Electronic Supplementary Material (ESI) for Chemical Communications

Accelerating Influence of the *gem*-Difluoromethylene Group in a Ring-Closing Olefin Metathesis reaction: A Thorpe Ingold Effect?

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Supporting Information

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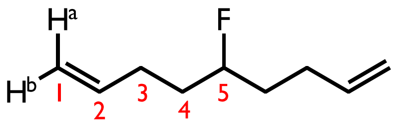
General considerations

All reagents were purchased from commercial supliers and used as received unles stated, 1,8-nonadiene was distilled prior tu use. Complex **M20** and **M23** were purchased from Umicore. Nona-1,8-dien-5-ol and nona-1,8-dien-5-one **(5)** were synthesized according to reported procedures.

Synthesis of the substrates

5-Fluoronona-1,8-diene (1b)



To a solution of nona-1,8-dien-5-ol (2.58 g, 18.4 mmol, 1 eq)[1] in DCM (40 mL), DAST (3.59 mL, 36.8 mmol, 2 eq) was added dropwise at −78 ºC. The resulting mixture was stirred for 5 h and gradually warmed to R.T. Stirring was continued for 2h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (80 mL) and extracted with DCM (3 × 40 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated by Vigreux distillation. The concentrate was purified over silica gel, eluting with pentane. Bulk solvent was removed by Vigreux distillation (atmospheric pressure, 55 ºC). Traces of solvent were removed by Vigreux distillation at reduced pressure (500 mbar, 40-50 ºC) yielding 5-fluoronona-1,8-diene (0.95 g, 36%) as a pale-yellow liquid:

$\mathbf{R_f}$ = 0.25 (pentane); $\mathbf{^1H}$ **NMR** (400 MHz, CD_2Cl_2) δ_H 5.83 (2H, ddt, *J* = 17.1, 10.2, 6.7 Hz, *CH*-2), 5.04 (2H, ddt, *J* = 17.1, 2.0, 1.6 Hz, *CH*-1a), 4.97 (2H, ddt, *J* = 10.2, 2.0, 1.3 Hz *CH*-1b), 4.49 (1H, dtt, *J* = 49.4, 8.2, 4.1 Hz, *CH*-5), 2.27-2.06 (4H, m, CH_2-3), and 1.79-1.53 (4H, m, CH_2-4); $\mathbf{\{^{19}F\}^1H}$ **NMR** (400 MHz, CD_2Cl_2) δ_H 5.83 (2H, ddt, *J* = 17.1, 10.2, 6.7 Hz, *CH*-2), 5.04 (2H, ddt, *J* = 17.1, 2.0, 1.6 Hz, *CH*-1a), 4.97 (2H, ddt, *J* = 10.2, 2.0, 1.3 Hz *CH*-1b), 4.49 (1H, tt, *J* = 8.2, 4.1 Hz, *CH*-5), 2.27-2.06 (4H, m, CH_2-3), and 1.77-1.57 (4H, m, CH_2-4); $\mathbf{^{13}C}$ **NMR** (100 MHz, CD_2Cl_2) δ_C 138.3 (*C*-2), 115.1 (*C*-1), 93.5 (d, *J* = 167.3 Hz, *C*-5), 34.7 (d, *J* = 21.1 Hz, *C*-4), and 29.7 (d, *J* =4.5 Hz, *C*-3); $\mathbf{\{^1H\}^{19}F}$ **NMR** (376 MHz, CD_2Cl_2) δ_F −182.97; $\mathbf{^{19}F}$ **NMR** (376 MHz, CD_2Cl_2) δ_F −182.97 (dtt, *J* = 49.4, 30.8, 16.9 Hz, *CF*-5). **HRMS** *m/z* (EI^+) Found: $[M]^+$ 142.1151. $C_9H_{15}F$ requires $[M]^+$ 142.1152; **LRMS** *m/z* (EI^+) 142.1 $[M]^+$.

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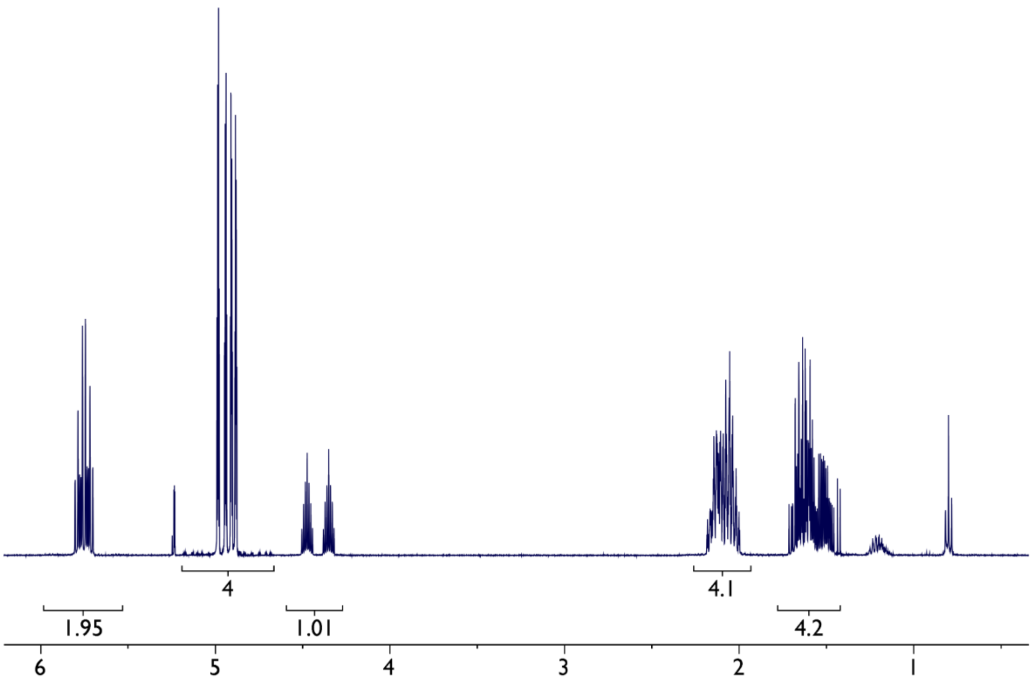
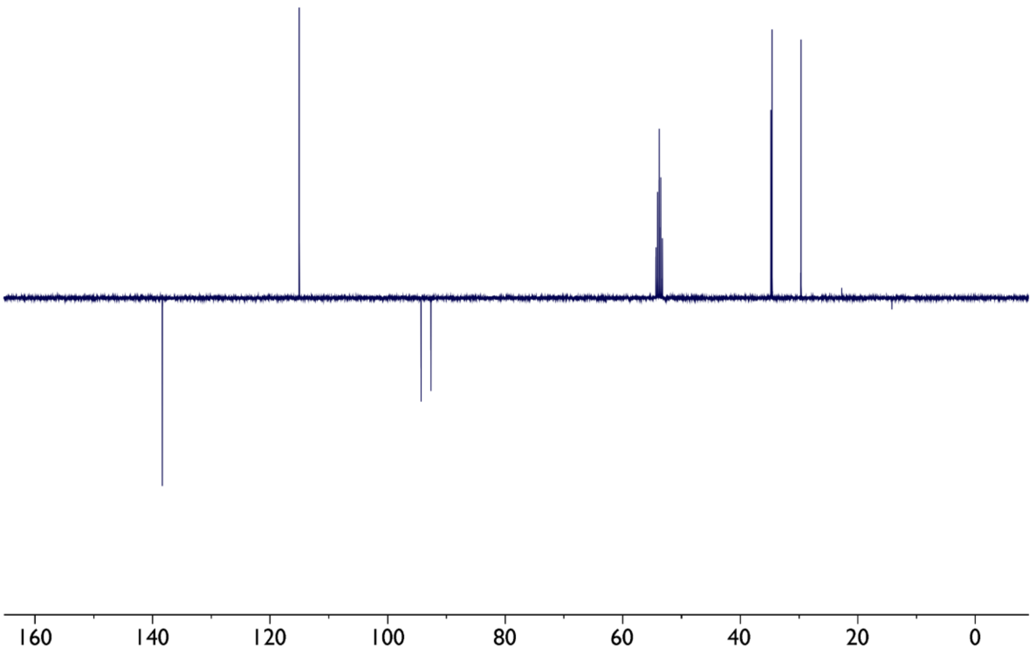
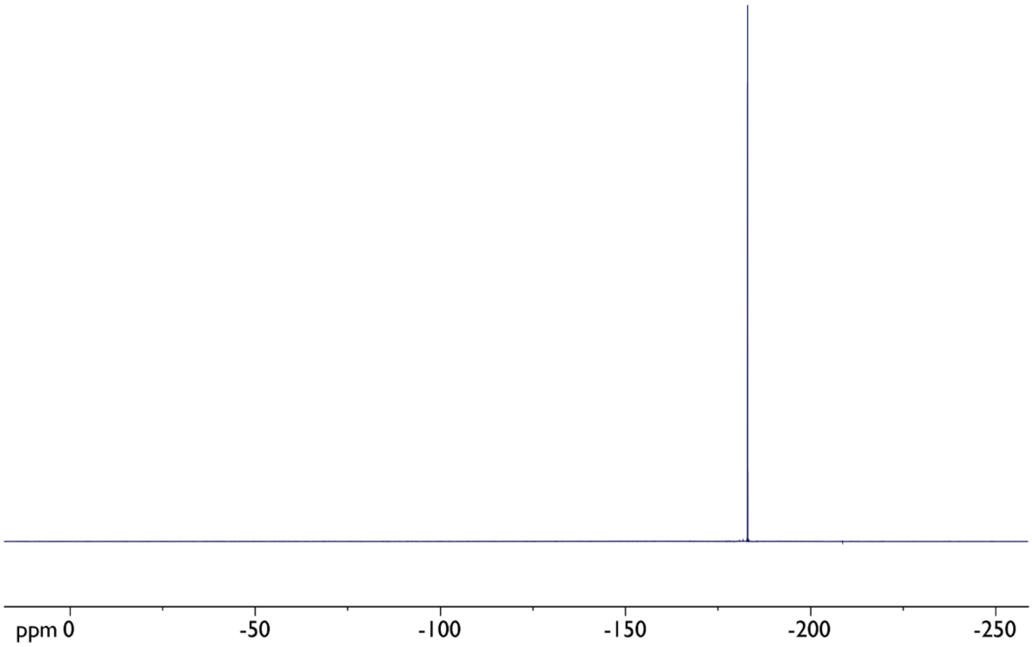
^{1}H NMR of **1b** (400 MHz, CD_2Cl_2)



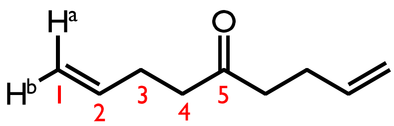
^{13}C NMR of **1b** (100 MHz, CD_2Cl_2)



{^{1}H}^{19}F NMR of **1b** (376 MHz, CD_2Cl_2)



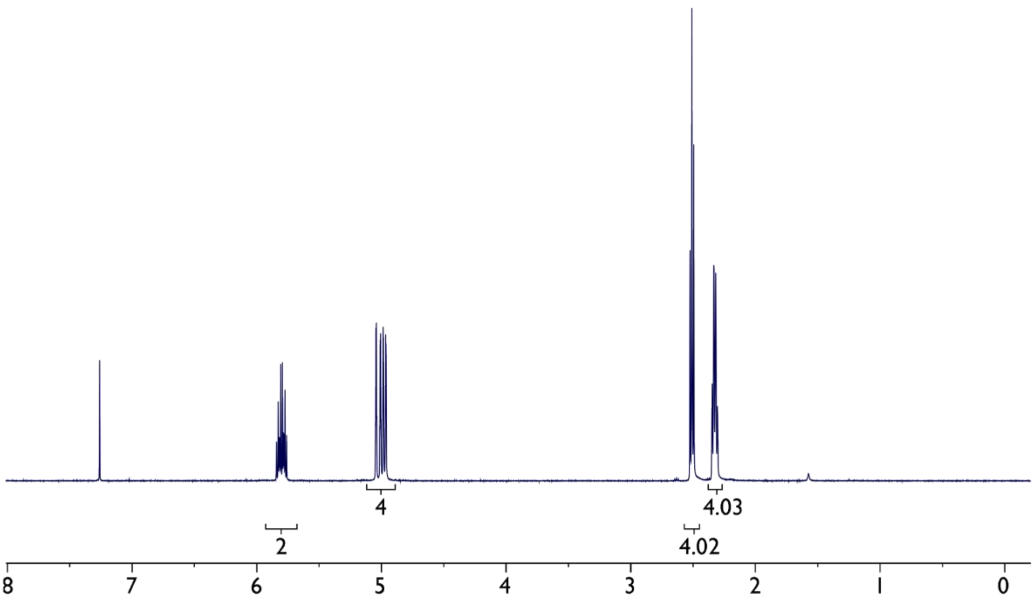
Nona-1,8-dien-5-one (5)



