A General and Efficient Aldehyde Decarbonylation Reaction by Palladium Catalyst

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Supporting Information

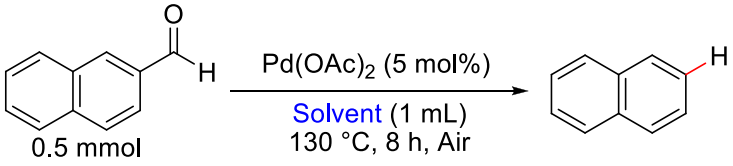
General consideration:

Reagent and reaction setup information. Unless otherwise stated, all reaction were carried out under air in screw cap reaction tube. All the solvents were bought from Aldrich in sure seal bottle and were used as received. Palladium catalysts and ligands were purchased from Aldrich and Merck. Moleculer sieves (4Å; particle size 2–3 μ) were bought from Aldrich. Moleculer sieves was always kept in oven in small amount before use. All aldehydes were bought from Aldrich. For column chromatography, silica gel (60–120 mesh or 100–200 mesh) from SRL Co. were used. A gradient elution using pet ether and ethyl acetate was performed, based on Merck aluminium TLC sheets (silica gel $60F_{254}$).

Analytical Information. **A**ll isolated compound are characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, Gas chromatography mass spectra (GC–MS). Copies of the ^{1}H NMR, ^{13}C NMR can be found in the Supporting Information. Unless otherwise stated, all Nuclear Magnetic Resonance spectra were recorded on a Bruker 400 MHz instrument. Some Nuclear Magnetic Resonance was taken on a VARIAN 300MHz instrument. All ^{1}H NMR experiments are reported in units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated. All ^{13}C NMR spectra were reported in ppm relative to deuterochloroform (77.23 ppm), unless otherwise stated, and all were obtained with ^{1}H decoupling. All GC analyses were performed on a Agilent 7890A GC system with an FID detector using a J & W DB–1 column (10 m, 0.1 mm I.D.). All GCMS analysis were done by Agilent 7890A GC system connected with 5975C inert XL EI/CI MSD (with triple axis detector).

Optimization details for palladium catalysed deformylation:

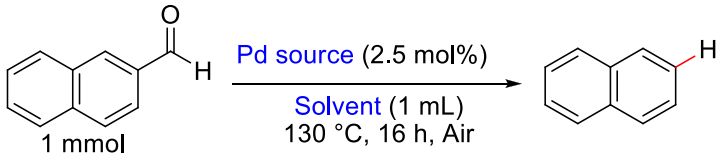
(i) Optimization by varying solvent:



Entry	Solvent	GC Yield (%)

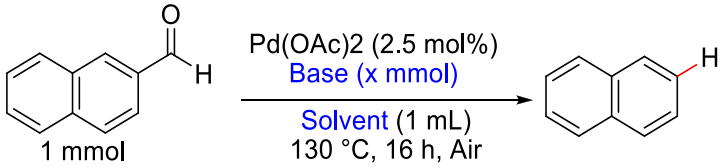
1	Cyclohexane	96
2	Dichloroethane(DCE)	95
3	Dimethoxyethane(DME)	79
4	2–Methyltetrahydrofuran	74
5	2–Methyl–2–butanol	75
6	Tetrahydropyran(THP)	76
7	Dioxane	49
8	Me_3CCN	55
9	$PhCF_3$	52
10	Bu_2O	36
11	C_6H_6	68
12	Methylcyclohexane	65
13	*m*–Xylene	29
14	Toluene	37
15	Butyronitrile	76
16	NMP	74
17	Anisole	65
18	PhCN	62
19	DMF	50
20	DMA	49
21	DIPEA	38

(ii) Optimization by varying Pd source and solvent:



Entry	Pd source	Solvent	GC Yield (%)
1	$Pd(OAc)_2$	Cyclohexane	75
2	$Pd(CF_3CO_2)_2$	Cyclohexane	71
3	$Pd(dba)_2$	Cyclohexane	68
4	$Pd(acac)_2$	Cyclohexane	71
5	$Pd(OAc)_2$	DCE	54
6	$Pd(CF_3CO_2)_2$	DCE	64
7	$Pd(dba)_2$	DCE	55

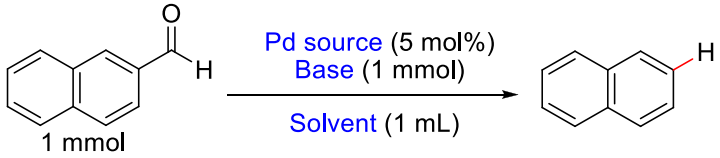
(iii) Optimization by varying solvent (type) and base (type and amount):



Entry	Base	Amount (mmol)	Solvent	GC Yield (%)
1	K_2CO_3	1.0	Cyclohexane	76
2	—	——	Cyclohexane	77
3	Cs_2CO_3	1.0	Cyclohexane	23
4	NaOAc	1.0	Cyclohexane	53
5	K_3PO_4	1.0	Cyclohexane	44
6	K_2CO_3	1.0	DCE	33
7	NaOAc	1.0	DCE	56

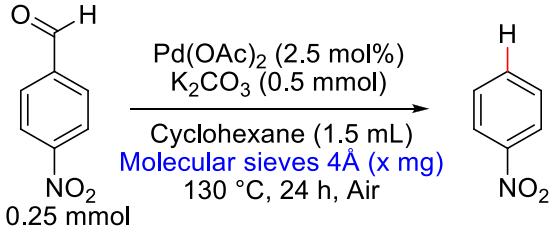
8	K_2CO_3	0.4	Cyclohexane	50
9	Cs_2CO_3	0.4	Cyclohexane	33
10	NaOAc	0.4	Cyclohexane	78
11	K_3PO_4	0.4	Cyclohexane	48

(iv) Optimization by varying Pd source, base and solvent:



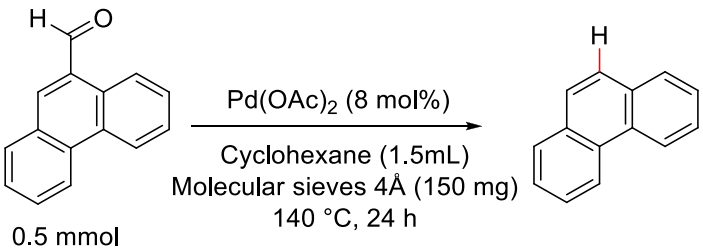
Entry	Pd source	Base	Solvent	GC Yield (%)
1	$Pd(OAc)_2$	K_2CO_3	Cyclohexane	99
2	$Pd(OAc)_2$	K_3PO_4	Cyclohexane	92
3	$Pd(OAc)_2$	Cs_2CO_3	Cyclohexane	55
4	$Pd(OAc)_2$	NaO^tBu	Cyclohexane	69
5	$Pd(acac)_2$	–	Cyclohexane	80
6	$Pd(CF_3CO_2)_2$	–	Cyclohexane	69
7	Pd(2,4–pentadiene)	–	Cyclohexane	76
8	$PdCl_2(CH_3CN)_2$	–	Cyclohexane	7
9	$Pd(acac)_2$	–	DCE	70
10	$Pd(CF_3CO_2)_2$	–	DCE	79
11	Pd(2,4–pentadiene)	–	DCE	53
12	$Pd(dba)_2$	–	DCE	73
13	$Pd_2(dba)_3$	–	DCE	78

(v) Optimization by varying amount of molecular sieves:



