Regioselective Mg-Promoted C-Acylation of Stilbene and Acenaphthylene Derivatives

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Abstract: Treatment of stilbene and acenaphthylene derivatives with Mg turnings in the presence of aliphatic acid anhydrides and trimethylsilyl chloride (TMSCl) in *N*,*N*-dimethylformamide (DMF) brought about a facile and efficient cross-coupling to give C-acylation products in moderate to good yields. The reaction may be initiated by electron transfer from magnesium to the carbon-carbon double bonds of the substrates to generate the corresponding anionic species which are subsequently subjected to regioselective electrophilic acylation with acid anhydrides.

Key words: acylation, electron transfer, magnesium, cross-coupling, regioselectivity

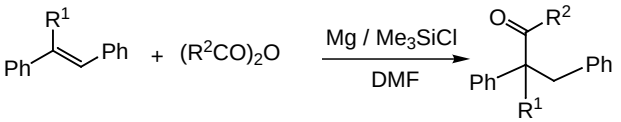
Introduction of an acyl group to the carbon-carbon double bonds of aromatic olefins may be useful and valuable in organic synthesis since the acylated products, benzyl alkyl ketones, are often used as potent synthetic intermediates of important specialty chemicals such as pharmaceutical drugs and agrochemicals.[2] Electrochemical acylation[3,4] has been reported as a hitherto known method for this purpose although its synthetic utility has been considerably limited owing to use of special equipment, much difficulty in scale-up under the controlled potential electrolysis condition, troublesome procedure and unsatisfactory yield. On the other hand, we have demonstrated selective electrochemical[5] and Mg-promoted carbon-acylation[6] of aromatic α,β-unsaturated systems to give those products as would be formed by nucleophilic attack of a difficult-to-generate acyl anion to the electron-deficient carbon-carbon double bonds.

In this study, we wish to report facile Mg-promoted C-acylation of stilbene and acenaphthylene derivatives to give the corresponding benzyl alkyl ketones in moderate to good yields. This reaction may be characterized with simple procedure, mild conditions, unusual regioselectivity, good yields, easy availability and non-polluted feature of Mg metal.

Mg-promoted reductive cross-coupling took place quite smoothly by treatment of stilbenes (**1a**,**b**) and acenaphthylenes (**5a**,**b**) with Mg turnings[7] in the presence of aliphatic acid anhydrides (**2a**–**d**) and trimethylsilyl chloride (TMSCl) in *N*,*N*-dimethylformamide (DMF) at 15–20 °C or -10 to 10 °C, giving the corresponding C-acylation products (**3a**–**d**, **4a**–**d**, **6a**–**c** and **7a**–**c**) in moderate to good yields, respectively, as shown in Tables 1 and 2.[8] It may be noteworthy that no addition of water into the reaction mixture resulted in much decrease in yield of the C-acylated products and formation of much tarry material.[13] Thus, in the case of **3a**, the yield was decreased from 73% to 44%. Increase in the carbon-number of acid anhydrides (**2a**–**d**) led to some decrease in yield of the products (**3a**–**d**), indicating some importance of steric hindrance in the present reaction.

Introduction of a methyl group to the either of the olefinic carbon atoms of the starting substrates **1** and **5** unexpectedly showed unusual regioselectivity of C-acylation. Thus, the reaction of α-methylstilbene (**1b**) and 1-methylacenaphtylene (**5b**) gave 2-acyl-1,2-diphenylpropanes (**4a**–**d**) and 1-acyl-1-methylacenaphthenes (**7a**–**c**) as the main products, respectively, with no formation of the corresponding regioisomers, 1-acyl-1,2-diphenylpropanes (**8a**–**d**) and 1-acyl-2-methylacenaphthenes (**9a**–**c**), as

Table 1 Mg-Promoted Cross-Coupling of Stilbene with Acid Anhydrides



1a,b **2a-d** **3a-d, 4a-d**

Entry	R^1 of **1a**,**b**	R^2 of **2a**,**b**	Conv. (%)	Product (%)[a] **3a–d** or **4a–d**
1	**1a**: H	**2a**: CH_3	100	**3a**: 73
2	**1a**: H	**2b**: C_2H_5	100	**3b**: 60
3	**1a**: H	**2c**: *n*-C_3H_7	100	**3c**: 59
4	**1a**: H	**2d**: $(CH_3)_2CH$	100	**3d**: 61
5	**1b**: CH_3	**2a**: CH_3	35	**4a**: 15 (43)[b]
6	**1b**: CH_3	**2b**: C_2H_5	38	**4b**: 30 (79)[b]
7	**1b**: CH_3	**2c**: *n*-C_3H_7	37	**4c**: 22 (59)[b]
8	**1b**: CH_3	**2d**: $(CH_3)_2CH$	40	**4d**: 21 (53)[b]

