Electronic Supplementary Material (ESI) for Dalton Transactions.


# Synthesis of disubstituted furans catalysed by $[(AuCl)_2(\mu\text{-bis(phosphino)metallocene})]$ and $Na[BArF_{24}]$

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**Supporting Information**

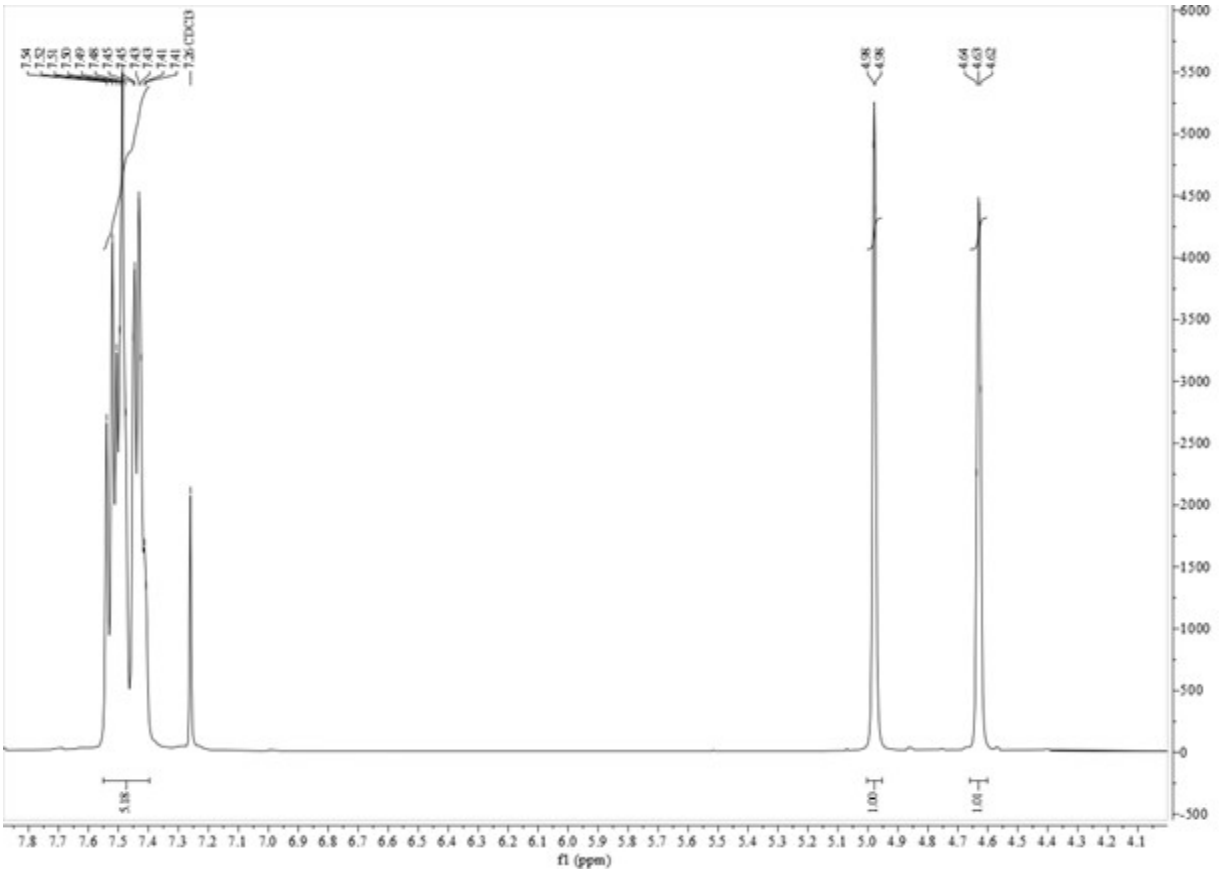



**Fig. S1.** $^{1}$H NMR spectrum of [$(AuCl)_2$(μ-dppr)] in $CDCl_3$.

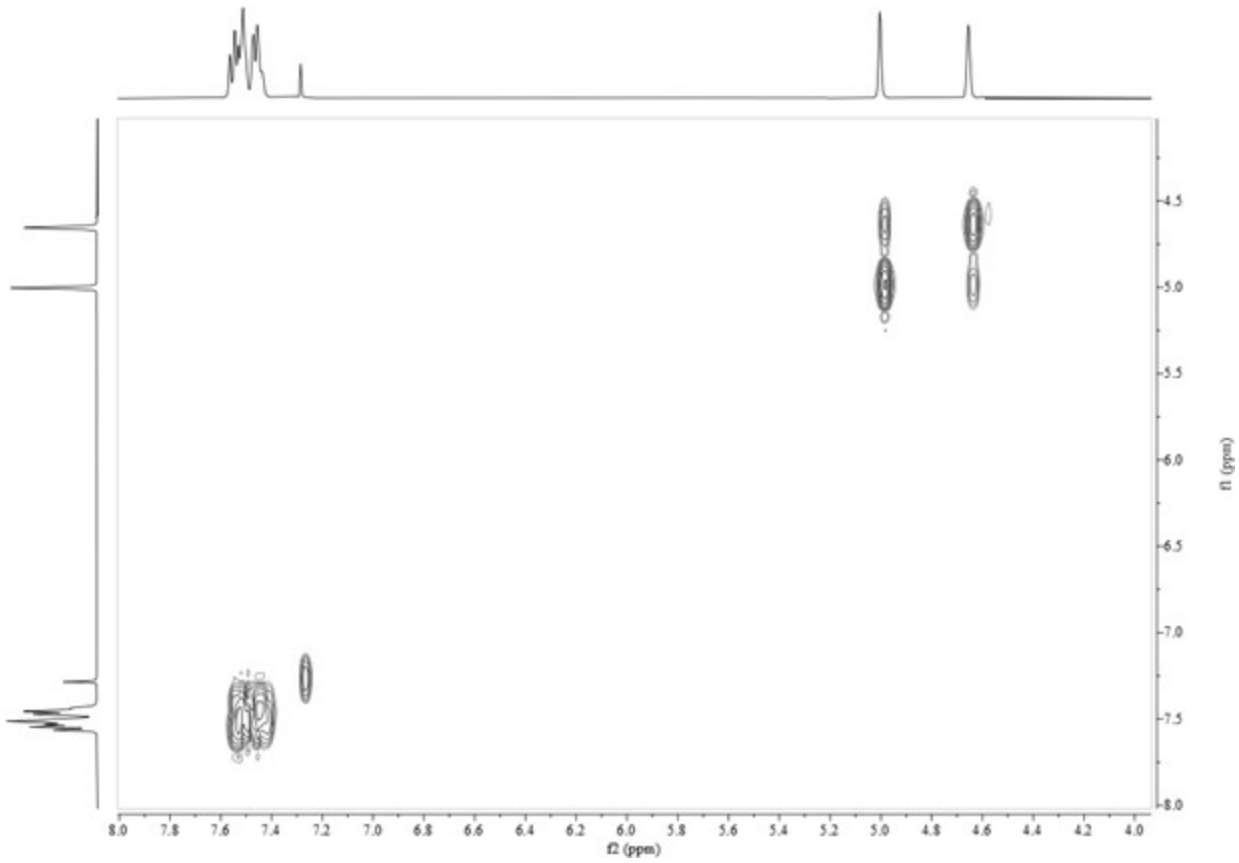



**Fig. S2.** $^{1}H$ COSY NMR spectrum of $[(AuCl)_2(\mu\text{-dppr})]$ in $CDCl_3$.

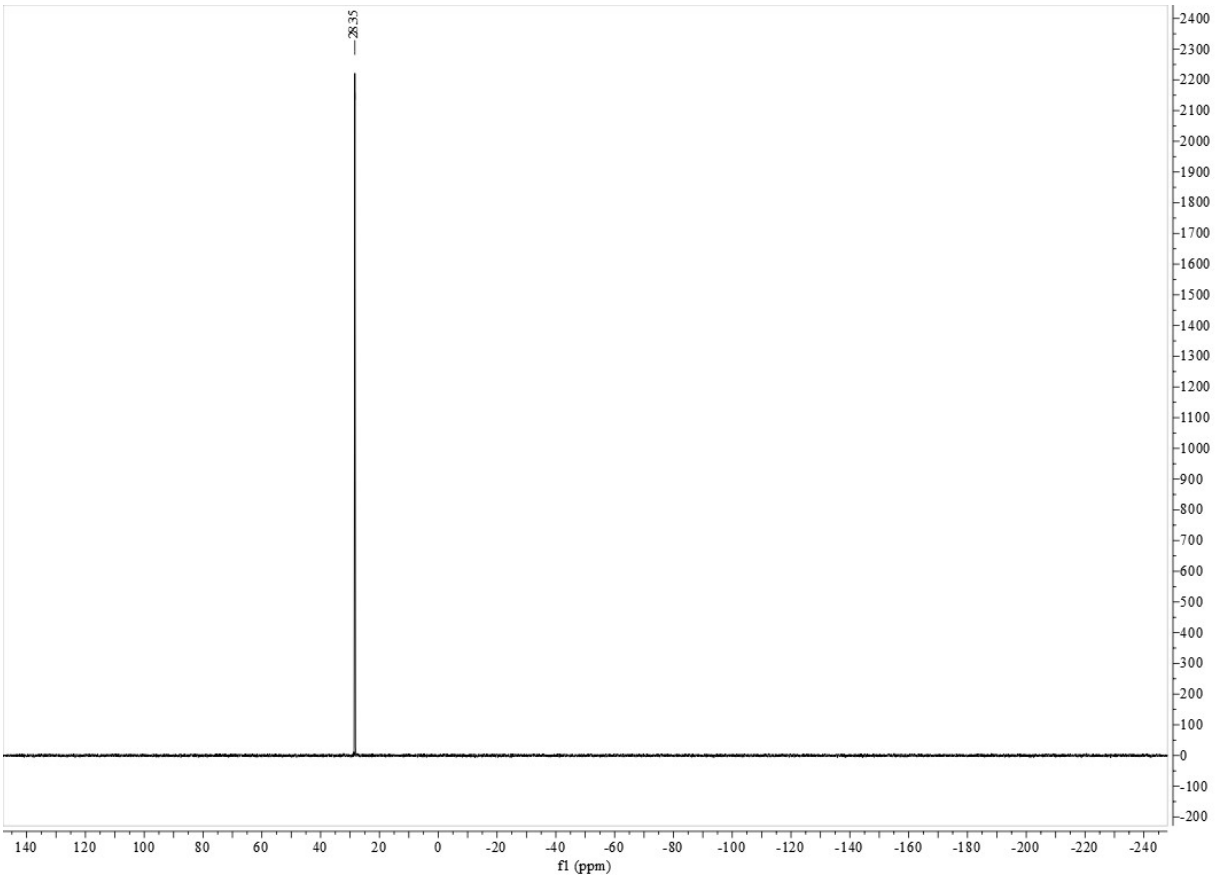



**Fig. S3.** $^{31}P\{^{1}H\}$ NMR spectrum of $[(AuCl)_2(\mu\text{-dppr})]$ in $CDCl_3$.


**Fig. S4.** $^{13}C\{^{1}H\}$ NMR spectrum of $[(AuCl)_2(\mu\text{-dppr})]$ in $CDCl_3$.

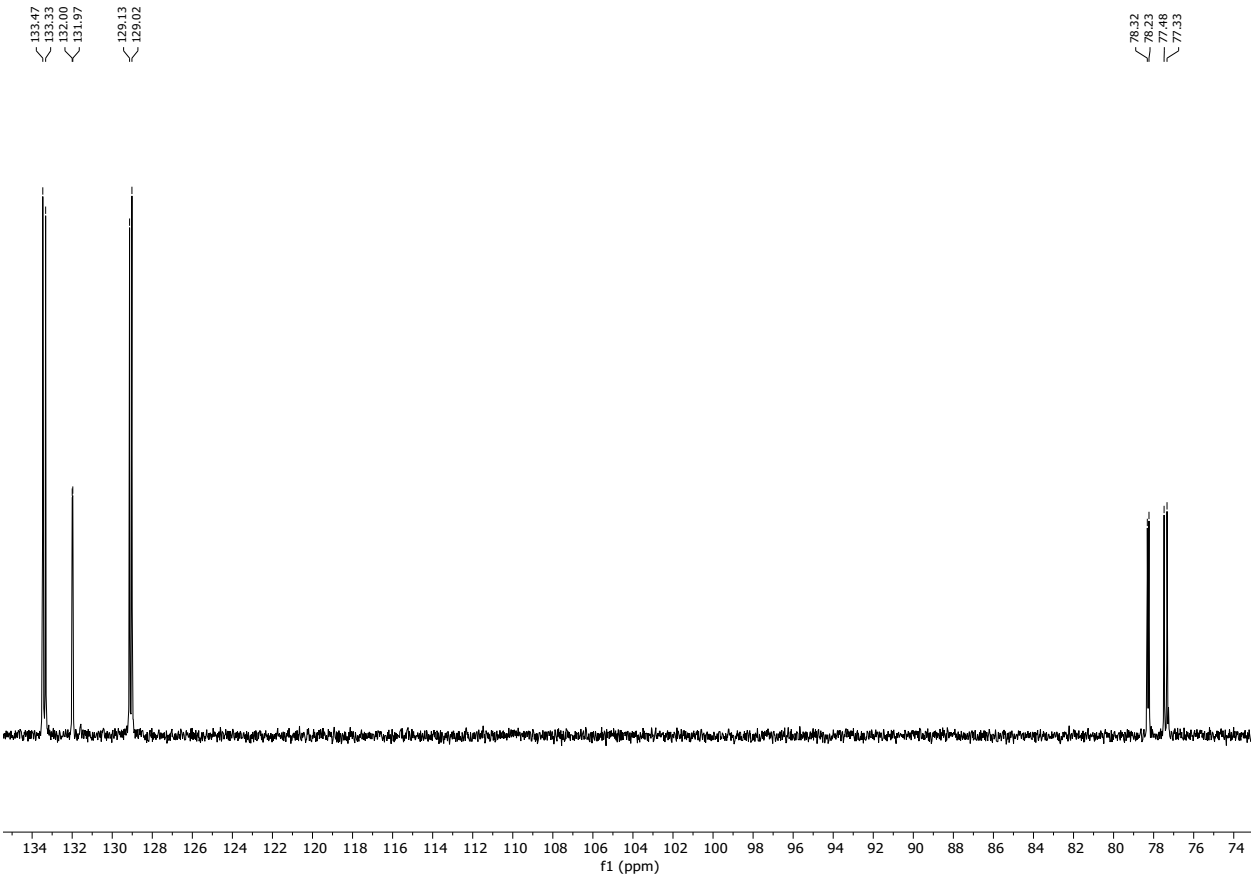



