



Supporting Information

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Carbynes: Useful Intermediates for Organic Synthesis !

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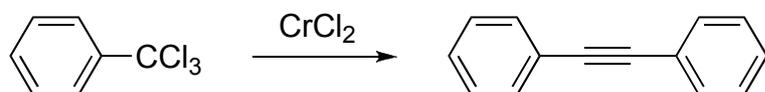
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GC/MS analyses were carried out using a Shimadzu GCMS-QP5050A with a SGE silica capillary 25 m x 0.22 mm BPX5 column (5% phenyl polysilphenylene-siloxane / 95% methylpolysiloxane), helium carrier gas (29 mL/min; 113 kPa), 260 °C interface, 80 °C column temp., 320°C detector, programmed for 2 min at 80°C, then heating at 25°C/min.

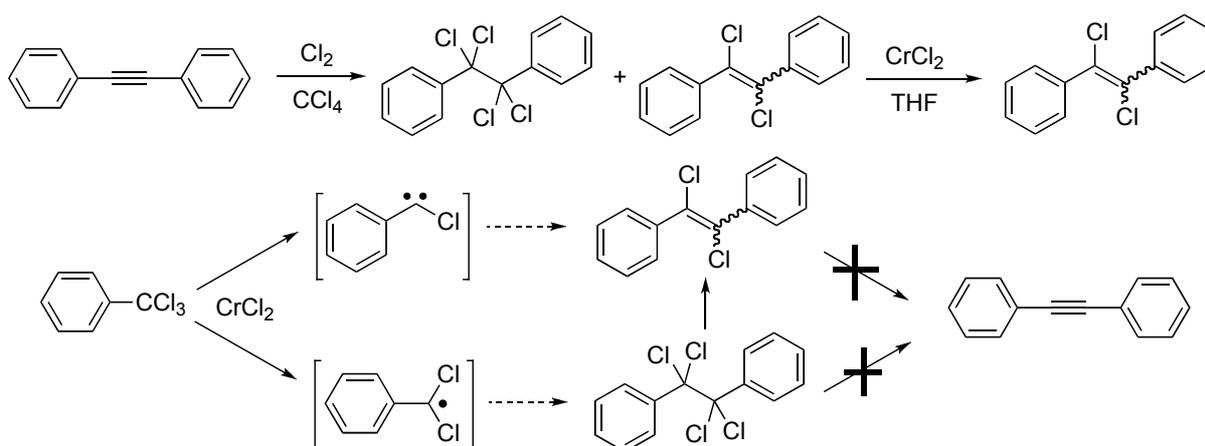
Anhydrous lithium iodide was purchased from Aldrich or prepared by reduction of iodine by lithium hydride and stored under argon as a 1.0 M solution in anhydrous THF.^[1] CrCl₂ was purchased from Strem. Tetrahydrofuran (THF) was distilled over Na/benzophenone ketyl. 1-butyl-3-methylimidazolium bromide ([bmim][Br]) and 1-butyl-3-methylimidazolium iodide ([bmim][I]) were synthesized and dried under vacuum before use.

Dimerization of trichloromethylaryls into diarylacetylenes.

1,1,1-trichloromethylaryls undergo a rapid dimerization upon treatment with CrCl₂ in THF, to yield diarylacetylenes.



The treatment of 1,2-dichloro-1,2-diphenylethene with CrCl₂ in THF do not lead to diphenylacetylene, thus excluding a dimerization of 1,1-dichlorobenzyl radical.



Experimental procedures

To a stirred suspension of chromium(II) chloride (368 mg, 3.0 mmol) in anhydrous THF (5 mL) at ambient temperature under argon was added benzotrichloride (72 μL, 0.5 mmol). The mixture was

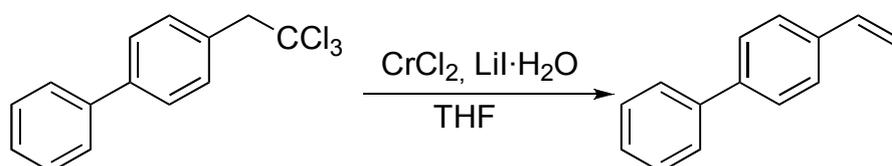
stirred 3 h at ambient temperature, quenched with aqueous ammonium oxalate and diluted with Et₂O. The layers were separated and the aqueous phase was extracted twice with Et₂O. The combined organic extracts were washed with aqueous ammonium oxalate, dried over anhydrous Na₂SO₄ and filtered. After concentration under vacuum, the crude product was purified chromatography (*n*-hexane) on silica gel to give 36 mg (81%) of diphenylacetylene as white crystals. ¹H (300 MHz, CDCl₃) δ: 7.59-7.54 (m, 2H), 7.40-7.35 ppm (m, 3H); ¹³C (75 MHz, CDCl₃) δ: 131.8, 128.5, 128.4, 123.4, 89.5 ppm; MS (CI, NH₃) m/z: 178.

Synthesis of 1,2-dichloro-1,2-diphenylethene according to literature.^[2] Dry Cl₂ was bubbled through a solution of diphenylacetylene (2.0g, 11.2 mmol) in anhydrous CCl₄ (20 mL) for 5 min until no more heat was evolved. The solution was stirred overnight, then concentrated until formation of a white precipitate. The mixture was refrigerated to induce more precipitation. The white solid was filtered and washed with CCl₄ to afford a mixture of (*E*)-1,2-dichloro-1,2-diphenylethene and 1,1,2,2-tetrachloro-1,2-diphenylethane as a white solid. ¹H (300 MHz, CDCl₃) δ: 7.68 (d, *J* = 7.2 Hz, 4H_{*E*}), 7.53-7.37 (m, 9.9H), 7.28-7.24 ppm (m, 3.7H). (*E*)-1,2-dichloro-1,2-diphenylethene: ¹³C (75 MHz, CDCl₃) δ: 137.5, 129.7, 129.1, 129.0, 128.2 ppm; MS (EI) m/z: 178, 213, 215, 233, 248, 250, 252. 1,1,2,2-tetrachloro-1,2-diphenylethane: ¹³C (75 MHz, CDCl₃) δ: 136.2, 130.8, 129.8, 126.6 ppm; MS (EI) m/z: 159, 161, 163, 178, 212, 214, 248, 250, 283, 320.

