Synthesis F.-F. Pan et al. Special Topic

Synthesis of Dibenzyls by Nickel-Catalyzed Homocoupling of Benzyl Alcohols

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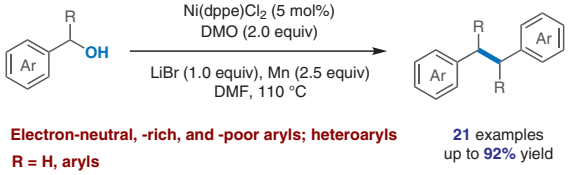

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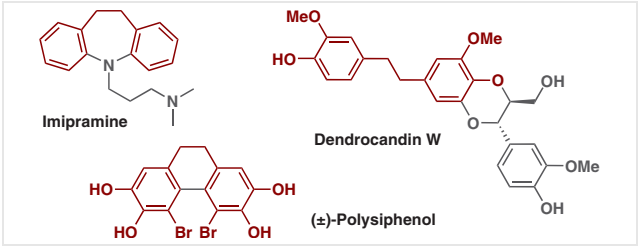
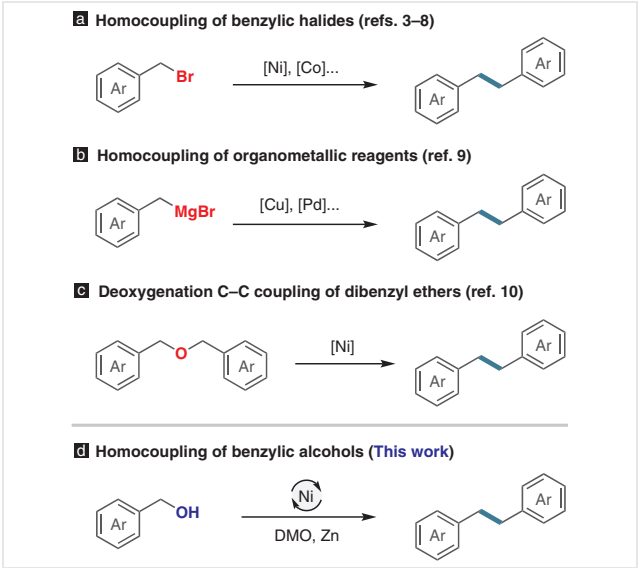
Abstract Dibenzyls are essential building blocks that are widely used in organic synthesis, and they are typically prepared by the homocoupling of halides, organometallics, and ethers. Herein, we report an approach to this class of compounds using alcohols, which are more stable and readily available. The reaction proceeds via nickel-catalyzed and dimethyl oxalate assisted dynamic kinetic homocoupling of benzyl alcohols. Both primary and secondary alcohols are tolerated.

Key words homocoupling, nickel, dibenzyls, alcohols, synthetic methodology

Dibenzyls are key structural motifs found in a wide range of biologically active natural products and pharmaceuticals, such as imipramine, (±)-polysiphenol, and dendrocandin W (Scheme 1).[1] They also serve as important building blocks for the synthesis of agrochemicals, dyes, and polymers.[2] In general, these compounds are synthesized through the homocoupling reactions of benzylic halides under reductive conditions (Scheme 2a).[3–8] The substrate scope has been extended from bromides to iodide and chloride, and a wide range of catalysts have proven to be effective, including nickel,[3] cobalt,[4] titanium,[5] copper,[6] iron,[7] and rhodium.[8] They were also be prepared through oxidative homocoupling reactions using organometallic species (e.g., R–M: M = Mg, Zn) as coupling partners (Scheme 2b).[9] Very recently, the synthesis of dibenzyls from C–O electrophiles was realized via deoxygenative dimerization of benzyl ethers (Scheme 2c).[10] Despite these promising advances, alternative strategies for producing dibenzyls using stable, readily available, and naturally occurring functional groups remains desirable.