**Fig. S5.** DEPT-135 $^{13}C$ NMR spectrum of $[(AuCl)_2(\mu\text{-dppr})]$ in $CDCl_3$.

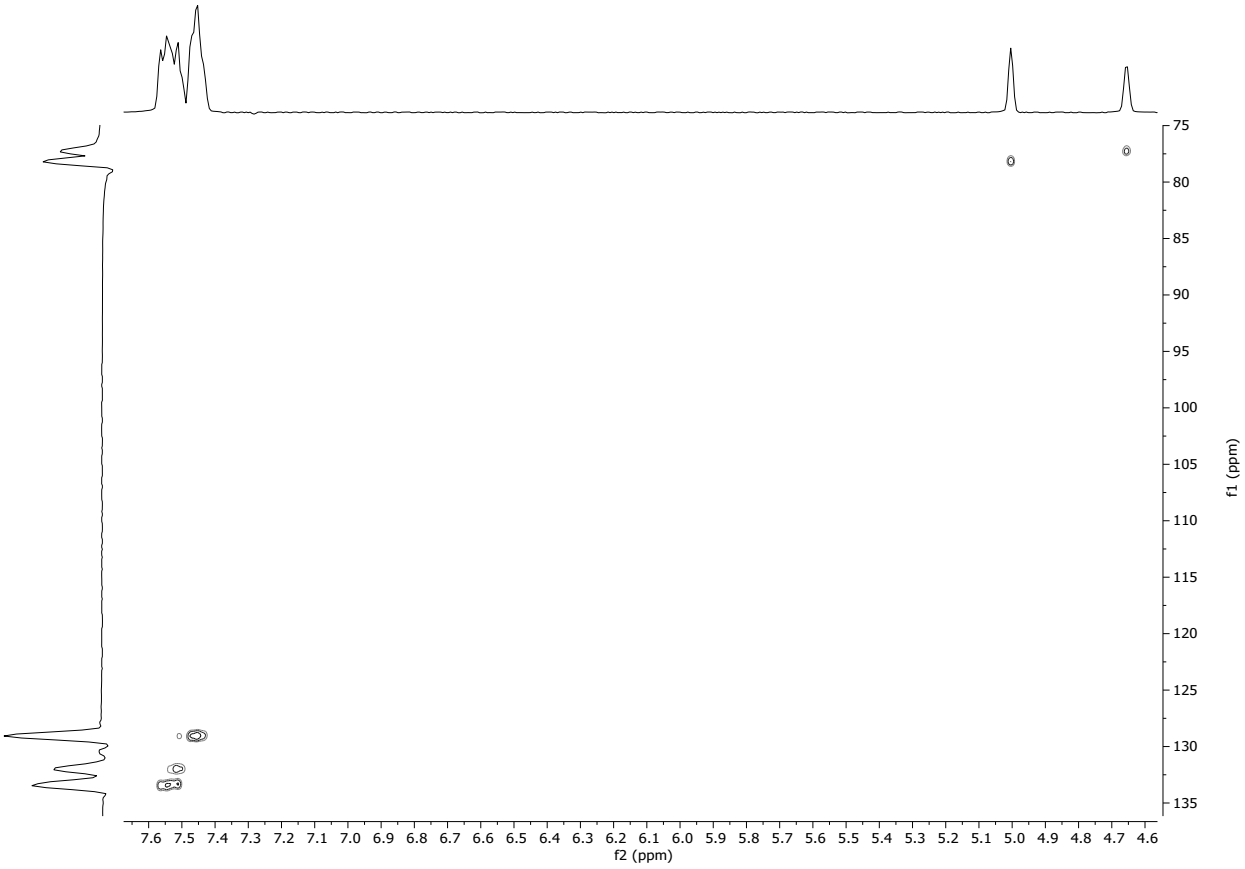



**Fig. S6.** $^{13}C$-$^{1}H$ HMBC NMR spectrum of $[(AuCl)_2(\mu\text{-dppr})]$ in $CDCl_3$.

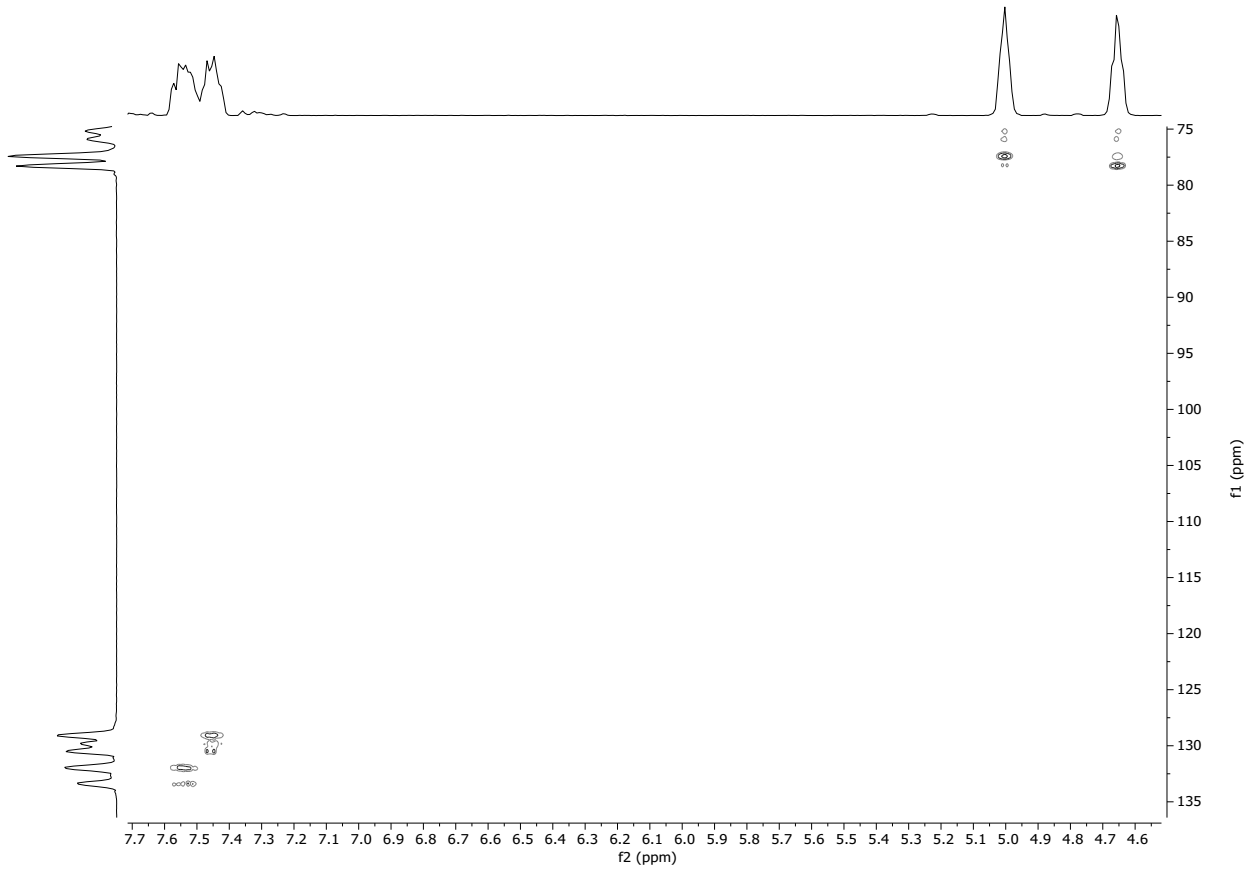



**Fig. S7.** $^{13}C$-$^{1}H$ HSQC NMR spectrum of $[(AuCl)_2(\mu\text{-dppr})]$ in $CDCl_3$.

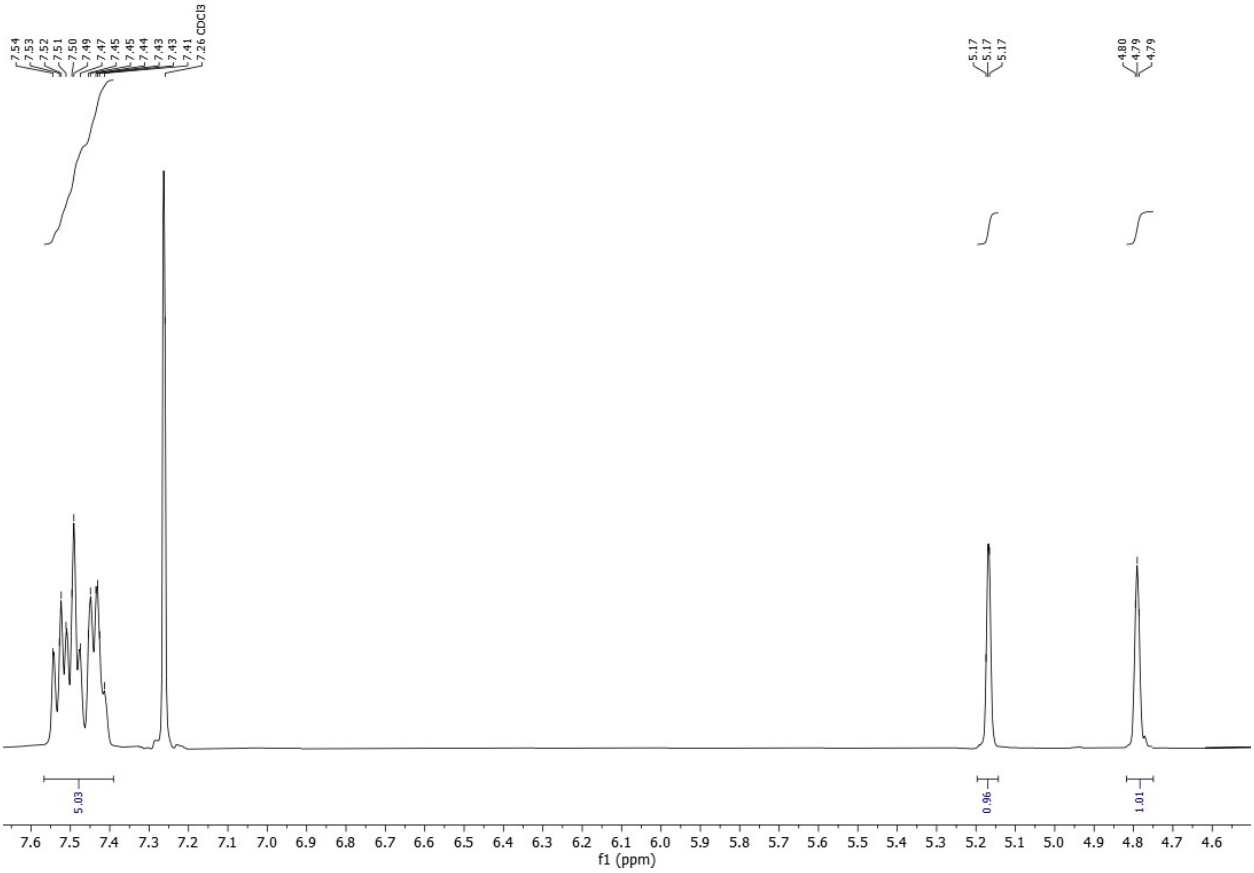



**Fig. S8.** $^{1}$H NMR spectrum of [$(AuCl)_2$(μ-dppo)] in $CDCl_3$.

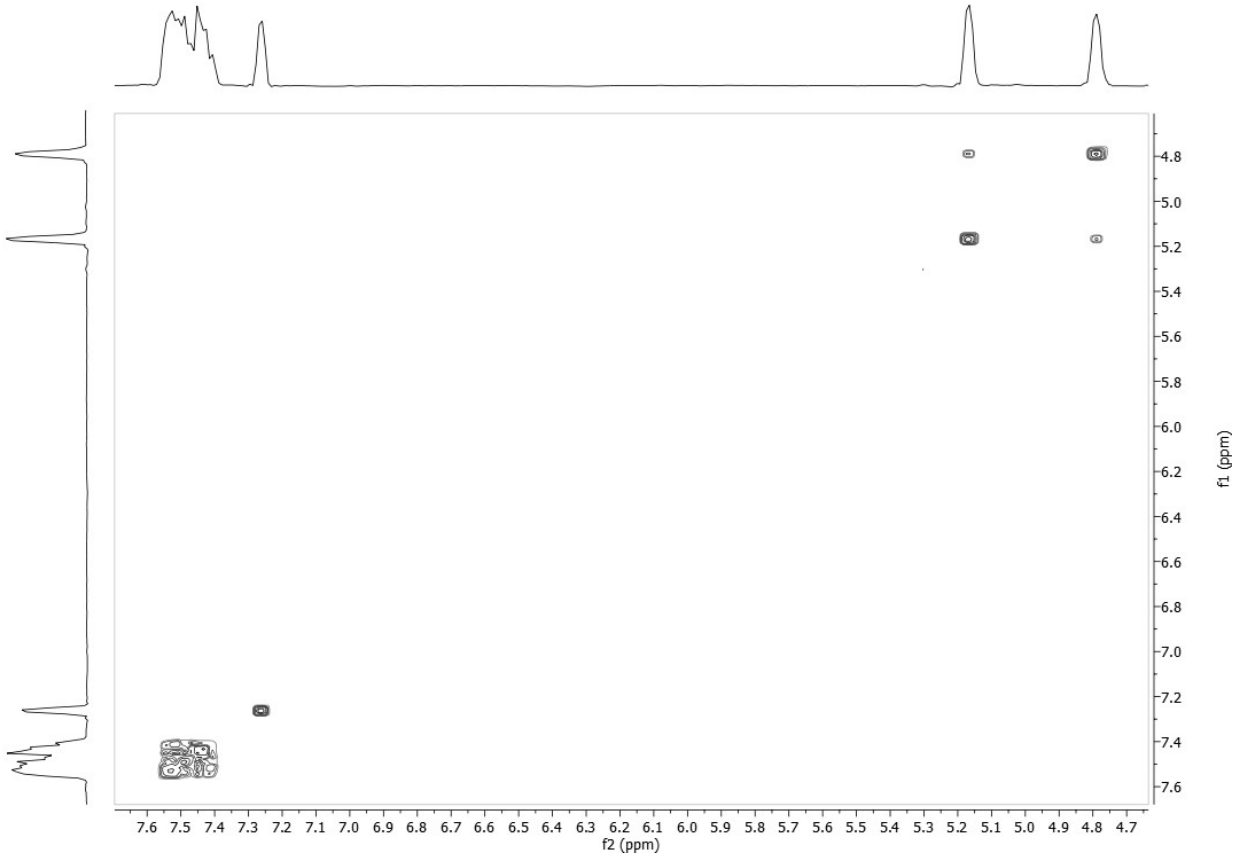



**Fig. S9.** $^{1}$H COSY NMR spectrum of $[(AuCl)_2(\mu\text{-dppo})]$ in $CDCl_3$.

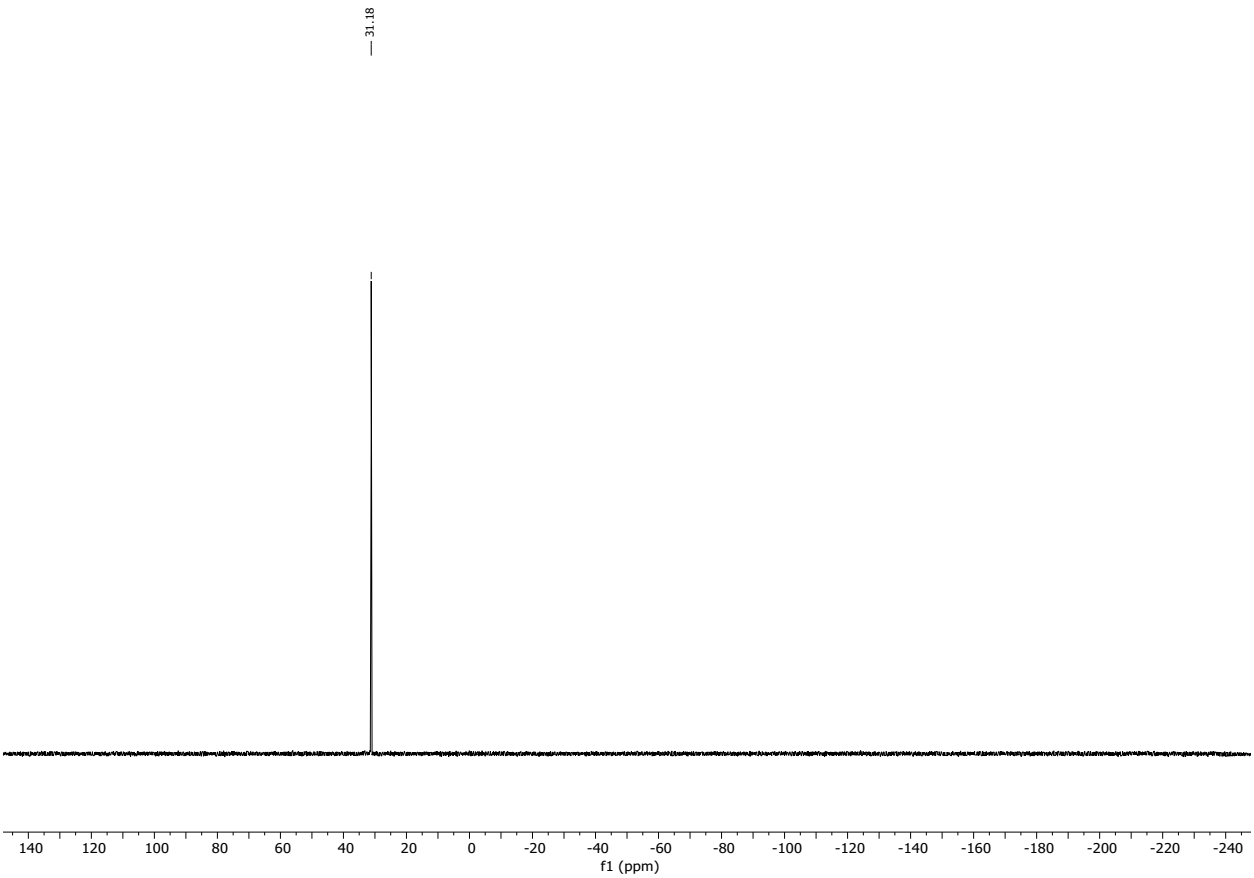



