

A Computational Triage Approach into the Synthesis of Novel Difluorocyclopentenes and Fluorinated Heptadienes using Thermal Rearrangements

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General Experimental

NMR spectra were recorded on Bruker DPX-400, AV-500 Avance-II+ 600 spectrometers. ^1H , ^{19}F and ^{13}C NMR spectra were recorded using the deuterated solvent as the lock and the residual solvent as the internal reference. The multiplicities of the spectroscopic data are presented in the following manner: s = singlet, d = doublet, dd = double doublet, ddd = doublet of double doublets, etc up to ddddd, dt = doublet of triplets, ddt = doublet of double triplet, dddt = doublet of double double triplet, dq = doublet of quartet; t = triplet, td = triple doublet; tt = triple triplet, q = quartet, ABq = AB system quartet, m = multiplet and br. = broad. Unless stated otherwise, all couplings refer to 3J homocouplings. All ^1H spectra are fully assigned as much as possible. Relevant 2D-NMR spectra are supplied to confirm assignment.

IR spectra were recorded on a Shimadzu IRAffinity-1 FT-IR Spectrophotometer using a MIRacle™ Single Reflection Horizontal ATR Accessory.

GC/MS spectra were obtained on an Agilent 7890A GC System fitted with a DB5-type column (30 m $\times$ 0.25 μm) running a 40–320 $^{\circ}\text{C}$ temperature program, ramp rate 20 $^{\circ}\text{C min}^{-1}$ with helium carrier gas flow at 1 $\text{cm}^3 \text{min}^{-1}$. Chemical ionisation (CI) (methane) mass spectra were recorded on an Agilent Technologies 5975C mass spectrometer.

HRMS measurements were obtained from a Waters GCT Premier MS (CI-MS), Finnigan MAT 95 XP (EI-MS and/or APCI-MS) or Thermo Scientific LTQ Orbitrap XL via Advion TriVersa NanoMate infusion (NSI-ES) spectrometers (EPSRC National Mass Spectrometry Service Centre, Swansea).

Melting points were recorded on a Griffin melting point apparatus and are uncorrected.

Thin layer chromatography was performed on pre-coated aluminium-backed silica gel plates (E.Merck, A.G.Darmstadt, Germany. Silica gel 60 F254, thickness 0.2 mm). Visualisation was achieved using potassium permanganate or UV detection at 254 nm. Column

chromatography was performed on silica gel (Zeochem, Zeoprep 60 HYD, 40-63 μm) using a Büchi Sepacore system. Hexane was distilled before chromatography.

Preparative HPLC was performed using Grace Reveleris PREP purification system with a Kromasil 100-10-C18 column (L = 250 mm, ID = 200 mm). Compound was loaded in a minimum volume of 1:1 DMSO:MeOH in a 5 mL sample loop. Flow rates varied depending on separation (5-30 mL/min) and peaks determined using ELSD and UV detection.

Commercial furfural (black) was percolated through a pad of alumina to afford an orange solution which was used immediately in reactions. 2-Formyl-pyrrole-1-carboxylic acid tert-butyl ester **12f** was synthesised from NaH and Boc anhydride using conditions described by Carreira and co-workers.^{S1} 2-thiazolyl-carboxaldehyde **12g** was synthesised from thiazole, BuLi and DMF using conditions described by Glorius and co-workers.^{S2} Due to the volatility of the aldehyde, crude product was used directly in subsequent Wittig olefinations.

Diglyme was distilled from CaH_2 (60 $^\circ\text{C}$ /23 mbar) and stored under nitrogen over CaH_2 . Trimethylsilyl chloride was distilled from CaH_2 (60 $^\circ\text{C}$ /430 mbar) and stored under nitrogen over CaH_2 in the refrigerator. Methyl 2,2-difluoro-2-(fluorosulfonyl)acetate (MDFA) and trimethylsilyl 2,2-difluoro-2-(fluorosulfonyl)acetate (TFDA) were purchased from Fluorochem and stored under a headspace of nitrogen. Potassium iodide (Sigma Aldrich) and magnesium sulfate (MgSO_4 , VWR Chemicals) were dried in the oven (150 $^\circ\text{C}$) before use. DCM (for tandem oxidation/olefination, acetylation and cyclopropanation reactions) and toluene (for reduction reactions) were dried using a PureSolv system from Innovative Technology, Inc..

All other chemicals were purchased from Sigma Aldrich, Apollo Scientific, Alfa Aesar, or Fluorochem and used as received.

Computational Methodology

Structures were built in Spartan'10 using previously published compounds as models and geometry optimisation calculations were carried out for all closed shell compounds. For known diradical compounds unrestricted methodology was invoked using the keywords MIX and SCF=UNRESTRICTED, with CONVERGE deprecated. In cases where SCF convergence was difficult, the keyword NODIIS was used. All calculations were performed *in vacuo*. Spartan'10 was run on a Dell Precision T7500 (2 x Intel E5530 processors, four cores each, 2.40 GHz) with 24 GB RAM Debian GNU/Linux 5.

The calculation methods used in Spartan have been documented in: Y. Shao, L.F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S.T. Brown, A.T.B. Gilbert, L.V. Slipchenko, S.V. Levchenko, D.P. O'Neill, R.A. DiStasio Jr., R.C. Lochan, T. Wang, G.J.O. Beran, N.A. Besley, J.M. Herbert, C.Y. Lin, T. Van Voorhis, S.H. Chien, A. Sodt, R.P. Steele, V.A. Rassolov, P.E. Maslen, P.P. Korambath, R.D. Adamson, B. Austin, J. Baker, E.F.C. Byrd, H. Dachsel, R.J. Doerksen, A. Dreuw, B.D. Dunietz, A.D. Dutoi, T.R. Furlani, S.R. Gwaltney, A. Heyden, S. Hirata, C-P. Hsu, G. Kedziora, R.Z. Khalliulin, P. Klunzinger, A.M. Lee, M.S. Lee, W.Z. Liang, I. Lotan, N. Nair, B. Peters, E.I. Proynov, P.A. Pieniazek, Y.M. Rhee, J. Ritchie, E. Rosta, C.D. Sherrill, A.C. Simmonett, J.E. Subotnik, H.L. Woodcock III, W. Zhang, A.T. Bell, A.K. Chakraborty, D.M. Chipman, F.J. Keil, A. Warshel, W.J. Hehre, H.F. Schaefer, J. Kong, A.I. Krylov, P.M.W. Gill and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, **2006**, *8*, 3172.

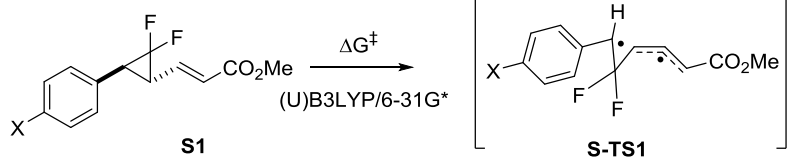
Full reference for the Gaussian09 programme: Gaussian 09, Revision A.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

Hammett Plot Data

The lower activation energy calculated for the more electron rich phenyl-substituted **9f** ($-2.3 \text{ kcal mol}^{-1}$) prompted further investigations into the electronic effects of phenyl ring substitution. The VCPR activation energies for a range of precursors with electron-donating and -withdrawing groups were assessed (**Table S1**), focusing solely on *para*-substituents, since these show the greatest effects for resonance stabilisation of benzylic radicals. Substrates containing electron-donating groups were predicted to undergo faster rearrangement (**Table S1**, Entries 1-6) than unsubstituted **9j** (**Table S1**, Entry 7), whereas substrates bearing electron-withdrawing groups only showed a modest increase in activation energy (**Table S1**, Entries 8-12). The Hammett plot^{S3} (**Figure S1**) constructed from this data gave an extremely low ρ value of 0.05 and supported a radical mechanism. A variety of free radical substituent constants ($\sigma^\bullet$) have been reported in the literature^{S4-7} but only those reported by Creary and co-workers ($\sigma_c^\bullet$) are applicable to the more commonly used substituents.^{S8} Our calculated activation energies correlated poorly when $\sigma_c^\bullet$ constants were used ($R^2 = 0.4259$) but still gave a ρ value close to zero (**Figure S1**). The relatively small increases in activation barriers, suggest that even substrates bearing electron-deficient phenyl rings should undergo VCPR at or close to 100 °C.

Both Hammett plots were generated using Excel from calculated free energies of activation ((U)B3LYP/6-31G*, gas phase, 298 K, kcal mol^{-1}) manipulated into $\log(\Delta G^\ddagger(\text{X})/\Delta G^\ddagger(\text{H}))$ values and literature σ values^{S3} (**Figure S1**) or $\sigma^\bullet$ values^{S8} (**Table S1** and **Figure S2**). Graphs were generated on Excel and a straight line fitted using the trendline function for **Figure S1** and **Figure S2**.

Table S1: Calculated free energies of activation (298 K) and $\sigma^\bullet$ data used to generate Hammett Plot in **Figure S1**.

						
VCP	X	$\Delta G^\ddagger$	$\Delta\Delta G^\ddagger$	$\log \frac{\Delta G(X)}{\Delta G(X=H)}$	σ^{S3}	$\sigma^\bullet$ ref. S8
a	N(Me) ₂	21.2	-4.1	-0.056	-0.83	0.9
b	NH ₂	21.9	-3.4	-0.042	-0.66	0.7
c	OH	23.5	-1.8	-0.011	-0.37	0.26
d	OMe	23.3	-2.0	-0.015	-0.27	0.27
e	NHC(O)Me	23.7	-1.6	-0.007	-0.17	0.34
f	Me	24.5	-0.8	-0.072	0	0.16
9j	H	25.3	0	0.000	0	-
i	Cl	25.3	0	0.021	0.23	0.11
j	Br	25.4	0.1	0.023	0.23	0.11
k	CF ₃	25.4	0.1	0.023	0.54	0.05
l	CN	25.6	0.3	0.026	0.66	0.47
m	NO ₂	25.9	0.6	0.031	0.78	0.57

^[a] $\Delta\Delta G^\ddagger_{B3LYP} = (\Delta G^\ddagger_{B3LYP} \text{ S1x}) - (\Delta G^\ddagger_{B3LYP} \text{ 9j})$

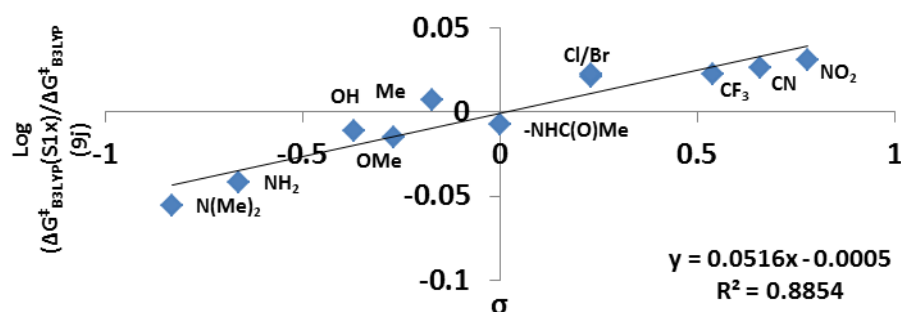


Figure S1: Hammett plot generated from calculated free energies of activation and σ values.

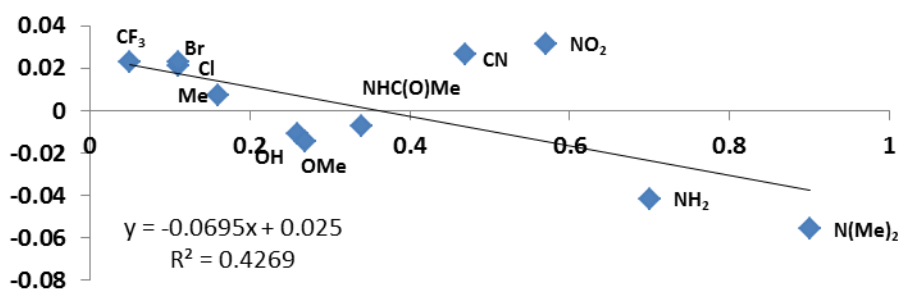
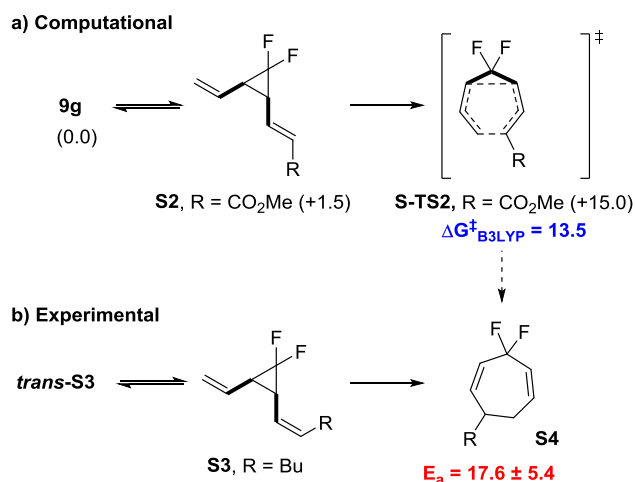


Figure S2: Hammett plot generated from calculated free energies of activation and σ^* values.

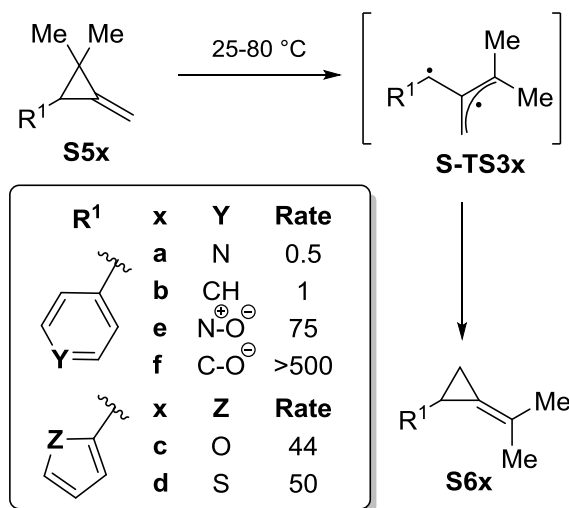
Radical Stabilising Effects

As our prime goal was to lower VCPR reaction temperatures, our screening was directed towards vinyl, (hetero)aryl and alkynyl substituents because the most effective mechanism for radical stabilisation is delocalisation through adjacent π -systems.^{S9,10} The lower activation energy observed for **9g** (ethenyl, 24.5 kcal mol⁻¹) compared with **9j** (phenyl, 25.3 kcal mol⁻¹) and **9l** (ethynyl, 25.9 kcal mol⁻¹) showed good correlation with the increased radical stabilisation energy reported for these substituents (calculated as 17.6, 14.6 and 14.5 kcal mol⁻¹, respectively).^{S10} The higher activation energy observed for **9p** (cyano, 29.3 kcal mol⁻¹) can be rationalised by a decreased radical stabilisation energy (7.9 kcal mol⁻¹),^{S10} which arises from the higher electronegativity of the nitrogen atom. These calculations suggested that *bis*-vinyl VCP-**9g** has the potential to rearrange at temperatures lower than 100 °C, but electronic structure calculations predicted that *cis*-isomer **S2** would favour divinylcyclopropane rearrangement via **S-TS2** ($\Delta G^\ddagger_{\text{B3LYP}} = 13.5$ kcal mol⁻¹, VCPR vs [3,3] difference of 11.5 kcal mol⁻¹, **Scheme S1a**). Erbes and Boland showed experimentally that a similar dialkenyl-substituted *gem*-difluorocyclopropane (**S3**) exclusively favoured the [3,3]-pathway through to heptadiene **S4** (**Scheme S1b**).^{S11} Dialkenyl-**9g** was omitted from any subsequent synthetic investigations due to the unlikelihood of selective VCPR.



Scheme S1: a) Predicted lower energy [3,3]-pathway for bis-vinyldifluorocyclopropane **S2** (free energies are relative to **9h**). b) Experimental example of preferential divinylcyclopropane rearrangement from bis-vinyldifluorocyclopropane **S3** to difluoroheptadiene **S4**^{S11} (experimental activation energy (E_a) is derived from an Arrhenius determination of reported kinetic data^{S11}).

Of the heteroaromatic substituents examined, only the 2- and 4-pyridyl species gave higher VCPR barriers compared with **9j** (**9o**, +2.9 kcal/mol⁻¹ and **9m**, +1.1 kcal/mol⁻¹); the nitrogen atom cannot help stabilise radicals in these cases. Creary and co-workers reported similar results during investigations into the radical rearrangement of methylenecyclopropane **S5** to isopropylidenecyclopropane **S6** (Scheme S2).^{S8,12}



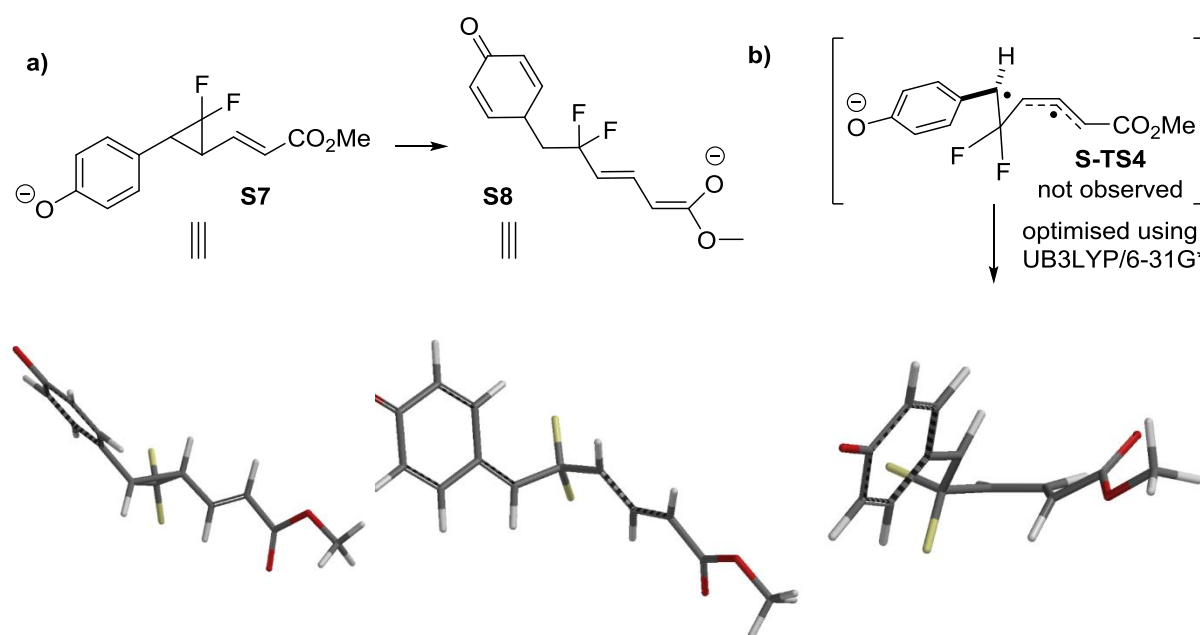
Scheme S2: Substituent group radical stability determined from the rate of rearrangement of **S5** to **S6**.^{S8}

They reported higher rearrangement rates when heterocycles **S5c-e** and phenolate **S5f** were present. These substituents were dubbed “super radical stabilisers”. Unfortunately all computational attempts at incorporating the most strongly-activating 4-phenoxide

substituent into a VCPR failed; a diradicaloid transition state could not be obtained. Ring opening occurred via a donor-acceptor mechanism when the rearrangement precursor was optimised^{S13,14} (*vide infra*).

Computational Searches Involving Phenolate S7

Intermediate VCP **S7** and transition state **S-TS4** were built from previously optimised structure of phenyl VCP **9j** and **TS1j** and optimised using B3LYP/6-31G* or UB3LYP/6-31G*, respectively (Spartan'10, gas phase, 298 K, multiplicity = 1). It was observed that closed shell intermediate **S7** optimised to ring opened cyclopropane intermediate **S8** (Scheme **S3a**); desired VCP **S7** was never observed after optimisation. An optimised transition state structure could be obtained from **S-TS4** ($\nu_i = i107\text{ cm}^{-1}$) but the lack of diradical character ($S^2 = 0.0001$) suggested that the process had a donor-acceptor mechanism rather than VCPR (Scheme **S3b**).



Scheme S3: Failed attempts at obtaining optimised structures for a) intermediate **S7** and b) transition state **STS4**. The resulting structures strongly suggest the process proceeds *via* a donor-acceptor mechanism.

Regioselectivity with Heteroarene Precursors

When, the heteroarenes were embedded in our VCPR system, the calculated activation energies (for **9b-9d**) were consistently lower (ranging from -5.3 to -4.2 kcal mol⁻¹ lower) than for phenyl **9j**. Two regioisomeric transition-states exist for the unsymmetrical species; the 2-pyrrolyl and 2-thiophenyl species favoured **TS1a** whilst the 2-furyl favoured **TS1b** (**Figure S3a**).

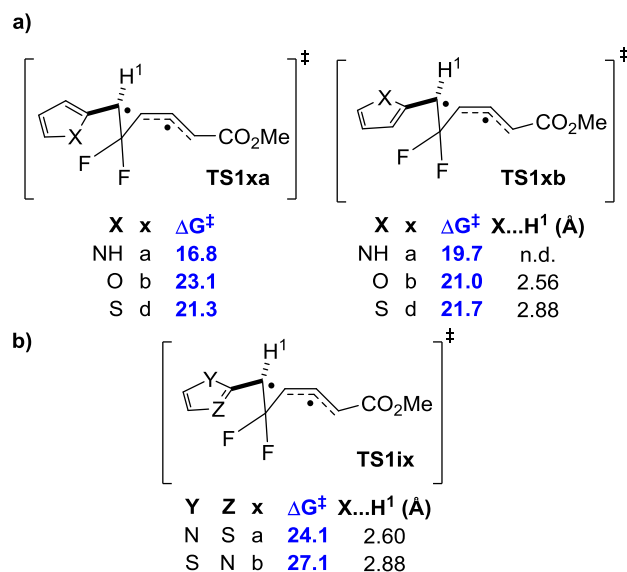


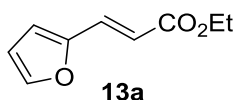
Figure S3: Two alternative VCPR transition states available for difluoro-VCPR substituted with heteroarenes ($\Delta G^\ddagger$ energies calculated on Spartan'10, (U)B3LYP/6-31G*, 298 K, gas phase, energies quoted in kcal mol⁻¹).

We propose that the lower energies observed for **TS1bb** compared with **S-TS1ba** arose from a complementary polar interaction between the δ^+ proton (H¹) and the oxygen atom in the furan ring (calculated distances are within the sum of the Van der Waals radii used in Spartan'10). The absence of additional stabilisation observed in **S-TS1cb** over **S-TS1ca** can be attributed to lower strength S...H interactions. This was consistent with calculated activation energies for thiazolyl **TS1i**, favouring the stronger N...H interaction over S...H (**Figure S3b**).^{S15} Furthermore, 2-pyrrolyl **9a** favoured **S-TS1xa** due to an unfavourable N-H...H interaction in **S-TS1ab**. The extra stabilisation experience by furyl **9b** over thiophenyl **XXc** offered some explanation as to why our calculated rearrangement rates were ordered differently from those reported by Creary and co-workers. Our lowest calculated activation energy was observed with 2-pyrrolyl **9a** (-8.5 kcal mol⁻¹), a substituent which to our knowledge has not previously been reported as a strong radical stabiliser.

Synthetic Procedures

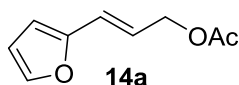
General Procedure A: Synthesis of Alkenoates from Commercial Aldehydes

Preparation of ethyl 3-(2'-furyl) prop-2*E*-enoate (**13a**)



(Carbethoxymethylene)triphenylphosphorane (3.7 g, 10.4 mmol) was added to a solution of furfural **12a** (0.79 mL, 9.5 mmol) in anhydrous DCM (50 mL) and the reaction mixture stirred at room temperature under nitrogen for 7 hours. An aliquot was taken and TLC confirmed full conversion of aldehyde. The reaction mixture was concentrated under reduced pressure and column chromatography on silica gel (1:9 Et₂O in hexane) afforded alkenoate **13a** (1.36 g, 82%) as a yellow oil. R_f = 0.31 (1:4 Et₂O in hexane); ¹H NMR (400 MHz, CDCl₃): δ = 7.49 (d, J = 1.8 Hz; ArH, 1H), 7.45 (d, J = 15.8 Hz, ArCH=CH, 1H), 6.62 (d, J = 3.4 Hz, ArH, 1H), 6.48 (dd, J = 3.4, 1.8 Hz, ArH, 1H), 6.33 (d, J = 15.8 Hz, ArCH=CH, 1H), 4.26 (q, J = 7.1 Hz, OCH₂CH₃, 2H), 1.34 ppm (t, J = 7.1 Hz, OCH₂CH₃, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 166.5, 150.5, 144.1, 130.4, 115.5, 114.0, 111.7, 59.9, 13.8 ppm; $\bar{\nu}$ /(film) = 2361, 2342, 1703, 1638, 1302, 1258, 1207, 1159, 1017 cm⁻¹; MS (CI): m/z (%): 195 (12) [M+C₂H₅]⁺, 167 (100) [M+H]⁺, 139 (61), 121 (80) [M-OEt]⁺; t_R (GC) = 9.62 minutes. The data was in agreement with that reported by Lebel and Davi.^{S16}

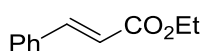
Preparation of (*E*)-3-(furan-2-yl)allyl acetate (**14a**)



Diisobutylaluminum hydride (14.0 mL of a 1.1 M solution in cyclohexane, 15.0 mmol)) was added dropwise to a solution of ester **13a** (1.12 g, 5.0 mmol) in anhydrous toluene (40 mL) under nitrogen at 0 °C for 10 minutes. The reaction mixture was allowed to warm to room temperature and stirred for a further 8 hours, cooled to 0 °C and quenched by dropwise addition of H₂O (1 mL), 0.1 M aqueous NaOH (1 mL) and H₂O (1 mL) in that order. MgSO₄ was added to quenched mixture until the solid was free flowing and the mixture was left overnight at room temperature (17 h). The resulting white emulsion was washed with EtOAc (3 x 50 mL) and the organic extracts were combined and concentrated under reduced

pressure. ^1H NMR spectrum confirmed full conversion to the corresponding alcohol (603 mg, 97%) which was directly acetylated without further purification. Acetic anhydride (0.78 ml, 8.3 mmol) was added dropwise to a solution of crude alcohol (860 g, 6.9 mmol) and pyridine (0.67 ml, 8.3 mmol) in DCM (7 mL) under nitrogen and the reaction mixture was heated to 45 °C for 5 hours. The TLC of the reaction mixture showed complete consumption of alcohol. H_2O (20 mL) was added to the reaction mixture and the organic layer separated. The aqueous layer was extracted with DCM (2 x 10 mL) and the organic layer and extracts were combined and backwashed with HCl (2 x 20 mL of a 1 M aqueous solution), NaOH (3 x 20 mL of a 10 M aqueous solution) and aqueous NaCl (20 mL) in that order. The resulting organic layer was dried (MgSO_4) and concentrated under reduced pressure. Any remaining pyridine in the resulting oil was removed by co-evaporation with toluene (2 x 25 mL) to afford acetate **14a** as a colourless oil (950 g, 83%). R_f = 0.43 (1:4 Et_2O in hexane); ^1H NMR (400 MHz, CDCl_3): δ = 7.37 (d, J = 1.8 Hz, ArH, 1H), 6.49 (dt, J = 15.8 Hz, 4J = 1.3 Hz, ArCH=CHCH₂, 1H), 6.40 (dd, J = 3.5, 1.8 Hz, ArH, 1H), 6.30 (d, J = 3.4 Hz, ArH, 1H), 6.23 (dt, J = 15.8, 6.5 Hz, CH=CHCH₂, 1H), 4.72 (dd, J = 6.4 Hz, 4J = 1.3 Hz, CH₂OAc, 2H), 2.12 ppm (s, COCH₃, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ = 170.3, 151.3, 141.9, 121.6, 121.2, 110.9, 108.4, 64.1, 20.5 ppm; $\bar{\nu}$ /(film) = 2359, 1734, 1377, 1360, 1223, 1013 cm^{-1} ; MS (CI): m/z (%): 166 (5) [M], 123 (8) [M-COMe]⁺, 107 (100) [M-OAc]⁺, 61 (75); t_R (GC) = 10.26 minutes. The data were in agreement with those reported by Iwasaki and co-workers.^{S17}

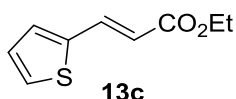
Preparation of cinnamyl acetate (**13b**)



13b

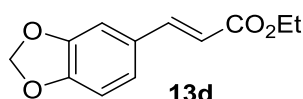
Ester **13b** was prepared from benzaldehyde **12b** (1.06 ml, 10 mmol), (carbethoxymethylene)triphenylphosphorane (3.83 g, 11.0 mmol) and DCM (20 ml) according to General Procedure A. Column chromatography on silica gel (1:4 Et_2O in hexane) afforded ester **13b** as a yellow oil (930 mg, 87%). ^1H NMR data was consistent with a commercial sample.

Preparation of ethyl 3-(2'-thiophenyl)-prop-2E-enoate (**13c**)



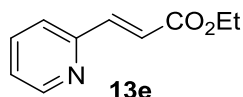
Ester **13c** was prepared from thiophene-2-carbaldehyde **12c** (0.92 ml, 10 mmol), (carbethoxymethylene)triphenylphosphorane (4.6 g, 11.2 mmol) and DCM (30 ml) over 20 hours according to General Procedure A. Column chromatography on silica gel (1:4 Et₂O in hexane) afforded ester **13c** as a yellow oil (1.79 g, 98%). *R_f* = 0.31 (1:1 Et₂O in hexane); ¹H NMR (400 MHz, CDCl₃): δ = 7.81 (d, *J* = 15.7 Hz, ArCH=CH, 1H), 7.39 (d, *J* = 5.1 Hz, ArH, 1H), 7.27 (d, *J* = 3.6 Hz, ArH, 1H), 7.07 (dd, *J* = 5.1, 3.6 Hz, ArH, 1H), 6.26 (d, *J* = 15.7 Hz, ArCH=CH, 1H), 4.27 (q, *J* = 7.0 Hz, OCH₂CH₃, 2H), 1.35 ppm (t, *J* = 7.0 Hz, OCH₂CH₃, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 166.4, 139.1, 136.5, 130.3, 127.8, 127.6, 116.5, 60.0, 13.8 ppm; $\bar{\nu}$ /(film) = 2358, 2342, 1703, 1624, 1369, 1304, 1202, 1159, 1042 cm⁻¹; MS (CI): *m/z* (%): 211 (13) [M+C₂H₅]⁺, 183 (100) [M+H]⁺, 137 (80) [M-OEt]⁺; *t_R* (GC) = 11.85 minutes. The data was in agreement with that reported by Lebel and Davi.^{S16}

Preparation of ethyl 3-(5'-benzo[d][1,3]dioxolyl)-prop-2E-enoate (**13d**)



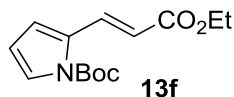
Ester **13d** was prepared from benzo[d][1,3]dioxole-5-carbaldehyde **12d** (1.39 g, 6.3 mmol), (carbethoxymethylene)triphenylphosphorane (3.47 g, 8.4 mmol) and DCM (30 ml) over 18 hours according to General Procedure A. Column chromatography on silica gel (1:4 Et₂O in hexane) afforded ester **13d** as a white solid (1.88 g, 98%). m.p. = 63-65 °C (obtained from powdered solid isolated after chromatography); *R_f* = 0.38 (1:4 Et₂O in hexane); ¹H NMR (400 MHz, CDCl₃): δ = 7.63 (d, *J* = 15.9 Hz, ArCH=CH, 1H), 7.06 (d, ⁴*J* = 1.6 Hz, ArH, 1H), 7.03 (dd, *J* = 8.1, ⁴*J* = 1.6 Hz, ArH, 1H), 6.83 (d, *J* = 8.1 Hz, ArH, 1H), 6.29 (d, *J* = 15.9 Hz, ArCH=CH, 1H), 6.03 (s, O₂CH₂, 2H), 4.28 (q, *J* = 7.1 Hz, OCH₂CH₃, 2H), 1.35 ppm (t, *J* = 7.1 Hz, OCH₂CH₃, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 166.7, 149.1, 147.8, 143.8, 128.4, 123.9, 115.7, 108.1, 106.0, 101.1, 59.9, 13.9 ppm; $\bar{\nu}$ /(film) = 2359, 2342, 1701, 1632, 1489, 1445, 1236, 1163 cm⁻¹; MS (CI): *m/z* (%): 249 (19) [M+C₂H₅]⁺, 221 (95) [M+H]⁺, 193 (12), 175 (100) [M-OEt]⁺, 147 (10) [M-CO₂Et]⁺; *t_R* (GC) = 13.91 minutes. The data was in agreement with that reported by Lebel and Davi.^{S16}

Preparation of ethyl 3-(2'-pyridyl)-prop-2E-enoate (**13e**)



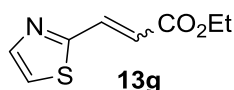
Ester **13e** was prepared from picolinaldehyde **12e** (0.57 ml, 6 mmol), (carbethoxymethylene)triphenylphosphorane (2.7 g, 6.6 mmol) and DCM (25 ml) according to General Procedure A. Column chromatography on silica gel (1:1 Et₂O in hexane) afforded ester **13e** as a yellow oil (930 mg, 87%). *R_f* = 0.34 (1:1 Et₂O in hexane); ¹H NMR (400 MHz, CDCl₃): δ = 8.66 (br. d, *J* = 4.7 Hz, *ArH*, 1H), 7.72 (td, *J* = 7.8 Hz, ⁴*J* = 1.9 Hz, *ArH*, 1H), 7.70 (d, *J* = 15.7 Hz, *ArCH=CH*, 1H), 7.44 (dt, *J* = 7.8 Hz, ⁴*J* = 1.0 Hz, *ArH*, 1H), 7.27 (ddd, *J* = 7.8, 4.7 Hz, ⁴*J* = 1.0 Hz, *ArH*, 1H), 6.93 (d, *J* = 15.7 Hz, *ArCH=CH*, 1H), 4.29 (q, *J* = 7.14 Hz, OCH₂CH₃, 2H), 1.35 ppm (t, *J* = 7.14 Hz, OCH₂CH₃, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 166.3, 152.5, 149.6, 142.8, 136.2, 123.7, 123.6, 122.0, 60.2, 13.8 ppm; $\bar{\nu}$ /(film) = 2981, 2359, 2342, 1717, 1201, 1167 cm⁻¹; MS (CI): *m/z* (%): 218 (5) [M+C₃H₅]⁺, 206 (10) [M+C₂H₅]⁺, 178 (100) [M+H]⁺, 150 (15), 132 (20) [M-OEt]⁺; *t_R* (GC) = 12.10 minutes. The data was in agreement with that reported by Lebel and Davi.^{S16}

Preparation of ethyl 3-(2'-pyrrolyl-1-carboxylic acid *tert*-butyl ester)-prop-2E-enoate (**13f**)



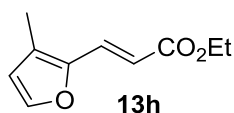
Ester (**13f**) was prepared from aldehyde **12f** (3.9 g, 20 mmol), (carbethoxymethylene)triphenylphosphorane (9.25 g, 26 mmol) and DCM (125 ml) according to General Procedure A. Column chromatography (1:19 Et₂O in hexane to 1:4 Et₂O in hexane) afforded alkenoate **13f** as a yellow oil (3.4 g, 60%). *R_f* = 0.40 (1:4 Et₂O in hexane); ¹H NMR (400 MHz, CDCl₃): δ = 8.30 (d, *J* = 15.9 Hz, *ArCH=CH*, 1H), 7.42 (br. dd, *J* = 3.6 Hz, ⁴*J* = 1.6 Hz, *ArH*, 1H), 6.72-6.70 (m, *ArH*, 1H), 6.23 (t, *J* = 3.6 Hz, *ArH*, 1H), 6.22 (d, *J* = 15.9 Hz, CH=CHCO₂Et, 1H), 4.26 (q, *J* = 7.1 Hz, OCH₂CH₃, 2H), 1.65 (s, OC(CH₃)₃, 9H), 1.3 ppm (t, *J* = 7.1 Hz, OCH₂CH₃, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 166.6, 148.5, 134.4, 130.6, 124.3, 116.1, 114.3, 110.9, 84.4, 59.8, 27.5, 13.9 ppm; $\bar{\nu}$ /(film) = 2976, 1742, 1705, 1621, 1316, 1299, 1245, 1158, 1117 cm⁻¹; MS (CI): *m/z* (%): 194 (12) [M+ C₂H₅-Pyrrolyl-N-Boc]⁺, 166 (50) [M-Pyrrolyl-N-Boc]⁺, 120 (100); *t_R* (GC) = 12.58 minutes. The data was in agreement with that reported by Jeffrey and co-workers.^{S18}

Preparation of ethyl 3-(2'-thiazolyl)-prop-2E-enoate (**13g**)



Aldehyde **12g** was synthesised from thiazole (1.75 mL, 25 mmol), DMF (3.9 mL, 20 mmol), BuLi (14.3 mL of a 2.1 M in THF, 30 mmol) in THF (100 mL) according to Glorius and co-workers^{S2} as a yellow oil. ¹H NMR confirmed full conversion to aldehyde. Ester **13f** was prepared from crude aldehyde **12g** (assumed 25 mmol), (carbethoxymethylene)triphenylphosphorane (9.75 g, 27 mmol) and DCM (150 mL) according to general procedure A. Column chromatography (7:20 Et₂O in hexane) afforded ester **13f** as a yellow oil (3.38 g, 74%) with a 4:1 mixture of alkene isomers (*E*-isomer major). **Data for Mixture:** *R*_f = 0.20 (1:4 Et₂O in hexane); $\bar{\nu}$ /(film) = 2978, 1708, 1630, 1468, 1480, 1299, 1266, 1175 1030 cm⁻¹; HRMS (FTMS): calcd. for C₈H₁₀O₂N₁S₁, 184.0423 [M+H]⁺ found 184.0427. **Data for E-13f:** ¹H NMR (400 MHz, CDCl₃): δ = 7.94 (d, *J* = 3.3 Hz, ArH, 1H), 7.82 (d, *J* = 15.9 Hz, ArCH=CH, 1H), 7.45 (d, *J* = 3.3 Hz, ArH, 1H), 6.77 (d, *J* = 15.9 Hz, CH=CHCO₂Et, 1H), 4.31 (q, *J* = 7.3 Hz, OCH₂CH₃, 2H), 1.36 ppm (t, *J* = 7.3 Hz, CH₂CH₃, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 165.3, 162.9, 144.2, 135.2, 122.5, 120.8, 60.3, 13.7 ppm; MS (CI): *m/z* (%): 224 (17), [M+C₃H₅]⁺, 212 (25) [M+C₂H₅]⁺, 184 (100) [M+H]⁺, 156 (42), 138 (59) [M-OEt]; *t*_R (GC) = 11.83 minutes. **Data for Z-13f:** ¹H NMR (400 MHz, CDCl₃): δ = 7.97 (d, *J* = 3.3 Hz, ArH, 1H), 7.57 (dd, *J* = 3.3 Hz, ⁵*J* = 1.0 Hz, ArH, 1H), 7.37 (dd, *J* = 12.7 Hz, ⁵*J* = 1.0 Hz, ArCH=CH, 1H), 6.15 (d, *J* = 12.7 Hz, CH=CHCO₂Et, 1H), 4.32 (q, *J* = 7.2 Hz, OCH₂H₃, 2H), 1.37 ppm (t, *J* = 7.2 Hz, CH₂H₃, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 165.3, 160.2, 142.6, 136.4, 123.7, 118.9, 60.2, 13.6 ppm; MS (CI): *m/z* (%): 224 (11), [M+C₃H₅]⁺, 212 (18) [M+C₂H₅]⁺, 184 (100) [M+H]⁺, 156 (20), 138 (97) [M-OEt]; 112 (14); *t*_R (GC) = 11.59 minutes.

Preparation of ethyl 3-(2'-furyl-3-methyl)-prop-2E-enoate (**13h**)

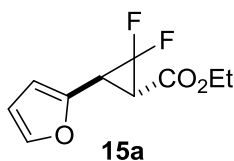


Diisobutylaluminium hydride (50 mL of a 0.9 M solution in cyclohexane, 45 mmol) was added dropwise to a solution of methyl 3-methyl-2-furoate (2.04 g, 14.6 mmol) in anhydrous toluene (120 mL) under nitrogen at -78 °C for 5 minutes. The reaction mixture

was allowed to warm to room temperature and stirred for a further 8 hours, cooled to -78 °C and quenched with aqueous potassium sodium tartrate tetrahydrate (sat. Rochelle salt, 40 mL) and EtOAc (50 mL). The resulting organic layer was separated and collected. The aqueous layer was extracted further with EtOAc (50 mL x 6) and the separated extracts combined with the original organic layer, dried (MgSO₄) and concentrated under reduced pressure to afford (3-methylfuran-2-yl)methanol as a yellow oil (1.33 g 81%). ¹H NMR confirmed full conversion to desired alcohol which was used without further purification. Bis(acetoxy)iodobenzene (BAIB, 4.18 g, 13 mmol) was added to a solution of (3-methylfuran-2-yl)methanol (1.33 g, 11.8 mmol), TEMPO (184 mg, 1.18 mmol), in anhydrous DCM (90 mL) and the reaction mixture was stirred at room temperature under nitrogen for 4 hours. The ¹H NMR spectrum of a reaction aliquot showed complete conversion to corresponding aldehyde **12h**. (Carbethoxymethylene)triphenylphosphorane (5.2 g, 15 mmol) was then added and the reaction mixture stirred for 17 hours. ¹H NMR of a reaction aliquot showed complete consumption of aldehyde. The resulting orange solution was concentrated under reduced pressure and column chromatography on silica gel (2:25 Et₂O in hexane) afforded alkenoate **13h** as a yellow oil (1.26 g, 45%). R_f = 0.44 (1:10 Et₂O in hexane); $\bar{\nu}$ /(film) = 2976, 1703, 1632, 1299, 1253, 1164 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.50 (d, *J* = 15.5 Hz, ArCH=CH, 1H), 7.40 (dq, *J* = 1.6 Hz, ⁴*J* = 0.5 Hz, ArH, 1H), 6.34 (d, *J* = 1.6 Hz, ArH, 1H), 6.26 (d, *J* = 15.5 Hz, CH=CHCO₂Et, 1H), 4.27 (q, *J* = 7.1 Hz, OCH₂H₃, 2H), 2.18 (s, ArCH₃, 3H), 1.35 ppm (t, *J* = 7.1 Hz, CH₂CH₃, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 166.9, 146.6, 143.4, 128.5, 125.1, 114.1, 113.5, 59.7, 13.8, 9.7 ppm; MS (CI): *m/z* (%): 209 (18), [M+C₂H₅]⁺, 181 (100), [M+H]⁺, 153 (12), 135 (72), [M-OEt]; HRMS (NSI): calcd. for C₁₀H₁₃O₃, 181.0859 [M+H]⁺ found 184.0857; t_R (GC) = 11.43 minutes.

General Procedure B: Difluorocyclopropanation of Alkenoates **13** with MDFA

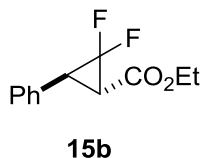
Preparation of ethyl (1*S**,3*S**)-2,2-difluoro-3-(fur-2-yl)cyclopropane-1-carboxylate (**15a**)



An oven dried two-necked round bottom flask containing potassium iodide (1.87 g, 11.2 mmol) was sealed with a SubaSeal, and the salt was stirred and lightly flame dried under an atmosphere of argon. A low boiling point water condenser with a gas outlet connected to an argon/vacuum manifold was fitted to the reaction flask and the atmosphere was purged three times. Alkenoate **13a** (1.48 g, 8.9 mmol) followed by diglyme (1.43 mL) were added and the yellow suspension purged with argon/vacuum once and then heated to 120 °C. Once the reaction temperature had been reached, TMSCl (2.9 mL, 22.3 mmol) and MDFA (2.9 mL, 22.3 mmol) were added dropwise in that order. After 4 hours, the black reaction mixture was allowed to cool to room temperature and the reaction mixture was quenched with aqueous NH₄Cl (10 mL) and diethyl ether (10 mL) was added. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The original organic layer and the extracts were combined, dried (MgSO₄) and concentrated under reduced pressure to remove volatile materials. The ¹H NMR spectrum of the resulting brown oil confirmed 66% conversion to difluorocyclopropyl **15a**. Column chromatography on silica gel (1:20 Et₂O in hexane) afforded difluorocyclopropyl **15a** as a yellow oil (760 mg, 40%) and recovered starting alkenoate **13a** (340 mg, 23%). *R_f* = 0.4 (1:19 Et₂O in hexane); ¹H NMR (400 MHz, CDCl₃): δ = 7.39 (dd, *J* = 2.0 Hz, ⁴*J* = 0.8 Hz, *ArH*, 1H), 6.38 (dd, *J* = 3.4, 2.0 Hz, *ArH*, 1H), 6.29 (dd, *J* = 3.4 Hz, ⁴*J* = 0.8 Hz, *ArH*, 1H), 4.28 (q, *J* = 7.1 Hz, OCH₂CH₃, 2H), 3.48 (ddd, *J*_{H-F} = 12.3 Hz, *J* = 7.7 Hz, ⁴*J*_{H-F} = 1.8 Hz, *ArCHCF*₂, 1H), 2.79 (dd, *J*_{H-F} = 13.4 Hz, *J* = 7.7 Hz, CF₂CHCO₂Et, 1H), 1.34 ppm (t, *J* = 7.2 Hz, OCH₂CH₃, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 165.5, 145.1, 142.6, 110.6, 108.8 (dd, ¹*J*_{C-F} = 294.6, 289.7 Hz) 108.4, 61.9, 32.1 (t, ²*J*_{C-F} = 10.9 Hz), 26.7 (dd, ²*J*_{C-F} = 13.3, 8.9 Hz) 14.1 ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ = -133.1 (dd, ²*J* = 151.7 Hz, *J*_{F-H} = 13.4 Hz, 1F), -135.1 ppm (dd, ²*J* = 152.8 Hz, *J*_{F-H} = 12.2 Hz, 1F); $\bar{\nu}$ /(film) = 2986, 2932, 2359, 2342, 1736, 1447, 1331, 1290, 1153, 1009 cm⁻¹; MS (CI): *m/z* (%): 257 (4) [M+C₃H₅]⁺, 245 (9) [M+C₂H₅]⁺, 217 (45) [M+H]⁺, 197 (100) [M-F]⁺, 189 (58), 171 (42) [M-

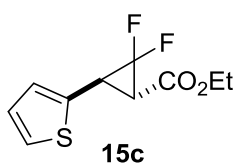
OEt]⁺, 169 (70) [(M+H)-F-Et]⁺, 143 (20), 125 (16); *t_R* (GC) = 9.49 minutes; HRMS (APCI): calcd for C₁₀H₁₁F₂O₃, 217.0668 [M+H]⁺ found 217.0671.

Preparation of ethyl (1S*,3S*)-2,2-difluoro-3-phenylcyclopropane-1-carboxylate (**15b**)



The preparation of ester **15b** was attempted from alkenoate **13b** (0.67 mL, 4.03 mmol), MDFA (2.6 mL, 10 mmol), TMSCl (2.6 mL, 10 mmol), potassium iodide (1.87 g, 11.2 mmol) and diglyme (1.4 mL) according to General Procedure B with a total reaction time of 24 hours. The resulting ¹H NMR of the crude reaction mixture after work up confirmed incomplete conversion of **13b** (28% conv. to **15b**). The reaction was repeated using commercial ethyl cinnamate (**13b**) according to general procedure B on twice the scale. The resulting ¹H spectrum of the resulting brown oil confirmed incomplete conversion of **13b** (29% conv. to **15b**).

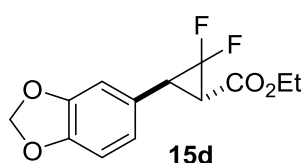
Preparation of ethyl (1S*,3R*)-2,2-difluoro-3-(thiophen-2-yl)cyclopropane-1-carboxylate (**15c**)



Ester **15c** was prepared from alkenoate **13c** (1.45 mg, 8 mmol), MDFA (2.6 mL, 20 mmol), TMSCl (2.6 mL, 20 mmol), potassium iodide (3.68 g, 22.6 mmol) and diglyme (1.3 mL) according to general procedure B with a reaction time of 4 hours. ¹H NMR of the resulting crude product showed 77% conversion to desired ester **15c**. Column chromatography on silica gel (1:19 Et₂O in hexane) afforded ester **15c** as a yellow oil (1.32 g, 71%) and recovered alkenoate **13c** (310 mg, 21%). *R_f* = 0.42 (1:24 Et₂O in hexane); ¹H NMR (500 MHz, CDCl₃): δ = 7.26 (dd, *J* = 3.3, 3.1 Hz, Ar*H*, 1H), 7.00 (d, *J* = 3.3 Hz, Ar*H*, 1H), 7.00 (d, *J* = 3.1 Hz, Ar*H*, 1H), 4.27 (q, *J* = 7.2 Hz, OCH₂CH₃, 2H), 3.63 (ddd, *J*_{H-F} = 13.1, 2.3 Hz, *J* = 7.7 Hz, ArCH, 1H), 2.67 (dd, *J*_{H-F} = 13.6, *J* = 7.7 Hz, CHCO₂Et, 1H), 1.33 ppm (t, *J* = 7.2 Hz, OCH₂CH₃, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 165.7, 133.3, 127.0, 126.7, 125.4, 110.4 (dd, ¹*J*_{C-F} = 296.8, 290.3 Hz), 61.9,

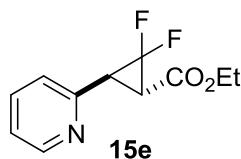
34.5 ($^2J_{C-F} = 10.9$ Hz), 28.6 (dd, $^2J_{C-F} = 13.0$, 9.2 Hz), 14.1 ppm; ^{19}F NMR (376 MHz, CDCl_3): $\delta = -132.8$ (ddd, $^2J_{F-F} = 151.7$ Hz, $J_{F-H} = 13.6$, 2.4 Hz, 1F), -134.2 ppm (dd, $^2J_{F-F} = 151.2$ Hz, $J_{F-H} = 13.3$ Hz, 1F); $\bar{\nu}/(\text{film}) = 2965, 2359, 2342, 1732, 1466, 1431, 1325, 1285, 1215, 1152, 1009\text{ cm}^{-1}$; MS (CI): m/z (%): 261 (7) $[\text{M}+\text{C}_2\text{H}_5]^+$, 233 (33) $[\text{M}+\text{H}]^+$, 213 (100) $[\text{M}-\text{F}]^+$, 205 (43), 187 (36), 185 (66) $[\text{M}-(\text{F}+\text{Et})]^+$, 159 (16), 139 (18); HRMS (APCI): calcd for $\text{C}_{10}\text{H}_{14}\text{F}_2\text{O}_2\text{S}_1\text{N}_1$, 250.0708 $[\text{M}+\text{NH}_4]^+$ found 250.0706; t_R (GC) = 11.15 minutes.

Preparation of ethyl (1S*,3S*)-3-(benzo[d][1,3]dioxol-5-yl)-2,2-difluorocyclopropane-1-carboxylate (**15d**)



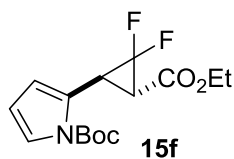
Ester **15d** was prepared from alkenoate **13d** (1.66 g, 7.5 mmol), MDFA (2.4 mL, 18.5 mmol), TMSCl (2.4 mL, 18.5 mmol), potassium iodide (3.45 g, 20.7 mmol) and diglyme (1.2 mL) according to general procedure B. ^1H NMR of the resulting crude product showed 50% conversion to desired ester **15d**. Column chromatography on silica gel (1:9 Et_2O in hexane) afforded ester **15d** as a yellow oil (880 mg, 43%) and recovered alkenoate **13d** (700 mg, 42%). $R_f = 0.59$ (1:4 Et_2O in hexane); ^1H NMR (400 MHz, CDCl_3): $\delta = 6.82$ -6.73 (m, ArH, 3H), 6.00 (s, OCH_2O , 2H), 4.28 (q, $J = 7.2$ Hz, OCH_2CH_3 , 2H), 3.44 (ddd, $J_{H-F} = 13.2$, 2.9 Hz, $J = 7.9$ Hz, ArCH, 1H), 2.65 (dd, $J_{H-F} = 13.2$ Hz, $J = 7.9$ Hz, CHCO_2Et , 1H), 1.34 (t, $J = 7.2$ Hz, OCH_2CH_3 , 3H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 165.8, 147.5, 146.9, 124.1, 121.3, 110.2$ (t, $^1J_{C-F} = 294.2, 287.2$ Hz), 107.9 (represents 2 carbons), 100.8, 61.3, 32.4 (dd, $^2J_{C-F} = 11.2, 8.8$ Hz), 32.0 (t, $^2J_{C-F} = 11.1$ Hz) 13.6 ppm; ^{19}F NMR (376 MHz, CDCl_3): $\delta = -133.1$ (dd, $^2J_{F-F} = 151.9$ Hz, $J_{F-H} = 13.6$ Hz, 1F), -134.1 (ddd, $^2J_{F-F} = 151.3$ Hz, $J_{F-H} = 13.5, 2.7$ Hz, 1F), $\bar{\nu}/(\text{film}) = 2359, 2342, 1732, 1506, 1466, 1449, 1290, 1242, 1213, 1152, 1038, 1013, 989\text{ cm}^{-1}$; MS (CI): m/z (%): 299 (19) $[\text{M}+\text{C}_2\text{H}_5]^+$, 271 (44) $[\text{M}+\text{H}]^+$, 251 (94) $[\text{M}-\text{F}]^+$, 223 (75) $[(\text{M}+\text{H})-\text{F}-\text{OEt}]^+$, 206 (24), 197 (26) $[\text{M}-\text{CO}_2\text{Et}]^+$, 177 (100); HRMS (APCI): calcd for $\text{C}_{13}\text{H}_{13}\text{F}_2\text{O}_4$, 271.0776 $[\text{M}+\text{H}]^+$ found 271.0776; t_R (GC) = 13.50 minutes.

Preparation of ethyl (1S*,3S*)-2,2-difluoro-3-(pyridin-2-yl)cyclopropane-1-carboxylate (15e)



The preparation of ester **15e** was attempted from alkenoate **13e** (400 mg, 2.3 mmol), MDFA (0.74 mL, 5.7 mmol), TMSCl (0.74 mL, 5.7 mmol), potassium iodide (1.1 g, 6.6 mmol) and diglyme (0.45 mL) according to general procedure B with a total reaction time of 4 hours. The resulting ^1H NMR of the resulting crude black solid showed diglyme and diethyl ether with trace amounts of alkenoate **13e**. The desired product **15e** was not observed (0% conversion).

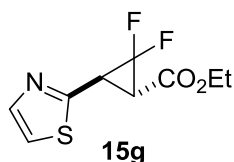
Preparation of ethyl (1S*,3S*)-2,2-difluoro-3-(2'-pyrrolyl-1-carboxylic acid *tert*-butyl ester)cyclopropane-1-carboxylate (15f)



Ester **15f** was prepared from alkenoate **13f** (2.12 g, 8 mmol), MDFA (2.6 mL, 20 mmol), TMSCl (2.6 mL, 20 mmol), potassium iodide (3.74 g, 22.4 mmol) and diglyme (1.6 mL) according to general procedure B. ^1H NMR of the resulting crude product showed 92% conversion to desired product. Column chromatography on silica gel (1:20 Et₂O in hexane) afforded ester **15f** as a yellow oil (1.37 g, 54%) and recovered alkenoate **13f** (140 mg, 7%). R_f = 0.35 (1:4 Et₂O in hexane); ^1H NMR (400 MHz, CDCl₃): δ = 7.29 (ddd, J = 3.3 Hz, 4J = 1.7 Hz, 5J = 0.7 Hz, ArH, 1H), 6.17-6.15 (br. m, ArH, 1H), 6.14 (t, J = 3.4 Hz, ArH, 1H), 4.28 (ABq, J = 7.4 Hz, 2J = 3.1 Hz, OCH_aH_bCH₃, 2H), 3.73 (br. dd, $J_{\text{H-F}}$ = 12.8 Hz, J = 7.8 Hz, ArCH, 1H), 2.63 (dd, J = 13.4 Hz, J = 7.8 Hz, HCCO₂Et, 1H), 1.63 (s, C(CH₃)₃, 9H), 1.34 (t, J = 7.2 Hz, CH₂CH₃, 3H); ^{13}C NMR (100 MHz, CDCl₃): δ = 165.7, 148.4, 124.0, 122.1, 112.9, 110.3 (dd, $^1J_{\text{C-F}}$ = 297.3, 287.2 Hz), 109.6, 84.1, 61.1, 31.7 (t, $^2J_{\text{C-F}}$ = 10.9 Hz), 27.6 (t, $^2J_{\text{C-F}}$ = 12.9, 8.0 Hz), 27.5, 13.7 ppm; ^{19}F NMR (376 MHz, CDCl₃): δ = -133.4 (dd, 2J = 149.8 Hz, $J_{\text{F-H}}$ = 12.8 Hz, CF_aF_b, 1F), -134.9 ppm (dd, 2J = 149.8 Hz, $J_{\text{F-H}}$ = 13.4 Hz, CF_aF_b, 1F); $\bar{\nu}$ /(film) = 2980, 1742, 1459, 1325, 1158, 1128

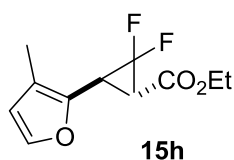
cm⁻¹; MS (CI): *m/z* (%): 224 (17) [M-(F+CO₂Et)+H]⁺, 196 (100) [M-(F+Boc)+H]⁺, 168 (29), 150 (72) [M-(*N*-Boc-pyrrolyl)+H]⁺; HRMS (APCI): calcd for C₁₅H₂₃F₂N₂O₄, 333.1620 [M+NH₄]⁺ found 333.1623; *t_R* (GC) = 12.07 minutes.

Preparation of ethyl (1*S,3*S**)-2,2-difluoro-3-(2'-thiazolyl)cyclopropane-1-carboxylate (15g)**



The preparation of ester **15g** was attempted from alkenoate **13g** (1.18 g, 6.4 mmol), MDFA (2.1 mL, 16.2 mmol), TMSCl (2.1 mL, 16.2 mmol), potassium iodide (3.0 g, 18 mmol) and diglyme (1.28 mL) according to general procedure B with a total reaction time of 4 hours. The resulting ¹H NMR of the resulting crude black solid showed diglyme and diethyl ether the desired product **15g** was not observed (0% conversion).

Preparation of ethyl (1*S,3*S**)-2,2-difluoro-3-(2'-furyl-3-methyl) cyclopropane-1-carboxylate (15h)**

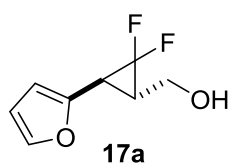


Ester **15h** was prepared from alkenoate **13h** (721 mg, 4.0 mmol), MDFA (1.3 mL, 10 mmol), TMSCl (1.3 mL, 10 mmol), potassium iodide (1.84 g, 12 mmol) and diglyme (0.7 mL) according to general procedure B. ¹H NMR of the resulting crude product showed 80% conversion to desired product. Column chromatography on silica gel (1:20 Et₂O in hexane) afforded ester **15h** as a yellow oil (417 mg, 45%) and recovered alkenoate **13h** (136 mg, 19%). *R_f* = 0.56 (1:4 Et₂O in hexane); ¹H NMR (400 MHz, CDCl₃): δ = 7.26 (d, *J* = 1.8 Hz, Ar*H*, 1H), 6.23 (d, *J* = 1.8 Hz, Ar*H*, 1H), 4.26 (q, *J* = 7.1 Hz, OCH₂CH₃, 2H), 3.67 (ddd, *J*_{H-F} = 12.2, 2.3 Hz, *J* = 7.7 Hz, ArCH, 1H), 2.92 (dd, *J*_{H-F} = 13.5 Hz, *J* = 7.7 Hz, HCCO₂Et, 1H), 2.05 (s, ArCH₃, 3H), 1.33 ppm (t, *J* = 7.1 Hz, CH₂CH₃, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 165.9, 141.4, 139.8, 119.0, 113.4, 110.1 (t, ¹*J*_{C-F} = 294.1, 287.4 Hz), 61.9, 30.8 (t, *J*_{C-F} = 11.0 Hz), 25.5 (dd, *J*_{C-F} = 13.5, 9.5 Hz), 14.1, 9.6 ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ = -132.8 (ddd, ²*J* = 150.5 Hz, *J*_{F-H} =

13.5, 2.3 Hz, CF_aF_b , 1F), -131.5 ppm (dd, $^2J = 150.5$ Hz, $J_{F-H} = 12.2$ Hz, CF_aF_b , 1F); $\bar{\nu}/(\text{film}) = 2985, 1738, 1454, 1329, 1290, 1208, 1154, 1091, 1013, 989$ cm $^{-1}$; MS (CI): m/z (%): 259 (6) $[M+C_2H_5]^+$, 231 (25) $[M+H]^+$, 211 (100) $[M-F]^+$, 203 (23), 185 (25) $[M-OEt]^+$, 183 (28); HRMS (APCI): calcd for $C_{11}H_{11}F_2O_3$, 229.0671 $[M-H]^+$ found 229.0676; t_R (GC) = 10.61 minutes.

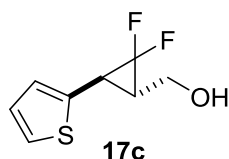
General Procedure C: Reduction of Difluorocyclopropyl Ethyl Esters

Preparation of ethyl ((1S*,3S*)-2,2-difluoro-3-(furan-2-yl)cyclopropyl)methanol (**17a**)



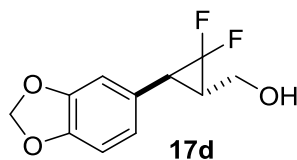
Diisobutylaluminium hydride (24 ml of a 1.1 M solution in cyclohexane, 23.7 mmol) was added dropwise to a solution of ester **15a** (1.71 g, 7.9 mmol) in anhydrous toluene (70 mL) under nitrogen at -78 °C over 10 minutes. The reaction mixture was allowed to warm to room temperature and stirred for a further 8 hours, then cooled to 0 °C and quenched by dropwise addition of H₂O (2 mL), 0.1 M aqueous NaOH (2 mL) and H₂O (2 mL) in that order. MgSO₄ was added to the quenched mixture until the solid was free flowing and the mixture was left overnight at room temperature (14-17 h). The resulting white emulsion was washed with EtOAc (4 x 50 mL) and the organic extracts were combined and concentrated under reduced pressure to afford alcohol **17a** as a pale yellow oil (1.3 g, 94%). $R_f = 0.19$ (1:2 Et₂O in hexane); 1H NMR (400 MHz, CDCl₃): $\delta = 7.37$ (dd, $J = 1.9$ Hz, $^4J = 0.8$ Hz, ArH, 1H), 6.38 (dd, $J = 3.3, 1.9$ Hz, ArH, 1H), 6.21 (br. d, $J = 3.3$ Hz, ArH, 1H), 3.99-3.91 (br. m, CH_aH_bOH , 1H), 3.90-3.83 (br. m, CH_aH_bOH , 1H), 2.64 (dd, $J_{H-F} = 13.1$ Hz, $J = 7.3$ Hz, ArCH, 1H), 2.32-2.23 (m, $CHCH_2O$, 1H), 1.62 ppm (br. s, CH_2OH , 1H); ^{13}C NMR (100 MHz, CDCl₃): $\delta = 146.6, 141.6, 112.1$ (t, $^1J_{C-F} = 289.0$ Hz), 110.1, 106.9, 58.6 (d, $J_{C-F} = 5.9$ Hz), 30.4 (t, $^2J_{C-F} = 9.5$ Hz), 24.2 ppm (dd, $^2J_{C-F} = 13.6, 10.6$ Hz); ^{19}F NMR (376 MHz, CDCl₃): $\delta = -135.5$ (ddd, $^2J = 158.7$ Hz, $J_{F-H} = 13.6, 2.0$ Hz, 1F), -138.3 ppm (dd, $^2J = 158.8$ Hz, $J_{F-H} = 13.1$ Hz, 1F); $\bar{\nu}/(\text{film}) = 2926, 2359, 2342, 1458, 1263, 1167, 1009, 736$ cm $^{-1}$; MS (CI): m/z (%): 175 (13) $[M+H]^+$, 157 (100) $[M-OH]^+$, 139 (13), 127 (12), 109 (18); HRMS (TOF): calcd for $C_8H_8O_2F_2$, 174.0492 $[M]$ found 174.0496; t_R (GC) = 9.39 minutes.

Preparation of ((1S*,3R*)-2,2-difluoro-3-(thiophen-2-yl)cyclopropyl)methanol (**17c**)



Alcohol **17c** was prepared from ester **15c** (272 mg, 0.85 mmol), DIBAL (2.3 ml of a 1.1 M solution in cyclohexane, 2.55 mmol) and DCM (6 mL) according to general procedure B. ^1H NMR of the result crude reaction mixture confirmed 83% conversion. Column chromatography on silica gel (2:3 Et₂O in hexane) afforded alcohol **17c** as a yellow oil (81 mg, 50%). R_f = 0.19 (1:2 Et₂O in hexane); ^1H NMR (400 MHz, CDCl₃): δ = 7.23 (dd, J = 5.2, 4J = 1.3 Hz, ArH, 1H), 6.99 (dd, J = 5.2, 3.6 Hz, ArH, 1H), 6.95 (br. d, J = 3.6 Hz, ArH, 1H), 3.94 (dddd, 2J = 12.1 Hz, J = 6.6, 1.1 Hz, $^4J_{\text{H-F}}$ = 2.7 Hz, CH_oH_bOH, 1H), 3.84 (ddd, 2J = 12.1 Hz, J = 7.8, 1.6 Hz, CH_aH_bOH, 1H), 2.77 (dd, $J_{\text{H-F}}$ = 13.6 Hz, J = 7.3 Hz, ArCH, 1H), 2.33 (br. s, CH₂OH, 1H), 2.17 ppm (dddd, $J_{\text{H-F}}$ = 13.4 Hz, J = 7.8, 7.4, 6.6 Hz, 4J = 0.9 Hz, CHCH₂OH, 1H); ^{13}C NMR (100 MHz, CDCl₃): δ = 135.1, 126.5, 125.4, 124.2, 112.7 (t, $^1J_{\text{C-F}}$ = 290.1 Hz), 58.7 (d, $J_{\text{C-F}}$ = 5.7 Hz), 32.9 (t, $^2J_{\text{C-F}}$ = 9.6 Hz), 26.1 ppm (dd, $^2J_{\text{C-F}}$ = 12.5, 11.1 Hz); ^{19}F NMR (376 MHz, CDCl₃): δ = -135.4 (ddd, 2J = 158.0 Hz, $J_{\text{F-H}}$ = 13.5 Hz, $^4J_{\text{F-H}}$ = 2.7 Hz, 1F), -137.5 ppm (dd, 2J = 158.0 Hz, $J_{\text{F-H}}$ = 13.5 Hz, 1F); $\bar{\nu}$ /(film) = 3324, 2930, 2885, 1472, 1435, 1245, 1080, 1037, 1007 cm⁻¹; MS (CI): m/z (%): 219 (6) [M+C₂H₅]⁺, 191 (26) [M+H]⁺, 173 (100) [M-OH]⁺, 153 (42) [M-F₂]⁺, 123 (22); HRMS (ASAP): calcd for C₈H₇F₂S₁, 173.0231 [M-H₂O+H]⁺ found 173.0229; t_R (GC) = 10.51 minutes.

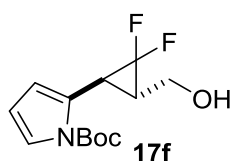
Preparation of ((1S*,3R*)-2,2-difluoro-3-(benzo[d][1,3]dioxol-5-yl)cyclopropyl)methanol (**17d**)



Alcohol **17d** was prepared from ester **15d** (550 mg, 2 mmol), DIBAL (1.0 M in cyclohexane, 6.0 mL, 6 mmol) and toluene (30 mL) according to general procedure C. Column chromatography on silica gel (1:1 Et₂O in hexane) afforded desired alcohol **17d** as a colourless oil (342 mg, 75%). R_f = 0.35 (1:1 Et₂O in hexane); ^1H NMR (400 MHz, CDCl₃): δ =

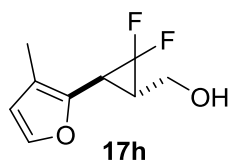
6.80-6.72 (m, ArH, 3H), 5.97 (s, OCH₂O, 2H), 3.95-3.83 (m, CHCH₂OH, 2H), 2.57 (ddd, $J_{\text{H-F}} = 11.2$ Hz, $J = 7.6$ Hz, $^4J = 3.3$ Hz, ArCH, 1H), 2.12 (dddd, $J_{\text{H-F}} = 11.2$ Hz, $J = 7.6, 7.5, 7.1$ Hz, $^4J = 3.3$ Hz, CHCH₂OH, 1H), 1.92 ppm (br. s, CH₂OH, 1H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 147.3, 146.4, 126.1, 121.1, 113.1$ (t, $^1J_{\text{C-F}} = 289.1$ Hz), 108.0, 107.8, 100.6, 59.1 (d, $J_{\text{C-F}} = 4.3$ Hz), 30.8 (t, $^2J_{\text{C-F}} = 9.1$ Hz), 30.7 ppm (t, $^2J_{\text{C-F}} = 11.1$ Hz); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -136.5$ (ddd, $^2J = 158.2$ Hz, $J_{\text{F-H}} = 10.8$ Hz, $^4J_{\text{F-H}} = 4.2$ Hz, CHCF_aF_bCHCH₂, 1F), -136.6 ppm (ddt, $^2J = 157.8$ Hz, $J_{\text{F-H}} = 10.8$ Hz, $^4J_{\text{F-H}} = 3.7$ Hz, CHCF_aF_bCHCH₂, 1F). Reported chemical shifts are representative of an AB system; $\bar{\nu}/(\text{film}) = 3292, 1495, 1476, 1437, 1236, 1167, 1036, 1011, 930$ cm⁻¹; MS (CI): m/z (%): 269 (2) [M+C₃H₅]⁺, 257 (10) [M+C₂H₅]⁺, 229 (32) [M+H]⁺, 211 (100) [M-OH]⁺, 191 (90) [(M+H)-F₂]⁺, 181 (48), 161 (74), 131 (26); HRMS (APCI): calcd for C₁₁H₁₁F₂O₃, 229.0671 [M+H]⁺ found 229.0668; t_{R} (GC) = 12.96 minutes.

Preparation of ((1S*,3R*)-2,2-difluoro-3-(2'-pyrrolyl-1-carboxylic acid *tert*-butyl ester)methanol (17f)



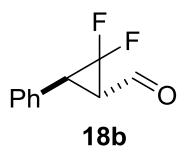
Alcohol **17f** was prepared from ester **15f** (600 mg, 1.9 mmol), DIBAL (1.0 M in cyclohexane, 5.7 mL, 5.7 mmol) and toluene (40 mL) according to general procedure C. Column chromatography on silica gel (1:1 Et₂O in hexane) afforded desired alcohol **17f** as a pale yellow oil (30 mg, 6%). $R_f = 0.32$ (1:1 Et₂O in hexane); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.23$ (ddd, $J = 3.4$ Hz, $^4J = 1.8$ Hz, $^5J = 0.8$ Hz, ArH, 1H), 6.25 (m, ArH, 1H), 6.14 (t, $J = 3.4$ Hz, ArH, 1H), 3.98 (ddd, $^2J = 12.0$ Hz, $J = 5.7, 1.8$ Hz, CHCH_aH_bOH, 1H), 3.74 (dt, $^2J = 11.9$ Hz, $J = 1.8$ Hz, CHCH_aH_bOH, 1H), 2.96 (br. s, OH, 1H), 2.86 (dd, $^3J_{\text{H-F}} = 15.3$ Hz, $J = 7.3$ Hz, ArCH, 1H), 1.99 (m, CHCH₂OH, 1H), 1.63 ppm (s, OC(CH₃)₃, 9H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 149.3, 126.5, 121.2, 113.3$ (dd, $^1J_{\text{C-F}} = 290.3, 287.3$ Hz), 112.3 (d, $^4J_{\text{C-F}} = 3.3$ Hz), 110.0, 84.2, 59.0 (d, $J_{\text{C-F}} = 4.4$ Hz), 32.9 (t, $^2J_{\text{C-F}} = 9.3$ Hz), 23.5, 23.3 ppm (dd, $^2J_{\text{C-F}} = 13.0, 9.6$ Hz); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -132.6$ (dd, $^2J = 160.0$ Hz, $J_{\text{F-H}} = 13.6$ Hz, CF_aF_b, 1F), -134.7 ppm (dd, $^2J = 159.0$ Hz, $J_{\text{F-H}} = 15.1$ Hz, CF_aF_b, 1F); $\bar{\nu}/(\text{film}) = 3443, 2982, 2835, 1740, 1478, 1405, 1372, 1323, 1260, 1164, 1128$ cm⁻¹; MS (CI): m/z (%): 180 (23), 152 (100); t_{R} (GC) = 10.12 minutes. Due to lack of m/z consistent with product accurate mass analysis was not attempted.

Preparation of ((1S*,3R*)-2,2-difluoro-3-(2'-furyl-3-methyl)cyclopropyl)methanol (**17h**)



Alcohol **17h** was prepared from ester **15h** (234 mg, 1.0 mmol), DIBAL (1.0 M in cyclohexane, 3.0 mL, 3.0 mmol) and toluene (6.2 mL) according to general procedure C to afford desired alcohol **17h** as a pale yellow oil (160 mg, 84%). R_f = 0.21 (1:1 Et₂O in hexane); ¹H NMR (400 MHz, CDCl₃): δ = 7.25 (d, J = 1.8 Hz, ArH, 1H), 6.22 (d, J = 1.8 Hz, ArH, 1H), 3.97-3.84 (br. m., CHCH₂OH, 2H), 2.52 (dd, J_{H-F} = 12.7, J = 7.3 Hz, ArCH, 1H), 2.40 (dddd, J_{H-F} = 13.9, 2.0 Hz, J = 7.6, 7.3, 6.4 Hz), 2.04 (s, ArCH₃, 3H), 1.62 ppm (br. s, OH, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 141.5, 141.0, 118.2, 113.3, 113.0 (t, $^1J_{C-F}$ = 289.0 Hz), 59.1 (d, J_{C-F} = 5.6 Hz), 29.5 (t, $^2J_{C-F}$ = 9.5 Hz), 23.4 (dd, $^2J_{C-F}$ = 13.4, 10.8 Hz), 9.6 ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ = -134.8 (ddd, 2J = 157.3 Hz, J_{F-H} = 13.9, 2.2 Hz, CF_aF_b, 1F), -138.4 ppm (dd, 2J = 157.3 Hz, J_{F-H} = 12.7 Hz, CF_aF_b, 1F); $\bar{\nu}$ /(film) = 3333, 2928, 2887, 1632, 1455, 1271, 1180, 1041, 1013 cm⁻¹; MS (CI): m/z (%): 189 (9) [M+H]⁺, 171 (100) [M-OH]⁺, 153 (16), 121 (14); HRMS (APCI): calcd for C₉H₉F₂O₁, 171.0616 [M-H₂O+H]⁺ found 171.0615; t_R (GC) = 9.99 minutes.

Preparation of (1S*,3S*)-2,2-difluoro-3-phenylcyclopropane-1-carbaldehyde (**18b**)

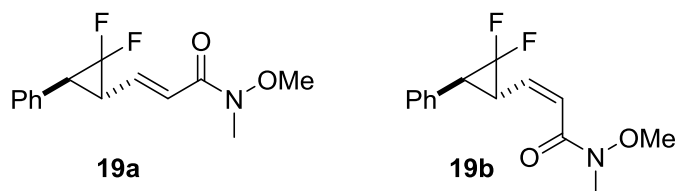


BAIB (3.0 g, 9.3 mmol) was added to a solution of ((1S*,3S*)-2,2-difluoro-3-phenylcyclopropyl)methanol (**17b**) (1.58 g, 8.6 mmol) and TEMPO (133 mg, 0.9 mmol) in anhydrous DCM (45 mL) and the reaction mixture was stirred at room temperature under nitrogen for 6 hours. The ¹H NMR spectrum showed complete conversion to aldehyde **18b**. Kugelrohr distillation (50 °C, 20 mbar) removed iodobenzene side product then (60 °C, 0.1 mbar) afforded aldehyde **18b** as a pale yellow oil (1.17 g, 75%). R_f = 0.26 (1:4 Et₂O in hexane); ¹H NMR (400 MHz, CDCl₃): δ = 9.51 (dd, J = 4.4 Hz, 4J = 2.0 Hz, C(O)H, 1H), 7.42-7.34 (m, ArH, 3H), 7.29-7.27 (m, ArH, 2H), 3.63 (ddd, J_{H-F} = 14.8 Hz, J = 7.6 Hz, 4J = 2.1 Hz, ArCH, 1H), 2.97 (ddd, J_{H-F} = 12.8 Hz, J = 7.5, 4.4 Hz, CHC(O)H, 1H); ¹³C NMR (100 MHz, CDCl₃): δ =

191.8 (d, J_{C-F} = 3.9 Hz), 130.0, 128.4, 127.8, 127.6, 111.0 (t, $^2J_{C-F}$ = 291.3 Hz), 40.3 (t, J_{C-F} = 40.4 Hz), 32.8 ppm (dd, J_{C-F} 12.1, 8.8 Hz); ^{19}F NMR (376 MHz, CDCl_3): δ = -129.4 (dd, 2J = 158.0 Hz, J_{F-H} = 15.0 Hz, 1F), -133.4 ppm (dd, 2J = 157.9 Hz, J_{F-H} = 12.9 Hz, 1F); $\bar{\nu}$ /(film) = 1738, 1634, 1059, 980 cm^{-1} ; MS (CI): m/z (%): 183 (11) $[\text{M}+\text{H}]^+$, 163 (73) $[\text{M}-\text{F}]^+$, 135 (100) $[(\text{M}+\text{H})-\text{F}-\text{CO}]$, 115 (24) $[(\text{M}+\text{H})-\text{F}_2-\text{CO}]$; HRMS (APCI): calcd for $\text{C}_{10}\text{H}_9\text{F}_2\text{O}$, 183.0616 $[\text{M}+\text{H}]^+$ found 183.0615; t_R (GC) = 10.03 minutes.

General Procedure D: Tandem Oxidation/Olefination of Difluorocyclopropyl Alcohols

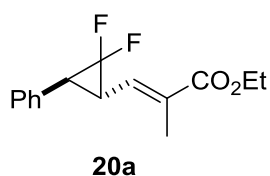
Preparation of (*E*)-3-((1*R,3*S**)-2,2-difluoro-3-phenylcyclopropyl)-*N*-methoxy-*N*-methylacrylamide (19a) and (*Z*)-3-((1*R**,3*S**)-2,2-difluoro-3-phenylcyclopropyl)-*N*-methoxy-*N*-methylacrylamide (19b)**



Bis(acetoxyl)iodobenzene (BAIB, 304 mg, 0.92 mmol) was added to a solution of alcohol **17b** (148 mg, 0.8 mmol) and TEMPO (12 mg, 0.08 mmol) in anhydrous DCM (3.2 mL) and the reaction mixture was stirred at room temperature under nitrogen for 6 hours. The ^1H NMR spectrum showed complete conversion to the corresponding aldehyde. *N*-methoxy-*N*-methyl(triphenylphosphoranylidene)acetamide (378 mg, 1.04 mmol) was then added, and the reaction mixture stirred for 16 hours until the ^1H or ^{19}F NMR spectrum showed complete conversion. The resulting orange solution was concentrated under reduced pressure and column chromatography on silica gel (1:1 to 3:2 diethyl ether in hexane) afforded **19a** (157 mg, 74%) as a pale yellow solid and **19b** (25 mg, 9%) as a yellow oil. Data for **19a**: m.p. = 52-55 °C (chloroform/pentane); R_f = 0.14 (1:1 Et_2O in hexane); ^1H NMR (400 MHz, CDCl_3): δ = 7.39-7.31 (m, ArH , 3H), 7.30-7.25 (m, ArH , 2H), 6.82 (dd, J = 15.6, 9.6 Hz, $\text{CHCH}=\text{CH}$, 1H), 6.69 (d, J = 15.4 Hz, $\text{CH}=\text{CHCO}$, 1H), 3.74 (s, OCH_3 , 3H), 3.28 (s, NCH_3 , 3H), 2.91 (dd, J_{H-F} = 14.6 Hz, J = 7.1 Hz, ArCHCF_2CH , 1H), 2.70 ppm (ddd, J_{H-F} = 13.1 Hz, J = 9.6, 7.2 Hz, CHCH , 1H); ^{13}C NMR (100 MHz, CDCl_3): δ = 165.3, 138.5 (d, $^4J_{C-F}$ = 4.8 Hz), 132.1, 128.2, 127.4, 127.1, 120.6, 112.9 (t, $^1J_{C-F}$ = 292.7 Hz), 61.3, 35.6 (dd, J_{C-F} = 11.2, 9.0 Hz), 33.8 (t, J_{C-F} = 11.5), 31.9 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ = -130.5 (dd, 2J = 156.1 Hz, J_{F-H} = 14.1 Hz, 1F), -135.7 ppm

(dd, $^2J = 156.0$ Hz, $J_{F-H} = 13.5$ Hz, 1F); $\bar{\nu}/(\text{film}) = 1661, 1630, 1383, 1273, 1152, 986$ cm $^{-1}$; MS (CI): m/z (%): 288 (8) [(M-F)+C₃H₅] $^+$, 276 (9) [(M-F)+C₂H₅] $^+$, 248 (100) [M-F] $^+$; HRMS (APCI): calcd for C₁₄H₁₆F₂NO₂, 268.1144 [M+H] $^+$ found 268.1145; t_R (GC) = 11.30 minutes. Data for **19b**: $R_f = 0.33$ (1:1 Et₂O in hexane); ^1H NMR (400 MHz, CDCl₃): $\delta = 7.36$ -7.34 (m, ArH, 4H), 7.32-7.27 (m, ArH, 1H), 6.53 (d, $J = 11.4$ Hz, CH=CHCO, 1H), 5.95 (dddd, $J = 11.4, 10.1$ Hz, $^4J_{H-F} = 1.4, 1.3$ Hz, CHCH=CH, 1H), 4.29 (br. ddd, $J_{H-F} = 14.0$ Hz, $J = 10.1, 7.2$ Hz, CHCH=CH, 1H), 3.74 (s, OCH₃, 3H), 3.27 (s, NCH₃, 3H), 2.81 (dd, $J_{H-F} = 14.9$ Hz, $J = 7.2$ Hz, ArCHCF₂CH, 1H); ^{13}C NMR (100 MHz, CDCl₃): $\delta = 166.2$ (d, $^5J_{C-F} = 3.7$ Hz), 133.3 (d, $^4J_{C-F} = 6.0$ Hz), 131.8, 128.1, 127.7, 126.9, 119.0, 113.7 (t, $^1J_{C-F} = 291.3$ Hz), 61.3, 36.1 (dd, $^2J = 11.5, 8.9$ Hz), 31.5, 29.8 ppm (dd, $^2J = 13.2, 9.8$ Hz); ^{19}F NMR (376 MHz, CDCl₃): $\delta = -132.6$ (dd, $^2J = 153.9$ Hz, $J_{F-H} = 14.8$ Hz, 1F), -136.3 ppm (dd, $^2J = 153.8$ Hz, $J_{F-H} = 14.0$ Hz, 1F); $\bar{\nu}/(\text{film}) = 2982, 2360, 2343, 1656, 1627, 1425, 1354, 1252, 1169, 1001$ cm $^{-1}$; MS (CI): m/z (%): 296 (12) [M+C₂H₅] $^+$, 268 (52) [M+H] $^+$, 248 (100) [M-F] $^+$, 217 (8) [M-(F-OMe)], 187 (8); HRMS (APCI): calcd for C₁₄H₁₆F₂NO₂, 268.1144 [M+H] $^+$ found 268.1145; t_R (GC) = 13.37 minutes.

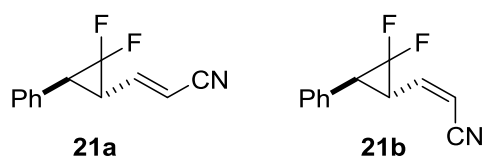
Preparation of ethyl (E)-3-((1R*,3S*)-2,2-difluoro-3-phenylcyclopropyl)-2-methylacrylate (20a)



Ester **20a** was prepared from alcohol **17b** (340 mg, 1.47 mmol), TEMPO (26 mg, 0.47 mmol), BAIB (512 mg, 1.62 mmol), (carbethoxyethylidene)triphenylphosphorane (692 mg, 1.9 mmol) and anhydrous DCM (10 mL) according to general procedure D with an oxidation time of 4 hours and an olefination time of 17 hours. Column chromatography on silica gel (1:19 Et₂O in hexane) afford ester **20a** as a yellow oil (290 mg, 74%); $R_f = 0.47$ (1:4 Et₂O in hexane); ^1H NMR (400 MHz, CDCl₃): $\delta = 7.39$ -7.30 (m, ArH, 3H), 7.29-7.25 (m, ArH, 2H), 6.59 (ddd, $J = 9.7$ Hz, $^4J_{H-F} = 3.0$ Hz, $^4J = 1.5$ Hz, CH=CCH₃, 1H), 4.25 (q, $J = 7.2$ Hz, OCH₂CH₃, 2H), 2.86 (dd, $J_{H-F} = 14.9$ Hz, $J = 7.2$ Hz, ArCHCF₂CH, 1H), 2.70 (ddd, $J_{H-F} = 13.3$ Hz, $J = 9.7, 7.3$ Hz, CHCH=CH₃, 1H), 2.00 (d, $^4J = 1.2$ Hz, CH=C(CH₃), 3H), 1.34 ppm (t, $J = 7.2$ Hz, OCH₂CH₃, 3H); ^{13}C NMR (100 MHz, CDCl₃): $\delta = 167.2, 133.4$ (d, $^4J_{C-F} = 4.9$ Hz) 132.6, 130.8, 128.7, 127.9, 127.6, 113.8 (t, $^1J_{C-F} = 292.5$ Hz), 60.8, 36.2 (dd, $^2J_{C-F} = 11.8, 9.6$ Hz), 31.2 (t, $^2J_{C-F} = 11.2$ Hz),

14.3, 13.1 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ = -130.73 (dd, 2J = 154.4 Hz, $J_{\text{F-H}}$ = 14.6 Hz, 1F), -135.5 (dd, 2J = 154.8 Hz, $J_{\text{F-H}}$ = 13.5 Hz, 1F); $\bar{\nu}$ /(film) = 2984, 2359, 2342, 1705, 1441, 1259 cm^{-1} ; MS (CI): m/z (%): 275 (8) $[(\text{M-F})+\text{C}_2\text{H}_5]^+$, 247 (100), $[\text{M-F}]^+$, 219 (11), $[(\text{M+H})-\text{F-Et}]$, 201 (20), 173 (39); HRMS (APCI): calcd for $\text{C}_{15}\text{H}_{17}\text{F}_2\text{O}_2$, 267.1191 $[\text{M+H}]^+$ found 267.1192; t_{R} (GC) = 12.46 minutes.

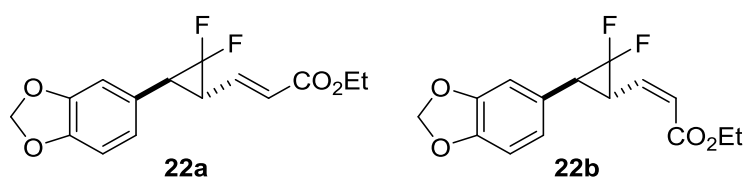
Preparation of ethyl (*E*)-3-((1*R,3*S**)-2,2-difluoro-3-phenylcyclopropyl)acrylonitrile (**21a**) and (*Z*)-3-((1*R**,3*S**)-2,2-difluoro-3-phenylcyclopropyl)acrylonitrile (**21b**) mixture**



(Triphenylphosphoranylidene)acetonitrile (536 mg, 1.8 mmol) was added to a colourless solution of aldehyde **18b** (250 mg, 1.37 mmol) in anhydrous DCM (6 mL) at room temperature under nitrogen. The resulting yellow reaction mixture changed to a red solution after being stirred for 2.5 hours. The reaction mixture was concentrated under reduced pressure and the resulting ^1H NMR of crude product confirmed complete conversion of **18b**. Column chromatography on silica gel (1:4 Et_2O in hexane) afforded a 3:2 diastereoisomeric mixture of cyano-**21a** and **21b** (237 mg, 84%). Mixed data for **21a** and **21b**: R_{f} = 0.29 (1:4 Et_2O in hexane); HRMS (APCI): calcd for $\text{C}_{12}\text{H}_{10}\text{F}_2\text{N}$, 206.0776 $[\text{M+H}]^+$ found 206.0774; $\bar{\nu}$ /(film) = 3291, 2912, 1495, 1476, 1437, 1236, 1167, 1103, 1036, 1011, 930 cm^{-1} ; Extracted data for **21a**: ^1H NMR (400 MHz, CDCl_3): δ = 7.42-7.24 (m, ArH, 5H), 6.53 (ddt, J = 16.3, 9.6 Hz, $^4J_{\text{H-F}}$ = 1.3 Hz, $\text{CH}=\text{CHCN}$, 1H), 5.60 (d, J = 16.4 Hz, $\text{CH}=\text{CHCN}$, 1H), 3.00-2.93 (m, ArCH, 1H), 2.65 ppm (ddd, $J_{\text{H-F}}$ = 12.3 Hz, J = 9.6, 7.2 Hz, $\text{CHCH}=\text{CH}$, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ = 146.9 (d, $^4J_{\text{C-F}}$ = 4.9 Hz), 131.5, 128.9, 128.1, 127.9, 116.8, 112.8 (t, $^1J_{\text{C-F}}$ = 293.6 Hz), 101.8, 36.4 (dd, $^2J_{\text{C-F}}$ = 11.9, 9.6 Hz), 34.2 ppm (t, $^2J_{\text{C-F}}$ = 11.6 Hz); ^{19}F NMR (376 MHz, CDCl_3): δ = -129.9 (dd, 2J = 158.1 Hz, $J_{\text{F-H}}$ = 15.3 Hz, 1F), -135.5 ppm (dd, 2J = 158.1 Hz, $J_{\text{F-H}}$ = 12.10 Hz, 1F); MS (CI): m/z (%): 246 (11) $[\text{M}+\text{C}_3\text{H}_5]^+$, 234 (23) $[\text{M}+\text{C}_2\text{H}_5]^+$, 206 (94) $[\text{M+H}]^+$, 186 (100) $[\text{M-F}]^+$; t_{R} (GC) = 11.45 minutes. Extracted data for **21b**: ^1H NMR (400 MHz, CDCl_3): δ = 7.42-7.24 (m, ArH, 5H), 6.32 (ddt, J = 11.0, 9.8 Hz, $^4J_{\text{H-F}}$ = 1.1 Hz, $\text{CHCH}=\text{CHCN}$, 1H), 5.55 (d, J = 11.1 Hz, $\text{CH}=\text{CHCN}$, 1H), 3.09 (ddd, $J_{\text{H-F}}$ = 12.3 Hz, J = 9.8, 6.9 Hz, $\text{CHCH}=\text{CH}$, 1H), 3.00-2.93 ppm (m, ArCH, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ = 146.2 (d, $^4J_{\text{C-F}}$ =

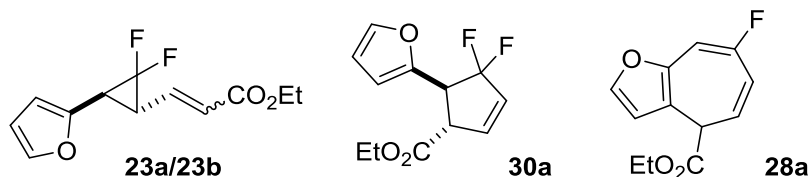
5.4 Hz), 131.2, 128.9, 128.1, 127.9, 115.8, 112.8 (t, $^1J_{C-F}$ = 293.1 Hz), 101.4, 36.6 (d, $^2J_{C-F}$ = 11.8, 9.22), 33.1 ppm (d, $^2J_{C-F}$ = 13.3, 10.4); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -130.0 (dd, 2J = 156.9, J_{H-F} = 15.0 Hz, 1F), -135.8 ppm (dd, 2J = 156.9, J_{H-F} = 12.2 Hz, 1F); MS (CI): m/z (%): 246 (6) $[M+C_3H_5]^+$, 234 (15) $[M+C_2H_5]^+$, 206 (22) $[M+H]^+$, 186 (100) $[M-F]^+$; t_R (GC) = 11.86 minutes.

Preparation of ethyl (E)-3-((1R*,3S*)-3-(benzo[d][1,3]dioxol-5-yl)-2,2-difluorocyclopropyl)acrylate (22a) and of ethyl (Z)-3-((1R*,3S*)-3-(benzo[d][1,3]dioxol-5-yl)-2,2-difluorocyclopropyl)acrylate (22b)



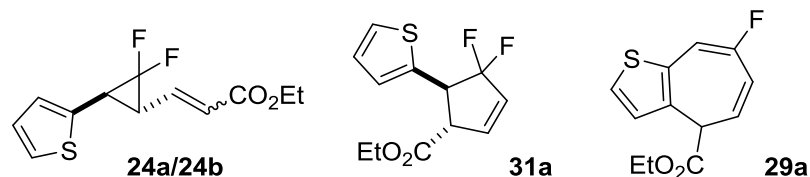
Ester **22a** was prepared from alcohol **17d** (36.5 mg, 0.16 mmol), TEMPO (3.7 mg, 0.02 mmol), BAIB (57 mg, 0.18 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (85 mg, 0.21 mmol) and anhydrous DCM (2 mL) according to General Procedure D with an oxidation time of 4 hours and an olefination time of 4 hours. Column chromatography on silica gel (1:9 diethyl ether in hexane) afforded **22a** (23.5 mg, 50%) and a mixture of **22a** and **22b** (10 mg, 21%) as pale yellow oils. Data for **22a**: R_f = 0.25 (1:4 Et_2O in hexane); 1H NMR (400 MHz, $CDCl_3$): δ = 6.81-6.72 (m, ArH, 3H), 6.77 (dd, J = 15.3, 8.9 Hz, $CH=CHCO_2Et$, 1H), 6.08 (d, J = 15.5 Hz, $CH=CHCO_2Et$, 1H), 5.98 (s, OCH_2O , 2H), 4.23 (q, J = 7.1 Hz, OCH_2CH_3 , 2H), 2.84 (J_{H-F} = 14.7 Hz, J = 7.1 Hz, ArCH, 1H), 2.54 (ddd, J_{H-F} = 13.0 Hz, J = 8.9, 7.1 Hz, $CHCH=CH$, 1H), 1.33 (t, J = 7.1 Hz, OCH_2CH_3 , 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.2, 147.5, 146.7, 139.8 (d, J_{C-F} = 4.7 Hz), 125.2, 123.1, 121.2, 112.7 (t, $^1J_{C-F}$ = 292.4 Hz), 107.9, 107.7, 100.8, 60.1, 35.2 (dd, $^2J_{C-F}$ = 12.1, 9.3 Hz), 33.4 (t, $^2J_{C-F}$ = 11.7 Hz), 13.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -130.6 (dd, 2J = 156.5 Hz, J_{F-H} = 14.7 Hz, 1F), -135.5 (dd, 2J = 156.2 Hz, J_{F-H} = 13.0 Hz, 1F); $\bar{\nu}$ /(film) = 2924, 2359, 2342, 1715, 1505, 1493, 1445, 1256, 1188 1165, 1096, 1038, 1018, 789 cm^{-1} ; MS (CI): m/z (%): 325 (4) $[M+C_2H_5]^+$, 305 (9) $[(M-F)+C_2H_5]^+$, 277 (100) $[M-F]^+$, 259 (11) $[M-F_2]^+$, 231 (44), 203 (24), 175 (5); HRMS (APCI): calcd for $C_{15}H_{18}F_2O_4N$, 314.1198 $[M+NH_4]^+$ found 314.1199; t_R (GC) = 14.30 minutes. Extracted Data for **22b**: R_f = 0.40 (1:4 Et_2O in hexane); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -132.5 (dd, 2J = 154.4 Hz, J_{F-H} = 14.8 Hz, 1F), -136.1 (dd, 2J = 153.6 Hz, J_{F-H} = 13.5 Hz, 1F).

Attempted preparation of ethyl (E)-3-((1R*,3S*)-2,2-difluoro-3-(furan-2-yl)cyclopropyl)acrylate (23a/23b**)**



The synthesis of ester **23a** was attempted from alcohol **17a** (1.33 g, 7.6 mmol), BAIB (2.67 mg, 8.36 mmol), TEMPO (60 mg, 1.52 mmol), (ethoxycarbonylmethylene)-triphenylphosphorane (5.3 g, 9.8 mmol) and DCM (30 mL) according to general procedure D with an oxidation time of 3 h and olefination time of 16 h. The ^{19}F NMR of the resulting crude reaction mixture confirmed complete consumption of **17a**. Column chromatography on silica gel (1:19 Et₂O in hexane) afforded a set of fractions containing rearrangement product **28a** with trace amounts of difluorocyclopentene **30a** (1.06 g, 80%) as a pale yellow oil. Further purification attempts failed as isolated compounds showed signs of decomposition (solution turned black). No evidence of ester **23** was observed during the reaction and initial purification, consistent with rearrangement occurring at room temperature. ^1H and ^{19}F NMR spectra are consistent with heptadiene **28a** and show similarities with the corresponding thiophene based product (**29a**) which was fully characterised (*vide infra*). Extracted data for **28a**: R_f = 0.38 (1:4 Et₂O in hexane); ^1H NMR (400 MHz, CDCl₃): δ = 7.54 (d, J = 2.0 Hz, ArH, 1H), 6.57 (dddd, $J_{\text{H-F}}$ = 15.2 Hz, 4J = 2.0 Hz, 5J = 0.7, 0.5 Hz, C-CH=CF, 1H), 6.28 (dd, J = 2.0 Hz, 4J = 0.6 Hz, ArH, 1H), 6.17 (dddd, $J_{\text{H-F}}$ = 11.5 Hz, J = 10.7 Hz, 4J = 2.0 Hz, 0.5 Hz, (F)CCH=CH, 1H), 5.89 (ddd, J = 10.7, 7.2 Hz, $^4J_{\text{H-F}}$ = 4.1 Hz, 5J = 0.5 Hz), 4.23 (ABq, J = 7.4 Hz, 2J = 1.4 Hz, OCH_aH_bCH₃, 2H), 4.18 (br. d, J = 7.5 Hz, C(H)CO₂Et, 1H), 1.29 ppm (t, J = 7.2 Hz, CH₂CH₃, 3H); ^{19}F NMR (376 MHz, CDCl₃): δ = -105.67 ppm (ddd, $J_{\text{F-H}}$ = 15.2, 11.5 Hz, $^4J_{\text{F-H}}$ = 4.2 Hz).

