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MCM-41-supported bidentate phosphine palladium(0) complex as an efficient catalyst for the heterogeneous Stille reaction

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ABSTRACT

A Stille coupling reaction of organostannanes with organic halides has been developed in the presence of a catalytic amount of MCM-41-supported bidentate phosphine palladium(0) complex (0.5 mol %) in DMF/H_2O (9:1) under air atmosphere in high yields. This polymeric palladium catalyst exhibits higher activity than $Pd(PPh_3)_4$ and can be reused at least 10 times without any decrease in activity.

1. Introduction

The palladium-catalyzed cross-coupling of organostannanes with organic halides and triflates, known as Stille reaction, is one of the most important, powerful, and versatile tools for the formation of carbon–carbon bonds.[1] This coupling reaction has been widely applied in organic synthesis[2] since a variety of functionality can be tolerated on either partner. The yields of coupled products are often high, and the organotin reagents can be readily synthesized, purified, and stored. However, the reaction generally proceeds in the presence of a homogeneous palladium catalyst such as $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, and $PdCl_2(MeCN)_2$, which makes the recovery of the metal tedious if not impossible and might result in unacceptable palladium contamination of the product. The forcing conditions are typically at reflux in THF or dioxane and the requirement for dry, oxygen-free environments is also the limitation of the Stille reaction. From the standpoint of green chemistry, the development of more environmentally benign conditions for the reaction, for example, the use of a heterogeneous palladium catalyst would be desirable.[3] So far, polymer-supported palladium catalysts have successfully been used for Heck reactions,[4] Suzuki reactions,[5] Sonogashira reactions,[6] etc. However, to the best of our knowledge, Stille reactions catalyzed by polymer-supported palladium complexes have received less attention.[7] Unfortunately, they have lower catalytic activity compared with their soluble counterparts in Stille reactions. In addition, the activity of the recycled catalysts gradually decreases because the palladium species leaches from the supporting polymer or silica gel. To overcome these limitations, a novel methodology for creating insoluble and highly active catalysts is needed. Our approach was guided by three imperatives: (1) the polymeric reagent should be easily accessible, (2) starting from readily available and cheap reagents, and (3) the polymeric ligand should be air stable at room temperature, which should allow its storage in normal bottles with unlimited shelf life. Recent developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support to immobilize homogeneous catalysts.[8] MCM-41 has a regular pore diameter of ca. 5 nm and a specific surface area $>700\ m^2\ g^{-1}$.[9] Its large pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to reach to the surface of the channel.[10–12] To date, a few palladium complexes on functionalized MCM-41 support have been prepared and used in organic reactions.[13–17] Very recently, we have reported the synthesis of the MCM-41-supported bidentate phosphine palladium(0) complex [abbreviated as MCM-41-2P-Pd(0)] and found that this complex is a highly active and recyclable catalyst for Sonogashira reactions of aryl iodides.[6e] In this paper, we wish to report that Stille coupling reactions of organostannanes with organic halides can be easily achieved in the presence of a catalytic amount of MCM-41-supported bidentate phosphine palladium(0) complex [MCM-41-2P-Pd(0)] under aqueous and aerobic conditions in high yields.

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2. Results and discussion

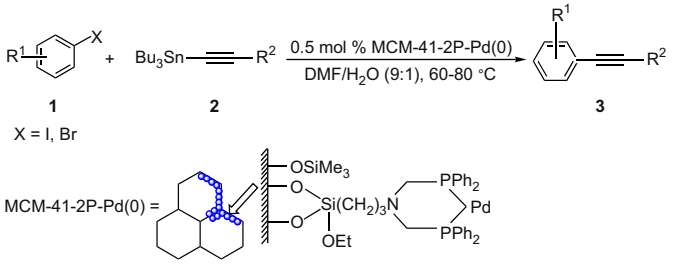
The MCM-41-supported bidentate phosphine palladium(0) complex [MCM-41-2P-Pd(0)] was prepared according to our previous procedure.[6e] The phosphine and palladium content was 1.15 and 0.52 mmol/g, respectively. Initially, to determine the optimum conditions, the cross-coupling reaction of 1-(tributylstannyl)-2-phenylethyne with iodobenzene was examined in different solvents under aerobic conditions and found that DMF/H_2O (9:1) was the best choice as a solvent. The results are summarized in Table 1. For the temperatures evaluated [25, 40, 60, and 80 °C], 60 °C gave the best result. The use of DMF, NMP, and HMPA at 60 °C gave good yields (81–84%), and the use of THF, PhH, and CH_3CN gave lower yields (23–35%). Running the reaction in DMF/H_2O (9:1) at 60 °C for 6 h gave 1,2-diphenylethyne (**3a**) in 86% yield. Increasing the amount of palladium catalyst shortened the reaction time, but did not increase the yield of 1,2-diphenylethyne (entry 12). The low palladium concentration usually led to a long period of reaction, which was consistent with our experimental result (entry 13). Taken together, good result was obtained when the coupling reaction was carried out with 0.5 mol % of MCM-41-2P-Pd(0) in DMF/H_2O (9:1) at 60 °C under aerobic conditions.

Table 1
Stille coupling of iodobenzene with 1-(tributylstannyl)-2-phenylethyne under the various reaction conditions[a]

Entry	Solvent	MCM-41-2P-Pd(0) (mol %)	Temp (°C)	Time (h)	Yield[b] (%)
1	DMF	0.5	25	24	38
2	DMF	0.5	40	24	62
3	DMF	0.5	60	6	84
4	DMF	0.5	80	5	79
5	NMP	0.5	60	6	83
6	HMPA	0.5	60	6	81
7	DMF/H_2O (9:1)	0.5	60	6	86
8	THF	0.5	60	24	27
9	PhH	0.5	60	24	23
10	CH_3CN	0.5	60	24	35
11	CH_3CN/H_2O (9:1)	0.5	60	24	30
12	DMF/H_2O (9:1)	1.0	60	4	85
13	DMF/H_2O (9:1)	0.2	60	15	83

[a] All reactions were performed using 1.0 mmol of iodobenzene, 1.1 mmol of 1-(tributylstannyl)-2-phenylethyne in 2 mL of solvent under aerobic conditions.
[b] Isolated yield based on the iodobenzene used.

To examine the scope for this coupling reaction, a variety of alkynylstannanes were coupled with aryl halides in DMF/H_2O (9:1) in the presence of a catalytic amount of MCM-41-2P-Pd(0) (Scheme 1). The experimental results are summarized in Table 2. As shown in Table 2, the Stille coupling reaction of aryl iodides with a variety of alkynylstannanes proceeded smoothly under mild conditions giving the corresponding coupled products in high yields. This polymeric palladium catalyst exhibits higher activity than $Pd(PPh_3)_4$. For example, the coupling reaction of 3-nitroiodobenzene with 1-(tributylstannyl)-2-phenylethyne in the



Scheme 1.