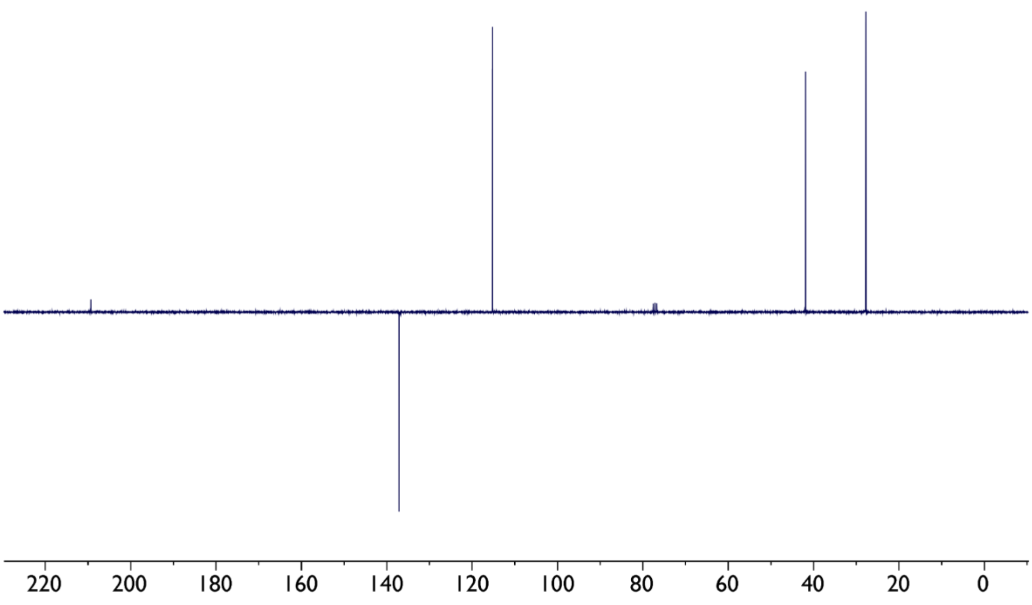
Concentrated sulfuric acid (16.3 mL) was added dropwise to a solution of chromium trioxide (19.35 g, 193.5, 2.5 eq) in water (56.4 mL). The resulting Jones reagent was added dropwise to a solution of nona-1,8-dien-5-ol[1] (10.75 g, 76.6 mmol, 1 eq) at 0 ºC. Reaction mixture was left to stir overnight at RT and quenched with isopropanol (10 mL). Acetone was removed under reduced pressure and the residue extracted with Et_2O (4 × 150 mL). Combined organic extracts were washed with water (150 mL), saturated aqueous $NaHCO_3$ solution (150 mL), brine (150 mL), dried over $MgSO_4$ and concentrated. Purification by distillation under reduced pressure (2.6 mBar, 42-44 ºC) yielded nona-1,8-dien-5-one (9.64 g, 91%) as a pale-yellow oil:

R_f = 0.61 (DCM); **^{1}H NMR** (300 MHz, $CDCl_3$) δ_H 5.76 (2H, ddt, *J* = 17.0, 10.3, 6.6 Hz, *CH*-2), 4.98 (2H, ddt, *J* = 17.0, 1.8, 1.6 Hz, *CH*-1a), 4.93 (2H, ddt, *J* = 10.3, 1.8, 1.3 Hz *CH*-1b), 2.51-2.43 (4H, m, CH_2-4), 2.34-2.23 (4H, m, CH_2-3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ_C 209.5 (*C*-5), 137.2 (*C*-2), 115.4 (*C*-1), 42.0 (*C*-4), 27.8 (*C*-3). **LRMS** *m/z* (ES$^+$) 161.09 $[M+Na]^+$.

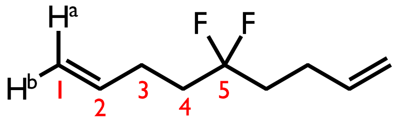
^{1}H NMR of **5** (300 MHz, $CDCl_3$)



^{13}C NMR of **5** (125 MHz, $CDCl_3$)



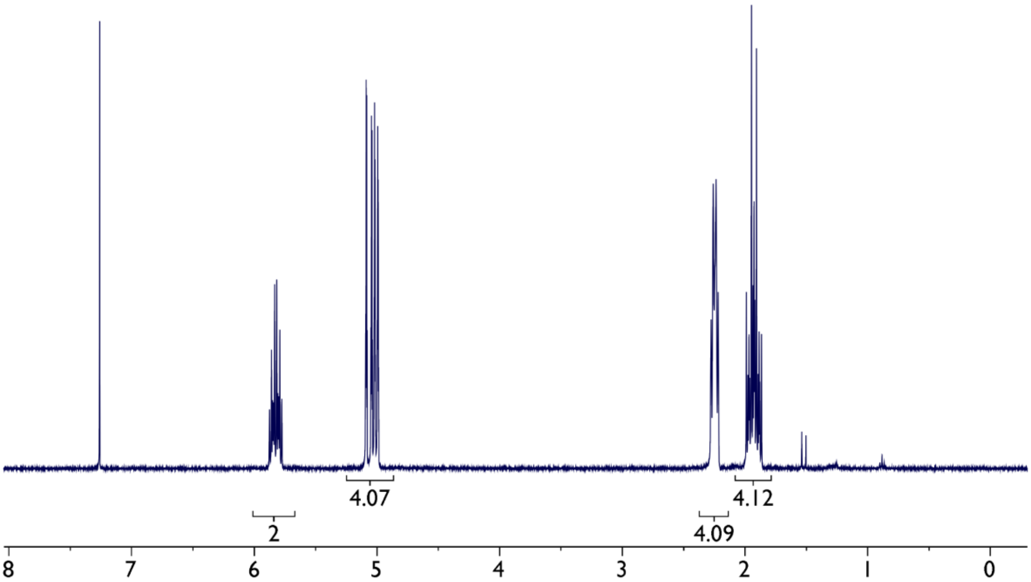
5,5-Difluoronona-1,8-diene (1c)



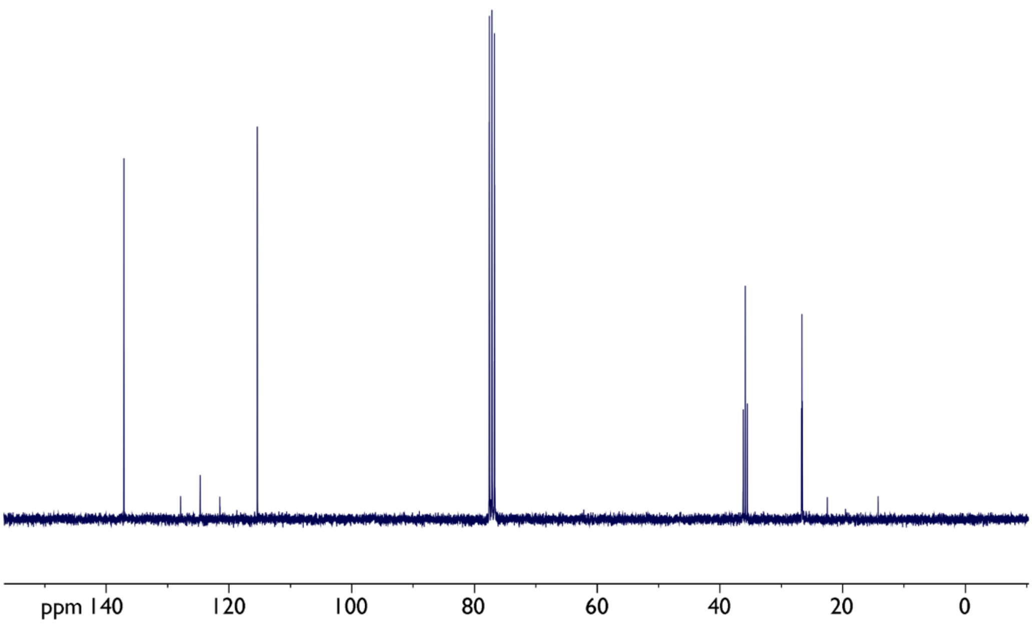
A mixture of nona-1,8-dien-5-one (3.86 g, 27.9 mmol, 1 eq) and neat DAST (10.9 mL, 111.7 mmol, 4 eq) was stirred for 6 days at 45 ºC. Crude reaction was added portionwise to a biphasic mixture of saturated aqueous $NaHCO_3$ solution (300 mL) and pentane (150 mL) at 0 ºC. The aqueous layer was separated and extracted with pentane (3 × 100 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated by Vigreux distillation. The concentrate was purified over silica gel, eluting with pentane. Bulk solvent was removed by Vigreux distillation (atmospheric pressure, 55 ºC). Traces of solvent were removed by Vigreux distillation at reduced pressure (700 mbar, 45-60 ºC) yielding 5,5-difluoronona-1,8-diene (2.47 g, 55%) as a pale-yellow oil:

R_f = 0.44 (pentane); **^{1}H NMR** (300 MHz, $CDCl_3$) δ_H 5.83 (2H, ddt, *J* = 17.1, 10.2, 6.6 Hz, *CH*-2), 5.07 (2H, ddt, *J* = 17.1, 1.7, 1.7 Hz, *CH*-1a), 5.01 (2H, ddt, *J* = 10.2, 1.7, 1.3 Hz *CH*-1b), 2.30-2.19 (4H, m, CH_2-3), and 2.03-1.83 (4H, m, CH_2-4); **^{13}C NMR** (75 MHz, $CDCl_3$) δ_C 137.1 (*C*-2), 124.7 (t, *J* = 241.0 Hz, *C*-5), 115.4 (*C*-1), 35.9 (t, *J* = 25.4 Hz, *C*-4), 26.6 (t, *J* = 5.2 Hz, *C*-3); **{^{19}F}^{1}H NMR** (300 MHz, $CDCl_3$) δ_H 5.83 (2H, ddt, *J* = 17.1, 10.2, 6.6 Hz, *CH*-2), 5.07 (2H, ddt, *J* = 17.1, 1.7, 1.7 Hz, *CH*-1a), 5.01 (2H, ddt, *J* = 10.2, 1.7, 1.3 Hz *CH*-1b), 2.30-2.19 (4H, m, CH_2-3), and 1.97-1.88 (4H, m, CH_2-4); **^{13}C NMR** (75 MHz, $CDCl_3$) δ_C 137.1 (*C*-2), 124.7 (t, *J* = 241.0 Hz, *C*-5), 115.4 (*C*-1), 35.9 (t, *J* = 25.4 Hz, *C*-4), 26.6 (t, *J* =5.2 Hz, *C*-3); **{^{1}H}^{19}F NMR** (282 MHz, $CDCl_3$) δ_F −99.06; **^{19}F NMR** (282 MHz, $CDCl_3$) δ_F −99.06 (quintet, *J* = 16.51 Hz, CF_2-5). **HRMS** *m/z* (EI^+) Found: $[M]^+$ 160.1056. $C_9H_{14}F_2$ requires $[M]^+$ 160.1058; **LRMS** *m/z* (EI^+) 160.0 $[M]^+$.

