A Novel Nickel(0)-Catalyzed Cascade Ullmann–Pinacol Coupling: From *o*-Bromobenzaldehyde to *trans*-9,10-Dihydroxy-9,10-dihydrophenanthrene

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Received 9 April 2007

Abstract: Using 5 mol% of $(Ph_3P)_2NiCl_2$ as a catalyst, Zn powder as a reductant, *ortho*-carbonyl-substituted aryl halides could be coupled to form *trans*-9,10-dihydroxy-9,10-dihydrophenanthrenes in a one-pot cascade reaction.

Key words: Nickel catalysis, Ullmann–pinacol coupling, cascade reaction, *trans*-selectivity, *trans*-9,10-dihydroxy-9,10-dihydrophenanthrene

Chiral diols, especially TADDOL[1] and BINOL,[2] are versatile chiral ligands in asymmetric synthesis. However, to the best of our knowledge, there are few reports about *trans*-9,10-dihydroxy-9,10-dihydrophenanthrene (phendiol) as chiral ligand in asymmetric synthesis.[3] Possessing a rigid cyclic vicinal diol structure, *trans*-phendiol could serve as a potential diol skeleton in asymmetric synthesis (Figure 1). Moreover, phendiols are the key structural units in various important natural products, such as pradimicinone and related compounds.[4] There are many methods to synthesize the phendiol structure: reduction of phenanthraquinone;[5] combination of enantioselective dihydroxylation with intramolecular Ullmann coupling;[4b] or intramolecular pinacol coupling.[4a,6] Described herein is the development of a novel $(Ph_3P)_2NiCl_2$-catalyzed cascade Ullmann–pinacol coupling reaction and its application to a highly *trans*-selective preparation of phendiols.

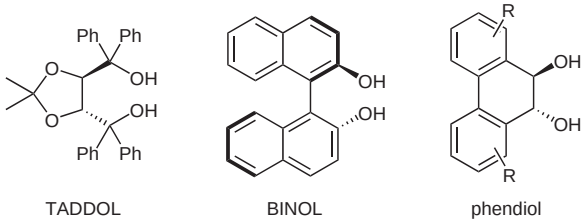
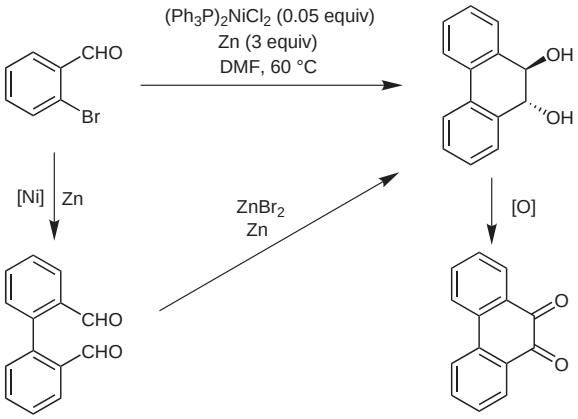


Figure 1

The Ullmann reaction[7] can be induced by Cu, Ni, and Pd. Generally, nickel(0)-mediated Ullmann reaction of aryl halides can tolerate a broad variety of functional groups. In addition, the reaction condition is mild and the nickel reagent is inexpensive. We also noted that zinc halide produced in situ from the coupling of aryl halides was a promoter for the pinacol couping.[8] Exhilaratingly, the *trans*-phendiol was really obtained as the major product in the homocoupling reaction of *o*-bromobenzaldehyde under the conditions of Ni-catalyzed Ullmann reaction in the presence of Zn metal (Scheme 1).[9]



Scheme 1

In the homocoupling experiment of 2-bromobenzaldehyde with excess zinc powder[10] catalyzed by $(Ph_3P)_2NiCl_2$,[11] an Ullmann coupling was believed to occur first. As the biphenyl-2,2′-dialdehyde was formed, an intramolecular pinacol cyclization was then induced by the $ZnBr_2$ engendered in the Ullmann coupling step to produce *trans*-phendiol. If the reaction was stopped in a shorter reaction time, the biphenyl-2,2′-dialdehyde could be isolated as the main product.[12] It should also be noted that phenanthrenequinone was usually isolated as a byproduct. We suspected that the phenanthrenequinone was the oxidation product of the phendiol in the workup process.[13]

