Catalytic Asymmetric Arylative Cyclization of Alkynals: Phosphine-Free Rhodium/Diene Complexes as Efficient Catalysts

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Supporting Information

I. General

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under argon.

Et₂O, THF, and 1,4-dioxane were distilled over benzophenone ketyl under nitrogen. Methanol was distilled over magnesium turnings under nitrogen. Dichloromethane was distilled over CaH under nitrogen. DMF was distilled over CaH under vacuum.

Dimethyl malonate (Wako Chemicals), bromoacetaldehyde dimethyl acetal (Aldrich), bromopropionaldehyde dimethyl acetal (Wako Chemicals), 1-bromo-2-butyne (Wako Chemicals), 1-bromo-2-pentyne (Wako Chemicals), benzyl bromide (Wako Chemicals), bromoacetone (TCI), *p*-toluenesulfonyl chloride (Wako Chemicals), iodomethane (Wako Chemicals), trimethylsilylacetylene (Aldrich), 3-aminopropionaldehyde diethyl acetal (TCI), trimethyl orthoformate (Wako Chemicals), 4-dimethylaminopyridine (Wako Chemicals), Et₃N (Wako Chemicals), trifluoroacetic acid (Wako Chemicals), *p*-toluenesulfonic acid (Nacalai Tesque; monohydrate), PhB(OH)₂ (TCI), NaOMe (Wako Chemicals), K₂CO₃ (Wako Chemicals), NaH (Kanto Chemicals; 60 wt% in mineral oil), LiAlH₄ (Wako Chemicals), *n*-BuLi (Kanto Chemicals; 1.50 M solution in hexane), CuI (Nacalai Tesque), P(*t*-Bu)₃ (Kanto Chemicals), 1,3-bis(diphenylphosphino)propane (Kanto Chemicals), 1,4-bis(diphenylphosphino)butane (TCI), 1,1'-bis(diphenylphosphino)ferrocene (Fluka), and PPh₃ (Wako Chemicals) were used as received. Diisopropylamine (Aldrich) was distilled over KOH under vacuum prior to use. Other arylboronic acids were synthesized from the corresponding aryl bromides with B(OMe)₃ (Wako Chemicals). PdCl₂(PhCN)₂,¹ [RhCl(C₂H₄)₂]₂,² [RhCl(cod)]₂,³ [Rh(OH)(cod)]₂,⁴ (*R,R*)-**3**,⁵ and (*S,S*)-**4**⁶ were synthesized following the literature procedures.

All other chemicals and solvents were purchased from Aldrich, Wako Chemicals, TCI, or Kanto Chemicals and used as received.

¹ Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.

² Cramer, R. *Inorg. Synth.* **1974**, *15*, 16.

³ Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218.

⁴ Uson, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126.

⁵ Hayashi, T.; Ueyama, K.; Tokunaga, N.; Yoshida, K. *J. Am. Chem. Soc.* **2003**, *125*, 11508.

⁶ Tokunaga, N.; Otomaru, Y.; Okamoto, K.; Ueyama, K.; Shintani, R.; Hayashi, T. *J. Am. Chem. Soc.* **2004**, *126*, 13584.

II. Synthesis of Substrates

The yields have not been optimized.

3,3-Bis(benzyloxymethyl)-5-heptynal (1a)

Dimethyl malonate (2.45 mL, 21.3 mmol) was added to a solution of NaOMe (1.27 g, 23.4 mmol) in MeOH (16 mL), and the mixture was stirred for 15 min at 50 °C. Bromoacetaldehyde dimethyl acetal (3.00 mL, 22.5 mmol) was then added to this mixture, and the resulting solution was stirred for 72 h at 80 °C. After cooling to room temperature, the mixture was poured into NaCl (aqueous, saturated) and extracted with Et₂O. The organic layer was dried over MgSO₄, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane=2/3 to afford dimethyl 2,2-dimethoxyethylmalonate (CAS 51534-81-7) as a pale yellow oil (2.37 g, 10.8 mmol; 50% yield).

¹H NMR (CDCl₃): δ 4.41 (t, ³J_{HH} = 5.5 Hz, 1H), 3.75 (s, 6H), 3.54 (t, ³J_{HH} = 7.2 Hz, 1H), 3.32 (s, 6H), 2.23 (dd, ³J_{HH} = 7.2 and 5.5 Hz, 2H).

Dimethyl 2,2-dimethoxyethylmalonate (2.18 g, 9.90 mmol) was added dropwisely to a suspension of NaH (478 mg, 12.0 mmol; 60 wt% in mineral oil) in THF (50 mL) at 0 °C, and the mixture was stirred for 30 min. 1-Bromo-2-butyne (1.09 mL, 12.4 mmol) was then added to it at 0 °C, and the resulting mixture was stirred for 4 h at room temperature. The reaction was quenched with water, and then extracted with Et₂O. The organic layer was dried over MgSO₄, filtered, and concentrated under vacuum to afford 3,3-bis(methoxycarbonyl)-5-heptynal dimethyl acetal as a pale yellow oil quantitatively.

A solution of this oil in Et₂O (15 mL) was added to a suspension of LiAlH₄ (758 mg, 20.0 mmol) in Et₂O (25 mL) at 0 °C, and the mixture was stirred for 17 h at room temperature. After quenching with water, the precipitate was removed by filtration. The resulting solution was dried over MgSO₄, filtered, and concentrated under vacuum to afford the diol as a colorless oil quantitatively.

A solution of this diol in THF (10 mL) was added to a suspension of NaH (1.22 g, 30.5 mmol; 60 wt% in mineral oil) in THF (30 mL) and DMF (5 mL) at 0 °C. After stirring for 15 min at 0 °C, benzyl bromide (2.59 mL, 21.8 mmol) was added to it, and the mixture was stirred for 36 h at room temperature. The reaction was quenched with water, and then extracted with Et₂O. The organic layer was dried over MgSO₄, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Et₂O/hexane=1/4 to afford 3,3-bis(benzyloxymethyl)-5-heptynal dimethyl acetal as a colorless oil (2.26 g, 5.70 mmol; 58% yield).

