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Cationic palladium(II)–acetylacetonate complexes bearing pyridinyl imine ligands as catalysts for the hydroamination of phenylacetylene and polymerization of norbornene

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CONTENTS

1 General procedures and materials

All air- and/or moisture-sensitive compounds were manipulated by using standard high-vacuum line, Schlenk, or cannula techniques under an argon atmosphere. Argon (Arnika-Prom-Service) was purified before feeding to the reactor by passing through columns packed with oxygen scavenger and molecular sieve 4Å (Aldrich), respectively. Diethyl ether, benzene, toluene, (AO Vekton), norbornene (Acros, 99%) were distilled from sodium benzophenone ketyl. CH_2Cl_2 (AO Vekton), MeCN (AO Vekton), methanol (AO Vekton), phenylacetylene (99%, Aldrich) were distilled from CaH_2. Solvents were stored over molecular sieves. Other chemicals were purchased from Acros Organic, Sigma-Aldrich, ABCR and employed without drying or any further purification. All glassware was dried for at least 3 h in a 150°C oven and cooled under an argon atmosphere. $Pd(acac)_2$ and $[Pd(acac)(MeCN)_2]BF_4$ were synthesized according to published procedures [S1,S2]. The pyridinyl imine ligands **L1**–**L5** (Figure S1) were synthesized by slightly modified literature procedures [S3–S5] (see below) by condensation of pyridine-2-carboxaldehyde with the corresponding amines. All other reagents were obtained commercially and used as received. NMR spectra were recorded at room temperature on Bruker DPX-400 spectrometer. ESI-MS spectra were recorded on a HR-TOF-ESI-MS Agilent 6210. IR spectra were recorded on a Simex Infralum FT 801 spectrometer. HPLC analyses were performed on a Thermo-Dionex HPLC system. GC-FID and GC–MS analyses were performed on Chromatec Crystall 5000.2 (SGE BPX-5 capillary column, benzene internal standard) and Shimadzu QP2010 Ultra (GSBP-5 MS capillary column), respectively.

2 Synthesis of ligands and palladium complexes

Ligands **L1–L5** were obtained as a result of condensation reactions of the appropriate aldehydes with the corresponding amines (**Figure S1**) using published procedures [S3–S5].

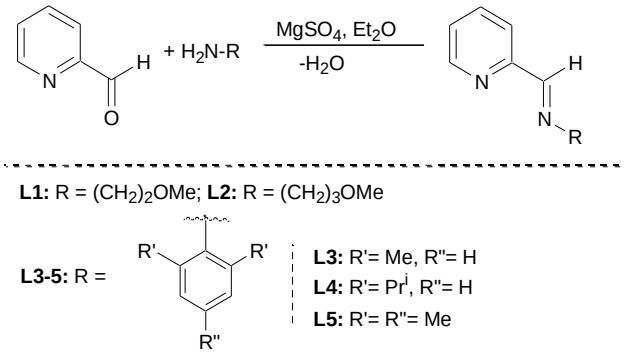


Figure S1 Synthesis of pyridinyl imine ligands **L1–L5**

2-Methoxy-N-[(pyridin-2-yl)methylene]ethanamine **L1**. 2-Methoxyethylamine (0.89 ml, 10.3 mmol) was added to a stirred solution of pyridine-2-carboxaldehyde (0.89 ml, 9.34 mmol) in diethyl ether (15 ml). Anhydrous magnesium sulfate (2 g) was added, and the reaction mixture left stirred at room temperature for 4 hours. The resulting mixture was filtered, and the solvent and unreacted amine were removed from the filtrate under reduced pressure to give of pure product **L1** as a yellow oil. Purity was checked by GS-MS. Yield: 1.23 g (80%, 4 mmol).

3-Methoxy-N-[(pyridin-2-yl)methylene]propan-1-amine **L2** was obtained out similarly from 3-methoxypropan-1-amine (1.0 ml, 9.8 mmol) and pyridine-2-carboxaldehyde (0.89 ml, 9.34 mmol). Product **L2** appeared as an orange oil. Purity was checked by GS-MS. Yield: 1.24 g (74%, 9.34 mmol).

2,6-Dimethyl-N-(pyridin-2-ylmethylene)aniline **L3** was obtained similarly from 2,6-dimethylaniline (1.73 ml, 14 mmol) and pyridine-2-carboxaldehyde (1.48 ml, 15.5 mmol). Product **L3** appeared as a red-orange oil. Purity was checked by GS-MS. Yield: 2.42 g (82%, 14 mmol).

2,6-Diisopropyl-N-(pyridin-2-ylmethylene)aniline **L4** was obtained similarly from 2,6-diisopropylaniline (2.29 ml, 12 mmol) and pyridine-2-carboxaldehyde (1.26 ml, 13.2 mmol). Product **L4** appeared as an orange oil. Purity was checked by GS-MS. Yield: 2.85 g (89%, 12 mmol).

2,4,6-Trimethyl-N-(pyridin-2-ylmethylene)aniline **L5** was obtained similarly from2,4,6-trimethylaniline (2.06 ml, 14.3 mmol) and pyridine-2-carboxaldehyde (1.43 ml, 15 mmol). Product **L5** appeared as an yellow oil. Purity was checked by GS-MS. Yield: 2.74 g (87%, 14.3 mmol).

The synthesis of complexes **1–5** was achieved by reacting bis(acetonitrile)(acetylacetonate)palladium(II) tetrafluoroborate with one equivalent of **L1–L5** in CH_2Cl_2, which led to [Pd(acac) (L)][BF_4] (**1–5**), as depicted in Figure S2.

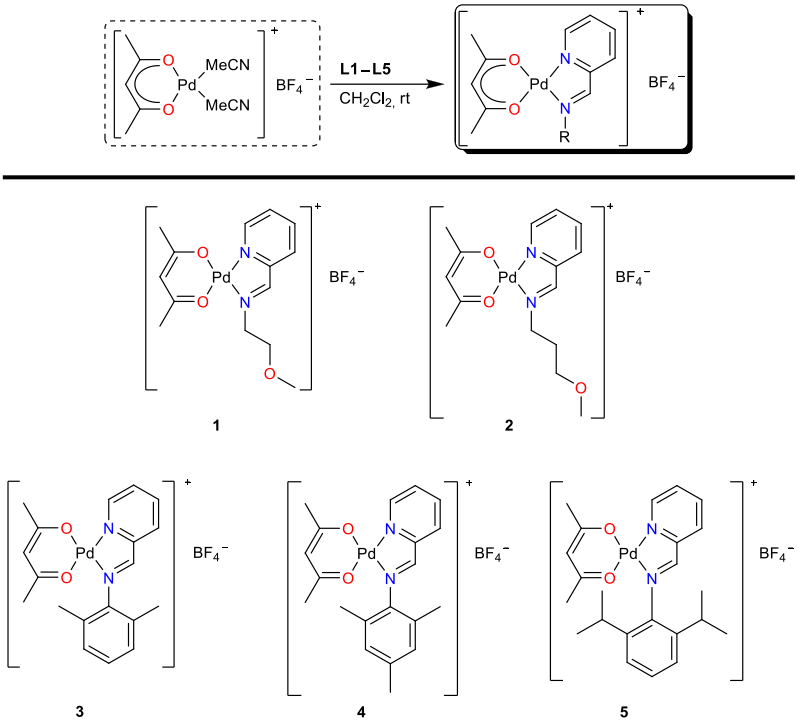


Figure S2 – Synthesis of palladium pyridinyl-imine complexes **1-5**

(Acetylacetonate-κ^2O,O')[N-(2-methoxyethyl)-1-(pyridin-2-yl)methanimine-κ^2N,N']palladium(II) tetrafluoroborate **1**. Complex [Pd(acac)$(MeCN)_2$]BF_4 (192.4 mg, 0.51 mmol) was dissolved in CH_2Cl_2 (24 ml). The CH_2Cl_2 solution of ligand **L1** (0.8 ml, 0.51 mmol) was added dropwise to the resulting mixture over 30-40 min. The mixture was stirred at room temperature for 3 h. The resulting yellow solution was concentrated to ~3 ml under vacuum. The addition of diethyl ether (20 ml) resulted in an orange precipitate, which was collected, washed with diethyl ether (2×10 ml), and dried (8 h) under vacuum to afford complex **1** as a light orange powder (204 mg, 87%). Anal. Calcd for $C_{14}H_{19}BF_4N_2O_3Pd$: C, 36.83; H, 4.20; N, 6.14. Found: C, 36.76; H, 4.16; N, 6.20. ESI-MS (positive ion mode, MeCN): *m/z* 369.04 [M^+]. ^{1}H NMR (400 MHz, CD_3CN, 25°C): δ 8.68 (d, br., *J* = 5.5, 1H, 6-py), 8.42 (s, 1H, HC=N), 8.42 (ddd, overlapped with HC=N, *J* = 7.8, 1.4 Hz, 1H, 4-py), 8.16 (dd, *J* = 7.8, 1.6 Hz, 1H, 3-py), 7.95 (ddd, *J* = 7.8, 6.0, 1.5 Hz, 1H, 5-py), 5.86 (s, 1H, CH_{acac}), 3.95 – 3.89 (m, 2H, CH_2–N), 3.87 – 3.81 (m, 2H, CH_2–O), 3.47 (s, 3H, CH_3–O), 2.32 (s, 3H, $CH_{3,acac}$, «*cis*-Py»), 2.26 (s, 3H, $CH_{3,acac}$, «*trans*-Py»). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN, 25°C): 188.69 ($C_{CO\text{-}acac}$), 188.60 ($C_{CO\text{-}acac}$), 171.53 (C=N), 155.60 (2-py), 148.82 (6-py), 142.71 (4-py), 129.33 (5-py), 128.97 (3-py), 102.65 ($C_{CH\text{-}acac}$), 69.12

(CH_2–O), 58.44(CH_3–O), 57.03 (CH_2–N), 25.45($C_{Me\text{-}acac}$), 25.36($C_{Me\text{-}acac}$). ^{19}F NMR (376 MHz, CD_3CN, 25°C): δ −151.18 (s, 1F), −151.23 (s, 4F) (BF_4, intensity ratio of approximately 20:80 corresponding to the natural abundances of ^{10}B and ^{11}B, respectively). ^{15}N NMR (41 MHz, CD_3CN, 25°C, from HMBC experiment): δ −162.33 (Py), −135.34.

(Acetylacetonate-κ^{2}O,O')[N-(3-methoxypropyl)-1-(pyridin-2-yl)methanimine-κ^{2}N,N']palladium(II) tetrafluoroborate **2**. Complex [Pd(acac)$(MeCN)_2$]BF_4 (214.6 mg, 0.57 mmol) was dissolved in CH_2Cl_2 (26 ml). The ligand **L2** solution (1 ml, 0.57 mmol) was added dropwise to the resulting mixture over 30-40 min. The mixture was stirred at room temperature for 3 h. The resulting yellow solution was concentrated to approximately 3 ml under vacuum. Addition of diethyl ether (20 ml) resulted in an orange precipitate, which was collected, washed with diethyl ether (2×10 ml), and dried (8 h) under vacuum to afford complex **2** as a light orange powder (236.6 mg, 88%). Anal. Calcd for $C_{15}H_{21}BF_4N_2O_3Pd$: C, 38.29; H, 4.50; N, 5.95. Found: C, 38.89; H, 4.66; N, 5.61. ESI-MS (positive ion mode, MeCN): *m/z* 383.06 [M^+] . ^{1}H NMR (400 MHz, CD_3CN, 25°C): δ 8.56 (дд, *J* = 5.5, 1.5 Hz, 1H, 6-py), 8.34 (s, 1H, HC=N), 8.30 (ddd, overlapped with HC=N, *J* = 7.8, 1.4 Hz, 1H, 4-py), 8.02 (d, *J* = 7.6 Hz, 1H, 3-py), 7.83 (ddd, *J* = 7.8, 5.9, 1.4 Hz, 1H, 5-py), 5.74 (s, 1H, CH_{acac}), 3.72 (t, *J* = 7.0, Hz, 2H, CH_2–N), 3.47 (t, *J* = 5.9 Hz, 2H, CH_2–O), 3.29 (s, 3H, CH_3), 2.20 (s, 3H, $CH_{3,acac}$, *«cis*-Py»), 2.16 (s, 3H, $CH_{3,acac}$, *«trans*-Py»), 2.06 (quint., *J* = 6.5 Hz, 2H, CH_2). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN, 25°C): δ 188.18 ($C_{CO\text{-}acac}$), 187.95 ($C_{CO\text{-}acac}$), 170.27 (C=N), 155.22 (2-py), 148.17 (6-py), 142.14 (4-py), 128.66 (5-py), 128.25 (3-py), 102.08 ($C_{CH\text{-}acac}$), 68.78 (CH_2–O), 57.68 (CH_3–O), 55.15 (CH_2–N), 29.23 (CH_2), 24.95 ($C_{Me\text{-}acac}$), 24.84 ($C_{Me\text{-}acac}$).^{19}F NMR (376 MHz, CD_3CN, 25°C): δ −151.16 (s, 1F), −151.21 (s, 4F) (BF_4, intensity ratio of approximately 20:80 corresponding to the natural abundances of ^{10}B and ^{11}B, respectively).^{15}N NMR (41 MHz, CD_3CN, 25°C, from HMBC experiment): δ −168.25 (Py), −134.62.

(Acetylacetonate-κ^{2}O,O')[N-(2,6-dimethylphenyl)-1-(pyridin-2-yl)methanimine-κ^{2}N,N']palladium(II) tetrafluoroborate **3**. Complex [Pd(acac)$(MeCN)_2$]BF_4 (186.3 mg, 0.498 mmol) was dissolved in CH_2Cl_2 (23 ml) The ligand **L3** solution (1.2 ml, 0.548 mmol) was added dropwise to the resulting mixture over 30-40 min. The mixture was stirred at room temperature for 3 h. The resulting yellow solution was concentrated to approximately 3 ml under vacuum. The addition of diethyl ether (25 ml) resulted in a yellow precipitate which was collected, washed with diethyl ether (2×10 ml), and dried (8 h) under vacuum to afford complex **3** as a light yellow powder (213.7 mg, 85%). The product contained traces (< 1%) of Et_2O by ^{1}H NMR analysis. Anal. Calcd for $C_{19}H_{21}BF_4N_2O_2Pd$: C, 45.40; H, 4.21; N, 5.57. Found: C, 45.89; H, 4.39; N, 5.78. ESI-MS (positive ion mode, MeCN): *m/z* 415.06 [M^+]. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 8.65 (dd, *J* = 5.6, 1.5 Hz, 1H, 6-py), 8.58 (s, 1H, HC=N), 8.58 (d, overlapped with HC=N, *J* = 7.0, 1H, 3-py),

8.32 (td, *J* = 7.8, 1.5 Hz, 1H, 4-Py), 7.93 (ddd, *J* = 8.0, 5.5, 1.4 Hz, 1H, 5-py), 7.24 – 7.16 (m, 1H, Ar), 7.15 – 7.05 (m, 2H, Ar), 5.50 (s, 1H, CH_{acac}), 2.33 (s, 6H, CH_3), 2.20 (s, 3H, $CH_{3,acac}$, *«cis*-Py»), 1.74 (s, 3H, $CH_{3,acac}$, *«trans*-Py»). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25°C): δ 187.98 ($C_{CO\text{-}acac}$), 187.28 ($C_{CO\text{-}acac}$), 173.63 (C=N), 154.95 (2-py), 148.21 (6-py), 142.60 (4-py), 142.52 (1-Ar), 131.16 (3-py), 130.71 (2,6-Ar), 129.60 (5-py), 128.76 (4-Ar), 128.41 (3,5-Ar), 102.36 ($C_{CH\text{-}acac}$), 25.86 ($C_{Me\text{-}acac}$), 25.21 ($C_{Me\text{-}acac}$), 18.47 (CH_3-Ar). ^{19}F NMR (376 MHz, $CDCl_3$, 25°C): δ −152.08 (s, 1F), −152.13 (s, 4F) (BF_4, intensity ratio of approximately 20:80 corresponding to the natural abundances of ^{10}B and ^{11}B, respectively). ^{15}N NMR (41 MHz, $CDCl_3$, 25°C, from HMBC experiment): δ −162.36 (Py), −127.42.

(Acetylacetonate-κ²O,O')[N-mesityl-1-(pyridin-2-yl)methanimine-κ²N,N']palladium(II) tetrafluoroborate **4**. Complex $[Pd(acac)(MeCN)_2]BF_4$ (186.3 mg, 0.498 mmol) was dissolved in CH_2Cl_2 (25 ml). The ligand **L4** solution (1.4 ml, 0.516 mmol) was added dropwise to the resulting mixture over 30-40 min. The mixture was stirred at room temperature for 3 h. The resulting yellow solution was concentrated to approximately 3 ml under vacuum. The addition of diethyl ether (25 ml) resulted in a yellow precipitate which was collected, washed with diethyl ether (2×10 ml), and dried (8 h) under vacuum to produce complex **4** as a yellow powder (237.5 mg, 95%). The product contained traces (< 0.5%) of Et_2O by ^1H NMR analysis. Anal. Calcd for $C_{20}H_{23}BF_4N_2O_2Pd$: C, 46.50; H, 4.49; N, 5.42. Found: C, 46.14; H, 4.75; N, 5.31. ESI-MS (positive ion mode, MeCN): *m/z* 429.08 $[M^+]$ ^1H NMR (400 MHz, $CDCl_3$, 25°C): δ 8.65 (dd, *J* = 5.6, 1.5 Hz, 1H, 6-py), 8.54 (dd, overlapped with HC=N, *J* = 7.6, 1.3 Hz, 1H, 3-py), 8.53 (s, 1H, HC=N), 8.31 (td, *J* = 7.8, 1.6 Hz, 1H, 4-Py), 7.93 (ddd, *J* = 7.9, 5.5, 1.5 Hz, 1H, 5-py), 6.89 (s, 2H, Ar), 5.50 (s, 1H, CH_{acac}), 2.27 (s, 6H), 2.27 (s, 3H, CH_3), 2.19 (s, 3H, $CH_{3,acac}$, *«cis*-Py»), 1.77 (c 3H, $CH_{3,acac}$, *«trans*-Py»). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25°C): δ 188.38 ($C_{CO\text{-}acac}$), 187.65 ($C_{CO\text{-}acac}$), 173.93 (C=N), 155.29 (2-py), 148.62 (6-py), 142.84 (4-py), 140.75 (1-Ar), 138.96 (4-Ar), 131.31 (3-py), 130.83 (2,6-Ar), 129.95 (5-py), 129.44 (3,5-Ar), 102.73 ($C_{CH\text{-}acac}$), 26.23 ($C_{Me\text{-}acac}$), 25.69 ($C_{Me\text{-}acac}$), 21.51 (4-CH_3-Ar), 18.77 (2,6-CH_3-Ar). ^{19}F NMR (376 MHz, $CDCl_3$, 25°C): δ −152.15 (s, 1F), −152.20 (s, 4F) (BF_4, intensity ratio of approximately 20:80 corresponding to the natural abundances of ^{10}B and ^{11}B, respectively). ^{15}N NMR (41 MHz, $CDCl_3$, 25°C, from HMBC experiment): δ −162.77 (Py), −127.04.

(Acetylacetonate-κ²O,O')[N-(2,6-diisopropylphenyl)-1-(pyridin-2-yl)methanimine-κ²N,N']palladium(II) tetrafluoroborate **5**. Complex $[Pd(acac)(MeCN)_2]BF_4$ (171.3 mg, 0.458 mmol) was dissolved in CH_2Cl_2 (25 ml). The ligand **L5** solution (1.4 ml, 0.479 mmol) was added dropwise to the resulting mixture over 30-40 min. The mixture was stirred for 3 h at room temperature. The resulting yellow solution was concentrated to approximately 3 ml under vacuum. The addition of diethyl ether (28 ml) resulted in a yellow precipitate, which was collected, washed

with diethyl ether (2×10 ml), and dried (8 h) under vacuum to produce complex **5** as a yellow powder (203.2 mg, 81%). The product contained traces (< 0.5%) of Et_2O by ^1H NMR analysis. Anal. Calcd for $C_{23}H_{29}BF_4N_2O_2Pd$: C, 49.44; H, 5.23; N, 5.01. Found: C, 49.61; H, 5.15; N, 5.01. ESI-MS (positive ion mode, MeCN): *m/z* 471.12 [M^+]. ^1H NMR (400 MHz, $CDCl_3$, 25°C): δ 8.69 (dd, *J* = 5.5, 1.5 Hz, 1H, 6-py), 8.64 (dd, *J* = 7.8, 1.4 Hz, 1H, 3-py), 8.59 (s, 1H, HC=N), 8.35 (td, *J* = 7.8, 1.5 Hz, 1H, 4-Py), 7.97 (ddd, *J* = 8.0, 5.5, 1.5 Hz, 1H, 5-py), 7.38 (t, *J* = 7.8 Hz, 1H, Ar), 7.20 (d, *J* = 7.8 Hz, 2H, Ar), 5.49 (s, 1H, CH_{acac}), 3.21 (sept., *J* = 6.8 Hz, 2H, $(CH_3)_2CH$), 2.20 (s, 3H, $CH_{3,acac}$, *«cis*-Py»), 1.72 (s, 3H, $CH_{3,acac}$, *«trans*-Py»), 1.24 (dd, *J* = 8.5, 6.8 Hz, 12H, $(CH_3)_2CH$). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25°C): δ 187.68 ($C_{CO\text{-}acac}$), 187.51 ($C_{CO\text{-}acac}$), 173.01 (C=N), 154.72 (2-py), 148.41 (6-py), 142.71 (4-py), 141.24 (2,6-Ar), 139.84 (1-Ar), 131.34 (3-py), 129.85(5-py), 129.52 (4-Ar), 123.67 (3,5-Ar), 102.49 ($C_{CH\text{-}acac}$), 28.81($(CH_3)_2CH$), 25.91 ($C_{Me\text{-}acac}$), 25.21 ($C_{Me\text{-}acac}$), 23.96 ($(CH_3)_2CH$), 23.32 ($(CH_3)_2CH$). ^{19}F NMR (376 MHz, $CDCl_3$, 25°C): δ −152.15 (s, 1F), −152.20 (s, 4F) (BF_4, intensity ratio of approximately 20:80 corresponding to the natural abundances of ^{10}B and ^{11}B, respectively). ^{15}N NMR (41 MHz, $CDCl_3$, 25°C, from HMBC experiment): δ −162.90 (Py), −127.40.