Scheme 1 Dibenzyl moiety in biologically active molecules



Scheme 2 Formation of dibenzyl derivatives by homocoupling reactions

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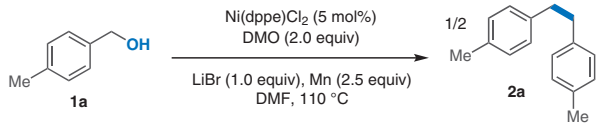
Alcohols are among the most accessible organic compounds and can be readily found in a wide range of biologically active molecules. The formation of the C–C bond from alcohols via coupling reactions catalyzed by transition metals is synthetically appealing.[11] Studies in this field have resulted in many useful methods, including the coupling between electrophiles.[12] In general, these reactions require preactivation of alcohols to better leaving groups, using highly reactive activators such as $(CF_3SO)_2O$, RSO_2Cl, and RCOCl. Such a requirement is costly and time-consuming, and it can constrain functional-group compatibility. New coupling technology for direct functionalization of alcohols could have a substantial effect on organic synthesis but remains largely undeveloped.[13–17] Very recently, we found that dimethyl oxalate (DMO) can undergo equilibrium reaction with alcohols, and the formed alkyl oxalates can participate in coupling reactions when generated.[18] Based on this finding, we established a nickel-catalyzed dynamic kinetic cross-electrophile coupling of benzyl alcohols and aryl halides. Herein, we demonstrate a nickel-catalyzed homocoupling of benzyl alcohols by this dynamic kinetic strategy, which offers convenient access to dibenzyls (Scheme 2d).

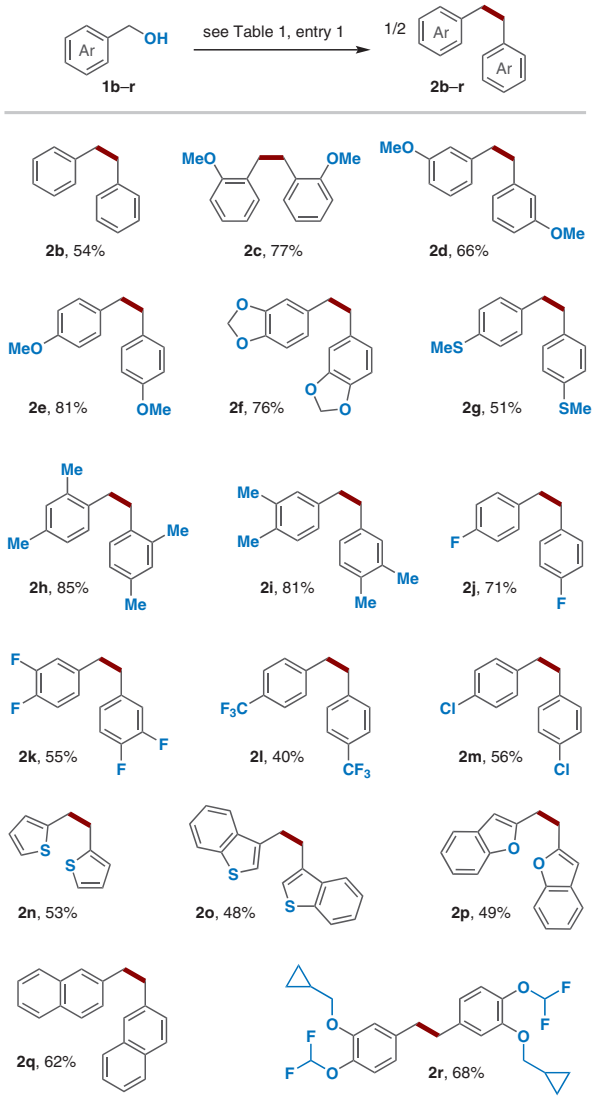
Table 1 Screening of Reaction Conditions[a]



Entry	Variation from standard conditions	Yield of **2a** (%)[b]
1	None	81 (78)[c]
2	$Ni(dppp)Cl_2$ instead of $Ni(dppe)Cl_2$	79
3	$Ni(dppf)Cl_2$ instead of $Ni(dppe)Cl_2$	61
4	$Ni(PPh_3)_2Cl_2$ instead of $Ni(dppe)Cl_2$	48
5	$NiCl_2$ instead of $Ni(dppe)Cl_2$	69
6	$Ni(COD)_2$ instead of $Ni(dppe)Cl_2$	73
7	no LiBr	58
8	LiI instead of LiBr	79
9	$MgBr_2$ instead of LiBr	75
10	$CaBr_2$ instead of LiBr	73
11	reaction at 30 °C	0
12	Zn instead of Mn	35
13	no Ni	18
14	no Mn or DMO	0

[a] Reaction conditions: **1a** (0.2 mmol), $Ni(dppe)Cl_2$ (5 mol%), LiBr (1.0 equiv), DMO (2.0 equiv), and Mn (2.5 equiv) in DMF (0.7 mL) at 110 °C for 16 h.
[b] Yields were determined by GC analysis with dodecane as internal standard.
[c] Isolated yield.

