Supporting information

Stabilization of Pd NPs over the surface of a *β*-cyclodextrin incorporated UiO-66-NH_2 for the C-C coupling reaction

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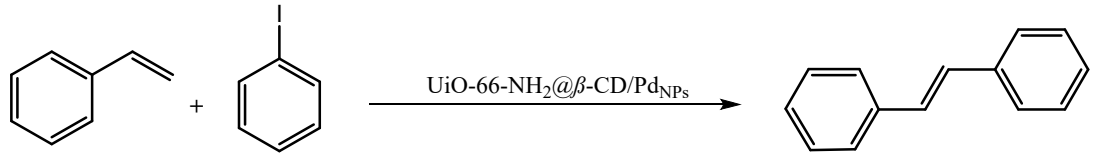
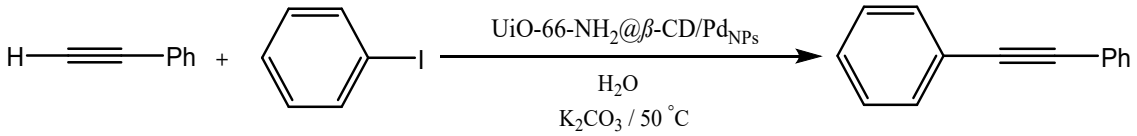
Table S1. The results of the optimization studies on the Heck reaction.



Entry	Catalyst (mg)	Solvent	T (°C)	Base	Time (min)	Yield (%)
1	5	H_2O	25	K_2CO_3	240	-
2	10	H_2O	25	K_2CO_3	240	10
3	20	H_2O	30	K_2CO_3	240	25
4	25	H_2O	45	K_2CO_3	240	35
5	30	H_2O	55	K_2CO_3	200	60
6	30	H_2O	80	K_2CO_3	100	98
7	30	H_2O	90	K_2CO_3	100	94
8	30	H_2O	100	K_2CO_3	100	90
9	30	H_2O	80	K_2CO_3	240	-
10	30	H_2O	90	KOH	240	76
11	30	DMSO	80	K_2CO_3	100	90
12	30	DMAc	80	K_2CO_3	100	90
13	30	NMP	80	K_2CO_3	100	90
14	30	DMF	80	K_2CO_3	100	87
15	30	H_2O	80	Et_3N	100	87
16	30	H_2O	80	Na_2CO_3	100	88
17	30	H_2O	80	NaOH	100	88
18	30	H_2O	80	NaOAc	100	80
19	30	CH_3CN	80	K_2CO_3	100	60
20	30	$C_6H_5CH_3$	80	K_2CO_3	100	65

Reaction condition: iodobenzene (1 mmol), styrene (1.1 mmol), base (2 mmol), solvent (3 ml)

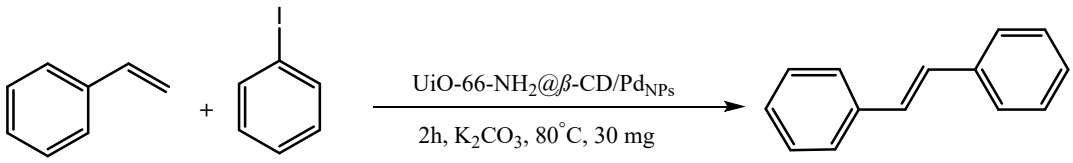
Table S2. The results of the optimization studies on the Sonogashira reaction.

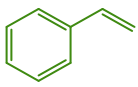
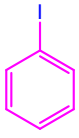
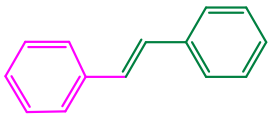