A suspension of 1,2-dichloro-1,2-diphenylethene and 1,1,2,2-tetrachloro-1,2-diphenylethane (125 mg), and CrCl₂ (367 mg, 3.0 mmol) in anhydrous THF was stirred overnight at RT under an argon atmosphere. The reaction mixture was quenched with aqueous ammonium oxalate and diluted with Et₂O. The layers were separated and the aqueous phase was extracted twice with Et₂O. The combined organic extracts were washed with aqueous ammonium oxalate, dried over anhydrous Na₂SO₄ and filtered. Concentration under vacuum afforded 1,2-dichloro-1,2-diphenylethene as a mixture of isomers *E/Z* = 66:33. No trace of diphenylacetylene could be detected. ¹H (300 MHz, CDCl₃) δ: 7.68 (d, *J* = 7.2 Hz, 4H_{*E*}), 7.53-7.44 (m, 6H_{*E*}), 7.30-7.17 ppm (m, 5H_{*Z*}). (*E*)-1,2-dichloro-1,2-diphenylethene: ¹³C (75 MHz, CDCl₃) δ: 137.5, 129.7, 129.1, 129.0, 128.2 ppm. (*Z*)-1,2-dichloro-1,2-diphenylethene: ¹³C (75 MHz, CDCl₃) δ: 137.2, 130.8, 129.7, 128.6, 128.1 ppm.

Reduction of 2,2,2-trichloroethylaryls into alkenes in presence hydrated lithium iodide.

2,2,2-trichloroethylaryls undergo a 1,2-hydride migration and an hydrolysis upon treatment with CrCl₂ and hydrated LiI in THF, to yield terminal alkenes.



Previous work have demonstrated that intramolecular 1,2-suprafacial migration of the hydride group in carbene complexes affords selectively *Z* isomers, due to steric repulsions between hexacoordinated chromium and the R¹ group (R = R¹CH₂).^[3] In contrast, 1,2-hydride migration in carbyne complexes should afford both isomers. So, the formation of allylic alcohols and an isotopically labelled terminal alkene as mixtures of *Z/E* isomers implies that both pathways are involved.

Experimental procedures

To a stirred suspension of chromium(II) chloride (368 mg, 3.0 mmol) and hydrated lithium iodide (75 mg, 0.5 mmol) in anhydrous THF (3 mL) at ambient temperature under argon was added 4-(2,2,2-trichloroethyl)-biphenyl (143 mg, 0.5 mmol) in THF (2 mL). The mixture was stirred overnight at ambient temperature, quenched with aqueous ammonium oxalate and diluted with Et₂O. The layers were separated and the aqueous phase was extracted twice with Et₂O. The combined organic extracts were washed with aqueous ammonium oxalate, dried over anhydrous Na₂SO₄ and filtered. After concentration under vacuum, the crude product was purified chromatography (*n*-hexane) on silica gel to give 81 mg (90%) of 4-vinylbiphenyl as white solid. ¹H (300 MHz, CDCl₃) δ: 7.28-7.61 (m, 9H), 6.80 (dd, *J* = 17.8, 10.9 Hz, 1H), 5.81 (d, *J* = 17.8 Hz, 1H), 5.28 ppm (d, *J* = 10.9 Hz, 1H); ¹³C (50 MHz, CDCl₃) δ: 140.9, 140.7, 136.7, 136.5, 128.9, 127.44, 127.37, 127.1, 126.8, 114.0 ppm; MS (CI, NH₃) *m/z*: 180, 181; mp : 118-119°C (lit. 119-121°C).

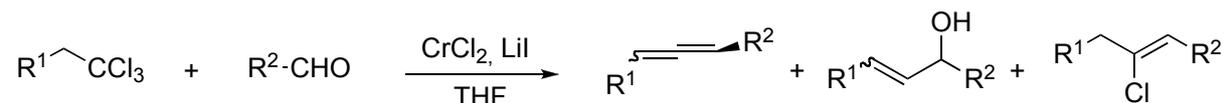
To a stirred suspension of chromium(II) chloride (368 mg, 3.0 mmol) and hydrated lithium iodide (75 mg, 0.5 mmol) in anhydrous THF (3 mL) at ambient temperature under argon was added 4-(2,2,2-trichloro-1,1-*d*₂-ethyl)-biphenyl (143 mg, 0.5 mmol) in THF (2 mL). The mixture was stirred overnight at ambient temperature, quenched with aqueous ammonium oxalate and diluted with Et₂O. The layers were separated and the aqueous phase was extracted twice with Et₂O. The combined organic extracts were washed with aqueous ammonium oxalate, dried over anhydrous Na₂SO₄ and filtered. After concentration under vacuum, the crude product was purified chromatography (*n*-hexane) on silica gel to yield 4-(1,2-*d*₂-vinyl)biphenyl as a mixture of isomers *E/Z* = 70:30. (*E*)-4-(1,2-*d*₂-vinyl)biphenyl : ¹H (300 MHz, CDCl₃) δ: 7.28-7.61 (m, 9H), 5.82 ppm (t, *J* = 2.5 Hz, 1H); ²H NMR (46 MHz, CHCl₃) δ: 5.37 ppm (brs, 1D); MS (CI, NH₃) *m/z*: 182, 183. (*Z*)-4-(1,2-*d*₂-vinyl)biphenyl : ¹H (300 MHz, CDCl₃) δ: 7.28-7.61 (m, 9H), 5.31 ppm (s, 1H); ²H NMR (46 MHz, CHCl₃) δ: 5.89 ppm (brs, 1D); MS (CI, NH₃) *m/z*: 182, 183.

To a stirred suspension of chromium(II) chloride (368 mg, 3.0 mmol), anhydrous lithium iodide (0.5 mmol) and deuterium oxide (9 μL, 0.5 mmol) in anhydrous THF (3 mL) at ambient temperature under argon was added 4-(2,2,2-trichloroethyl)-biphenyl (143 mg, 0.5 mmol) in THF (2 mL). The mixture was stirred overnight at ambient temperature, quenched with aqueous ammonium oxalate and diluted with Et₂O. The layers were separated and the aqueous phase was extracted twice with Et₂O. The combined organic extracts were washed with aqueous ammonium oxalate, dried over anhydrous Na₂SO₄ and filtered. After concentration under vacuum, the crude product was purified

chromatography (*n*-hexane) on silica gel to yield 4-(2-*d*₁-vinyl)biphenyl as a mixture of isomers *Z/E* = 60:40.

Reduction of trichloromethylalkyls in presence anhydrous lithium iodide and aldehydes.

