SUPPORTING INFORMATION
for

Palladate pre-catalysts for the formation of C-N and C-C bonds

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1. General information

All aryl halides and boronic acids were used as received. All bases were used as received (in air) or dried under vacuum at 100 °C (under inert atmosphere). All solvents were used as received when experiments were conducted in air. Degassed solvents were used when experiments were conducted under inert atmosphere. All $[\text{NHC}\cdot\text{H}][\text{Pd}(\text{R-allyl})\text{Cl}_2]$ were prepared from commercially available $\text{NHC}\cdot\text{HCl}$ and $[\text{Pd}(\text{R-allyl})\text{Cl}]_2$.

Flash chromatography was performed on silica gel 60 Å pore diameter and 40-63 µm particles size.

^1H , $^{19}\text{F}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker-400 and 500 MHz spectrometers at 298K in CDCl_3 , purchased from Acros and dried over molecular sieves. Chemical shifts (expressed in parts per million, ppm) are referenced to the residual solvent peak. Coupling constants, J , are given in hertz. Abbreviations used in the designation of the signals: s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, t = triplet, td = triplet of doublets, m = multiplet,

Elemental analyses were performed at London Metropolitan University 166-220 Holloway Road, London, N7 8DB.

2. Synthesis of $[\text{NHC}\cdot\text{H}][\text{Pd}(\eta^3\text{-R-allyl})\text{Cl}_2]$ complexes

General procedure:

In air, the $\text{NHC}\cdot\text{HCl}$ and $[\text{Pd}(\eta^3\text{-R-allyl})(\mu\text{-Cl})_2]$ were added to a mortar. The two solids were mixed and grinded using a pestle for 5 min. A crystalline solid was obtained.

Synthesis of $[\text{IPr}\cdot\text{H}][\text{Pd}(\eta^3\text{-cin})\text{Cl}_2]^1$

Following the general procedure from $\text{IPr}\cdot\text{HCl}$ (82.1 mg, 0.19 mmol) and $[\text{Pd}(\eta^3\text{-cin})(\mu\text{-Cl})_2]$ (35.3 mg, 0.09 mmol), the product was obtained as a yellow powder in 99% yield (117. mg).

^1H NMR (400 MHz, CDCl_3): δ (ppm) = δ 9.19 (s, 1H, C_{NCHN}), 8.32 (d, J = 1.6 Hz, 2H, CH_{Imid}), 7.54 (t, J = 8.1 Hz, 2H, CH_{Ar}), 7.45 (dd, J = 6.1 Hz, 2H, $\text{CH}_{\text{Ar(cin)}}$), 7.33 (d, J = 7.9 Hz, 4H, CH_{Ar}), 7.21 (m, 3H, $\text{CH}_{\text{Ar(cin)}}$), 5.69-5.62 (m, 1H, $\text{CH}_{\text{(cin)}}$), 4.46 (m, 1H, $\text{CH}_{2\text{(cin)}}$), 3.86 (d, J = 6.6 Hz, 1H, $\text{CH}_{2\text{(cin)}}$), 2.90 (d, J = 11.9 Hz, 1H, $\text{CH}_{\text{(cin)}}$), 2.48-2.41 (m, 4H, $\text{CH}_{\text{(IPr)}}$), 1.27 (d, J = 6.8 Hz, 12H, $\text{CH}_3\text{(IPr)}$), 1.19 (d, J = 6.7 Hz, 12H, $\text{CH}_3\text{(IPr)}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3): δ (ppm) = δ 145.1 (C_{Ar}), 136.9 (CH_{NCHN}), 132.1 (CH_{Ar}), 129.9 (C_{Ar}), 128.7 (CH_{cin}), 127.9 (CH_{cin}), 127.7 (CH_{Imid}), 124.7 (CH), 105.2 (CH_{cin}), 81.8 (CH_{cin}), 58.4 ($\text{CH}_{2\text{(cin)}}$), 29.0 ($\text{CH}_{\text{(IPr)}}$), 24.7 ($\text{CH}_3\text{(IPr)}$), 23.9 ($\text{CH}_3\text{(IPr)}$).

Anal. Calcd. for $\text{C}_{36}\text{H}_{46}\text{Cl}_2\text{N}_2\text{Pd}$: C 63.21, H 6.78, N 4.10. Found: C 63.11, H 6.95, N 4.14.

Synthesis of $[\text{IPent}\cdot\text{H}][\text{Pd}(\eta^3\text{-cin})\text{Cl}_2]^1$

Following the general procedure from $\text{IPent}\cdot\text{HCl}$ (62.2 mg, 0.12 mmol) and $[\text{Pd}(\eta^3\text{-cin})(\mu\text{-Cl})_2]$ (30. mg, 0.06 mmol), the product was obtained as a yellow powder in 99% (92 mg).

^1H NMR (400 MHz, CDCl_3): δ (ppm) = δ 8.43 (d, J = 1.6 Hz, 2H, CH_{Imid}), 8.37 (br. s, 1H, C_{NCHN}), 7.60 (t, J = 7.9 Hz, 2H, CH_{Ar}), 7.50 (d, J = 7.5 Hz, 2H, $\text{CH}_{\text{Ar(cin)}}$), 7.27 (m, 7H, CH_{Ar}), 5.75 (br. s, 1H, $\text{CH}_{\text{(cin)}}$), 4.60 (br. s, 1H, $\text{CH}_{2\text{(cin)}}$), 3.93 (br. s, 1H, $\text{CH}_{2\text{(cin)}}$), 3.00 (br. s, 1H, $\text{CH}_{\text{(cin)}}$), 1.96 (sept, J = 8.1 Hz, 4H, $\text{CH}_{\text{(IPent)}}$), 1.75-1.60 (m, 16H, $\text{CH}_2\text{(IPent)}$), 0.86 (t, J = 7.1 Hz, 12H, $\text{CH}_3\text{(IPent)}$), 0.76 (t, J = 7.4 Hz, 12H, $\text{CH}_3\text{(IPent)}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) = δ 142.7 (C_{Ar}), 134.9 (CH_{NCHN}), 132.8 (C_{Ar}), 132.0 (CH_{Ar}), 129.2 (CH_{cin}), 128.9 (CH_{cin}), 128.3 (C_{cin}), 128.1 (CH_{Imid}), 125.4 (CH_{Ar}), 105.6 (CH_{cin}), 81.2 (CH_{cin}), 59.2 ($\text{CH}_{2\text{(cin)}}$), 43.5 ($\text{CH}_{\text{(IPent)}}$), 29.4 ($\text{CH}_2\text{(IPent)}$), 28.5 ($\text{CH}_2\text{(IPent)}$), 12.6 ($\text{CH}_3\text{(IPent)}$), 12.4 ($\text{CH}_3\text{(IPent)}$).

Anal. Calcd. for $C_{44}H_{62}Cl_2N_2Pd \cdot 0.33CH_2Cl_2$: C 64.57, H 7.66, N 3.40. Found: C 64.77, H 7.94, N 3.68. Traces of DCM in the final the compound proved highly difficult to completely remove.

Synthesis of $[IPr^* \cdot H][Pd(\eta^3\text{-cin})Cl_2]^1$

Following the general procedure from $IPr^* \cdot HCl$ (108.6 mg, 0.12 mmol) and $[Pd(\eta^3\text{-cin})(\mu\text{-Cl})_2]$ (30.0 mg, 0.06 mmol), the product was obtained as a yellow powder in 99% yield (147.0 mg).

1H NMR (400 MHz, $CDCl_3$): δ (ppm) = δ 12.52 (s, 1H, C_{NCHN}), 7.31-7.23 (m, 20H, CH_{Ar}), 7.19-7.06 (m, 19H, CH_{Ar}), 6.77-6.75 (m, 10H, CH_{Ar}), 5.87-5.75 (br. m, 1H, CH_{cin}), 5.41 (s, 4H, CH_{IPr}), 5.33 (s, 2H, CH_{cin}), 4.60-3.85 (br. m, 2H, CH_{cin}), 2.97-2.58 (m, 1H, CH_{cin}), 2.18 (s, 6H, CH_3).

^{13}C { 1H } NMR (100 MHz, $CDCl_3$): δ (ppm) = δ 142.6 (C_{Ar}), 142.5 (CH_{NCHN}), 142.1 (C_{Ar}), 140.7 (C_{Ar}), 140.6 (C_{Ar}), 130.7 (CH_{Ar}), 130.2 (CH_{Ar}), 129.1 (CH_{Ar}), 128.3 (CH_{Ar}), 127.9 (CH_{Ar}), 126.6 (CH_{Ar}), 126.5 (CH_{Ar}), 122.8 (CH_{imid}), 105.6 (CH_{cin}), 82.2 (CH_{cin}), 59.3 (CH_{cin}), 51.0 ($CH_{(IPr^*)}$), 21.7 ($CH_3(IPr^*)$).

Anal. Calcd. for $C_{78}H_{66}Cl_2N_2Pd$ C 77.51, H 5.50, N 2.32; Found: C 77.25, H 5.47, N 2.36.

