Ru-Catalyzed Cyclization of Terminal Alkynals to Cycloalkenes

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I. General

Acetic acid (99.8%, Fluka) was used as received. All other reagents and solvents: toluene, THF and Et₂O (99.5-99.8%, GC, over molecular sieves) were used as received without further purification, unless otherwise noted.

All reactions were carried out under an atmosphere of argon in flame-dried glassware with magnetic stirring, unless otherwise indicated.

II. Preparation of starting materials and catalysts

- Starting materials **1a**,¹ **1b**,² **1c**,³ **1d**⁴ and **12**,⁵ were prepared following published procedures or with appropriate modifications.
- Alkynals **1e** and **1f** were synthesized following the procedure for **1a**,¹ but using 2-(2-bromoethyl)-1,3-dioxolane or 2-(3-chloropropyl)-1,3-dioxolane as first alkylating agents. For preparation of **9**, 1-bromo-2-butyne were used as alkylating agent.
- Alkynes **7a**, **7b** and **4** were synthesized using methyl 2-chloroacetate, 2-chloroacetonitrile and chloropropanone, respectively, as the first alkylating agents.
- [Cp*Ru(CH₃CN)₃]PF₆,^{6,7} [CpRu(CH₃CN)₃]PF₆,^{7,8} [CpRu(dppm)Cl],⁸ [CpRu(PPh₃)₂Cl],⁹ and [Cp*Ru(COD)Cl]¹⁰ were prepared following literature procedures.
- Vinyl acetate **IIa** was prepared by Pd-catalyzed alkylation¹¹ of dimethyl 2-(2,2-diethoxyethyl)malonate¹ with the dimethyl acetal of acrolein:¹² To a solution of dimethyl 2-(2,2-diethoxyethyl)malonate (1.2 mmol), prop-2-ene-1,1-diyl diacetate (1.2 mmol) and BSA (1.3 mmol) in THF (10 mL) was added Pd(PPh₃)₄ (0.12 mmol) and the resulting mixture was refluxed for 24 h. Once the reaction mixture reached room temperature, water (10 mL) was added. The aqueous layer was extracted with diethyl ether (3x10 mL), and the combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under vacuum. The resulting residue was chromatographed on silica gel using ethyl ether/hexane (4:6) as eluent affording the final vinyl acetate **IIa** as a pale oil (37%).

¹ Carretero, J. C.; Adrio, J. *Synthesis*. **2001**, 12, 1888.

² Shintani, R.; Okamoto, K.; Otomaru, Y.; Ueyama, K.; Hayashi, T. *J. Am. Chem. Soc.* **2005**, 127, 54.

³ Feldman, K. S.; Bruendl, M. M.; Schildknecht, K.; Bohnstedt, A. C. *J. Org. Chem.* **1996**, 61, 5440.

⁴ Shizaki, M.; Hoshino, O. *Tetrahedron* **2000**, 56, 8813.

⁵ Bashiardes, G.; Safir, I.; Mohamed, A. Said; Barbot, F.; Laduranty, J. *Org. Lett.* **2003**, 5, 4915.

⁶ Trost, B. M.; Older, C. M. *Organometallics* **2002**, 21, 2544.

⁷ Schenk, J. L.; McNair, A. M.; McCormick, F. B. Mann, K. R. *Inorg. Chem.* **1986**, 25, 3501.

⁸ Ashby, G. S.; Bruce, M. I. Tomkins, I. B.; Wallis, R. C. *Aust. J. Chem.* **1979**, 32, 1003.

⁹ Bruce, M. I.; Windsor, N. J. *Aust. J. Chem.* **1977**, 30, 1601.

¹⁰ Masuda, K.; Ohkita, H.; Kurumatani, S.; Itoh, K. *Organometallics* **1993**, 12, 2221.

¹¹ Trost, B.M., Vercauteren J. *Tetrahedron Lett.* **1985**, 26, 131.

