Electronic Supplementary Information (ESI) I – Syntheses and NMR spectra
for
Isoelectronic Pt(II) Complexes of Cyclometalating C^N^N Ligands with Phenyl/(Benzo)thiophenyl/Pyridyl/(Benzo)thiazole Moieties

Maren Krause,[a] Stefan Buss,[b] Dana Brünink,[c] Annemarie Berger,[a] Cristian A. Strassert,[b,*] Nikos L. Doltsinis,[c,*] Axel Klein[a,*]

* to whom the correspondence should be addressed: e-mail: axel.klein@uni-koeln.de

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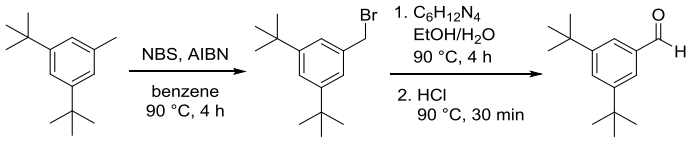
Syntheses

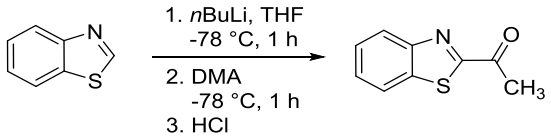
Syntheses of ligand precursors

Synthesis of 3,5-di-*tert*-butylbenzaldeyde



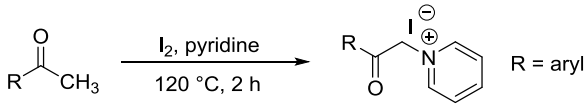
A solution of 8.91 g 3,5-di-*tert*-butyltoluene (11 mL, 43.6 mmol, 1.00 eq.), 12.8 g *N*-bromosuccinimide (NBS) (71.9 mmol, 1.65 eq.) and 0.35 g azobisisobutyronitrile (AIBN) (2.13 mmol, 5 mol%) in 20 mL benzene was heated up to 90 °C for 4 h. After cooling to room temperature the solid (precipitate of succinimide) was filtered off. The filtrat was concentrated and the residue was treated with a mixture of EtOH/water (1:1, 40 mL) and 19.0 g hexamethylentetramin (135.5 mmol, 3.1 eq.) and heated up to 90 °C for another 4 h. Then 8 mL of hydrochloric acid (37% w/w in H_2O) were added and heating was continued for 30 min. The solvent was removed under reduced pressure and the aqueous phase was extracted with diethyl ether (3 x 100 mL). The combinded organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure to obtain the product as colourless solid. Yield: 9.00 g (41.2 mmol, 95%, Lit.[1]: 88%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.01 (s, 1H, CHO), 7.73-7.71 (m, 3H, H-Ph), 1.37 (s, 18H, CH_3) ppm.

Synthesis of 2-acetylbenzothiazole



A solution of 4.06 g benzothiazole (30 mmol, 1 eq.) in 60 mL THF was cooled down to −78 °C and a solution of 2.5 M *n*BuLi in *n*-hexane (13.2 mL, 33 mmol, 1.1 eq.) was added dropwise. The mixture was stirred for 1 h at −78 °C. Then, 2.61 g *N*,*N*-dimethylacetamide (30 mmol, 1 eq.) was added and stirring continued for another 1 h at −78 °C. The cooling bath was removed and after 10 min the reaction mixture was treated with 6 mL hydrochloric acid (37% w/w in H_2O). Under continuous stirring the mixture was allowed to warm up to room temperature. Then it was poured into the same amount of water. The aqueous phase was extracted with ethylacetate (EtOAc) three times. The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reducted pressure. The residue was purified by column chromatography (*c*Hex/EtOAc = 10/1) giving the product as yellow solid. Yield: 3.24 g (18 mmol, 61%, Lit.[2]: 58%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.23-8.20 (m, 1H), 8.02-7.99 (m, 1H), 7.63-7.53 (m, 2H), 2.85 (s, 3H, CH_3) ppm.

Syntheses of acylmethylpyridinium iodids (*Kröhnke* reagent) – General description



The methylketone (50 mmol) and 12.69 g iodine (50 mmol) were dissolved in 60 mL pyridine and heated up to 120 °C for 2 h. After cooling down to room temperature, the precipitate was filtered off, washed thoroughly with pyridine and acetone and dried. The product was obtained as crystalline solid.

1-[2-oxo-2-(naphthalin-2-yl)ethyl]pyridinium iodide

From 2-acetylnaphtalene (50 mmol); yellow solid; Yield: 15.83 g (42.2 mmol, 84%); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.04 (d, *J* = 5,5 Hz, 2H), 8.83 (s, 1H), 8.76 (t, *J* = 7,9 Hz, 1H), 8.31 (t, *J* = 7,1 Hz, 2H), 8.24 (d, *J* = 7.9 Hz, 1H), 8.16 (d, *J* = 8.7 Hz, 1H), 8.10-8.03 (m, 2H), 7.80-7.69 (m, 2H), 6.60 (s, 2H, CH_2) ppm.

1-[2-oxo-2-(thiazol-2-yl)ethyl]pyridinium iodide

From 2-acetylthiazole (18 mmol); yellow-golden solid; Yield: 5.15 g (15.5 mmol, 86%); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.03 (d, *J* = 6.9 Hz, 2H), 8.75 (t, *J* = 7.8 Hz, 1H), 8.44 (d, *J* = 3.0 Hz, 1H), 8.34 (d, *J* = 3.0 Hz, 1H), 8.29 (dd, *J* = 7.7, 6.7 Hz, 2H), 6.46 (s, 2H, CH_2) ppm.

1-[2-oxo-2-(benzothiazol-2-yl)ethyl]pyridinium iodide

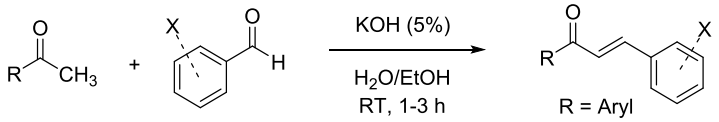
From 2-acetylbenzothiazole (17 mmol); green-golden solid; Yield: 5.03 g (13.2 mmol, 78%); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.04 (d, J = 6.9 Hz, 2H), 8.77 (t, J = 7.6 Hz, 1H), 8.38-8.29 (m, 4H), 7.80-7.70 (m, 2H), 6.58 (s, 2H, CH_2) ppm.

1-[2-oxo-2-(pyridin-2-yl)ethyl]pyridinium iodide

From 2-acetylpyridine (50 mmol); black solid; yield: 13.5 g (41 mmol, 83%); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.00 (d, J = 5.5 Hz, 2H), 8.87 (d, J = 4.7 Hz, 1H), 8.73 (t, J = 7.8 Hz, 1H), 8.27 (d, J = 14.4 Hz, 2H), 8.14 (t, J = 7.6 Hz, 1H), 8.08 (d, J = 7.5 Hz, 1H), 7.84 (t, J = 6.0 Hz, 1H), 6.51 (s, 2H, CH_2) ppm.

Syntheses of chalcones – General description

Method A



Methylketone (30 mmol) and aldehyde (30 mmol) were dissolved in 50 mL EtOH and a solution of KOH (5 wt%, 2.5 g, 45 mmol, 1.5 eq.) was added dropwise. After 1-3 h stirring at room temperature the precipitate was filtered off. The crude product was washed with water und EtOH and recrystallised from EtOH if necessary.

1-(naphthalin-2-yl)-3-phenylprop-2-en-1-one

From 2-acetylnaphthalene (30 mmol) and benzaldehyde (30 mmol); pale yellow solid; yield: 6.43 g (24.9 mmol, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.55 (s, 1H), 8.11 (dd, J = 1.7, 8.6 Hz, 1H), 8.02-7.86 (m, 4H), 7.73-7.67 (m, 3H), 7.65-7.55 (m, 2H), 7.46-7.43 (m, 3H) ppm.

1-(thiophen-2-yl)-3-phenylprop-2-en-1-one

From 2-acetylthiophene (30 mmol) and benzaldehyde (30 mmol); colourless solid; Yield: 6.02 g (28.2 mmol, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88-7.83 (m, 2H), 7.70-7.64 (m, 3H), 7.45-7.40 (m, 4H), 7.19 (t, 1H) ppm.

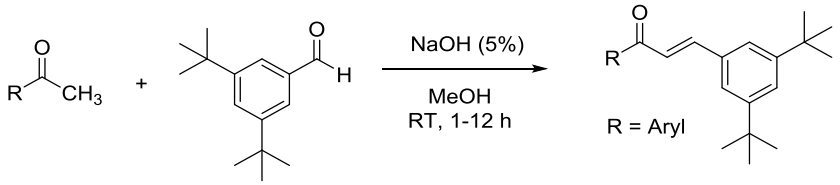
1-(benzothiophen-2-yl)-3-phenylprop-2-en-1-one

From 2-acetylbenzothiophene (5 mmol) and benzaldehyde (5 mmol); yield: 1.16 g (4.39 mmol, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.09 (s, 1H), 7.92-7.86 (m, 3H), 7.68-7.66 (m, 2H), 7.55-7.38 (m, 6H) ppm.

1-phenyl-3-phenylprop-2-en-1-one

From acetophenone (30 mmol) and benzaldehyde (30 mmol); recrystallised from EtOH; colourless solid; Yield: 3.55 g (17 mmol, 57%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04-8.01 (m, 2H), 7.82 (d, J = 15.9 Hz, 1H), 7.66-7.40 (m, 6H), 7.44-7.40 (m, 3H) ppm.

Method B



Methylketone (10 mmol) and 2.18 g 3,5-di-*tert*-butylbenzaldeyde (10 mmol) were dissolved in 10 mL of MeOH. A solution of 0.48 g NaOH (5 wt%, 12 mmol) in 10 mL MeOH was added dropwise. The reaction mixture was stirred for 1 h at room temperature. If precipitation was not completed then, stirring was continued over night. The precipitate was filtered off, washed with small amounts of cold MeOH and dried.

1-phenyl-3-(3,5-di-*tert*-butyl-phenyl)prop-2-en-1-one

From acetophenone (5 mmol) and 3,5-di-*tert*-butylbenzaldeyde (5 mmol) after 12 h reaction time; light yellow solid; Yield: 1.14 g (3.56 mmol, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 15.7 Hz, 1H), 7.62-7.45 (m, 7H), 1.36 (s, 18H) ppm.

1-(naphthalin-2-yl)-3-(3,5-di-*tert*-butyl-phenyl)prop-2-en-1-one

From 2-acetylnaphthalene (10 mmol) and 3,5-di-*tert*-butylbenzaldeyde (10 mmol) after 1 h reaction time; colourless solid; Yield: 1.54 g (4.16 mmol, 42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.56 (s, 1H), 8.12 (dd, J = 1.7, 8.6 Hz, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.99-7.88 (m, 3H), 7.66-7.59 (m, 3H), 7.54 (s, 3H), 1.40 (s, 18H) ppm.

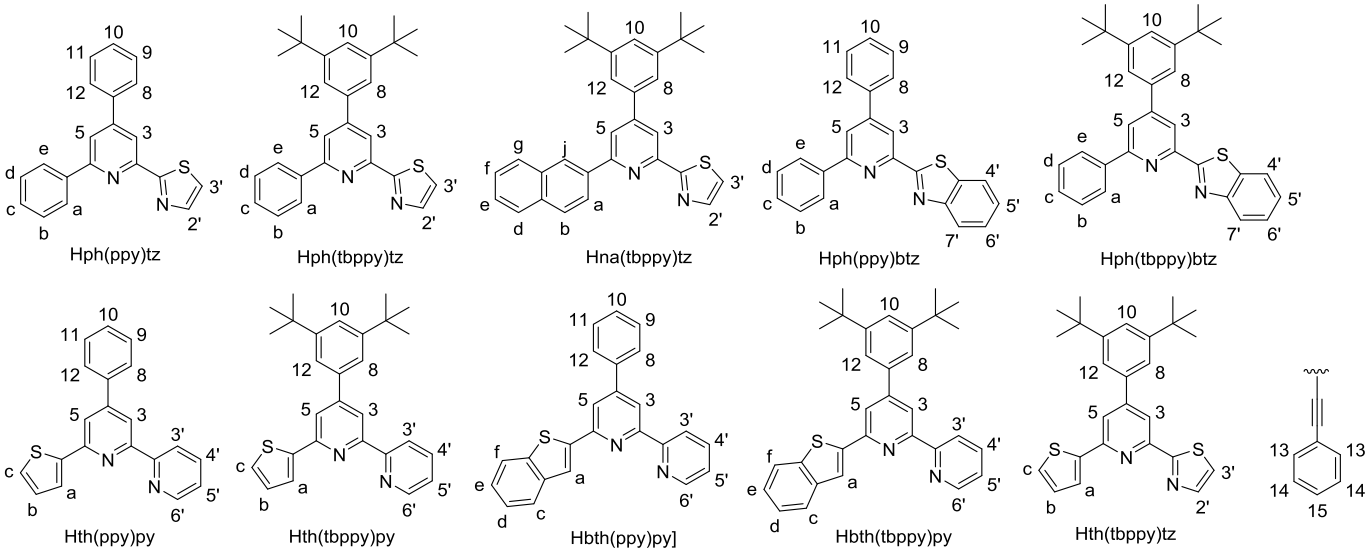
1-(thiophen-2-yl)-3-(3,5-di-*tert*-butyl-phenyl)prop-2-en-1-one

From 2-acetylthiophene (10 mmol) and 3,5-di-*tert*-butylbenzaldeyde (10 mmol) after 1 h reaction time; colourless solid; Yield: 1.67 g (5.11 mmol, 51%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 (dd, J = 0.9, 3.8 Hz, 1H), 7.89 (d, J = 15.6 Hz, 1H), 7.68 (dd, J = 0.9, 4.9 Hz, 1H), 7.51-7.48 (m, J = 2.9 Hz, 3H), 7.39 (d, J = 15.6 Hz, 1H), 7.19 (dd, J = 3.9, 4.9 Hz, 1H), 1.37 (s, 18H) ppm.

1-(benzthiophen-2-yl)-3-(3,5-di-*tert*-butyl-phenyl)prop-2-en-1-one

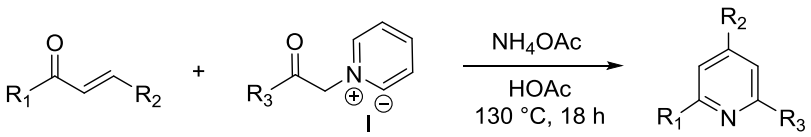
From 2-acetylbenzothiophene (15 mmol) and 3,5-di-*tert*-butylbenzaldeyde (15 mmol) after 1 h reaction time; yellow solid; Yield: 4.13 g (10.9 mmol), 73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (s, 1H), 7.98-7.92 (m, 3H), 7.56-7.42 (m, 6H), 1.41 (s, 18H) ppm.

Syntheses of the ligands



Scheme S1. Ligands with numbering of atoms for NMR assignment.

Syntheses of 2,4,6-trisubstited pyridines – General description



The corresponding *Kröhnke* reagent (5 mmol, 1 eq.) and 3.85 g NH_4OAc (50 mmol, 10 eq.) in 20 mL acetic acid were heated up to 130 °C. After 10 min at 130 °C the chalcone (5 mmol, 1 eq.) was added. The reaction mixture was heated for another 18 h. Then the solution was concentrated under reduced pressure. The oily residue was dissolved in $CHCl_3$ (50 mL) and washed with water (2 x 50 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography. The product was obtained as colourless to light yellow solid.

6-(thiophen-2-yl)-4-phenyl-2,2'-bipyridine (Hth(ppy)py)

From 3.26 g 1-(2-oxo-2-(pyridin-2-yl)ethyl)pyridinium iodide (10 mmol) and 2.14 g 1-(thiophen-2-yl)-3-phenylprop-2-en-1-one (10 mmol); column chromatography (*c*Hex/EtOAc = 10/1); Yield: 2.26 g (7.19 mmol, 72%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.73 (dq, *J* = 0.9, 4.8 Hz, 1H, H6'), 8.66-8.63 (m, 2H, H3'/py), 7.97-7.85 (m, 4H, py/H4'/H8/H12), 7.81 (dd, *J* = 1.1, 3.7 Hz, 1H, H-th), 7.61-7.50 (m, 4H, H9-H11, th), 7.42-7.38 (m, 1H, H5'), 7.23-7.21 (m, 1H, Hd) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 156.2 (C_q), 155.7 (C_q), 152.4 (C_q), 150.2 (C_q), 149.1 (CH, C6'), 145.4 (C_q), 138.5 (C_q), 136.9 (CH, C4'), 129.1 (CH, C10), 129.0 (CH, C9/C11), 128.1 (CH, Cd), 127.7 (CH, th), 127.1 (CH, C8/C12), 124.7 (CH, th), 123.9 (CH, C5'), 121.2 (CH, C3'), 117.2 (CH, py), 116.5 (CH, py) ppm.

6-(thiophen-2-yl)-4-(3,5-di-*tert*-butyl-phenyl)-2,2'-bipyridine (Hth(tbppy)py)

From 0.75 g 1-(2-oxo-2-(pyridin-2-yl)ethyl)pyridinium iodide (2.3 mmol) and 0.75 g 1-(thiophen-2-yl)-3-(3,5-di-*tert*-butyl-phenyl)prop-2-en-1-one (2.3 mmol); column chromatography (*c*Hex/EtOAc = 10/1); Yield: 0.49 g (1.2 mmol, 50%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.71 (d, *J* = 3.9 Hz, 1H, H6'), 8.62 (d, *J* = 8.0 Hz, 1H, H3'), 8.52 (d, *J* = 1.5 Hz, 1H, H5), 7.87 (dd, *J* = 1.8, 7.7 Hz, 1H, H4'), 7.85 (d, *J* = 1.5 Hz, 1H, H3), 7.73 (dd, *J* = 1.0, 3.6 Hz, 1H, H-th), 7.55 (m, *J* = 2.6 Hz, 3H, H8/H10/H12), 7.43 (dd, *J* = 1.0, 5.0 Hz, 1H, th), 7.33 (ddd, *J* = 1.1, 4.8, 7.4 Hz, 1H, H5'), 7.16 (dd, *J* = 5.0, 3.7 Hz, 1H, Hd), 1.41 (s, 18H) ppm. ^{13}C (HSQC) NMR (125 MHz, $CDCl_3$): δ = 149.1 (CH, C6'), 121.7 (CH, C3'), 117.9 (CH, C5), 137.0 (CH, C4'), 117.3 (CH, C3), 124.7 (CH, th), 121.7 (CH, C8/C12), 123.4 (CH, C10), 127.5 (CH, th), 123.7 (CH, C5'), 128.2 (CH, Cd), 31.7 (CH_3, *t*Bu) ppm. HR-ESI-MS (+) m/z = 427.22021 $[M+H]^+$ (calc. 427.22025).

6-(benzothiophen-2-yl)-4-phenyl-2,2'-bipyridine (Hbth(ppy)py)

From 2.45 g 1-(2-oxo-2-(pyridin-2-yl)ethyl)pyridinium iodide (7.5 mmol) and 1.98 g 1-(benzthiophen-2-yl)-3-phenylprop-2-en-1-one (7.5 mmol); column chromatography (*c*Hex/EtOAc = 10/1); Yield: 0.35 g (0.96 mmol, 13%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.76-8.74 (m, 1H, H6'), 8.71-8.68 (m, 2H, H3'/py), 8.12 (d, *J* = 1.6 Hz, 1H, py), 8.07 (s, 1H, Ha), 7.99-7.88 (m, 5H, H4'/H8/H12/bth), 7.64-7.54 (m, 3H, H9-H12), 7.46-7.40 (m, 3H, H5'/bth) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 149.2 (CH, C6'), 136.9 (CH), 129.2 (CH, C10), 129.1 (CH, C9/C11), 127.2 (CH, C8/C12), 125.1 (CH), 124.5 (CH), 124.2 (CH), 124.1 (CH), 122.5 (CH), 121.2 (CH, C3'), 121.2 (CH, Ca), 117.9 (CH, py), 117.3 (CH, py) ppm.

6-(benzothiophen-2-yl)-4-(3,5-di-*tert*-butyl-phenyl)-2,2'-bipyridine (Hbth(tbppy)py)

From 1.31 g 1-(2-oxo-2-(pyridin-2-yl)ethyl)pyridinium iodide (4 mmol) and 1.51 g 1-(benzothiophen-2-yl)-3-(3,5-di-*tert*-butyl-phenyl)prop-2-en-1-one (4 mmol); column chromatography (*c*Hex/EtOAc = 25/1); Yield: 0.92 g (1.9 mmol, 48%). Elemental analysis calculated (%) for $C_{32}H_{32}N_2S$: C 80.63, H 6.77, N 5.88, S 6.73; found: C 80.82, H 7.04, N 5.23, S 6.44. ^{1}H NMR (500 MHz, $CDCl_3$): δ = (d, *J* = 4.9 Hz, 1H, H6'), 8.68 (d, *J* = 7.9 Hz, 1H, Bth), 8.58 (d, *J* = 1.4 Hz, 1H, H3), 7.99 (d, *J* = 1.5 Hz, 1H, H5), 7.98 (s, 1H, Ha), 7.88 (m, 3H, bth/py), 7.59 (d, *J* = 1.7 Hz, 2H, H8/H12), 7.56 (t, *J* = 1.7 Hz, 1H, H10), 7.37 (m, 3H, bth/py), 1.43 (s, 18H, *t*Bu) ppm. ^{13}C (HSQC) NMR (125 MHz, $CDCl_3$): δ = 149.2 (CH, C6'), 136.8 (CH), 124.6 (CH), 124.6 (CH), 124.1 (CH), 123.7 (CH), 123.4 (CH, C10), 122.3 (CH), 121.6 (CH, C8/C12), 121.3 (CH, bth), 120.7 (CH, Ca), 118.6 (CH, C3), 117.9 (CH, C5), 31.6 (CH_3, *t*Bu) ppm. HR-ESI-MS (+) m/z = 477.23590 $[M+H]^+$ (calc. 477.23570);

2-(4,6-diphenylpyridin-2-yl)thiazole (Hph(ppy)tz)

From 3.32 g 1-(2-oxo-2-(thiazol-2-yl)ethyl)pyridinium iodide (10 mmol) and 2.08 g 1-phenyl-3-phenylprop-2-en-1-one (10 mmol); column chromatography (*c*Hex/EtOAc = 10/1); Yield: 2.59 g (8.2 mmol, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.41 (s, 1H), 8.21 (d, *J* = 8.3 Hz, 2H), 8.01-7.98 (m, 2H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.58-7.50 (m, 7H) ppm.

2-(4-(3,5-di-*tert*-butylphenyl)-6-phenylpyridin-2-yl)thiazole (Hph(tbppy)tz)

From 1.66 g 1-(2-oxo-2-(thiazol-2-yl)ethyl)pyridinium iodide (5 mmol) and 1.60 g 1-phenyl-3-(3,5-di-*tert*-butyl-phenyl)prop-2-en-1-one (5 mmol); column chromatography (*c*Hex/EtOAc = 25/1); Yield: 1.78 g (4.2 mmol, 83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.35 (d, *J* = 1.4 Hz, 1H, py), 8.18 (d, *J* = 7.1 Hz, 2H, Ha/He), 7.97 (d, *J* = 3.2 Hz, 1H, H-tz), 7.95 (d, *J* = 1.5 Hz, 1H, py), 7.56 (s, 3H, H8/H10/H12), 7.54 (t, *J* = 7.5 Hz, 2H, Hb/Hd), 7.47 (m, 2H, Hc/tz), 1.41 (s, 18H, *t*Bu) ppm. ^{13}C (HSQC) NMR (125 MHz, $CDCl_3$): δ = 143.9 (CH, C-tz), 129.3 (CH, Cc), 128.7 (CH, Cb/Cd), 126.9 (CH, Ca/Ce), 123.5 (CH), 121.6 (CH, C-tz), 121.4 (CH), 119.6 (CH, C-tz), 116.2 (CH, C-py), 31.6 (CH_3, *t*Bu) ppm. HR-ESI-MS (+) m/z = 427.22027 $[M+H]^+$ (calc. 427.22025).

