Reaction of difluorocarbene with acetylene ethers generates novel fluorinated 5- and 7-membered carbacycles.

Poh Wai Chia, Davide Bello, Alexandra M. Z. Slawin and David O’Hagan.*

University of St Andrews, School of Chemistry and Centre for Biomolecular Sciences, North Haugh, St Andrews, Fife, KY16 9ST, UK Fax: 01334 463800; Tel: 01334 467171; E-mail: do1@st-andrews.ac.uk

- General information

All commercially available reagents were purchased from Acros, Alfa Aesar, Fisher Scientific, Fluorochem or Sigma-Aldrich and used without further purification. Reactions were performed under an atmosphere of argon using standard vacuum line techniques, unless otherwise stated. All glassware was flame-dried and allowed to cool down under high vacuum. Dry solvents diethyl ether and tetrahydrofuran were obtained from the MBraun SPS-800 Solvent Purification System, by passing the solvent through two drying columns under an argon atmosphere. Reaction temperatures of -78 °C to -10 °C were obtained using an isopropyl alcohol bath together with LabPlant Refrigerated Immersion Probe. A temperature of 0°C was obtained using an ice/water bath. Reactions requiring heating or reflux were carried out using a heating block with a contact thermometer.

Thin layer chromatography (TLC) was performed using Merck TLC silica gel 60 F_{254} glass-backed plates. Compounds were visualised by either UV light (254 nm) or by the use of potassium permanganate stain or molybdenum-based stain. Reverse-phase preparative HPLC column chromatography were performed using a Waters 600E multisolvant HPLC system coupled to a Waters 2487 dual wavelength absorbance detector and a Phenomenex Kingsorb® C_{18} 250 × 21.20 mm 5µ column.
NMR spectra were acquired on Bruker Avance 300 (\(^1\)H at 300 MHz, \(^{13}\)C at 75 MHz, \(^{19}\)F at 282 MHz) or Bruker Avance II 400 spectrometer (\(^1\)H at 400 MHz, \(^{13}\)C at 100 MHz, \(^{19}\)F at 376 MHz), or Bruker Avance 500 spectrometer (\(^1\)H at 500 MHz, \(^{13}\)C at 126 MHz, \(^{19}\)F at 470 MHz). Chemical shifts (\(\delta\)) are reported in parts per million (ppm) and are quoted relative to the residual peak of CDCl\(_3\). Coupling constants (\(J\)) are given in Hertz (Hz). \(^{13}\)C NMR and \(^{19}\)F NMR spectra were recorded with \(^1\)H decoupling. Signal splitting patterns are described as: \(s\) – singlet, \(br\ s\) – broad singlet, \(d\) – doublet, \(t\) – triplet, \(tt\) – triplet of triplets, \(m\) – multiplet.

Mass spectrometric data were acquired by electron impact ionisation (EI), electrospray ionisation (ESI) or chemical ionisation (CI), using Waters Micromass LCT (ESI) or GCT (CI) spectrometers (University of St Andrews), or a Thermofisher LTQ Orbitrap XL spectrometer (APCI) (National Mass Spectrometry Service Centre, Swansea). Values are reported as a ratio of mass to charge (m/z).

IR spectra were recorded on a Perkin-Elmer Spectrum GX IR spectrometer as thin films between sodium chloride disks as indicated. Absorption maxima are reported in wavenumbers (cm\(^{-1}\)). Intensities of the maxima are quoted as strong (s), medium (m), weak (w).

Single crystal X-ray Diffraction analysis was carried out by Prof Alexandra M. Z. Slawin at the University of St Andrews.