Reaction conditions: Substrate (10 mmol), Acid anhydride (10 equiv-mol), Mg (4 equiv mol), H_2O (0.56 equiv mol), DMF (60 mL), Temp. 15~20 °C, 15 h, under N_2 atmosphere.
[a] GC Yield.
[b] Yield based on the consumed starting substrates.

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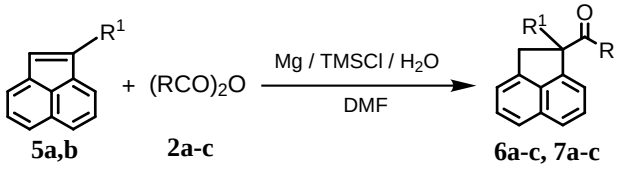
shown in Tables 1 (entries 5–8) and 2 (entries 4–6). This unusual regioselectivity in the exclusive acylation of more sterically hindered carbon atoms may suggest specific reactivity and behaviors of the anionic species, generated through electron transfer from Mg metal.[14]

Table 2 Mg-Promoted Acylation of Acenaphthylene with Acid Anhydrides



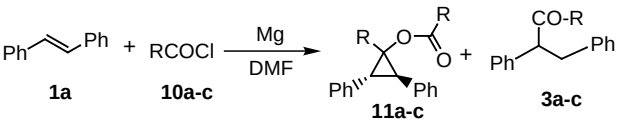
5a,b **2a-c** **6a-c, 7a-c**

Entry	R^1	R	Product (%)[a]
1	**5a**: H	**2a**: CH_3	**6a**: 70
2	**5a**: H	**2b**: C_2H_5	**6b**: 57
3	**5a**: H	**2c**: *n*-C_3H_7	**6c**: 53
4	**5b**: CH_3	**2a**: CH_3	**7a**: 87 (80)[b]
5	**5b**: CH_3	**2b**: C_2H_5	**7b**: 76 (74)[b]
6	**5b**: CH_3	**2c**: *n*-C_3H_7	**7c**: 72 (66)[b]

Reaction conditions: Substrate (10 mmol), Acid anhydride (10 equiv mol), Mg (4 equiv mol), H_2O (0.56 equiv mol), DMF (60 mL), Temp. –10 to 10 °C, 3 h, under N_2 atmosphere.
[a] GC Yield.
[b] Isolated Yield.

Furthermore, use of acid chlorides (**10a**–**c**) instead of a combination reagent of acid anhydride and TMSCl in this reductive cross-coupling of stilbene (**1a**) brought about novel tandem intramolecular cyclization to form the corresponding cyclopropanol esters (**11a**–**c**) as well as normal acylated products (**3a**–**c**) although the yield was not so good, as shown in Table 3.[15]