2-(4-(3,5-di-*tert*-butylphenyl)-6-(naphthalen-2-yl)pyridin-2-yl)thiazole (Hna(tbppy)tz)

From 1.66 g 1-(2-oxo-2-(thiazol-2-yl)ethyl)pyridinium iodide (5 mmol) and 1.85 g 1-(naphthalin-2-yl)-3-(3,5-di-*tert*-butyl-phenyl)prop-2-en-1-one (5 mmol); column chromatography (*c*Hex/EtOAc = 20/1); Yield: 1.43 g (3,0 mmol, 60%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.63 (s, 1H, Hg), 8.37 (d, *J* = 1.4 Hz, 1H, py), 8.34 (dd, *J* = 1.7, 8.6 Hz, 1H, Ha), 8.09 (d, *J* = 1.4 Hz, 1H, py), 8.02-7.99 (m, 3H, na/tz), 7.91 (t, *J* = 4.7 Hz, 1H, na), 7.59-7.57 (m, 3H, H8/H10/H12), 7.55-7.53 (m, 2H, na), 7.50 (d, *J* = 3.2 Hz, 1H, tz), 1.43 (s, 18H, *t*Bu) ppm. ^{13}C HSQC NMR (125 MHz, $CDCl_3$): δ = 149.0 (CH, tz), 128.6 (CH, na), 127.7 (CH, na), 126.5 (CH, Cg), 126.5 (CH, na), 124.6 (CH, Ca), 123.4 (CH, ph), 121.6 (CH, ph), 121.5 (CH, tz), 120.0 (CH, py), 116.3 (CH, py), 31.5 (CH_3, *t*Bu) ppm. HR-ESI-MS (+) m/z = 477.23573 $[M+H]^+$ (calc. 477.23590).

2-(4,6-diphenylpyridin-2-yl)benzothiazole (Hph(ppy)btz)

From 3.27 g 1-(2-oxo-2-(benzothiazol-2-yl)ethyl)pyridinium iodide (8.6 mmol) and 1.78 g 1-phenyl-3-phenylprop-2-en-1-one (8.6 mmol); column chromatography (*c*Hex/EtOAc = 10/1) and recrystallisation from EtOH; Yield: 0.79 g (2.2 mmol, 25%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.58 (d, 1H, *J* = 1.5 Hz, py), 8.27-8.24 (m, 2H, Ha/He), 8.15 (d, 1H, *J* = 7.8 Hz, btz), 8.08 (d, 1H, *J* = 1.5 Hz, py), 8.01 (d, 1H, *J* = 7.8 Hz, btz), 7.88-7.84 (m, 2H, H8/H12), 7.60-7.43 (m, 8H, Hb-d/H9-11/H3'/H4') ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.3 (C_q), 157.6 (C_q), 154.4 (C_q), 151.6 (C_q), 150.6 (C_q), 138.4 (C_q), 138.0 (C_q), 136.4 (C_q), 129.5 (CH), 129.5 (CH), 129.2 (CH), 128.9 (CH), 127.3 (CH, C8/C12), 127.1 (CH, Ca/Ce), 126.2 (CH), 125.6 (CH), 123.6 (CH, btz), 122.0 (CH, btz), 119.8 (CH, py), 117.0 (CH, py) ppm.

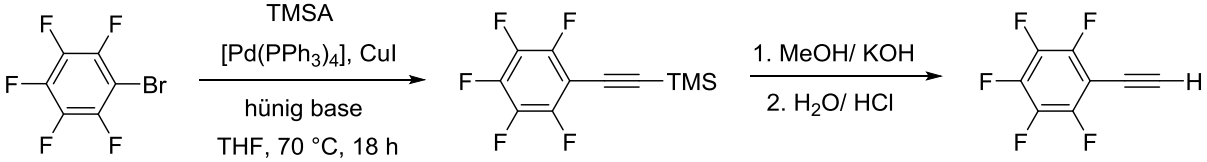
2-(4-(3,5-di-*tert*-butylphenyl)-6-phenylpyridin-2-yl)benzothiazole (Hph(tbppy)btz)

From 1.53 g 1-(2-oxo-2-(benzothiazol-2-yl)ethyl)pyridinium iodide (4 mmol) and 1.28 g 1-phenyl-3-(3,5-di-*tert*-butyl-phenyl)prop-2-en-1-one (4 mmol); column chromatography (*c*Hex/EtOAc = 25/1); Yield: 1.40 g (2.9 mmol, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 1.5 Hz, 1H), 8.26-8.23 (m, 2H), 8.16 (d, *J* = 7.8 Hz, 1H), 8.04-8.00 (m, 2H), 7.61-7.43 (m, 8H), 1.45 (s, 18H, *t*Bu) ppm.

2-(4-(3,5-di-*tert*-butylphenyl)-6-(thiophen-2-yl)-pyridin-2-yl)thiazole (Hth(tbppy)tz)

From 0.47 g 1-(2-oxo-2-(thiazol-2-yl)ethyl)pyridinium iodide (1.4 mmol) and 0.46 g 1-(thiophen-2-yl)-3-(3,5-di-*tert*-butyl-phenyl)prop-2-en-1-one (1.4 mmol); column chromatography (*c*Hex/EtOAc = 20/1); Yield: 0.30 g (0.69 mmol, 50%). Elementar analysis calculated for $C_{26}H_{28}N_2S_2$: C 72.18, H 6.52, N 6.48, S 14.82; found: C 72.18, H 6.62, N 5.14, S 14.62%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.25 (d, 1H, *J* = 1.4 Hz, H2'), 7.96 (d, 1H, *J* = 3.1 Hz, py), 7.83 (d, 1H, *J* = 1.4 Hz, H3'), 7.74 (d, 1H, *J* = 4.6 Hz, th), 7.56 (t, 1H, *J* = 1.7 Hz, H10), 7.54 (d, 2H, *J* = 1.7 Hz, H8/H12), 7.48 (d, 1H, *J* = 3.2 Hz, py), 7.45 (d, 1H, *J* = 6.0 Hz, th), 7.16 (dd, 1H, *J* = 5.0, 3.7 Hz, Hb), 1.41 (s, 18H) ppm. ^{13}C HSQC NMR (125 MHz, $CDCl_3$): δ = 143.9 (CH, py), 128.1 (CH, Cb), 128.0 (CH, th), 125.1 (CH, th), 123.6 (CH, C10), 121.6 (CH, py), 121.5 (CH, C8/C12), 117.9 (CH, C3'), 115.9 (CH, C2'), C31.6 (CH_3, *t*Bu) ppm.

Synthesis of pentafluorphenylacetylene



Under inert gas atmosphere 300 mg CuI (1.6 mmol, 4 mol%), 920 mg $[Pd(PPh_3)_4]$ (0.8 mmol, 2 mol%) and 10 g bromopentafluorbenzene (40.5 mmol, 1 eq.) were dissolved in 100 mL dry THF. Then 26 mL diisopropyl ethylamine (*Hünig* base) (150 mmol, 3.7 eq.) and 11.5 mL trimethylsilylacetylen (TMSA) (81 mmol, 2 eq.) were added. The reaction mixture was stirred over night at 70°C. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica; *c*Hex). The obtained trimethyl((perfluorophenyl)ethynyl)silane (3.39 g, 12.8 mmol) was directly used in for the next reaction step. Therefore, it was dissolved in 40 mL MeOH and 45 µL of KOH solution in MeOH (50%) were added. After 10 min the reaction was quenched with water (17 mL) and 1 mL hydrochloric acid (10%), which lead to the formation of two phases. The lightyellow oily phase was separated. The crude product was used for further

synthesis without purification. Yield: 2.6 g (13.5 mmol, 33%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.61 (s) ppm. ^{19}F NMR (282 MHz, CD_2Cl_2): δ = −135.78 (dd, 1F, *J* = 6.9, 23.1 Hz), −151.40 (t, 2F, *J* = 20.8 Hz), −161.43 and −161.61) (m, 2F) ppm.

Syntheses of the complexes [Pt(C^N^N)Cl] – General description.
The corresponding ligand and 208 mg $K_2[PtCl_4]$ (0.5 mmol) were suspended in acetic acid (60 mL). The suspention was heated up to 110 °C for 3 d. Formation of a precipitate was observed over time. After cooling down to room temperature, the precipitate was filtered off and washed with acetic acid, water and diethyl ether consecutively. The products were obtained as yellow to red solids. In case of incomplete conversions, $K_2[PtCl_4]$ was regained from the aqueos phase.

[Pt(th(ppy)py)Cl]: From 189 mg Hth(ppy)py (0.6 mmol) and 208 mg $K_2[PtCl_4]$ (0.5 mmol); orange solid; Yield: 250 mg (0.46 mmol, 92%). Elemental analysis for $C_{20}H_{13}ClN_2PtS$ (543.93): C 35.87, H 2.41, N 5.15, S 5.89; found: C 35.81, H 2.49, N 5.18, S 5.90%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.98 (d, 1H, *J* = 5.3 Hz, J_{Pt-H} = 15.3 Hz, H6'), 8.10 (dt, 1H, *J* = 7.8, 1.5 Hz, H4'), 7.99 (d, 1H, *J* = 8.0 Hz, H3'), 7.76-7.73 (m, 2H, H8/H12), 7.65 (t, 1H, *J* = 7.0 Hz, H5'), 7.61-7.52 (m, 5H, Hc/H9-11/py), 7.43 (d, 1H, *J* = 1.4 Hz, J_{Pt-H} = 13.3 Hz, py), 7.10 (d, 1H, *J* = 4.8 Hz, J_{Pt-H} = 20.2 Hz, Hb) ppm. EI-MS (+) (70 eV) m/z = 544 $[M]^+$, 508 $[M–Cl]^+$, 314 $[Hth(ppy)py]^+$.
[Pt(th(tbppy)py)Cl]: From 256 mg Hth(tbppy)py (0.6 mmol) und 20 mg $K_2[PtCl_4]$ (0.5 mmol); yellow solid; Yield: 280 mg (0.43 mmol, 71%). Elemental analysis calculated for $C_{28}H_{29}ClN_2PtS$ (656.15): C 51.25, H 4.46, N 4.27, S 4.89; found: C 51.31, H 4.49, N 4.22, S 4.86%. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 8.71 (d, 1H, *J* = 4.6 Hz, H6'), 7.95 (t, 1H, *J* = 7.7 Hz, H4'), 7.90 (d, 1H, *J* = 7.8 Hz, H3'), 7.62 (t, 1H, *J* = 1.5 Hz, H10), 7.57 (d, 2H, *J* = 1.6 Hz, H8/H12), 7.50 (d, 1H, *J* = 1.1 Hz, py), 7.48 (d, 1H, *J* = 4.7 Hz, Hc), 7.43 (t, 1H, *J* = 6.3 Hz, H5'), 7.20 (d, 1H, *J* = 1.2 Hz, py), 6.95 (d, 1H, *J* = 4.7 Hz, Hb), 1.45 (s, 18H, *t*Bu) ppm. ^{195}Pt NMR (54 MHz, CD_2Cl_2): δ = −3835 ppm. EI-MS(+) (70 eV) m/z = 656 $[M]^+$, 426 $[Hth(tbppy)py]^+$.
[Pt(bth(ppy)py)Cl]: From 220 mg Hbth(ppy)py (0.6 mmol) and 208 mg $K_2[PtCl_4]$ (0.5 mmol); red solid; Yield: 285 mg (0.48 mmol, 96%). Elemental analysis calculated for $C_{24}H_{15}ClN_2PtS$ (593.99): C 48.53, H 2.55, N 4.72, S 5.40; found: C 48.43, H 2.58, N 4.72, S 5.46%. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.96 (d, 1H, *J* = 4.6 Hz, H6'), 8.77 (d, 1H, *J* = 7.4 Hz, bth), 8.71 (d, 1H, *J* = 8.0 Hz, H3'), 8.38-8.35 (m, 2H, H4'/py), 8.06-8.04 (m, 2H, H8/H12), 7.93 (t, 2H, *J* = 7.3 Hz, bth/H5'), 7.86 (s, 1H, py), 7.60-7.55 (m, 3H, H9-H11), 7.36-7.30 (m, 2H, He/Hd) ppm. EI-MS(+) (70 eV) m/z = 594 $[M]^+$, 557 $[M-Cl]^+$, 364 $[Hbth(ppy)py]^+$.
[Pt(bth(tbppy)py)Cl]: From 286 mg Hbth(tbppy)py (0.6 mmol) and 208 mg $K_2[PtCl_4]$ (0.5 mmol); orange solid; Yield: 345 mg (0.49 mmol, 98%). Elemental analysis calculated for $C_{32}H_{31}ClN_2PtS$ (706.21): C 54.42, H 4.42, N 3.97, S 4.54; found: C 54.45, H 4.44, N 3.92, S 4.54%. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.99 (d, 1H, *J* = 5.3 Hz, H6'), 8.79 (d, 1H, *J* = 8.0 Hz, bth), 8.74 (d, 1H, *J* = 8.0 Hz, H3'), 8.40 (dt, 1H, *J* = 7.8, 1.5 Hz, H4'), 8.22 (d, 1H, *J* = 1.2 Hz, py), 7.96 (dd, 1H, *J* = 6.5, 5.5 Hz, H5'), 7.92 (d, 1H, *J* = 7.3 Hz, bth), 7.83 (d, 1H, *J* = 1.3 Hz, py), 7.72 (d, 2H, *J* = 1.7 Hz, H8/H12), 7.57 (t, 1H, *J* = 1.6 Hz, H10), 7.37-7.31 (m, 2H, He/Hd), 1.38 (s, 18H, *t*Bu) ppm. EI-MS (+) (70 eV) m/z = 706 $[M]^+$, 476 $[Hbth(tbppy)py]^+$.
[Pt(ph(ppy)tz)Cl]: From 220 mg Hph(ppy)tz (0.7 mmol) and 208 mg $K_2[PtCl_4]$ (0.5 mmol); orange solid; incomplete conversion (57%); Yield: 155 mg (0.29 mmol, 57%). Elemental analysis calculated $C_{20}H_{13}ClN_2PtS$ (543.93): C 44.16, H 2.41, N 5.15, S 5.89; found: C 44.15, H 2.44, N 5.12, S 5.88%. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 8.07 (d, 1H, *J* = 3.2 Hz, tz), 7.86 (d, 1H, *J* = 3.2 Hz, tz), 7.78-7.76 (m, 2H, H8/H12), 7.69 (d, 1H, *J* = 1.4 Hz, py), 7.65 (d, 1H, *J* = 1.3 Hz, py), 7.59-7.56 (m, 4H, H9-H11/Hb), 7.43 (dd, 1H, *J* = 7.6, 1.0 Hz, He), 7.16 (t, 1H, *J* = 7.4 Hz, Hc), 7.11 (t, 1H, *J* = 7.4 Hz, Hd) ppm. EI-MS(+) (70 eV) m/z = 544 $[M]^+$, 508 $[M–Cl]^+$, 314 $[Hph(ppy)tz]^+$.
[Pt(ph(tbppy)tz)Cl]: From 256 mg Hph(tbppy)tz (0.6 mmol) and 208 mg $K_2[PtCl_4]$ (0.5 mmol); yellow solid; Yield: 257 mg (0.4 mmol, 80%). Elemental analysis calculated for $C_{28}H_{29}ClN_2PtS$ (656.15): C 51.25, H 4.46, N 4.27, S 4.89; found: C 51.23, H 4.46, N 4.24, S 4.82%. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 7.84 (d, 1H, *J* = 3.2 Hz, tz), 7.71 (d, 1H, *J* = 3.2 Hz, tz), 7.64 (t, 1H, *J* = 1.7 Hz, H10), 7.57-7.56 (m, 3H, H8/H12/H3), 7.43-7.42 (m, 2H, *J* = 2.7 Hz, J^{Pt-H} = 45.3 Hz, Hb/H5), 7.32 (dd, 1H, *J* = 7.4, 1.4 Hz, He), 7.05-6.99 (m, 2H, *J* = 3.2 Hz, Hc/Hd), 1.45 (s, 18H, *t*Bu); EI-MS (+) (70 eV) m/z = 656 $[M]^+$, 426 $[Hph(tbppy)tz]^+$.

[Pt(na(tbppy)tz)Cl]: From 286 mg Hna(tbppy)tz (0.6 mmol) and 208 mg $K_2[PtCl_4]$ (0.5 mmol); brownish red solid; yield: 330 mg (0.47 mmol, 93%). Elemental analysis calculated $C_{32}H_{31}ClN_2PtS$ (706.21): C 54.42, H 4.42, N 3.97, S 4.54; found: C 54.44, H 4.40, N 3.99, S 4.57%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.16 (d, J = 3.2 Hz, 1H), 7.98 (s, 1H), 7.93 (s, 1H), 7.88-7.81 (m, 2H), 7.73-7.60 (m, 6H), 7.48-7.36 (m, 2H), 1.49 (s, 18 H, *t*Bu) ppm.
[Pt(ph(ppy)btz)Cl]: From 200 mg Hph(ppy)btz (0.6 mmol) and 208 mg $K_2[PtCl_4]$ (0.5 mmol); orange solid; Yield: 214 mg (0.36 mmol, 72%). Elemental analysis calculated for $C_{24}H_{15}ClN_2PtS$ (593.99): C 48.53, H 2.55, N 4.72, S 5.40; found: C 48.53, H 2.51, N 4.74, S 5.42%. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.03 (d, 1H, J = 7.7 Hz), 8.48 (s, 1H), 8.43 (d, J = 7.5 Hz, 1H), 8.33-8.06 (m, J = 10.3 Hz, 4H), 7.85 (d, J = 6.3 Hz, 1H), 7.78-7.54 (m, 6H), 7.21-7.09 (m, 2H) ppm.
[Pt(ph(tbppy)btz)Cl]: From 286 mg Hph(tbppy)btz (0.6 mmol) and 208 mg $K_2[PtCl_4]$ (0.5 mmol); orange solid; Yield: 311 mg (0.44 mmol, 88%). Elemental analysis calculated for $C_{32}H_{31}ClN_2PtS$ (706.21): C 54.42, H 4.42, N 3.97, S 4.54; found: C 54.50, H 4.41, N 3.92, S 4.47%. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 8.82 (d, 1H, J = 2.3 Hz, H7′), 7.70 (d, 1H, J = 1.4 Hz, H3), 7.64 (m, 2H, H4′/H10), 7.60 (d, 2H, J = 1.7 Hz, H8/H12), 7.44 (m, 1H, Hb, J_{Pt-H} = 44.2 Hz), 7.35 (m, 2H, H5′/H6′), 7.15 (d, 1H, J = 1.3 Hz, H5), 7.07 (m, 1H, He), 6.92 (m, 2H, Hc/Hd), 1.48 (s, 18H, *t*Bu) ppm. EI-MS (+) (70 eV) m/z = 706 $[M]^+$.
[Pt(th(tbppy)tz)Cl]: From 216 mg Hth(tbppy)tz (0.5 mmol) and 174 mg $K_2[PtCl_4]$ (0.42 mmol); orange solid; **yield**: 161 mg (0.24 mmol, 58%). Elemental analysis calculated for $C_{26}H_{27}ClN_2PtS_2$ (662.17): C 47.16, H 4.11, N 4.23, S 9.68; found: C 47.16, H 4.02, N 4.20, S 9.63%. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 7.94 (d, 1H, J = 3.2 Hz, tz), 7.77 (d, 1H, J = 3.2 Hz, tz), 7.62 (t, 1H, J = 1.7 Hz, H10), 7.55 (d, 1H, J = 4.7 Hz, Hc), 7.52 (d, 2H, J = 1.7 Hz, H8/H12), 7.44 (d, 1H, J = 1.4 Hz, py), 7.28 (d, 1H, J = 1.4 Hz, py), 7.03 (d, 1H, J = 4.7 Hz/Hb), 1.44 (s, 18H, *t*Bu) ppm. EI-MS(+) (70 ev) m/z = 662 $[M]^+$, 432 $[Hth(tbppy)tz)]^+$.

Syntheses of the complexes [Pt(C^N^N)(R)] (R = alkynyl) – General description.
The chlorido complexes [Pt(C^N^N)Cl] were dissolved in degassed CH_2Cl_2. The corresponding acetylene, CuI (8 mol%) and NEt_3 were added. The reaction mixture was stirred at room temperature over night in the absence of light. The resulting dark solution was treated with diethyl ether until no further solid precipitated. The precipitate was filtered off and washed thoroughly with diethyl ether and water. If necessary, the product was recrystallised from CH_2Cl_2 and diethyl ether for a second time. The products were obtained as dark yellow to red solids.
[Pt(th(tbppy)py)(C≡CPh)]: From 100 mg [Pt(th(tbppy)py)Cl] (0.152 mmol), 50 µL phenylacetylene (0.456 mmol), 2.3 mg CuI (0.012 mmol), 1.4 mL NEt_3 in 25 mL CH_2Cl_2; dark yellow solid; Yield: 81 mg (0.112 mmol, 84%). Elemental analysis calculated for $C_{36}H_{34}N_2PtS$ (721.83): C 59.90, H 4.75, N 3.88, S 4.44; found: C 59.85, H 4.74, N 4.66, S 4.42%. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 9.16 (d, 1H, J = 4.9 Hz, J_{Pt-H} = 21.6 Hz, H6′), 8.09 (t, 1H, J = 7.4 Hz, H4′), 7.98 (d, 1H, J = 7.9 Hz, H3′), 7.61 (s, 1H, H10), 7.60 (s, 1H, py), 7.56 (t, 1H, J = 6.2 Hz, H5′), 7.50-7.48 (m, 3H, J = 8.9 Hz, H8/H12/th), 7.46 (d, 2H, J = 7.3 Hz, H13), 7.39 (s, 1H, py), 7.28 (t, 3H, J = 7.6 Hz, H14), 7.19-7.16 (m, 2H, H15/th), 1.42 (s, 18H, *t*Bu) ppm. ^{195}Pt NMR (54 MHz, CD_2Cl_2): δ = −3821 ppm. HR-ESI-MS (+) m/z = 754.24293 $[M+CH_3OH+H]^+$.
[Pt(th(tbppy)py)(C≡CC$_6$F$_5$)]: From 100 mg [Pt(th(tbppy)py)Cl] (0.152 mmol, 1 eq.), 62 µL pentafluoro-phenylacetylene (0.456 mmol, 3 eq.), 2.3 mg CuI (0.012 mmol, 0.08 eq.), 1.4 mL NEt_3 in 24 mL CH_2Cl_2; yellow solid; Yield: 115 mg (0.142 mmol, 93%). Elemental analysis calculated for $C_{36}H_{29}F_5N_2PtS$ (811.78): C 53.27, H 3.60, N 3.45, S 3.95; found: C 53.33, H 3.71, N 3.42, S 3.92%. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 9.01 (dd, 1H, J = 5.3, 0.8 Hz, J_{Pt-H} = 21.3 Hz, H6′), 8.07 (dt, J = 11.7, 1.5 Hz, 1H, H4′), 7.99 (d, 1H, J = 8.0 Hz, H3′), 7.61 (t, 1H, J = 1.7 Hz, H10), 7.59 (d, 1H, J = 1.0 Hz, py), 7.54 (dd, 1H, J = 5.3, 8.6 Hz, H5′), 7.49 (d, 2H, J = 1.7 Hz, H8/H12), 7.44 (d, 1H, J = 4.7 Hz, th), 7.35 (d, 1H, J = 1.1 Hz, py), 7.12 (d, 1H, J = 4.6 Hz, J_{Pt-H} = 27.2 Hz, th), 1.41 (s, 18H, *t*Bu) ppm. ^{19}F NMR (282 MHz, CD_2Cl_2): δ = −140.30 (dd, 1F, J = 23.1, 7.1, Hz), −161.51 (t, 2F, J = 20.8 Hz), −165.33 (dt, 2F, J = 25.8, 18.4 Hz) ppm. ^{195}Pt NMR (54 MHz, CD_2Cl_2): δ = −3840 ppm.
[Pt(bth(tbppy)py)(C≡CPh)]: From 100 mg [Pt(bth(tbppy)py)Cl] (0.142 mmol, 1 eq.), 46 µL phenylacetylene (0.425 mmol, 3 eq.), 2.1 mg CuI (0.011 mmol, 0.08 eq.), 1.3 mL NEt_3 in 85 mL CH_2Cl_2; orange-red solid; Yield: 82 mg (0.11 mmol, 75%). Elemental analysis calculated for $C_{40}H_{36}N_2PtS$ (771.89): C 62.24, H 4.70, N 3.63, S 4.15; found: C 62.43, H 4.71, N 3.62, S 4.12%. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 9.27 (d, 1H, J = 5.0 Hz, H6′), 8.84 (d, 1H, J

= 7.6 Hz, Hc), 7.88 (t, 1H, *J* = 7.5 Hz, H4'), 7.76 (d, 1H, *J* = 7.6 Hz, Hf), 7.71 (d, 1H, *J* = 7.8 Hz, H3'), 7.61 (s, 1H, H10), 7.51 (d, 2H, *J* = 7.0 Hz, H13), 7.48 (d, 2H, *J* = 1.6 Hz, H8/H12), 7.45 (t, 1H, *J* = 6.4 Hz, H5'), 7.43 (s, 1H, py), 7.33-7.27 (m, 5H, py/H14/Hd/He), 7.21 (t, 1H, *J* = 7.4 Hz, H15), 1.42 (s, 18H, *t*Bu) ppm. ^{13}C NMR (HMQC) (151 MHz, CD_2Cl_2): δ = 151.6 (CH, C6'), 139.0 (CH, C4'), 131.5 (CH, C13), 130.1 (CH, Cc), 127.9 (CH, C14), 125.8 (CH, Ce), 125.4 (CH, C15), 124.4 (CH, C10), 124.3 (CH, Cd), 122.9 (CH, C3'), 122.1 (CH, Cf), 121.2 (CH, C8/C12), 115.1 (CH, py), 114.1 (CH, py), 31.5 (CH_3, *t*Bu) ppm. HR-ESI-MS(+) m/z = 804.25888 $[M+CH_3OH+H]^+$ (calc. 804.25910).

