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Photochemical Rearomatization and Dearomatization of Tricarbonyl(η^5-cyclohexadienyl)manganese Complexes

Li Zhou,[†,‡] Li-Zhu Wu,[*,†] Li-Ping Zhang,[†] and Chen-Ho Tung[*,†]

*Technical Institute of Physics and Chemistry, The Chinese Academy of Sciences,
Beijing 100101, China, and Graduate University of Chinese Academy of Sciences, Beijing 100049, China*

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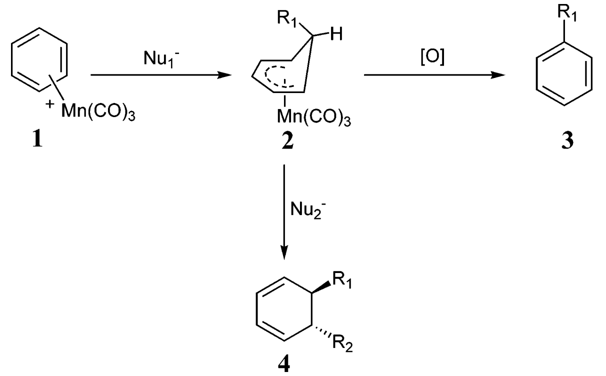
Photoirradiation of the tricarbonyl(η^5-cyclohexadienyl)manganese complexes **2** in dichloromethane or cyclohexane leads to the formation of the rearomatization products **3** in high yield, while photoirradiation of **2** in acetonitrile or dimethylformamide results in **3** and dearomatization products **5** and **6** with the ratio **3**:(**5** + **6**) of ca. 1:1. In the presence of acetic acid the photochemical reaction of **2** both in dichloromethane and in acetonitrile exclusively yields **5** and **6**. The photochemical reaction of **2** might be of significant utility in the synthesis of functionalized arenes and substituted cyclohexadienes.

Introduction

Transition-metal-assisted reactions of arenes with nucleophiles have received particular attention as a unique and potentially useful method of arene reduction and/or functionalization.[1−5] $[(\eta^6\text{-Arene})\text{Mn(CO)}_3]^+$ and its ring-substituted derivatives (**1** in Scheme 1) are among the transition-metal complexes that have been extensively investigated in this regard.[1−8] The electrophilic nature of the complex fragment makes the arene in **1** electron deficient and renders it susceptible to nucleophilic attack. A variety of nucleophiles, including Grignard reagents, organolithium reagents, ketone enolates, malonates, and hydride, have been used in this nucleophilic addition. Nucleophilic addition to such complexes typically yields the corresponding exo-substituted cyclohexadienyl complexes **2**.[2,9] The tricarbonyl(η^5-cyclohexadienyl)manganese complexes can be converted to the corresponding substituted arenes **3** under strongly oxidizing conditions (for example, treatment with a stoichiometric amount of Jones reagent, CrO_3/H_2SO_4/acetone).[10−12] This rearomatization reaction has been successfully applied in the synthesis of various substituted arenes. On the other hand, after reactivation by substitution of a CO ligand with NO^+ (treatment of **2** with $NOPF_6$), the cyclohexadienyl complexes **2** also can react with a second nucleophile and generate either a cis- or trans-disubstituted cyclohexadiene (**4**), depending very much on the nature of the nucleophiles involved.[11,13−16] Through this reaction, a number of dearomatization products have been synthesized with interesting selectivity.

Scheme 1. Rearomatization and Dearomatization of Tricarbonyl(η^5-cyclohexadienyl)manganese Complexes



Although the thermal transformations of tricarbonyl(η^5-cyclohexadienyl)manganese complexes have been extensively studied, their photochemical reactions have rarely been reported. In this work we report the photochemical conversions of several such complexes (**2a−f** in Scheme 2). We have found that the

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* To whom correspondence should be addressed. E-mail: lzwu@mail.ipc.ac.cn (L.-Z.W.); chtung@mail.ipc.ac.cn (C.-H.T.).

[†] Technical Institute of Physics and Chemistry.

[‡] Graduate University of Chinese Academy of Sciences.