3 NMR spectra

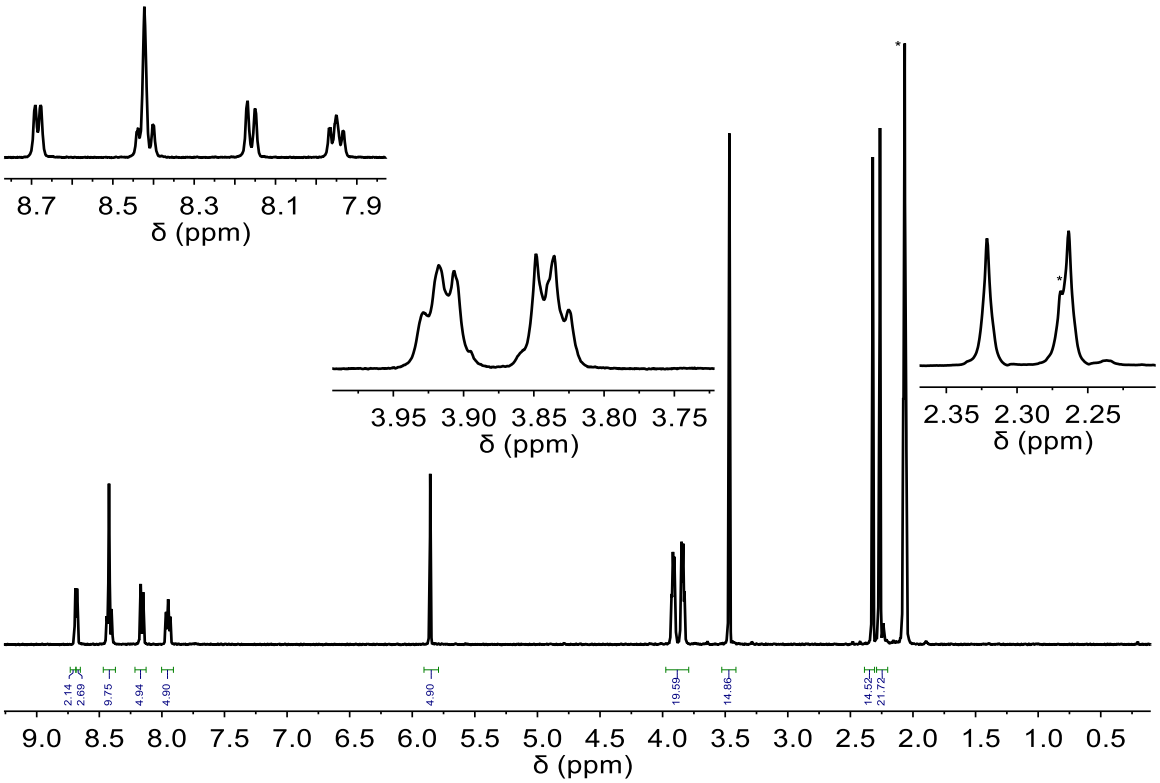


Figure S3 – ^{1}H NMR (400 MHz, CD_3CN, 25°C): spectrum of **1**

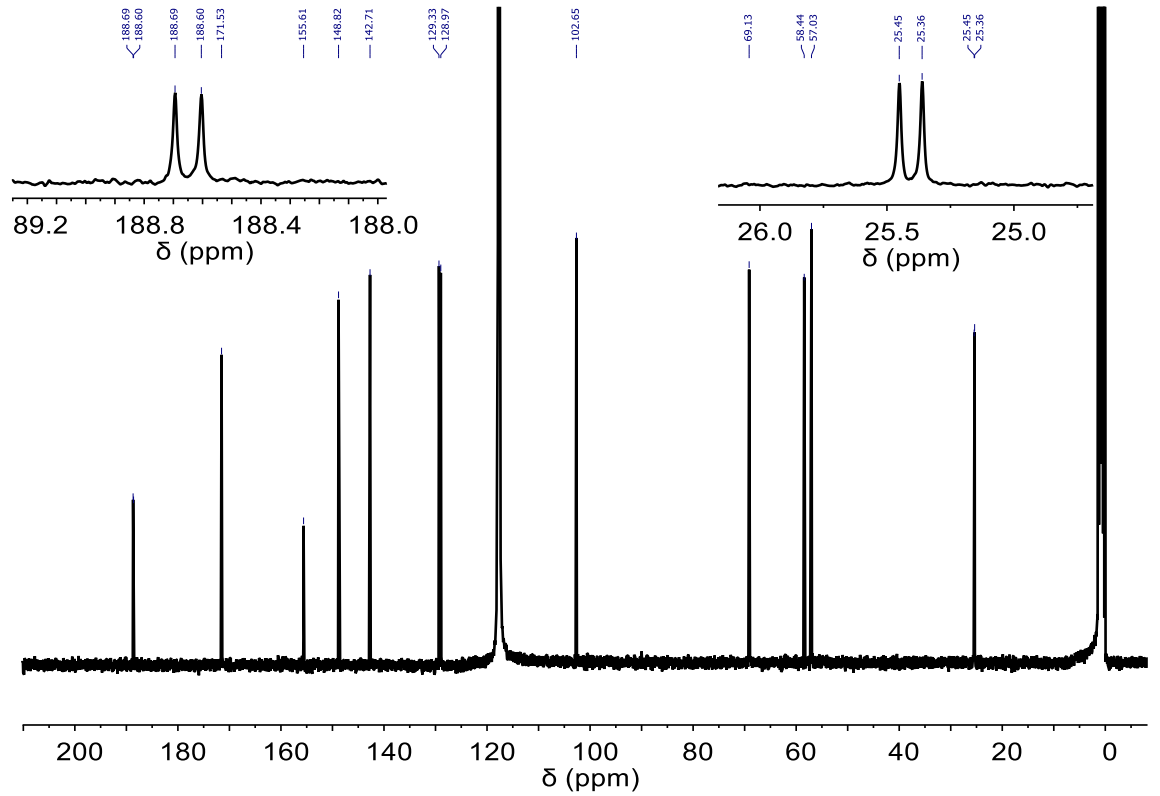


Figure S4 – ^{13}C NMR (101 MHz, CD3CN, 25°C): spectrum of **1**

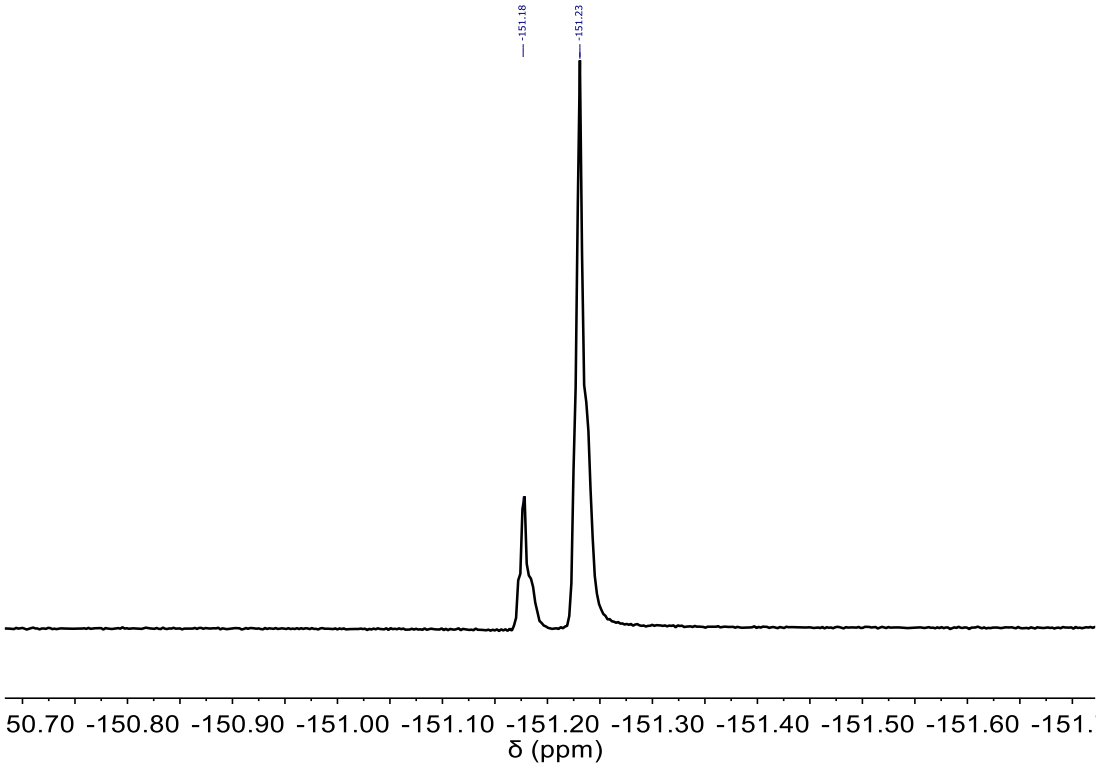


Figure S5 – ^{19}F NMR (376 MHz, CD_3CN, 25°C): spectrum of **1**

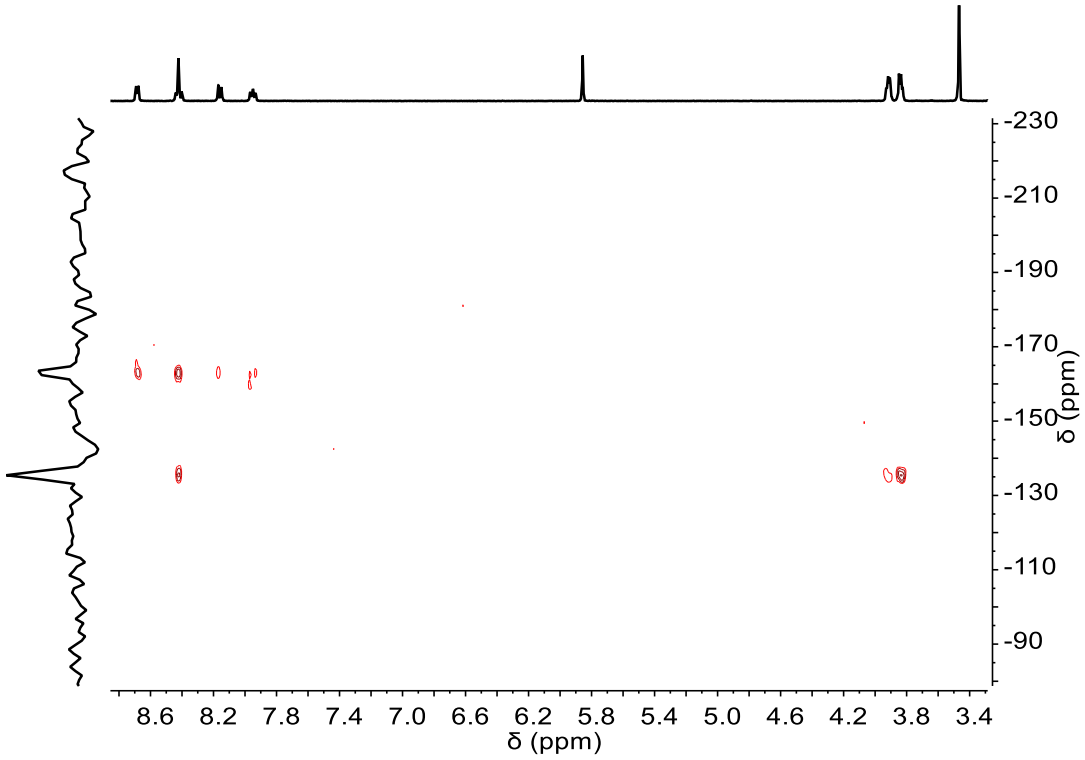


Figure S6 – ^{15}N-^{1}H HMBC (CD_3CN, 25°C): spectrum of **1**

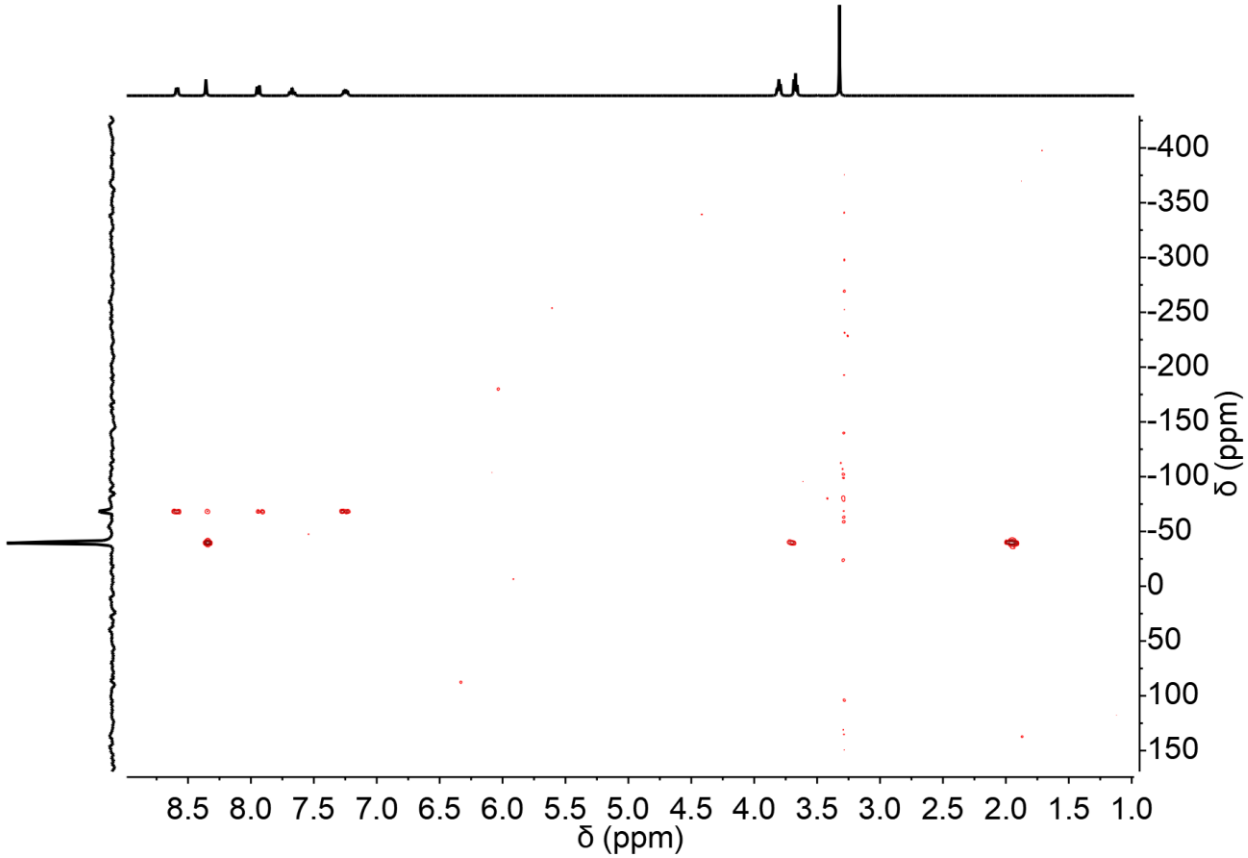


Figure S7 – ^{15}N-^{1}H HMBC (CD_3CN, 25°C): spectrum of **L1**

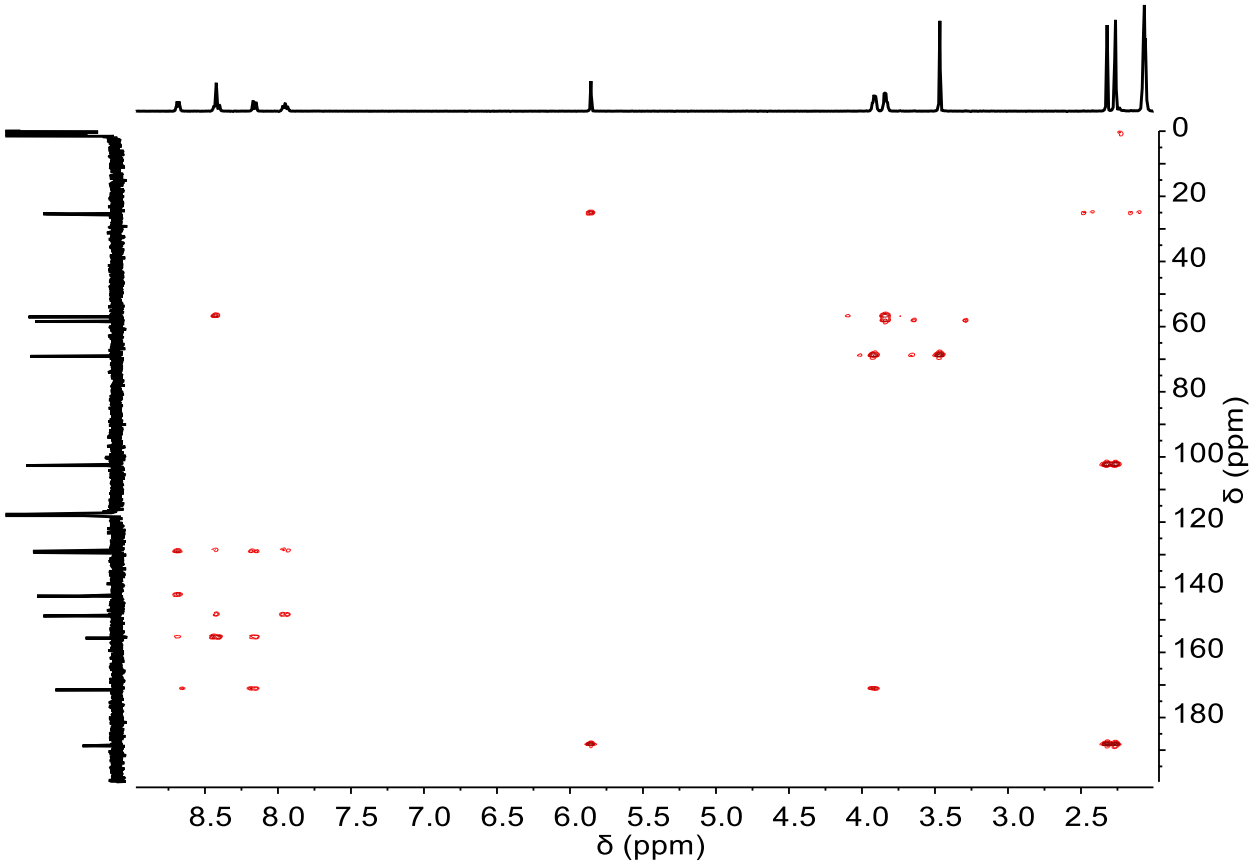


Figure S8 – ^{13}C-^{1}H HMBC (CD_3CN, 25°C): spectrum of **1**

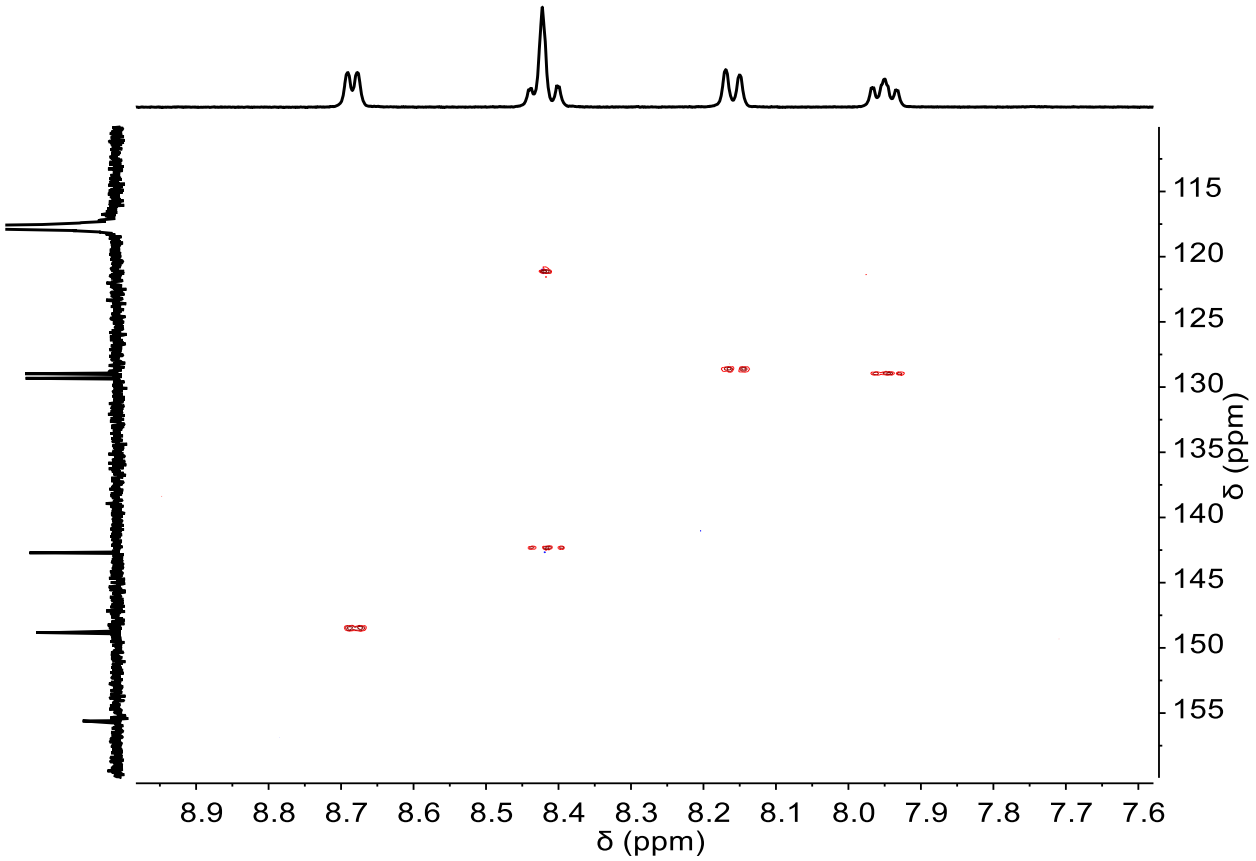


Figure S9 – ^{13}C-^{1}H HSQC (CD_3CN, 25°C): spectrum of **1**

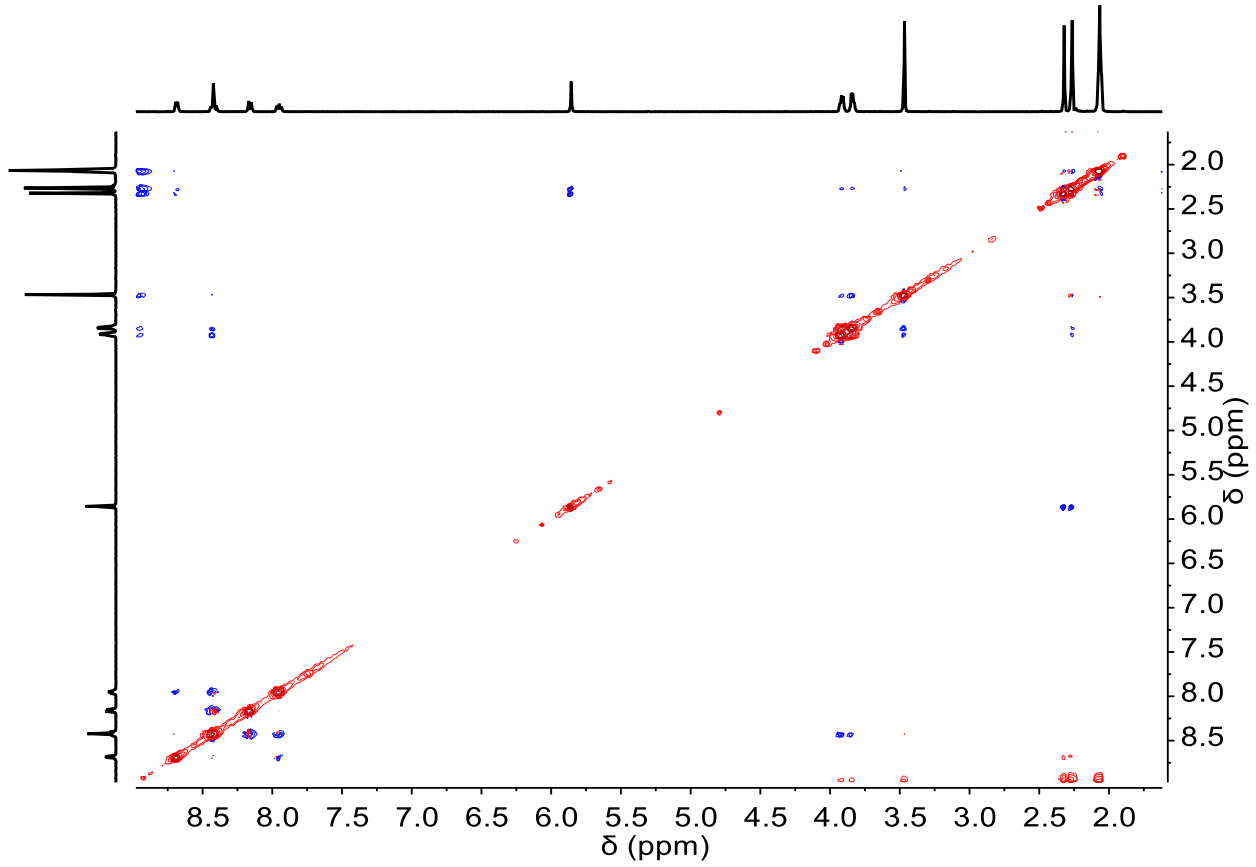


Figure S10 – ^{1}H-^{1}H NOESY (400 MHz, CD3CN, 25°C): spectrum of **1**

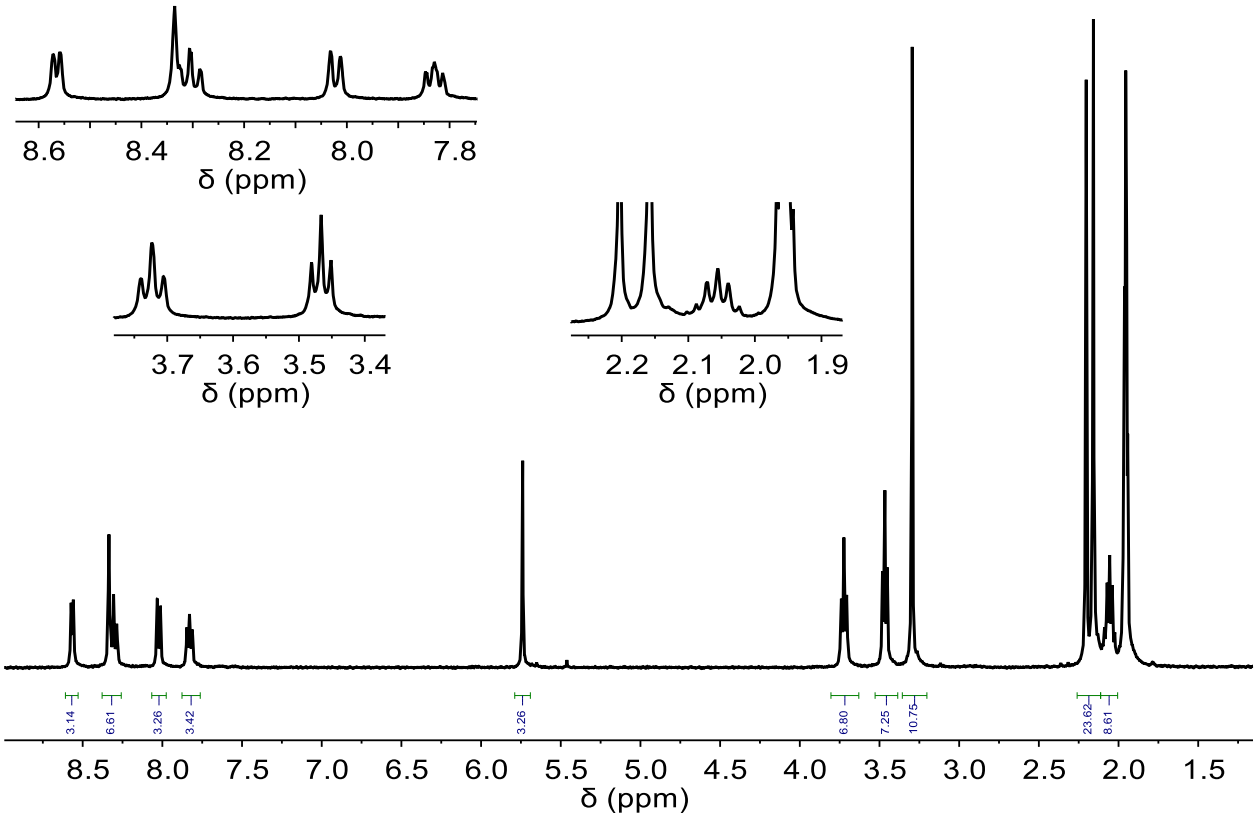


Figure S11 – ^{1}H NMR (400 MHz, CD_3CN, 25°C): spectrum of **2**

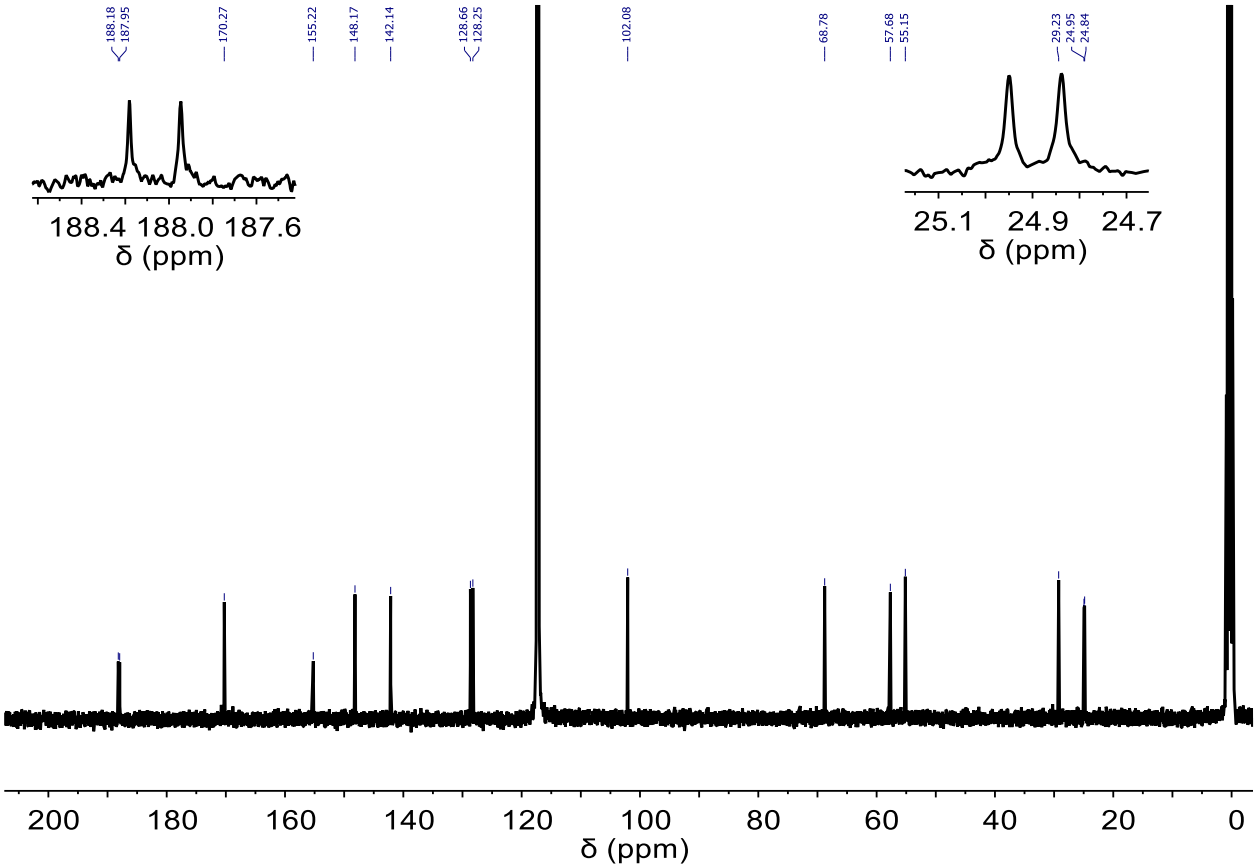


Figure S12 – ^{13}C NMR (101 MHz, CD_3CN, 25°C): spectrum of **2**

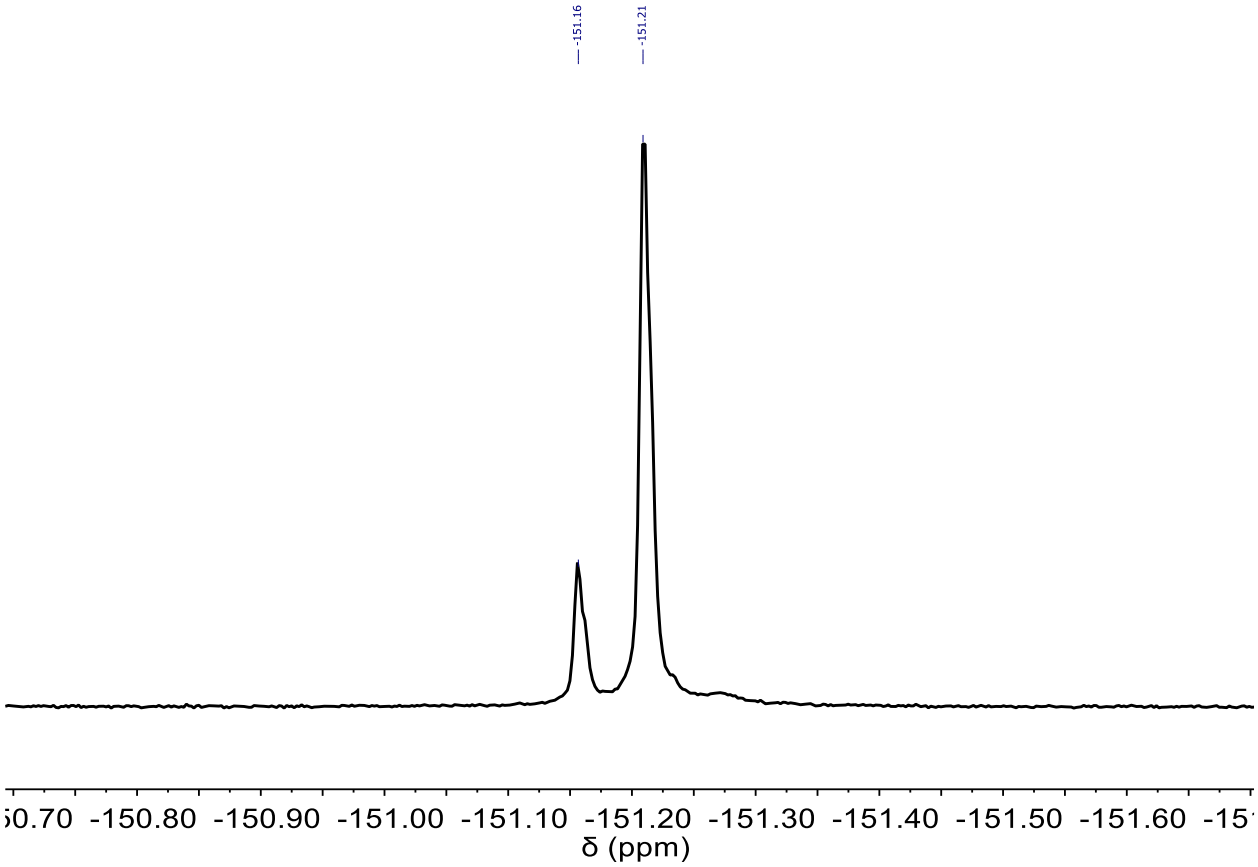


Figure S13 – ^{19}F NMR (376 MHz, CD_3CN, 25°C): spectrum of **2**

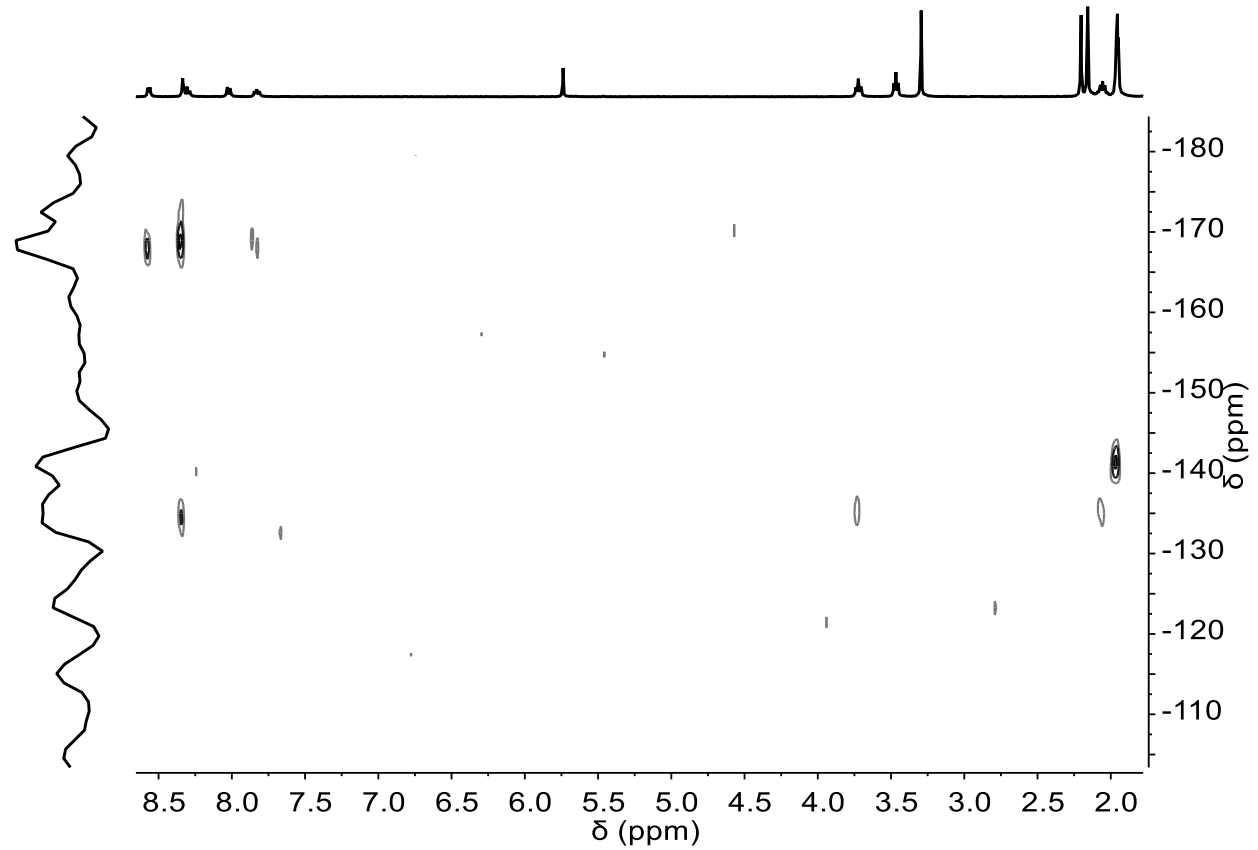


Figure S14 – ^{15}N-^{1}H HMBC (CD_3CN, 25°C): spectrum of **2**

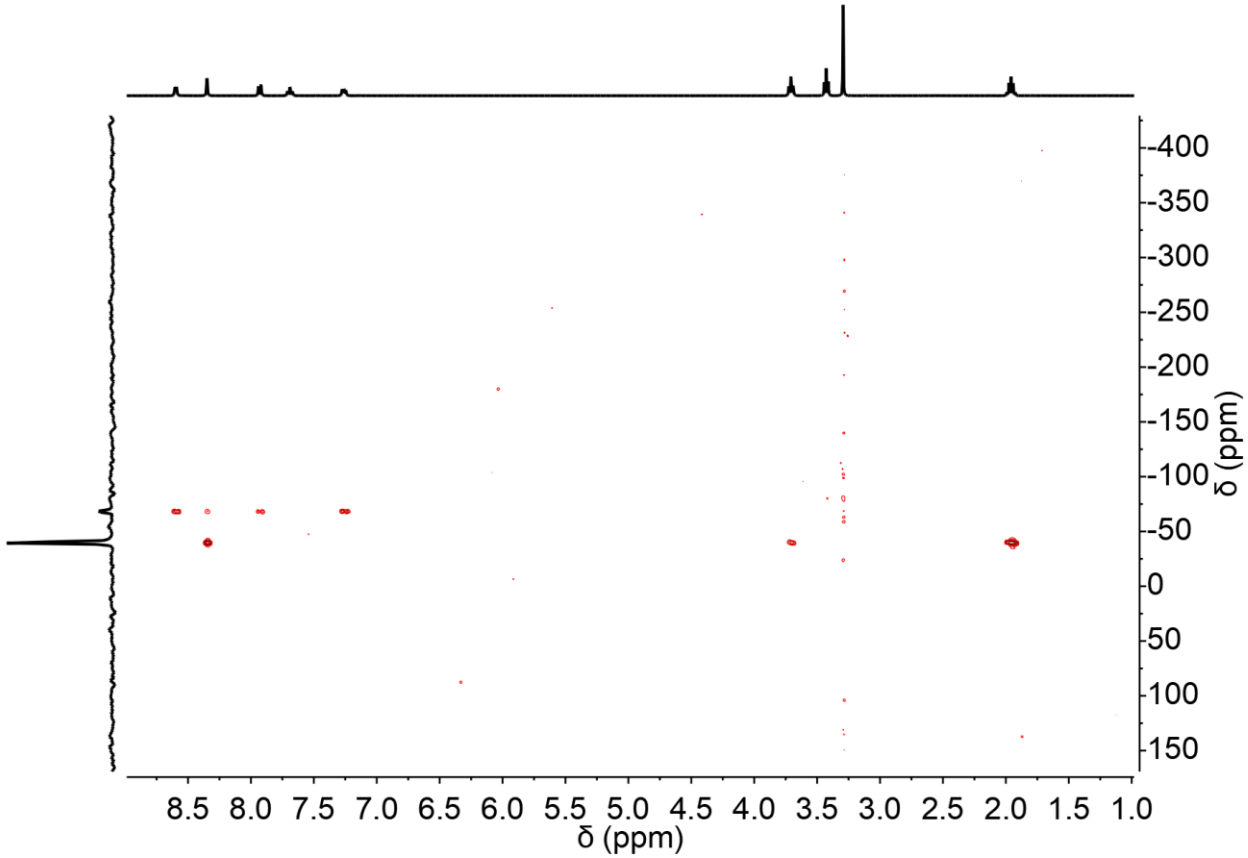