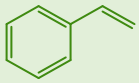
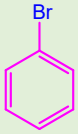
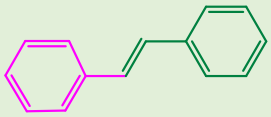
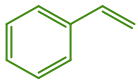
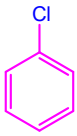
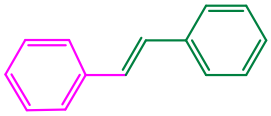
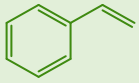
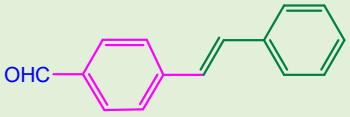
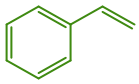
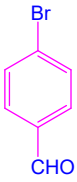
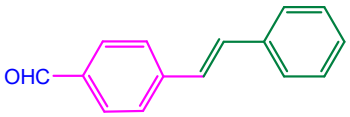
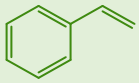
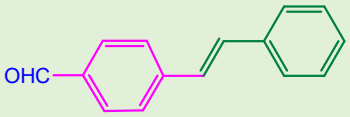
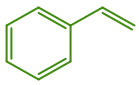
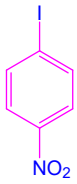
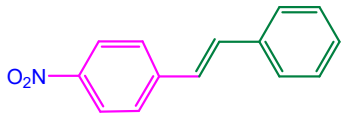
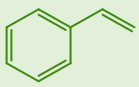
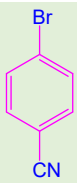
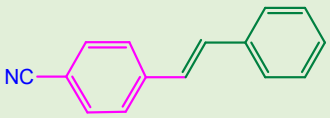
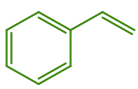
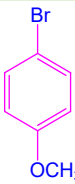
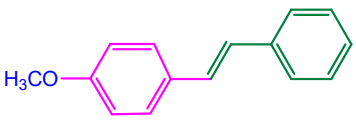
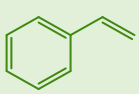
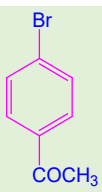
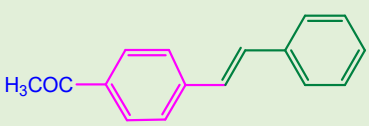
Entry	Catalyst (mg)	Solvent	T (°C)	Base	Time (h)	Yield (%)
1	10	H_2O	50	K_2CO_3	15	70
2	20	H_2O	50	K_2CO_3	15	95
3	30	H_2O	50	K_2CO_3	15	98
4	20	H_2O	25	K_2CO_3	15	35
5	20	H_2O	100	K_2CO_3	15	80
6	20	EtOH	50	K_2CO_3	15	83
7	20	H_2O	50	$NaCO_3$	15	15
8	20	H_2O	50	$CsCO_3$	15	85
9	20	H_2O	50	NaOH	15	70
10	20	H_2O	50	KOH	15	25

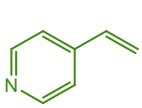
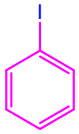
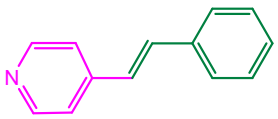
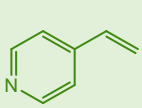
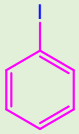
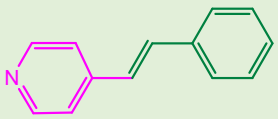
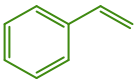
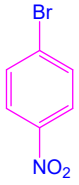
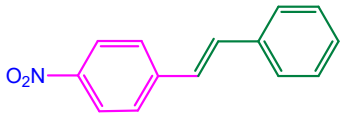
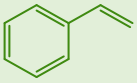
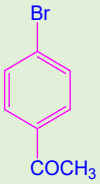
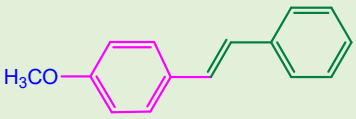
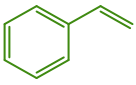
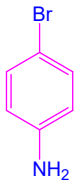
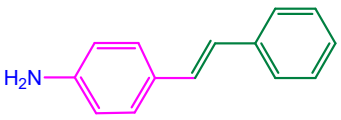
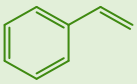
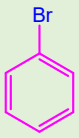
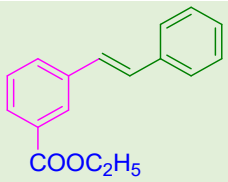
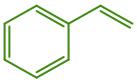
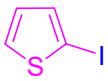
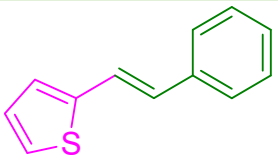
Reaction condition: Aryl halide (1 mmol), terminal alkynes (1.2 mmol), base (2 mmol), solvent (3 mL)

Table S3. Preparation of various organic compounds by Heck reaction under optimum conditions.



