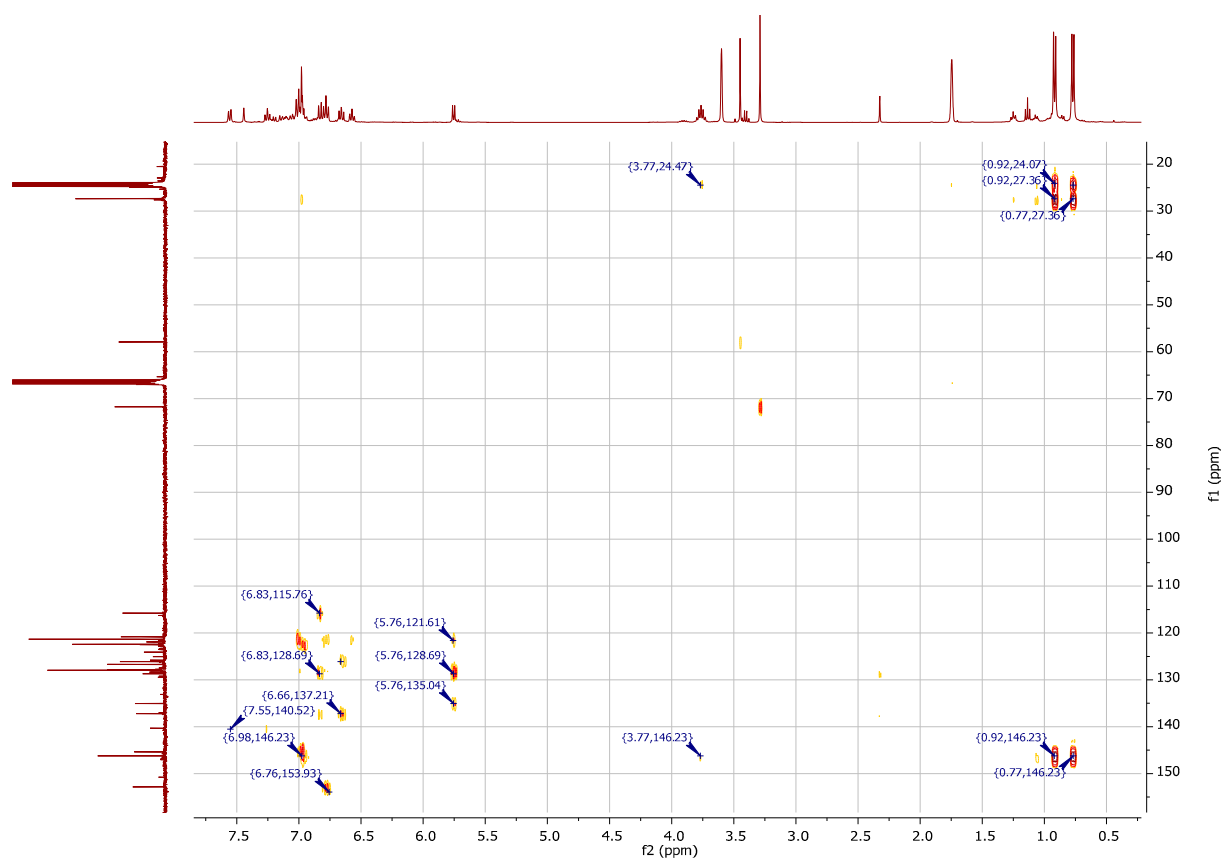


Figure S7. ^1H - ^{13}C HMBC NMR spectrum of compound 2 in THF-d_8 .

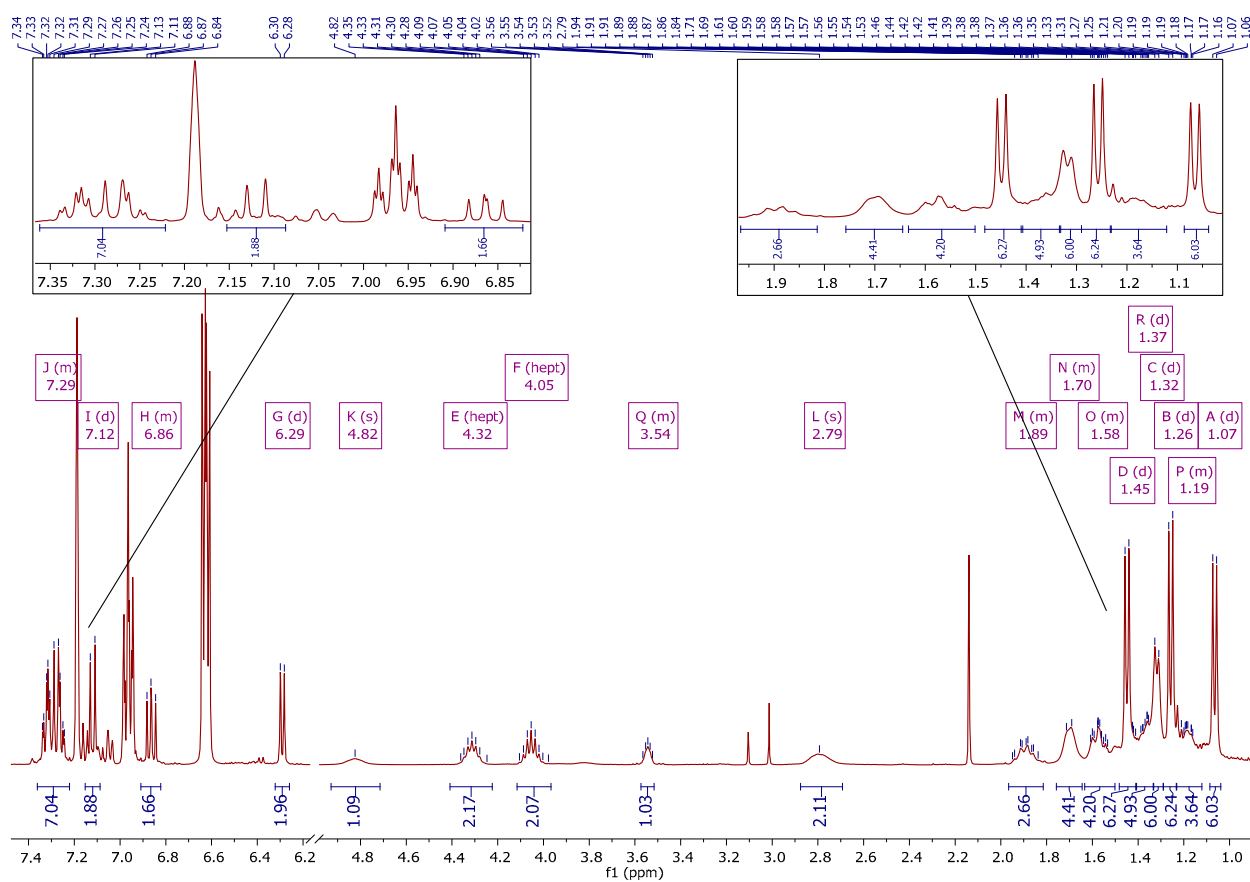


Figure S8. ^1H NMR spectrum of compound 5 in C_6D_6 .

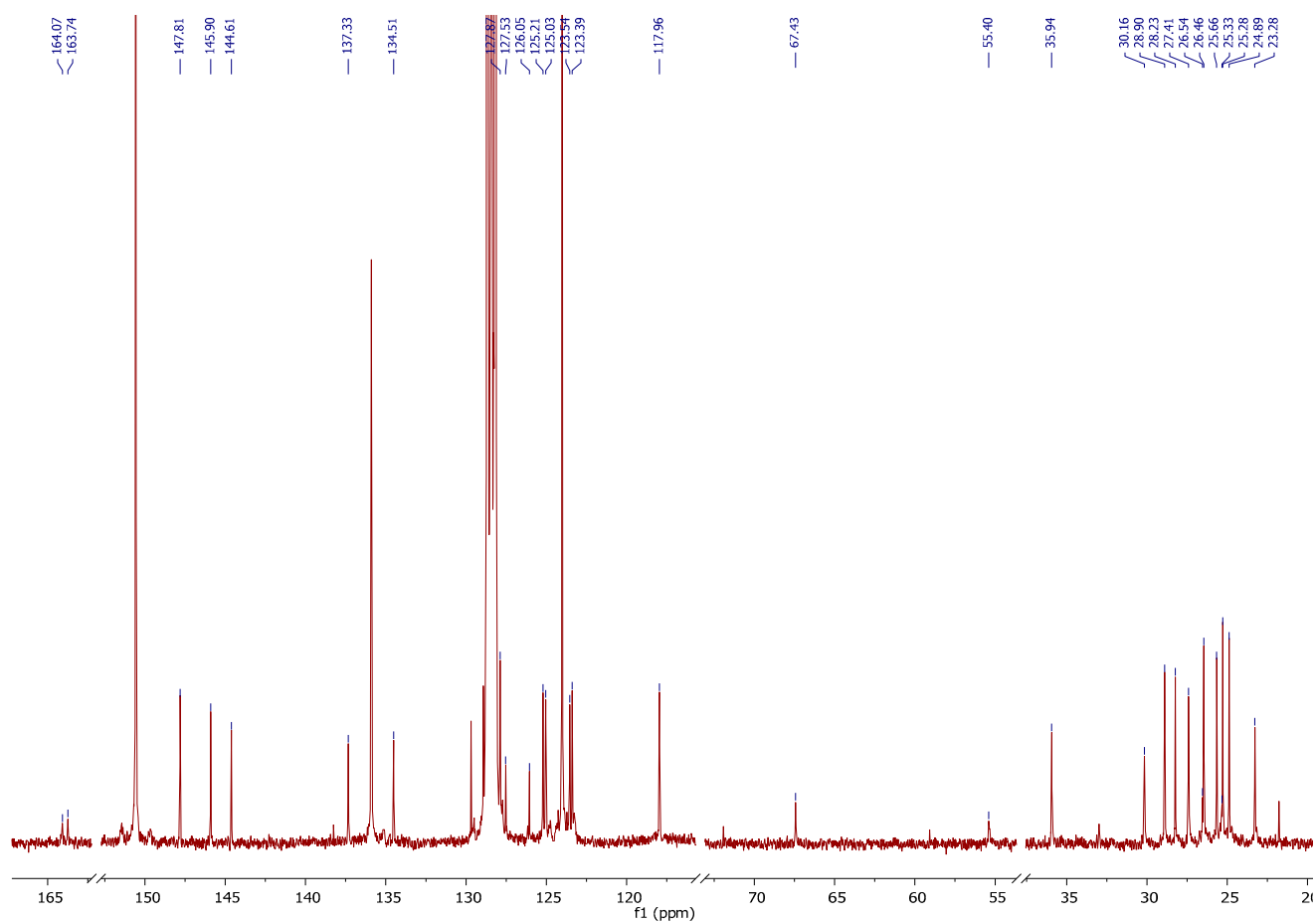


Figure S9. Selected area of ^{13}C NMR spectrum of compound **5** in C_6D_6 .

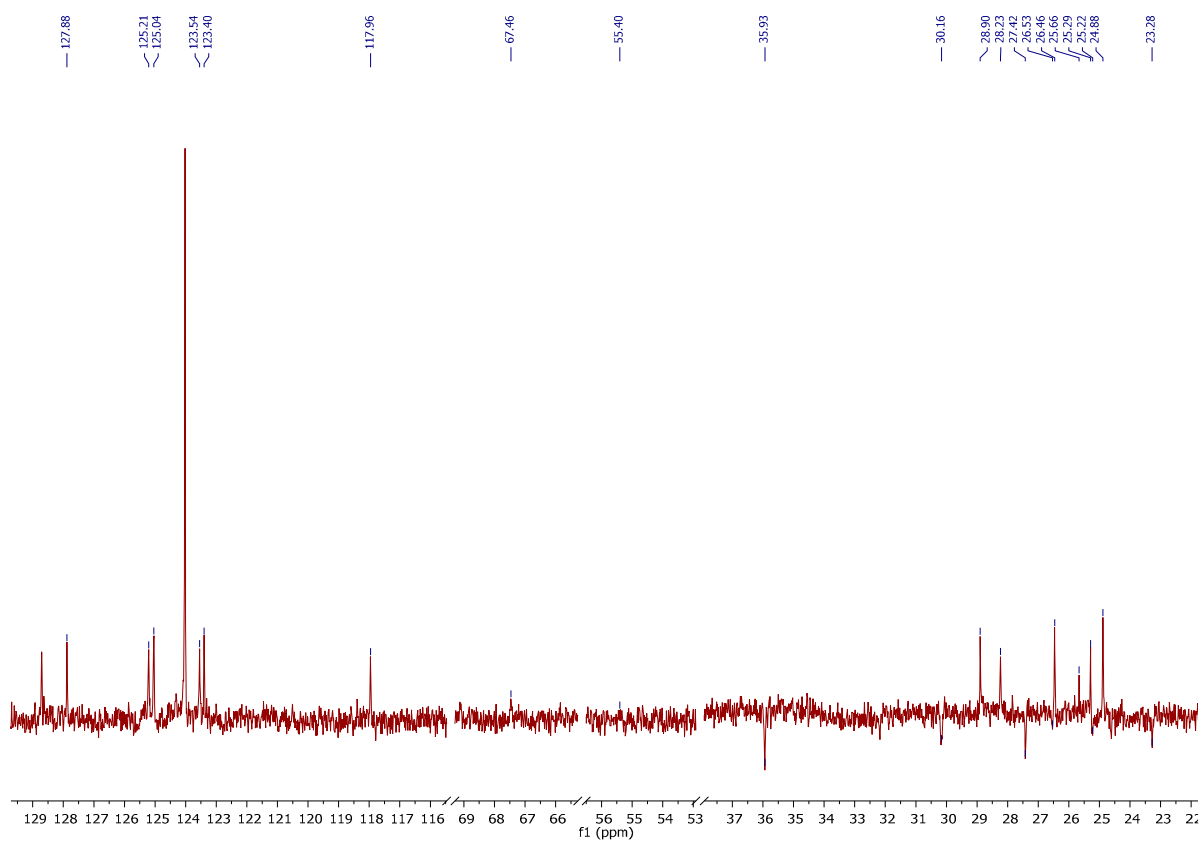


Figure S10. Selected area of DEPT135 NMR spectrum of compound **5** in C_6D_6 .

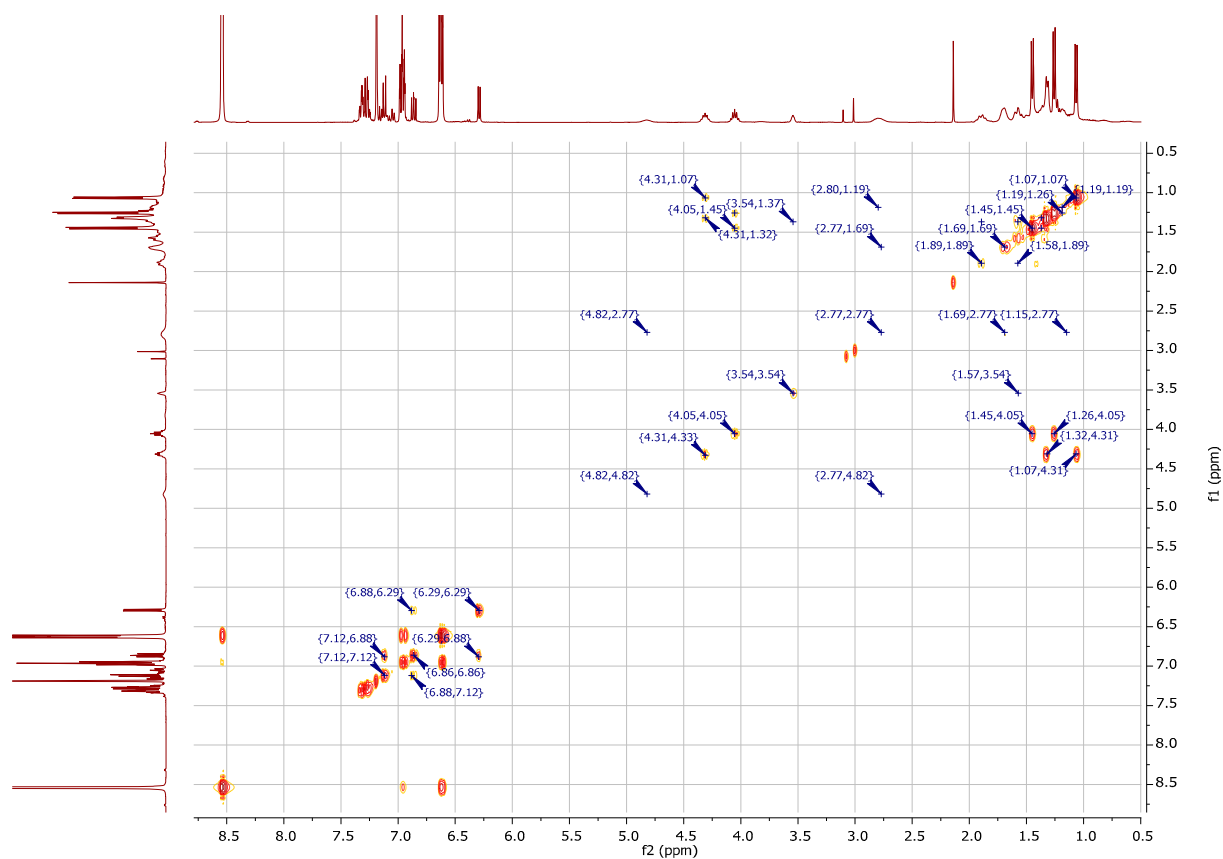


Figure S11. ^1H - ^1H COSY NMR spectrum of compound 5 in C_6D_6 .