**Fig. S10.** $^{31}P\{^{1}H\}$ NMR spectrum of $[(AuCl)_2(\mu\text{-dppo})]$ in $CDCl_3$

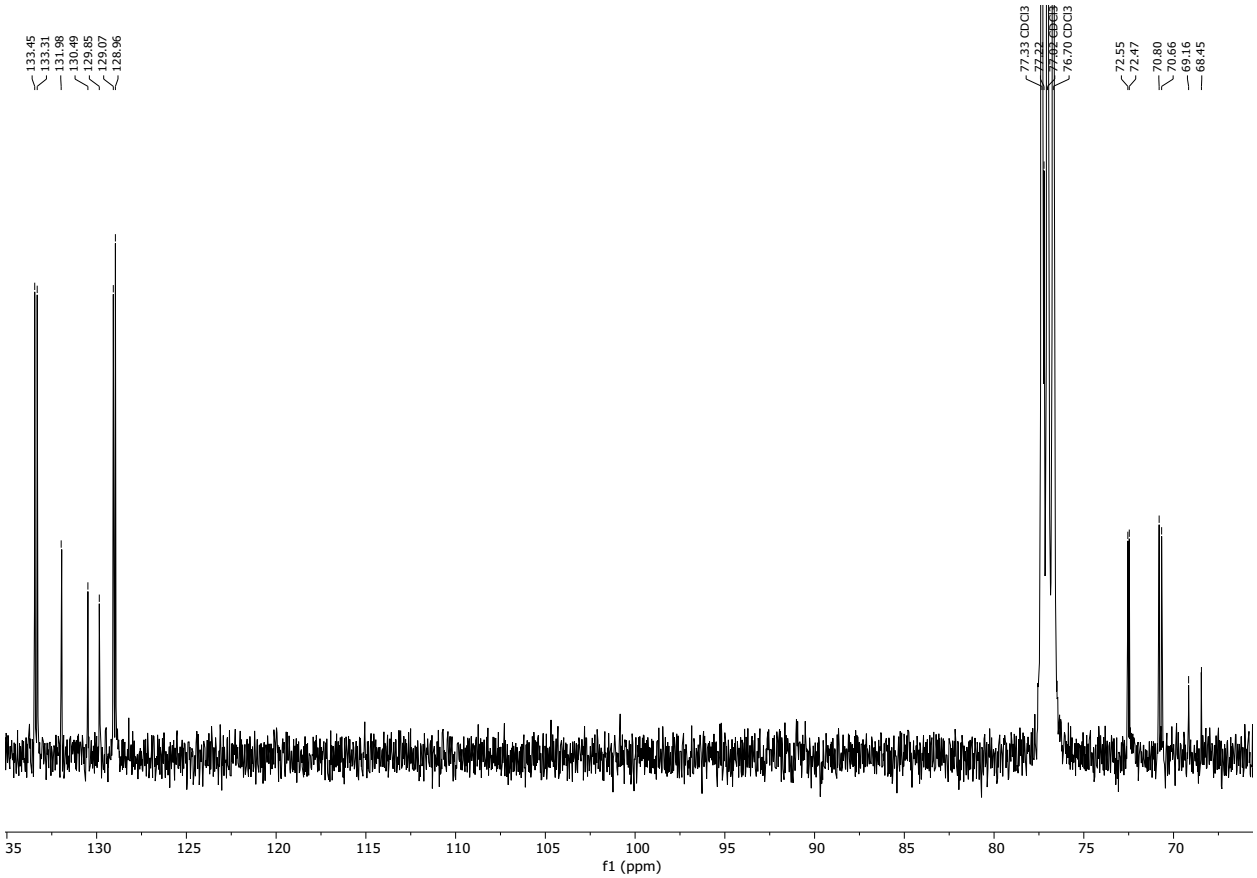



**Fig. S11.** $^{13}C\{^{1}H\}$ NMR spectrum of $[(AuCl)_2(\mu\text{-dppo})]$ in $CDCl_3$.

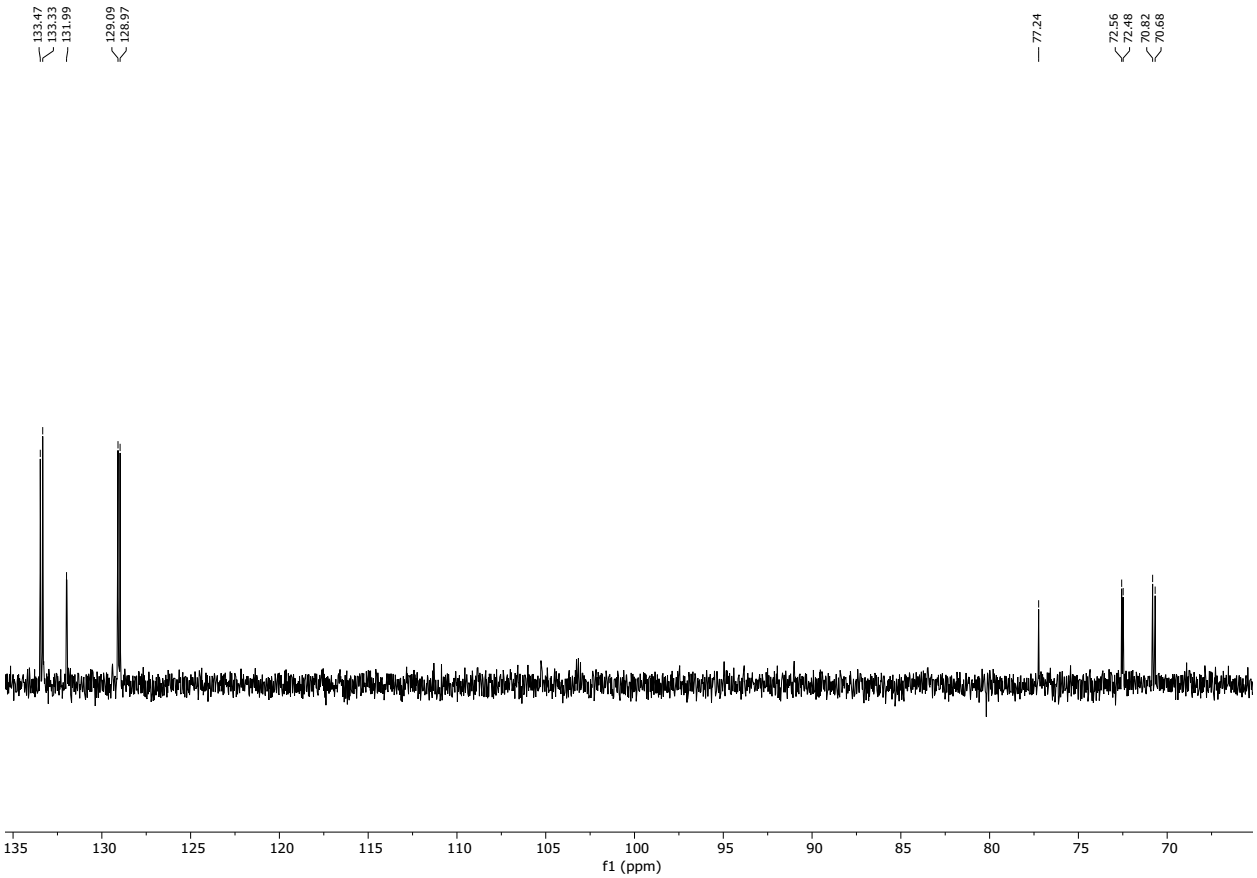



**Fig. S12.** DEPT-135 $^{13}C$ NMR spectrum of $[(AuCl)_2(\mu\text{-dppo})]$ in $CDCl_3$.

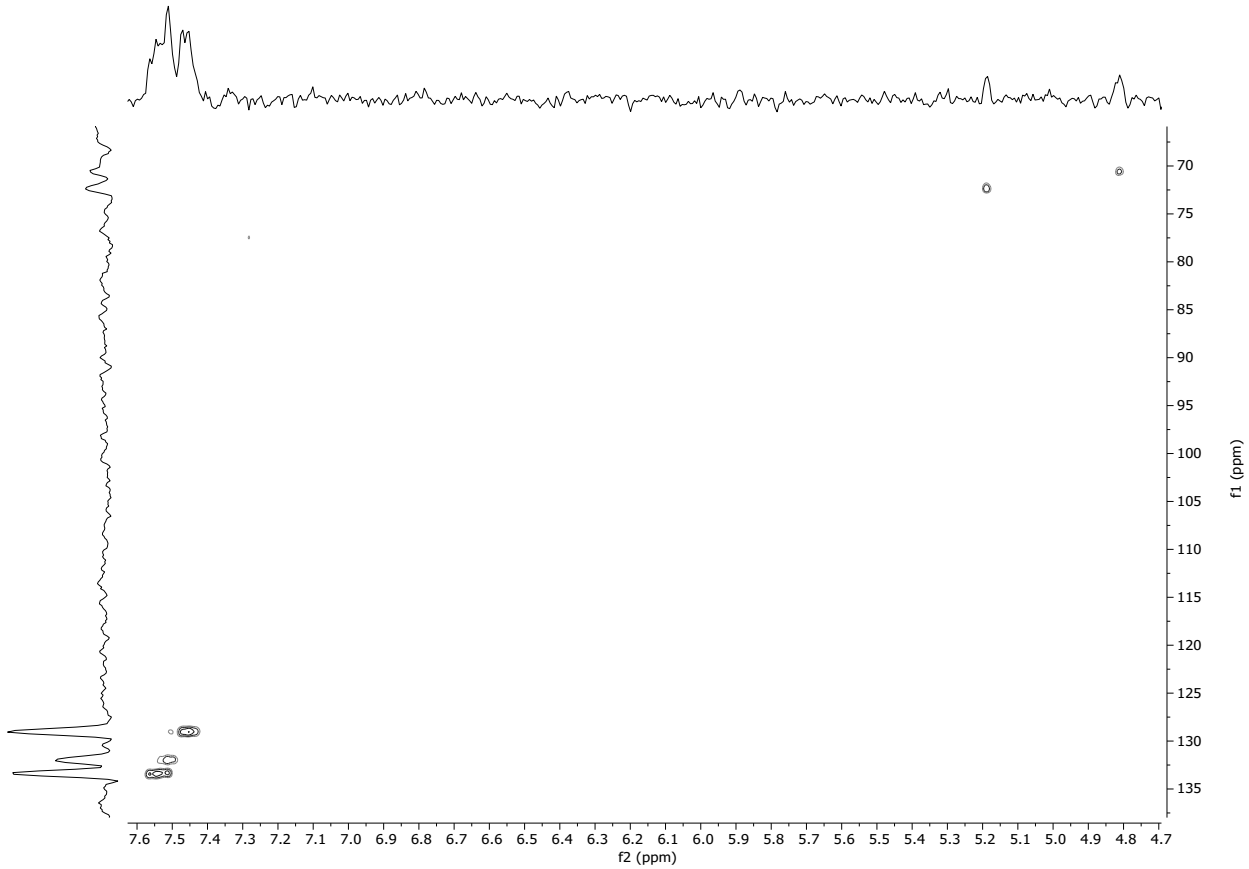



**Fig. S13.** $^{13}C$-$^{1}H$ HMBC NMR spectrum of $[(AuCl)_2(\mu\text{-dppo})]$ in $CDCl_3$.

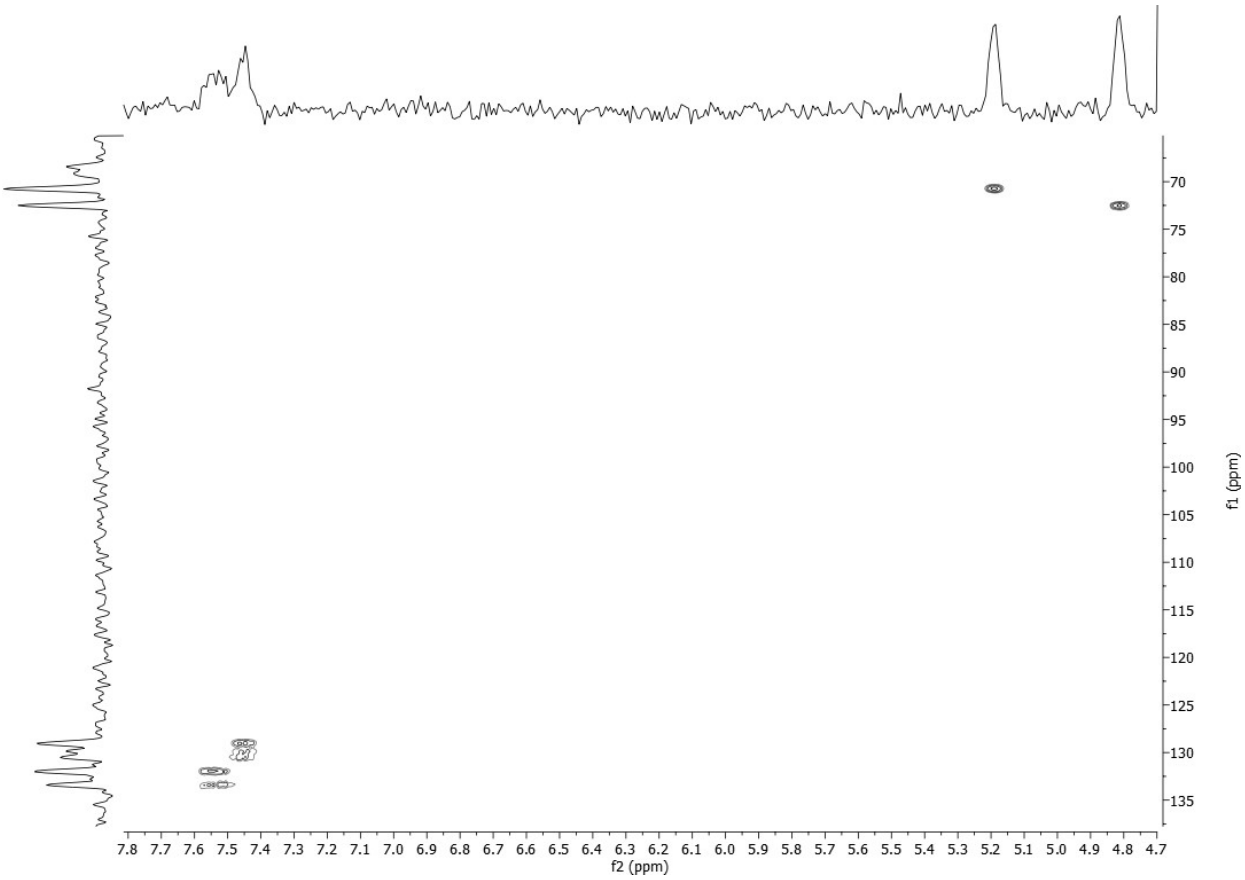
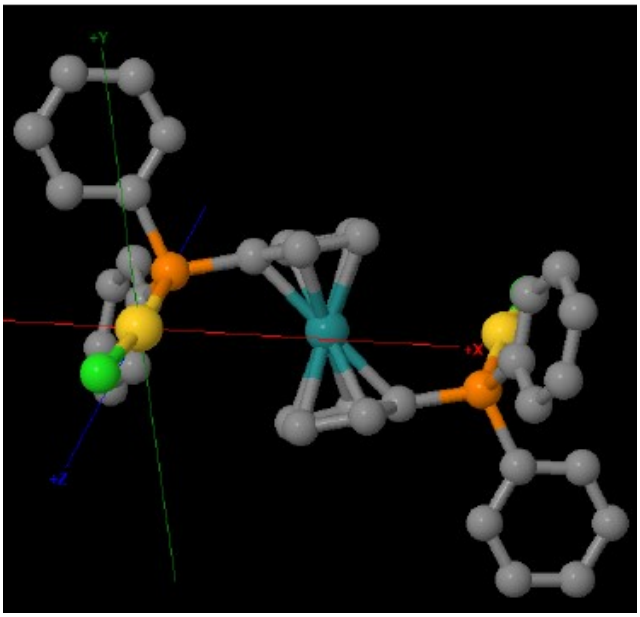



**Fig. S14.** $^{13}C$-$^{1}H$ HSQC NMR spectrum of $[(AuCl)_2(\mu\text{-dppo})]$ in $CDCl_3$.

**Table S1.** Crystallographic data for [$(AuCl)_2$(μ-dppr)] and [$(AuCl)_2$(μ-dppo)].

| | **[$(AuCl)_2$(μ-dppr)]** | **[$(AuCl)_2$(μ-dppo)]** |