Figure S15 – ^{15}N-^{1}H HMBC (CD_3CN, 25°C): spectrum of **L2**

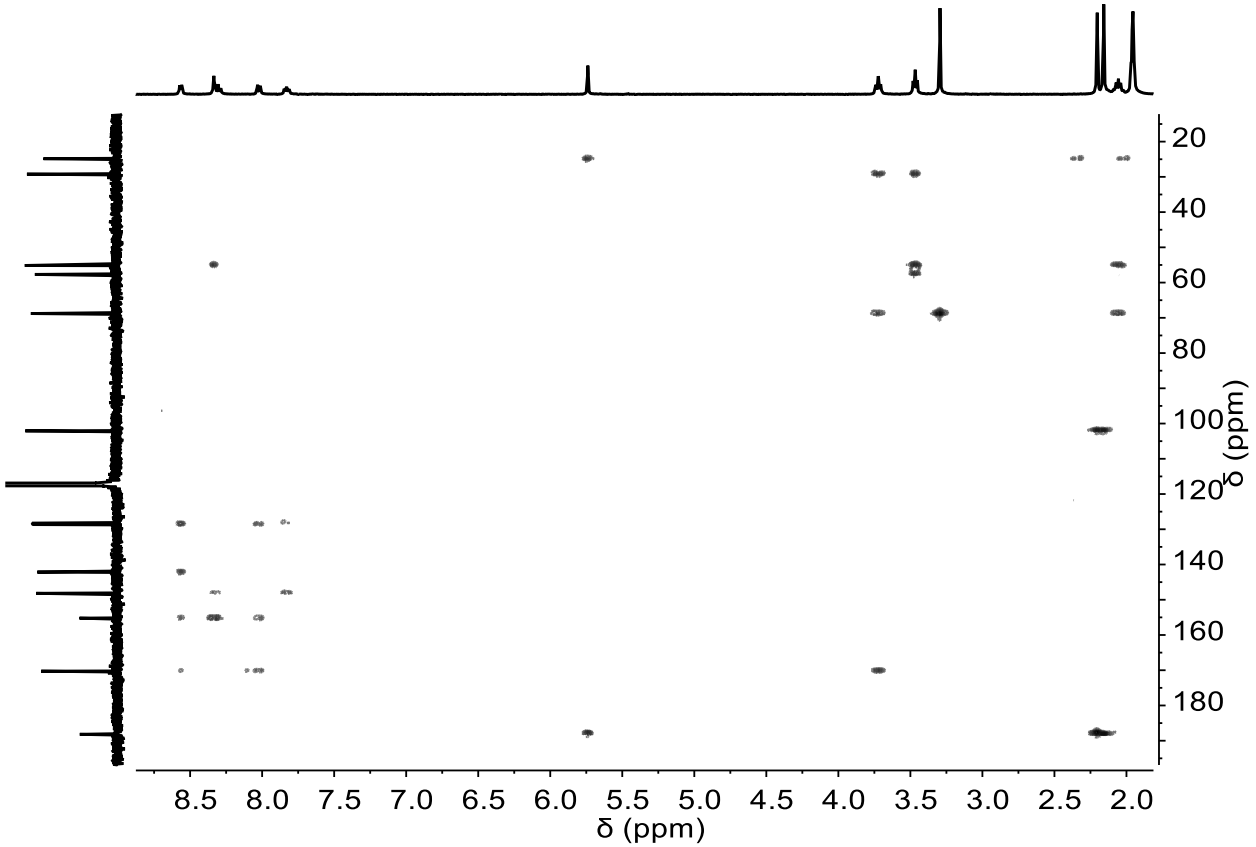


Figure S16 – ^{13}C-^{1}H HMBC (CD_3CN, 25°C): spectrum of **2**

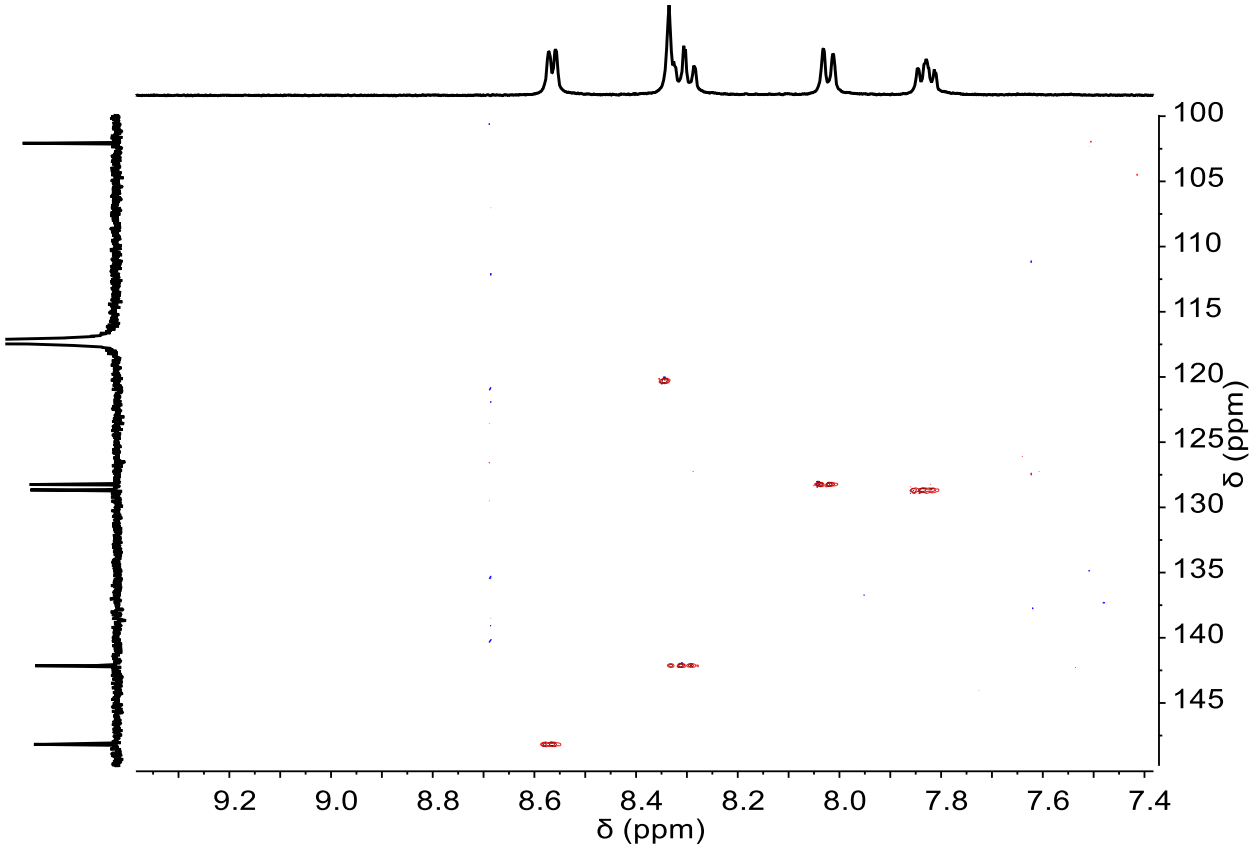


Figure S17 – ^{13}C-^{1}H HSQC (CD_3CN, 25°C): spectrum of **2**

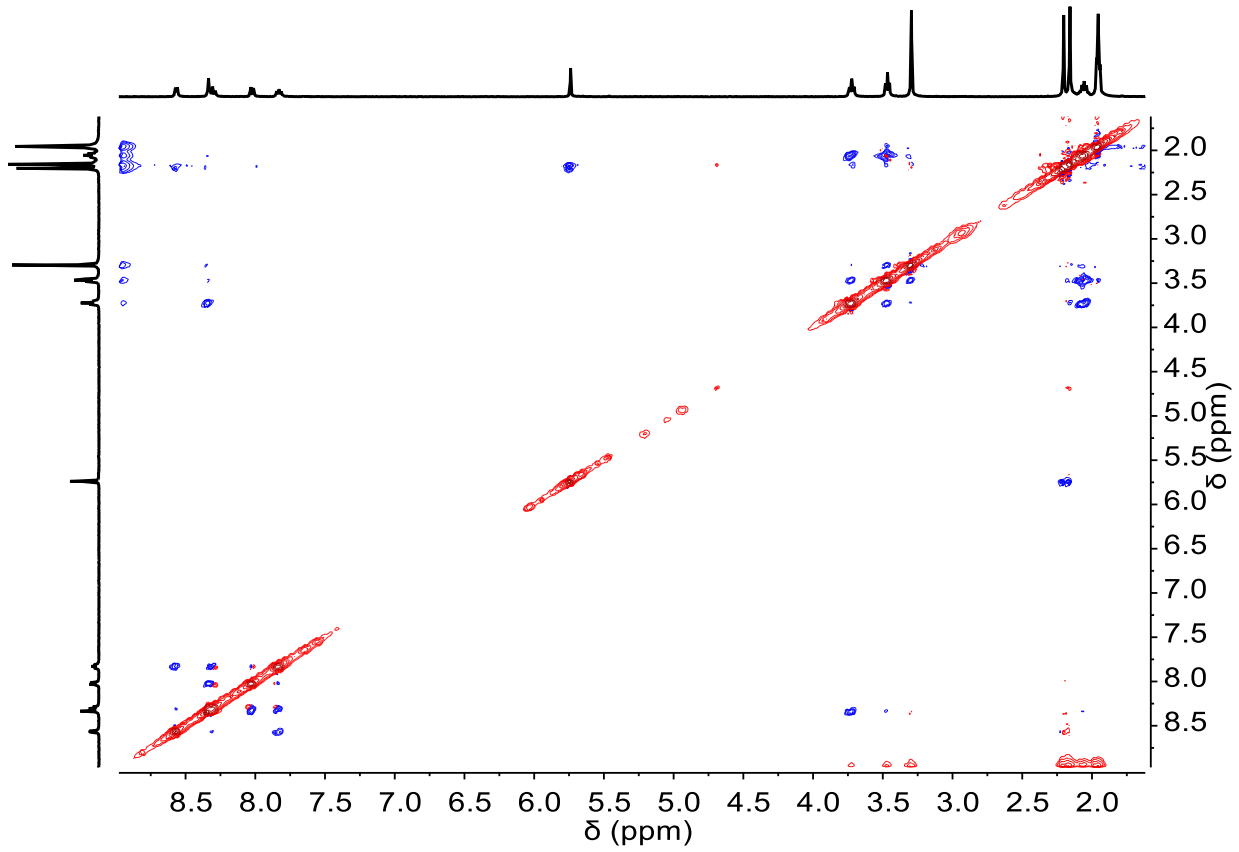


Figure S18 – ^{1}H-^{1}H NOESY (CD_3CN, 25°C): spectrum of **2**

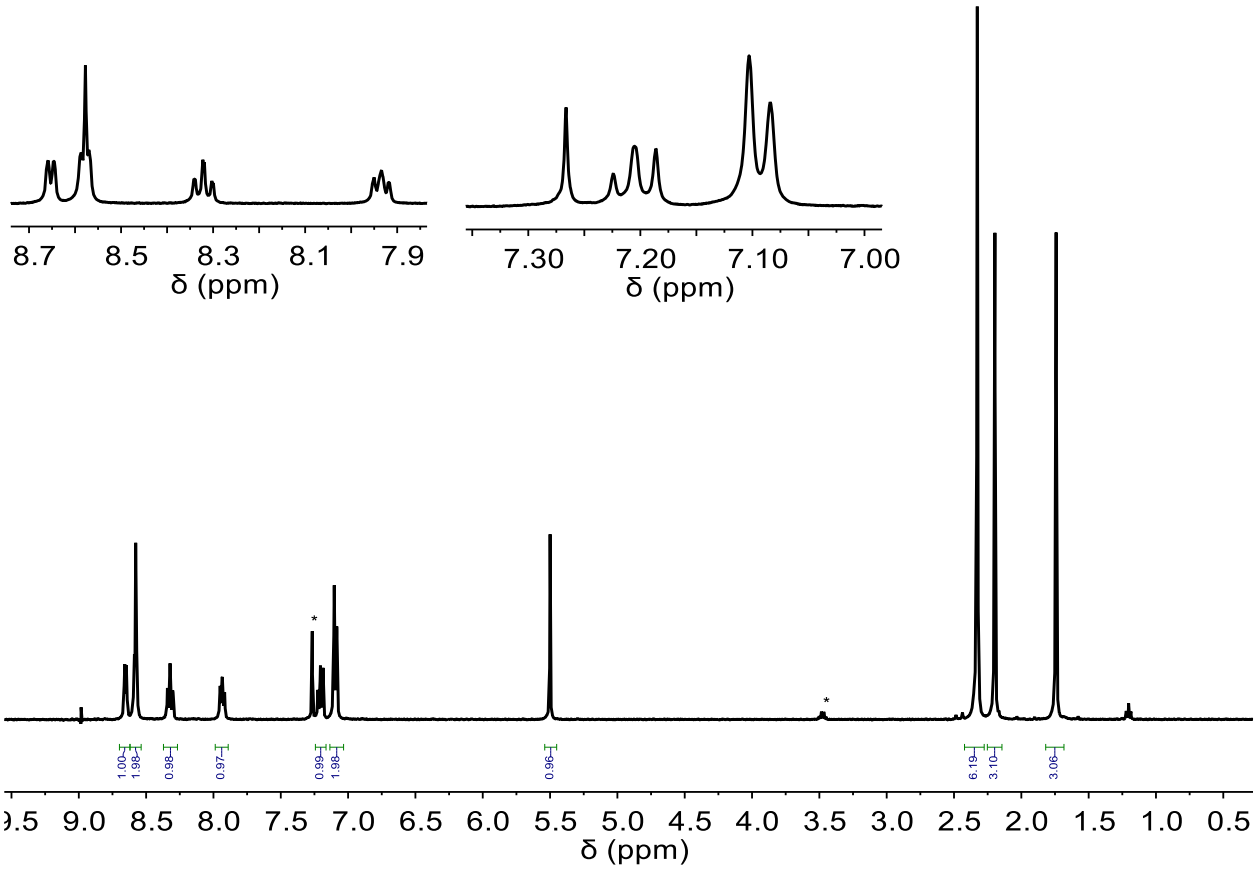


Figure S19 – NMR (400 MHz, $CDCl_3$, 25°C): spectrum of **3**

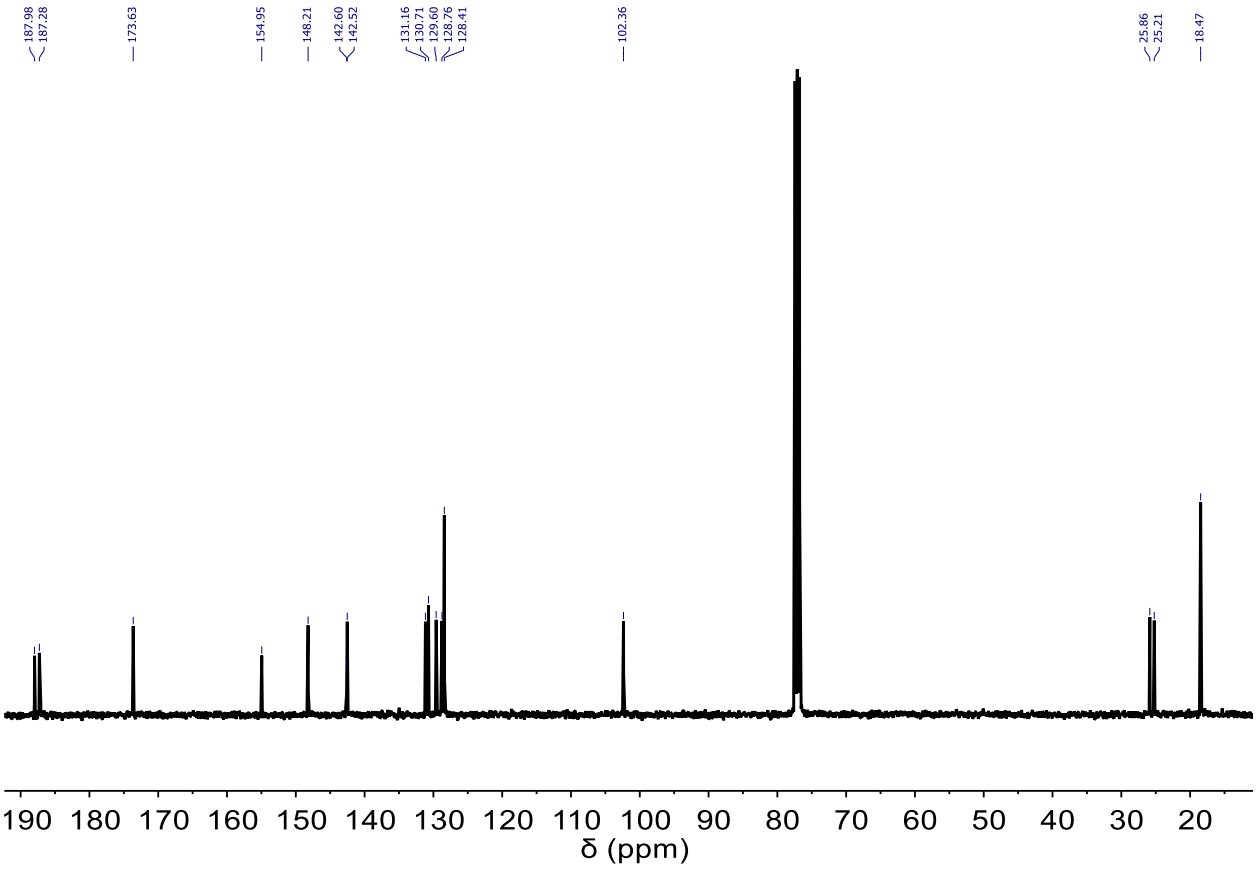


Figure S20 – ^{13}C NMR (101 MHz, $CDCl_3$, 25°C): spectrum of **3**

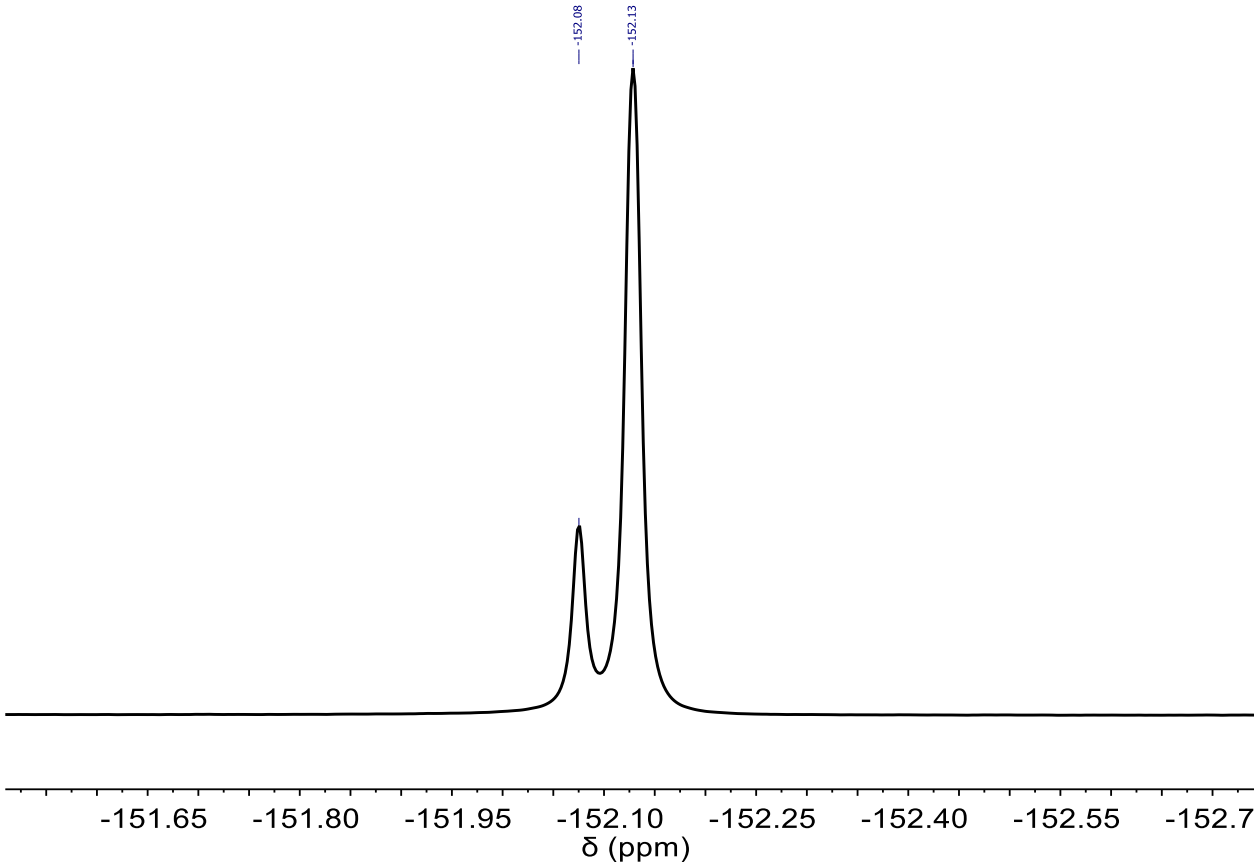


Figure S21 – ^{19}F NMR (376 MHz, $CDCl_3$, 25°C): spectrum of **3**

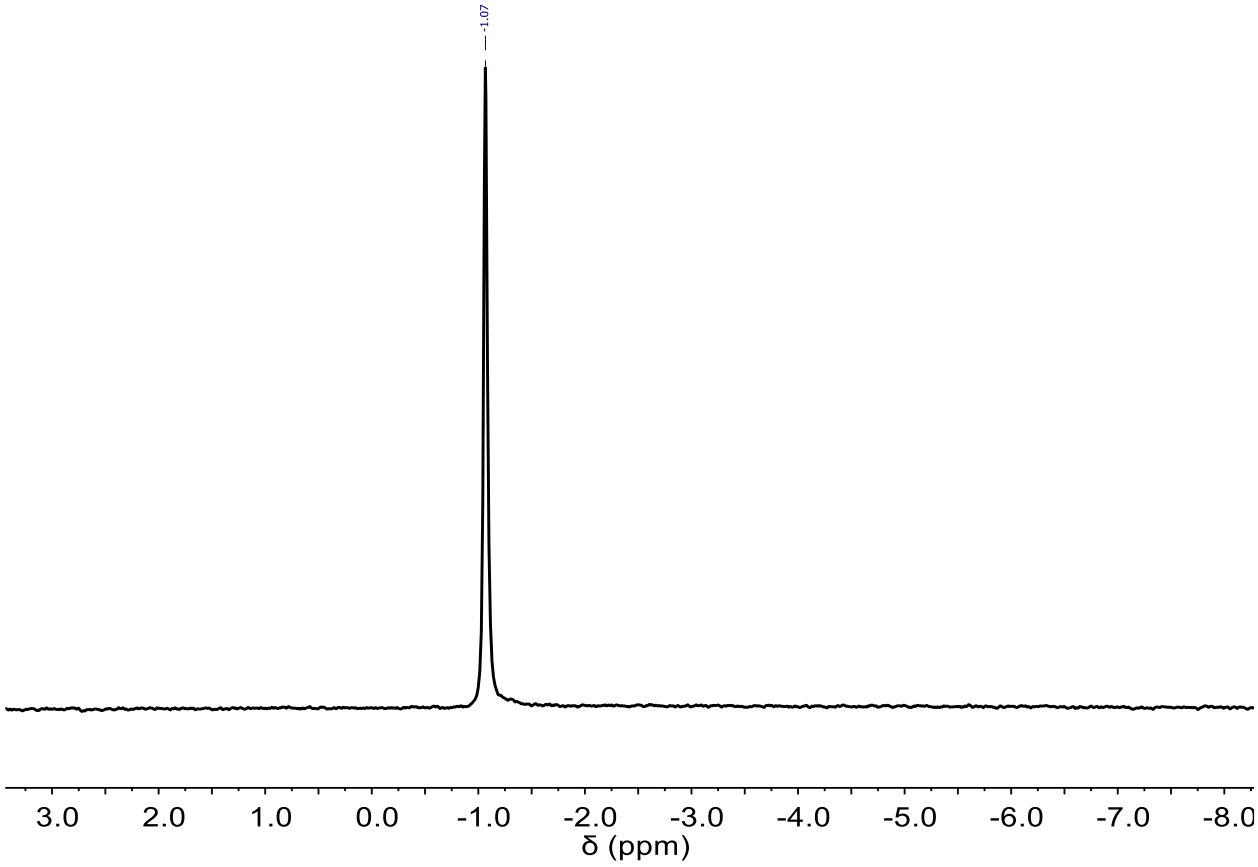


Figure S22 – ^{11}B NMR (128 MHz, $CDCl_3$, 25°C): spectrum of **3**

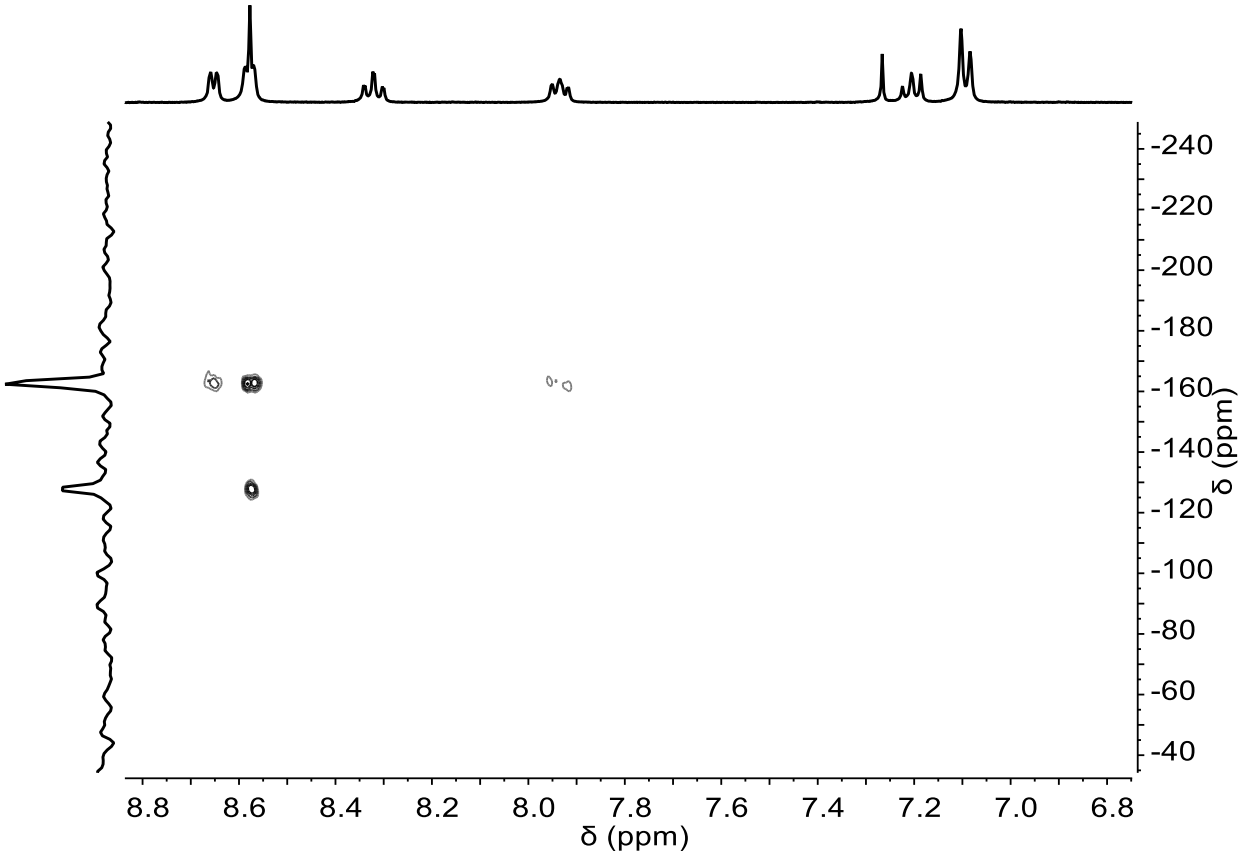


Figure S23 – ^{15}N-^{1}H HMBC ($CDCl_3$, 25°C): spectrum of **3**

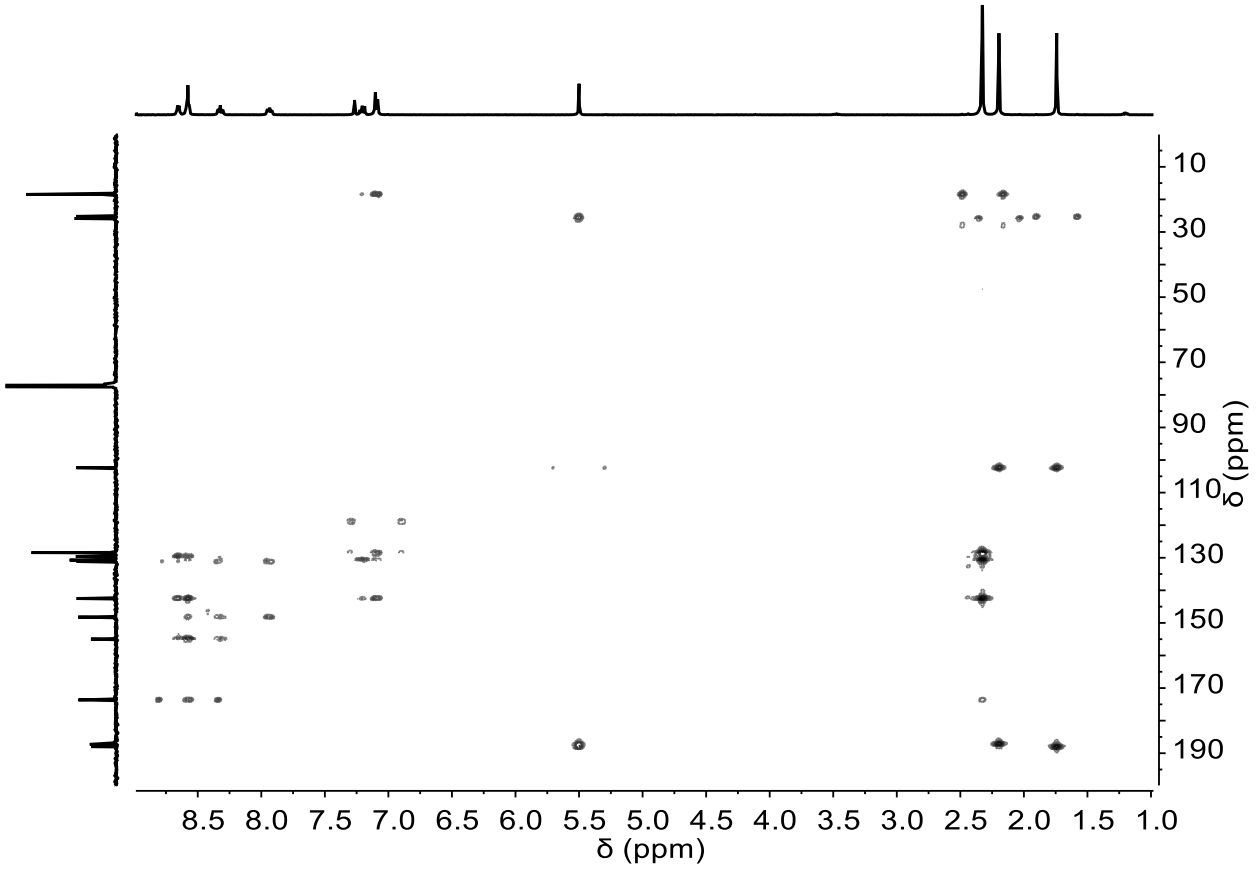


Figure S24 – ^{13}C-^{1}H HMBC ($CDCl_3$, 25°C): spectrum of **3**

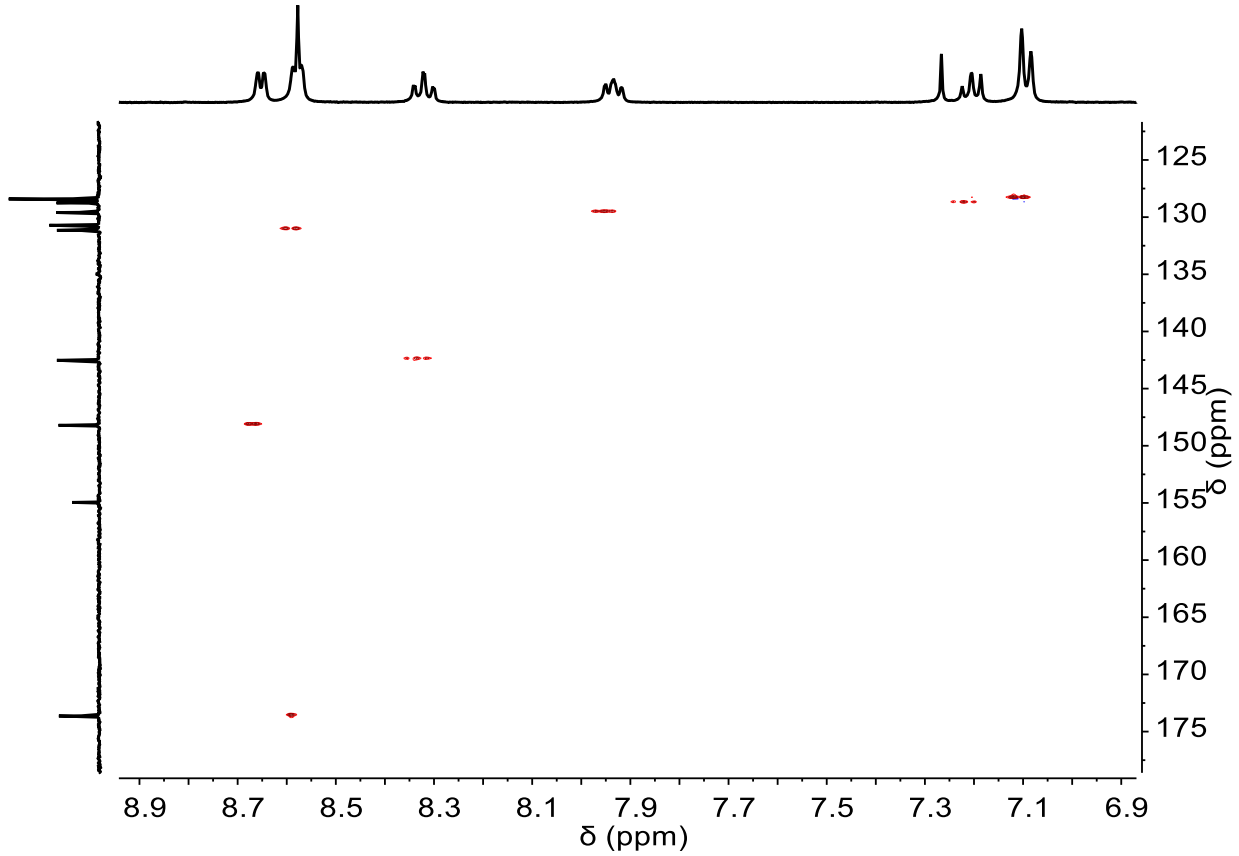


Figure S25 – ^{13}C-^{1}H HSQC ($CDCl_3$, 25°C): spectrum of **3**

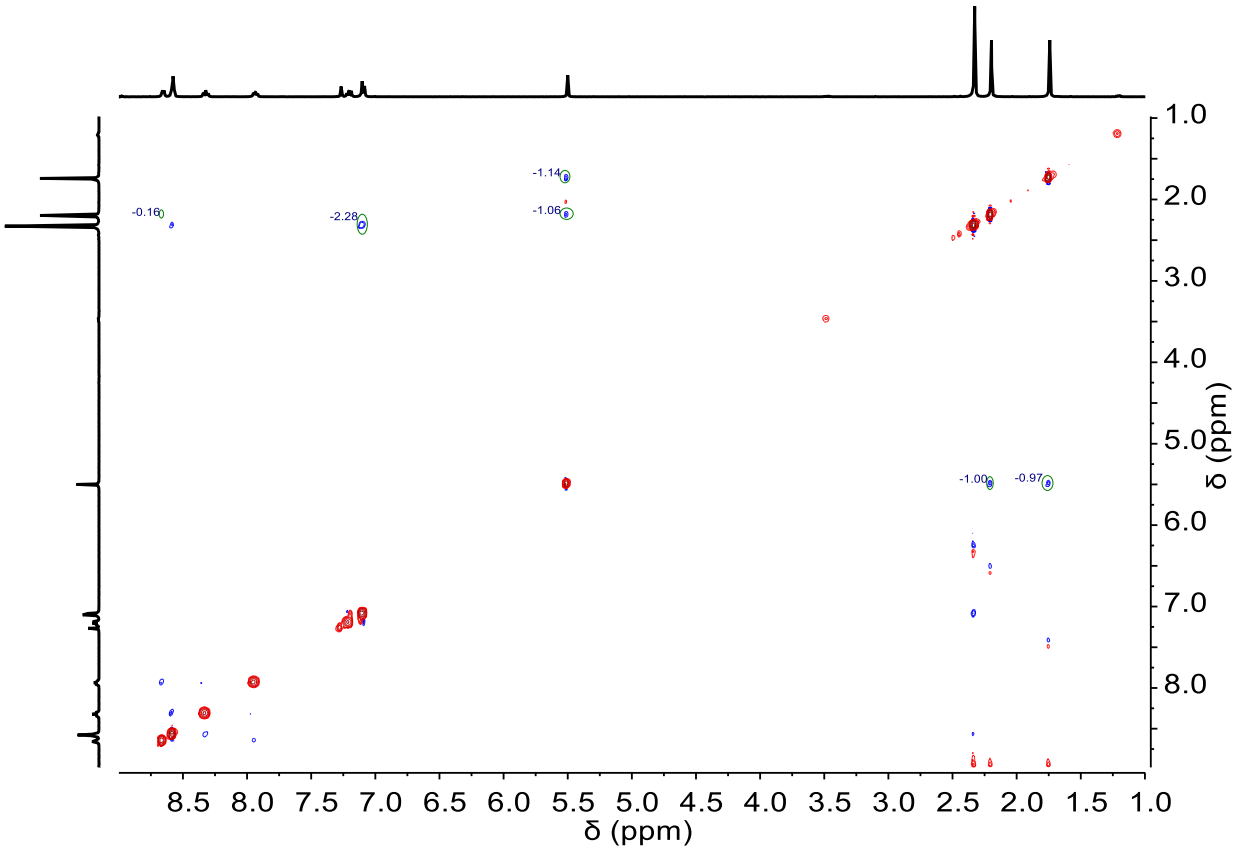


Figure S26 – ^{1}H-^{1}H NOESY ($CDCl_3$, 25°C): spectrum of **3**

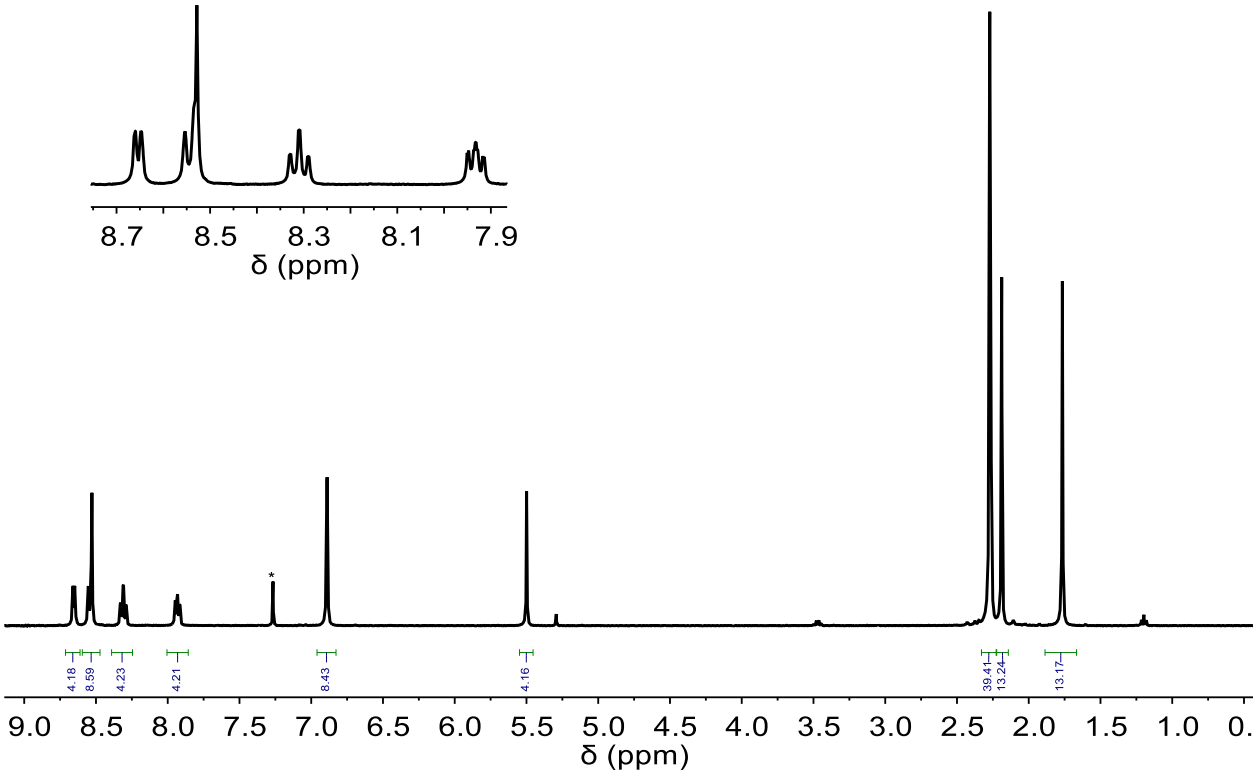


Figure S27 – ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): spectrum of **4**