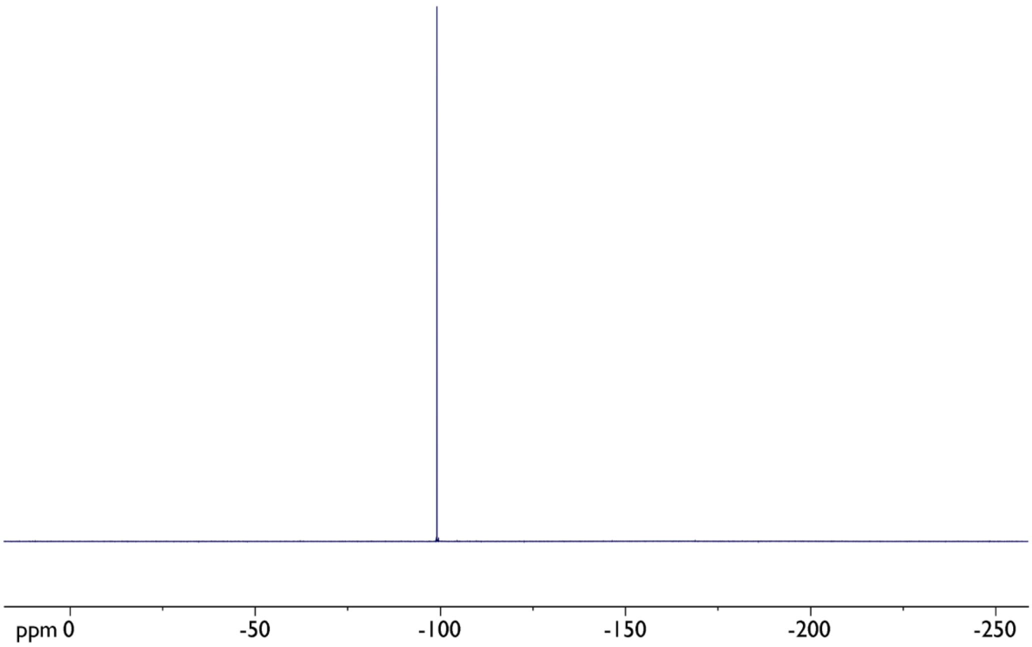
^{1}H NMR of **1c** (300 MHz, $CDCl_3$)



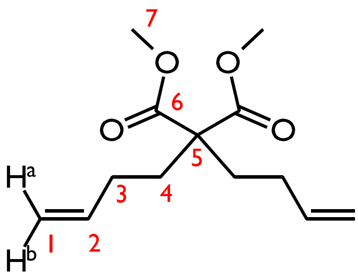
^{13}C NMR of **1c** (75 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ NMR of **1c** (282 MHz, $CDCl_3$)



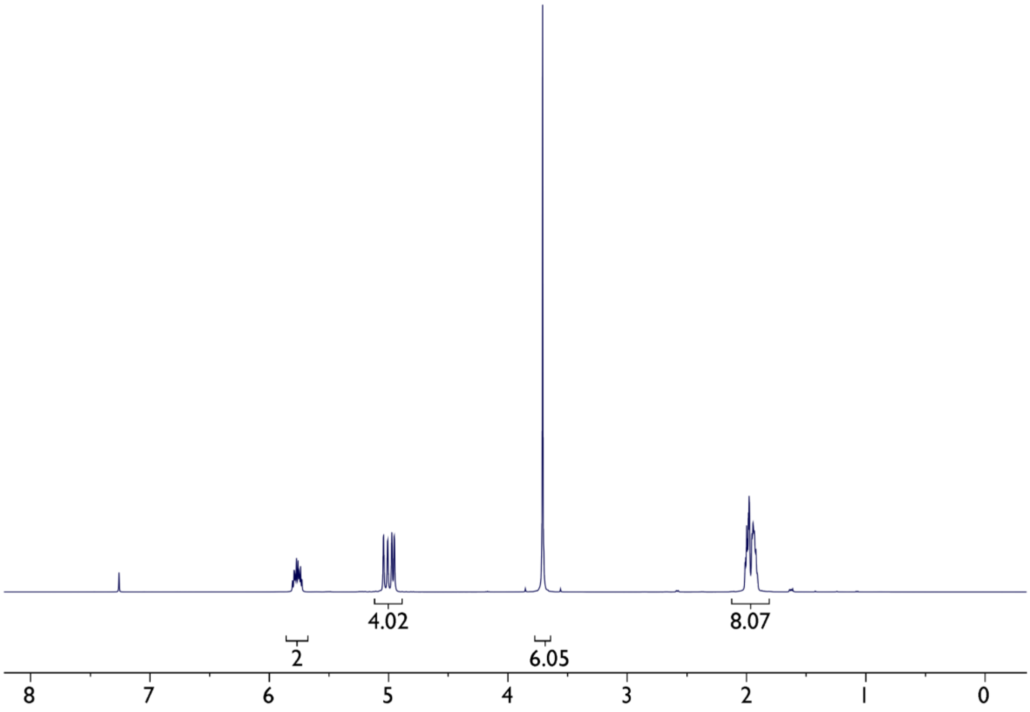
5,5-bis(dimethylcarboxyl)-nona-1,8-diene (1d)



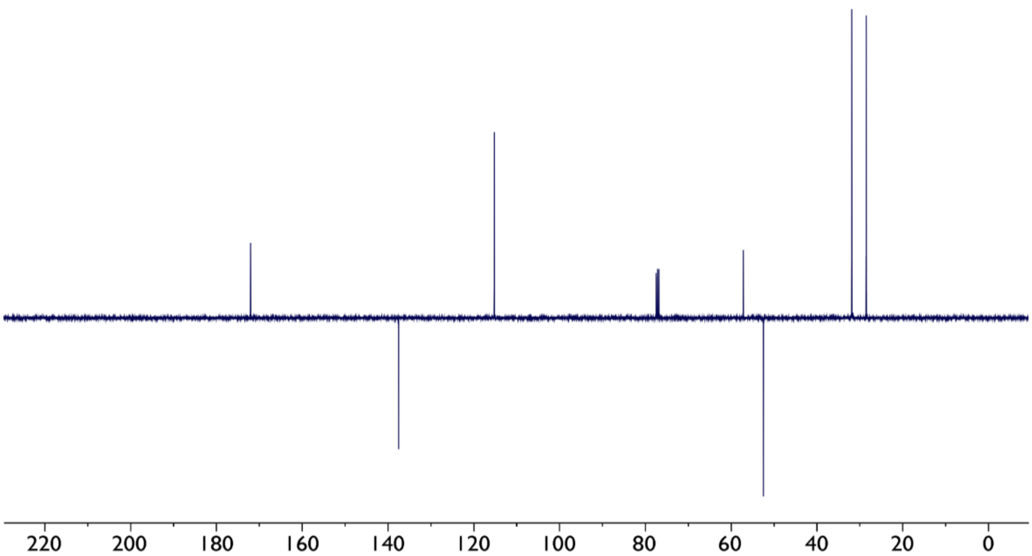
To a suspension of NaH (1.30 g, 51.5 mmol) in DMF (80 mL) dimethyl malonate (4 mL, 34.4 mmol) was added dropwise at 0 ºC. After 20 min, 4-bromo-1-butene (4.68 mL, 44.7 mmol) was added dropwise, the mixture was stirred for 2 h at room temperature. A further aliquot of NaH (1.30 g, 51.5 mmol) and 4-bromo-1-butene (4.68 mL, 44.7 mmol) were added at 0 ºC and stirred for 12 h at RT. A third aliquot of NaH (0.87 g, 34.4 mmol) followed by 4-bromo-1-butene (3.60 mL, 34.4 mmol) was added at 0 ºC and stirring continued for 4 h. Reaction was quenched with saturated aqueous NH_4Cl solution (50 mL), diluted with DCM (150 mL) and washed with brine (5 × 100 mL). Organic extracts were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification over silica gel, eluting with pentane and DCM (30:70), followed by Vigreux distillation at reduced pressure (3 mBar, 101-102 ºC) yielded 5,5-bis(dimethylcarboxyl)-nona-1,8-diene (5.33 g, 64%) as a colourless oil:

R$_f$ = 0.41 (DCM); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 5.76 (2H, ddt, *J* = 17.0, 10.3, 6.4 Hz, *CH*-2), 5.02 (2H, ddt, *J* = 17.0, 1.8, 1.4 Hz, *CH*-1a), 4.96 (2H, ddt, *J* = 10.3, 1.8, 1.2 Hz, *CH*-1b), 3.71 (6H, s, CH_3-7), 2.02-1.90 (8H, m, CH_2-3, 4); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 172.0 (*C*-6), 137.5 (*C*-2), 115.2 (*C*-1), 57.2 (*C*-5), 52.5 (*C*-7), 31.9 (CH_2), 28.5 (CH_2). **HRMS** *m/z* (ES^+) Found: $[M+Na]^+$ 263.1254. $C_{13}H_{20}NaO_4$ requires $[M+Na]^+$ 263.1259; **LRMS** *m/z* (ES^+) 263.03 $[M+Na]^+$.

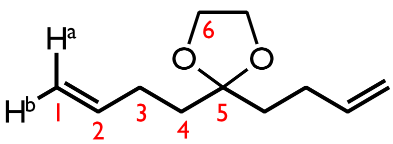
^{1}H NMR of **1d** (500 MHz, $CDCl_3$)



^{13}C NMR of **1d** (100 MHz, $CDCl_3$)



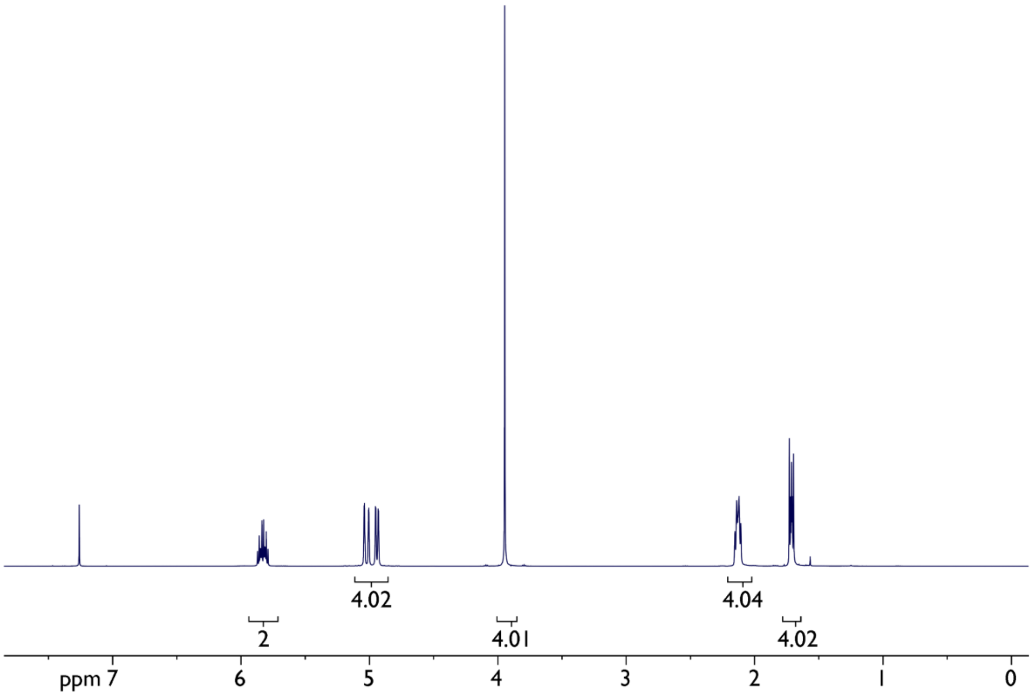
2,2-bis(but-3-en-1-yl)-1,3-dioxolane (1e)