2,2,2-trichloroethylalkyls and aldehydes afford allylic alcohols, allenes and vinylic chlorides upon treatment with CrCl₂ and anhydrous LiI in THF.

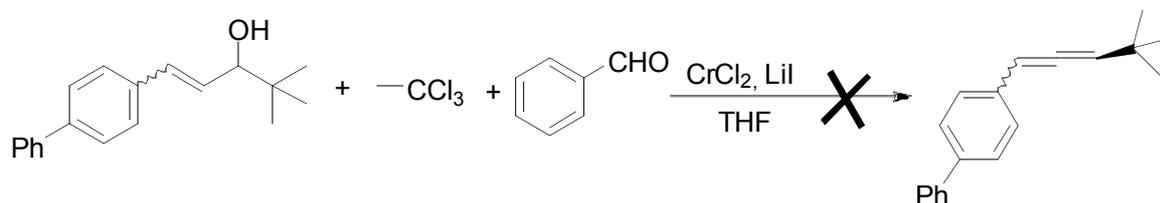


R¹ = phenyl, biphenyl, hydrocinnamyl

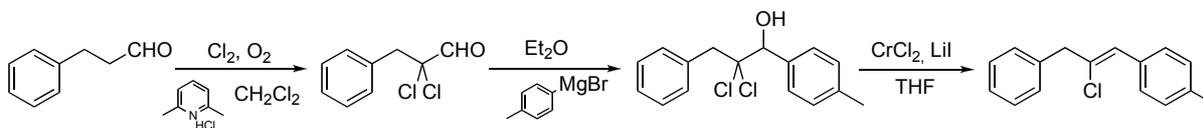
R² = *p*-tolyl, *t*-butyl

CrCl₂-LiI reduction of a ²H labelled substrate indicated complete migration of the deuterium label.

The formation of allenes was determined not to proceed via an allylic alcohol. Treatment of 1-biphenyl-4-yl-4,4-dimethylpent-1-en-3-ol under the standard reaction conditions did not lead to (4,4-dimethylpenta-1,2-dienyl)-benzene and 1-biphenyl-4-yl-4,4-dimethylpent-1-en-3-ol could be recovered in quantitative yield.



The formation of vinylic chlorides was determined to proceed through a 1,1-dichloro-1-chromium alkane carbenoid. Addition to the carbonyl of an aldehyde gives a chromium(III) 2,2-dichloroalcoholate. Further elimination yields a vinylic chloride.



Experimental procedures

To a stirred suspension of chromium(II) chloride (368 mg, 3.0 mmol), anhydrous lithium iodide (0.5 mmol) and *p*-tolualdehyde (90 μL, 0.75 mmol) in anhydrous THF (3 mL) at ambient temperature under argon was added 2,2,2-trichloroethyl-benzene (105 mg, 0.5 mmol) in THF (2 mL). The mixture was stirred overnight at ambient temperature, quenched with aqueous ammonium oxalate and diluted with Et₂O. The layers were separated and the aqueous phase was extracted twice with Et₂O. The combined organic extracts were washed with aqueous ammonium oxalate, dried over anhydrous

Na₂SO₄ and filtered. After concentration under vacuum, the crude product was purified chromatography (*c*-hexane / Et₂O = 100:0 to 85:15) on silica gel to yield 42 mg (41%) of 1-phenyl-3-(*p*-tolyl)-1,2-propadiene, 6 mg (5%) of 1-(2-chloro-3-phenyl-propenyl)-4-methyl-benzene and 50 mg (45%) of 3-phenyl-1-*p*-tolyl-prop-2-enol as a mixture of isomers *Z/E* = 80:20. 1-Phenyl-3-(*p*-tolyl)-1,2-propadiene (NMR spectra in accordance with the literature ^[4]): ¹H (300 MHz, CDCl₃) δ: 7.39-7.23 (m, 7H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.60 (s, 2H), 2.36 ppm (s, 3H); ¹³C (50 MHz, CDCl₃) δ: 207.7, 137.3, 134.0, 130.7, 129.6, 128.9, 127.4, 127.12, 127.06, 98.5, 98.4, 21.4 ppm. 3-Phenyl-1-*p*-tolyl-prop-2-enol (NMR spectra in accordance with the literature.^[5] *Z/E* = 80:20 determined by ¹H NMR and GC). (*Z*)-3-Phenyl-1-*p*-tolyl-prop-2-enol: ¹H (200 MHz, CDCl₃) δ: 7.40-7.18 (m, 9H), 6.70 (d, *J* = 11.3 Hz, 1H), 5.96 (dd, *J* = 11.3 Hz, *J* = 9.3 Hz, 1H), 5.63 (d, *J* = 9.3 Hz, 1H), 2.38 ppm (s, 3H), 2.04 (brs, 1H); ¹³C (50 MHz, CDCl₃) δ: 140.4, 137.6, 136.6, 133.5, 131.2, 129.5, 129.0, 128.4, 127.5, 126.4, 70.0, 21.3 ppm; MS (CI, NH₃) *m/z*: 223, 207; GC: *t*_R = 9.08 min. (*E*)-3-Phenyl-1-*p*-tolyl-prop-2-enol: ¹H (200 MHz, CDCl₃) δ: 7.40-7.18 (m, 9H), 6.70 (d, *J* = 15.9 Hz), 6.40 (dd, *J* = 15.9 Hz, *J* = 6.3 Hz, 1H), 5.37 (d, *J* = 6.3 Hz), 2.38 (s, 3H), 2.04 ppm (brs, 1H); ¹³C (50 MHz, CDCl₃) δ: 140.0, 137.7, 136.7, 131.8, 130.4, 129.4, 129.3, 128.7, 127.8, 126.5, 75.1, 21.3 ppm; MS (CI, NH₃) *m/z*: 225, 209; GC: *t*_R = 9.20 min. 1-(2-Chloro-3-phenyl-propenyl)-4-methyl-benzene: ¹H (300 MHz, CDCl₃) δ: 7.52 (d, *J* = 8.1 Hz, 2H), 7.33-7.26 (m, 5H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.52 (s, 1H), 3.80 (s, 2H), 2.36 ppm (s, 3H); ¹³C (50 MHz, CDCl₃) δ: 137.7, 137.6, 132.7, 132.2, 129.2, 129.1, 129.0, 128.7, 127.0, 125.9, 47.4, 21.4 ppm; MS (CI, NH₃) *m/z*: 242, 244, 260, 262.

