Supplementary Information

Cationic indium catalysts for ring opening polymerization: Tuning reactivity with hemilabile ligands

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A. Experimental procedures

General Considerations. Unless otherwise indicated, all air- and/or water-sensitive reactions were carried out under dry nitrogen using either an MBraun glove box or standard Schlenk line techniques. NMR spectra were recorded on a Bruker Avance 300 MHz, 400 MHz and 600 MHz spectrometers. ^{1}H NMR chemical shifts are reported in ppm versus residual protons in deuterated solvents as follows: δ 7.27 $CDCl_3$, δ 7.16 C_6D_6, δ 7.16 C_6D_5Br $^{13}C\{^{1}H\}$ NMR chemical shifts are reported in ppm versus residual ^{13}C in the solvent: δ 77.2 $CDCl_3$. $^{19}F\{^{1}H\}$ NMR chemical shifts are reported in ppm and externally referenced to neat $CFCl_3$ at 0 ppm. $^{31}P\{^{1}H\}$ NMR chemical shifts are reported in ppm and externally referenced to 85% H_3PO_4 at 0 ppm.

Diffraction measurements for X-ray crystallography were made on a Bruker X8 APEX II diffraction and a Bruker APEX DUO diffraction with graphite monochromated Mo-Kα radiation. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELXTL crystallographic software of Bruker-AXS. Unless specified, all non-hydrogens were refined with anisotropic displacement parameters, and all hydrogen atoms were constrained to geometrically calculated positions but were not refined.

EA CHN analysis was performed using a Carlo Erba EA1108 elemental analyzer. The elemental composition of unknown samples was determined by using a calibration factor. The calibration factor was determined by analyzing a suitable certified organic standard (OAS) of a known elemental composition.

Polymer molecular weights were determined by triple detection gel permeation chromatography (GPC-LLS) using a Waters liquid chromatograph equipped with a Water 515 HPLC pump, Waters 717 plus autosampler, Waters Styragel columns (4.6 × 300 mm) HR5E, HR4 and HR2, Water 2410 differential refractometer, Wyatt tristar miniDAWN (laser light scattering detector) and a Wyatt ViscoStar viscometer. A flow rate of 0.5 mL min^{-1} was used and samples were dissolved in THF (2 mg mL^{-1}). Narrow molecular weight polystyrene standards were used for calibration purposes. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometric analysis of isolated polymers was performed on a Bruker Autoflex MALDI-TOF equipped with a nitrogen laser (337 nm). The accelerating potential of the Bruker instrument was 19.5 kV. The polymer samples were dissolved in tetrahydrofuran (ca. 1 g/mL). The concentration of a cationization agent, sodium trifluoroacetate, in tetrahydrofuran was 1 mM. The matrix used was *trans*-[3-(4-*tert*-butylphenyl)2-methyl-2-propenylidene]malononitrile (DCTB) at the concentration of 20 mg/mL. A sample solution was prepared by mixing polymer, matrix, and salt in a volume ratio of 5:5:1, respectively.

Materials. Solvents (THF, pentane, toluene, hexane and diethyl ether) were collected from a Solvent Purification System from Innovative Technology, Inc. whose columns were packed with activated alumina. $CDCl_3$ was dried over CaH_2, collected by vacuum distillation and degassed through a series of freeze-pump-thaw cycles. Dimethylanilinium Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate ($[HNMe_2Ph][BAr^F]$) was generated by reacting dimethylanilinium chloride with sodium BAr^F in diethyl ether at room temperature for 4 h.[1] The solvent was removed under high vacuum, and addition of hexane to the residual precipitated a

white solid. The white solid was isolated by vacuum filtration and dried in *vacuo* for 4 h. $InCl_3$ was purchased from Strem Chemicals and used without further purification. Isobutylmagnesium chloride (2.0 M in Et_2O) and dimethylanilinium chloride ([$HNMe_2Ph$]Cl) were purchased from Aldrich and Alfa Aesar, respectively, and used as received. *Rac*-lactide was recrystallized 3 times from dry toluene and dried under vacuum. ε-caprolactone were dried over CaH_2, distilled and stored under molecular sieves. In(^{i}Bu)$_3$ was synthesized according to a previously reported procedure.[2] Proligands L_{a-d} were synthesized by the modification of a previously reported procedure.[3]

Syntheais of proligand L_a

(±)- trans-N-(thiophen-2-ylmethyl)cyclohexane-1,2-diamine (4.38 g, 20.8 mmol) was dissolved in 50 ml of acetonitrile (ACN) and 3,5-dicumylsalicylaldehyde (7.45 g, 20.8 mmol) was added while stirring. The solution was heated under reflux for 8 hours, and the solvent was removed under reduced pressure. The residue was dissolved in a minimum amount of ethyl acetate and crystallized by slow evaporation at low temperature to yield a pale yellow solid (yield 63%). HRMS $[M+H]^+$, calculated m/z = 551.3096. Found m/z = 551.3100. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 13.23 (1H, br. s., Ar-OH), 8.33 (1H, s, -N=CH-Ar), 7.03 - 7.41 (11H, m, ArH), 7.05 (1H, s, ArH), 7.13 (1H, m,Thioph α), 6.89 (1H, m, Thioph β), 6.74 (1H, m, Thioph γ), 3.97 (1H, d, $^2J_{H-H}$ = 14 Hz, -CH_2- of thiophenyl), 3.86 (1H, d, $^2J_{H-H}$ = 14 Hz, -CH_2- of thiophenyl), 2.95 (1H, m, -CH- of DACH), 2.63 (1H, m, -CH- of DACH), 1.02 - 1.74 (17H, m, -CH_2- of DACH and -CH_3 of cumyl), ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.7 (N=CH-Ar), 157.8 (Ar C), 150.9 (Ar C), 139.8 (Ar C), 129.2 (Ar C-H), 128.2 (Ar C-H), 128.1 (Ar C-H), 126.9 (Ar C-H), 125.0 (Ar C-H), 124.3 (Thioph α), 126.8 (Thioph β), 125.2 (Thioph γ), 74.4 (C-H of DACH), 59.5 (C-H of DACH), 42.8 (-CH_2- of thiophenyl) 31.1 (-CH_3 of cumyl), 30.0 (-CH_3 of cumyl), 29.3 (-CH_3 of cumyl).

Synthesis of proligand L_b

(±)- trans-N-(furan-2-ylmethyl)cyclohexane-1,2-diamine (6.28 g, 32.3 mmol) was dissolved in 100 ml of acetonitrile (ACN) and 3,5-dicumylsalicylaldehyde (11.6 g, 32.3 mmol) was added while stirring. The solution was heated under reflux for 8 hours, and the solvent was removed under reduced pressure. The residue was dissolved in a minimum amount of hot hexane and crystallized by slow evaporation at low temperature to yield a yellow solid (yield 61%). HRMS $[M+H]^+$, calculated m/z = 535.3325. Found m/z = 535.3334. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 13.22 (1H, br. s., Ar-OH), 8.35 (1H, s, -N=CH-Ar), 7.02 - 7.43 (11H, m, ArH), 7.07 (1H, s, ArH), 7.16 (1H, m, furan α), 6.24 (1H, m, furan β), 5.98 (1H, m, furan γ), 3.73 (1H, d, $^2J_{H-H}$ = 15 Hz, -CH_2- of furfuryl), 3.69 (1H, d, $^2J_{H-H}$ = 15 Hz, -CH_2- of furfuryl), 2.95 (1H, m, -CH- of DACH), 2.57 (1H, m, -CH- of DACH), 1.06 – 2.12 (17H, m, -CH_2- of DACH and -CH_3 of cumyl), ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.8 (N=CH-Ar), 157.8 (Ar C), 153.8 (Ar C), 150.8 (Ar C), 139.8 (Ar C), 136.2 (Ar C), 142.0 (Ar C-H), 128.2 (Ar C-H), 128.1 (Ar C-H), 126.9 (Ar C-H), 125.2 (Furan α), 110.1 (Furan β), 107.0 (Furan γ), 74.2 (C-H of DACH), 59.3 (C-H of DACH), 43.1 (-CH_2- of furfuryl), 31.1 (-CH_3 of cumyl), 29.8 (-CH_3 of cumyl), 29.2 (-CH_3 of cumyl).

Synthesis of proligand L_c

(±)- trans-N-(pyridin-2-ylmethyl)cyclohexane-1,2-diamine (7.54 g, 36.8 mmol) was dissolved in 100 ml of acetonitrile (ACN) and 3,5-dicumylsalicylaldehyde (13.2 g, 36.8 mmol) was added while stirring. The solution was heated under reflux for 8 hours, and the solvent was removed under reduced pressure. The residue was dissolved in a minimum amount of hot pentane and crystallized by slow evaporation at low temperature to yield a bright yellow solid (yield 64%). HRMS $[M+H]^+$, calculated m/z = 546.3484. Found m/z = 546.3483. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.37 (1H, s, -N=CH-Ar), 7.03 - 7.41 (12H, m, ArH),

7.42 (1H, m,Pyr. α), 7.08 (1H, m, Pyr β), 8.25 (1H, m, Pyr γ), 7.01 (1H, m, Pyr δ), 3.88 (1H, d, $^{2}J_{H-H}$ = 15 Hz, -CH_2- of pyridyl), 3.82 (1H, d, $^{2}J_{H-H}$ = 15 Hz, -CH_2- of pyridyl), 3.05 (1H, m, -CH- of DACH), 2.52 (1H, m, -CH- of DACH), 1.09 – 2.14 (20H, m, -CH_2- of DACH and -CH_3 of cumyl),$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 165.3 (N=CH-Ar), 159.7 (Ar C), 157.6 (Ar C), 150.8 (Ar C), 139.6 (Ar C), 128.9 (Ar C-H), 126.7 (Ar C-H), 125.6 (Ar C-H), 125.1 (Ar C-H), 136.3 (Pyr α), 127.9 (Pyr β), 149.2 (Pyr γ), 122.0 (Pyr δ), 74.4 (C-H of DACH), 59.5 (C-H of DACH), 51.8 (-CH_2- of pyridyll), 30.9 (-CH_3 of cumyl), 30.1 (-CH_3 of cumyl).

Synthesis of proligand L_d

(±)- trans-N-benzylcyclohexane-1,2-diamine (5.62 g, 27.4 mmol) was dissolved in 100 ml of acetonitrile (ACN) and 3,5-dicumylsalicylaldehyde (9.83 g, 27.4 mmol) was added while stirring. The solution was heated under reflux for 8 hours, and the solvent was removed under reduced pressure. The residue was dissolved in a minimum amount of pentane and crystallized by slow evaporation at low temperature to yield a bright yellow solid (yield 71%). HRMS $[M+H]^+$, calculated m/z = 545.3532. Found m/z = 545.3543.^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.35 (1H, s, -N=CH-Ar), 7.03 - 7.45 (17H, m, ArH, 3.81 (1H, d, $^{2}J_{H-H}$ = 14 Hz, -CH_2- of benzyl), 3.61 (1H, d, $^{2}J_{H-H}$ = 14 Hz, -CH_2- of benzyl), 2.97 (1H, m, -CH- of DACH), 2.61 (1H, m, -CH- of DACH), 1.00 – 2.24 (20H, m, -CH_2- of DACH and -CH_3 of cumyl),$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 165.6 (N=CH-Ar), 157.8 (Ar C), 150.7 (Ar C), 140.4 (Ar C), 139.7 (Ar C), 136.0 (Ar C), 129.1 (Ar C-H), 128.5 (Ar C-H), 127.9 (Ar C-H), 126.7 (Ar C-H), 125.6 (Ar C-H), 125.0 (Ar C-H), 74.2 (C-H of DACH), 59.8 (C-H of DACH), 50.9 (-CH_2- of benzyl), 30.9 (-CH_3 of cumyl), 29.7 (-CH_3 of cumyl), 29.2 (-CH_3 of cumyl).

Synthesis of complex 1a

A 20 mL scintillation vial was charged with proligand $\mathbf{L_a}$ (186 mg, 0.345 mmol) in hexane (5 ml). triisobutylindium, $In(CH_2CH(CH_3)_2)_3$ (100 mg, 0.345 mmol) was added to the stirring mixture. The reaction mixture was stirred for 4 h at room temperature. The concentrated in vacuo, the residue was cooled to -30 °C give yellow crystals. The solid was washed with hexane (3 × 3 mL) and dried under high vacuum for 4 hours. (Yield 94%) Anal. Calcd. For $C_{44}H_{59}InN_2OS$: C 67.84; H 7.65; N 3.60. Found: C 67.56; H 7.55; N 3.70.^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.02 (1H, s, -N=CH-Ar), 7.10 - 7.32 (11H, m, ArH), 7.18 (1H, m,Thioph α), 6.93 (1H, m, Thioph β), 6.86 (1H, m, Thioph γ), 6.79 (1H, s, ArH), 3.96 (1H, dd, $^{2}J_{H-H}$ =7, 15 Hz, -CH_2- of thiophenyl), 3.69 (1H, d, $^{2}J_{H-H}$ = 7, 15 Hz, -CH_2- of thiophenyl), 2.94 (1H, m, -CH- of DACH), 2.58 (1H, m, -CH- of DACH), 0.95 – 2.29 (20H, m, -CH_2- of DACH, -CH_3 of cumyl and -CH- of ^{i}Bu), 0.84 (6H, d, $^{3}J_{H-H}$ =6 Hz, -CH_3 of ^{i}Bu), 0.75 (6H, d, $^{3}J_{H-H}$ =6 Hz, -CH_3 of ^{i}Bu), 0.47 (2H, d, $^{3}J_{H-H}$ =7 Hz, -CH_2- of ^{i}Bu), 0.24 (2H, d, $^{3}J_{H-H}$ =7 Hz, -CH_2- of ^{i}Bu),$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 171.2 (N=CH-Ar), 168.1 (Ar C), 151.8 (Ar C), 151.5 (Ar C), 143.1 (Ar C), 141.3 (Ar C), 132.0 (Ar C-H), 131.7 (Ar C-H), 127.9 (Thioph α), 127.5 (Thioph β), 125.4 (Thioph γ), 72.4 (C-H of DACH), 60.9 (C-H of DACH), 44.6 (-CH_2- of thiophenyl) 31.0 (-CH_3 of cumyl), 29.6 (-CH_3 of cumyl), 28.1 (-CH_3 of ^{i}Bu), 27.9 (-CH_3 of ^{i}Bu), 29.5 (-CH_2- of ^{i}Bu), 29.3 (-CH_2- of ^{i}Bu).

Synthesis of complex 1b

Complex **1b** was generated using a similar procedure to complex **1a** (187 mg of L_b, 0.350 mmol, yield=95%). Anal. Calcd. For $C_{44}H_{59}InN_2O_2$: C 69.27; H 7.81; N 3.67. Found: C 69.10; H 7.69; N 3.64.^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.06 (1H, s, -N=CH-Ar), 7.02 - 7.36 (11H, m, ArH), 7.34 (1H, m, Furan α), 6.80 (1H, ArH), 6.28 (1H, m, Furan β), 6.14 (1H, m, Furan γ), 3.81 (1H, dd, $^{2}J_{H-H}$ =6, 14 Hz, -CH_2- of furfuryl), 3.71 (1H, d, $^{2}J_{H-H}$ =6, 14 Hz, -CH_2- of furfuryl), 2.94 (1H, m, -CH- of DACH), 2.58 (1H, m, -CH- of DACH), 0.97 – 2.31 (16H, m, -CH_2- of DACH, -CH_3 of cumyl and -CH- of ^{i}Bu), 0.88 (6H, m, -CH_3

of ^{i}Bu), 0.74 (6H, m, -CH_3 of ^{i}Bu), 0.50 (2H, m, -CH_2- of ^{i}Bu), 0.11 (2H, m, -CH_2- of ^{i}Bu),$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 171.7 (N=CH-Ar), 168.8 (Ar C), 152.9 (Ar C), 151 (Ar C), 152.0 (Ar C), 151.8 (Ar C), 142.3 (Furan α), 141.5 (Ar C), 132.2 (Ar C-H), 131.8 (Ar C-H), 128.2 (Ar C-H), 127.8 (Ar C-H), 127.1 (Ar C-H), 127.1 (Ar C-H), 124.6 (Ar C-H), 110.8 (Furan β), 107.8 (Furan γ), 70.6 (C-H of DACH), 61.1 (C-H of DACH), 42.5(-CH_2- of furfuryl) 31.1 (-CH_3 of cumyl), 29.8 (-CH_3 of cumyl), 29.5 (-CH_3 of cumyl), 28.5 (-CH_3 of ^{i}Bu), 28.4(-CH_3 of ^{i}Bu), 28.9 (-CH_2- of ^{i}Bu), 29.4 (-CH_2- of ^{i}Bu).

Synthesis of complex 1c

Complex **1c** was generated using a similar procedure to complex **1a** (191 mg of L_c, 0.350 mmol, yield=95%). Anal. Calcd. For $C_{45}H_{60}InN_3O$: C 68.83; H 7.83; N 5.43. Found: C 69.87; H 7.61; N 5.70.^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.52 (1H, m, Pyr γ), 8.11 (1H, s, -N=CH-Ar), 7.09 - 7.35 (11H, m, ArH), 7.61 (1H, m, Pyr α), 7.16 (1H, m, Pyr δ), 7.03 (1H, m, Pyr β), 6.79 (1H, ArH), 3.84 (2H, m, -CH_2- of pyridyl), 3.01 (1H, m, -CH- of DACH), 2.63 (1H, m, -CH- of DACH), 0.93 – 2.18 (17H, m, -CH_2- of DACH, -CH_3 of cumyl and -CH- of ^{i}Bu), 0.88 (6H, m, -CH_3 of ^{i}Bu), 0.60 (6H, m, -CH_3 of ^{i}Bu), 0.52 (2H, m, -CH_2- of ^{i}Bu), -0.07 (2H, m, -CH_2- of ^{i}Bu),$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 171.3 (N=CH-Ar), 169.3 (Ar C), 158.4 (Ar C), 151 (Ar C), 152.0 (Ar C), 142.3 (Pyr γ), 141.3 (Ar C), 136.6 (Pyr α), 131.9 (Ar C-H), 131.4 (Ar C-H), 128.0 (Ar C-H), 127.1 (Ar C-H), 125.4 (Pyr δ), 124.4 (Pyr β), 68.4 (C-H of DACH), 61.5 (C-H of DACH), 49.5 (-CH_2- of pyridyl) 31.0 (-CH_3 of cumyl), 29.9 (-CH_3 of cumyl), 29.0 (-CH_3 of cumyl), 28.3 (-CH_3 of ^{i}Bu), 27.9(-CH_3 of ^{i}Bu), 28.2 (-CH_2- of ^{i}Bu), 28.1 (-CH_2- of ^{i}Bu).

Synthesis of complex 1d

Complex **1d** was generated using a similar procedure to complex **1a** (191 mg of L_d, 0.350 mmol, yield=96%). Anal. Calcd. For $C_{46}H_{61}InN_2O$: C 71.48; H 7.97; N 3.63. Found: C 71.74; H 7.99; N 3.57.^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.85 (1H, s, -N=CH-Ar), 6.80 - 7.20 (11H, m, ArH), 6.61 (1H, m, ArH), 3.61 (1H, dd, $^{2}J_{H\text{-}H}$=7, 13 Hz -CH_2- of benzyl), 3.50 (1H, dd, $^{2}J_{H\text{-}H}$=7, 13 Hz -CH_2- of benzyl), 2.75 (1H, m, -CH- of DACH), 2.41 (1H, m, -CH- of DACH), 0.77 – 2.13 (17H, m, -CH_2- of DACH, -CH_3 of cumyl and -CH- of ^{i}Bu), 0.68 (6H, d, $^{3}J_{H\text{-}H}$=7 Hz, -CH_3 of ^{i}Bu), 0.53 (6H, d, $^{3}J_{H\text{-}H}$=7 Hz, -CH_3 of ^{i}Bu), 0.32 (2H, d, $^{3}J_{H\text{-}H}$=7 Hz, -CH_2- of ^{i}Bu), -0.01 (2H, d, $^{3}J_{H\text{-}H}$=7 Hz, -CH_2- of ^{i}Bu),$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 171.0 (N=CH-Ar), 168.2 (Ar C), 151.7 (Ar C), 151.5 (Ar C), 141.2 (Ar C), 139.8 (Ar C), 132.0 (Ar C-H), 131.5 (Ar C-H), 128.7 (Ar C-H), 127.9 (Ar C-H), 124.4 (Ar C-H), 71.7 (C-H of DACH), 61.1 (C-H of DACH), 50.1 (-CH_2- of benzyl) 30.9(-CH_3 of cumyl), 29.4 (-CH_3 of cumyl), 29.5 (-CH_3 of cumyl), 27.8 (-CH_3 of ^{i}Bu), 28.1 (-CH_3 of ^{i}Bu), 29.4 (-CH_2- of ^{i}Bu), 29.4 (-CH_2- of ^{i}Bu).

Synthesis of complex 2a

A 20 mL scintillation vial was charged with **1a** (200 mg, 0.257 mmol) in C_6H_6 (3 ml). [$HNMe_2Ph$][$BAr^{F}{}_{24}$] (253 mg, 0.266 mmol) in C_6H_6 (2 ml) was added to the stirring solution of **1a**. The reaction mixture was stirred for 4 h at r.t. The solvent was removed in vacuo to obtain a yellow residue and cold hexane (3 ml) was added to the residue. After stirring for 1 h, the supernatant was decanted off to remove the byproduct NMe_2Ph. This step was repeated at least 3 times until a pale-yellow solid precipitate formed. The product was washed with hexane (2 × 3 ml) and dried under high vacuum for a few hours. (70%). Anal. Calcd. For $C_{72}H_{62}BF_{24}InN_2OS$: C 54.79; H 4.10; N 1.75. Found: C 55.16; H 4.57; N 2.02. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.22 (1H, s, -N=CH-Ar), 7.76 (8H, br. s., *ortho H* of BAr^{F}), 7.62 (1H, m, ArH), 7.57 (4H, br. s., *para H* of BAr^{F}), 6.94 - 7.42 (14H, m, ArH), 7.36 (1H, m,Thioph α), 7.05 (1H, m, Thioph β), 6.86 (1H, m, Thioph γ), 4.38 (1H, d, $^{2}J_{H\text{-}H}$=13 Hz, -CH_2- of thiophenyl), 3.75 (1H, m, -CH_2- of thiophenyl), 3.17 (1H, m, -CH- of DACH), 2.29 (1H, m, -CH- of DACH), 0.83 – 2.04 (16H, m, -CH_2- of DACH, -CH_3 of cumyl and -CH- of ^{i}Bu), 0.66 (6H, m, -CH_3 of ^{i}Bu), 0.73 (2H, m, -CH_2- of ^{i}Bu),$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

δ 169.3 (N=CH-Ar), 163.9 (Ar C), 161.3-162.4 (B-C), 151.7 (Ar C), 150.0 (Ar C), 141.8 (Ar C), 140.2 (Ar C), 138.8 (Ar C), 134.9 (*ortho* C-H of BAr^F), 134.4 (ArC-H), 131.7 (ArC-H), 130.9 (ArC-H), 129.6 (Thioph γ), 128.6-129.4 (qq, $^2J_{C-F}$ = 3, 32 Hz, *meta* C of BAr^F), 127.4,125.6,123.8,121.9 (q, $^1J_{C-F}$ = 273 Hz, $-CF_3$), 128.8 Thioph β), 128.3 (Thioph α), 118.1 (Ar C), 117.6 (*para* C-H of BAr^F), 65.5 (C-H of DACH), 62.6 (C-H of DACH), 46.6 ($-CH_2$- of furfuryl) 32.2 ($-CH_2$- of ^{i}Bu), 30.7 ($-CH_3$ of cumyl), 30.8 ($-CH_3$ of cumyl), 28.7 ($-CH_3$ of cumyl), 27.6 ($-CH_3$ of ^{i}Bu),$^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$): δ -61.9.

Synthesis of complex 2b

Complex **2b** was generated using a similar procedure to complex **2a** (200 mg of **1b**, 0.262 mmol, yield=75%). Anal. Calcd. For $C_{72}H_{62}BF_{24}InN_2O_2$: C 55.35; H 4.15; N 1.77. Found: C 54.86; H 4.18; N 1.89.^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.19 (1H, s, -N=CH-Ar), 7.71 (8H, br. s., *ortho H* of BAr^F), 7.62 (1H, m, ArH), 7.53 (4H, br. s., *para H* of BAr^F), 6.90 - 7.36 (12H, m, ArH), 6.21 (1H, m, Furan α), 6.14 (1H, m, Furan β), 6.13 (1H, m, Furan γ), 4.03 (1H, d, $^2J_{H-H}$ =15 Hz, $-CH_2$- of furfuryl), 3.80 (1H, m, $-CH_2$- of furfuryl), 3.12 (1H, m, -CH- of DACH), 2.33 (1H, m, -CH- of DACH), 0.85 – 2.29 (19H, m, $-CH_2$- of DACH, $-CH_3$ of cumyl, -CH- of ^{i}Bu and $-CH_2$- of ^{i}Bu), 0.83 (6H, m, $-CH_3$ of ^{i}Bu), $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.7 (N=CH-Ar), 165.7 (Ar C), 161.2-162.4 (B-C), 150.0 (Ar C), 146.1 (Furan δ), 144.2.0 (Furan γ), 141.5 (Ar C), 139.4 (Ar C), 134.9 (*ortho* C-H of BAr^F), 134.8 (ArC-H), 132.4 (ArC-H), 128.7-129.4 (qq, $^2J_{C-F}$ = 3, 32 Hz, *meta* C of BAr^F), 127.4,125.6,123.8,121.9 (q, $^1J_{C-F}$ = 273 Hz, $-CF_3$), 126.2 (Ar C-H), 125.5 (Ar C-H), 122.0 (Ar C), 117.6 (*para* C-H of BAr^F), 117.3 (Ar C),112.3 (Furan β), 110.9 (Furan α), 64.7 (C-H of DACH), 61.6 (C-H of DACH), 42.5 ($-CH_2$- of furfuryl) 31.3 ($-CH_3$ of cumyl), 30.9 ($-CH_3$ of cumyl), 30.8 ($-CH_2$- of DACH), 30.3 ($-CH_2$- of ^{i}Bu), 28.4 ($-CH_3$ of cumyl), 27.9 ($-CH_2$- of DACH), 27.8 ($-CH_3$ of ^{i}Bu), 23.9 ($-CH_2$- of DACH), 23.5 (-CH- of ^{i}Bu), $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$): δ -62.0.

Synthesis of complex 2c

Complex **2c** was generated using a similar procedure to complex **2a** (200 mg of **1c**, 0.259 mmol, yield=86%). Anal. Calcd. For $C_{73}H_{63}BF_{24}InN_3O$: C 55.72; H 4.18; N 2.64. Found: C 55.60; H 4.28; N 2.82.^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.20 (1H, s, -N=CH-Ar), 7.76 (9H, br. s., *ortho H* of BAr^F and Pyr γ), 7.61 (1H, m, ArH), 7.54 (4H, br. s., *para H* of BAr^F), 7.19 - 7.39 (10H, m, ArH), 7.16 (1H, m, Pyr α), 7.10 (1H, m, Pyr δ), 6.95 (2H, m, Pyr β and ArH), 4.02 (2H, m, $-CH_2$- of pyridyl), 3.12 (1H, m, $-CH_2$- of thiophenyl), 3.17 (1H, m, -CH- of DACH), 0.95 – 2.56 (20H, m, $-CH_2$- of DACH, $-CH_3$ of cumyl, -CH- of ^{i}Bu and $-CH_2$- of ^{i}Bu), 0.87 (6H, m, $-CH_3$ of ^{i}Bu), $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.0 (N=CH-Ar), 167.1 (Ar C), 161.8 (B-C), 152.2 (Ar C), 152.1 (Ar C), 150.0 (Pyr β), 149.9 (Ar C), 141.9 (Pyr γ), 135.1 (*ortho* C-H of BAr^F), 134.2 (ArC-H), 132.8 (Pyr δ), 128.7-129.4 (qq, $^2J_{C-F}$ = 3, 32 Hz, *meta* C of BAr^F), 127.4,125.6,123.8,121.9 (q, $^1J_{C-F}$ = 273 Hz, $-CF_3$), 126.2 (Ar C-H), 125.5 (Ar C-H), 124.0 (Pyr α), 117.6 (*para* C-H of BAr^F), 64.2 (C-H of DACH), 60.6 (C-H of DACH), 47.3 ($-CH_2$- of pyridyl) 33.8 ($-CH_3$ of cumyl), 30.9 ($-CH_3$ of cumyl), 25.9 ($-CH_3$ of cumyl), 27.8 ($-CH_3$ of ^{i}Bu), 27.3 ($-CH_2$- of ^{i}Bu),$^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$): δ -61.8.

Synthesis of complex 2d

Complex **2d** was generated using a similar procedure to complex **2a** but was obtained in a mixture of decomposition products and could not be purified. Synthesis of **2d** in THF at -30 °C resulted in less decomposition products. However, **2d** could not be isolated. Anal. Calcd. For $C_{74}H_{64}BF_{24}InN_2O$: C 56.70; H 4.20; N 1.70. Found: C 55.10; H 4.50; N 1.71.^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.36 (1H, s, -N=CH-Ar), 7.70 (8H, br. s., *ortho H* of BAr^F), 7.52 (4H, br. s., *para H* of BAr^F), 7.07 - 7.45 (14H, m, ArH), 4.17 (1H, m, $-CH_2$- of benzyl), 3.98 (1H, m, $-CH_2$- of benzyl), 3.76 ($-CH_2$-of THF), 3.50 (1H, m, -CH- of

DACH), 3.14 (1H, m, -CH- of DACH), -0.22 – 2.31 (24H, m, -CH_2- of DACH, -CH_3 of cumyl, -CH- of ^{i}Bu, -CH_2- of ^{i}Bu and -CH_3 of ^{i}Bu).

Representative polymerization of epoxides using cationic complexes (2a)

A 7 mL scintillation vial was charged with a solution of complex **2a** (19.0 mg, 0.012 mmol) in 0.3 ml of C_6D_6. Epichlorohydrin (0.30 mL, 3.8 mmol) was added directly to the vial by a syringe. The mixture was stirred at 25 °C for 24 h. The resulting solution was concentrated under vacuum for 3 h and then cold methanol was added to it (0 °C, 15 mL). The polymer precipitated from solution and was isolated by decantation or centrifugation. The isolated polymer was dried under high vacuum for at least 3 h prior to analysis.

Representative polymerization of ε-CL using cationic complexes (2b)

A 20 ml scintillation vial was charged with a solution of complex **2b** (20.0 mg, 0.013 mmol) in 0.5 ml of toluene. A solution of ε-CL (0.5 ml, 4.5 mmol) in 0.5 ml of toluene was added to the vial. The mixture was stirred at 100 °C for 24 h. The resulting solution was concentrated under vacuum for 3 h and then cold methanol was slowly added to the vial (0 °C, 15 mL). The polymer precipitated from the solution and was isolated by decantation of the supernatant. The isolated polymer was dried under high vacuum for at least 3 h prior to analysis.

Representative polymerization of *rac*-LA using cationic complexes (2c)

A 20 ml scintillation vial was charged with a solution of complex **2c** (10.1 mg, 0.006 mmol) in 1 ml of toluene. *Rac*-LA (230 mg, 1.6 mmol) was directly added to the vial. The mixture was stirred at 100 °C for 24 h. The resulting solution was concentrated under vacuum for 3 h and then cold methanol was slowly added to the vial (0 °C, 15 mL). The polymer precipitated from the solution and was isolated by decantation of the supernatant. The isolated polymer was dried under high vacuum for at least 3 h prior to analysis.

Table S1 Summary of cationic complex synthesis, storage and shelf life.

Complex	**2a**	**2b**	**2c**	**2d**
Pendant group donor strength (D_s)[4]	11	10	33	38
Synthesis temperature	Ambient temperature	Ambient temperature	Ambient temperature	-30 °C
Synthesis solvents	THF, DCM, C_6D_6	THF, DCM, C_6D_6	THF, DCM, C_6D_6	THF
Shelf life*	~48 h at r.t. ~2 weeks at -30 °C	Stable up to 10 weeks at r.t.	Stable up to 10 weeks at r.t. Up to 10 days exposed to moist air	~20 mins at r.t. ~ 1 day at -30 °C

*Stored under dry N_2 unless otherwise stated.

B. Characterization of metal complexes and ligands in solution

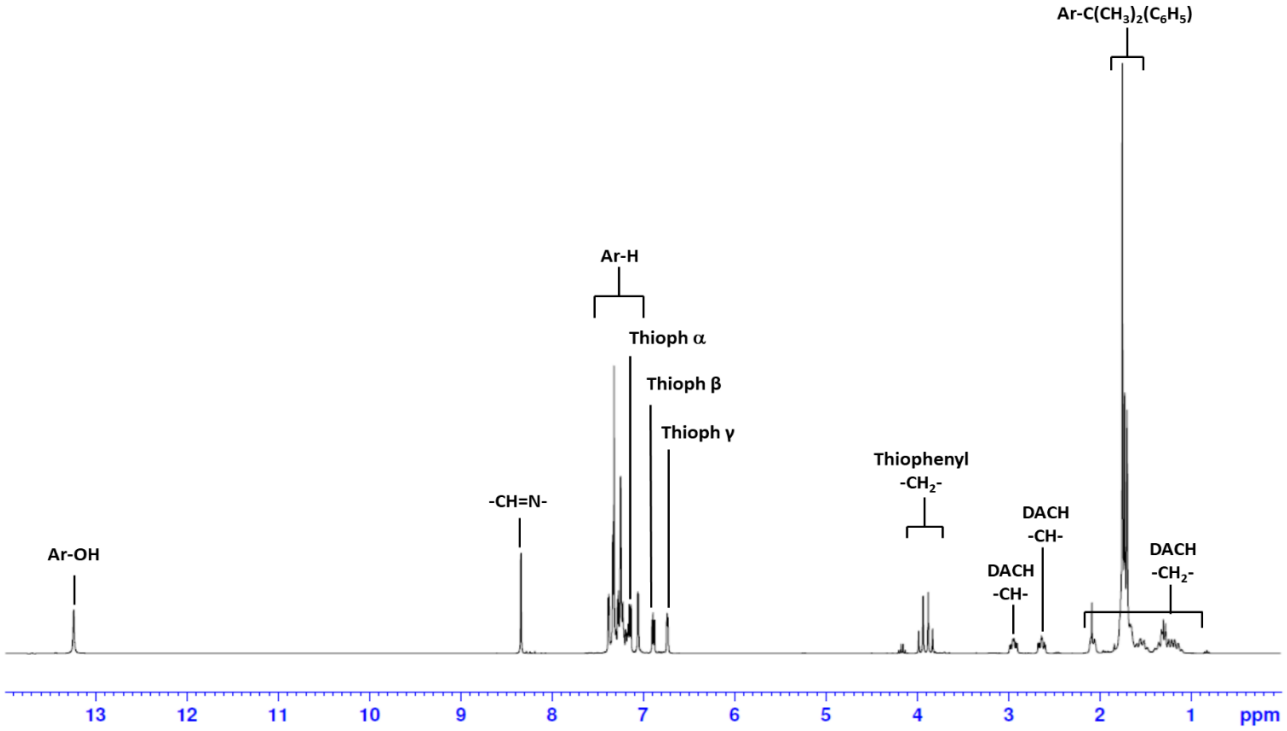


Figure S1 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of $\mathbf{L_a}$.