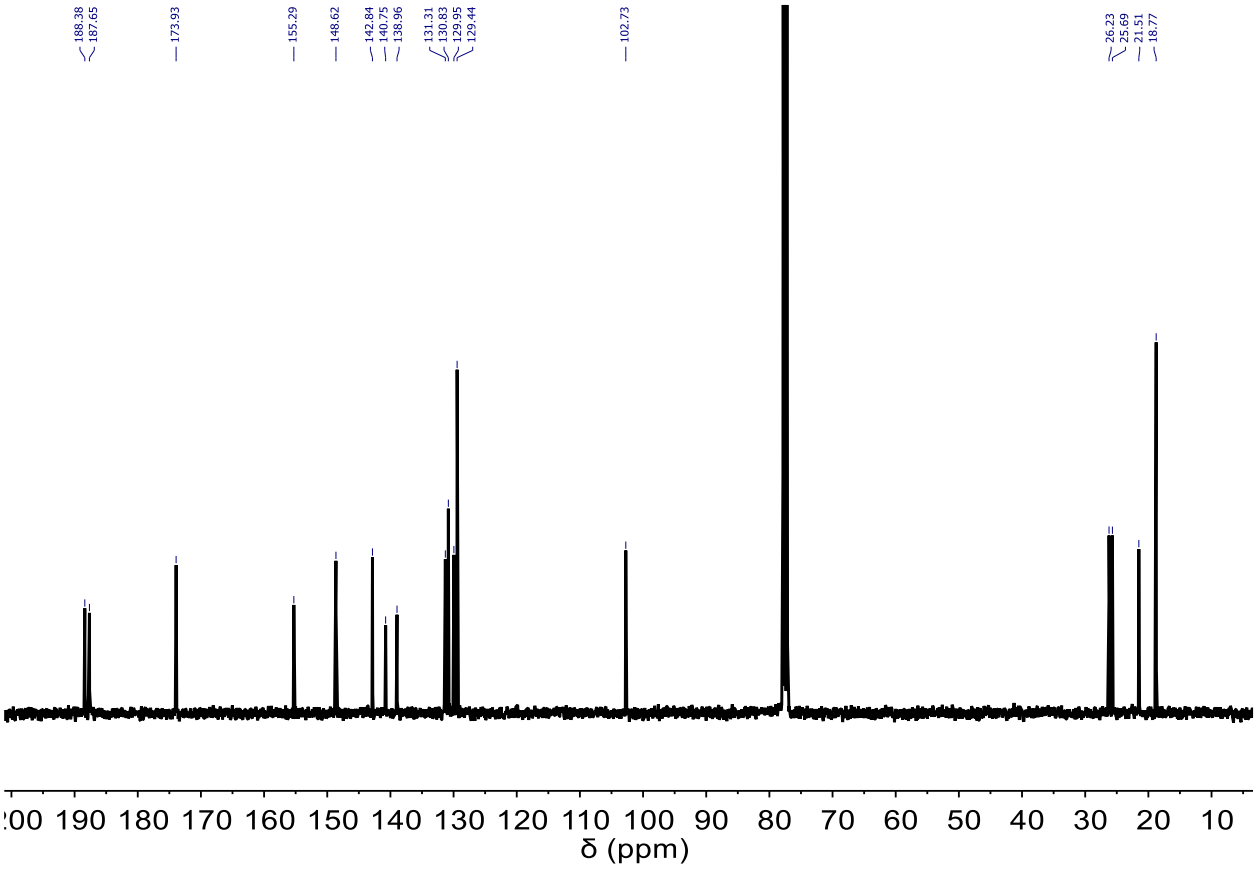


Figure S28 – ^{13}C NMR (101 MHz, $CDCl_3$, 25°C): spectrum of **4**

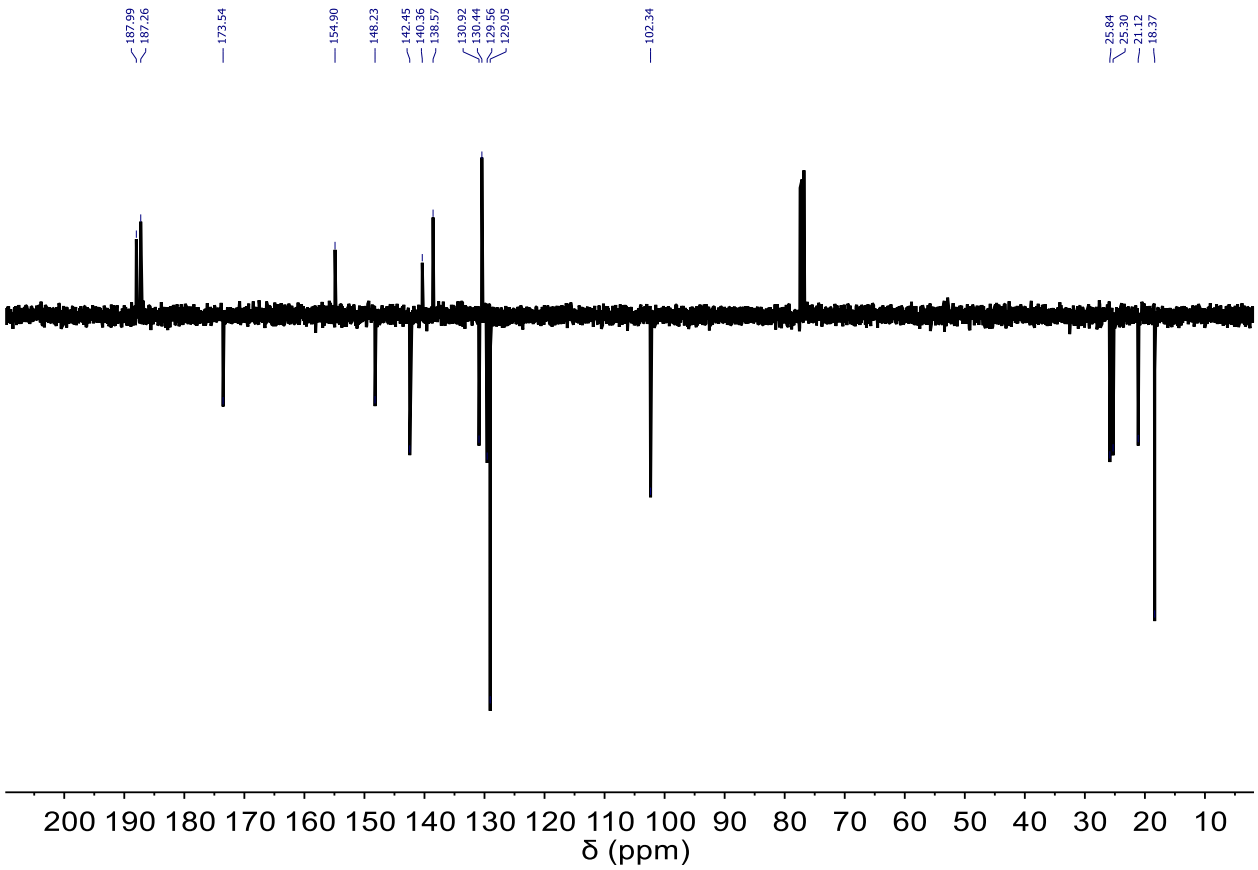


Figure S29 – $^{13}C\{^{1}H\}$ DEPT ($CDCl_3$, 25°C): spectrum of **4**

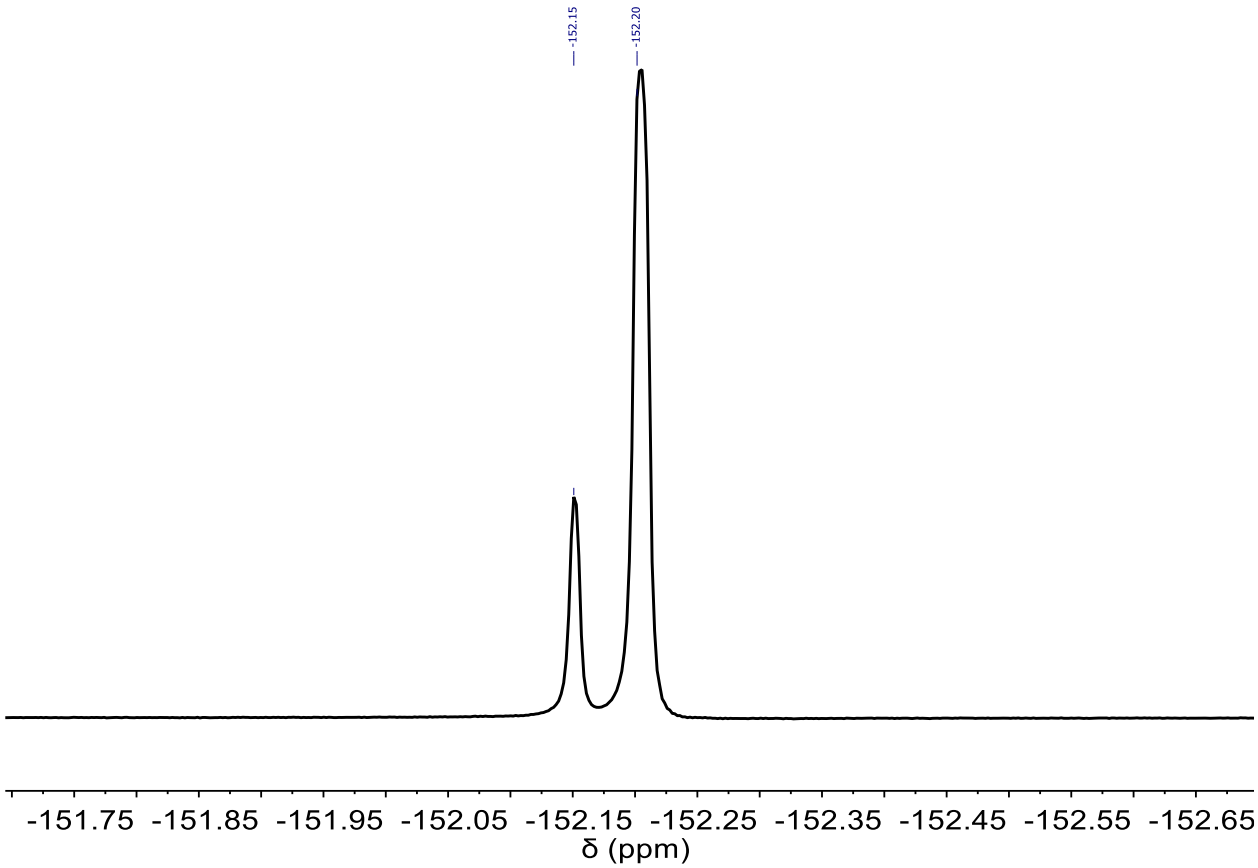


Figure S30 – ^{19}F NMR (376 MHz, $CDCl_3$, 25°C): spectrum of **4**

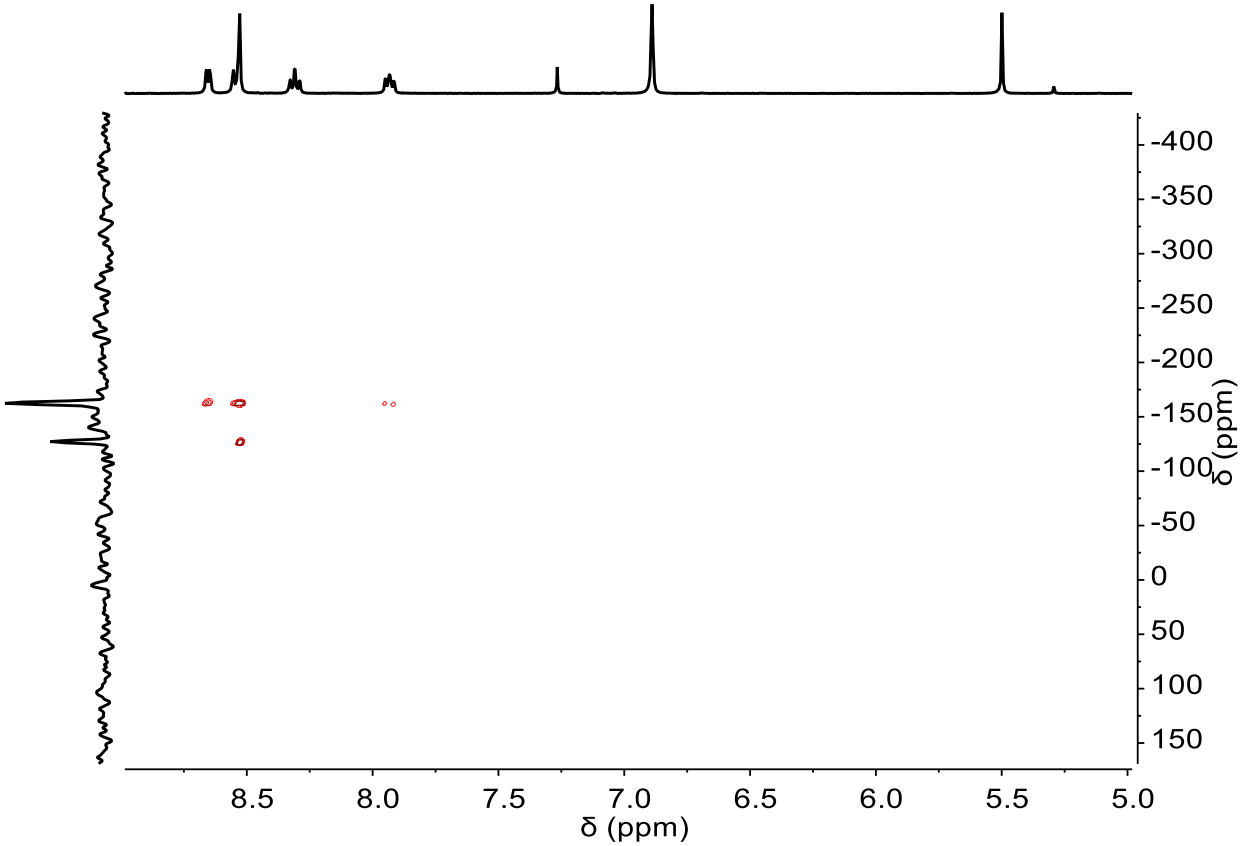


Figure S31 – ^{15}N-^{1}H HMBC ($CDCl_3$, 25°C): spectrum of **4**

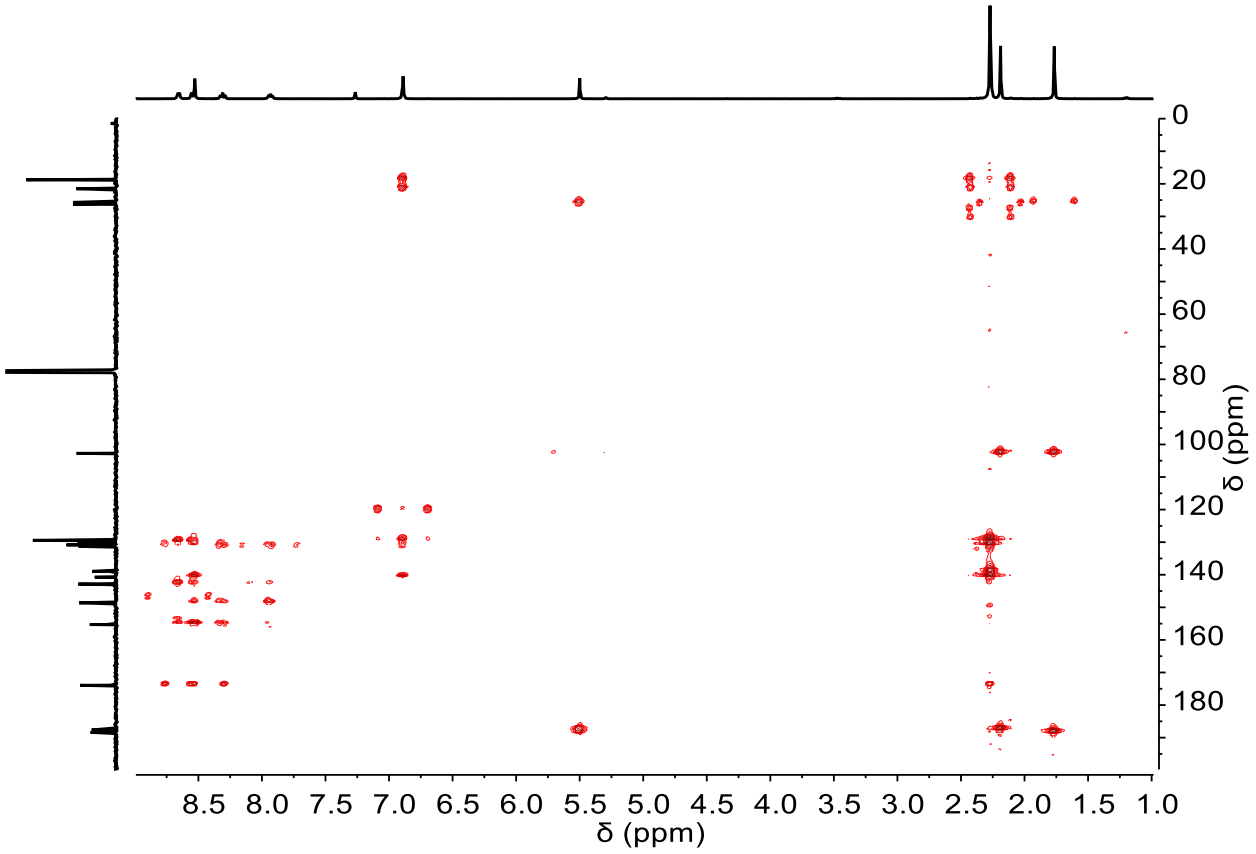


Figure S32 – ^{13}C-^{1}H HMBC ($CDCl_3$, 25°C): spectrum of **4**

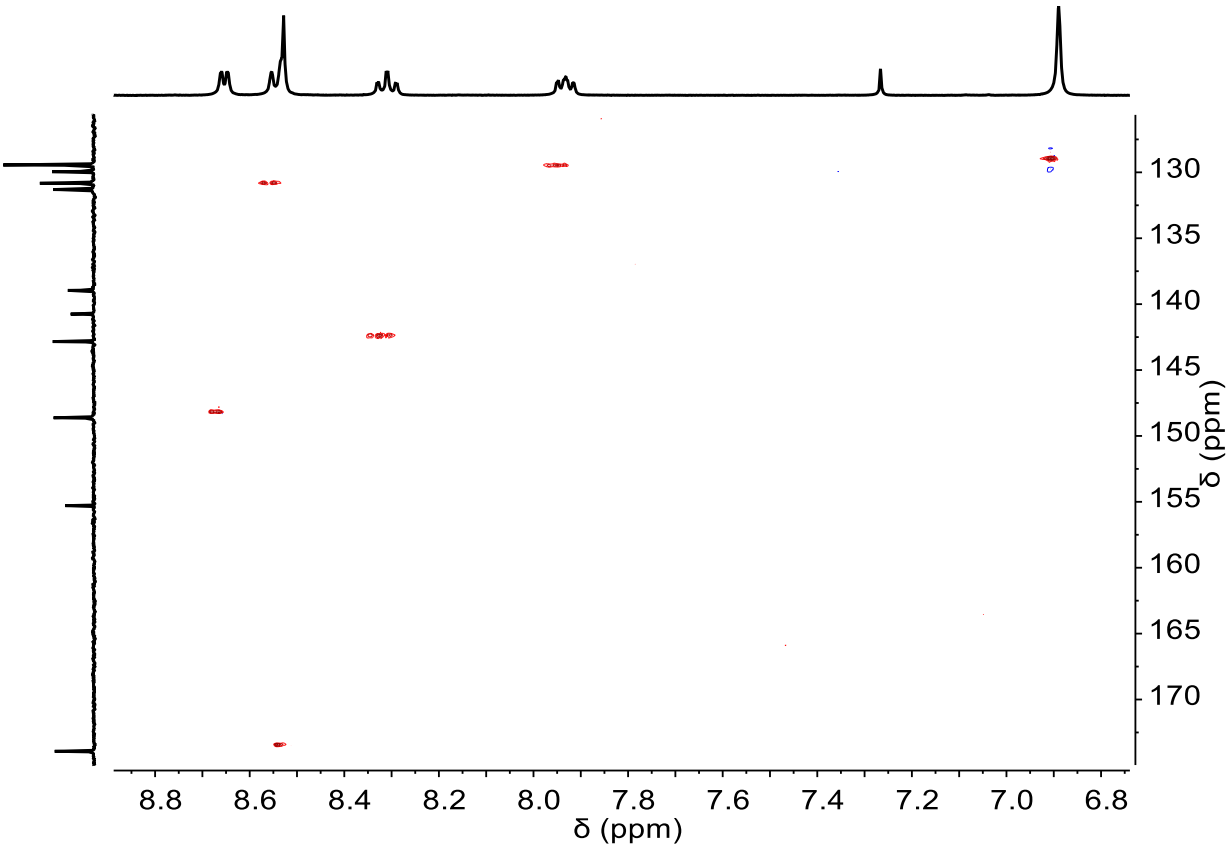


Figure S33 – ^{13}C-^{1}H HSQC ($CDCl_3$, 25°C): spectrum of **4**

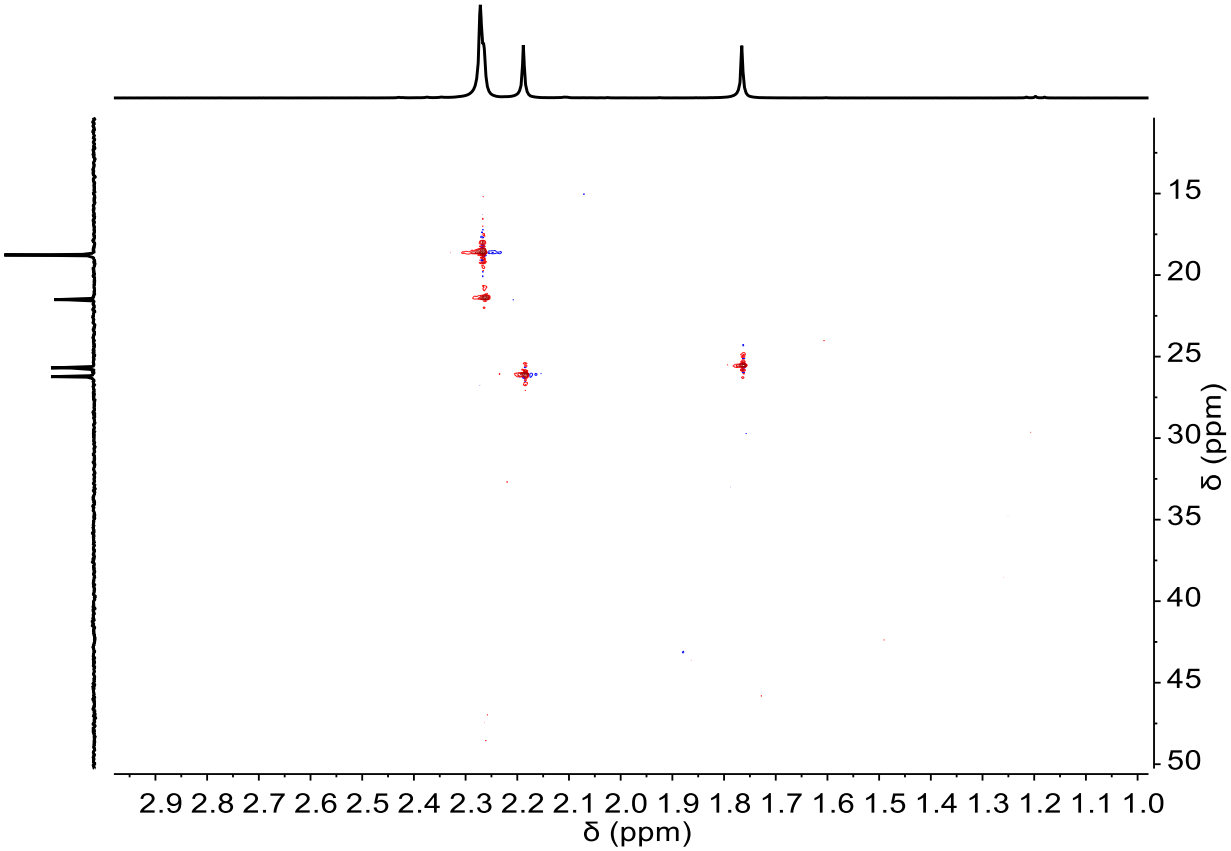


Figure S34 – ^{13}C-^{1}H HSQC ($CDCl_3$, 25°C): spectrum of **4**

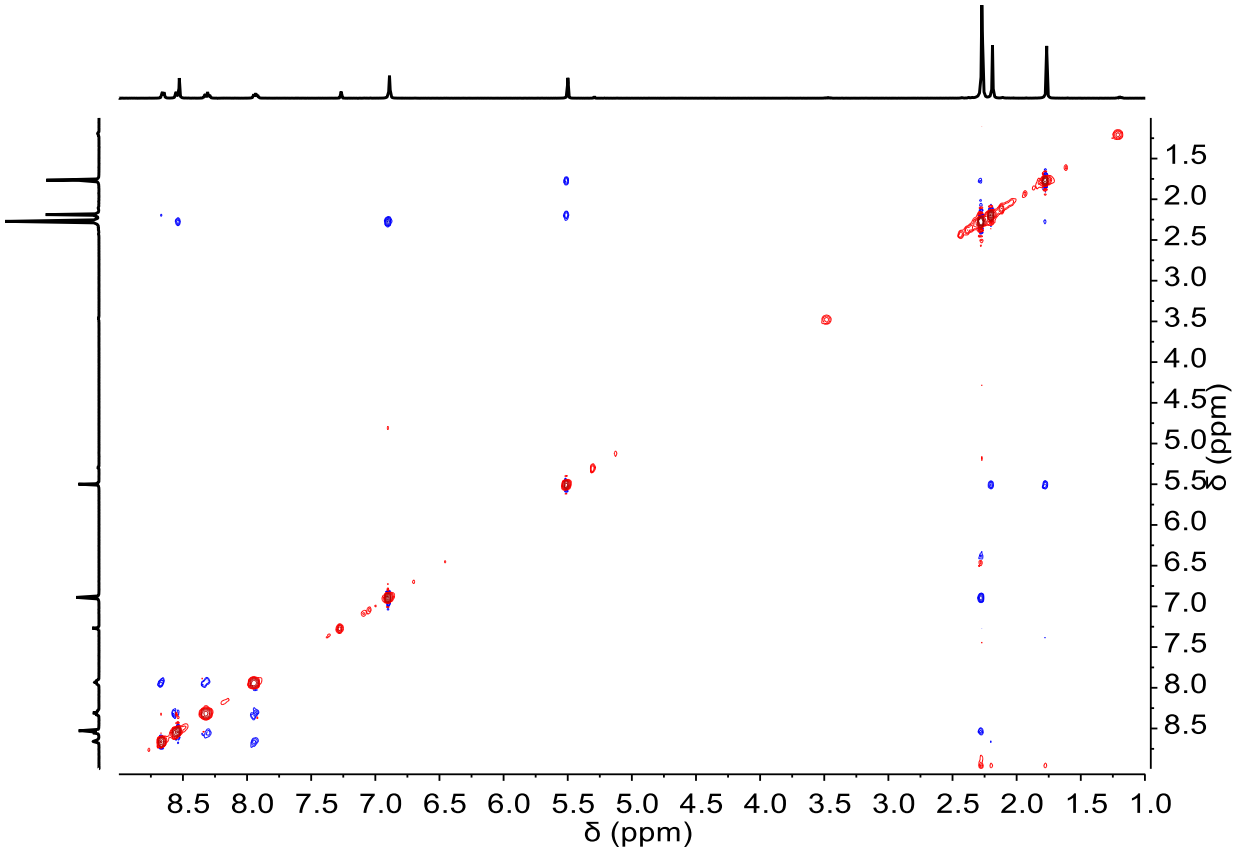


Figure S35 – ^{1}H-^{1}H NOESY ($CDCl_3$, 25°C): spectrum of **4**

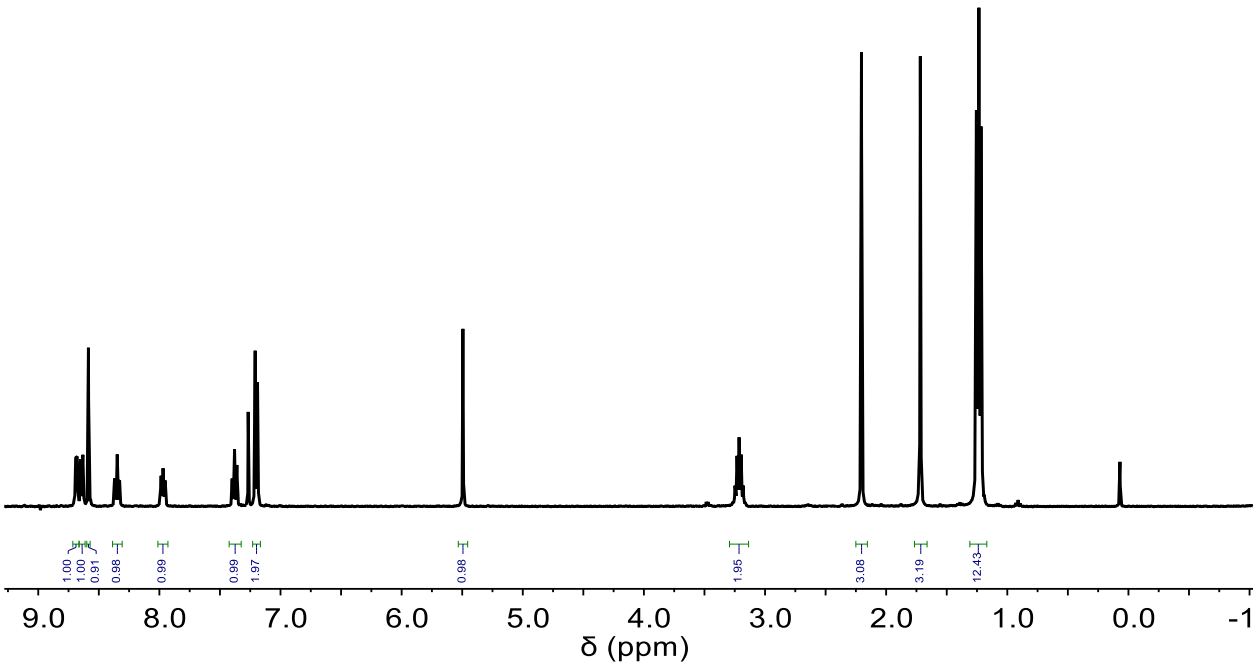


Figure S36 – ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): spectrum of **5**