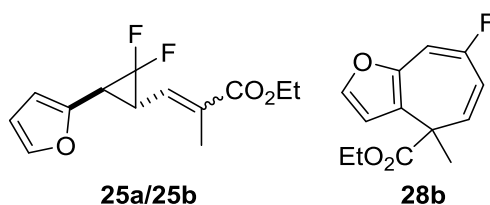
Attempted preparation of ethyl (E)-3-((1R*,3S*)-2,2-difluoro-3-(thiophen-2-yl)cyclopropyl)acrylate (24a/24b**)**



The synthesis of ester **24a** was attempted from alcohol **17c** (684 mg, 3.6 mmol), BAIB (1.26 g, 3.96 mmol), TEMPO (28 mg, 0.72 mmol), (ethoxycarbonylmethylene)-triphenylphosphorane (1.64 g, 4.68 mmol) and DCM (15 mL) according to general procedure D with an oxidation time of 3 h and an olefination time of 16 h. The ^1H NMR spectrum of the crude reaction mixture confirmed complete consumption of **17c**. Column chromatography on silica gel (1:19 Et₂O in hexane) afforded a set of fractions containing **24b** (12 mg), a mixture of rearrangement products and alkenoate **24a** (420 mg) and a mixture of rearrangement products **29a** and **31a** (212 mg). A solution of crude product containing **24a** in CDCl₃ (1 mL) and **24b** in CDCl₃ (1 mL) were heated at 40 °C and 50 °C, respectively for 17 h. ^1H and ^{19}F NMR showed complete consumption of VCP-precursors. Product samples containing a clean mixture of **29a** and **31a** were combined and concentrated under reduced pressure to afford a brown oil (488 mg). HPLC purification on a Kromasil C18 cartridge (2:5 to 1:1 gradient of MeCN containing 0.1% ammonia solution in 10 mM ammonium bicarbonate for 10 minutes then 1:1 to 9.9:10 of the same eluent for 30 minutes) afforded clean heptadiene **29a** (112 mg, 14%) as an orange oil and a brown oil containing a mixture of **29a** and difluorocyclopentene **31a** (24 mg, 1:1 by ^1H NMR, the latter characterised by the distinctive ^{19}F NMR signals). Data for **29a**: R_f = 0.42 (1:4 Et₂O in hexane); ^1H NMR (400 MHz, CDCl₃): δ = 7.38 (d, J = 5.2 Hz, ArH, 1H), 6.80 (dd, $J_{\text{H-F}}$ = 15.6 Hz, 4J = 1.7 Hz, C-CH=CF, 1H), 6.77 (d, J = 5.24 Hz, ArH, 1H), 6.21 (dddd, J = 10.9 Hz, $J_{\text{H-F}}$ = 7.3 Hz, 4J = 1.7, 0.8 Hz, CHCH=CH-CF, 1H), 6.01 (ddd, J = 10.9, 7.0 Hz, $^4J_{\text{H-F}}$ = 4.6 Hz, CH-CH=CH, 1H), 4.29 (ABq, J = 7.2 Hz, 2J = 1.4 Hz, OCH₂H_bCH₃, 2H), 3.98 (d, J = 7.0 Hz, C(H)CO₂Et, 1H), 1.32 ppm (t, J = 7.2 Hz, CH₂CH₃, 3H); ^{13}C NMR (100 MHz, CDCl₃): δ = 170.6, 158.8 (d, $^1J_{\text{C-F}}$ = 246 Hz), 132.3 (d, $J_{\text{C-F}}$ = 14.9 Hz), 129.7, 126.8 (d, $^5J_{\text{C-F}}$ = 3.1 Hz), 125.8 (d, $J_{\text{C-F}}$ = 13.0 Hz), 125.5, 120.5 (d, $^2J_{\text{C-F}}$ = 35.2 Hz), 106.1 (d, $^2J_{\text{C-F}}$ = 31.4 Hz), 60.9, 44.7, 13.7 ppm; ^{19}F NMR (376 MHz, CDCl₃): δ = -103.4 ppm (ddd, $J_{\text{F-H}}$ = 15.6, 7.3 Hz, $^4J_{\text{F-H}}$ = 4.6 Hz); $\bar{\nu}$ /(film) = 2980, 2937, 1733, 1632, 1444, 1402, 1370, 1333,

1308, 1186, 1137 cm^{-1} ; MS (CI): m/z (%): 239 (41) $[\text{M}+\text{H}]^+$, 219 (35) $[\text{M}-\text{F}]^+$, 193 (25) $[\text{M}-\text{OEt}]^+$, 165 (100) $[\text{M}-\text{CO}_2\text{Et}]^+$, 147 (9); HRMS (APCI): calcd for $\text{C}_{12}\text{H}_{12}\text{FSO}_2$, 239.0542 $[\text{M}+\text{H}]^+$ found 239.0548; t_R (GC) = 12.91 minutes. Extracted data for **31a**: ^1H NMR (400 MHz, CDCl_3): δ = 7.31 (dd, J = 5.1 Hz, 4J = 1.3 Hz, ArH, 1H), 7.09-7.07 (br m, containing d J = 3.7 Hz, ArH, 1H), 7.04 (dd, J = 5.1, 3.7 Hz, ArH, 1H), 6.46 (dt, J = 6.0, 1.9 Hz, 4J = 1.9 Hz, $\text{CF}_2\text{-CH=CH}$, 1H), 6.10 (dd, J = 6.0 Hz, 4J = 2.7 Hz, $\text{CF}_2\text{-CH=CH}$, 1H), 4.34-4.24 (m, under peak for **29a**, ArCH, 1H), 4.21 (q, J = 7.2 Hz, OCH_2CH_3 , 2H), 3.94-3.88 (m, CHCO_2Et , 1H), 1.28 ppm (t, J = 7.2 Hz, CH_2CH_3 , 3H); ^{19}F NMR (376 MHz, CDCl_3): δ = -92.4 (ddd, 2J = 250.5 Hz, $J_{\text{F-H}}$ = 14.8 Hz, $^4J_{\text{F-H}}$ = 7.6 Hz, CF_aF_b , 1F), -93.7 ppm (ddd, 2J = 250.5 Hz, $J_{\text{F-H}}$ = 14.6 Hz, $^4J_{\text{F-H}}$ = 5.4 Hz, CF_aF_b , 1F); MS (CI): m/z (%): 267 (7) $[\text{M}-\text{F}+\text{C}_2\text{H}_5]^+$, 239 (100) $[\text{M}-\text{F}]^+$, 221 (8) $[\text{M}-\text{F}_2+\text{H}]^+$, 193 (25), 165 (12); t_R (GC) = 12.11 minutes.

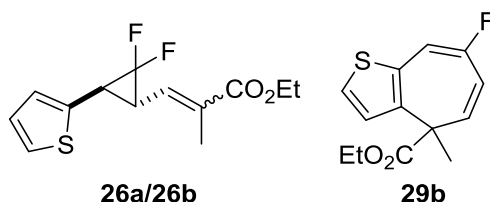
Attempted preparation of ethyl (E)-3-((1R*,3S*)-2,2-difluoro-3-(furan-2-yl)cyclopropyl)acrylate (25a/25b**)**



The synthesis of ester **25a** was attempted from alcohol **17a** (52 mg, 0.3 mmol), BAIB (106 mg, 0.33 mmol), TEMPO (5 mg, 0.03 mmol), (carbethoxyethylidene)triphenylphosphorane (142 mg, 0.39 mmol) and DCM (2 mL) according to general procedure D with an oxidation time of 3 h and an olefination time of 14 h. The ^1H NMR spectrum of the crude reaction mixture confirmed complete consumption of **17a**, forming cycloheptadiene **28b** exclusively. The crude reaction mixture was transferred onto a pad of silica (10 g) in a sinter funnel which had been conditioned with hexane. The pad was eluted with 0:1 to 1:9 Et_2O in hexane to afford cycloheptadiene **28b** as a pale yellow oil (34 mg, 48%). R_f = 0.41(1:4 Et_2O in hexane); ^1H NMR (400 MHz, CDCl_3): δ = 7.53 (d, J = 2.0 Hz, ArH, 1H), 6.57 (dddd, $J_{\text{H-F}}$ = 14.9 Hz, 4J = 2.0, 0.7 Hz, 5J = 0.6 Hz, C-CH=CF , 1H), 6.28 (dd, J = 2.0 Hz, 4J = 0.7 Hz, ArH, 1H), 6.14 (ddd, J = 11.7 Hz, $J_{\text{H-F}}$ = 10.3 Hz, 4J = 2.0 Hz, C(F)-CH=CH , 1H), 5.76 (dd, J = 11.7 Hz, $^4J_{\text{H-F}}$ = 4.2 Hz, C(F)-CH=CH , 1H), 4.18 (q, J = 7.2 Hz, OCH_2CH_3 , 2H), 1.64 (s, CH_3 , 3H), 1.25 ppm (t, J = 7.2 Hz, CH_2CH_3 , 3H); ^{13}C NMR (150 MHz, CDCl_3): δ = 173.9, 157.8 (d, $^1J_{\text{C-F}}$ = 241.0 Hz), 146.2 (d,

$^4J_{C-F} = 15.9$ Hz), 144.4 (d, $^5J_{C-F} = 4.1$ Hz), 133.2 (d, $J_{C-F} = 13.1$ Hz), 120.5 (d, $^2J_{C-F} = 37.7$ Hz), 120.3 (d, $J_{C-F} = 3.9$ Hz), 109.9, 102.5 (d, $J_{C-F} = 33.7$ Hz), 61.4, 44.9, 24.0, 14.1 ppm; ^{19}F NMR (376 MHz, CDCl_3): $\delta = -107.05$ (ddd, $J_{F-H} = 14.9, 10.3$ Hz, $^4J_{F-H} = 4.2$ Hz); $\bar{\nu}/(\text{film}) = 2980, 2934, 1794, 1731, 1641, 1459, 1405, 1376, 1251, 1216, 1149, 1108, 1017$ cm^{-1} ; MS (CI): m/z (%): 237 (33) $[\text{M}+\text{H}]^+$, 217 (30) $[\text{M}-\text{F}]^+$, 191 (15) $[\text{M}-\text{OEt}]^+$, 189 (13) $[\text{M}-(\text{F}+\text{Et})+\text{H}]^+$, 163 (100) $[\text{M}-\text{CO}_2\text{Et}]^+$, 145 (8) $[\text{M}-(\text{CO}_2\text{Et}+\text{F})+\text{H}]^+$; HRMS (APCI): calcd for $\text{C}_{13}\text{H}_{17}\text{F}_1\text{N}_1\text{O}_3$, 254.1187 $[\text{M}+\text{NH}_4]^+$ found 254.1189; t_R (GC) = 12.05 minutes.

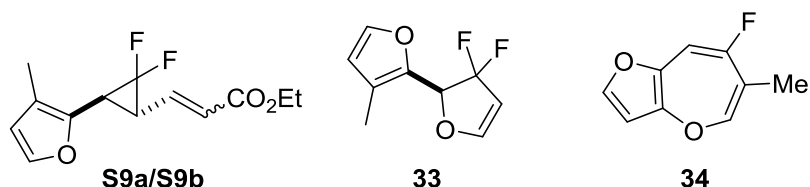
Attempted preparation of ethyl (*E*)-3-((1*R**,3*S**)-2,2-difluoro-3-(thiophen-2-yl)cyclopropyl)acrylate (**26a/26b**)



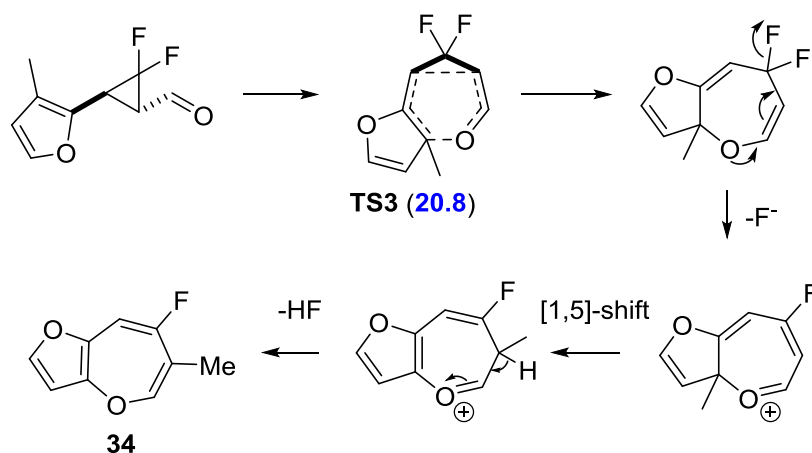
The synthesis of ester **26a** was attempted from alcohol **17c** (93 mg, 0.48 mmol), BAIB (171 mg, 0.53 mmol), TEMPO (7.5 mg, 0.05 mmol), (carbethoxyethylidene)triphenylphosphorane (226 mg, 0.62 mmol) and DCM (3.2 mL) according to general procedure D with an oxidation time of 3 h and an olefination time of 14 h. The ^1H NMR spectrum of the crude reaction mixture confirmed complete consumption of **17c**, forming cycloheptadiene **29b** exclusively. The crude reaction mixture was transferred onto a pad of silica (10 g) in a sinter funnel which had been conditioned with hexane. The pad was eluted with 0:1 to 1:9 Et_2O in hexane to afford cycloheptadiene **29b** as a pale yellow oil (66 mg, 55%). $R_f = 0.39$ (1:4 Et_2O in hexane); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.39$ (d, $J = 5.4$ Hz, ArH , 1H), 6.88 (d, $J = 5.4$ Hz, ArH , 1H), 6.76 (dd, $J_{H-F} = 15.4$ Hz, $^4J = 2.0$ Hz, $\text{C}-\text{CH}=\text{CF}$, 1H), 6.24 (ddd, $J = 11.1$ Hz, $J_{H-F} = 8.2$ Hz, $^4J = 2.0$ Hz, $\text{CF}-\text{CH}=\text{CH}$, 1H), 5.80 (dd, $J = 11.1$ Hz, $^4J_{H-F} = 4.6$ Hz, $\text{CF}-\text{CH}=\text{CH}$, 1H), 4.14 (q, $J = 7.2$ Hz, OCH_2CH_3 , 2H), 1.79 (s, $\text{C}-\text{CH}_3$, 3H), 1.20 ppm (t, $J = 7.2$ Hz, CH_2CH_3 , 3H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 173.8, 158.2$ (d, $^1J_{C-F} = 244.5$ Hz), 135.4 (d, $^4J_{C-F} = 2.0$ Hz), 132.9 (d, $J_{C-F} = 13.1$ Hz), 132.0 (d, $J_{C-F} = 13.5$ Hz), 126.4 (d, $^5J_{C-F} = 3.3$ Hz), 125.3, 120.0 (d, $^2J_{C-F} = 36.0$ Hz), 105.9 (d, $^2J_{C-F} = 31.3$ Hz), 60.8, 47.6, 23.3, 13.6 ppm; ^{19}F NMR (376 MHz, CDCl_3): $\delta = -106.10$ (ddd, $J_{F-H} = 15.4, 8.2$ Hz, $^4J_{F-H} = 4.6$ Hz); $\bar{\nu}/(\text{film}) = 2980, 2937, 1733, 1632, 1444, 1402, 1370, 1333, 1308, 1186, 1137$ cm^{-1} ; MS (CI): m/z (%): 253 (31) $[\text{M}+\text{H}]^+$, 233 (53) $[\text{M}-\text{F}]^+$, 207 (19) $[\text{M}-\text{OEt}]^+$, 179

(100) $[M-CO_2Et]^+$, 161 (8) $[M-(CO_2Et+F)+H]^+$; HRMS (APCI): calcd for $C_{13}H_{14}F_1S_1O_2$, 253.0693 $[M+H]^+$ found 253.0696; t_R (GC) = 13.17 minutes.

Attempted preparation of ethyl (*E*)-3-((1*R,3*S**)-2,2-difluoro-3-(2'-furyl-3-methyl)cyclopropyl)acrylate (**S9a/S9b**)**



The synthesis of ester **S9a** was attempted from alcohol **17h** (71 mg, 0.38 mmol), BAIB (144 mg, 0.45 mmol), TEMPO (11 mg, 0.08 mmol), (carbethoxyethylidene)triphenylphosphorane (183 mg, 0.53 mmol) and DCM (3 mL) according to general procedure D with an oxidation time of 6 h and an olefination time of 16 h. Crude 1H and ^{19}F NMR after oxidation suggested rearrangement had occurred before addition of phosphorane. The reaction mixture was concentrated under reduced pressure and crude 1H and ^{19}F NMR showed no new formation of rearrangement products. Attempted chromatographic purification on silica gel (0:1 to 1:4 Et_2O in hexane) failed to isolated desired rearrangement products either due to product volatility or decomposition on silica. ^{19}F NMR of crude products showed strong similarities to 3,3-difluoro-4,5-dihydrofurans reported by Hammond and Arimitsu (^{19}F NMR: δ = -84.6 (ddd, J = 248.0, 23.1, 19.8 Hz, 1F) -87.2 ppm (ddd, J = 248.0, 13.2, 13.2 Hz, 1F))^{S19} and benzoheptadiene compounds reported previously by ourselves (^{19}F NMR: δ = -100.7 ppm (dt, J_{F-H} = 18.2, 5.2 Hz, $^4J_{F-H}$ = 5.2 Hz, 1F).^{S20} Due to these similarities the crude products were tentatively assigned as dihydrofuran **33** and ether **34** (1:2.5 ratio respectively by ^{19}F NMR); the doublet of doublet observed for the latter suggest the methyl group underwent [1,5]-shift during the re-aromatisation of the furan (**Scheme S4**).

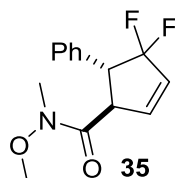


Scheme S4: Proposed mechanism rearrangement of **18h** to **34** through rearrangements ($\Delta G^\ddagger$ value (blue) quoted in kcal mol⁻¹)

Data for **33**: ¹⁹F NMR (376 MHz, CDCl₃): δ = -81.9 (dd, ²*J* = 248.0 Hz, *J*_{F-H} = 20.0 Hz, 1F), -89.3 ppm (dt, ²*J* = 248.0 Hz, *J*_{F-H} = 13.8 Hz, 1F). Data for **34**: ¹⁹F NMR (376 MHz, CDCl₃): δ = -99.4 ppm (dd, *J*_{F-H} = 34.0 Hz, ⁴*J*_{F-H} = 18.5 Hz).

General Procedure E: Thermal Rearrangement of Vinyl Difluorocyclopropanes

Preparation of (1*R**,5*R**)-4,4-difluoro-*N*-methoxy-*N*-methyl-5-phenylcyclopent-2-ene-1-carboxamide (**35**)



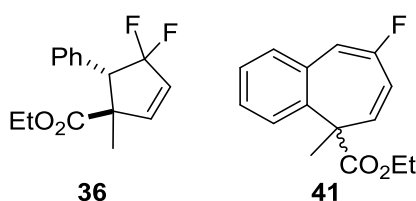
A solution of **19a** (7.0 mg, 0.026 mmol) in toluene (0.3 mL) was heated to 95 °C in a sealed microwave vial for 17 hours in a DrySyn block. After cooling and venting the vial, ¹⁹F NMR confirmed complete consumption of **19a**. The reaction mixture was transferred to a round bottom flask using DCM (5 mL) and concentrated under reduced pressure to afford difluorocyclopentene **35** (6.8 mg, 97%) as a yellow oil. *R*_f = 0.36 (1:1 Et₂O in hexane); ¹H NMR (400 MHz, CDCl₃): δ = 7.40-7.31 (m, ArH, 5H), 6.40 (dt, *J* = 6.0, 1.6 Hz, *J*_{H-F} = 1.6 Hz, =CHCHCO, 1H), 6.10 (dd, *J* = 6.0 Hz, ⁴*J* = 2.5 Hz, CF₂CH=CH, 1H), 4.34 (dddd, ⁴*J*_{H-F} = 8.9, 5.2 Hz, *J* = 6.7, 1.6 Hz, COCH, 1H), 4.11 (ddd, *J*_{H-F} = 16.1, 15.4 Hz, *J* = 6.7 Hz, PhCH, 1H), 3.49 (s, OCH₃, 3H), 3.20 ppm (s, OCH₃, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 170.5, 139.1 (t, *J*_{C-F} = 10.0 Hz), 134.1, 129.6 (t, ¹*J*_{C-F} = 254.7 Hz), 128.9, 128.3 (dd, ²*J*_{C-F} = 30.1, 25.2 Hz), 128.0, 127.3, 60.9, 53.2 (t,

$^2J_{C-F} = 24.5$ Hz), 51.4 (d, $J_{C-F} = 5.3$ Hz), 31.9 ppm; ^{19}F NMR (376 MHz, CDCl_3): $\delta = -90.2$ (ddd, $^2J = 251.0$ Hz, $J_{F-H} = 16.1$, $^4J_{H-F} = 8.9$ Hz, 1F), -92.0 ppm (ddd, $^2J = 251.1$ Hz, $J_{F-H} = 15.4$, $^4J_{H-F} = 5.2$ Hz, 1F); $\bar{\nu}/(\text{film}) = 2963, 2940, 2361, 2342, 1661, 1456, 1418, 1387, 1364, 1350, 1169, 1051, 1034, 1026, 1093\text{ cm}^{-1}$; MS (CI): m/z (%): 296 (19) $[(M+H)-F]^+$, 276 (26) $[(M+H)-F]^+$, 248 (100) $[M-F]^+$, 218 (10) $[(M+H)-\text{OMe}-F]^+$, 187 (16), 161 (6); HRMS (APCI): calcd for $\text{C}_{14}\text{H}_{15}\text{F}_2\text{NO}_2\text{Na}$, 290.0963 $[M+\text{Na}]^+$ found 290.0964; t_R (GC) = 12.97 minutes.

Thermolysis of (Z)-3-((1R*,3S*)-2,2-difluoro-3-phenylcyclopropyl)-N-methoxy-N-methylacrylamide (**19b**)

A solution of **19b** (126 mg, 0.47 mmol) in Ph_2O (0.5 mL) was heated at 165°C for 17 h according to General Procedure E. The crude reaction mixture was loaded onto a silica pad (10 g) conditioned with hexane. Ph_2O was eluted with hexane then crude products were eluted with Et_2O , collected and concentrated under reduced pressure to afford a brown oil (53 mg). ^1H and ^{19}F NMR confirmed full consumption of alkenoate **19b**. Column chromatography on silica gel (1:9 to 2:5 EtOAc in hexane) was used to separated two major unknown products as yellow oils; unknown **S10a** (13 mg) and unknown **S10b** (7 mg). Lack of distinctive Weinreb amide signals in the ^1H NMR suggests decomposition had occurred. Data for **S10a**: $R_f = 0.21$ (1:1 Et_2O in hexane); ^{19}F NMR (376 MHz, CDCl_3): $\delta = -100.41$ (d, $J_{F-H} = 15.9$ Hz). Data for **S10b**: $R_f = 0.39$ (1:1 Et_2O in hexane); ^{19}F NMR (376 MHz, CDCl_3): $\delta = -87.39$ (s).

Attempted preparation of ethyl (1R*,5S*)-4,4-difluoro-1-methyl-5-phenylcyclopent-2-ene-1-carboxylate (**36**)

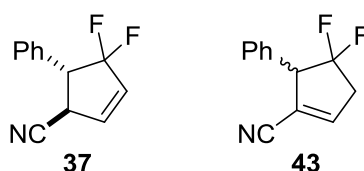


A solution of **20** (100 mg, 0.37 mmol) in Ph_2O (0.45 mL) was heated at 155°C for 17 h according to General Procedure E. The crude reaction mixture was loaded onto a silica pad (16 g) conditioned with hexane. Ph_2O was eluted with hexane then crude products were eluted with Et_2O , collected and concentrated under reduced pressure to afford crude reaction mixture as a brown oil (100 mg). ^1H and ^{19}F NMR confirmed full consumption of alkenoate **20**. Column chromatography on silica gel (0:1 to 1:19 EtOAc in hexane) was used

to separated two major unknown products as yellow oils; unknown **S11a** (8 mg) and unknown **S11b** (29 mg). Product assignment could not be determined due to complexity in ^1H NMR spectra. However, the major ^{19}F NMR signal for **S11b** was consistent with previously observed benzoheptadiene compounds and tentatively assigned as benzoheptadiene **41**. No evidence for VCPR rearrangement to difluorocyclopentene **36**.

Data for **S11a**: R_f = 0.18 (1:19 EtOAc in hexane); ^{19}F NMR (CDCl_3 , 376 MHz): δ = -103.67 (minor peak, dd, $J_{\text{F-H}}$ = 12.0, 7.5 Hz), -110.58 ppm (major peak, s). Data for **S11b**: R_f = 0.28 (1:19 EtOAc in hexane); ^{19}F NMR (CDCl_3 , 376 MHz): δ = -95.84 (minor peak, dd, $J_{\text{F-H}}$ = 32.9, 15.0 Hz), -104.43 ppm (major peak, dt, $J_{\text{F-H}}$ = 17.8, 5.4 Hz, $^4J_{\text{F-H}}$ = 5.4 Hz).

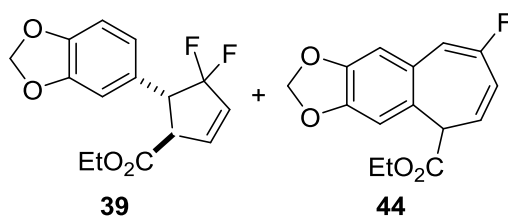
Preparation of (1*R**,5*R**)-4,4-difluoro-5-phenylcyclopent-2-ene-1-carbonitrile (**37**) and 4,4-difluoro-5-phenylcyclopent-1-ene-1-carbonitrile (**43**)



A solution of mixture **21a/21b** (100 mg, 0.48 mmol) in Ph_2O (1.0 mL) was heated to 90 °C in a sealed microwave vial for 17 hours in a DrySyn block. After cooling and venting, the resulting ^{19}F NMR spectrum confirmed full conversion of **21a**. The microwave vial was resealed and heated to 160 °C for 17 hours in a DrySyn block. After cooling and venting, the resulting ^{19}F NMR spectrum confirmed full consumption of **21b**. The crude reaction mixture was transferred onto a pad of silica (15 g) in a sinter funnel which has been conditioned with hexane. Ph_2O was eluted using hexane and then crude product fractions were eluted using Et_2O , collected and concentrated under reduced pressure to afford a red oil (106 mg). Column chromatography on silica gel (0:1 to 1:9 Et_2O in hexane) afforded a mixture difluorocyclopentenenes **37** and **43** (6:1 ratio by ^1H NMR) as a yellow oil (44.7 mg, 48%). Data for mixture of **37** and **43**: R_f = 0.21 (1:9 Et_2O in hexane); $\bar{\nu}/(\text{film})$ = 3091, 3069, 3036, 2915, 2249, 2229, 1502, 1457, 1349, 1178 cm^{-1} ; HRMS (APCI): calcd for $\text{C}_{12}\text{H}_8\text{F}_2\text{N}$, 204.0625 [M-H] found 204.0634; Data for **37**: ^1H NMR (400 MHz, CDCl_3): δ = 7.47-7.40 (m, ArH, 3H), 7.35-7.32 (m, ArH, 2H), 6.45 (dt, J = 6.0, 1.9 Hz, $^4J_{\text{H-F}}$ = 1.3 Hz, $\text{C}(\text{F}_2)\text{CH}=\text{CH}$, 1H) 6.26 (dd, J = 6.0 Hz, $J_{\text{H-F}}$ = 2.6 Hz, $\text{C}(\text{F}_2)-\text{CH}=\text{CH}$, 1H), 3.99 (dddd, J = 7.6, 2.0 Hz, $^4J_{\text{H-F}}$ = 9.6, 5.0 Hz, $\text{C}(\text{H})\text{CN}$, 1H),

3.90 ppm (ddd, $J = 7.6$ Hz, $J_{\text{H-F}} = 14.6, 13.7$ Hz, ArCH, 1H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 134.8$ (t, $J_{\text{C-F}} = 10.0$ Hz), 131.0, 130.4 (dd, $^2J_{\text{C-F}} = 30.1, 24.1$ Hz), 128.5, 128.4 (represents 2 carbon atoms), 127.4 (t, $^1J_{\text{C-F}} = 246.7$ Hz), 117.3 (d, $^4J_{\text{C-F}} = 5.2$ Hz), 5.4 (t, $^2J_{\text{C-F}} = 25.4$ Hz), 38.3 ppm (d, $J_{\text{C-F}} = 6.4$ Hz); ^{19}F NMR (376 MHz, CDCl_3): $\delta = -90.98$ (ddd, $^2J = 255.6$ Hz, $J_{\text{F-H}} = 14.9$ Hz, $^4J_{\text{F-H}} = 9.6$ Hz, CF_aF_b , 1F), -93.00 ppm (ddd, $^2J = 255.6$ Hz, $J_{\text{F-H}} = 13.7$ Hz, $^4J_{\text{F-H}} = 14.6$ Hz, CF_aF_b , 1F); MS (CI): m/z (%): 246 (10) $[\text{M}+\text{C}_3\text{H}_5]^+$, 234 (20) $[\text{M}+\text{C}_2\text{H}_5]^+$, 206 (77) $[\text{M}+\text{H}]^+$, 186 (100) $[\text{M-F}]^+$; t_{R} (GC) = 11.31 minutes. Data for **47**: ^1H NMR (400 MHz, CDCl_3): $\delta = 7.47$ -7.40 (m, ArH, 3H), 7.24-7.22 (m, ArH, 2H), 6.87 (dtt, $J = 5.0$ Hz, $^4J_{\text{H-F}} = 2.6$ Hz, $^4J = 2.2$ Hz, $\text{CF}_2\text{-CH}_2\text{-CH=}$, 1H), 4.36 (dddt, $J_{\text{H-F}} = 18.0, 7.9$ Hz, $^4J = 2.2, 1.4$ Hz, ArCH, 1H), 3.17-3.09 (m, $\text{CF}_2\text{-CH}_2\text{-CH=}$, 2H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 143.9$ (t, $J_{\text{C-F}} = 4.1$ Hz), 129.9, 128.3, 128.2 (represents 2 carbon atoms), 127.1 (t, $^1J_{\text{C-F}} = 255.1$ Hz), 115.9 (dd, $J_{\text{C-F}} = 6.7, 2.8$ Hz), 114.1, 58.7 (dd, $^2J_{\text{C-F}} = 26.7, 25.4$ Hz), 41.9 ppm (dd, $J_{\text{C-F}} = 28.9, 28.3$ Hz); ^{19}F NMR (376 MHz, CDCl_3): $\delta = (-90.62)$ -(-91.40) (m, CF_aF_b , underneath ^{19}F signal for major product **37**), (-98.05)-(-98.76) ppm (m, containing d, $^2J = 233.1$ Hz, CF_aF_b); MS (CI): m/z (%): 246 (7) $[\text{M}+\text{C}_3\text{H}_5]^+$, 234 (17) $[\text{M}+\text{C}_2\text{H}_5]^+$, 206 (100) $[\text{M}+\text{H}]^+$, 186 (35) $[\text{M-F}]^+$; t_{R} (GC) = 11.50 minutes.

Preparation of ethyl (1R,5R)-5-(benzo[d][1,3]dioxol-5-yl)-4,4-difluorocyclopent-2-ene-1-carboxylate (39**) and ethyl 8-fluoro-5H-cyclohepta[4,5]benzo[1,2-d][1,3]dioxole-5-carboxylate (**44**)**



A solution of **22a** (445 mg, 0.07 mmol) in a toluene (7.5 mL) was heated to 70 °C for 17 h according the General Procedure E. ^1H and ^{19}F NMR showed full consumption of **22a** to a mixture of difluorocyclopentene **39** and benzoheptadiene **44** (42:58 respectively, relative ratio by ^{19}F NMR). HPLC purification on a Kromasil C18 cartridge (3:10 to 9.9:10 gradient of MeCN containing 0.1% ammonia solution in 10 mM ammonium bicarbonate) afford clean fluoroheptadiene **44** (45 mg, 11%) as a white solid and difluorocyclopentene **39** (82 mg, 18%). Note: poor yield could be due to partial solubility of crude reaction mixture in loading solvent for HPLC purification (1:1 DMSO/MeOH). Data for **39**: $R_f = 0.35$ (1:4 Et_2O in hexane);

^1H NMR (400 MHz, CDCl_3): δ = 6.81 (s, ArH, 3H), 6.48 (ddd, J = 6.0 Hz, $J_{\text{H-F}}$ = 1.7 Hz, 4J = 1.7 Hz, $\text{CF}_2\text{-CH=CH}$, 1H), 6.07 (dd, J = 6.0, 2.5 Hz, CH=CH , 1H), 5.98 (s, O_2CH_2 , 2H), 4.19 (q, J = 7.0 Hz, OCH_2CH_3 , 2H), 3.95-3.82 (m, ArCH and HCCO_2Et , 2H), 1.26 ppm (t, J = 7.0 Hz, CH_2CH_3 , 3H); ^{13}C NMR (100 MHz, CDCl_3): δ = 170.2 (d, $^4J_{\text{C-F}}$ = 2.7 Hz), 147.3, 146.8, 138.4 (t, $J_{\text{C-F}}$ = 10.4 Hz), 129.0 (t, $^1J_{\text{C-F}}$ = 245.7 Hz), 128.4 (dd, $^2J_{\text{C-F}}$ = 30.8, 24.5 Hz), 127.2, 122.3, 108.8, 107.7, 100.6, 61.0, 54.2 (d, $J_{\text{C-F}}$ = 5.8 Hz), 53.1 (t, $^2J_{\text{C-F}}$ = 24.0 Hz), 13.6 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ = -90.21 (ddd, 2J = 252.5 Hz, $J_{\text{F-H}}$ = 16.4, $^4J_{\text{F-H}}$ = 8.6 Hz, CF_aF_b , 1F), -93.07 ppm (ddd, 2J = 252.5 Hz, $J_{\text{F-H}}$ = 14.1, $^4J_{\text{F-H}}$ = 5.1 Hz, CF_aF_b , 1F); $\bar{\nu}$ /(film) = 2982, 2904, 1614, 1731, 1506, 1493, 1446, 1245, 1167, 1018 cm^{-1} ; MS (CI): m/z (%): 277 (100) $[\text{M-F}]^+$, 231 (16), 203 (15), 175 (4) $[\text{M-C}_7\text{O}_2\text{H}_5]^+$; HRMS (APCI): calcd for $\text{C}_{15}\text{H}_{14}\text{FO}_4$, 277.0876 $[\text{M-F}]$ found 277.0905; t_R (GC) = 14.09 minutes. Data for **44**: m.p. = 118-120 °C (chloroform/pentane); R_f = 0.40 (1:4 Et_2O in hexane); ^1H NMR (400 MHz, CDCl_3): δ = 6.82 (s, ArH, 1H), 6.80 (d, $J_{\text{H-F}}$ = 18.1 Hz, C-CH=CF , 1H), 6.59 (s, ArH, 1H), 6.22-6.14 (m, representing CF-CH=CH and C(H)-CH=CH , 2H), 6.01 (d, 2J = 1.4 Hz, $\text{OCH}_a\text{H}_b\text{O}$, 1H), 5.98 (d, 2J = 1.4 Hz, $\text{OCH}_a\text{H}_b\text{O}$, 1H), 4.30 (ABq, J = 7.2 Hz, 2J = 1.9 Hz, $\text{OCH}_a\text{H}_b\text{CH}_3$, 2H), 3.69 (d, J = 5.2 Hz, HCCO_2Et , 1H), 1.31 ppm (t, J = 7.2 Hz, CH_2CH_3 , 3H); ^{13}C NMR (100 MHz, CDCl_3): δ = 171.0, 158.6 (d, $^2J_{\text{C-F}}$ = 245.5 Hz), 148.6, 146.1, 127.7 (d, $J_{\text{C-F}}$ = 12.5 Hz), 126.0 (d, $J_{\text{C-F}}$ = 11.4 Hz), 125.8, 119.3 (d, $^2J_{\text{C-F}}$ = 35.1 Hz), 113.0 (d, $^2J_{\text{C-F}}$ = 27.9 Hz), 107.0 (d, $^5J_{\text{C-F}}$ = 3.8 Hz), 105.1, 101.1, 60.9, 48.9, 13.7 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ = -102.97 ppm (ddd, $J_{\text{F-H}}$ = 18.1, 4.8 Hz, $^4J_{\text{C-F}}$ = 4.8 Hz); $\bar{\nu}$ /(film) = 2982, 2904, 1733, 1645, 1506, 1485, 1374, 1333, 1305, 1238, 1193 cm^{-1} ; MS (CI): m/z (%): 305 (11) $[\text{M}+\text{C}_2\text{H}_5]^+$, 277 (65) $[\text{M}+\text{H}]^+$, 257 (41) $[\text{M}+\text{H}]^+$, 231 (100) $[\text{M-OEt}]^+$, 203 (40) $[\text{M-CO}_2\text{Et}]^+$, 57 (80); HRMS (ASAP+): calcd for $\text{C}_{15}\text{H}_{14}\text{FO}_4$, 277.0876 $[\text{M}+\text{H}]^+$ found 277.0884; t_R (GC) = 14.97 minutes.

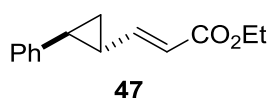
Preparation of ((1S*,2S*)-2-phenylcyclopropyl)methanol (**S12**)



Diiodomethane (1 ml, 12.5 mmol) was added dropwise to a solution of diethylzinc (6.25 mL of a 1 M solution in hexane, 6.25 mmol) in DCM (2 mL) at 0 °C over a period of 5 minutes and stirred for 20 minutes under nitrogen. A solution of cinnamyl alcohol (335 mg, 1.25 mmol) in DCM (1.5 mL) was added dropwise and the reaction mixture and stirred for 2.5 hours at 0 °C. The reaction mixture was quenched with saturated aqueous NH_4Cl (10 ml) and

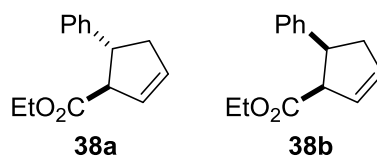
EtOAc (10 ml). The organic layer was separated and the aqueous layer extracted further with EtOAc (3 x 10 ml). The original organic layer and extracts were combined, dried (MgSO₄) and concentrated under reduced pressure to remove volatile organic solvent. Column chromatography on silica gel (2:3 EtOAc in hexane) afforded alcohol **S12** as a yellow oil (93 mg, 52%). *R*_f = 0.23 (1:1 Et₂O in hexane); ¹H NMR (400 MHz, CDCl₃): δ = 7.29-7.26 (m, *ArH*, 2H), 7.17 (tt, *J* = 7.3 Hz, ⁴*J* = 1.2 Hz, *ArH*, 1H), 7.10-7.08 (m, *ArH*, 2H), 3.64 (dd, ²*J* = 11.3 Hz, *J* = 6.8 Hz, CH₆H₆OH, 1H), 3.62 (dd, ²*J* = 11.3 Hz, *J* = 6.8 Hz, CH₆H₆OH, 1H), 1.84 (td, *J* = 9.8, 4.9 Hz, PhCH, 1H), 1.78 (br. s, OH, 1H), 1.50-1.44 (m, CH₂CH(CH₂)CH, 1H), 1.00-0.92 ppm (m, CH₂, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 142.5, 128.4, 125.9, 125.7, 66.5, 25.3, 21.3, 13.8 ppm; $\bar{\nu}$ /(film) = 3333, 3026, 3003, 2361, 2342, 1605, 1497, 1018, 743, 696 cm⁻¹; MS (CI): *m/z* (%): 159 (14) [(M+H)-OH]⁺, 131 (100) [M-OH]⁺; 117 (29), 91 (28); *t*_R (GC) = 11.10 minutes. Data was in agreement with those reported by Charette and co-workers.^{S21}

Preparation of ethyl (*E*)-3-((1*R**,2*S**)-2-phenylcyclopropyl)acrylate (**47**)



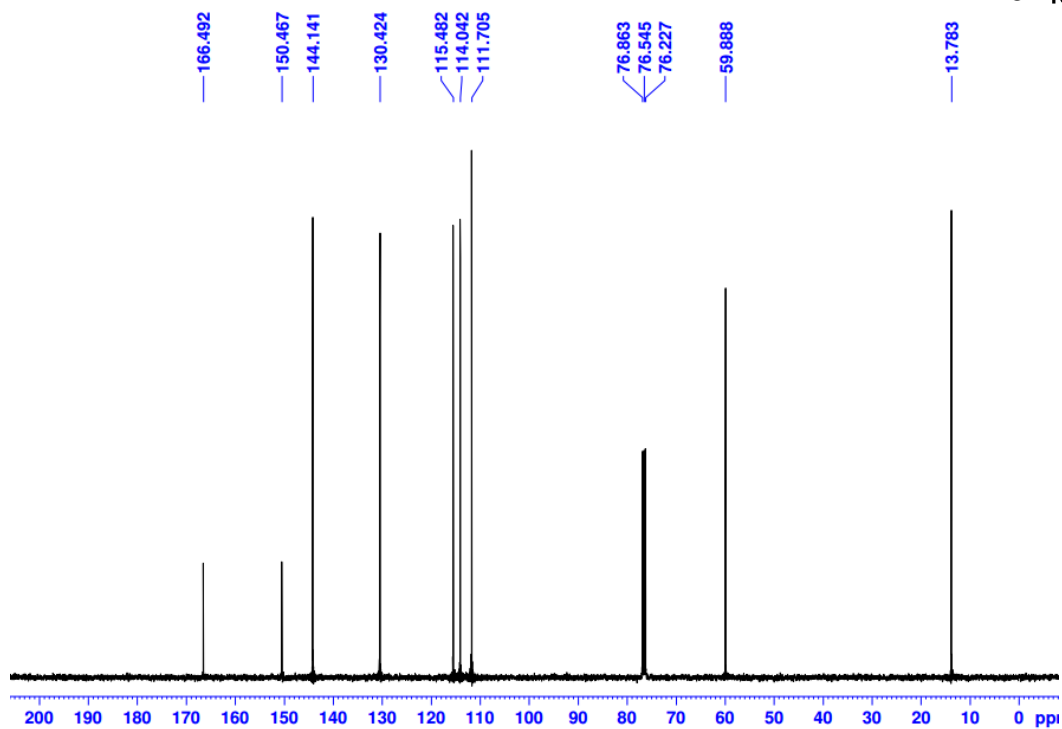
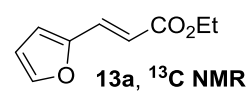
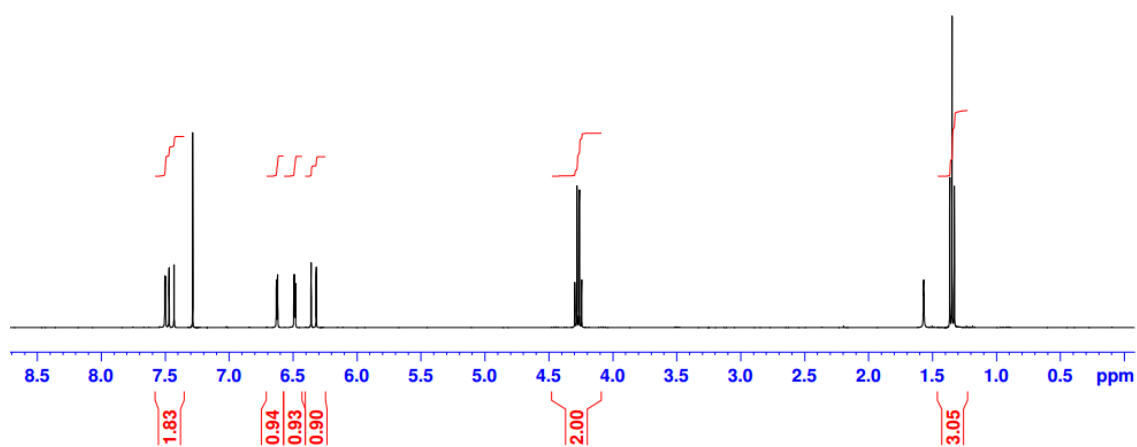
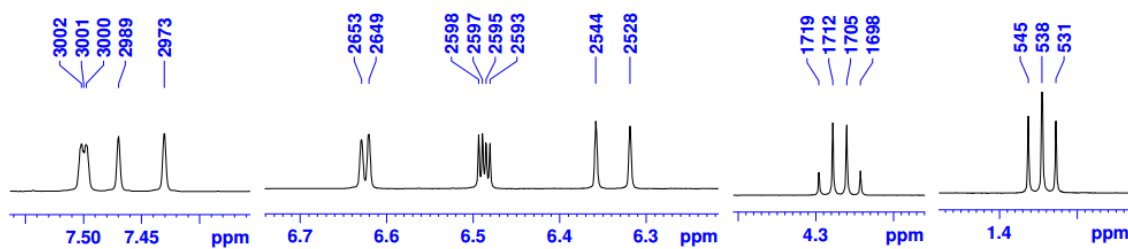
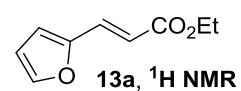
Ester **47** was prepared from alcohol **S12** (100 mg, 0.67 mmol), TEMPO (10 mg, 0.067 mmol), BAIB (237 mg, 0.74 mmol), (carbethoxyethylidene)triphenylphosphorane (303 mg, 0.87 mmol) and anhydrous DCM (1 mL) according to general procedure D with an oxidation time of 3.5 hours and an olefination time of 20 hours. Column chromatography on silica gel (1:9 Et₂O in hexane) afforded ester **47** as a colourless oil (100 mg, 67%). *R*_f = 0.42 (1:4 Et₂O in hexane); ¹H NMR (400 MHz, CDCl₃): δ = 7.33-7.28 (m, *ArH*, 2H), 7.21 (tt, *J* = 7.3 Hz, ⁴*J* = 1.3 Hz, *ArH*, 1H), 7.12-7.09 (m, *ArH*, 2H), 6.62 (dd, *J* = 15.5, 9.9 Hz, CHCH=CH, 1H), 5.92 (d, *J* = 15.5 Hz, CH=CH, 1H), 4.21 (q, *J* = 7.2 Hz, OCH₂CH₃, 2H), 2.20 (ddd, *J* = 9.5, 6.2, 4.3 Hz, PhCH, 1H), 1.84 (dddd, *J* = 9.9, 8.4, 5.4, 4.1 Hz, CH₂CHCH=CH, 1H), 1.47 (ddd, ²*J* = 8.5, *J* = 6.6, 5.2 Hz, CHCH₆H₆CH, 1H), 1.36-1.30 ppm (m, (incl. 1.31 ppm, t, *J* = 7.2 Hz, OCH₂CH₃, 3H), 4H); ¹³C NMR (100 MHz, CDCl₃): δ = 166.2, 151.0, 140.3, 128.0, 125.7, 125.4, 118.4, 59.6, 26.4, 26.2, 17.2, 13.8 ppm; $\bar{\nu}$ /(film) = 2980, 2359, 2342, 1709, 1643, 1256, 1175, 1036 cm⁻¹; MS (CI): *m/z* (%): 245 (6) [M+C₂H₅]⁺, 217 (56) [M+H]⁺, 171 (50) [M-OEt]⁺, 143 (100) [M-CO₂Et]⁺, HRMS (APCI): calcd for C₁₄H₁₇O₂, 217.1223 [M+H]⁺ found 217.1224; *t*_R (GC) = 13.57 minutes.

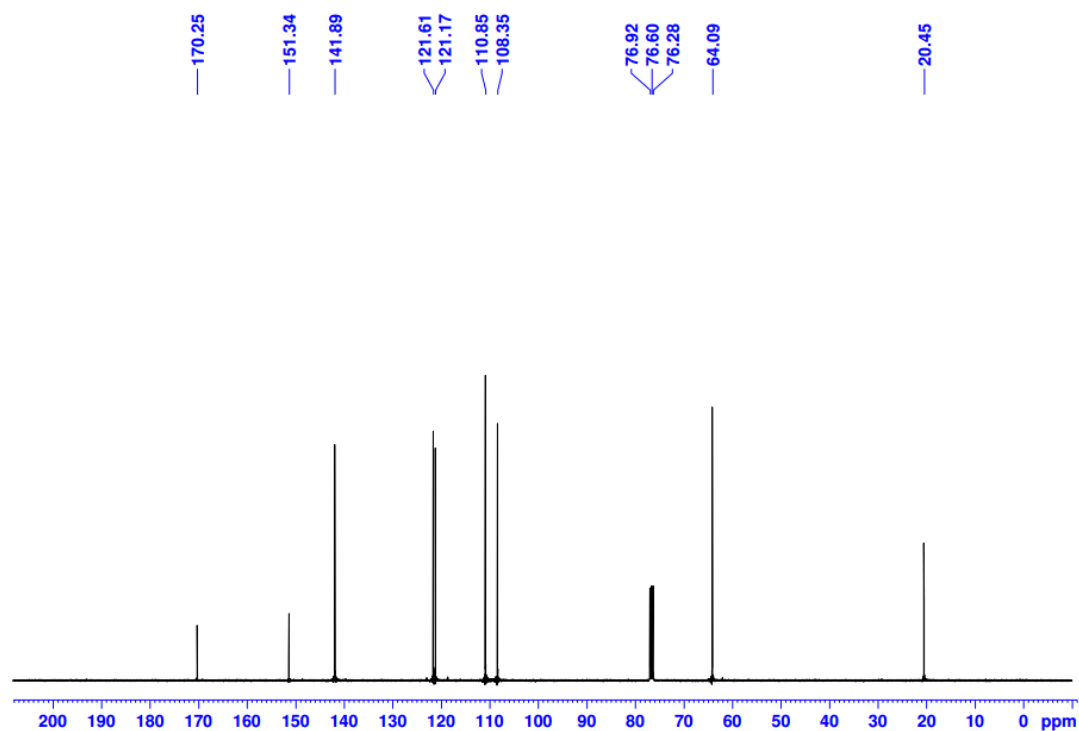
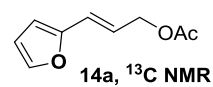
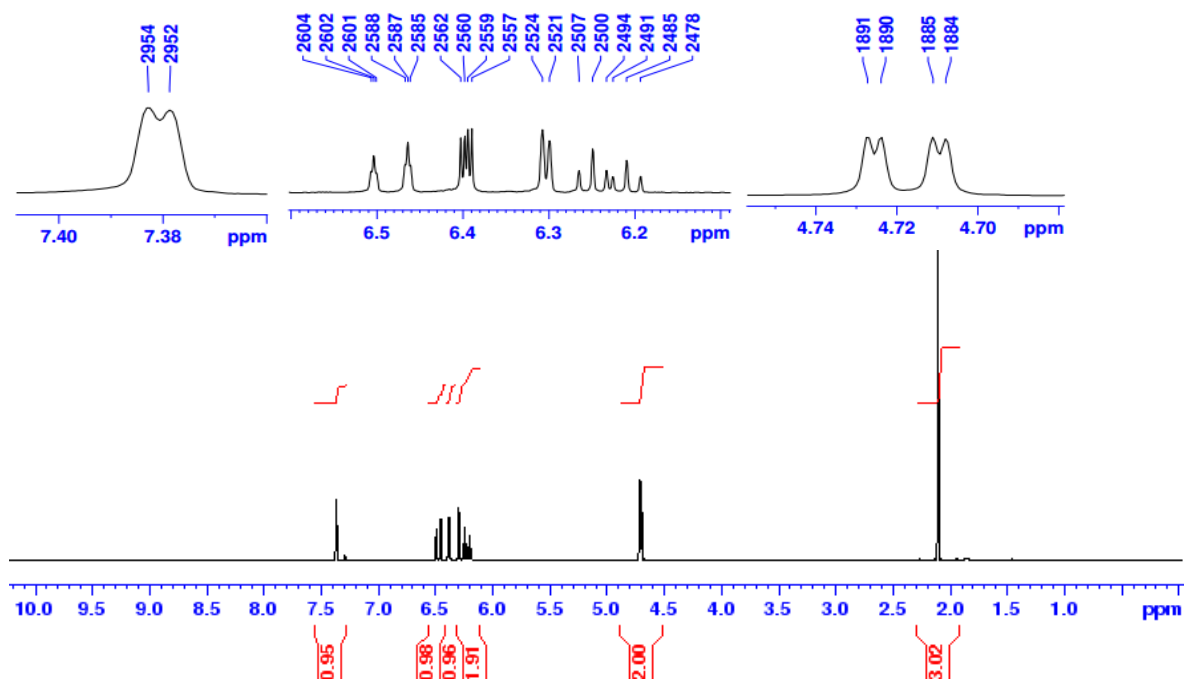
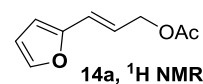
Preparation of ethyl (1R*,5R*)-5-phenylcyclopent-2-ene-1-carboxylate (38a**) and ethyl (1R*,5S*)-5-phenylcyclopent-2-ene-1-carboxylate (**38b**)**

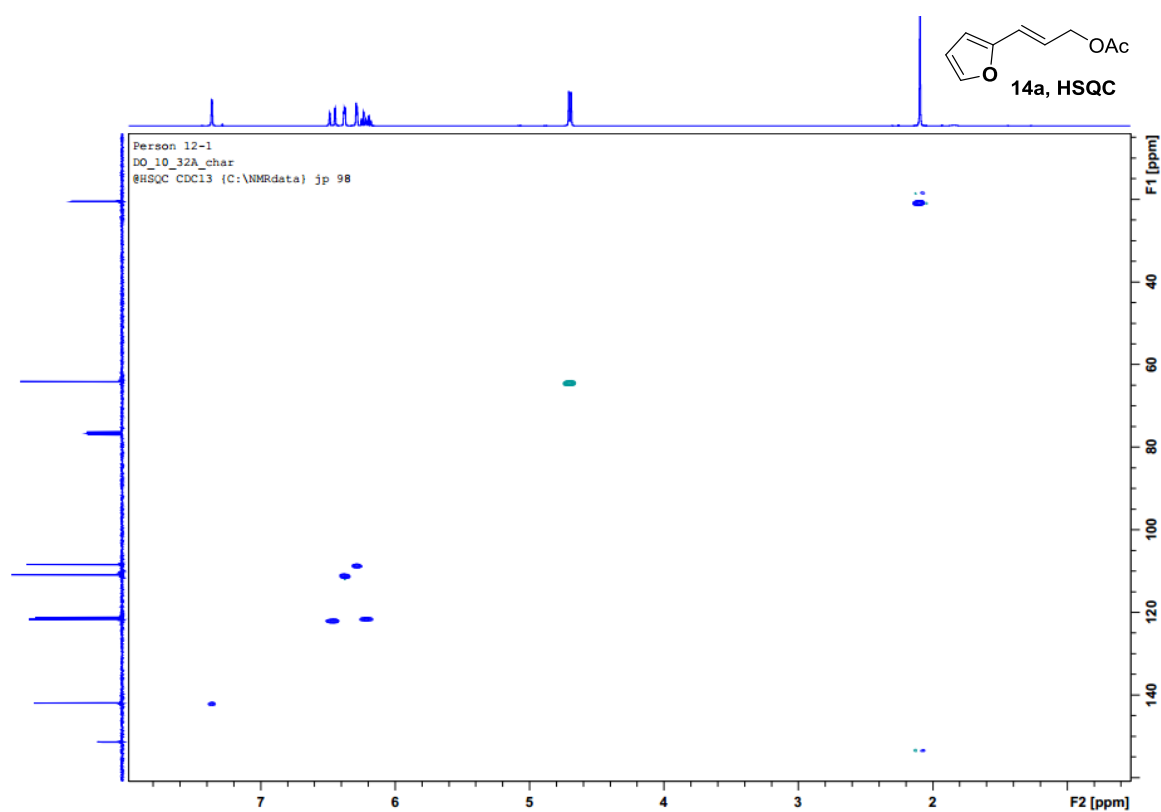


A solution of **47a** (100 mg, 0.46 mmol) in a Ph₂O (0.5 mL) was heated to 220 °C for 17 h according the General Procedure E. The crude reaction mixture was transferred onto a pad of silica (10 g) in a sinter funnel which has been conditioned with hexane. Ph₂O was eluted using hexane and then crude product fractions were eluted using Et₂O, collected and concentrated under reduced pressure to afford an orange oil (80 mg). Column chromatography on silica gel (0:1 to 1:9 Et₂O in hexane) afforded a *trans*-**38a** (40 mg, 40%) and *cis*-**38b** (22 mg, 22%, compound started to decompose slowly after isolation to an unknown side product) as pale yellow oils. Data for *trans*-**38a**: *R*_f = 0.65 (1:4 Et₂O in hexane); ¹H NMR (400 MHz, CDCl₃): δ = 7.35-7.27 (m, ArH, 3H), 7.25-7.21 (m, ArH, 2H), 5.96 (ddt, *J* = 5.7, 2.5 Hz, ⁴*J* = 2.3 Hz, CH₂CH=CH, 1H), 5.79 (ddt, *J* = 5.7, 2.4 Hz, ⁴*J* = 2.2 Hz, CH₂CH=CH, 1H), 4.17 (q, *J* = 7.2 Hz, OCH₂CH₃, 2H), 3.83 (dt, *J* = 9.2, 6.6 Hz, ArCH, 1H), 3.67 (dddd, *J* = 9.2, 2.5 Hz, ⁴*J* = 2.5, 2.2 Hz, HCCO₂Et, 1H), 3.00 (dddd, ²*J* = 16.9 Hz, *J* = 9.2, 2.4 Hz, ⁴*J* = 2.6, 2.3 Hz, -CH_αH_β-, 1H), 2.56 (dddd, ²*J* = 16.9 Hz, *J* = 6.6, 2.4 Hz, ⁴*J* = 2.6, 2.3 Hz, -CH_αH_β-, 1H), 1.27 ppm (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 173.6, 145.0, 132.2, 128.1, 127.7, 126.6, 125.9, 60.2, 59.0, 45.8, 41.1, 13.7 ppm; $\bar{\nu}$ /(film) = 3060, 3029, 2980, 2932, 2906, 2854, 1731, 1495, 1457, 1245, 1176 cm⁻¹; MS (CI): *m/z* (%): 245 (2) [M+C₂H₅]⁺, 217 (8) [M+H]⁺, 171 (19) [M-OEt]⁺, 143 (100) [M-CO₂Et]⁺, HRMS (APCI): calcd for C₁₄H₁₇O₂, 217.1228 [M+H]⁺ found 217.1229; *t*_R (GC) = 12.44 minutes. Data *cis*-**38b**: *R*_f = 0.52 (1:4 Et₂O in hexane); ¹H NMR (400 MHz, CDCl₃): δ = 7.27-7.28 (m, ArH, 4H), 7.22-7.17 (m, ArH, 1H), 6.15 (ddt, *J* = 5.7, 2.2 Hz, ⁴*J* = 2.1 Hz, CH₂CH=CH, 1H), 5.85 (ddt, *J* = 5.7, 2.3 Hz, ⁴*J* = 1.9 Hz, CH₂CH=CH, 1H), 3.93 (dddt, *J* = 9.1, 2.1 Hz, ⁴*J* = 2.0, 1.9 Hz, HCCO₂Et, 1H), 3.85 (dt, *J* = 9.1, 7.2 Hz, ArCH, 1H), 3.78-3.61 (m, OCH_αH_βCH₃, 2H); 2.83 (dddd, *J* = 7.2, 2.3 Hz, ⁴*J* = 2.2, 1.9 Hz, CH-CH₂-CH=CH-, 2H), 0.85 ppm (t, *J* = 7.0 Hz, CH₂CH₃, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 172.2, 141.5, 133.8, 128.0, 127.5, 127.4, 126.0, 59.6, 55.9, 46.3, 38.4, 13.2 ppm; $\bar{\nu}$ /(film) = 3060, 3029, 2980, 2932, 2904, 1729, 1495, 1457, 1370, 1178 cm⁻¹; MS (CI): *m/z* (%): 245 (5) [M+C₂H₅]⁺, 217 (14) [M+H]⁺, 171 (20) [M-OEt]⁺, 143 (100) [M-CO₂Et]⁺; HRMS (TOF): calcd for C₁₄H₁₇O₂, 216.1150 [M] found 216.1155; *t*_R (GC) = 12.28 minutes.

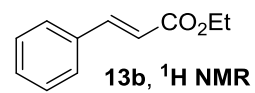
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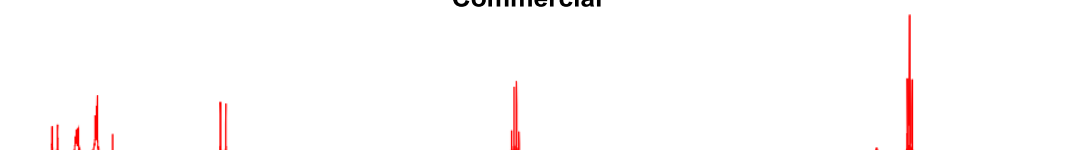




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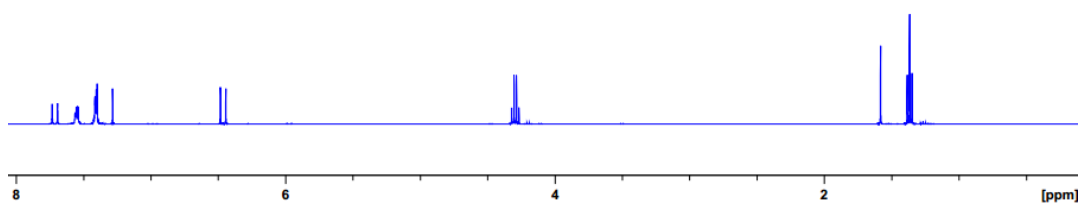


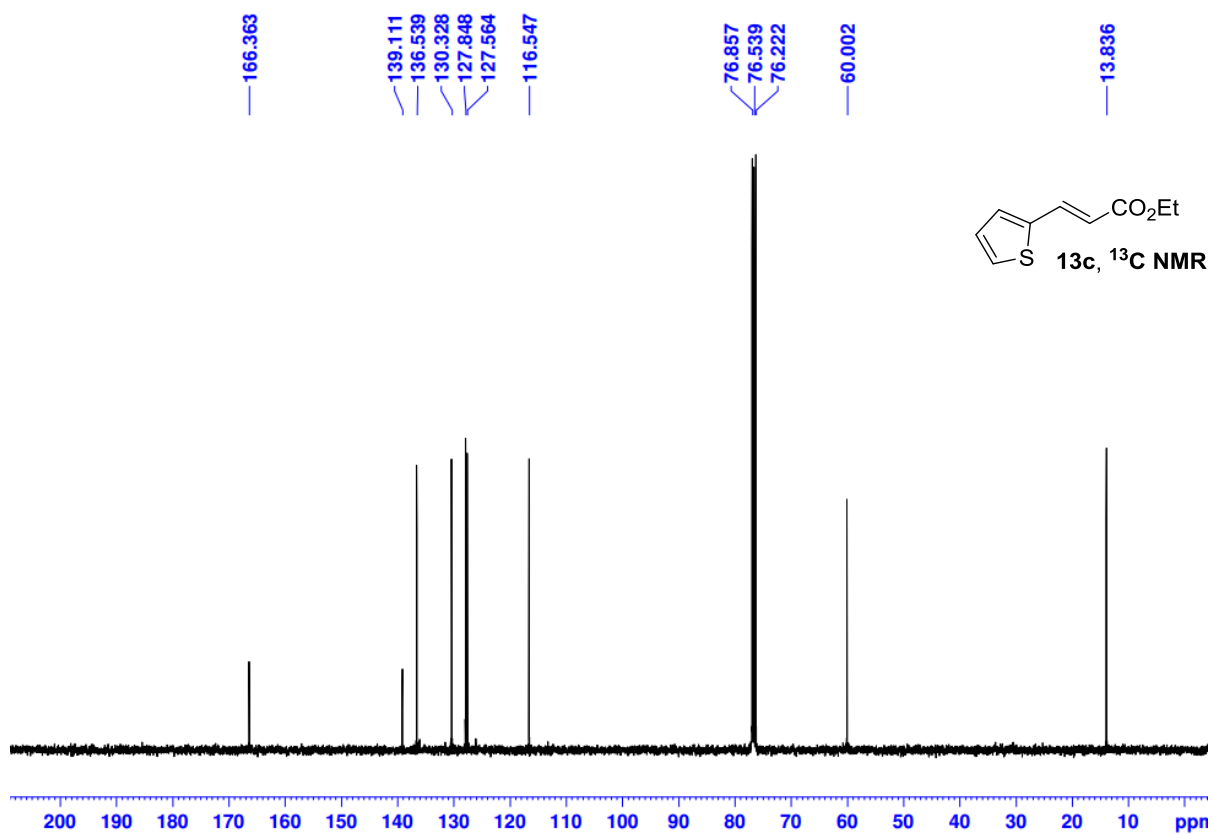
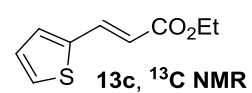
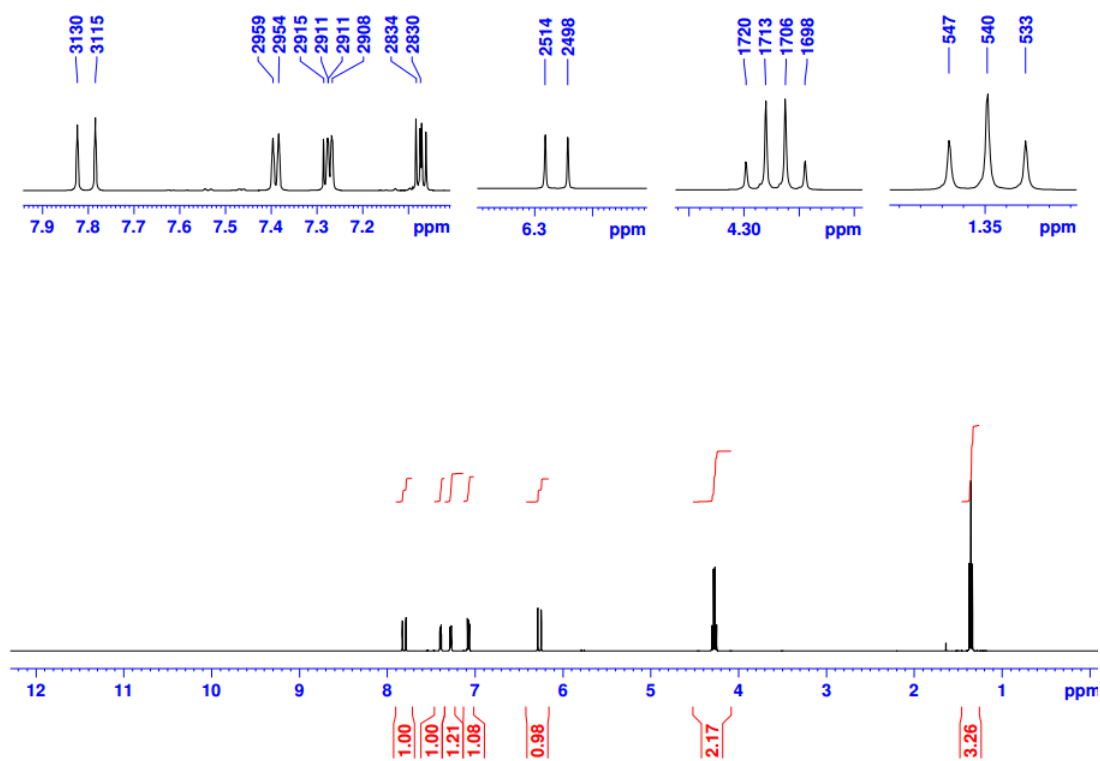
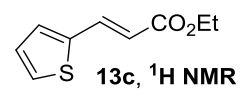
Commercial

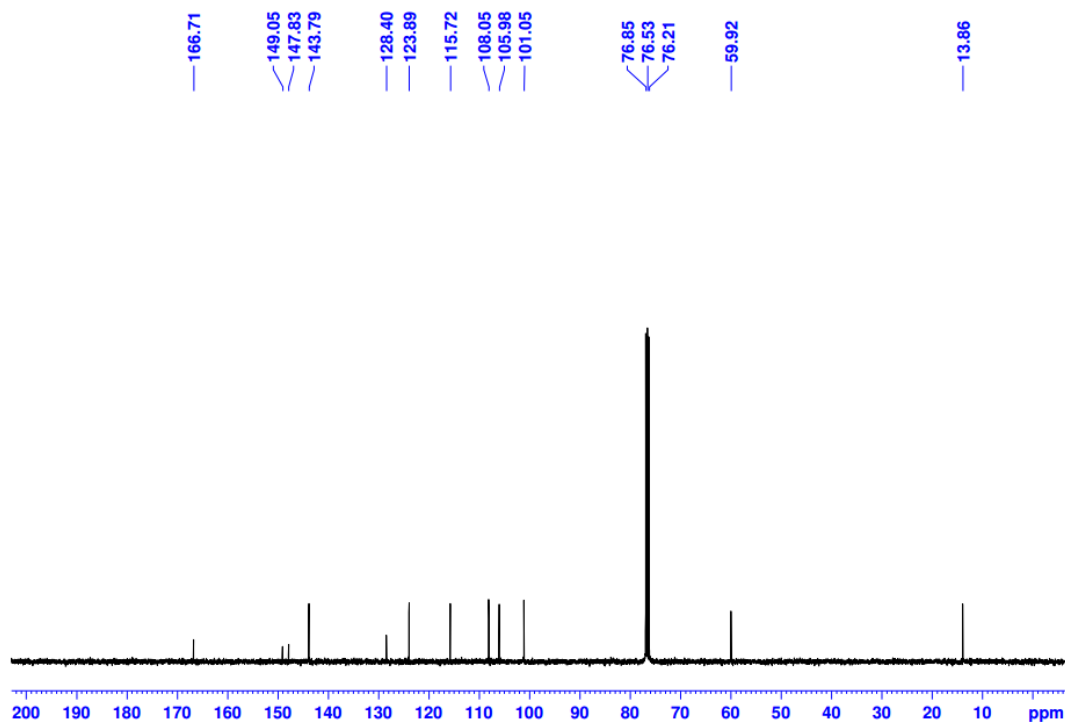
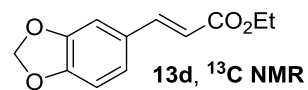
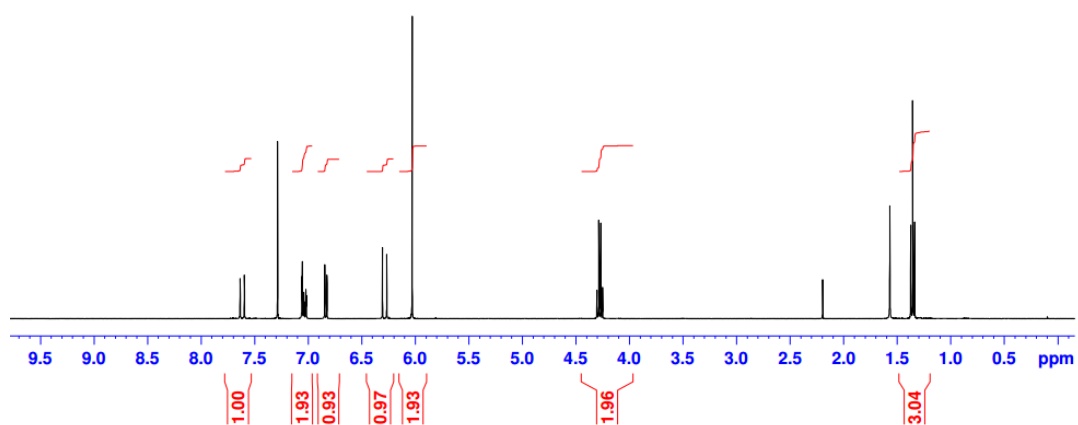
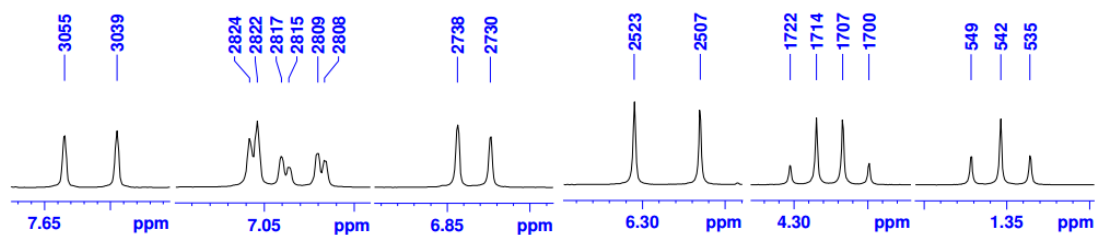
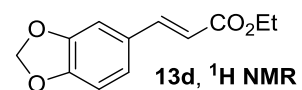


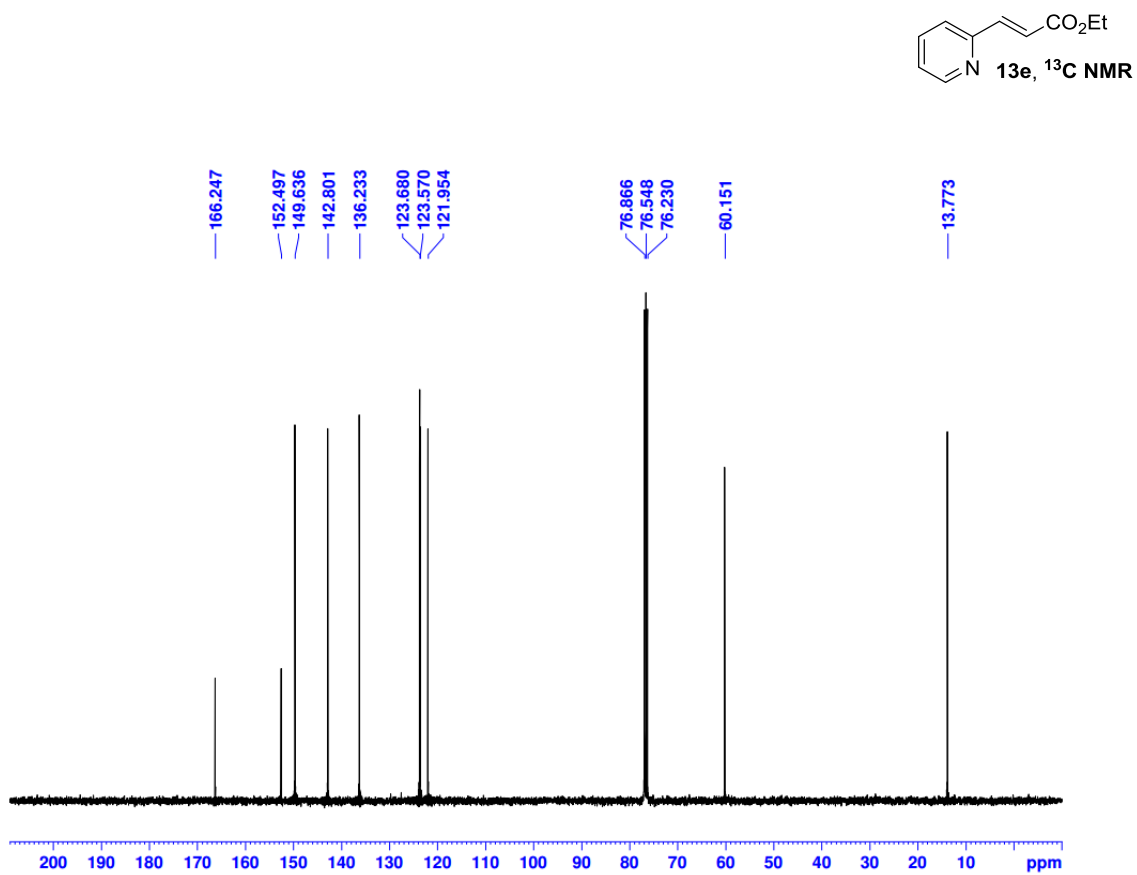
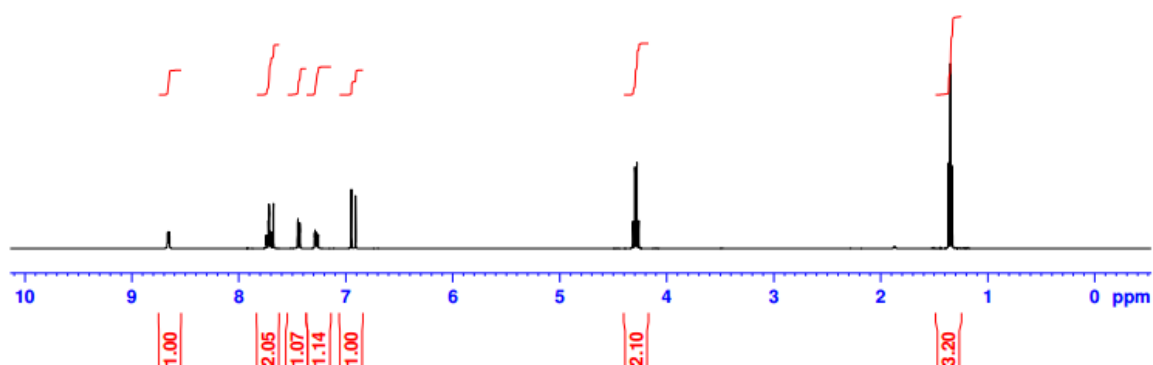
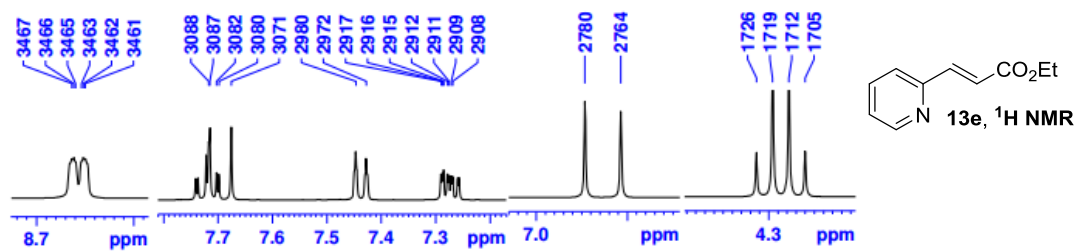
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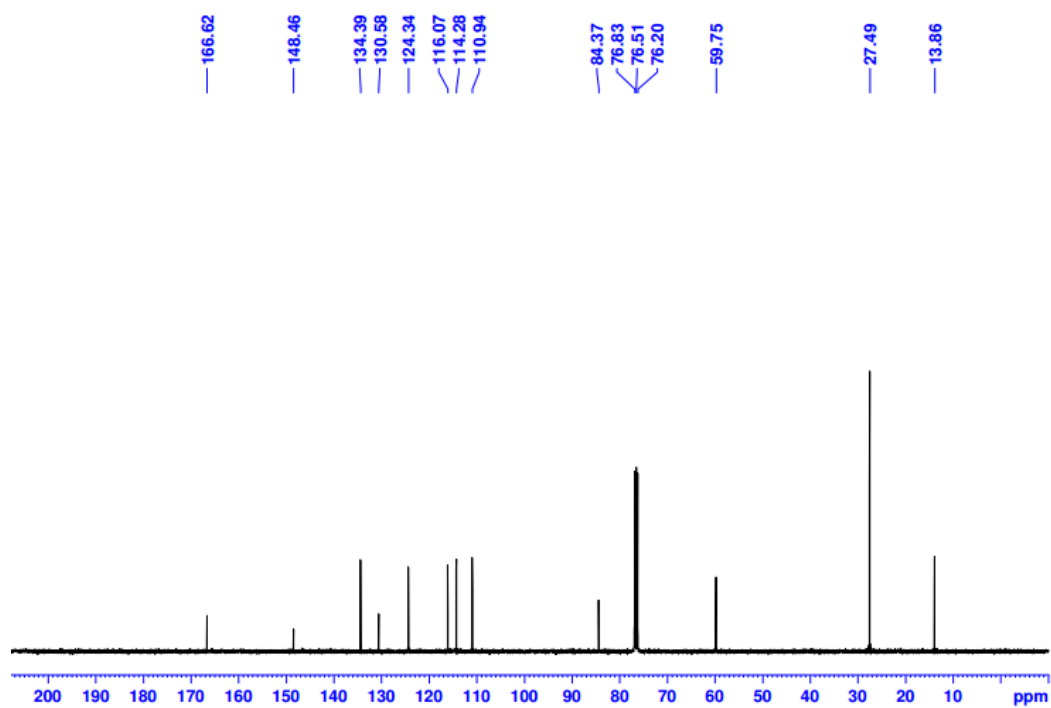
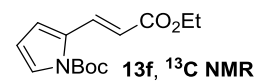
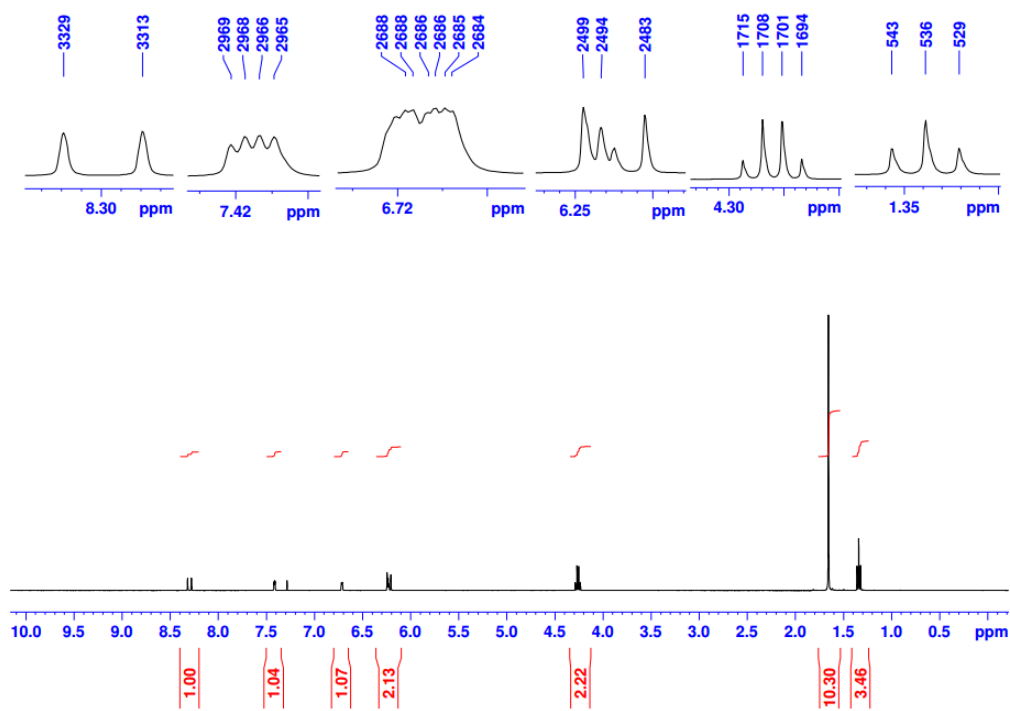
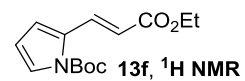
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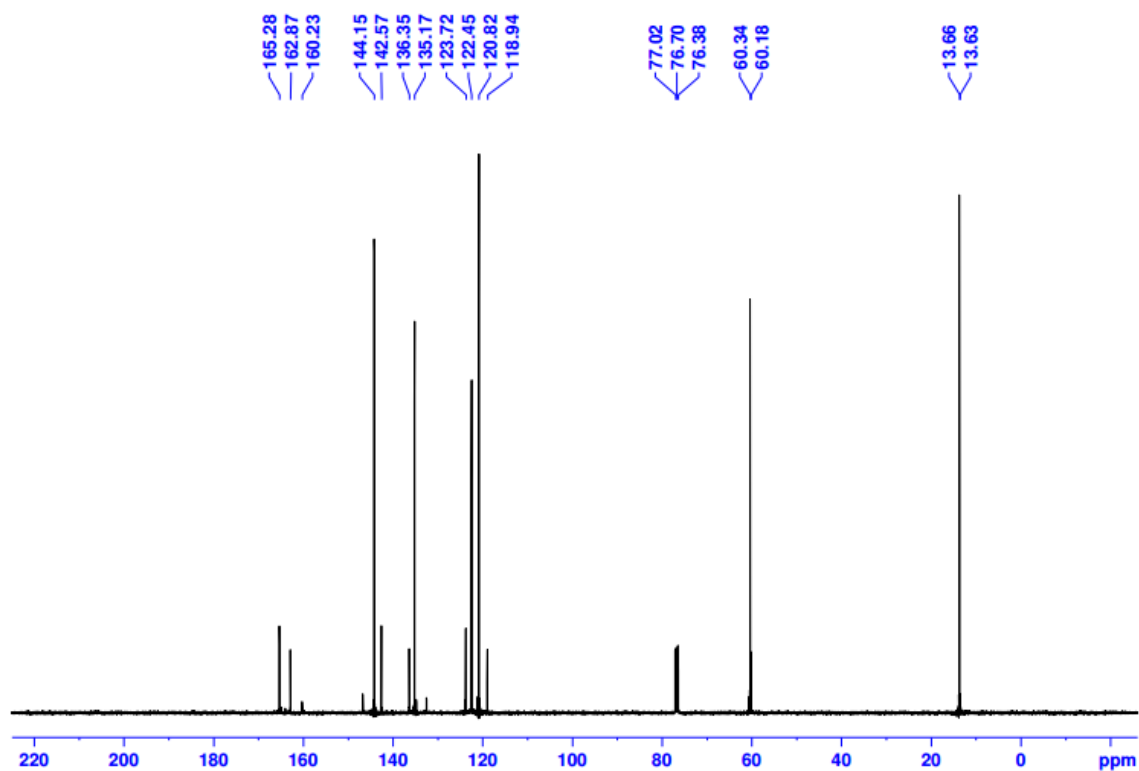
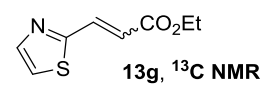
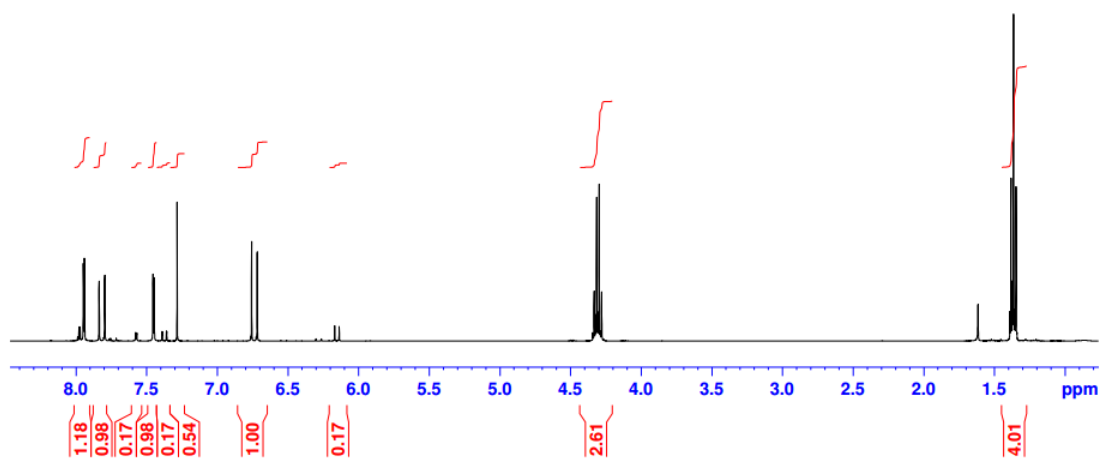
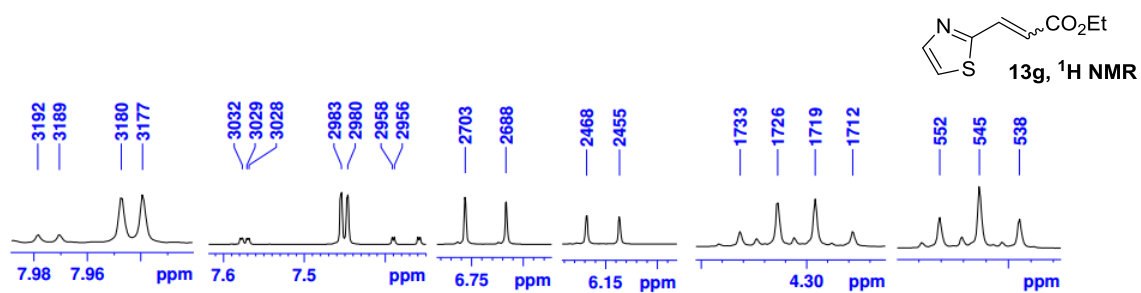


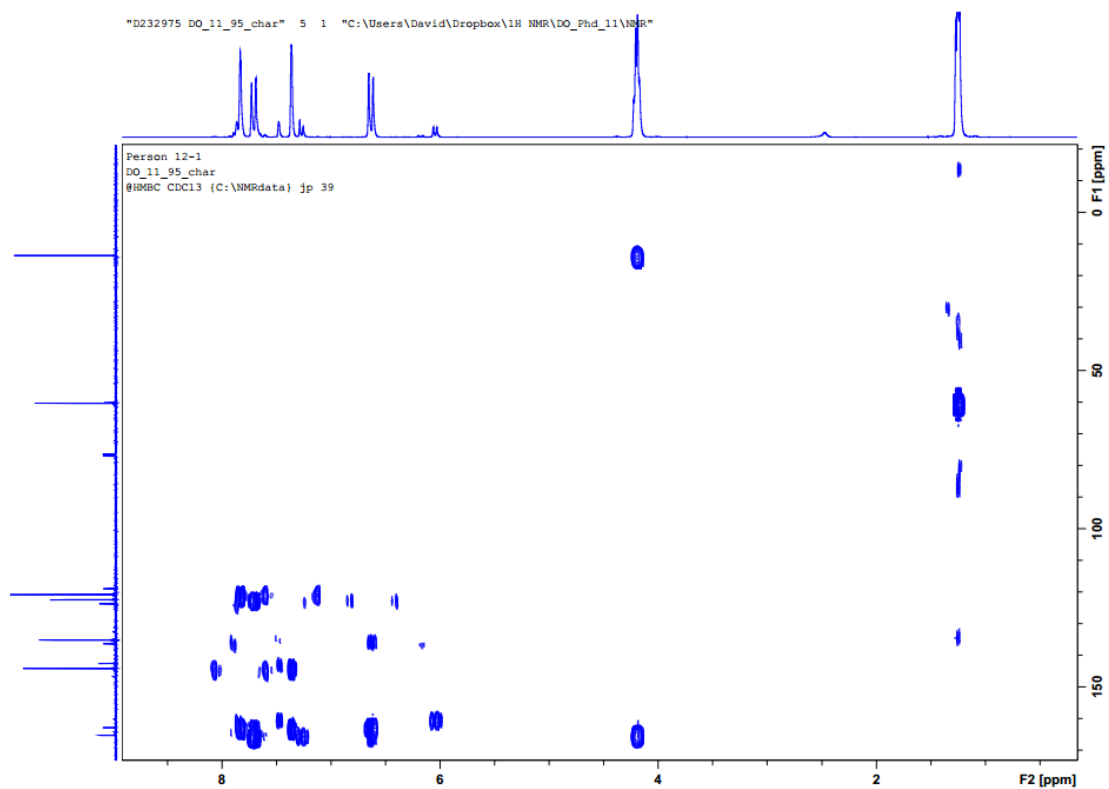
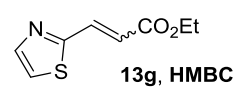
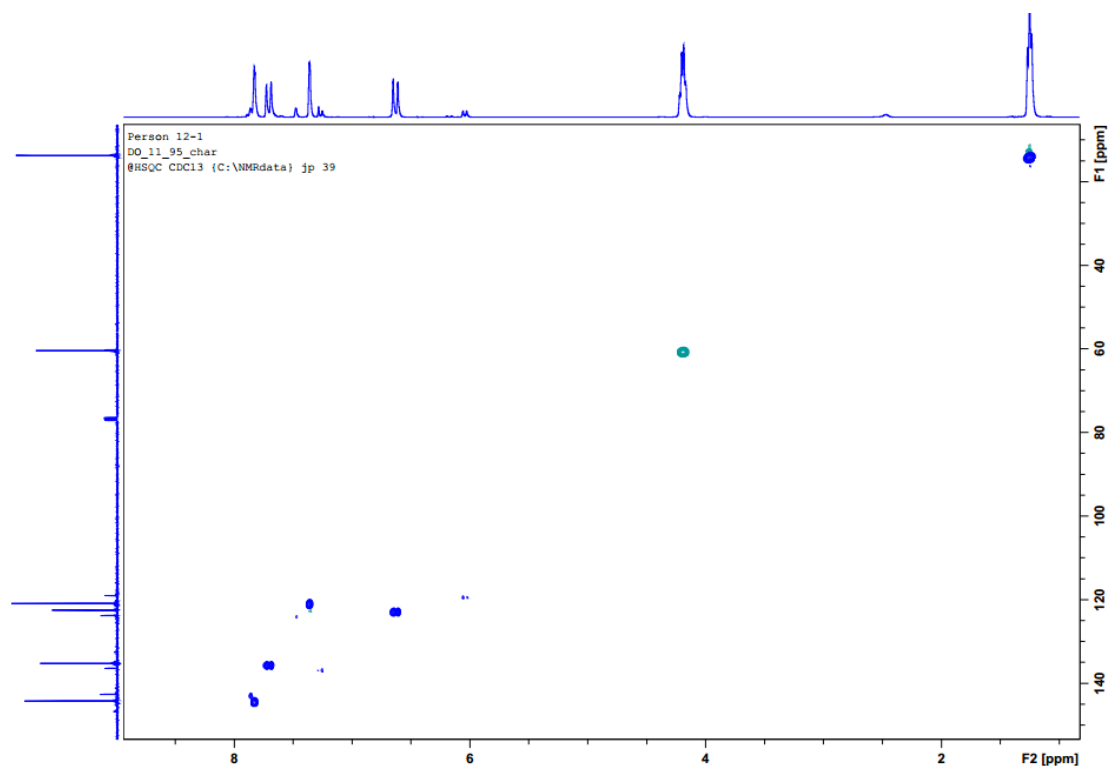
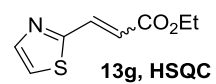


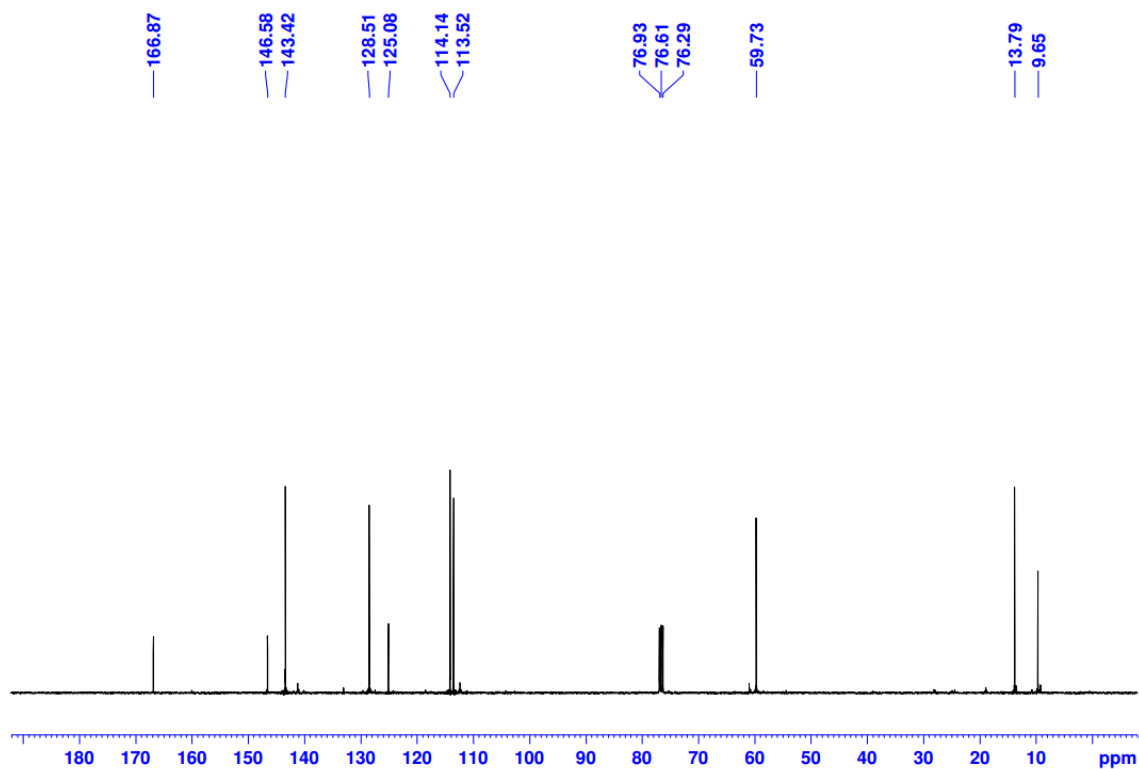
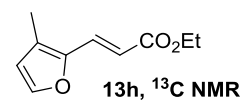
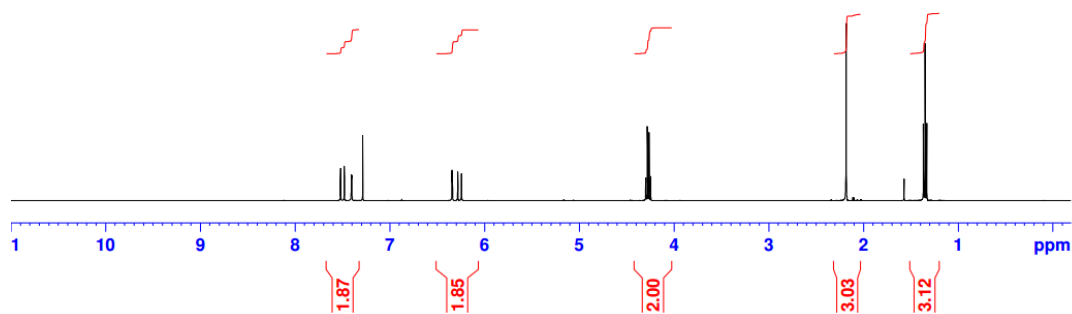
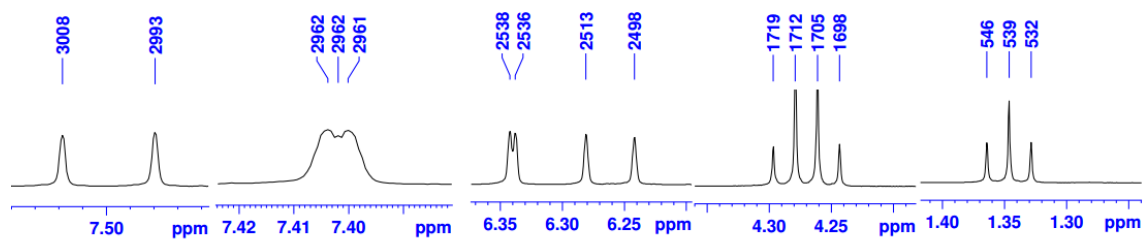
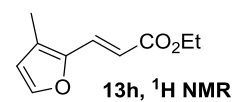


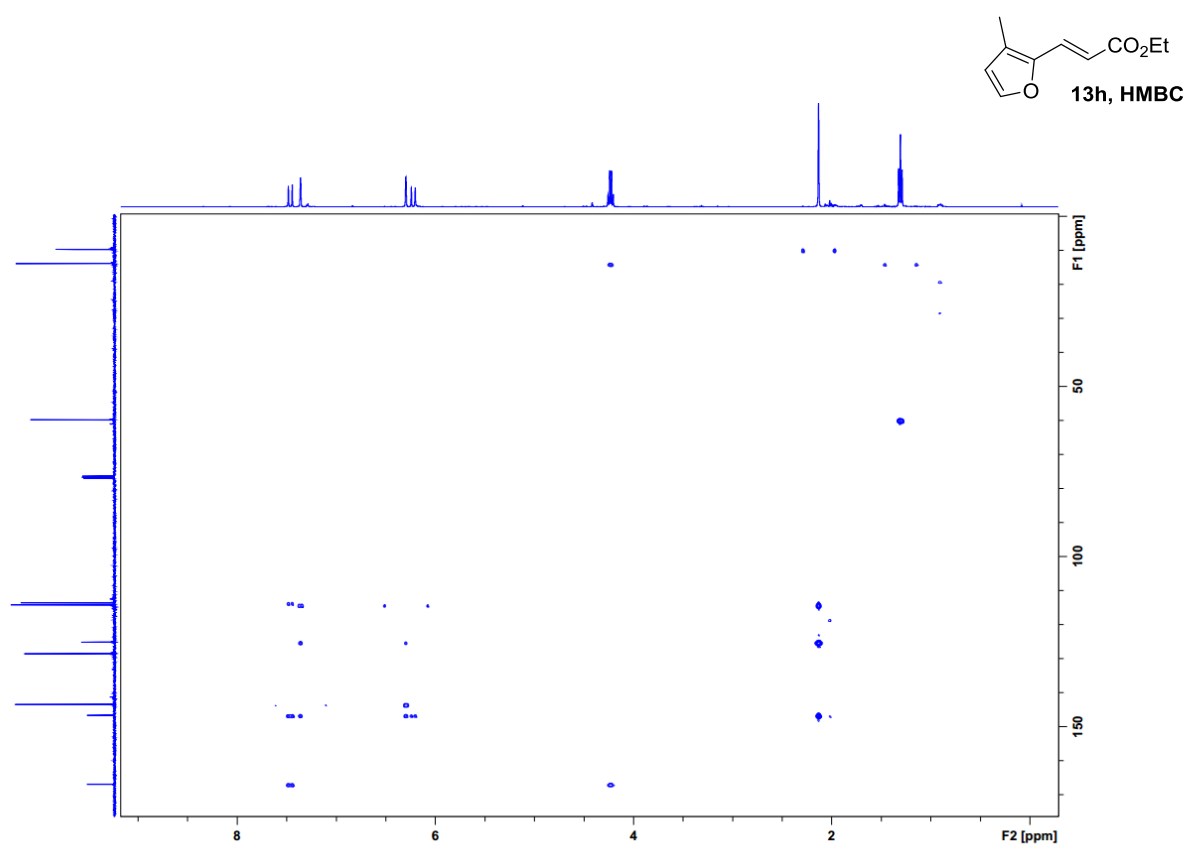
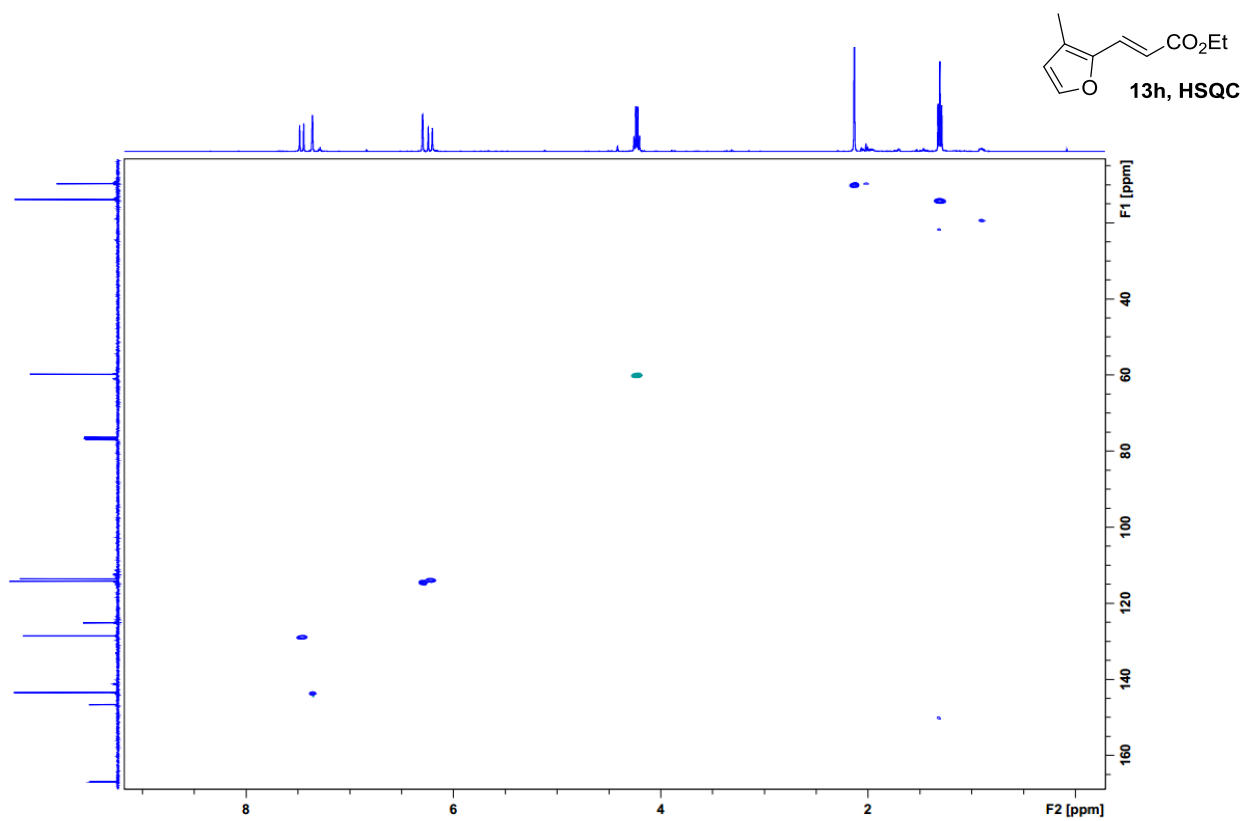