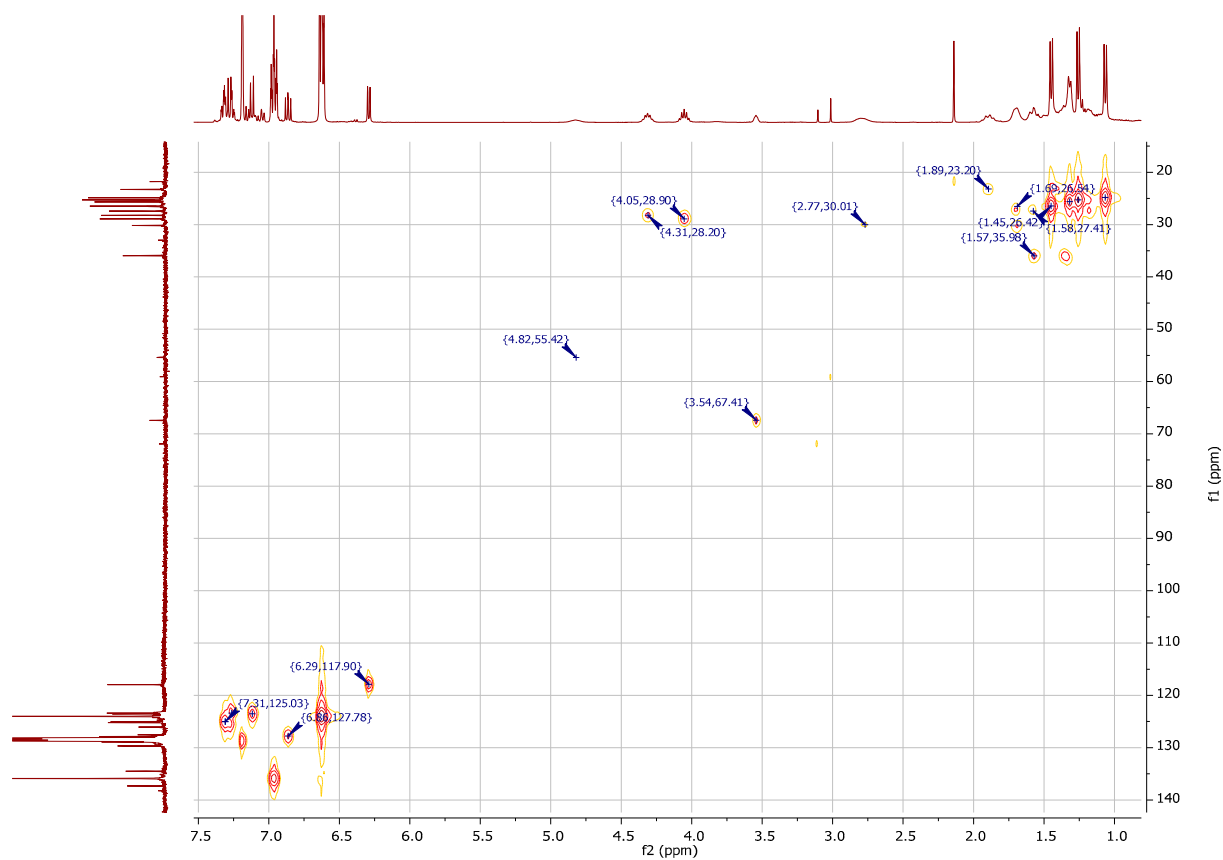


Figure S12. ^1H - ^{13}C HSQC NMR spectrum of compound 5 in C_6D_6 .

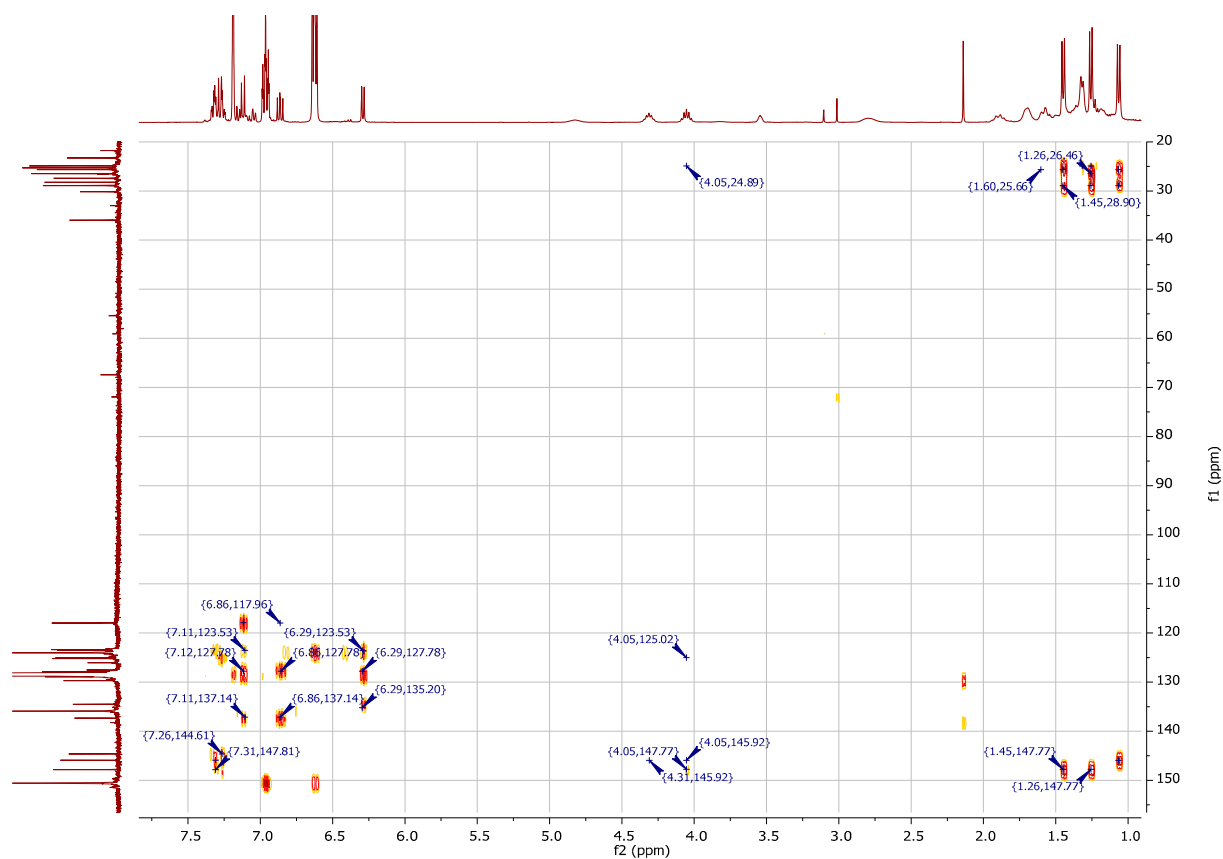


Figure S13. ^1H - ^{13}C HMBC NMR spectrum of compound 5 in C_6D_6 .

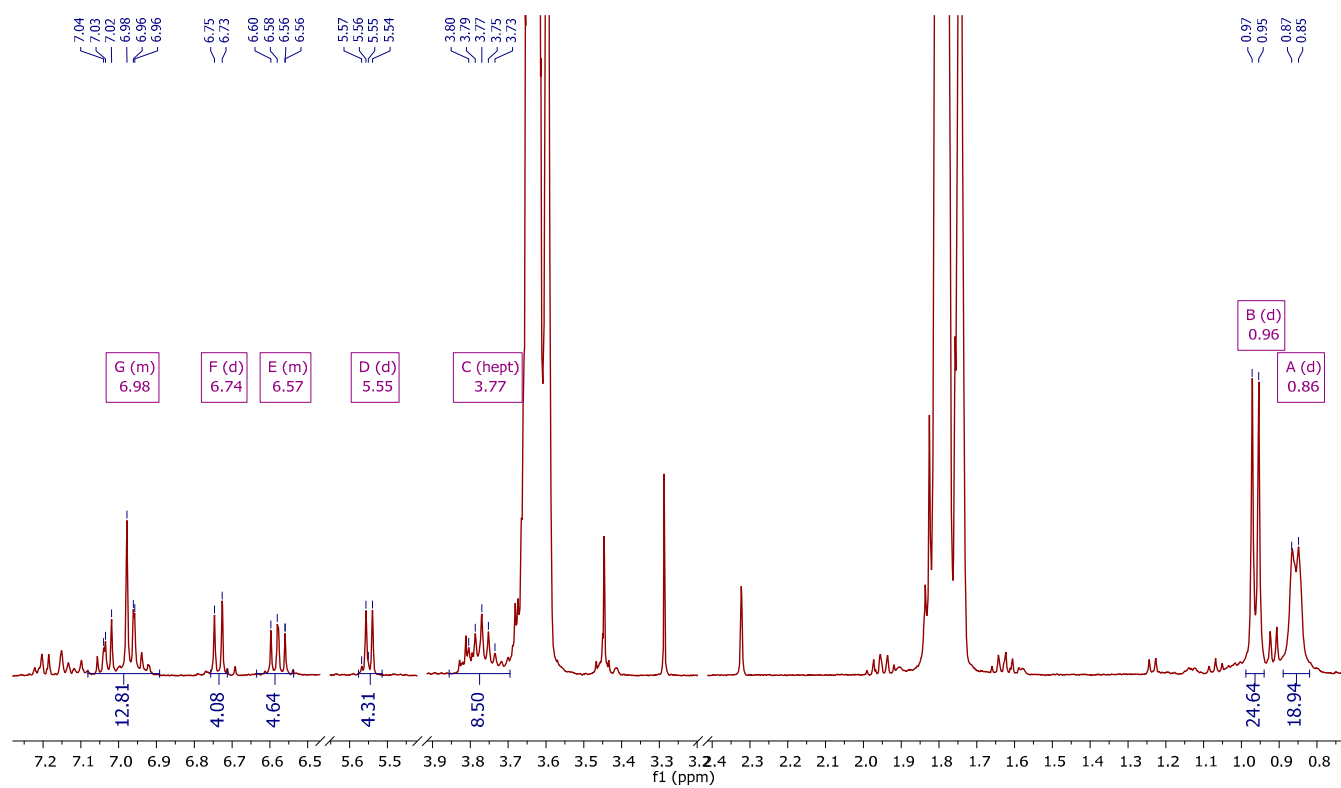


Figure S14. Selected area of ^1H NMR spectrum of compound 6 in $\text{THF-}d_8$.

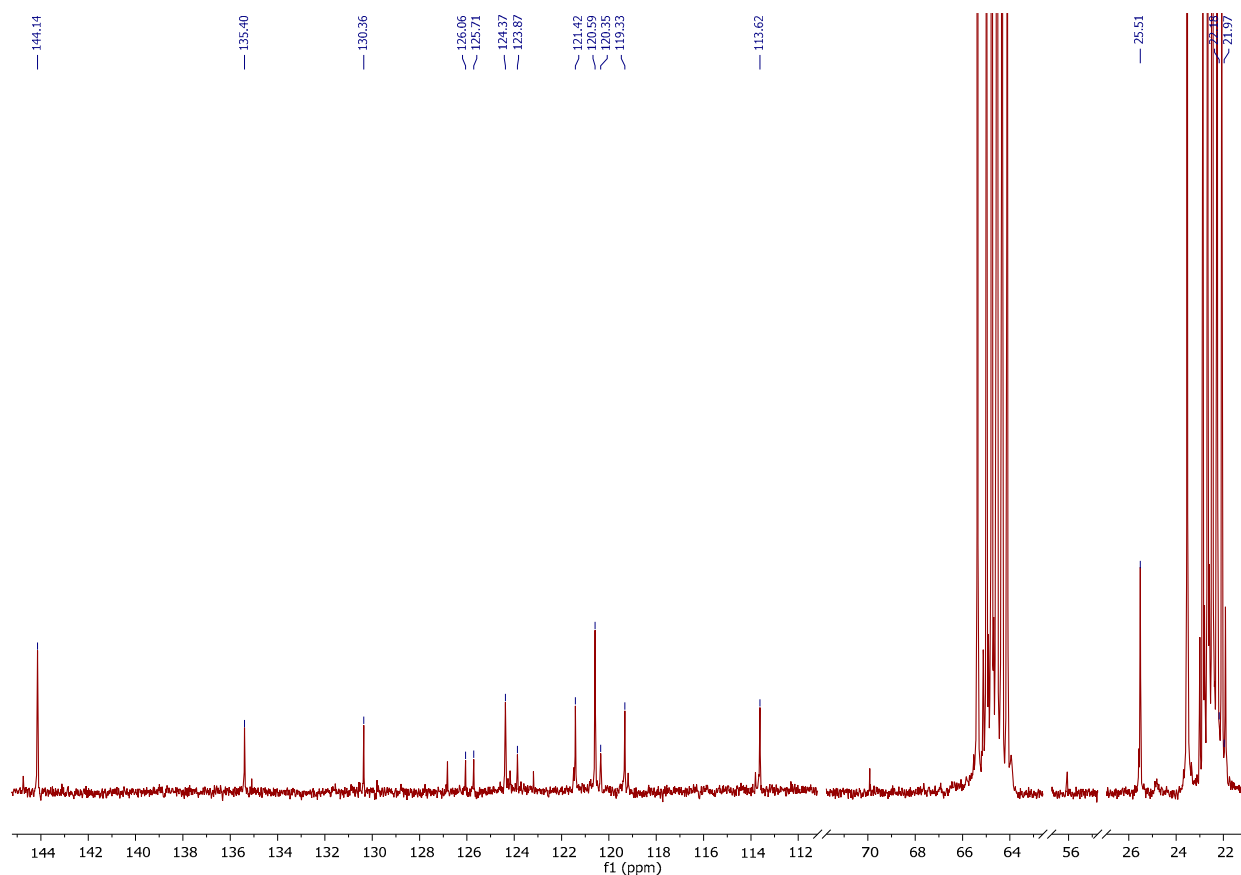


Figure S15. Selected area of ^{13}C NMR spectrum of compound **6** in $\text{THF-}d_8$.