|---|---|---|
| formula | $C_{34}H_{28}Au_2Cl_2P_2Ru$ | $C_{34}H_{28}Au_2Cl_2OsP_2$ |
| fw | 1064.41 | 1153.54 |
| crystal system | monoclinic | monoclinic |
| space group | $P2_1/n$ | $P2_1/n$ |
| *a*, Å | 8.7596(7) | 8.7482(2) |
| *b*, Å | 16.7100(12) | 16.7111(5) |
| *c*, Å | 10.6881(7) | 10.6925(3) |
| $\alpha$, deg | 90 | 90 |
| $\beta$, deg | 94.805(6) | 94.880(2) |
| $\gamma$, deg | 90 | 90 |
| *V*, Å$^3$ | 1559.0(2) | 1557.49(7) |
| Z | 2 | 2 |
| cryst. size, mm | 0.453 x 0.400 x 0.214 | 0.517 x 0.412 x 0.188 |
| cryst. color | Yellow | Colorless |
| radiation | 0.71073 | 0.71073 |
| temp, K | 100.0(1) | 100.1(1) |
| 2$\theta$ range, deg | 4.536-61.136 | 4.534-61.112 |
| data collected | | |
| *h* | -12 to 12 | -12 to 12 |
| *k* | -23 to 23 | -23 to 23 |
| *l* | -13 to 14 | -15 to 15 |
| no. of data collected | 15987 | 15974 |
| no. of unique data | 4527 | 4523 |
| abs. corr. | SCALE3 ABSPACK | SCALE3 ABSPACK |
| final *R* indices | | |
| R1 | 0.0251 | 0.0321 |
| wR2 | 0.0663 | 0.0814 |
| goodness of fit | 1.103 | 1.050 |



| %V Free | %V Buried | %V Tot/V Ex |
|---|---|---|
| 64.5 | 35.5 | 99.9 |

| Quadrant | V f | V b | V t | %V f | %V b |
|---|---|---|---|---|---|
| SW | 30.3 | 14.6 | 44.9 | 67.5 | 32.5 |
| NW | 28.3 | 16.6 | 44.9 | 63.1 | 36.9 |
| NE | 31.3 | 13.5 | 44.9 | 69.8 | 30.2 |
| SE | 25.8 | 19.1 | 44.9 | 57.5 | 42.5 |

**Steric Map**

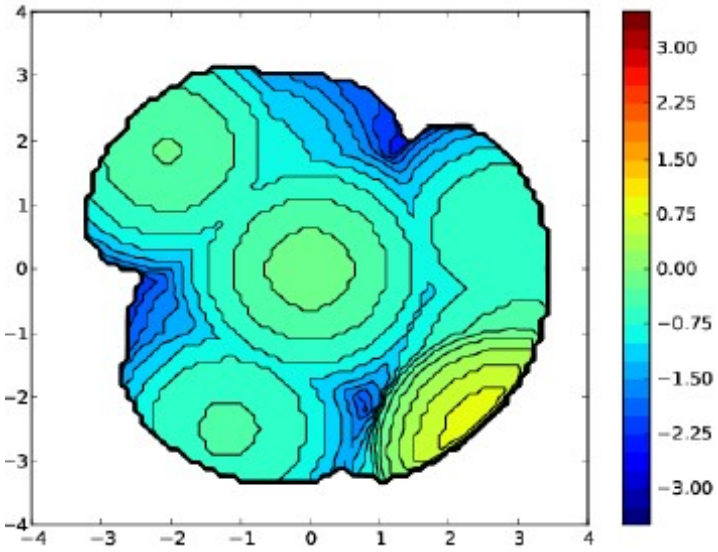
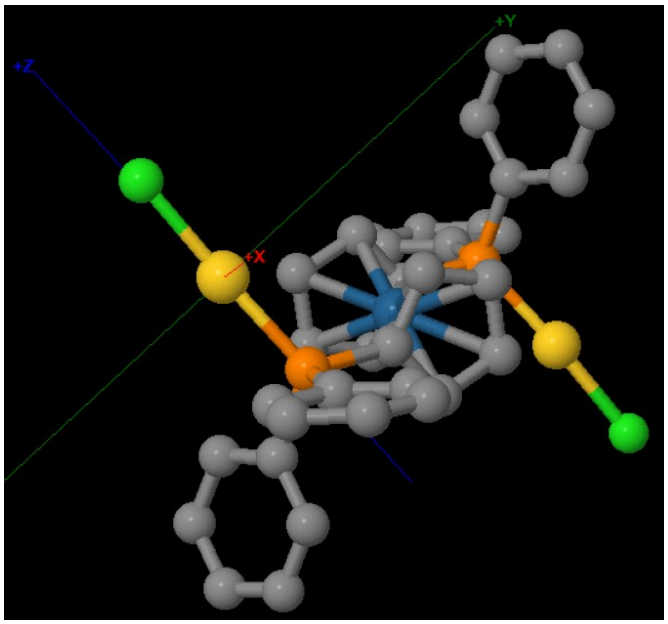