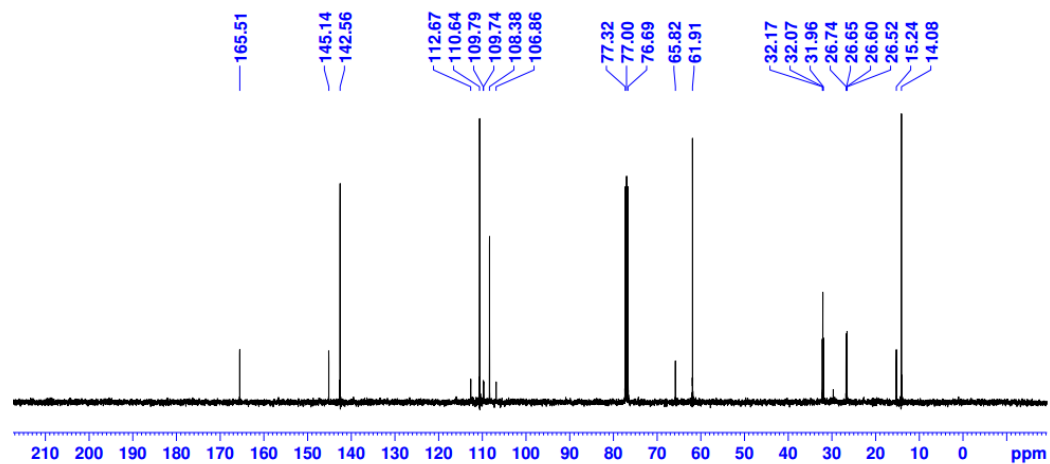
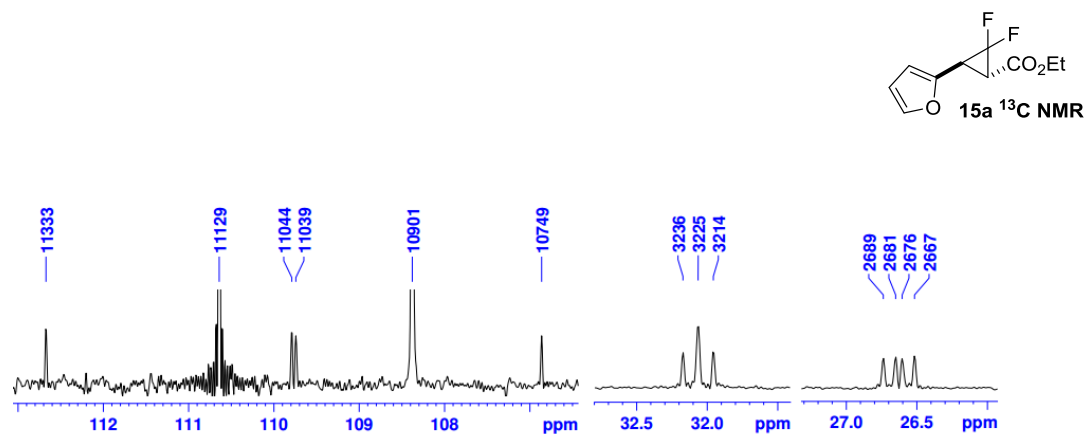
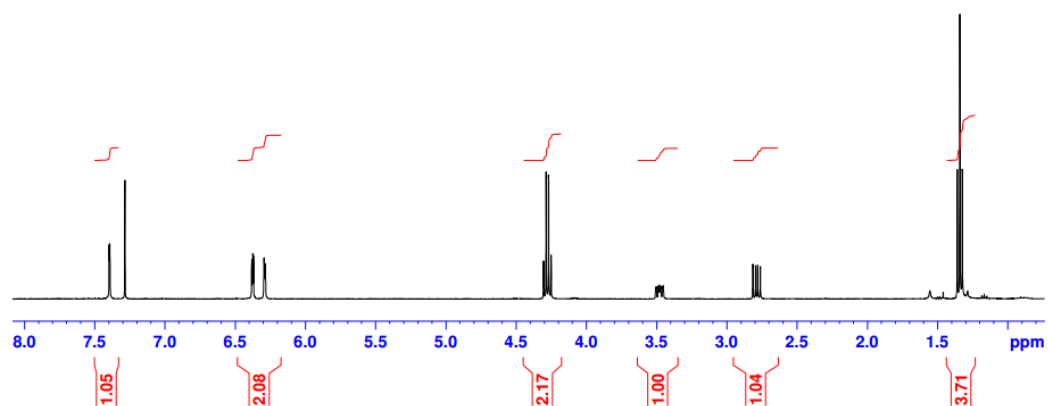
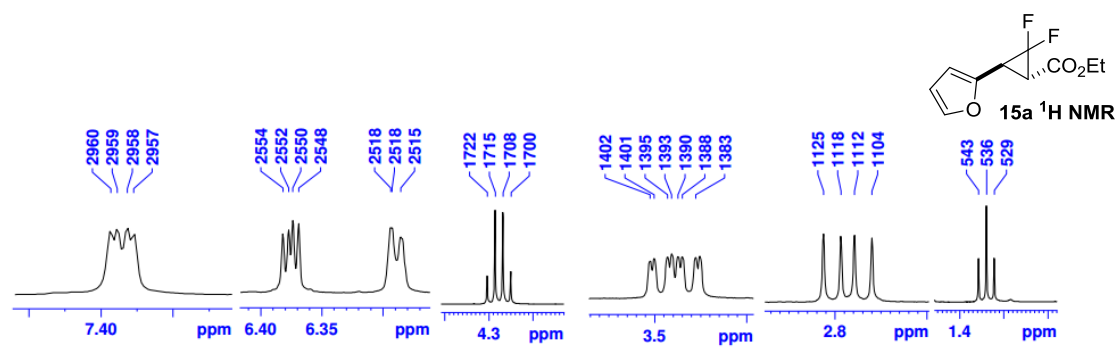


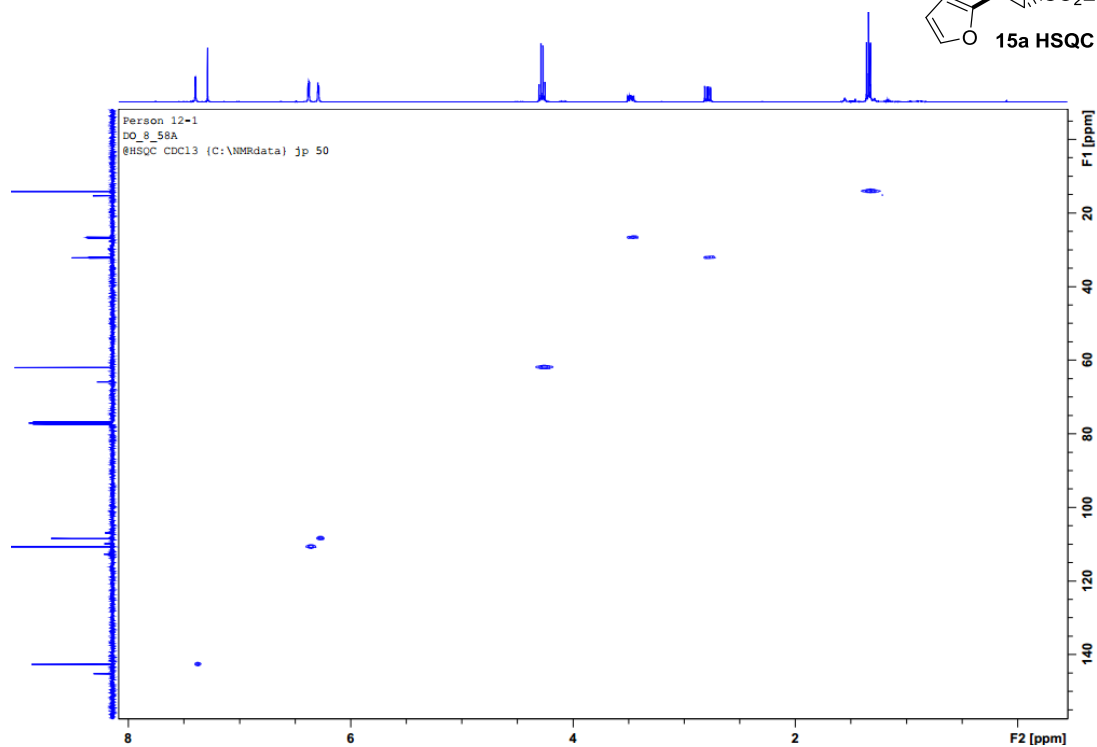
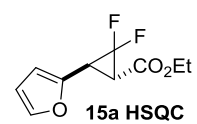
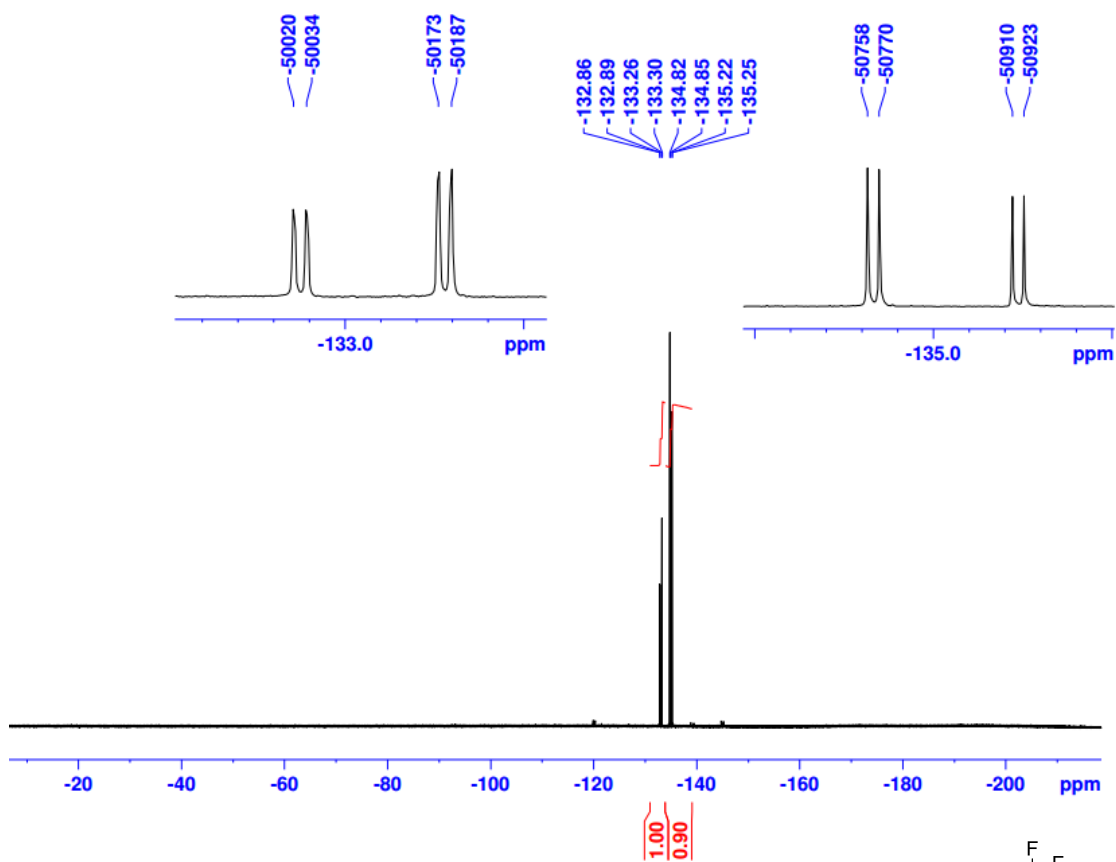
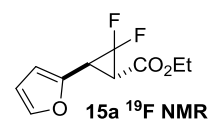


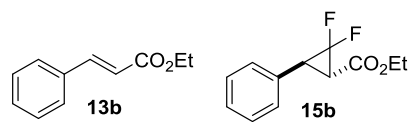




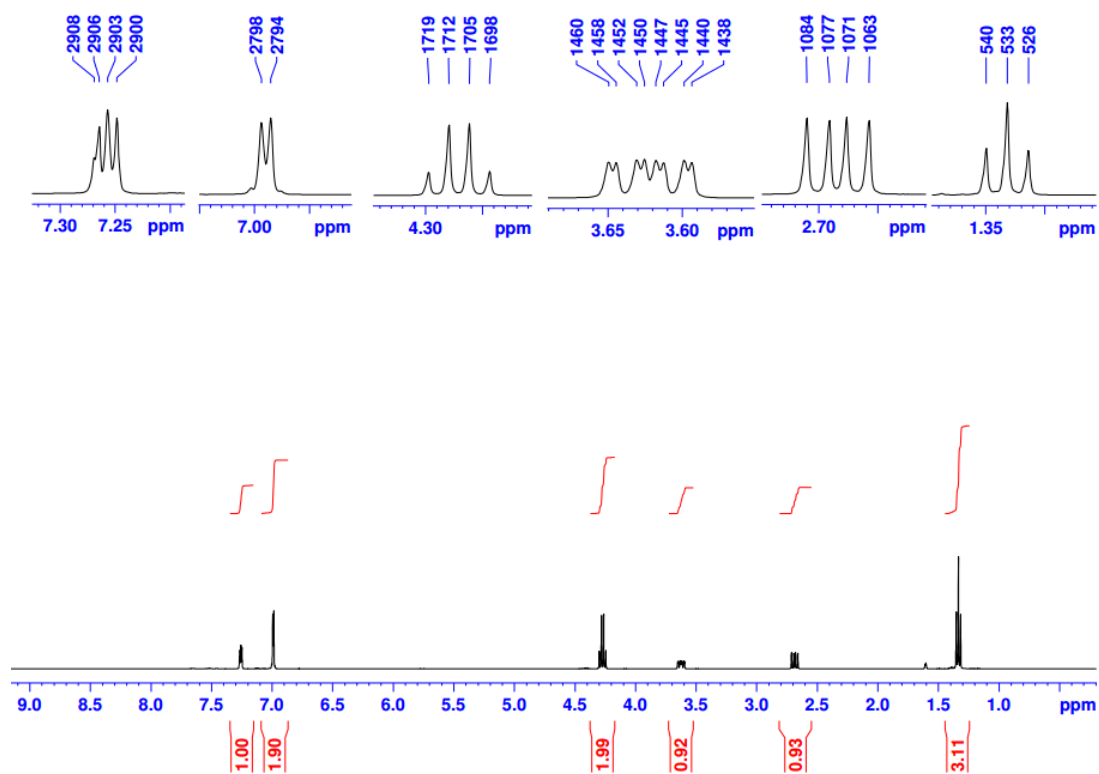
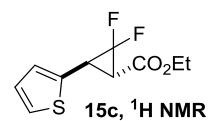
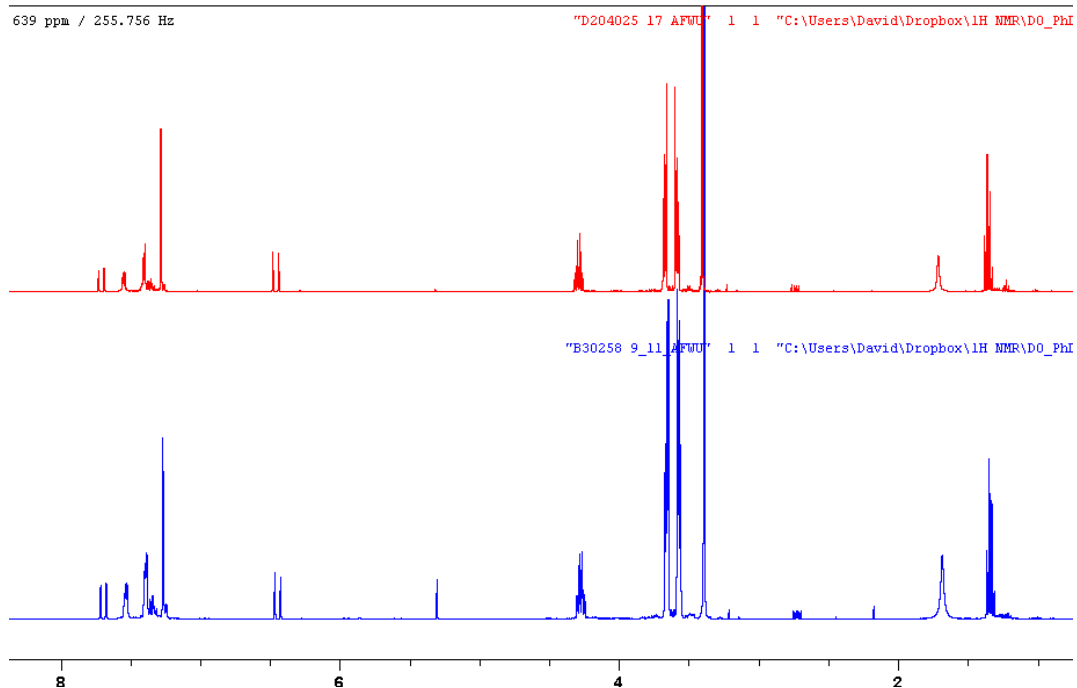


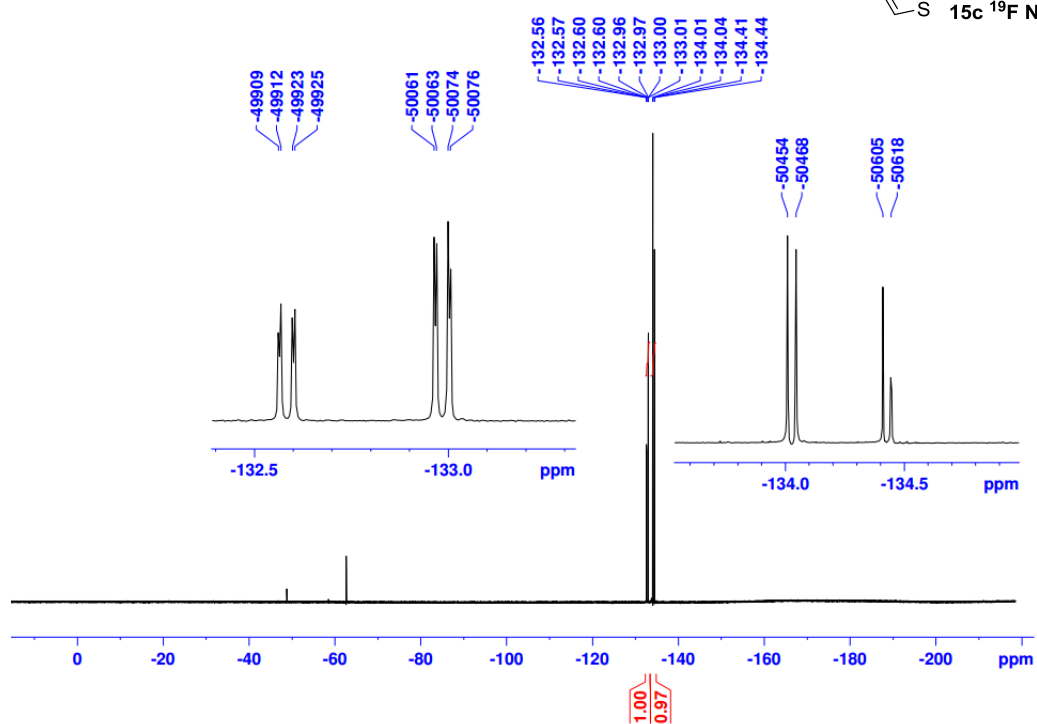
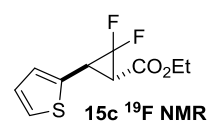
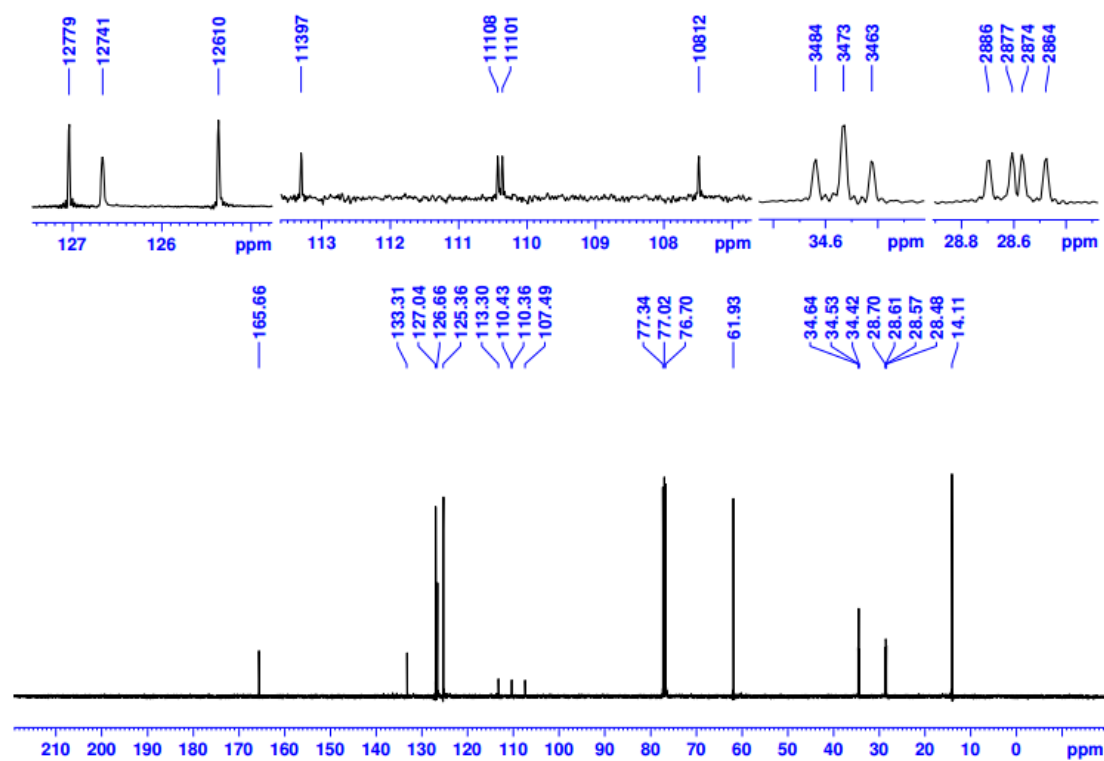
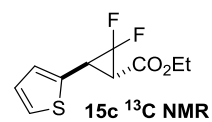


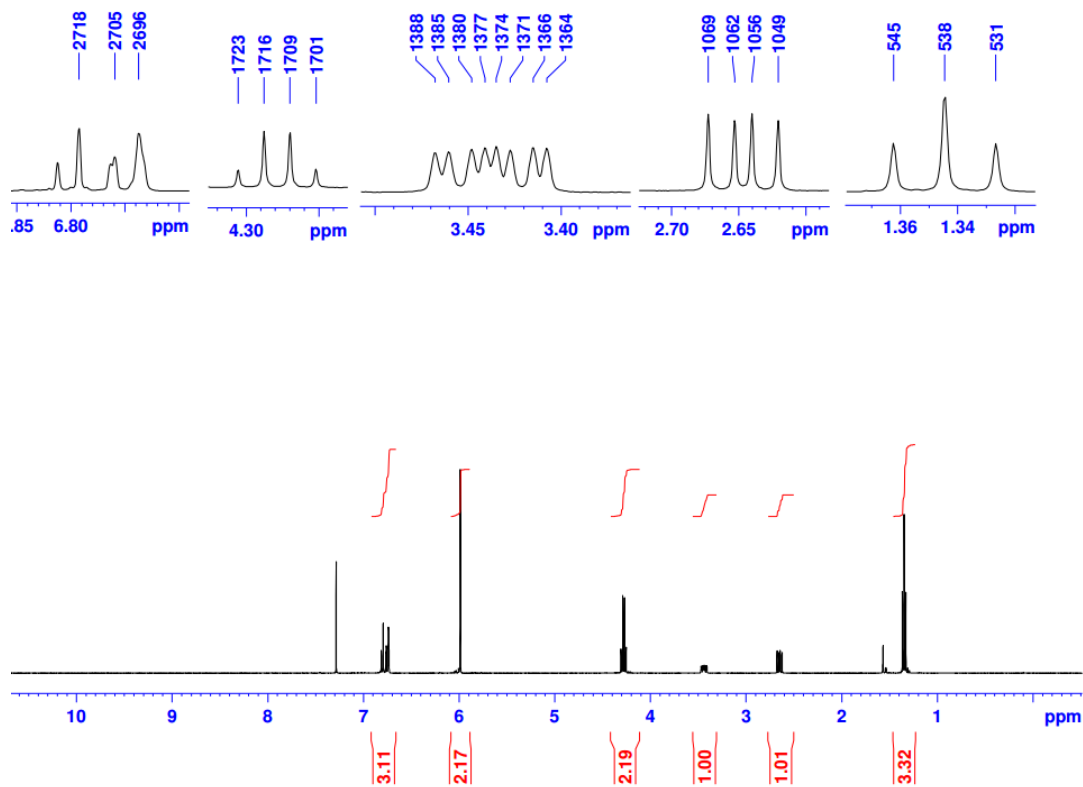
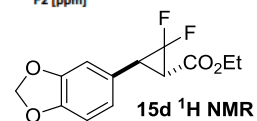
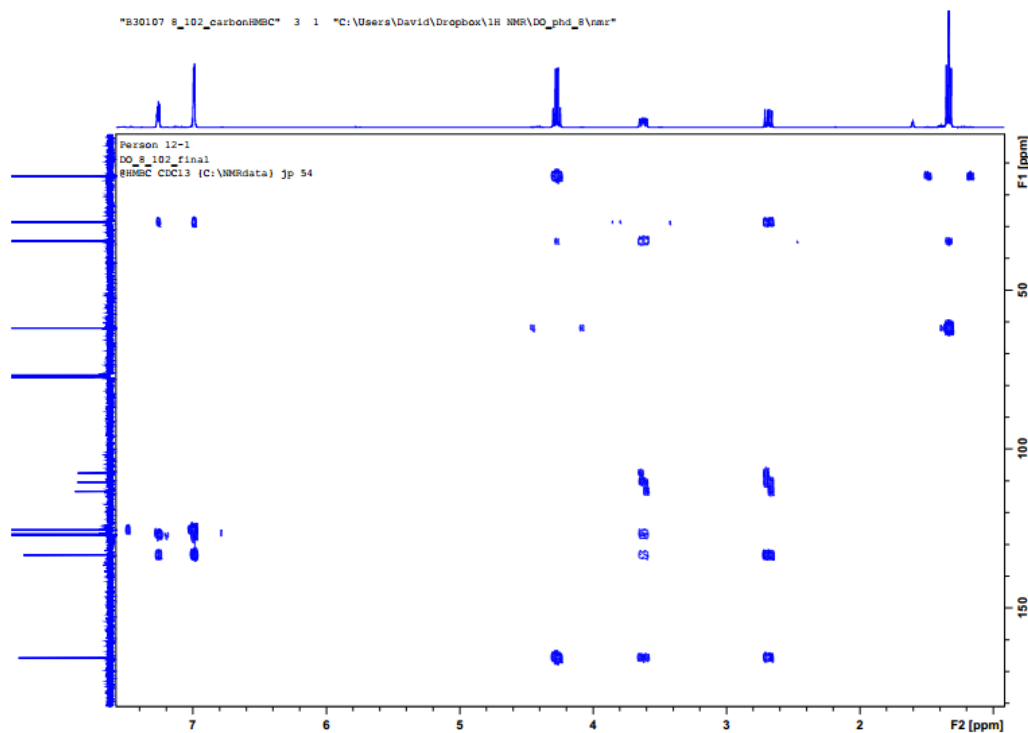
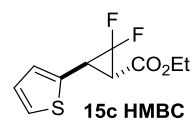


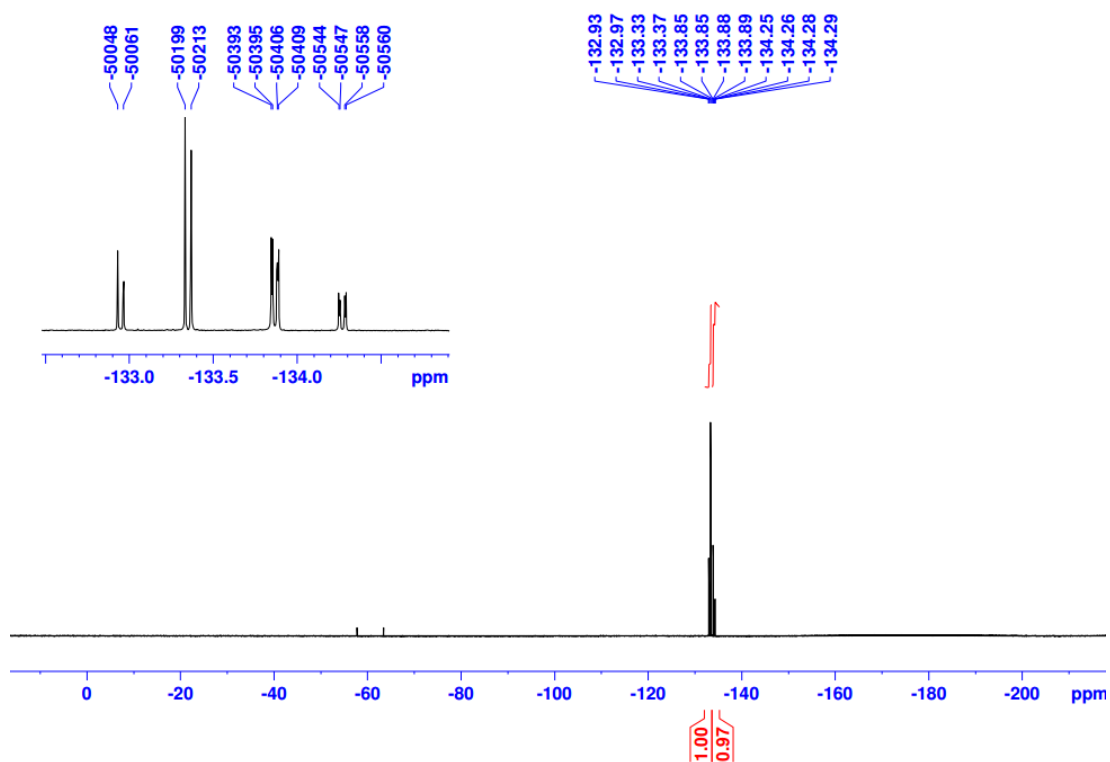
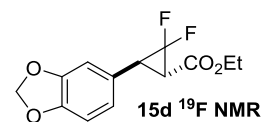
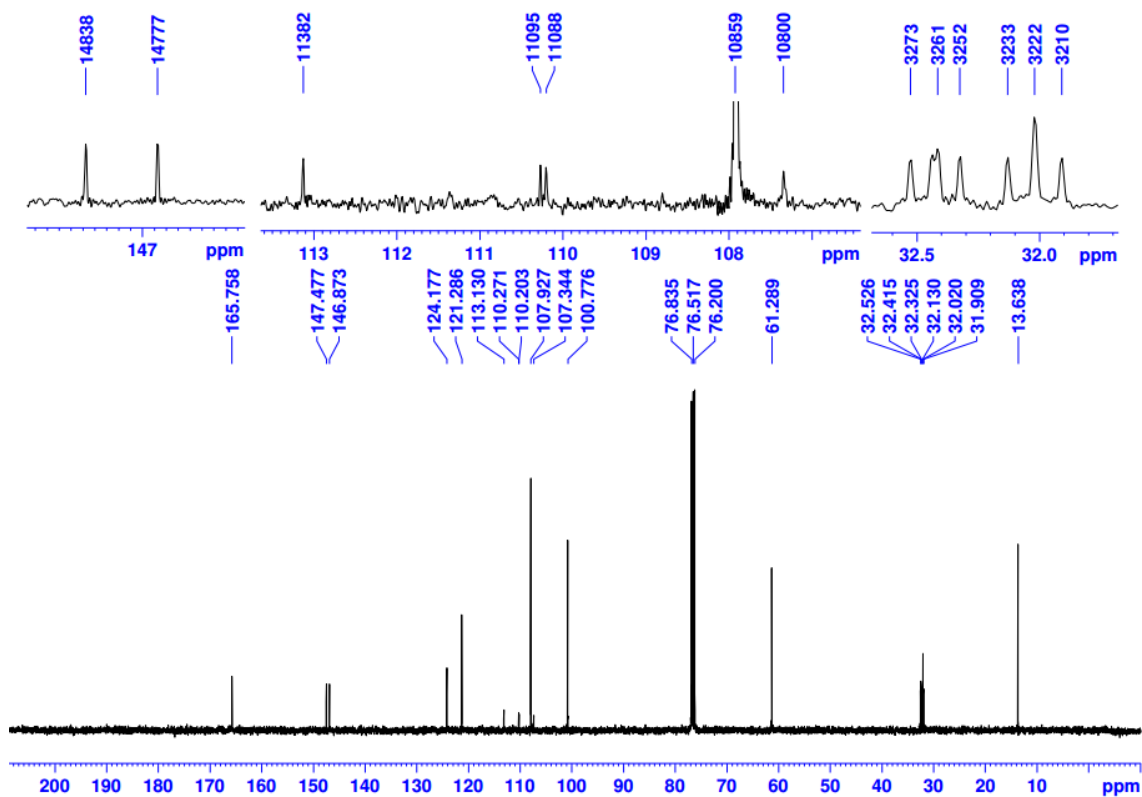
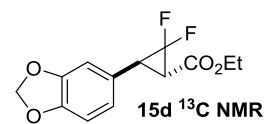


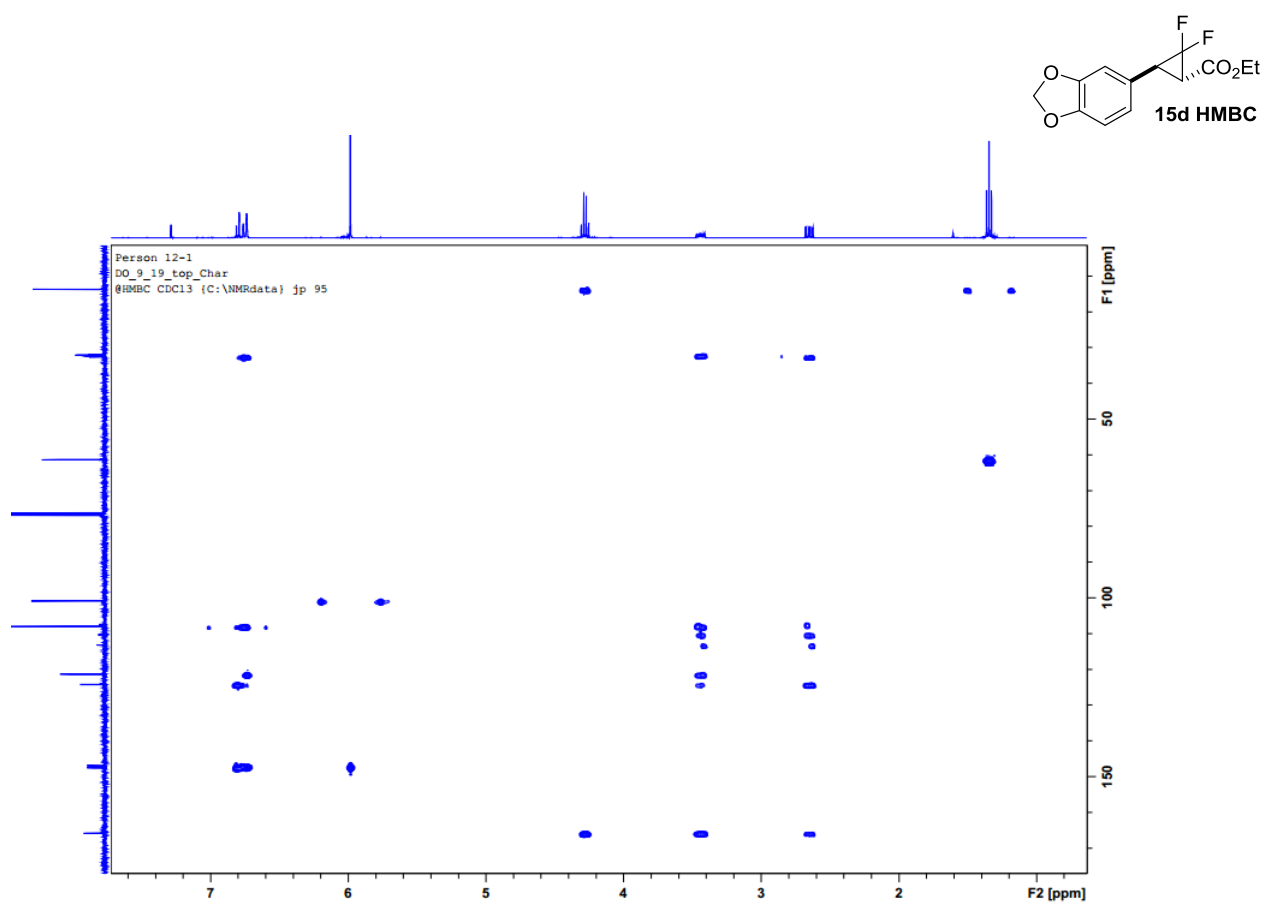
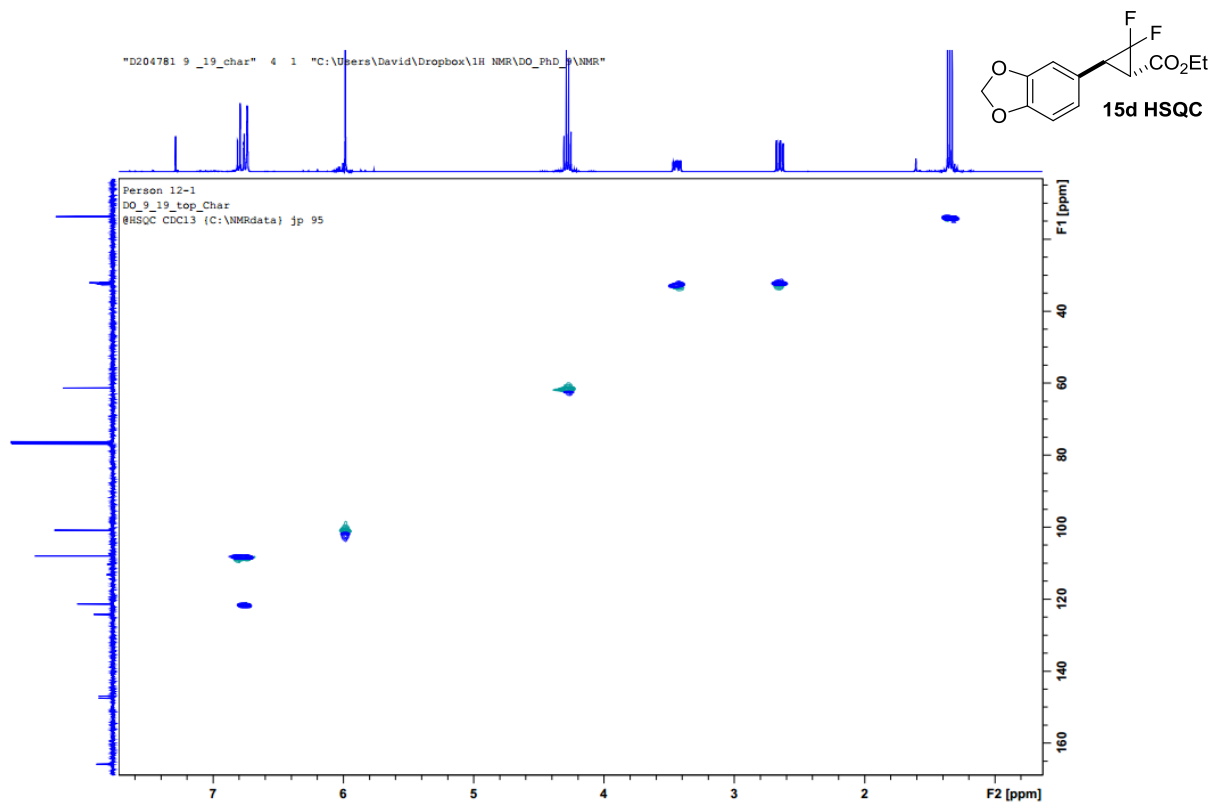
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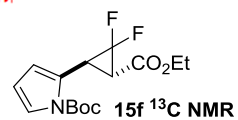
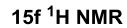


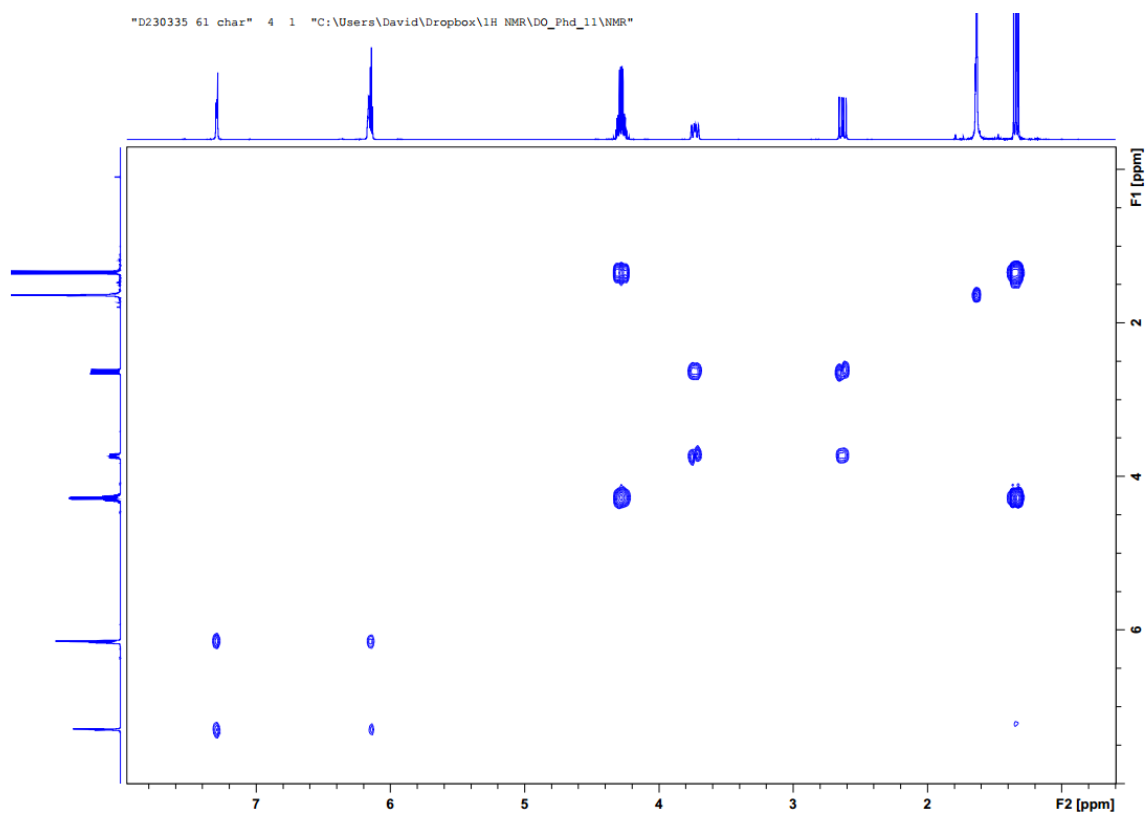
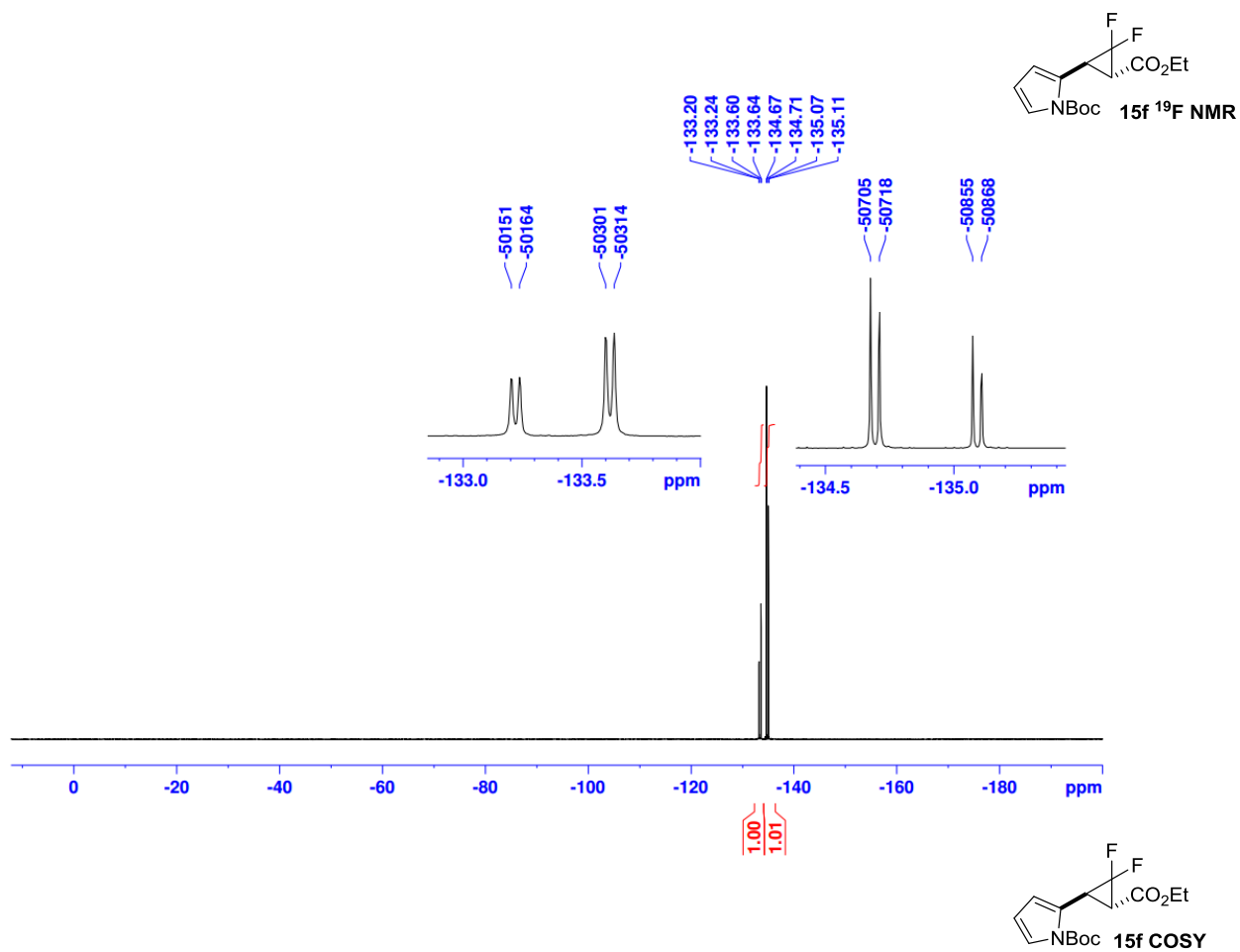


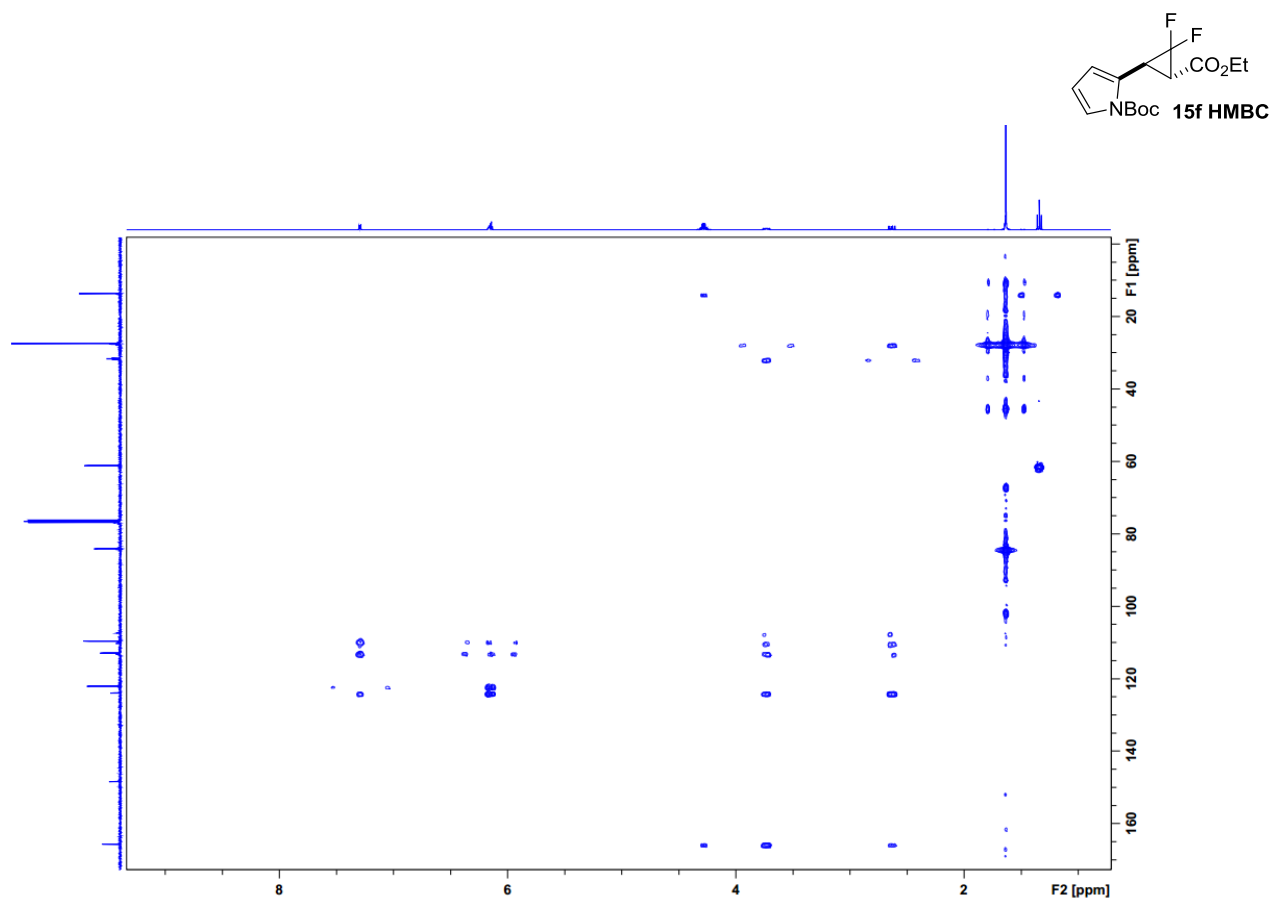
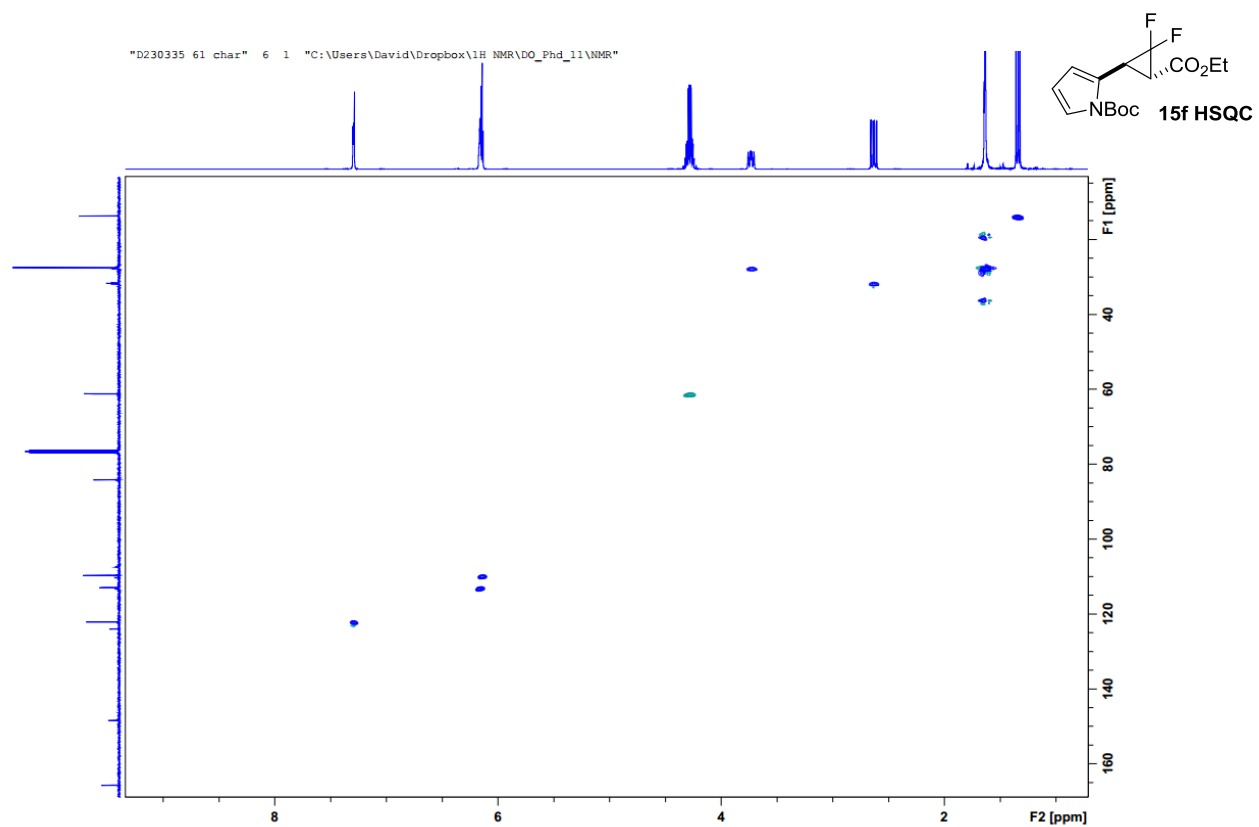


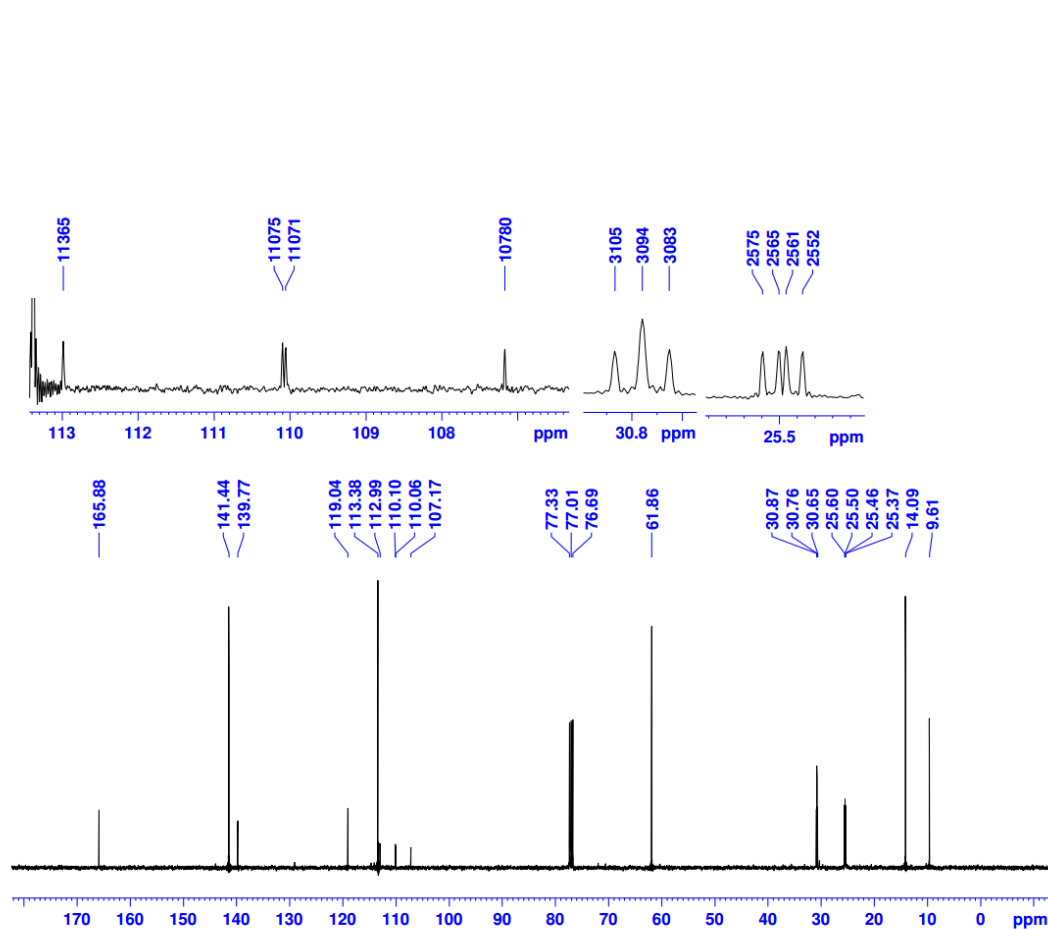
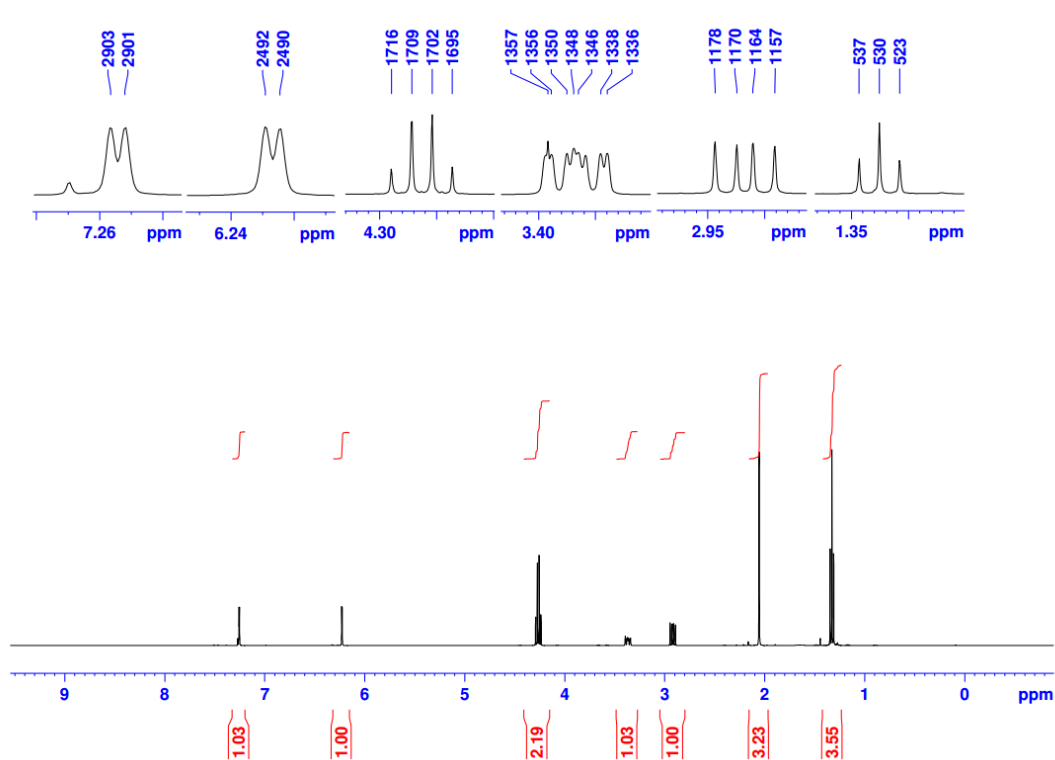


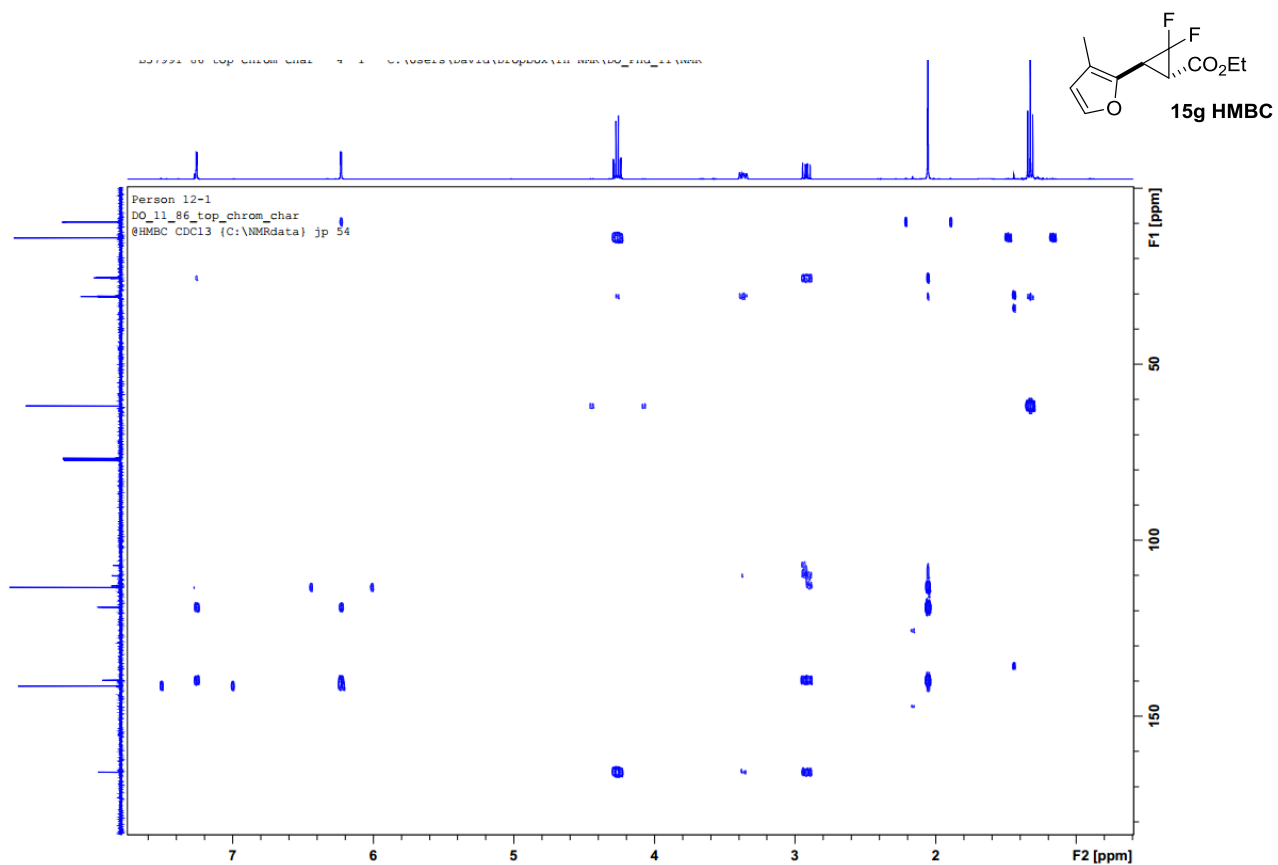
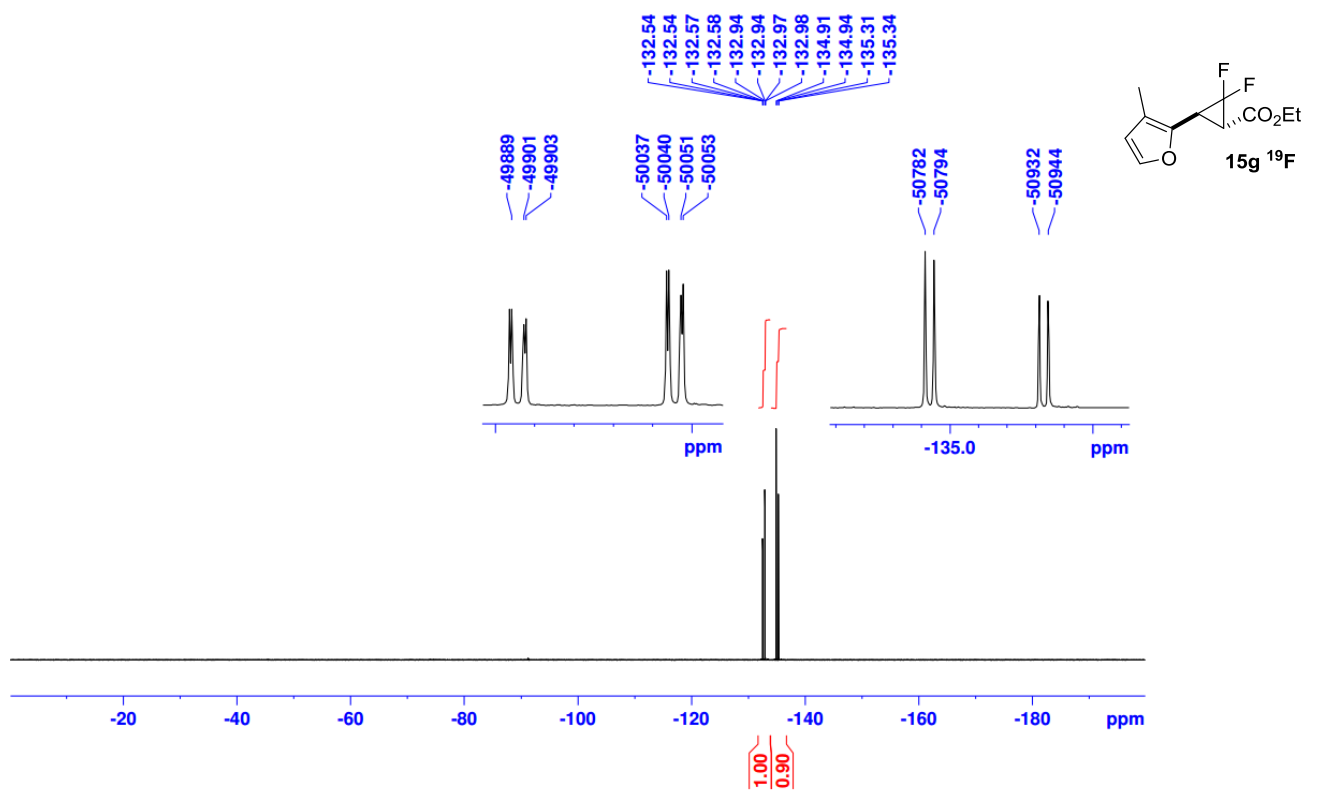


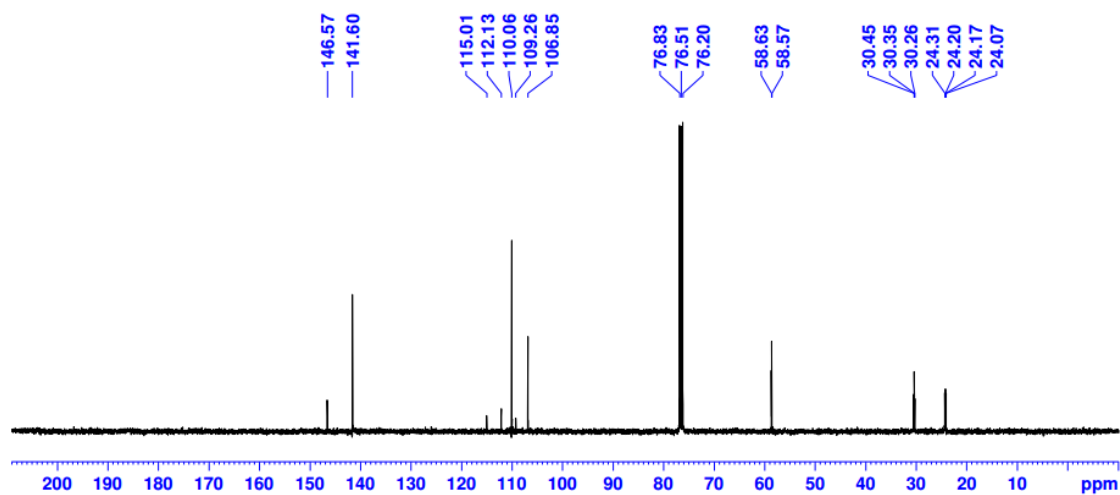
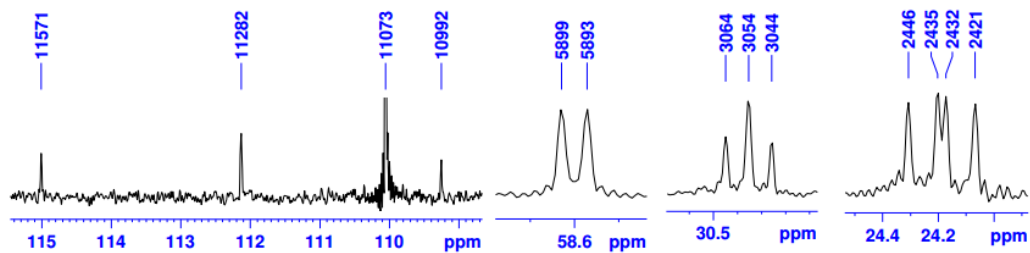
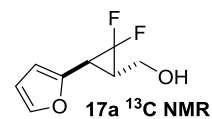
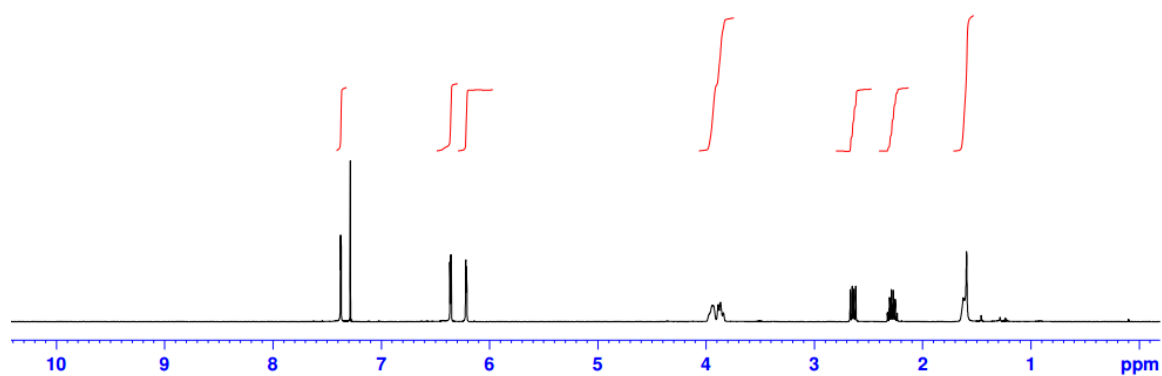
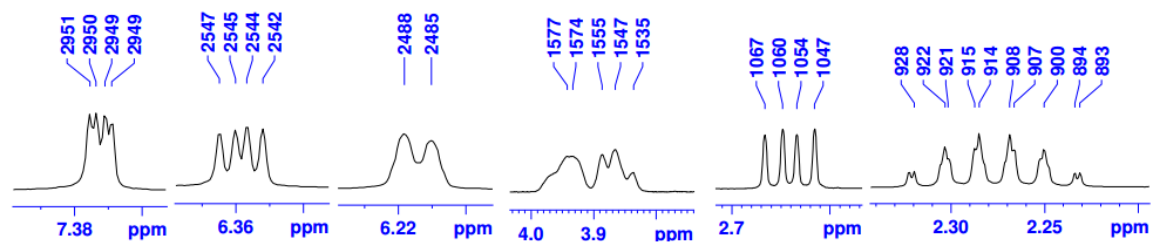
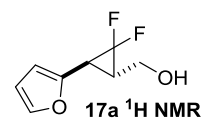


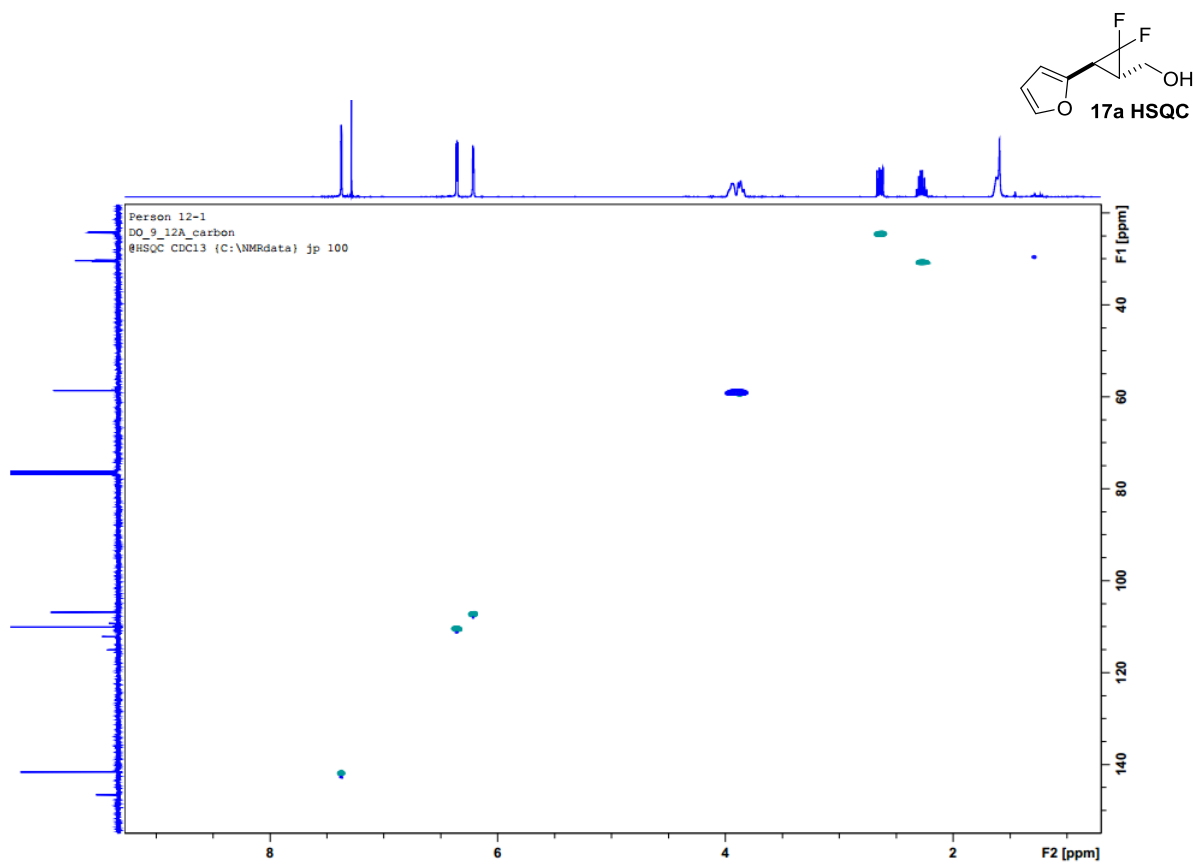
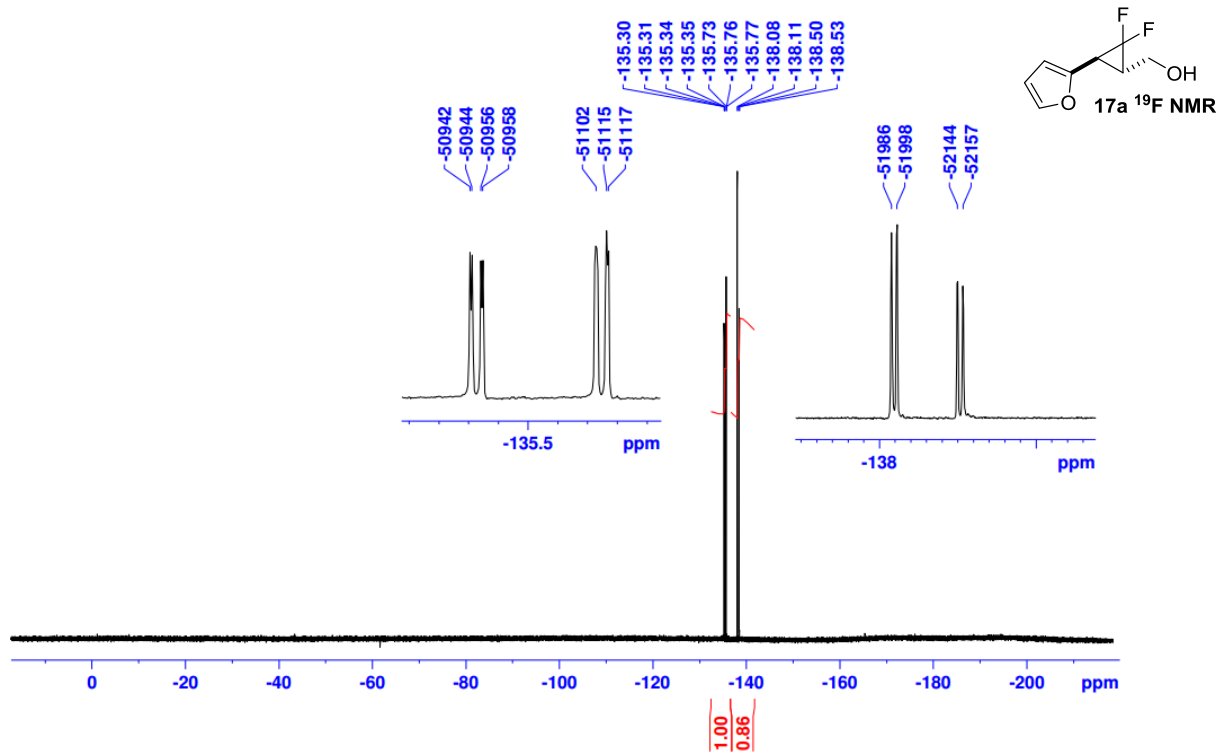


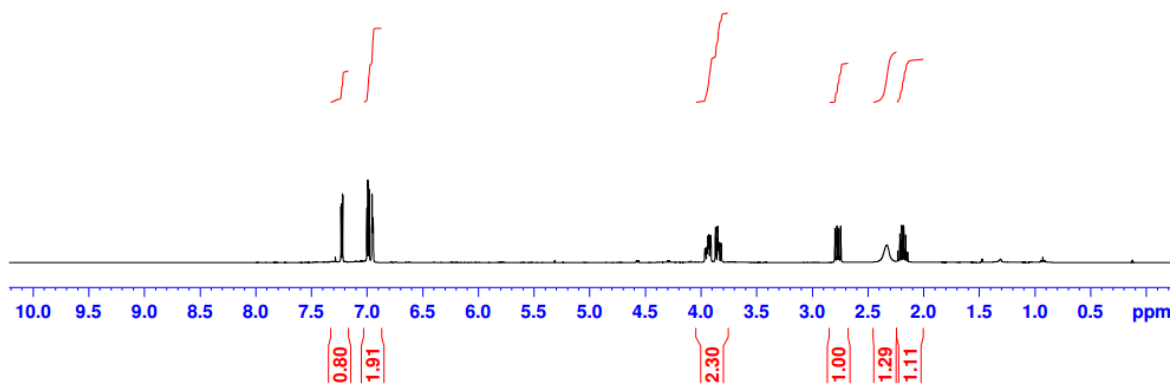
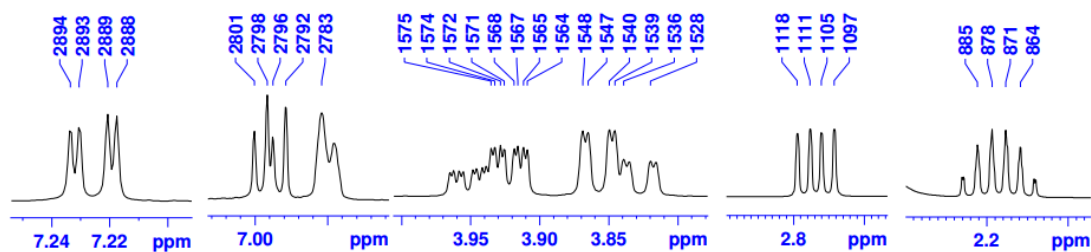
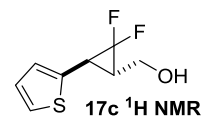
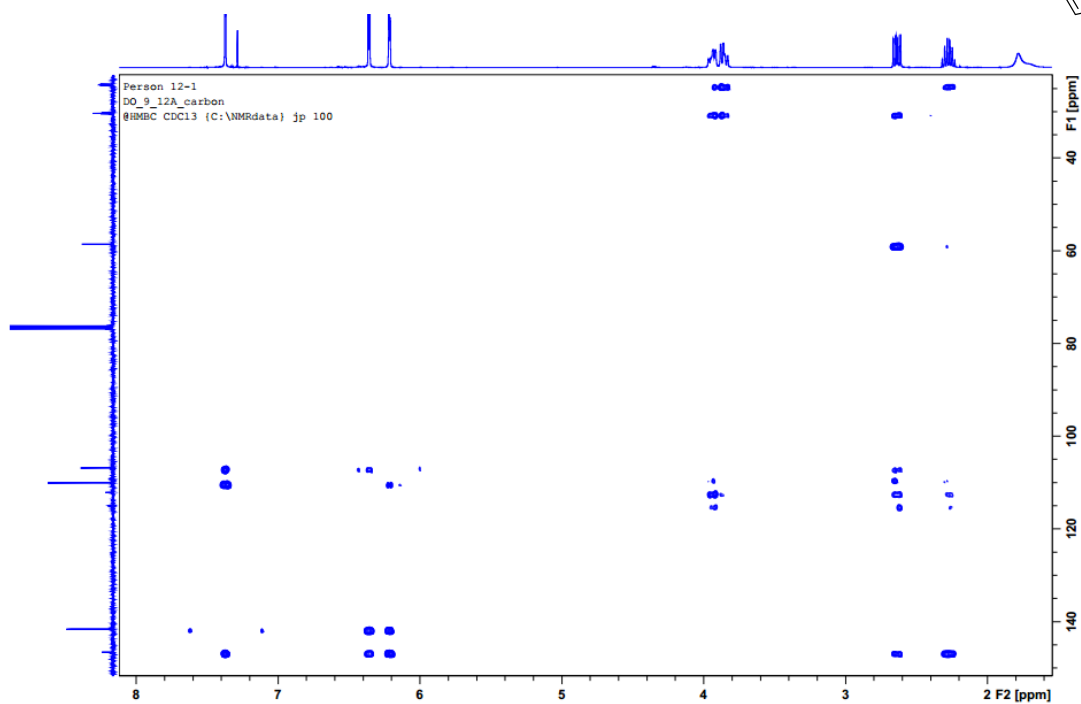
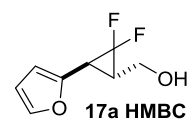


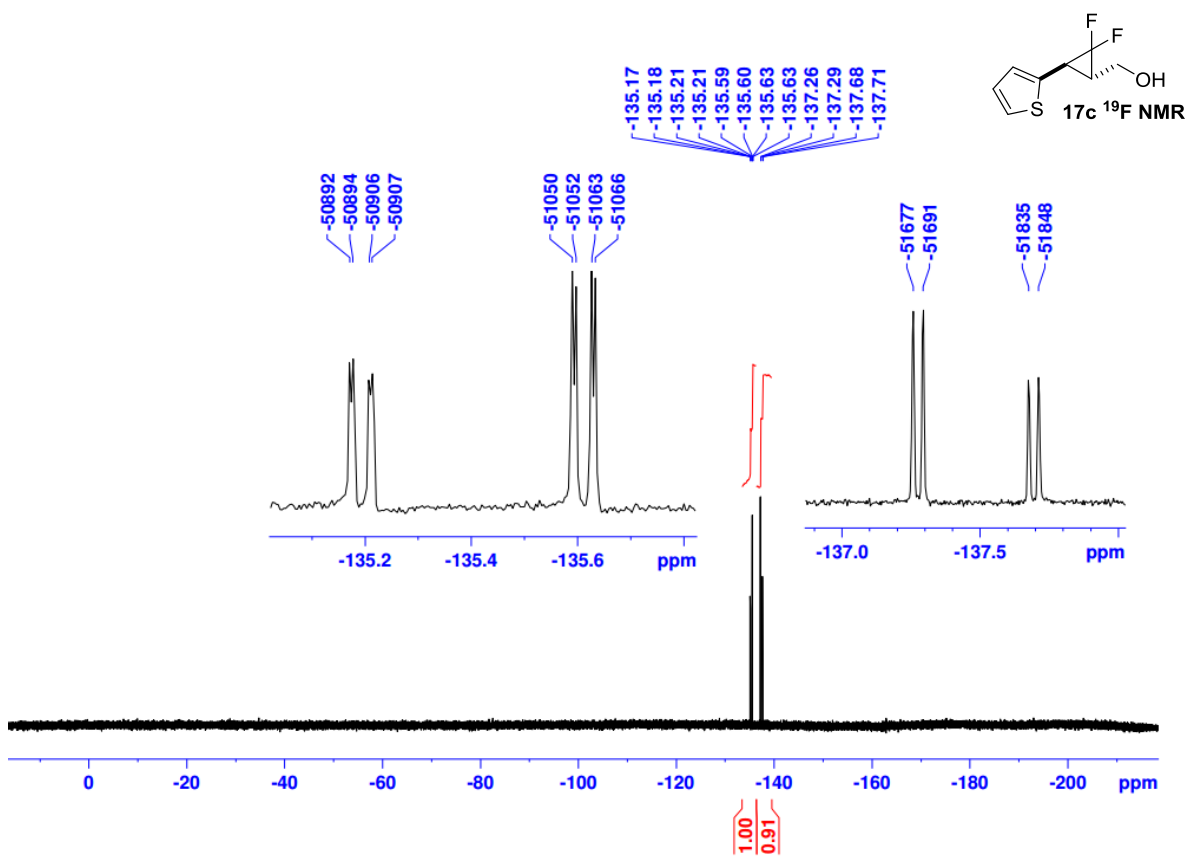
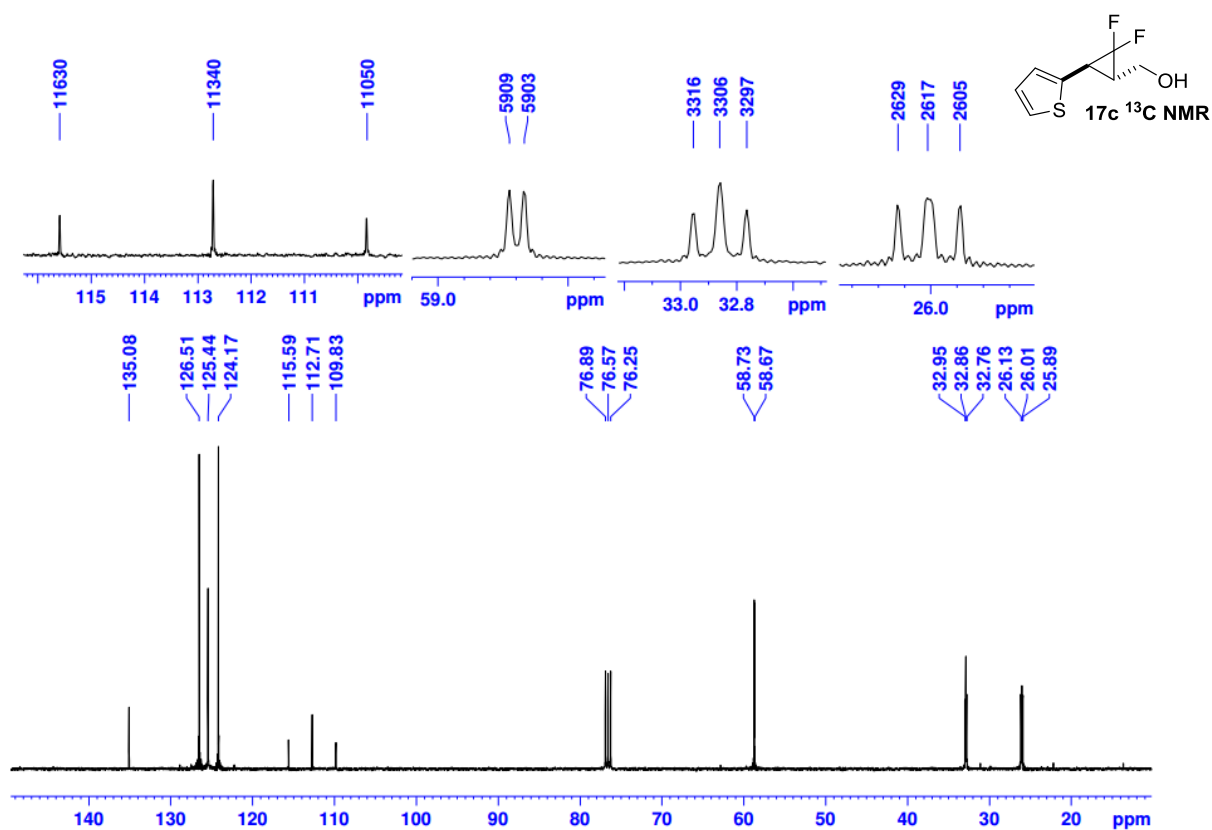


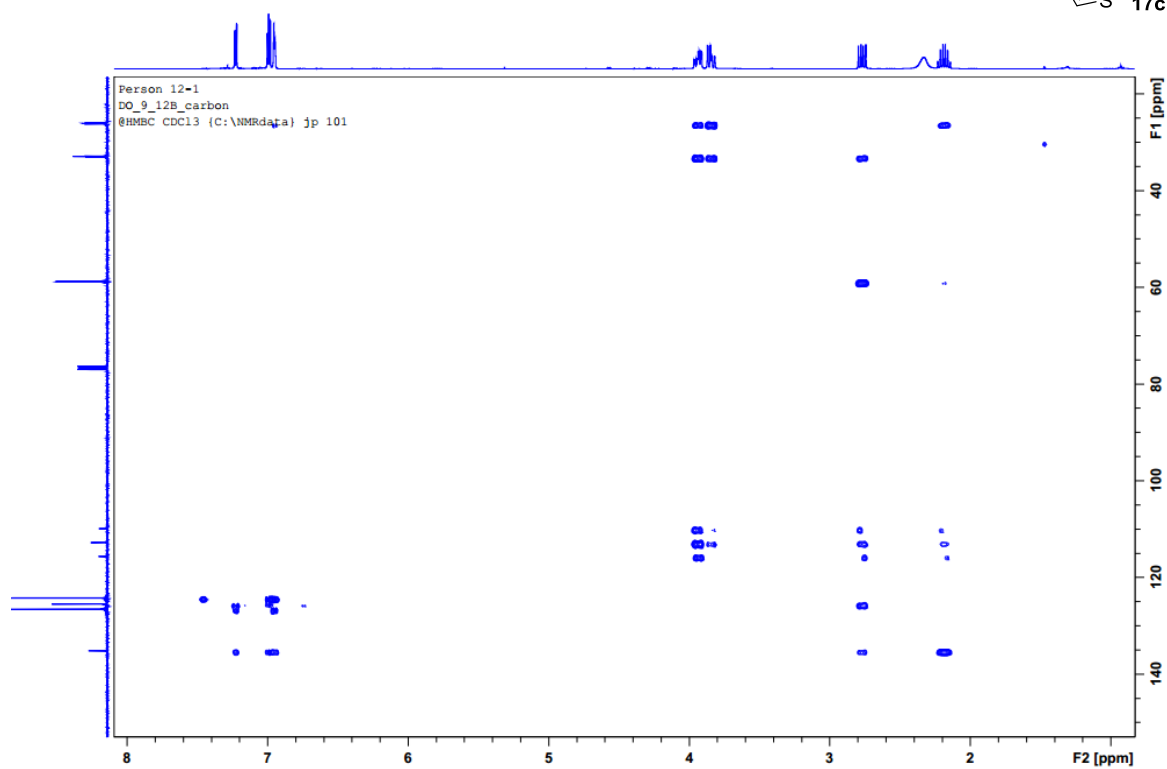
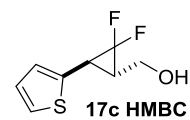
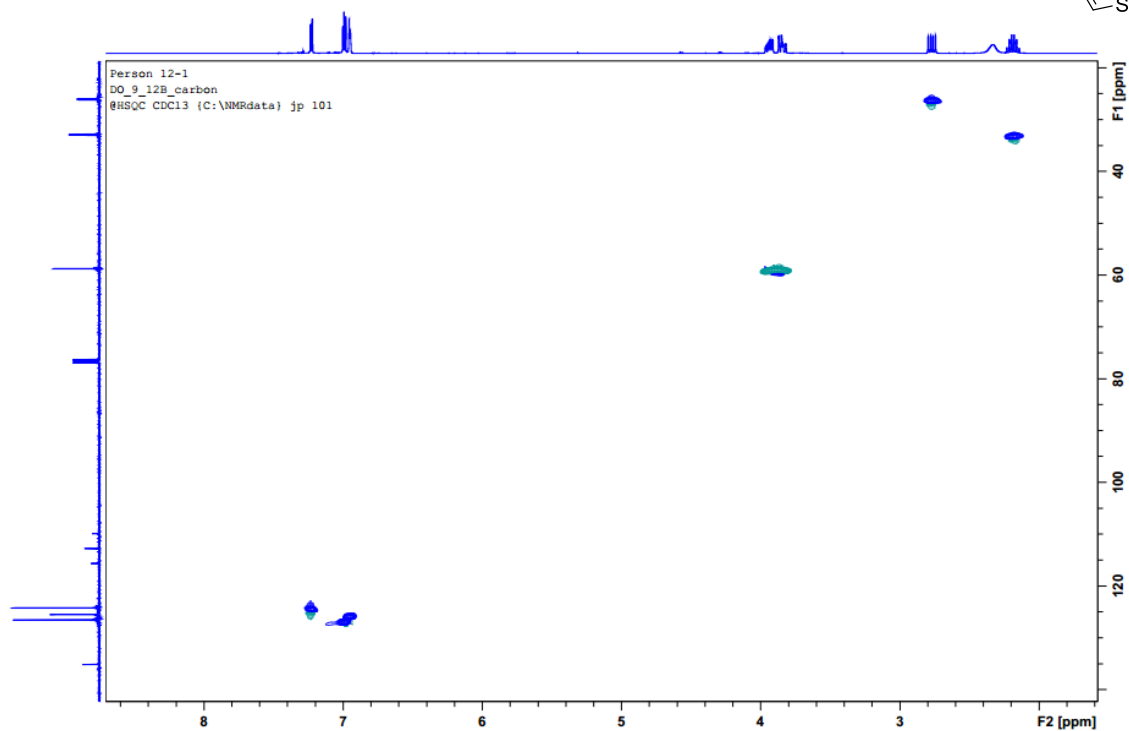
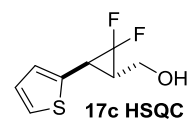


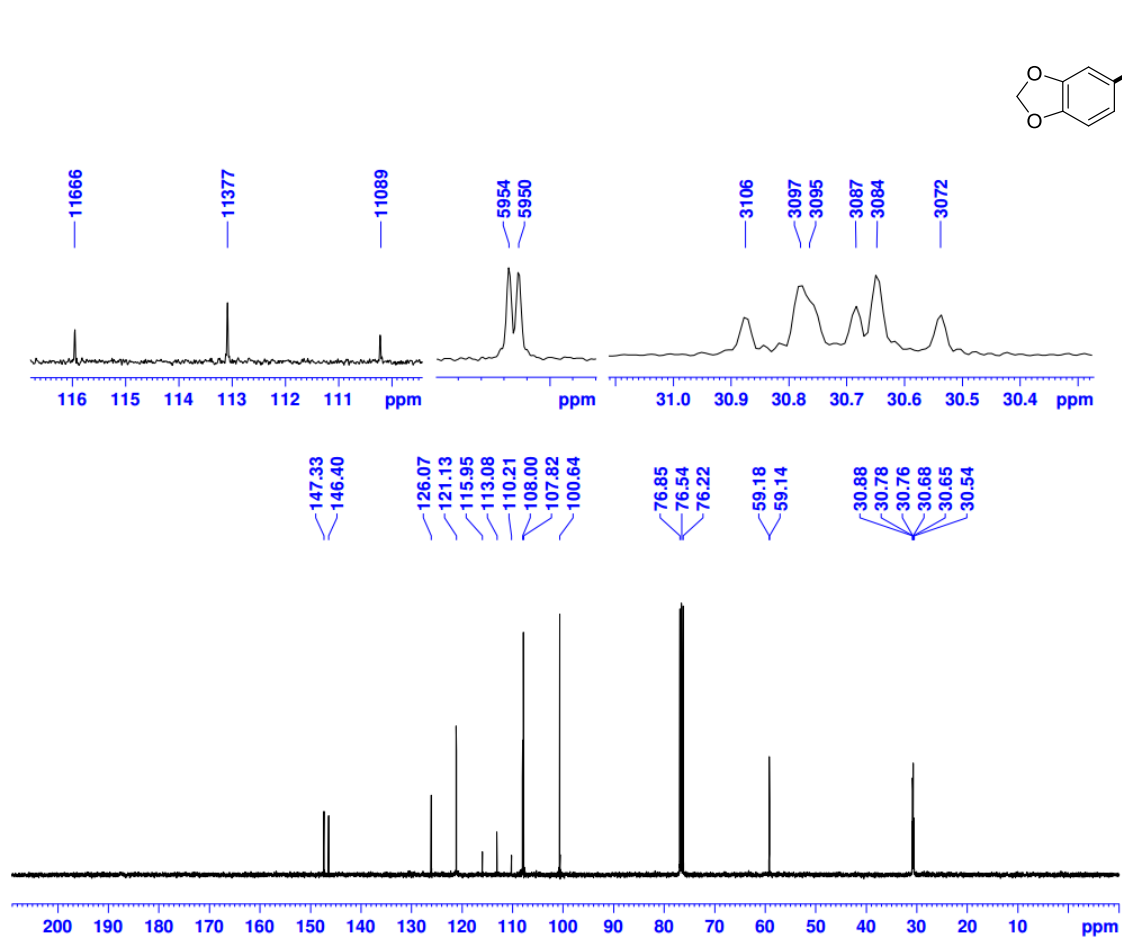
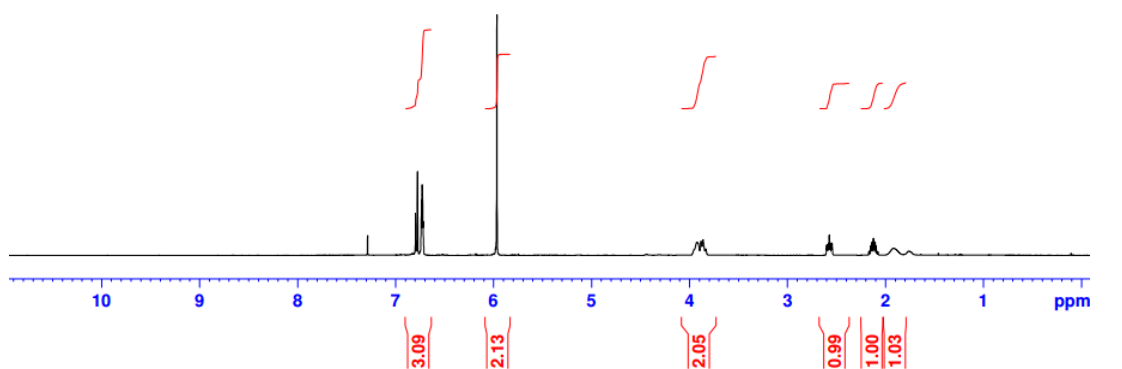
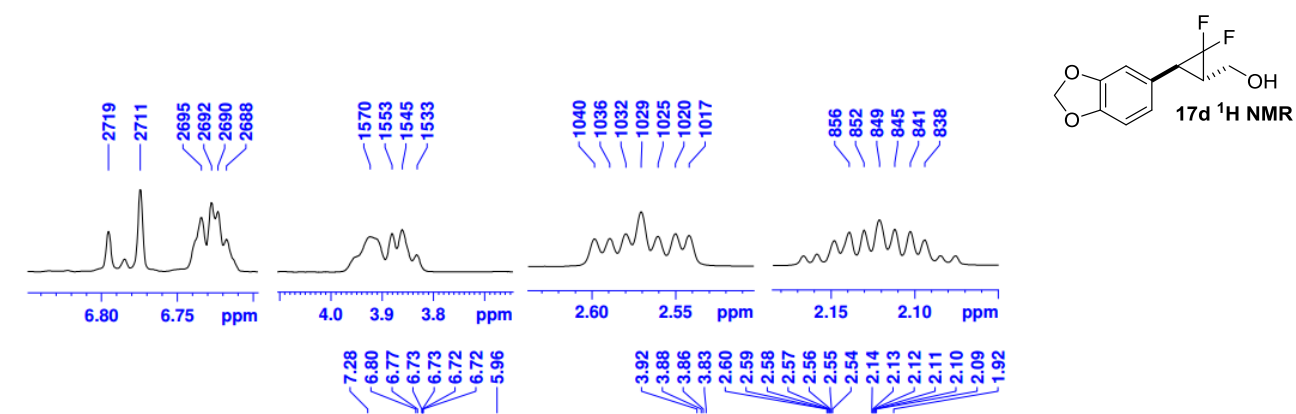