3. Optimization of the Buchwald-Hartwig Reaction

General procedure

In a glovebox, a vial was charged with the pre-catalyst, base, solvent (1 mL) and a magnetic stir bar and sealed with a screw cap. The mixture was let to stir at the 110 °C for the stated time (10 mins – 1 h, **activation time**). The sample was removed from the heating block and the corresponding aniline was added followed by the corresponding aryl chloride. The reaction was left stirring (910 rpm) for 16 h at varying temperatures.

3.1. Catalyst screening

The general procedure was followed using 4-fluoroaniline (61.1 mg, 0.55 mmol), 4-chloroanisole (61 μ L, 0.5 mmol) with KO^tAm (69.8 mg, 0.55 mmol) in 1,4-dioxane (1 mL) with activation and experimental temperatures at 110 °C.

Table S1: Optimisation of Pd pre-catalyst for 0.2 - 0.5% mol reaction

Entries	Pd pre-catalyst	Mass (mg)	Catalyst loading (mol%)	GC Conversion ^{a,b} (%)
1	$[IPent \cdot H][Pd(\eta^3\text{-cin})Cl_2]$	2.0	0.5	86
2	$[IHept \cdot H][Pd(\eta^3\text{-cin})Cl_2]$	2.3	0.5	88
3	$[INon \cdot H][Pd(\eta^3\text{-cin})Cl_2]$	2.6	0.5	93
4	$[IPr^* \cdot H][Pd(\eta^3\text{-cin})Cl_2]$	3.0	0.5	99
5	$[Pr^{*OMe} \cdot H][Pd(\eta^3\text{-cin})Cl_2]$	3.1	0.5	95
6	$[IPent^{Cl} \cdot H][Pd(\eta^3\text{-cin})Cl_2]$	2.2	0.5	87
7	$[IPr \cdot H][Pd(\eta^3\text{-cin})Cl_2]$	1.7	0.5	63
8	$[IPr^* \cdot H][Pd(\eta^3\text{-cin})Cl_2]$	3.0	0.5	99
9	$[IPr^* \cdot H][Pd(\eta^3\text{-crotyl})Cl_2]$	2.8	0.5	96
10	$[IPr^* \cdot H][Pd(\eta^3\text{-2-Me-allyl})Cl_2]$	2.8	0.5	95
11	$[IPr^* \cdot H][Pd(Ind^{tBu})Cl_2]$	3.2	0.5	87
12	$[INon \cdot H][Pd(\eta^3\text{-cin})Cl_2]$	2.7	0.5	98

13	[IPr*·H][Pd(η^3 -cin)Cl ₂]	1.2	0.2	99 ^c
14	[IPr*·H][Pd(η^3 -crotyl)Cl ₂]	1.2	0.2	90 ^c
15	[IPr*·H][Pd(η^3 -2-Me-allyl)Cl ₂]	1.2	0.2	88 ^c
16	[IPr*·H][Pd(Ind ^{tBu})Cl ₂]	1.3	0.2	56 ^c
17	[INon·H][Pd(η^3 -cin)Cl ₂]	1.0	0.2	83 ^c

^a GC conversion based on 4-chloroanisole disappearance. Value calculated from an average of two reactions.

^b GC yield, mesitylene is used as internal standard. ^c 0.2 mol% of catalyst used.

3.2. Activation time Optimization

The general procedure was followed using [IPr*·H][Pd(η^3 -cin)Cl₂] (0.5 mol%), 4-fluoroaniline (61.1 mg, 0.55 mmol), 4-chloroanisole (61 μ L, 0.5 mmol) with KO^tAm (69.8 mg, 0.55 mmol) in 1,4-dioxane at 110 °C with varying activation times.

Table S2: Activation time optimization

Entries	Time (min)	GC conversion (%) ^a
1	10	88
2	30	80
3	60	99

^a GC conversion is based on 4-chloroanisole. Value calculated from an average of two reactions.

3.3. Temperature optimization

The general procedure was followed using pre-catalyst (0.5 ml%), 4-fluoroaniline (61.1 mg, 0.55 mmol), 4-chloroanisole (61 μ L, 0.5 mmol) with KO^tAm (69.8 mg, 0.55 mmol) in 1,4-dioxane at with varying activation temperatures for 1 h and varying experimental temperature.

Table S3: Temperature optimisation using [IPr*·H][Pd(η^3 -cin)Cl₂]

Entries	Activation Temperature (°C)	Reaction Temperature (°C)	GC conversion (%) ^a
1	60	60	83
2	70	70	80
3	80	80	92
4	90	90	85
5	70	100	76
6	80	100	85
7	90	100	90
8	100	100	95

^a GC conversion is based on 4-chloroanisole. Value calculated from an average of two reactions

Table S4: Temperature optimisation using [IPr*·H][Pd(η^3 -cin)Cl₂]

Entries	Activation Temperature (°C)	Reaction Temperature (°C)	GC conversion (%) ^a
1	60	80	99
2	80	80	90
2	90	90	88

^a GC conversion is based on 4-chloroanisole. Value calculated from an average of two reactions

3.4. Solvent Optimization

The general procedure was followed using [IPr*·H][Pd(η^3 -cin)Cl₂] (0.5 ml%), 4-fluoroaniline (61.1 mg, 0.55 mmol), 4-chloroanisole (61 μ L, 0.5 mmol) with KO^tAm (69.8 mg, 0.55 mmol) in varying solvents, activating at 80 °C for 1 h and running at 80 °C for 16h.

Table S5: Solvents used in solvent optimisation in air

Entries	Solvent	GC conversion (%) ^a
1	Toluene	80
2	THF	64
3	Ethanol	n.r.
4	<i>iso</i> -Propanol	n.r.
5	<i>n</i> -Butanol	n.r.
6	1,4-Dioxane	93

^a GC conversion based on 4-chloroanisole. Value calculated from an average of two reactions. n.r. = no reaction.

Table S6: Solvents used in solvent optimization under inert atmosphere

Entries	Solvent	GC conversion (%) ^a
1	Toluene	90
2	THF	92
3	<i>iso</i> -Propanol	19
4	Acetonitrile	n.r.

5	Hexane	89
6	1,2-Dimethoxyethane	90
7	1,4-Dioxane	90
8	Cyclohexane	94
9	CPME	97
10	2-MeTHF	87
11	Heptane	87
12	1,4-Dioxane ^b	97
13	THF ^b	99
14	CPME ^b	96
15	Cyclohexane ^b	94
16	Ethanol ^c	n.r.

^a GC conversion based on 4-chloroanisole. Value calculated from an average of two reactions. ^b The substrates were added in reverse order; 4-fluoroaniline followed by 4-chloroanisole. ^c K₂CO₃ as the base.

3.5. Base Optimization

The general procedure was followed using [IPr*·H][Pd(η³-cin)Cl₂] (0.5 mol%), 4-fluoroaniline (61.1 mg, 0.55 mmol), 4-chloroanisole (61 μL, 0.5 mmol) with the corresponding base (0.55 mmol) and corresponding solvent (1 mL), activating at 80 °C for 1 h and running at 80 °C for 16h.

Table S7: Base optimization in 1,4-dioxane

Entries	Base (0.55 mmol)	GC conversion (%) ^a
1	KO ^t Bu	93
2	K ₂ CO ₃	n.r.
3	K ₃ PO ₄	n.r.
4	KOH	57
5	NaOH	45
6	Cs ₂ CO ₃	<1
7	LiOH	n.r.
8	CsOH	22
9	Na ₂ CO ₃	n.r.
10	NaO ^t Bu	91
11	KF/K ₂ CO ₃ (1:1)	n.r.
12	KO ^t Bu ^b	83

^a GC conversion based on 4-chloroanisole. Value calculated from an average of two reactions. ^b The substrates were added in reverse order; 4-fluoroaniline followed by 4-chloroanisole.

Table S8: Base optimization in THF

Entries	Base (0.55 mmol)	GC conversion (%) ^a
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1	KO ^t Am	92
2	KO ^t Bu	98
3	K ₂ CO ₃	n.r.
4	K ₃ PO ₄	n.r.
5	KOH	57
6	NaOH	19
7	Cs ₂ CO ₃	7
8	LiOH	n.r.
9	CsOH	22
10	Na ₂ CO ₃	n.r.
11	KO ^t Bu	99

^a GC conversion based on 4-chloroanisole. Value calculated from an average of two reactions.

Table S9: Base optimization in cyclohexane

Entries	Base (0.55 mmol)	GC conversion (%) ^a
1	KO ^t Am	94
2	KO ^t Bu	86
3	KOH	12
4	NaOH	<1
5	CsOH	n.r.

^a GC conversion based on 4-chloroanisole. Value calculated from an average of two reactions.

Table S10: Base optimization in CPME

Entries	Base (0.55 mmol)	GC Conversion (%) ^a
1	KO ^t Am	99
2	KO ^t Bu	99
3	KOH	42
4	NaOH	32
5	CsOH	38
6	NaO ^t Bu	98

^a GC conversion based on 4-chloroanisole. Value calculated from an average of two reactions.