We then investigated this Ullmann–pinacol cascade reaction of various *ortho*-carbonyl-substituted aryl halides (Table 1). Replacing the bromide **1a** with the less reactive chloride **1a′** led to a comparable yield of phendiol though the reaction time was longer (entries 1 and 2). The product yield was found to decrease for extensively conjugated systems (entries 3–5).[14] When ketone **1e** was tested, the main product was 2,2′-diacetylbiphenyl instead of phendiol **2e** (entry 6). The yield of **2e** was only 19% even the reaction time was prolonged to 24 hours, presumably because the lower reactivity of ketone and the increased steric hinderance of the methyl groups that was an obstacle to the subsequent pinacol coupling step. The reaction went smoothly if the substituent on the aromatic

SYNLETT 2007, No. 13, pp 2101–2105
Advanced online publication: 27.06.2007
DOI: 10.1055/s-2007-984543; Art ID: W07007ST

ring was electron-withdrawing but was retarded in the first step if the substituent was electron-donating (entries 7 and 8). For heterocyclic **1h**, the dialdehyde intermediate was reduced to an unexpected alcohol instead of phendiol compound (entry 9).[15]

Although Ni-catalyzed pinacol couplings have been reported,[24] it seemed that $(Ph_3P)_2NiCl_2$ did not induce the pinacol reaction in our experiment. This was supported by the fact that phendiol was not obtained when biphenyl-2,2′-dialdehyde was treated with $(Ph_3P)_2NiCl_2$. On the other hand, when the nickel catalyst was replaced by $ZnCl_2$, the dialdehyde was smoothly converted into *trans*-phendiol in 4 hours (Scheme 2).

Table 1 Cascade Reaction of Various *ortho*-Carboxyl Aryl Halides[16,17]

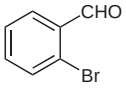
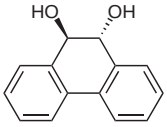
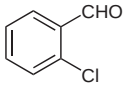
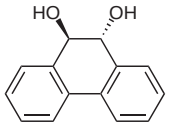
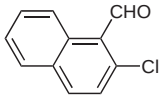
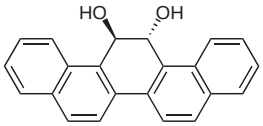
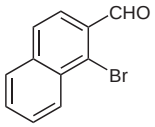
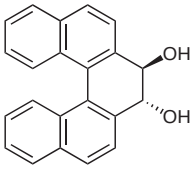
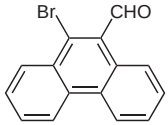
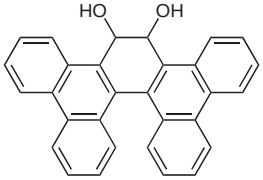
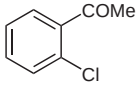
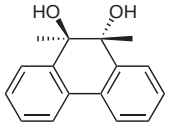
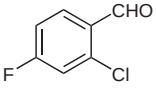
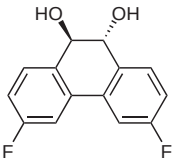
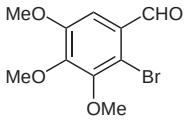
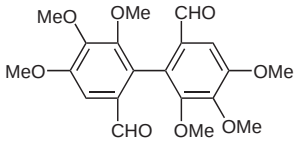
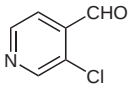
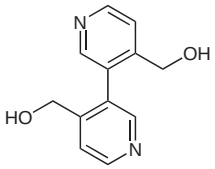
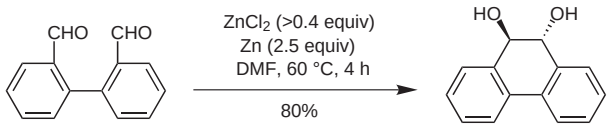
Entry	Substrate[a]	Time (h)	Product	Isolated yield[b] (%)
1	 **1a**	7	 **2a**[6b]	80
2	 **1a′**	10	 **2a**[6b]	76
3	 **1b**[18]	12	 **2b**	71
4	 **1c**[19]	9	 **2c**[6a]	63
5	 **1d**[20]	9	 **2d**[21]	51
6	 **1e**	24	 **2e**[22]	19[c]
7	 **1f**	12	 **2f**	73