¹H NMR (CDCl₃): δ 7.35-7.29 (m, 8H), 7.29-7.23 (m, 2H), 4.58 (t, ³J_{HH} = 5.5 Hz, 1H),

4.50 (s, 4H), 3.43 (s, 4H), 3.26 (s, 6H), 2.31 (q, $^4J_{\text{HH}} = 1.9$ Hz, 2H), 1.77 (d, $^3J_{\text{HH}} = 5.5$ Hz, 2H), 1.75 (t, $^4J_{\text{HH}} = 2.4$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 138.8, 128.2, 127.4, 127.3, 102.3, 77.5, 75.8, 73.2, 72.4, 52.5, 40.7, 34.7, 23.2, 3.6. Anal. Calcd for $\text{C}_{25}\text{H}_{32}\text{O}_4$: C, 75.73; H, 8.13. Found: C, 75.52; H, 8.09.

Trifluoroacetic acid (6 mL) was added to a mixture of 3,3-bis(benzyloxymethyl)-5-heptynal dimethyl acetal (1.93 g, 4.94 mmol) in CHCl_3 (12 mL) and water (6 mL) at 0°C . The resulting heterogeneous mixture was stirred for 9 h at room temperature. The reaction was quenched with NaHCO_3 (aqueous, saturated), and then extracted with CHCl_3 . The organic layer was dried over MgSO_4 , filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Et_2O /hexane=1/2 to afford 3,3-bis(benzyloxymethyl)-5-heptynal as a pale yellow oil (1.17 g, 3.34 mmol; 68% yield).

^1H NMR (CDCl_3): δ 9.80 (t, $^3J_{\text{HH}} = 2.8$ Hz, 1H), 7.35-7.31 (m, 4H), 7.31-7.25 (m, 6H), 4.48 (s, 4H), 3.52 (d, $^2J_{\text{HH}} = 8.9$ Hz, 2H), 3.48 (d, $^2J_{\text{HH}} = 9.1$ Hz, 2H), 2.49 (d, $^3J_{\text{HH}} = 2.8$ Hz, 2H), 2.41 (q, $^4J_{\text{HH}} = 2.6$ Hz, 2H), 1.75 (t, $^4J_{\text{HH}} = 2.5$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 201.6, 138.1, 128.2, 127.4, 127.3, 78.4, 74.8, 73.2, 72.3, 47.0, 42.6, 23.5, 3.4. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{26}\text{O}_3\text{Na}$ ($\text{M}+\text{Na}^+$) 373.1774, found 373.1775.

3,3-Bis(benzyloxymethyl)-5-octynal (1b)

This was synthesized using 1-bromo-2-pentyne instead of 1-bromo-2-butyne, following the procedure for 3,3-bis(benzyloxymethyl)-5-heptynal. Pale yellow oil, 49% overall yield from dimethyl 2,2-dimethoxyethylmalonate.

^1H NMR (CDCl_3): δ 9.81 (t, $^3J_{\text{HH}} = 2.8$ Hz, 1H), 7.35-7.23 (m, 10H), 4.48 (s, 4H), 3.53 (d, $^2J_{\text{HH}} = 9.0$ Hz, 2H), 3.49 (d, $^2J_{\text{HH}} = 9.0$ Hz, 2H), 2.49 (d, $^3J_{\text{HH}} = 2.8$ Hz, 2H), 2.42 (t, $^4J_{\text{HH}} = 2.4$ Hz, 2H), 2.12 (qt, $^3J_{\text{HH}} = 7.4$ Hz and $^4J_{\text{HH}} = 2.4$ Hz, 2H), 1.08 (t, $^3J_{\text{HH}} = 7.5$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 201.7, 138.2, 128.2, 127.44, 127.38, 84.7, 75.0, 73.3, 72.4, 47.0, 42.6, 23.5, 14.1, 12.3. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{28}\text{O}_3\text{Na}$ ($\text{M}+\text{Na}^+$) 387.1931, found 387.1938.

4,4-Bis(benzyloxymethyl)-6-octyn-2-one (1f)

Dimethyl malonate (2.29 mL, 20.0 mmol) was added to a suspension of NaH (880 mg, 22.0 mmol; 60 wt% in mineral oil) in THF (40 mL) at 0°C , and the mixture was stirred for 15 min at 0°C . Bromoacetone (2.24 mL, 24.0 mmol) was then added to it, and

the resulting mixture was stirred for 15 h at room temperature. After being quenched with water, NaCl (aqueous, saturated) was added to it and the mixture was then extracted with Et₂O. The organic layer was dried over MgSO₄, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Et₂O/hexane=2/1 to afford dimethyl acetonylmalonate (CAS 24889-15-4) as a pale yellow oil (3.06 g, 16.3 mmol; 81% yield).

A solution of dimethyl acetonylmalonate (1.21 g, 6.42 mmol) and *p*-toluenesulfonic acid (7.5 mg, 39 μmol; monohydrate) in trimethyl orthoformate (8 mL) and MeOH (2 mL) was refluxed for 56 h. After cooling to room temperature, the mixture was poured into NaCl (aqueous, saturated) and extracted with Et₂O. The organic layer was dried over MgSO₄, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Et₂O/hexane=1/1 to afford dimethyl 2,2-dimethoxypropylmalonate (CAS 133494-04-9) as an almost colorless oil (1.22 g, 5.22 mmol; 81% yield).

¹H NMR (CDCl₃): δ 3.74 (s, 6H), 3.51 (t, ³J_{HH} = 6.7 Hz, 1H), 3.16 (s, 6H), 2.31 (d, ³J_{HH} = 6.6 Hz, 2H), 1.25 (s, 3H).

This was synthesized following the procedure for 3,3-bis(benzyloxymethyl)-5-heptynal (**1a**). Pale yellow oil, 50% overall yield from dimethyl 2,2-dimethoxypropylmalonate.

