An Efficient, Stereoselective Approach to syn-1,2-Diols Protected as Cyclic Carbonates

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Preparation of 6a: The general procedure for the synthesis of alkyl 4-hydroxybut-2-ynyl carbonates was followed for: Zn(OTf)₂ (200 mg, 0.55 mmol), (–)-NME (108 mg, 0.60 mmol), toluene (1 mL) and Et₃N (84 μl, 0.60 mmol) at rt for 2 h 30 min. Alkyne **3**¹ (92.9 mg, 0.5 mmol), toluene (0.5 mL) at rt for 30 min. Cyclohexanecarbaldehyde (73 μL, 0.60 mmol) for 4 h. Purification by flash chromatography with gel (CH₂Cl₂/MeOH : 99/1) gave **6a** (137.2 mg, 93%) as a colorless oil: $[\alpha]^{25}_{D}$ +2.62 (*c* 0.98, CHCl₃) for 98% ee;² IR (film) 3444, 2929, 1752, 1451, 1391, 1263 cm⁻¹. ¹H NMR (200 MHz, CDCl₃) δ 7.40–7.35 (5H, m), 5.19 (2H, s), 4.79 (2H, d, *J* = 1.8 Hz), 4.18 (2H, dt, *J* = 6.2, 1.8 Hz), 1.85–1.51 (7H, m), 1.32–0.99 (5H, m); ¹³C NMR (50 MHz, CDCl₃) δ 154.5, 134.9, 128.6, 128.5, 128.3, 87.7, 78.9, 70.0, 67.1, 55.8, 43.9, 28.4, 28.1, 26.3, 25.8, 25.8; HRMS(ESI) calcd for C₁₈H₂₂NaO₄ (M + Na⁺) 325.1416, found 325.1413.

Preparation of 7a: The general procedure for the synthesis of alkyl 4-hydroxybut-2-ynyl carbonates was followed for: Zn(OTf)₂ (200 mg, 0.55 mmol), (–)-NME (108 mg, 0.60 mmol), toluene (1 mL), and Et₃N (84 μl, 0.60 mmol) at rt for 2 h 30 min. Alkyne **4**³ (58.0 mg, 0.5 mmol), toluene (0.5 mL) at rt for 30 min. Cyclohexanecarbaldehyde (73 μl, 0.60 mmol) for 5 h. Purification by flash chromatography on silica gel (CH₂Cl₂/MeOH : 99/1) gave **7a** (100.3 mg, 87%) as a colorless oil: $[\alpha]^{25}_{D}$ +3.17 (*c* 1.12, CHCl₃) for 97% ee;² IR (film) 3436, 2929, 1756, 1447, 1376, 1270 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.78 (2H, d, *J* = 1.7 Hz), 4.19 (1H, dt, *J* = 6.1, 1.7 Hz), 3.82 (3H, s), 1.85–1.50 (7H, m), 1.32–0.99 (5H, m); ¹³C NMR (50 MHz, CDCl₃) δ 155.1, 87.6, 78.9, 67.0, 55.7, 55.1, 43.9, 28.4, 28.1, 26.3, 25.8, 25.8; HRMS(ESI) calcd for C₁₂H₁₈NaO₄ (M + Na⁺) 249.1103, found 249.1100.

General procedure for the synthesis of alkyl (Z)-4-hydroxybut-2-enyl carbonates (8a–d, 8f, 9a, 10a, and 13e): the alkyl 4-hydroxybut-2-ynyl carbonate, Pd/CaCO₃ (5%) poisoned with lead, quinoline, and AcOEt were added in a flask which was purged with N_2 and then with H_2 . The reaction mixture was shaken and monitored for completion by TLC. The mixture was filtered through a short pad of Celite. The organic layer was washed with aqueous HCl 2 N and brine, dried over MgSO₄, and evaporated under reduced pressure. The mixture was purified by flash chromatography on silica gel to give the (Z)-alkene.

Compound 8a: The general procedure was followed for: alkyne **5a** (95.9 mg, 0.36 mmol), Pd/CaCO₃ (27.0 mg), quinoline (8 μ L), and AcOEt (2.5 mL) for 90 min. Purification of the crude mixture by flash chromatography on silica gel (Hexane/AcOEt : 80/20) gave **8a** (81.2 mg, 84%) as a colorless oil: $[\alpha]_{D}^{25}$

¹Zhang, H. X.; Guibé, F.; Balavoine, G. Tetrahedron Lett. 1988, 29, 619–622.

² Determined by HPLC of the corresponding Mosher's esters.

³ Allcock, S. J.; Gilchrist, T. L.; Shuttleworth, S. J.; King, F. D. *Tetrahedron* **1991**, *47*, 10053–10064.

-14.7 (*c* 1.71, CHCl₃) for >96% ee; IR (film) 3427, 2927, 1743, 1451, 1370, 1277 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 5.67 (2H, m), 4.82 (1H, dd, *J* = 12.6, 6.6 Hz), 4.50 (1H, dd, *J* = 12.6, 4.0 Hz), 4.19 (1H, t, *J* = 7.2 Hz), 1.97–0.82 (12H, m), 1.48 (9H, s); ¹³C NMR (50 MHz, CDCl₃) δ 153.5, 136.3, 125.1, 82.4, 71.6, 62.7, 43.4, 28.7, 28.5, 27.7, 26.5, 26.0, 25.9; HRMS(ESI) calcd for C₁₅H₂₆NaO₄ (M + Na⁺) 293.1729, found 291.1739.

Compound 8b: The general procedure was followed for: alkyne **5b** (39.0 mg, 0.17 mmol), Pd/CaCO₃ (7.0 mg), quinoline (2.8 μ L), and AcOEt (1.3 mL) for 30 min. Purification of the crude mixture by flash chromatography on silica gel (Hexane/Et₂O : 9/1) gave **8b** (32.8 mg, 83%) as a colorless oil: $[\alpha]_{D}^{25}$ –2.26 (*c* 1.00, CHCl₃) for 96% ee; IR (film) 3467, 2964, 1742, 1457, 1370 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.71–5.63 (2H, m), 4.83 (1H, dd, *J* = 12.7, 7.2 Hz), 4.52 (1H, dd, *J* = 12.7, 4.3 Hz), 4.18 (1H, dd, *J* = 7.8, 6.8 Hz), 1.72 (1H, oct, *J* = 6.7 Hz), 1.48 (9H, s), 0.98 (3H, d, *J* = 6.7 Hz), 0.87 (3H, d, *J* = 6.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 153.6, 136.2, 125.4, 82.5, 72.4, 62.7, 33.7, 27.7, 18.1, 18.1; HRMS(ESI) calcd for C₁₂H₂₂NaO₄ (M + Na⁺) 253.1416, found 253.1413.

Compound 8c: The general procedure was followed for: alkynol **5c** (32.9 mg, 0.136 mmol), Pd/CaCO₃ (6.5 mg), and quinoline (4 μ L) in AcOEt (1.3 mL) for 30 min. Purification of the crude mixture by flash chromatography on silica gel (CH₂Cl₂) gave **8c** (27.5 mg, 83%) as a colorless oil: $[\alpha]^{25}_{\ D}$ –18.0 (*c* 1.31, CHCl₃) for 89% ee; IR (film) 3436, 2958, 1742, 1459, 1370, 1279 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.69–5.56 (2H, m), 4.85 (1H, ddt, *J* = 12.7, 8.2, 1.1 Hz), 4.58 (1H, td, *J* = 7.0, 6.0 Hz), 4.52 (1H, ddd, *J* = 12.7, 5.7, 1.2 Hz), 2.11 (1H, bs), 1.72 (1H, m), 1.53 (1H, m), 1.48 (9H, s), 1.28, (1H, m), 0.94 (3H, d, *J* = 6.6 Hz), 0.92 (3H, d, *J* = 6.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 153.6, 138.3, 124.3, 82.5, 65.5, 62.5, 45.9, 27.7, 24.4, 23.0, 22.4; HRMS(ESI) calcd for C₁₃H₂₄NaO₄ (M + Na⁺) 267.1572, found 267.1609.

Compound 8d: The general procedure was followed for: alkynol **5d** (82.5 mg, 0.314 mmol), Pd/CaCO₃ (25 mg), and quinoline (16 μ L) in AcOEt (5 mL). Purification of the crude mixture by flash chromatography on silica gel (CH₂Cl₂/MeOH : 99/1) gave **8d** (74.7 mg, 90%) as a colorless oil: $[\alpha]_{D}^{25}$ –105.1 (*c* 0.95, CHCl₃) for >96% ee; IR (film) 3446, 2981, 1740, 1457, 1370, 1277 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.41–7.28 (5H, m), 5.88 (1H, ddt, *J* = 11.0, 8.5, 1.2 Hz), 5.69 (1H, m), 5.62 (1H, bd, *J* = 8.8 Hz), 4.95 (1H, ddd, *J* = 12.8, 8.2, 1.2 Hz), 4.63 (1H, ddd, *J* = 12.8, 5.9, 1.2 Hz), 1.49 (9H, s); ¹³C NMR (75 MHz, CDCl₃) δ 153.6, 142.5, 136.9, 128.6, 127.6, 126.0, 124.6, 82.6, 69.5, 62.5, 27.7; HRMS(ESI) calcd for C₁₅H₂₀NaO₄ (M + Na⁺) 287.1259, found 287.1281.

Compound 8f: The general procedure was followed for: alkynol **5f** (42.4 mg, 0.16 mmol), Pd/CaCO₃ (12.4 mg), and quinoline (3.5 μ L) in AcOEt (1.5 mL) for 2 h. Washings with HCl 2 N were substituted by washings with a 7% aqueous citric acid solution. Purification of the crude mixture by flash chromatography on silica gel (Hexane/AcOEt : 7/3) gave **8f** (38.9 mg, 91%) as a colorless oil: $[\alpha]^{25}_{D}$ +19.5 (*c* 1.00, CHCl₃); IR (film) 3467, 2985, 1740, 1456, 1372, 1277 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.76 (1H, ddt, *J* = 11.2, 7.9, 1.1 Hz), 5.65 (1H, dddd, *J* = 11.2, 7.9, 5.7, 1.1 Hz), 4.82 (1H, ddd, *J* = 12.9, 7.9, 1.1 Hz), 4.60–4.54 (2H, m), 4.11–4.02 (2H, m), 3.94 (1H, dd, *J* = 8.1, 6.1 Hz), 1.48 (9H, s), 1.43 (3H, s), 1.36 (3H, s); ¹³C NMR (50 MHz, CDCl₃) δ 153.4, 132.6, 127.4, 109.4, 82.6, 77.9, 67.8, 65.6, 62.7, 27.8, 26.5, 25.1; HRMS(ESI) calcd for C₁₄H₂₄NaO₆ (M + Na⁺) 311.1471, found 311.1486.

Compound 9a: The general procedure was followed for: alkyne **6a** (90.2 mg, 0.36 mmol), Pd/CaCO₃ (27.0 mg), quinoline (8 μ L), and AcOEt (2.5 mL) for 2 h. Purification of the crude mixture by flash chromatography on silica gel (Hexane/AcOEt : 80/20) gave **9a** (72.3 mg, 80%) as a colorless oil: $[\alpha]^{25}_{D}$ –19.5 (*c* 1.74, CHCl₃) for >96% ee;⁴ IR (film) 3444, 2929, 1752, 1451, 1391, 1263 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.39–7.32 (5H, m), 5.67 (2H, m), 5.15 (2H, s), 4.87 (1H, m), 4.57 (1H, m), 4.17 (1H, t, *J* = 7.3 Hz), 2.25 (1H, bs), 1.95–1.59 (5H, m), 1.47–0.86 (6H, m); ¹³C NMR (50 MHz, CDCl₃) δ 155.0, 136.7, 135.0 128.5, 128.5, 128.2, 124.6, 71.7, 69.7, 63.7, 43.4, 28.6, 28.5, 26.4, 26.0, 25.9; HRMS(ESI) calcd for C₁₈H₂₄NaO₄ (M + Na⁺) 327.1572, found 327.1565.