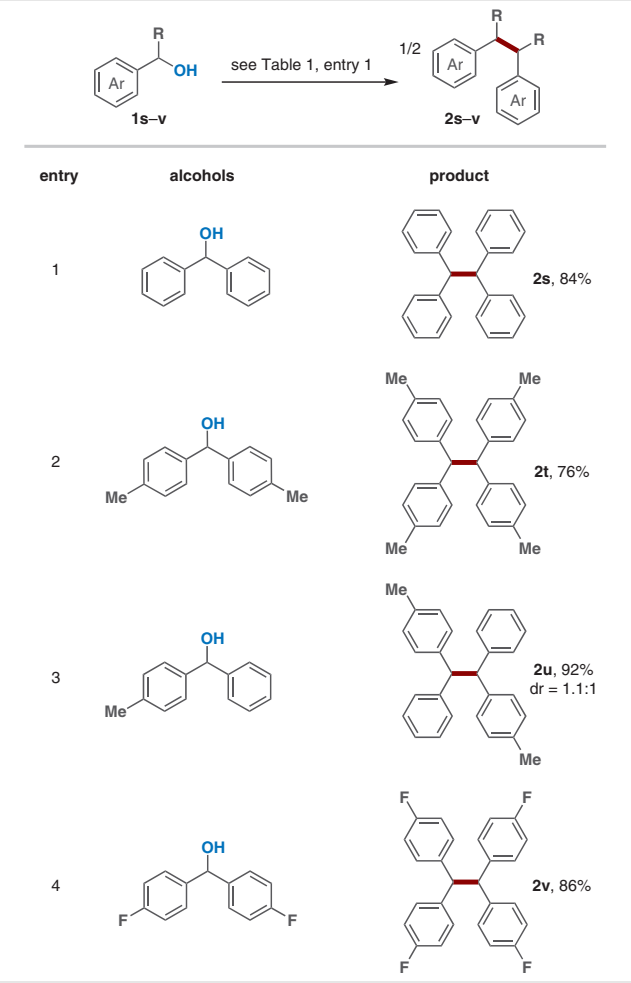
We started our investigation by studying the reaction of alcohol **1a**. After numerous trials, we determined that the combination of $Ni(dppe)Cl_2$ (5 mol%), LiBr (1.0 equiv), DMO (2.0 equiv), and Mn (2.5 equiv) in DMF (0.7 mL) at 110 °C gave the best result; the reaction afforded **2a** in 78% isolated yield (Table 1, entry 1). A comparable result was obtained when $Ni(dppp)Cl_2$ was used, whereas the reactions with $Ni(dppf)Cl_2$ or $Ni(PPh_3)_2Cl_2$ resulted in lower yields (entries 2–4). The reactions also worked well when either $NiCl_2$ or $Ni(COD)_2$ was used in the absence of a ligand, affording **2a** in 69% and 73% yields, respectively (entries 5 and 6). Although the role of halide additives remains to be disclosed, they play an essential role in this reaction; the use of LiBr (1.0 equiv) improved the yield from 58% to 81%, and similar



Scheme 3 Scope of reactions with primary benzyl alcohols. Reaction conditions as shown in Table 1, entry 1, but alcohol **1** (0.4 mmol) was used; isolated yields are given.

improvement was also observed when LiI, $MgBr_2$, and $CaBr_2$ were employed (entries 7–10).[19] Reaction at 30 °C did not yield any desired product, probably because the transesterification between alcohol and DMO to form active benzylic oxalate did not proceed at this temperature (entry 11).[18] A low yield was obtained when Zn was used instead of Mn (entry 12). In the absence of a nickel catalyst, the reactions afforded **2a** in a low yield of 18% (entry 13). No reaction was observed when the reaction was conducted in the absence of Mn or DMO (entry 14).