To a stirred suspension of chromium(II) chloride (368 mg, 3.0 mmol), anhydrous lithium iodide (0.5 mmol) and *p*-tolualdehyde (90 μL, 0.75 mmol) in anhydrous THF (3 mL) at ambient temperature under argon was added perdeuterated 2,2,2-trichloroethyl-benzene (108 mg, 0.5 mmol) in THF (2 mL). The mixture was stirred overnight at ambient temperature, quenched with aqueous ammonium oxalate and diluted with Et₂O. The layers were separated and the aqueous phase was extracted twice with Et₂O. The combined organic extracts were washed with aqueous ammonium oxalate, dried over anhydrous Na₂SO₄ and filtered. After concentration under vacuum, the crude product was purified chromatography (*c*-hexane / Et₂O = 100:0 to 85:15) on silica gel to yield 1,2,3,4,5-*d*₅-6-(1-*d*₁-3-*p*-tolyl-propa-1,2-dienyl)-benzene, 1-(2-chloro-1,1-*d*₂-3-*p*-tolyl-allyl)-2,3,4,5,6-*d*₅-benzene and 3-(2,3,4,5,6-*d*₅-phenyl)-2,3-*d*₂-1-*p*-tolyl-prop-2-en-1-ol as a mixture of isomers *Z/E* = 80:20. 1,2,3,4,5-*d*₅-6-(1-*d*₁-3-*p*-tolyl-propa-1,2-dienyl)-benzene: ¹H (300 MHz, CDCl₃) δ: 7.26 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.59 (s, 1H), 2.35 ppm (s, 3H). 3-(2,3,4,5,6-*d*₅-phenyl)-2,3-*d*₂-1-*p*-tolyl-prop-2-en-1-ol: ¹H (300 MHz, CDCl₃) δ: 7.36 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 5.63 (s, 0.8H), 5.37 (s, 0.2H), 2.38 ppm (s, 3H); ¹³C (75 MHz, CDCl₃) δ: 140.4, 137.6, 129.5, 128.4, 126.4, 70.0, 21.3 ppm. 1-(2-Chloro-1,1-*d*₂-3-*p*-tolyl-allyl)-2,3,4,5,6-*d*₅-benzene: ¹H (300 MHz, CDCl₃) δ: 7.52 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 6.52 (s, 1H), 2.36 ppm (s, 3H).

To a stirred suspension of chromium(II) chloride (368 mg, 3.0 mmol), anhydrous lithium iodide (0.5 mmol) and pivaldehyde (55 μ L, 0.5 mmol) in anhydrous THF (3 mL) at ambient temperature under argon was added 4-(2,2,2-trichloroethyl)-biphenyl (143 mg, 0.5 mmol) in THF (2 mL). The mixture was stirred overnight at ambient temperature, quenched with aqueous ammonium oxalate and diluted with Et₂O. The layers were separated and the aqueous phase was extracted twice with Et₂O. The combined organic extracts were washed with aqueous ammonium oxalate, dried over anhydrous Na₂SO₄ and filtered. After concentration under vacuum, the crude product was purified chromatography (*c*-hexane / Et₂O = 100:0 to 90:10) on silica gel to yield 8 mg (7%) of 4-(4,4-dimethylpenta-1,2-dienyl)-biphenyl and 86 mg (65%) of 1-biphenyl-4-yl-4,4-dimethylpent-1-en-3-ol as a equimolar mixture of isomers. 4-(4,4-Dimethylpenta-1,2-dienyl)-biphenyl (NMR spectra in accordance with NMR data of (4,4-dimethylpenta-1,2-dienyl)-benzene described in the literature [6]) : ¹H (200 MHz, CDCl₃) δ : 7.58-7.34 (m, 9H), 6.25 (d, *J* = 6.4 Hz, 1H), 5.63 (d, *J* = 6.4 Hz, 1H), 1.16 ppm (s, 9H); ¹³C (50 MHz, CDCl₃) δ : 202.9, 139.6, 134.5, 132.2, 129.0, 127.7, 127.3, 127.1, 126.9, 107.1, 96.0, 33.0, 30.4 ppm; MS (CI, NH₃) *m/z*: 248; mp: 58°C (lit. 59-61 °C). 1-Biphenyl-4-yl-4,4-dimethylpent-1-en-3-ol (NMR spectra in accordance with NMR data of (4,4-dimethylpent-1-en-3-ol)-benzene described the literature.[7,8] *Z/E* \approx 50:50 determined by ¹H NMR) : ¹³C (50 MHz, CDCl₃) δ : 25.6 (*Z*), 25.9 (*E*), 35.1 (*Z*), 35.5 (*E*), 74.9 (*Z*), 81.1 (*E*), 127.1, 127.4, 128.9, 129.4, 129.8, 131.1, 131.4, 132.2, 132.7, 135.9, 136.0, 140.0, 140.4, 140.8 ppm; MS (CI, NH₃) *m/z*: 266, 249, 233; HRMS (EI) calcd for C₁₉H₂₂O (M⁺) *m/z* 266.1671, found 266.1650 ; mp = 70°C. (*Z*)-1-Biphenyl-4-yl-4,4-dimethyl-pent-1-en-3-ol : ¹H (200 MHz, CDCl₃) δ : 7.66-7.35 (m, 9H), 6.71 (d, *J* = 11.9 Hz, 1H), 5.84 (dd, *J* = 11.9 Hz, *J* = 9.7 Hz, 1H), 4.31 (d, *J* = 9.7 Hz, 1H), 1.78 (brs, 1H), 1.01 ppm (s, 9H). (*E*)-1-Biphenyl-4-yl-4,4-dimethyl-pent-1-en-3-ol : ¹H (200 MHz, CDCl₃) δ : 7.66-7.35 (m, 9H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.37 (dd, *J* = 15.9, 7.0 Hz, 1H), 3.98 (d, *J* = 7.0 Hz, 1H), 1.02 ppm (s, 9H).