Compound 10a: The general procedure was followed for: alkyne **7a** (34.0 mg, 0.15 mmol), Pd/CaCO₃ (5.7 mg), quinoline (4.5 μ L), and AcOEt (1.4 mL) for 1 h. Purification of the crude mixture by flash chromatography on silica gel (CH₂Cl₂/MeOH : 99/1) gave **10a** (31.9 mg, 93%) as a colorless oil: $[\alpha]^{25}_{D}$ –20.3 (*c* 0.93, CHCl₃) for 97% ee;² IR (film) 3435, 2927, 1750, 1447, 1362, 1270 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 5.68 (2H, m), 4.87 (1H, dd, *J* = 12.4, 7.2 Hz), 4.58 (1H, dd, *J* = 12.4, 4.0 Hz), 4.20 (1H, t, *J* = 7.3 Hz), 3.78 (3H, s), 2.19 (1H, bs), 1.97–1.60 (5H, m), 1.44–0.88 (6H, m); ¹³C NMR (100 MHz, CDCl₃) δ 155.8, 136.7, 124.8, 71.7, 63.6, 54.8, 43.4, 28.6, 28.5, 26.4, 26.0, 25.9; HRMS(ESI) calcd for C₁₂H₂₀NaO₄ (M + Na⁺) 251.1259, found 251.1263.

Compound 13e: The general procedure was followed for: alkynol **5e** (67.5 mg, 0.26 mmol), Pd/CaCO₃ (12.0 mg), and quinoline (4 μ L) in AcOEt (2 mL) for 30 min. Purification of the crude mixture by flash chromatography on silica gel (CH₂Cl₂) gave (2Z,4S)-4-hydroxynon-2-enyl benzoate (**13e**, 60.7 mg, 89%) as a colorless oil: [α]²⁵_D –27.4 (*c* 0.82, CHCl₃) for 80% ee; IR (film) 3423, 2930,

⁴ Determined by ¹H and ¹⁹F NMR of the corresponding Mosher's esters.

1721, 1603, 1272 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.04 (2H, m), 7.56 (1H, m), 7.43 (2H, m), 5.70 (2H, m), 5.08 (1H, m), 4.79 (1H, dd, J = 12.7, 4.5 Hz), 4.59 (1H, q, J = 6.7 Hz), 1.64 (2H, m), 1.53–1.28 (6H, m), 0.88 (3H, d, J = 6.8 Hz); ¹³C NMR (50 MHz, CDCl₃) δ 166.5, 137.8, 133.0, 129.6, 129.6, 128.3, 124.6, 67.6, 60.8, 37.0, 31.8, 25.0, 22.6, 14.0; HRMS(ESI) calcd for C₁₆H₂₂NaO₃ (M + Na⁺) 285.1467, found 285.1458.

Cyclization of 8a catalyzed by 0.5% Pd(PPh₃)₄: A solution of Pd(PPh₃)₄ (2.31 mg, 0.002 mmol) in CH₂Cl₂ (0.4 mL) was added to a flask (sealed with a septum) that contained the alkenol **8a** (108.1 mg, 0.4 mmol) under N₂. Then, Et₃N (11 μ L, 0.08 mmol) was added and the mixture was stirred for 24 h at rt. The solvent was removed in vacuo and the crude mixture was purified by flash chromatography on silica gel (CH₂Cl₂/Hexane : 1/1) to afford a mixture 84:16 of *trans*-**1a** and *cis*-**1a** as a colorless oil (23.8 mg, 30%) and starting material **8a** (47.8 mg, 44%). Spectra of *cis*-**1a**: ¹H NMR (400 MHz, CDCl₃) δ 5.92 (1H, ddd, *J* = 17.1, 10.4, 7.4 Hz), 5.52 (1H, dt, *J* = 17.1, 1.0 Hz), 5.50 (1H, dt, *J* = 10.4, 1.0 Hz), 5.04 (1H, ddt, *J* = 7.4, 7.1, 1.0 Hz), 4.36 (1H, dd, *J* = 9.0, 7.1 Hz), 1.92–1.63 (5H, m), 1.35–1.00 (6H, m); ¹³C NMR (100 MHz, CDCl₃) δ 154.6, 129.2, 122.0, 83.9, 80.2, 37.2, 28.8, 28.1, 25.9, 25.1, 25.0.

Isomerization of *cis*-1a: The above mixture of *trans*-1a and *cis*-1a (84:16, 23.8 mg, 0.12 mmol) was dissolved in CDCl₃ (1.0 mL) and Pd(PPh₃)₄ (7.0 mg, 0.006 mmol) was added. The isomerization rate at rt was: 16% *cis*-1a at 0 min, 9.6% at 30 min, 8.5% at 1 h, 5.9% at 5 h, 3.7% at 24 h.

Preparation of *E*-**8a**: A 1.6M solution of BuLi in hexanes (13.75 mL, 22 mmol) was added to a solution of 2-propyn-1-ol (561 mg, 10.0 mmol) in anhyd THF (20 mL) at -78 °C. Cyclohexanecarbaldehyde (1.45 mL, 12.0 mmol) was added and the mixture was warmed up to rt and stirred for additional 20 min. The reaction was quenched with an aqueous saturated solution of NH₄Cl and extracted with CH₂Cl₂. The organic layer was washed with brine and dried with anhyd MgSO₄. Then, the crude mixture can be purified by flash chromatography on silica gel (from CH₂Cl₂ to CH₂Cl₂/MeOH : 95/5) to afford 1-cyclohexylbut-2-yne-1,4-diol as colorless oil (1.379 g, 82%). Alternatively, the above crude mixture (without chromatography) was dissolved in anhyd Et₂O (30 mL) and LiAlH₄ (1.33 g, 35 mmol) was added at 0 °C. The suspension was quenched with a saturated solution of Rochelle salt and was extracted with Et₂O. The organic layer was washed with brine and was dried with anhyd MgSO₄. The crude mixture was purified by flash chromatography on silica gel (from CH₂Cl₂ to CH₂Cl₂/MeOH : 95/5) to afford (*E*)-1-cyclohexylbut-2-ene-1,4-diol as colorless oil (377 mg, 22% for the two steps). The purified diol (128 mg, 0.75 mmol) was dissolved in anhyd THF (2 mL) at -78 °C. A 1.6 M solution of BuLi in hexanes (516 μ L, 0.83 mmol) was added and stirred for 10 min. Then, a solution of Boc₂O (180

mg, 0.83 mmol) in THF (2 mL) was added at -78 °C and stirred for 45 min. The reaction mixture was quenched by addition of an aqueous saturated solution of NH₄Cl and extracted with CH₂Cl₂. The organic layer was washed with brine and dried over anhyd MgSO₄. The crude mixture was purified by flash chromatography on silica gel (from CH₂Cl₂ to CH₂Cl₂/MeOH : 99/1) to afford *tert*-butyl (*E*)-4-cyclohexyl-4-hydroxybut-2-enyl carbonate (*E*-**8a**) as a colorless oil (128 mg, 63%), IR (film) 3436, 2981, 1742, 1451, 1370, 1279 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 5.85–5.74 (2H, m), 4.56 (2H, dd, *J* = 5.4, 1.0 Hz), 3.88 (1H, t, *J* = 6.1 Hz), 1.85–0.94 (11H, m), 1.49 (9H, s); ¹³C NMR (100 MHz, CDCl₃) δ 153.3, 136.5, 125.0, 82.2, 76.5, 66.7, 43.5, 28.7, 28.3, 27.7, 26.4, 26.1, 26.0. HRMS(ESI) calcd for C₁₅H₂₆NaO₄ (M + Na⁺) 293.1729, found 293.1738.

Preparation of 12e: A solution of Et₂Zn (1.1M) in toluene (909 μL, 1.00 mmol) was added at rt to a solution of **11**⁵ (163.6 mg, 1.00 mmol) in anhyd toluene (1 mL), and the mixture was refluxed for 1 h. A catalyst solution of (*R*)-BINOL (28.6 mg, 0.1 mmol), phenol (9.4 mg, 0.1mmol), Ti(*i*PrO)₄ (74 μL, 0.25 mmol) in anhyd Et₂O (3 mL) was stirred for 30 min. This solution was added to the reaction mixture and it was stirred for one additional hour at rt before adding hexanal (30 μL, 0.25 mmol). The reaction mixture was stirred for 4 h at rt. Finally, the reaction was quenched with NH₄Cl, the organic layer was washed with HCl (2 N), NaHCO₃, brine, dried over MgSO₄, and evaporated under reduced pressure. The crude mixture was purified on silica gel (CH₂Cl₂/MeOH : 99/1) to give (*S*)-4-hydroxynon-2-ynyl benzoate (**12e**, 65.1 mg, 100%) as colorless oil: [α]²⁵_D +1.16 (*c* 0.97, CHCl₃) for 80% ee;² IR (film) 3440, 2932, 1726, 1269, 712 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.06 (2H, m), 7.58 (1H, m), 7.45 (2H, m), 4.96 (2H, d, *J* = 1.6 Hz), 4.43 (1H, tt, *J* = 6.6, 1.6 Hz), 2.11 (1H, bs), 1.72 (2H, m), 1.46 (2H, m), 1.31 (4H, m), 0.88 (3H, t, *J* = 6.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 165.9, 133.3, 129.8, 129.5, 128.4, 88.0, 78.8, 62.4, 52.8, 37.5, 31.4, 24.7, 22.5, 13.9; HRMS(ESI) calcd for C₁₆H₂₀NaO₃ (M + Na⁺) 283.1310, found 283.1300.