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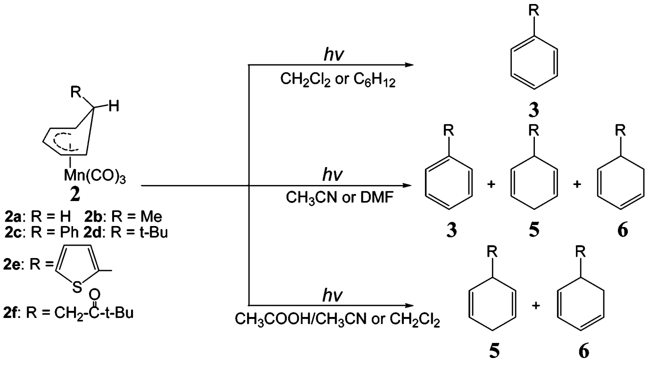
Scheme 2. Photochemical Conversion of Tricarbonyl(η^5-cyclohexadienyl)manganese Complexes



photochemical reactions of these complexes are very dependent on the solvents. Upon exposure to ultraviolet light in dichloromethane or in cyclohexane **2** was converted to the corresponding substituted benzene **3** in high yield. In contrast, photoirradiation of **2** in acetonitrile or in dimethylformamide leads to the formation of **3** and the substituted cyclohexadienes **5** and **6** with the ratio of benzene to dienes of ca. 1:1. Irradiation of **2** both in dichloromethane and in acetonitrile in the presence of a stoichiometric amount of acetic acid resulted in the formation of **5** and **6** exclusively. Thus, the photochemistry of **2** provides useful methods for the synthesis of functionalized arenes and substituted cyclohexadienes under mild conditions.

Results and Discussion

General Considerations. [(Benzene)Mn(CO)$_3$]ClO$_4$ (**1**) was readily synthesized according to the method in ref 17. Reaction of **1** with an excess of Grignard reagents under a nitrogen atmosphere produced the corresponding substituted-cyclohexadienyl complexes **2b**−**e** in high yields.[10,18,19] Complex **2a** was prepared by reduction of a suspension of **1** in ether with lithium aluminum hydride.[19] Complex **2f** was synthesized by ketone enolate addition to **1**.[10] The assignments of the structures of **2a**−**f** mainly rely on their ^{1}H NMR and ^{13}C NMR spectra as well as MS spectra, which are consistent with those in the literature.[10,18−21] The synthetic procedure and characterization of these complexes are given in the Experimental Section.

Complexes **2a**−**f** are quite thermally stable. They are electrically neutral and readily soluble in a variety of organic solvents. Their solutions in organic solvents are pale yellow. Figure 1 presents the UV−vis spectrum of **2c** in acetonitrile. Other complexes show similar absorption spectra. They exhibit absorption in the region of 220−400 nm with λ_{max} at ca. 250 nm. Irradiation of the degassed solutions of **2a**−**f** in organic solvents (ca. 1×10^{-3} M) in quartz tubes with a 450 W Hanovia high-pressure mercury lamp resulted in precipitation. After filtration of the resulting inorganic compound(s), the products in solution were analyzed by ^{1}H NMR and ^{13}C NMR as well as gas chromatography and separated by column chromatography. In all cases the yields of the product(s) were close to 100% on the basis of the consumption of the starting material. This photochemical reaction is very efficient. Generally, after 1 h of irradiation the conversion of the starting material is greater than 95%. The quantum yield of this photochemical reaction was determined by using a potassium ferrioxalate solution as an actinometer.[22] To avoid the absorption of the product(s) in the determination of the quantum yield, the conversion of the starting material was controlled to be less than 10%.

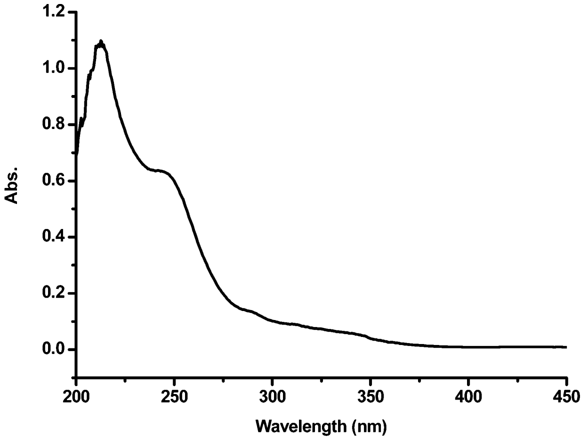


Figure 1. Absorption spectrum of **2c** in acetonitrile. [**2c**] = 2×10^{-4} M.