3.6. Catalyst loading optimization

The general procedure was followed using [IPr*·H][Pd(η³-cin)Cl₂] (mol%), 4-fluoroaniline (61.00 mg, 0.55 mmol), 4-chloroanisole (61.00 μL, 0.50 mmol) with KO^tBu (62.00 mg, 0.55 mmol) in CPME (2 mL), activating at 60 °C for 1 h and running at 80 °C for 16 h. An aliquot was taken to determine the conversion of 4-chloroanisole by GC using mesitylene as internal standard.

Table S11: Catalyst loading optimization

Entries	mol%	GC yield (%) ^a
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1	0.5	99
2	0.5 ^b	70
3	0.3	99
4	0.2	99
5	0.1	50

^aGC yield, internal standard = mesitylene 0.1 mmol. Value calculated from an average of two reactions. ^bno activation step was used.

3.7. Reaction time optimization

The general procedure was followed using [IPr*H][Pd(η^3 -cin)Cl₂] (0.20 mol%), 4-fluoroaniline (61 mg, 0.55 mmol), 4-chloroanisole (61 μ L, 0.50 mmol) with KO^tBu (62.00 mg, 0.55 mmol) in CPME (2 mL), activating at 60 °C for 1 h and running at 80 °C for the corresponding time. An aliquot was taken to determine the conversion of 4-chloroanisole by GC using mesitylene as internal standard.

Table S12: Time optimization

Activation time (min)	Reaction time (min)	GC yield (%)
60	15	30
60	30	34
60	45	43
60	60	75
60	90	83
60	120	99

GC yield, internal standard = mesitylene 0.10 mmol. Value calculated from an average of two reactions.

Figure S1: Time optimization of the Buchwald-Hartwig amination. GC yield, internal standard = mesitylene 0.1mmol. Value calculated from an average of two reactions.

4. Buchwald-Hartwig reaction scope

General procedure

A vial was charged with [IPr*H][Pd(η^3 -cin)Cl₂] (1.2 mg, 0.2 mol%), KO^tBu (62 mg, 0.55 mmol), CPME (1 mL) and a magnetic stir bar and sealed with a screw cap. The mixture was let to stir

at 60 °C for 1 h. The vial was removed from the heating block and the corresponding solution of aniline and aryl chloride in CPME (1 mL) was added. The reaction was left to stir (910 rpm) for 2 h at 80 °C. The crude mixture was purified by a filtration through silica gel.

Compound 4a

Chemical Formula: C₁₃H₁₂FNO

Molecular Weight: 217.24

Following the general procedure, from 4-chloroanisole (71 mg, 0.5 mmol) and 4-fluoroaniline (56 mg, 0.55 mmol), the product yielded 107 mg (99 %) as an oil.

Large scale:

Following the general procedure, from 4-chloroanisole (784 mg, 5.5 mmol) and 4-fluoroaniline (672 mg, 6.05 mmol), the product yielded 1193 mg (99 %) as an oil.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = δ 7.02 (dt, *J* = 9.1 Hz, 2H), 6.95 (m, 6H), 5.38 (s, 1H), 3.80 (s, 3H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = δ 157.2 (d, CF, *J* = 238.1), 155.1 (C), 141.2 (d, C, *J* = 1.9 Hz), 136.6 (C), 121.3 (CH), 117.9 (d, CH, 7.6 Hz), 117.9 (CH), 115.9 (d, CH, *J* = 22.4 Hz), 114.9 (CH), 55.7 (CH₃).

Analytical data obtained were in agreement with the reported values.²

Compound 4b

Chemical Formula: C₁₃H₁₂FN

Molecular Weight: 201.24

Following the general procedure, from 3-chlorotoluene (63 mg, 0.5 mmol) and 3-fluoroaniline (56 mg, 0.55 mmol), the product yielded 99.8 mg (99 %) as an oil.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = δ 7.25 (m, 2H), 6.97 (m, 2H), 6.89 (d, *J* = 8.7 Hz, 1H), 6.81 (m, 2H), 6.65 (t, *J* = 7.1 Hz, 1H), 5.74 (s, 1H), 2.38 (s, 3H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = δ 1632.9 (d, CF, *J* = 243.8 Hz), 145.6 (d, C, 10.55 Hz), 142.0 (C), 139.5 (C), 130.5 (d, CH, *J* = 10.0 Hz), 129.4 (CH), 123.1 (CH), 119.9 (CH), 116.2 (CH), 112.6 (CH), 107.0 (d, CH, *J* = 21.5 Hz), 103.6 (d, CH, *J* = 25.1 Hz), 21.6 (CH₃).

Analytical data obtained were in agreement with the reported values.³

Compound 4c

Chemical Formula: C₁₃H₁₂FNO

Molecular Weight: 217.24

Following the general procedure, from 2-chloroanisole (72 mg, 0.5 mmol) and 2-fluoroaniline (56 mg, 0.55 mmol), the product yielded 86 mg (80 %) as an oil.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.43 (td, *J* = 8.3, 1.5 Hz, 1H), 7.31-7.29 (m, 1H), 7.13 (ddd, *J* = 11.3, 8.1, 1.4 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 6.93-6.86 (m, 4H), 6.23 (s, 1H), 3.91 (s, 3H).

^{13}C { ^1H } NMR (100 MHz, CDCl_3): δ (ppm) = δ 153.7 (d, CF, J = 241.7 Hz), 149.0 (C), 132.0 (C), 131.4 (d, C, J = 11 Hz), 124.3 (d, CH, J = 3.6 Hz), 120.9 (d, CH, J = 7.0 Hz), 120.8 (d, CH, J = 8.1), 118.1 (2CH), 115.6 (d, CH, J = 19.4 Hz), 115.5 (CH), 110.7 (CH), 55.7 (CH_3).
Analytical data obtained were in agreement with the reported values.⁴

Compound 4d

Chemical Formula: $\text{C}_{14}\text{H}_{15}\text{NO}$
Molecular Weight: 213.28

Following the general procedure, from 4-chlorotoluene (63 mg, 0.5 mmol) and 4-methoxyaniline (68 mg, 0.55 mmol), the product yielded 105 mg (99 %) as a black powder.

^1H NMR (400 MHz, CDCl_3): δ (ppm) = δ 7.66 (m, 4H), 6.88 (m, 4H), 5.41 (s, 1H), 3.80 (s, 3H), 2.29 (s, 3H).

^{13}C { ^1H } NMR (100 MHz, CDCl_3): δ (ppm) = δ 154.6 (C), 142.2 (C), 136.5 (C), 129.6 (C), 129.2 (CH), 120.9 (CH), 116.4 (CH), 114.5 (CH), 55.4 (CH_3), 20.4 (CH_3).

Analytical data obtained were in agreement with the reported values.⁵

Compound 4e

Chemical Formula: $\text{C}_{15}\text{H}_{17}\text{NO}_3$
Molecular Weight: 259.31

Following the general procedure, from 4-chloroanisole (71 mg, 0.5 mmol) and 3,5-dimethoxyaniline (67 mg, 0.55 mmol), the product yielded 122.7 mg (95 %) as a yellow oil.

^1H NMR (400 MHz, CDCl_3): δ (ppm) = δ 7.10 (d, J = 9.2 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.07 (m, 3H), 5.52 (br. s, 1H), 3.80 (m 9H).

^{13}C { ^1H } NMR (100 MHz, CDCl_3): δ (ppm) = δ 171.2 (C), 161.3 (C), 155.5 (C), 148.5 (C), 147.4 (C), 135.2 (CH), 123.0 (CH), 114.6 (CH), 93.8 (CH), 93.7 (CH), 91.6 (CH), 90.9 (CH), 60.4 (CH_3), 55.5 (CH_3), 55.1 (CH_3).

Analytical data obtained were in agreement with the reported values.⁶

Compound 4f

Chemical Formula: $\text{C}_{13}\text{H}_{14}\text{N}_2$
Molecular Weight: 198.27

Following the general procedure, from 2-chloropyridine (57 mg, 0.5 mmol) and 3,5-dimethylaniline (67 mg, 0.55 mmol), the product yielded 74.5 mg (75 %) as a yellow oil.

^1H NMR (400 MHz, CDCl_3): δ (ppm) = 8.22 (s, 1H), 7.53 (m, 1H), 6.96 (m, 3H), 6.77 (br. s, 1H), 6.75 (m, 2H), 2.34 (s, 6H).

^{13}C { ^1H } NMR (100 MHz, CDCl_3): δ (ppm) = δ 156.3 (C), 148.4 (CH), 140.4 (C), 139.1 (CH), 137.9 (C), 125.0 (CH), 118.5 (CH), 114.9 (CH), 108.3 (CH), 221.5 (CH_3).

Analytical data obtained were in agreement with the reported values.⁷

Compound 4g

Chemical Formula: C₁₄H₁₅NO
Molecular Weight: 213.28

Following the general procedure, from 4-chloroanisole (63 mg, 0.5 mmol) and *o*-toluidine (59 mg, 0.55 mmol), the product yielded 106 mg (99 %) as a oil.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = δ 7.20 (d, *J* = 8.2 Hz, 1H), 7.14 (t, *J* = 8.3 Hz, 1H), 7.07 (m, 3H), 6.92 (m, 3H), 5.25 (s, 1H), 3.84 (s, 3H), 2.29 (s, 3H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = δ 155.2 (C), 143.4 (C), 136.4 (C), 130.8 (C), 126.9 (CH), 125.4 (CH), 122.2 (CH), 120.1 (CH), 115.2 (CH), 114.8 (CH), 55.7 (CH₃), 17.9 (CH₃).

