Synthesis B. Heid, B. Plietker Feature

Iron-Catalyzed C-Allylating Partial Dearomatization of Naphthols

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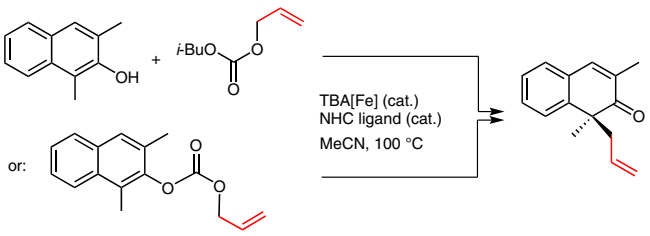

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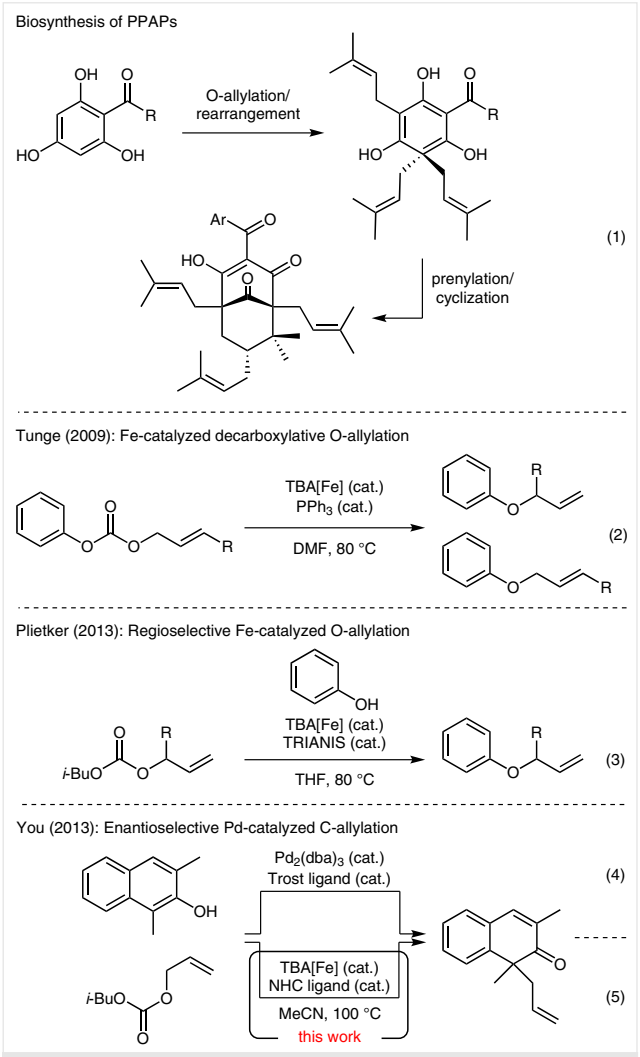
Abstract The iron complex $Bu_4N[Fe(CO)_3(NO)]$ (TBA[Fe]) catalyzes the intermolecular allylation of naphthol derivatives to give the corresponding partially dearomatized allylated chromenones in good to excellent yields. The scope and limitations are reported. An efficient decarboxylative intramolecular C-allylation, starting from allyl naphthyl carbonates, was developed. From a mechanistic point of view, the overall process is the result of a fast O-allylation followed by a sigmatropic rearrangement to the desired product.

Key words iron catalysis, allylation, decarboxylation, dearomatization, substitution, rearrangement

The synthesis of carbocyclic products with defined stereochemistry remains a central topic within organic synthesis. Amongst the various strategies developed to date, dearomatization of aromatic compounds has only recently attracted significant attention. This is mostly due to the significant amount of energy required to overcome the resonance energy present in aromatic groups.[1]

In nature, dearomatization is usually the consequence of an allyl phenyl ether rearrangement, that is a [3,3]-sigmatropic Claisen rearrangement. Within the past years, our group has been involved in developing short total syntheses of polyprenylated polycyclic acylphloroglucines (PPAP).[2] Biosynthesis studies of these natural products revealed that per-prenylation of an acylphloroglucine derivative via sequences of O-allylation and subsequent allyl phenyl ether rearrangement results in the formation of a tris-prenylated cyclohexadienones, which undergo further prenylation and cyclization to give natural products with the unusual [3.3.1]-nonatrione core (Scheme 1, eq. 1).[3] Parallel to our synthetic investigations, we developed efficient protocols for regioselective Tsuji–Trost-type allylations by using the iron complex $Bu_4N[Fe(CO)_3(NO)]$ (TBA[Fe]).[4] On the basis of



Scheme 1 O- versus C-allylation: state of research

this work, the group of Tunge reported a TBA[Fe]-catalyzed decarboxylative O-allylation by using aryl allyl carbonates as starting materials (Scheme 1, eq. 2).[5]

Whereas only moderate regioselectivities were reported for the decarboxylative intramolecular O-allylation, our group was later on able to show that the use of triazolium-based carbene ligands allows a selective *ipso*-substitution to take place in the intermolecular O-allylation of various phenol derivatives (Scheme 1, eq. 3).[6]

At the same time, landmark reports on a dearomatizing palladium-catalyzed Tsuji–Trost allylation of dialkylnaphthols were reported by You (Scheme 1, eq. 4).[7] On the basis of their experimental results, they proposed that direct C-allylation takes place instead of O-allylation–[3,3]-sigmatropic rearrangement. In light of the potential application in total synthesis and with regard to our and others' previous work in allylating dearomatization, we became interested in developing a TBA[Fe]-catalyzed version of You's transformation. Herein we report the successful realization of this concept (Scheme 1, eq. 5).

We initiated our studies by employing 1,3-dimethyl-2-naphthol (**1**) as starting material, and were pleased to find that the reaction in tetrahydrofuran as a solvent and by using TBA[Fe] (10 mol%) and NHC-ligand **L1** (12 mol%) (Figure 1) already gave the desired product **3** in a promising yield of 62% (Table 1, entry 1).

A subsequent evaluation of the scope and limitations was performed. Various substituted allylic carbonates were employed under the standard reaction conditions (Table 2).

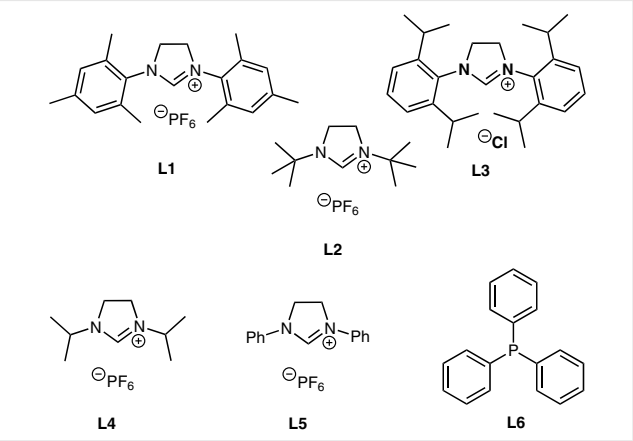


Figure 1 Ligand structures

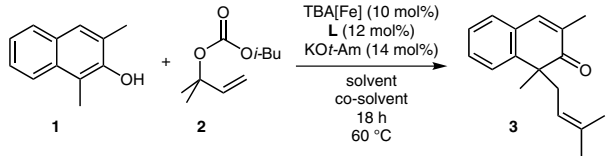
The carbonate structure has a strong influence on the reactivity. Moderate reactivities were observed alongside with significant formation of the O-allylation product B. These results indicate the process to be rather a sequence of O-allylation–sigmatropic rearrangement than a direct dearomatizing C-allylation. To prove this assumption, the O-allylated product **15** (see product B, entry 2), was reacted at 80 °C for 18 hours in acetonitrile; this resulted in a 1:1 mixture of **15** and **14**. This result proves that an iron-catalyzed O-allylation followed by [3,3]-sigmatropic rearrangement takes place. Introduction of additional substituents at the olefinic moiety led to a significant erosion in reactivity (entries 6

Biographical sketches

Berenice Heid was born in 1987. She obtained her diploma degree in Chemistry at the University of Stuttgart (Germany) in 2012. Since graduation she has been a Ph.D. student in the group of Prof. Dr. B. Plietker at the same university. She is focusing on the development of iron-catalyzed allylic substitutions and dearomatizations.

Bernd Plietker studied chemistry in Münster, Germany, and received his diploma degree in 1995. He obtained his Dr. rer. nat. under the supervision of Peter Metz in the field of intramolecular Diels–Alder reactions at the Technische Universität Dresden, Germany. He spent one year as a postdoc with Jan-Erling Bäckvall, Stockholm Universitet, Sweden, followed by a second year with Barry M. Trost, Stanford University, USA, working in the field of palladium catalysis. In 2001 he founded a research group at the Universität Dortmund, Germany, supported by a Liebig fellowship of the Fonds der chemischen Industrie and an Emmy-Noether-grant of the Deutsche Forschungsgemeinschaft. Since 2007 he has been a professor of organic chemistry at the Universität Stuttgart, Germany. The research in his group focuses on the development of sustainable catalytic transformations by employing highly oxidized ruthenium complexes or subvalent iron complexes in catalysis and natural product synthesis.