Photoirradiation of 2 in Noncoordinating Solvents. Photoirradiation of **2** in a solvent without coordination ability such as dichloromethane or cyclohexane results in rearomatization to give the functionalized benzene **3**. For all of the substrates, the isolated yield of the rearomatization products was greater than 95%. The combination of the ready synthesis of **2** with its photochemical transformation proceeding under mild conditions provides a useful synthetic route to functionalized arenes. It has been established[1] that the arene unit can be attached to the Mn(CO)$_3^+$ moiety (synthesis of **1**) under conditions which are mild enough to preclude any reaction or isomerization of arene ring substitutes. Upon binding of the arene to the cationic Mn(CO)$_3^+$ fragment, it becomes substantially electrophilic and can react with a variety of nucleophiles to produce **2**. However, under thermal conditions the rearomatization of **2** requires powerful oxidizing agents, such as the Jones reagent.[10−12] This fact seriously limits the application of this series of reactions as a synthetic method for functionalized arenes. Sweigart and co-workers have demonstrated[10] that common oxidizing agents failed to oxidize **2** to a significant extent. These oxidizing agents include I$_2$ in THF, KMnO$_4$ in water, 30% H$_2$O$_2$, and 4 M (NH$_4$)$_2$Ce(NO$_3$)$_6$ in 2 M H$_2$SO$_4$. In contrast, the photolytic conditions for the rearomatization of **2** employed in this work are much milder. The photochemical rearomatization was carried out at room temperature or below and in the absence of strong oxidizing agents, thereby avoiding the generation of byproduct(s). Indeed, photoirradiation of **2** in cyclohexane or dichloromethane at room temperature for 1 h led to **3** in greater than 95% yield.

Photoirradiation of 2 in Coordinating Solvents. In contrast to the photochemistry above, irradiation of the degassed solutions of **2a**−**f** in a solvent such as acetonitrile or dimethylformamide, which can act as a ligand to bond to the manganese metal, produced both the rearomatization product **3** and the dearomatization products **5** and **6**. The product distribution was slightly dependent on the substrates. For most of the substrates, the ratio of the three products **3**:**5**:**6** = 50:25:25 and the yield of the three products was greater than 95%. The assignment of the product structures mainly relies on their ^{1}H NMR, ^{13}C NMR, and GC-MS spectra and UV absorption spectra. The spectral data and distribution of the products are

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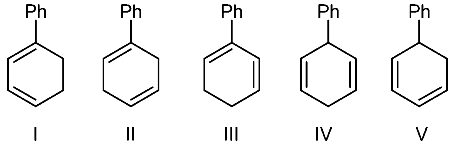
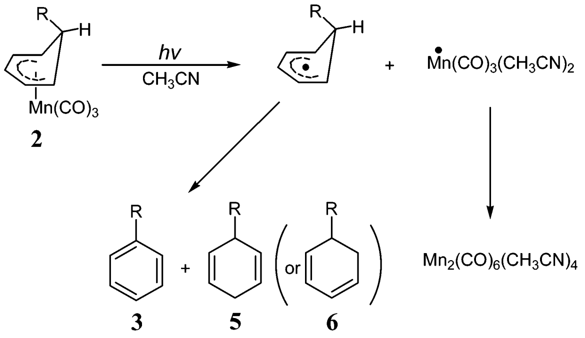
Chart 1. Isomers of Phenylcyclohexadiene



Scheme 3. Plausible Mechanism for the Photochemical Reaction of 2 in Acetonitrile



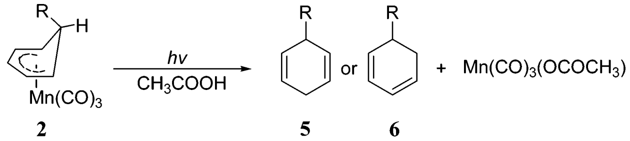
given in the Experimental Section. For all of the substrates, photoirradiation of their solutions for 1 h led to complete conversion of the starting material into the products. The quantum yields for the photochemical conversion of **2a**−**f** in acetonitrile were determined to be 0.06, 0.16, 0.25, 0.20, 0.18, and 0.22, respectively.