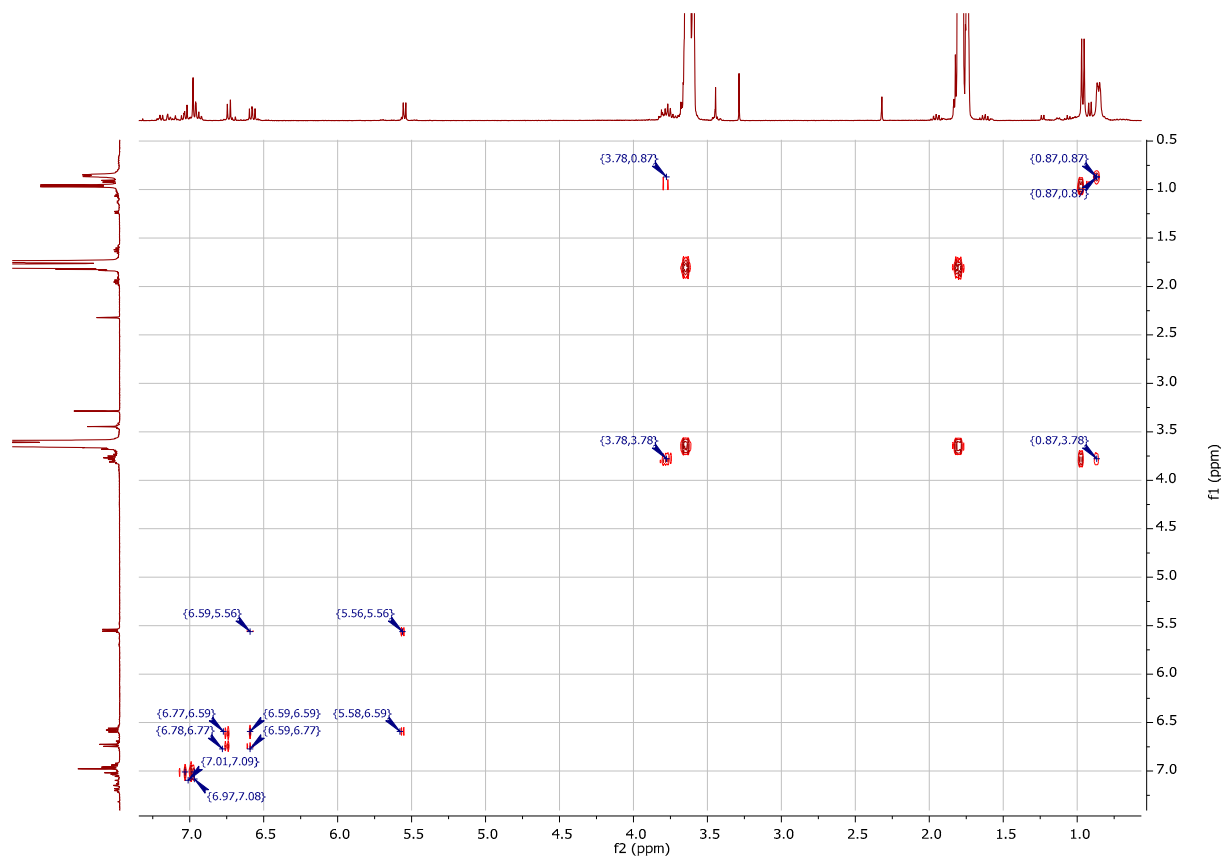


Figure S16. ^1H - ^1H COSY NMR spectrum of compound **6** in $\text{THF-}d_8$.

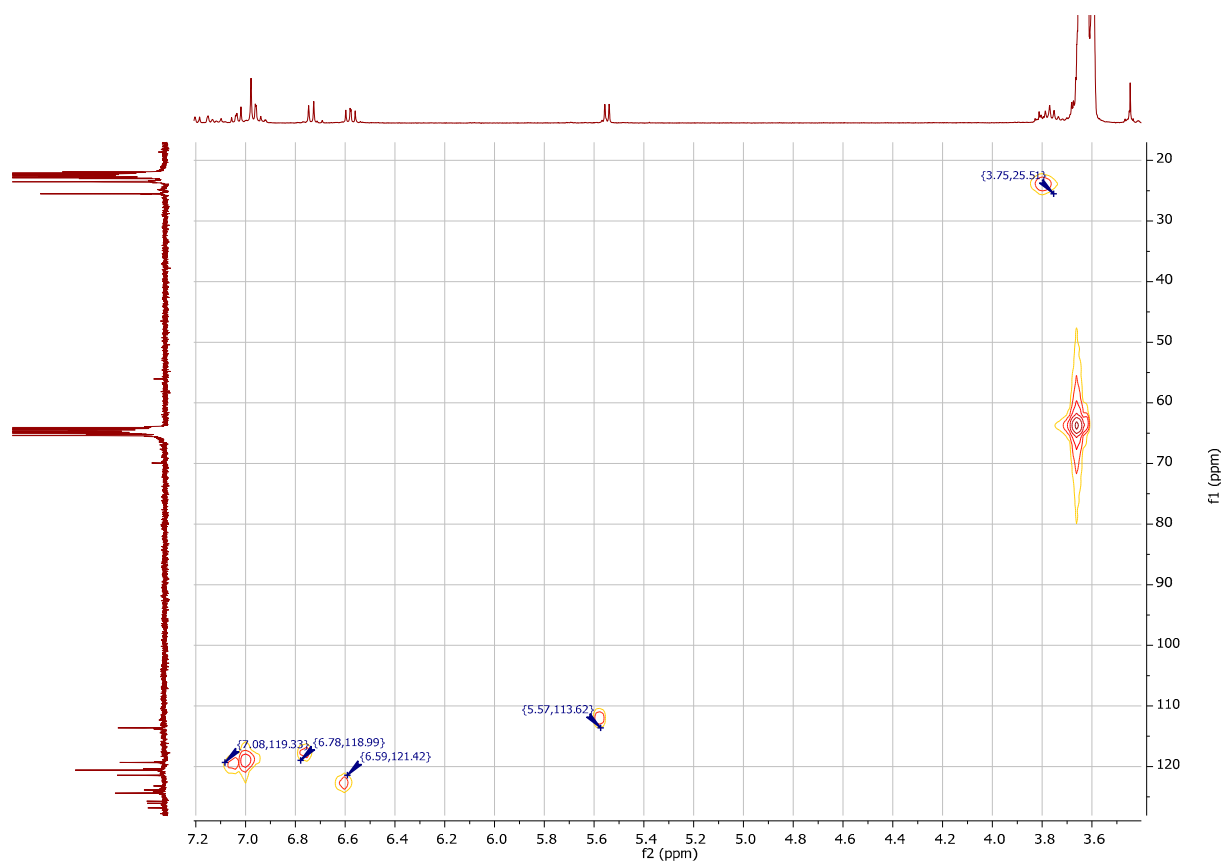


Figure S17. ^1H - ^{13}C HSQC NMR spectrum of compound **6** in THF-d_8 .

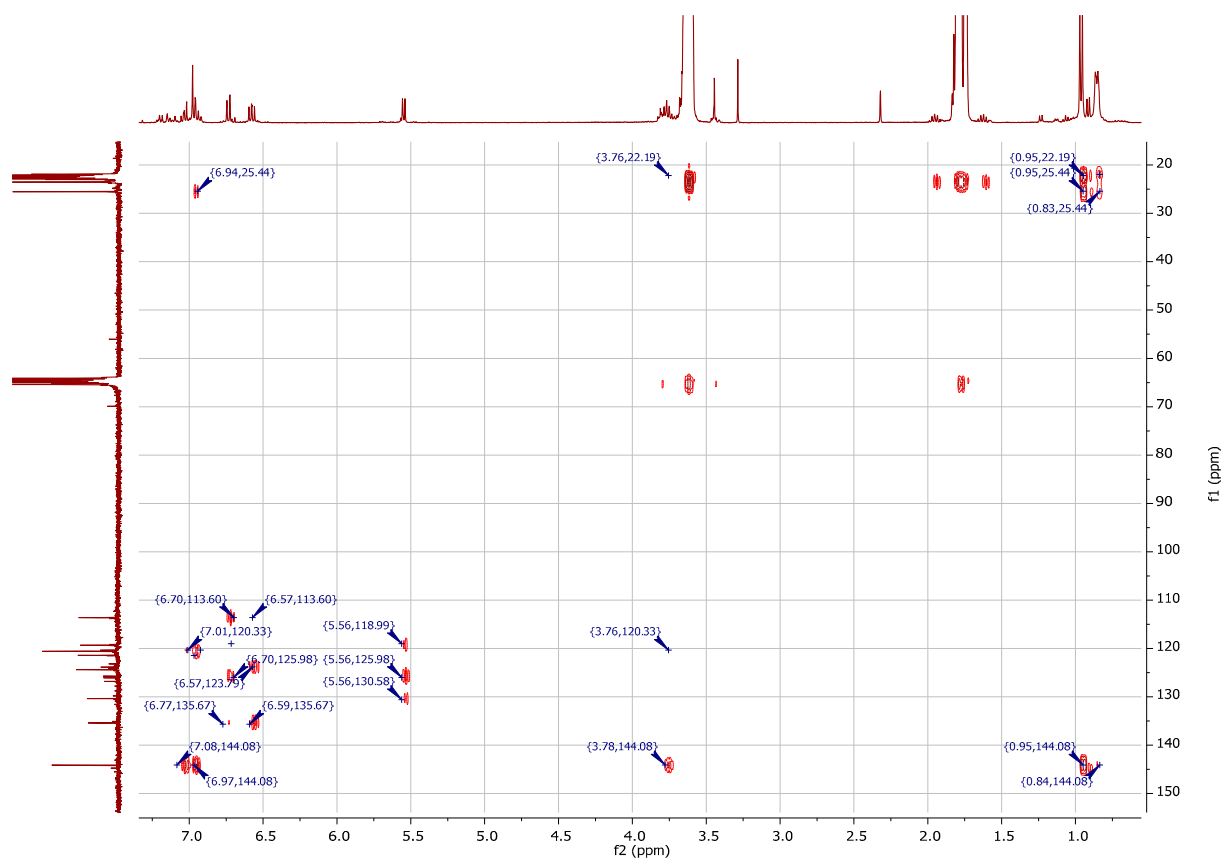


Figure S18. ^1H - ^{13}C HMBC NMR spectrum of compound **6** in THF-d_8 .

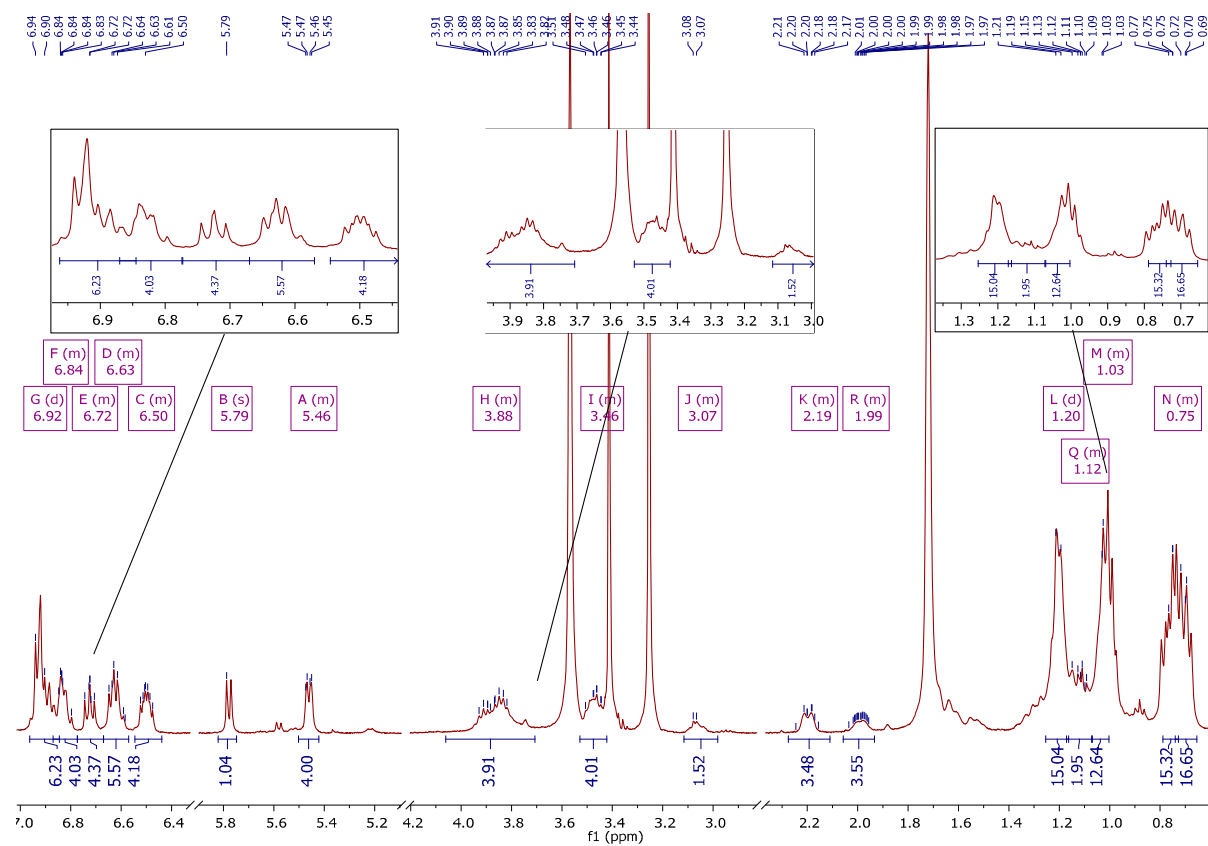


Figure S19. ^1H NMR spectrum of compound **8** in $\text{THF-}d_8$.

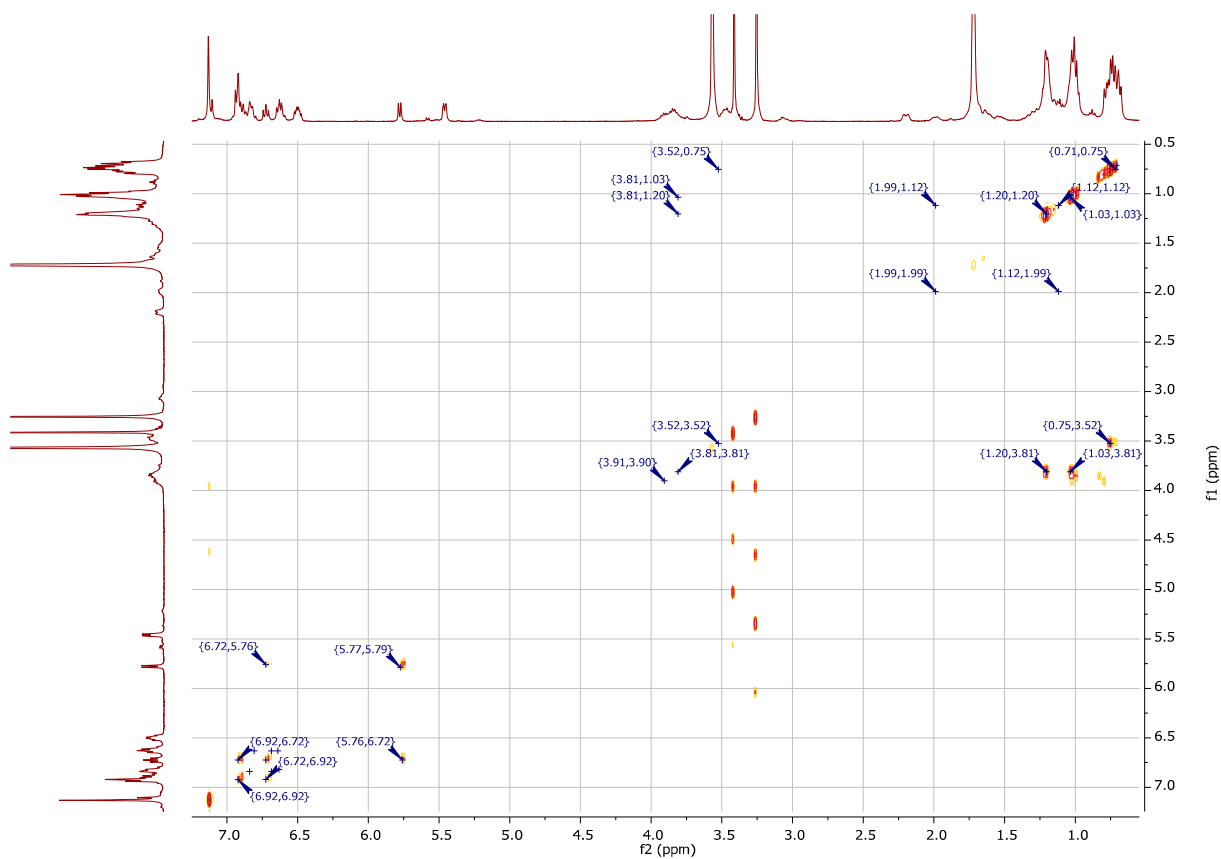


Figure S20. ^1H - ^1H COSY NMR spectrum of compound **8** in $\text{THF-}d_8$.