[Pt(ph(tbppy)tz)(C≡CPh)]: From 30 mg [Pt(ph(tbppy)tz)Cl] (0.046 mmol, 1 eq.), 15 µL phenylacetylene (0.137 mmol, 3 eq.), 0.7 mg CuI (0.004 mmol, 0.08 eq.), 0.4 mL NEt_3 in 15 mL CH_2Cl_2; orange solid; Yield: 32 mg (0.044 mmol, 96%); Elemental analysis calculated for $C_{36}H_{34}N_2PtS$ (721.83): C 59.90, H 4.75, N 3.88, S 4.44; found: C 59.80, H 4.71, N 3.83, S 4.45. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 8.11 (d, *J* = 3.1 Hz, 1H, tz), 7.78-7.76 (m, J_{Pt-H} = 62.1 Hz, 1H, Hb), 7.72 (d, *J* = 3.2 Hz, 2H, tz), 7.65 (s, 1H, py), 7.63 (s, 1H, H10), 7.58 (s, 1H, py), 7.51 (d, *J* = 1.4 Hz, 2H, H8/H12), 7.45-7.42 (m, 3H, H13/He), 7.27 (t, *J* = 7.6 Hz, 2H, H14), 7.16 (t, *J* = 7.4 Hz, 1H, H15), 7.07-7.06 (m, 2H, Hc/Hd), 1.42 (s, 18H, *t*Bu) ppm. ^{195}Pt NMR (54 MHz, CD_2Cl_2): δ = −3850 ppm. HR-ESI-MS(+) m/z = 754.24284 $[M+CH_3OH+H]^+$ (calc. 754.24312), 743.19723 $[M+Na]^+$ (calc. 743.196155), 721.21424 $[M+H]^+$ (calc. 721.21421).

[Pt(ph(tbppy)tz)(C≡CC$_6$F$_5$)]: From 100 mg [Pt(ph(tbppy)tz)Cl] (0.152 mmol, 1 eq.), 125 µL pentafluorophenylacetylene (0.912 mmol, 6 eq.), 2.3 mg CuI (0.012 mmol, 0.08 eq.), 1.4 mL NEt_3 in 25 mL CH_2Cl_2; yellow solid; Yield: 99 mg (0.122 mmol, 80%). Elemental analysis calculated for $C_{36}H_{29}F_5N_2PtS$ (811.78): C 53.27, H 3.60, N 3.45, S 3.95; found: C 53.29, H 3.65, N 3.49, S 3.94%. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 7.99 (d, 1H, *J* = 3.1 Hz, tz), 7.71-7.68 (m, 3H, tz/Hb/py), 7.62 (t, 1H, *J* = 1.7 Hz, H10), 7.56 (s, 1H, py), 7.49 (d, 2H, *J* = 1.7 Hz, H8/H12), 7.41 (d, 1H, *J* = 6.7 Hz, He), 7.05 (dt, 1H, *J* = 11.0, 1.3 Hz, Hd), 7.01 (dt, 1H, *J* = 10.9, 1.3 Hz, Hc), 1.41 (s, 18H, *t*Bu) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −140.26 (dd, 1F, *J* = 23.3, 6.6 Hz), −161.62 (t, 2F, *J* = 20.8 Hz), −165.25 to −165.44 (m, 2F) ppm. ^{195}Pt NMR (54 MHz, CD_2Cl_2): δ = −3871 ppm. HR-ESI-MS **(+)** m/z = 661.19645 $[M-C{\equiv}CC_6F_5+CH_3CN]^+$ (calc. 661.19673), 833.14963 $[M+Na]^+$ (calc. 833.14905), 811.16773 $[M+H]^+$ (calc. 811.16710).

[Pt(na(tbppy)tz)(C≡CPh)]: From 233 mg [Pt(na(tbppy)tz)Cl] (0.330 mmol, 1 eq.), 110 µL phenylacetylene (1 mmol, 3 eq.), 5.0 mg CuI (0.026 mmol, 0.08 eq.), 3.0 mL NEt_3 in 45 mL CH_2Cl_2; purified by recrystallisation from CH_2Cl_2/Et_2O; dark red solid; Yield: 205 mg (0.266 mmol, 80%); Elemental analysis calculated for $C_{40}H_{36}N_2PtS$ (771.89): C 62.24, H 4.70, N 3.63, S 4.15; found: C 62.21, H 4.66, N 3.61, S 4.11%. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 8.12-8.11 (m, 2H, J_{Pt-H} = 73.4 Hz, Hb), 7.90 (s, 1H), 7.76 (dd, 1H, *J* = 6.0, 3.3 Hz), 7.77-7.73 (m, 3H), 7.66 (t, 1H, *J* = 1.7 Hz), 7.57-7.56 (m, 3H), 7.52 (d, 2H, *J* = 7.0 Hz, H13), 7.35-7.33 (m, 2H), 7.30 (t, 2H, *J* = 7.7 Hz, H14), 7.19 (t, 1H, *J* = 7.4 Hz, H15), 1.44 (s, 18H, *t*Bu) ppm. EI-MS (+) (70 eV) m/z = 771 $[M]^+$, 476 $[Hna(tbppy)tz]^+$. HR-ESI-MS(+) m/z = 804.25861 $[M+CH_3OH+H]^+$ (calc. 804.25910), 793.21263 $[M+Na]^+$ (calc. 793.21181), 771.22944 $[M+H]^+$ (calc. 771.22986).

[Pt(ph(tbppy)btz)(C≡CPh)]: From 150 mg [Pt(ph(tbppy)btz)Cl] (0.212 mmol, 1 eq.), 70 µL phenylacetylene (0.636 mmol, 3 eq.), 3.2 mg CuI (0.017 mmol, 0.08 eq.), 3.0 mL NEt_3 in 45 mL CH_2Cl_2; purified by column chromatography (silica, CH_2Cl_2) and recrystallisation from CH_2Cl_2/Et_2O; orange solid; Yield: 137 mg (0.178 mmol, 85%); Elemental analysis calculated for $C_{40}H_{36}N_2PtS$ (771.89): C 62.24, H 4.70, N 3.63, S 4.15; found: C 62.42, H 4.64, N 3.66, S 4.15%. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 8.99 (d, 1H, *J* = 8.0 Hz, btz), 7.82 (m, 3H, btz/Hb/H3), 7.65 (t, 1H, *J* = 1.5 Hz, H10), 7.54 (d, 2H, *J* = 1.6 Hz, H8/H12), 7.46 (m, 5H, H5/H5'/H6'/H13), 7.34 (t, 1H, *J* = 3.5 Hz, He), 7.28 (t, 2H, *J* = 7.6 Hz, H14), 7.18 (t, 1H, *J* = 7.4 Hz, H15), 7.04 (t, 2H, *J* = 4.3 Hz, Hc/Hd), 1.44 (s, 18H, *t*Bu) ppm. HR-ESI-MS(+) m/z = 804.25897 $[M+CH_3OH+H]^+$ (calc. 804.25910), 793.21344 $[M+Na]^+$ (calc. 793.21181), 771.22933 $[M+H]^+$ (calc. 771.22986).

[Pt(th(tbppy)tz)(C≡CPh)]: From 70 mg [Pt(th(tbppy)tz)Cl] (0.11 mmol, 1 eq.), 35 µL phenylacetylene (0.317 mmol, 3 eq.), 1.6 mg CuI (0.009 mmol, 0.08 eq.), 1.0 mL NEt_3 in 17 mL CH_2Cl_2; Yield: 63 mg (0.09 mmol, 82%); Elemental analysis calculated for $C_{34}H_{32}N_2PtS_2$ (727.85): C 56.11, H 4.43, N 3.85, S 8.81; found: C 56.15, H 4.44, N 3.86, S 8.86%. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 8.23 (d, 1H, *J* = 3.3 Hz, tz), 7.80 (d, 1H, *J* = 3.2 Hz, tz), 7.65 (t, 1H, *J* = 1.7 Hz, H10), 7.58-7.57 (m, 2H, py/Hc), 7.52 (d, 2H, *J* = 1.7 Hz, H8/H12), 7.49-7.46 (m, 3H, py/H13), 7.32-7.30 (m, 3H, Hb/H14), 7.19 (t, 1H, *J* = 7.4 Hz, H15), 1.45 (s, 18H, *t*Bu) ppm. EI-MS (+) (70 eV) m/z = 727 $[M]^+$, 432 $[Hth(tbppy)tz]^+$.

References

1) T. A. Pham, F. Song, M. N. Alberti, M.-T. Nguyen, N. Trapp, C. Thilgen, F. Diederich, M. Stohr, *Chem. Comm.* **2015**, *51*, 14473–14476.

2) H. Yang, N. Huo, P. Yang, H. Pei, H. Lv, X. Zhang, *Org. Lett.* **2015**, *17*, 4144–4147.

Supporting Fig.s

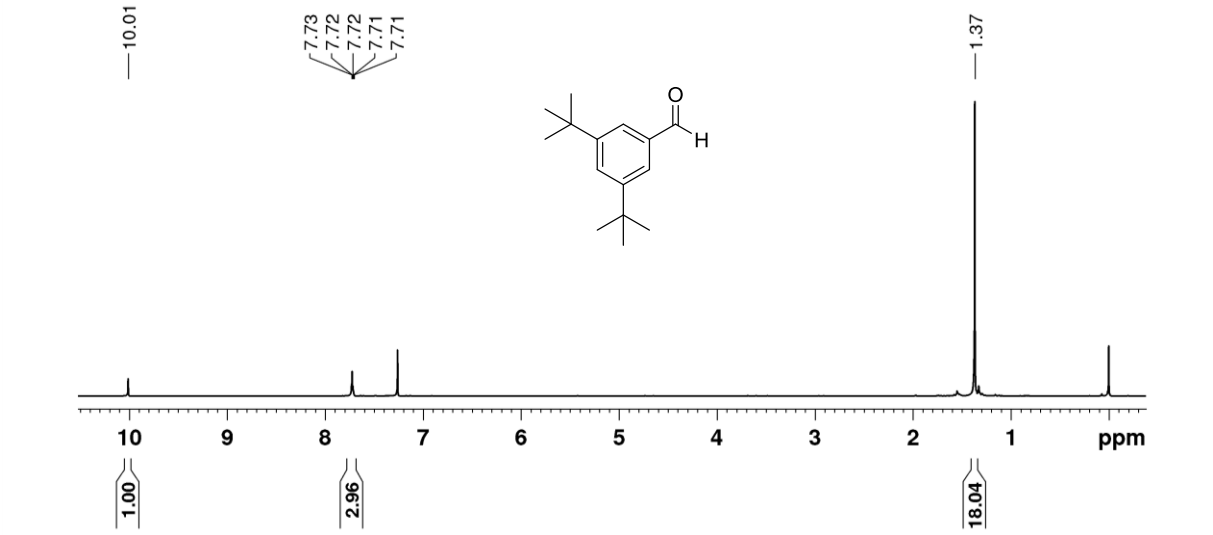


Fig. S001 300 MHz ^{1}H NMR spectrum of 3,5-di-*tert*-butylbenzaldeyde in $CDCl_3$.

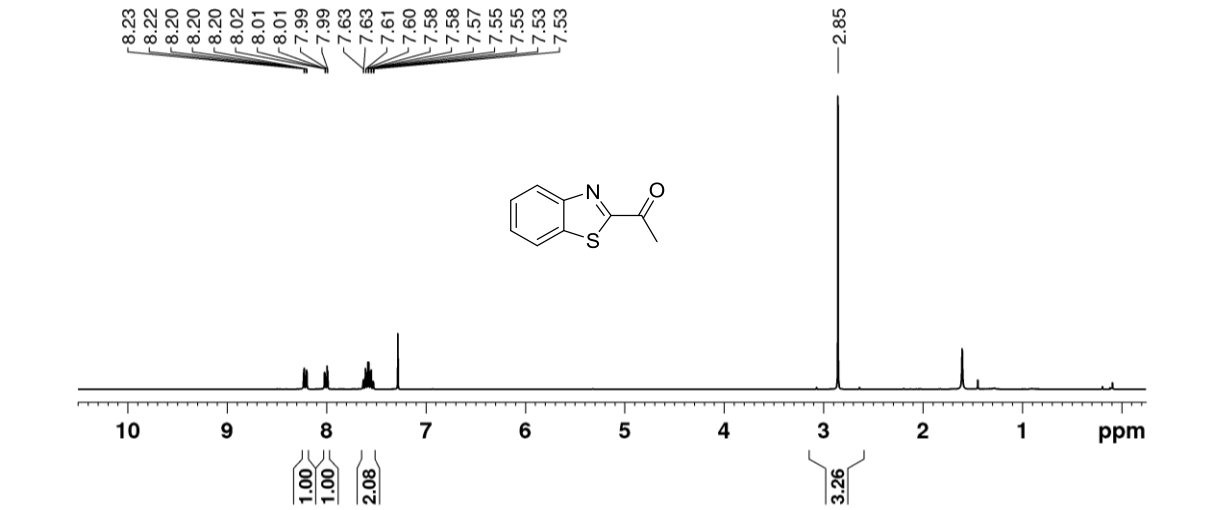


Fig. S002 300 MHz ^{1}H NMR spectrum of 2-acetylbenzthiazole in $CDCl_3$.

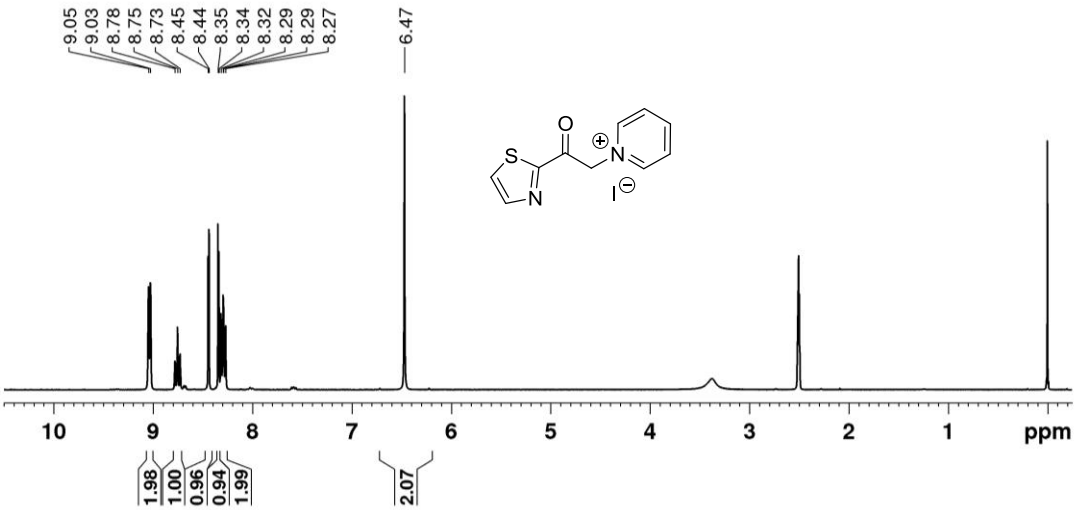


Fig. S003 300 MHz ^{1}H NMR spectrum of 1-(2-oxo-2-(thiazol-2-yl)ethyl)pyridinium iodide in DMSO-d_6.

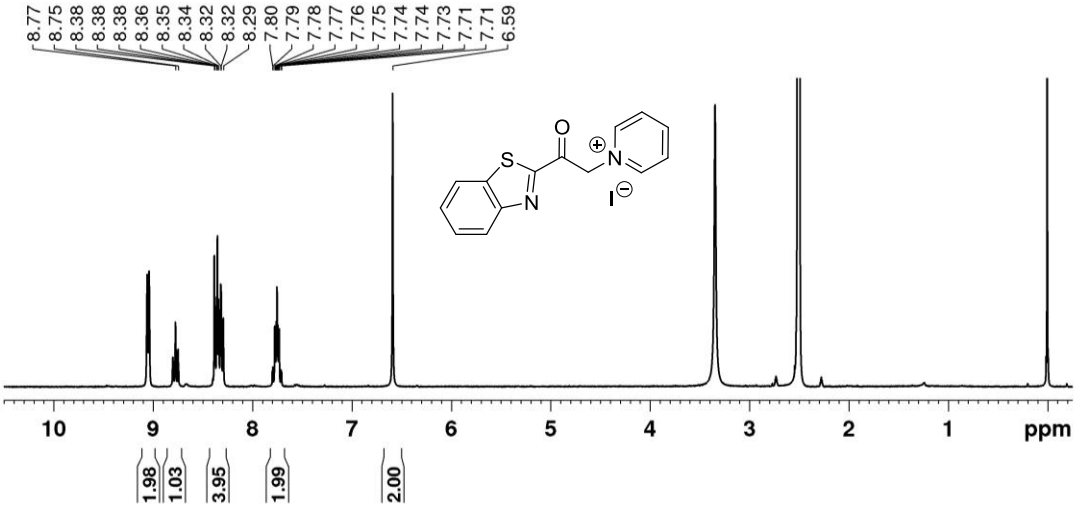


Fig. S004 300 MHz ^{1}H NMR spectrum of 1-(2-oxo-2-(benzthiazol-2-yl)ethyl)pyridinium iodide in DMSO-d_6.

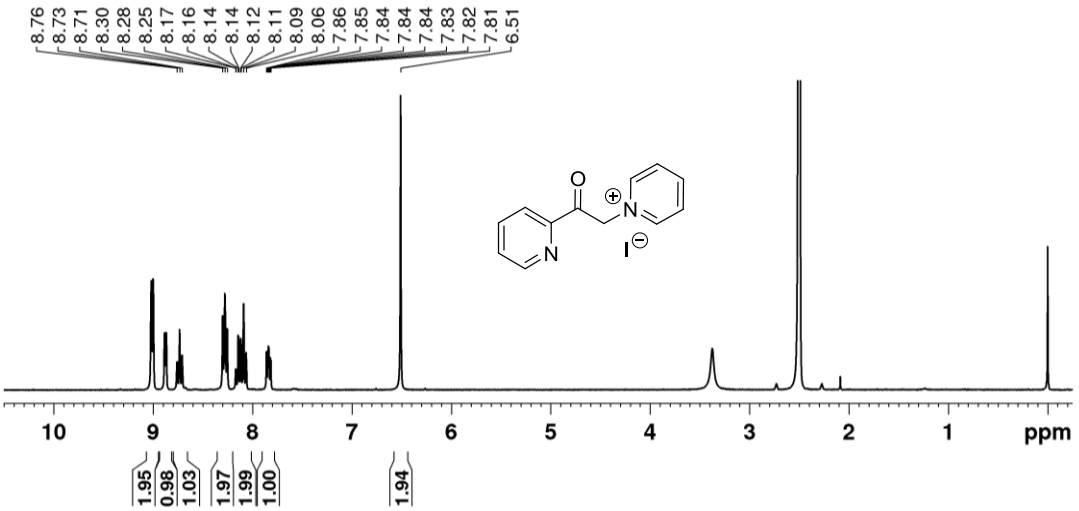


Fig. S005 300 MHz ^{1}H NMR spectrum of 1-(2-oxo-2-(pyridin-2-yl)ethyl)pyridinium iodide in DMSO-d_6.

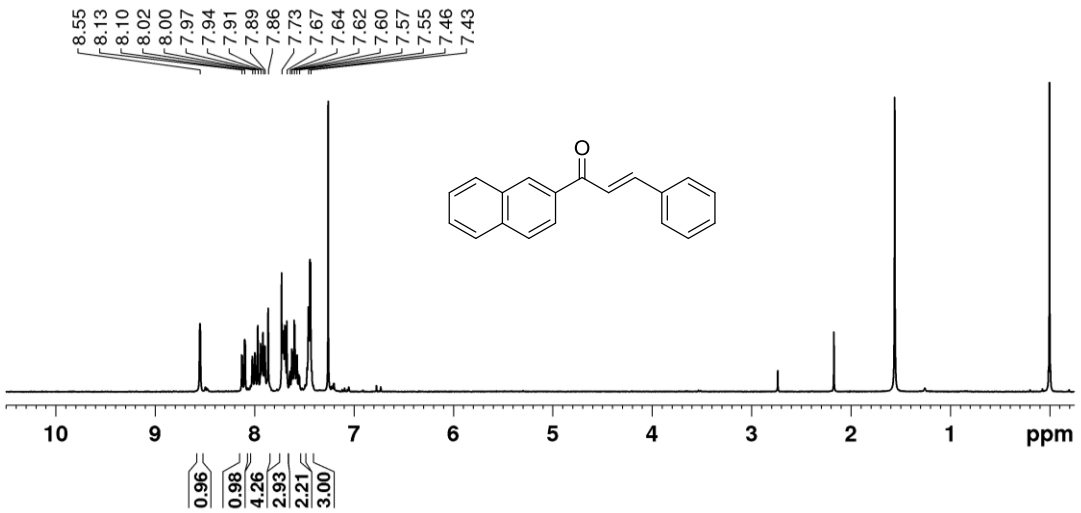


Fig. S006 300 MHz ^{1}H NMR spectrum of 1-(naphthalin-2-yl)-3-phenylprop-2-en-1-one in $CDCl_3$.

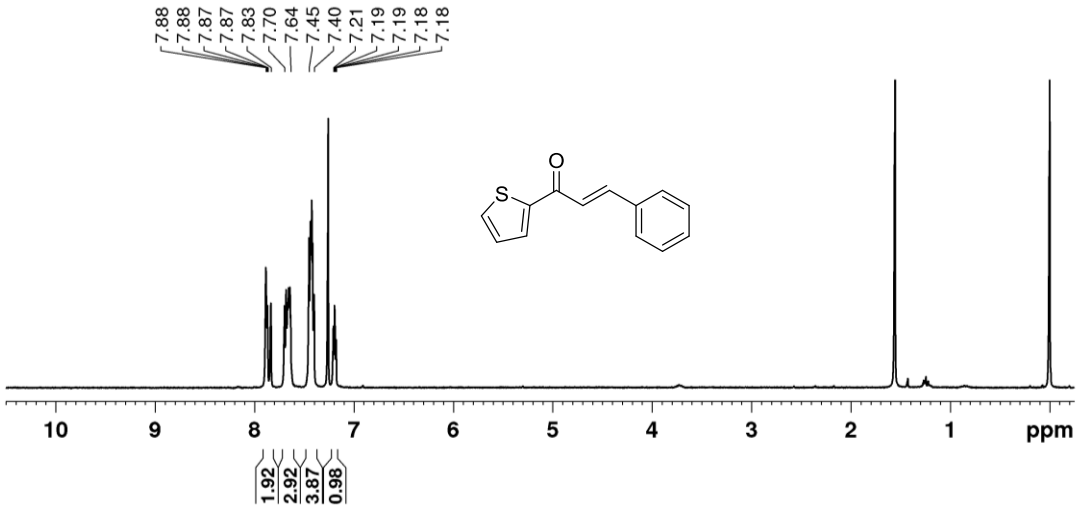


Fig. S007 300 MHz ^{1}H NMR spectrum of 1-(thiophen-2-yl)-3-phenylprop-2-en-1-one in $CDCl_3$.