With the optimized conditions in hand, we studied the scope of the reaction for primary benzylic alcohols (Scheme 3). While electron-rich, -neutral, and -poor benzyl alcohols all worked well to afford **2b–m** in moderate to high yields, the electron-rich substrates generally gave better results (**2e** vs. **2b**, **2l**, **2m**; **2i** vs. **2k**). A substituent at the *ortho*-, *meta*- or *para*-position was tolerated (**2c–e** and **2h–i**). Aryl chloride was reported to couple with benzyl alcohols, and it

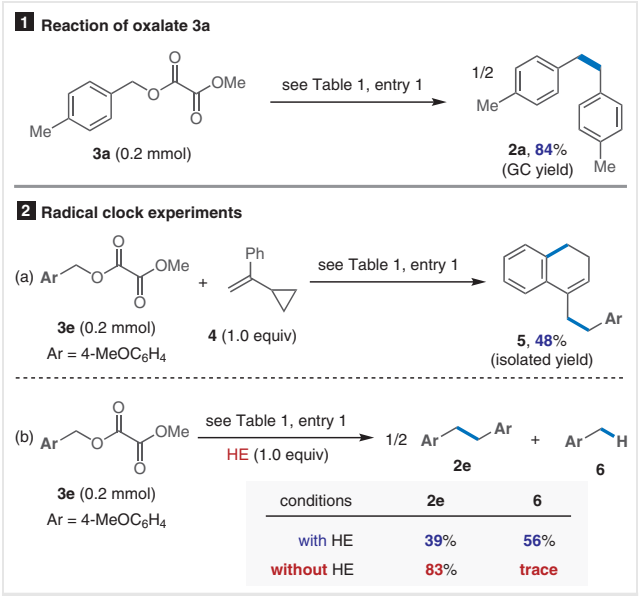


Scheme 4 Scope of reactions with secondary benzyl alcohols. Reaction conditions as shown in Table 1, entry 1, but alcohol **1** (0.4 mmol) was used; isolated yields are given.

was tolerated here (**2m**).[18] The reactions of heterobenzylic alcohols afforded product **2n–p** in moderate yields. The dimerization of polyarene substrate and the complex molecule is also feasible, and they afforded **2q** and **2r** in 62% and 68% yield, respectively.

The substrate scope of secondary benzyl alcohols is shown in Scheme 4. Diaryl substituted substrates coupled efficiently under our conditions, affording tetraaryl products **2s–v** in high yields. Both symmetric and asymmetric alcohols were tolerated (entries 2 and 3). The electron effect of the aryl group is not apparent; comparable results were obtained for both electron-rich and -poor substrates (entries 2–4).

In the absence of DMO, the reaction of alcohol **1a** did not afford any desired product, and alcohol **1a** was recovered quantitatively (Table 1, entry 14). Our previous studies reveal that transesterification between alcohol and DMO proceeded smoothly in the presence of either Ni(0) or Mn.[18] Moreover, without DMO, the reaction of preformed oxalate **3a** afforded **2a** in 84% GC yield under the standard conditions (Scheme 5, part 1). These results suggest that the homocoupling of alcohols may proceed through the intermediacy of benzyl oxalates.

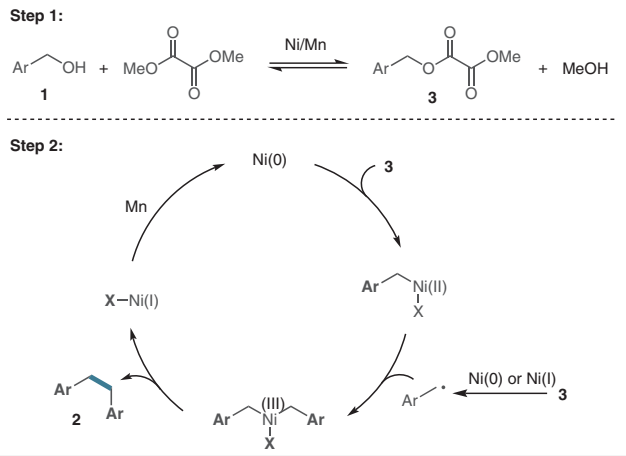


Scheme 5 Mechanistic investigation. Reaction conditions as shown in Table 1, entry 1, but DMO was not used; GC yield is given; HE: Hantzsch ester.

