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Supporting Information

For

Symmetrical Non-Chelating Poly-*N*-Heterocyclic Carbenes

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General information:

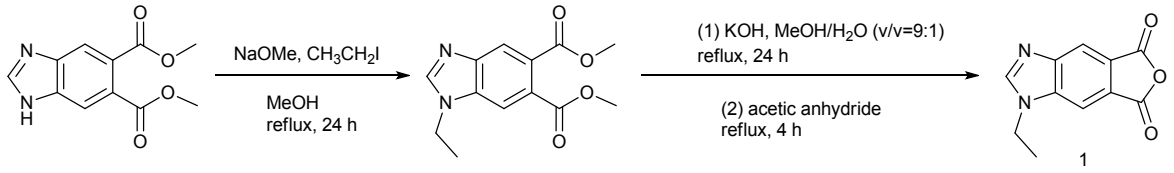
Air and moisture sensitive reactions were carried out under an atmosphere of N2 using standard Schlenk techniques or inside the glovebox. Dichloromethane was dried via passing through the molecular sieves packed drying column under nitrogen. THF was dried using Na/K alloy, and distilled under inert atmosphere. 1,3,5-tri (4-aminophenyl) benzene[1] and tetra-(4-aminophenyl) methane[2] were synthesized according to published procedures. ^{1}H and ^{13}C NMR spectra were recorded using Bruker Avance III 400 MHz NMR and Bruker AVIII 500MHz FT-NMR. The ^{1}H and ^{13}C NMR spectra reported in ppm (δ) are relative to the chemical shift of solvent residual signals for CDCl3 at 7.26 and 77.00 ppm, DMSO-d6 at 2.50 and 39.52 ppm, The elemental analysis was recorded on Thermo Flash 2000. The ESI MASS was recorded on Bruker micrOTOF-QII.

X-ray Crystallography:

Diffraction data of [**2a**][I]$_2$ and [**2a**-(NiCpI)$_2$] were collected at T = 150(2) K with a NONIUS KappaCCD diffractometer and [**5**][I] was collected at T = 150(2) K with a BRUKER SMART APEXCCD area detector diffractometer. Both of the diffractometers were equipped with a rotation anode using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. Cell parameters were retrieved and refined using DENZO-SMN for [**2a**][I]$_2$ and [**2a**-(NiCpI)$_2$] and Bruker SAINT software for [**5**][I] on all reflections. Data reduction was performed with DENZO-SMN ([**2a**][I]$_2$ and [**2a**-(NiCpI)$_2$]) and Bruker SAINT software ([**5**][I]). Structural analysis was conducted using the SHELXTL program on a personal computer. All the structures were solved and refined using the SHELXL-97 program by full-matrix least-squares on F^2 values. Hydrogen atoms were added to the structure models in calculated positions. Crystallographic data have been deposited at the Cambridge Crystallographic Data Center with deposition number CCDC-1020160, CCDC-1020161, and CCDC-1020162, for [**2a**][I]$_2$, [**2a**-(NiCpI)$_2$], and [**5**][I], respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

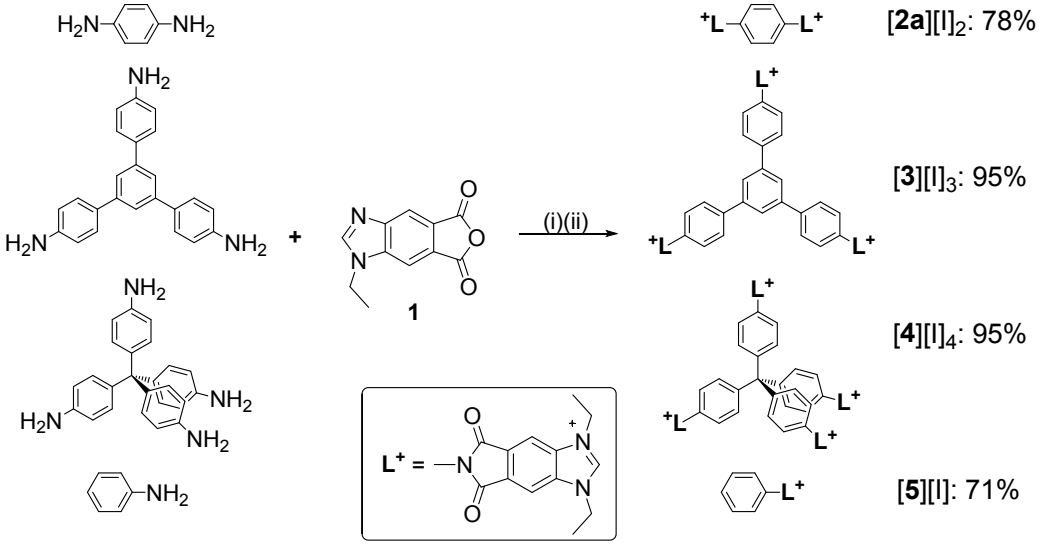
Syntheses:

***N*-alkyl-benzimidazole-5,6-dicarboxylic anhydride (1).**



Sodium (0.35 g, 15.3 mmol) was dissolved in 85 mL anhydrous MeOH under nitrogen atmosphere in iced bath. Dimethyl 5,6-benzimidazoledicarboxylate[3] (3 g, 12.8 mmol) was added into the solution, and the reaction mixture was allowed to stir for 30 min at room temperature. Ethyl iodide 4 mL (8 g, 51.2 mmol) was then added to give a light yellow solution. The mixture was stirred at room temperature for 18 h, and then refluxed for another 5 h. The light yellow solution was concentrated under reduced pressure to give light yellow oil. After purification with silica gel column chromatography ($MeOH/CH_2Cl_2$ = 3:97), dimethyl *N*-ethyl-5,6-benzimidazolate was obtained as pale yellow solid (2.53 g, yield 73%). The *N*-ethyl derivative (3 g, 12.1 mmol) was then dissolved in a mixture of 100 mL $MeOH/H_2O$ (v/v = 9:1), and then KOH (2.04 g, 36.3 mmol) was added. After addition, the light yellow solution was refluxed for 18 h. After cooling to room temperature and concentrated under reduced pressure, the resulting yellow oil was acidified with 5 mL 12 M HCl aqueous solution. The whole mixture was brought to dryness under vacuum, and then was mixed with 20 mL of acetic anhydride. After refluxing for 3 h, the resulting heterogeneous solution was filtered while the solution was warm. The collected filtrate was mixed with 30 mL of diethyl ether to yield light yellow precipitates. The solid was collected by filtration and washed with diethyl ether (10 mL x 2) to give compound **1** as light yellow solid (2.23 g, yield 91%). ^{1}H NMR (DMSO-d^6, 400 MHz):δ 8.76 (s, 1H, CH), 8.50 (s, 1H, Ar-H), 8.31 (s, 1H, Ar-H), 4.47 (q, J = 7.3 Hz, 2H, NCH_2), 1.45 (t, J = 7.3 Hz, 3H, NCH_2CH_3) ppm. ^{13}C NMR (d^6-DMSO, 100 MHz):δ 163.7, 149.5, 148.4, 138.6, 124.6, 124.1, 227.4, 109.5, 40.1, 15.3 ppm. HRMS (ESI-TOF) calcd for $C_{11}H_9N_2O_3$ $[M+H]^+$ 217.0608, found: 217.0605.

General Synthetic Procedure for Poly-benzimidazolium salts.



Compound **1** (208 mg for [**2a**]I_2, 312 mg for [**3**]I_3, 416 mg for [**4**]I_4, and 104 mg for [**5**]I) and 0.4 mmol of polyamine were dissolved in 20 mL of CH_3CN/DMF (v/v = 1:1). The solution was refluxed for 18 h to yield pale yellow precipitates. The precipitates were collected and refluxed in 30 mL DMF in the presence of ethyl iodide(1.28 mL for [**2a**]I_2, 1.92 mL for [**3**]I_3, 2.56 mL for [**4**]I_4, and 0.64 mL for [**5**]I). After refluxing for 18 h, the mixture turned from opaque to clear yellow solution. The solution was then cooled to room temperature, and mixed with 30 mL of diethyl ether to yield yellow precipitates. The solid was collected and washed with diethyl ether (5 mL x 2) to give product as yellow solid.

[**2a**][I]$_2$. Yellow solid (255 mg, yield: 78 %). M.p.: > 290 ^oC. ^1H NMR (DMSO-d_6, 400 MHz): δ 10.07 (s, 2H, CH), 8.88 (s, 4H, Ar-H), 7.72 (s, 4H, Ar-H), 4.67 (q, J = 7.2 Hz, 8H, NCH_2), 1.59 (t, J = 7.2 Hz, 12H, NCH_2CH_3) ppm.^{13}C NMR (DMSO-d_6, 100 MHz): δ 165.8, 145.5, 134.7, 131.4, 129.3, 127.9, 110.7, 42.9, 14.3 ppm. HRMS (ESI-TOF) calcd for $C_{32}H_{30}N_6O_4$ $[M\text{-}2I^-]^{2+}$ 281.1159, found: 281.1148.

[**2b**][I]$_2$. Yellow solid (39 mg, yield: 12%). M.p.: 167 ^oC (dec). ^1H NMR (DMSO-d_6, 400 MHz): δ 10.02 (s, 2H, CH), 8.74 (S, 4F, Ar-H), 7.74 (m, 4H, Ar-H), 4.56 (q, J = 7.2 Hz, 8H, NCH_2), 1.52 (t, J = 7.2 Hz, 12H, NCH_2CH_3) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ 165.3, 146.2, 135.3, 130.3, 130.1, 129.2, 129.1, 111.3, 43.3, 14.7 ppm. HRMS (ESI-TOF) calcd for $C_{32}H_{30}N_6O_4I$ $[M\text{-}I^-]^{1+}$ 689.1368, found: 689.1357; calcd for $C_{32}H_{30}N_6O_4$ $[M\text{-}2I^-]^{2+}$ 281.1159, found: 281.1163.

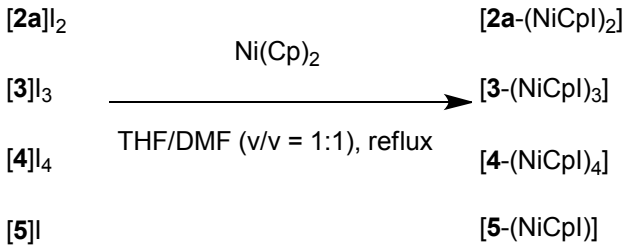
[**3**][I]$_3$. Yellow solid (536 mg, yield: 95%). M.p.: 250 ^oC (dec). ^1H NMR (DMSO-d_6, 400 MHz): δ 10.07 (s, 3H, CH), 8.87 (s, 6H, Ar-H), 8.14 (d, J = 8.5 Hz, 6H, Ar-H),

8.13 (s, 3H, Ar-H), 7.69 (d, J = 8.5 Hz, 6H, Ar-H), 4.68 (q, J = 7.2 Hz, 12H, NCH_2), 1.60 (t, J = 7.2 Hz, 18 H, NCH_2CH_3) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ 166.4, 145.9, 141.5, 140.3, 135.2, 131.9, 129.9, 128.3, 128.2, 125.6, 111.1, 43.4, 14.8 ppm. HRMS (ESI-TOF) calcd for $C_{63}H_{54}N_9O_6$ $[M\text{-}3I^-]^{3+}$ 344.1394, found: 344.1394.

[**4**][I]$_4$. Yellow solid (682 mg, yield: 95%). M.p.: 264 ^oC (dec). ^1H NMR (DMSO-d_6, 400 MHz): δ 10.05 (s, 4H, CH), 8.84 (s, 8H, Ar-H), 7.57 (m, 16H, Ar-H), 4.66 (q, J = 7.2 Hz,16H, NCH_2), 1.58 (t, J = 7.2 Hz, 24H, NCH_2CH_3) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ 166.3, 146.3, 146.0, 135.3, 131.2, 130.3, 129.7, 127.2, 111.1, 43.4, 14.8 ppm; HRMS (ESI-TOF) calcd for $C_{77}H_{68}N_{12}O_8I_2$ $[M\text{-}2I^-]^{2+}$ 771.1681, found: 771.1659; calcd for $C_{77}H_{68}N_{12}O_8I$ $[M\text{-}3I^-]^{3+}$ 471.8104, found: 471.8111; calcd for $C_{77}H_{68}N_{12}O_8$ $[M\text{-}4I^-]^{4+}$ 322.1315, found: 322.1319; Anal. Calcd. for $C_{77}H_{68}N_{12}O_8I_4 \cdot H_2O$: C, 50.95; H, 3.89; N, 9.26%, found: C, 50.14; H, 4.22; N, 8.96%.

[**5**][I]. Yellow solid (127 mg, yield: 71 %). ^1H NMR (DMSO-d_6, 400 MHz): δ 10.05 (s, 1H, CH), 8.84 (s, 2H, Ar-H), 7.58 (m, 2H, Ar-H), 7.51 (m, 3H, Ar-H), 4.67 (q, J = 7.2 Hz, 4H, NCH_2), 1.59 (t, J = 7.2 Hz, 6H, NCH_2CH_3) ppm.^{13}C NMR (DMSO-d_6, 100 MHz): δ 165.8, 145.4, 134.6, 131.7, 129.3, 128.9, 128.8, 128.3, 127.2 42.9, 14.3 ppm. HRMS (ESI-TOF) calcd for $C_{19}H_{18}N_3O_2$ $[M\text{-}I^-]^+$ 320.1394, found: 320.1401; Anal. Calcd. for $C_{19}H_{18}N_3O_2I \cdot H_2O$: C, 49.05; H, 4.33; N, 9.03%, found: C, 49.91; H, 4.11; N, 9.26%.

General Synthetic Procedure for Poly-nuclear Ni-NHC complexes.



0.07 mmol of poly-benzimidazolium salt and $NiCp_2$ (29 mg for [**2a**-$(NiCpI)_2$], 44 mg for [**3**-$(NiCpI)_3$], 58 mg for [**4**-$(NiCpI)_4$], and 15 mg for [**5**-(NiCpI)]) were dissolved in 10 mL of anhydrous THF/DMF (v/v = 1:1). The reaction mixture was refluxed for two days under N_2 to yield a dark red solution. After reaction, 20 mL of diethyl ether and 10 mL of hexane were added to the solution to yield dark red precipitates. The solid was collected and washed with hexane (5 mL) and diethyl ether (5 mL x 2). The nickel complex was further purified by re-precipitation of product from CH_2Cl_2 solution with diethyl ether, and dried under vacuum.

[**2a**-$(NiCpI)_2$]. Crimson solid (44 mg, yield: 59%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90 (s, 4H, Ar-H), 7.67 (s, 4H, Ar-H), 5.48 (s, 10H, Cp), 5.29 (m, 4H, NCH_2), 5.08 (m, 4H, NCH_2), 1.69 (t, J = 7.2 Hz, 12H, NCH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.7, 166.4, 138.8, 131.2, 126.9, 126.3, 105.8, 92.7, 46.0, 14.7 ppm. HRMS (ESI-TOF) calcd for $C_{42}H_{38}N_6O_4Ni_2I$ $[M\text{-}I^-]^{1+}$ 933.0701, found: 933.0685; calcd for $C_{42}H_{38}N_6O_4Ni_2$ $[M\text{-}2I^-]^{2+}$ 403.0825, found: 403.0829; Anal. Calcd. for $C_{42}H_{38}N_6O_4Ni_2I_2$: C, 47.50; H, 3.61; N, 7.91%, found: C, 46.69; H, 3.64; N, 7.43%.

[**3**-$(NiCpI)_3$]. Crimson solid (50 mg, yield: 40%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (m, 15H, Ar-H), 7.62 (d, *J = 7.2 Hz*, 6H, Ar-H), 5.48 (s, 15H, Cp), 5.30 (m, 6H, NCH_2), 5.04 (m, 6H, NCH_2), 1.67 (m, 18H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.5, 166.7, 141.5, 140.6, 138.8, 131.2, 128.1, 126.9, 126.4, 125.4, 105.7, 92.6, 46.0, 14.7 ppm. HRMS (ESI-TOF) calcd for $C_{78}H_{66}N_9O_6Ni_3I$ $[M\text{-}2I^-]^{2+}$ 762.6115, found: 762.6084; calcd for $C_{78}H_{66}N_9O_6Ni_3$ $[M\text{-}3I^-]^{3+}$ 466.1060, found: 466.1077; Anal. Calcd. for $C_{78}H_{66}N_9O_6Ni_3I_3$: C, 52.57; H, 3.73; N, 7.07%, found: C, 52.68; H, 4.06; N, 7.19%

[**4**-$(NiCpI)_4$]. Crimson solid (125 mg, yield: 78%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (s, 8H, Ar-H), 7.47 (m, 24H, Ar-H), 5.46 (s, 20H, Cp), 5.27 (m, 8H, NCH_2), 5.06 (m, 8H, NCH_2), 1.67 (s, 24H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.6, 191.4, 166.6, 138.8, 131.7, 126.4, 125.4, 105.7, 92.6, 46.0, 14.7 ppm. HRMS (ESI-TOF) calcd for $C_{97}H_{84}N_{12}O_8Ni_4I_2$ $[M\text{-}2I^-]^{2+}$ 1015.1014, found: 1015.1027; calcd for $C_{97}H_{84}N_{12}O_8Ni_4I$ $[M\text{-}3I^-]^{3+}$ 634.4326, found: 634.4326; calcd for $C_{97}H_{84}N_{12}O_8Ni_4$ $[M\text{-}4I^-]^{4+}$ 444.0982, found: 444.0973; Anal. Calcd. for $C_{97}H_{84}N_{12}O_8Ni_4I_4$: C, 50.92; H, 3.70; N, 7.35%, found: C, 50.36; H, 3.90; N, 6.75%.

[**5**-(NiCpI)]. Crimson solid (20 mg, yield: 52%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (s, 2H, Ar-H), 7.49 (m, 2H, Ar-H), 7.42 (m, 3H, Ar-H), 5.44 (s, 5H, Cp), 5.24 (m, 2H, NCH_2), 5.03 (m, 2H, NCH_2), 1.65 (t, J = 7.2 Hz, 6H, NCH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.4, 166.7, 138.7, 131.6, 129.2, 128.3, 126.5, 105.7, 92.6, 45.9, 14.7 ppm. HRMS (ESI-TOF) calcd for $C_{24}H_{22}N_3O_2Ni$ $[M\text{-}I^-]^+$ 442.1060, found: 442.1068; Anal. Calcd. for $C_{24}H_{22}N_3O_2NiI \bullet C_4H_{10}O$: C, 52.21; H, 5.01; N, 6.52%, found: C, 52.52; H, 4.34; N, 6.68%

General Synthetic Procedure for Poly-nuclear Rh-NHC complexes. 0.04 mol of Poly-benzimidazolium salt and K^{t}OBu (8.8 mg for [**2a**-$[Rh(COD)I]_2$], 13 mg for [**3**-

[Rh(COD)I]$_3$], and 18 mg for [**4**-[Rh(COD)I]$_4$]) were dissolved in 10 mL of anhydrous THF/DMF (v/v = 3:2). After stirring for 1 h at room temperature, [Rh(COD)Cl]$_2$ (22 mg for [**2a**-[Rh(COD)I]$_2$], 33 mg for [**3**-[Rh(COD)I]$_3$], and 44 mg for [**4**-[Rh(COD)I]$_4$]) was added and stirred for 18 h at room temperature to yield a yellow solution. After reaction, the insoluble solids were filtered off, and 20 mL of diethyl ether was added to the filtrate to give yellow precipitates. The precipitates were then collected and washed with diethyl ether (2 mL x 2) and hexane (2 mL).

[**2a**-[Rh(COD)I]$_2$]. Yellow brown solid (7 mg, yield: 15%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (s, 4H, Ar-H), 7.66 (s, 4H, Ar-H), 5.44 (s, 4H, COD), 5.14 (q, *J* = 7.2 Hz, 4H, NCH_2), 4.84 (q, *J = 7.2 Hz,* 4H, NCH_2), 3.55 (s, 4H, COD), 2.41 (m, 8H, COD), 2.09 (m, 4H, COD), 1.92 (m, 4H, COD), 1.70 (t, *J = 7.2 Hz,* 12H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 204.3, 204.1, 166.6, 138.5, 131.2, 126.9, 126.0, 105.7, 105.5, 105.2, 99.6, 99.5, 73.0, 72.9, 44.4, 32.2, 29.4, 14.4 ppm. HRMS (ESI-TOF) calcd for $C_{48}H_{52}N_6O_4Rh_2$ $[M\text{-}2I^-]^{2+}$ 491.1075, found: 491.1085

[**3**-[Rh(COD)I]$_3$]. Yellow brown solid (11 mg, yield: 13%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (m, 15H, Ar-H), 7.62 (d, 6H, *J* = 8.4 Hz, Ar-H), 5.45 (s, 6H, COD), 5.14 (m, 6H, NCH_2), 4.85 (m, 6H, NCH_2), 3.56 (s, 6H, COD), 2.42 (m, 12H, COD), 2.09 (m, 6H, COD), 1.92 (m, 6H, COD), 1.70 (t, *J* = 7.2 Hz, 18H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 203.9, 166.9, 141.6, 140.7, 138.5, 131.3, 128.1, 128.0, 126.9, 126.2, 125.5, 105.6, 99.6, 73.0, 72.9, 44.4, 32.2, 29.4, 28.0, 14.4 ppm. HRMS (ESI-TOF) calcd for $C_{87}H_{87}N_9O_6Rh_3I$ $[M\text{-}2I^-]^{2+}$ 894.6489, found: 894.6455; calcd for $C_{87}H_{88}N_9O_6Rh_3$ $[M\text{-}3I^-]^{3+}$ 554.1309, found: 554.1322.

