Tetrahedron xxx (xxxx) xxx

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Practical acetalization and transacetalization of carbonyl compounds catalyzed by recyclable PVP-I

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ARTICLE INFO

Article history:
Received 3 April 2021
Received in revised form
11 May 2021
Accepted 21 May 2021
Available online xxx

Keywords:
PVP-I
Acetalization
Transacetalization
Non-toxic
Recyclable catalyst

ABSTRACT

A novel PVP-I catalyzed acetalizations/transacetalizations of carbonyl compounds has been developed processing with a mild and easy handling fashion. Different types of Acyclic and cyclic acetals were prepared from carbonyl compounds or their acetals successfully. Further applications of newly developed catalytic combination were testified. This protocol featured with simplicity of operation, mild reaction condition, short reaction time, recyclable of catalyst and broad substrates scope with excellent yields.

1. Introduction

Protection of carbonyl groups plays an important role in multistep organic synthesis [1] and industrial manufacturing [2]. Acetalization of carbonyl groups is now commonly used in the total synthesis of natural compounds. Moreover, acetals could present in natural products such as Anthogorgiene D and Incargutine B [3] (Scheme 1). Till now, numerous endeavors have been devoted to developing the protocol of acetals preparation. Traditional methods for the formation of acetals and ketals involve condensation of an aldehyde or ketone with alcohols or diols using protic or Lewis acid [4–9] catalysts equipped with a Dean-Stark trap or using dehydration agents to remove water. However, these approaches have the drawbacks of corrosive acid catalyst handling, high temperature, toxic solvent, long reaction time and some limitations on substrates scope. Recently, complementary catalytic protocols including ionic liquid catalysts [10], photo-redox catalysts [11], solid acid catalysts [12], electrochemical oxidation catalysis [13] or transition-metal catalysts [14] have been reported to show several advantages over conventional acid methods. In addition, acetaliaztion of carbonyl compounds catalyzed by molecular Iodine were reported by K. Banik and B. Karimi respectively [15]. Molecular Iodine used in this protocol has its own nature of easy sublimate and tedious work-up process using sodium thiosulfate. Therefore, the development of an economic, green and sustainable method for this acetalization is highly desirable. Our previous researches using Povidone-iodine (PVP—I) as catalyst in the organic transfermations [16] urge us to investigate the efficacy of PVP-I in the application of acetalization.

2. Results and discussion

The research work was initiated using *p*-chlorobenzaldehyde as model substrates. As shown in Table 1, when reaction was conducted using 0.03 eq. of PVP-I in methanol under 30 °C for 3h, the conversion rate of **2aa** was 96.8% (Table 1, entry 1). However, TLC inspected that there was a little surplus of raw materials. The starting material cannot be consumed completely by changing reaction temperature, time and the loading amount of PVP-I (Table 1, entries 2—8). In the next trail, When trimethyl orthoformate [17] (1.0 eq.) was added, the starting material could be completely converted into target product (Table 1, entry 9). This should be due to the fact that trimethyl orthoformate could act as both methoxy source and dehydration agents. Any further alteration of reaction time, temperature, loading amount of catalyst and trimethyl orthoformate all led to slight reduction of the yield (Table 1, entries 10—13). The product **2aa** could also be afforded in the absence of

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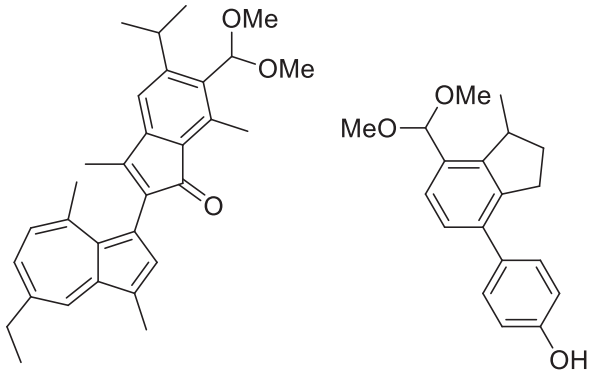
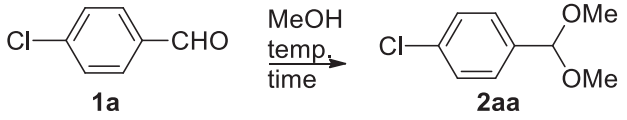
https://doi.org/10.1016/j.tet.2021.132250
0040-4020/



Scheme 1. Selected examples of natural products with dimethyl acetal.

Table 1
Optimization of reaction Conditions.



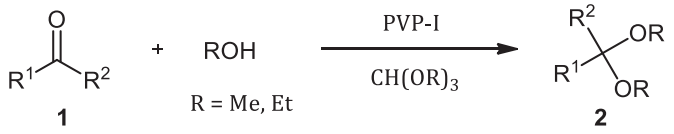
Entry	PVP-I (equiv.)	Solvent	T (°C)	Time (h)	yield (%)[b]
1	0.03	MeOH	30	3	96.8
2	0.04	MeOH	30	3	96.5
3	0.02	MeOH	30	3	96.3
4	0.03	MeOH	20	3	95.6
5	0.03	MeOH	40	3	96.8
6	0.03	MeOH	30	2	95.7
7	0.03	MeOH	30	4	96.7
8	0.03	MeOH	30	10	97.0
9 [d]	0.03	MeOH	30	3	quant.(94.2)[c]
10 [d]	0.02	MeOH	30	3	98.7
11 [d]	0.03	MeOH	30	2	99.0
12 [d]	0.03	MeOH	30	1	97.6
13 [e]	0.03	MeOH	30	3	96.5
14 [d]	0.03	–	30	3	29.5
15 [d]	0.03	DCM	30	3	15.3
16 [d]	0.03	MeCN	30	3	20.5
17 [d]	0.03	THF	30	3	0.9
18 [d]	–	MeOH	30	3	23.2

[a]Reaction condition: 1a (1.0 mmol), MeOH (2 mL).
[b] Determined by GC-MS of the crude reaction mixture.
[c] Isolated yield was given in parentheses.
[d] Trimethyl orthoformate (1.0 mmol).
[e] Trimethyl orthoformate (0.5 mmol).

MeOH with a low conversion rate (Table 1, entry 14). Even the solvent was switched to DCM, CH_3CN and THF, the production yields were still low (Table 1, entries 15–17). Furthermore, the conversion rate was less than 25% in the absence of catalyst (Table 1, entry 18). Therefore, the current optimal condition for the acetalization was obtained with a loading of 0.03 eq. of PVP-I and trimethyl orthoformate (1.0 eq.) in MeOH at 30 °C for 3h. These results indicated that PVP-I/$CH(OMe)_3$/MeOH is an excellent catalytic system for the acetalization of carbonyl compounds. Similarly, diethyl acetal can also be obtained under the catalytic system of PVP-I/$CH(OEt)_3$/EtOH.

Having the optimized reaction conditions in hand, the investigation of substrate scope was conducted and the results were summarized in Table 2. The reactions worked smoothly with all tested aldehydes and ketones to give their corresponding dimethyl/diethyl acetal products in good to excellent yields. Substrates

Table 2
Substrate scope for acetalization of aldehydes and Ketones[a].