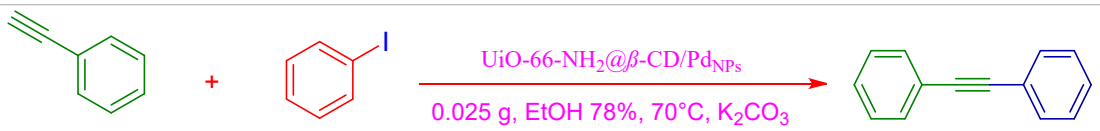
Entry	Alkene	Aryl halide	Product	Time (h)	Yield (%)
1				2	98

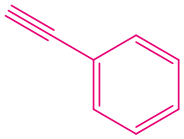
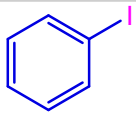
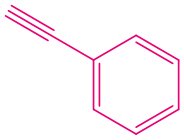
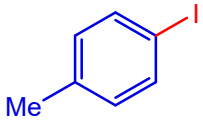
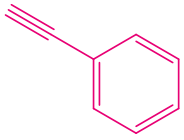
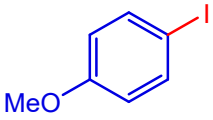
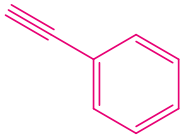
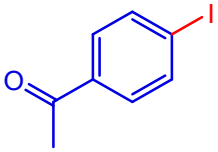
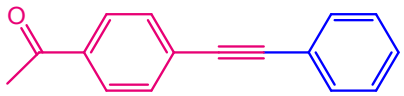
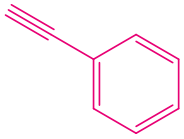
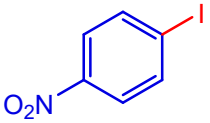
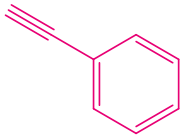
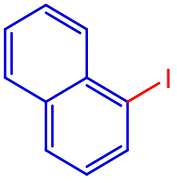
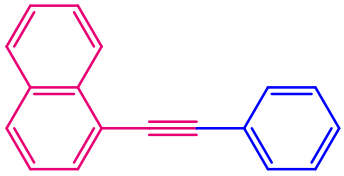
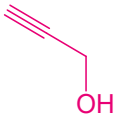
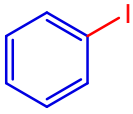
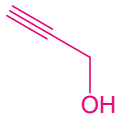
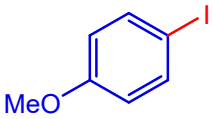
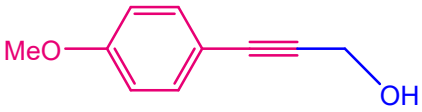
2				2	88
3				2	80
4				2	97
5				2	93
6				2	82
7				2	98
8				2	97
9				2	92
10				2	96

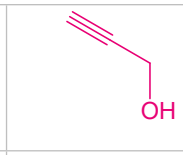
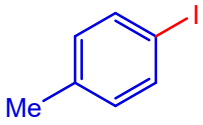
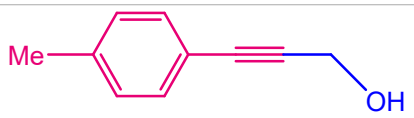
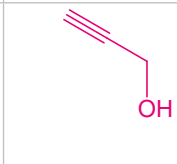
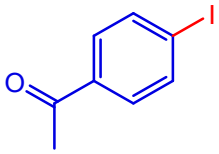
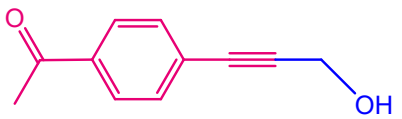
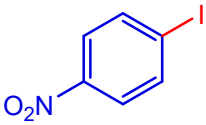
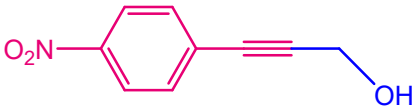
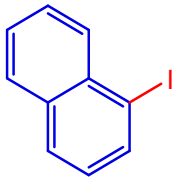
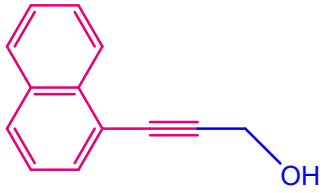
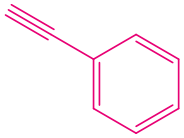
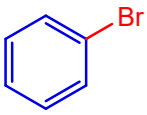
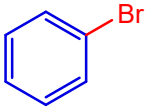
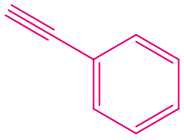
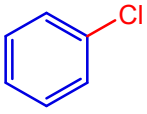
11				2	93
12				2	89
13				2	96
14				2	82
15				2	84
16				2	90
17				2	87

Reaction conditions: 1 mmol of aryl halide, 1 mmol of terminal alkyne, 2 mmol of base, 3 mL of solvent.