Formally, a monosubstituted cyclohexadiene has five isomers. Indeed, some of these isomers have been reported.[23] Grisdale and co-workers examined the methods for the reduction of biphenyl in detail and isolated four of the five isomers of phenylcyclohexadiene (Chart 1). In the photochemical conversion of **2c**, only two isomers of the phenylcyclohexadiene were produced. The two isolated isomers show the characteristic benzylic proton (1 H) resonance signals at δ 4.14 and 3.78 ppm and allylic proton (2 H) signals at δ 2.90 and 2.60 ppm, respectively. This observation rules out the possibility of structures I−III and is consistent with IV and V. Furthermore, the UV absorption and ^{13}C NMR spectra of the two isolated isomers also confirmed the above assignments. The two isolated phenylcyclohexadienes **5c** and **6c** show UV absorptions in the region of 220−300 nm with $\lambda_{\max}$ at 260 and 248 nm, respectively, which are consistent with those reported in the literature.[23] In the conversion of **2b**, **d**−**f**, the ^{1}H NMR, ^{13}C NMR, and GC-MS spectra also suggested the formation of the two cyclohexadienes **5** and **6**.

This photochemical reaction might proceed via a radical intermediate. In the presence of a solvent known to compete with the arene for coordination sites on the $Mn(CO)_3^+$ moiety, excitation of the complex yields a cyclohexadienyl radical, which then undergoes disproportionation to produce the substituted arene and cyclohexadiene (Scheme 3). The driving force for this reaction is the ready arene displacement by the solvent and the photoinduced cleavage of the arene−metal bond.

Photoirradiation in the Presence of Acetic Acid. Irradiation of the degassed solutions of **2a**−**f** both in dichloromethane or cyclohexane and in acetonitrile or dimethylformamide in the presence of a stoichiometric amount of acetic acid exclusively leads to the formation of **5** and **6**. No substituted benzene (**3**) was detected. The mass balance for this reaction is generally greater than 97%. The ratio of the two dienes was estimated from their ^{1}H NMR data to be 1:1 for most of the substrates. The efficiency of this photochemical conversion is comparable to that in the absence of CH_3COOH. This photochemical reaction can be contrasted with the thermochemical reactions of tricarbonyl(η^5-cyclohexadienyl)manganese complexes in the presence of an acid. It has been established[10] that refluxing **2** in acetonitrile in the presence of CF_3COOH exclusively produces **3** rather than **5** and **6**.

Scheme 4. Plausible Mechanism for the Photochemical Reaction of 2 in the Presence of CH$_3$COOH



The conversion of benzene to substituted cyclohexadienes via manganese-mediated nucleophilic addition and photochemical dearomatization under acidic conditions described above is particularly interesting from a synthetic standpoint. As mentioned above, **2** can be readily synthesized. However, the decomplexation of **2** via a thermal reaction under acidic oxidative conditions generally leads to the rearomatization product. To synthesize substituted cyclohexadienes, one has to carry out double nucleophilic addition to **1**. For example, first, treatment of **1** with $LiAlH_4$ results in the formation of **2a**, and then reaction of **2a** with a C-nucleophile produces substituted cyclohexadienes. The photochemical method for the synthesis of substituted cyclohexadienes reported here only requires one nucleophilic addition and can proceed under mild conditions.

The mechanism for the photochemical conversion of **2** in the presence of acetic acid is not yet fully understood. The following observations facilitate a clarification of this reaction. First, acetic acid serves here as a bidentate ligand and hydrogen source for the reduction of **2** and does not act as an acidic medium provider. The acidity of the reaction medium is not important in the determination of the products. For example, addition of HCl to a solution of **2** either in dichloromethane or in acetonitrile does not influence the product distribution. Second, when CH_3COOD is used instead of CH_3COOH to perform the photochemical reaction, one proton at the 4-position in product **5** and one proton at the 2-position in **6** were replaced by deuterium. These observations suggested that the reaction involves a cyclohexadienyl anion. We propose a plausible mechanism for this reaction in Scheme 4.

Summary

The photochemistry of tricarbonyl(η^5-cyclohexadienyl)manganese complexes is very much dependent on the solvent. In noncoordinating solvents the photochemical reactions of these complexes produce functionalized arenes in high yields. In contrast, in the presence of acetic acid photoirradiation of these complexes exclusively yields substituted cyclohexadienes. In comparison with thermal reactions that require treatment with powerful oxidizing agents (for the synthesis of **3**) or double nucleophilic addition (for the synthesis of substituted cyclohexadienes) and high temperature, the photochemical reactions proceed under mild conditions, thereby providing useful synthetic methods for functionalized arenes and substituted cyclohexadienes. Work on the mechanism and on the scope of substrates is currently in progress.

