Supporting Information

For

A Simple Synthetic Entryway into Palladium Cross Coupling Catalysis

Caroline M. Zinser,[a] Fady Nahra,[a],[b] Marcel Brill,[a] Rebecca E. Meadows,[c] David B. Cordes,[a] Alexandra M. Z. Slawin,[a] Steven P. Nolan[b],[d]* and Catherine S. J. Cazin [a],[b]*

[a] C. M. Zinser, Dr. F. Nahra, Dr. M. Brill, Dr. D. B. Cordes, Prof. A. M. Z. Slawin, Dr. C. S. J. Cazin
School of Chemistry
University of St Andrews
St Andrews, KY16 9ST, UK

[b] Dr. F. Nahra, Dr. C. S. J. Cazin, Prof. Dr. S. P. Nolan
Department of Physical and Inorganic Chemistry
Ghent University, Krijgslaan 281, S-3, B-9000 Ghent, Belgium. E-mail: steven.nolan@ugent.be; catherine.cazin@ugent.be

[c] Dr. Rebecca E. Meadows, AstraZeneca, Chemical Development, Pharmaceutical Technology and Development, Etherow T46/10, Silk Road Business Park, Charter Way, Maccelsfield, Cheshire, SK10 2NA, UK, rebecca.meadows@astrazeneca.com

[d] Prof. Dr. S. P. Nolan
Chemistry Department, College of Science
King Saud University
PO Box 2455, Riyadh, 11451, Saudi Arabia

Table of Contents

General information: S3

Synthesis and optimisation of [Pd(IPr)(η^3-cin)Cl] S3

Synthesis and optimisation of [Pd(IPr)(η^3-allyl)Cl] S4

Synthesis and optimisation of [Pd(IPr*)(η^3-cin)Cl] S5

Synthesis of [Pd(SIPr)(η^3-cin)Cl] S7

Synthesis of [Pd(SIMes)(η^3-cin)Cl] S7

Synthesis of [Pd(IPr*$^{2\text{-Np}}$)(η^3-cin)Cl] S7

Synthesis of [Pd(IPent)(η^3-cin)Cl] S8

Synthesis of [Pd(IHept)(η^3-cin)Cl] S8

Synthesis of [Pd(IPr*$^{\text{OMe}}$)(η^3-cin)Cl] S9

Table for large scale synthesis of [Pd(NHC)(η^3-R-allyl)Cl] pre-catalysts S9

Synthesis and analysis of the palladate intermediates S9

Synthesis of [IPrH][Pd(η^3-cin)Cl_2] (**7a**) S10

Synthesis of [IPrH][Pd(η^3-allyl)Cl_2] (**7b**) S10

Synthesis of [IPr*H][Pd(η^3-cin)Cl_2] (**7c**) S10

Synthesis of [SIPrH][Pd(η^3-cin)Cl_2] (**7d**) S11

The Suzuki-Miyaura coupling S12

Method A S12

Method B S12

Methods C1, C3 ..... S12

Method C2 ..... S12

Preliminary scope S13

The Mizoroki-Heck reaction S15

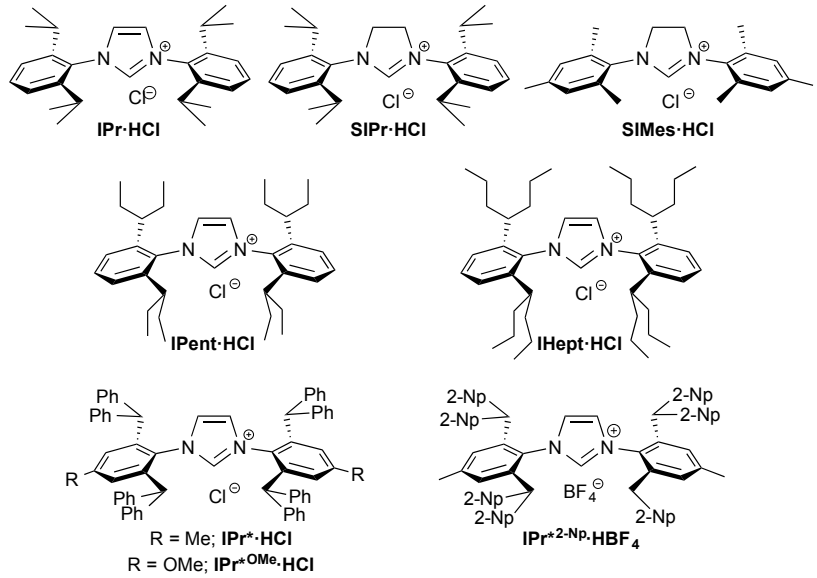
NMR spectra S17

References S39

General information

All complex syntheses were performed in air. Solvents and all other reagents were purchased and used as received without further purification unless otherwise stated. ^{1}H and ^{13}C $\{^{1}H\}$ Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Advance 400 Ultrashield spectrometer at 298K. Chemical shifts (expressed by parts per million) are referenced to residual solvent peaks. Elemental analyses were performed by London Metropolitan University, Service 166-220 Holloway Road, London, N7 8DB.

Structures of NHC•HCl used in this study



Synthesis and optimisation of [Pd(IPr)(η^3-cin)Cl]

Small scale:

IPr•HCl (50.0 mg, 0.117 mmol), [Pd(η^3-cin)(μ-Cl)]$_2$ (25.3 mg, 0.048 mmol), a magnetic stir bar and acetone (0.5 mL) were charged into a vial or round-bottomed flask, followed by K_2CO_3 (13.5 mg, 0.097 mmol). The mixture was stirred at 60 °C for 5 h. After the reaction was complete, the solvent was removed under vacuum. The residue was re-dissolved in dichloromethane (1-2 mL) and filtered through a pad of silica. The silica was washed with DCM (20 mL). The resulting solution was concentrated and dried under vacuum until a powder was obtained. In some cases, washing with pentane (5 mL) was necessary in order to remove the residual DCM. The product was obtained as a microcrystalline material in 98% (60.9 mg) yield.

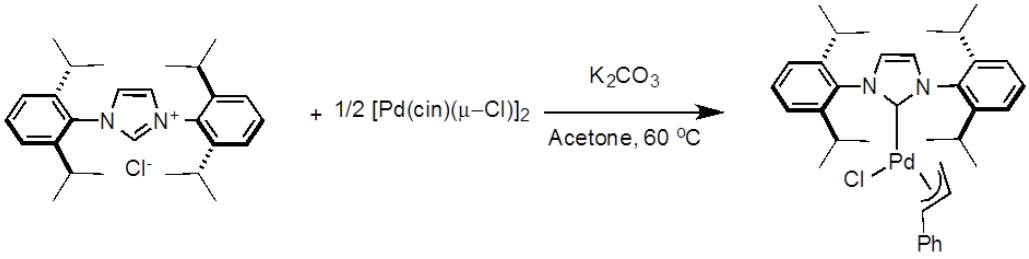
Large scale:

IPr•HCl (4.01 g, 9.44 mmol), [Pd(η^3-cin)(μ-Cl)]$_2$ (2.04 g, 3.93 mmol) and a magnetic stir bar were charged into a scintillation vial or round bottom flask. Acetone (30 mL) was then added, followed by K_2CO_3 (1.08 g, 7.87 mmol) and the reaction mixture was refluxed for 24 h. The same general work up as above afforded the product in 97% (4.94 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.50 (t, *J* = 7.7 Hz, 2H), 7.48-7.28 (d, *J* = 7.7 Hz, 4H), 7.12 (m, 7H), 5.09 (m, 1H), 4.36 (d, *J* = 12.9 Hz, 1H), 3.06 (m, 5H), 1.77 (d, *J* = 11.4 Hz, 1H), 1.43-1.36 (m, 12H), 1.16 (d, *J* = 7.1 Hz, 12H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = δ 184.8, 145.9, 137.7, 135.7, 129.7 128.0, 127.9, 127.1, 126.5, 124.0, 123.6, 108.6, 90.0, 46.1, 28.4, 26.0, 22.8.
Elemental Analysis: Expected: C 66.66, H 7.15, N 4.32. Found: C 66.73, H 7.27, N 4.38.
Analytical data obtained are in agreement with the reported values.[1]

Table S-1: Optimisation of the synthesis of [Pd(IPr)(η^3-cin)Cl]



Entry	IPr·HCl (equiv.)	K_2CO_3 (equiv.)	t (h)	Yield (%)[a]
1	1	2	3	94*
2	1.1	2	3	100*
3	1.2	1.1	5	98*
4	1.3	1.1	5	100*
5	1.5	1.1	5	100*
6	1.2	0.9	5	99*
7	**1.2**	**1**	**5**	**98**
8	1.2	1.3	5	100*
9	1.2	1.5	5	96*
10	1.2	0.6	5	65*
11	1.2	0.4	5	69*
12	1.2	0.2	5	52*
13	1.2	1	5	94*[b]
14	1.2	1	5	99*[c]
15	1.2	1	6	99[d]

*^{1}H NMR shows impurities in the spectra. [a]Isolated yield. All reactions were carried out in air using technical grade acetone (0.235 M in respect to IPr·HCl). [b]Concentration = 0.117 M. [c]Concentration = 0.058M. [d]IPr·HCl and [Pd((η^3-cin)(μ-Cl)]$_2$ were stirred in acetone for 1 h at 60 °C, then K_2CO_3 was added and the mixture was left to stir for 5h at 60 °C.

Synthesis and optimisation of [Pd(IPr)(η^3-allyl)Cl]

Small scale: IPr•HCl (50.0 mg, 0.117 mmol), [Pd(η^3-allyl)(μ-Cl)]$_2$ (17.8 mg, 0.048 mmol), a magnetic stir bar and acetone (0.5 mL) were charged into a vial or round bottom flask followed by K_2CO_3 (13.5 mg, 0.097 mmol). The mixture was stirred at 60 °C for 5 h. After the reaction was complete, the solvent was removed under vacuum. The residue was re-dissolved in dichloromethane (1-2 mL) and filtered through a pad of silica. The silica was washed with DCM (20 mL). The resulting solution was concentrated and dried in vacuum until a powder was obtained. In some cases washing with pentane (5 mL) was necessary in order to remove the residual DCM. The product was obtained as microcrystalline material in 85% (47.6 mg) yield.

Large scale: IPr•HCl (2.70 g, 6.55 mmol), [Pd(η^3-allyl)(μ-Cl)]$_2$ (1 g, 2.73 mmol) and a magnetic stir bar were charged into a scintillation vial or round bottom flask. Acetone (28 mL) was then added followed by K_2CO_3 (755 mg, 5.47 mmol) and the reaction mixture was refluxed for 10 h. The same general work up as above afforded the product in 92% (2.87 g) yield.

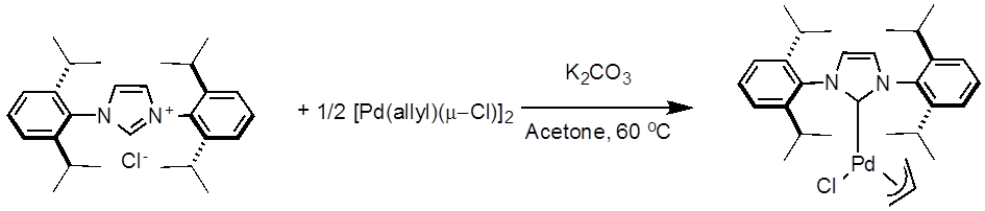
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.42 (t, *J* = 7.3 Hz, 2H), 7.28 (m, 4H), 7.15 (s, 2H), 4.86-4.76 (m, 1H), 3.91 (dd, *J*=5.6 Hz, 1H), 3.16-3.03 (m, 2H), 3.04 (d, *J*=6.3 Hz, 1H), 2.89-2.82 (m, 2H), 2.77 (d, *J*=13.6 Hz, 1H), 1.59 (d, *J*=12.1 Hz, 1H), 1.39 (d, *J*=7.1 Hz, 6H), 1.34 (d, *J*=6.8 Hz, 6H), 1.18 (d, *J*=7.1, 6H), 1.09 (d, *J*=7.1 Hz, 6H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 186.1, 146.2, 146.0, 135.8, 129.9, 124.1, 123.9, 123.8, 114.2, 72.5, 49.5, 28.6, 28.5, 26.5, 25.8, 22.9, 22.8.

Elemental Analysis: Expected: C 62.93, H 7.39, N 4.89. Found: C 63.06, H 7.55, N 5.02.

Analytical data obtained are in agreement with the reported values.[2]

Table S-2: Optimisation of the synthesis of [Pd(IPr)(η^3-allyl)Cl]



Entry	IPr•HCl (equiv.)	[Pd(η^3-allyl)Cl]$_2$ (equiv.)	K_2CO_3 (equiv.)	t (h)	Yield (%)
1	1	0.5	2	5	85*
2	1.1	0.5	2	5	75*
3	1	0.55	1.1	5	60*
4	1	0.6	1.1	5	57*
5	**1.2**	**0.5**	**1**	**5**	**85**

* ^{1}H NMR shows impurities in the spectra. [a]Isolated yield after filtration through silica using DCM. All reactions were carried out in air using technical grade acetone (0.235 M).

Synthesis and optimisation of [Pd(IPr*)(η^3-cin)Cl]

Small scale:

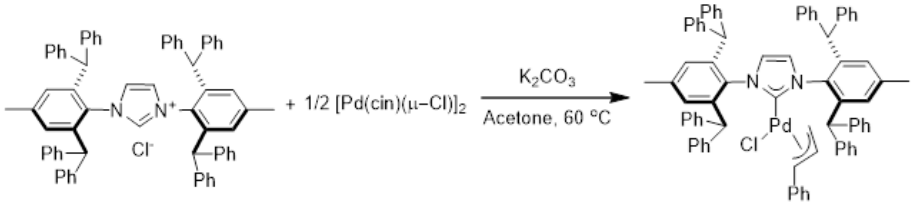
IPr*•HCl (110 mg, 0.116 mmol), [Pd(η^3-cin)(μ-Cl)]$_2$ (30.0 mg, 0.058 mmol), a magnetic stir bar and acetone (0.5 mL) were charged into a vial or round bottom flask , the reaction was stirred at 60 °C for 1 h. Then K_2CO_3 (32.0 mg, 0.232 mmol) was added and the mixture was stirred at 60 °C for 24 h. After the reaction was complete, the solvent was removed under vacuum. The residue was re-dissolved in dichloromethane (1-2 mL) and filtered through a pad of silica. The silica was washed with DCM (20 mL). The resulting solution was concentrated and dried in vacuum, until a powder was obtained. In some cases washing with pentane (5 mL) was necessary in order to remove the residual DCM. The product was obtained as microcrystalline material in a 94% (127 mg) yield.

Large scale:

IPr*•HCl (3.66 g, 3.86 mmol), [Pd(η^3-cin)(μ-Cl])$_2$ (1 g, 1.93 mmol) and a magnetic stir bar were charged into a scintillation vial or round bottom flask. Acetone (13 mL) was then added and the reaction was refluxed for 3 h (65 °C). Then, K_2CO_3 (1.07 g, 7.72 mmol) was added and the reaction mixture refluxed for 30 h. The same general work up as above afforded the product in a 98% (4.23 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.50 (d, *J* = 7.1 Hz, 2H), 7.41 (t, *J* = 7.4, 2H), 7.30-7.19 (m, 21H), 7.10-7.08 (m, 12H), 6.84-6.79 (m, 12H), 6.09 (s, 2H), 5.70 (s, 2H), 5.31 (s, 2H), 5.01-4.96 (m, 1H), 4.64 (d, *J* = 12.8 Hz, 1H), 2.59 (d, *J* = 5.8 Hz, 1H), 2.23 (s, 6H), 1.2-1.3 (m, 1H).
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 182.3, 144.3, 143.4, 141.1, 140.3, 138.1, 137.5, 135.6, 130.3, 130.0, 129.0, 128.9, 128.3, 128.1, 127.9, 127.4, 126.9, 126.1, 123.2, 108.7, 91.0, 53.3, 47.1, 21.7.
Elemental Analysis: Expected: C 79.85, H 5.67, N 2.39. Found: C 79.64, H 5.81, N 2.36.
Analytical data obtained are in agreement with the reported values.[3]

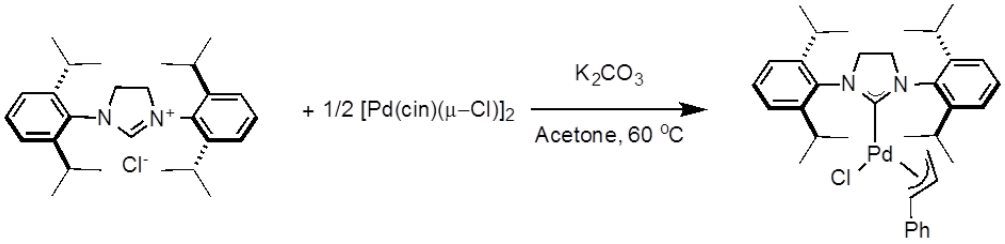
T**able S-3:** Optimisation of the synthesis of [Pd(IPr*)(η^3-cin)Cl]



Entry	IPr*•HCl(equiv.)	K_2CO_3(equiv.)	t (h)	Yield[a] (%)	Acetone (M)
1	2	4	5	80*[b]	0.1158
2	2	4	20	81*	0.1158
3	2	4	5	70*	0.1158
4	2.2	2	5	84*	0.105
5	2	4	5	74*[c]	0.105
6	2	2	5	59*	0.105
7	2	4	5	73*[c]	0.105
8	2	2	5	60*	0.105
9	2	4	5	78*[d]	0.105
10	2	4	20	99[d]	0.105
11	**2**	**4**	**24**	**94[d]**	**0.2316**
12	2	3	20	73*	0.2316
13	2	4	24	93[e]	0.105
14	2	4	24	98*	0.0579

* ^{1}H NMR shows impurities in the spectra. [a]Isolated yield after filtration through silica using DCM. All reactions were carried out in air using technical grade acetone. [b]Clean NMR spectrum obtained but difficulties in reproducing it. [c]IPr*·HCl and [Pd(η^3-cin)(μ-Cl)]$_2$ in acetone were stirred at 60 °C for 7 min, then K_2CO_3 was added and left to stir and heat for 5 h. [d]IPr*·HCl and [Pd(η^3-cin)(μ-Cl)]$_2$ in acetone were stirred at 60 °C for 1 h, then K_2CO_3 was added and the mixture was stirred at 60 °C for the indicated time. [e]IPr*·HCl and [Pd(η^3-cin)(μ-Cl)]$_2$ in acetone were stirred at 60 °C for 3 h, then K_2CO_3 was added and the mixture was stirred at 60 °C for 24 h.

Synthesis of [Pd(SIPr)(η^3-cin)Cl]



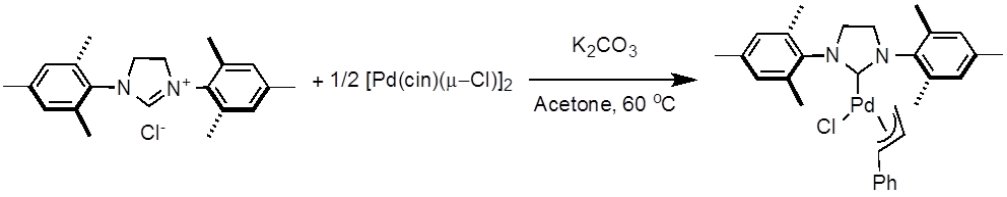
SIPr•HCl (110 mg, 0.234 mmol), [Pd(η^3-cin)(μ-Cl)]$_2$ (49.7 mg, 0.096 mmol) and a magnetic stir bar were charged into a vial or round bottom flask. Acetone (1 mL) was then added, followed by K_2CO_3 (26.9 mg, 0.192 mmol) and the mixture was left to stir for 5 h at 60 °C. The same general work up as above afforded the desired complex as microcrystalline material in 78% (122 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.38-7.35 (m, 2H), 7.26 (d, *J* = 7.5 Hz, 4H), 7.14-7.13 (m, 5H), 5.09-5.01 (m, 1H), 4.33 (d, *J* = 13.3 Hz, 1H), 4.02 (s, 4H), 3.44 (br s, 4H), 2.86 (br s, 1H), 1.54 (br s, 1H), 1.43 (m, 12H), 1.27 (d, *J* = 6.3 Hz, 12H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 212.1, 147.2, 137.7, 136.4, 129.1, 128.3, 127.4, 126.8, 124.3, 109.2, 91.7, 54.1, 46.0, 28.6, 26.7, 23.9.

Elemental analysis: Expected: C 66.56, H 7.29, N 4.31. Found: C 66.62, H 7.36, N 4.27. Analytical data obtained are in agreement with the reported values.[1]

Synthesis of [Pd(SIMes)(η^3-cin)Cl]



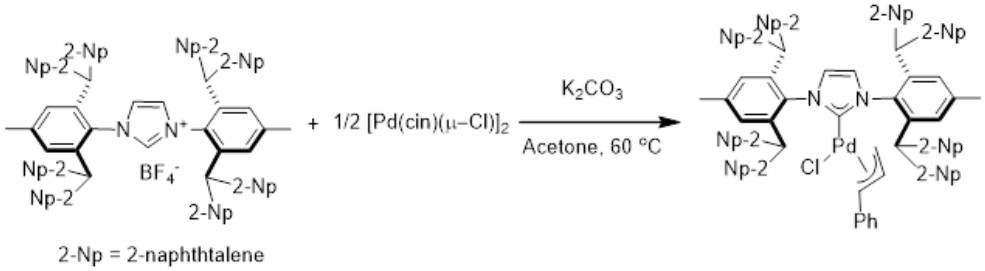
SIMes•HCl (100 mg, 0.292 mmol), [Pd(η^3-cin)(μ-Cl)]$_2$ (62.9 mg, 0.122 mmol), a magnetic stir bar and acetone (1.2 mL) were charged into a vial or round bottom flask , followed by K_2CO_3 (33.5 mg, 0.243 mmol). The mixture was stirred at 60 °C for 5 h. The general work up procedure was then followed, affording the product as microcrystalline material in 80% (135 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.12 (m, CH_{Ar}, 3H), 7.06 (m, CH_{Ar}, 2H), 6.96 (s, 2H), 6.93 (s, 2H), 5.12-5.04 (m, CH_{cin}, 1H), 4.27 (d, CH_{cin}, *J* = 12.9 Hz, 1H), 3.99 (m, $CH_{2imid,}$ 4H), 3.27 (d, CH_{cin}, *J* = 6.9 Hz, 1H), 2.44 (s, CH_3, 6H), 2.41 (s, CH_3, 6H), 2.31 (s, CH_3, 6H), 1.92 (d, CH_{cin}, *J* = 12 Hz, 1H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = δ 211.2, 138.3, 138.1, 136.6, 136.0, 129.5, 128.3 , 127.4 , 126.7 , 109.7 , 90.3, 51.3, 46.8, 21.2 , 18.7 , 18.6 .

Elemental analysis: Expected: C 63.72, H 6.24, N 4.95. Found: C 63.84, H 6.35, N 4.96.

Synthesis of [Pd(IPr*$^{2\text{-Np}}$)(η^3-cin)Cl]

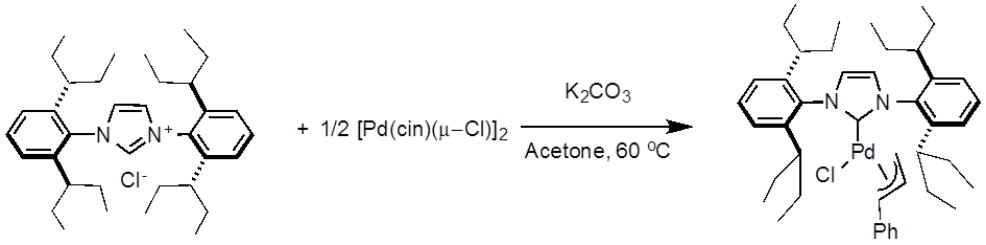


2-Np = 2-naphthtalene

IPr*$^{2\text{-Np}}$•BF_4 (171.2 mg, 0.115 mmol), [Pd(η^3-cin)(μ-Cl)]$_2$ (30.0 mg, 0.058 mmol), a magnetic stir bar and acetone (1.1 mL) were charged into a vial or round bottom flask. The reaction was stirred at 60 °C for 1 h.