Table 3 Mg-Promoted Tandem C-Acylation-Cyclization of Stilbene

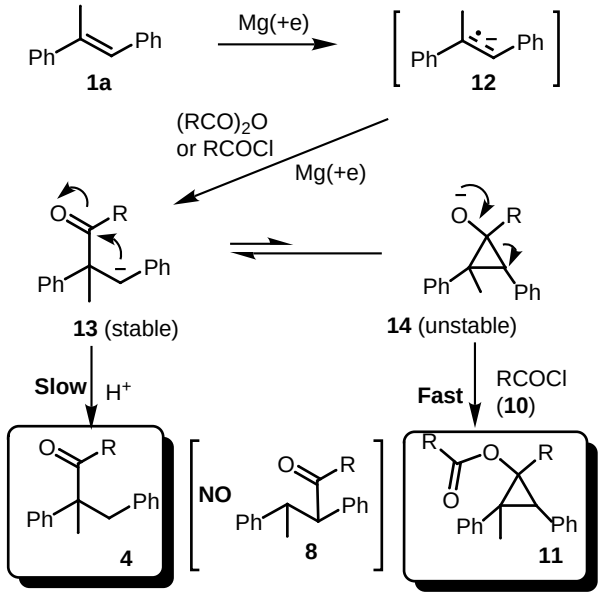


1a **10a-c** **11a-c** **3a-c**

			Product (%)[a]	
Entry	R in **10a-c**	Conv. (%)	**11a–c**	**3a–c**
1	**10a**: CH_3	100	**11a**: 48	**3a**: 13
2	**10b**: C_2H_5	84	**11b**: 36	**3b**: 8
3	**10c**: *n*-C_3H_7	87	**11c**: 34	**3c**: 8

Reaction conditions: Substrate (10 mmol), Acid chloride (20 equiv mol), Mg (12 equiv mol), H_2O (2 equiv mol), DMF (60 mL), Temp: 15–20 °C, 15 h, under N_2 atmosphere.
[a] GC Yield.

From reduction potential of stilbene (**1a** : Ep = –2.35 V vs Ag/AgCl), α-methylstilbene(**1b**: Ep = –2.49 V), acid anhydrides (**2a**–**d**: no peak at 0 → –3.00 V), and TMSCl (no peak at 0 → –3.00 V) in cyclic voltammetry, the present reaction may be initiated by one electron transfer from Mg metal to aromatic olefins to generate the corresponding anion radicals **12**, which are subjected to electrophilic acylation in a regioselective manner. Subsequent fast second electron transfer to **12** may give stable benzyl anions **13** which may relatively slowly react with acid anhydrides to afford the normal C-acylated products **3**, and be in equilibrium with unstable cyclopropanol anions **14**, which are trapped very fast with more reactive acid chlorides **10**, forming cyclopropanol esters **11**, as shown in Scheme.



Scheme Proposed reaction mechanism

In conclusion, Mg-promoted reduction of stilbene and acenaphthylene derivatives in the presence of acid anhydrides and TMSCl brought about versatile and efficient C-acylation possessing unusual regioselectivity, which may provide a facile methods for introduction of acyl group on an aromatic carbon-carbon double bond. Use of acid chloride as the acylating agent led to convenient formation of difficult-to-prepare cyclopropanol esters in a one pot procedure.

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(7) Commercially available Mg turnings for Grignard reaction was used without any pre-treatment.
(8) Typical procedure is as follows: Into a *N*,*N*-dimethylformamide (DMF, 20 mL) solution containing commercially available Mg turnings (40 mmol) for Grignard reaction and H_2O (5.6 mmol) was added dropwise a DMF solution (40 mL) of stilbene (**1a**, 10 mmol), trimethylsilyl chloride (TMSCl, 20 mmol), and acid anhydride(**2a**–**d**: 100 mmol) at 15–20 °C with magnetic stirring under nitrogen atmosphere during a period of 45 min. After the addition, the mixture was stirred at room temperature overnight. Treatment of the reaction mixture according to usual work-up gave 2-acyl-1,2-diphenylethanes (**3a**–**d**) in 73–59% yields accompanying a small amount (4–9%yield) of dibenzyl as a by-product. The products, **3,4-diphenyl-2-butanone**(**3a**),[3a] **1,2-diphenyl-3-pentanone**(**3b**),[9] **4-methyl-1,2-diphenyl-3-pentanone**(**3d**),[10] **3-methyl-3,4-diphenyl -2-butanone**(**4a**),[11] **2-methyl-1,2-diphenyl-3-pentanone**(**4b**),[12] and **1-acetylacenaphthene**(**6a**)[3a] were identified by comparison of their gas chromatography and spectroscopic behaviors with those of their authentic samples. The other products were characterized by spectroscopic methods (^{1}H- and ^{13}C NMR, IR, MASS) and elemental analysis.