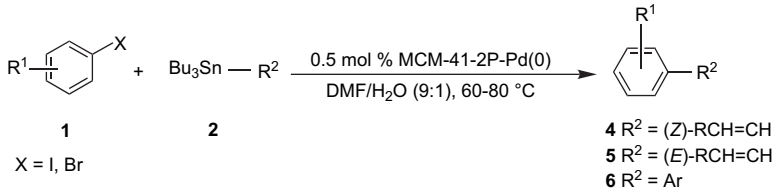
Table 2
Stille reactions of alkynylstannanes with aryl halides[a]

Entry	R^1	X	R^2	Temp (°C)	Time (h)	Product	Yield[b] (%)
1	H	I	Ph	60	6	**3a**	86
2	4-Me	I	Ph	60	6	**3b**	84
3	3-Me	I	Ph	60	6	**3c**	86
4	4-O_2N	I	Ph	60	6	**3d**	87
5	3-O_2N	I	Ph	60	6	**3e**	89
6	4-MeOCO	I	Ph	60	6	**3f**	87
7	3-Me	I	n-C_4H_9	60	8	**3g**	85
8	4-O_2N	I	n-C_4H_9	60	6	**3h**	88
9	3-CN	I	n-C_4H_9	60	6	**3i**	88
10	H	I	$MeOCH_2$	60	8	**3j**	85
11	4-MeO	I	Me_3Si	60	6	**3k**	84
12	4-Cl	I	Me_3Si	60	6	**3l**	86
13	4-MeCO	I	Ph	60	6	**3m**	87
14	4-OH	I	H	60	8	**3n**	85
15	3-CN	I	H	60	8	**3o**	86
16	H	Br	Ph	80	18	**3a**	78
17	4-Cl	Br	n-C_4H_9	80	12	**3p**	82
18	4-MeO	Br	Ph	80	24	**3q**	75
19	4-O_2N	Br	Ph	80	10	**3d**	84

[a] All reactions were performed using 1.0 mmol of aryl halide, 1.1 mmol of alkynylstannane, and 0.005 mmol of MCM-41-2P-Pd(0) in DMF/H_2O (9:1) (2 mL) under aerobic conditions.
[b] Isolated yield based on aryl halide used.

presence of 0.5 mol % of MCM-41-2P-Pd(0) in DMF/H_2O (9:1) at 60 °C for 6 h gave the coupled product **3e** in 89% yield, the same reaction in the presence of 2 mol % of $Pd(PPh_3)_4$ in DMF at 60 °C for 6 h gave **3e** in 84% yield. The heterogeneous Stille coupling of aryl iodides with ethynyltributylstannane provides a direct and practical route for the synthesis of functionalized terminal arylacetylenes (entries 14 and 15). As expected, the reactivity of aryl bromides was lower than that of aryl iodides and the coupling reactions of aryl bromides with alkynylstannanes required slightly higher temperature (80 °C) and longer times. The substituent effects in the aryl iodides appeared to be less significant than in the aryl bromides and the reactivity of aryl bromides with electron-withdrawing substituents was higher than that of aryl bromides with electron-donating substituents. The Stille reaction of alkynylstannanes with the electron-deficient aryl bromides proceeded smoothly at 80 °C using MCM-41-2P-Pd(0) complex as catalyst to afford the corresponding coupled products in high yields after 10–12 h of reaction time (entries 17 and 19). The Stille reaction of alkynylstannanes with bromobenzene or aryl bromides having electron-donating substituents also proceeded under the same conditions giving the corresponding coupled products in good yields, but longer reaction time (18–24 h) was required (entries 16 and 18). The optimized catalyst system was quite general and compatible with a wide range of functional groups such as nitro, cyano, halogen, methoxy, carbonyl, hydroxy, and silyl on either partner. We attempted to carry out the coupling reactions of heteroaryl iodides such as 2-iodothiophene or 3-iodopyridine with alkynylstannanes under the same reaction conditions, but this is unsuccessful, no desired coupled product was detected after 24 h of reaction time.

The developed methodology was also applicable for the Stille coupling reactions of vinylstannanes and arylstannanes with aryl halides. The Stille coupling of aryl halides with a variety of vinylstannanes or arylstannanes was investigated (Scheme 2), the experimental results are summarized in Table 3. The Stille coupling reactions of a variety of aryl iodides with (*Z*)- or (*E*)-vinylstannanes proceeded smoothly in the presence of a catalytic amount of MCM-41-2P-Pd(0) in DMF/H_2O (9:1) at 60 °C to afford the corresponding coupled products in high yields with retention of the configuration (entries 1–10). As expected, the coupling reaction of aryl bromides with vinylstannanes at 60 °C was very slow, only traces of coupled products were formed after 24 h. However, the Stille reaction of aryl bromides with (*E*)-vinylstannanes could also proceed smoothly



Scheme 2.

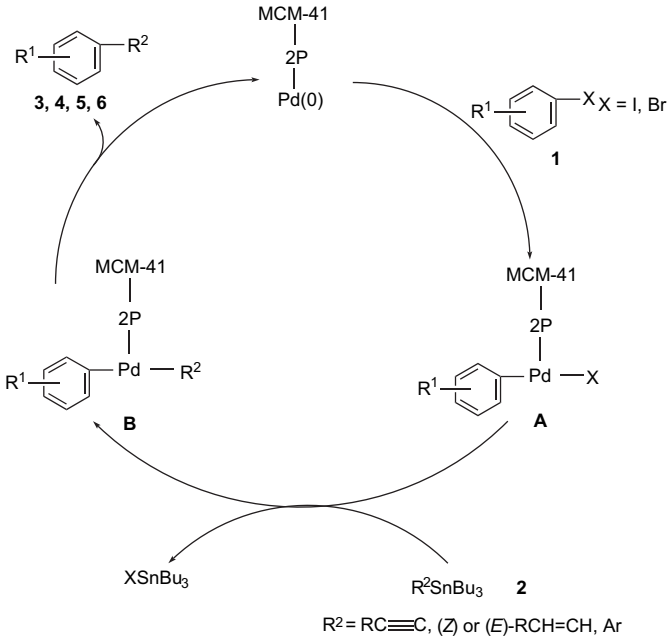
at 80 °C to give (*E*)-1,2-disubstituted ethenes in good yields after 12–20 h of reaction time (entries 17 and 18), the reactivity of the electron-deficient aryl bromides was higher than that of the electron-rich aryl bromides. As shown in Table 3, the Stille coupling reactions of a variety of aryl iodides with different arylstannanes also proceeded smoothly under mild conditions giving a variety of unsymmetrical biaryls in high yields (entries 11–16). A range of functional groups on either coupling partner can be tolerated. Although the Stille coupling of aryl bromides with arylstannanes was also very slow at 60 °C giving traces of cross-coupling products after 24 h of reaction time, the same coupling reactions at 80 °C proceeded smoothly affording the corresponding unsymmetrical biaryls in good yields. For the electron-deficient aryl bromides, the coupling reactions were completed within 10–12 h (entries 19 and 20), and the others required longer times (entries 21 and 22). In all reactions, only 0.5 mol % of MCM-41-2P-Pd(0) based on the aryl halides was used, the molar turnover numbers (TON) were much larger than those in the corresponding coupling reaction catalyzed by the homogeneous palladium complexes or other heterogeneous palladium catalysts reported.[7]

Table 3
Stille reactions of vinylstannanes and arylstannanes with aryl halides[a]