Table 1 Optimization of the Reaction Conditions: Variation of Solvent and Ligand[a]



1 2 3

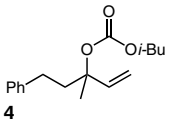
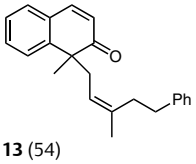
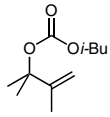
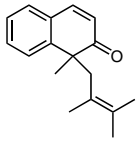
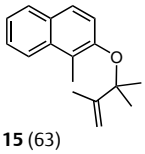
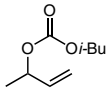
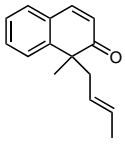
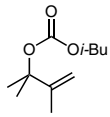
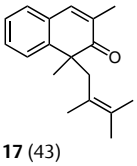
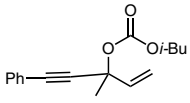
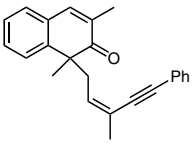
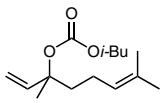
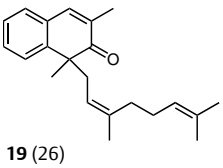
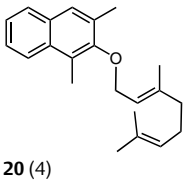
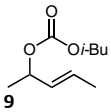
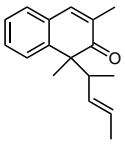
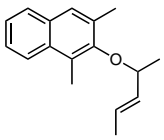
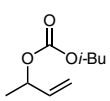
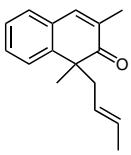
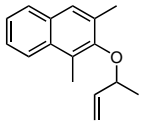
Entry	Solvent	Co-solvent[b]	Ligand[c]	Yield of **3** (%)[d]
1	THF	–	**L1**	62
2	CH_2Cl_2	–	**L1**	18
3	toluene	–	**L1**	49
4	MTBE	–	**L1**	56
5	DMF	–	**L1**	49
6	MeCN	–	**L1**	80 (73)[e]
7	1,4-dioxane	–	**L1**	30
8	MeCN	THF	**L1**	81
9	MeCN	CH_2Cl_2	**L1**	72
10	MeCN	MTBE	**L1**	75
11	**MeCN**	**THF**	**L2**	**91**
12	MeCN	THF	**L3**	–
13	MeCN	THF	**L4**	90
14	MeCN	THF	**L5**	84
15	MeCN	THF	**L6**	–

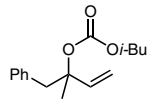
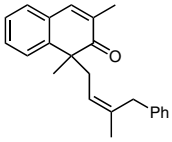
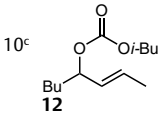
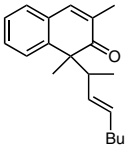
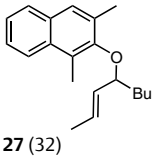
[a] Reaction conditions: $Bu_4N[Fe(CO)_3NO]$ (10 mol%), ligand (12 mol%), potassium *tert*-pentoxide (KO*t*-Am) (14 mol%), naphthol **1** (0.2 mmol), carbonate **2** (0.2 mmol), THF (0.05 mmol), MeCN (1 mL), 60 °C.
[b] Co-solvent (0.05 mmol).
[c] For ligand structures, see Figure 1.
[d] Yield of the crude reaction mixture determined by ^{1}H NMR analysis; mesitylene (0.2 mmol) used as internal standard.
[e] Isolated yield.

and 8). Using monosubstituted olefins possessing different substituents at the quaternary allylic C-atom led to the formation of the desired product in low to good yields along with varying amounts of the undesired O-allylation product.

A screening of the naphthol scope using carbonate **2** as allylating agent resulted in significantly improved yields and conversions (Table 3). Various substituted naphthol derivatives were successful dearomatized. Importantly, functional groups such as halides and carbonyl groups remain intact. Hence, this transformation sets the stage for employing di- and monosubstituted β-naphthols as building blocks to allow the generation of molecular complexity within a few synthetic operations. Unfortunately, the use of 1-naphthols was not successful so far.

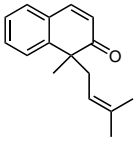
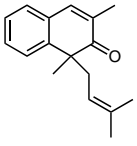
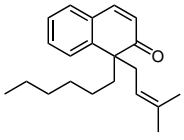
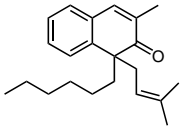
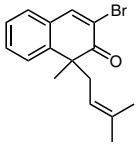
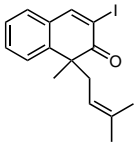
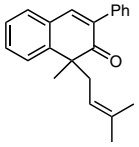
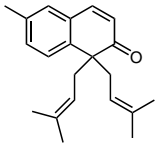
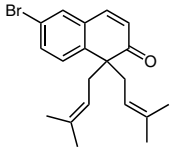
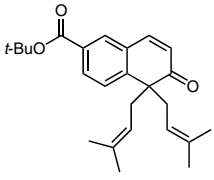
Table 2 Iron-Catalyzed Partially Dearomatizing C-Allylation: Allyl Carbonate Scope

Entry	Carbonate	Product A[a]	Product B[a]
1[b]	 **4**	 **13** (54)	
2[b]	 **5**	 **14** (12)	 **15** (63)
3[b]	 **6**	 **16** (14)	
4[c]	 **5**	 **17** (43)	
5[c]	 **7**	 **18** (4)	
6[c]	 **8**	 **19** (26)	 **20** (4)
7[c]	 **9**	 **21** (10)	 **22** (43)
8[c]	 **10**	 **23** (23)	 **24** (39)

Entry	Carbonate	Product A[a]	Product B[a]
9[c]	 **11**	 **25** (11)	
10[c]	 **12**	 **26** (18)	 **27** (32)

[a] Isolated yield (%) given in parentheses.
[b] Reaction conditions: TBA[Fe] (1 mol%), **L2** (3 mol%), KO*t*-Am (5 mol%), naphthol (0.2 mmol), carbonate (0.2 mmol), EtOAc as co-solvent (0.05 mmol), MeCN (1 mL), 60 °C.
[c] Reaction conditions: TBA[Fe] (5 mol%), **L2** (7 mol%), KO*t*-Am (9 mol%), naphthol (0.2 mmol), carbonate (0.2 mmol), THF as co-solvent (0.05 mmol), MeCN (0.5 mL), 60 °C.

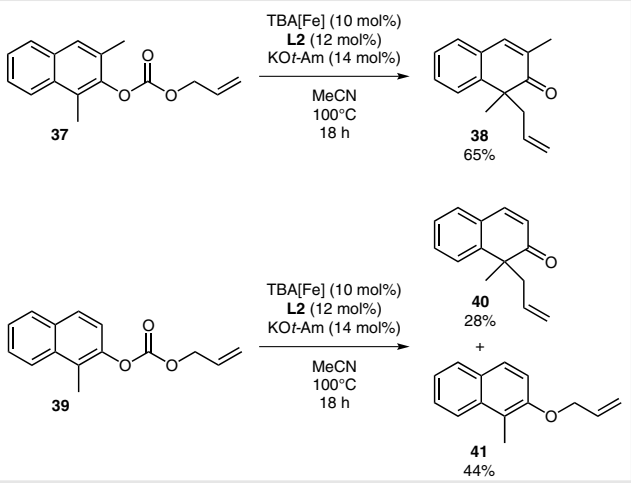
Table 3 Scope and Limitations of Naphthol Derivatives

Entry	Product	Yield (%)[a]
1[b]	**28** 	82
2[c]	**3** 	91
3[b]	**29** 	54
4[c]	**30** 	74
5[c]	**31** 	92
6[c]	**32** 	66
7[c]	**33** 	65
8[d]	**34** 	80
9[d]	**35** 	72
10[d]	**36** 	19

[a] Isolated yield.
[b] Reaction conditions: TBA[Fe] (1 mol%), **L2** (3 mol%), KO*t*-Am (5 mol%), naphthol (0.2 mmol), carbonate (0.2 mmol), EtOAc as co-solvent (0.05 mmol), MeCN (1 mL), 60 °C.
[c] Reaction conditions: TBA[Fe] (5 mol%), **L2** (7 mol%), KO*t*-Am (9 mol%), naphthol (0.2 mmol), carbonate (0.2 mmol), THF as co-solvent (0.05 mmol), MeCN (0.5 mL), 60 °C.
[d] Reaction conditions: TBA[Fe] (10 mol%), **L2** (12 mol%), KO*t*-Am (16 mol%), naphthol (0.2 mmol), carbonate (0.4 mmol), no co-solvent, MeCN (1 mL), 100 °C.

Despite the overall usefulness of this transformation, we considered the rather narrow scope of allylic carbonates to be a limitation and were wondering whether simple allyloxycarbonyl-protected β-naphthols would decarboxylate in the presence of TBA[Fe] to form the corresponding naphtholates. These naphtholates could then react with the allyl–Fe complex to give α-allylated naphthones, to which more complex olefinic substitution could be introduced by employing, for example, ruthenium-catalyzed cross-metathesis. We were pleased that this transformation worked particularly well for the disubstituted β-naphthol **37** to give the corresponding product **38** in 65% isolated yield (Scheme 2). Using monosubstituted naphthol **39** under otherwise

identical reaction conditions led to a mixture of partially dearomatized product **40** alongside with allyl ether **41** (Scheme 2).