¹H NMR (CDCl₃): δ 7.33-7.24 (m, 10H), 4.47 (s, 4H), 3.52 (s, 4H), 2.56 (s, 2H), 2.42 (q, ⁴J_{HH} = 2.4 Hz, 2H), 2.10 (s, 3H), 1.74 (t, ⁴J_{HH} = 2.5 Hz, 3H). ¹³C NMR (CDCl₃): δ 208.3, 138.6, 128.2, 127.4, 127.3, 77.6, 75.5, 73.2, 71.7, 44.2, 42.3, 32.0, 22.9, 3.5. Anal. Calcd for C₂₄H₂₈O₃: C, 79.09; H, 7.74. Found: C, 78.93; H, 7.76.

(2-(1'-Propynyl)phenyl)acetaldehyde (**1c**)

A solution of (2-bromophenyl)acetaldehyde dimethyl acetal⁷ (3.28 g, 13.4 mmol; CAS 112396-13-1) in 1,4-dioxane (15 mL) and trimethylsilylacetylene (2.27 mL, 16.1 mmol) were successively added to a mixture of PdCl₂(PhCN)₂ (154.2 mg, 0.40 mmol), P(*t*-Bu)₃ (162.7 mg, 0.80 mmol), CuI (51.0 mg, 0.27 mmol), and (*i*-Pr)₂NH (2.25 mL, 16.1 mmol) in 1,4-dioxane (15 mL). The resulting mixture was stirred for 42 h at 50 °C. After cooling to room temperature, this was passed through a pad of silica gel with Et₂O and concentrated under vacuum. The residue was dissolved in MeOH (90 mL), and NaOH (30 mL; aqueous, 3 N) was then added at 0 °C. The reaction mixture was stirred for 1 h

⁷ Wunsch, B. *Arch. Pharm. (Weinheim, Ger.)* **1990**, 323, 493-499.

at room temperature, and then neutralized by NH_4Cl (aqueous, saturated) at 0 °C. After extraction with Et_2O , the organic layer was dried over MgSO_4 , filtered, and concentrated. The residue was chromatographed on silica gel with Et_2O /hexane=1/6 to afford (2-ethynylphenyl)acetaldehyde dimethyl acetal as an orange oil (1.59 g, 8.36 mmol; 63% yield).

^1H NMR (CDCl_3): δ 7.49 (d, $^3J_{\text{HH}} = 7.9$ Hz, 1H), 7.30-7.27 (m, 2H), 7.20-7.16 (m, 1H), 4.66 (t, $^3J_{\text{HH}} = 5.6$ Hz, 1H), 3.35 (s, 6H), 3.30 (s, 1H), 3.13 (d, $^3J_{\text{HH}} = 5.7$ Hz, 2H). ^{13}C NMR (CDCl_3): δ 139.6, 132.9, 130.5, 128.9, 126.5, 122.2, 104.6, 82.4, 81.3, 53.7, 38.4. Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2$: C, 75.76; H, 7.42. Found: C, 75.70; H, 7.55.

n-BuLi (5.58 mL, 8.37 mmol; 1.50 M in hexane) was added to a solution of (2-ethynylphenyl)acetaldehyde dimethyl acetal (1.59 g, 8.37 mmol) in THF (25 mL) at -78 °C. After stirring for 15 min, iodomethane (1.04 mL, 16.7 mmol) was added to it at -78 °C. The reaction mixture was stirred for 3 h at room temperature and was quenched with water. After extraction with Et_2O , the organic layer was dried over MgSO_4 , filtered, and concentrated to afford (2-(1'-propynyl)phenyl)acetaldehyde dimethyl acetal as an orange oil (1.63 g). This orange oil (736 mg) was dissolved in CHCl_3 (10 mL) and water (5 mL) was then added. Trifluoroacetic acid (5 mL) was added to this at 0 °C, and the resulting heterogeneous mixture was stirred for 21 h at room temperature. The reaction was quenched with NaHCO_3 (aqueous, saturated), and then extracted with CHCl_3 . The organic layer was dried over MgSO_4 , filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Et_2O /hexane=1/3 to afford (2-(1'-propynyl)phenyl)acetaldehyde as an orange-brown oil (395 mg, 2.50 mmol; 66% yield).

^1H NMR (CDCl_3): δ 9.73 (t, $^3J_{\text{HH}} = 2.2$ Hz, 1H), 7.47-7.43 (m, 1H), 7.30-7.22 (m, 2H), 7.21-7.17 (m, 1H), 3.83 (d, $^3J_{\text{HH}} = 2.0$ Hz, 2H), 2.06 (s, 3H). ^{13}C NMR (CDCl_3): δ 199.7, 134.2, 132.3, 130.0, 128.1, 127.4, 124.6, 91.1, 78.0, 49.2, 4.3. Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{O}$: C, 83.51; H, 6.37. Found: C, 83.25; H, 6.51.

4,4-Bis(methoxycarbonyl)-6-octaynal (1d)

Dimethyl malonate (2.29 mL, 20.0 mmol) was added to a solution of NaOMe (1.19 g, 22.0 mmol) in MeOH (15 mL), and the mixture was stirred for 15 min at 50 °C. Bromopropionaldehyde dimethyl acetal (3.28 mL, 24.0 mmol) was then added to this mixture, and the resulting solution was stirred for 61 h at 80 °C. After cooling to room temperature, the mixture was poured into NaCl (aqueous, saturated) and extracted

with Et₂O. The organic layer was dried over MgSO₄, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Et₂O/hexane=1/2 to afford dimethyl 3,3-dimethoxypropylmalonate (CAS 53744-52-8) as a pale yellow oil (2.72 g, 11.6 mmol; 58% yield).

Dimethyl 3,3-dimethoxypropylmalonate (1.43 g, 6.10 mmol) was added dropwisely to a suspension of NaH (292 mg, 7.30 mmol; 60 wt% in mineral oil) in THF (23 mL) at room temperature, and the mixture was stirred for 20 min. 1-Bromo-2-butyne (700 μ L; 8.00 mmol) was then added to it at 0 °C, and the resulting mixture was stirred for 5 h at room temperature. The reaction was quenched with water, and then extracted with Et₂O. The organic layer was dried over MgSO₄, filtered, and concentrated under vacuum to afford 4,4-bis(methoxycarbonyl)-6-octynal dimethyl acetal as a pale yellow oil quantitatively.