[**4**-[Rh(COD)I]$_4$]. Light brown solid (17 mg, yield: 16%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84 (s, 8H, Ar-H), 7.48 (m, 16H, Ar-H), 5.43 (s, 8H, COD), 5.13 (q, *J* = 7.2 Hz, 8H, NCH_2), 4.83 (q, *J* = 7.2 Hz, 8H, NCH_2), 3.54 (s, 8H, COD), 2.41 (m, 16H, COD), 2.06 (m, 8H, COD), 1.91 (m, 8H, COD), 1.69 (t, *J* = 7.2 Hz, 24H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 204.2, 203.8, 166.7, 145.4, 138.5, 131.7, 130.1, 128.7, 126.2, 125.4, 105.6, 99.5, 99.4, 73.0, 72.9, 65.8, 64.4, 44.4, 32.2, 29.4, 14.4 ppm. HRMS (ESI-TOF) calcd for $C_{109}H_{112}N_{12}O_8Rh_4I_2$ $[M\text{-}2I^-]^{2+}$ 1191.1512, found: 1191.1505; calcd for $C_{109}H_{112}N_{12}O_8Rh_4I$ $[M\text{-}3I^-]^{3+}$ 751.7991, found: 751.8009; Anal. Calcd. for $C_{109}H_{112}N_{12}O_8Rh_4I_4$: C, 49.64; H, 4.28; N, 6.37%, found: C, 48.91; H, 4.55; N, 6.40%.

Hydrothiolation of 1-Heptyne. A stock solution containing thiophenol (8.95 mmole), 1-heptyne (3.60 mmole), and triethylamine (0.215 mmole) in 4 mL of $CDCl_3$ was

prepared in a glove box. To the stock solution 8.95 mmole of naphthalene was added as internal standard. Then, 0.8 mL of the resulting solution was added to Young's NMR tube loaded with catalysts consisting of 3 mol% of Ni atom (12.2 mg of [**5**-(NiCpI)], 11.4 mg of [**2a**-$(NiCpI)_2$], 12.8 mg of [**3**-$(NiCpI)_3$], or 12.2 mg of [**4**-$(NiCpI)_4$]). The solution was heated at 60 ^oC and was monitored with NMR spectroscopy. Product yield was calculated based on the integration of the multiplets centered at 8.61 ppm (naphthalene) and the terminal alkene $C=CH_2$ detected at 5.43 and 5.22 ppm.

Reaction time (h)	Yield of alkene (%)			
	[**5**-(NiCpI)]	[**2a**-$(NiCpI)_2$]	[**3**-$(NiCpI)_3$]	[**4**-$(NiCpI)_4$]
4	3	7	6	8
8	11	13	13	17
12	26	22	23	30
16	50	38	38	41
24	58	54	52	61
36	68	77	76	72

References:

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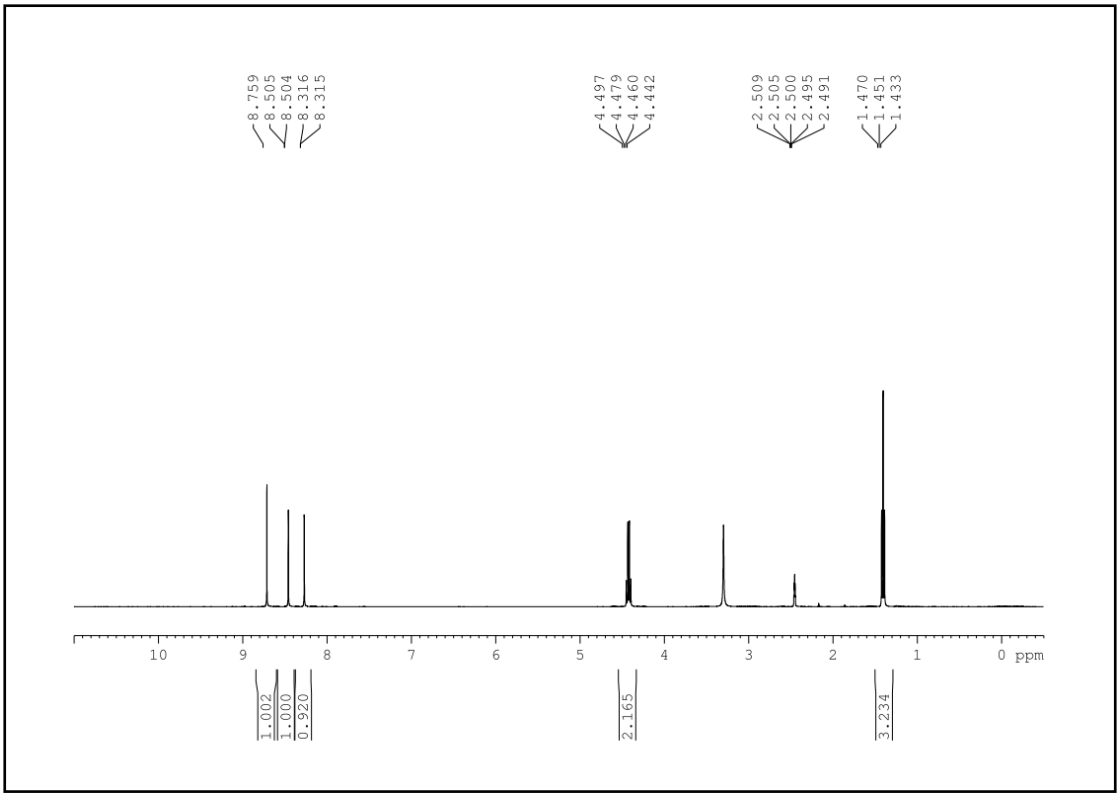


Figure S1 ^{1}H NMR spectrum of compound **1** (400 MHz, DMSO-d_6)

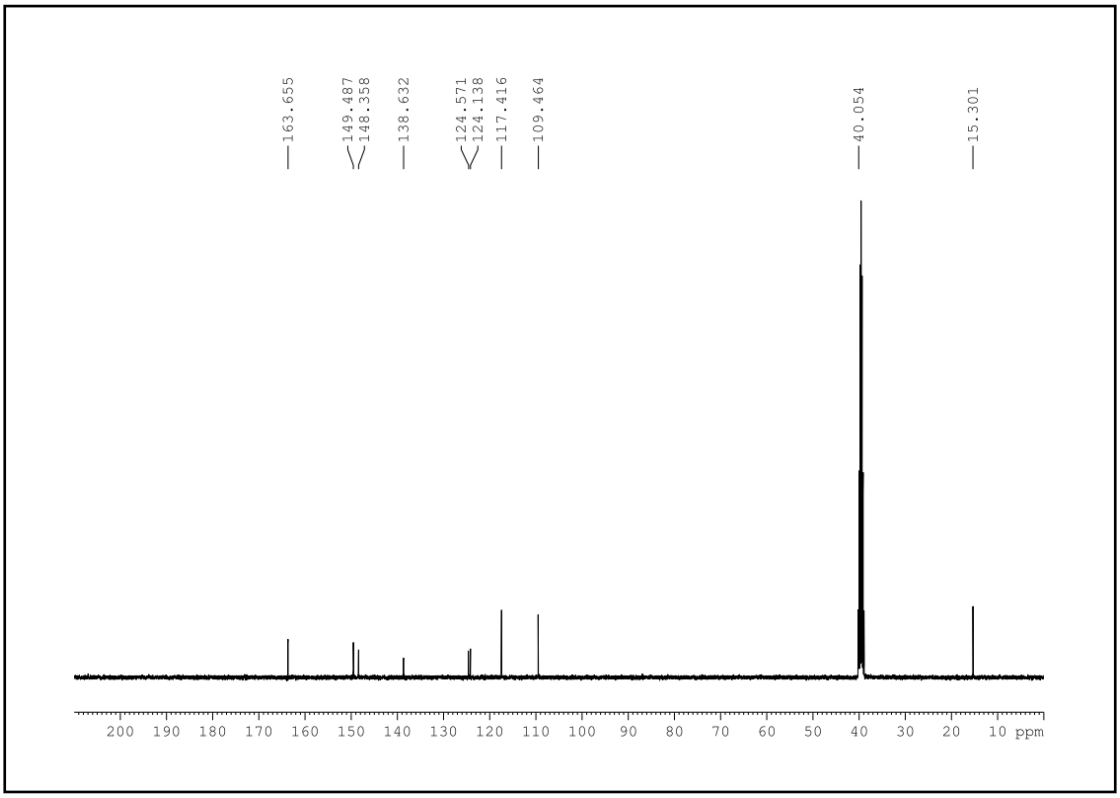


Figure S2 ^{13}C NMR spectrum of compound **1** (100 MHz, DMSO-d_6)

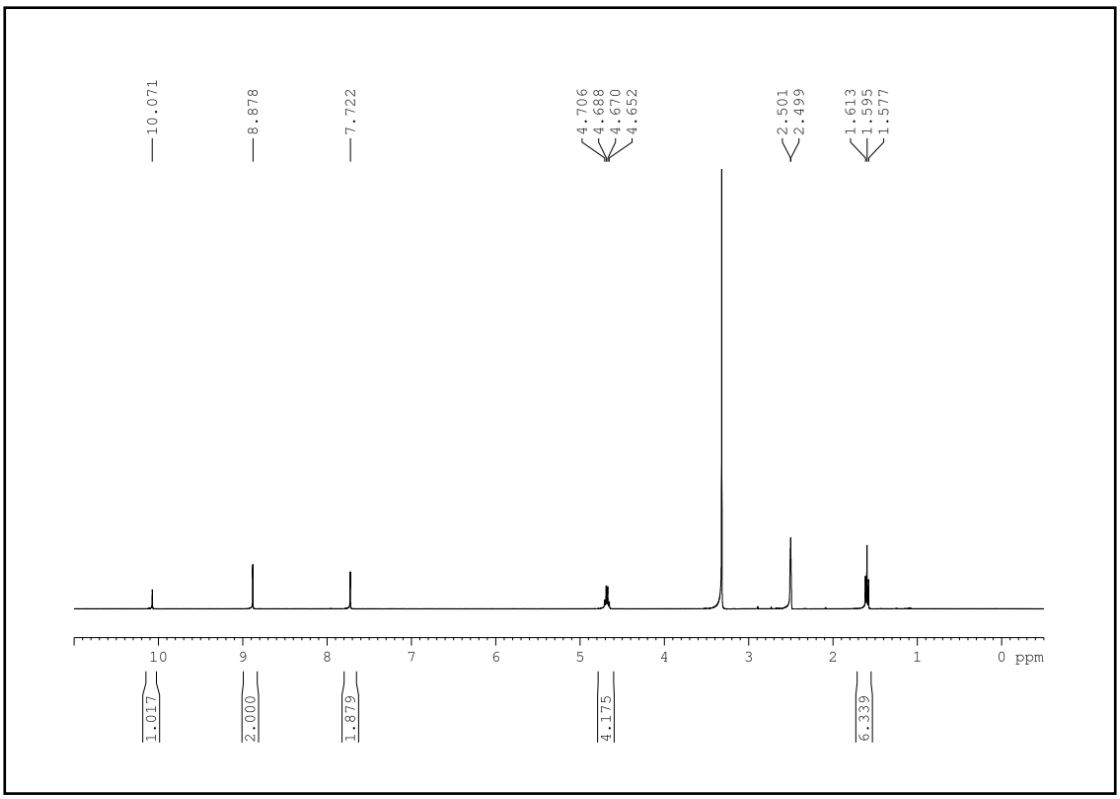


Figure S3 ^{1}H NMR spectrum of compound [**2a**][I]$_2$ (400 MHz, DMSO-d_6)

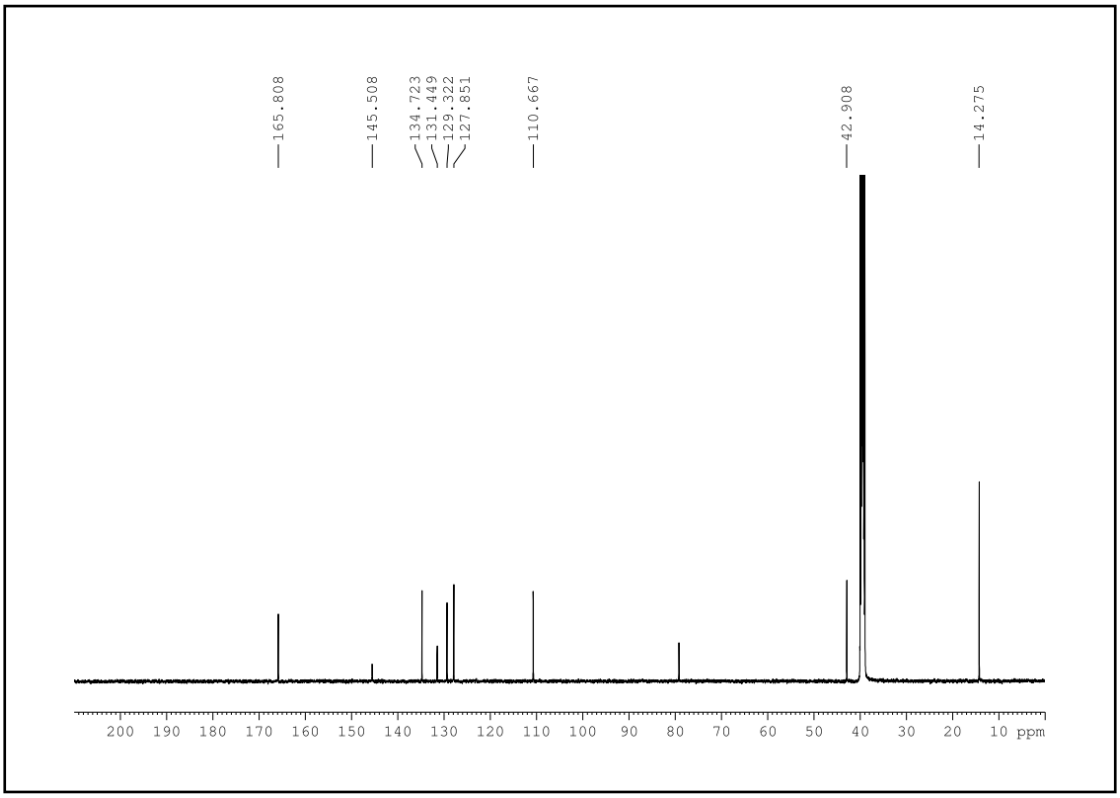


Figure S4 ^{13}C NMR spectrum of compound [**2a**][I]$_2$ (100 MHz, DMSO-d_6)

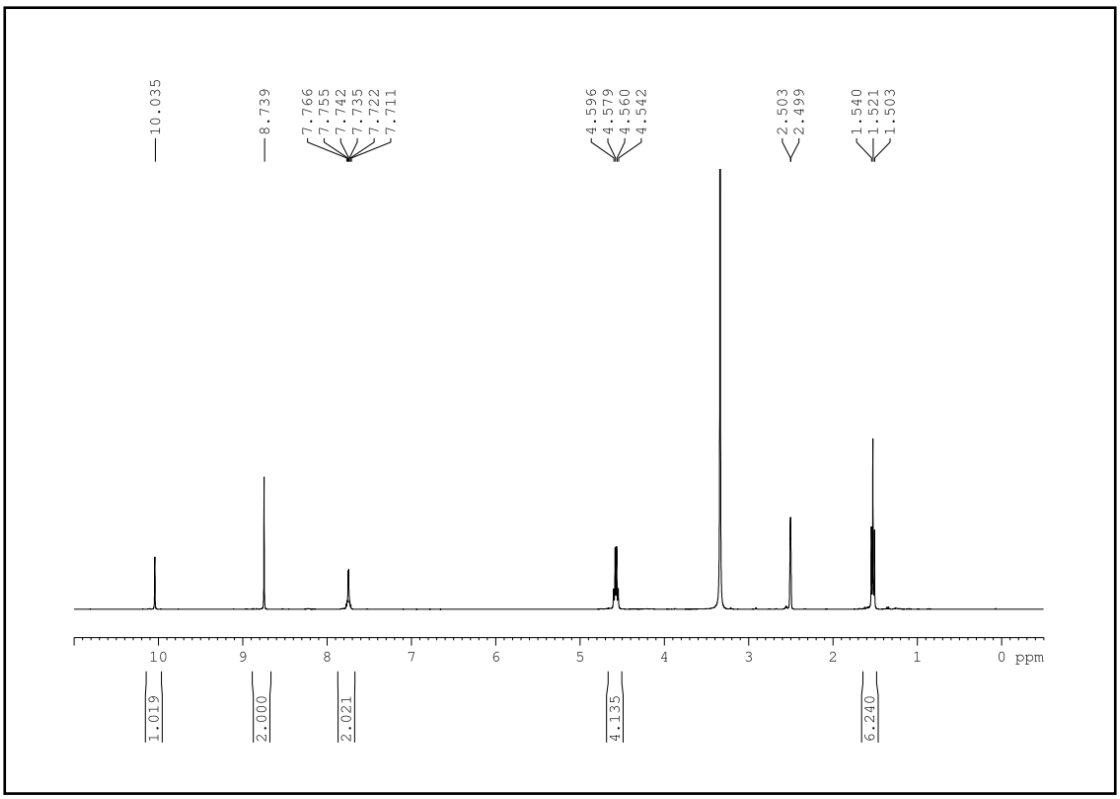


Figure S5 ^{1}H NMR spectrum of compound [**2b**][I]$_2$ (400 MHz, DMSO-d_6)

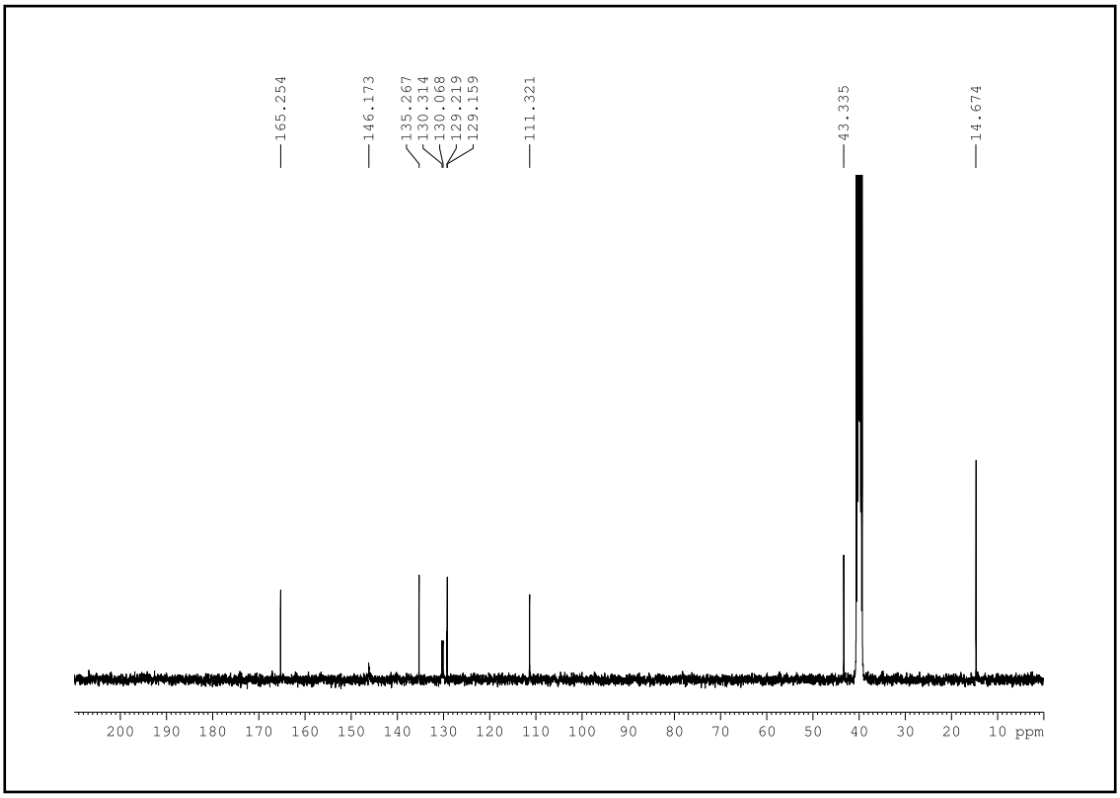


Figure S6 ^{13}C NMR spectrum of compound [**2b**][I]$_2$ (100 MHz, DMSO-d_6)