Scheme 2 Intermolecular dearomatization of naphthol derivatives

Herein we reported an operationally simple procedure for the allylating partial dearomatization of substituted naphthol derivatives by using catalytic amounts of the iron complex $Bu_4N[Fe(CO)_3(NO)]$ (TBA[Fe]). Reasonable functional group tolerance was observed. The obtained products were formed in moderate to good yields. With regard to the usefulness of this particular reaction, future work will focus on the development of more efficient iron-based catalysts and the elaboration of an asymmetric version of this transformation.

Reactions which are sensitive to air or moisture were performed under anhyd N_2 using standard Schlenk techniques. All solvents were purified prior to use. All chemicals were purchased from Sigma Aldrich, Acros Organics, or Alfa Aesar. Mass spectra were measured using electronspray ionization on a Bruker Micro-TOF-Q. IR spectra were measured on a Bruker Vector 22 FT-IR spectrometer in an ATR mode (b = broad, w = weak, vw = very weak, s = strong, vs = very strong). NMR spectra were recorded on a Bruker AV 300 spectrometer (^{1}H NMR, 300 MHz; ^{13}C NMR, 75 MHz), a Bruker AV 250 spectrometer (^{1}H NMR, 250 MHz; ^{13}C NMR, 62.5 MHz), or a Bruker AV 500 spectrometer (^{1}H NMR, 500 MHz;^{13}C NMR, 125 MHz). Chemical shifts were reported in ppm downfield from tetramethylsilane as an internal standard.

Dearomatization of 1,3-Disubstituted Naphthols Catalyzed by the Iron Complex $Bu_4N[Fe(CO)_3(NO)]$ (TBA[Fe]); General Procedure I (GP I)

A 10 mL Schlenk tube was charged with **L2** (4.5 mg, 0.014 mmol, 0.07 equiv) and MeCN (0.5 mL). Afterwards KO*t*-Am solution (1.7 M in toluene, 11 µL, 0.018 mmol, 0.09 equiv) was added and the reaction mixture was stirred for 20 min at r.t. Then $Bu_4N[Fe(CO)_3NO]$ (4.2 mg, 0.01 mmol, 0.05 equiv) was added and the mixture was heated for 1 h at 80 °C to coordinate the ligand. At r.t. the carbonate (0.2 mmol, 1 equiv) was added to the mixture, followed by the naphthol (0.2 mmol, 1 equiv) and the co-solvent THF (0.05 mmol). The reaction mixture was stirred for 18 h at 60 °C. After filtration through a silica plug (Et_2O) the crude product was purified by column chromatography.

1,3-Dimethyl-1-(3-methylbut-2-en-1-yl)naphthalen-2-one (3)

The product was prepared according to GP I by using 1,3-dimethyl-2-naphthol and 2-methylbut-3-en-2-yl isobutyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 44 mg, 0.18 mmol (91%). R_f = 0.41 (PE–EtOAc, 20:1).

IR (film): 3392 (b), 3025 (w), 2970 (w), 2924 (vw), 1715 (vw), 1650 (vs), 1447 (w), 1376 (w), 1275 (w), 1061 (vw), 969 (vw), 908 (vw), 754 (s), 523 (vw), 462 (vw), 411 (vw) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.22 (m, 5 H, ArH), 4.66–4.57 (m, 1 H, prenyl-sp^2-CH), 2.80–269 (m, 1 H, prenyl-sp^3-CH_2), 2.47–2.37 (m, 1 H, prenyl-sp^3-CH_2), 1.97 (d, *J* = 1.3 Hz, 3 H, enone-CH_3), 1.48 (s, 3 H, prenyl-CH_3), 1.45 (s, 3 H, enone-CH_3), 1.39 (s, 3 H, prenyl-CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.3, 145.4, 141.3, 134.3, 132.5, 130.3, 128.5, 128.3, 126.4, 118.8, 51.4, 41.9, 25.7, 25.6, 17.7, 15.9.

GC/MS (EI, 70 eV): *m*/*z* (%) = 240 (3), 172 (100), 157 (5), 142 (6), 128 (6), 115 (2), 97 (6), 69 (10), 41 (5).

ESI-HRMS: *m*/*z* calcd for $C_{17}H_{20}O$: 240.1514; found: 240.1513.

1-(2,3-Dimethylbut-2-en-1-yl)-1,3-dimethylnaphthalen-2-one (17)

The product was prepared according to GP I by using 1,3-dimethyl-2-naphthol and 2,3-dimethylbut-3-en-2-yl isobutyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 22 mg, 0.08 mmol (43%). R_f = 0.43 (PE–EtOAc, 20:1).

IR (film): 2921 (w), 2862 (w), 1717 (w), 1651 (vs), 1441 (s), 1372 (s), 1275 (w), 1263 (w), 1243 (w), 1028 (w), 967 (w), 875 (w), 754 (vs), 586 (s) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.15 (m, 5 H, ArH), 2.83 (d, *J* = 13.6 Hz, 1 H, olefin-sp^3-CH_2), 2.53 (d, *J* = 13.6 Hz, 1 H, olefin- sp^3-CH_2), 1.97 (d, *J* = 1.2 Hz, 3 H, enone-CH_3), 1.52 (s, 3 H, olefin-CH_3), 1.45 (s, 3 H, enone-CH_3), 1.35 (s, 3 H, olefin-CH_3), 1.15 (s, 3 H, olefin-CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.4, 145.5, 140.9, 132.4, 130.2, 128.4, 128.2, 127.0, 126.4, 123.7, 52.0, 48.5, 26.9, 25.5, 20.7, 20.6, 19.5, 16.1.

GC/MS (EI, 70 eV): *m*/*z* (%) = 254 (1), 172 (100), 157 (5), 3), 128 (5), 115 (2), 83 (9), 55 (5).

ESI-HRMS: *m*/*z* calcd for $C_{18}H_{22}O$: 254.1671; found: 254.1676.

1,3-Dimethyl-1-(3-methyl-5-phenylpent-2-en-4-yn-1-yl)naphthalen-2-one (18)

The product was prepared according to GP I by using 1,3-dimethyl-2-naphthol and isobutyl 3-methyl-5-phenylpent-1-en-4-yn-3-yl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 2.6 mg, 0.008 mmol (4%). R_f = 0.4 (PE–EtOAc, 20:1).

IR (film): 2971 (w), 2920 (w), 1740 (w), 1720 (w), 1651 (s), 1488 (w), 1441 (w), 1373 (w), 1275 (w), 1260 (w), 1083 (w), 1069 (w), 1027 (s), 909 (w), 801 (w), 752 (vs), 690 (vs) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.41 (m, 3 H, ArH), 7.38–7.26 (m, 4 H, ArH), 7.25–7.20 (m, 3 H, ArH), 5.31–5.22 (m, 1 H, olefin- sp^2-CH), 3.07–2.95 (m, 1 H, olefin- sp^3-CH_2), 2.92–2.81 (m, 1 H, olefin- sp^3-CH_2), 2.00 (d, *J* = 1.22 Hz, 3 H, enone-CH_3), 1.75 (d, *J* = 1.2 Hz, 3 H, olefin-CH_3), 1.49 (s, 3 H, enone-CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.3, 132.4, 131.1, 130.0, 128.7, 128.4, 128.2, 128.0, 126.6, 120.5, 51.5, 43.3, 26.9, 25.9, 22.9, 16.0.

GC/MS (EI, 70 eV): *m*/*z* (%) =326 (6), 172 (21), 155 (100), 128 (7), 115 (20).

ESI-HRMS: *m*/*z* calcd for $C_{24}H_{22}O$: 326.1671; found: 326.1664.

1-(3,7-Dimethylocta-2,6-dien-1-yl)-1,3-dimethylnaphthalen-2-one (19)

The product was prepared according to GP I by using 1,3-dimethyl-2-naphthol and 3,7-dimethylocta-1,6-dien-3-yl isobutyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 16 mg, 0.052 mmol (26%). R_f = 0.45 (PE–EtOAc, 20:1).

IR (film): 2967 (w), 2919 (w), 2854 (w), 1650 (vs), 1441 (w), 1374 (w), 1275 (w), 1031 (w), 968 (w), 906 (w), 753 (vs) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.18 (m, 5 H, ArH), 5.11–4.86 (m, 1 H, olefin-sp^2-CH), 4.69–4.54 (m, 1 H, olefin- sp^2-CH), 2.85–2.67 (m, 1 H, olefin- sp^3-CH_2), 2.49–2.36 (m, 1 H, olefin-sp^3-CH_2), 1.97 (s, 3 H, enone-CH_3), 1.93–1.72 (m, 4 H, 2 × olefin-sp^3-CH_2), 1.71–1.61 (m, 3 H, CH_3), 1.54–1.47 (m, 3 H, CH_3), 1.47–1.34 (m, 6 H, 2 × olefin-CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.3, 145.4, 141.4, 137.9, 132.6, 131.4, 131.2, 130.3, 128.5, 128.2, 126.5, 126.4, 124.3, 124.1, 118.6, 51.4, 42.2, 39.7, 26.9, 25.6, 17.5, 15.9.