¹² Deka, N., Kalita, D.J., Borah, R., Sarma, J. C. *J. Org. Chem.* **1997**, 62, 1563

III. General conditions for the Ru-catalyzed cyclization of alkynals

Condition A. To a mixture of ruthenium catalyst (5% mmol) in acetic acid (4 mL) was added alkynal **1a** (0.5 mmol) and then heated in an oil bath for 12-24 h at 90°C. After reaching rt, diethyl ether was added to the solution and washed with water and saturated aqueous NaHCO₃. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under vacuum. The residue obtained was chromatographed on silica gel using ethyl acetate/hexane as eluents to afford the final cycloalkenes.*

* Additives used for reaction of entry 6, (Table 1):

- Use of dppf (5% mmol) gave exclusively **2a** (see Table 1).
- Use of dppe, P(OPh)₃ and PPh₃ (5% mmol) gave no modification of **2a:3a** ratio.

Condition B. To a mixture of ruthenium catalyst (5%, mmol) in acetic acid (4 mL) in a screw-capped vial was added alkynal **1a** (0.5 mmol) and then heated in an oil bath for 1-12 h at 130°C. After reaching rt, diethyl ether was added to the solution and washed with water and saturated aqueous NaHCO₃. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under vacuum. The residue obtained was chromatographed on silica gel using ethyl acetate/hexane as eluents to afford the final products.

Condition C.¹³ To a mixture of [CpRu(dppm)Cl] (10%, mmol) in a mixture of H₂O (0.4 mL) and 2-propanol (1.3 mL) in a screw-capped vial was added alkynal **1** (0.5 mmol). The reaction mixture was stirred for 24 h at 130 °C. After reaching rt, diethyl ether was added to the solution, dried over anhydrous Na₂SO₄ and concentrated under vacuum. The residue obtained was chromatographed on silica gel using ethyl acetate/hexane as eluents to afford the final aldehydes.

¹³ Suzuki, T.; Tokunaga, M.; Wakatsuki, Y. *Org. Lett.* **2001**, 3, 735

IV. Optimization conditions for the Ru-catalyzed reactions.

Besides the experimental conditions showed in the main text, the following catalyst and solvents were also used for the optimization of the Ru-catalyzed cyclization of alkynal **1a** (Table 1).

Table 1. Ru-catalyzed cyclization of alkynal **1a** [X = C(CO₂Me)₂, n = 1].

entry	catalyst ^a	solvent	t°C	time	yield ^b	2a : 3a
1	Cp*RuCl(cod)	AcOH	90	5.5 h	94% ^c	80 : 20
2	CpRuCl(PPh ₃) ₂	AcOH	90	24 h	58%	95 : 5
3	RuCl ₂ (PPh ₃) ₃	AcOH	90	24 h	20%	95 : 5
4	(ArRuCl ₂) ₂	AcOH	90	24 h	50%	95 : 5
5	[CpRuL ₃]PF ₆	AcOH/H ₂ O 90:10	90	24 h	90%	96 : 4
6	[CpRuL ₃]PF ₆	AcOH/H ₂ O 50:50	90	24 h	55%	94 : 6
7	[CpRuL ₃]PF ₆	C ₂ H ₅ COOH	90	24h	90%	90 : 10

^a L= CH₃CN, Ar= *p*-cymene. ^b Isolated yields. ^c GC yields.

V. Deuteration experiments.

The reaction was carried out in an NMR tube equipped with a J Young valve under argon atmosphere. Benzaldehyde **12** (40 mg, 0.25 mmol) was added over a mixture of Cp*Ru(CH₃CN)₃PF₆ (6mg, 0.013mmol) in CD₃COOD (0.75 mL), and the mixture was heated at 90°C. The course of the experiment was monitorized by ¹H NMR (300 MHz) during 12h. After partial deuteration of starting alkynal **12** (S27),¹⁴ evolution to the deuterated chromene **13** was observed.

VI. Mechanistic probes.

- A solution of vinyl acetate **11a** (0.5 mmol) in AcOH (4 mL) was heated at 90°C in an oil bath. The reaction was monitored by GC-MS, showing a slow (24 h) quantitative conversion to the cyclic α,β-unsaturated aldehyde **11a**.
- A solution of vinyl acetate **11a** (0.5 mmol) and CpRu(CH₃CN)₃PF₆ (0.05 mmol) in AcOH (4 mL) was heated at 90°C in an oil bath. The reaction was monitored by GC-MS showing a faster conversion (4-5 h) to the cyclic α,β-unsaturated aldehyde **11a**.
- To a mixture of CpRu(CH₃CN)₃PF₆ (0.05 mmol) in AcOH (4 mL) placed in a screw-capped vial was added the α,β-unsaturated aldehyde **11a** (0.5 mmol). The mixture was heated at 90 °C in an oil bath and monitored by GC-MS. After 24 h the starting aldehyde **11a** was recovered unaffected.
A second run of the same experiment performed at 130 °C gave the same result.