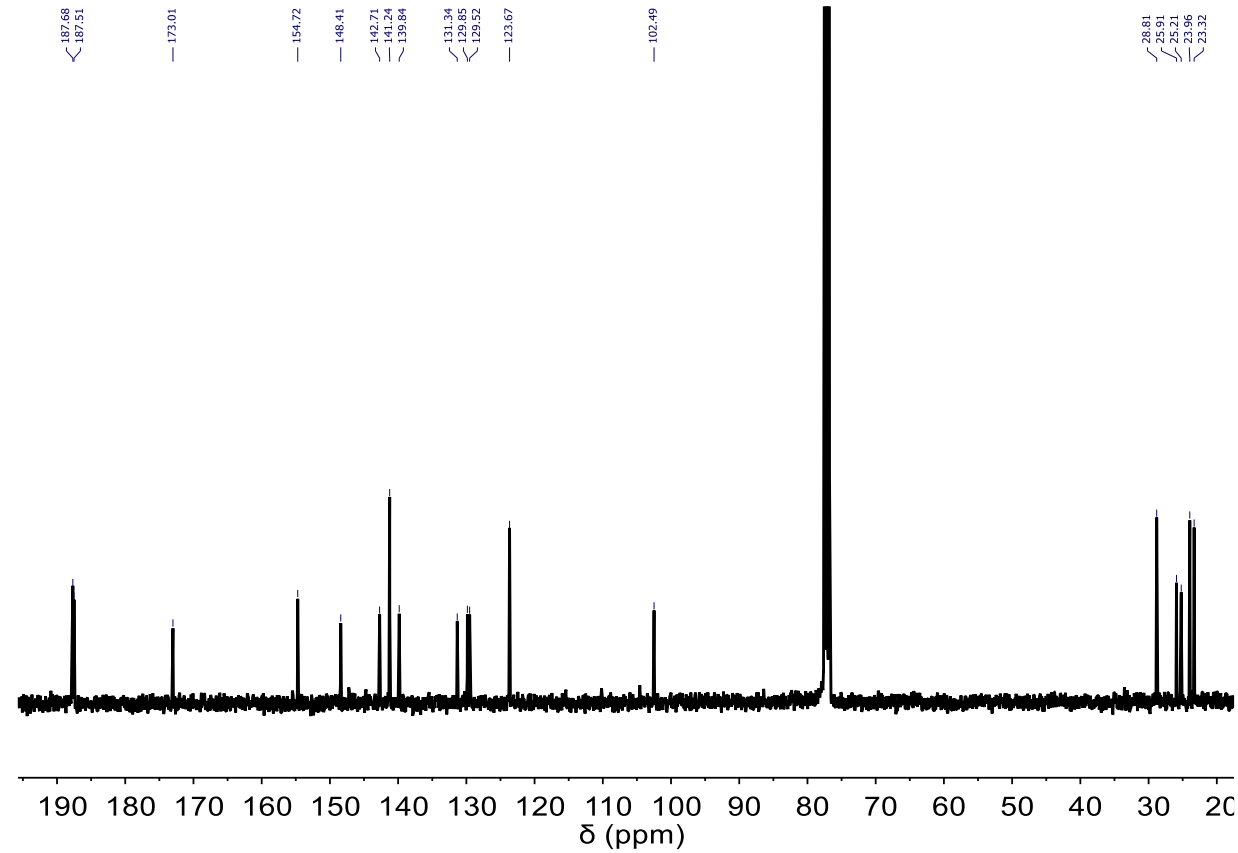


Figure S37 – ^{13}C NMR (101 MHz, $CDCl_3$, 25°C): spectrum of **5**

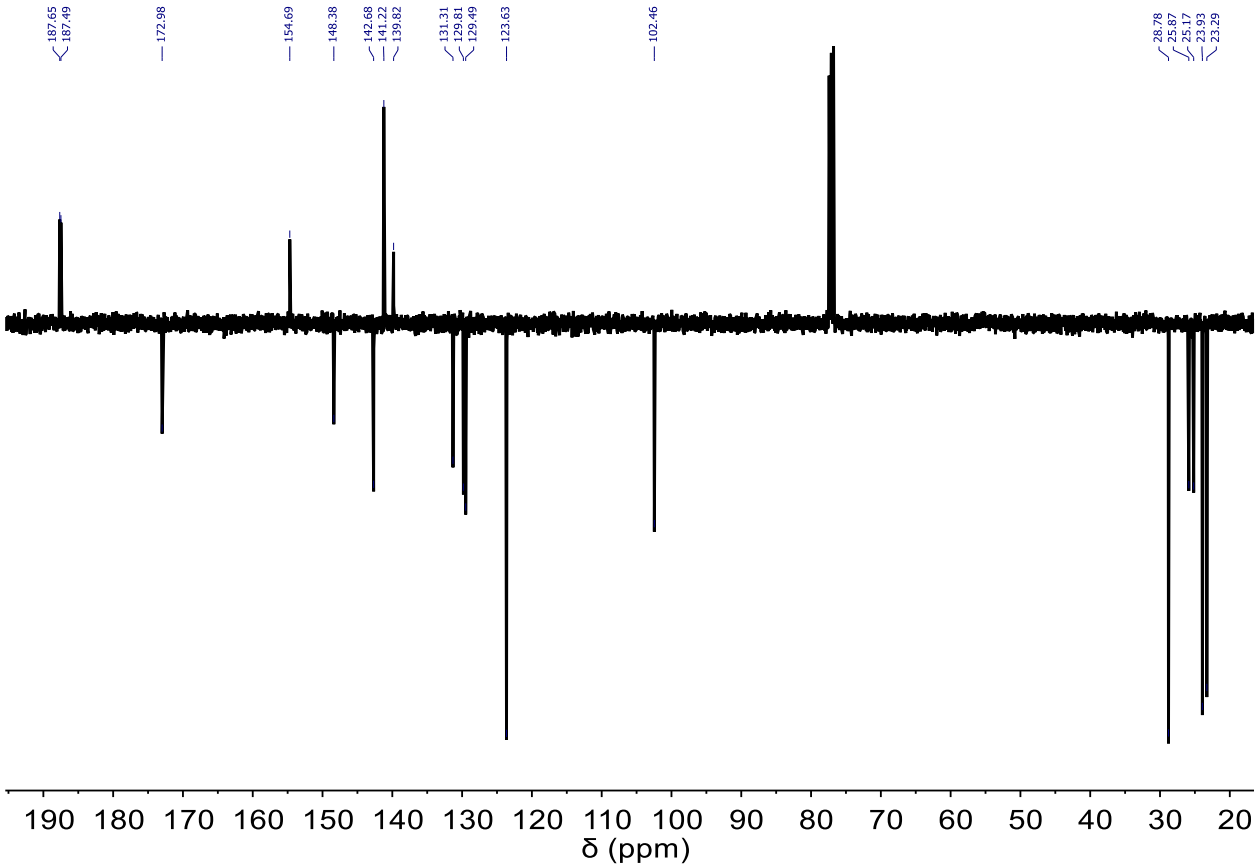


Figure S38 – $^{13}C\{^1H\}$ DEPT ($CDCl_3$, 25°C): spectrum of **5**

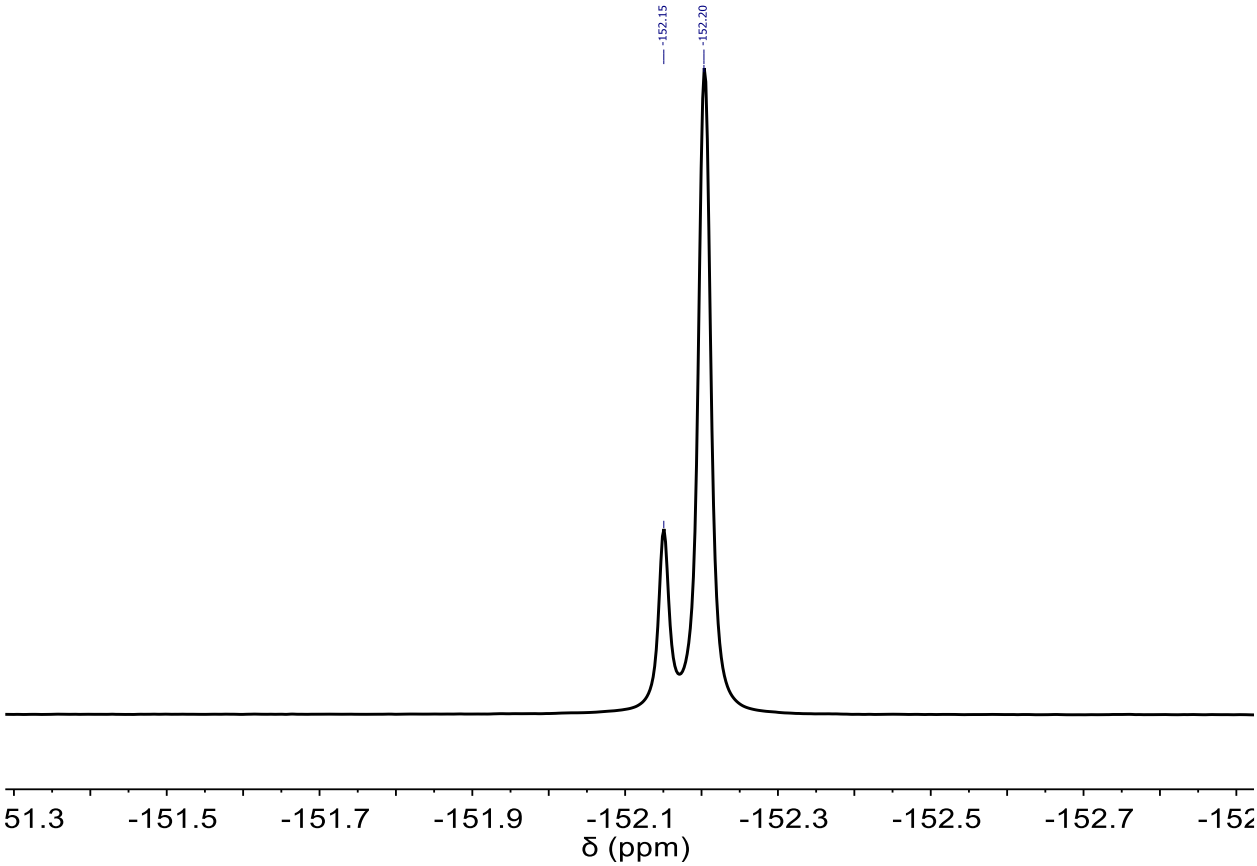


Figure S39 – ^{19}F NMR (376 MHz, $CDCl_3$, 25°C): spectrum of **5**

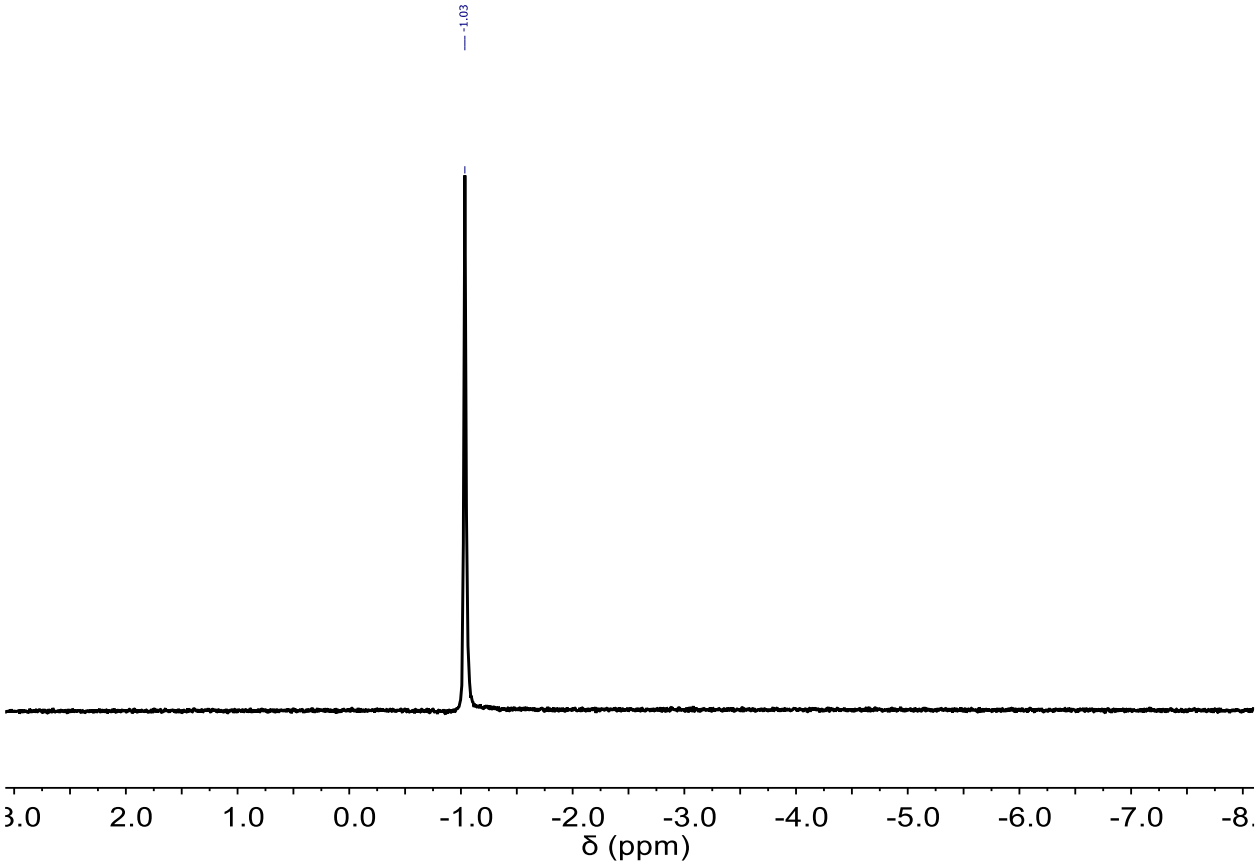


Figure S40 – ^{11}B NMR (128 MHz, $CDCl_3$, 25°C): spectrum of **5**

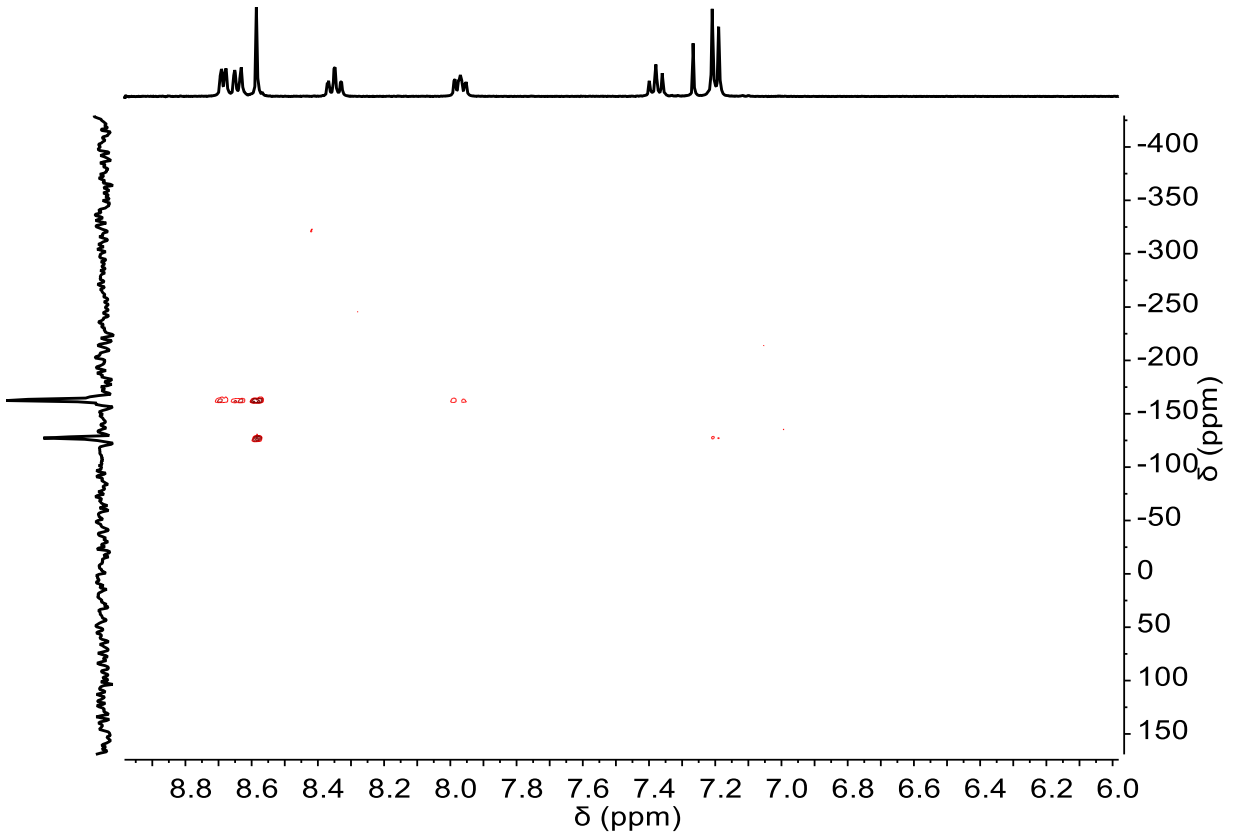


Figure S41 – ^{15}N-^{1}H HMBC ($CDCl_3$, 25°C): spectrum of **5**

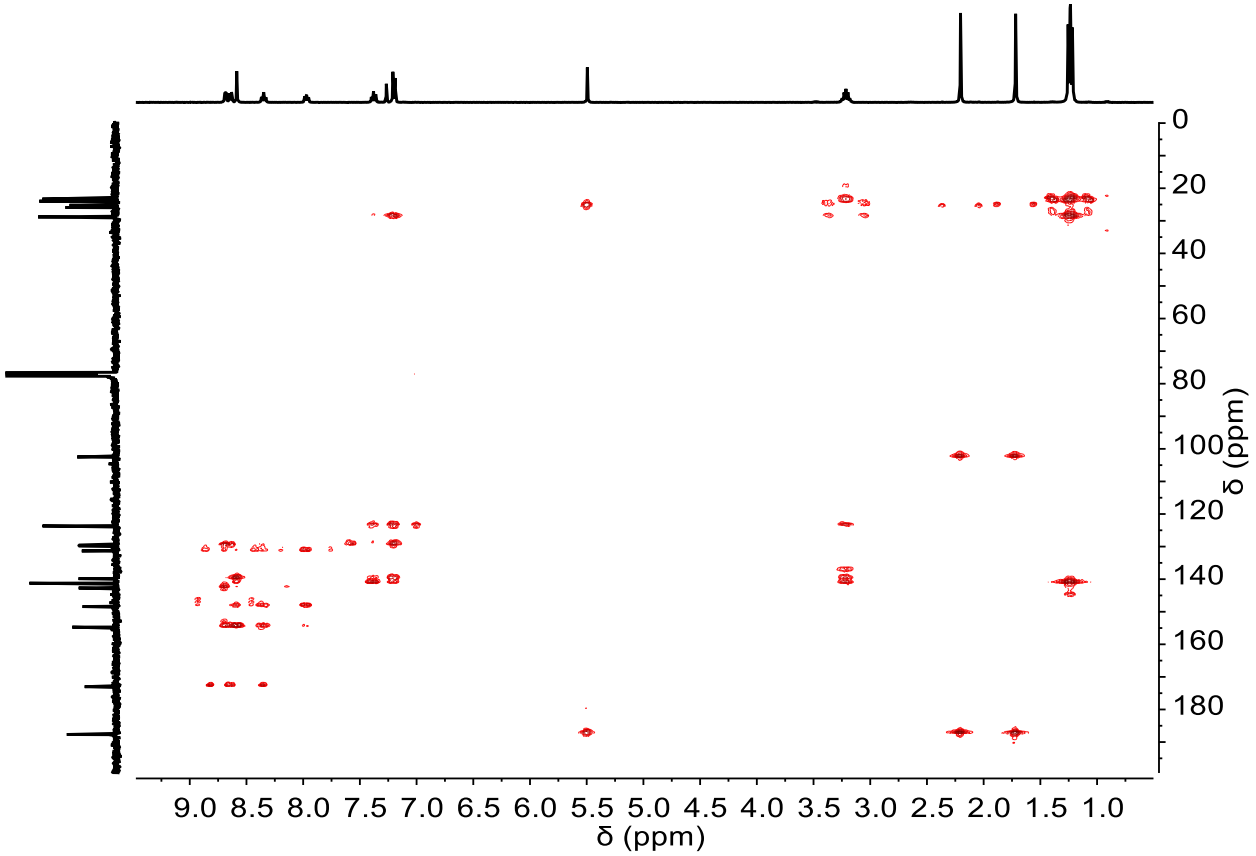


Figure S42 – ^{13}C-^{1}H HMBC ($CDCl_3$, 25°C): spectrum of **5**

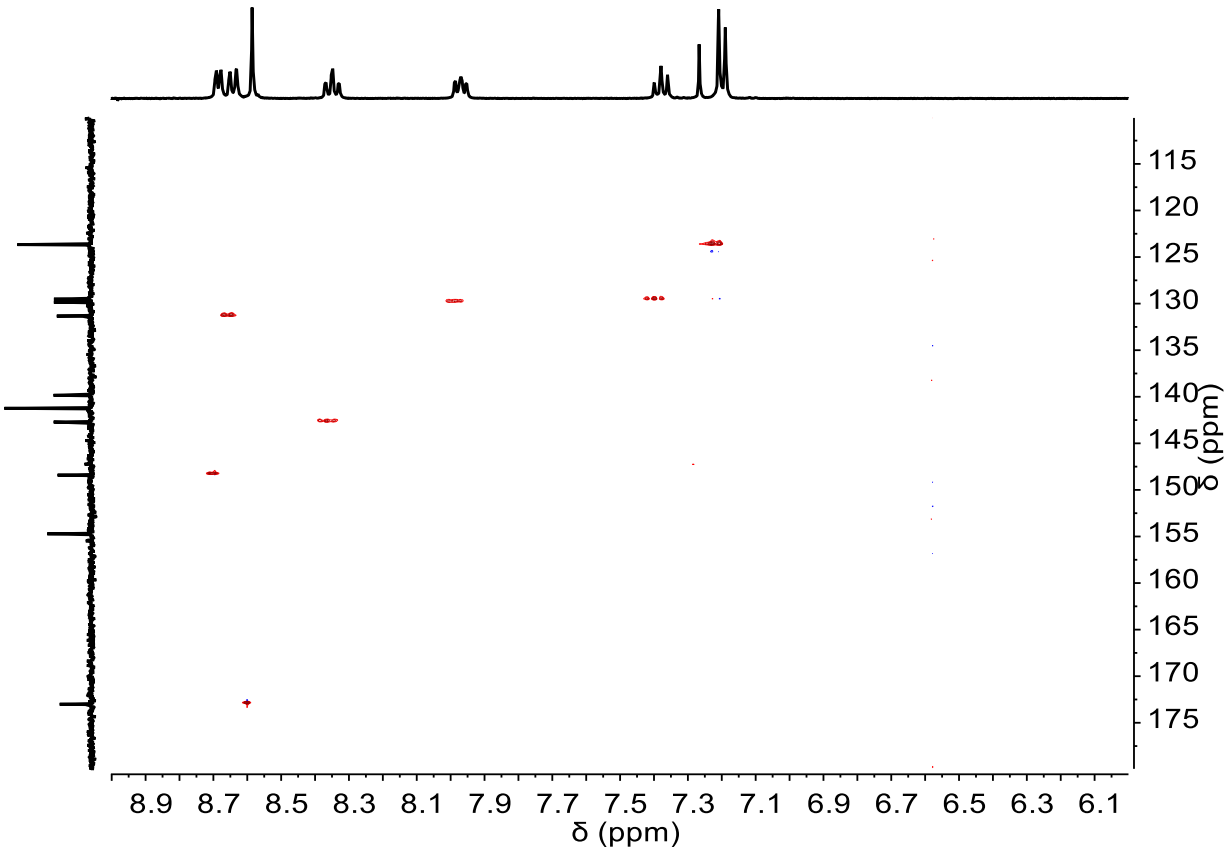


Figure S43 – ^{13}C-^{1}H HSQC ($CDCl_3$, 25°C): spectrum of **5**

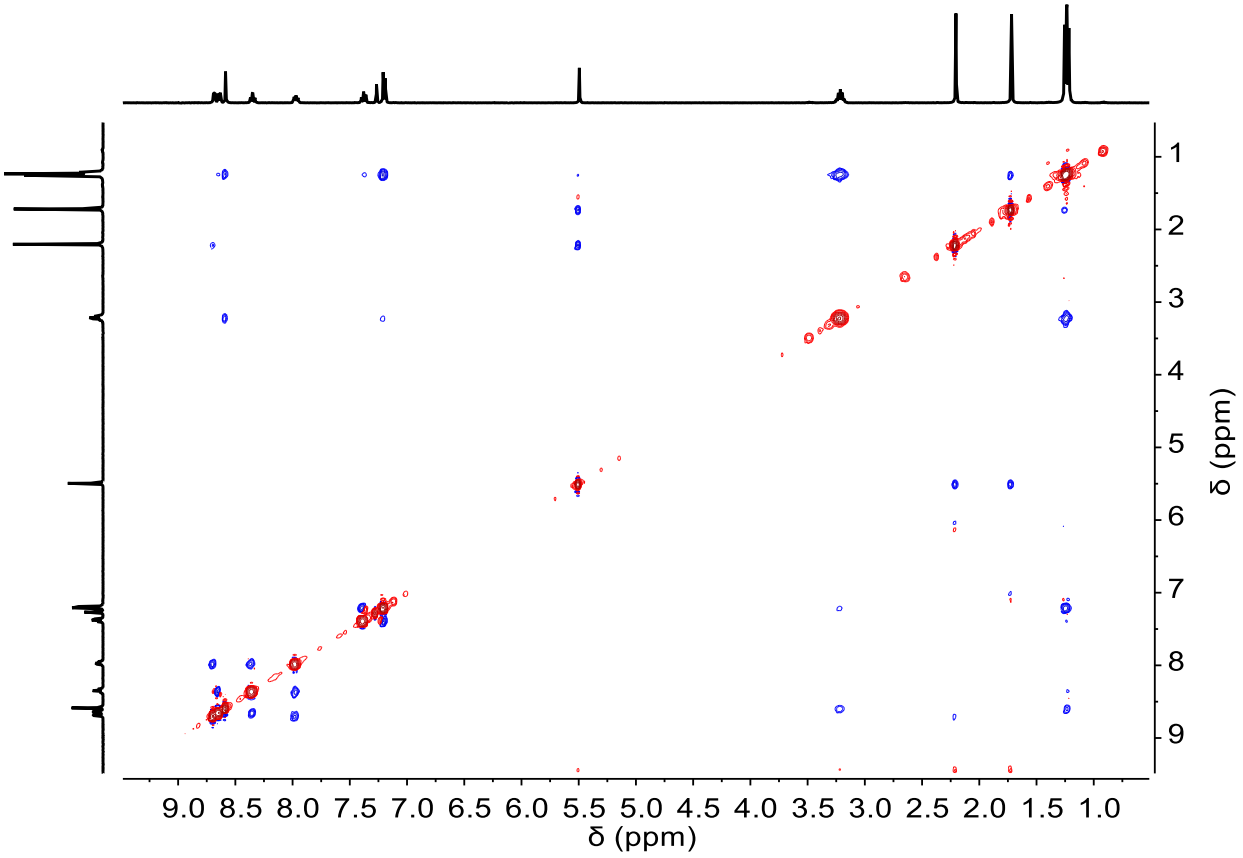
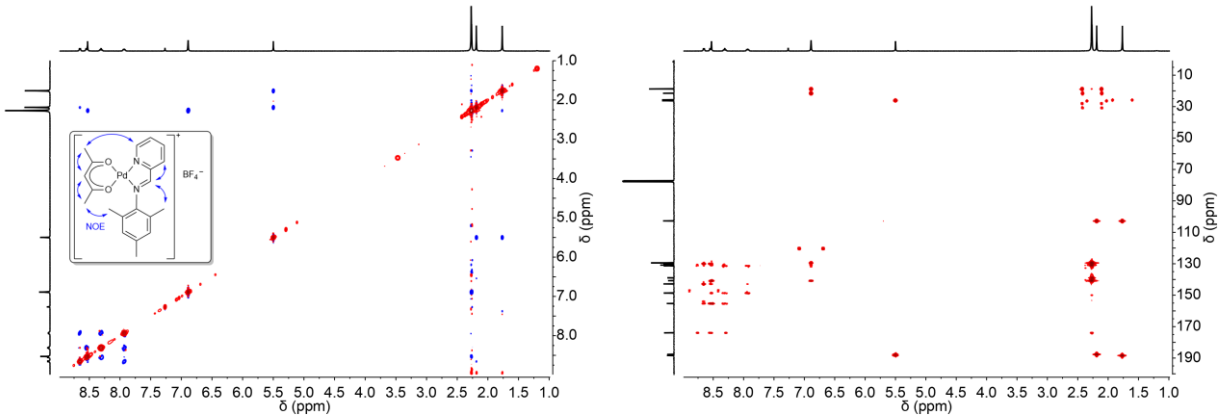


Figure S44 – ^{1}H-^{1}H NOESY ($CDCl_3$, 25°C): spectrum of **5**

Table S1 – Selected ^{1}H Chemical Shift Values (ppm) for Free Ligands and Cationic Palladium Complexes

Ligand/ complex	H^3	H^4	H^5	H^6	CH_3-acac ("*cis*-Py")	CH-acac	CH_3-acac ("*trans*-Py")
L1[S6]	7.94	7.79	7.37	8.60	–	–	–
L2[S3]	7.99	7.74	7.28	8.66	–	–	–
L3[S5]	8.30	7.85	7.42	8.73	–	–	–
L4[S7]	8.28	7.84	7.41	8.70	–	–	–
L5[S5]	8.27	7.86	7.42	8.73	–	–	–
1	8.16	8.42	7.95	8.68	2.32	5.86	2.26
2	8.02	8.30	7.83	8.56	2.20	5.74	2.16
3	8.58	8.32	7.93	8.65	2.20	5.50	1.74
4	8.54	8.31	7.93	8.65	2.19	5.50	1.77
5	8.64	8.35	7.97	8.69	2.20	5.49	1.72



(b) (b)

Figure S45 – NMR spectra of **4**: {^{1}H–^{1}H} NOESY (a) and {^{13}C–^{1}H} HMBC (b) [$CDCl_3$, 298K]

Table S2 – ^{15}N NMR Data[a] for Complexes **1**–**5**

Compound	**1**[b]	**2**[b]	**3**[c]	**4**[c]	**5**[c]
2-R′-Py, δ(^{15}N), ppm	−162.33	−168.25	−162.36	−162.77	−162.90
R-C=N, δ(^{15}N), ppm	−135.34	−134.62	−127.42	−127.04	−127.40

[a]As determined by {^{1}H,^{15}N}-HMBC experiments. [b]In CD_3CN at 298 K. [c]In $CDCl_3$ at 298 K

4 ESI-MS spectra

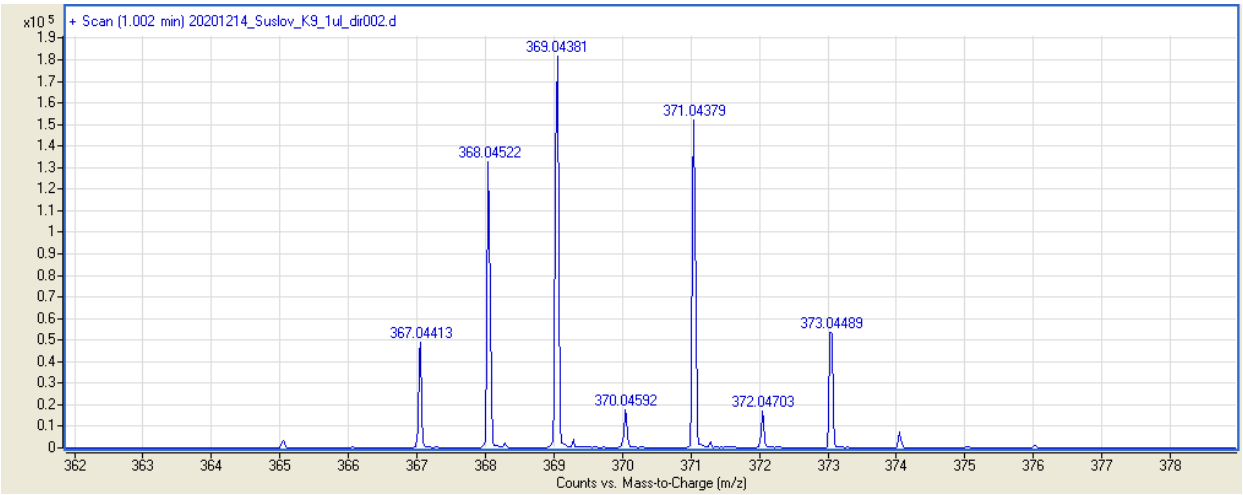


Figure S46 – MS spectrum of **1** (MeCN)

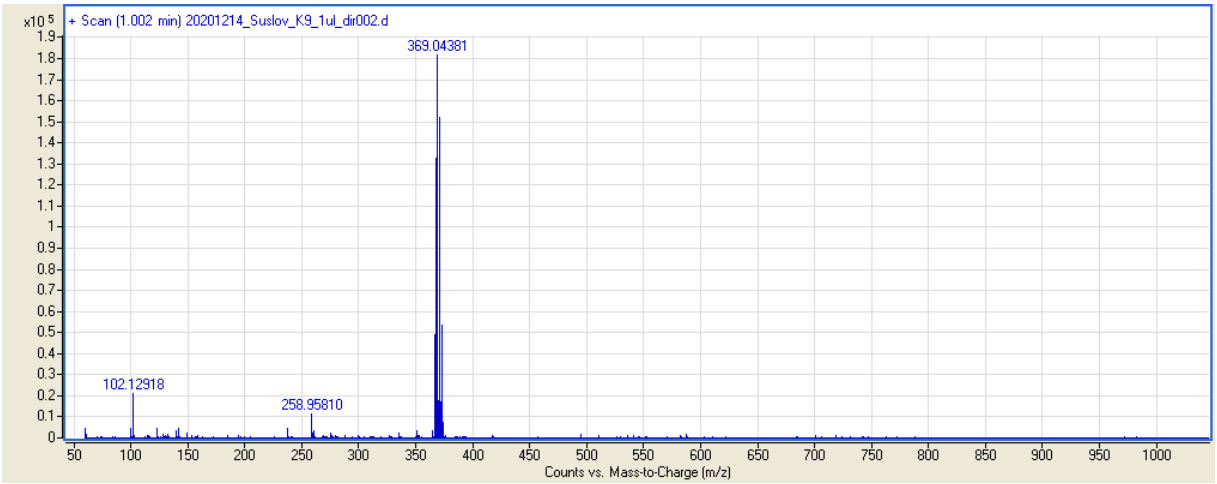


Figure S47 – MS spectrum of **1** (MeCN)

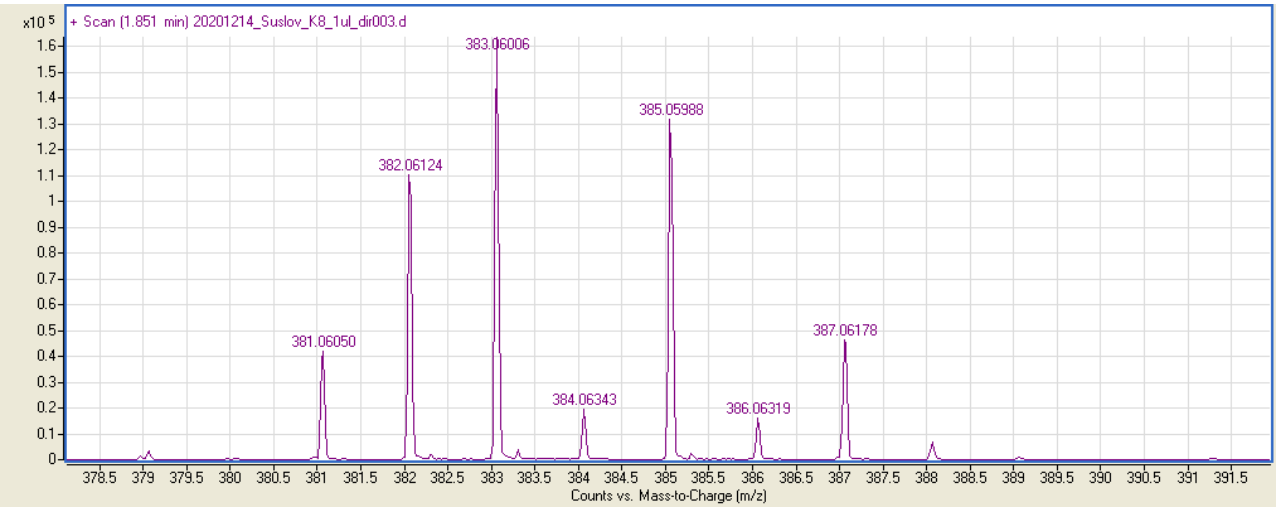


Figure S48 – MS spectrum of **2** (MeCN)

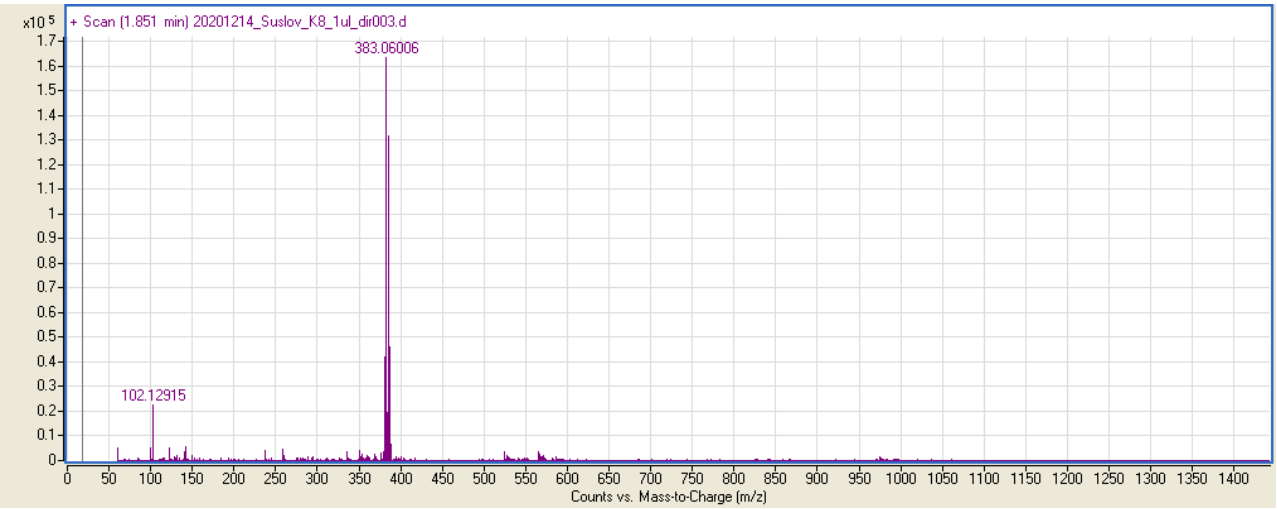


Figure S49 – MS spectrum of **2** (MeCN)

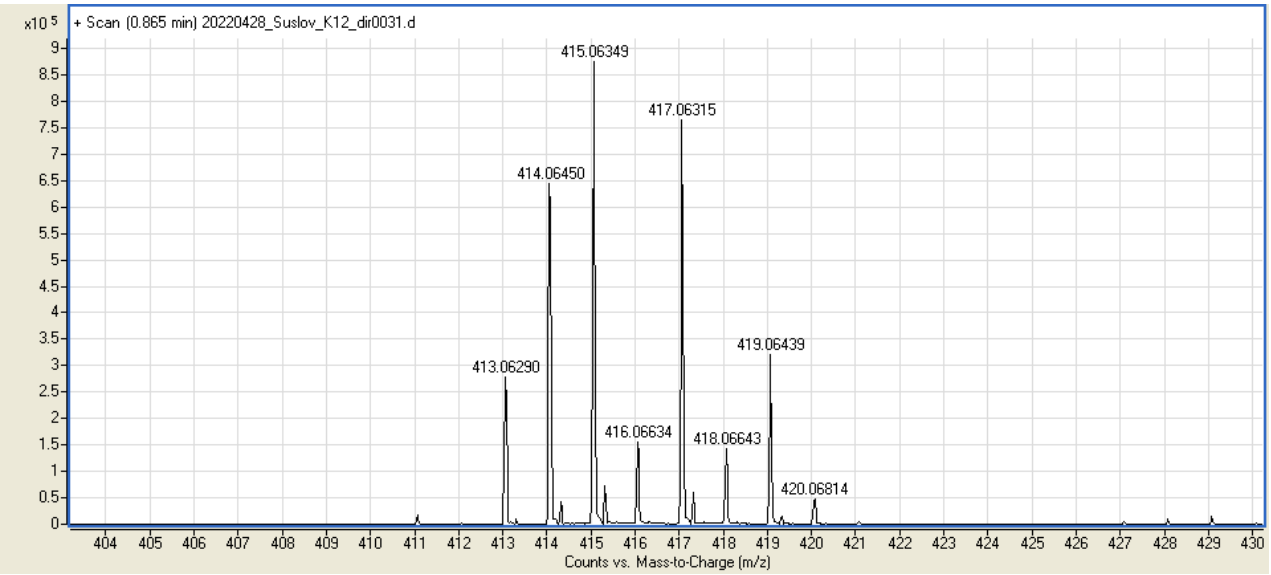


Figure S50 – MS spectrum of **3** (MeCN)

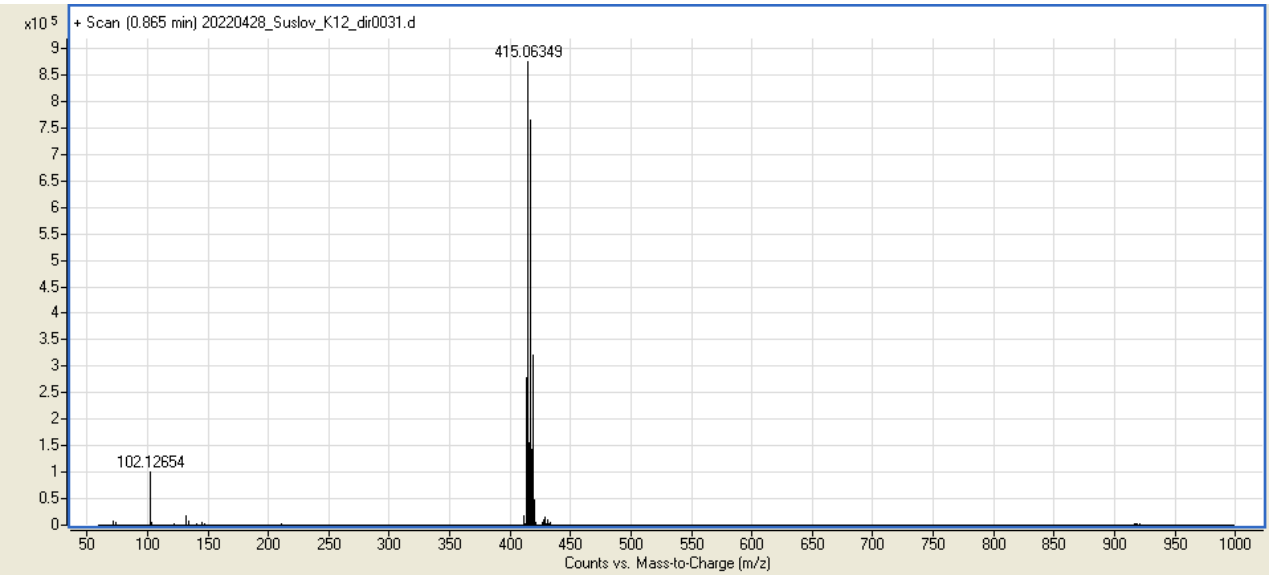


Figure S51 – MS spectrum of **3** (MeCN)

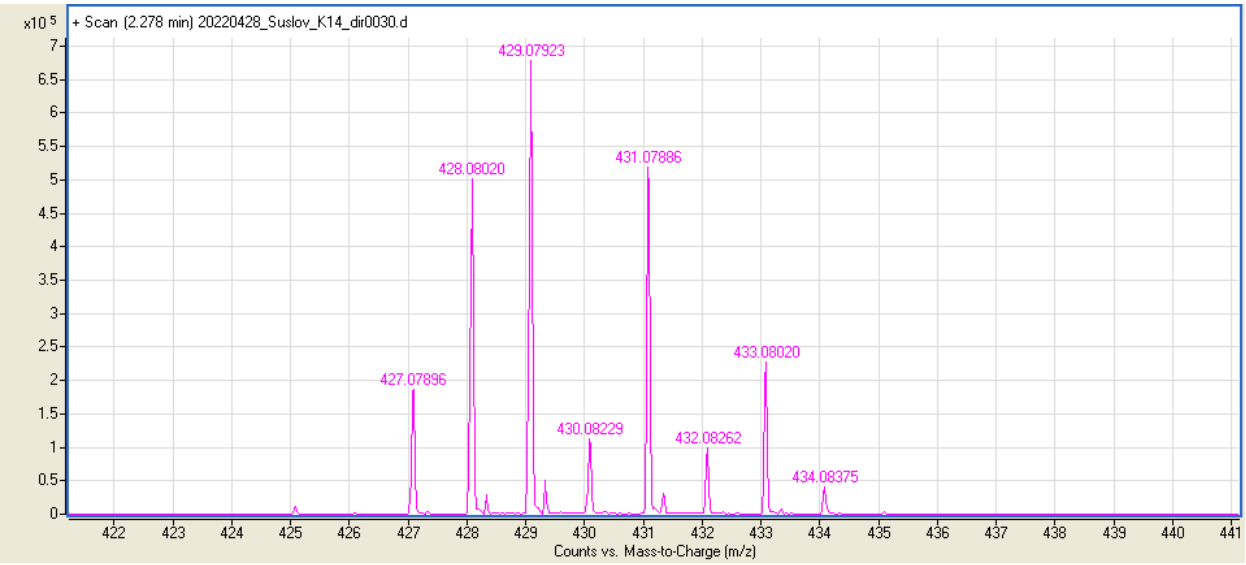


Figure S52 – MS spectrum of **4** (MeCN)

