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Supporting Information

Bidentate Cycloimidate Complexes with Aliphatic and Aromatic Anagostic Bonds

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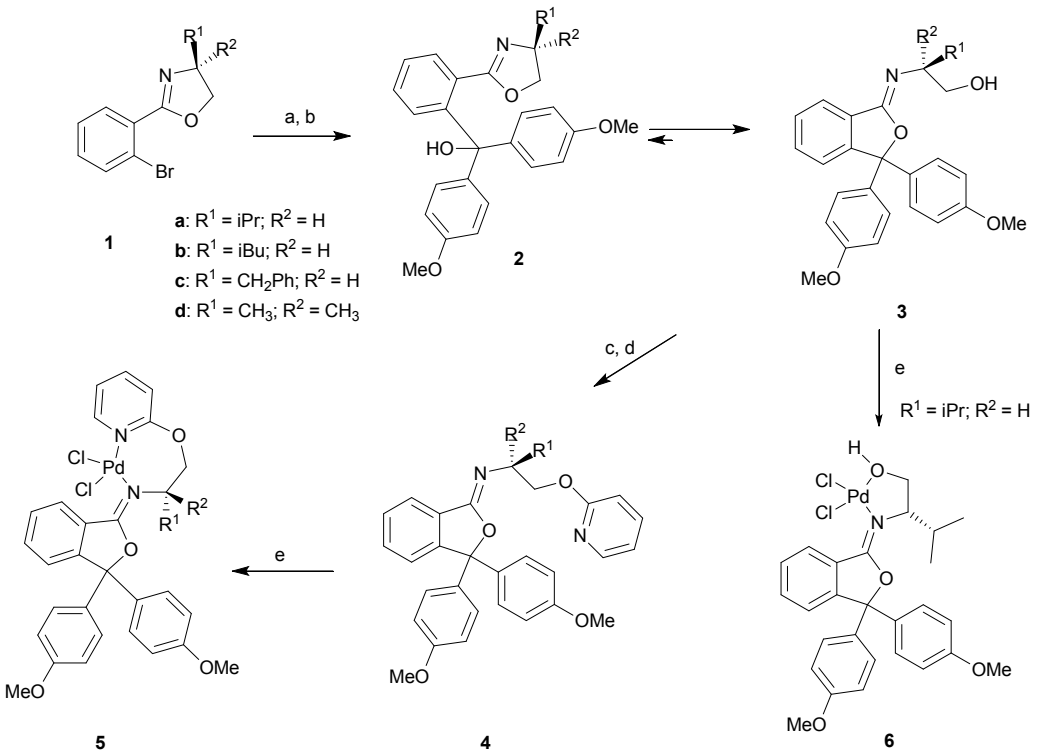
Materials and Methods

All chemicals were purchased from Sigma Aldrich, Acros Organics or Alfa Aesar and were used directly without purification unless stated otherwise. Anhydrous solvents were dried according to literature known procedures and stored under argon (99.996 %). NMR spectra were recorded on a Bruker Advance DRX-400 (^{1}H: 400.13 MHz, ^{13}C: 101.26 MHz) using the residual solvent signal as the internal standard ($CHCl_3$ = 7.26 ppm). A Bruker EQUINOX 55 FT-IR was used to record the IR spectra with a resolution of 2 cm^{-1}. Melting points were determined with the model by Dr. Tottoli from Büchi and are uncorrected. Flash column chromatography was performed with silica gel from Merck (40 – 63 µm) in glass columns applying air pressure. Using Olex2[1], the structures were solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL[2] refinement package using Least Squares minimisation. Phenyloxazolines **1a-c** were synthesized according literature procedures.[3] For the QTAIM analysis of **5d** we started from the refined structure obtained by ShelXL and re-optimized the positions of the hydrogen atoms by a geometry optimization at theDFT/BP86/def-SVP level. Then a refined electron density was computed at the DFT/BP86/def2-TZVP level. The DFT calculations were carried out with the TURBOMOLE program package[6] with the defs-SVP and def2-TZVP basis set developed by Ahlrichs *et al.*[7,8,9,10] and the QTAIM analysis with the AIMPAC[11] program suite.



2-(2-Bromophenyl)-4,4-dimethyl-2-oxazoline 1d:

The synthesis was based on the method of Marxer *et al.* with some variations.[4] 2-Bromobenzoic acid (4.00 g, 19.8 mmol) was suspended in CH_2Cl_2 (100 ml) and three drops of DMF. Thionyl chloride (2.17 ml, 3.54 g, 29.8 mmol) was added and the solution was stirred for 2 h at reflux temperature. The solvent and the excess thionyl chloride were removed in vacuum. The crude product was redissolved in CH_2Cl_2 (30 ml) and added to a solution of 2-amino-2-methyl-propan-1-ol (3.72 g, 4.00 ml, 2.00 mmol) in CH_2Cl_2 (100 ml) under ice cooling. The reaction mixture was stirred for 4 h at room temperature and filtered to remove the hydrochloride salt. The filtrate was washed with 1N hydrochloric acid (30 ml), dried over Na_2SO_4 and the solvent was removed in vacuum. Trituration with diethyl ether gave 4.80 (89 %) 2-bromo-*N*-(2-hydroxy-1,1-dimethylethyl)benzamide as a colorless solid. The benzamide (3.63 g, 16.7 mmol) was dissolved in thionyl chloride (15 ml, 24.4 g, 205 mmol) under ice cooling. The reaction mixture was stirred at room temperature for 24 h. Diethyl ether (100 ml) was added, the suspension filtered with suction and the colorless salt redissolved in CH_2Cl_2 (100ml). The solution was washed with aqueous $NaHCO_3$ solution until neutral, then dried over Na_2SO_4 and the solvent was removed in vacuum to yield **1d** (3.63 g, 85 %) as a colorless solid with mp. 36 - 38 °C (lit. 38 - 40 °C[5]).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.41 ppm (s, 6H), 4.13 (s, 2H), 7.19 – 7.38 (m, 2H), 7.54 – 7.68 (m, 2H).

General procedure for the preparation of compounds 3a-d

A solution of phenyloxazoline (6.0 - 10 mmol) **1a-d** in anhydrous THF (100 ml), cooled to -89 °C and (3.0 - 7.0 ml) *n*-butyllithium (1.6 M in hexane) was added dropwise within 10 min. The deep orange solution was stirred for 40 min at this temperature and 4,4'-dimethoxybenzophenone was added. The reaction mixture was warmed to room temperature and stirred for 16 h. The mixture was hydrolysed with brine (30 ml), diluted with MTBE (100 ml) and the phases were separated. The organic phase was dried over Na_2SO_4 and the solvent was evaporated in vacuum. The crude product was purified by flash column chromatography to yield **3a-d**.

(S,Z)-2-((3,3-Bis(4-methoxyphenyl)isobenzofuran-1(3H)-ylidene)amino)-3-methylbutan-1-ol 3a:

According to the general procedure phenyl oxazoline **1a** (2.53 g, 9.00 mmol), *n*-butyllithium (6.9 ml, 11.0 mmol) and 4,4'-dimethoxybenzophenone (1.46 g, 6.00 mmol) were used. The crude product was purified by flash column chromatography (SiO_2, PE/EtOAc 1:3). The fraction with R_f = 0.30 gave imidate **3a** (2.25 g, 87 %) as a colourless solid with mp. 43 - 47 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.78 ppm (d, J = 6.8 Hz, 3H), 0.86 (d, J = 6.7 Hz, 3H), 1.78 – 1.88 (m, 1H), 2.57 (s, 1H), 3.66 (d, J = 1.8 Hz, 7H), 3.84 (td, J = 6.8, 4.3 Hz, 1H), 6.69 – 6.76 (m, 5H), 7.10 (d, J = 8.8 Hz, 2H), 7.14 (d, J = 8.8 Hz, 2H), 7.18 – 7.25 (m, 2H), 7.31 – 7.37 (m, 1H), 7.77 (d, J = 7.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 19.59 ppm (CH_3), 19.76 (CH_3), 30.45 (CH), 55.31 (OMe), 64.12 (CH), 64.74 (CH_2O), 92.94 (Ar_3C), 113.58, 113.73, 123.56, 123.80, 128.34, 128.64, 128.67, 130.18, 131.36, 134.74, 149.31 (all Ar), 159.15 (C=N), 159.38 (COMe), 159.40 (COMe).

MS(FAB): *m/z* (%): 456 (20) $[M+Na]^+$, 435 (30), 434 (93), 433 (60) $[M]^+$, 416 (15), 329 (75), 330 (100).

IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1} (w), 3225 (w), 3064 (w), 2954 (w), 1622 (m), 1550 (s), 1508 (s), 1465 (w), 1248 (s), 1175 (m), 1030 (m), 844 (w), 568 (w).

(S,Z)-2-((3,3-Bis(4-methoxyphenyl)isobenzofuran-1(3H)-ylidene)amino)-4-methylpentan-1-ol 3b:

According to the general procedure phenyloxazoline **1b** (2.50 g, 8.90 mmol), *n*-butyllithium (5.70 ml, 9.12 mmol) and 4,4'-dimethoxybenzophenone (1.44 g, 5.93 mmol) were used. The crude product was purified by flash column chromatography (SiO_2, PE/EtOAc 1:3). The fraction with R_f = 0.33 gave imidate **3b** (2.29 g, 88 %) as a colourless solid with mp. 57 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80 ppm (d, *J* = 6.4 Hz, 3H), 0.87 (d, *J* = 6.5 Hz, 3H), 1.20 – 1.38 (m, 1H), 1.40 – 1.63 (m, 2H), 2.38 (s, 1H), 3.68 (tdd, *J* = 17.7, 10.4, 6.9 Hz, 2H), 3.78 (d, *J* = 3.1 Hz, 6H), 4.21 – 4.29 (m, 1H), 6.83 (dd, *J* = 8.6, 7.1 Hz, 4H), 7.18 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 2H), 7.37 (dd, *J* = 12.4, 7.6 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 22.49 (CH_3) ppm, 23.45 (CH_3), 25.17 (CH_2), 41.83 (CH_2), 55.40 (OMe), 56.54 (CH), 67.08 (CH_2O), 93.18 (Ar_3C), 113.59, 113.80, 123.71, 123.82, 128.34, 128.77, 130.24, 131.47, 134.71, 134.81, 149.25, 159.33 (C=N), 159.46 (OMe), 159.51 (COMe).

MS(FAB): *m/z* (%): 446 (100) $[M+H]^+$, 414 (18) $[M-CH_2OH]^+$, 330 (14),238 (12).

IR(KBr): $\tilde{\nu}$ = 3359 cm^{-1} (b), 3072 (w), 3001 (w), 2952 (s), 2931 (s), 2866 (m), 2836 (m), 1688 (vs), 1608 (s),1582 (w), 1511 (vs), 1465 (s), 1441 (m), 1299 (s), 1252 (vs), 1176 (s), 1162 (m), 1105 (m), 1071 (m), 1033 (s), 969 (m), 949 (m), 830 (s), 776 (w), 751 (m), 677 (w), 603 (w), 599 (m).

(S,Z)-2-((3,3-Bis(4-methoxyphenyl)isobenzofuran-1(3H)-ylidene)amino)-3-phenylpropan-1-ol 3c:

According to the general procedure phenyloxazoline **1c** (1.96 g, 6.12 mmol), *n*-butyllithium (3.90 ml, 6.20 mmol) and 4,4'-dimethoxybenzophenone (753 mg, 3.11 mmol) were used. The crude product was purified by flash column chromatography (SiO_2, PE/EtOAc 1:4). The fraction with R_f = 0.37 gave imidate **3c** (1.37 g, 92 %) as a colourless solid with mp. 51 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.34 ppm (s, 2H), 2.80 – 2.98 (m, 2H), 3.60 – 3.77 (m, 2H), 3.78 (s, 3H), 4.31 – 4.44 (m, 1H), 6.76 – 6.85 (m, 4H), 7.01 – 7.05 (m, 2H), 7.12 – 7.27 (m, 7H), 7.34 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.40 (td, *J* = 7.5, 1.1 Hz, 1H), 7.47 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.87 (dt, *J* = 7.5, 1.0 Hz, 1H).

^{13}C NMR (101 MHz, CDCl3) δ = 38.93 ppm ($PhCH_2$), 55.39 (OMe), 55.41 (OMe), 59.88 (CH), 65.63 (CH_2O), 93.40 (Ar_3C), 113.75, 113.78, 113.90, 123.69, 123.71, 123.83, 126.06, 128.31, 128.37, 128.61, 128.68, 128.71, 128.78, 129.29, 129.34, 129.59, 130.14, 131.56, 134.64, 134.80, 139.57, 149.28, 159.38 (C=N), 159.53 (COMe).

MS(FAB) *m/z* (%): 480 (100) $[M]^+$, 388 (12) , 330 (10), 307 (12), 154 (63), 136 (43), 107 (13), 91 (20) .

IR(KBr): $\tilde{\nu}$ = 3368 cm^{-1} (w), 2930 (m), 1685 (s), 1510 (s), 1252 (s), 1032 (s).

(Z)-2-((3,3-Bis(4-methoxyphenyl)isobenzofuran-1(3H)-ylidene)amino)-2-methylpropan-1-ol 3d:

According to the general procedure phenyloxazoline **1d** (2.57 g, 9.71 mmol), *n*-butyllithium (6.1 ml, 9.71 mmol) and 4,4'-dimethoxybenzophenone (1.81g , 7.47 mmol) were used. The crude reaction product was purified by flash column chromatography (SiO_2, PE/EtOAc 1:4). The fraction with R_f = 0.25 gave imidate **3d** (2.57 g, 82 %) as a colourless solid with mp. 127 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.39 ppm (s, 6H), 3.08 (t, *J* = 6.1 Hz, 1H), 3.44 (d, *J* = 5.8 Hz, 2H), 3.79 (s, 6H), 6.84 (d, *J* = 8.8 Hz, 4H), 7.22 (d, *J* = 8.8 Hz, 4H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.42 (dd, *J* = 7.1, 1.2 Hz, 1H), 7.46 – 7.52 (m, 1H), 7.78 (d, *J* = 7.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 22.56 ppm (CH_3), 55.40 (OCH_3), 73.12 (CH_2O), 113.07 (Ar_3C), 113.73, 123.68, 123.90, 128.53, 128.72, 129.15, 131.37, 131.41, 134.93, 148.35, 157.07 (C=N), 159.44 (COMe).
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MS(FAB) *m/z* (%): 440 (5) $[M+Na]^+$, 418 (100) $[M+H]^+$.

IR(KBr): $\tilde{\nu}$ = 3363 cm^{-1} (m), 2953 (m), 2834 (m), 1650 (s), 1608 (s), 1583 (s), 1500 (s), 1462 (s), 1440 (m), 1416 (m), 1307 (s), 1295 (s), 1280 (s), 1175 (s), 1161 (s), 1067 (s), 1032 (s), 964 (s), 830 (s), 590 (s).

General procedure for the preparation of ligands 4a-d

Sodium hydride (60% in mineral oil, 2 eq.) was added to a solution of dihydroisobenzofuran **3a-d** in THF (10 ml). The reaction mixture was stirred for 5 min and 2-fluoropyridine (2 eq.) was added. The solution was further stirred over night at room temperature. The suspension was treated with water (10 ml) and diluted with MTBE (50 ml). The organic phase was separated, washed with brine (30 ml), dried over Na_2SO_4 and the solvent was evaporated in vacuum. The crude product was purified by flash column chromatography (SiO_2) to give a viscous colourless oil.

(S,Z)-*N*-(3,3-Bis(4-methoxyphenyl)isobenzofuran-1(3H)-ylidene)-3-methyl-1-(pyridin-2-yloxy)butan-2-amine 4a:

According to the general procedure **3a** (300 mg, 0.695 mmol) was dissolved in THF and sodium hydride (169 mg, 2.43 mmol) was added. Subsequently 2-fluoropyridine (236 mg, 209 µl, 2.43 mmol) was added and the reaction mixture was stirred overnight. The crude product was purified by flash column chromatography (PE/EtOAc 1:1). The fraction with $R_f = 0.45$ resulted in **4a** (241 mg, 68 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.01 ppm (dd, J = 12.4, 6.7 Hz, 6H), 1.98 – 2.09 (m, 1H), 3.79 (d, J = 4.1 Hz, 6H), 4.24 – 4.37 (m, 2H), 4.60 (dd, J = 9.9, 3.5 Hz, 1H), 6.39 (d, J = 8.4 Hz, 1H), 6.77 (ddd, J = 7.0, 5.1, 0.8 Hz, 1H), 6.79 – 6.85 (m, 4H), 7.24 (dd, J = 16.4, 8.9 Hz, 4H), 7.35 – 7.50 (m, 4H), 7.89 (d, J = 7.5 Hz, 1H), 8.11 (ddd, J = 5.1, 2.0, 0.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 19.06 (CH_3) ppm, 20.05 (CH_3), 30.83 (CH), 55.38 (OMe), 55.40 (OMe), 61.40 (CH), 68.39 (CH_2O), 92.47 (Ar_3C), 111.47, 113.62, 113.65, 116.34, 123.53, 123.96, 128.58, 128.62, 130.67, 131.19, 135.20, 135.32, 138.18, 146.87, 149.39, 158.39 (C=N), 159.35 (COMe), 159.37 (COMe), 164.31 (PyO).

MS(FAB) *m/z* (%): 531 (8), 510 (36), 509 (100), 415 (26), 414 (73), 400 (18), 330 (19), 238 (16).

IR(KBr): $\tilde{\nu}$ = 2956 cm^{-1} (w), 2835 (w), 1696 (s), 1609 (m), 1594 (m), 1569 (w), 1510 (s), 1474 (m), 1462 (m), 1430 (m), 1309 (m), 1287 (m), 1252 (s), 1176 (m), 1034 (w), 830 (w), 751 (w), 584 (w).