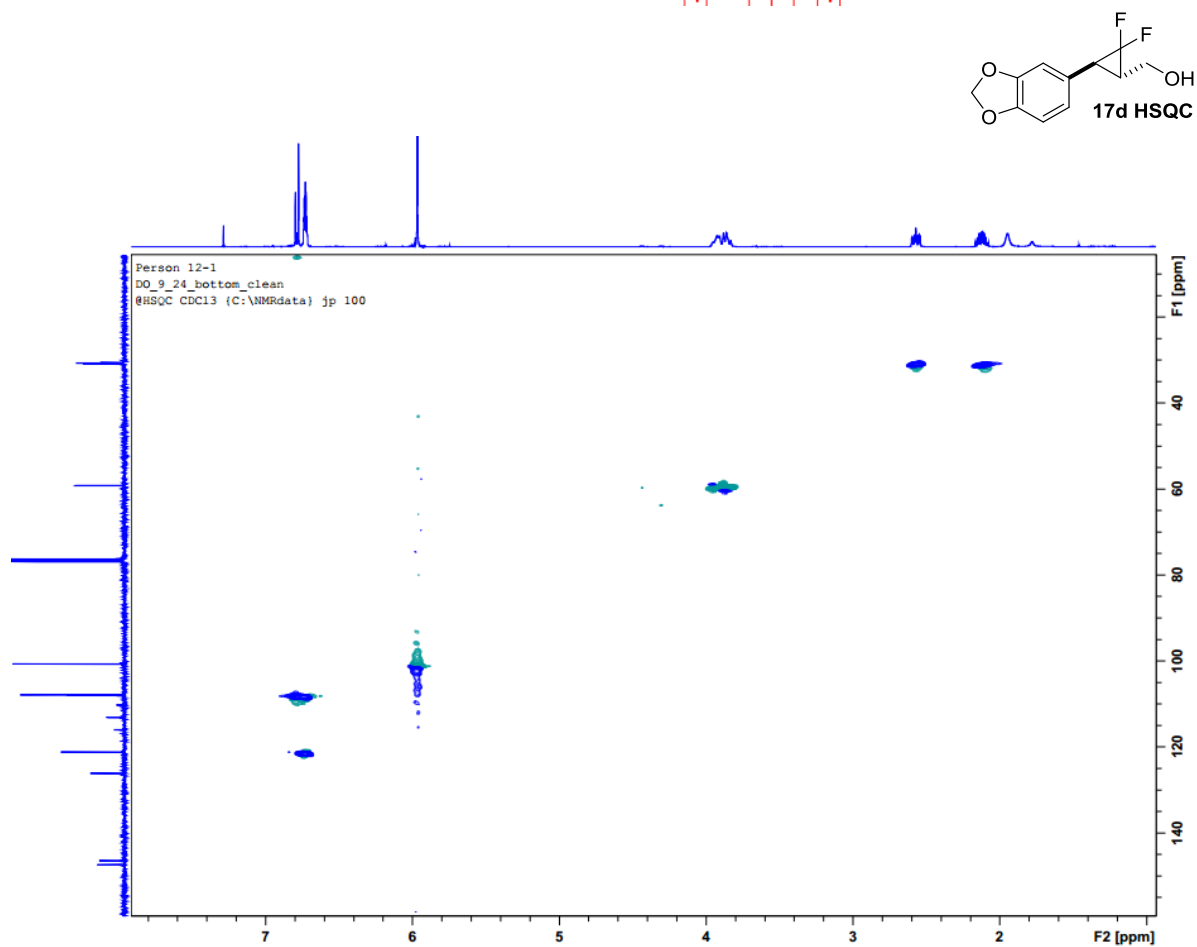
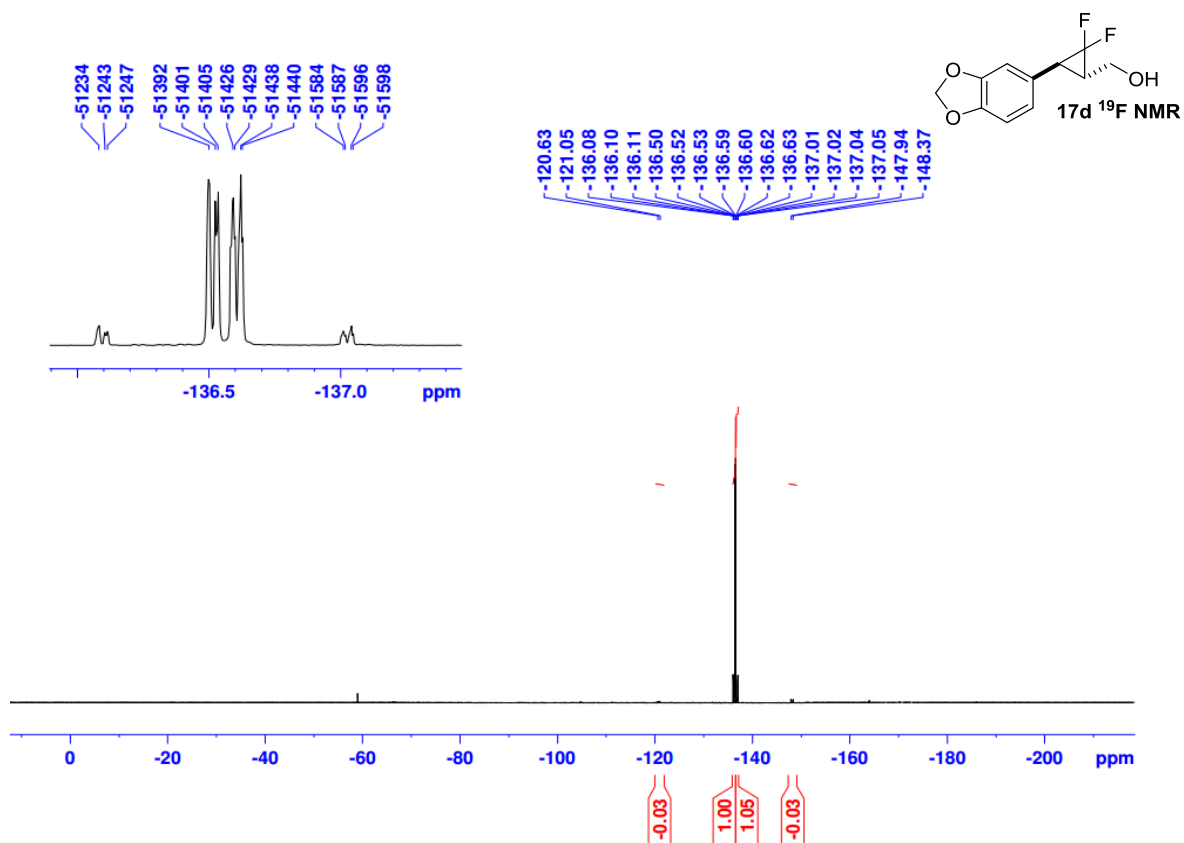


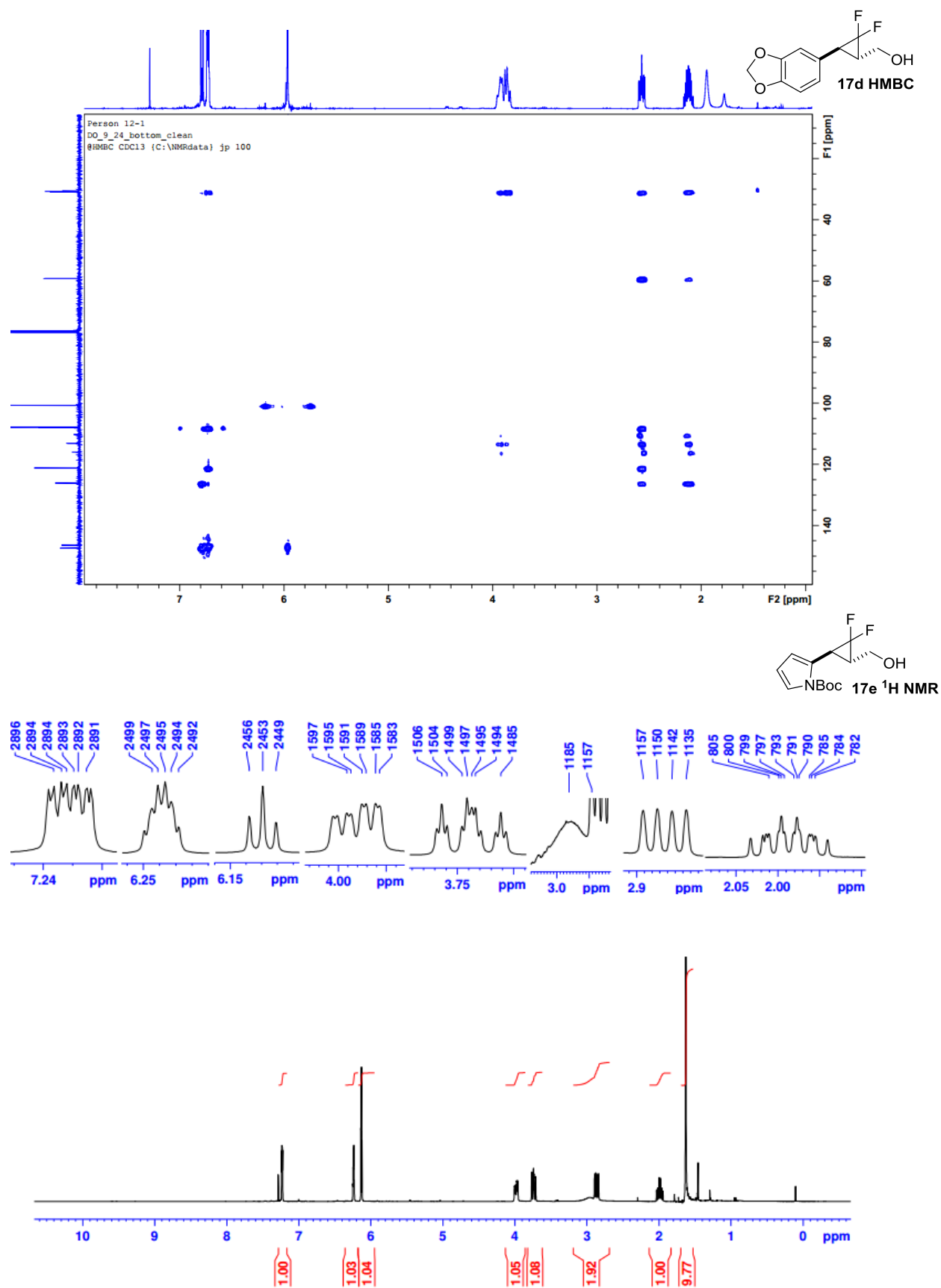


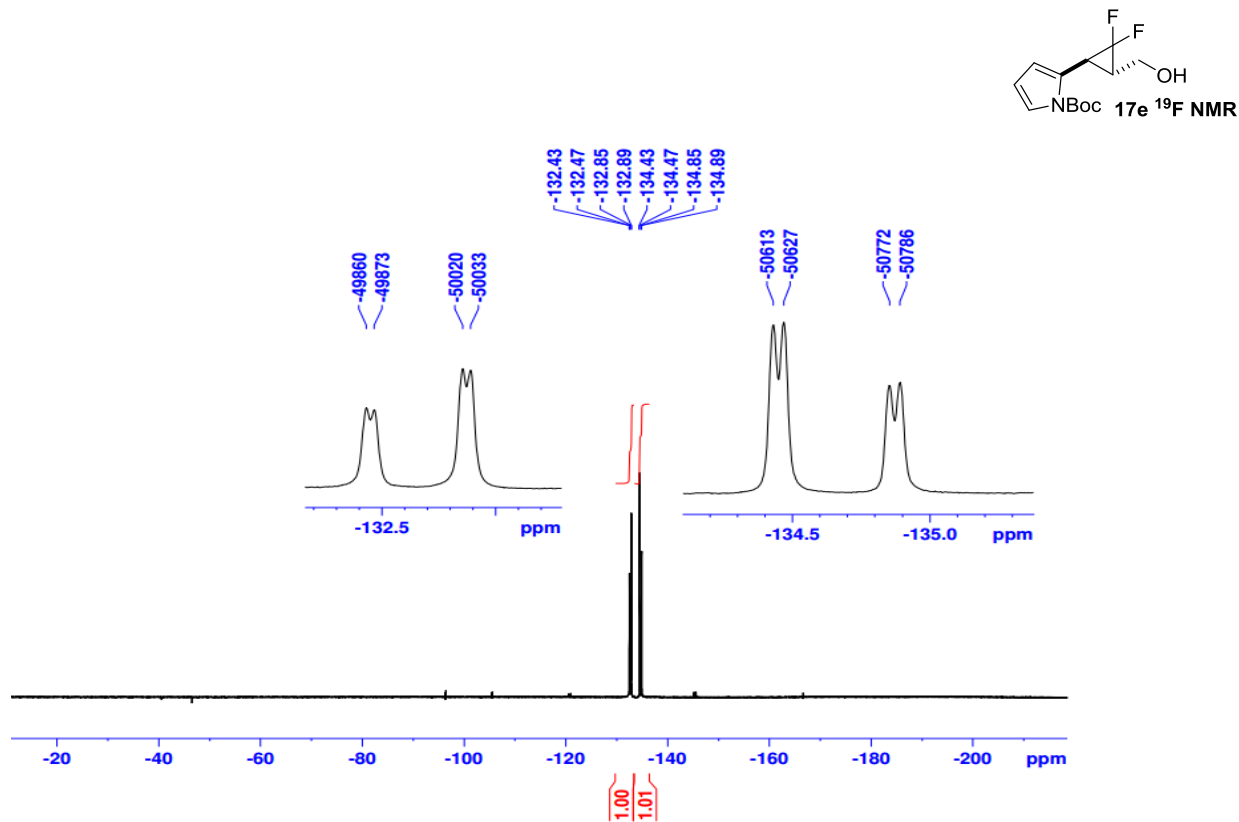
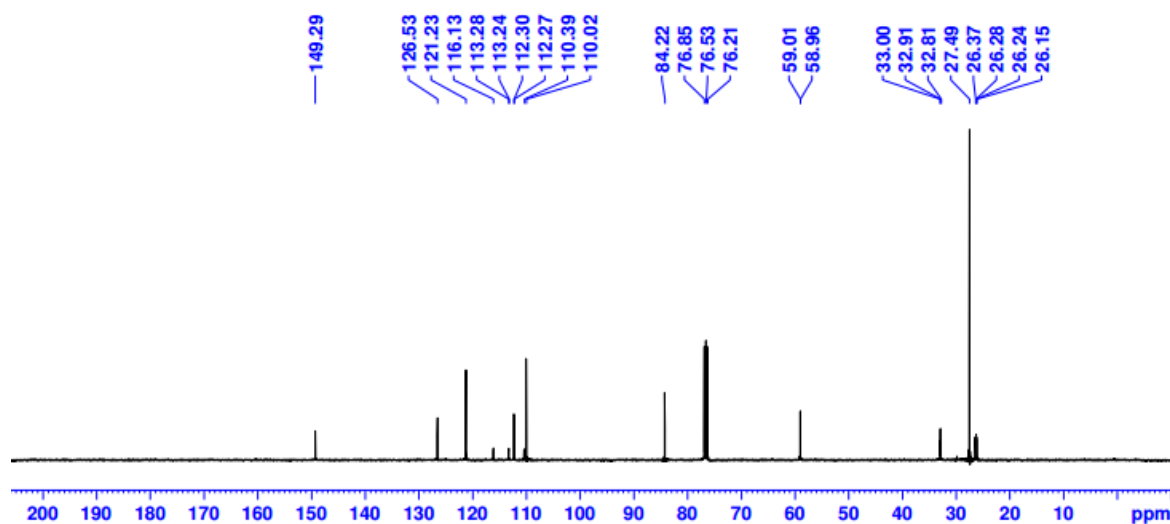
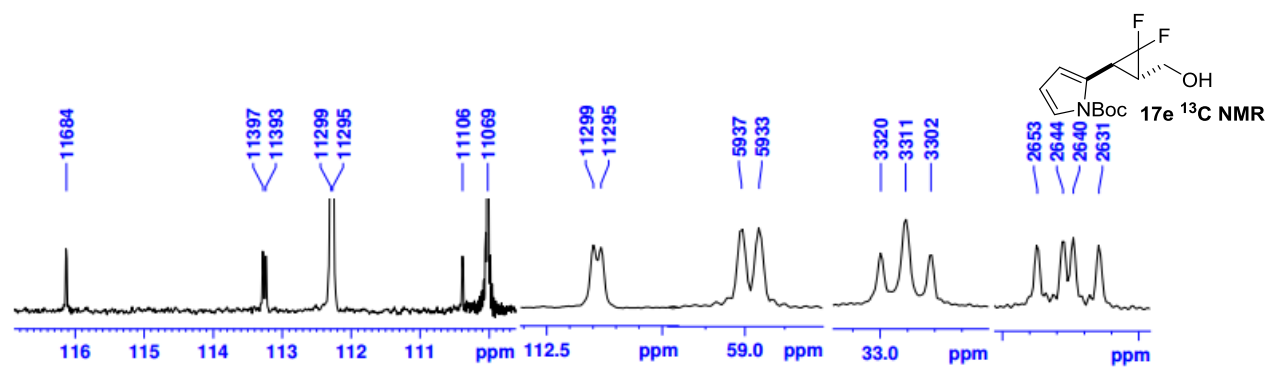


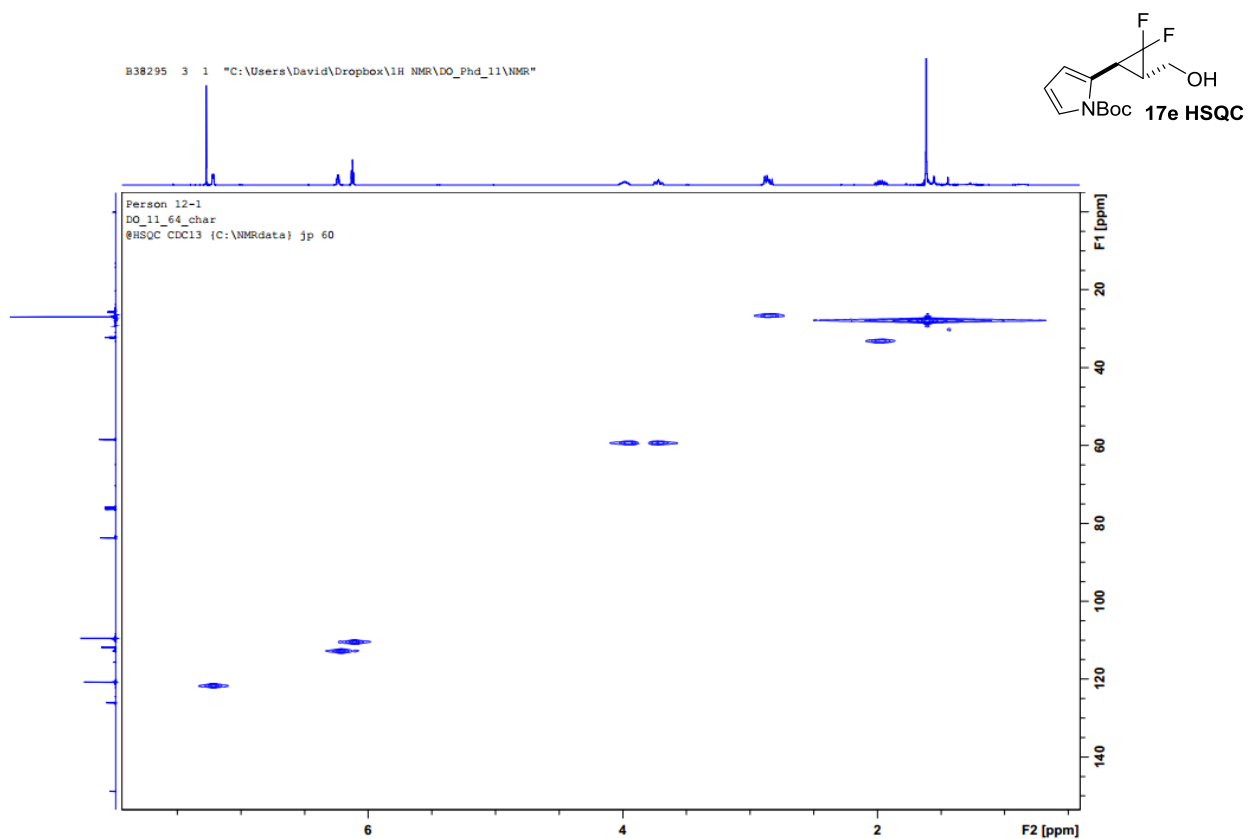
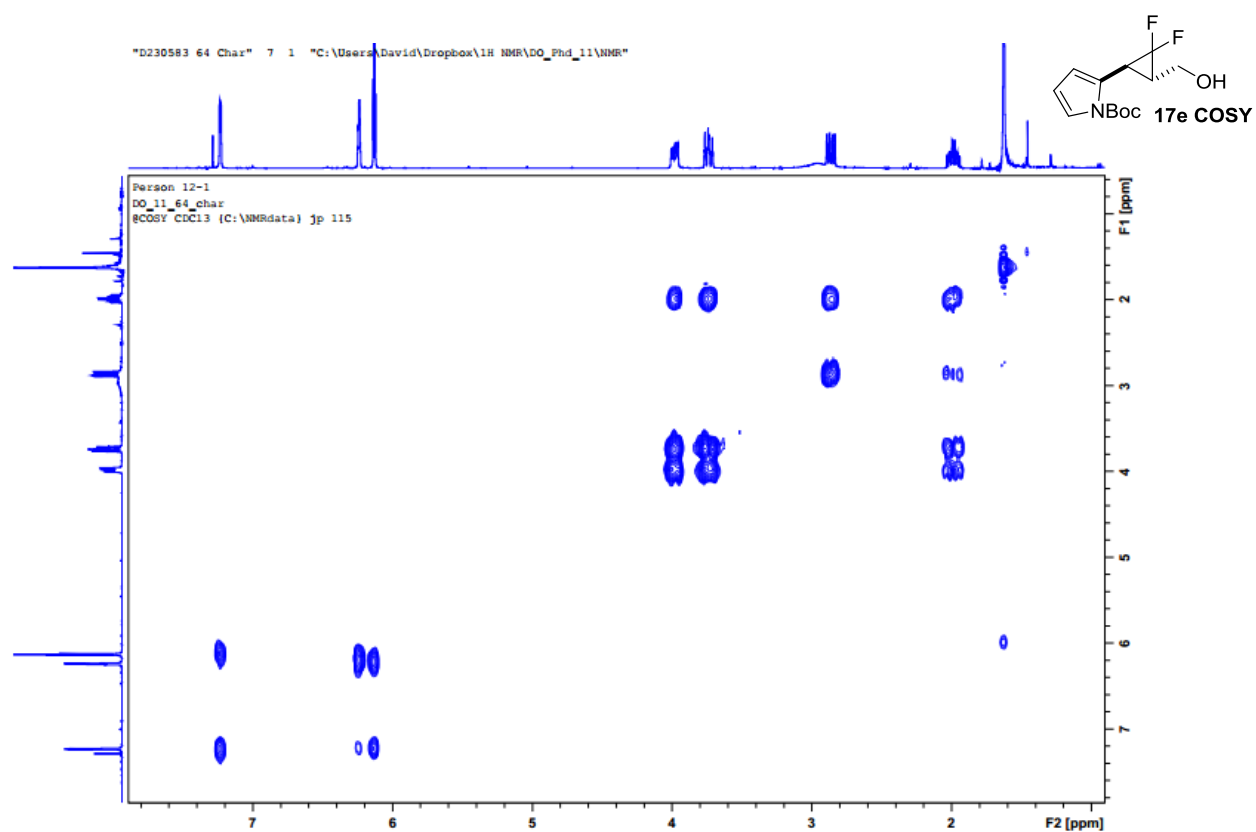


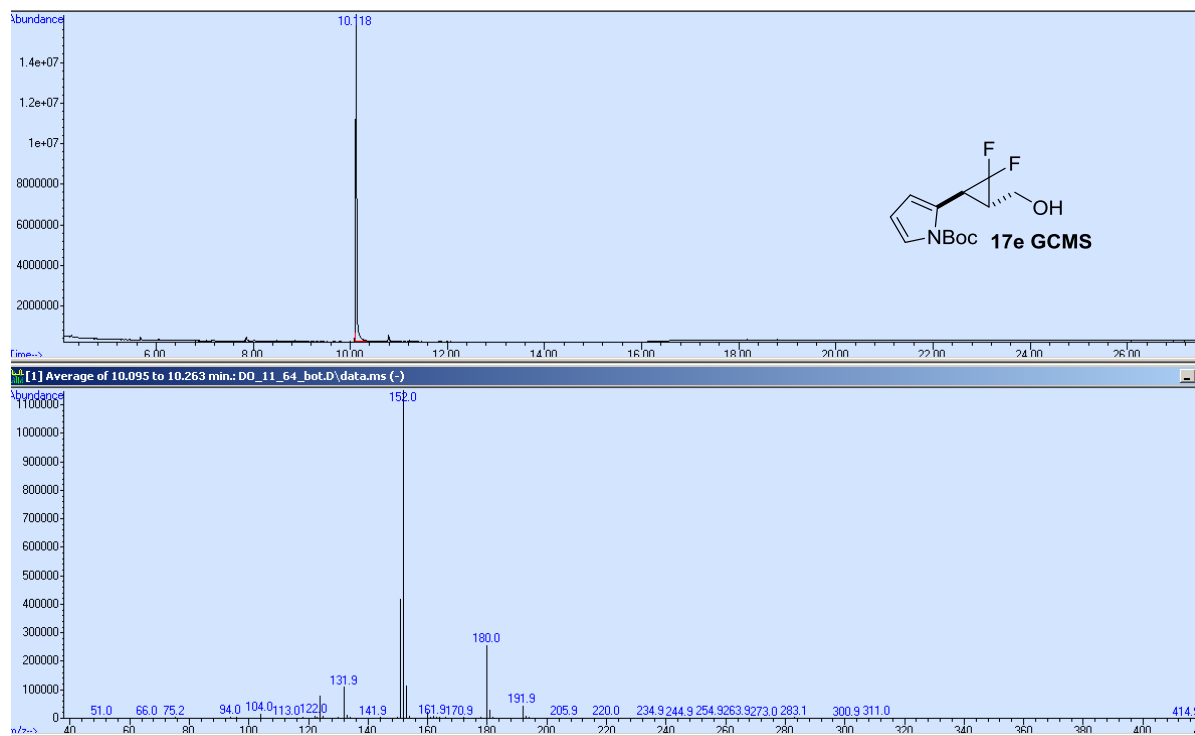
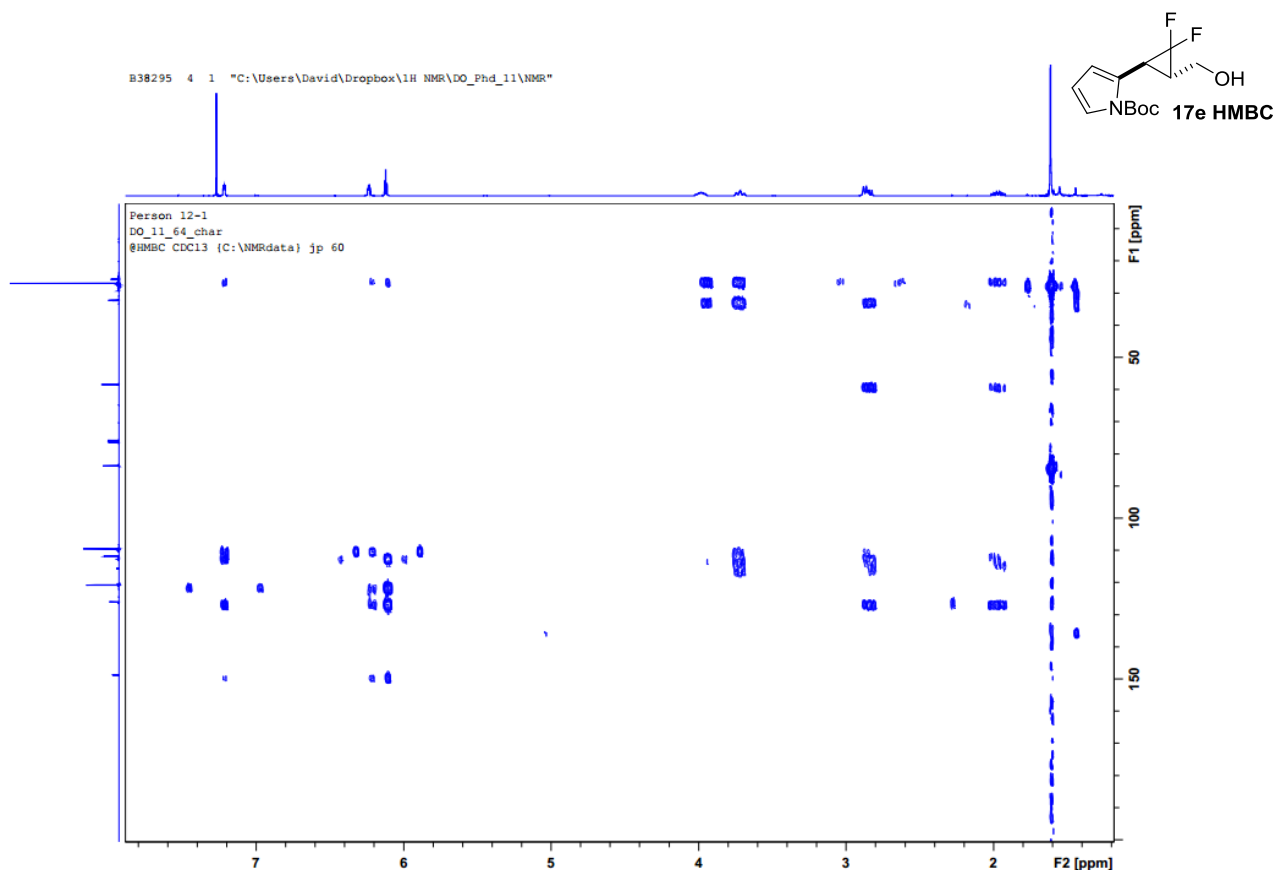


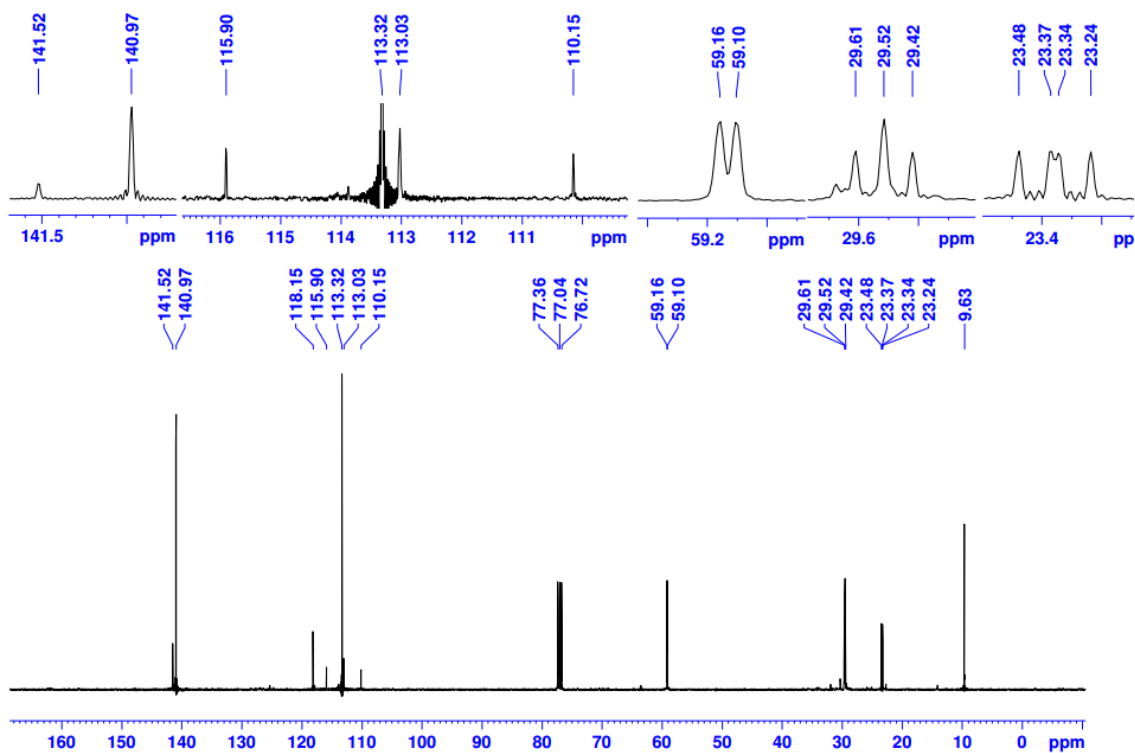
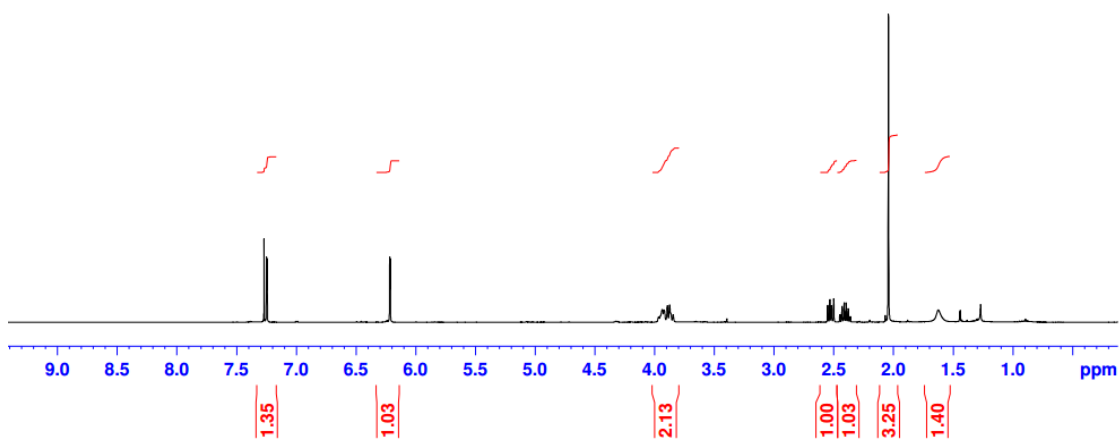
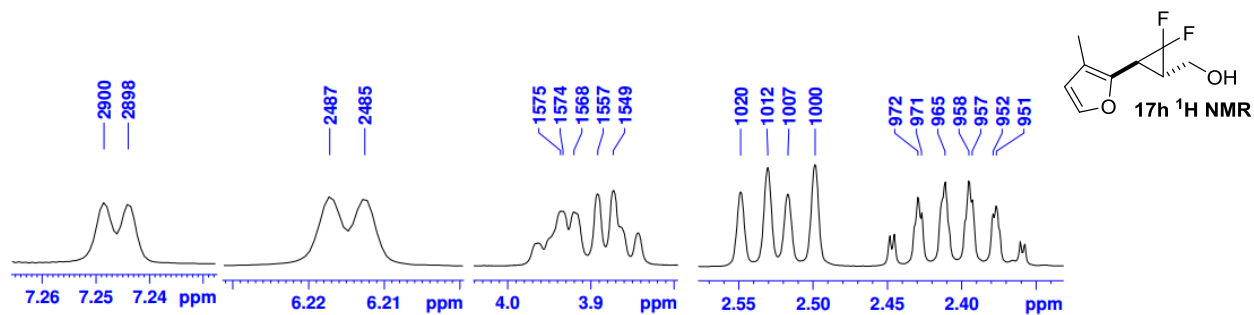


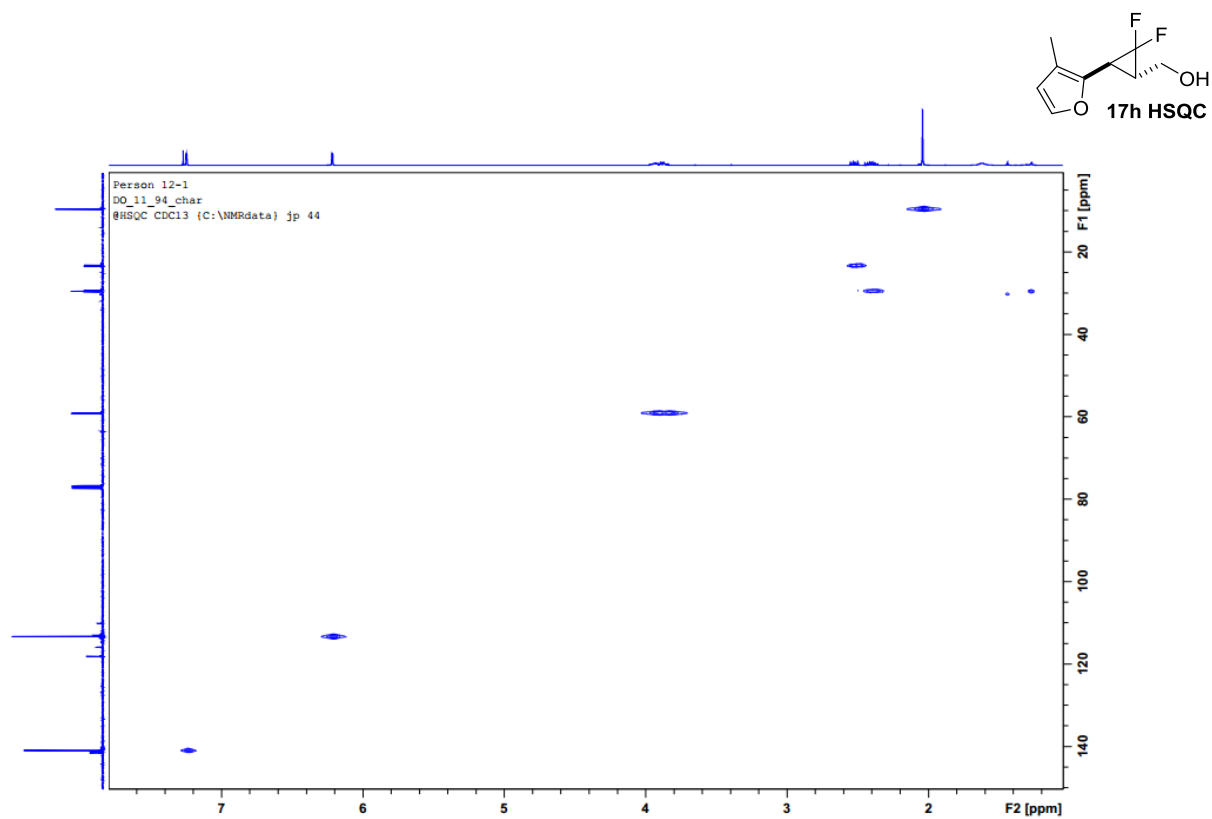
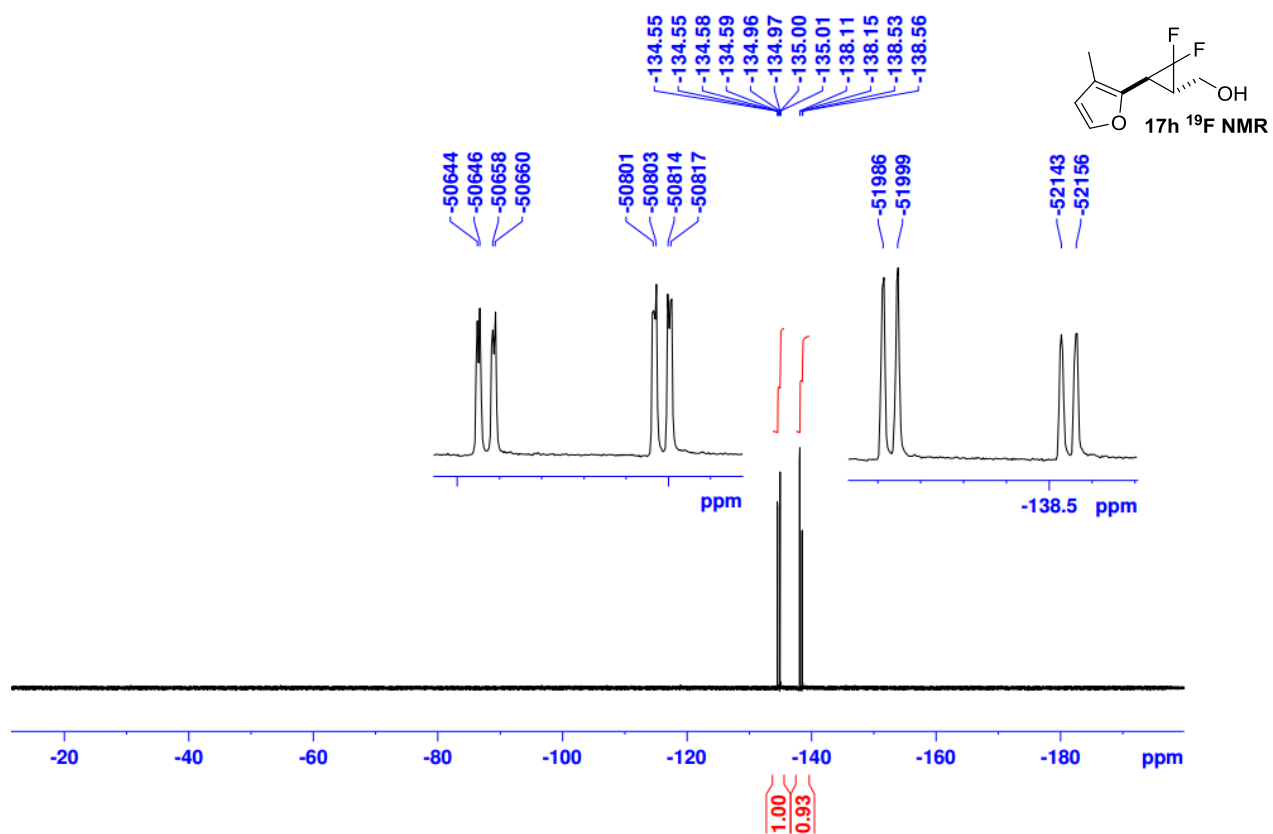


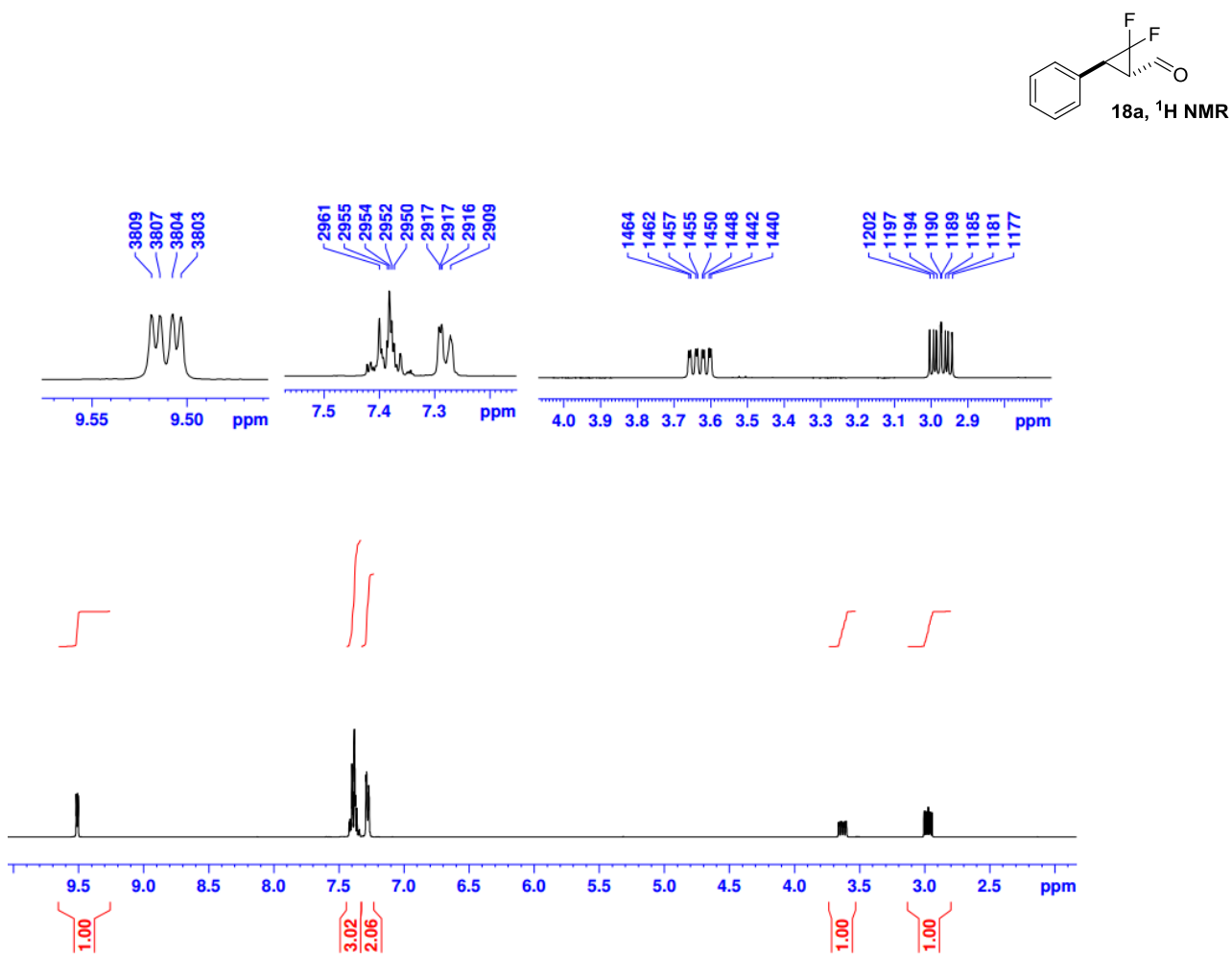
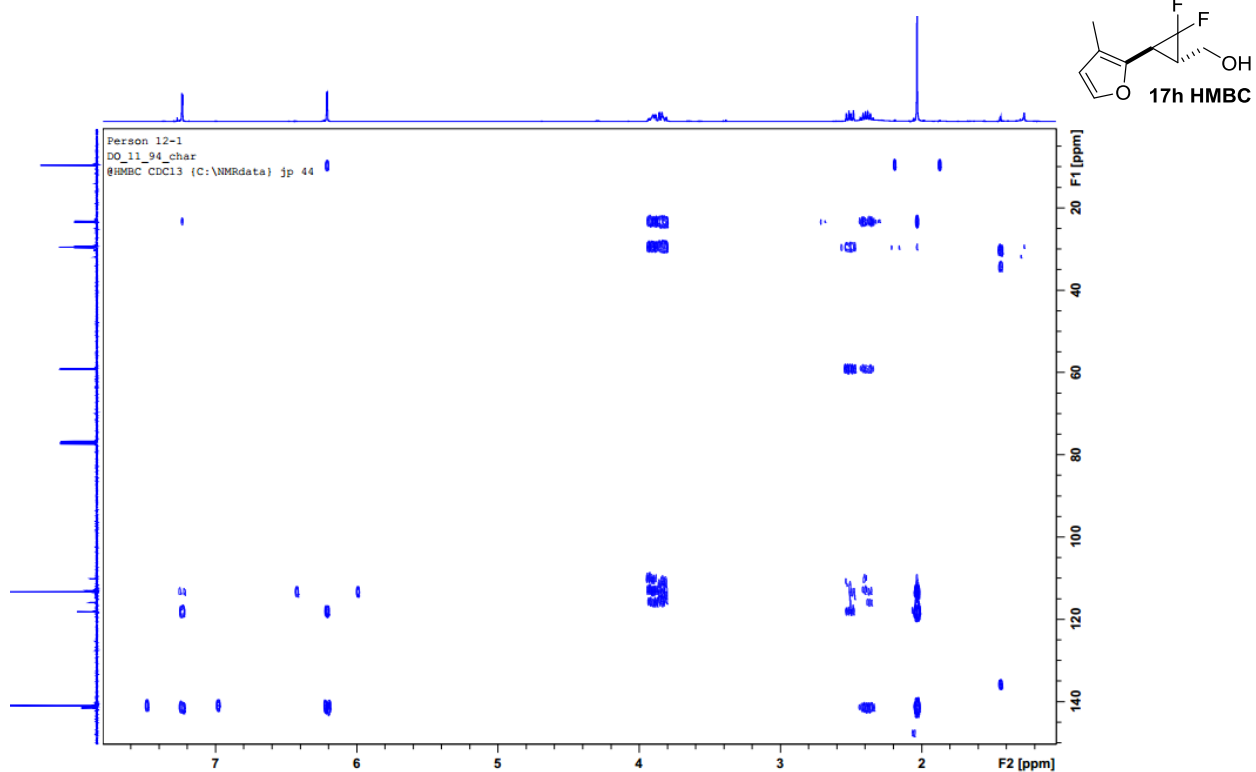


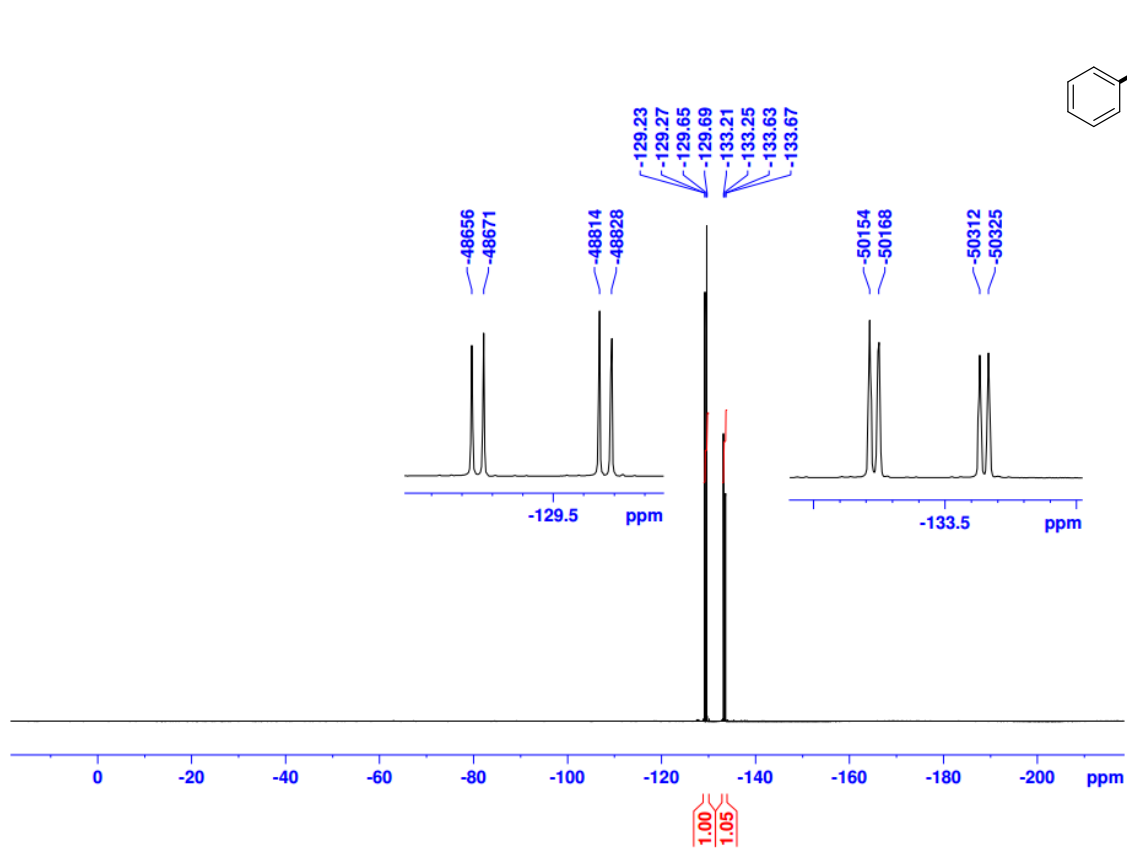
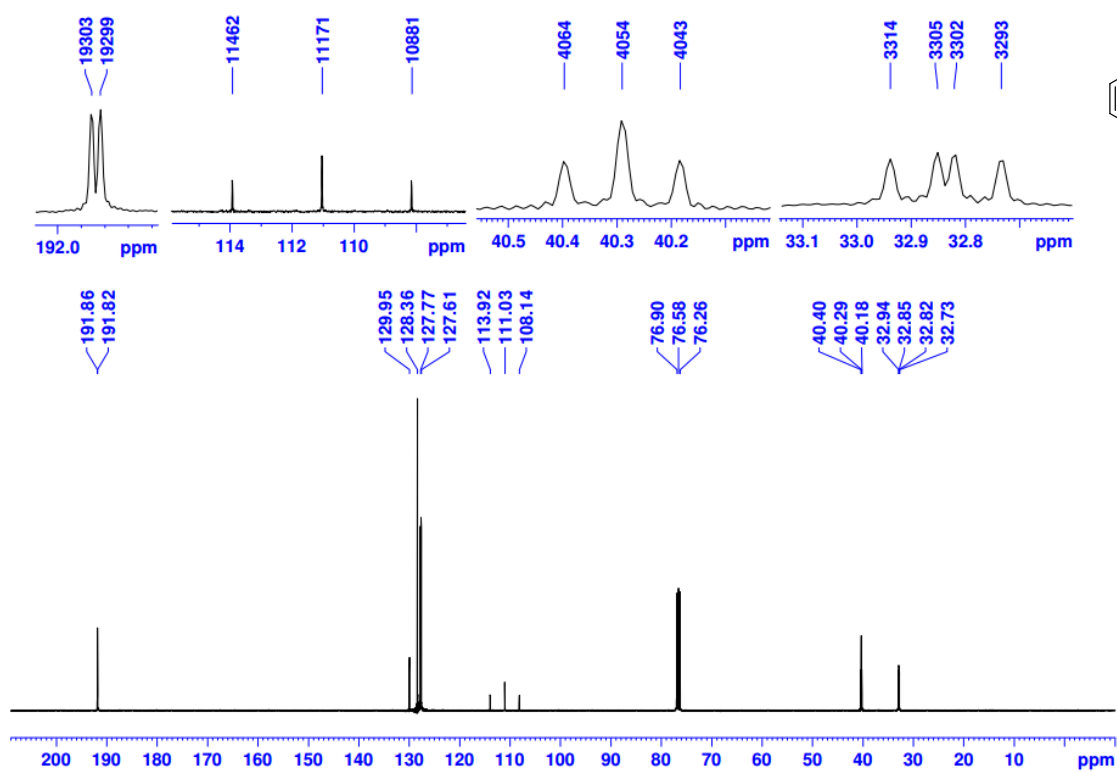


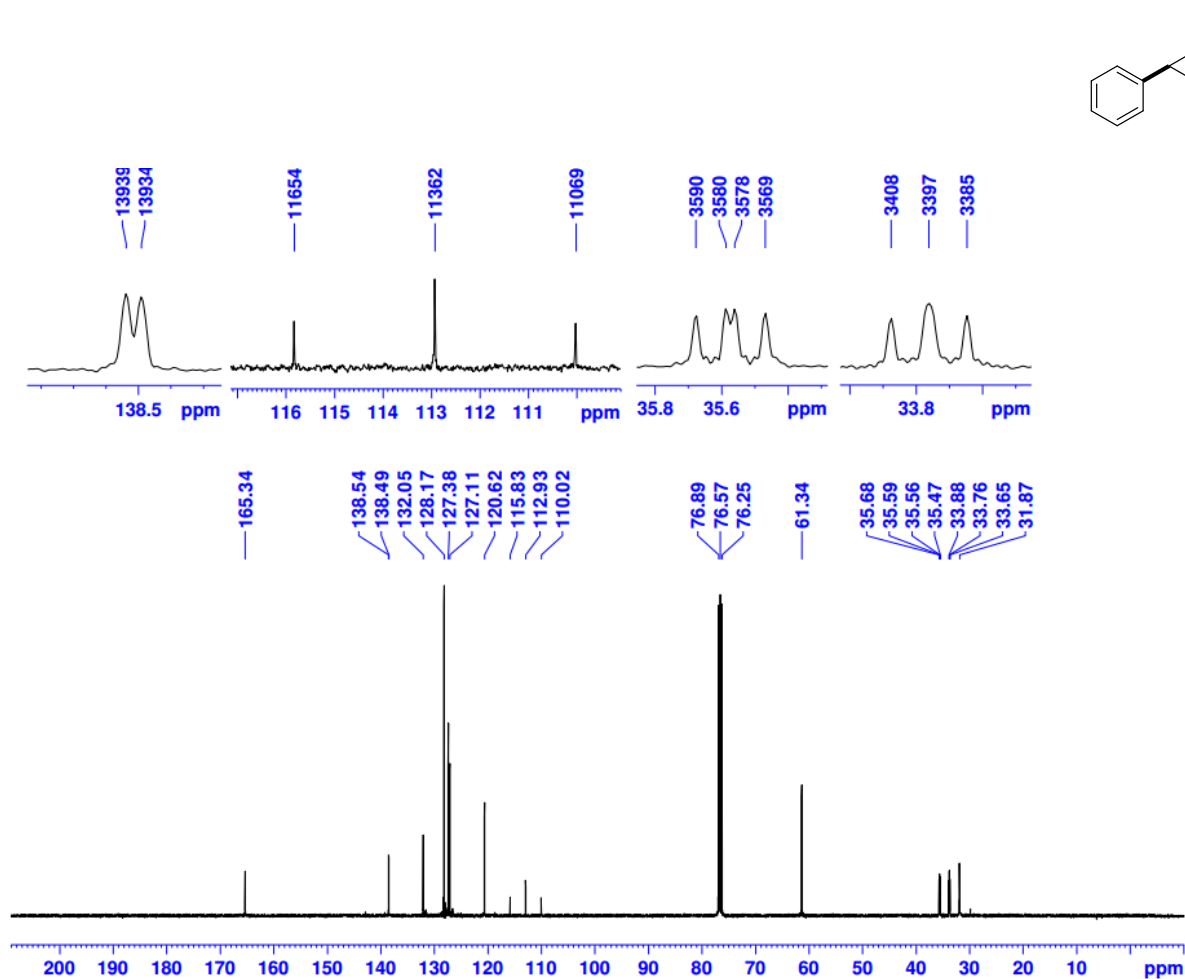
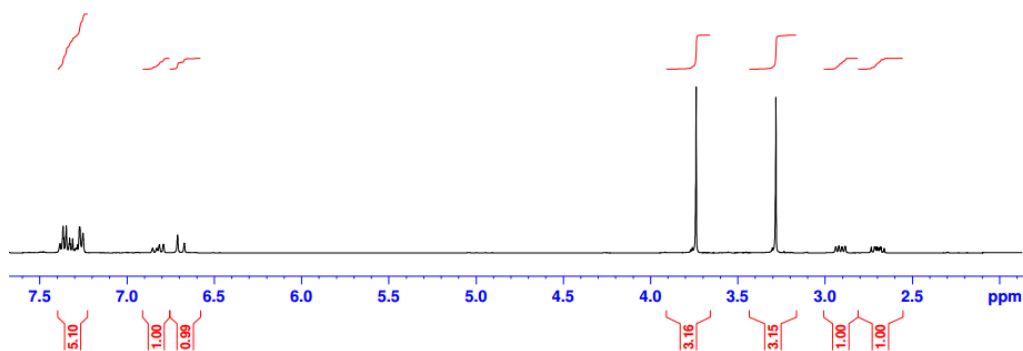
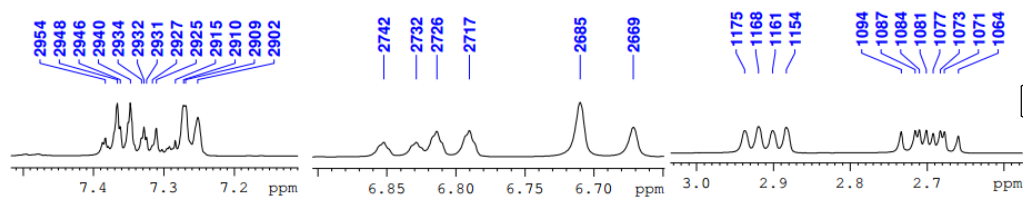


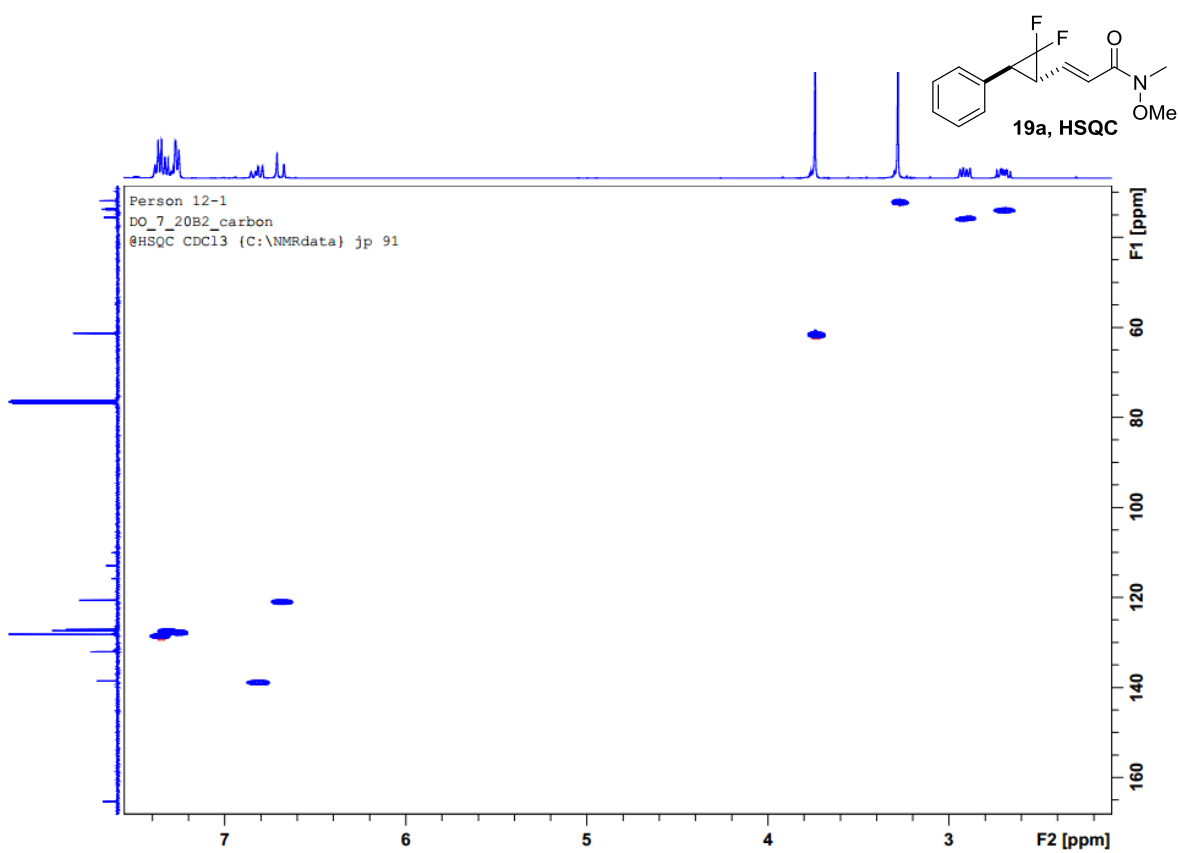
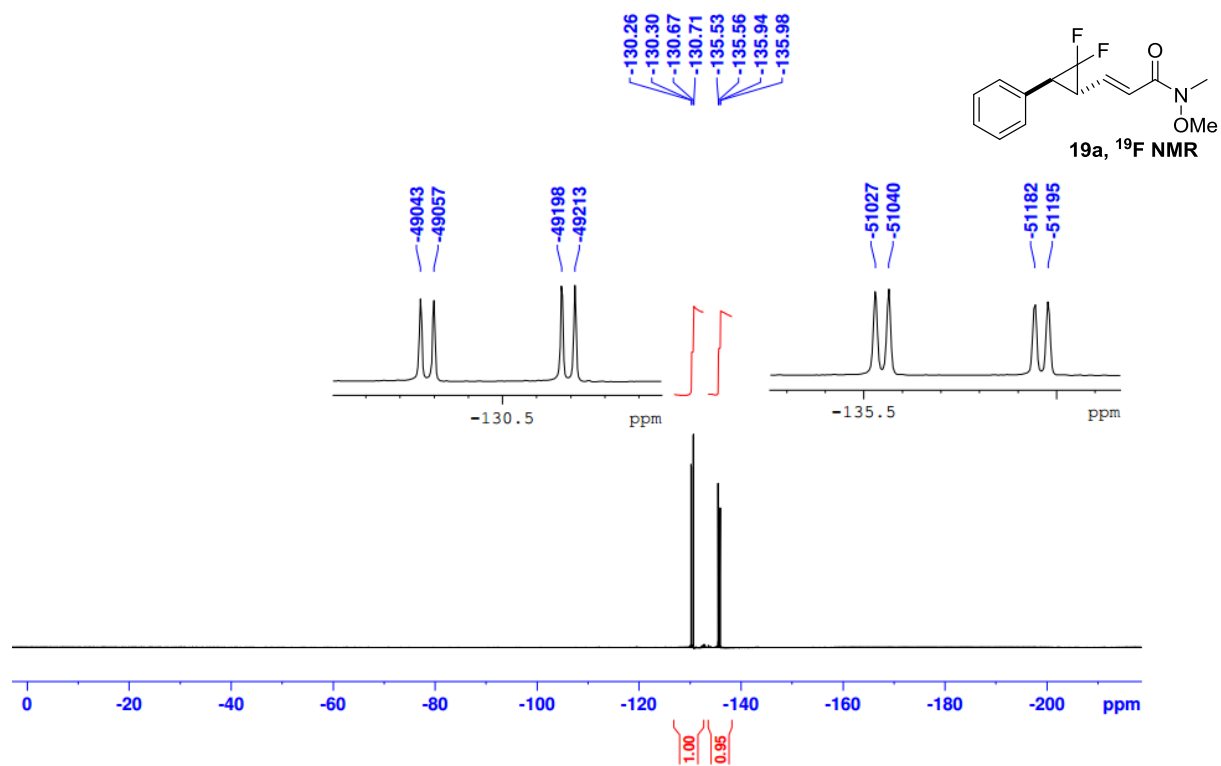


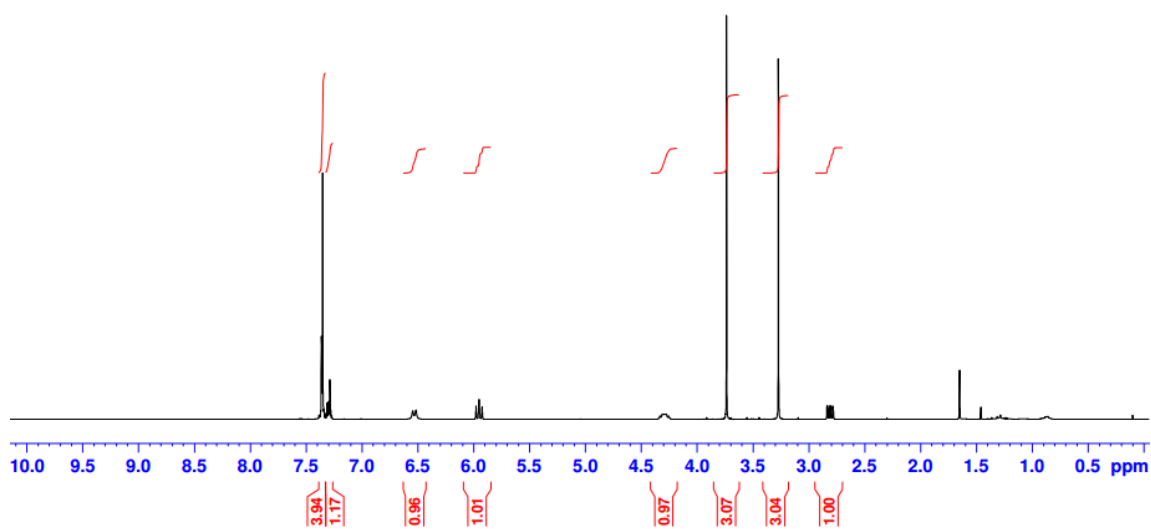
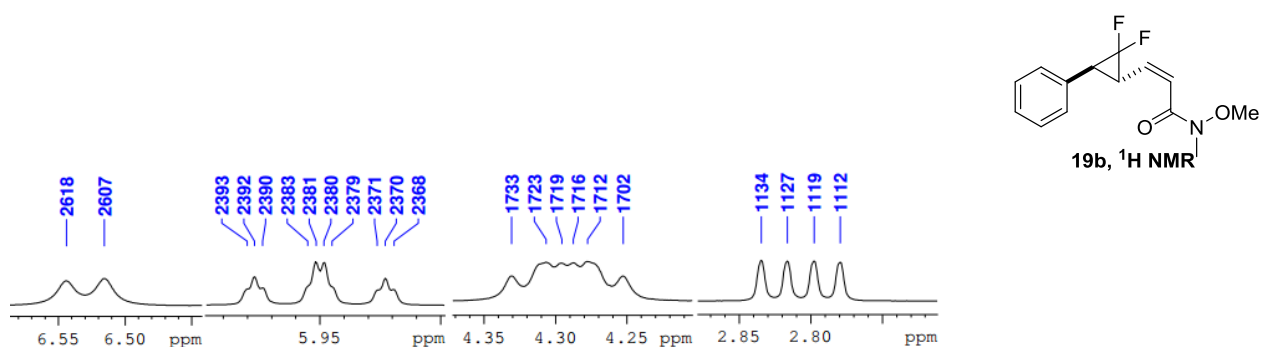
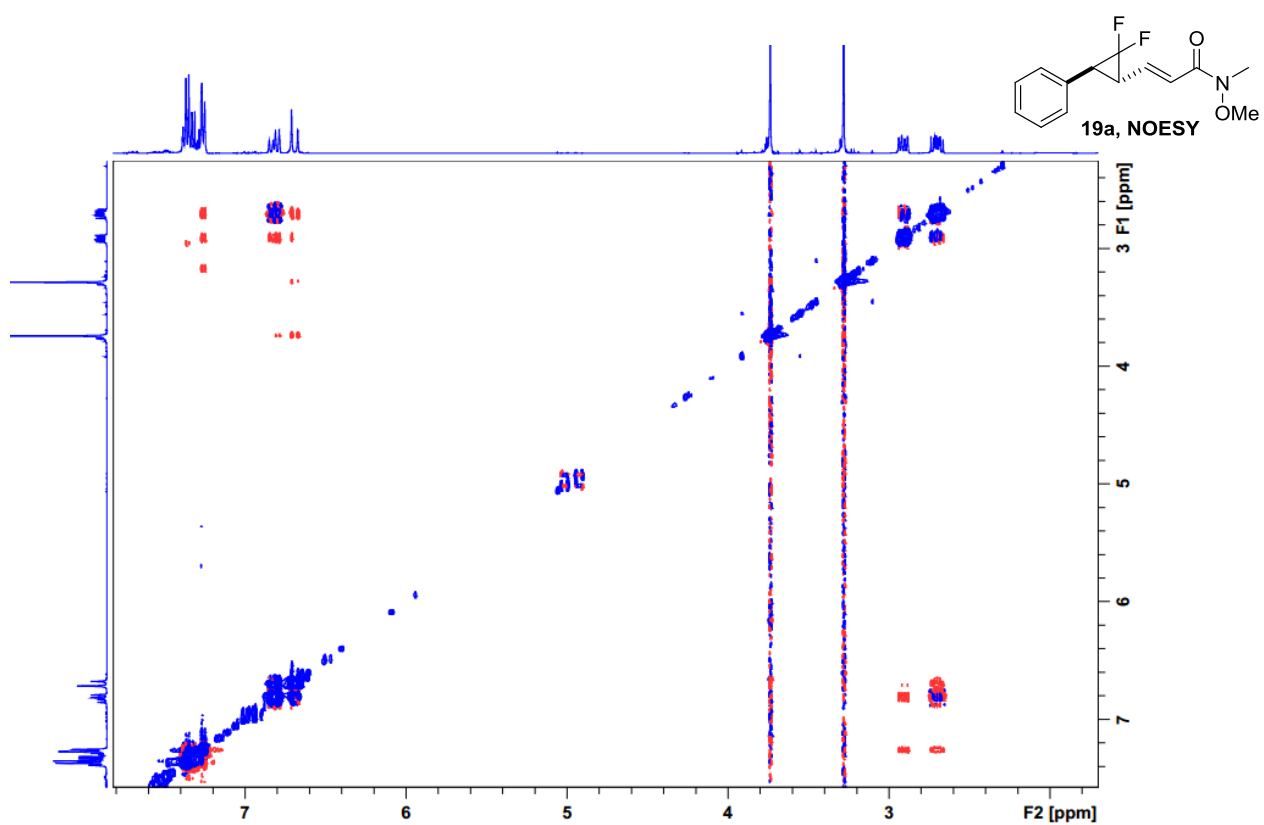


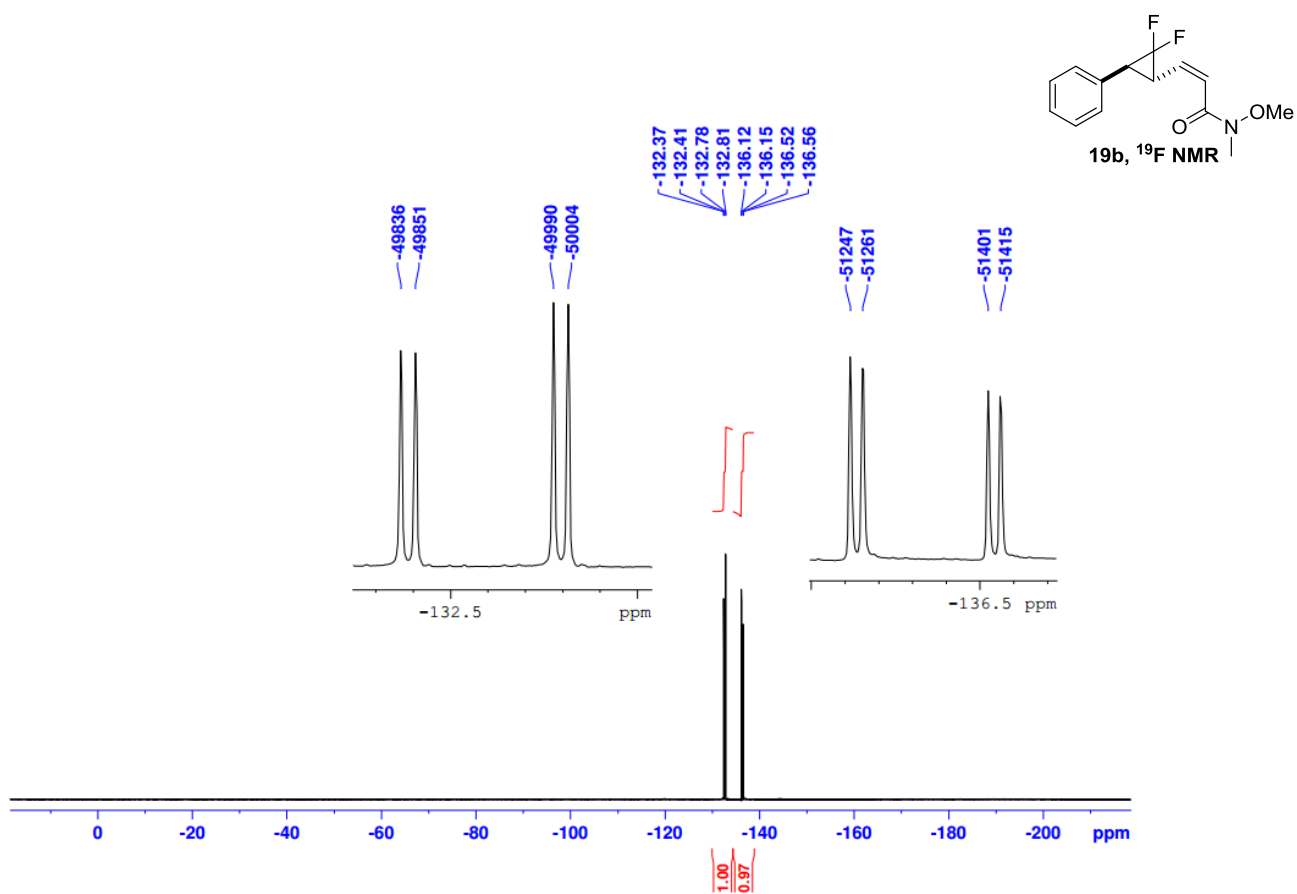
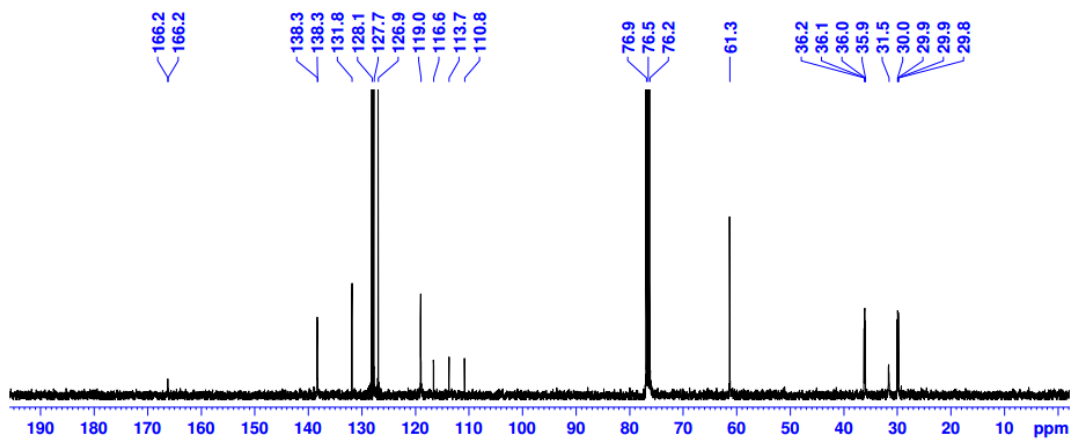
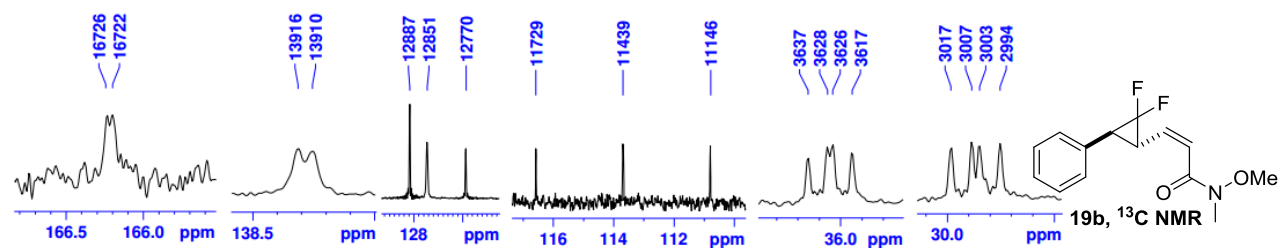


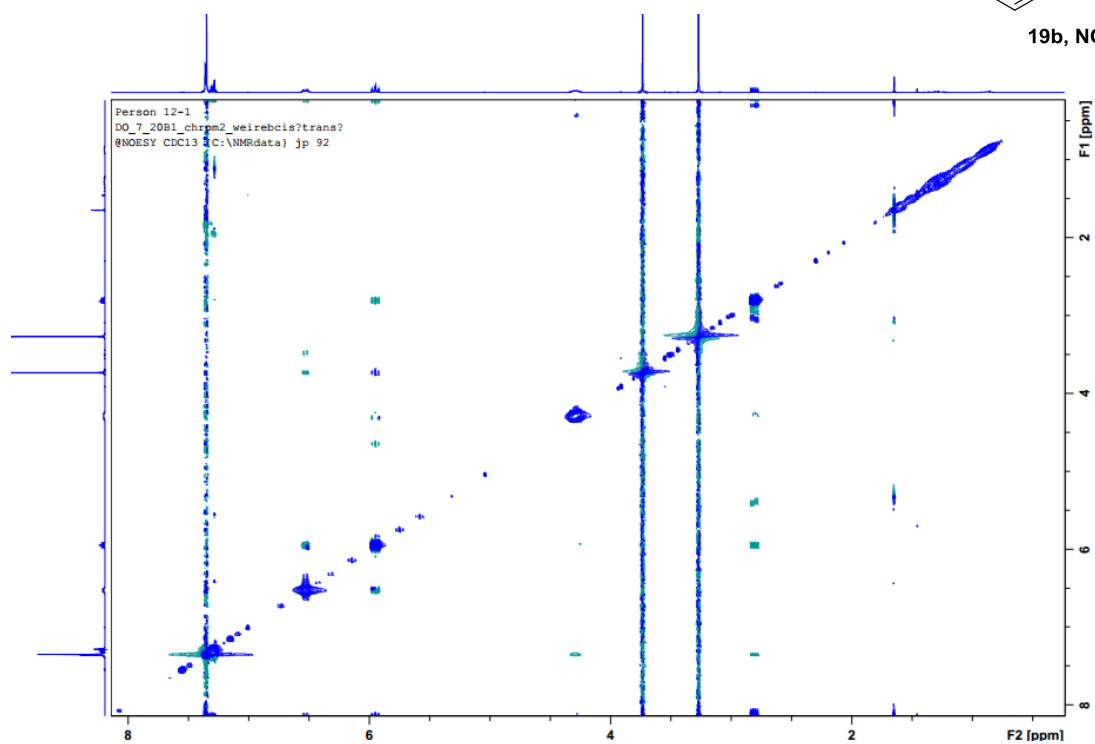
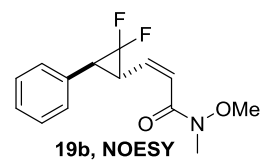
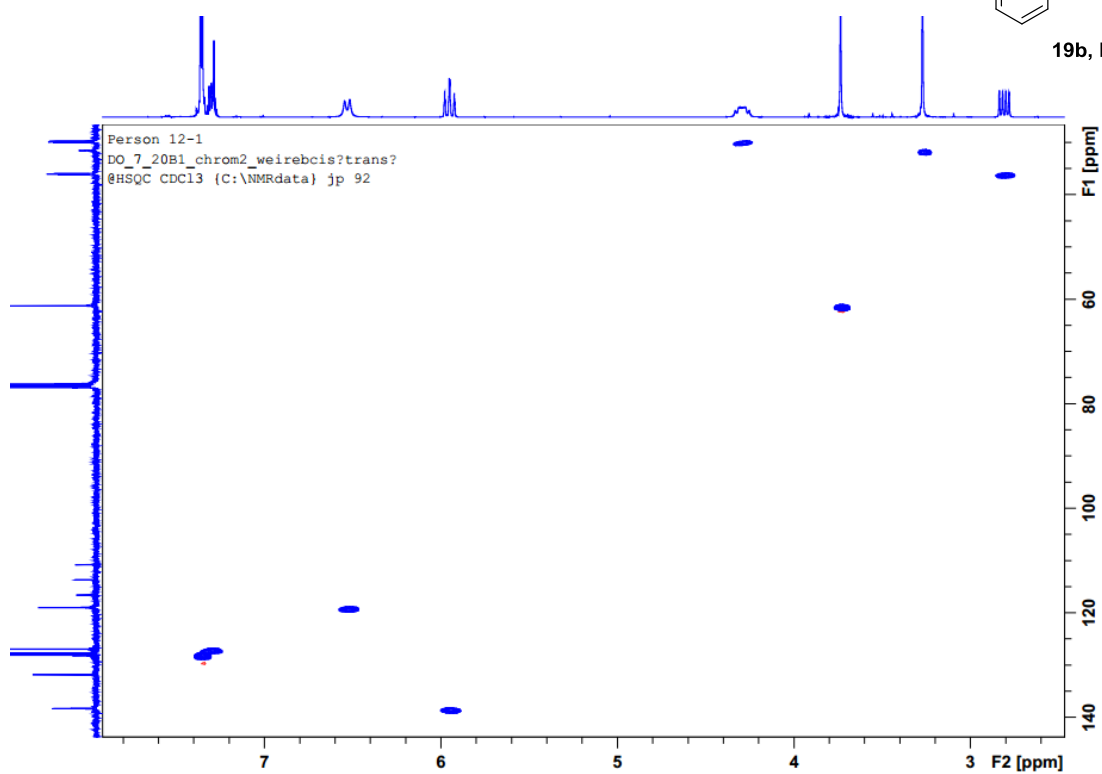
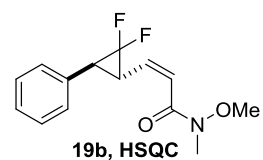


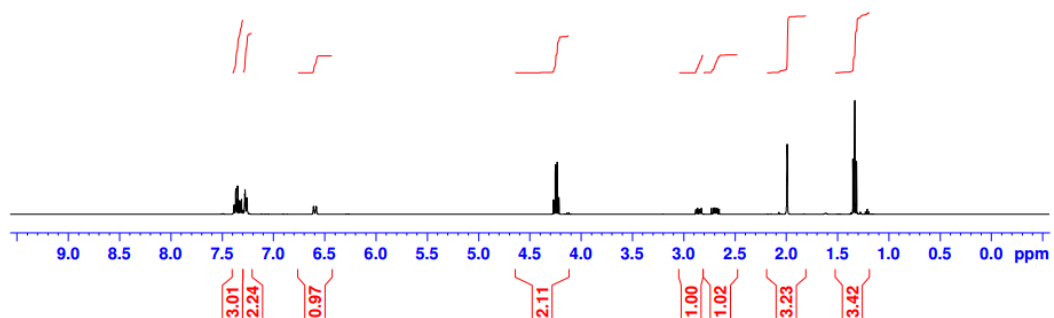
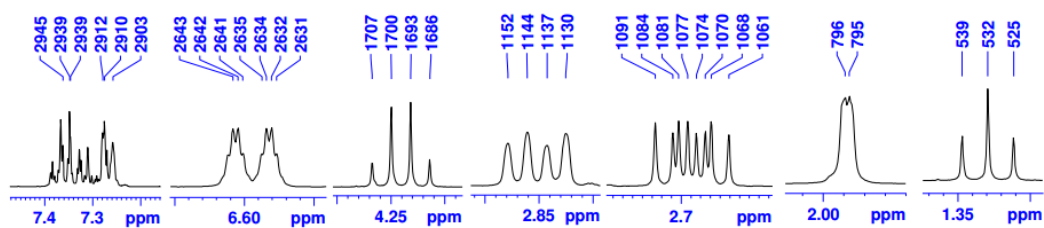


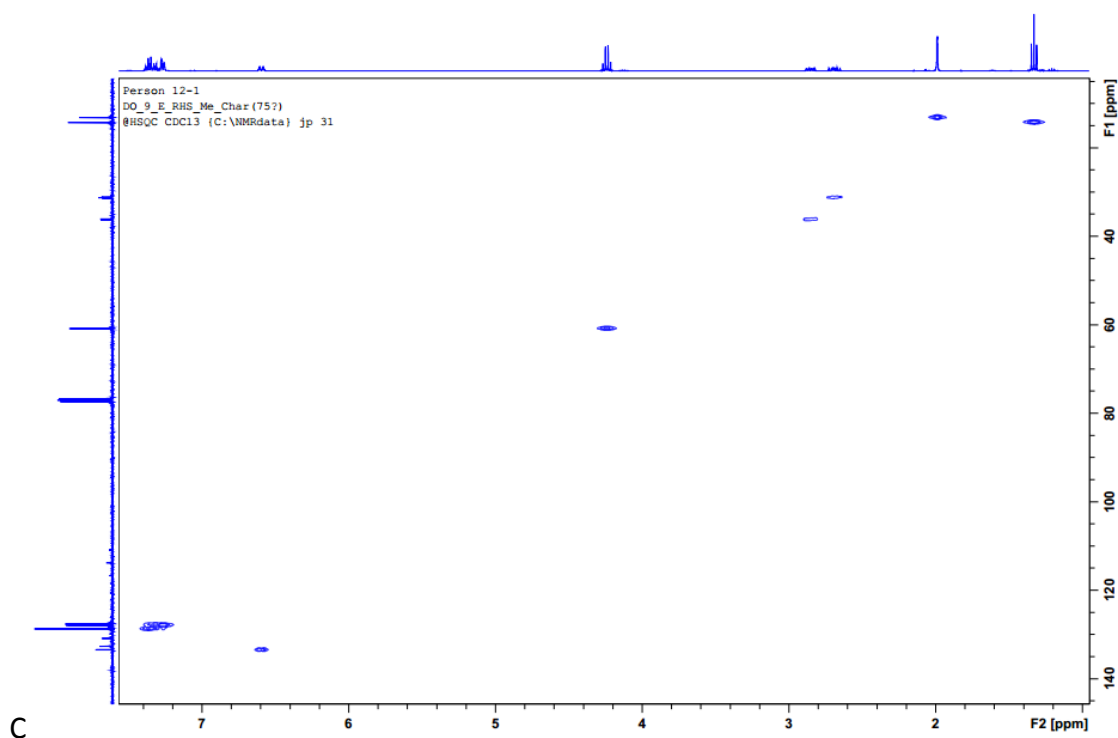
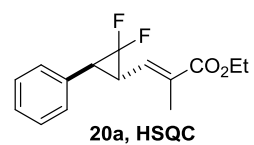
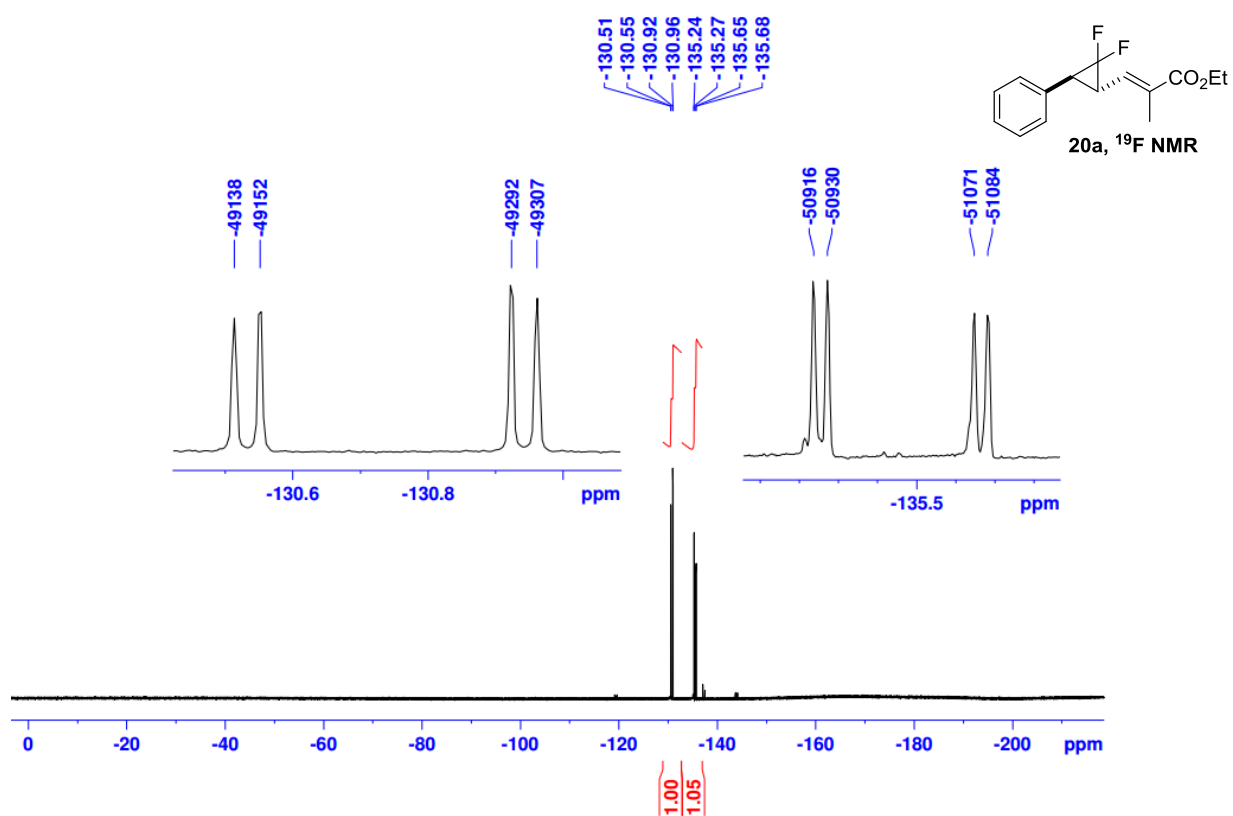


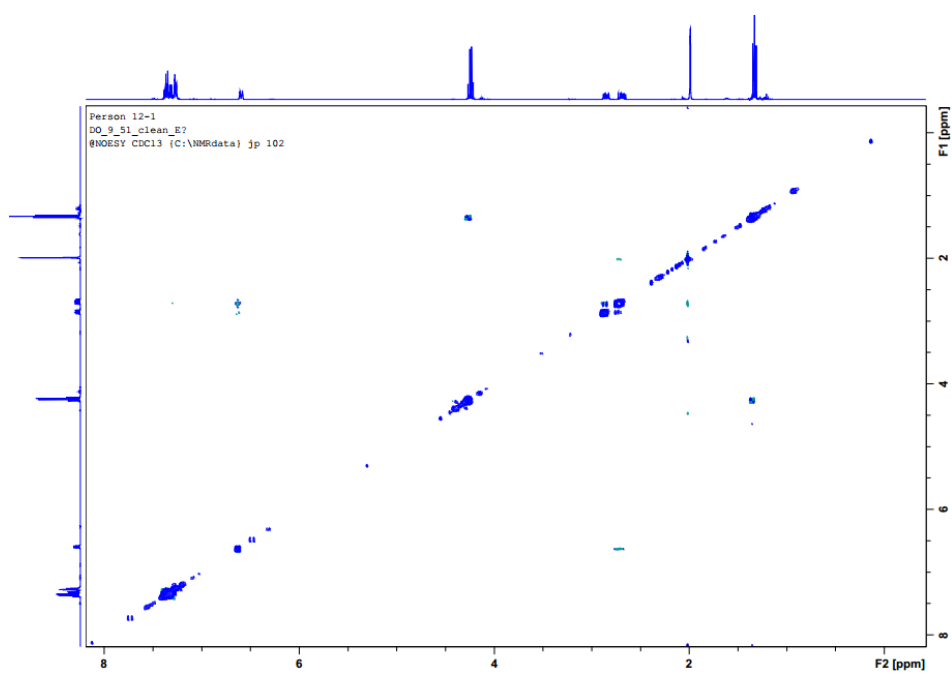
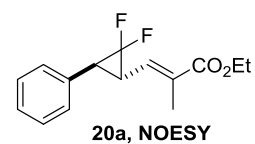
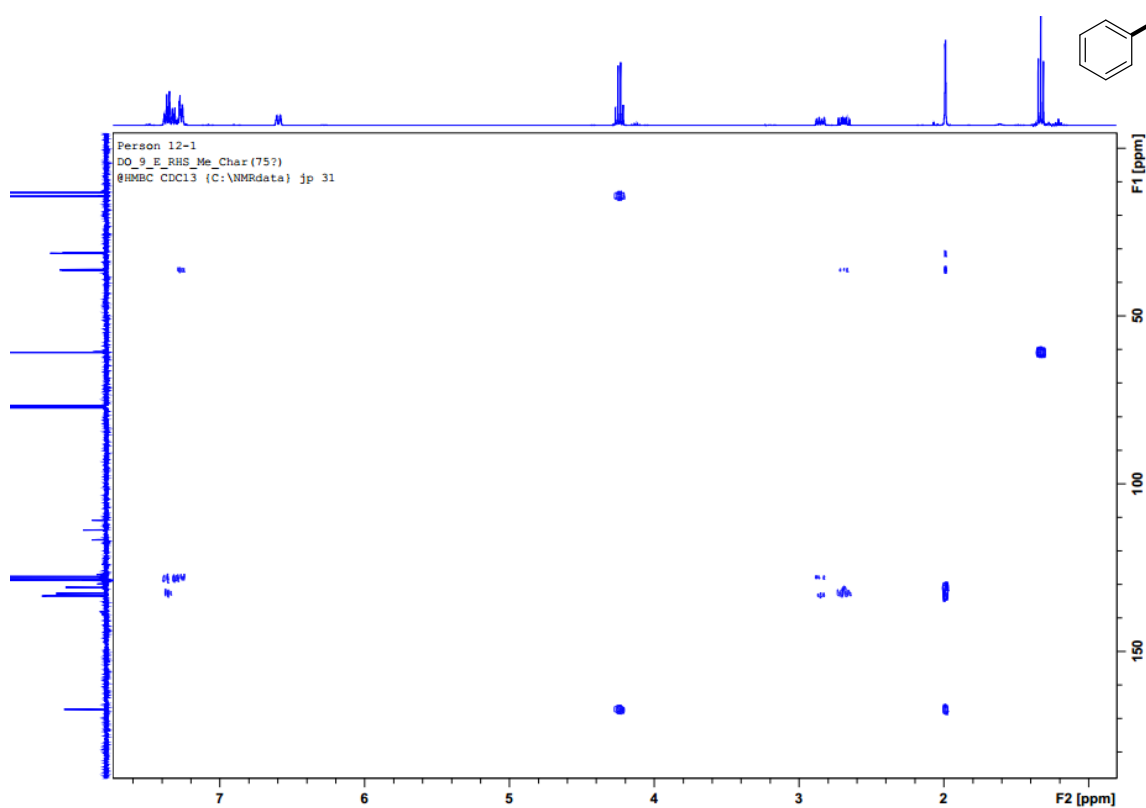
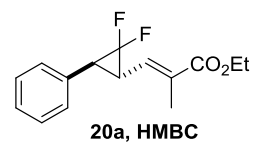