Table 1 Cascade Reaction of Various *ortho*-Carboxyl Aryl Halides[16,17] (continued)

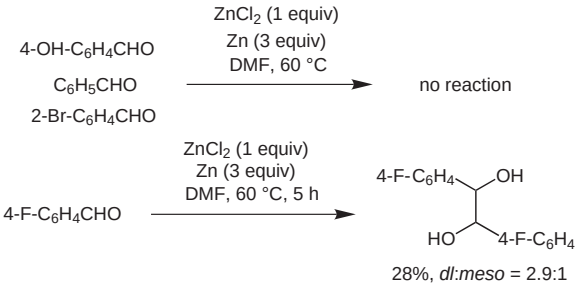
Entry	Substrate[a]	Time (h)	Product	Isolated yield[b] (%)
8	 **1g**[23]	9	 **3**[23]	50[d]
9	 **1h**	12	 **4**	45

[a] The reagents are commercially available unless otherwise noted.
[b] Uncorrected.
[c] The main product is the diketone[22] (54% yield).
[d] 3,4,5-Trimethoxybenzaldehyde is isolated with 30% yield.



Scheme 2

Despite its excellent efficiency in the intramolecular pinacol cyclization above, $ZnCl_2$ was not responsible for the intermolecular pinacol coupling of benzaldehyde under similar conditions. Even the substituent on the aromatic ring was strong electron-withdrawing, such as 4-fluorobenzaldehyde, the yield of pinacol was only 28% after 5 hours (Scheme 3).



Scheme 3

Thus, based on the experimental results of the tandem reactions and of the intermolecular pinacol coupling, it seemed that an electron-withdrawing substituent on the aromatic ring would favor this cascade reaction and an electron-donating substituent would retard the second step of pinacol coupling.

In conclusion, a highly stereoselective Ullmann–pinacol reaction to prepare *trans*-9,10-dihydroxy-9,10-dihydrophenanthrene was discovered.[25] The reason of the highly *trans*-selectivity[26] in the intramolecular pinacol coupling is still under investigation. We are trying to expand this reaction to *ortho*-halogen-substituted aromatic imines and to apply these chiral phendiols in asymmetric catalysis.

Acknowledgment

Project supported by the National Natural Science Foundation of China (No. 20472077). In addition, we thank the referees for very valuable advice.

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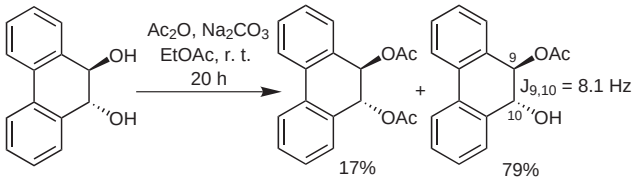
(9) (a) Scherf group reported a similar reaction to *cis*-phendiol with excess $Ni(COD)_2$ in 1999: Reisch, H. A.; Enkelmann, V.; Scherf, U. *J. Org. Chem.* **1999**, *64*, 655. (b) The *trans*-structure of **2a** was determined by the $J_{9,10}$ = 8.1 Hz and the singlet for acetate at δ = 2.11 ppm of *trans*-9-acetoxy-10-hydroxy-9,10-dihydrophenanthrene (Scheme 4). (c) For *cis*-9-acetoxy-10-hydroxy-9,10-dihydrophenanthrene, $J_{9,10}$ = 3.8 Hz and the singlet for acetate is at δ = 1.92 ppm, see: Jerina, D. M.; Selander, H.; Yagi, H.; Wells, M. C.; Davey, J. F.; Mahadevan, V.; Gilbson, D. T. *J. Am. Chem. Soc.* **1976**, *98*, 5988.



Scheme 4

(10) The zinc powder was purchased from SCRC (Sinopharm Chemical Reagent Co., Ltd). The activation procedure was conducted as follows: The zinc powder was stirred in 1 M HCl for a few minutes to remove the oxide, then filtered and washed successively with H_2O, EtOH, and Et_2O. The material was dried in vacuum for 24 h and then stored in a sealed bottle.