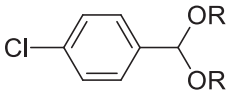
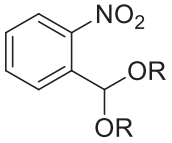
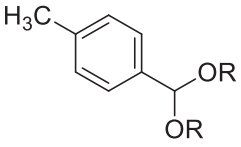
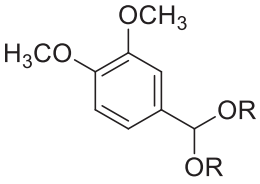
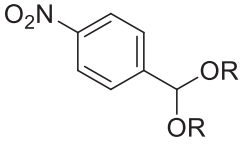
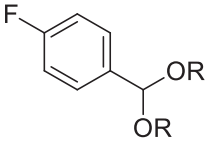
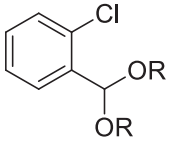
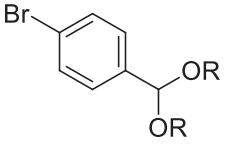
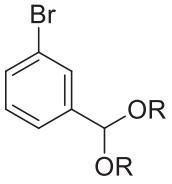
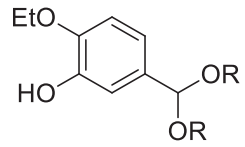
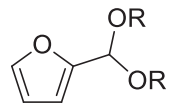
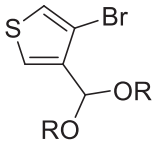
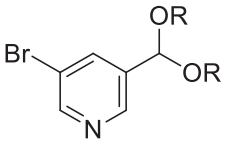
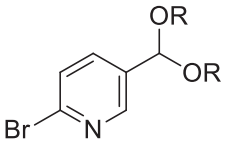
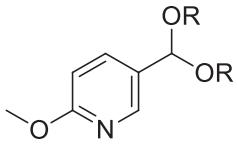
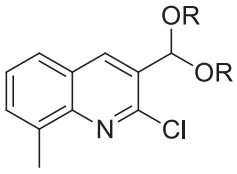
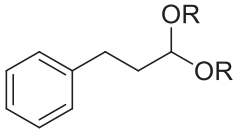
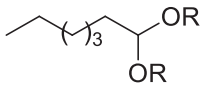
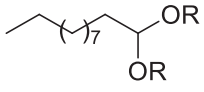
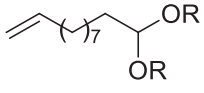
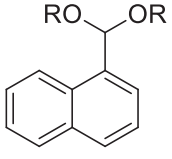
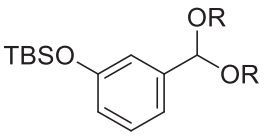
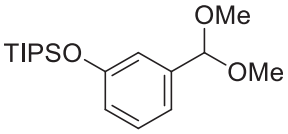
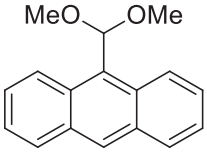
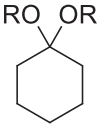
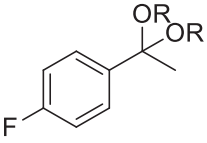
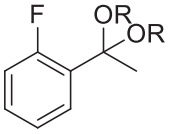
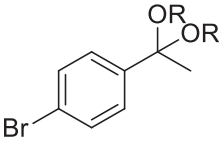
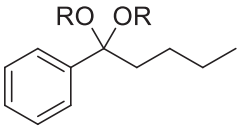
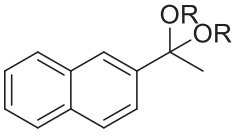
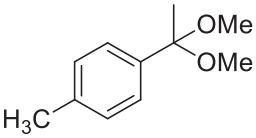
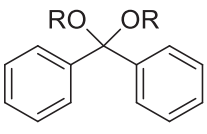
Entry	Product	Yield[b] (%)
1		**2aa**, quant., (94.2), R = Me **2 ab**, quant., R = Et
2		**2ba**, quant., (97.0), R = Me **2bb**, quant., R = Et
3		**2ca**, 93.0(89.0), R = Me **2 cb**, 87.0, R = Et
4		**2da**, 92.1, R = Me **2 db**, 92.0, R = Et
5		**2ea**, quant., (99.0), R = Me **2eb**, quant., R = Et
6		**2fa**, quant., (90.1), R = Me **2 fb**, 94.0, R = Et
7		**2ga**, 98.0, R = Me **2gb**, 94.6, R = Et
8		**2ha**, quant., (91.7), R = Me **2 hb**, 97.8, R = Et
9		**2ia**, quant., R = Me **2ib**, 96.0, R = Et

Table 2 (*continued*)

Entry	Product	Yield[b] (%)
10		**2ja**, 93.6, R = Me **2jb**, 91.8, R = Et
11		**2ka**, quant., R = Me **2 kb**, quant., R = Et
12		**2la**, quant., R = Me **2lb**, quant., R = Et
13		**2ma**, 95.0 (93.0), R = Me **2 mb**, 90.1 (87.0), R = Et
14		**2na**, quant., (96.0), R = Me **2 nb**, quant., R = Et
15		**2oa**, 99.0, R = Me **2ob**, 95.0, R = Et
16		**2pa**, 90.6, R = Me **2 pb**, 83.0, R = Et
17		**2qa**, quant., R = Me **2qb**, quant., R = Et
18		**2ra**, quant., R = Me **2rb**, quant., R = Et
19		**2sa**, quant., (98.0), R = Me **2sb**, quant., (97.0), R = Et
20		**2ta**, quant., (97.6), R = Me **2tb**, quant., (96.1), R = Et
21		**2ua**, 99.0 (93.0), R = Me **2ub**, 85.0, R = Et

(*continued on next column*)

Table 2 (*continued*)

Entry	Product	Yield[b] (%)
22		**2va**, 98.0 (95.1), R = Me **2vb**, 97.5, R = Et
23		**2wa**, 96.0 (93.0)
24		**2xa**, 98.2
25[c]		**2aaa**, quant., R = Me **2aab**, quant., R = Et
26[c]		**2aba**, 99.0, R = Me **2abb**, 94.0, R = Et
27[c]		**2aca**, quant., R = Me **2acb**, 99.0, R = Et
28[c]		**2ada**, 99.5, R = Me **2adb**, 95.0, R = Et
29[c]		**2aea**, 94.1, R = Me **2aeb**, 93.7, R = Et
30[c]		**2afa**, 97.1, R = Me **2afb**, 93.0, R = Et
31[c]		**2aga**, 97.8
32[c,d]		**2 aha** 96.0 (92.1), R = Me **2ahb** 79.9 (75.4), R = Et

[a] Reaction condition: aldehyde/ketone (1.0 mmol), alcohol (2 mL), PVP-I (3.0 mol %), Trimethyl orthoformate (for methanol) or Triethyl orthoformate (for ethanol) (1.0 mmol) at 30 °C for 3 h.

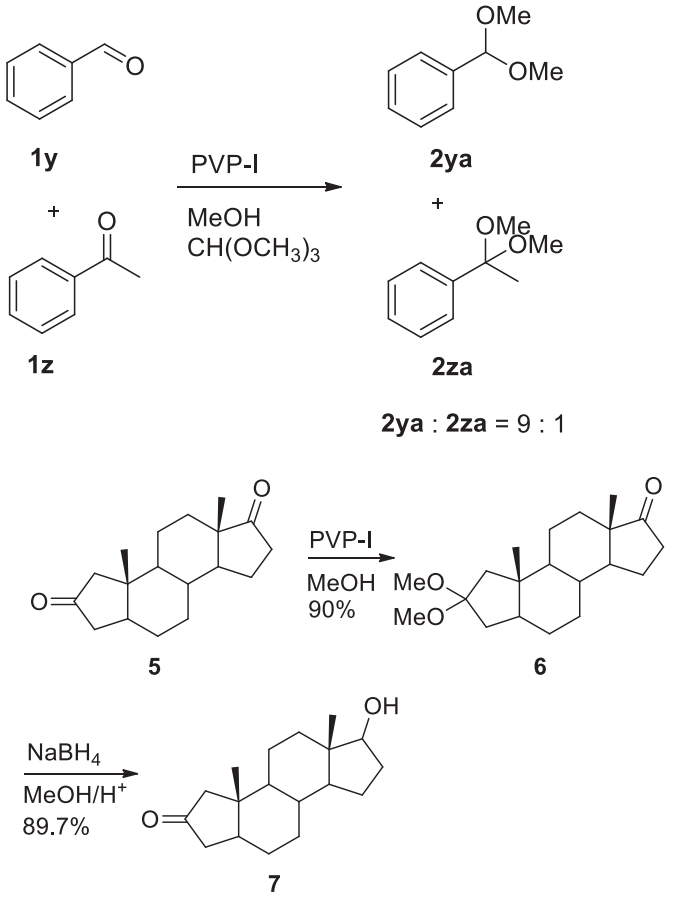
[b] Determined by GC-MS of the crude reaction mixture. Isolated yields were shown in parentheses.

[c] Trimethyl orthoformate or Triethyl orthoformate (3.0 mmol) at 30 °C for 6 h.

[d] 5.0 mmol of starting material for 2 aha and 2.0 mmol starting material for 2ahb.

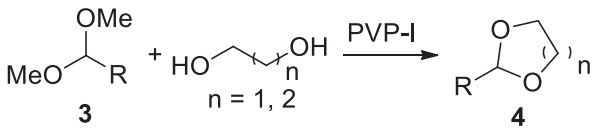
bearing electron-withdrawing group on the benzene ring (Table 2, entries 1–2 and 5–9) seemed to be better than that with electron-donating group (Table 2, entries 3, 4 and 10). This system was also compatible with a wide range of functional groups such as -Me, -OMe, –F, -Cl, -Br, $-NO_2$, –OH, providing the possibility for further organic transformations. Besides aromatic substrates mentioned above, the heteroaromatic and aliphatic aldehydes also worked well and could be transferred into their corresponding acetals in good to excellent yields (Table 2, entries 11–20). It was interesting that *ortho*-substituted aldehydes could also afford target acetal products with excellent yield under standard conditions (Table 2, entries 2, 7, 12, 16 and 21). It was worth mentioning that the acid-sensitive groups such as TBS-ethers and TIPS-ethers were both survived under the optimal reaction condition (Table 2, entries 22, 23). It was reported that **2xa** could be used as fluorescent probe for Fe^{3+}. This probe was successfully applied in the bioimaging [18]. Moreover, this catalytic system was found to be effective on ketones. Nevertheless, less reactive ketones require longer reaction time and 3.0 equivalents of trimethyl orthoformate in order to gain satisfactory results.

In order to demonstrate the chemoselectivity of PVP-I catalyzed acetalization, the controlled reaction was performed using benzaldehyde and acetophenone under current reaction condition. After 30 min, the ratio of the dimethyl acetals of benzaldehyde and acetophenone was found to be 9 : 1 (determined by GC-MS) (Scheme 2). The method also showed selectivity for different type of ketones as demonstrated in Scheme 2. Current method could selectively protect carbonyl group with less steric hindrance. The compound **7** was obtained in a total yield of 80.7% over two steps by



Scheme 2. Chemoselective acetalization.

Table 3
Transacetalizations catalyzed by PVP-I[a].