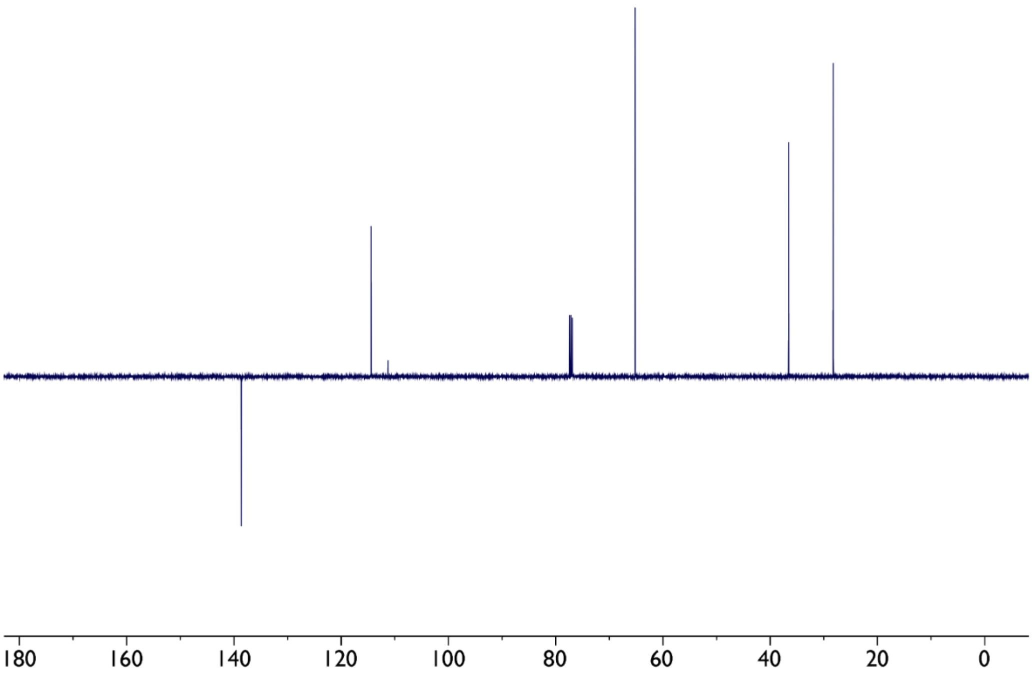
p-Toluenesulfonic acid monohydrate (0.04 g, 0.2 mmol) was added to a mixture of nona-1,8-dien-5-one (3.05 g, 22.1 mmol, 1 eq) and ethane-1,2-diol (1.60 mL, 28.7 mmol, 1.3 eq) in toluene (60 mL). Resulting solution was refluxed for 2.5 h, until 0.4 mL of water had been collected in a Dean-Stark trap. Solution was washed with aqueous NaOH solution (10% w/v, 15 mL), water (5 × 10 mL), and brine (20 mL). The organic extracts were dried over $MgSO_4$ and concentrated. Purification by Vigreux distillation under reduced pressure (2.6 mBar, 62-64 ºC) yielded 2,2-bis(but-3-en-1-yl)-1,3-dioxolane (2.17 g, 54%) as a colourless oil:

R_f = 0.5 (pentane:Et_2O, 92:8); **^{1}H NMR** (500 MHz, $CDCl_3$) **δ_H** 5.83 (2H, ddt, *J* = 17.0, 10.2, 6.5 Hz, *CH*-2), 5.02 (2H, ddt, *J* = 17.0, 1.7, 1.7 Hz, *CH*-1a), 4.97-4.91 (2H, m, *CH*-1b), 3.95 (4H, s, CH_3-6), 2.16-2.10 (4H, m, CH_2-3), 1.74-1.68 (4H, m, CH_2-4); **^{13}C NMR** (125 MHz, $CDCl_3$) **δ_C** 138.6 (*C*-2), 114.4 (*C*-1), 111.3 (*C*-5), 65.2 (*C*-6), 36.6 (*C*-4), 28.2 (*C*-3). **HRMS** *m/z* (ES^+) Found: $[M+H]^+$ 183.1387. $C_{11}H_{19}O_2$ requires $[M+H]^+$ 183.1385; **LRMS** *m/z* (ES^+) 183.12 $[M+H]^+$.

^{1}H NMR of **1e** (500 MHz, $CDCl_3$)

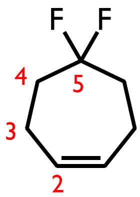


^{13}C NMR of **1e** (125 MHz, $CDCl_3$)



Synthesis of the products

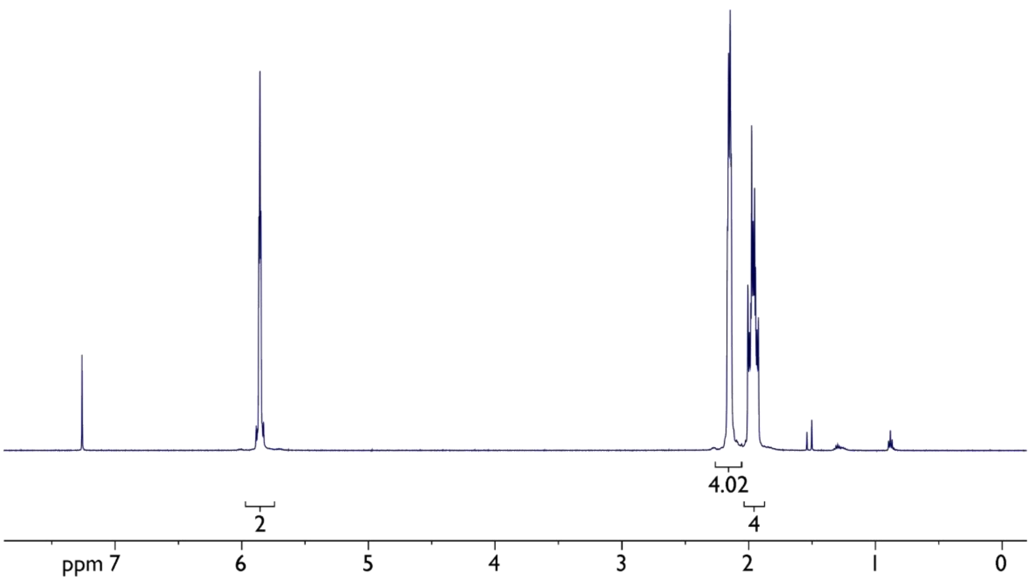
5,5-Difluocyclohept-1-ene (2c)



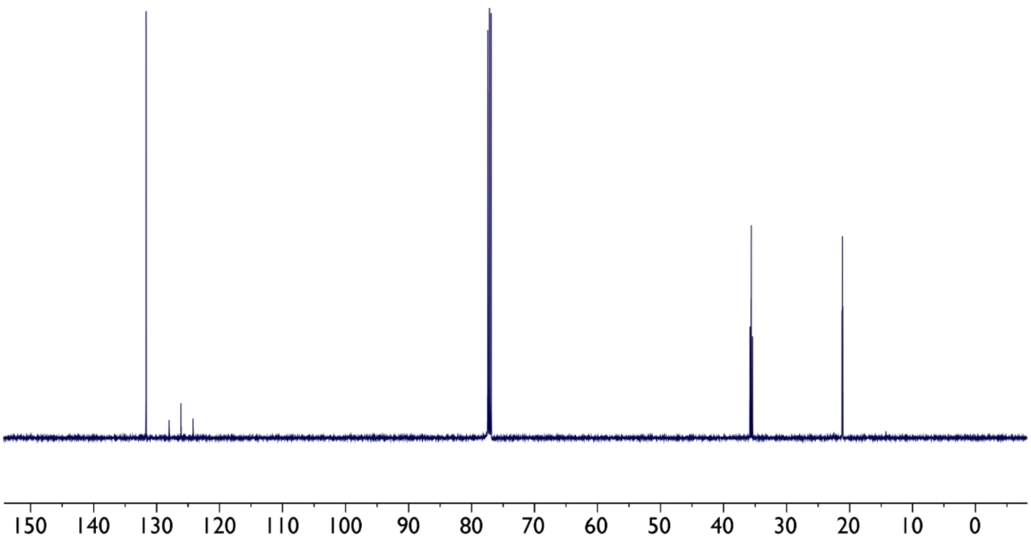
To a solution of 5,5-difluoronona-1,8-diene (1.67 g, 10.4 mmol) in pentane (520 mL) was added M23 (0.10 g, 0.10 mmol). The reaction was stirred for 3 h at RT. The bulk solvent was removed by Vigreux distillation. The concentrate was purified over silica gel, eluting with pentane. Bulk solvent was removed by Vigreux distillation (amospheric pressure, 45-55 ºC). Traces of pentane were removed by Vigreux distillation at reduced pressure (700 mbar, 45-60 ºC) yielding 5,5-difluorocyclohept-1-ene (0.92 g, 67%) as a pale-yellow liquid:

R_f = 0.44 (pentane); **^{1}H NMR** (500 MHz, $CDCl_3$) **δ_H** 5.90-5.81 (2H, m, *CH*-2), 2.22-2.08 (4H, m, *CH_2*-3), 2.04-1.89 (4H, m, *CH_2*-4); **^{1}H NMR** (500 MHz, C_7D_8) δ_H 5.60-5.51 (2H, m, *CH*-2), 1.85-1.76 (4H, m, *CH_2*-3), 1.75-1.65 (4H, m, *CH_2*-4); **{^{19}F}^{1}H NMR** (500 MHz, $CDCl_3$) **δ_H** 5.90-5.81 (2H, m, *CH*-2), 2.20-2.10 (4H, m, *CH_2*-3), 2.01-1.92 (4H, m, *CH_2*-4); **^{13}C NMR** (125 MHz, $CDCl_3$) **δ_C** 131.7 (*C*-2), 126.1 (t, *J* = 239.4 Hz, *C*-5), 35.6 (t, *J* = 25.4 Hz, *C*-4), 21.1 (t, *J* =6.8 Hz, *C*-3); **{^{1}H}^{19}F NMR** (470 MHz, $CDCl_3$) **δ_F** −89.98; **{^{1}H}^{19}F NMR** (470 MHz, C_7D_8) **δ_F** −89.85; **^{19}F NMR** (470 MHz, $CDCl_3$) **δ_F** −89.98 (quintet, *J* = 15.0 Hz, *CF_2*-5). **HRMS** *m/z* (EI^+) Found: $[M]^+$ 132.0755. $C_7H_{10}F_2$ requires $[M]^+$ 132.0751; **LRMS** *m/z* (EI^+) 132.08 $[M]^+$.

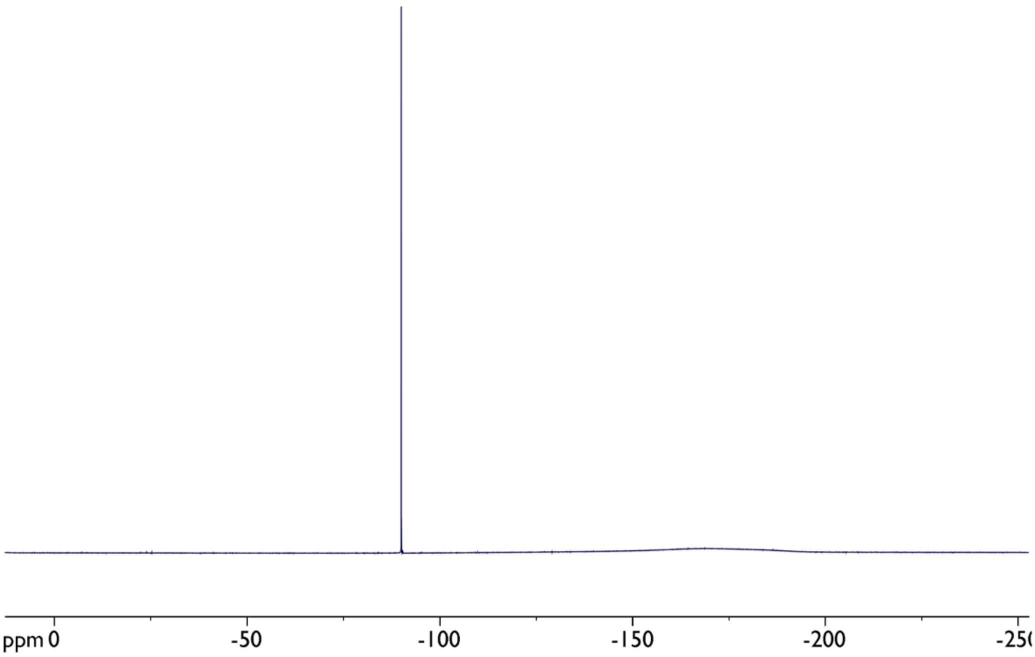
^{1}H NMR of **2c** (500 MHz, $CDCl_3$)



^{13}C NMR of **2c** (125 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ NMR of **2c** (470 MHz, $CDCl_3$)