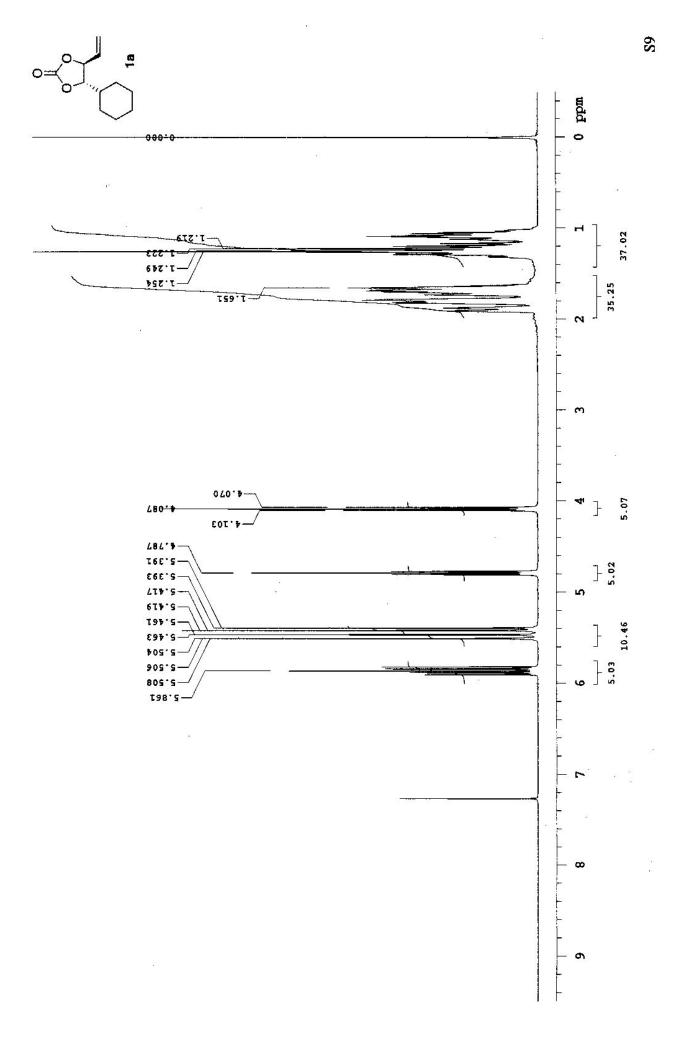
Synthesis of 1e: Potassium *tert*-butyl carbonate was prepared by bubbling CO₂ through a solution of potassium *tert*-butoxide (224 mg, 2.00 mmol) in anhyd THF (20 mL) for 2 h at rt. A solution of Pd(PPh₃)₄ (6.5 mg, 0.006 mmol) and alkenol **8e** (23.5 mg, 0.11 mmol) in CH₂Cl₂ (1 mL) was added to another solution of potassium *tert*-butyl carbonate (88 mg, 0.56 mmol) in CH₂Cl₂ (0.8 mL) under N₂ atmosphere. The mixture was stirred at rt until TLC showed complete disappearance of **8e**. The reaction mixture was quenched with an aqueous phosphate buffer (pH=7). The organic layer was washed with brine, dried over MgSO₄, and evaporated under reduced pressure. The crude mixture was purified by

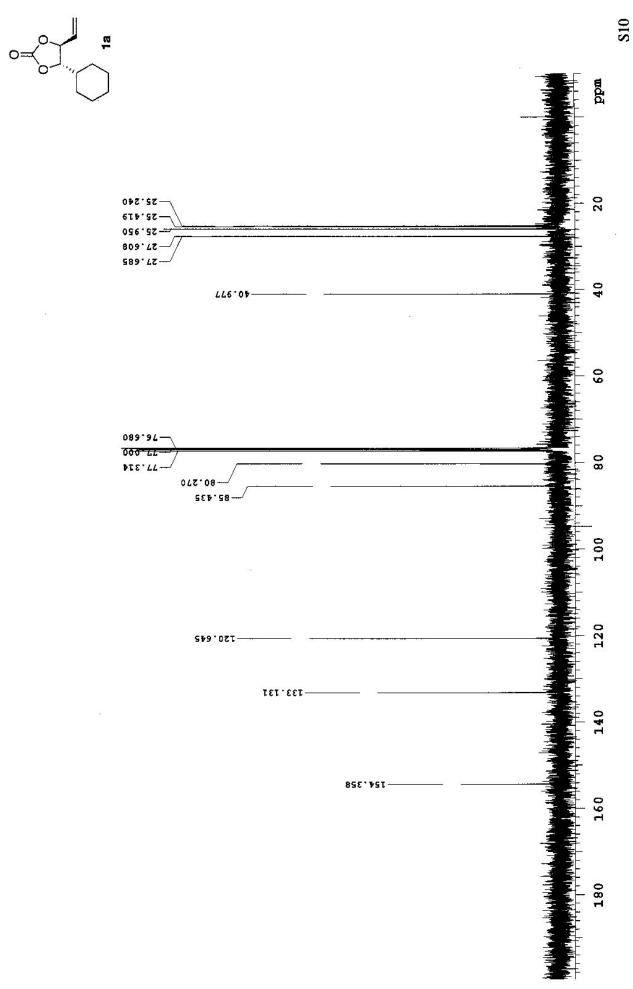
⁵ Bandgar, B. P.; Kamble, V. T.; Sadavarte, V. S.; Uppalla, L. S. Synlett 2002, 735–738.

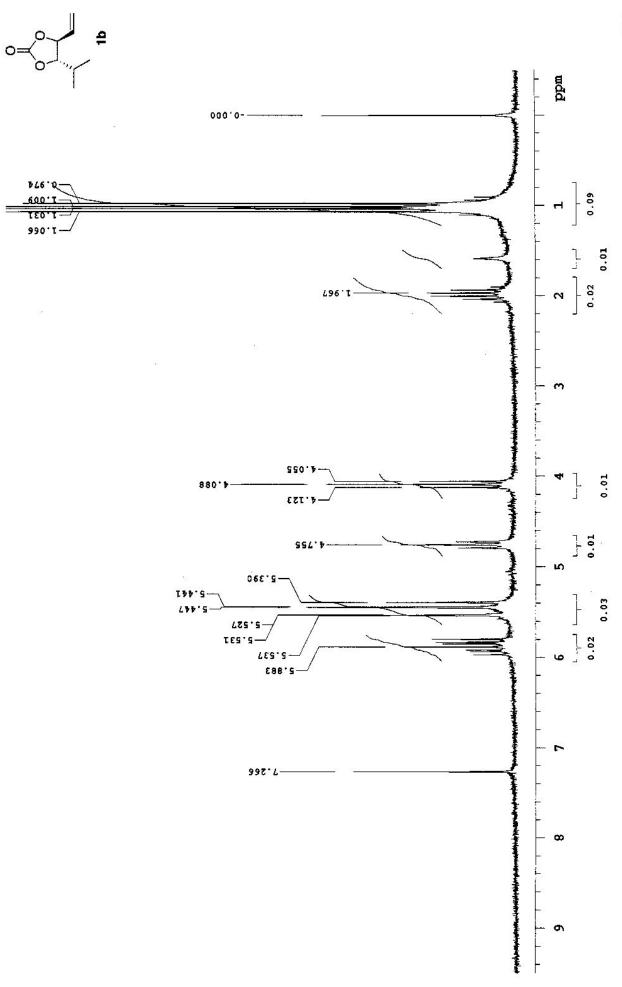
flash chromatography on silica gel (hexane/Et₂O : 9/1) to afford **1e** as a colorless oil (16.3 mg, 80%); $[\alpha]_{D}^{25}$ -38.5 (*c* 0.98, CHCl₃) for 80% ee; IR (film) 2931, 1806, 1459, 1366, 1266 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.87 (1H, ddd, *J* = 17.1, 10.5, 7.1 Hz), 5.49 (1H, d, *J* = 17.1 Hz), 5.43 (1H, dt, *J* = 10.5 Hz), 4.64 (1H, t, *J* = 7.2, 1.0 Hz), 4.30 (1H, td, *J* = 7.6, 5.1 Hz), 1.72 (2H, m), 1.56–1.30 (6H, m), 0.90 (3H, t, *J* = 7.0 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 154.3, 132.2, 121.2, 82.6, 81.9, 32.9, 31.3, 24.3, 22.3, 13.9.

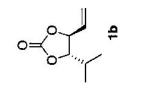
Formation of 14f: Cyclic carbonate **1f** (18.0 mg, 0.084 mmol) was stirred in a mixture of NaOH 1 M (1 mL) and 1,4-dioxane (1 mL) for 2 h. A saturated solution of NH₄Cl was added and the mixture was extracted with CH₂Cl₂. The organic layer was washed with brine and dried over anhyd MgSO₄. The solvent was evaporated in vacuo and the crude mixture was purified by flash chromatography on silica gel (CH₂Cl₂/MeOH from 98:2 to 95:5) to afford **14f** (7.6 mg, 48%) as a colorless oil:⁶ $[\alpha]^{25}_{D}$ +23.4 (*c* 0.63, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 5.96 (1H, ddd, *J* = 17.4, 10.6, 5.7 Hz), 5.39 (1H, dt, *J* = 17.4, 1.5 Hz), 5.28 (1H, dt, *J* = 10.6, 1.4 Hz), 4.27 (1H, m), 4.16 (1H, q, *J* = 6.3 Hz), 4.08 (1H, dd, *J* = 8.4, 6.3 Hz), 3.97 (1H, dd, *J* = 8.4, 6.3 Hz), 3.62 (1H, m), 2.34 (1H, d, *J* = 4.2 Hz), 2.28 (1H, d, *J* = 4.2 Hz), 1.43 (3H, s), 1.37 (3H, s); ¹³C NMR (50 MHz, CDCl₃) δ 137.2, 117.1, 109.2, 76.0, 73.7, 72.1, 66.0, 26.7, 25.2.

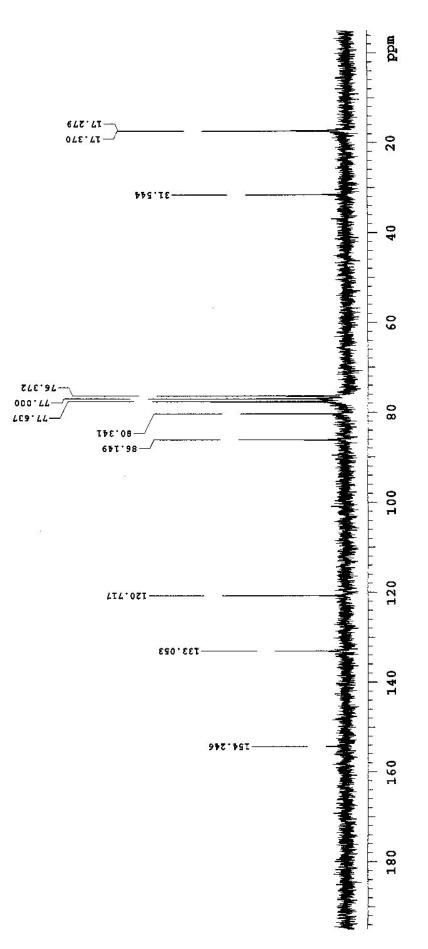
⁶ (a) Sato, A.; Ito, H.; Taguchi, T. *J. Org. Chem.* **2000**, *65*, 918–921. (b) Yadav, J. S.; Reddy, B. V. S.; Reddy, K. S. *Tetrahedron*, **2003**, *59*, 5333–5336. (c) Lee, H. W.; Yoon, H. K.; Lee, I.-Y. C. *Bull. Korean Chem. Soc.* **1998**, *19*, 916–917.