Melting points were determined in Pyrex capillaries using a Griffin Melting Point Apparatus and are uncorrected.
### Experimental section

*General procedure (A) for the synthesis of dichloro-aryloxy alkenes*: Compounds **6b**, **6c** and **6d** were prepared following a modified version of the method previously reported by Tanaka.\(^1\)

Potassium hydride (slurry in mineral oil, approx. 50.0 mmol, 2.2 equiv) was transferred in a three-necked flask under an atmosphere of argon. The slurry was washed twice with tetrahydrofuran (20 mL) in order to remove the mineral oil. The resulting potassium hydride was then suspended in tetrahydrofuran (30 mL) and the mixture cooled to 0 °C. A solution of the corresponding phenol (23.1 mmol, 1.0 equiv) in dry tetrahydrofuran (30 mL) was then added dropwise over 10 min, while the hydrogen, formed in the reaction, was vented to the atmosphere through an outlet connected to a bubbler using a positive pressure of argon. After the evolution of gas had ceased, the resulting mixture was stirred at 0 °C for a further 10 min before adding a solution of trichloroethylene (90.2 mmol, 3.9 equiv) in tetrahydrofuran over a period of 10 min. The resulting mixture was then allowed to warm to room temperature and stirred for 14 h. The mixture was then cooled to 0 °C and the residual potassium hydride quenched by adding an excess of 2-propanol. The resulting mixture was warmed to room temperature, stirred for a further 15 min, then concentrated under reduced pressure. The residue was taken up with diethyl ether (20 mL) and a saturated aqueous solution of ammonium chloride (20 mL), the layers were separated and the aqueous layer extracted into diethyl ether (3 × 20 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure to furnish an oily residue. Depending on the starting material employed, the crude oils were in some instances used without any further purification, or were purified by flash column chromatography.

\[
(E)-1\text{-Bromo-4-(1,2-dichlorovinyloxy)benzene (6b)}
\]

Compound **6b** was prepared accordingly to General Procedure A and it was obtained as a yellow oil in 92% yield. The oil was used in the next synthetic step without any
further purification. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51-7.43 (m, 2H), 6.99-6.91 (m, 2H), 5.98 (s, 1H). These data are in good agreement with the literature.$^1$

**(E)-2-(1,2-Dichlorovinyl)oxy)naphthalene (6c)**

![Image of compound 6c]

Compound 6c was prepared accordingly to General Procedure A and obtained as a colourless oil in 76% yield after purification by silica gel flash column chromatography eluting with 1/99 ethyl acetate/hexane. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.94-7.73 (m, 3H), 7.58-7.39 (m, 3H), 7.33-7.20 (dd, $J$ = 9.0, 2.6, 1H), 6.04 (s, 1H). These data are in good agreement with the literature.$^1$

**(E)-1-(1,2-Dichlorovinyl)oxy)-4-methoxybenzene (6d)**

![Image of compound 6d]

Compound 6d was prepared accordingly to the General Procedure A and obtained as a colourless oil in 55% yield after purification by silica gel flash column chromatography eluting with 5/95, then 10/90, then 20/80 ethyl acetate/hexane. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.06-6.93 (m, 2H), 6.93-6.84 (m, 2H), 5.88 (s, 1H), 3.80 (s, 3H). These data are in good agreement with the literature.$^1$

*General Procedure (B) for the synthesis of aryloxy acetylenes:* Compounds 1b, 1c and 1d were prepared according to the method reported by Tanaka.$^1$

The corresponding dichloro-aryloxy alkene (21.0 mmol, 1.0 equiv) was dissolved in dry diethyl ether (90 mL) under an atmosphere of argon. The resulting mixture was cooled to -78 ºC and a solution of butyllithium in hexanes (1.6M, 84 mmol, 4.0 equiv) was added dropwise over 20 min. The resulting mixture was stirred at -78ºC for 30 min, then allowed to warm to -40 ºC over 2 h and stirred for a further 1 h at -40 ºC. The
residual butyllithium was quenched by adding 2-propanol (10 mL), the mixture was warmed to room temperature and a saturated aqueous solution of ammonium chloride (40 mL) added. The layers were separated and the aqueous layer was extracted into diethyl ether (2 × 40 mL). The combined organic layers were washed with saturated brine, dried over magnesium sulfate, filtered and concentrated under reduced pressure to furnish a brown residue. Purification by silica gel flash column chromatography eluting with 1/99 ethyl acetate/hexane yielded the required products.