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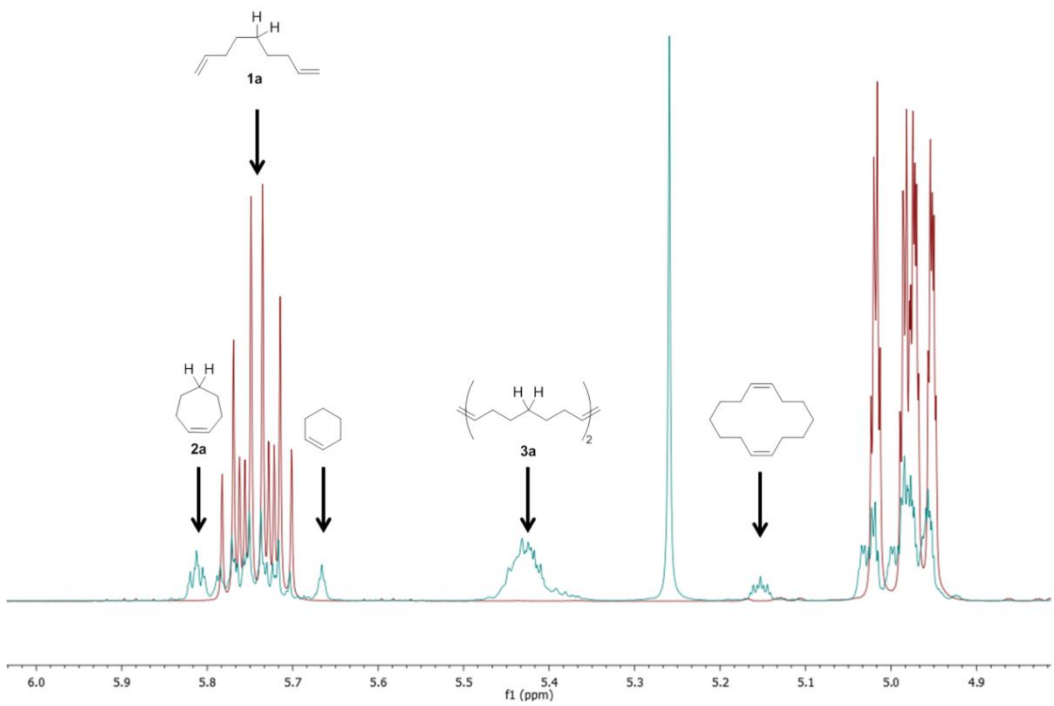
Procedure for the reaction kinetics

Inside a glovebox, 800 μL of a stock solution of the substrate in toluene-d_8 (0.25 mmol/800 μL; 0.3125 mmol/5 mL) and the internal standard (1,3,5–trimethoxybenzene or α,α,α-trifluorotolune, 0.125 mmol/800 μL; 0.1562 mmol/5 mL) were introduced in a Wilmad® screw-cap NMR tube. The NMR tube was left to equilibrate at 15 °C inside the NMR after and then 200 μL of a stock solution of the catalysts (0.05mmol/200μL; 0.125mmol/5mL) were injected into the NMR tube. The progress of the reaction was followed by ^{1}H NMR and ^{19}F{^{1}H}NMR. (1 scan per datapoint).

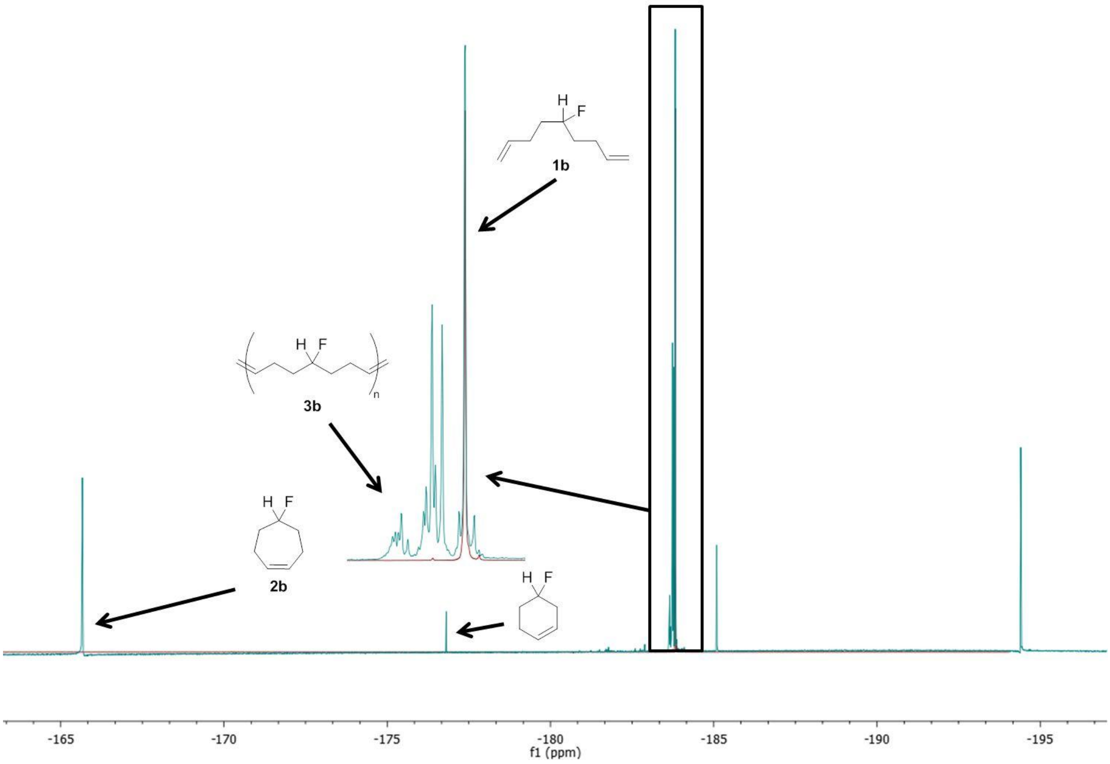
Representative NMR indicating the chemical shifts used

^{1}H NMR of the RCM of **1a** (500 MHz, toluene-d$_8$)



Electronic Supplementary Material (ESI) for Chemical Communications

$^{19}F\{^{1}H\}$ NMR of the RCM of **1b** (500 MHz, toluene-d_8)



5-Fluorocycloheptene **2b** is an unknown compound. The signal at ^{19}F-NMR δ = -165.8 ppm is assigned to **2b** based on expectation. It is alone in this region and has a similar chemical shift to related cycloalkanes. Eg fluorocycloheptane has a chemical shift of δ_F = -165 ppm (see I. Busci, B. Torok, A. I. Marko, G. Rasul, G. K. S Prakash, G. A. Olah., *J. Am. Chem. Soc*., 2002, **124**, 7728 – 7736) and fluorocyclooctane has a chemical shift of δ_F = -160 ppm (see H. J. Schneider, W. Gschwendtner, D. Heiske, V. Hoppen, F. Thomas, *Tetrahedron*, 1977, **33**, 1769 – 1773). The signal at δ_F = -177 ppm is assigned to 4-fluorocyclohexene (see F. J. Weigert, *J. Org. Chem.,* 1980, **45**, 3476 – 3483).

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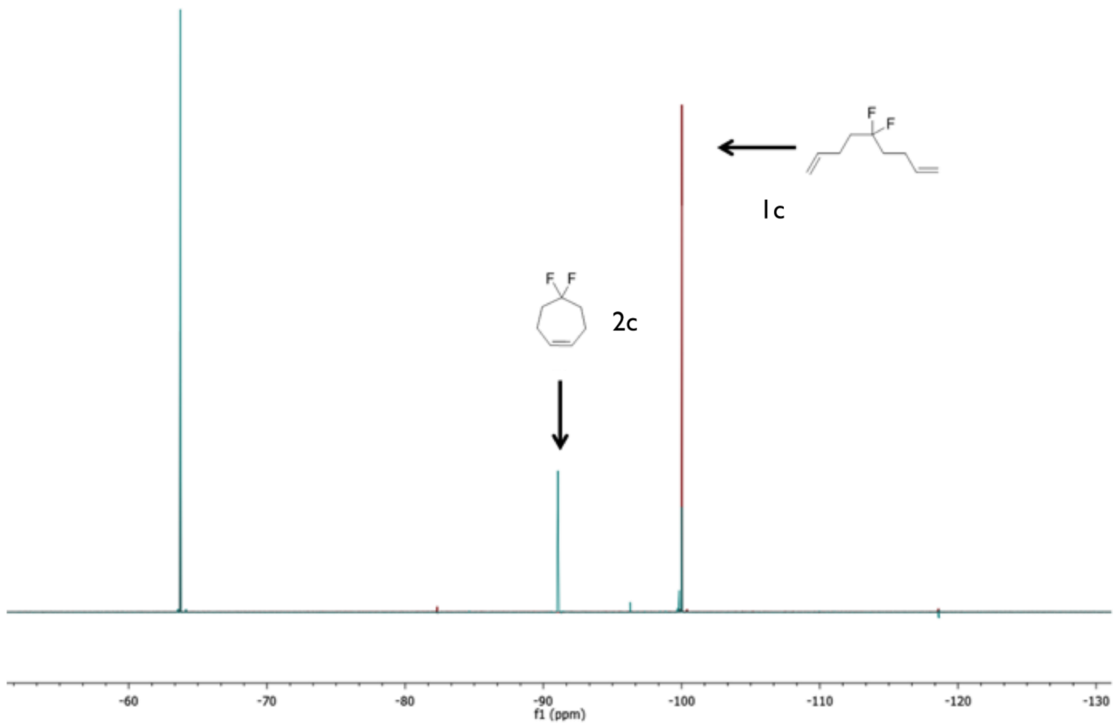
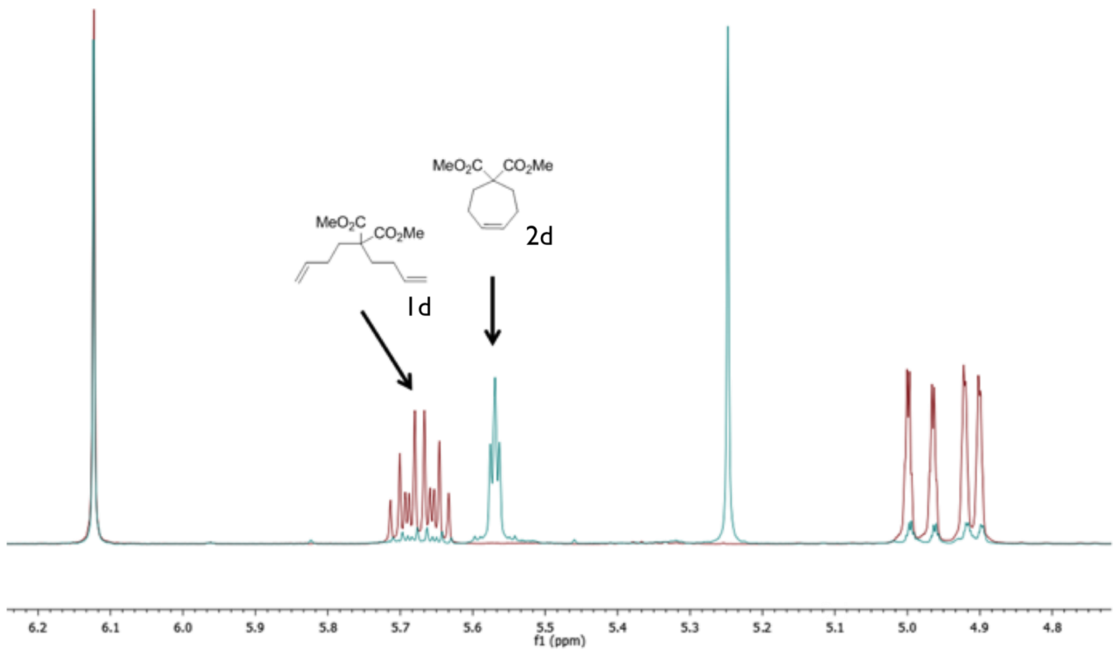
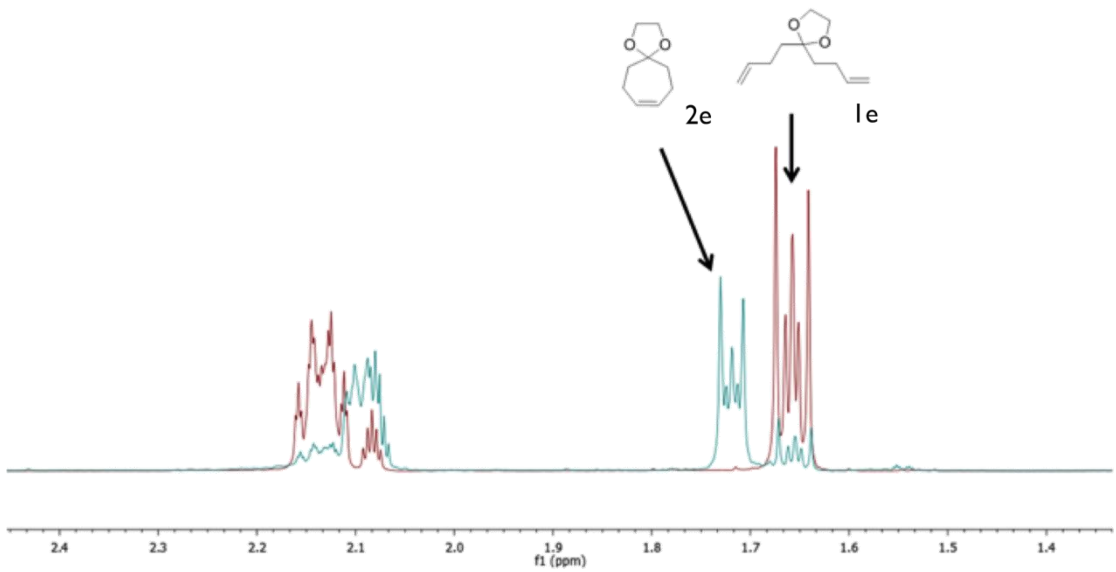
$^{19}F\{^{1}H\}$ NMR of the RCM of **1c** (470 MHz, toluene-d_8)