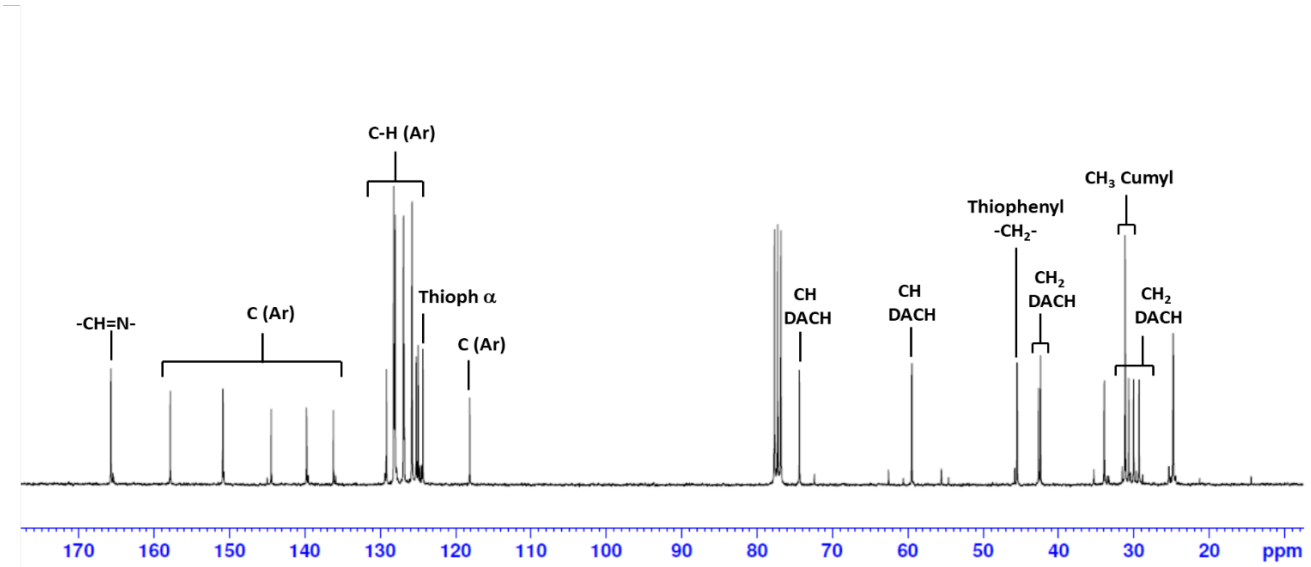


Figure S2 ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of $\mathbf{L_a}$.

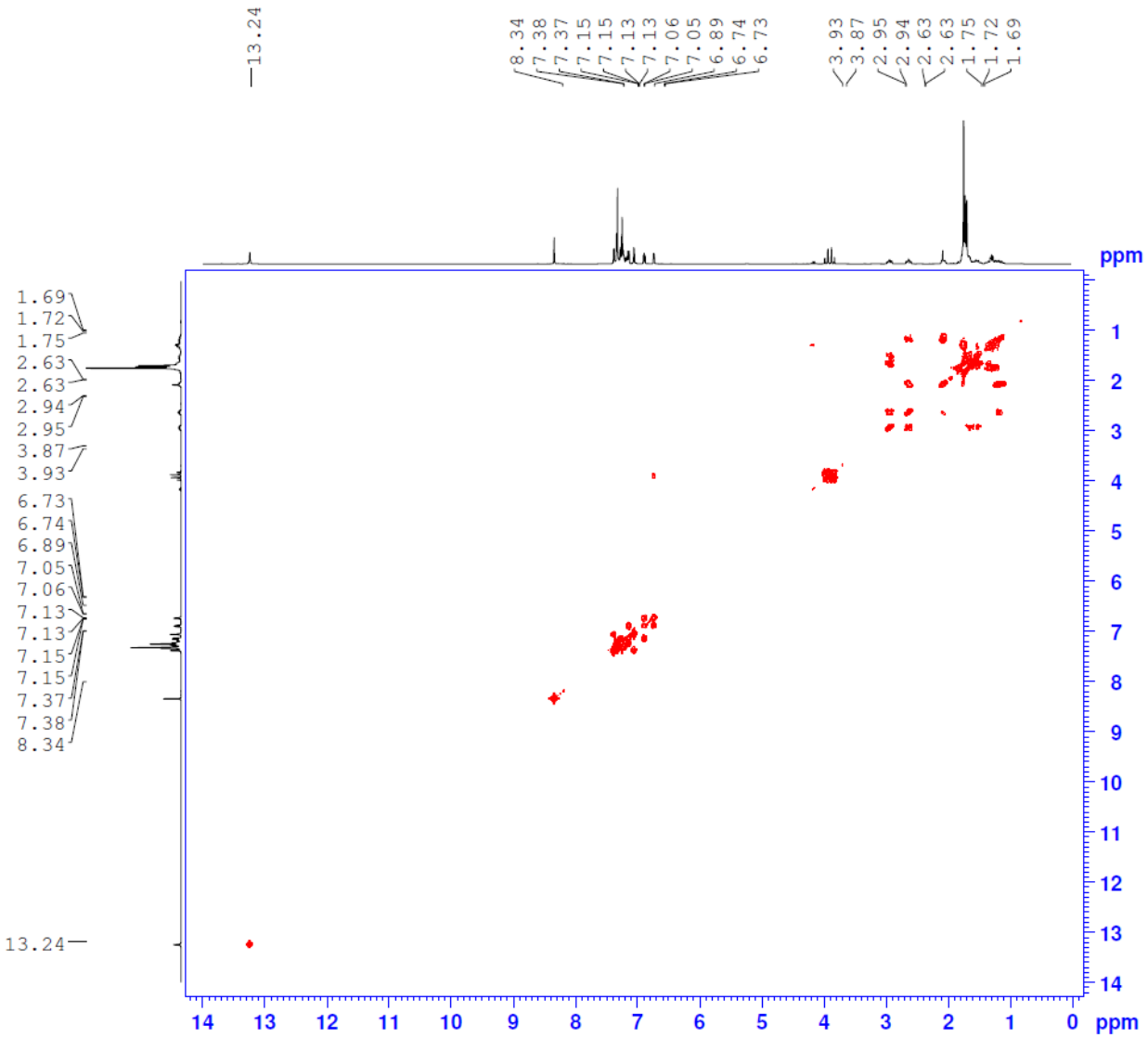


Figure S3 2D ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of $\mathbf{L_a}$.

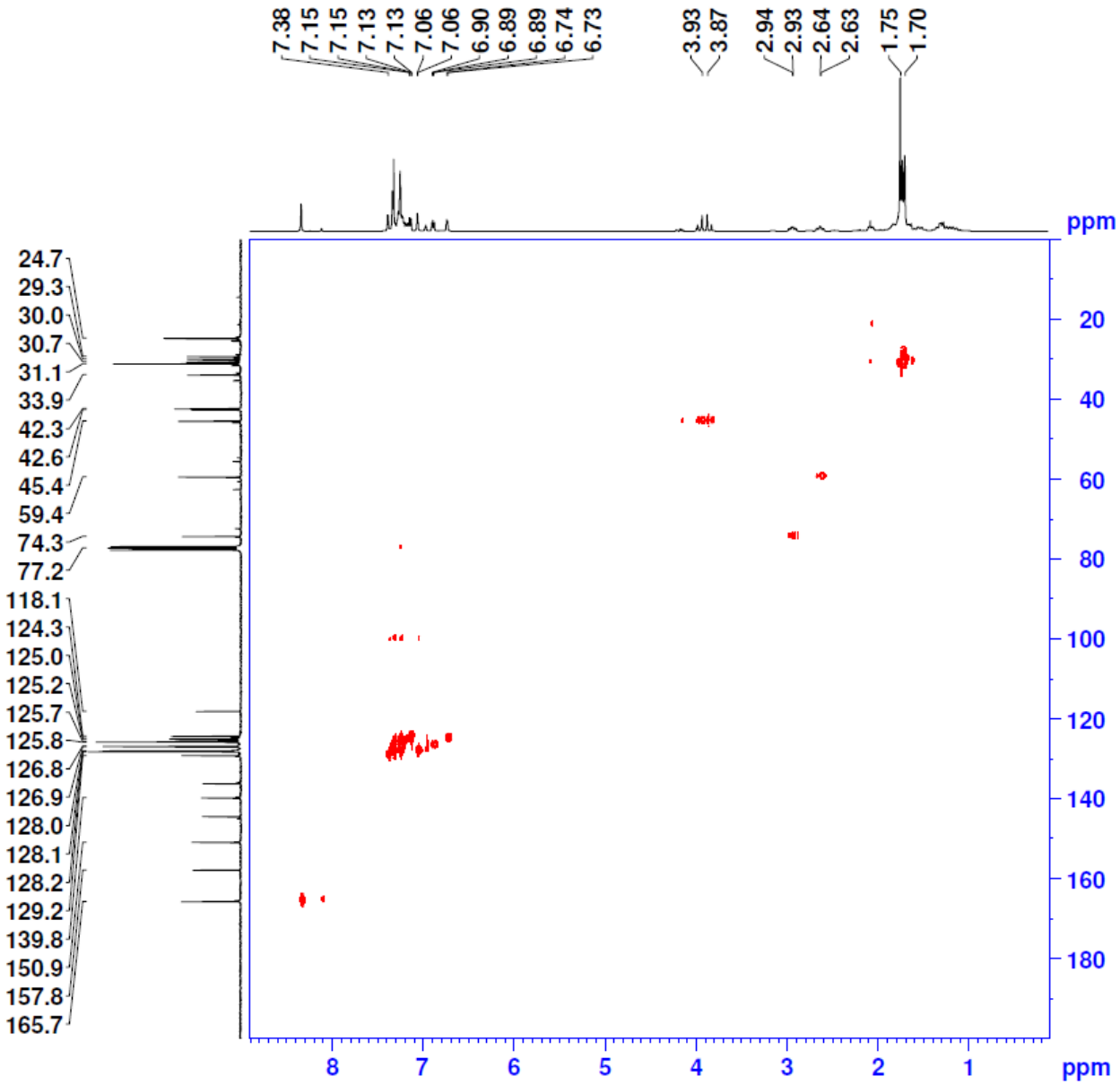


Figure S4 ^{1}H-^{13}C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum ($CDCl_3$, 25 °C) of $\mathbf{L_a}$.

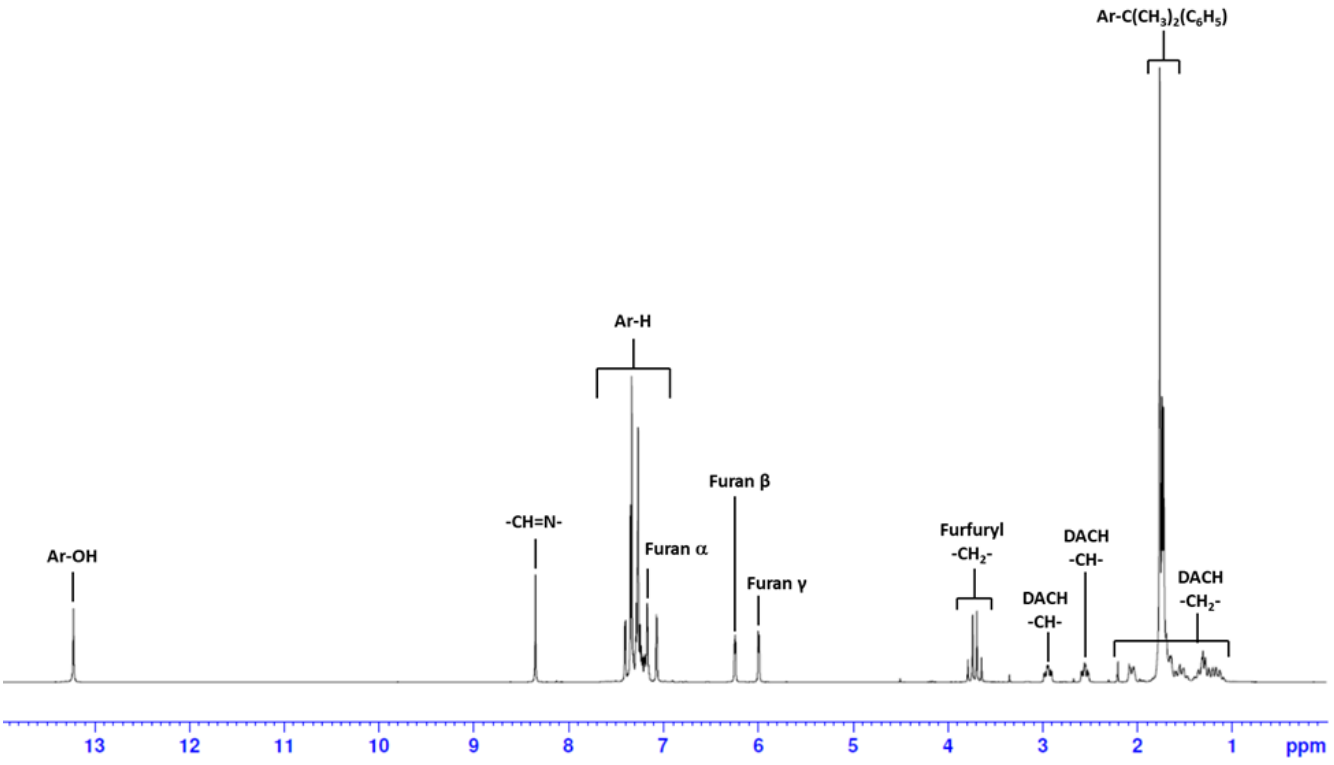


Figure S5 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of $\mathbf{L_b}$

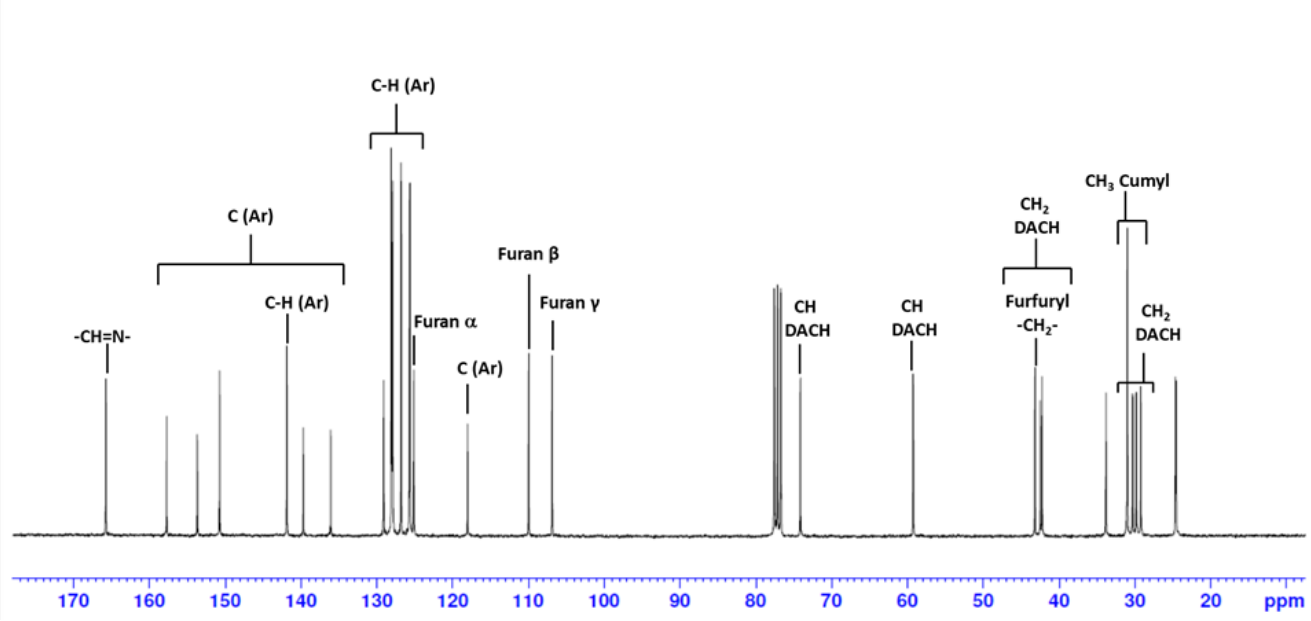


Figure S6 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of $\mathbf{L_b}$.

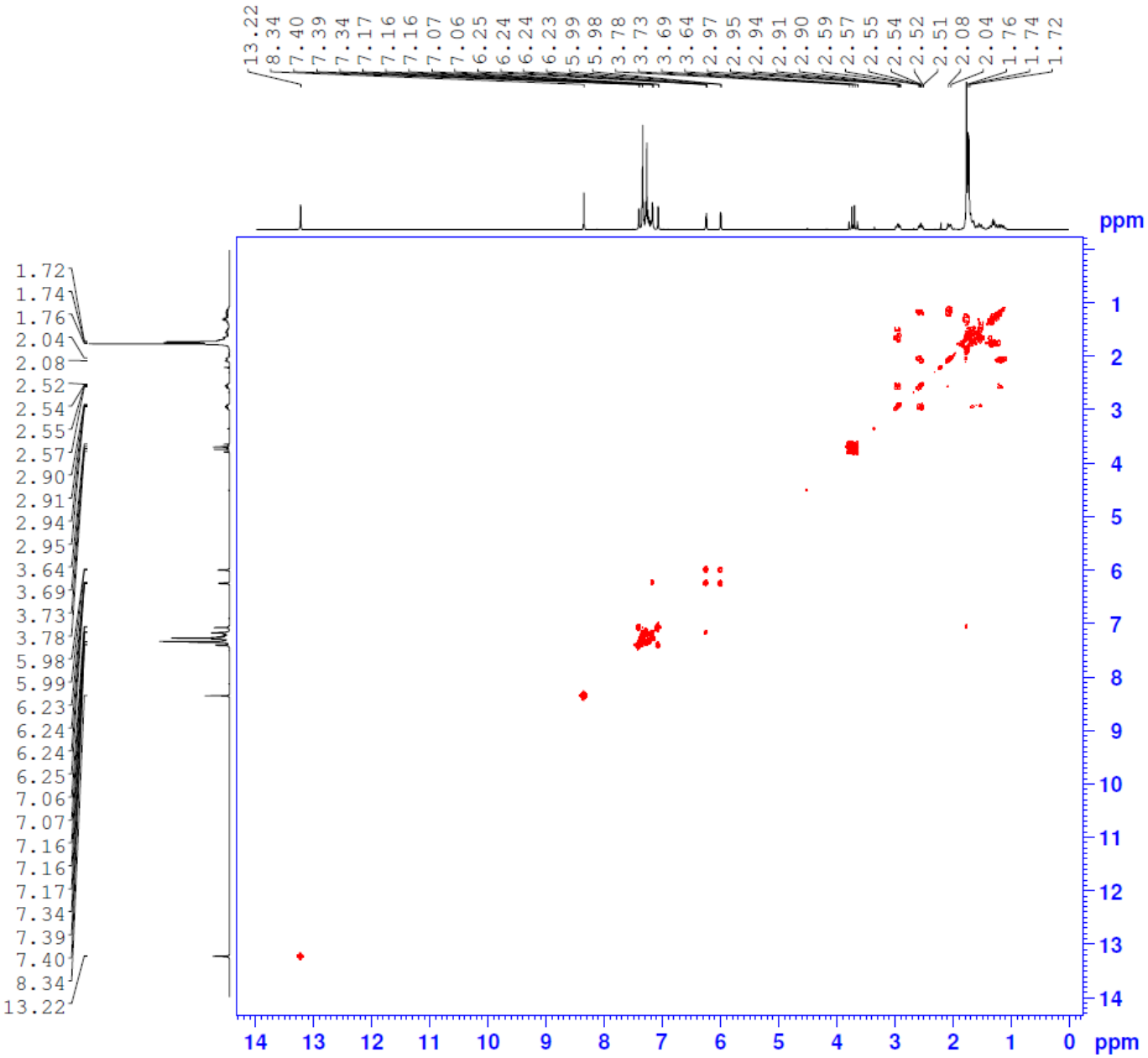


Figure S7 ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of $\mathbf{L_b}$.

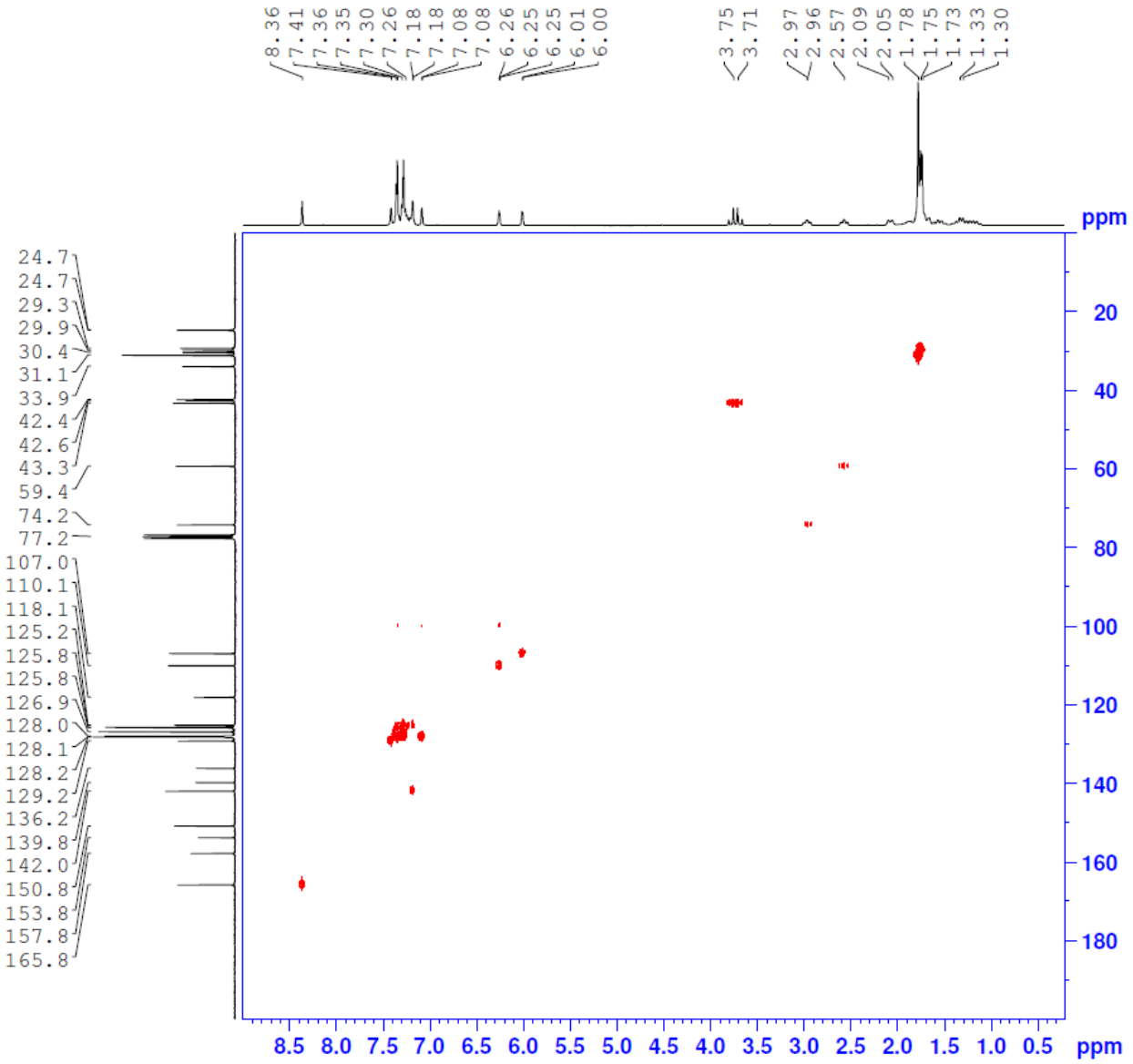


Figure S8 ^{1}H-^{13}C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum ($CDCl_3$, 25 °C) of $\mathbf{L_b}$.

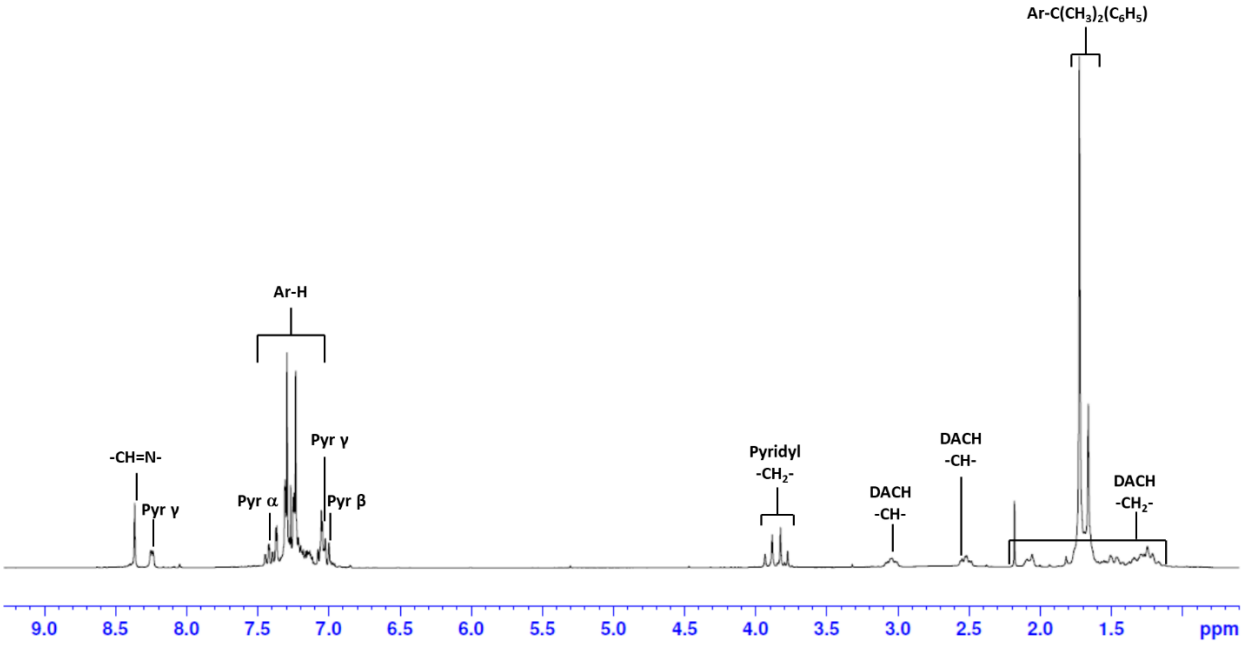


Figure S9 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of $\mathbf{L_c}$

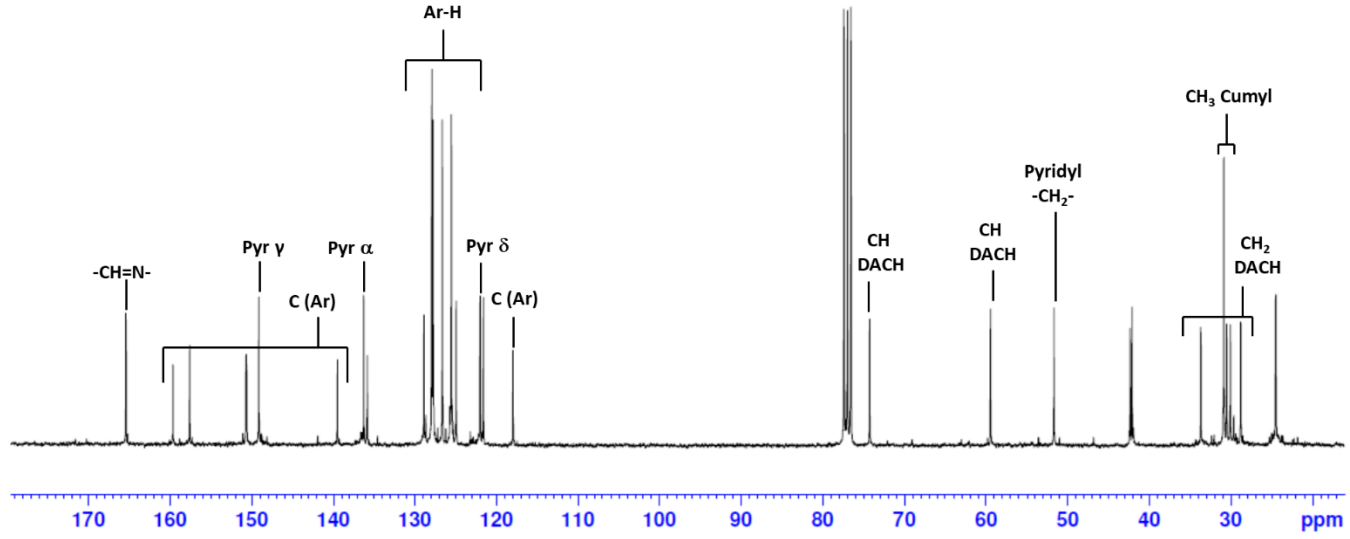


Figure S10 ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of $\mathbf{L_c}$.

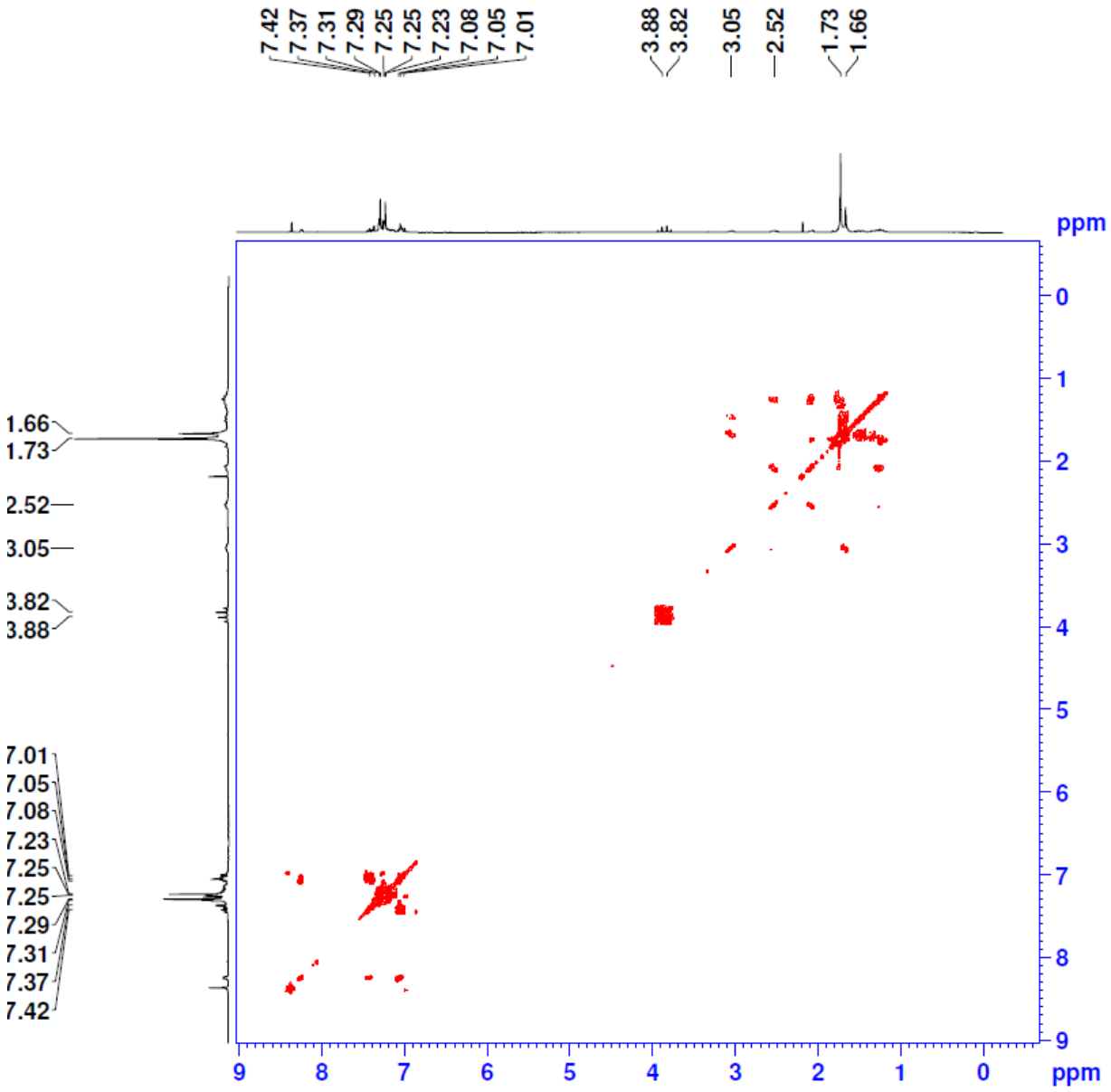


Figure S11 ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of $\mathbf{L_c}$.