GC/MS (EI, 70 eV): *m*/*z* (%) = 308 (1), 172 (100), 128 (5), 81 (6), 69 (14), 41 (4).

ESI-HRMS: *m*/*z* calcd for $C_{22}H_{28}O$: 308.2140; found: 308.2143.

2-[(3,7-Dimethylocta-2,6-dien-1-yl)oxy]-1,3-dimethylnaphthalene (20)

The product was prepared according to GP I by using 1,3-dimethyl-2-naphthol and 3,7-dimethylocta-1,6-dien-3-yl isobutyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 2.3 mg, 0.007 mmol (4%). R_f = 0.54 (PE–EtOAc, 20:1).

IR (film): 2921 (vs), 2851 (s), 1459 (w), 1376 (w), 1237 (w), 1209 (vw), 1177 (w), 1151 (vw), 1102 (w), 1062 (vw), 1028 (vw), 971 (w), 746 (w) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.1 Hz, 1 H, ArH), 7.72 (d, *J* = 8.1 Hz, 1 H, ArH), 7.52 (s, 1 H, ArH), 7.47–7.33 (m, 2 H, ArH), 5.71–5.62 (m, 1 H, olefin-sp^2-CH), 5.16–5.09 (m, 1 H, olefin-sp^2-CH), 4.38 (d, *J* = 6.9 Hz, 2 H, olefin-sp^3-CH_2), 2.62 (s, 3 H, CH_3), 2.47 (s, 3 H, CH_3), 2.22–2.05 (m, 4 H, 2 × olefin-sp^3-CH_2), 1.70 (d, *J* = 3.8 Hz, 6 H, 2 × olefin-CH_3), 1.43 (s, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.0, 141.0, 132.5, 131.8, 131.4, 130.8, 127.5, 127.2, 124.9, 124.4, 123.8, 120.0, 69.9, 39.6, 31.9, 29.7, 26.7, 26.3, 22.3, 17.7, 17.4, 16.5, 14.1, 14.0, 11.7.

GC/MS (EI, 70 eV): *m*/*z* (%) = 308 (1), 172 (100), 128 (5), 81 (4), 69 (11), 41 (3).

ESI-HRMS: *m*/*z* calcd for $C_{22}H_{28}O$ [M + Na]$^+$: 331.2032; found: 331.2016.

1,3-Dimethyl-1-(pent-3-en-2-yl)naphthalen-2-one (21)

The product was prepared according to GP I by using 1,3-dimethyl-2-naphthol and (*E*)-pent-3-en-2-yl isobutyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 4.8 mg, 0.02 mmol (10%). R_f = 0.51 (PE–EtOAc, 20:1).

IR (film): 2969 (w), 2928 (w), 1716 (w), 1649 (s), 1597 (vw), 1503 (vw), 1446 (s), 1373 (s), 1235 (s), 1211 (w), 1178 (s), 1102 (s), 1036 (vs), 964 (vs), 908 (s), 876 (w), 845 (w), 747 (vs), 530 (w) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.26 (m, 2 H, ArH), 7.25–7.17 (m, 3 H, ArH), 5.40–5.26 (m, 1 H, olefin-sp^2-CH), 5.26–5.13 (m, 1 H, olefin-sp^2-CH), 2.58–2.32 (m, 1 H, olefin-sp^3-CH), 2.00–1.93 (m, 3 H, CH_3), 1.66–1.59 (m, 3 H, CH_3), 1.47–1.42 (m, 3 H, CH_3), 0.78–0.66 (m, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.8, 143.8, 141.4, 140.9, 133.4, 131.8, 131.1, 128.1, 127.8, 127.7, 126.7, 126.5, 54.1, 50.4, 49.6, 30.9, 22.4, 17.9, 15.8, 15.0.

GC/MS (EI, 70 eV): *m*/*z* (%) = 240 (14), 172 (100), 157 (8), 128 (5), 69 (10), 41 (5).

ESI-HRMS: *m*/*z* calcd for $C_{17}H_{20}O$: 240.1514; found: 240.1516.

1,3-Dimethyl-2-(pent-3-en-2-yloxy)naphthalene (22)

The product was prepared according to GP I by using 1,3-dimethyl-2-naphthol and (*E*)-pent-3-en-2-yl isobutyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as colorless oil.

Yield: 20.6 mg, 0.09 mmol (43%). R_f = 0.58 (PE–EtOAc, 20:1).

IR (film): 2971 (w), 2927 (w), 1650 (w), 1597 (w), 1503 (w), 1451 (s), 1372 (s), 1235 (vs), 1211 (s), 1178 (vs), 1151 (s), 1101 (vs), 1062 (s), 1036 (vs), 964 (vs), 908 (vs), 876 (vs), 844 (w), 746 (vs), 530 (s) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.3 Hz, 1 H, ArH), 7.70 (d, *J* = 8.3 Hz, 1 H, ArH), 7.49 (s, 1 H, ArH), 7.46–7.31 (m, 2 H, ArH), 5.70–5.59 (m, 1 H, olefin- sp^2-CH), 5.50–5.35 (m, 1 H, olefin-sp^2-CH), 4.45–4.32 (q, *J* = 6.7 Hz, 1 H, olefin- sp^3-CH), 2.55 (s, 3 H, enone-CH_3), 2.41 (s, 3 H, enone-CH_3), 1.60 (dd, *J* = 1.6 Hz, *J* = 6.4 Hz, 3 H, olefin-CH_3), 1.43 (d, *J* = 6.4 Hz, 3 H, olefin-CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.6, 132.6, 132.2, 131.9, 130.6, 127.9, 127.4, 127.2, 125.0, 124.8, 124.2, 123.8, 80.2, 21.1, 18.1, 17.6, 12.8.

GC/MS (EI, 70 eV): *m*/*z* (%) = 240 (10), 172 (100), 157 (3), 128 (6), 69 (9), 41 (4).

ESI-HRMS: *m*/*z* calcd for $C_{17}H_{20}O$: 240.1514; found: 240.1517.

1-(But-2-en-1-yl)-1,3-dimethylnaphthalen-2-one (23)

The product was prepared according to GP I by using 1,3-dimethyl-2-naphthol and but-3-en-2-yl isobutyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 10.3 mg, 0.045 mmol (23%). R_f = 0.38 (PE–EtOAc, 20:1).

IR (film): 3024 (vw), 2967 (w), 2920 (w), 1716 (w), 1649 (vs), 1598 (vw), 1572 (vw), 1488 (vw), 1440 (s), 1373 (s), 1272 (s), 1198 (w), 1025 (s), 966 (vs), 910 (w), 753 (vs), 566 (s), 510 (w) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.29 (m, 2 H, ArH), 7.28–7.19 (m, 3 H, ArH), 5.32–5.16 (m, 1 H, olefin-sp^2-CH), 4.96–4.82 (m, 1 H, olefin-sp^2-CH), 2.75–2.65 (m, 1 H, olefin-sp^3-CH_2), 2.49–2.38 (m, 1 H, olefin-sp^3-CH_2), 1.97 (d, *J* = 1.2 Hz, 3 H, enone-CH_3), 1.49–1.36 (m, 6 H, 1 × enone-CH_3, 1 × olefin-CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.1, 145.3, 141.3, 132.5, 130.2, 128.6, 128.4, 128.3, 126.5, 126.4, 125.5, 51.4, 46.3, 26.1, 17.7, 15.8.

GC/MS (EI, 70 eV): *m*/*z* (%) = 226 (15), 172 (199), 157 (6), 143 (14), 128 (13), 115 (4), 55 (6).

ESI-HRMS: *m*/*z* calcd for $C_{16}H_{18}O$: 226.1358; found: 226.1356.

2-(But-3-en-2-yloxy)-1,3-dimethylnaphthalene (24)

The product was prepared according to GP I by using 1,3-dimethyl-2-naphthol and but-3-en-2-yl isobutyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 17.6 mg, 0.08 mmol (39%). R_f = 0.51 (PE–EtOAc, 20:1).

IR (film): 3067 (w), 2975 (w), 2926 (w), 1597 (vw), 1502 (w), 1456 (w), 1420 (w), 1372 (w), 1236 (vs), 1212 (w), 1178 (s), 1152 (w), 1101 (vs), 1047 (s), 989 (s), 918 (s), 878 (s), 845 (w), 746 (vs), 530 (s) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.0 Hz, 1 H, ArH), 7.70 (d, *J* = 8.0 Hz, 1 H, ArH), 7.50 (s, 1 H, ArH), 7.47–7.32 (m, 2 H, ArH), 6.10–5.93 (m, 1 H, olefin-sp^2-CH), 5.15–5.03 (m, 2 H, olefin-sp^2-CH_2), 4.52–4.40 (q, *J* = 6.5 Hz, 1 H, olefin-sp^3-CH), 2.57 (s, 3 H, enone-CH_3), 2.43 (s, 3 H, enone-CH_3), 1.44 (dd, *J* = 5.3 Hz, *J* = 6.4 Hz, 3 H, olefin-CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.5, 139.1, 132.6, 131.7, 130.7, 127.4, 127.3, 124.9, 124.3, 123.8, 116.2, 80.3, 20.8, 18.1, 12.9.