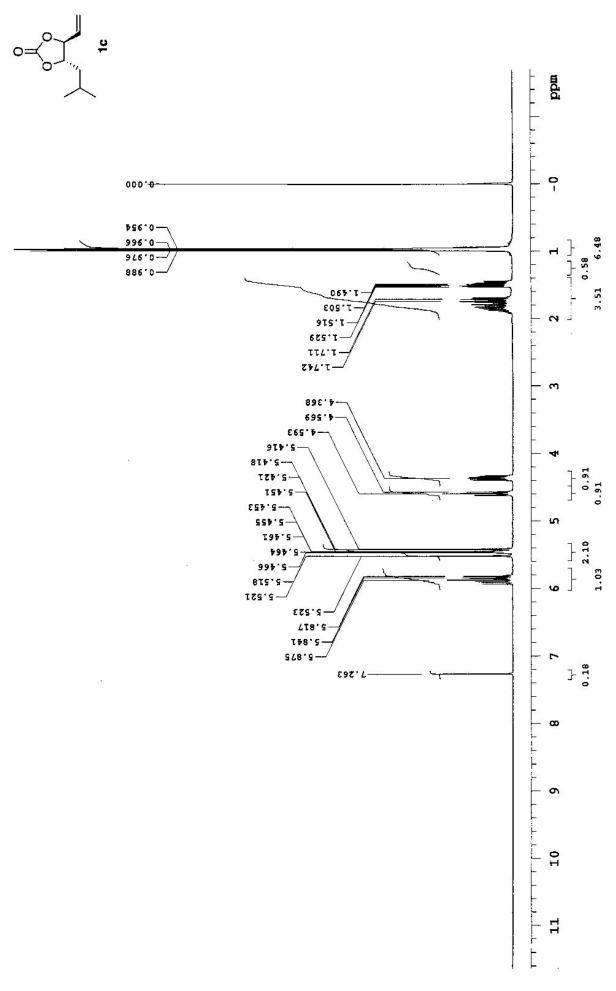


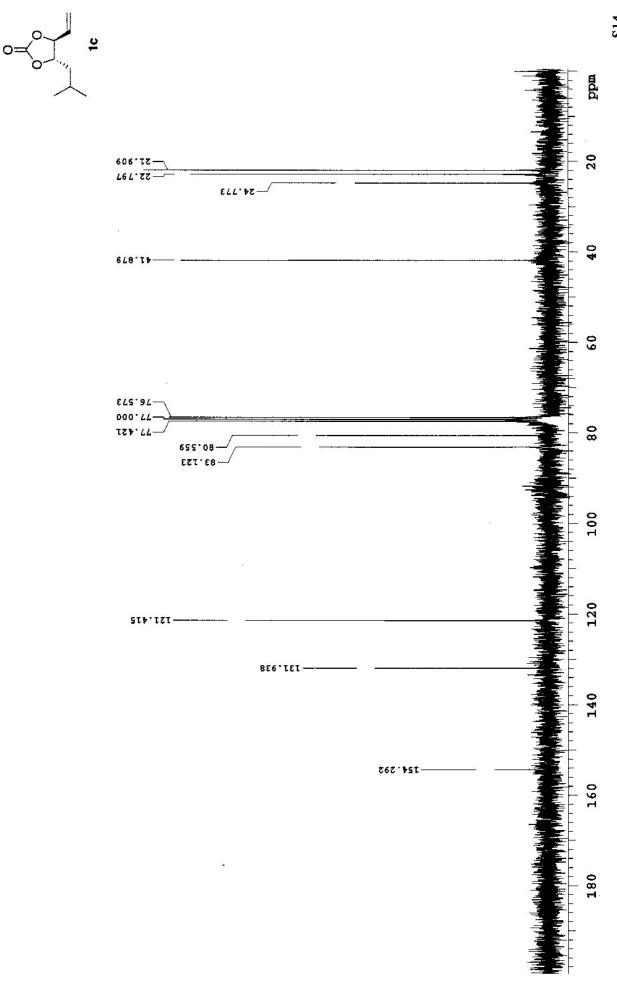


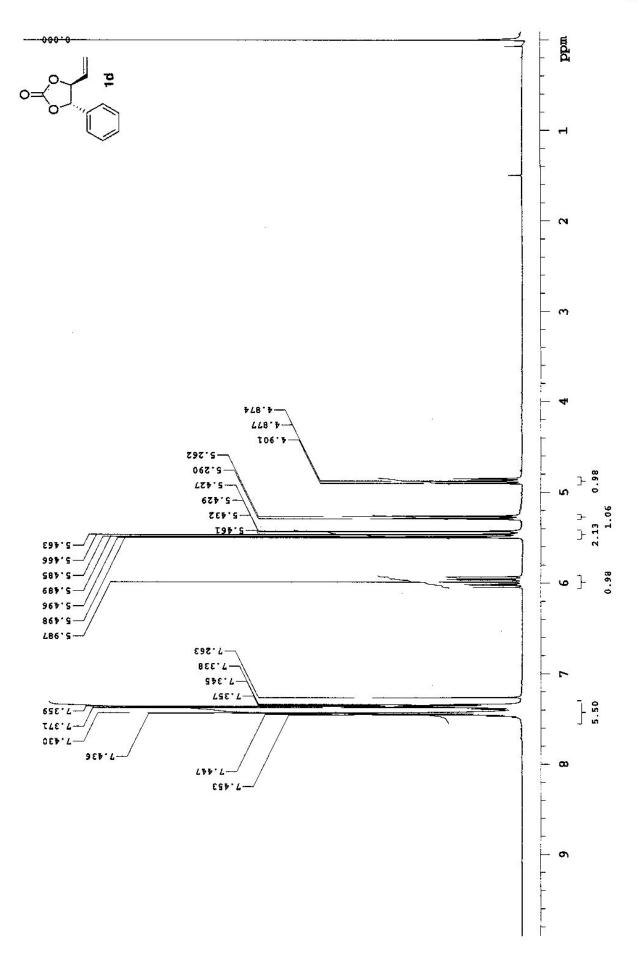


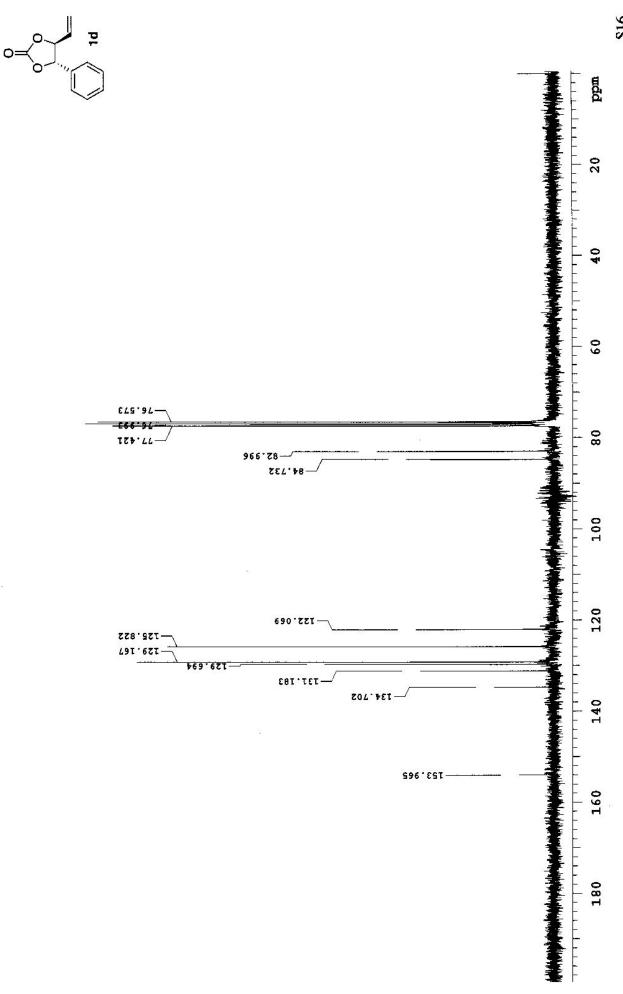


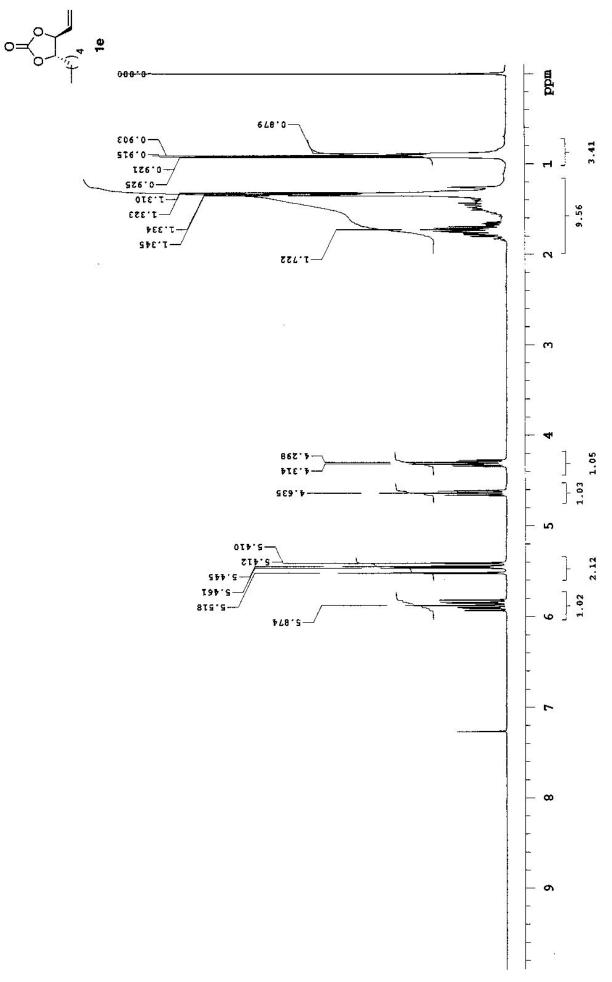
S12

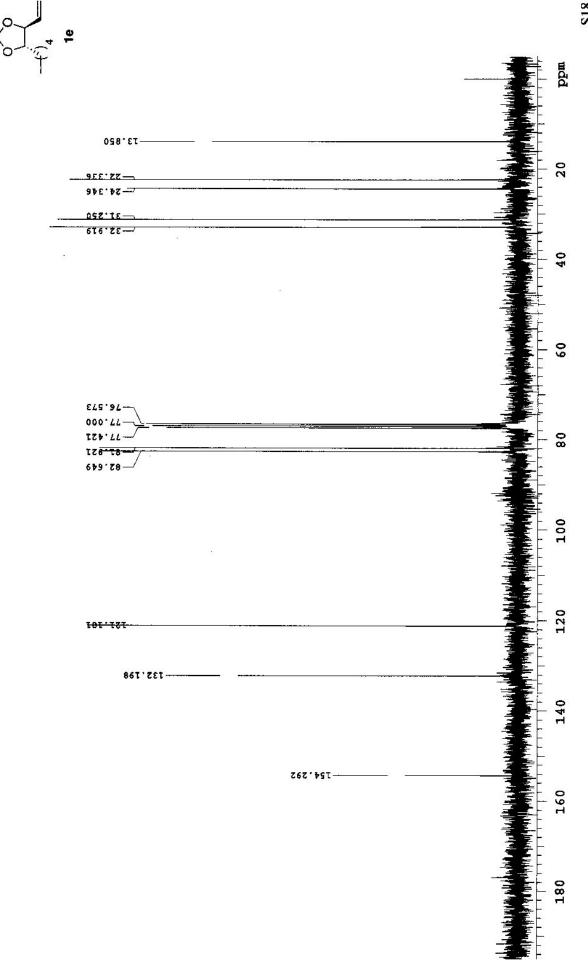




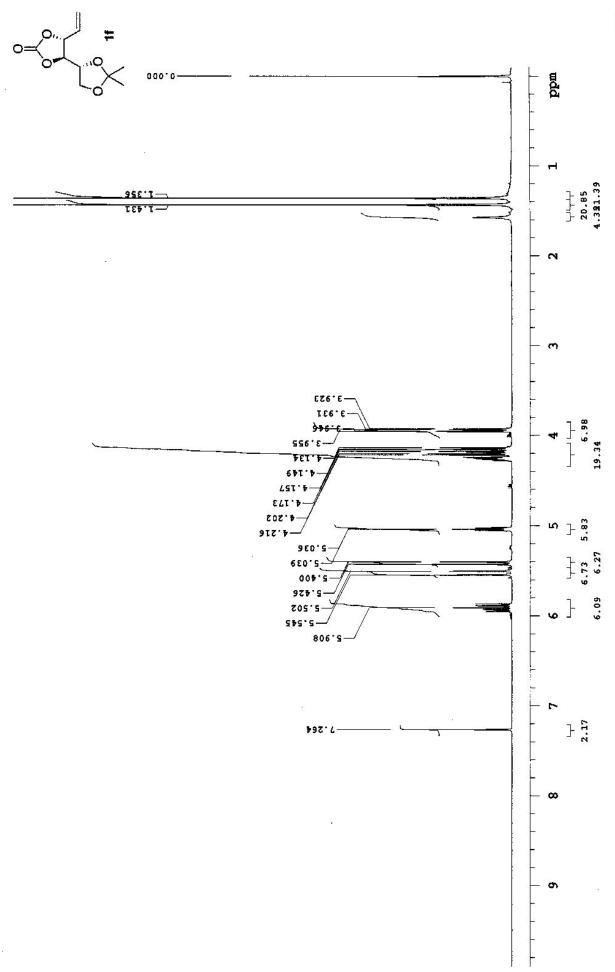