Trifluoroacetic acid (8 mL) was added to a mixture of 4,4-bis(methoxycarbonyl)-6-octynal dimethyl acetal in CHCl₃ (16 mL) and water (8 mL) at 0 °C. The resulting heterogeneous mixture was stirred for 7 h at 0 °C. The reaction was quenched with NaHCO₃ (aqueous, saturated), and then extracted with CHCl₃. The organic layer was dried over MgSO₄, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Et₂O/hexane=2/3 to afford 4,4-bis(methoxycarbonyl)-6-octynal as a pale yellow oil (1.03 g, 4.29 mmol; 70% yield).

¹H NMR (CDCl₃): δ 9.76 (t, ³J_{HH} = 1.2 Hz, 1H), 3.74 (s, 6H), 2.77 (q, ⁴J_{HH} = 2.6 Hz, 2H), 2.52-2.48 (m 2H), 2.38-2.35 (m, 2H), 1.75 (t, ⁴J_{HH} = 2.5 Hz, 3H). ¹³C NMR (CDCl₃): δ 200.5, 170.3, 79.1, 72.6, 56.0, 52.5, 38.7, 24.6, 23.7, 3.1. HRMS (ESI) calcd for C₁₂H₁₆O₅Na (M+Na⁺) 263.0890, found 263.0890.

***N*-(2'-Pentynyl)-*N*-(*p*-tosyl)-3-aminopropionaldehyde (1e)**

A solution of *p*-toluenesulfonyl chloride (2.10 g, 11.0 mmol) in dichloromethane (10 mL) was added to a mixture of 3-aminopropionaldehyde diethyl acetal (1.62 mL, 10.0 mmol), Et₃N (2.79 mL, 20.0 mmol), and 4-dimethylaminopyridine (6.1 mg, 50 μ mol) in dichloromethane (20 mL) at 0 °C. The resulting mixture was stirred for 10 h at room temperature, and then quenched with water. After extraction with Et₂O, the organic layer was dried over MgSO₄, filtered, and concentrated under vacuum to afford *N*-(*p*-tosyl)-3-aminopropionaldehyde diethyl acetal (CAS 164532-58-5) as a yellow oil quantitatively.

¹H NMR (CDCl₃): δ 7.74 (d, ³J_{HH} = 8.0 Hz, 2H), 7.30 (d, ³J_{HH} = 8.4 Hz, 2H), 5.11 (bs, 1H), 4.48 (t, ³J_{HH} = 4.9 Hz, 1H), 3.61 (dq, ²J_{HH} = 8.8 Hz and ³J_{HH} = 7.2 Hz, 2H), 3.43 (dq,

$^2J_{\text{HH}} = 8.8$ Hz and $^3J_{\text{HH}} = 7.1$ Hz, 2H), 3.05 (td, $^3J_{\text{HH}} = 6.1$ Hz and 5.9 Hz, 2H), 2.42 (s, 3H), 1.76 (dt, $^3J_{\text{HH}} = 6.2$ Hz and 5.3 Hz, 2H), 1.17 (t, $^3J_{\text{HH}} = 7.1$ Hz, 6H).

1-Bromo-2-pentyne (530 μL , 5.18 mmol) was added to a mixture of *N*-(*p*-tosyl)-3-propionacetaldehyde diethyl acetal (1.12 g, 3.72 mmol) and K_2CO_3 (1.02 g, 7.38 mmol) in DMF (12 mL) at room temperature, and the resulting mixture was stirred for 20 h at 80 $^\circ\text{C}$. The reaction was quenched with water, and then extracted with Et_2O . The organic layer was dried over MgSO_4 , filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Et_2O /hexane=1/2 to afford *N*-(2'-pentynyl)-*N*-(*p*-tosyl)-3-aminopropionaldehyde diethyl acetal as a pale yellow oil (1.27 g, 3.46 mmol; 93% yield).

^1H NMR (CDCl_3): δ 7.73 (d, $^3J_{\text{HH}} = 8.3$ Hz, 2H), 7.28 (d, $^3J_{\text{HH}} = 8.1$ Hz, 2H), 4.59 (t, $^3J_{\text{HH}} = 5.5$ Hz, 1H), 4.09 (t, $^4J_{\text{HH}} = 2.2$ Hz, 2H), 3.66 (dq, $^2J_{\text{HH}} = 9.3$ Hz and $^3J_{\text{HH}} = 7.1$ Hz, 2H), 3.52 (dq, $^2J_{\text{HH}} = 9.2$ Hz and $^3J_{\text{HH}} = 7.0$ Hz, 2H), 3.26 (t, $^3J_{\text{HH}} = 7.0$ Hz, 2H), 2.41 (s, 3H), 1.95-1.87 (m, 4H), 1.21 (t, $^3J_{\text{HH}} = 7.0$ Hz, 6H), 0.90 (t, $^3J_{\text{HH}} = 7.5$ Hz, 3H).

Trifluoroacetic acid (1.0 mL) was added to a mixture of *N*-(2'-pentynyl)-*N*-(*p*-tosyl)-3-aminopropionaldehyde dimethyl acetal (366 mg, 1.00 mmol) in CHCl_3 (2 mL) and water (1 mL) at 0 $^\circ\text{C}$. The resulting heterogeneous mixture was stirred for 8 h at room temperature. The reaction was quenched with NaHCO_3 (aqueous, saturated), and then extracted with CHCl_3 . The organic layer was dried over MgSO_4 , filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Et_2O /hexane=1/2 to afford *N*-(2'-pentynyl)-*N*-(*p*-tosyl)-3-aminopropionaldehyde as a pale yellow oil (224 mg, 0.76 mmol; 76% yield).

^1H NMR (CDCl_3): δ 9.80 (t, $^3J_{\text{HH}} = 1.2$ Hz, 1H), 7.74 (d, $^3J_{\text{HH}} = 8.3$ Hz, 2H), 7.30 (d, $^3J_{\text{HH}} = 7.9$ Hz, 2H), 4.08 (t, $^4J_{\text{HH}} = 2.2$ Hz, 2H), 3.50 (t, $^3J_{\text{HH}} = 6.9$ Hz, 2H), 2.83 (td, $^3J_{\text{HH}} = 6.9$ Hz and 1.2 Hz, 2H), 2.42 (s, 3H), 1.94 (qt, $^3J_{\text{HH}} = 7.4$ Hz and $^4J_{\text{HH}} = 2.3$ Hz, 2H), 0.91 (t, $^3J_{\text{HH}} = 7.6$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 200.2, 143.6, 135.5, 129.4, 127.8, 87.8, 71.8, 43.0, 40.4, 38.0, 21.5, 13.4, 12.1. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{20}\text{NO}_3\text{S}$ ($\text{M}+\text{H}^+$) 294.1158, found 294.1158.

