Ortho Metalation of Intramolecular (η^2-Arene)palladium Species and Reactivities of the Resulting Palladacycles

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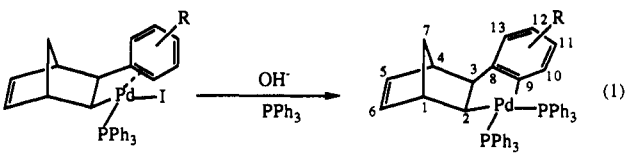
*Summary: Treatment of the intramolecular η^2-arene complexes Pd[C_7H_8(η^2-Ar)](PPh$_3$)I, where Ar = C_6H_5, p-$CH_3C_6H_4$, and p-$CH_3OC_6H_4$, in dichloromethane with aqueous sodium hydroxide in the presence of PPh$_3$ led to isolation of the corresponding yellow ortho-metalation products Pd[C_7H_8(C_6H_3R)](PPh$_3$)$_2$ (R = H (**2a**), p-CH_3 (**2b**), and p-OCH_3 (**2c**)). **2a** reacts with CH_3I to give the o-methyl product Pd[C_7H_8(C_6H_4-o-CH_3)](PPh$_3$)I (**1d**) and with HCl, HC≡CPh, $CH_3OCOC{\equiv}CCOOCH_3$, and $(NC)_2C{=}C(CN)_2$ to afford the substituted nortricyclene C_7H_9Ph (**4a**), the exo-disubstituted norbornene derivative $C_7H_8(C{\equiv}CC_6H_5)(C_6H_5)$ (**5a**), the insertion product C_7H_8-[C_6H_4($C(COOCH_3){=}CCOOCH_3$)] (**6a**), and the benzocyclobutane product C_7H_8(C_6H_4) (**8a**), respectively.*

In the C–H bond activation of arenes, it is believed that coordination of an arene to a metal atom in a η^2 fashion generally takes place prior to the C–H bond cleavage.[1] This mechanism provides a low-activation-energy pathway for the C–H bond activation of arenes and explains the observations that many more arenes than alkanes are activated by metal complexes, although the C–H bond strength in an arene is greater than that in an alkane. A considerable number of η^2-bound arene complexes have been isolated or characterized,[2-7] but examples demonstrating the transformation of η^2-bound arene complexes into metalation products are hardly known. In the reaction of Cp*Rh(PMe$_3$)(C_2H_4) with ArH to give RhCp*(H)(Ar)-PMe$_3$, an η^2-bound arene intermediate was detected by NMR spectroscopy at low temperature. Treatment of RhCp*(H)(Ar)PMe$_3$ with naphthalene produced a η^2-bound (naphthalene)rhodium complex.[8] In spite of the rich chemistry on the C–H bond activation of arenes by palladium complexes, there has been no report of a η^2-bound arene complex of palladium being transformed into a palladation product.[9] Recently, we isolated the series of intramolecular (η^2-arene)palladium(II) species Pd[C_7H_8-(η^2-Ar)](PPh$_3$)I (1) from the reaction of norbornadiene with Pd(PPh$_3$)$_2$(Ar)I.[10-12] These complexes appear suitable for the C–H bond activation of arenes by palladium. We report here the first examples of (η^2-arene)palladium complexes that have been transformed into ortho-metalation products and the reactivities of these resulting palladacycles with substrates to give interesting organometallic and organic products.

Treatment of the complex Pd(C_7H_8Ph)(PPh$_3$)I (**1a**) in dichloromethane with aqueous sodium hydroxide in the presence of 1.5 equiv of PPh$_3$ led to the isolation of the yellow palladacyclic complex **2a** (eq 1)in 70% yield. The



(1)

R = H **1a** **2a**

R = p-CH_3 **1b** **2b**

R = p-OCH_3 **1c** **2c**

NMR spectra of this ortho-metalation product provided the key information for structure assignment.[13] In the $^{13}C\{^1H\}$ spectrum of **2a**, the signals at δ 162 (dd, J = 112 and 12 Hz) and 58.9 (dd, J = 82 and 5 Hz) are assigned to carbons C9 and C2 (see eq 1), respectively, which are attached to the metal center. The observed chemical shifts, coupling patterns, and coupling constants strongly support the notion that C2 and C9 are σ-bonded to palladium and that two phosphines are coordinated to palladium. The large coupling constants (J = 112 and 82 Hz) reflect coupling of these two carbons with the respective trans phosphine ligands, while the small constants (J = 12 and