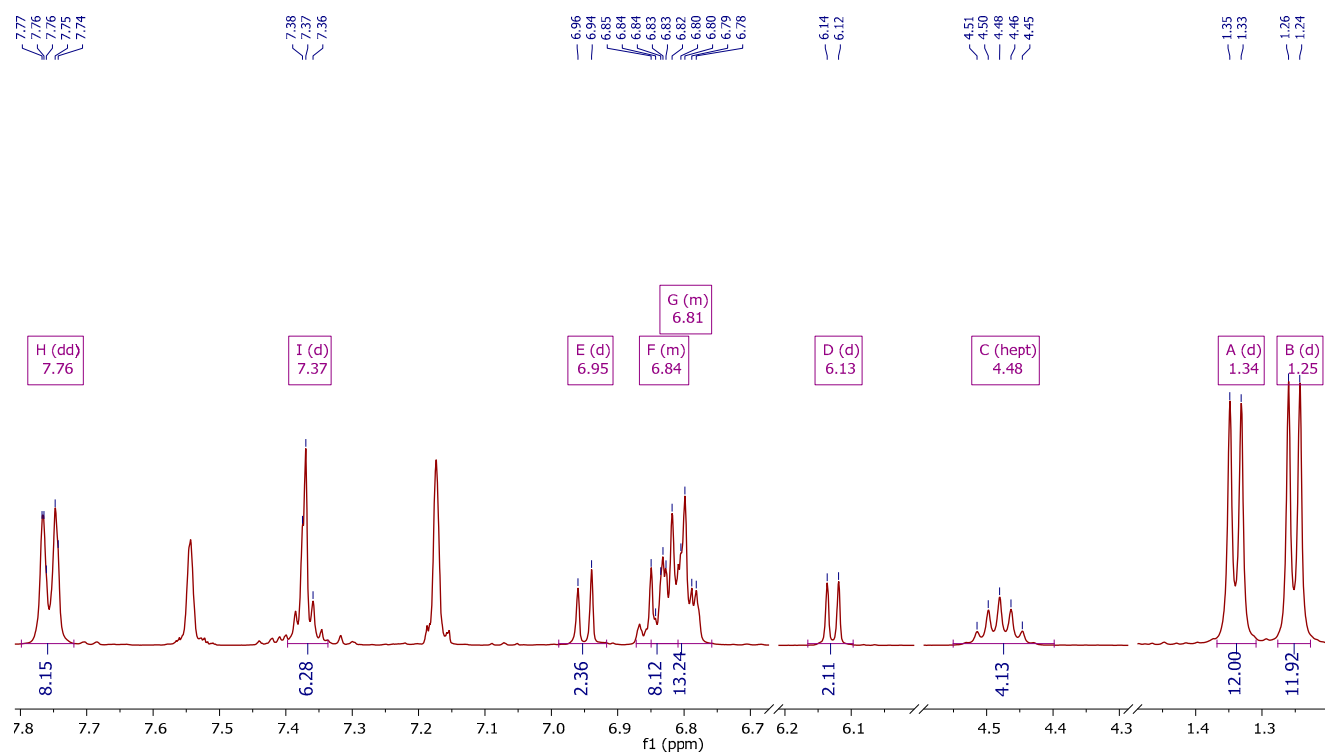


Figure S21. Selected area of ^1H NMR spectrum of compound **9** in Pyridine- d_5 .

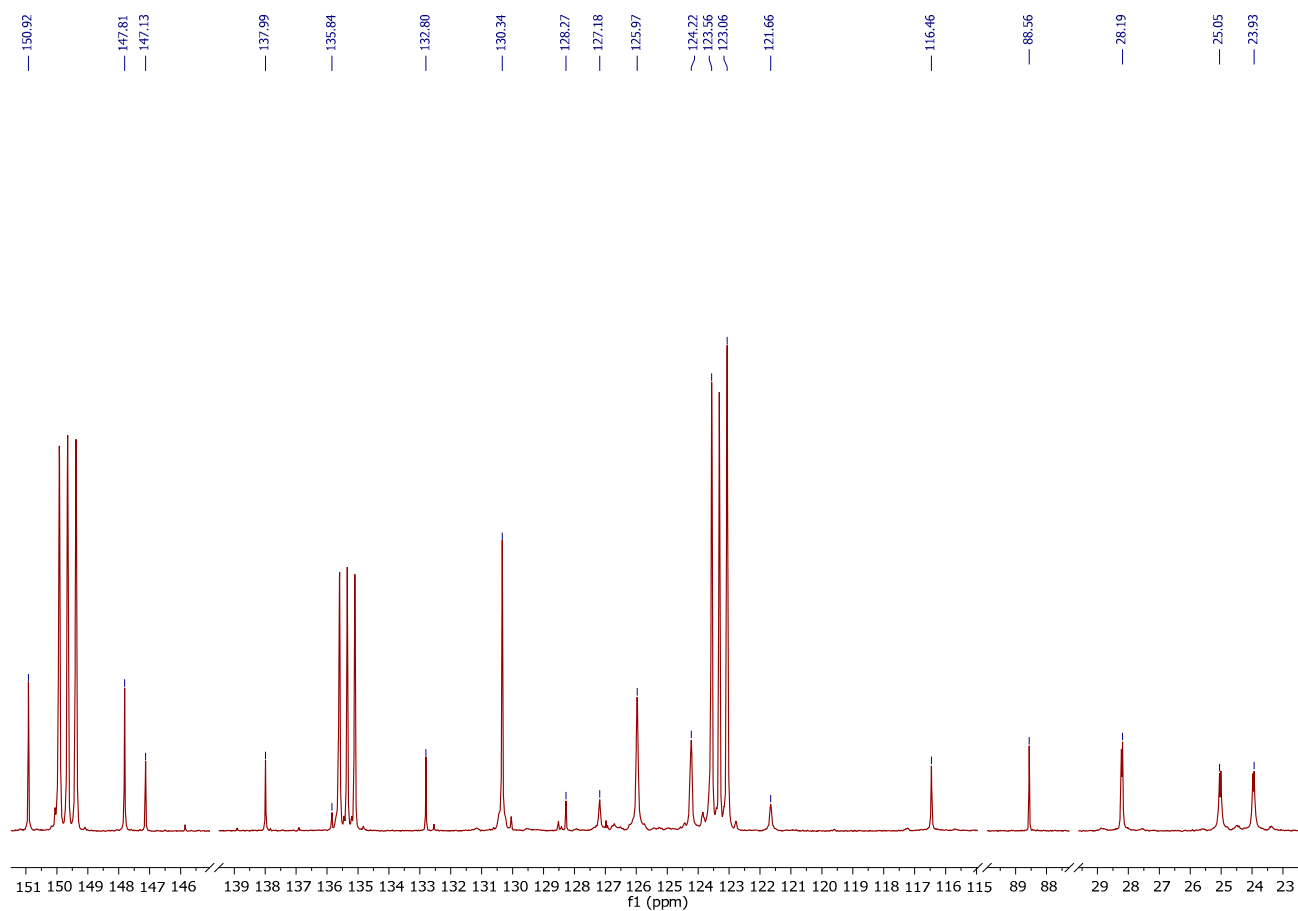


Figure S22. Selected area of ^{13}C NMR spectrum of compound **9** in Pyridine- d_5 .

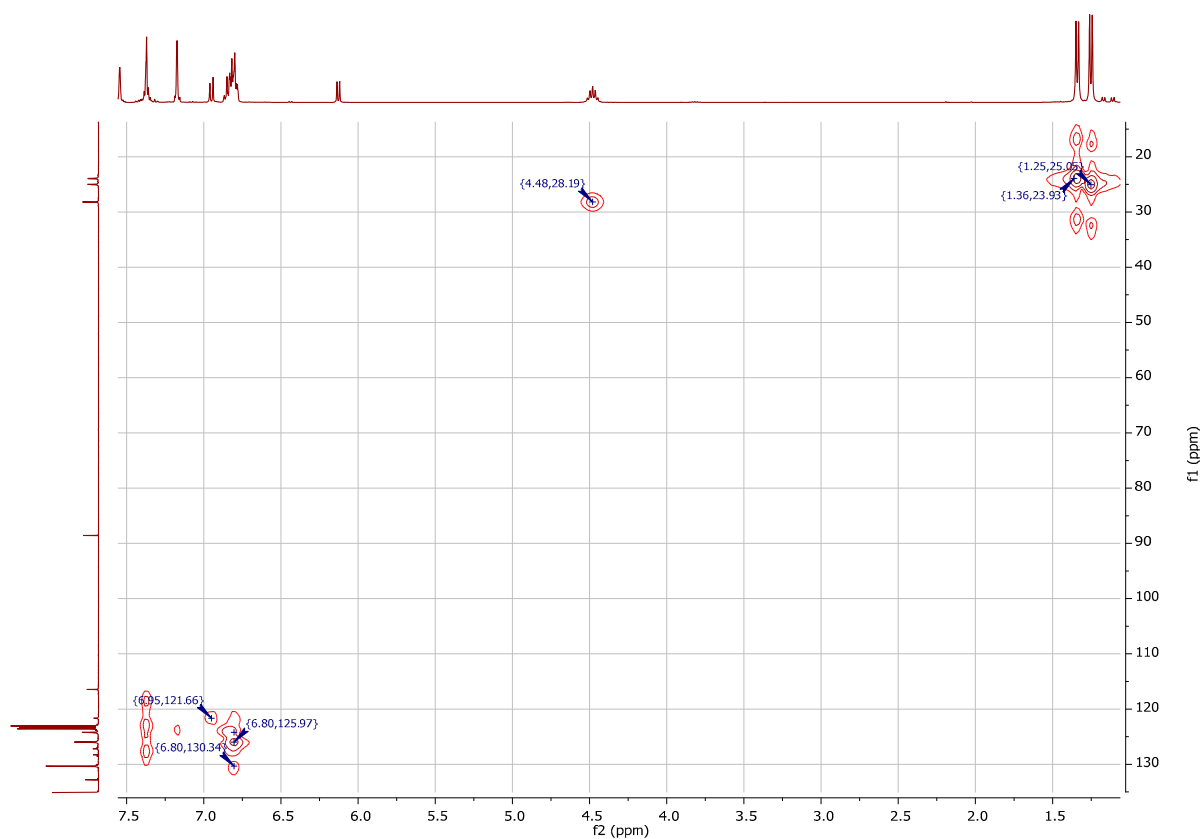


Figure S23. ^1H - ^{13}C HSQC NMR spectrum of compound **9** in Pyridine- d_5 .

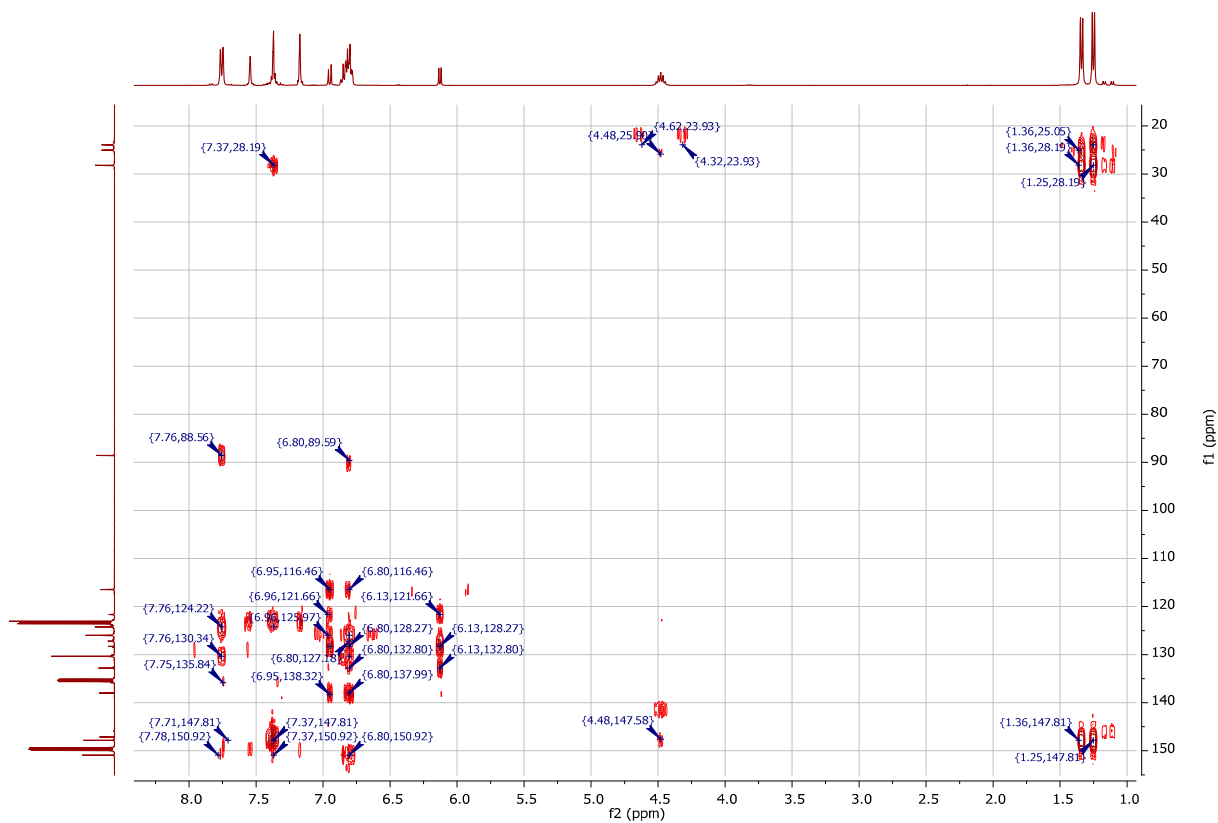


Figure S24. ^1H - ^{13}C HMBC NMR spectrum of compound **9** in Pyridine- d_5 .

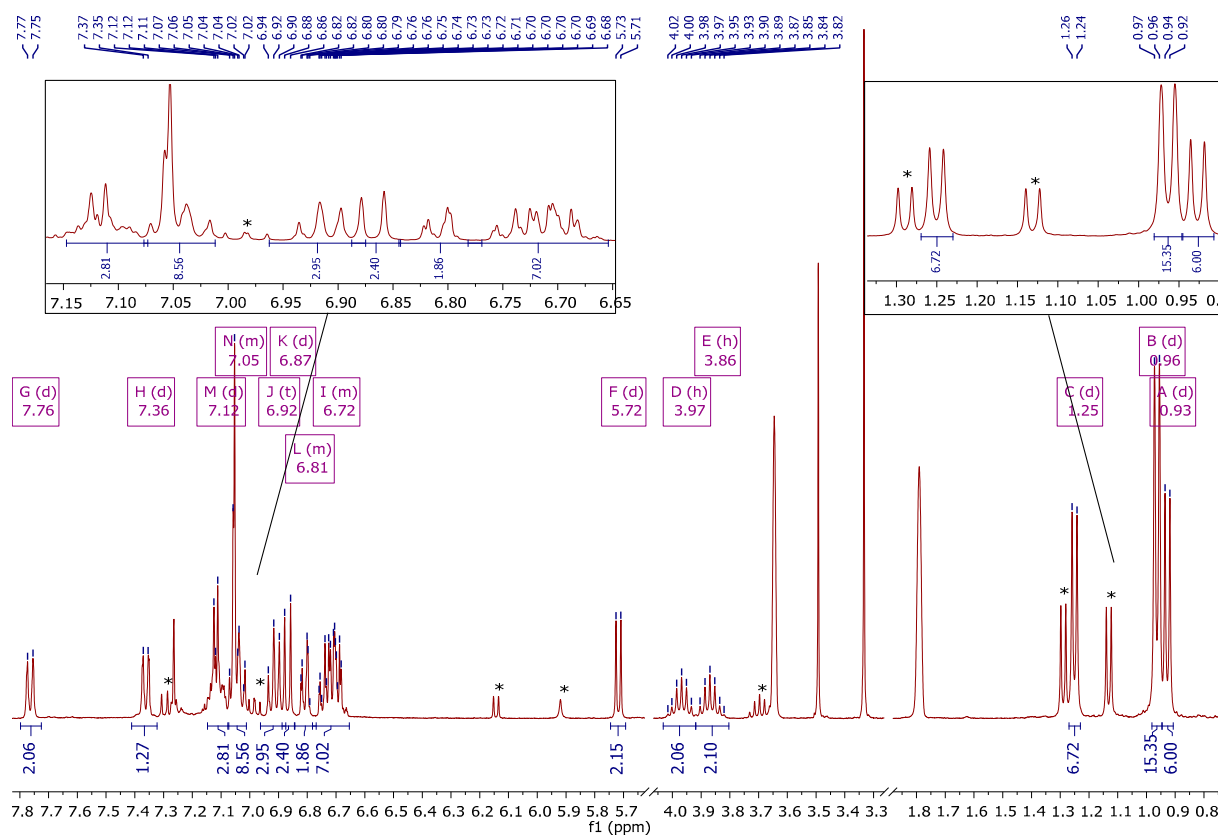


Figure S25. Selected area of ^1H NMR spectrum of compound 10 in THF- d_8 .