To a stirred suspension of chromium(II) chloride (368 mg, 3.0 mmol), anhydrous lithium iodide (0.5 mmol) and pivaldehyde (55 μ L, 0.5 mmol) in anhydrous THF (3 mL) at ambient temperature under argon was added (4,4,4-trichlorobutyl)-benzene (119 mg, 0.5 mmol) in THF (2 mL). The mixture was stirred overnight at ambient temperature, quenched with aqueous ammonium oxalate and diluted with Et₂O. The layers were separated and the aqueous phase was extracted twice with Et₂O. The combined organic extracts were washed with aqueous ammonium oxalate, dried over anhydrous Na₂SO₄ and filtered. After concentration under vacuum, the crude product was purified chromatography (*c*-hexane / Et₂O = 100:0 to 90:10) on silica gel to yield 48 mg (44%) of 2,2-dimethyl-7-phenyl-hept-4-en-3-ol as a mixture of isomers *Z/E* = 64:36. 2,2-Dimethyl-7-phenyl-hept-4-en-3-ol (*Z/E* = 64:36 determined by ¹H NMR and GC) : ¹H (300 MHz, CDCl₃) δ : 7.34-7.18 (m, 5H), 5.76-5.43 (m, 2H), 3.97 (d, *J* = 9.1 Hz, 0.64H_Z), 3.69 (d, 7.5 Hz, 0.36H_E), 2.87-2.30 (m, 4H), 0.89 (s, 5.8H_Z), 0.88 ppm (s, 3.2H_E); ¹³C (75 MHz, CDCl₃) δ : 141.7, 132.6 (*E*), 132.1 (*Z*), 130.7 (*E*), 130.2 (*Z*), 128.7, 128.6, 128.4, 126.1 (*Z*), 125.9 (*E*), 81.1 (*E*), 74.9 (*Z*), 35.9 (*Z*), 35.8 (*E*), 35.0 (*Z*),

34.8 (*E*), 34.2 (*E*), 29.9 (*Z*), 25.8 (*E*), 25.6 (*Z*) ppm; MS (CI, NH₃) *m/z*: 217, 200. (*Z*) isomer : GC : t_R = 7.69 min. (*E*) isomer : GC : t_R = 7.77 min.

A suspension of chromium(II) chloride (148 mg, 1.2 mmol), anhydrous lithium iodide (0.2 mmol), 1-biphenyl-4-yl-4,4-dimethylpent-1-en-3-ol (50 mg, 0.2 mmol), *p*-tolualdehyde (24 μL, 0.2 mmol) and 1,1,1-trichloroethane (20 μL, 0.2 mmol) in anhydrous THF (1.5 mL) at ambient temperature under argon was stirred overnight at ambient temperature, quenched with aqueous ammonium oxalate and diluted with Et₂O. The layers were separated and the aqueous phase was extracted twice with Et₂O. The combined organic extracts were washed with aqueous ammonium oxalate, dried over anhydrous Na₂SO₄ and filtered. ¹H NMR of the crude material indicated no trace of (4,4-dimethylpenta-1,2-dienyl)-benzene.

To 2,6-lutidine (262 μL, 2.25 mmol) is added 0.2 mL aqueous HCl 37% (10% excess) at ambient temperature.^[9] 2,6-lutidine hydrochloride is then dried at the rotavapor and diluted with in CH₂Cl₂ (5 mL). The solution is flushed with O₂, maintaining a small and steady flow for the duration of the reaction. Then a flow of Cl₂ is turned on to saturate the mixture, the flask wrapped with a black cloth and the mixture warmed to 50°C. 3-Phenyl-propionaldehyde (2.0 mL, 14.9 mmol) is then added dropwise for 10 min, and the mixture heated for 0.5 h at 50°C. After cooling at ambient temperature, the reaction mixture is stripped with O₂ to remove residual Cl₂. Dilution with Et₂O salt out 2,6-lutidine hydrochloride, which is filtered off. After concentration of the filtrate, 2,2-dichloro-3-phenyl-propionaldehyde was obtained as a yellow oil in quantitative yield (3.0 g). ¹H (300 MHz, CDCl₃) δ : 9.34 (s, 1H), 7.37 (s, 5H), 3.62 ppm (s, 2H); ¹³C (75 MHz, CDCl₃) δ : 185.4, 132.6, 131.5, 128.4, 128.1, 87.4, 46.2 ppm.

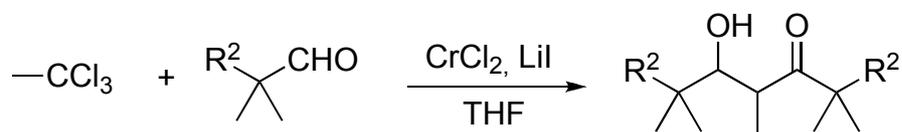
To magnesium turnings (270 mg, 11 mmol) and a crystal of iodine, under argon, is added anhydrous Et₂O (5 mL) and 4-bromotoluene (1.25 mL, 10 mmol). The reaction mixture is stirred with heating at reflux for 1 h, then cooled to 0°C and 2,2-dichloro-3-phenyl-propionaldehyde (2.03 g, 10 mmol) in anhydrous Et₂O (5 mL) is added dropwise. The mixture is stirred for 1 h at ambient temperature, quenched with aqueous NH₄Cl and extracted twice with AcOEt. The combined organic extracts were washed with aqueous NH₄Cl, dried over anhydrous Na₂SO₄. Purification by chromatography on silica gel (Et₂O / *c*-hexane = 1:9) gives 620 mg (21%) of 2,2-dichloro-3-phenyl-1-*p*-tolyl-propan-1-ol. ¹H (200 MHz, CDCl₃) δ : 7.56-7.27 (m, 9H), 5.06 (d, *J* = 4.4 Hz, 1H), 3.71 (d, *J* = 14.0 Hz, 1H), 3.50 (d, *J* = 14.0, 1H), 3.26 (d, *J* = 4.4 Hz, 1H), 2.49 ppm (s, 3H); ¹³C (50 MHz, CDCl₃) δ : 138.7, 134.2, 134.0, 131.7, 128.9, 128.6, 127.9, 127.6, 96.1, 80.7, 48.2, 21.3 ppm; MS (CI, NH₃) *m/z*: 276, 261, 259, 241, 243, 223, 221.

A suspension of chromium(II) chloride (184 mg, 1.5 mmol), anhydrous lithium iodide (0.5 mmol) and 2,2-dichloro-3-phenyl-1-*p*-tolyl-propan-1-ol (148 mg, 0.5 mmol) in anhydrous THF (5 mL) at ambient temperature under argon was stirred overnight at ambient temperature, quenched with aqueous ammonium oxalate and diluted with Et₂O. The layers were separated and the aqueous

phase was extracted twice with Et₂O. The combined organic extracts were washed with aqueous ammonium oxalate, dried over anhydrous Na₂SO₄ and filtered. After concentration under vacuum, the ¹H NMR of the crude material revealed the formation of 1-(2-chloro-3-phenyl-propenyl)-4-methyl-benzene in 2%. Stirring 2,2-dichloro-3-phenyl-1-*p*-tolyl-propan-1-ol under the same conditions, overnight at reflux gives 1-(2-chloro-3-phenyl-propenyl)-4-methyl-benzene in 40% yield

Reduction of 1,1,1-trichloroethane in presence anhydrous lithium iodide and neopentanal derivatives.