¹⁴ Tokunaga, M.; Suzuki, T.; Koga, N.; Fukushima, T.; Horiuchi, A.; Wakatsuki, Y. *J. Am. Chem. Soc.* **2001**, *123*, 11917.

VII. Spectral data.

Dimethyl cyclopent-3-ene-1, 1-dicarboxylate (2a)¹⁵

¹H NMR (300 MHz, CDCl₃), δ (ppm): 5.61 (s, 1H), 3.74 (s, 6H), 3.02 (s, 4H). ¹³C NMR, DEPT (75 MHz, CDCl₃), δ (ppm): 172.6 (2 $\times$ CO), 127.8 (2 $\times$ CH), 58.7 (C), 52.8 (2 $\times$ CH₃), 40.9 (2 $\times$ CH₂). MS, m/z (% relative intensity): 184 (M⁺, 10), 152 (21), 124 (100), 93 (61). HRMS calculated for C₉H₁₂O₄: 184.0735; found: 184.0742.

4, 4-Bis (benzyloxymethyl)cyclopent-1-ene (2b)¹⁶

¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.32-7.28 (m, 10H), 5.58 (s, 2H), 4.53 (s, 4H), 3.44 (s, 4H), 2.24 (s, 4H). ¹³C NMR, DEPT (75 MHz, CDCl₃), δ (ppm): 138.9 (C), 128.9 (CH), 128.2 (2 $\times$ CH), 127.4 (2 $\times$ CH), 127.3 (CH), 74.1 (2 $\times$ CH₂), 73.2 (2 $\times$ CH₂), 46.7 (C), 39.4 (2 $\times$ CH₂). MS, m/z (% relative intensity): 309 (M⁺+1, 77), 308 (9), 307 (24), 183 (32), 182 (20), 181 (100). HRMS calculated for C₂₁H₂₅O₂: 309.1854; found: 309.1864.

1-(2-(Cyclopent-2-enyl)ethyl)benzene (2c)¹⁷

¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.31-7.14 (m, 5H), 5.77-5.67 (m, 2H), 2.65 (t, *J*=7.8 Hz, 2H), 2.38-2.27 (m, 2H), 2.14-1.99 (m, 1H), 1.92-1.41 (m, 4H). ¹³C NMR, DEPT (75 MHz, CDCl₃), δ (ppm): 142.8 (C), 134.9 (CH), 130.5 (CH), 128.4 (2 $\times$ CH), 128.3 (2 $\times$ CH), 125.6 (CH), 45.2 (CH), 37.9 (CH₂), 34.3 (CH₂), 31.9 (CH₂), 29.8 (CH₂). MS, m/z (% relative intensity): 173 (M⁺+1, 21), 172 (6), 171 (21), 131 (13), 119 (33), 105 (15), 91 (100). HRMS calculated for C₁₃H₁₇: 173.1330; found: 173.1329.

¹⁵ Depres, J. P.; Greene, A. E. *J. Org. Chem.* **1984**, 49, 928.

¹⁶ Legraverend, M.; Huel, C.; Bisagni, E. *J. Chem. Res., Synopses.* **1990**, 4, 102.

¹⁷ Ellis-Davies, G. C. R.; Gilbert, A.; Heath, P.; Lane, J. C.; Warrington, J. V.; Westover, D. L. *J. Chem Soc, Perkin Trans. 2* **1984**, 11, 1833.