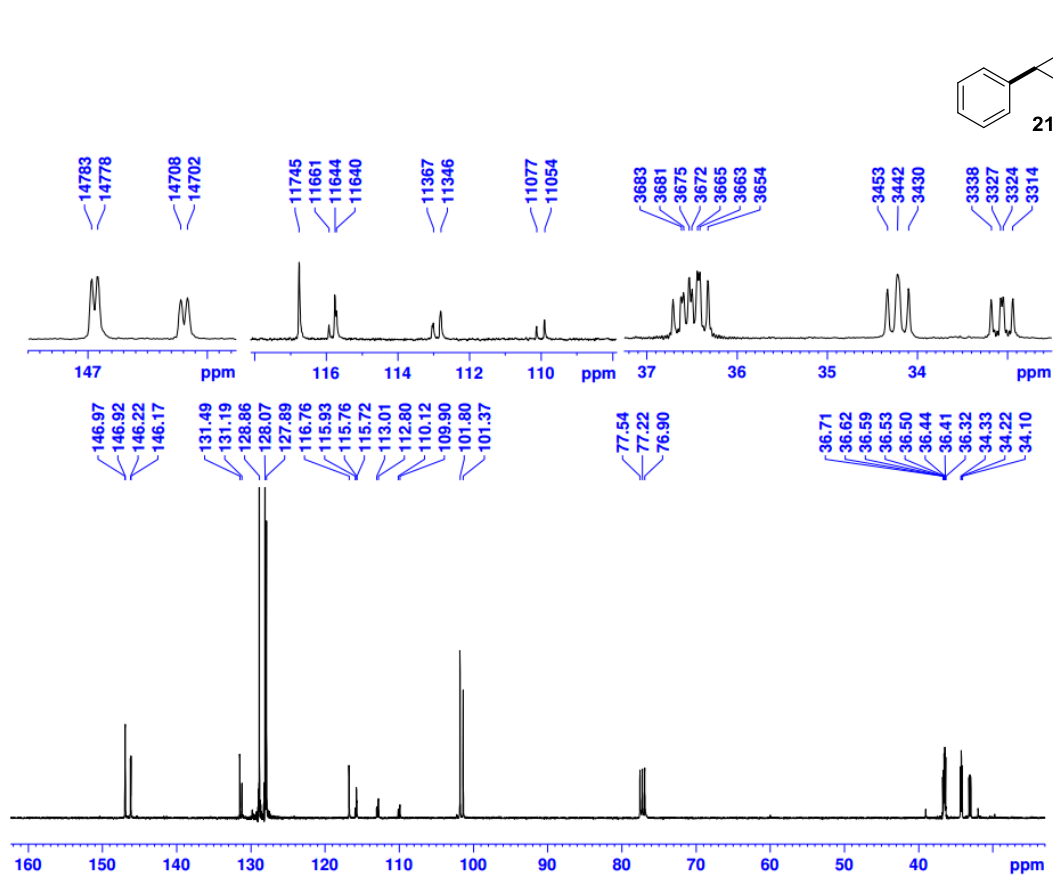
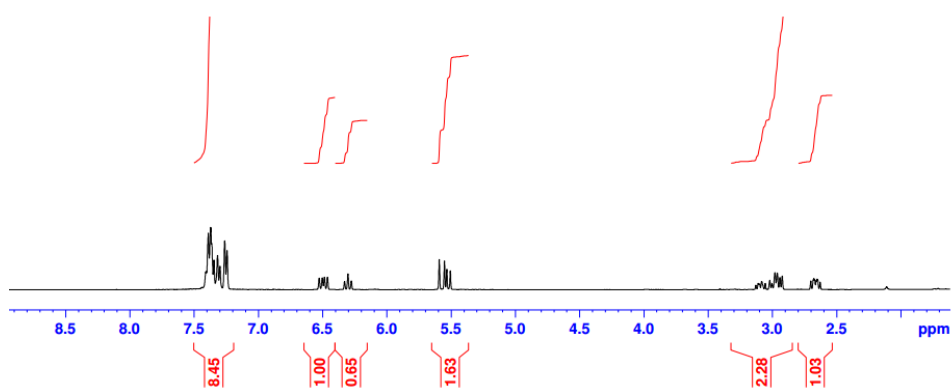
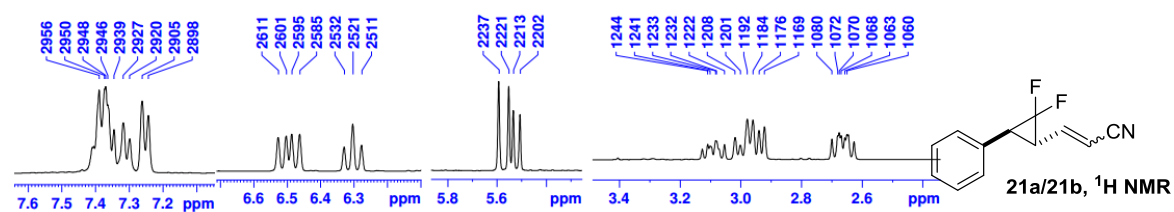


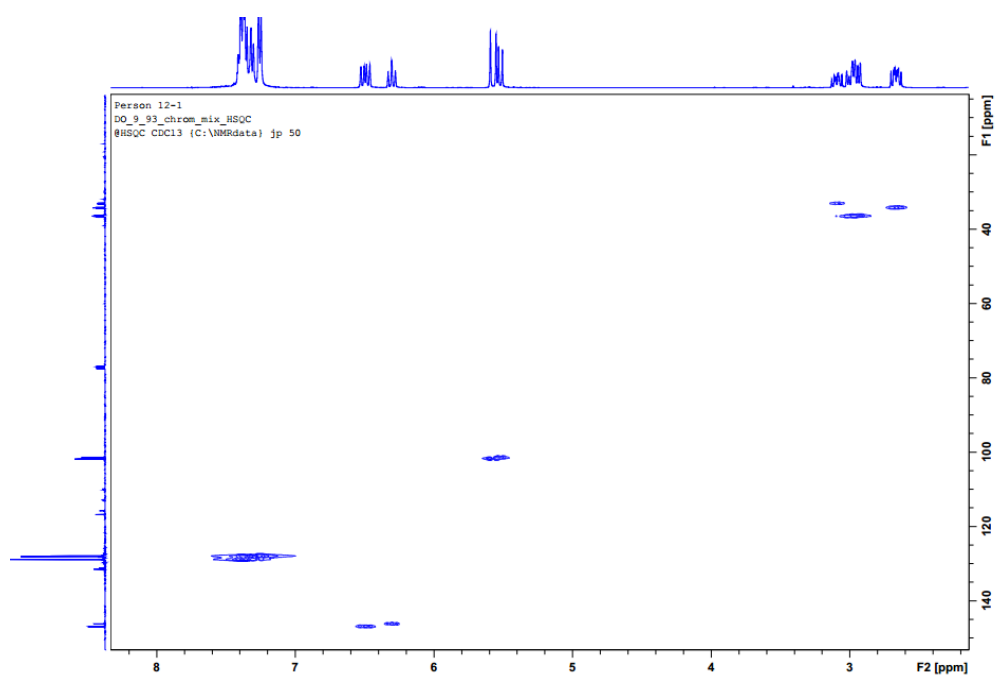
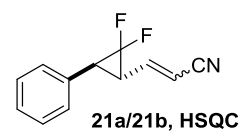
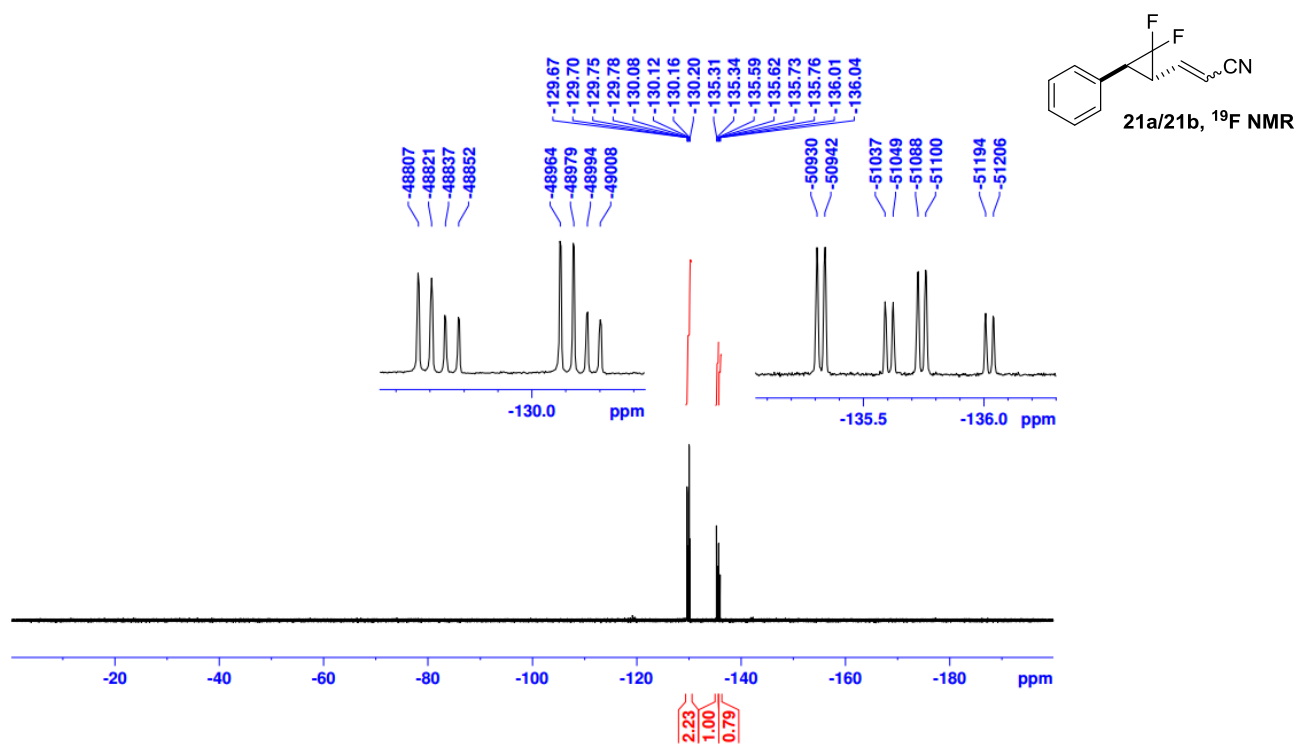


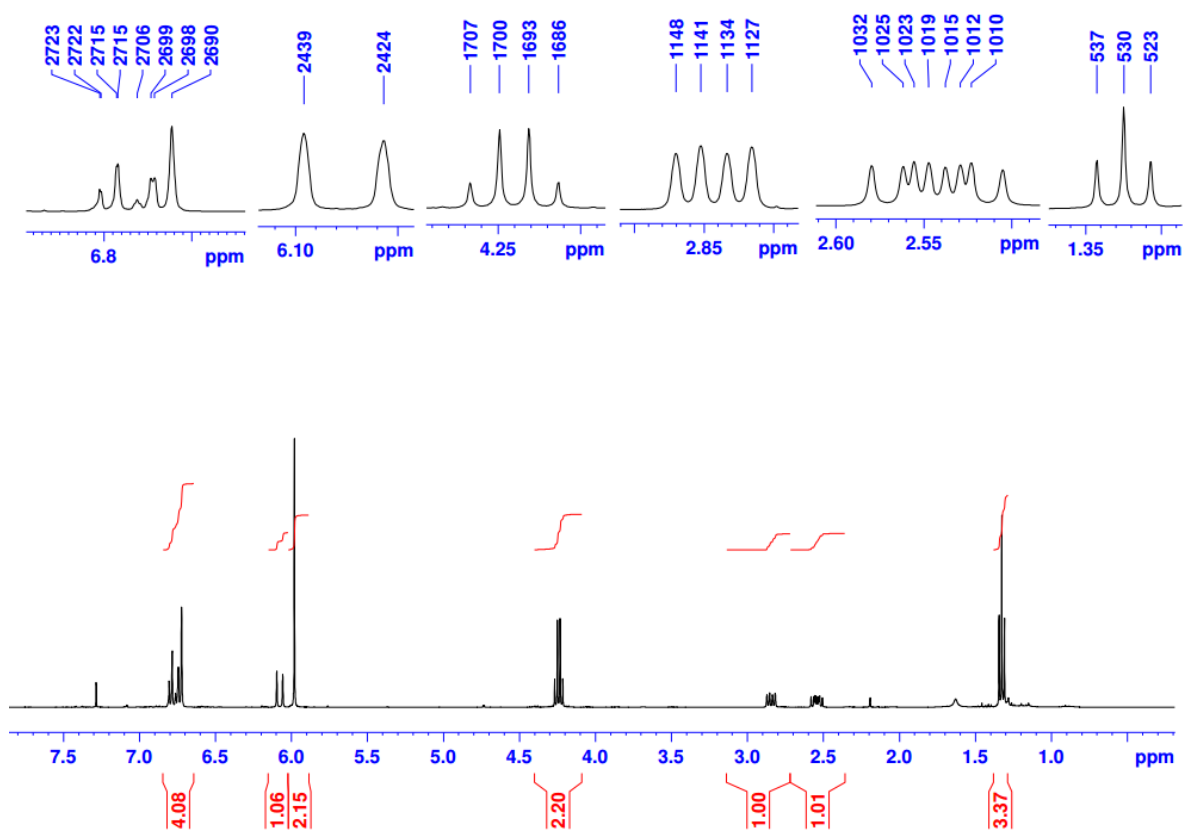
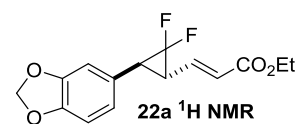
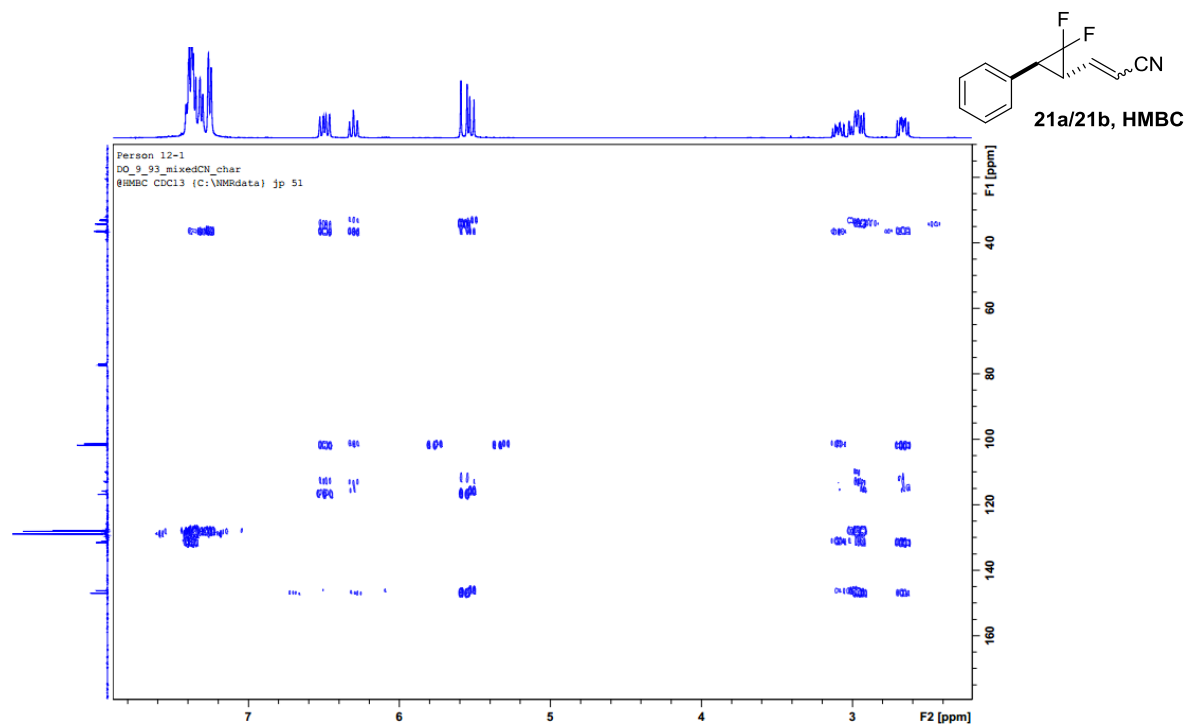


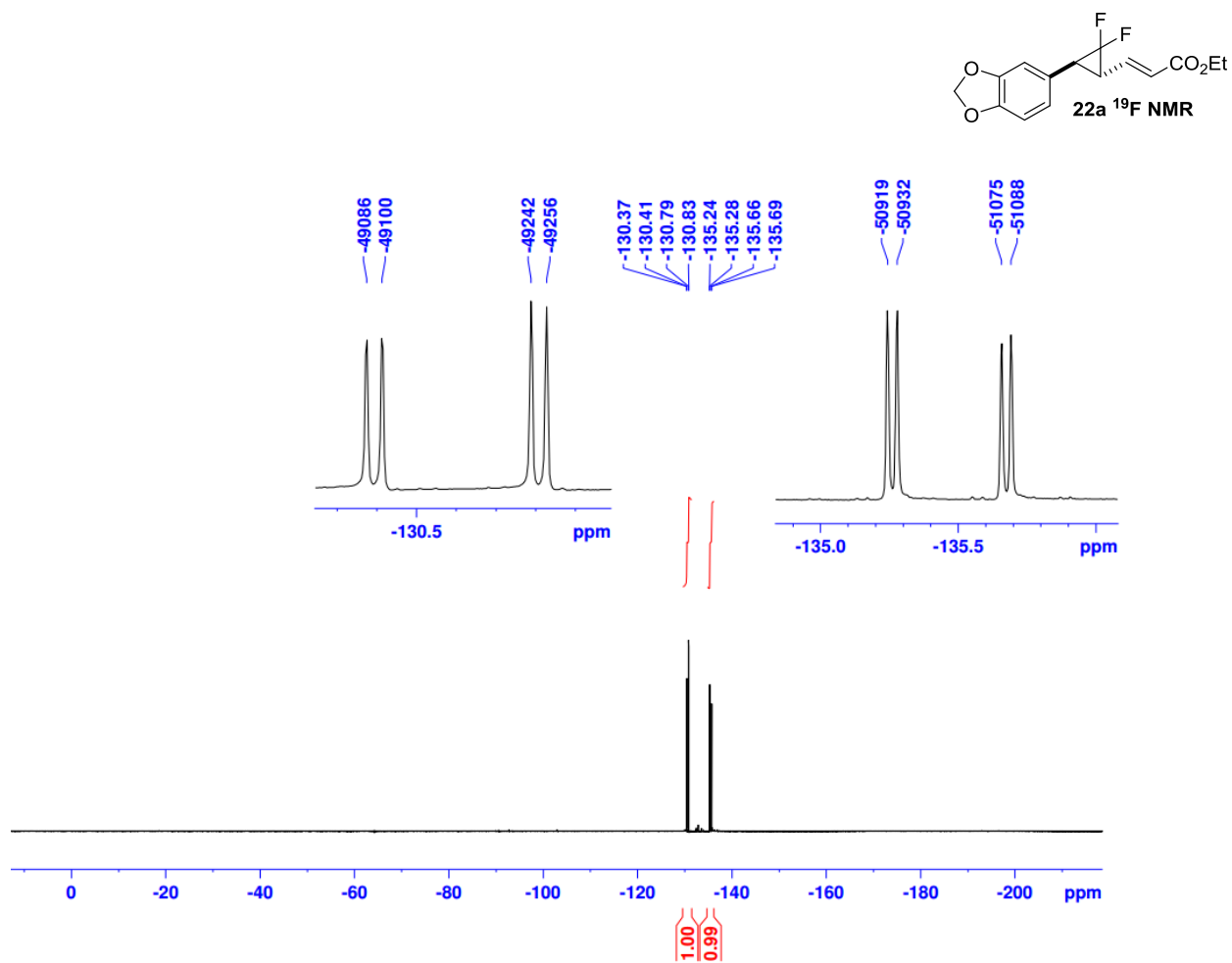
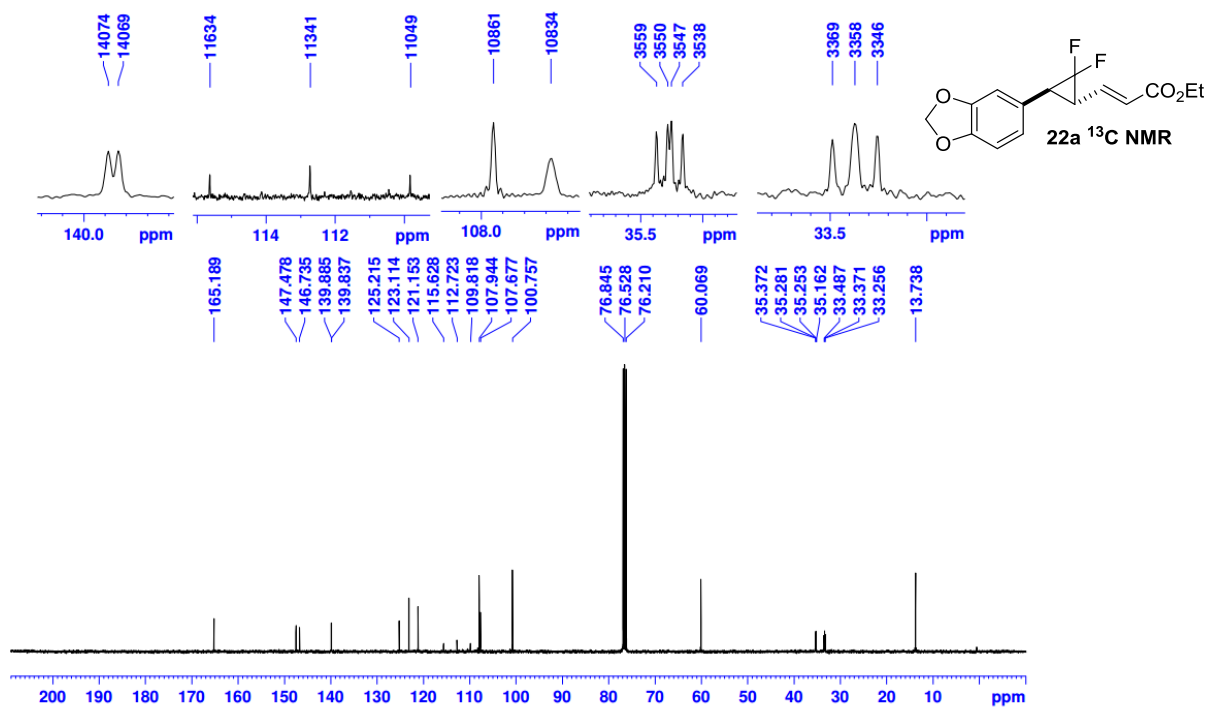


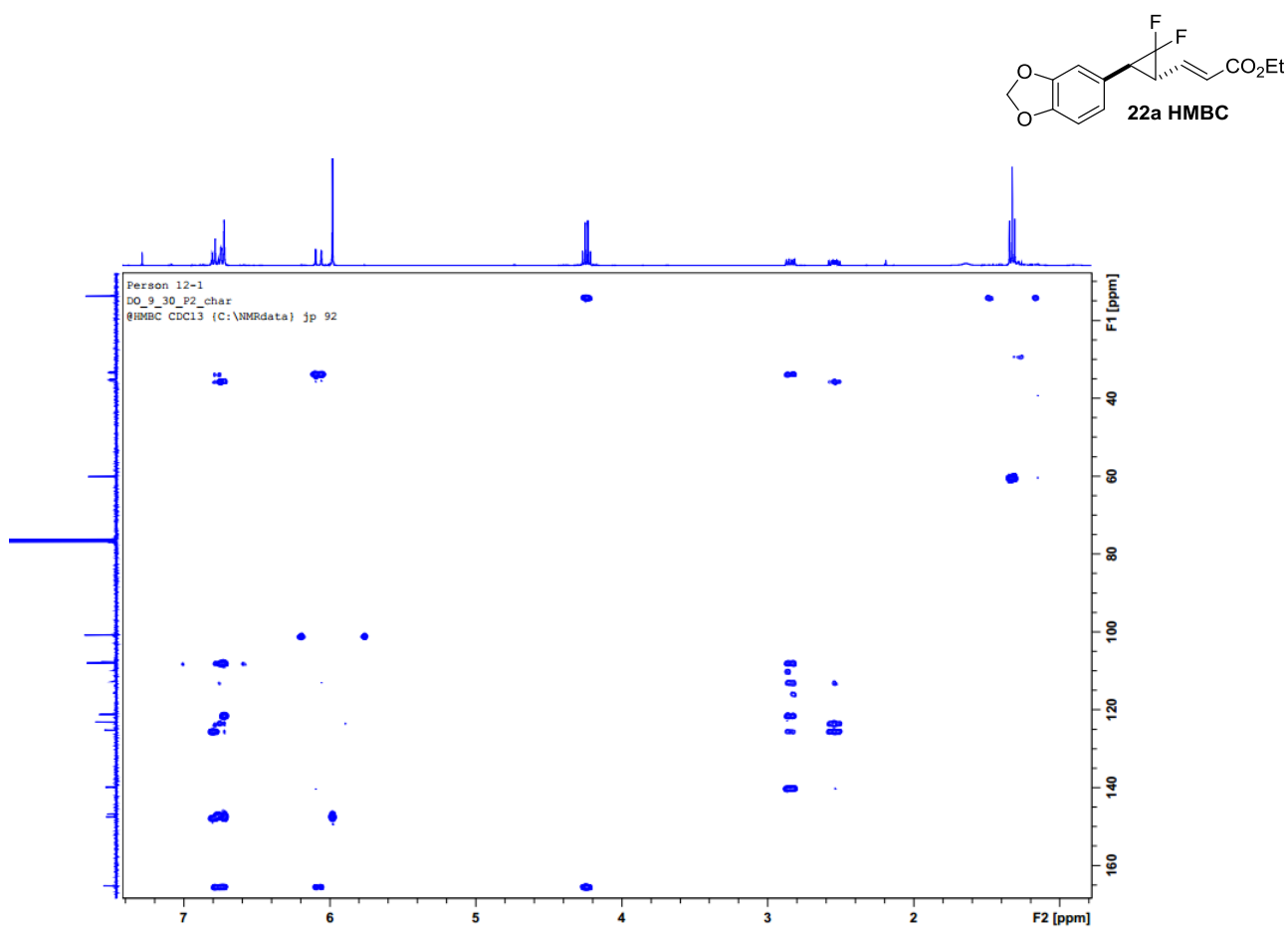
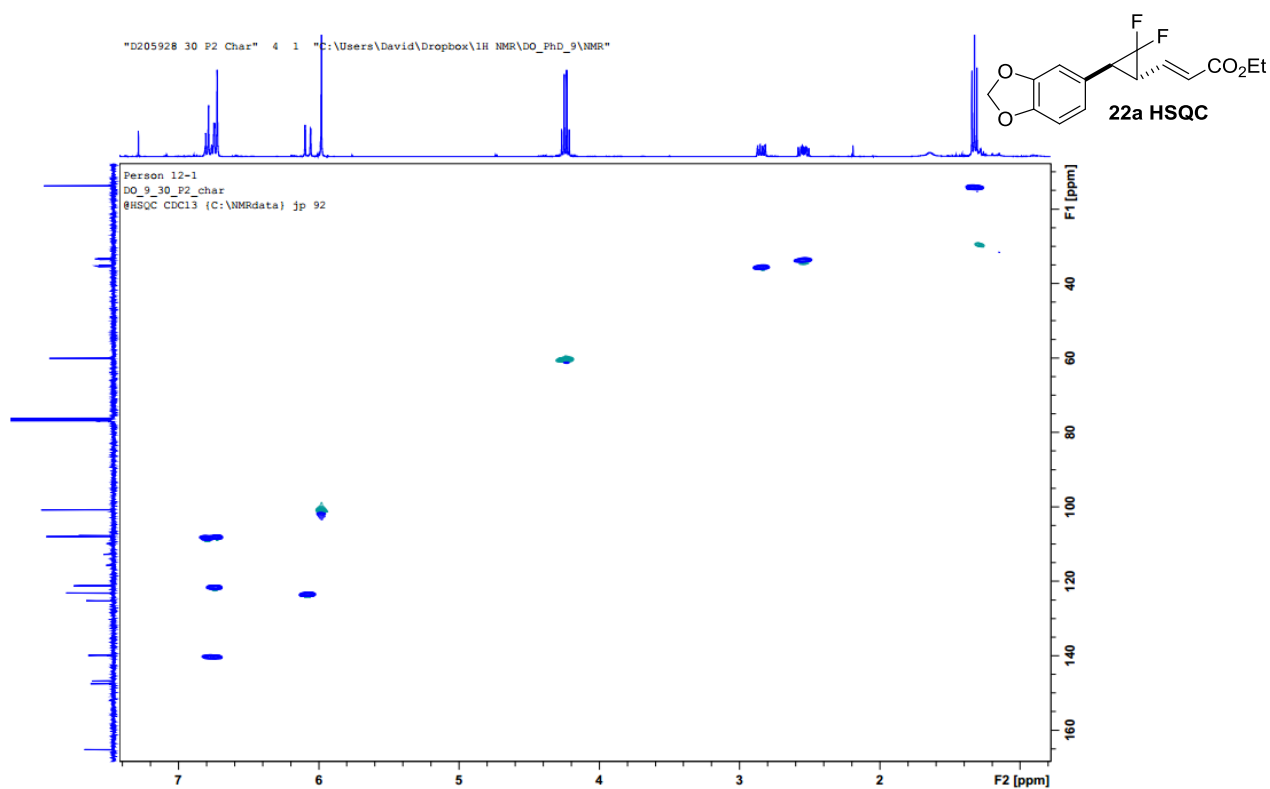


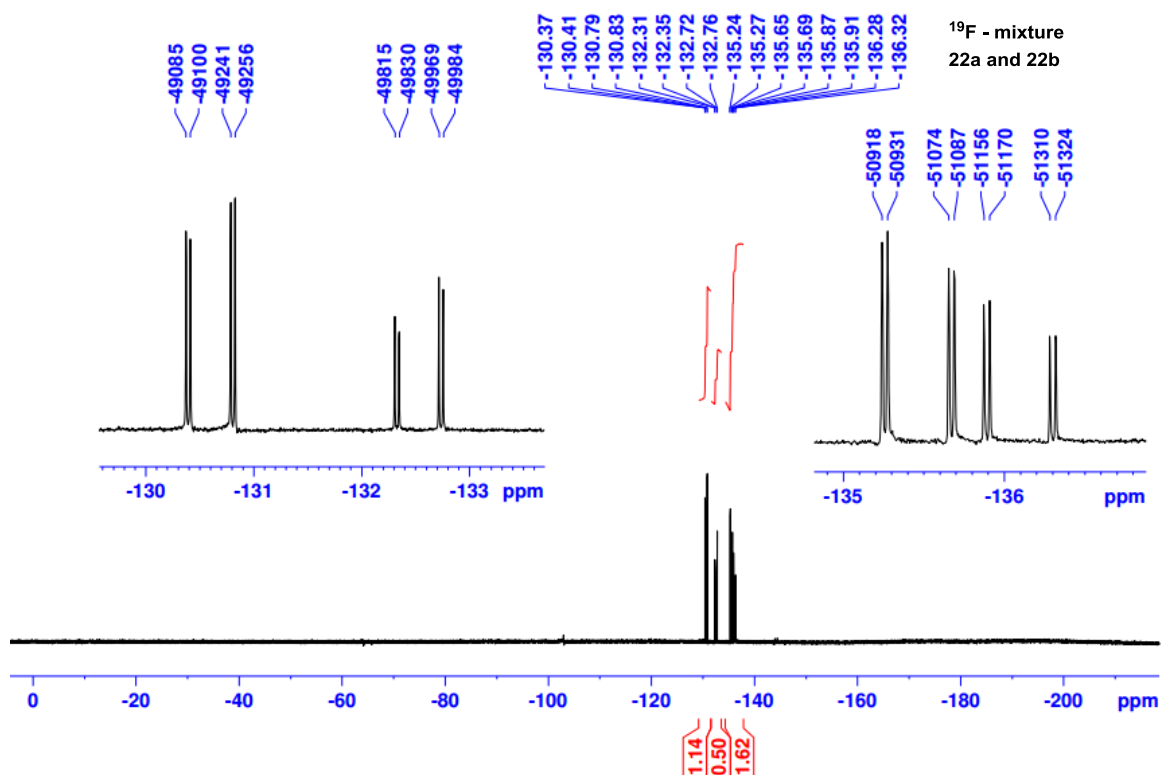
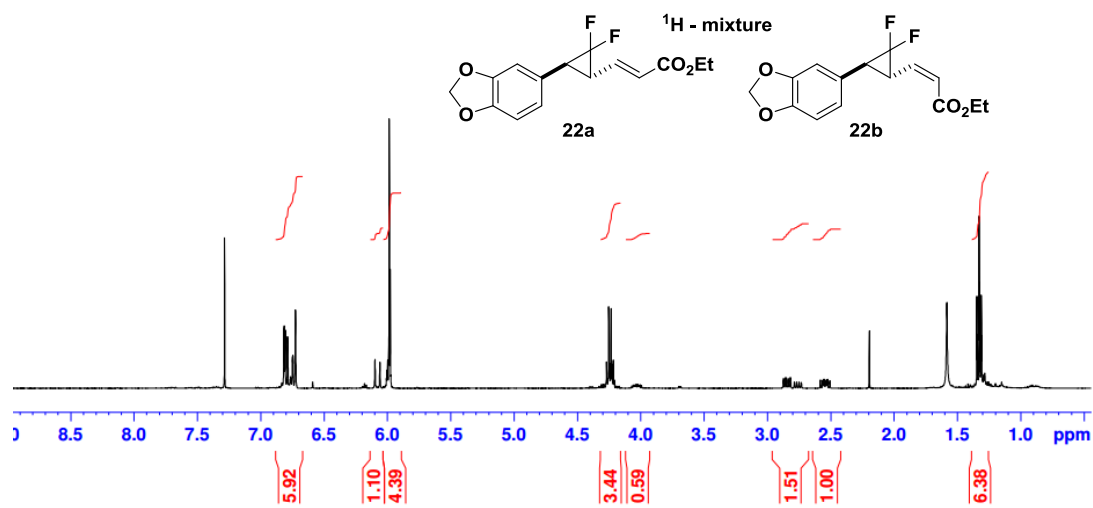
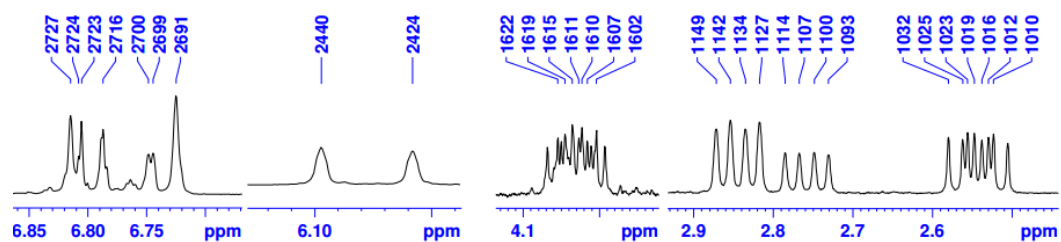


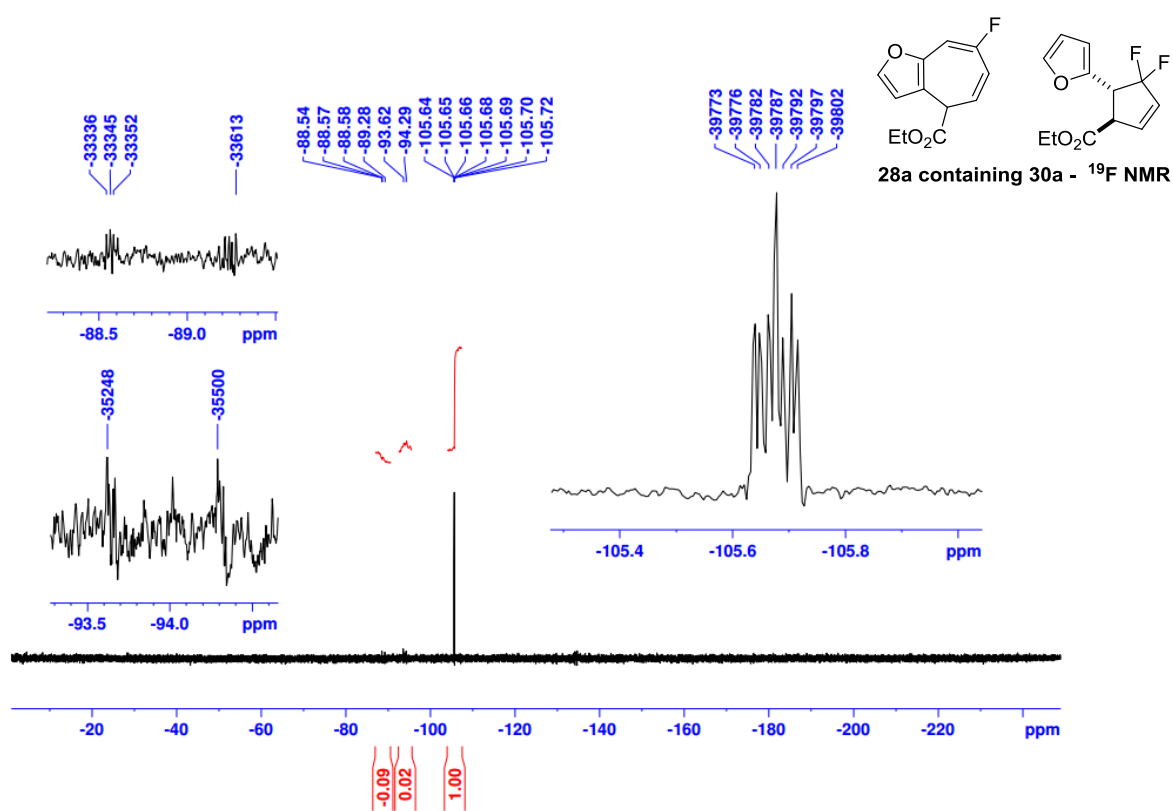
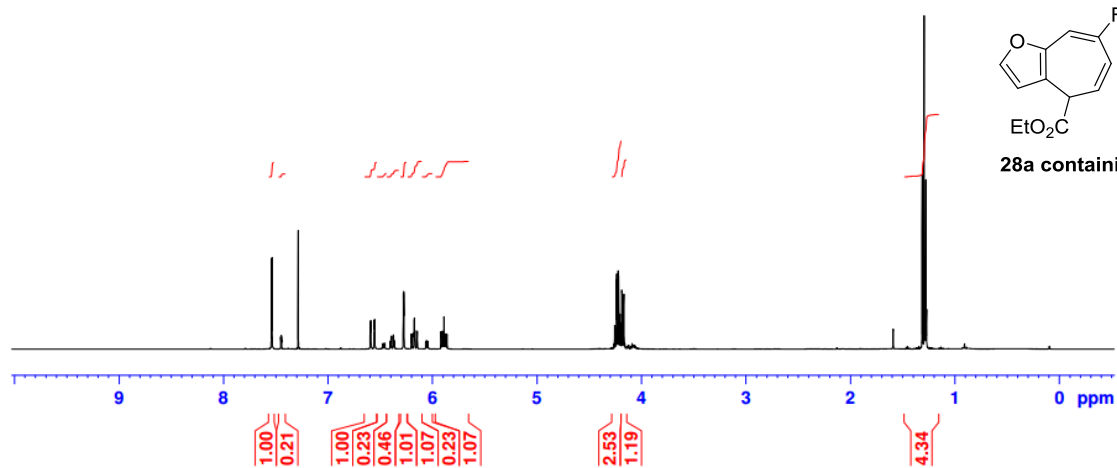
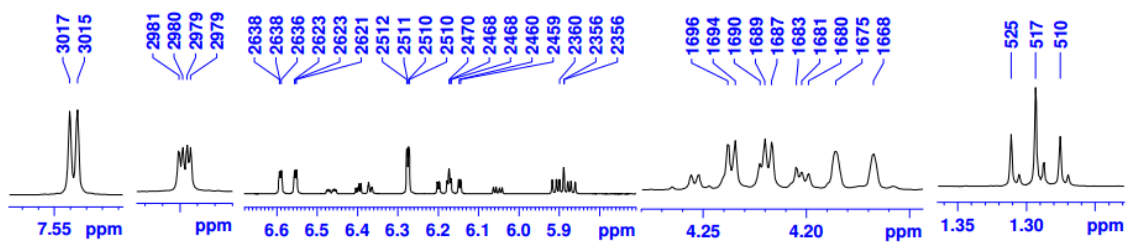


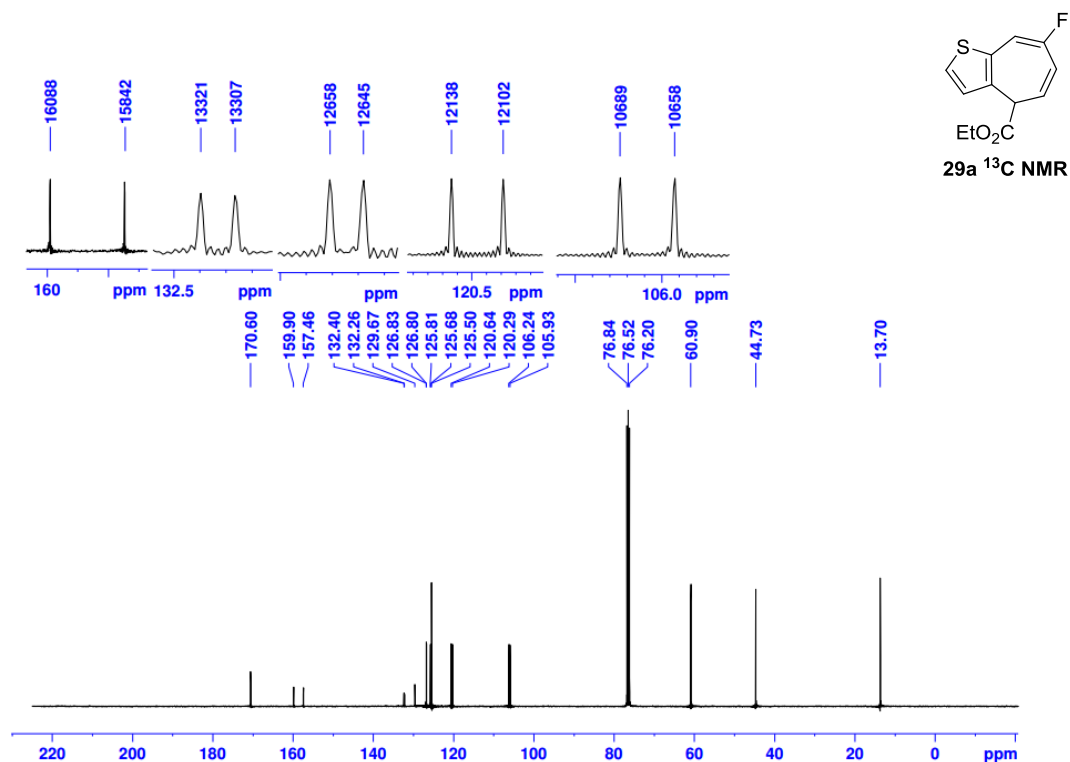
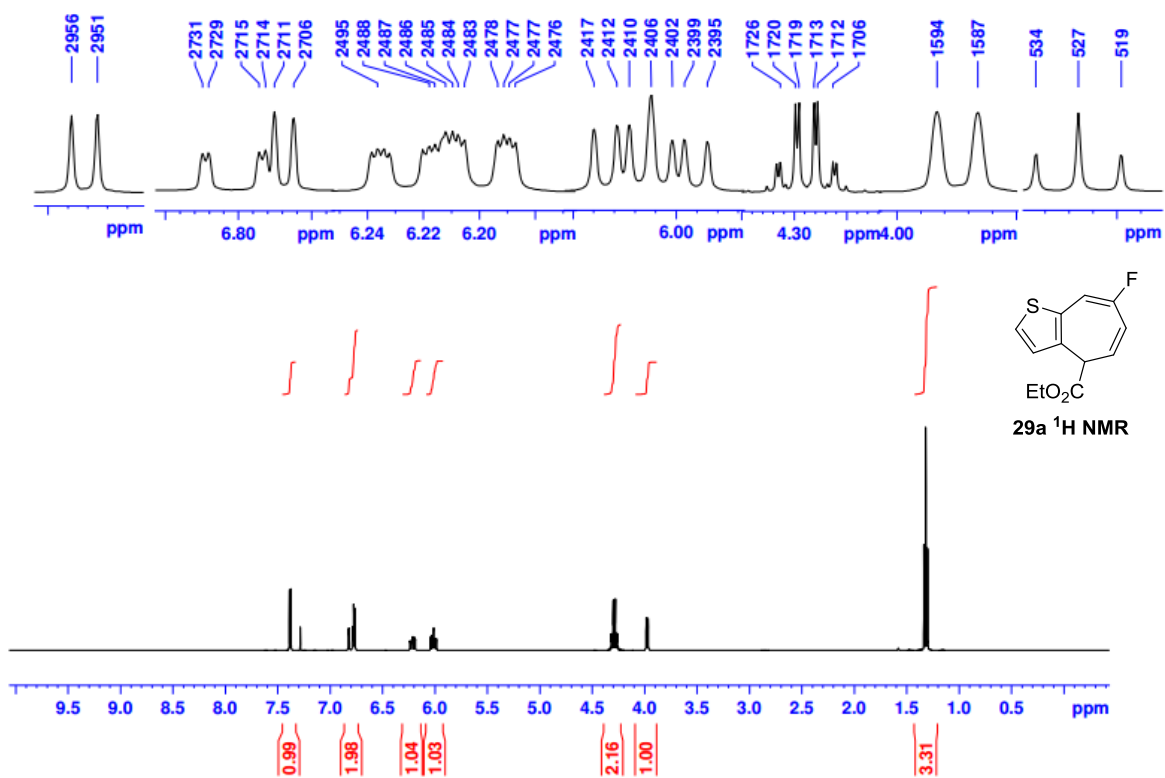


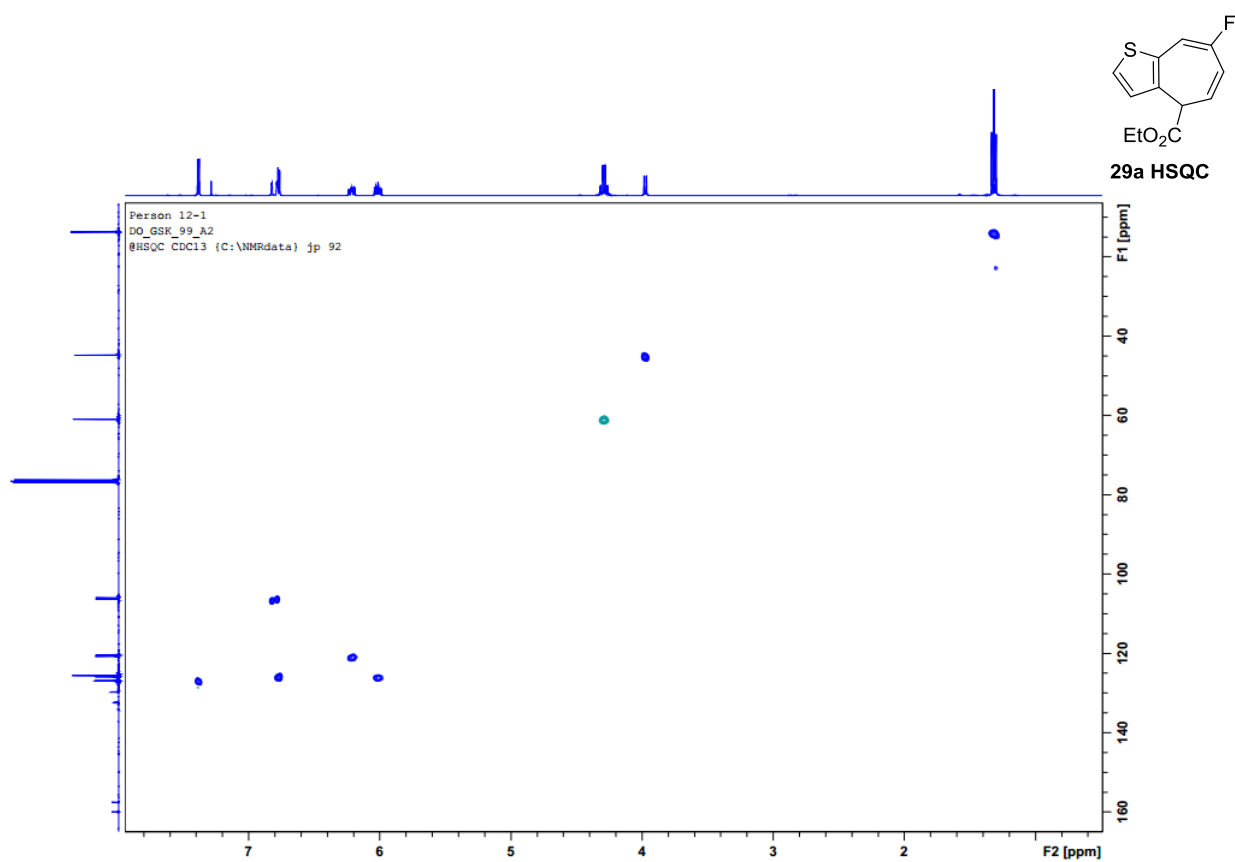
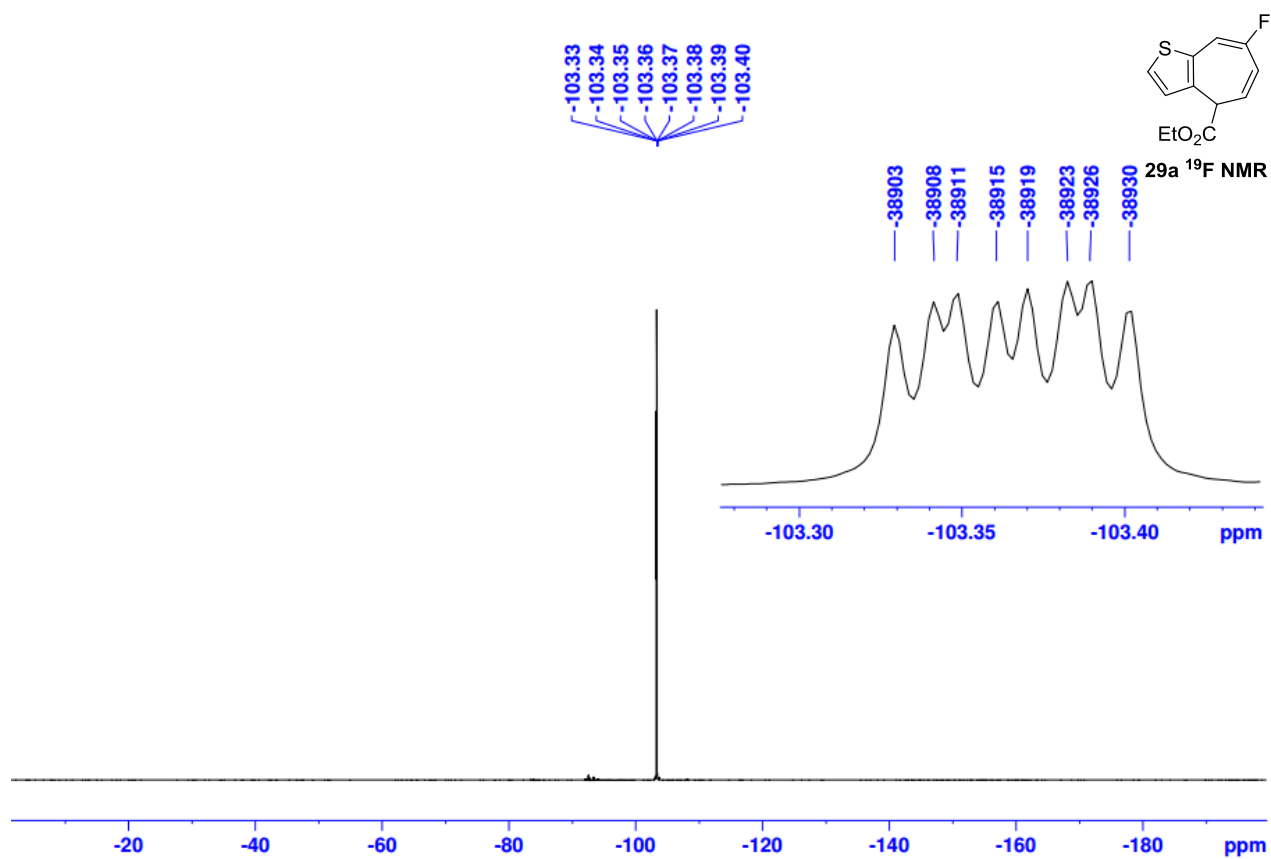


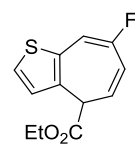




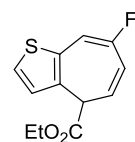
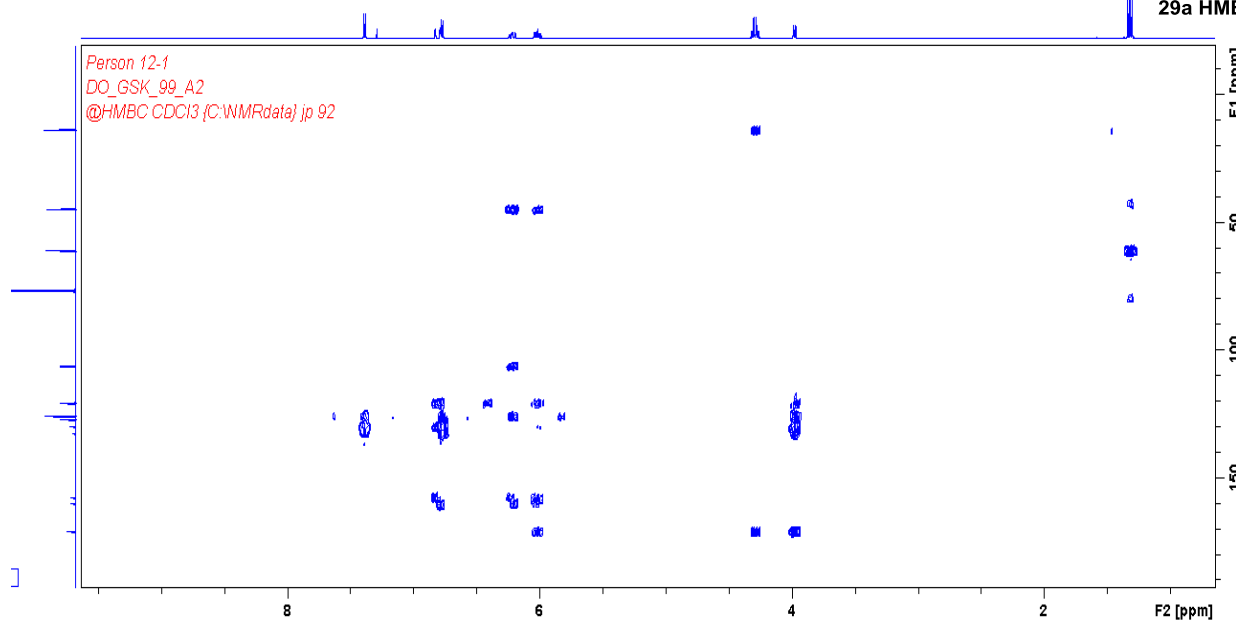




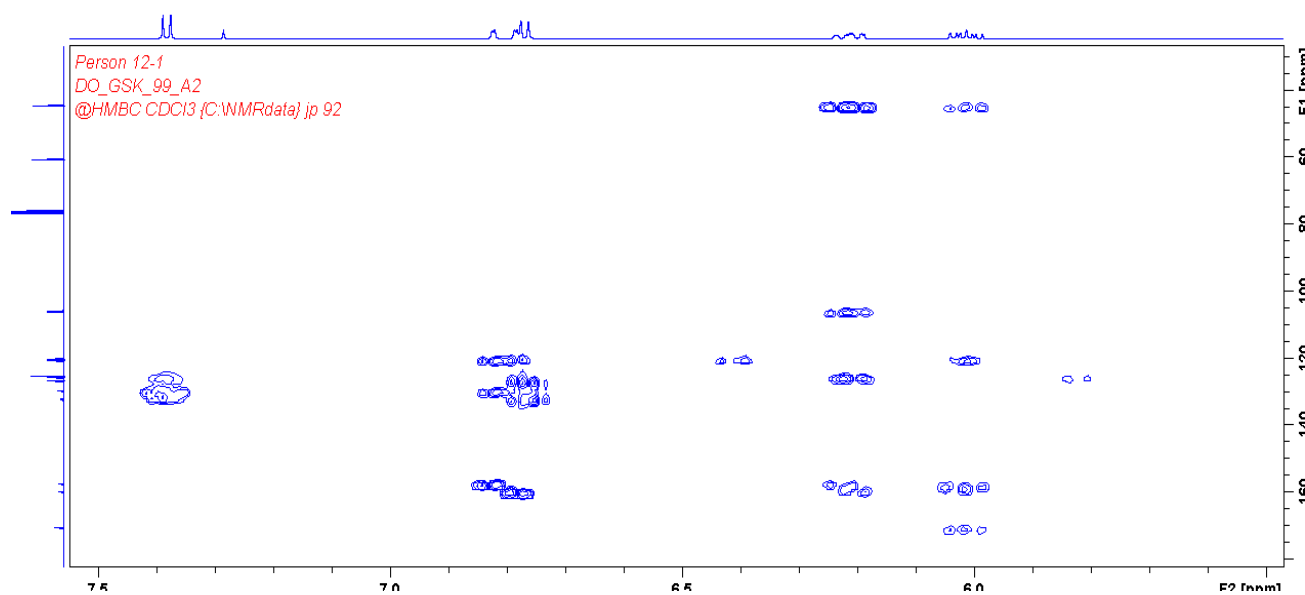


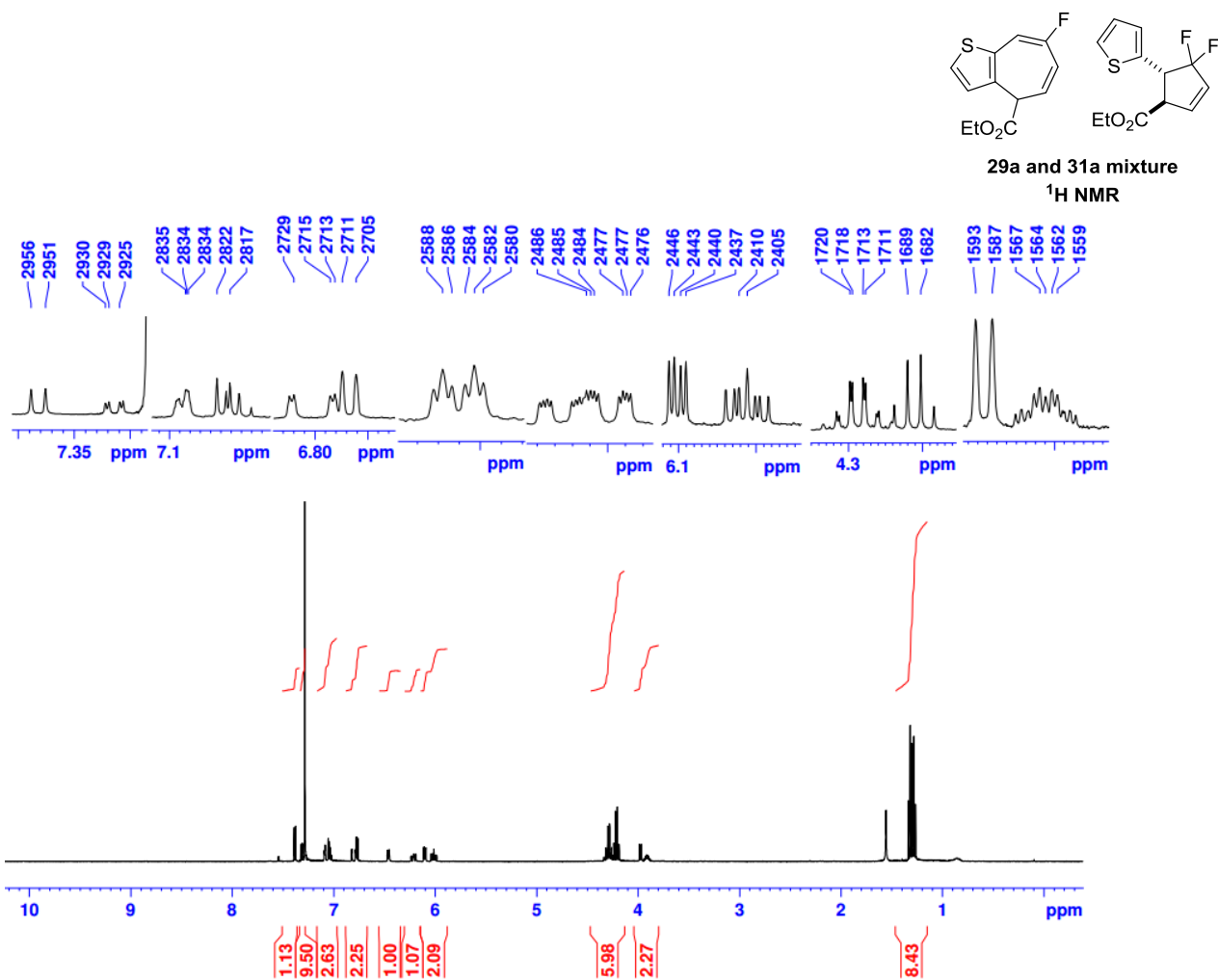
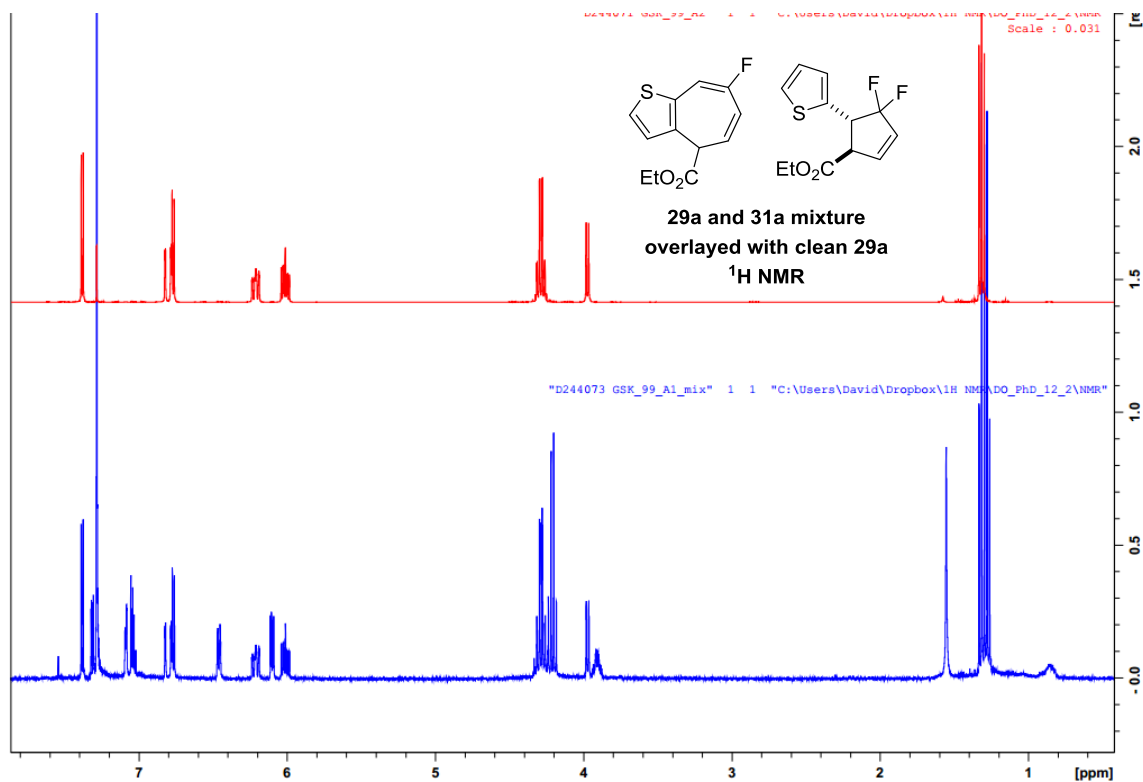


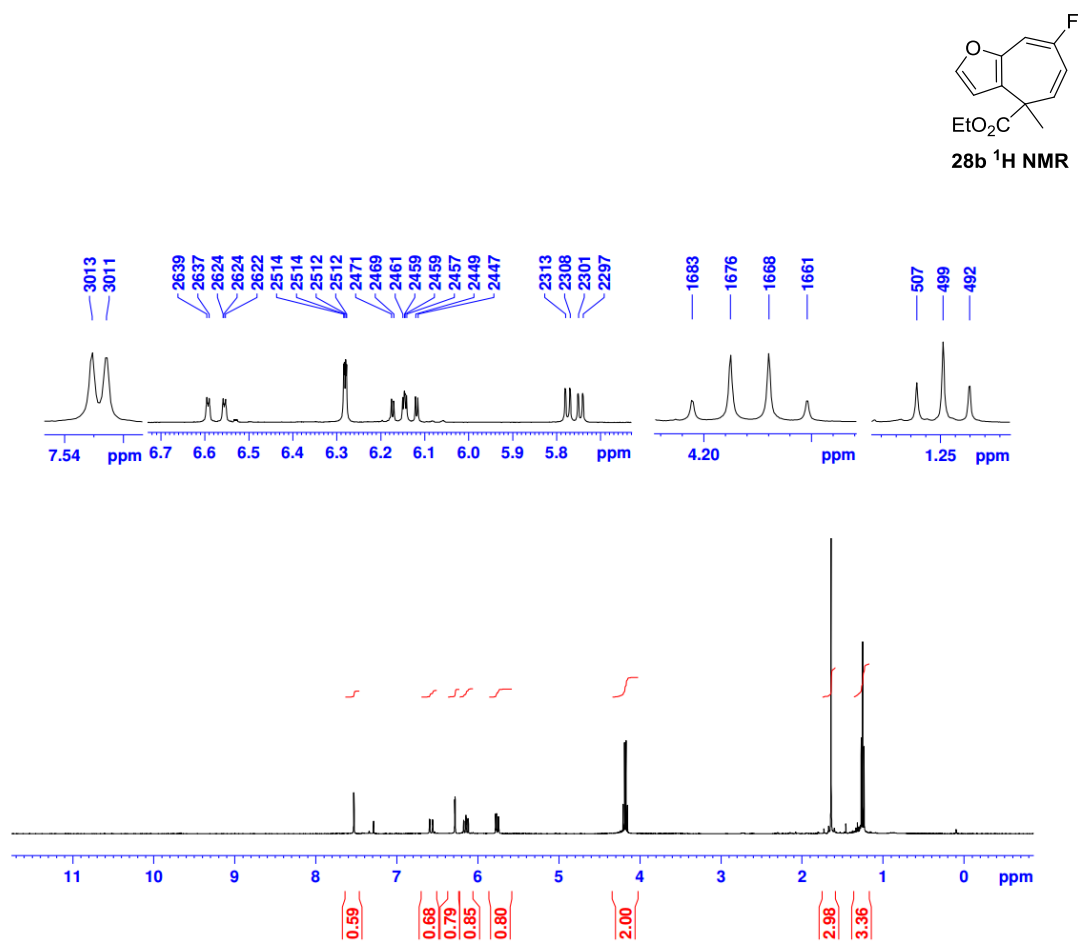
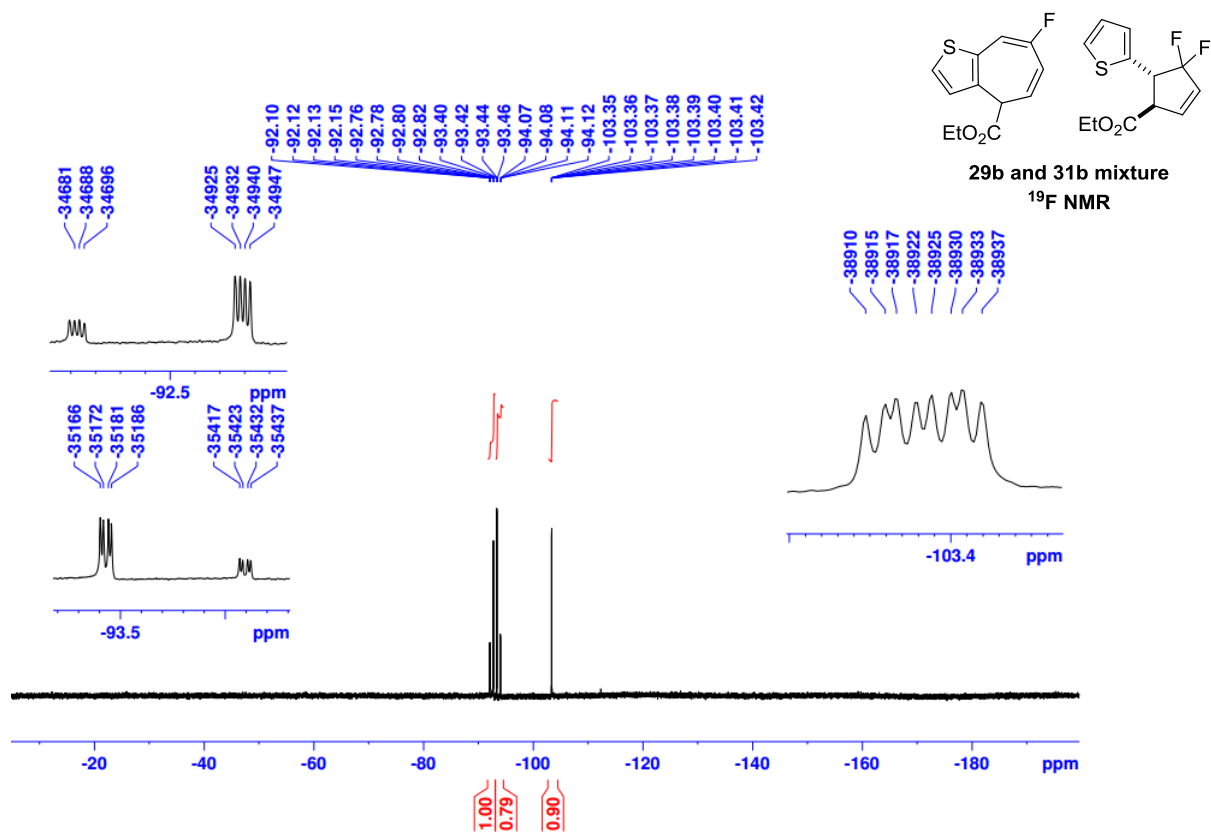
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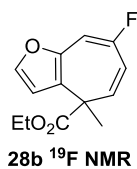
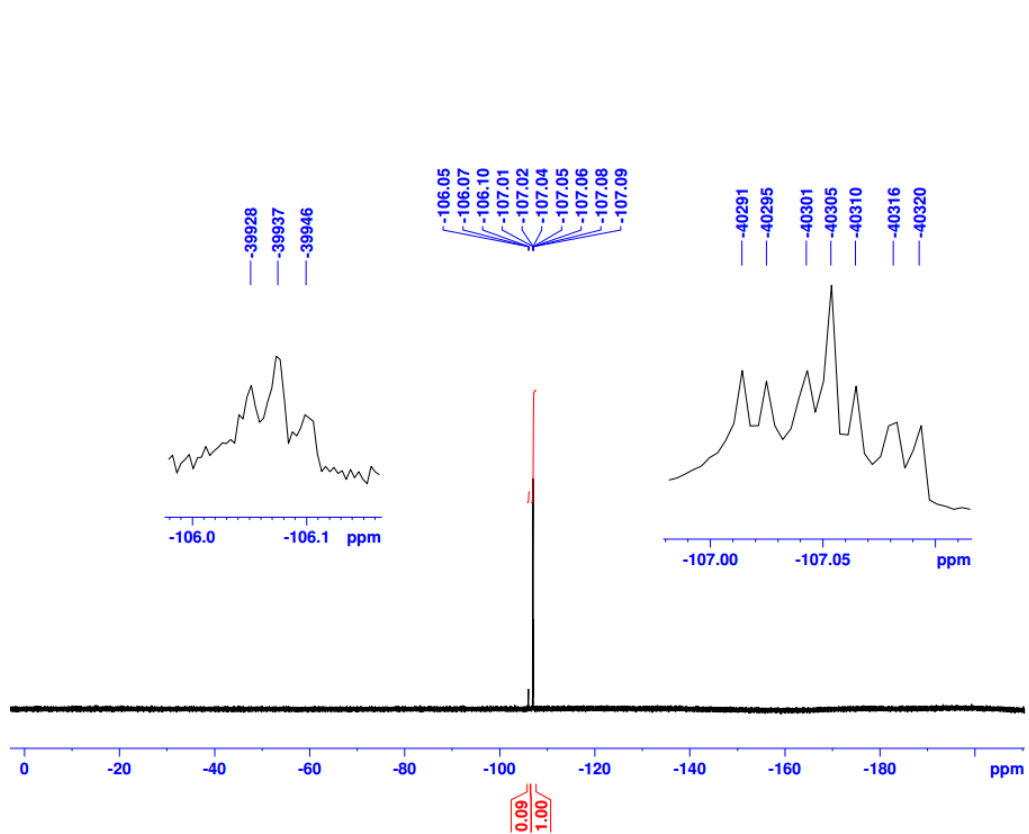
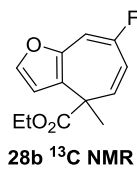
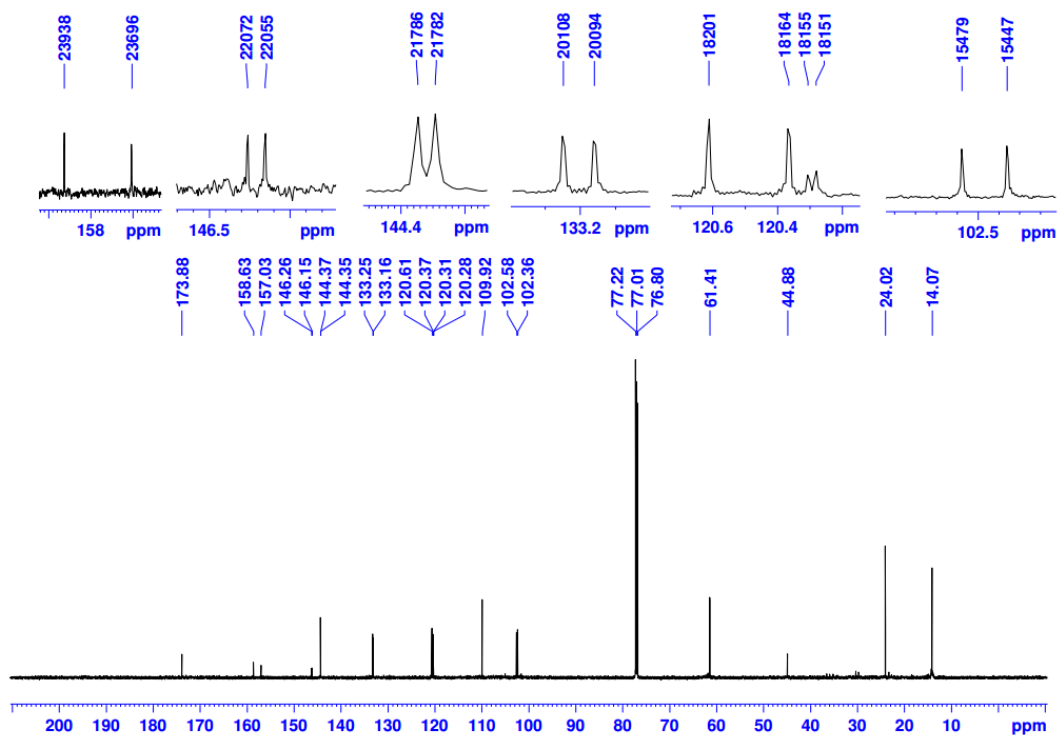


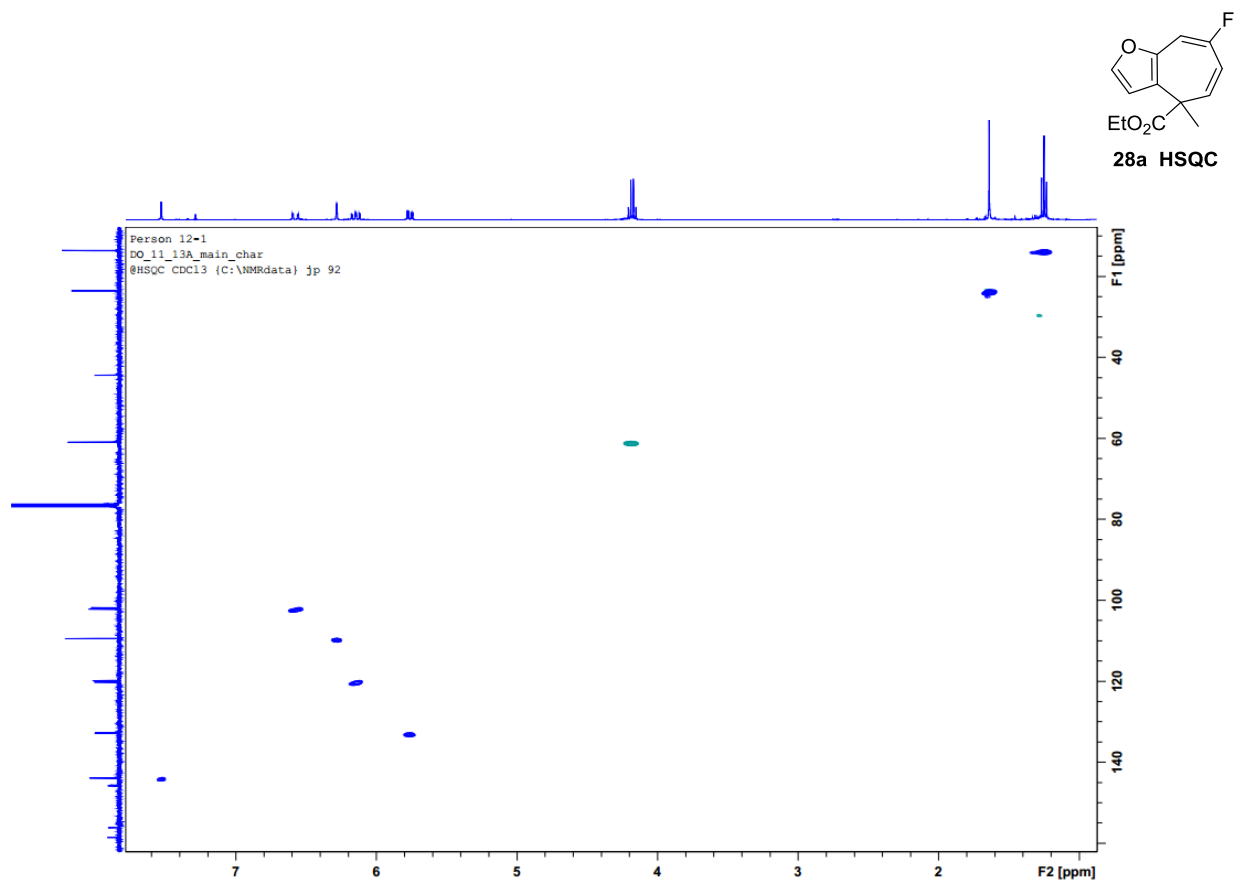
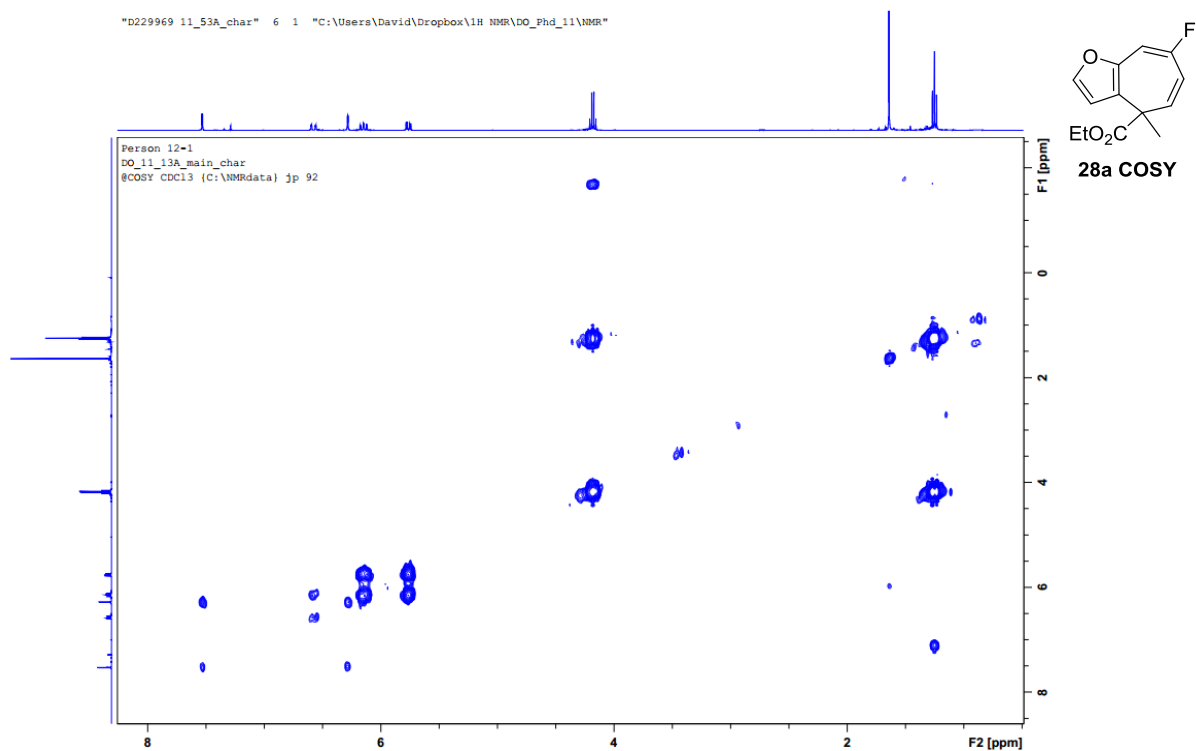
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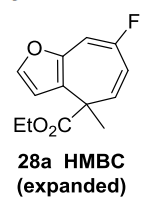
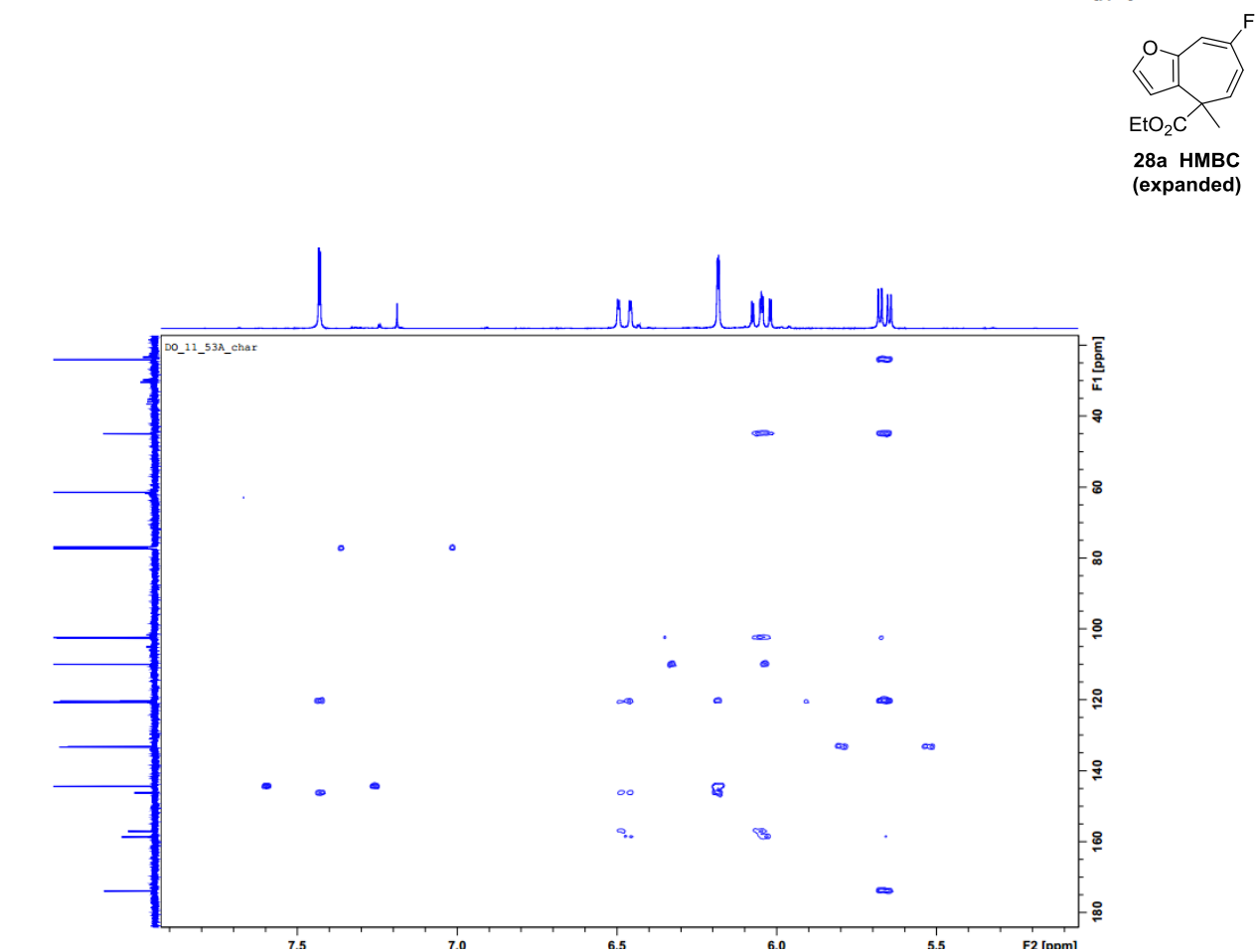
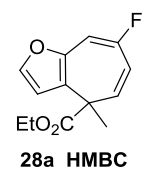
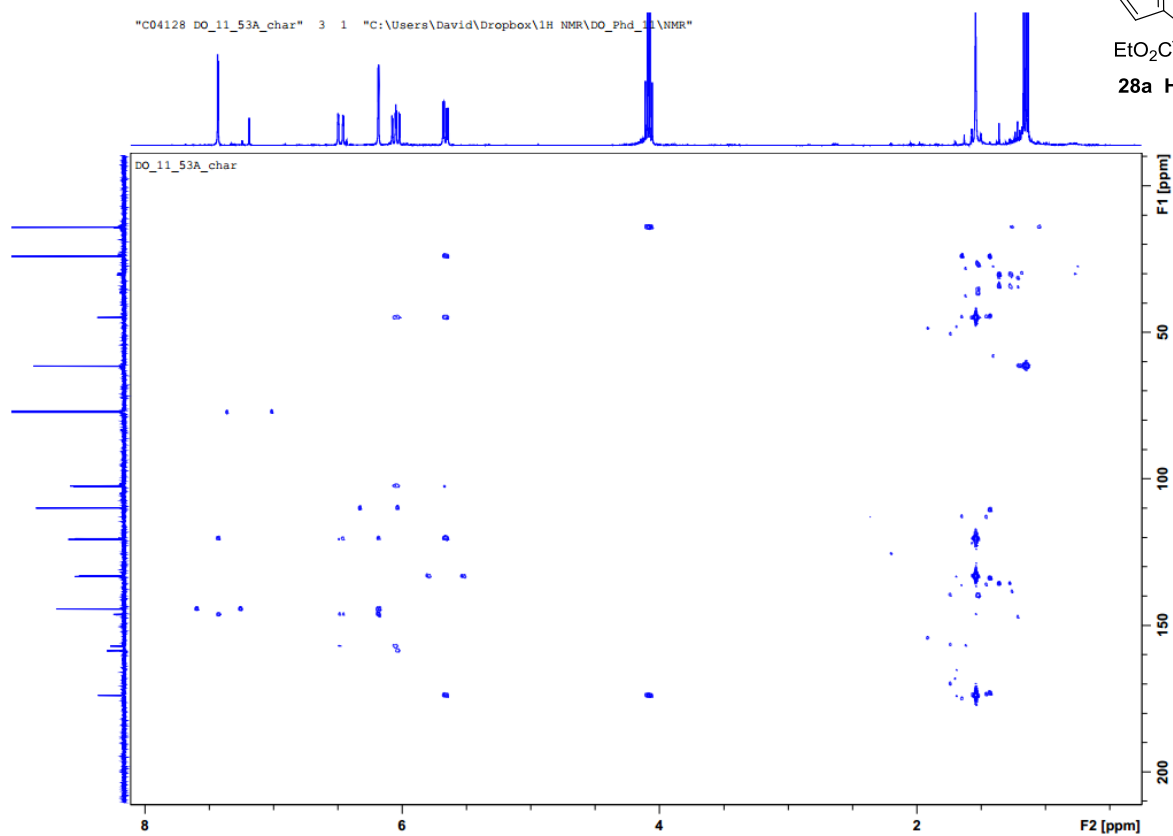


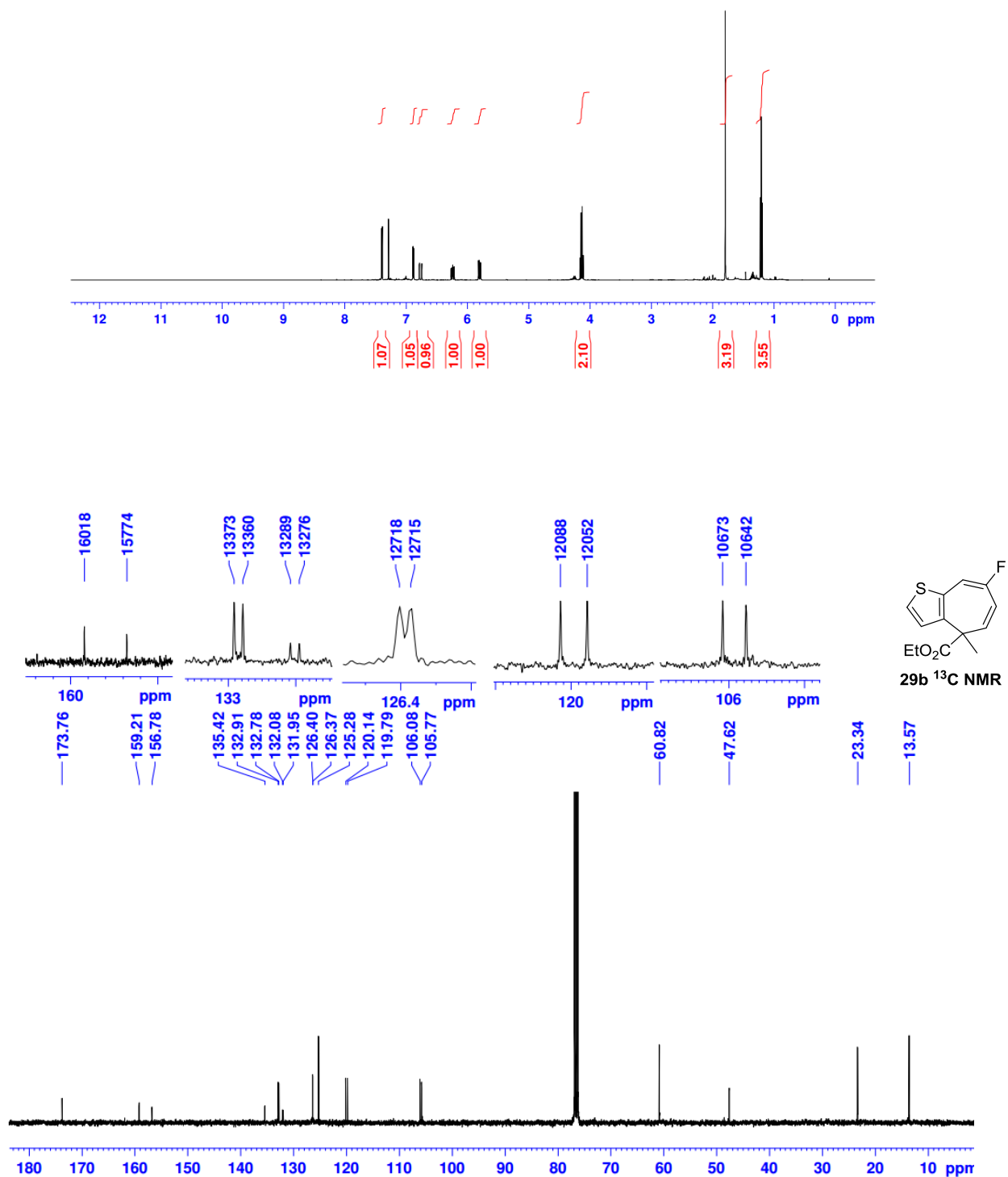
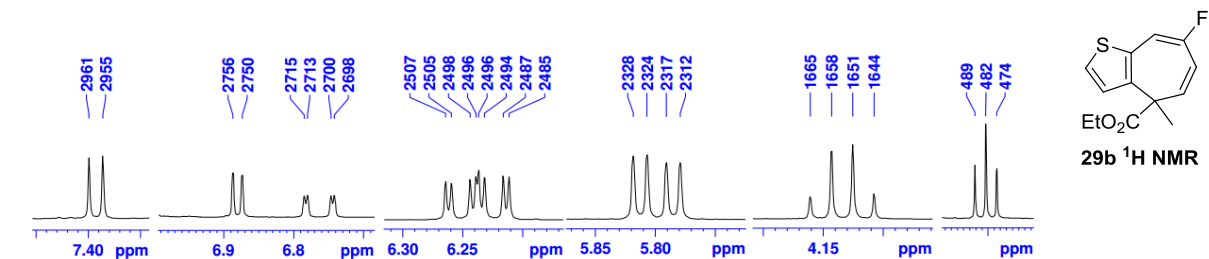


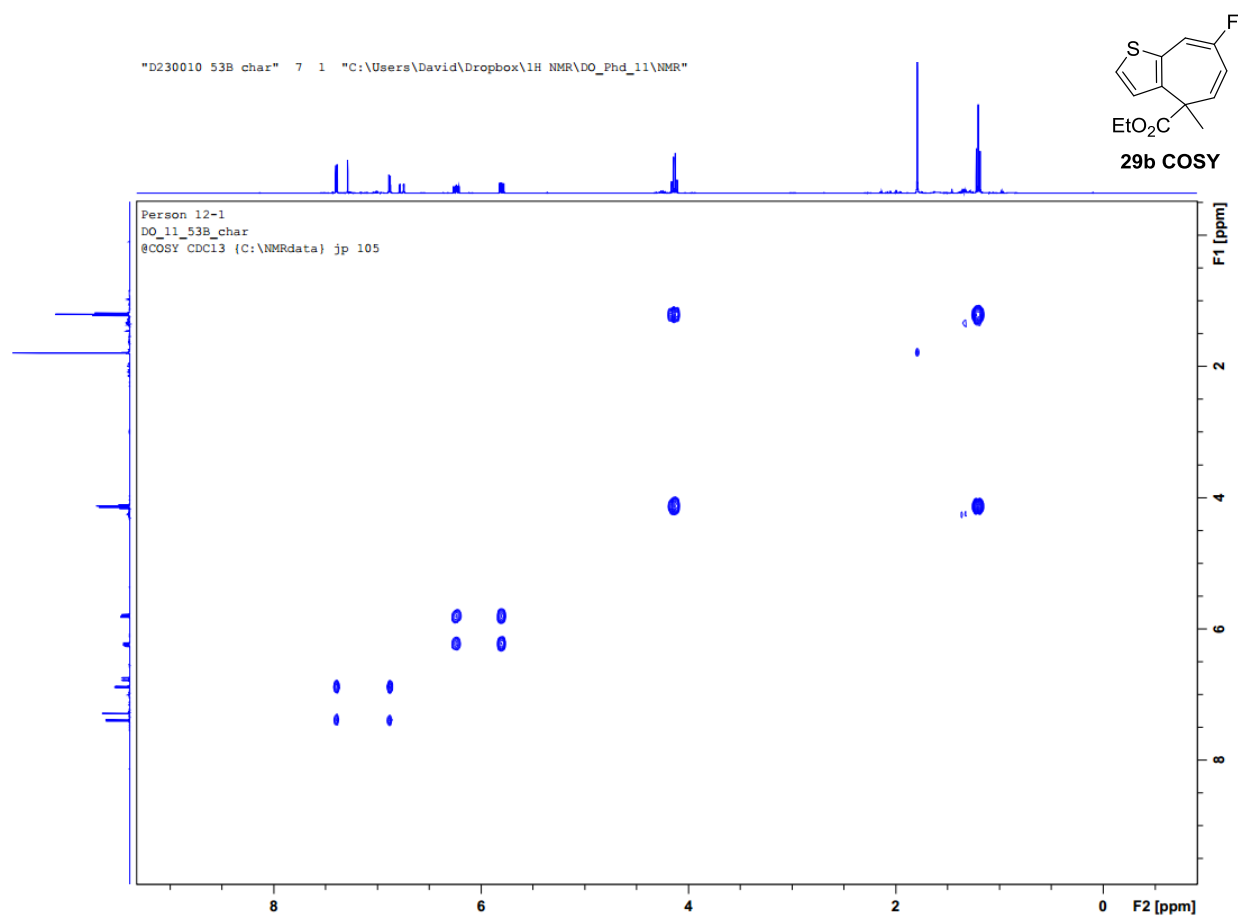
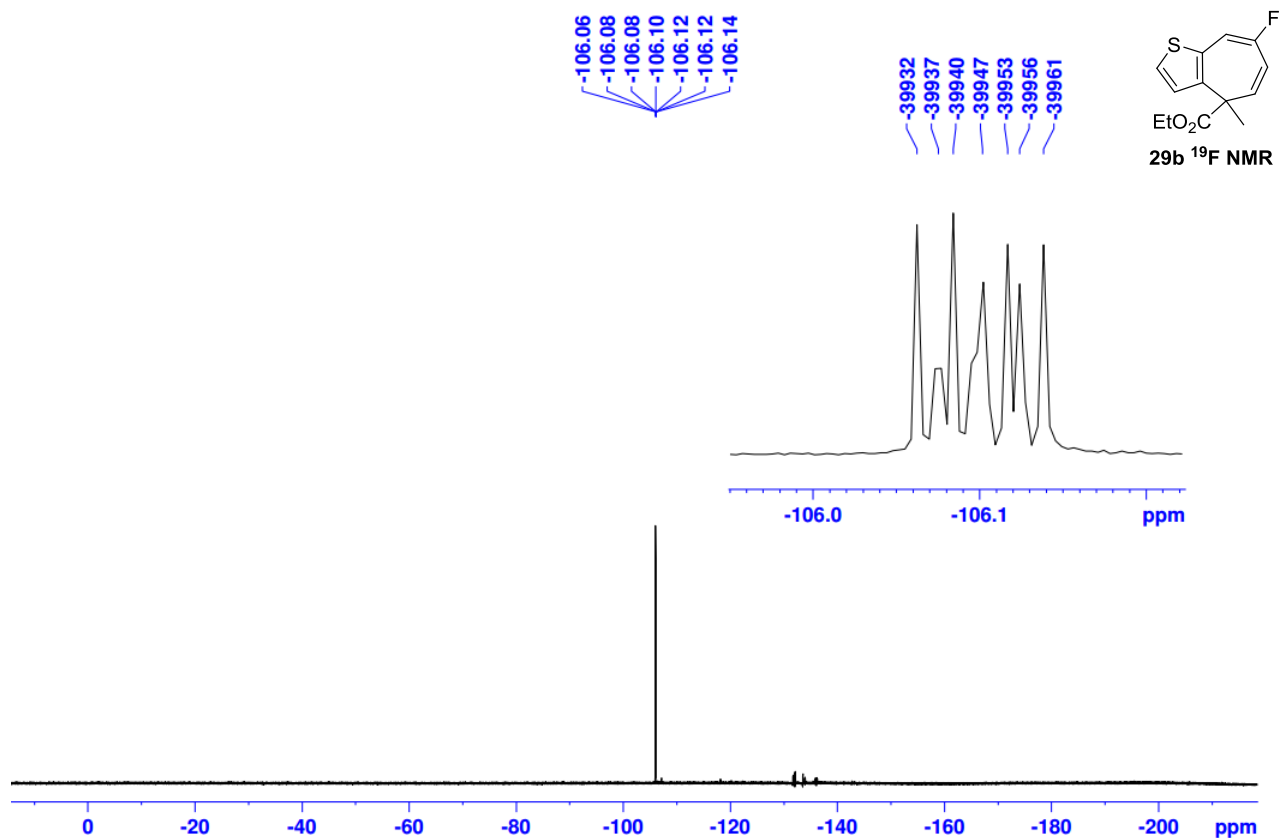