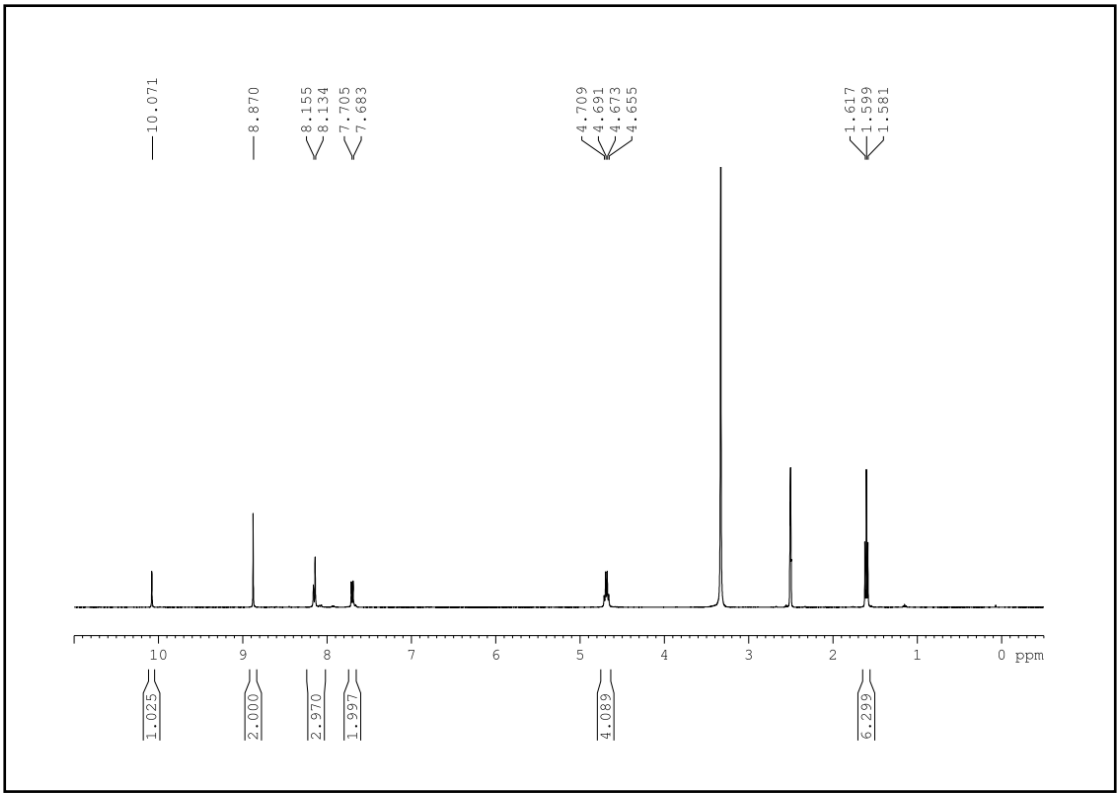


Figure S7 ^{1}H NMR spectrum of compound [**3**][I]$_3$ (400 MHz, DMSO-d_6)

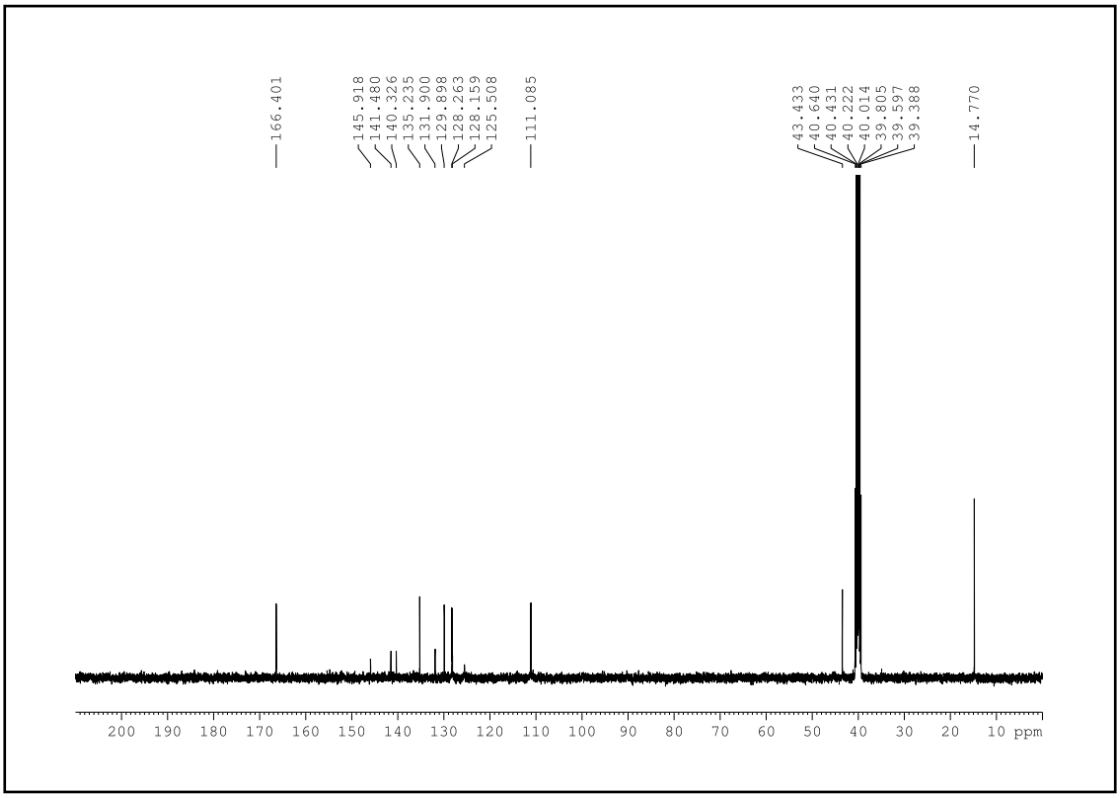


Figure S8 ^{13}C NMR spectrum of compound [**3**][I]$_3$ (100 MHz, DMSO-d_6)

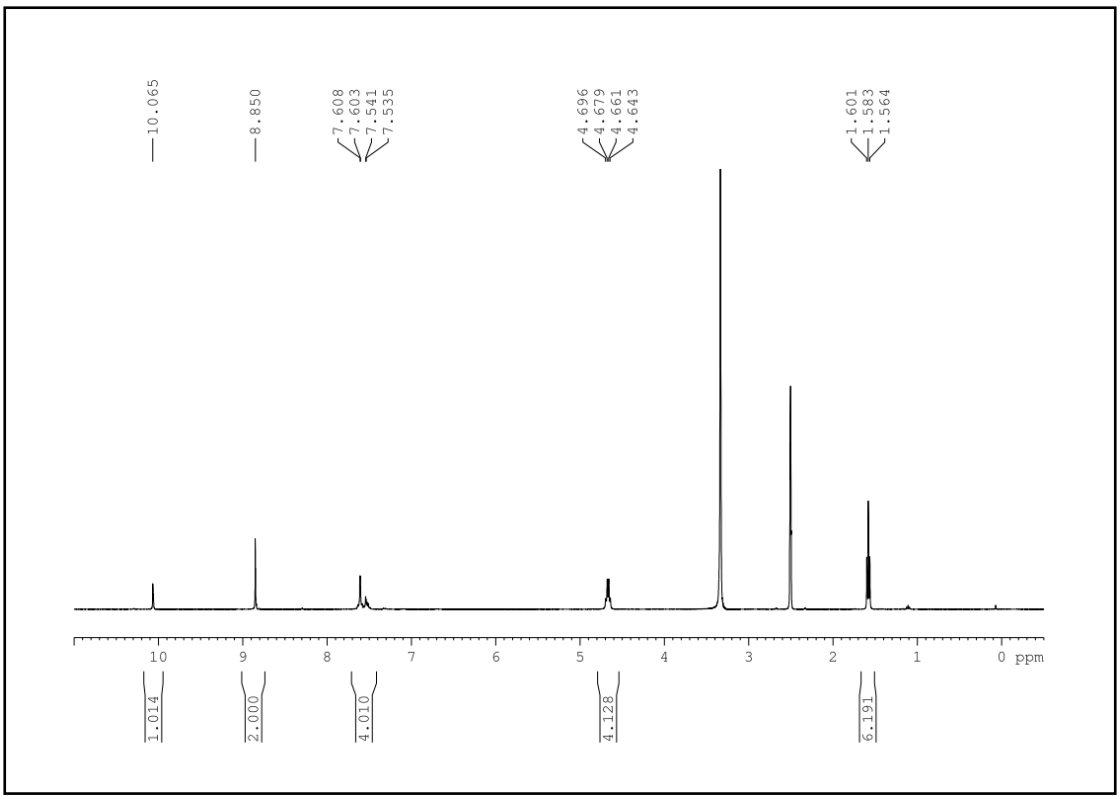


Figure S9 ^{1}H NMR spectrum of compound [**4**][I]$_4$ (400 MHz, DMSO-d_6)

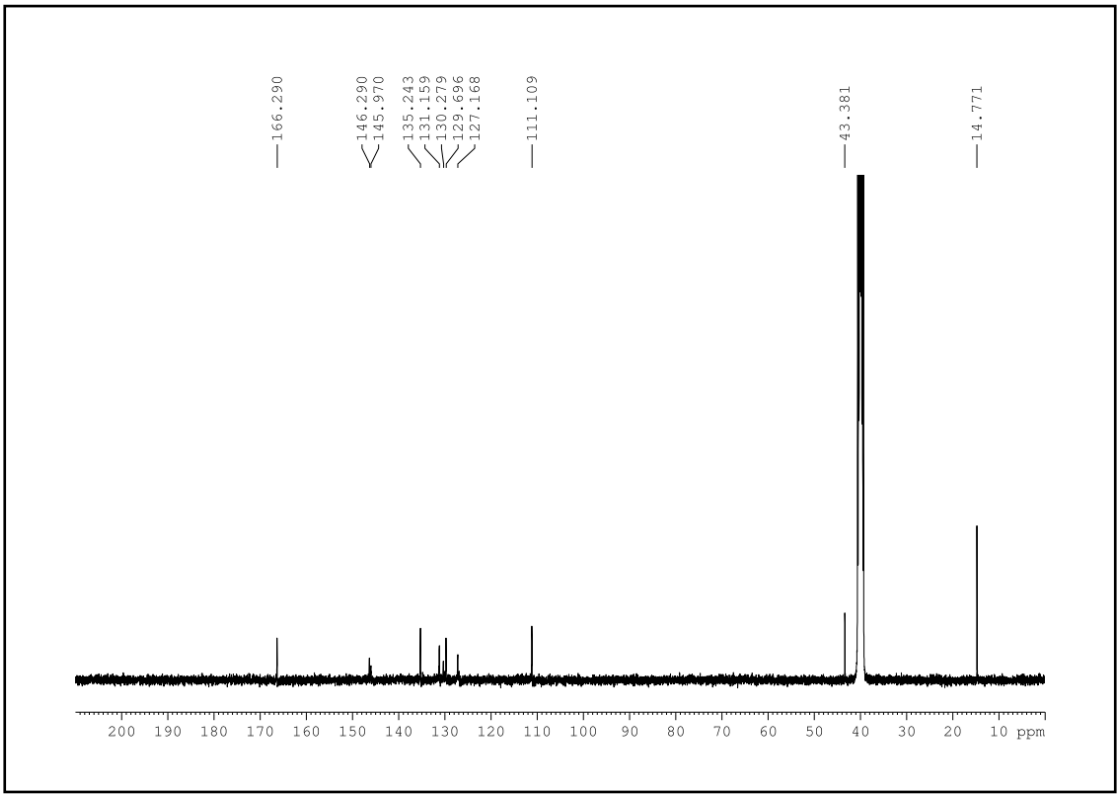


Figure S10 ^{13}C NMR spectrum of compound [**4**][I]$_4$ (100 MHz, DMSO-d_6)

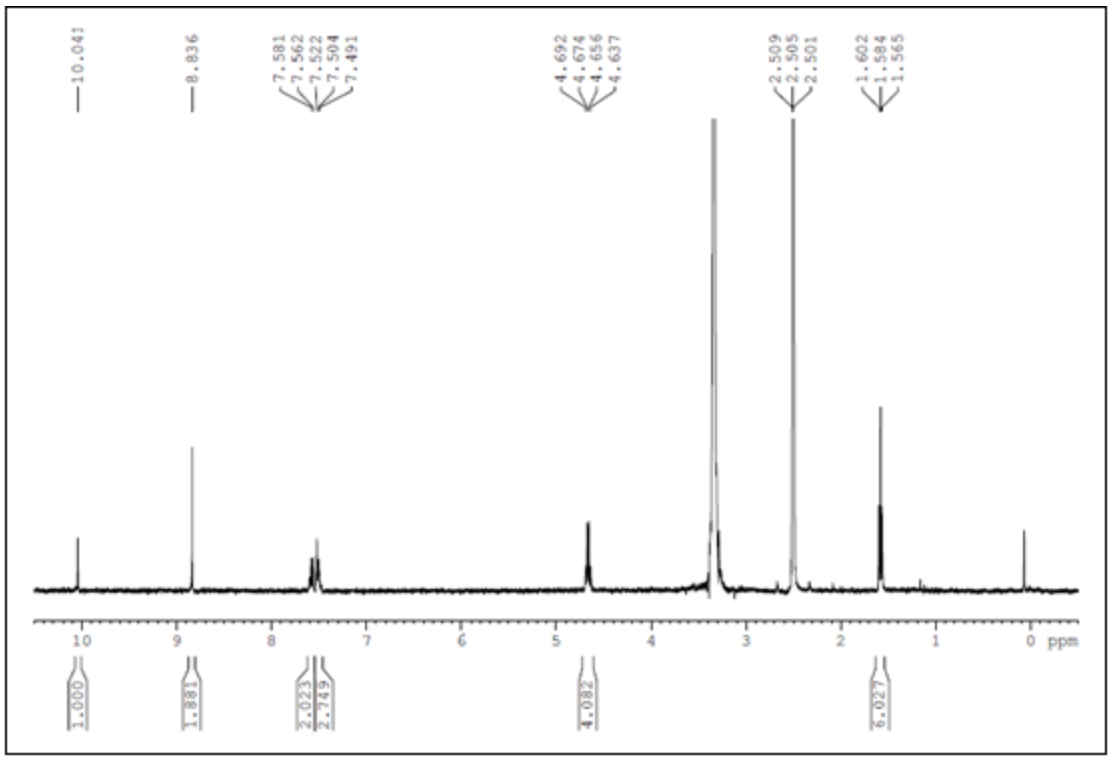


Figure S11 ^{1}H NMR spectrum of compound [**5**][I] (400 MHz, DMSO-d_6)

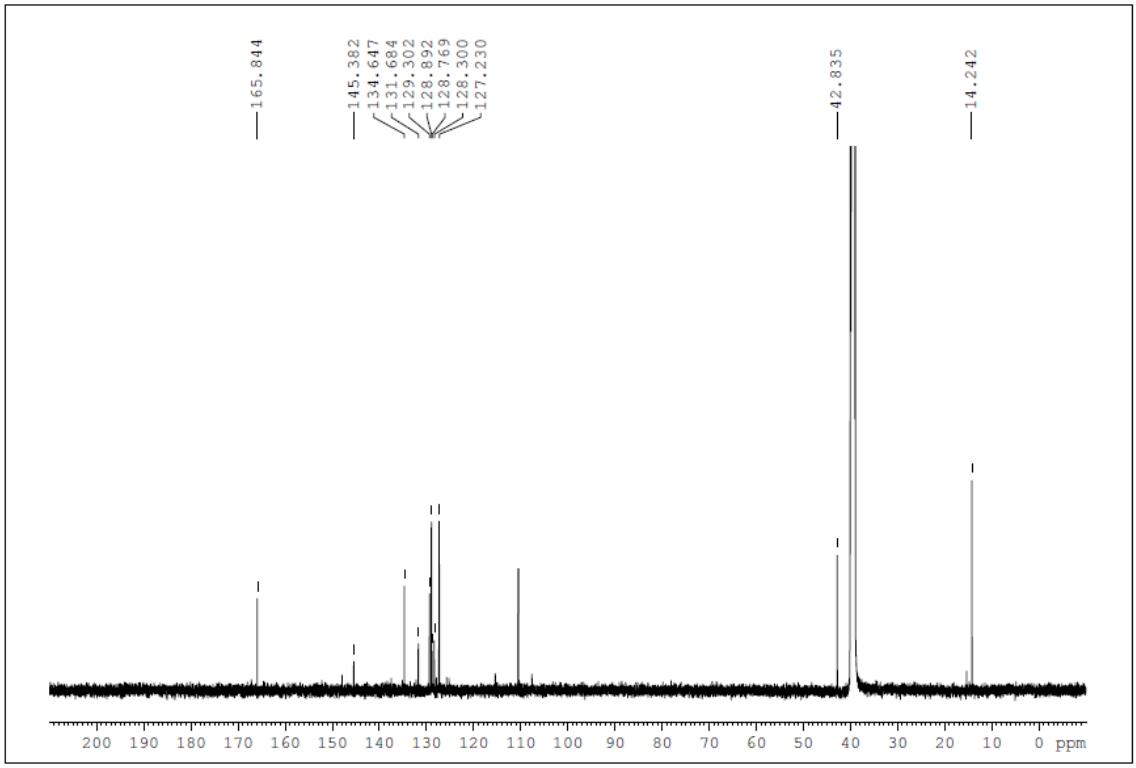


Figure S12 ^{13}C NMR spectrum of compound [**5**][I] (100 MHz, DMSO-d_6)

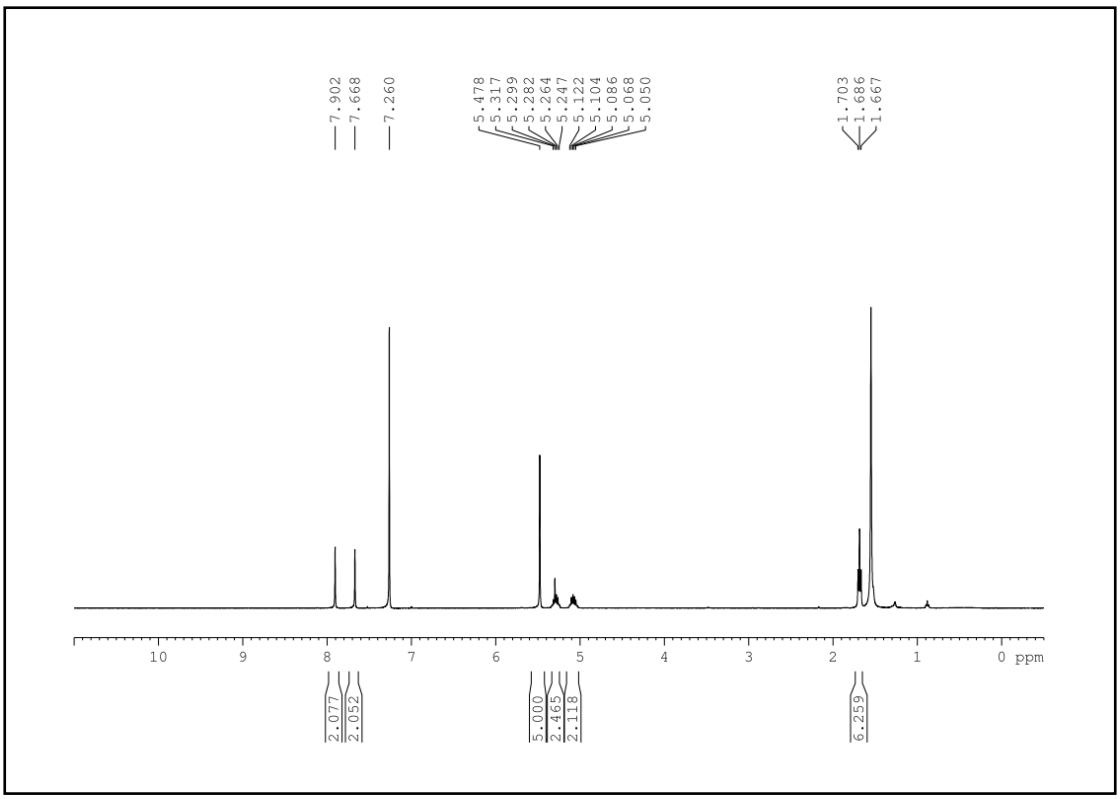


Figure S13 ^{1}H NMR spectrum of compound [**2a**-$(NiCpI)_2$] (400 MHz, $CDCl_3$)