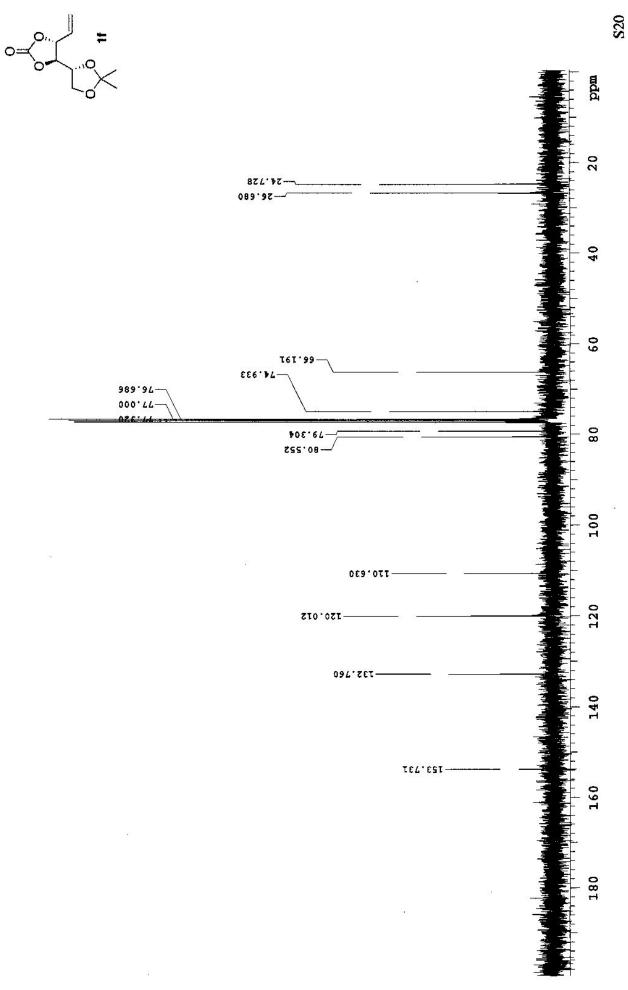


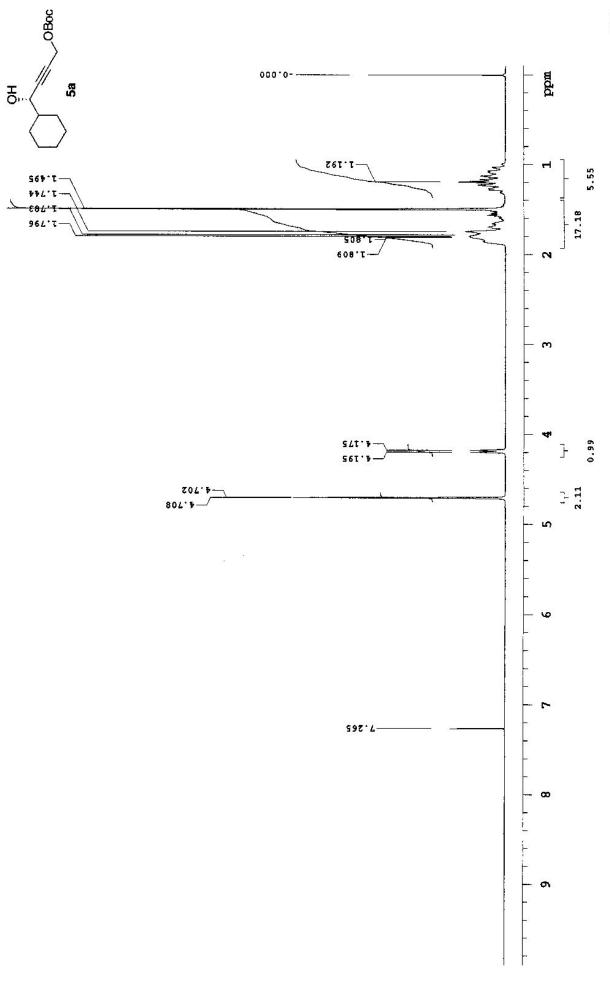


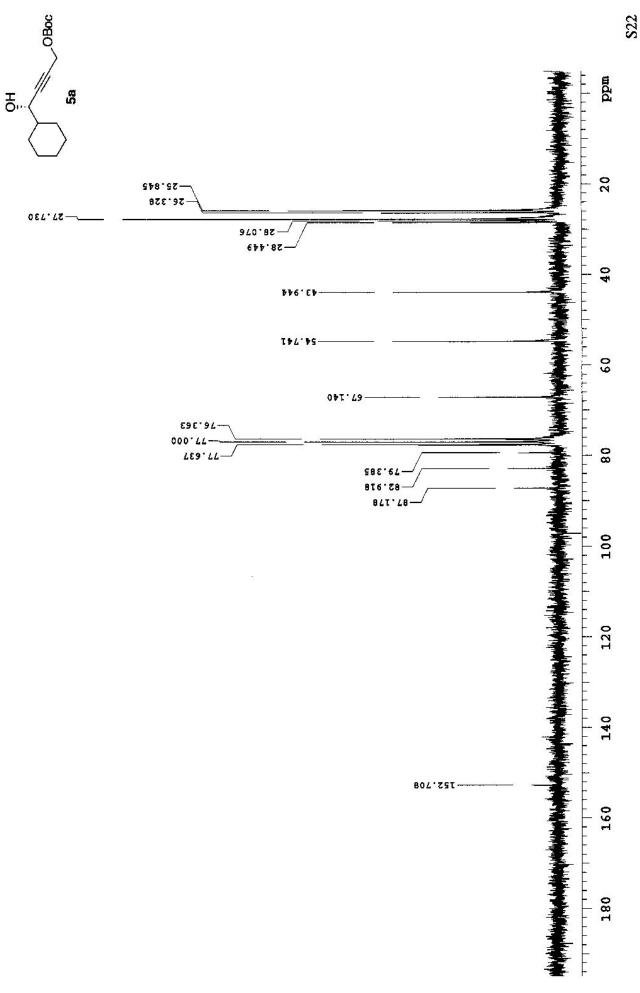


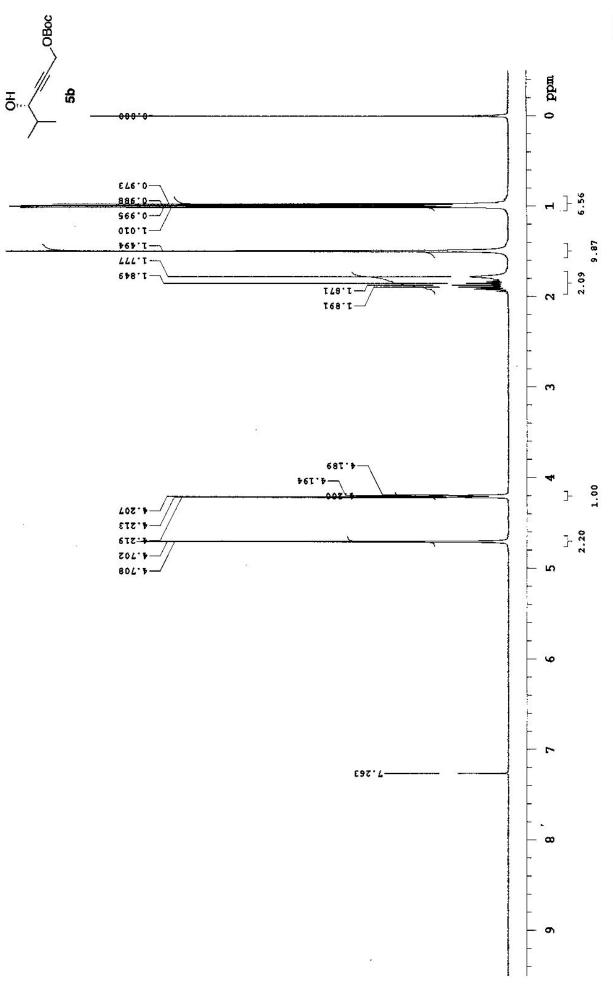
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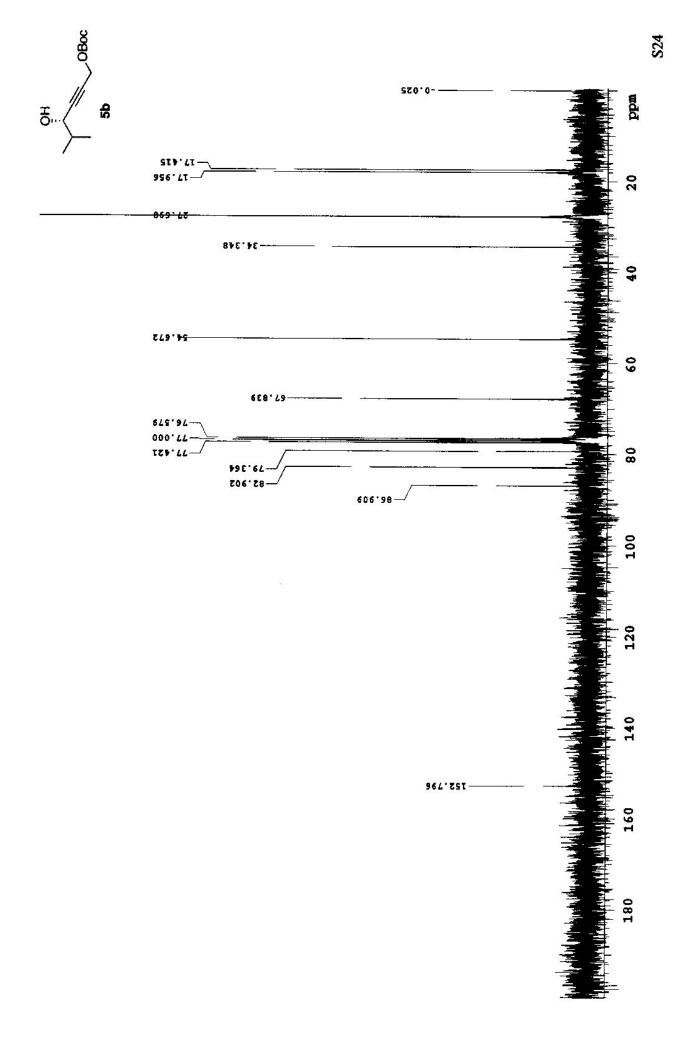