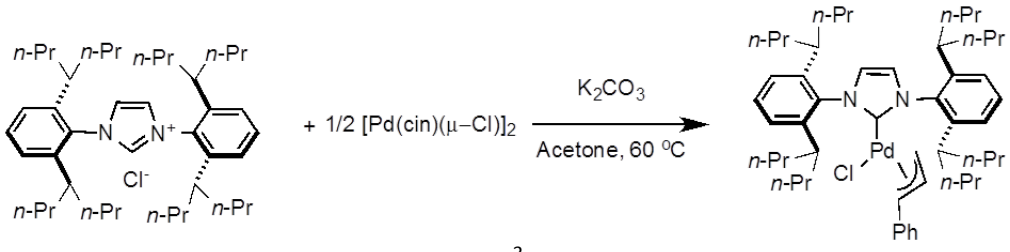
Then K_2CO_3 (32.0 mg, 0.232 mmol) was added and the mixture was stirred at 60 °C for 24 h. The general work up procedure was followed; affording the product as microcrystalline material in 94% (170 mg) yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.96-7.78 (m, 12H), 7.76-7.57 (m, 13H), 7.53-7.35 (m, 20H), 7.35-7.26 (m, 8H), 7.14 (d, *J* = 15.8 Hz, 4H), 6.94 (s, 4H), 6.84 (d, *J* = 8.3 Hz, 2H), 6.71 (d, *J* = 8.3 Hz, 2H), 6.49 (s, 2H), 6.20 (s, 2H), 5.45-5.28 (m, 1H), 5.19 (s, 2H), 5.03 (d, *J* = 13.1 Hz, 1H), 3.14 (d, *J* = 6.5 Hz, 1H), 2.24 (s, 6H), 1.92 (d, *J* = 11.3 Hz, 1H).
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 182.0, 141.4, 141.2, 141.1, 140.6, 140.2, 138.5, 137.5, 135.9, 133.0, 132.9, 132.1, 132.0, 131.8, 130.7, 129.2, 128.9, 128.6, 128.0, 127.9, 127.8, 127.7, 127.6, 127.4, 127.3, 127.2, 127.0 , 125.7, 125.6, 125.5, 123.0, 109.6 , 92.1, 51.5, 47.1, 21.7.
Elemental analysis: Expected: C 84.01, H 5.19, N 1.78. Found: C 83.87, H 5.23, N 1.91. Analytical data obtained are in agreement with the reported values.[4]

Synthesis of [Pd(IPent)(η^3-cin)Cl]



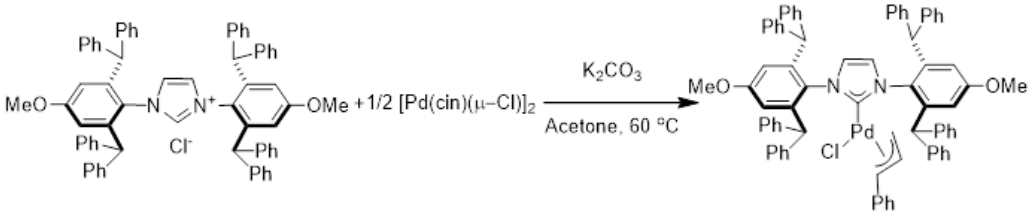
IPent•HCl (100 mg, 0.186 mmol), [Pd(η^3-cin)(μ-Cl)]$_2$ (48.2 mg, 0.093 mmol), a magnetic stir bar and acetone (0.8 mL) were charged into a vial or round bottom flask, the reaction was stirred at 60 °C for 1 h. Then, K_2CO_3 (51.4 mg, 0.372 mmol) was added and the mixture was stirred at 60 °C for 24 h. The general work up procedure was followed, affording the product as microcrystalline material in 85% (123 mg) yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.41-7.37 (m, 2H), 7.18-7.12 (m, 9 H), 7.09 (s, 2H), 5.21-5.13 (m, 1H), 4.40 (d, *J* = 13.4 Hz, 1H), 2.53 (br. m, 4H), 2.11-1.97 (m, 4H), 1.76-1.72 (m, 4H), 1.63-1.60 (m, 4H), 1.52-1.43 (m, 6H), 0.99 (t, *J* = 6.9 Hz, 12H), 0.75 (t, *J* = 7.4 Hz, 12H).
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 181.5, 143.6, 137.5, 128.8, 128.2, 127.2, 126.6, 124.8 , 124.2, 108.2, 91.4, 41.5, 27.9, 27.2, 12.8, 11.2.
Elemental analysis: Expected: C 69.55 H 8.09, N 3.69. Found: C 69.49, H 8.19, N 3.80. Analytical data obtained are in agreement with the reported values.[5]

Synthesis of [Pd(IHept)(η^3-cin)Cl]



IHept•HCl (100 mg, 0.154 mmol), [Pd(η^3-cin)(μ-Cl)]$_2$ (39.8 mg, 0.076 mmol), a magnetic stir bar and acetone (0.7 mL) were charged into a vial or round bottom flask, the reaction was stirred for at 60 °C for 1 h. Then, K_2CO_3 (42.5 mg, 0.308 mmol) was added and the mixture was stirred at 60 °C for 24 h. The general work up procedure was followed, affording the product as microcrystalline material in 81% (109 mg) yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = δ 7.40-7.36 (m, 2H), 7.19-7.13 (m, 9H), 7.06 (s, 2H), 5.18-5.10 (m, 1H), 4.44 (d, *J* = 13.8 Hz, 1H), 2.61 (br. s, 4H), 1.98-1.91 (m, 4H), 1.56-1.26 (m, 22H), 1.15-1.11 (m, 8H), 0.90-0.80 (m, 24H).
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = δ 181.4, 144.2, 137.5, 137.2, 128.9, 128.1, 127.3, 126.5, 124.7, 124.2, 108.1, 91.5, 39.1, 39.0, 37.8, 21.4, 20.3, 14.5.
Elemental analysis: Expected: C 71.62 H 8.90, N 3.21. Found: C 71.5, H 8.75, N 3.30. Analytical data obtained are in agreement with the reported values.[5]

Synthesis of [Pd(IPr*^{OMe})(η^3-cin)Cl]



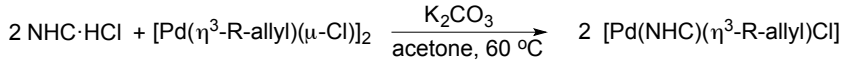
IPr^{*OMe}·HCl (100 mg, 0.103 mmol), [Pd((η^3-cin)(μ-Cl)]$_2$ (26.7 mg, 0.051 mmol), a magnetic stir bar and acetone (0.5 mL) were charged into a vial or round bottom flask and the reaction was stirred at 60 °C for 1 h. Then, K_2CO_3 (28.5 mg, 0.206 mmol) was added and heated at 60 °C for 24 h. The general work up procedure was followed, affording the product as microcrystalline material in 85% (107 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.49 (d, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.1 Hz, 2H), 7.30-7.19 (m, 22H), 7.10-7.09 (m, 11H), 6.85 (d, *J* = 7.2 Hz, 4H), 6.80 (d, *J* = 6.6 Hz, 4H), 6.55 (s, 4H), 6.07 (s, 2H), 5.73 (s, 2H), 5.23 (s, 2H), 5.13-5.05 (m, 1H), 4.67 (d, *J* = 13.1 Hz, 1H), 3.57 (s, 6H), 2.67 (d, *J* = 6.9 Hz, 1H), 1.36-1.26 (m, 1H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 182.9, 158.6, 144.0, 143.31, 143.05, 142.28, 137.48, 131.3, 130.2, 129.0, 128.9, 128.4, 128.1, 128.0, 127.4, 127.0, 126.3, 126.1, 123.3, 114.8, 114.7, 108.7, 91.7, 54.8, 51.4, 47.0.

Elemental analysis: Expected: C 77.80, H 5.44 N 2.33 Found: C 77.59 H 5.35 N 2.36. Analytical data obtained are in agreement with the reported values.[6]

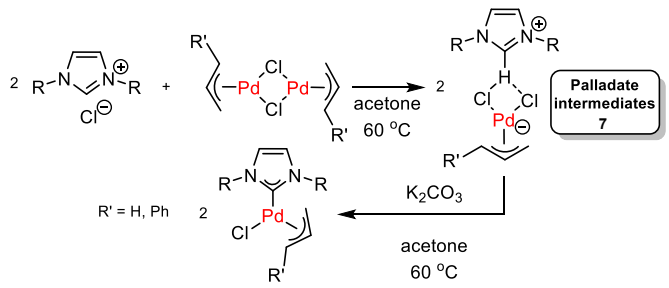
Table S-4: Table for large scale synthesis of [Pd(NHC)(η^3-R-allyl)Cl] pre-catalysts



Entry	[Pd] Complex (1 g)	NHC.HCl (g)	K_2CO_3 (equiv.)	Yield, %[b] (g)
1	[Pd(IPr)(η^3-cin)Cl]	4.0	1	97 (4.9)
2	[Pd(IPr)(η^3-allyl)Cl]	2.7	1	92 (2.9)
3	[Pd(IPr*)(η^3-cin)Cl]	3.7	2	98 (4.2)

[a]Reaction conditions: NHC·HCl (1.2 equiv. for entries 1-2 and 1 equiv. for entry 3), [Pd((η^3-R-allyl)(μ-Cl)]$_2$ (0.5 equiv.), K_2CO_3 and acetone at 60 °C for the corresponding time. **Protocol A** was used for entries 1-2; the NHC salt and palladium dimer were pre-mixed in acetone at room temperature, followed immediately by K_2CO_3 then heating for 10 h at 60 °C. **Protocol B** was used for entry 3; the NHC salt and palladium dimer were pre-mixed in acetone for 1 h at 60 °C, then K_2CO_3 was added and the mixture was stirred for 24 h at 60 °C. [b]Isolated yield.

Synthesis and analysis of the palladate intermediates



Synthesis of [IPrH][Pd(η^3-cin)Cl_2] (**7a**)

IPr·HCl (82.1 mg, 0.193 mmol), [Pd(η^3-cin)(μ-Cl)]$_2$ (50.0 mg, 0.096 mmol), a magnetic stir bar and acetone (0.8 mL) were charged into a vial. The mixture was stirred at 60 °C for 1 h. The solvent was removed and the product was dried under vacuum. The product was obtained as a dark orange powder in a 99% (132 mg) yield. Single crystals were grown by vapour diffusion of hexane into a saturated solution of the complex in DCM.
Elemental analysis: Expected: C 63.02, H 7.05 N 4.08 Found: C 62.92 H 7.14 N 4.15.

Large scale synthesis:
IPr·HCl (3.15 g, 7.4 mmol), [Pd(η^3-cin)(μ-Cl)]$_2$ (1.92 g, 3.7 mmol), a magnetic stir bar and acetone (31 mL) were charged to a vial. The mixture was stirred at 60 °C for 1 h. Then the solvent was removed and dried under vacuum. The product was obtained as a yellow powder in a 99% (5.0 g) yield.
Elemental analysis: Expected: C 63.02, H 7.05 N 4.08, Found: C 63.13 H 7.17 N 4.17.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.19 (s, H_{NCHN}, 1H), 8.32 (d, *J* = 1.6 Hz, H_{imid}, 2H), 7.56-7.52 (m, H_{Ar}, 2H), 7.46 (d, *J* = 7.4 Hz, H_{Ar}, 2H), 7.33 (d, *J* = 7.7 Hz, $H_{Ar,}$ 4H), 7.21 (m, H_{Ar}, 3H), 5.66 (s, H_{cin}, 1H), 4.46 (s, H_{cin}, 1H), 3.83 (s, H_{cin}, 1H), 2.90 (s, H_{cin}, 1H), 2.48-2.41 (m, C*H*(CH_3)$_2$, 4H), 1.26 (d, *J* = 6.8 Hz, CH(C*H*$_3$)$_2$, 12H), 1.18 (d, *J* = 6.7 Hz, CH(C*H*$_3$)$_2$, 12H).
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = δ 144.9, 136.7, 131.8, 129.7, 128.4, 127.7, 127.5, 124.5, 105.0, 28.8, 24.4, 23.7.

Synthesis of [IPrH][Pd(η^3-allyl)Cl_2] (**7b**)

IPr·HCl (82.04 mg, 0.193 mmol), [Pd(η^3-allyl)(μ-Cl)]$_2$ (35.3 mg, 0.096 mmol), a magnetic stir bar and acetone (0.8 mL) were charged to a vial. The mixture was stirred at 60 °C for 1 h. Then the solvent was removed and dried under vacuum. The product was obtained as a yellow powder in a 99% (117 mg).
Elemental analysis: Expected: C 59.07, H 7.27 N 4.59, Found: C 58.90 H 7.17 N 4.57.
Large scale:
IPr·HCl (816.1 mg, 1.92 mmol), [Pd(η^3-allyl)(μ-Cl)]$_2$ (351.2 mg, 0.96 mmol), a magnetic stir bar and acetone (2.5 mL) were charged to a vial. The mixture was stirred at 60 °C for 1 h. Then, the solvent was removed and dried under vacuum. The product was obtained as a yellow powder in a 98% (1.1 g) yield.
Elemental analysis: Expected: C 59.07, H 7.27 N 4.59, Found: C 59.11 H 6.97 N 4.73.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.16 (s, H_{NCHN}, 1H), 8.28 (d, *J* = 1.6 Hz, H_{imid}, 2H), 7.54-7.50 (m, H_{Ar}, 2H), 7.32 (d, H_{Ar}, *J* = 7.2 Hz, 4H), 5.16-5.10 (m, H_{allyl}, 1H), 3.76 (d, *J* = 8 Hz, H_{allyl}, 2H), 2.65 (d, *J* = 11.6 Hz, H_{allyl}, 2H), 2.48-2.44 (m, C*H*(CH_3)$_2$, 4H), 1.27 (d, *J* = 6.8 Hz, CH(C*H*$_3$)$_2$, 12H), 1.20 (d, *J* = 7.2 Hz, CH(C*H*$_3$)$_2$, 12H).
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = δ145.2, 137.0, 132.0, 130.0, 127.5, 124.7, 109.2, 60.3, 28.8, 24.4, 23.8.

Synthesis of [IPr*H][Pd(η^3-cin)Cl_2] (**7c**)

IPr*·HCl (109.9 mg, 0.115 mmol), [Pd(η^3-cin)(μ-Cl)]$_2$ (30.0 mg, 0.058 mmol), a magnetic stir bar and acetone (1.1 mL) were charged to a vial. The mixture was stirred at 60 °C for 1 h. Then, the solvent was removed and dried under vacuum. The product was obtained as a yellow powder in a 99% (139 mg) yield. Single crystals were grown by vapour diffusion of hexane into a solution of the complex in DCM.
Elemental analysis: Expected: C 77.38 H 5.66 N 2.31 Found: C 77.25 H 5.47 N 2.36.

Large scale:
IPr*·HCl (949.6 mg, 1 mmol), [Pd(η^3-cin)(μ-Cl)]$_2$ (259 mg, 0.5 mmol), a magnetic stir bar and acetone (2.5 mL) were charged to a vial. The mixture was stirred at 60 °C for 1 h. Then, the solvent was removed and dried under vacuum. The product was obtained as a yellow powder in a 99% (1.2 g) yield. Single crystals

were grown by vapour diffusion of hexane into a solution of the complex in DCM. **Elemental analysis**: Expected: C 77.38 H 5.66 N 2.31 Found: C 77.52 H 5.43 N 2.35.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 12.52 (s, H_{NCHN}, 1H), 7.31-7.23 (m, H_{Ar}, 19H), 7.19-7.06 (m, H_{Ar}, 20H), 6.77-6.75 (m, H_{Ar}, 10H), 5.87-5.75 (br. m, H_{cin}, 1H), 5.41 (s, C*H*$(Ph)_2$, 4H), 5.33 (s, H_{imid}, 2H), 4.68-3.68 (br. m, H_{cin}, 2H), 3.15-2.45 (m, H_{cin}, 1H), 2.18 (s, CH_3, 6H).
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 142.9, 142.8, 142.3, 140.7, 131.1, 130.4, 129.4, 129.2, 128.7, 128.1, 126.9, 126.8, 123.3, 106.1, 82.0, 59.0, 51.3, 22.0.

Synthesis of [SIPrH][Pd(η^3-cin)Cl_2] (**7d**)

SIPr·HCl (65 mg, 0.152 mmol), [Pd(η^3-cin)(μ-Cl)]$_2$ (40.0 mg, 0.076 mmol), a magnetic stir bar and acetone (1 mL) were charged to a vial. The mixture was stirred at 60 °C for 1 h. Then, the solvent was removed and dried under vacuum. The product was obtained as a yellow powder in a 99% yield (106.7 mg). **Elemental analysis**: Expected: C 63.02 H 7.05 N 4.08 Found: C 63.28 H 6.96 N 4.15.

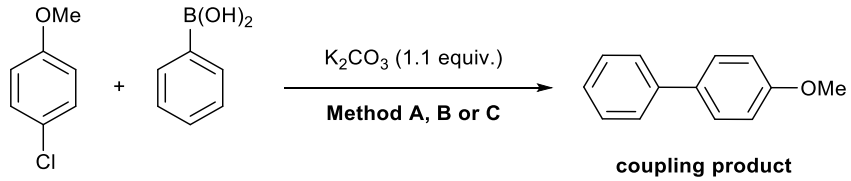
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.75 (s, H_{NCHN}, 1H), 7.52-7.43 (m, H_{Ar}, 4H), 7.30-7.19 (m, H_{Ar}, 7H), 5.72 (br. s, H_{cin}, 1H), 4.95 (s, H_{imid}, 4H), 4.51 (br. s, H_{cin}, 1H), 3.93 (d, *J* = 6.9 Hz, H_{cin}, 1H), 3.15-3.02 (m, C*H*$(CH_3)_2$, 4H), 2.97 (d, *J* = 12.5 Hz, H_{cin}, 1H), 1.40 (d, *J* = 6.8 Hz, CH(C*H*$_3$)$_2$, 12H), 1.22 (d, *J* = 6.9 Hz, CH(C*H*$_3$)$_2$, 12H).
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 157.2 , 146.5, 131.5, 129.5, 128.7, 128.1, 127.4, 125.0, 105.2, 58.3, 56.0, 29.1, 25.5, 24.0.

Table S-5: Table for synthesis of [NHCH][Pd(η^3-R-allyl)Cl_2]

Complex	Small scale	Large scale
[Pd(η^3-cin)Cl_2][IPrH]	99% (132 mg)	99% (5.0 g)
[Pd(η^3-allyl)Cl_2][IPrH]	99% (117 mg)	98% (1.1 g)
[Pd(η^3-cin)Cl_2][IPr*H]	99% (139 mg)	99% (1.2 g)

[a]Reaction conditions: NHC·HCl (1. equiv.)[Pd(η^3-R-allyl)(μ-Cl)]$_2$ (0.5 equiv.) in acetone at 60 ^{o}C for 1 h.

The Suzuki-Miyaura coupling



Method A:[1]

The vial containing the pre-catalyst **7a-c** was transferred into the glovebox. Inside the glovebox, the vial was charged with a stirring bar, 4-chloroanisole (0.5 mmol), phenylboronic acid (1 equiv.) and K_2CO_3 (1.1 equiv.). The vial was then sealed with a screw cap fitted with a septum. The reaction mixture was taken outside the glovebox. 1 mL of an ethanol/water (1:1) mixture (degassed) was added and the reaction was left to stir at 80 ^oC for 4 h.

Method B:

A vial containing the pre-catalyst **7a-c** was transferred into the glovebox. Inside the glovebox, the vial was charged with a stirring bar, 4-chloroanisole (0.5 mmol), phenylboronic acid (1 equiv.) and K_2CO_3 (1.1 equiv.). The vial was sealed with a screw cap fitted with a septum. The reaction mixture was taken outside the glovebox. 1 mL of ethanol (degassed) was added and the reaction was left to stir at RT for 20 h.

Methods C1, C3:

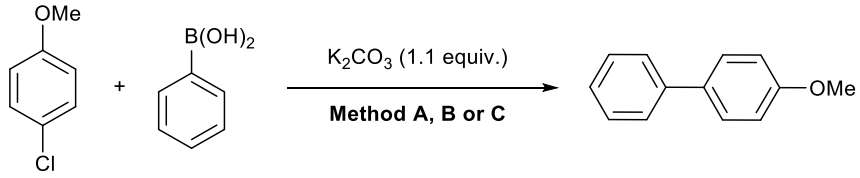
A vial was charged with a stirring bar, **7a-c** (0.3 mol%) and K_2CO_3 (1.1 equiv.) under argon. the mixture was stirred for; 1 h at 60 °C (**C1**) or 30 min at 60 °C (**C3**), then 4-chloroanisole (0.5 mmol) and phenylboronic acid (1 equiv.) were added and the reaction was left stirring at RT for 20 h.

Method C2:

A vial containing **7a-c** (0.3 mol%) was transferred into the glovebox. Inside the glovebox, the vial was charged with a stirring bar, 4-chloroanisole (0.5 mmol), phenylboronic acid (1 equiv.) and K_2CO_3 (1.1 equiv.). The vial was sealed with a screw cap fitted with a septum. The reaction mixture was taken outside the glovebox. 1 mL of ethanol (degassed) was added and the reaction was stirred for 1 h at 60 °C, then 20 h at RT.

For entries 7-9: Pd dimer (0.15 mol%) and NHC·HCl (0.3 mol%) were used instead of **7a-c**.

Table S-6: Table for the investigation of the Suzuki-Miyaura coupling of phenylboronic acid and 4-chloroanisole[a]



Entry	Catalyst (0.3 mol%)	**Meth. A** (Conv. %)[b]	**Meth. B** (Conv. %)[b]	**Meth. C** (Conv. %)[b]		
				C1	C2	C3
1	[Pd(IPr)(cin)Cl] **4**	71	**82**			
2	[Pd(IPr)(allyl)Cl] **5**	61	58			
3	[Pd(IPr*)(cin)Cl] **6**	70	**73**			
4	**7a**	NR	NR	**82**	9	43
5	**7b**	NR	NR	50	NR	13
6	**7c**	NR	NR	**83**	28	**97**
7	$[Pd(cin)Cl]_2$ + 2 IPr·HCl	NR	NR	NR		
8	$[Pd(allyl)Cl]_2$ + 2 IPr·HCl	NR	NR	NR		
9	$[Pd(cin)Cl]_2$ + 2 IPr*·HCl	NR	NR	NR		

[a]NR: no reaction. Reaction conditions: 4-chloroanisole (0.5 mmol), phenylboronic acid (1 equiv.), K_2CO_3 (1.1 equiv.) in 1 mL of solvent. The reactions were all charged under inert atmosphere and all reagents and catalysts were charged initially except for **Methods C1** and **C3**. **Method A:** Ethanol/water (1:1) at 80 °C for 4 h. **Method B:** Ethanol at RT for 20 h. **Method C: 7a-c** (entries 4-6) (or Pd dimer, 0.15 mol%, and NHC·HCl, 0.3 mol%, for entries 7-9), K_2CO_3 and ethanol were heated for; 1 h at 60 °C (**C1**) or 30 min at 60 °C (**C3**), then the coupling partners were added and the reaction was left stirring at RT for 20 h. **C2:** All reagents and catalysts were added from the start and heated for 1 h at 60 °C then stirred at RT for 20 h. [b]Conversion determined by GC.

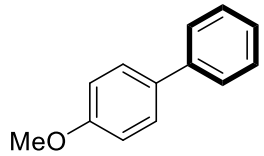
Coupling product: 4-methoxy-1,1'-biphenyl
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.59-7.50 (m, 4H), 7.45-7.39 (m, 2H), 7.33-7.28 (m, 1H), 7.02-6.95 (m, 2H), 3.86 (s, 3H).
Analytical data obtained were in agreement with the reported information.[1]

Preliminary scope:

General procedure: In air, a vial was charged with [Pd(η^3-cinnamyl)Cl_2][IPrH] **7a** (0.5 mol%, 1.7 mg), K_2CO_3 (0.55 mmol, 79 mg), ethanol (1 mL) and a magnetic stir bar and sealed with a screw cap. The mixture was let to stir at the 60 °C for 1 h. The vial was removed from the heating block and the corresponding aryl boronic acid was added followed by the corresponding aryl chloride. The reaction was left to stir (1000 rpm) for the corresponding time at room temperature (20 °C.)