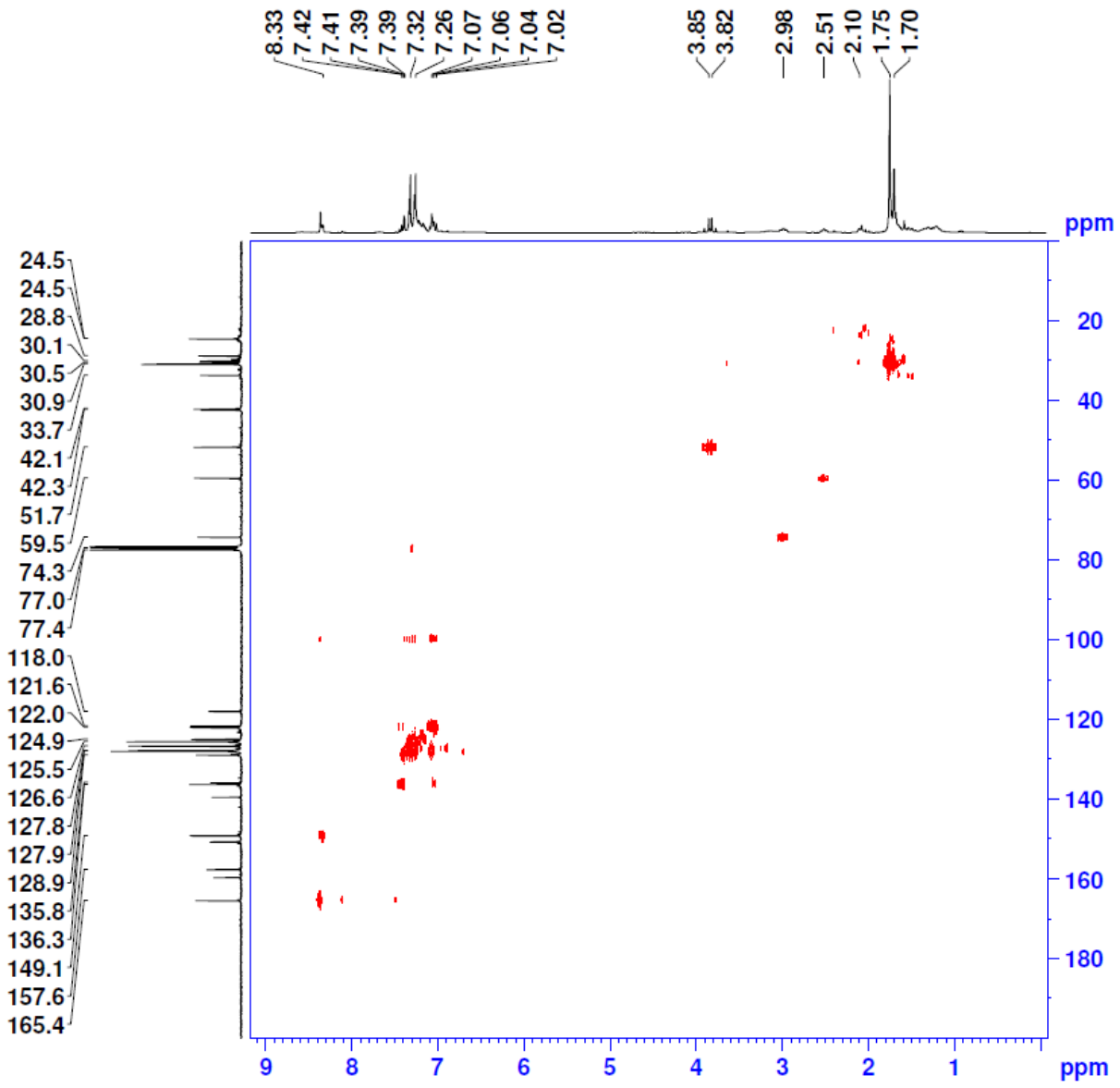


Figure S12 ^{1}H-^{13}C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum ($CDCl_3$, 25 °C) of $\mathbf{L_c}$

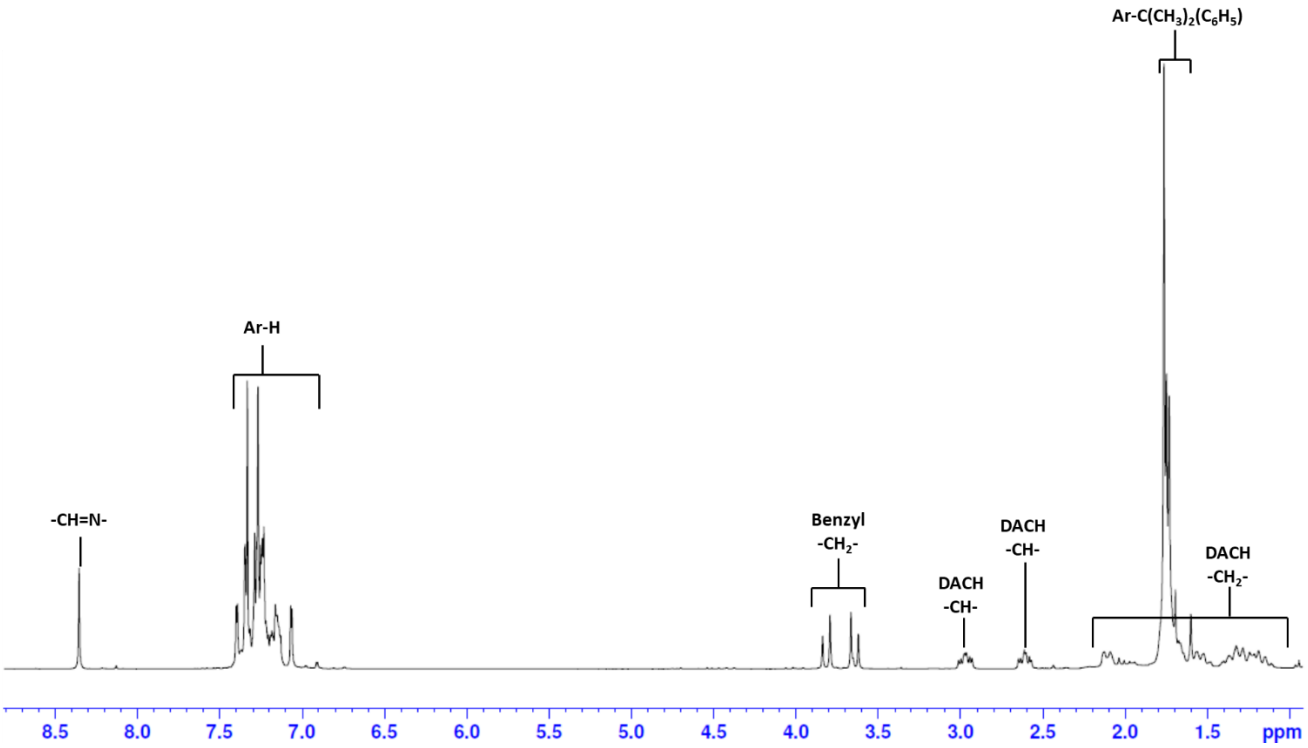


Figure S13 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of $\mathbf{L_d}$

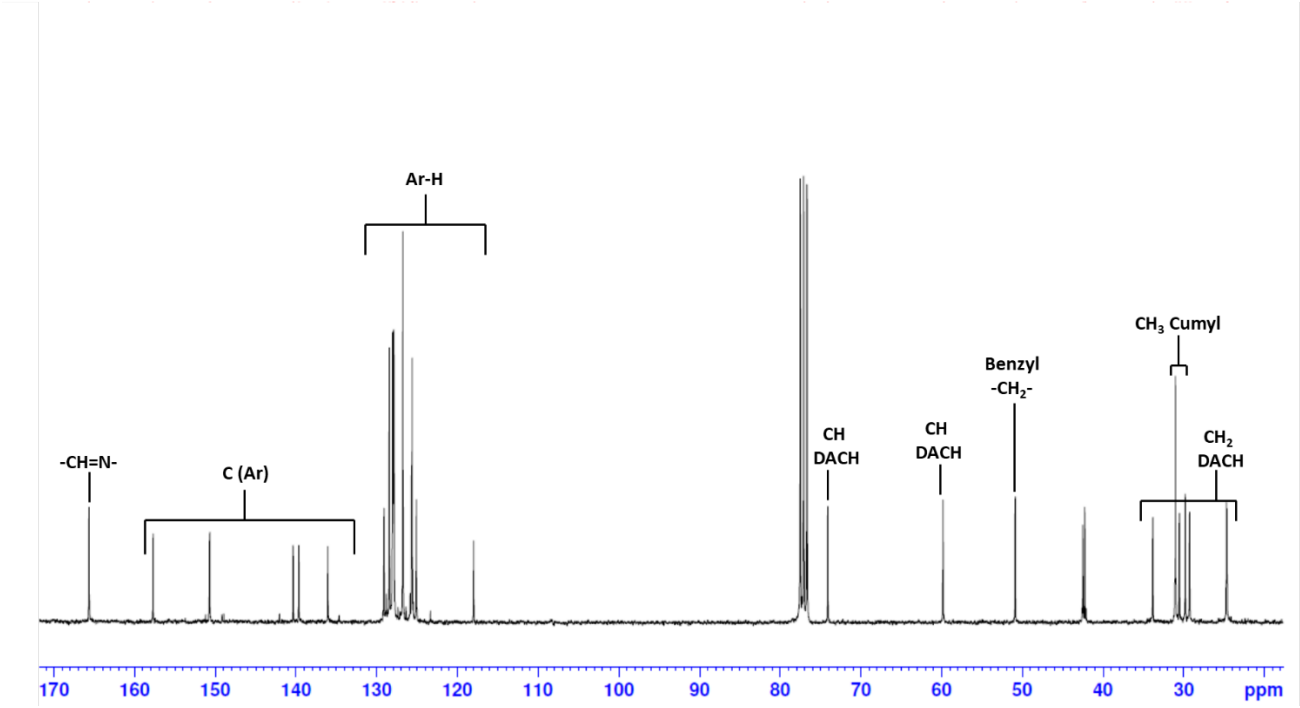


Figure S14 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of $\mathbf{L_d}$.

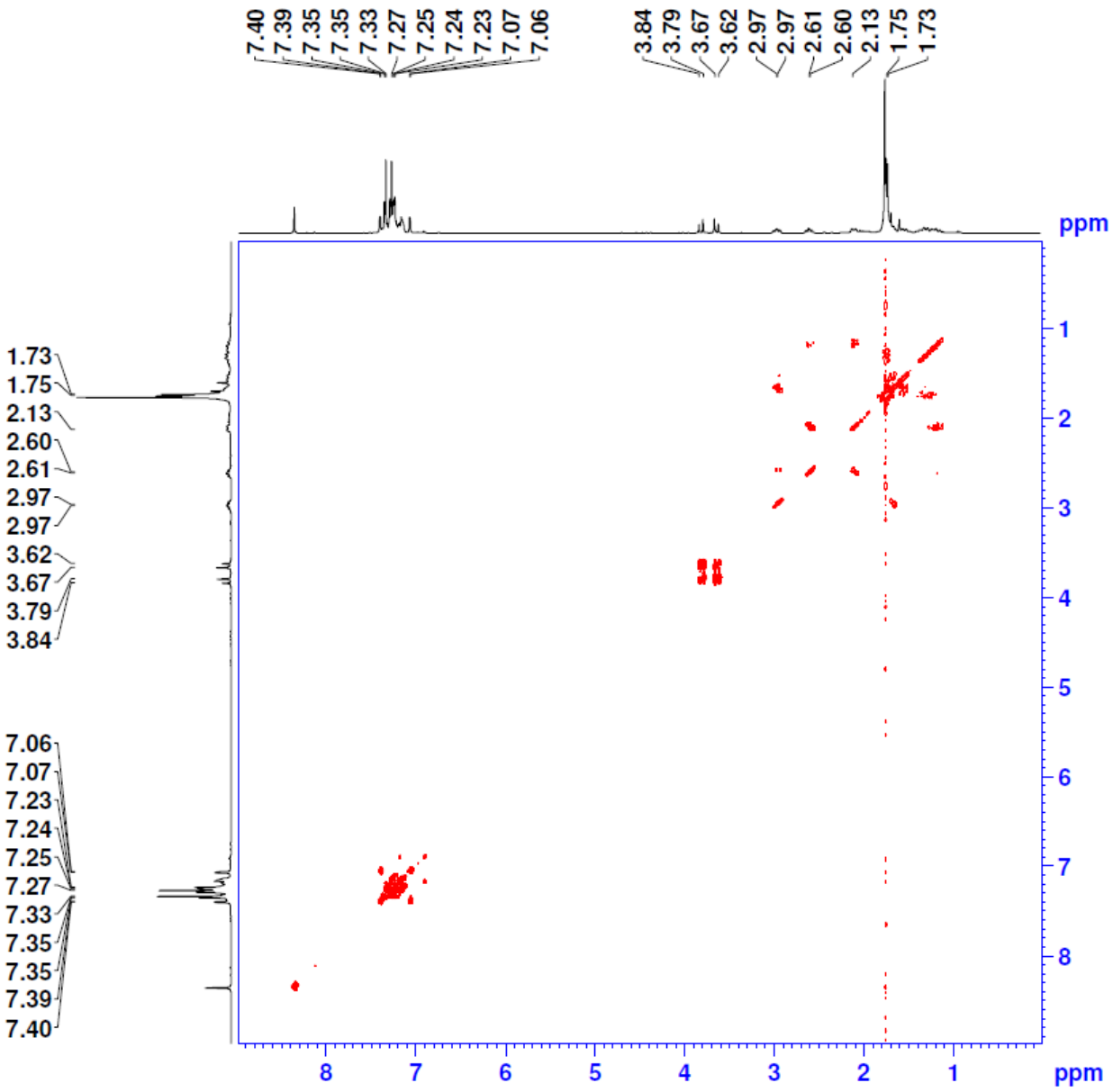


Figure S15 2D ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of $\mathbf{L_d}$.

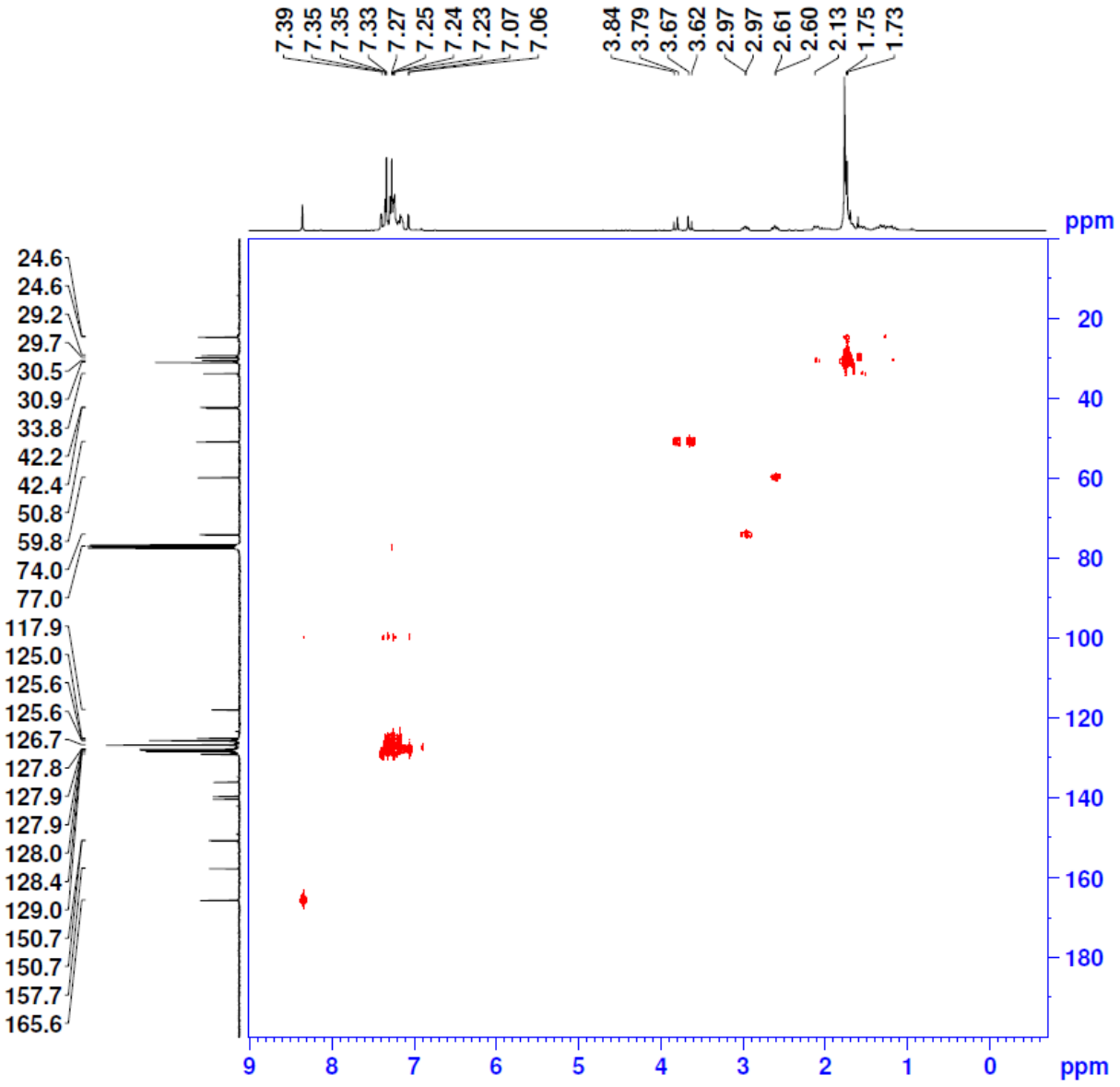


Figure S16 ^{1}H-^{13}C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum ($CDCl_3$, 25 °C) of $\mathbf{L_d}$

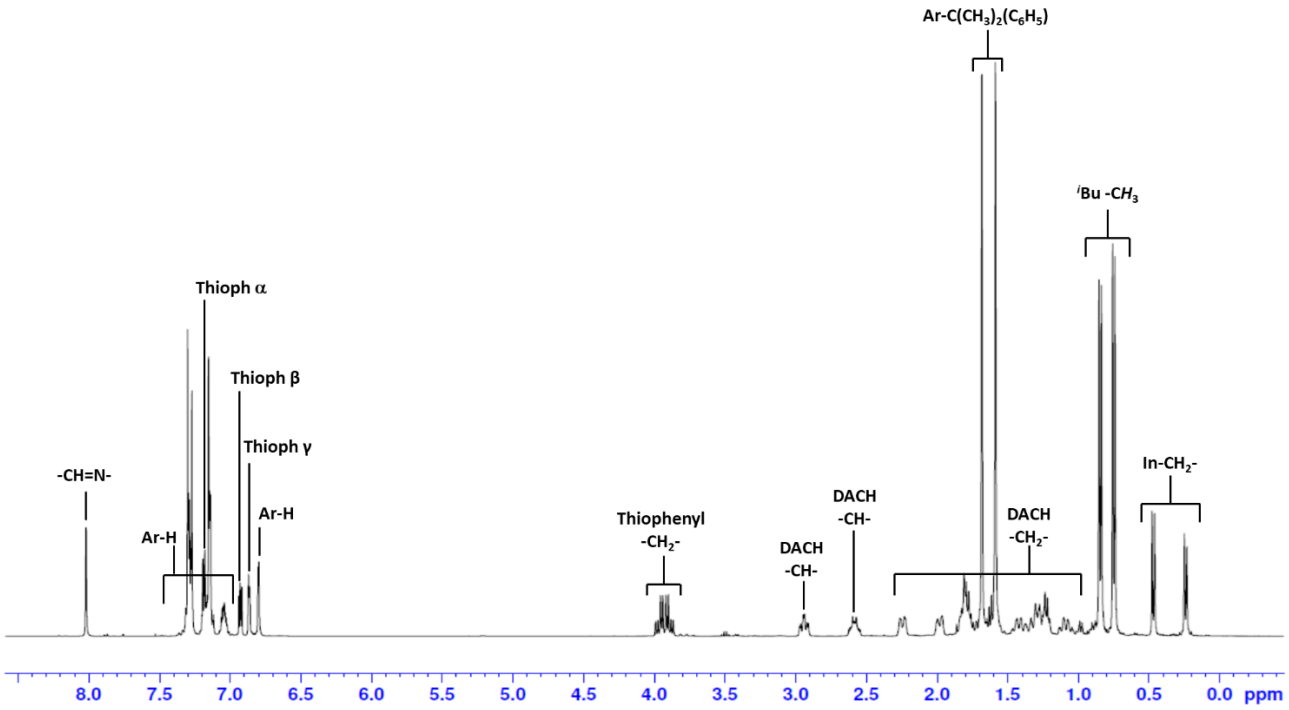


Figure S17 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **1a**

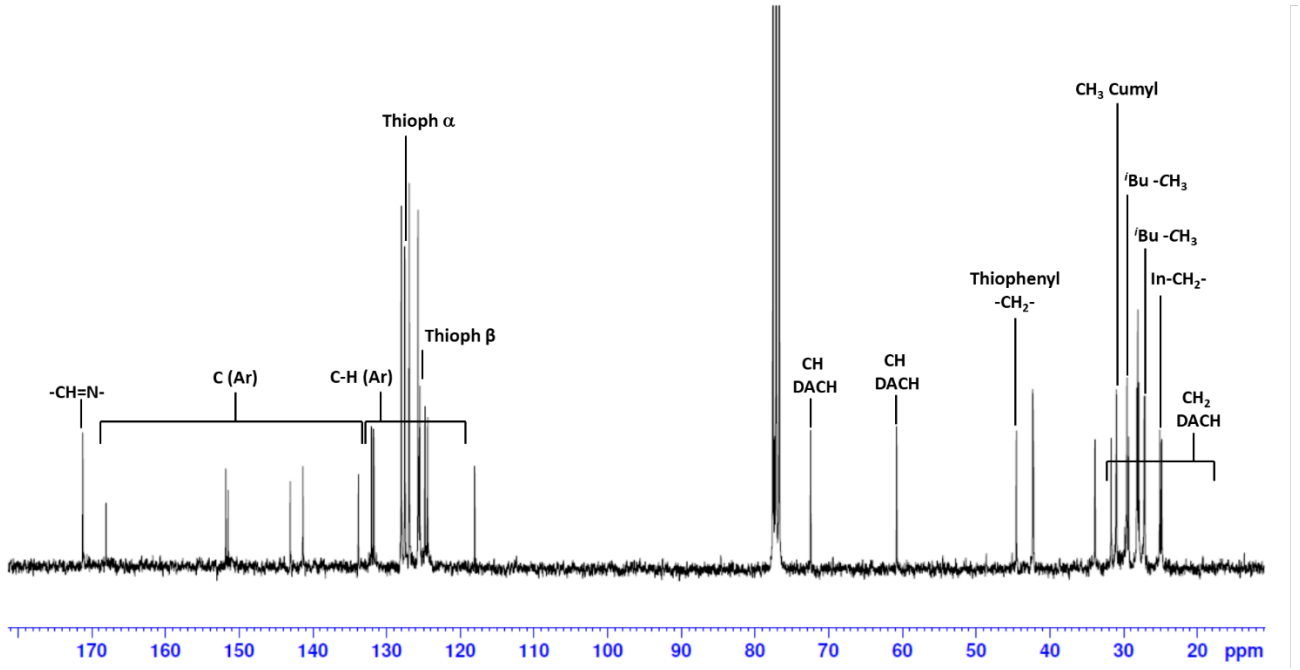


Figure S18 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of **1a**

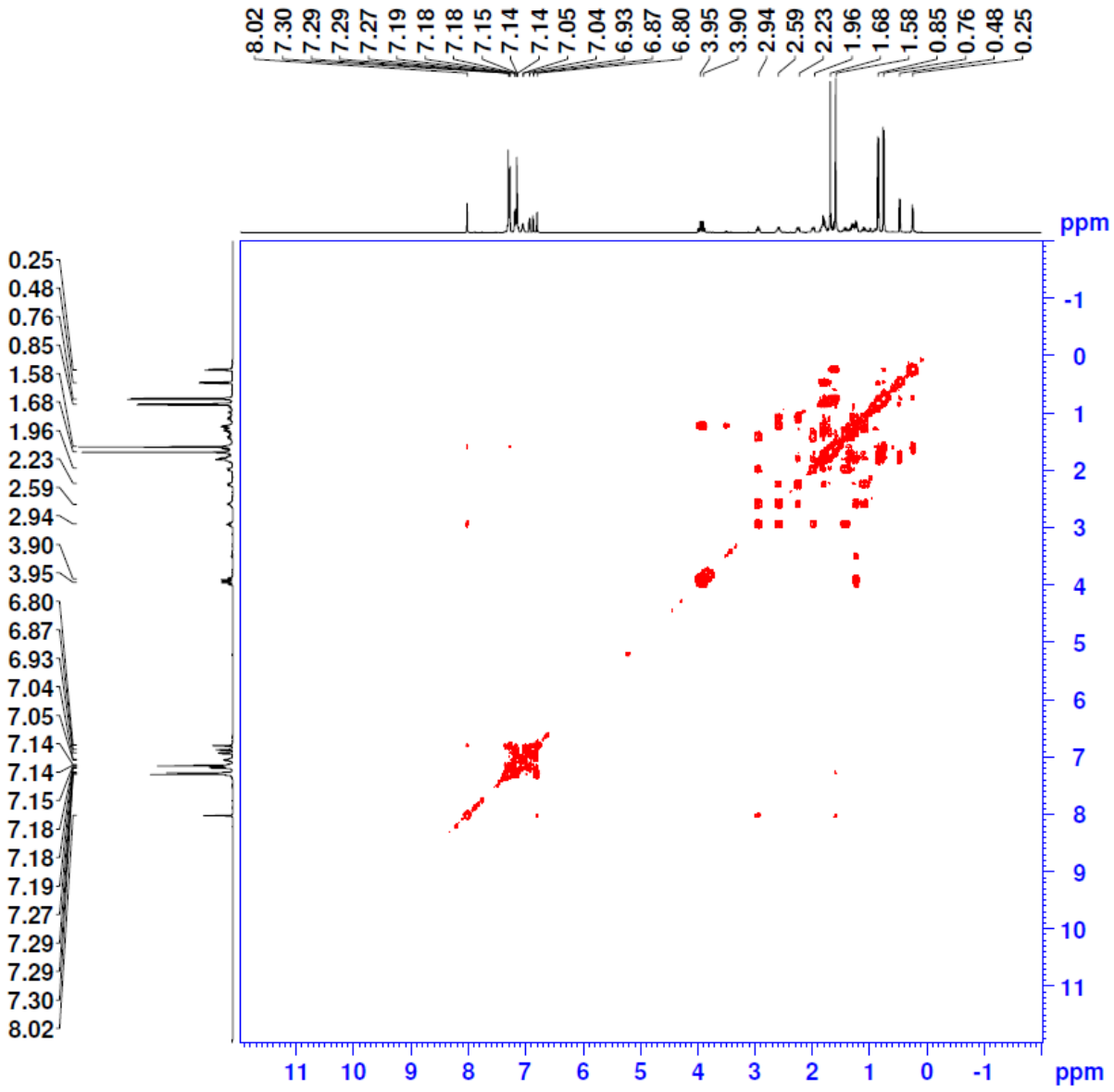


Figure S19 ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **1a**.

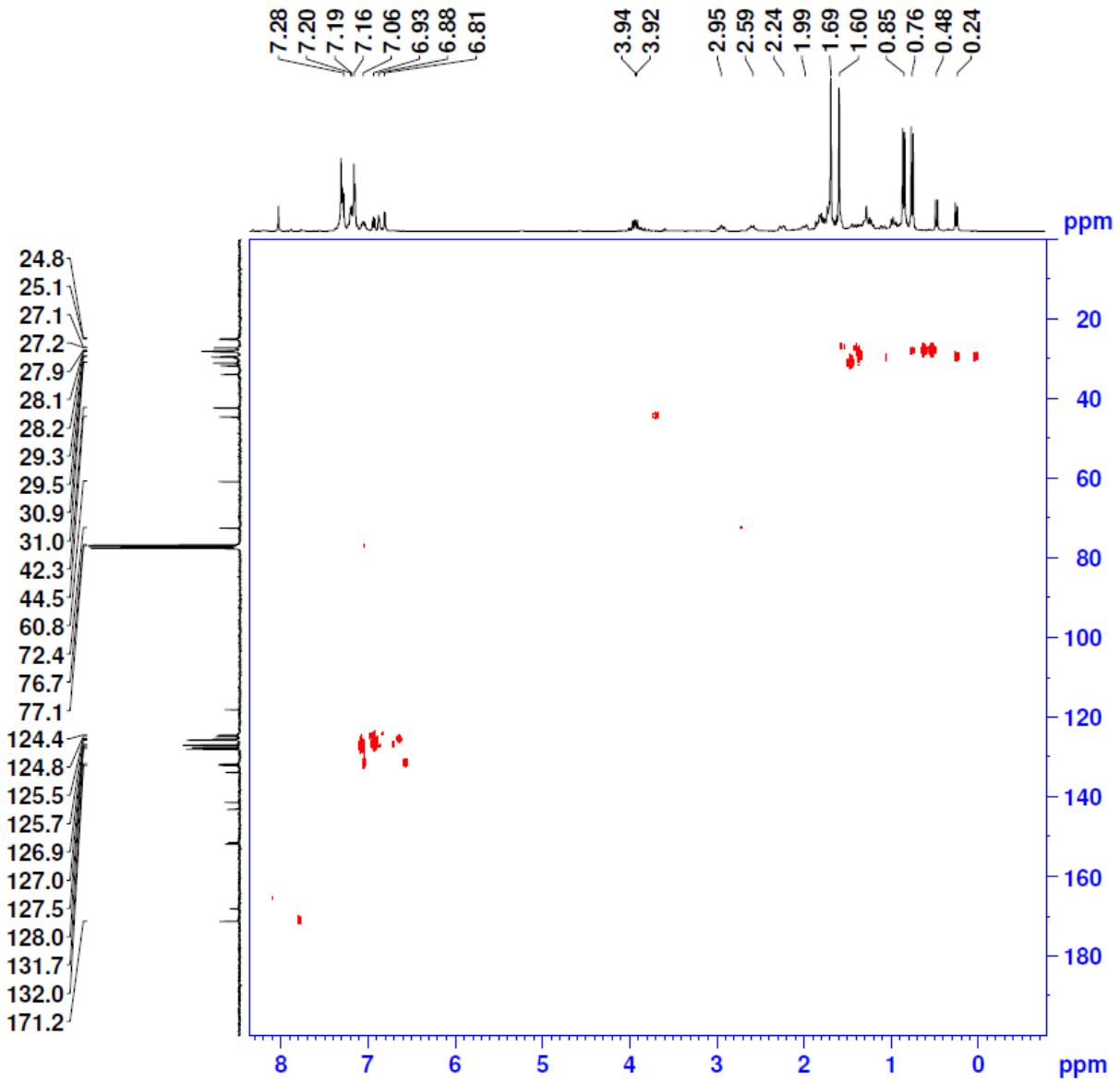


Figure S20 ^{1}H-^{13}C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum ($CDCl_3$, 25 °C) of **1a.**

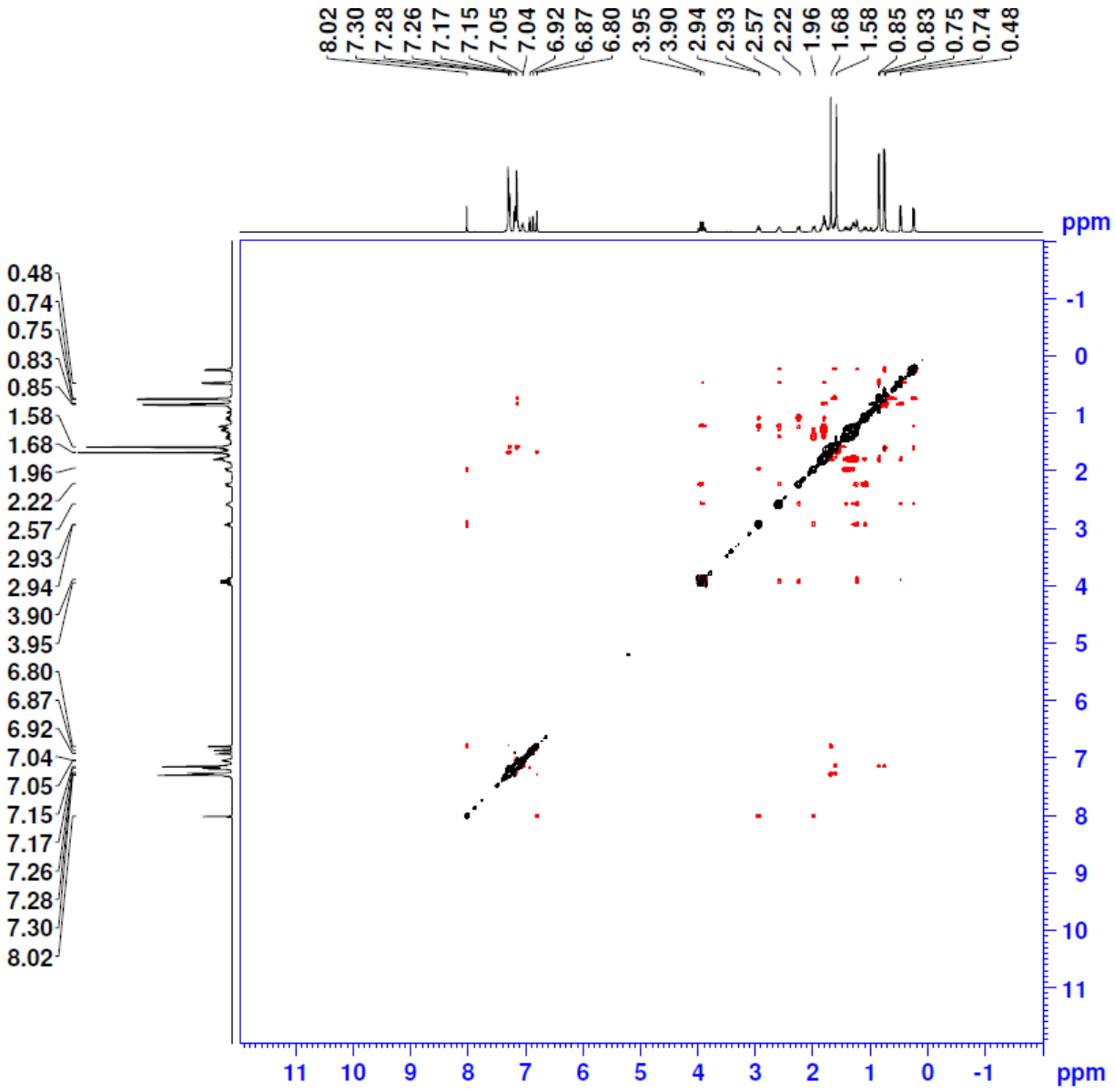


Figure S21 Nuclear Overhauser Effect spectroscopy (NOESY) NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **1a**