Entry	R^1	X	R^2	Temp (°C)	Time (h)	Product	Yield[b] (%)
1	3-CN	I	(*Z*)-BuCH=CH	60	6	**4a**	91
2	4-O_2N	I	(*Z*)-BuCH=CH	60	6	**4b**	90
3	4-Me	I	(*Z*)-PhCH=CH	60	9	**4c**	87
4	4-O_2N	I	(*Z*)-PhCH=CH	60	7	**4d**	89
5	4-MeO	I	(*E*)-BuCH=CH	60	6	**5a**	85
6	4-Cl	I	(*E*)-BuCH=CH	60	6	**5b**	88
7	4-Me	I	(*E*)-PhCH=CH	60	8	**5c**	84
8	4-MeO	I	(*E*)-PhCH=CH	60	9	**5d**	87
9	H	I	(*E*)-$MeOCH_2CH$=CH	60	6	**5e**	86
10	4-Cl	I	(*E*)-$MeOCH_2CH$=CH	60	6	**5f**	87
11	4-MeO	I	Ph	60	8	**6a**	85
12	4-MeCO	I	4-$MeOC_6H_4$	60	7	**6b**	87
13	4-O_2N	I	4-$MeOC_6H_4$	60	6	**6c**	88
14	4-MeO	I	4-ClC_6H_4	60	8	**6d**	84
15	3-O_2N	I	4-ClC_6H_4	60	6	**6e**	89
16	4-MeOCO	I	4-ClC_6H_4	60	8	**6f**	87
17	4-Cl	Br	(*E*)-BuCH=CH	80	12	**5b**	82
18	4-MeO	Br	(*E*)-BuCH=CH	80	20	**5a**	76
19	4-O_2N	Br	Ph	80	10	**6g**	85
20	4-CHO	Br	Ph	80	12	**6h**	81
21	4-Me	Br	4-$MeOC_6H_4$	80	24	**6i**	78
22	4-MeO	Br	Ph	80	24	**6a**	74

[a] All reactions were performed using 1.0 mmol of aryl halide, 1.1 mmol of vinylstannane or arylstannane, and 0.005 mmol of MCM-41-2P-Pd(0) in DMF/H_2O (9:1) (2 mL) under aerobic conditions.
[b] Isolated yield based on aryl halide used.

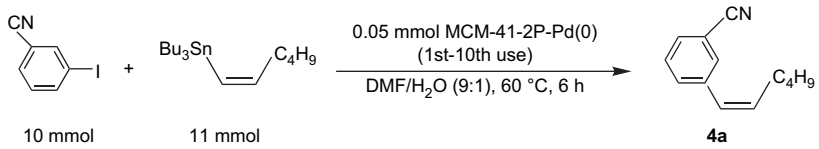
In order to determine whether the catalysis was due to the MCM-41-2P-Pd(0) complex or due to a homogeneous palladium complex that comes off the support during the reaction and then returns to the support at the end, we performed the hot filtration test.[18] We focused on the coupling reaction of iodobenzene with 1-(tributylstannyl)-2-phenylethyne. We filtered off the MCM-41-2P-Pd(0) complex after 1 h of reaction time and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (60 °C) in order to avoid possible recoordination or precipitation of soluble palladium upon cooling. We found that, after this hot filtration, no further reaction was observed. This result suggests that the palladium catalyst remains on the support at elevated temperatures during the reaction. A plausible mechanism is shown in Scheme 3. Oxidative addition of aryl halides **1** to MCM-41-2P-Pd(0) could give the MCM-41-bound arylpalladium complexes **A**, and the reaction of **A** with R^2SnBu_3 **2** could afford the intermediates **B**. The reductive elimination of the intermediates **B** could afford the coupling products **3**, **4**, **5**, **6** and regenerate the MCM-41-2P-Pd(0) complex.



Scheme 3.

The MCM-41-2P-Pd(0) complex catalyst can be easily recovered by simple filtration. We also examined the possibility to reuse of the catalyst by using the coupling reaction of 3-iodobenzonitrile with (*Z*)-1-tributylstannyl-1-hexene. In general, the continuous recycle of resin-supported palladium catalysts is difficult owing to leaching of the palladium species from the polymer supports, which often reduces their activity within a five-recycle run. Kang et al.[7a] reported that a silica-supported poly[3-(2-cyanoethylsulfanyl)-propylsiloxane palladium] complex was an efficient catalyst for Stille reaction of aryl iodides with organostannanes; the activity of the recovered catalyst was tested for the coupling of iodobenzene with 2-thienylstannane for two recycles and it was found that the yield of the coupled product decreased by 8 and 5% in each cycle, respectively. However, when the reaction of 3-iodobenzonitrile with (*Z*)-1-tributylstannyl-1-hexene was performed even with 0.5 mol % of MCM-41-2P-Pd(0), the catalyst could be recycled 10 times without any loss of activity. The reaction promoted by the

Table 4
Stille reaction of 3-iodobenzonitrile with (*Z*)-1-tributylstannyl-1-hexene catalyzed by recycled catalyst



10 mmol 11 mmol **4a**

Entry	Catalyst cycle	Isolated yield (%)	TON
1	1st	91	182
2	10th	89	178
3	1st to 10th consecutive	Average of 90	Total of 1800

10th recycled catalyst gave **4a** in 89% yield (Table 4, entry 2). The average yield of **4a** in consecutive reactions promoted by the 1st through the 10th recycled catalyst was 90% (entry 3). The high stability and excellent reusability of the catalyst are resulted from the chelating action of bidentate phosphine ligand on palladium and the mesoporous structure of MCM-41 support. The result is important from a practical point of view. The high catalytic activity, excellent reusability, and the easy accessibility of the MCM-41-2P-Pd(0) make them a highly attractive supported palladium catalyst for the parallel solution phase synthesis of diverse libraries of compounds.

3. Conclusions

In summary, the Stille coupling of organostannanes with aryl halides in the presence of MCM-41-supported bidentate phosphine palladium(0) complex as catalyst was accomplished in high yields in aqueous medium under aerobic conditions. This polymeric palladium catalyst exhibits higher activity than $Pd(PPh_3)_4$ and can be reused 10 times without any decrease in activity. The advantages of our heterogeneous catalytic system over others are: (1) the preparation of the heterogeneous MCM-41-2P-Pd(0) catalyst is simple and convenient from commercially available and cheap reagents, (2) the reaction conditions are very mild, i.e., only 0.5 mol % palladium catalyst, aqueous medium, and air atmosphere, and (3) excellent performance and reusability of the catalyst.

4. Experimental

4.1. Materials

All chemicals were reagent grade and used as purchased. Alkynylstannanes,[19] ethynyltributylstannane,[20] arylstannanes,[21] (*Z*)-vinylstannanes,[22] and (*E*)-vinylstannanes[23] were prepared according to the literature methods. All coupling products were characterized by comparison of their spectra and physical data with authentic samples. IR spectra were determined on a Perkin–Elmer 683 instrument. ^{1}H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. ^{13}C NMR spectra were recorded on a Bruker AC-P400 (100 MHz) spectrometer in $CDCl_3$ as solvent. Mass spectra were determined on a Finnigan 8230 mass spectrometer. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyzer.

