Reductive Coupling of Aromatic Aldehydes and Ketones Under Electrochemical Conditions

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Reductive Coupling of Aromatic Aldehydes and Ketones Under Electrochemical Conditions

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Reductive coupling of *o*-substituted carbonyl compounds and *m*-substituted carbonyl compounds by the direct transfer of electron to carbonyl group respectively gave 1-(4-(1-hydroxy-1-phenylethyl/methyl)phenyl)ethanones/methanones and 2,3-bis(3-substitutedphenyl)butane/ethane-2,3-diols. 4-Methoxyacetophenone surprisingly gave 4-methoxybenzoic acid as oxidation product. Even acetophenone conjugated with alkyne group afforded interesting reductive addition product. Finally, imine also furnished reductively coupled diamino compound. Probable mechanisms for the formation of products is proposed.
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Electrochemistry involves addition or removal of electrons from molecules or ions by the application of electrical potential. Its application in organic chemistry has gained great attention and termed as electro-synthesis. In electro-synthesis, potential is applied across the electrodes with the flow of current through reaction mixture. The reaction mixture contains some electrolytes to carry electricity.[1–10] Reactions are carried out at constant potential and also at constant current.[1–10] Various heterocyclic structures can be constructed by employing electrochemical technique.[9] Since electron is a mass-free reagent which avoids usage of equivalent amount of reagents taken up in conventional synthesis, thus eliminates the produce of waste. Interestingly, electron transfer to a functional group changes its polarity, which is difficult to achieve by other synthetic approaches.

Electro-reductive formation of C–C bonds in organic halides,[11–16] ketones,[17–23] imines[24–26] and imides[27,28] are well known. Direct transfer of electron from electrode to carbonyl group for the synthesis of indolealkanones,[29] isoindolinones,[28] cyclohexanols,[30] pyrrolizinones and indolizinones[26] are reported. Similarly, electron transfer to imines for the synthesis of azetidine,[31] pyrrolidinone and piperidinone[32] derivatives are also reported.

Further, phenyl-carbonyl coupling reactions are induced by SmI_2 and hexamethylphosphoramide (HMPA) are known (Scheme 1a).[28] Besides, coupling of aromatic carbonyl compounds and imines are induced by electro-generated SmI_2 are also known (Scheme 1b).[33] But these methods have severe drawbacks due to the use of stoichiometric amounts of SmI_2-HMPA[28] and Sm as sacrificial anode.[33] To the best of our knowledge, phenyl-carbonyl coupling reactions are not reported under electrochemical conditions. In continuation of our efforts in organic synthesis,[34–47] we report here-in phenyl-carbonyl reductive coupling of *o*-substituted aromatic carbonyl compounds (Scheme 1c) and carbonyl-carbonyl reductive coupling of *m*-substituted carbonyl compounds (Scheme 1d).

Results and Discussion

Initially electrolysis of acetophenone **1a** in DMSO using platinum as anode and cathode by passing 20 mA of current in the presence of 15 mol% of *tetra*-butylammonium iodide (TBAI) gave 1-(4-(1-hydroxy-1-phenylethyl)phenyl)ethanone **2a** in 45% yield as an unexpected product (Scheme 2, entry 1, Table I). In the absence of electricity, there was no progress in the reaction (entry 2). Only a trace of product was observed in THF (entry 3). In methanol, **2a** was not observed (entry 4). In acetonitrile and DMF, the required product was isolated in 46 and 35% yield respectively (entry 5 and 6). Toluene was not a suitable solvent for this reaction (entry 7). A mixture of acetonitrile and DMF furnished **2a** in 33% yield (entry 8). Use of ferrocene as an electron transfer reagent also did not improve the yield (entry 9). With 30 mol% of the TBAI, yield of **2a** was slightly improved to 48% (entry 10). But, the reaction mixture was intractable with 100 mol% of the TBAI (entry 11). *Tetra*-butyl ammonium tetrafluroroborate in DMSO and ACN furnished product **2a** in 30 and 35% yield respectively (entries 12 and 13). Using Pt as cathode and RVC as anode, the desired product **2a** was observed in trace (entry 14). On increasing the current to 40 mA in DMSO, yield of **2a** was improved to 59% (entry 15). Further increase in current to 60 mA, slightly reduced the yield. (55%, entry 16). With 40 mA of current in ACN and DMF, the product was formed in 37 and 30% yield respectively (entries 17 and 18). *Tetra*-butylammonium bromide gave the best result by yielding the required product in 72% (entry 19). *Tetra*-butylammonium hexafluorophosphate, *tetra*-butylammonium chloride and *tetra*-butylammonium tosylate gave product **2a** in 40, 50 and 37% yield respectively (entries 20, 21 and 22).

We extended the generality of the protocol for the synthesis of 1-(4-(1-hydroxy-1-phenylethyl)phenyl)ethanone by taking other *o*-substituted acetophenones (Table II). Thus, *o*-methoxyacetophenone and *o*-methylacetophenone bearing electron donating groups furnished corresponding products **2b** and **2c** in 60 and 78% yield respectively. *o*-Fluoroacetophenone containing electron withdrawing group formed product **2d** in 70% yield. A representative example for α-substituted acetophenone—propiophenone also gave 1-(4-(1-hydroxy-1-phenylpropyl)phenyl)propan-1-one **2e** in 82% yield. Later, we elaborated the methodology for aldehyde substrates. In the same way, electrolysis of benzaldehyde gave 4-(hydroxy(phenyl)methyl) benzaldehyde **2f** in 57% yield. *o*-Methoxy benzaldehyde, *o*-methyl benzaldehyde and *o*-chloro benzaldehyde also underwent smooth reaction to produce respective products **2g**, **2h** and **2i** in 60, 65 and 51% yield respectively. Even *o*-disubstituted benzaldehyde such as 2-chloro-6-flurobenzaldehyde yielded desired product **2j** in 55%. Finally, *o*-nitroacetophenone and benzophenone on electrolysis under the optimized reaction condition did not furnish any product (**2k** and **2l**) with complete recovery of substrate, probably because the intermediate radical formed (blue in colour) was very stable and was not much reactive to react further with another molecule of it.