Work up: To the crude mixture ethyl acetate (10 mL) and water (10 mL) were added. The aqueous phase was extracted with ethyl acetate (3 x 10 mL). The organic phase was dried over $MgSO_4$. The solution of the crude was filtered through silica gel, the volatiles removed in vacuum and the residue was recrystallized from dichloromethane/pentane.

4-methoxy-1,1'-biphenyl :

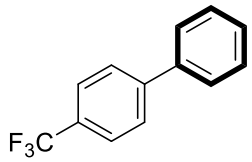


4-methoxy-1,1'-biphenyl
Chemical Formula: $C_{13}H_{12}O$
Molecular Weight: 184.24

Following the general procedure, from phenylboronic acid (60.9 mg, 0.5 mmol) and 4-chloroanisole (61 µL, 0.5 mmol), the reaction yielded 97% (89.3 mg, 0.48 mmol) of a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = δ 7.57 (tt, *J* = 8.1 Hz, 4H), 7.42 (tt, *J* = 7.3 Hz, 2H), 7.31 (tt, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 2.9 Hz, 1H), 6.98 (t, *J* = 2.1 Hz, 1H), 3.86 (s, 3H).
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = δ 159.3 (CH_{Ar}), 141.0 (CH_{Ar}), 133.9 (CH_{Ar}), 128.9 (CH_{Ar}), 128.3 (CH_{Ar}), 126.9 (CH_{Ar}), 126.8 (CH_{Ar}), 114.3 (CH_{Ar}), 55.5 (CH_3).
Analytical data obtained was in accordance with the reported values.[7]

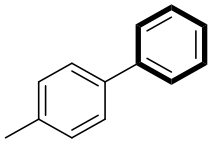
4-(trifluoromethyl)-1,1'-biphenyl



4-(trifluoromethyl)-1,1'-biphenyl
Chemical Formula: $C_{13}H_9F_3$
Molecular Weight: 222.21

Following the general procedure, from phenylboronic acid (60.9 mg, 0.5 mmol) and 1-chloro-4-trifluoromethyl benzene (122 µL, 0.5 mmol), the reaction yielded 98% (108 mg, 0.48 mmol) of a white solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = δ 7.70 (s, 4H), 7.61 (td, *J* = 6.9 Hz, 2H), 7.48 (tt, *J* = 7.2 Hz, 2H), 7.41 (tt, *J* = 6.7 Hz, 1H).
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = δ 144.9 (C_{Ar}), 139.9 (C_{Ar}), 129.6 (CH_{Ar}), 129.3 (CH_{Ar}), 129.1 (CH_{Ar}), 129.0 (CH_{Ar}), 128.3 (CH_{Ar}), 127.6 (CH_{Ar}), 127.4 (CH_{Ar}), 127.3 (CH_{Ar}), 125.9 (CH_{Ar}), 125.8 (CH_{Ar}), 123.1 (CF_3).
Analytical data obtained were in accordance with the reported values.[7]

4-methyl-1,1´-biphenyl

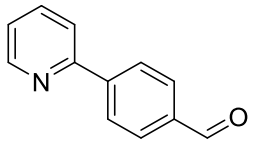


4-methyl-1,1'-biphenyl
Chemical Formula: $C_{13}H_{12}$
Molecular Weight: 168.24

Following the general procedure, from phenylboronic acid (60.9 mg, 0.5 mmol) and 1-chlorotoluene (63.3 mg, 0.5 mmol), the reaction yielded 99% (83 mg, 0.49 mmol) of a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = δ 7.62 (d, *J* = 6.3 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 5.4 Hz, 2H), 7.37 (m, 1H), 7.29 (d, *J* = 7.4 Hz, 2H), 2.43 (s, 3H).
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = δ 141.3 (C), 138.5 (C), 137.2 (C), 135.8 (CH), 129.6 (CH), 128.8 (CH), 128.1 (CH), 127.1 (CH), 21.2 (CH_3).
Analytical data obtained were in agreement with the reported values.[7]

4-(pyridin-2-yl)benzaldehyde



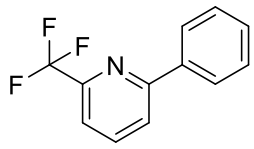
4-(pyridin-2-yl)benzaldehyde
Chemical Formula: $C_{12}H_9NO$
Molecular Weight: 183.21

Following the general procedure, from 4-formylboronic acid (75 mg, 0.5 mmol) and 2-chloropyridine (68 µL, 0.5 mmol), the product yielded 85% (78.2 mg, 0.43 mmol) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = δ 10.09 (s, 1H), 8.75 (dt, *J* = 4.8 Hz, 1H), 8.19 (d, *J* = 8.7 Hz, 2H), 8.00 (td, *J* = 8.7 Hz, 2H), 7.82 (m, 2H), 7.33 (q, *J* = 4.5 Hz, 1H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = δ 192.1 (CH_{COH}), 156.0 (CH), 150.1 (CH), 145.0 (CH), 137.2 (CH), 136.5 (CH), 130.5 (CH), 130.3 (CH), 128.1 (CH), 127.6 (CH), 123.3 (CH), 121.4 (CH).
Analytical data obtained were in agreement with the reported values.[8]

2-phenyl-6-(trifluoromethyl)pyridine

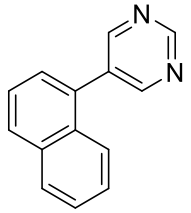


2-phenyl-6-(trifluoromethyl)pyridine
Chemical Formula: $C_{12}H_8F_3N$
Molecular Weight: 223.20

Following the general procedure, from phenylboronic acid (61 mg, 0.5 mmol) and 2-chloro-6-trifluoromethyl pyridine (91 mg, 0.5 mmol), the product yielded 99% (110.3 mg, 0.49 mmol) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = δ 8.67 (dd, *J* = 6.5 Hz, 2H), 7.91 (d, *J* = 3.9 Hz, 2H), 7.61 (t, *J* = 4.3 Hz, 1H), 7.52 – 7.46 (m, 3H).
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = δ 157.9 (C), 148.5 (C), 148.1 (C), 147.8 (CH), 138.2 (C), 137.9 (CH), 129.9 (CH), 129.0 (CH), 127.3 (CH), 122.9 (CH), 120.4 (CF_3), 118.6 (CH).
Analytical data obtained were in agreement with the reported values.[9]

5-(naphthalen-1-yl)pyrimidine

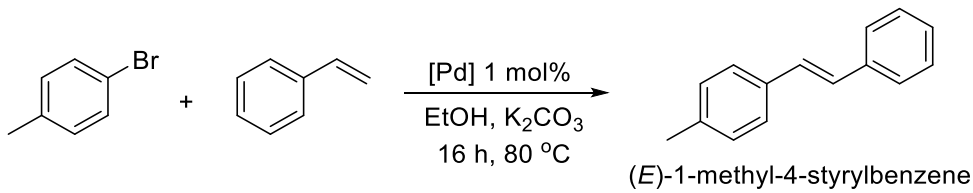


5-(naphthalen-1-yl)pyrimidine
Chemical Formula: $C_{14}H_{10}N_2$
Molecular Weight: 206.25

Following the general procedure, from 1-naphthalene boronic acid (86 mg, 0.5 mmol) and 2-bromopyrimidine (79.5 mL, 0.5 mmol), the product yielded 99% (102.5 mg, 0.49 mmol) as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = δ 9.31 (s, 1H), 8.90 (s, 1H), 7.98 (m, 2H), 7.77 (d, *J* = 8.9 Hz, 1H), 7.61 – 7.42 (m, 4H).
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = δ 157.7 (CH), 157.4 (CH), 134.5 (C), 133.9 (C), 132.5 (C), 131.3 (C), 129.5 (CH), 128.8 (CH), 127.8 (CH), 127.2 (CH), 126.5 (CH), 125.5 (CH), 124.6 (CH).
Analytical data obtained were in agreement with the reported values.[10]

The Mizoroki-Heck reaction



(*E*)-1-methyl-4-styrylbenzene

The vial containing [Pd(cin)Cl_2][SIPrH] (1 mol%, 3.4 mg) was transferred into the glovebox. Inside the glovebox, the vial was charged with a stirring bar, 4-bromotoluene (0.5 mmol, 85.5 mg), styrene (0.75 mmol, 78 mg, 1.5 equiv.) and K_2CO_3 (0.75 mmol, 103.6 mg, 1.5 equiv.). The vial was then sealed with a screw cap fitted with a septum. The reaction mixture was taken outside the glovebox. 2 mL of ethanol (degassed) was added and the reaction was left to stir at 80 °C for 16 h.

Pre-catalysts 1 mol% (mg)	Isolated yield[a]
[Pd(cin)Cl_2][SIPrH] (3.4)	87.5 mg, 90%

[a]Average of two reactions

Coupling product: (E)-1-methyl-4-styrylbenzene

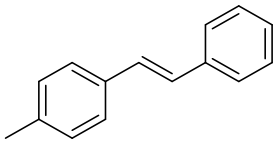
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.52 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 9.3 Hz, 2H), 7.35 (t, *J* = 8.5 Hz, 2H), 7.25 (m, 1H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 2.2 Hz, 2H), 2.36 (s, 3H).

Analytical data obtained were in accordance with the reported values.[11]

Preliminary scope:

The vial containing [Pd(cin)Cl_2][SIPrH] (1.6 mg, 0.0025 mmol, 0.5 mol%) was transferred into the glovebox. Inside the glovebox, the vial was charged with a stirring bar, bromoaryl, styrene (0.75 mmol, 78 mg, 1.5 equiv.) and K_2CO_3 (0.75 mmol, 103.6 mg, 1.5 equiv.) The vial was then sealed with a screw cap fitted with a septum. The reaction mixture was taken outside the glovebox. 2 mL of an ethanol (degassed) was added and the reaction was left to stir at 80 °C for 16 h. The product was isolated as for the Suzuki-Miyaura products, see above.

(E)-1-methyl-4-styrylbenzene



(*E*)-1-methyl-4-styrylbenzene
Chemical Formula: $C_{15}H_{14}$
Molecular Weight: 194.28

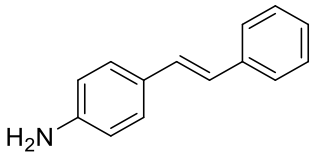
Following the general procedure, from 4-bromotoluene (85.5 mg, 0.5 mmol), the reaction yielded 92% (89 mg, 0.46 mmol) of a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = δ 7.52 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 9.32 Hz, 2H), 7.35 (t, *J* = 8.5 Hz, 8.56 Hz, 2H), 7.25 (m, 1H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 2.2 Hz, 2H), 2.36 (s, 3H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = δ 141.5 (C), 138.7 (C), 137.4 (C), 136.0 (CH), 133.1 (CH), 129.9 (CH), 129.1 (CH), 128.4 (CH), 127.6 (CH), 127.4 (CH), 21.5 (CH_3).

Analytical data obtained were in agreement with the reported values.[10]

(E)-4-styrylaniline



(*E*)-4-styrylaniline
Chemical Formula: $C_{14}H_{13}N$
Molecular Weight: 195.27

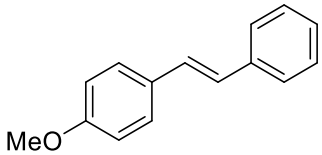
Following the general procedure, from 4-bromoaniline (86 mg, 0.5 mmol), the reaction yielded 76% (75 mg, 0.38 mmol) of a brown solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = δ 7.47 (d, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 9.1 Hz, 4H), 7.21 (t, *J* = 6.0 Hz, 1H), 7.05 (m, 1H), 6.94 (m, 1H), 3.75 (bs, 2H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = δ 146.2 (C), 145.0 (C), 137.6 (C), 132.3 (CH), 128.6 (CH), 127.8 (CH), 126.9 (CH), 126.1 (CH), 125.1 (CH), 124.8 (CH), 115.2 (CH).

Analytical data obtained were in agreement with the reported values.[12]

(E)-1-methoxy-4-styrylbenzene



(*E*)-1-methoxy-4-styrylbenzene
Chemical Formula: $C_{15}H_{14}O$
Molecular Weight: 210.28

Following the general procedure, from 4-bromoanisole (98 mg, 0.5 mmol), the reaction yielded 85% (89.1 mg, 0.42 mmol) of a yellow solid.

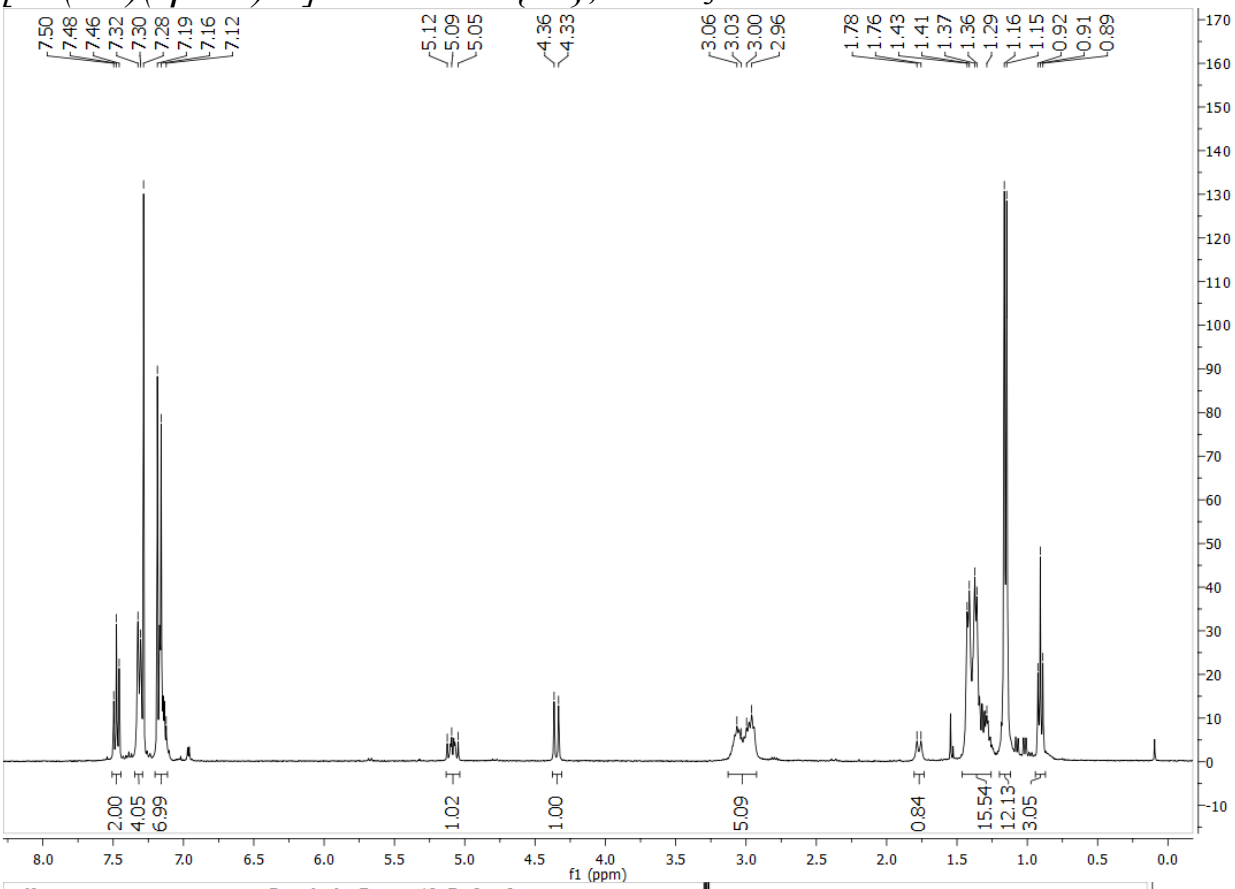
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = δ 7.50-7.45 (m, 4H), 7.36 (t, *J* = 8.5 Hz, 4H), 7.24 (m, 2H), 7.09 (m, 1H), 7.00 (m, 1H), 6.91 (d, *J* = 8.5 Hz, 2H), 3.84 (s, 3H).

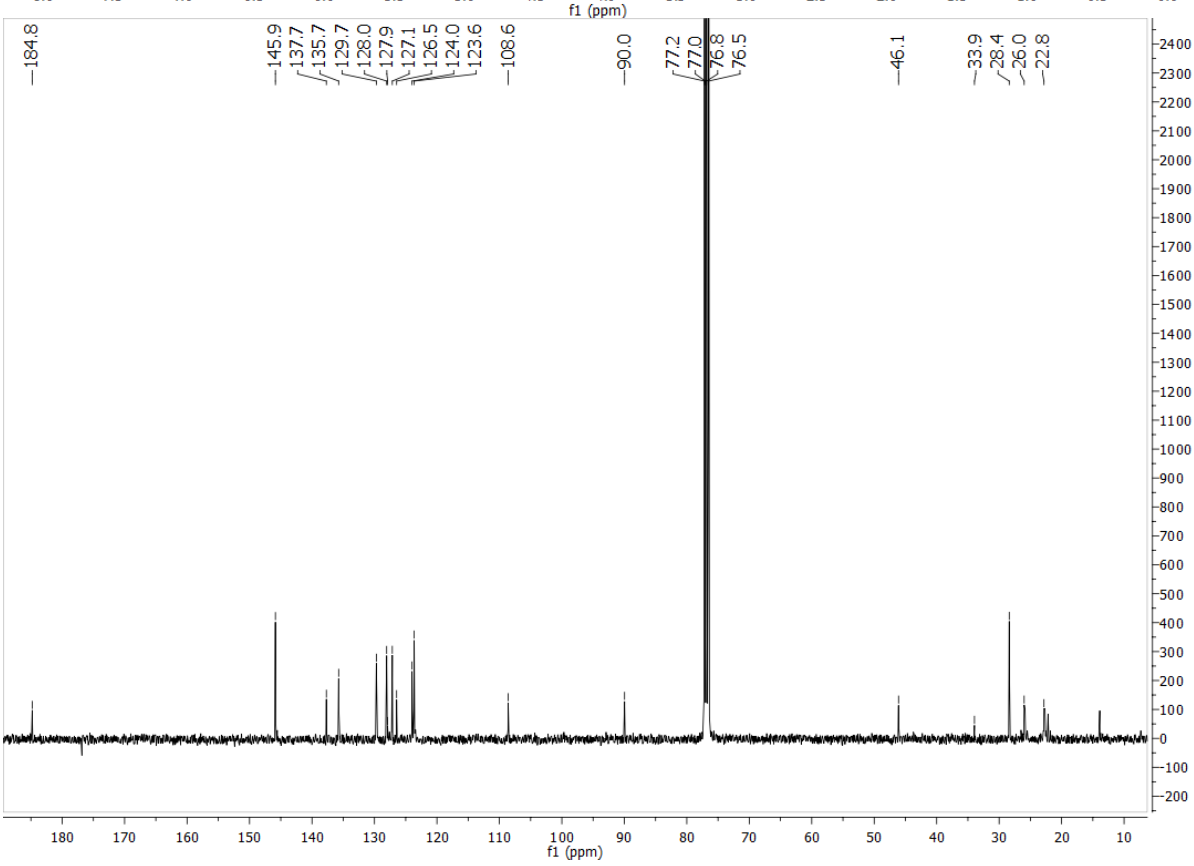
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = δ 159.4 (C), 137.8 (C), 130.3 (CH), 128.8 (C), 128. (CH), 127.9 (CH), 126.7 (CH), 126.4 (CH), 114.3 (CH), 55.5 (CH_3).

Analytical data obtained were in agreement with the reported values.[10]