**Fig. S15.** SambVca results for [$(AuCl)_2$(μ-dppr)].




| %V Free | %V Buried | %V Tot/V Ex |
|---|---|---|
| 64.4 | 35.6 | 99.9 |

| Quadrant | V f | V b | V t | %V f | %V b |
|---|---|---|---|---|---|
| SW | 28.8 | 16.1 | 44.9 | 64.2 | 35.8 |
| NW | 24.9 | 20.0 | 44.9 | 55.5 | 44.5 |
| NE | 32.1 | 12.7 | 44.9 | 71.7 | 28.3 |
| SE | 29.7 | 15.2 | 44.9 | 66.2 | 33.8 |

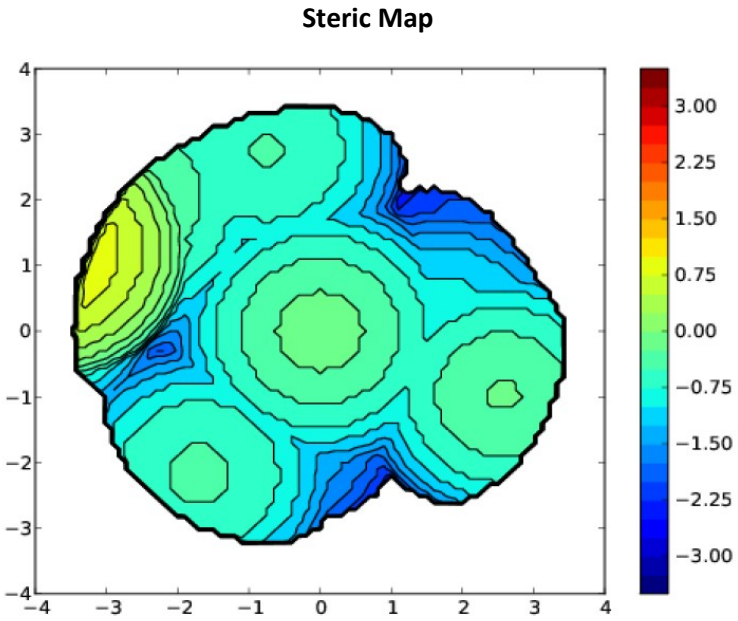



**Fig. S16.** SambVca results for [$(AuCl)_2$(μ-dppo)].

**Characterization of furan products**

2,5-diphenylfuran: $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra were in good agreement with the literature.[1]

2,5-di(3-tolyl)furan: $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra were in good agreement with the literature.[2]

2,5-di(4-*tert*-butylphenyl)furan: $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra were in good agreement with the literature.[2]

2,5-di-n-pentylfuran: $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra were in good agreement with the literature.[3]

2,5-dicyclopropylfuran: The $^{1}H$ NMR spectrum was in good agreement with the reported spectrum.[4] $^{13}C\{^{1}H\}$ NMR: $\delta$ (ppm) 152.6 (s, No DEPT), 106.1 (s, DEPT +), 10.5 (s, DEPT +), 6.5 (s, DEPT -).

2,5-dibenzylfuran: $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.24 (m, 4H, -*Ph*), 7.17 (m, 6H, -*Ph*), 5.94 (s, 2H, =C*H*), 3.79 (m, 4H, -C$H_2$-). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 153.7 (s, No DEPT), 137.6 (s, No DEPT), 130.1 (S, DEPT +), 128.8 (s, DEPT +), 124.0 (s, No DEPT), 108.7 (s, DEPT +), 38.9 (s, DEPT -).

2,5-di(4-pentynyl)furan: $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 6.02 (s, 2H, =C*H*), 2.74 (m, 4H, -C$H_2$-), 2.42 (m, 4H, -C$H_2$-), 2.10 (t, *J* = 2.6 Hz, 2H, ≡C*H*), 1.82 (m, 4H, -C$H_2$-). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 152.2 (s, No DEPT), 107.1 (s, DEPT +), 84.1 (s, no DEPT), 70.4 (s, DEPT +), 28.1 (s, DEPT -), 25.7 (s, DEPT -), 17.5 (s, DEPT -).

2,5-di(5-hexynyl)furan: $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 5.96 (s, 2H, =C*H*), 2.69 (m, 4H, -C$H_2$-), 2.44 (m, 4H, -C$H_2$-), 2.00 (t, *J* = 2.5 Hz, 2H, ≡C*H*), 1.71 (m, 4H, -C$H_2$-), 1.52 (m, 2H, -C$H_2$-). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 153.0 (s, No DEPT), 106.3 (s, DEPT +), 84.0 (s, no DEPT), 68.7 (s, DEPT +), 29.4 (s, DEPT -), 27.3 (s, DEPT -), 26.3 (s, DEPT -), 18.3 (s, DEPT -).

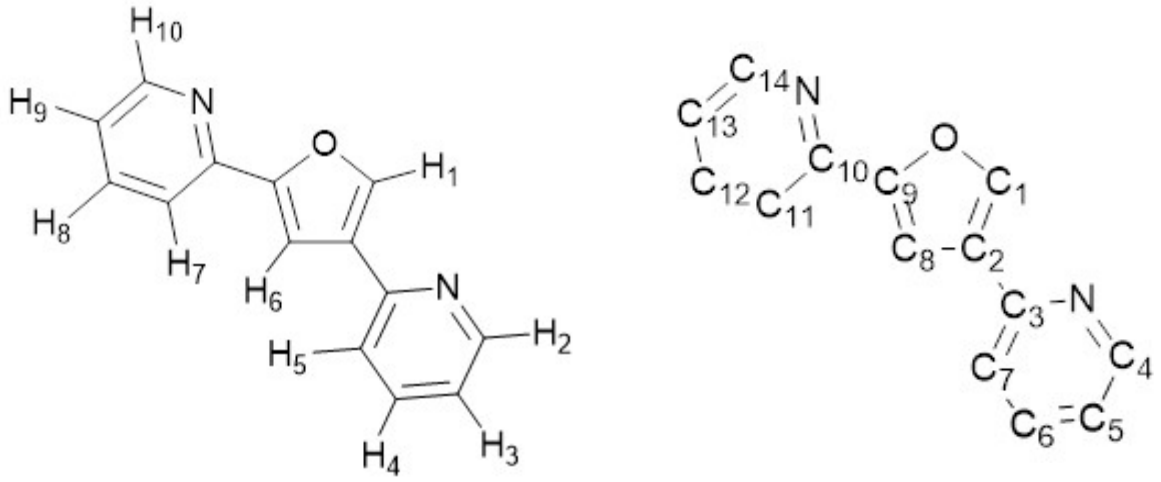
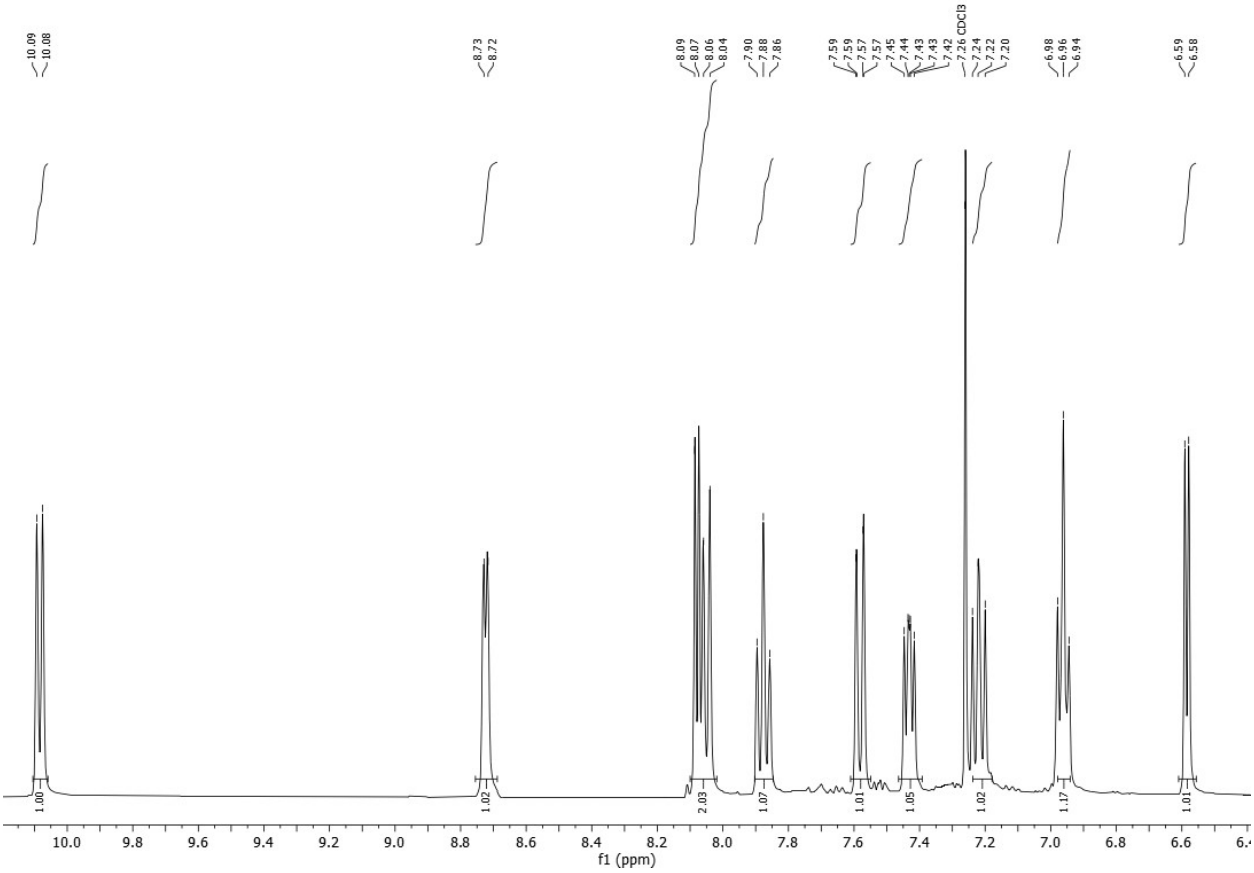
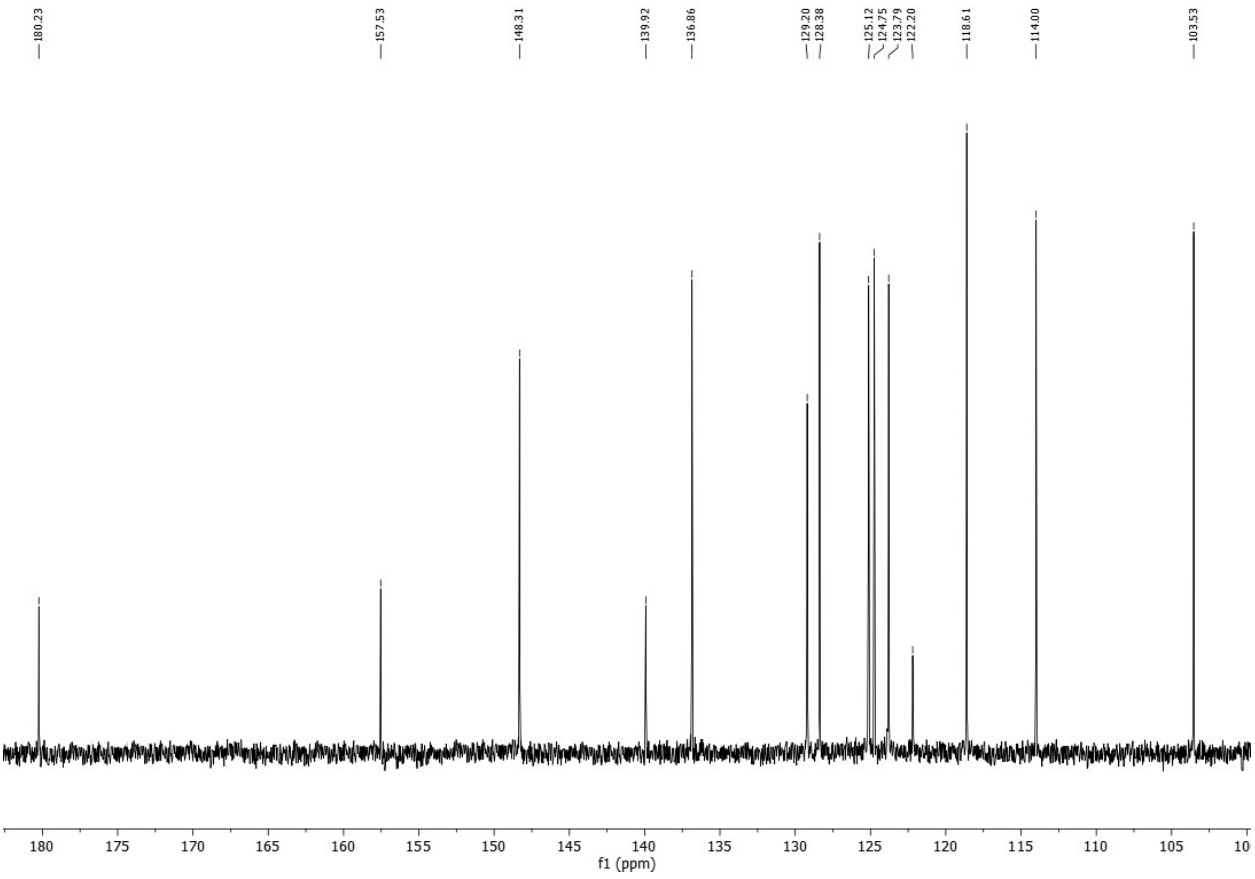