Further, electrolysis of *m*-substituted acetophenones gave 2,3-bis (3-substitutedphenyl)butane-2,3-diols as diastereomers (Table III, diastereomeric ratios are given in parenthesis). Thus, *m*-methylacetophenone, *m*-methoxyacetophenone and *m*-fluoroacetophenone gave 2,3-bis(3-methoxy/methyl/fluorophenyl)butane-2,3-diol **4a**, **4b** and **4c** in 85, 66 and 69% yield respectively. Similarly, *m*-substituted aldehydes also furnished 2,3-bis(3-substitutedphenyl)ethane-2,3-diols. Thus, *m*-methylbenzaldehyde and *m*-methoxybenzaldehyde

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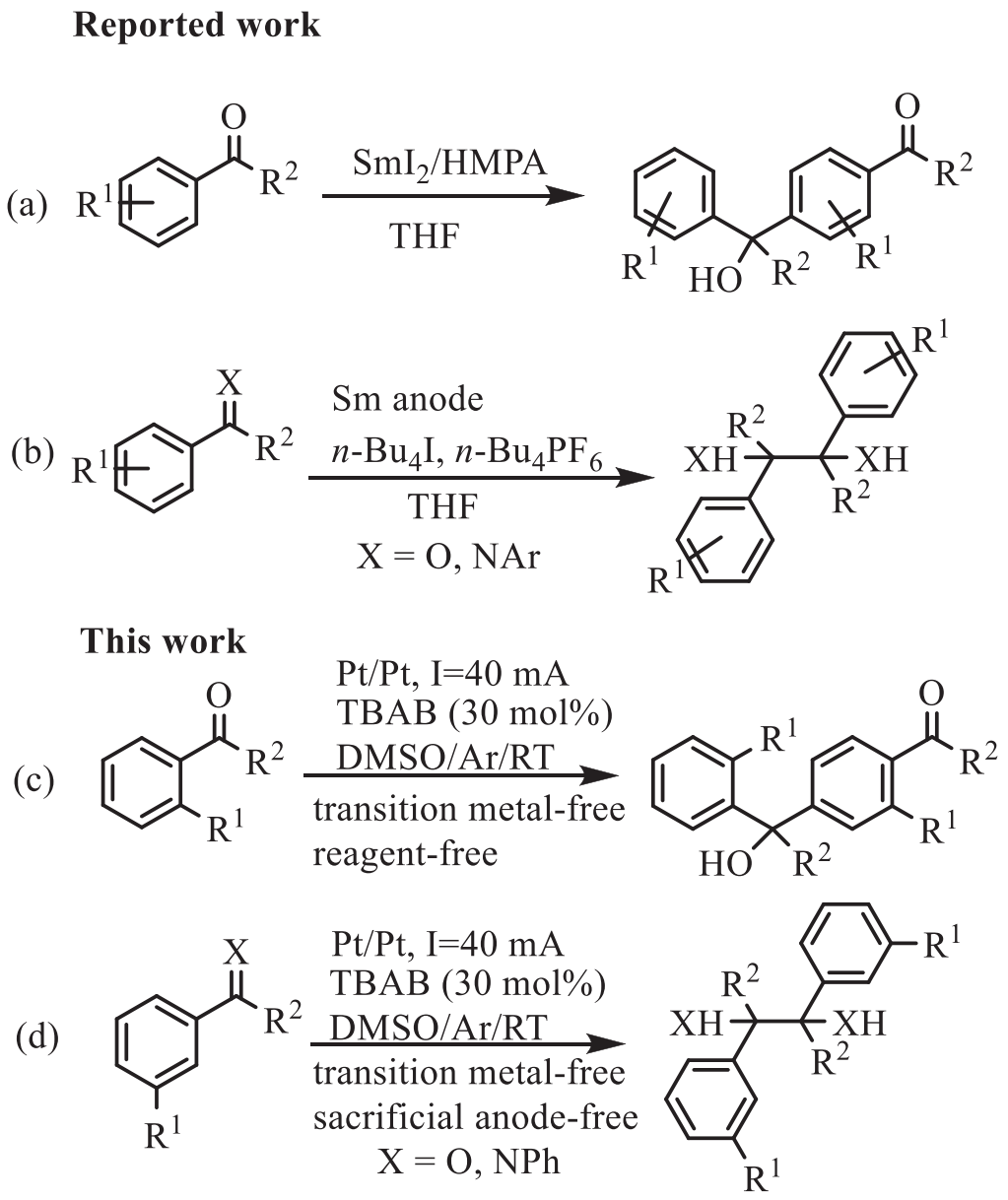


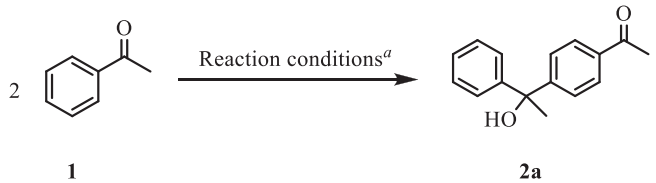
Scheme 1. Comparison of reported work and present work.

substituted with electron donating groups afforded 2,3-bis(3-methyl/methoxyphenyl)ethane-2,3-diols **4d** and **4e** in 81 and 69% yield respectively. Similarly, *m*-fluorobenzaldehyde and *m*-chlorobenzaldehyde substituted with electron withdrawing groups furnished 2,3-bis(3-fluoro/chlorophenyl)ethane-2,3-diols **4f** and **4g** in 75 and 73% yield respectively.

Surprisingly, electrolysis of 4-methoxyacetophenone 5 gave 4-methoxy benzoic acid 7 in 63% yield *via* the formation of 2,3-bis(4-methoxyphenyl)butane-2,3-diol 6, which was formed as diastereomer in the ratio 1:8.1 (Scheme 3). Further, 1-(4-ethynylphenyl) ethanone 8 under the aforementioned conditions furnished 1-(4-(3-(4-ethynylphenyl)-3-hydroxybut-1-yn-1-yl)phenyl)ethanone 9 in 56% yield (Scheme 4). On the other hand, electrolysis of *N*-(1-phenylethylidene)aniline 10 furnished 2,3-diphenyl-2,3-phenylaminobutane 11 in 55% yield (Scheme 5).