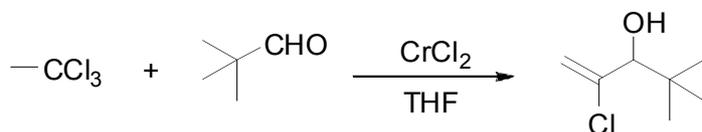
With neopentanal derivatives, insertion of alkylidene **14** into the aldehydic C–H bond gives β-hydroxyketones.



R² = methyl, 2-propenyl

Insertion into the aldehydic C–H bond was evidenced by reacting ²H labeled pivaldehyde.

The reaction of 1,1,1-trichloroethane with chromous chloride in presence of pivaldehyde was performed without LiI and gives the hydroxy-chloroalkene adduct described in literature.^[10]



Experimental procedures

To a stirred suspension of chromium(II) chloride (615 mg, 5.0 mmol), anhydrous lithium iodide (1.0 mmol) and pivaldehyde (110 μL, 1.0 mmol) in anhydrous THF (5 mL) at ambient temperature under argon was added 1,1,1-trichloroethane (100 μL, 1.0 mmol). The mixture was stirred overnight at ambient temperature, quenched with aqueous ammonium oxalate and diluted with Et₂O. The layers were separated and the aqueous phase was extracted twice with Et₂O. The combined organic extracts were washed with aqueous ammonium oxalate, dried over anhydrous Na₂SO₄ and filtered. After concentration under vacuum, the crude product was purified chromatography (*c*-hexane / Et₂O = 95:5) on silica gel to yield 78 mg (78%) of 5-hydroxy-2,2,4,6,6-pentamethylheptan-3-one as a mixture of isomers *like/unlike* = 84:16. *like*-5-hydroxy-2,2,4,6,6-pentamethylheptan-3-one (erythro, configuration assigned according to literature^[11]): ¹H NMR (300 MHz, CDCl₃) δ: 0.97 (s, 9H), 1.10 (d, *J* = 6.8 Hz, 3H), 1.17 (s, 9H), 3.28 (s, 1H), 3.36 ppm (q, *J* = 6.8 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ: 222.7, 77.7, 45.1, 39.1, 35.9, 27.3, 26.2, 12.0 ppm; MS (CI, NH₃) *m/z* 183 ([M-OH]⁺), 201 ([M+H]⁺); GC: t_R

= 5.15 min. *unlike*-5-hydroxy-2,2,4,6,6-pentamethylheptan-3-one (threo): ^1H NMR (300 MHz, CDCl_3) δ : 0.91 (s, 9H), 1.19 (s, 3H), 1.27 (d, $J = 6.8$ Hz, 3H), 3.21-3.30 ppm (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ : 224.8, 84.7, 45.4, 39.0, 36.0, 27.5, 26.8, 19.6 ppm; MS (CI, NH_3) m/z 183 ($[\text{M}-\text{OH}]^+$), 201 ($[\text{M}+\text{H}]^+$); GC: $t_{\text{R}} = 5.25$ min.

To a stirred suspension of chromium(II) chloride (615 mg, 5.0 mmol), anhydrous lithium iodide (1.0 mmol) and 2,2-dimethyl-4-pentenal (technical grade, 90%, 150 μL , 1.0 mmol) in anhydrous THF (5 mL) at ambient temperature under argon was added 1,1,1-trichloroethane (100 μL , 1.0 mmol). The mixture was stirred overnight at ambient temperature, quenched with aqueous ammonium oxalate and diluted with Et_2O . The layers were separated and the aqueous phase was extracted twice with Et_2O . The combined organic extracts were washed with aqueous ammonium oxalate, dried over anhydrous Na_2SO_4 and filtered. After concentration under vacuum, the crude product was purified chromatography (*c*-hexane / $\text{Et}_2\text{O} = 90:10$) on silica gel to yield 73 mg (58%) of 7-hydroxy-4,4,6,8,8-pentamethyl-undeca-1,10-dien-5-one as a mixture of isomers *like/unlike* = 90:10. *like*-7-Hydroxy-4,4,6,8,8-pentamethyl-undeca-1,10-dien-5-one (*like/unlike* configuration determined by analogy with 5-hydroxy-2,2,4,6,6-pentamethylheptan-3-one): ^1H NMR (300 MHz, CDCl_3) δ : 5.91-5.61 (m, 2H), 5.10-5.02 (m, 4H), 3.36 (s, 1H), 3.32 (q, $J = 6.9$ Hz, 1H), 2.28-2.19 (m, 3H), 1.98 (dd, $J_1 = 13.5$ Hz, $J_2 = 7.5$ Hz, 1H), 1.16 (s, 3H), 1.15 (s, 3H), 1.11 (d, $J = 6.9$ Hz, 3H), 0.96 (s, 3H), 0.92 ppm (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ : 222.0, 135.3, 134.0, 118.5, 117.5, 75.9, 48.4, 44.7, 43.5, 39.2, 38.8, 24.2, 24.1, 24.0, 23.9, 12.0 ppm. *unlike*-7-Hydroxy-4,4,6,8,8-pentamethyl-undeca-1,10-dien-5-one: ^1H NMR (300 MHz, CDCl_3) δ : 5.91-5.63 (m, 2H), 5.11-5.01 (m, 4H), 3.38 (d, $J = 4.2$ Hz, 1H), 3.31-2.20 (m, 1H), 2.33-2.14 (m, 3H), 1.97 (dd, $J_1 = 13.5$ Hz, $J_2 = 7.3$ Hz, 1H), 1.26 (d, $J = 6.9$ Hz, 3H), 1.21 (s, 3H), 1.18 (s, 3H), 0.88 ppm (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ : 223.2, 135.3, 134.2, 118.5, 117.5, 82.9, 48.5, 44.4, 43.9, 39.3, 38.9, 24.9, 24.7, 24.1, 23.5, 19.2 ppm.