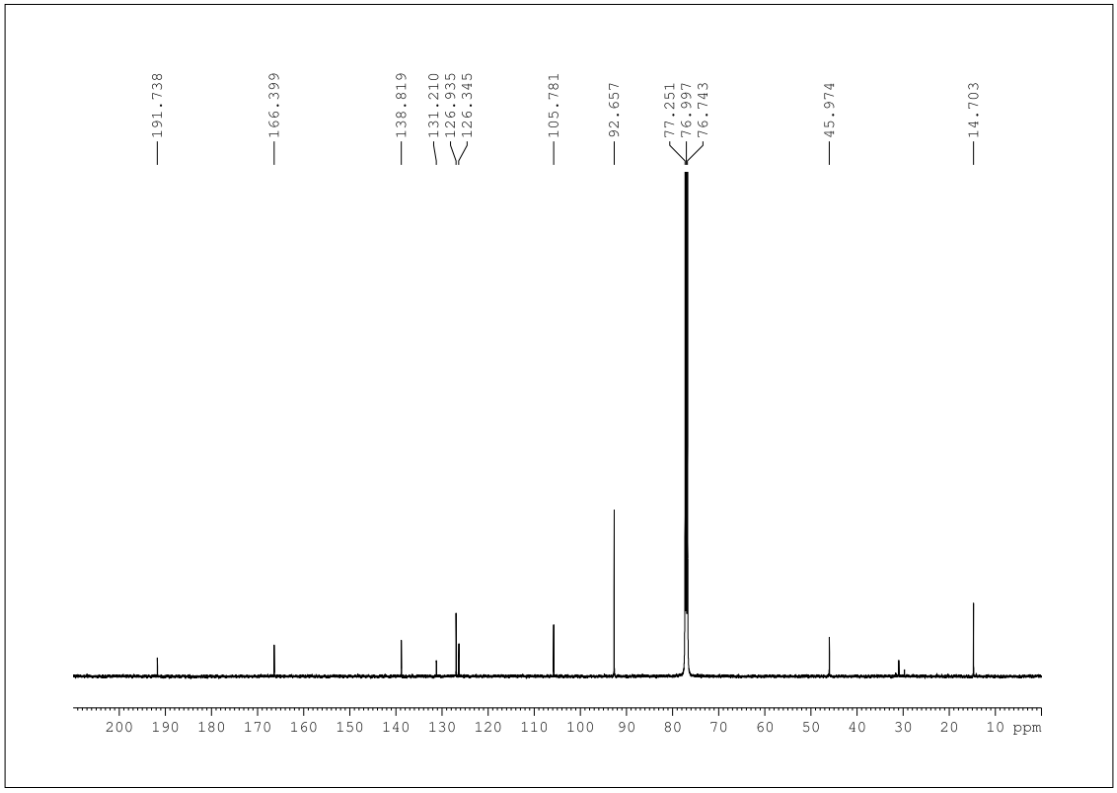


Figure S14 ^{13}C NMR spectrum of compound [**2a**-$(NiCpI)_2$] (100 MHz, $CDCl_3$)

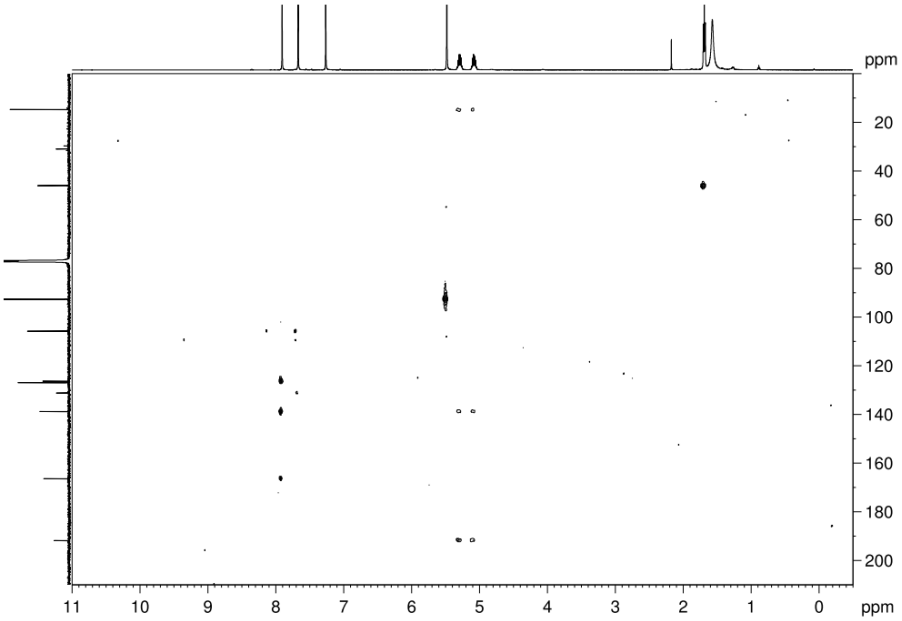


Figure S15 HMBC spectrum of compound [**2a**-$(NiCpI)_2$]

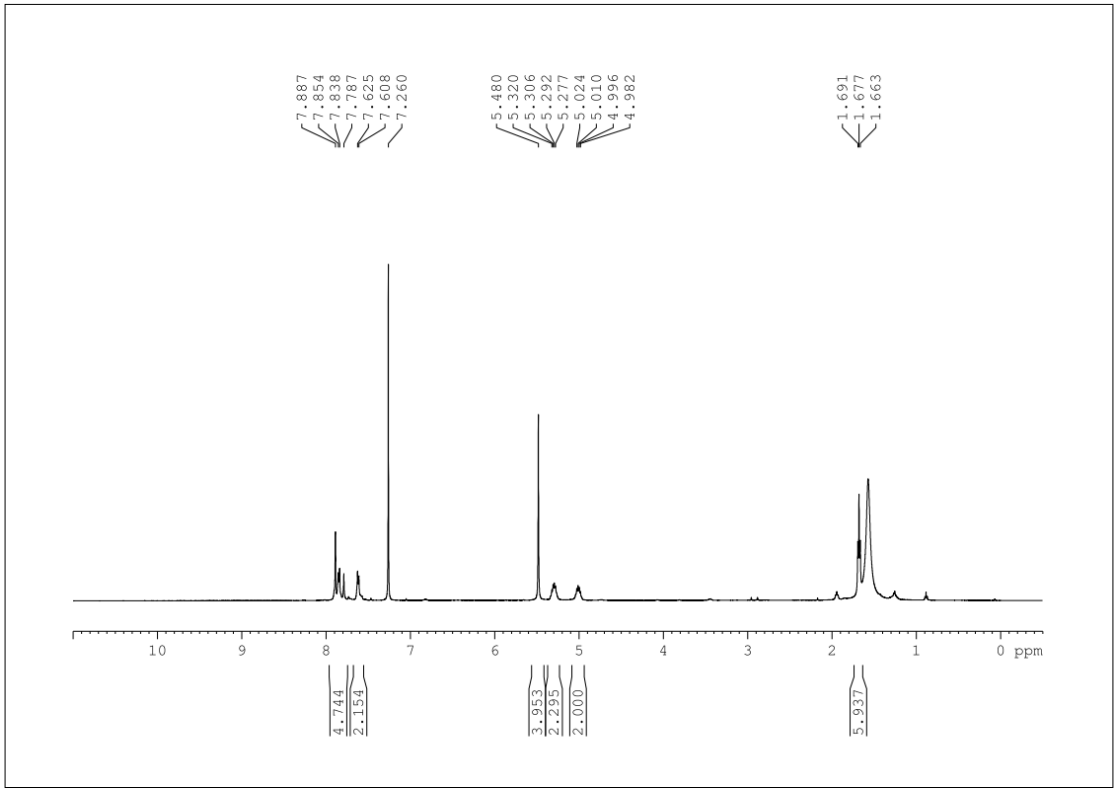


Figure S16 ^{1}H NMR spectrum of compound [**3**-$(NiCpI)_3$] (400 MHz, $CDCl_3$)

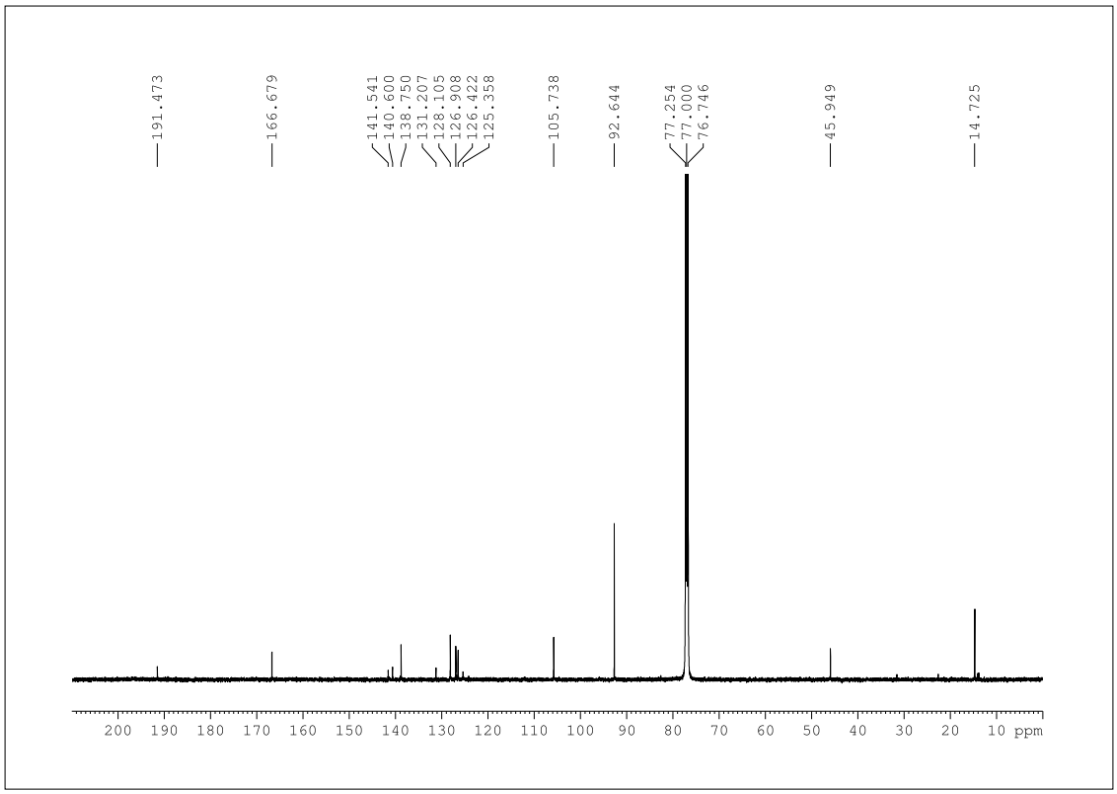


Figure S17 ^{13}C NMR spectrum of compound [**3**-$(NiCpI)_3$] (100 MHz, $CDCl_3$)

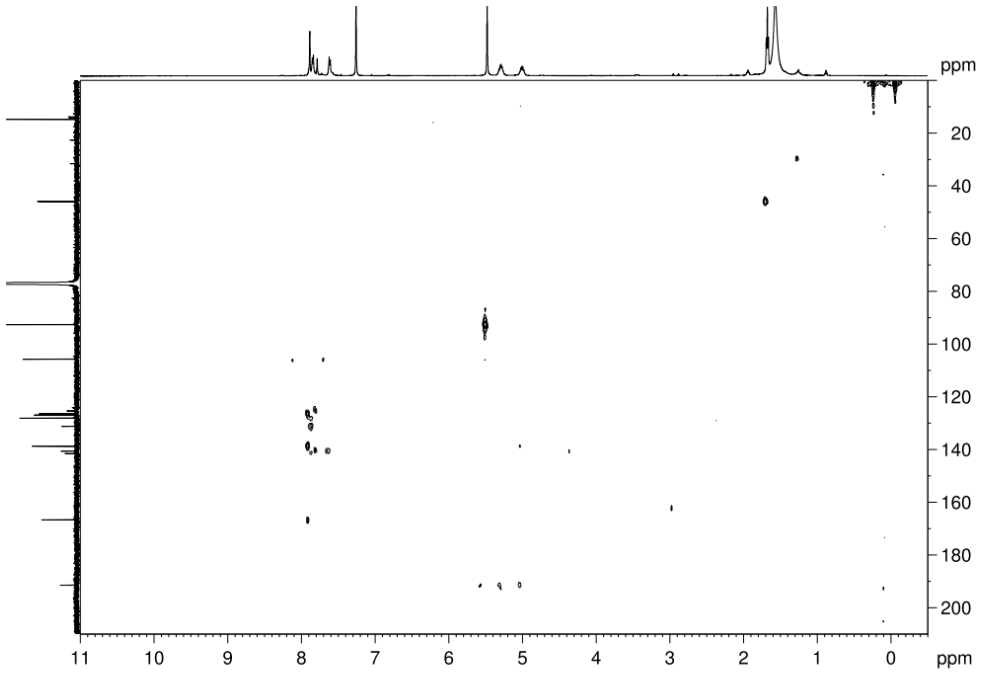


Figure S18 HMBC spectrum of compound [**3**-$(NiCpI)_3$]

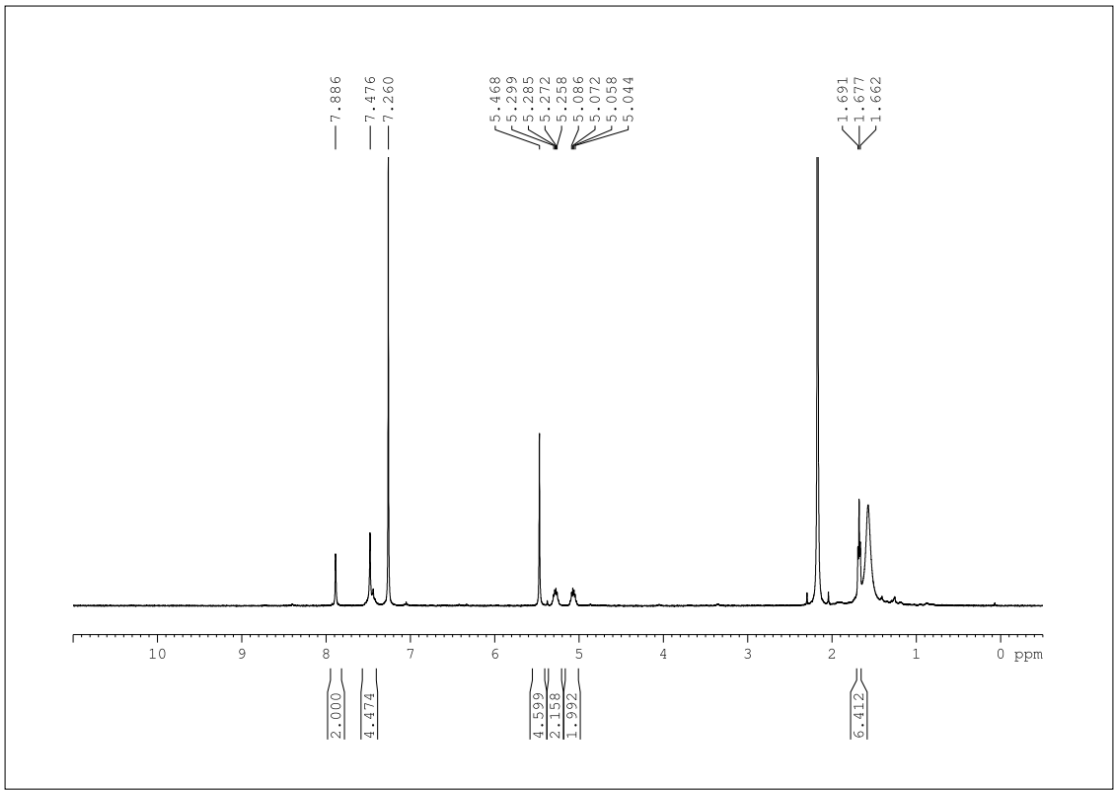


Figure S19 ^{1}H NMR spectrum of compound [**4**-$(NiCpI)_4$] (400 MHz, $CDCl_3$)

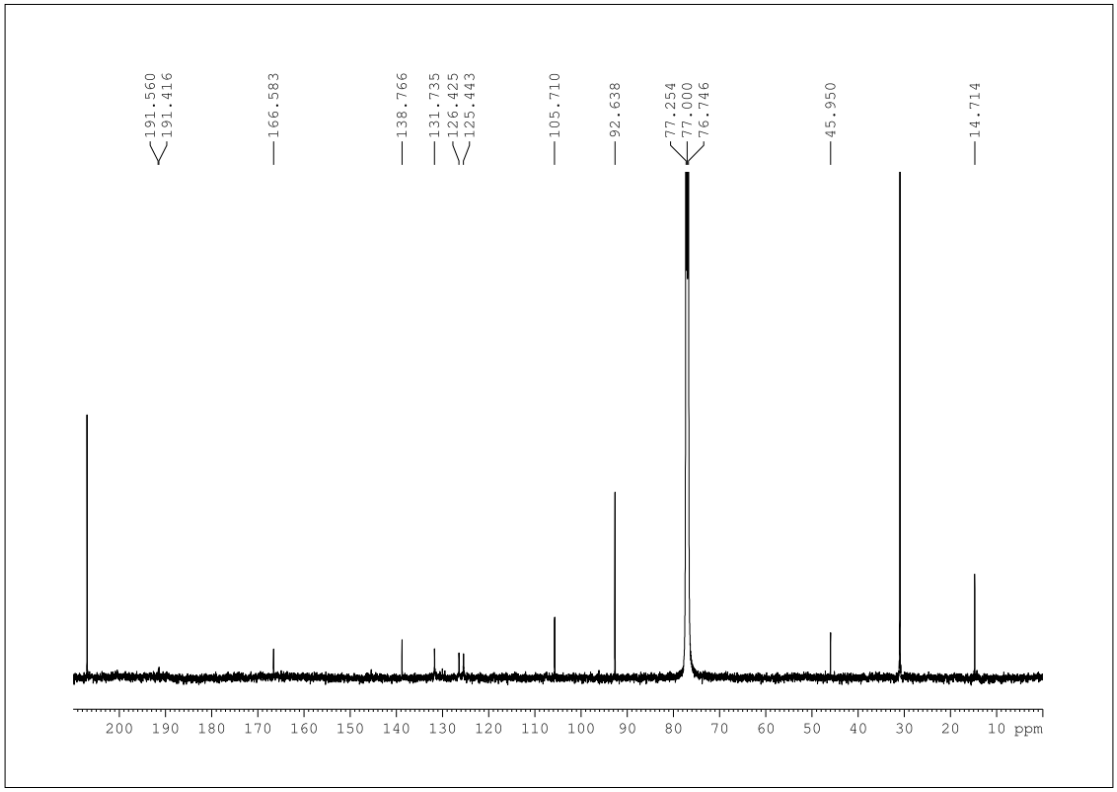


Figure S20 ^{13}C NMR spectrum of compound [**4**-$(NiCpI)_4$] (100 MHz, $CDCl_3$)

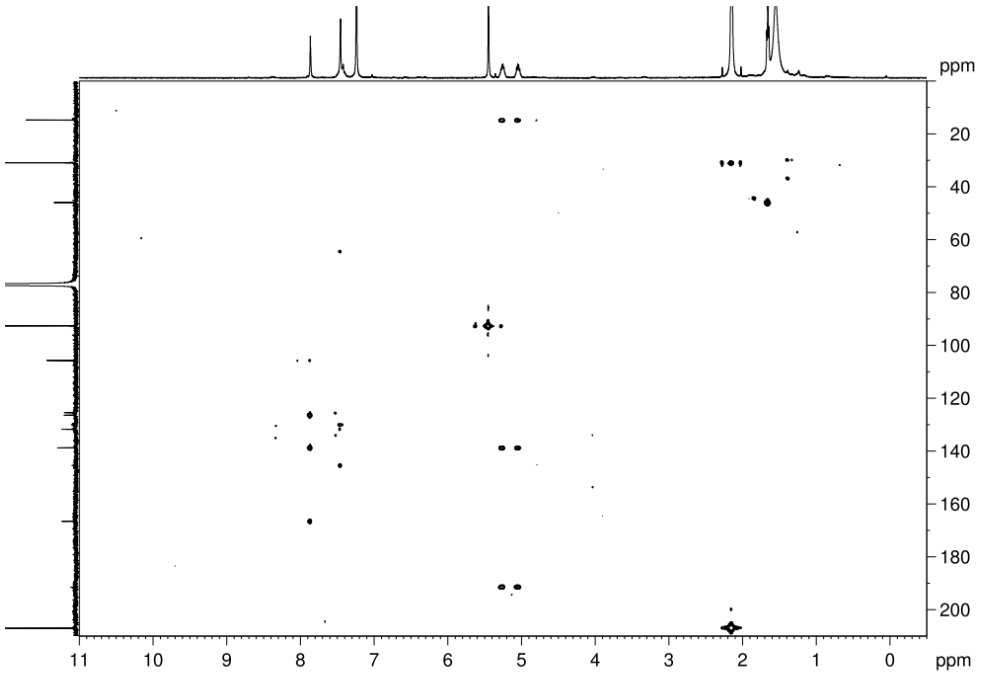


Figure S21 HMBC spectrum of compound [**4**-$(NiCpI)_4$]