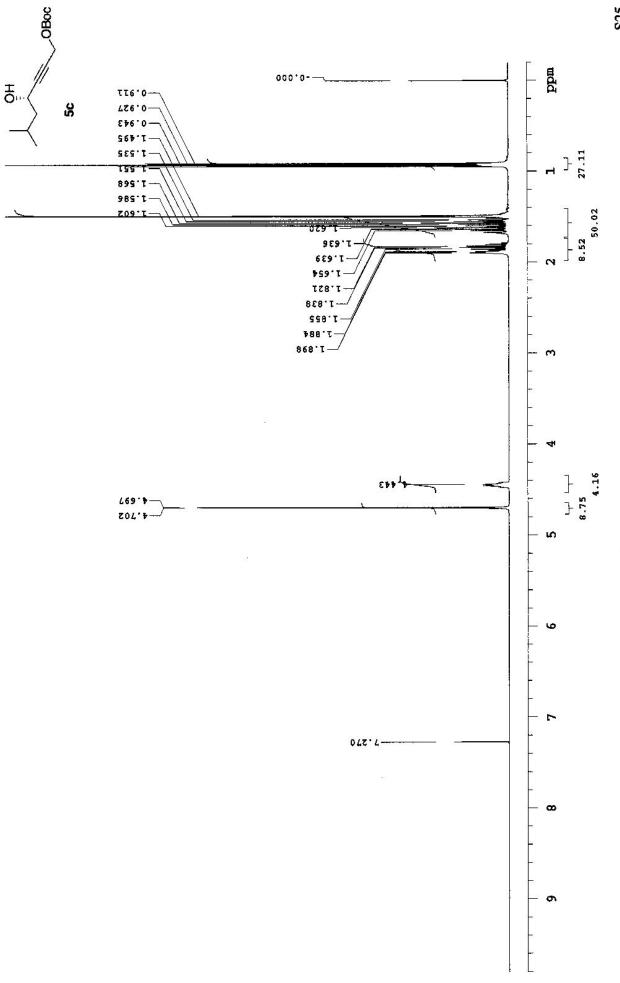


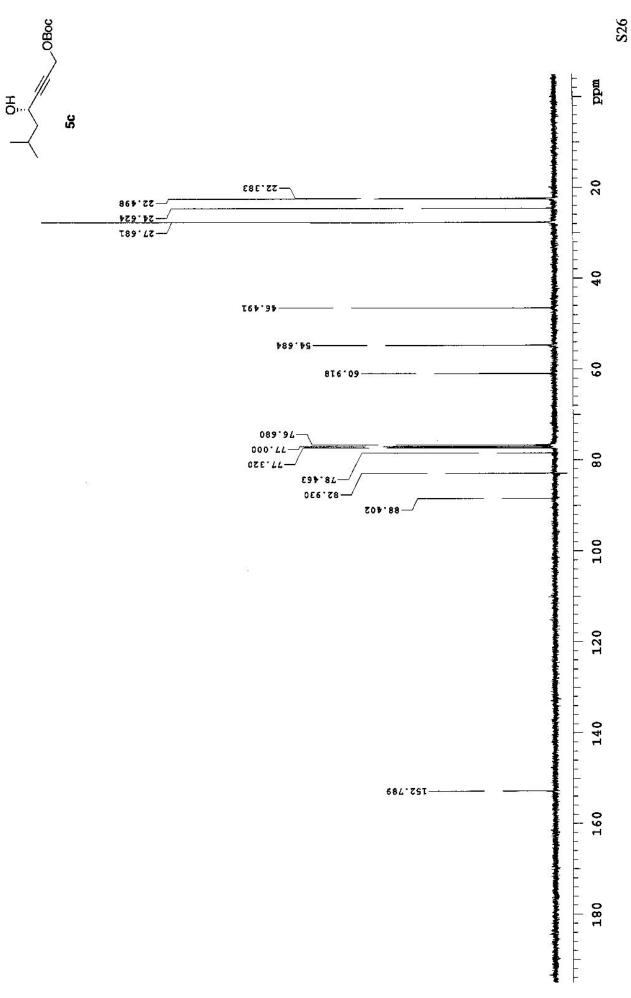


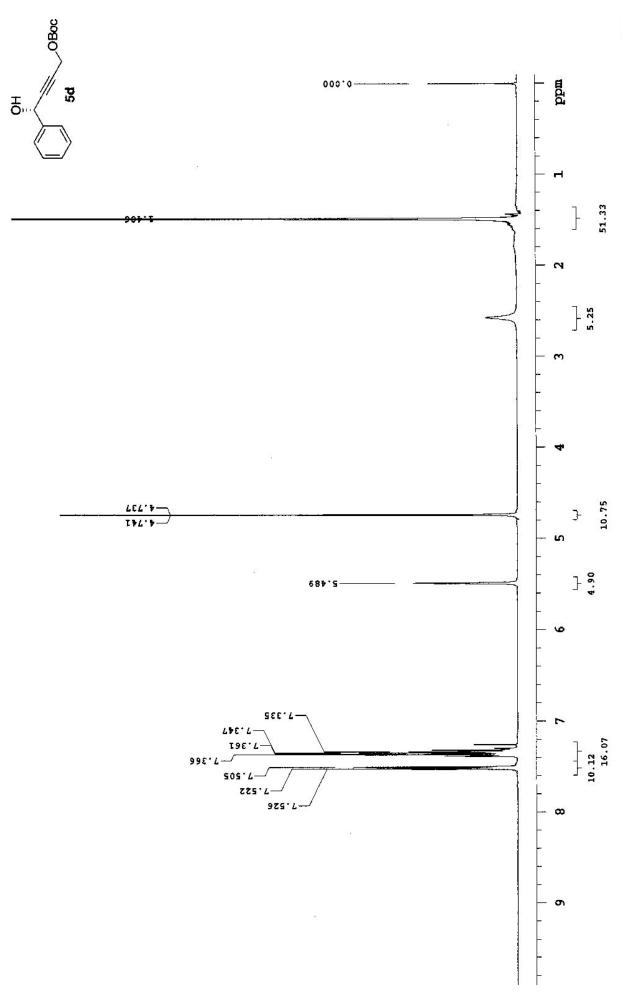


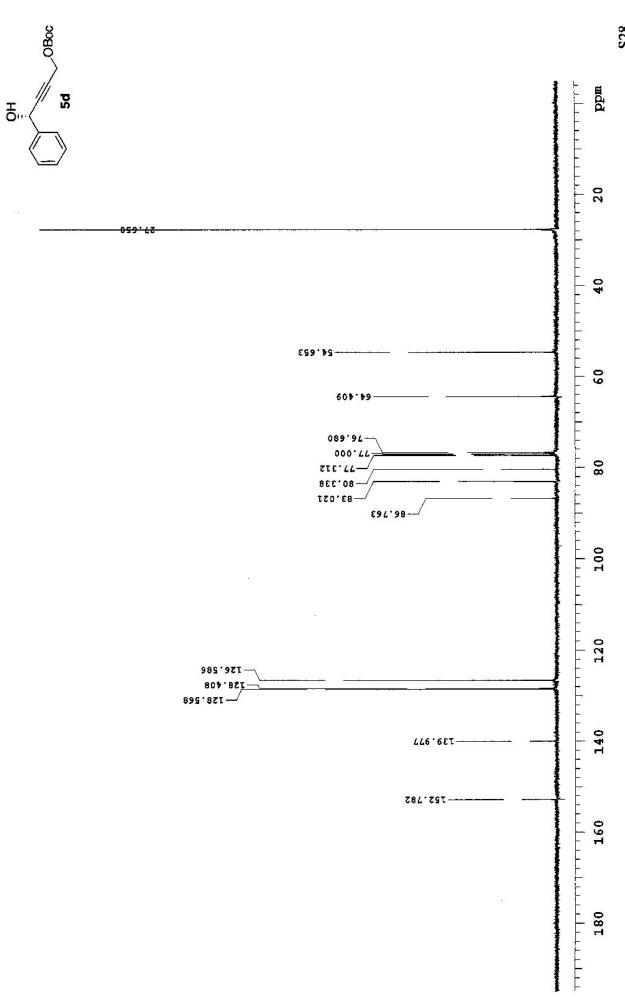


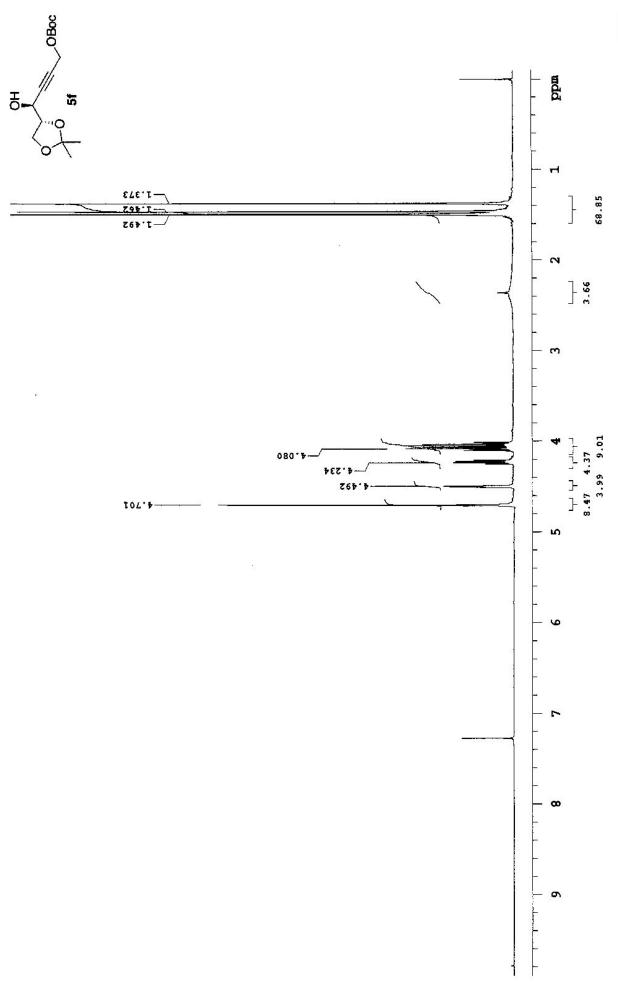


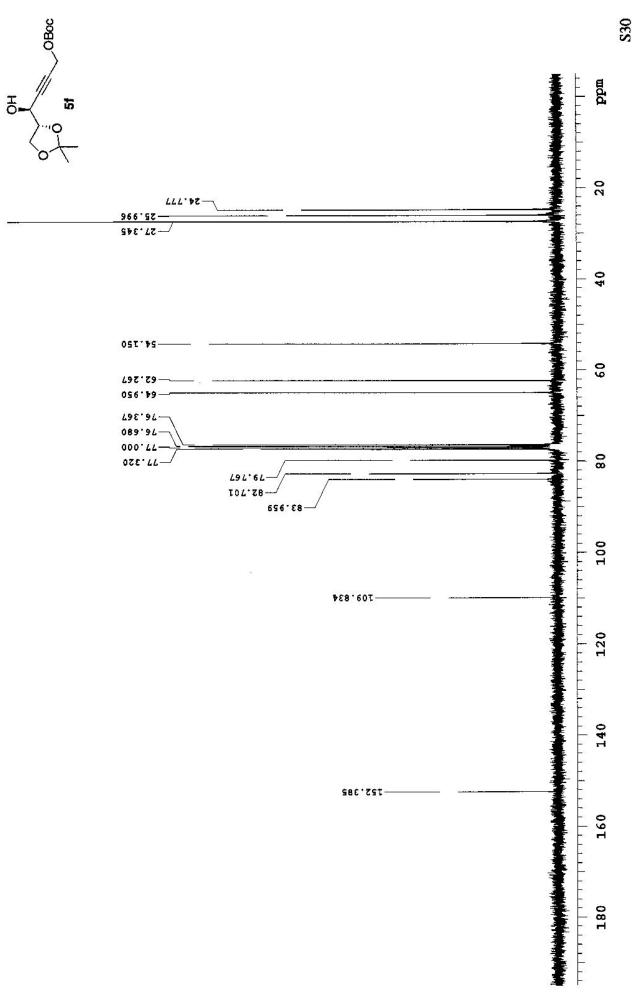