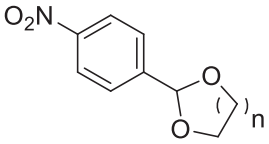
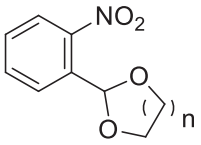
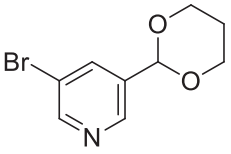
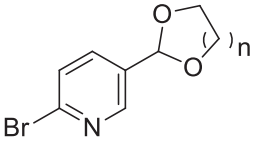
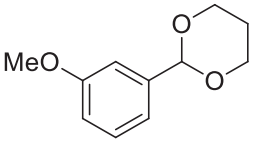
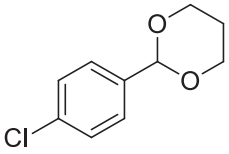
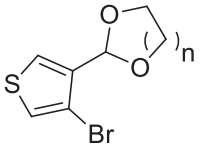
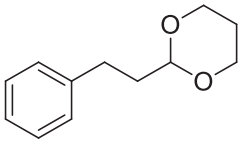
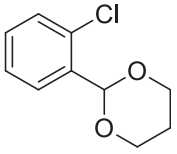
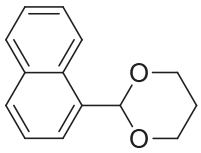
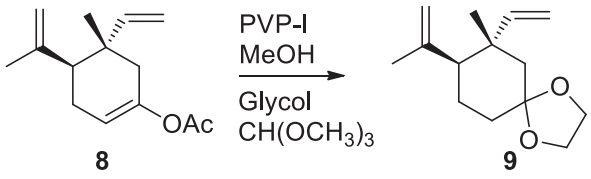
Entry	Product	Yield (%)[b]
1		**4aa**, 99.0, n = 1 **4 ab**, 98.0, n = 2
2		**4ba**, 98.3, n = 1 **4bb**, 97.5, n = 2
3		**4 cb**, 91.0
4		**4da**, 96.0, n = 1 **4 db**, 93.0, n = 2
5		**4eb**, 95.2
6		**4 fb**, 94.0
7		**4ga**, 94.0, n = 1 **4gb**, 97.0, n = 2
8		**4 hb**, 96.0
9		**4ib**, 95.0

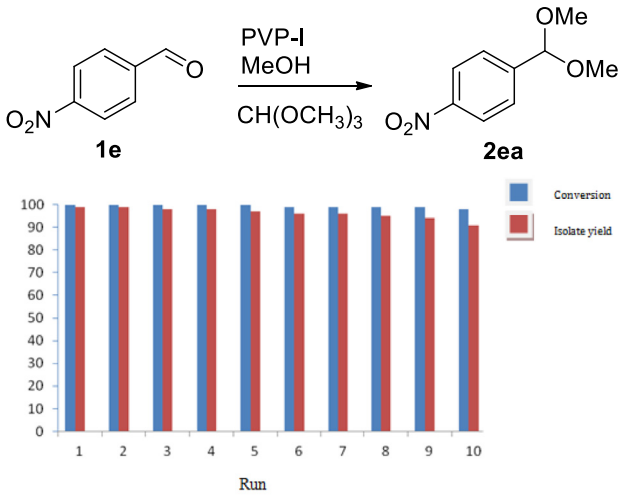
Table 3 (*continued*)

Entry	Product	Yield (%)[b]
10		**4jb**, 94.0

[a] Reaction condition: acetal (1.0 mmol), diol (6.0 mmol), PVP-I (3.0 mol%), CH_3CN (2 mL) at 60 °C for 3 h.
[b] Isolated yield.



Scheme 3. Application of newly developed transacetalization.



Reaction conditions: 4-nitrobenzaldehyde: 5.0 mmol; methanol: 10 mL; PVP-I: 3.0 mol%; trimethyl orthoformate (1.0 equiv.); temperature: 30℃; time: 3h. The conversion of **2ea** was determined by GC-MS.

Scheme 4. Recycling of PVP-I catalyst.

a facile protection-reduction/deprotection process from diketone **5**.

Inspired by Brendan M. Smith [19], PVP-I catalyzed transacetalization using 1,2-ethylene glycol/1.3-propylene glycol were also conducted and the results were summarized in Table 3. The presence of electron-withdrawing/donating group on the aromatic ring of acetals does not show significant influence on the yield information in this catalytic transacetalization (Table 3, entries 1–6). Besides aromatic substrates, the heteroaromatic and aliphatic dimethyl acetals also worked well and gave the corresponding cyclic acetals with excellent yields (Table 3, entry 7). At the same time, this transacetalization could also process smoothly on those substrates with some steric hindrance (Table 3, entries 9–10). Compound **9** is an intermediate for the synthesis of Bolivianine [20]. The target compound could be obtained in 91% under newly developed catalytic combination (Scheme 3). Compared with the original route, this method showed advantages of simple operation and more environmental friendly.

The recyclability of PVP-I for the acetalization of 4-nitrobenzaldehyde with methanol was also investigated and the results were illustrated in Scheme 4. PVP-I could be used 10 cycles to catalyze the reaction without significant loss of its activity. It demonstrated that PVP-I was very stable at the ambient temperature and could be reused expediently.

Reaction conditions: 4-nitrobenzaldehyde: 5.0 mmol; methanol: 10 mL; PVP-I: 3.0 mol%; trimethyl orthoformate (1.0 equiv.); temperature: 30 °C; time: 3h. The conversion of **2ea** was determined by GC-MS.

3. Conclusion

In conclusion, a simple and efficient method for the acetalization/transacetalization of carbonyl compounds catalyzed by non-toxic PVP-I was developed. A variety of dialkyl acetals/ketals could be achieved in excellent yields under mild condition. Furthermore, dimethyl acetals could be transferred into *O,O*-cyclic acetals in high yield catalyzed by PVP-I. The significant advantages offered by this method are: (a) general applicability to all types of carbonyl compounds (b) high yields and selectivity, (c) considerably lower catalyst loading amount and recyclability, (d) the acid-sensitive group's tolerance, (e) ease of handling. Thus, this procedure will provide a practical and better alternative to the existing procedures for acetalization.

4. Experimental section

All the reagents and solvents were commercial grade and used without further purifications unless otherwise stated. All the anhydrous solvents were freshly prepared before use according to Purification of Laboratory Chemicals-fifth edition. ^{1}H and ^{13}C NMR spectra were recorded at 400/600 MHz and 100/151 MHz. Chemical shifts were reported in parts per million (ppm), using the residual solvent signal as an internal standard: $CDCl_3$ (^{1}H NMR: δ 7.26 ppm, singlet; ^{13}C NMR: δ 77.0 ppm, triplet); DMSO-d_6 (^{1}H NMR: δ 2.50 ppm, quintet; ^{13}C NMR: δ 39.5 ppm, heptet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplets), dd (doublet of doublets), dt (doublet of triplets), and br (broad). Coupling constants (*J*) were recorded in Hertz (Hz). The number of proton atoms (n) for a given resonance was indicated by nH. Mass samples were dissolved in DCM and MeOH (HPLC grade) unless otherwise stated. Column chromatography was carried out with silica gel 60 (200–400 mesh) and commercially available solvents. Thin-Layer Chromatography (TLC) was conducted on aluminum sheets coated with silica gel 60 F254 with visualization by a UV lamp (254 nm).

5. General procedures

To a 25 mL round-bottomed flask was charged with starting material (1.0 mmol), PVP-I (76 mg, 0.03 mmol of effective iodine), Trimethyl orthoformate (1.0 mmol, 0.24 mL) and MeOH (2.0 mL). The mixture was stirred for 3 h at 30 °C. After that, the solvent was evaporated. The resulting mixture was suspended in water (20 mL) and extracted with EA (10 mL x 3). The combined organic layer was washed with brine (20 mL) and dried over anhydrous Na_2SO_4. After, filtration and concentrated under reduced pressure, most of the products were pure enough. The residue could be further purified by flash column chromatography to give the fine products.

5.1. *1-Chloro-4-(dimethoxymethyl)benzene (2aa)* [16a]

186.6 mg, quant. yield (94.2% after column); Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 8.4 Hz, 2H), 7.32 (d,

J = 8.4 Hz, 2H), 5.37 (s, 1H), 3.31 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.9, 134.4, 128.6, 128.4, 102.4, 52.7 ppm. MS (EI, m/z) $[M]^+$: 186.0; $[M+2]^+$: 188.0.

5.2. 1-Chloro-4-(diethoxymethyl)benzene (2 ab) [16a]

212.5 mg, quant. yield; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 5.48 (s, 1H), 3.63–3.48 (m, 4H), 1.23 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.9, 134.2, 128.5, 128.3, 100.9, 61.1, 15.4 ppm. MS (EI, m/z) $[M]^+$: 214.0; $[M+2]^+$: 216.0.

5.3. 1-(Dimethoxymethyl)-2-nitrobenzene (2ba) [16a]

197.1 mg, quant. yield(97.0% after column); Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 (t, J = 8.0 Hz, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 8.0 Hz, 1H), 5.92 (s, 1H), 3.41 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.2, 132.8, 132.6, 129.6, 128.3, 124.3, 100.0, 54.7 ppm. MS (EI, m/z) $[M]^+$: 197.0.