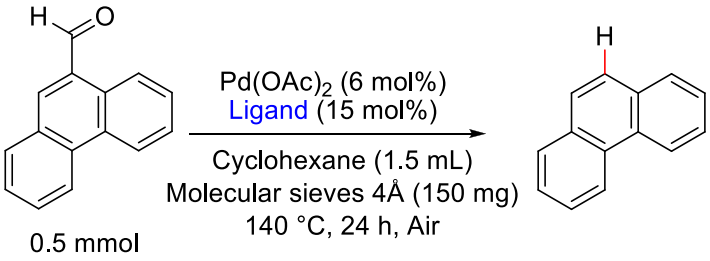
Entry	Amount of Molecular sieves (mg)	GC Yield (%)
1	0	56
2	50	84
3	100	82
4	200	96

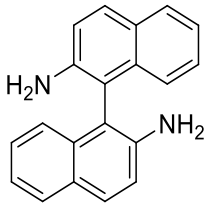
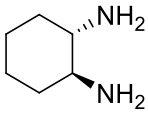
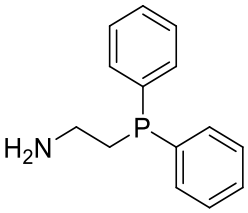
(vi) Optimization ***of reaction atmosphere and necessity of base:***

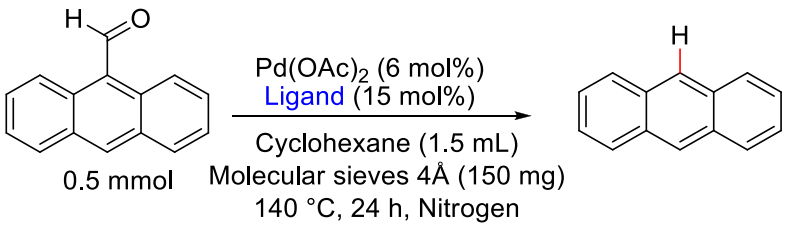


Entry	Reaction condition	GC Yield (%)
1	Under air	100
2	Under N_2	92
3	With base	88
4	Without base	100

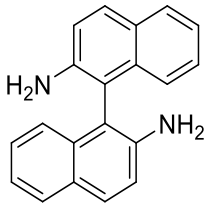
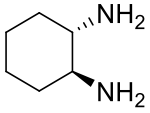
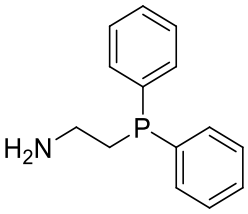
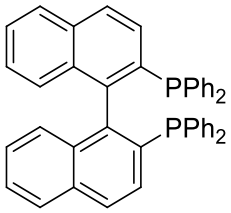
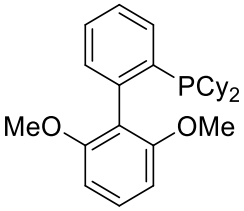
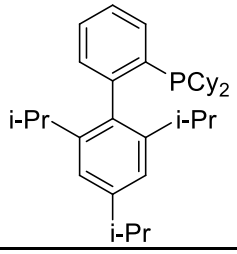
(vii) ***Optimization of ligand for decarbonylation of aldehyde:***



Entry	Ligand	GC Yield (%)
1	No ligand	52
2	PCy_3	38
3	PPh_3	39
4		32
5		33
6		30
7	Bipyridine	21
8	$P(OEt)_3$	20



Entry	Ligand	GC Yield (%)
1	No ligand	37
2	PPh_3	29

3		34
4		7
5		35
6	Bipyridine	22
7		32
8		16
9		11

Experimental procedure for *decarbonylation of aldehyde*.

General Procedure A for deformylation of aldehydes with 5–16 mol% palladium catalyst loading under air

A clean, oven–dried screw cap reaction tube with previously placed magnetic stir–bar was charged with molecular sieves (4Å, 150 mg), aldehyde (0.5 mmol), palladium acetate (5–16 mol%). Cyclohexane (1.3 mL) was added to this mixture by syringe. The tube was tightly closed by screw cap and placed in a preheated oil bath at required temperature. The reaction mixture was vigorously stirred for 24 h. The reaction mixture was cooled to room temperature and filtered through celite. Reaction tube and residue was washed with ethyl acetate (20 mL). The filtrate was concentrated and resulting deformylated product was purified via column chromatography using silica gel and pet ether, ethyl acetate as eluent.

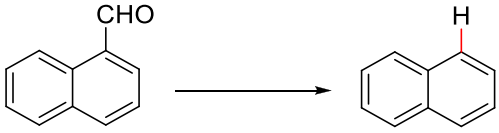
General Procedure B for deformylation of aldehydes with 5–16 mol% palladium catalyst loading under nitrogen

A clean, oven–dried screw cap reaction tube with previously placed magnetic stir–bar was charged with molecular sieves (4Å, 150 mg), aldehyde (0.5 mmol), palladium acetate (5–16 mol%). The tube was then evacuated and back–filled with nitrogen. The evacuation/backfill sequence was repeated two additional times. Under a counter flow of nitrogen, remaining liquid reagents were added, followed by cyclohexane (1.3 mL) by syringe. The tube was tightly closed by screw cap and placed in a preheated oil bath at required temperature. The reaction mixture was vigorously stirred for 24 h. The reaction mixture was cooled to room temperature and filtered through celite. Reaction tube and residue was washed with ethyl acetate (20 mL). The filtrate was concentrated and resulting deformylated product was purified via column chromatography using silica gel and pet ether, ethyl acetate as eluent.

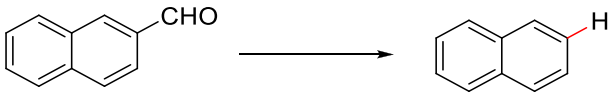
Fig. 1. Pictorial description of reaction tube for deformylation: Fisherbrand Disposable Borosilicate Glass Tubes(16*125mm) with Threaded End (Fisher Scientific Order No. 1495935A) [left]; Kimble Black Phenolic Screw Thread Closures with Open Tops (Fisher Scientific Order No. 033407E) [middle]; Thermo Scientific National PTFE/Silicone Septa for Sample Screw Thread Caps (Fisher Scientific Order No. 03394A) [right].

General Procedure C for preparation of starting materials by C–N Coupling

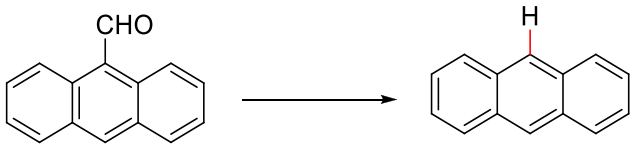
In an oven dried schlenk reaction tube, charged with magnetic stir bar *p*–tolyl iodide (1.5 mmol); heterocyclic aldehyde (1.5 mmol), CuI (20 mol%, 0.3 mmol, 57 mg), 1,10–phenanthrolene (40 mol%, 0.6 mmol, 119 mg) and base (3 mmol) were added. Then using schlenk technique the reaction tube was evacuated and back filled with nitrogen. This vacuum/ nitrogen sequence was repeated for two times, toluene (3 mL) was added under the positive pressure of nitrogen and the resealed tube was immersed in a preheated oil bath at 130 ºC and stirred vigorously for 24 hours. The reaction mixture was cooled to room temperature, diluted with 5 mL ethyl acetate and filtered through celite using additional 10 mL ethyl acetate. The filtrate was concentrated and purified by column chromatography (100–200 mesh) eluting with pet ether– ethyl acetate mixture.



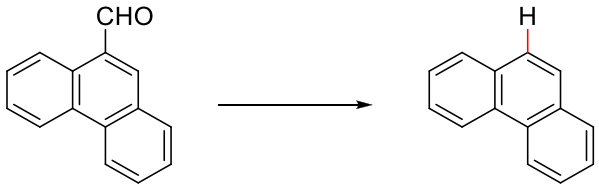
Naphthalene (Table 1, entry a). Deformylation was done by general procedure A with 1–naphthaldehyde (0.5 mmol, 78 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White crystalline naphthalene was eluted by pet ether only. Isolated yield 92% (59 mg). Same reaction was carried out following general procedure A with 12 mol% palladium acetate (0.06 mmol, 14 mg) at 120°C temperature, yield 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86–7.83 (m, 4H), 7.49–7.47 (m, 4H). GC–MS (*m/z*): 128.2 $[M]^+$.