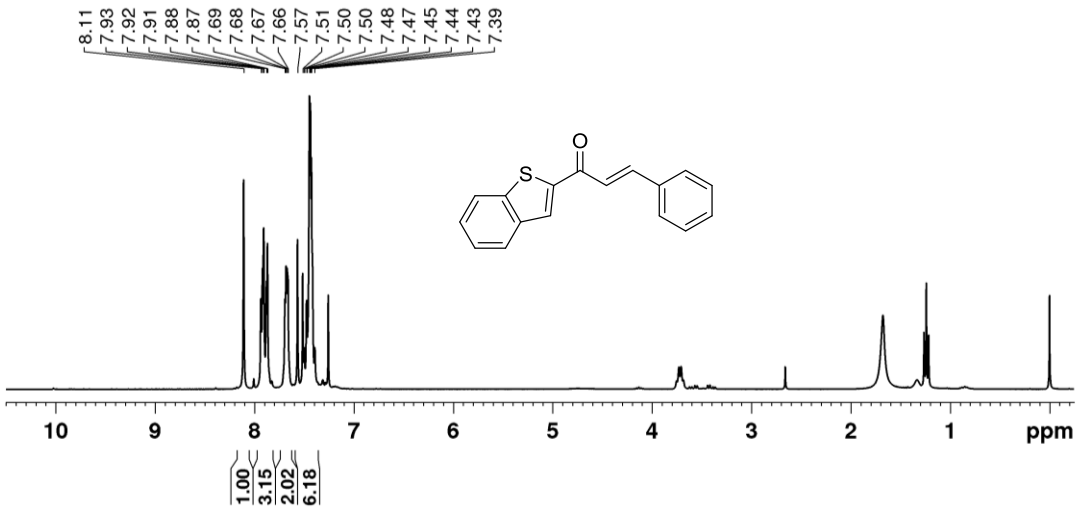


Fig. S008 300 MHz ^{1}H NMR spectrum () of 1-(benzothiophen-2-yl)-3-phenylprop-2-en-1-one in $CDCl_3$.

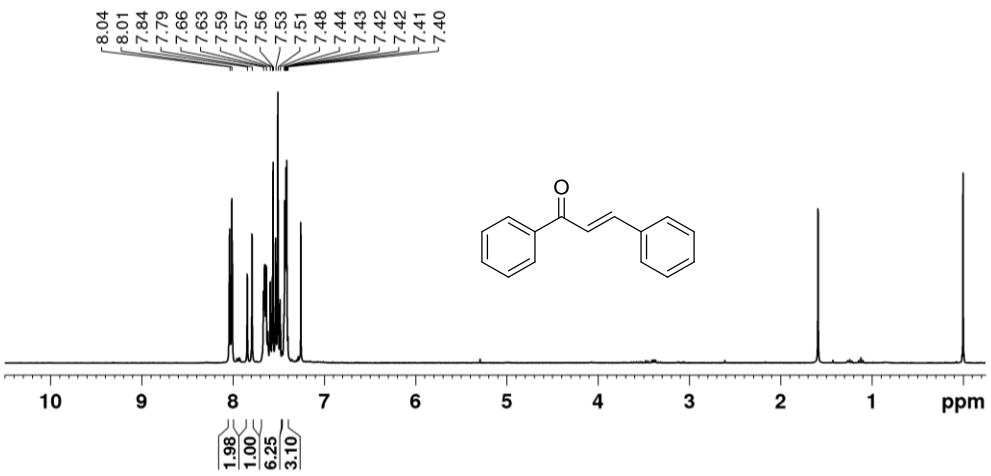


Fig. S009 300 MHz ^{1}H NMR spectrum of 1-phenyl-3-phenylprop-2-en-1-one in $CDCl_3$.

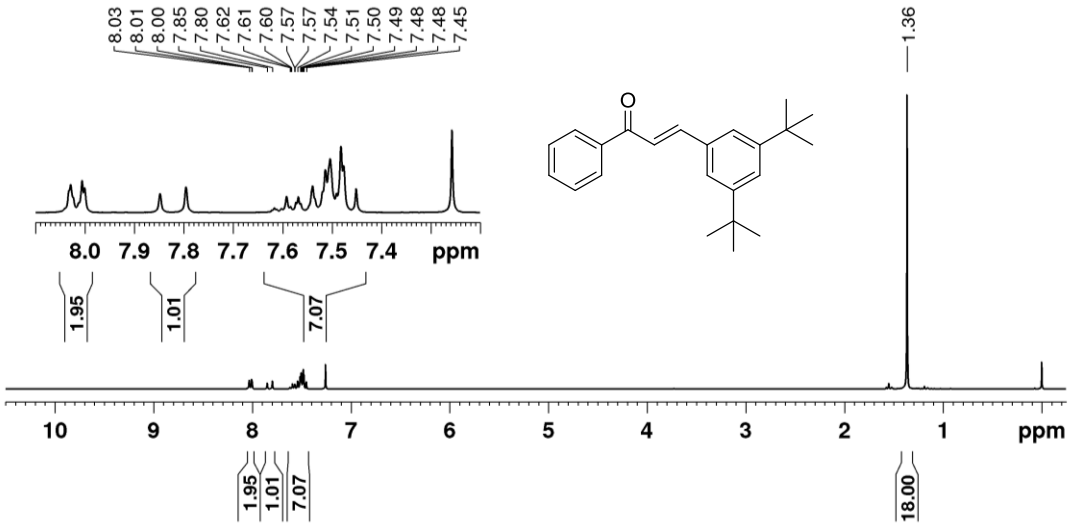


Fig. S010 300 MHz ^{1}H NMR spectrum of 1-phenyl-3-phenylprop-2-en-1-one in $CDCl_3$.

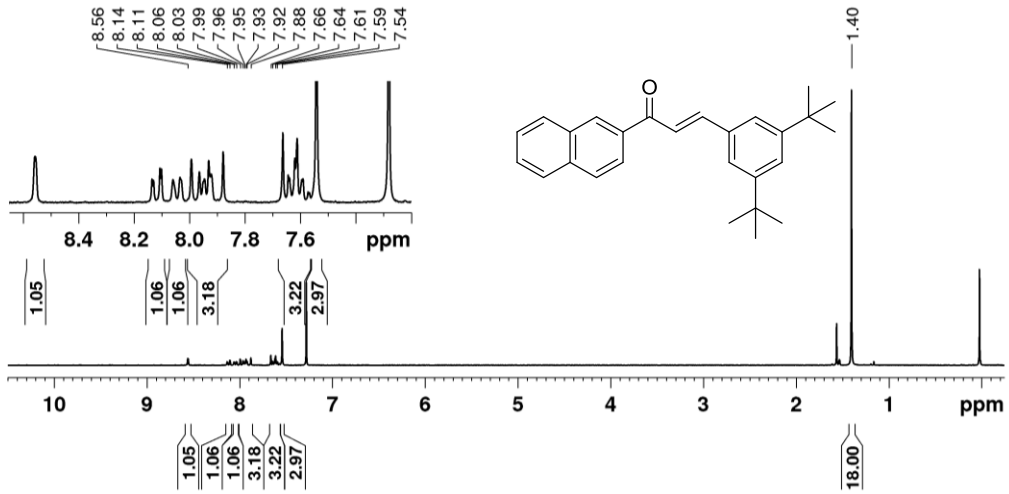


Fig. S011 300 MHz ^{1}H NMR spectrum of 1-(naphthalin-2-yl)-3-(3,5-di-*tert*-butyl-phenyl)prop-2-en-1-one in $CDCl_3$.

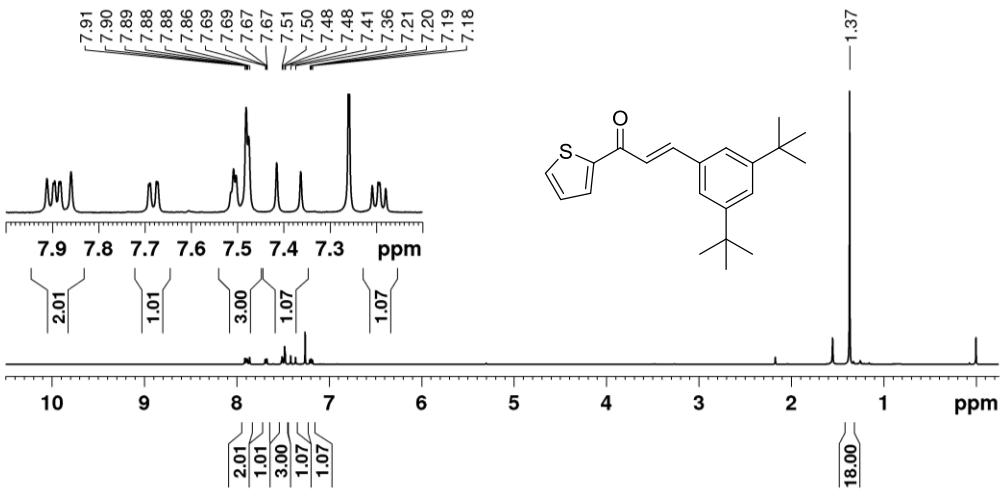


Fig. S012 300 MHz ^{1}H NMR spectrum of 1-(thiophen-2-yl)-3-(3,5-di-*tert*-butyl-phenyl)prop-2-en-1-one in $CDCl_3$.

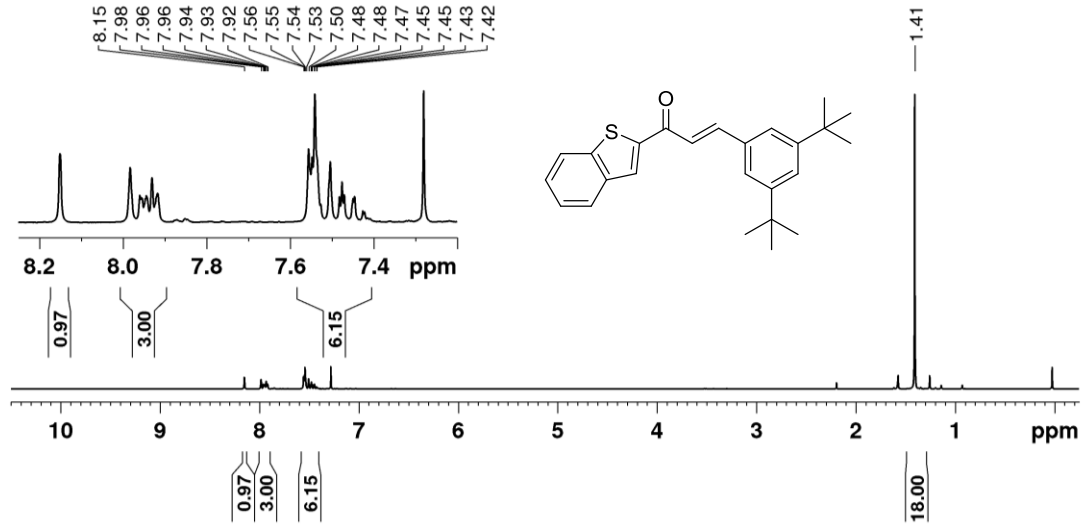


Fig. S013 300 MHz ^{1}H NMR spectrum of 1-(benzothiophen-2-yl)-3-(3,5-di-*tert*-butyl-phenyl)prop-2-en-1-one in $CDCl_3$.

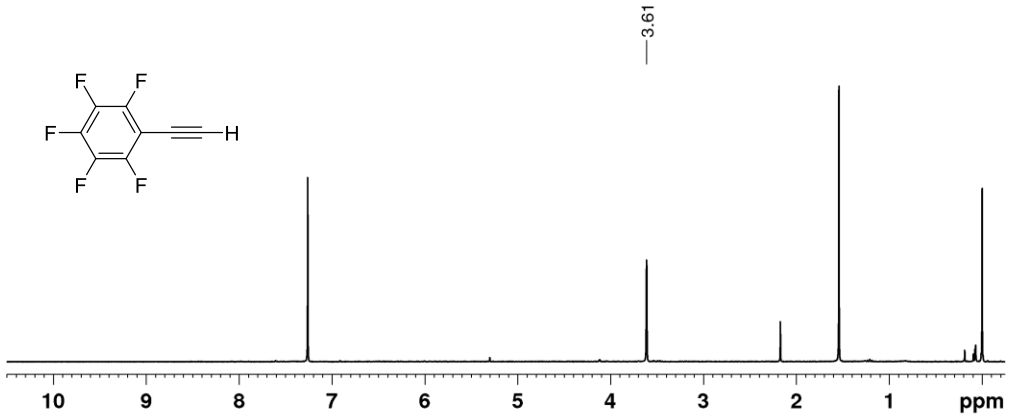


Fig. S014 300 MHz ^{1}H NMR spectrum of pentafluorphenylacetylene in $CDCl_3$.

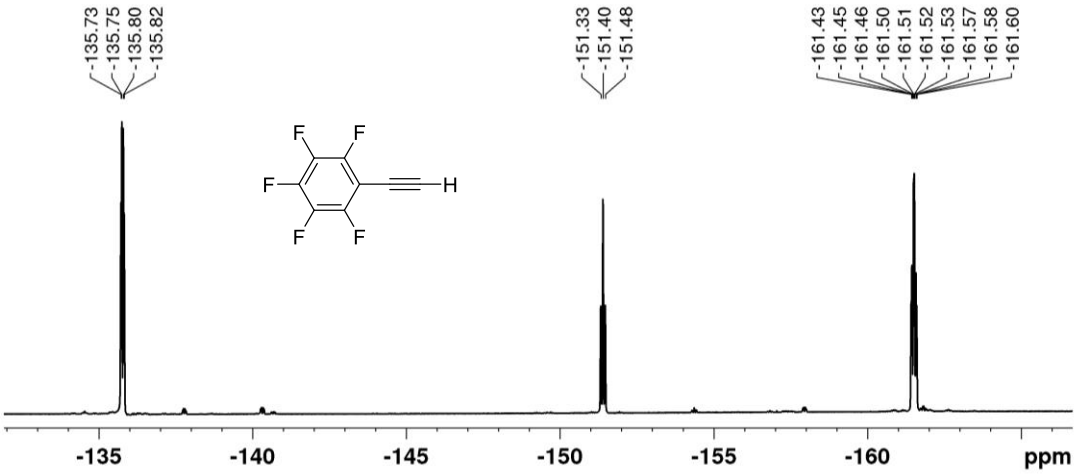


Fig. S015 284 MHz ^{19}F NMR spectrum of pentafluorphenylacetylene in $CDCl_3$.

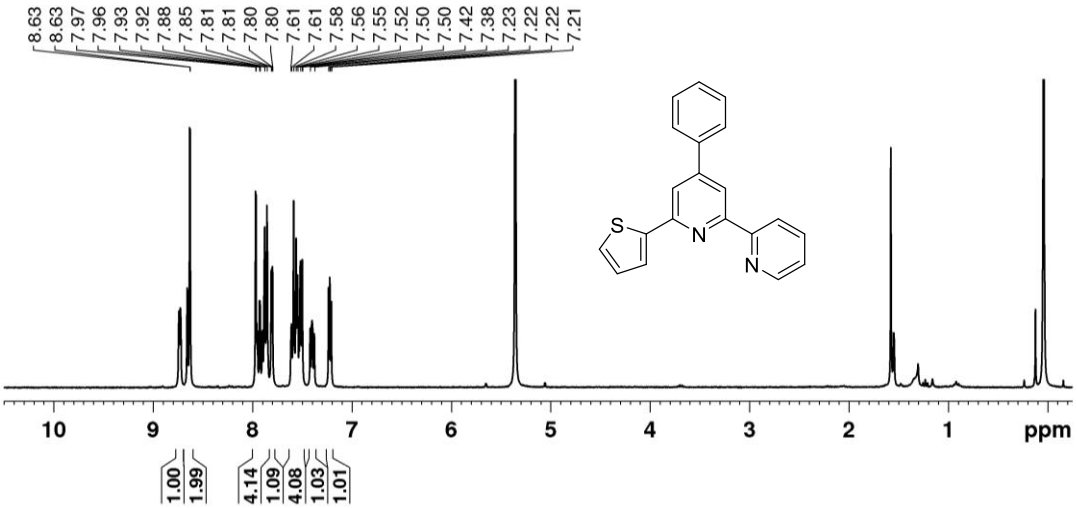


Fig. S016 300 MHz ^{1}H NMR spectrum of 6-(thiophen-2-yl)-4-phenyl-2,2'-bipyridine (Hth(ppy)py) in CD_2Cl_2.

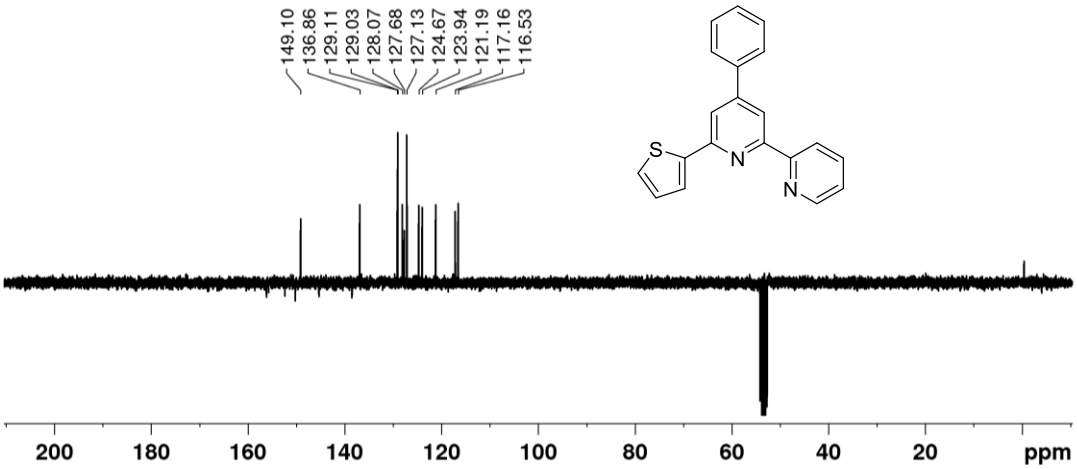


Fig. S017 75 MHz ^{13}C NMR spectrum of 6-(thiophen-2-yl)-4-phenyl-2,2'-bipyridine (Hth(ppy)py) in CD_2Cl_2.

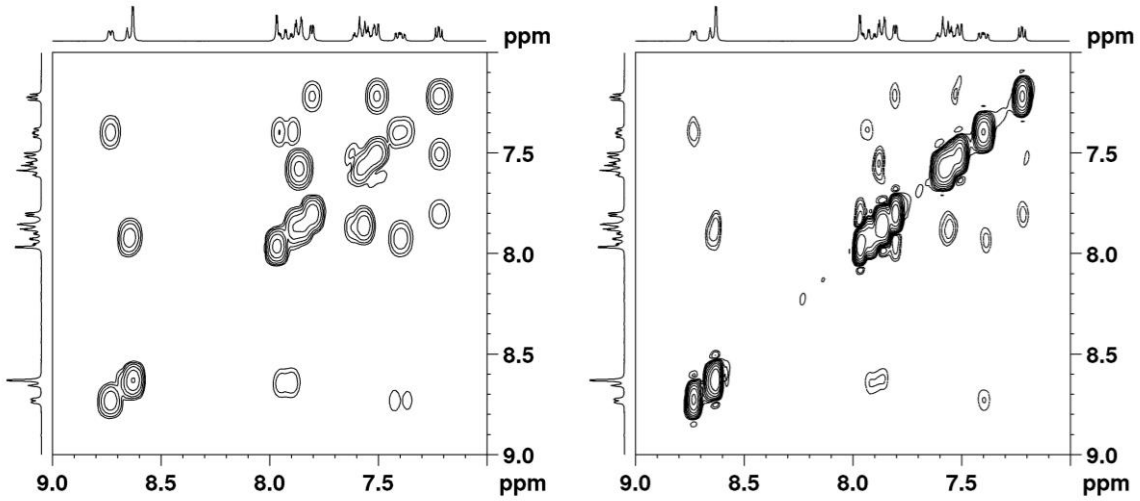


Fig. S018 300 MHz $^{1}H/^{1}H$ COSY (left) and $^{1}H/^{1}H$-NOESY NMR spectra (right) of 6-(thiophen-2-yl)-4-phenyl-2,2'-bipyridine (Hth(ppy)py) in CD_2Cl_2.

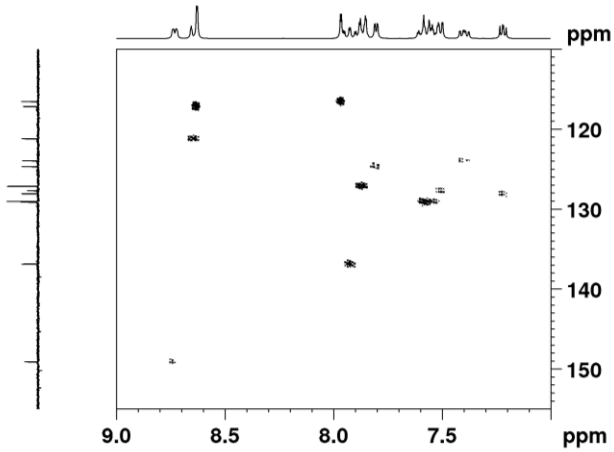


Fig. S019 300 MHz $^{1}H/^{13}C$ HMQC NMR spectrum of 6-(thiophen-2-yl)-4-phenyl-2,2'-bipyridine (Hth(ppy)py) in CD_2Cl_2.

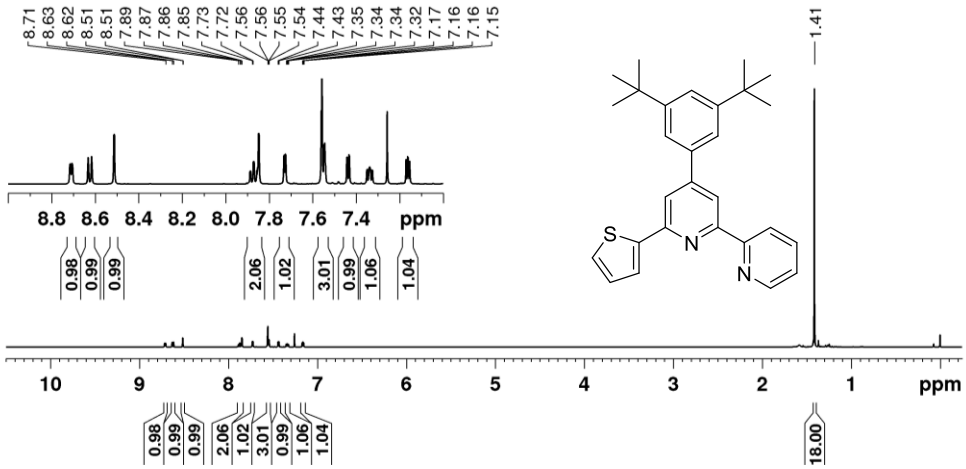


Fig. S020 500 MHz ^{1}H NMR spectrum of 6-(thiophen-2-yl)-4-(3,5-di-*tert*-butyl-phenyl)-2,2'-bipyridine (Hth(bppy)py) in $CDCl_3$.