(S,Z)-*N*-(3,3-Bis(4-methoxyphenyl)isobenzofuran-1(3H)-ylidene)-1-phenyl-3-(pyridin-2-yloxy)propan-2-amine 4b:

According to the general procedure **3b** (457 mg, 1.02 mmol) was dissolved in THF and sodium hydride (82 mg, 2.04 mmol) was added. Subsequently 2-fluoropyridine (198 mg, 168 µl, 2.04 mmol) was added and the reaction mixture was stirred overnight. The crude product was purified by flash column chromatography (PE/EtOAc 1:1). The fraction with $R_f = 0.53$ resulted in **4b** (341 mg, 65 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80 ppm (d, J = 6.3 Hz, 4H), 0.90 (d, J = 6.3 Hz, 4H), 1.46 (td, J = 10.5, 5.2 Hz, 1H), 1.63 (td, J = 11.0, 9.1, 4.1 Hz, 2H), 3.79 (d, J = 3.1 Hz, 7H), 4.30 (dd, J = 10.2, 7.8 Hz, 1H), 4.44 (dd, J = 10.2, 4.3 Hz, 1H), 4.55 – 4.67 (m, 1H), 6.45 – 6.52 (m, 1H), 6.74 – 6.84 (m, 6H), 7.18 – 7.22 (m, 2H), 7.25 – 7.31 (m, 3H), 7.35 – 7.51 (m, 5H), 7.89 (d, J = 7.5 Hz, 1H), 8.09 – 8.15 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 21.89 ppm (CH_3), 23.78 (CH_3), 25.07 (CH_2), 42.14 (CH_2), 53.99 (CH), 55.41 (OMe), 70.22 (CH_2O), 92.72 (Ar_3C), 111.38, 113.56, 113.60, 113.68, 116.42, 123.61, 123.95, 128.47, 128.51,

128.65, 128.69, 128.77, 130.54, 131.27, 134.98, 135.29, 138.27, 146.92, 149.29, 158.70 (C=N), 159.35 (COMe), 159.44 (COMe), 164.25 (PyO).

MS(FAB) *m/z* (%): 523 (40) $[M+H]^+$, 428 (100) $[M-C_5H_4NO]^+$, 414 (18) $[M-C_7H_6O]^+$, 330 (24) $[M-C_{11}H_{16}N_2O]^+$, 238 (18) $[M-C_{18}H_{23}NO_2]^+$, 178 (29), 96 (41) $[M-C_{28}H_{28}NO_3]$+.

IR(KBr): $\tilde{\nu}$= 2953 cm^{-1} (m), 2931 (m), 2867 (w), 2835 (w), 1695 (s), 1609 (m), 1596 (m), 1569 (m), 1511 (s), 1475 (m), 1464 (m), 1431 (s), 1309 (m), 1287 (s), 1252 (s), 1176 (m), 1162 (w), 1102 (w), 1075 (w), 1034 (m), 1017 (m), 949 (w), 969 (w),830 (m), 778 (m), 751 (w), 678 (w).

(S,Z)-*N*-(3,3-Bis(4-methoxyphenyl)isobenzofuran-1(3H)-ylidene)-4-methyl-1-(pyridin-2-yloxy)pentan-2-amine 4c:

According to the general procedure **3c** (400 mg, 0.834 mmol) was dissolved in THF and sodium hydride (100 mg, 2.50 mmol) was added. Subsequently 2-fluoropyridine (244 mg, 214 µl, 2.50 mmol) was added and the reaction mixture was stirred overnight. The crude product was purified flash column by chromatography (PE/EtOAc 1:2). The fraction with R_f = 0.28 resulted in **4c** (406 mg, 88 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.97 ppm (dd, *J* = 13.4, 8.4 Hz, 1H), 3.11 (dd, *J* = 13.5, 5.0 Hz, 1H), 3.79 (d, *J* = 1.3 Hz, 6H), 4.38 (dd, *J* = 10.3, 7.3 Hz, 1H), 4.51 (dd, *J* = 10.3, 4.7 Hz, 1H), 4.78 (ddt, *J* = 8.3, 7.2, 4.9 Hz, 1H), 6.49 (dt, *J* = 8.4, 0.9 Hz, 1H), 6.71 – 6.84 (m, 5H), 6.88 – 6.92 (m, 2H), 7.10 – 7.25 (m, 5H), 7.25 – 7.33 (m, 3H), 7.37 – 7.49 (m, 3H), 7.88 (dt, *J* = 7.4, 1.1 Hz, 1H), 8.10 (ddd, *J* = 5.1, 2.2, 0.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 39.55 ppm (CH_2), 55.39 (OMe), 55.41 (OMe), 57.55 ($PhCH_2$), 69.16 (CH_2O), 92.82 (Ar_3C), 111.33, 113.65, 113.67, 116.51, 123.51, 123.93, 125.88, 128.15, 128.29, 128.62, 128.78, 129.64, 130.35, 131.31, 134.94, 135.11, 138.32, 139.72, 146.91, 149.34, 158.90 (C=N), 159.24 (COMe), 159.42 (COMe), 164.13 (PyO).

MS(FAB) *m/z* (%): 557 (67) $[M]^+$, 462 (100) $[M-C_5H_4NO]^+$, 330 (23) $[M-C_{14}H_{14}N_2O]^+$, 212 (23), 91 (50) $[C_7H_7]^+$.

IR(KBr): $\tilde{\nu}$= 2933 cm^{-1} (w), 1696 (s), 1510 (s), 1252 (s), 1034 (s).

(Z)-*N*-(3,3-Bis(4-methoxyphenyl)isobenzofuran-1(3H)-ylidene)-2-methyl-1-(pyridin-2-yloxy)propan-2-amine 4d:

According to the general procedure **3a** (208 mg, 0.500 mol) was dissolved in THF and sodium hydride (60.0 mg, 1.50 mmol) was added. Subsequently 2-fluoropyridine (145 mg, 128 µl, 1.50 mmol) was added and the reaction mixture was stirred for 16 h. The crude product was purified by flash column chromatography (PE/EtOAc 1:1). The fraction with $R_f = 0.41$ resulted in **4a** (177 mg, 72 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.52 ppm (s, 6H), 3.76 (s, 6H), 4.45 (s, 2H), 6.72 – 6.78 (m, 1H), 6.83 (ddd, *J* = 7.0, 5.0, 1.0 Hz, 1H), 7.17 – 7.21 (m, 4H), 7.31 (dt, *J* = 7.5, 0.9 Hz, 1H), 7.39 (td, *J* = 7.4, 1.2 Hz, 1H), 7.46 (td, *J* = 7.4, 1.2 Hz, 1H), 7.52 (ddd, *J* = 8.5, 7.1, 2.0 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 8.14 (dd, *J* = 5.4, 1.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 25.15 ppm (CH_3), 55.35 (OMe), 56.34 (OMe), 74.54 (CH_2O), 93.64 (Ar_3C), 111.40, 113.59, 116.42, 123.52, 124.24, 128.54, 128.57, 131.09, 131.76, 135.16, 138.38, 147.00, 148.27, 155.72 (C=N), 159.30 (COMe), 164.70 (PyO)

MS(FAB) *m/z* (%): 517 (7) $[M+Na]^+$, 495 (100) $[M+H]^+$.

IR(KBr): $\tilde{\nu}$= 3430 cm^{-1} (w), 2966 (m), 2834 (m), 1696 (s), 1608 (s), 1568 (s), 1510 (s), 1465 (s), 1431 (s), 1287 (s), 1252 (s), 1175 (s), 1074 (m), 1033 (m), 966 (m), 949 (m), 829 (m), 829 (m), 777 (m), 750 (m), 677 (m), 585 (m).

General procedure for the complexation of ligands 4a-d with $(MeCN)_2PdCl_2$

Ligand **4a-d** and $(MeCN)_2PdCl_2$ were dissolved in 10 ml dichloromethane and stirred for 1h at room temperature, the yellow solution changed to orange within minutes. The solvent was removed in vacuum and the resulting orange crude product was washed with *n*-hexane (3 x 2 ml) in order to remove the excess ligand. Analytically pure samples and crystals suitable for X-ray analysis could be prepared by recrystallization from CH_2Cl_2 / *n*-hexane.

<u>Palladium complex 5a:</u>

According to the general procedure $(MeCN)_2PdCl_2$ (39.4 mg, 152 µmol) and **4a** (79 mg, 155 µmol) were used to give the complex **5a** after evaporation of the solvent and washing with *n*-hexane in almost quantitative yield (101 mg, 97 %) as an orange solid with mp. 213 °C (dec.).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.83 ppm (d, *J* = 6.5 Hz, 3H), 1.13 (d, *J* = 6.7 Hz, 3H), 2.87 – 2.98 (m, 1H), 3.77 (d, *J* = 0.5 Hz, 6H), 4.02 (td, *J* = 10.6, 3.4 Hz, 1H), 4.73 (dd, *J* = 12.5, 3.4 Hz, 1H), 6.57 (dd, *J* = 8.4, 0.9 Hz, 1H), 6.71 – 6.83 (m, 5H), 6.89 (dd, *J* = 9.3, 2.6 Hz, 2H), 7.03 – 7.09 (m, 2H), 7.30 (dd, *J* = 15.5, 7.9 Hz,

2H), 7.49 (ddd, *J* = 8.6, 7.1, 1.9 Hz, 1H), 7.64 (td, *J* = 7.6, 0.9 Hz, 1H), 7.71 – 7.78 (m, 1H), 8.94 (dd, *J* = 6.2, 1.7 Hz, 1H), 11.04 (d, *J* = 7.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 19.37 ppm (CH_3), 21.24 (CH_3), 29.68 (*i*Pr), 55.45 (OMe), 55.50 (OMe), 70.43 (CH_2O), 71.31 (CH_2O), 97.73 (Ar_3C), 113.91, 113.93, 113.97, 115.14, 117.87, 123.74, 126.16, 127.71, 127.77, 127.80, 129.24, 129.26, 129.78, 131.23, 132.71, 134.01, 140.89, 151.31, 151.50 (PyH), 159.85 (COMe), 160.26 (COMe), 164.94 (C=N), 166.61 (PyO).

MS(FAB) *m/z* (%): 1335 (17), 1300 (4), 781 (4), 709 (24), 613 (72), 509 (40), 414 (72), 301 (100).

IR(KBr): $\tilde{\nu}$ = 3452 cm^{-1} (w), 2958 (w), 2928 (w), 1735 (w), 1658 (s), 1607 (s), 1510 (s), 1480 (m), 1465 (m), 1297 (m), 1255 (s), 1177 (m), 1027 (m), 835 (m), 776 (m), 583 (w).

Elemental analysis **$C_{32}H_{32}Cl_2N_2O_2Pd \cdot 1.2\ CH_2Cl_2$**:
calculated: C 52.76 H 4.59 N 3.71
found: C 52.57 H 4.80 N 3.71

<u>Palladium complex 5b:</u>

According to the general procedure $(MeCN)_2PdCl_2$ (47.0 mg, 181 µmol) and **4b** (97.0 mg, 186 µmol) were used to give the complex **5b** after evaporation of the solvent and washing with *n*-hexane in 94 % yield (125 mg) as an orange solid with mp. 142 °C (dec.).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.72 ppm (d, *J* = 5.9 Hz, 3H), 0.86 (d, *J* = 6.1 Hz, 4H), 1.54 (dd, *J* = 13.5, 4.1 Hz, 1H), 2.43 (t, *J* = 9.2 Hz, 1H), 3.77 (d, *J* = 2.0 Hz, 7H), 4.40 (d, *J* = 3.3 Hz, 0H), 4.50 (dd, *J* = 12.7, 3.5 Hz, 1H), 6.64 (dd, *J* = 8.5, 1.4 Hz, 1H), 6.73 – 6.83 (m, 5H), 6.96 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.9 Hz, 2H), 7.20 – 7.29 (m, 1H), 7.29 – 7.34 (m, 1H), 7.49 – 7.55 (m, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 8.96 (dd, *J* = 6.3, 2.0 Hz, 1H), 10.96 (d, *J* = 7.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 22.05 (CH_3) ppm, 22.77 (CH_3), 24.90 (CH_2), 39.11 (CH), 55.49 (OMe), 62.67 (CH), 72.26 (CH_2O), 97.93 (Ar_3C), 113.91, 114.02, 115.27, 117.99, 123.76, 126.25, 127.75, 127.83, 128.65, 129.36, 129.73, 131.38, 132.54, 134.00, 140.94, 151.10, 151.56 (PyH), 159.88 (COMe), 160.30 (COMe), 164.88 (C=N), 166.40 (PyO).

MS(FAB): *m/z* (%): 723 (30) $[M+Na]^+$, 627 (100) $[M-C_5H_{12}]^+$, 523 (16), 428 (53) $[M-C_5H_4Cl_2NOPd]^+$, 307 (31).

IR(KBr): $\tilde{\nu}$ = 2955 cm^{-1} (w), 2926 (w), 1653 (s), 1608 (m), 1511 (s), 1489 (m), 1465 (m), 1428 (w), 1296 (m), 1255 (s), 1177 (m), 1133 (w), 1027 (m), 824 (w), 776 (w), 738 (w), 625 (w).

Elemental analysis **$C_{33}H_{34}Cl_2N_2O_2Pd$**:
calculated: C 56.63 H 4.90 N 4.00
found: C 56.21 H 4.76 N 3.82

Palladium complex 5c:

According to the general procedure $(MeCN)_2PdCl_2$ (44.1 mg, 170 µmol) and **4c** (100 mg, 179 µmol) were used to give the complex **5c** after evaporation of the solvent and washing with *n*-hexane in 92 % yield (115 mg) as an orange solid with mp. 184 - 188°C (dec.).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.40 – 3.45 ppm (m, 2H), 3.77 (s, 6H), 4.40 – 4.54 (m, 2H), 6.57 (dd, *J* = 8.5, 1.3 Hz, 1H), 6.74 – 6.82 (m, 5H), 6.87 – 6.96 (m, 4H), 7.12 – 7.17 (m, 1H), 7.19 – 7.24 (m, 2H), 7.29 – 7.37 (m, 3H), 7.52 (ddd, *J* = 8.7, 7.1, 1.9 Hz, 1H), 7.59 (dd, *J* = 12.6, 10.5 Hz, 1H), 7.66 (td, *J* = 7.6, 1.1 Hz, 1H), 7.76 (td, *J* = 7.6, 1.0 Hz, 1H), 8.94 (dd, *J* = 6.2, 1.8 Hz, 1H), 10.92 (dt, *J* = 7.8, 0.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 36.84 ppm ($PhCH_2$), 55.45 (OMe), 55.49 (OMe), 66.36 (CH), 71.48 (CH_2O), 98.23 (Ar_3C), 113.99, 114.14, 115.44, 118.01, 123.80, 126.29, 126.83, 127.82, 128.25, 128.66, 128.79, 129.54, 129.76, 131.55, 132.31, 134.09, 137.41, 140.88, 151.05, 151.36, 160.00 (COMe), 160.09 (COMe), 164.68 (C=N), 166.95 (PyO).

MS (FAB) *m/z* (%) = 1431 (13) $[2M\text{-}Cl]^+$, 755 (14), 699 (55) $[M\text{-}Cl]^+$, 661 (82) $[M\text{-}2Cl]^+$, 570 (15) $[M\text{-}PdCl_2]^+$, 555 (40), 522 (14), 462 (60) $[M\text{-}C_6H_6NO]$, 154 (100).

IR (KBr): $\tilde{\nu}$= 3446 cm^{-1} (w), 2932 (s), 1654 (m), 1509 (m), 1478 (m), 1254 (m).

Elemental analysis **$C_{36}H_{32}Cl_2N_2O_2Pd \cdot 0.6\ CH_2Cl_2$**:
calculated: C 58.38 H 4.44 N 3.72
found: C 58.26 H 4.57 N 3.71

Palladium complex 5d:

According to the general procedure $(MeCN)_2PdCl_2$ (126 mg, 254 µmol) and **4d** (62.7 mg , 242 µmol) were used to give the complex **5d** after evaporation of the solvent and washing with *n*-hexane in almost quantitative yield (161 mg, 99 %) as an orange solid with mp. 205 °C (dec.).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.52 ppm (s, 3H), 1.75 (s, 3H), 3.77 (d, *J* = 4.9 Hz, 7H), 4.25 (d, *J* = 13.0 Hz, 1H), 6.75 (dd, *J* = 8.5, 1.3 Hz, 1H), 6.80 – 6.86 (m, 4H), 6.93 (ddd, *J* = 7.3, 6.2, 1.4 Hz, 1H), 7.04 – 7.12 (m, 2H), 7.13 – 7.21 (m, 2H), 7.29 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.58 – 7.68 (m, 2H), 7.74 – 7.79 (m, 1H), 8.55 (d, *J* = 12.9 Hz, 1H), 8.96 (dd, *J* = 6.2, 1.8 Hz, 1H), 11.17 (dt, *J* = 7.9, 0.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 21.57 ppm (CH_3), 23.85 (CH_3), 55.45 (OMe), 67.47 (C_{quart}), 79.73 (CH_2), 99.09 (Ar_3C), 113.87, 114.21, 115.42, 118.11, 123.77, 128.12, 128.68, 128.85, 129.14, 129.35, 131.43, 132.26, 133.58, 140.90, 150.16, 151.05, 159.98 (COMe), 160.07 (COMe), 164.06 (C=N), 167.32 (PyO).

MS (FAB): *m/z* (%) = 495 (7), 599 (25) $[M\text{-}2Cl]^+$, 635 (7) $[M\text{-}Cl]^+$, 1309 (8) $[2M\text{-}Cl]^+$.

IR (KBr): $\tilde{\nu}$ = 2929 cm^{-1} (w), 1637 (s), 1615 (m), 1511 (m), 1480 (m), 1414 (m), 1366 (m), 1176 (m), 832 (w), 821 (w), 781 (w), 584 (w).

Palladium complex 6:

Imidate **3a** (100 mg, 231 µmol) and $(MeCN)_2PdCl_2$ (57.0 mg, 220 µmol) were dissolved in 10 ml dichloromethan and stirred for 1h at room temperature, the yellow solution changed to orange within minutes. The solvent was removed in vacuum and the resulting orange crude product was washed with n-hexane (3 x 2 ml) in order to remove the excess ligand. The orange powder was dried in vacuum to yield complex **6** (118 mg, 88 %) with mp. 166 °C (dec.). Analytically pure samples and crystals suitable for x-ray analysis could be prepared by recrystallization from CH_2Cl_2 / n-hexane.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.27 (d, J = 6.4 Hz, 1 H), 0.52 (d, J = 6.4 Hz, 2 H), 0.80 (d, J = 6.6 Hz, 1 H), 1.07 (d, J = 6.6 Hz, 2 H), 2.11 (dtd, J = 5.7, 10.1, 10.7, 13.0 Hz, 0.31 H), 2.45 (ddt, J = 6.2, 10.1, 13.0 Hz, 0.77 H), 3.47 (dd, J = 5.0, 10.6 Hz, 0.77 H), 3.54 – 3.70 (m, 1.63 H), 3.78 (d, J = 13.9 Hz, 6 H), 3.88 – 4.01 (m, 1 H), 4.81 (s, 1 H), 6.74 – 6.86 (m, 5 H), 7.04 – 7.23 (m, 5 H), 7.46 (d, J = 7.9 Hz, 0.38 H), 7.53 (d, J = 7.4 Hz, 0.69 H), 7.78 – 7.92 (m, 1 H), 7.98 – 8.05 (m, 0.73 H), 8.05 – 8.10 (m, 0.36 H), 11.99 – 12.09 (m, 1 H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 19.46, 19.58, 21.07, 21.41, 29.93, 30.09, 55.44, 55.47, 64.02, 70.88, 71.22, 97.75, 97.89, 113.79, 113.95, 114.22, 124.05, 124.26, 126.77, 127.02, 127.84, 127.89, 128.59, 129.19, 129.35, 129.65, 129.83, 131.67, 131.92, 132.29, 132.43, 134.11, 134.16, 152.21, 152.64, 159.89, 159.94, 160.21, 160.35, 167.62, 167.68 ppm.