(11) **Synthesis of $(Ph_3P)_2NiCl_2$ from $NiCl_2·6H_2O$ and PPh_3**
Nickel(II) chloride hexahydrate and PPh_3 were purchased from SCRC and used as available. Then, PPh_3 (10.50 g, 40 mmol) was dissolved in 100 mL of warm AcOH, and then cooled to r.t. To this solution, $NiCl_2·6H_2O$ (4.76 g, 20 mmol) in H_2O (4 mL) was added dropwise. The mixture was stirred at r.t. for 48 h. The dark green solution was filtered, yielding deep green solid, which was washed successively with AcOH, EtOH, and Et_2O. The material was dried in vacuum for 24 h and then stored in a sealed bottle.

(12) Addition of PPh_3 seems to accelerate the Ullmann coupling step. When 28 mol% of PPh_3 was added and the reaction was ceased in 53 min, the biphenyl-2,2′-dialdehyde can be isolated with 80% yield. But the second step of pinacol coupling was not affected by PPh_3.

(13) The phendiol **2a** is stable in solid. But, in our observation, it could be oxidized to phenanthrenequinone in solution. The colorless solution of phendiol **2a** changed to yellow in several hours, indicated that some phenanthrenequinone was formed. This conversion could be accelerated by silica gel or light, see: Barbas, J. T.; Sigma, M. E.; Dabestani, R. *Environ. Sci. Technol.* **1996**, *30*, 1776; thus, the diol products must be separated as quickly as possible after ceasing the reaction to assure high yields.

(14) In solution, **2b** and **2c** were oxidized faster than **2a** in our observation. That resulted in lower yield of **2b** and **2c**.

(15) The coordination of the Zn^{2+} with both the carbonyls, which brings the two carbonyls together, is essential to the intramolecular pinacol coupling. In the reaction of heterocyclic **1h**, this effect may be disturbed by the competitive coordination of the nitrogen atom on the heterocycle.

(16) **Typical Procedure for the $(Ph_3P)_2NiCl_2$-Catalyzed Ullmann–Pinacol Coupling**
To a mixture of $(Ph_3P)_2NiCl_2$ (33 mg, 0.05 mmol) and zinc powder (196 mg, 3 mmol) in anhyd DMF (0.5 ml) was added the 2-bromobenzaldehyde (**1a**, 185 mg, 117 μL, 1 mmol) at 60 °C under a nitrogen atmosphere. This mixture was stirred for 7 h. After cooling to ambient temperature, 5 mL 1 M HCl and 10 mL CH_2Cl_2 were added. The mixture was stirred for 10 min, and then filtered to remove the unreacted zinc powder. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were dried over $MgSO_4$ for 1 h and concentrated. Purification of the residue by chromatography gave the phendiol **2a** (85 mg, 80% yield).