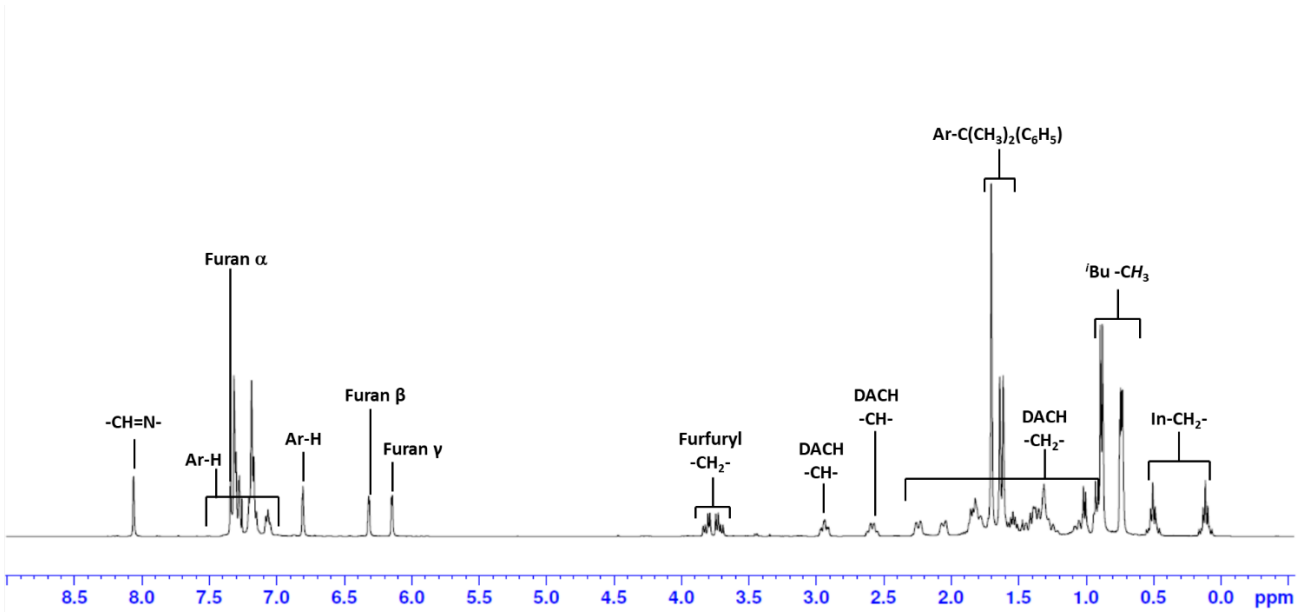


Figure S22 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **1b.**

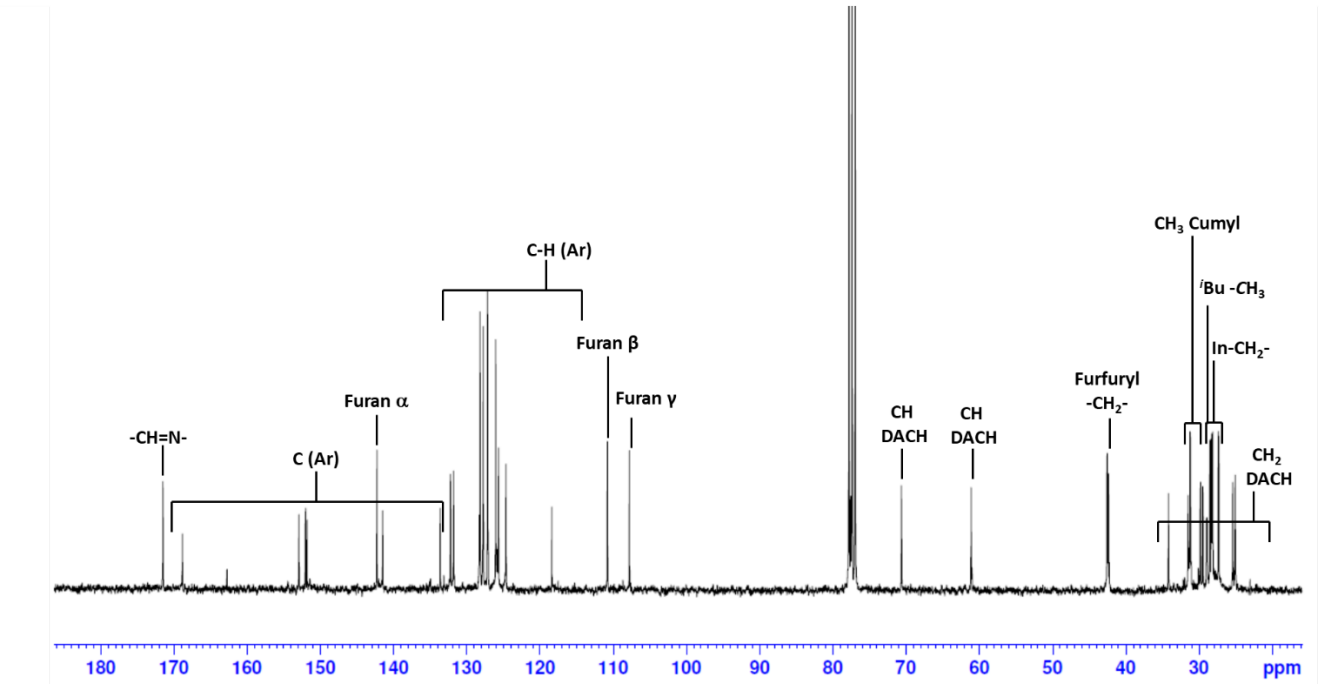


Figure S23 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of **1b**

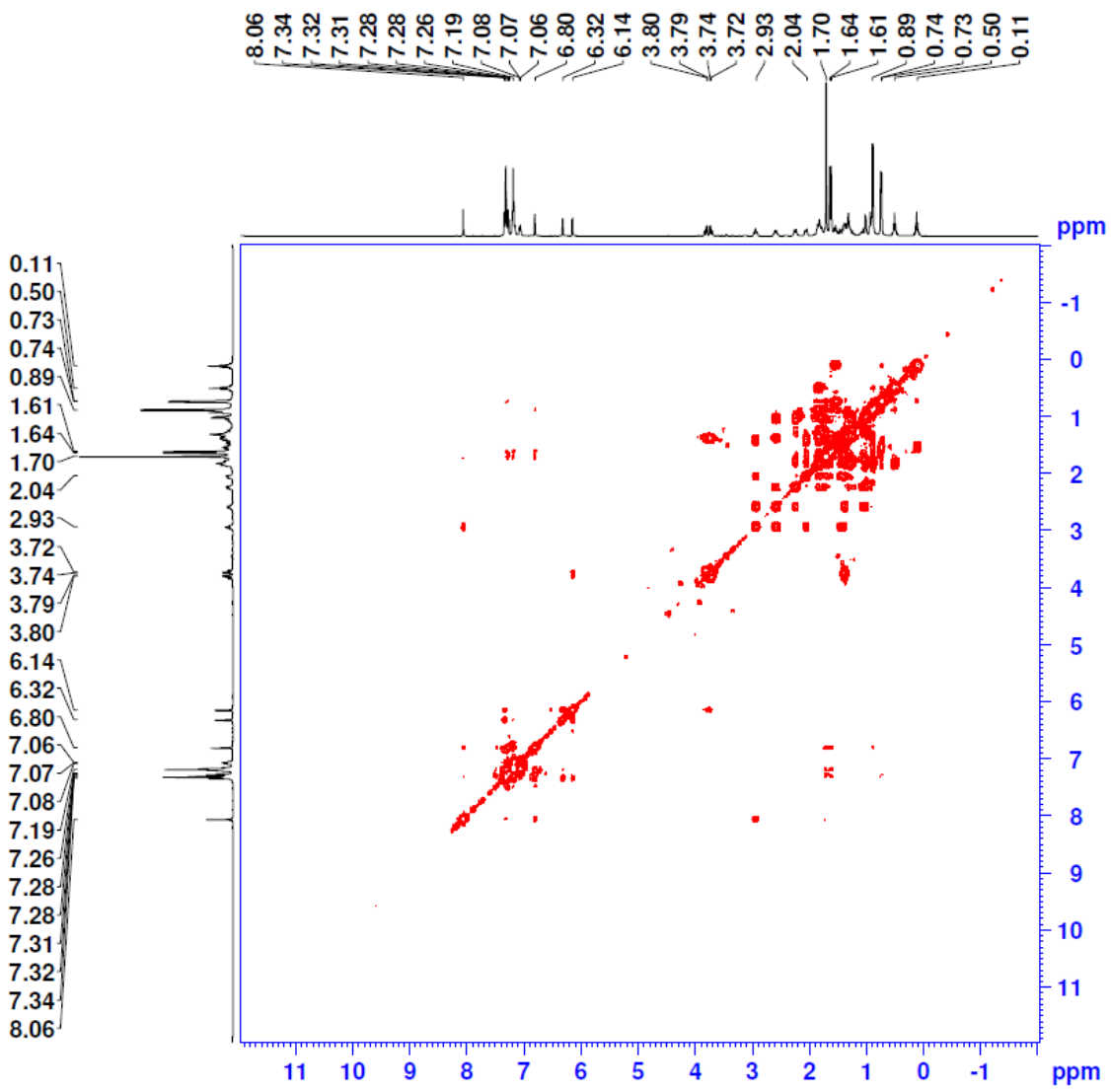


Figure S24 ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **1b**

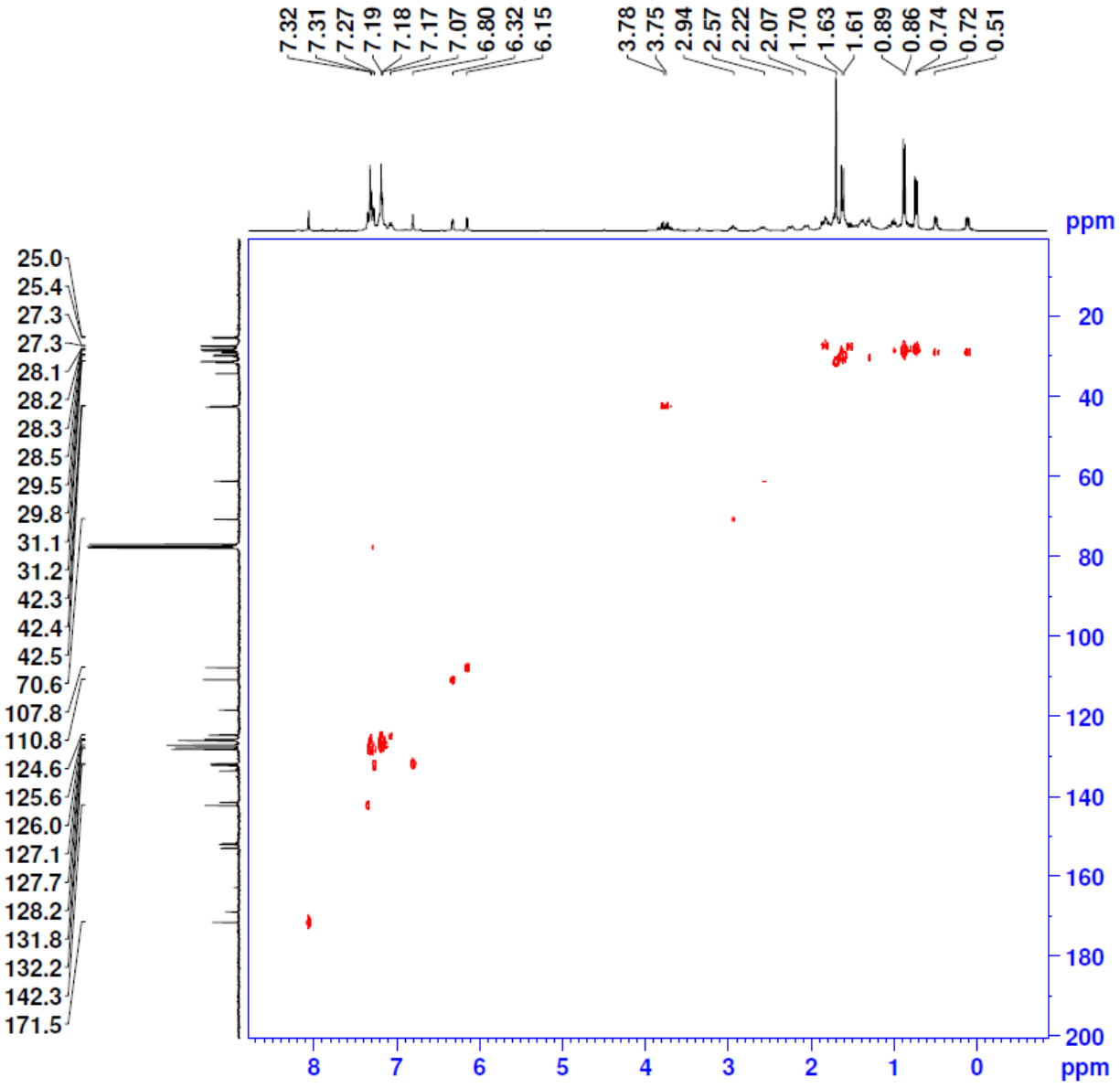


Figure S25 ^{1}H-^{13}C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum ($CDCl_3$, 25 °C) of **1b.**

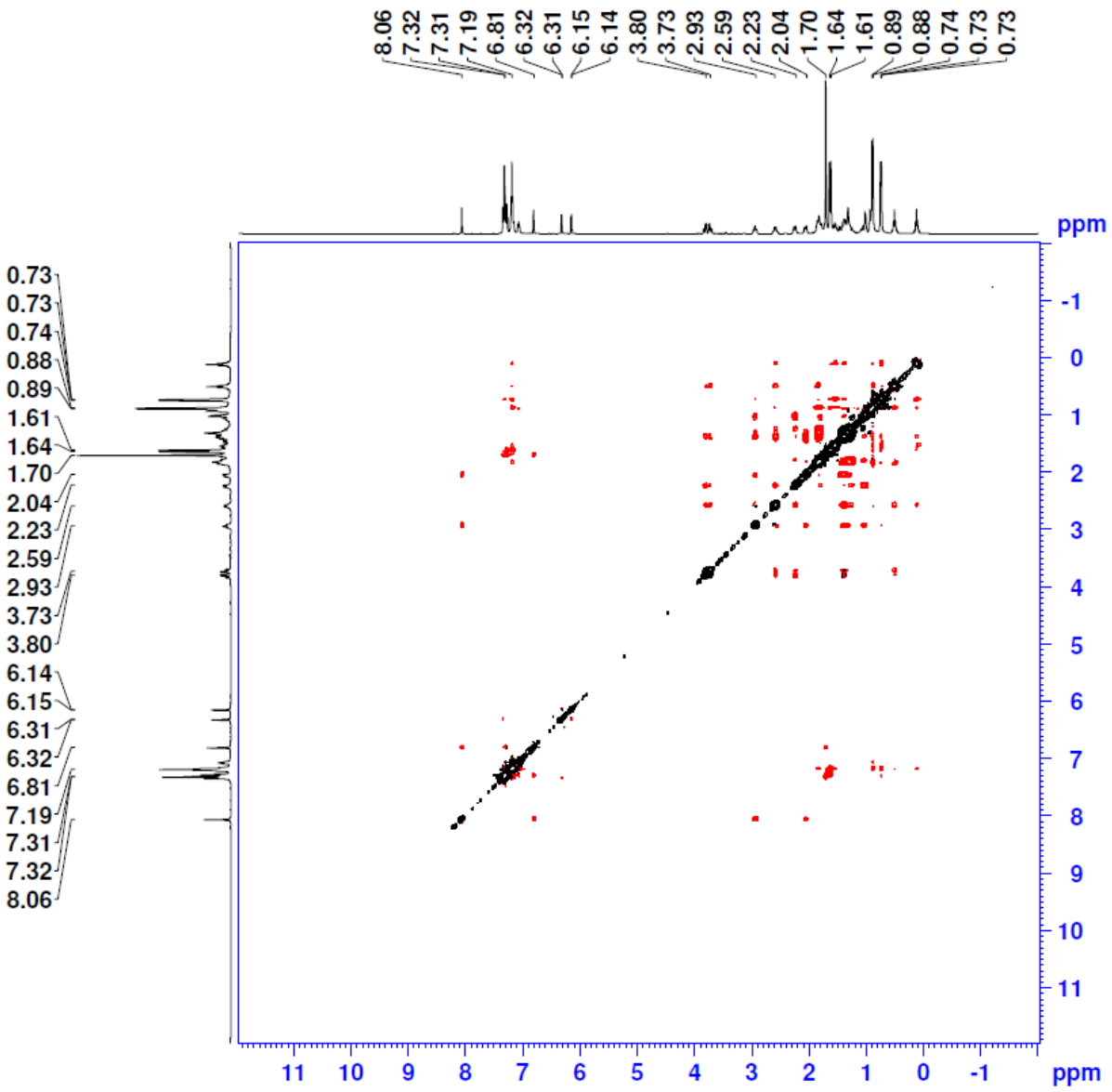


Figure S26 Nuclear Overhauser Effect spectroscopy (NOESY) NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **1b.**

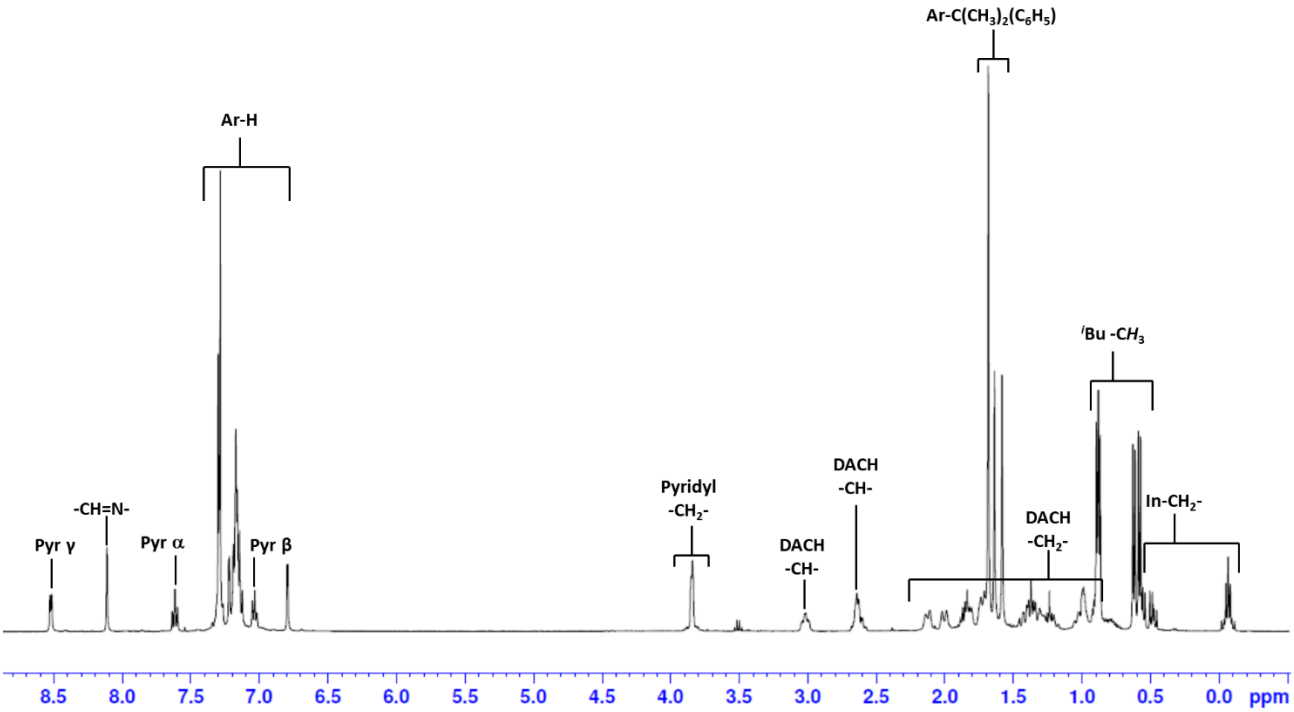


Figure S27 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **1c.**

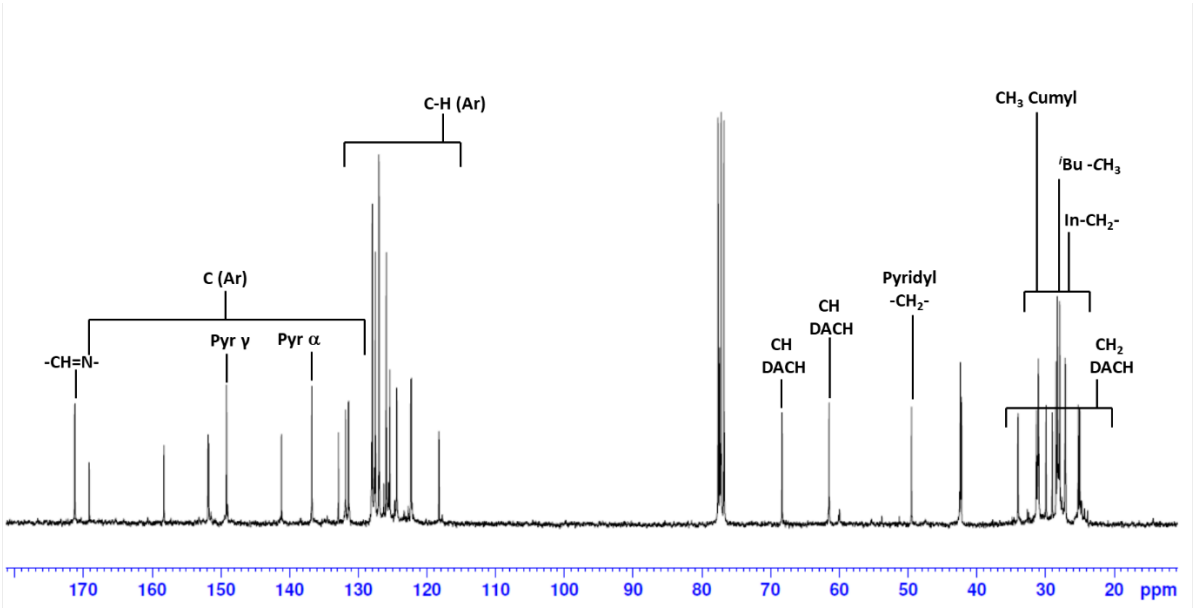


Figure S28 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of **1c**

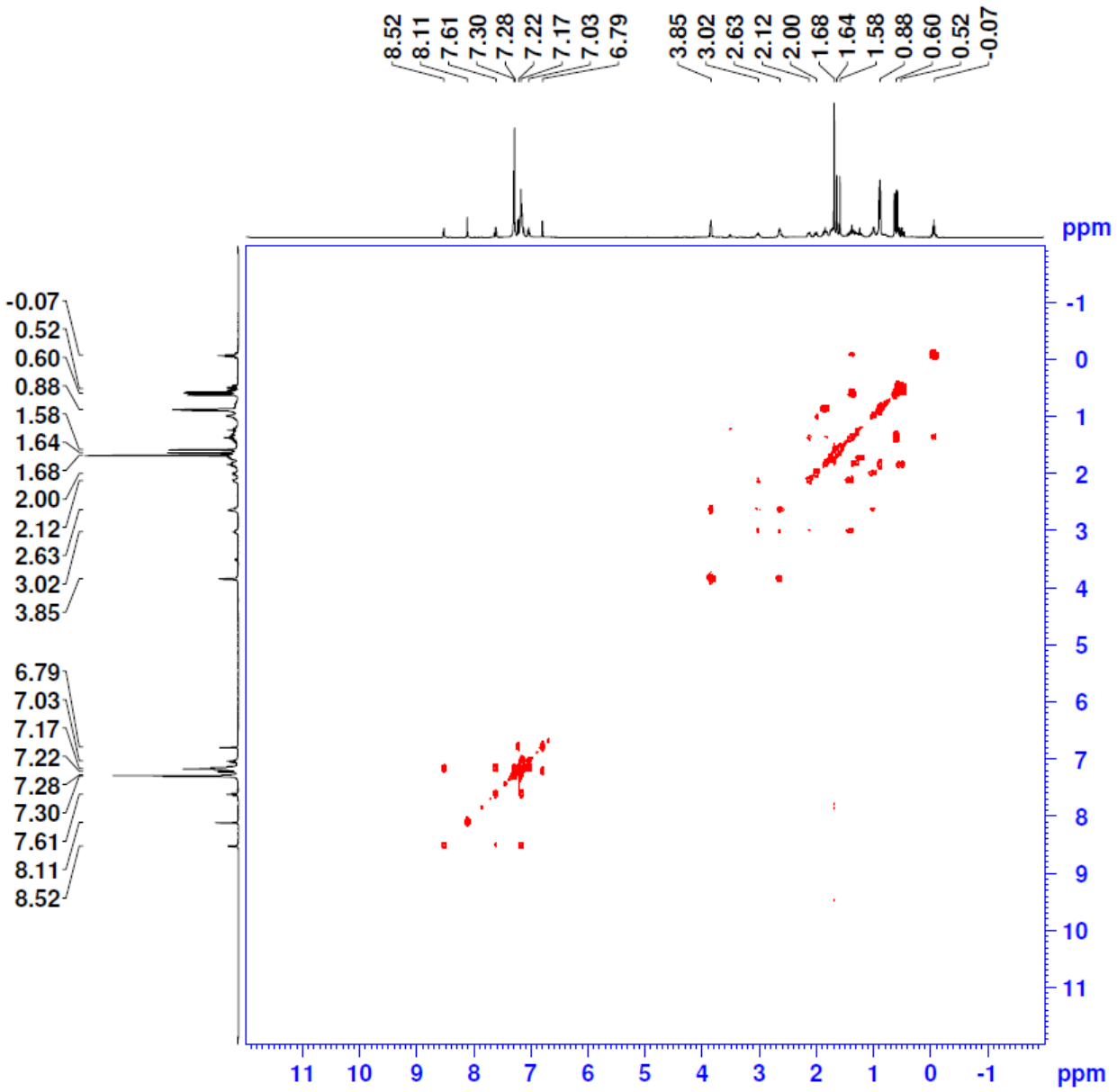


Figure S29 ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **1c**

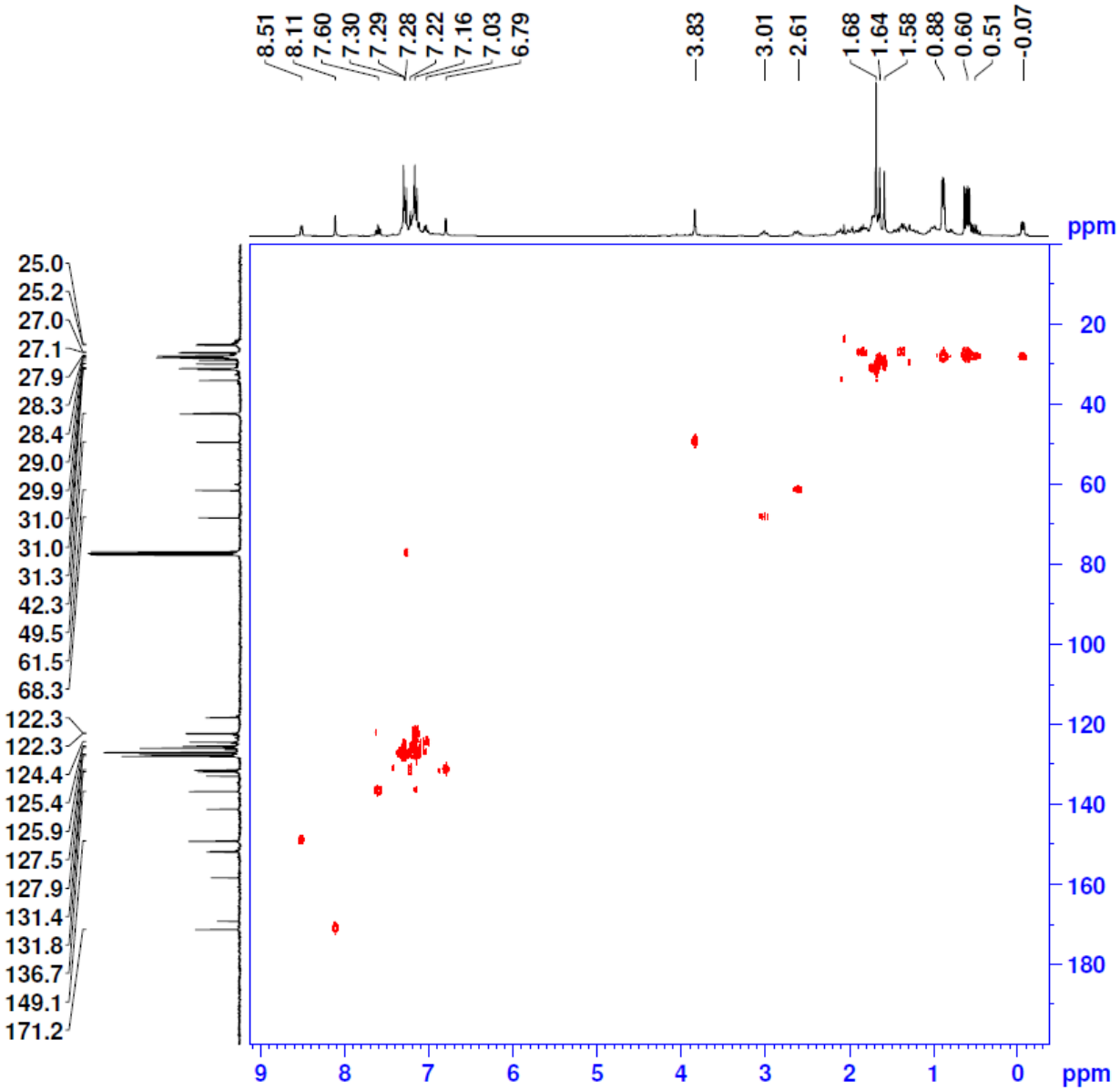


Figure S30 ^{1}H-^{13}C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum ($CDCl_3$, 25 °C) of **1c.**

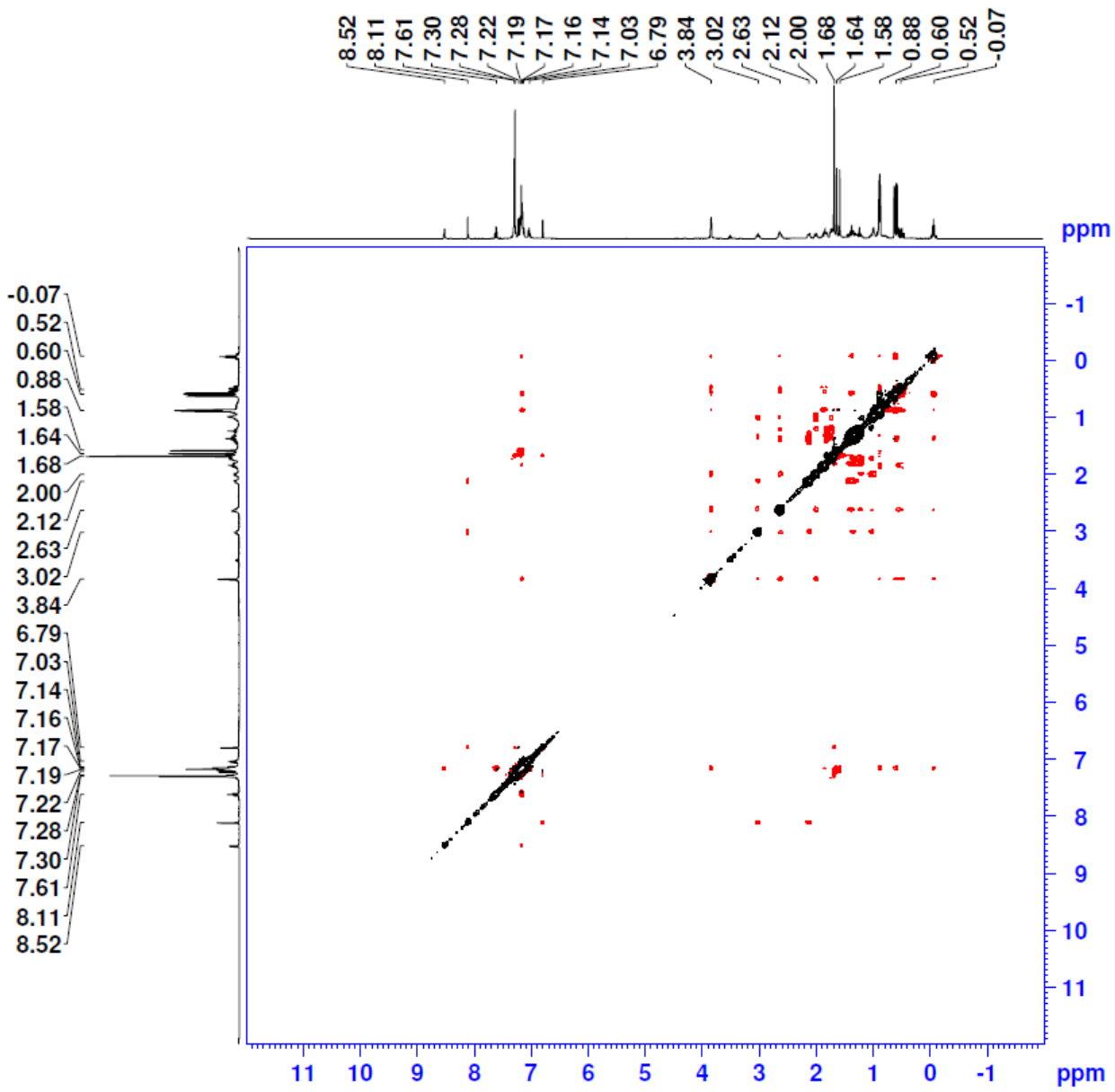


Figure S31 Nuclear Overhauser Effect spectroscopy (NOESY) NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **1c.**