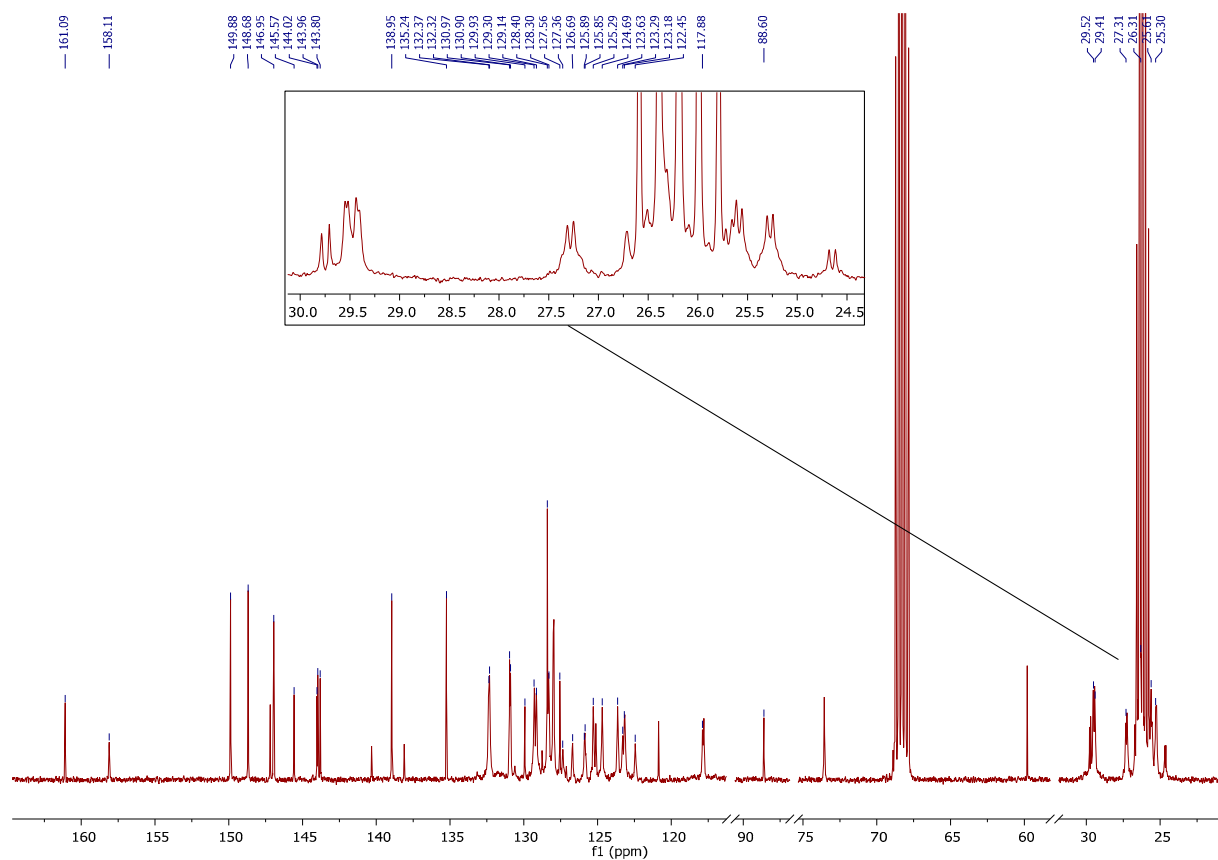


Figure S26. Selected area of ^{13}C NMR spectrum of compound 10 in THF- d_8 .

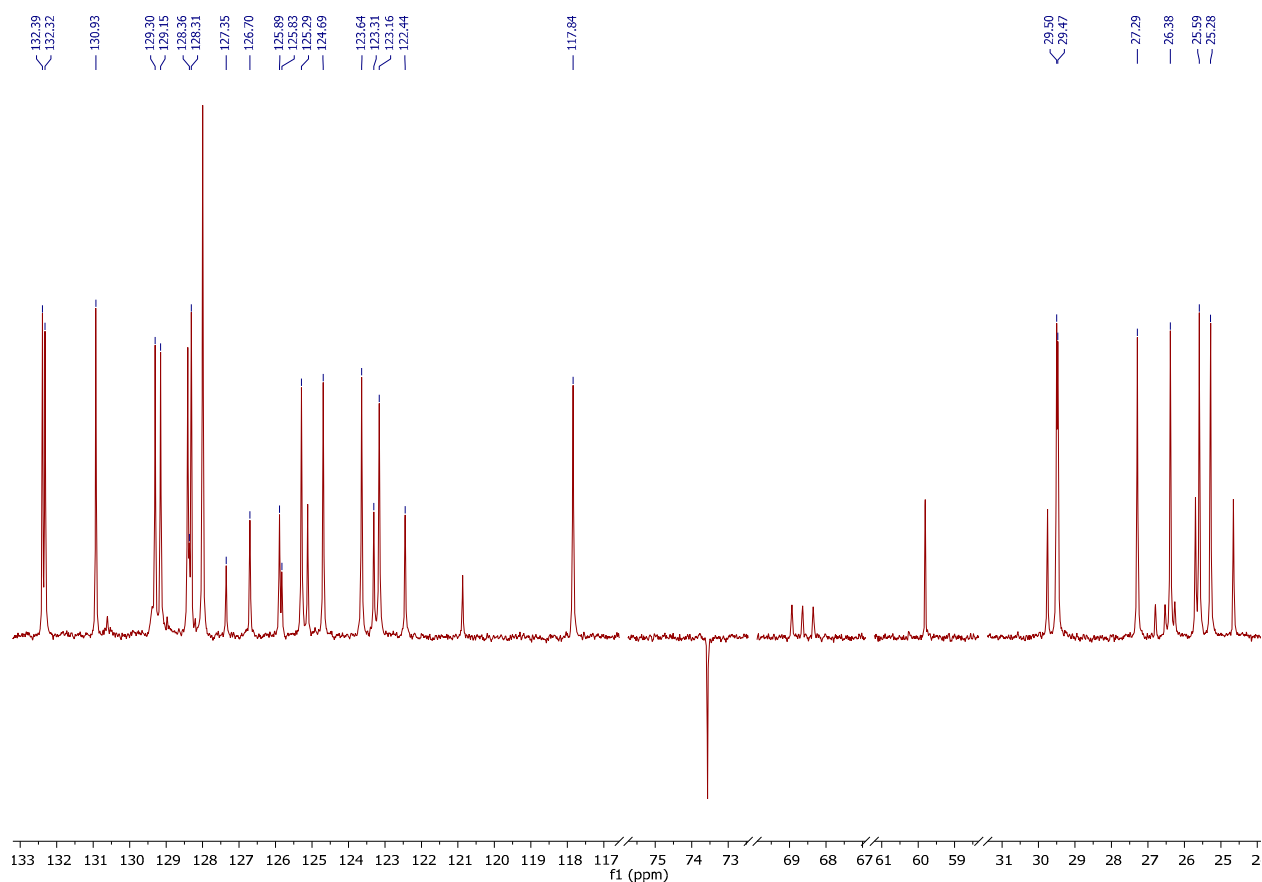


Figure S27. Selected area of DEPT135 NMR spectrum of compound **10** in THF-*d*₈.

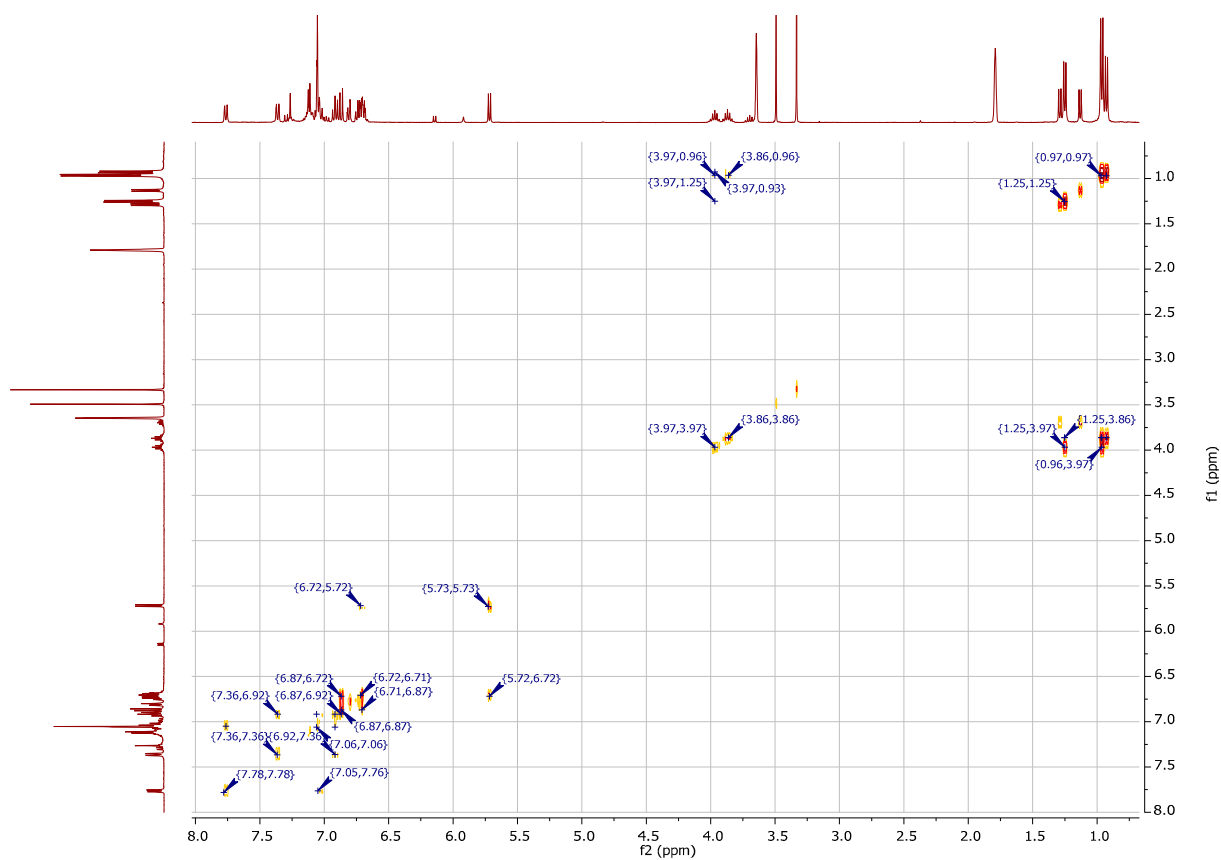


Figure S28. ¹H-¹H COSY NMR spectrum of compound **10** in THF-*d*₈.

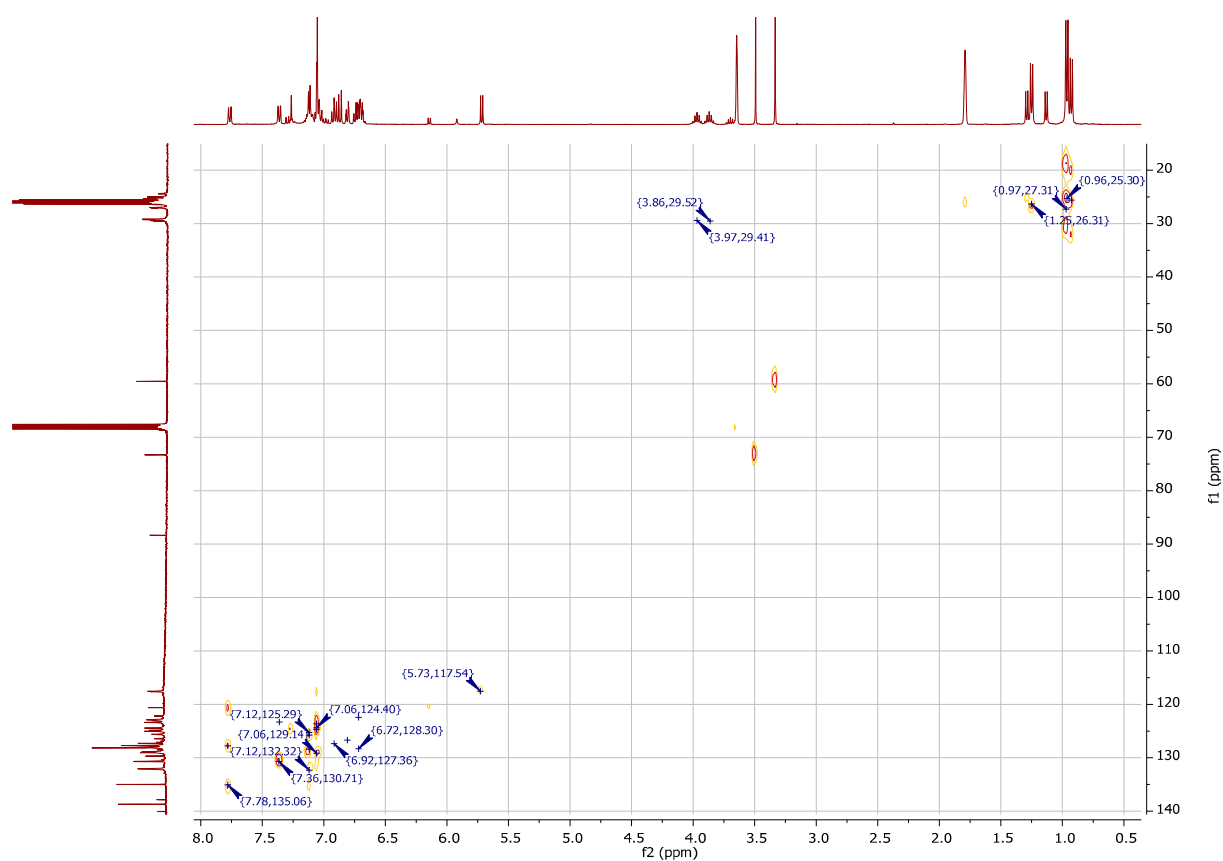


Figure S29. ^1H - ^{13}C HSQC NMR spectrum of compound **10** in $\text{THF-}d_8$.