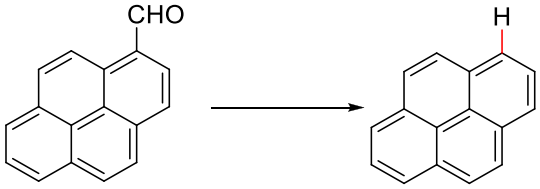
Naphthalene (Table 1, entry b). Deformylation was done by general procedure A with 2–naphthaldehyde (0.5 mmol, 78 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White crystalline naphthalene was eluted by pet ether only. Isolated yield 82% (52 mg). Same reaction was carried out following general procedure A with 12 mol% palladium acetate (0.06 mmol, 14 mg) at 110°C temperature, yield 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86–7.82 (m, 4H), 7.50–7.46 (m, 4H). GC–MS (*m/z*): 128.1 $[M]^+$.



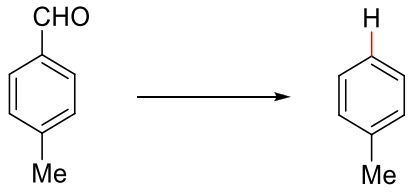
Anthracene (Table 1, entry c). Deformylation was done by general procedure A with anthracene–9–aldehyde (0.5 mmol, 104 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White crystalline anthracene was eluted by pet ether only. Isolated yield 97% (86 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.42(s, 2H), 8.02–7.98 (m, 4H), 7.48–7.45 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.85, 128.34, 126.40, 125.52. GC–MS (*m/z*): 178.2 $[M]^+$.



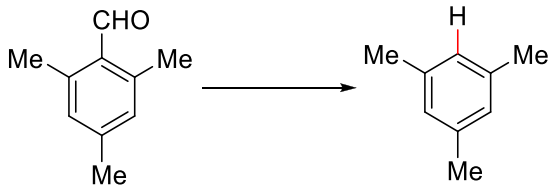
Phenanthrene (Table 1, entry d). Deformylation was done by general procedure A with phenanthrene–9–aldehyde (0.5 mmol, 104 mg) and 3 mol% palladium acetate (0.015 mmol, 4 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 100–200). White crystalline phenanthrene was eluted by pet ether only. Isolated yield 94% (84 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.69 (d, 2H, J= 8.1), 7.89 (dd, 2H, J= 7.8, 1.4), 7.74 (s, 2H), 7.68–7.57 (m,4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.22, 130.48, 128.75, 127.10, 126.75, 122.84. GC–MS (*m/z*): 178.2 $[M]^+$.



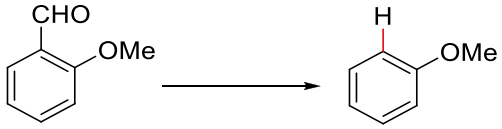
Pyrene (Table 1, entry e). Deformylation was done by general procedure A with pyrene–1–carbaldehyde (0.5 mmol, 115 mg) and 3 mol% palladium acetate (0.015 mmol, 4 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White crystalline pyrene was eluted by pet ether only. Isolated yield 95% (96 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18 (d, 4H, J= 7.7), 8.08 (s, 4H), 8.00 (t, 2H, J = 7.7). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.32, 127.57, 126.05, 125.13. GC–MS (*m/z*): 202.1 $[M]^+$.



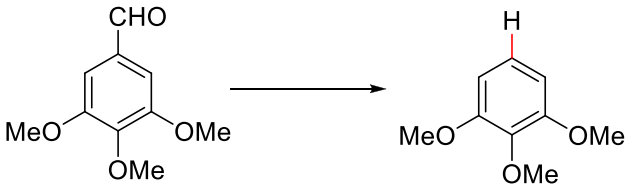
Toluene (Table 1, entry f). Deformylation was done by general procedure A with 4–methylbenzaldehyde (0.5 mmol, 60 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Yield was determined by gas chromatography using naphthalene as internal standard. GC yield 100%. Same reaction was carried out following general procedure A with 12 mol% palladium acetate (0.06 mmol, 14 mg) at 120°C temperature, yield 83%. GC–MS (*m/z*): 91.1 $[M]^+$.



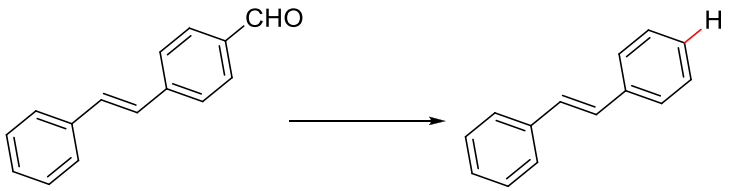
Mesitylene (Table 1, entry g). Deformylation was done by general procedure A with 2,4,6–trimethylbenzaldehyde (0.5 mmol, 74 mg) and 16 mol% palladium acetate (0.08 mmol, 18 mg) loading at 140°C. Yield was determined by gas chromatography using naphthalene as internal standard. GC yield 100%. GC–MS (*m/z*): 120.1 $[M]^+$.



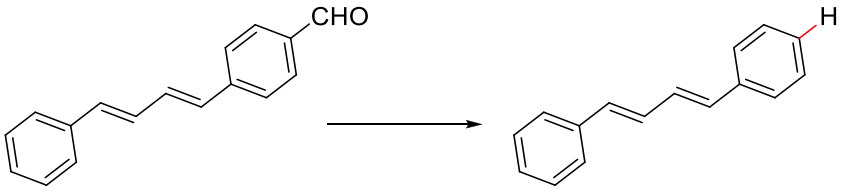
Anisole (Table 1, entry h). Deformylation was done by general procedure A with 2–methoxybenzaldehyde (0.5 mmol, 68 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Colourless liquid anisole was eluted by pet ether only. Isolated yield 81% (44 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30–7.25 (m, 2H), 6.95–6.89 (m, 3H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.69, 129.60, 120.80, 114.03, 55.26. GC–MS (*m/z*): 108.0 $[M]^+$.



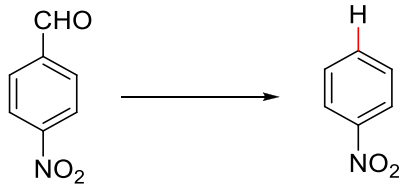
1,2,3–trimethoxybenzene (Table 2, entry i). Deformylation was done by general procedure A with 3,4,5–trimethoxybenzaldehyde (0.5 mmol, 98 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White solid product was eluted by pet ether–ethyl acetate mixture (98:2 v/v). Isolated yield 68% (57 mg). Recovered starting materials 24% (23 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.00 (t, 1H, J = 8.4), 6.58 (d, 2H,), 3.81 (t, 2H, J = 8.4), 3.86 (s, 6H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.65, 338.15, 123.82, 105.26, 60.99, 56.19 . GC–MS (*m/z*): 168.1 $[M]^+$.



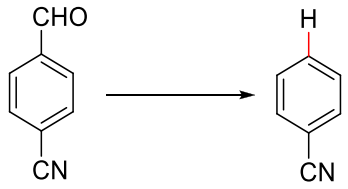
(E)–1,2–Diphenylethene (Table 1, entry j). Deformylation was done by general procedure A with (E)–4–styrylbenzaldehyde (0.5 mmol, 104 mg), cyclohexane (1 mL) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White crystalline product was eluted by pet ether only. Isolated yield 94% (84 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53–7.50 (m, 4H), 7.38–7.34 (m, 4H), 7.28–7.24 (m, 2H), 7.11(s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.50, 128.86, 127.80, 126.69. GC–MS (*m/z*): 180.2 $[M]^+$.