To determine whether benzyl oxalates were activated via radical process under the current conditions, several radical clock experiments were investigated. (1) The reaction of **3e** with α-cyclopropylstyrene **4** afforded ring-expanded product **5** in 48% yield (Scheme 5, part 2a).[21] (2) Hantzsch ester (HE) has been widely used as a hydrogen atom donor capable of trapping carbon radicals.[22] In the presence of HE, the formation of dimer **2e** was inhibited,

whereas a significant increase of benzyl–H was observed (Scheme 5, part 2b). These results suggest that the activation of benzyl oxalates might involve a radical process.

The catalytic cycle for this reaction is shown in Scheme 6, which is proposed based on our previous finding[18] and on reported work. Step 1: Transesterification of benzyl alcohols and DMO to form benzylic oxalates, which are highly reactive towards low-valent metals.[12e,f] Step 2: Reaction of oxalates with Ni(0) affords benzyl–Ni(II)–X species, which undergoes radical trapping and reductive elimination processes to afford dimer **2**.[20] Benzyl radicals can be generated either by Ni(0) or Ni(I) species.[18] Alternatively, dimerization of benzyl radicals may also result in the desired products.



Scheme 6 Proposed mechanism

In conclusion, we have reported a nickel-catalyzed deoxygenative dimerization reaction of benzyl alcohols and thereby established a new method for the synthesis of dibenzyls. The reaction proceeds with broad substrate scope of benzyl alcohols, with heteroaryl substrates and complex molecules included. Both primary and secondary alcohols were tolerated.

All reactions were carried out under an atmosphere of argon in a sealed tube with magnetic stirring. Nickel catalysts, reductants, and other chemicals are commercially available and were used as received. ^{1}H and ^{13}C NMR spectra were collected with Bruker AVANCE III 400 MHz, JEOL JNM-ECS 400M, and Agilent-NMR-inova 600 MHz spectrometers at room temperature. ^{1}H NMR spectra are reported in parts per million (ppm) downfield of tetramethylsilane (TMS) and referenced to the signal of TMS (0.00 ppm). ^{13}C NMR spectra are reported in ppm relative to residual $CHCl_3$ (77.16 ppm). Coupling constants, *J*, are reported in hertz (Hz). ^{19}F NMR spectra were collected with a Bruker AVANCE III 400 MHz spectrometer and an Agilent-NMR-inova 600 MHz spectrometer at room temperature. IR spectra were collected with a Bruker-TENSOR 27 spectrometer and Agilent Technologies Cary 630 FTIR; peaks are given on the cm^{-1} scale, and only major peaks are reported. HRMS was performed with a Bruker Apex II FT-ICR mass instrument (ESI) and waters GCT Premier TOFMS (EI). GC analysis was performed with Thermo Scientific TRACE 1300. GC-MS data were collected with a Thermo Scientific TRACE DSQ GC-MS. Thin-layer chromatography was carried out using XINNUO SGF254 TLC plates. Flash chromatography was performed using XINNUO silica gel (200–300 mesh).

Synthesis of 2a; Typical Procedure

The procedure was conducted in an argon-filled glove box. A reaction tube equipped with a magnetic stir bar was charged with Ni(dppe)Cl_2 (10.6 mg, 0.02 mmol), Mn (44.0 mg, 0.8 mmol), alcohol **1a** (48.8 mg, 0.4 mmol), DMO (94.5 mg, 0.8 mmol), LiBr (34.7 mg, 0.4 mmol), and DMF (1.5 mL). The reaction tube was then sealed and removed from the glove box. The reaction mixture was stirred at 110 °C for 16 h. After cooling to r.t., the mixture was diluted with EtOAc (40 mL) and washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated in vacuum. The residue was purified by flash chromatography on silica gel to afford the desired product **2a**.

1,2-Di-*p*-tolylethane (2a, known)[23]

Yield: 38.2 mg (78%); white solid; mp: 79–80 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (s, 8 H), 2.85 (s, 4 H), 2.31 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.0, 135.4, 129.1, 128.4, 37.8, 21.2.

IR (neat): 2920, 2857, 1515, 1454, 813, 716 cm^{-1}.

1,2-Diphenylethane (2b, known)[23]

Yield: 19.7 mg (54%); white solid; mp: 43–45 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.24 (m, 4 H), 7.21–7.18 (m, 6 H), 2.92 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.9, 128.6, 128.5, 126.1, 38.1.