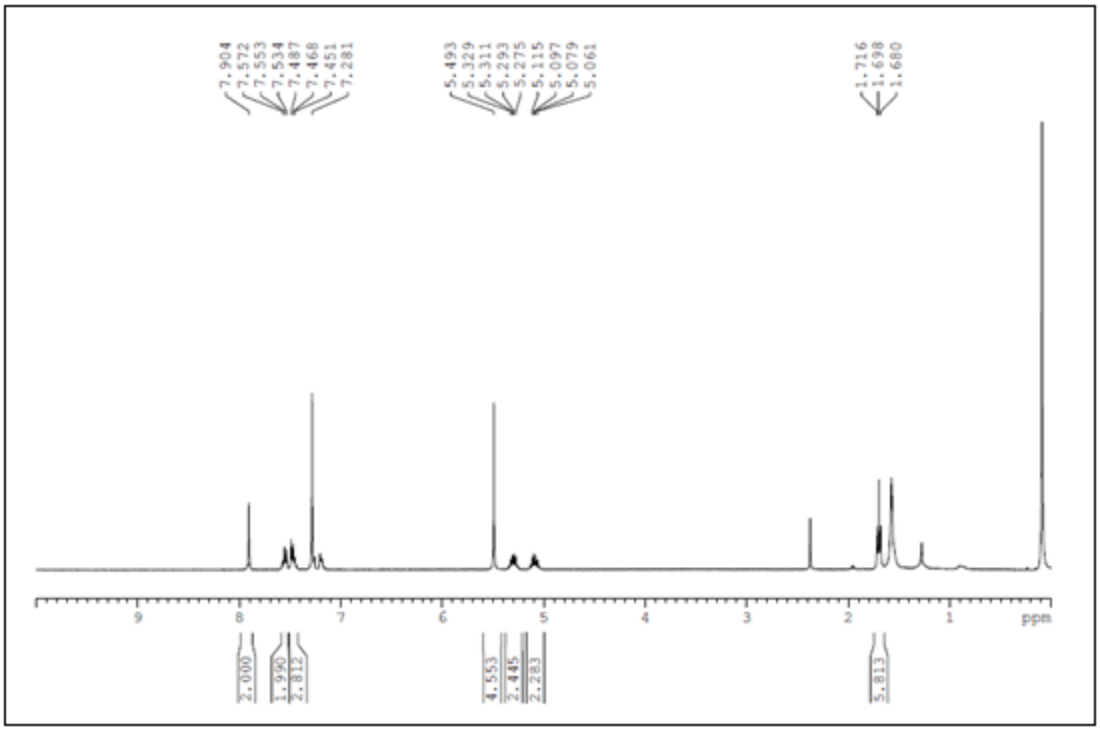


Figure S22 ^{1}H NMR spectrum of compound [**5**-(NiCpI)] (400 MHz, $CDCl_3$)

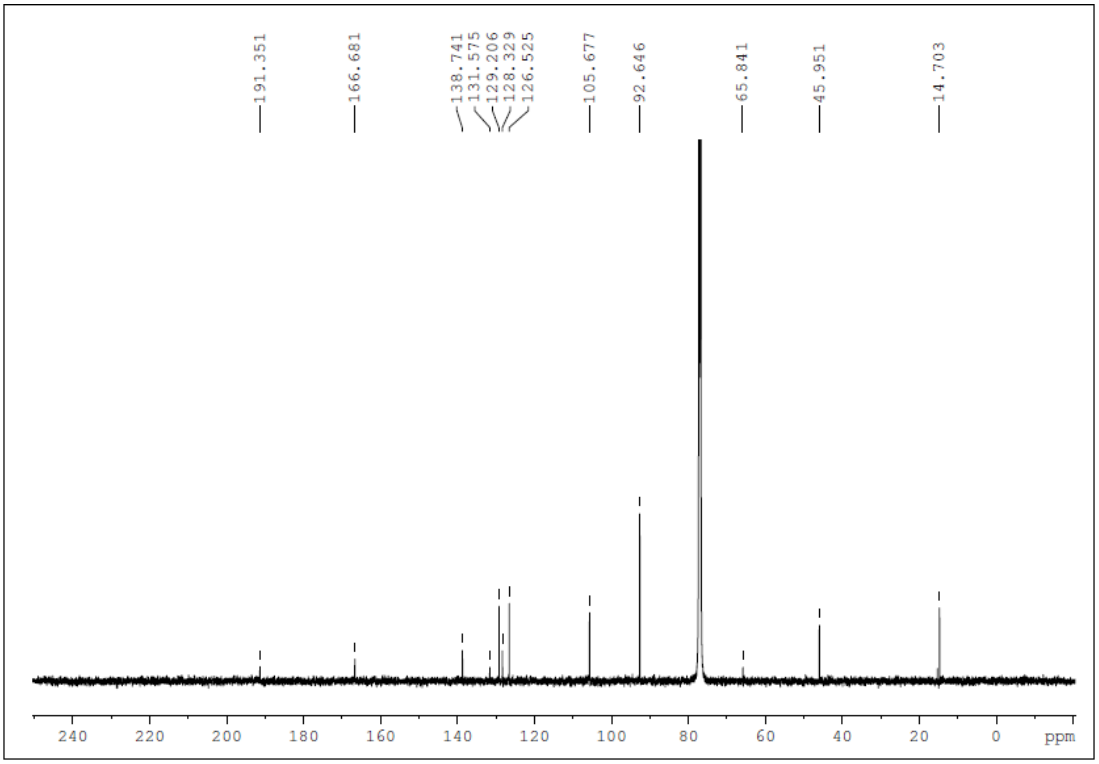


Figure S23 ^{13}C NMR spectrum of compound [**5**-(NiCpI)] (100 MHz, $CDCl_3$)

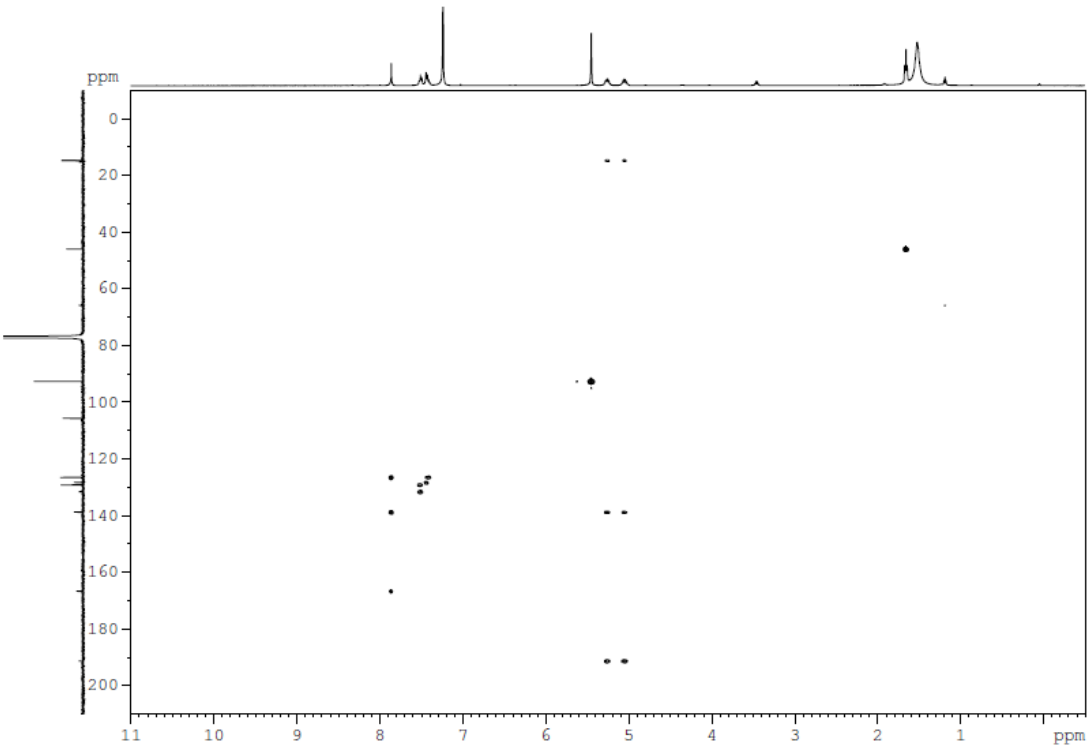


Figure S24 HMBC spectrum of compound [**5**-(NiCpI)]

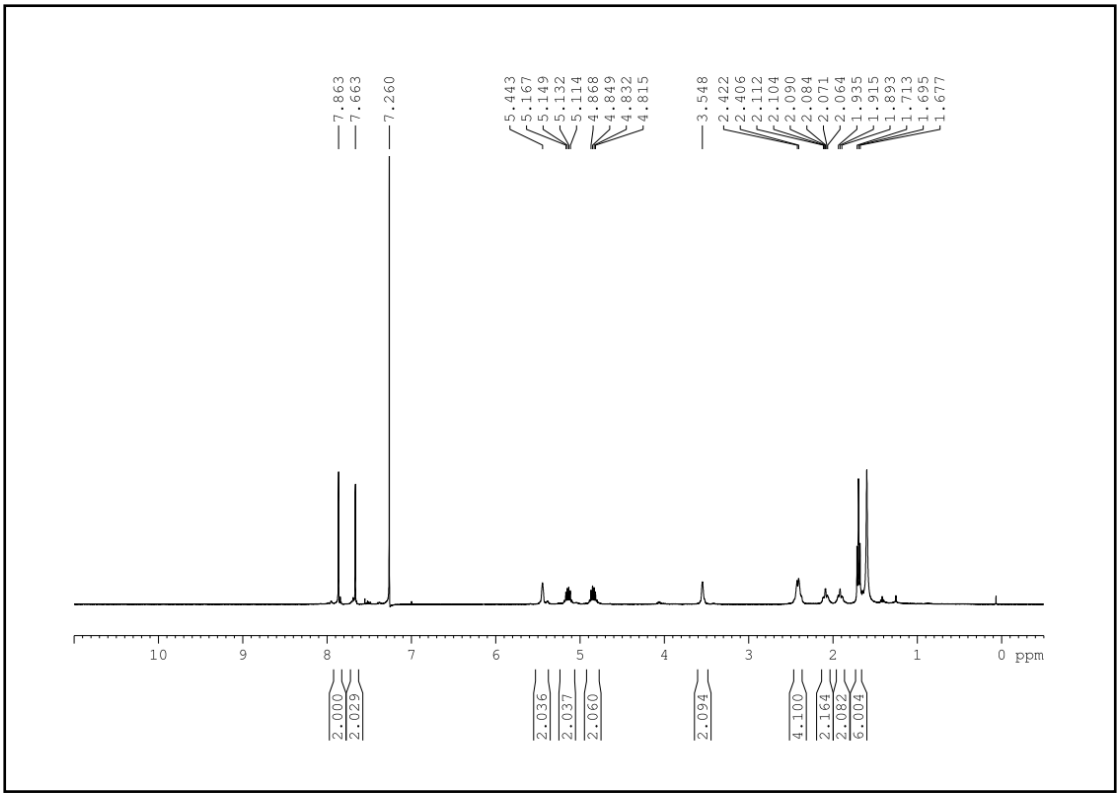


Figure S25 ^{1}H NMR spectrum of compound [**2a**-[Rh(COD)I]$_2$] (400 MHz, $CDCl_3$)

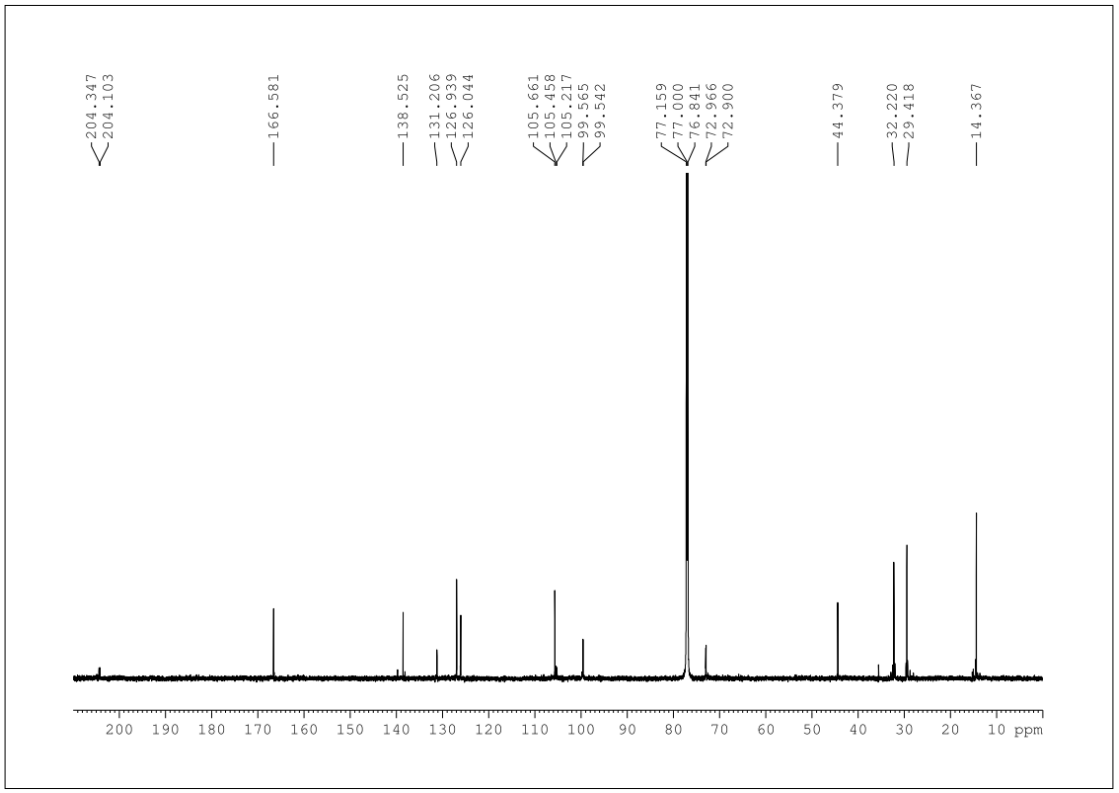


Figure S26 ^{13}C NMR spectrum of compound [**2a**-[Rh(COD)I]$_2$] (100 MHz, $CDCl_3$)

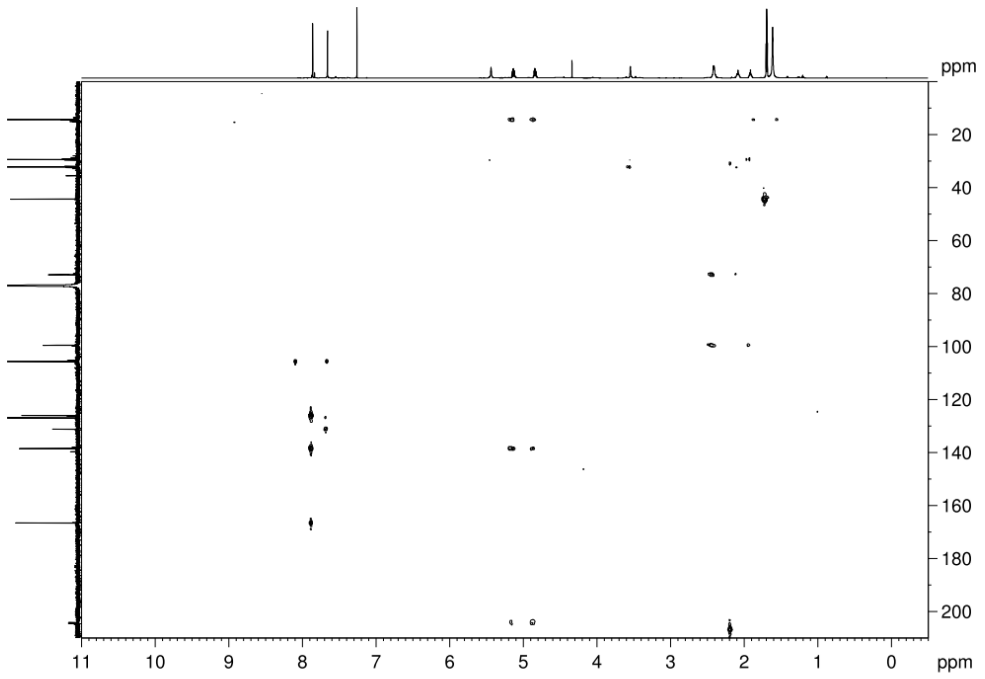


Figure S27 HMBC spectrum of compound [**2a**-[Rh(COD)I]$_2$]

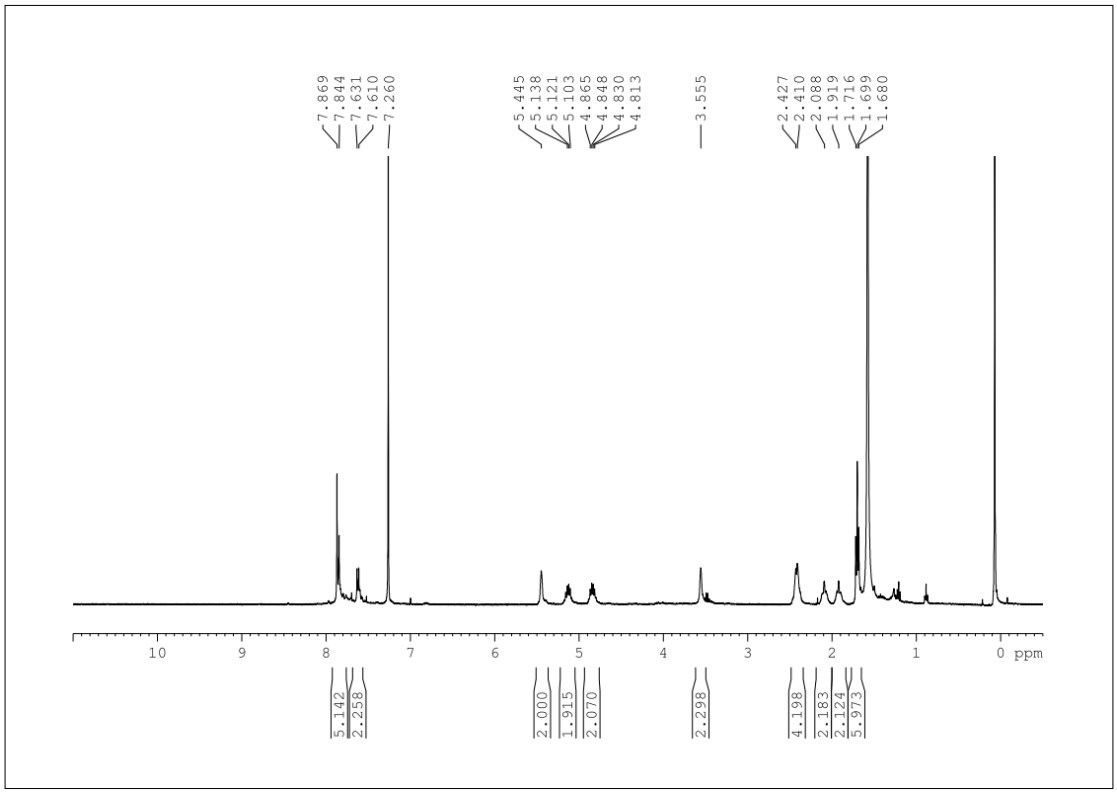


Figure S28 ^{1}H NMR spectrum of compound [**3**-[Rh(COD)I]$_3$] (400 MHz, $CDCl_3$)

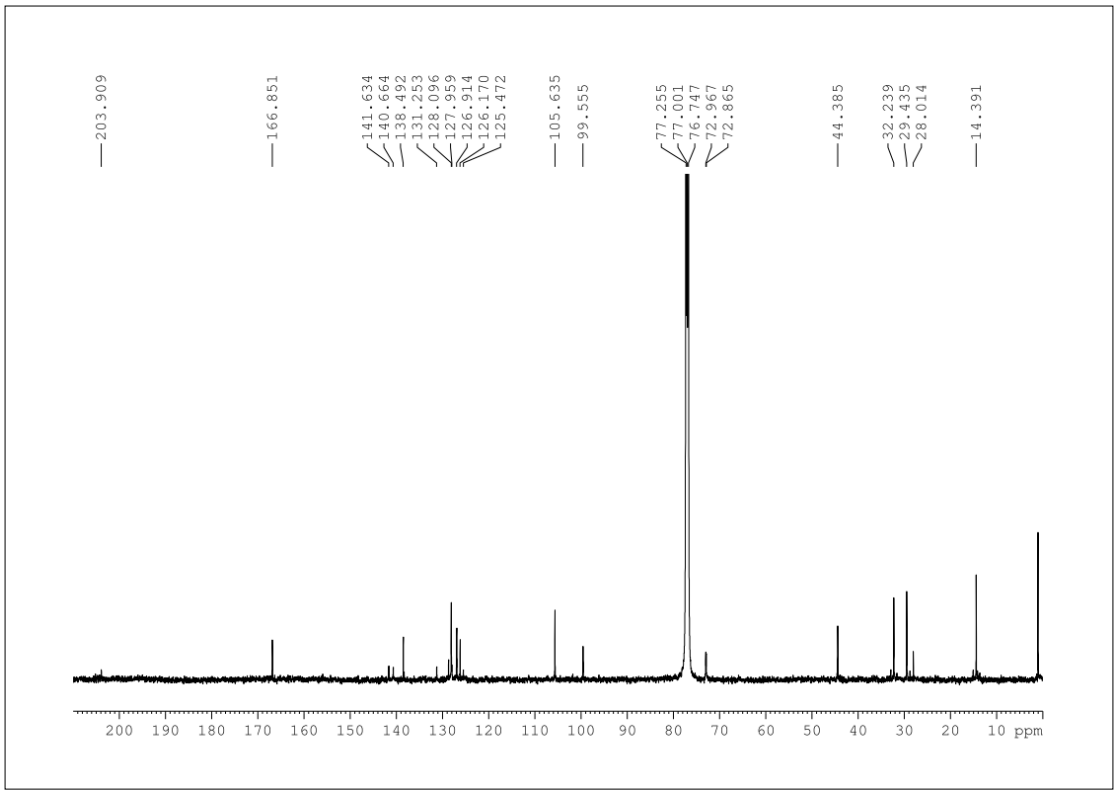


Figure S29 ^{13}C NMR spectrum of compound [**3**-[Rh(COD)I]$_3$] (100 MHz, $CDCl_3$)