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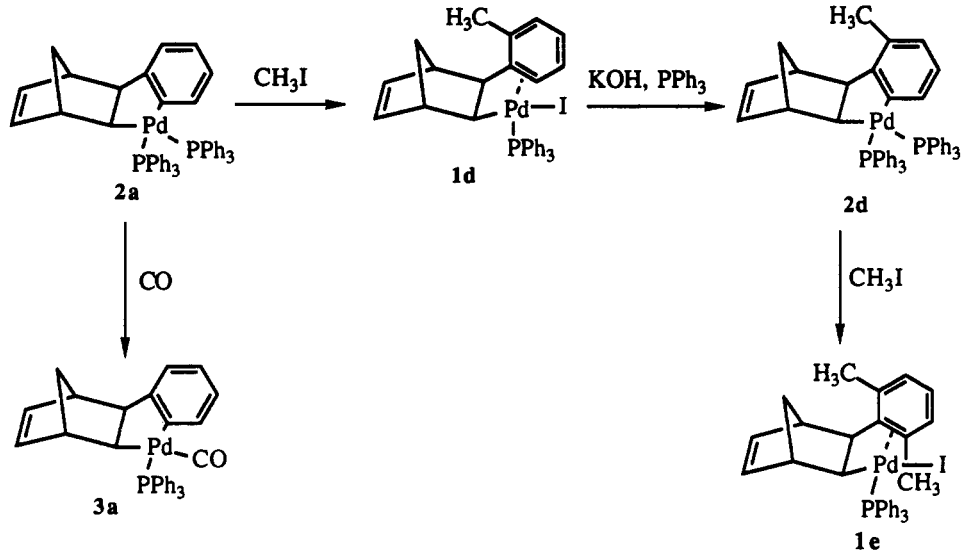
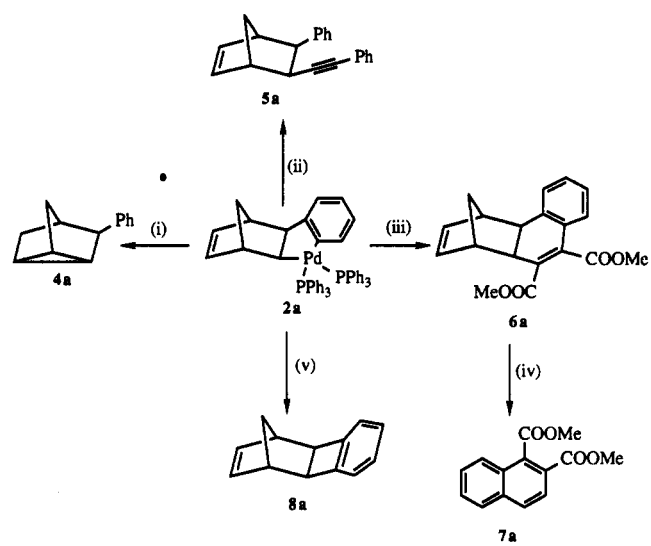
Scheme 1



5 Hz) result from the coupling with cis phosphines. In agreement with the ^{13}C NMR results, the endo proton on C2 couples with the trans phosphorus nucleus with coupling constants of 15 Hz. Similarly, **2b** and **2c** were prepared from the reaction of the corresponding η^2-arene species **1b** and **1c** with hydroxide ion in the presence of PPh_3 in 68% and 65% yields, respectively. These two products also show characteristic ^{13}C resonances of the corresponding C2 and C9 atoms at δ 59.0 (dd, J = 82.4, 5.8 Hz) 163.2 (dd, J = 114.5, 12.1 Hz) for **2b** and at δ 58.8 (dd, J = 82.2, 4.7 Hz) and 164.0 (dd, J = 111.8, 11.9 Hz) for **2c**. In the ^1H NMR spectra of these palladacyclic species **2a–c**, the protons of the metalated aryl group except that at the meta position (H10) appear in the region 6–7 ppm. For instance, the proton signals of the metalated aryl group of **2a** occur at δ 6.31 (t, H(11)), 6.79 (d, H(13)), and 6.84 (t, H(12)). Assignments of the spectra data are based on 2D NMR spectra of this complex. These resonances do not overlap with other signals and are useful for identification of the ortho-metalated products. The ^1H signals for the meta proton (H10) are buried in the region 7–8 ppm for phenyl proton resonances of PPh_3. Similar palladacyclic species were isolated previously from the reaction of norbornene, aryl bromide, and $Pd(PPh_3)_4$ in anisole at 105 °C in the presence of potassium phenoxide.[14] We believe that the corresponding η^2-arene intermediates were involved, although these intermediates were not previously isolated.