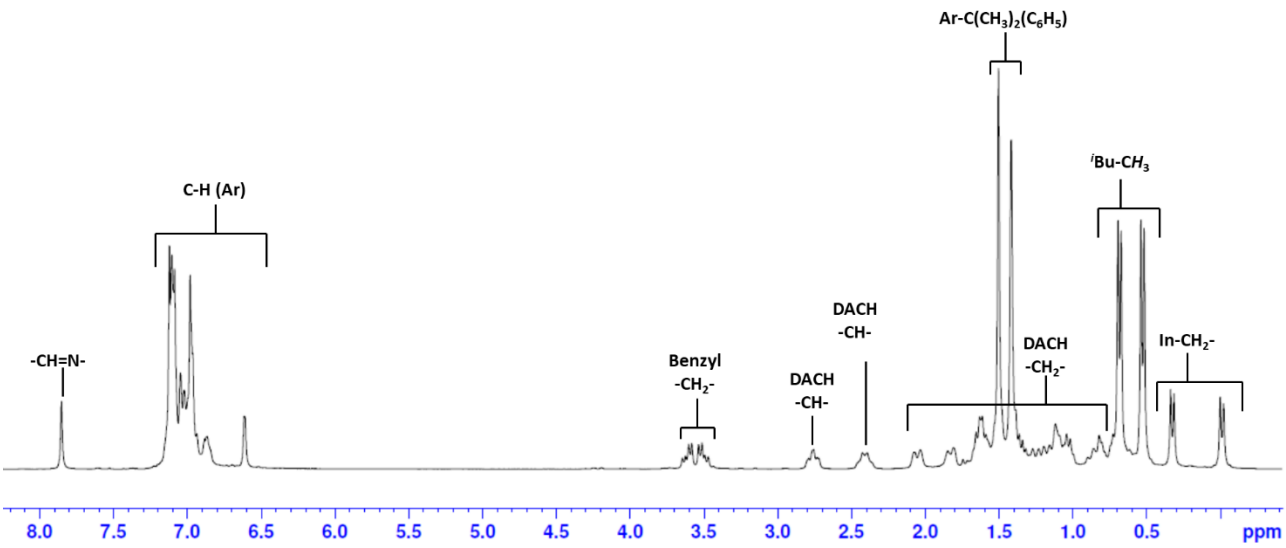


Figure S32 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **1d.**

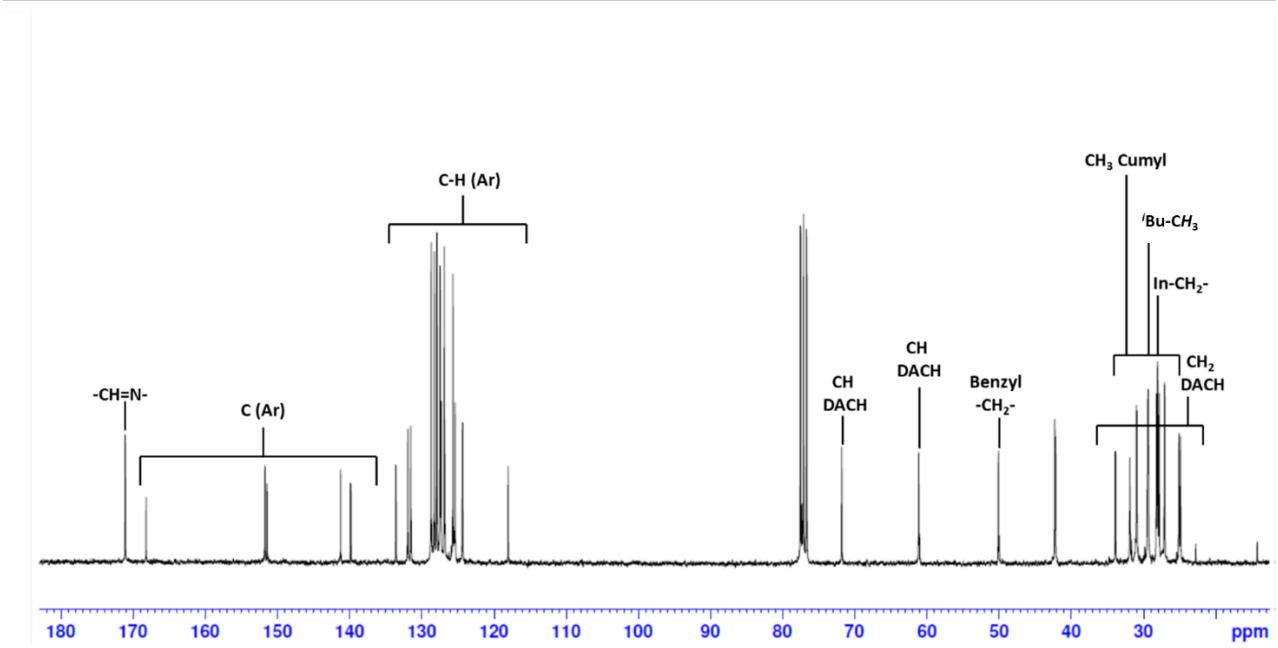


Figure S33 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of **1d**

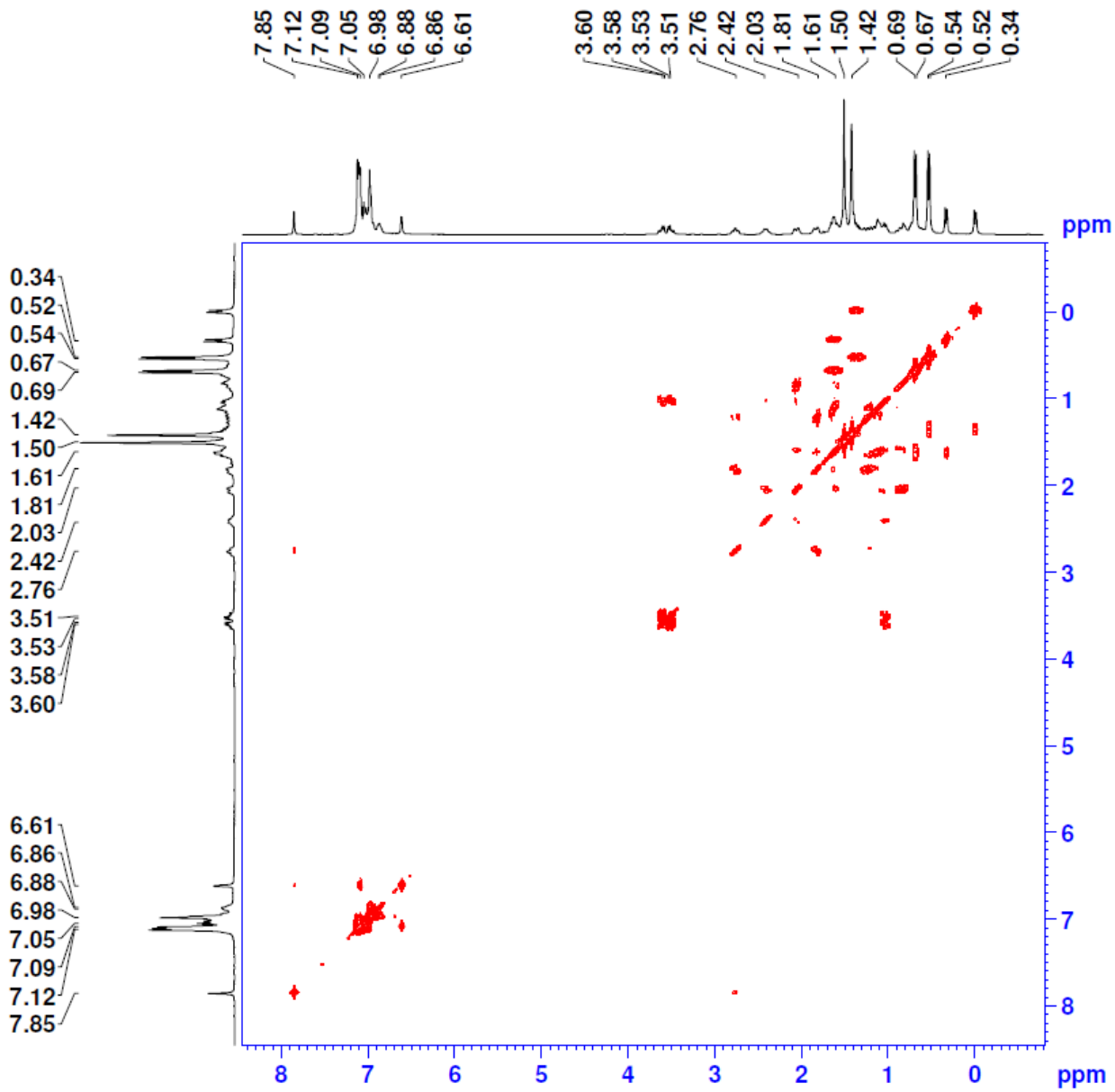


Figure S34 ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **1d.**

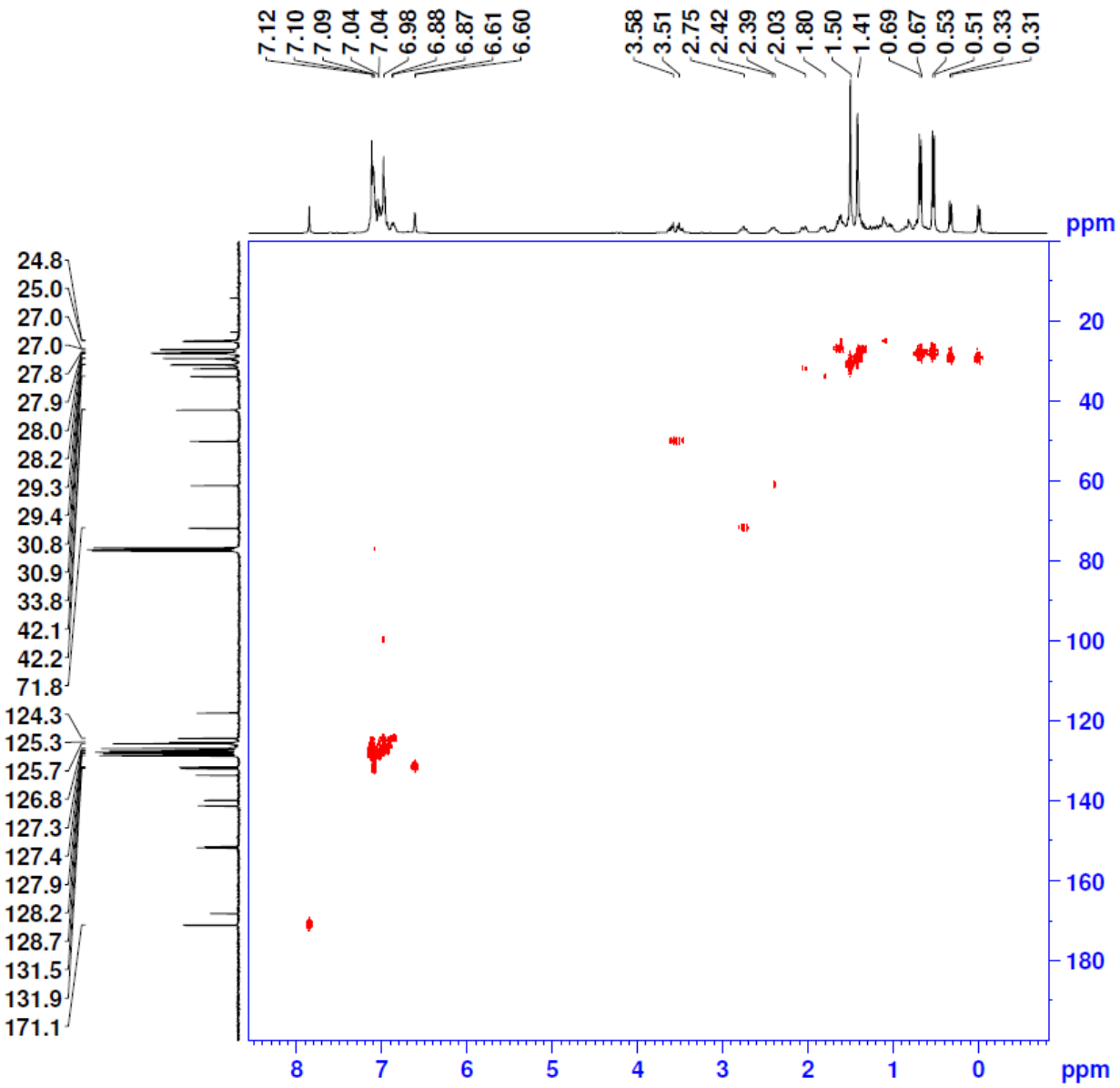


Figure S35 ^{1}H-^{13}C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum ($CDCl_3$, 25 °C) of **1d.**

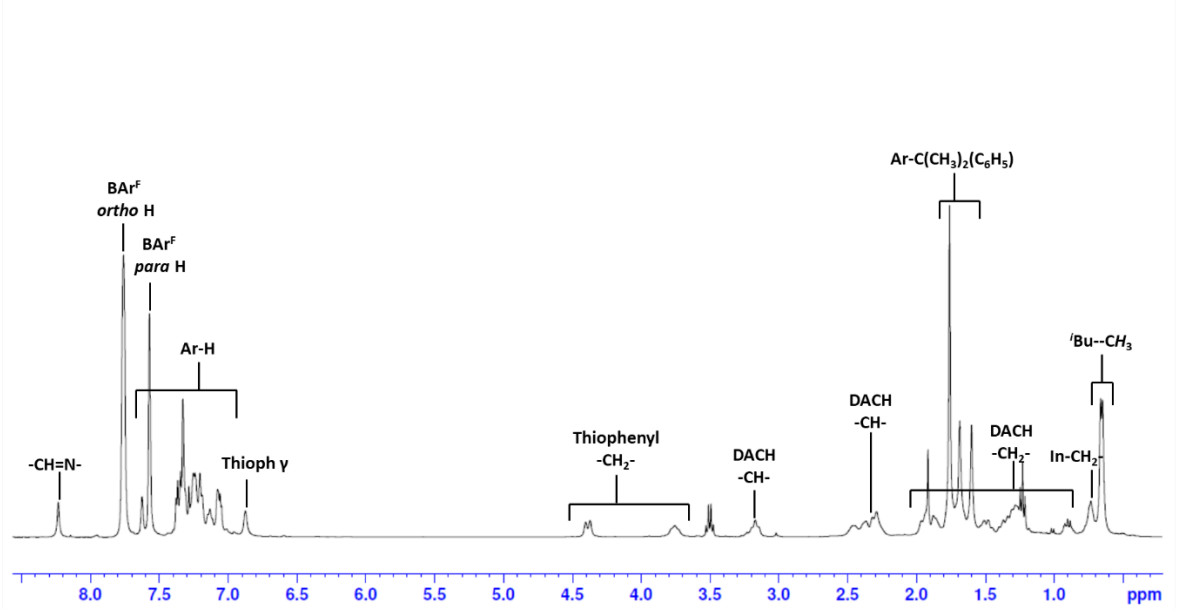


Figure S36 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of **2a**. (Residual diethyl ether q, 3.48 and t, 1.22 ppm)

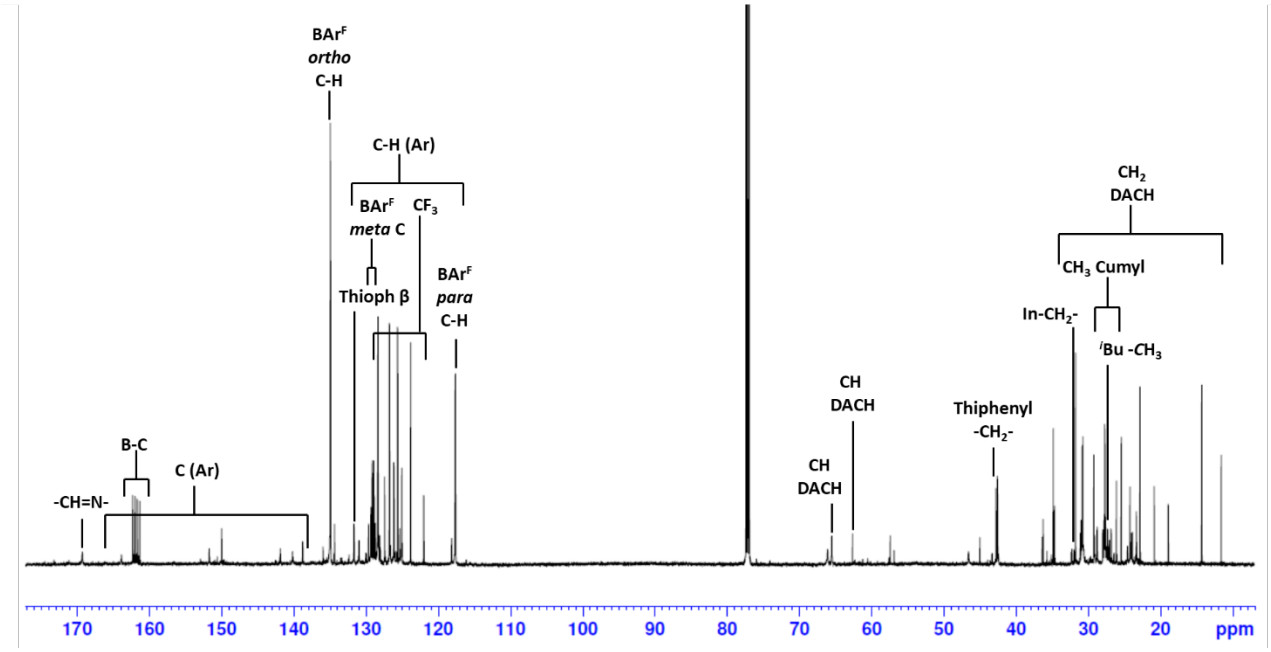


Figure S37 $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$, 25 °C) of **2a**

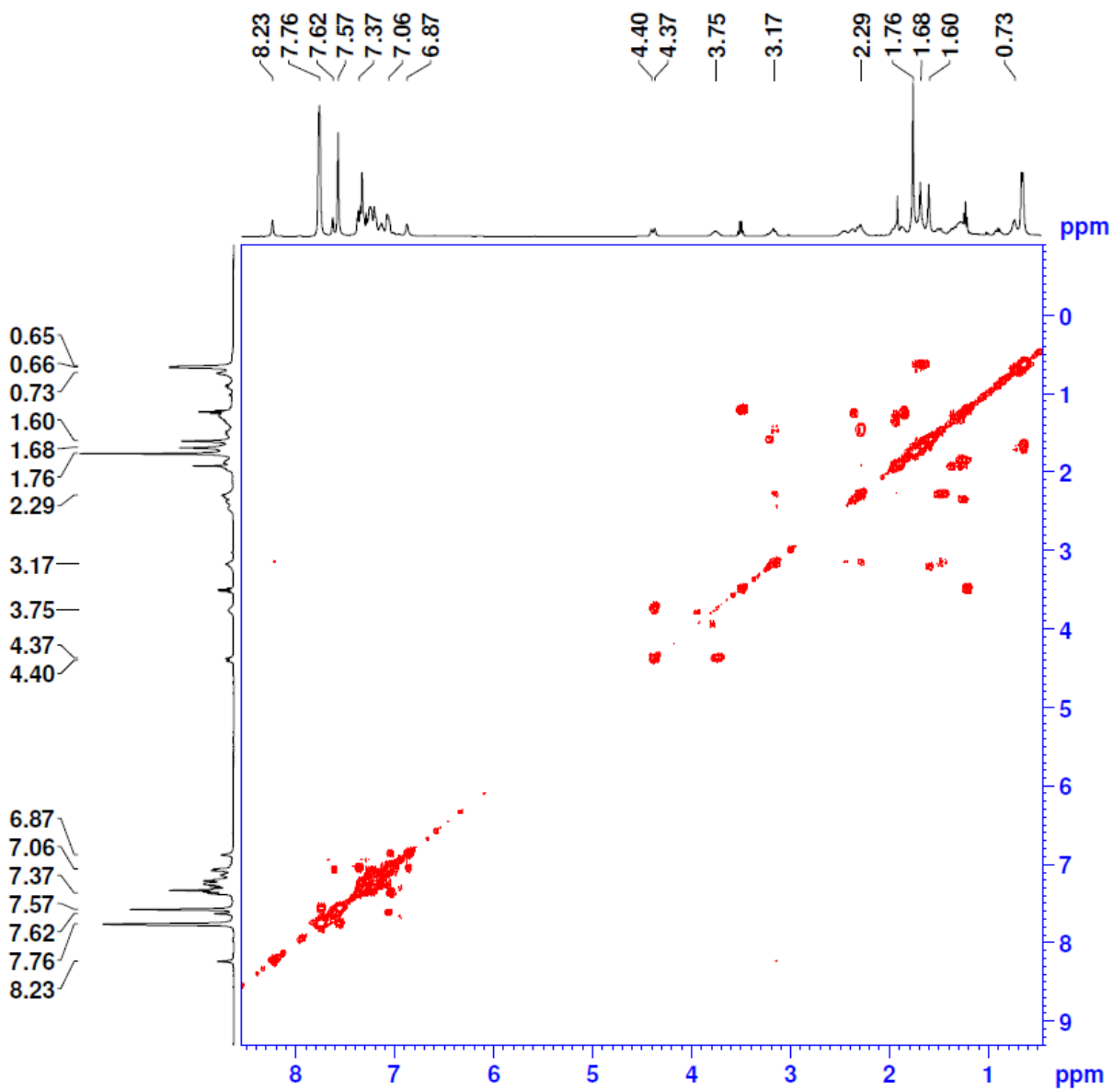


Figure S38 ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **2a.**

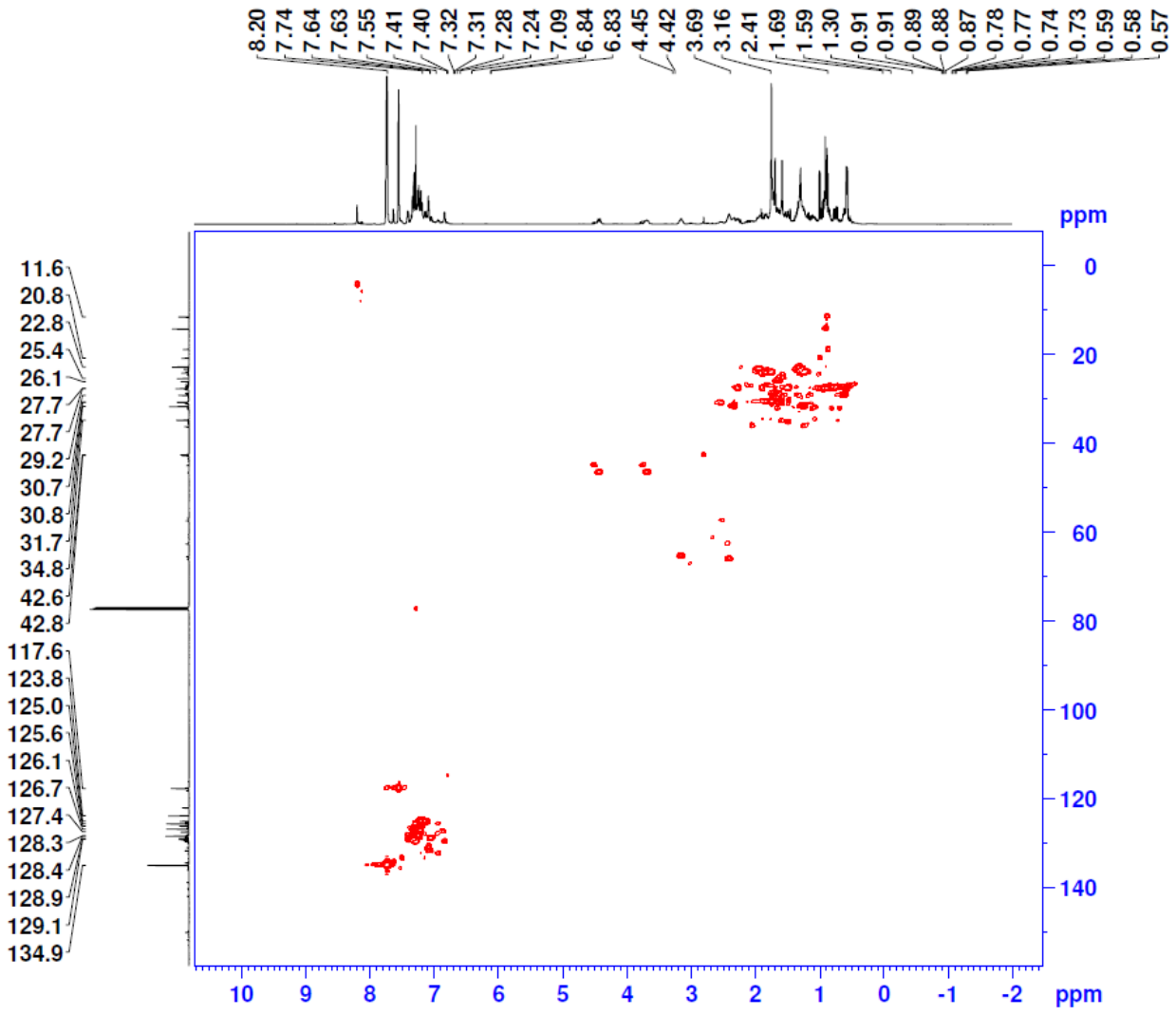


Figure S39 ^{1}H-^{13}C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum ($CDCl_3$, 25 °C) of **2a.**

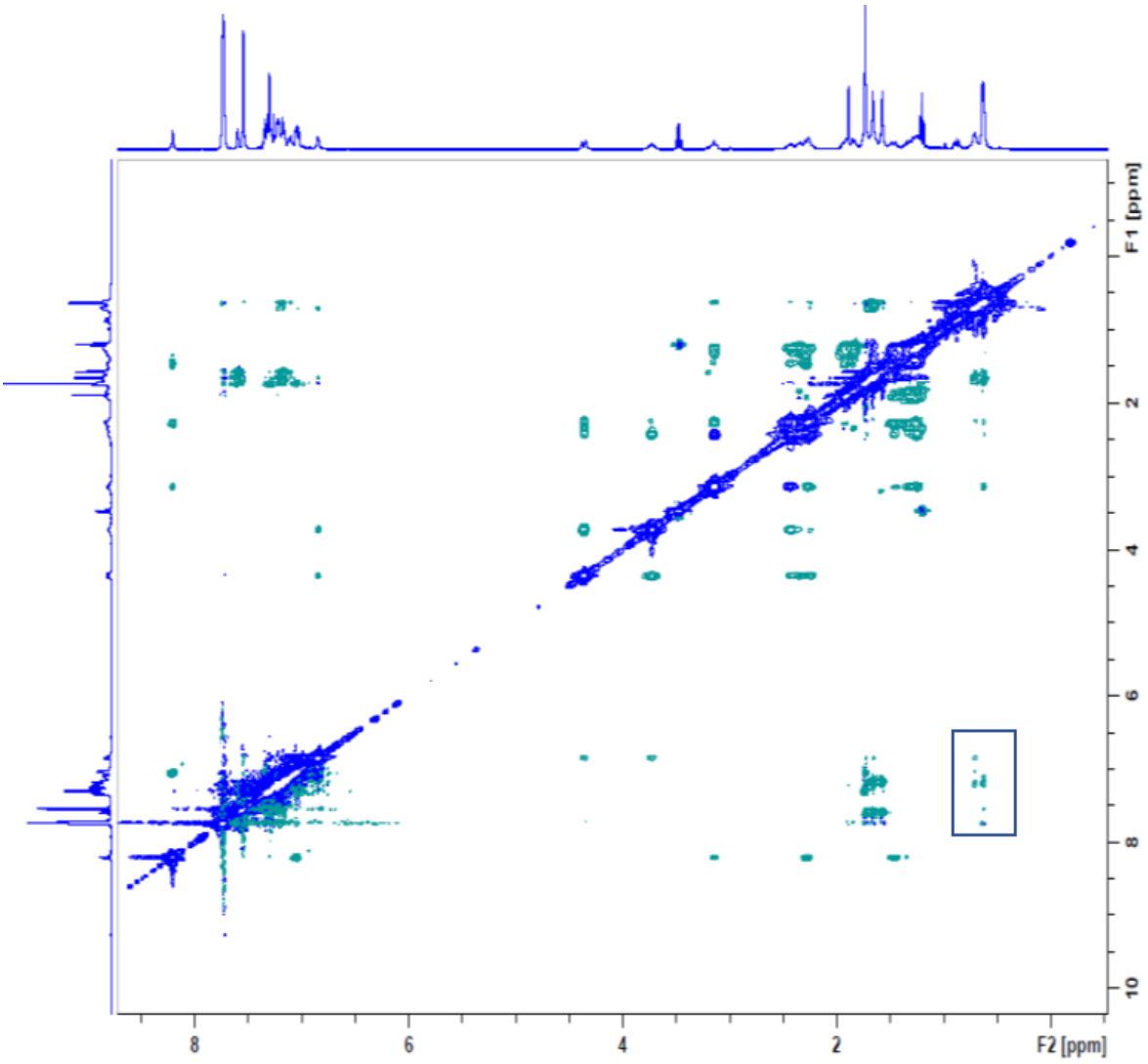


Figure S40 Nuclear Overhauser Effect spectroscopy (NOESY) NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **2a.**

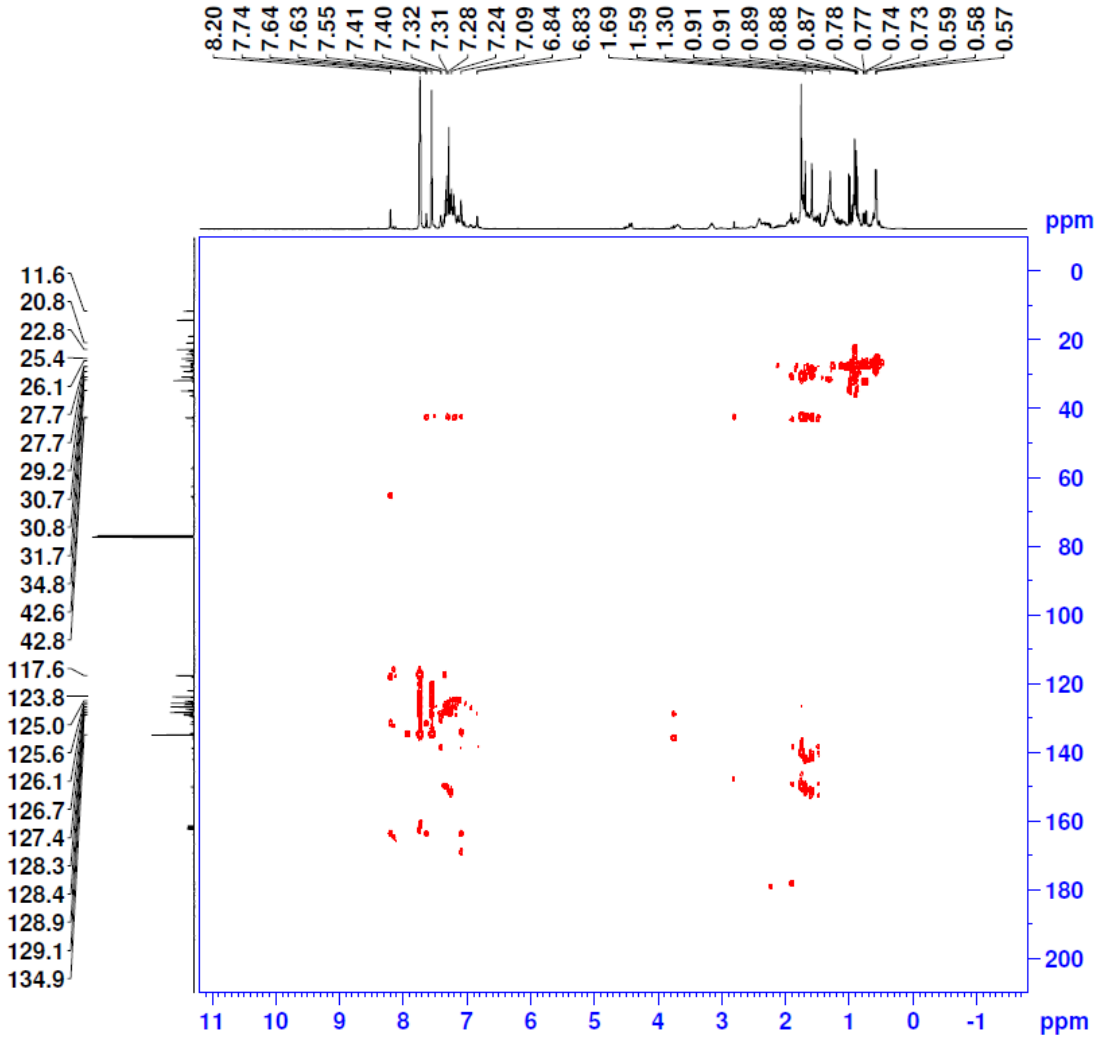


Figure S41 ^{1}H-^{13}C Heteronuclear Multiple Bond Correlation (HMBC) NMR spectrum ($CDCl_3$, 25 °C) of **2b**.