(1E,3E)–1,4–Diphenylbuta–1,3–diene (Table 2, entry k). Deformylation was done by general procedure A with 4–((1E,3E)–4–phenylbuta–1,3–dienyl)benzaldehyde (0.25 mmol, 59 mg) and 8 mol% palladium acetate (0.02 mmol, 5 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White crystalline product was eluted by pet ether only. Isolated yield 64% (33 mg). Recovered starting materials 27% (16 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45–7.42 (m, 4H), 7.35–7.31 (m, 4H), 7.25–7.21 (m, 2H), 6.96 (dd, 2H, J= 11.9, 2.9), 6.67 (dd, 2H, J= 11.9, 2.9). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.52, 132.99, 129.42, 128,84, 127.74, 126.56. GC–MS (*m/z*): 206.1 $[M]^+$.

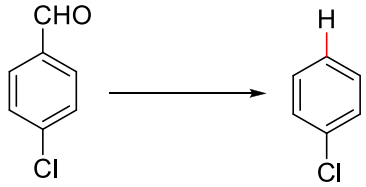


Nitrobenzene (Table 2, entry a). Deformylation was done by general procedure A with 4–nitrobenzaldehyde (0.5 mmol, 76 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Yellow liquid nitrobenzene was eluted by pet ether only. Isolated yield 80% (49 mg). Same reaction was carried out following general procedure A with 8 mol% palladium acetate (0.04 mmol, 9 mg) at 120°C temperature, yield 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25–8.22 (m, 2H), 7.71 (tt, 1H, J = 7.4, 1.2), 7.58–7.53 (m, 2H). GC–MS (*m/z*): 123.1 $[M]^+$.

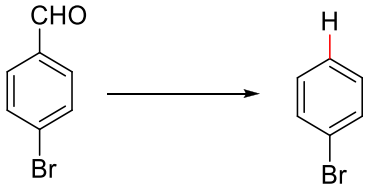


Benzonitrile (Table 2, entry b). Deformylation was done by general procedure A with 4–formylbenzonitrile (0.5 mmol, 66 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 120°C. Pure deformylated product was isolated by column chromatography through a silica gel column

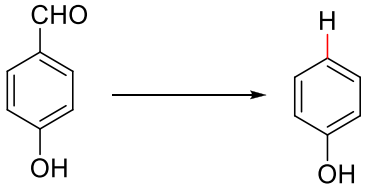
(mesh 60–120). Colourless liquid benzonitrile was eluted by pet ether only. Isolated yield 85% (44 mg). Same reaction was carried out following general procedure A with 10 mol% palladium acetate (0.05 mmol, 11 mg) at 110°C temperature, yield 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66–7.64 (m, 2H), 7.61 (tt, 1H, J = 7.5, 1.4), 7.49–7.46 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.91, 132.26, 129.25, 118.98, 112.52 . GC–MS (*m/z*): 103.0 $[M]^+$.



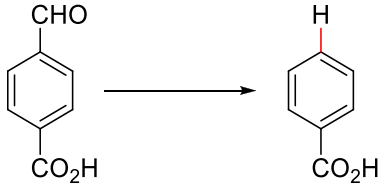
Chlorobenzene (Table 2, entry c). Deformylation was done by general procedure A with 4–chlorobenzaldehyde (0.5 mmol, 70 mg) and 12 mol% palladium acetate (0.06 mmol, 14 mg) loading at 110°C. Yield was determined by gas chromatography using naphthalene as internal standard. GC yield 93%. GC–MS (*m/z*): 112.0 $[M]^+$.



Bromobenzene (Table 2, entry d). Deformylation was done by general procedure A with 4–bromobenzaldehyde (0.5 mmol, 93 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Yield was determined by gas chromatography using naphthalene as internal standard. GC yield 28%. GC–MS (*m/z*): 159.9, 161.9 $[M]^+$.

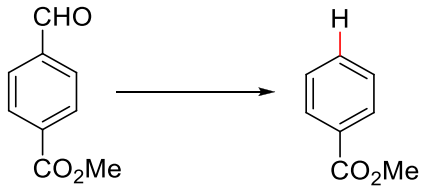


Phenol (Table 2, entry e). Deformylation was done by general procedure A with 4–hydroxybenzaldehyde (0.5 mmol, 61 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Colourless liquid product was eluted by pet ether–ethyl acetate mixture (95:5 v/v). Isolated yield 64% (30 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27–7.21 (m, 2H), 6.93 (tt, 1H, J = 7.4, 1.0), 6.85–6.81 (m, 2H), 5.01 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.53, 129.75, 120.87, 115.36. ^{13}C NMR was done by VRIAN instrument. GC–MS (*m/z*): 94.0 $[M]^+$.

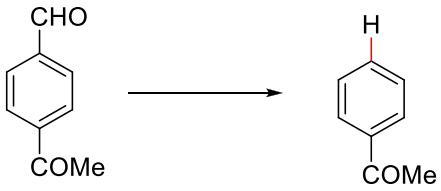


Benzoic acid (Table 2, entry f). Deformylation was done by general procedure A with 4–formylbenzoic acid (0.5 mmol, 75 mg) and 5 mol% palladium acetate (0.025 mmol, 6 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White solid benzoic acid was eluted by pet ether–ethyl acetate mixture (9:1 v/v). Isolated yield

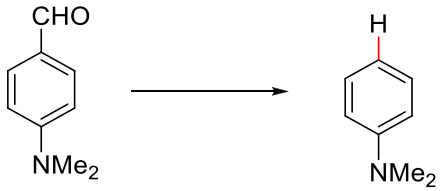
86% (52 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14–8.11 (m, 2H), 7.62 (tt, 1H, J = 7.4, 1.3), 7.51–7.46 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.78, 133.97, 130.39, 129.44, 128.68. GC–MS (*m/z*): 122.0 $[M]^+$.



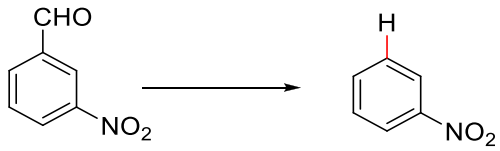
Methyl benzoate (Table 2, entry g). Deformylation was done by general procedure A with methyl 4–formylbenzoate (0.5 mmol, 82 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 120°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Colorless liquid methyl benzoate was eluted by pet ether only. Isolated yield 86% (58 mg). Same reaction was carried out following general procedure A with 12 mol% palladium acetate (0.06 mmol, 14 mg) at 100°C temperature, yield 69%. Defomylation in decaline (1.3 mL) instead of cyclohexane with 10 mol% palladium acetate (0.05 mmol, 11 mg) at 140°C following general procedure A yielded 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05–8.02 (m, 2H), 7.54 (tt, 1H, J = 7.4, 1.3), 7.44–7.41 (m, 2H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.22, 133.02, 130.27, 129.68, 128.47, 52.20. GC–MS (*m/z*): 136.0 $[M]^+$.



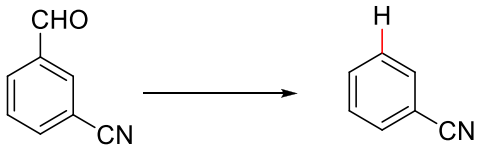
Acetophenone (Table 2, entry h). Deformylation was done by general procedure A with methyl 4–acetylbenzaldehyde (0.5 mmol, 74 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Colorless liquid acetophenone was eluted by pet ether only. Isolated yield 80% (48 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97–7.94 (m, 2H), 7.55 (tt, 1H, J = 7.3, 1.5), 7.47–7.43 (m, 2H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.26, 137.17, 133.20, 128.65, 128.38, 26.68. GC–MS (*m/z*): 120.1 $[M]^+$.