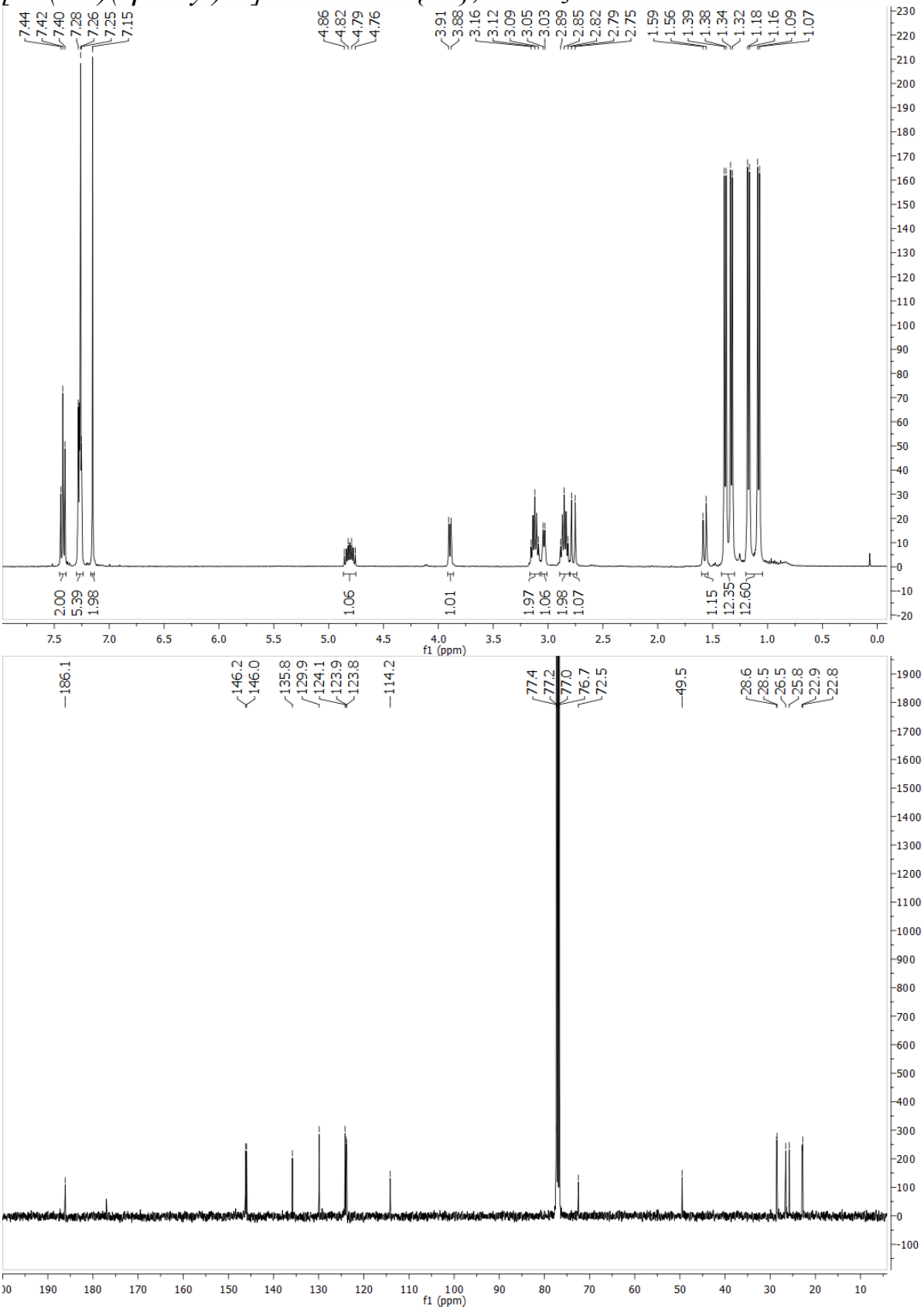
NMR spectra

[Pd(IPr)(η³-cin)Cl] ^{1}H and $^{13}C\{^{1}H\}$, $CDCl_3$

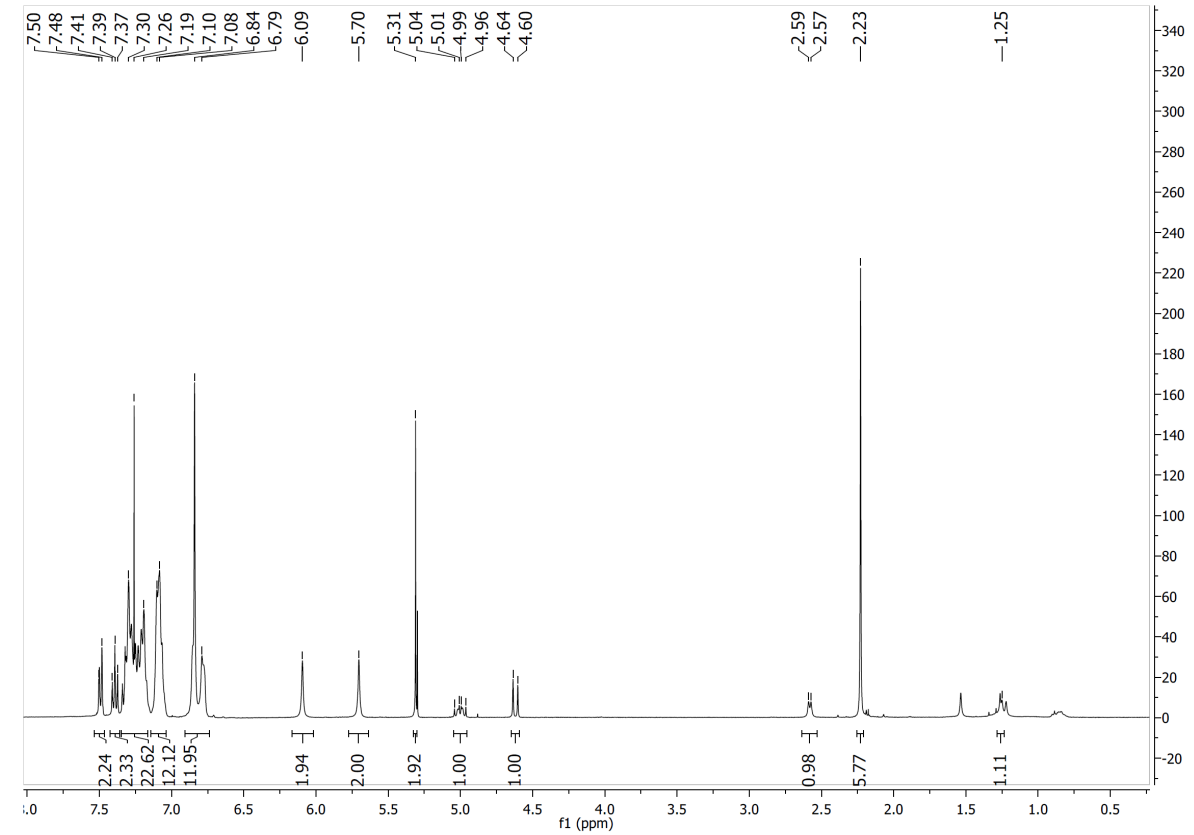


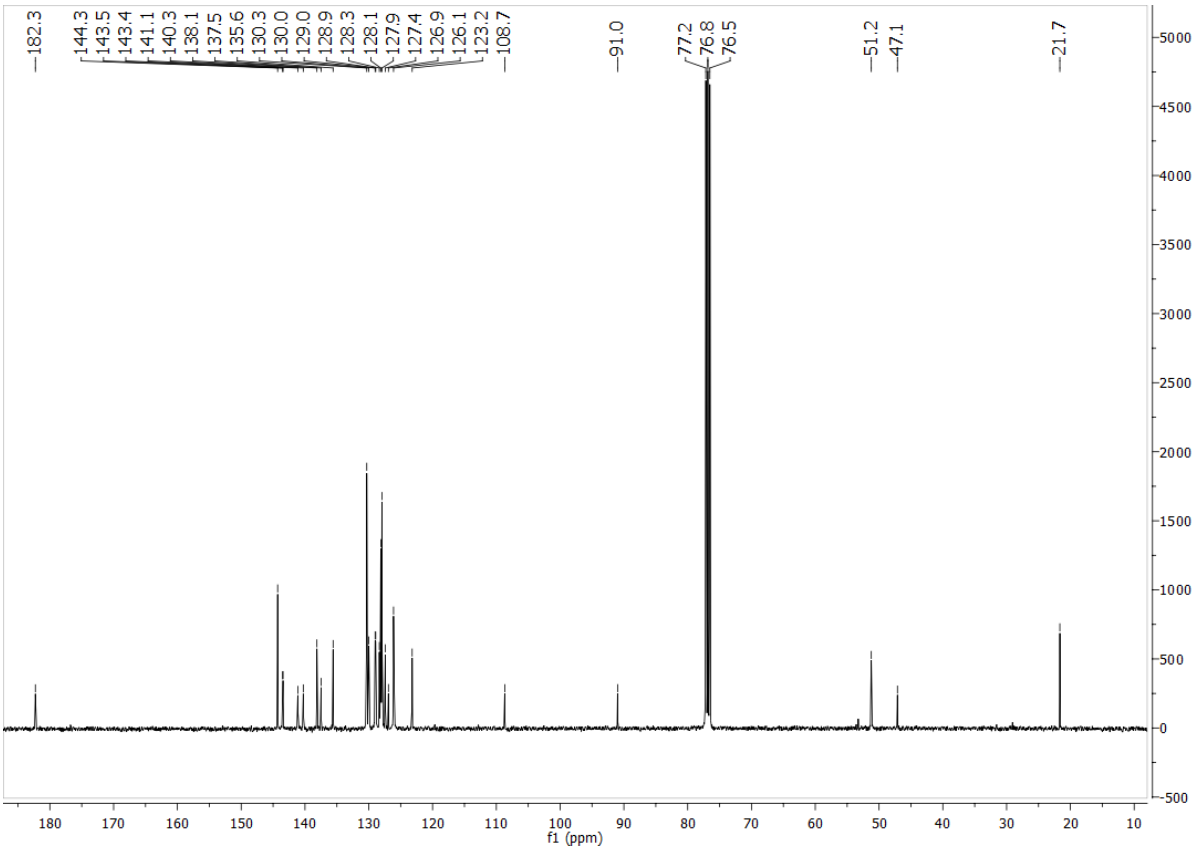


[Pd(IPr)(η³-allyl)Cl] ^{1}H and $^{13}C\{^{1}H\}$, $CDCl_3$

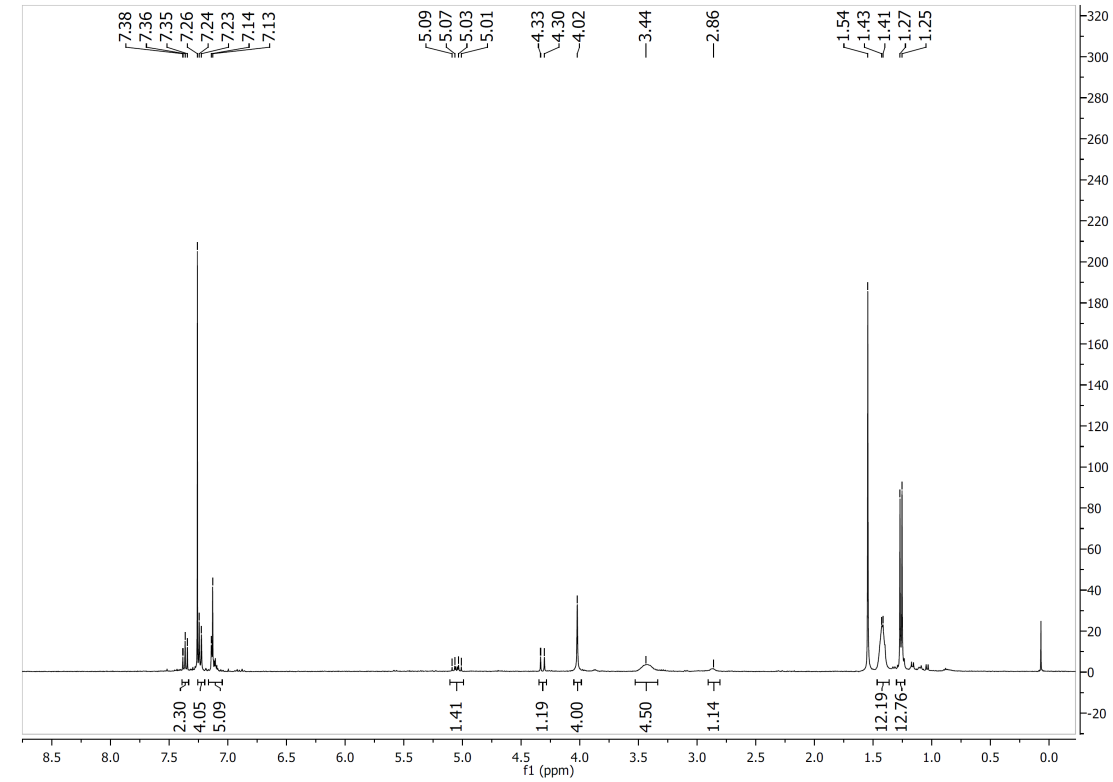


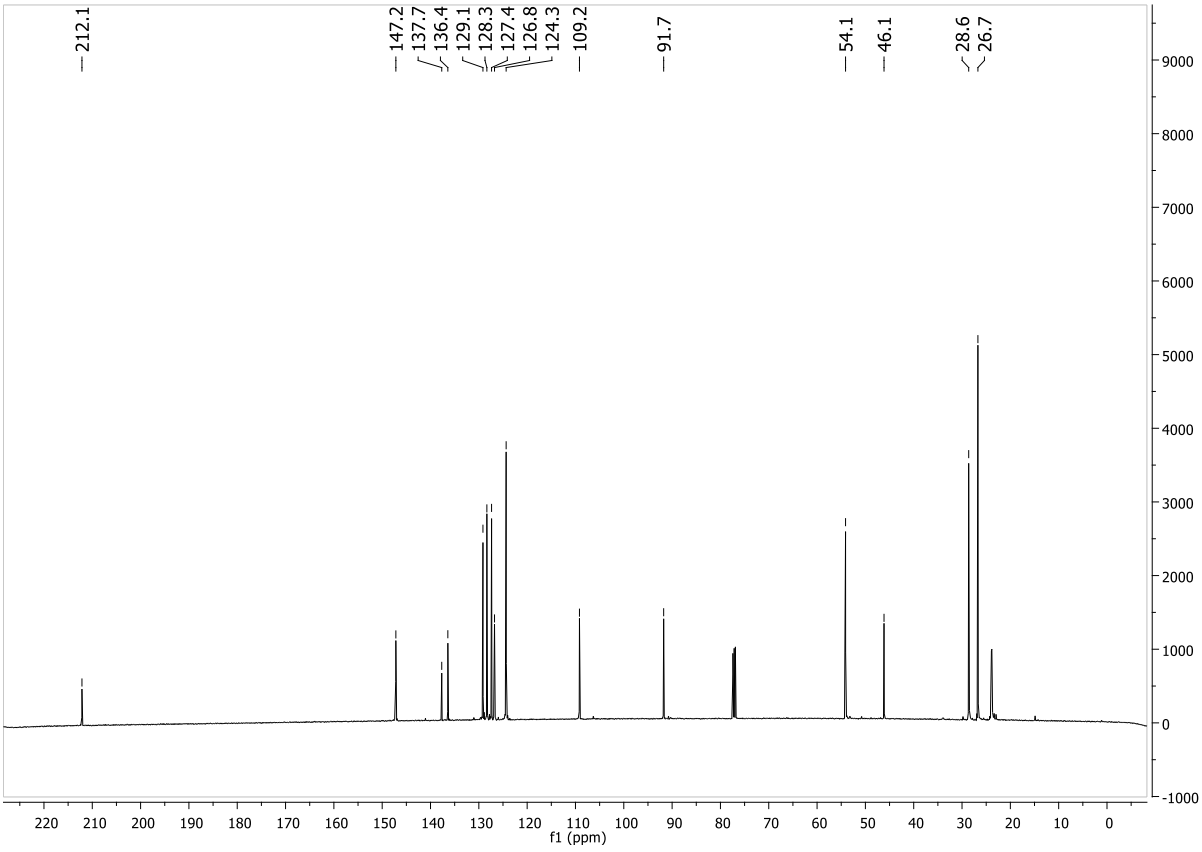
[Pd(IPr)(η³-cin)Cl] ^{1}H and $^{13}C\{^{1}H\}$, $CDCl_3$*



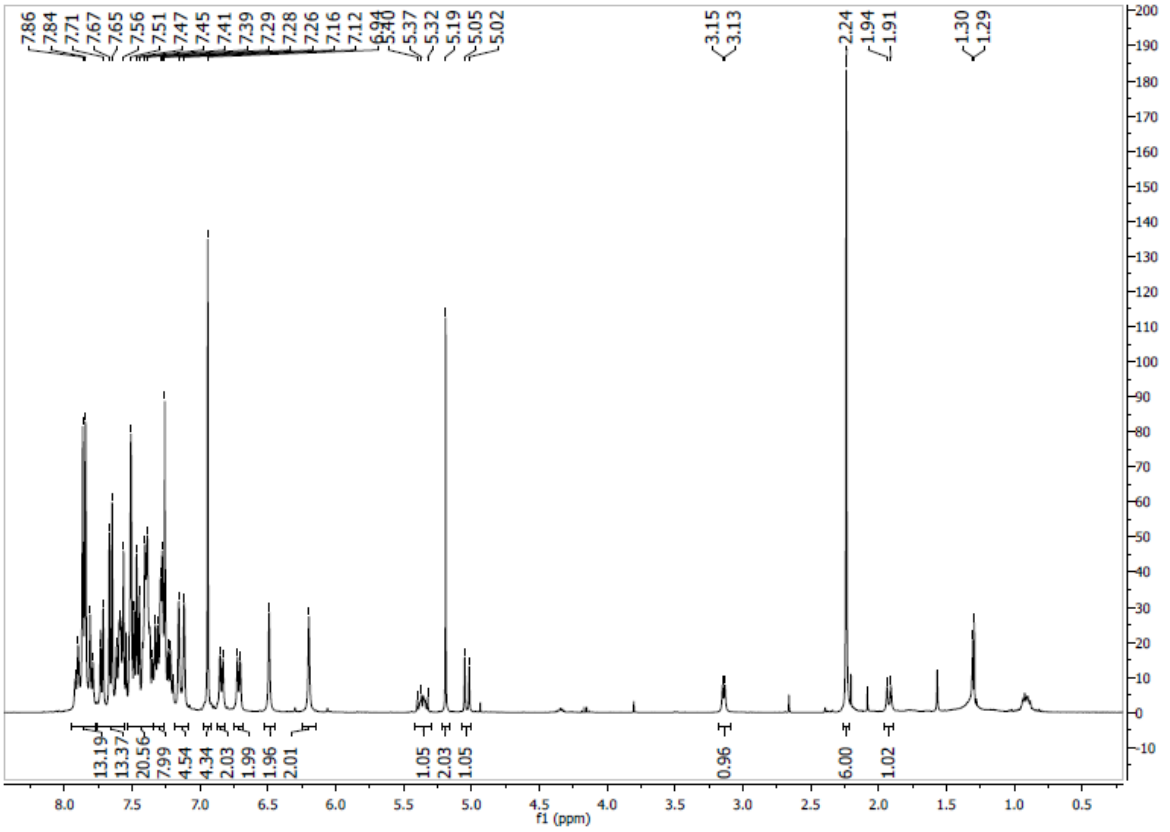


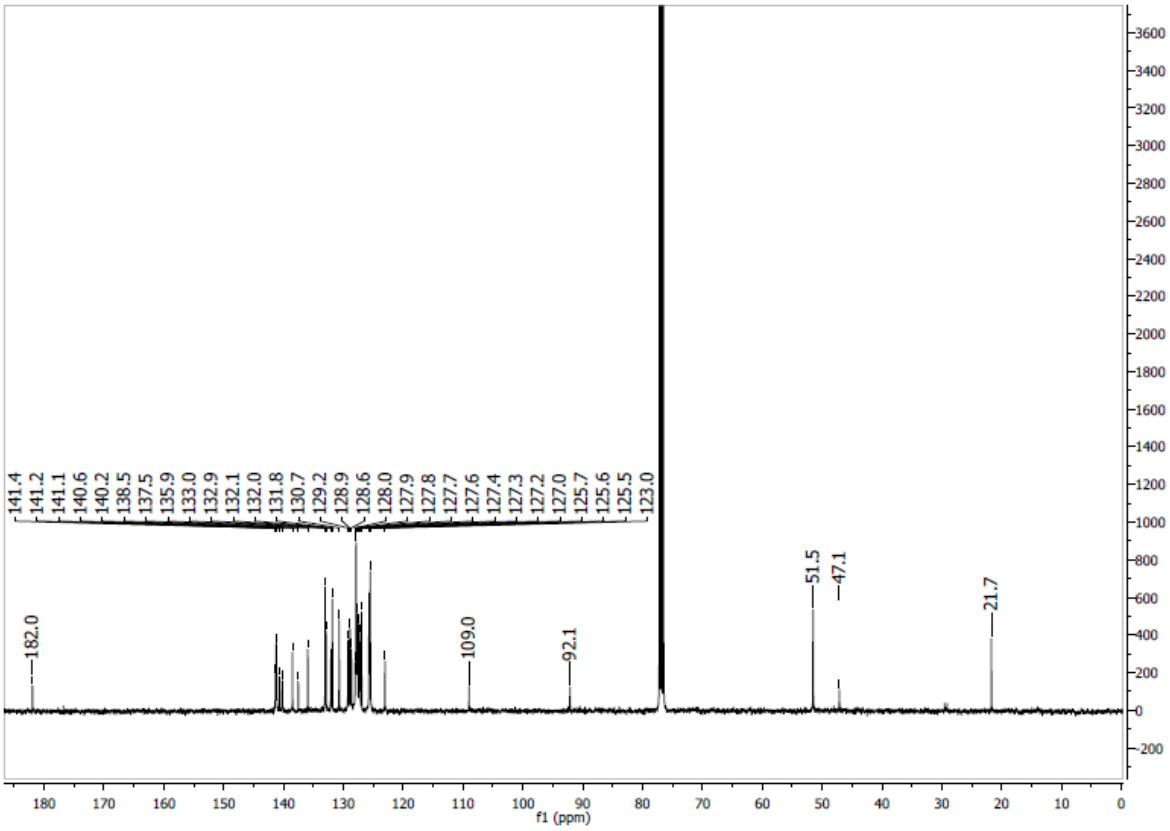
[Pd(SIPr)(η³-cin)Cl] ^{1}H and $^{13}C\{^{1}H\}$, $CDCl_3$



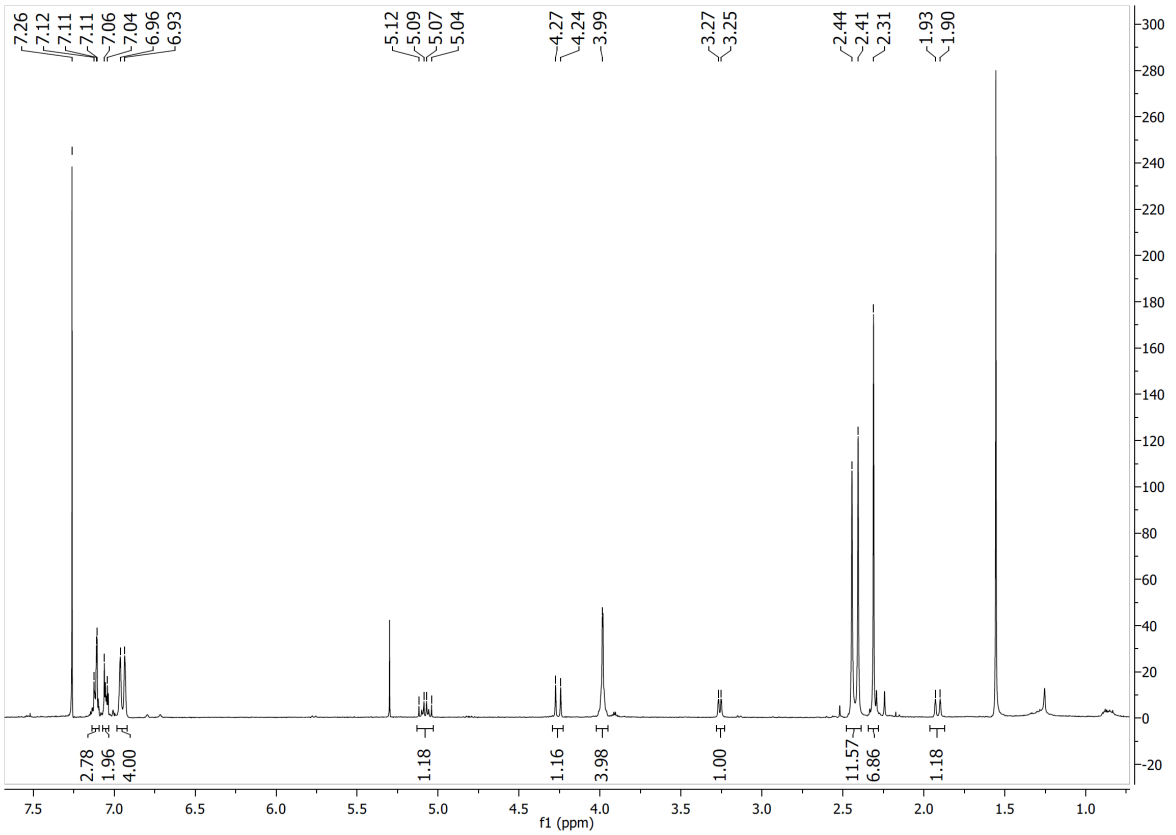


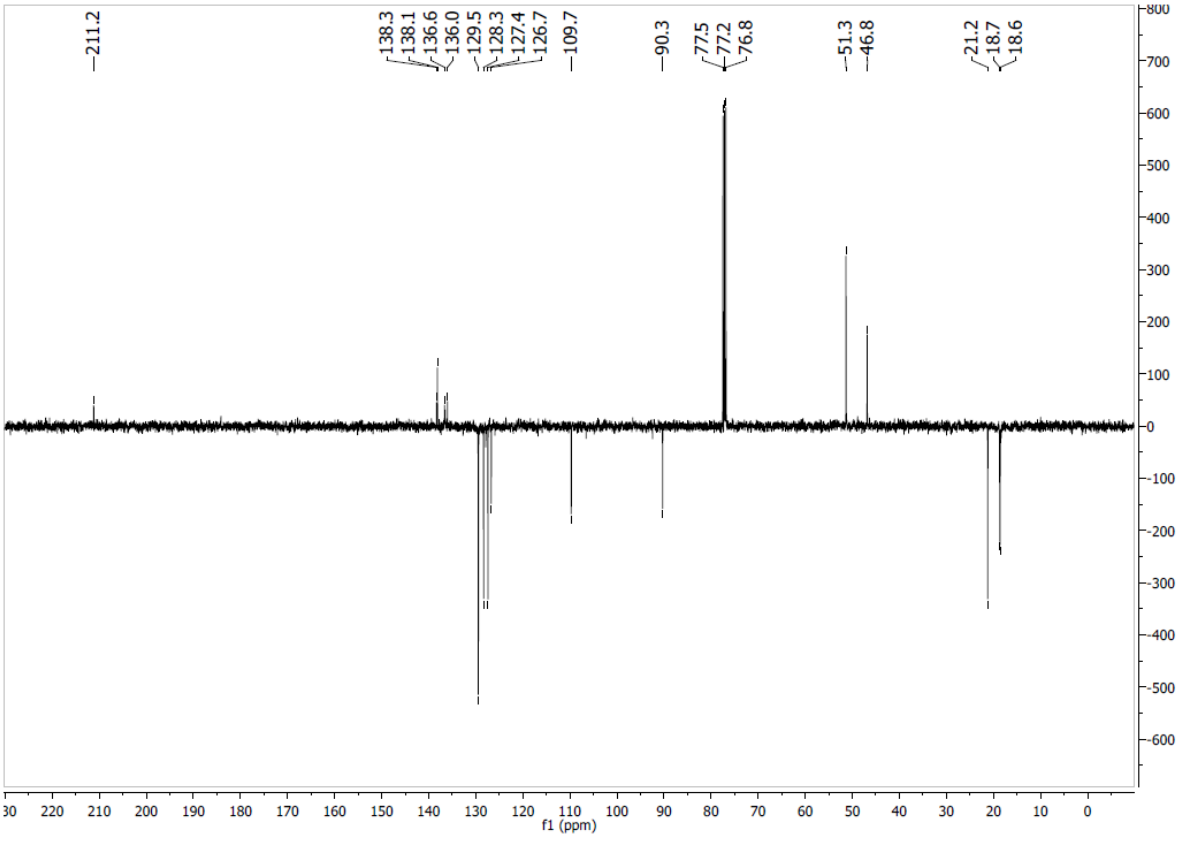
[Pd(IPr$^{*2\text{-}Np}$)(η^3-cin)Cl] ^{1}H and ^{13}C {^{1}H}, $CDCl_3$



