An Efficient Preparation of Chroman Derivatives from 3-Aryl-1-propanols and Related Compounds with 1,3-Diiodo-5,5-dimethylhydantoin under Irradiation Conditions

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Abstract: Treatment of various 3-aryl-1-propanols with 1,3-diiodo-5,5-dimethylhydantoin (DIH) in ethyl acetate or 1,2-dichloroethane under irradiation with a tungsten lamp gave the corresponding chroman derivatives in good to moderate yields.

The present reaction proceeds via the initial formation of an alkoxyl radical and the radical cyclization onto the aromatic ring, followed by the oxidation of the formed radical intermediate with DIH to provide the chroman derivative. The same treatment of *o*-biphenyldimethylcarbinol, *o*-phenylbenzoic acid, and *o*-alkylbenzoic acids with DIH provided the corresponding chroman derivatives and lactone derivatives in good yields, respectively.

Key words: 1,3-diiodo-5,5-dimethylhydantoin, 3-aryl-1-propanol, chroman, alkoxyl radical, cyclization, aroyloxyl radical

The use of trivalent iodines for organic synthesis has been studied widely.[1] Among them, (diacetoxyiodo)benzene (DIB) is the most popular and useful trivalent iodine reagent for organic synthesis and is used as an alternative to toxic heavy-metal reagents.[2] The advantages of DIB are that it is a nonmetal oxidant and can be used not only for polar reactions, but also for radical reactions to generate oxygen-centered radicals, nitrogen-centered radicals, and carbon-centered radicals.[3] In radical reactions, the initial formation of an unstable acetyl hypoiodite ($MeCO_2I$) from the reaction with DIB and molecular iodine is the key step, and acetyl hypoiodite reacts with alcohols to form alkyl hypoiodites that would serve as the precursors of alkoxyl radicals.[4,5] Synthetic studies of alkoxyl radicals derived from substrates, such as steroidal alcohols and sugars, with DIB and molecular iodine have been well carried out by Suarez et al.[3] We have also studied the synthetic use of oxygen-centered radicals for the construction of chromans from 3-aryl-1-propanols[6] and nitrogen-centered radicals for the construction of tetrahydroquinolines, benzosultams, and saccharins from sulfonamides[7] with DIB and molecular iodine under irradiation with a tungsten lamp. On the other hand, 1,3-diiodo-5,5-dimethylhydantoin (DIH, Figure 1) is not a hypervalent iodine compound, but it may work as a synthon of unstable acetyl hypoiodite derived from the reaction with DIB and molecular iodine. Thus, this suggests that the above reactions can be carried out with DIH alone, instead of a DIB and molecular iodine system. As far as we know, the synthetic studies of DIH are extremely limited. There is one study where DIH was used for the iodination of aromatic compounds.[8] The chroman skeleton is a very important unit and is contained in some natural products, such as vitamin E and flavonoid compounds. Therefore, its synthetic study is very attractive. An extensive study of the preparation of the chroman skeleton has been carried out.[9]

DIH :

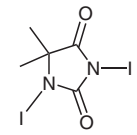

Figure 1

Here, as part of our explorative work on the synthetic use of DIH,[10] we would like to report an efficient preparation of the chroman skeleton from 3-aryl-1-propanols and related reactions with DIH under irradiation with a tungsten lamp. Table 1 shows the results of the reaction of 3-phenyl-1-propanol with DIH under irradiation with a tungsten lamp (300 W) in ethyl acetate and 1,2-dichloroethane (DCE). When the reaction was carried out in ethyl acetate, chroman (**2A-I**) was obtained mainly (entries 1–6). In contrast, 6-iodochroman (**2A-II**) was obtained mainly when the reaction was carried out in DCE (entries 7, 8, 11–13).[11] These results indicate that less polar solvents than ethyl acetate, such as DCE, induce the 6-iodination of the formed chromans. *N*-Iodosuccinimide (NIS) also worked to give chroman in moderate yield (entry 9), although 3.2 equivalents of NIS were required. When the reaction was carried out in the presence of galvinoxyl free radical under the same conditions, chromans were not formed at all, and the starting 3-phenyl-1-propanol was recovered quantitatively (entry 10). Thus, this result indicates that the present reaction proceeds through the formation of radical species.