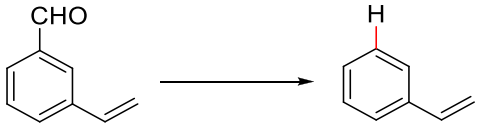
N,N–dimethylaniline (Table 2, entry i). Deformylation was done by general procedure A with methyl 4–(dimethylamino)benzaldehyde (0.5 mmol, 74 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Colourless liquid N,N–dimethylaniline was eluted by pet ether–ethyl acetate mixture (97.5:2.5 v/v). Isolated yield 85% (51 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25–7.20 (m, 2H), 6.74–6.66 (m, 3H), 2.92 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.79, 129.73, 116.76, 112.79, 40.75. GC–MS (*m/z*): 121.1 $[M]^+$.



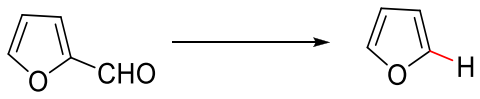
Nitrobenzene (Table 2, entry j). Deformylation was done by general procedure A with 3–nitrobenzaldehyde (0.5 mmol, 76 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 120°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Yellow liquid nitrobenzene was eluted by pet ether only. Isolated yield 80% (49 mg). Same reaction was carried out following general procedure A with 10 mol% palladium acetate (0.05 mmol, 11 mg) at 110°C temperature, yield 70%. Defomylation in decaline (1.3 mL) instead of cyclohexane with 10 mol% palladium acetate (0.05 mmol, 11 mg) at 140°C following general procedure A yielded 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25–8.22 (m, 2H), 7.71 (tt, 1H, J = 7.4, 1.2), 7.58–7.53 (m, 2H). GC–MS (*m/z*): 123.1 $[M]^+$.



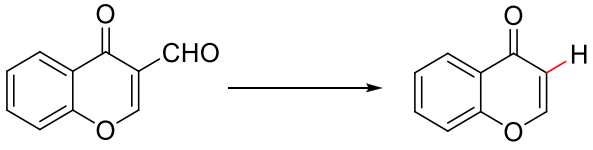
Benzonitrile (Table 2, entry k). Deformylation was done by general procedure A with 3–formylbenzonitrile (0.5 mmol, 66 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 120°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Colorless liquid benzonitrile was eluted by pet ether only. Isolated yield 77% (40 mg). Same reaction was carried out following general procedure A with 10 mol% palladium acetate (0.05 mmol, 11 mg) at 110°C temperature, yield 70%. Same reaction was carried out following general procedure A with 12 mol% palladium acetate (0.06 mmol, 14 mg) at 100°C temperature, yield 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71–7.65 (m, 2H), 7.61 (tt, 1H, J = 7.6, 1.4), 7.51–7.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.81, 132.18, 129.15, 118.88, 112.46. GC–MS (*m/z*): 103.1 $[M]^+$.



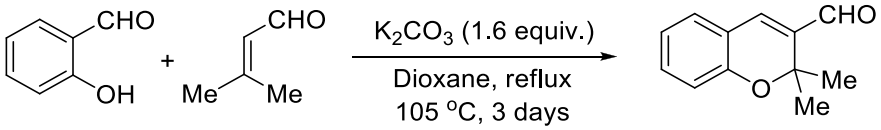
Styrene (Table 2, entry l). Deformylation was done by general procedure A with 3–vinylbenzaldehyde (0.5 mmol, 66 mg) and 12 mol% palladium acetate (0.06 mmol, 14 mg) loading at 110°C. Yield was determined by gas chromatography using naphthalene as internal standard. GC yield 79%. GC–MS (*m/z*): 104.1$[M]^+$, two peaks at (*m/z*): 206.1$[M]^+$ (yield~ 5%), (*m/z*): .206.1$[M]^+$ (yield~ 8%).



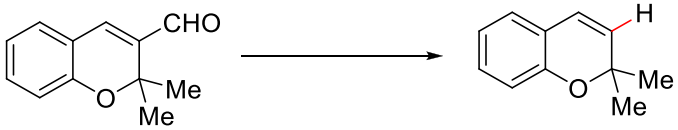
Furan (Table 3, entry a). Deformylation was done by general procedure A with furan–2–carbaldehyde (0.5 mmol, 48 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Yield was determined by gas chromatography using naphthalene as internal standard. GC yield 100%.



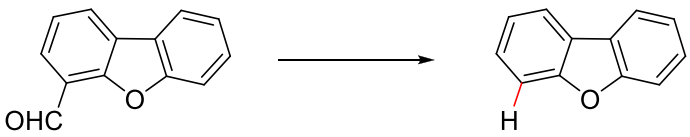
4H–Chromen–4–one (Table 3, entry b). Deformylation was done by general procedure A with 4–oxo–4H–chromene–3–carbaldehyde (0.5 mmol, 87 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Yellow solid 4H–chromen–4–one was eluted by pet ether–ethyl acetate mixture (95:5 v/v). Isolated yield 87% (64 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (dd, 1H, J = 8.0, 1.6), 7.86 (d, 1H, J = 6.0), 7.70–7.66 (m, 1H), 7.47–7.39 (m, 2H), 6.35 (d, 1H, J = 6.0). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.86, 156.67, 155.51, 133.96, 125.96, 125.43, 125.02, 118.34, 113.13. GC–MS (*m/z*): 146.0 $[M]^+$.



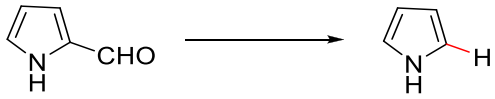
2,2-Dimethyl-2H-chromene-3-carbaldehyde. 2-Hydroxybenzaldehyde (5 mmol, 610 mg) was taken in a RB with magnetic stirbar. 10 mL dry dioxane and K_2CO_3 (4 mmol, 552 mg) were added. 3-methyl crotonaldehyde (7.5 mmol, 0.718 mL) was added dropwise under constant stirring. Then the mixture was refluxed for 3 days. Solvent was evaporated under reduced pressure; the residue was dissolved in DCM and distributed between DCM and 20% aq. NaOH soln. The organic layer was extracted finally with brine solution, dried over anhydrous Na_2SO_4, concentrated and purified by column (100-200 mesh silica) using pet ether–ethyl acetate mixture (95:5 v/v) as eluent to give the Pale White solid. Isolated yield 40% (376 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.45 (s, 1H), 7.31-7-27 (m, 1H), 7.16 (dd, 1H, J = 7.5, 1.7), 7.10 (s, 1H), 6.90 (td, 1H, J = 7.5, 1.1), 6.82 (d, 1H, J = 7.5), 1.62 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.54, 154.41, 142.67, 139.18, 133.69, 128.95, 121.40, 119.81, 117.01, 78.83, 26.75. GC–MS (*m/z*): 188.1 $[M]^+$.



2,2-Dimethyl-2H-chromene (Table 3, entry c). Deformylation was done by general procedure A with 2,2-dimethyl-2H-chromene-3-carbaldehyde (0.25 mmol, 47 mg), cyclohexane (0.7 mL) and 16 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Yellow liquid methyl 2,2-dimethyl-2H-chromene was eluted by pet ether–ethyl acetate mixture (95:5 v/v). Isolated yield 88% (32 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.08 (td, 1H, J = 7.8, 1.8), 6.96-6.94 (m, 1H), 6.82 (td, 1H, J = 7.4, 1.2), 6.76 (d, 1H, J = 8.1), 6.30 (d, 1H, J = 9.8), 5.58 (d, 1H, J = 9.8), 1.41 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.05, 130.84, 129.19, 126.44, 122.46, 121.41, 120.85, 116.45, 76.24, 28.14. GC–MS (*m/z*): 168.1 $[M]^+$.