Finally, cross coupling of *o*-methoxyacetophenone and *o*-methylacetophenone under optimized reaction conditions furnished four products **2b**, **2c**, **2m** and **2n** in 14%, 18%, 15% and 13% respectively (Scheme 6). These products were inseparable in column chromatography and identified in LCMS.

The probable mechanism involves transfer of electron from platinum cathode to carbonyl group of **1** to give radical anion **12** which undergo resonance stabilization to give radical anion **13**. The coupling of **13** with another molecule of **1** forms intermediate **14**. Hydrogen migration in **14** forms another radical anion **15**, which is stabilized by resonance to produce **16**. Finally, oxidation of **16** at anode gives product **2** (Scheme 7). On the other hand, similar electron transfer to **3** gives radical anion **17**, which undergo coupling with carbonyl carbon of another molecule of **3** to form dianion **18**, oxidation of which generates biradical **19**. Its protonation during work-up gives product **4** (Scheme 8). The mechanism of formation

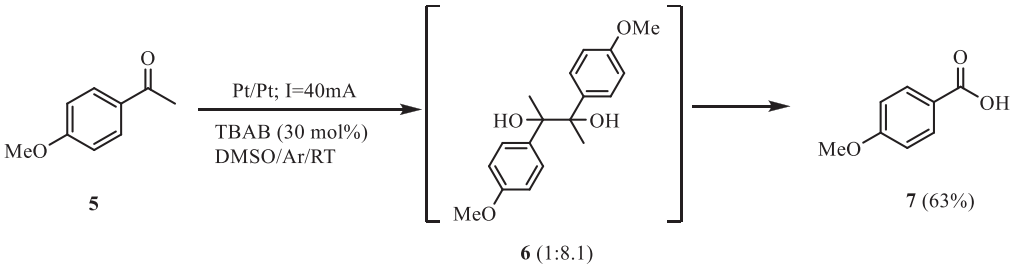


Scheme 2. Synthesis of 1-(4-(1-hydroxy-1-phenylethyl)phenyl)ethanone **2a**.

Table I. Optimization of reaction conditions[a)].

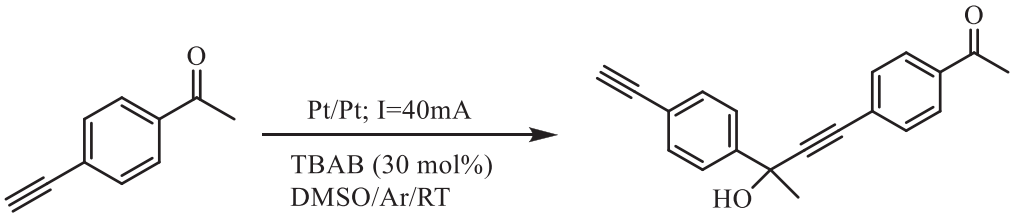
Entry	Cathode/Anode/Current (mA)	Electrolyte(15 mol%)	Solvent	Time	% Yield of **2**
1	Pt/Pt/20	TBAI	DMSO	12 h	45%
2	Pt/Pt/00	TBAI	DMSO	15 h	0%
3	Pt/Pt/20	TBAI	THF	15 h	trace
4	Pt/Pt/20	TBAI	MeOH	12 h	0%
5	Pt/Pt/20	TBAI	ACN	24 h	46%
6	Pt/Pt/20	TBAI	DMF	5 h	35%
7	Pt/Pt/20	TBAI	Toluene	12 h	0%
8	Pt/Pt/20	TBAI	ACN:DMF	16 h	33%
9	Pt/Pt/20	TBAI[b)]	DMSO	12 h	43%
10	Pt/Pt/20	TBAI[c)]	DMSO	7	48%
11	Pt/Pt/20	TBAI[d)]	DMSO	4 h	0%
12	Pt/Pt/20	n-Bu_4NBF_4[c)]	DMSO	12 h	30%
13	Pt/Pt/20	n-Bu_4NBF_4[c)]	ACN	12 h	35%
14	Pt/RVC/20	TBAI[c)]	DMSO	12 h	trace
15	Pt/Pt/40	TBAI[c)]	DMSO	3 h	59%
16	Pt/Pt/60	TBAI[c)]	DMSO	3 h	55%
17	Pt/Pt/40	TBAI[c)]	ACN	2.5 h	37%
18	Pt/Pt/40	TBAI[c)]	DMF	2 h	30%
19	Pt/Pt/40	n-Bu_4NBr[c)]	DMSO	2.5 h	72%
20	Pt/Pt/40	n-Bu_4NPF_6[c)]	DMSO	2.5 h	40%
21	Pt/Pt/40	n-Bu_4NCl[c)]	DMSO	4 h	50%
22	Pt/Pt/40	n-Bu_4NOTs[c)]	DMSO	6 h	37%

a) Reaction conditions: **1a** (0.5 mmol), Pt as anode and cathode; b) with 5 mol% Cp_2Fe; c) 30 mol% was used; d) 100 mol% was used.



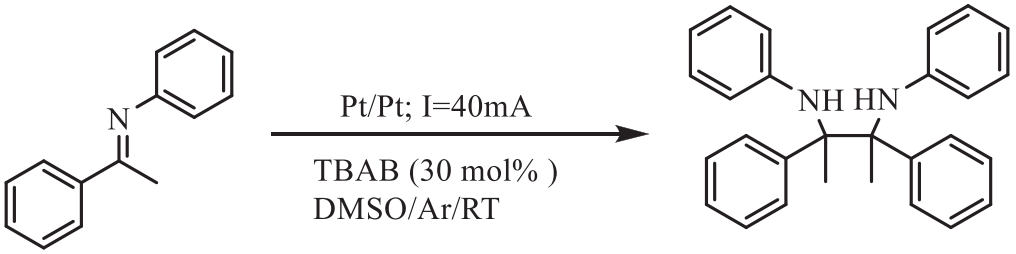
5 **6** (1:8.1) **7** (63%)

Scheme 3. Formation of 4-methoxybenzoic acid from 4-methoxy acetophenone.