4.2. General procedure for the Stille coupling reaction

Aryl halide (1.0 mmol), MCM-41-2P-Pd(0) (10 mg, 0.005 mmol Pd), and DMF/H_2O (9:1) (2 mL) were added to a flask, and the resulting mixture was stirred at room temperature for 5 min. To this suspension was added organostannane (1.1 mmol) and the reaction mixture was stirred at 60–80 °C for 6–24 h. The mixture was dissolved in Et_2O (30 mL). The MCM-41-2P-Pd(0) catalyst was separated from the mixture by filtration, washed with distilled water (2×10 mL), EtOH (3×10 mL), and Et_2O (2×10 mL) and reused in the next run. The ethereal solution was treated with 20% aqueous KF (10 mL) for 30 min before being dried and concentrated. The solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel to give the desired product.

4.2.1. *PhC≡CPh* (***3a***)[24]

White solid, mp 60–61 °C. IR (KBr): ν (cm^{-1}) 3063, 1599, 1492, 756, 689 (CH_{arom}). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.52 (m, 4H_{arom}), 7.37–7.32 (m, 6H_{arom}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.6 (2CH_{arom}), 128.4 (2CH_{arom}), 128.3 (CH_{arom}), 123.3 (C_{arom}), 89.4 (C).

4.2.2. *4-$CH_3C_6H_4C$≡CPh* (***3b***)[24]

White solid, mp 73–74 °C. IR (KBr): ν (cm^{-1}) 3029 (CH_{arom}), 2968, 2859 (CH_3), 2215 (C≡C), 1594, 1509, 818, 690 (CH_{arom}). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.51 (m, 2H_{arom}), 7.42 (d, J=8.0 Hz, 2H_{arom}), 7.36–7.27 (m, 3H_{arom}), 7.14 (d, J=8.0 Hz, 2H_{arom}), 2.36 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4 (C_{arom}), 131.6 (2CH_{arom}), 131.5 (2CH_{arom}), 129.1 (2CH_{arom}), 128.3 (2CH_{arom}), 128.1 (CH_{arom}), 123.5 (C_{arom}), 120.2 (C_{arom}), 89.6 (C), 88.7 (C), 21.5 (CH_3).

4.2.3. *3-$CH_3C_6H_4C$≡CPh* (***3c***)

Colorless oil. IR (neat): ν (cm^{-1}) 3056 (CH_{arom}), 2957 (CH_3), 2207 (C≡C), 1602, 1580, 1494, 783, 755, 689 (CH_{arom}). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.51 (m, 2H_{arom}), 7.37–7.32 (m, 5H_{arom}), 7.26–7.21 (m, 1H_{arom}), 7.16–7.13 (m, 1H_{arom}), 2.35 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0 (C_{arom}), 132.2 (CH_{arom}), 131.6 (2CH_{arom}), 129.2 (CH_{arom}), 128.7 (CH_{arom}), 128.4 (2CH_{arom}), 128.3 (CH_{arom}), 128.2 (CH_{arom}), 123.4 (C_{arom}), 123.1 (C_{arom}), 89.6 (C), 89.0 (C), 21.3 (CH_3). Anal. Calcd for $C_{15}H_{12}$: C, 93.71; H, 6.29. Found: C, 93.42; H, 6.38.

4.2.4. *4-$O_2NC_6H_4C$≡CPh* (***3d***)[24]

Yellow solid, mp 120–121 °C. IR (KBr): ν (cm^{-1}) 3082 (CH_{arom}), 2217 (C≡C), 1592 (CH_{arom}), 1511 (NO_2), 1495, 858, 765, 690 (CH_{arom}). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J=8.8 Hz, 2H_{arom}), 7.67 (d, J=8.8 Hz, 2H_{arom}), 7.58–7.55 (m, 2H_{arom}), 7.41–7.37 (m, 3H_{arom}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9 (C_{arom}), 132.3 (2CH_{arom}), 131.8 (2CH_{arom}), 130.3 (C_{arom}), 129.3 (CH_{arom}), 128.5 (2CH_{arom}), 123.7 (2CH_{arom}), 122.1 (C_{arom}), 94.7 (C), 87.5 (C).

4.2.5. *3-$O_2NC_6H_4C$≡CPh* (***3e***)[25]

Yellow solid, mp 69–70 °C. IR (KBr): ν (cm^{-1}) 3081 (CH_{arom}), 2210 (C≡C), 1597 (CH_{arom}), 1530, 1517, 1347 (NO_2), 810, 759, 692 (CH_{arom}). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H_{arom}), 8.19–8.16 (m, 1H_{arom}), 7.82 (d, J=7.6 Hz, 1H_{arom}), 7.57–7.51 (m, 3H_{arom}), 7.40–7.37 (m, 3H_{arom}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2 (C_{arom}), 137.2 (CH_{arom}), 131.8 (2CH_{arom}), 129.4 (CH_{arom}), 129.1 (CH_{arom}), 128.5 (2CH_{arom}), 126.4 (CH_{arom}), 125.2 (C_{arom}), 122.9 (CH_{arom}), 122.2 (C_{arom}), 92.0 (C), 86.9 (C).

4.2.6. 4-$CH_3OCOC_6H_4C{\equiv}CPh$ (**3f**)

White solid, mp 120 °C. IR (KBr): ν (cm^{-1}) 2948 (CH_3), 2218 (C≡C), 1717 (C=O), 1605 (CH_{arom}), 1438 (CH_3), 1109 (C–O), 770 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 8.04–8.02 (m, $2H_{arom}$), 7.61–7.58 (m, $2H_{arom}$), 7.56–7.54 (m, $2H_{arom}$), 7.38–7.36 (m, $3H_{arom}$), 3.93 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6 (C=O), 131.8 ($2CH_{arom}$), 131.5 ($2CH_{arom}$), 129.5 ($2CH_{arom}$), 129.4 (C_{arom}), 128.8 (CH_{arom}), 128.5 ($2CH_{arom}$), 128.0 (C_{arom}), 122.7 (C_{arom}), 92.4 (C), 88.6 (C), 52.3 (CH_3). Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.07; H, 4.93.

4.2.7. 3-$CH_3C_6H_4C{\equiv}C(CH_2)_3CH_3$ (**3g**)

Colorless oil. IR (neat): ν (cm^{-1}) 3037 (CH_{arom}), 2959 (CH_3), 2932 (CH_2), 2228 (C≡C), 1603, 1580, 783 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 7.22–7.13 (m, $3H_{arom}$), 7.06 (d, J=7.2 Hz, $1H_{arom}$), 2.40 (t, J=7.2 Hz, 2H, CH_2), 2.30 (s, 3H, CH_3), 1.60–1.54 (m, 2H, CH_2), 1.51–1.39 (m, 2H, CH_2), 0.94 (t, J=7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8 (C_{arom}), 132.2 (CH_{arom}), 128.6 (CH_{arom}), 128.4 (CH_{arom}), 128.1 (CH_{arom}), 123.9 (C_{arom}), 90.0 (C), 80.7 (C), 30.9 (CH_2), 22.1 (CH_2), 21.2 (CH_3), 19.1 (CH_2), 13.7 (CH_3). Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.48; H, 9.23.