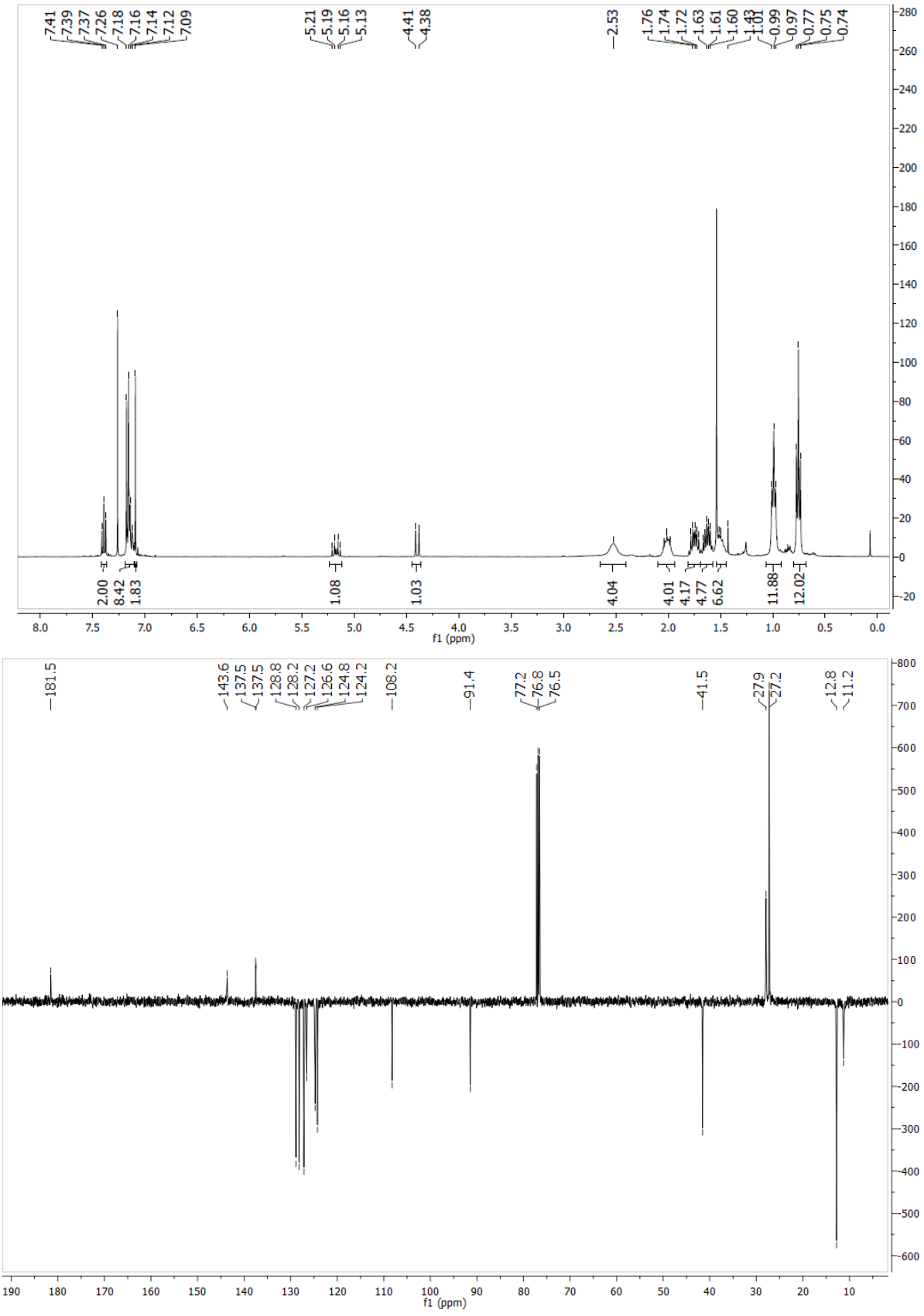


[Pd(SIMes)(η^3-cin)Cl] ^1H and $^{13}C\{^1H\}$, $CDCl_3$

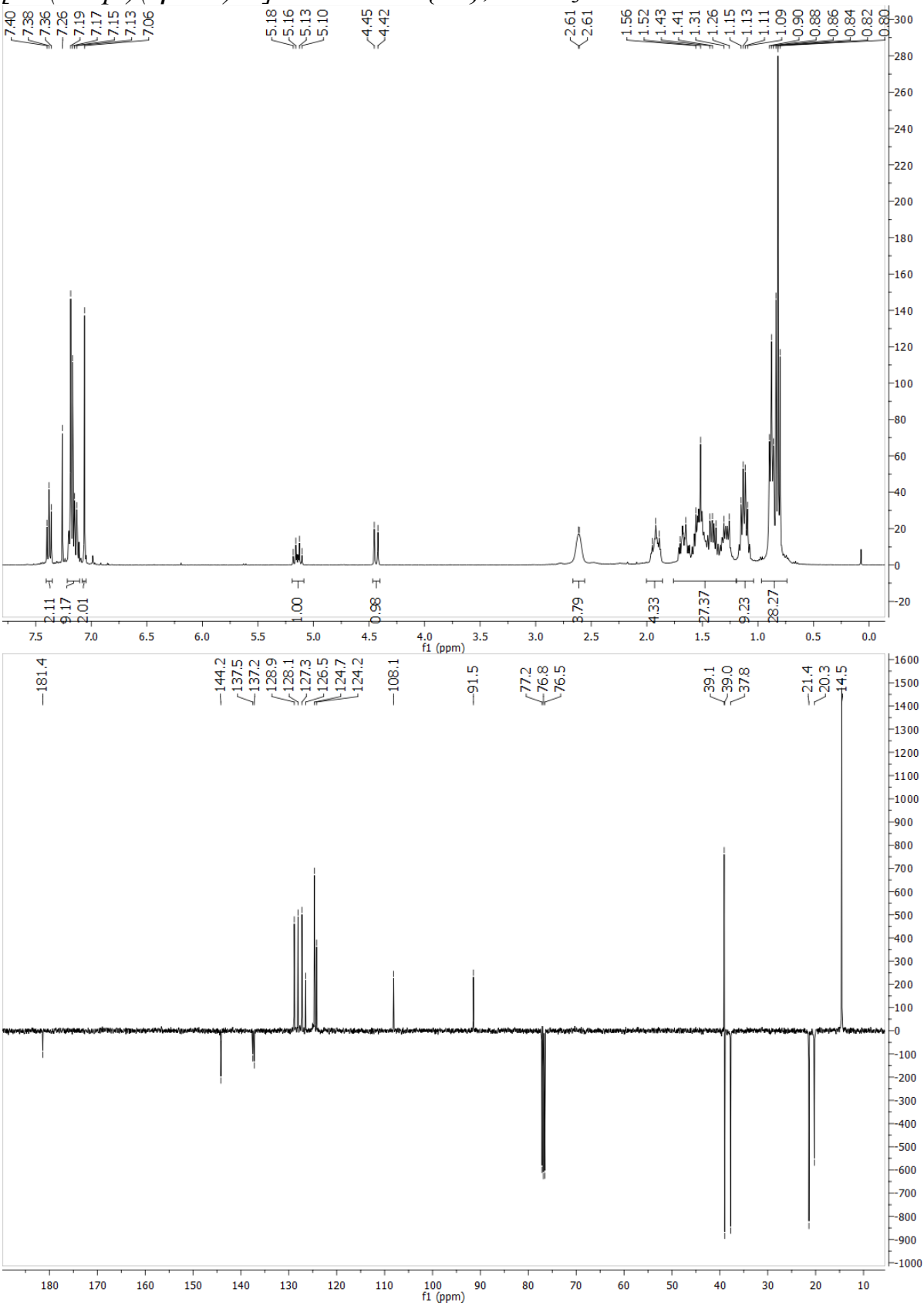




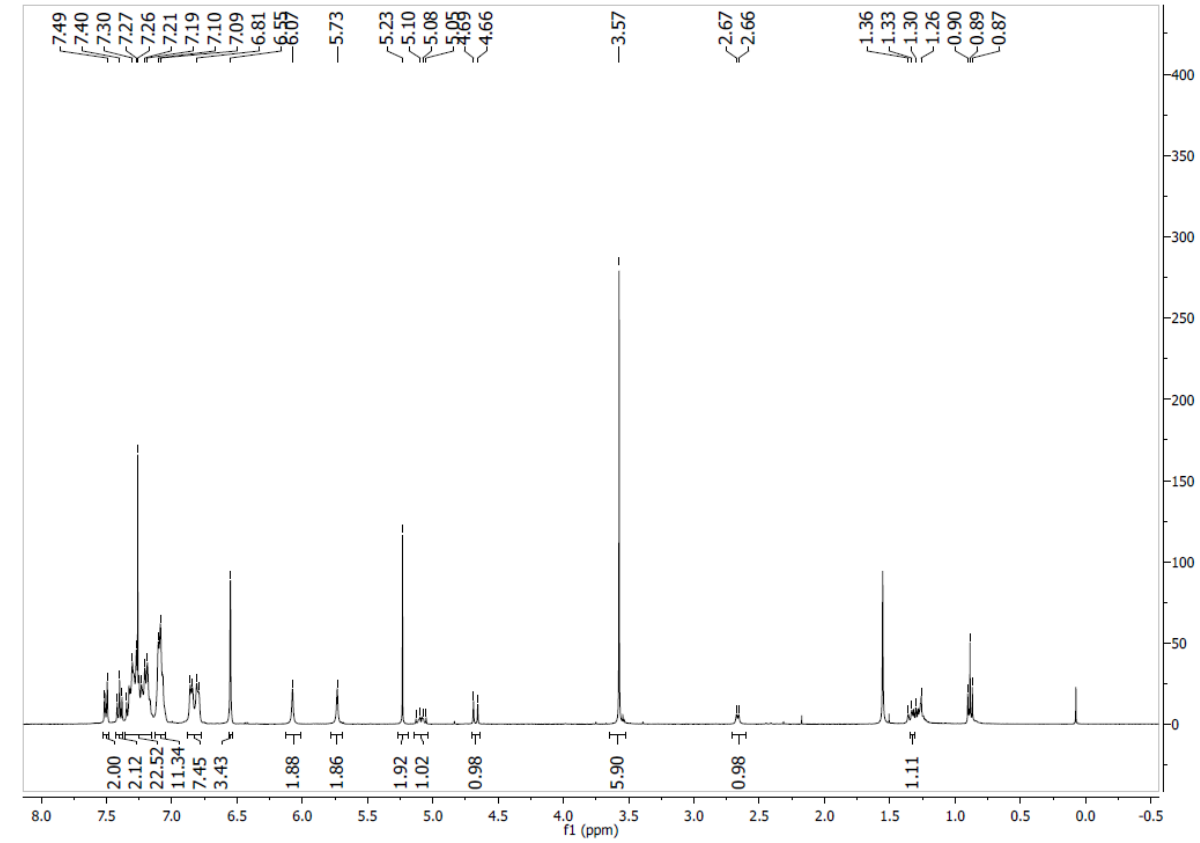
[Pd(IPent)(η³-cin)Cl] ^{1}H and $^{13}C\{^{1}H\}$, $CDCl_3$

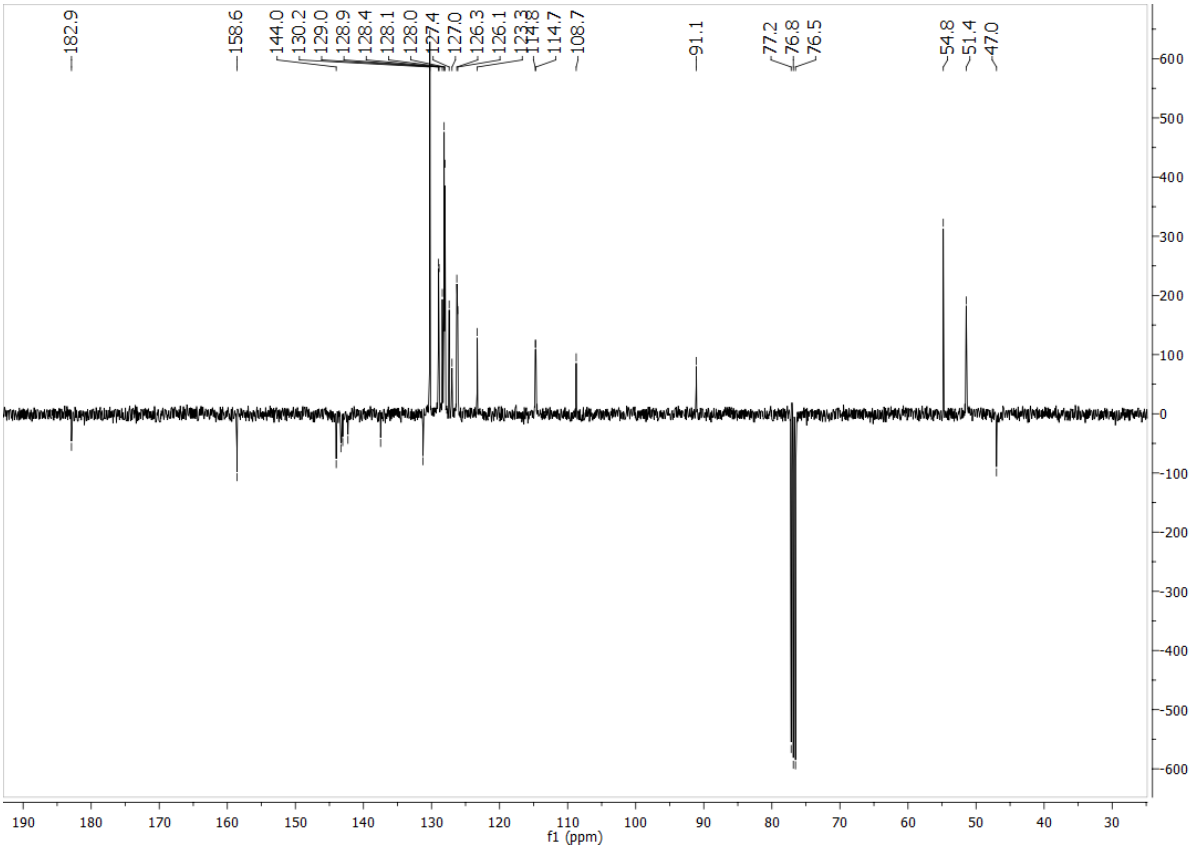


[Pd(IHept)(η³-cin)Cl] ^{1}H and ^{13}C {^{1}H}, $CDCl_3$

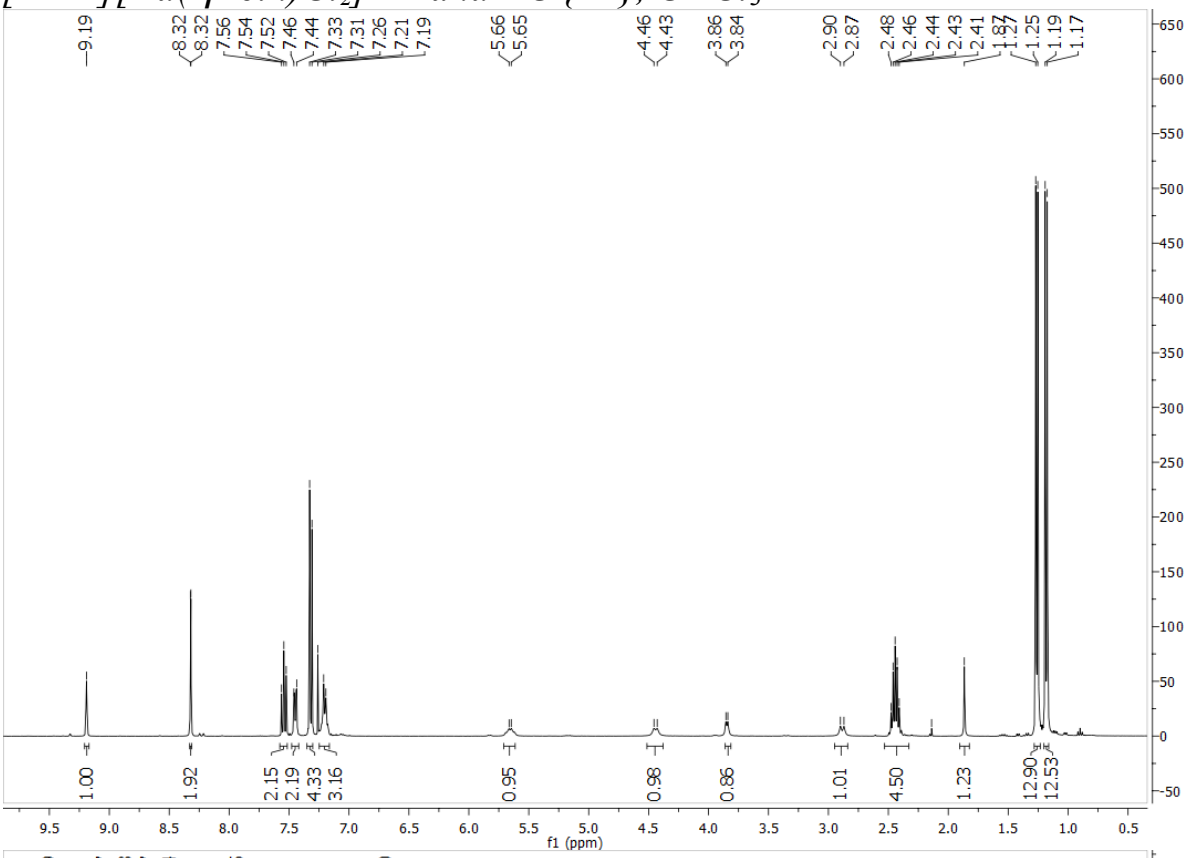


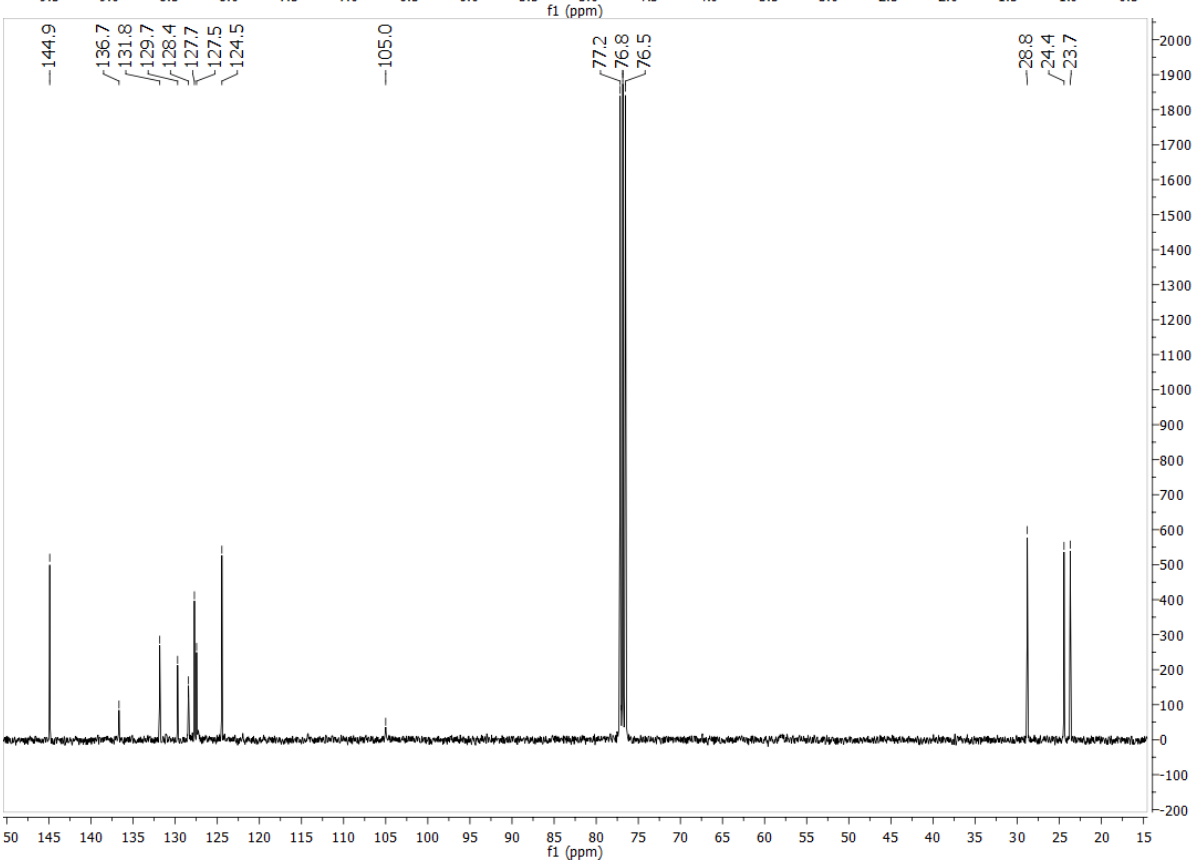
[Pd(IPr^{OMe})(η^3-cin)Cl] ^{1}H and ^{13}C {^{1}H}, $CDCl_3$*



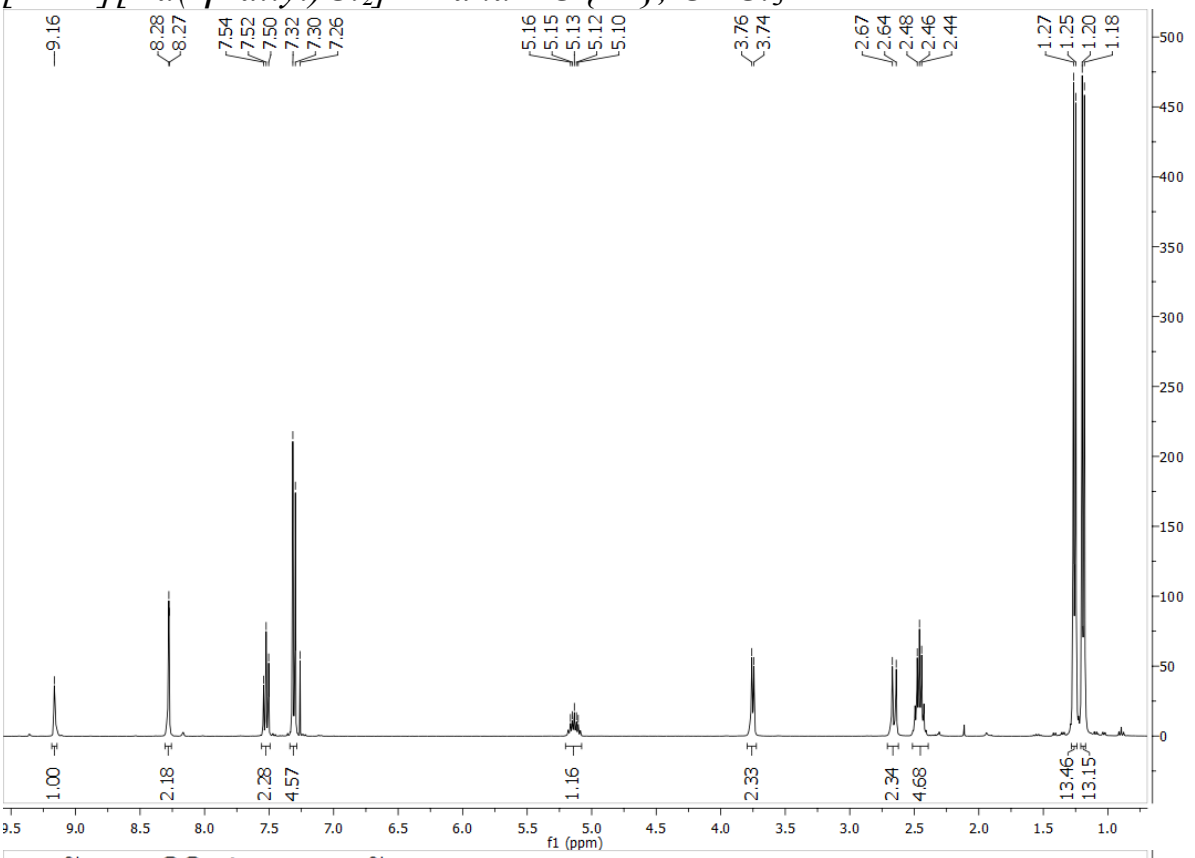


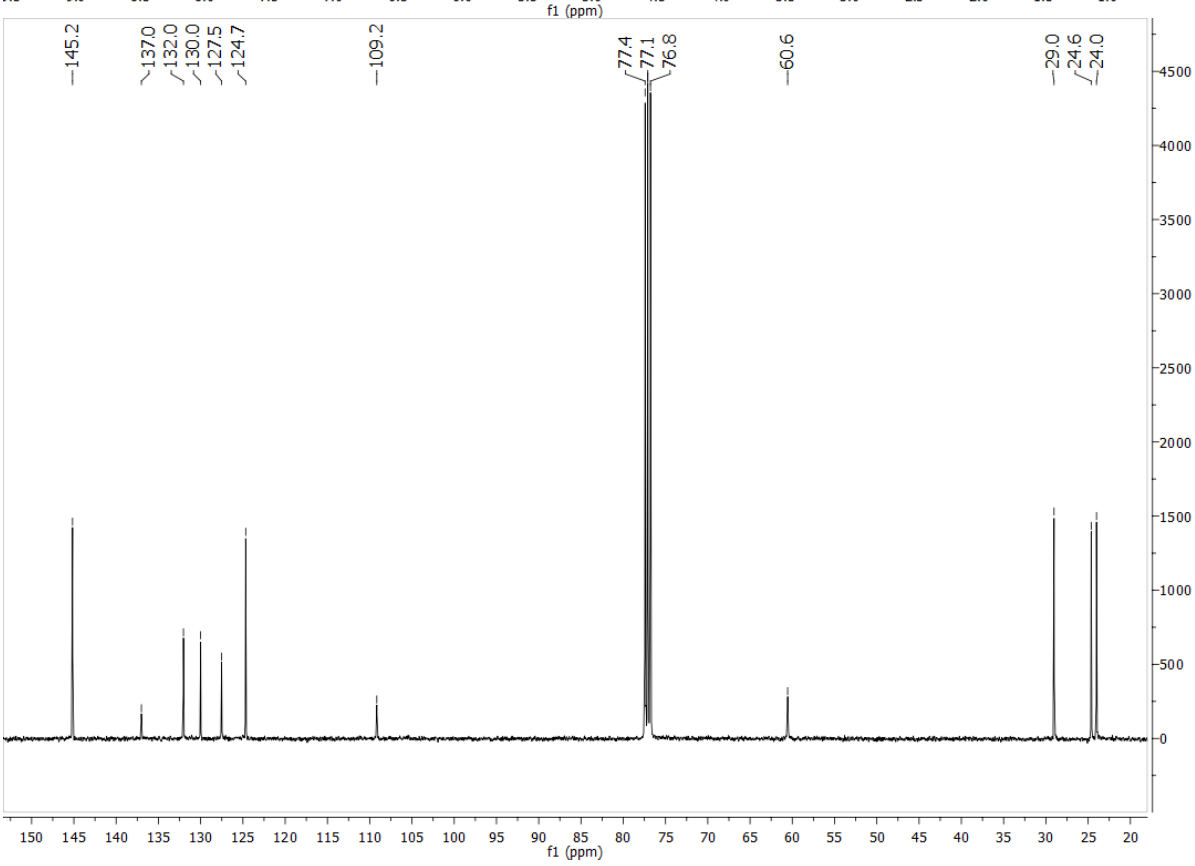
[IPrH][Pd(η^3-cin)Cl_2] ^1H and ^{13}C {^1H}, $CDCl_3$