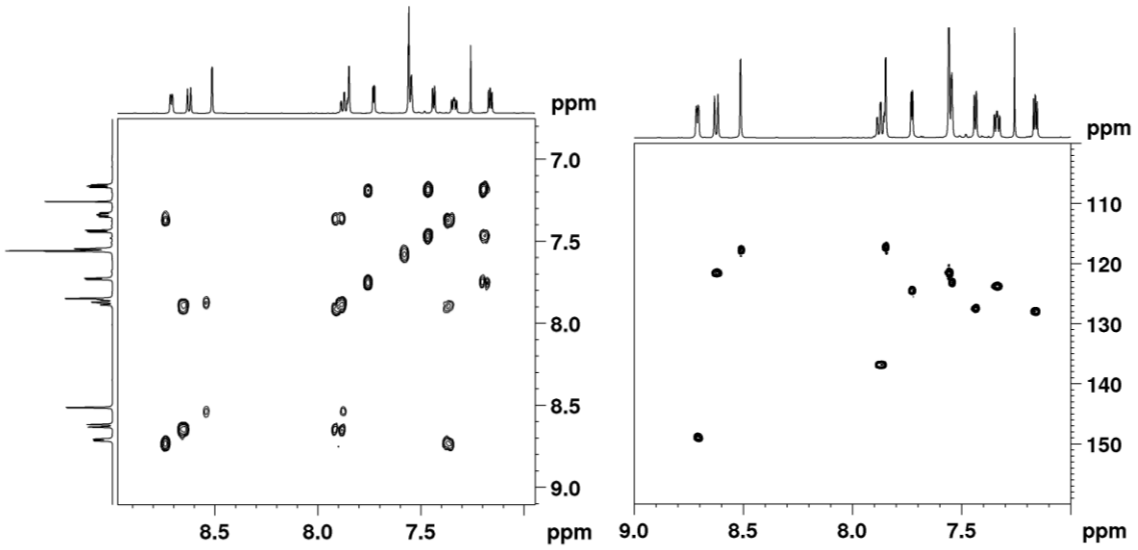


Fig. S021 500 MHz $^{1}H/^{1}H$ COSY NMR spectrum (left) and part of the 500 MHz ^{13}C-HSQC-NMR spectrum (right) of 6-(thiophen-2-yl)-4-(3,5-di-*tert*-butyl-phenyl)-2,2'-bipyridine (Hth(bppy)py) in $CDCl_3$.

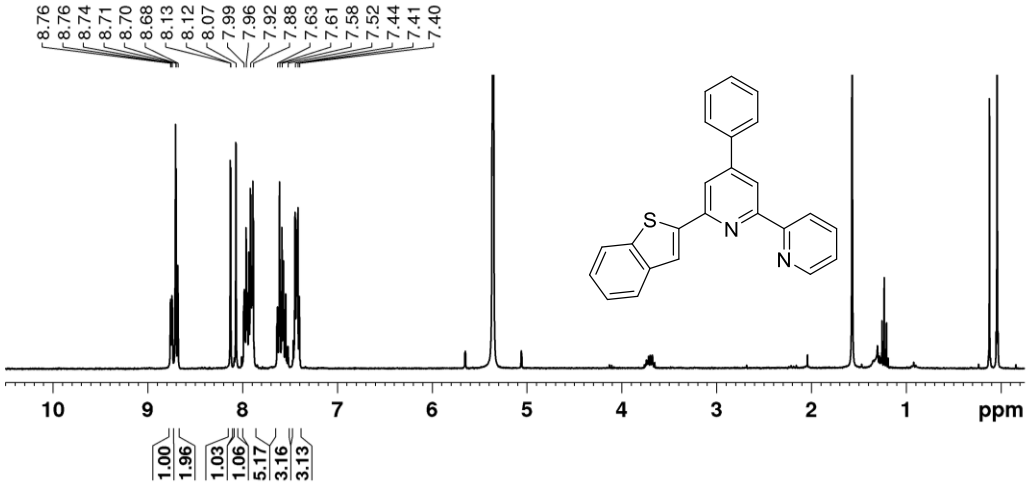


Fig. S022 300 MHz ^{1}H NMR spectrum of 6-(benzothiophen-2-yl)-4-phenyl-2,2'-bipyridine (Hbth(ppy)py) in CD_2Cl_2.

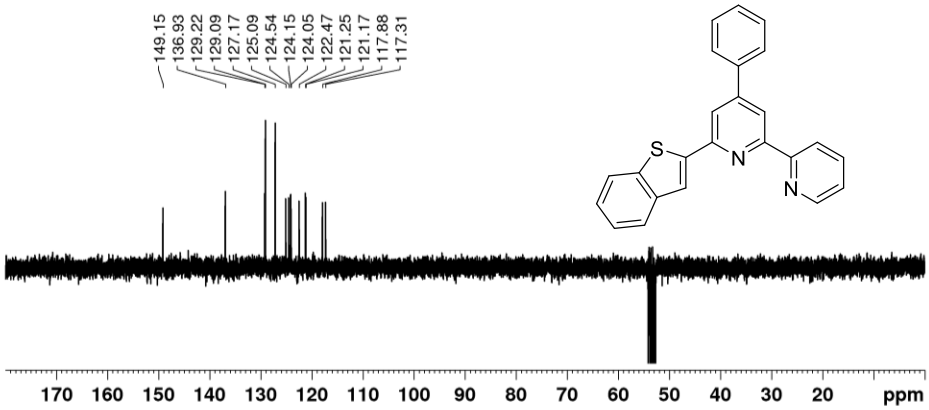


Fig. S023 75 MHz ^{13}C NMR spectrum of 6-(benzothiophen-2-yl)-4-phenyl-2,2'-bipyridine (Hbth(ppy)py) in CD_2Cl_2.

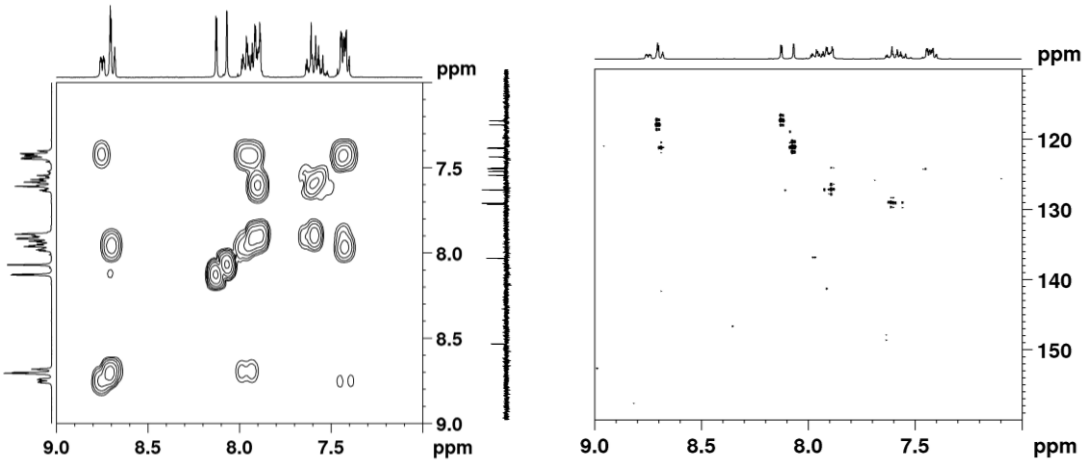


Fig. S024 300 MHz $^{1}H/^{1}H$ COSY (left) and $^{1}H/^{13}C$-HSQC (right) NMR spectra of 6-(benzothiophen-2-yl)-4-phenyl-2,2'-bipyridine (Hbth(ppy)py) in CD_2Cl_2.

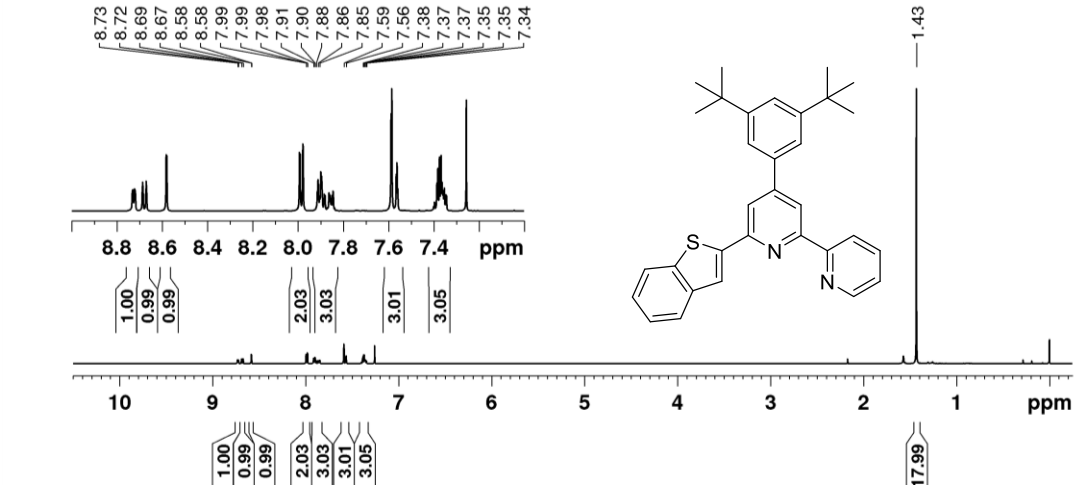


Fig. S025 500 MHz ^{1}H NMR spectrum of 6-(benzothiophen-2-yl)-4-(3,5-di-*tert*-butyl-phenyl)-2,2'-bipyridine (Hbth(tbppy)py) in $CDCl_3$.

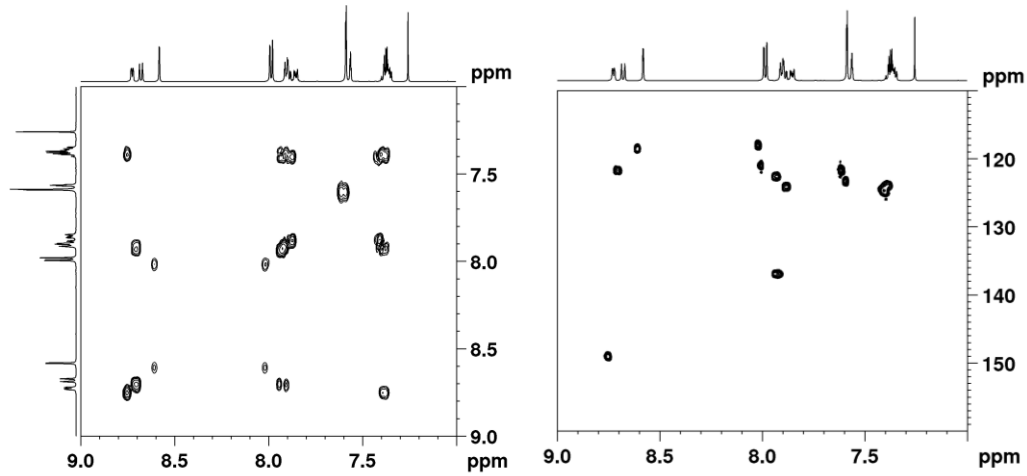


Fig. S026 500 MHz $^{1}H/^{1}H$ COSY NMR spectrum (left) and part of the 500 MHz $^{1}H/^{13}C$ HSQC NMR spectrum (right) of 6-(benzothiophen-2-yl)-4-(3,5-di-*tert*-butyl-phenyl)-2,2'-bipyridine (Hbth(tbppy)py) in $CDCl_3$.

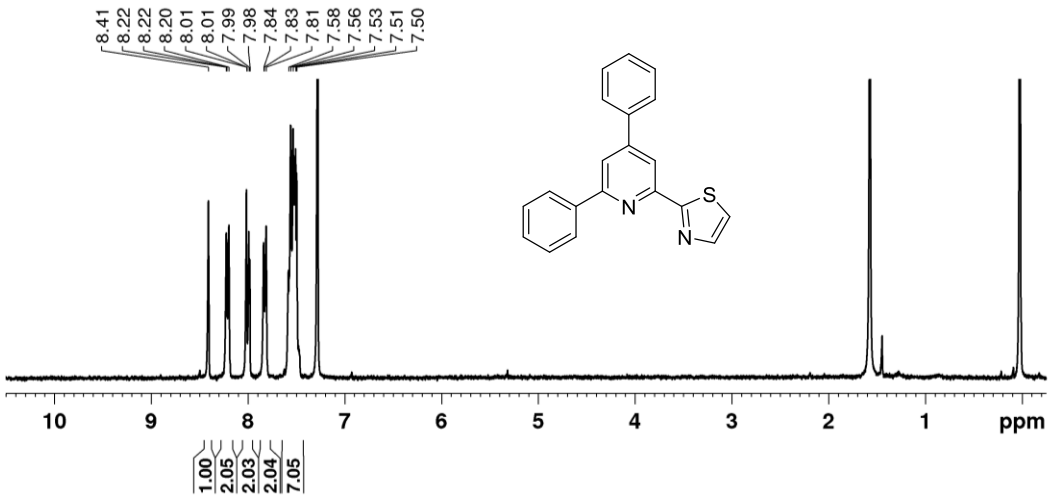


Fig. S027 300 MHz ^{1}H NMR spectrum of 2-(4,6-diphenylpyridin-2-yl)thiazole (Hph(ppy)tz) in $CDCl_3$.

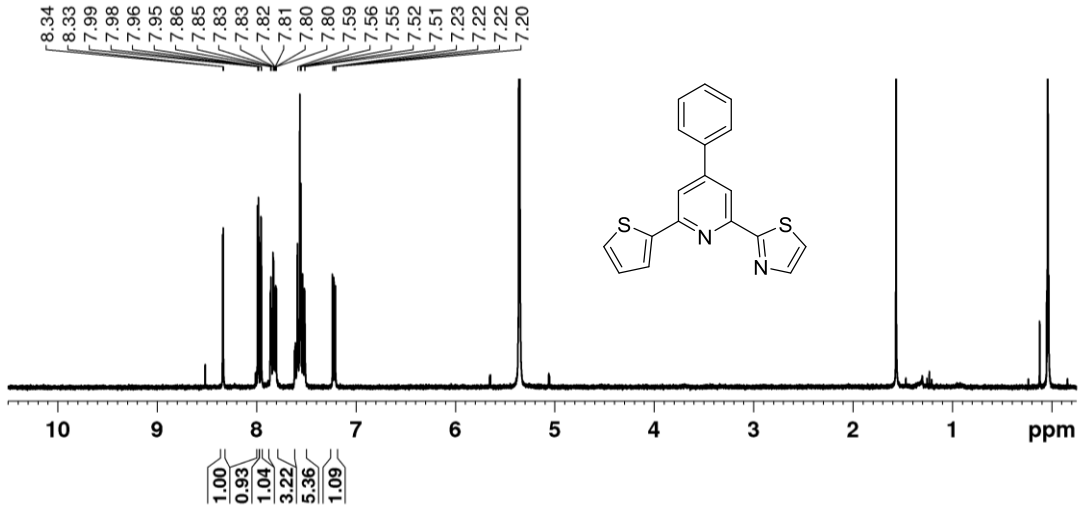


Fig. S028 300 MHz ^{1}H NMR spectrum of 2-(4-phenyl-6-(thiophen-2-yl)pyridin-2-yl)thiazole (Hth(ppy)tz) in $CDCl_3$.

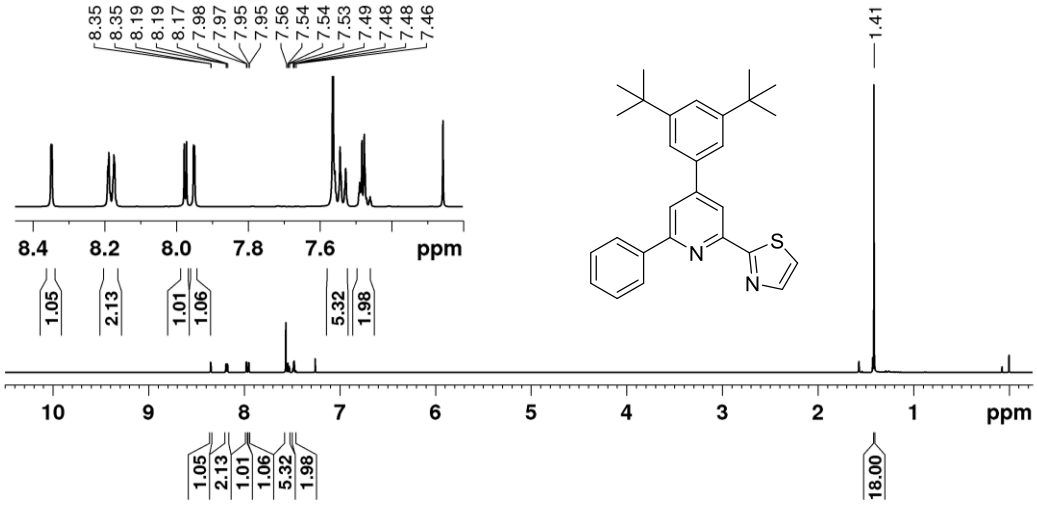


Fig. S029 500 MHz ^{1}H NMR spectrum of 2-(4-(3,5-di-*tert*-butylphenyl)-6-phenylpyridin-2-yl)thiazole (Hph(tbppy)tz) in $CDCl_3$.

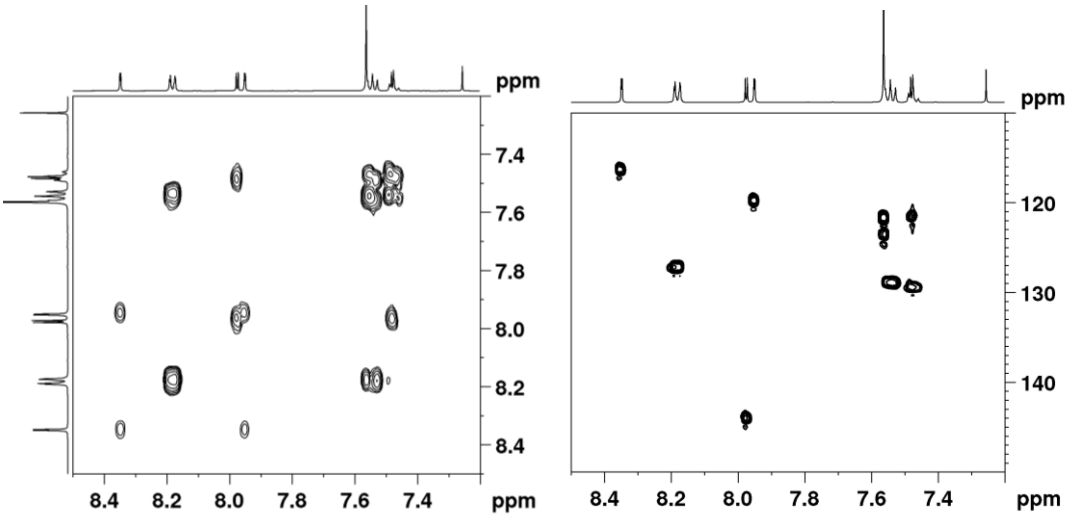


Fig. S030 500 MHz ^{1}H/^{1}H COSY (left) and ^{1}H/^{13}C-HSCQ (right) NMR spectra of 2-(4-(3,5-di-*tert*-butylphenyl)-6-phenylpyridin-2-yl)thiazole (Hph(tbppy)tz) in $CDCl_3$.

Fig. S031 300 MHz ^{1}H NMR spectrum of 2-(6-(naphthalen-2-yl)-4-phenylpyridin-2-yl)thiazole (Hna(ppy)tz) in $CDCl_3$.

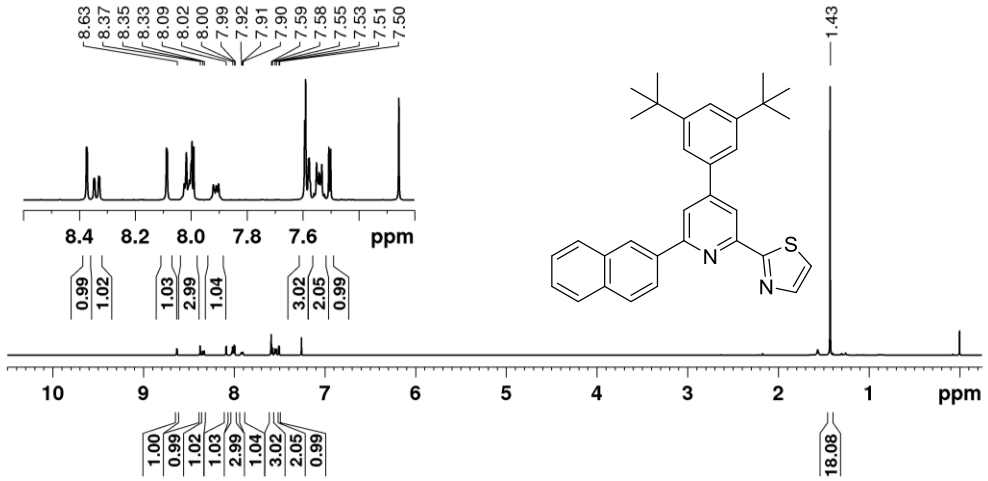


Fig. S032 500 MHz ^{1}H NMR spectrum of 2-(4-(3,5-di-*tert*-butylphenyl)-6-(naphthalen-2-yl)pyridin-2-yl)thiazole (Hna(tbppy)tz) in $CDCl_3$.

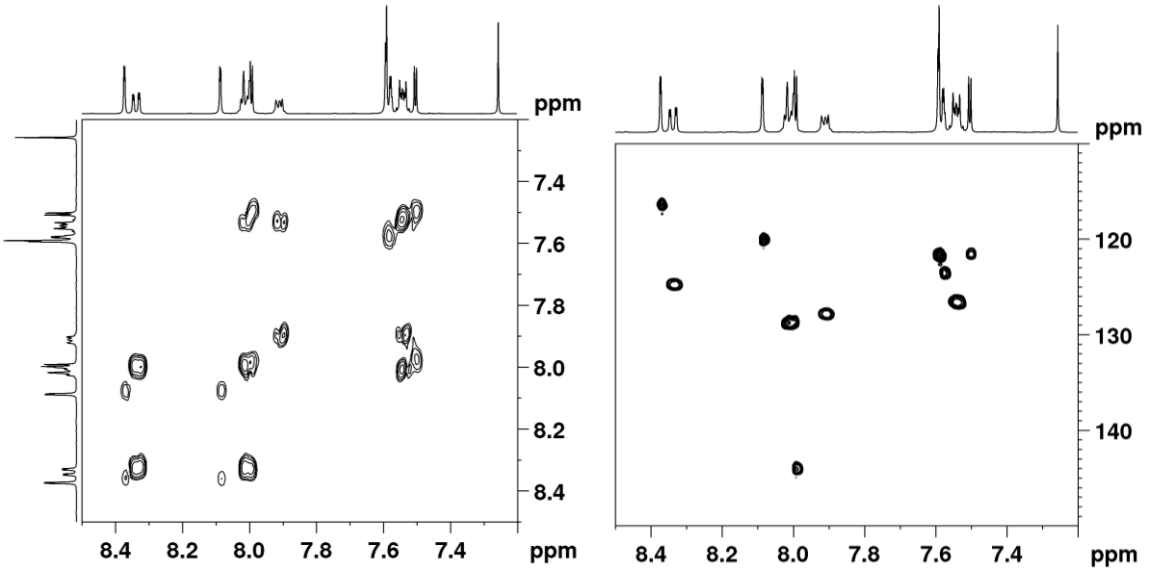


Fig. S033 500 MHz ^{1}H/^{1}H COSY (left) and ^{1}H/^{13}C-HSCQ (right) NMR spectra of 2-(4-(3,5-di-*tert*-butylphenyl)-6-(naphthalen-2-yl)pyridin-2-yl)thiazol (Hna(tbppy)tz) in $CDCl_3$.

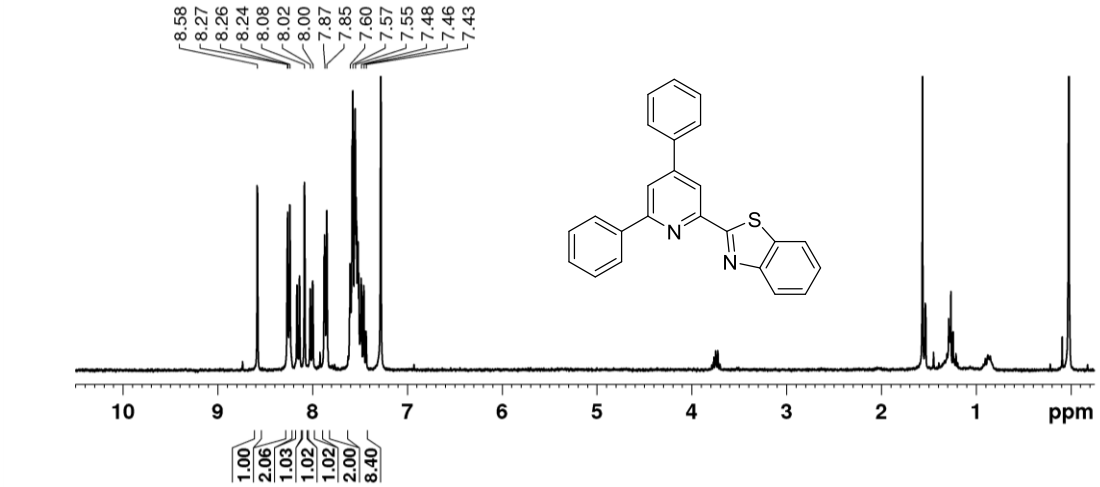


Fig. S034 300 MHz ^{1}H NMR spectrum of 2-(4,6-diphenylpyridin-2-yl)benzothiazole (Hph(ppy)btz) in $CDCl_3$.