Table S4. Preparation of various organic compounds by Sonogashira reaction under optimum conditions.



Entry	Alkyne	Aryl halide	Product	Time (min)	Yield (%)
1				15	95
2				30	85
3				45	80
4				75	98
5				75	95
6				75	60
7				15	95
8				45	80

9				30	85
10				75	98
11				75	95
12				75	60
13				80	80
14				75	80
15				80	55

Reaction conditions: 1 mmol of arylhalide, 1 mmol of terminal alkyne, 2 mmol of base, 3 mL of solvent.

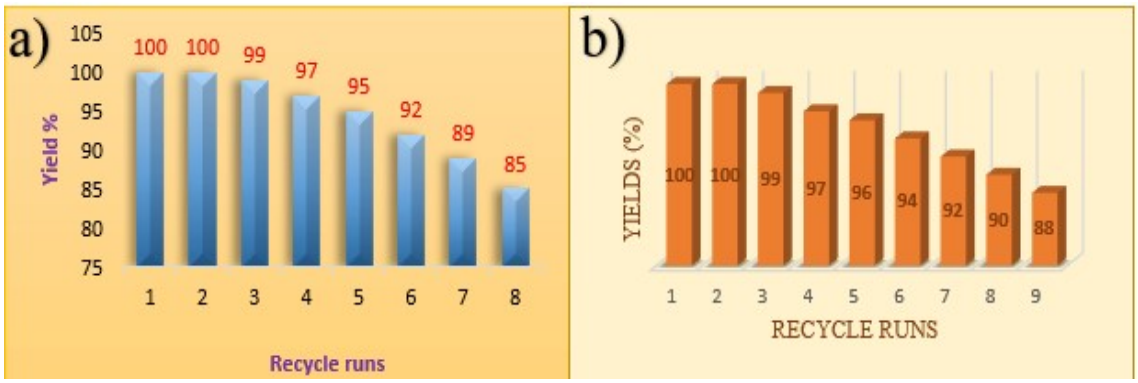
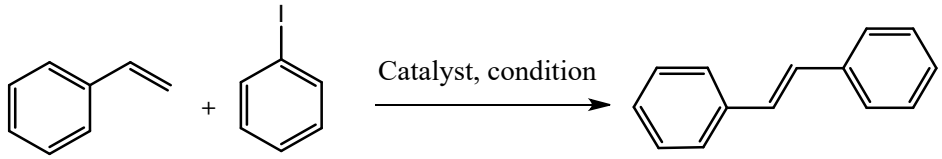


Fig. S1. Reusability of catalyst for a) Heck and b) Sonogashira reaction.

Table S5: Comparison of the catalytic performance of the proposed catalyst for Heck reaction with some related reports in the *literature*

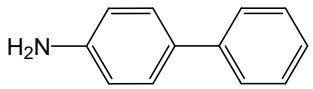


Entry	Catalyst	Reaction condition	Time (h)	Yield %	Reference
1	GA-FSNP@Pd (0.47)	DMF: H_2O (2: 1), Cs_2CO_3, 110°C	0.5	95	[1]
2	Pd-biomagnetic (5)	DMF, TEA, 120°C	3	100	[2]
3	Pd/N-MCNPs	DMAN, TEA, 120°C	3	97.6	[3]
4	SBA-TMG[a] –Pd (0.05)	Solvent-free, 140°C	4	90	[4]
5	Fe_3O_4@PUNP[b]-Pd (0.1)	H_2O, K_2CO_3, reflux	12	trace	[5]
6	Pd/graphene oxide (0.54)	toluene, NEt_3, reflux	5	62	[6]
7	Pd/MCPPY	DMA, TBA, 120°C	3	97	[7]
8	Pd/HCN (0.255)	DMF, K_2CO_3, 120°C	1	100	[8]
9	Pd/Fe_3O_4@C (0.308)	DMF, K_2CO_3, 120°C	2	66	[9]
10	PdNs-PAMAM-g-MWCNTs (0.3)	NMP, K_2CO_3, 100°C	2.5	95	[10]
11	Pd-MNPSS (0.36)	K_2CO_3, H_2O, 100°C	4	90	[11]
12	$PdCl_2$ (1.5), TDTAT (3 W%)	K_2CO_3, H_2O, 80°C	6	96	[12]
13	hydrogel@Pd NPs	K_2CO_3, H_2O, 85°C	0/5	98	[13]
14	*h*-BN@Sal@$Pd(OAc)_2$ (0.05 mol)	H_2O, 90°C	3.5	92	[14]
15	PdL_n@*β*-CD (3)	K_2CO_3, H_2O, reflux	4	94	[15]
16	Pd-MPTA-1 (10 mg)	K_2CO_3, H_2O, 100°C	6	92	[16]