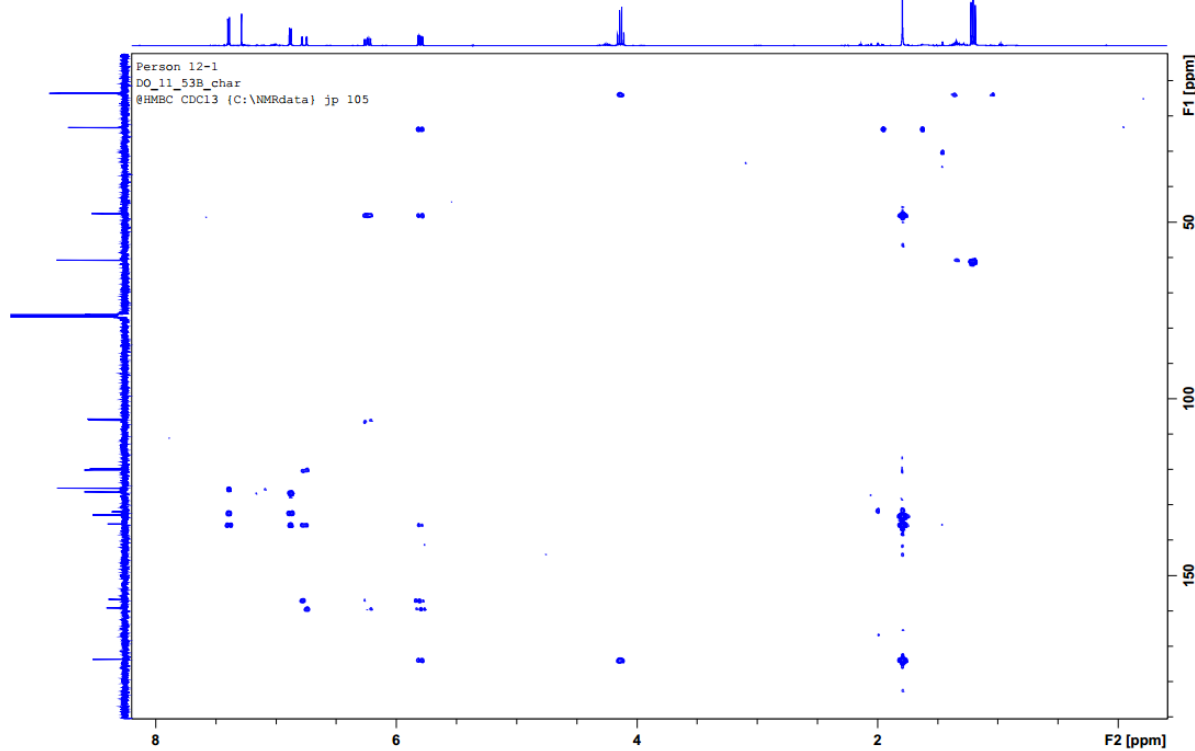
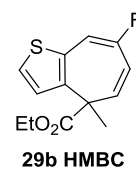
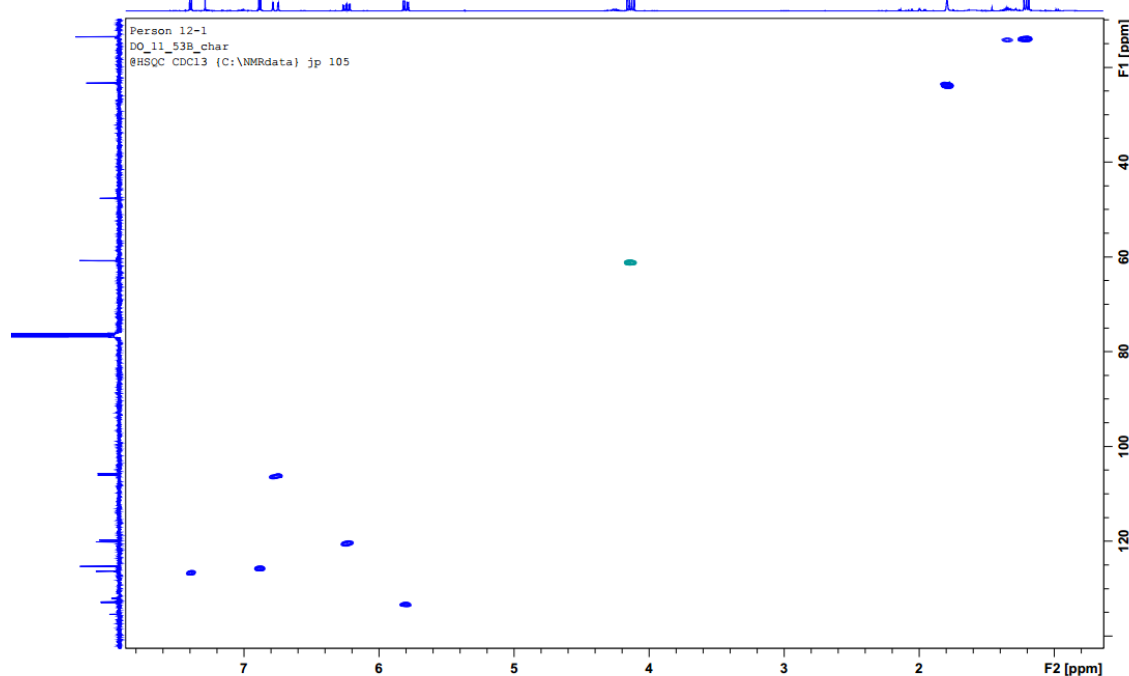
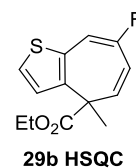


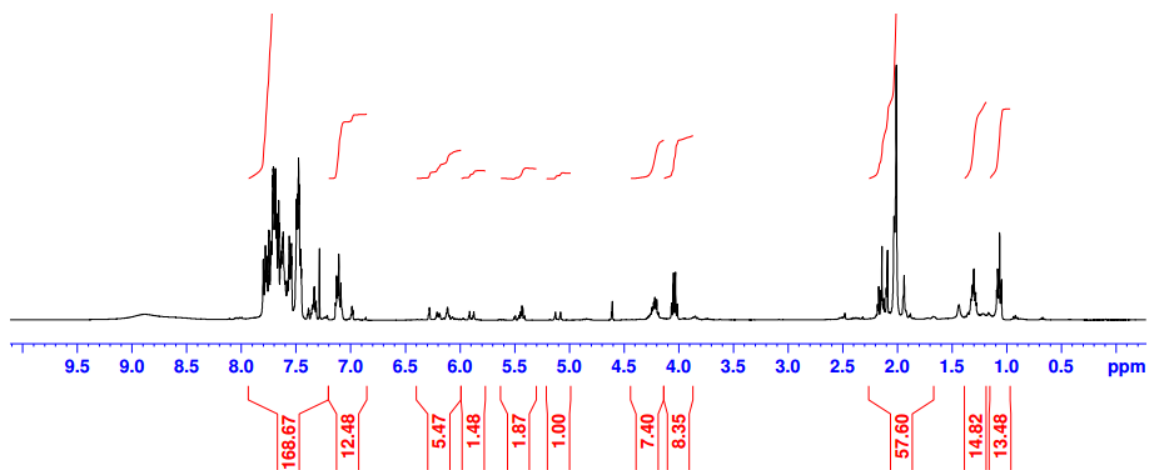
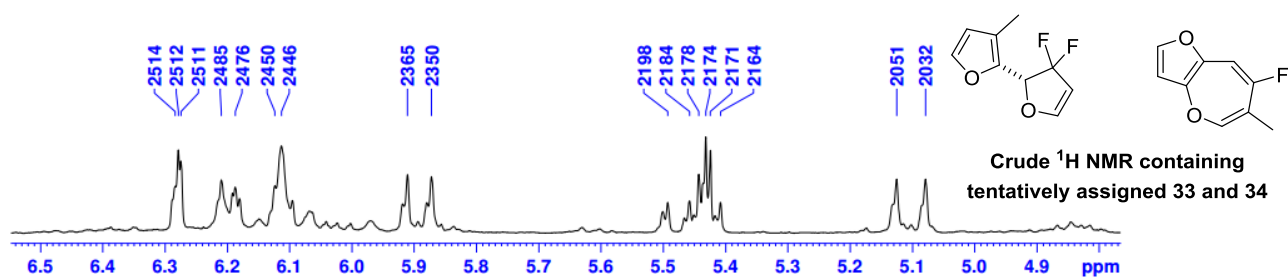
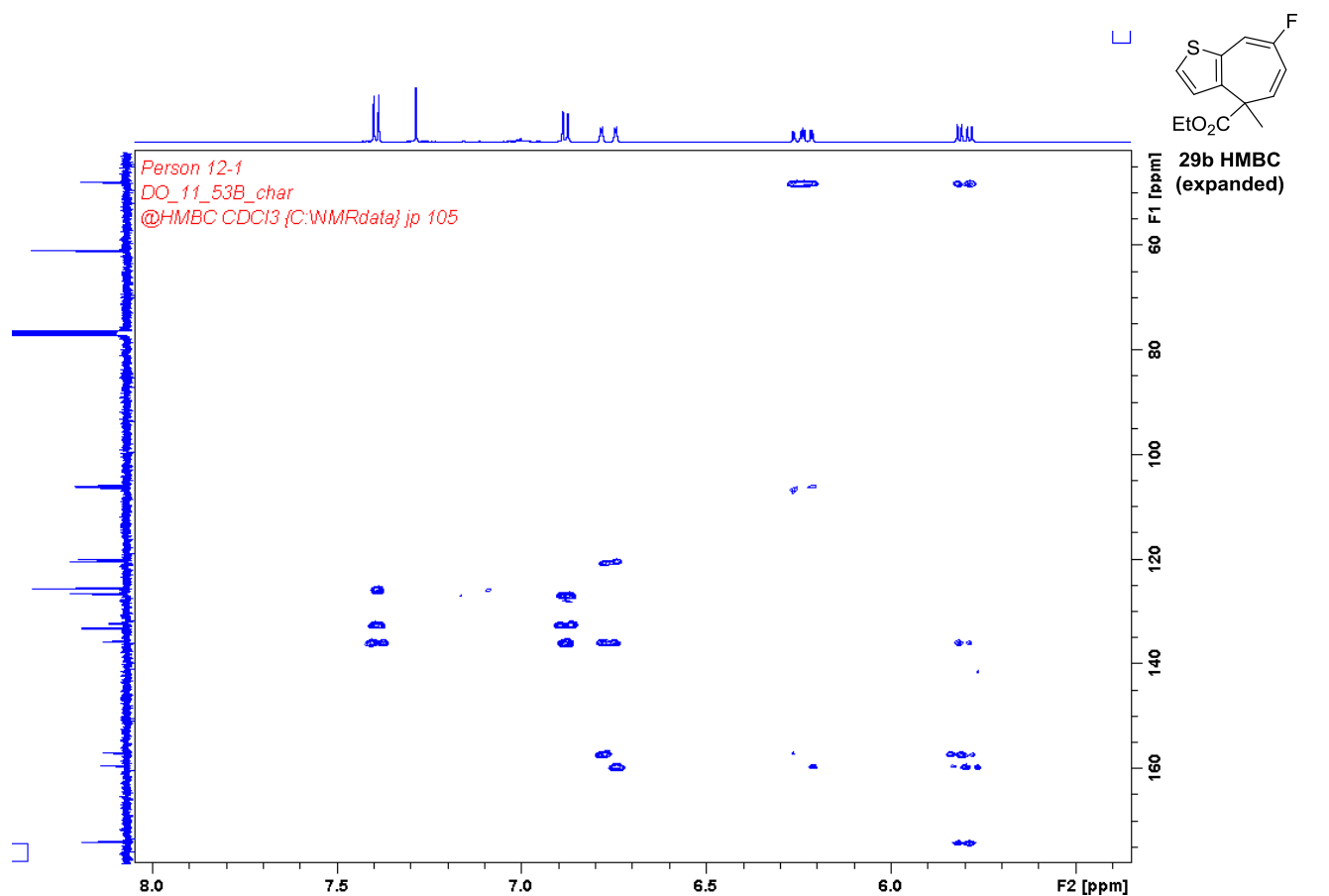


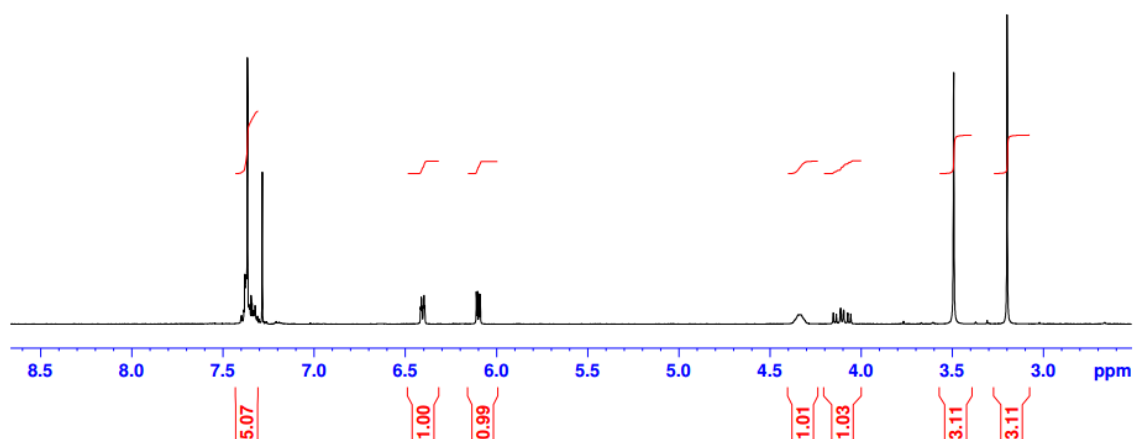
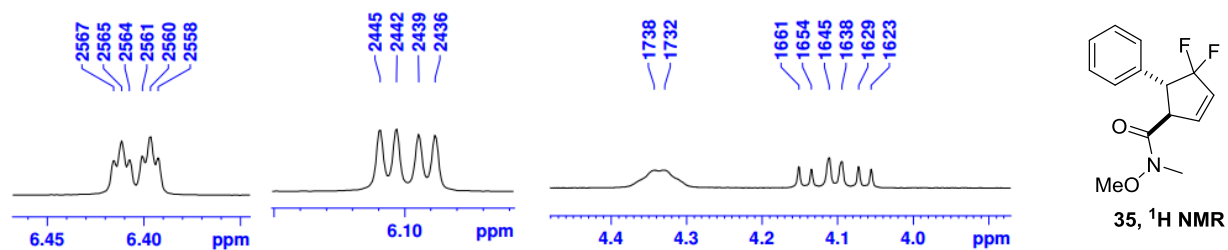
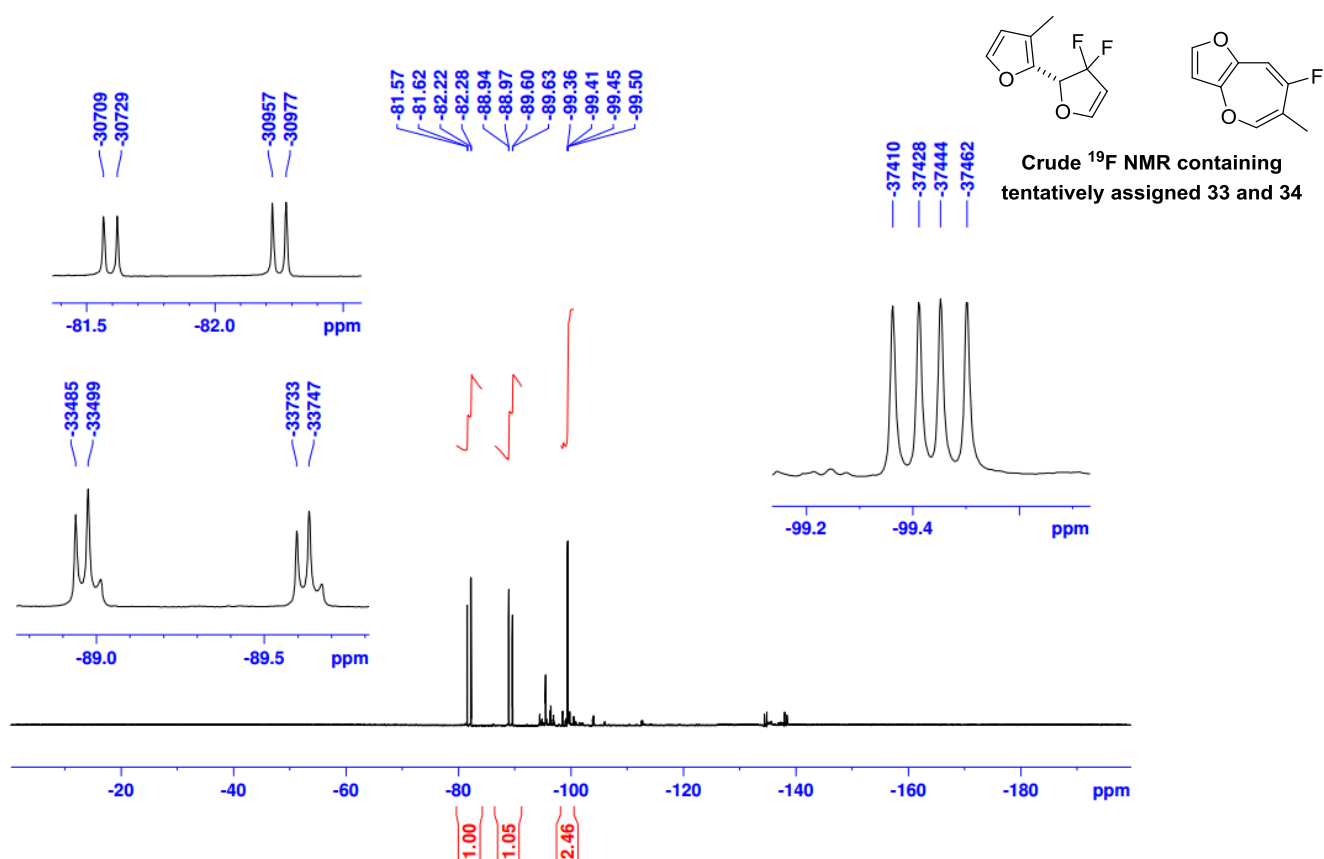


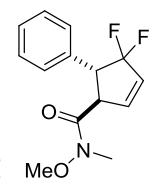
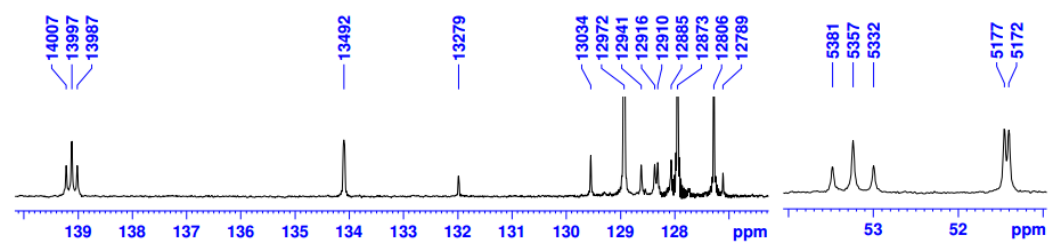


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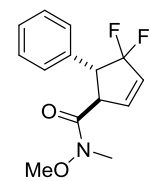
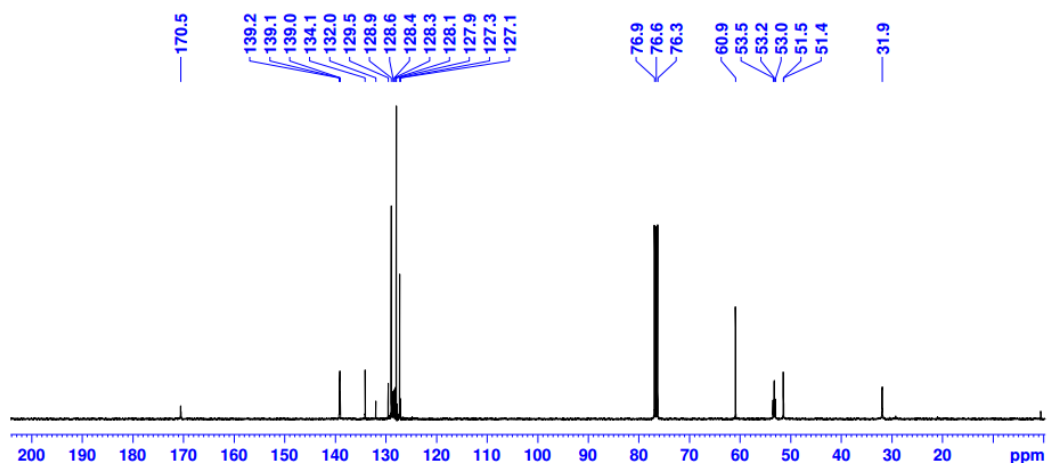




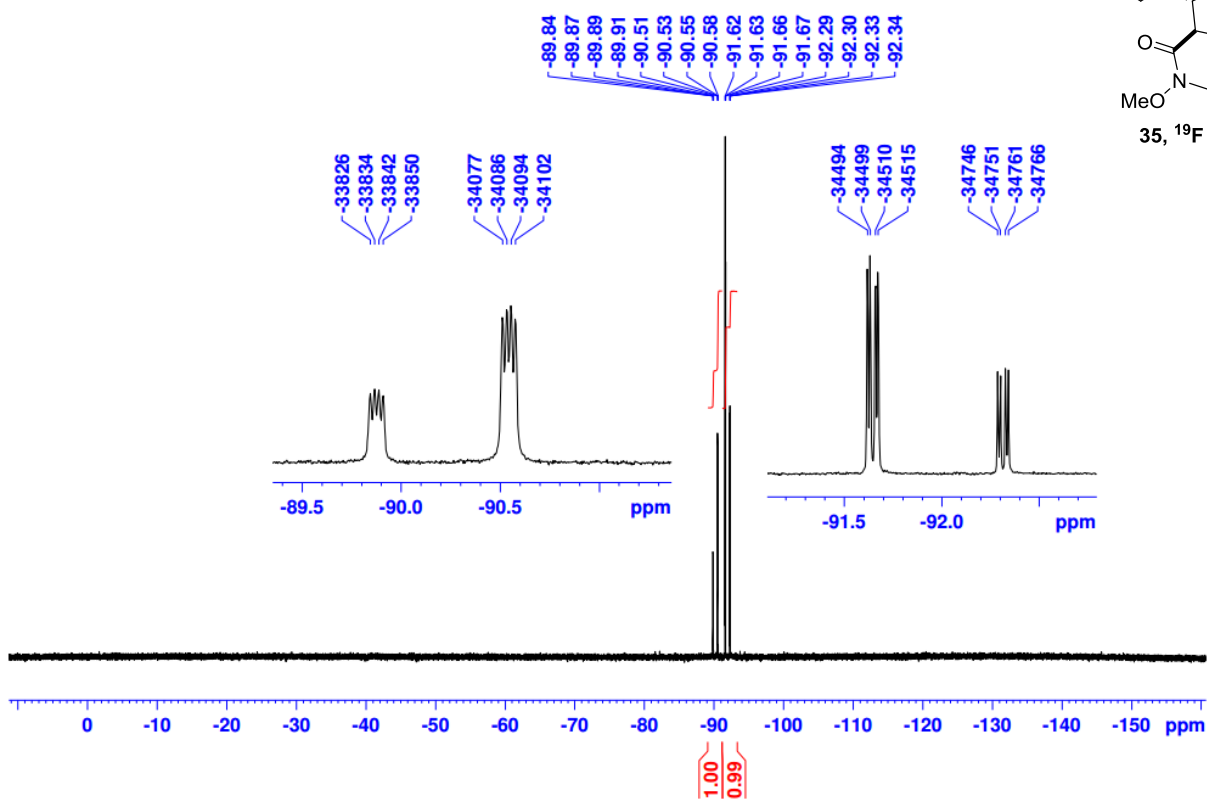


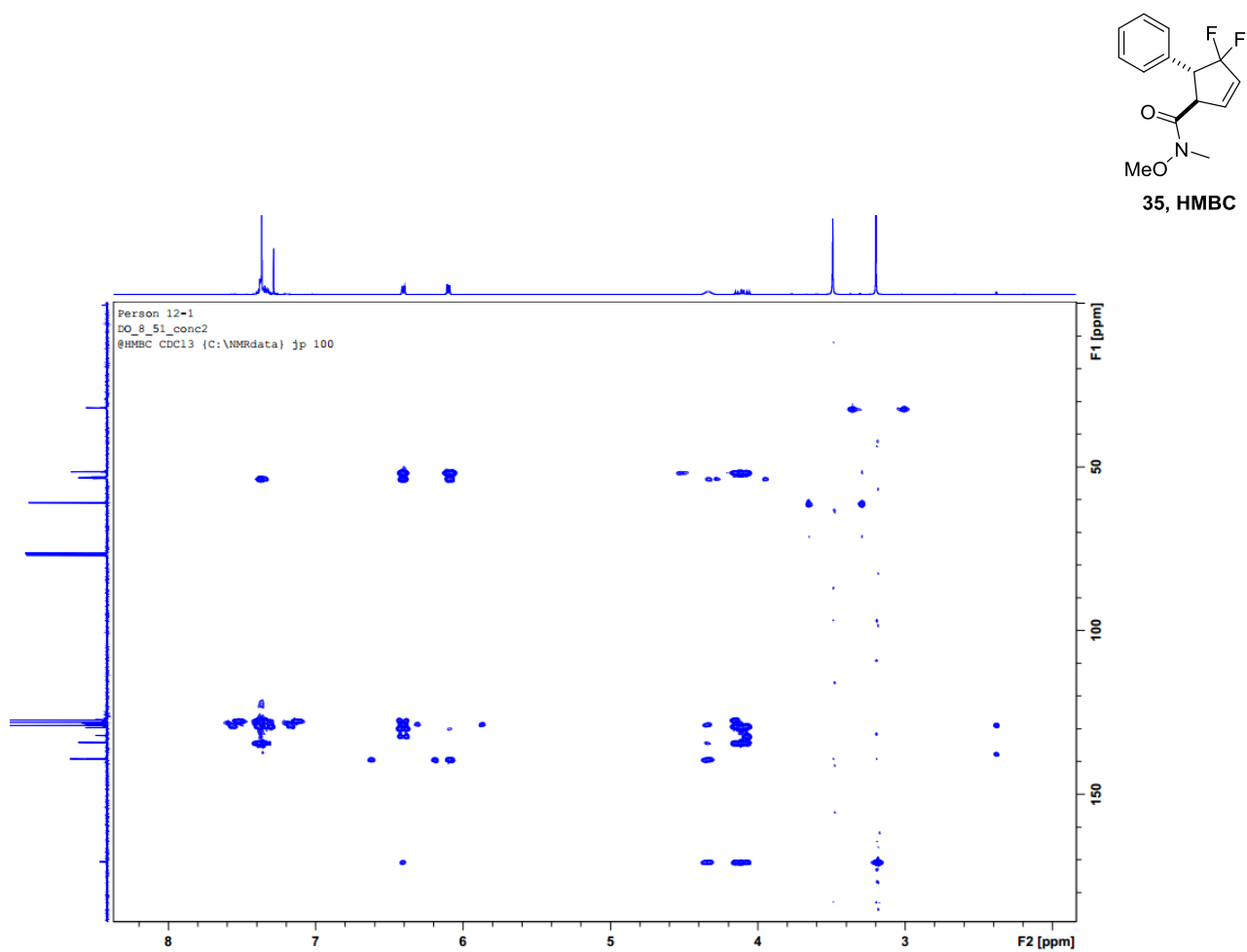
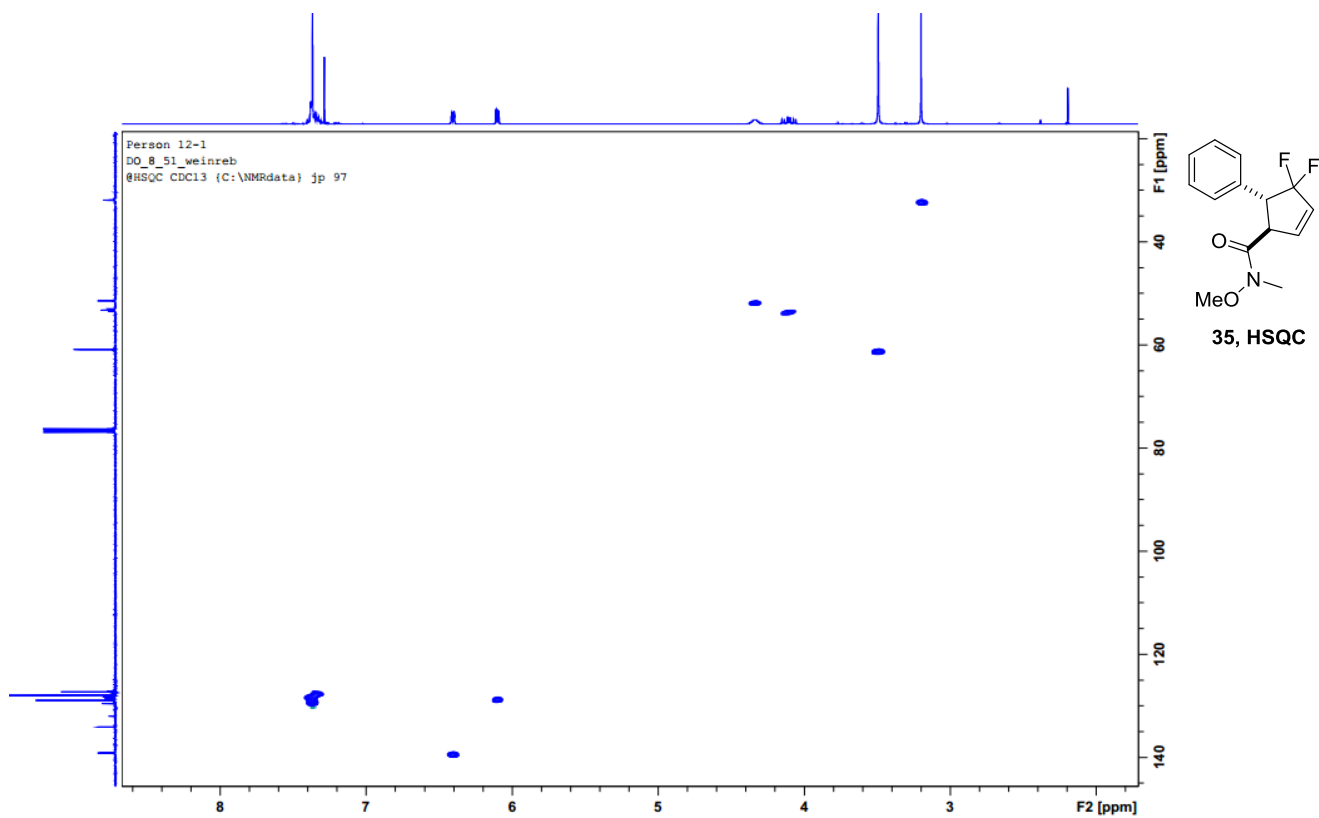


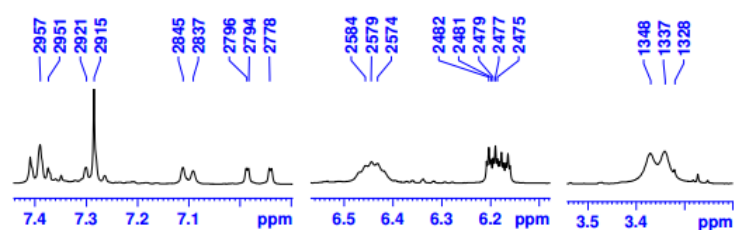
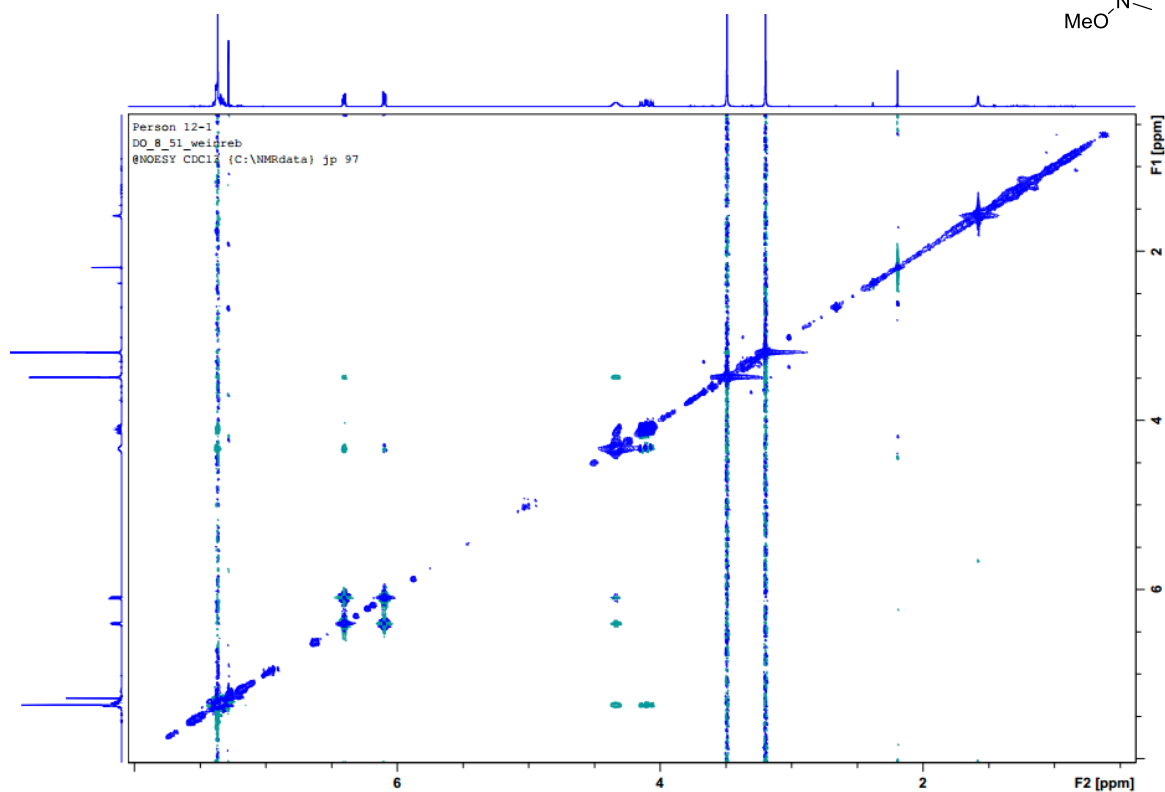
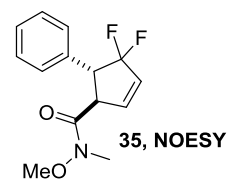
35, ^{13}C NMR



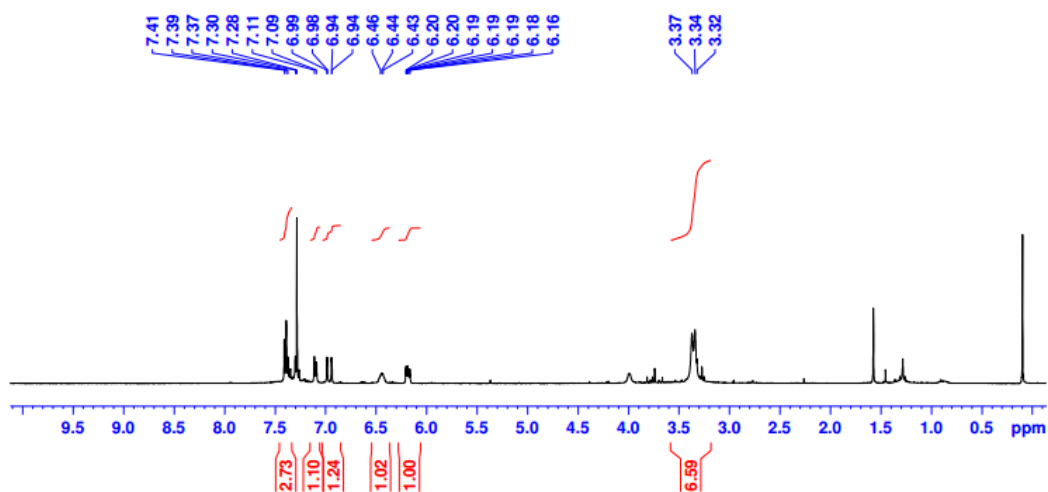
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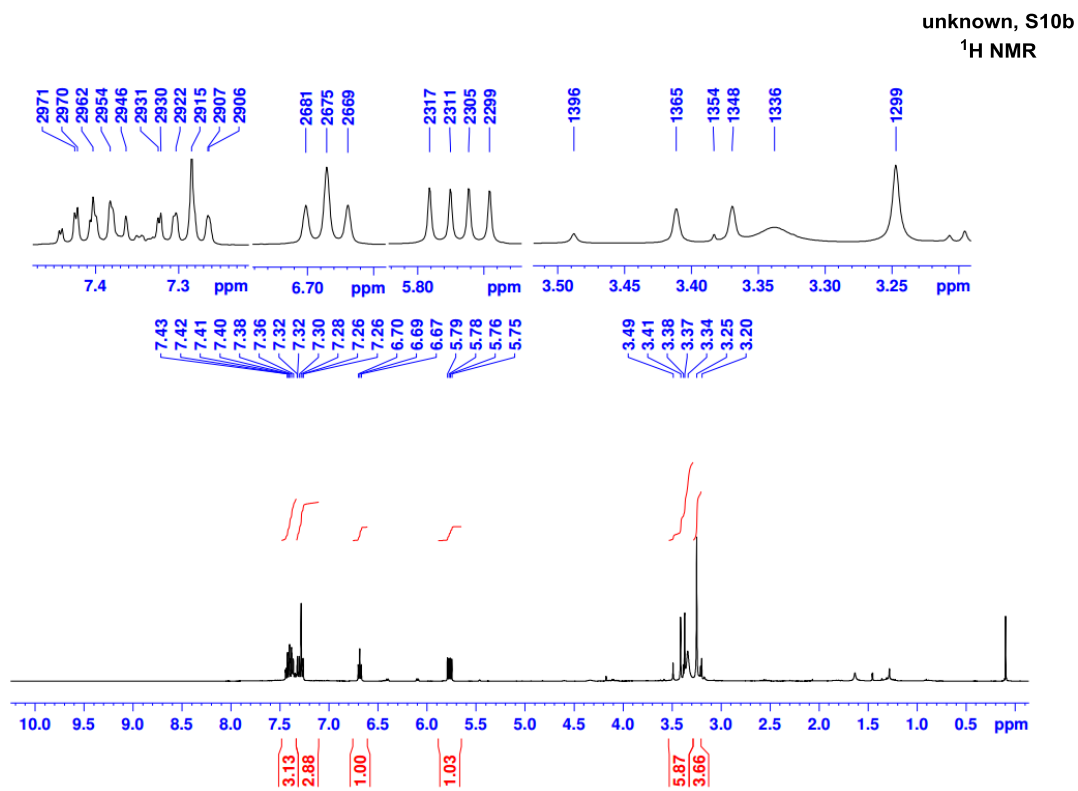
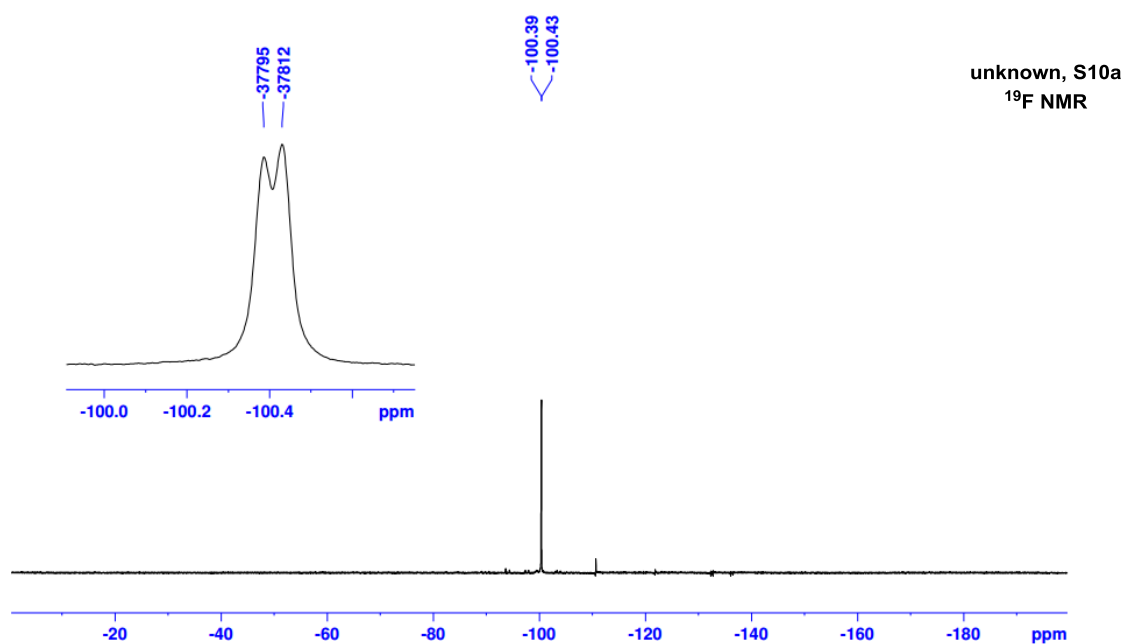


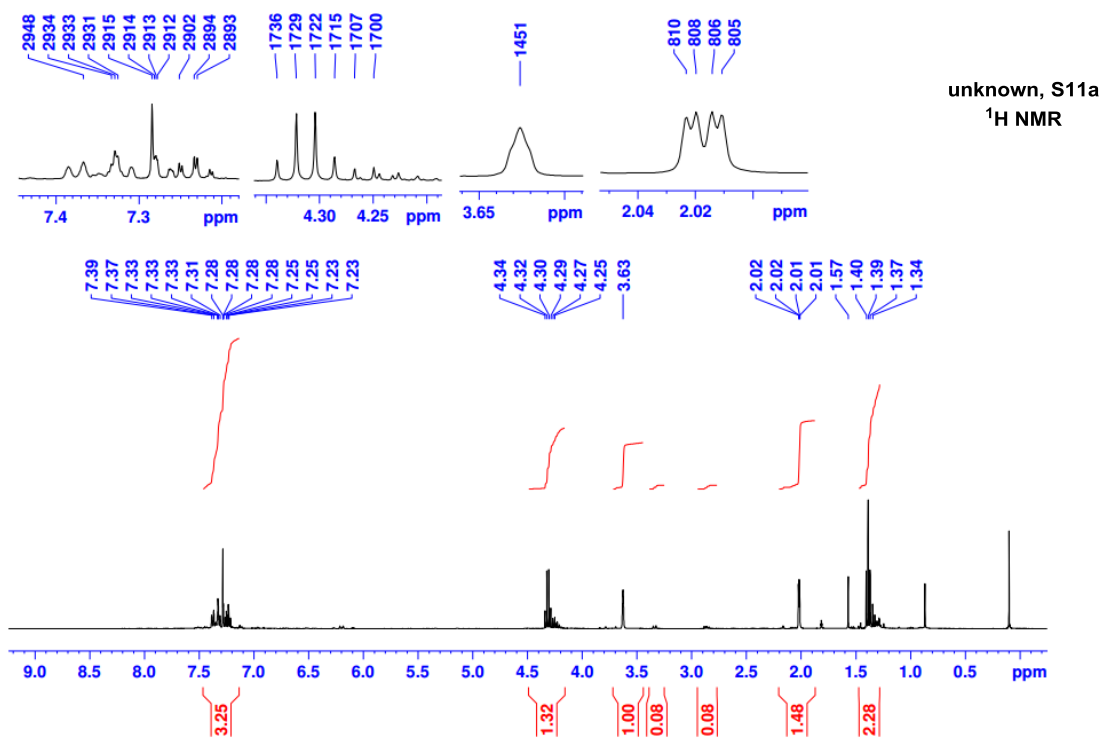
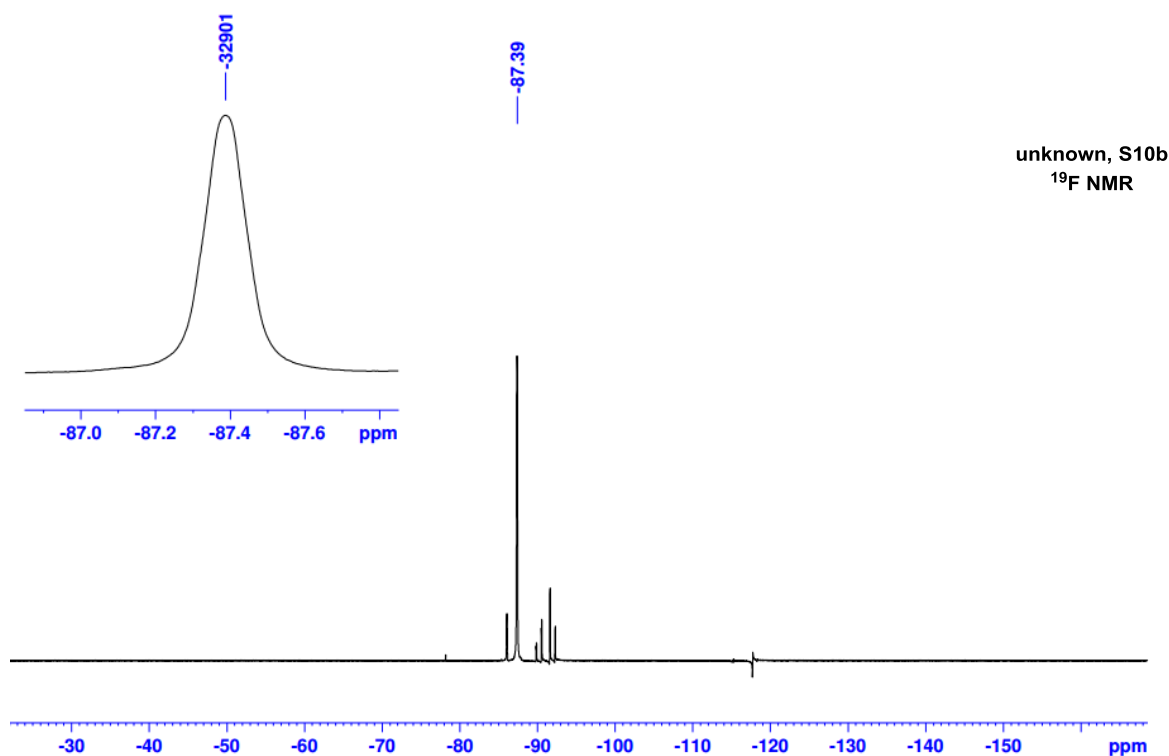


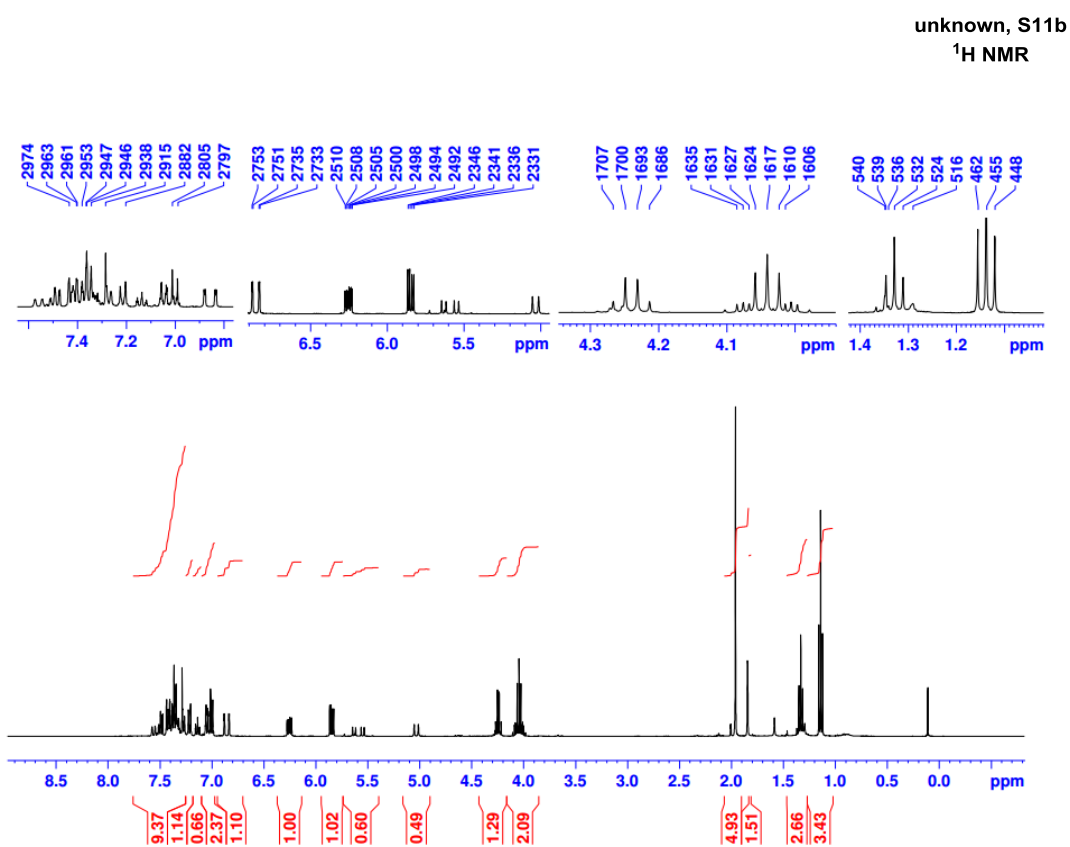
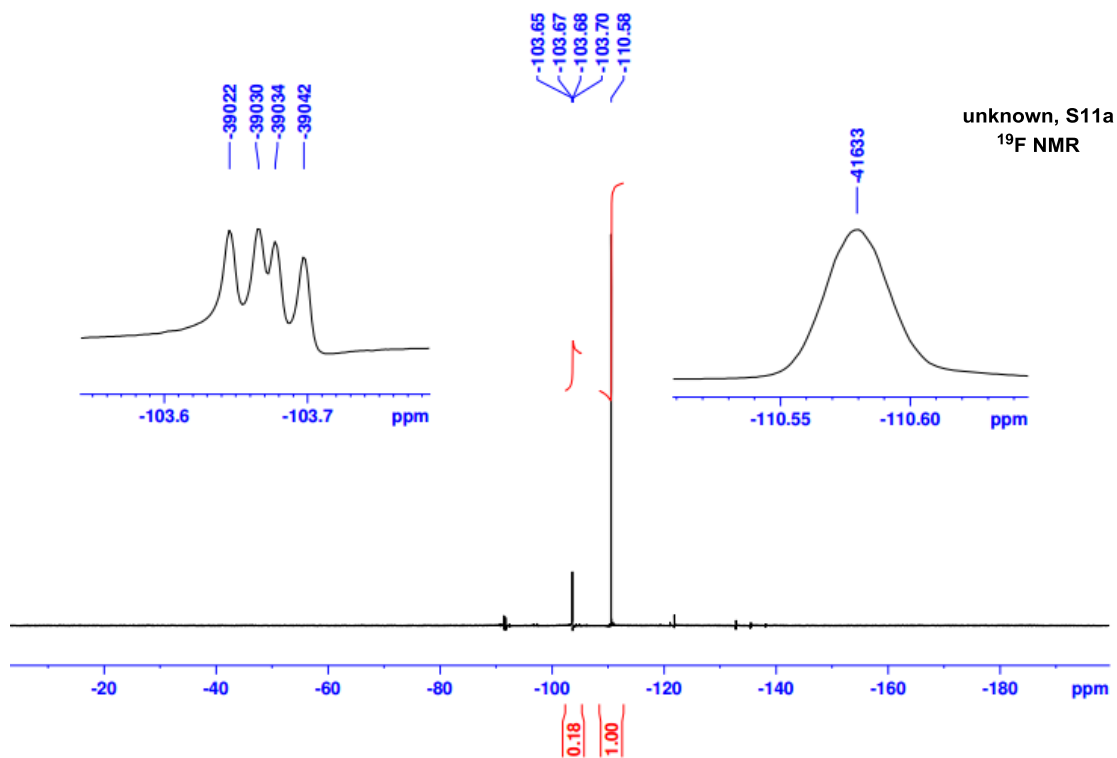


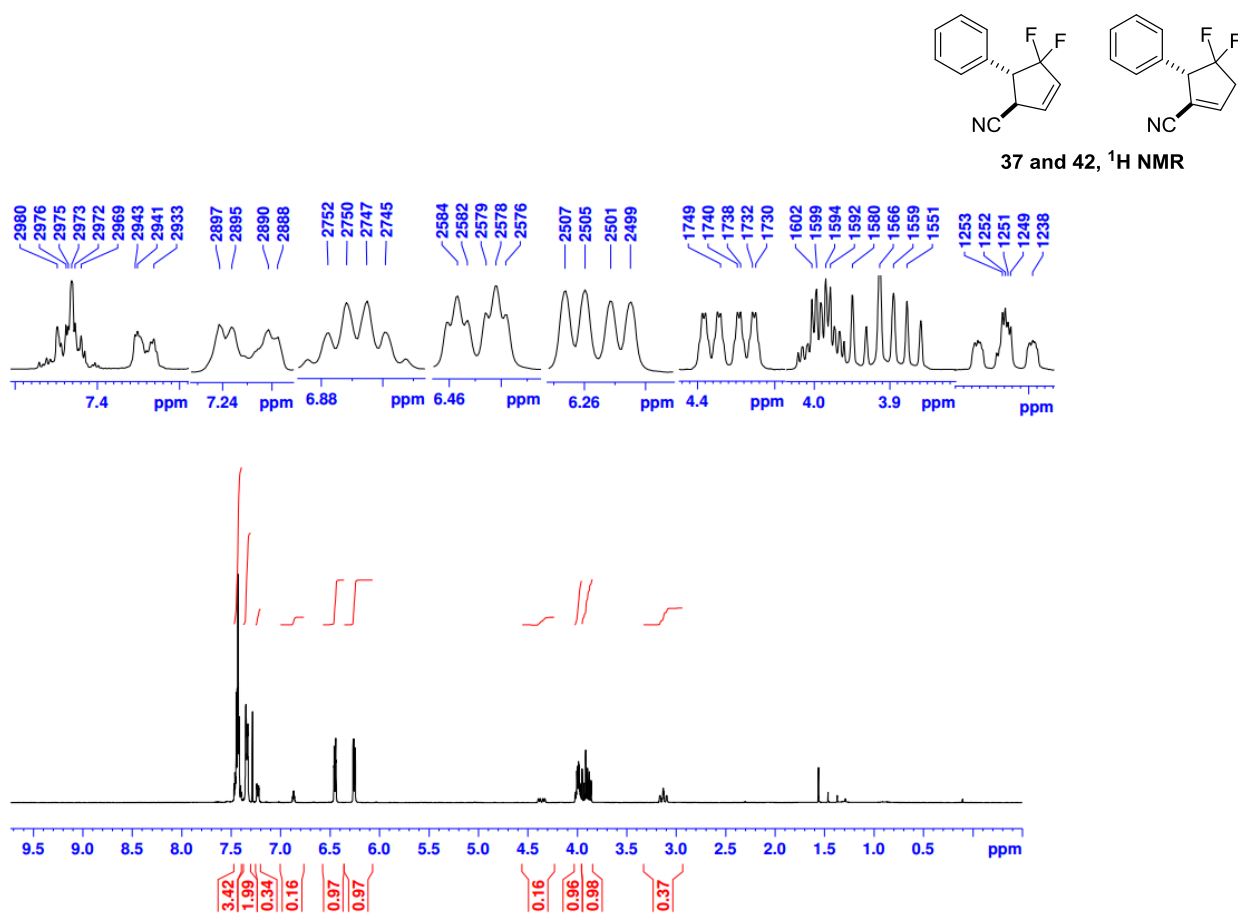
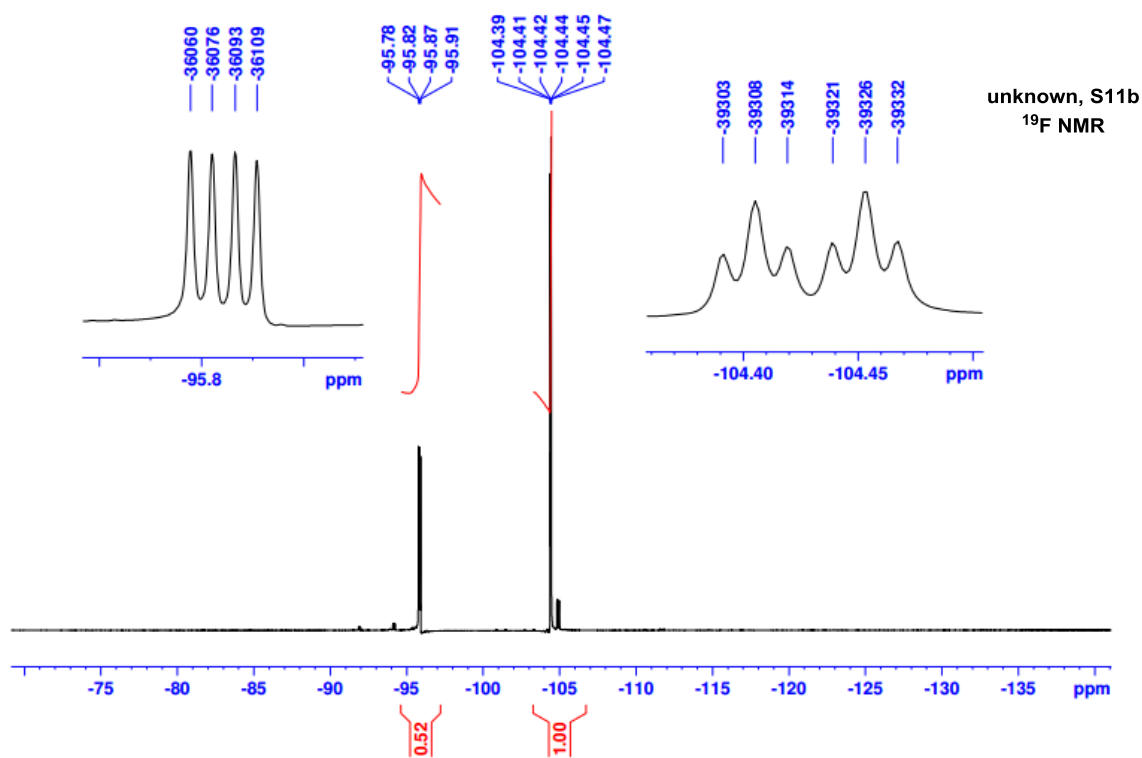
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¹H NMR

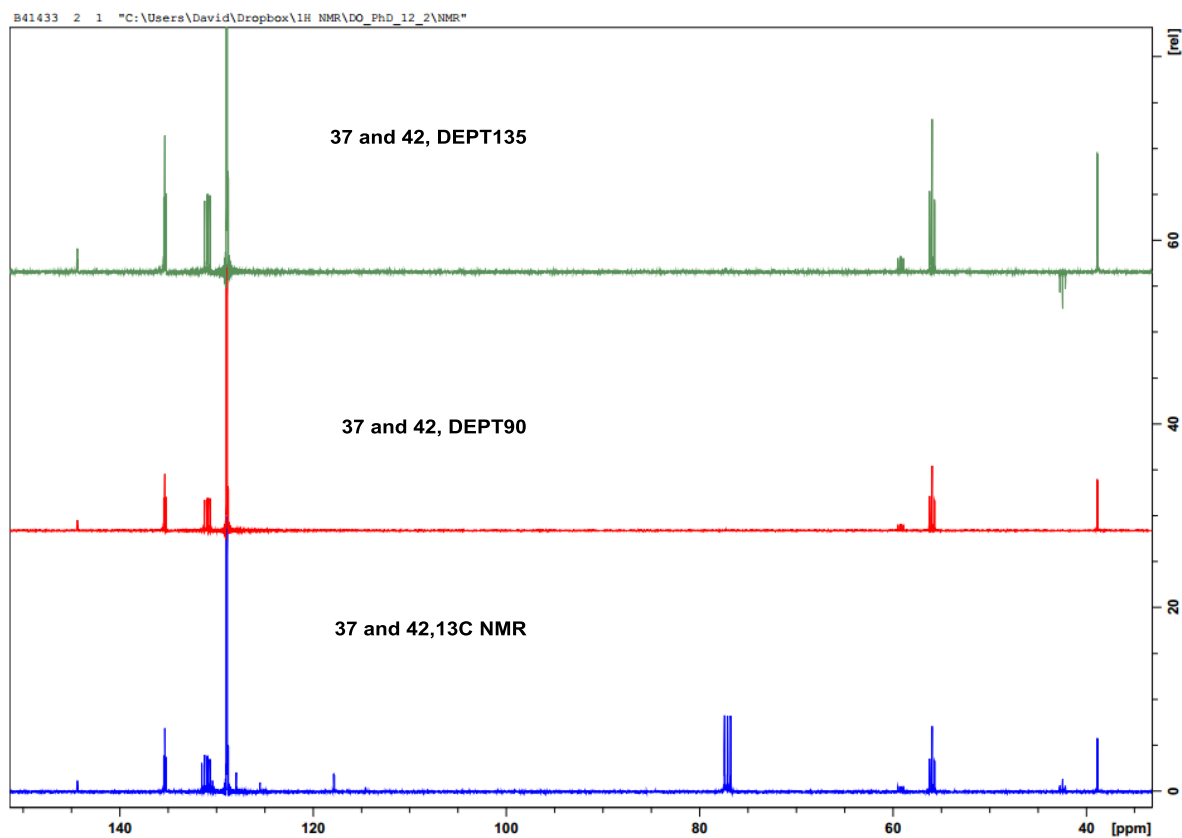
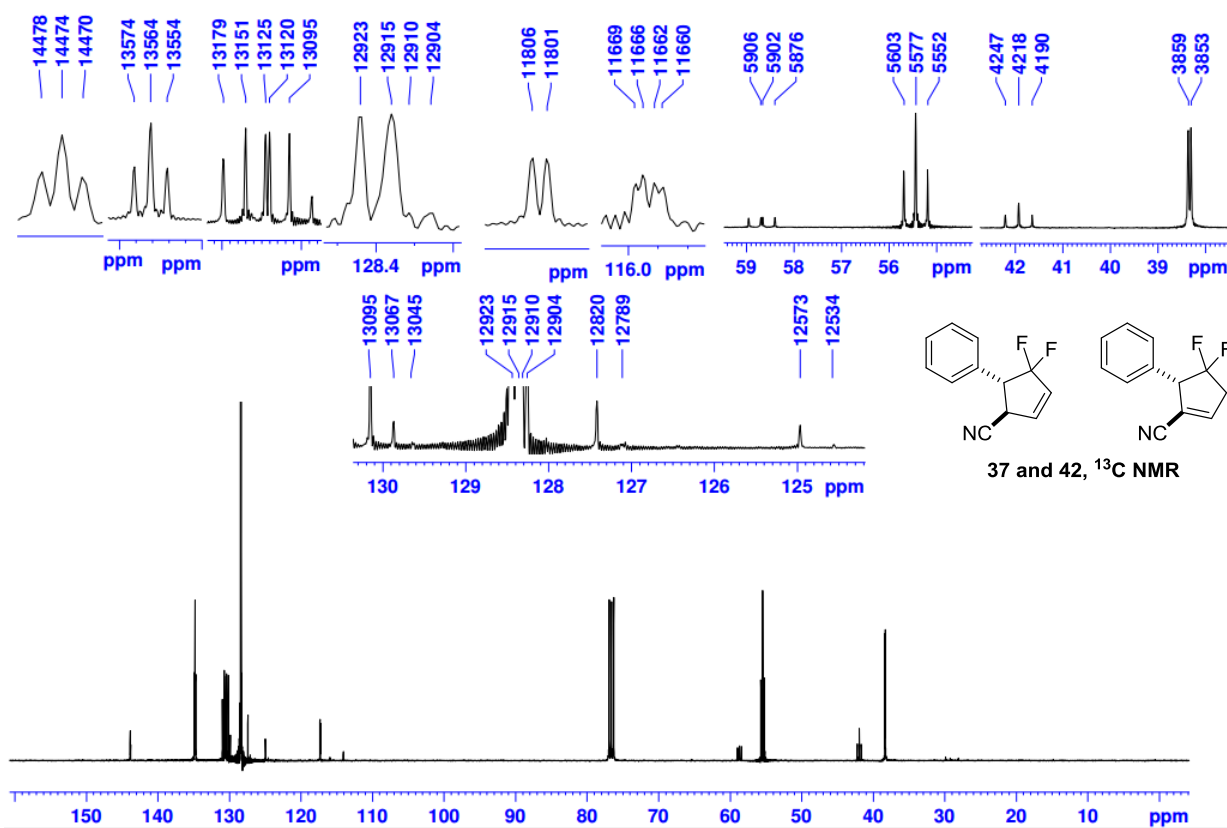


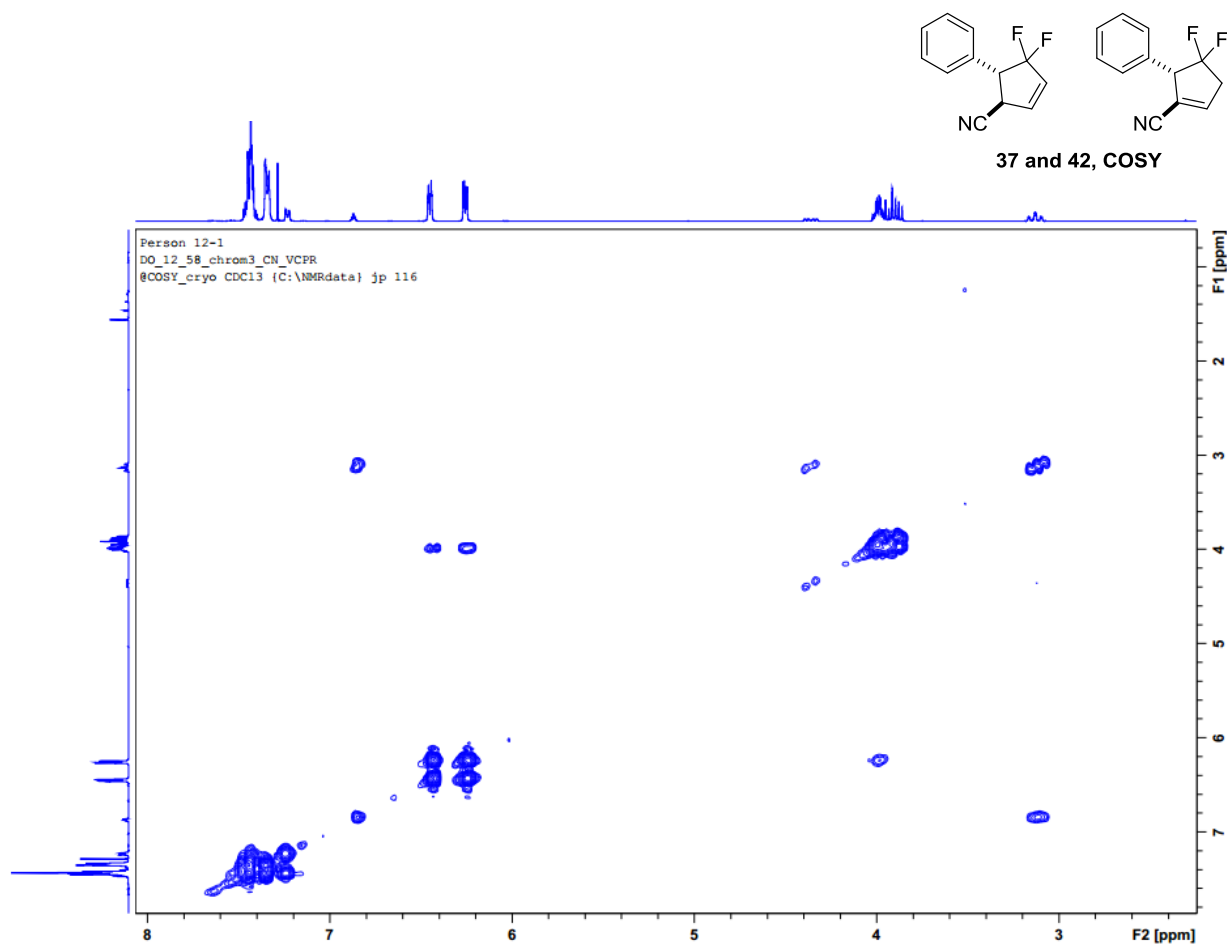
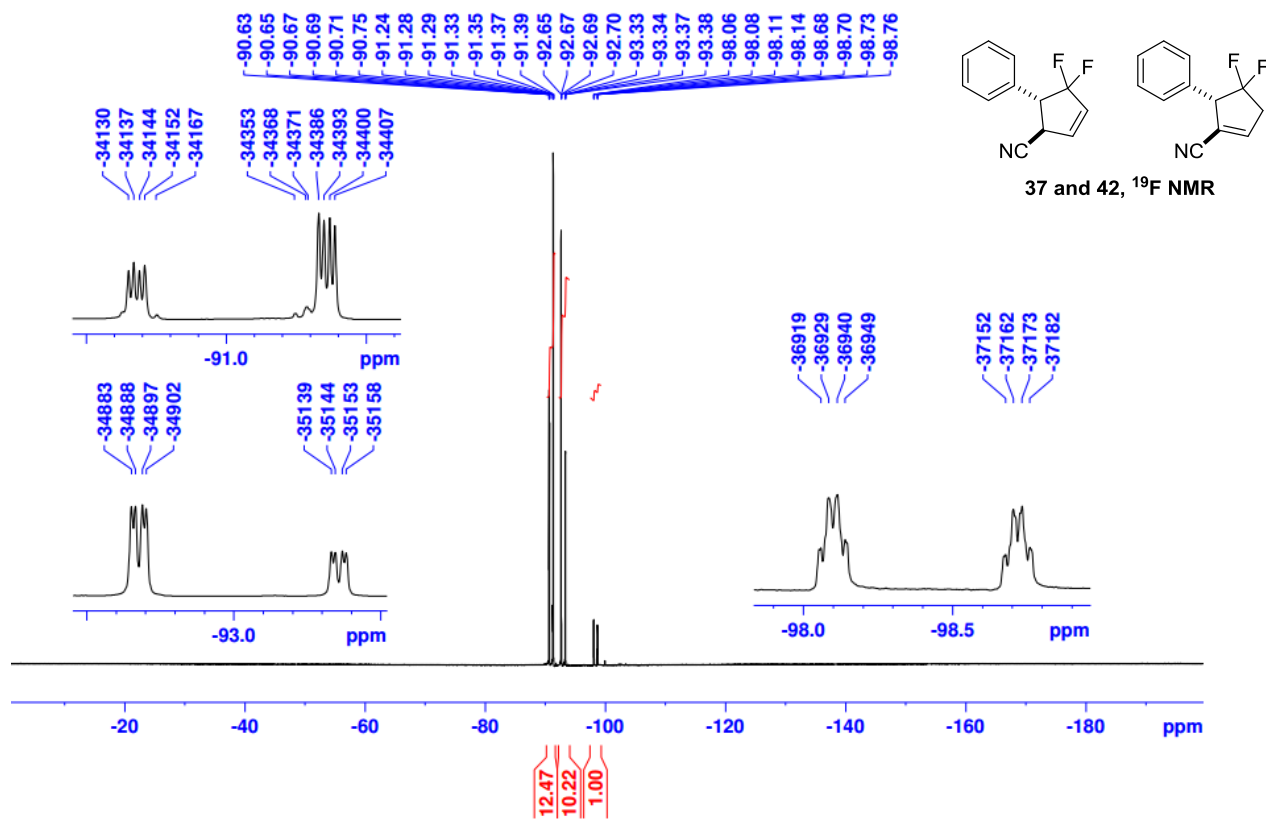


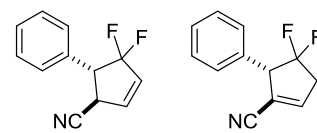




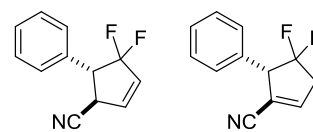
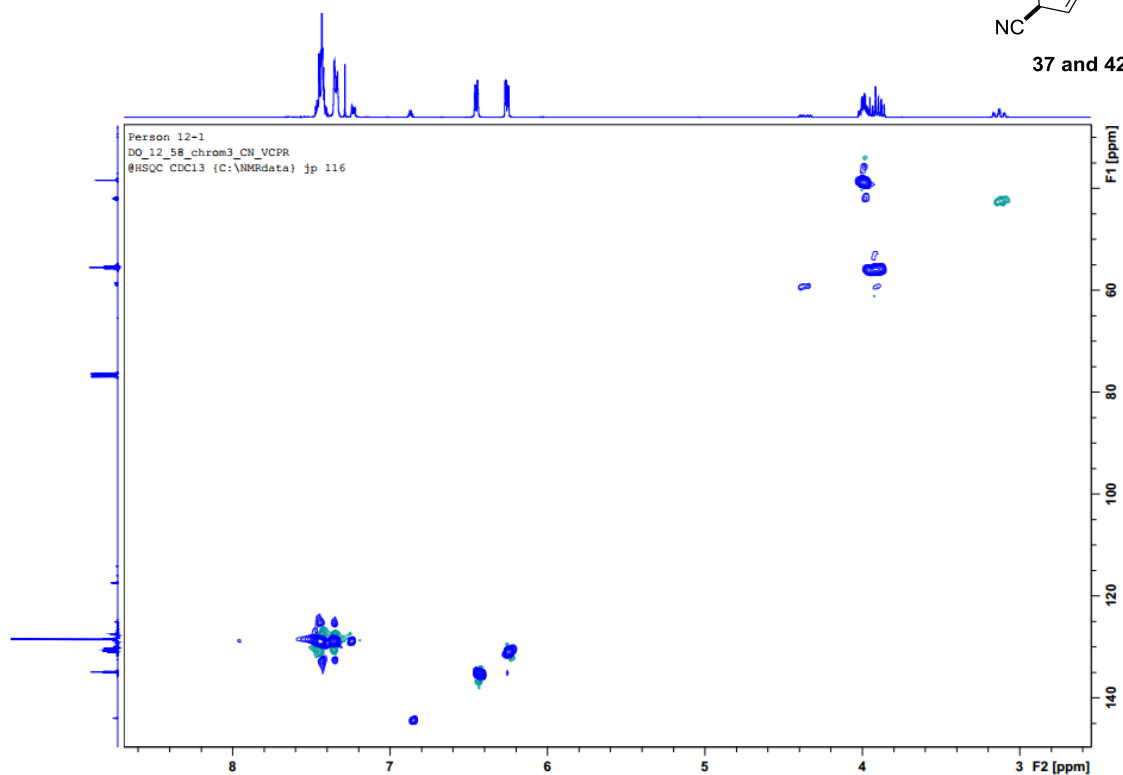




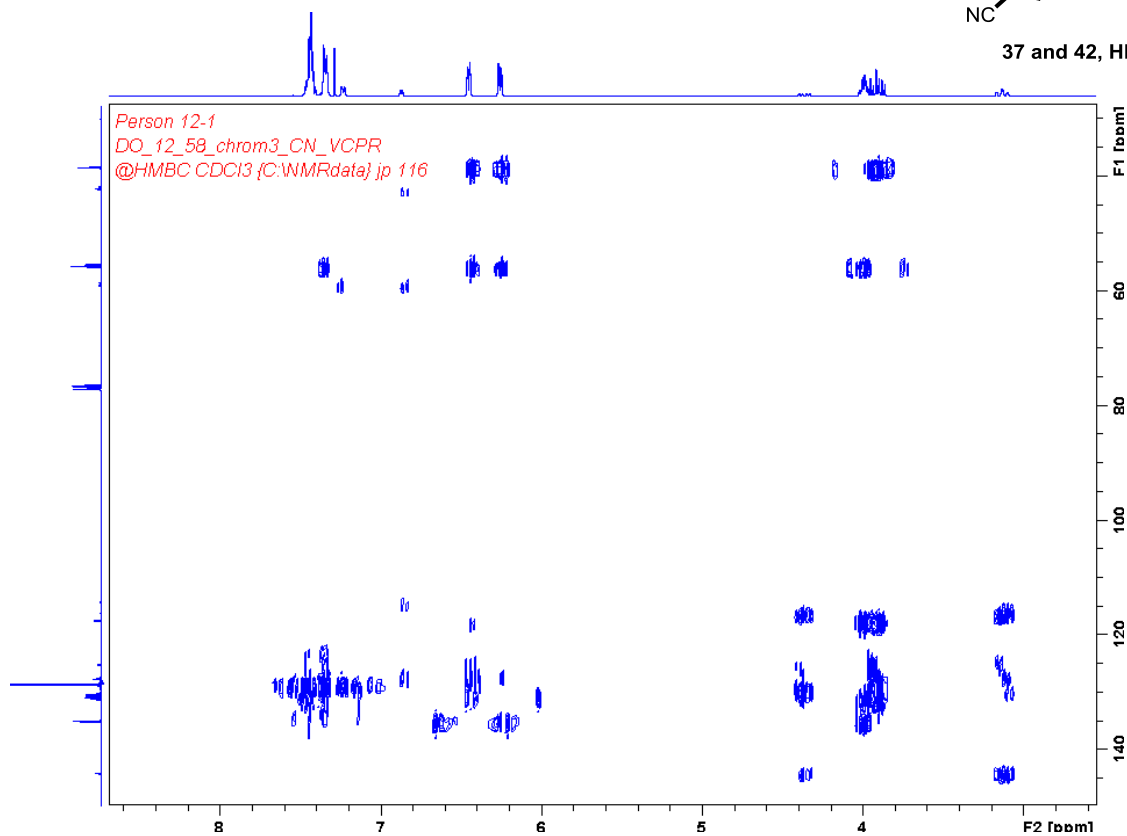


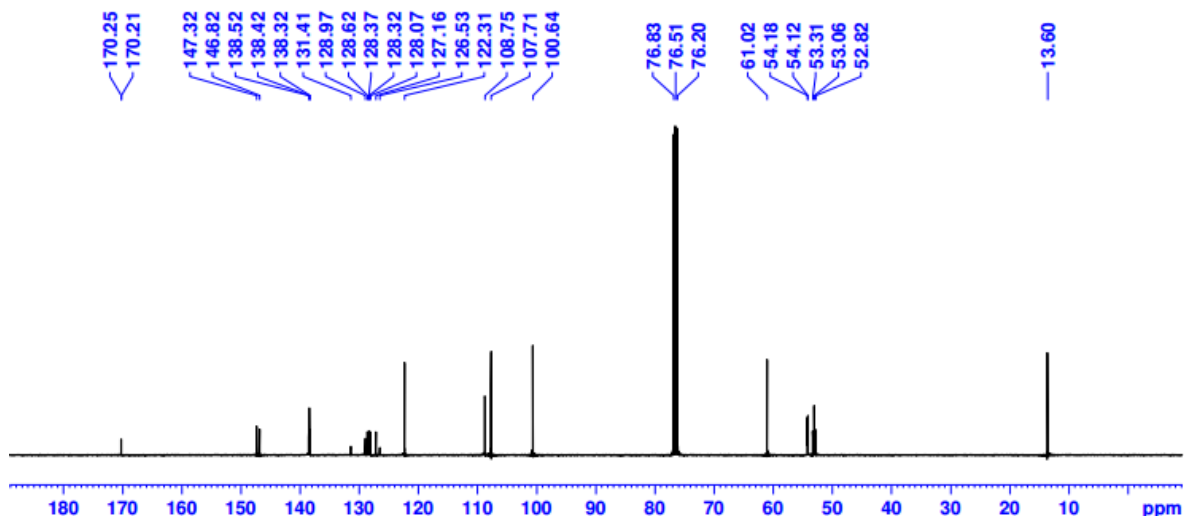
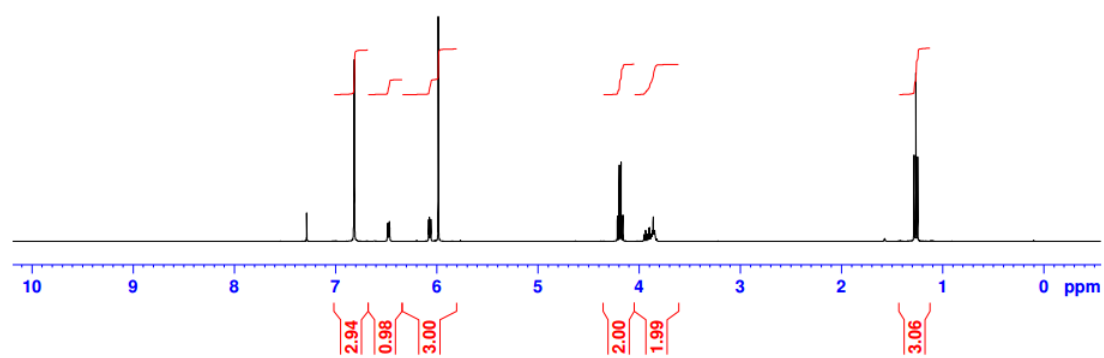
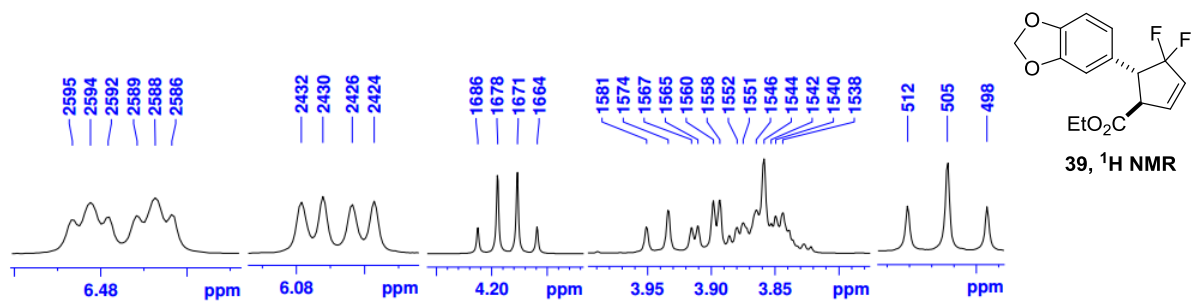


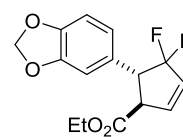
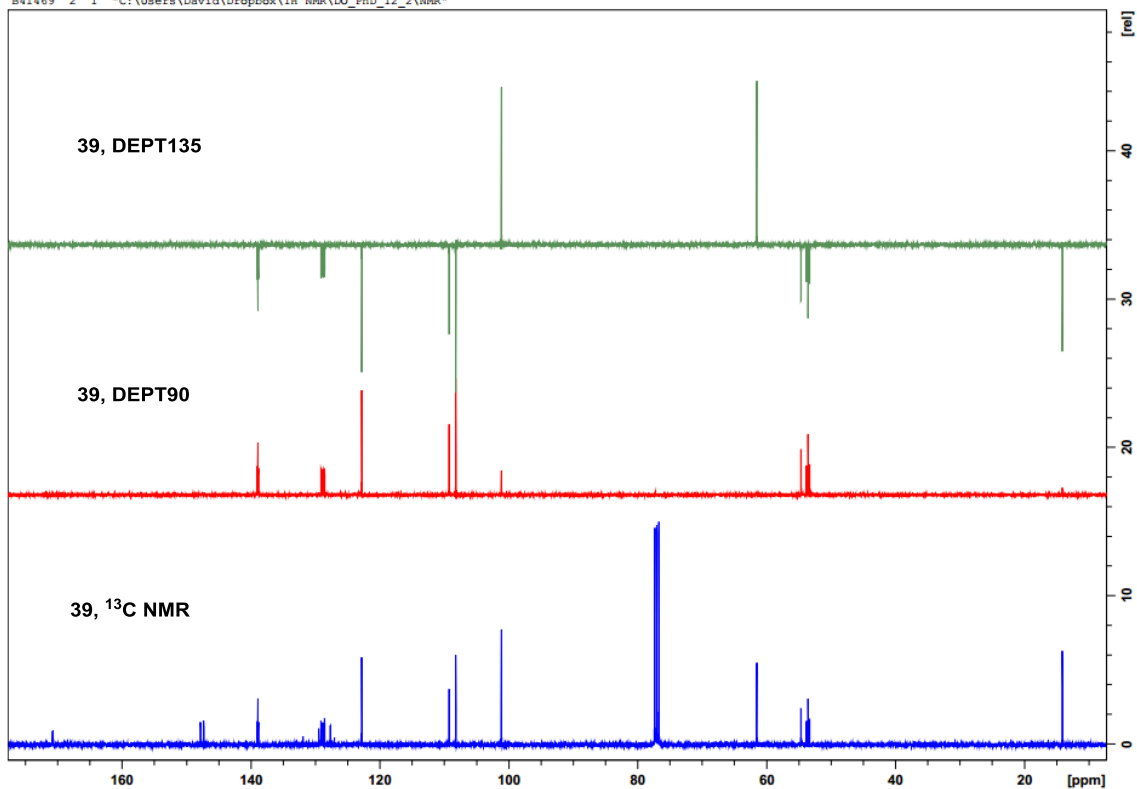
37 and 42, HSQC



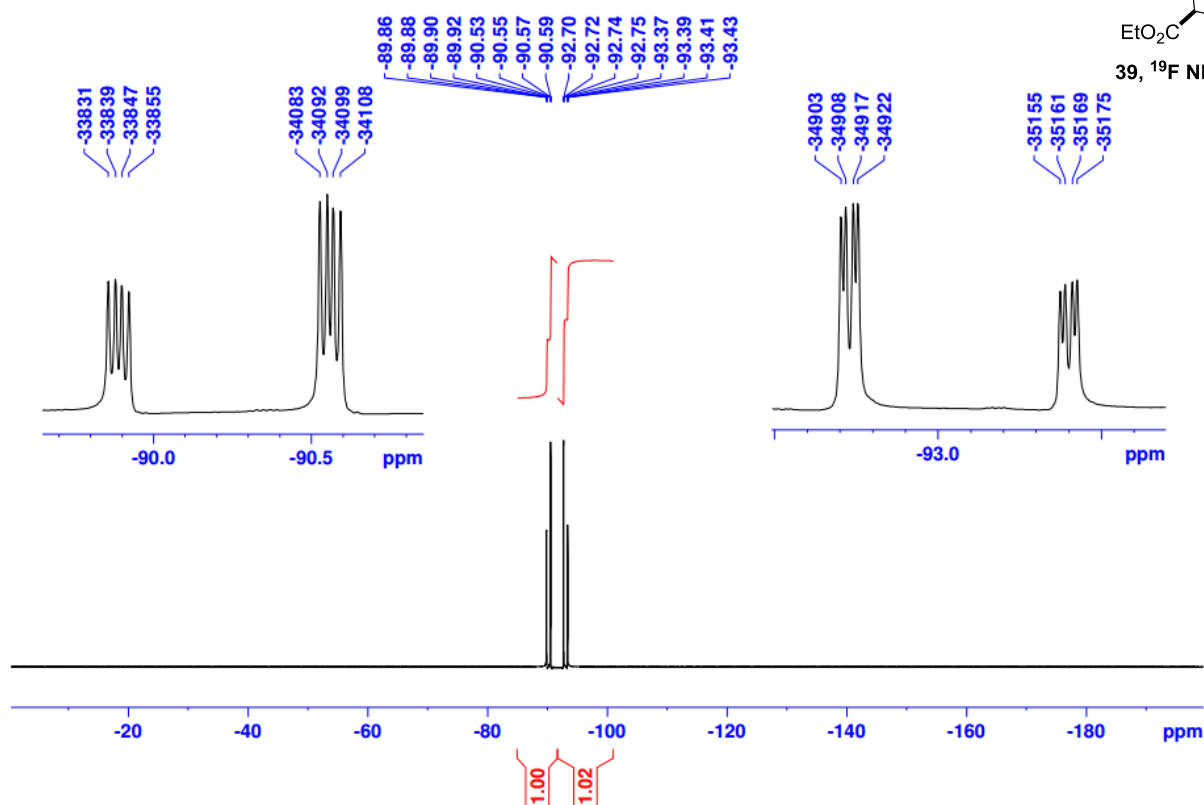
37 and 42, HMBC

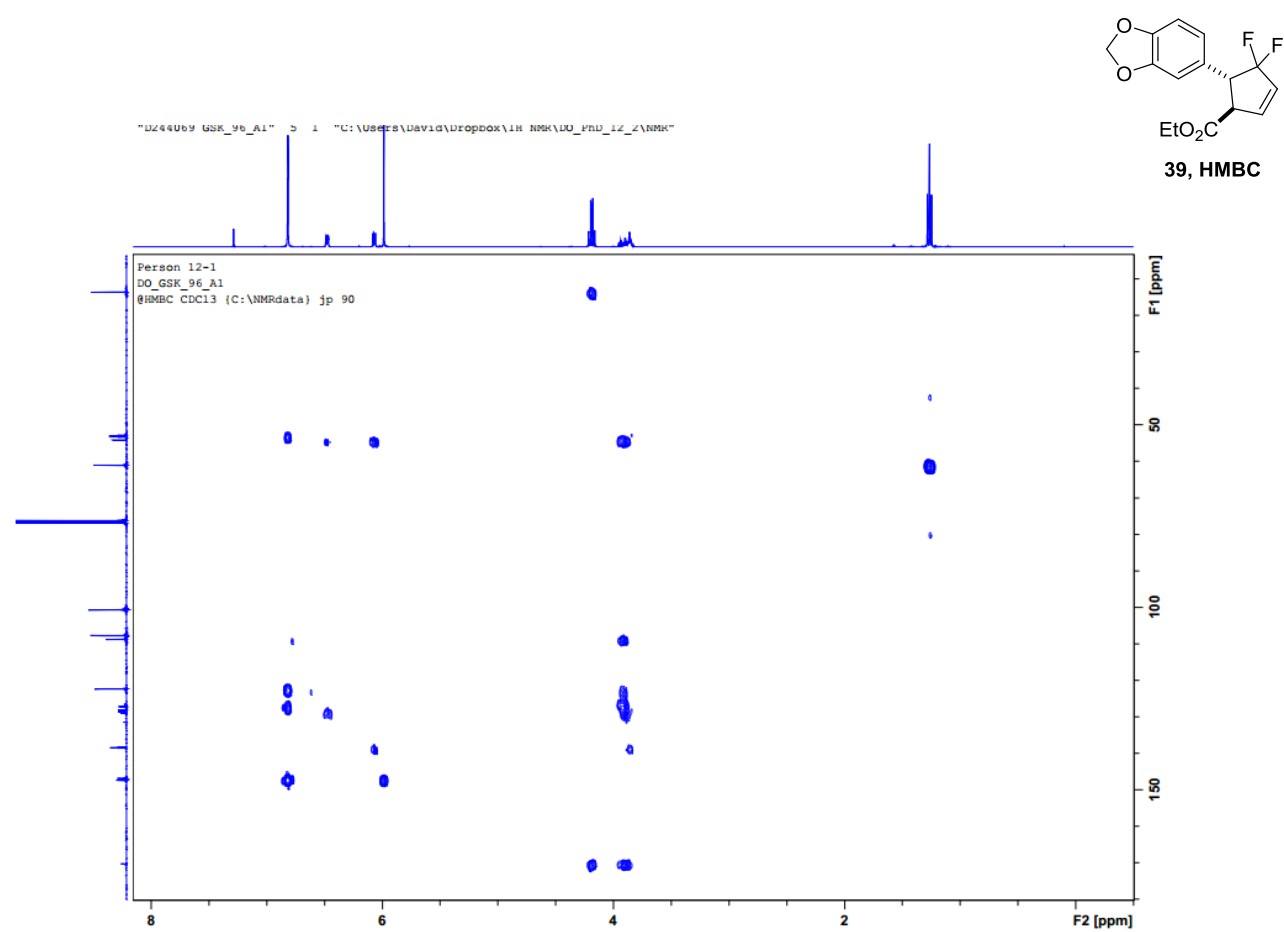
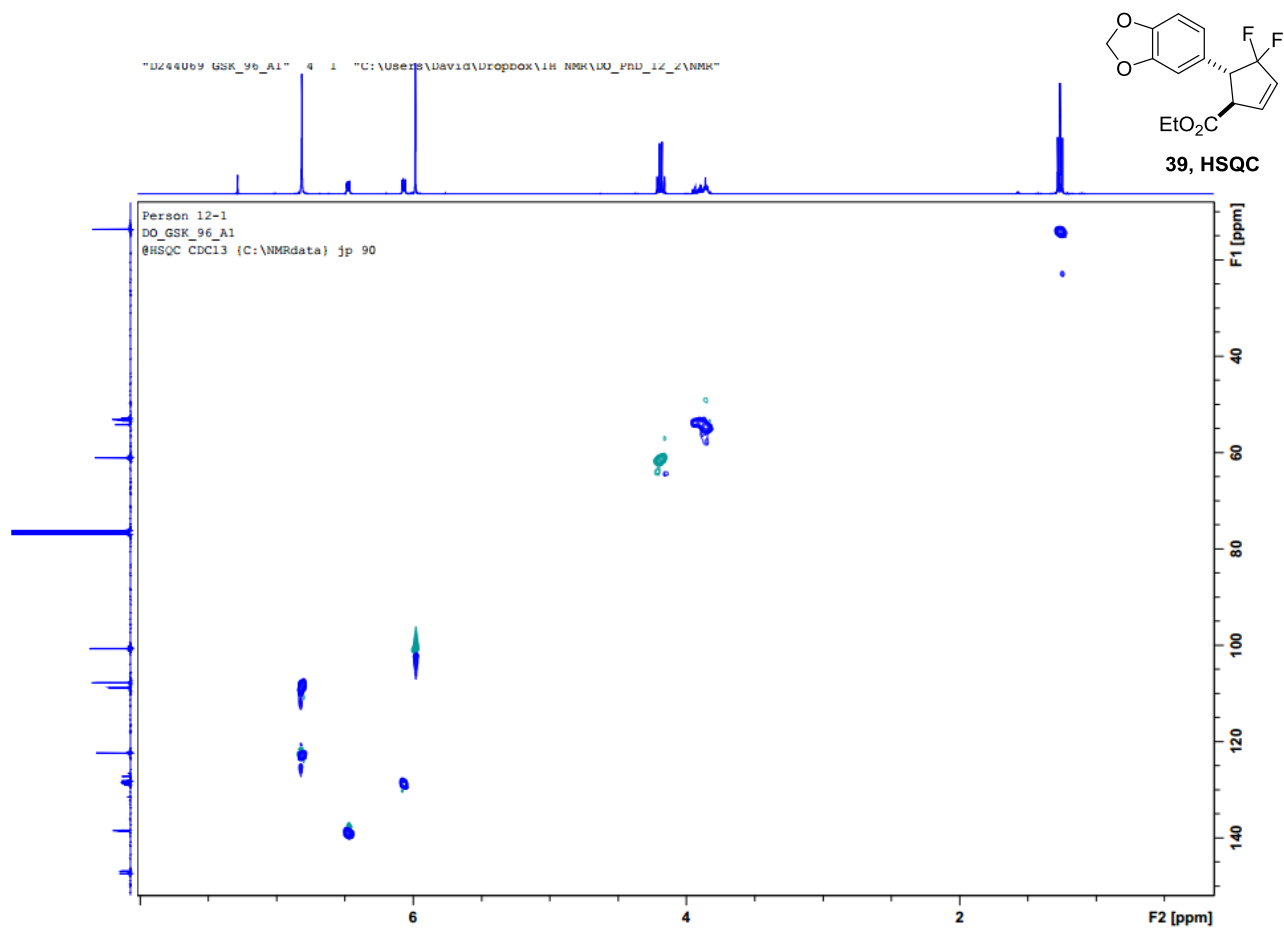


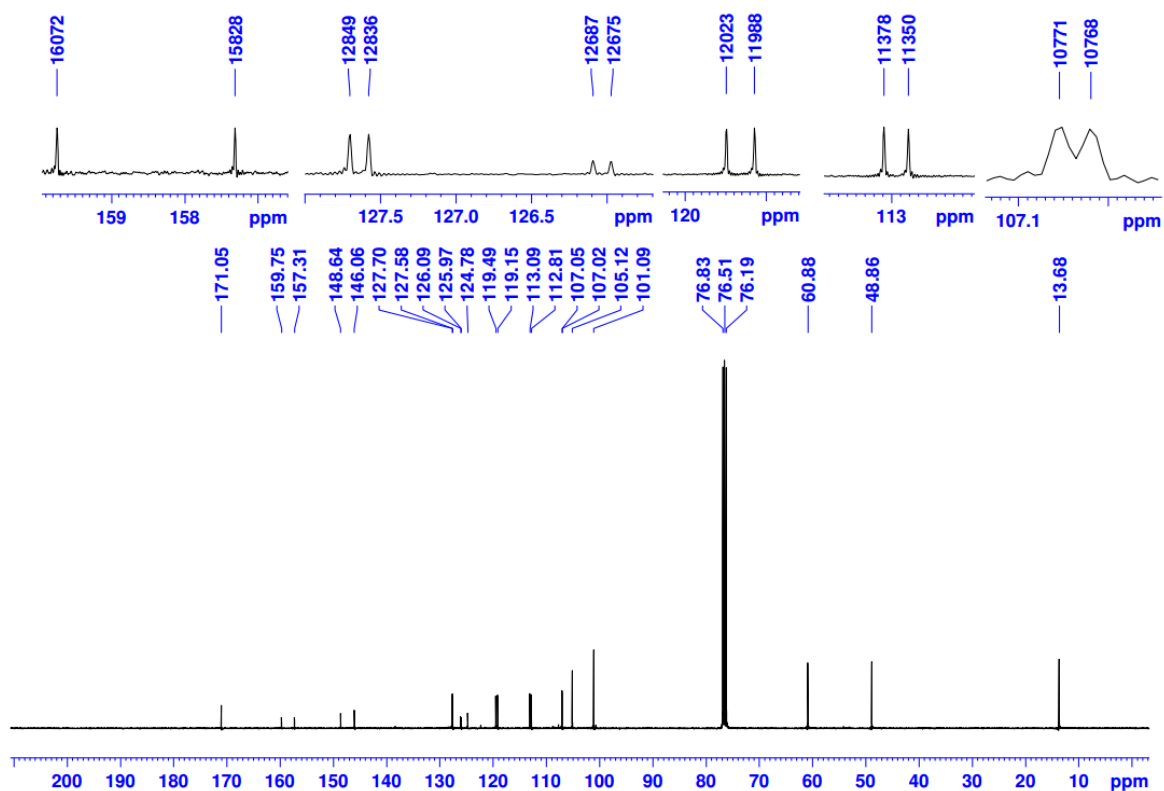
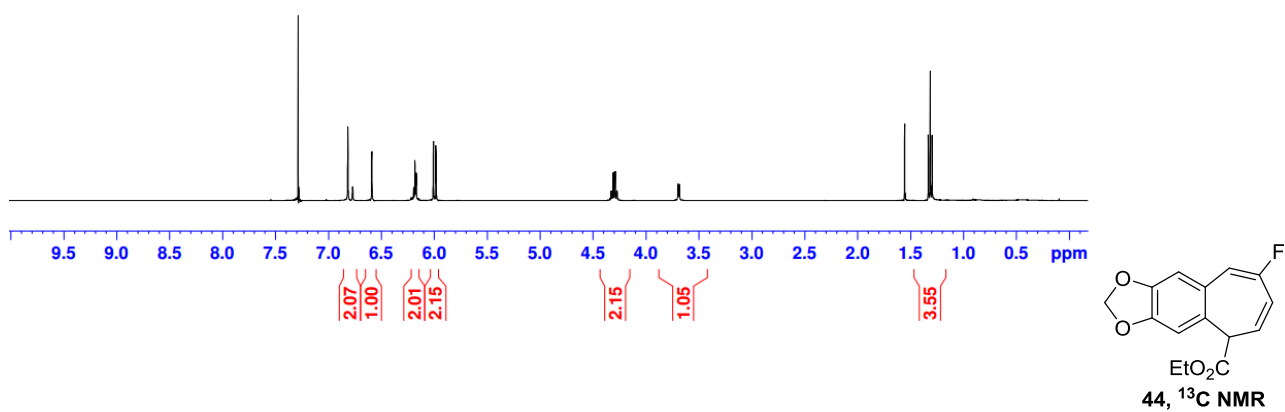
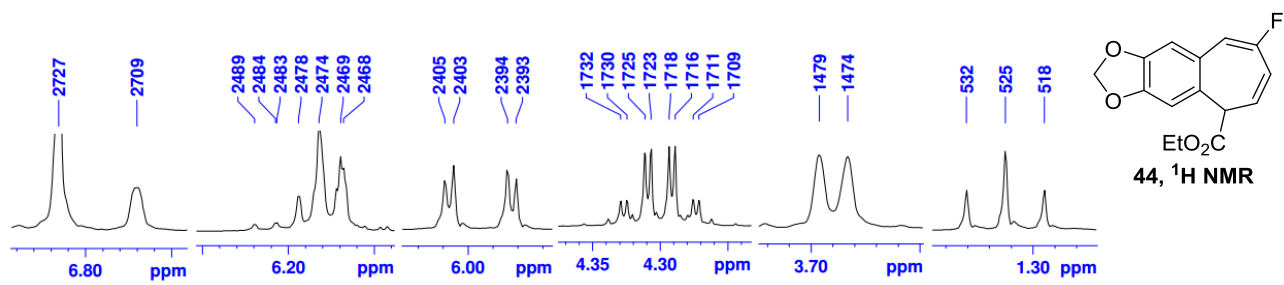