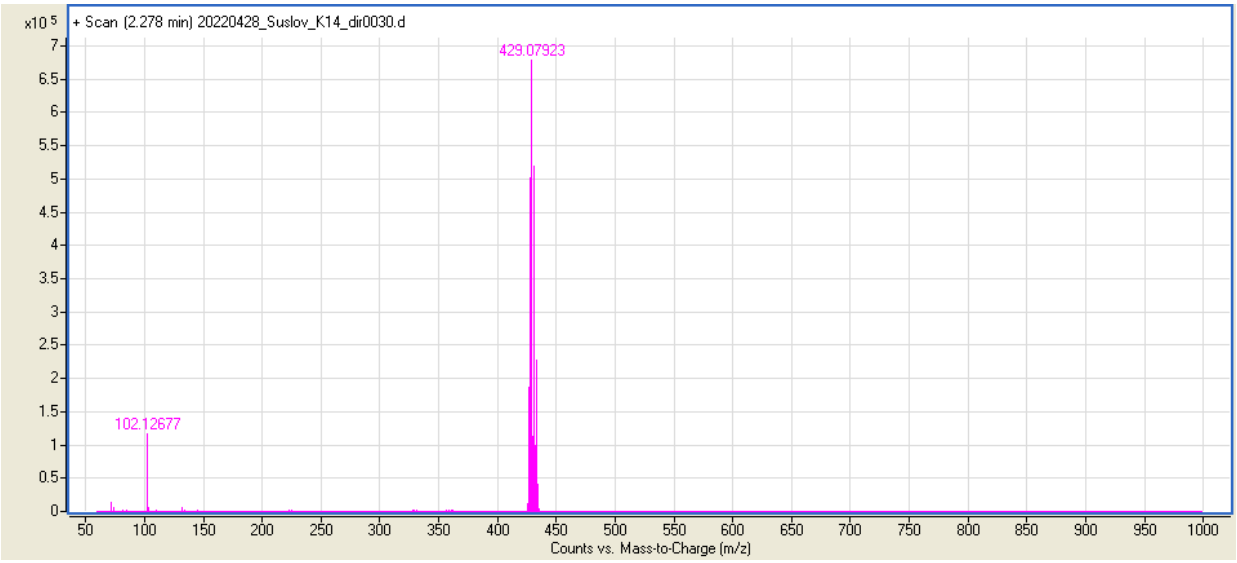


Figure S53 – MS spectrum of **4** (MeCN)

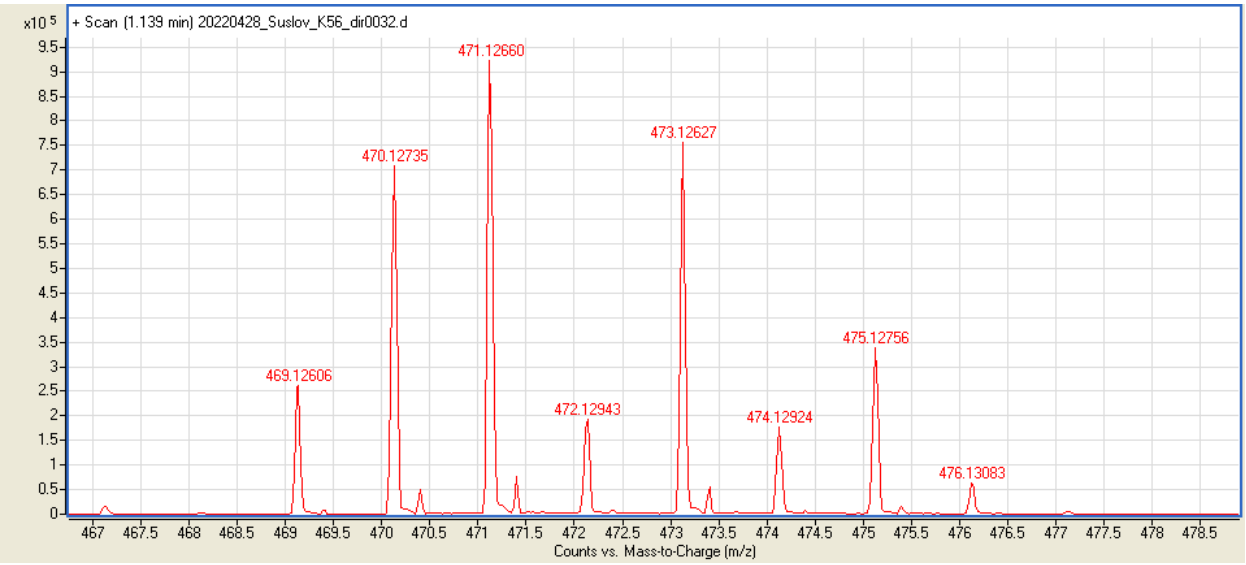


Figure S54 – MS spectrum of **5** (MeCN)

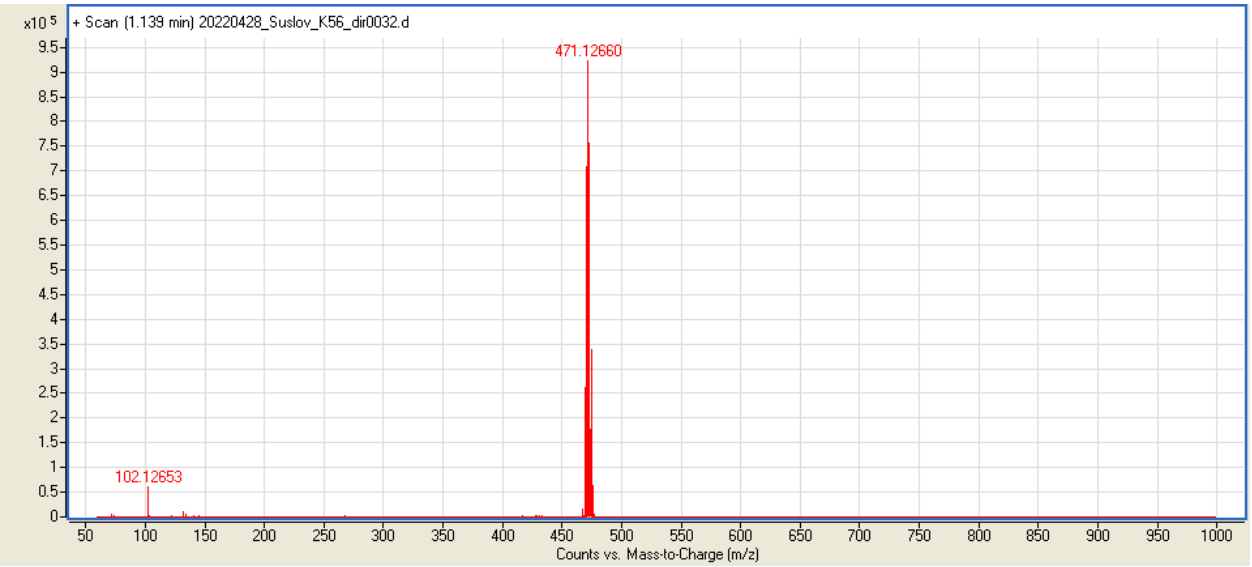


Figure S55 – MS spectrum of **5** (MeCN)

5 X-ray crystallographic studies

Data were collected on a BRUKER D8 VENTURE PHOTON 100 CMOS diffractometer with MoK_α radiation (λ = 0.71073 Å) using the φ and ω scans technique. Using Olex2 [S8], the structure was solved with the ShelXS [S9] structure solution program using Direct Methods and refined with the XL [S9] refinement package using Least Squares minimization. Data were corrected for absorption effects using the multi-scan method (SADABS) [S10]. All non-hydrogen atoms were refined anisotropically using SHELX [S9]. The coordinates of the hydrogen atoms were calculated from geometrical positions. Crystal data and experimental details selective bond lengths, bond angles and torsion angles are given in Tables S.2– S.6 (Supplementary Information). Table S.2 contains CCDC reference number of the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk

Table S3 – X-ray crystallographic data for compounds **3** and **5**

Compound	**3**	**5**
CCDC number	2162440	2162442
Empirical formula	$C_{19}H_{21}N_2O_2Pd$, BF_4	$C_{23}H_{29}N_2O_2Pd$, BF_4
Formula weight/ g·mol^{-1}	502.59	558.69
Crystal system	Orthorhombic	Monoclinic
Space group	*C222$_1$*	*P21/n*
a/ Å	11.476(10)	8.679(4)
b/ Å	29.30(3)	16.948(9)
c/ Å	25.25(2)	17.691(9)
α, β, γ/ °	90.00, 90.00, 90.00	90.00, 103.378(15), 90.00
Volume/ Å^3	8490(13)	2532(2)
Z	16	4
Density (calculated)/ g·cm^{-3}	1.573	1.466
Absorptions coefficient/ mm^{-1}	0.925	0.784
Radiation (λ / Å)	MoKα (0.71073)	MoKα (0.71073)
Temperature/ K	293(2)	293(2)
2Θ range/ °	2.50 – 30.12	2.37 – 30.12
Crystal size/ mm	0.24 × 0.14 × 0.14	0.60 × 0.45 × 0.10
Crystal habit	yellow, prism	yellow, prism
F(000)	4032	1136
Index ranges	-16 ≤ h ≤ 15, -41 ≤ k ≤ 17, -29 ≤ l ≤ 35	-12 ≤ h ≤ 12, -23 ≤ k ≤ 23, -24 ≤ l ≤ 24
Reflections collected	24321	76229
Independent reflections	12329 [R(int) = 0.0574]	7445 [R(int) = 0.0534]
Number of ref. parameters	532	307
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0520 / 0.1060	0.0379 / 0.1013
R_1 / wR_2 (all data)	0.1250 / 0.1383	0.0547 / 0.1117
Goodness-of-fit on F^2	0.991	1.038
Completeness [%]	98.8	99.8
Largest diff. peak and hole/ e·Å^{-3}	0.56/ -0.53	0.70/ -0.51
Weight scheme	$w=1/[\sigma^2(F_o^2)+(0.0605P)^2+0.0000P]$ where $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F_o^2)+(0.0566P)^2+1.5228P]$ where $P=(F_o^2+2F_c^2)/3$

Table S4 – Selected bond lengths, bond angles and torsion angles for **3**

Bond	*l*, Å	Angle	*φ*, ˚	Torsion angle	*θ*, ˚
Pd1-N2	2.007(5)	N1-Pd1-N2	81.0(2)	Pd1-N2-C11-C10	-2.8(7)
Pd1-N1	2.000(5)	O1-Pd1-N2	172.5(2)	Pd1-N2-C12-C13	76.4(7)
Pd1-O1	1.976(4)	O1-Pd1-N1	91.8(2)	Pd1-N2-C12-C17	-102.4(6)
Pd1-O2	1.959(5)	O2-Pd1-N2	93.0(2)	Pd1-N1-C10-C11	4.0(7)
Pd2-N4	2.007(5)	O2-Pd1-N1	174.0(2)	Pd1-N1-C10-C9	-179.9(5)
Pd2-O3	1.964(5)	O2-Pd1-O1	94.2(2)	Pd1-N1-C6-C7	179.7(5)
Pd2-O4	1.966(4)	O3-Pd2-N4	171.91(19)	Pd1-O1-C2-C3	4.0(11)
Pd2-N3	1.983(5)	O3-Pd2-O4	93.5(2)	Pd1-O1-C2-C1	-175.4(6)
N2-C11	1.278(7)	O3-Pd2-N3	91.7(2)	Pd1-O2-C4-C3	0.3(12)
N2-C12	1.442(8)	O4-Pd2-N4	94.0(2)	Pd1-O2-C4-C5	-180.0(7)
N1-C10	1.357(8)	O4-Pd2-N3	174.7(2)	Pd2-N4-C31-C30	-1.5(8)
N1-C6	1.336(8)	N3-Pd2-N4	80.7(2)	Pd2-N4-C32-C33	68.8(7)
O1-C2	1.277(9)	C11-N2-Pd1	113.9(5)	Pd2-N4-C32-C37	-109.4(6)
F5-B2	1.283(7)	C11-N2-C12	119.7(5)	Pd2-O3-C22-C23	7.9(11)
F6-B2	1.392(8)	C12-N2-Pd1	126.4(4)	Pd2-O3-C22-C21	-169.8(6)
N4-C31	1.264(8)	C10-N1-Pd1	112.6(4)	Pd2-O4-C24-C23	-3.7(12)
N4-C32	1.443(8)	C6-N1-Pd1	127.5(5)	Pd2-O4-C24-C25	178.0(5)
O3-C22	1.262(9)	C6-N1-C10	119.9(6)	Pd2-N3-C30-C31	2.0(7)
O4-C24	1.253(9)	C2-O1-Pd1	122.0(4)	Pd2-N3-C30-C29	-177.7(6)
C11-C10	1.441(9)	C31-N4-Pd2	113.9(4)	Pd2-N3-C26-C27	-178.8(5)
O2-C4	1.276(8)	C31-N4-C32	120.4(6)	N2-Pd1-N1-C10	-4.2(4)
N3-C30	1.333(7)	C32-N4-Pd2	125.7(4)	N2-Pd1-N1-C6	175.0(5)
N3-C26	1.334(8)	C22-O3-Pd2	123.4(5)	N2-Pd1-O1-C2	159.1(13)
F7-B3	1.354(11)	C24-O4-Pd2	123.1(5)	N2-Pd1-O2-C4	-173.9(6)
F3-B1	1.228(12)	N2-C11-C10	117.7(6)	N2-C11-C10-N1	-0.8(8)
C10-C9	1.363(9)	C4-O2-Pd1	122.6(4)	N2-C11-C10-C9	-176.7(6)
C12-C13	1.386(9)	C30-N3-Pd2	114.2(4)	N2-C12-C13-C14	178.7(6)
C12-C17	1.384(9)	C30-N3-C26	119.4(5)	N2-C12-C13-C18	-1.1(10)
C6-C7	1.384(10)	C26-N3-Pd2	126.5(5)	N2-C12-C17-C16	-176.0(6)
C7-C8	1.341(11)	N1-C10-C11	114.7(6)	N2-C12-C17-C19	1.6(9)
C8-C9	1.402(11)	N1-C10-C9	120.2(6)	N1-Pd1-N2-C11	3.9(4)
C13-C14	1.395(11)	C9-C10-C11	125.0(6)	N1-Pd1-N2-C12	-176.6(5)

C13-C18	1.494(10)	C13-C12-N2	117.1(5)	N1-Pd1-O1-C2	174.5(5)
C14-C15	1.367(13)	C17-C12-N2	119.5(6)	N1-Pd1-O2-C4	178(26)
C15-C16	1.406(13)	C17-C12-C13	123.4(6)	N1-C10-C9-C8	-0.5(10)
C16-C17	1.362(12)	N1-C6-C7	122.9(7)	N1-C6-C7-C8	1.2(10)
C17-C19	1.497(11)	C8-C7-C6	116.5(7)	O1-Pd1-N2-C11	19.4(17)
C2-C3	1.346(10)	C7-C8-C9	122.2(7)	O1-Pd1-N2-C12	-161.0(13)
C2-C1	1.516(10)	C10-C9-C8	118.3(7)	O1-Pd1-N1-C10	177.8(4)
C3-C4	1.347(10)	C12-C13-C14	116.6(7)	O1-Pd1-N1-C6	-2.9(5)
C4-C5	1.514(12)	C12-C13-C18	122.9(6)	O1-Pd1-O2-C4	4.2(6)
B2-F51	1.283(7)	C14-C13-C18	120.5(7)	O1-C2-C3-C4	2.6(15)
B2-F61	1.392(8)	C15-C14-C13	121.8(8)	N4-Pd2-O3-C22	147.9(15)
C31-C30	1.464(9)	C14-C15-C16	119.1(8)	N4-Pd2-O4-C24	-169.0(6)
C30-C29	1.391(9)	C17-C16-C15	121.1(8)	N4-Pd2-N3-C30	-2.1(5)
C26-C27	1.392(10)	C12-C17-C19	120.7(7)	N4-Pd2-N3-C26	178.8(6)
C27-C28	1.378(12)	C16-C17-C12	117.9(8)	N4-C31-C30-N3	-0.3(10)
C28-C29	1.360(11)	C16-C17-C19	121.3(7)	N4-C31-C30-C29	179.3(7)
C32-C33	1.364(11)	O1-C2-C3	126.2(6)	N4-C32-C33-C34	-178.5(7)
C32-C37	1.386(10)	O1-C2-C1	113.2(7)	N4-C32-C33-C38	3.7(10)
C33-C34	1.404(13)	C3-C2-C1	120.6(7)	N4-C32-C37-C36	178.6(6)
C33-C38	1.498(13)	C2-C3-C4	128.3(7)	N4-C32-C37-C39	-1.0(10)
C34-C35	1.317(17)	O2-C4-C3	126.2(7)	O3-Pd2-N4-C31	24(2)
C35-C36	1.369(17)	O2-C4-C5	113.5(7)	O3-Pd2-N4-C32	-156.1(15)
C36-C37	1.394(10)	C3-C4-C5	120.3(7)	O3-Pd2-O4-C24	8.0(6)
C37-C39	1.472(11)	F51-B2-F5	123.3(13)	O3-Pd2-N3-C30	-179.2(5)
C22-C23	1.356(12)	F51-B2-F6	106.8(5)	O3-Pd2-N3-C26	1.8(6)
C22-C21	1.520(12)	F5-B2-F61	106.8(5)	O3-C22-C23-C24	-0.3(15)
C23-C24	1.364(12)	F5-B2-F6	104.7(5)	O4-Pd2-N4-C31	-178.5(5)
C24-C25	1.523(12)	F51-B2-F61	104.7(5)	O4-Pd2-N4-C32	1.8(6)
F8-B3	1.212(12)	F61-B2-F6	110.3(9)	O4-Pd2-O3-C22	-10.0(6)
B3-F72	1.354(11)	N4-C31-C30	117.6(6)	O4-Pd2-N3-C30	-7(2)
B3-F82	1.212(12)	N3-C30-C31	113.6(5)	O4-Pd2-N3-C26	174(2)
F4-B1	1.262(15)	N3-C30-C29	122.9(6)	C11-N2-C12-C13	-104.1(7)
F1-B1	1.345(12)	C29-C30-C31	123.5(6)	C11-N2-C12-C17	77.2(8)
F2-B1	1.326(14)	N3-C26-C27	119.7(7)	C11-C10-C9-C8	175.2(6)

C28-C27-C26	121.1(7)	O2-Pd1-N2-C11	-175.3(4)
C29-C28-C27	118.3(7)	O2-Pd1-N2-C12	4.3(5)
C28-C29-C30	118.5(7)	O2-Pd1-N1-C10	4(2)
C33-C32-N4	116.9(8)	O2-Pd1-N1-C6	-176.6(18)
C33-C32-C37	123.5(8)	O2-Pd1-O1-C2	-6.2(6)
C37-C32-N4	119.5(7)	N3-Pd2-N4-C31	2.0(5)
C32-C33-C34	115.9(10)	N3-Pd2-N4-C32	-177.7(6)
C32-C33-C38	123.3(8)	N3-Pd2-O3-C22	169.3(6)
C34-C33-C38	120.8(9)	N3-Pd2-O4-C24	-164(2)
C35-C34-C33	122.9(11)	N3-C30-C29-C28	-4.1(12)
C34-C35-C36	120.0(10)	N3-C26-C27-C28	-3.4(12)
C35-C36-C37	120.9(10)	C10-N1-C6-C7	-1.2(9)
C32-C37-C36	116.6(8)	C12-N2-C11-C10	177.6(5)
C32-C37-C39	122.7(7)	C12-C13-C14-C15	-1.9(12)
C36-C37-C39	120.7(9)	C6-N1-C10-C11	-175.3(5)
O3-C22-C23	125.2(8)	C6-N1-C10-C9	0.8(9)
O3-C22-C21	114.0(9)	C6-C7-C8-C9	-0.8(11)
C23-C22-C21	120.7(9)	C7-C8-C9-C10	0.5(11)
C22-C23-C24	127.9(8)	C13-C12-C17-C16	5.3(10)
O4-C24-C23	126.0(8)	C13-C12-C17-C19	-177.1(7)
O4-C24-C25	113.5(9)	C13-C14-C15-C16	3.5(14)
C23-C24-C25	120.5(8)	C14-C15-C16-C17	-0.7(13)
F72-B3-F7	105.2(12)	C15-C16-C17-C12	-3.6(11)
F8-B3-F7	106.5(7)	C15-C16-C17-C19	178.8(8)
F82-B3-F7	112.5(10)	C17-C12-C13-C14	-2.6(10)
F8-B3-F72	112.5(10)	C17-C12-C13-C18	177.6(7)
F82-B3-F72	106.5(7)	C18-C13-C14-C15	177.9(8)
F82-B3-F8	113(2)	C2-C3-C4-O2	-5.1(16)
F3-B1-F4	109.4(13)	C2-C3-C4-C5	175.1(9)
F3-B1-F1	115.3(11)	C1-C2-C3-C4	-178.0(9)
F3-B1-F2	112.7(13)	C31-N4-C32-C33	-110.9(8)
F4-B1-F1	106.4(12)	C31-N4-C32-C37	71.0(8)
F4-B1-F2	103.9(14)	C31-C30-C29-C28	176.3(8)
F2-B1-F1	108.3(10)	C30-N3-C26-C27	2.3(10)

C26-N3-C30-C31	-178.9(6)
C26-N3-C30-C29	1.5(11)
C26-C27-C28-C29	0.7(13)
C27-C28-C29-C30	2.9(13)
C32-N4-C31-C30	178.2(6)
C32-C33-C34-C35	2.6(15)
C33-C32-C37-C36	0.6(10)
C33-C32-C37-C39	-179.0(7)
C33-C34-C35-C36	-4.8(18)
C34-C35-C36-C37	4.8(17)
C35-C36-C37-C32	-2.7(13)
C35-C36-C37-C39	176.9(9)
C37-C32-C33-C34	-0.5(11)
C37-C32-C33-C38	-178.2(7)
C38-C33-C34-C35	-179.6(10)
C22-C23-C24-O4	-2.1(16)
C22-C23-C24-C25	176.0(9)
C21-C22-C23-C24	177.3(9)

Table S5 – Selected bond lengths, bond angles and torsion angles for **5**

Bond	*l*, Å	Angle	*φ*, ˚	Torsion angle	*θ*, ˚
Pd1-N1	1.995(2)	N2-Pd1-N1	80.91(8)	Pd1-N1-C10-C11	2.9(3)
Pd1-N2	1.993(2)	O1-Pd1-N1	92.71(8)	Pd1-N1-C10-C9	179.8(2)
Pd1-O1	1.972(2)	O1-Pd1-N2	173.47(8)	Pd1-N1-C6-C7	-179.3(2)
Pd1-O2	1.956(2)	O2-Pd1-N1	173.10(8)	Pd1-N2-C11-C10	-3.9(3)
N1-C10	1.356(3)	O2-Pd1-N2	92.28(8)	Pd1-N2-C12-C13	90.6(3)
N1-C6	1.329(3)	O2-Pd1-O1	94.12(8)	Pd1-N2-C12-C17	-83.2(3)
N2-C11	1.278(3)	C10-N1-Pd1	113.54(16)	Pd1-O1-C2-C1	-179.0(2)
N2-C12	1.443(3)	C6-N1-Pd1	127.0(2)	Pd1-O1-C2-C3	0.8(4)
O1-C2	1.276(4)	C6-N1-C10	119.4(3)	Pd1-O2-C4-C3	-1.9(5)
O2-C4	1.281(4)	C11-N2-Pd1	114.40(16)	Pd1-O2-C4-C5	178.0(4)
C11-C10	1.456(4)	C11-N2-C12	122.5(2)	N1-Pd1-N2-C11	4.25(18)
F1-B1	1.356(6)	C12-N2-Pd1	123.08(16)	N1-Pd1-N2-C12	-173.4(2)
F2-B1	1.270(5)	C2-O1-Pd1	123.33(19)	N1-Pd1-O1-C2	176.9(2)
F3-B1	1.326(5)	C4-O2-Pd1	123.5(2)	N1-Pd1-O2-C4	-169.2(7)
F4-B1	1.320(5)	N2-C11-C10	117.5(2)	N1-C10-C9-C8	-0.3(4)
C10-C9	1.371(4)	N1-C10-C11	113.4(2)	N2-Pd1-N1-C10	-3.84(17)
C9-C8	1.380(5)	N1-C10-C9	121.3(3)	N2-Pd1-N1-C6	174.4(2)
C8-C7	1.362(5)	C9-C10-C11	125.2(3)	N2-Pd1-O1-C2	-170.8(6)
C7-C6	1.368(5)	C10-C9-C8	118.8(3)	N2-Pd1-O2-C4	-178.6(3)
C12-C13	1.392(4)	C7-C8-C9	119.2(3)	N2-C11-C10-N1	0.6(3)
C12-C17	1.388(4)	C8-C7-C6	120.0(3)	N2-C11-C10-C9	-176.1(3)
C13-C18	1.521(4)	N1-C6-C7	121.3(3)	N2-C12-C13-C18	3.1(4)
C13-C14	1.386(4)	C13-C12-N2	118.1(2)	N2-C12-C13-C14	-176.1(2)
C18-C20	1.507(6)	C17-C12-N2	118.7(2)	N2-C12-C17-C16	176.3(3)
C18-C19	1.517(5)	C17-C12-C13	122.9(2)	N2-C12-C17-C21	-4.2(4)
C14-C15	1.369(5)	C12-C13-C18	122.8(2)	O1-Pd1-N1-C10	174.75(18)
C15-C16	1.379(5)	C14-C13-C12	117.3(3)	O1-Pd1-N1-C6	-7.0(2)
C16-C17	1.385(4)	C14-C13-C18	119.9(2)	O1-Pd1-N2-C11	-8.2(8)
C17-C21	1.519(4)	C20-C18-C13	111.8(3)	O1-Pd1-N2-C12	174.2(6)
C21-C23	1.517(6)	C20-C18-C19	110.5(3)	O1-Pd1-O2-C4	2.6(3)
C21-C22	1.537(6)	C19-C18-C13	111.5(3)	O1-C2-C3-C4	1.0(6)
C2-C1	1.498(4)	C15-C14-C13	121.0(3)	O2-Pd1-N1-C10	-13.4(8)
C2-C3	1.372(5)	C14-C15-C16	120.6(3)	O2-Pd1-N1-C6	164.8(7)

C3-C4	1.371(5)	C15-C16-C17	120.7(3)	O2-Pd1-N2-C11	-176.90(19)
C4-C5	1.494(6)	C12-C17-C21	122.3(2)	O2-Pd1-N2-C12	5.50(19)
		C16-C17-C12	117.4(3)	O2-Pd1-O1-C2	-2.1(2)
		C16-C17-C21	120.3(3)	C11-N2-C12-C13	-86.8(3)
		C17-C21-C22	111.0(3)	C11-N2-C12-C17	99.4(3)
		C23-C21-C17	110.3(3)	C11-C10-C9-C8	176.2(3)
		C23-C21-C22	112.4(4)	C10-N1-C6-C7	-1.1(4)
		O1-C2-C1	114.4(3)	C10-C9-C8-C7	-1.1(5)
		O1-C2-C3	126.0(3)	C9-C8-C7-C6	1.5(6)
		C3-C2-C1	119.6(3)	C8-C7-C6-N1	-0.4(5)
		C4-C3-C2	126.9(3)	C6-N1-C10-C11	-175.5(2)
		O2-C4-C3	126.1(3)	C6-N1-C10-C9	1.4(4)
		O2-C4-C5	113.5(3)	C12-N2-C11-C10	173.7(2)
		C3-C4-C5	120.4(3)	C12-C13-C18-C20	110.5(3)
		F2-B1-F1	107.2(5)	C12-C13-C18-C19	-125.4(3)
		F2-B1-F3	113.5(4)	C12-C13-C14-C15	0.9(5)
		F2-B1-F4	114.4(5)	C12-C17-C21-C23	-103.8(4)
		F3-B1-F1	109.8(4)	C12-C17-C21-C22	131.1(4)
		F4-B1-F1	100.3(4)	C13-C12-C17-C16	2.7(4)
		F4-B1-F3	110.7(4)	C13-C12-C17-C21	-177.8(3)
				C13-C14-C15-C16	0.3(6)
				C18-C13-C14-C15	-178.3(3)
				C14-C13-C18-C20	-70.3(4)
				C14-C13-C18-C19	53.8(4)
				C14-C15-C16-C17	0.0(6)
				C15-C16-C17-C12	-1.4(5)
				C15-C16-C17-C21	179.1(4)
				C16-C17-C21-C23	75.7(5)
				C16-C17-C21-C22	-49.5(5)
				C17-C12-C13-C18	176.7(3)
				C17-C12-C13-C14	-2.5(4)
				C2-C3-C4-O2	-0.3(6)
				C2-C3-C4-C5	179.8(4)
				C1-C2-C3-C4	-179.2(3)

Despite attempts at crystallization from different common organic solvents, the quality of the single crystals of **4** was not sufficient to avoid the disorder of the $[BF_4]^-$ anions. Therefore, the molecular structure of cation of **4** in the crystal is shown in Figure S. 56 and Tables S. 6 and 7 is for illustration purposes only.

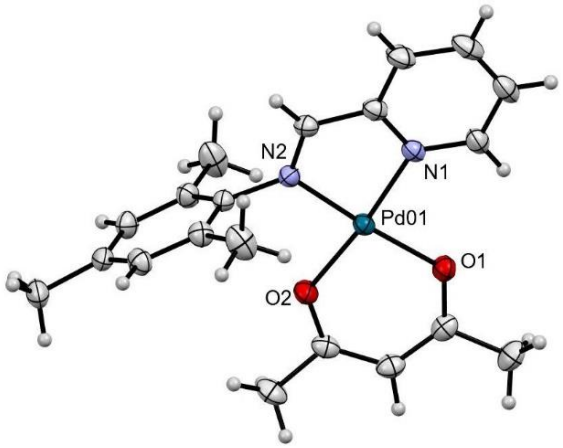


Figure S56 – ORTEP plot of cation of **4** of compounds **4** at 25% thermal ellipsoid probability)

Table S6 – X-ray crystallographic data for compounds **4**

CCDC number	2162441
Empirical formula	$C_{20}H_{23}N_2O_2Pd$, $2(B_{0.5}F_3)$
Formula weight/ g·mol^{-1}	554.61
Crystal system	Monoclinic
Space group	*C2/c*
a/ Å	16.731(7)
b/ Å	15.323(7)
c/ Å	17.700 (7)
α, β, γ/ °	90.00, 101.869(11), 90.00
Volume/ Å^3	4441(3)
Z	8
Density (calculated)/ g·cm^{-3}	1.659
Absorptions coefficient/ mm^{-1}	0.905
Radiation (λ / Å)	MoKα (0.71073)
Temperature/ K	293(2)
2Θ range/ °	2.66 – 30.03
Crystal size/ mm	0.60 × 0.25 × 0.24

Crystal habit	yellow, prism
F(000)	2224
Index ranges	$-23 \le h \le 23$, $-21 \le k \le 21$, $-24 \le l \le 24$
Reflections collected	72502
Independent reflections	6478 [R(int) = 0.0329]
Number of ref. parameters	296
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0457 / 0.1361
R_1 / wR_2 (all data)	0.0590 / 0.1475
Goodness-of-fit on F^2	1.068
Completeness [%]	99.7
Largest diff. peak and hole/ e·Å^{-3}	0.68/ -0.92
Weight scheme	$w=1/[\sigma^2(F_o^2)+ (0.0823P)^2+8.3602P]$ where $P=(F_o^2+2F_c^2)/3$

Table S7 – Selected bond lengths, bond angles and torsion angles for **4**

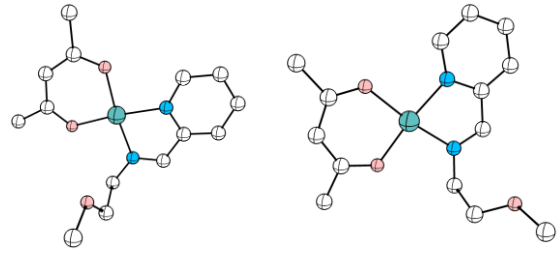
Bond	*l*, Å	Angle	*φ*, ˚	Torsion angle	*θ*, ˚
Pd01-O1	1.984(3)	O1-Pd01-N1	92.99(12)	O2 -Pd01-O1-C2	-13.6(3)
Pd01-O2	1.971(2)	O1-Pd01-N2	172.72(11)	N1 -Pd01-O1 -C2	165.9(3)
Pd01-N1	2.003(3)	O2-Pd01-O1	93.71(11)	N2 -Pd01-O1-C2	131.3(8)
Pd01-N2	2.009(3)	O2-Pd01-N1	173.28(11)	O1 -Pd01-O2-C4	10.3(3)
F4-B2	1.466(8)	O2-Pd01-N2	92.25(11)	N1 -Pd01-O2-C4	-165.0(9)
F5-B2	1.378(8)	N1-Pd01-N2	81.03(12)	N2 -Pd01-O2-C4	-165.6(3)
F6-B2	1.433(8)	C2-O1-Pd01	122.6(2)	O1 -Pd01-N1-C6	3.6(3)
O1-C2	1.281(5)	C4-O2-Pd01	123.8(2)	O1 -Pd01-N1-C10	-173.6(2)
O2-C4	1.274(4)	C6-N1-Pd01	127.2(3)	O2 -Pd01-N1-C6	178.8(8)
N1-C6	1.334(4)	C6-N1-C10	119.6(3)	O2 -Pd01-N1 -C10	2(1)
N1-C10	1.359(5)	C10-N1-Pd01	113.1(2)	N2 -Pd01 -N1 -C6	179.4(3)
N2-C11	1.285(4)	C11-N2-Pd01	114.1(2)	N2 -Pd01 -N1 -C10	2.3(2)
N2-C12	1.443(4)	C11-N2-C12	122.7(3)	O1 -Pd01 -N2 -C11	32(1)
C1-C2	1.506(6)	C12-N2-Pd01	122.8(2)	O1 -Pd01 -N2 -C12	-140.3(8)
C2-C3	1.381(6)	O1-C2-C1	114.4(4)	O2 -Pd01 -N2 -C11	177.1(2)
C3-C4	1.399(6)	O1-C2-C3	126.2(3)	O2 -Pd01 -N2 -C12	4.6(2)
C4-C5	1.515(5)	C3-C2-C1	119.3(4)	N1 -Pd01 -N2 -C11	-2.9(2)

C6-C7	1.391(6)	C2-C3-C4	126.3(3)	N1 -Pd01 -N2 -C12	-175.3(3)
C7-C8	1.370(7)	O2-C4-C3	125.6(3)	Pd01 -O1 -C2 -C1	-170.0(3)
C8-C9	1.393(7)	O2-C4-C5	114.1(4)	Pd01 -O1 -C2 -C3	9.8(5)
C9-C10	1.385(5)	C3-C4-C5	120.3(4)	Pd01 -O2 -C4 -C3	-2.7(5)
C10-C11	1.453(5)	N1-C6-C7	121.4(4)	Pd01 -O2 -C4 -C5	177.9(3)
C12-C13	1.390(5)	C8-C7-C6	119.2(4)	Pd01-N1 -C6 -C7	-177.6(3)
C12-C17	1.393(5)	C7-C8-C9	119.9(4)	C10 -N1 -C6 -C7	-0.7(6)
C13-C14	1.390(5)	C10-C9-C8	118.2(4)	Pd01 -N1 -C10 -C9	177.6(3)
C13-C18	1.509(6)	N1-C10-C9	121.6(4)	Pd01 -N1 -C10 -C11	-1.4(4)
C14-C15	1.379(6)	N1-C10-C11	114.4(3)	C6 -N1 -C10 -C9	0.2(5)
C15-C16	1.381(6)	C9-C10-C11	124.1(4)	C6 -N1 -C10 -C11	-178.8(3)
C15-C19	1.520(5)	N2-C11-C10	117.4(3)	Pd01 -N2 -C11 -C10	3.0(4)
C16-C17	1.386(5)	C13-C12-N2	118.8(3)	C12 -N2 -C11 -C10	175.4(3)
C17-C20	1.506(6)	C13-C12-C17	122.4(3)	Pd01 -N2 -C12 -C13	-76.5(4)
B2-F41	1.466(8)	C17-C12-N2	118.4(3)	Pd01 -N2 -C12 -C17	97.0(3)
B2-F51	1.378(8)	C12-C13-C14	118.0(3)	C11 -N2 -C12 -C13	111.7(4)
B2-F61	1.432(8)	C12-C13-C18	121.8(3)	C11 -N2 -C12 -C17	-74.8(4)
F1-B1	1.487(8)	C14-C13-C18	120.2(3)	O1 -C2 -C3 -C4	2.3(6)
F2-B1	1.301(6)	C15-C14-C13	121.6(3)	C1 -C2 -C3 -C4	-177.9(4)
F3-B1	1.432(9)	C14-C15-C16	118.2(3)	C2 -C3 -C4 -O2	-6.4(6)
B1-F12	1.487(8)	C14-C15-C19	120.6(4)	C2 -C3 -C4 -C5	172.9(4)
B1-F22	1.301(6)	C16-C15-C19	121.1(4)	N1 -C6 -C7 -C8	0.7(7)
B1-F32	1.432(9)	C15-C16-C17	123.0(4)	C6 -C7 -C8 -C9	-0.3(7)
		C12-C17-C20	122.3(3)	C7 -C8 -C9 -C10	-0.2(7)
		C16-C17-C12	116.7(3)	C8 -C9 -C10 -N1	0.3(6)
		C16-C17-C20	121.0(4)	C8 -C9 -C10 -C11	179.1(4)
		F4-B2-F41	179.999(1)	N1 -C10 -C11 -N2	-1.1(4)
		F5-B2-F41	91.6(5)	C9 -C10 -C11 -N2	-180.0(4)
		F51-B2-F41	88.4(5)	N2 -C12 -C13 -C14	173.6(3)
		F5-B2-F4	88.4(5)	N2 -C12 -C13 -C18	-6.1(5)
		F51-B2-F4	91.6(5)	C17 -C12 -C13 -C14	0.3(5)
		F5-B2-F51	179.998(2)	C17 -C12 -C13 -C18	-179.4(4)
		F5-B2-F61	92.2(5)	N2 -C12 -C17 -C16	-174.4(3)