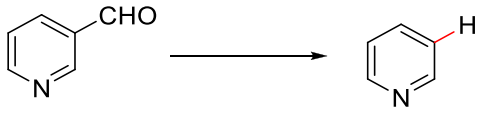
Dibenzo[b,d]furan (Table 3, entry d). Deformylation was done by general procedure A with dibenzo[b,d]furan–4–carbaldehyde (0.5 mmol, 98 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White crystalline dibenzo[b,d]furan was eluted by pet ether only. Isolated yield 89% (75 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, 2H, J = 7.7), 7.58–7.55 (m, 2H), 7.47–7.43 (m, 2H), 7.36–7.32 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.35, 127.30, 124.39, 122.86, 120.82, 111.84. GC–MS (*m/z*): 168.1 $[M]^+$.



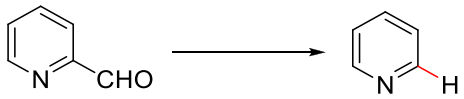
1H–Pyrrole (Table 3, entry e). Deformylation was done by general procedure A with 1H–pyrrole–2–carbaldehyde (0.5 mmol, 48 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Yield was determined by gas chromatography using naphthalene as internal standard. GC yield 58%. GC–MS (*m/z*): 67.1 $[M]^+$. Starting materials remained unreacted ~37% GC–MS (*m/z*): 95.1 $[M]^+$.

pyridine

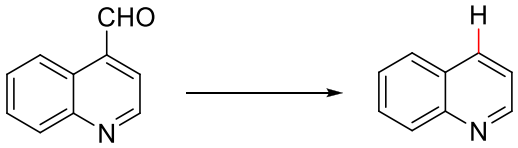
Pyridine (Table 3, entry f). Deformylation was done by general procedure A with isonicotinaldehyde (0.5 mmol, 54 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading. Yield was determined by gas chromatography using naphthalene as internal standard. GC yield 83%. GC–MS (*m/z*): 79.1 $[M]^+$. Starting materials remained unreacted ~10% GC–MS (*m/z*): 107.1 $[M]^+$.



Pyridine (Table 3, entry g). Deformylation was done by general procedure A with nicotinaldehyde (0.5 mmol, 54 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading. Yield was determined by gas chromatography using naphthalene as internal standard. GC yield 80%. GC–MS (*m/z*): 79.1 $[M]^+$. Starting materials remained unreacted ~10% GC–MS (*m/z*): 107.1 $[M]^+$.

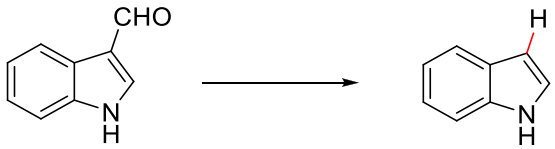


Pyridine (Table 3, entry h). Deformylation was done by general procedure A with picolinaldehyde (0.5 mmol, 54 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading. Yield was determined by gas chromatography using naphthalene as internal standard. GC yield 72%. GC–MS (*m/z*): 79.1 $[M]^+$. Starting materials remained unreacted ~20% GC–MS (*m/z*): 107.1 $[M]^+$.

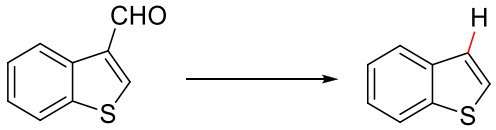


Quinoline (Table 3, entry i). Deformylation was done by general procedure A with quinoline–4–carbaldehyde (0.5 mmol, 78 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Yellow liquid quinoline was eluted by pet ether–ethyl acetate mixture (92:8 v/v). Isolated yield 85% (55 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.91 (dd, 1H, J = 4.2, 1.7), 8.15–8.11 (m, 2H), 7.80 (dd, 1H, J = 8.1, 1.2), 7.73–7.69 (m, 1H), 7.55–7.51 (m, 1H), 7.38 (dd, 1H, J = 8.3, 4.2). ^{13}C NMR (100 MHz,

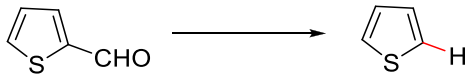
$CDCl_3$) δ: 150.43, 148.27, 136.19, 129.56, 129.44, 128.35, 127.87, 126.63, 121.15. GC–MS (*m/z*): 129.1 $[M]^+$.



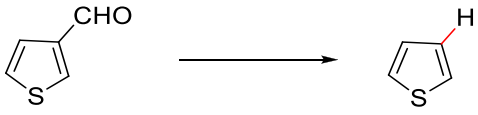
1H–Indole (Table 3, entry j). Deformylation was done by general procedure A with 1H–indole–3–carbaldehyde (0.25 mmol, 36 mg), cyclohexane (0.7 mL) and 8 mol% palladium acetate (0.02 mmol, 5 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White crystalline solid 1H–indole was eluted by pet ether –ethyl acetate mixture (98:2 v/v). Isolated yield 81% (23 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15 (b, 1H), 7.68–7.66 (m, 1H), 7.42–7.40 (m, 1H), 7.23–7.20 (m, 2H), 7.19–7.12 (m, 1H), 6.58–6.57 (m, 1H). GC–MS (*m/z*): 117.1 $[M]^+$.



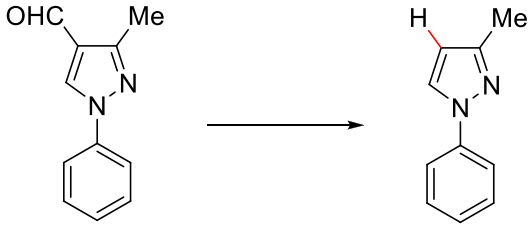
Benzo[b]thiophene (Table 3, entry k). Deformylation was done by general procedure A with benzo[b]thiophene–3–carbaldehyde (0.5 mmol, 81 mg) and 16 mol% palladium acetate (0.08 mmol, 18 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Colorless liquid benzo[b]thiophene was eluted by pet ether only. Isolated yield 66% (44 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87–7.84 (m, 1H), 7.81–7.78 (m, 1H), 7.40 (d, 1H, J = 5.5), 7.36–7.29 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.84, 139.72, 126.45, 124.35, 124.30, 123.99, 123.76, 123.63. GC–MS (*m/z*): 134.0 $[M]^+$.



Thiophene (Table 3, entry l). Deformylation was done by general procedure A with thiophene–2–carbaldehyde (0.5 mmol, 56 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Yield was determined by gas chromatography using naphthalene as internal standard. GC yield 55%.

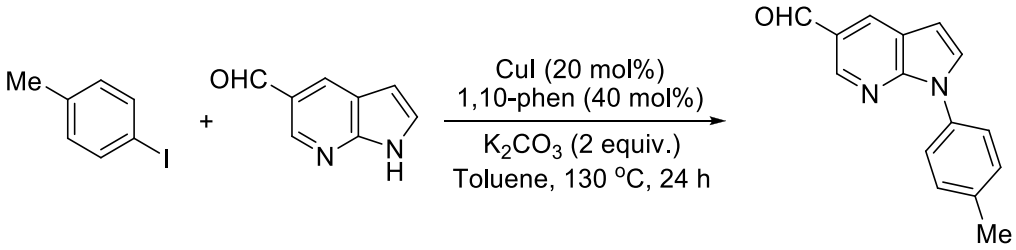


Thiophene (Table 3, entry m). Deformylation was done by general procedure A with thiophene–3–carbaldehyde (0.5 mmol, 56 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Yield was determined by gas chromatography using naphthalene as internal standard. GC yield 55%.