Analytical data obtained were in agreement with the reported values.⁵

Compound 4h

Chemical Formula: C₁₆H₁₉NO
Molecular Weight: 241.33

Following the general procedure, from 4-chloroanisole (71 mg, 0.5 mmol) and 2-isopropylaniline (75 mg, 0.55 mmol), the product yielded 120 mg (99 %) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = δ 7.20 (d, *J* = 7.5 Hz, 1H), 7.03-6.98 (m, 2H), 6.89 (m, 3H), 6.79 (m, 2H), 5.22 (br. s, 1H), 3.72 (s, 3H), 3.05 (sept, *J* = 6.8 Hz, 1H), 1.22 (dd, *J* = 5.2 Hz, 6H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = δ 154.8 (C), 141.8 (C), 137.6 (C), 137.3 (C), 126.5 (CH), 125.9 (CH), 121.4 (CH), 121.1 (CH), 118.1 (CH), 114.8 (CH), 55.7 (CH₃), 27.6 (CH), 22.9 (CH₃), 22.4 (CH₃).

Analytical data obtained were in agreement with the reported values.⁸

Compound 4i

Chemical Formula: C₁₆H₁₉N
Molecular Weight: 225.34

Following the general procedure, from 2-chloroanisole (63 mg, 0.5 mmol) and 2-isopropylaniline (71 mg, 0.55 mmol), the product yielded 111.9 mg (99 %) as a beige solid.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = δ 7.33 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.16-7.05 (m, 4H), 6.93 (m, 2H), 5.24 (s, 1H), 3.17 (q, *J* = 5.8 Hz, 1H), 2.29 (s, 3H), 1.29 (d, *J* = 7.0 Hz, 6H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = δ 143.2 (C), 140.4 (C), 139.5 (C), 130.8 (CH), 127.0 (C), 126.6 (CH), 126.5 (CH), 126.1 (CH), 122.8 (CH), 121.0 (CH), 120.7 (CH), 119.1 (CH), 117.0 (CH), 27.9 (CH), 23.1 (CH₃), 17.9 (CH₃).

Analytical data obtained were in agreement with the reported values.⁸

Compound 4j

Chemical Formula: C₁₅H₁₇N
Molecular Weight: 211.31

Following the general procedure, from 4-chlorotoluene (63 mg, 0.5 mmol) and 2,6-dimethylaniline (67 mg, 0.55 mmol), the product yielded 104 mg (99 %) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = δ 7.14-7.08 (m, 3H), 7.00 (d, *J* = 7.8 Hz, 2H); 6.46 (d, *J* = 7.9 Hz, 2H), 5.11 (s, 1H), 2.26 (s, 3H), 2.23 (s, 6H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = δ 144.0 (C), 138.8 (C), 135.6 (C), 129.8 (CH), 128.6 (CH), 127.5 (C), 125.5 (CH), 113.9 (CH), 20.6 (CH₃), 18.5 (CH₃).

Analytical data obtained were in agreement with the reported values.⁸

Compound 4k

Chemical Formula: C₁₅H₁₇NO

Molecular Weight: 227.31

Following the general procedure, from 4-chloroanisole (71 mg, 0.5 mmol) and 2,6-dimethylaniline (67 mg, 0.55 mmol), the product yielded 112 mg (99 %) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = δ 7.12 (d, *J* = 7.1 Hz, 2H), 7.16 (m, 1H), 6.76 (d, *J* = 8.5 Hz, 2H). 6.51 (d, *J* = 9.4 Hz, 2H), 5.03 (s, 1H), 3.75 (s, 3H), 2.20 (s, 3H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = δ 152.8 (C), 140.2 (C), 139.4 (C), 135.0 (C), 128.7 (CH), 128.3 (CH), 125.0 (CH), 121.8 (CH), 118.1 (CH), 115.3 (CH), 114.8 (CH), 55.9 (CH₃), 18.5 (CH₃).

Analytical data obtained were in agreement with the reported values.⁵

Compound 4l

Chemical Formula: C₁₅H₁₇NO

Molecular Weight: 227.31

Following the general procedure, from 2-chloroanisole (71 mg, 0.5 mmol) and 2,6-dimethylaniline (67 mg, 0.55 mmol), the product yielded 91 mg (80 %) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = δ 7.13 (m, 3H), 6.87 (m, 1H), 6.70 (m, 2H), 6.14 (m, 1H), 5.65 (s, 1H), 3.95 (s, 3H), 2.21 (s, 6H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = δ 146.9 (C), 138.5 (C), 136.3 (C), 136.1 (C), 128.6 (CH), 125.8 (CH), 121.2 (CH), 117.4 (CH), 111.2 (CH), 110. (CH), 55.8 (CH₃), 18.4 (CH₃).

Analytical data obtained were in agreement with the reported values.⁹

Compound 4m

Chemical Formula: C₁₃H₁₄N₂

Molecular Weight: 198.27

Following the general procedure, from 2-chloropyridine (57 mg, 0.5 mmol) and 2,6-dimethylaniline (67 mg, 0.55 mmol), the product yielded 72 mg (73%) as a beige solid.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = δ 8.15 (m, 1H), 7.35 (td, *J* = 6.7 Hz, 1H), 7.13 (s, 3H), 6.64 (t, *J* = 6.5 Hz, 1H), 6.27 (br. s, 1H), 6.01 (dt, *J* = 8.5 Hz, 1H), 2.23 (s, 6H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = δ 157.9 (C), 148.6 (CH), 138.0 (C), 136.9 (CH), 136.6 (C), 128.7 (C), 126.9 (CH), 113.8 (CH), 105.8 (CH), 18.5 (CH₃).

Analytical data obtained were in agreement with the reported values.⁵

Compound 4n

Chemical Formula: C₁₉H₂₅NO

Molecular Weight: 283.42

Following the general procedure, from 4-chloroanisole (71 mg, 0.5 mmol) and *o*-toluidine (59 mg, 0.55 mmol), the product yielded 142 mg (99%) as a oil.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = δ 7.39 (m, 1H), 7.31 (m, 2H), 7.14 (t, *J* = 8.1 Hz, 1H), 6.37 (dd, *J* = 8.1 Hz, 1H), 6.21 (dd, *J* = 8.0 Hz, 1H), 6.12 (t, *J* = 2.0 Hz, 1H), 5.23 (s, 1H), 3.78 (s, 3H), 3.34 (q, *J* = 7.2 Hz, 2H), 1.25 (d, *J* = 6.9 Hz, 12H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = δ 160.9 (C), 149.7 (C), 147.7 (C), 135.1 (C), 130.0 (CH), 127.4 (CH), 123.9 (CH), 106.2 (CH), 103.2 (CH), 99.1 (CH), 55.1 (CH₃), 28.3 (CH), 24.0 (CH₃).

Analytical data obtained were in agreement with the reported values.⁵

Compound 4o

Chemical Formula: C₁₇H₂₁NO

Molecular Weight: 255.36

Following the general procedure, from 4-chloroanisole (71 mg, 0.5 mmol) and 2,6-diethylaniline (75 mg, 0.55 mmol), the product yielded 126 mg (99 %) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = δ 7.17 (m, 3H), 6.76 (dt, *J* = 9.1 Hz, 2H), 6.49 (dt, *J* = 8.5 Hz, 2H), 5.01 (s, 1H), 3.77 (s, 3H), 2.61-2.56 (q, *J* = 7.5 Hz, 4H), 1.18 (t, *J* = 6.3 Hz, 6H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = δ 152.6 (C), 141.6 (C), 141.3 (C), 136.0 (C), 126.8 (CH), 126.0 (CH), 114.9 (CH), 114.8 (CH), 55.7 (CH₃), 24.8 (CH₂), 14.8 (CH₃).

Analytical data obtained were in agreement with the reported values.⁸

Compound 5a

Chemical Formula: C₁₂H₁₂N₂

Molecular Weight: 184.24

Following the general procedure, from 4-chloropyridine (57 mg, 0.5 mmol) and N-methylaniline (59 mg, 0.55 mmol), the product yielded 89.5 mg (99 %) as a yellow oil.

Large scale:

Following the general procedure, from 4-chloropyridine (624.5 mg, 5.5 mmol) and N-methylaniline (648.3 mg, 6.05 mmol), the product yielded 1013 mg (99 %) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = δ 8.24 (m, 1H), 7.42 (t, *J* = 6.5 Hz, 2H), 7.31-1.22 (m, 4H), 6.62 (m, 1H), 6.55 (m, 1H), 3.48 (s, 3H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = δ 158.9 (C), 147.9 (C), 146.9 (CH), 136.6 (CH), 129.8 (CH), 129.2 (CH), 126.4 (CH), 125.5 (CH), 113.2 (CH), 112.5 (CH), 109.2 (CH), 38.2 (CH₃).