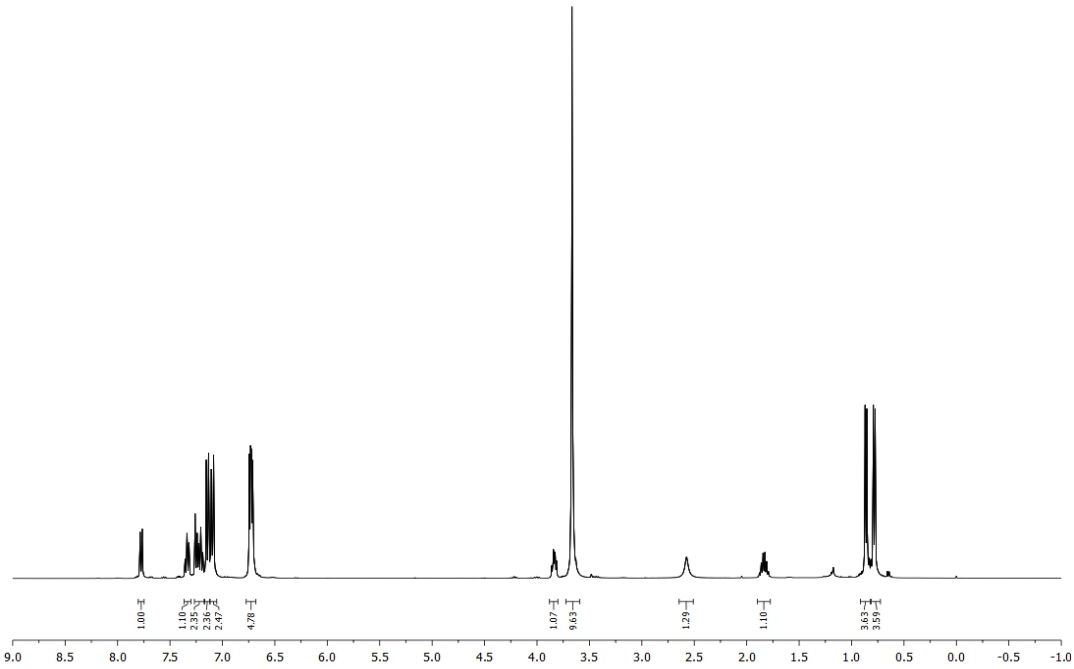
MS(FAB): *m/z* (%) = 538 (5) $[M\text{-}2Cl]^+$, 432 (100) $[M\text{-}PdCl_2]^+$.

IR(KBr): $\tilde{\nu}$= 3440 (m), 2959 (m), 2835 (w), 1634 (s), 1607 (s), 1582 (m), 1465 (s), 1301 (s), 1255 (s), 1177 (s), 1142 (s), 1115 (m), 1070 (m), 1031 (s), 958 (m), 829 (m), 538 (m) cm^{-1}.

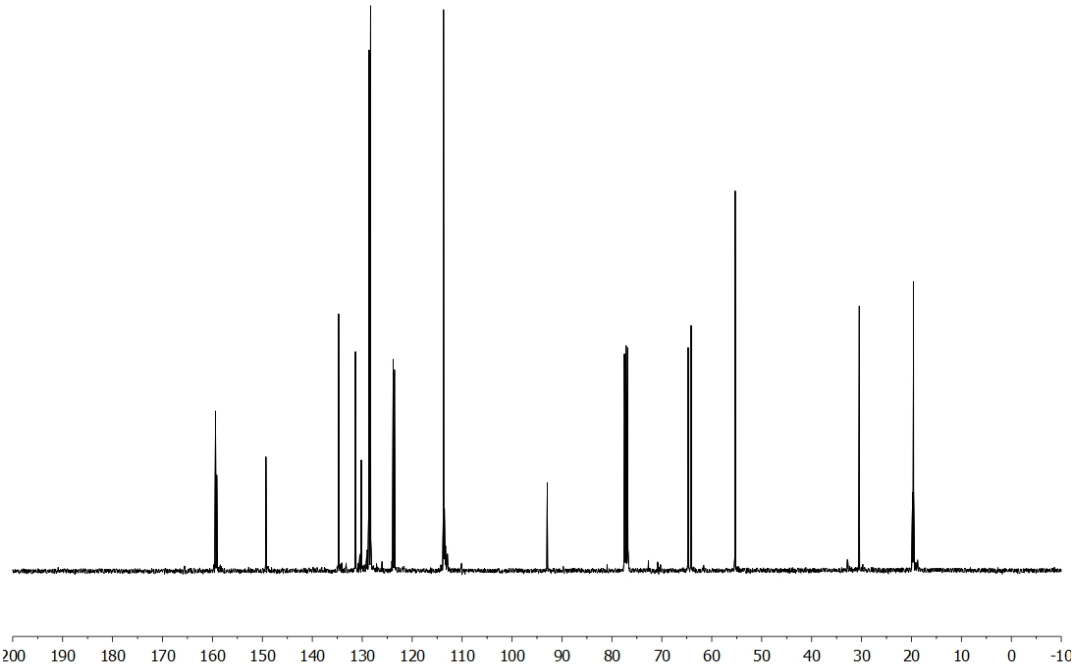
NMR Spectra

(S,Z)-2-((3,3-Bis(4-methoxyphenyl)isobenzofuran-1(3H)-ylidene)amino)-3-methylbutan-1-ol_3a:

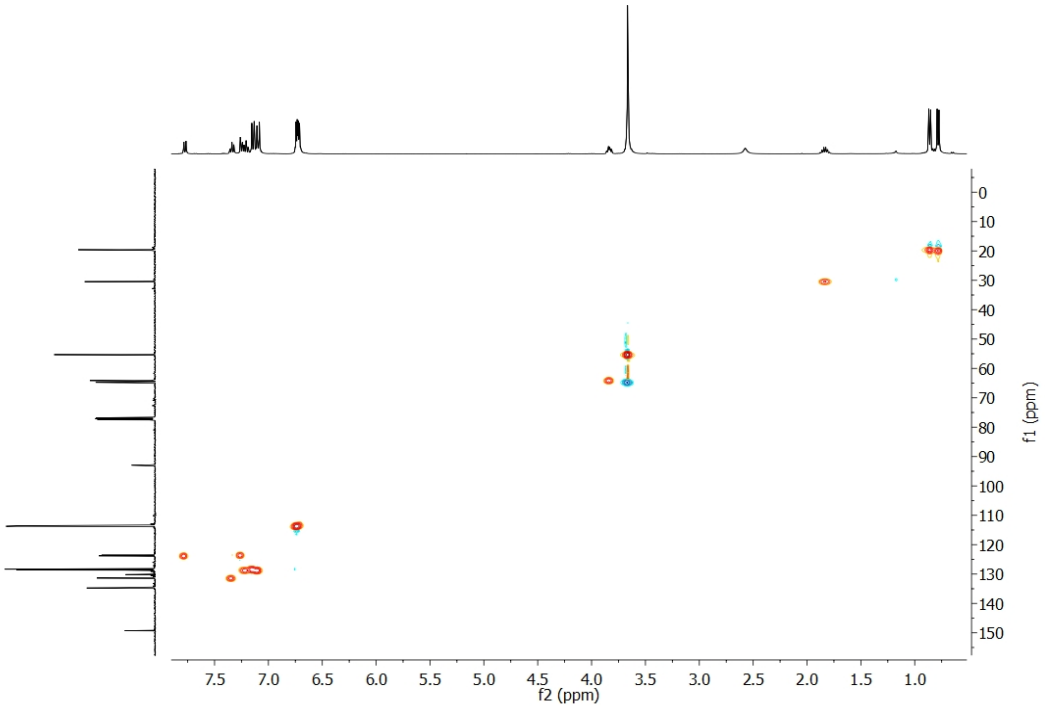
^{1}H NMR:



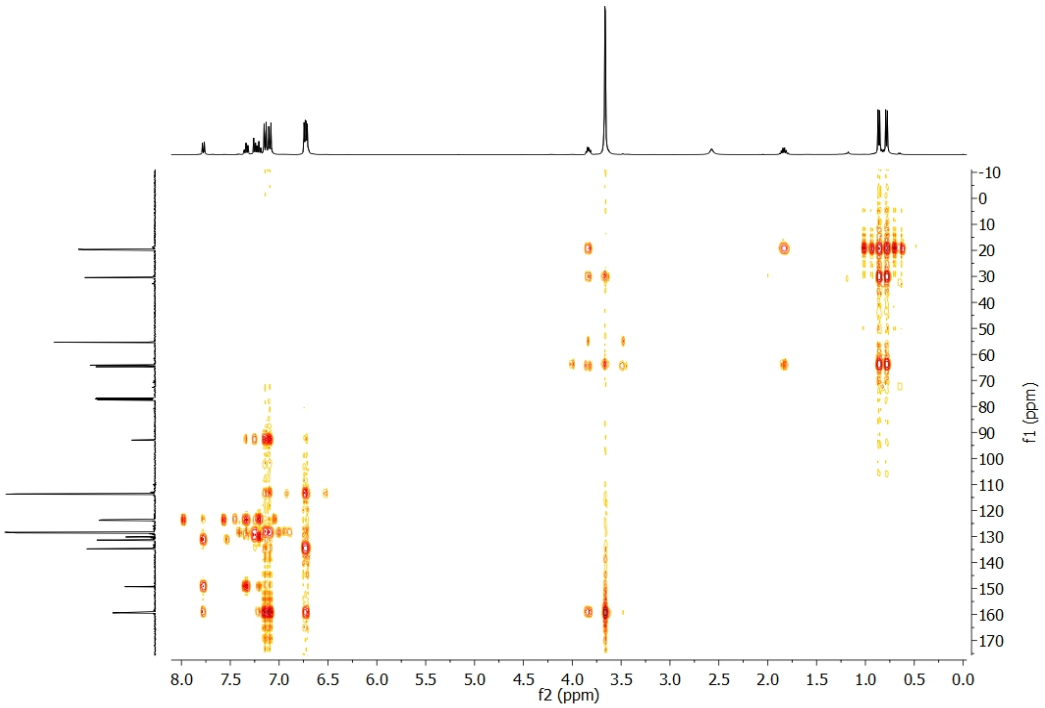
^{13}C NMR:



$^{1}H,^{13}C$ HSQC:

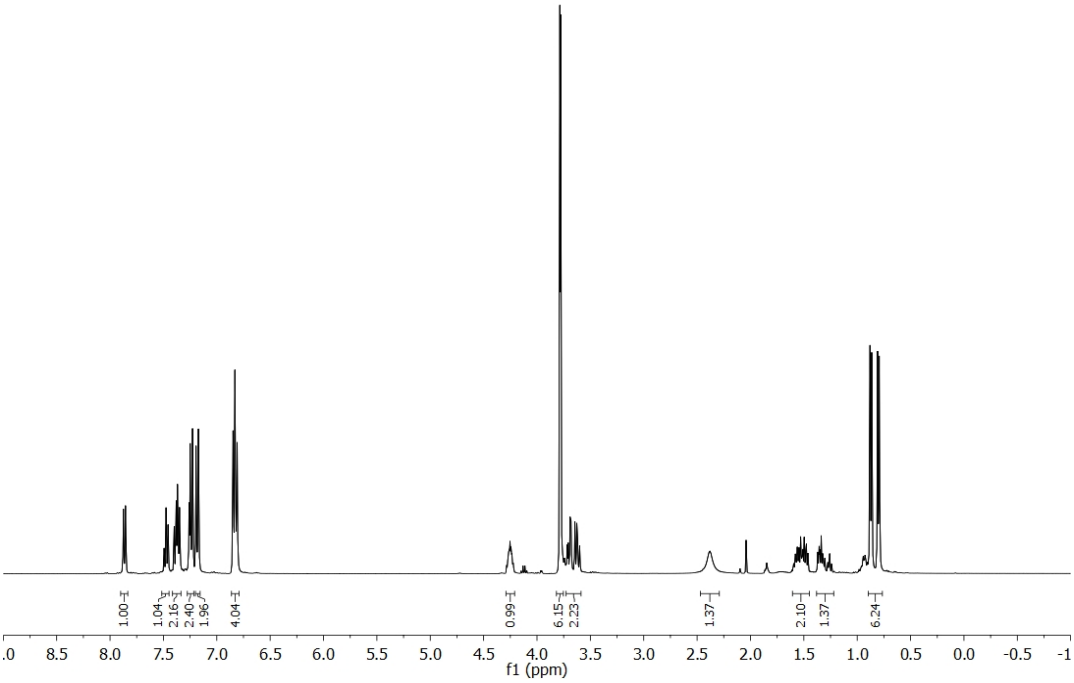


$^{1}H,^{13}C$ HMBC:

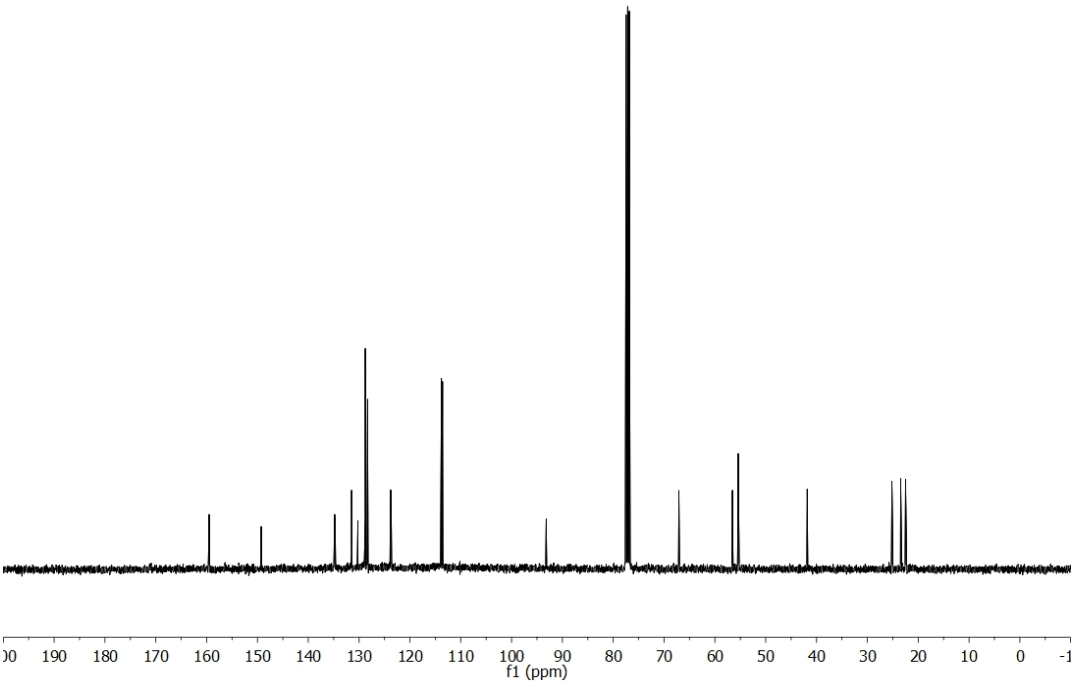


(S,Z)-2-((3,3-Bis(4-methoxyphenyl)isobenzofuran-1(3H)-ylidene)amino)-4-methylpentan-1-ol 3b:

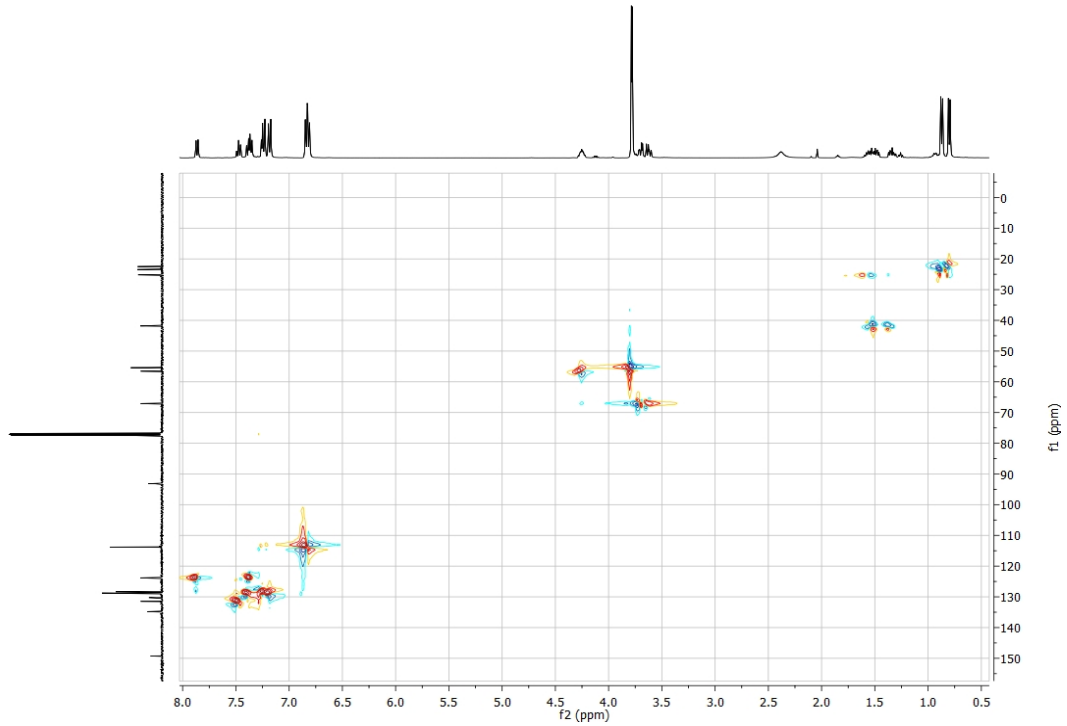
^{1}H NMR:



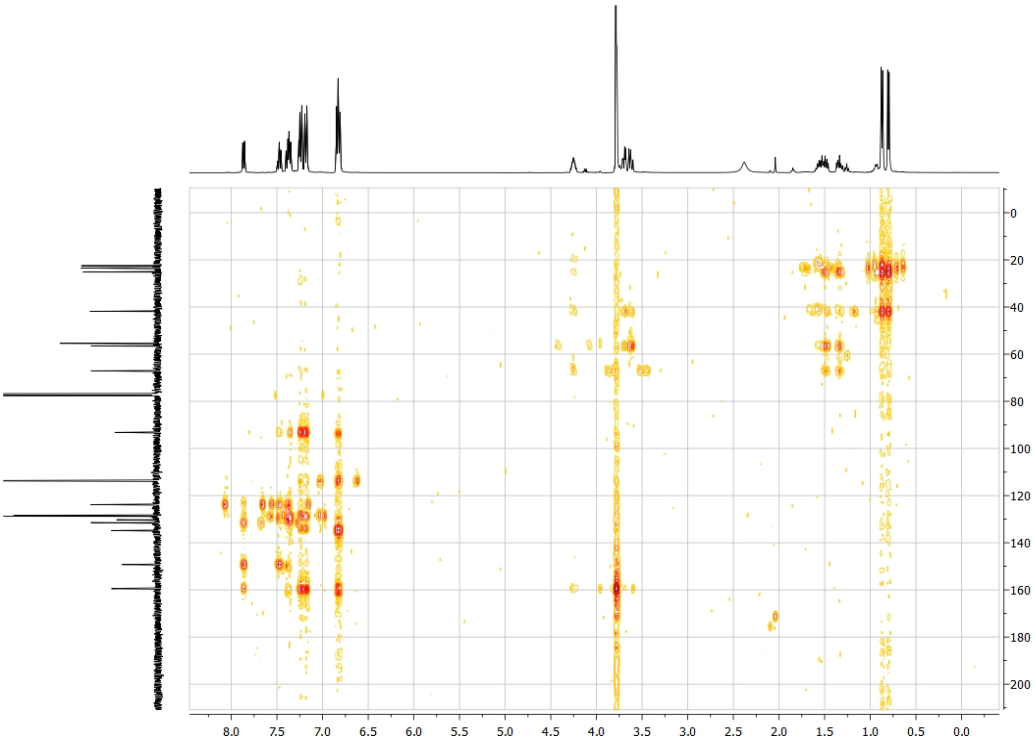
^{13}C NMR:



$^{1}H,^{13}C$ HSQC:

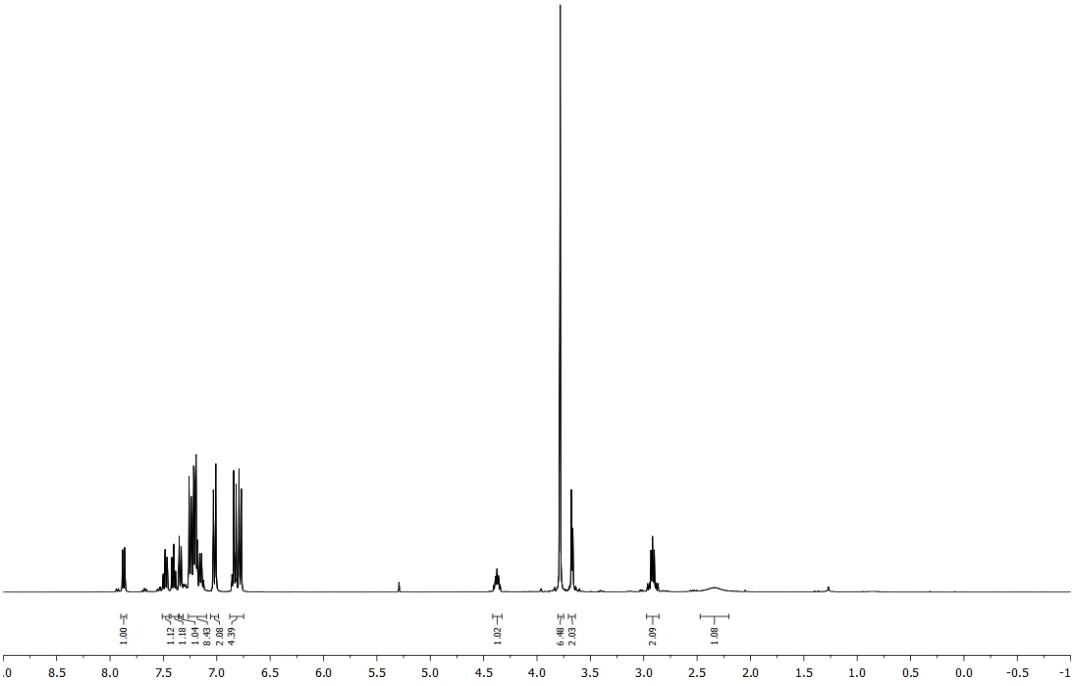


$^{1}H,^{13}C$ HMBC:

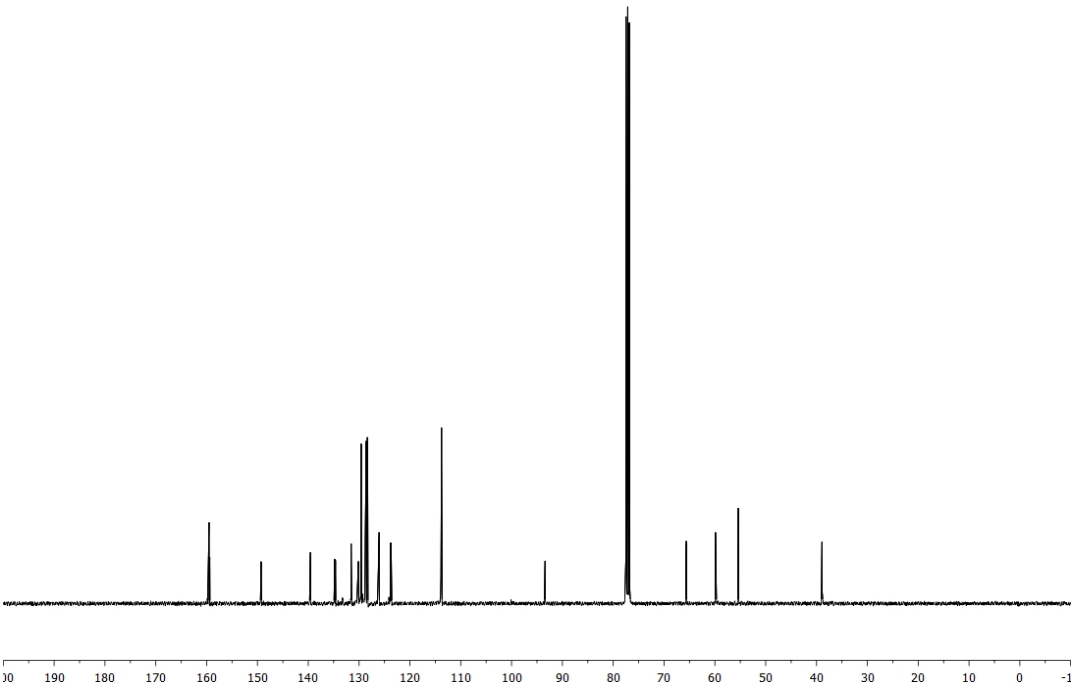


(S,Z)-2-((3,3-Bis(4-methoxyphenyl)isobenzofuran-1(3H)-ylidene)amino)-3-phenylpropan-1-ol 3c:

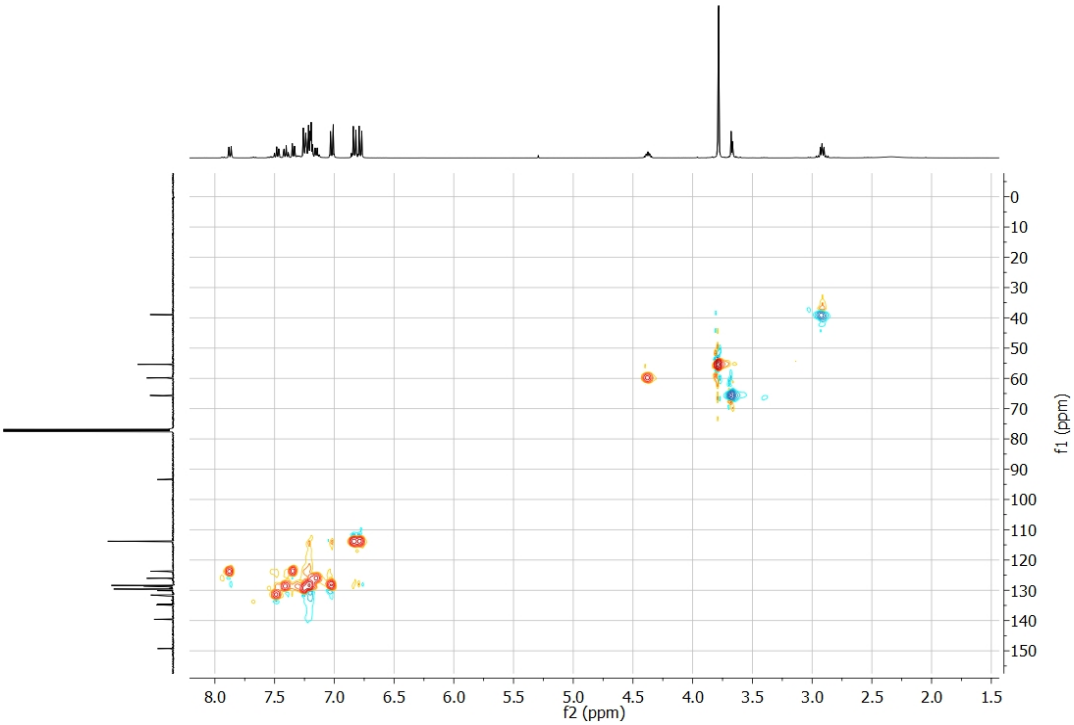
^{1}H NMR:



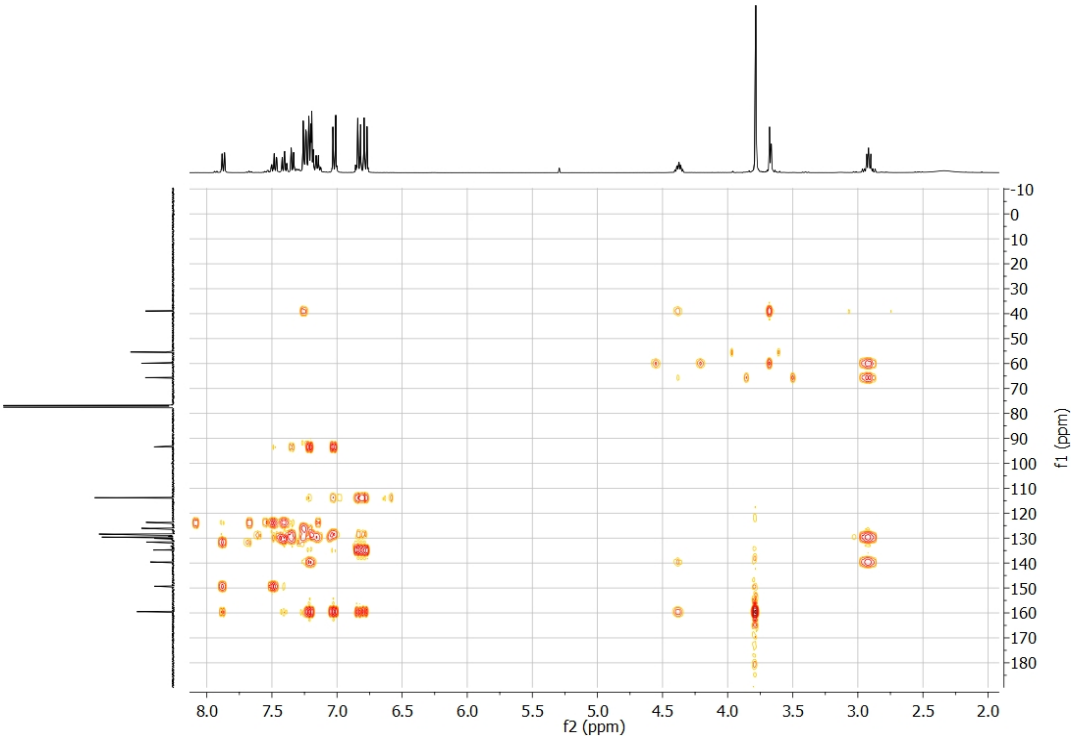
^{13}C NMR:



$^{1}H,^{13}C$ HSQC:

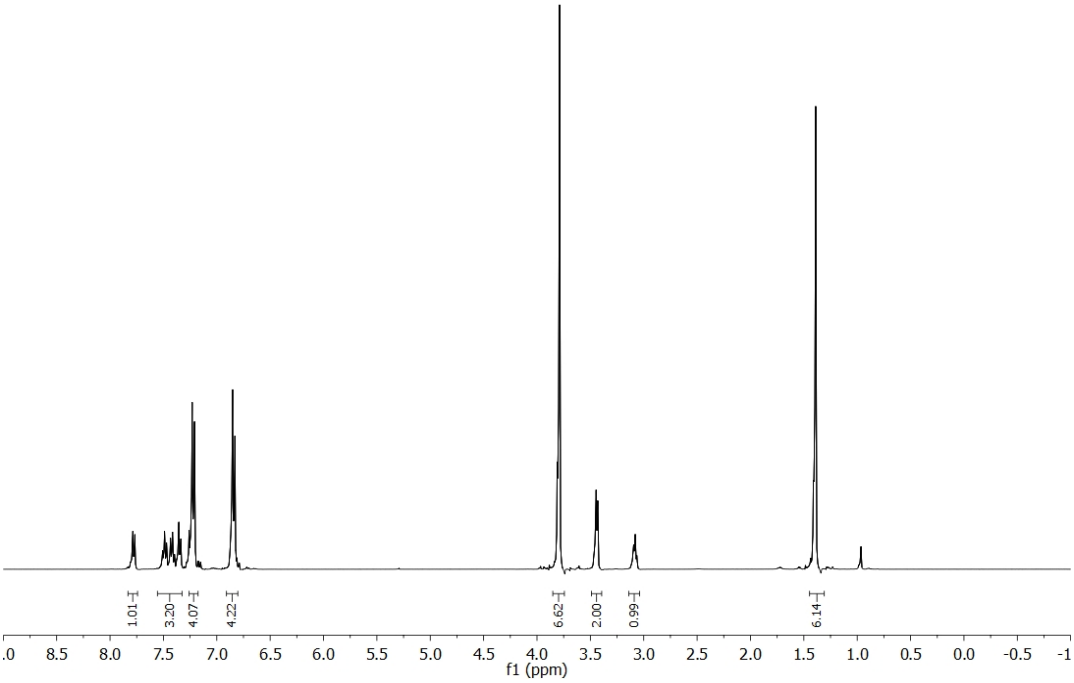


$^{1}H,^{13}C$ HMBC:

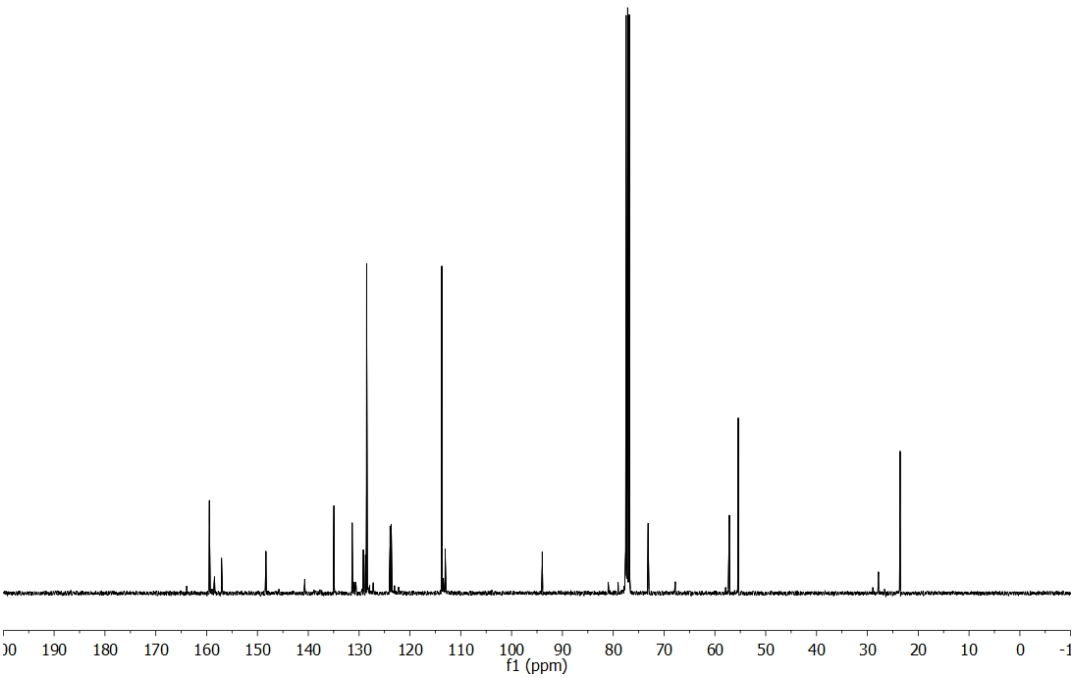


(Z)-2-((3,3-Bis(4-methoxyphenyl)isobenzofuran-1(3H)-ylidene)amino)-2-methylpropan-1-ol 3d:

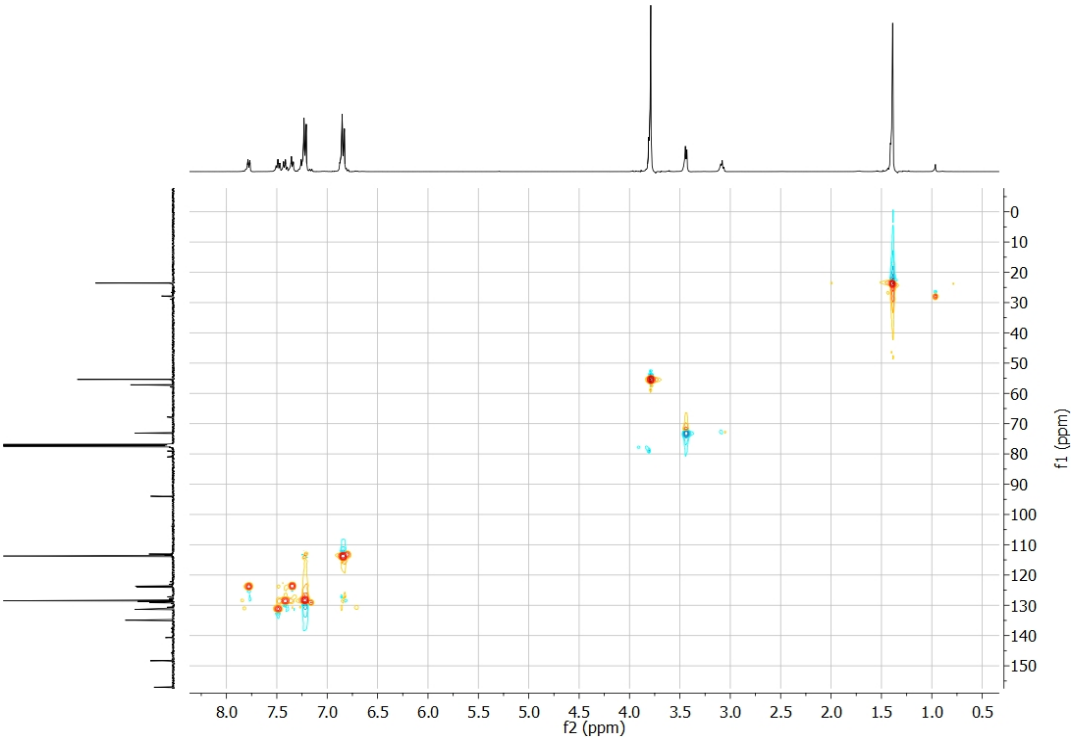
^{1}H NMR:



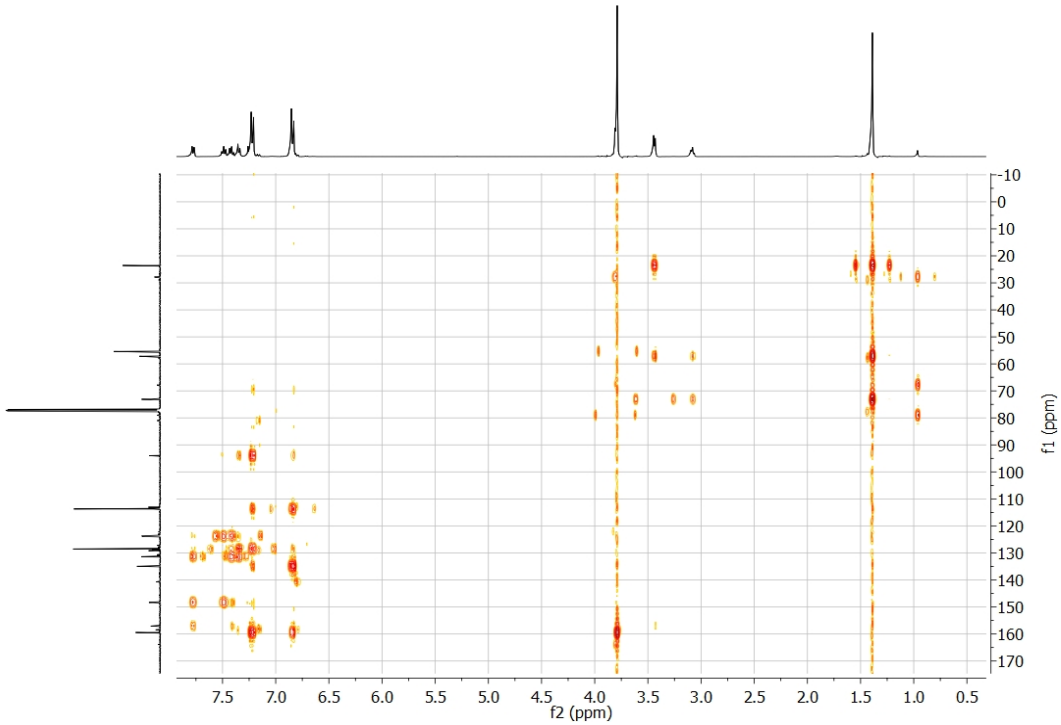
^{13}C NMR:



$^{1}H,^{13}C$ HSQC:

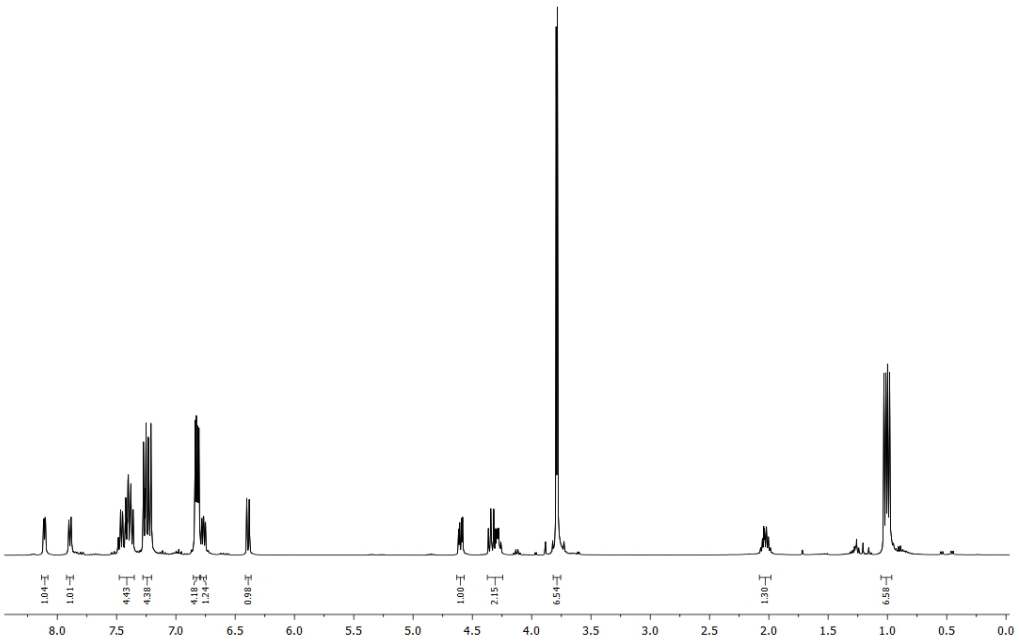


$^{1}H,^{13}C$ HMBC:

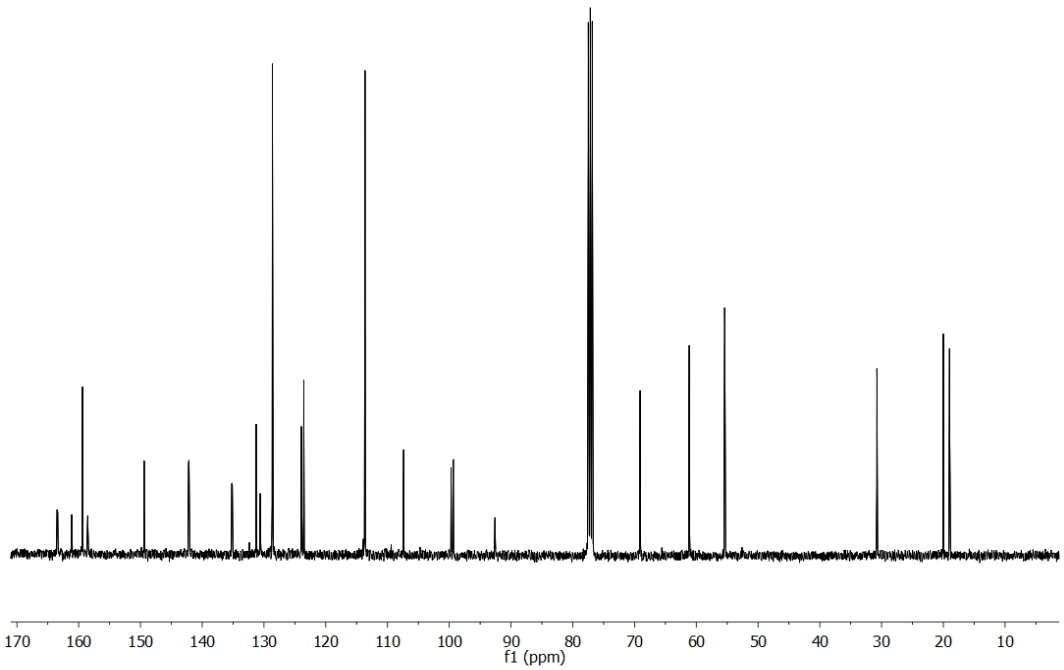


(S,Z)-*N*-(3,3-Bis(4-methoxyphenyl)isobenzofuran-1(3H)-ylidene)-3-methyl-1-(pyridin-2-yloxy)butan-2-amine 4a:

^{1}H NMR:

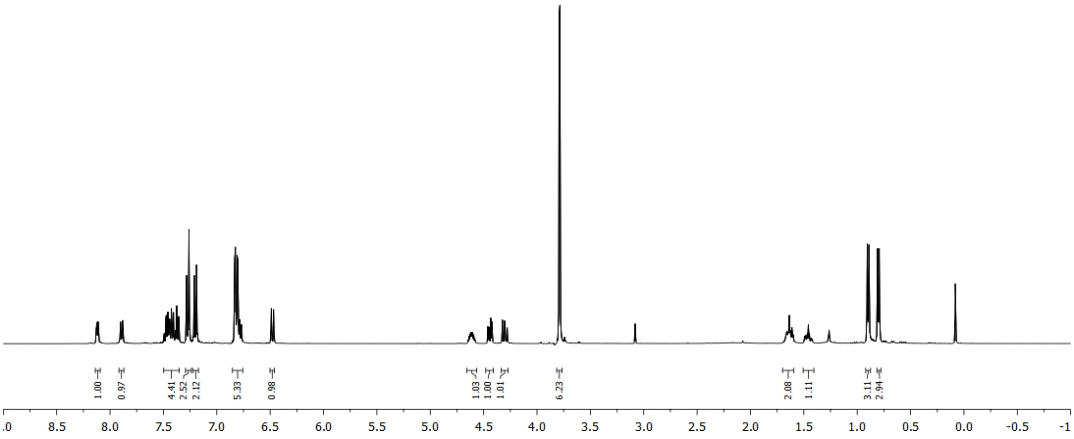


^{13}C NMR:

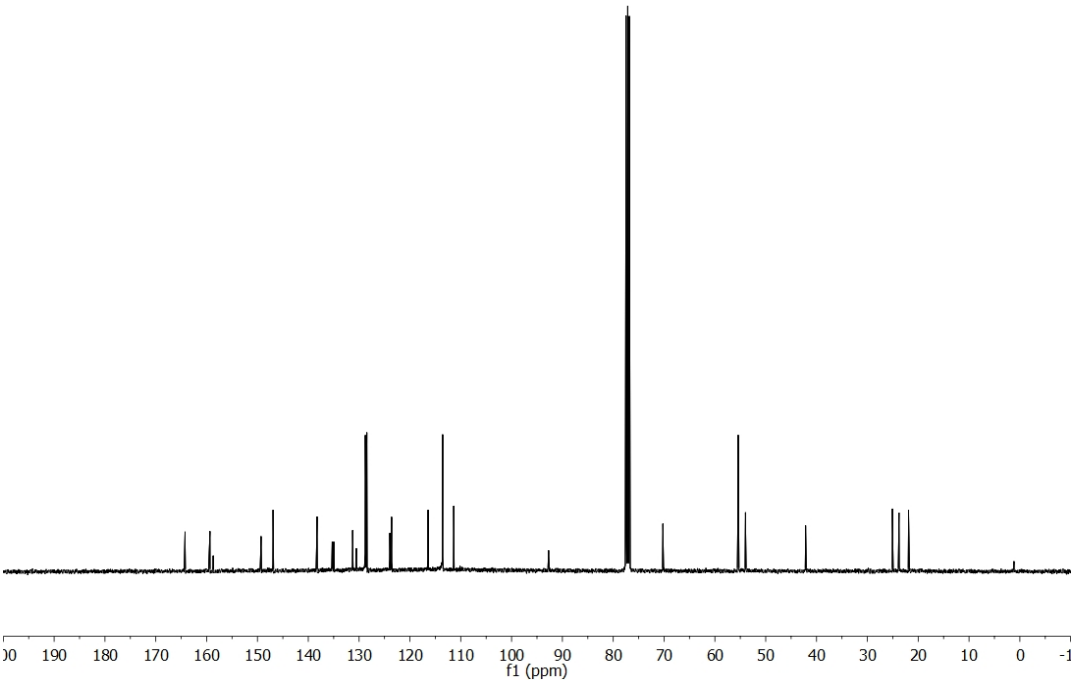


(S,Z)-*N*-(3,3-Bis(4-methoxyphenyl)isobenzofuran-1(3H)-ylidene)-1-phenyl-3-(pyridin-2-yloxy)propan-2-amine 4b:

^{1}H NMR:

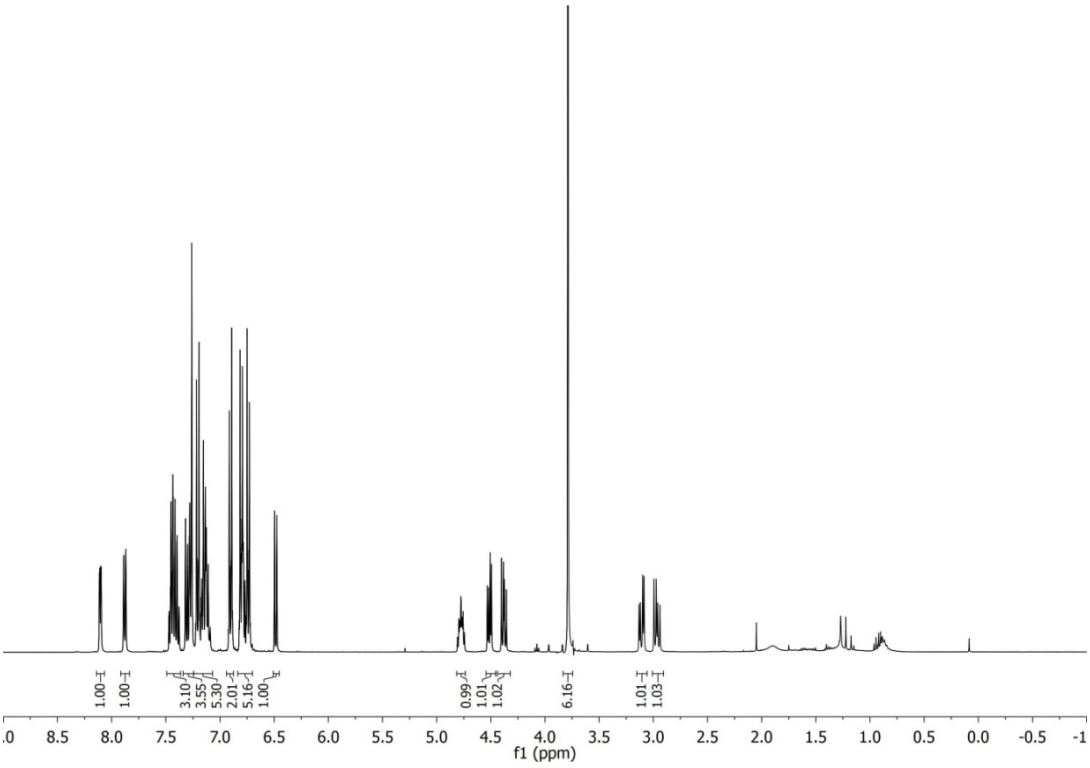


^{13}C NMR

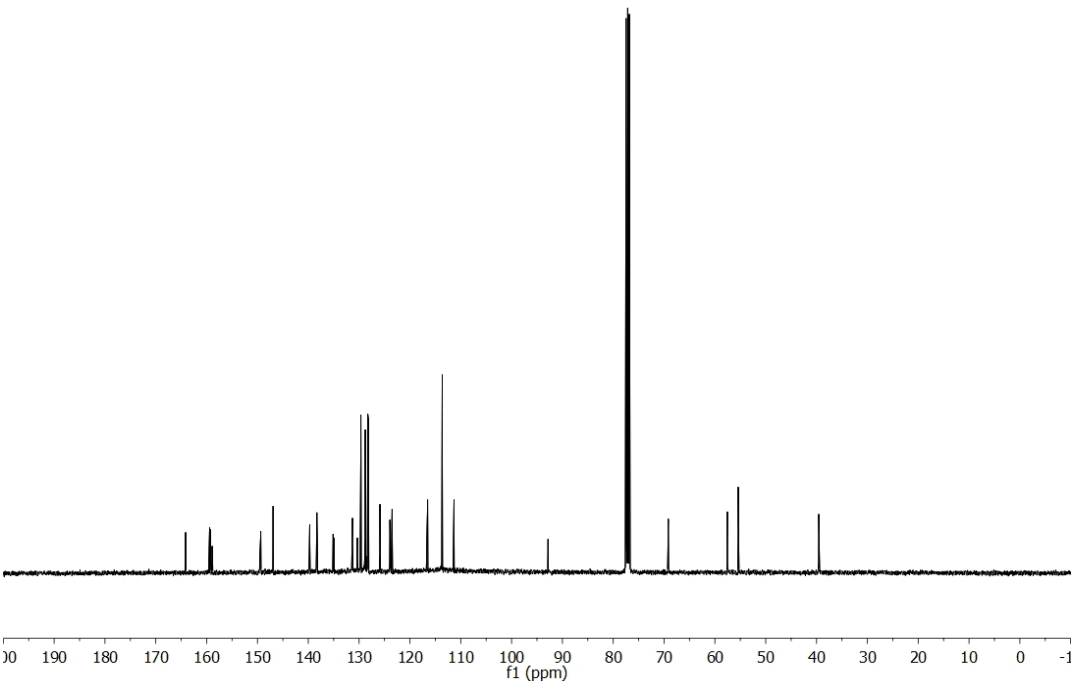


(S,Z)-*N*-(3,3-Bis(4-methoxyphenyl)isobenzofuran-1(3H)-ylidene)-4-methyl-1-(pyridin-2-yloxy)pentan-2-amine 4c:

^{1}H NMR:

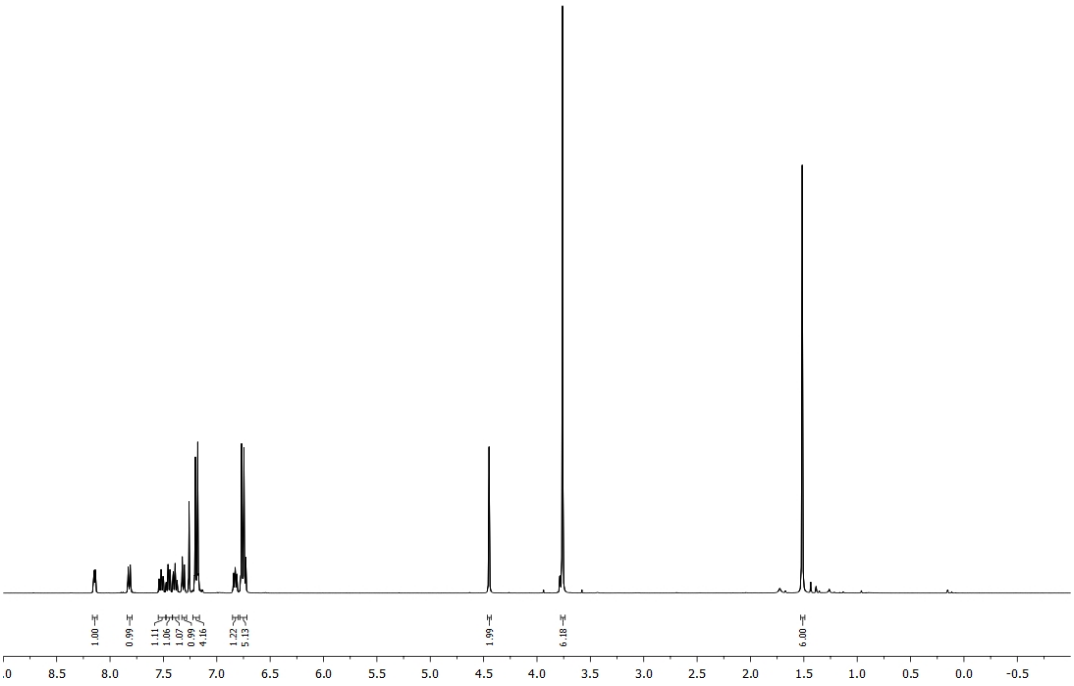


^{13}C NMR:

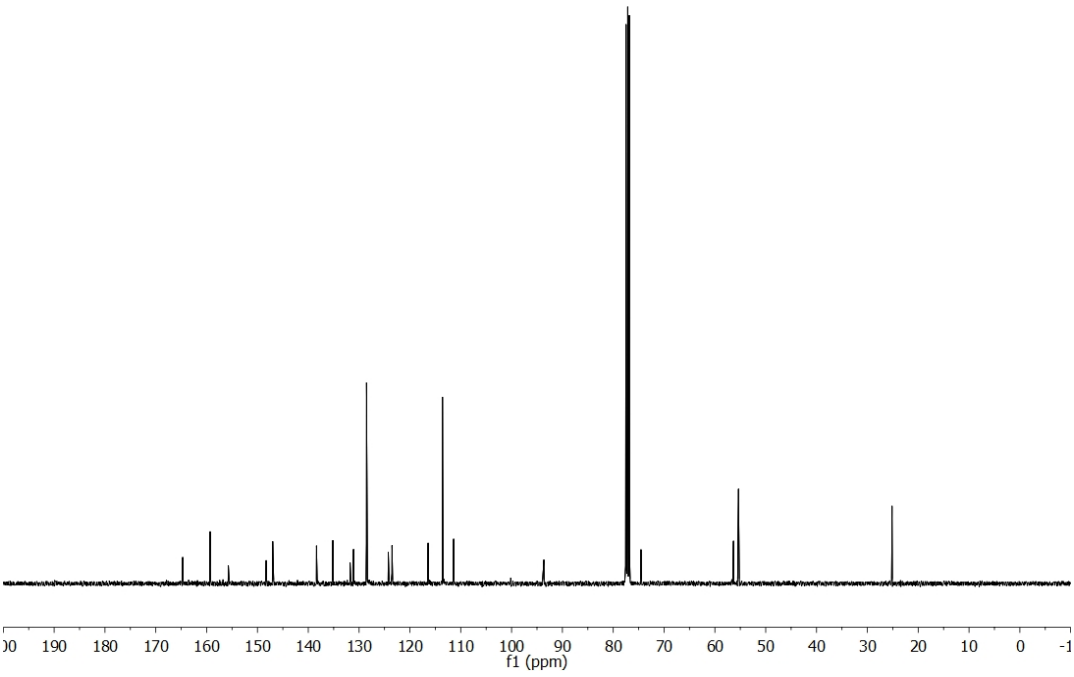


(Z)-*N*-(3,3-Bis(4-methoxyphenyl)isobenzofuran-1(3H)-ylidene)-2-methyl-1-(pyridin-2-yloxy)propan-2-amine 4d:

^{1}H NMR:

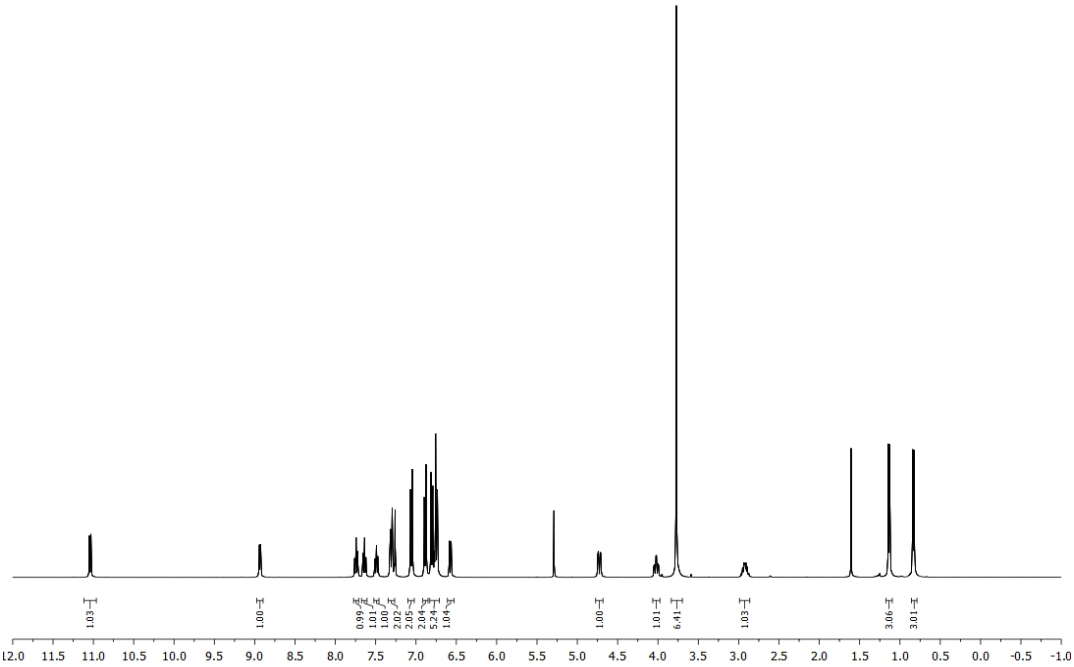


^{13}C NMR:

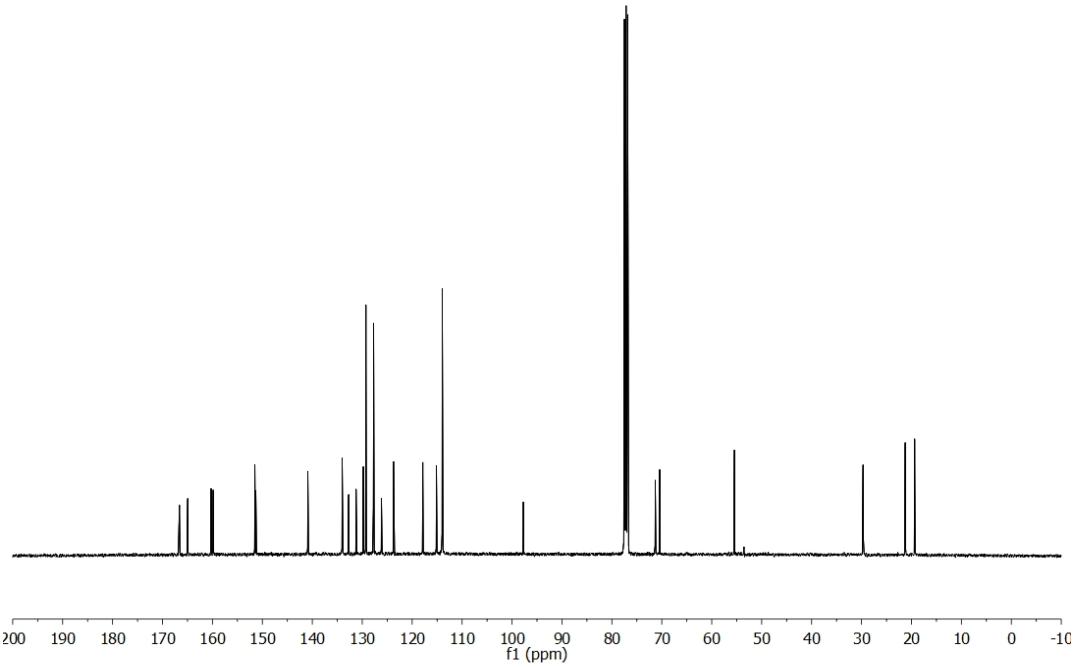


Palladium complex 5a:

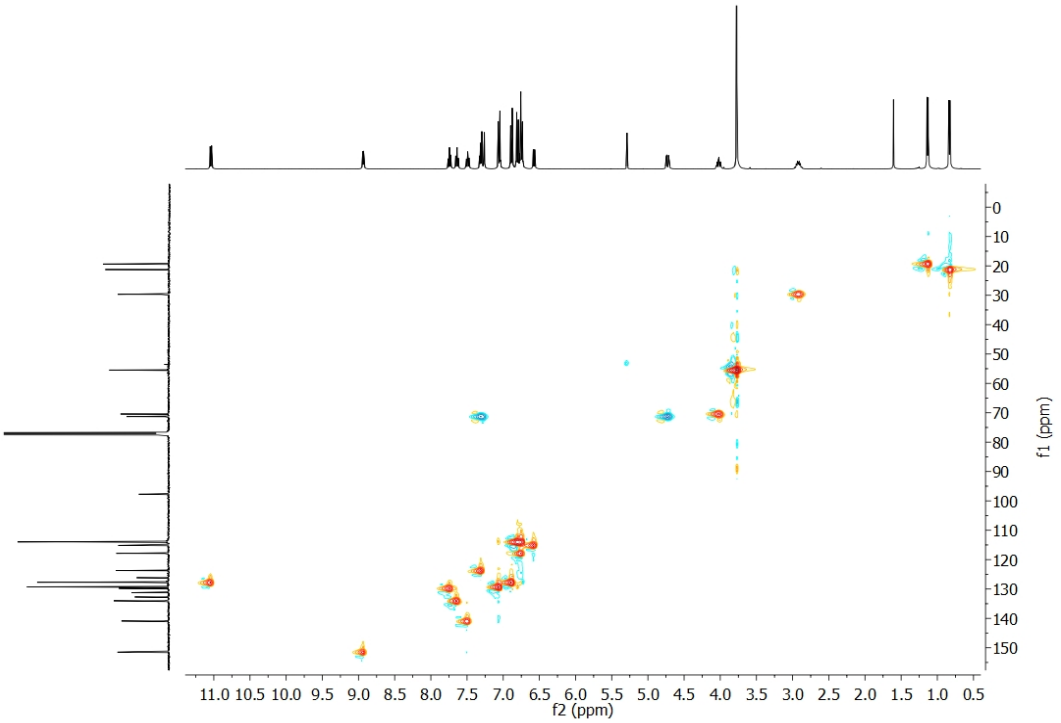
^{1}H NMR:



^{13}C NMR

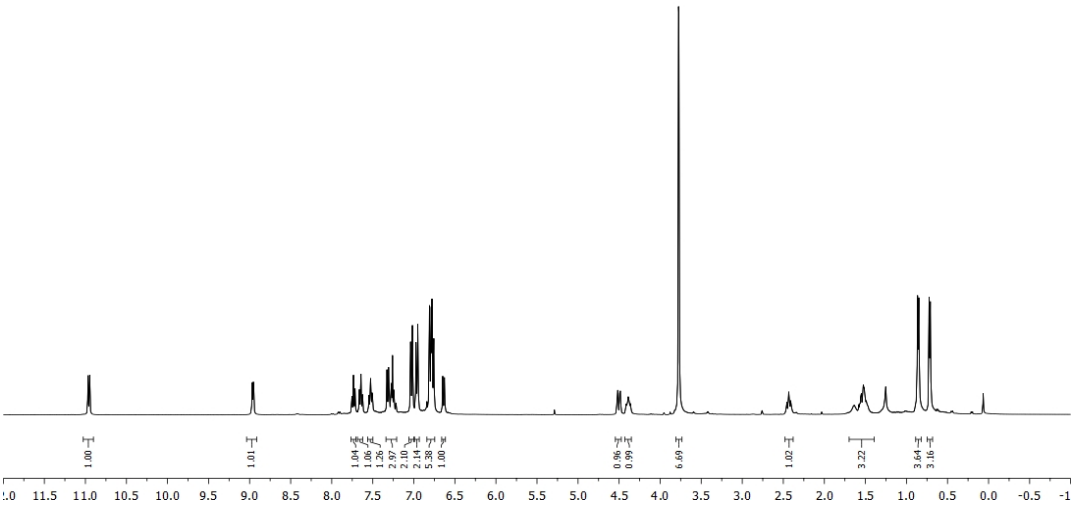


$^{1}H,^{13}C$ HSQC:

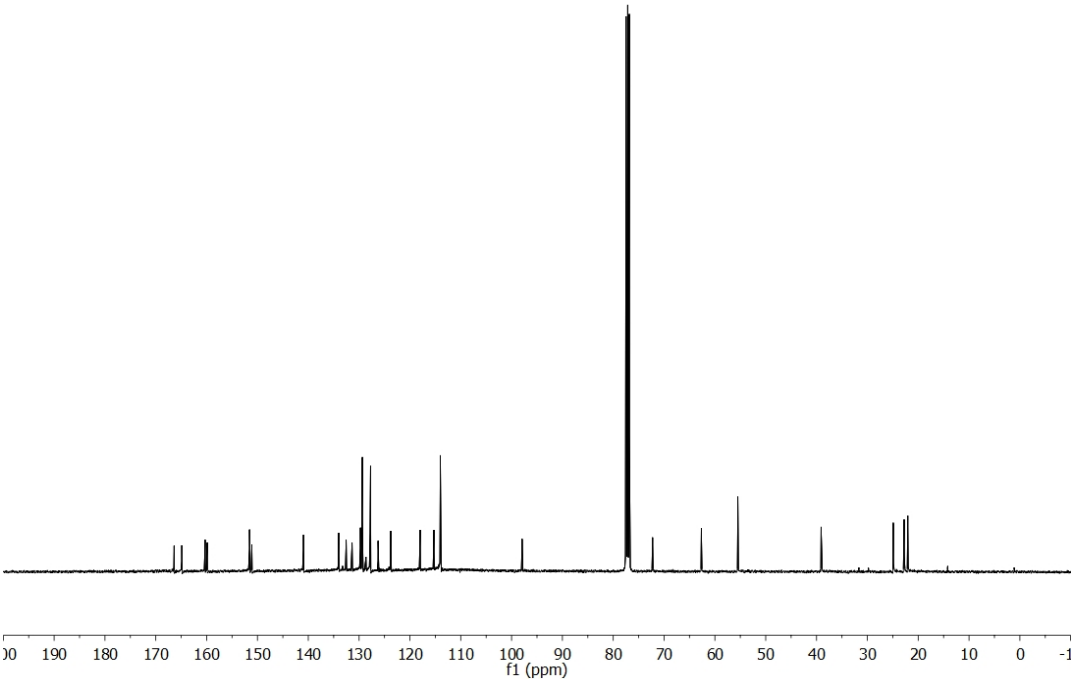


Palladium complex 5b:

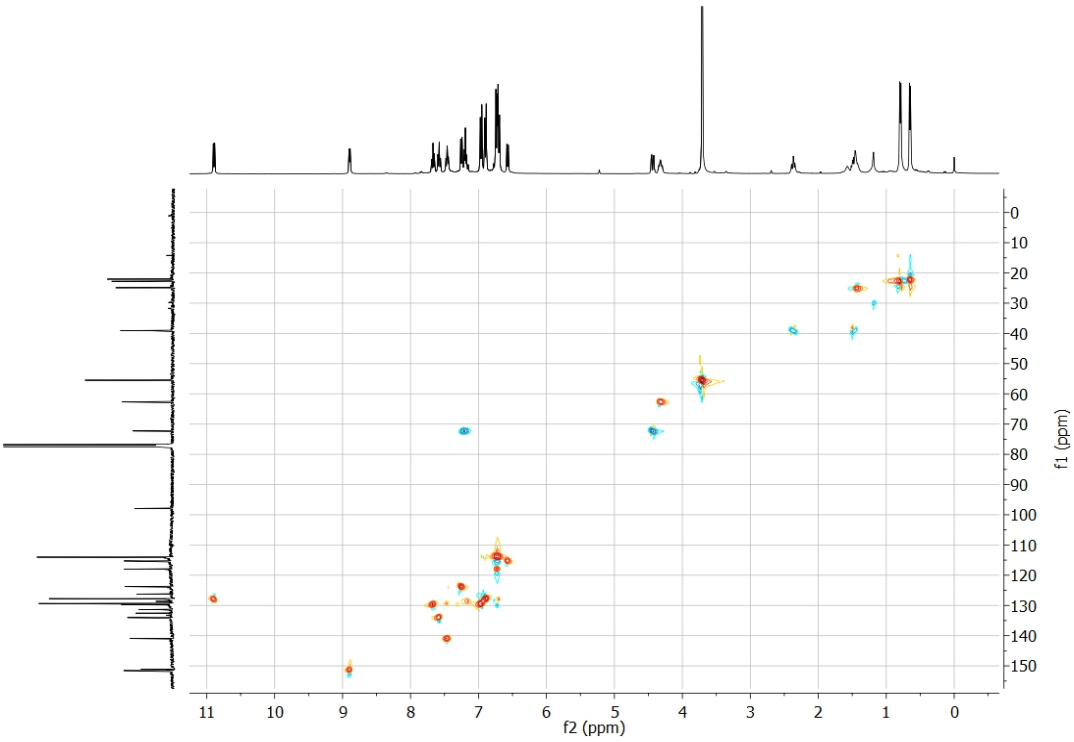
^{1}H NMR:



^{13}C NMR

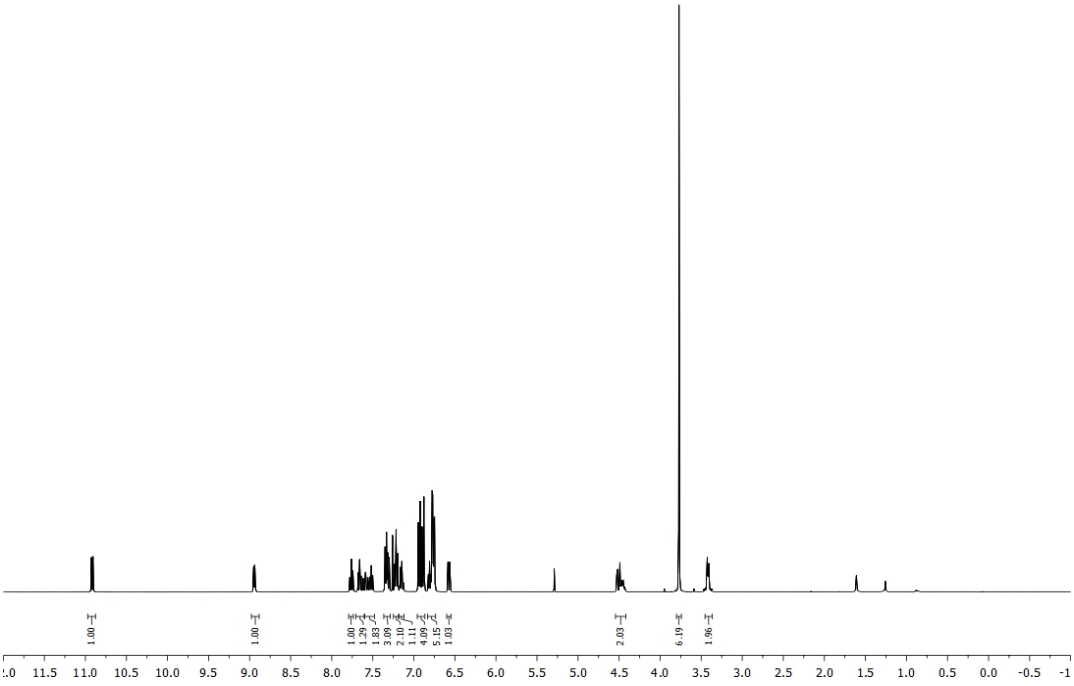


^{1}H,^{13}C HSQC:

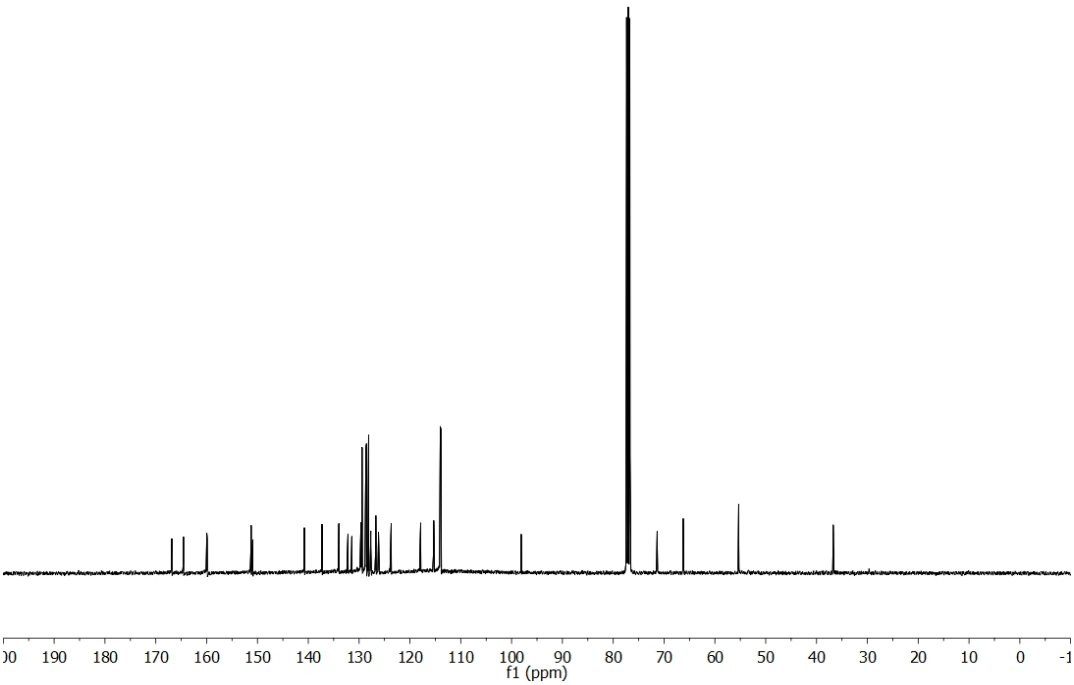


Palladium complex 5c:

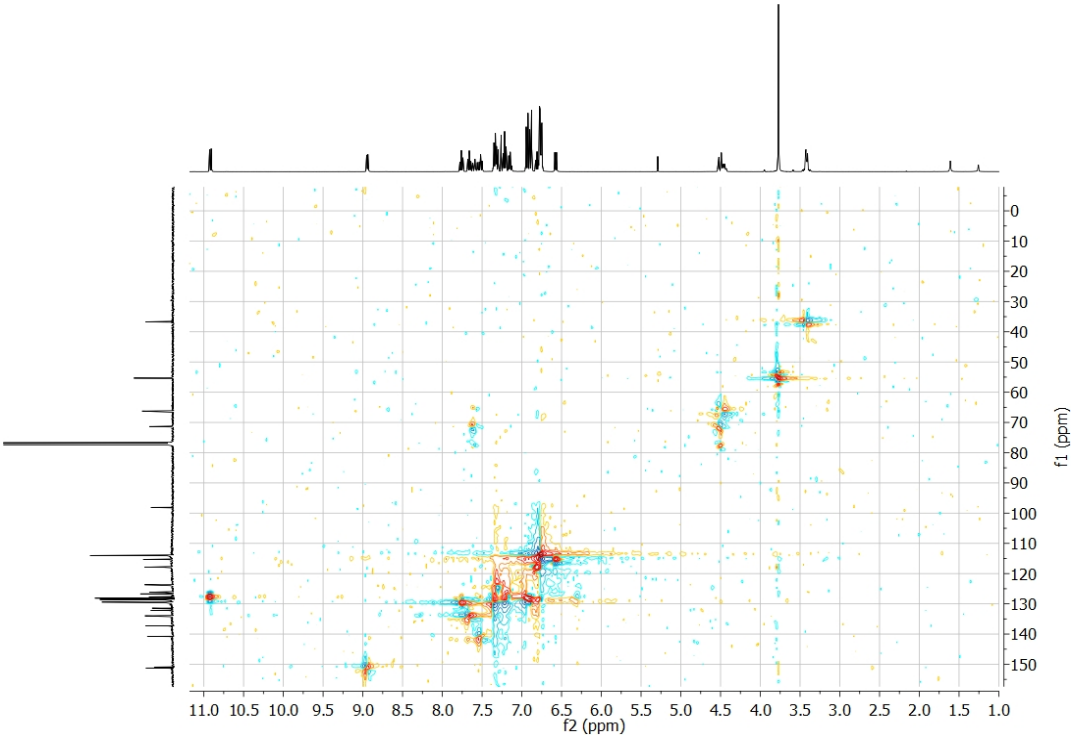
^{1}H NMR:



^{13}C NMR:

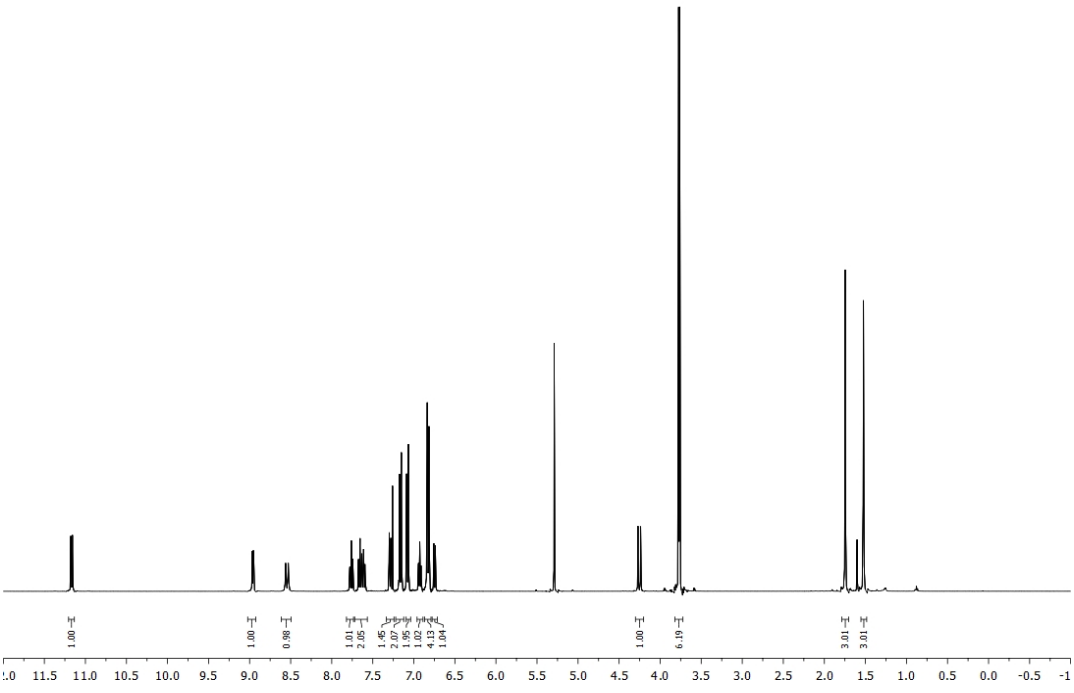


$^{1}H,^{13}C$ HSQC:

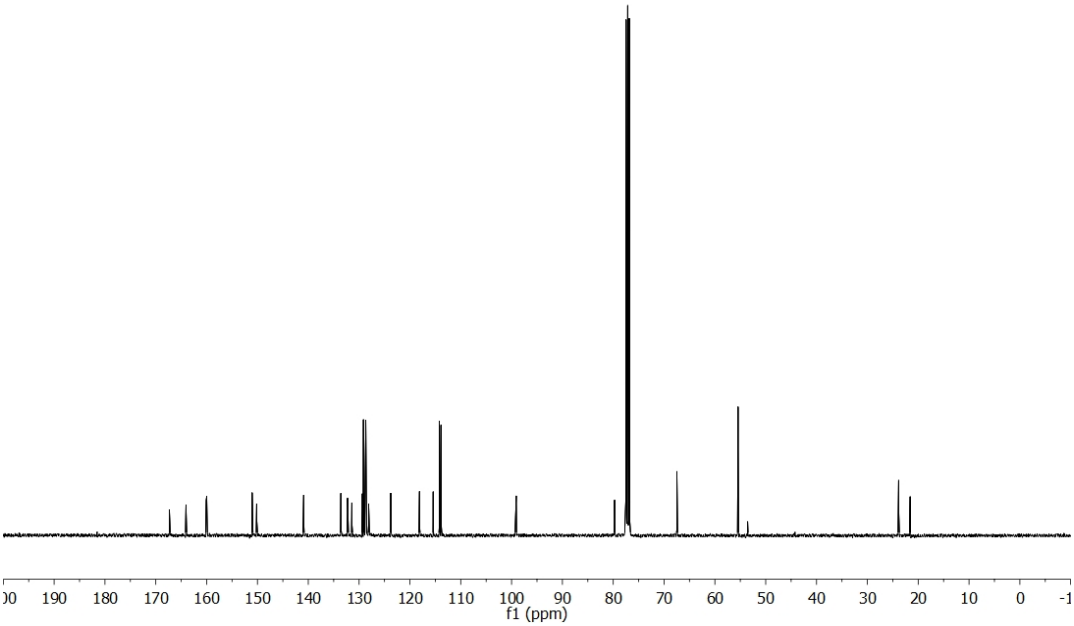


<u>Palladium complex 5d:</u>

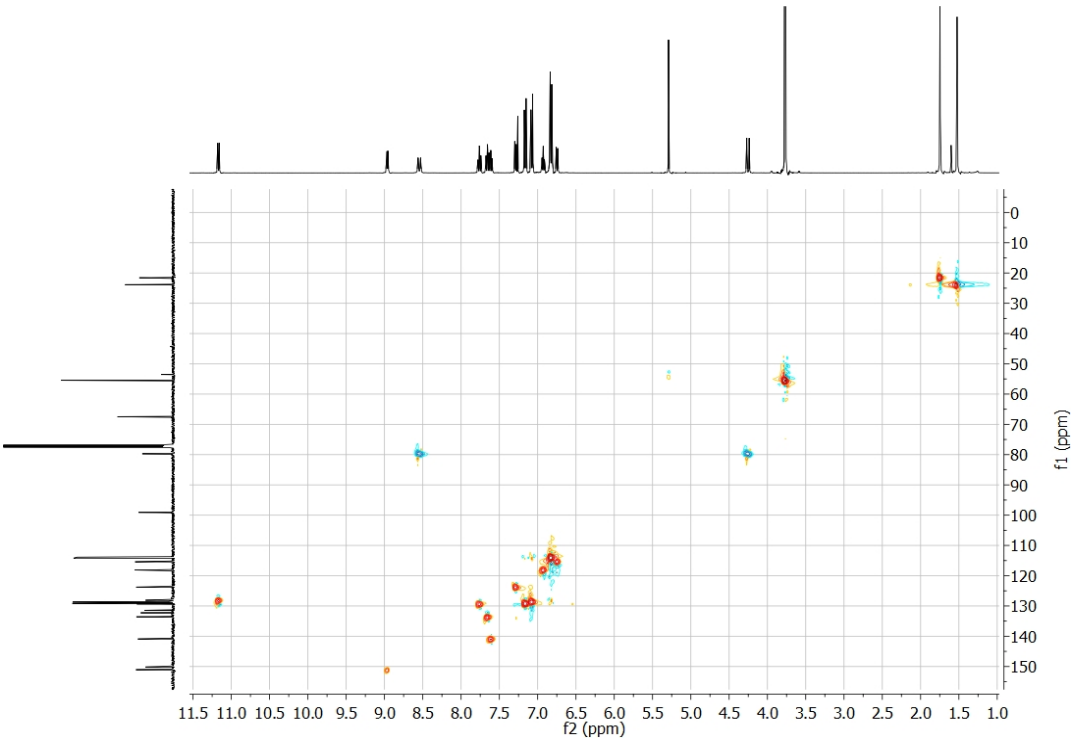
^{1}H NMR:



^{13}C NMR:

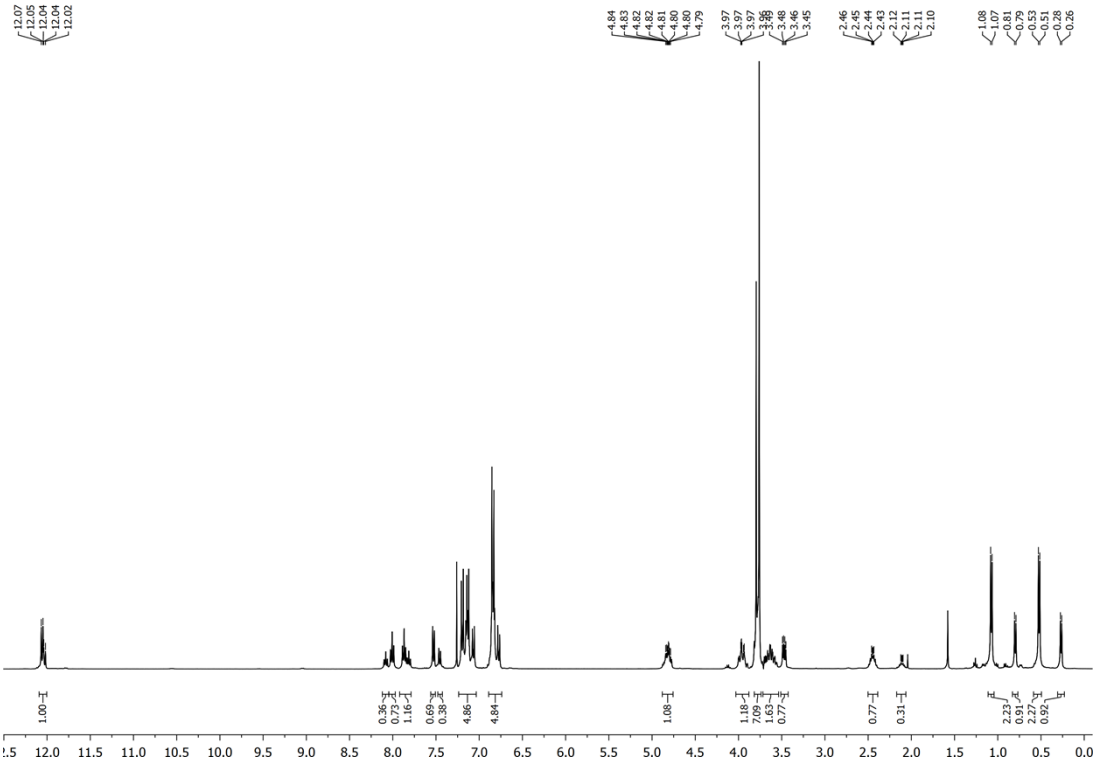


^{1}H,^{13}C HSQC:

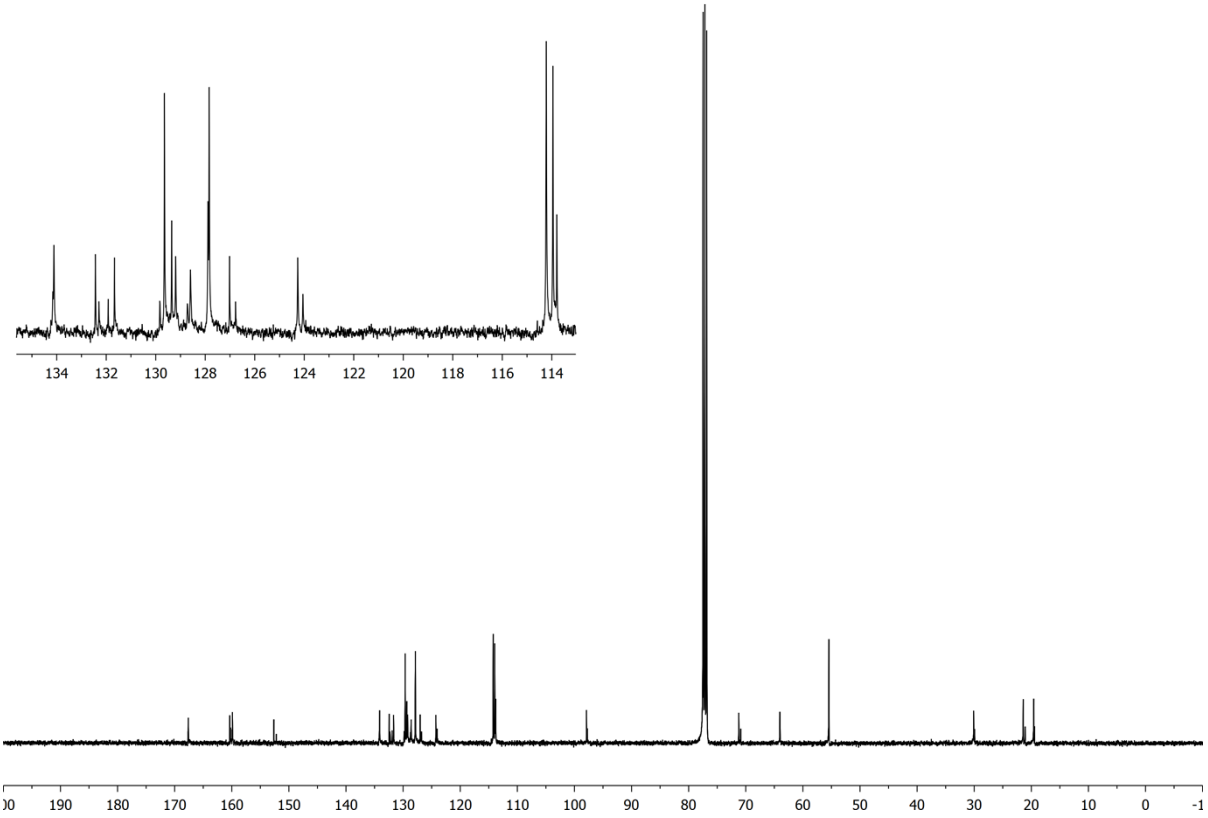


Palladium complex 6:

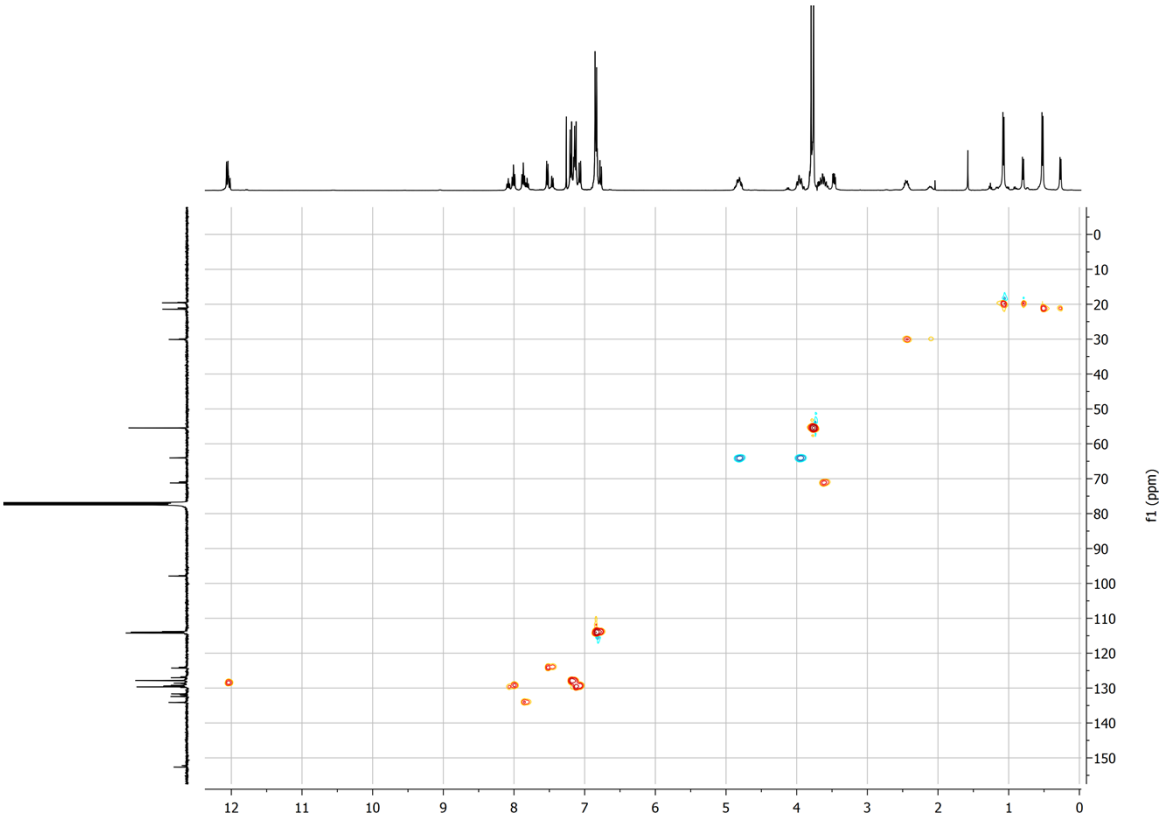
^{1}H NMR:



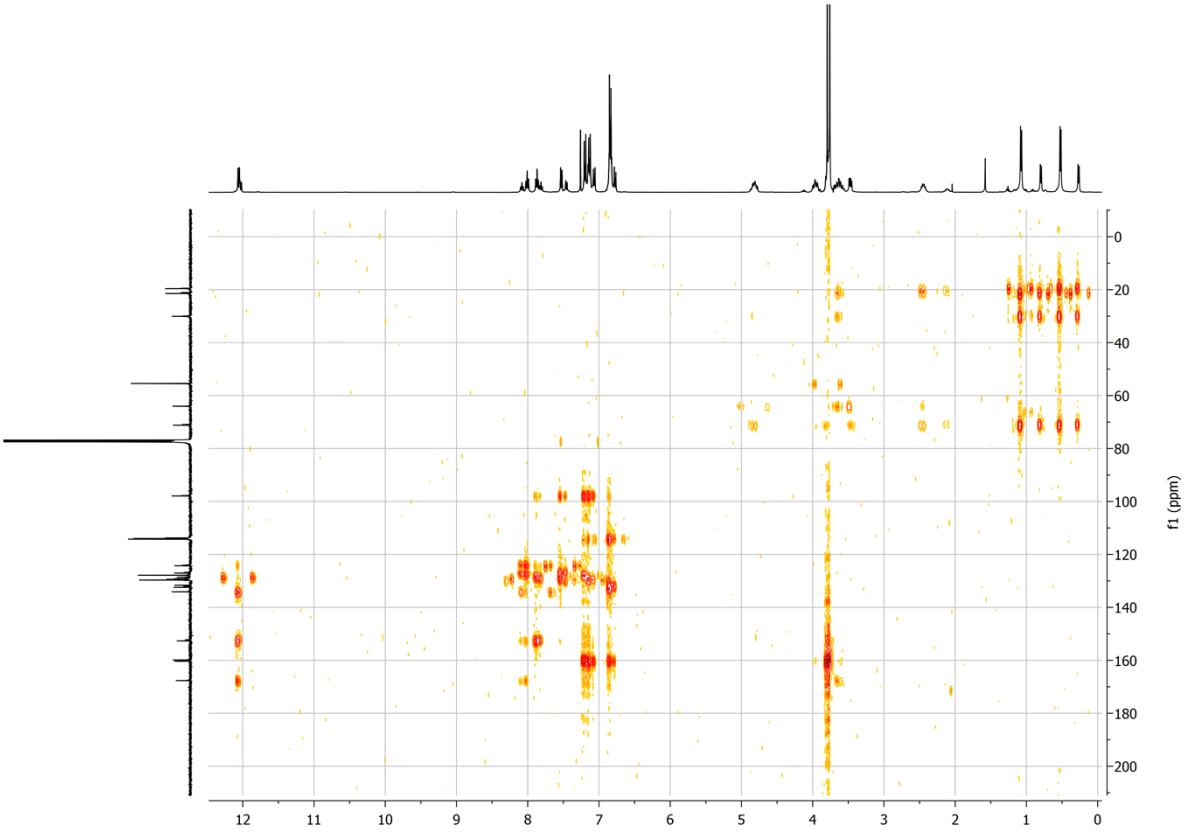
^{13}C NMR:



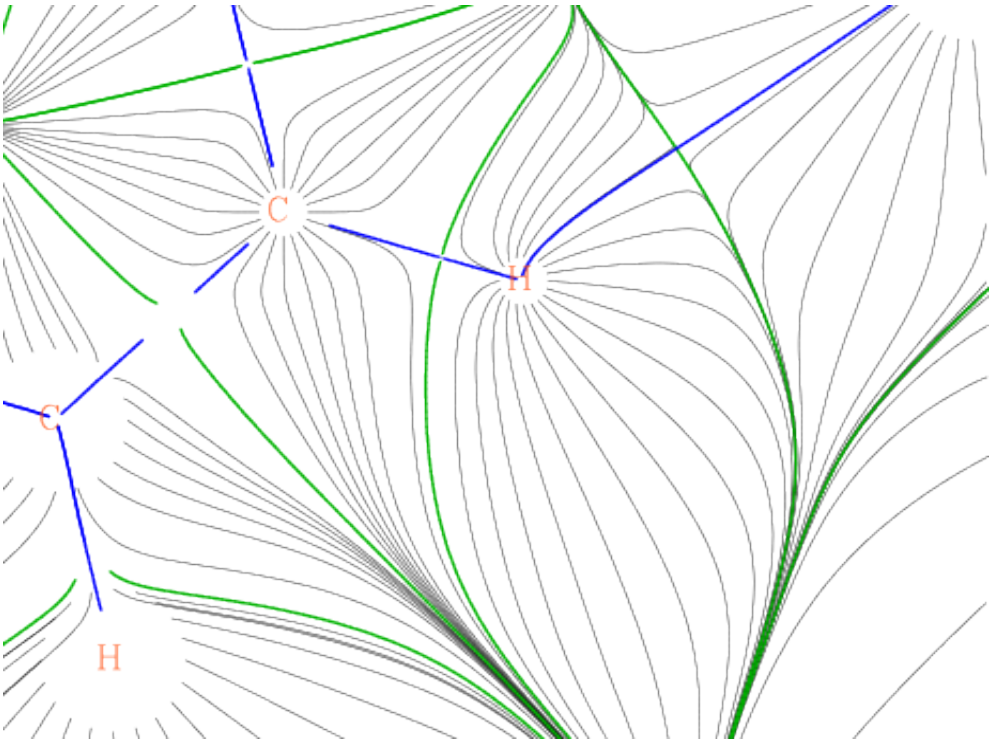
$^{1}H,^{13}C$ HSQC:



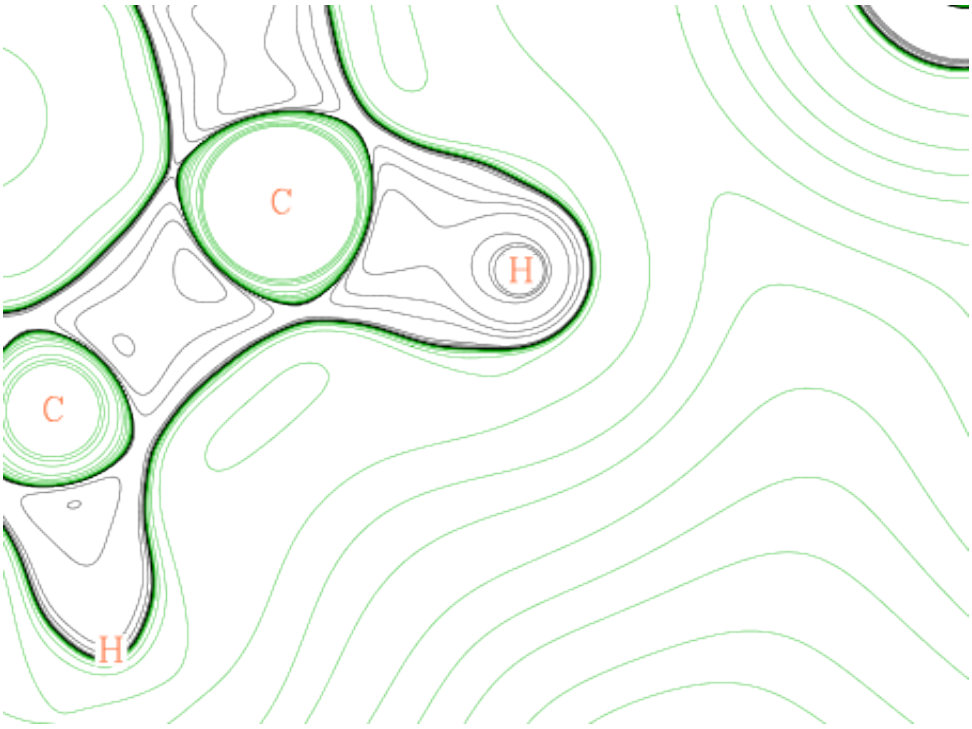
$^{1}H,^{13}C$ HMBC:



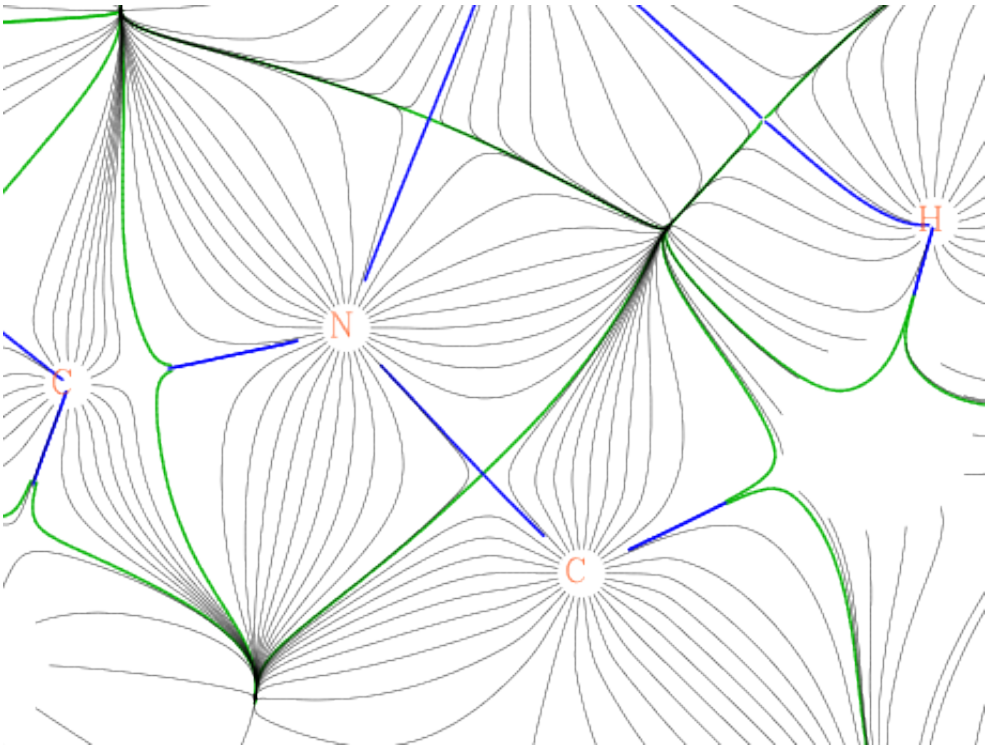
Gradient vector field of the electron density in the region of the Pd-H3 anagostic interaction:



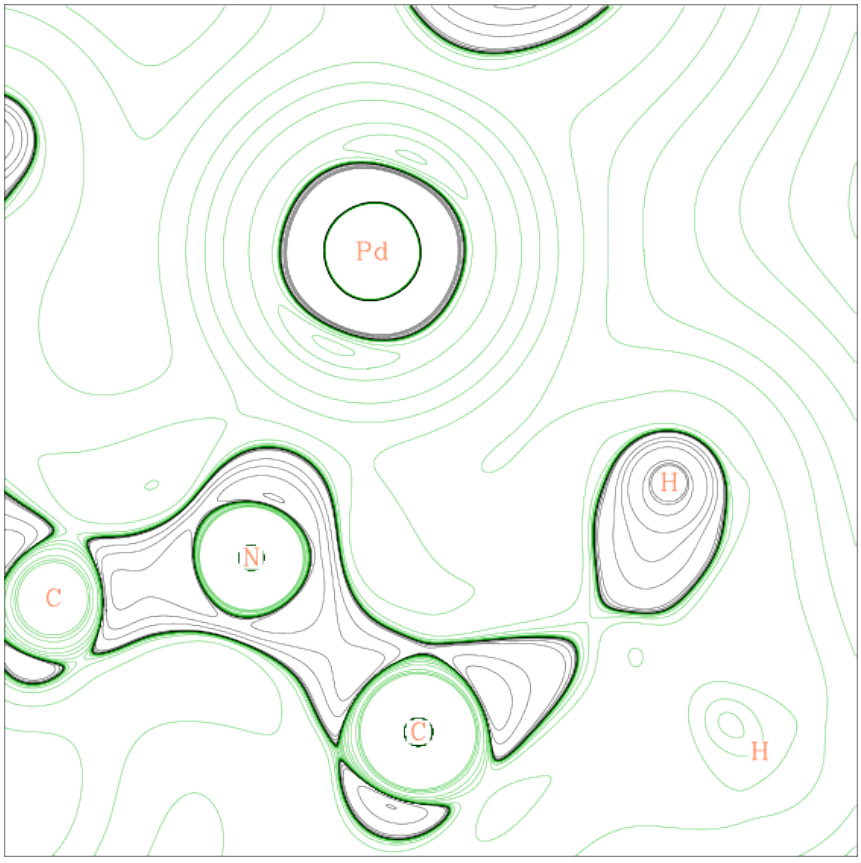
Laplacian of the electron density in the region of the Pd-H3 anagostic interaction:



Gradient vector field of the electron density in the region of the Pd-H24b anagostic interaction:



Laplacian of the electron density in the region of the Pd-H24b anagostic interaction:



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