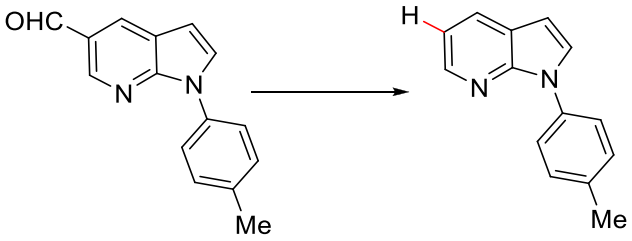


3–Methyl–1–phenyl–1H–pyrazole (Table 3, entry n). Deformylation was done by general procedure A with 3–methyl–1–phenyl–1H–pyrazole–4–carbaldehyde (0.5 mmol, 93 mg) and 8 mol% palladium

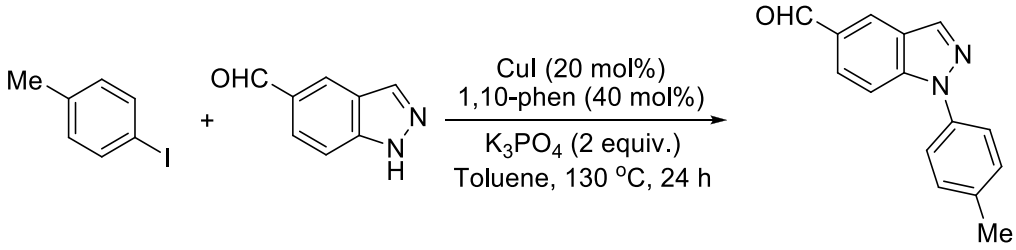
acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Colorless liquid 3–methyl–1–phenyl–1H–pyrazole was eluted by pet ether–ethyl acetate mixture (99:1 v/v). Isolated yield 66% (52 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, 1H, J = 2.2), 7.64–7.62 (m, 2H), 7.42–7.38 (m, 2H), 7.24–7.20 (m, 1H), 6.22 (d, 1H, J = 2.2), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.62, 140.30, 129.45, 127.45, 126.00, 118.89, 107.62, 13.84. GC–MS (*m/z*): 158.1 $[M]^+$.



1–p–tolyl–1H–pyrrolo[2,3–b]pyridine–5–carbaldehyde. Following general procedure C, *p*–tolyl iodide (1.5 mmol, 327 mg); 7–azaindole–5–carbaldehyde (1.5 mmol, 219 mg); CuI (0.3 mmol, 28 mg); 1,10–phenanthrolene (0.6 mmol, 59 mg) and K_2CO_3 (3 mmol, 414 mg) were used. Column chromatography provided the desired compound as white solid using pet ether–ethyl acetate mixture (80:20 v/v) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.06 (s, 1H), 8.62 (dd, 1H, J = 7.9, 1.6), 8.45 (dd, 1H, J = 4.7, 1.6), 8.08 (s, 1H), 7.59 (d, 2H, 8.3), 7.36 (d, 2H, J = 8.2), 7.30 (dd, 1H, J = 7.9, 4.7), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.06, 148.76, 145.85, 138.28, 137.98, 134.56, 130.92, 130.35, 124.67, 119.56, 118.26, 117.49, 21,29. GC–MS (*m/z*): 236.1 $[M]^+$.

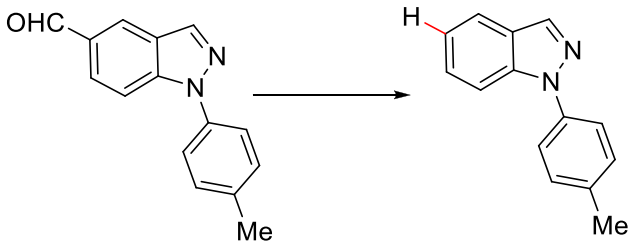


1–*p*–Tolyl–1H–pyrrolo[2,3–b]pyridinepyrazole (Table 3, entry o). Deformylation was done by general procedure A with 1–p–tolyl–1H–pyrrolo[2,3–b]pyridine–5–carbaldehyde (0.25 mmol, 59 mg), cyclohexane (0.7 mL) and 16 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Yellow oily liquid 1–*p*–Tolyl–1H–pyrrolo[2,3–b]pyridinepyrazole was eluted by pet ether –ethyl acetate mixture (93:7 v/v). Isolated yield 65% (31 mg). Recovered starting material 33% (19 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35 (dd, 1H, J = 4.6, 1.6), 7.94 (dd, 1H, J = 7.9, 1.4), 7.61–7.58 (m, 2H), 7.45 (d, 1H, J = 3.4), 7.30 (d, 2H, J = 8.4), 7.10 (dd, 1H, J = 4.7, 0.4), 6.59–6.58 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.67, 143.66, 136.34, 136.09, 130.05, 129.13, 128.17, 124.22, 121.55, 116.64, 101.36, 21.19. GC–MS (*m/z*): 208.0 $[M]^+$.

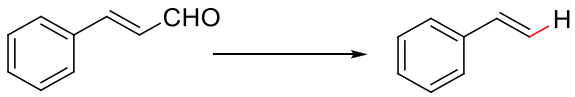


1–*p*–Tolyl–1H–indazole–5–carbaldehyde. Following general procedure C, *p*–tolyl iodide (1.5 mmol, 327 mg); 1*H*–indazole–5–carbaldehyde (1.5 mmol, 219 mg); CuI (0.3 mmol, 28 mg); 1,10–

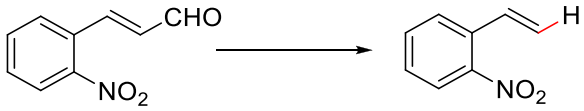
phenanthrolene (0.6 mmol, 59 mg) and K_3PO_4 (3 mmol, 637 mg) were used. Column chromatography provided the desired product as white crystalline solid using pet ether–ethyl acetate mixture (95:5 v/v) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.08 (s, 1H), 8.35–8.32 (m, 2H), 7.97 (dd, 1H, J = 8.8, 1.5), 7.77–7.75 (m, 1H), 7.60–7.51 (m, 2H), 7.38–7.36 (m, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.57, 141.40, 137.84, 137.07, 131.22, 130.37, 127.60, 126.27, 125.08, 123.33, 111.36, 21.33. GC–MS (*m/z*): 236.1 $[M]^+$.



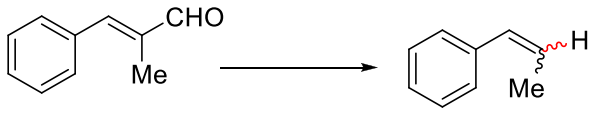
1–p–Tolyl–1H–indazole (Table 3, entry p). Deformylation was done by general procedure A with 1–p–tolyl–1H–indazole–5–carbaldehyde (0.25 mmol, 59 mg), cyclohexane (0.7 mL) and 16 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Yellow liquid 1–p–Tolyl–1H–indazole was eluted by pet ether –ethyl acetate mixture (98:2 v/v). Isolated yield 88% (46 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.17 (s, 1H), 7.77 (dt, 1H, J = 8.1, 0.9), 7.69 (dq, 1H, J = 8.6, 0.9), 7.60–7.58 (m, 2H), 7.41–7.37 (m, 1H), 7.33–7.29 (m, 2H), 7.22–7.17 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.92, 137.86, 136.66, 135.17, 130.12, 127.12, 125.28, 122.88, 121.48, 121.39, 110.53, 21.21. GC–MS (*m/z*): 208.1 $[M]^+$.