Based on these results, 1-methyl-, 1-ethyl-, 1-butyl-, 1,1-dimethyl-, 1-dodecyl, and 1-tridecyl-3-phenyl-1-propanols were treated with DIH in ethyl acetate and DCE to provide the corresponding chroman derivatives in good to moderate yields as shown in Table 2 (entries 1–11). Under the same conditions, 3-(4′-methylphenyl)-1-propanol and 3-(4′-chlorophenyl)-1-propanol provided the corresponding chroman derivatives in good to moderate yields (en-

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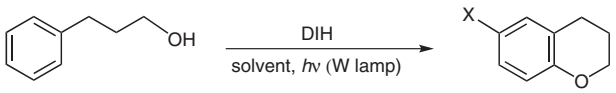
Table 1 Preparation of Chroman from 3-Phenyl-1-propanol with DIH

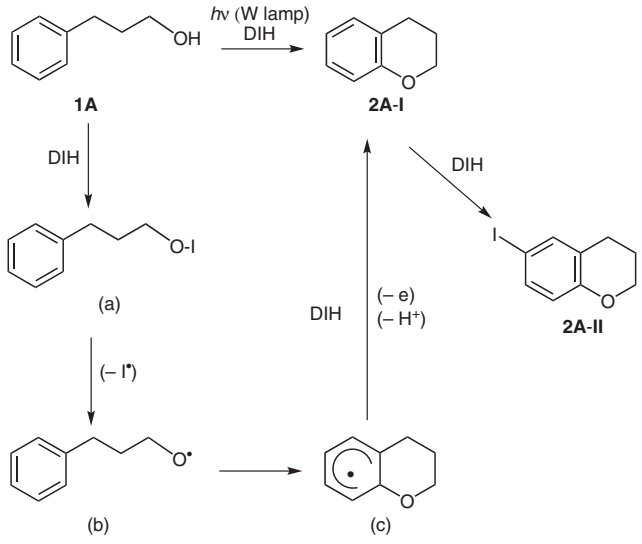


1A **2A-I** X = H **2A-II** X = I

Entry	Solvent (mL)	DIH (equiv)	Temp (°C)	Time (h)	Yield of **2A-I** (%)	Yield of **2A-II** (%)
1	EtOAc (10)	1.0	40	9	32	3
2	EtOAc (10)	1.6	40	9	53	11
3	EtOAc (10)	1.6	55	10	48	5
4	EtOAc (10)	2.0	40	9	52	5
5	EtOAc (10)	2.0	55	10	52	14
6	EtOAc (10)	2.4	40	9	39	18
7	DCE (10)	1.0	40	7	18	34
8	DCE (10)	1.6	40	7	30	60
9[a]	DCE (10)	3.2	40	7	3	57
10[b]	DCE (10)	1.6	40	7	0	0
11	DCE (15)	3.0	40	9	8	75
12	DCE (15)	3.5	40	9	7	79
13	DCE (15)	4.0	40	9	3	82

[a] Instead of DIH (1.6 mmol) NIS (3.2 mmol) was used.
[b] Reaction was carried out in the presence of galvinoxyl free radical (1 mmol).

tries 12–16). However, the same treatment of 3-(4′-nitrophenyl)-1-propanol did not give the cyclized product at all (entry 17). These results suggest that the cyclization onto the aromatic ring by the oxygen-centered radical of the formed alkoxyl radical proceeds in an electrophilic manner. A plausible reaction mechanism is shown in Scheme 1.



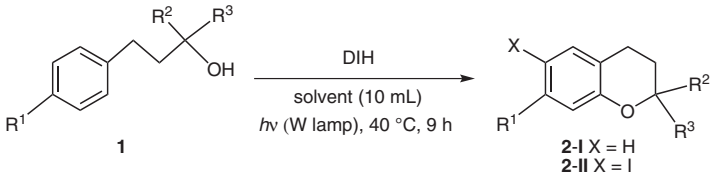
Scheme 1

Alkyl hypoiodite **a** is formed by the reaction of 3-phenyl-1-propanol (**1A**) with DIH. Homolytic O–I bond cleavage of hypoiodite **a** occurs to provide oxygen-centered radical **b**. Then, oxygen-centered radical **b** cyclizes onto the aromatic ring in an electrophilic manner to generate radical intermediate **c**, which is further oxidized to chroman **2A-I**. Chroman **2A-I** is iodinated at 6-position by DIH in an electrophilic manner to give 6-iodochroman **2A-II**.