1,2-Diphenyl-3-hexanone(**3c**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.71 (t, *J* = 7.6 Hz, 3 H), 1.39–1.50 (m, 2 H), 2.17–2.35 (m, 2 H), 2.90 (dd, *J* = 7.3 Hz, *J* = 13.7 Hz, 1 H), 3.42 (dd, *J* = 7.3 Hz, 13.7 Hz, 1 H), 3.91 (t, *J* = 7.3 Hz, 1 H) and 7.03–7.35 (m, 10 H) ppm. ^{13}C NMR ($CDCl_3$) δ 13.43, 17.01, 38.69, 44.28, 60.82, 126.05, 127.24, 128.21, 128.33, 128.79, 128.99, 138.59, 139.82 and 209.77 ppm.. IR(neat): 3010, 2960, 1720, 1600, 1490, 1450, 1380 and 1110 cm^{-1}. EI–MS: *m/z* 252 (M^+). Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.25; H, 8.01.

2-Methyl-1,2-diphenyl-3-hexanone(**4c**): ^{1}H NMR (400M Hz, $CDCl_3$) δ 0.77 (t, *J* = 7.3 Hz, 3 H), 1.41 (s, 3 H), 1.48–1.58 (m, 2 H), 2.14–2.25 (m, 2 H), 3.17 (d, *J* = 13.7 Hz, 1 H), 3.22 (d, *J* = 13.7 Hz, 1 H) and 6.65–7.33 (m, 10 H) ppm. ^{13}C NMR ($CDCl_3$) δ 13.63, 17.73, 19.89, 40.06, 44.39, 56.35, 125.97, 126.94, 127.02, 127.46, 128.44, 130.53, 137.84, 141.76 and 212.49 ppm.. IR(neat): 3020, 2950, 1710, 1590, 1490, 1450, 1380 and 1120 cm^{-1}. EI–MS: *m/z* 266 (M^+). Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.43; H, 8.45.

2,4-Dimethyl-1,2-diphenyl-3-pentanone(**4d**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (d, *J* = 6.8 Hz, 3 H), 1.02 (d, *J* = 6.8 Hz, 3 H), 1.45 (s, 3 H), 2.65 (sept, *J* = 6.8 Hz, 1 H), 3.16 (d, *J* = 13.7 Hz, 1 H), 3.22 (d, *J* = 13.7 Hz, 1 H) and 6.61–7.36 (m, 10 H) ppm. ^{13}C NMR ($CDCl_3$) δ 19.23, 21.02, 21.17, 36.26, 44.27, 56.94, 125.92, 127.09, 127.46, 127.49, 128.37, 130.53, 137.94, 140.71 and 216.99 ppm. IR(neat): 3020, 2960, 1720, 1600, 1490, 1450, 1380 and 1110 cm^{-1}. EI–MS: *m/z* 266 (M^+). Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.66; H, 8.32. Mp: 66–68 °C.

1-Propionylacenaphthene(6b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (t, *J* = 7.2 Hz, 3 H), 2.48 (dq, *J* = 7.2 Hz, *J* = 16.0 Hz, 1 H), 2.64 (dq, *J* = 7.2 Hz, *J* = 16.0 Hz, 1 H), 3.53 (dd, *J* = 8.4 Hz, *J* = 17.4 Hz, 1 H), 3.70 (dd, *J* = 3.4 Hz, *J* = 17.4 Hz, 1 H), 4.57 (dd, *J* = 3.4 Hz, *J* = 8.4 Hz, 1 H), 7.29 (d, *J* = 7.5 Hz, 1 H), 7.33 (d, *J* = 7.5 Hz, 1 H), 7.44 (t, *J* = 7.5 Hz, 1 H), 7.45 (t, *J* = 7.5 Hz, 1 H), 7.60 (d, *J* = 7.5 Hz, 1 H) and 7.64 (d, *J* = 7.5 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$) δ 7.85, 33.37, 33.86, 56.34, 119.61, 119.85, 122.63, 123.80, 127.64, 128.10, 131.68, 138.56, 142.49, 143.37 and 209.31 ppm. IR(neat): 3040, 2940, 1710, 1600, 1490, 1450, 1370 and 1110 cm^{-1}. EI–MS: *m/z* 210 (M^+).