Analytical data obtained were in agreement with the reported values.²

Compound 5b

Chemical Formula: C₁₄H₁₅NO

Molecular Weight: 213.28

Following the general procedure, from 4-chloroanisole (71 mg, 0.5 mmol) and N-methyl aniline (59 mg, 0.55 mmol), the product yielded 106 mg (99 %) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = δ 7.23 (t, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 9.1 Hz, 2H), 6.91 (d, *J* = 9.6 Hz, 2H), 6.81 (m, 3H), 3.82 (s, 3H), 3.27 (s, 3H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = δ 156.4 (C), 149.8 (C), 142.3 (C), 129.3 (CH), 129.0 (CH), 126.3 (CH), 118.4 (CH), 115.8 (CH), 114.8 (CH), 114.7 (CH), 112.4 (CH), 55.5 (CH₃), 40.5 (CH₃).

Analytical data obtained were in agreement with the reported values.²

Compound 5c

Chemical Formula: C₁₄H₁₂F₃N

Molecular Weight: 251.25

Following the general procedure, from 4-chlorobenzotrifluoride (90 mg, 0.5 mmol) and N-methyl aniline (59 mg, 0.55 mmol), the product yielded 123.9 mg (99 %) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = δ 7.44 (m, 4H), 7.21 (m, 3H), 6.86 (d, *J* = 8.9 Hz, 2H), 3.35 (s, 3H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = δ 151.6 (C), 147.8 (C), 129.9 (CH), 126.3 (dd, CH, *J* = 3.6, 7.6 Hz), 125.4 (CH), 125.1 (CH), 125.1 (q, CF₃, *J* = 270.5 Hz), 120.1 (q, C-CF₃, *J* = 32.6 Hz), 114.9 (CH), 40.2 (CH₃).

Analytical data obtained were in agreement with the reported values.³

Compound 5d

Chemical Formula: C₁₅H₂₅NO

Molecular Weight: 235.3710

Following the general procedure, from 4-chloroanisole (71 mg, 0.5 mmol) and dibutylamine (71 mg, 0.55 mmol), the product yielded 100 mg (80 %) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = δ 6.83-6.81 (m, 2H), 6.67-6.65 (m, 2H), 3.76 (s, 3H), 3.20 (t, *J* = 7.1 Hz, 4H), 1.56-1.48 (q, *J* = 7.7 Hz, 4H), 1.38-1.29 (sep, *J* = 8.4 Hz, 4H), 0.95 (t, *J* = 7.2 Hz, 6H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = δ 151.1 (C), 143.5 (C), 115.0 (CH), 114.5 (CH), 56.0 (CH₃), 51.8 (CH₂), 29.6 (CH₂), 20.6 (CH₂), 14.2 (CH₃).

Analytical data obtained were in agreement with the reported values.⁸

Compound 5e

Chemical Formula: $C_{11}H_{15}NO_2$

Molecular Weight: 193.25

Following the general procedure, from 4-chloroanisole (71 mg, 0.5 mmol) and morpholine (107 mg, 0.55 mmol), the product yielded 96 mg (99 %) as a white solid.

Large scale:

Following the general procedure, from 4-chloroanisole (784 mg, 5.5 mmol) and morpholine (1175.4 mg, 6.05 mmol), the product yielded 1061 mg (99 %) as a white solid.

1H NMR (400 MHz, $CDCl_3$): δ (ppm) = δ 6.91-6.84 (m, 4H), 3.87-3.77 (m, 4H), 3.77 (s, 3H), 3.07 (m, 4H).

^{13}C { 1H } NMR (100 MHz, $CDCl_3$): δ (ppm) = δ 154.1 (C), 145.8 (C), 118.0 (CH), 114.6 (CH), 67.2 (CH_2), 55.7 (CH_3), 51.0 (CH_2).

Analytical data obtained were in agreement with the reported values.²

Compound 5f

Chemical Formula: $C_{11}H_{15}NO$

Molecular Weight: 177.25

Following the general procedure, from 4-chlorotoluene (63 mg, 0.5 mmol) and morpholine (107 mg, 0.55 mmol), the product yielded 86 mg (97 %) as a white solid.

1H NMR (400 MHz, $CDCl_3$): δ (ppm) = δ 7.10 (d, J = 8.73 Hz, 2H), 6.85 (d, J = 7.79 Hz, 2H), 3.87 (m, 4H), 3.12 (m, 4H), 2.28 (s, 3H).

^{13}C { 1H } NMR (100 MHz, $CDCl_3$): δ (ppm) = δ 149.9 (C), 129.9 (C), 129.7 (CH), 116.2 (CH), 67.1 (CH_2), 50.1 (CH_2), 20.6 (CH_3).

Analytical data obtained were in agreement with the reported values.⁸

Compound 5g

Chemical Formula: $C_{13}H_{19}NO$

Molecular Weight: 205.30

Following the general procedure, from 4-chloroanisole (71 mg, 0.5 mmol) and Hexamethyleneimine (55 mg, 0.55 mmol), the product yielded 103 mg (99 %) as a yellow oil.

1H NMR (400 MHz, $CDCl_3$): δ (ppm) = δ 6.84 (dt, J = 9.2 Hz, 2H), 6.66 (bd, J = 8.4 Hz, 2H), 3.76 (s, 3H), 3.43 (t, J = 7.9 Hz, 4H), 1.78 (m, 4H), 1.56 (m, 4H).

^{13}C { 1H } NMR (100 MHz, $CDCl_3$): δ (ppm) = δ 150.5 (C), 143.9 (C), 115.1 (CH), 112.4 (CH), 56.0 (CH_3), 49.7 (CH_2), 28.1 (CH_2), 27.3 (CH_2).

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

Compound 5h

Chemical Formula: $C_{13}H_{19}N$

Molecular Weight: 189.30

Following the general procedure, from 2-chloropyridine (57 mg, 0.5 mmol) and Hexamethylenimine (55 mg, 0.55 mmol), the product yielded 94 mg (99 %) as a beige solid. **¹H NMR (400 MHz, CDCl₃):** δ (ppm) = 7.16 (m, 2H), 7.07 (dd, *J* = 6.5 Hz, 1H), 6.94 (td, *J* = 12.6 Hz, 1H), 3.10 (t, *J* = 5.5 Hz, 4H), 2.33 (s, 3H), 1.78 (m, 8H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = δ 155.0 (C), 133.0 (C), 131.0 (CH), 126.5 (CH), 122.4 (CH), 120.9 (CH), 56.0 (CH₂), 29.7 (CH₂), 27.1 (CH₂), 19.0 (CH₃).

Analytical data obtained were in agreement with the reported values.¹¹

Compound 5i

Chemical Formula: C₁₁H₁₅NO

Molecular Weight: 177.25

Following the general procedure, from 4-chloroanisole (71 mg, 0.5 mmol) and pyrrolidine (67 mg, 0.55 mmol), the product yielded 71 mg (80 %) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = δ 6.90 (dt, *J* = 8.7 Hz, 2H), 6.59 (dt, *J* = 9.5 Hz, 2H), 3.79 (s, 3H), 3.29 (m, 4H), 2.04 (m, 4H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = δ 150.8 (C), 143.3 (C), 115.1 (CH), 112.7 (CH), 56.0 (CH₃), 48.3 (CH₂), 25.2 (CH₂).

Analytical data obtained were in agreement with the reported values.⁵

5. Synthesis of coupling substrates

Scheme S1: Synthesis of starting materials **6a-b**

General procedure: In a round bottom flask, *N*-ethylacetoindole (1.00 g, 5.34 mmol), and the corresponding aldehyde (8.00 mmol, 1.50 equiv.) were dissolved in ethanol (20 mL). Then, NaOH (853.00 mg, 16.00 mmol, 4.00 equiv.) in 10 ml water was added and the mixture was stirred at room temperature for 24 hours. The solid was then collected by filtration and washed with hexane to give the pure product.

X=Cl, 95%
Br, 93%

(E)-3-(4-chlorophenyl)-1-(1-ethyl-1H-indol-3-yl)prop-2-en-1-one: Following the general procedure using 4-chloroaldehyde (1.12 g, 8.00 mmol) the product was obtained in 95% (1.56 g) yield. Melting point: 118 – 119 °C. **¹H NMR (400 MHz, CDCl₃):** δ (ppm) = 8.54-8.51 (m, 1H, H₁), 7.91 (s, 1H, H₇), 7.76 (d, *J* = 15.6 Hz, 1H, H₄), 7.56 (d, *J* = 7.7 Hz, 2H, H_{8,9}), 7.37 (m, 6H, H_{2,3,10,11}), 4.23 (m, 2H, H₆), 1.57 (t, *J* = 7.2 Hz, 3H, H₅) **¹³C {¹H} NMR (100 MHz, CDCl₃):** δ (ppm) = δ 184.0 (C=O), 139.6 (C=C), 136.9 (C-N), 135.7 (C_{Ar}), 134.1 (C_{Ar}), 133.9 (C_{Ar}), 129.4

(CH_{Ar}), 129.2 (CH_{Ar}), 127.1 (CHN), 124.5 (CH_{Ar}), 123.7 (CH_{Ar}), 123.2 (CH_{Ar}), 122.9 (CH_{Ar}), 117.8 (CH_{Ar}), 42.0 (CH₂), 15.3 (CH₃). IR (KBr, cm⁻¹) $\nu_{\max}$ = 3046, 2971, 2926, 1653, 1595, 1527, 1480, 1464, 1392, 1238, 1200, 1145, 1098, 1089, 1057, 967, 939, 856, 811, 750, 701, 426. **Elemental analysis:** Expected C, 73.66; H, 5.21; N, 4.52; Found: C, 73.75; H, 5.42; N, 4.39]. LC/MS (ESI, *m/z*): [M⁺], found 309.10, C₁₉H₁₆ClNO for 309.09.