The same treatment of *o*-biphenyldimethylcarbinol (**3**) with DIH under irradiation with a tungsten lamp generated corresponding benzochroman (**4**) in good yield, as shown in Scheme 2.

However, *o*-biphenylcarbinol and *o*-biphenylmethylcarbinol, which are primary and secondary alcohols, respectively, gave the corresponding benzochromans in low yields due to the formation of the corresponding aldehyde and methylketone via the oxidation of the formed alkoxyl radicals. Treatment of *o*-phenylbenzoic acid (**5**) and *o*-alkylbenzoic acids **7** with DIH under irradiation with a tungsten lamp provided the corresponding δ-lactone **6** and γ-lactones **8** in good yields, respectively. A plausible reaction mechanism for the formation of γ-lactones **8** from the reaction of *o*-alkylbenzoic acids **7** with DIH is shown in Scheme 3. The initial formation of aroyl hypoiodite **d** and the homolytic cleavage of the O–I bond occurs to provide aroyloxyl radical **e**. Then, the 1,5-H shift occurs to form benzylic radical, which reacts with aroyl hypoiodite

Table 2 Preparation of Chroman Derivatives from 3-Aryl-1-propanols with DIH



Entry	R^1	R^2	R^3	DIH (equiv)	Solvent	Yield of **2-I** (%)	Yield of **2-II** (%)
1	H	H	Me	1.6	EtOAc	50	6
2	H	H	Me	2.5	DCE	14	64
3	H	H	Et	1.6	EtOAc	46	2
4	H	H	Et	1.6	DCE	58	24
5	H	H	Et	2.5	DCE	11	57
6	H	H	Bu	1.6	EtOAc	37	3
7	H	H	Bu	2.5	DCE	21	21
8	H	Me	Me	1.6	DCE	19	41
9	H	Me	Me	2.5	DCE	8	29
10	H	H	n-$C_{12}H_{25}$	1.6	DCE	22	1
11	H	H	n-$C_{12}H_{25}$	2.5	DCE	27	7
12	Me	H	H	1.6	EtOAc	30	28
13	Me	H	H	1.6	DCE	40	39
14	Me	H	H	2.5	DCE	26	40
15	Cl	H	H	1.6	EtOAc	12	3
16	Cl	H	H	1.6	DCE	41	19
17	NO_2	H	H	1.6	EtOAc	0	0
18	Me	H	Me	2.5	DCE	31	20

d to generate benzylic iodide **g** and aroyloxyl radical **e** again. Finally, the ionic cyclization of *o*-(α-iodo)alkylbenzoic acid occur to provide γ-lactone **8**.

In conclusion, treatment of 3-aryl-1-propanols with 1,3-diiodo-5,5-dimethylhydantoin (DIH) in ethyl acetate or 1,2-dichloroethane under irradiation with a tungsten lamp provided the corresponding chroman derivatives in good to moderate yields. The same treatment of *o*-biphenyldimethylcarbinol, *o*-phenylbenzoic acid, and *o*-alkylbenzoic acids with DIH gave the corresponding chroman derivatives and lactone derivatives, respectively, in good yields.