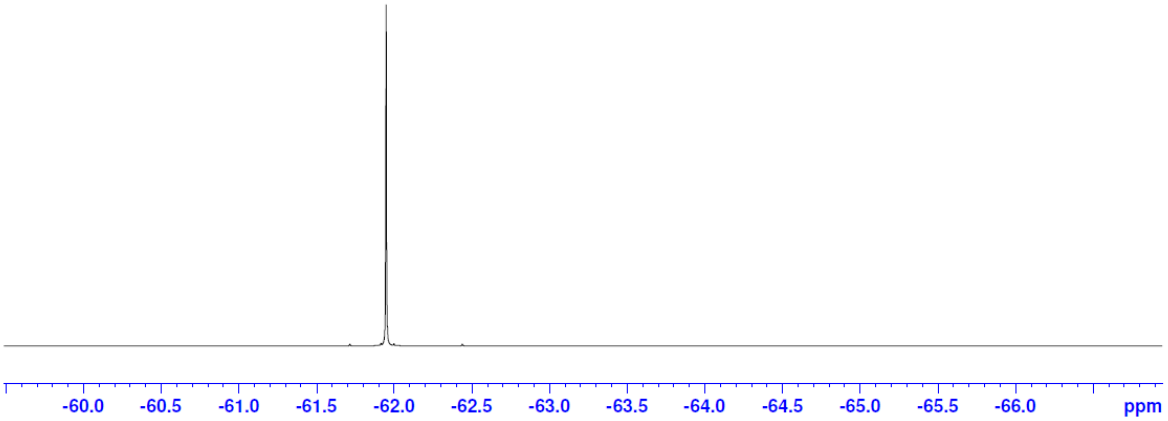


Figure S42 $^{19}F\{^{1}H\}$ NMR spectrum (282 MHz, $CDCl_3$, 25 °C) of **2a**

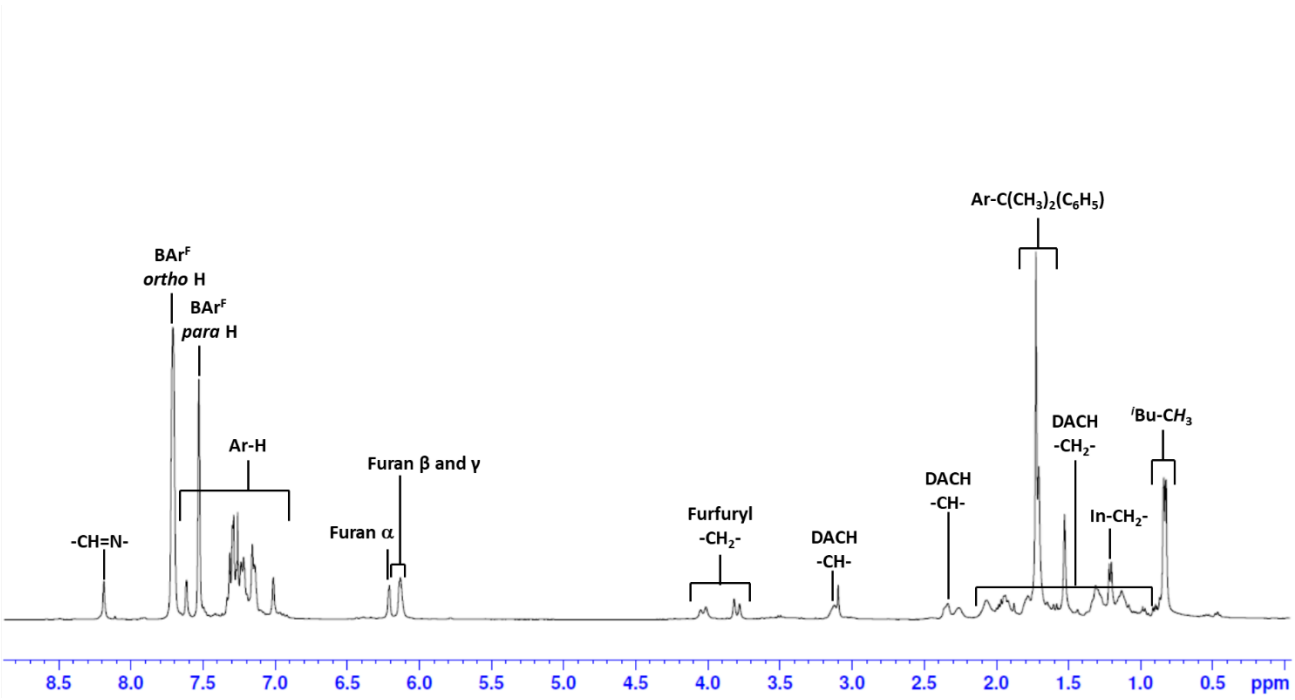


Figure S43 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of **2b**.

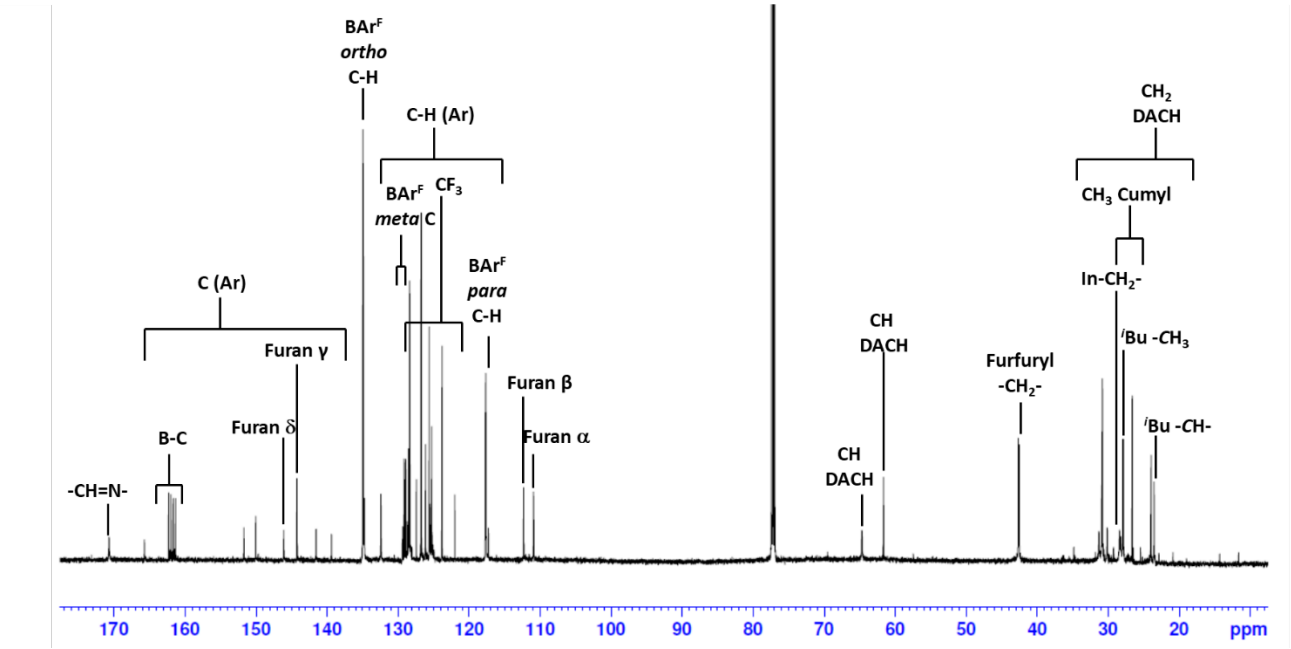


Figure S44 $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$, 25 °C) of **2b**

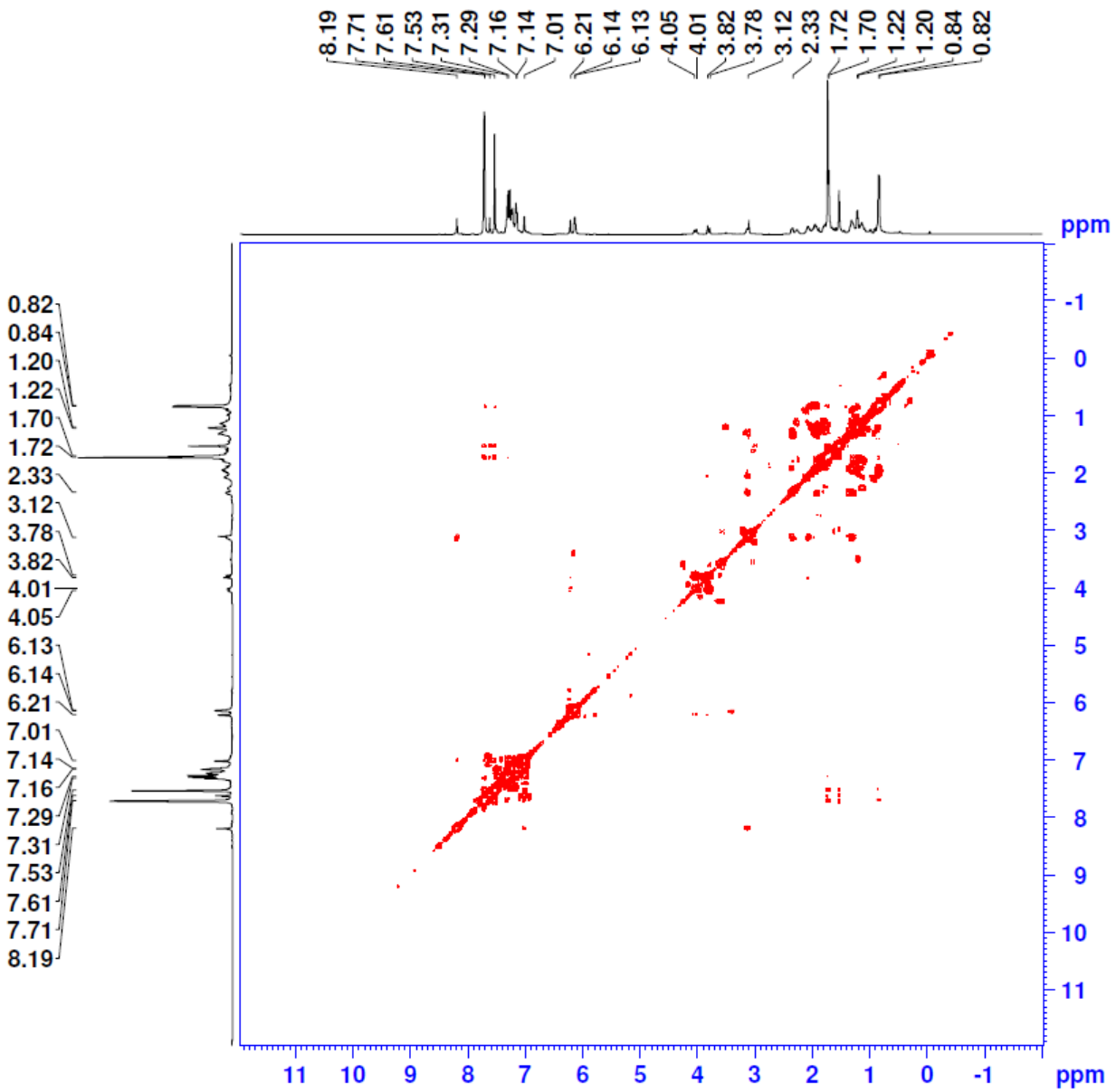


Figure S45 ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **2b.**

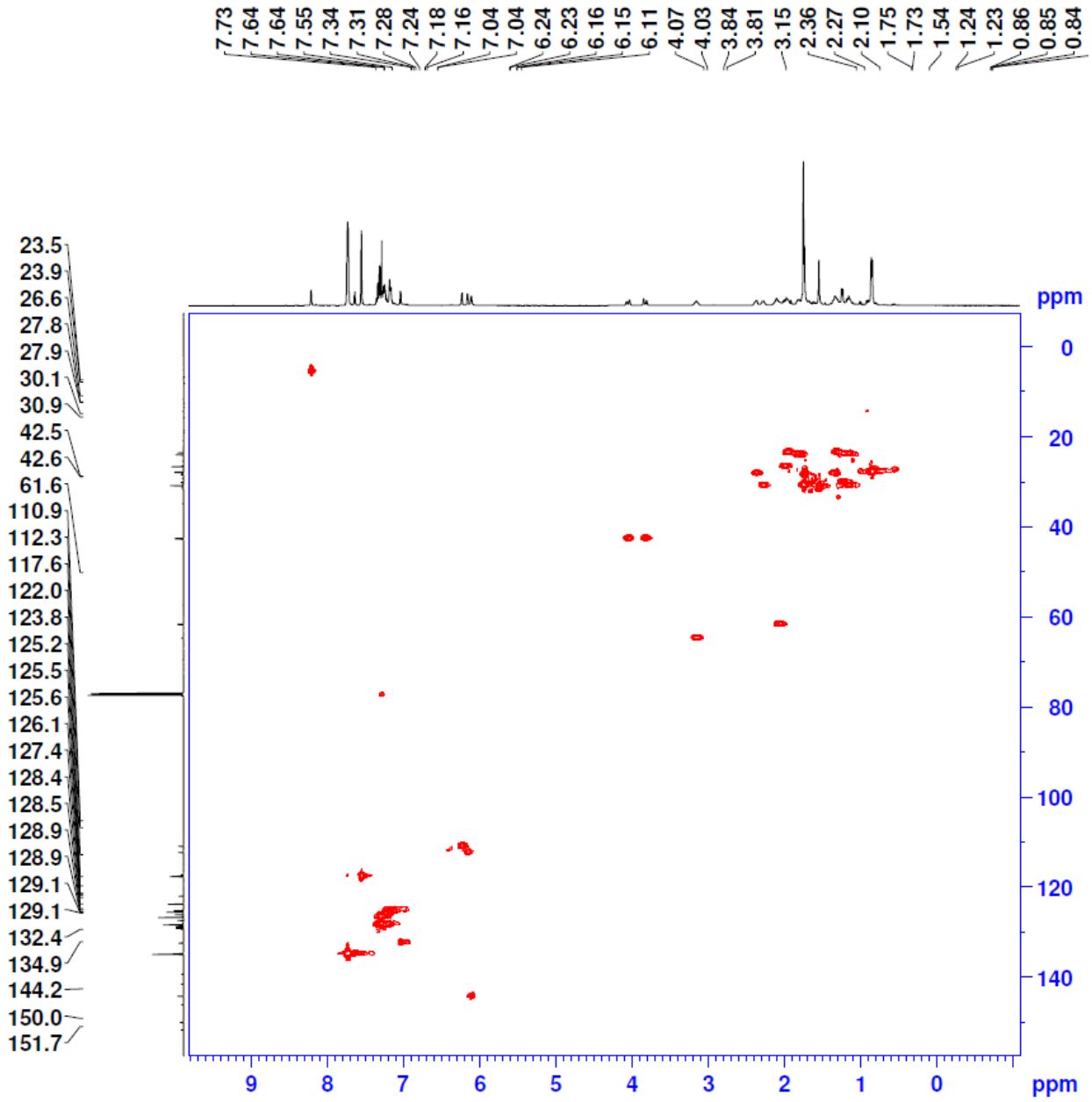


Figure S46 ^{1}H-^{13}C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum ($CDCl_3$, 25 °C) of **2b.**

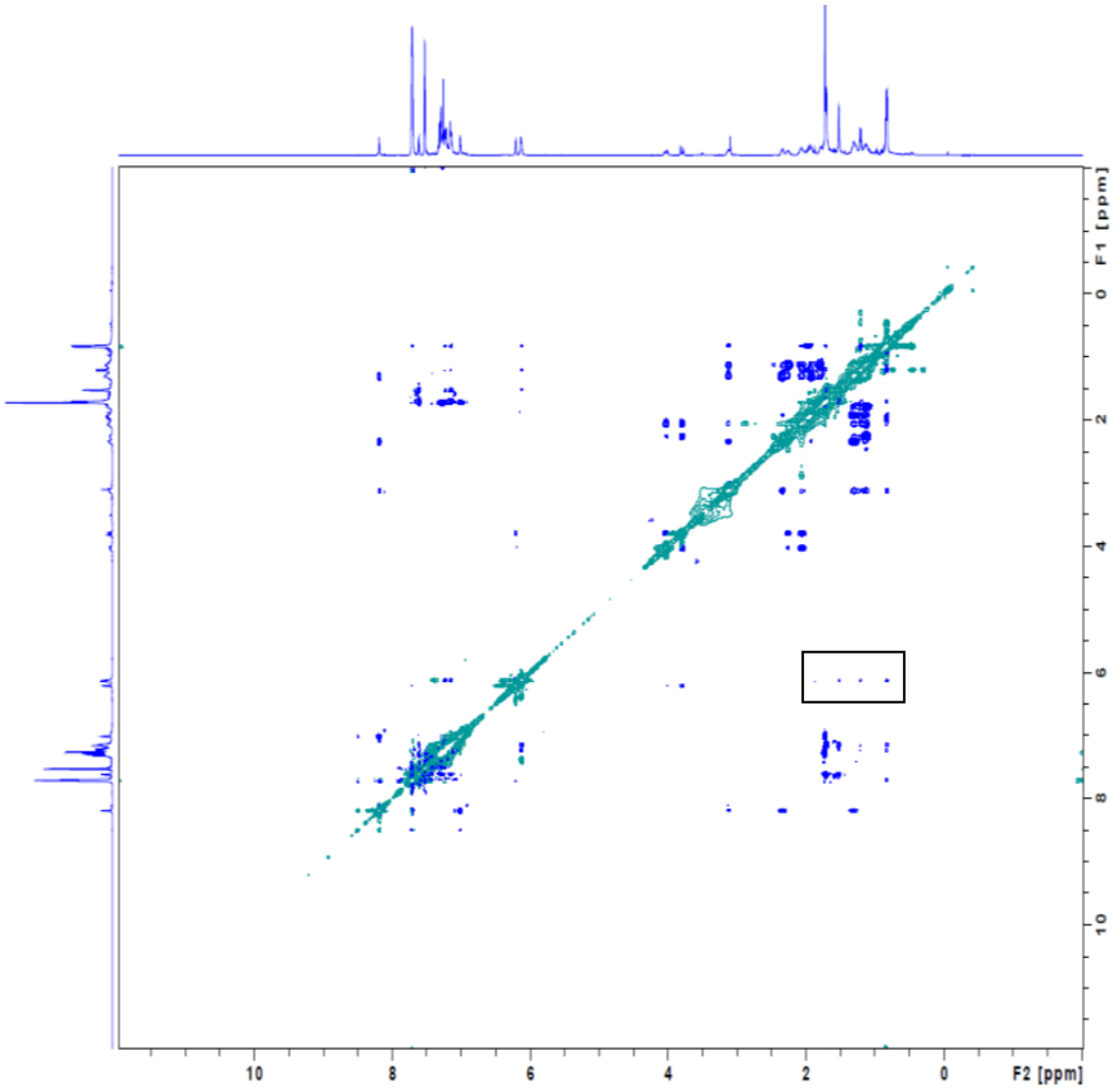


Figure S47 Nuclear Overhauser Effect spectroscopy (NOESY) NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **2b.**

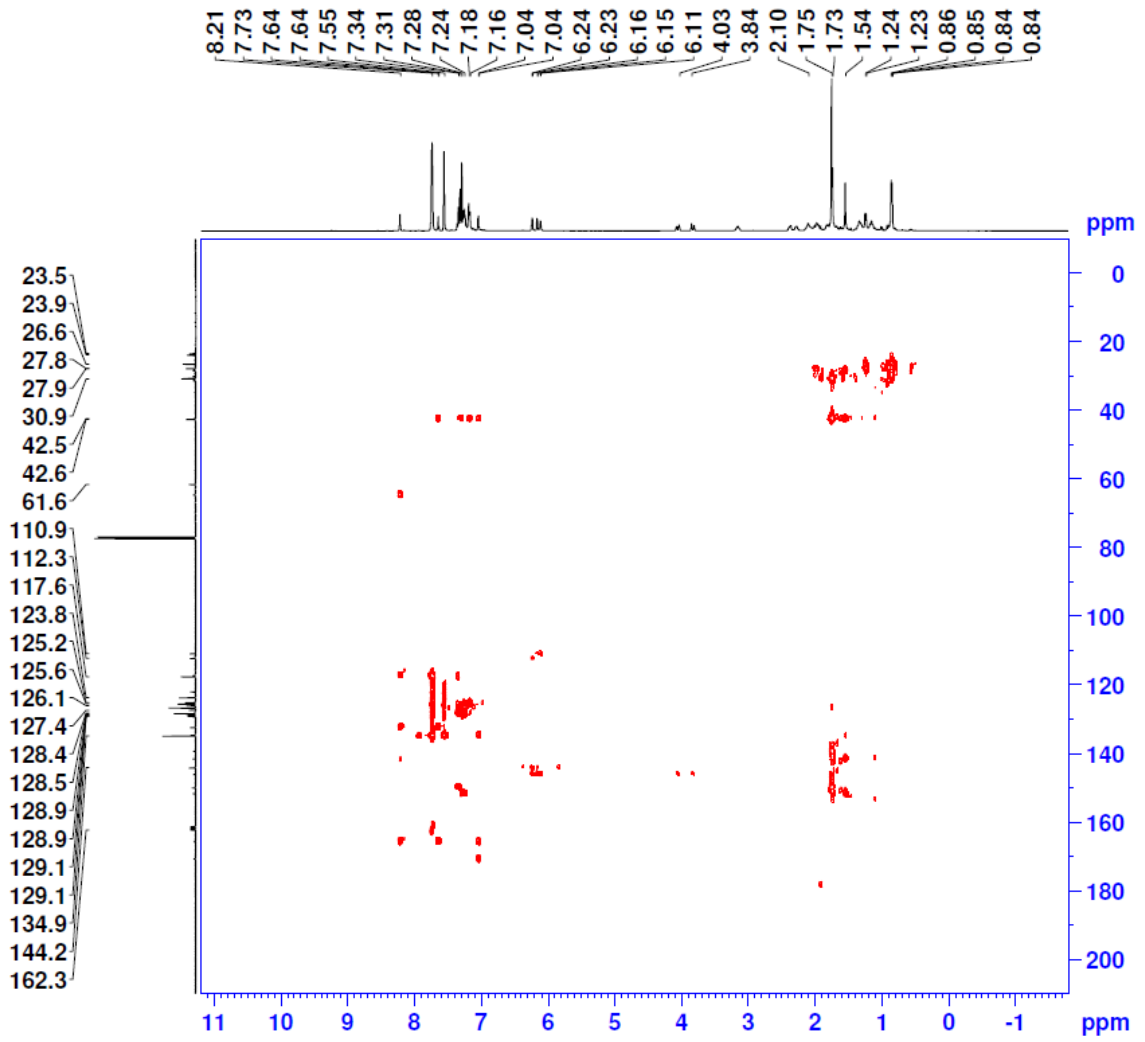


Figure S48 ^{1}H-^{13}C Heteronuclear Multiple Bond Correlation (HMBC) NMR spectrum ($CDCl_3$, 25 °C) of **2b**.

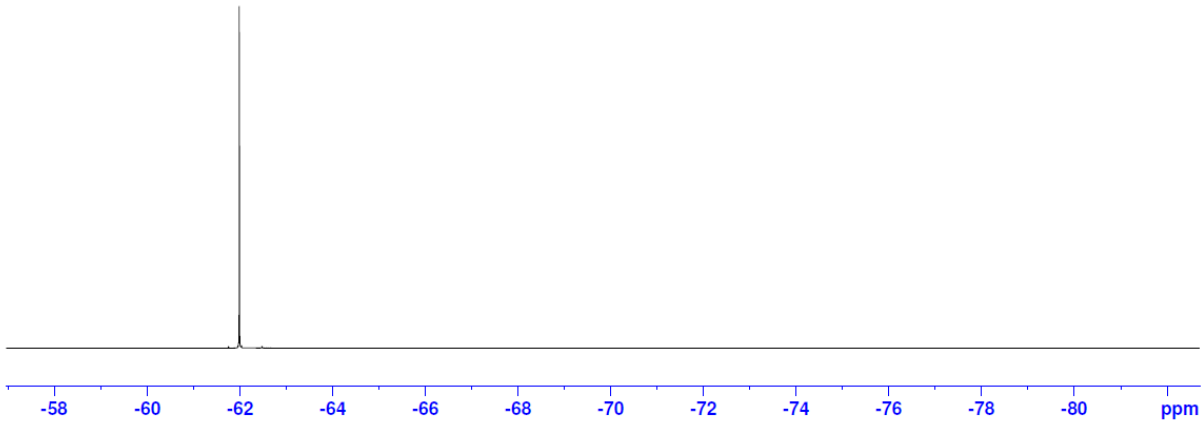


Figure S49 $^{19}F\{^{1}H\}$ NMR spectrum (282 MHz, $CDCl_3$, 25 °C) of **2b**

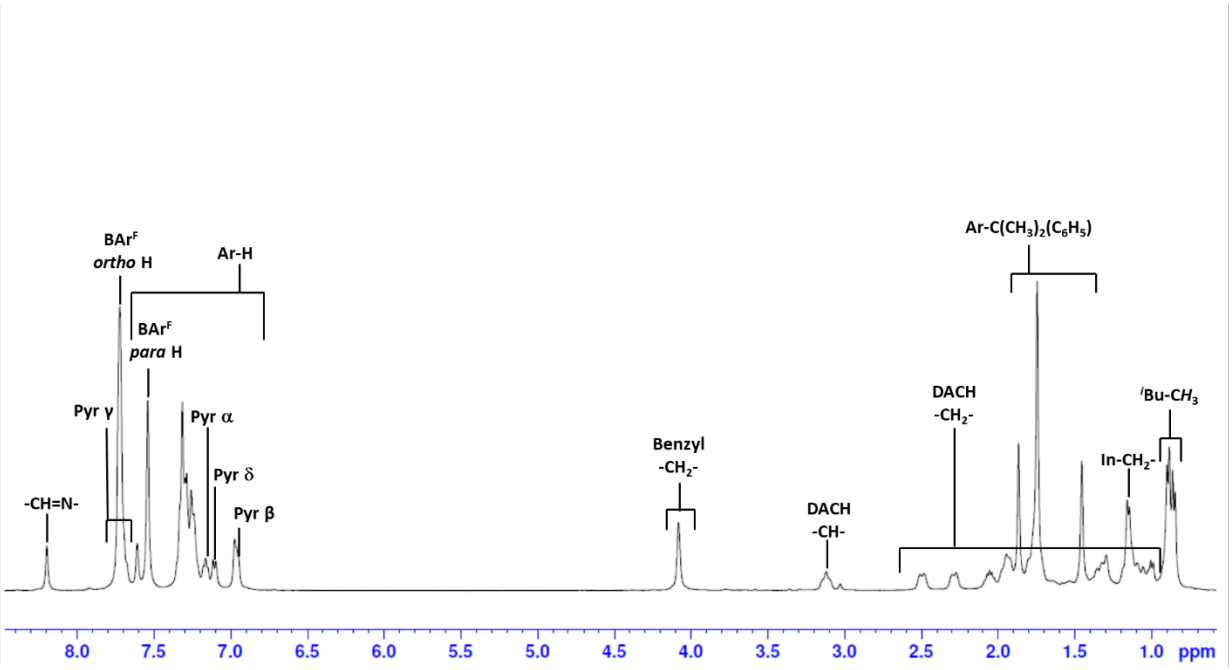


Figure S50 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of **2c**

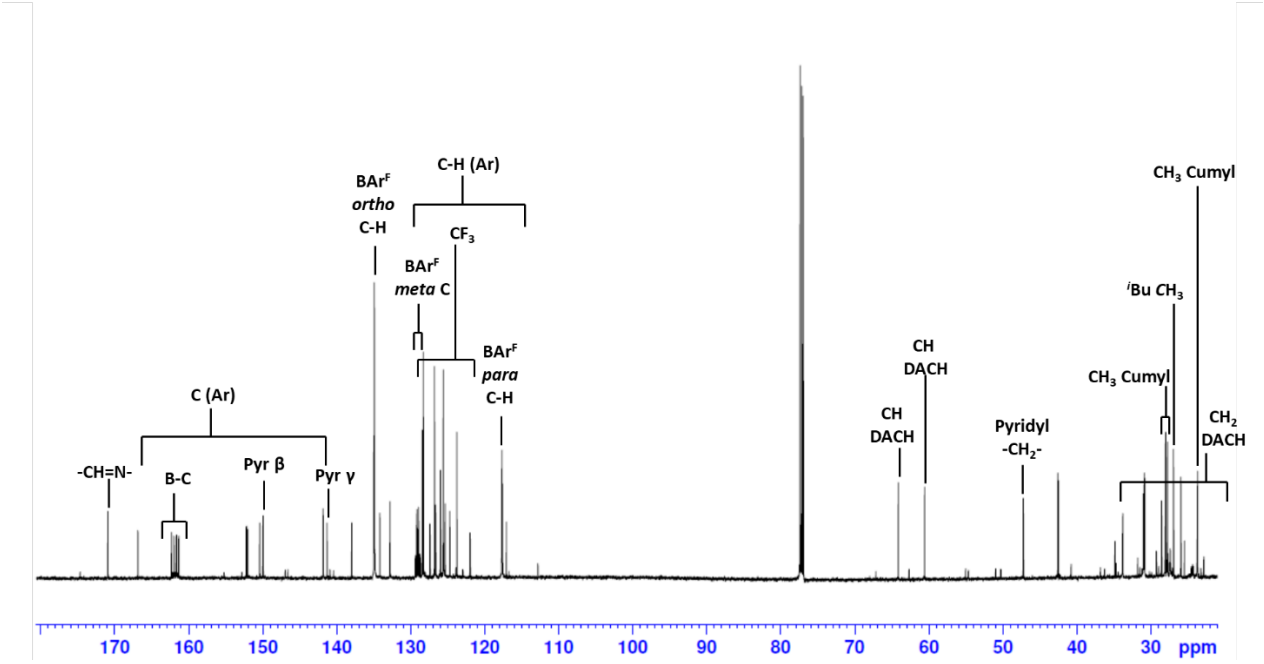


Figure S51 $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$, 25 °C) of **2c**

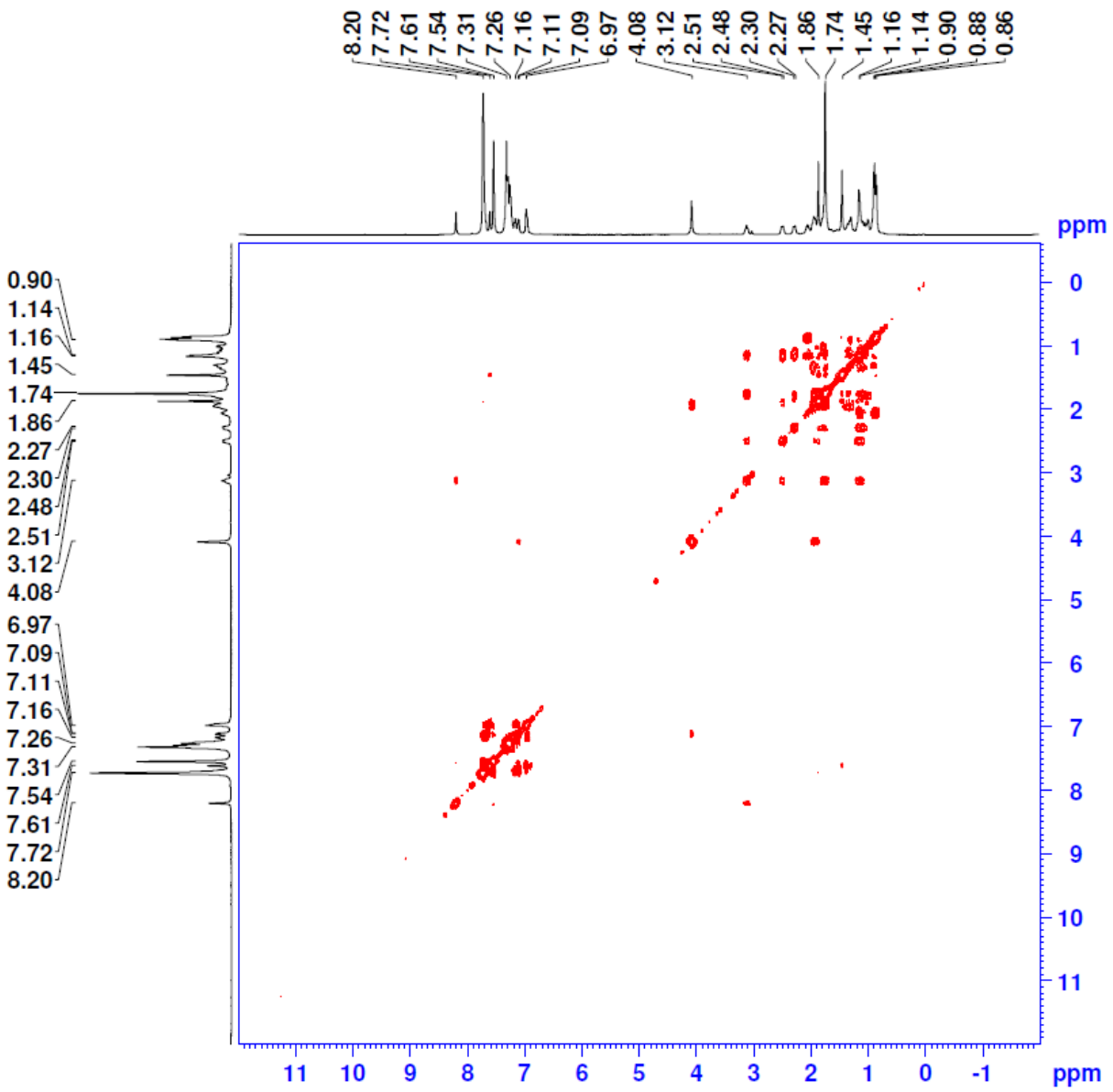


Figure S52 ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **2c.**

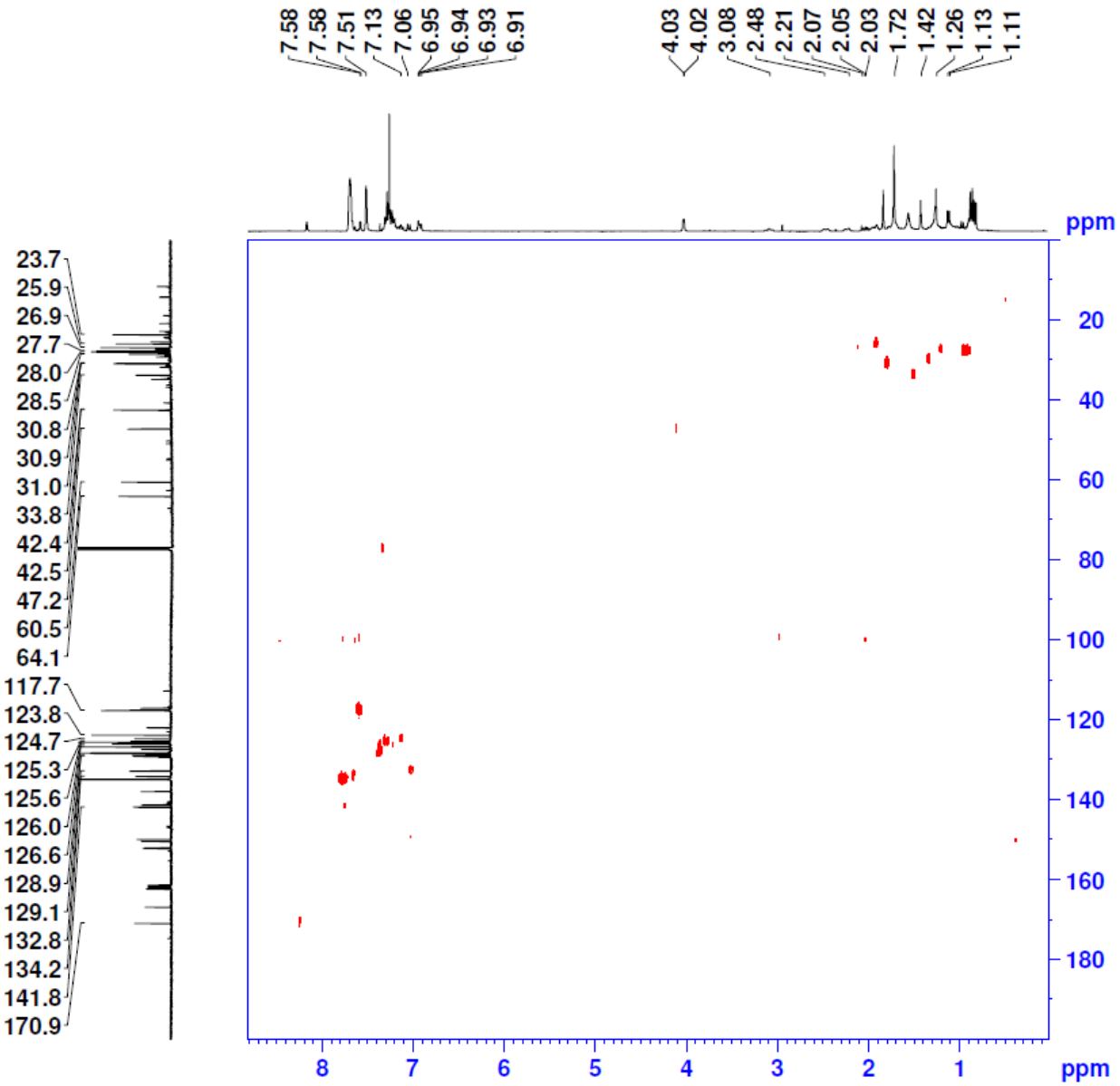


Figure S53 ^{1}H-^{13}C Heteronuclear Single Quantum Coherence (HSQC) NMR spectrum ($CDCl_3$, 25 °C) of **2c**.