(E)-3-(4-bromophenyl)-1-(1-ethyl-1H-indol-3-yl)prop-2-en-1-one: Following the general procedure using 4-bromoaldehyde (1.48 g, 8.00 mmol) the product was obtained in 93% (1.75 g) yield. Melting point: 139 – 140 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.54-8.52 (m, 1H, H₁), 7.93 (s, 1H, H₇), 7.74 (d, *J* = 15.6 Hz, 1H, H₄), 7.53 (d, *J* = 7.7 Hz, 2H, H_{8,9}), 7.40 (m, 6H, H_{2,3,10,11}), 4.28 (m, 2H, H₆), 1.57 (t, *J* = 7.2 Hz, 3H, H₅) ¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = δ 184.0 (C=O), 139.6 (C=C), 136.9 (C-N), 135.7 (C_{Ar}), 134.1 (C_{Ar}), 133.9 (C_{Ar}), 129.4 (CH_{Ar}), 129.2 (CH_{Ar}), 127.1 (CHN), 124.5 (CH_{Ar}), 123.7 (CH_{Ar}), 123.2 (CH_{Ar}), 122.9 (CH_{Ar}), 117.8 (CH_{Ar}), 42.0 (CH₂), 15.3 (CH₃). IR (KBr, cm⁻¹) $\nu_{\max}$ = 3049, 2977, 1646, 1611, 1588, 1524, 1463, 1449, 1391, 1311, 1268, 1260, 1089, 1062, 993, 975, 858, 835, 779, 741, 717, 671, 561, 520, 478. **Elemental Analysis** Expected: C 64.42, H 4.55, N 3.95. Found: C 64.31, H 4.67, N 4.15 LC/MS (ESI, *m/z*): [M⁺], found 353.00, C₁₉H₁₆BrNO for 353.04.

C-N amination procedure: A vial was charged with [IPr*·H][Pd(η³-cin)Cl₂] (12.0 mg, 2.0 mol%), KO^tBu (11.2 mg, 0.10 mmol), CPME (0.2 mL) and a magnetic stir bar and sealed with a screw cap. The mixture was left to stir at the 60 °C for 1 h. The vial was removed from the heating block and the corresponding solution of aniline and aryl chloride in CPME (0.5 mL) was added. The reaction was left to stir (910 rpm) at 80 °C for 20 h. The reaction was purified using flash column chromatography, gradient from 10:90 to 50:50 ethyl acetate/petroleum ether.

Compounds 7a and 7b

Following the general procedure, from *N*-Et-Indenone (17.6 mg, 0.05 mmol) and 4-methoxyaniline (6.8 mg, 0.05 mmol), the product was obtained in 80% yield (15.6 mg) as an orange/brown oil. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = δ 8.53 (m, 1H₁), 7.91 (s, 1H₇), 7.79 (d, *J* = 15.5 Hz, 1H₉), 7.53 (d, *J* = 8.6 Hz, 2H_{11 and 12}), 7.39 (m, 1H₂), 7.33 (m, 2H_{10 and 13}), 7.29-7.24 (m, 2H_{3 and 4}), 7.14 (d, *J* = 8.9 Hz, 2H_{15 and 17}), 6.91 (m, 3H_{8, 16 and 18}), 5.77 (br. s, 1H₁₄), 4.25 (q, *J* = 7.3 Hz, 2H₅), 3.82 (s, 3H₁₉), 1.56 (t, *J* = 7.3 Hz, 3H₆). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = δ 184.9 (C=O), 156.2 (C-OMe), 147.3 (C=C), 141.4 (C-NH), 136.8 (C-N), 134.3 (C-NH), 133.4 (CH), 130.1 (CH), 127.2 (CH(N)), 126.4 (CH), 123.7 (CH), 123.5 (CH), 123.3 (C=C), 122.6 (CH), 114.9 (C(C=O)), 114.8 (CH), 109.8 (CH), 55.7 (OCH₃), 41.9 (CH₂), 15.4 (CH₃(CH₂)).

7a HRMS (ESI/Q-TOF) *m/z*: [M+H]⁺ Calcd for C₂₆H₂₄N₂O₂ 397.1916. Found: 397.1910

7b HRMS (ESI/Q-TOF) *m/z*: [M+H]⁺ Calcd for C₂₆H₂₄N₂O₂ 397.1916. Found: 397.1910

Compound 7c

Following the general procedure, from *N*-Et-Indenone (17.60 mg, 0.05 mmol) and morpholine (4.80 mg, 0.05 mmol), the product was obtained in 74% (13.40 mg) as an orange/brown oil.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.41 (m, 1H₁), 7.78 (d, *J* = 30.0 Hz, 1H₇), 7.38 (m, 2H₈ and 9), 7.31 (m, 3H_{2,11} and 12), 7.19 (d, *J* = 8.4 Hz, 2H₃ and 4), 6.87 (d, *J* = 8.5 Hz, 2H₁₀ and 13), 4.22 (m, 2H₅), 4.23-4.18 (m, 2H₁₅ and 16), 3.87-3.82 (m, 2H₁₄ and 17), 3.17 (m, 4H₁₄ and 17; 15 and 16), 1.25 (s, 3H₆).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) = 194.9 (C=O), 193.2 (C-N), 149.7 (C=C), 136.7 (C-N), 134.2 (CH), 133.7 (CH), 133.6 (C), 129.2 (CH), 126.6 (C), 124.8 (CH), 123.3 (CH), 122.9 (C=C), 122.7 (CH), 117.2 (C), 116.7 (CH), 116.2 (CH), 109.8 (CH), 67.1 (CH₂), 49.8 (CH₂), 42.1 (CH₂), 41.9 (CH₂), 41.8 (CH₂), 15.3 (CH₃).

HRMS (ESI/Q-TOF) *m/z*: [M+H]⁺ Calcd for C₂₃H₂₄N₂O₂ 361.1916. Found: 361.1916.

6. Optimization of the ketone arylation

General procedure: A vial was charged with the pre-catalyst, base, solvent (1 mL) and a magnetic stir bar and sealed with a screw cap. The mixture was let to stir at 60 °C for 1 h. The sample was removed from the heating block and the corresponding aryl ketone was added followed by the corresponding aryl chloride. The reaction was left to stir (910 rpm) at 80 °C for 3 h.

6.1. Catalyst Screening

The general procedure was followed using propiophenone (74 mg, 0.55 mmol), 4-chloroanisole (63 mg, 0.5 mmol) with NaO^tBu (53 mg, 0.55 mmol) in CPME (1 mL).

Table S13: Pre-catalyst optimisation using 0.20 mol%

Entries	Pd Pre-catalyst	GC conversion (%) ^a
1	[IPent·H][Pd(η ³ -cin)Cl ₂]	99
2	[IHept·H][Pd(η ³ -cin)Cl ₂]	99
3	[IPr*·H][Pd(η ³ -cin)Cl ₂]	99
4	[Pr* ^{OMe} ·H][Pd(η ³ -cin)Cl ₂]	99
5	[IPr*·H][Pd(η ³ -crotyl)Cl ₂]	94
6	[IPr*·H][Pd(η ³ -2-Me-allyl)Cl ₂]	99

^a GC conversion based on 4-chlorotoluene. Value calculated from an average of two reactions.

Table S14: Pre-catalyst optimization using 0.1 mol%

Entries	Pd Pre-catalyst	GC conversion (%) ^a
1	[IPent·H][Pd(η ³ -cin)Cl ₂]	83
2	[IHept·H][Pd(η ³ -cin)Cl ₂]	77
3	[IPr*·H][Pd(η³-cin)Cl₂]	86
4	[Pr* ^{OMe} ·H][Pd(η ³ -cin)Cl ₂]	72
5	[IPr*·H][Pd(η ³ -2-Me-allyl)Cl ₂]	79

^a GC conversion based on 4-chlorotoluene. Value calculated from an average of two reactions.

6. 2. Base/Solvent screening

The general procedure was followed using [IPr*·H][Pd(η³-cin)Cl₂] (1.2 mg, 0.001 mmol), propiophenone (74 mg, 0.55 mmol) and 4-chloroanisole (63 mg, 0.5 mmol).

Table S15: Base optimization using cyclopentylmethyl ether (CPME)

Entries	Base (0.55 mmol)	GC conversion (%)
1	KO ^t Bu	n.r.
2	LiO ^t Bu	31
3	NaO ^t Bu	99
4	KOH	n.r.
5	NaOH	n.r.