2d**2,5-Dihydro-1-tosyl-1H-pyrrole (2d)¹⁸**

¹H NMR (250 MHz, CDCl₃), δ (ppm): 7.72 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 5.65 (s, 2H), 4.12 (s, 4H), 2.43 (s, 3H). ¹³C NMR, DEPT (63 MHz, CDCl₃), δ (ppm): 143.4 (C), 134.3 (C), 129.7 (2 $\times$ CH), 127.4 (2 $\times$ CH), 125.4 (2 $\times$ CH), 54.8 (2 $\times$ CH₂), 21.5 (CH₃). MS, m/z (% relative intensity): 224 (M^+ +1, 100), 223 (6), 222 (17), 149 (23). HRMS calculated for C₁₁H₁₄N₁O₂S: 224.0745; found: 224.0748.

2e**Dimethyl cyclohex-3-ene-1,1-dicarboxylate (2e)¹⁹**

¹H NMR (250 MHz, CDCl₃), δ (ppm): 5.65 (s, 2H), 3.71 (s, 6H), 2.56 (s, 2H), 2.17-2.06 (m, 4H). ¹³C NMR, DEPT (63 MHz, CDCl₃), δ (ppm): 171.9 (2 $\times$ CO), 126.0 (CH), 123.8 (CH), 53.0 (C), 52.6 (2 $\times$ CH₃), 30.6 (CH₂), 27.6 (CH₂), 22.4 (CH₂). MS, m/z (% relative intensity): 199 (M^+ +1, 28), 197 (7), 167 (95), 139 (100), 79 (15). HRMS calculated for C₁₀H₁₅O₄: 199.0970; found: 199.0978.

5**Dimethyl 3-methylcyclopent-3-ene-1,1-dicarboxylate (5)²⁰**

¹H NMR (400 MHz, CDCl₃), δ (ppm): 5.18 (m, 1H), 3.73 (s, 6H), 2.97 (m, 2H), 2.91 (broad s, 2H), 1.70 (broad s, 3H). ¹³C NMR, DEPT (100 MHz, CDCl₃), δ (ppm): 172.8 (2 $\times$ CO), 137.4 (C), 121.2 (CH), 59.3 (C), 52.7 (2 $\times$ CH₃), 44.7 (CH₂), 40.9 (CH₂), 16.0 (CH₃). MS, m/z (% relative intensity): 199 (M^+ +1, 17), 198 (2), 197 (6), 167 (37), 139 (100), 123 (8).

6**Dimethyl-2-[4,4-di(methylcarbonyloxy)butyl]-2-ethylmalonate (6)**

¹⁸ Kimura, M.; Harayama, H.; Tanaka, S.; Tamaru, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 21, 2531.

¹⁹ Baylouny, R. A. *J. Am. Chem. Soc.* **1971**, 93, 4621.

²⁰ Furstner, A.; Ackermann, L. *Chem. Commun.* **1999**, 1, 95.

^1H NMR (400 MHz, CDCl_3), δ (ppm): 6.75 (t, J = 5.6 Hz, 1H), 3.72 (s, 6H), 2.07 (s, 6H), 1.98-1.86 (m, 4H), 1.78 (m, 2H), 1.31-1.18 (m, 2H), 0.81 (t, J = 7.5 Hz, 3H) ^{13}C NMR, DEPT (100 MHz, CDCl_3), δ (ppm): 171.9 (2xCO), 168.9 (2xCO), 90.0 (CH), 57.9 (C), 52.3 (2xCH₃), 33.2 (CH₂), 31.6 (CH₂), 25.6 (CH₂), 20.8 (2xCH₃), 18.1 (CH₂), 8.5 (CH₃), MS, m/z (% relative intensity): 355 ($\text{M}^+ + \text{Na}$, 6), 295 (14), 254 (20), 253 (100), 179 (13). HRMS calculated for $\text{C}_{15}\text{H}_{24}\text{O}_8\text{Na}$: 355.1369; found: 355.1363.

8a

Trimethyl butane-1,2,2-tricarboxylate (8a)

^1H NMR (250 MHz, CDCl_3), δ (ppm): 3.72 (s, 6H), 3.64 (s, 3H), 2.94 (s, 2H), 2.01 (q, J = 7.5 Hz, 2H), 0.84 (t, J = 7.5 Hz, 3H). ^{13}C NMR, DEPT (63 MHz, CDCl_3), δ (ppm): 170.9 (2xCO), 170.8 (CO), 56.0 (C), 52.7 (2xCH₃), 51.8 (CH₃), 36.9 (CH₂), 26.5 (CH₂), 8.8 (CH₃). MS, m/z (% relative intensity): 233 ($\text{M}^+ + 1$, 6), 202 (10), 201 (100), 141 (3). HRMS calculated for $\text{C}_{10}\text{H}_{17}\text{O}_6$: 233.1025; found: 233.1025.