To a stirred suspension of chromium(II) chloride (358 mg, 2.5 mmol), anhydrous lithium iodide (0.5 mmol) and 2,2-dimethylpropan-1-*d*-al (55 μL , 0.5 mmol) in anhydrous THF (2.5 mL) at ambient temperature under argon was added 1,1,1-trichloroethane (50 μL , 0.5 mmol). The mixture was stirred overnight at ambient temperature, quenched with aqueous ammonium oxalate and diluted with Et_2O . The layers were separated and the aqueous phase was extracted twice with Et_2O . The combined organic extracts were washed with aqueous ammonium oxalate, dried over anhydrous Na_2SO_4 and filtered. After concentration under vacuum, the crude product was purified chromatography (*c*-hexane / $\text{Et}_2\text{O} = 90:10$) on silica gel to yield 4,5-*d*₂-5-hydroxy-2,2,4,6,6-pentamethylheptan-3-one. ^1H NMR (300 MHz, CDCl_3) δ : 0.98 (s, 9H), 1.10 (d, $J = 6.8$ Hz, 3H), 1.18 (s, 9H), 3.18 ppm (brs, 1H); ^1H NMR (300 MHz, $\text{CDCl}_3 + \text{MeOD}$) δ : 0.93 (s, 9H), 1.06 (d, $J = 6.8$ Hz, 3H), 1.14 ppm (s, 9H).

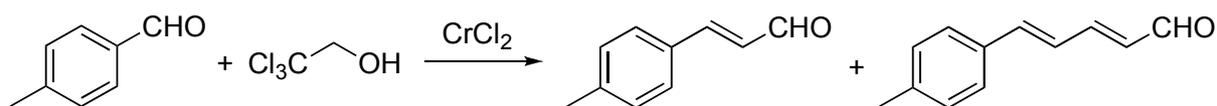
To a stirred suspension of chromium(II) chloride (615 mg, 5.0 mmol) and pivaldehyde (110 μL , 1.0 mmol) in anhydrous THF (5 mL) at ambient temperature under argon was added 1,1,1-trichloroethane (100 μL , 1.0 mmol). The mixture was stirred overnight at ambient temperature,

quenched with aqueous ammonium oxalate and diluted with Et₂O. The layers were separated and the aqueous phase was extracted twice with Et₂O. The combined organic extracts were washed with aqueous ammonium oxalate, dried over anhydrous Na₂SO₄ and filtered. After concentration under vacuum, 2-chloro-4,4-dimethyl-pent-1-en-3-ol was identified as a volatile compound. ¹H (200 MHz, CDCl₃) δ: 5.42 (s, 1H), 5.38 (s, 1H), 3.96 (s, 1H), 1.01 ppm (s, 9H).

Reduction of 2,2,2-trichloroethanol with CrCl₂-LiI in presence of aldehydes.

Upon treatment with CrCl₂-LiI in THF or AcOEt, aldehydes and 2,2,2-trichloroethanol give rise to α,β-unsaturated aldehydes. This result could be reproduced with CrCl₂ in 1-butyl-3-methylimidazolium bromide ([bmim][Br]) or 1-butyl-3-methylimidazolium iodide ([bmim][I]).

1,2-Hydride migration was evidenced by reacting 2H labelled 2,2,2-trichloro-1,1-d₂-ethanol, bis- and mono-deuterated vinylic aldehydes were obtained in a 2:1 ratio (the latter adduct formation probably involves an enolization equilibrium).



Experimental procedures

To a stirred suspension of chromium(II) chloride (368 mg, 3.0 mmol), anhydrous lithium iodide (0.5 mmol) and *p*-tolualdehyde (60 μL, 0.5 mmol) in anhydrous THF (5 mL) at ambient temperature under argon was added 2,2,2-trichloroethanol (145 μL, 1.5 mmol). The mixture was refluxed for 3 h, quenched with aqueous HCl 5% and diluted with Et₂O. The layers were separated and the aqueous phase was extracted twice with Et₂O. The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄ and filtered over Florisil®. After concentration under vacuum, the crude product was purified chromatography (*c*-hexane / Et₂O = 90:10) on silica gel to yield 40 mg as a mixture aldehydes: (*E*)-3-*p*-tolyl-propenal (38 %) and (*E,E*)-5-*p*-tolyl-penta-2,4-dienal (12 %). (*E*)-3-*p*-Tolyl-propenal : ¹H NMR (300 MHz, CDCl₃) δ: 9.67 (d, *J* = 8.0 Hz, 1H), 7.47-7.20 (m, 5H), 6.67 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.38 ppm (s, 3H); ¹³C NMR (50 MHz, CDCl₃) δ: 193.8, 153.0, 142.1, 131.4, 129.9, 128.6, 127.8, 21.6 ppm; IR ν: 1685 cm⁻¹; MS (CI, NH₃) *m/z* 147 ([M+H]⁺). (*E,E*)-5-*p*-Tolyl-penta-2,4-dienal : ¹H NMR (300 MHz, CDCl₃) δ: 9.59 (d, *J* = 8.0 Hz, 1H), 7.42-6.97 (m, 7H), 6.24 (dd, *J* = 15.0, 8.0 Hz, 1H), 2.36 ppm (s, 3H); ¹³C NMR (50 MHz, CDCl₃) δ: 193.6, 152.4, 142.6, 140.1, 132.9, 131.1, 129.7-127.5, 125.2, 21.4 ppm; IR ν: 1683 cm⁻¹; MS (CI, NH₃) *m/z* 173 ([M+H]⁺).

To a stirred suspension of chromium(II) chloride (512 mg, 4.1 mmol), anhydrous lithium iodide (1.1 g, 8.2 mmol) and *p*-tolualdehyde (41 μL, 0.34 mmol) in anhydrous AcOEt (5.2 mL) at ambient temperature under argon was added 2,2,2-trichloroethanol (100 μL, 1.0 mmol). The mixture was

stirred for 3 h at 70°C, quenched with aqueous HCl 5% and diluted with Et₂O. The layers were separated and the aqueous phase was extracted twice with Et₂O. The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄ and filtered over Florisil®. After concentration under vacuum, the crude product was purified chromatography (*c*-hexane / Et₂O = 95:5) on silica gel to yield 35 mg (70 %) of (*E*)-3-*p*-tolyl-propenal and 9 mg (15 %) of (*E,E*)-5-*p*-tolyl-penta-2,4-dienal.