GC conversion based on 4-chlorotoluene. Value calculated from an average of two reactions.

Table S16: Base optimization using toluene

Entries	Base (0.55 mmol)	GC conversion (%)
1	KO ^t Bu	72
2	LiO ^t Bu	5
3	NaO ^t Bu	91
4	KOH	n.r.
5	NaOH	n.r.

GC conversion based on 4-chlorotoluene. Value calculated from an average of two reactions.

Table S17: Base optimization using THF

Entries	Base (0.55 mmol)	GC conversion (%)
1	KO ^t Bu	n.r.
2	LiO ^t Bu	traces
3	NaO ^t Bu	31
4	KOH	n.r.
5	NaOH	n.r.

GC conversion based on 4-chlorotoluene. Value calculated from an average of two reactions.

Table S18: Base optimization using 1,4-dioxane

Entries	Base (0.55 mmol)	GC conversion (%)
1	KO ^t Bu	11
2	LiO ^t Bu	n.r.
3	NaO ^t Bu	11
4	KOH	n.r.
5	NaOH	n.r.

GC conversion based on 4-chlorotoluene. Value calculated from an average of two reactions.

7. Scope

General procedure: A vial was charged with [IPr*·H][Pd(η³-cin)Cl₂] (1.2 mg, 0.2 mol%), NaO^tBu (53 mg, 0.55 mmol), CPME (1 mL) and a magnetic stir bar and sealed with a screw cap. The mixture was let to stir at 60 °C for 1 h. The vial was removed from the heating block and the corresponding solution of aryl ketone and aryl chloride in CPME (1 mL) was added. The reaction was left to stir (910 rpm) for 1-3 h at 80 °C. The reaction was purified using flash chromatography, 5:95 ethyl acetate/petroleum ether.

Compound 10a

Chemical Formula: C₁₆H₁₆O

Molecular Weight: 224.30

Following the general procedure, from 4-chlorotoluene (63 mg, 0.5 mmol) and propiophenone (74 mg, 0.55 mmol), the product yielded 111 mg (99 %) as a colorless oil. **¹H NMR (400 MHz, CDCl₃):** δ (ppm) = δ 7.96 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.49 (tt, *J* = 7.4 Hz, 1H), 7.39 (tt, *J* = 7.5 Hz, 2H), 7.18 (dt, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 4.55 (q, *J* = 6.8 Hz, 1H), 2.28 (s, 3H), 1.51 (d, *J* = 6.8 Hz, 3H). **¹³C {¹H} NMR (100 MHz, CDCl₃):** δ (ppm) = δ 200.4 (C=O), 138.3 (C), 136.4 (C), 136.4 (C), 132.6 (CH), 129.6 (CH), 128.7 (CH), 128.3 (CH), 127.5 (CH), 47.4 (CH), 20.9 (CH₃), 19.4 (CH₃).

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

Compound 10b

Chemical Formula: C₁₆H₁₆O₂

Molecular Weight: 240.30

Following the general procedure, from 4-chloroanisole (72 mg, 0.5 mmol) and propiophenone (74 mg, 0.55 mmol), the product yielded 117.4 mg (98 %) as a colorless oil. **¹H NMR (400 MHz, CDCl₃):** δ (ppm) = δ 7.98 (d, *J* = 7.1 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.68 (q, *J* = 6.8 Hz, 1H), 3.74 (s, 3H), 1.53 (d, *J* = 6.9 Hz, 3H). **¹³C {¹H} NMR (100 MHz, CDCl₃):** δ (ppm) = δ 200.6 (C=O), 158.5 (C), 136.5 (C), 133.5 (C), 132.8 (CH), 128.8 (CH), 128.8 (CH), 128.5 (CH), 114.4 (CH), 55.2 (CH₃), 47.0 (CH), 19.6 (CH₃).

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

Compound 10c

Chemical Formula: C₁₆H₁₃F₃O

Molecular Weight: 278.27

Following the general procedure, from 4-chlorobenzotrifluoride (90.3 mg, 0.5 mmol) and propiophenone (74 mg, 0.55 mmol), the product yielded 134.7 mg (97 %) as a colorless oil. **¹H NMR (400 MHz, CDCl₃):** δ (ppm) = δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.43 (m, 4H), 4.80 (q, *J* = 6.9 Hz, 1H), 1.57 (d, *J* = 6.9 Hz, 3H). **¹³C {¹H} NMR (100 MHz, CDCl₃):** δ (ppm) = δ 199.8 (C=O), 145.5 (C), 136.2 (C), 133.3 (CH), 129.3 (q, C(CF₃), *J* = 32.5 Hz), 128.8 (CH), 128.8 (CH), 128.3 (CH), 126.0 (q, CH, *J* = 3.6 Hz), 125.3 (q, CF₃, *J* = 272.0 Hz), 47.6 (CH), 19.5 (CH₃).

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

Compound 10d

Chemical Formula: C₁₇H₁₆O₂
Molecular Weight: 252.31

Following the general procedure, from 4-chloroanisole (71 mg, 0.5 mmol) and α -tetralone (73.1 mg, 0.55 mmol), the product yielded 88.5 mg (70 %) as a colorless oil. **¹H NMR (400 MHz, CDCl₃):** δ (ppm) = δ 8.18 (d, J = 9.0 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.22 (m, 3H), 6.81 (d, J = 8.9 Hz, 2H), 4.13 (s, 1H), 3.75 (s, 3H), 2.94 (m, 1H), 2.76 (m, 2H), 2.47-2.40 (m, 1H). **¹³C {¹H} NMR (100 MHz, CDCl₃):** δ (ppm) = δ 201.0 (C=O), 159.5 (C), 144.4 (C), 134.3 (CH), 132.9 (C), 131.8 (C), 129.2 (CH), 127.8 (CH), 127.6 (CH), 127.1 (CH), 114.1 (CH), 77.5 (CH), 55.4 (CH₃), 36.5 (CH₂), 26.8 (CH₂).

Analytical data obtained were in agreement with the reported values.¹³

Compound 10e

Chemical Formula: C₁₇H₁₆O₂
Molecular Weight: 252.31

Following the general procedure, from 2-chloroanisole (71 mg, 0.5 mmol) and α -tetralone (73.1 mg, 0.55 mmol), the product yielded mg (70 %) as a colorless oil. **¹H NMR (400 MHz, CDCl₃):** δ (ppm) = δ 8.12 (d, J = 7.8 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.30 (m, 2H), 7.13 (d, J = 9.1 Hz, 1H), 6.96 (dd, J = 17.4, 7.9 Hz, 2H), 4.08 (dd, J = 12.3, 4.7 Hz, 1H), 3.76 (s, 3H), 3.18-3.14 (m, 1H), 3.04-3.01 (m, 1H), 2.55 (qd, J = 27.2, 14.3 Hz, 1H), 2.30-2.26 (m, 1H). **¹³C {¹H} NMR (100 MHz, CDCl₃):** δ (ppm) = δ 198.3 (C=O), 157.2 (C), 144.2 (C), 133.2 (CH), 129.5 (C + CH), 129.3 (C), 128.8 (CH), 128.3 (CH), 127.8 (CH), 126.7 (CH), 120.9 (CH), 111.2 (CH), 55.6 (CH₃), 50.1 (CH), 30.0 (CH₂), 29.6 (CH₂).

Analytical data obtained were in agreement with the reported values.¹⁴

Compound 10f

Chemical Formula: C₁₇H₁₆O
Molecular Weight: 236.31

Following the general procedure, from 4-chlorotoluene (63.3 mg, 0.5 mmol) and α -tetralone (73.1 mg, 0.55 mmol), the product yielded 112 mg (95 %) as a colorless oil. **¹H NMR (400 MHz, CDCl₃):** δ (ppm) = δ 8.18 (dd, J = 7.8, 0.8 Hz, 1H), 7.53 (t, J = 8.1 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.20 (m, 3H), 7.09 (d, J = 8.1 Hz, 2H), 4.17 (s, 1H), 2.93 (m, 1H), 2.77 (m, 2H), 2.47-2.41 (m, 1H), 2.29 (s, 3H). **¹³C {¹H} NMR (100 MHz, CDCl₃):** δ (ppm) = δ 201.0 (C=O), 144.4 (C), 138.1 (C), 137.9 (C), 134.3 (C), 131.8 (CH), 129.4 (CH), 129.2 (CH), 127.8 (CH), 127.1 (CH), 126.2 (CH), 77.7 (CH), 36.5 (CH₂), 26.8 (CH₂), 21.2 (CH₃).

Analytical data obtained were in agreement with the reported values.¹⁵

Compound 10g

Chemical Formula: C₁₅H₁₄O₂
Molecular Weight: 226.28

Following the general procedure, from 4-chlorotoluene (63.3 mg, 0.5 mmol) and acetophenone (60 mg, 0.55 mmol), the product yielded 110 mg (98 %) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = δ 8.08 (d, *J* = 7.1 Hz, 2H), 7.57 (t, *J* = 6.8 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 8.7 Hz, 1H), 7.22 (d, *J* = 8.9 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 4.31 (s, 2H), 3.80 (s, 3H). **¹³C {¹H} NMR (100 MHz, CDCl₃):** δ (ppm) = δ 198.0 (C=O), 157.2 (C), 137.0 (C), 133.0 (CH), 131.1 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 123.7 (C), 120.7 (CH), 110.6 (CH), 55.4 (CH₃), 40.1 (CH₂).