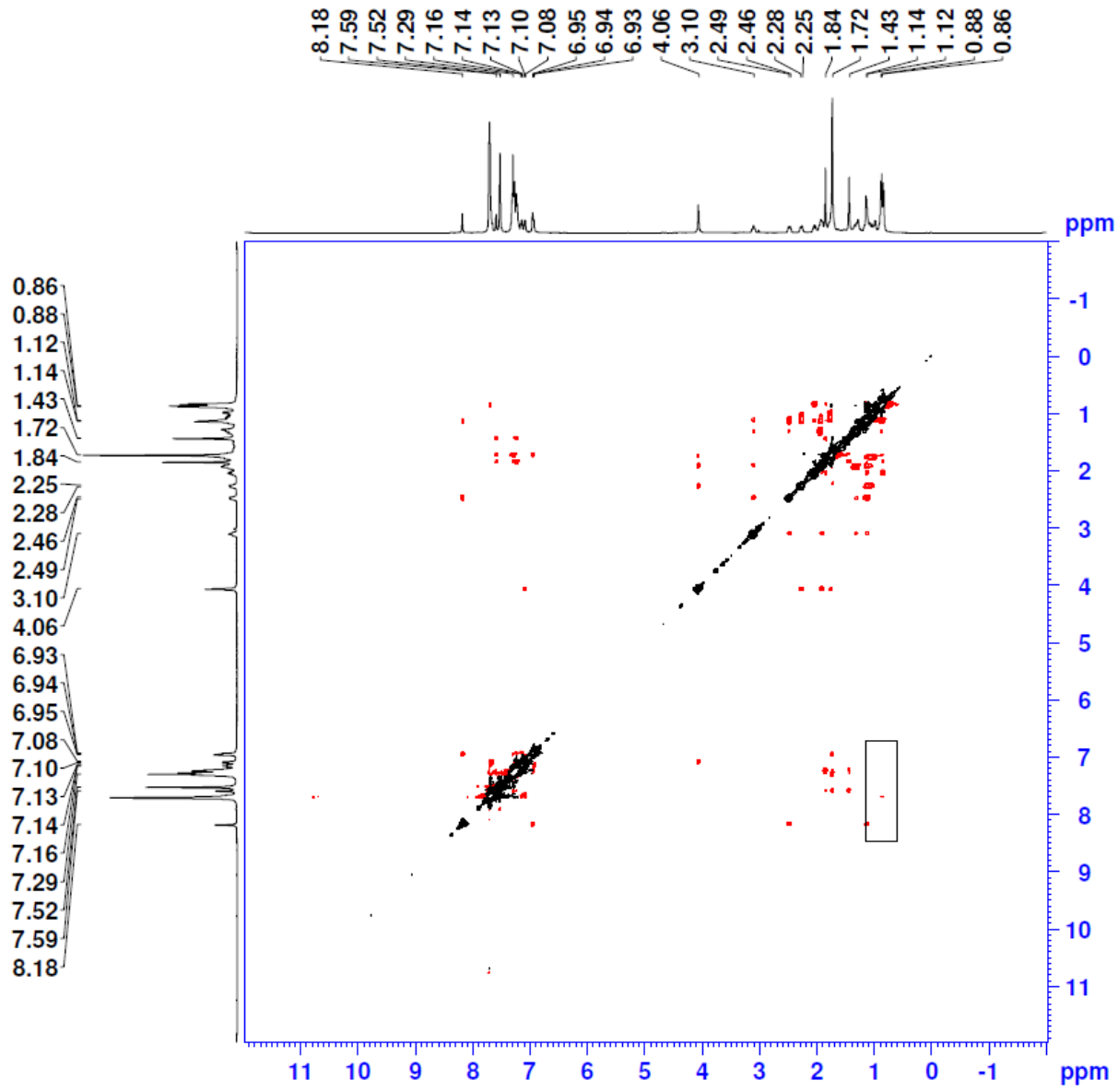


Figure S54 Nuclear Overhauser Effect spectroscopy (NOESY) NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **2c.**

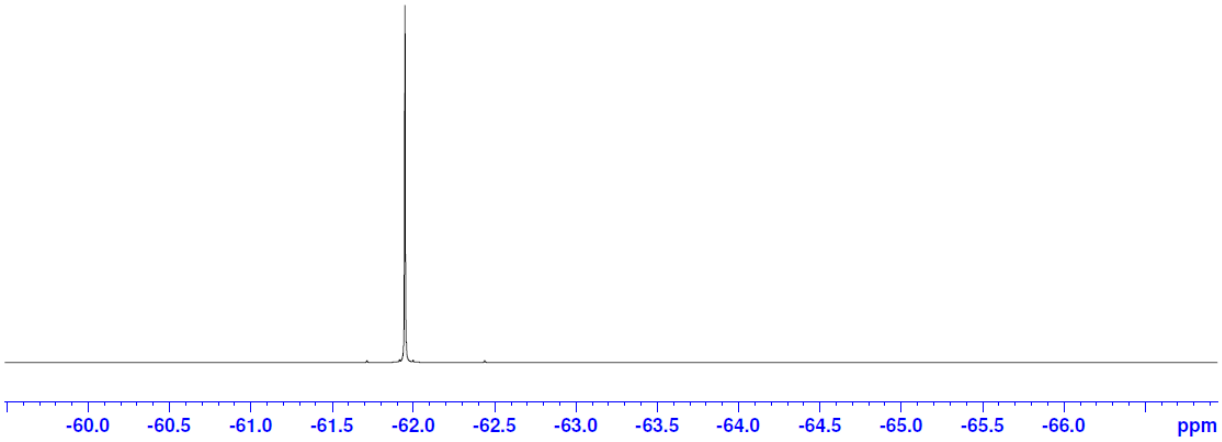


Figure S55 $^{19}F\{^{1}H\}$ NMR spectrum (282 MHz, $CDCl_3$, 25 °C) of **2c**

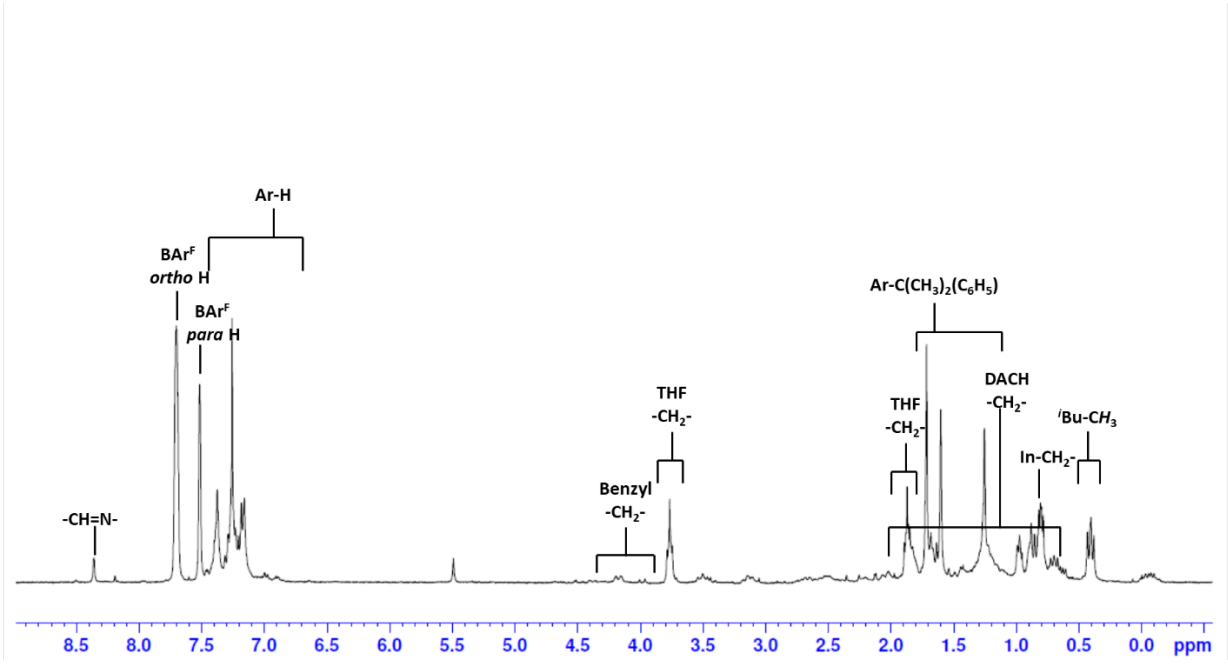
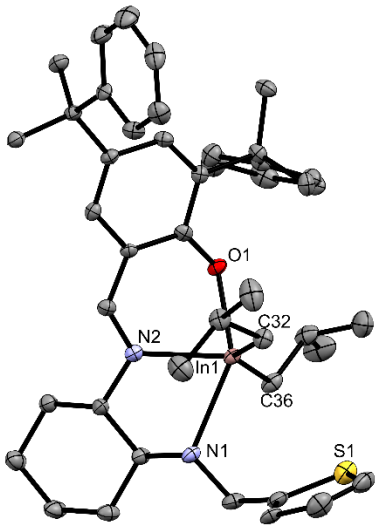


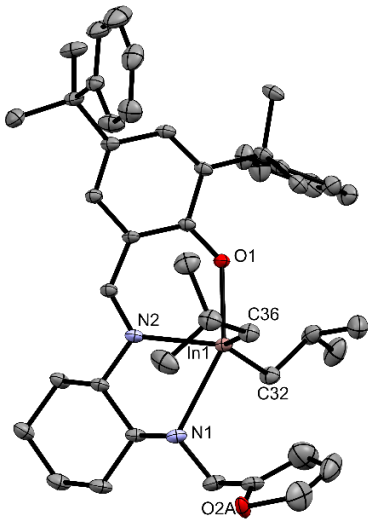
Figure S56 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of **2d**

C. Characterization of metal complexes in the solid state



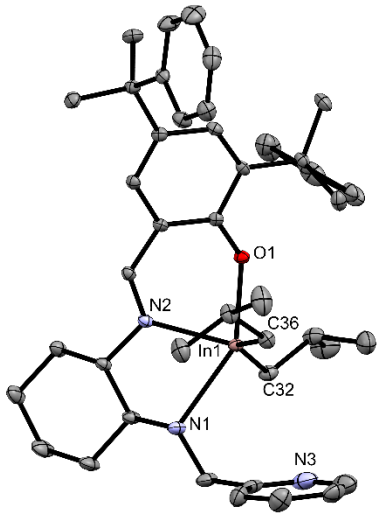
Selected bond distance (Å) and angles (°) for complex **1a**.				
Bond distances	In1-N1	2.510(3)	In1-C32	2.165(4)
	In1-N2	2.293(3)	In1-C36	2.169(4)
	In1-O1	2.205(3)		
Bond Angles	O1-In1-C32A	98.0(1)	O1-In1-N1	147.4(1)
	O1-In-C36	95.0(1)	N1-In1-C32	99.4(1)
	C32-In1-C36	135.0(2)	N1-In1-C36	91.9(1)
	N1-In1-N2	69.6(1)		

Figure S57 Molecular structure of complex **1a**. (depicted with thermal ellipsoids at 50% probability and H atoms, as well as solvent molecules omitted for clarity).



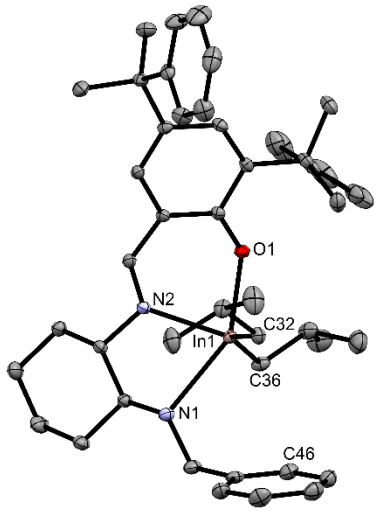
Selected bond distance (Å) and angles (°) for complex **1b**.				
Bond distances	In1-N1	2.548(1)	In1-C32	2.178(2)
	In1-N2	2.269(2)	In1-C36	2.187(3)
	In1-O1	2.203(1)		
Bond Angles	O1-In1-C32A	94.00(7)	O1-In1-N1	148.60(6)
	O1-In-C36	101.95(8)	N1-In1-C32	90.98(8)
	C32-In1-C36	129.61(9)	N1-In1-C36	98.52(8)
	N1-In1-N2	70.31(6)		

Figure S58 Molecular structure of complex **1b**. (depicted with thermal ellipsoids at 50% probability and H atoms, minor disorders as well as solvent molecules omitted for clarity).



Selected bond distance (Å) and angles (°) for complex **1c**.				
Bond distances	In1-N1	2.510(2)	In1-C32	2.174(2)
	In1-N2	2.286(1)	In1-C36	2.170(2)
	In1-O1	2.209(2)		
Bond Angles	O1-In1-C32A	94.72(7)	O1-In1-N1	148.01(6)
	O1-In-C36	97.68(7)	N1-In1-C32	92.82(7)
	C32-In1-C36	135.39(8)	N1-In1-C36	98.55(7)
	N1-In1-N2	69.95(6)		

Figure S59 Molecular structure of complex **1c**. (depicted with thermal ellipsoids at 50% probability and H atoms, as well as solvent molecules omitted for clarity).



Selected bond distance (Å) and angles (°) for complex **1d**.				
Bond distances	In1-N1	2.516(2)	In1-C32	2.170(1)
	In1-N2	2.286(1)	In1-C36	2.176(1)
	In1-O1	2.206(1)		
Bond Angles	O1-In1-C32A	97.49(5)	O1-In1-N1	148.14(4)
	O1-In-C36	94.38(5)	N1-In1-C32	98.34(5)
	C32-In1-C36	136.55(6)	N1-In1-C36	92.87(5)
	N1-In1-N2	69.81(4)		

Figure S60 Molecular structure of complex **1d**. (depicted with thermal ellipsoids at 50% probability and H atoms, as well as solvent molecules omitted for clarity).

D. Characterization of complex behavior

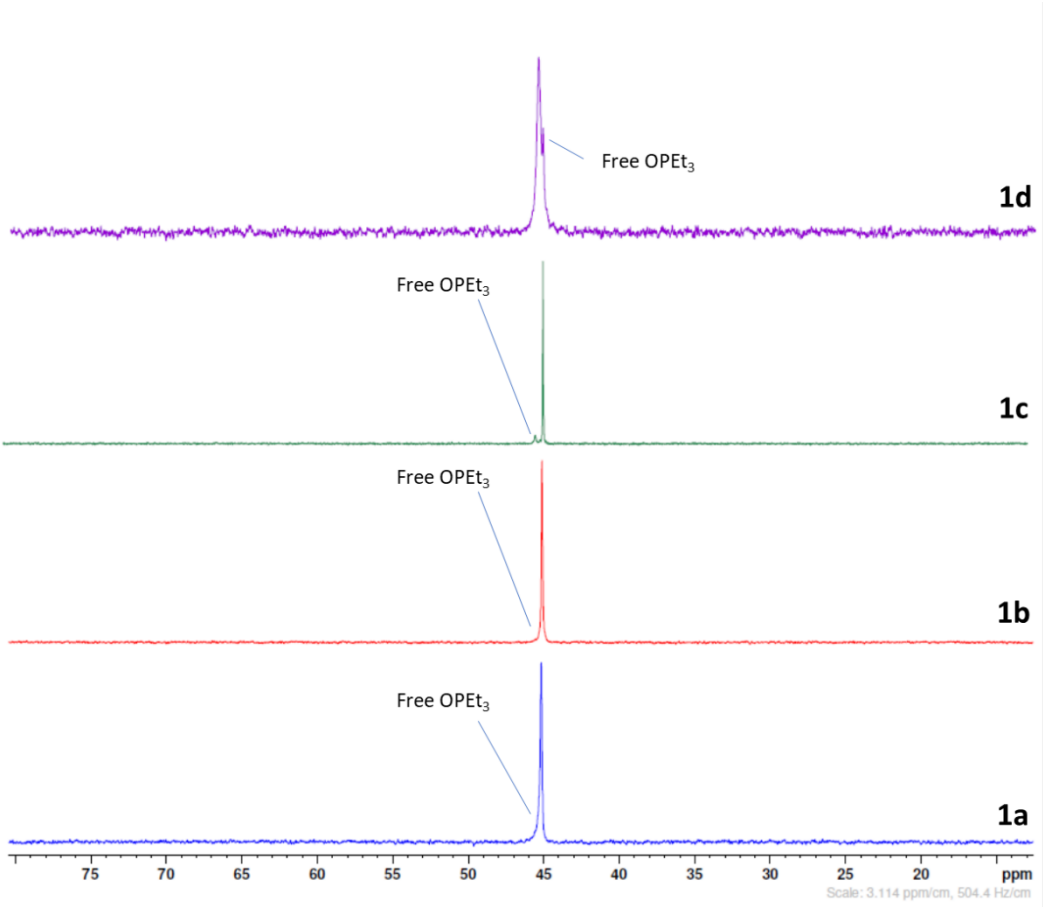


Figure S61 $^{31}P\{^{1}H\}$ NMR spectra (162 MHz, C_6D_6, 25 °C) of **1a**, **1b**, **1c** and **1d** after the addition of 0.8 equivalents of $OPEt_3$. The free triethylphosphine oxide shift is determined by the addition of a capillary inside the NMR tube containing a solution of triethylphosphine oxide in C_6D_6.

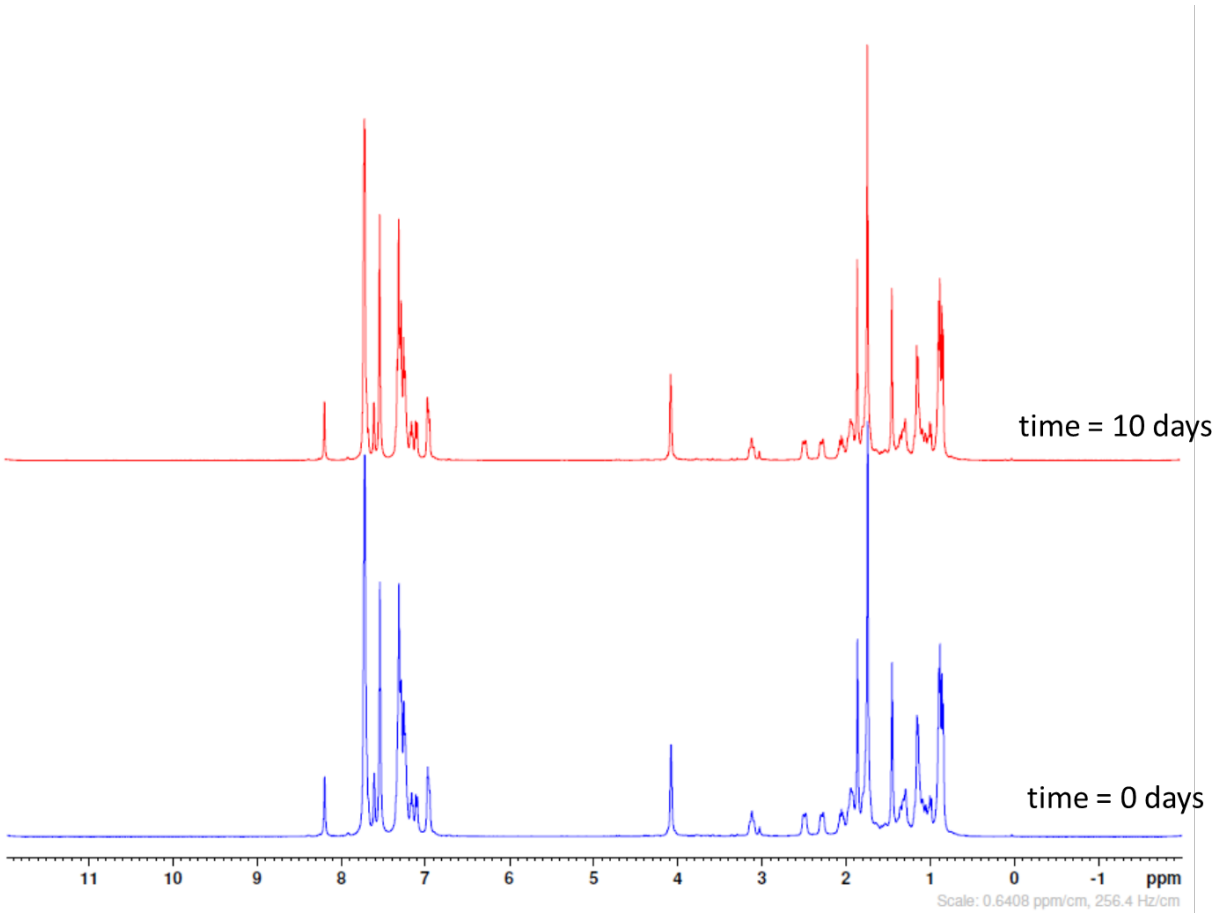


Figure S62 ^{1}H NMR spectra of **2c** before (time = 0 days) and after (time = 10 days) exposure to air for 10 days continuously. No significant changes were observed.

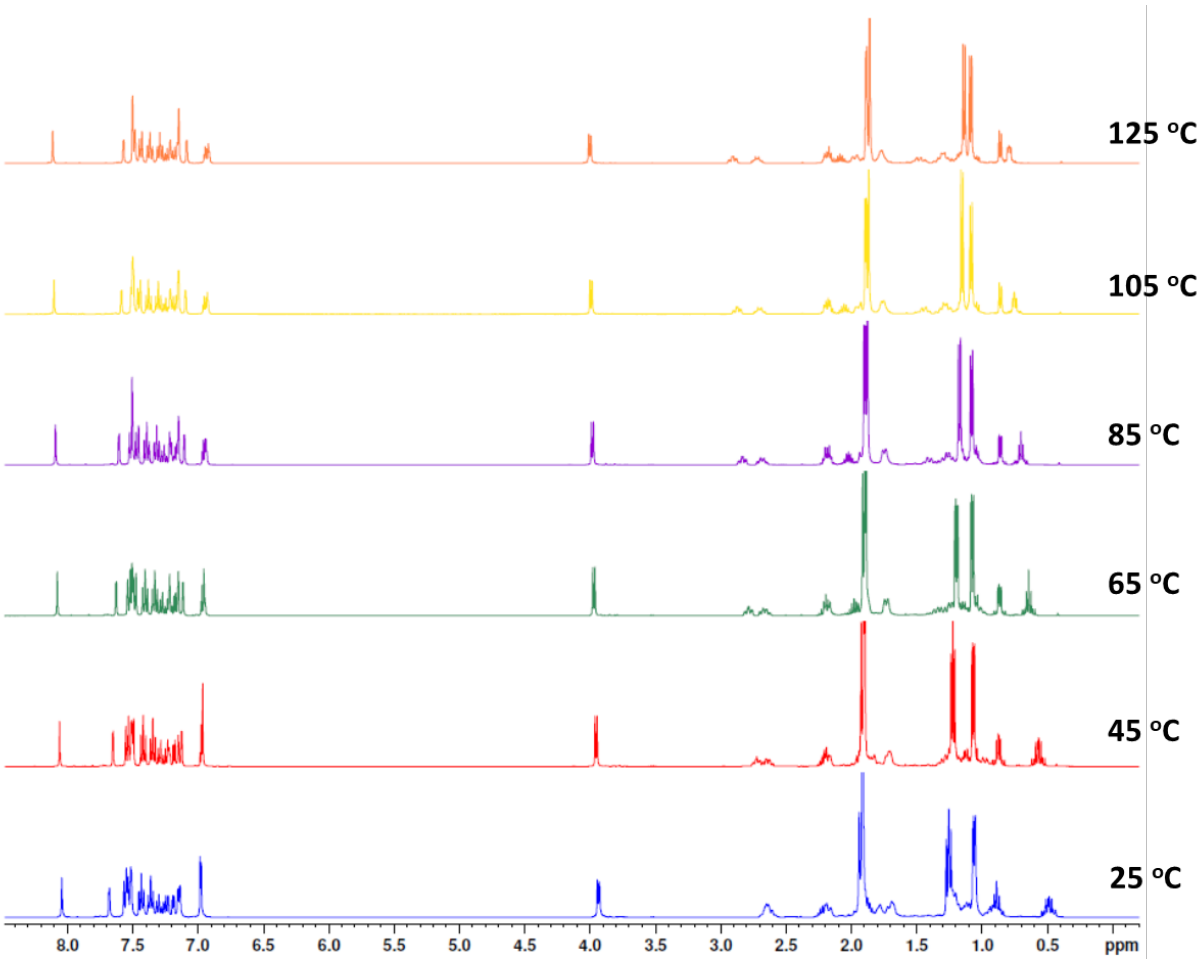


Figure S63 Variable temperature (VT) ^{1}H NMR spectra (400 MHz, C_6D_5Br, 25 to 125 °C) of **1a**. Shifts observed were reversible. C_6D_5Br is taken as a reference.

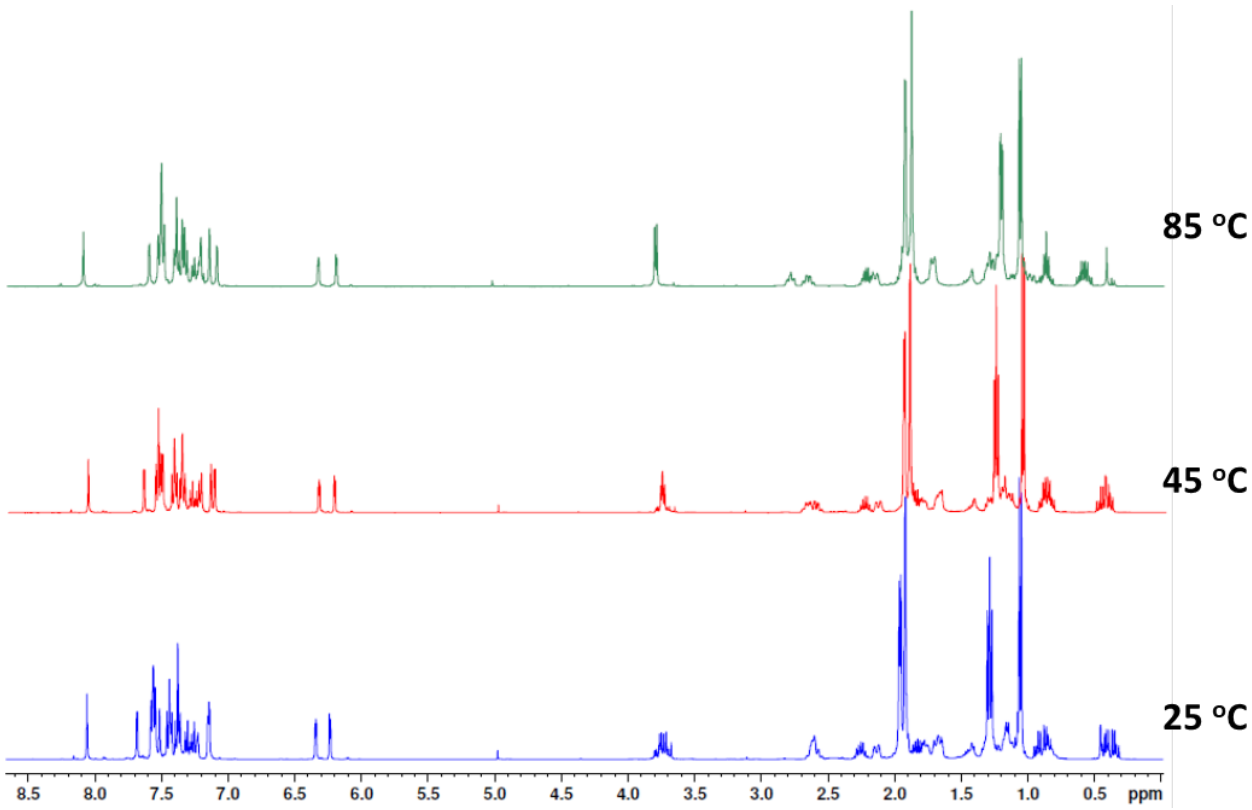


Figure S64 Variable temperature (VT) ^{1}H NMR spectra (400 MHz, C_6D_5Br, 25 to 85 °C) of **1b**. Shifts observed were reversible. C_6D_5Br is taken as a reference.

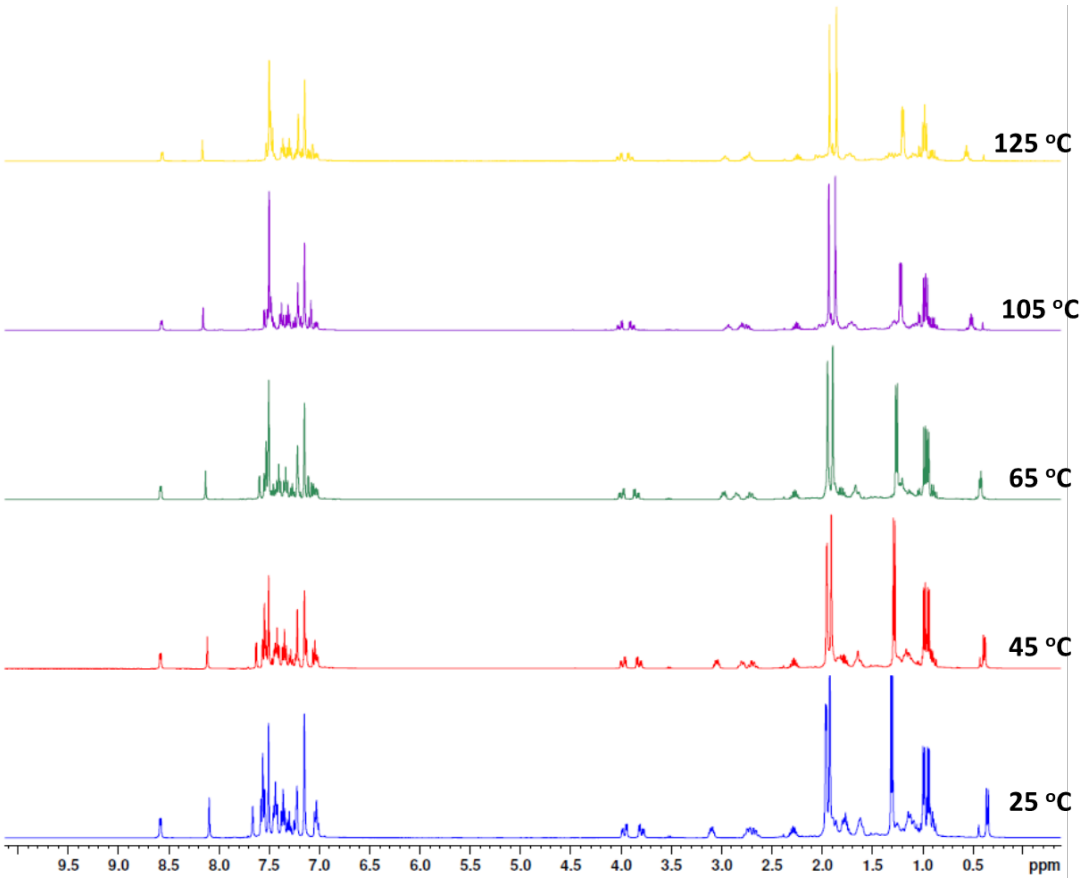


Figure S65 Variable temperature (VT) ^{1}H NMR spectra (400 MHz, C_6D_5Br, 25 to 85 °C) of **1c**. Shifts observed were reversible. C_6D_5Br is taken as a reference.