5.4. 1-(Diethoxymethyl)-2-nitrobenzene (2bb) [16a]

225.2 mg, quant. yield; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82 (t, J = 8.0 Hz, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 8.0 Hz, 1H), 6.03 (s, 1H), 3.75–3.67 (m, 2H), 3.64–3.56 (m, 2H), 1.24 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.3, 133.9, 132.7, 129.4, 128.2, 124.3, 98.6, 63.6,15.3 ppm. MS (EI, m/z) $[M]^+$: 225.0.

5.5. 1-(Dimethoxymethyl)-4-methylbenzene (2ca) [11a]

147.9 mg, 93.9% (89.0% after column); Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, J = 7.6 Hz, 2H), 7.19 (d, J = 7.6 Hz, 2H), 5.38 (s, 1H), 3.33 (s, 6H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.2, 138.3, 135.4, 129.1, 126.9, 103.4, 52.8, 21.4 ppm. MS (EI, m/z) $[M]^+$: 166.1.

5.6. 1-(Diethoxymethyl)-4-methylbenzene (2 cb) [21]

169.0 mg, 87.0%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, J = 7.6 Hz, 2H), 7.19 (d, J = 7.6 Hz, 2H), 5.49 (s, 1H), 3.67–3.51 (m, 4H), 2.36 (s, 3H), 1.25 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.2, 136.4, 135.4, 129.1, 126.8, 101.8, 61.2, 18.0, 15.4 ppm. MS (EI, m/z) $[M]^+$: 194.1.

5.7. 4-(Dimethoxymethyl)-1,2-dimethoxybenzene (2da) [22]

195.5 mg, 92.1%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.97 (d, J = 5.6 Hz, 2H), 6.84 (d, J = 8.4 Hz, 1H), 5.32 (s, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.32 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.0, 130.9, 119.4, 110.7, 109.6, 103.3, 56.0, 52.8 ppm. MS (EI, m/z) $[M]^+$: 212.0.

5.8. 4-(Diethoxymethyl)-1,2-dimethoxybenzene (2 db) [23]

221.1 mg, 92.0%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.02 (d, J = 10.0 Hz, 2H), 6.85 (d, J = 8.0 Hz, 1H), 5.43 (s, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.66–3.58 (m, 2H), 3.56–3.48 (m, 2H), 1.24 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.2, 149.1, 132.1, 119.3, 110.8, 109.7, 101.9, 61.3, 56.1, 56.0, 15.4 ppm. MS (EI, m/z) $[M]^+$: 240.0.

5.9. 1-(Dimethoxymethyl)-4-nitrobenzene (2ea) [16a]

197.1 mg, quant. yield (99.0% after column); Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 5.45 (s, 1H), 3.32 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.2, 145.3, 128.0, 123.6, 101.8, 52.9 ppm. MS (EI, m/z) $[M]^+$: 197.0.

5.10. 1-(Diethoxymethyl)-4-nitrobenzene (2eb) [16a]

225.2 mg, quant. yield; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 5.56 (s, 1H), 3.62–3.53 (m, 4H), 1.23 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.1, 146.4, 127.9, 123.6, 100.3, 61.5, 15.3 ppm. MS (EI, m/z) $[M]^+$: 225.0.

5.11. 1-(Dimethoxymethyl)-4-fluorobenzene (2fa) [11a]

170.1 mg, quant. yield (90.1% after column); Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 (dd, J = 5.6, 8.8 Hz, 2H), 7.04 (t, J = 8.8 Hz, 2H), 5.37 (s, 1H), 3.31 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.2 (d, $J_{C,F}$ = 245.5 Hz), 134.2, 128.7 (d, $J_{C,F}$ = 7.4 Hz), 115.3 (d, $J_{C,F}$ = 21.7 Hz), 102.7, 52.8 ppm. MS (EI, m/z) $[M]^+$: 170.0.

5.12. 1-(Diethoxymethyl)-4-fluorobenzene (2 fb) [24]

186.3 mg, 94.0%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (dd, J = 5.6, 8.6 Hz, 2H), 7.03 (t, J = 8.8 Hz, 2H), 5.48 (s, 1H), 3.64–3.48 (m, 4H), 1.23 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.2 (d, $J_{C,F}$ = 241.6 Hz), 135.2, 128.6 (d, $J_{C,F}$ = 8.0 Hz), 115.3 (d, $J_{C,F}$ = 21.2 Hz), 101.1, 61.2, 15.4 ppm. MS (EI, m/z) $[M]^+$: 198.1.

5.13. 1-Chloro-2-(dimethoxymethyl)benzene (2ga) [12c]

182.9 mg, 98.0%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (d, J = 7.2 Hz, 1H), 7.38 (d, J = 7.2 Hz, 1H), 7.29–7.26 (m, 2H), 5.64 (s, 1H), 3.39 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 135.6, 133.4, 130.0, 129.8, 128.3, 126.8, 101.2, 54.0 ppm. MS (EI, m/z) $[M]^+$: 186.0; $[M+2]^+$: 188.0.

5.14. 1-Chloro-2-(diethoxymethyl)benzene (2gb) [24]

203.1, mg, 94.6%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (d, J = 7.2 Hz, 1H), 7.386 (d, J = 7.2 Hz, 1H), 7.30–7.23 (m, 2H), 5.74 (s, 1H), 3.72–3.35 (m, 4H), 1.25 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.7, 133.4, 129.8, 129.7, 128.2, 126.8, 99.5, 62.6, 15.4 ppm. MS (EI, m/z) $[M]^+$: 214.0; $[M+2]^+$: 216.0.

5.15. 1-Bromo-4-(dimethoxymethyl)benzene (2ha) [11a]

231.0 mg, quant. yield (91.7% after column); Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 5.36 (s, 1H), 3.31 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.4, 131.6, 128.8, 122.7, 102.5, 52.7 ppm. MS (EI, m/z) $[M]^+$: 229.9; $[M+2]^+$: 231.9.

5.16. 1-Bromo-4-(diethoxymethyl)benzene (2 hb) [11a]

253.4 mg, 97.8%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 5.46 (s, 1H), 3.63–3.49 (m, 4H), 1.22 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.4, 131.5, 128.7, 122.5, 101.0, 61.2, 15.4 ppm. MS (EI, m/z) $[M]^+$: 258.0; $[M+2]^+$: 260.0.

5.17. 1-Bromo-3-(dimethoxymethyl)benzene (2ia) [15a]

231.0 mg, quant. yield; Pale yellow liquid. ^{1}H NMR (400 MHz,

$CDCl_3$) δ = 7.62 (s, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 7.6 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 5.36 (s, 1H), 3.31 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.9, 131.0, 129.4, 129.3, 124.9, 121.9, 101.6, 52.2 ppm. MS (EI, m/z) $[M]^+$: 229.9; $[M+2]^+$: 231.9.

5.18. *1-Bromo-3-(diethoxymethyl)benzene (2ib)* [21]

248.8 mg, 96.0%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (s, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 7.2 Hz, 1H), 7.23 (t, J = 8.0 Hz, 1H), 5.47 (s, 1H), 3.64–3.49 (m, 4H), 1.24 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.7, 131.5, 130.1, 130.0, 125.6, 122.6, 100.7, 61.3, 15.4 ppm.

5.19. *5-(Dimethoxymethyl)-2-ethoxyphenol (2ja)* [25a]

198.7 mg, 93.6%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.02 (s, 1H), 6.90 (d, J = 8.4 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 5.82 (s, 1H), 5.30 (s, 1H), 4.11 (q, J = 6.8 Hz, 2H), 2.76 (s, 3H), 3.30 (s, 6H), 1.43 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.2, 145.8, 131.5, 118.6, 113.3, 111.4, 103.2, 64.7, 52.8, 15.1 ppm. MS (EI, m/z) $[M]^+$: 212.1.

5.20. *5-(Diethoxymethyl)-2-ethoxyphenol (2jb)* [25b]

220.6 mg, 91.8%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.05 (s, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 5.67 (s, 1H), 5.41 (s, 1H), 4.11 (q, J = 6.8 Hz, 2H), 2.76 (s, 3H), 1.45 (t, J = 7.2 Hz, 3H), 1.22 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.0, 145.8, 132.6, 118.6, 113.3, 111.4, 101.5, 64.7, 61.1, 15.4, 15.1 ppm. MS (EI, m/z) $[M]^+$: 240.1.

5.21. *2-(Dimethoxymethyl)furan (2ka)* [16a]

142.1 mg, quant. yield; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 (s, 1H), 6.42 (s, 1H), 6.37 (d, J = 1.6 Hz, 1H), 5.44 (s, 1H), 3.55 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.1, 142.7, 110.3, 108.7, 98.2, 63.1 ppm. MS (EI, m/z) $[M]^+$: 142.1.

5.22. *2-(Diethoxymethyl)furan (2 kb)* [16a]

170.2 mg, quant. yield; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 (s, 1H), 6.40 (d, J = 1.6 Hz, 1H), 6.35 (s, 1H), 5.53 (s, 1H), 3.65–3.56 (m, 4H), 1.23 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.1, 142.5, 110.3, 108.2, 96.6, 61.5, 15.4 ppm. MS (EI, m/z) $[M]^+$: 170.1.