1-Bromo-4-ethynyloxybenzene (1b)

Compound 1b was prepared by following the General Procedure B and isolated as a brown oil in 63% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.45-7.35 (m, 2H), 7.13-7.07 (m, 2H), 2.06 (s, 1H). These data are in good agreement with the literature.$^1$

2-Ethynyloxynaphthalene (1c)

Compound 1c was prepared by following the General Procedure B and isolated as an off-cream solid in 68% yield. Mp: 39.0-40.1 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.87-7.76 (m, 4H), 7.57-7.41 (m, 2H), 7.37 (dd, $J$ = 9.0, 2.6, 1H), 2.20 (s, 1H). These data are in good agreement with the literature.$^1$
1-Methoxy-4-ethynloxybenzene (1d)

Compound 1d was prepared by following the General Procedure B and isolated as a yellow oil in 71% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.24-7.17 (m, 2H), 6.91-6.84 (m, 2H), 3.79 (s, 3H), 2.03 (s, 1H). These data are in good agreement with the literature.$^1$

General procedure (C) for the synthesis of 5- and 7-membered ring poly-fluorinated compounds 4a, 4b, 4c, 4d, and 5a, 5b, 5c, 5d.

The corresponding acetylene ether (5.0 mmol, 1.0 equiv) was dissolved in tetrahydrofuran (13 mL) and sodium iodide (1.0 mmol, 0.2 equiv) was added, followed by trifluoromethyl-trimethylsilane (11.17 mmol, 2.2 equiv). The resulting mixture was heated to reflux for 2 h. The mixture was then allowed to cool to room temperature and a 10% aqueous solution of sodium sulfite was added (5 mL). Diethyl ether (20 mL) was added to the mixture, the layers separated and the aqueous layer extracted into diethyl ether (2 × 10 mL). The combined organic layers were washed with a saturated aqueous solution of sodium hydrogen carbonate (20 mL), saturated brine (10 mL) and dried over magnesium sulfate. The solution was filtered and dried to furnish a brown oily residue. Purification of the products required both silica gel flash column chromatography and then reverse-phase C$_{18}$ preparative HPLC.

2,4-Diethoxy-3,3,6,6,7,7-hexafluorocyclohepta-1,4-diene (4a)

Compound 4a was prepared accordingly to the General Procedure C. Purification by silica gel flash column chromatography (x 3) eluting with hexane, then 1/99 diethyl ether/hexane, afforded compound 4a as a colourless solid in 32% yield. Mp: 45 – 46 $^\circ$C; $\nu_{max}$ (NaCl disc/cm$^{-1}$) 2996.7 (w), 2925.3 (w), 1689.1 (s), 1671.9 (m), 1479.5 (m), 1442.1 (m), 1380.4 (m), 1325.6 (m), 1291.4 (m), 1212.7 (m), 1154.7 (s), 1122.7 (s),
1053.4 (s), 867.2 (s), 800.1 (s), 742.6 (s), 658.2 (m); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 5.11 – 5.01 (m, 2H), 3.89 (q, \(J = 6.9, 4H\)), 1.44 (t, \(J = 6.9, 6H\)); \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) \(\delta\) -99.23 – -99.25 (m, 2F), -102.03 (s, 4F); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 154.5 – 152.7 (m), 114.1 (tt, \(J = 244.6, 33.2\)), 109.8 (t, \(J = 245.8\)), 96.5 – 95.3 (m), 65.1, 13.7; \(m/z\) (Cl+), 271 ([M-F]+, 100%), 215 (30), 243 (30); \(m/z\) (Cl+): Found [M-F]+ 271.0753. \(C_{11}H_{12}F_{6}O_{2}\) requires \(M^{+}\), 271.0757.

2,4-Bis(Compound 4-bromophenoxy)-3,3,6,6,7,7-hexafluorocyclohepta-1,4-diene (4b)