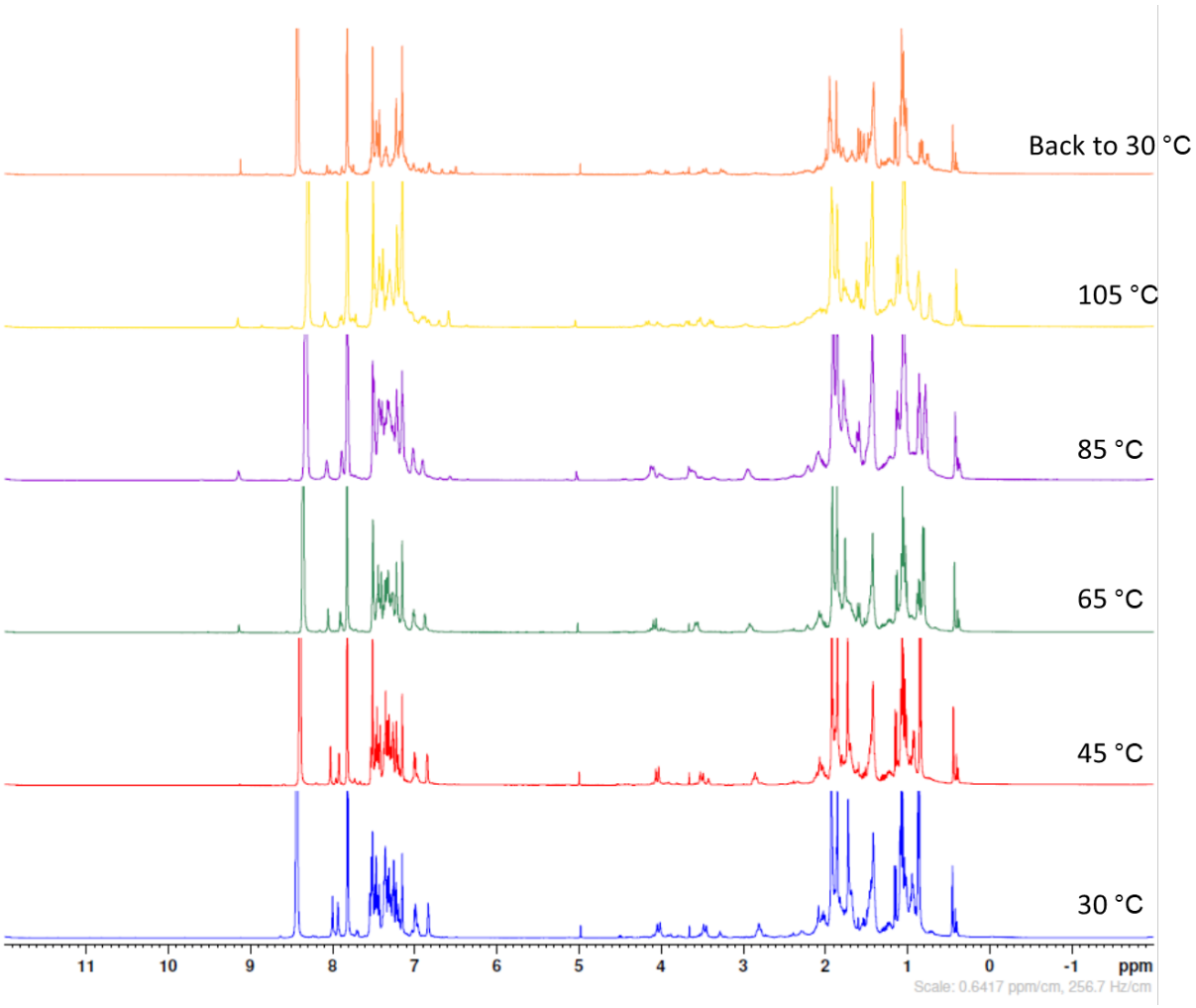


Figure S66 Variable temperature (VT) ^{1}H NMR spectra (400 MHz, C_6D_5Br, 30 to 105 °C) of **2a**. Shifts observed were irreversible. C_6D_5Br is taken as a reference.

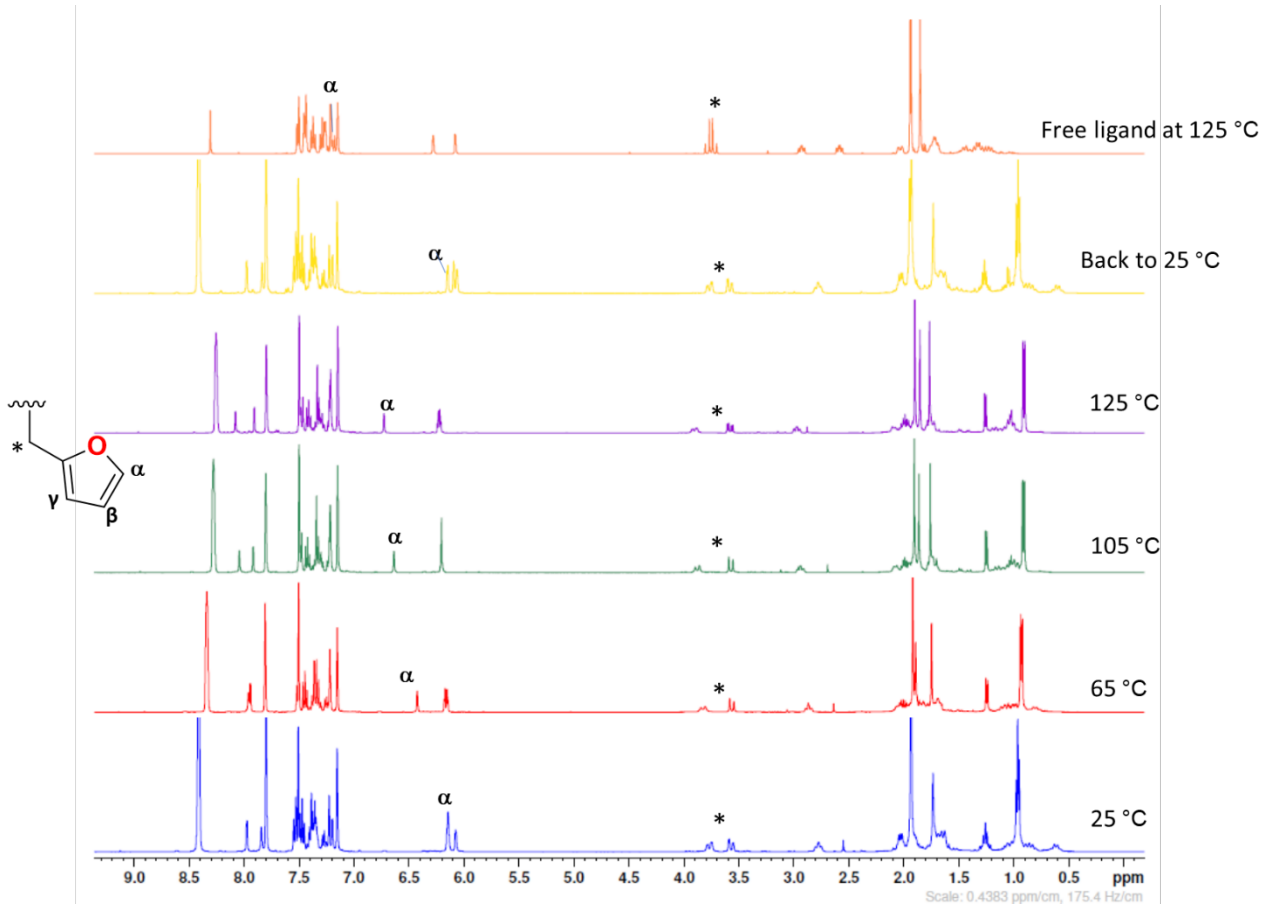


Figure S67 Variable temperature (VT) ^{1}H NMR spectra (400 MHz, C_6D_5Br, 25 to 125 °C) of **2b** free ligand **L2**. Shifts observed were reversible. C_6D_5Br is taken as a reference.

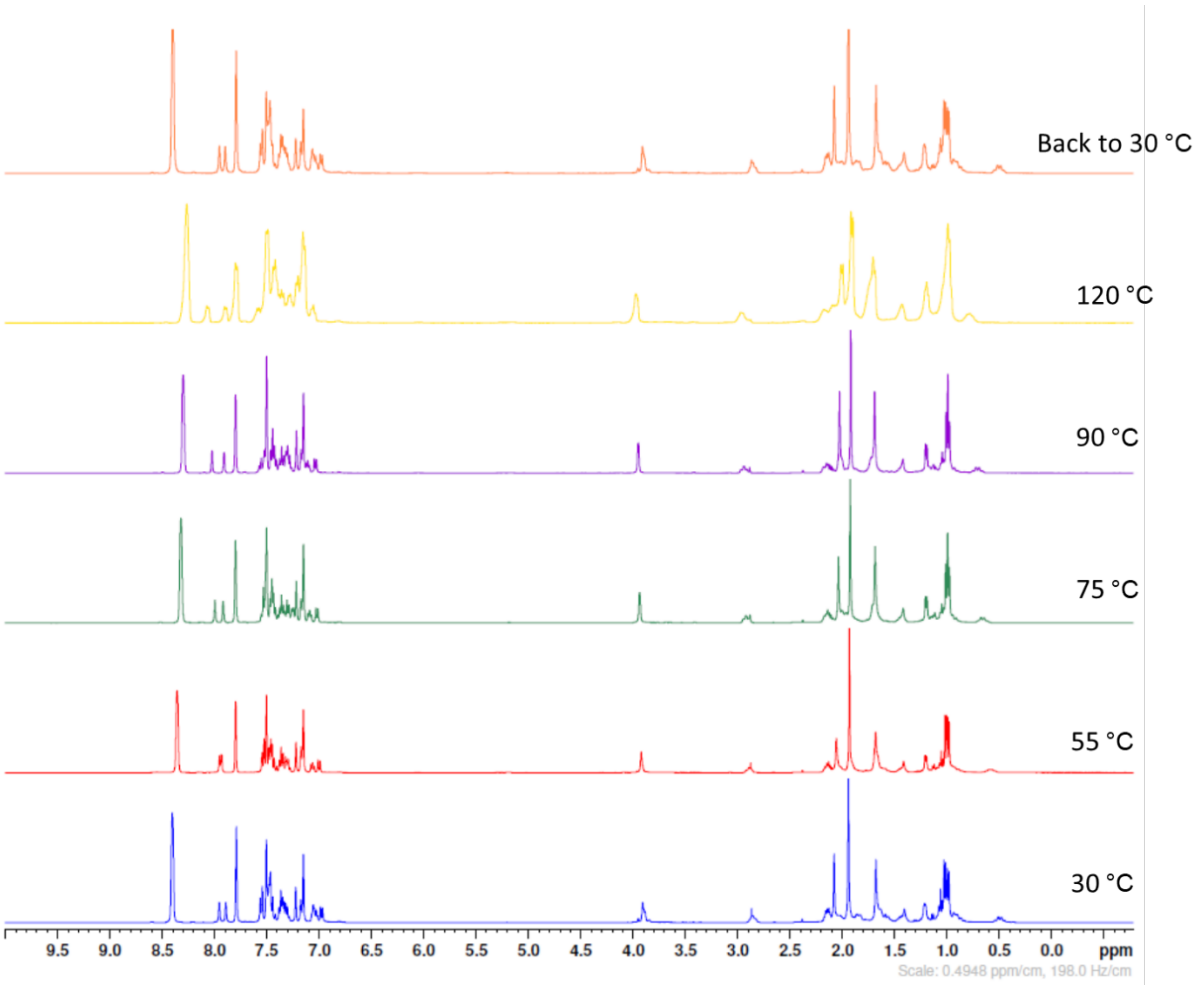
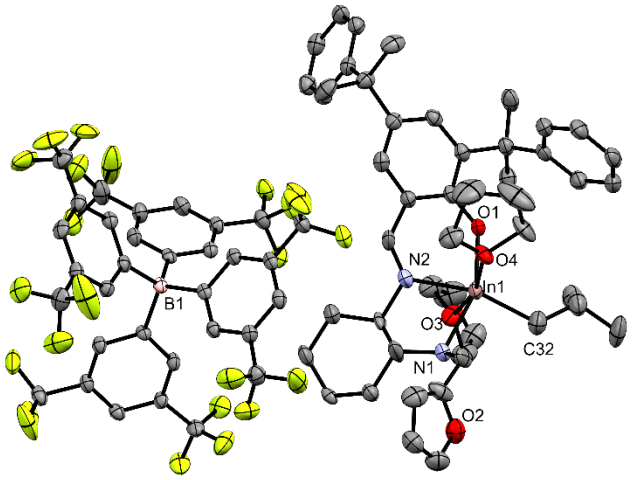


Figure S68 Variable temperature (VT) ^{1}H NMR spectra (400 MHz, C_6D_5Br, 30 to 120 °C) of **2c**. Shifts observed were reversible. C_6D_5Br is taken as a reference.



Selected bond distance (Å) and angles (°) for complex **2b.2THF**.				
Bond distances	In1-N1	2.468(5)	In1-O3	2.392(4)
	In1-N2	2.179(5)	In1-O4	2.354(4)
	In1-O1	2.127(3)	In1-C32	2.128(7)
Bond Angles	O1-In1-C32	112.9(2)	O1-In1-N1	156.3(1)
	O3-In1-O4	166.3(1)	N1-In1-C32	90.4(2)
	N1-In1-N2	72.9(2)		

Figure S69 Molecular structures of complex **2b.2THF** (depicted with thermal ellipsoids at 50% probability and H atoms, minor disorders as well as solvent molecules omitted for clarity)

Table S2 Selective crystal data for **1b**, **1d**, **1a**, **1c** and **2b.2THF**.

	1b	**1d**	**1a**	**1c**	**2b.2THF**
empirical formula	C_{44} H_{59} In N_2 O_2	C_{46} H_{61} In N_2 O	C_{44} H_{59} In N_2 O S	C_{45} H_{60} In N_3 O	C_{88} H_{92} B F_{24} In N_2 O_6
Fw	762.75	772.78	778.81	773.78	1855.26
T (K)	296.15	273(2)	100	296.15	100
a (Å)	17.5732(15)	18.4020(6)	18.3672(15)	18.3804(16	12.616(3)
b (Å)	13.8493(11)	13.9008(5)	14.0583(12)	13.9887(12)	13.343(3)
c (Å)	18.4226(15)	18.4542(7)	17.9736(14)	18.328(2)	26.255(5)
α (deg)	90	90	90	90	80.163(3
β (deg)	117.891(2)	119.051(2)	118.8140(10)	119.839(2)	76.369(3
γ (deg)	90	90	90	90	85.869(3)
volume (Å^3)	3962.81	4126.72	4066.39	4087.71	4229.90
Z	4	4	4	4	2
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	*P* 2_1 / *c*	*P* 2_1 / *n*	*P* 2_1 / *c*	*P* 2_1 / *c*	*P* -1
d_{calc} (g/cm^3)	1.278	1.244	1.272	1.257	1.457
μ (Mo Kα) (cm^{-1})	6.34	6.08	6.67	6.14	3.87
$2\theta_{max}$ (deg)	61.3	61.2	55.8	61.0	54.6
absor corr (T_{min}, T_{max})	0.7005, 0.7461	0.909, 0.986	0.982, 0.997	0.6730, 0.7461	0.9887, 0.9977
total no. of reflns	63957	65464	9204	56696	18759
no. of indep reflns (R_{int})	12154 (0.0394)	12665 (0.0445)	9204 (0.0890)	12417 (0.0461)	18759(0.1605)
residuals (refined on F^2): R_1; wR_2	0.0523, 0887	0.0354, 0.0634	0.0773, 0.1436	0.0465, 0.0808	0.0983, 2141
GOF	1.023	1.032	1.067	1.094	1.036
no. obsrvns [$I > 2\sigma(I)$]	9858	9908	9510	9643	9841
residuals (refined on F^2: $R_1{}^a$; $wR_2{}^b$)	0.0524, 0.0802	0.0273, 0.0600	0.0550, 0.1339	0.0373, 0.0772	0.0794, 2047

$^a R_1 = \Sigma \, ||F_o| - |F_c|| \, / \Sigma \, |F_o|$. $^b wR_2 = [\, \Sigma \, (w \, (F_o^2 - F_c^2)^2 \,) / \, \Sigma \, w(F_o^2)_2]^{1/2}$

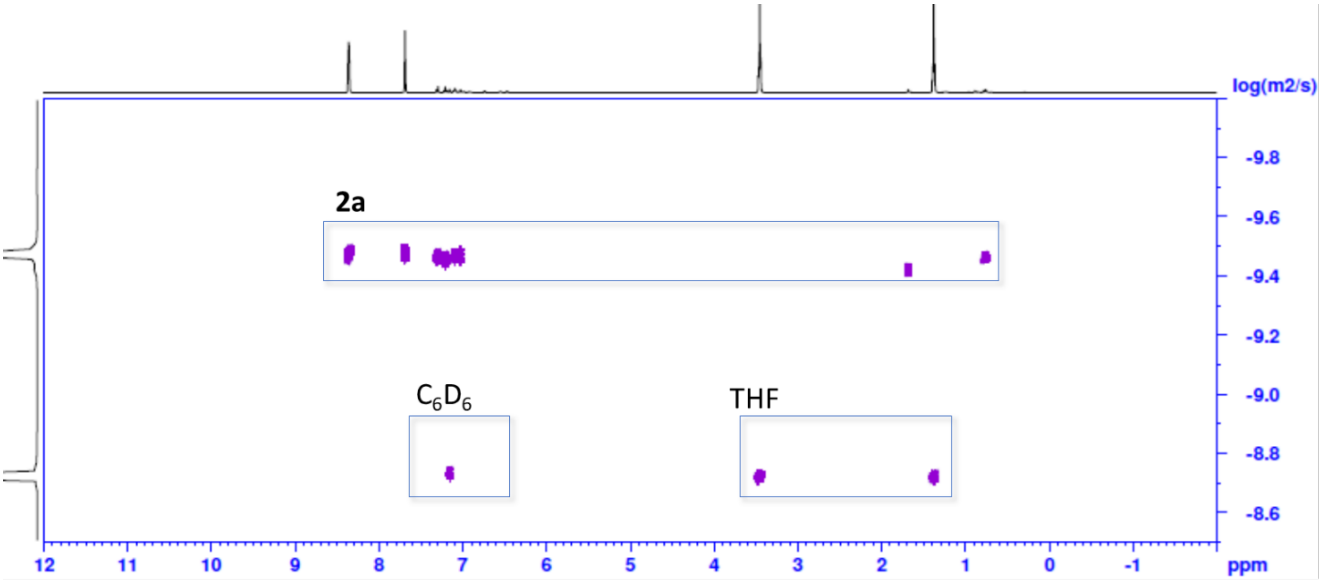


Figure S70 DOSY-NMR of the mixture of THF and **2a** (400MHz, diffusion time (Δ) = 0.85 s, gradient length (δ) = 400 μs, C_6D_6, 25 °C).

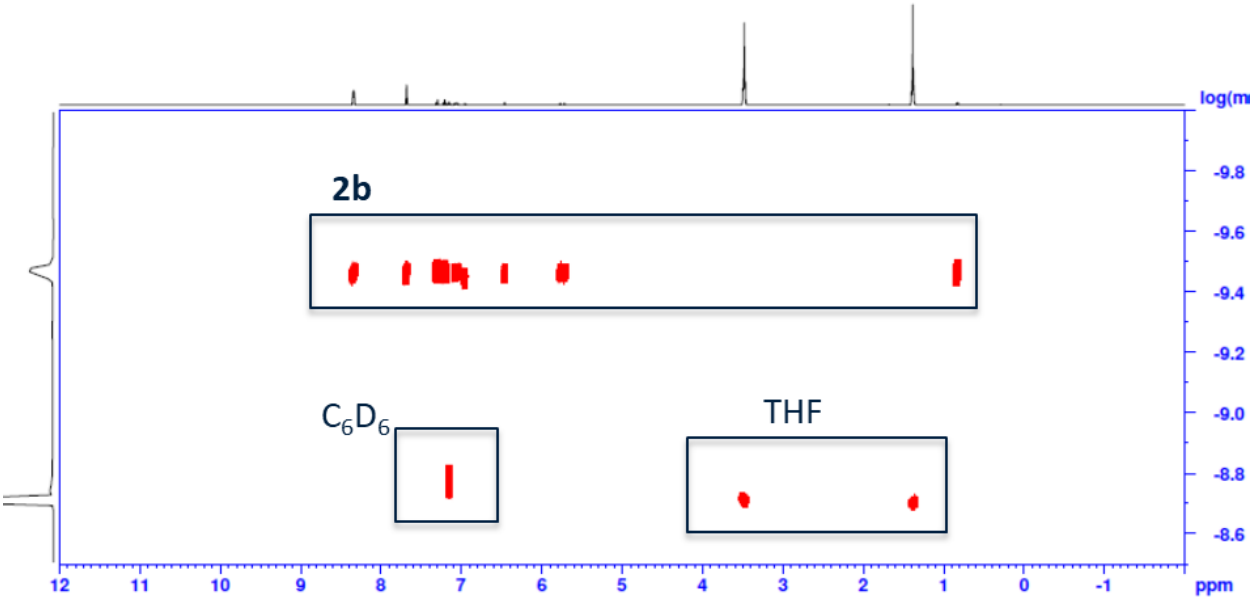


Figure S71 DOSY-NMR of the mixture of THF and **2b** (400MHz, Δ = 1.2 s, δ = 400 μs, C_6D_6, 25 °C).

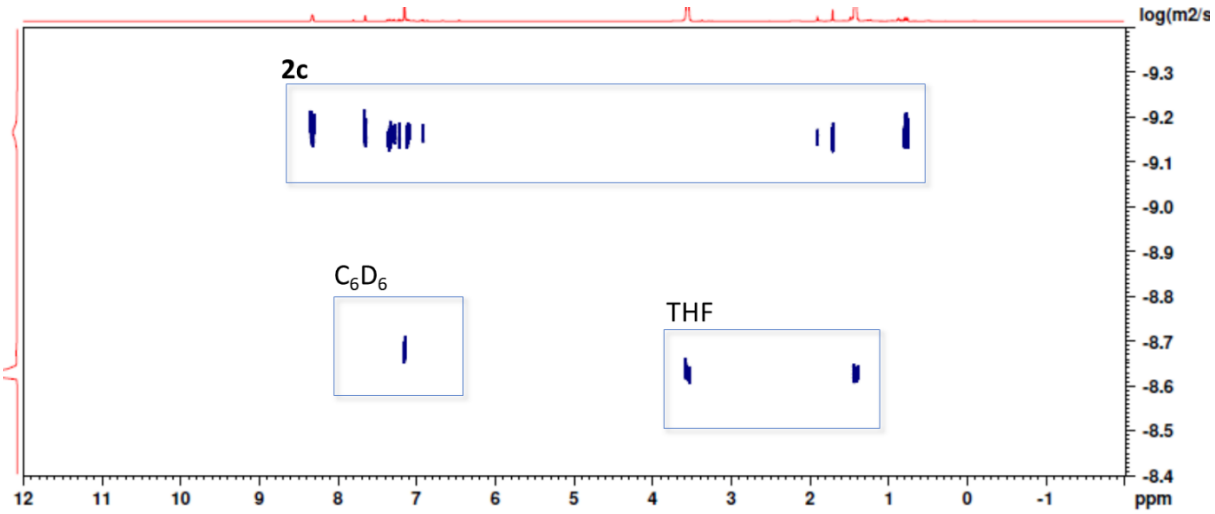


Figure S72 DOSY-NMR of the mixture of THF and **2c** (400MHz, Δ = 0.55 s, δ = 400 µs, C_6D_6, 25 °C).

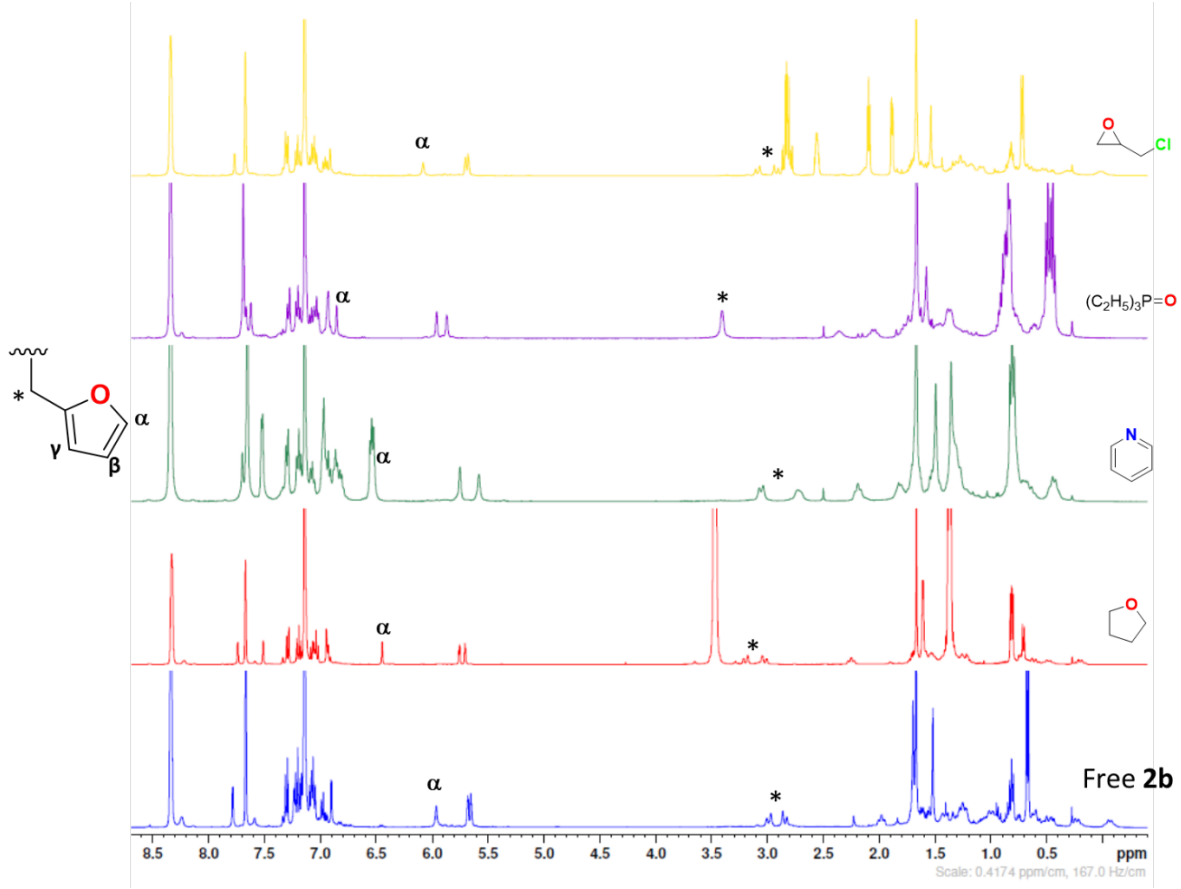


Figure S73 ^{1}H NMR of spectra of **2b** in the presence of THF, pyridine, triethylphosphine oxide and epichlorohydrin (400 MHz in C_6D_6 at 25 °C).

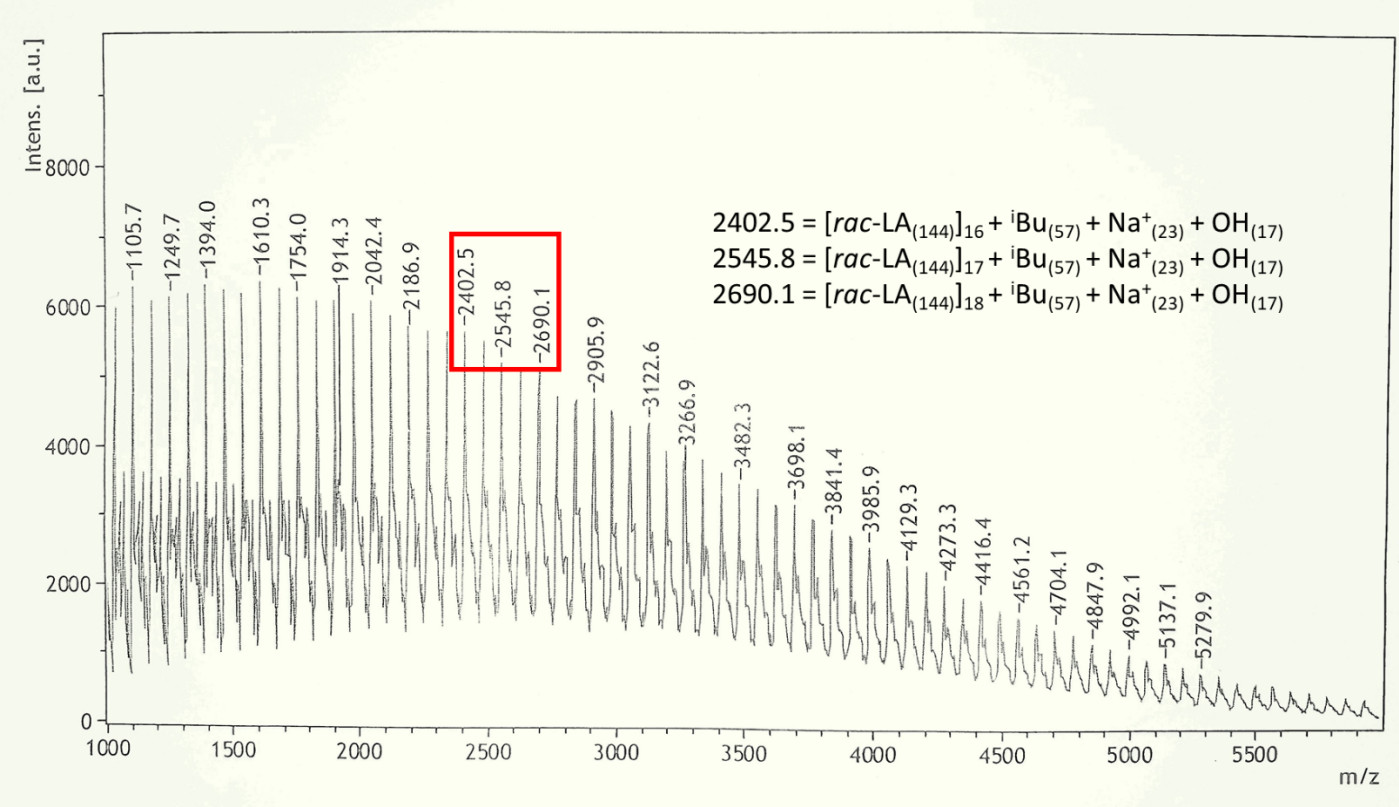


Figure S74 MALDI-TOF spectrum of PLA isolated from polymerization of 250 equivalents of rac-LA with **2c** in toluene at 100 °C for 24 hours

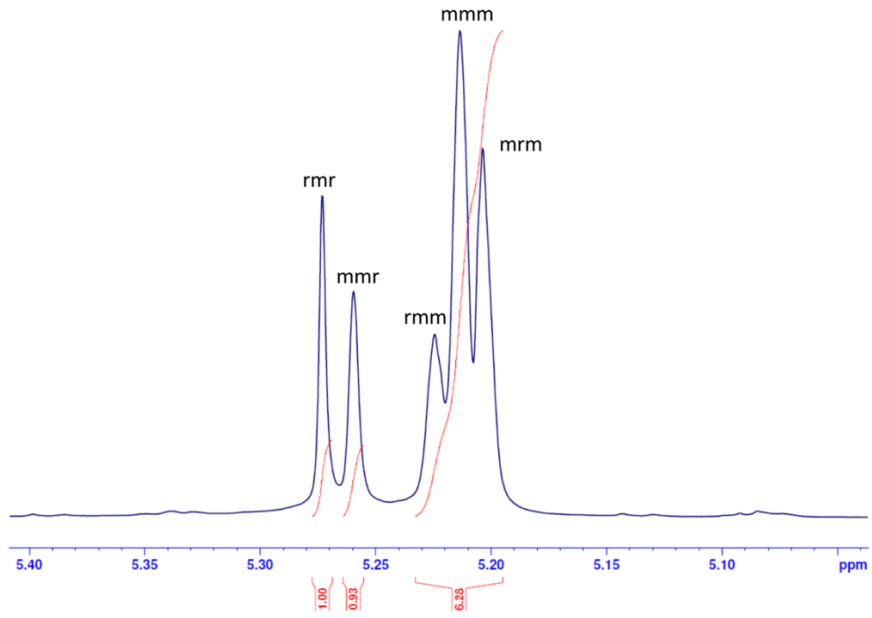


Figure S75 $^{1}H\{^{1}H\}$ NMR spectrum (600 MHz, $CDCl_3$, 25 °C) of PLA as the product of the polymerization of 250 equivalents of rac-LA **2c** in toluene at 100 °C for 24 hours. The methine protons of the polymer are decoupled. (P_m = 0.46)

E. References

1. Jung, H. J.; Chang, C.; Yu, I.; Aluthge, D. C.; Ebrahimi, T.; Mehrkhodavandi, P., Coupling of Epoxides and Lactones by Cationic Indium Catalysts To Form Functionalized Spiro-Orthoesters. *ChemCatChem* **2018,** *10* (15), 3219-3222.
2. Beachley, O. T.; Rusinko, R. N., Preparation and properties of ((trimethylsilyl)methyl)indium(iii) compounds. *Inorg. Chem.* **1979,** *18* (7), 1966-1968.
3. Murphy, A.; Pace, A.; Stack, T. D. P., Ligand and pH influence on manganese-mediated peracetic acid epoxidation of terminal olefins. *Org. Lett.* **2004,** *6* (18), 3119-3122.
4. Sandstrom, M.; Persson, I.; Persson, P., A study of solvent electron-pair donor ability and lewis basicity scales. *Acta. Chem. Scand.* **1990,** *44* (7), 653-675.