5.23. *3-Bromo-4-(dimethoxymethyl)thiophene (2la)* [26a]

237.1 mg, quant. yield; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (s, 1H), 7.28 (s, 1H), 5.51 (s, 1H), 3.34 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.6, 125.2, 123.9, 109.9, 99.8, 63.1 ppm. MS (EI, m/z) $[M]^+$: 235.9; $[M+2]^+$: 237.9.

5.24. *3-Bromo-4-(diethoxymethyl)thiophene (2lb)* [26b]

265.1 mg, quant. yield; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (d, J = 4.4 Hz, 1H), 7.25 (d, J = 4.4 Hz, 1H), 5.51 (s, 1H), 3.64–3.56 (m, 4H), 1.24 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.8, 124.8, 123.8, 110.1, 98.3, 61.7, 15.4 ppm. MS (EI, m/z) $[M]^+$: 263.9; $[M+2]^+$: 265.9.

5.25. *3-Bromo-5-(dimethoxymethyl)pyridine (2ma)* [27]

220.3 mg, 95.0% (93.0% after column); Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.62 (d, J = 2.4 Hz, 1H), 8.57 (d, J = 1.8 Hz, 1H), 7.92 (t, J = 1.8 Hz, 1H), 5.42 (s, 1H), 3.32 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.8, 146.7, 137.2, 134.4, 120.6, 100.2, 52.7 ppm. MS (EI, m/z) $[M]^+$: 230.9; $[M+2]^+$: 232.9.

5.26. *3-Bromo-5-(diethoxymethyl)pyridine (2 mb)*

209.0 mg, 90.1% (87.0% after column); Pale yellow liquid. ^{1}H NMR (600 MHz, DMSO-d_6) δ = 8.69 (d, J = 2.4 Hz, 1H), 8.58 (d, J = 1.8 Hz, 1H), 7.92 (t, J = 1.8 Hz, 1H), 5.60 (s, 1H), 3.60–3.43 (m, 4H), 1.17 (t, J = 7.2 Hz 6H) ppm; ^{13}C NMR (151 MHz, DMSO-d_6) δ = 150.6, 146.9, 137.3, 137.0, 120.5, 99.0, 61.9, 15.5 ppm. MS (EI, m/z) $[M]^+$: 230.9; $[M+2]^+$: 232.9.

5.27. *2-Bromo-5-(dimethoxymethyl)pyridine (2na)* [28a]

232.0 mg, quant. Yield (96.0% after column); Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.42 (s, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 5.41 (s, 1H), 3.31 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.3, 142.4, 137.5, 133.3, 127.9, 100.7, 52.8 ppm. MS (EI, m/z) $[M]^+$: 230.9; $[M+2]^+$: 232.9.

5.28. *2-Bromo-5-(diethoxymethyl)pyridine (2 nb)* [28b]

260.1 mg, quant. yield; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.43 (s, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 5.51 (s, 1H), 3.63–3.49 (m, 4H), 1.22 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.2, 142.2, 137.4, 134.3, 127.9, 99.3, 61.4, 15.3 ppm. MS (EI, m/z) $[M]^+$: 259.0; $[M+2]^+$: 261.0.

5.28.1. *5-(Dimethoxymethyl)-2-methoxypyridine (2oa)* [29]

181.4 mg, 99.0%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (s, 1H), 7.63 (d, J = 8.4 Hz, 1H), 6,72 (d, J = 8.8 Hz, 1H), 5.35 (s, 1H), 3.91 (s, 3H), 3.29 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.6, 145.8, 137.4, 126.8, 110.6, 101.6, 53.5, 52.6 ppm. MS (EI, m/z) $[M]^+$: 183.0.

5.29. *5-(Diethoxymethyl)-2-methoxypyridine (2ob)* [29]

200.7 mg, 95.0%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.22 (s, 1H), 7.68 (d, J = 8.4 Hz, 1H), 6,74 (d, J = 8.0 Hz, 1H), 5.48 (s, 1H), 3.93 (s, 3H), 3.63–3.58 (m, 2H), 3.56–3.48 (m, 2H), 1.22 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.6, 145.7, 137.4, 127.8, 110.7, 100.2, 61.2, 53.6, 15.3 ppm. MS (EI, m/z) $[M]^+$: 211.1.

5.30. *2-Chloro-3-(dimethoxymethyl)-8-methylquinoline (2pa)*

228.0 mg, 90.6%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.36 (s, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 6.8 Hz, 1H), 7.45 (t, J = 7.2 Hz, 1H), 5.73 (s, 1H), 3.43 (s, 6H), 2.77 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.5, 146.9, 137.7, 136.6, 131.1, 129.1, 127.2, 127.0, 126.2, 100.7, 54.0, 18.0 ppm. MS (EI, m/z) $[M]^+$: 251.0; $[M+2]^+$: 253.0.

5.31. *2-Chloro-3-(diethoxymethyl)-8-methylquinoline (2 pb)*

232.2 mg, 83.0%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.39 (s, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 7.2 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 5.82 (s, 1H), 3.76–3.62 (m, 4H), 2.76 (s, 3H), 1.28 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.6, 146.9, 137.4, 136.6, 130.9, 130.3, 127.2, 127.1, 126.2, 99.3, 62.9, 18.0, 15.4 ppm. MS (EI, m/z) $[M]^+$: 279.1; $[M+2]^+$: 281.1.

5.32. ***(3,3-Dimethoxypropyl)benzene (2qa)*** *[11a]*

180.2 mg, quant. yield; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 (t, J = 6.8 Hz, 2H), 7.22–7.18 (m, 3H), 4.38 (t, J = 6.0 Hz, 1H), 3.35 (s, 6H), 2.69 (t, J = 8.0 Hz, 2H), 1.97–1.91 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.9, 128.6, 126.1, 104.0, 52.9, 34.4, 31.1 ppm. MS (EI, m/z) $[M]^+$: 180.1.

5.33. ***(3,3-Diethoxypropyl)benzene (2qb)*** *[24]*

208.3 mg, quant. yield; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 (t, J = 7.2 Hz, 2H), 7.22–7.17 (m, 3H), 4.50 (t, J = 5.6 Hz, 1H), 3.70–3.63 (m, 2H), 3.55–3.47 (m, 2H), 2.70 (t, J = 7.6 Hz, 2H), 1.98–1.93 (m, 2H), 1.24 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 142.0, 128.6, 128.5, 126.0, 102.4, 61.3, 35.4, 31.1, 15.6 ppm. MS (EI, m/z) $[M]^+$: 208.1.

5.34. ***1,1-Dimethoxyheptane (2ra)*** *[30]*

160.2 mg, quant. yield; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.35 (t, J = 6.0 Hz, 1H), 3.30 (s, 6H), 1.61–1.56 (m, 2H), 1.28 (br, 8H), 0.87 (t, J = 6.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 104.8, 52.7, 32.7, 32.0, 29.3, 24.8, 22.8, 14.2 ppm. MS (EI, m/z) $[M]^+$: 160.1.

5.35. ***1,1-Diethoxyheptane (2rb)*** *[30]*

188.3 mg, quant. yield; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.48 (t, J = 5.6 Hz, 1H), 3.67–3.60 (m, 2H), 3.53–3.45 (m, 2H), 1.63–1.58 (m, 2H), 1.28 (br, 8H), 1.20 (t, J = 7.2 Hz, 6H), 0.88 (t, J = 6.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 103.2, 61.0, 33.8, 32.0, 29.4, 24.9, 22.8, 15.6, 14.3 ppm. MS (EI, m/z) $[M]^+$: 188.1.

5.36. ***1,1-Dimethoxyundecane (2sa)*** *[31a]*

211.9 mg, quant. yield (98.0% after column); Colorless liquid. ^{1}H NMR (600 MHz, DMSO-d_6) δ = 4.32 (t, J = 6.0 Hz, 1H), 3.20 (s, 6H), 1.49 (q, J = 6.0 Hz, 2H), 1.25 (br, 16H), 0.87 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (151 MHz, DMSO-d_6) δ = 104.4, 52.8, 32.5, 31.8, 29.4, 29.3, 29.2, 24.5, 22.6, 14.4 ppm. MS (EI, m/z) $[M]^+$: 216.2.

5.37. ***1,1-Diethoxyundecane (2sb)*** *[31b]*

236.9 mg, quant. yield (97.0% after column); Colorless liquid. ^{1}H NMR (600 MHz, DMSO-d_6) δ = 4.32 (t, J = 6.0 Hz, 1H), 3.57–3.51 (m, 2H), 3.43–3.38 (m, 2H), 1.48 (q, J = 6.0 Hz, 2H), 1.25 (br, 16H), 1.10 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (151 MHz, DMSO-d_6) δ = 102.6, 60.8, 33.7, 31.8, 29.4, 29.3, 29.2, 24.9, 22.6, 15.8, 14.4 ppm. MS (EI, m/z) $[M]^+$: 244.2.