IR (neat): 3029, 2922, 2855, 1601, 1493, 1452, 1064, 1027, 751, 699 cm^{-1}.

1,2-Bis(2-methoxyphenyl)ethane (2c, known)[23]

Yield: 37.3 mg (77%); white solid; mp: 76–78 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17 (dt, *J* = 7.8 Hz, *J* = 1.7 Hz, 2 H), 7.12 (dd, *J* = 7.3 Hz, *J* = 1.6 Hz, 2 H), 6.89–6.82 (m, 4 H), 3.81 (s, 6 H), 2.89 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.7, 131.0, 129.9, 127.1, 120.4, 110.3, 55.4, 30.6.

IR (neat): 2963, 2933, 1599, 1493, 1465, 1245, 1180, 1096, 1047, 1031, 753 cm^{-1}.

1,2-Bis(3-methoxyphenyl)ethane (2d, known)[23]

Yield: 32.0 mg (66%); white solid; mp: 47–49 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (t, *J* = 7.7 Hz, 2 H), 6.79 (d, *J* = 7.5 Hz, 2 H), 6.77–6.72 (m, 4 H), 3.78 (s, 6 H), 2.89 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 143.5, 129.4, 121.0, 114.3, 111.4, 55.2, 38.0.

IR (neat): 2926, 1601, 1586, 1489, 1454, 1260, 1152, 1044, 779, 695 cm^{-1}.

1,2-Bis(4-methoxyphenyl)ethane (2e, known)[23]

Yield: 39.3 mg (81%); white solid; mp: 138–140 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (d, *J* = 8.4 Hz, 4 H), 6.82 (d, *J* = 8.4 Hz, 4 H), 3.78 (s, 6 H), 2.82 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 134.1, 129.5, 113.8, 55.4, 37.4.

IR (neat): 2965, 2920, 2855, 1612, 1511, 1456, 1441, 1305, 1247, 1176, 1094, 1031, 833, 725 cm^{-1}.

1,2-Bis(benzo[d][1,3]dioxol-5-yl)ethane (2f, known)[23]

Yield: 41.1 mg (76%); white solid; mp: 149–151 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.72 (d, *J* = 8.0 Hz, 2 H), 6.66 (d, *J* = 1.2 Hz, 2 H), 6.60 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 2 H), 5.92 (s, 4 H), 2.78 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.6, 145.7, 135.5, 121.3, 109.0, 108.2, 100.9, 38.0.

IR (neat): 2947, 2928, 1500, 1487, 1441, 1247, 1036, 936, 919, 874, 814 cm^{-1}.

1,2-Bis(4-(methylthio)phenyl)ethane (2g, known)[24]

Yield: 28.0 mg (51%); white solid; mp: 129–131 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.18 (d, *J* = 8.2 Hz, 4 H), 7.08 (d, *J* = 8.2 Hz, 4 H), 2.85 (s, 4 H), 2.46 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.8, 135.6, 129.1, 127.2, 37.4, 16.4.

IR (neat): 2922, 2851, 1495, 1435, 1090, 1016, 813 cm^{-1}.

1,2-Bis(2,4-dimethylphenyl)ethane (2h)

Yield: 40.5 mg (85%); white solid; mp: 64–66 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.07 (d, *J* = 7.6 Hz, 2 H), 7.01–6.96 (m, 4 H), 2.78 (s, 4 H), 2.30 (s, 6 H), 2.29 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.4, 135.8, 135.6, 131.1, 128.9, 126.8, 34.1, 21.1, 19.4.

IR (neat): 3008, 2943, 2878, 1504, 1463, 1154, 1038, 882, 814 cm^{-1}.

GC-MS (EI): *m*/*z* (%) = 238.11 (14.20) $[M]^+$.

1,2-Bis(3,4-dimethylphenyl)ethane (2i, known)[25]

Yield: 38.6 mg (81%); white solid; mp: 92–94 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.06 (d, *J* = 7.6 Hz, 2 H), 7.01 (s, 2 H), 6.96 (d, *J* = 7.6 Hz, 2 H), 2.82 (s, 4 H), 2.25 (s, 6 H), 2.23 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.7, 136.6, 134.1, 129.9, 129.7, 125.8, 38.0, 19.9, 19.5.

IR (neat): 2941, 2857, 1452, 1021, 891, 818, 716 cm^{-1}.