Scheme 2[a]



[a] Reagents and conditions: (i) excess HCl, CH_2Cl_2, room temperature 1 h, 71% yield; (ii) phenylacetylene, CH_2Cl_2, room temperature, 4 h, 78% yield; (iii) dimethyl acetylenedicarboxylate, CH_2Cl_2, room temperature, 1 h, 68% yield; (iv) pyrolysis, 300 °C, 92% yield; (v) tetracyanoethylene, CH_2Cl_2, room temperature 1 h, 51% yield.

As shown in Schemes 1 and 2, complex **2a** shows interesting reactivities with various substrates. The reaction of **2a** with methyl iodide led to the methylation of the aryl carbon bonded to palladium to give the η^2-arene species **1d**. Treatment of **1d** in dichloromethane in the presence of PPh_3 with an aqueous solution of sodium hydroxide resulted in removal of the proton at the ortho position and afforded the corresponding palladacycle **2d** in good yield. The reaction of **2d** with methyl iodide led

(13) Important spectral data for **2a** are as follows. ^1H NMR (300 MHz, $CDCl_3$): δ 1.15 (d, J = 7.7 Hz, 1 H, H(7b)), 2.12 (d, J = 7.7 Hz, 1 H, H(7a)), 2.29 (dd, J_{PH} = 15.4 Hz, J = 7.5 Hz, 1 H, H(2)), 2.77 (br s, 1 H, H(1)), 2.82 (br s, 1 H, H(4)), 2.88 (m, 1 H, H(3)), 4.95 (dd, J = 5.5 Hz, J = 2.7 Hz, 1 H, H(6)), 5.83 (dd, J = 5.5 Hz, J = 2.7 Hz, 1 H, H(5)), 6.31 (t, J = 7.5 Hz, 1 H, H(11)), 6.79 (d, J = 7.5 Hz, 1 H, H(13)), 6.84 (t, J = 7.5 Hz, 1 H, H(12)), 7.05–7.61 (m, 31 H, PPh_3, H(10)). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 44.36 (C(7)), 49.11 (C(1)), 52.39 (C(4)), 55.27 (d, $^3J_{PC}$ = 4.6 Hz, C(3)), 58.87 (dd, $^2J_{PC}$ = 82.2 Hz, $^2J_{PC}$ = 4.9 Hz, C(2)), 122.26 (C(10)), 122.39 (dd, $^4J_{PC}$ = 7.6 Hz, $^4J_{PC}$ = 3.5 Hz, C(11)), 123.02 (C(12)), 127.57, 127.97, 129.25, 129.65, 133.75, 134.16, 134.76, 135.41 (C of PPh_3), 132.77 (C(5)), 136.44 (dd, $^4J_{PC}$ = 7.1 Hz, $^4J_{PC}$ = 4.5 Hz, C(6)), 142.21 (dd, $^4J_{PC}$ = 12.8 Hz, $^4J_{PC}$ = 5.8 Hz, C(13)), 162.92 (dd, $^2J_{PC}$ = 111.7 Hz, $^2J_{PC}$ = 11.8 Hz, C(9)), 166.07 (dd, $^3J_{PC}$ = 6.1 Hz, $^3J_{PC}$ = 3.8 Hz, C(8)). IR (KBr): 3052, 1479, 1434, 1002, 695 cm^{-1}. Anal. Calcd for $C_{49}H_{42}P_2Pd$: C, 73.68; H, 5.26. Found: C, 73.23; H, 5.26. MS (FAB): m/z 799 (M^+ + 1). Mp: 103 °C dec. Important spectral data for **2d** are as follows. ^1H NMR (300 MHz, $CDCl_3$): δ 1.18 (d, J = 7.1 Hz, 1 H, H(7b)), 2.20 (dd, J_{PH} = 14.9 Hz, J = 7.1 Hz, 1 H, H(2)), 2.25 (d, J = 7.6 Hz, 1 H, H(7a)), 2.38 (s, 3 H, CH_3), 2.81 (s, 1 H, H(1)), 2.86 (br s, 2 H, H(3), H(4)), 5.02 (dd, J = 5.1 Hz, J = 2.7 Hz, 1 H, H(6)), 5.87 (dd, J = 5.1 Hz, J = 2.7 Hz, 1 H, H(5)), 6.26 (td, J = 7.14 Hz, J = 1.5 Hz, 1 H, H(11)), 6.63 (d, J = 7.14 Hz, 1 H, H(12)), 6.69 (t, J = 7.14 Hz, 1 H, H(10)), 7.02–7.57 (m, 30 H, PPh_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 21.59 (CH_3), 45.26 (C(7)), 49.10 (C(4)), 49.59 (C(1)), 54.12 (d, $^3J_{PC}$ = 4.8 Hz, C(3)), 58.08 (dd, $^2J_{PC}$ = 80.8 Hz, $^2J_{PC}$ = 4.8, C(2)), 123.18 (d, $^3J_{PC}$ = 5.7 Hz, C(10)), 125.13 (C(12)), [127.53, 127.86, 129.13, 129.47, 133.62, 134.03, 134.72, 135.32, C of PPh_3], 131.92 (C(13)), 133.35 (C(5)), 136.15 (dd, $^4J_{PC}$ = 7.2 Hz, $^4J_{PC}$ = 4.8 Hz, C(6)), 140.26 (dd, $^4J_{PC}$ = 12.3 Hz, $^4J_{PC}$ = 5.5 Hz, C(11)), 163.47 (dd, $^2J_{PC}$ = 110.5 Hz, $^2J_{PC}$ = 11.1 Hz, C(9)), 163.58 (dd, $^3J_{PC}$ = 5.0 Hz, $^3J_{PC}$ = 3.6 Hz, C(8)). IR (KBr): 3050, 1481, 1434, 1000, 690 cm^{-1}. Anal. Calcd for $C_{50}H_{44}P_2Pd$: C, 73.89; H, 5.42. Found: C, 73.23; H, 5.42. MS (FAB): m/z 813 (M^+ + 1). Mp: 101 °C dec.