GC/MS (EI, 70 eV): *m*/*z* (%) = 226 (15), 172 (100), 157 (5), 143 (6), 128 (13), 115 (3), 55 (3).

ESI-HRMS: *m*/*z* calcd for $C_{16}H_{18}O$: 226.1358; found: 226.1355.

1,3-Dimethyl-1-(3-methyl-4-phenylbut-2-en-1-yl)naphthalen-2-one (25)

The product was prepared according to GP I by using 1,3-dimethyl-2-naphthol and isobutyl 2-methyl-1-phenylbut-3-en-2-yl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 6.8 mg, 0.02 mmol (11%). R_f = 0.55 (PE–EtOAc, 20:1).

IR (film): 3060 (vw), 3024 (vw), 2974 (w), 2917 (w), 1648 (vs), 1599 (vw), 1572 (vw), 1492 (w), 1450 (s), 1374 (s), 1275 (w), 1028 (s), 755 (vs), 732 (vs), 698 (vs) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.26 (m, 3 H, ArH), 7.25–7.09 (m, 5 H, ArH), 7.04–6.80 (m, 2 H, ArH), 4.83–4.66 (m, 1 H, olefin-sp^2-CH), 3.04 (s, 2 H, benzyl-CH_2), 2.89–2.76 (m, 1 H, olefin-sp^3-CH_2), 2.55–2.45 (m, 1 H, olefin-sp^3-CH_2), 1.93 (m, 3 H, enone-CH_3), 1.48 (s, 3 H, olefin-CH_3), 1.31 (m, 3 H, enone-CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.2, 145.4, 141.7, 139.9, 136.9, 132.6, 128.6, 128.5, 128.3, 128.2, 128.0, 126.5, 125.7, 121.0, 51.3, 46.0, 42.4, 26.1, 15.9.

GC/MS (EI, 70 eV): *m*/*z* (%) = 316 (5), 172 (100), 145 (13), 128 (4), 91 (5).

ESI-HRMS: *m*/*z* calcd for $C_{23}H_{24}O$ [M + Na]$^+$: 339.1719; found: 339.1712.

1,3-Dimethyl-1-(oct-3-en-2-yl)naphthalen-2-one (26)

The product was prepared according to GP I by using 1,3-dimethyl-2-naphthol and isobutyl oct-2-en-4-yl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 10.3 mg, 0.036 mmol (18%). R_f = 0.40 (PE–EtOAc, 20:1).

IR (film): 2957 (w), 2925 (w), 2871 (w), 1649 (vs), 1453 (s), 1375 (s), 1236 (w), 1102 (vw), 1029 (vw), 965 (s), 907 (w), 752 (vs) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.15 (m, 5 H, ArH), 5.41–4.97 (m, 2 H, 2 × olefin-sp^2-CH), 2.57–2.32 (m, 1 H, olefin-sp^3-CH), 2.00–1.96 (m, 2 H, alkyl-CH_2), 1.95–1.86 (m, 3 H, CH_3), 1.50–1.38 (m, 3 H, CH_3), 1.31–1.17 (m, 4 H, alkyl-CH_2), 0.96–0.83 (m, 3 H, CH_3), 0.81–0.66 (m, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.6, 144.8, 144.0, 141.5, 141.0, 133.5, 133.4, 132.3, 131.5, 130.5, 128.1, 127.8, 127.6, 127.1, 126.5, 54.0, 50.4, 49.7, 32.2, 32.1, 31.6, 22.1, 16.3, 15.8, 15.7, 13.7.

GC/MS (EI, 70 eV): *m*/*z* (%) = 282 (8), 172 (100), 157 (5), 128 (4), 69 (11), 55 (10).

ESI-HRMS: *m*/*z* calcd for $C_{20}H_{26}O$ [M + Na]$^+$: 305.1876; found: 305.1863.

1,3-Dimethyl-2-(oct-2-en-4-yloxy)naphthalene (27)

The product was prepared according to GP I by using 1,3-dimethyl-2-naphthol and isobutyl oct-2-en-4-yl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 18.2 mg, 0.06 mmol (32%). R_f = 0.45 (PE–EtOAc, 20:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.2 Hz, 1 H, ArH), 7.70 (d, *J* = 8.2 Hz, 1 H, ArH), 7.48 (s, 1 H, ArH), 7.45–7.31 (m, 2 H, ArH), 5.65–5.46 (m, 1 H, olefin-sp^2-CH), 5.44–5.21 (m, 1 H, olefin-sp^2-CH), 4.46–4.35 (m, 1 H, olefin-sp^3-CH), 2.56 (s, 3 H, enone-CH_3), 2.46 (s, 3 H, enone-CH_3), 1.93 (q, *J* = 6.4 Hz, 2 H, olefin-CH_2), 1.45 (d, *J* = 6.4 Hz, 3 H, olefin-CH_3), 1.26–1.07 (m, 4 H, 2 × alkyl-CH_2), 0.77 (t, *J* = 7.3 Hz, 3 H, alkyl-CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.6, 133.5, 132.6, 131.8, 130.6, 127.4, 127.1, 125.0, 124.8, 124.2, 123.8, 80.3, 31.7, 30.9, 22.0, 21.2, 18.1, 17.6, 13.8, 12.8.

IR (film): 2955 (w), 2926 (w), 2858 (w), 1651 (w), 1502 (w), 1455 (s), 1374 (s), 1235 (vs), 1211 (w), 1178 (w), 1151 (w), 1102 (s), 1037 (s), 967 (s), 915 (w), 844 (w), 745 (vs), 529 (s) cm^{-1}.

GC/MS (EI, 70 eV): *m*/*z* (%) = 282 (1), 172 (100), 157 (6), 128 (8), 69 (12), 55 (10).

ESI-HRMS: *m*/*z* calcd for $C_{20}H_{26}O$ [M + Na]$^+$: 305.1876; found: 305.1873.

1-Hexyl-3-methyl-1-(3-methylbut-2-en-1-yl)naphthalen-2-one (30)

The product was prepared according to GP I by using 1-hexyl-3-methyl-2-naphthol and 2-methylbut-3-en-2-yl isobutyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 45.7 mg, 0.15 mmol (74%). R_f = 0.51 (PE–EtOAc, 20:1).

IR (film): 3023 (vw), 2954 (s), 2855 (w), 1714 (vw), 1649 (vs), 1441 (s), 1376 (s), 1273 (w), 1196 (w), 1109 (vw), 976 (w), 947 (w), 909 (w), 753 (vs) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.27 (m, 2 H, ArH), 7.25–7.18 (m, 3 H, ArH), 4.60–4.50 (m, 1 H, prenyl-sp^2-CH), 2.81–2.70 (m, 1 H, prenyl-sp^3-CH_2), 2.48–2.35 (m, 1 H, prenyl-sp^3-CH_2), 2.29–2.14 (m, 1 H, alkyl-CH_2), 1.95 (d, *J* = 1.4 Hz, 3 H, enone-CH_3), 1.87–1.73 (m, 1 H, alkyl-CH_2), 1.44 (s, 3 H, prenyl-CH_3), 1.37 (s, 3 H, prenyl-CH_3), 1.22–0.99 (m, 6 H, 3 × alkyl-CH_2), 0.85–0.65 (m, 5 H, alkyl-CH_2 + alkyl-CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.3, 144.3, 141.6, 133.9, 133.4, 131.5, 128.5, 128.2, 126.4, 126.3, 118.4, 55.9, 42.5, 41.6, 31.4, 29.6, 25.6, 24.5, 22.5, 17.7, 15.7, 13.9.

GC/MS (ESI): *m*/*z* (%) = 333 [M + Na$^+$].

ESI-HRMS: *m*/*z* calcd for $C_{22}H_{30}O$ [M + Na]$^+$: 333.2189, found: 333.2172.

3-Bromo-1-methyl-1-(3-methylbut-2-en-1-yl)naphthalen-2-one (31)

The product was prepared according to GP I by using 3-bromo-1-methyl-2-naphthol and 2-methylbut-3-en-2-yl isobutyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 55.8 mg, 0.18 mmol (92%). R_f = 0.18 (PE–EtOAc, 20:1).

IR (film): 2975 (w), 2927 (w), 1734 (w), 1672 (vs), 1608 (w), 1415 (w), 1375 (w), 1347 (w), 1260 (w), 1224 (w), 756 (s) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (s, 1 H, ArH), 7.46–7.36 (m, 2 H, ArH), 7.33–7.36 (m, 2 H, ArH), 4.67–4.57 (m, 1 H, prenyl-sp^2-CH), 2.85–2.74 (m, 1 H, prenyl-sp^3-CH_2), 2.50–2.40 (m, 1 H, prenyl-sp^3-CH_2), 1.53 (s, 3 H, enone-CH_3), 1.50 (s, 3 H, prenyl-CH_3), 1.39 (s, 3 H, prenyl-CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.6, 146.3, 145.3, 135.4, 130.0, 129.9, 128.9, 127.0, 126.8, 122.1, 117.8, 53.9, 42.5, 25.9, 25.6, 17.7.