Dimethyl (2-pentynyl)(2-methylallyl)malonate (5)

Dimethyl (2-methylallyl)malonate⁸ (215.6 mg, 1.16 mmol) was added to a suspension of NaH (55.6 mg, 1.39 mmol; 60 wt% in mineral oil) in THF (5 mL) at 0 $^\circ\text{C}$, and the mixture was stirred for 15 min. 1-Bromo-2-pentyne (148 μL ; 1.45 mmol) was then added to it at 0 $^\circ\text{C}$, and the resulting mixture was stirred for 3 h at room temperature. The reaction was quenched with water, and then extracted with Et_2O . The organic layer was dried over MgSO_4 , filtered, and concentrated under vacuum. The residue was

⁸ Harrowven, D. C.; May, P. J.; Bradley, M. *Tetrahedron Lett.* **2003**, *44*, 503–506.

chromatographed on silica gel with Et₂O/hexane=1/4 to afford dimethyl (2-pentynyl)(2-methylallyl)malonate as a pale yellow oil (250.6 mg, 0.99 mmol; 86% yield).

¹H NMR (CDCl₃): δ 4.90 (s, 1H), 4.82 (s, 1H), 3.73 (s, 6H), 2.83 (s, 2H), 2.79 (t, ⁴J_{HH} = 2.4 Hz, 2H), 2.12 (qt, ³J_{HH} = 7.5 Hz and ⁴J_{HH} = 2.3 Hz, 2H), 1.66 (s, 3H), 1.09 (t, ³J_{HH} = 7.4 Hz, 3H). ¹³C NMR (CDCl₃): δ 171.0, 140.2, 116.1, 85.4, 74.1, 57.0, 52.7, 39.6, 23.3, 23.1, 14.3, 12.4. Anal. Calcd for C₁₄H₂₀O₄: C, 66.65; H, 7.99. Found: C, 66.41; H, 8.18.

III. Arylative Cyclization Reactions

General Procedure for Table 1.

KOH (0.15 mL, 45 μ mol; 0.3 M in H₂O) was added to a solution of [RhCl(C₂H₄)₂]₂ (2.0 mg, 10 μ mol Rh) and ligand (11.3 μ mol) in 1,4-dioxane (1.0 mL), and the mixture was stirred for 5 min at room temperature. PhB(OH)₂ (64.0 mg, 0.52 mmol) and alkynal **1a** (52.6 mg, 0.15 mmol) were added to it with additional 1,4-dioxane (0.5 mL), and the resulting solution was stirred for 4 h at 60 °C. The reaction mixture was directly passed through a pad of silica gel with Et₂O and the solvent was removed under vacuum. The residue was purified by silica gel PTLC with Et₂O/hexane = 1/2 to afford the desired allylic alcohol **2a** as a yellow oil.

¹H NMR (CDCl₃): δ 7.37-7.27 (m, 14H), 7.22-7.19 (m, 1H), 4.62 (d, ²J_{HH} = 12.1 Hz, 1H), 4.59 (d, ²J_{HH} = 12.1 Hz, 1H), 4.49 (s, 2H), 4.34 (bt, ³J_{HH} = 6.6 Hz, 1H), 3.59 (d, ²J_{HH} = 8.5 Hz, 1H), 3.55 (d, ²J_{HH} = 8.5 Hz, 1H), 3.43 (d, ³J_{HH} = 7.7 Hz, 1H), 3.30 (d, ²J_{HH} = 12.1 Hz, 1H), 3.28 (d, ²J_{HH} = 12.0 Hz, 1H), 2.62 (d, ²J_{HH} = 17.5 Hz, 1H), 2.42 (d, ²J_{HH} = 17.3 Hz, 1H), 1.98 (s, 3H), 1.82 (dd, ²J_{HH} = 14.4 Hz and ²J_{HH} = 6.0 Hz, 1H), 1.75 (d, ²J_{HH} = 14.4 Hz, 1H). ¹³C NMR (CDCl₃): δ 143.2, 141.5, 138.4, 137.8, 131.4, 128.4, 128.3, 128.0, 127.83, 127.81, 127.7, 127.5, 127.4, 126.5, 76.0, 75.7, 73.6, 73.2, 72.3, 46.1, 42.9, 36.1, 21.4. Anal. Calcd for C₂₉H₃₂O₃: C, 81.27; H, 7.53. Found: C, 81.07; H, 7.64.

General Procedure for Table 2.

A solution of [Rh(OH)(cod)]₂ (2.4 mg, 11 μ mol Rh), PhB(OH)₂ (64.0 mg, 0.52 mmol), and alkynal (0.15 mmol) in 1,4-dioxane (1.5 mL) and water (0.15 mL) was stirred for 4 h at 60 °C. The reaction mixture was directly passed through a pad of silica gel with Et₂O and the solvent was removed under vacuum. The residue was purified by silica gel PTLC with Et₂O/hexane to afford the desired allylic alcohol.

Pale yellow oil. 93% yield.