(17) **Selective NMR Data of Products**
Compound **2a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (dd, *J* = 6.2, 2.8 Hz, 2 H), 7.67 (dd, *J* = 9.4, 3.1 Hz, 2 H), 7.42–7.36 (m, 4 H), 4.76 (s, 2 H), 1.65 (br, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.2, 132.6, 128.6, 128.5, 125.3, 123.9, 74.2.
Compound **2b**: ^{1}H NMR (300 MHz, acetone-d_6): δ = 8.41 (d, *J* = 8.4 Hz, 2 H), 8.21 (d, *J* = 8.7 Hz, 2 H), 8.02 (d, *J* = 8.7 Hz, 2 H), 7.95 (d, *J* = 7.8 Hz, 2 H), 7.64–7.51 (m, 4 H), 5.69 (s, 2 H), 3.13 (s, 2 H). ^{13}C NMR (75 MHz, acetone-d_6): δ = 134.3, 133.9, 132.1, 131.5, 129.8, 129.2, 127.5, 126.6, 124.8, 123.5, 67.9.
Compound **2c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.4 Hz, 2 H), 7.95–7.91 (m, 4 H), 7.56 (d, *J* = 8.4 Hz, 2 H), 7.46 (t, *J* = 7.5 Hz, 2 H), 7.27 (t, *J* = 6.6 Hz, 2 H), 4.73 (s, 2 H), 2.61 (br, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.2, 133.8, 130.2, 129.1, 129.1, 128.5, 127.6, 125.6, 125.4, 121.4, 75.0.
(18) Compound **2e**: ^{1}H NMR (300 MHz, acetone-d_6): δ = 7.78–7.72 (m, 4 H), 7.34–7.29 (m, 4 H), 3.04 (s, 2 H), 1.24 (s, 6 H). ^{13}C NMR (75 MHz, acetone-d_6): δ = 144.8, 132.7, 128.8, 128.0, 125.1, 124.0, 77.3, 25.0.
Compound **2f**: ^{1}H NMR (300 MHz, acetone-d_6): δ = 7.71 (dd, *J* = 8.4, 6.0 Hz, 2 H), 7.60 (dd, *J* = 10.3, 2.5 Hz, 2 H), 7.13 (td, *J* = 8.6, 2.5 Hz, 2 H), 4.60 (s, 2 H), 3.12 (s, 2 H). ^{13}C NMR (75 MHz, acetone-d_6): δ = 163.7 (d, *J* = 241.0 Hz), 135.1 (d, *J* = 2.9 Hz), 134.7 (dd, *J* = 8.0, 2.3 Hz), 129.0 (d, *J* = 8.4 Hz), 115.6 (d, *J* = 21.5 Hz), 111.2 (d, *J* = 23.1 Hz), 73.416.
Compound **4**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.48 (s, 4 H), 7.55 (d, *J* = 4.5 Hz, 2 H), 4.81 (s, 4 H), 2.96 (br, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.7, 148.1, 147.8, 129.8, 122.08, 61.28.

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(20) Compound **1d** was prepared from 9-bromophenanthrene in five steps (Scheme 5).

(21) Pure diol product was not obtained. The most polar product was supposed to be the mixture of *cis*-diol and *trans*-diol by NMR analysis.

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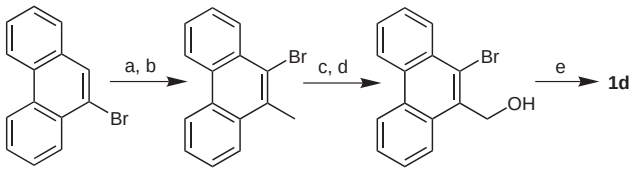

Scheme 5 Preparation of **1d**. *Reagents and conditions*: (a) *n*-BuLi (1.1 equiv), Et_2O, r.t., 1 h; then Me_2SO_4 (2 equiv), Et_2O, reflux, 5 h, 99%; (b) NBS (1.1 equiv), MeCN, r.t. in dark, 24 h, 92%; (c) NBS (1.01 equiv), BPO (0.02 equiv), CCl_4, reflux, 7 h; (d) $CaCO_3$ (5 equiv), dioxane–H_2O (1:1), reflux, 10 h, 92% (2 steps); (e) PCC (1.3 equiv), CH_2Cl_2, 2 h, 84%.

(24) (a) Shi, L.; Fan, C.-A.; Tu, Y.-Q.; Wang, M.; Zhang, F.-M. *Tetrahedron* **2004**, *60*, 2851. (b) Ogoshi, S.; Kamada, H.; Kurosawa, H. *Tetrahedron* **2006**, *62*, 7583.

(25) Preparation in multigram scale is feasible, the dosage of nickel catalyst can be reduced to 0.03 equiv: To a mixture of $(Ph_3P)_2NiCl_2$ (392 mg, 0.60 mmol) and zinc powder (3.930 g, 60.1 mmol) in anhyd DMF (10 mL) was added the 2-bromobenzaldehyde (**1a**, 3.70 g, 2.34 mL, 20 mmol) at 60 °C under nitrogen atmosphere. After stirring for 7 h, the mixture was poured into ice water (50 mL) and filtered. The filtrate was discarded. The filter residue was dissolved in hot EtOAc and filtered again. Concentration of the filtrate gave crude phendiol **2a**, which is easily recrystallized in EtOAc or EtOH to afford pure product (1.683 g, 79% yield).

(26) The *trans*-structures of the phendiols in Table 1 were confirmed based on NMR analysis of the diols and the corresponding monoacetates (see ref. 9).