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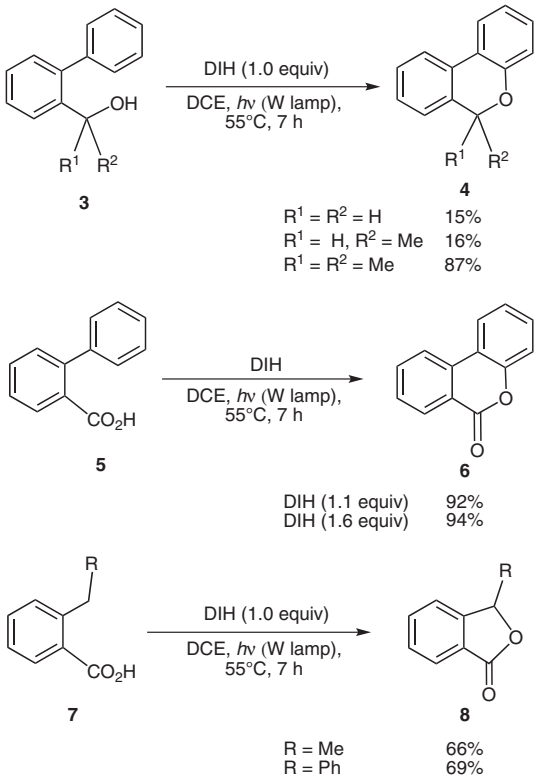
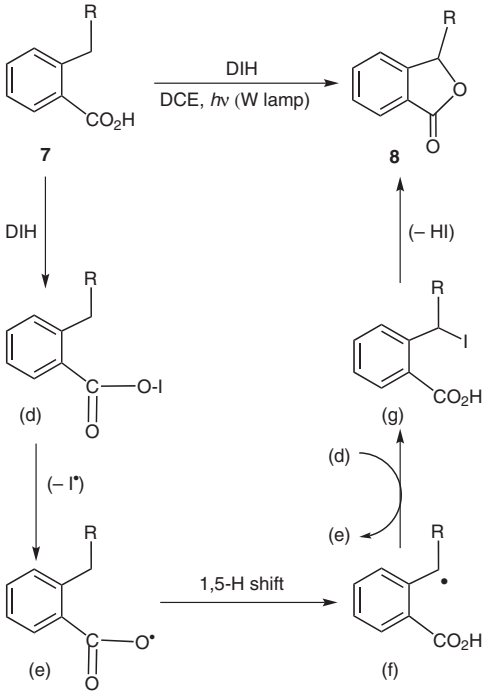


Scheme 2



Scheme 3

Zhdankin, V. *Synlett* **2007**, 527.

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(11) **Typical Procedure for Preparation of Chromane from 3-Phenyl-1-propanol with DIH**

1,2-Dichloroethane (15 mL) was added to the mixture of 3-phenyl-1-propanol (1.0 mmol, 136.2 mg) and DIH (1.6 mmol, 607.8 mg, commercially available from Tokyo Kasei Co.). The mixture was irradiated with a tungsten lamp (300 W) at 40 °C for 9 h under an argon atmosphere. After the

reaction, the mixture was poured into a sat. aq Na_2SO_4 solution and extracted with $CHCl_3$ (3 × 15 mL). The organic layer was dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure, and the residue was treated with flash column chromatography on silica gel using a mixture of hexane and EtOAc (1: 5) as an eluent to provide chroman and 6-iodochroman.

Chromane

Oil. IR (neat): 2935, 2861, 1581, 1488, 1227, 1115 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.98–2.04 (m, 2 H), 2.79 (t, *J* = 6.5 Hz, 2 H), 4.18 (t, *J* = 5.2 Hz, 2 H), 6.78 (d, *J* = 8.1 Hz, 1 H), 6.83 (dd, *J* = 8.1, 7.5 Hz, 1 H), 7.03 (d, *J* = 7.5 Hz, 1 H), 7.08 (dd, *J* = 7.5, 8.1 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 22.46 (s), 24.96 (s), 66.51 (s), 116.78 (t), 120.18 (t), 122.31 (q), 127.28 (t), 129.90 (t), 154.97 (q). HRMS (APPI): *m/z* calcd for $C_9H_{10}O$ [M]: 134.0732; found [M^+]: 134.0726.

6-Iodochromane

Oil. IR (neat): 2900, 2850, 1560, 1480, 1230, 1120, 810 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.97 (tt, *J* = 6.4, 5.1 Hz, 2 H), 2.74 (t, *J* = 6.4 Hz, 2 H), 4.16 (t, *J* = 5.1 Hz, 2 H), 6.56 (d, *J* = 9.2 Hz, 1 H), 7.33 (d, *J* = 9.2 Hz, 1 H), 7.34 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 21.87 (s), 24.53 (s), 66.40 (s), 81.99 (q), 119.01 (t), 124.99 (q), 135.91 (t), 138.21 (t), 154.79 (q). HRMS (EI): *m/z* calcd for C_9H_9OI [M]: 259.9698; found [M^+]: 259.9689.