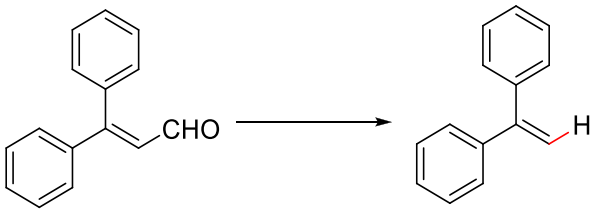
Styrene (Table 4, entry a). Deformylation was done by general procedure A with trans–cinnamaldehyde (0.5 mmol, 66 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Colourless liquid styrene was eluted by pet ether only. Isolated yield 74% (40 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56–7.54 (m, 2H), 7.47–7.43 (m, 2H), 7.40–7.36 (m, 1H), 6.76 (dd, 1H, J = 17.6, 10.8), 5.88 (dd, 1H, J = 17.6, 0.9), 5.38 (dd, 1H, J = 10.8, 0.9). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.69, 137.02, 128.65, 127.93, 126.35, 113. 90. GC–MS (*m/z*): 104.0 $[M]^+$. Styrene homo coupled product fromed as a side product (yield ~ 15 %). GC–MS (*m/z*): 206.1 $[M]^+$.



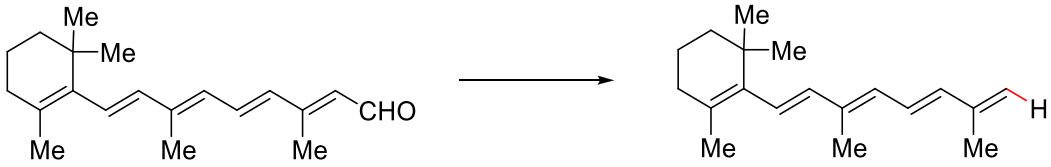
1–Nitro–2–vinylbenzene (Table 4, entry b). Deformylation was done by general procedure A with (E)–3–(2–nitrophenyl)acrylaldehyde (0.5 mmol, 82 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Yellow coloured liquid 1–nitro–2–vinylbenzene was eluted by pet ether only. Isolated yield 84% (57 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (dd, 1H, J = 8.2, 1.2), 7.63–7.55 (m, 2H), 7.42–7.38 (m, 1H), 7.16 (dd, 1H, J = 17.3, 10.9), 5.78 (dd, 1H, J = 17.3, 0.9), 5.47 (dd, 1H, J = 10.9, 0.9). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.99, 133.51, 133.30, 132.63, 128.66, 128. 51, 124.57, 119.14.



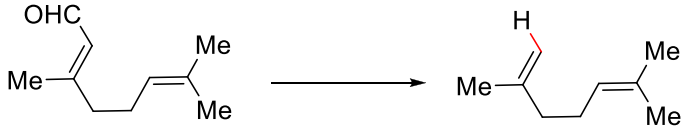
Prop–1–enylbenzene (Table 4, entry c). Deformylation was done by general procedure A with (E)–2–methyl–3–phenylacrylaldehyde (0.5 mmol, 73 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Colourless liquid prop–1–enylbenzene (cis : trans ~1:1) was eluted by pet ether only. Isolated yield 59% (35 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33–7.30 (m, 4H), 7.24–7.19 (m, 1H), 6.45–6.41 (m, 1H), 5.83–5.74 (m, 1H), 1.90 (dd, 3H, J = 1.8). GC–MS: two peaks with almost same area at different retention times, (*m/z*): 118.1 $[M]^+$. Other side products (yield ~5%) were characterized. GCMS (*m/z*): 134.1 $[M]^+$.



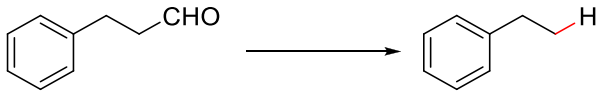
Ethene–1,1–diyldibenzene (Table 4, entry d). Deformylation was done by general procedure A with 3,3–diphenylacrylaldehyde (0.5 mmol, 104 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Yellow liquid ethene–1,1–diyldibenzene was eluted by pet ether only. Isolated yield 92% (82 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36–7.27 (m, 10H), 5.44 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.19, 141.63, 128.43, 128.33, 127.88, 114.49. GC–MS (*m/z*): 180.1 $[M]^+$. Other side product (yield ~5%) were characterized. GCMS (*m/z*): 358.1 $[M]^+$.



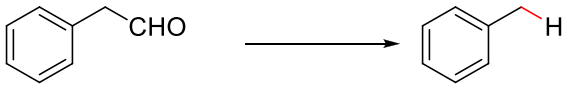
Retinal (Table 4, entry e). Deformylation was done by general procedure B with retinal (0.5 mmol, 142 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Yellow liquid 2–((1E,3E,5E)–3,7–dimethylocta–1,3,5,7–tetraenyl)–1,3,3–trimethylcyclohex–1–ene was eluted by pet ether only. Isolated yield 70% (80 mg). GC–MS (*m/z*): 256.1 $[M]^+$.



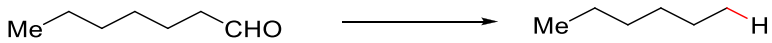
Citral (Table 4, entry f). Deformylation was done by general procedure B with citral (0.5 mmol, 76 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loading at 140°C. Yield was determined by gas chromatography using naphthalene as internal standard. GC yield 93%. GC–MS (*m/z*): 124.1 $[M]^+$.



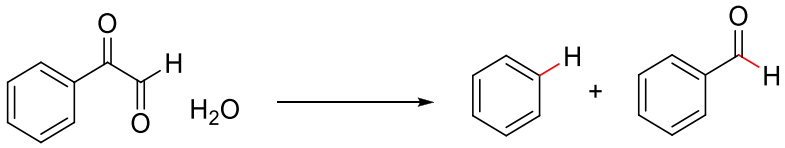
3–Phenylpropanal (Table 4, entry g). Deformylation was done by general procedure B with 3–phenylpropanal (0.5 mmol, 67 mg) and 16 mol% palladium acetate (0.08 mmol, 18 mg) loading at 140°C. Yield was determined by gas chromatography using naphthalene as internal standard. GC yield 62%.



Toluene (Table 4, entry h). Deformylation was done by general procedure B with 2-phenylacetaldehyde (0.5 mmol, 60 mg) and 12 mol% palladium acetate (0.06 mmol, 14 mg) loading at 120°C. Yield was determined by gas chromatography using n-decane as internal standard. GC yield 81%.

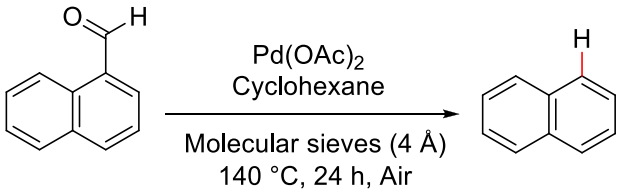


Heptanal (Table 4, entry i). Deformylation was done by general procedure B with heptanal (0.5 mmol, 57 mg) and 16 mol% palladium acetate (0.08 mmol, 18 mg) loading. Yield was determined by gas chromatography using naphthalene as internal standard. GC yield 74%. GC–MS (*m/z*): 100.1 $[M]^+$.



Deformylation of Phenylglyoxal hydrate (Scheme 2). Deformylation was done by general procedure A with phenylglyoxal hydrate (0.5 mmol, 67 mg) and 16 mol% palladium acetate (0.08 mmol, 18 mg) loading at 140°C. Yield was determined by gas chromatography using naphthalene as internal standard. Same reactions were done with 5 mol% (0.025 mmol, 6 mg) and 12 mol% (0.06 mmol, 14 mg) palladium acetate loading.

Deformylation of 1-Naphthaldehyde



1-Naphthaldehyde (5 mmol, 0.78 gm), palladium acetate (8 mol%, 0.4 mmol, 90 mg), molecular sieves (1 gm) were taken in a dry 100 mL round-bottom flusk, charged with magnetic stir-bar. Then 20 mL cyclohexane was added to it. The flusk containing reaction mixture was connected with a reflux condenser and heated at 140°C for 24 h with vigorously stirring. Reaction mixture was cooled and filtered through celite.