Compound 4b was prepared accordingly to the General Procedure C. Purification by silica gel flash column chromatography (x 3), eluting with hexane and then 1/99 diethyl ether/hexane afforded compound 4b as a colourless solid in 47% yield. Mp: 123 – 125 °C (from diethyl ether/hexane); \(\nu_{\text{max}}\) (NaCl disc/cm\(^{-1}\)) 3095.6 (w), 2925.4 (w), 2853.9 (w), 1698.2 (m), 1683.4 (m), 1582.4 (w), 1484.0 (s), 1364.2 (m), 1323.6 (m), 1281.2 (w), 1196.1 (s), 1162.8 (m), 1093.2 (s), 1054.1 (s), 1012.2 (s), 872.2 (s), 829.6 (m), 678.9 (m); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.69 – 7.53 (m, 4H), 7.09 – 6.99 (m, 4H), 5.30 – 5.02 (m, 2H); \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -100.34 – -100.40 (m, 2F), -104.12 (s, 4F); \(m/z\) (APCI+), 525 ([M-F]+, 100%), 527 (50), 545 (50), 543 (59), 547 (30), 465 (70), 467 (70), 445 (50), 447 (50), 351 (50), 353 (59), 273 (40); \(m/z\) (APCI+): Found [M]+ 541.8946. \(C_{19}H_{10}Br_{2}F_{6}O_{2}\) requires \(M^{+}\), 541.8946.
2,4-Bis(2-naphthoxy)-3,3,6,6,7,7-hexafluorocyclohepta-1,4-diene (4c)

Compound 4c was prepared accordingly to the General Procedure C. Purification by silica gel flash column chromatography (x 3), eluting with diethyl ether/hexane 1/99 afforded compound 4c as a colourless solid in 41% yield. Mp: 138 – 140 °C (from diethyl ether/hexane); ν\text{max} (NaCl disc/cm\textsuperscript{-1}) 3055.4 (w), 2987.1 (w), 1692.8 (w), 1631.5 (w), 1600.6 (w), 1510.0 (m), 1465.6 (w), 1321.2 (w), 1265.7 (s), 1199.2 (m), 1160.6 (s), 1124.9 (w), 1064.2 (w), 1041.9 (w), 893.8 (m), 870.3 (w), 813.9 (w), 738.6 (s), 705.2 (m); \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) δ 7.97 (d, \textit{J} = 9.0, 2H), 7.94 – 7.84 (m, 4H), 7.63 (d, \textit{J} = 2.4, 2H), 7.61 – 7.51 (m, 4H), 7.29 (dd, \textit{J} = 8.9, 2.4, 2H), 5.28 – 5.17 (m, 2H); \textsuperscript{19}F NMR (282 MHz, CDCl\textsubscript{3}) δ -100.18 – -100.23 (p, \textit{J} = 3.6, 2F), -103.91 (s, 4F); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) δ 154.9 – 154.3 (m), 150.2, 134.1, 131.6, 131.1 128.0, 127.7, 127.2, 126.4, 120.0, 118.4, 113.6 (tt, \textit{J} = 244.2, 30.1), 110.2 (t, \textit{J} = 246.4), 102.4 (t, \textit{J} = 35.5); \textit{m/z} (ES\textsuperscript{+}), 509 ([M+Na]\textsuperscript{+}, 50%); 435 (100), 429 (70), \textit{m/z} (ES\textsuperscript{+}): Found [M+Na]\textsuperscript{+} 509.0958. C\textsubscript{27}H\textsubscript{16}F\textsubscript{6}O\textsubscript{2}Na requires M\textsuperscript{+}, 509.0952.

2,4-Bis(4-methoxyphenoxy)-3,3,6,6,7,7-hexafluorocyclohepta-1,4-diene (4d)

Compound 4d was prepared accordingly to the General Procedure C. Purification by silica gel flash column chromatography (x 2), eluting with hexane and then diethyl ether/hexane 1/99 afforded compound 4d as a colourless solid in 46% yield. Mp: 145-146 °C (from diethyl ether/hexane); ν\text{max} (NaCl disc/cm\textsuperscript{-1}) 2951.3 (w), 2845.5 (w), 1684.0 (m), 1669.8 (w), 1605.7 (w), 1507.8 (s), 1547.5 (w), 1357.0 (m), 1326.4 (m), 1253.5 (m), 1191.5 (s), 1179.3 (s), 1137.7 (m), 1097.2 (m), 1070.6 (s), 1039.6 (s), 869.9 (s), 823. (m), 730.1 (m); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.12-7.01 (m, 4H), 7.01-6.89 (m, 4H), 5.12 (m, 2H), 3.83 (s, 6H); \textsuperscript{19}F NMR (471 MHz, CDCl\textsubscript{3}) δ -99.95 (br s, 2F), -103.19 (s, 4F); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) δ 157.9, 155.3 – 155.1 (m), 145.8, 122.3,
115.6, 113.8 (tt, $J = 245.6, 32.5$), 110.2 (t, $J = 247.3$), 101.0 (t, $J = 32.9$), 55.7; $m/z$ (APCI+), 447 ([M+H]$^+$, 100%), 427 (30), 397 (100), 377 (90); $m/z$ (APCI+): Found [M+H]$^+$ 447.1024. C$_{21}$H$_{17}$F$_6$O$_4$ requires $M^+$, 447.1026.