Analytical data obtained were in agreement with the reported values.¹⁴

Compound 10h

Chemical Formula: C₁₆H₁₆O
Molecular Weight: 224.30

Following the general procedure, from 2-chloro,1-3-dimethylbenzene (70 mg, 0.5 mmol) and acetophenone (60 mg, 0.55 mmol), the product yielded 105 mg (95 %) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = δ 8.12 (d, *J* = 7.4 Hz, 2H), 7.64 (t, *J* = 7.0 Hz, 1H), 7.55 (t, *J* = 7.3 Hz, 2H), 7.14 (m, 3H), 4.40 (s, 2H), 2.24 (s, 6H). **¹³C {¹H} NMR (100 MHz, CDCl₃):** δ (ppm) = δ 197.0 (C=O), 137.2 (C), 137.1 (C), 133.3 (CH), 132.5 (C), 128.8 (CH), 128.2 (CH), 128.1 (CH), 127.0 (CH), 39.7 (CH₂), 20.5 (CH₃).

Analytical data obtained were in agreement with the reported values.¹⁶

Compound 10i

Chemical Formula: C₁₅H₁₄O₂
Molecular Weight: 226.28

Following the general procedure, from 4-chloroanisole (72 mg, 0.5 mmol) and acetophenone (60 mg, 0.55 mmol), the product yielded 110 mg (97 %) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ (ppm) = δ 8.03-8.01 (m, 2H), 7.58 (tt, *J* = 7.2, 1.3 Hz, 1H), 7.48 (tt, *J* = 6.8, 1.3 Hz, 2H), 7.20-7.18 (m, 2H), 6.89-6.86 (m, 2H), 4.23 (s, 2H), 3.79 (s, 3H). **¹³C {¹H} NMR (100 MHz, CDCl₃):** δ (ppm) = δ 198.0 (C=O), 158.6 (C), 136.7 (C), 133.2 (CH), 130.6 (CH), 128.7 (CH), 128.7 (CH), 126.6 (C), 114.3 (CH), 55.3 (CH₃), 44.7 (CH₂).

Analytical data obtained were in agreement with the reported values.¹⁵

8. NMR spectra: ^1H and ^{13}C $\{^1\text{H}\}$, CDCl_3 (solvent signal at 7.26 ppm)

8.1. Palladates

$[\text{IPent} \cdot \text{H}][\text{Pd}(\eta^3\text{-cin})\text{Cl}_2]$: ^1H NMR

$[\text{IPent} \cdot \text{H}][\text{Pd}(\eta^3\text{-cin})\text{Cl}_2]$: ^{13}C $\{^1\text{H}\}$ NMR

[IHept-H][Pd(η³-cin)Cl₂]: ¹H NMR

[IHept·H][Pd(η^3 -cin)Cl₂]: ¹³C {¹H} NMR

[INon·H][Pd(η^3 -cin)Cl₂]: ¹H NMR

[INon·H][Pd(η^3 -cin)Cl₂]: ¹³C {¹H} NMR

[IPr*·H][Pd(η³-cin)Cl₂]: ¹H NMR

[IPr*OMe.H][Pd(η^3 -cin)Cl₂]: ¹H NMR

[IPr*OMe.H][Pd(η^3 -cin)Cl₂]: ¹³C {¹H} NMR

[IPent^{Cl}·H][Pd(η³-cin)Cl₂]: ¹H NMR

[IPent^{Cl}·H][Pd(η³-cin)Cl₂]: ¹³C {¹H} NMR

[IPr*·H][Pd(η³-crotyl)Cl₂]: ¹H NMR

[IPr*·H][Pd(η³-crotyl)Cl₂]: ¹³C {¹H} NMR

[IPr*·H][Pd(η^3 -2-Me-allyl)Cl₂]: ¹H NMR

[IPr*·H][Pd(η^3 -2-Me-allyl)Cl₂]: ¹³C {¹H} NMR

[IPr*·H][Pd(Ind^tBu)Cl₂]: ¹H NMR

[IPr*·H][Pd(Ind^tBu)Cl₂]: ¹³C {¹H} NMR

8.2 Cross coupling products

Compound **4a**: ^1H NMR

Compound **4a**: ^{13}C $\{^1\text{H}\}$ NMR

Compound **4b**: ^1H NMR

Compound **4b**: ^{13}C $\{^1\text{H}\}$ NMR

Compound **4c**: ^1H NMR

Compound **4c**: ^{13}C $\{^1\text{H}\}$ NMR

Compound **4d**: ^1H NMR

Compound **4d**: ^{13}C $\{^1\text{H}\}$ NMR

Compound **4e**: ^1H NMR

Compound **4e**: ^{13}C $\{^1\text{H}\}$ NMR

Compound **4f**: ^1H NMR

Compound **4f**: ^{13}C $\{^1\text{H}\}$ NMR

Compound **4g**: ^1H NMR

Compound **4g**: ^{13}C $\{^1\text{H}\}$ NMR

Compound **4h**: ^1H NMR

Compound **4h**: ^{13}C $\{^1\text{H}\}$ NMR

Compound **4i**: ^1H NMR

Compound **4i**: ^{13}C { ^1H } NMR

Compound **4j**: ^1H NMR

Compound **4j**: ^{13}C $\{^1\text{H}\}$ NMR

Compound **4k**: ^{13}C $\{^1\text{H}\}$ NMR

Compound **4k**: ^1H NMR

Compound **4l**: ^1H NMR

Compound **4l**: ^{13}C $\{^1\text{H}\}$ NMR

Compound **4m** : ^1H NMR

Compound **4m** : ^{13}C $\{^1\text{H}\}$ NMR

Compound **4n** : ^1H NMR

Compound **4n** : ^{13}C $\{^1\text{H}\}$ NMR

Compound **4o** : ¹H NMR

Compound **4o** : ^{13}C $\{^1\text{H}\}$ NMR

Compound **5a** : ^1H NMR

Compound **5a** : ^{13}C $\{^1\text{H}\}$ NMR

Compound **5b** : ¹H NMR

Compound **5b** : ^{13}C $\{^1\text{H}\}$ NMR

Compound **5c** : ^1H NMR

Compound **5c** : ^{13}C $\{^1\text{H}\}$ NMR

Compound **5d** : ^1H NMR

Compound **5d** : ^{13}C { ^1H } NMR

Compound **5e** : ^1H NMR

Compound **5e** : ^{13}C $\{^1\text{H}\}$ NMR

Compound **5f**: ^1H NMR

Compound **5f**: ^{13}C $\{^1\text{H}\}$ NMR

Compound **5g** : ^1H NMR

Compound **5g** : ^{13}C $\{^1\text{H}\}$ NMR

Compound **5h** : ¹H NMR

Compound **5h** : ¹³C {¹H} NMR

Compound 5i: ^1H NMR

Compound **5i**: ^{13}C $\{^1\text{H}\}$ NMR

(E)-3-(4-chlorophenyl)-1-(1-ethyl-1H-indol-3-yl)prop-2-en-1-one (**6a**) : ^1H NMR

(E)-3-(4-chlorophenyl)-1-(1-ethyl-1H-indol-3-yl)prop-2-en-1-one (6a) : ^{13}C $\{^1\text{H}\}$ NMR

(E)-3-(4-bromophenyl)-1-(1-ethyl-1H-indol-3-yl)prop-2-en-1-one (**6b**) : ^1H NMR

(E)-3-(4-bromophenyl)-1-(1-ethyl-1H-indol-3-yl)prop-2-en-1-one (**6b**) : ^{13}C { ^1H } NMR

Compounds **7a** and **7b** : ^1H NMR

Compounds **7a** and **7b** : ^{13}C { ^1H } NMR

Compound **7c** : ^1H NMR

Compound **7c** : ^{13}C { ^1H } NMR

Compound **10a** : ^1H NMR

Compound **10a** : ^{13}C { ^1H } NMR

Compound **10b** : ^1H NMR

Compound **10b** : ^{13}C { ^1H } NMR

Compound **10c**: ¹H NMR

Compound **10c**: ^{13}C $\{^1\text{H}\}$ NMR

Compound **10d**: ^1H NMR

Compound **10d** : ^{13}C $\{^1\text{H}\}$ NMR

Compound **10e** : ^1H NMR

Compound **10e** : ^{13}C { ^1H } NMR

Compound **10f** : ^1H NMR

Compound **10f** : ^{13}C $\{^1\text{H}\}$ NMR

Compound **10g** : ^1H NMR

Compound **10g** : ^{13}C { ^1H } NMR

Compound **10h** : ^1H NMR

Compound **10h** : ^{13}C { ^1H } NMR

Compound **10i** : ^1H NMR

Compound **10i** : ^{13}C $\{^1\text{H}\}$ NMR

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