¹H NMR (CDCl₃): δ 7.36-7.20 (m, 15H), 4.60 (d, ²J_{HH} = 12.2 Hz, 1H), 4.57 (d, ²J_{HH} = 12.2 Hz, 1H), 4.50 (s, 2H), 4.30 (bt, ³J_{HH} = 6.1 Hz, 1H), 3.58 (d, ²J_{HH} = 8.5 Hz, 1H), 3.55 (d, ²J_{HH} = 8.5 Hz, 1H), 3.32 (d, ²J_{HH} = 8.8 Hz, 1H), 3.29 (d, ²J_{HH} = 8.8 Hz, 1H), 2.97 (d, ³J_{HH} = 6.8 Hz, 1H), 2.60 (d, ²J_{HH} = 17.0 Hz, 1H), 2.45 (d, ²J_{HH} = 17.0 Hz, 1H), 2.37-2.30 (m, 2H), 1.81 (dd, ²J_{HH} = 14.3 Hz and ³J_{HH} = 6.2 Hz, 1H), 1.70 (d, ²J_{HH} = 14.3 Hz, 1H), 0.90 (t, ³J_{HH} = 7.4 Hz, 3H). ¹³C NMR (CDCl₃): δ 141.8, 140.7, 138.5, 138.2, 138.0, 128.40, 128.37, 128.3,

128.0, 127.7, 127.6, 127.5, 127.4, 126.5, 75.6, 75.4, 73.5, 73.2, 72.4, 46.1, 42.1, 35.1, 28.4, 12.4. Anal. Calcd for C₃₀H₃₄O₃: C, 81.41; H, 7.74. Found: C, 81.21; H, 7.81.

Pale yellow solid. 76% yield.

¹H NMR (CDCl₃): δ 7.69 (d, ³J_{HH} = 7.6 Hz, 1H), 7.42-7.37 (m, 4H), 7.31-7.22 (m, 4H), 4.66 (d, ³J_{HH} = 5.5 Hz, 1H), 3.13 (dd, ²J_{HH} = 16.6 Hz and ³J_{HH} = 5.7 Hz, 1H), 2.79 (d, ²J_{HH} = 16.7 Hz, 1H), 2.43 (s, 3H), 1.69 (bs, 1H). ¹³C NMR (CDCl₃): δ 144.2, 144.1, 140.9, 139.4, 135.5, 128.4, 127.8, 127.7, 127.1, 126.6, 125.7, 125.6, 74.1, 40.6, 22.1. HRMS (ESI) calcd for C₁₇H₁₆ONa (M+Na⁺) 259.1093, found 259.1087.

Colorless oil. 75% yield.

¹H NMR (CDCl₃): δ 7.32-7.29 (m, 2H), 7.24 (t, ³J_{HH} = 7.3 Hz, 1H), 7.05 (d, ³J_{HH} = 7.0 Hz, 2H), 4.30 (bs, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.24 (d, ²J_{HH} = 13.7 Hz, 1H), 2.87 (d, ²J_{HH} = 13.8 Hz, 1H), 2.23-2.20 (m, 2H), 2.01 (d, ⁴J_{HH} = 1.2 Hz, 3H), 1.77-1.72 (m, 2H), 1.21 (bs, 1H). ¹³C NMR (CDCl₃): δ 172.3, 171.0, 143.4, 135.3, 131.0, 128.3, 127.6, 126.6, 66.5, 56.5, 52.7, 52.2, 30.4, 29.5, 25.5, 20.7. HRMS (ESI) calcd for C₁₈H₂₂O₅Na (M+Na⁺) 341.1359, found 341.1357.

Colorless viscous oil. 64% yield.

¹H NMR (CDCl₃): δ 7.72 (d, ³J_{HH} = 8.0 Hz, 2H), 7.36-7.24 (m, 5H), 7.05 (d, ³J_{HH} = 7.7 Hz, 2H), 4.57 (d, ²J_{HH} = 12.7 Hz, 1H), 4.23-4.20 (m, 1H), 3.65-3.61 (m, 1H), 3.27 (d, ²J_{HH} = 12.7 Hz, 1H), 2.85 (td, ²J_{HH} = 12.1 Hz and ³J_{HH} = 3.2 Hz, 1H), 2.57-2.44 (m, 2H), 2.45 (s, 3H), 1.77 (tdd, ²J_{HH} = 14.2 Hz and ³J_{HH} = 4.9 Hz and 2.9 Hz, 1H), 1.70 (dq, ²J_{HH} = 13.8 Hz and ³J_{HH} = 2.7 Hz, 1H), 1.67 (bs, 1H), 0.94 (t, ³J_{HH} = 7.7 Hz, 3H). ¹³C NMR (CDCl₃): δ 143.4, 142.1, 141.0, 133.6, 129.6, 128.7, 128.2, 128.0, 127.7, 126.9, 64.9, 43.1, 40.9, 32.5, 27.4, 21.5, 12.8. HRMS (ESI) calcd for C₂₁H₂₅NO₃SNa (M+Na⁺) 394.1447, found 394.1446.

General Procedure for Table 3.

KOH (0.15 mL, 45 μmol; 0.3 M in H₂O) was added to a solution of [RhCl(C₂H₄)₂]₂

(2.0 mg, 10 μ mol Rh) and ligand (11.3 μ mol) in 1,4-dioxane (1.0 mL), and the mixture was stirred for 5 min at room temperature. ArB(OH)₂ (0.53 mmol) and **1** (0.15 mmol) were added to it with additional 1,4-dioxane (0.5 mL), and the resulting solution was stirred for 4 h at 60 °C. The reaction mixture was directly passed through a pad of silica gel with Et₂O and the solvent was removed under vacuum. The residue was purified by silica gel PTLC with Et₂O/hexane to afford the desired allylic alcohol.

Entry 3. Yellow oil. 78% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane : isopropanol = 95 : 5, flow = 0.5 mL/min. Retention times: 22.8 min [(*S*)-enantiomer], 28.6 min [(*R*)-enantiomer]. 95% ee. $[\alpha]_D^{20} +51.0$ (*c* 1.02, CHCl₃). The absolute configuration was determined by the Mosher's analysis after converting it to the corresponding (*R*)-MTPA ester.⁹

Entry 4. Pale yellow oil. 89% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane : isopropanol = 95 : 5, flow = 0.5 mL/min. Retention times: 19.7 min [(*S*)-enantiomer], 22.1 min [(*R*)-enantiomer]. 94% ee. $[\alpha]_D^{20} +48.9$ (*c* 0.80, CHCl₃). The absolute configuration was assigned by analogy with entry 3.