^{1}H NMR of the RCM of **1d** (500 MHz, toluene-d_8)



^{1}H NMR of the RCM of **1e** (500 MHz, toluene-d$_8$)



Conversion (%) *vs* time (s) for compounds 2a-2e

Time	% 2a	Time	% 2b	Time	% 2c	Time	% 2d	Time	% 2e
0	0	0	0.0	0	0.0	0	0.0	0	0.0
300	1.35	960	6.4	1200	33.1	660	19.0	240	11.8
378	1.63	1923	9.7	1849	43.6	792	24.1	379	16.8
990	3.10	2885	11.4	2500	51.7	1407	41.3	990	36.3
1604	4.37	3848	12.5	3150	57.7	2020	52.9	1602	49.4
2219	5.37	4811	13.3	3800	62.2	2634	61.0	2217	58.1
2833	6.08	5774	13.8	4452	65.6	3249	66.7	2832	63.9
3447	6.65	6736	14.0	5103	67.9	3863	70.3	3449	67.7
4062	7.11	7695	14.3	5753	69.7	4479	72.6	4064	70.5
4675	7.44	8658	14.5	6403	71.0	5094	74.3	4680	72.1
5290	7.56	9621	14.7	7053	71.9	5711	75.3	5294	73.4
5905	7.77	10583	14.9	7702	72.6	6328	76.1	5908	74.2
6519	7.97	11546	15.0	8354	73.2	6941	76.6	6523	74.9
7134	8.21	12509	15.2	9004	73.7	7555	77.0	7139	75.5
7748	8.38	13472	15.3	9654	74.0	8169	77.3	7753	75.9
8363	8.43	14434	15.4	10304	74.3	8783	77.5	8369	76.4
8977	8.74	15398	15.5	10954	74.6	9398	77.7	8983	76.6
9592	8.79	16360	15.5	11605	74.7	10013	77.9	9596	76.7
10202	8.93	17323	15.6	12255	74.9	10627	78.1	10212	76.7
10817	9.01	18285	15.7	12905	75.1	11242	78.2	10827	77.2
11431	9.05	19249	15.7	13555	75.3	11857	78.2	11442	77.3
12045	9.18	20211	15.8	14205	75.3	12478	78.3	12057	77.7
12659	9.25	21173	15.8	14855	75.4	13094	78.3	12671	77.6
13274	9.27	22136	15.9	15505	75.4	13709	78.4	13286	77.5
13888	9.43	23099	15.9	16155	75.6	14324	78.5	13900	77.7
14503	9.50	24062	16.0	16805	75.7	14938	78.5	14515	77.6
15117	9.64	25025	15.9	17455	75.6	15553	78.5	15131	77.6
15733	9.61	25987	16.0	18105	75.7	16168	78.4	15746	77.8
16347	9.64	26950	16.0	18755	75.9	16785	78.5	16361	77.9
16961	9.71	27913	16.0	19405	75.8	17400	78.5	16975	77.9
17576	9.81	28876	16.0	20055	76.0	18015	78.5	17591	78.1
18190	9.84	29839	16.1	20705	75.9	18629	78.5	18205	77.8
18804	9.87			21355	75.9	19244	78.6	18821	78.2
19418	9.91			22007	76.0	19859	78.5	19435	78.0
20032	9.97			22657	76.0	20472	78.6	20049	78.0
20645	9.99			23307	76.1	21087	78.6	20663	78.2

DFT calculated energies of compounds 1a-1e and 2a-2e

All the DFT static calculations were performed at the GGA level with the Gaussian09 set of programs, [2] using the B3LYP functional.[3] with a 6-311+G(d,p) basis set.

E+ZP	Sum of Electronic and zero-point Energies
E+T	Sum of Electronic and thermal Energies
H	Sum of Electronic and thermal Enthalpies
G	Sum of Electronic and thermal Free Energies

	Energy (a.u.)			
	E+ZP	E+T	H	G
1a	-352.429617	-352.418183	-352.417239	-352.467425
1b	-451.709611	-451.697518	-451.696574	-451.749228
1c	-550.998900	-550.986162	-550.985218	-551.039279
1d	-808.215158	-808.194809	-808.193864	-808.266378
1e	-580.292019	-580.277674	-580.276730	-580.334249
2a	-273.856657	-273.849919	-273.848975	-273.887144
2b	-373.137716	-373.130230	-373.129286	-373.169553
2c	-472.428809	-472.420744	-472.419799	-472.461306
2d	-729.648091	-729.632349	-729.631404	-729.690767
2e	-501.722891	-501.713052	-501.712108	-501.758252

XYZ coordinates of compounds 1a-1e

1a

C	0.00000	0.54807	0.16656
C	1.28116	-0.13211	-0.32807
H	1.28454	-0.14763	-1.42529
H	1.28963	-1.18044	-0.00761
C	-1.28116	-0.13212	-0.32807
H	-1.28963	-1.18045	-0.00762
H	-1.28454	-0.14763	-1.42529
C	2.56463	0.55488	0.17262
H	2.58317	0.55206	1.26813
H	2.54019	1.60843	-0.13806
C	-2.56463	0.55488	0.17262
H	-2.54019	1.60843	-0.13806
H	-2.58317	0.55206	1.26813
C	-3.81843	-0.08311	-0.35476
H	-3.92388	-0.09549	-1.43936
C	3.81843	-0.08311	-0.35476
H	3.92388	-0.09548	-1.43936
C	4.77823	-0.62963	0.38884
H	4.71882	-0.64336	1.47340
H	5.65793	-1.07980	-0.05753
C	-4.77824	-0.62962	0.38884
H	-5.65793	-1.07980	-0.05754
H	-4.71883	-0.64335	1.47340
H	0.00000	1.59799	-0.15413
H	0.00000	0.56561	1.26401

1b

C	0.00000	0.17438	0.45385
H	0.00000	0.29691	1.54394
C	-1.27706	-0.51638	-0.00020
H	-1.25787	-1.54402	0.38235
H	-1.27445	-0.58501	-1.09328
C	1.27706	-0.51639	-0.00020
H	1.27445	-0.58501	-1.09328
H	1.25787	-1.54402	0.38234
C	-2.55990	0.19033	0.47274
H	-2.57976	1.21053	0.08181
H	-2.53265	0.26954	1.56818
C	2.55990	0.19033	0.47274
H	2.53265	0.26953	1.56818
H	2.57976	1.21053	0.08181
C	3.80621	-0.54267	0.06294
H	3.90928	-1.55869	0.44369
C	-3.80621	-0.54267	0.06294
H	-3.90928	-1.55869	0.44370
C	-4.76388	-0.05100	-0.72022
H	-4.70586	0.95510	-1.12513
H	-5.63992	-0.63384	-0.98208
C	4.76388	-0.05099	-0.72022
H	5.63992	-0.63384	-0.98208
H	4.70586	0.95510	-1.12513
F	0.00000	1.49625	-0.06680

1c

C	0.00000	0.30981	0.00701
C	1.28513	-0.39452	-0.39688
H	1.27006	-0.50709	-1.48573
H	1.26555	-1.40138	0.03018
C	-1.28513	-0.39452	-0.39688
H	-1.26555	-1.40138	0.03018
H	-1.27006	-0.50709	-1.48573
C	2.56427	0.33913	0.04487
H	2.58919	0.41124	1.13476
H	2.53181	1.36223	-0.34514
C	-2.56427	0.33913	0.04487
H	-2.53181	1.36223	-0.34514
H	-2.58919	0.41124	1.13476
C	-3.80402	-0.34809	-0.45505
H	-3.90684	-0.41739	-1.53767
C	3.80402	-0.34809	-0.45505
H	3.90684	-0.41738	-1.53767
C	4.75824	-0.86534	0.31555
H	4.70133	-0.81972	1.39918
H	5.63215	-1.34727	-0.10821
C	-4.75824	-0.86534	0.31555
H	-5.63215	-1.34727	-0.10821
H	-4.70133	-0.81971	1.39918
F	0.00000	0.49759	1.38323
F	0.00000	1.59194	-0.52974

1d

C	-0.05579	0.14924	-0.31508
C	1.17523	-0.27218	-1.18260
H	1.27865	0.47915	-1.97370
H	0.92773	-1.19994	-1.70197
C	-1.35986	-0.14504	-1.11867
H	-1.27768	-1.13161	-1.57943
H	-1.39211	0.57505	-1.94023
C	2.53475	-0.44557	-0.47559
H	2.45620	-1.16931	0.34166
H	2.82499	0.50450	-0.02188
C	-2.68287	-0.06791	-0.33242
H	-2.74174	0.90405	

1e

C	0.00001	-0.03080	-0.13133
C	1.26659	-0.89269	-0.23155
H	1.22943	-1.42876	-1.18580
H	1.22881	-1.64539	0.56169
C	-1.26656	-0.89271	-0.23152
H	-1.22878	-1.64538	0.56175
H	-1.22939	-1.42882	-1.18575
C	2.57967	-0.10174	-0.12872
H	2.63145	0.40093	0.84112
H	2.57973	0.67290	-0.90500
C	-2.57966	-0.10176	-0.12874
H	-2.57973	0.67282	-0.90508

0.16505
H -2.71154 -0.83379
0.44971
C -3.86942 -0.23456 -
1.23970
H -3.97856 0.51995 -
2.01773
C 3.59979 -0.89026 -
1.43918
H 3.78258 -0.22761 -
2.28474
C 4.31764 -2.00677 -
1.33339
H 4.17964 -2.69724 -
0.50614
H 5.07761 -2.26547 -
2.06209
C -4.76889 -1.21299 -
1.15862
H -5.60742 -1.27326 -
1.84338
H -4.70483 -1.98281 -
0.39483
C -0.13476 -0.50641
1.08767
C 0.01033 1.67667 -
0.06231
O 1.16052 2.04591
0.52090
O -0.32874 0.15811
2.07167
O -0.84310 2.46167 -
0.39421
C 1.27352 3.43932
0.87191
H 0.48975 3.70822
1.58057
H 2.25469 3.54296
1.32963
H 1.19203 4.06634 -
0.01665
O -0.02648 -1.92054
1.27049
C -0.20573 -2.23822
2.65318
H -0.14932 -3.29847
2.78576
H 0.56133 -1.76532
3.23014
H -1.16332 -1.88857
2.97824

H -2.63144 0.40096
0.84106
C -3.78782 -0.97662 -
0.31141
H -3.86311 -1.48752 -
1.27100
C 3.78785 -0.97656 -
0.31143
H 3.86316 -1.48740 -
1.27105
C 4.74304 -1.17125
0.59549
H 4.71183 -0.68716
1.56736
H 5.58996 -1.81948
0.39974
C -4.74301 -1.17127
0.59552
H -5.58992 -1.81952
0.39980
H -4.71181 -0.68711
1.56735
O 0.00001 0.68456
1.10748
O 0.00001 0.94852 -
1.17404
C 0.00006 2.09126 0.88974
H -0.88855 2.52844
1.35529
H 0.88886 2.52835 1.35502
C -0.00017 2.26864 -
0.64046
H 0.88841 2.80047 -
0.99386
H -0.88904 2.80016 -
0.99363