4.2.8. 4-$O_2NC_6H_4C{\equiv}C(CH_2)_3CH_3$ (**3h**)[24]

Yellow liquid. IR (neat): ν (cm^{-1}) 3081 (CH_{arom}), 2934 (CH_2), 2873 (CH_3), 2230 (C≡C), 1594 (CH_{arom}), 1519, 1343 (NO_2), 854 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J=8.8 Hz, $2H_{arom}$), 7.52 (d, J=8.8 Hz, $2H_{arom}$), 2.46 (t, J=7.2 Hz, 2H, CH_2), 1.63–1.57 (m, 2H, CH_2), 1.51–1.46 (m, 2H, CH_2), 0.96 (t, J=7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5 (C_{arom}), 132.3 ($2CH_{arom}$), 131.2 (C_{arom}), 123.5 ($2CH_{arom}$), 96.8 (C), 79.3 (C), 30.5 (CH_2), 22.1 (CH_2), 19.3 (CH_2), 13.6 (CH_3).

4.2.9. 3-$NCC_6H_4C{\equiv}C(CH_2)_3CH_3$ (**3i**)

Colorless liquid. IR (neat): ν (cm^{-1}) 3069 (CH_{arom}), 2958 (CH_3), 2873 (CH_3), 2232 (C≡C), 2227 (C≡N), 1597, 1478, 896, 798, 683 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, $1H_{arom}$), 7.60–7.53 (m, $2H_{arom}$), 7.39 (t, J=7.6 Hz, $1H_{arom}$), 2.42 (t, J=7.2 Hz, 2H, CH_2), 1.61–1.56 (m, 2H, CH_2), 1.50–1.45 (m, 2H, CH_2), 0.96 (t, J=7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.7 (CH_{arom}), 135.0 (CH_{arom}), 130.7 (CH_{arom}), 129.1 (CH_{arom}), 125.7 (C≡N), 118.3 (C_{arom}), 112.6 (C_{arom}), 93.4 (C), 78.5 (C), 30.5 (CH_2), 22.0 (CH_2), 19.1 (CH_2), 13.7 (CH_3). Anal. Calcd for $C_{13}H_{13}N$: C, 85.26; H, 7.10. Found: C, 85.02; H, 6.91.

4.2.10. $PhC{\equiv}CCH_2OCH_3$ (**3j**)

Colorless liquid. IR (neat): ν (cm^{-1}) 2930 (CH_2), 2237 (C≡C), 1599, 1490 (CH_{arom}), 1099 (C–O), 757, 691 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 7.46–7.44 (m, $2H_{arom}$), 7.32–7.30 (m, $3H_{arom}$), 4.32 (s, 2H, CH_2), 3.46 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.8 ($2CH_{arom}$), 128.4 (CH_{arom}), 128.3 ($2CH_{arom}$), 122.7 (C_{arom}), 86.4 (C), 84.9 (C), 60.4 (CH_2), 57.7 (CH_3). Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.84. Found: C, 81.93; H, 6.61.

4.2.11. 4-$CH_3OC_6H_4C{\equiv}CSiMe_3$ (**3k**)[26]

Colorless liquid. IR (neat): ν (cm^{-1}) 2156 (C≡C), 1606, 1508 (CH_{arom}), 1249, 834 (C–Si), 756, 699 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, J=8.8 Hz, $2H_{arom}$), 6.81 (d, J=8.8 Hz, $2H_{arom}$), 3.81 (s, 3H, OCH_3), 0.24 (s, 9H, $SiCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7 (C_{arom}), 133.5 ($2CH_{arom}$), 115.3 (C_{arom}), 113.8 ($2CH_{arom}$), 105.2 (C), 92.5 (C), 55.3 (CH_3), 0.08 ($3SiCH_3$).

4.2.12. 4-$ClC_6H_4C{\equiv}CSiMe_3$ (**3l**)[26]

Colorless liquid. IR (neat): ν (cm^{-1}) 3030 (CH_{arom}), 2159 (C≡C), 1590, 1488 (CH_{arom}), 1250, 844 (C–Si), 759, 685 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J=8.4 Hz, $2H_{arom}$), 7.26 (d, J=8.4 Hz, $2H_{arom}$), 0.24 (s, 9H, $SiCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.6 (C_{arom}), 133.2 ($2CH_{arom}$), 128.6 ($2CH_{arom}$), 121.7 (C_{arom}), 103.9 (C), 95.4 (C), −0.07 ($3SiCH_3$).

4.2.13. 4-$CH_3COC_6H_4C{\equiv}CPh$ (**3m**)[24]

White solid, mp 98–99 °C. IR (KBr): ν (cm^{-1}) 2218 (C≡C), 1680 (C=O), 1604 (CH_{arom}), 833, 693 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J=8.0 Hz, $2H_{arom}$), 7.62 (d, J=8.0 Hz, $2H_{arom}$), 7.59–7.50 (m, $2H_{arom}$), 7.38–7.36 (m, $3H_{arom}$), 2.62 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3 (C=O), 136.2 (C_{arom}), 131.8 ($2CH_{arom}$), 131.7 ($2CH_{arom}$), 128.8 (CH_{arom}), 128.5 (C_{arom}), 128.3 ($2CH_{arom}$), 128.2 ($2CH_{arom}$), 122.7 (C_{arom}), 92.7 (C), 88.6 (C), 26.6 (CH_3).

4.2.14. 4-$HOC_6H_4C{\equiv}CH$ (**3n**)

Colorless liquid. IR (neat): ν (cm^{-1}) 3289 (OH), 2154 (C≡C), 1609, 1585, 1510 (CH_{arom}), 1093 (C–O), 836 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, J=8.4 Hz, $2H_{arom}$), 6.80 (d, J=8.4 Hz, $2H_{arom}$), 4.93 (br, 1H, OH), 3.02 (s, 1H, ≡CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3 (C_{arom}), 133.8 ($2CH_{arom}$), 115.5 ($2CH_{arom}$), 114.2 (C_{arom}), 104.3 (C), 83.7 (C). MS (EI): m/z 118 (M^+, 100), 93 (89), 77 (56). Anal. Calcd for C_8H_6O: C, 81.34; H, 5.12. Found: C, 81.56; H, 5.35.

4.2.15. 3-$NCC_6H_4C{\equiv}CH$ (**3o**)

Colorless liquid. IR (neat): ν (cm^{-1}) 3293 (≡CH), 2233 (C≡N), 2109 (C≡C), 1594, 1573, 800 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 7.78–7.61 (m, $3H_{arom}$), 7.45 (t, J=8.0 Hz, $1H_{arom}$), 3.19 (s, 1H, ≡CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.2 (CH_{arom}), 135.5 (CH_{arom}), 132.1 (CH_{arom}), 129.3 (CH_{arom}), 123.8 (C≡N), 117.9 (C_{arom}), 113.0 (C_{arom}), 81.2 (C), 79.8 (C). MS (EI): m/z 127 (M^+, 100), 101 (84), 75 (41). Anal. Calcd for C_9H_5N: C, 85.02; H, 3.96. Found: C, 84.78; H, 3.81.