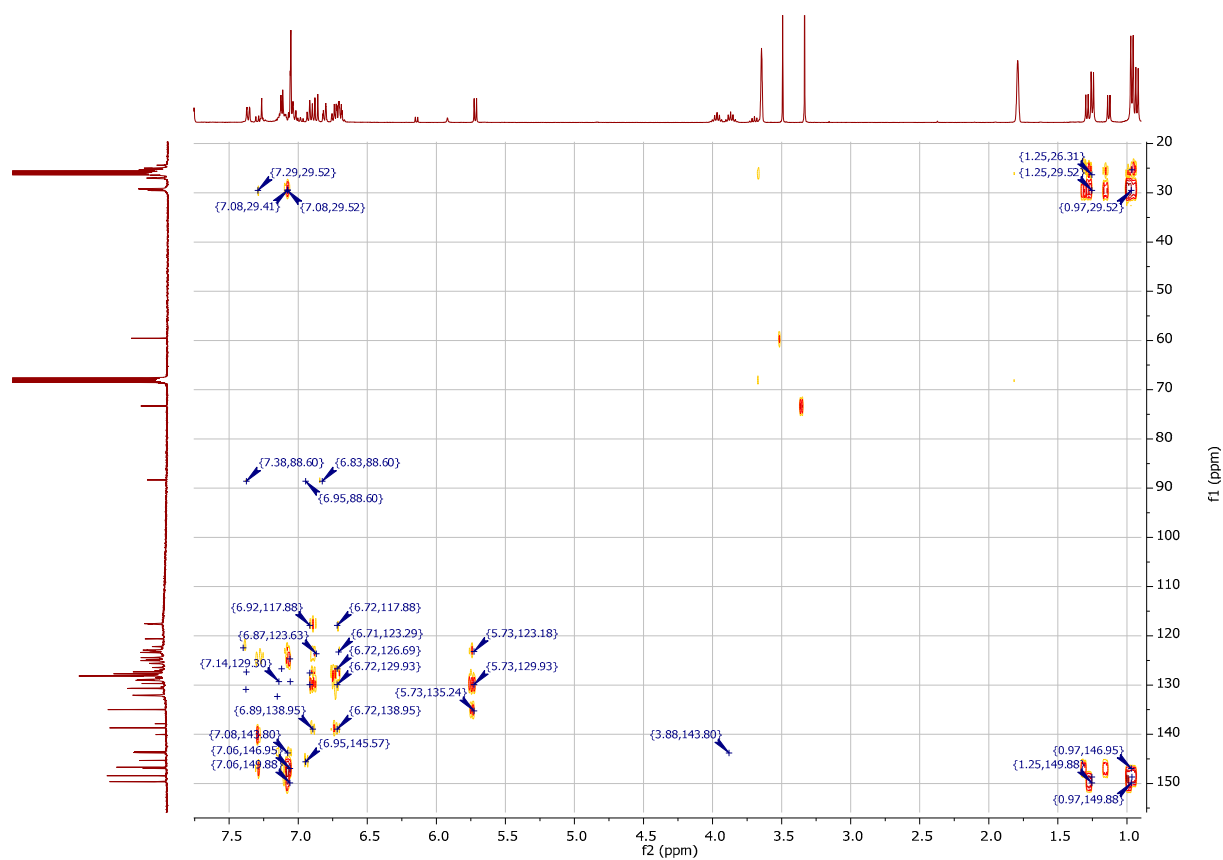
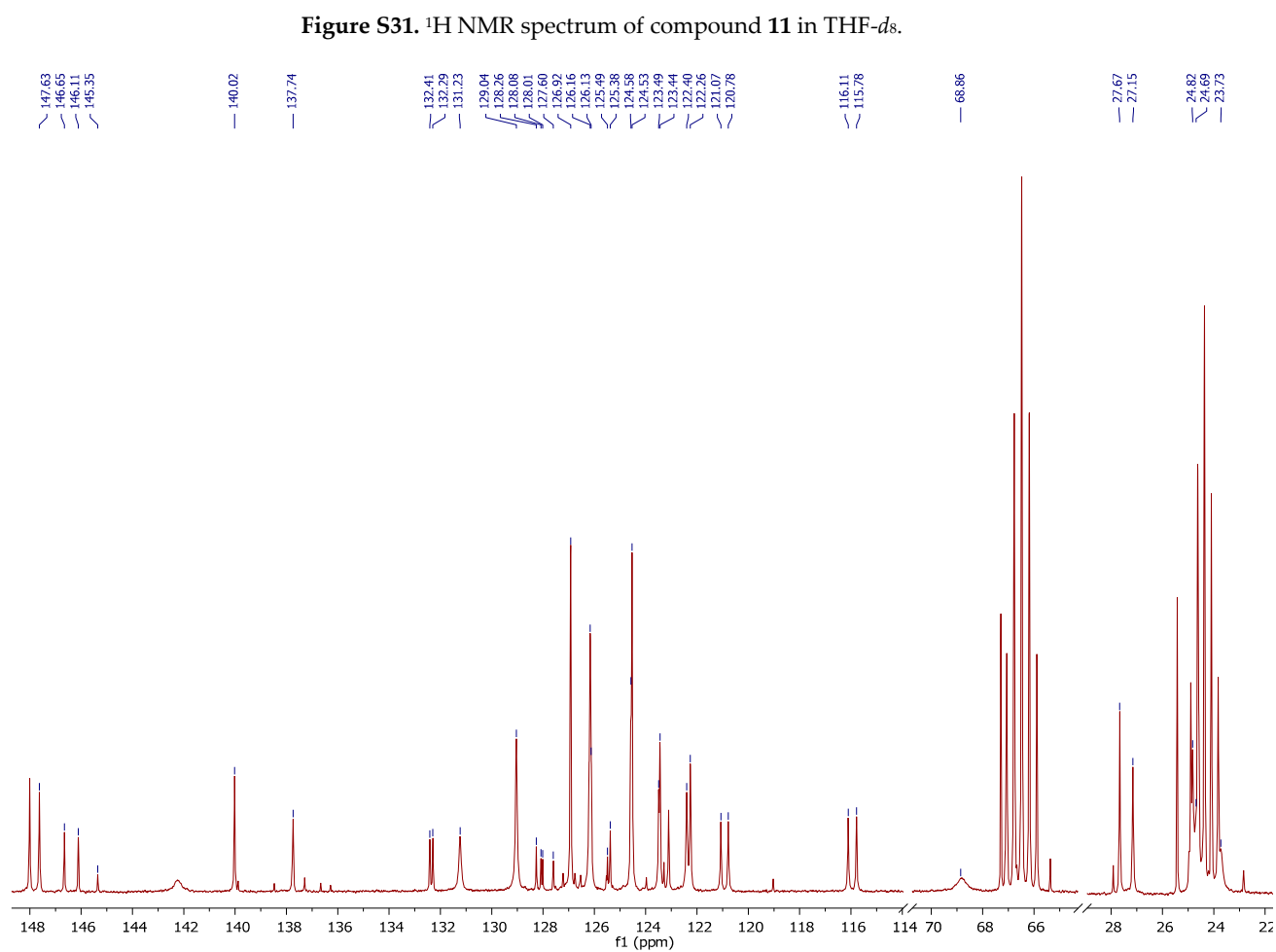
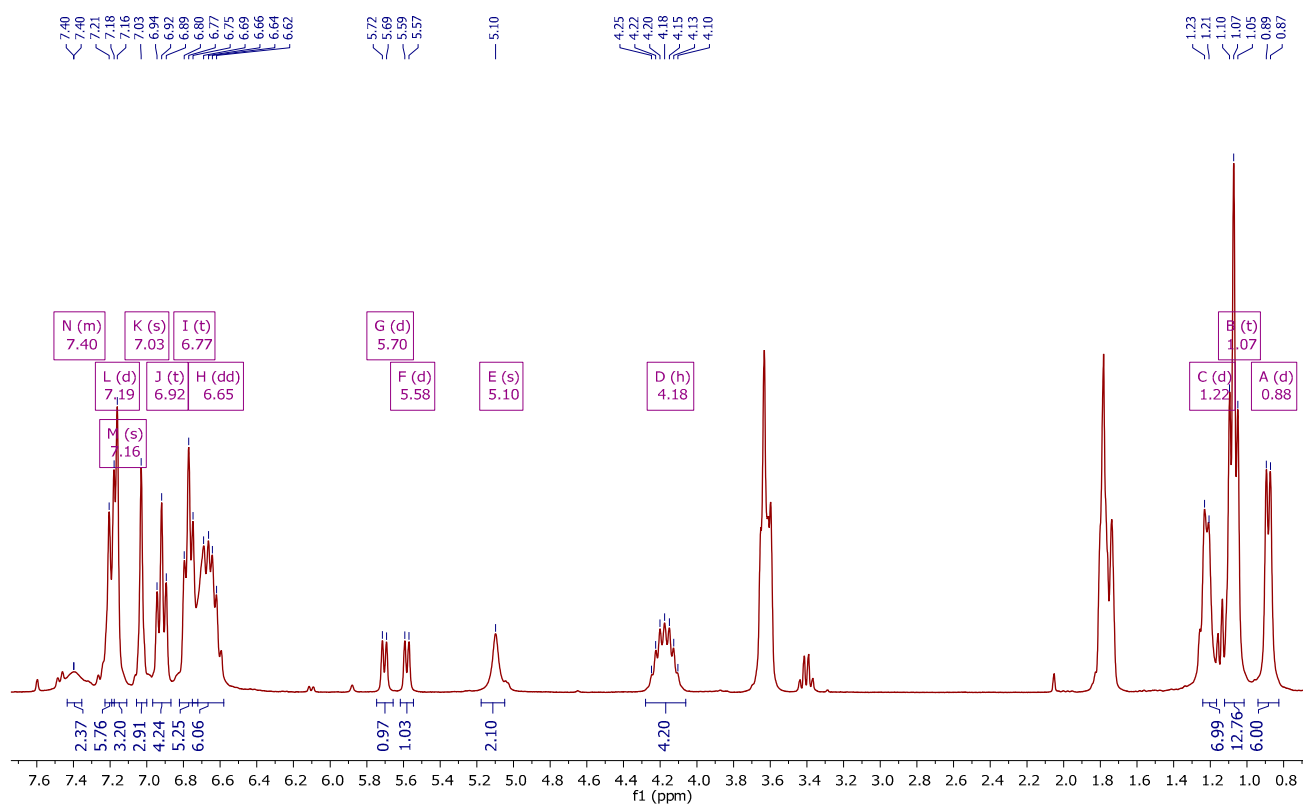


Figure S30. ^1H - ^{13}C HMBC NMR spectrum of compound **10** in $\text{THF-}d_8$.



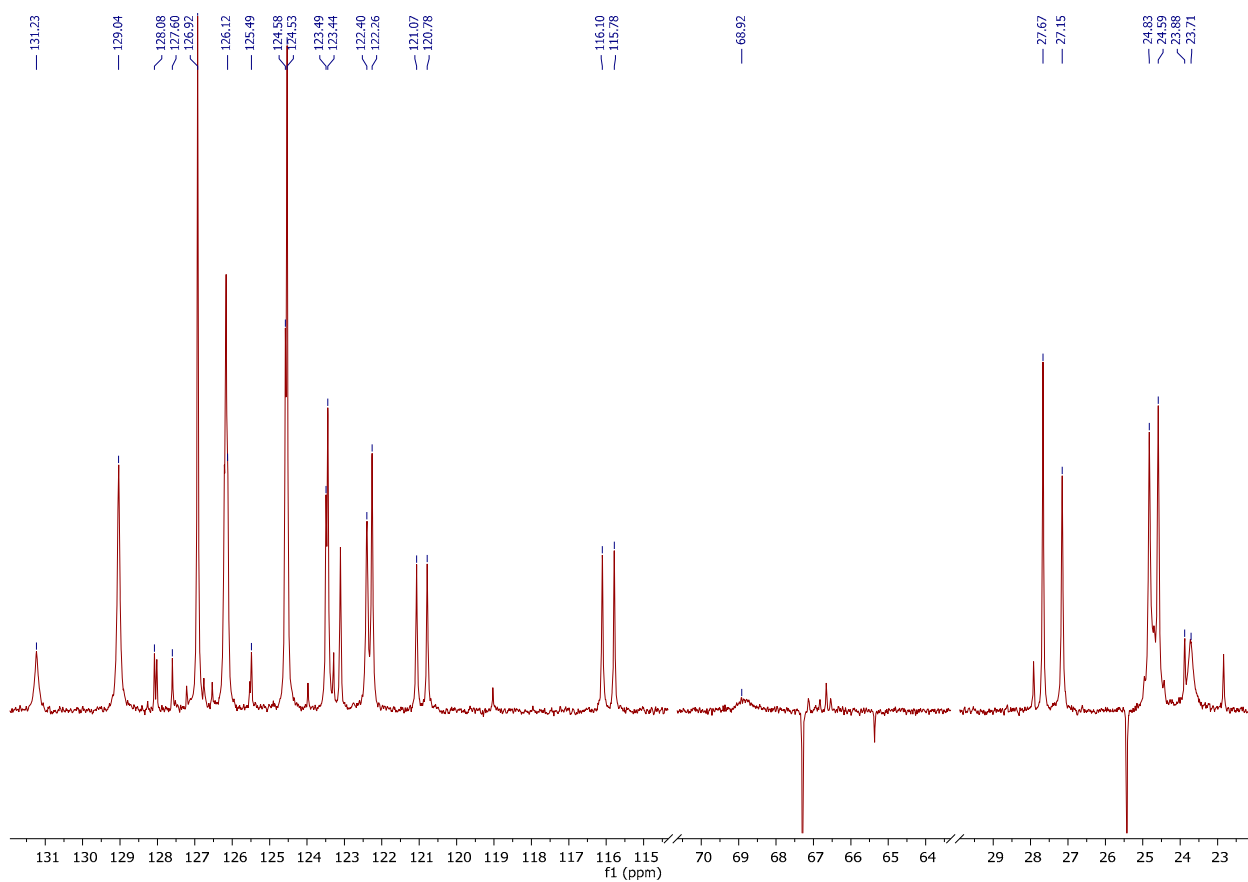


Figure S33. Selected area of DEPT135 NMR spectrum of compound **11** in THF-*d*₈.

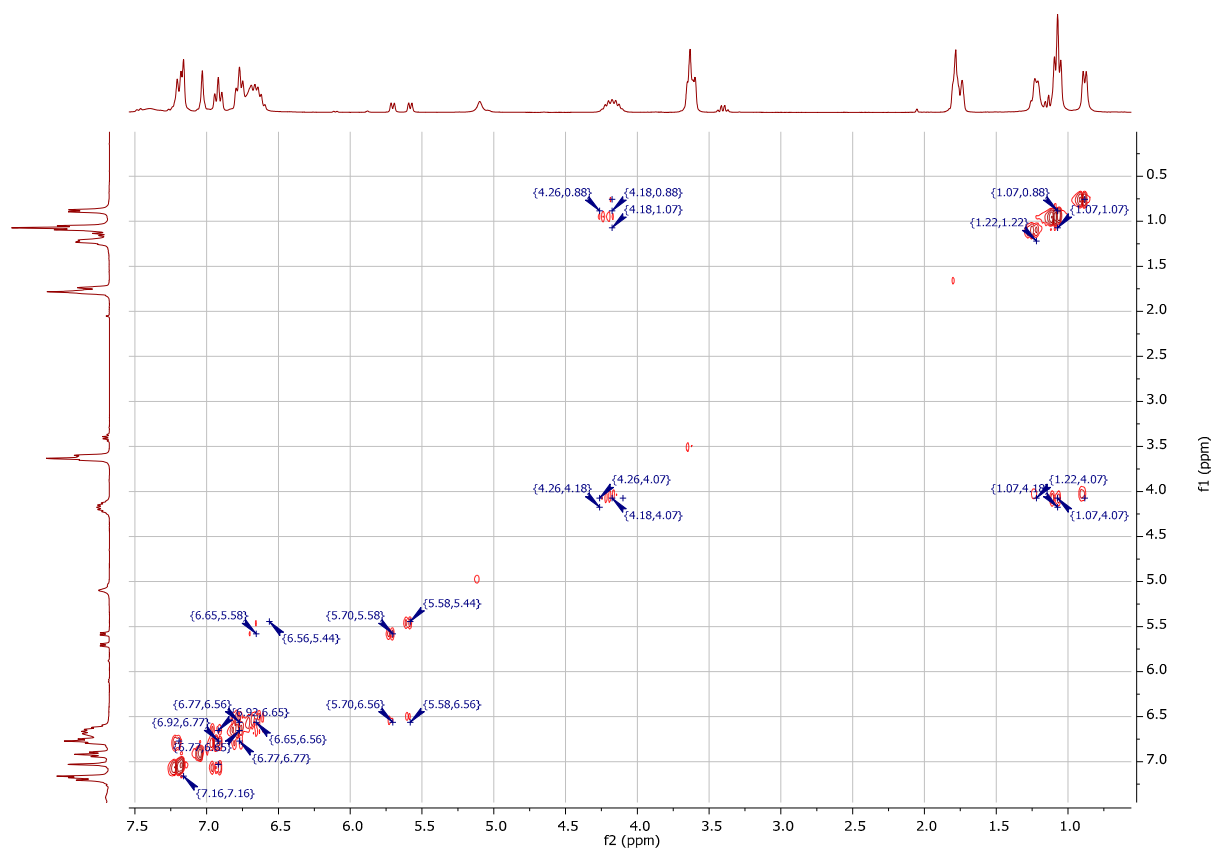


Figure S34. ¹H-¹H COSY NMR spectrum of compound **11** in THF-*d*₈.