Rotational energies for 1a-1e

1a		1b	
Angle	Energy (a.u)	Angle	Energy (a.u)
-179.964	-352.6558313	-180.285	-451.9283047
-171.605	-352.6555624	-172.547	-451.9279916
-163.198	-352.6548012	-164.250	-451.9269954
-153.659	-352.6537149	-155.523	-451.9255246
-143.170	-352.6525192	-145.432	-451.9237942
-131.797	-352.6515666	-134.038	-451.9223436
-119.459	-352.6511801	-121.270	-451.9215244
-107.370	-352.6514441	-108.597	-451.9216932
-96.500	-352.6522392	-97.134	-451.9226672
-87.309	-352.6531762	-87.034	-451.9239951
-78.985	-352.6539396	-78.271	-451.9253230
-70.668	-352.6543899	-69.749	-451.9263181
-62.683	-352.6544449	-61.449	-451.9268735
-54.913	-352.6539061	-53.304	-451.9268009
-46.984	-352.6527711	-45.216	-451.9260293
-38.503	-352.6511323	-36.724	-451.9246526
-28.620	-352.6492558	-27.465	-451.9229226
-16.808	-352.6475799	-16.751	-451.9212259
-2.076	-352.6467547	-4.452	-451.9201148
13.220	-352.6472572	9.388	-451.9200634
26.027	-352.648809	22.170	-451.9210886
36.423	-352.6506971	33.554	-451.9227098
45.503	-352.6524072	43.972	-451.9244413
53.836	-352.6536561	53.300	-451.9258403
62.013	-352.6542947	62.304	-451.9266590
70.325	-352.6543676	71.292	-451.9268520
78.765	-352.6539753	80.216	-451.9265168
87.155	-352.6532454	89.271	-451.9257760
96.751	-352.6522972	98.682	-451.9248427
107.601	-352.6514952	109.210	-451.9240029
119.462	-352.6512007	120.417	-451.9236255
131.943	-352.6515665	132.095	-451.9238964
143.414	-352.6524856	143.107	-451.9247830
153.914	-352.6536694	153.626	-451.9259711
163.003	-352.6547929	162.958	-451.9271593
171.745	-352.6555567	171.677	-451.9279976
180.041	-352.6558312	179.712	-451.9283047

1c		1e	
Angle	Energy (a.u)	Angle	Energy (a.u)
-179.256	-551.2097073	-184.954	-580.5630165
-171.477	-551.2093756	-174.954	-580.5626784
-163.212	-551.2084686	-164.954	-580.5617529
-154.346	-551.2071454	-154.954	-580.5604967
-143.995	-551.2056825	-144.954	-580.5591820
-132.454	-551.2045309	-134.954	-580.5582450
-120.5	-551.2040291	-124.954	-580.5579009
-108.168	-551.2044094	-114.954	-580.5581629
-97.0802	-551.2054381	-104.954	-580.5591817
-87.277	-551.2067396	-94.954	-580.5606362
-78.5122	-551.2079073	-84.954	-580.5620508
-69.9539	-551.2086600	-74.954	-580.5629771
-61.549	-551.2089092	-64.954	-580.5632121
-53.2186	-551.2084890	-54.954	-580.5627327
-44.6027	-551.2074134	-44.954	-580.5615717
-35.3313	-551.2058651	-34.954	-580.5599044
-25.125	-551.2041348	-24.954	-580.5580934
-13.5568	-551.2026903	-14.954	-580.5565954
-0.59065	-551.2020731	-4.954	-580.5557730
12.60209	-551.2025893	5.046	-580.5560498
24.30318	-551.2039590	15.046	-580.5573230
34.70406	-551.2056170	25.046	-580.5591901
44.21369	-551.2071509	35.046	-580.5611020
53.09049	-551.2082041	45.046	-580.5626054
61.82354	-551.2086307	55.046	-580.5633691
70.41695	-551.2083939	65.046	-580.5632666
79.19634	-551.2076200	75.046	-580.5624989
88.27514	-551.2064088	85.046	-580.5613055
98.32812	-551.2051201	95.046	-580.5598333
109.8903	-551.2041345	105.046	-580.5585031
122.0624	-551.2038787	115.046	-580.5577591
134.0159	-551.2044621	125.046	-580.5578503
145.2761	-551.2056444	135.046	-580.5587426
155.4278	-551.2071290	145.046	-580.5601166
164.5491	-551.2084563	155.046	-580.5615742
172.9152	-551.2093808	165.046	-580.5626336
180.7442	-551.2097073	175.046	-580.5630164

1d			
Angle	Energy (a.u)	Angle	Energy (a.u)
181.757	-808.5275066	-8.243	-808.5214351
176.757	-808.5274610	-13.243	-808.5219539
171.757	-808.5273026	-18.243	-808.5227095
166.757	-808.5270416	-23.243	-808.5236048
161.757	-808.5266626	-28.243	-808.5245938
156.757	-808.5261488	-23.243	-808.5236048
151.757	-808.5255254	-28.243	-808.5245938
146.757	-808.5248024	-33.243	-808.5256009
141.757	-808.5239611	-38.243	-808.5265348
136.757	-808.5230650	-43.243	-808.5273620
131.757	-808.5221957	-48.243	-808.5280312
126.757	-808.5214157	-53.243	-808.5285220
121.757	-808.5207870	-58.243	-808.5288260
116.757	-808.5203776	-63.243	-808.5289173
111.757	-808.5202059	-68.243	-808.5287781
106.757	-808.5202504	-73.243	-808.5284352
101.757	-808.5205129	-78.243	-808.5278927
96.757	-808.5209477	-83.243	-808.5271716
91.757	-808.5215333	-88.243	-808.5263289
86.757	-808.5222634	-93.243	-808.5254018
81.757	-808.5230355	-98.243	-808.5244756
76.757	-808.5238029	-103.243	-808.5236367
71.757	-808.5245670	-108.243	-808.5229547
66.757	-808.5254224	-113.243	-808.5224710
61.757	-808.5261810	-118.243	-808.5222216
56.757	-808.5267090	-123.243	-808.5222112
51.757	-808.5269538	-128.243	-808.5224290
46.757	-808.5269063	-133.243	-808.5228505
41.757	-808.5266328	-138.243	-808.5234169
36.757	-808.5261292	-143.243	-808.5240668
31.757	-808.5254298	-148.243	-808.5247802
26.757	-808.5246237	-153.243	-808.5255379
21.757	-808.5237557	-158.243	-808.5262433
16.757	-808.5229134	-163.243	-808.5268217
11.757	-808.5221692	-168.243	-808.5271897
6.757	-808.5215983	-173.243	-808.5274510
1.757	-808.5212504	-178.243	-808.5275066
-3.243	-808.5211913		

XYZ coordinates of compounds 2a-2e

2a				2b			
C	-0.66691	1.54461	-0.15640	C	-1.91891	-0.66764	-0.21134
H	-1.16944	2.43313	-0.53115	H	-2.78327	-1.17266	-0.63473
C	0.66837	1.54399	-0.15640	C	-1.91891	0.66764	-0.21134
H	1.17174	2.43204	-0.53113	H	-2.78327	1.17266	-0.63473
C	-1.56224	0.43003	0.33455	C	-0.82880	-1.55891	0.33634
H	-1.47485	0.34659	1.42786	H	-0.80270	-1.47991	1.43257
H	-2.60256	0.70775	0.14148	H	-1.08545	-2.59953	0.12370
C	1.56265	0.42856	0.33455	C	-0.82880	1.55891	0.33634
H	2.60323	0.70529	0.14148	H	-1.08545	2.59953	0.12370
H	1.47519	0.34519	1.42786	H	-0.80270	1.47991	1.43257
C	-1.30220	-0.95559	-0.28474	C	0.58586	-1.29453	-0.21611
H	-2.13929	-1.61002	-0.01565	H	1.24560	-2.11139	0.09225
H	-1.31597	-0.86773	-1.37766	H	0.56509	-1.28979	-1.31057
C	1.30129	-0.95682	-0.28475	C	0.58586	1.29453	-0.21611
H	1.31513	-0.86898	-1.37767	H	0.56509	1.28979	-1.31057
H	2.13775	-1.61205	-0.01567	H	1.24560	2.11139	0.09225
C	-0.00077	-1.63819	0.15973	C	1.21495	0.00000	0.27615
H	-0.00081	-1.72589	1.25503	H	1.25356	0.00000	1.37253
H	-0.00126	-2.66485	-0.22401	F	2.56894	0.00000	-0.14918

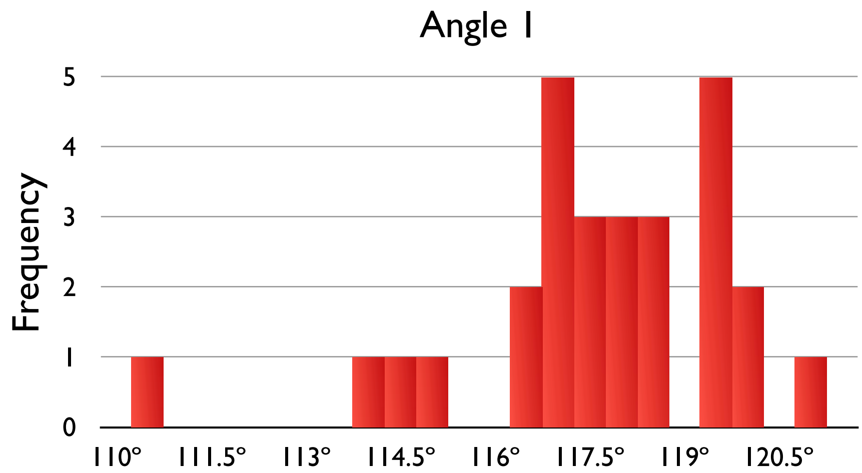
2c				2d				2e			
C	-2.09670	-0.66760	-0.18870	C	0.00000	1.58985	2.15337	C	-2.70300	-0.65097	-0.01510
H	-2.97999	-1.17992	-0.56037	H	0.49464	2.51816	2.45868	H	-3.63659	-1.14221	-0.27739
C	-2.09673	0.66740	-0.18880	H	-1.01559	1.89227	1.87377	C	-2.69519	0.68121	0.07118
H	-2.98007	1.17962	-0.56049	C	0.75351	1.05659	0.92365	H	-3.62250	1.21320	-0.12594
C	-0.96278	-1.53985	0.29650	H	1.69701	0.61748	1.26320	C	-1.51268	-1.54619	0.23481
H	-0.81724	-1.40482	1.37493	H	1.01020	1.88992	0.26865	H	-1.20699	-1.47722	1.28609
H	-1.23402	-2.58899	0.15880	C	0.00000	0.00000	0.07291	H	-1.81036	-2.58547	0.07300
C	-0.96298	1.53984	0.29647	C	-0.75351	-1.05659	0.92365	C	-1.49263	1.52280	0.42645
H	-1.23439	2.58892	0.15866	H	-1.01020	-1.88992	0.26865	H	-1.77454	2.57830	0.38875
H	-0.81758	1.40488	1.37493	H	-1.69701	-0.61748	1.26320	H	-1.18587	1.32646	1.46086
C	0.38446	-1.30800	-0.41333	C	0.00000	-1.58985	2.15337	C	-0.27919	-1.26548	-0.64406
H	1.08581	-2.10169	-0.14076	H	-0.49464	-2.51816	2.45868	H	0.42761	-2.09472	-0.54306
H	0.25394	-1.34149	-1.49832	H	1.01559	-1.89227	1.87377	H	-0.56565	-1.21838	-1.69907
C	0.38447	1.30825	-0.41311	C	0.02023	-0.66722	3.34986	C	-0.26958	1.32400	-0.48942
H	0.25417	1.34206	-1.49810	H	0.04842	-1.16622	4.31606	H	-0.57139	1.38970	-1.53881
H	1.08566	2.10188	-0.14004	C	-0.02023	0.66722	3.34986	H	0.44746	2.12995	-0.30544
C	1.07322	0.00005	-0.06656	H	-0.04842	1.16622	4.31606	C	0.49455	0.01075	-0.30047
F	2.31219	0.00001	-0.69504	C	1.02965	-0.69677	-0.83165	O	1.66614	0.02735	-1.13622
F	1.35958	-0.00011	1.29458	C	-1.02965	0.69677	-0.83165	O	0.97675	-0.04180	1.05462
				O	1.55760	0.17698	-1.71337	C	2.37391	-0.32885	1.02167
				O	1.36227	-1.85299	-0.76359	H	2.83968	0.13503	1.89245
				O	-1.55760	-0.17698	-1.71337	H	2.55147	-1.41139	1.04769
				O	-1.36227	1.85299	-0.76359	C	2.80101	0.27463	-0.30937
				C	-2.55583	0.34795	-2.60951	H	2.99409	1.35125	-0.21845
				H	-3.41070	0.72578	-2.04722	H	3.66720	-0.21033	-0.76191
				H	-2.84996	-0.48968	-3.23789				
				H	-2.13715	1.15450	-3.21267				