4.2.16. 4-$ClC_6H_4C{\equiv}C(CH_2)_3CH_3$ (**3p**)

Colorless liquid. IR (neat): ν (cm^{-1}) 2959 (CH_3), 2932 (CH_2), 2232 (C≡C), 1489 (CH_{arom}), 1466 (CH_2), 827, 753 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J=8.4 Hz, $2H_{arom}$), 7.24 (d, J=8.4 Hz, $2H_{arom}$), 2.40 (t, J=7.2 Hz, 2H, CH_2), 1.60–1.55 (m, 2H, CH_2), 1.50–1.44 (m, 2H, CH_2), 0.95 (t, J=7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.4 (C_{arom}), 132.8 ($2CH_{arom}$), 128.5 ($2CH_{arom}$), 122.6 (C_{arom}), 91.5 (C), 79.5 (C), 30.7 (CH_2), 22.0 (CH_2), 19.1 (CH_2), 13.7 (CH_3). Anal. Calcd for $C_{12}H_{13}Cl$: C, 74.78; H, 6.80. Found: C, 74.52; H, 6.91.

4.2.17. 4-$CH_3OC_6H_4C{\equiv}CPh$ (**3q**)[24]

White solid, mp 58–59 °C. IR (KBr): ν (cm^{-1}) 3024 (CH_{arom}), 2212 (C≡C), 1602, 1498 (CH_{arom}), 1185 (C–O), 835, 750, 690 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 7.52–7.43 (m, $4H_{arom}$), 7.32–7.29 (m, $3H_{arom}$), 6.86–6.83 (m, $2H_{arom}$), 3.76 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5 (C_{arom}), 133.0 ($2CH_{arom}$), 131.4 ($2CH_{arom}$), 128.3 ($2CH_{arom}$), 127.9 ($2CH_{arom}$), 123.4 (CH_{arom}), 115.5 (C_{arom}), 113.9 (C_{arom}), 89.4 (C), 88.1 (C), 55.2 (CH_3).

4.2.18. (Z)-3-$NCC_6H_4CH{=}CHBu$-n (**4a**)

Colorless oil. IR (neat): ν (cm^{-1}) 3065 (CH_{arom}), 2958 (CH_3), 2927 (CH_2), 2230 (C≡N), 1643 (C=C), 1597, 1575 (CH_{arom}), 1465 (CH_2), 806, 687 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (s, $1H_{arom}$), 7.51–7.40 (m, $3H_{arom}$), 6.36 (d, J=11.6 Hz, 1H, =CH), 5.78 (dt, J=11.6, 7.2 Hz, 1H, =CH), 2.31–2.25 (m, 2H, CH_2), 1.48–1.32 (m, 4H, $2CH_2$), 0.90 (t, J=7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9 (C_{arom}), 135.8 (CH), 133.1 (CH_{arom}), 132.1 (CH), 129.9 (CH_{arom}), 129.0 (CH_{arom}), 126.6 (CH_{arom}), 119.0 (C≡N), 112.3 (C_{arom}), 31.9 (CH_2), 28.3 (CH_2), 22.4 (CH_2), 13.9 (CH_3). Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16. Found: C, 84.05; H, 7.97.

4.2.19. (Z)-4-$O_2NC_6H_4CH{=}CHBu$-n (**4b**)

Yellow oil. IR (neat): ν (cm^{-1}) 2958 (CH_3), 2929 (CH_2), 1640 (C=C), 1596 (CH_{arom}), 1516, 1343 (NO_2), 856 (CH_{arom}). ^1H NMR

(400 MHz, $CDCl_3$): δ 8.18 (d, J=8.8 Hz, $2H_{arom}$), 7.41 (d, J=8.8 Hz, $2H_{arom}$), 6.44 (d, J=11.6 Hz, 1H, =CH), 5.87 (dt, J=11.6, 7.2 Hz, 1H, =CH), 2.34–2.30 (m, 2H, CH_2), 1.48–1.44 (m, 2H, CH_2), 1.38–1.32 (m, 2H, CH_2), 0.90 (t, J=7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2 (C_{arom}), 144.6 (C_{arom}), 137.2 (CH), 129.3 ($2CH_{arom}$), 127.0 (CH), 123.5 ($2CH_{arom}$), 31.8 (CH_2), 28.5 (CH_2), 22.4 (CH_2), 13.9 (CH_3). Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37. Found: C, 70.42; H, 7.51.

4.2.20. (Z)-4-MeC_6H_4CH=CHPh (**4c**)

Colorless oil. IR (neat): ν (cm^{-1}) 3012 (=CH), 1629 (C=C), 1599, 1492, 821, 772 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 7.28–7.19 (m, $5H_{arom}$), 7.15 (d, J=8.0 Hz, $2H_{arom}$), 7.03 (d, J=8.0 Hz, $2H_{arom}$), 6.56 (s, 2H, 2CH), 2.32 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4 (C_{arom}), 136.9 (C_{arom}), 134.3 (C_{arom}), 130.2 (CH), 129.6 (CH), 128.9 ($2CH_{arom}$), 128.8 ($2CH_{arom}$), 128.7 ($2CH_{arom}$), 128.2 ($2CH_{arom}$), 127.0 (CH_{arom}), 21.3 (CH_3). Anal. Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.50; H, 7.31.

4.2.21. (Z)-4-$O_2NC_6H_4CH$=CHPh (**4d**)

Yellow solid, mp 60.5–61.5 °C. IR (KBr): ν (cm^{-1}) 1627 (C=C), 1592 (CH_{arom}), 1505, 1342 (NO_2), 856, 778, 696 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J=8.8 Hz, $2H_{arom}$), 7.37 (d, J=8.8 Hz, $2H_{arom}$), 7.26–7.19 (m, $5H_{arom}$), 6.82 (d, J=12.4 Hz, 1H, =CH), 6.62 (d, J=12.4 Hz, 1H, =CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6 (C_{arom}), 144.2 (C_{arom}), 136.1 (C_{arom}), 134.0 (CH), 129.7 ($2CH_{arom}$), 128.8 ($2CH_{arom}$), 128.6 ($2CH_{arom}$), 128.0 (CH_{arom}), 127.9 (CH), 123.6 ($2CH_{arom}$). Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92. Found: C, 74.38; H, 4.71.

4.2.22. (E)-4-$MeOC_6H_4CH$=CHBu-n (**5a**)

Colorless oil. IR (neat): ν (cm^{-1}) 2957 (CH_3), 1608, 1577 (CH_{arom}), 1464 (CH_2), 1174, 1038 (C–O), 965 (*E*-CH=CH), 804 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, J=8.4 Hz, $2H_{arom}$), 6.83 (d, J=8.4 Hz, $2H_{arom}$), 6.32 (d, J=16.0 Hz, 1H, =CH), 6.09 (dt, J=16.0, 7.2 Hz, 1H, =CH), 3.80 (s, 3H, OCH_3), 2.22–2.16 (m, 2H, CH_2), 1.47–1.34 (m, 4H, $2CH_2$), 0.93 (t, J=7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6 (C_{arom}), 130.9 (CH), 129.1 (CH), 129.0 (C_{arom}), 127.0 ($2CH_{arom}$), 113.9 ($2CH_{arom}$), 55.3 (OCH_3), 32.7 (CH_2), 31.7 (CH_2), 22.3 (CH_2), 14.0 (CH_3). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 82.25; H, 9.71.