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to further methylation of the ortho aryl carbon attached to palladium to form the dimethylation product **1e** (Scheme 1). Both **1d** and **1e** exhibit characteristic ^{13}C NMR signals for the π-bonded ipso carbon of the *o*-tolyl group at δ 105.9 (d, $^2J_{PC}$ = 11.0 Hz) and 104.6 (d, $^2J_{PC}$ = 15.0 Hz). In addition, the methyl carbon signals appear at δ 21.6 for **1d** and at δ 22.9 and 24.2 for **1e**.[15] Similar to the case for complexes **2a–c**, important spectral data for structural assignment of the palladacyclic species **2d** include the observed ^{13}C NMR signals at δ 58.08 and 163.47, both as doublets of doublets for the C2 and C9 atoms coordinated to palladium. In the reaction of carbon monoxide with **2a**, substitution of the coordinated PPh_3 trans to C2 by carbon monoxide takes place to give complex **3a**. Evidence to support this substitution is provided by the $^{13}C\{^1H\}$ NMR signals of carbons C2 and C9 attached to the palladium center appearing as doublets at δ 58.56 (d, $^2J_{PC}$ = 5.5 Hz) and 161.67 (d, $^2J_{PC}$ = 101.8 Hz), respectively. The observed large coupling constant of C9 strongly indicates that a PPh_3 is trans to C9, while the small coupling constant of 5.5 Hz for C2 is in agreement with the assignment that a coordinated PPh_3 is cis to the carbon. This product is unstable, readily losing the carbonyl group in solution in the absence of CO gas at room temperature. Attempts to isolate this species in a pure form failed.

Surprisingly, reaction of **2a** with the hydrochloric acid afforded the nortricyclene derivative **4a** in essentially quantitative yield. This product was identified by comparing its spectra data with those of an authentic sample which we had prepared previously.[16] Treatment of **2a** with phenylacetylene led to the isolation of 2,3-disubstituted norbornene derivative **5a**.[17] In this reaction, the acetylenic hydrogen is selectively transferred to the aryl carbon, consistent with the reactions of **2a** and **2d** with methyl iodide in which methylation occurred at the aryl carbons. The reaction of **2a** with dimethyl acetylenedicarboxylate resulted in the insertion of the alkyne into a palladium–carbon bond, followed by a reductive ring closure to afford the six-membered-ring product **6a**.[17] The product underwent retro Diels–Alder reaction at 300 °C, affording the corresponding naphthalene derivative **7a**.[18] In the presence of tetracyanoethylene, the ring-closure reaction of **2a** led to the four-membered organic product **8a**.[19] No insertion product was observed in this case. The reaction conditions and product yields for the reaction of **2a** with various substrates are summarized in Scheme 2.