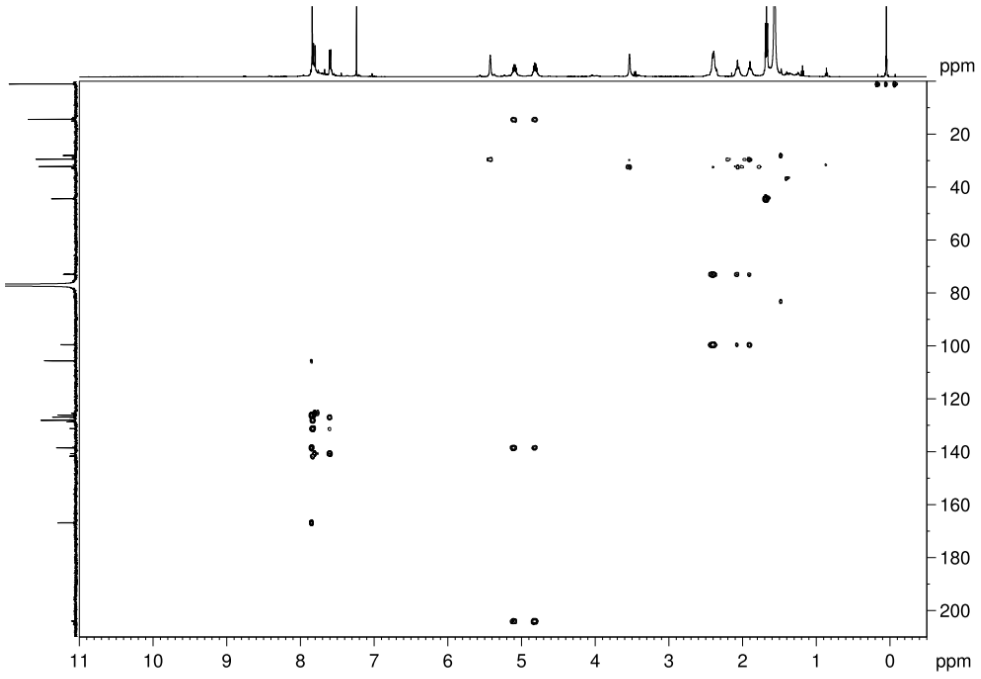


Figure S30 HMBC spectrum of compound [**3**-[Rh(COD)I]$_3$]

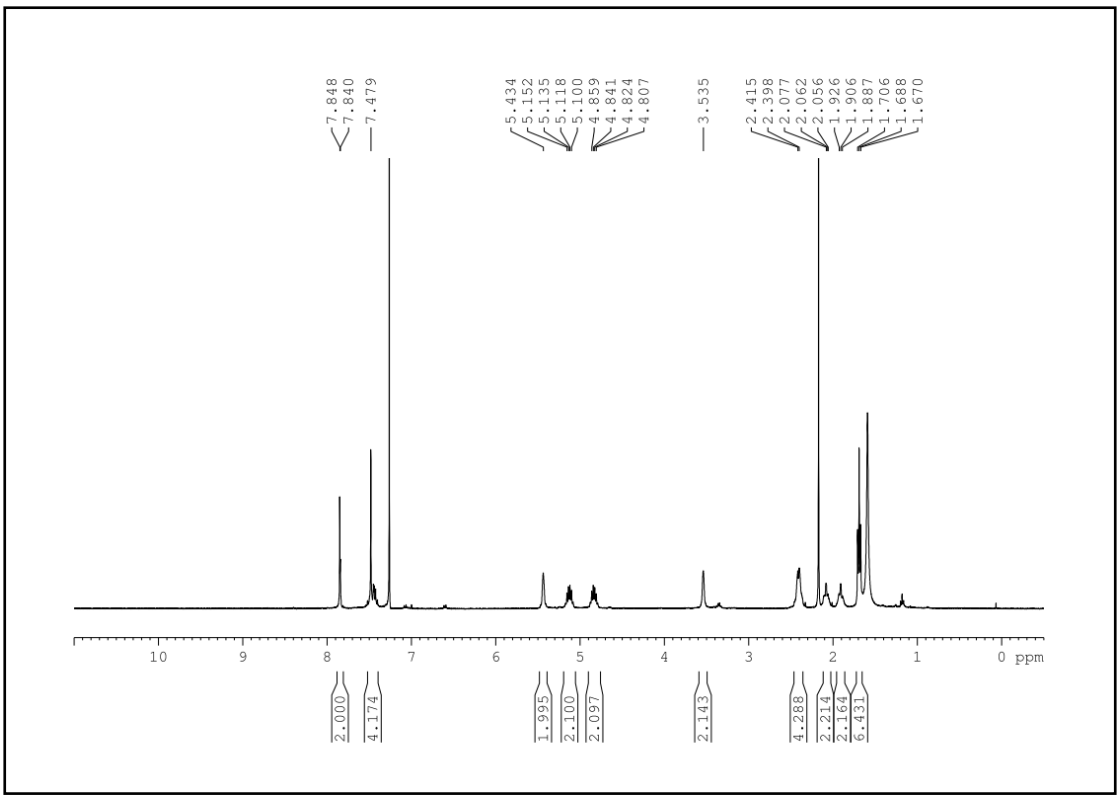


Figure S31 ^{1}H NMR spectrum of compound [**4**-[Rh(COD)I]$_4$] (400 MHz, $CDCl_3$)

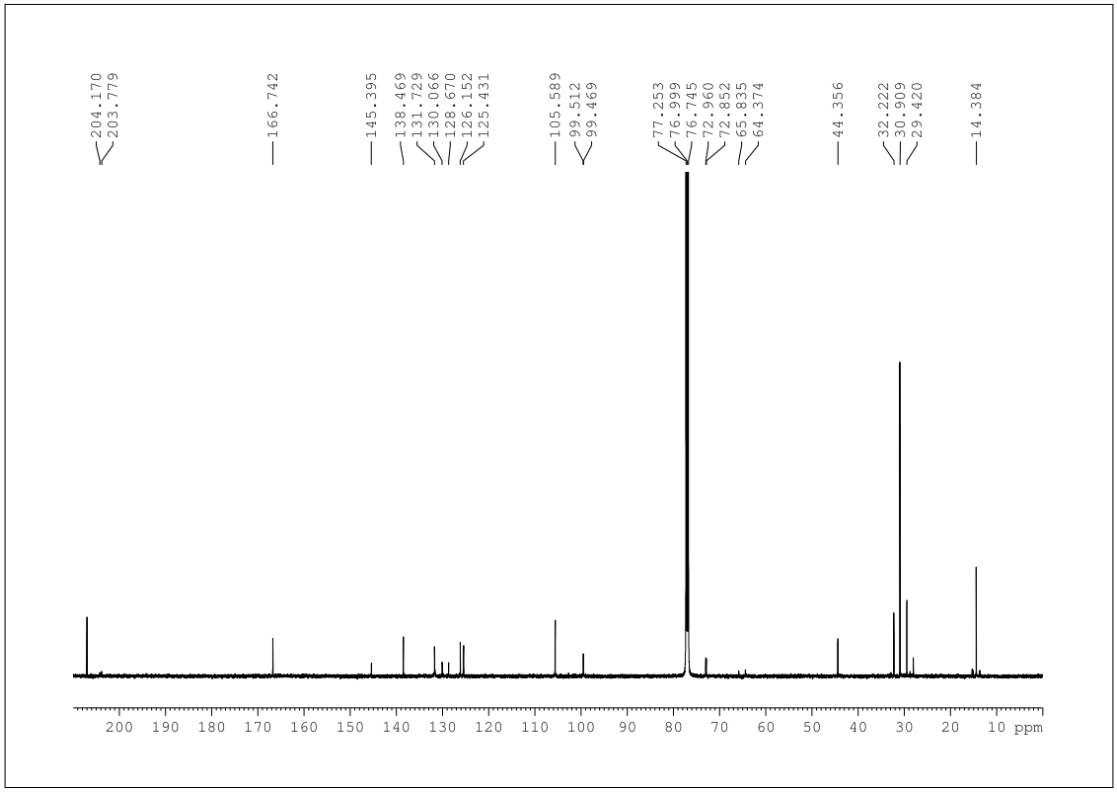


Figure S32 ^{13}C NMR spectrum of compound [**4**-[Rh(COD)I]$_4$] (100 MHz, $CDCl_3$)

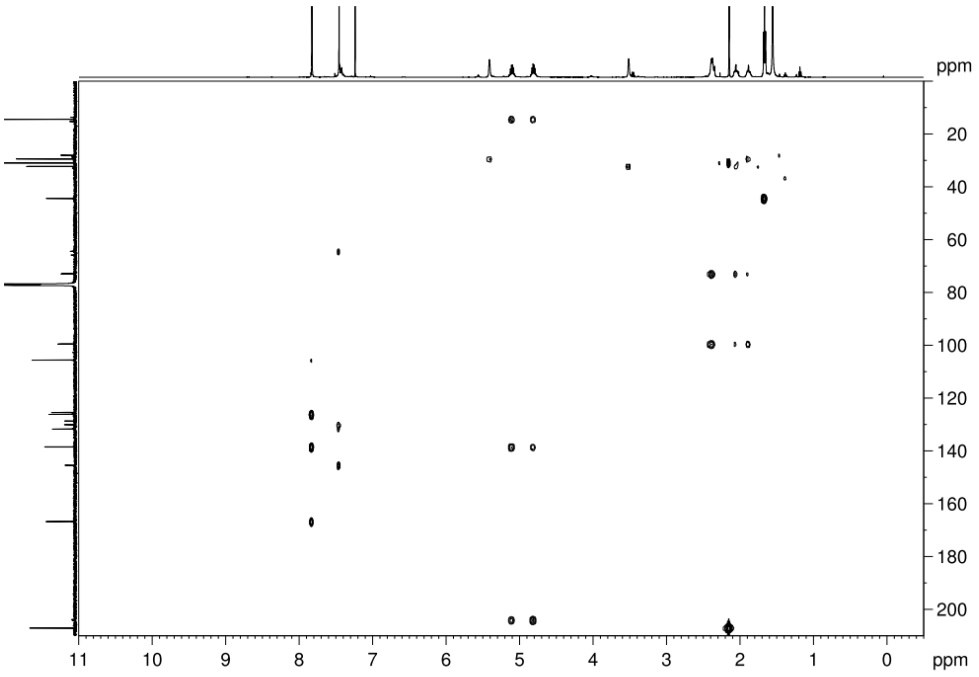


Figure S33 HMBC spectrum of compound [**4**-[Rh(COD)I]$_4$]