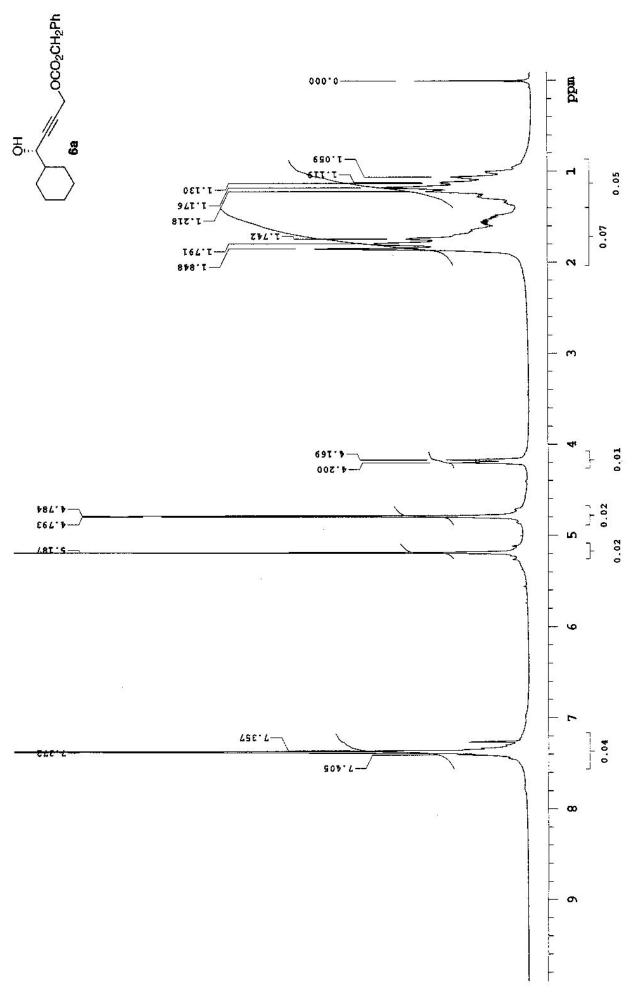


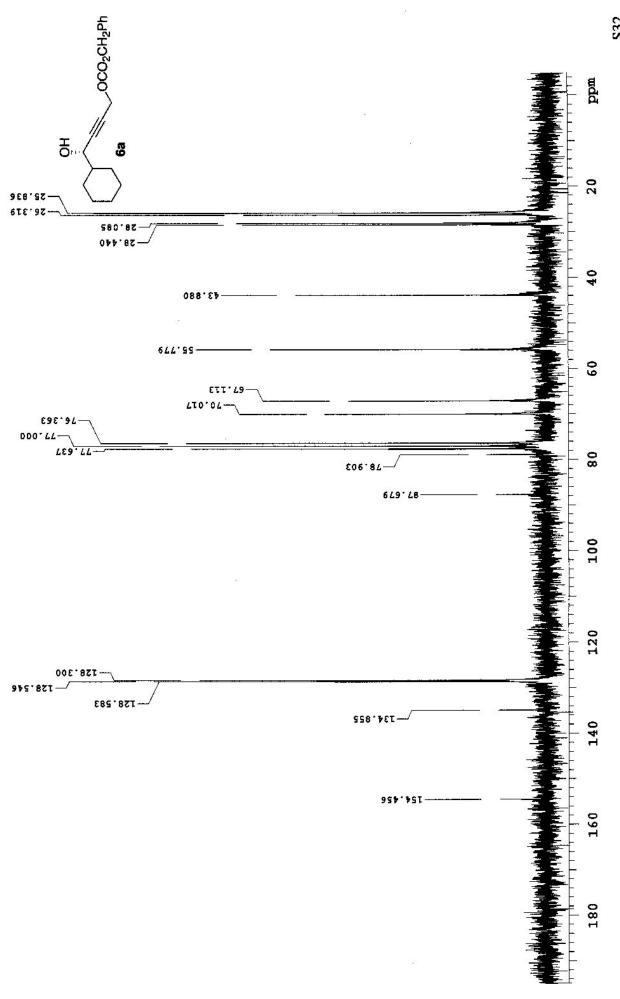


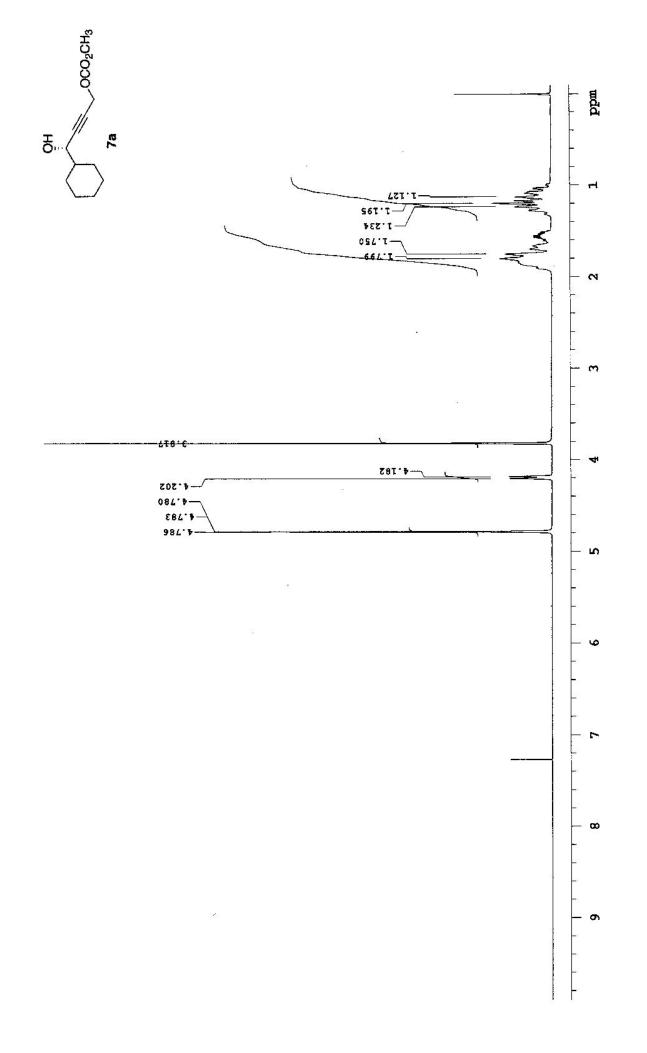


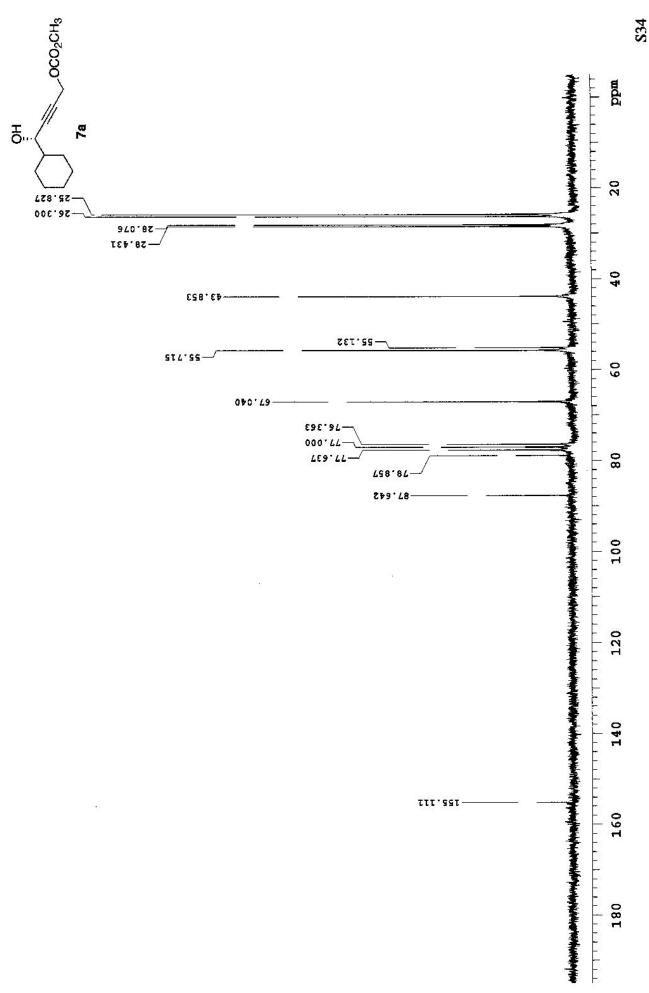


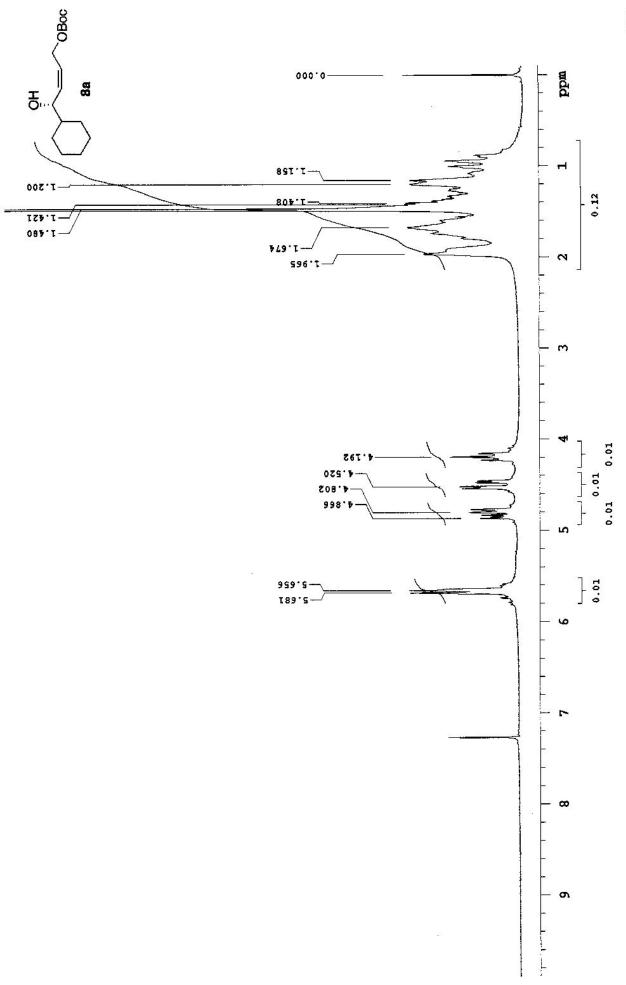


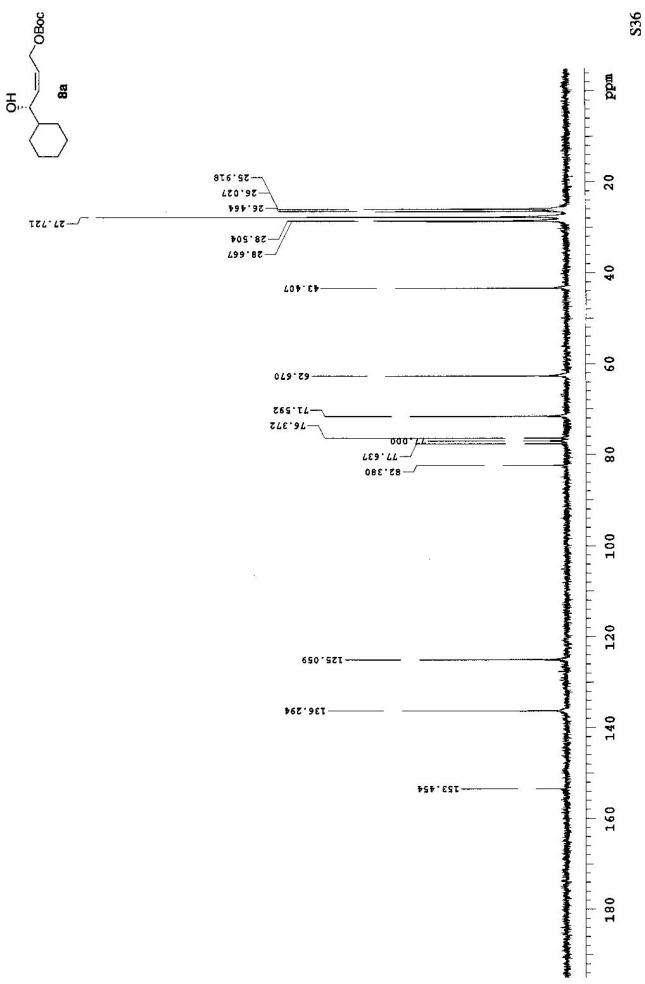