GC/MS (EI, 70 eV): *m*/*z* (%) = 304 (5), 261 (4), 250 (11), 236 (100), 143 (8), 128 (25), 69 (28), 41 (16).

ESI-HRMS: *m*/*z* calcd for $C_{16}H_{17}BrO$: 304.0463, 306.0444; found: 304.0455, 306.0439.

3-Iodo-1-methyl-1-(3-methylbut-2-en-1-yl)naphthalen-2-one (32)

The product was prepared according to GP I by using 3-iodo-1-methyl-2-naphthol and 2-methylbut-3-en-2-yl isobutyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 8:1) as a colorless oil.

Yield: 46.2 mg, 0.13 mmol (66%). R_f = 0.63 (PE–EtOAc, 8:1).

IR (film) ν 3062 (w), 2970 (w), 2927 (w), 2910 (w), 1665 (vs), 1602 (w), 1555 (w), 1449 (w), 1344 (w), 1300 (w), 1222 (w), 915 (w), 834 (w), 754 (vs), 575 (w) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.17 (s, 1 H, ArH), 7.46–7.37 (m, 2 H, ArH), 7.31–7.21 (m, 2 H, ArH), 4.65–4.56 (m, 1 H, prenyl-sp^2-CH), 2.82–2.71 (m, 1 H, prenyl-sp^3-CH_2), 2.47–2.36 (m, 1 H, prenyl-sp^3-CH_2), 1.53 (s, 3 H, enone-CH_3), 1.50 (s, 3 H, prenyl-CH_3), 1.39 (s, 3 H, prenyl-CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.7, 153.9, 145.8, 135.3, 131.0, 130.2, 128.7, 126.8, 117.9, 101.8, 52.8, 42.7, 34.1, 25.9, 25.7, 17.8.

GC/MS (EI, 70 eV): *m*/*z* (%) = 352 (4), 298 (3), 284 (100), 128 (9), 69 (8), 41 (3).

ESI-HRMS: *m*/*z* calcd for $C_{16}H_{17}IO$: 352.0324; found: 352.0327.

1-Methyl-1-(3-methylbut-2-en-1-yl)-3-phenylnaphthalen-2-one (33)

The product was prepared according to GP I by using 1-methyl-3-phenyl-2-naphthol and 2-methylbut-3-en-2-yl isobutyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 39.4 mg, 0.13 mmol (65%). R_f = 0.45 (PE–EtOAc, 20:1).

IR (film): 3055 (w), 3024 (w), 2969 (w), 2912 (w), 1655 (vs), 1619 (w), 1597 (w), 1490 (w), 1447 (s), 1373 (s), 1358 (s), 1292 (s), 1210 (w), 1157 (w), 1076 (vw), 910 (vw), 755 (vs), 710 (s), 694 (vs), 578 (w), 509 (w) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51–7.45 (m, 3 H, ArH), 7.44–7.27 (m, 7 H, ArH), 4.80–4.72 (m, 1 H, prenyl-sp^2-CH), 2.86–2.76 (m, 1 H, prenyl-sp^3-CH_2), 2.54–2.44 (m, 1 H, prenyl-sp^3-CH_2), 1.55 (s, 3 H, CH_3), 1.51 (s, 3 H, CH_3), 1.40 (s, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.6, 145.7, 142.0, 136.1, 135.4, 134.6, 130.2, 129.5, 129.3, 128.6, 128.1, 127.9, 126.7, 126.5, 118.7, 52.6, 42.2, 25.7, 24.9, 17.8.

GC/MS (EI, 70 eV): *m*/*z* (%) = 302 (1), 287 (3), 234 (100), 205 (5), 69 (6).

ESI-HRMS: *m*/*z* calcd for $C_{22}H_{22}O$ [M + H]$^+$: 303.1743; found: 303.1728.

Dearomatization of 1-Substituted Naphthols Catalyzed by the Iron Complex $Bu_4N[Fe(CO)_3(NO)]$ (TBA[Fe]); General Procedure II (GP II)

A 10 mL Schlenk tube was charged with **L2** (2.1 mg, 0.006 mmol, 0.03 equiv) and MeCN (1 mL). Afterwards KO*t*-Am solution (1.7 M in toluene, 6 μL, 0.01 mmol, 0.05 equiv) was added and the reaction mixture was stirred for 20 min at r.t. Then $Bu_4N[Fe(CO)_3NO]$ (1.1 mg, 0.002 mmol, 0.01 equiv) was added and the mixture was heated for 1 h at 80 °C to coordinate the ligand. At r.t. the carbonate (0.2 mmol, 1 equiv) was added to the mixture, followed by the naphthol (0.2 mmol, 1 equiv) and the co-solvent EtOAc (0.05 mmol). The reaction mixture was stirred for 18 h at 60 °C. After filtration through a silica plug (Et_2O), the crude product was purified by column chromatography.

1-Methyl-1-(3-methyl-5-phenylpent-2-en-1-yl)naphthalen-2-one (13)

The product was prepared according to GP II by using 1-methyl-2-naphthol and isobutyl 3-methyl-5-phenylpent-1-en-3-yl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 34.3 mg, 0.10 mmol (54%). R_f = 0.28 (PE–EtOAc, 20:1).

IR (film): 3061 (vw), 3025 (vw), 2970 (vw), 2929 (vw), 1655 (vs), 1620 (vw), 1599 (vw), 1564 (w), 1494 (w), 1452 (w), 1396 (w), 834 (w), 755 (s), 699 (s) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–727 (m, 6 H, ArH), 7.25–7.11 (m, 3 H, ArH), 7.08–7.02 (m, 1 H, ArH), 6.16–6.13 (dd, *J* = 2.9 Hz, *J* = 9.8 Hz, 1 H, ArH), 4.74–4.60 (m, 1 H, olefin-sp^2-CH), 2.81–2.69 (m, 1 H, olefin-sp^3-CH_2), 2.57–2.31 (m, 2 H, CH_2), 2.25–2.03 (m, 1 H, olefin-sp^3-CH_2), 1.52 (d, *J* = 1.3 Hz, 2 H, CH_2), 1.47–1.40 (m, 6 H, 2 × CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.3, 144.8, 142.2, 129.8, 129.2, 128.3, 128.2, 126.8, 126.7, 126.6, 125.7, 125.6, 125.3, 119.1, 51.8, 41.7, 41.4, 34.5, 34.0, 33.8, 25.4, 23.3, 16.2.

GC/MS (EI, 70 eV): *m*/*z* (%) = 316 (9), 173 (3), 158 (100), 128 (5), 91 (27), 55 (1).

ESI-HRMS: *m*/*z* calcd for $C_{23}H_{24}O$ [M + Na]$^+$: 339.1711; found: 339.1719.

1-(2,3-Dimethylbut-2-en-1-yl)-1-methylnaphthalen-2-one (14)

The product was prepared according to GP II by using 1-methyl-2-naphthol and 2,3-dimethylbut-3-en-2-yl isobutyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 6 mg, 0.025 mmol (12%). R_f = 0.32 (PE–EtOAc, 20:1).

IR (film): 2961 (w), 2924 (w), 1720 (w), 1260 (s), 1085 (s), 1018 (vs), 798 (vs) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.31 (m, 3 H, ArH), 7.30–7.24 (m, 2 H, ArH), 6.15 (d, *J* = 9.8 Hz, 1 H, ArH), 2.87 (d, *J* = 13.6 Hz, 1 H, olefin-sp^3-CH_2), 2.57 (d, *J* = 1 Hz, 1 H, olefin-sp^3-CH_2), 1.52 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 1.18 (s, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.4, 146.0, 144.3, 129.6, 129.3, 129.2, 128.7, 127.2, 126.5, 125.2, 123.6, 52.4, 47.8, 25.6, 20.7, 20.6, 19.5.

GC/MS (EI, 70 eV): *m*/*z* (%) = 240 (7), 158 (100), 128 (6), 83 (9), 55 (6).

ESI-HRMS: *m*/*z* calcd for $C_{17}H_{20}O$: 240.1514; found: 240.1521.

2-[(2,3-Dimethylbut-3-en-2-yl)oxy]-1-methylnaphthalene (15)

The product was prepared according to GP II by using 1-methyl-2-naphthol and 2,3-dimethylbut-3-en-2-yl isobutyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 30.5 mg, 0.13 mmol (63%). R_f = 0.64 (PE–EtOAc, 20:1).

IR (film): 3402 (b), 2974 (s), 2864 (w), 1719 (vs), 1594 (w), 1509 (w), 1466 (s), 1376 (s), 1244 (s), 1132 (s), 1082 (s), 901 (w), 831 (w), 810 (w), 755 (s), 528 (w) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.5 Hz, 1 H, ArH), 7.75 (d, *J* = 8.0 Hz, 1 H, ArH), 7.54 (d, *J* = 9.1 Hz, 1 H, ArH), 7.50–7.43 (m, 1 H, ArH), 7.37–7.30 (m, 1 H, ArH), 7.27 (d, *J* = 9.2 Hz, 1 H, ArH), 5.02 (s, 1 H, olefin-sp^2-CH_2), 4.99–4.96 (m, 1 H, olefin-sp^2-CH_2), 2.57 (s, 3 H, enone-CH_3), 1.97 (s, 3 H, CH_3), 1.49 (s, 6 H, 2 × CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 251.1, 129.5, 128.1, 126.0, 125.7, 123.7, 123.5, 120.2, 110.8, 81.4, 27.1, 19.1, 11.6.