Typical Procedure for Phendiol Monoacetate

Method A (**2a**, **2c**, **2f**): To a suspension of phendiol (0.05 mmol) and Na_2CO_3 (16 mg, 0.15 mmol) in anhyd EtOAc (0.5 mL), Ac_2O (15 mg, 14 μL, 0.15 mmol) was added at r.t. After the reaction was complete (monitored by TLC), the mixture was poured into 2 mL of cold H_2O and the phases were separated. The aqueous phase was extracted with EtOAc (3 × 1 mL). The combined organic extracts were concentrated. Purification of the residue by chromatography gave the monoacetate.

Method B (**2b**): To a solution of **2b** (18 mg, 0.058 mmol) in 0.5 mL pyridine, Ac_2O (8.9 mg, 8.2 μL, 0.087 mmol) was added at r.t. The reaction was conducted for 10 h. Conventional procedures led to the isolation of the monoacetate (5 mg, 24.5%).

Selective NMR Data of Phendiol Monoacetates

Monoacetate of **2a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (m, 2 H), 7.55 (d, *J* = 7.2 Hz, 1 H), 7.41–7.22 (m, 5 H), 6.02 (d, *J* = 8.1 Hz, 1 H), 4.82 (d, *J* = 8.1 Hz, 1 H), 2.48 (s, 1 H), 2.11 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.3, 135.5, 133.1, 132.3, 132.0, 129.2, 128.9, 128.5, 128.1, 127.6, 127.1, 123.9, 123.8, 74.5, 71.1, 21.1.

Monoacetate of **2b**: ^{1}H NMR (300 MHz, acetone-d_6): δ = 8.38 (d, *J* = 8.4 Hz, 1 H), 8.28–8.25 (m, 3 H), 8.13–8.06 (m, 2 H), 8.00–7.96 (m, 2 H), 7.67–7.53 (m, 4 H), 7.06 (d, *J* = 2.4 Hz, 1 H), 5.66 (d, *J* = 2.4 Hz, 1 H), 3.07 (br, 1 H), 1.84 (s, 3 H). ^{13}C NMR (75 MHz, acetone-d_6): δ = 171.0, 134.5, 134.3, 133.6, 133.5, 133.4, 131.4, 131.3, 131.1, 130.3, 129.5, 129.3, 128.2, 127.8, 127.2, 126.9, 124.7, 124.0, 123.5, 123.4, 68.7, 65.1, 20.9.

Monoacetate of **2c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00–7.90 (m, 5 H), 7.57–7.43 (m, 5 H), 7.29–7.24 (m, 2 H), 6.06 (d, *J* = 11.1 Hz, 1 H), 4.92 (d, *J* = 11.1 Hz, 1 H), 2.65 (br, 1 H), 2.38 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.0, 136.1, 133.9, 133.8, 132.8, 130.2, 130.0, 129.3, 129.0, 128.8, 128.44, 128.39, 127.6, 127.5, 125.8, 125.7, 126.5, 125.4, 121.6, 121.0, 76.6, 73.4, 21.1.

Monoacetate of **2f**: ^{1}H NMR (300 MHz, acetone-d_6): δ = 7.73–7.63 (m, 3 H), 7.45 (dd, *J* = 8.4, 5.7 Hz, 1 H), 7.19–7.07 (m, 2 H), 5.96 (d, *J* = 7.2 Hz, 1 H), 4.84 (d, *J* = 7.2 Hz, 1 H), 3.03 (s, 1 H), 2.09 (s, 3 H). ^{13}C NMR (75 MHz, acetone-d_6): δ = 170.9, 165.8 (d, *J* = 17.1 Hz), 162.6 (d, *J* = 16.2 Hz), 135.8 (dd, *J* = 8.2, 2.4 Hz), 134.7 (dd, *J* = 8.0, 2.2 Hz), 133.6 (d, *J* = 2.9 Hz), 131.3 (d, *J* = 8.6 Hz), 130.9 (d, *J* = 8.5 Hz), 130.0 (d, *J* = 3.0 Hz), 116.2 (d, *J* = 14.3 Hz), 115.8 (d, *J* = 14.5 Hz), 112.0 (d, *J* = 15.9 Hz), 111.6 (d, *J* = 15.9 Hz), 74.2, 70.1, 21.0.