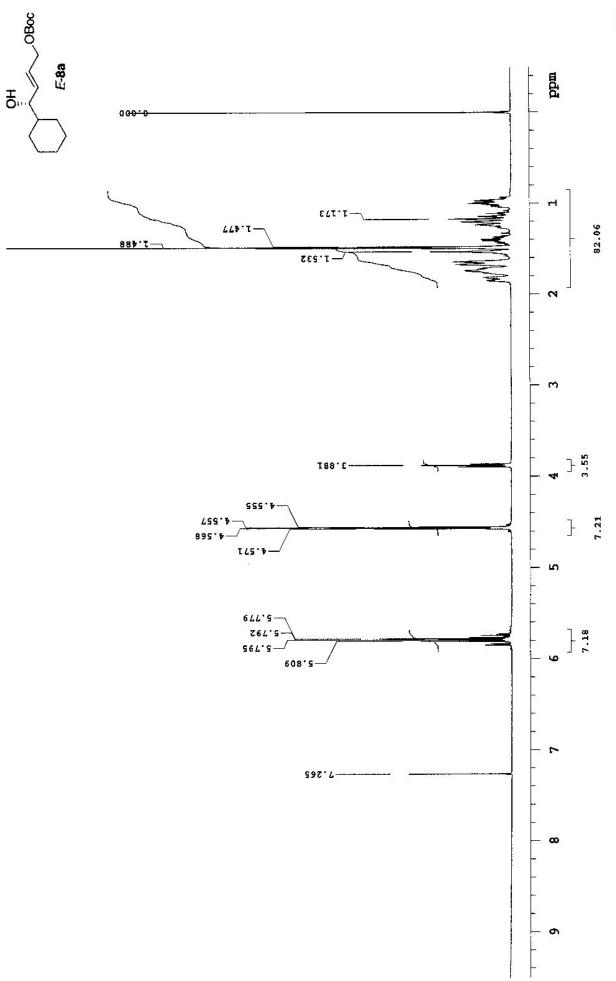


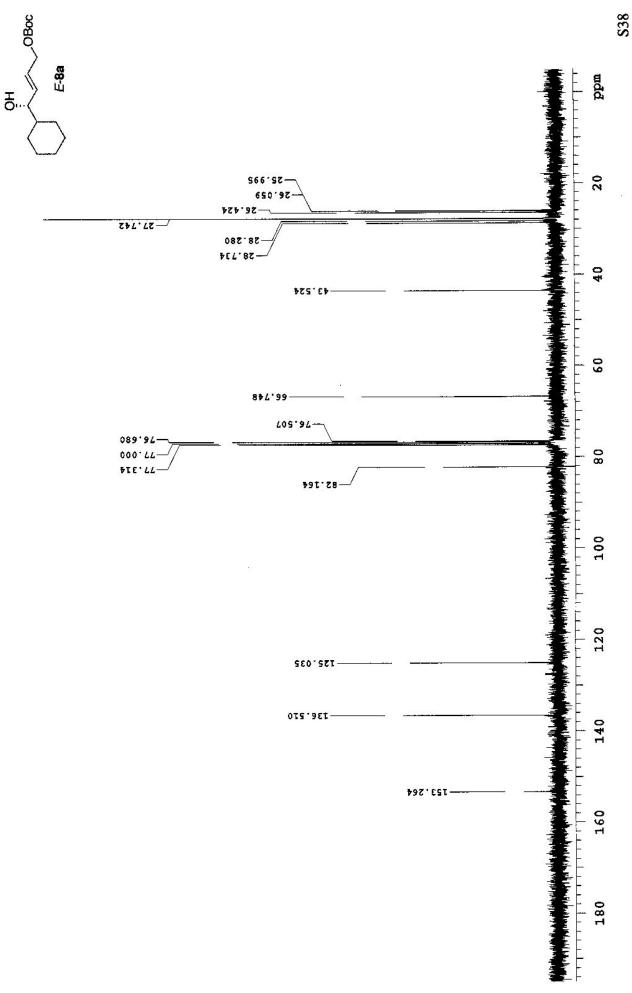


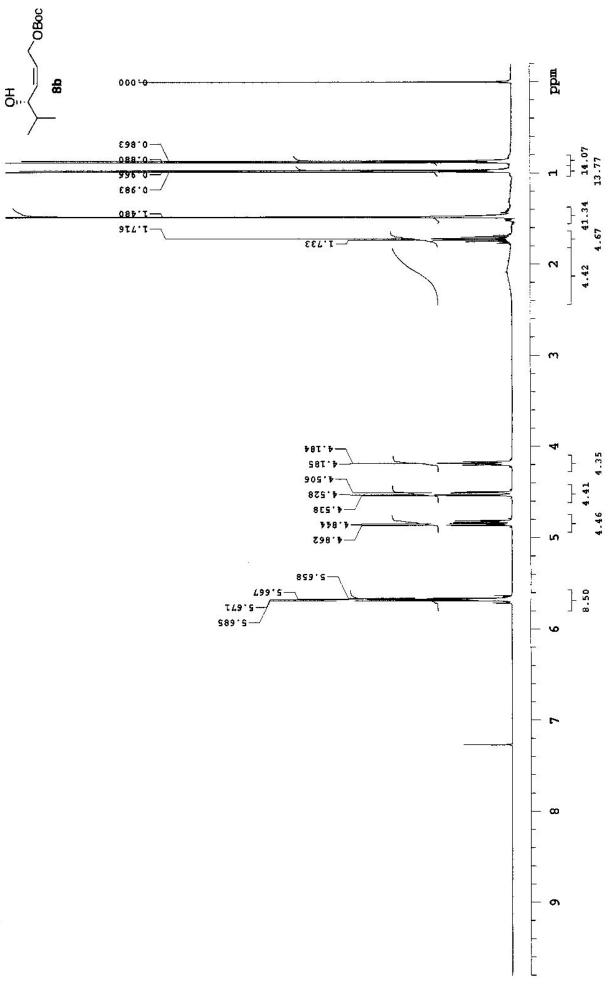




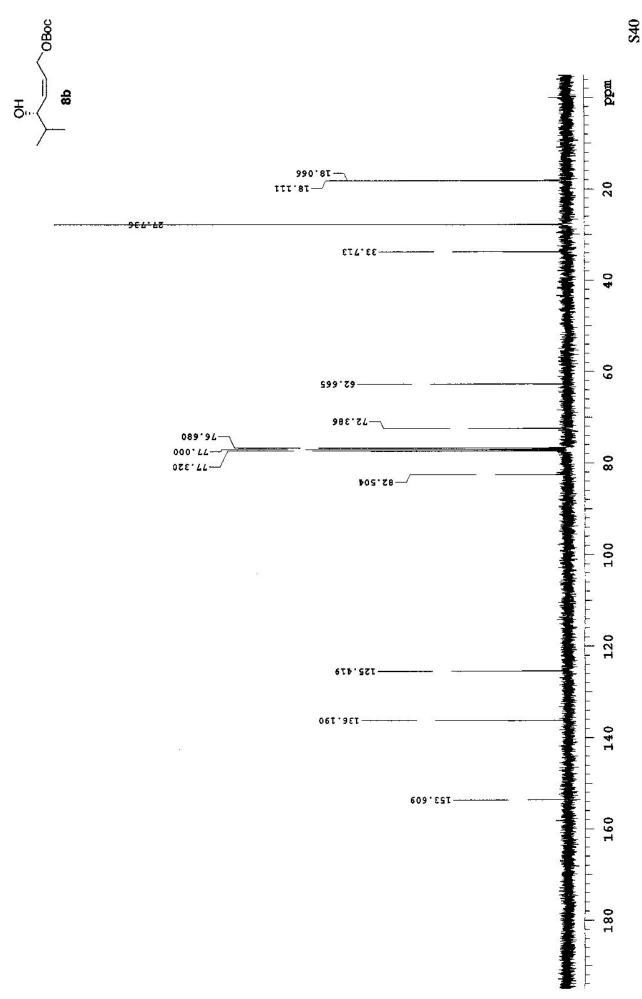


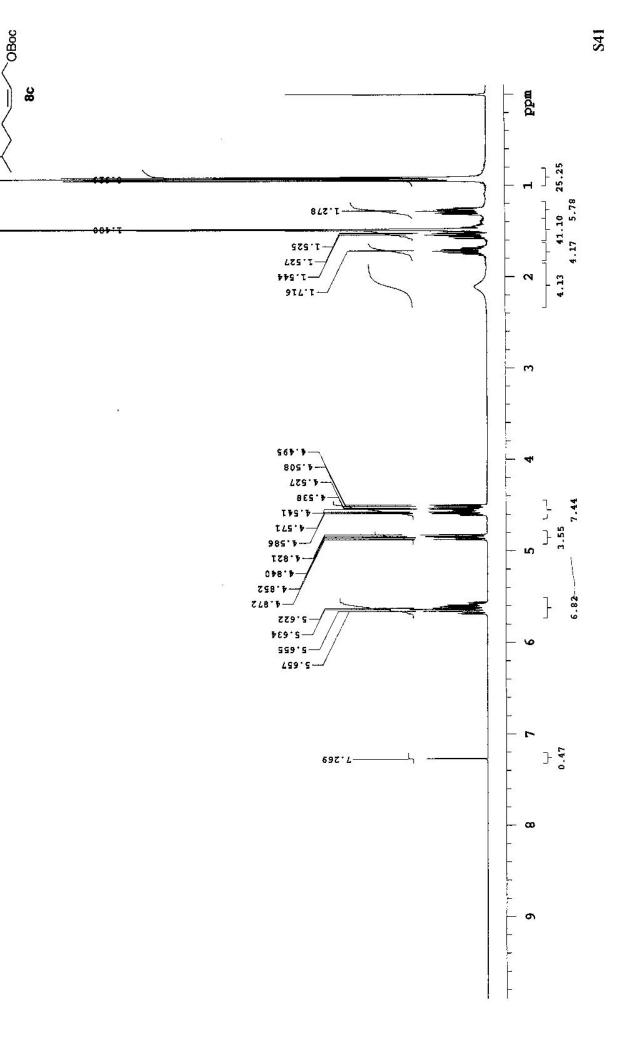












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