4.2.23. (E)-4-ClC_6H_4CH=CHBu-n (**5b**)

Colorless oil. IR (neat): ν (cm^{-1}) 2957 (CH_3), 1593, 1490 (CH_{arom}), 1469 (CH_2), 966 (*E*-CH=CH), 809 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J=8.4 Hz, $2H_{arom}$), 7.07 (d, J=8.4 Hz, $2H_{arom}$), 6.30 (d, J=16.0 Hz, 1H, =CH), 6.20 (dt, J=16.0, 7.2 Hz, 1H, =CH), 2.21–2.18 (m, 2H, CH_2), 1.47–1.32 (m, 4H, $2CH_2$), 0.92 (t, J=7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7 ($2CH_{arom}$), 134.2 (C_{arom}), 132.0 (C_{arom}), 130.5 ($2CH_{arom}$), 128.6 (CH), 127.1 (CH), 32.7 (CH_2), 31.5 (CH_2), 22.3 (CH_2), 14.0 (CH_3). Anal. Calcd for $C_{12}H_{15}Cl$: C, 74.01; H, 7.76. Found: C, 73.79; H, 7.57.

4.2.24. (E)-4-MeC_6H_4CH=CHPh (**5c**)[4b]

White solid, mp 117–118 °C. IR (KBr): ν (cm^{-1}) 3023 (=CH), 1643 (C=C), 1594, 1511 (CH_{arom}), 970 (*E*-CH=CH), 809, 690 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J=7.6 Hz, $2H_{arom}$), 7.41 (d, J=8.0 Hz, $2H_{arom}$), 7.35 (t, J=7.6 Hz, $2H_{arom}$), 7.26–7.22 (m, $1H_{arom}$), 7.16 (d, J=8.0 Hz, $2H_{arom}$), 7.07 (s, 2H, 2CH), 2.36 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6 (C_{arom}), 137.5 (C_{arom}), 134.6 (C_{arom}), 129.4 ($2CH_{arom}$), 128.7 ($2CH_{arom}$), 128.6 (CH), 127.7 (CH_{arom}), 127.4 (CH), 126.5 ($2CH_{arom}$), 126.4 ($2CH_{arom}$), 21.3 (CH_3).

4.2.25. (E)-4-$MeOC_6H_4CH$=CHPh (**5d**)[4b]

White solid, mp 134–135 °C. IR (KBr): ν (cm^{-1}) 2963 (CH_3), 1602, 1513 (CH_{arom}), 1112 (C–O), 967 (*E*-CH=CH), 813 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J=7.6 Hz, $2H_{arom}$), 7.45 (d, J=8.4 Hz, $2H_{arom}$), 7.34 (t, J=7.6 Hz, $2H_{arom}$), 7.25–7.23 (m, $1H_{arom}$), 7.07 (d, J=16.4 Hz, 1H, =CH), 6.97 (d, J=16.4 Hz, 1H, =CH), 6.90 (d, J=8.4 Hz, $2H_{arom}$), 3.83 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3 (C_{arom}), 137.7 (C_{arom}), 130.2 (C_{arom}), 128.6 ($2CH_{arom}$), 128.2 (CH), 127.7 ($2CH_{arom}$), 127.2 (CH), 126.7 (CH_{arom}), 126.3 ($2CH_{arom}$), 114.2 ($2CH_{arom}$), 55.3 (CH_3).

4.2.26. (E)-PhCH=$CHCH_2OMe$ (**5e**)

Colorless oil. IR (neat): ν (cm^{-1}) 1657 (C=C), 1599, 1577, 1495 (CH_{arom}), 1449 (CH_2), 1121 (C–O), 966 (*E*-CH=CH). ^1H NMR (400 MHz, $CDCl_3$): δ 7.40–7.22 (m, $5H_{arom}$), 6.61 (d, J=16.0 Hz, 1H, =CH), 6.29 (dt, J=16.0, 6.0 Hz, 1H, =CH), 4.09 (d, J=6.0 Hz, 2H, OCH_2), 3.39 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.7 (C_{arom}), 132.5 (CH), 128.6 ($2CH_{arom}$), 127.7 (CH), 126.5 ($2CH_{arom}$), 126.0 (CH_{arom}), 73.1 (CH_2), 58.0 (CH_3). Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.79; H, 7.94.

4.2.27. (E)-4-ClC_6H_4CH=$CHCH_2OMe$ (**5f**)

Colorless oil. IR (neat): ν (cm^{-1}) 2925 (CH_2), 1593, 1491 (CH_{arom}), 1191, 1090 (C–O), 968 (*E*-CH=CH), 846, 796 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 7.32–7.26 (m, $4H_{arom}$), 6.56 (d, J=16.0 Hz, 1H, =CH), 6.27 (dt, J=16.0, 6.0 Hz, 1H, =CH), 4.08 (d, J=6.0 Hz, 2H, OCH_2), 3.39 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.3 (C_{arom}), 133.3 (C_{arom}), 131.0 (CH), 128.7 ($2CH_{arom}$), 127.7 ($2CH_{arom}$), 126.7 (CH), 72.9 (CH_2), 58.1 (CH_3). Anal. Calcd for $C_{10}H_{11}OCl$: C, 65.74; H, 6.07. Found: C, 65.85; H, 6.31.

4.2.28. 4-$MeOC_6H_4$–Ph (**6a**)[27]

White solid, mp 89–90 °C. IR (KBr): ν (cm^{-1}) 2961 (CH_3), 1606, 1486 (CH_{arom}), 1038 (C–O), 832, 759 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 7.56–7.51 (m, $4H_{arom}$), 7.42 (t, J=7.6 Hz, $2H_{arom}$), 7.32–7.28 (m, $1H_{arom}$), 6.98 (d, J=8.4 Hz, $2H_{arom}$), 3.85 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1 (C_{arom}), 140.9 (C_{arom}), 133.8 (C_{arom}), 128.7 ($2CH_{arom}$), 128.2 ($2CH_{arom}$), 126.8 ($2CH_{arom}$), 126.7 (CH_{arom}), 114.2 ($2CH_{arom}$), 55.4 (OCH_3).

4.2.29. 4-$MeCOC_6H_4$–C_6H_4OMe-4′ (**6b**)

White solid, mp 152 °C. IR (KBr): ν (cm^{-1}) 2957 (CH_3), 1675 (C=O), 1601, 1581, 1497 (CH_{arom}), 1033 (C–O), 818 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J=8.4 Hz, $2H_{arom}$), 7.65 (d, J=8.4 Hz, $2H_{arom}$), 7.58 (d, J=8.8 Hz, $2H_{arom}$), 7.01 (d, J=8.8 Hz, $2H_{arom}$), 3.87 (s, 3H, OCH_3), 2.63 (s, 3H, $COCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8 (C=O), 159.9 (C_{arom}), 145.4 (C_{arom}), 135.3 (C_{arom}), 132.3 (C_{arom}), 129.0 ($2CH_{arom}$), 128.4 ($2CH_{arom}$), 126.6 ($2CH_{arom}$), 114.4 ($2CH_{arom}$), 55.4 (OCH_3), 26.7 ($COCH_3$). Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.37; H, 6.11.