8 **9** (56%)

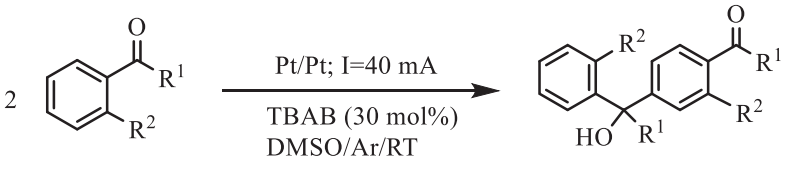
Scheme 4. Synthesis of 1-(4-(3-(4-ethynylphenyl)-3-hydroxybut-1-yn-1-yl)phenyl)ethanone from 1-(4-ethynylphenyl)ethanone **9**.



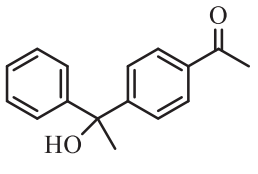
10 **11** (55%)

Scheme 5. Synthesis of 2,3-diphenyl-2,3-phenylaminobutane **11** from *N*-(1-phenylethylidene)aniline **10**.

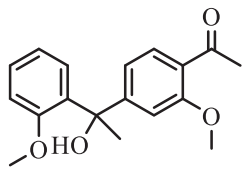
Table II. Synthesis of 1-(4-(1-hydroxy-1-phenylethyl/methyl)phenyl)ethanones/methanones 2.



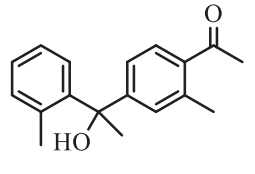
1 **2**



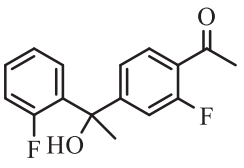
2a, 72%



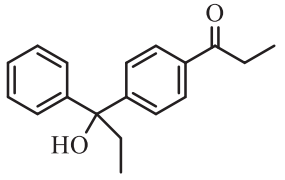
2b, 60%



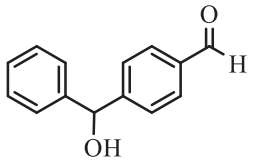
2c, 78%



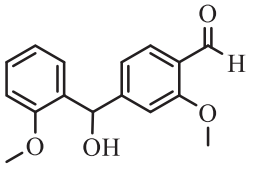
2d, 70%



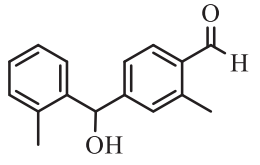
2e, 82%



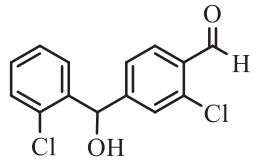
2f, 57%



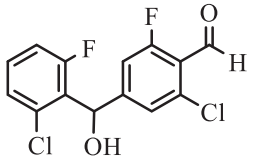
2g, 60%



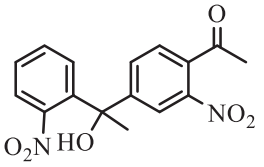
2h, 65%



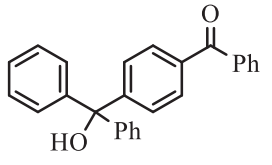
2i, 51%



2j, 55%

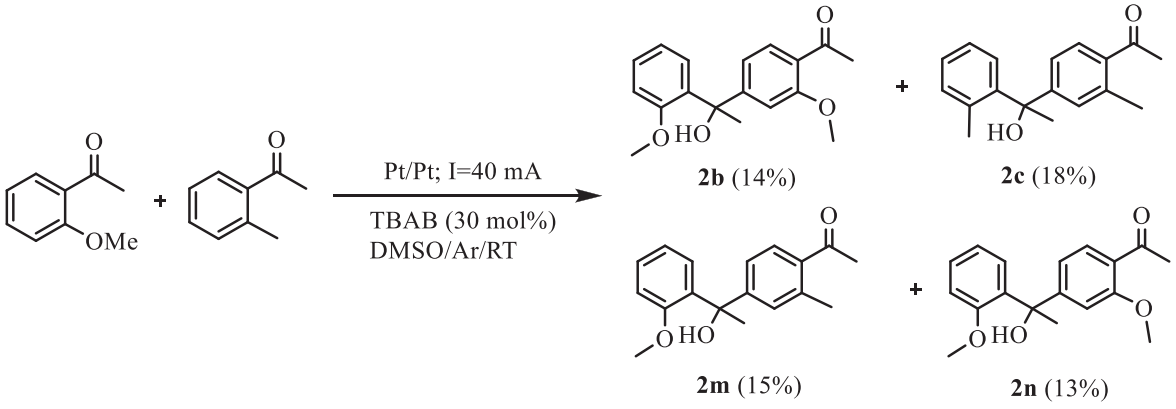


2k, 0%



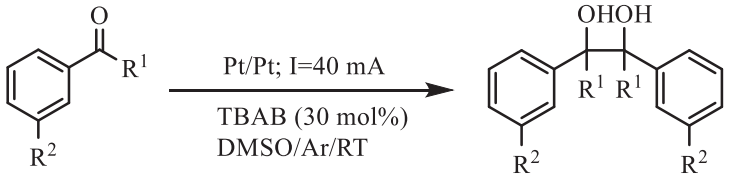
2l, 0%

Reaction conditions: **1** (0.5 mmol), Pt as anode and cathode, 1-3 h.

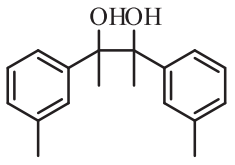


Scheme 6. Cross coupling of *o*-methoxyacetophenone and *o*-methylacetophenone.