1-(*n*-Butyryl)acenaphthene(6c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.4 Hz, 3 H), 1.61 (sext, *J* = 7.4 Hz, 2 H), 2.45 (dt, *J* = 7.4 Hz, *J* = 17.2 Hz, 1 H), 2.58 (dt, *J* = 7.4 Hz, *J* = 17.2 Hz, 1 H), 3.54 (dd, *J* = 8.5 Hz, *J* = 17.5 Hz, 1 H), 3.70 (dd, *J* = 3.6 Hz, *J* = 17.5 Hz, 1 H), 4.57 (dd, *J* = 3.6 Hz, *J* = 8.5 Hz, 1 H), 7.31 (d, *J* = 7.5 Hz, 1 H), 7.34 (d, *J* = 7.5 Hz, 1 H), 7.45 (t, *J* = 7.5 Hz, 1 H), 7.46 (t, *J* = 7.5 Hz, 1 H), 7.61 (d, *J* = 7.5 Hz, 1 H) and 7.66 (d, *J* = 7.5 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$) δ 13.67, 17.09, 33.80, 42.03, 56.61, 119.67, 119.92, 122.68, 123.84, 127.68, 128.13, 131.75, 138.65, 142.45, 143.40 and 208.71 ppm. IR(neat): 3040, 2960, 1710, 1600, 1500, 1450, 1370 and 1120 cm^{-1}. EI–MS: *m/z* 224 (M^+).

1-Acetyl-1-methylacenaphthene(**7a)**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60 (s, 3 H), 1.92 (s, 3 H), 3.23 (d, *J* = 18.0 Hz, 1 H), 3.82 (d, *J* = 18.0 Hz, 1 H), 7.22 (d, *J* = 7.8 Hz, 1 H), 7.34 (d, *J* = 7.8 Hz, 1 H), 7.48 (t, *J* = 7.8 Hz, 1 H), 7.51 (t, *J* = 7.8 Hz, 1 H), 7.67 (d, *J* = 7.8 Hz, 1 H) and 7.69(d, *J* = 7.8Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$) δ 24.04, 25.31, 43.46, 60.34, 118.95, 119.89, 122.94, 123.96, 128.02, 128.26, 131.74, 138.25, 142.27, 148.07 and 208.58 ppm. IR(neat): 3050, 2960, 1700, 1600, 1490, 1420 and 1350 cm^{-1}. EI–MS: *m/z* 210 (M^+).

1-Methyl-1-propionylacenaphthene(**7b)**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.2 Hz, 3 H), 1.61 (s, 3 H), 2.14 (dq, *J* = 7.2 Hz, *J* = 17.6 Hz, 1 H), 2.29 (dq, *J* = 7.2 Hz, *J* = 17.6 Hz, 1 H), 3.23 (d, *J* = 17.6 Hz, 1 H), 3.79 (d, *J* = 17.6 Hz, 1 H), 7.20 (d, *J* = 7.5 Hz, 1 H), 7.33 (d, *J* = 7.5 Hz, 1 H), 7.47 (t, *J* = 7.5 Hz, 1 H), 7.50 (t, *J* = 7.5 Hz, 1 H), 7.66 (d, *J* = 7.5 Hz, 1 H) and 7.68 (d, *J* = 7.5 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$) δ 8.42, 24.28, 30.70, 43.66, 60.01, 118.95, 119.81, 122.90, 123.84, 128.00, 128.22, 131.70, 138.36, 142.42, 148.34 and 211.52 ppm. IR(neat): 3050, 2970, 1710, 1600, 1500, 1450 and 1370 cm^{-1}. EI–MS: *m/z* 224 (M^+).

1-(*n*-Butyryl)-1-methylacenaphthene(**7c)**:^{1}H NMR (400 MHz, $CDCl_3$) δ 0.71 (t, *J* = 7.4 Hz, 3 H), 1.43–1.53 (m, 2 H), 1.60 (s, 1 H), 2.10 (dt, *J* = 7.3 Hz, *J* = 17.0 Hz, 1 H), 2.24 (dt, *J* = 7.3 Hz, *J* = 17.0 Hz, 1 H), 3.21 (d, *J* = 17.8 Hz, 1 H), 3.80 (d, *J* = 17.8 Hz, 1 H), 7.20 (d, *J* = 7.4 Hz, 1 H), 7.34 (d, *J* = 7.4 Hz, 1 H), 7.47 (t, *J* = 7.4 Hz, 1 H), 7.51 (t, *J* = 7.4 Hz, 1 H), 7.66 (d, *J* = 7.4 Hz, 1 H) and 7.68 (d, *J* = 7.4 Hz, 1 H) ppm. ^{13}C NMR($CDCl_3$) δ 13.54, 17.40, 24.26, 39.29, 43.44, 60.10, 119.03, 119.81, 122.90, 123.84, 127.99, 128.21, 131.70, 138.39, 142.45, 148.23 and 210.65 ppm. IR(neat): 3050, 2950, 1710, 1600, 1490, 1460 and 1370cm^{-1}.EI–MS: *m/z* 238 (M^+).