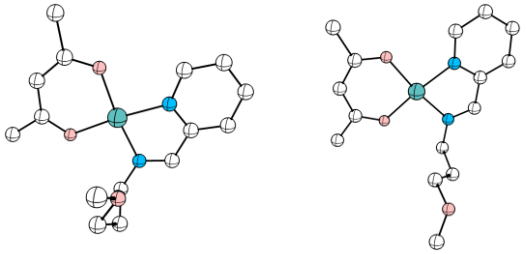
F5-B2-F6	87.8(5)	N2 -C12 -C17 -C20	3.7(5)
F51-B2-F61	87.8(5)	C13 -C12 -C17 -C16	-1.1(5)
F51-B2-F6	92.2(5)	C13 -C12 -C17 -C20	177.0(4)
F61-B2-F4	91.5(4)	C12 -C13 -C14 -C15	-0.6(6)
F61-B2-F41	88.5(4)	C18 -C13 -C14 -C15	179.1(4)
F6-B2-F4	88.5(4)	C13 -C14 -C15 -C16	1.7(6)
F6-B2-F41	91.5(4)	C13 -C14 -C15 -C19	-177.0(4)
F61-B2-F6	180.0(3)	C14 -C15 -C16 -C17	-2.6(5)
F12-B1-F1	95.8(7)	C19 -C15 -C16 -C17	176.1(3)
F22-B1-F12	98.2(5)	C15 -C16 -C17 -C12	2.3(5)
F22-B1-F1	81.8(5)	C15 -C16 -C17 -C20	-175.8(4)
F2-B1-F12	81.8(5)		
F2-B1-F1	98.2(5)		
F2-B1-F22	180.0(12)		
F22-B1-F3	82.4(5)		
F2-B1-F3	97.6(6)		
F2-B1-F32	82.4(5)		
F22-B1-F32	97.6(6)		
F32-B1-F12	164.2(4)		
F3-B1-F12	87.5(4)		
F32-B1-F1	87.5(4)		
F3-B1-F1	164.2(4)		
F32-B1-F3	93.5(8)		

6 Cartesian coordinates (Å) for palladium complexes computed with the BP86 functional

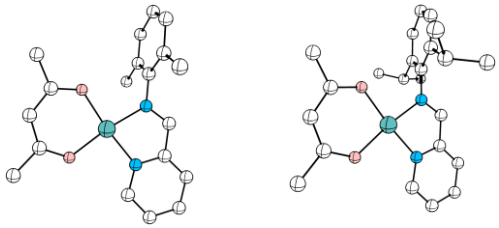
All density functional theory calculations were performed with the ORCA program [S11]. All geometry optimizations were run with tight convergence criteria, using the BP86 functional [S12,S13], making use of the resolution of the identity technique [S14]. The applicability of gradient-corrected functionals as BP86 for the structural prediction of transition metal compounds and reliable determination of the kinetic balance are well documented [S15–S20]. The basis sets that were used were the Weigend−Ahlrichs basis sets [S21,S22]. Triple-ξ-quality basis sets with one set of polarization functions (def2-TZVP) were used for the palladium in connection with effective core potentials for Pd. The remaining atoms were described by slightly smaller def2-SVP basis sets.



endo-[**1**]$^+$ *exo*-[**1**]$^+$



endo-[**2**]$^+$ *exo*-[**2**]$^+$



[**3**]$^+$ [**4**]$^+$

[**5**]$^+$

Figure S57 – Structures of the calculated cation at DFT/BP86 level (hydrogen atoms are omitted for clarity)

1_endo

39

H	-13.7395600000	8.2484010000	1.2793880000
H	-14.2928290000	2.1018570000	0.4180310000
H	-14.2328840000	8.5773230000	-0.4019420000
C	-14.2952350000	7.8297370000	0.4149380000
C	-13.6408680000	6.5447100000	-0.0307940000
O	-12.4119300000	6.6812420000	-0.4083950000
H	-15.4037990000	5.3796120000	0.3417230000
C	-14.3638740000	5.3308220000	-0.0062690000
C	-13.8713470000	4.0602280000	-0.3688780000
Pd	-11.2665220000	5.1960860000	-1.0750250000
C	-14.7559100000	2.8414730000	-0.2672600000
O	-12.6743220000	3.8128120000	-0.8004010000
H	-14.8361860000	2.3559510000	-1.2616290000
H	-15.3521350000	7.6851610000	0.7005540000
H	-15.7683580000	3.0882810000	0.0981770000
C	-8.6161540000	5.7999540000	-1.8220220000
C	-10.1210010000	2.4967380000	-1.7970090000
C	-9.0933800000	1.6258730000	-2.1962970000
C	-7.8223150000	2.1478880000	-2.4855440000
C	-7.6091430000	3.5309770000	-2.3706230000
C	-8.6771310000	4.3520260000	-1.9704840000
N	-9.9130420000	3.8214000000	-1.6900340000
H	-11.1381250000	2.1538650000	-1.5493630000
H	-9.2994510000	0.5487900000	-2.2749350000
H	-7.0025810000	1.4839290000	-2.7975440000
N	-9.7039410000	6.4118320000	-1.4421080000
H	-7.6843600000	6.3542880000	-2.0381370000
H	-6.6276470000	3.9772450000	-2.5875400000
C	-9.7662550000	7.8739710000	-1.3530370000
H	-10.5932220000	8.1264650000	-0.6624600000
C	-10.0260930000	8.5206670000	-2.7198950000
H	-8.8120510000	8.2655310000	-0.9415550000
H	-10.0145740000	9.6312240000	-2.5793900000
O	-11.2566370000	8.0683950000	-3.2212440000
H	-9.1833540000	8.2752000000	-3.4181270000
C	-11.6102420000	8.6658830000	-4.4598560000
H	-12.5913160000	8.2515720000	-4.7576560000
H	-10.8650400000	8.4382900000	-5.2582980000
H	-11.6988720000	9.7744210000	-4.3728860000

1_exo

39

H	-13.6959240000	8.3038850000	1.2289080000
H	-14.0590040000	2.0910670000	0.7082370000
H	-14.2802400000	8.5146060000	-0.4422970000
C	-14.2695780000	7.8122380000	0.4161810000
C	-13.5802350000	6.5304870000	0.0157350000
O	-12.3732090000	6.6933450000	-0.4256230000
H	-15.2757110000	5.3252390000	0.5319660000
C	-14.2503840000	5.2943560000	0.1411430000
C	-13.7305830000	4.0225180000	-0.1822900000
Pd	-11.1869820000	5.2055350000	-1.0203680000
C	-14.5719610000	2.7845160000	0.0103310000
O	-12.5451140000	3.7925920000	-0.6506830000
H	-14.6758640000	2.2516670000	-0.9572870000

H	-15.3055370000	7.6408110000	0.7581660000
H	-15.5766450000	3.0175660000	0.4050180000
C	-8.5851850000	5.8635290000	-1.8945470000
C	-9.9918680000	2.5189830000	-1.7034650000
C	-8.9633670000	1.6678720000	-2.1413360000
C	-7.7295020000	2.2190270000	-2.5219970000
C	-7.5529610000	3.6106410000	-2.4563420000
C	-8.6186550000	4.4112110000	-2.0125140000
N	-9.8181950000	3.8515230000	-1.6438500000
H	-10.9817520000	2.1533290000	-1.3876920000
H	-9.1401360000	0.5833740000	-2.1782710000
H	-6.9100650000	1.5710600000	-2.8667470000
N	-9.6657730000	6.4513290000	-1.4577020000
H	-7.6919970000	6.4467110000	-2.1742830000
H	-6.6017850000	4.0811120000	-2.7448740000
C	-9.7447080000	7.9111050000	-1.3929520000
H	-10.5998380000	8.1798960000	-0.7451570000
C	-9.9450090000	8.5157330000	-2.7874690000
H	-8.8082020000	8.3119490000	-0.9511190000
H	-10.0824860000	9.6180630000	-2.6622750000
H	-10.8816080000	8.1147220000	-3.2491880000
O	-8.8138110000	8.2142770000	-3.5695400000
C	-8.9168650000	8.6495650000	-4.9196500000
H	-7.9860810000	8.3477320000	-5.4354200000
H	-9.0194680000	9.7570390000	-4.9864650000
H	-9.7868800000	8.1825850000	-5.4378740000

2_endo

42

H	-13.4027320000	8.3519890000	1.2858480000
H	-13.8160100000	2.1738900000	0.6750610000
H	-13.9535470000	8.6168610000	-0.3885420000
C	-13.9678230000	7.8905770000	0.4494860000
C	-13.2865250000	6.6103550000	0.0287720000
O	-12.0774990000	6.7700270000	-0.4059990000
H	-14.9956740000	5.4117400000	0.5175180000
C	-13.9678050000	5.3780420000	0.1336490000
C	-13.4541320000	4.1062700000	-0.2002830000
Pd	-10.8823540000	5.2756260000	-0.9802870000
C	-14.3081450000	2.8727910000	-0.0325080000
O	-12.2650470000	3.8725780000	-0.6557470000
H	-14.3929110000	2.3431920000	-1.0036300000
H	-15.0116260000	7.7244050000	0.7696210000
H	-15.3200210000	3.1105980000	0.3404830000
C	-8.2383380000	5.8991660000	-1.7255610000
C	-9.6797290000	2.5712990000	-1.5726870000
C	-8.6370550000	1.7058360000	-1.9420720000
C	-7.3779480000	2.2414420000	-2.2582540000
C	-7.1919990000	3.6315920000	-2.1983170000
C	-8.2736080000	4.4469950000	-1.8235320000
N	-9.4972550000	3.9031610000	-1.5168820000
H	-10.6891070000	2.2185090000	-1.3082090000
H	-8.8217470000	0.6226090000	-1.9765790000
H	-6.5465980000	1.5821940000	-2.5488030000
N	-9.3335960000	6.5054430000	-1.3625160000
H	-7.3169760000	6.4610430000	-1.9643000000
H	-6.2211360000	4.0886860000	-2.4388840000
C	-9.4083860000	7.9704790000	-1.3027090000
H	-10.2843790000	8.2229880000	-0.6746790000
C	-9.5362460000	8.6339940000	-2.6904960000
H	-8.4950890000	8.3475920000	-0.7948170000
H	-9.4894130000	9.7312810000	-2.5278190000

H	-8.6559060000	8.3697110000	-3.3155360000
C	-10.8119210000	8.3159070000	-3.4607010000
H	-11.7124530000	8.5810330000	-2.8516810000
O	-10.8291550000	6.9412860000	-3.8053500000
H	-10.8466260000	8.9484270000	-4.3821410000
C	-11.9433100000	6.5838840000	-4.6082310000
H	-11.8655240000	5.5016290000	-4.8252870000
H	-11.9483350000	7.1431400000	-5.5732010000
H	-12.9112220000	6.7781900000	-4.0885750000

2_exo

42

H	-14.7025390000	7.1465340000	1.1205560000
H	-16.0936060000	1.4640940000	-1.0646440000
H	-14.6823320000	7.8107160000	-0.5338750000
C	-15.0773690000	6.9823340000	0.0891580000
C	-14.5596010000	5.6637370000	-0.4316080000
O	-13.2674910000	5.5807340000	-0.4735860000
H	-16.5317100000	4.8763260000	-0.7262160000
C	-15.4617620000	4.6490490000	-0.8181900000
C	-15.1220580000	3.3689750000	-1.3053340000
Pd	-12.2639090000	3.9703080000	-1.0864450000
C	-16.2026170000	2.3832240000	-1.6766030000
O	-13.9165370000	2.9249890000	-1.4735230000
H	-16.0827800000	2.0821360000	-2.7376690000
H	-16.1807580000	7.0260860000	0.0941880000
H	-17.2156040000	2.7974940000	-1.5295340000
C	-9.4488380000	4.0417880000	-0.9864780000
C	-11.4703930000	1.2215490000	-2.0528610000
C	-10.5464990000	0.2111660000	-2.3687790000
C	-9.1732640000	0.4632420000	-2.2199450000
C	-8.7550250000	1.7219630000	-1.7589630000
C	-9.7259510000	2.6933140000	-1.4614230000
N	-11.0650630000	2.4262340000	-1.6128600000
H	-12.5602560000	1.0895910000	-2.1428380000
H	-10.9128730000	-0.7614800000	-2.7271940000
H	-8.4326240000	-0.3137700000	-2.4605180000
N	-10.4666530000	4.8274480000	-0.7642070000
H	-8.4099630000	4.3852680000	-0.8290550000
H	-7.6885510000	1.9571850000	-1.6293680000
C	-10.2674690000	6.2207160000	-0.3359650000
H	-11.2209120000	6.5569410000	0.1156130000
C	-9.8573100000	7.1502950000	-1.4953950000
H	-9.4851560000	6.2351090000	0.4521430000
H	-9.6179400000	8.1371170000	-1.0456210000
H	-8.9164080000	6.7831340000	-1.9603500000
C	-10.9215250000	7.3111110000	-2.5960730000
H	-11.8545810000	7.7485520000	-2.1605030000
O	-10.4578590000	8.0673770000	-3.6902340000
H	-11.1945930000	6.3119410000	-3.0024100000
C	-10.5231980000	9.4734410000	-3.5189040000
H	-10.2096410000	9.9333080000	-4.4753530000
H	-9.8452250000	9.8485780000	-2.7161170000
H	-11.5609250000	9.8123240000	-3.2847350000

3

45

H	-11.1325060000	-11.0055730000	-1.1570820000
H	-11.0524320000	-4.7454610000	-1.1817510000

H	-12.0563650000	-11.0305800000	0.3639150000
C	-11.8215200000	-10.4092770000	-0.5239510000
C	-11.1282230000	-9.1421080000	-0.0855910000
O	-10.0657980000	-9.3410170000	0.6240340000
H	-12.5629580000	-7.8819720000	-1.0649020000
C	-11.6473750000	-7.8814200000	-0.4592570000
C	-11.1011980000	-6.6237780000	-0.1301250000
Pd	-8.9050810000	-7.8922360000	1.3451420000
C	-11.7722810000	-5.3550150000	-0.5980360000
O	-10.0281350000	-6.4303960000	0.5708460000
H	-12.0728150000	-4.7481510000	0.2811320000
H	-12.7492930000	-10.2063630000	-1.0875260000
H	-12.6637210000	-5.5570980000	-1.2177310000
C	-6.6041630000	-8.6256680000	2.8106930000
C	-7.6652880000	-5.2340950000	2.0673970000
C	-6.6879100000	-4.4122140000	2.6535730000
C	-5.6098700000	-5.0013280000	3.3338150000
C	-5.5348000000	-6.4013040000	3.4119990000
C	-6.5435910000	-7.1700150000	2.8066030000
N	-7.5903390000	-6.5750350000	2.1460790000
H	-8.5342960000	-4.8380840000	1.5182340000
H	-6.7819800000	-3.3198870000	2.5709710000
H	-4.8334730000	-4.3765560000	3.7996700000
N	-7.6139790000	-9.1933890000	2.2064790000
H	-5.8298520000	-9.2309690000	3.3146990000
H	-4.7060360000	-6.9008250000	3.9347210000
C	-7.7365420000	-10.6208600000	2.1477960000
C	-6.9965230000	-11.3277310000	1.1632370000
C	-7.1558380000	-12.7264590000	1.1214290000
C	-8.0136180000	-13.3868820000	2.0135690000
C	-8.7423230000	-12.6574590000	2.9648760000
C	-8.6304810000	-11.2566280000	3.0492500000
C	-6.0897230000	-10.6139260000	0.1883750000
H	-6.5969380000	-13.3021960000	0.3674630000
H	-8.1197590000	-14.4809940000	1.9628230000
H	-9.4174090000	-13.1794020000	3.6607560000
C	-9.4067910000	-10.4641380000	4.0717770000
H	-5.1868650000	-10.1947280000	0.6819720000
H	-6.6079830000	-9.7680020000	-0.3107880000
H	-5.7355030000	-11.3070710000	-0.5974680000
H	-9.9926540000	-9.6492480000	3.5951180000
H	-8.7404430000	-9.9843320000	4.8203220000
H	-10.1107560000	-11.1135190000	4.6251370000

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H	-11.1949900000	-10.5414840000	-0.7767560000
H	-11.0912780000	-4.3074120000	-0.8022380000
H	-12.0766100000	-10.5915860000	0.7690190000
C	-11.8692210000	-9.9575770000	-0.1164500000
C	-11.1692750000	-8.6924260000	0.3184510000
O	-10.1014220000	-8.8949150000	1.0182010000
H	-12.6098780000	-7.4289980000	-0.6479590000
C	-11.6884670000	-7.4305090000	-0.0511840000
C	-11.1342640000	-6.1740990000	0.2696090000
Pd	-8.9262600000	-7.4478970000	1.7258010000
C	-11.8042340000	-4.9040590000	-0.1969280000
O	-10.0539660000	-5.9830120000	0.9593850000
H	-12.0803760000	-4.2851900000	0.6817350000
H	-12.8124340000	-9.7521140000	-0.6528990000
H	-12.7099950000	-5.1041760000	-0.7961870000
C	-6.5837130000	-8.1774160000	3.1256000000

C	-7.6743330000	-4.7878630000	2.4174850000
C	-6.6785650000	-3.9645580000	2.9692130000
C	-5.5755740000	-4.5525260000	3.6097030000
C	-5.4947840000	-5.9521060000	3.6834090000
C	-6.5237880000	-6.7228840000	3.1147160000
N	-7.5947280000	-6.1287640000	2.4935070000
H	-8.5620700000	-4.3934890000	1.8979730000
H	-6.7778180000	-2.8723540000	2.8915790000
H	-4.7840730000	-3.9266660000	4.0478730000
N	-7.6170020000	-8.7505140000	2.5649730000
H	-5.7929130000	-8.7795640000	3.6067230000
H	-4.6461480000	-6.4504650000	4.1743400000
C	-7.7297380000	-10.1749590000	2.5024290000
C	-6.9177280000	-10.8937730000	1.5839330000
C	-7.0726420000	-12.2904280000	1.5410010000
C	-7.9877580000	-12.9767310000	2.3663070000
C	-8.7760930000	-12.2175980000	3.2557080000
C	-8.6817780000	-10.8176730000	3.3375090000
C	-5.9427130000	-10.1957410000	0.6630350000
H	-6.4556000000	-12.8632430000	0.8298650000
C	-8.1410630000	-14.4745580000	2.2751330000
H	-9.4921370000	-12.7334540000	3.9157810000
C	-9.5220120000	-10.0335970000	4.3151250000
H	-5.0477140000	-9.8163940000	1.2008150000
H	-6.4084460000	-9.3266770000	0.1530540000
H	-5.5768390000	-10.8902750000	-0.1163320000
H	-10.0848090000	-9.2211790000	3.8081620000
H	-8.9003830000	-9.5518690000	5.0999770000
H	-10.2517670000	-10.6892580000	4.8260240000
H	-8.5005590000	-14.9095720000	3.2280870000
H	-7.1862020000	-14.9687600000	2.0080250000
H	-8.8797950000	-14.7491830000	1.4909100000

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H	-6.8563540000	-11.9983720000	4.1671280000
H	-13.0946940000	-12.0497100000	3.7355160000
H	-6.9212080000	-10.6553320000	5.3328320000
C	-7.5085660000	-11.4958970000	4.9106180000
C	-8.7378010000	-10.9557850000	4.2196610000
O	-8.4851910000	-10.0925840000	3.2914570000
H	-10.0675070000	-12.1439140000	5.4140690000
C	-10.0224710000	-11.4021400000	4.6061370000
C	-11.2509810000	-10.9853520000	4.0539120000
Pd	-9.8776500000	-9.1701030000	2.2012250000
C	-12.5507490000	-11.5565750000	4.5674190000
O	-11.3912370000	-10.1169430000	3.1021250000
H	-13.1987750000	-10.7350350000	4.9362640000
H	-7.7590860000	-12.2095430000	5.7153450000
H	-12.3946440000	-12.2874890000	5.3804270000
C	-9.0504890000	-7.2277390000	0.3245380000
C	-12.4800930000	-8.1980780000	1.0161320000
C	-13.2615690000	-7.3931400000	0.1705090000
C	-12.6300550000	-6.4692730000	-0.6780860000
C	-11.2296040000	-6.3726090000	-0.6609330000
C	-10.5018250000	-7.2065770000	0.2054970000
N	-11.1379620000	-8.1038300000	1.0274930000
H	-12.9101660000	-8.9391710000	1.7084510000
H	-14.3558470000	-7.4986170000	0.1856580000
H	-13.2228710000	-5.8286510000	-1.3476610000
N	-8.5204240000	-8.0713470000	1.1705240000
H	-8.4155290000	-6.5609690000	-0.2848850000

H	-10.6977540000	-5.6606420000	-1.3088180000
C	-7.0993140000	-8.1310120000	1.3643800000
C	-6.3970780000	-9.2327210000	0.7970950000
C	-5.0041510000	-9.2741470000	0.9862080000
C	-4.3409800000	-8.2795770000	1.7208300000
C	-5.0636200000	-7.2245430000	2.2918970000
C	-6.4610360000	-7.1217170000	2.1393240000
H	-4.4239880000	-10.0987020000	0.5468610000
H	-4.5313740000	-6.4610440000	2.8795890000
H	-3.2496190000	-8.3316090000	1.8532370000
C	-7.2182030000	-5.9803570000	2.8201460000
C	-7.1146140000	-10.2785640000	-0.0550370000
C	-7.0084020000	-5.9961070000	4.3495920000
H	-8.3041930000	-6.1350460000	2.6504120000
C	-6.5702260000	-11.7042280000	0.1413080000
H	-8.1804830000	-10.2901360000	0.2677130000
H	-5.9494430000	-5.8098830000	4.6221670000
H	-7.3043220000	-6.9695240000	4.7894220000
H	-7.6176270000	-5.2030270000	4.8292030000
C	-6.8430650000	-4.6092240000	2.2182680000
H	-5.7711040000	-4.3745090000	2.3819020000
H	-7.4359350000	-3.7995040000	2.6907260000
H	-7.0233160000	-4.5712250000	1.1240700000
H	-7.2072450000	-12.4345900000	-0.3974260000
H	-6.5531720000	-11.9906100000	1.2116980000
H	-5.5427080000	-11.8191460000	-0.2608640000
C	-7.0886000000	-9.8777940000	-1.5476910000
H	-7.6519040000	-10.6109640000	-2.1606870000
H	-6.0476340000	-9.8429770000	-1.9303560000
H	-7.5342800000	-8.8762740000	-1.7205200000

7 Norbornene polymerization results

Polymerizations were performed in a 25 ml glass reactor equipped with a magnetic stirrer. The reactor was filled with norbornene as a solution in CH_2Cl_2; the solution was kept at the desired temperature for 15 min before the palladium complex was added. Polymerizations were initiated by the injection of boron compound. After stirring, the polymers formed were precipitated in ethanol. The precipitated polymers were washed three times with ethanol and dried in vacuum at 80 °C for 6 h.

The monomer conversion/time relationship was monitored by GC-FID (Fig. S. 58).

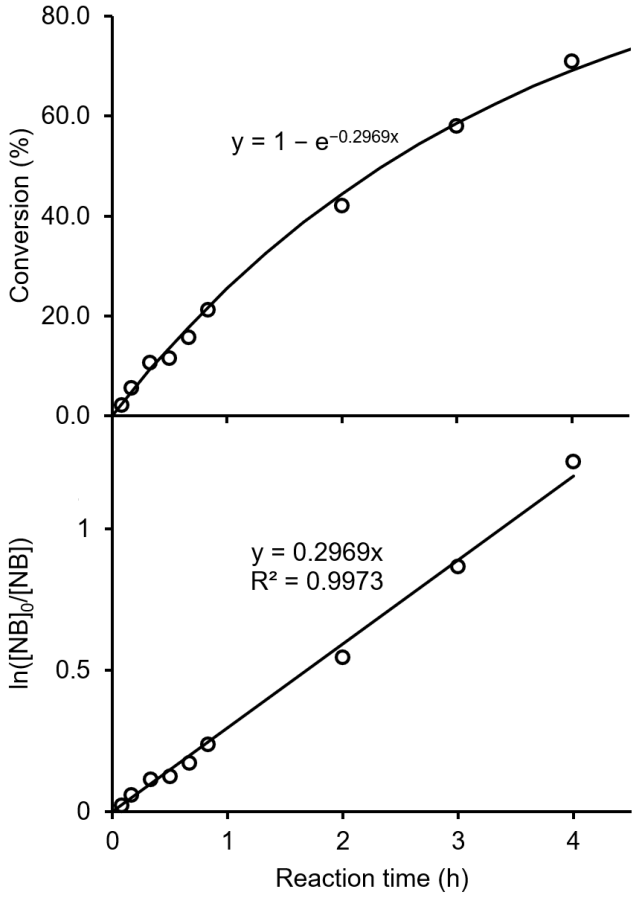


Figure S58 – Conversion/time and first-order plots for the polymerization of NB with Pd catalyst system **2**/50BF_3·OEt_2. Conditions: V_0 = 9 mL, $[NB]_0$=2.25 M, $[NB]_0/[Pd]_0$ = 2500 in dichloromethane at 25 °C .

The effect of $[NB]_0/[Pd]_0$ ratio on the norbornene polymerization is shown in Figure S. 59. A linear relation between *TON* and the initial molar ratio of monomer to precatalyst of up to $[NB]_0/[Pd]_0$ of 7500 for the most active pre-catalyst (**2**) was found. A further increase of $[NB]_0/[Pd]_0$ lowered the activity. Such concentration effect of palladium pre-catalyst was reported for norbornene polymerization by C. Janiak et al [S23] and may be explained by impurities which

are contained in the monomer and eventually decrease the number of active centers. Reaction time of 10 min was chosen intentionally. The polymerization was stopped after this time by the addition of EtOH/HCl. Such short reaction times with conversions still below 10% allow for a better differentiation or comparison of catalyst activities. With PNB formation the active complex becomes more and more embedded in the polymer matrix which represents a transfer to a heterogeneous phase, that is, a heterogeneous active complex form, and this leads to a diffusion-controlled reaction [S24].

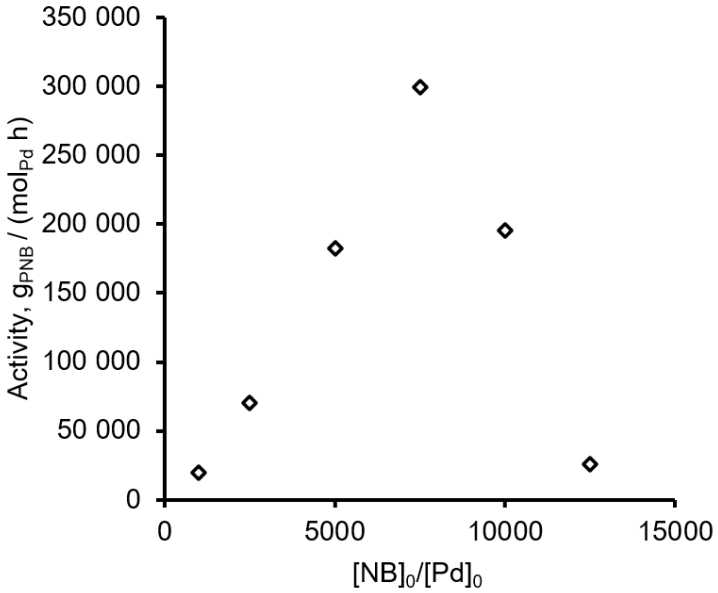


Figure S59 – Plot of *TON* vs. $[NB]_0/[Pd]_0$ for **2** at 25 °C in CH_2Cl_2 (n_{Pd} = 4.6 μmol, V_0 = 9 mL, τ = 10 min, $[B]_0/[Pd]_0$ = 50)

Variations of the ratio of $BF_3{\cdot}OEt_2$ in **2** showed a significant effect on catalytic activity. The catalytic activity of **2** firstly increased rapidly with increases in B/Pd ratios, and then increases smoothly after the $[B]_0/[Pd]_0$ ratio reached about 30:1. Thus, as exemplified with complex **2** an optimal amount of the cocatalyst around B/Pd = 50–100 can be recommended. The results obtained might be explained by the equilibrium between active and inactive (initial κ^2-O,O-acetylacetonate complex) palladium species (see Figures S. 59 and S. 60). The increasing amount of the $BF_3{\cdot}OEt_2$ cocatalyst shifts the equilibrium to the active form [S25,S26].

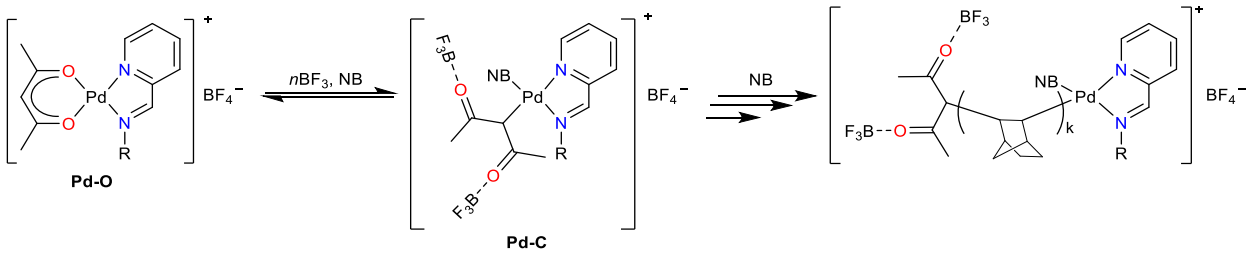


Figure S60 – Proposed mechanism of the formation of the active species using (**1**-**5**)/$n$$BF_3{\cdot}OEt_2$

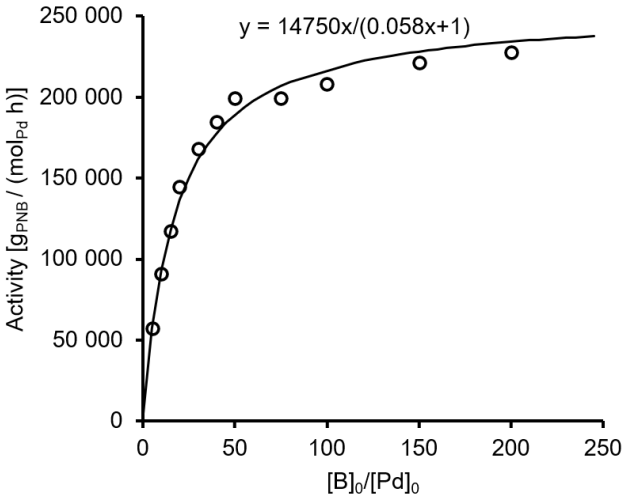


Figure S61 – Plot of activity vs. $[B]_0/[Pd]_0$ for **2**/*n*BF_3·OEt_2 at 25 ◦C in CH_2Cl_2; 4.6 μmol **2**, $[NB]_0$:$[Pd]_0$ = 5000, V_0 = 9 mL, reaction time – 10 min (curve parameters were found by linearizing the data in coordinates 1/*A* vs $[Pd]_0/[B]_0$, see Figure S62).

For the Figure S60 curve parameters were found by linearizing the data in coordinates 1/*A* vs $[Pd]_0/[B]_0$. Simplified hypothetical mechanism was used for this model (see Figure S60), but obtained curve parameters (Figure S62) were in good agreement with the experimental data:

$$\mathbf{Pd\text{-}O} + \mathbf{BF_3} \overset{K}{\rightleftharpoons} \mathbf{Pd\text{-}C}$$

$$\mathbf{Pd\text{-}C} + \mathbf{NB} \overset{k}{\rightarrow} \mathbf{P}\ \text{(Addition polymerization)}$$

$$r = k[\text{Pd-C}][\text{NB}], K = \frac{[\text{Pd-C}]}{[\text{Pd-O}][\text{BF}_3]}, [\text{Pd}]_0 = [\text{Pd-C}] + [\text{Pd-O}]$$

$$r = \frac{kK[\text{Pd}]_0[\text{NB}][\text{BF}_3]}{1 + K[\text{BF}_3]}, TOF = \frac{kK[\text{NB}][\text{BF}_3]}{1 + K[\text{BF}_3]}, TOF_0 = \frac{kK[\text{NB}]_0[\text{BF}_3]_0}{1 + K[\text{BF}_3]_0}$$

$$\frac{1}{TOF_0} = \frac{1}{k[\text{NB}]_0} + \frac{1}{kK[\text{NB}]_0[\text{BF}_3]_0} = \frac{1}{k[\text{NB}]_0} + \frac{1}{kK[\text{NB}]_0[\text{Pd}]_0}\frac{[\text{Pd}]_0}{[\text{BF}_3]_0}$$

$$A = TOF \cdot M_{\text{NB}}, \frac{1}{A_0} = \frac{1}{kM_{\text{NB}}[\text{NB}]_0} + \frac{1}{kKM_{\text{NB}}[\text{NB}]_0[\text{Pd}]_0}\frac{[\text{Pd}]_0}{[\text{BF}_3]_0}$$

$$\frac{1}{A_0} = a + b\frac{[\text{Pd}]_0}{[\text{BF}_3]_0}$$

$$A_0 = \frac{b^{-1}x}{1 + \frac{a}{b}x}, \text{where } x = \frac{[\text{BF}_3]_0}{[\text{Pd}]_0}$$

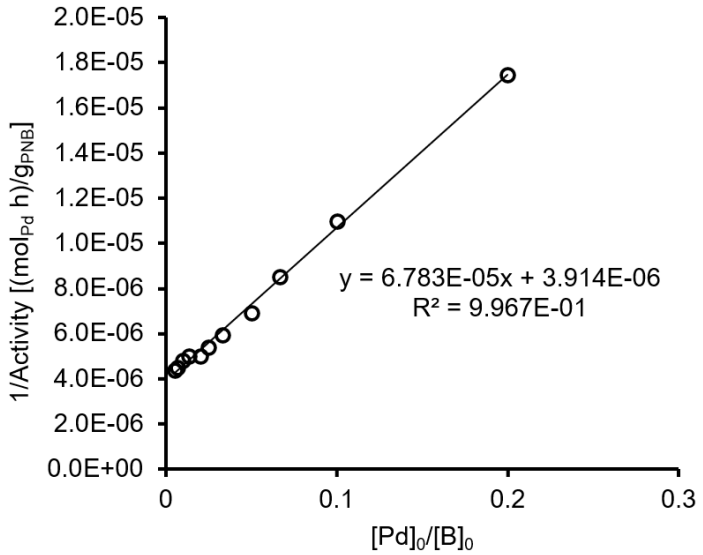


Figure S62 – Plot 1/*A* vs $[Pd]_0/[B]_0$

The resulting polynorbornenes were insoluble in common solvents, such as benzene, chloroform, methylene chloride, THF, toluene, and 1,2,4-trichlorobenzene. Insolubility of addition PNBs is frequently observed and considered indicative of high stereoregularity or the existence of a cross-linking structure by the C7-linkage, since intramolecular σ-bond metathesis leads to a rigid helical structure of the PNB, which strongly affects its solubility [S27–S29]. IR (KBr disk) analysis of polynorbornene (Figure S. 63) showed no absorbance in the 1600–1670 cm^{-1} range, indicating that polymerization occurred via a vinyl addition pathway [S30].

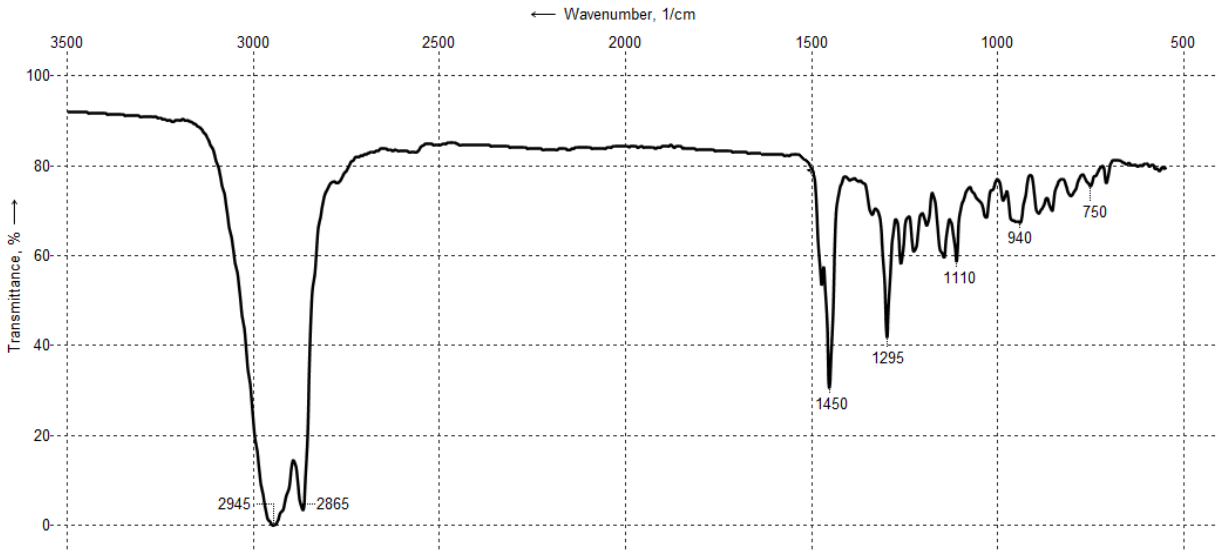
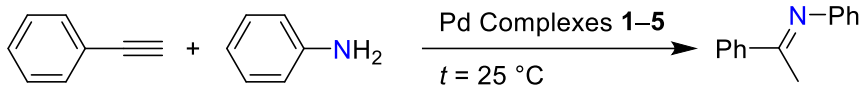


Figure S63 – IR spectrum of polynorbornene sample (KBr), obtained using **1**/50BF_3·OEt_2

8 Hydroamination of phenylacetylene results

Table S8 – Hydroamination of Phenylacetylene with Aniline.