2-Methyl-6-iodochromane

Mp 43.0–44.0 °C. IR (neat): 2920, 1550, 1460, 1240, 1110, 820 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.38 (dd, *J* = 6.2, 2.9 Hz, 3 H), 1.63–1.73 (m, 1 H), 1.97 (ddd, *J* = 13.5, 7.5, 2.9 Hz, 1 H), 2.67–2.85 (m, 2 H), 4.07–4.13 (m, 1 H), 6.56 (d, *J* = 8.0 Hz, 1 H), 7.34 (d, *J* = 8.0 Hz, 1 H), 7.35 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 21.20 (p), 24.50 (s), 28.72 (s), 72.32 (t), 81.85 (q), 119.01 (t), 124.64 (q), 135.88 (t), 137.98 (t), 154.95 (q). HRMS (EI): *m/z* calcd for $C_{10}H_{11}OI$ [M]: 273.9855; found [M^+]: 273.9840.

2-Ethylchromane

Oil. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.04 (t, *J* = 7.5 Hz, 3 H), 1.62–1.82 (m, 3H), 1.97–2.02 (m, 1 H), 2.75 (ddd, *J* = 16.3, 5.7, 3.1 Hz, 1 H), 2.84 (ddd, *J* = 16.3, 11.3, 6.1 Hz, 1 H), 3.88–3.94 (m, 1 H), 6.80 (d, *J* = 7.9 Hz, 1 H), 6.81 (dd, *J* = 7.9, 7.4 Hz, 1 H), 7.03 (d, *J* = 7.4 Hz, 1 H), 7.07 (dd, *J* = 7.9, 7.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 9.65 (p), 24.80 (s), 26.84 (s), 28.28 (s), 77.16 (t), 116.70 (t), 119.84 (t), 122.10 (q), 127.10 (t), 129.48 (t), 155.11 (q). HRMS (APCI): *m/z* calcd for $C_{11}H_{14}O$ [M] 162.1039; found [M^+]: 162.1040.

2-Ethyl-6-iodochromane

Oil. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.03 (t, *J* = 7.4 Hz, 3 H), 1.59–1.82 (m, 3 H), 1.94–2.00 (m, 1 H), 2.70 (ddd, *J* = 16.6, 5.2, 3.4 Hz, 1 H), 2.75–2.83 (m, 1 H), 3.85–3.91 (m, 1 H), 6.57 (d, *J* = 8.0 Hz, 1 H), 7.33 (d, *J* = 8.6 Hz, 1 H), 7.34 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 9.71 (p), 24.58 (s), 26.50 (s), 28.26 (s), 77.45 (t), 81.82 (q), 119.16 (t), 125.06 (q), 135.96 (t), 138.06 (t), 155.15 (q). HRMS (APCI): *m/z* calcd for $C_{11}H_{13}OI$ [M]: 288.0006; found [M^+]: 288.0005.

2-Butyl-6-iodochromane

Oil. IR (neat): 2900, 2830, 1560, 1470, 1240, 1120, 820 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.92 (t, *J* = 7.1 Hz, 3 H), 1.32–2.00 (m, 8 H), 2.70 (ddd, *J* = 16.7, 5.5, 3.3 Hz, 1 H), 2.79 (ddd, *J* = 16.7, 10.6, 5.1 Hz, 1 H), 3.94 (tdd, *J* = 10.3, 5.5, 2.2 Hz, 1 H), 6.56 (d, *J* = 8.2 Hz, 1 H), 7.33 (d, *J* = 8.2 Hz, 1 H), 7.34 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 14.04 (p), 22.65 (s), 24.46 (s), 26.87 (s), 27.39 (s), 34.92 (s), 76.11 (t), 81.71 (q), 119.05 (t), 124.93 (q), 135.82 (t), 137.94 (t), 155.00 (q). HRMS (EI): *m/z* calcd for $C_{13}H_{17}OI$ [M]: 316.0324; found [M^+]: 316.0323.