1,2-Bis(4-fluorophenyl)ethane (2j, known)[23]

Yield: 31.0 mg (71%); white solid; mp: 88–90 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.08–7.05 (m, 4 H), 6.97–6.92 (m, 4 H), 2.85 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.5 (d, J_{C-F} = 244.5 Hz), 137.1 (d, J_{C-F} = 3.2 Hz), 130.0 (d, J_{C-F} = 7.7 Hz), 115.2 (d, J_{C-F} = 21.2 Hz), 37.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –117.5.

IR (neat): 2930, 1601, 1510, 1221, 1087, 835.

1,2-Bis(3,4-difluorophenyl)ethane (2k)

Yield: 27.9 mg (55%); white solid; mp: 37–39 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.05 (dt, *J* = 10.3, 8.4 Hz, 2 H), 6.93 (ddd, *J* = 11.3, 7.6, 2.2 Hz, 2 H), 6.83–6.79 (m, 2 H), 2.85 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.2 (dd, J_{C-F} = 248.7 Hz, J_{C-F} = 12.7 Hz), 149.0 (dd, J_{C-F} = 246.8 Hz, J_{C-F} = 12.6 Hz), 137.9 (dd, J_{C-F} = 5.6 Hz, J_{C-F} = 3.9 Hz), 124.4 (dd, J_{C-F} = 5.9 Hz, J_{C-F} = 3.6 Hz), 117.3 (d, J_{C-F} = 9.4 Hz), 117.1 (d, J_{C-F} = 9.6 Hz), 36.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –138.1(d, J_{F-F} = 20.8 Hz), –141.7(d, J_{F-F} = 20.5 Hz).

IR (neat): 2941, 2872, 1610, 1519, 1433, 1293, 1269, 1206, 1111, 878, 818, 777 cm^{-1}.

GC-MS (EI): *m*/*z* (%) = 254.02 (12.44) $[M]^+$.

1,2-Bis(4-(trifluoromethyl)phenyl)ethane (2l, known)[23]

Yield: 25.4 mg (40%); white solid; mp: 78–80 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 8.0 Hz, 4 H), 7.23 (d, *J* = 8.0 Hz, 4 H), 2.97 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.3, 128.9, 128.7 (q, J_{C-F} = 32.2 Hz), 125.5 (q, J_{C-F} = 3.7 Hz), 124.5 (q, J_{C-F} = 270.4 Hz), 37.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.4.

IR (neat): 2934, 2866, 1619, 1416, 1329, 1173, 1118, 1067, 835 cm^{-1}.

1,2-Bis(4-chlorophenyl)ethane (2m, known)[24]

Yield: 28.1 mg (56%); white solid; mp: 117–119 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.24–7.22 (m, 4 H), 7.06–7.03 (m, 4 H), 2.85 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.7, 131.8, 130.0, 128.6, 37.2.

IR (neat): 2928, 2861, 1489, 1088, 1016, 826, 800 cm^{-1}.

1,2-Di(thiophen-2-yl)ethane (2n, known)[26]

Yield: 20.6 mg (53%); white solid; mp: 74–76 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.13 (dd, *J* = 5.1, 1.0 Hz, 2 H), 6.92 (dd, *J* = 5.1, 3.5 Hz, 2 H), 6.80 (d, *J* = 3.2 Hz, 2 H), 3.20 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.8, 126.9, 124.8, 123.5, 32.3.

IR (neat): 3103, 2950, 2919, 2853, 1441, 1267, 1105, 1031, 852, 829, 695 cm^{-1}.

1,2-Bis(benzo[*b*]thiophen-3-yl)ethane (2o, known)[26]

Yield: 28.3 mg (48%); white solid; mp: 149–151 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.88–7.84 (m, 2 H), 7.77–7.73 (m, 2 H), 7.40–7.32 (m, 4 H), 7.07 (s, 2 H), 3.27 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.6, 139.0, 136.1, 124.4, 124.1, 123.1, 121.74, 121.65, 28.4.

IR (neat): 3060, 2915, 2841, 1424, 1229, 1078, 1018, 847, 759, 733, 713 cm^{-1}.