GC/MS (EI, 70 eV): *m*/*z* (%) = 241 (6), 171 (100), 157 (78), 143 (48), 128 (10), 99 (6).

ESI-HRMS: *m*/*z* calcd for $C_{17}H_{20}O$ [M + H]$^+$: 241.1589; found: 241.1587.

1-(But-2-en-1-yl)-1-methylnaphthalen-2-one (16)

The product was prepared according to GP II by using 1-methyl-2-naphthol and but-3-en-2-yl isobutyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 6.2 mg, 0.027 mmol (14%). R_f = 0.32 (PE–EtOAc, 20:1).

IR (film): 3025 (w), 2968 (w), 2931 (w), 1719 (vw), 1652 (vs), 1620 (w), 1596 (vw), 1564 (w), 1448 (w), 1396 (w), 1375 (vw), 1298 (vw), 1238 (w), 1207 (w), 966 (s), 834 (s), 755 (vs) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.36 (m, 3 H, ArH), 7.34–7.27 (m, 2 H, ArH), 6.14 (d, *J* = 9.8 Hz, 1 H, ArH), 5.32–5.18 (m, 1 H, olefin-sp^2-CH), 5.00–4.85 (m, 1 H, olefin-sp^2-CH), 2.80–2.68 (m, 1 H, olefin-sp^3-CH_2), 2.51–2.41 (m, 1 H, olefin-sp^3-CH_2), 1.46–1.40 (m, 6 H, 2 × CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.1, 146.0, 144.9, 129.8, 129.7, 129.3, 128.6, 126.7, 126.6, 125.3, 125.2, 51.8, 45.9, 26.2, 17.8.

GC/MS (EI, 70 eV): *m*/*z* (%) = 212 (16), 158 (100), 129 (11), 55 (7).

ESI-HRMS: *m*/*z* calcd for $C_{15}H_{16}O$ [M + Na]$^+$: 235.1093; found: 235.1079.

1-Methyl-1-(3-methylbut-2-en-1-yl)naphthalen-2-one (28)

The product was prepared according to GP II by using 1-methyl-2-naphthol and 2-methylbut-3-en-2-yl isobutyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 37.1 mg, 0.16 mmol (82%). R_f = 0.28 (PE–EtOAc, 20:1).

IR (film): 3306 (w), 2969 (w), 2912 (w), 1652 (vs), 1564 (w), 1448 (w), 1396 (vw), 1375 (vw), 1229 (vw), 1239 (vw), 1207 (vw), 835 (s), 755 (vs) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.35 (m, 3 H, ArH), 7.33–7.27 (m, 2 H, ArH), 6.14 (d, *J* = 9.9 Hz, 1 H, ArH), 4.69–4.60 (m, 1 H, prenyl-sp^2-CH), 2.82–2.72 (m, 1 H, prenyl-sp^3-CH_2), 2.50–2.39 (m, 1 H, prenyl-sp^3-CH_2), 1.49 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 1.40 (s, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.3, 146.1, 144.9, 134.5, 129.8, 129.7, 129.3, 126.7, 126.5, 125.2, 118.6, 51.8, 41.6, 25.7, 25.6, 17.7.

GC/MS (EI, 70 eV): *m*/*z* (%) = 226 (13), 211 (5), 195 (2), 181 (4), 165 (1), 158 (100), 141 (3), 128 (14), 115 (4), 83 (1), 69 (11), 41 (9).

ESI-HRMS: *m*/*z* calcd for $C_{16}H_{18}O$: 226.1352; found: 226.1364.

1-Hexyl-1-(3-methylbut-2-en-1-yl)naphthalen-2-one (29)

The product was prepared according to GP II by using 1-hexyl-2-naphthol and 2-methylbut-3-en-2-yl isobutyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 32.4 mg, 0.11 mmol (54%). R_f = 0.43 (PE–EtOAc, 20:1).

IR (film): 2955 (w), 2924 (s), 2855 (w), 1654 (vs), 1621 (w), 1564 (w), 1450 (w), 1396 (vw), 1377 (vw), 1236 (w), 827 (s), 755 (vs) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.38 (m, 3 H, ArH), 7.33–7.26 (m, 2 H, ArH), 6.15 (d, *J* = 9.9 Hz, 1 H, ArH), 4.63–4.53 (m, 1 H, prenyl-sp^2-CH), 2.83–2.72 (m, 1 H, prenyl-sp^3-CH_2), 2.49–2.37 (m, 1 H, prenyl-sp^3-CH_2), 2.19–2.25 (m, 1 H, alkyl-CH_2), 1.90–1.77 (m, 1 H, alkyl-CH_2), 1.44 (s, 3 H, prenyl-CH_3), 1.38 (s, 3 H, prenyl-CH_3), 1.23–1.00 (m, 6 H, 3 × alkyl-CH_2), 0.97–0.83 (m, 2 H, alkyl-CH_2), 0.78 (t, *J* = 7.3 Hz, 3 H, alkyl-CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.5, 145.1, 145.0, 134.2, 131.0, 129.7, 129.2, 126.6, 126.4, 126.2, 118.2, 56.2, 42.4, 41.7, 31.4, 29.6, 25.6, 24.4, 22.5, 17.7, 13.9.

GC/MS (EI, 70 eV): *m*/*z* (%) = 297 (100), 241 (60), 229 (5), 213 (6), 171 (6), 157 (12), 145 (3).

ESI-HRMS: *m*/*z* calcd for $C_{21}H_{28}O$ [M + H]$^+$: 297.2213; found: 297.2223.

Dearomatization of 6-Substituted Naphthols Catalyzed by the Iron Complex $Bu_4N[Fe(CO)_3(NO)]$ (TBA[Fe]); General Procedure III (GP III)

A 10 mL Schlenk tube was charged with **L2** (8.0 mg, 0.024 mmol, 0.12 equiv) and MeCN (1 mL). Afterwards KO*t*-Am solution (1.7 M in toluene, 19 µL, 0.032 mmol, 0.16 equiv) was added and the reaction mixture was stirred for 20 min at r.t. Then $Bu_4N[Fe(CO)_3NO]$ (8.2 mg, 0.02 mmol, 0.1 equiv) was added and the mixture was heated for 1 h at 80 °C to coordinate the ligand. At r.t. the carbonate (0.4 mmol, 2 equiv) was added to the mixture, followed by the naphthol (0.2 mmol, 1 equiv). The reaction mixture was stirred for 18 h at 100 °C. After filtration through a silica plug (Et_2O), the crude product was purified by column chromatography.

6-Methyl-1,1-bis(3-methylbut-2-en-1-yl)naphthalen-2-one (34)

The product was prepared according to GP III by using 6-methyl-2-naphthol and 2-methylbut-3-en-2-yl isobutyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 47.1 mg, 0.16 mmol (80%). R_f = 0.39 (PE–EtOAc, 20:1).

IR (film): 2968 (w), 2912 (w), 2857 (vw), 1652 (vs), 1564 (w), 1438 (s), 1376 (s), 1219 (w), 824 (vs) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.26 (m, 2 H, ArH), 7.22–7.16 (m, 1 H, ArH), 7.09 (s, 1 H, ArH), 6.09 (d, *J* = 9.83 Hz, 1 H, ArH), 4.62–4.52 (m, 2 H, 2 × prenyl-sp^2-CH), 2.91–2.78 (m, 2 H, 2 × prenyl-sp^3-CH_2), 2.52–2.41 (m, 2 H, 2 × prenyl-sp^3-CH_2), 2.37 (s, 3 H, CH_3), 1.45 (s, 12 H, 4 × prenyl-CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.3, 145.1, 140.6, 135.9, 133.9, 130.8, 130.4, 129.7, 126.9, 126.0, 118.7, 56.0, 40.4, 26.9, 25.6, 20.8, 17.9.

GC/MS (EI, 70 eV): *m*/*z* (%) = 294 (11), 226 (80), 209 (7), 183 (12), 171 (100), 141 (5), 69 (14), 41 (10).

ESI-HRMS: *m*/*z* calcd for $C_{21}H_{26}O$ [M + Na]$^+$: 317.1876; found: 317.1878.

6-Bromo-1,1-bis(3-methylbut-2-en-1-yl)naphthalen-2-one (35)

The product was prepared according to GP III by using 6-bromo-2-naphthol and 2-methylbut-3-en-2-yl isobutyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 51.5 mg, 0.14 mmol (72%). R_f = 0.43 (PE–EtOAc, 20:1).