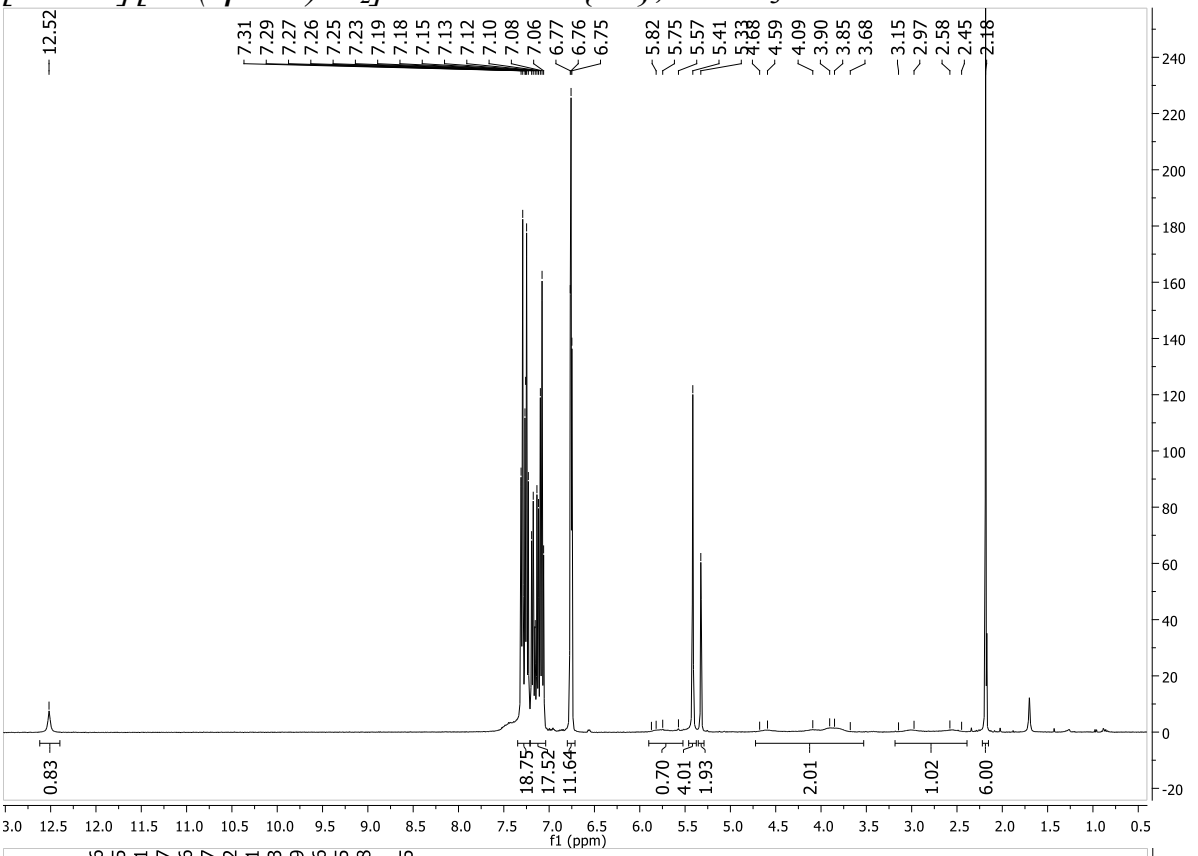


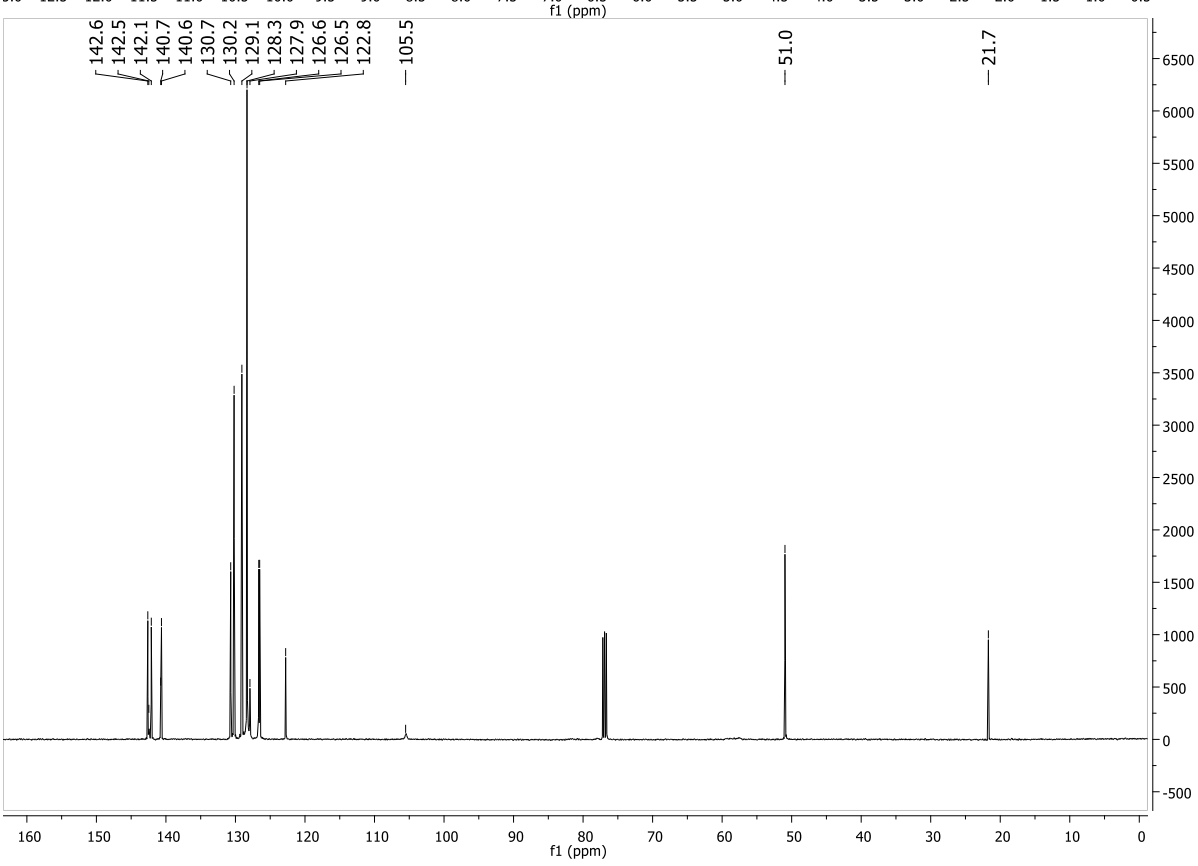
[IPrH][Pd(η³-allyl)Cl₂] ^{1}H and $^{13}C\{^{1}H\}$, $CDCl_3$



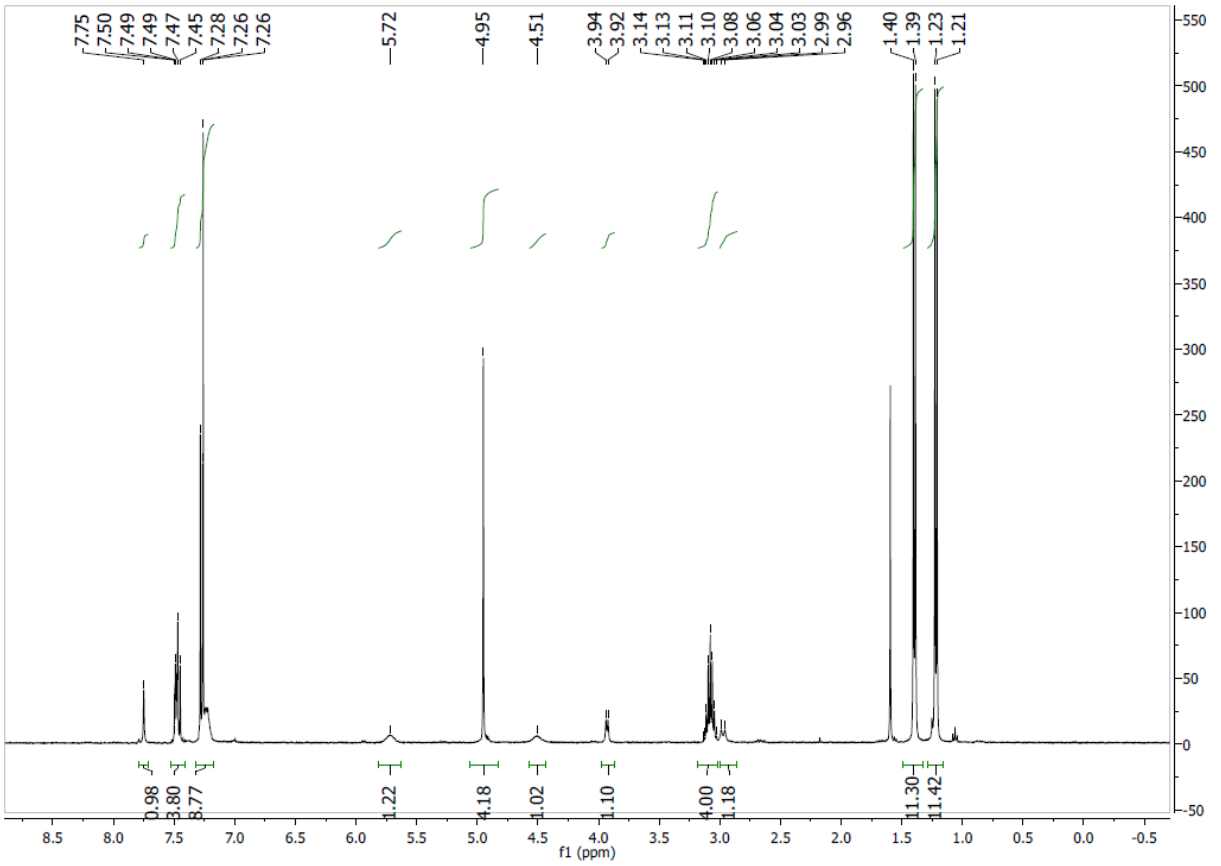


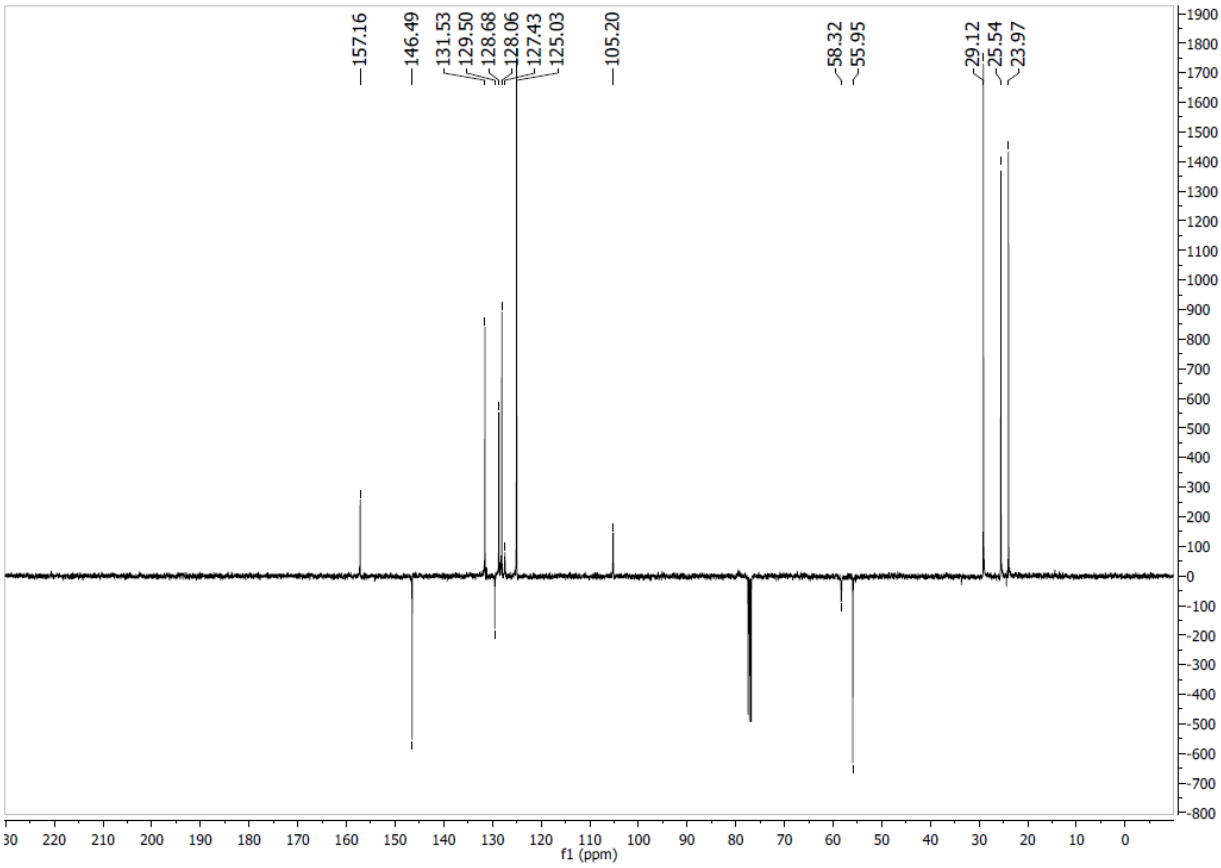
*[IPr*H][Pd(η³-cin)Cl₂] ^{1}H and $^{13}C\{^{1}H\}$, $CDCl_3$*



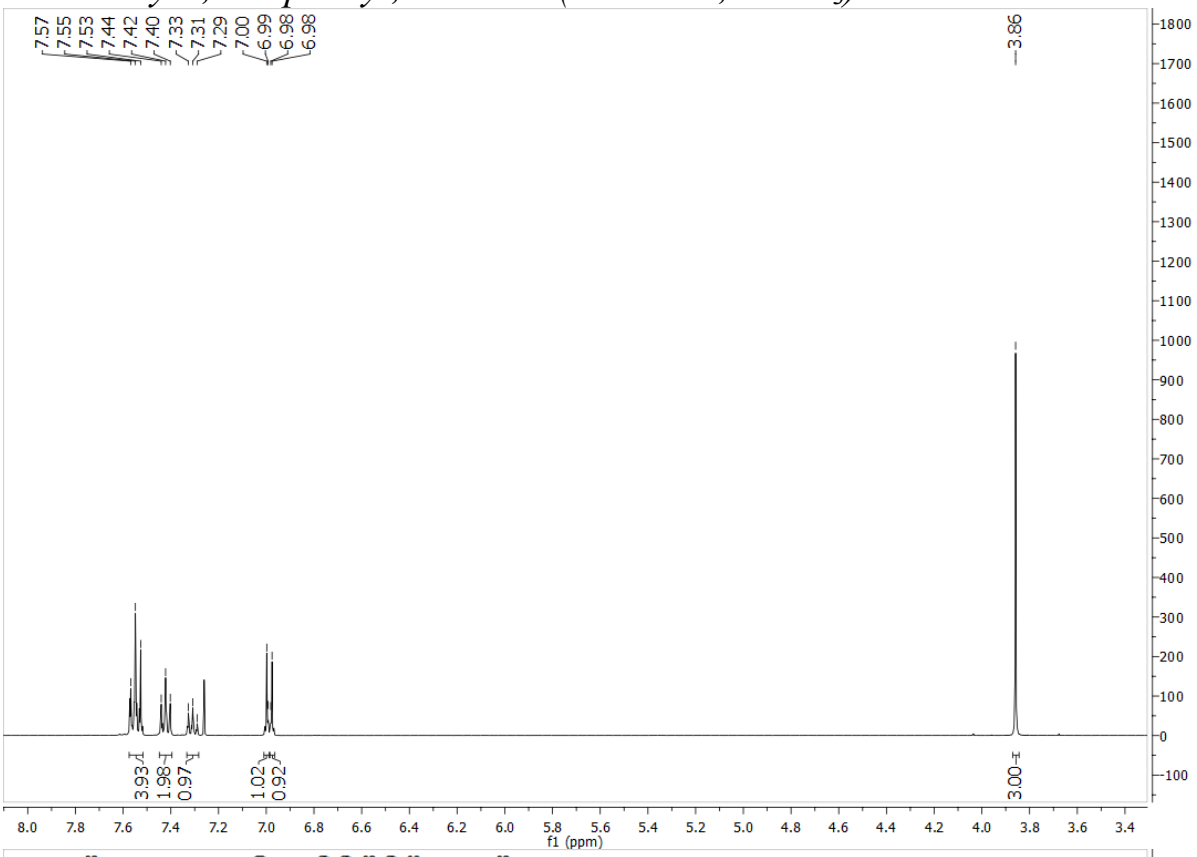


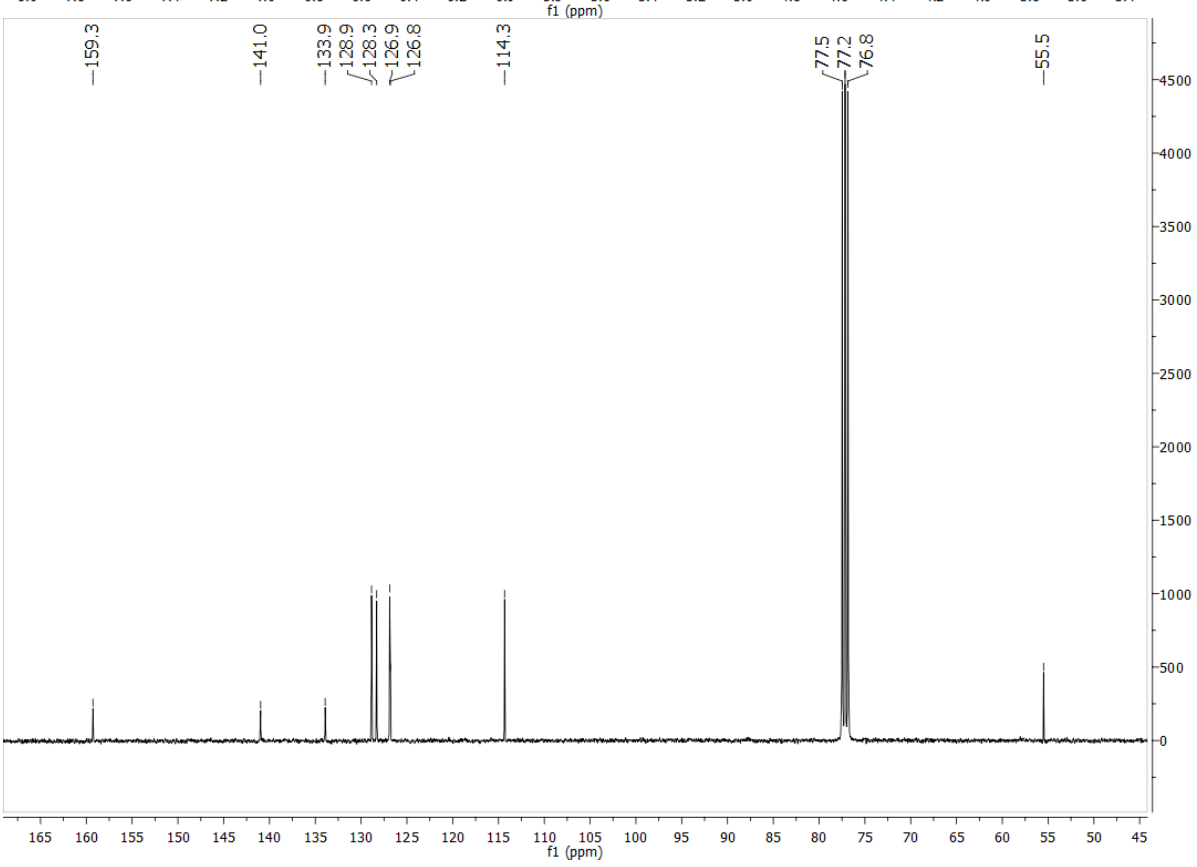
[SIPrH][Pd(η³-cin)Cl₂] ^{1}H and $^{13}C\{^{1}H\}$, $CDCl_3$