8b

Dimethyl 2-(cyanomethyl)-2-ethylmalonate (8b)

^1H NMR (250 MHz, CDCl_3), δ (ppm): 3.72 (s, 6H), 2.90 (s, 2H), 2.09 (q, J = 7.5 Hz, 2H), 0.85 (t, J = 7.5 Hz, 3H). ^{13}C NMR, DEPT (75 MHz, CDCl_3), δ (ppm): 169.2 (2xCO), 116.2 (CN), 55.8 (C), 53.3 (2xCH₃), 26.1 (CH₂), 21.3 (CH₂), 8.5 (CH₃). MS, m/z (% relative intensity): 200 ($\text{M}^+ + 1$, 100), 169 (4), 168 (40), 140 (13).

8c

Dimethyl 2-ethyl-2-(2-oxopropyl)malonate (8c)²¹

^1H NMR (400 MHz, CDCl_3), δ (ppm): 3.72 (s, 6H), 3.10 (s, 2H), 2.16 (s, 3H), 2.04 (q, J = 7.6 Hz, 2H), 0.83 (t, J = 7.6 Hz, 3H). ^{13}C NMR, DEPT (100 MHz, CDCl_3), δ (ppm): 205.2 (CO), 171.3 (2xCO), 55.7 (C), 52.6 (2xCH₃), 45.6 (CH₂), 30.3 (CH₃), 26.7 (CH₂), 9.1 (CH₃). MS, m/z (% relative intensity): 217 ($\text{M}^+ + 1$, 6), 186 (10), 185 (100), 157 (7), 129 (17). HRMS calculated for $\text{C}_{10}\text{H}_{17}\text{O}_5$: 217.1076; found: 217.1080.

²¹ Hosomi, A.; Shirahata, A.; Araki, Y.; Sakurai, H. *J. Org. Chem.* **1981**, *46*, 4631.

10**Dimethyl 3-acetylcyclopent-3-ene-1,1-dicarboxylate (10)**²²

¹H NMR (300 MHz, CDCl₃), δ (ppm): 6.52 (m, 1H), 3.68 (s, 6H), 3.20-3.19 (m, 2H), 3.18-3.16 (m, 2H), 2.25 (s, 3H). ¹³C NMR, DEPT (75 MHz, CDCl₃), δ (ppm): 195.6 (C), 171.7 (2 $\times$ CO), 142.6 (C), 139.8 (CH), 58.1 (C), 52.9 (2 $\times$ CH₃), 41.5 (CH₂), 38.8 (CH₂), 26.3 (CH₃). MS, m/z (% relative intensity): 227 (M⁺+1, 89), 226 (6), 195 (100), 167 (69), 135 (26), 125 (77). HRMS calculated for C₁₁H₁₅O₅: 227.0919; found: 227.0913.

11a**Dimethyl 3-formylcyclopent-3-ene-1,1-dicarboxylate (11a)**

¹H NMR (300 MHz, CDCl₃), δ (ppm): 9.72 (s, 1H), 6.71 (m, 1H), 3.76 (s, 6H), 3.31 (m, 2H), 3.23 (m, 2H). ¹³C NMR, DEPT (75 MHz, CDCl₃), δ (ppm): 188.5 (CHO), 171.5 (2 $\times$ CO), 147.5 (CH), 144.2 (C), 58.3 (C), 53.1 (2 $\times$ CH₃), 41.5 (CH₂), 37.0 (CH₂). MS, m/z (% relative intensity): 213 (M⁺+1, 84), 182 (10), 181 (100), 153 (98). HRMS calculated for C₁₀H₁₃O₅: 213.0762; found: 213.0762.