2,2-Dimethyl-6-iodochromane

Oil. IR (neat): 2950, 2900, 1560, 1470, 1260, 1220, 1160, 1120, 820 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.31 (s, 6 H), 1.77 (t, *J* = 6.6 Hz, 2 H), 2.73 (t, *J* = 6.6 Hz, 2 H), 6.54 (d, *J* = 8.6 Hz, 1 H), 7.34 (d, *J* = 8.6 Hz, 1 H), 7.34 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 22.14 (s), 26.75 (p), 32.34 (s), 74.50 (q), 81.44 (q), 119.60 (t), 123.79 (q), 135.99 (t), 137.91 (t), 153.96 (q). HRMS (EI): *m/z* calcd for $C_{11}H_{13}OI$ [M]: 288.0011; found [M^+]: 288.0027.

7-Methyl-6-iodochromane

Oil. H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.93–1.98 (m, 2 H), 2.32 (s, 3 H), 2.71 (t, *J* = 6.4 Hz, 2 H), 4.14 (t, *J* = 5.1 Hz, 2 H), 6.69 (s, 1 H), 7.44 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 22.09 (s), 24.06 (s), 27.56 (p), 66.43 (s), 89.03 (q), 118.01 (t), 122.12 (q), 139.31 (t), 140.00 (q), 155.08 (q).

3,4-Benzocoumarin

Mp 91.0–92.0 °C. IR (KBr): 1720, 1600, 1480, 1300, 1205, 1100, 900, 760, 730 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.31–7.36 (m, 2 H), 7.47 (t, *J* = 7.7 Hz, 1 H), 7.57 (t, *J* = 8.0 Hz, 1 H), 7.81 (t, *J* = 8.0 Hz, 1 H), 8.04 (d, *J* = 7.7 Hz, 1 H), 8.10 (d, *J* = 8.0 Hz, 1 H), 8.39 (d, *J* = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 117.75 (t), 118.02 (q), 121.23 (q), 121.67 (t), 122.76 (t), 124.54 (t), 128.86 (t), 130.42 (t), 130.54 (t), 134.74 (q), 134.83 (t), 151.27 (q), 161.16 (q). HRMS–FAB: *m/z* calcd for $C_{13}H_9O_2$ [M + H]: 197.0603; found [M + H]$^+$: 197.0610.

3-Methylphthalide

Oil. IR (neat): 2940, 1740, 1590, 1450, 1210, 1030, 760, 740 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.64 (d, *J* = 6.5 Hz, 3 H), 5.57 (q, *J* = 6.5 Hz, 1 H), 7.64 (d, *J* = 7.7 Hz, 1 H), 7.53 (t, *J* = 7.7 Hz, 1 H), 7.68 (t, *J* = 7.7 Hz, 1 H), 7.89 (d, *J* = 7.7 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 20.39 (p), 77.76 (t), 121.59 (t), 125.65 (t), 125.75 (q), 129.07 (t), 134.09 (t), 151.21 (q). HRMS–FAB: *m/z* calcd for $C_9H_9O_2$ [M + H]: 149.0603; found [M + H]$^+$: 149.0627.

3-Phenylphthalide

Mp 113.0–114.0 °C. IR (KBr): 3000, 1740, 1580, 1455, 1280, 1060, 970, 740 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 6.41 (s, 1 H), 7.27–7.40 (m, 6 H), 7.56 (t, *J* = 7.3 Hz, 1 H), 7.65 (t, *J* = 7.3 Hz, 1 H), 7.97 (d, *J* = 7.3 Hz, 1 H). HRMS (EI): *m/z* calcd for $C_{14}H_{10}O_2$ [M]: 210.0680; found [M^+]: 210.0678.

6,6-Dimethyl-6*H*-dibenzo[*b*,*d*]pyran

Oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.64 (s, 6 H), 6.95 (d, *J* = 8.2 Hz, 1 H), 7.02 (t, *J* = 7.5 Hz, 1 H), 7.20–7.36 (m, 4 H), 7.70–7.75 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 27.68 (p), 77.63 (q), 118.15 (t), 121.62 (t), 122.32 (t), 122.57 (q), 122.97 (t), 123.30 (t), 127.79 (t), 128.04 (t), 128.69 (q), 129.52 (t), 139.61 (q), 152.85 (q). HRMS (APCI): *m/z* calcd for $C_{15}H_{14}O$ [M]: 210.1045; found [M^+]: 210.1043.