17	Pd@CSP (0.5), TBAB	NEt_3, H_2O, reflux	7	90	[17]
18	Hall/TMSPMA@PGMA@5Aminotetrazole @Pd NPs	K_2CO_3, H_2O, 80°C, 2h	2	95	This research

Suzuki derivatives

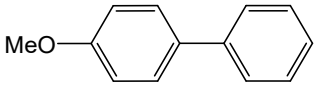
4-amine-[1,1'-biphenyl]



m.p. = 67-68 ºC.

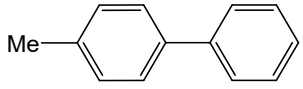
^{1}HNMR (400 MHz, DMSO): δ = 5.23 (2H, NH_2), 6.67 (2H, d, J = 8.3), 7.20 (1H, t, J = 7.2), 7.34-7.38 (4H, m), 7.53 (2H, d, J = 7.6). ^{13}CNMR (100 MHz, DMSO): δ = 114.3, 125.4, 125.7, 127.2 (4 × CH Ar), 127.5 (Ar), 128.8 (CH, Ar), 140.7, 148.4 (Ar). m/z: 170.1

4-Methoxy-1,1'-biphenyl



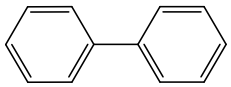
White waxy solid, yield 90%, ^{1}HNMR (500 MHz, $CDCl_3$): 7.57-7.52 (m, 4H), 7.41 (t, J = 8.0 Hz, 2H), 7.30 (t, J = 8.0 Hz, 1H), 6.98 (d, J = 8.5 Hz, 2H), and 3.86 (s, 3H).

4-methyl-1,1'-bipheny



white yellow solid in 92% yield, MP: 46-48 °C; ^{1}HNMR (500 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.51 (t, J = 7.8 Hz, 1H), 7.39 (m, 3H), 7.34 (m, 1H), 7.24 (t, J = 7.2 Hz, 1H), 7.16 (t, J = 8.1 Hz, 2H), 2.31 (s, 3H); ^{13}CNMR (126 MHz, $CDCl_3$): δ 141.19, 139.80, 138.34, 137.05, 136.72, 129.48, 129.01, 128.74, 128.21, 127.38, 127.01, 126.83, 125.73, 21.11; FTIR (cm^{-1}): 2918, 2318, 1743, 1521, 1325, 1114, 802; GC-MS m/z: 168.

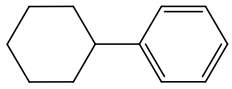
Biphenyl



white solid in 94% yield, MP: 69-71 °C

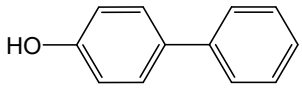
^{1}HNMR (500 MHz, $CDCl_3$): δ 7.59 (d, J =7.7 Hz, 4H), 7.44 (t, J = 7.7 Hz, 4H), 7.34 (t, J = 7.4 Hz, 2H); ^{13}CNMR (126 MHz, $CDCl_3$): δ141.29, 128.82, 127.27; FTIR (cm^{-1}): 2358, 1510, 1029, 580; GC-MS (EI, 70ev) m/z: found: 154 ($C_{12}H_{10}$).