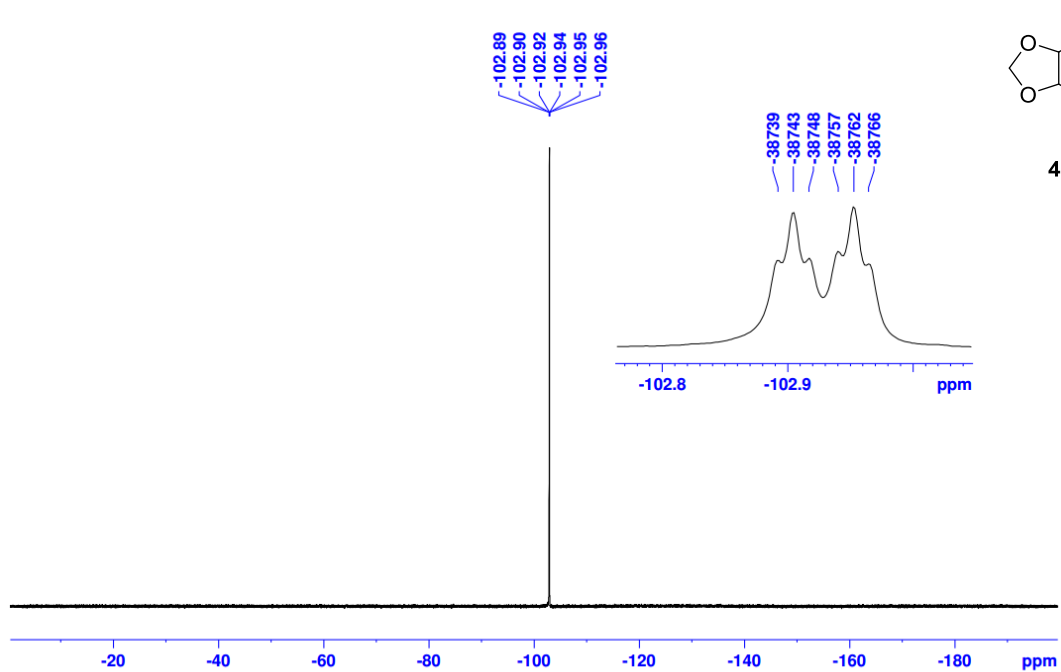
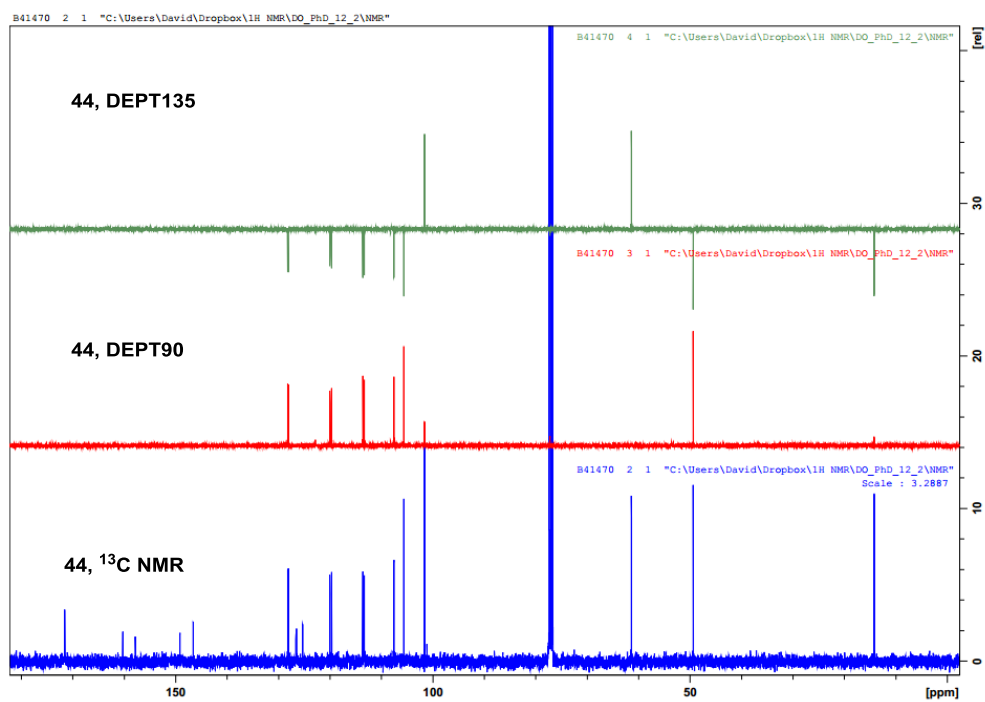


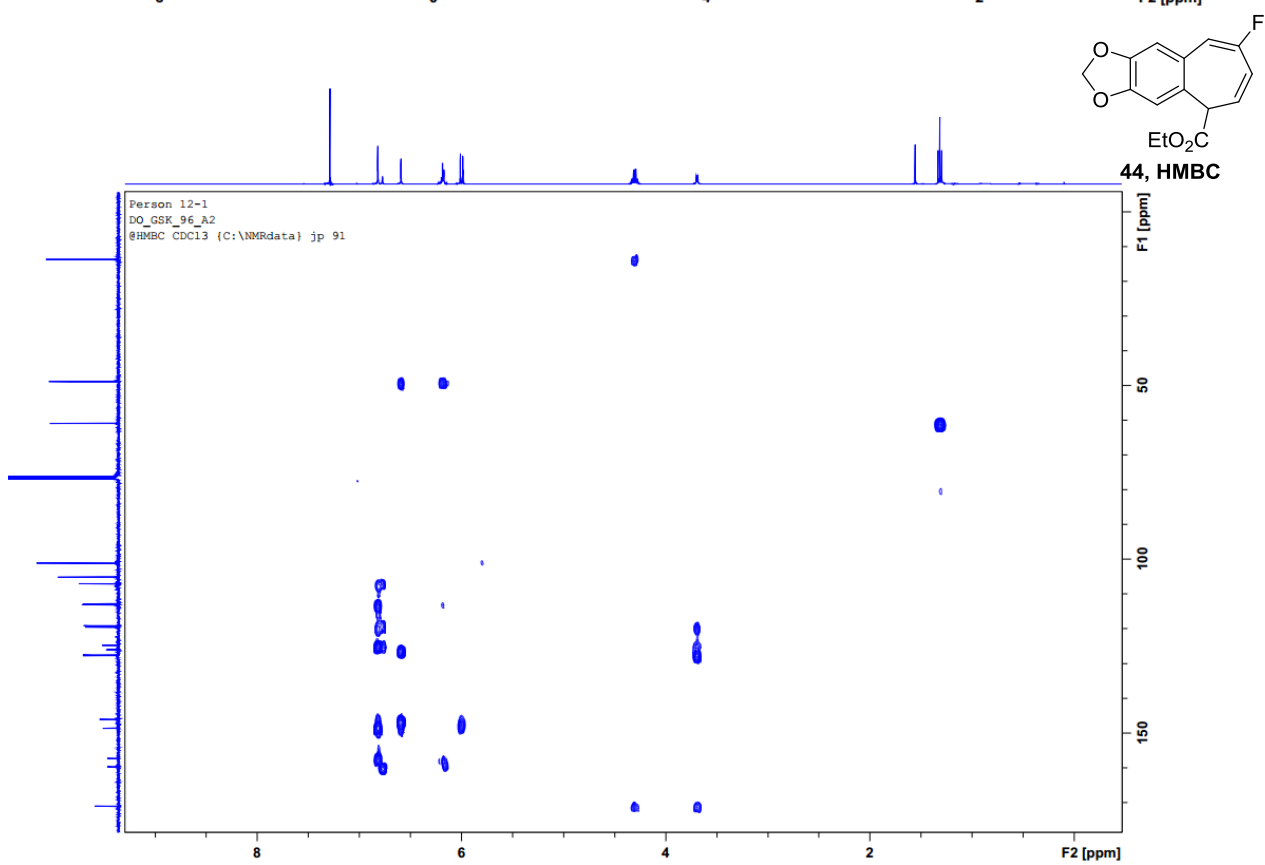
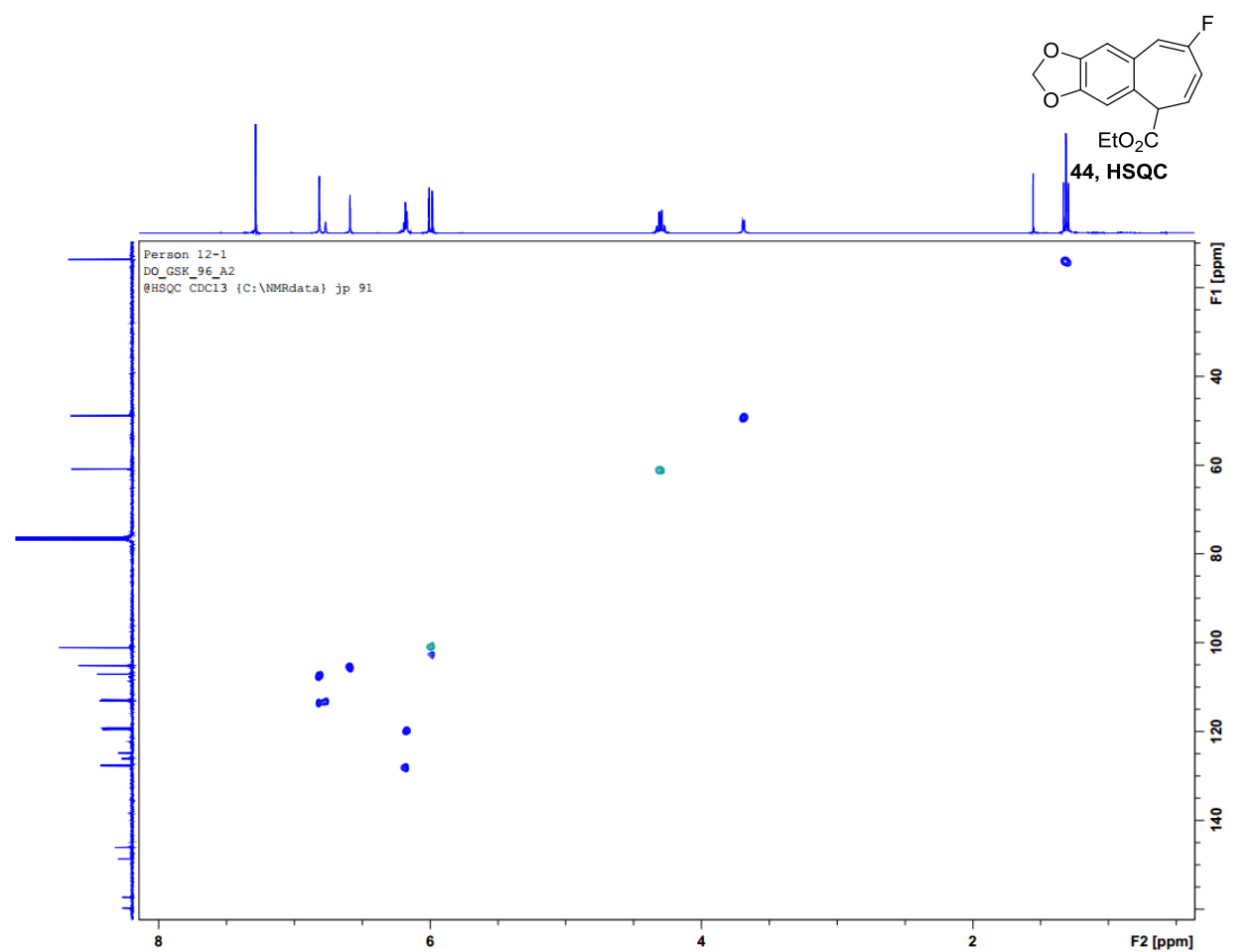
39, ^{19}F NMR

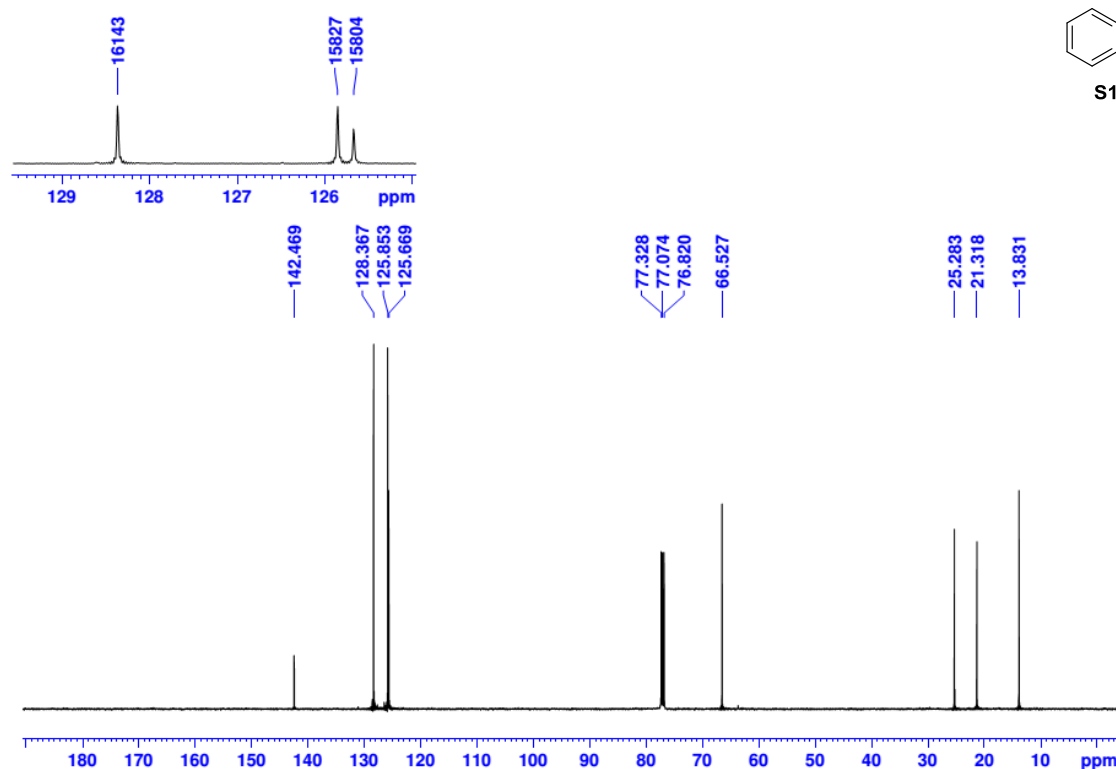
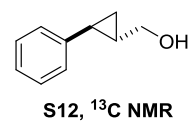
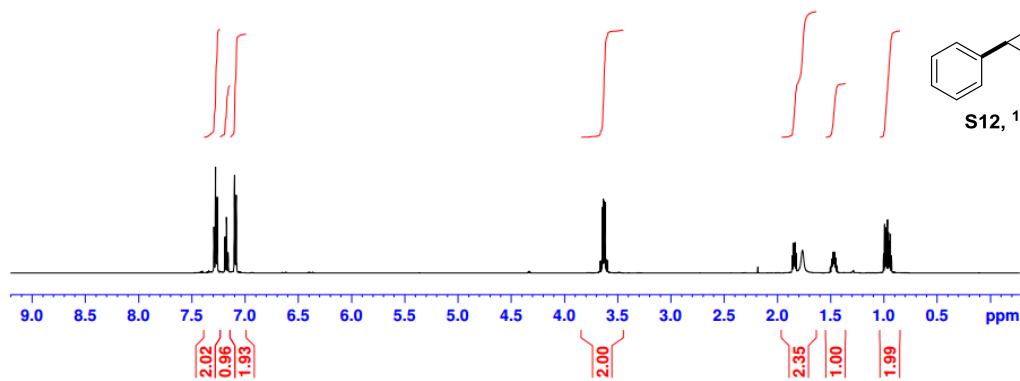
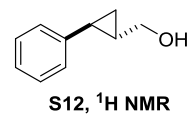
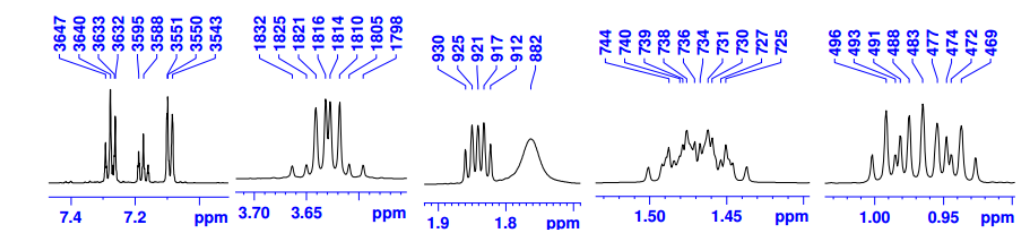


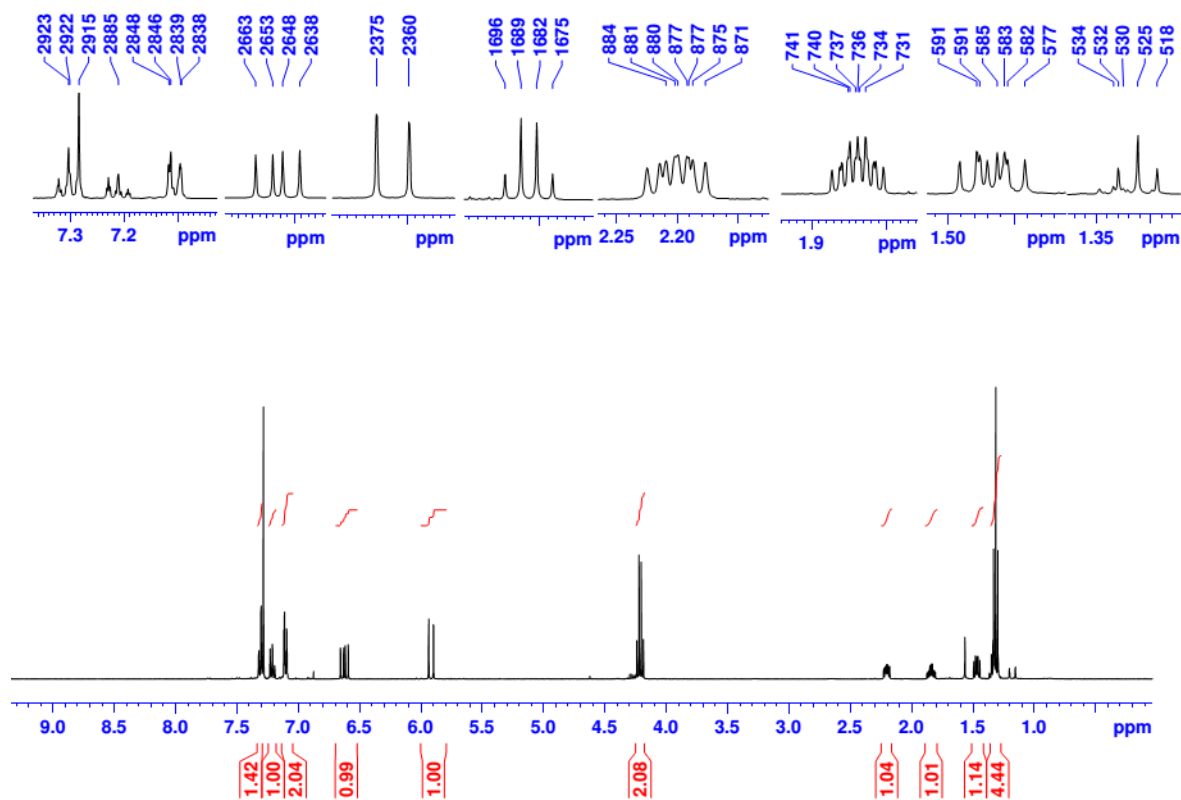
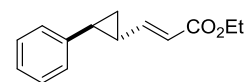
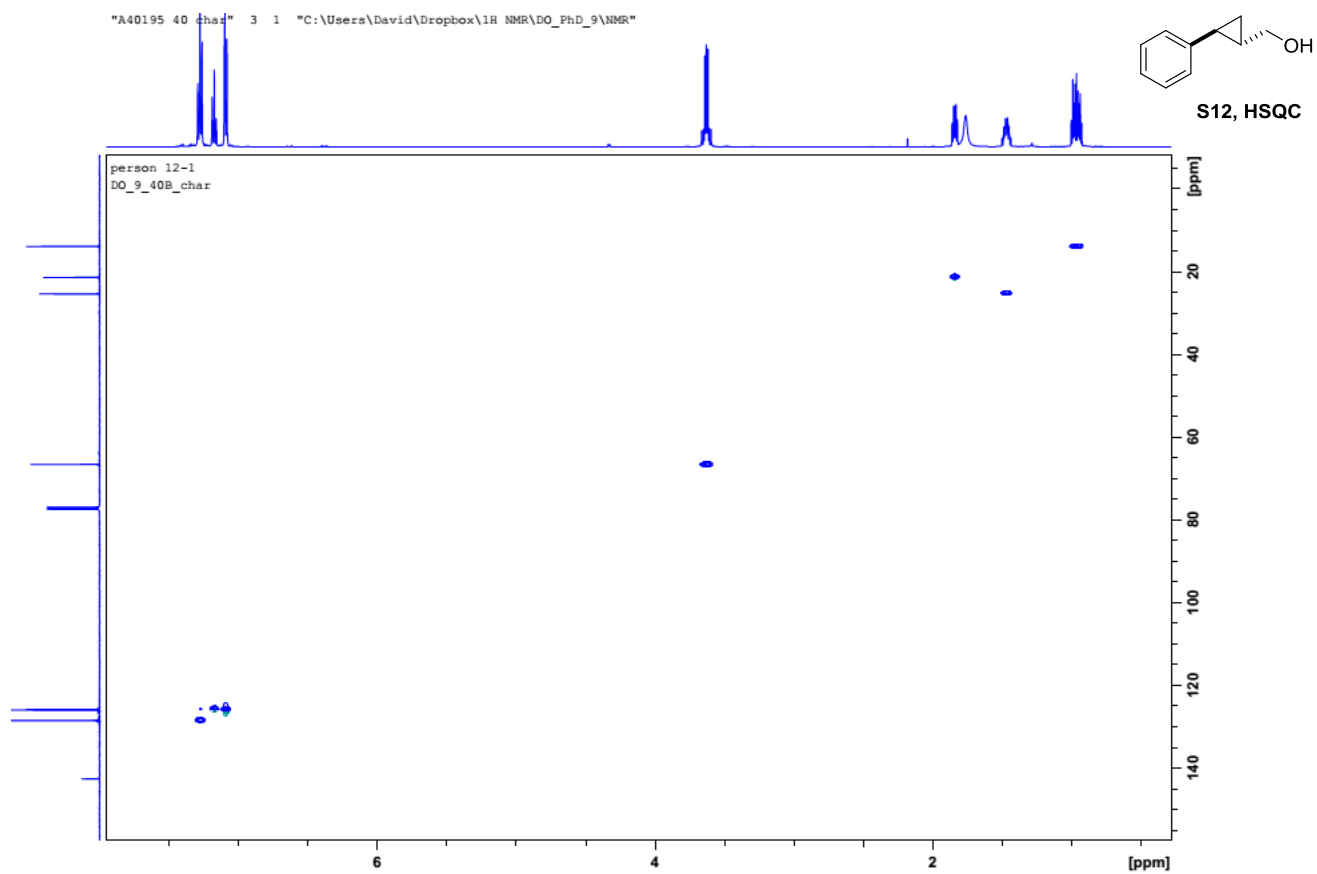


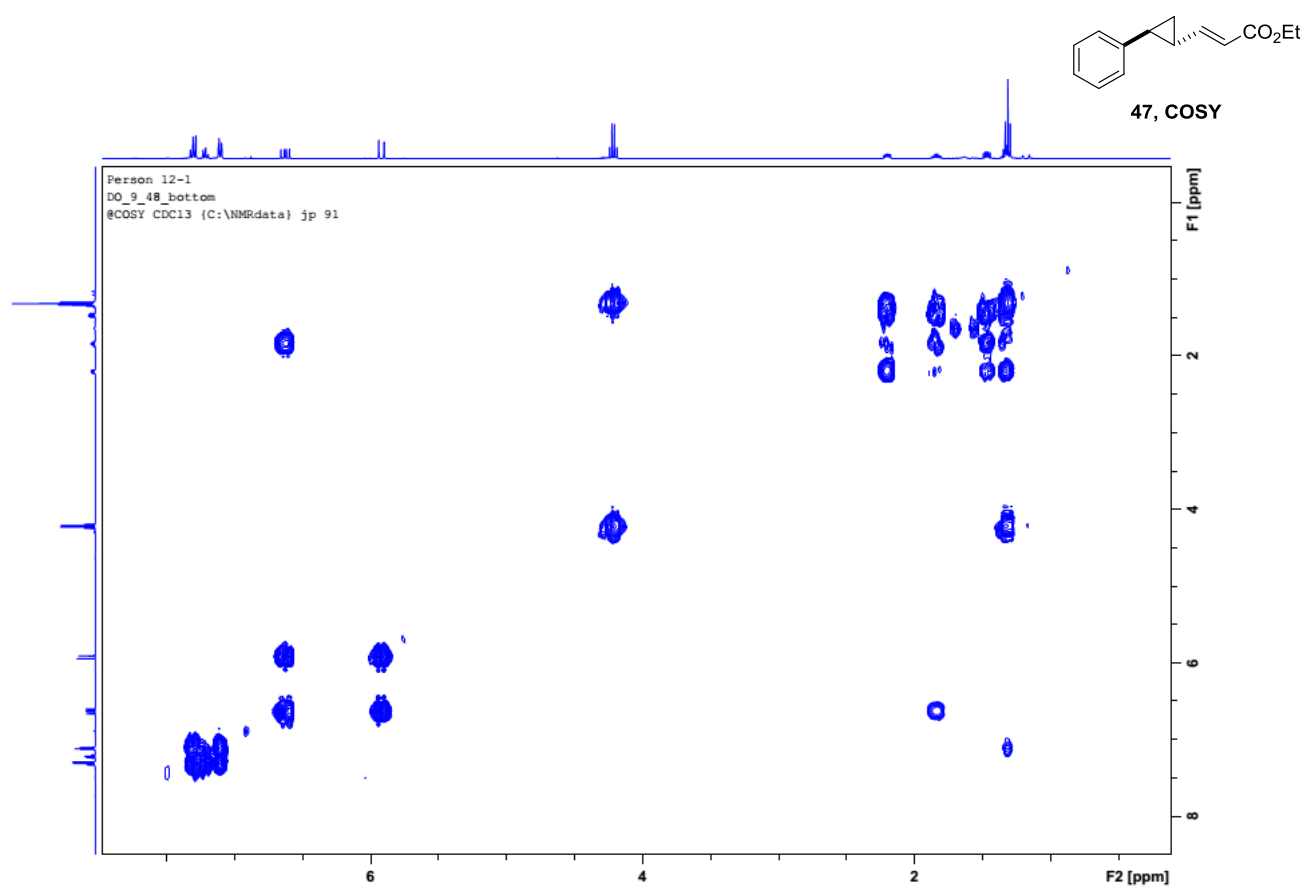
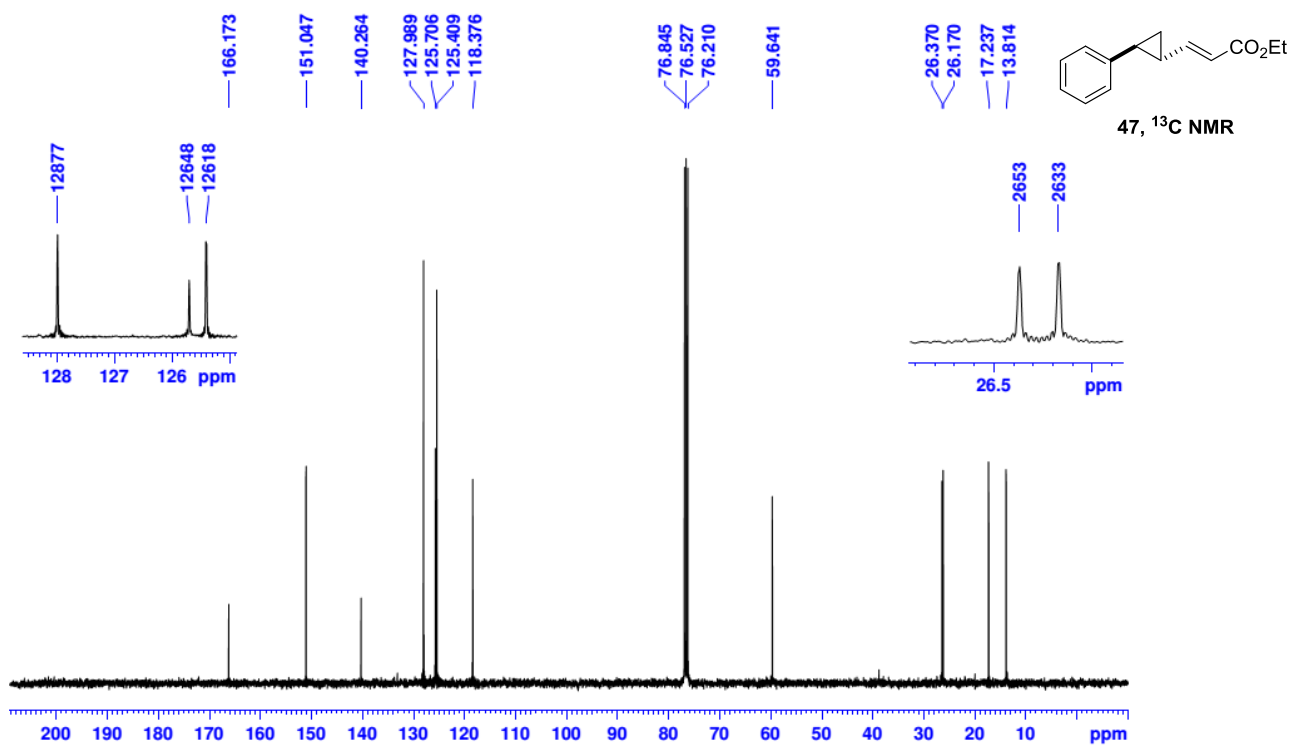


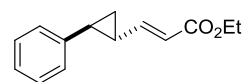




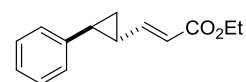
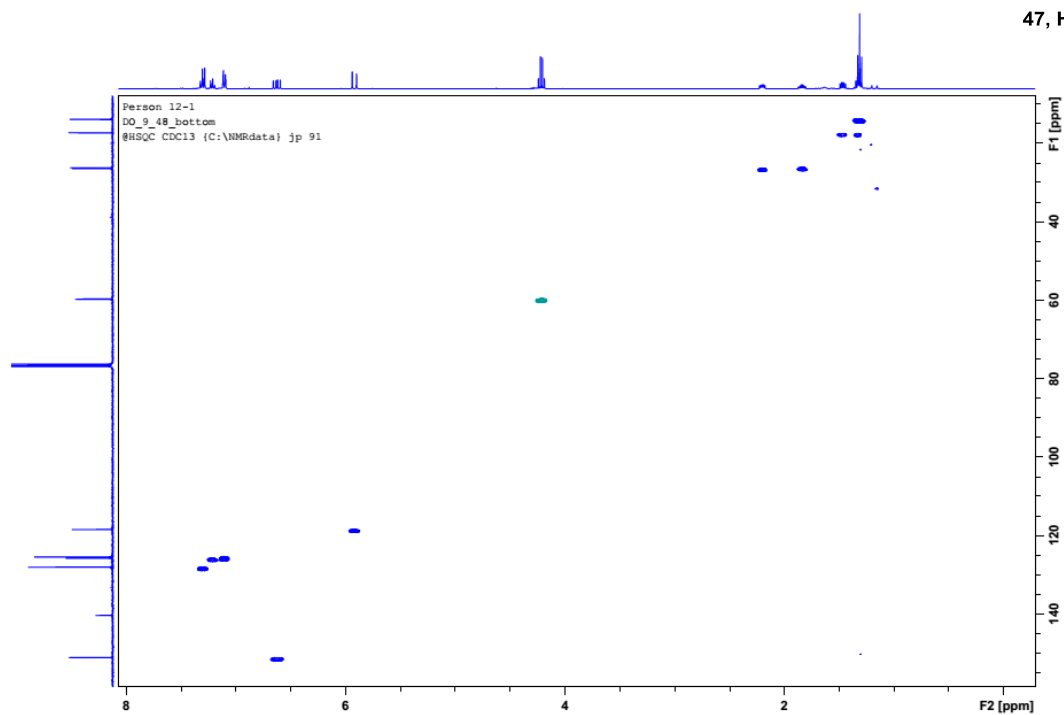




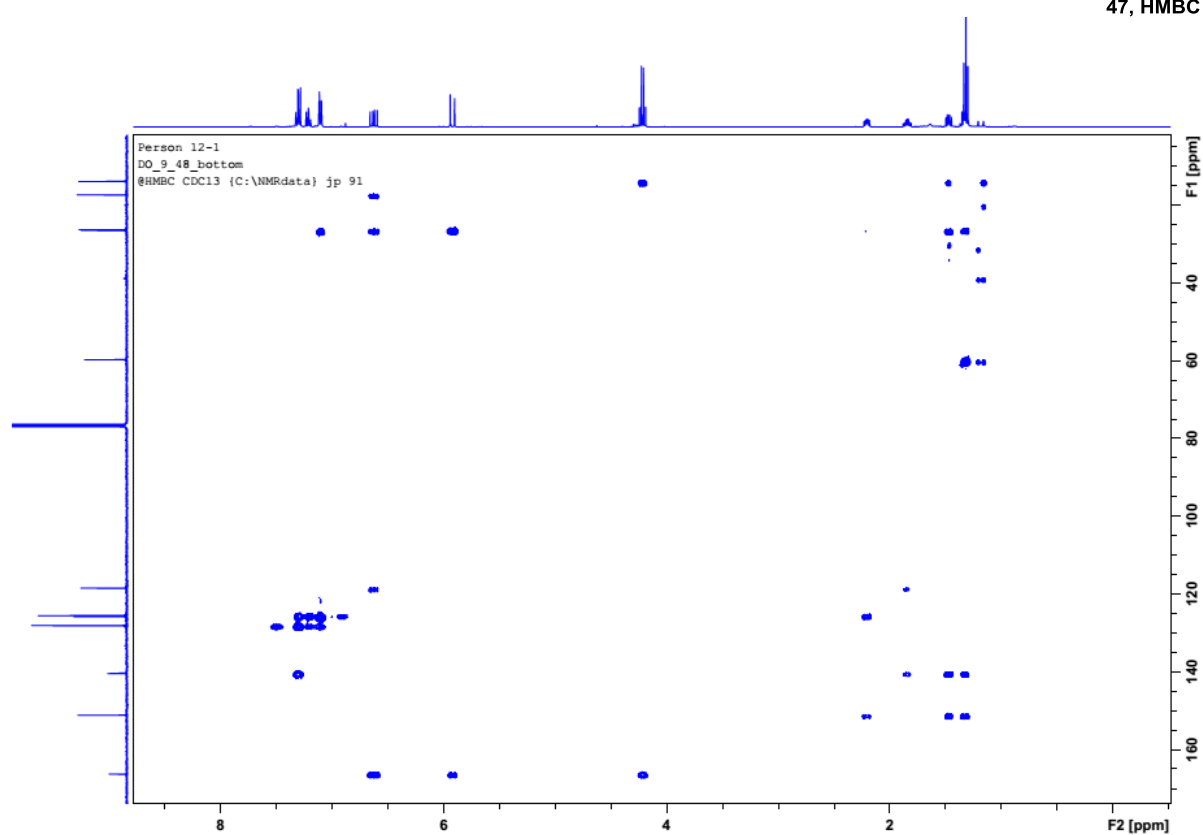


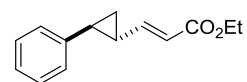


47, HSQC

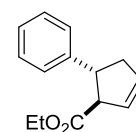
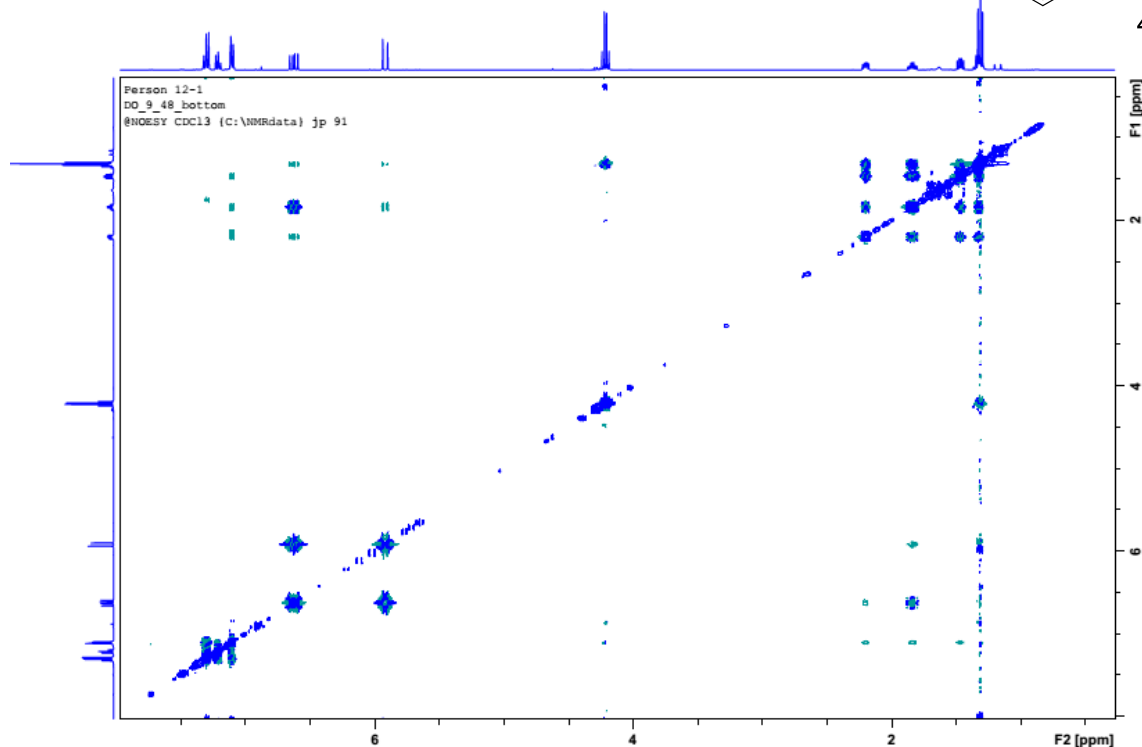


47, HMBC

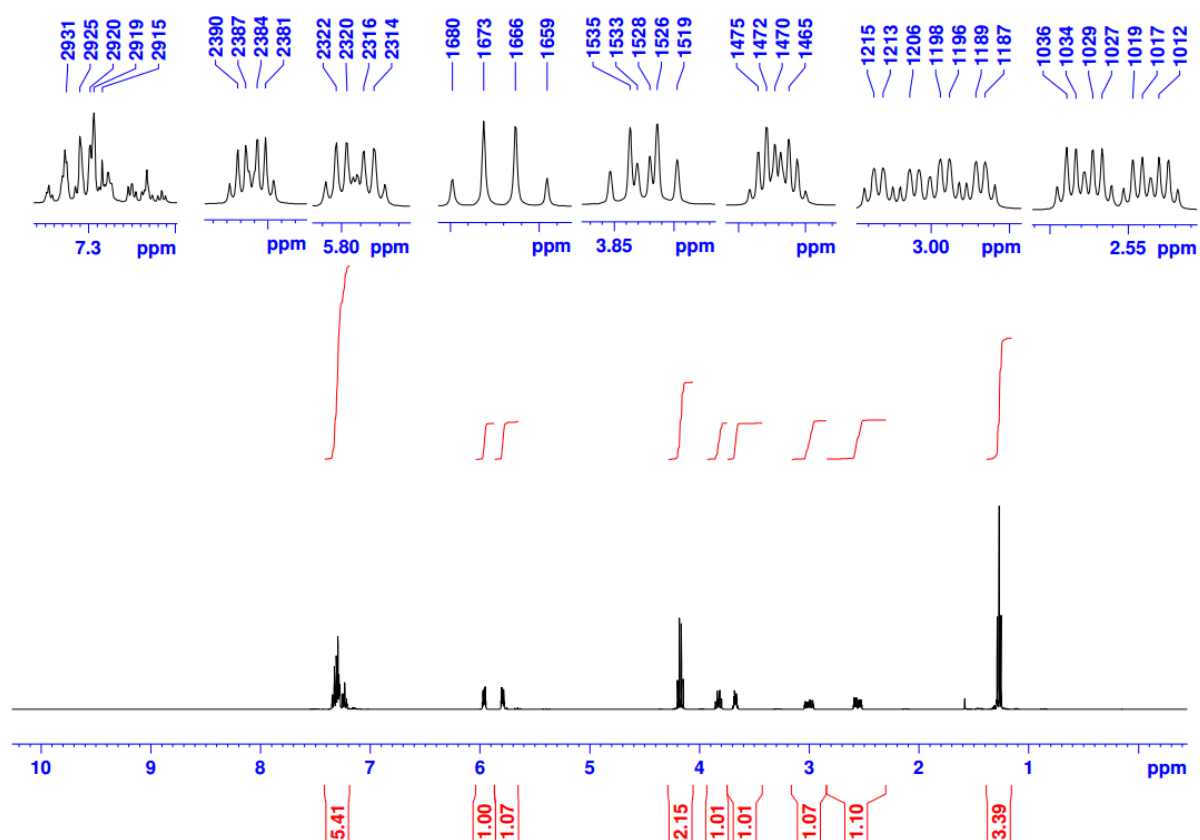


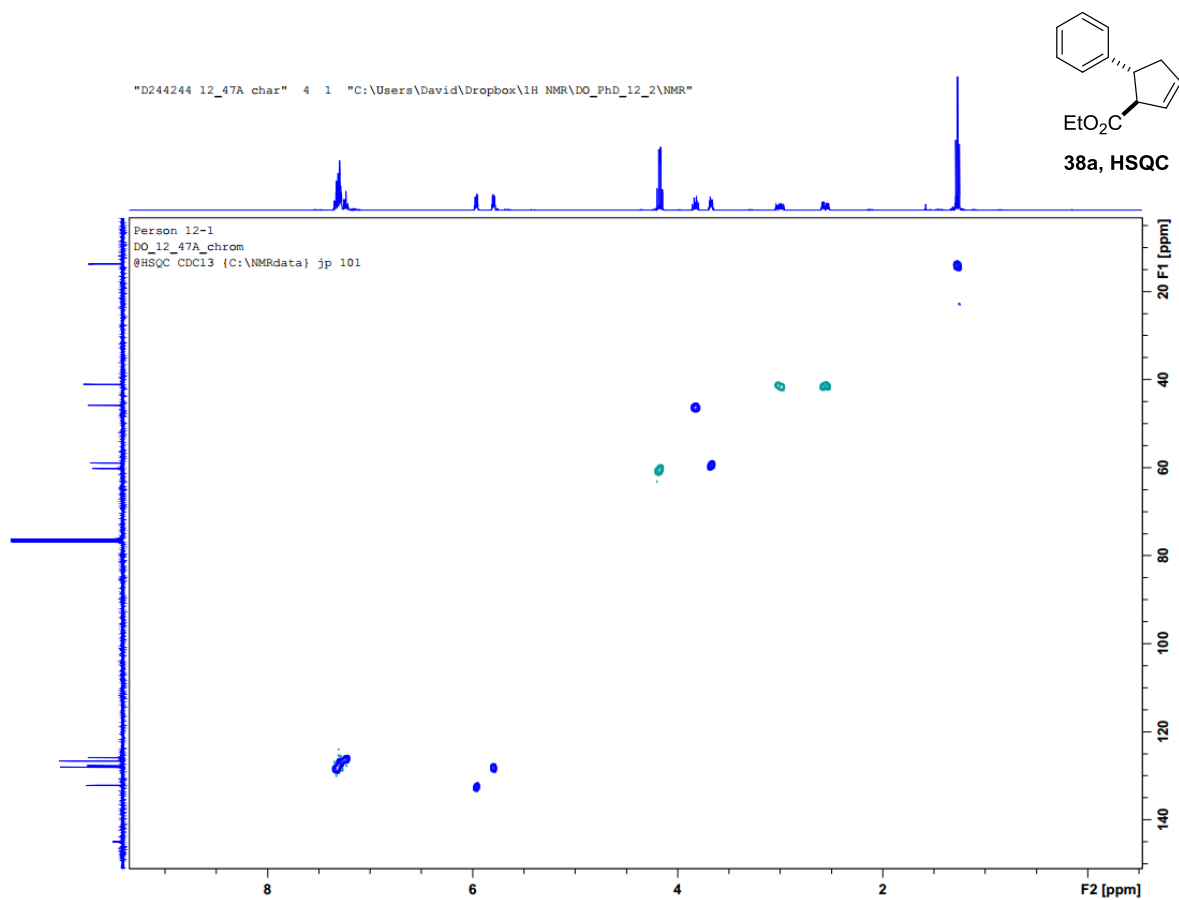
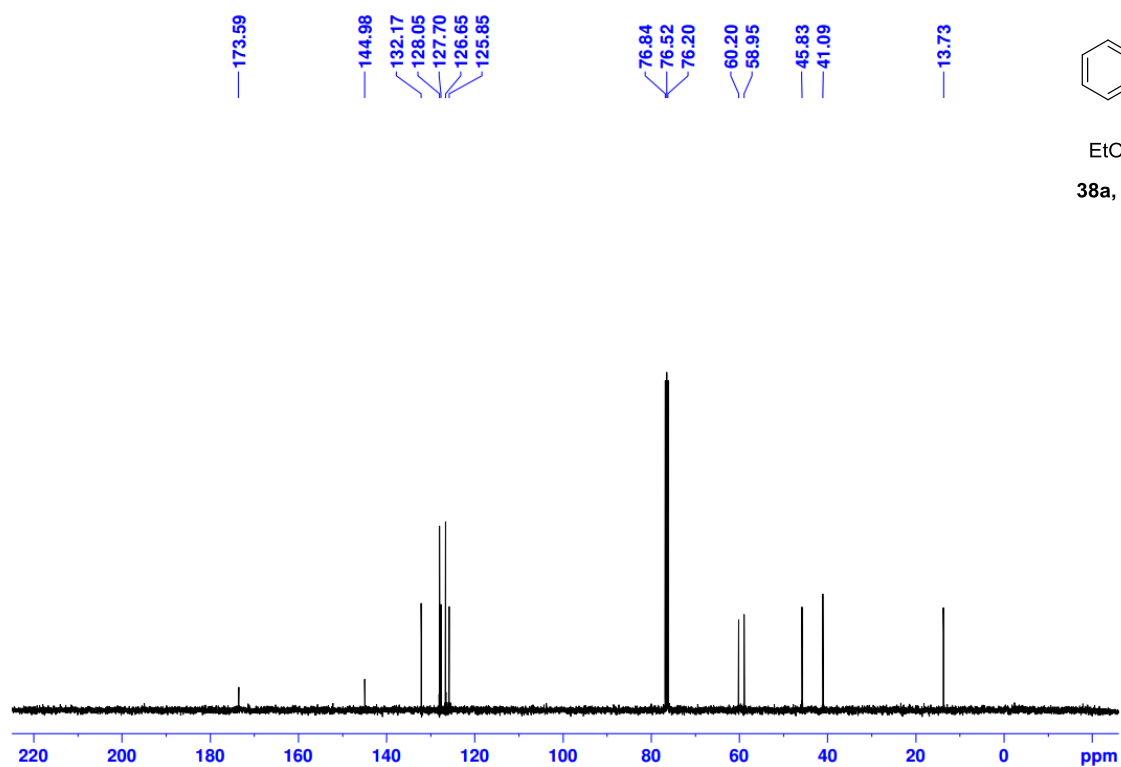


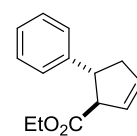
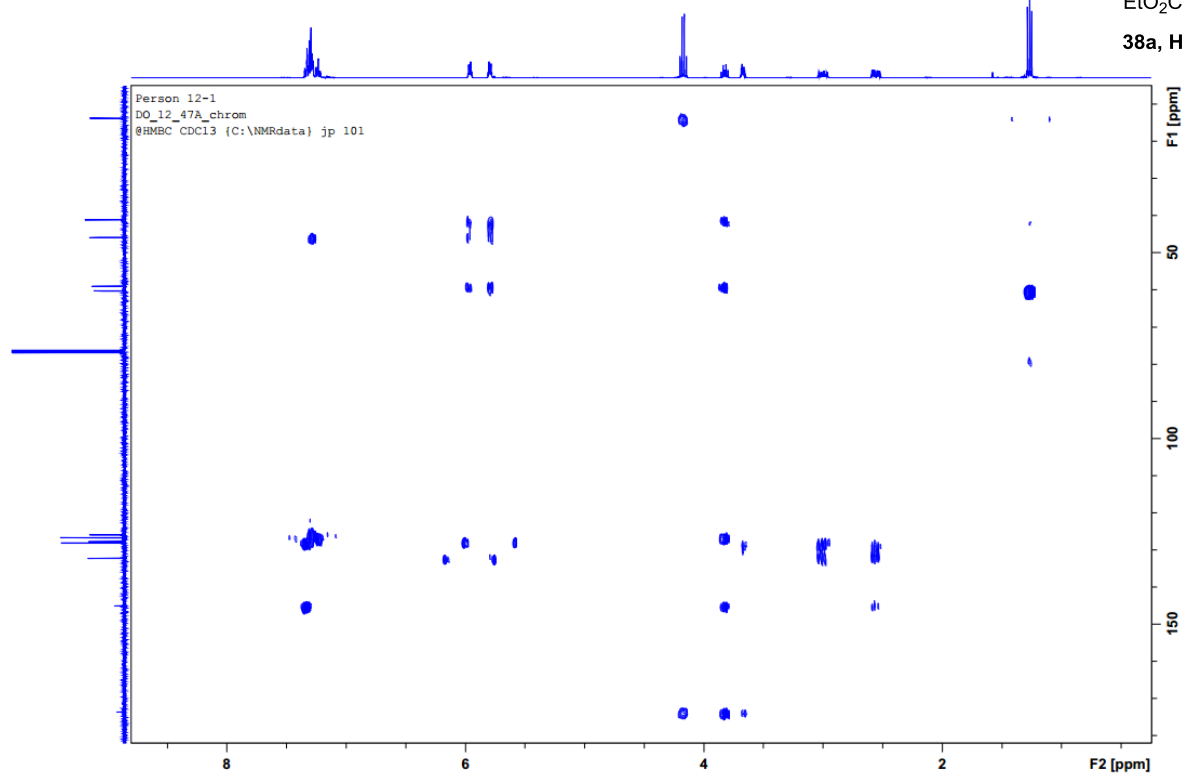
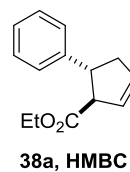
47, NOESY



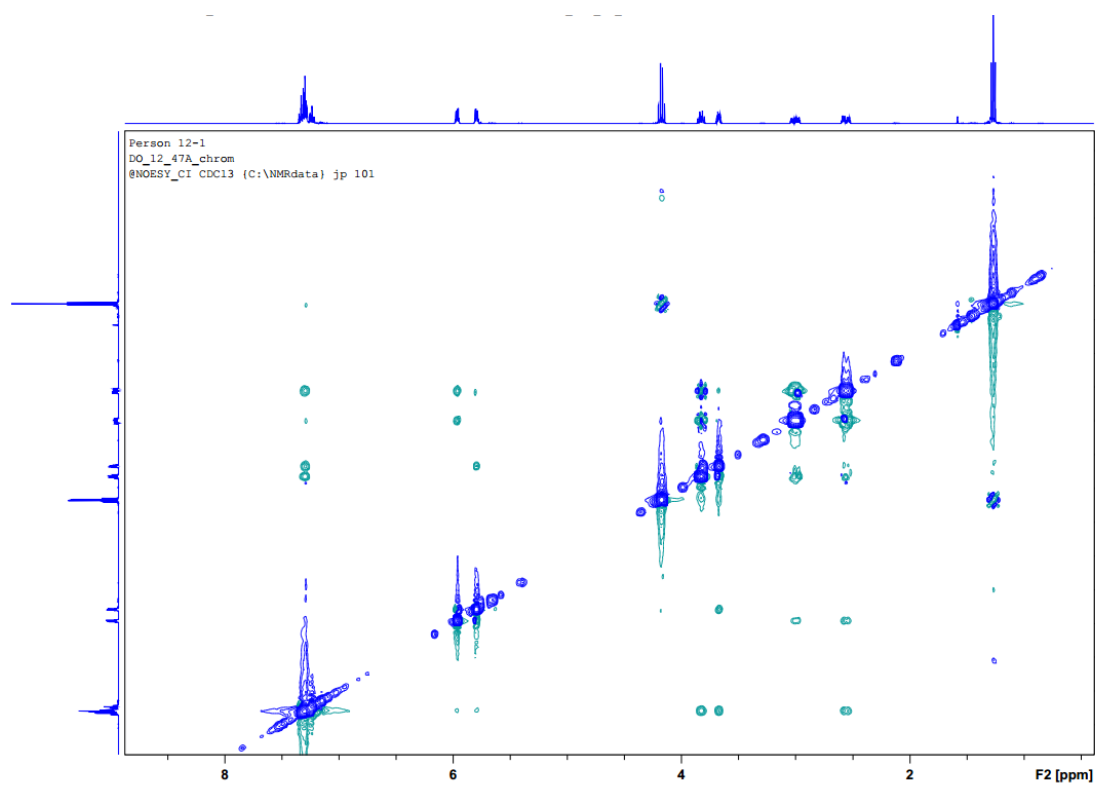
38a, ¹H NMR

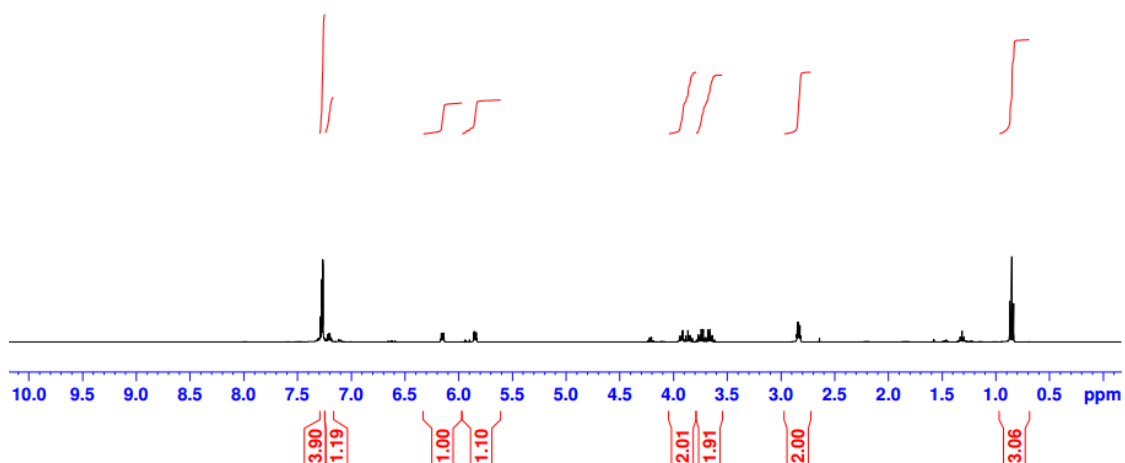
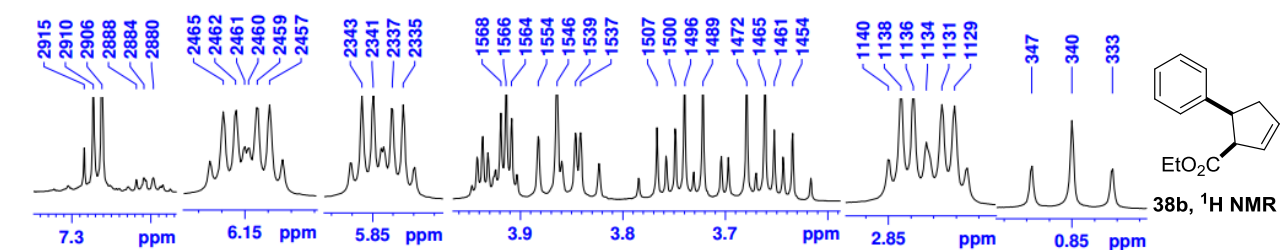


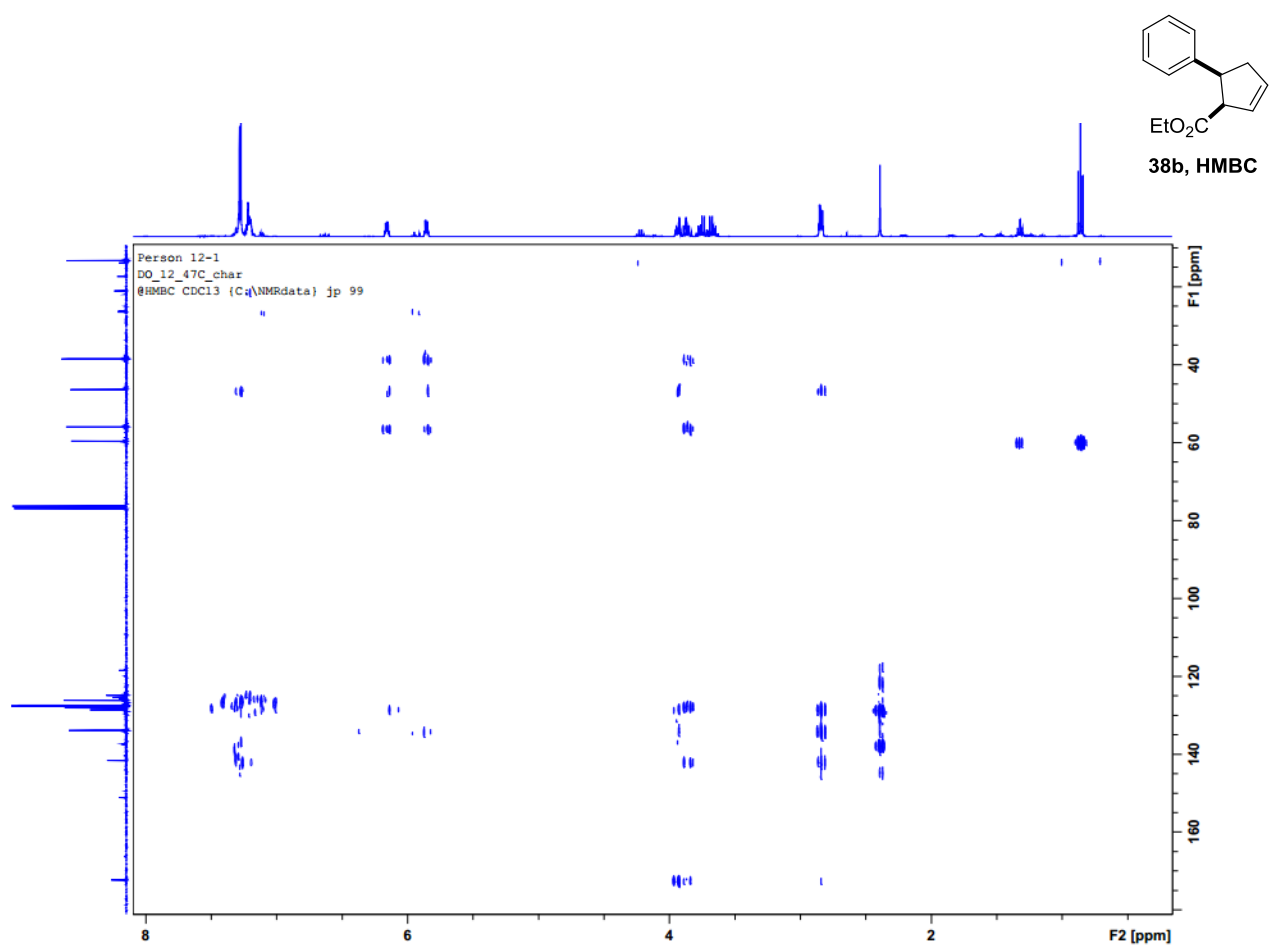
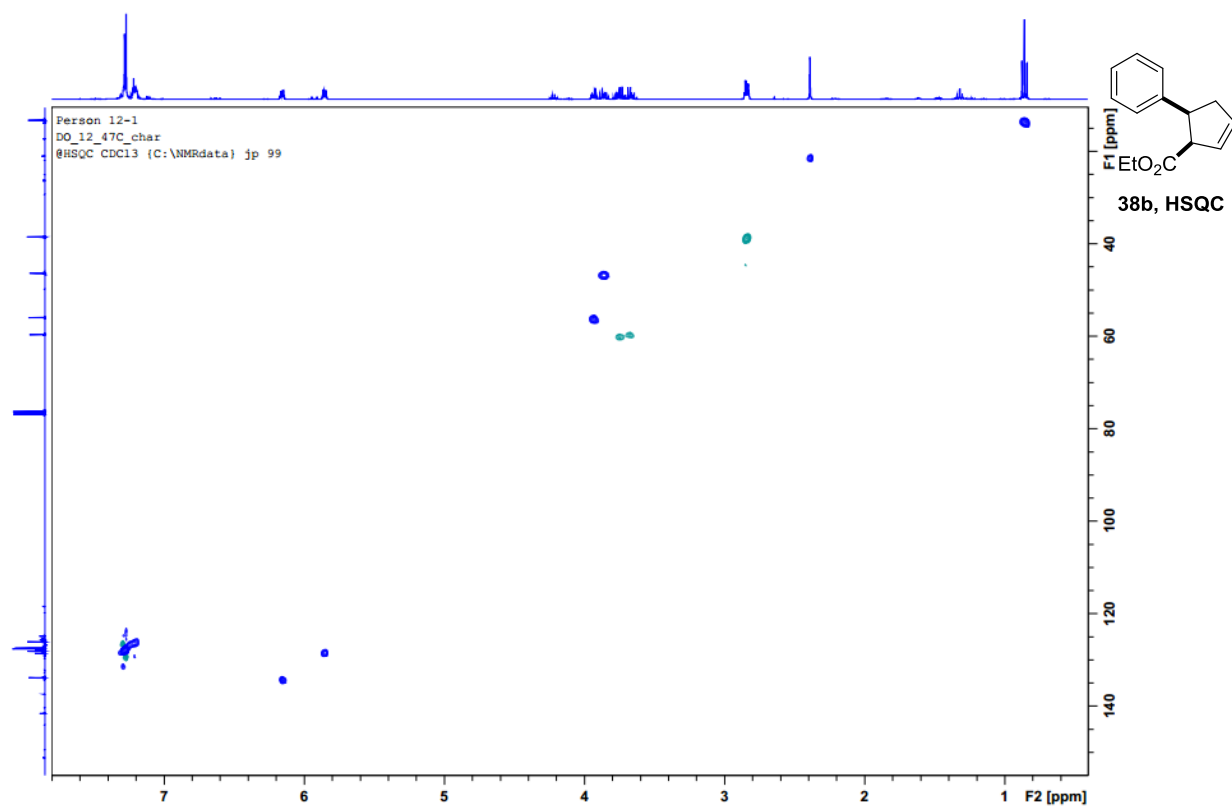


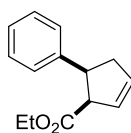


no Et-Ar through
space interactions
trans-relationship

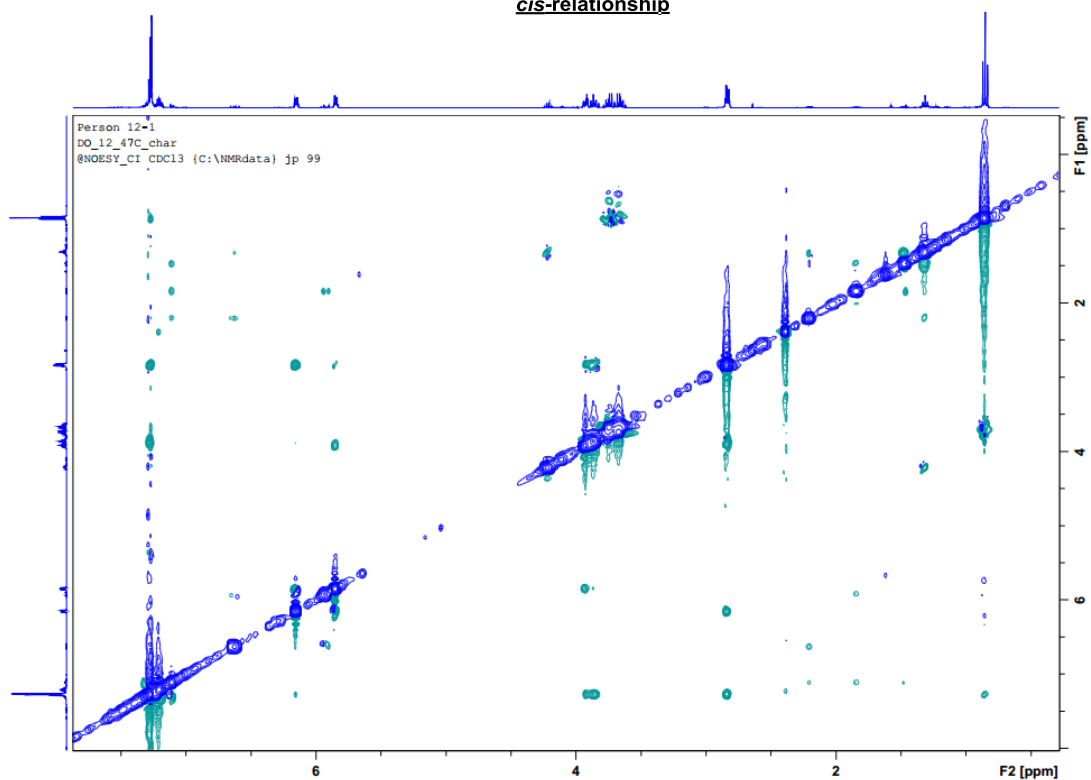








38b, NOESY
 observed Et-Ar through
 space interactions
cis-relationship



Decomposition Evidence for Furyl Vinyl Acetate **14a**

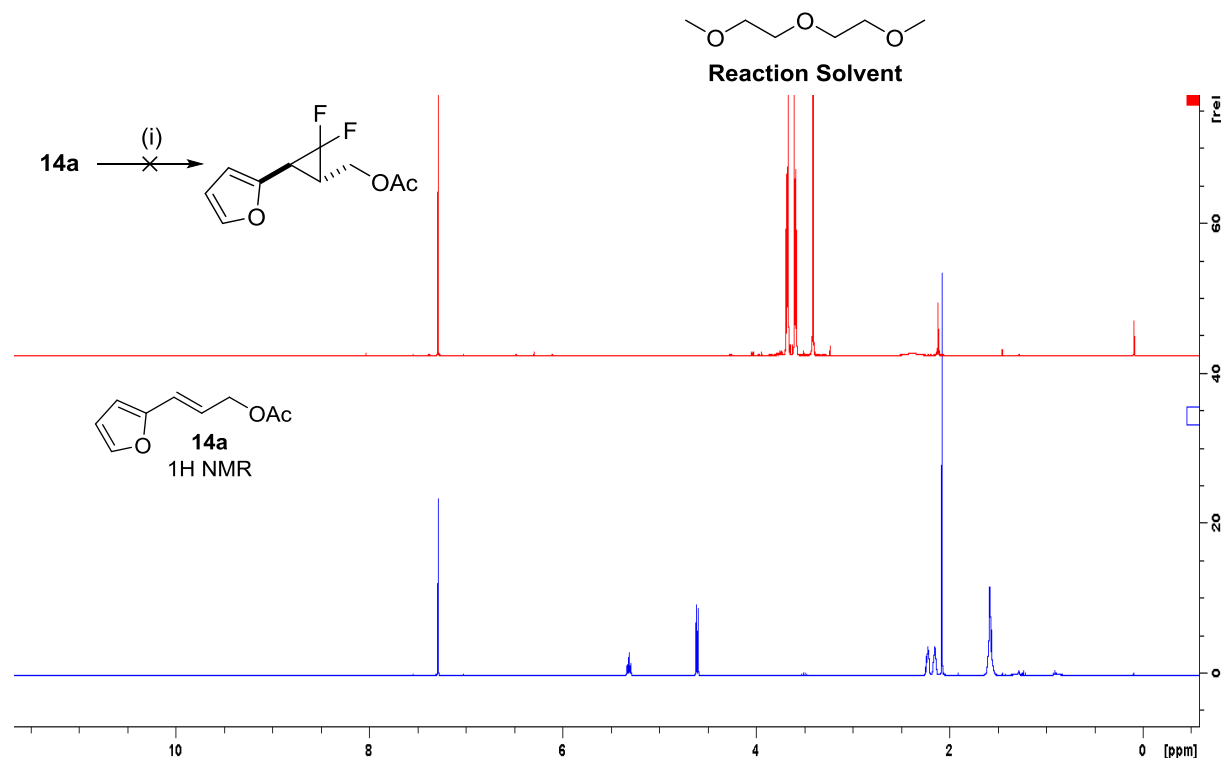


Figure S4: Overlay of ^1H NMR spectra representing 2-furyl vinyl acetate **14a** (bottom) and the resulting crude mixture from the failed difluorocyclopropanation. Conditions: (i) MDFA (2.5 eq.), TMSCl (2.5 eq.), KI (2.8 eq.), diglyme (1.17 eq.), 120 °C, 24 h.

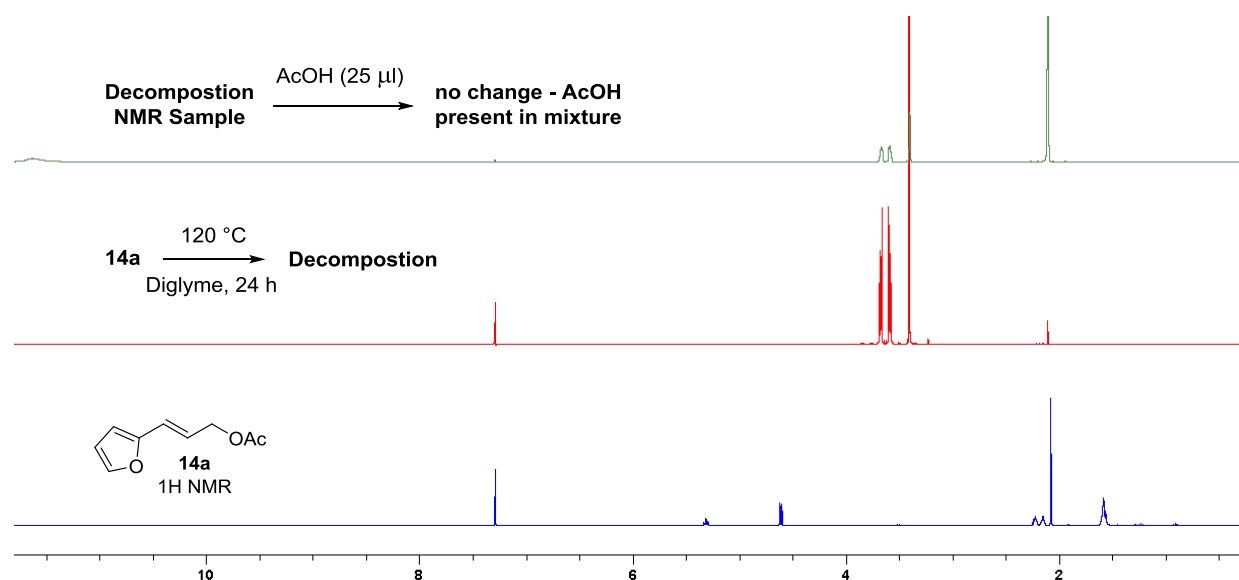
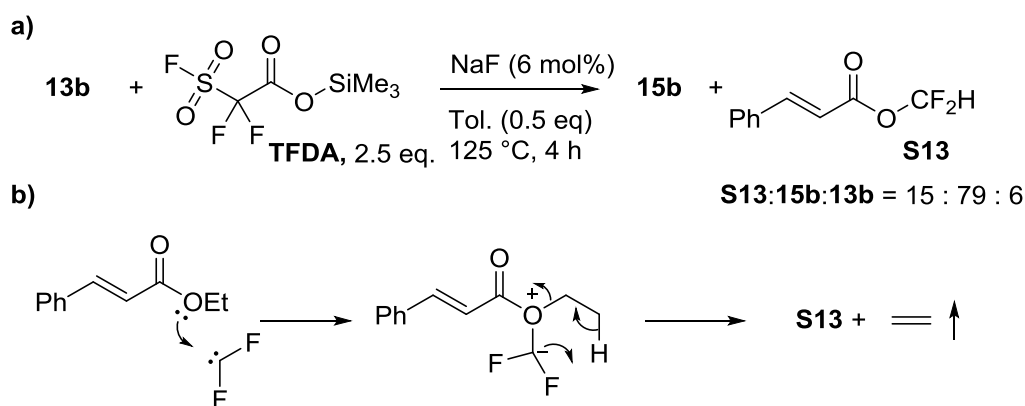


Figure S5: Overlay of ^1H NMR spectra representing 2-furyl vinyl acetate **14a** (bottom), resulting mixture after heating **14a** at 120 °C for 24 hours (middle) and spiking the middle NMR sample with 25 μl of AcOH which showed no change suggesting that the AcOH was the only visible side product from the decomposition experiment (top).

Difluorocyclopropanation of Ethyl Cinnamate

Both synthesised and commercial ethyl cinnamate **13b** gave similarly low conversion after difluorocyclopropanation (28% and 29%, respectively) so we were confident that there were no side products from the previous olefination step which were responsible for the poor conversion (**Table 3**, Entries 2-3). Again, slightly higher conversions could be obtained by decreasing the reaction time to 4 hours (**Table 3**, Entry 4, 37% conversion) but **15b** could not be separated from **13b** using either chromatography or distillation. Under the same conditions, cinnamyl acetate (**14b**) had given 100% conversion to the desired difluorocyclopropane.^{S20} The dramatic reactivity difference between **14b** and **13b** can be attributed to increased electron-deficiency of the alkene in **13b**. Selectivity experiments carried out by Dolbier and co-workers showed that difluorocarbene addition to a 1:1 mixture of butyl acrylate and 1-octene favoured the latter at 120 °C (product ratio of 1:3.3), consistent with the lower reactivity observed for **13b**.^{S22} Other literature methods^{S23,24} using commercial reagents were previously unsuccessful when used for the difluorocyclopropanation of cinnamyl acetate (**14b**)^{S20} and were therefore not investigated for these less reactive alkenoates.

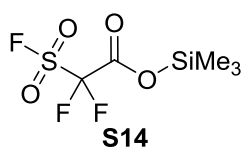
Dolbier and co-workers reported more success in the synthesis of **15b** using alternative MDFA conditions (64%, ¹⁹F NMR conversion);^{S25} we were able to replicate their results (69% ¹H NMR conversion) but felt that the longer reaction time of 48 hours would be detrimental to the product recovery of the more reactive alkenoates. Higher conversion of 81% was achieved for this substrate by the same group using trimethylsilyl 2,2-difluoro-2-(fluorosulfonyl)acetate (TFDA) as the difluorocarbene precursor but it is unclear if this is an isolated or NMR yield.^{S22} This reagent is less practical than others since it is prone to hydrolysis; purification is necessary before every reaction. We observed similar conversion with TFDA (79%, determined by ¹H NMR) but the isolation of synthetically useful quantities of **15b** proved difficult due to the presence of starting alkenoate **13b** and the previously unreported difluoromethyl ester side product **S13** (**Scheme S4a**, see below for a full discussion on difluorocyclopropanation of **13b** with TFDA). We currently do not have a reason for the formation of **S13** but it is proposed to proceed via a mechanism similar to that of the difluoromethylation of acids reported by Wu and Chen^{S26} and driven by the elimination of ethene (**Scheme S4a**).



Scheme 5: a) Difluorocyclopropanation of **13b** using TFDA (ratios determined by ^1H NMR). b) Proposed mechanism for the formation of side product **S13**.

Reported difluorocyclopropanation methodologies are generally screened against a set of simple alkene substrates but reactivity issues are rarely discussed. We have used alkenoates **13a** and **13b** to assess the most reactive procedures in the literature and highlighted the synthetic limitations for electron deficient olefins. For this study, the main purpose of the synthetic investigations was to obtain a range of substituted cyclopropane precursors in order to test computational predictions. No further screening of conditions was carried out, but recent synthetic advances with metal-mediated difluorocyclopropanation reported by Ichikawa and co-worker, look to be a more promising method for the synthesis of difluorocyclopropyl esters **15b**.^{S27}

Preparation of trimethylsilyl 2,2-difluoro-2-(fluorosulfonyl)acetate (**S14**)



A mixture of chlorotrimethylsilane (4.9 mL, 38.8 mmol) and commercial trimethylsilyl 2,2-difluoro-2-(fluorosulfonyl)acetate (TFDA, **S14**, 1 mL, 9.7 mmol, 80% purity determined by ^{19}F NMR) was refluxed (110 $^{\circ}\text{C}$) for 1 hour under an atmosphere of argon. The reaction mixture was cooled to room temperature and the water condenser was replaced with an oven dried distillation apparatus and the glassware cooled under an atmosphere of argon. Excess TMSCl was removed (90 $^{\circ}\text{C}$, 600 mbar) and the residual **S14** was stored under argon at room temperature. The ^{19}F NMR spectrum of the residue confirmed reagent purity at > 95% and **S14** used immediately for a difluorocyclopropanation reaction. ^{19}F NMR (376 MHz,

CDCl_3): $\delta = -41.2$ (dd, $J = 4.6, 4.2$ Hz, FSO_2CF_2 , 1F), -103.1 ppm (d, $J = 4.4$ Hz, FSO_2CF_2 , 2F). The data was in agreement with that reported by Tian and co-workers.^{S28}

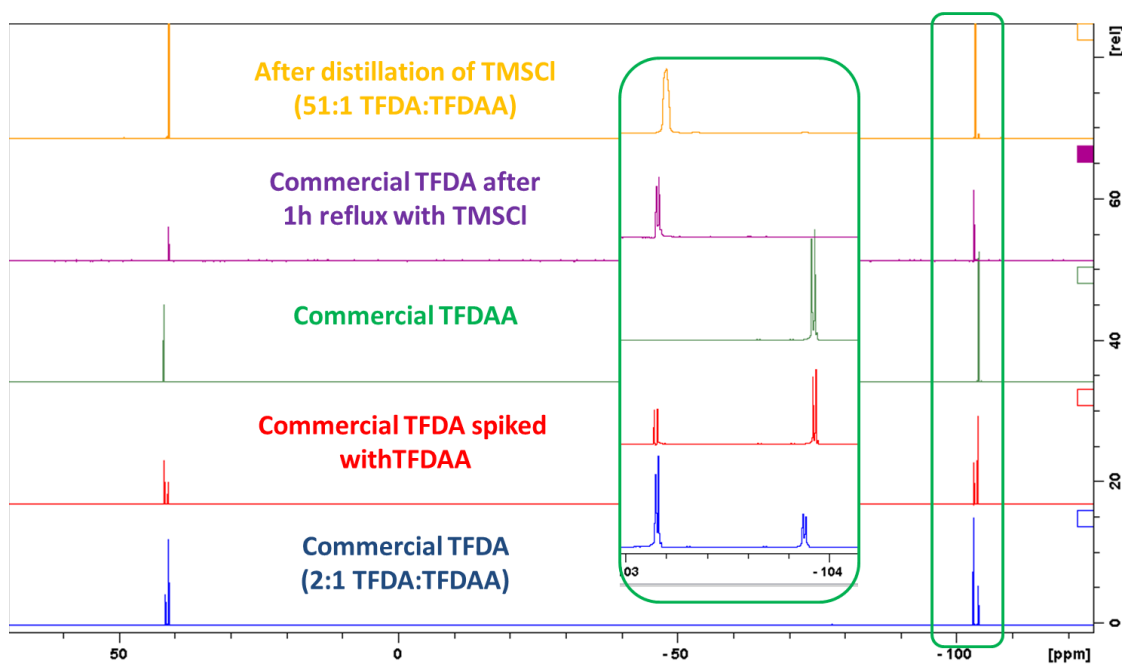


Figure S6: ^{19}F NMR analysis of the synthesis and purification of TFDA.

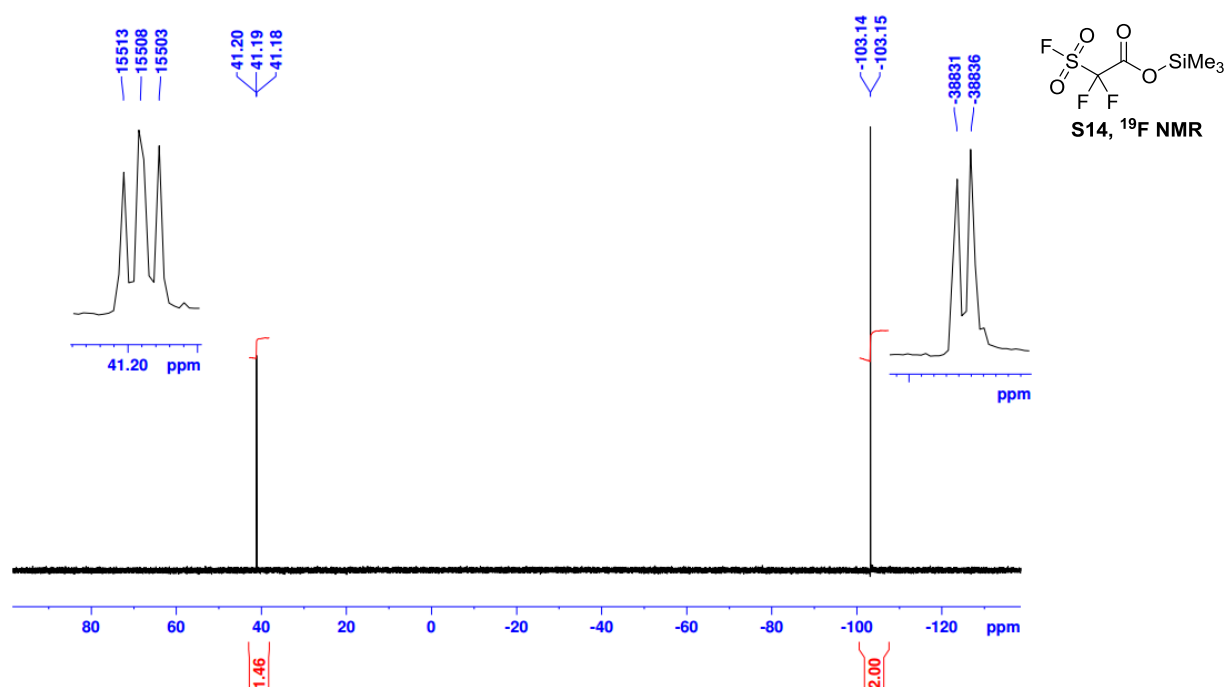
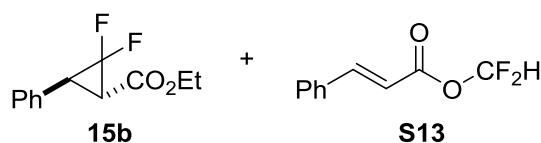


Figure S7: ^{19}F NMR for clean TFDA used in difluorocyclopropanation reaction.

Attempted difluorocyclopropanation of ethyl cinnamate with TFDA



An oven dried two-necked round bottom flask containing sodium fluoride (7 mg, 0.17 mmol) was sealed with a SubaSeal, and the salt was stirred and lightly flame dried under an atmosphere of argon. A low boiling point water condenser with a gas outlet connected to an argon/vacuum manifold was attached to the reaction flask and the atmosphere was purged three times. Ethyl cinnamate (0.48 mL, 2.84 mmol) followed by toluene (0.15 mL, 1.42 mmol) were added and the colourless suspension was heated to 125 °C. Once the reaction temperature had been reached, freshly distilled TFDA (1.4 mL, 7.1 mmol) was added dropwise over a period of 3 hours using a syringe pump. The mixture was stirred for a further 1 hour (total reaction time of 4 hours). The reaction mixture was cooled to room temperature and the reaction mixture was quenched with addition of water (10 mL) and diethyl ether (10 mL). The organic layer was separated and the aqueous layer was extracted with diethyl ether (4 x 10 mL). The original organic layer and the extracts were combined, dried (MgSO₄) and concentrated under reduced pressure to remove volatile materials. The ¹H NMR spectrum of the crude reaction mixture was used to determine the ratio of **13b**, **15b** and **S13**.

A similar crude reaction mixture was purified by column chromatography on silica gel (1:19 to 1:9 Et₂O in hexane) and a mixture of **S13** and **13b** (4:1 ratio determined by NMR) was isolated.

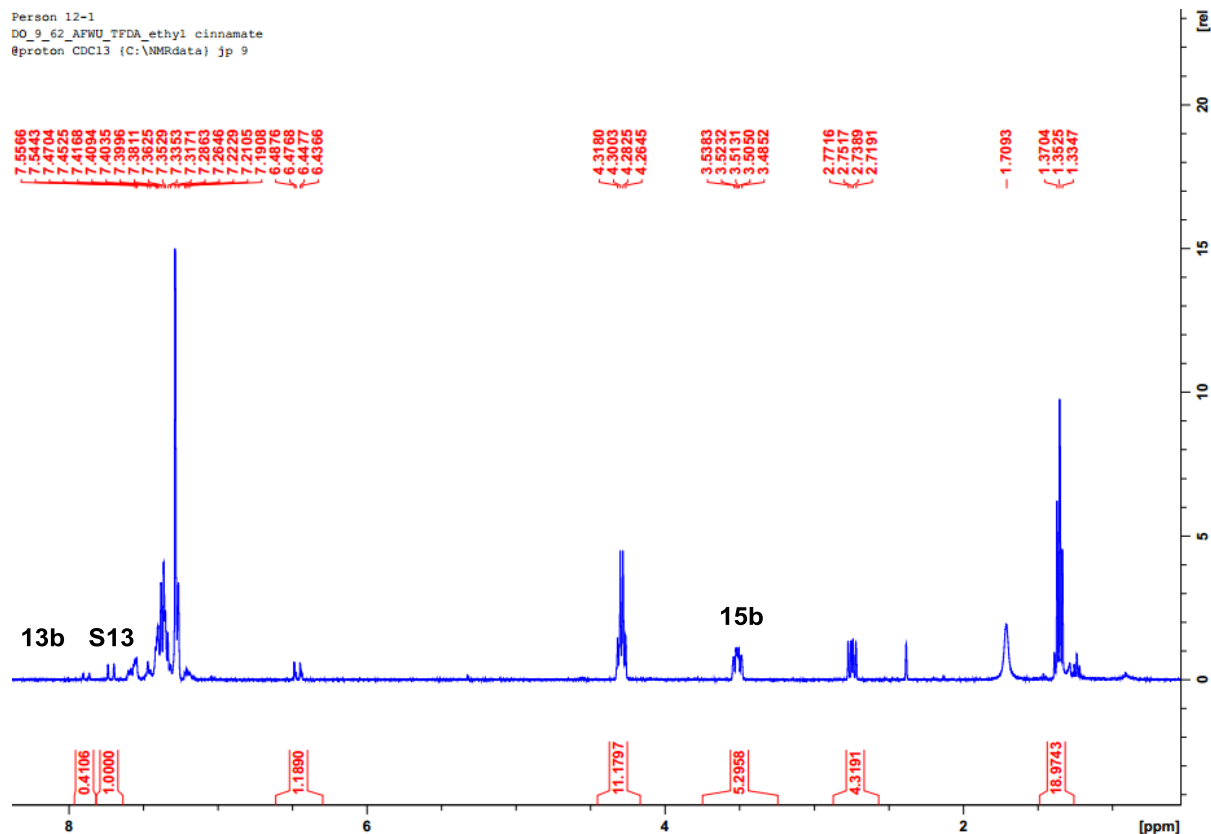
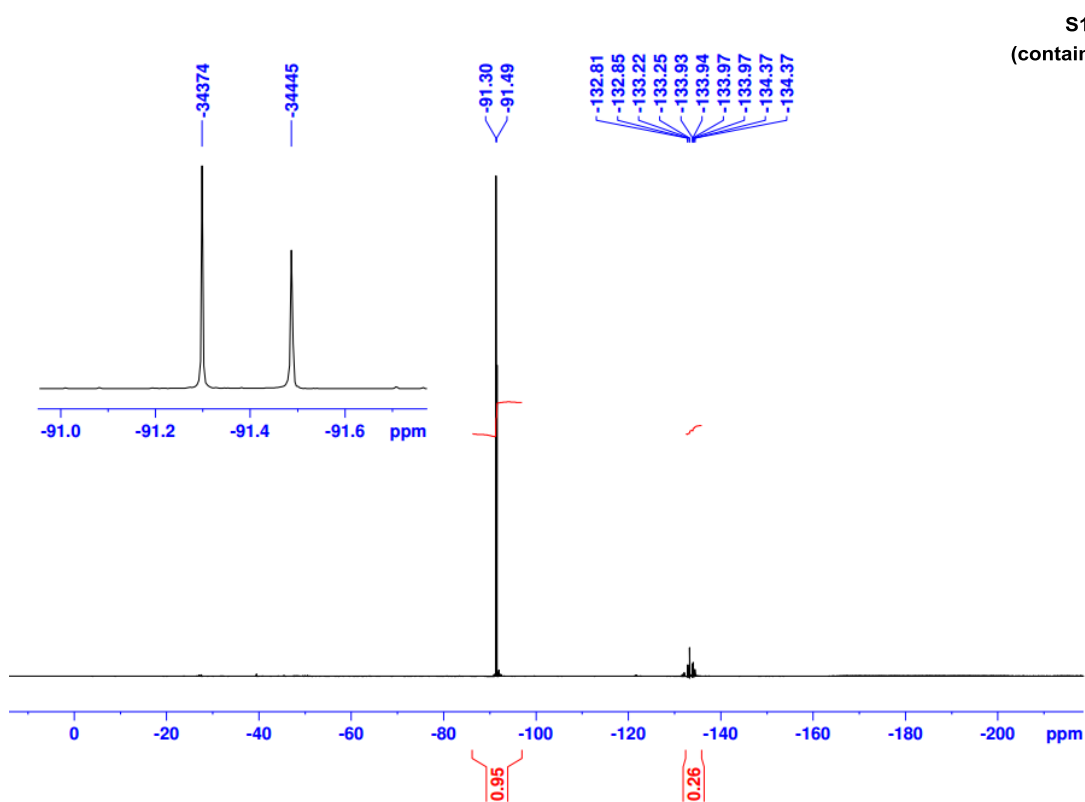
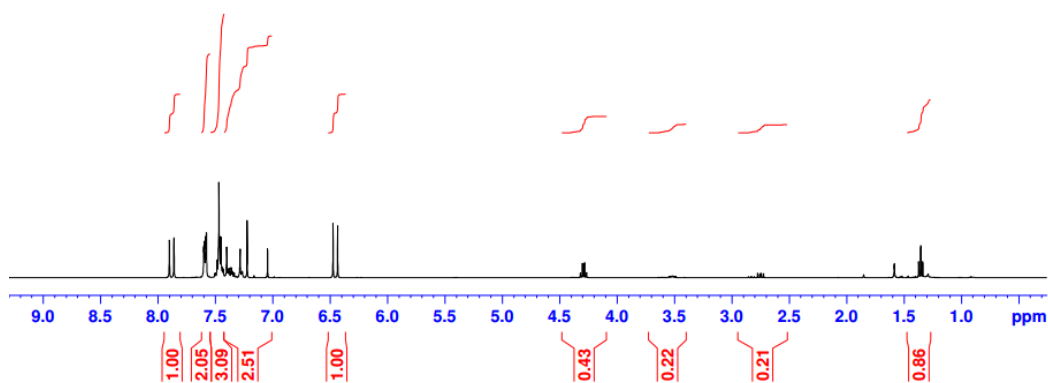
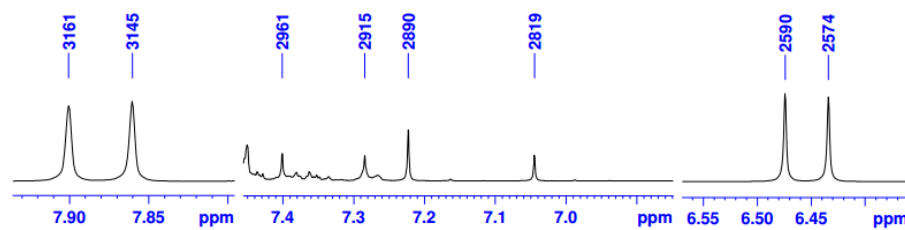
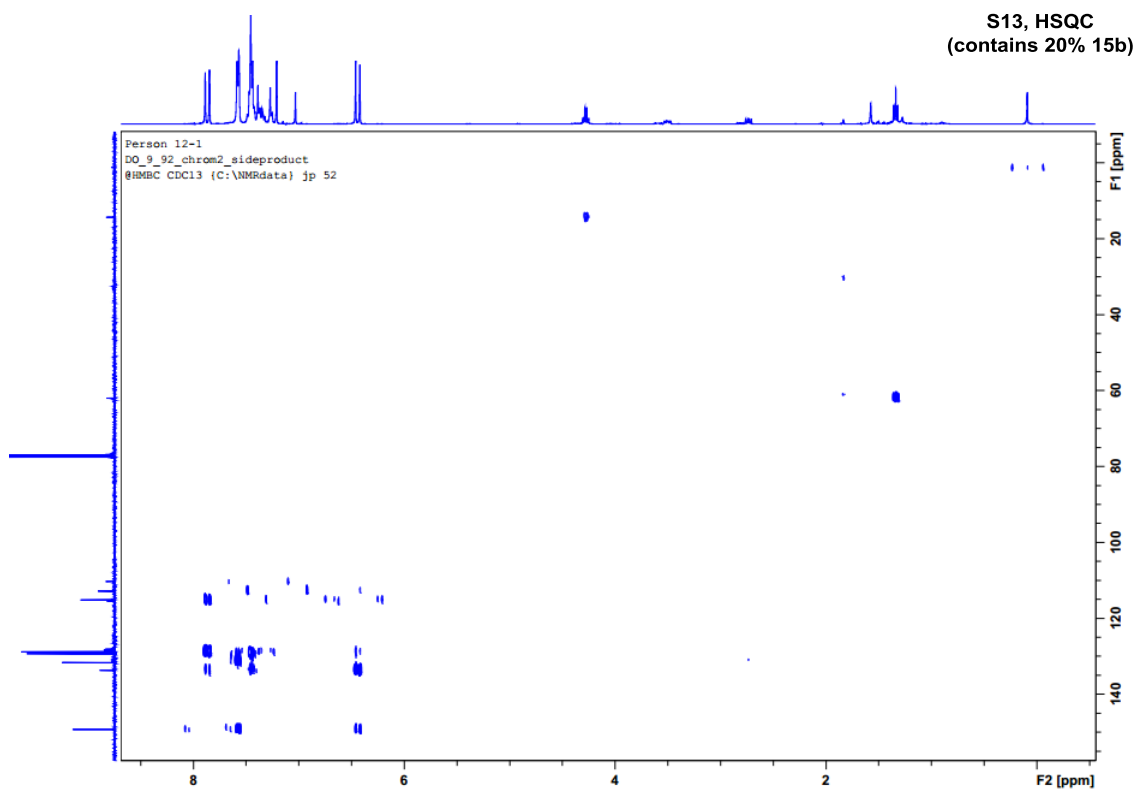
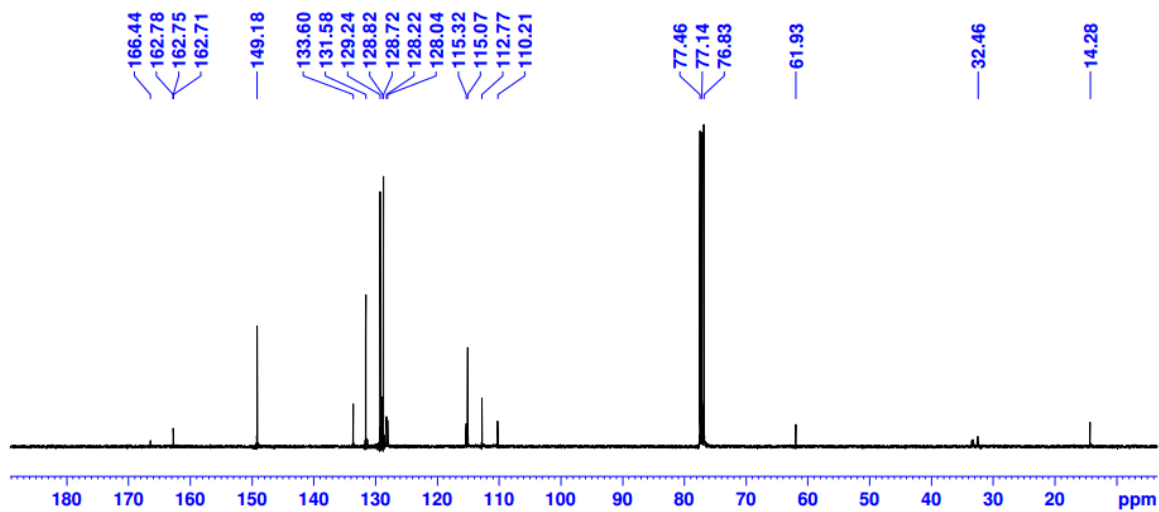
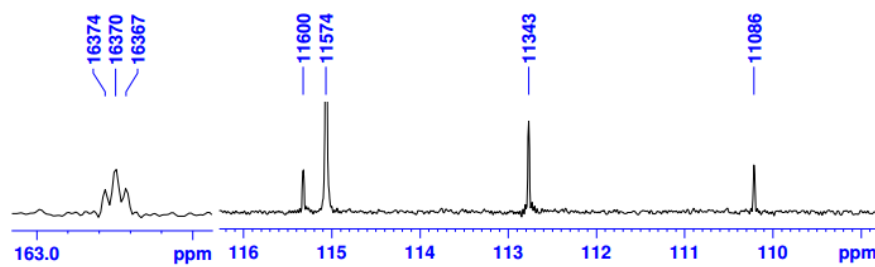


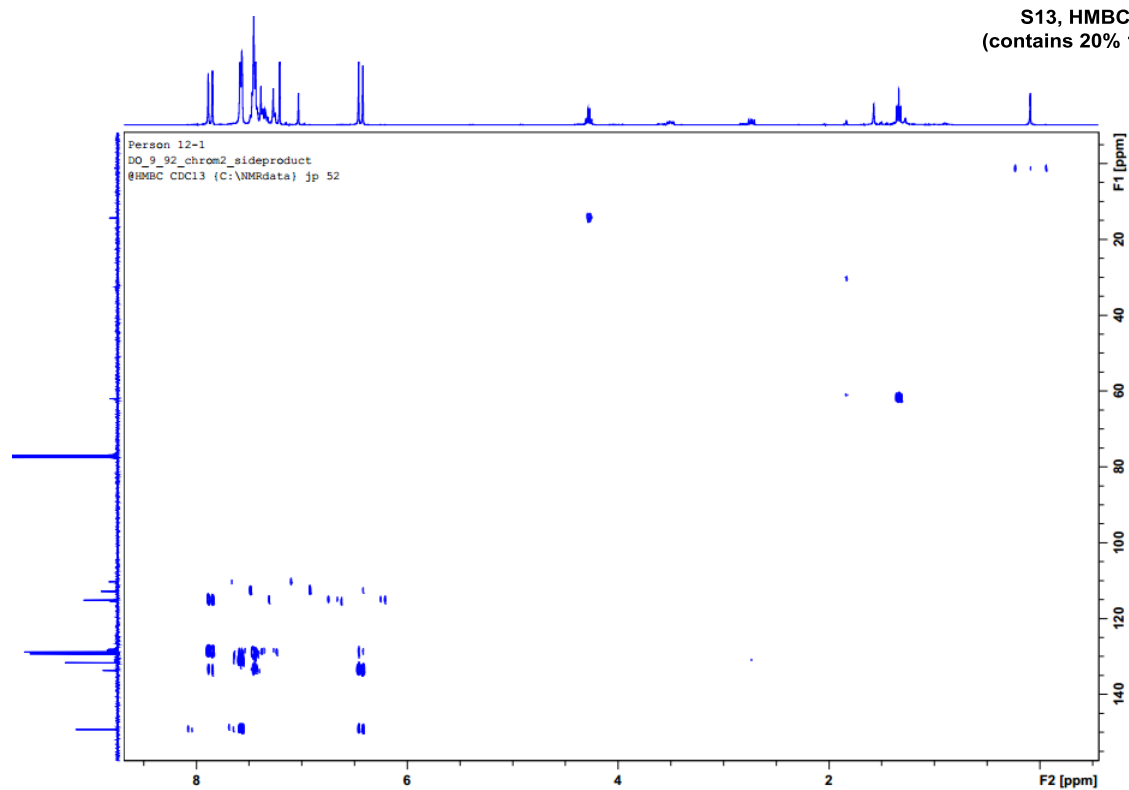
Figure S8: Crude ^1H NMR used to relative conversion ratio from TFDA difluorocyclopropanation.

Extracted data for **S13**: $R_f = 0.26$ (1:4 Et_2O in hexane); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.88$ (d, $J = 16.0$ Hz, $\text{ArCH}=\text{CH}$, 1H), 7.60–7.58 (m, ArH , 3H), 7.49–7.43 (m, ArH , 2H), 7.22 (t, $^2J_{\text{H-F}} = 71.2$ Hz, CF_2H , 1H), 6.56 ppm (d, $J = 16.0$ Hz, $\text{CH}=\text{CHCO}$, 1H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 162.8$ (t, $J_{\text{C-F}} = 3.4$ Hz), 149.2, 133.6, 131.6, 129.2, 128.8, 115.1, 112.8 ppm (t, $^1J_{\text{C-F}} = 257.1$ Hz); ^{19}F NMR (376 MHz, CDCl_3): $\delta = -91.4$ ppm (d, $^2J_{\text{F-H}} = 71.2$ Hz); $\bar{\nu}/(\text{film}) = 1738, 1634, 1059, 980$ cm^{-1} ; MS (CI): m/z (%): 227 (4) $[\text{M}+\text{C}_2\text{H}_5]^+$, 199 (47) $[\text{M}+\text{H}]^+$, 157 (6), 131 (100) $[\text{M}-\text{OCF}_2\text{H}]^+$; t_R (GC) = 10.45 minutes.