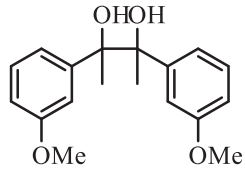
Table III. Synthesis of 2,3-bis(3-substitutedphenyl)butane/ethane-2,3-diols 4.



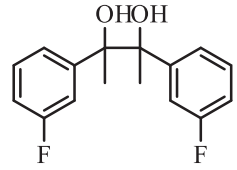
3 **4**



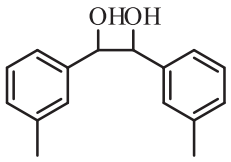
4a (1:6.5), 85%



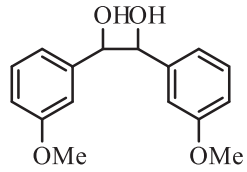
4b (1:4.6), 66%



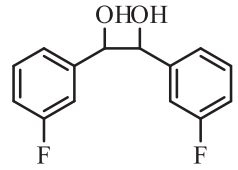
4c (1:1.97), 69%



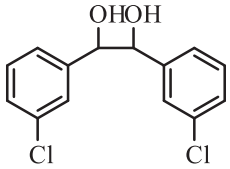
4d (1:1.2), 81%



4e (1:1.1), 69%



4f (1:1), 75%

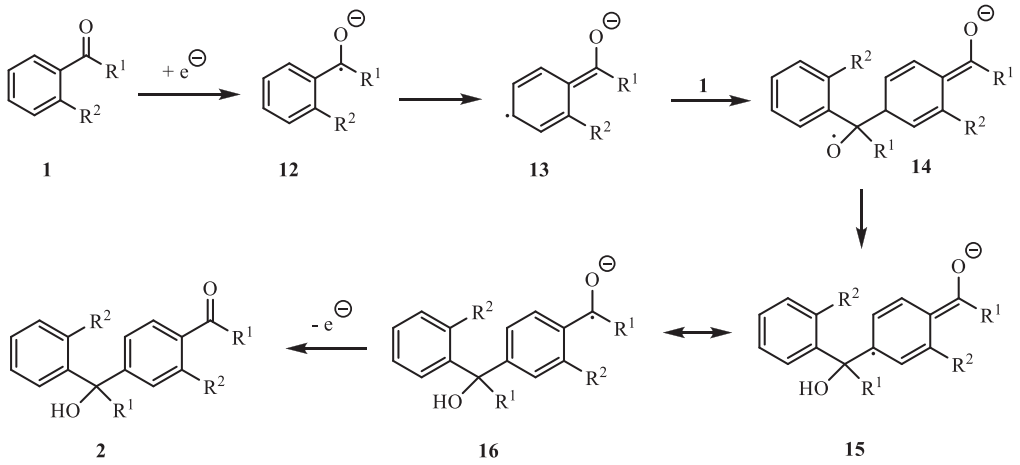


4g (1:1), 73%

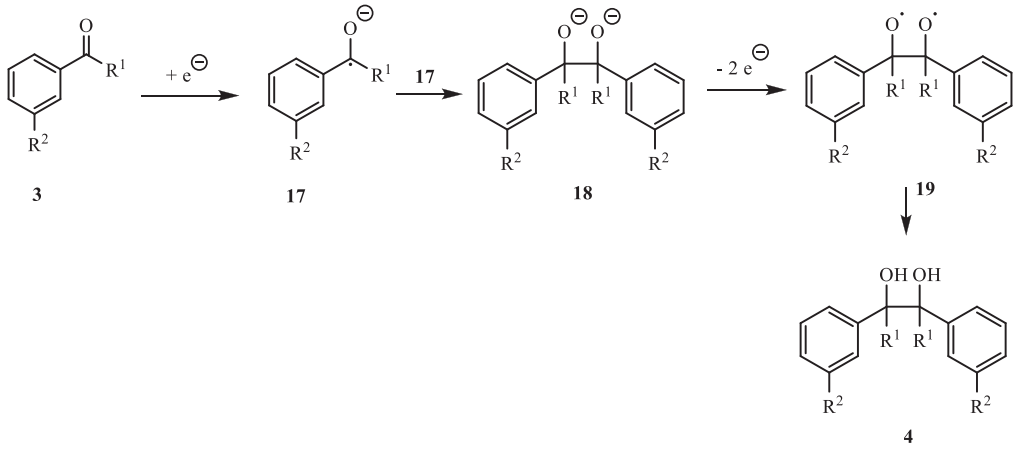
Reaction conditions: **3** (0.5 mmol), Pt as anode and cathode, 1-2 h.

of 4-methoxybenzoic acid from 4-methoxycetophenone is not clear at this stage.

To confirm the above-proposed radical mechanism, we conducted a control experiment involving electrolysis of acetophenone 1a in the presence of butylated hydroxyl toluene (BHT), which did not furnish the required product thus pointing out the radical mechanism of this reductive coupling. To further shed light on the mechanism and to know the redox pattern of reactants we performed



Scheme 7. Probable mechanism for the formation of **2**.



Scheme 8. Probable mechanism for the formation of **4**.

cyclic voltammetric studies. Unfortunately, the reduction-oxidation peaks were too weak to identify in the cyclic voltagram.

Experimental

The starting materials were commercially available and were used without further purification. Reactions were monitored by TLC using precoated sheets with UV light for visualization. Products were purified by preparative TLC. NMR spectra were recorded using 400 MHz Brucker spectrometer using the residual solvent peaks as reference relative to TMS. High resolution mass spectra were recorded using ESI-Q-TOF mass spectrometer.

General procedure for the synthesis of 2/4/7/9/11.—To a solution of 0.5 mmol of **2/4/7/9/11** in DMSO (3 ml) in a three neck round bottom flask fitted with platinum electrodes (1 cm × 1 cm) and passed a constant current of 15 mA was passed for 1–3 h from an amperostate. Reaction was monitored by thin layer chromatography. After the completion of the reaction, the reaction mixture was diluted with ethyl acetate (30 ml), washed with brine (20 ml). The aqueous layer was extracted with ethyl acetate (30 ml). The combined ethyl acetate layer was washed with brine (20 ml). The organic layer was evaporated under reduced pressure. The crude products were purified by preparative TLC.