5.38. ***11,11-Dimethoxyundec-1-ene (2ta)*** *[32a]*

Yield: 209.0 mg, quant. yield (97.6% after column); Colorless liquid. ^{1}H NMR (600 MHz, DMSO-d_6) δ = 5.83–5.76 (m, 1H), 5.01 (ddd, J = 16.8, 3.6, 1.8 Hz, 1H), 4.95 (ddt, J = 10.2, 1.8, 1.2 Hz, 1H), 4.32 (t, J = 6.0 Hz, 1H), 2.02 (q, J = 7.2 Hz, 2H), 1.49 (q, J = 5.4 Hz, 2H), 1.38–1.32 (m, 2H), 1.25 (br, 10H) ppm; ^{13}C NMR (151 MHz, DMSO-d_6) δ = 139.3, 115.1, 104.4, 52.7, 33.7, 32.5, 29.4, 29.3, 29.2, 28.9, 28.7, 24.5 ppm. MS (EI, m/z) $[M]^+$: 214.1.

5.39. ***11,11-Diethoxyundec-1-ene (2tb)*** *[32b]*

232.8 mg, quant. yield (96.1% after column); Colorless liquid. ^{1}H NMR (600 MHz, DMSO-d_6) δ = 5.83–5.76 (m, 1H), 5.01 (ddd, J = 17.4, 3.0, 1.8 Hz, 1H), 4.95 (ddt, J = 10.2, 1.8, 1.2 Hz, 1H), 4.43 (t, J = 5.4 Hz, 1H), 3.57–3.52 (m, 2H), 3.43–3.38 (m, 2H), 2.02 (q, J = 7.2 Hz, 2H), 1.48 (q, J = 6.6 Hz, 2H), 1.38–1.32 (m, 2H), 1.25 (br, 10H), 1.10 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (151 MHz, DMSO-d_6) δ = 139.3, 115.1, 102.6, 60.8, 33.7, 33.6, 29.4, 29.3, 29.2, 28.9, 28.7, 24.7, 15.8 ppm. MS (EI, m/z) $[M]^+$: 242.2.

5.40. ***1-(Dimethoxymethyl)naphthalene (2ua)*** *[33a]*

200.1 mg, 99.0% (93.0% after column); Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.32 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 7.2 Hz, 1H), 7.57–7.47 (m, 3H), 5.95 (s, 1H), 3.43 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 134.1, 133.4, 131.1, 129.5, 128.8, 126.5, 125.9, 125.3, 125.1, 124.5, 102.6, 53.4 ppm. MS (EI, m/z) $[M]^+$: 202.0.

5.41. ***1-(Diethoxymethyl)naphthalene (2ub)*** *[33b]*

195.6 mg, 85.0%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.34 (d, J = 8.0 Hz, 1H), 7.88 (dd, J = 9.2, 8.0 Hz, 2H), 7.77 (d, J = 7.6 Hz, 1H), 7.55–7.45 (m, 3H), 6.05 (s, 1H), 3.69–3.61 (m, 4H), 1.25 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 134.4, 134.2, 131.2, 129.4, 128.8, 126.3, 125.9, 125.2, 125.0, 124.7, 100.9, 61.7, 15.6 ppm. MS (EI, m/z) $[M]^+$: 230.1.

5.42. ***tert-Butyl(3-(dimethoxymethyl)phenoxy)dimethylsilane (2va)*** *[34]*

276.6 mg, 98.0% (95.1% after column); Colorless liquid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.25 (t, J = 7.8 Hz, 1H), 6.98 (d, J = 7.2 Hz, 1H), 6.84 (t, J = 1.8 Hz, 1H), 6.82–6.80 (m, 1H), 5.33 (s, 1H), 3.32 (s, 6H), 0.94 (s, 9H), 0.17 (s, 6H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ = 155.4, 140.3, 129.8, 120.2, 118.4, 102.6, 52.8, 26.0, 18.4, 4.1 ppm. MS (EI, m/z) $[M]^+$: 282.2.

5.43. tert-Butyl(3-(diethoxymethyl)phenoxy)dimethylsilane (2vb)

302.7 mg, 97.5%; Colorless liquid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.24 (t, J = 7.8 Hz, 1H), 6.99 (d, J = 7.2 Hz, 1H), 6.85 (t, J = 1.8 Hz, 1H), 6.81–6.78 (m, 1H), 5.43 (s, 1H), 3.54–3.43 (m, 4H), 1.13 (t, J = 6.6 Hz, 6H), 0.94 (s, 9H), 0.17 (s, 6H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ = 155.4, 141.4, 129.7, 120.1, 120.0, 118.2, 100.9, 61.1, 26.0, 18.4, 15.6, 4.1 ppm. MS (EI, m/z) $[M]^+$: 310.2.

5.44. (3-(Dimethoxymethyl)phenoxy)triisopropylsilane (2wa)

311.5 mg, 96.0% (93.0% after column); Colorless liquid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.26 (t, J = 7.8 Hz, 1H), 6.96 (d, J = 7.2 Hz, 1H), 6.88 (t, J = 1.8 Hz, 1H), 6.84 (dd, J = 2.4, 7.8 Hz, 1H), 5.34 (s, 1H), 3.21 (s, 6H), 1.26–1.21 (m, 3H), 1.06 (d, J = 7.2 Hz, 18H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ = 155.7, 140.3, 129.8, 120.1, 119.9, 118.1, 102.6, 52.8, 26.0, 18.2, 12.5 ppm. MS (EI, m/z) $[M]^+$: 324.2.

5.44.1. ***9-(Dimethoxymethyl)anthracene (2xa)*** *[33a]*

247.7 mg, 98.2%; Colorless liquid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.75 (d, J = 9.0 Hz, 2H), 8.62 (s, 1H), 8.09 (d, J = 7.2 Hz, 2H), 7.56–7.50 (m, 4H), 6.65 (s, 1H), 3.47 (s, 6H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ = 130.9, 129.5, 129.2, 128.8, 128.6, 128.5, 125.3, 1250, 103.3, 55.6 ppm. MS (EI, m/z) $[M]^+$: 252.1.

5.45. ***1,1-Dimethoxycyclohexane (2aa)*** *[16a]*

144.2 mg, quant. yield; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.16 (s, 6H), 1.62 (t, J = 6.0 Hz, 4H), 1.51–1.47 (m, 4H), 1.40–1.36 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 100.2, 47.6, 32.9, 25.8, 23.1 ppm. MS (EI, m/z) $[M]^+$: 144.1.

5.46. ***1,1-Diethoxycyclohexane (2aab)*** *[16a]*

172.2 mg, quant. yield; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.47–3.42 (m, 4H), 1.69–1.60 (m, 4H), 1.52–1.43 (m, 4H), 1.42–1.30 (m, 2H), 1.17 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 100.2, 55.0, 34.0, 25.9, 23.2, 15.8 ppm. MS (EI, m/z) $[M]^+$: 172.1.

5.47. ***1-(1,1-Dimethoxyethyl)-4-fluorobenzene (2aba)*** *[35]*

182.4 mg, 99.0%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (dd, J = 7.6, 5.6 Hz, 2H), 7.03 (t, J = 8.8 Hz, 2H), 3.18 (s, 6H), 1.52 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.6 (d, $J_{C,F}$ = 244.4 Hz), 138.9, 128.3 (d, $J_{C,F}$ = 8.2 Hz), 115.1 (d, $J_{C,F}$ = 21.3 Hz), 101.5, 49.1, 26.3 ppm. MS (EI, m/z) $[M]^+$: 184.0.

5.48. ***1-(1,1-Diethoxyethyl)-4-fluorobenzene (2abb)*** *[35]*

203.3 mg, 94.0%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 (t, J = 8.8 Hz, 2H), 7.02 (t, J = 8.8 Hz, 2H), 3.54–3.31 (m, 4H), 1.54 (s, 3H), 1.21 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.6 (d, $J_{C,F}$ = 244.1 Hz), 139.9, 128.2 (d, $J_{C,F}$ = 8.1 Hz), 115.0 (d, $J_{C,F}$ = 21.1 Hz), 101.1, 56.8, 27.4, 15.5 ppm. MS (EI, m/z) $[M]^+$: 212.1.

5.49. 1-(1,1-Dimethoxyethyl)-2-fluorobenzene (2aca)

184.2 mg, quant. yield; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (t, J = 8.0 Hz, 1H), 7.30–7.26 (m, 1H), 7.12 (t, J = 7.6 Hz, 1H), 7.04 (dd, J = 11.6, 8.0 Hz, 1H), 3.20 (s, 6H), 1.65 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.2 (d, $J_{C,F}$ = 248.9 Hz), 129.9 (d, $J_{C,F}$ = 8.4 Hz), 129.5, 129.3 (d, $J_{C,F}$ = 10.2 Hz), 123.9, 116.4 (d, $J_{C,F}$ = 22.9 Hz), 100.1, 49.0, 23.9 ppm. MS (EI, m/z) $[M]^+$: 184.0.

5.50. 1-(1,1-Diethoxyethyl)-2-fluorobenzene (2acb)

210.1 mg, 99.0%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (t, J = 8.0 Hz, 1H), 7.29–7.24 (m, 1H), 7.11 (t, J = 7.2 Hz, 1H), 7.02 (dd, J = 11.6, 8.4 Hz, 1H), 3.54–3.33 (m, 4H), 1.67 (s, 3H), 1.22 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.3 (d, $J_{C,F}$ = 248.9 Hz), 130.3 (d, $J_{C,F}$ = 10.0 Hz), 129.7 (d, $J_{C,F}$ = 8.4 Hz), 129.4, 123.8, 116.3 (d, $J_{C,F}$ = 22.9 Hz), 99.5, 56.8, 24.9, 15.5 ppm. MS (EI, m/z) $[M]^+$: 212.1.