**Fig. S17.** Proton (left) and carbon (right) numbering scheme for 2,4-di(2-pyridyl)furan.




$^1$H NMR (400 MHz, $CDCl_3$) δ 10.08 (d, *J* = 7.1 Hz, 1H, H2), 8.72 (d, *J* = 4.9 Hz, 1H, H10), 8.06 (dd, *J* = 12.4, 6.3 Hz, 2H), 7.88 (t, *J* = 7.8 Hz, 1H), 7.58 (dd, *J* = 8.7, 1.2 Hz, 1H), 7.46 – 7.39 (m, 1H), 7.21 (d, *J* = 8.7 Hz, 1H), 6.95 (d, *J* = 7.0 Hz, 1H), 6.59 (d, *J* = 4.8 Hz, 1H).

**Fig. S18.** $^1$H NMR spectrum of 2,4-di(2-pyridyl)furan in $CDCl_3$.




$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 180.23 (C9), 157.53 (C3), 148.31 (C14), 139.92, 136.86, 129.20 (C4), 128.38, 125.12, 124.75, 123.79, 122.20, 118.61, 114.00, 103.53.

**Fig. S19.** $^{13}C\{^{1}H\}$ NMR spectrum of 2,4-di(2-pyridyl)furan in $CDCl_3$.

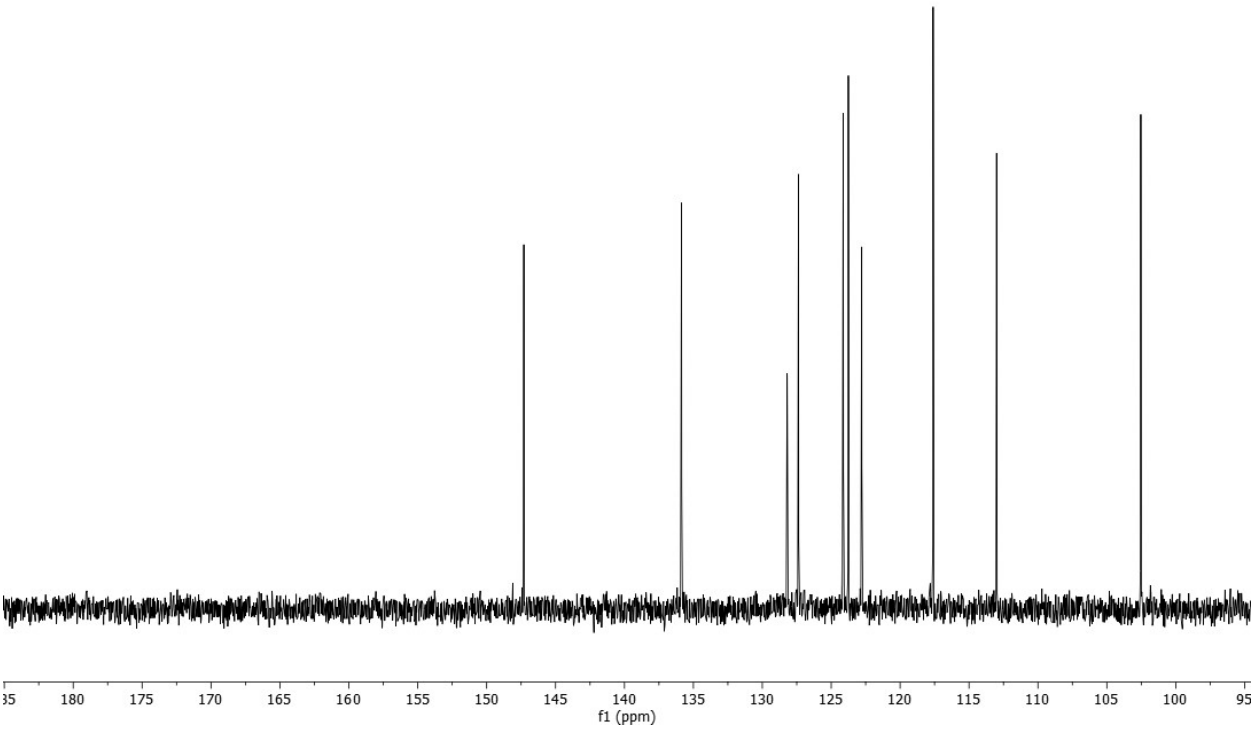



**Fig. S20.** $^{13}C$ DEPT NMR spectrum of 2,4-di(2-pyridyl)furan in $CDCl_3$.

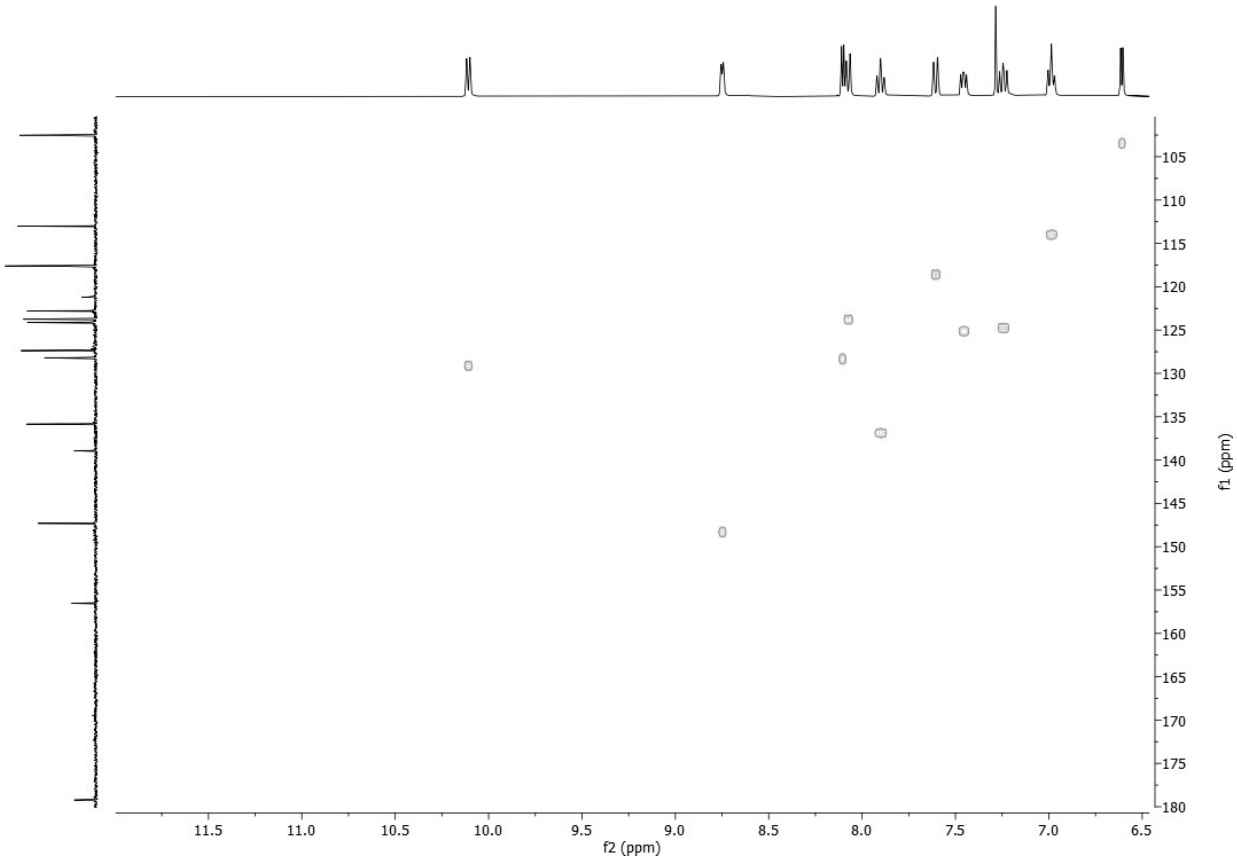



**Fig. S21.** $^{13}C$-$^{1}H$ HMBC NMR spectrum of 2,4-di(2-pyridyl)furan in $CDCl_3$.

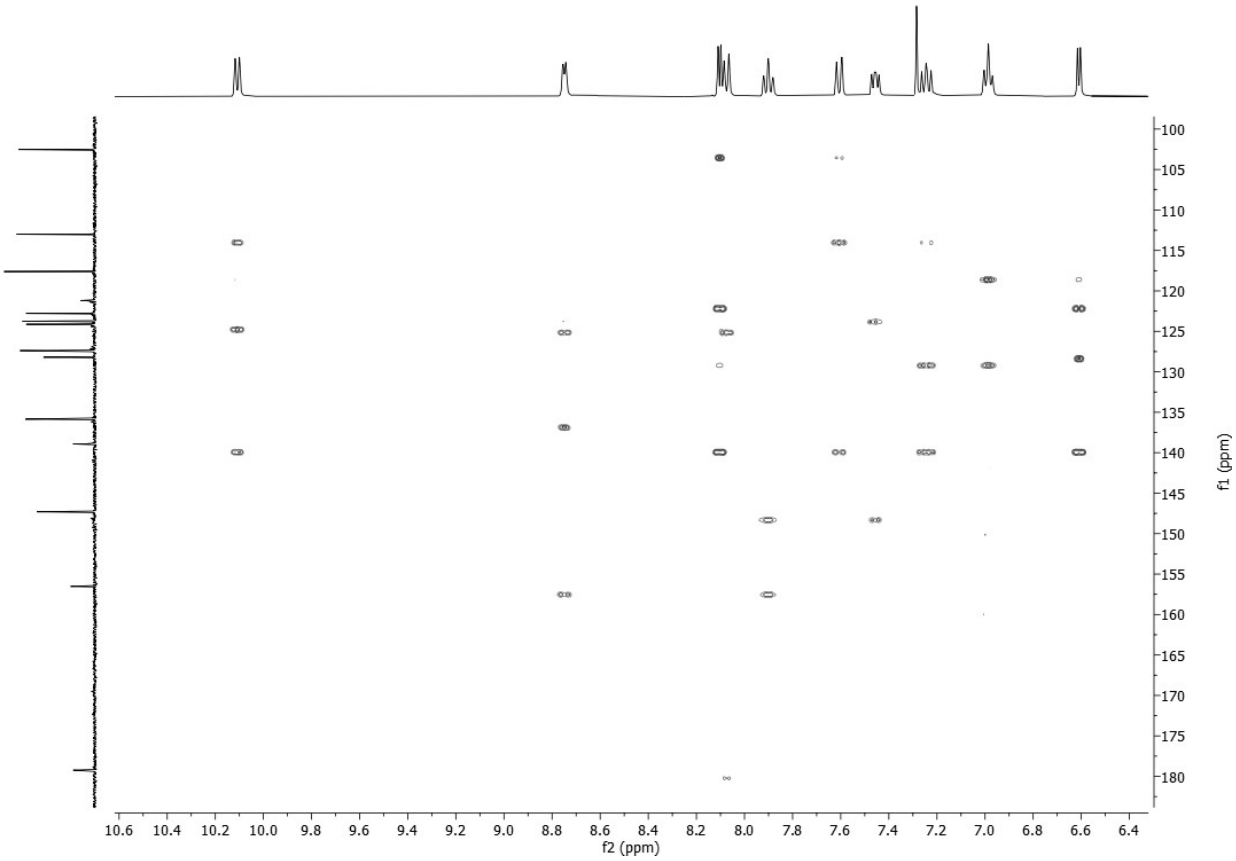



**Fig. S22.** $^{13}C$-$^{1}H$ HSQC NMR spectrum of 2,4-di(2-pyridyl)furan in $CDCl_3$.

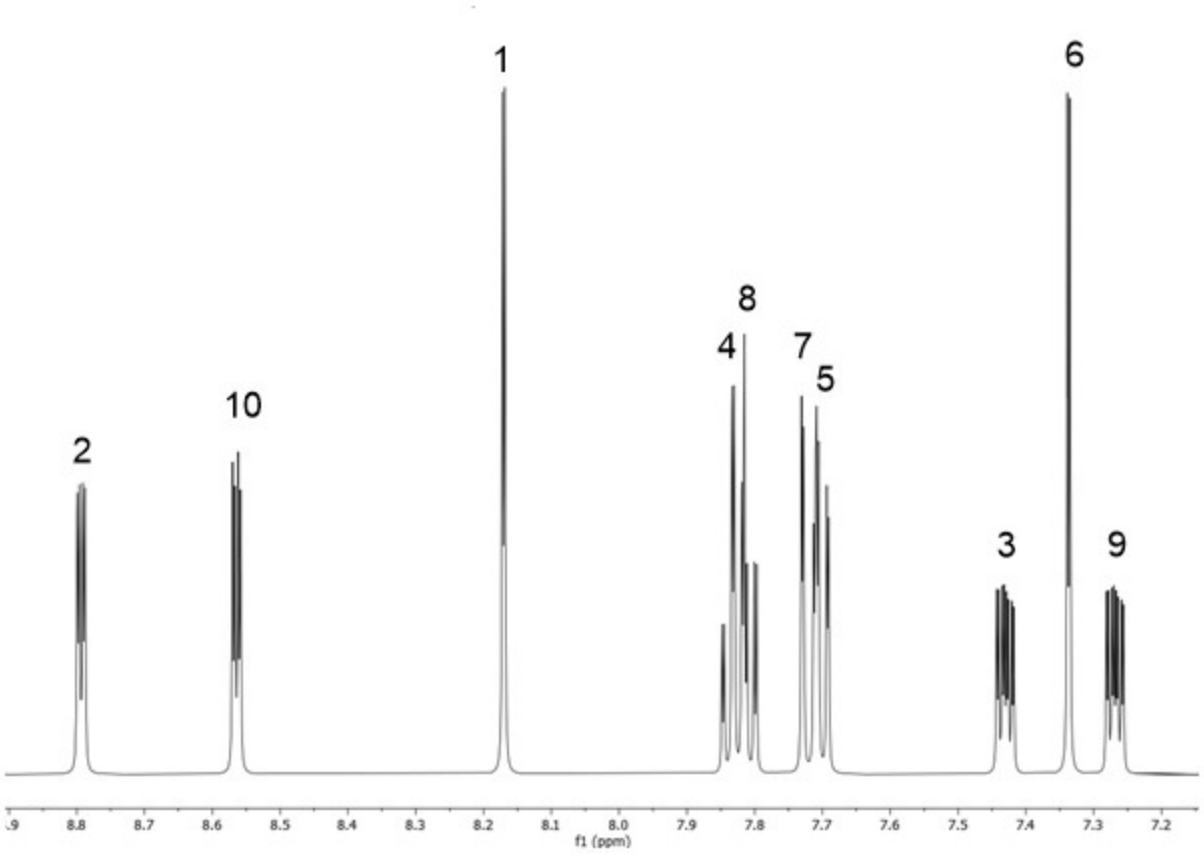