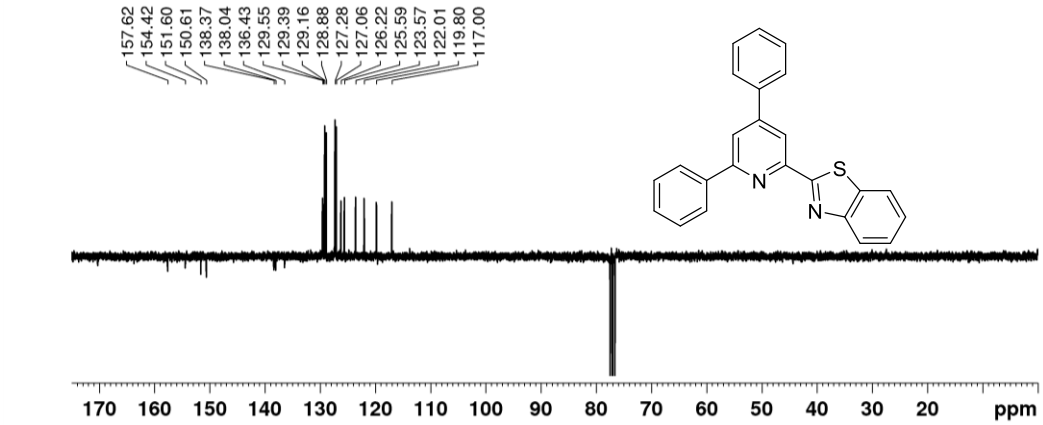


Fig. S035 75 MHz ^{13}C NMR spectrum of 2-(4,6-diphenylpyridin-2-yl)benzothiazole (Hph(ppy)btz) in $CDCl_3$.

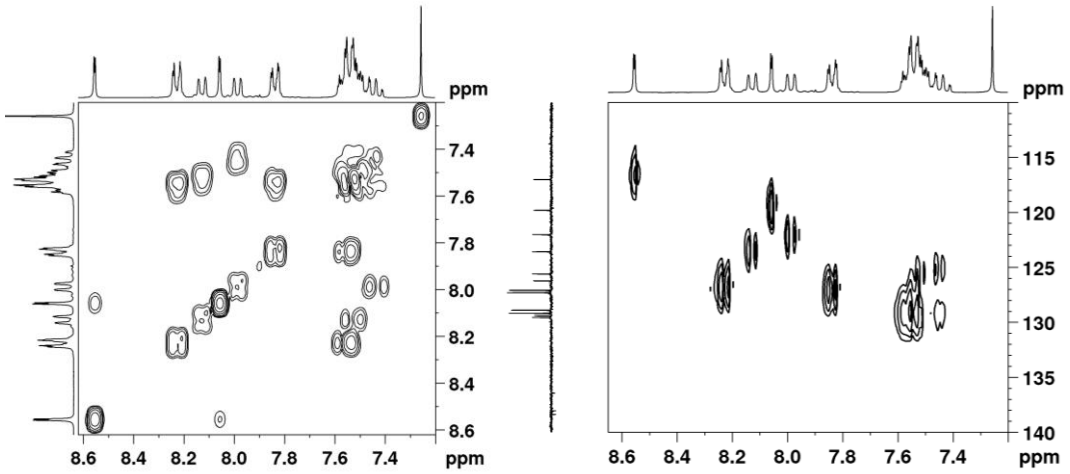


Fig. S036 300 MHz $^{1}H/^{1}H$ COSY (left) and $^{1}H/^{13}C$-HSCQ (right) NMR spectra of 2-(4,6-diphenylpyridin-2-yl)benzothiazole (Hph(ppy)btz) in $CDCl_3$.

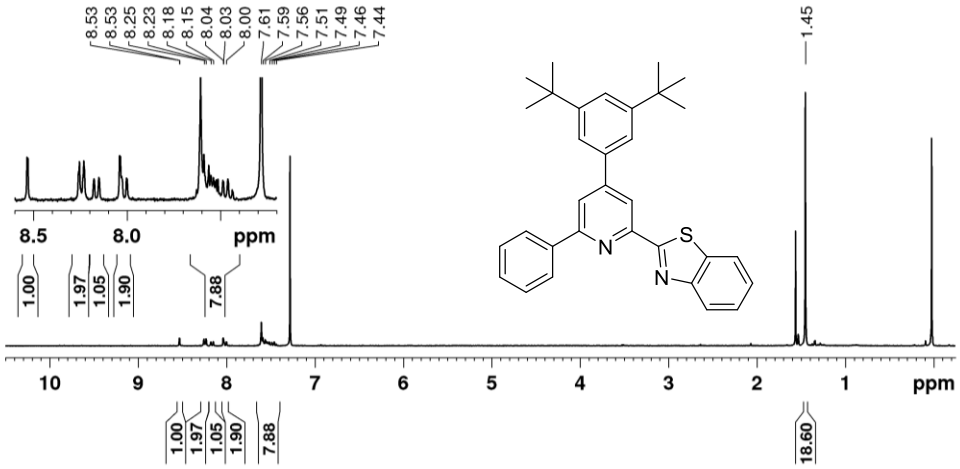


Fig. S037 300 MHz ^{1}H NMR spectrum of 2-(4-(3,5-di-*tert*-butylphenyl)-6-phenylpyridin-2-yl)benzothiazole (Hph(tbppy)btz) in $CDCl_3$.

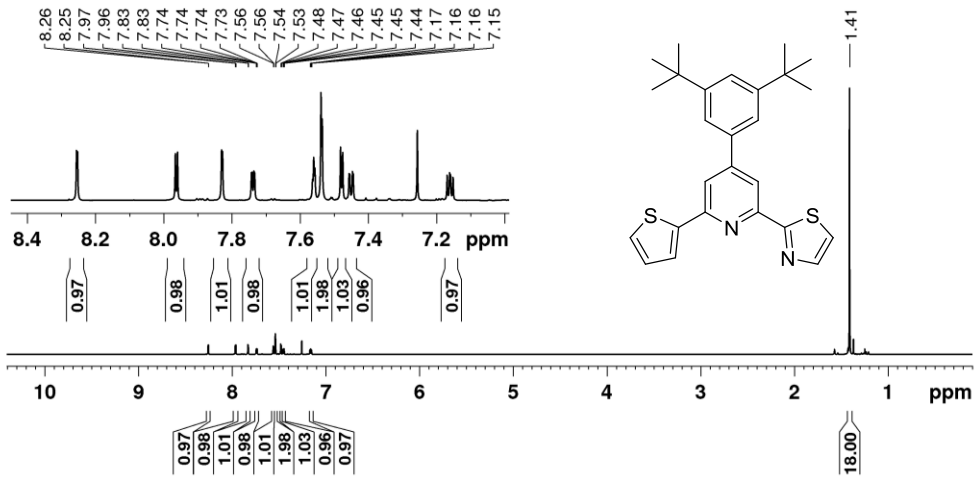


Fig. S038 300 MHz ^{1}H NMR spectrum of 2-(4-(3,5-di-*tert*-butylphenyl)-6-(thiophen-2-yl)-pyridin-2-yl)thiazole (Hth(tbppy)tz) in $CDCl_3$.

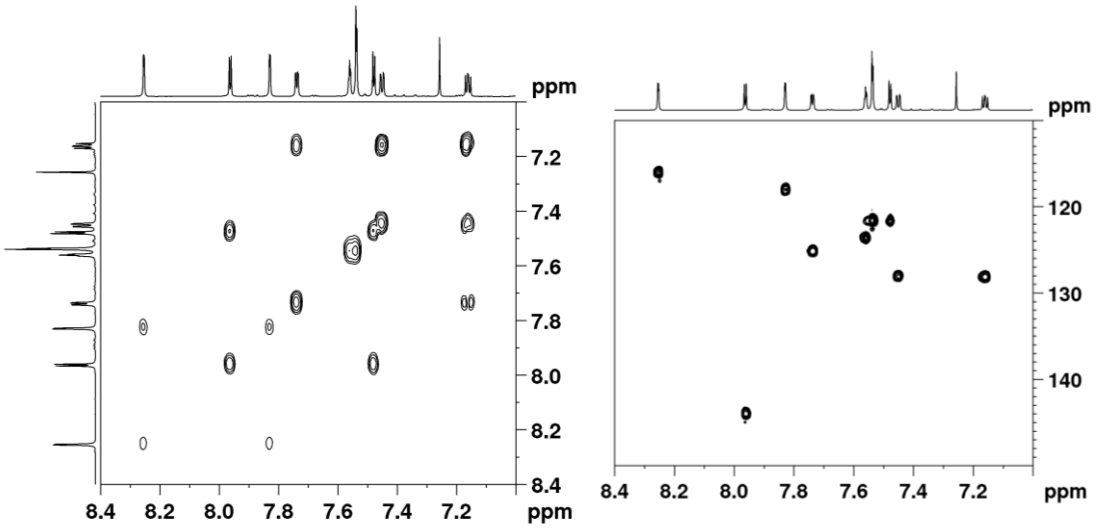


Fig. S039 500 MHz $^{1}H/^{1}H$ COSY (left) and $^{1}H/^{13}C$-HSCQ (right) NMR spectra of 2-(4-(3,5-Di-tert-butylphenyl)-6-(thiophen-2-yl)-pyridin-2-yl)thiazole (Hth(tbppy)tz) in $CDCl_3$.

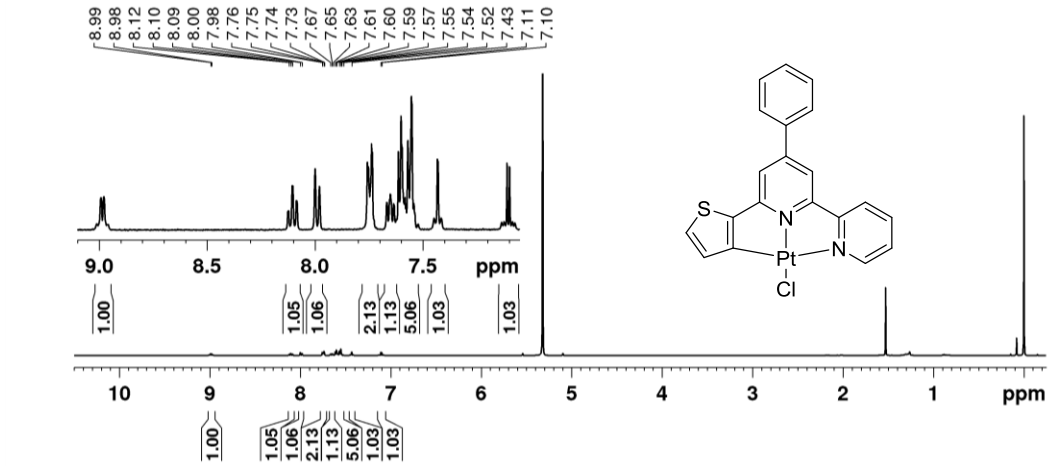


Fig. S040 400 MHz ^{1}H NMR spectrum of [Pt(th(ppy)py)Cl] in CD_2Cl_2.

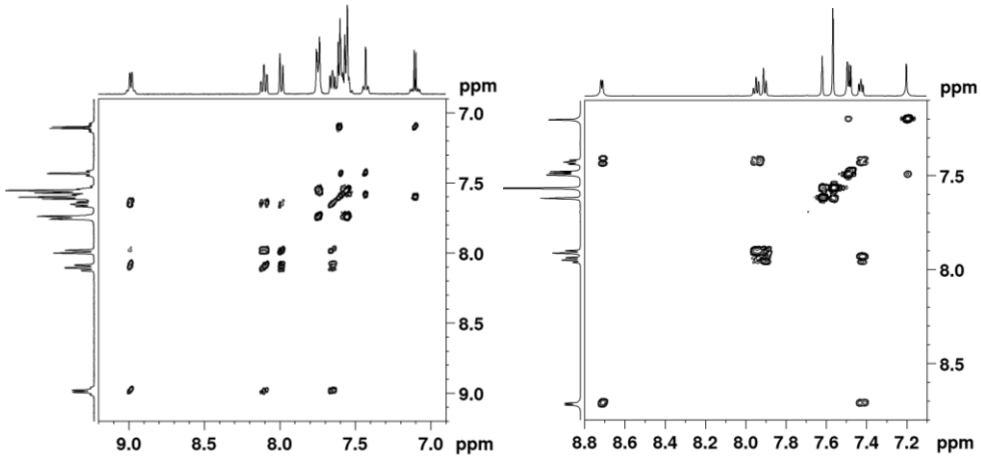


Fig. S041 400 MHz $^{1}H/^{1}H$ COSY NMR spectrum of [Pt(th(ppy)py)Cl] (left) and 600 MHz $^{1}H/^{1}H$-COSY NMR spectrum of [Pt(th(tbppy)py)Cl] (right) in CD_2Cl_2.

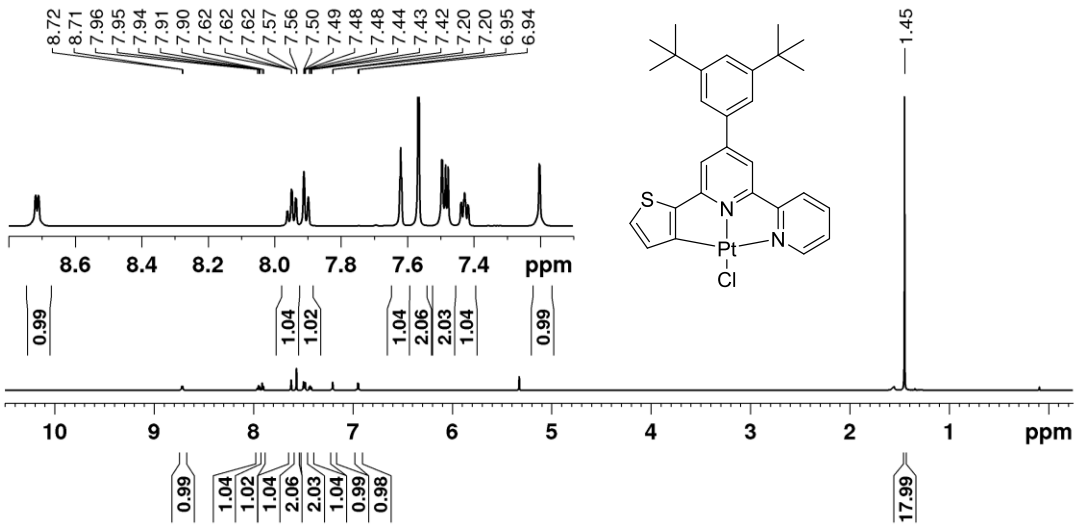


Fig. S042 600 MHz ^{1}H NMR spectrum of [Pt(th(tbppy)py)Cl] in CD_2Cl_2.

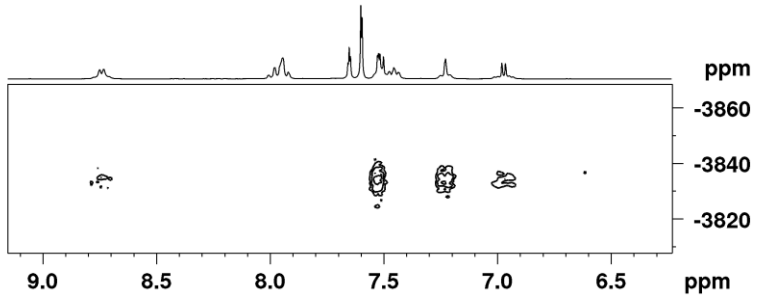


Fig. S043 300 MHz ^{1}H/^{195}Pt HMBC NMR spectrum of [Pt(th(tbppy)py)Cl] in CD_2Cl_2.

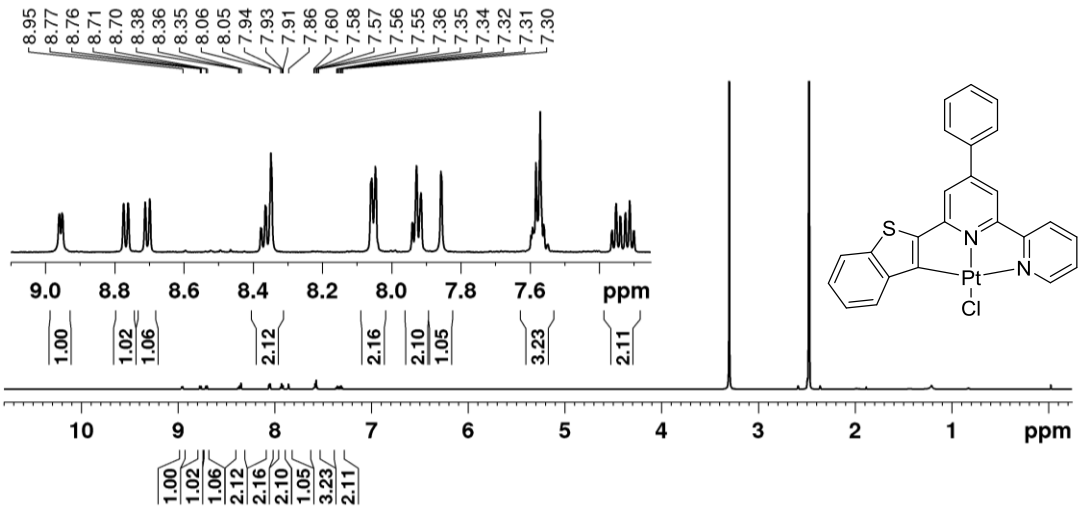


Fig. S044 600 MHz ^{1}H NMR spectrum of [Pt(bth(ppy)py)Cl] in DMSO-*d*$_6$.

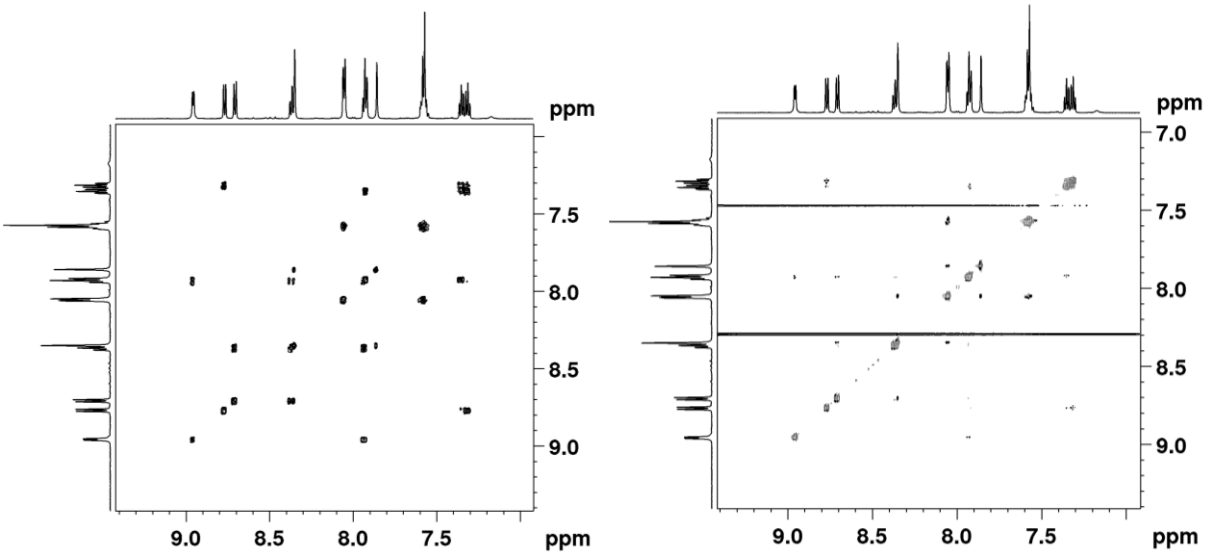


Fig. S045 600 MHz ^{1}H/^{1}H COSY (left) and ^{1}H/^{1}H NOESY (right) NMR spectra of [Pt(bth(ppy)py)Cl] in DMSO-*d*$_6$.

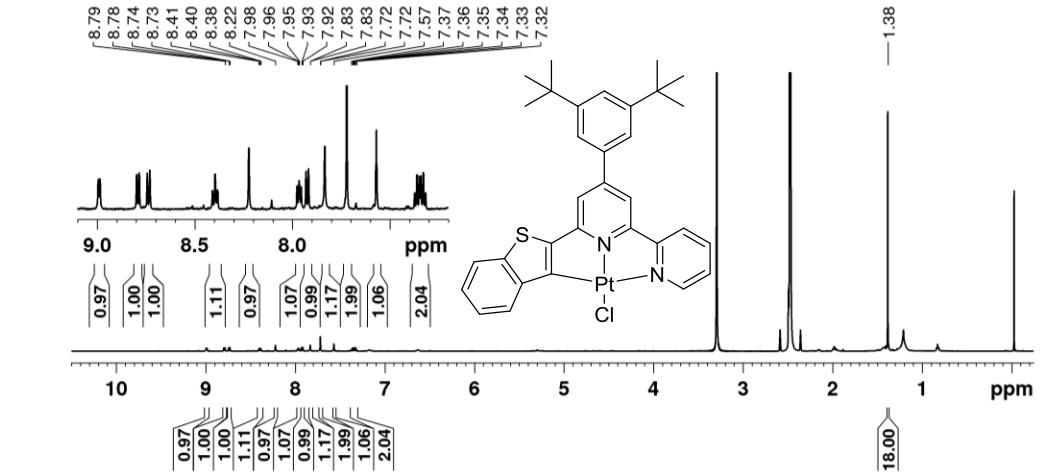


Fig. S046 600 MHz ^{1}H NMR spectrum of [Pt(bth(tbppy)py)Cl] in DMSO-*d*$_6$.

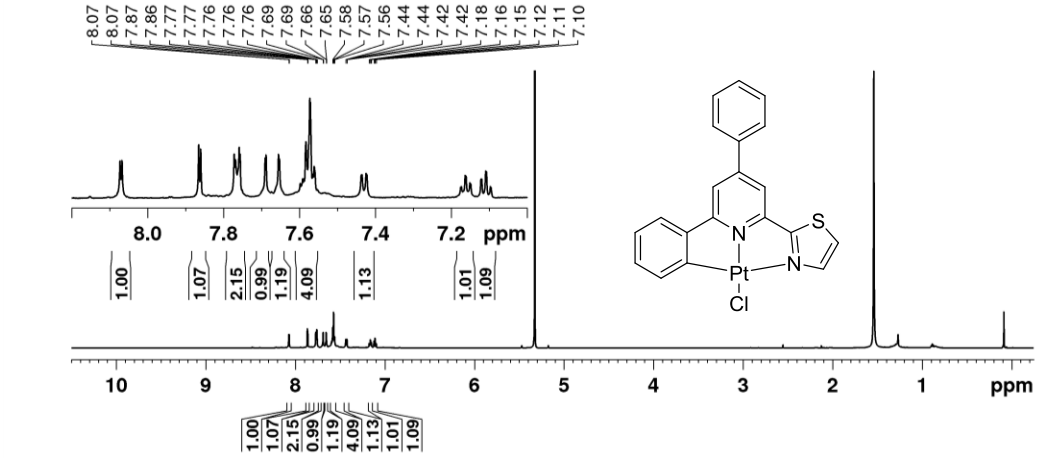


Fig. S047 600 MHz ^{1}H NMR spectrum of [Pt(ph(ppy)py)Cl] in CD_2Cl_2.