5.51. ***1-Bromo-4-(1,1-dimethoxyethyl)benzene (2ada)*** *[36a]*

243.9 mg, 99.5%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (d, J = 8.8 Hz, 2H), 7.38 (d, J = 8.8 Hz, 2H), 3.17 (s, 6H), 1.51 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 142.2, 131.4, 128.4, 121.9, 101.5, 49.2, 26.2 ppm. MS (EI, m/z) $[M]^+$: 244.0; $[M+2]^+$: 246.0.

5.52. ***1-Bromo-4-(1,1-diethoxyethyl)benzene (2adb)*** *[36b]*

259.5 mg, 95.0%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 3.51–3.30 (m, 4H), 1.53 (s, 3H), 1.21 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.2, 131.3, 128.3, 121.7, 101.1, 56.9, 27.3, 15.6 ppm. MS (EI, m/z) $[M]^+$: 272.0; $[M+2]^+$: 274.0.

5.53. (1,1-Dimethoxypentyl)benzene (2aea) [37a]

196.0 mg, 94.1%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (d, J = 8.8 Hz, 2H), 7.35 (t, J = 8.0 Hz, 2H), 7.30 (t, J = 7.2 Hz, 1H), 3.16 (s, 6H), 1.90 (t, J = 8.4 Hz, 2H), 1.21–1.15 (m, 2H), 0.99–0.93 (m, 2H), 0.79 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.3, 128.1, 127.7, 127.2, 103.9, 48.7, 37.2, 25.7, 22.9, 14.2 ppm. MS (EI, m/z) $[M\text{-}OCH_3]^+$: 177.1.

5.54. ***(1,1-Diethoxypentyl)benzene (2aeb)*** *[37b]*

221.5 mg, 93.7%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.28 (t, J = 7.2 Hz, 1H), 3.45–3.31 (m, 4H), 1.90 (t, J = 8.4 Hz, 2H), 1.20 (t, J = 7.2 Hz, 6H), 1.16–1.12 (m, 2H), 0.99–0.89 (m, 2H), 0.78 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 142.3, 127.9, 127.5, 127.0, 103.4, 56.3, 38.1, 25.7, 22.9, 15.5, 14.2 ppm. MS (EI, m/z) $[M\text{-}OCH_2CH_3]^+$: 191.1.

5.55. ***2-(1,1-Dimethoxyethyl)naphthalene (2afa)*** *[38a]*

210.0 mg, 97.1%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (s, 1H), 7.89–7.84 (m, 3H), 7.60 (d, J = 8.4 Hz, 1H), 7.50–7.48 (m, 2H), 3.26 (s, 6H), 1.64 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.6, 133.4, 133.2, 128.7, 128.2, 127.8, 126.3, 125.8, 124.6, 102.1, 49.4, 26.3 ppm. MS (EI, m/z) $[M]^+$: 216.1.

5.56. ***2-(1,1-Diethoxyethyl)naphthalene (2afb)*** *[38b]*

227.2 mg, 93.0%; Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (s, 1H), 7.89–7.84 (m, 3H), 7.64 (d, J = 8.4 Hz, 1H), 7.51–7.48 (m, 2H), 3.60–3.43 (m, 4H), 1.66 (s, 3H), 1.28 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.5, 133.4, 133.1, 128.7, 128.0, 127.8, 126.2, 125.5, 124.6, 101.6, 57.1, 27.4, 15.7 ppm. MS (EI, m/z) $[M]^+$: 244.1.

5.57. ***1-(1,1-Dimethoxyethyl)-4-methylbenzene (2aga)*** *[39]*

176.2 mg, 97.8%; Pale yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (d, J = 6.4 Hz, 2H), 7.18 (d, J = 7.2 Hz, 2H), 3.19 (s, 6H), 2.36 (s, 3H), 1.04 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.2, 137.4, 129.0, 126.4, 101.9, 49.1, 26.4, 21.3 ppm. MS (EI, m/z) $[M]^+$: 180.1.

5.58. Dimethoxydiphenylmethane (2 aha) [40a]

1050 mg, 96.0% (92.1% after column) White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.4 Hz, 4H), 7.21 (t, J = 7.5 Hz, 4H), 7.13 (t, J = 7.3 Hz, 2H), 3.05 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.37, 127.24, 126.94, 126.38, 125.84, 48.25 ppm. MS (EI, m/z) $[M]^+$: 228.1.

5.59. ***Diethoxydiphenylmethane(2ahb)*** *[40b]*

386 mg, 79.9% (75.4% after column); White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (dd, J = 8.2, 1.1 Hz, 4H), 7.24 (t, J = 7.7 Hz, 4H), 7.18–7.14 (m, 2H), 3.31 (q, J = 7.1 Hz, 4H), 1.19 (t, J = 7.1 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 143.35, 127.84, 127.19, 126.79, 57.04, 15.12 ppm. MS (EI, m/z) $[M]^+$: 256.1.

5.60. 2-(4-Nitrophenyl)-1,3-dioxolane (4aa) [23]

193.0 mg, 99.0%; Pale yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, J = 9.0 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 5.90 (s, 1H), 4.01–4.14 (m, 4H) ppm; ^{13}C NMR (151 MHz, DMSO-d_6) δ = 148.4, 145.7, 128.3, 123.9, 101.8, 65.5 ppm. MS (EI, m/z) $[M]^+$: 195.0.

5.61. ***2-(4-Nitrophenyl)-1,3-dioxane (4 ab)*** *[23]*

204.8 mg, 98.0%; Pale yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, J = 9.0 Hz, 2H), 7.65 (d, J = 9.0 Hz, 2H), 5.57 (s, 1H), 4.31–4.28 (m, 2H), 4.03 (td, J = 12.6, 2.4 Hz, 2H), 2.27–2.19 (m, 1H),

1.51–1.47 (m, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ = 148.1, 145.7, 127.2, 123.4, 99.9, 67.5, 25.6 ppm. MS (EI, *m*/*z*) $[M]^+$: 209.0.

5.62. 2-(2-Nitrophenyl)-1,3-dioxolane (4ba) [23]

191.7 mg, 98.3%; Pale yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 1.2, 7.8 Hz, 1H), 7.80 (dd, *J* = 1.2, 7.8 Hz, 1H), 7.62 (td, *J* = 7.8, 1.2 Hz, 1H), 7.50 (td, *J* = 7.8, 1.2 Hz, 1H), 6.48 (s, 1H), 4.08–4.04 (m, 2H), 4.03–4.00 (m, 2H) ppm; ^{13}C NMR (151 MHz, DMSO-d_6) δ = 149.0, 133.5, 132.7, 130.6, 127.9, 124.6, 99.2, 65.2 ppm. MS (EI, *m*/*z*) $[M]^+$: 195.0.

5.63. 2-(2-Nitrophenyl)-1,3-dioxane (4bb) [41]

203.8 mg, 97.5%; Pale yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.83 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.61 (td, *J* = 7.8, 1.2 Hz, 1H), 7.47 (td, *J* = 7.8, 1.2 Hz, 1H), 6.09 (s, 1H), 4.25–4.22 (m, 2H), 4.01 (td, *J* = 12.6, 2.4 Hz, 2H), 2.23–2.15 (m, 1H), 1.51–1.47 (m, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ = 148.3, 132.7, 132.6, 129.4, 127.7, 124.1, 97.1, 67.6, 25.6 ppm.

5.64. 3-Bromo-5-(1,3-dioxan-2-yl)pyridine (4 cb)

222.1 mg, 91.0%; Pale yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 (d, *J* = 2.4 Hz, 1H), 8.60 (d, *J* = 1.8 Hz, 1H), 7.98 (t, *J* = 1.8 Hz, 1H), 5.53 (s, 1H), 4.29–4.25 (m, 2H), 3.98 (td, *J* = 2.4, 12.0 Hz, 2H), 2.26–2.17 (m, 1H), 1.49–1.45 (m, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ = 150.9, 145.9, 136.7, 135.9, 120.6, 98.6, 67.4, 25.6 ppm. MS (EI, *m*/*z*) $[M]^+$: 242.9; $[M+2]^+$: 244.9.

5.65. 2-Bromo-5-(1,3-dioxolan-2-yl)pyridine (4da) [42a]

234.3 mg, 96.0%; Pale yellow liquid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.46 (d, *J* = 2.4 Hz, 1H), 7.80 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.49 (d, *J* = 7.71 Hz,1H), 5.84 (s, 1H), 4.08–4.04 (m, 2H), 4.00–3.96 (m, 2H) ppm; ^{13}C NMR (151 MHz, DMSO-d_6) δ = 148.8, 142.0, 137.8, 133.7, 128.0, 100.4, 65.0 ppm. MS (EI, *m*/*z*) $[M]^+$: 242.9; $[M+2]^+$: 244.9.