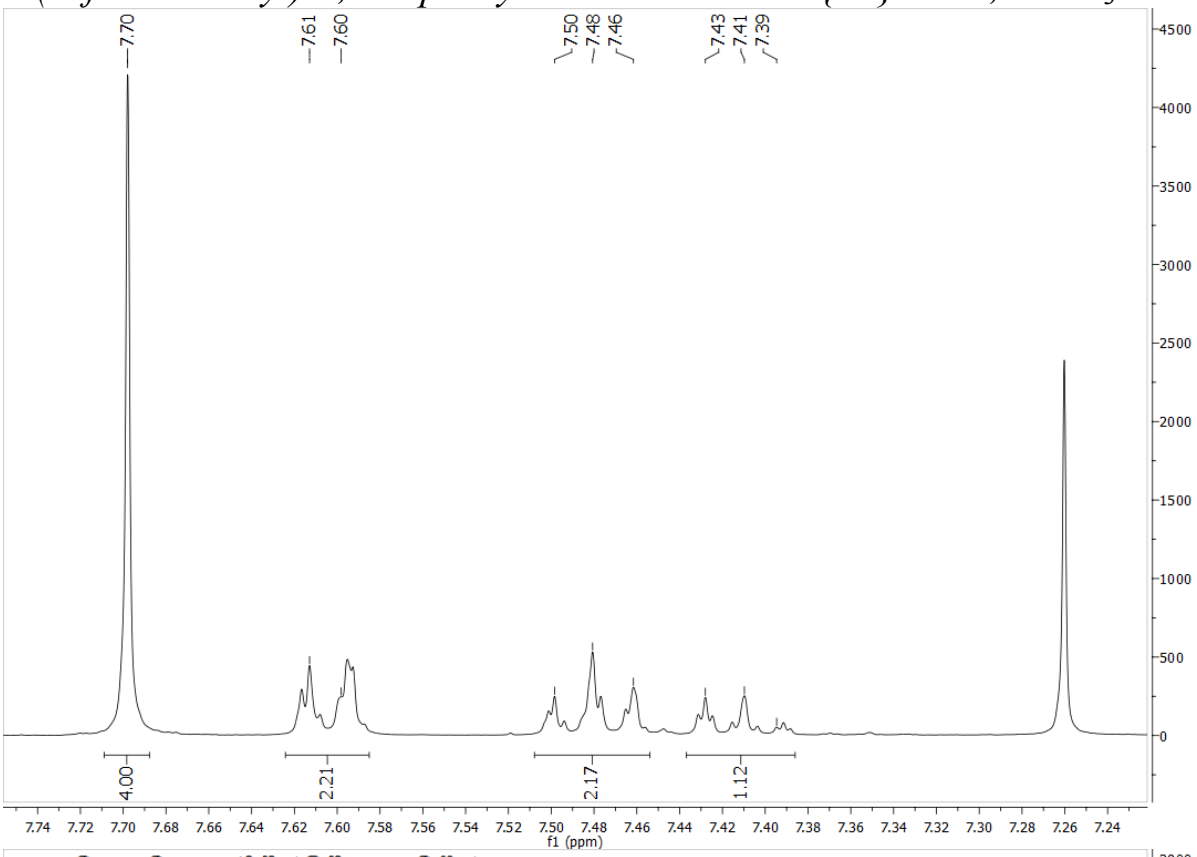


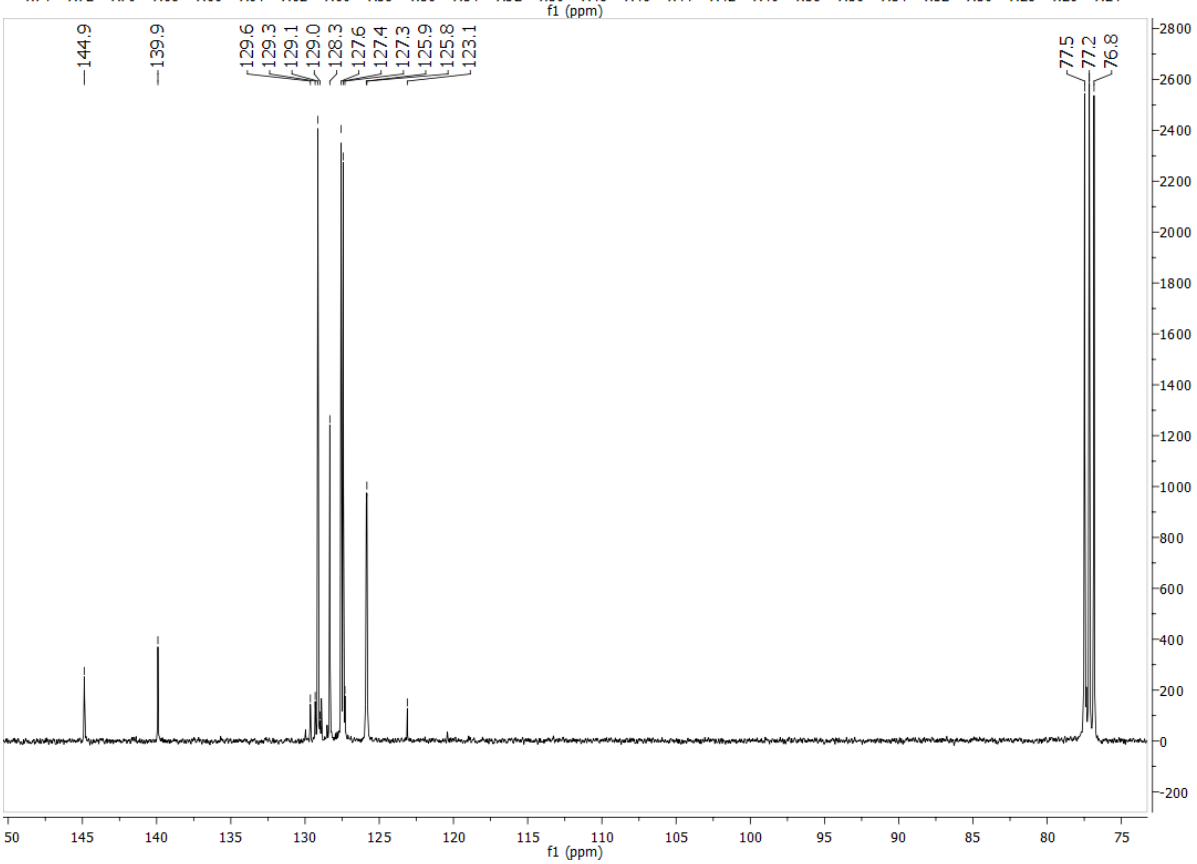
4-methoxy-1,1'-biphenyl, ^{1}H NMR (400 MHz, $CDCl_3$):



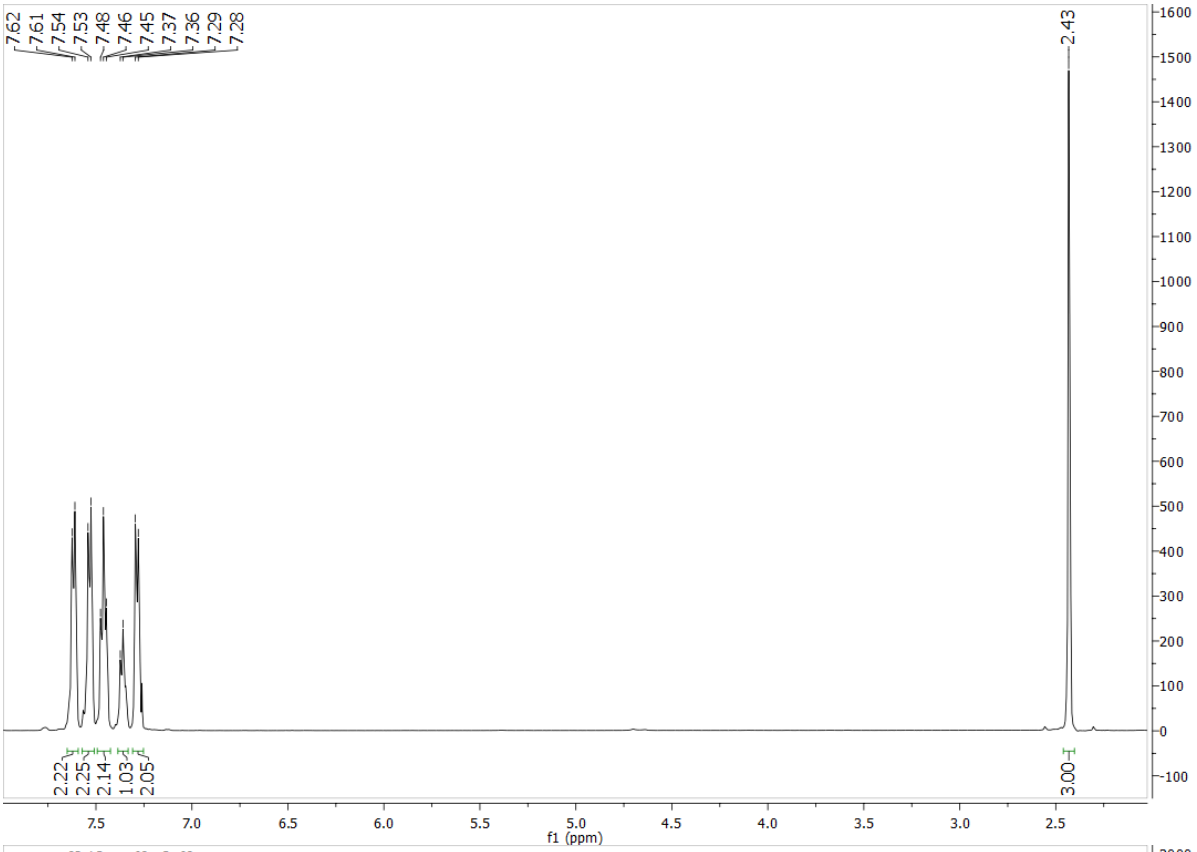


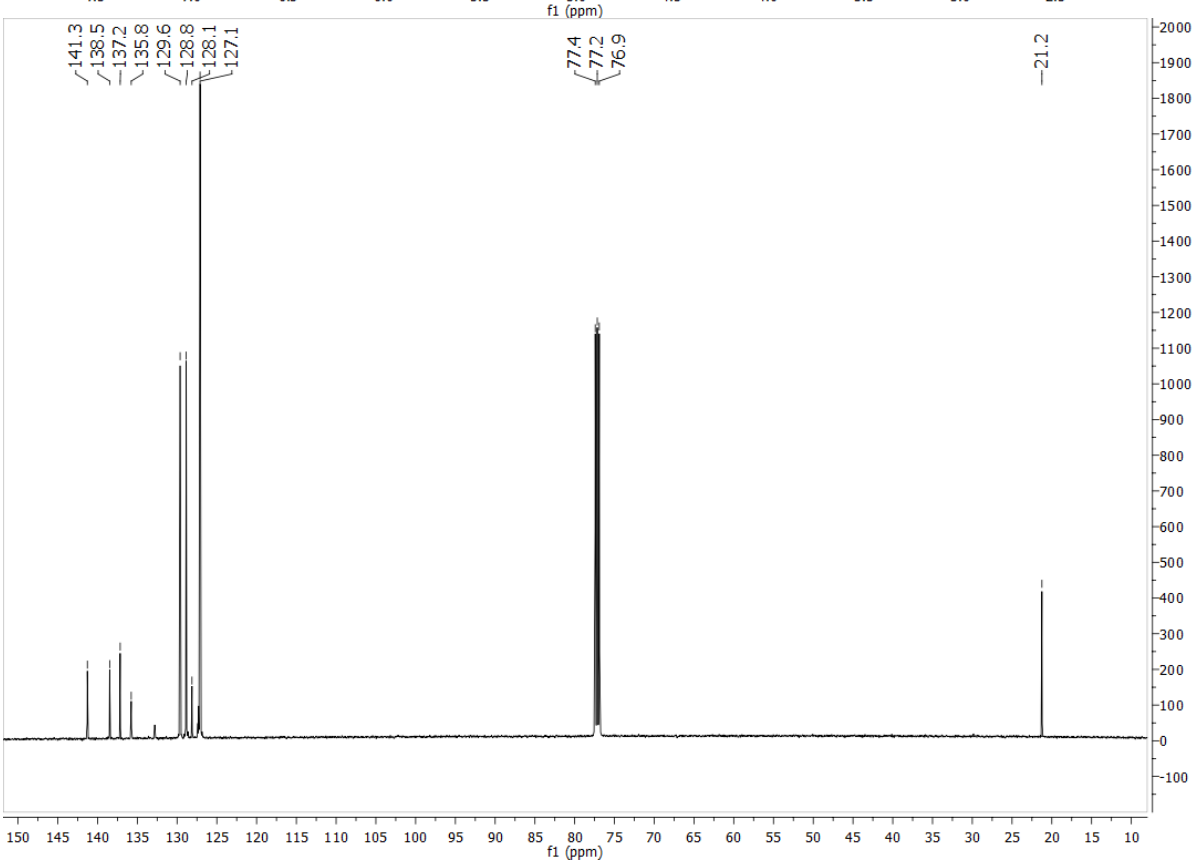
4-(trifluoromethyl)-1,1'-biphenyl ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR, $CDCl_3$



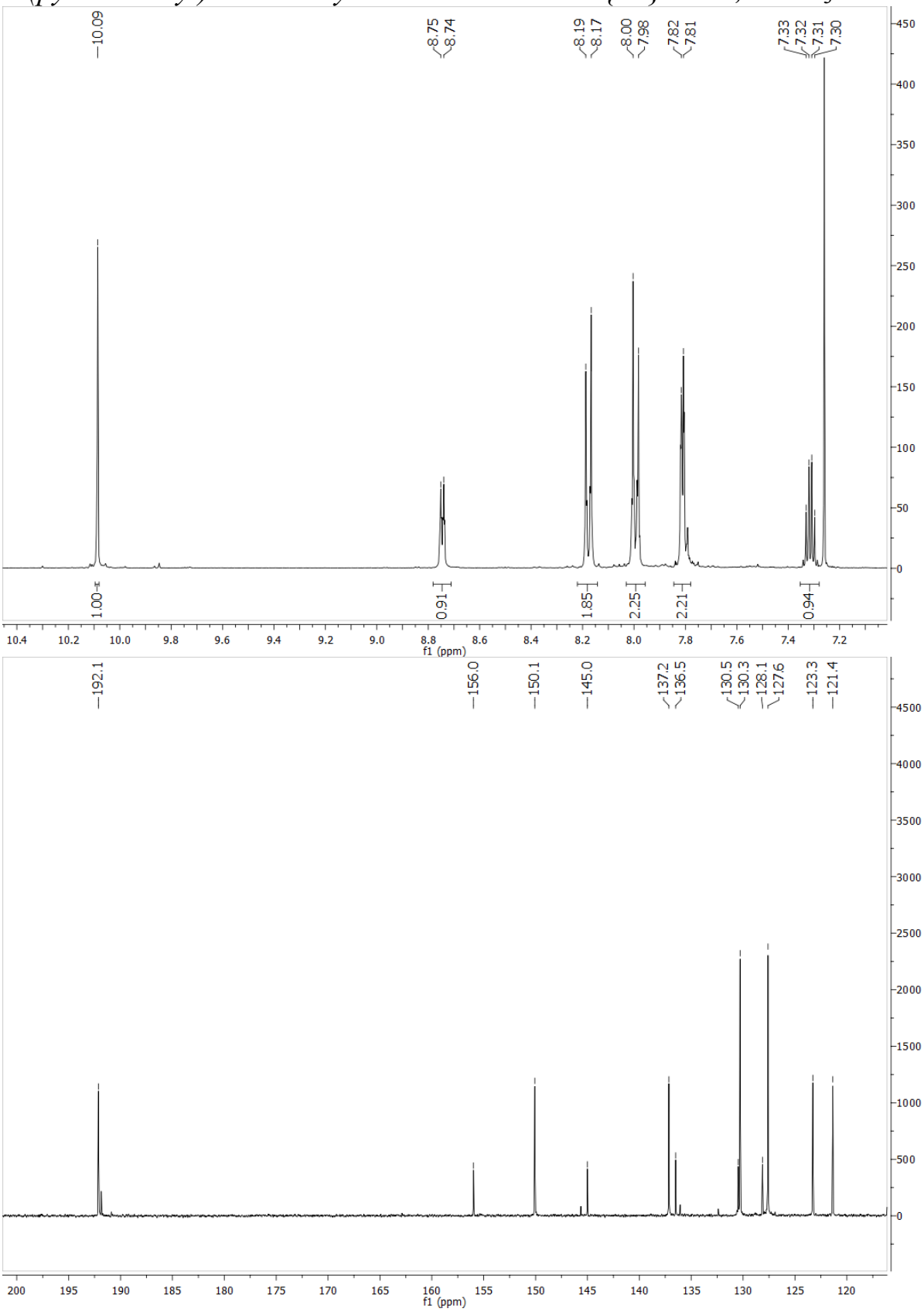


4-methyl-1,1′-biphenyl ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR, $CDCl_3$

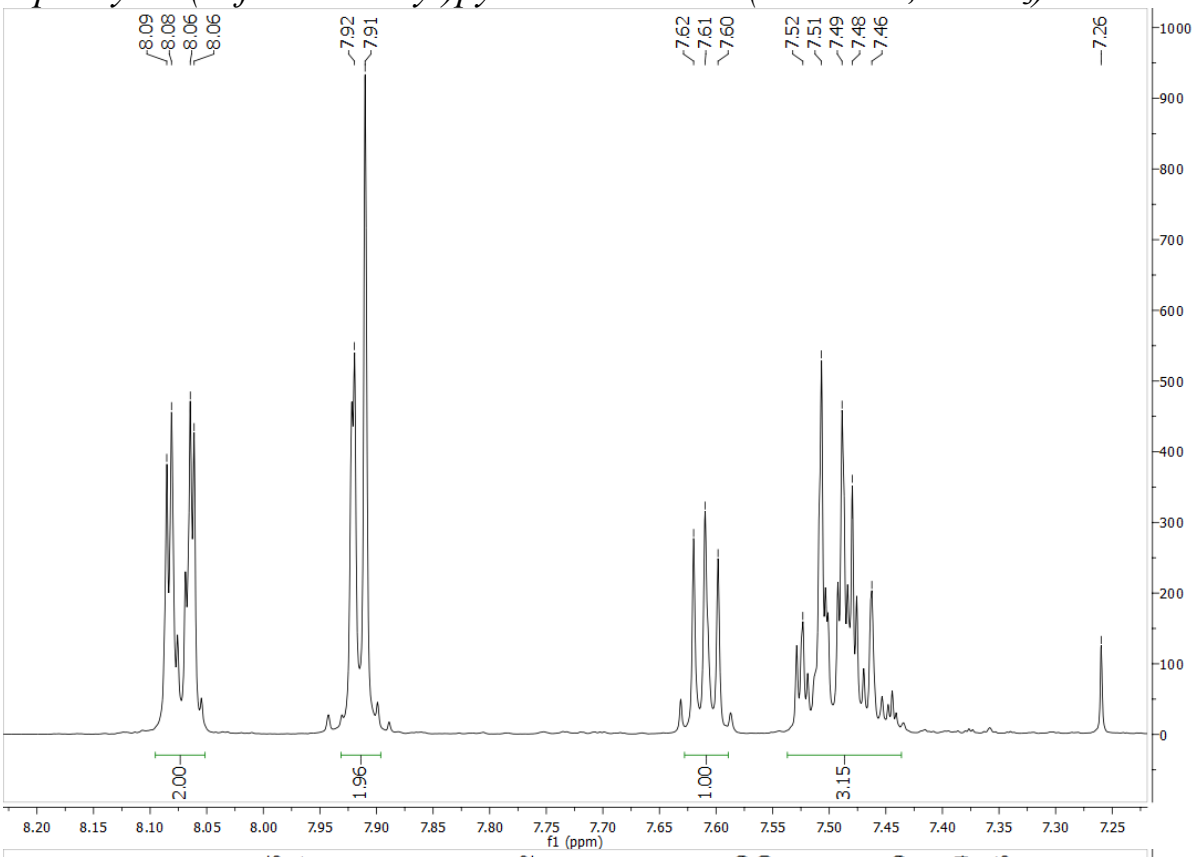


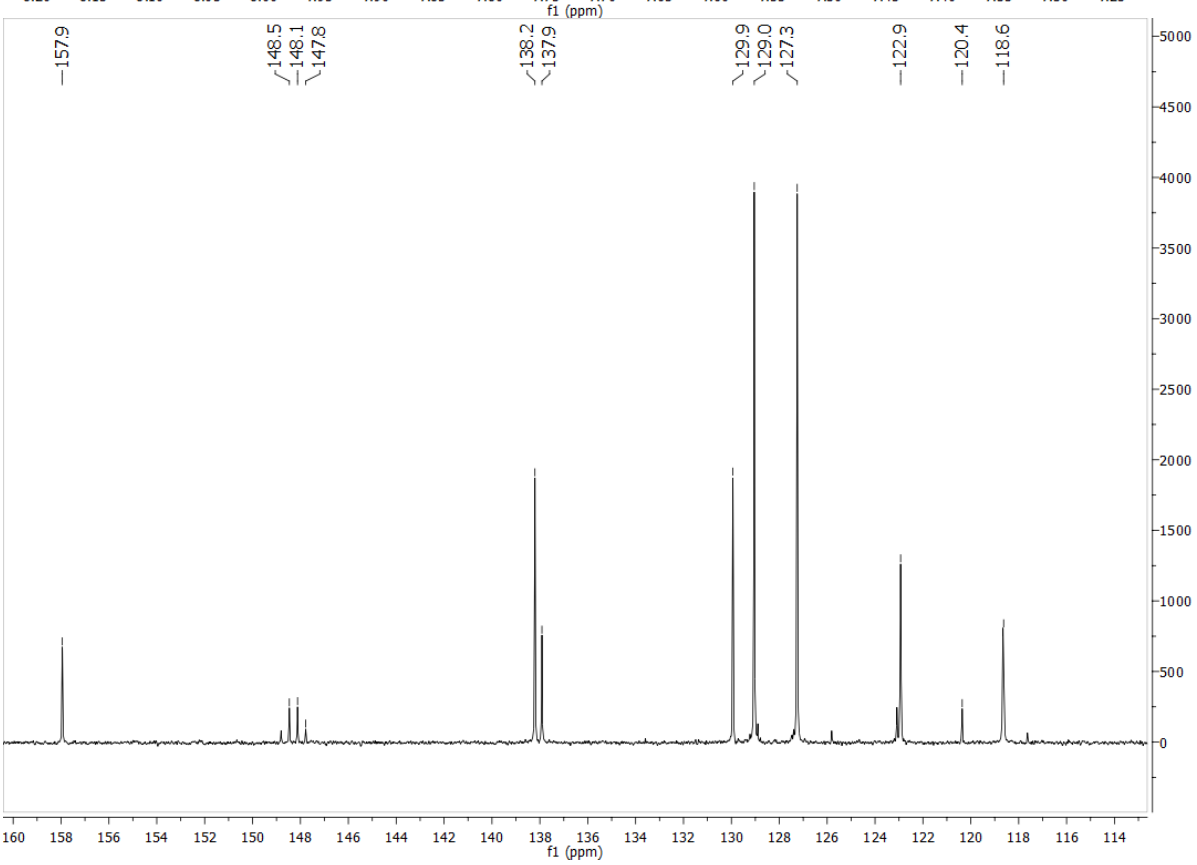


4-(pyridine-2-yl)benzaldehyde ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR, $CDCl_3$