Cyclohexylbenzene



Colorless oil in 73% yield ^{1}HNMR (400 MHz, chloroform-d) δ = 7.31 – 7.25 (m, 2H), 7.23 – 7.13 (m, 3H), 2.49 (m, 1H), 1.92 – 1.82 (m, 4H), 1.74 (m, 1H), 1.51 – 1.34 (m, 4H), 1.25 (m, 1H); ^{13}CNMR (100 MHz, chloroform-d) δ = 148.2, 128.4, 127.0, 125.9, 44.8, 34.6, 27.1, 26.3.

4-hydroxyl-[1,1'-biphenyl]

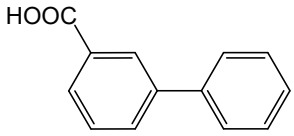


m.p. = 161-162 °C.

^{1}HNMR (400 MHz, DMSO): δ = 6.85 (2H, d, J = 8.5), 7.27 (1H, t, J = 7.4), 7.40 (2H, t, J = 7.4), 7.48

(2H, d, J = 8.5), 7.57 (2H, d, J = 8.5), 9.58 (1H, br s, OH). 13 C NMR (100 MHz, DMSO): δ = 115.8, 126.0, 126.4, 127.8, 128.8 (5 × CH, Ar), 131.0, 140.3, 157.2 (Ar). m/z: 169.1.

3-carboxylic acid-[1,1'-biphenyl]

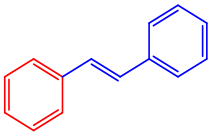


m.p. = 160-161 °C. ^{1}HNMR (400 MHz, DMSO): δ = 7.42 (1H, tt, J = 7.3, 1.1), 7.50 (2H, t, J = 7.3), 7.58 (1H, t, J = 7.7), 7.66 (2H, m), 7.87 (1H, dq, J = 7.7, 1.4), 8.14 (1H, dt, J = 7.7, 1.4), 8.40 (1H, t, J = 1.4).

^{13}CNMR (100 MHz, DMSO): δ = 127.2, 127.8, 128.85, 128.93, 128.96, 128.99 (CH, Ar), 129.8 (Ar), 132.4 (CH Ar), 139.9, 141.6 (2 × CH Ar), 172.3 (C=O). m/z: 197.0

Heck derivatives

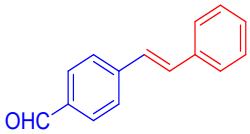
Trans-1, 2-diphenylethene (*E*-Stilbene)



White solid, Mp. 123-124°C (lit. 123.9-124.6°C)

GC–MS (m/z): 180; ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.07-7.08 (s, 2H), 7.21-7.23 (m, 2H), 7.32- 7.34 (m, 4H,) 7.46-7.48 (m, 21H) ppm. ^{13}CNMR (100 MHz, $CDCl_3$) δ 122.1, 123.2, 124.3, 132.9.

(*E*)-4-styrylbenzaldehyde

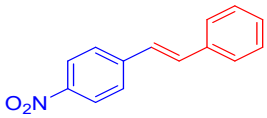


White solid, Mp. 116°C (lit. 116.0-116.8°C)

GC–MS (m/z): 208; ^{1}HNMR (400 MHz, $CDCl_3$): δ = 9.97 (s, 1H), 7.84 (d, J=8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.52 (d, J= 7.6 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.28 (t, J= 7.6 Hz, 1H), 7.22 (d, J = 5.2 Hz, 1H), 7.11 (d, J=16.4 Hz, 1H).

^{13}CNMR (100 MHz, $CDCl_3$): δ = 191.5, 143.4, 136.5, 135.3, 132.2, 130.2, 128.8, 128.4, 127.3, 126.9. MS (EI) m/z: 208, 179, 165, 152, 102, 89, 76, 63, 51.

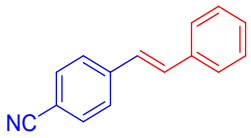
(*E*)-4-Nitrostilbene



Yellow solid, Mp. 154-155°C (lit. 154.2-155.0°C)

GC–MS (m/z): 225; ^{1}HNMR (400 MHz, $CDCl_3$) δ: 8.22 (d. *J* = 8.6 Hz, 2H, Ar-H), 7.63 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.55 (d, *J* = 7.7 Hz, 2H, Ar-H), 7.40 (t, *J* = 7.6 Hz, 2H, Ar-H), 7.36-7.31 (m, 1H, Ar-H), 7.27 (d, *J* = 16.3 Hz, 1H, CH=), 7.14 (d, *J* = 16.3, 1H, Hz, CH=). ^{13}CNMR (100 MHz, $CDCl_3$), δ = 125.2, 127.4, 128.0, 128.2, 130.0, 134.4, 137.3, 145.0, 147.8 ppm.