**Fig. S23.** Predicted[5] $^{1}$H NMR spectrum of 2,4-di(2-pyridyl)furan in $CDCl_3$.

$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.79 (dd, *J* = 4.0, 1.7 Hz, 1H), 8.56 (dd, *J* = 4.0, 1.7 Hz, 1H), 8.17 (d, *J* = 1.8 Hz, 1H), 7.82 (qd, *J* = 7.3, 1.6 Hz, 2H), 7.76 – 7.67 (m, 2H), 7.43 (ddd, *J* = 7.2, 4.0, 1.5 Hz, 1H), 7.33 (s, 0H), 7.27 (ddd, *J* = 7.0, 4.0, 1.5 Hz, 1H).

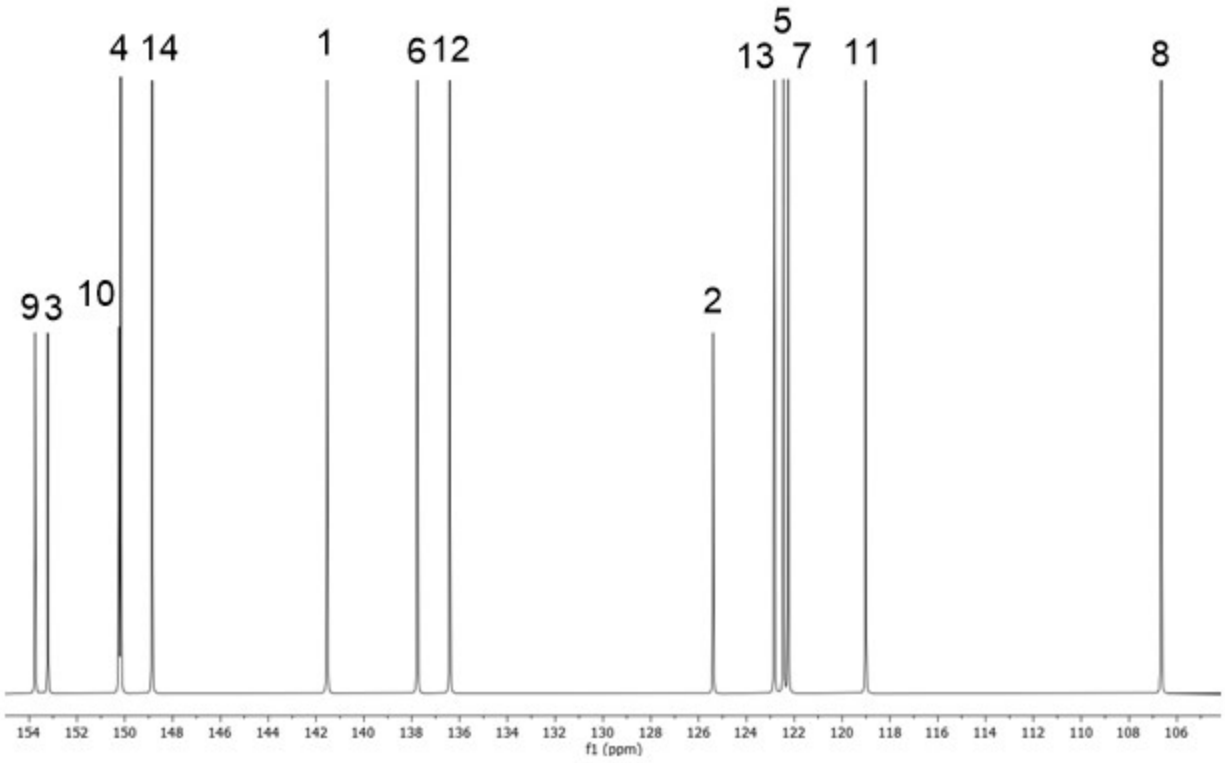



**Fig. S24.** Predicted[5] $^{13}C\{^{1}H\}$ NMR spectrum of 2,4-di(2-pyridyl)furan in $CDCl_3$.

$^{13}C$ NMR (100 MHz, Chloroform-*d*) δ 153.75, 153.22, 150.24, 150.17, 148.86, 141.54, 137.76, 136.41, 125.39, 122.83, 122.46, 122.25, 119.02, 106.65.

## References


1 D. Alickmann, R. Fröhlich, A. H. Maulitz and E. U. Würthwein, *Eur. J. Org. Chem.*, 2002, 1523–1537.

2 M. Zhang, H. F. Jiang, H. Neumann, M. Beller and P. H. Dixneuf, *Angew. Chem., Int. Ed.*, 2009, **48**, 1681–1684.

3 K. Tanaka, T. Shoji and M. Hirano, *Eur. J. Org. Chem.*, 2007, 2687–2699.

4 Spectrum available from Enamine Ltd. (EN300-378678.nmr.y2020).

5 Predicted using MestReNova ver. 14.3.0-30573.