1,2-Di(benzofuran-2-yl)ethane (2p, known)[10]

Yield: 25.7 mg (49%); white solid; mp: 119–121 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.38 (m, 4 H), 7.25–7.14 (m, 4 H), 6.41 (s, 2 H), 3.22 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.6, 154.8, 128.9, 123.5, 122.7, 120.6, 110.9, 102.7, 27.0.

IR (neat): 2919, 2850, 1636, 1454, 1253, 1168, 952, 940, 811, 741 cm^{-1}.

1, 2-Di(naphthalen-2-yl)ethane (2q, known)[23]

Yield: 35.0 mg (62%); white solid; mp: 189–191 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.77–7.75 (m, 6 H), 7.65 (s, 2 H), 7.47–7.39 (m, 4 H), 7.36 (dd, *J* = 8.4, 1.6 Hz, 2 H), 3.18 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.4, 133.8, 132.2, 128.1, 127.8, 127.6, 127.5, 126.7, 126.0, 125.3, 38.1.

IR (neat): 2919, 964, 900, 863, 822, 744 cm^{-1}.

1,2-Bis(3-(cyclopropylmethoxy)-4-(difluoromethoxy)phenyl)ethane (2r)

Yield: 61.8 mg (68%); white solid; mp: 111–113 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.05 (d, *J* = 8.1 Hz, 2 H), 6.71 (dd, *J* = 8.1, 1.8 Hz, 2 H), 6.63 (d, *J* = 1.8 Hz, 2 H), 6.58 (t, *J* = 75.8 Hz, 2 H), 3.78 (t, *J* = 6.9 Hz, 4 H), 2.84 (s, 4 H), 1.28–1.17 (m, 2 H), 0.66–0.59 (m, 4 H), 0.35–0.30 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.4, 140.2, 138.8, 122.8, 121.1, 116.5 (t, *J* = 257.5 Hz), 115.1, 74.0, 37.7, 10.3, 3.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –81.6.

IR (neat): 3016, 2930, 2868, 1600, 1514, 1391, 1261, 1217, 1135, 1025, 1008, 829, 635 cm^{-1}.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd. for $C_{24}H_{26}F_4NaO_4$: 477.1659; found: 477.1674.

1,1,2,2-Tetraphenylethane (2s, known)[27]

Yield: 56.2 mg (84%); white solid; mp: 228–231 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (d, *J* = 7.4 Hz, 8 H), 7.09 (t, *J* = 7.6 Hz, 8 H), 6.99 (t, *J* = 7.2 Hz, 4 H), 4.77 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6, 128.6, 128.3, 126.0, 56.4.

IR (neat): 3027, 1493, 1450, 1072, 1031, 746, 695 cm^{-1}.

1,1,2,2-Tetra-*p*-tolylethane (2t, known)[27]

Yield: 59.4 mg (76%); white solid; mp: 286–289 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.04 (d, *J* = 8.0 Hz, 8 H), 6.89 (d, *J* = 8.0 Hz, 8 H), 4.68 (s, 2 H), 2.16 (s, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2, 135.0, 129.0, 128.3, 55.5, 21.1.

IR (neat): 2920, 1513, 1182, 1120, 801, 751 cm^{-1}.

1,2-Diphenyl-1,2-di-*p*-tolylethane (2u, known)[28]

Yield: 66.7 mg (92%); white solid; mp: 203–206 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18–7.02 (m, 24 H), 7.00–6.86 (m, 12 H), 4.72 (s, 4 H), 2.15 (s, 6 H), 2.14 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.05, 143.99, 140.67, 140.61, 135.2, 129.02, 128.97, 128.5, 128.4, 128.23, 128.19, 125.8, 56.0, 21.10, 21.07.

IR (neat): 3027, 2920, 1515, 1495, 1452, 727, 695 cm^{-1}.

1,1,2,2-Tetrakis(4-fluorophenyl)ethane (2v, known)[27]

Yield: 69.5 mg (86%); white solid; mp: 311–314 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07–7.01 (m, 8 H), 6.86–6.79 (m, 8 H), 4.62 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.3 (d, J_{C-F} = 246.1 Hz), 138.7 (d, J_{C-F} = 3.2 Hz), 129.9 (d, J_{C-F} = 7.9 Hz), 115.4 (d, J_{C-F} = 21.4 Hz), 55.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –116.5.

IR (neat): 2920, 1605, 1510, 1234, 1159, 1096, 1016, 826, 770 cm^{-1}.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

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