IR (film): 2968 (w), 2911 (w), 2856 (vw), 1655 (vs), 1586 (vw), 1551 (w), 1482 (w), 1489 (s), 1375 (s), 1320 (vw), 1288 (vw), 1231 (s), 1198 (s), 1121 (vw), 1105 (vw), 1082 (w), 873 (s), 819 (vs), 686 (w), 581 (w), 555 (w), 460 (w) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49 (dd, *J* = 2.2 Hz, *J* = 8.3 Hz, 1 H, ArH), 7.42 (d, *J* = 2.2 Hz, 1 H, ArH), 7.30–7.24 (m, 2 H, ArH), 6.14 (d, *J* = 9.8 Hz, 1 H, ArH), 4.60–4.50 (m, 2 H, 2 × prenyl-sp^2-CH), 2.92–2.78 (m, 2 H, 2 × prenyl-sp^3-CH_2), 2.53–2.38 (m, 2 H, 2 × prenyl-sp^3-CH_2), 1.45 (d, *J* = 7.0 Hz, 12 H, 4 × prenyl-CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 203.3, 143.4, 143.3, 134.5, 132.9, 132.1, 131.6, 128.8, 127.1, 120.1, 118.1, 56.3, 40.3, 25.6, 17.9.

GC/MS (EI, 70 eV): *m*/*z* (%) = 358 (15), 290 (98), 235 (100), 195 (40), 168 (24), 152 (9), 128 (9), 83 (7), 69 (62), 41 (26).

ESI-HRMS: *m*/*z* calcd for $C_{20}H_{23}BrO$ [M + Na]$^+$: 381.0824, 383.0806; found: 381.0822, 383.0806.

tert-Butyl 5,5-Bis(3-methylbut-2-en-1-yl)-6-oxo-5,6-dihydronaphthalene-2-carboxylate (36)

The product was prepared according to GP III by using 6-*tert*-butoxycarbonyl-2-naphthol and 2-methylbut-3-en-2-yl isobutyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 10:1) as a colorless oil.

Yield: 11.5 mg, 0.03 mmol (19%). R_f = 0.72 (PE–EtOAc, 10:1).

IR (film): 2973 (w), 2928 (w), 1713 (vs), 1658 (vs), 1624 (w), 1452 (w), 1368 (s), 1293 (vs), 1256 (w), 1229 (s), 1203 (vw), 1162 (vs), 1125 (s), 1107 (s), 916 (vw), 848 (w), 827 (w), 761 (w) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99 (dd, *J* = 6.4 Hz, *J* = 8.2 Hz, 1 H, ArH), 7.90 (d, *J* = 1.8 Hz, 1 H, ArH), 7.48–7.39 (m, 2 H, ArH), 6.17 (d, *J* = 9.9 Hz, 1 H, ArH), 4.58–4.49 (m, 2 H, 2 × prenyl-sp^2-CH), 2.95–2.84 (m, 2 H, 2 × prenyl-sp^3-CH_2), 2.58–2.44 (m, 2 H, 2 × prenyl-sp^3-CH_2), 1.62 (s, 9 H, ^{t}Bu-CH_3), 1.44 (s, 12 H, 4 × prenyl-CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 203.4, 165.1, 149.3, 144.3, 134.5, 131.0, 130.4, 130.1, 130.0, 127.1, 126.7, 118.1, 81.4, 56.7, 40.5, 28.2, 25.6, 17.9.

GC/MS (EI, 70 eV): *m*/*z* (%) =380 (15), 312 (40), 256 (97), 239 (19), 201 (100), 69 (27), 57 (12), 41 (22).

ESI-HRMS: *m*/*z* calcd for $C_{25}H_{32}O_3$ [M + Na]$^+$: 403.2244, found: 403.2245.

Intramolecular Dearomatization Catalyzed by the Iron Complex $Bu_4N[Fe(CO)_3(NO)]$ (TBA[Fe]); General Procedure VII (GP VII)

A 10 mL Schlenk tube was charged with **L2** (8.0 mg, 0.024 mmol, 0.12 equiv) and MeCN (1 mL). Afterwards KO*t*-Am solution (1.7 M in toluene, 16 µL, 0.028 mmol, 0.14 equiv) was added and the reaction mixture was stirred for 20 min at r.t. Then $Bu_4N[Fe(CO)_3NO]$ (8.2 mg, 0.02 mmol, 0.1 equiv) was added and the mixture was heated for 1 h at 80 °C to coordinate the ligand. At r.t. the naphthol (0.2 mmol, 1 equiv) was added. The reaction mixture was stirred for 18 h at 100 °C. After filtration through a silica plug (Et_2O), the crude product was purified by column chromatography.

1-Allyl-1,3-dimethylnaphthalen-2-one (38)

The product was prepared according to GP VII by using allyl 1,3-dimethyl-2-naphthyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 27.5 mg, 0.13 mmol (65%). R_f = 0.43 (PE–EtOAc, 20:1).

IR (film): 3070 (vw), 2976 (vw), 2922 (vw), 1649 (vs), 1438 (w), 1371 (w), 1275 (w), 1199 (vw), 1026 (w), 992 (w), 912 (s), 754 (vs), 738 (s), 657 (vw), 631 (vw), 494 (w) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.29 (m, 2 H, ArH), 7.26–7.21 (m, 3 H, ArH), 5–34–5.19 (m, 1 H, allyl-sp^2-CH), 4.86–4.74 (m, 2 H, allyl-sp^3-CH_2), 2.87–2.77 (m, 1 H, allyl-sp^3-CH_2), 2.58–2.48 (m, 1 H, allyl-sp^3-CH_2), 1.98 (d, *J* = 1.3 Hz, 3 H, enone-CH_3), 1.45 (s, 3 H, enone-CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 203.7, 145.0, 141.5, 133.2, 132.5, 130.2, 128.7, 128.5, 126.6, 126.4, 117.6, 51.1, 47.1, 26.7, 15.8.

GC/MS (EI, 70 eV): *m*/*z* (%) = 212 (51), 197 (5), 171 (100), 143 (56), 128 (45), 115 (14).

ESI-HRMS: *m*/*z* calcd for $C_{15}H_{16}O$ [M + Na]$^+$: 235.1092; found: 235.1105.

1-Allyl-1-methylnaphthalen-2-one (40)

The product was prepared according to GP VII by using allyl 1-methyl-2-naphthyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 10.8 mg, 0.06 mmol (28%). R_f = 0.25 (PE–EtOAc, 20:1).

IR (film): 2974 (vw), 1716 (vw), 1655 (vw), 952 (s), 835 (vw), 757 (vw), 707 (vs), 676 (vs) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.38 (m, 3 H, ArH), 7.34–7.27 (m, 2 H, ArH), 6.16 (d, *J* = 10.0 Hz, 1 H, ArH), 5.39–5.22 (m, 1 H, allyl-sp^2-CH), 4.88–4.75 (m, 2 H, allyl-sp^3-CH_2), 2.90–2.80 (m, 1 H, allyl-sp^3-CH_2), 2.60–2.50 (m, 1 H, allyl-sp^3-CH_2), 1.46 (s, 3 H, enone-CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 203.7, 145.7, 145.0, 133.0, 129.9, 129.7, 129.4, 126.76, 126.72, 125.2, 117.9, 51.5, 46.7, 26.7.

GC/MS (EI, 70 eV): *m*/*z* (%) = 198 (84), 183 (8), 170 (23), 157 (100), 143 (53), 129 (67), 115 (12).

ESI-HRMS: *m*/*z* calcd for $C_{14}H_{14}O$ [M + Na]$^+$: 221.0937; found: 221.0932.

2-(Allyloxy)-1-methylnaphthalene (41)

The product was prepared according to GP VII by using allyl 1-methyl-2-naphthyl carbonate and obtained after purification by column chromatography (silica gel, PE–EtOAc, 20:1) as a colorless oil.

Yield: 17.4 mg, 0.09 mmol (44%). R_f = 0.49 (PE–EtOAc, 20:1).

IR (film): 2921 (vw), 2862 (vw), 1624 (w), 1594 (w), 1510 (w), 1468 (w), 1382 (vw), 1337 (vw), 1261 (s), 1243 (vs), 1218 (vs), 1180 (vw), 1147 (w), 1087 (s), 1020 (s), 989 (s), 920 (s), 799 (vs), 769 (s), 742 (vs), 701 (w), 522 (w), 416 (w) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.8 Hz, 1 H, ArH), 7.77 (d, *J* = 8.2 Hz, 1 H, ArH), 7.68 (d, *J* = 9.1 Hz, 1 H, ArH), 7.52–7.43 (m, 1 H, ArH), 7.40–7.30 (m, 1 H, ArH), 7.22 (d, *J* = 8.9 Hz, 1 H, ArH), 6.19–6.03 (m, 1 H, allyl-sp^2-CH), 5.51–5.23 (m, 2 H, allyl-sp^3-CH_2), 4.65 (dt, *J* = 1.5 Hz, 5.3 Hz, 2 H, allyl-sp^2-CH_2), 2.58 (s, 3 H, enone-CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.4, 133.8, 133.7, 129.2, 128.3, 127.0, 126.0, 123.5, 123.4, 120.1, 117.1, 115.4, 70.5, 10.7.

GC/MS (EI, 70 eV): *m*/*z* (%) = 198 (92), 157 (100), 129 (38).

ESI-HRMS: *m*/*z* calcd for $C_{14}H_{14}O$: 198.1045; found: 198.1047.

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Supporting Information

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