Spectral data.—1-(4-(1-Hydroxy-1-phenylethyl)phenyl)ethanone (**2a**): Viscous liquid; 84 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.97 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 7.27 (t, J = 8.0 Hz, 1H, Ar-H), 7.33 (t, J = 8.0 Hz, 2H, Ar-H), 7.41 (d, J = 8.0 Hz, 2H, Ar-H), 7.52 (d, J = 8.0 Hz, 2H, Ar-H), 7.90 (d, J = 8.0 Hz, 2H, Ar-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.6, 30.6, 76.1, 125.8, 126.0, 127.3, 128.3, 128.4, 135.7, 147.2, 153.4, 197.9. HRMS (APPI+) m/z calcd for [$C_{16}H_{16}O_2$]: 240.1150, found 240.1144.

1-(4-(1-Hydroxy-1-(2-methoxyphenyl)ethyl)-2-methoxyphenyl) ethanone (**2b**): White solid; M. P. 84 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.82 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 3.62 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 6.69 (dd, J = 12.0 Hz, 4.0 Hz, 1H, Ar-H) , 6.90 (d, J = 12.0 Hz, 1H, Ar-H),7.04 (t, J = 8.0 Hz, 1H, Ar-H), 7.13 (s, 1H, Ar-H), 7.32 (t, J = 8.0 Hz, 1H, Ar-H), 7.44 (d, J = 8.0 Hz, 1H, Ar-H), 7.60 (d, J = 8.0 Hz, 1H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.9, 31.9, 55.5, 55.6, 76.3, 108.2, 112.0, 117.3, 121.0, 126.2, 127.0, 129.2, 130.0, 134.1, 156.5, 156.9, 159.0, 199.5. HRMS (APPI +) m/z calcd for [$C_{18}H_{20}O_4$]: 300.1362, found 300.1357.

1-(4-(1-Hydroxy-1-(*o*-tolyl)ethyl)-2-methylphenyl)ethanone (**2c**): Viscous liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.91 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 7.11–7.26 (m, 5H, Ar-H), 7.62–7.66 (m, 2H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 22.0, 29.5, 32.6, 76.7, 122.7, 125.5, 126.0, 128.0, 128.9, 129.7, 132.6, 135.7, 137.4, 138.8, 143.8, 151.7, 201.3. HRMS (APPI+) m/z calcd for [$C_{18}H_{20}O_2$]: 268.1463, found 268.1459.

1-(2-Fluoro-4-(1-(2-fluorophenyl)-1-hydroxyethyl)phenyl)ethanone (**2d**): Viscous liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.94 (s, 3H, CH_3), 2.61 (s, 3H, CH_3), 6.93–7.03 (m, 1H, Ar-H), 7.15–7.23 (m, 3H, Ar-H), 7.30–7.35 (m, 1H, Ar-H), 7.58–7.62 (t, J = 8.0 Hz, 1H, Ar-H), 7.80 (m, 1H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.3 (d, J = 1.0 Hz), 31.4 (d, J = 28.0 Hz), 74.7, 113.7 (d, J = 25.0 Hz), 116.4 (d, J = 22.0 Hz), 121.3 (d, J = 2.0 Hz), 123.6 (d, J = 3.0 Hz), 124.3 (d, J = 3.0 Hz), 127.2 (d, J = 4.0 Hz), 130.0 (d, J = 9.0 Hz), 130.6 (d, J = 55.0 Hz), 133.1 (d, J = 11.0 Hz), 155.5 (d, J = 8.0 Hz), 161.5 (d, J = 58.0 Hz), 163.5, 195.6 (d, J = 4.0 Hz). HRMS (APPI+) m/z calcd for [$C_{16}H_{14}F_2O_2$]: 276.0962, found 276.0958.

1-(4-(1-Hydroxy-1-phenylpropyl)phenyl)propan-1-one (**2e**): Viscous liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.89 (t, J = 8.0 Hz, 3H, CH_3), 1.20 (t, J = 8.0 Hz, 3H, CH_3), 2.34 (q, J = 8.0 Hz, 2H, CH_2), 2.97 (q, J = 8.0 Hz, 2H, CH_2), 7.15 (s, 1H, OH), 7.23–7.26 (m, 1H, Ar-H), 7.31 (t, J = 8.0 Hz, 2H, Ar-H), 7.41 (d, J = 8.0 Hz, 2H, Ar-H), 7.51 (d, J = 8.0 Hz, 2H, Ar-H), 7.90 (d, J = 8.0 Hz, 2H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 8.0, 8.3, 31.8, 34.3, 78.4, 126.1, 126.3, 127.2, 127.9, 128.4, 135.3, 146.4, 151.9, 200.6. HRMS (APPI+) m/z calcd for [$C_{18}H_{20}O_2$]: 268.1463, found 268.1456.

4-(Hydroxy(phenyl)methyl)benzaldehyde (**2f**): Viscous liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ ^{1}H NMR ($CDCl_3$, 400 MHz): 5.91 (s, 1H, CH), 7.26–7.37 (m, 5H, Ar-H),7.58 (d, J = 8.0 Hz, 2H, Ar-H), 7.86 (d, J = 8.0 Hz, 2H, Ar-H),9.99 (s, 1H, CHO) ^{13}C NMR ($CDCl_3$, 100 MHz) δ 76.0, 126.7, 126.9, 128.2, 128.8, 130.0, 135.7, 143.1, 150.3, 191.9. HRMS (APPI+) m/z calcd for [$C_{14}H_{12}O_2$]: 212.0837, found 212.0832.