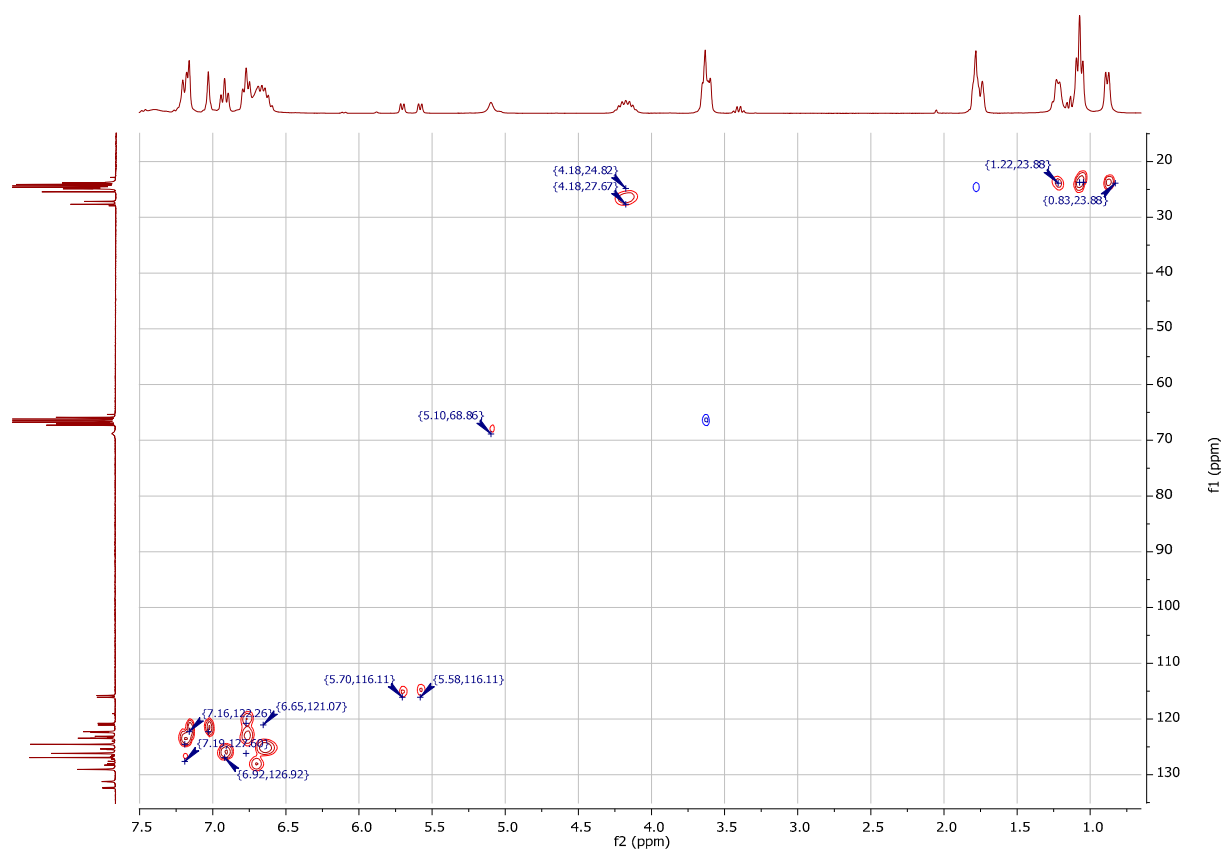


Figure S35. ^1H - ^{13}C HSQC NMR spectrum of compound 11 in THF-d_8 .

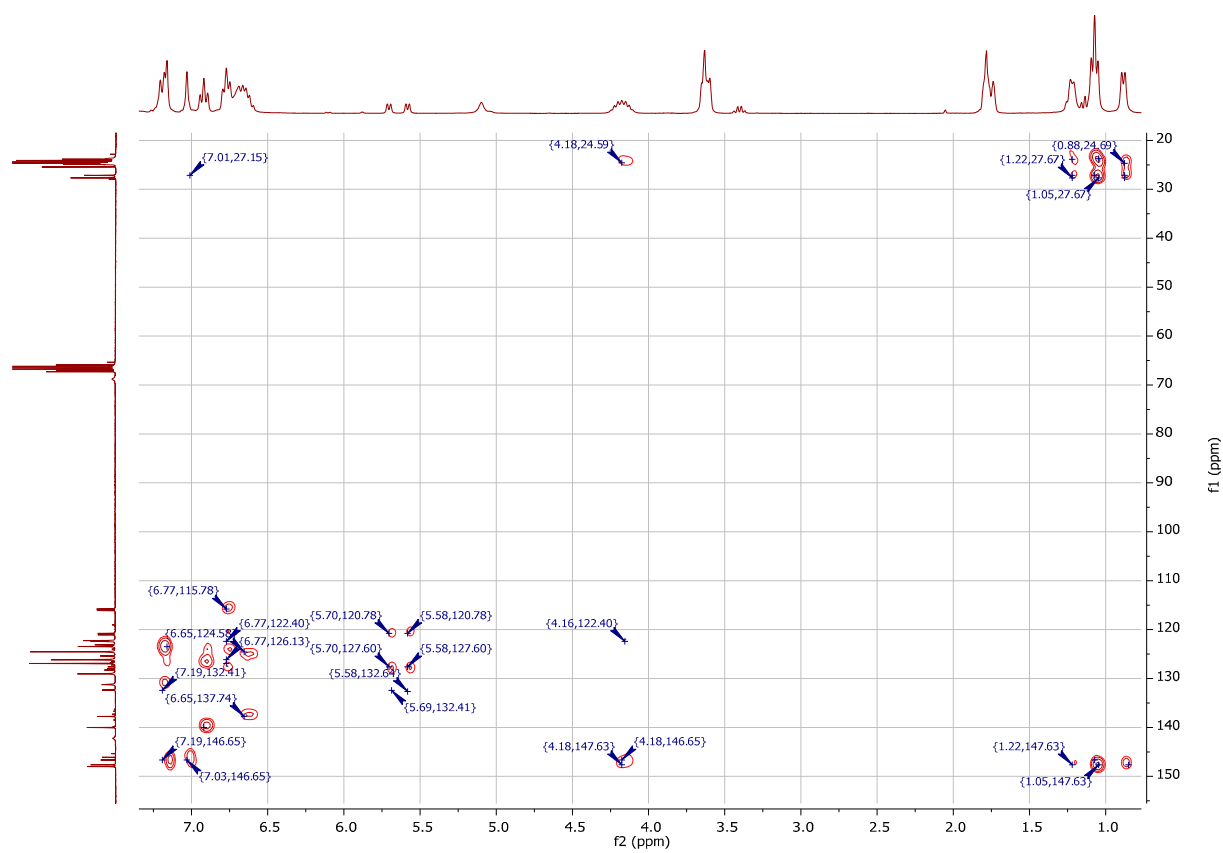


Figure S36. ^1H - ^{13}C HMBC NMR spectrum of compound 11 in THF-d_8 .

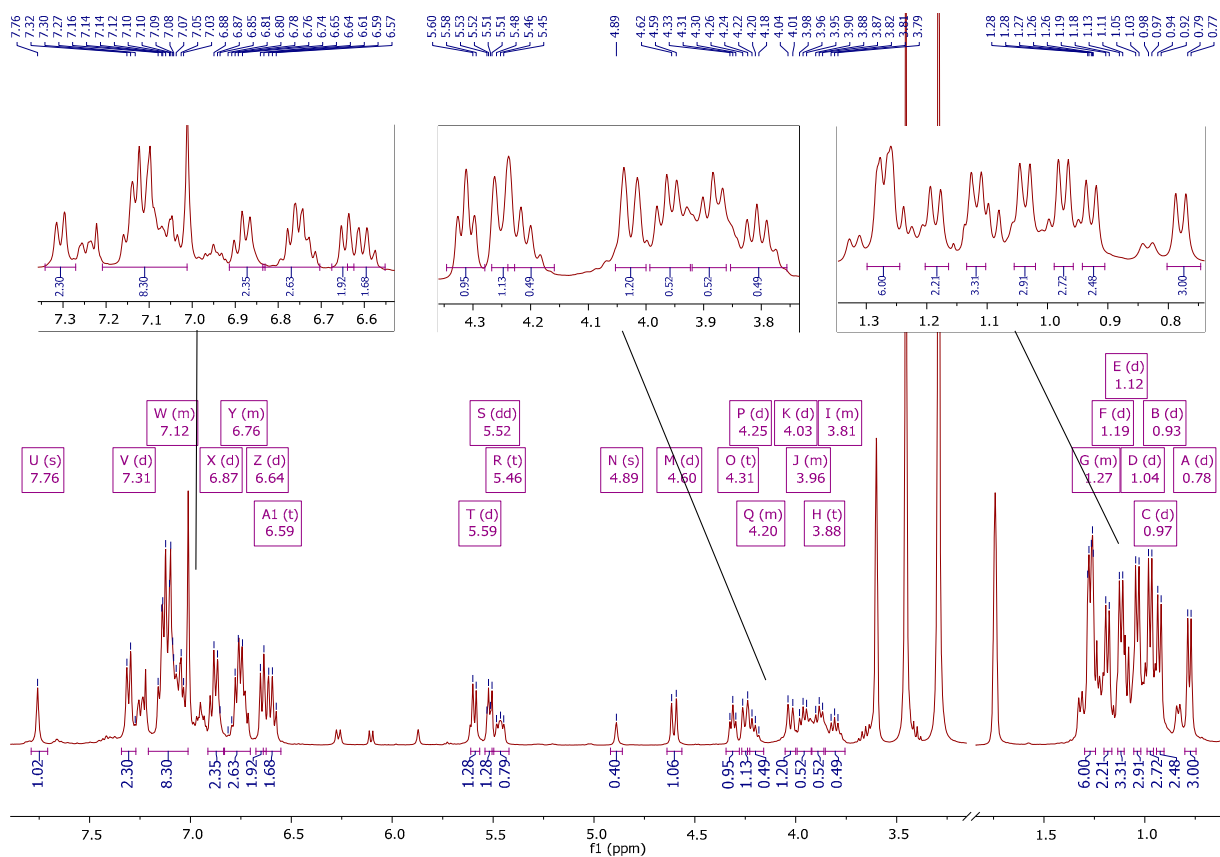


Figure S37. Selected area of ^1H NMR spectrum of compound **12** in THF-d_8 .

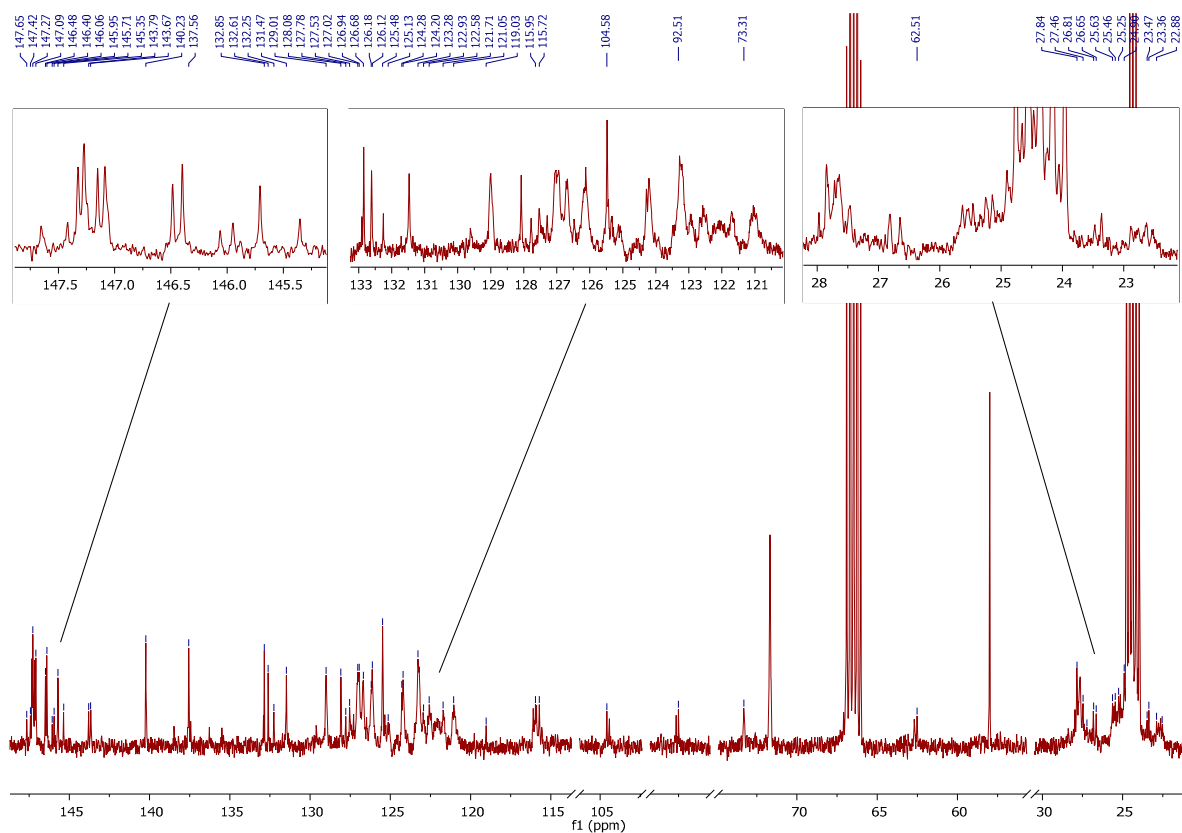


Figure S38. Selected area of ^{13}C NMR spectrum of compound **12** in THF-d_8 .

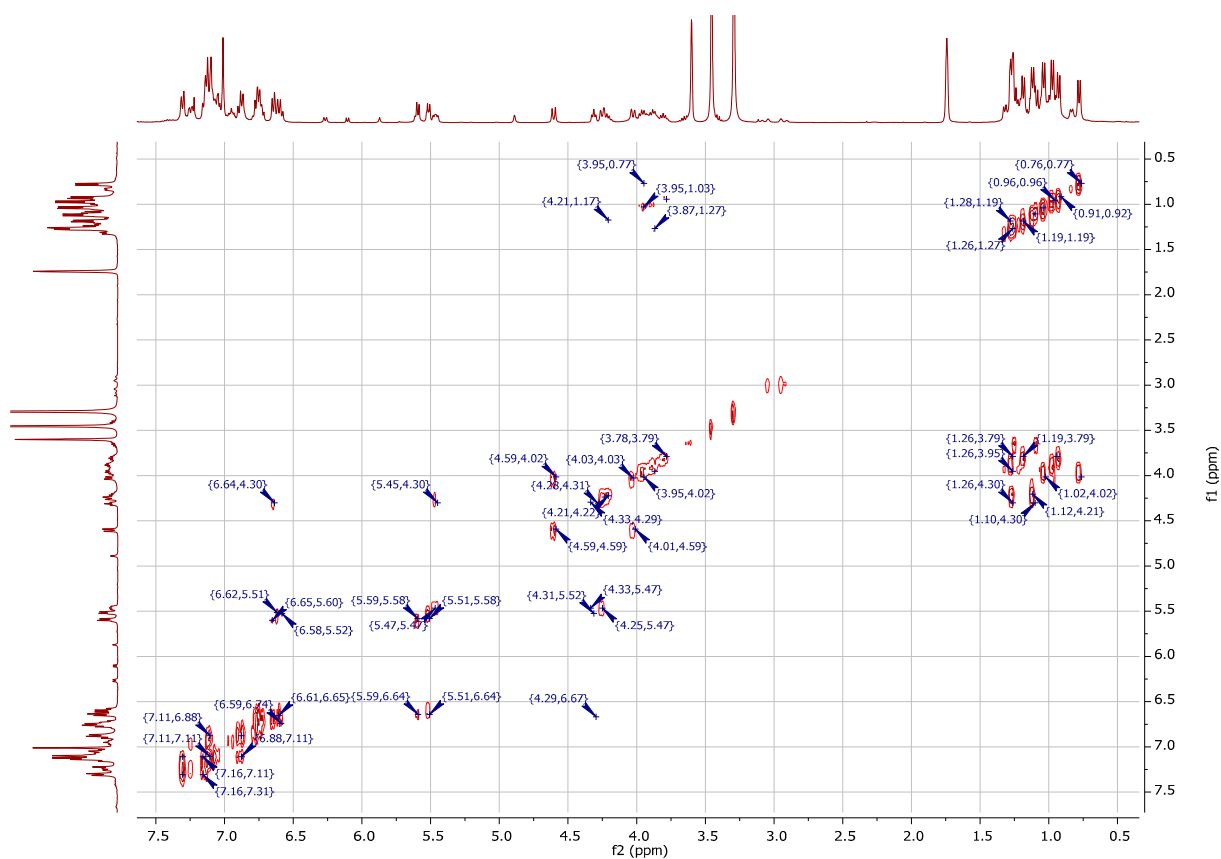


Figure S39. ^1H - ^1H COSY NMR spectrum of compound **12** in THF-d_8 .