Entry[a]	Pd	*t*, °C	Reaction time, h	Conv. PA %[b]	Yield, %	Chemo, mol%[c]	*TON*[d]
1	**2**	40	3	12	1	8	8
2	**2**	55	3	17	2	10	15
3	**2**	70	3	20	6	19	35
4	**2**	85	3	29	9	20	54
5	**2**	100	3	43	14	22	87
6	**4**	40	3	25	9	23	55
7	**4**	55	3	33	16	32	100
8	**4**	70	3	63	29	30	180
9	**4**	85	3	56	24	28	150
10	**4**	100	3	54	22	27	140
11[e]	**2**	70	3	36	6	18	35
12[e]	**2**	70	6	45	8	21	50
13[e]	**2**	70	9	54	10	23	65
14[e]	**2**	70	12	58	12	24	75
15[e]	**2**	70	15	62	14	27	90
16[e]	**5**	70	1	37	13	41	80
17[e]	**5**	70	2	62	21	41	135
18[e]	**5**	70	3	74	25	40	155
19[e]	**5**	70	6	92	32	41	200
20[e]	**5**	70	9	96	33	41	210
21[e]	**2**	25	24	27	2	10	15
22[e]	**5**	25	24	49	13	31	80
23[e]	**2**	25	96	34	9	31	55
24[e]	**5**	25	96	62	41	79	260

[a] Reaction conditions: $[PA]_0/[AN]_0/[Pd]_0$ = 945/630/1, n_{Pd} = 8.6 μmol.
[b] Phenylacetylene conversion.
[c] Chemoselectivity = $(n_{N\text{-(1-Phenylethyl)benzenamine}})(n_{PA})^{-1}$.
[d] In units of (mol of *N*-(1-Phenylethyl)benzenamine)(mol of Pd)$^{-1}$.
[e] $[PA]_0/[AN]_0/[Pd]_0$ = 630/530/1, n_{Pd} = 8.6 μmol, V_0 = 1.0 mL.

In a typical experiment, a mixture of phenylacetylene (500 μL, 4.55 mmol) and a slight excess of aniline (500 μL, 5.20 mmol) was added using syringe to complex **4** (4.3 mg) in a glass vial under argon at room temperature. Afterwards the reactor was closed and placed in an oil bath at 70 °C. The mixture was then stirred or 15 h, after which the reaction mixture was poured into a large amount of methanol to precipitate the PA oligomer byproduct as yellow powder. Analyses of the catalytic reactions have been performed on a GC-FID. The pure product was isolated by distillation under reduced pressure (t_b = 114°C, p = 0.57 Torr) and used for the experimental determination of relative response factors for GC-FID.

N-(1-Phenylethylidene)benzenamine **6**. Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 8.08 – 8.05 (m, 2H), 7.48 – 7.45 (m, 3H), 7.42 – 7.38 (m, 2H), 7.19 – 7.11 (m, 1H), 6.92 – 6.85 (m, 2H), 2.22 (s, 3H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25°C): δ 165.37 (C=N), 152.05, 139.67, 130.69, 129.24, 128.57, 127.48, 123.45, 119.66, 17.38 (Me). The spectroscopic data of the product are consistent with literature values [S31].

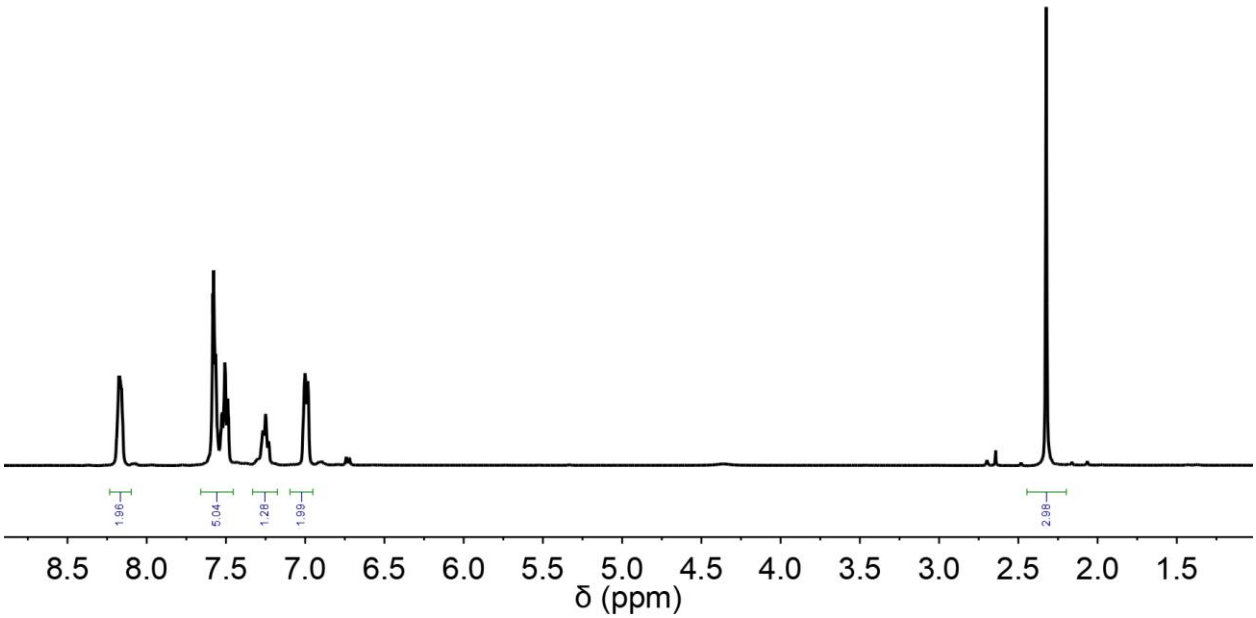


Figure S64 – ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) spectrum of *N*-(1-phenylethylidene)benzenamine **6**

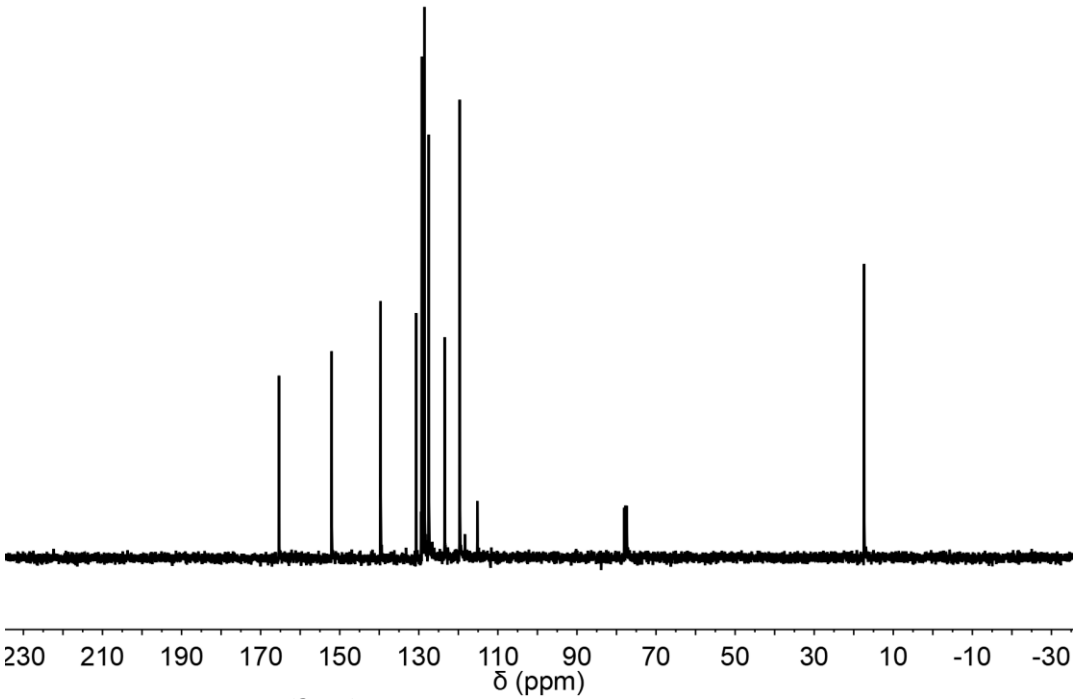


Figure S65 – $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 25°C) spectrum of *N*-(1-phenylethylidene)benzenamine **6**

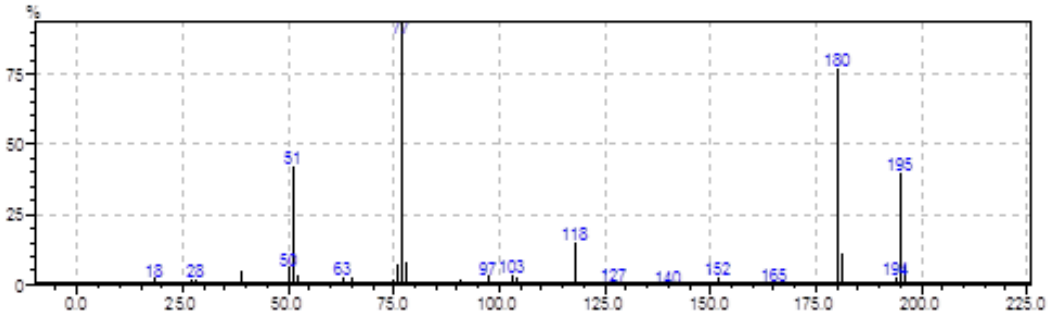
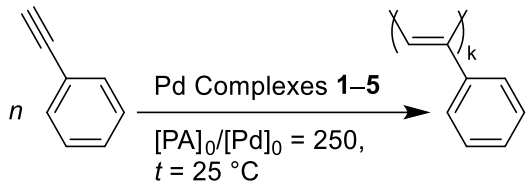


Figure S66 – EI MS spectrum of *N*-(1-phenylethylidene)benzenamine **6**

Table S9 – Oligo-/polymerization of PA with Pd Catalysts



Entry[a]	Complex	Yield (%)	*TON*[b]	Activity[c]	*Cis*[d] (%)	M_w (/10^3)[e]	M_w/M_n[e]
1	**1**	1.4	4	15	73	0.8	1.5
2	**2**	0.7	2	7	84	2.2	1.5
3	**3**	—	—	—	—	—	—
4	**4**	—	—	—	—	—	—
5	**5**	—	—	—	—	—	—

[a] Reaction conditions: $[PA]_0/[Pd]_0 = 250$, $n_{Pd} = 18$ μmol, $V_{PA} = 0.5$ mL, $V_{solvent} = 0.5$ mL, t = 25°C, reaction time – 24 h, solvent – THF. [b] In units of (mol of PA) (mol of Pd)$^{-1}$. [c] In units of (g of polymer) (mol of Pd)$^{-1}$ h^{-1} [d] The percentages of *cis* sequences determined as prescribed in ref [S32]. [e] Estimated by GPC in THF (polystyrene standard).

All the polymerizations were carried out in a 5 ml glass reactor equipped with a magnetic stirrer under Ar. Pd catalyst was stirred in the solvent (0.5 ml), after which a PA (0.5 ml, 4.55 mmol) was added. After being stirred for 24 h, the reaction mixture was poured into a large amount of acidified methanol to precipitate the polymer as yellow powder. The product was isolated by filtration and dried under vacuum to constant weight. Polymer samples were characterized by FT-IR and GPC analysis. The polyphenylacetylene (PPA) produced showed IR absorption bands characteristic of mixture of head-to-tail *cis-transoidal* PPA or *trans-cisoidal* PPA isomers [S32–S34].

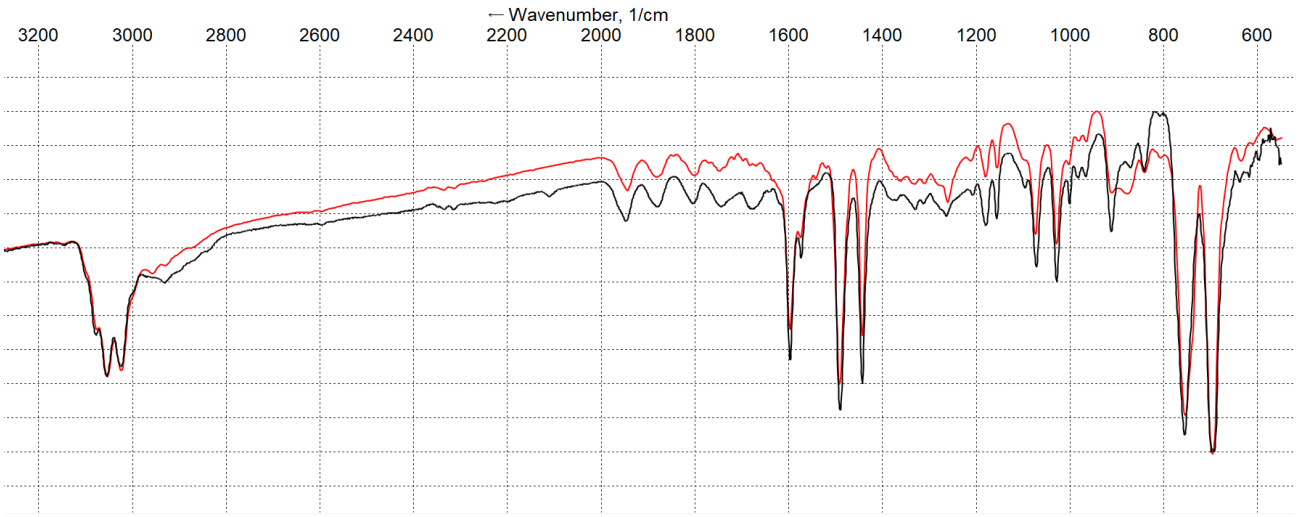


Figure S67 – IR spectrum of polyphenylacetylene sample (KBr), obtained using **1** as catalyst (—) and as byproduct in phenylacetylene hydroamination of phenylacetylene with aniline (—) in the presence of **3** as catalyst

We have also preliminarily examined computationally the intermediates energetics involved, using DFT at the BP86 (CH_2Cl_2/CPCM) level of theory, for the reaction between PA, AN, and cation of **3**; the computed energies (ΔE_{ZPE}) are given in Figure S68. All reported energies are in kcal mol^{-1} and include zero-point energy (ZPE) at the optimized level. It is reasonable to assume that the initial reaction involved the binding of PA or AN followed by acetylacetonate isomerization. The first step in Path A, involving coordination of the alkyne, has a positive ΔE_{ZPE} of 22.7 kcal mol^{-1}. The binding of the alkyne is asymmetric and the ipso carbon carry positive Mulliken charge. This appears to be quite similar to that proposed by Leong and Virant for a cationic alkyne Pd(II) and Rh(III) complexes [S35,S36]. The coordination of aniline is more energetically preferrable (ΔE_{ZPE} = 11.2 kcal mol^{-1}). The second step in Path B which involves proton transfer to acac ligand give amide-intermediate that lies 9.6 kcal mol^{-1} higher (total ΔE_{ZPE} = 20.0 kcal mol^{-1}). The possibility of direct migration of the Pd-bound **PA** to the Pd-N bond has a computed formation of intermediate **D'** with ΔE_{ZPE} of −14.6 kcal mol^{-1}. Despite the mechanism in Path B is rather tentative, it seems to be preferable, since explains the formation of phenylacetylene oligomers only in the presence of aniline.

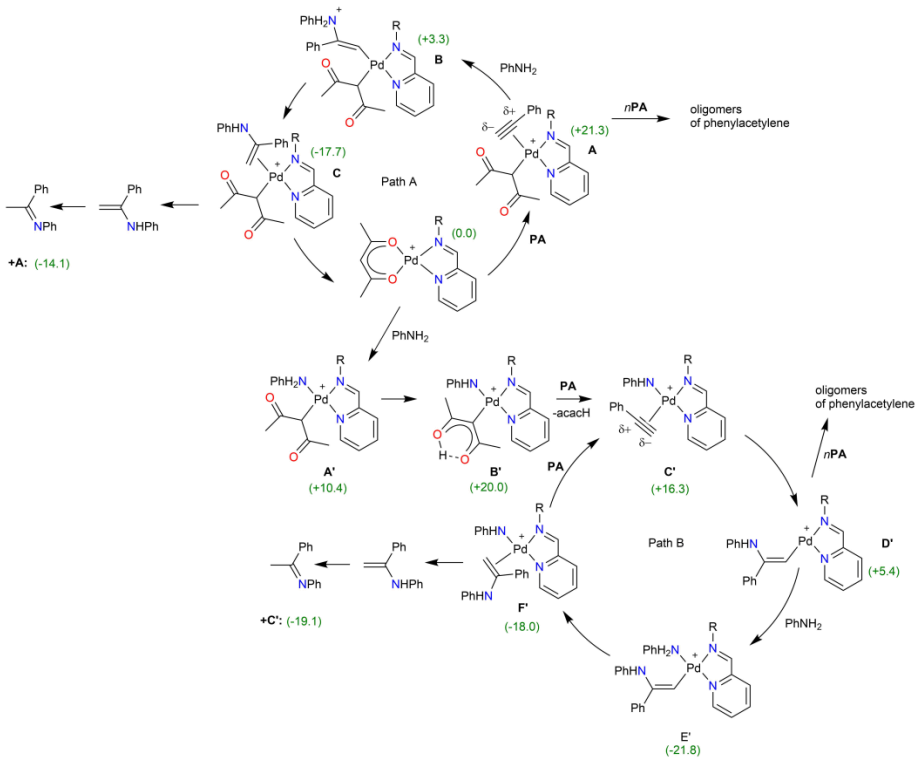


Figure S68 – Proposed mechanisms for the hydroamination reaction of phenylacetylene with aniline in the presence of a cationic catalyst **1**–**5**. $[BF_4]^-$ anion is omitted for clarity. In parentheses (marked in green) is DFT calculated relative intermediates E_{ZPE} at BP86 (CH_2Cl_2/CPCM) level of theory using cation of **3** (R = 2,6-$Me_2C_6H_3$).

Cartesian coordinates (Å) for intermediates computed with the BP86 functional

A

```
59
Coordinates from ORCA-job PhCCH_tr_c3acac_PyPhMe2
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  H   -8.18432604828355    -12.86305747167983      2.98673524492951
  C   -9.17564747980035    -12.45342890365537      2.71885296554294
  C   -9.03480526944321    -11.19132372465577      1.92845470859387
  O   -7.94225095656164    -10.81572296993705      1.46745115535342
  H   -10.49999650192901     -9.65969203269075      2.47779637001539
  C   -10.22049575646032    -10.29896230578551      1.61159941437103
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B

73
Coordinates from ORCA-job AN_PA_c3acac_PyPhMe2

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C

73
Coordinates from ORCA-job AFA_c3acac_PyPhMe2

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C	-10.16975149205656	-8.04022160388876	-3.34807540498002
H	-10.35313187095455	-5.67182190005720	-0.85986979198193
H	-9.63165970152392	-4.21039088435679	-2.75532168285514
H	-9.29899329047550	-5.18525613281921	-5.04308010999827
H	-9.65643259084294	-7.64131766781848	-5.42095098173629
H	-10.33149626037179	-9.11632906382700	-3.51712808268526
N	-11.89861128633205	-8.14573083239049	-0.24350261325624
C	-12.96612342527698	-7.22673897048825	-0.44864400511926
C	-13.38031473794197	-6.79096340070801	-1.72694933037401
C	-14.47570020253448	-5.92284109371253	-1.83747057910937
C	-15.16648147750135	-5.48802903417792	-0.69226095246474
C	-14.76766951767383	-5.94432841903511	0.57565047709964
C	-13.67712038057426	-6.81559505346997	0.70221061968081
H	-12.87174142181721	-7.14567358278749	-2.63256551612463
H	-14.80132173224659	-5.59320672791855	-2.83567339755549
H	-16.02539896283250	-4.80752035964345	-0.79100722801989
H	-15.31391987360284	-5.62603987828897	1.47630485154707
H	-13.36991621861968	-7.20005119778542	1.68639886354868
H	-11.97675967455520	-8.71657938498878	0.65096185650643
H	-10.55670950958844	-10.37218939210990	-0.20823848794724

A′

59
Coordinates from ORCA-job NH2Ph__tr_c3acac_PyPhMe2

H	-9.84435693447876	-13.18320914224356	2.83806688650362
H	-12.75832069962463	-8.79871201138657	3.01073978369881
H	-11.44896510526053	-12.38367414675860	2.92605907056536
C	-10.45955555222124	-12.36650356862186	2.41850569642505
C	-9.79971430054303	-11.03621552441057	2.72071936585979
O	-8.92975621533896	-10.95578132291975	3.59195096327247
H	-10.10861567500102	-8.92647096814663	2.72172649885809
C	-10.25081420673490	-9.76721412103352	2.01658806183480
C	-11.62162319934454	-9.72012758036433	1.41597366715775
Pd	-8.79660748019214	-9.31248442282177	0.52474140524596
C	-12.56565507467674	-8.65211446326405	1.92656100751909
O	-12.00037452223339	-10.52348835852760	0.54286213469112
H	-13.52223005639107	-8.69188822531921	1.37452174350520
H	-10.66381067185448	-12.53039924646109	1.34547172912218
H	-12.10932894432239	-7.64537366605183	1.82256118571934
C	-6.79094546167256	-7.43161472072822	-0.32702073009573
C	-7.50351627073929	-8.30009428896597	3.13476508077356
C	-6.60673699041916	-7.51070623576707	3.87989930883908
C	-5.77284061532094	-6.59888408296474	3.21990785319705
C	-5.82498895461218	-6.53363294492642	1.81786086844734
C	-6.72651175519804	-7.36156751622860	1.12890351665616
N	-7.58411711984914	-8.20625698720230	1.79254400965567
H	-8.14489293654177	-9.06952805613726	3.60690869882527
H	-6.57800162368319	-7.62633681112322	4.97300773552297
H	-5.07605272377645	-5.96026067409153	3.78292431199641
N	-7.56349700520910	-8.32415840079145	-0.87408423511143
H	-6.18393512535104	-6.74139197777406	-0.94297470649488
H	-5.16358182854962	-5.86031174898218	1.25292858953832
C	-7.66708409669752	-8.41312661458064	-2.30270333569792

C	-8.72774826035154	-7.72058320074918	-2.94772202986243
C	-8.83076103383858	-7.84934642792453	-4.34785551048639
C	-7.91462901637111	-8.62546928767616	-5.07353972618511
C	-6.87842394843950	-9.29667454874338	-4.40831818976059
C	-6.73232464066405	-9.21499137264412	-3.00895994417165
C	-9.67757809239784	-6.83571014193648	-2.17278978712225
H	-9.63993944040803	-7.31784610307988	-4.87270881724471
H	-8.00935632810804	-8.70680370210440	-6.16680343340880
H	-6.16244774255062	-9.90726587611154	-4.98002579159077
C	-5.62510707901379	-9.94839026846053	-2.29089362560888
H	-9.18542997815468	-5.89162525247117	-1.85314856917353
H	-10.04566721021835	-7.32253370121418	-1.24329558144555
H	-10.55266342900776	-6.55454946937128	-2.78867141015522
H	-6.02114768263705	-10.57550128828927	-1.46461418299123
H	-4.88449205262876	-9.25196105766231	-1.84305359740143
H	-5.07483003252121	-10.60836770615519	-2.98684022570624
N	-9.76864901526290	-10.51141410565108	-0.87607077167098
H	-10.05986098140917	-9.90977782832029	-1.66376629874091
H	-10.67234607871303	-10.79651436849349	-0.38071637162684
C	-9.02316992250685	-11.64137700741143	-1.40020779198503
C	-9.04210313907202	-11.90879312301217	-2.78250342781534
C	-8.36199708550709	-13.02892694799512	-3.28693926061716
C	-7.65656551570944	-13.87940196416896	-2.41927740064038
C	-7.62783386204336	-13.60187613342591	-1.04120096886059
C	-8.30484943210401	-12.48417950457849	-0.52893487636708
H	-9.59970328031621	-11.24769685079765	-3.46472117574598
H	-8.38878311983677	-13.23754104453345	-4.36703857569437
H	-7.12692649305242	-14.75815233531375	-2.81655902283563
H	-7.07094631459144	-14.25875795946120	-0.35614909393416
H	-8.26784664672541	-12.25848059364759	0.54711629281879

B′

59
Coordinates from ORCA-job 4trans_amid_acacH_PyPhMe2

H	-10.93569650366522	-12.49247317826752	4.10380849702901
H	-13.22372527465241	-7.74261624069394	2.15256814253700
H	-9.61030690230780	-12.83682200885632	2.97203503417985
C	-10.20829395166905	-12.01477586846355	3.41391093289646
C	-10.95738308909755	-11.29920948794593	2.33357280345723
O	-11.65761345250975	-12.02288093848121	1.53293351413395
H	-10.62104726111447	-9.27970482817072	3.04229888849595
C	-10.93628202410513	-9.86544506347607	2.16664677195964
C	-12.00071894180941	-9.28874869412879	1.33084287551591
Pd	-9.18589926643213	-9.49896879576611	0.77829397985970
C	-12.36842051164229	-7.83282758029589	1.44746826658754
O	-12.64180383225053	-10.03552185565876	0.54001690135794
H	-12.71673852602794	-7.44862158125162	0.47001730166622
H	-9.55001755523320	-11.34170390937420	3.99084655809761
H	-11.53795054816329	-7.21279591860812	1.83369646664052
C	-6.80179952022759	-8.01482360916681	0.15034748106255
C	-8.16365851223649	-8.23867161020794	3.50979470292837
C	-7.25497635318934	-7.52629786961846	4.30767001039870
C	-6.12155763120264	-6.95340501882214	3.70765947313585
C	-5.94457210825689	-7.11522959502734	2.32805545104075
C	-6.89826565392820	-7.84426472367621	1.58965392125298
N	-8.00351329873839	-8.40882388409102	2.18173708812028
H	-9.05261771548244	-8.69947684076631	3.96536377221419
H	-7.44007598304484	-7.43346358492138	5.38745678201359
H	-5.38977426230038	-6.39046301780599	4.30558404173962
N	-7.74206127376878	-8.66160097335813	-0.48630994837633
H	-5.96335426290958	-7.55101348495215	-0.39971459402506
H	-5.07588060067024	-6.68229365842925	1.81052220103548
C	-7.66888963307017	-8.79177695760494	-1.90872538681264

C	-8.68411100194497	-8.16580000655081	-2.68750115967936
C	-8.61208785833155	-8.29652218983920	-4.08612839933472
C	-7.57993151223314	-9.02711043668240	-4.69379203143888
C	-6.59444756495262	-9.63556358790358	-3.90632743997356
C	-6.60548241731548	-9.52970572483427	-2.50073815390809
C	-9.75778725505379	-7.31906578250670	-2.04926251078394
H	-9.37793663651566	-7.80508651047188	-4.70633460457379
H	-7.54523644260824	-9.12317732628943	-5.78945425320827
H	-5.79243701287720	-10.21786513289017	-4.38587769608498
C	-5.51382829357588	-10.19340109924387	-1.69171381312054
H	-9.33729739434778	-6.37931101033499	-1.63040188208067
H	-10.25246050356038	-7.84113614684567	-1.20184120696380
H	-10.53151315474404	-7.03655677079367	-2.78784515474015
H	-5.87152166525516	-10.54591233603895	-0.70508538907021
H	-4.65519498960777	-9.50935955705180	-1.51748099014221
H	-5.11622392380846	-11.07193153871566	-2.23470581808042
N	-10.06246328393776	-10.72896246828071	-0.54253964322143
H	-10.78199746337074	-10.25137050493752	-1.10573920738952
H	-12.17723317839077	-11.30263384226517	0.89590582131488
C	-9.31194475833608	-11.58811234366170	-1.31967233295915
C	-9.61005060520794	-11.80917350757271	-2.69780001535225
C	-8.91887195394741	-12.77852507719103	-3.43062624386032
C	-7.88667243810524	-13.52782341140694	-2.83167528471985
C	-7.56231932578487	-13.30521521456987	-1.47827595679976
C	-8.26848022371931	-12.36113846499160	-0.72683722443065
H	-10.40830472101652	-11.21882562902141	-3.17436576483537
H	-9.17995528490164	-12.94839968030535	-4.48657653558398
H	-7.34628273082842	-14.28942782796839	-3.41334310266416
H	-6.76604321227510	-13.89683302437330	-1.00065920392422
H	-8.05116574373918	-12.21878906857380	0.34416926746653

C′

58
Coordinates from ORCA-job amid_PA_PyPhMe2

Pd	-8.68025862198146	-9.87297786149627	0.72622775805760
C	-6.46900283094648	-8.33296904037019	-0.30685964567979
C	-7.17373370070426	-8.79767405494165	3.22698843886205
C	-6.12807988515295	-8.13397344586901	3.88592594892259
C	-5.12244254532409	-7.51057291150712	3.12659210037254
C	-5.20306465125398	-7.56968544912572	1.72971424487327
C	-6.27977425361578	-8.25339676568575	1.13040224502743
N	-7.25409581261131	-8.86685956525537	1.88134881091074
H	-7.97712148842330	-9.29907925333044	3.78740335356551
H	-6.10654876619171	-8.11829264693917	4.98512057309917
H	-4.28910084504763	-6.98698911848893	3.61782142519514
N	-7.51398502094042	-8.96256674298822	-0.78039517750881
H	-5.76185753738518	-7.81905717409664	-0.98247396119653
H	-4.44262170024451	-7.09261215121643	1.09398452399589
C	-7.73132148223639	-9.00059572762987	-2.19274991617336
C	-8.89733341915581	-8.36009726719416	-2.70299284980346
C	-9.10959576050317	-8.39348067670050	-4.09281488840342
C	-8.21271500269294	-9.05034407339801	-4.94844046331715
C	-7.07663382236492	-9.67901534006492	-4.42320662087716
C	-6.80055645325496	-9.66449794762251	-3.04116461900197
C	-9.84525372007867	-7.61197089869064	-1.79867905503169
H	-9.99535582576037	-7.88737688618155	-4.50738289875896
H	-8.40189845996198	-9.07251741688457	-6.03222369593059
H	-6.37900239181113	-10.20134973740882	-5.09618947885623
C	-5.55106481609542	-10.33978154028436	-2.52145643179328
H	-9.35172595490162	-6.74260254169578	-1.31426727349397
H	-10.22264374860062	-8.25351179390032	-0.97314842476904
H	-10.71387793281868	-7.22914852326242	-2.36689644898216
H	-5.68316812107409	-10.75911686729077	-1.50520464729132

H	-4.68928125602339	-9.63895403571340	-2.48384972733475
H	-5.25410719300986	-11.16897468499187	-3.19199714510622
N	-9.86018160227738	-11.07336113618248	-0.33744358812369
H	-10.82912897151869	-10.73271631703398	-0.40785369943656
C	-9.47625881786497	-11.77806722169152	-1.45318731144466
C	-10.32561549056176	-11.90298758755313	-2.59593277344045
C	-9.95672478972787	-12.71411193192053	-3.67143608398811
C	-8.72703597490582	-13.40363441007155	-3.65847693312580
C	-7.87187203152213	-13.28261081634260	-2.54465978117463
C	-8.23834092989667	-12.49170376605964	-1.45292919851547
H	-11.28212553571093	-11.35652703804496	-2.61498541501183
H	-10.63012224582506	-12.80856304074125	-4.53710122589244
H	-8.44410042856809	-14.04455932639238	-4.50677456791188
H	-6.92250401715172	-13.83957739810880	-2.51941835036172
H	-7.60535701225358	-12.44131804304343	-0.55300675031416
C	-10.64641401281843	-9.58446581253810	2.44952425289872
C	-9.80013290361222	-10.52449079333892	2.38509571346394
H	-9.51488166217215	-11.47306954877175	2.85317757190865
C	-11.60452796211326	-8.54575500548248	2.50476662460078
C	-11.32986464755492	-7.33058579040404	3.20133141854988
C	-12.29980436890604	-6.32702123527577	3.27084020861489
C	-13.55568549861252	-6.51076926762789	2.65947780795689
C	-13.84328259555211	-7.70710281382096	1.97404356879946
C	-12.88225312959858	-8.71858623724814	1.89086231391149
H	-10.35097005092570	-7.19505481856718	3.68385517957322
H	-12.08250161234243	-5.39319908579629	3.81084833044565
H	-14.31706189670989	-5.71851088568250	2.72253019911794
H	-14.82883643962933	-7.85047374651601	1.50612227737139
H	-13.10522335149866	-9.66063578551609	1.36843715795651

D′

58
Coordinates from ORCA-job hydroamid_PyPhMe2

Pd	-8.71717757869961	-9.15094497619316	-0.21917778695346
C	-6.14584153454328	-7.78569265656709	-0.25082532673360
C	-7.86989375392369	-9.02298363688575	2.71635487537730
C	-7.04167489662853	-8.64631038380841	3.78547828553105
C	-5.84956534241426	-7.95377522437821	3.52073149091716
C	-5.52486629509965	-7.65335587101184	2.19078137138884
C	-6.39426784597920	-8.05797257198158	1.15992599897718
N	-7.55286835857585	-8.74409968236924	1.43427869575080
H	-8.81450736813689	-9.55877147663101	2.88161703870648
H	-7.33995223156880	-8.90259410075609	4.81211235282407
H	-5.18261978867032	-7.64882859999217	4.34067929761229
N	-7.06390448810425	-8.12404567511581	-1.11342714702260
H	-5.20577646895691	-7.29048426796973	-0.55481594332524
H	-4.60531394870486	-7.10506445796394	1.93808059702043
C	-6.86226641355908	-8.01103293803403	-2.51416326395514
C	-7.86378627916919	-7.33101124225421	-3.27263529049906
C	-7.68972060409377	-7.23372590120368	-4.66305048344755
C	-6.57973821775164	-7.81415836356807	-5.29636492004331
C	-5.62306808119194	-8.50474726202334	-4.54063407558867
C	-5.72944867574631	-8.61730919280437	-3.14017348763168
C	-9.04681284032683	-6.68041976145048	-2.60015281478277
H	-8.44281780906201	-6.69425882983761	-5.25793171797680
H	-6.46722087453132	-7.73859458610950	-6.38837685513074
H	-4.77004323404632	-8.98376123401914	-5.04594753685092
C	-4.68618444298786	-9.41263392027093	-2.38476268900354
H	-8.73997663511838	-5.81952947623530	-1.96906756045361
H	-9.57363416724087	-7.39449502917223	-1.92460479830515
H	-9.77662776807967	-6.31338512361751	-3.34583995104814
H	-5.10335117578399	-9.93829963331263	-1.50282613560939

H	-3.84973177748012	-8.77543067429936	-2.02631119869738
H	-4.23679153059463	-10.17669016496041	-3.04795405755054
N	-12.49429124936647	-10.87445244027293	0.95730293230735
H	-13.41151500924723	-10.42576497374946	1.05348827052502
C	-12.54810268158630	-12.24855362344970	0.62527999900859
C	-13.69352044208950	-12.73527556725704	-0.04446827274181
C	-13.81431646111606	-14.10219591588648	-0.33475611298467
C	-12.79422069220113	-14.99662658673544	0.02889144305899
C	-11.65676877363195	-14.51420759127089	0.70291120285736
C	-11.52967455417187	-13.15254655696614	1.00783167444149
H	-14.48898732790278	-12.03414582954706	-0.34349085706442
H	-14.71211674544345	-14.46761945405443	-0.85575453006358
H	-12.88709304788764	-16.06789001448695	-0.20327886811397
H	-10.86364686397065	-15.21201388253707	1.01212008897885
H	-10.65540195380044	-12.79233702006699	1.56863383779498
C	-11.42396201012295	-9.99045731136962	0.95272119142219
C	-10.24519007756202	-10.23885284188214	0.25656634679029
H	-10.05778466676765	-11.27978779401365	-0.08147103539767
C	-11.66433473014437	-8.74485451093075	1.72858458068414
C	-12.36138302654817	-8.81049186970307	2.96275264437593
C	-12.58698536252843	-7.65203642804361	3.72036422667654
C	-12.12502715490240	-6.40613663193654	3.25989738181663
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E′

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72
Coordinates from ORCA-job An_hydroamid_PyPhMe2
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F′

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Coordinates from ORCA-job Amid_hydroamid_PyPhMe2

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