4-(Hydroxy(2-methoxyphenyl)methyl)-2-methoxybenzaldehyde (**2g**): Viscous liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.84 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 6.1 (s, 1H, CH), 6.91–6.97 (m, 3H, Ar-H), 7.17–7.26 (m, 2H, Ar-H), 7.30 (m, 1H, Ar-H), 7.76 (d, J = 8.0 Hz, 1H, Ar-H), 10.42 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.5, 55.6, 72.0, 109.5, 110.9, 118.8, 121.0, 123.7, 128.0, 128.4, 139.3, 131.0, 152.1, 156.7, 161.9, 189.6. HRMS (APPI+) m/z calcd for [$C_{16}H_{16}O_4$]: 272.1049, found 272.1044.

4-(Hydroxy(*o*-tolyl)methyl)-2-methylbenzaldehyde (**2h**): Viscous liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.31 (s, 3H, CH_3), 2.65 (s, 3H, CH_3), 6.04 (s, 1H, CH), 7.19–7.24 (m, 4H, Ar-H), 7.34–7.40 (m, 2H, Ar-H), 7.76 (m, 1H, Ar-H), 10.24 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 9.4, 19.7, 73.0, 124.7, 126.4, 126.8, 128.1, 130.1, 130.9, 132.3, 133.4, 135.6, 140.8, 140.9, 148.7, 192.3. HRMS (APPI+) m/z calcd for [$C_{16}H_{16}O_2$]: 240.1150, found 240.1144.

2-Chloro-4-((2-chlorophenyl)(hydroxy)methyl)benzaldehyde (**2i**): Viscous liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.28 (s, 1H, CH), 7.27–7.29 (m, 2H, Ar-H), 7.29–7.32 (m, 2H, Ar-H), 7.38–7.40 (m, 1H, Ar-H), 7.56 (d, J = 1.0 Hz, 1H, Ar-H), 7.88 (d, J = 8.0 Hz, 1H, Ar-H), 10.44 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 71.6,

125.6, 127.6, 128.3, 128.6, 129.5, 129.6, 129.9, 131.7, 132.5, 138.1, 139.8, 150.1, 189.4. HRMS (APPI+) m/z calcd for $[C_{14}H_{10}Cl_2O_2]$: 280.058, found 280.00054.

2-Chloro-4-((2-chloro-6-fluorophenyl)(hydroxy)methyl)-6-fluorobenzaldehyde (**2j**): Viscous liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.00 (s, 1H, OH), 6.38 (s, 1H, CH), 7.03–7.08 (m, 2H, Ar-H), 7.30–7.31 (m, 3H, Ar-H), 10.42 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 186.6, 164.66 and 162.02 (d, J = 264.0 Hz), 162.7 and 160.2 (d, J = 250.0 Hz), 150.9 (d, J = 9.0 Hz), 137.2 (d, J = 4.0 Hz), 134.0 (d, J = 6.0 Hz), 130.9 (d, J = 10.0 Hz), 127.2 (d, J = 14.0 Hz), 126.3 (d, J = 4.0 Hz), 123.6 (d, J = 2.0 Hz), 120.6 (d, J = 9.0 Hz), 115.4 (d, J = 22.0 Hz), 112.9 (d, J = 23.0 Hz), 68.8. HRMS (APPI+) m/z calcd for $[C_{14}H_8Cl_2F_2O_2]$: 315.9869, found 315.9865.

2,3-Di-*m*-tolylbutane-2,3-diol (**4a**): Viscous liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.44 (s, 6H, $2CH_3$), 1.53 (s, 6H, $2CH_3$), 2.26 (s, 6H, $2CH_3$), 2.28 (s, 6H, $2CH_3$), 2.60 (4H, OH), 6.97–7.14 (m, 16H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 25.0, 25.1, 78.7, 78.9, 124.1, 124.6, 127.0, 127.2, 127.6, 127.8, 127.9, 128.3, 136.5, 136.7, 143.4, 143.7. HRMS (APPI+) m/z calcd for $[C_{18}H_{22}O_2]$: 270.1620, found 270.1617.

2,3-Bis(3-methoxyphenyl)butane-2,3-diol (**4b**): Viscous liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.5 (s, 6H, $2CH_3$), 1.56 (s, 6H, $2CH_3$), 3.69 (s, 6H, $2OCH_3$), 7.72 (s, 6H, $2OCH_3$), 6.78–6.81 (m, 12H, Ar-H), 7.14–7.25 (m, 4H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.0, 25.2, 55.1, 78.6, 78.9, 112.5, 112.6, 113.0, 133.4, 119.4, 114.0, 128.0, 128.2, 145.2, 145.6, 158.6, 158.8. HRMS (APPI+) m/z calcd for $[C_{18}H_{22}O_4]$: 302.1518, found 302.1514.

2,3-Bis(3-fluorophenyl)butane-2,3-diol (**4c**): Viscous liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.50 (s, 6H, CH_3), 1.54 (s, 6H, CH_3), 2.27 (s, 2H, OH), 2.60 (s, 2H, OH), 6.87–7.16 (m, 12H, Ar-H), 7.17–7.26 (m, 4H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.8, 25.1, 78.2, 78.5, 113.7, 113.9, 114.2, 114.3, 114.5, 114.7, 123.0 (d, J = 8.0 Hz), 128.7 (d, J = 8.0 Hz), 128.5, 146.1 (d, J = 7.0 Hz), 146.6 (d, J = 4.0 Hz), 161.0 (d, J = 14.0 Hz), 163.4 (d, J = 14.0 Hz). HRMS (APPI+) m/z calcd for $[C_{16}H_{16}F_2O_2]$: 278.1118, found 278.1115.

1,2-Di-*m*-tolylethane-1,2-diol (**4d**): Viscous liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.25 (s, 6H, $2CH_3$), 2.30 (s, 6H, $2CH_3$), 2.69 (s, 4H, OH), 4.56 (s, 2H, 2CH), 4.65 (s, 2H, 2CH), 6.84 (d, J = 8.0 Hz, 2H, Ar-H), 6.92 (s, 2H, Ar-H), 7.00–7.10 (s, 10H, Ar-H), 7.18 (t, J = 8.0 Hz, 2H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 21.5, 78.2, 78.8, 124.1, 124.3, 127.6, 127.9, 130.0, 128.2, 128.6, 128.9, 137.7, 137.9, 140.0, 140.0. HRMS (APPI+) m/z calcd for $[C_{16}H_{18}O_2]$: 242.1307, found 242.1304.