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Experimental Section

Preparation of $[(C_6H_6)Mn(CO)_3]ClO_4$ (1). (η^6-Benzene)manganese tricarbonyl perchlorate was prepared according to the literature method.[17]

Synthesis of Tricarbonyl(η^5-cyclohexadienyl)manganese Complexes 2a−f. 2a was prepared by reduction of **1** with lithium aluminum hydride according to the literature method.[19] To a suspension of **1** (0.2 g, 0.6 mM) in anhydrous diethyl ether (25 mL) was added 1.5 equiv of $LiAlH_4$. After the mixture was stirred at room temperature for 3 h, 20 mL of water was added dropwise to destroy the excess hydride. The ether layer was separated and washed three times with water. The ether solution was dried with $MgSO_4$, and the solvent was evaporated. Column chromatography on silica using hexane as an eluant gave **2a** as yellow crystals. Yield: 58%. ^1H NMR (CD_3CN): δ 5.82 (t, 1H), 4.85 (t, 2H), 2.95 (t, 2H), 2.60 (d, 1H) 2.02 (d, 1H). MS: *m*/*z* 218 (M^+).

2b−f were synthesized by the reaction of **1** with the corresponding Grignard reagent or organolithium reagent.[10,18,19] For example, **2c** was prepared as follows. To a stirred suspension of **1** (0.2 g, 0.6 mM) in 25 mL of dry dichloromethane was added 1.5 equiv of PhMgBr in ether under a nitrogen atmosphere at 0 °C. After 30 min, several drops of water were added to destroy the excess Grignard reagent. The solution was then warmed to room temperature, and the precipitate was filtered. The filtrate was washed three times with water, and the organic layer was dried with $MgSO_4$. Evaporation of the solvent gave a yellow solid. The crude product was purified by column chromatography on silica using hexane as an eluant. **2c** was obtained as yellow crystals in 90% yield. Mp: 117 °C. IR (KBr): 2015, 1960, 1925 cm^{-1}. ^1H NMR (CD_3CN): δ 7.21 (t, 2H), 7.14 (t, 1H), 6.99 (d, 2H), 5.86 (t, 1H), 5.07 (t, 2H), 3.82 (t, 1H), 3.56 (t, 2H). ^{13}C NMR (CD_3CN): δ 38.8 (1C), 58.3 (1C), 80.1 (1C), 97.0 (1C), 117.4 (2C), 125.4 (2C), 126.5 (1C), 128.2 (2C), 147.8 (1C), 223.4 (3C). MS: *m*/*z* 294 (M^+).

2b was obtained as a yellow solid. Yield: 65%. Mp: 38 °C. IR (KBr): 2010, 1945, 1910 cm^{-1}. ^1H NMR (CD_3CN): δ 5.88 (t, 1H), 4.87 (t, 2H), 3.31 (t, 2H), 2.52 (q, 1H), 0.38 (d, 3H). ^{13}C NMR (CD_3CN): δ 27.4 (1C), 29.7 (1C), 59.6 (1C), 80.1 (1C), 96.2 (1C), 117.5 (2C), 223.8 (3C). MS: *m*/*z* 232 (M^+).

2d was obtained as a yellow solid. Yield: 60%. IR (KBr): 2020, 1960, 1920 cm^{-1}. ^1H NMR (CD_3CN): δ 5.75 (t, 1H), 4.99 (t, 2H), 3.29 (t, 2H), 2.42 (t, 1H), 0.53 (s, 9H). ^{13}C NMR (CD_3CN): δ 24.6 (9C), 37.6 (1C), 46.0 (1C), 58.2 (1C), 79.2 (1C), 98.1 (1C), 117.5 (2C), 223.6 (3C). MS: *m*/*z* 274 (M^+).

2e was obtained as a yellow solid. Yield: 78%. Mp: 85 °C. IR (KBr): 2030, 1962, 1915 cm^{-1}. ^1H NMR (CD_3CN): δ 7.10 (d, 1H), 6.83 (t, 1H), 6.61 (d, 1H), 5.93 (t, 1H), 5.08 (t, 2H), 4.02 (t, 1H), 3.58 (t, 2H). ^{13}C NMR (CD_3CN): δ 34.5 (1C), 58.5 (1C), 80.5 (1C), 96.7 (1C), 117.5 (2C), 122.4 (1C), 123.9 (1C), 126.6 (1C), 153.1 (1C), 223.3 (3C). MS: *m*/*z* 300 (M^+).