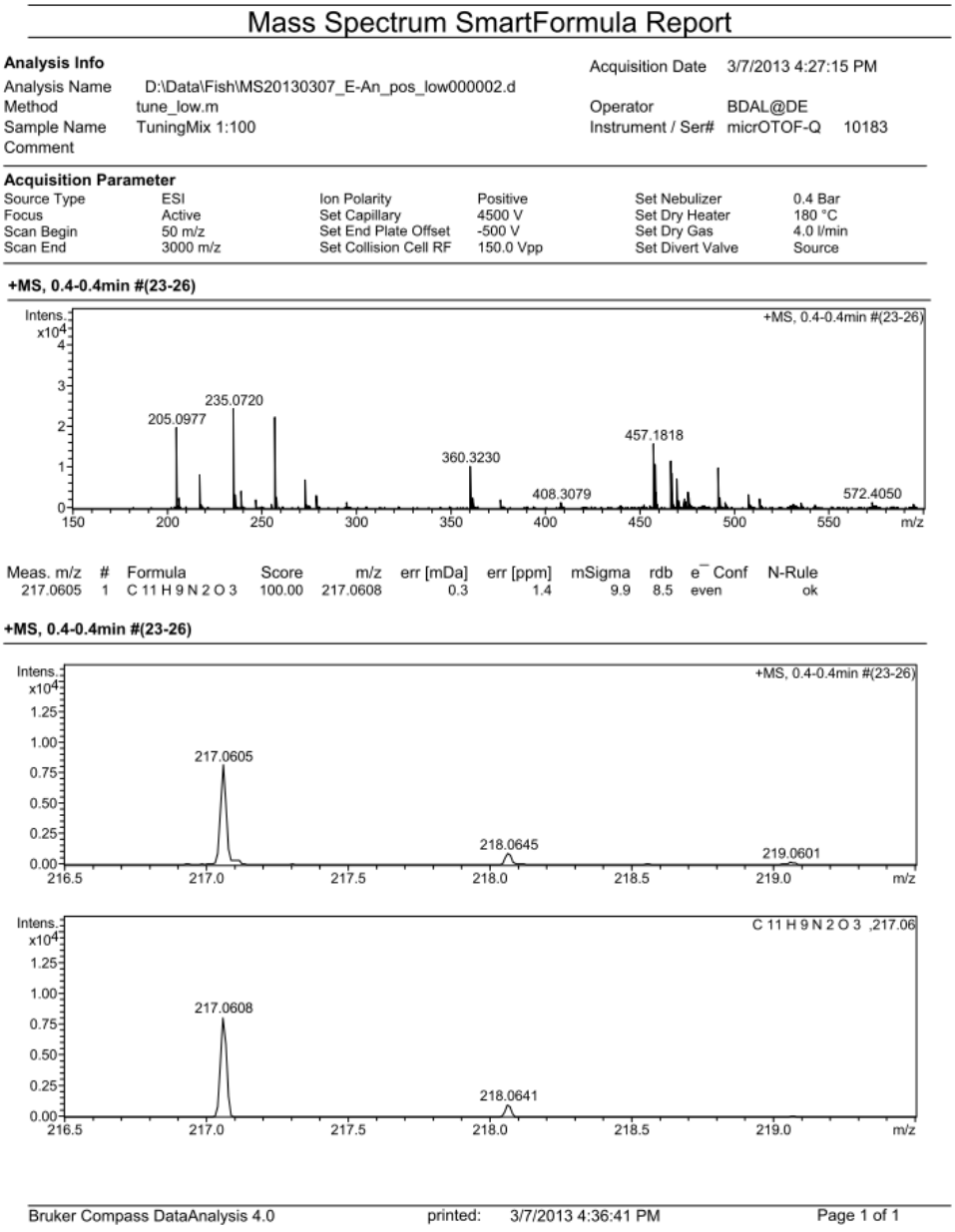


Figure S34 mass spectrum of compound **1**

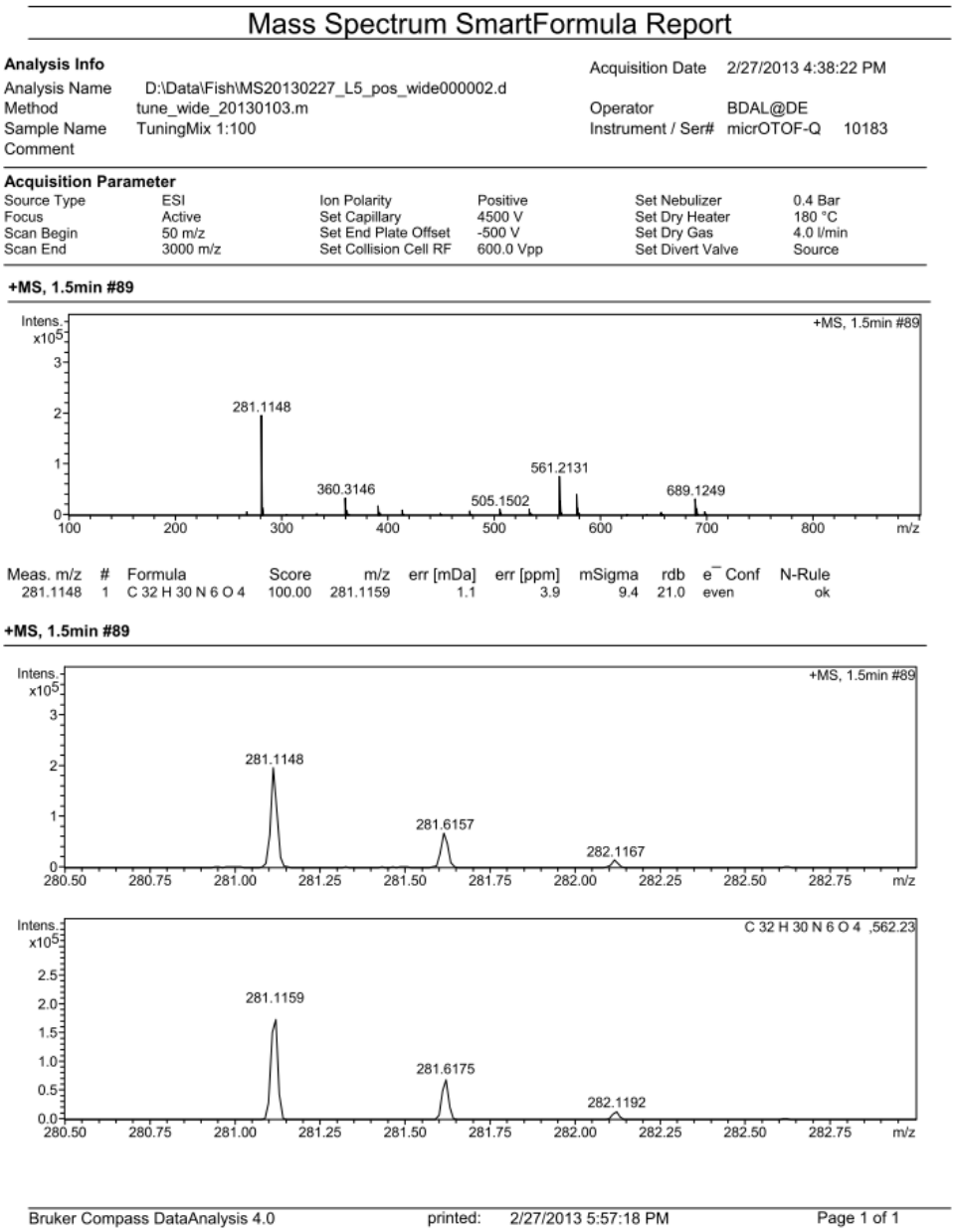


Figure S35 mass spectrum of compound [**2a**][I]$_2$

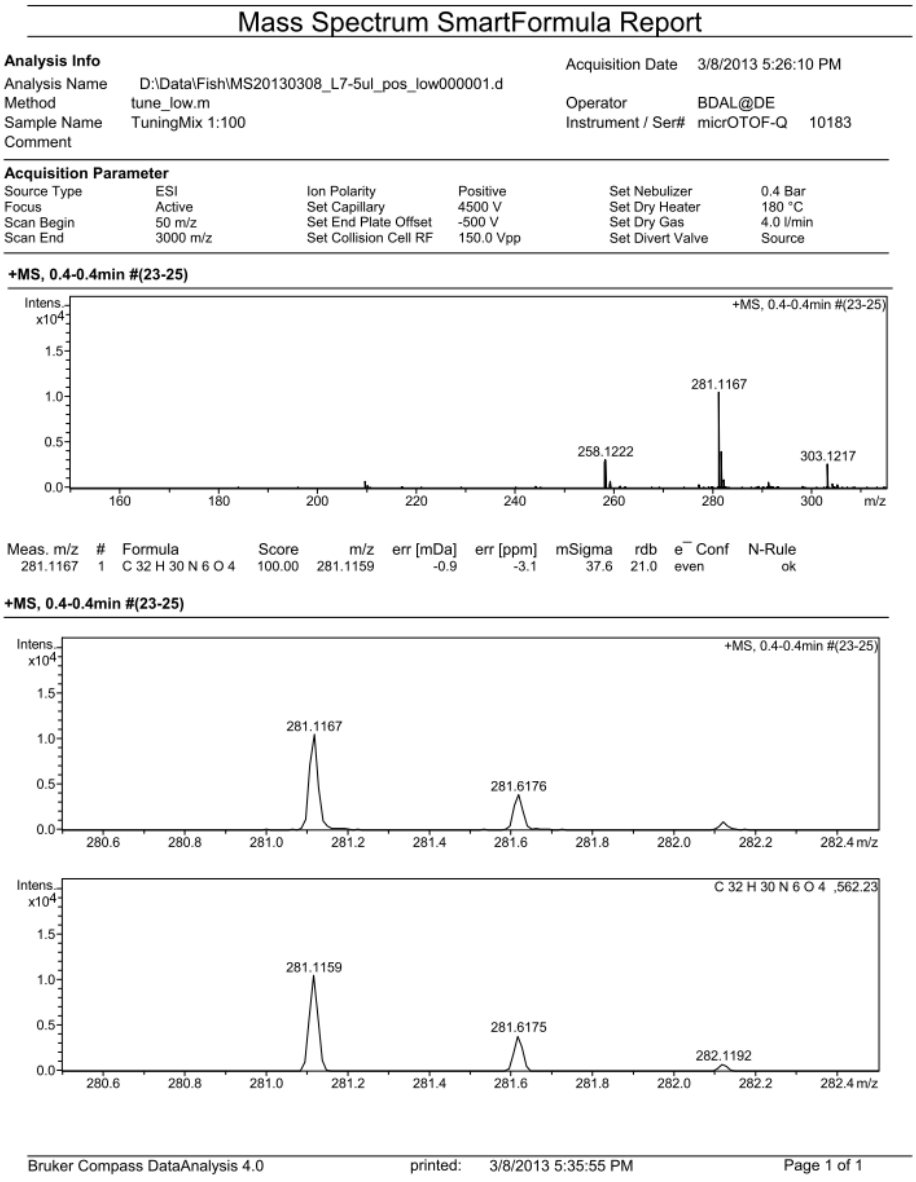


Figure S36 mass spectrum of compound [**2b**][I]$_2$

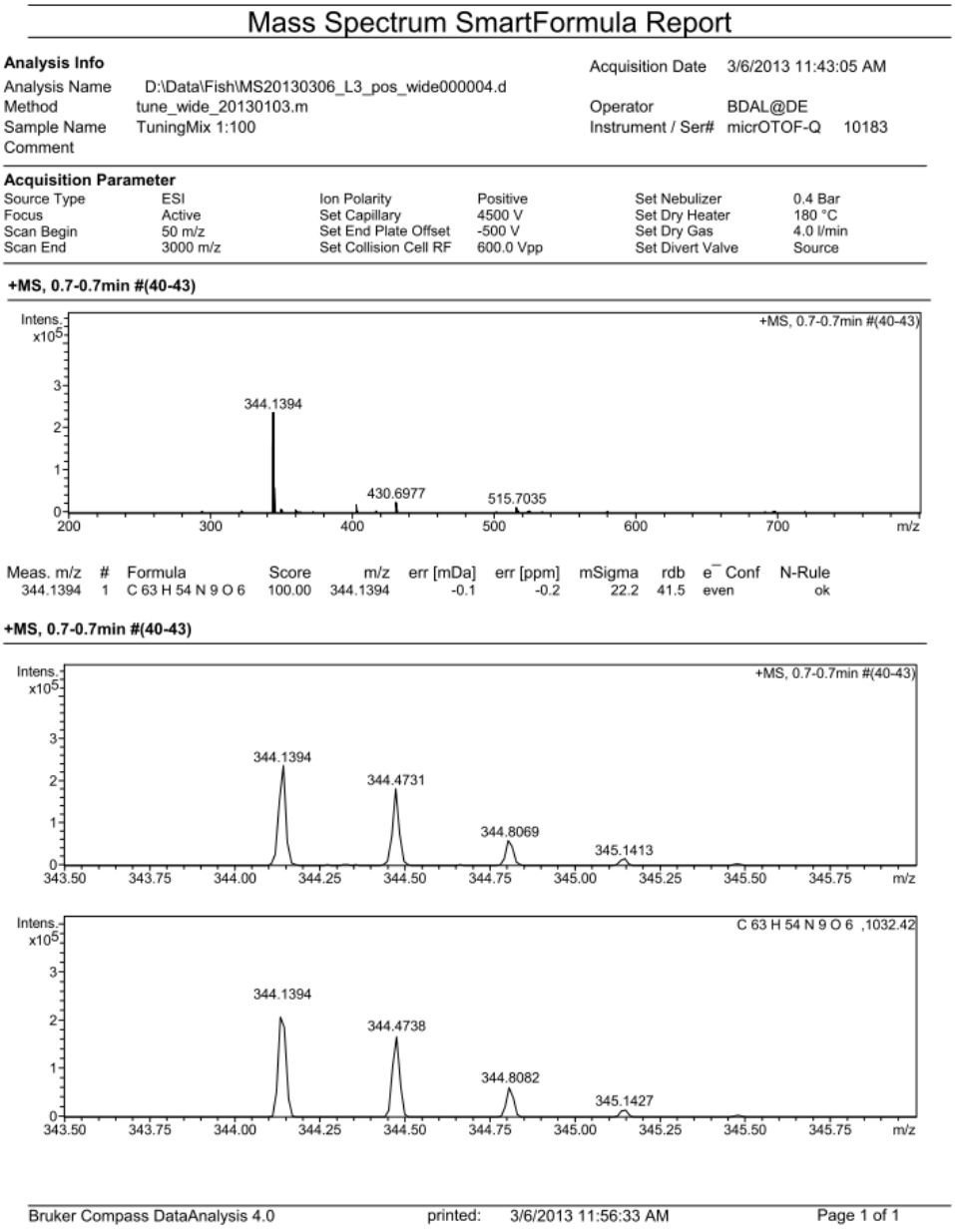


Figure S37 mass spectrum of compound [**3**][I]$_3$

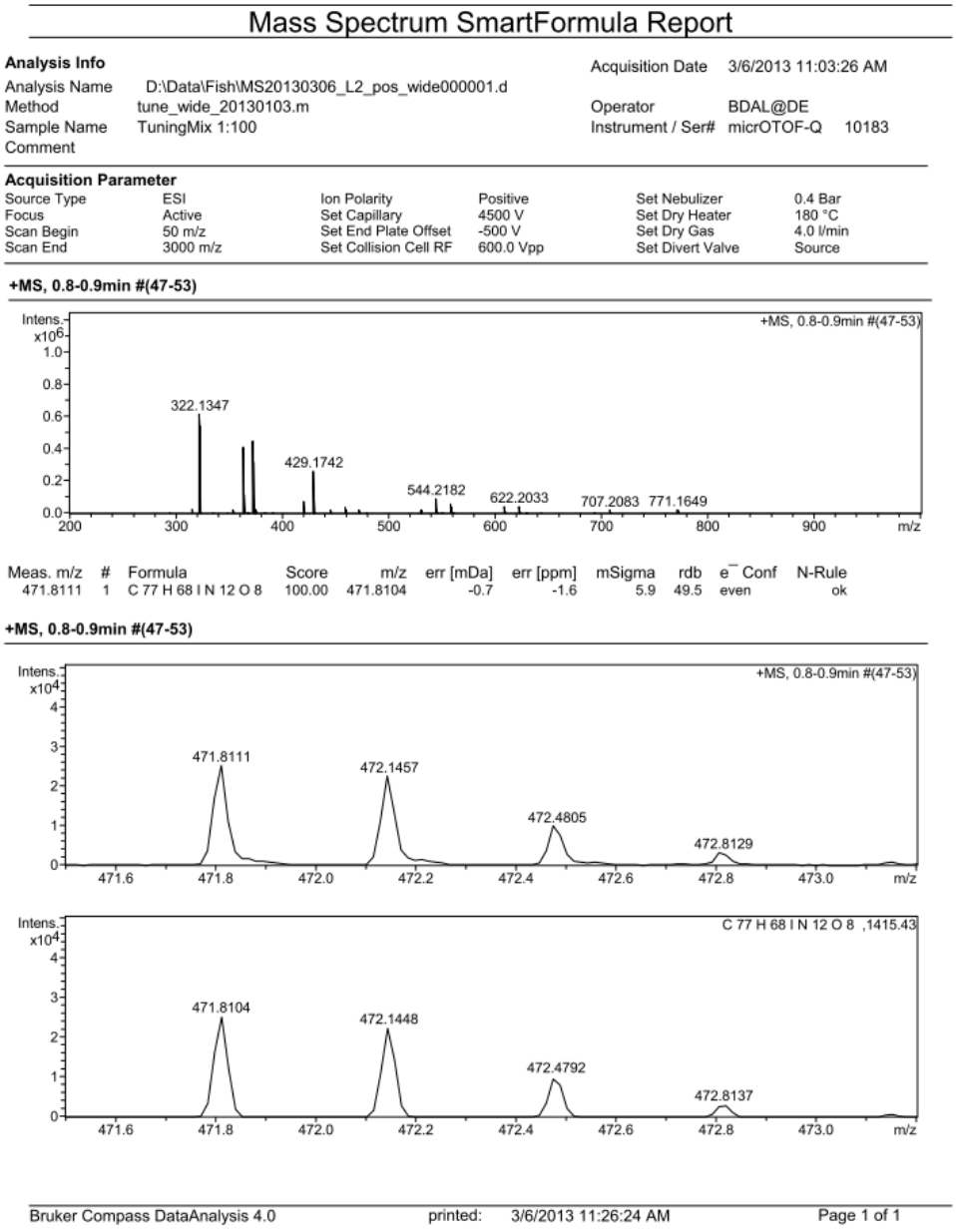


Figure S38 mass spectrum of compound [**4**][I]$_4$

Mass Spectrum SmartFormula Report

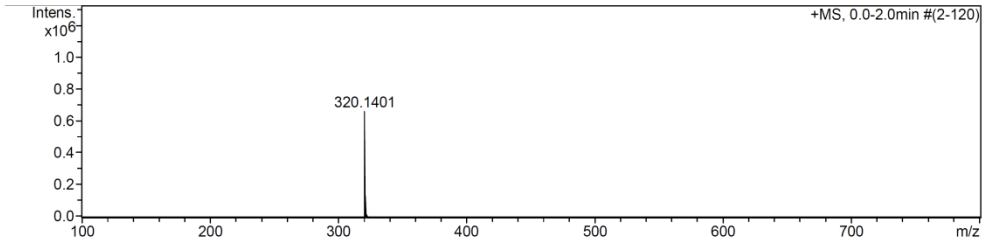
Analysis Info

Analysis Name	D:\Data\Fish\MS20140116_L9_pos_low000003.d	Acquisition Date	1/16/2014 10:34:58 AM
Method	tune_low.m	Operator	BDAL@DE
Sample Name		Instrument / Ser#	micrOTOF-Q 10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1300 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source

+MS, 0.0-2.0min #(2-120)



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	e⁻ Conf	rdb	N-Rule
320.1401	1	C 19 H 18 N 3 O 2	100.00	320.1394	-0.7	-2.2	11.3	even	12.5	ok

+MS, 0.0-2.0min #(2-120)

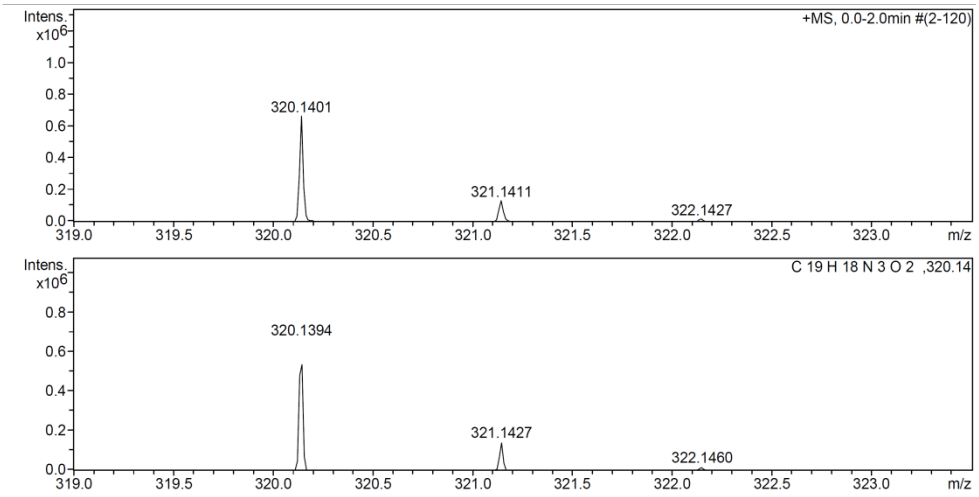


Figure S39 mass spectrum of compound [**5**][I]

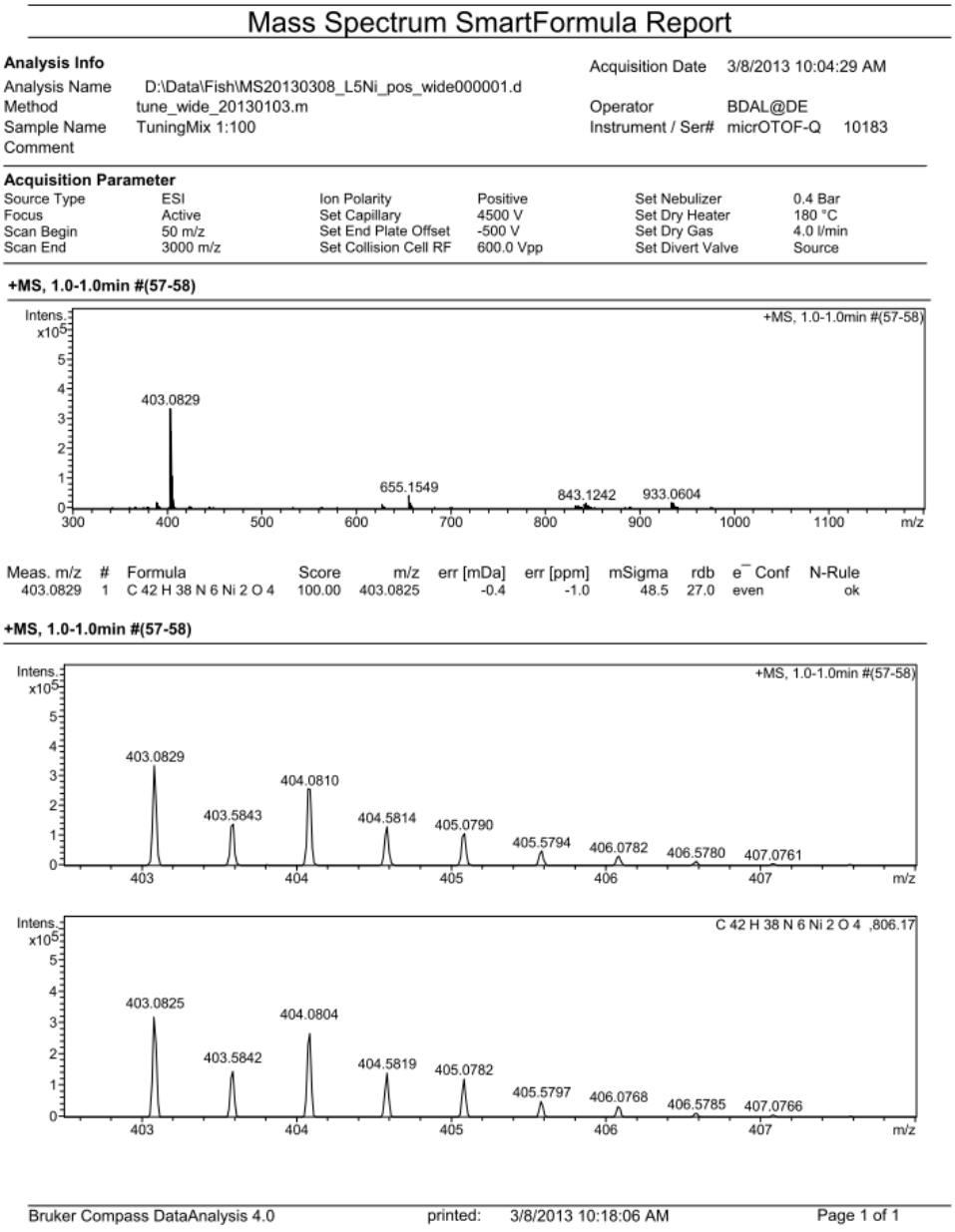


Figure S40 mass spectrum of compound [**2a**-$(NiCpI)_2$]

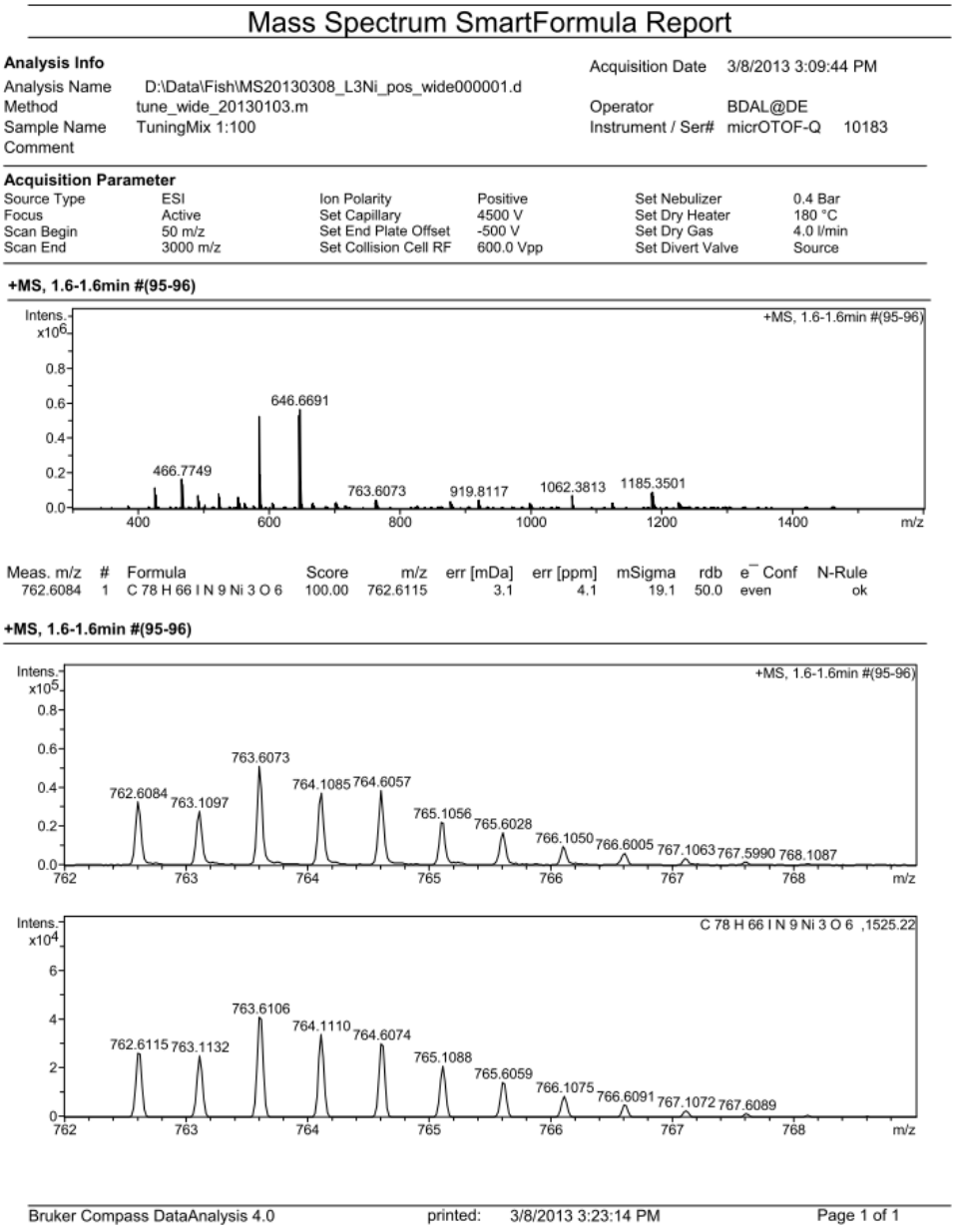


Figure S41 mass spectrum of compound [**3**-$(NiCpI)_3$]