4.2.30. 4-$O_2NC_6H_4$–C_6H_4OMe-4′ (**6c**)[28]

Yellow solid, mp 99–100 °C. IR (KBr): ν (cm^{-1}) 2956 (CH_3), 1601, 1594 (CH_{arom}), 1510, 1344 (NO_2), 1187, 1108 (C–O). ^1H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J=8.8 Hz, $2H_{arom}$), 7.70 (d, J=8.8 Hz, $2H_{arom}$), 7.58 (d, J=8.8 Hz, $2H_{arom}$), 7.02 (d, J=8.8 Hz, $2H_{arom}$), 3.88 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5 (C_{arom}), 147.2 (C_{arom}), 146.6 (C_{arom}), 131.1 (C_{arom}), 128.6 ($2CH_{arom}$), 127.1 ($2CH_{arom}$), 124.2 ($2CH_{arom}$), 114.6 ($2CH_{arom}$), 55.4 (CH_3).

4.2.31. 4-ClC_6H_4–C_6H_4OMe-4′ (**6d**)

White solid, mp 123–124 °C. IR (KBr): ν (cm^{-1}) 2963 (CH_3), 1606, 1484 (CH_{arom}), 1199, 1101 (C–O), 822, 737 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 7.50–7.46 (m, $4H_{arom}$), 7.37 (d, J=8.4 Hz, $2H_{arom}$), 6.97 (d, J=8.4 Hz, $2H_{arom}$), 3.85 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3 (C_{arom}), 139.3 (C_{arom}), 132.7 (C_{arom}), 132.5 (C_{arom}), 128.9 ($2CH_{arom}$), 128.1 ($2CH_{arom}$), 128.0 ($2CH_{arom}$), 114.3 ($2CH_{arom}$), 55.4 (CH_3). MS (EI): m/z 219 (M^+, 100), 204 (95), 176 (92), 140 (90). Anal. Calcd for $C_{13}H_{11}OCl$: C, 71.39; H, 5.07. Found: C, 71.16; H, 4.89.

4.2.32. 3-$O_2NC_6H_4$–C_6H_4Cl-4′ (**6e**)

Yellow solid, mp 91–92 °C. IR (KBr): ν (cm^{-1}) 3087, 1595 (CH_{arom}), 1525 (NO_2), 1497 (CH_{arom}), 1353 (NO_2), 908, 877, 824 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, $1H_{arom}$), 8.23–8.20 (m, $1H_{arom}$), 7.88 (d, J=8.0 Hz, $1H_{arom}$), 7.63 (t, J=8.0 Hz, $1H_{arom}$), 7.56 (d, J=8.4 Hz, $2H_{arom}$), 7.47 (d, J=8.4 Hz, $2H_{arom}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7 (C_{arom}), 141.6 (C_{arom}), 137.1 (C_{arom}), 134.8 (C_{arom}), 132.9 (CH_{arom}), 129.9 (CH_{arom}), 129.4 ($2CH_{arom}$), 128.5 ($2CH_{arom}$), 122.4 (CH_{arom}), 121.8 (CH_{arom}). MS (EI): m/z 234 (M^+, 95), 153 (100). Anal. Calcd for $C_{12}H_8NO_2Cl$: C, 61.67; H, 3.45. Found: C, 61.41; H, 3.24.

4.2.33. 4-$MeOCOC_6H_4$–C_6H_4Cl-4′ (**6f**)

White solid, mp 94 °C. IR (KBr): ν (cm^{-1}) 2959 (CH_3), 1725 (C=O), 1608, 1482 (CH_{arom}), 1105 (C–O), 828, 769 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J=8.4 Hz, $2H_{arom}$), 7.63 (d, J=8.4 Hz, $2H_{arom}$), 7.56 (d, J=8.4 Hz, $2H_{arom}$), 7.44 (d, J=8.4 Hz, $2H_{arom}$), 3.95 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9 (C=O), 144.3 (C_{arom}), 138.4 (C_{arom}), 134.3 (C_{arom}), 130.9 (C_{arom}), 130.2 ($2CH_{arom}$), 129.1 ($2CH_{arom}$), 128.5 ($2CH_{arom}$), 126.9 ($2CH_{arom}$), 52.2 (CH_3). Anal. Calcd for $C_{14}H_{11}O_2Cl$: C, 68.15; H, 4.49. Found: C, 67.87; H, 4.23.

4.2.34. 4-$O_2NC_6H_4$–Ph (**6g**)[27]

Yellow solid, mp 113 °C. IR (KBr): ν (cm^{-1}) 3076, 1595, 1576 (CH_{arom}), 1514 (NO_2), 1480 (CH_{arom}), 1346 (NO_2), 853, 740, 699 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J=8.4 Hz, $2H_{arom}$), 7.74 (d, J=8.4 Hz, $2H_{arom}$), 7.64–7.43 (m, $5H_{arom}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.7 (C_{arom}), 147.1 (C_{arom}), 138.8 (C_{arom}), 129.2 ($2CH_{arom}$), 128.9 (CH_{arom}), 127.8 ($2CH_{arom}$), 127.4 ($2CH_{arom}$), 124.1 ($2CH_{arom}$).

4.2.35. 4-$OHCC_6H_4$–Ph (**6h**)[29]

White solid, mp 59 °C. IR (KBr): ν (cm^{-1}) 1697 (C=O), 1603, 1562, 834, 764, 702 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 10.06 (s, 1H, CHO), 7.96 (d, J=8.0 Hz, $2H_{arom}$), 7.76 (d, J=8.0 Hz, $2H_{arom}$), 7.65–7.63 (m, $2H_{arom}$), 7.50–7.40 (m, $3H_{arom}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.9 (C=O), 147.2 (C_{arom}), 139.7 (C_{arom}), 135.2 (C_{arom}), 130.3 ($2CH_{arom}$), 129.0 ($2CH_{arom}$), 128.5 (CH_{arom}), 127.7 ($2CH_{arom}$), 127.4 ($2CH_{arom}$).

4.2.36. 4-MeC_6H_4–C_6H_4OMe-4′ (**6i**)

White solid, mp 111–112 °C. IR (KBr): ν (cm^{-1}) 2958 (CH_3), 1608, 1501 (CH_{arom}), 1183, 1038 (C–O), 842, 808 (CH_{arom}). ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J=8.8 Hz, $2H_{arom}$), 7.44 (d, J=8.0 Hz, $2H_{arom}$), 7.22 (d, J=8.0 Hz, $2H_{arom}$), 6.96 (d, J=8.8 Hz, $2H_{arom}$), 3.84 (s, 3H, OCH_3), 2.38 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0 (C_{arom}), 138.0 (C_{arom}), 136.3 (C_{arom}), 133.8 (C_{arom}), 129.4 ($2CH_{arom}$), 128.0 ($2CH_{arom}$), 126.6 ($2CH_{arom}$), 114.2 ($2CH_{arom}$), 55.3 (OCH_3), 21.0 (CH_3). MS (EI): m/z 199 (M^+, 100), 184 (93), 156 (89), 153 (72), 129 (68), 115 (58). Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 85.03; H, 7.23.

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