2f was obtained as a yellow solid. Yield: 50%. Mp: 98 °C. IR (KBr): 2022, 1930, 1905 cm^{-1}. ^1H NMR (CD_3CN): δ 5.79 (t, 1H), 4.76 (t, 2H), 3.34 (t, 2H), 2.97 (q, 1H), 1.88 (d, CH_2), 1.02 (s, CH_3). MS: *m*/*z* 316 (M^+).

Photoirradiation of 2a−f. The photochemical conversion of **2c** in acetonitrile is taken as an example. A solution of **2c** (1×10^{-3} M) in acetonitrile in a quartz tube was deoxygenated by bubbling nitrogen through it for 15 min, and then the solution was irradiated using a high-pressure mercury lamp as the light source. After 1 h, the slight yellow color of the solution disappeared and precipitates emerged at the bottom of the tube. After filtration of the precipitate, the solution was analyzed by gas chromatography and three products were found. The crude products were separated by column chromatography on silica using hexane as an eluant.

Characterization of 3a−f, 5a−f and 6a−f. 3a. Yield: 55%. ^1H NMR (CD_3CN): δ 7.3 (s, 6H). ^{13}C NMR (CD_3CN): δ 127.30 (6C); MS: *m*/*z* 78 (M^+).

5a. Yield: 23%. ^1H NMR (CD_3CN): δ 5.38 (m, 4H), 2.64 (m, 4H). ^{13}C NMR (CD_3CN): δ 31.72 (2C), 125.80 (4C); MS: *m*/*z* 80 (M^+).

6a. Yield: 22%. ^1H NMR (CD_3CN): δ 5.92 (m, 2H), 5.82 (m, 2H), 2.15 (d, 4H). ^{13}C NMR (CD_3CN): δ 27.83 (2C), 124.01 (2C), 127.21 (2C). MS: *m*/*z* 80 (M^+).

3b. Yield: 53%. ^1H NMR (CD_3CN): δ 7.0−7.3 (m, 5H), 2.30 (s, 3H). ^{13}C NMR (CD_3CN): δ 23.89 (1C), 125.66 (1C), 127.79 (2C), 129.01 (2C), 138.55 (1C). MS: *m*/*z* 154 (M^+).

5b. Yield: 25%. ^1H NMR (CD_3CN): δ 5.62 (m, 4H), 3.59 (s, 1H), 2.68 (m, 2H), 1.29 (t, 3H). ^{13}C NMR (CD_3CN): 23.22 (1C), 30.55 (1C), 35.65 (1C), 125.23 (2C), 129.57 (2C). MS: *m*/*z* 94 (M^+).

6b. Yield: 22%. ^1H NMR (CD_3CN): δ 5.82 (d, 2H), 5.72 (d, 2H), 2.55 (m, 2H), 2.20 (m, 1H), 1.00 (t, 3H). ^{13}C NMR (CD_3CN): δ 21.46 (1C), 32.23 (1C), 36.67 (1C), 119.32 (1C), 122.43 (1C), 127.89 (1C), 134.56 (1C). MS: *m*/*z* 94 (M^+).

3c. Yield: 51%. ^1H NMR (CD_3CN): δ 7.2−7.6 (m, 10H). ^{13}C NMR (CD_3CN): δ 127.83 (2C), 127.99 (4C), 129.87 (4C), 135.43 (2C). MS: *m*/*z* 154 (M^+).

5c. Yield: 26%. ^1H NMR (CD_3CN): δ 7.2−7.6 (m, 5H), 5.8 (d, 2H), 5.7 (d, 2H), 4.14 (s, 1H), 2.90 (s, 2H). ^{13}C NMR (CD_3CN): δ 31.2 (1C), 45.6 (1C), 125.8 (1C), 125.9 (2C), 128.3 (2C), 129.4 (2C), 135.2 (2C), 145.5 (1C). MS: *m*/*z* 156 (M^+).