11e**Dimethyl 4-formylcyclohex-3-ene-1,1-dicarboxylate (11e)**

¹H NMR (250 MHz, CDCl₃), δ (ppm): 9.45 (s, 1H), 6.77 (m, 1H), 3.73 (s, 6H), 2.78 (m, 2H), 2.49-2.41 (m, 2H), 2.21 (t, *J* = 6.4 Hz, 2H). ¹³C NMR, DEPT (63 MHz, CDCl₃), δ (ppm): 192.8 (CHO), 171.2 (2 $\times$ CO), 148.6 (CH), 138.6 (C), 52.7 (2 $\times$ CH₃), 52.2 (C), 27.2 (CH₂), 27.1 (CH₂), 23.7 (CH₂). MS, m/z (% relative intensity): 227 (M⁺+1, 52), 226 (6), 209 (32), 196 (11), 195 (100), 167 (60).

²² Beifuss, U.; Ledderhose, S. *Synlett*. **1995**, 9, 938.

13**2H-chromene (13)**²³

¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.09 (td, J = 7.5, 1.7 Hz, 1H), 6.95 (dd, J =7.5, 1.7 Hz, 1H), 6.85 (td, J = 7.5, 1.2 Hz, 1H), 6.76 (d, J = 7.4 Hz, 1H), 6.41 (td, J = 9.8, 1.7 Hz, 1H), 5.76 (td, J = 9.8, 3.6 Hz, 1H), 4.81 (dd, J = 3.6, 1.7 Hz, 1H). ¹³C NMR, DEPT (75 MHz, CDCl₃), δ (ppm): 154.0 (C), 129.1 (CH), 126.5 (CH), 124.5 (CH), 122.4 (C), 121.9 (CH), 121.3 (CH), 115.7 (CH), 65.5 (CH₂). MS, m/z (% relative intensity): 132 (M⁺, 27), 131 (100), 78 (58), 63 (94). HRMS calculated for C₉H₈O: 132.0575; found: 132.0574.

d-13**3-Deutero-2H-chromene (d-13)**²⁴

¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.08 (td, J = 7.5, 1.7 Hz, 1H), 6.94 (dd, J = 7.5, 1.7 Hz, 1H), 6.84 (td, J = 7.5, 1.2 Hz, 1H), 6.75 (d, J = 7.5 Hz, 1H), 6.40 (s, 1H), 4.80 (d, J = 1.7 Hz, 1H). ¹³C NMR, DEPT (75 MHz, CDCl₃), δ (ppm): 154.0 (C), 129.1 (CH), 126.5 (CH), 124.4 (CH), 122.4 (C), 121.9 (C), 121.3 (CH), 115.7 (CH), 65.5 (CH₂). MS, m/z (% relative intensity): 134 (M⁺+1, 100), 133 (29), 132 (8), 131 (3), 106 (6).

IIa**(E)-dimethyl 2-(3-acetoxyallyl)-2-(2-oxoethyl)malonate (IIa)**

¹H NMR (250 MHz, CDCl₃), δ (ppm): 9.69 (s, 1H), 7.06 (dt, J =12.4, 1.2 Hz, 1H), 5.26 (dt, J =12.4, 8.2 Hz, 1H), 3.74 (s, 6H), 2.98 (s, 2H), 2.70 (dd, J =8.2, 1.2 Hz, 2H), 2.09 (s, 3H). ¹³C NMR, DEPT (63 MHz, CDCl₃), δ (ppm): 198.4 (CHO), 170.1 (2 x C), 167.7 (C), 138.6 (CH), 108.2 (CH), 54.9 (C), 52.9 (2 x CH₃), 46.1 (CH₂), 32.1 (CH₂), 20.5 (CH₃). MS, m/z (% relative intensity): 273 (M⁺+1, 1), 213 (100), 199 (38), 181 (54), 153 (87).

²³ a) Baranton, F.; Fontaine, G.; Maitte, P. *Bull. Soc. Chim. Fr.* **1968**, 10, 4203. b) Koch-Pomeranz, U.; Hansen, H. J.; Schmid, H. *Helv. Chim. Acta.* **1973**, 56, 2981.

²⁴ Spilker, R.; Gruetzmacher, H. F. *Org. Mass Spectrom.* **1989**, 24, 47.

VIII. Spectra.

2a

H₂O

2b *H₂O

2d *H₂O

2e

*H₂O
+Solvent impurity

5

6 *H₂O

+ Impurity

8b

10

11e

13a