**1,3-Diethoxy-5,5,6,6-tetrafluorobicyclo[2.1.1]hex-2-ene (5a)**

![Diagram of compound 5a]

Compound 5a was prepared accordingly to the General Procedure C. However, purification proven to be difficult as 5a readily decomposed during column chromatography (using either silica gel or neutral alumina) or low-temperature vacuum distillation, as well as during preparative reverse-phase C$_{18}$-preparative HPLC.

A sample of 5a was isolated by silica gel column chromatography (twice) using 1/99 diethyl ether/hexane containing 0.1% of triethylamine as a clear oil in 5% yield. $\nu_{\text{max}}$ (NaCl disc/cm$^{-1}$) 3125.8 (w), 2986.9 (s), 2937.9 (s), 2904.9 (s), 184.4 (w), 1759.6 (w), 1738.9 (w), 1634.5 (w), 1479.3 (m), 1446.9 (m), 1384.5 (m), 1311.1 (s), 1251.8 (s), 1220.3 (s), 1108.9 (s), 1059.8 (s), 932.7 (m), 903.7 (m), 875.9 (m), 760.5 (m), 609.7 (s); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.01 (d, $J = 3.3$, 1H), 3.98 – 3.76 (m, 4H), 3.22 – 3.12 (m, 1H), 1.36 (t, $J = 7.1$, 3H), 1.28 (t, $J = 7.0$, 3H); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -109.13 – -110.58 (m, AA’BB’ system, 2F), -134.37 – -135.82 (m, AA’BB’ system, 2F). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 156.4, 134.2 – 126.6 (m), 94.0, 65.3, 64.4, 55.3, 15.5, 14.1 (note: the signal for the 1-position bridgehead quaternary carbon, expected at $\delta$ 89.5, is not visible due to the signal splitting by coupling with fluorine; increasing the number of scans over 2 hours in order to improve the signal/noise ratio resulted in compound 5a decomposing in the NMR tube); $m/z$ (ES+), 241 ([M+H]$^+$, 100%), 253 (70), 212 (30); $m/z$ (ES+): Found [M+H]$^+$ 241.0852. C$_{10}$H$_{13}$F$_4$O$_2$ requires $M^+$, 241.0852.
1,3-Bis(4-bromophenoxy)-5,5,6,6-tetrafluorobicyclo[2.1.1]hex-2-ene (5b)

Compound 5b was prepared accordingly to the general procedure C. Purification by silica gel flash column chromatography (x 2) followed by reverse-phase preparative HPLC (eluant initial composition: water/acetonitrile 30/70; linear gradient to 20/80 in 30 min; flow 15 mL/min) afforded compound 5b as a colourless solid in 2.3% yield. Mp: 114 – 115 °C; νmax (NaCl disc/cm⁻¹) 3421.9 (m), 3144.8 (w), 2926.1 (w), 2848.3 (w), 1624.5 (m), 1485.6 (s), 1388.6 (w), 1309.7 (m), 1267.8 (m), 1237.1 (s), 1200.1 (s), 1128.4 (m), 1068.2 (m), 1012.1 (m), 880.3 (m), 741.0 (m), 633.5 (w); ¹H NMR (300 MHz, CDCl₃) δ 7.53 – 7.46 (m, 2H), 7.43 – 7.37 (m, 2H), 7.06 – 6.99 (m, 2H), 6.92 – 6.85 (m, 2H), 5.09 (d, J = 3.3, 1H), 3.58 – 3.51 (m, 1H); ¹F NMR (470 MHz, CDCl₃) δ -108.14 – -108.73 (m, AA'BB' system, 2F), -132.24 – -132.95 (m, AA′BB′ system, 2F); ¹³C NMR (126 MHz, CDCl₃) δ 155.1, 153.4, 152.6, 133.2, 132.7, 132.2 – 127.0 (m) 121.8, 119.7, 118.8, 116.6, 98.5, 88.1 – 87.7 (m), 55.4 – 54.6 (m); m/z (ES⁻), 493 ([M-H]⁻, 20%), 495 (10), 491 (10), 255 (100); m/z (ES⁻): Found [M-H]⁻ 490.8913. C₁₈H₉Br₂F₄O₂ requires M⁻, 490.8911.