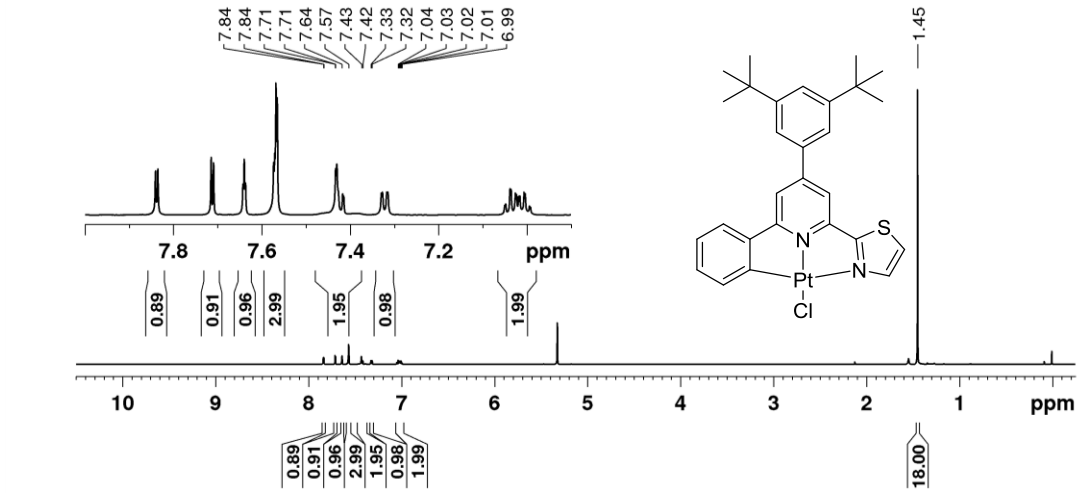


Fig. S048 600 MHz ^{1}H NMR spectrum of [Pt(ph(tbppy)tz)Cl] in CD_2Cl_2.

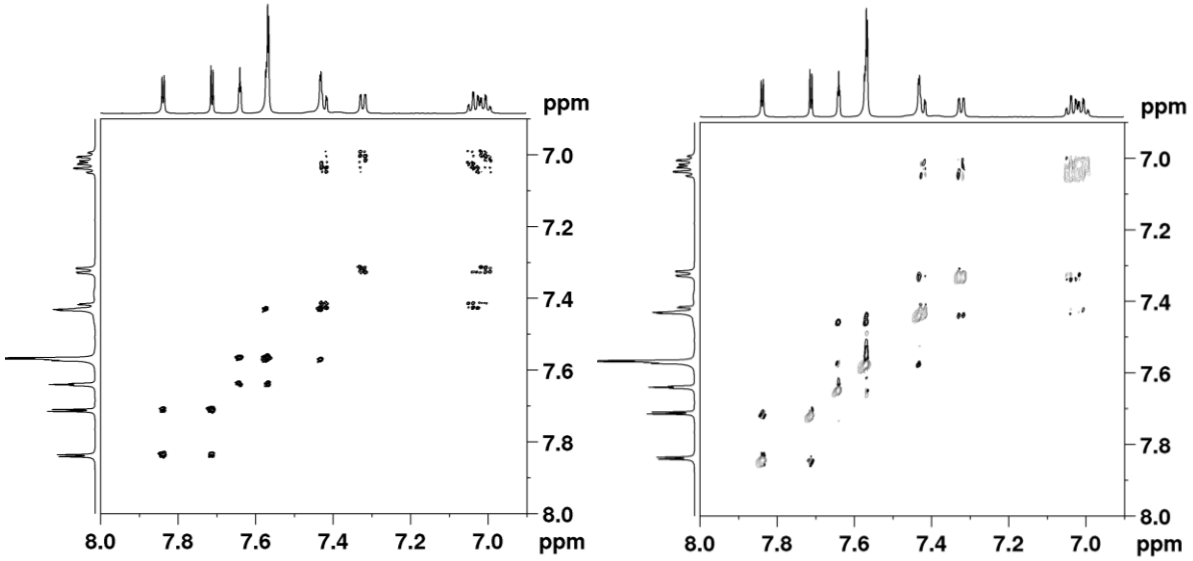


Fig. S049 600 MHz ^{1}H/^{1}H COSY (left) and ^{1}H/^{1}H NOESY (right) NMR spectra of [Pt(ph(tbppy)tz)Cl] in CD_2Cl_2.

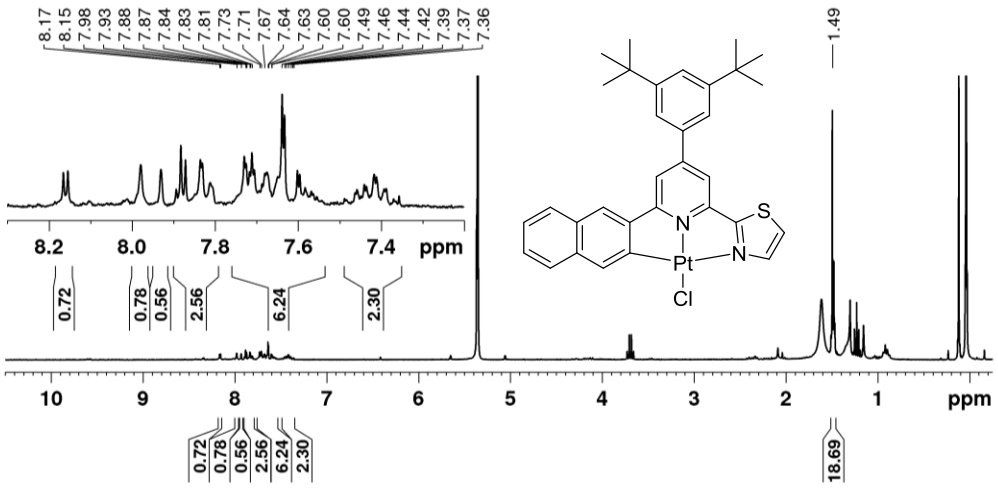


Fig. S050 300 MHz ^{1}H NMR spectrum of [Pt(na(tbppy)tz)Cl] in CD_2Cl_2.

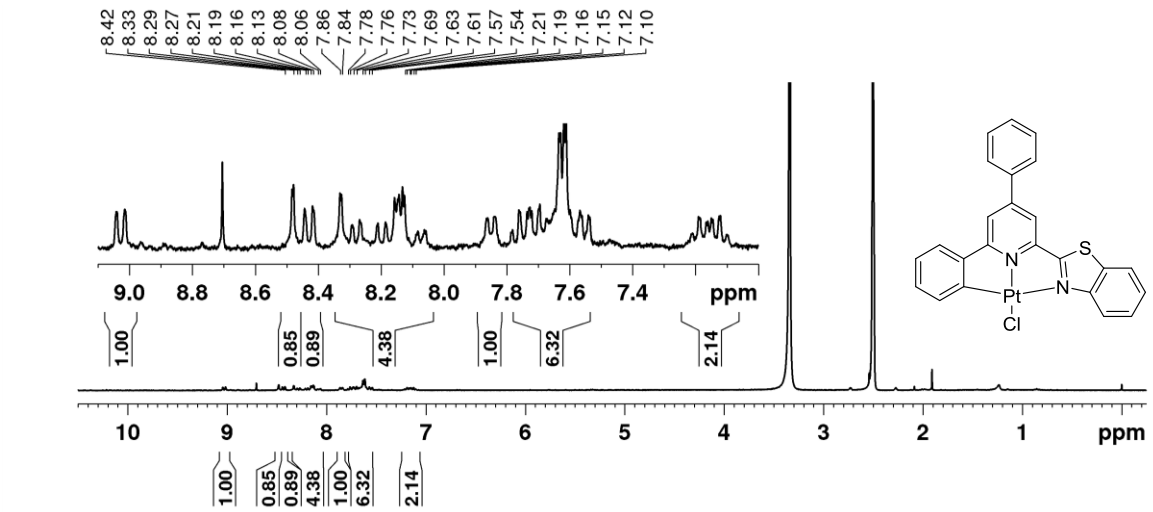


Fig. S051 300 MHz ^{1}H NMR spectrum of [Pt(ph(ppy)btz)Cl] in CD_2Cl_2.

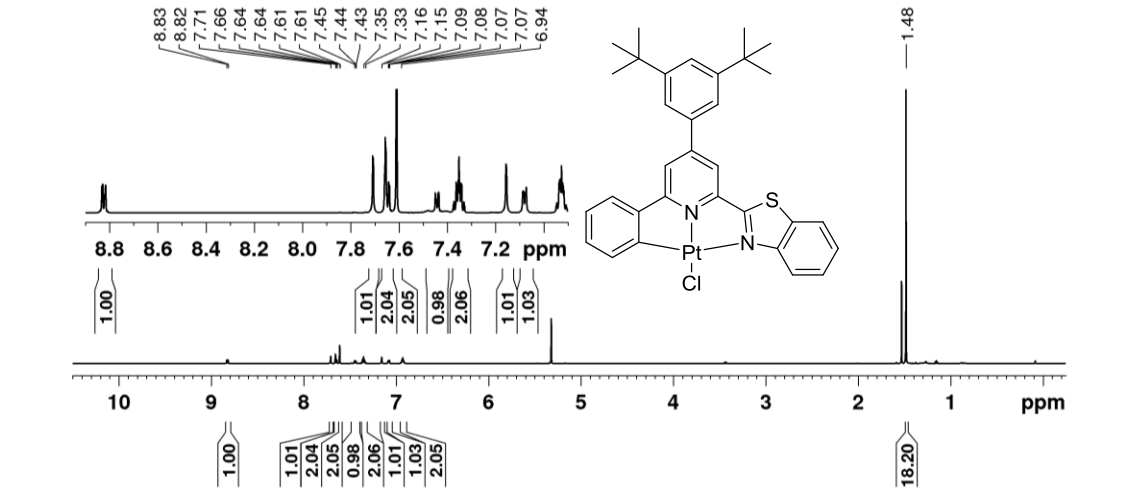


Fig. S052 600 MHz ^{1}H NMR spectrum of [Pt(ph(tbppy)btz)Cl] in CD_2Cl_2.

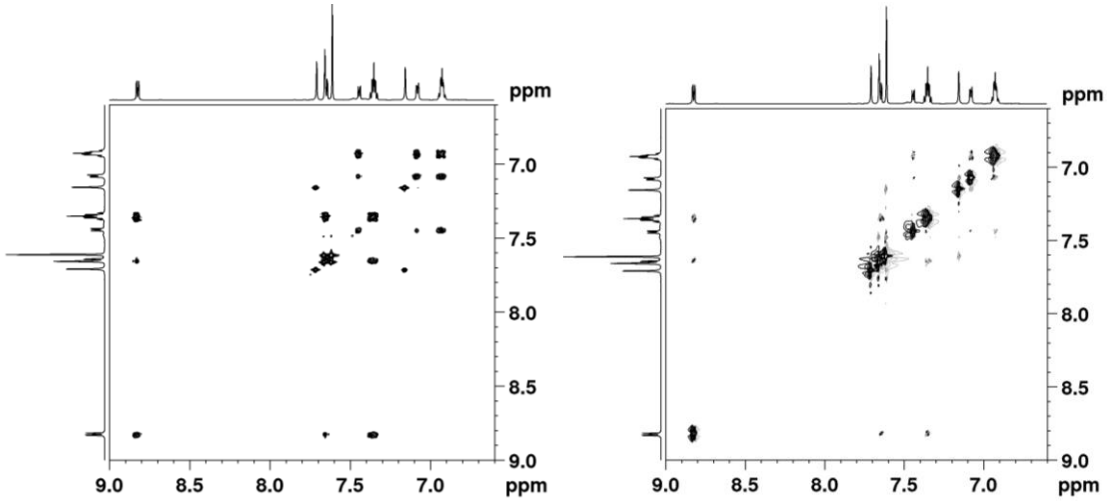


Fig. S053 600 MHz ^{1}H/^{1}H COSY (left) and ^{1}H/^{1}H NOESY (right) NMR spectra of [Pt(ph(tbppy)btz)Cl] in CD_2Cl_2.

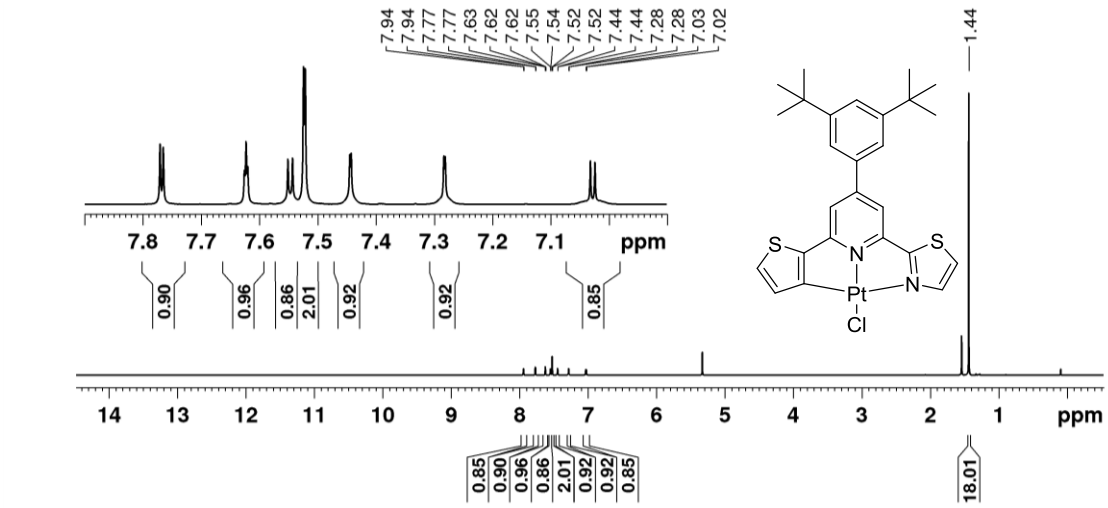


Fig. S054 300 MHz ^{1}H NMR spectrum of [Pt(th(tbppy)tz)Cl] in CD_2Cl_2.

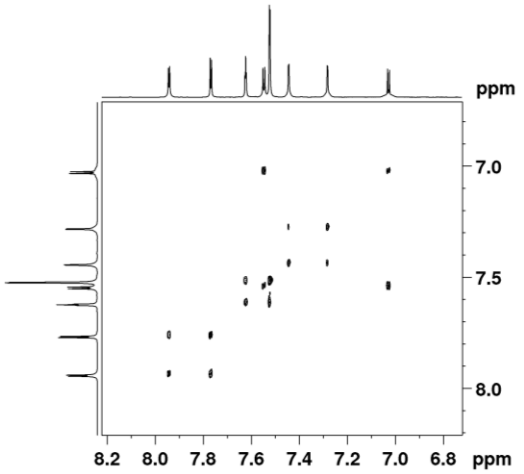


Fig. S055 600 MHz ^{1}H/^{1}H COSY NMR spectrum of [Pt(th(tbppy)tz)Cl] in CD_2Cl_2.

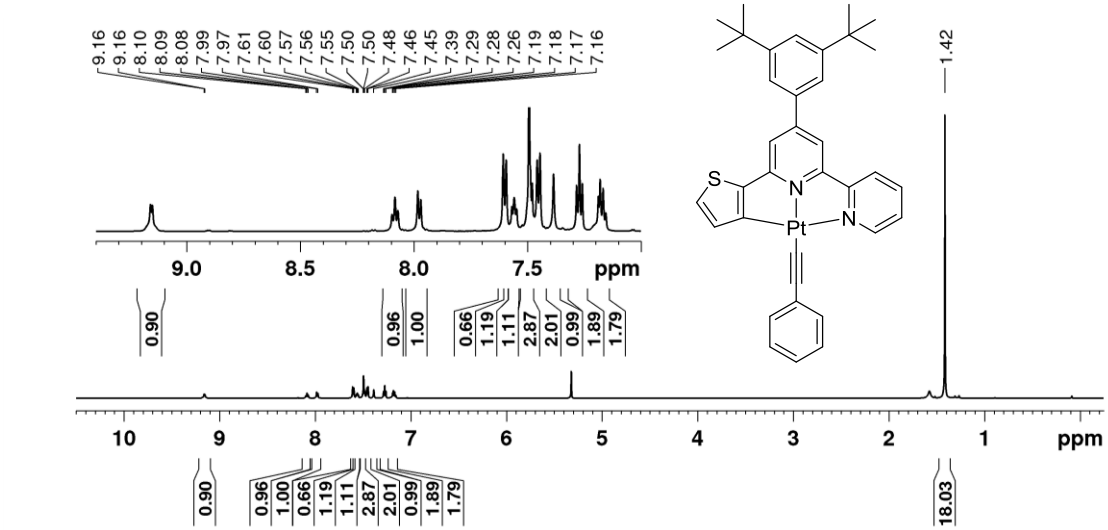


Fig. S056 600 MHz ^{1}H NMR spectrum of [Pt(th(tbppy)py)(C≡CPh)] in CD_2Cl_2.

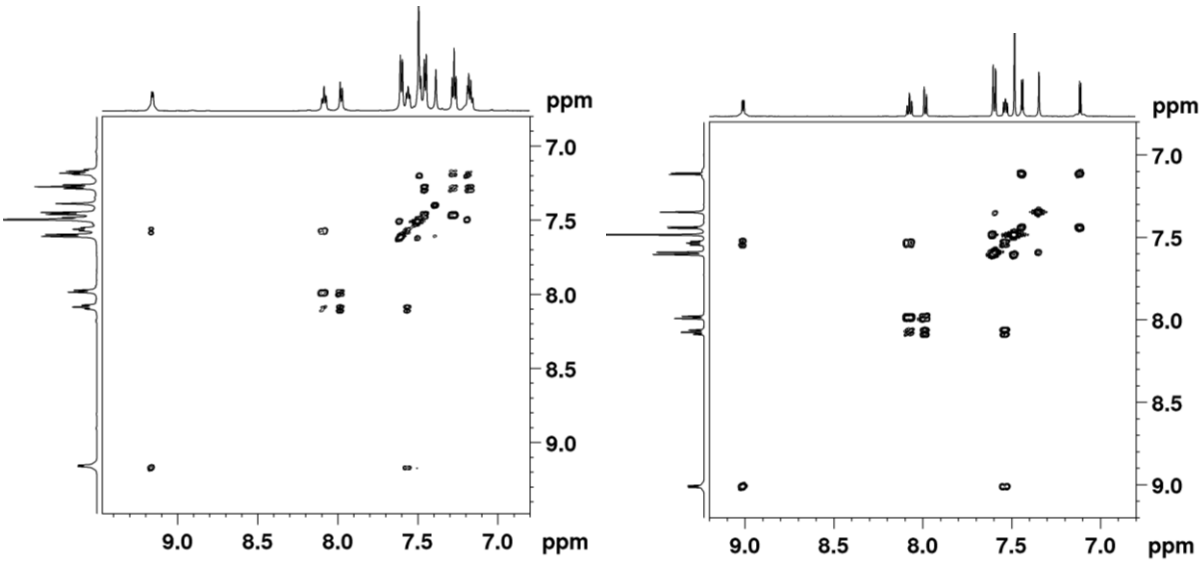


Fig. S057 600 MHz $^{1}H/^{1}H$ COSY NMR spectra of [Pt(th(tbppy)py)(C≡CPh)] (left) and [Pt(th(tbppy)py)(C≡CC_6F_5)] (right) in CD_2Cl_2.

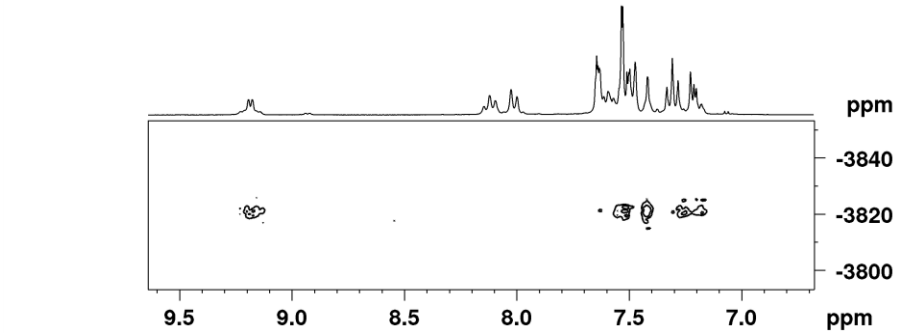


Fig. S058 300 MHz $^{1}H/^{195}Pt$ HMBC NMR spectrum of [Pt(th(tbppy)py)(C≡CPh)] in CD_2Cl_2.

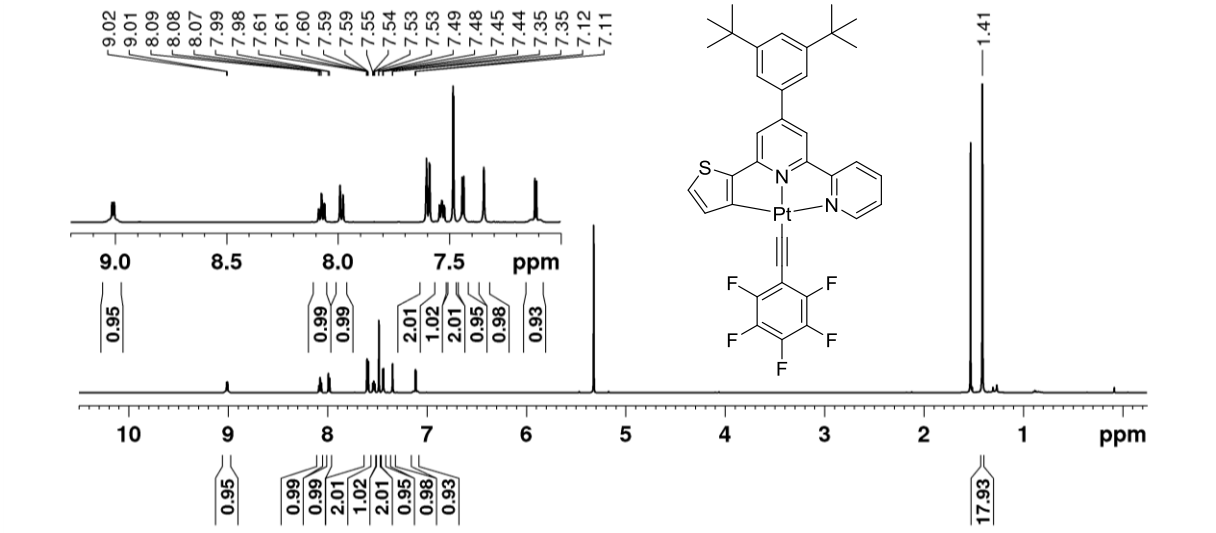


Fig. S059 600 MHz ^{1}H NMR spectrum of [Pt(th(tbppy)py)(C≡CC_6F_5)] in CD_2Cl_2.

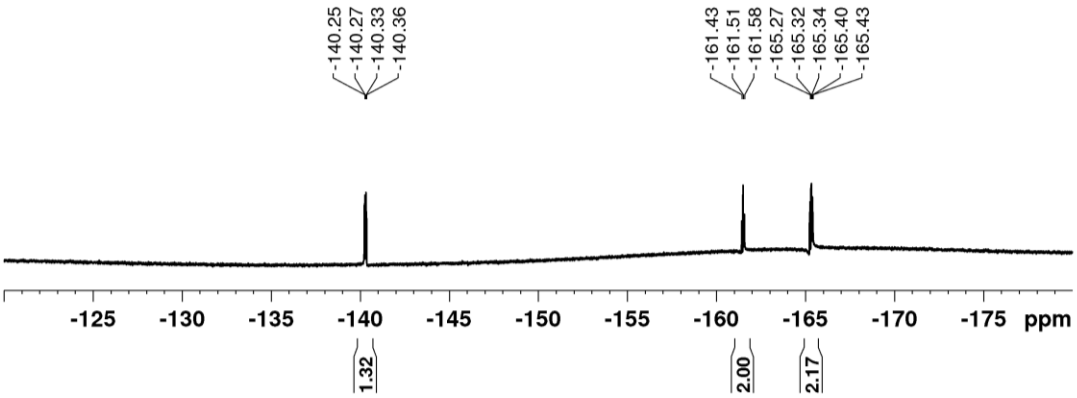


Fig. S060 282 MHz ^{19}F NMR spectrum of [Pt(th(tbppy)py)(C≡CC_6F_5)] in CD_2Cl_2.