We have shown for the first time that stable (η^2-arene)-palladium complexes may be readily converted into palladated species in the presence of a suitable base, thus providing evidence for the proposed mechanistic model of C–H bond activation of arenes by metal complexes. Methylation and protonation of the resulting palladacyclic complexes occur selectively at the aryl carbon attached to palladium, providing a convenient method for the ortho functionalization of the aryl group. In addition, the palladacyclic complexes exhibit several interesting reactions which are useful in organic synthesis.

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Supplementary Material Available: Text giving synthetic procedures and characterization data for the products in Schemes 1 and 2 (3 pages). Ordering information is given on any current masthead page.

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(15) Spectral data for **1d** are as follows. ^1H NMR (300 MHz, $CDCl_3$): δ 1.06 (ddd, J_{PH} = 13.2 Hz, J = 7.3 Hz, J = 2.1 Hz, 1 H, H(2)), 1.66 (d, J = 8.8 Hz, 1 H, H(7b)), 2.32 (br s, 1 H, H(1)), 2.74 (s, CH_3), 2.87 (d, J = 8.8 Hz, 1 H, H(7a)), 2.99 (br s, 1 H, H(4)), 3.20 (d, J = 7.3 Hz, 1 H, H(3)), 5.46 (dd, J = 5.2 Hz, J = 2.2 Hz, 1 H, H(6)), 6.13 (dd, J = 5.2 Hz, J = 2.2 Hz, 1 H, H(5)), 7.05–7.61 (m, 19 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 21.64 (CH_3), 37.37 (d, $^2J_{PC}$ = 11.0 Hz, C(2)), 46.33 (C(4)), 48.19 (C(1)), 48.70 (C(3)), 48.84 (C(7)), 105.92 (d, $^2J_{PC}$ = 11.0 Hz, C(8)), 128.43 (C(10)), [128.09, 130.54, 131.53, 134.79, C of PPh_3], 132.00 (C(12)), 132.37 (C(11)), 134.73 (C(9)), 136.99 (C(5)), 137.30 (d, $^4J_{PC}$ = 8.2 Hz, C(6)), 141.22 (C(13)). IR (KBr): 3057, 1479, 1434, 1093, 738, 695 cm^{-1}. Anal. Calcd for $C_{32}H_{30}$IPPd: C, 56.64; H, 4.42. Found: C, 56.58; H, 4.45. MS (FAB): m/z 551 (M^+ – I). Mp: 118 °C dec. Spectra data for **1e** are as follows. ^1H NMR (300 MHz, $CDCl_3$): δ 1.20 (dd, J_{PH} = 13.6 Hz, J = 6.7 Hz, 1 H, H(2)), 1.75 (d, J = 8.6 Hz, 1 H, H(7b)), 2.36 (br s, 1 H, H(1)), 2.72 (br s, 6 H, CH_3), 2.92 (d, J = 8.6 Hz, 1 H, H(7a)), 3.34 (d, J = 6.7 Hz, 1 H, H(3)), 3.45 (br s, 1 H, H(4)), 5.43 (dd, J = 5.1 Hz, J = 3.0 Hz, 1 H, H(6)), 6.08 (dd, J = 5.1 Hz, J = 3.0 Hz, 1 H, H(5)), 7.15–7.53 (m, 18 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 22.87 (CH_3), 24.15 (CH_3), 42.58 (d, $^2J_{PC}$ = 14.6 Hz, C(2)), 45.13 (C(4)), 48.01 (C(1)), 49.68 (C(7)), 52.49 (C(3)), 104.62 (d, $^2J_{PC}$ = 15.0 Hz, C(8)), 129.93 (C(10)), [128.08, 130.51, 131.60, 134.71, C of PPh_3], 131.34 (C(12)), 133.46 (C(11)), 136.92 (d, $^4J_{PC}$ = 7.3 Hz, C(6)), 137.47 (C(5)), 140.74 (C(13)), 145.66 (C(9)). IR (KBr): 3052, 1478, 1433, 1093, 736, 692 cm^{-1}. Anal. Calcd for $C_{33}H_{32}$IPPd: C, 57.23; H, 4.62. Found: C, 56.88; H, 4.56. MS (FAB): m/z 565 (M^+ – I), Mp: 125 °C dec.