5.66. 2-Bromo-5-(1,3-dioxan-2-yl)pyridine (4 db) [42b]

213.9 mg, 93.0%; Pale yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (d, *J* = 2.4 Hz, 1H), 7.66 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 5.50 (s, 1H), 4.26–4.23 (m, 2H), 3.98 (td, *J* = 12.0, 2.4, Hz, 2H), 2.24–2.16 (m, 1H), 1.48–1.44 (m, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ = 148.4, 142.3, 136.5, 133.7, 127.7, 98.9, 67.4, 25.6 ppm. MS (EI, *m*/*z*) $[M]^+$: 228.9; $[M+2]^+$: 230.9.

5.67. 2-(3-Methoxyphenyl)-1,3-dioxane (4eb) [43]

184.7 mg, 95.2%; Pale yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 8.4 Hz, 1H), 7.06–7.05 (m, 2H), 6.89–6.87 (m, 1H), 5.48 (s, 1H), 4.28–4.25 (m, 2H), 3.99 (td, *J* = 12.0, 2.4 Hz, 2H), 3.82 (s, 3H), 2.27–2.19 (m, 1H), 1.47–1.43 (m, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.6, 140.2, 129.3, 118.4, 15.1, 110.9, 101.5, 67.4, 55.3, 25.8 ppm. MS (EI, *m*/*z*) $[M]^+$: 194.0.

5.68. 2-(4-Chlorophenyl)-1,3-dioxane (4 fb) [44]

186.1 mg, 94.0%; Pale yellow liquid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 5.47 (s, 1H), 4.27–4.24 (m, 2H), 3.98 (td, *J* = 12.6, 2.4 Hz, 2H), 2.25–2.17 (m, 1H), 1.47–1.43 (m, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ = 137.3, 134.6, 128.4, 127.5, 100.8, 67.4, 25.7 ppm. MS (EI, *m*/*z*) $[M]^+$: 198.0; $[M+2]^+$: 200.0.

5.69. 2-(4-Bromothiophen-3-yl)-1,3-dioxolane (4ga) [45]

221.0 mg, 94.0%; Pale yellow liquid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.73 (d, *J* = 3.6 Hz, 1H), 7.71 (d, *J* = 3.6 Hz, 1H), 5.79 (s, 1H), 4.06–4.03 (m, 2H), 3.96–3.93 (m, 2H) ppm; ^{13}C NMR (151 MHz, DMSO-d_6) δ = 137.4, 126.3, 125.3, 108.7, 99.0, 64.7 ppm. MS (EI, *m*/*z*) $[M]^+$: 198.0; $[M+2]^+$: 200.0.

5.70. 2-(4-Bromothiophen-3-yl)-1,3-dioxane (4gb)

241.6 mg, 97.0%; Pale yellow liquid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.67 (d, *J* = 3.6 Hz, 1H), 7.65 (d, *J* = 3.0 Hz, 1H), 5.46 (s, 1H), 4.14–4.10 (m, 2H), 3.94 (td, *J* = 3.0, 12.6 Hz, 2H), 2.03–1.95 (m, 1H), 1.45–1.41 (m, 1H) ppm; ^{13}C NMR (151 MHz, DMSO-d_6) δ = 138.0, 125.6, 124.5, 108.7, 97.2, 66.7, 25.2 ppm. MS (EI, *m*/*z*) $[M]^+$: 198.0; $[M+2]^+$: 200.0.

5.71. 2-Phenethyl-1,3-dioxane (4 hb) [46]

184.4 mg, 96.0%; Pale yellow liquid. ^{1}H NMR (600 MHz, DMSO-d_6) δ7.27 (d, *J* = 7.8 Hz, 2H), 7.19–7.16 (m, 3H), 4.50 (t, *J* = 4.8 Hz, 1H), 4.02–3.99 (m, 2H), 3.69 (td, *J* = 12.6, 2.4 Hz, 2H), 2.64–2.60 (m, 2H), 1.91–1.83 (m, 1H), 1.78–1.74 (m, 2H), 1.35–1.31 (m, 1H) ppm; ^{13}C NMR (151 MHz, DMSO-d_6) δ = 142.0, 128.8, 128.7, 126.2, 101.1, 66.5, 336.8, 30.0, 25.9 ppm. MS (EI, *m*/*z*) $[M]^+$: 192.1.

5.72. 2-(2-Chlorophenyl)-1,3-dioxane (4ib) [44]

188.1 mg, 95.0%; Pale yellow liquid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.62 (dd, *J* = 7.2, 2.4 Hz, 1H), δ 7.44 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.40–7.35 (m, 2H), 5.74 (s, 1H), 4.16 (dd, *J* = 11.4, 5.4 Hz, 2H), 3.98 (td, *J* = 12.0, 1.8 Hz, 2H), 2.06–1.98 (m, 1H), 1.46 (d, *J* = 13.8 Hz, 1H) ppm; ^{13}C NMR (151 MHz, DMSO-d_6) δ = 136.4, 132.1, 130.9, 129.6, 128.4, 127.6, 98.4, 67.3, 25.7 ppm. MS (EI, *m*/*z*) $[M]^+$: 198.0; $[M+2]^+$: 200.0.

5.73. 2-(Naphthalen-1-yl)-1,3-dioxane (4jb) [47]

188.1 mg, 94.0%; Pale yellow liquid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.27 (d, *J* = 8.4 Hz, 1H), 7.92 (t, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.56–7.47 (m, 3H), 6.07 (s, 1H), 4.22 (dd, *J* = 11.4, 4.8 Hz, 2H), 4.09 (t, *J* = 12.0 Hz, 2H), 2.17–2.08 (m, 1H), 1.52 (d, *J* = 13.8 Hz, 1H) ppm; ^{13}C NMR (151 MHz, DMSO-d_6) δ = 134.3, 133.3, 130.1, 129.0, 128.3, 125.9, 125.7, 125.0, 124.7, 124.0, 100.0, 68.9, 25.5 ppm. MS (EI, *m*/*z*) [$[M]^+$: 198.0.

5.74. 2-((4S,5S)-5-methyl-4-(prop-1-en-2-yl)-5-vinylcyclohex-1-en-1-yl)-1,3-dioxolane (9) [20]

105.5 mg, 90.0%; Pale yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.79 (dd, *J* = 16.8, 11.4 Hz, 1H), 4.90 (s, 1H), 4.87 (d, *J* = 6.0 Hz, 1H), 4.84 (t, *J* = 1.8 Hz, 1H), 4.62 (s, 1H), 3.98–3.96 (m, 2H), 3.90–3.88 (m, 2H), 1.98–1.90 (m, 2H), 1.84–1.81 (m, 2H), 1.71 (s, 3H), 1.64 (d, *J* = 13.8 Hz, 1H), 1.59–1.54 (m, 2H), 1.52 (dd, *J* = 13.8, 3.0 Hz, 1H), 1.10 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ = 149.9, 146.8, 112.7, 110.1, 108.7, 77.3, 77.0, 76.8, 64.6, 63.6, 52.2, 46.2, 41.2, 35.5, 27.6, 24.6, 17.8 ppm. MS (EI, *m*/*z*) $[M]^+$: 222.1.

5.75. (3aS,5aS)-6-hydroxy-3a,5a-dimethyltetradecahydrodicyclopenta[a,f]naphthalen-2(1H)-one (7) [48]

To a stirring solution of Dione **3** (274 mg, 1.0 mmol) in methanol (2 mL) was added in PVP-I (102 mg, 0.04 mmol effective iodine) and Trimethyl orthoformate (1.0 mmol, 0.12 mL). The mixture was

stirred for 90 min at 30 °C. Then, $NaBH_4$ (8.0 mmol, 300 mg) was added under ice-bath and the mixture was stirred for another 1 h at room temperature. The reaction was quenched with water (20 mL). The resulting solution was then extracted with EA (10 mL x 3) and washed with brine (20 mL). Drying of organic layer over Na_2SO_4 and then removal of solvent under reduced pressure afforded crude dimethoxy compound which was directly used in hydrolysis under HCl (1 N, 5 mL) in MeOH (5 mL) at room temperature for 1 h. Upon finish, the reaction was quenched with $NaHCO_3$ solid and the organic solvent was evaporated under vacuum. The resulting solution was extracted with EA (15 mL x 3) and washed with brine (20 mL). Drying of organic layer over Na_2SO_4 and then removal of solvent under reduced pressure afforded crude material which was then purified with flash column to afford the final products as semi-solid 222.9 mg, 80.7% over two steps.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.63 (t, J = 8.4 Hz, 1H), 2.07–2.00 (m, 2H), 2.18–2.10 (m, 2H), 1.89 (d, J = 16.8 Hz, 1H), 1.81–1.74 (m, 3H), 1.72–1.67 (m, 1H), 1.61–1.55 (m, 1H), 1.51–1.38 (m, 4H), 1.36–1.32 (m, 1H), 1.30–1.22 (m, 1H), 1.09 (td, J = 12.6, 3.6 Hz, 1H), 0.83 (s, 3H), 0.74 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) 218.9, 81.7, 54.2, 54.0, 50.7, 47.6, 43.3, 42.1, 41.2, 36.4, 35.6, 31.2, 30.3, 24.5, 23.4, 23.1, 13.7, 11.3 ppm. MS (EI, m/z) $[M]^+$: 276.2.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was financially supported by Science and Technology Commission of Shanghai Municipality (14DZ1900102) and the Fundamental Research Funds for the Central University (WY1113007).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.132250.

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