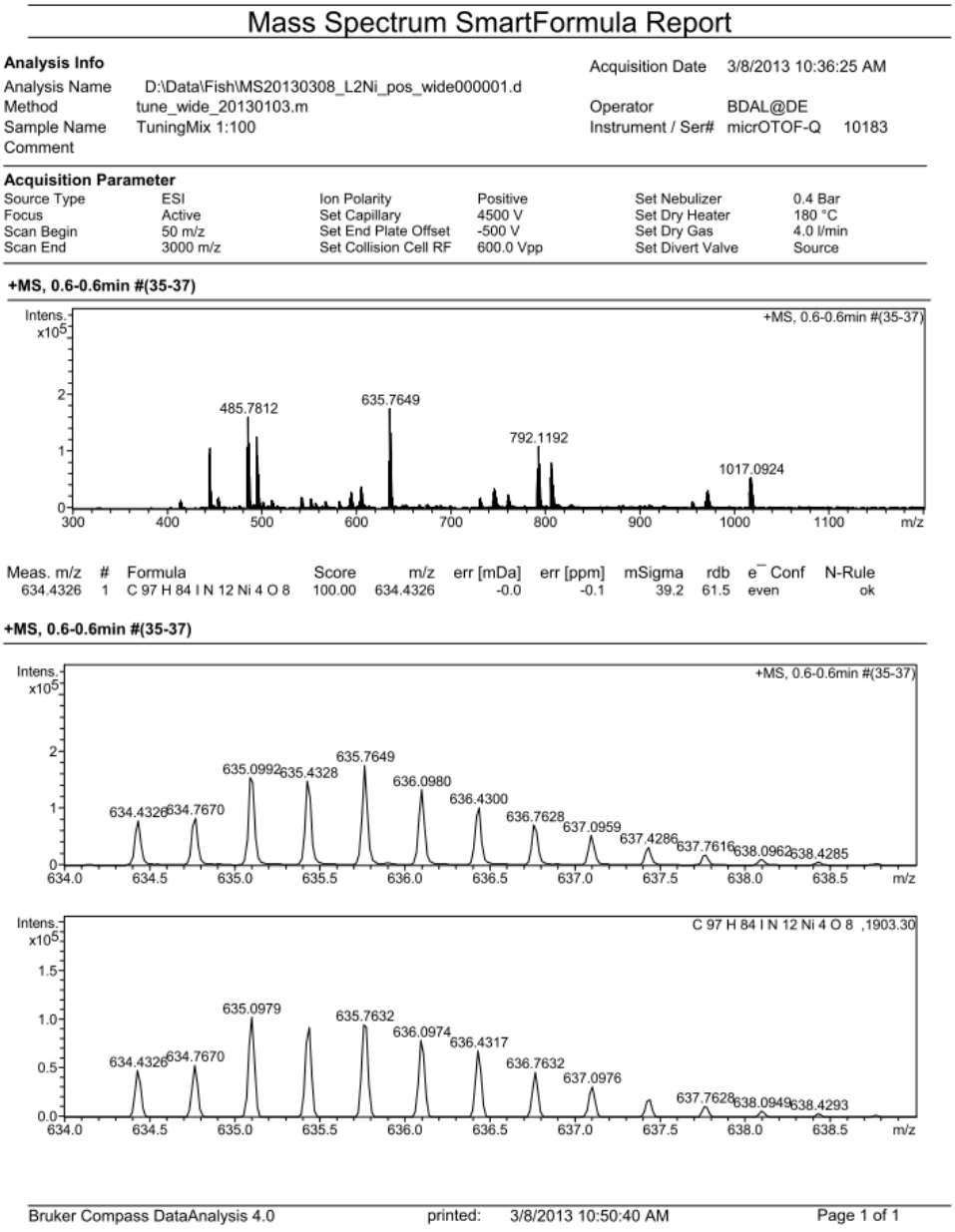


Figure S42 mass spectrum of compound [**4**-$(NiCpI)_4$]

Mass Spectrum SmartFormula Report

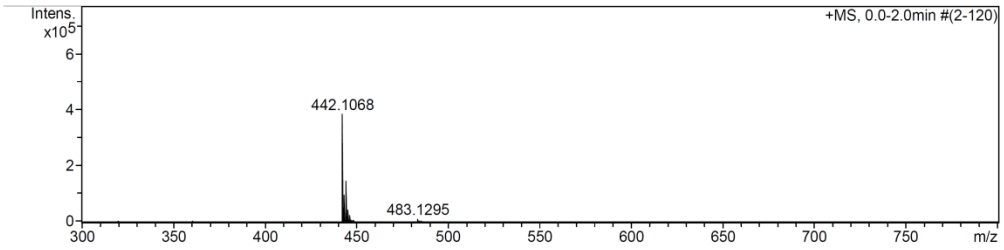
Analysis Info

Analysis Name	D:\Data\Fish\MS20140116_L9Ni_pos_low000001.d	Acquisition Date	1/16/2014 10:09:28 AM
Method	tune_low.m	Operator	BDAL@DE
Sample Name		Instrument / Ser#	micrOTOF-Q 10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1300 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source

+MS, 0.0-2.0min #(2-120)



Meas. m/z	#	Formula	m/z	Score	err [mDa]	err [ppm]	mSigma	e⁻ Conf	rdb	N-Rule
442.1068	1	C 24 H 22 N 3 Ni O 2	442.1060	100.00	-0.8	-1.9	19.1	even	15.5	ok

+MS, 0.0-2.0min #(2-120)

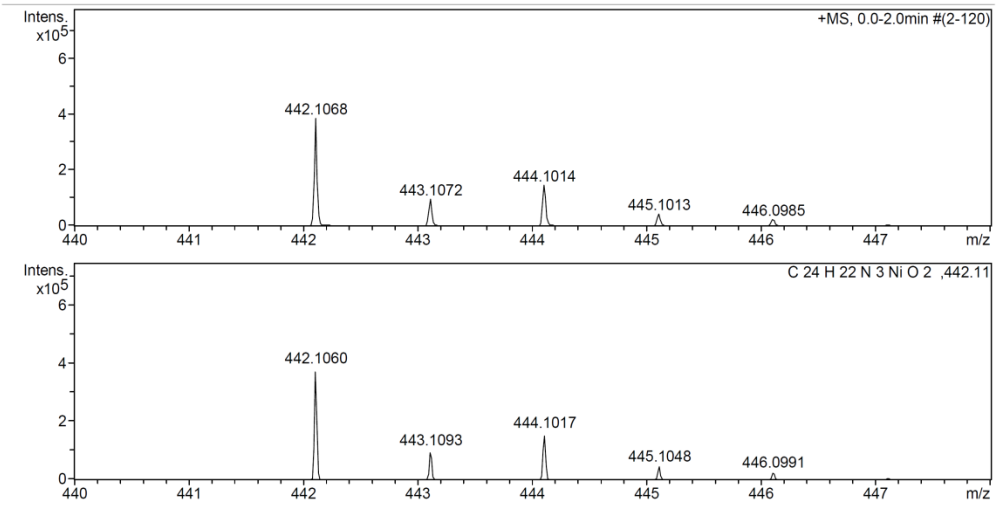


Figure S43 mass spectrum of compound [**5**-(NiCpI)]

Mass Spectrum SmartFormula Report

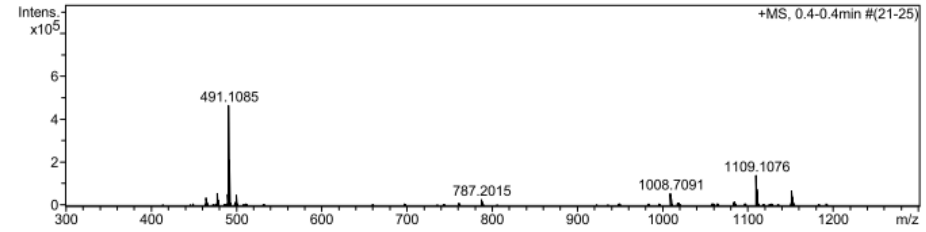
Analysis Info

Analysis Name	D:\Data\Fish\MS20130308_L5Rh_pos_wide000001.d	Acquisition Date	3/8/2013 12:07:27 PM
Method	tune_wide_20130103.m	Operator	BDAL@DE
Sample Name	TuningMix 1:100	Instrument / Ser#	micrOTOF-Q 10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

+MS, 0.4-0.4min #(21-25)



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
491.1085	1	C 48 H 52 N 6 O 4 Rh 2	100.00	491.1075	-1.0	-2.1	48.0	27.0	even	ok

+MS, 0.4-0.4min #(21-25)

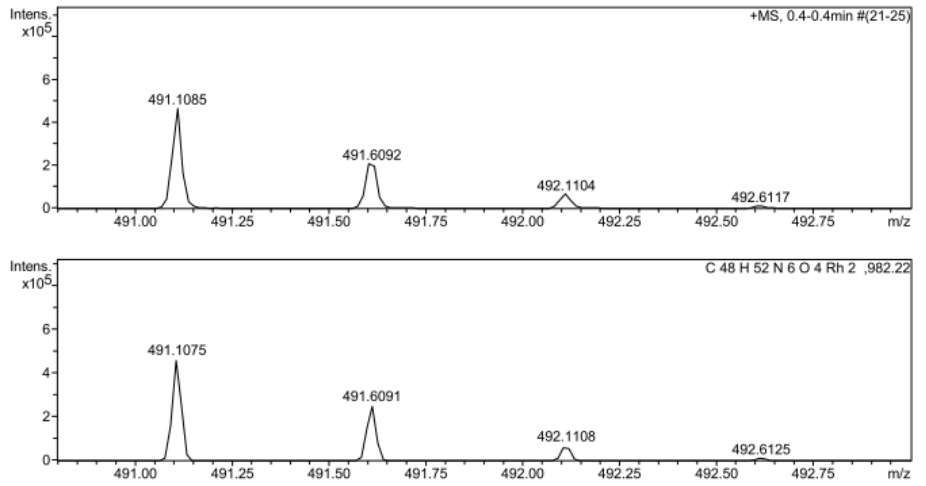


Figure S44 mass spectrum of compound [**2a**-[Rh(COD)I]$_2$]

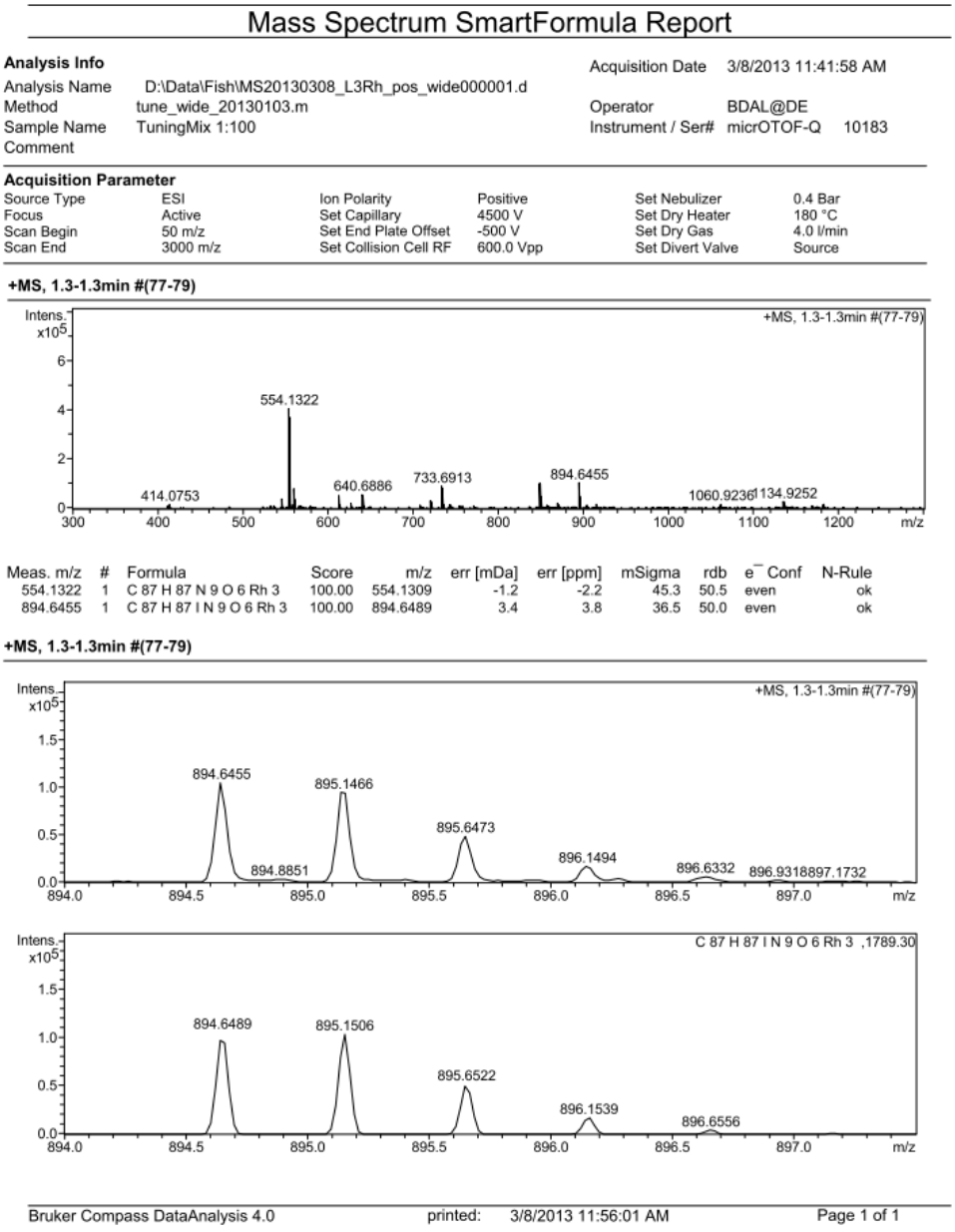


Figure S45 mass spectrum of compound [**3**-[Rh(COD)I]$_3$]

Mass Spectrum SmartFormula Report

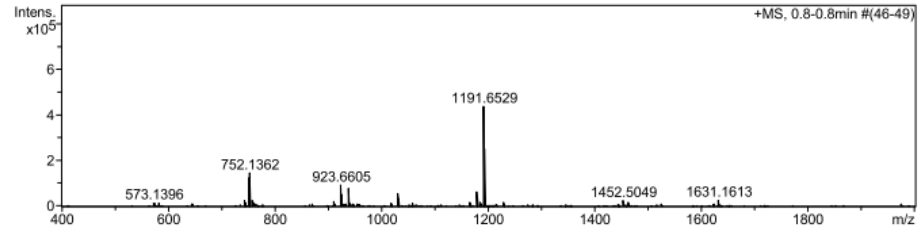
Analysis Info

Analysis Name	D:\Data\Fish\MS20130308_L2Rh_pos_wide000001.d	Acquisition Date	3/8/2013 11:17:52 AM
Method	tune_wide_20130103.m	Operator	BDAL@DE
Sample Name	TuningMix 1:100	Instrument / Ser#	micrOTOF-Q 10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

+MS, 0.8-0.8min #(46-49)



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
751.8009	1	C 109 H 112 I N 12 O 8 Rh 4	100.00	751.7991	-1.7	-2.3	19.3	61.5	even	ok
1191.1505	1	C 109 H 112 I 2 N 12 O 8 Rh 4	100.00	1191.1512	0.7	0.6	42.6	61.0	even	ok

+MS, 0.8-0.8min #(46-49)

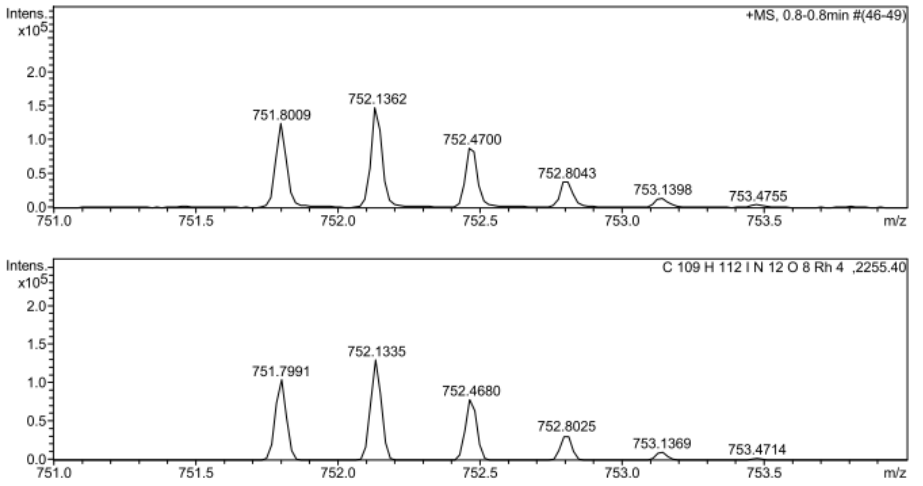


Figure S46 mass spectrum of compound [**4**-[Rh(COD)I]$_4$]

Crystal Data

Table 1 Crystal data and structure refinement for ic 15835 (compound [**2a**][$I]_2$).

Identification code	ic15835	
Empirical formula	C36 H36 I2 N8 O4	
Formula weight	898.53	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 21.0444(10) Å	α= 90°.
	b = 12.4275(5) Å	β= 114.665(2)°.
	c = 15.2824(7) Å	γ = 90°.
Volume	3632.1(3) $Å^3$	
Z	4	
Density (calculated)	1.643 g/cm^3	
Absorption coefficient	1.782 mm^{-1}	
F(000)	1784	
Crystal size	0.20 x 0.12 x 0.02 mm^3	
Theta range for data collection	1.95 to 25.00°.	
Index ranges	-23<=h<=24, -13<=k<=14, -18<=l<=18	
Reflections collected	11333	
Independent reflections	3201 [R(int) = 0.0566]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.952 and 0.865	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3201 / 0 / 229	
Goodness-of-fit on F^2	1.076	
Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.0802	
R indices (all data)	R1 = 0.0659, wR2 = 0.0968	
Largest diff. peak and hole	0.605 and -0.788 $e.Å^{-3}$	

Table 2 Crystal data and structure refinement for ic16141 (compound [**2a**-$(NiCpI)_2$])

Identification code	ic16141	
Empirical formula	C44 H40 Cl6 I2 N6 Ni2 O4	
Formula weight	1300.74	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.0998(3) Å	α= 90°.
	b = 24.2692(7) Å	β= 109.2740(13)°.
	c = 11.5148(4) Å	γ = 90°.
Volume	2400.45(13) $Å^3$	
Z	2	
Density (calculated)	1.800 g/cm^3	
Absorption coefficient	2.453 mm^{-1}	
F(000)	1284	
Crystal size	0.20 x 0.12 x 0.02 mm^3	
Theta range for data collection	1.68 to 25.00°.	
Index ranges	-10<=h<=10, -24<=k<=28, -13<=l<=13	
Reflections collected	12336	
Independent reflections	4218 [R(int) = 0.0562]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.940 and 0.674	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4218 / 15 / 288	
Goodness-of-fit on F^2	1.333	
Final R indices [I>2sigma(I)]	R1 = 0.1254, wR2 = 0.3282	
R indices (all data)	R1 = 0.1690, wR2 = 0.3470	
Largest diff. peak and hole	2.986 and -2.686 $e.Å^{-3}$	

Table 3 Crystal data and structure refinement for ic 16325 (compound [**5**][I]).

Identification code	ic16325	
Empirical formula	C19 H18 I N3 O2	
Formula weight	447.26	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 14.4332(10) Å	α= 90°.
	b = 8.5362(6) Å	β= 100.356(2)°.
	c = 15.4137(11) Å	γ = 90°.
Volume	1868.1(2) $Å^3$	
Z	4	
Density (calculated)	1.590 Mg/m^3	
Absorption coefficient	1.731 mm^{-1}	
F(000)	888	
Crystal size	0.25 x 0.25 x 0.13 mm^3	
Theta range for data collection	1.43 to 27.50°.	
Index ranges	-18<=h<=16, -11<=k<=11, -17<=l<=20	
Reflections collected	13991	
Independent reflections	4273 [R(int) = 0.0357]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8063 and 0.6715	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4273 / 0 / 228	
Goodness-of-fit on F^2	1.216	
Final R indices [I>2sigma(I)]	R1 = 0.0396, wR2 = 0.0955	
R indices (all data)	R1 = 0.0473, wR2 = 0.1068	
Largest diff. peak and hole	1.229 and -0.948 $e.Å^{-3}$	

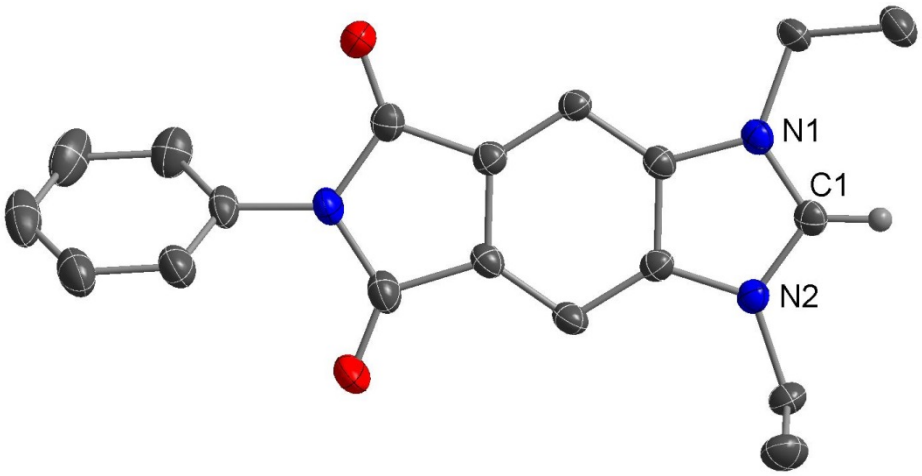


Figure S47. Molecular structure of [**5**][I]. Thermal ellipsoids were set at the 50% probability level and hydrogen atoms were omitted for clarity.