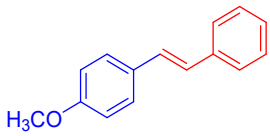
(*E*)-4-Styrylbenzonitrile



White solid, Mp. 114-115°C (lit. 114.9-115.2°C)

GC–MS (m/z): 205; ^{1}HNMR (400 MHz, $CDCl_3$): δ 7.09 (d, 1H, *J* = 16.0 Hz), 7.22 (d, 1H, *J* = 16.0 Hz), 7.31-7.34 (t, 1H, *J* = 4.0 Hz), 7.38-7.41 (t, 2H, *J* = 4.0 Hz), 7.54 (d, 2H, *J* = 7.2 Hz), 7.58 (d, 2H, *J* = 8.4 Hz), 7.64 (d, 2H, *J* = 8.4 Hz) ppm; ^{13}CNMR (100 MHz, $CDCl_3$), δ 111.7, 120.2, 127.8, 128.0, 128.1, 129.8, 130.0, 133.5, 133.6, 137.4, 142.9 ppm.

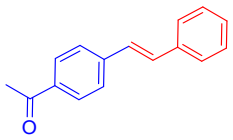
(*E*)-1-methoxy-4-styrylbenzene



White solid, Mp. 135-136°C (lit. 135.3-135.9°C)

GC–MS (m/z): 210; ^{1}H-NMR (400 MHz, $CDC1_3$) δ (ppm): 3.70 (3H, s), 6.78 (1H, d, *J* = 8.75 Hz), 6.90 (1H, d, *J* = 10.75 Hz), 7.00-7.38 (9H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 55.3, 114.2, 126.3, 126.6, 127.25, 127.8, 128.2, 128.7, 130.2, 137.7, 159.3.

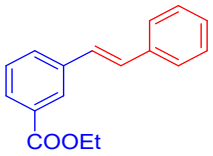
(*E*)-1-(4-styrylphenyl) ethanone



White solid, Mp. 141-142°C (lit. 141.3-142°C)

GC–MS (m/z): 222; ^{1}HNMR (400 MHz, $CDCl_3$): δ 7.97-7.95 (d, 2H), 7.58-7.57 (d, 2H), 7.53-7.52 (d, 2H), 7.40-7.36 (t, 2H), 7.29-7.25 (t, 1H), 7.22-7.20 (d, 1H), 7.12 (d, 1H), 2.64 (s, 3H), ^{13}CNMR (100 MHz, $CDCl_3$): δ 197.6, 142.1, 136.7, 136.1, 131.5, 128.9, 128.8, 128.4, 127.6, 126.8, 126.5, 26.8.

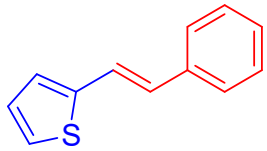
(*E*)-Ethyl-3-styrylbenzoate



Oily liquid

GC–MS (m/z): 252; ^{1}HNMR ($CDCl_3$, 400 MHz): δ (ppm) 8.22 (s, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 2H), 7.46–7.27 (m, 4H), 7.21 (d, *J* = 16.0 Hz, 1H), 7.15 (d, *J* = 16.0 Hz, 1H), 4.43 (q, *J* = 7.1 Hz3H), 1.44 (t, *J* = 7.1 Hz); ^{13}CNMR ($CDCl_3$, 100 MHz): δ (ppm) 166.6, 137.7, 137.0, 131.0, 130.7, 129.9, 128.8, 128.7, 128.5, 128.0, 127.6, 127.5, 126.7.

(*E*)-2-styrylthiophene



white solid, MP. 111-112°C (lit. 112°C)

GC–MS (m/z): 186; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.49 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 5.1 Hz, 1H), 7.24 (d, *J* = 16 Hz, 1H), 7.21 (d, *J* = 4.9 Hz, 1H), 7.09 (d, *J* = 3.4 Hz, 1H), 7.03 (t, *J* = 4 Hz, 1H), 6.95 (d, *J* = 16.2 Hz, 1H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ (ppm) 142.9, 137.0, 128.7, 128.4, 127.6, 126.3, 126.1, 124.3, 121.8.

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