6c. Yield: 23%. ^1H NMR (CD_3CN): δ 7.2−7.6 (m, 5H), 6.0 (d, 2H), 5.9 (d, 2H), 3.78 (s, 1 H), 2.60 (s, 2H). ^{13}C NMR (CD_3CN): δ 39.2 (1C), 41.6 (1C), 124.3 (2C), 125.5 (1C), 126.8 (1C), 127.7 (2C), 128.7 (2C), 129.9 (1C), 140.8 (1C). MS: *m*/*z* 156 (M^+).

3d. Yield: 55%. ^1H NMR (CD_3CN): δ 7.1−7.4 (m, 5H), 1.29 (s, 9H). ^{13}C NMR (CD_3CN): δ 30.9 (9C), 41.4 (1C), 125.7−128.9 (5C), 146.7 (1C). MS: *m*/*z* 136 (M^+).

5d. Yield: 25%. ^1H NMR (CD_3CN): δ 5.5 (t, 4H), 2.82 (s, 1H), 2.74 (s, 2H), 0.88 (s, 9H). ^{13}C NMR (CD_3CN): δ 24.3 (9C), 33.5 (1C), 40.1 (1C), 48.7 (1C), 122.2 (2C), 128.6 (2C). MS: *m*/*z* 136 (M^+).

6d. Yield: 20%. ^1H NMR (CD_3CN): δ 5.7−5.8 (m, 4H), 2.1 (m, 3H), 0.88 (s, 9H). ^{13}C NMR (CD_3CN): δ 26.8 (9C), 31.3 (1C), 41.6 (1C), 48.8 (1C), 120.2 (1C), 124.5 (1C), 131.1 (1C), 133.6 (1C). MS: *m*/*z* 136 (M^+).

3e. Yield: 52%. ^1H NMR (CD_3CN): δ 7.0−7.7 (m, 8H). ^{13}C NMR (CD_3CN): δ 125.52 (1C), 127.55 (2C), 127.61 (1C), 127.91 (1C), 128.85 (1C), 129.32 (2C), 133.32 (1C), 138.53 (1C). MS: *m*/*z* 160 (M^+).

5e. Yield: 24%. ^1H NMR (CD_3CN): δ 6.9−7.0 (m, 3H), 5.28 (m, 4H), 4.28 (m, 1H), 2.70 (m, 2H). ^{13}C NMR (CD_3CN): δ 31.45 (1C), 39.77 (1C), 121.23 (1C), 124.45 (2C), 126.33 (1C), 126.78 (1C), 133.23 (1C), 135.62 (1C), 138.78 (1C). MS: *m*/*z* 162 (M^+).

6e. Yield: 24%. ^1H NMR (CD_3CN): δ 6.9−7.0 (m, 3H), 5.8 (m, 4H), 3.57 (s, 1H), 2.72 (m, 2H). ^{13}C NMR (CD_3CN): δ 35.41 (1C), 37.88 (1C), 122.26 (1C), 124.21 (1C), 124.76 (1C), 126.74 (1C), 126.95 (1C), 127.33 (1C), 127.62 (1C), 139.50 (1C). MS: *m*/*z* 162 (M^+).

3f. Yield: 58%. ^1H NMR (CD_3CN): δ 7.29 (q, 5H), 3.92 (t, 1H), 1.22 (s, 9H). ^{13}C NMR (CD_3CN): δ 31.2 (9C), 43.5 (1C), 45.5 (1C), 127.4−135.6 (6C), 211.7 (1C). MS: *m*/*z* 176 (M^+).

5f. Yield: 21%.^1H NMR (CD_3CN): δ 5.56 (q, 4H), 3.12 (m, 1H), 2.72 (d, 1H), 2.74 (d, 1H), 2.43 (2H), 1.11 (s, 9H). ^{13}C NMR (CD_3CN): δ 24.1 (9C), 30.8 (1C), 33.1 (1C), 44.5 (1C), 45.6 (1C), 125.0−129.6 (4C), 213.9 (1C). MS: *m*/*z* 178 (M^+).

6f. Yield: 20%.^1H NMR (CD_3CN): δ 5.8−5.9 (q, 4H), 2.59 (t, 1H), 2.35 (m, 1H), 2.26 (m, 1H), 2.22 (m, 1H), 1.99 (m, 1H), 1.06 (s, 9H). ^{13}C NMR (CD_3CN): δ 26.9 (9C), 28.6 (1C), 33.9 (1C), 41.8 (1C), 44.8 (1C), 123−135.8 (4C), 214.2 (1C). MS: *m*/*z* 178 (M^+).

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