To a stirred suspension of chromium(II) chloride (512 mg, 4.1 mmol) and *p*-tolualdehyde (41 μL, 0.34 mmol) in anhydrous bmimBr (2.0 mL) at ambient temperature under argon was added 2,2,2-trichloroethanol (100 μL, 1.0 mmol). The mixture was stirred overnight at 65°C, quenched with aqueous HCl 5% and diluted with Et₂O. The layers were separated and the aqueous phase was extracted twice with Et₂O. The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄ and filtered over Florisil®. After concentration under vacuum, the crude product was purified chromatography (*c*-hexane / Et₂O = 90:10) on silica gel to yield 9 mg (18 %) of (*E*)-3-*p*-tolyl-propenal.

To a stirred suspension of chromium(II) chloride (256 mg, 2.1 mmol) and *p*-tolualdehyde (41 μL, 0.34 mmol) in anhydrous bmimI (2.0 mL) at ambient temperature under argon was added 2,2,2-trichloroethanol (100 μL, 1.0 mmol). The mixture was stirred overnight at 90°C, quenched with aqueous HCl 5% and diluted with Et₂O. The layers were separated and the aqueous phase was extracted twice with Et₂O. The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄ and filtered over Florisil®. After concentration under vacuum, the crude product was purified chromatography (*c*-hexane / Et₂O = 90:10) on silica gel to yield 21 mg as a mixture aldehydes: (*E*)-3-*p*-tolyl-propenal (31%) and (*E,E*)-5-*p*-tolyl-penta-2,4-dienal (10%).

To a stirred suspension of chromium(II) chloride (368 mg, 3.0 mmol), anhydrous lithium iodide (0.5 mmol) and *p*-tolualdehyde (60 μL, 0.5 mmol) in anhydrous THF (5 mL) at ambient temperature under argon was added 2,2,2-trichloroethan-1,1-*d*₂-ol (145 μL, 1.5 mmol). The mixture was refluxed for 3h, quenched with aqueous HCl 5% and diluted with Et₂O. The layers were separated and the aqueous phase was extracted twice with Et₂O. The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄ and filtered over Florisil®. After concentration under vacuum, the crude product was purified chromatography (*c*-hexane / Et₂O = 90:10) on silica gel to yield 23 mg (37%) of deuterium labelled (*E*)-3-*p*-tolyl-propenal as a mixture 2:1 of (*E*)-3-*p*-tolyl-1,2-*d*₂-propenal and (*E*)-3-*p*-tolyl-propen-1-*d*-al. (*E*)-3-*p*-tolyl-1,2-*d*₂-propenal : ¹H NMR (300 MHz, CDCl₃) δ : 7.47-7.20 (m, 5H), 2.38 ppm (s, 3H); ¹³C NMR (50 MHz, CDCl₃) δ : 193.6 (t, *J* = 26 Hz), 153.2, 142.0, 131.4, 129.9, 128.7, 127.7 (t, *J* = 3.7 Hz) 21,7 ppm; ²H NMR (46 MHz, CCl₄) δ : 9.61 (m, 1D), 6.64 ppm (m, 1D); MS (CI, NH₃) *m/z* 149 ([M+H]⁺). (*E*)-3-*p*-tolyl-propen-1-*d*-al : ¹H NMR (300 MHz, CDCl₃) δ : 7.47-7.20 (m, 5H), 6.67 (d, *J* = 16.2 Hz, 1H), 2.38 ppm (s, 3H); ¹³C NMR (50 MHz, CDCl₃) δ : 153.2, 142.0, 131.4, 129.9, 128.7, 127.8, 21,6 ppm; ²H NMR (46 MHz, CCl₄) δ : 9.61 ppm (m, 1D).

Synthesis of deuterated compounds

Experimental procedures

To a solution of biphenyl-4-carboxylic acid (2.0 g, 1 equiv) in anhydrous Et₂O (50 mL), LiAlD₄ (1.26 g, 3 equiv) was added carefully at 0°C, under an argon atmosphere. After 2 h warming from 0°C to room temperature, the reaction was quenched with water, extracted twice with Et₂O, washed with brine and dried over anhydrous Na₂SO₄ to give biphenyl-4-*d*₂-methanol in quantitative yield. ¹H NMR (200 MHz, CDCl₃) δ : 1.80 (brs, 1H), 7.36-7.50 (m, 5H), 7.59-7.64 ppm (m, 4H).

A suspension of biphenyl-4-*d*₂-methanol (1.8 g, 1 equiv), triphenylphosphine (2.9 g, 1.1 equiv) and tetrabromomethane (3.65 g, 1.1 equiv) in Et₂O (15 mL) was stirred at room temperature for 2 h. After evaporation of the solvent, purification by SiO₂ chromatography (*c*-hexane/Et₂O = 95:5) afforded 4-bromo-*d*₂-methyl-biphenyl as a white solid in 84% yield.

To a solution of 4-bromo-*d*₂-methyl-biphenyl (250 mg, 1 equiv) and chloroform (80 μL, 1 equiv) in anhydrous DMF (4 mL), sodium hydride (60% in mineral oil, 40 mg, 1 equiv) was added carefully at 0°C, under an argon atmosphere. After 1 h at 0°C, the reaction was quenched and diluted with water. Solid was filtrated, then dissolved in cyclohexane and dried over anhydrous Na₂SO₄. Purification by SiO₂ chromatography (*n*-hexane) afforded 4-(2,2,2-trichloro-1,1-*d*₂-ethyl)-biphenyl in 18% yield and 4-bromo-*d*₂-methyl-biphenyl in 73% yield. ²H NMR (46 MHz, CHCl₃) δ : 3.98 ppm (brs, 2D).

To a stirred solution of methyl trichloroacetate (3.0 mL, 24.4 mmol) and LiCl (2.2 g, 50.0 mmol) in anhydrous Et₂O (100 mL) was added carefully NaBD₄ (2.0 g, 50 mmol) at ambient temperature, under an argon atmosphere. The reaction mixture was stirred for 12 h at ambient temperature, then quenched with aqueous HCl 5% and diluted with Et₂O. The layers were separated and the aqueous phase was extracted with Et₂O. The combined organic extracts were dried over MgSO₄ and filtered. The crude material was distilled under vacuum (T_{eb} = 70°C / 25 mmHg) to yield 2.8 g (77%) of 2,2,2-trichloroethan-1,1-*d*₂-ol as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ : 3.24 ppm (brs, 1H); ¹³C NMR (50 MHz, CDCl₃) δ : 99.2, 75.9 ppm (quint); ²H NMR (46 MHz, CHCl₃) δ : 4.14 ppm (brs).

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