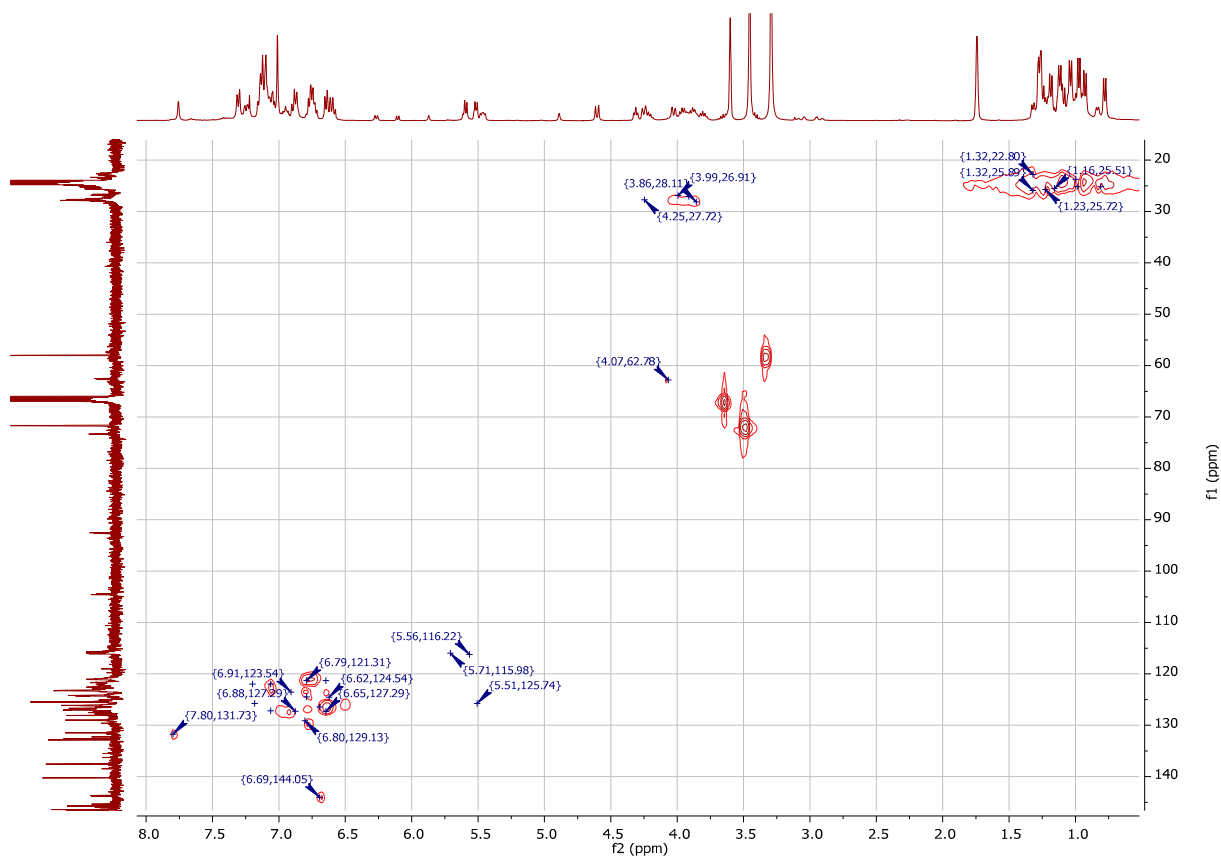


Figure S40. ^1H - ^{13}C HSQC NMR spectrum of compound **12** in THF-d_8 .

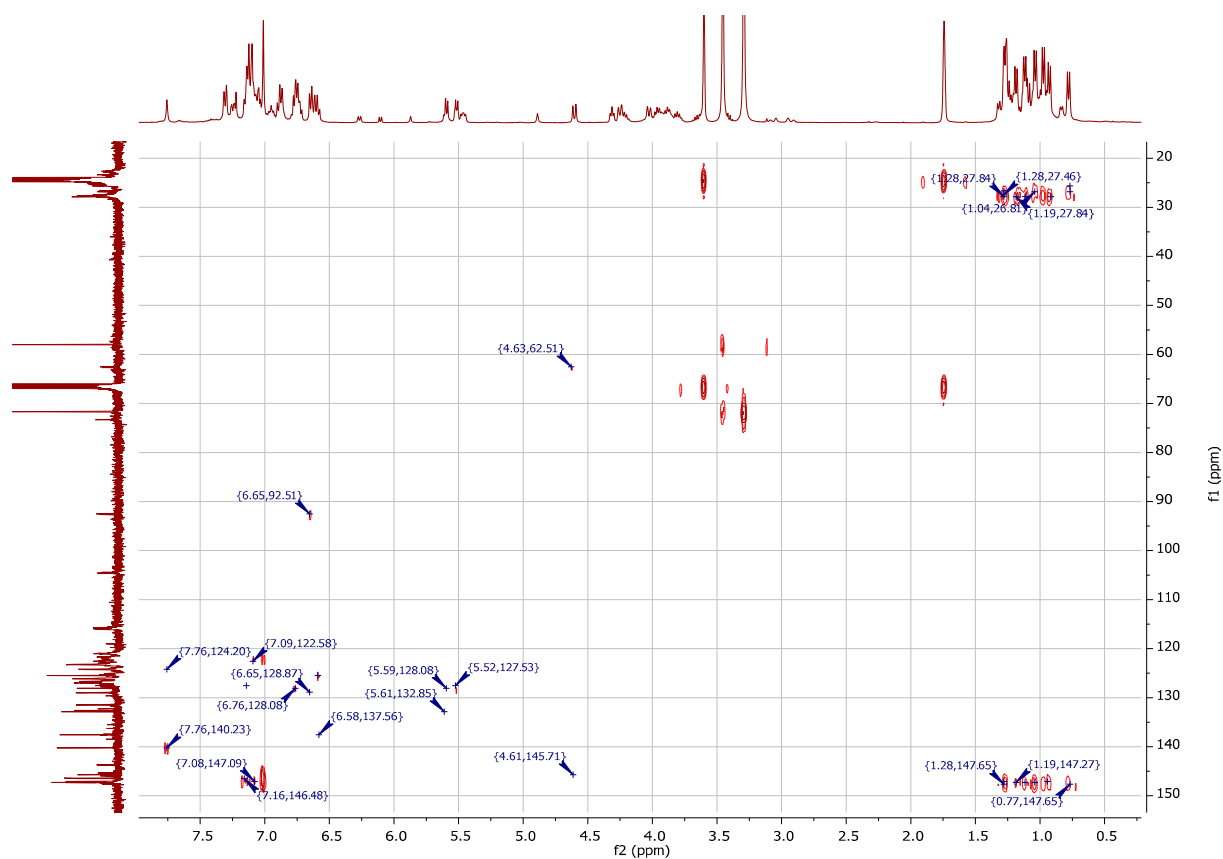


Figure S41. ^1H - ^{13}C HMBC NMR spectrum of compound **12** in THF-d_8 .

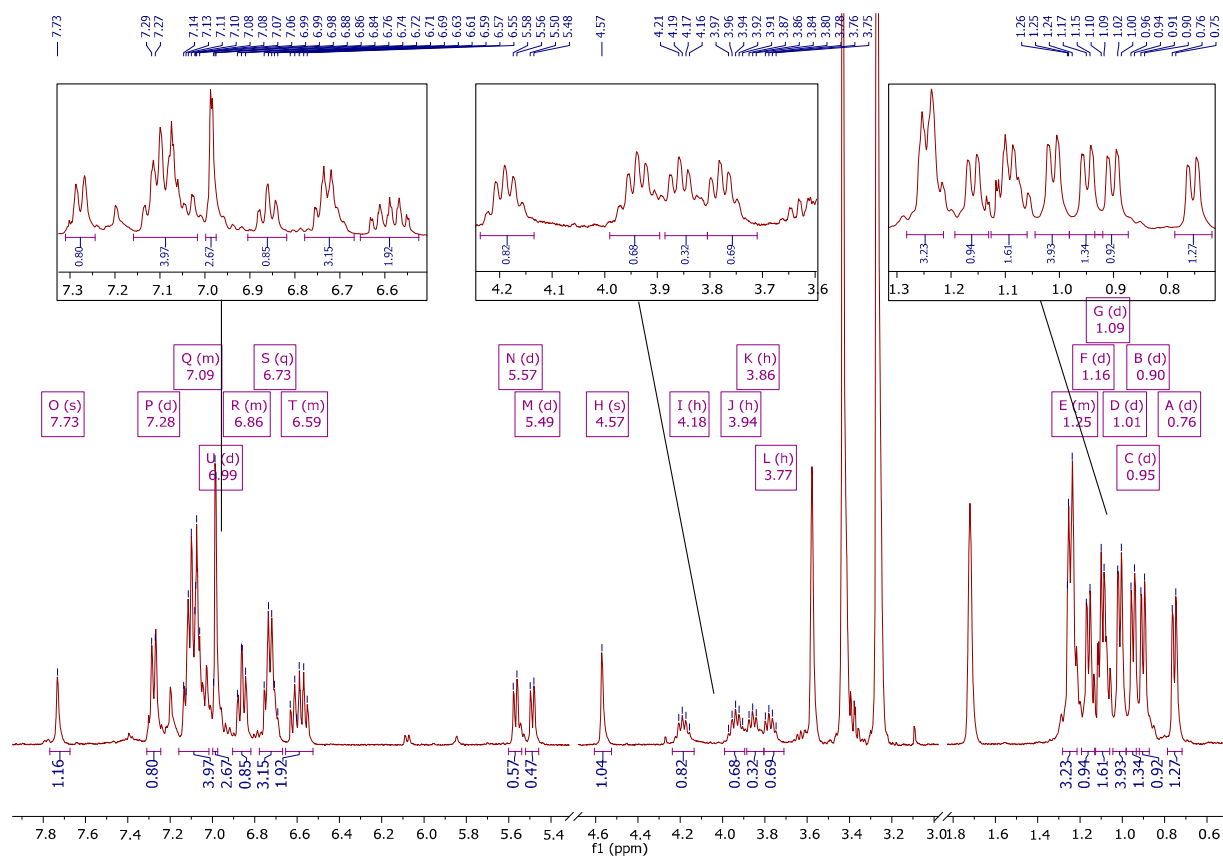


Figure S42. Selected area of ^1H NMR spectrum of compound **12-d₅** in THF-d_8 .

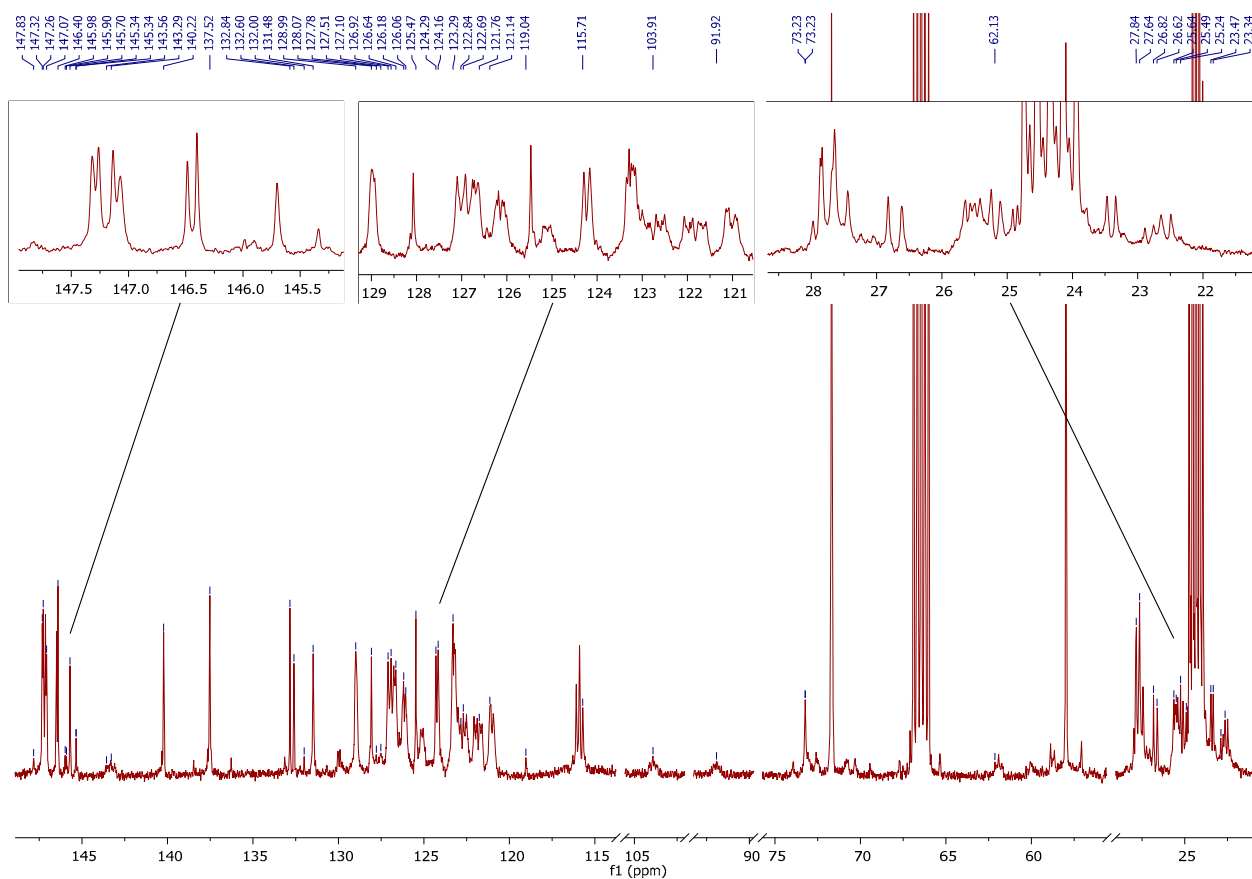


Figure S43. Selected area of ^{13}C NMR spectrum of compound **12-d⁵** in THF-d_8 .

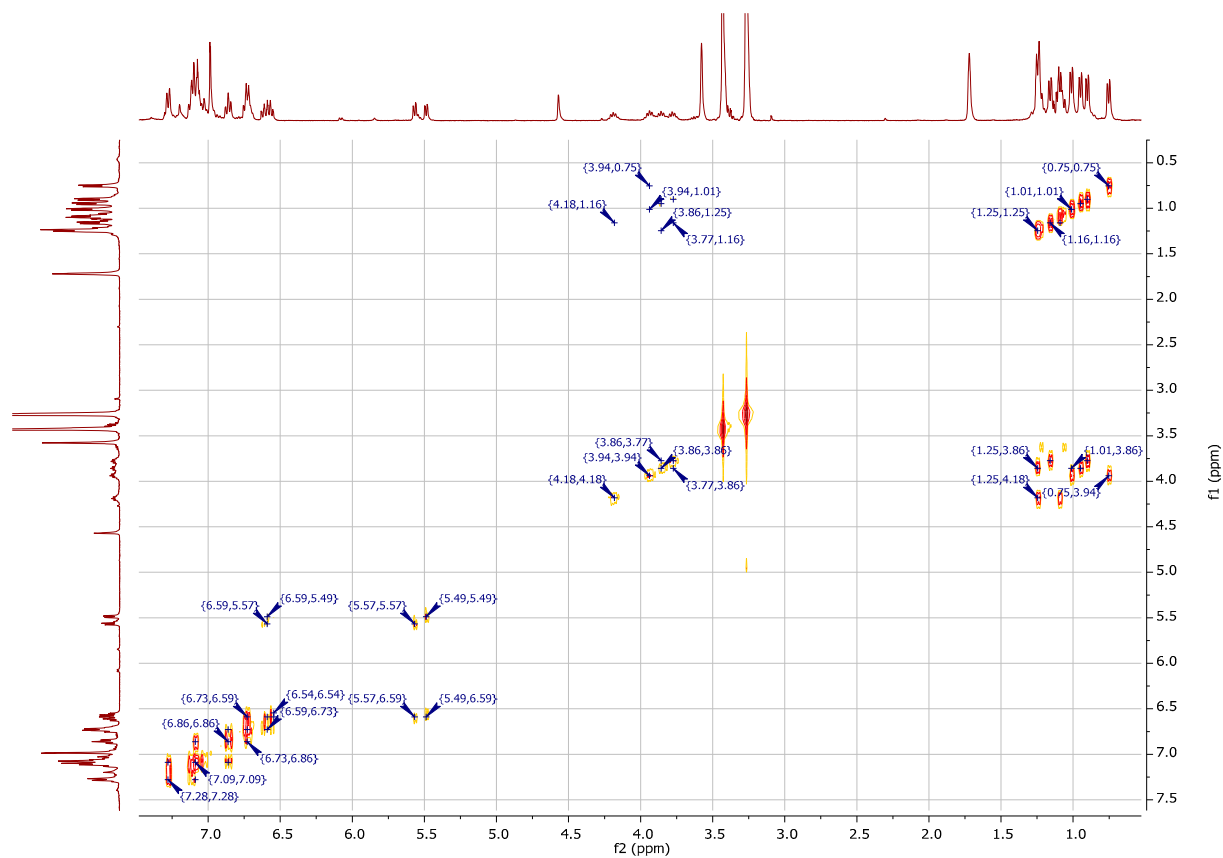


Figure S44. ^1H - ^1H COSY NMR spectrum of compound **12-d⁵** in THF-d_8 .

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