Entry 5. Yellow oil. 71% yield. The ee was determined on a Daicel Chiralcel OD-H column with hexane : isopropanol = 90 : 10, flow = 0.8 mL/min. Retention times: 14.9 min [(*R*)-enantiomer], 20.3 min [(*S*)-enantiomer]. 93% ee. $[\alpha]_D^{20} +67.4$ (*c* 1.07, CHCl₃). The absolute configuration was assigned by analogy with entry 3.

¹H NMR (CDCl₃): δ 7.37-7.26 (m, 12H), 6.89-6.82 (m, 2H), 4.62 (d, ²*J*_{HH} = 12.1 Hz, 1H), 4.59 (d, ²*J*_{HH} = 12.2 Hz, 1H), 4.49 (s, 2H), 4.35 (bt, ³*J*_{HH} = 6.8 Hz, 1H), 3.79 (s, 3H), 3.59 (d, ²*J*_{HH} = 8.7 Hz, 1H), 3.55 (d, ²*J*_{HH} = 8.6 Hz, 1H), 3.44 (d, ³*J*_{HH} = 7.7 Hz, 1H), 3.30 (d, ²*J*_{HH} = 12.1 Hz, 1H), 3.28 (d, ²*J*_{HH} = 12.2 Hz, 1H), 2.60 (d, ²*J*_{HH} = 17.4 Hz, 1H), 2.41 (d, ²*J*_{HH} = 17.1 Hz, 1H), 1.96 (s, 3H), 1.82 (dd, ²*J*_{HH} = 14.3 Hz and ³*J*_{HH} = 6.0 Hz, 1H), 1.75 (dd, ²*J*_{HH} = 14.4 Hz and ³*J*_{HH} = 1.8 Hz, 1H). ¹³C NMR (CDCl₃): δ 158.1, 140.9, 138.5, 137.8, 135.6, 130.9,

⁹ (a) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512–519. (b) Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc.* **1991**, *113*, 4092–4096.

128.9, 128.4, 128.3, 127.8, 127.7, 127.5, 127.4, 113.4, 76.1, 75.8, 73.6, 73.2, 72.3, 55.2, 46.0, 43.0, 36.3, 21.4. HRMS (ESI) calcd for C₃₀H₃₄O₄Na (M+Na⁺) 481.2349, found 481.2344.

Entry 6. Yellow oil. 77% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane : isopropanol = 95 : 5, flow = 0.5 mL/min. Retention times: 23.4 min [(*S*)-enantiomer], 29.3 min [(*R*)-enantiomer]. 93% ee. $[\alpha]_D^{20} +68.5$ (*c* 0.89, CHCl₃). The absolute configuration was assigned by analogy with entry 3.

¹H NMR (CDCl₃): δ 7.37-7.27 (m, 12H), 7.01-6.96 (m, 2H), 4.63 (d, ²*J*_{HH} = 12.1 Hz, 1H), 4.59 (d, ²*J*_{HH} = 12.1 Hz, 1H), 4.49 (s, 2H), 4.26 (bt, ³*J*_{HH} = 6.8 Hz, 1H), 3.65 (d, ³*J*_{HH} = 8.4 Hz, 1H), 3.59 (d, ²*J*_{HH} = 8.7 Hz, 1H), 3.55 (d, ²*J*_{HH} = 8.6 Hz, 1H), 3.28 (s, 2H), 2.61 (d, ²*J*_{HH} = 17.4 Hz, 1H), 2.41 (d, ²*J*_{HH} = 17.2 Hz, 1H), 1.96 (s, 3H), 1.82 (dd, ²*J*_{HH} = 14.4 Hz and ³*J*_{HH} = 5.7 Hz, 1H), 1.76 (dd, ²*J*_{HH} = 14.4 Hz and ³*J*_{HH} = 1.4 Hz, 1H). ¹³C NMR (CDCl₃): δ 161.5 (d, ¹*J*_{CF} = 245.0 Hz), 141.9, 139.1 (d, ⁴*J*_{CF} = 3.1 Hz), 138.4, 137.7, 130.3, 129.5 (d, ³*J*_{CF} = 7.8 Hz), 128.5, 128.3, 127.9, 127.8, 127.6, 127.5, 114.7 (d, ²*J*_{CF} = 21.2 Hz), 76.3, 76.0, 73.7, 73.3, 72.3, 46.2, 43.3, 36.2, 21.4. HRMS (ESI) calcd for C₂₉H₃₁FO₃Na (M+Na⁺) 469.2149, found 469.2147.

Entry 7. Yellow oil. 71% yield. The ee was determined on a Daicel Chiralcel OD-H column with hexane : isopropanol = 95 : 5, flow = 0.5 mL/min. Retention times: 28.9 min [(*S*)-enantiomer], 32.7 min [(*R*)-enantiomer]. 96% ee. $[\alpha]_D^{20} +77.4$ (*c* 0.86, CHCl₃). The absolute configuration was assigned by analogy with entry 3.

¹H NMR (CDCl₃): δ 7.38-7.27 (m, 14H), 7.24-7.17 (m, 3H), 4.62 (d, ²*J*_{HH} = 11.9 Hz, 1H), 4.59 (d, ²*J*_{HH} = 12.0 Hz, 1H), 4.49 (s, 2H), 4.28 (bt, ³*J*_{HH} = 6.6 Hz, 1H), 3.64 (d, ³*J*_{HH} = 8.3 Hz, 1H), 3.58 (d, ²*J*_{HH} = 8.1 Hz, 1H), 3.54 (d, ²*J*_{HH} = 8.6 Hz, 1H), 3.27 (s, 2H), 2.61 (d, ²*J*_{HH} = 17.5 Hz, 1H), 2.41 (d, ²*J*_{HH} = 17.5 Hz, 1H), 1.95 (s, 3H), 1.82 (dd, ²*J*_{HH} = 14.4 Hz and ³*J*_{HH} = 5.7 Hz, 1H), 1.77 (d, ²*J*_{HH} = 13.3 Hz, 1H). ¹³C NMR (CDCl₃): δ 145.0, 142.8, 138.4, 137.7, 133.8, 130.1, 129.2, 128.5, 128.3, 127.84, 127.83, 127.6, 127.5, 126.5, 126.3, 76.2, 75.8, 73.7, 73.3, 72.2, 46.2, 43.2, 36.3, 21.2. Anal. Calcd for C₂₉H₃₁ClO₃: C, 75.23; H, 6.75. Found: C, 74.95; H, 6.79.