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(13) It may be assumed that presence of water played a role in restraint of formation of tarry material by rapid protonation to the benzylic anion generated in the reaction system.

(14) This unique regioselectivity may be elucidated through higher reactivity of tertiary benzylic carbanion in the anion radical species **12** toward acylation, or preferential formation of more stable secondary carbanion species **13**, generated by electrophilic acylation followed by almost concerted second electron transfer, although any clear-cut explanation has not been available as yet.

(15) The reaction of stilbene(**1a**) with acid chlorides **10a**–**c** was also carried out according to the similar procedure except use of larger excess of acid chloride (20 equiv mol), Mg (12 equiv mol) and H_2O (2 equiv mol), and reaction at lower reaction temperature (–10~10 °C). The products, cyclopropanol esters (**11a**–**c**), were characterized by spectroscopic methods (^{1}H- and ^{13}C NMR, IR, MASS) and elemental analysis.

1-Acetoxy-1-methyl-2,3-*trans*-diphenylcyclo-propane(**11a**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (s, 3 H), 1.86 (s, 3 H), 2.51 (d, *J* = 7.6 Hz, 1 H), 2.87 (d, *J* = 7.6 Hz, 1 H) and 7.21–7.42 (m, 10 H) ppm. ^{13}C NMR ($CDCl_3$) δ 18.30, 21.02, 33.57, 34.26, 64.84, 126.32, 126.69, 128.00, 128.28 (× 2), 128.90, 136.56, 136.87 and 170.52 ppm. IR(neat): 3020, 2930, 1750, 1600, 1500, 1440, 1360, 1230, 1170 and 1100 cm^{-1}. EI–MS: *m/z* 223 (M – Ac)$^+$, 43(Ac). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.92; H, 6.85.

1-Propionyloxy-1-ethyl-2,3-*trans*-diphenylcyclo-propane(**11b**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.3 Hz, 3 H), 0.98 (t, *J* = 7.7 Hz, 3 H), 1.28 (dq, *J* = 7.3 Hz, 15.4 Hz, 1 H), 1.93 (dq, *J* = 7.3 Hz, 15.4 Hz, 1 H), 2.17 (q, *J* = 7.7 Hz, 2 H), 2.50 (d, *J* = 7.8 Hz, 1 H), 2.90 (d, *J* = 7.8 Hz, 1 H) and 7.17–7.48 (m, 10 H) ppm. ^{13}C NMR ($CDCl_3$) δ 8.90, 9.79, 24.88, 27.62, 32.21, 35.05, 68.55, 126.29, 126.63, 127.99, 128.22, 128.64, 128.99, 136.60, 137.00 and 174.16 ppm. IR(neat): 3030, 2920, 1750, 1610, 1490, 1440, 1360, 1230, 1160 and 1100 cm^{-1}. EI–MS: *m/z* 294 (M$^+$) Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.44; H, 7.54.

1-Butyryloxy-1-propyl-2,3-*trans*-diphenylcyclo-propane(**11c**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, *J* = 7.3 Hz, 3 H), 0.84 (t, *J* = 7.1 Hz, 3 H), 1.07–1.15 (m, 1 H), 1.42–1.53 (m, 4 H), 1.93–2.01 (m, 1 H), 2.11–2.15 (m, 2 H), 2.50 (d, *J* = 7.8 Hz, 1 H), 2.86 (d, *J* = 7.8 Hz, 1 H) and 7.21–7.49 (m, 10 H) ppm. ^{13}C NMR ($CDCl_3$) δ 13.51, 13.96, 18.21, 19.01, 32.43, 33.66, 34.70, 36.24, 67.53, 126.29, 126.63, 127.99, 128.22, 128.64, 129.01, 136.56, 137.04 and 173.43 ppm. IR(neat): 3030, 2910, 1740, 1600, 1500, 1450, 1350, 1240, 1160 and 1090 cm^{-1}. EI–MS: *m/z* 322 (M$^+$). Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 81.80; H, 8.18.