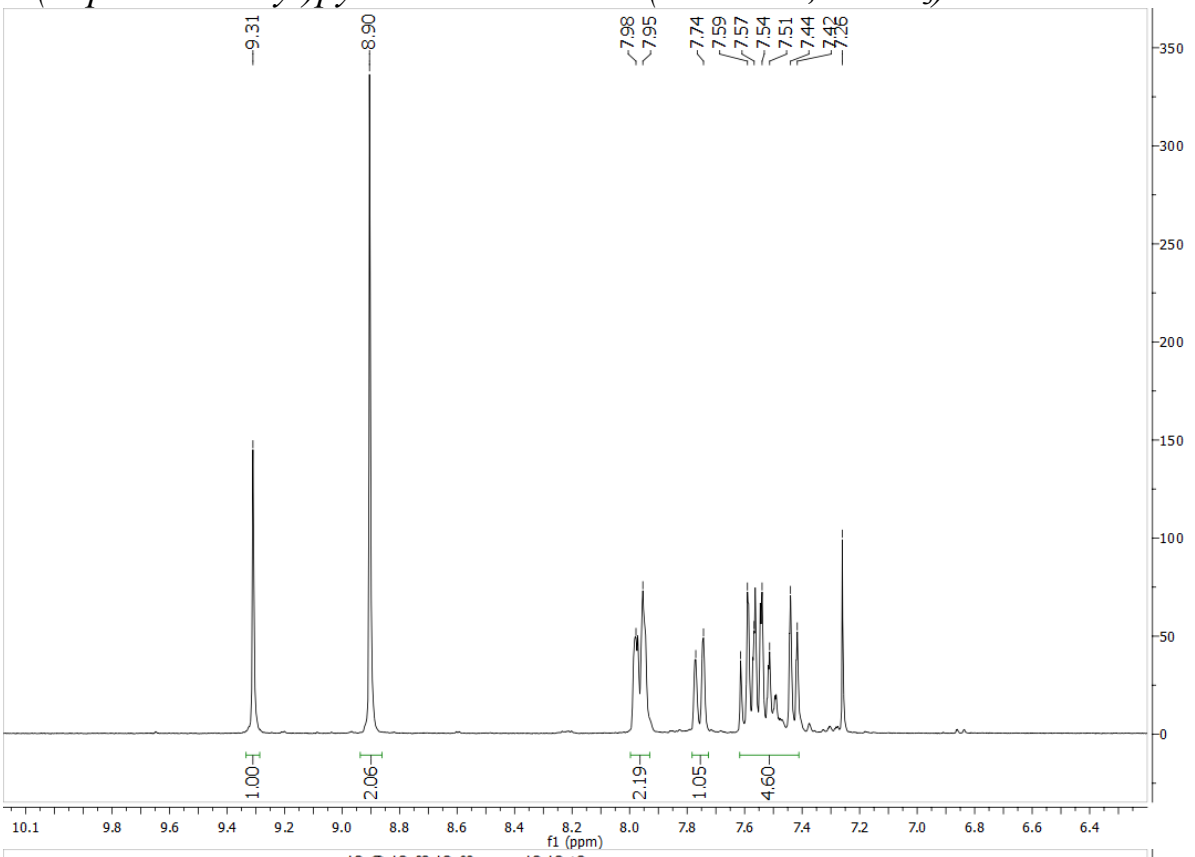


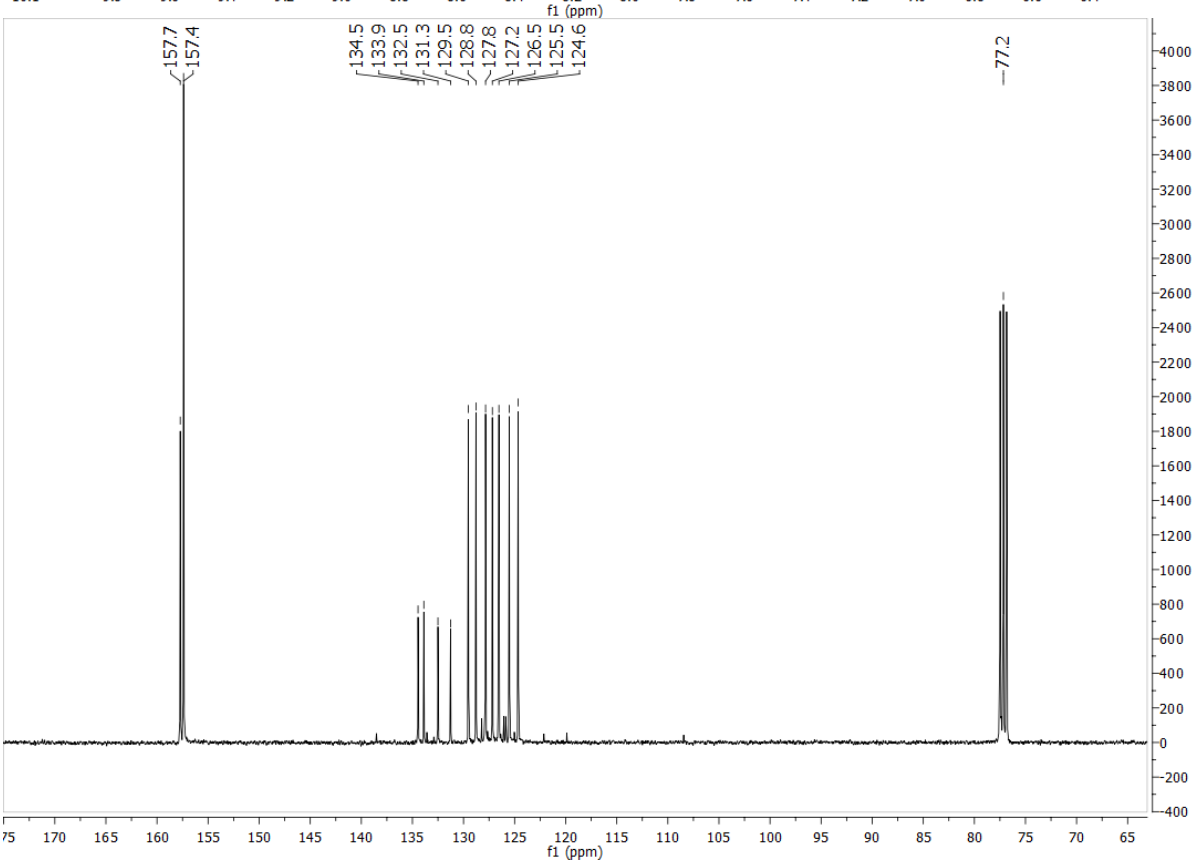
2-phenyl-6-(trifluoromethyl)pyridine ^{1}H NMR (400 MHz, $CDCl_3$)



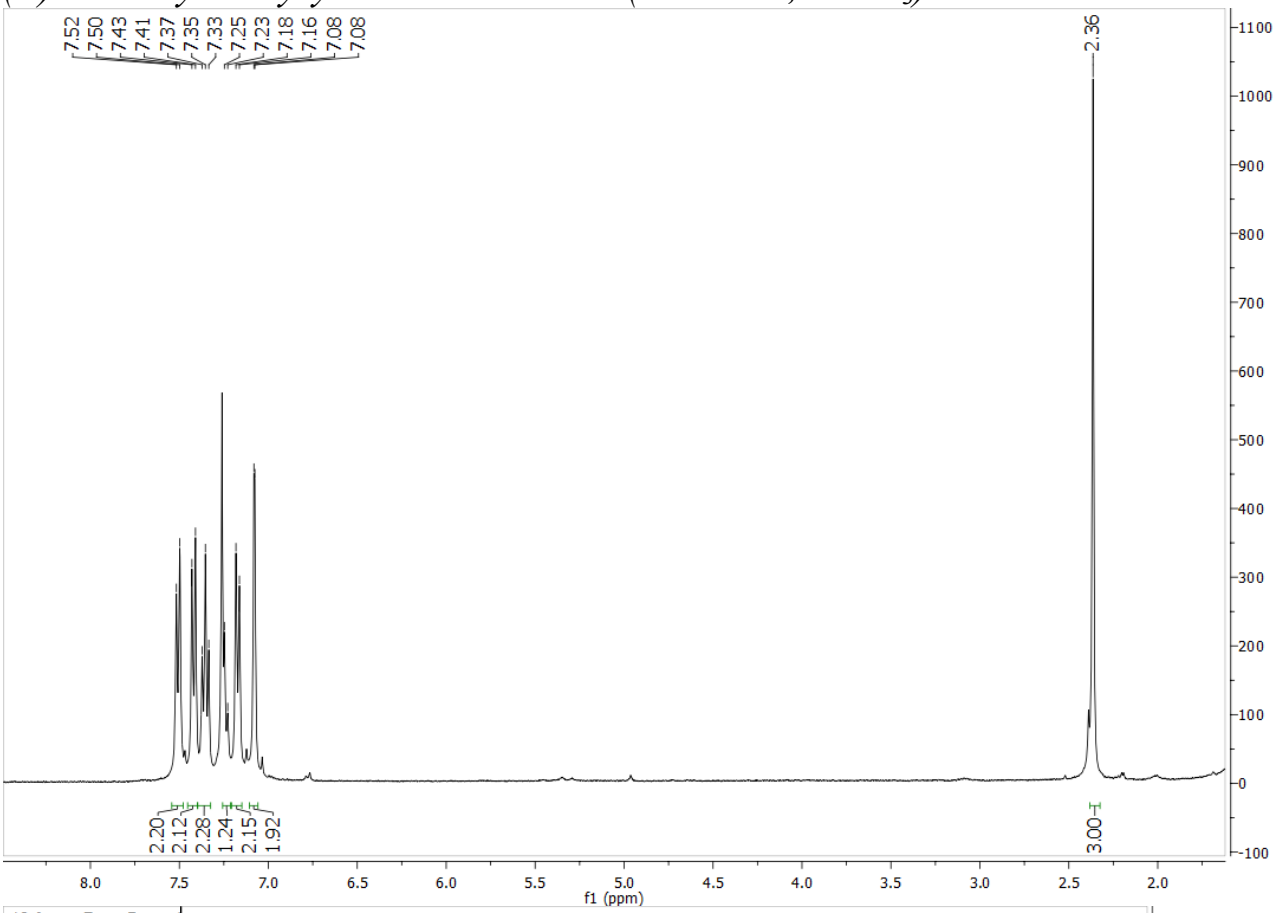


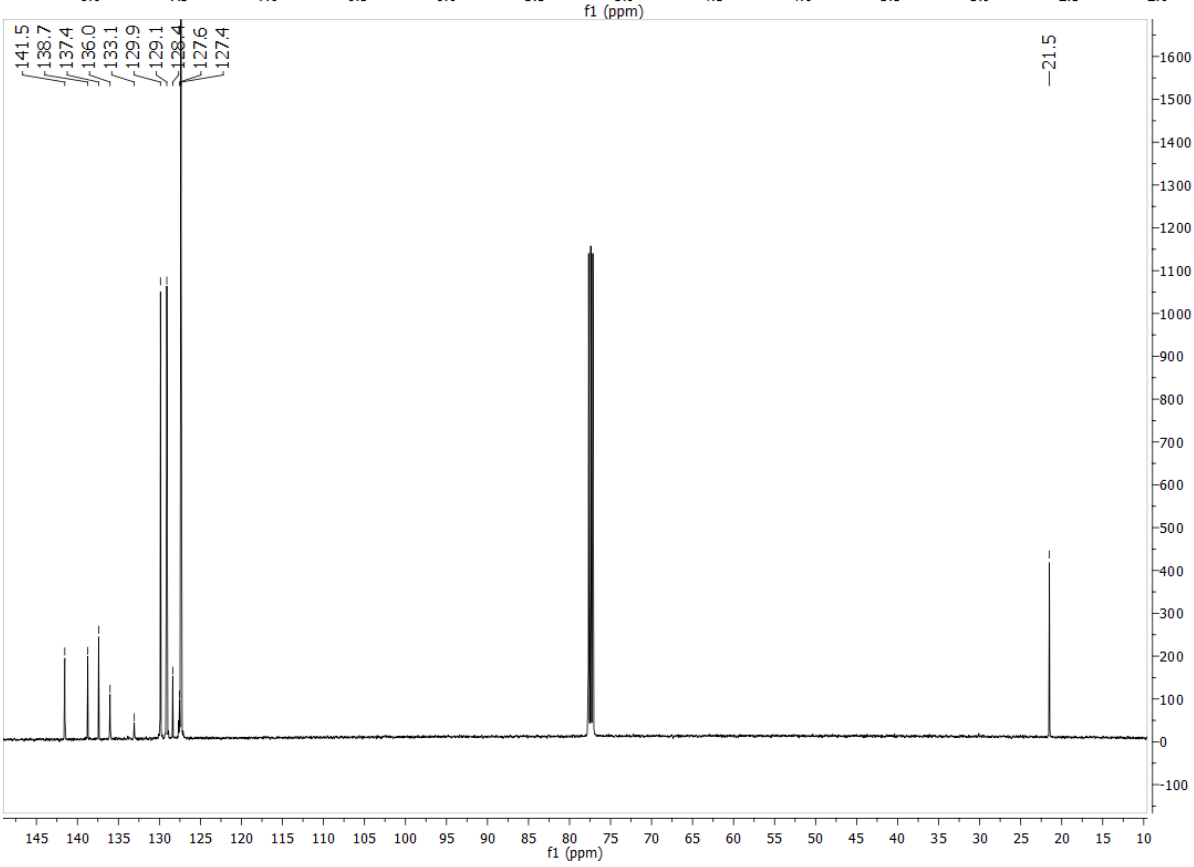
5-(naphthalen-1-yl)pyrimidine ^{1}H NMR (400 MHz, $CDCl_3$)



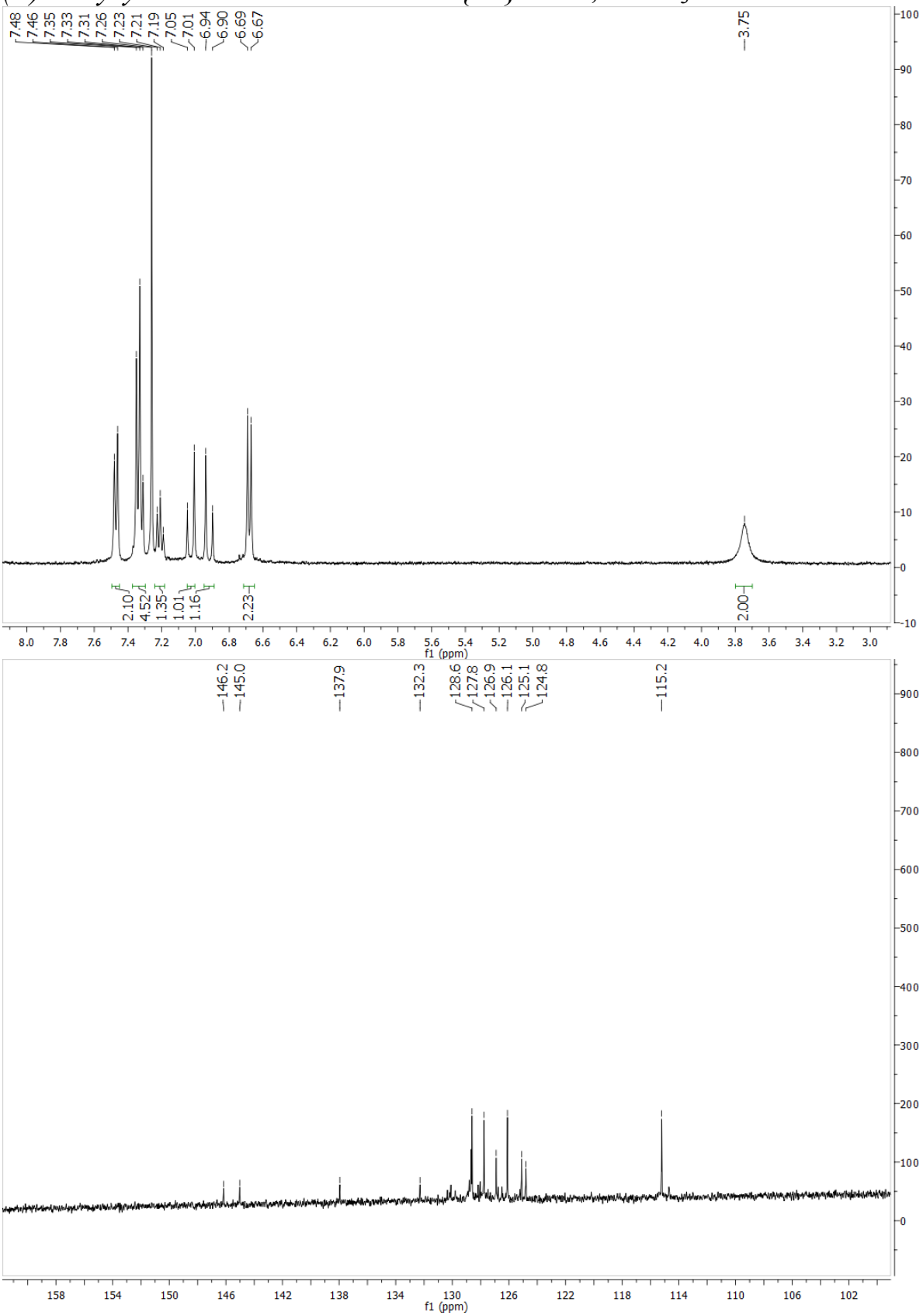


(E)-1-methyl-4-styrylbenzene ^{1}H NMR (400 MHz, $CDCl_3$)

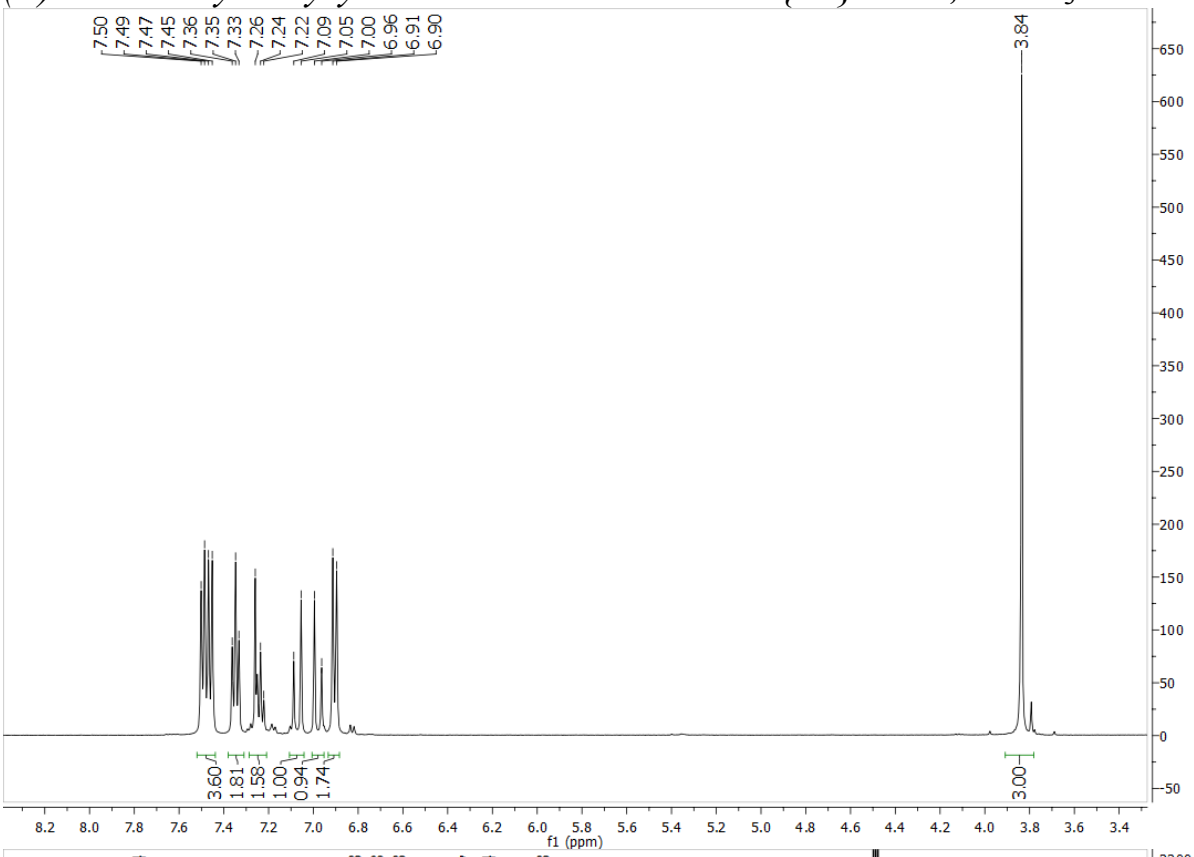


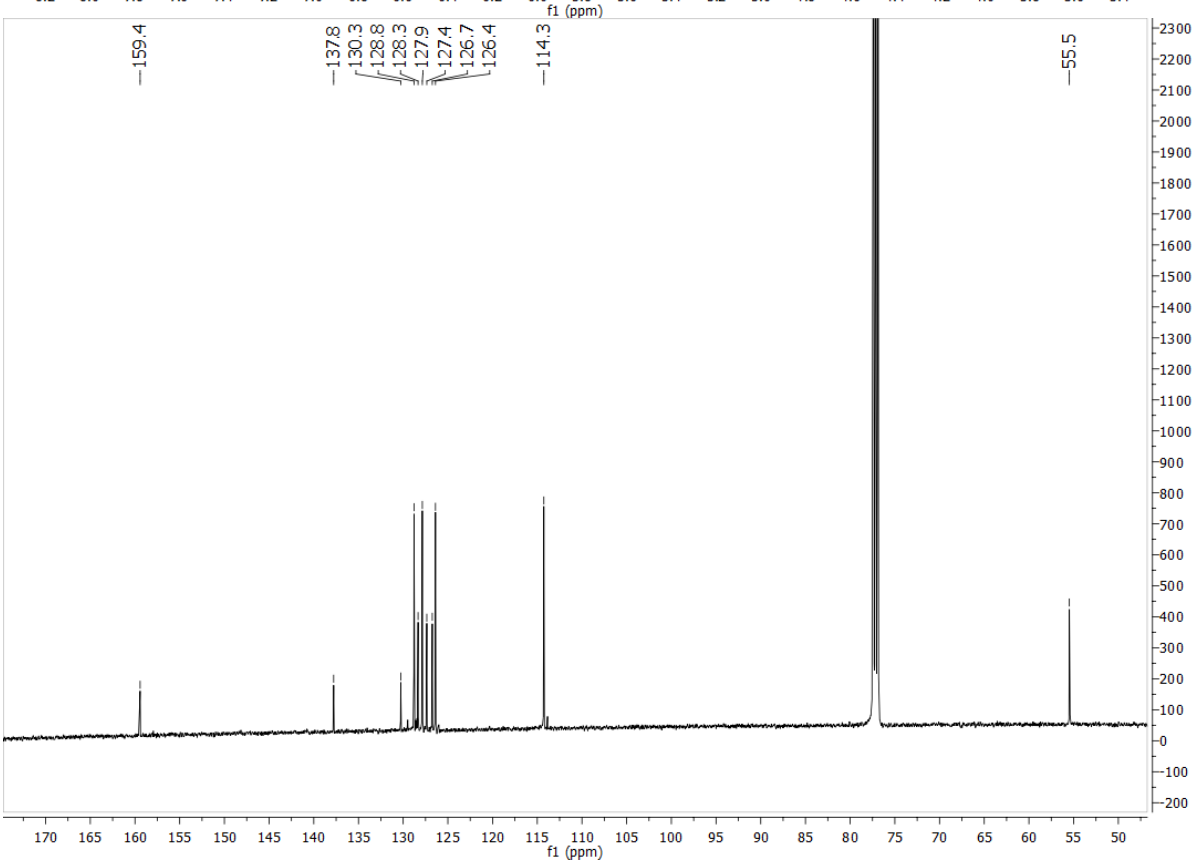


(E)-4-styrylaniline ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR, $CDCl_3$



(E)-1-methoxy-4-styrylbenzene ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR, $CDCl_3$





References

1. N. Marion, O. Navarro, J. Mei, E. D. Stevens, N. M:Scott, S. P. Nolan, *J. Am. Chem. Soc.* **2006**, *128*, 4101.
2. M. S. Viciu, O. Navarro, R. F. Germaneau, R. A. Kelly III, W. Sommer, N. Marion, E. D. Stevens, L. Cavallo, S. P. Nolan, *Organometallics* **2004**, *23*, 1629.
3. A. Chartoire, M. Lesieur, L. Falivene, A. M. Z. Slawin, L. Cavallo, C. S. J. Cazin, S. P. Nolan, *Chem. Eur. J.* **2012**, *18*, 4517.
4. S. Dierdrich, D. F. Dewez, I. E. Marko, *Organometallics* **2014**, 33, 3, 677.
5. S. Meiries, G. Le Duc, A. Chartoire, A. Collado, K. Speck, K. S. A. Arachchige, A. M. Z. Slawin, S. P. Nolan, *Chem. Eur. J.* **2013**, *19*, 17358.
6. G. Bastug, S. P. Nolan, *Organometallics* **2014**, *33*, 1253.
7. F. Izquierdo, M. Corpet and S. P. Nolan, *Eur. J. Org. Chem.* **2015**, 1920.
8. Y. Zou, G. Yue, J. Xu, J. Zhou, *Eur. J. Org. Chem*. **2014**, 5901.
9. P. Petiot, A. Gagnon, *Eur. J. Org. Chem.* **2013**, 5282.
10. S. Handa, M. P. Andersson, F. Gallou, J. Reille, B. H. Lipshutz, *Angew. Chem. Int. Ed.* **2016**, *55*, 4914.
11. U. I. Tessin, X. Bantreil, O. Songis, C.S.J. Cazin, *J. Inorg. Chem.* **2013**, 2007.
12. Y. Tang, Y. Zeng, O. Hu, F. Huang, L. Jin, W. Mo, N. Sun, B. Hu, Z. Shen, X. Hu, W. Sun, *Adv. Synth. Catal.* **2016**, *358*, 2642.