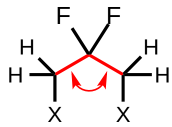
C	2.55583	-0.34795	-2.60951
H	2.84996	0.48968	-3.23789
H	2.13715	-1.15450	-3.21267
H	3.41070	-0.72578	-2.04722

Electronic Supplementary Material (ESI) for Chemical Communications

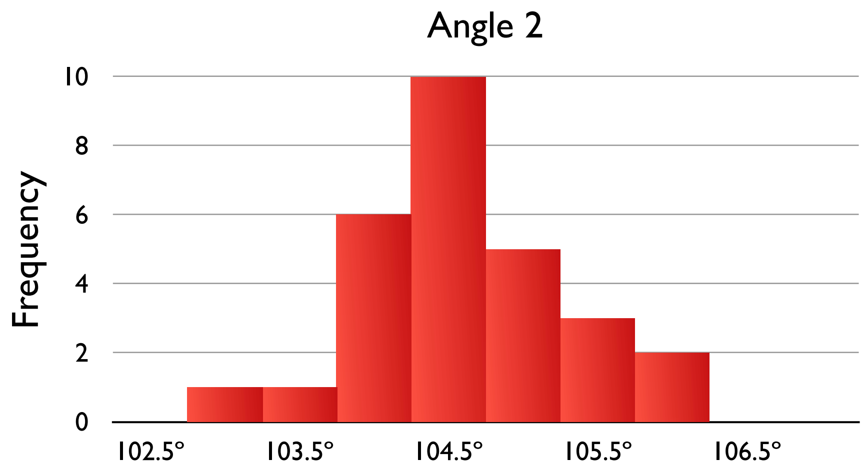
Cambridge Structural Database (CSD) Search

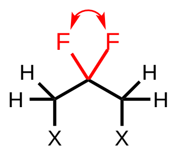
The Cambridge Structure Database (CSD) Search was conducted on 29.04.2013 using ConQuest and Mercury software. Histograms and a statistical summary of the relevant angles were obtained for organic species containing the specified motifs.





ANG 1

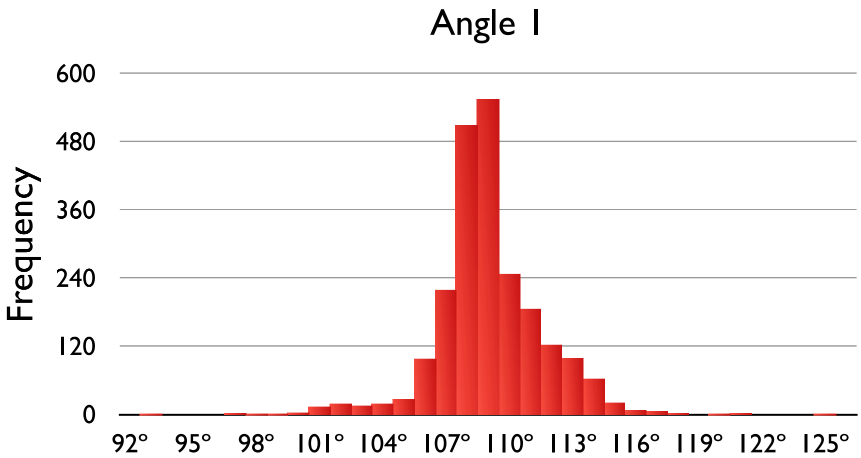


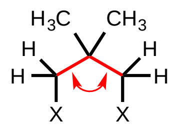


ANG 2

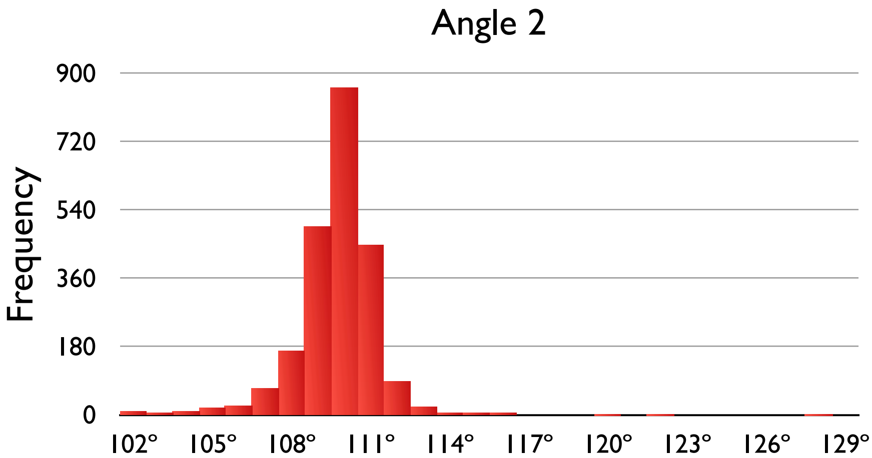
	max	min	range	count	average	st. dev.
ANG 1	120.73	110.42	10.31	28	117.34	2.17
ANG 2	105.83	102.93	2.89	28	104.33	0.67

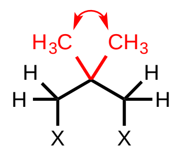
Electronic Supplementary Material (ESI) for Chemical Communications





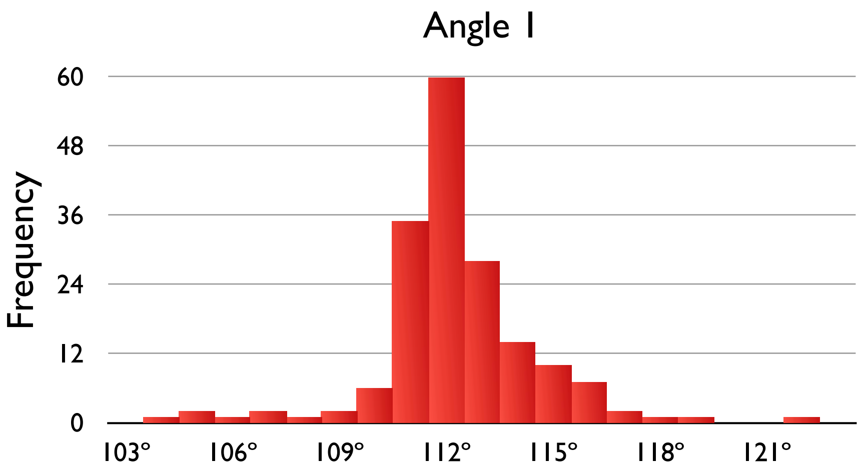
ANG 1

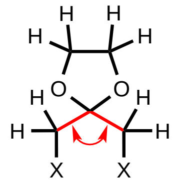




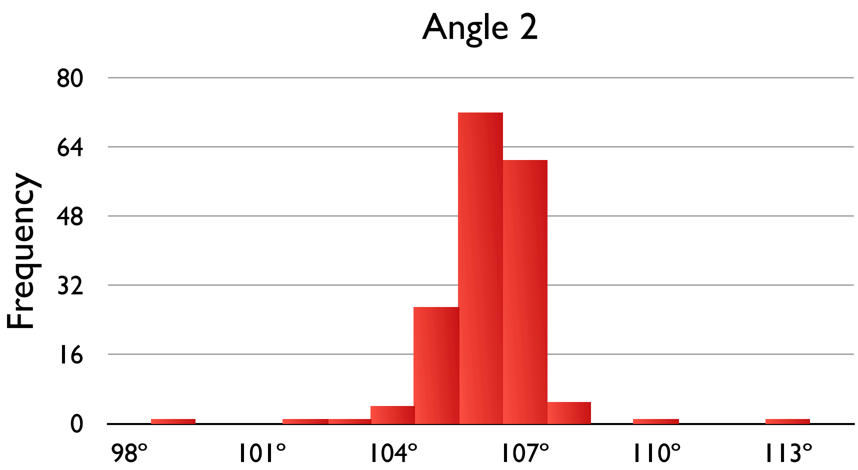
ANG 2

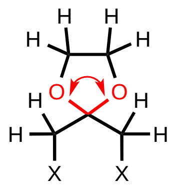
	max	min	range	count	average	st. dev.
ANG 1	124.42	92.72	31.70	2241	108.57	2.50
ANG 2	127.45	102.25	25.20	2241	109.24	1.61





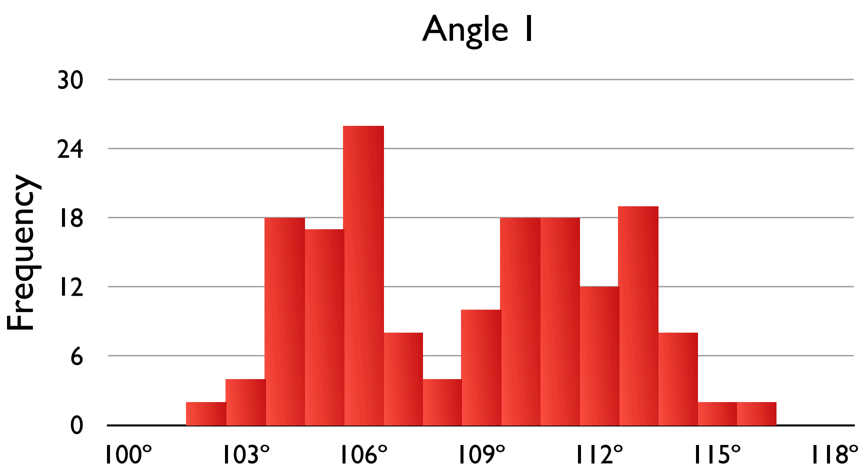
ANG I

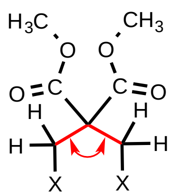




ANG 2

	max	min	range	count	average	st. dev.
ANG 1	121.27	103.75	17.52	174	111.79	2.18
ANG 2	112.60	98.91	13.69	174	105.68	1.15





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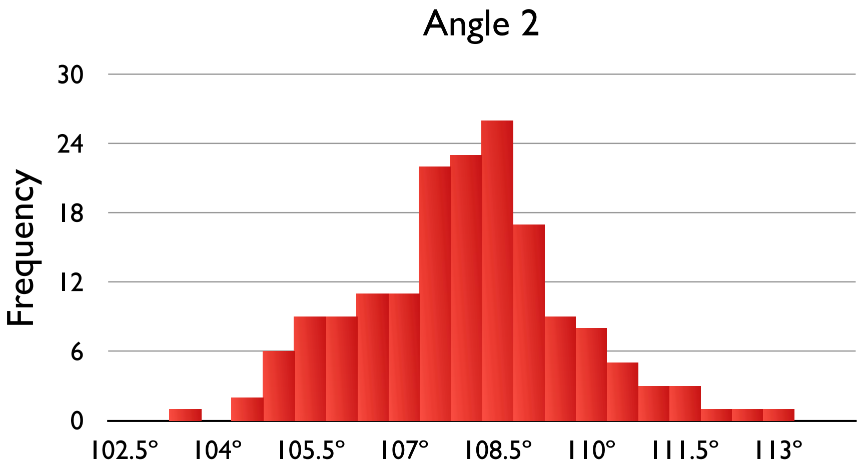

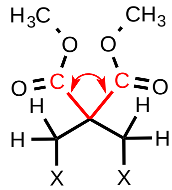

	max	min	range	count	average	st. dev.
ANG 1	115.97	101.45	14.52	168	108.12	3.55
ANG 2	112.67	103.30	9.38	168	107.72	1.65

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(3) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098-3100; (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789; (c) Vosko, S. H.; Wilk, L.; Nusair, M. *Canadian Journal of Physics* **1980**, *58*, 1200-1211; (d) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *The Journal of Physical Chemistry* **1994**, *98*, 11623-11627.