2a-Np

Entry 8. Yellow oil. 78% yield. The ee was determined on a Daicel Chiralcel OD-H column with hexane : isopropanol = 90 : 10, flow = 0.5 mL/min. Retention times: 30.2 min [(*R*)-enantiomer], 41.5 min [(*S*)-enantiomer]. 96% ee. $[\alpha]_D^{20} +42.1$ (*c* 1.18, CHCl₃). The absolute configuration was assigned by analogy with entry 3.

¹H NMR (CDCl₃): δ 7.82-7.77 (m, 4H), 7.49-7.28 (m, 13H), 4.63 (d, ²*J*_{HH} = 12.3 Hz, 1H), 4.60 (d, ²*J*_{HH} = 12.2 Hz, 1H), 4.51 (s, 2H), 4.42 (bt, ³*J*_{HH} = 6.4 Hz, 1H), 3.60 (d, ²*J*_{HH} = 8.6 Hz, 1H), 3.57 (d, ²*J*_{HH} = 8.5 Hz, 1H), 3.45 (d, ³*J*_{HH} = 7.4 Hz, 1H), 3.32 (d, ²*J*_{HH} = 12.1 Hz, 1H), 3.31 (d, ²*J*_{HH} = 12.0 Hz, 1H), 2.67 (d, ²*J*_{HH} = 17.3 Hz, 1H), 2.47 (d, ²*J*_{HH} = 17.5 Hz, 1H), 2.06 (s, 3H), 1.84 (dd, ²*J*_{HH} = 14.3 Hz and ³*J*_{HH} = 5.8 Hz, 1H), 1.76 (d, ²*J*_{HH} = 14.0 Hz, 1H). ¹³C NMR (CDCl₃): δ 142.2, 140.7, 138.5, 137.9, 133.3, 132.2, 131.4, 128.5, 128.4, 128.1, 127.9, 127.8, 127.57, 127.55, 127.52, 127.51, 126.5, 126.4, 125.9, 125.6, 76.1, 75.8, 73.7, 73.3, 72.4, 46.2, 43.0, 36.3, 21.5. Anal. Calcd for C₃₃H₃₄O₃: C, 82.81; H, 7.16. Found: C, 82.51; H, 7.29.

2f

Entry 9. Colorless oil. 89% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane : isopropanol = 98 : 2, flow = 0.5 mL/min. Retention times: 18.4 min [(*S*)-enantiomer], 28.3 min [(*R*)-enantiomer]. 75% ee. $[\alpha]_D^{20} +41.3$ (*c* 1.38, CHCl₃). The absolute configuration was assigned by analogy with entry 3.

¹H NMR (CDCl₃): δ 7.35-7.25 (m, 12H), 7.22-7.17 (m, 3H), 4.61 (d, ²*J*_{HH} = 12.0 Hz, 1H), 4.58 (d, ²*J*_{HH} = 11.9 Hz, 1H), 4.51 (s, 2H), 3.64 (d, ²*J*_{HH} = 8.6 Hz, 1H), 3.59 (d, ²*J*_{HH} = 8.7 Hz, 1H), 3.37 (d, ²*J*_{HH} = 8.8 Hz, 1H), 3.33 (d, ²*J*_{HH} = 8.8 Hz, 1H), 3.31 (s, 1H), 2.70 (d, ²*J*_{HH} = 17.2 Hz, 1H), 2.42 (d, ²*J*_{HH} = 17.2 Hz, 1H), 1.91 (s, 3H), 1.90 (d, ²*J*_{HH} = 14.3 Hz, 1H), 1.81 (dd, ²*J*_{HH} = 14.3 Hz, 1H), 0.89 (s, 3H). ¹³C NMR (CDCl₃): δ 143.8, 142.8, 138.6, 138.1, 131.1, 128.6, 128.4, 128.3, 127.8, 127.7, 127.6, 127.5, 127.4, 126.3, 78.1, 76.1, 75.6, 73.6, 73.3, 51.6, 44.1, 39.3, 28.4, 24.3. Anal. Calcd for C₃₀H₃₄O₃: C, 81.41; H, 7.74. Found: C, 81.14; H, 7.88.

Procedure for Equation 2.

6

A solution of [Rh(OH)(cod)]₂ (2.4 mg, 11 μmol Rh), PhB(OH)₂ (64.0 mg, 0.52 mmol),

and compound **5** (37.8 mg, 0.15 mmol) in 1,4-dioxane (1.5 mL) and water (0.15 mL) was stirred for 5 h at 70 °C. The reaction mixture was directly passed through a pad of silica gel with Et₂O and the solvent was removed under vacuum. The residue was purified by silica gel PTLC with Et₂O/hexane=1/3.5 to afford compound **6** as a white solid (39.5 mg, 0.13 mmol; 88% yield).

¹H NMR (CDCl₃): δ 7.35-7.21 (m, 3H), 7.17-6.92 (m, 2H), 3.79 (s, 3H), 2.95 (d, ²J_{HH} = 16.3 Hz, 1H), 2.62 (dd, ²J_{HH} = 16.1 Hz and ⁴J_{HH} = 2.5 Hz, 1H), 2.31-2.24 (m, 2H), 2.19-2.12 (m, 2H), 2.03 (dd, ²J_{HH} = 10.5 Hz and ⁴J_{HH} = 4.0 Hz, 1H), 1.97 (dd, ²J_{HH} = 9.8 Hz and ⁴J_{HH} = 2.7 Hz, 1H), 0.86 (t, ³J_{HH} = 7.1 Hz, 3H), 0.67 (s, 3H). ¹³C NMR (CDCl₃): δ 210.5, 170.5, 141.8, 136.2, 135.5, 128.1, 127.8, 126.8, 63.2, 52.4, 52.1, 50.0, 47.8, 36.8, 29.9, 20.2, 11.9. Anal. Calcd for C₁₉H₂₂O₃: C, 76.48; H, 7.43. Found: C, 76.11; H, 7.60.

IV. ¹H NMR Spectra