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(17) **5a** was prepared according to the following procedure. A round-bottom flask containing *cis,exo*-Pd[$C_7H_8(C_6H_4)$](PPh_3)$_2$ (**2a**; 0.262 g, 0.321 mmol) and phenylacetylene (0.061 g, 0.598 mmol) was purged by nitrogen gas three times. Into the system was syringed dichloromethane (10 mL), and the solution was stirred at ambient temperature for 1 h. The solution was condensed and separated on a silica gel column using *n*-hexane–ethyl acetate (30/1, v/v) as the eluent to give **5a** in 78% yield (0.074 g). ^1H NMR (300 MHz, $CDCl_3$): δ 1.71 (dt, J = 8.7 Hz, J = 1.5 Hz, 1 H), 2.19 (d, J = 8.7 Hz, 1 H), 2.97 (dd, J = 8.8 Hz, J = 1.5 Hz, 1 H), 3.06 (dd, J = 8.8 Hz, J = 1.5 Hz, 1 H), 3.17 (br s, 2 H), 6.26 (dd, J = 4.0 Hz, J = 2.1 Hz, 1 H), 6.41 (dd, J = 4.0 Hz, J = 2.1 Hz, 1 H), 6.86–6.89 (m, 2 H), 7.13–7.39 (m, 8 H), $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 37.08 (d), 45.83 (t), 46.15 (d), 48.15 (d), 49.64 (d), 84.23 (s), 92.41 (s), 124.00 (s), 125.92 (d), 127.35 (d), 127.98 (d), 128.02 (d), 128.81 (d), 131.48 (d), 136.77 (d), 140.08 (d), 143.13 (s). IR (KBr): 2965, 2218, 1598, 1499, 1451, 911, 749, 695, 668 cm^{-1}. HRMS: calcd for $C_{21}H_{18}$ 270.1410, found 270.1422. **6a** was prepared in 68% yield by following a procedure similar to that described for **5a**. ^1H NMR (300 MHz, $CDCl_3$): δ 1.26 (d, J = 7.6 Hz, 1 H), 1.47 (d, J = 7.6 Hz, 1 H), 2.90 (d, J = 10.4 Hz, 1 H), 3.00 (br s, 1 H), 3.03 (br s, 1 H), 3.10 (d, J = 10.4 Hz, 1 H), 3.85 (s, 3 H), 3.97 (s, 3 H), 6.31–6.33 (m, 2 H), 7.07 (d, J = 8.2 Hz, 1 H), 7.17–7.21 (m, 1 H), 7.31–7.34 (m, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): 38.73 (d), 41.41 (d), 43.07 (t), 51.60 (d), 52.16 (q), 52.28 (q), 55.47 (d), 126.68 (d), 126.81 (d), 127.60 (s), 128.87 (s), 129.39 (d), 130.63 (d), 137.60 (d), 138.07 (d), 138.55 (s), 139.86 (s), 167.40 (s), 169.81 (s). IR (KBr): 3022, 2951, 1723, 1622, 1438, 1261, 1139, 1038, 767, 736 cm^{-1}. MS: m/z 244 (M^+ – 66).

(18) Spectral data for **7a** are as follows. ^1H NMR (300 MHz, $CDCl_3$): δ 3.97 (s, 3 H), 4.08 (s, 3 H), 7.59–7.63 (m, 2 H), 7.86–7.92 (m, 2 H), 7.94 (d, J = 8.7 Hz, 1 H), 8.03 (d, J = 8.7 Hz, 1 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 52.67 (q), 52.89 (q), 124.73 (s) 124.94 (d), 126.11 (d), 127.73 (d), 128.10 (d), 128.51 (d), 129.27 (s), 129.54 (d), 134.94 (s), 135.09 (s), 166.23 (s), 169.53 (s). IR (KBr): 3015, 2951, 1732, 1466, 1434, 1286, 1262, 1235, 1038, 765, 732 cm^{-1}. HRMS: calcd for $C_{14}H_{12}O_4$ 244.0736, found 244.0729.

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