1,2-Bis(3-methoxyphenyl)ethane-1,2-diol (**4e**): Viscous liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.72 (s, 6H, $2OCH_3$), 3.74 (s, 6H, $2OCH_3$), 4.67 (s, 2H, 2CH), 4.78 (s, 2H, 2CH), 6.71–6.88 (m, 12H, ArH), 7.15 (t, J = 8.0 Hz, 2H, Ar-H), 7.22–7.26 (m, 2H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.2, 55.2, 78.0, 78.9, 112.2, 112.3, 113.7, 114.0, 119.2, 119.4, 129.2, 129.3, 141.4, 141.6, 159.5, 159.6. HRMS (APPI+) m/z calcd for $[C_{16}H_{18}O_4]$: 274.1205, found 274.1200.

1,2-Bis(3-fluorophenyl)ethane-1,2-diol (**4f**): Viscous liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.41 (s, 4H, OH), 4.58 (s, 2H, CH), 4.79 (s, 2H, CH), 6.75–6.96 (m,12H, Ar-H), 7.12–7.25 (m, 4H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 77.1 (d, J = 1.0 Hz), 78.4 (d, J = 2.0 Hz), 113.8 (d, J = 14.0. Hz), 114.0 (d, J = 14.0 Hz),114.9 (d, J = 5.0 Hz), 115.1 (d, J = 5.0 Hz), 112.6 (t, J = 3.0 Hz), 129.6 (d, J = 8.0 Hz), 129.7 (d, J = 9.0 Hz),141.9 (d, J = 7.0 Hz), 142.1 (d, J = 7.0 Hz), 163.9, 161.4. HRMS (APPI+) m/z calcd for $[C_{14}H_{12}F_2O_2]$: 250.0805, found 250.0801.

1,2-Bis(3-chlorophenyl)ethane-1,2-diol (**4g**): Viscous liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.56 (s, 4H, OH), 4.62 (d, J = 8.0 Hz, 2H, Ar-H), 4.79 (d, J = 8.0 Hz, 2H, Ar-H), 7.17–7.26 (m, 12H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 78.3, 125.2, 125.3, 127.0, 127.2, 128.3, 128.3, 129.4, 129.4, 134.2, 134.3, 141.6, 141.7. HRMS (APPI+) m/z calcd for $[C_{14}H_{12}Cl_2O_2]$: 282.0214, found 282.0211.

2,3-Bis(4-methoxyphenyl)butane-2,3-diol (**6**): Viscous liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.46 (s, 6H, CH_3), 1.55 (s, 6H, CH_3), 2.57 (s, 4H, OH), 3.79 (s, 6H, OCH_3), 3.80 (s, 6H, OCH_3), 6.75–6.78 (m, 8H, Ar-H), 7.09–7.12 (m, 8H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.0, 25.2, 55.2, 78.5, 78.7, 112.4, 112.6, 112.1, 128.6, 135.8, 136.1, 158.4, 158.5. HRMS (APPI+) m/z calcd for $[C_{18}H_{22}O_4]$: 302.1518, found 302.1514.

4-Methoxy benzoic acid (**7**): White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.88 (s, 3H, OCH_3), 6.94 (d, J = 8.0 Hz, 2H, Ar-H), 8.07 (d, J = 8.0 Hz, 2H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.5, 113.8, 121.7, 132.4, 164.1, 171.5. HRMS (APPI+) m/z calcd for $[C_{18}H_{22}O_4]$: 152.0473, found 152.0470.

1-(4-(3-(4-Ethynylphenyl)-3-hydroxybut-1-yn-1-yl)phenyl)ethanone (**9**): Viscous liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.78 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 3.08 (s, 1H, CH), 7.44–7.49 (m, 6H, Ar-H), 7.90 (d, J = 8.0 Hz, 2H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.6, 29.7, 74.6, 77.2, 77.2, 83.4, 124.9, 125.3, 126.7, 128.5, 128.8, 132.2, 136.2, 138.6, 146.8, 197.6. HRMS (APPI+) m/z calcd for $[C_{20}H_{16}O_2]$: 288.1150, found 288.1144.

2,3-Diphenyl-2,3-phenylaminobutane (**11**): Viscous liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.51 (s, 6H, $2CH_3$), 1.52 (s, 6H, $2CH_3$), 4.06 (s, 4H, NH), 6.36–6.50 (m, 4H, Ar-H), 6.51 (d, J = 8.0 Hz, 4H, Ar-H), 6.64 (t, J = 8.0Hz, 2H, Ar-H), 7.06–7.14 (m, 8H, Ar-H), 7.15–7.24 (m, 6H, Ar-H), 7.25–7.38 (m, 16H, Ar-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.9, 25.0, 53.5, 53.5, 108.9, 113.3, 114.9, 117.3, 125.8, 125.9, 128.6, 128.7, 129.1, 131.8, 144.6, 145.2, 146.2, 147.3. HRMS (APPI+) m/z calcd for $[C_{28}H_{28}N_2]$: 392.2252, found 392.2247.

Conclusions

In conclusion, we have reported electro-reductive phenyl-carbonyl coupling of *o*-substituted aromatic carbonyl compounds for the synthesis of 1-(4-(1-hydroxy-1-phenylethyl/methyl)phenyl)ethanones/methanones and reductive carbonyl-carbonyl coupling of *m*-substituted carbonyl compounds for the synthesis of 2,3-bis(3-substitutedphenyl)butane/ethane-2,3-diols. The present method avoids the use of stoichiometric amount of Sm and its compounds, and HMPA. Further, electrolysis of *p*-methoxy acetophenone surprisingly gave *p*-methoxy benzoic acid. Even conjugation extended system also furnished corresponding reductive addition product. Finally, imine also formed diamino compound as reductive coupling product. Thus, the present method describes an Umpolung reductive coupling of carbonyl compounds and imines. Radical mechanisms for the formation of products is proposed.

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