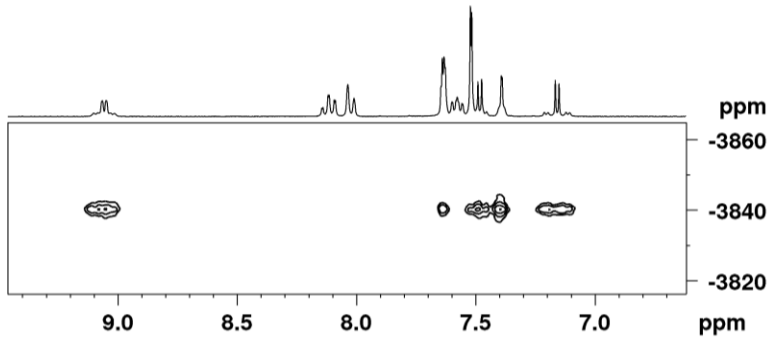


Fig. S061 300 MHz ^{1}H/^{195}Pt HMBC NMR spectrum of [Pt(th(tbppy)py)(C≡CC_6F_5)] in CD_2Cl_2.

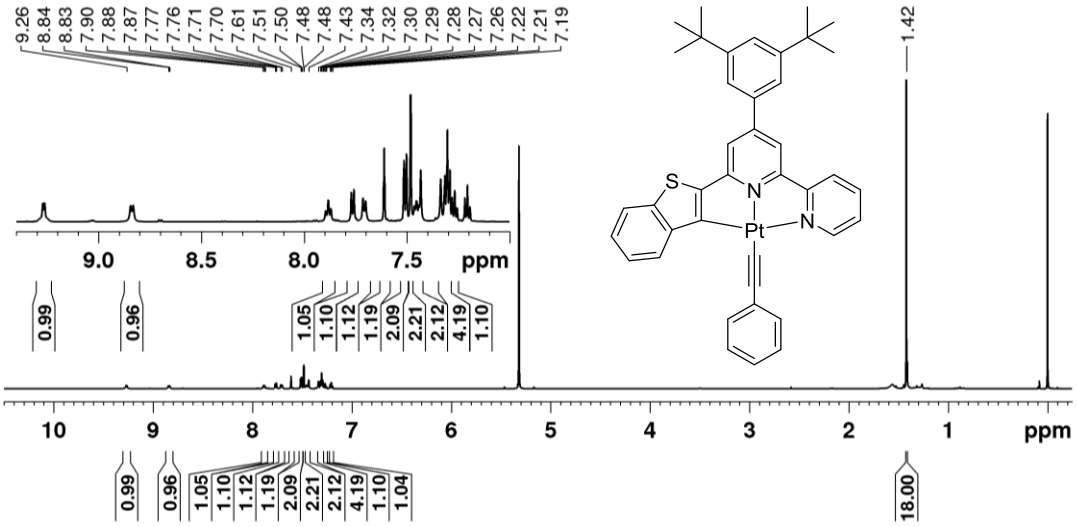


Fig. S062 600 MHz ^{1}H NMR spectrum of [Pt(bth(tbppy)py)(C≡CPh)] in CD_2Cl_2.

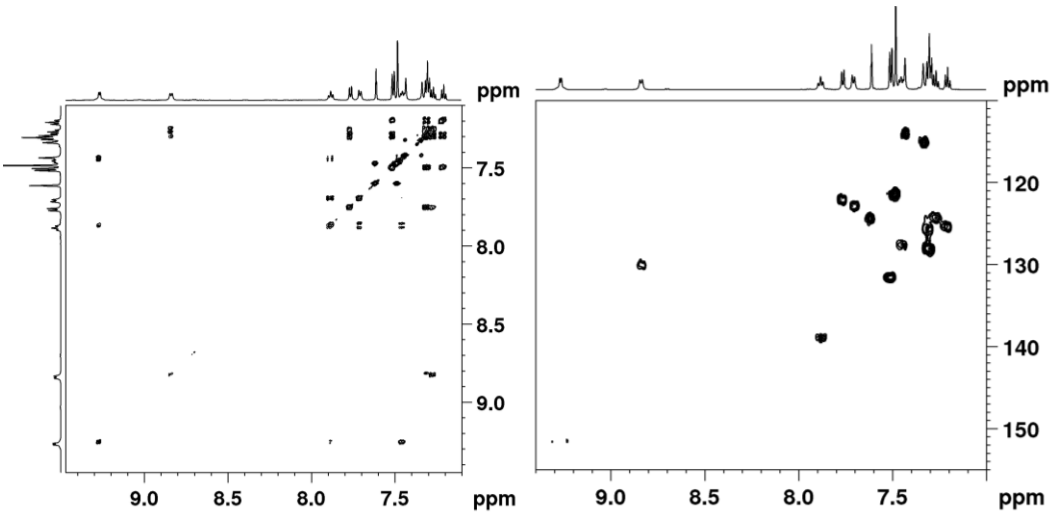


Fig. S063 600 MHz ^{1}H/^{1}H COSY NMR spectrum (left) and part of the 600 MHz ^{1}H/^{13}C HMQC NMR spectrum (right) of [Pt(bth(tbppy)py)(C≡CPh)] in CD_2Cl_2.

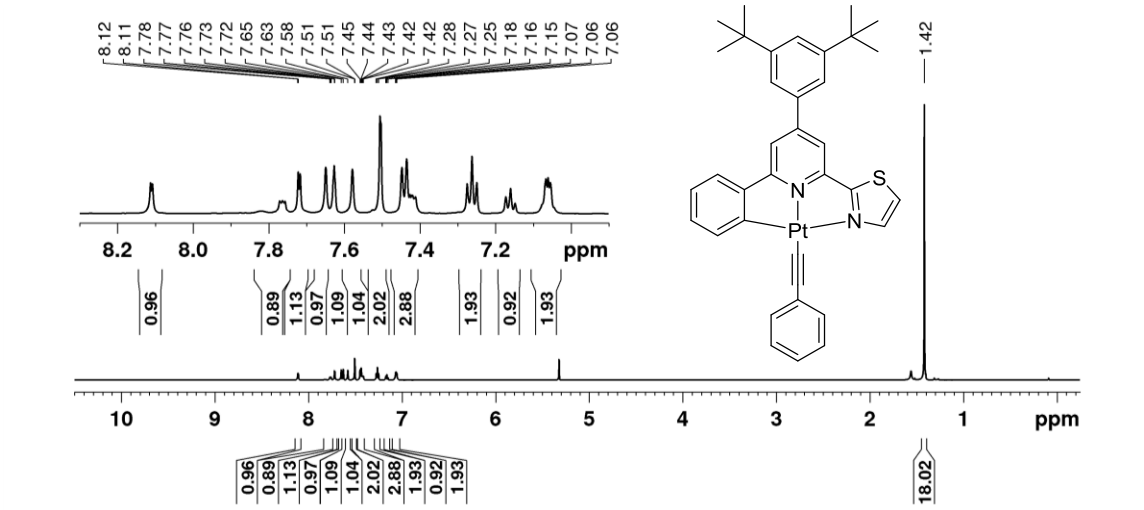


Fig. S064 600 MHz ^{1}H NMR spectrum of [Pt(ph(tbppy)tz)(C≡CPh)] in CD_2Cl_2.

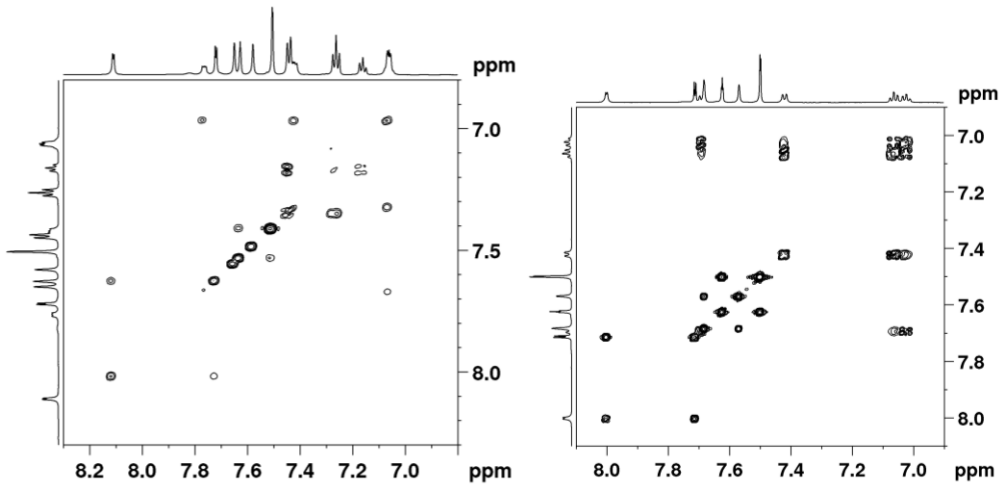


Fig. S065 600 MHz ^{1}H/^{1}H COSY NMR spectrum of [Pt(ph(tbppy)tz)(C≡CPh)] (left) and 600 MHz ^{1}H/^{1}H COSY NMR spectrum of [Pt(ph(tbppy)tz)(C≡CC_6F_5)] (right) in CD_2Cl_2.

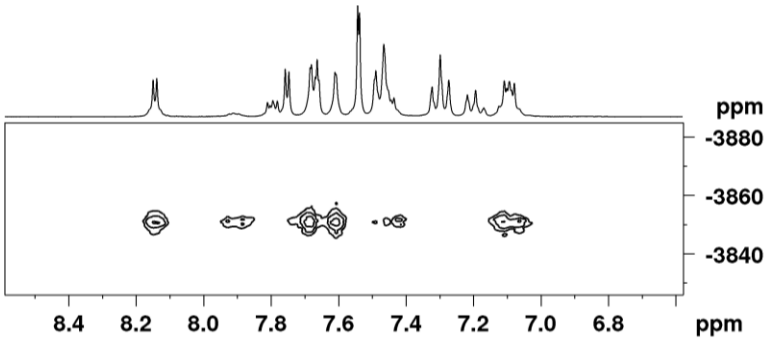


Fig. S066 300 MHz $^{1}H/^{195}Pt$ HMBC NMR spectrum of [Pt(ph(tbppy)tz)(C≡CPh)] in CD_2Cl_2.

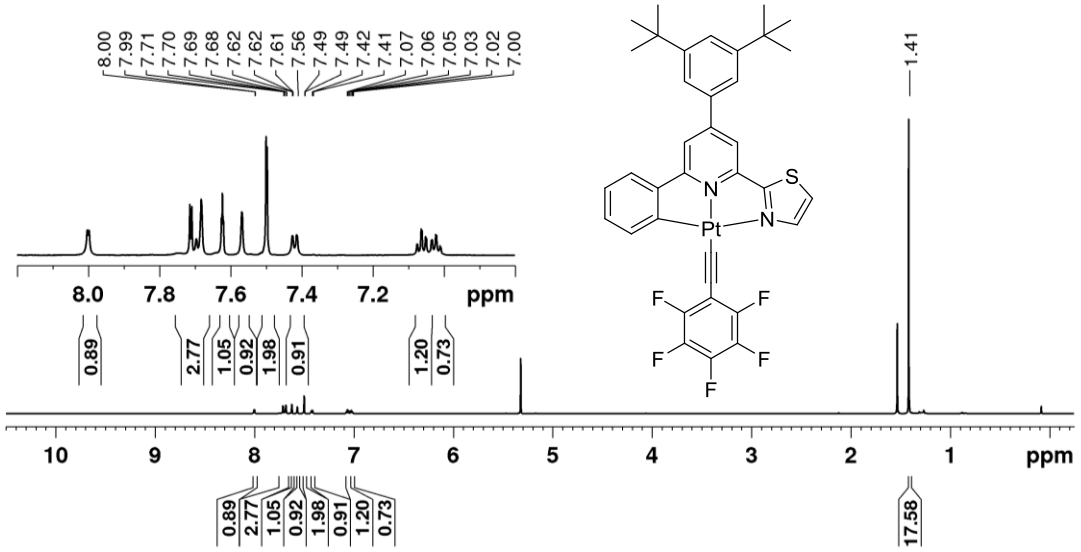


Fig. S067 600 MHz ^{1}H NMR spectrum of [Pt(ph(tbppy)tz)(C≡CC_6F_5)] in CD_2Cl_2.

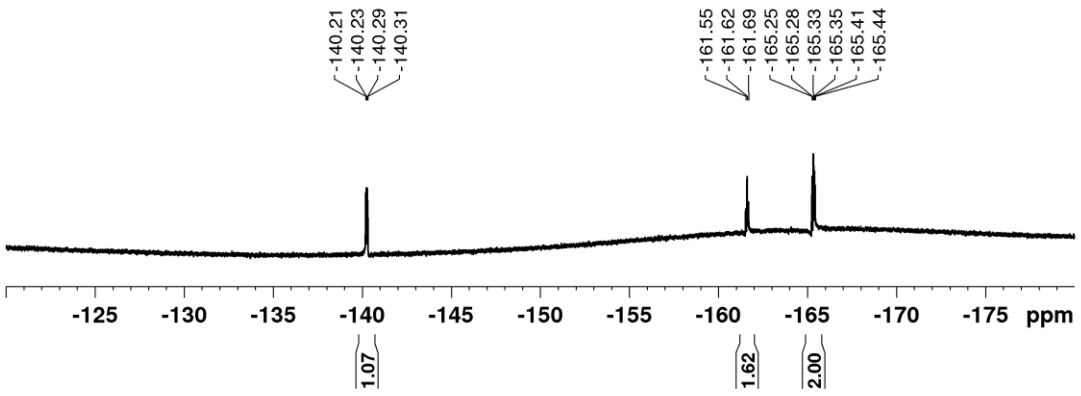


Fig. S068 282 MHz ^{19}F NMR spectrum of [Pt(ph(tbppy)tz)(C≡CC_6F_5)] in CD_2Cl_2.

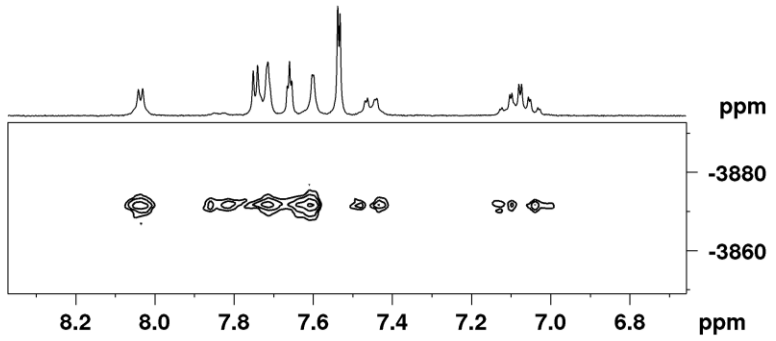


Fig. S069 300 MHz $^{1}H/^{195}Pt$ HMBC NMR spectrum of [Pt(ph(tbppy)tz)(C≡CC_6F_5)] in CD_2Cl_2.

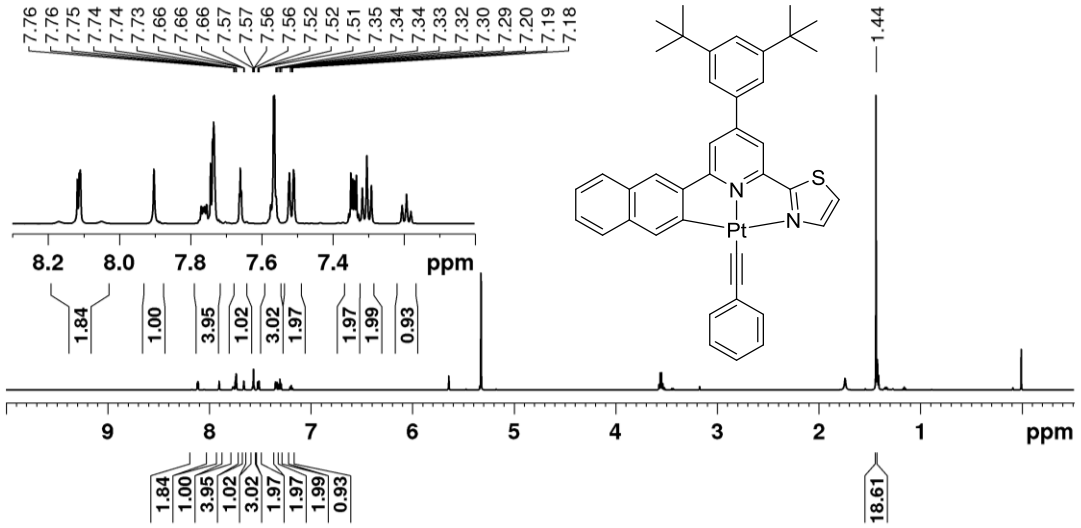


Fig. S070 600 MHz ^{1}H NMR spectrum of [Pt(na(tbppy)tz)(C≡CPh)] in CD_2Cl_2.

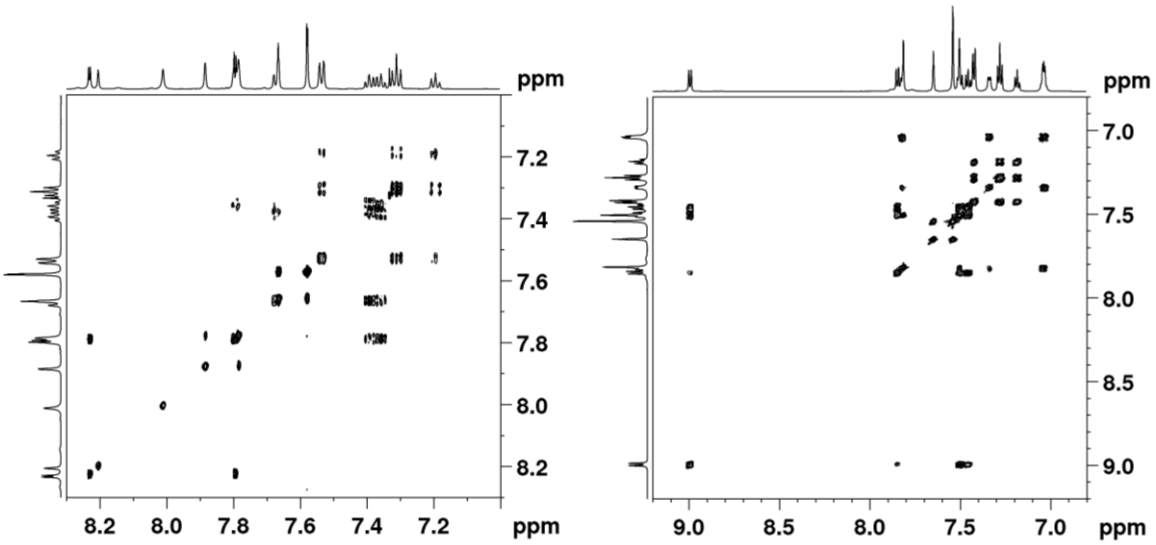


Fig. S071 600 MHz $^{1}H/^{1}H$ COSY NMR spectrum of [Pt(na(tbppy)tz)(C≡CPh)] (left) and 600 MHz $^{1}H/^{1}H$ COSY NMR spectrum of [Pt(ph(tbppy)btz)(C≡CPh)] (right) in CD_2Cl_2.

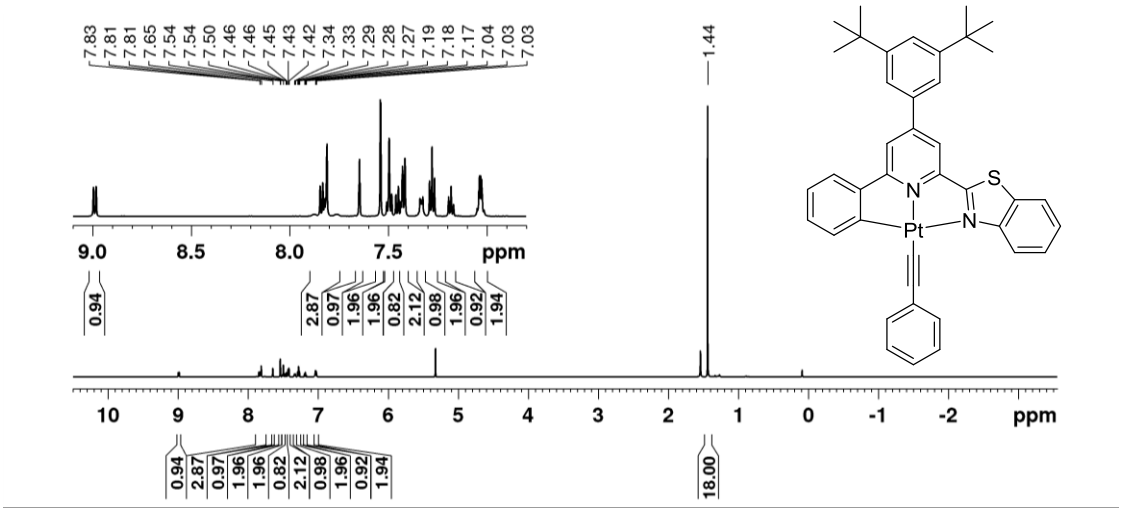


Fig. S072 600 MHz ^{1}H NMR spectrum of [Pt(ph(tbppy)btz)(C≡CPh)] in CD_2Cl_2.

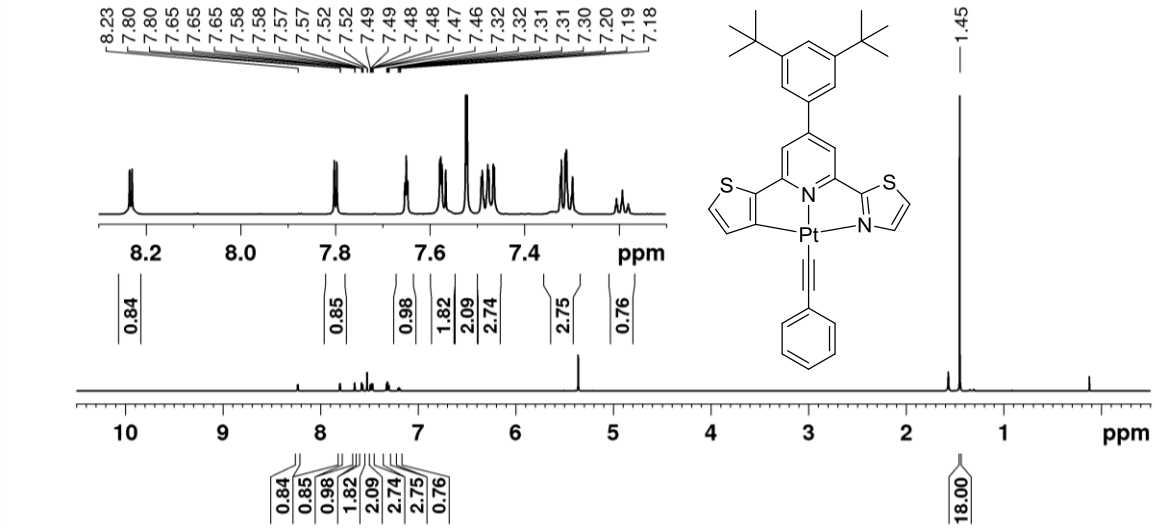


Fig. S073 600 MHz ^{1}H NMR spectrum of [Pt(th(tbppy)tz)(C≡CPh)] in CD_2Cl_2.

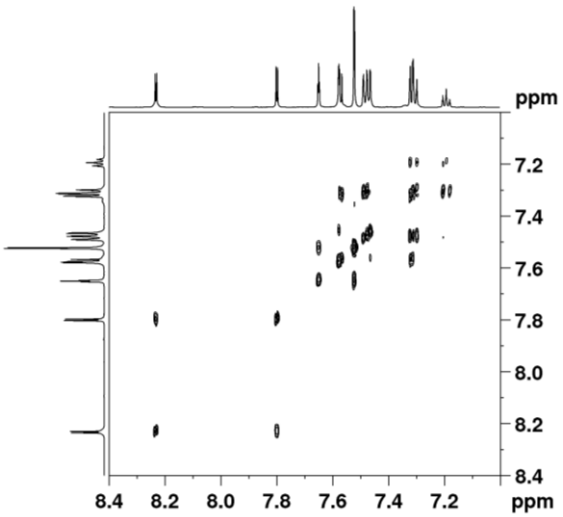


Fig. S074 600 MHz ^{1}H/^{1}H COSY NMR spectrum of [Pt(th(tbppy)tz)(C≡CPh)] in CD_2Cl_2.