1,3-Bis(2-naphthoxy)-5,5,6,6-tetrafluorobicyclo[2.1.1]hex-2-ene (5c)

Compound 5c was prepared accordingly to the general procedure C. Purification by silica gel flash column chromatography (x 2) followed by reverse-phase preparative HPLC (eluant initial composition: water/acetonitrile 35/65; linear gradient to 25/75 in 30 min; flow 15 mL/min) afforded compound 5c as a colourless solid in 4.1% yield. Mp: 83 – 85 °C; νmax (NaCl disc/cm⁻¹) 3092.7 (w), 3068.8 (w), 2850.9 (w), 1649.6 (s), 1581.6 (m), 1484.6 (s), 1435.9 (m), 1357.3 (m), 1313.4 (w), 1287.2 (m), 1205.1 (s), 1164.5 (m), 1145.1 (m), 1097.4 (w), 1068.6 (m), 1011.9 (m), 953.2 (w), 865.1 (w), 822.9 (m),
Compound 5d was prepared accordingly to the general procedure C. Purification by silica gel flash column chromatography (x2) followed by reverse-phase preparative HPLC (eluant initial composition: water/acetonitrile 35/65; linear gradient to 25/75 in 30 min; flow 15 mL/min) afforded compound 5d as a colourless solid in 2.2% yield. Mp: 62-64 °C; ν\textsubscript{max} (NaCl disc/cm\textsuperscript{-1}) 3138.0 (w), 3006.9 (w), 2961.9 (w), 2914.1 (w), 2836.7 (w), 1870.3 (w), 1741.3 (w), 1623.2 (s), 1595.9 (w), 1506.3 (s), 1463.1 (m), 1441.7 (m), 1386.4 (m), 1310.3 (m), 1247.2 (m), 1195.9 (m), 1130.8 (m), 1167.6 (m), 113.1, 99.1, 88.5 - 88.1 (m), 55.6 - 54.9 (m); m/z (ES+) 459 ([M+Na]\textsuperscript{+}, 100%), 585 (40), 475 (25), 413 (70), 309 (40), 239 (60); m/z (ES+): Found [M+Na]\textsuperscript{+} 459.0975. C\textsubscript{26}H\textsubscript{16}F\textsubscript{4}O\textsubscript{2}Na requires M\textsuperscript{+} 459.0984.

1,3-Bis(4-methoxyphenoxy)-5,5,6,6-tetrafluorobicyclo[2.1.1]hex-2-ene (5d)
Spectroscopic data

2,4-Diethoxy-3,3,6,6,7,7-hexafluorocyclohepta-1,4-diene (4a)

![Diagram of molecule 4a]
2,4-Bis(Compound 4-bromophenoxy)-3,3,6,6,7,7-hexafluorocyclohepta-1,4-diene (4b)
2,4-Bis(2-naphthoxy)-3,3,6,6,7,7-hexafluorocyclohepta-1,4-diene (4c)
2,4-Bis(4methoxyphenoxy)-3,3,6,6,7,7-hexafluorocyclohepta-1,4-diene (4d)
1,3-Diethoxy-5,5,6,6-tetrafluorobicyclo[2.1.1]hex-2-ene (5a)
1,3-Bis(4-bromophenoxy)-5,5,6,6-tetrafluorobicyclo[2.1.1]hex-2-ene (5b)
1,3-Bis(2-naphthoxy)-5,5,6,6-tetrafluorobicyclo[2.1.1]hex-2-ene (5c)
1,3-Bis(4-methoxyphenoxy)-5,5,6,6-tetrafluorobicyclo[2.1.1]hex-2-ene (5d)
• References