S13, HMBC
(contains 20% 15b)



Evidence of Difluorocarbene-Diglyme Reaction

An oven dried two-necked round bottom flask containing sodium chlorodifluoroacetate (275 mg, 1.8 mmol) was sealed with a SubaSeal, and the salt lightly flame dried under vacuum. The atmosphere was replaced with nitrogen and the flask allowed to cool to room temperature. A low boiling point water condenser with a gas outlet connected to an argon/vacuum manifold was attached to the reaction flask and the atmosphere was purged three times. Diglyme (1 mL) was added and a reaction aliquot (< 0.1 mL) was taken and analysed by ^{19}F NMR. The saturated mixture was heated to 180 °C and reaction aliquot taken at different time points and analysed by ^{19}F NMR (see **Figure S9**).

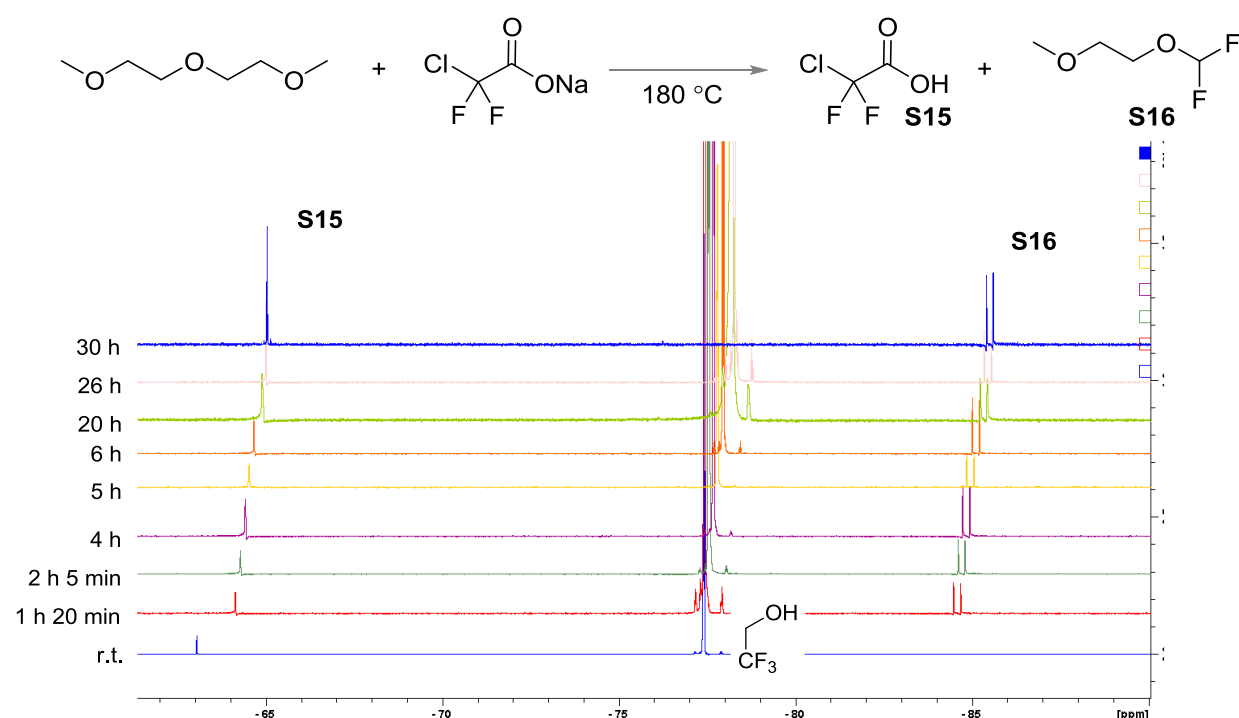
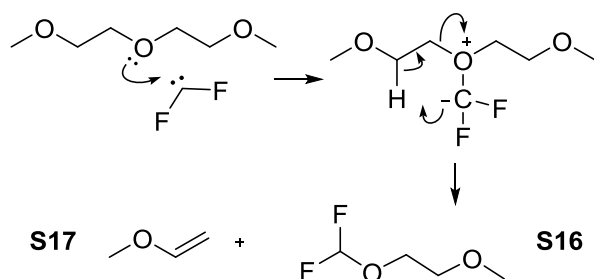


Figure S9: ^{19}F NMR (CDCl_3 , 400 MHz) spectrum of reaction time-points showing difluorocarbene generated from sodium chlorodifluoroacetate reacting with diglyme (horizontal offset = 0.15 ppm, trifluoroethanol used as external reference).

The observed ^{19}F NMR experimental data for the proposed side product **S16** (-84.6 ppm, d, $^2J_{\text{F-H}} = 74.6$ Hz) is extremely similar to 1,1-difluoro-3-(2-methoxyethoxy)propane reported by Rozen and co-workers^{S29} (-84.6 ppm, d, $^2J_{\text{F-H}} = 75.0$ Hz). Houk *et. al.* previously performed low level theoretical calculations (MP2/3-21G) showing that the attack by water on difluorocarbene resulted in a stabilisation of 9.7 kcal mol⁻¹ compared with the separate species, concluding that the ether stabilisation was greater than that seen with alkenes.^{S30}

This side product was common when less reactive alkenoates underwent difluorocyclopropanation attempts with MDFA and thought to proceed via the attack by solvent on difluorocarbene followed by elimination of vinyl ether **S17** (Scheme S5).



Scheme S6: Proposed mechanism for the reaction between diglyme and difluorocarbene.

Trend in Difluorocyclopropanation Conversion and Calculated HOMO Energies

The HOMO energy for a reactive species is generally considered to give a good representation of the compounds' nucleophilicity, but only a weak trend was observed between the reactivity of the alkenoates (determined by percentage conversion) and the HOMO energies of **13a-c**, **13f** and **13h** ($R^2 = 0.8287$, see Supporting Information for details). This model only assessed the reactivity of the olefin and did not take into consideration the alternative trapping reactions difluorocarbene can undergo; difluoromethylation of carboxylic acids, ketones, alcohols, thiols, heterocyclic amines and hydrophosphine oxides have all been reported.^{S31-35} Compounds which reacted slowly under the difluorocyclopropanation conditions contained common side products which were attributed to difluorocarbene reacting with the reaction solvent diglyme.

Aryl alkenoates were built *de novo* using Spartan'10 software and HOMO energies obtained after geometry optimisation using B3LYP/6-31G* methodology (gas phase, 298 K, orbitals and energies selected). Minimum energy structures were confirmed by a lack of imaginary frequency. HOMO energies are listed in **Table S2** alongside observed conversions.

Table S2: Difluorocyclopropanation conversion and calculated HOMO energies for (hetero)aromatic alkenoates.

$\text{R}^1 \text{---} \text{CH=CHCO}_2\text{Et}$ $\text{R}^1 =$	Percentage Conversion (%)	HOMO Energy (eV)
2-Pyridyl	0	-6.70
2-Thiazolyl	0	-6.47
Piperonyl	50	-5.68
Phenyl	37	-6.36
2-Furyl	66	-5.96
2-Thiophenyl	77	-6.10
3-Methyl-2-furyl	80	-5.84
2-NBoc-Pyrrolyl	92	-5.68

Both 2-pyridyl and 2-thiazoyl failed to show any reactivity and this could be due to their low calculated HOMO energies of -6.70 eV and -6.47 eV, respectively. However, the moderate conversion observed with piperonyl **13d** is not consistent with its higher HOMO energy of -5.68 eV, suggesting that alternative side reactions occur with these substituents. The remaining compounds show a slight trend relating percentage conversion with calculated HOMO energy but the data is not sufficient to make prediction on whether substrates will successfully undergo difluorocyclopropanation.

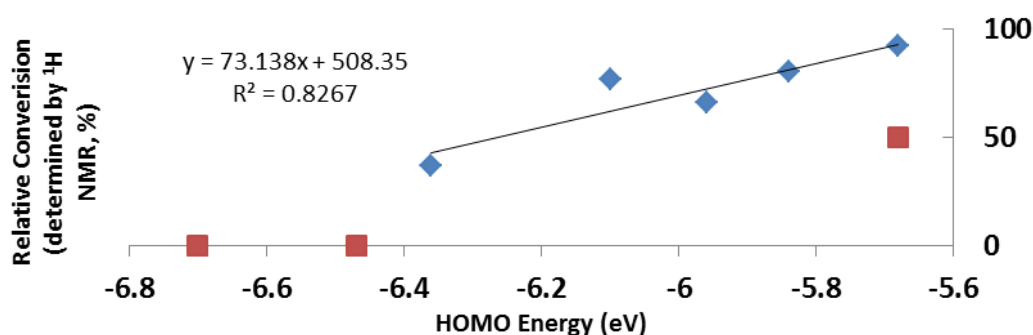


Figure S10: Plot of % conversion in difluorocyclopropanation reaction against calculated HOMO energies (eV) (data represented in Table SXX). ♦ = substrates which show slight trend, ■ = substrates which do not fit the trend.

Difluorocyclopropanation Functional Group Tolerance: Additive Experiment

We found that an indication of functional group tolerance was to measure the effects of heterocycles as additives in the previously successful difluorocyclopropanation of cinnamyl acetate **14b** (Table S3, Entry 1).^{S20}

Table S3: Effect of Heterocyclic Additives on the Difluorocyclopropanation of Cinnamyl Acetate **14b**.

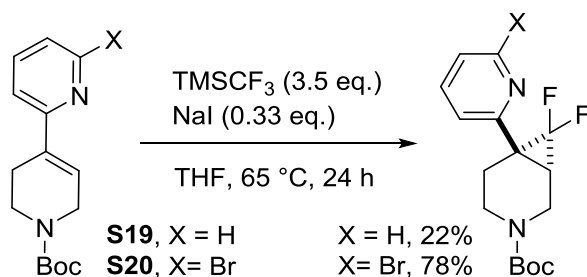
Entry ^[a]	Additive	Equivalents	Conversion to S18 (%) ^[b]
1 ^[c]	none	n.a.	100
2	Pyridine	1.0	0
3	Pyridine	0.5	4
4 ^[c]	Pyridine	0.1	85
5	Thiazole	0.5	34
6	Pyridine-N-oxide	0.5	14
7	N-Boc-pyrrole	0.5	88
8	Methyl-3-methyl-2-furoate	0.5	100
9	1,3-Benodioxole	0.5	50

^[a] All reactions run on an 8 mmol scale with respect to **14b** unless otherwise stated. ^[b]

Determined by ¹H NMR. ^[c] 16 mmol scale.

We observed that 1.0 and 0.5 equivalents of pyridine completely hindered the trapping of difluorocarbene with **14b** (Table S3, Entries 2-3); even small quantities of the heterocycle (10 mol%) lowered the conversion to **S18** by 15% (Table S3, Entry 4). Addition of thiazole to the reaction had a smaller effect, but a low 34% conversion confirmed that both of these

heterocycles do suppress the difluorocarbene-alkene reaction (**Table S3**, Entry 5). DeNinno and co-workers reported similar issues when the difluorocyclopropanation of **S19** gave a poor 22% yield, but shielding the pyridine nitrogen using *ortho*-bromo substitution gave a highly improved 78% yield from **S20** (**Scheme S6**).^{S36}



Scheme 7: Increased difluorocyclopropanation yields by blocking aromatic nitrogen atom.^{S36}

We hoped that blocking the nitrogen atom directly via the N-oxide would help the difluorocyclopropanation reaction in a similar way and potentially give access to a more reactive VCPR precursor. However, since a poor 14% conversion to **15b** was observed when pyridine-N-oxide was used as an additive, no further synthetic investigations were carried out (**Table S3**, Entry 6). Heterocycles which were tolerated during the difluorocyclopropanation of alkenoate **13**, gave higher 88-100% conversions to **15b** when used as additives (**Table S3**, Entries 7-8). This experimental approach of assessing functional group tolerance was a more effective way to prioritising the synthesis of heteroaromatic olefins and can be used to assess which substrates will be tolerated during difluorocyclopropanation without competing side reactions.

Methodology: An oven dried two-necked round bottom flask containing potassium iodide (3.68 g, 22.2 mmol) was sealed with a SubaSeal, and the salt was stirred and lightly flame dried under an atmosphere of argon. A low boiling point water condenser with a gas outlet connected to an argon/vacuum manifold was attached and the reaction flask and the atmosphere were purged three times. Cinnamyl acetate **14b** (1.34 mL, 8.0 mmol) followed by a solution of **additive (X eq.)** in diglyme (1.3 mL) were added and the resulting suspension was heated to 120 °C. Once the reaction temperature had been reached, TMSCl (2.6 mL, 19.7 mmol) and MDFA (2.6 mL, 19.7 mmol) were added dropwise in that order. After 5 hours, the reaction mixture had evaporated to dryness and a further portion of diglyme (1.3 mL) was added. The mixture was stirred for a further 19 hours (total reaction

time of 24 hours). The resulting brown solution was cooled to room temperature and the reaction mixture was quenched with aqueous NaCl (10 mL) and diethyl ether (10 mL) was added. The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 x 10 mL). The original organic layer and the extracts were combined, dried (MgSO₄) and concentrated under reduced pressure to remove volatiles. The ¹H NMR spectrum of the resulting brown oil was used to determine conversion of **13b** to difluorocyclopropyl **15b** and the results highlighted in **Table S3**.

Crude Spectra for Low Temperature Rearrangement Precursors

Spectra below highlight the results of oxidation/Wittig chemistry on highly reactive heteroaromatic substituents.

- Furyl Alcohol **17a** with (ethoxycarbonylmethylene)triphenylphosphorane

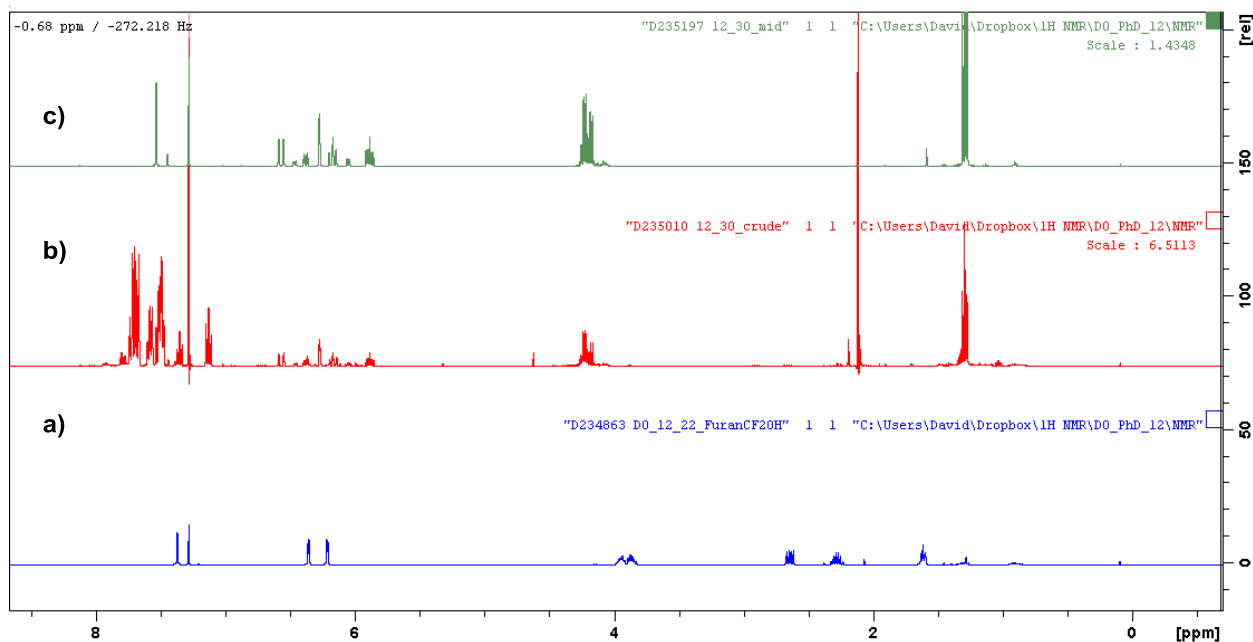


Figure S11: a) Isolated ^1H NMR for alcohol **17a** b) Crude ^1H NMR after oxidation/Wittig reaction showing no evidence of peaks relating to cyclopropane proton atoms. c) ^1H NMR of main fraction isolated from first purification on silica.

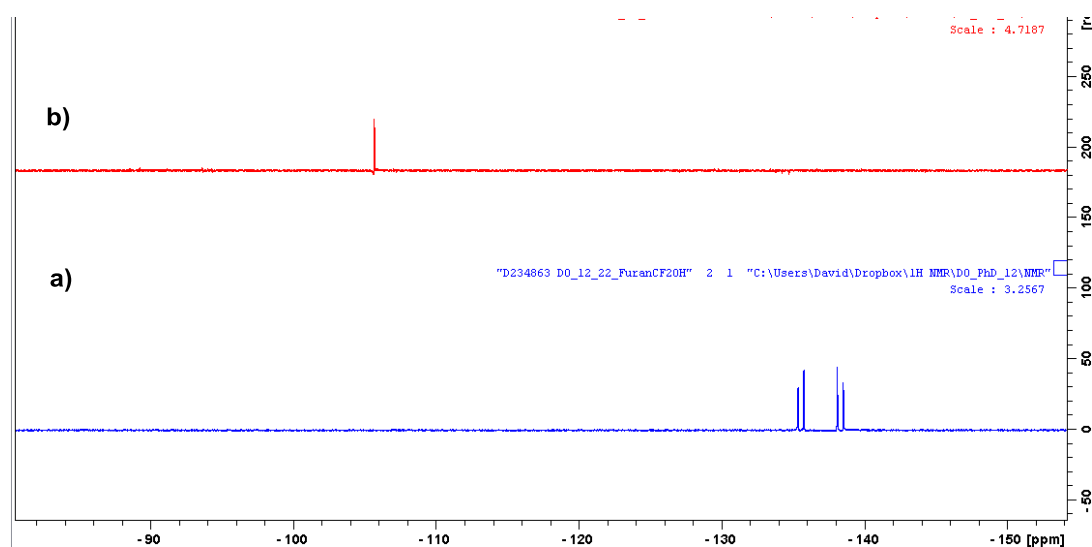


Figure S12: a) Isolated ^{19}F NMR for furyl alcohol **17a** b) ^{19}F NMR of main fraction isolated from first purification after oxidation/Wittig.

- Thiophenyl alcohol **17c** with (ethoxycarbonylmethylene)triphenylphosphorane

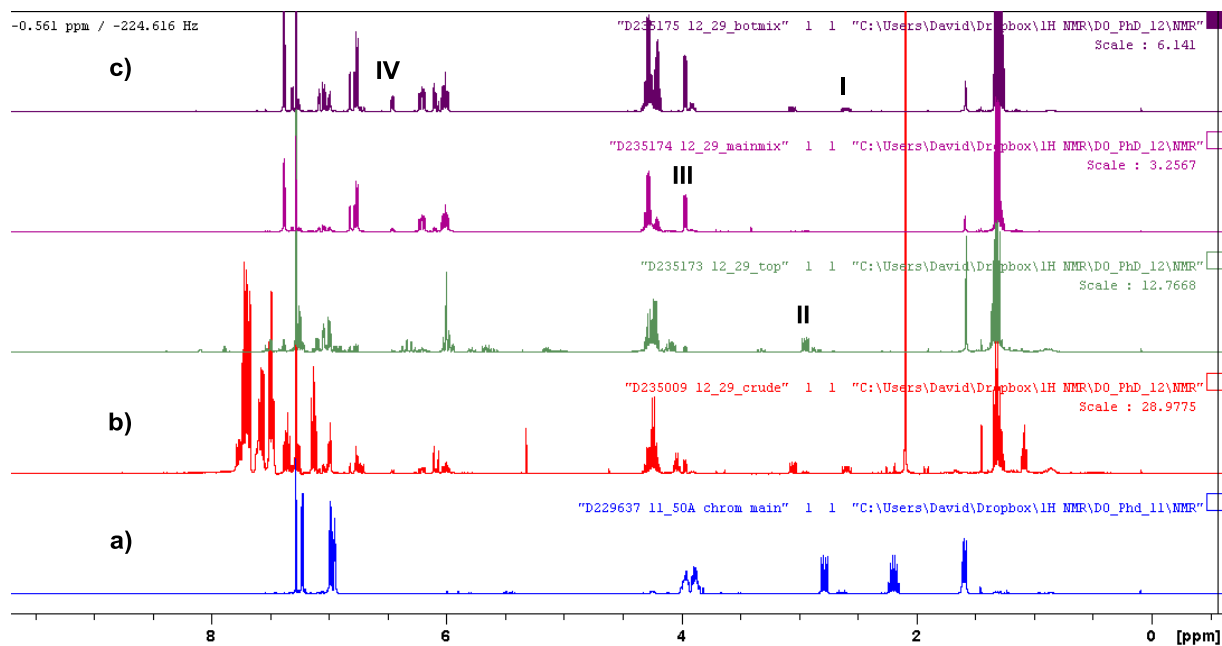
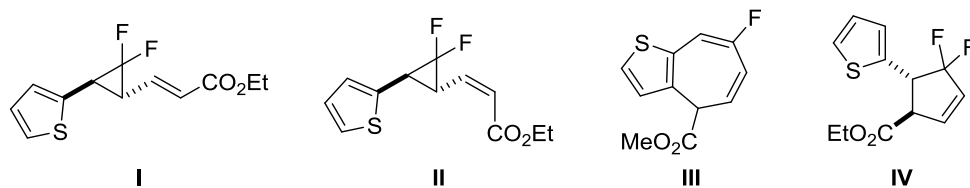


Figure S13: a) ^1H NMR of isolated thiophenyl alcohol **17c**. b) Crude ^1H NMR after oxidation/Wittig reaction. c) Three different fractions isolated after first purification on silica. (Assignment of crude spectra based on previous knowledge on *E/Z* cyclopropane isomers and ^{19}F NMR data for products which was confirmed on isolation of products).

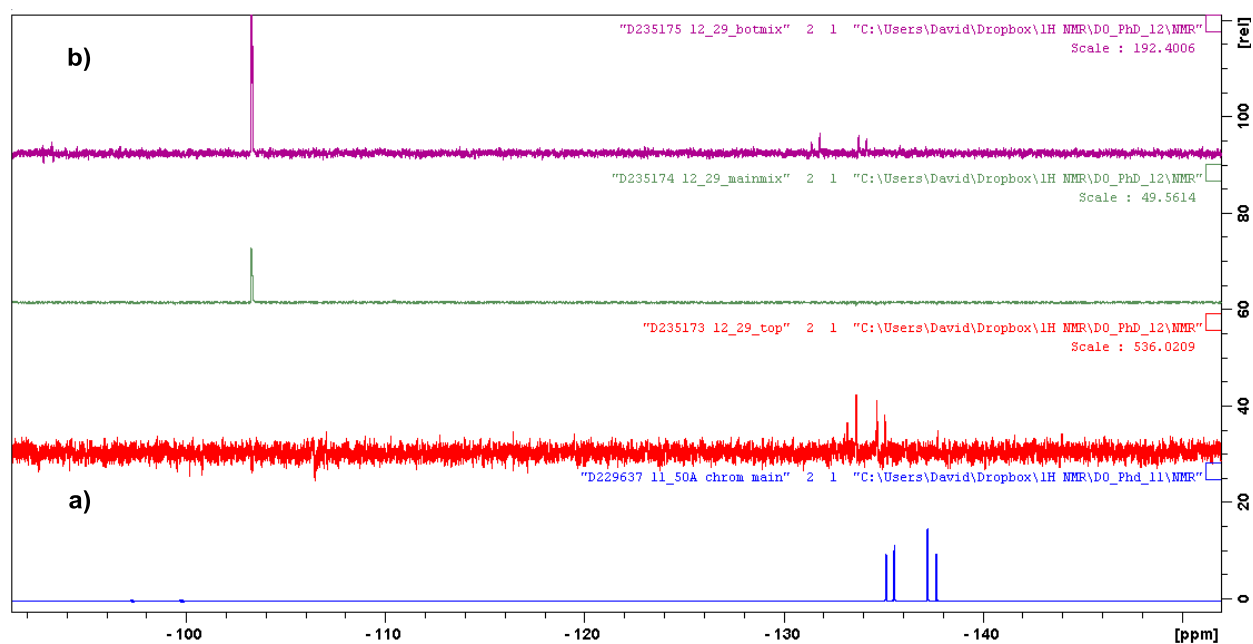


Figure S14: a) Crude ^{19}F NMR for isolated thiophenyl alcohol **17c**. b) ^{19}F NMR for isolated fractions highlighted in **Figure S13** from first purification on silica.

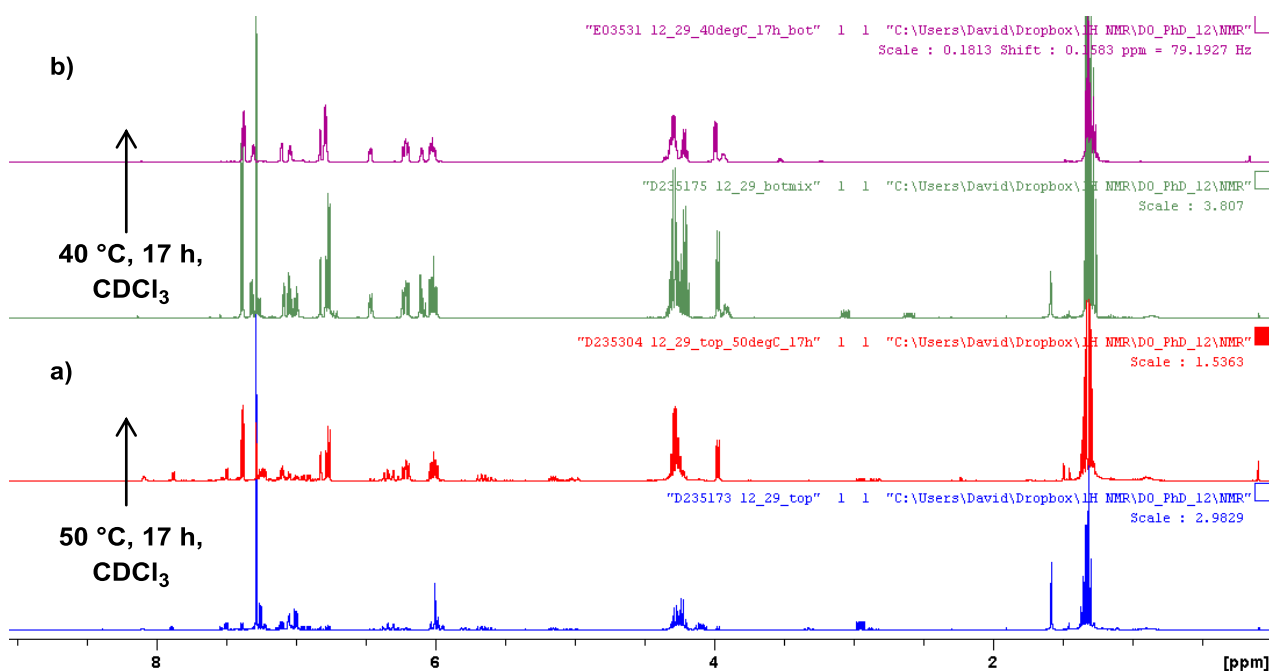


Figure S15: a) Thermolysis of < 10 mg sample containing *Z*-thiophenyl **24b** at 50 °C for 17 hours resulting in full conversion to heptadiene **29a** alongside other side products. b) Thermolysis of 420 mg sample containing *E*-thiophenyl **24a** at 40 °C for 17 hours resulting in full conversion to a mixture of VCPR and [3,3] product.

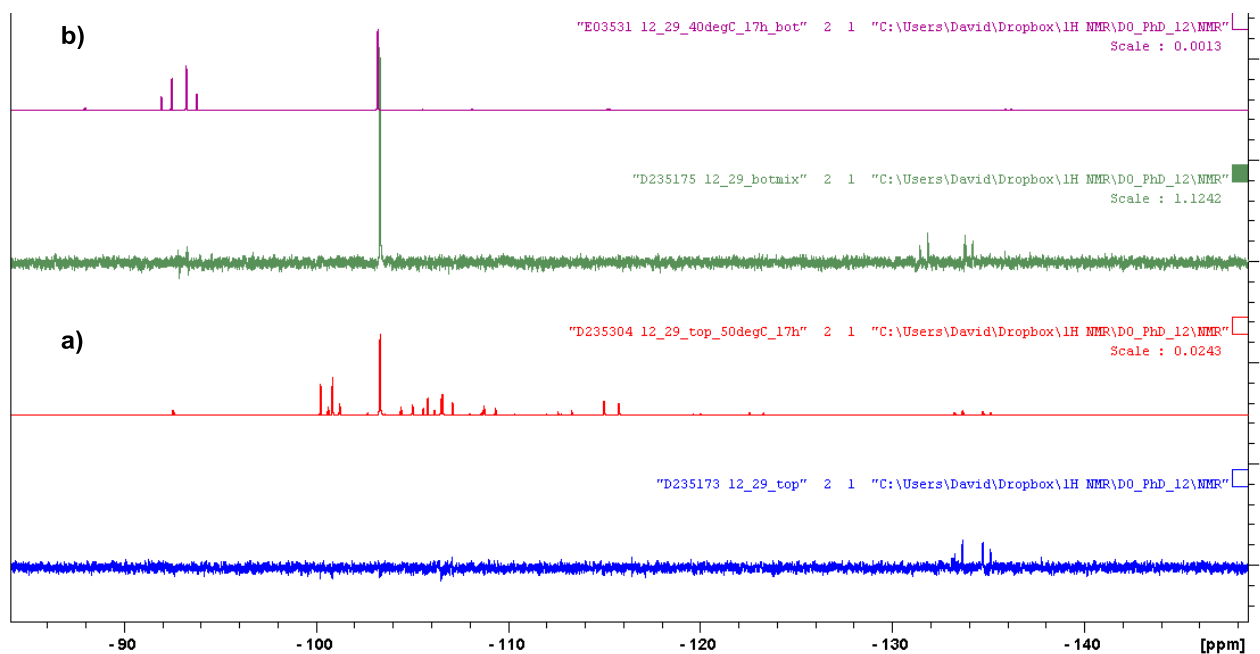


Figure S16: Corresponding ^{19}F NMR for ^1H NMR discussed in **Figure S15**.

- Furyl alcohol **17a** with (carbethoxyethylidene)triphenylphosphorane

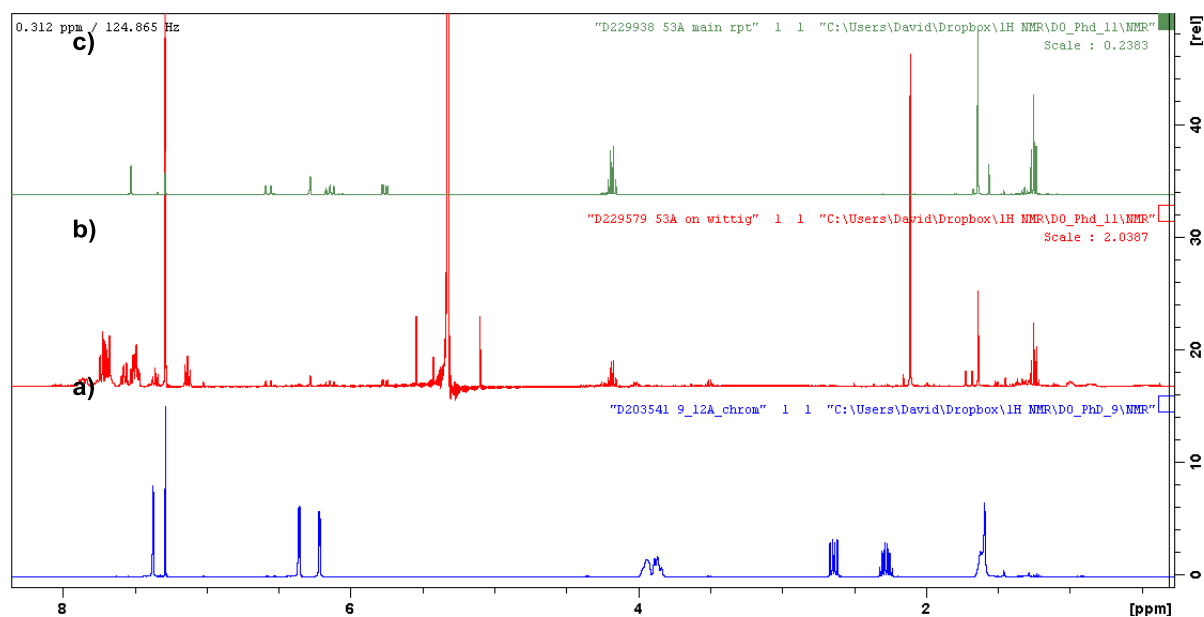


Figure S17: a) ^1H NMR of isolated furyl alcohol **17a**. b) Crude ^1H NMR after oxidation/Wittig with (carbethoxyethylidene)triphenylphosphorane c) ^1H NMR after 1st purification on silica.

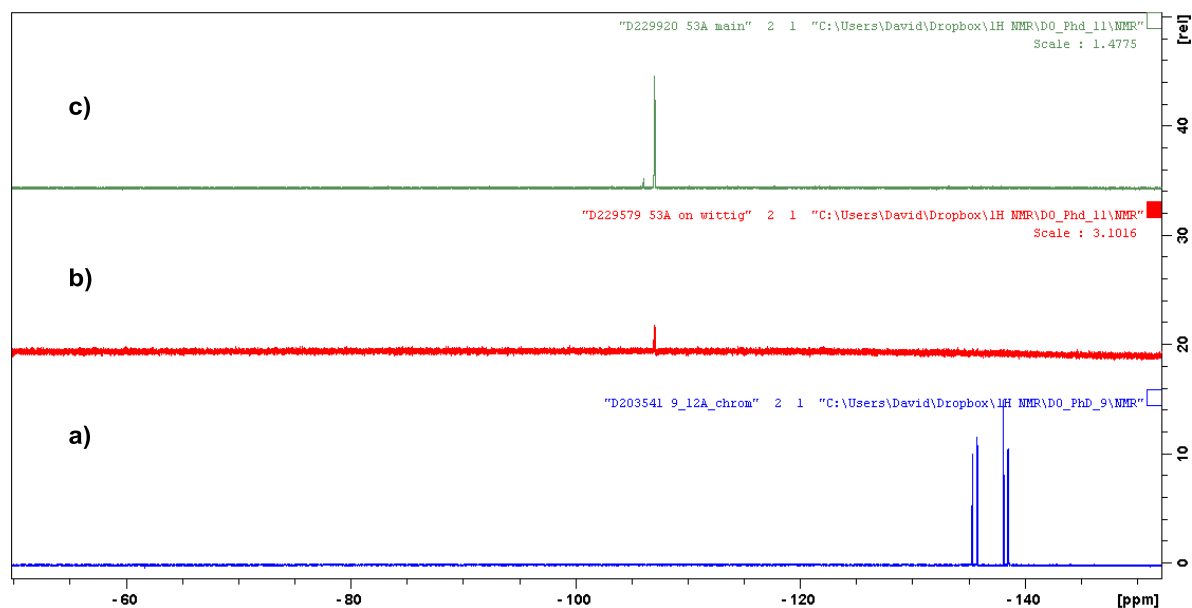


Figure S18: a) ^{19}F NMR for isolated furyl alcohol **17a** b) Crude ^{19}F NMR after oxidation/Wittig with (carbethoxyethylidene)triphenylphosphorane c) ^{19}F NMR after 1st purification on silica.

- Thiophenyl alcohol **17c** with (carbethoxyethylidene)triphenylphosphorane

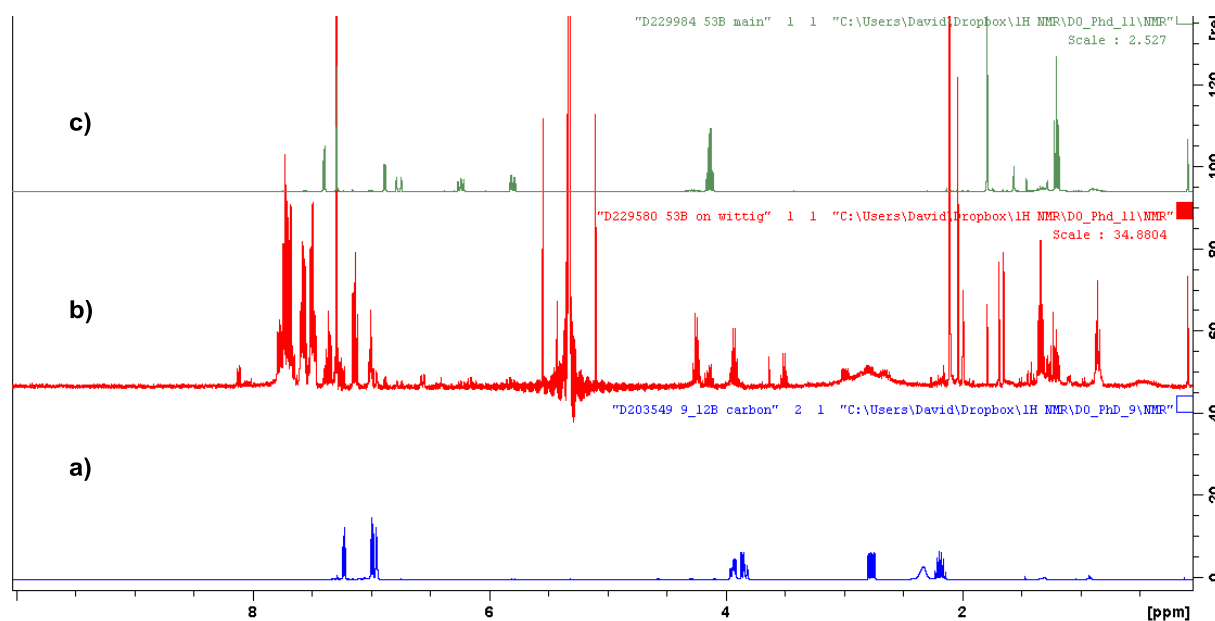


Figure S19: a) ^1H NMR for isolated thiophenyl alcohol **17c** b) Crude ^1H NMR after oxidation/Wittig with (carbethoxyethylidene)triphenylphosphorane c) ^1H NMR after 1st purification on silica.

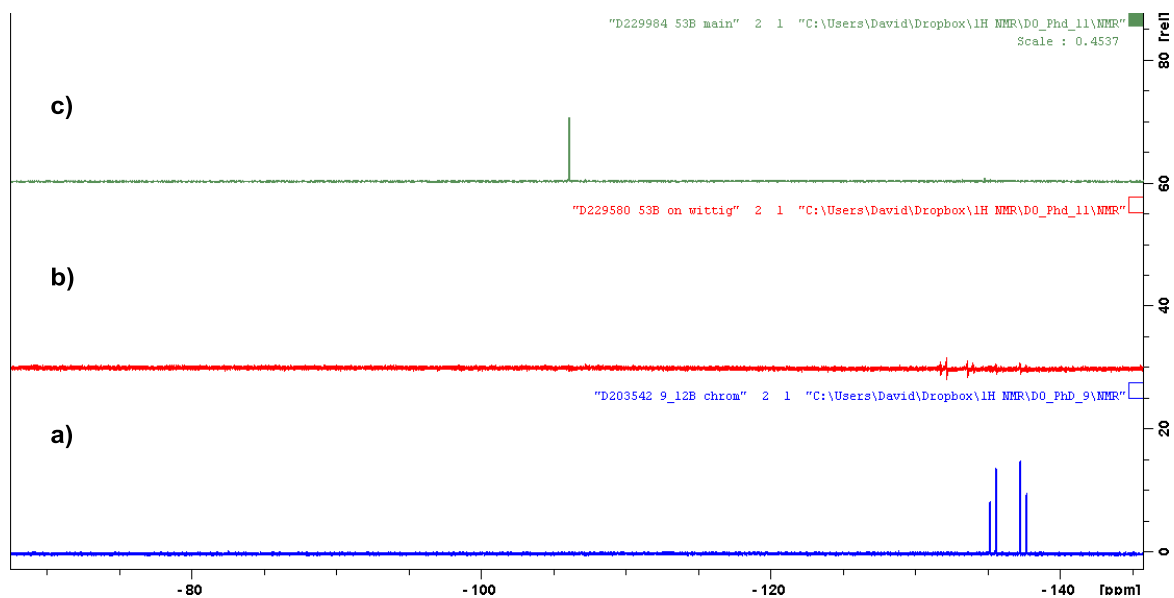


Figure S20: a) ^{19}F NMR for isolated thiophenyl alcohol **17c** b) Crude ^{19}F NMR after oxidation/Wittig with (carbethoxyethylidene)triphenylphosphorane c) ^{19}F NMR after 1st purification on silica.

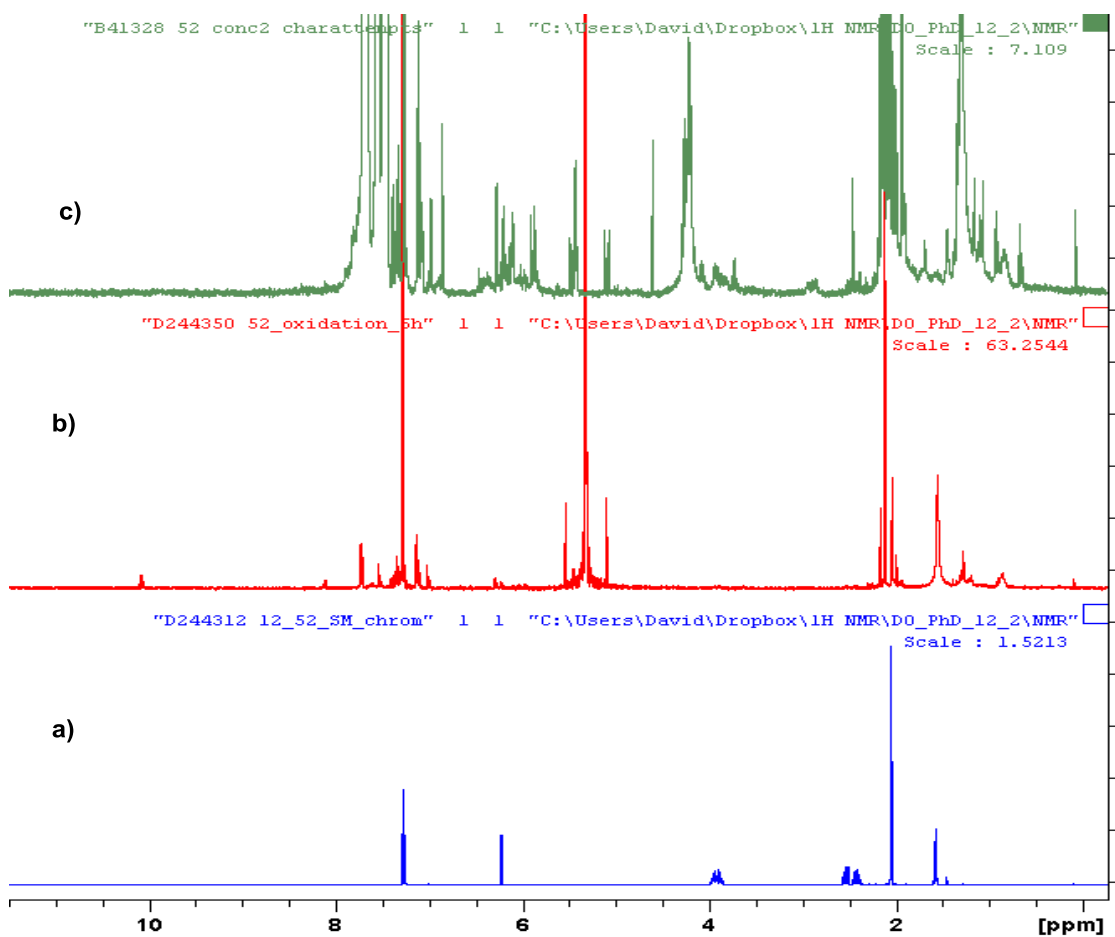


Figure S21: ^1H NMR for isolated 3-methyl-furyl alcohol **17h** b) Crude ^1H NMR after oxidation with (ethoxycarbonylmethylene)triphenylphosphorane c) ^1H NMR after olefination and concentration of reaction mixture.

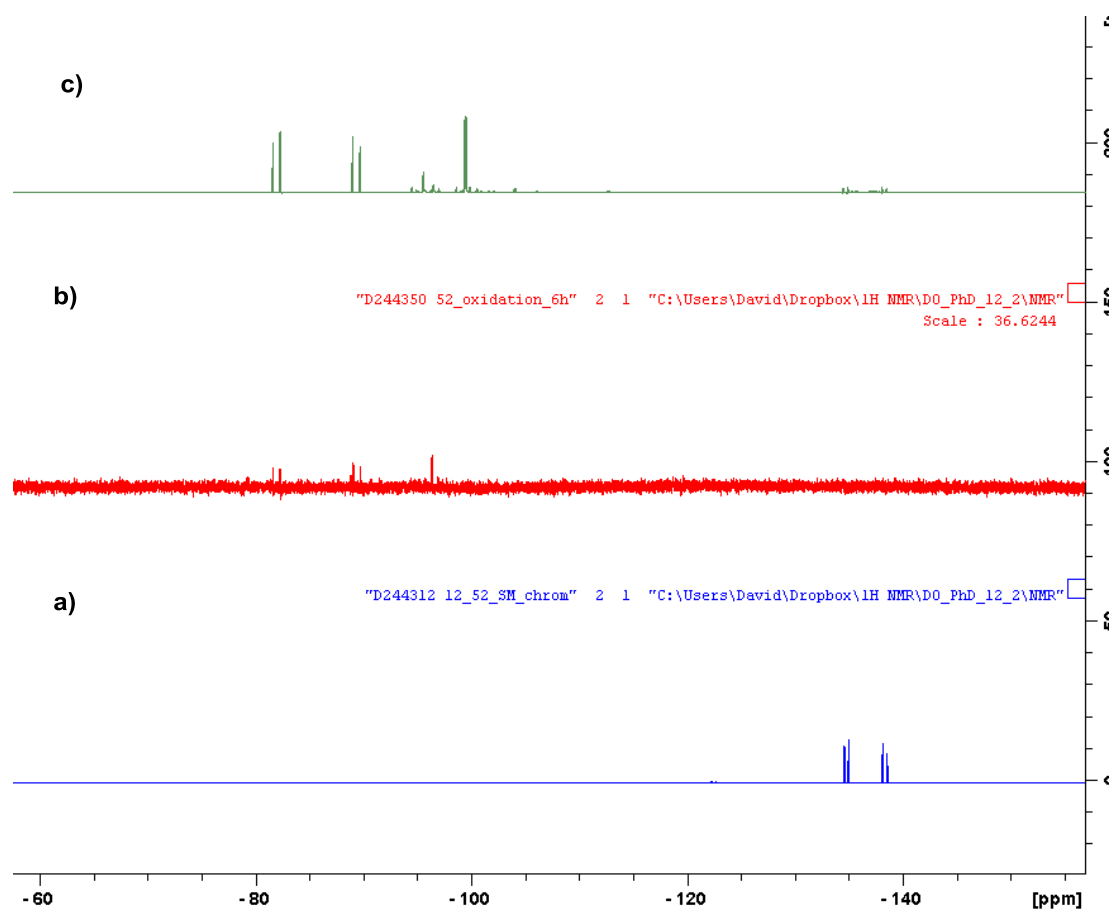


Figure S22: ^{19}F NMR for isolated 3-methyl-furyl alcohol **17h** b) Crude ^{19}F NMR after oxidation with (ethoxycarbonylmethylene)triphenylphosphorane c) ^{19}F NMR after olefination and concentration of reaction mixture.

Rearrangement of Isolated VCP – Crude Spectra

- (*E*)-Weinreb Amide **19a**

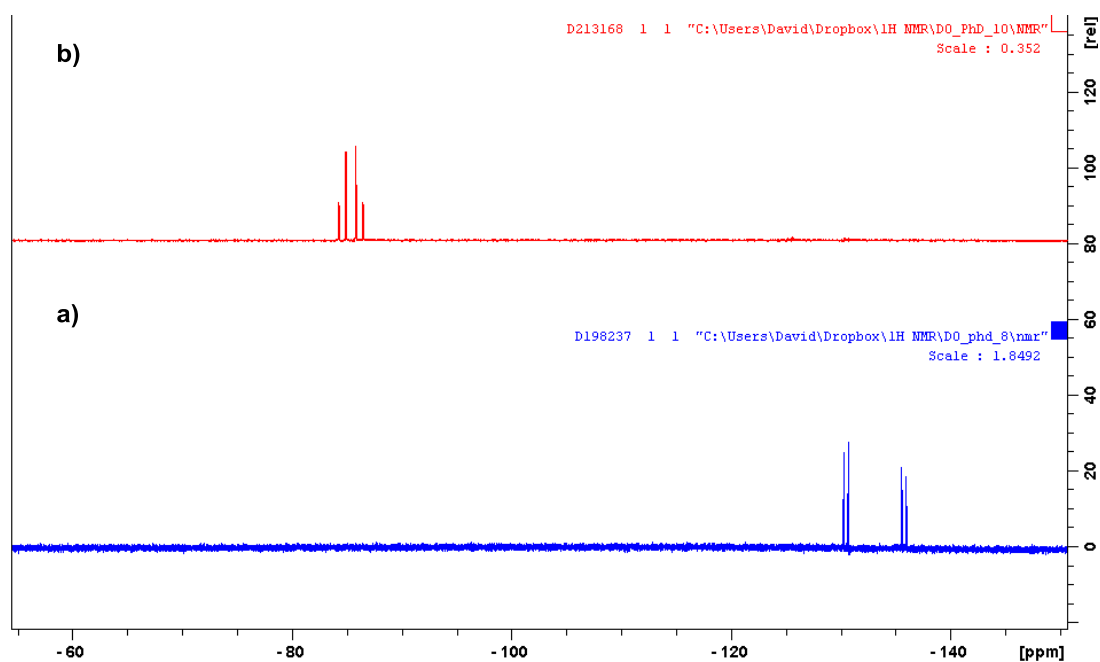


Figure S23: a) ^{19}F NMR of isolated *E*-Weinreb amide VCP **19a**. b) Crude ^{19}F NMR for rearrangement of **19a** at 95 °C for 17 hours.

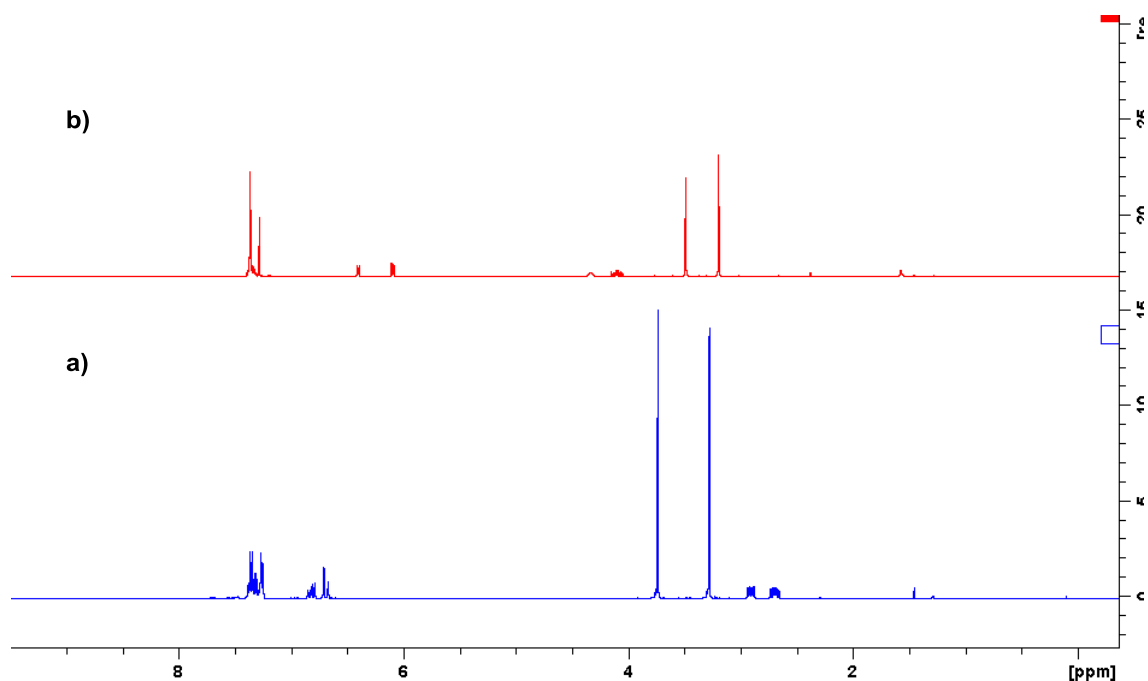


Figure S24: a) ^1H NMR of isolated *E*-Weinreb amide VCP **19a**. b) Crude ^1H NMR for rearrangement of **19a** at 95 °C for 17 hours.

- (Z)-Weinreb Amide (**19b**)

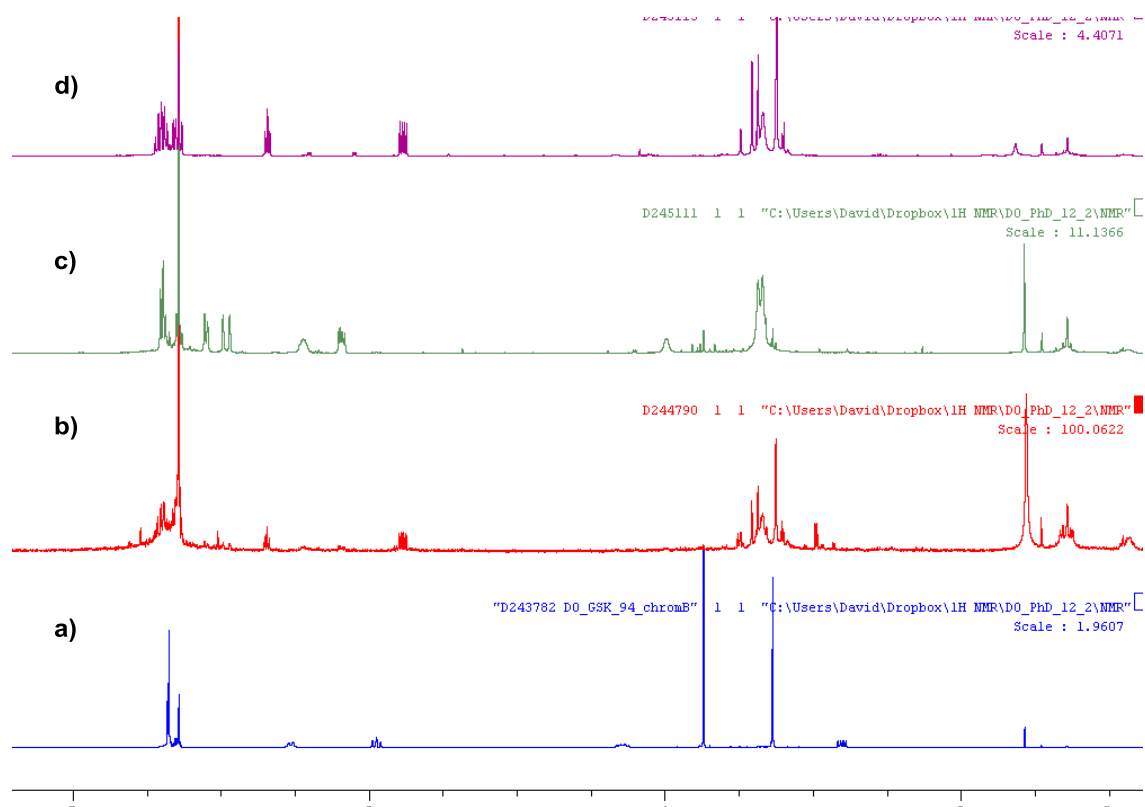


Figure S25: a) ^1H NMR of isolated ZWeinreb amide VCP **19b**. b) Crude ^1H NMR of **19b** after rearrangement at 165 °C for 17 hours (silica pad used to remove Ph_2O solvent c) and d) ^1H NMR of isolated products after chromatography.

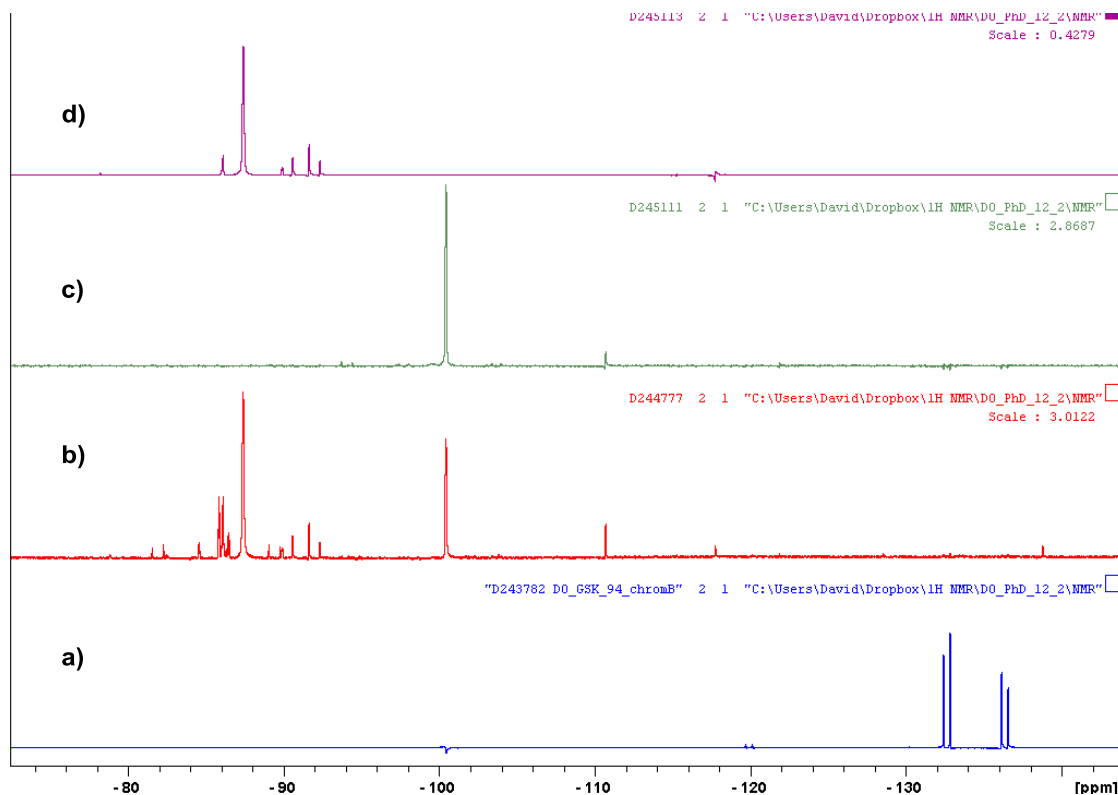


Figure S26: a) ^{19}F NMR of isolated Z-Weinreb amide VCP **19b**. b) Crude ^{19}F NMR of **19b** after rearrangement at 165 °C for 17 hours (silica pad used to remove Ph_2O solvent). c) and d) ^{19}F NMR of isolated products after chromatography.

- **α -Methyl Ester (20a)**

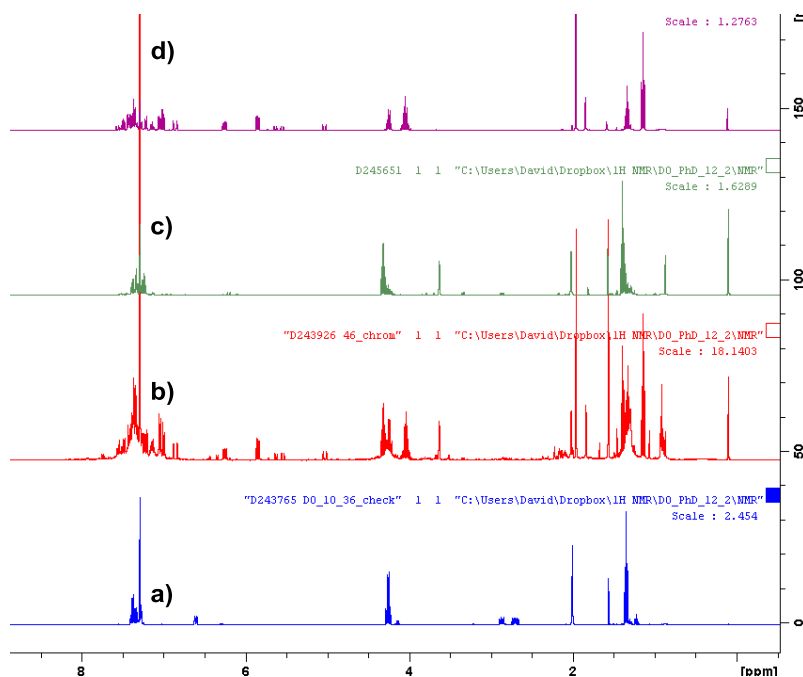


Figure S27: a) ^1H NMR of isolated alkenoate **20a** b) Crude ^1H NMR of **20a** after rearrangement at 155 °C for 17 hours (silica pad used to remove Ph_2O solvent). c) and d) ^1H NMR of isolated products after chromatography.

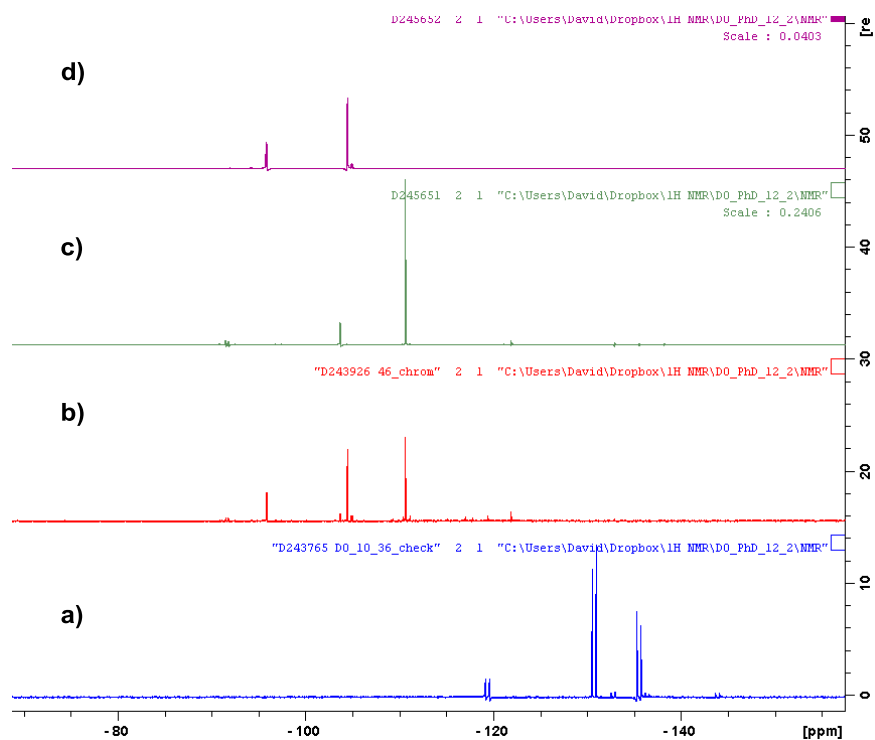


Figure S28: a) ^{19}F NMR of isolated alkenoate **20a**. b) Crude ^{19}F NMR of **20a** after rearrangement at 155 °C for 17 hours (silica pad used to remove Ph_2O solvent). c) and d) ^{19}F NMR of unknown products after chromatography.

- E/Z*-Cyano VCP mixture (**21a/21b**)**

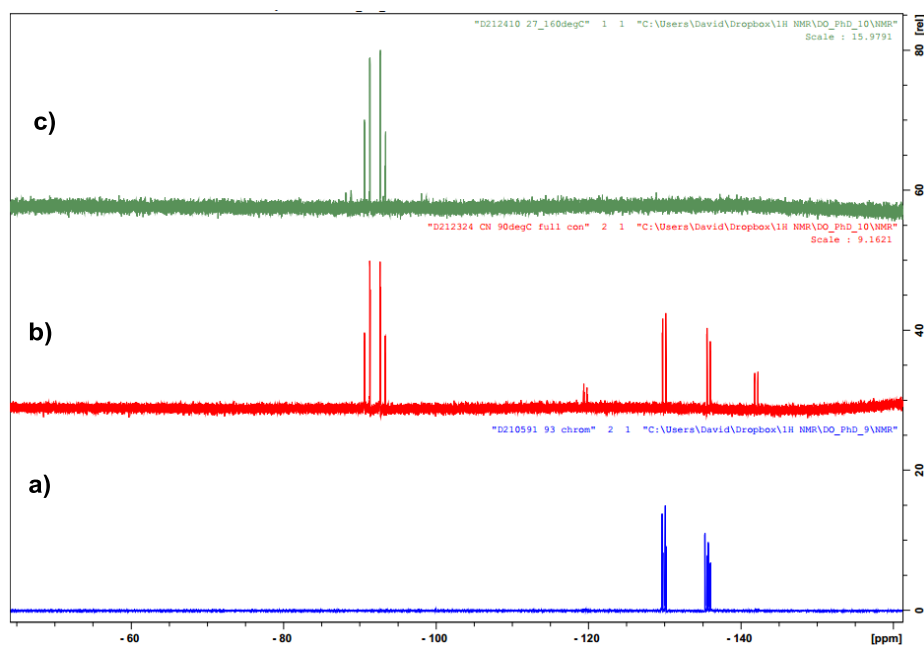


Figure S29: a) ^{19}F NMR spectra of **21a/21b** mixture. b) ^{19}F NMR spectra for the rearrangement of **21a/21b** at 90 °C for 17 h resulting in full conversion of **21a** to difluorocyclopentene **37** and only cyclopropane stereoisomerization of **21b** to **42**. c) ^{19}F NMR spectra after the rearrangement of crude mixture in b) at 160 °C for 17 h.

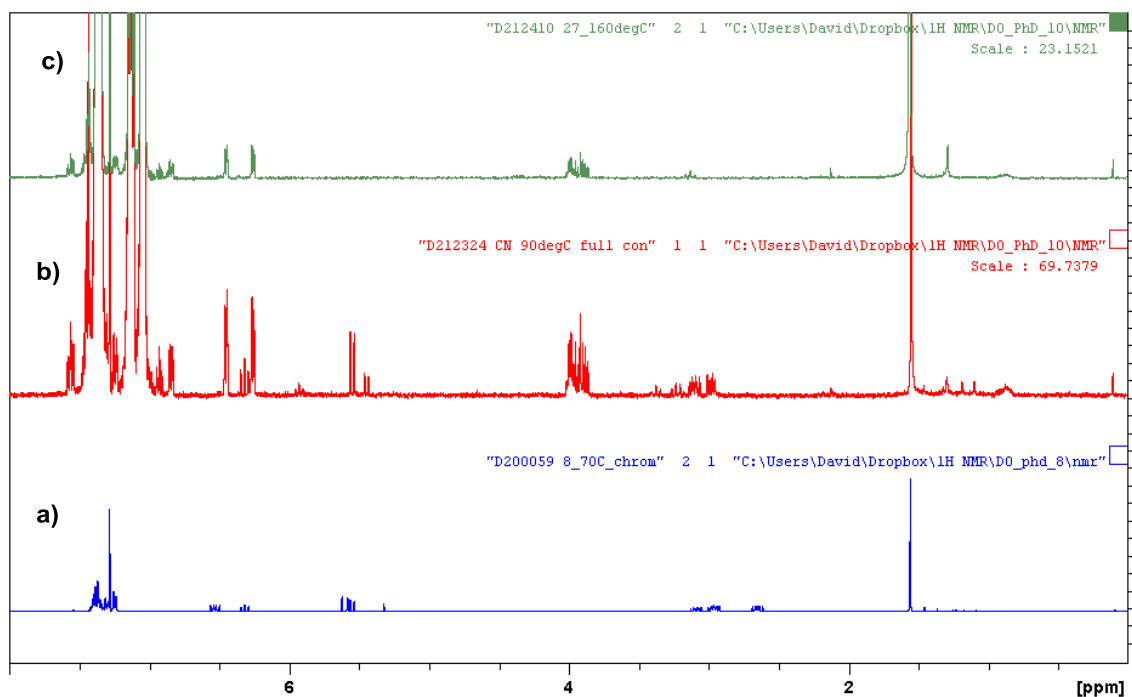


Figure S30: Corresponding ^1H spectra for mixtures in Figure 29.

- Piperonyl 22a

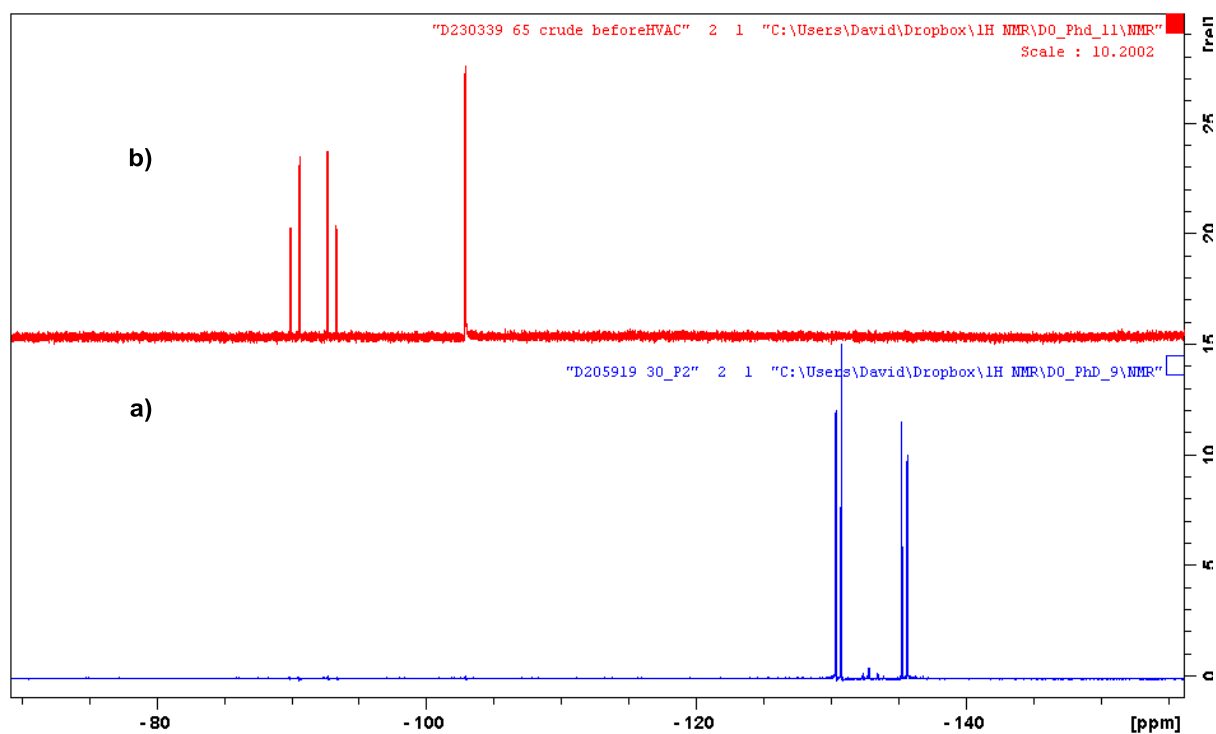


Figure S31: a) ^{19}F NMR of isolated piperonyl VCP 22a. b) ^{19}F NMR of crude reaction mixture after rearrangement at 70 °C for 17 h.

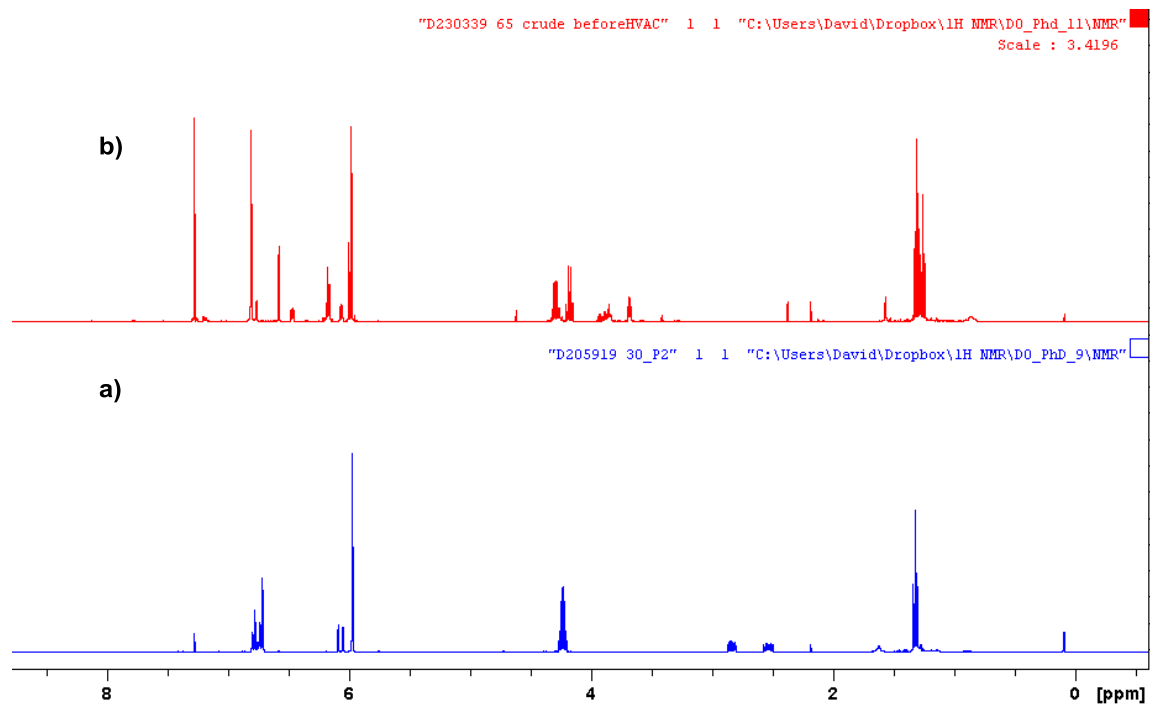


Figure S32: Corresponding ^1H NMR spectra for ^{19}F NMR discussed in **Figure S31**.

- **Non-fluorinated 47**

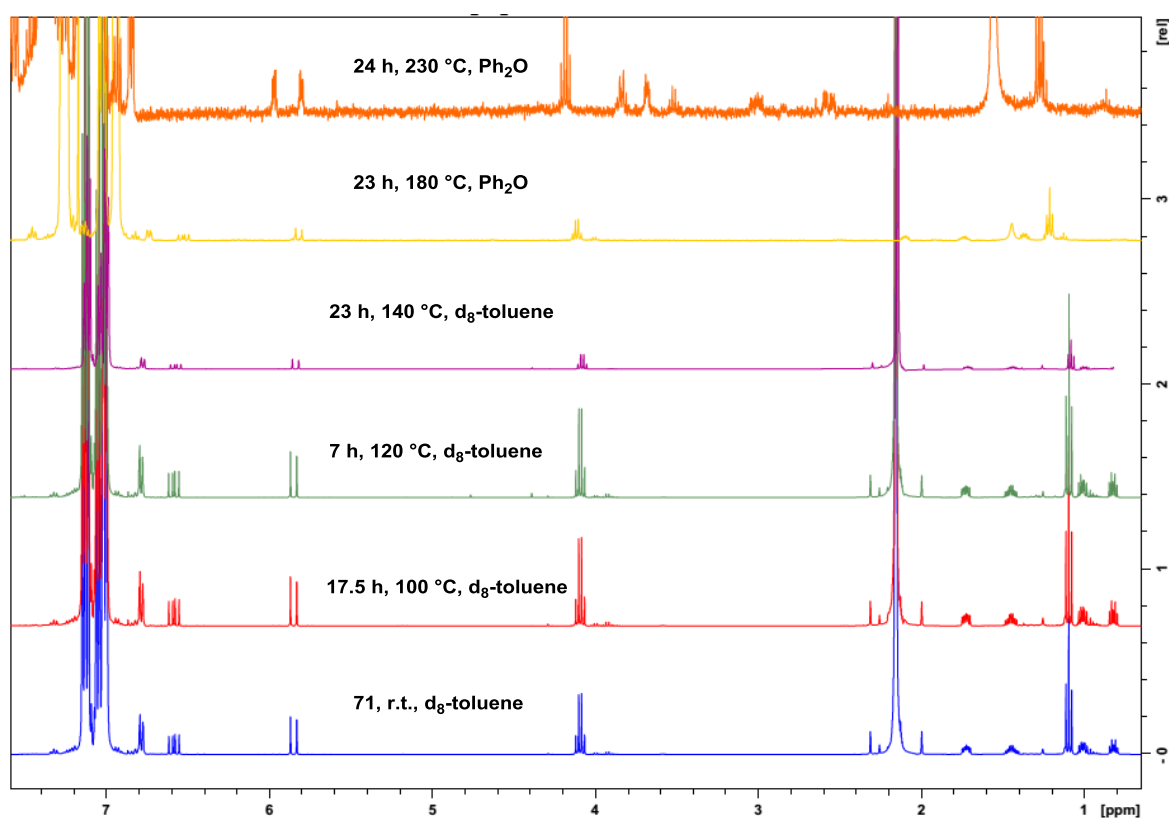


Figure S33: Rearrangement temperature screening show temperatures > 180 °C are required for the rearrangement of non-fluorinated VCP 47.

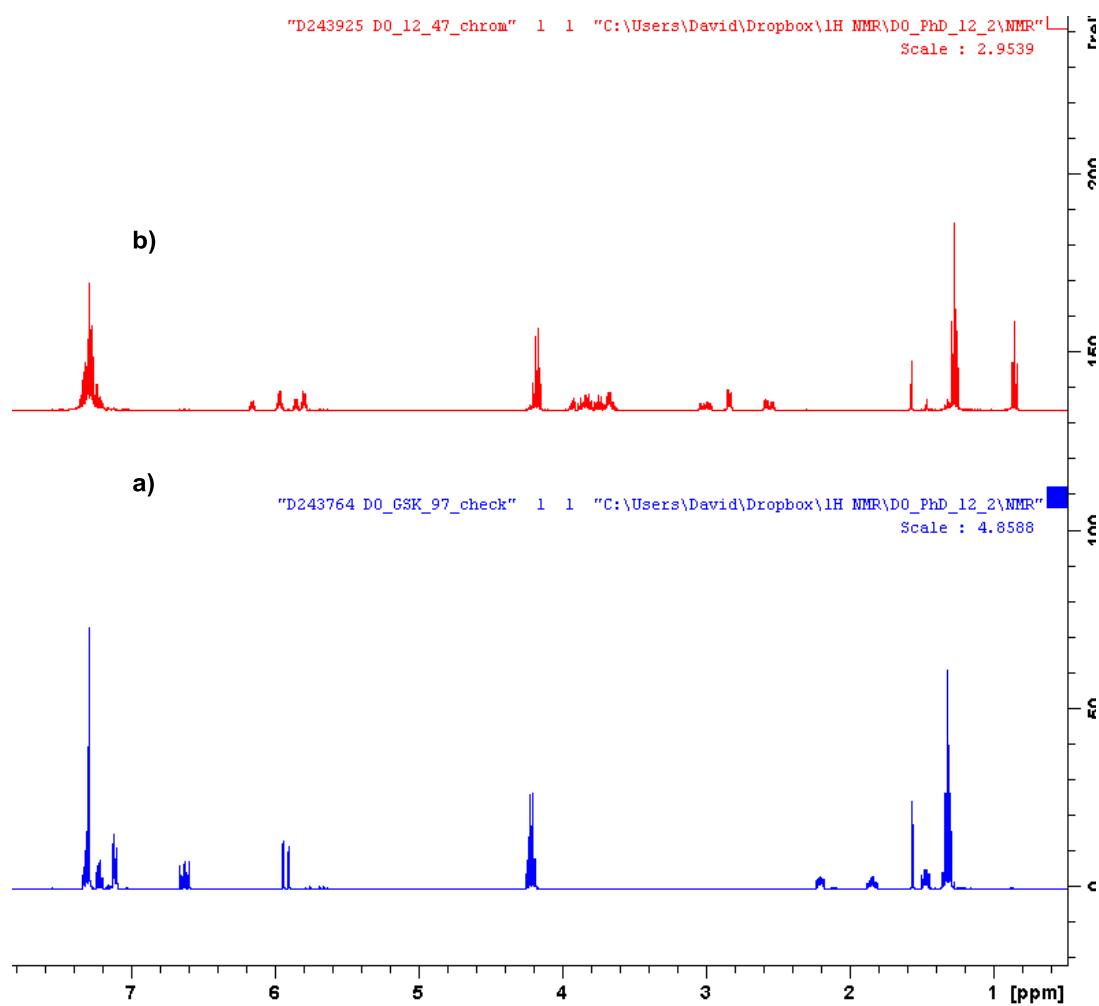


Figure S34: a) ^1H NMR for isolated alkenoate **47** b) Crude ^1H NMR for the rearrangement of isolated non-fluorinated **47** at 210 °C for 17 h (after removal of Ph_2O solvent).

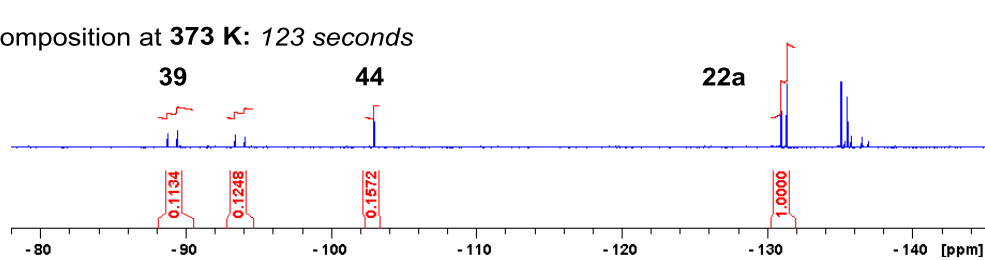
Piperonyl 22a Rearrangement: Kinetic Modelling

VT ^{19}F NMR Procedure for Piperonyl 22a

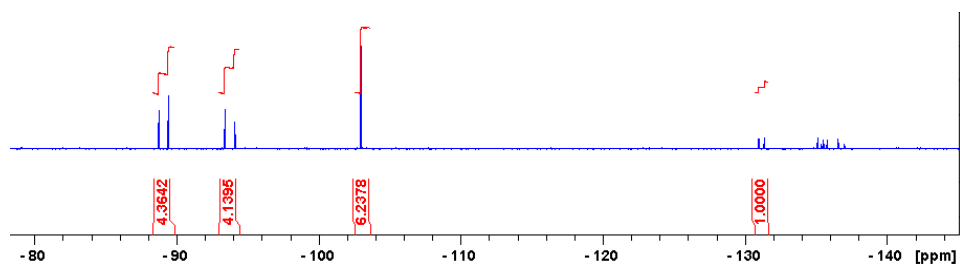
^{19}F NMR spectra were acquired on a Brüker AV400 instrument equipped with a QNP-z probe and a temperature control unit. Data was collected at 376 MHz using 8 scans per data point. Settings for spectra acquisition were as follows: NS = 8 scans; D1 = 1.5 s; SW = 199.77 ppm and O1P = -100 ppm. The samples were held at reaction temperature for the duration of the experiment: 343, 353, 363 and 373 K for Arrhenius plots with **22a**. d8-Toluene was purchased from and Sigma Aldrich and used as received. A solution of VCPR precursor (typically 0.13-0.15 M) was made up in a clean, dry NMR tube and the tube was capped. The tube was inserted into the magnet and the instrument's internal temperature was set to the desired reaction temperature and allowed to equilibrate (approx. 2 minutes heating time). The sample was then analysed at appropriate intervals using a Brüker Topspin automated script, *multi_zgvd2b*. Samples were automatically shimmed using *topshim* between acquisitions. In order to obtain sufficient data points for kinetic analysis; the above procedure was altered slightly for rearrangements at temperatures of 363 and 373 K. Reactions at both temperatures used *noshim* to cancel any shimming between spectra acquisition, allowing time points to be taken every 40 or 25 seconds (respectively) instead of 60 seconds with shimming between samples. A sacrificial sample was used to shim the reaction mixture at 373 K. This was ejected and replaced with a fresh sample which was locked and followed at 25 second intervals (*multi_zgvd2b*) after solvent locking. This procedure allowed the first time point to be taken after 50 seconds instead of 180 seconds. Relative percentages were determined by averaging the manual integration for each compound on the resulting spectra using proprietary software.

Example Spectra:

22a decomposition at **373 K**: 123 seconds



22a decomposition at **373 K**: 867 seconds



Raw Kinetic Data for Piperonyl 22a

¹⁹F NMR integration data for the VCPR of **22a** in d8-toluene (0.13 M) heated at 343 K (AV400, QNP-z probe); 8 scans, D1= 1.5 s, TE = 343 K.

Time	Average Integrations			Relative Percentage		
(s)	SM	VCPR	3,3	SM	VCPR	3,3
0	1.00	0.03	0.01	96.4	3.1	0.5
360	1.00	0.05	0.02	93.7	4.6	1.7
480	1.00	0.07	0.04	90.0	6.3	3.7
720	1.00	0.07	0.06	88.5	6.2	5.3
960	1.00	0.11	0.09	83.5	9.1	7.5
1200	1.00	0.11	0.09	83.0	9.3	7.7
1440	1.00	0.14	0.15	77.2	10.9	11.9
1680	1.00	0.16	0.17	74.9	12.2	12.8
1920	1.00	0.19	0.20	71.8	14.0	14.2
2160	1.00	0.22	0.22	69.5	15.0	15.6
2400	1.00	0.25	0.27	66.0	16.4	17.5
2640	1.00	0.28	0.30	63.2	17.7	19.1
2880	1.00	0.28	0.31	63.0	17.5	19.5
3120	1.00	0.32	0.36	59.6	19.0	21.4
3360	1.00	0.34	0.36	58.7	20.1	21.2
3600	1.00	0.40	0.44	54.4	21.6	24.0
3840	1.00	0.38	0.45	54.4	20.9	24.7
4080	1.00	0.46	0.52	50.7	23.1	26.2
4320	1.00	0.45	0.51	50.9	22.9	26.2
4560	1.00	0.50	0.55	48.8	24.2	27.0
4800	1.00	0.57	0.68	44.5	25.2	30.3
5040	1.00	0.60	0.70	43.5	26.1	30.4
5280	1.00	0.62	0.72	42.8	26.4	30.7
5520	1.00	0.62	0.77	41.9	26.1	32.1
5760	1.00	0.69	0.79	40.2	27.9	31.9
6000	1.00	0.76	0.83	38.5	29.5	32.0
6240	1.00	0.78	0.95	36.6	28.5	34.8
6480	1.00	0.82	0.99	35.7	29.1	35.2
6720	1.00	0.88	1.02	34.5	30.5	35.0
6960	1.00	0.90	1.08	33.6	30.3	36.1
7200	1.00	0.99	1.15	31.8	31.7	36.5
7440	1.00	1.02	1.23	30.8	31.3	37.9
7680	1.00	1.09	1.32	29.3	32.0	38.8
7920	1.00	1.15	1.38	28.4	32.6	39.0
8160	1.00	1.22	1.51	26.8	32.6	40.6
8400	1.00	1.26	1.45	27.0	34.0	39.1

Time	Average Integrations			Relative Percentage		
(s)	SM	VCPR	3,3	SM	VCPR	3,3
8640	1.00	1.27	1.56	26.1	33.2	40.6
8880	1.00	1.44	1.77	23.8	34.2	42.0
9120	1.00	1.54	1.84	22.8	35.2	42.0
9360	1.00	1.50	1.83	23.1	34.6	42.3
9600	1.00	1.66	1.96	21.6	35.9	42.5
9840	1.00	1.77	2.12	20.4	36.2	43.3
10080	1.00	1.81	2.20	19.9	36.1	43.9
10320	1.00	1.83	2.10	20.3	37.1	42.6
10560	1.00	1.89	2.37	19.0	36.0	45.0
10800	1.00	1.93	2.43	18.6	36.0	45.4
11280	1.00	2.09	2.60	17.6	36.7	45.7
63960	0.00	0.97	1.26	0.0	43.6	56.4

¹⁹F NMR integration data for the VCPR of **22a** in d8-toluene (0.13 M) heated at 353 K (AV400, QNP-z probe); 8 scans, D1= 1.0 s, TE = 353 K.

Time (s)	Average Integrations			Relative Percentage		
	SM	VCPR	3,3	SM	VCPR	3,3
0	1.00	0.04	0.02	94.0	3.9	2.2
240	1.00	0.06	0.05	90.1	5.8	4.1
420	1.00	0.12	0.06	84.4	10.2	5.4
600	1.00	0.18	0.18	73.8	13.1	13.2
780	1.00	0.23	0.24	67.6	15.8	16.5
960	1.00	0.27	0.31	63.2	17.1	19.7
1140	1.00	0.33	0.38	58.3	19.5	22.1
1320	1.00	0.43	0.49	52.1	22.3	25.6
1500	1.00	0.47	0.57	49.1	22.9	28.1
1680	1.00	0.55	0.65	45.6	25.0	29.4
1860	1.00	0.59	0.75	42.7	25.3	32.0
2040	1.00	0.73	0.89	38.2	27.9	33.8
2220	1.00	0.81	1.03	35.2	28.4	36.4
2400	1.00	0.94	1.15	32.3	30.5	37.2
2580	1.00	1.00	1.32	30.1	30.2	39.7
2760	1.00	1.20	1.55	26.7	32.1	41.3
2940	1.00	1.21	1.55	26.6	32.2	41.2
3120	1.00	1.40	1.78	23.9	33.5	42.6
3300	1.00	1.48	1.91	22.8	33.7	43.6
3480	1.00	1.71	2.24	20.2	34.6	45.2
3660	1.00	2.01	2.64	17.7	35.6	46.7
3840	1.00	2.03	2.59	17.8	36.1	46.1
4020	1.00	2.27	2.91	16.2	36.7	47.1
4200	1.00	2.85	3.80	13.1	37.3	49.6
4380	1.00	2.75	3.64	13.5	37.2	49.3
4560	1.00	3.23	4.31	11.7	37.8	50.5
4740	1.00	3.32	4.34	11.5	38.3	50.2
4920	1.00	4.35	5.59	9.1	39.8	51.1
5100	1.00	4.13	5.38	9.5	39.3	51.2
5280	1.00	4.26	5.65	9.2	39.1	51.8
5460	1.00	5.00	6.58	7.9	39.8	52.3
5640	1.00	4.81	6.06	8.4	40.5	51.1
5820	1.00	6.21	8.21	6.5	40.3	53.2
6000	1.00	6.75	8.85	6.0	40.7	53.3
6180	1.00	8.11	10.43	5.1	41.5	53.4
6360	1.00	5.79	7.55	7.0	40.4	52.7
6540	1.00	9.03	12.02	4.5	41.0	54.5
6720	1.00	9.71	12.64	4.3	41.6	54.1
6900	1.00	10.78	14.33	3.8	41.3	54.9
7080	1.00	9.40	12.23	4.4	41.5	54.0
7260	1.00	10.10	12.74	4.2	42.4	53.4
7440	1.00	12.65	16.46	3.3	42.0	54.7
7620	1.00	12.47	16.40	3.3	41.7	54.9
15120	0.00	1.01	1.61	0.0	38.4	61.6

¹⁹F NMR integration data for the VCPR of **22a** in d8-toluene (0.13 M) heated at 363 K (AV400, QNP-z probe); 8 scans, D1= 1.0 s, TE = 363 K.

Time	Average Integrations			Relative Percentage		
(s)	SM	VCPR	3,3	SM	VCPR	3,3
0	1.00	0.03	0.02	95.0	2.8	2.1
120	1.00	0.11	0.10	82.8	8.8	8.4
160	1.00	0.12	0.13	80.0	9.9	10.0
190	1.00	0.15	0.15	77.2	11.4	11.4
210	1.00	0.17	0.19	73.2	12.8	14.0
245	1.00	0.18	0.22	71.4	13.1	15.5
275	1.00	0.22	0.27	67.2	14.6	18.2
305	1.00	0.23	0.30	65.7	14.9	19.4
335	1.00	0.26	0.31	63.4	16.7	19.9
365	1.00	0.30	0.34	61.0	18.1	20.9
395	1.00	0.32	0.37	59.2	18.8	22.0
425	1.00	0.36	0.43	55.9	20.1	24.1
455	1.00	0.36	0.47	54.4	19.8	25.7
485	1.00	0.43	0.51	51.8	22.1	26.2
515	1.00	0.43	0.55	50.6	21.7	27.7
545	1.00	0.44	0.55	50.3	21.9	27.8
575	1.00	0.48	0.63	47.3	22.8	29.8
605	1.00	0.52	0.66	45.7	24.0	30.3
635	1.00	0.54	0.71	44.5	23.9	31.6
665	1.00	0.59	0.80	42.0	24.6	33.4
695	1.00	0.64	0.83	40.5	25.9	33.6
725	1.00	0.69	0.85	39.3	27.1	33.6
755	1.00	0.70	0.92	38.2	26.8	35.0
785	1.00	0.73	0.98	36.9	26.8	36.3
815	1.00	0.77	1.06	35.3	27.1	37.5
845	1.00	0.86	1.13	33.5	28.8	37.7
875	1.00	0.86	1.15	33.2	28.6	38.2
905	1.00	0.93	1.23	31.7	29.4	39.0
935	1.00	0.96	1.28	30.8	29.8	39.4
965	1.00	1.02	1.35	29.7	30.3	40.0
995	1.00	1.09	1.47	28.0	30.7	41.3
1025	1.00	1.16	1.64	26.3	30.5	43.2
1055	1.00	1.18	1.65	26.1	30.8	43.1
1085	1.00	1.30	1.72	24.9	32.4	42.7
1115	1.00	1.27	1.75	24.9	31.6	43.5
1145	1.00	1.41	1.91	23.2	32.6	44.2
1175	1.00	1.38	1.88	23.5	32.4	44.1
1205	1.00	1.56	2.07	21.6	33.7	44.7
1235	1.00	1.78	2.43	19.2	34.2	46.7
1265	1.00	1.72	2.35	19.7	34.0	46.3

Time	Average Integrations			Relative Percentage		
(s)	SM	VCPR	3,3	SM	VCPR	3,3
1295	1.00	1.69	2.41	19.6	33.1	47.3
1325	1.00	1.87	2.51	18.6	34.8	46.6
1355	1.00	1.86	2.60	18.3	34.1	47.6
1385	1.00	1.95	2.65	17.9	34.8	47.3
1415	1.00	2.48	3.36	14.6	36.2	49.1
1445	1.00	2.31	3.18	15.4	35.6	49.0
1475	1.00	2.65	3.57	13.9	36.6	49.5
1505	1.00	2.31	3.08	15.6	36.1	48.2
1535	1.00	2.70	3.55	13.8	37.2	49.0
1565	1.00	2.65	3.68	13.6	36.2	50.2
1595	1.00	3.04	4.27	12.0	36.5	51.4
1625	1.00	3.07	4.41	11.8	36.2	52.0
1655	1.00	2.96	4.16	12.3	36.5	51.2
1685	1.00	3.04	4.26	12.1	36.6	51.3
1715	1.00	3.22	4.44	11.6	37.2	51.3
1745	1.00	4.05	5.63	9.4	37.9	52.7
1775	1.00	3.50	4.64	10.9	38.3	50.8
1805	1.00	3.63	4.95	10.4	37.9	51.7
1835	1.00	4.26	5.99	8.9	37.9	53.2
1865	1.00	4.10	5.49	9.4	38.7	51.8
1895	1.00	4.71	6.66	8.1	38.1	53.9
1925	1.00	5.27	7.43	7.3	38.4	54.3
1955	1.00	4.75	6.31	8.3	39.4	52.3
1985	1.00	5.47	7.64	7.1	38.8	54.1
2015	1.00	4.68	6.58	8.2	38.2	53.7
2045	1.00	4.82	6.57	8.1	38.9	53.0
2075	1.00	6.13	8.45	6.4	39.4	54.2
2105	1.00	5.63	7.83	6.9	38.9	54.2
2135	1.00	5.74	8.28	6.7	38.2	55.1
2165	1.00	6.95	9.38	5.8	40.1	54.1
2315	1.00	12.12	16.74	3.3	40.6	56.1
2465	1.00	11.96	16.63	3.4	40.4	56.2
2525	1.00	10.33	14.72	3.8	39.6	56.5
2585	1.00	10.78	15.52	3.7	39.5	56.9
2645	1.00	14.73	21.04	2.7	40.0	57.2
6360	1.00	55.62	98.61	0.6	35.8	63.5

¹⁹F NMR integration data for the VCPR of **22a** in d8-toluene (0.15 M) heated at 373 K (AV400, QNP-z probe); 8 scans, D1= 1.0 s, TE = 373 K.

Time	Average Integrations			Relative Percentage		
(s)	SM	VCPR	3,3	SM	VCPR	3,3
51	1.00	0.07	0.04	90.6	6.1	3.4
75	1.00	0.08	0.04	90.0	6.8	3.3
99	1.00	0.10	0.11	82.6	7.9	9.5
123	1.00	0.12	0.16	78.4	9.3	12.3
147	1.00	0.18	0.22	71.1	13.1	15.8
171	1.00	0.24	0.29	65.2	15.9	18.9
195	1.00	0.28	0.35	61.6	17.0	21.4
219	1.00	0.32	0.42	57.2	18.6	24.2
243	1.00	0.35	0.52	53.4	18.9	27.6
267	1.00	0.43	0.58	49.7	21.3	29.0
291	1.00	0.51	0.68	45.7	23.2	31.1
315	1.00	0.56	0.77	42.8	24.2	33.0
339	1.00	0.61	0.85	40.5	24.9	34.6
363	1.00	0.66	0.95	38.3	25.2	36.5
387	1.00	0.76	1.08	35.2	26.7	38.1
411	1.00	0.85	1.23	32.5	27.6	39.9
435	1.00	0.93	1.36	30.4	28.4	41.2
459	1.00	0.99	1.41	29.4	29.1	41.4
483	1.00	1.10	1.57	27.2	30.0	42.8
507	1.00	1.22	1.83	24.7	30.2	45.1
531	1.00	1.34	1.88	23.7	31.7	44.6
555	1.00	1.52	2.20	21.2	32.2	46.6
579	1.00	1.59	2.34	20.3	32.3	47.5
603	1.00	1.76	2.58	18.7	33.0	48.3
627	1.00	1.97	2.92	17.0	33.4	49.6
651	1.00	2.21	3.16	15.7	34.7	49.7
675	1.00	2.13	3.13	16.0	34.0	50.0
699	1.00	2.43	3.56	14.3	34.8	50.9
723	1.00	2.70	3.87	13.2	35.6	51.2
747	1.00	2.88	4.15	12.4	35.8	51.7
771	1.00	2.98	4.32	12.0	35.9	52.1
795	1.00	3.59	5.19	10.2	36.7	53.1
819	1.00	3.78	5.38	9.8	37.2	53.0
843	1.00	3.36	4.88	10.8	36.3	52.8
867	1.00	4.25	6.24	8.7	37.0	54.3
891	1.00	5.13	7.42	7.4	37.9	54.7
915	1.00	6.12	8.78	6.3	38.5	55.2
939	1.00	5.47	7.85	7.0	38.2	54.8
963	1.00	6.99	10.23	5.5	38.4	56.2
987	1.00	6.75	9.82	5.7	38.4	55.9

Time	Average Integrations			Relative Percentage		
(s)	SM	VCPR	3,3	SM	VCPR	3,3
1011	1.00	7.67	10.89	5.1	39.2	55.7
1035	1.00	6.99	10.21	5.5	38.4	56.1
1059	1.00	6.96	9.74	5.6	39.3	55.0
1083	1.00	8.89	12.55	4.5	39.6	55.9
1107	1.00	10.62	14.97	3.8	39.9	56.3
1131	1.00	9.79	14.16	4.0	39.2	56.8
1155	1.00	14.57	21.05	2.7	39.8	57.5
1179	1.00	12.66	17.92	3.2	40.1	56.7
1203	1.00	16.53	23.12	2.5	40.7	56.9
1227	1.00	16.37	22.65	2.5	40.9	56.6
1251	1.00	16.80	23.88	2.4	40.3	57.3
1275	1.00	23.06	33.48	1.7	40.1	58.2
1299	1.00	20.64	28.65	2.0	41.0	57.0
1323	1.00	41.69	61.14	1.0	40.2	58.9
1347	1.00	22.65	32.25	1.8	40.5	57.7
1371	1.00	29.39	42.34	1.4	40.4	58.2
1395	1.00	28.58	40.41	1.4	40.8	57.7
1419	1.00	39.00	56.55	1.0	40.4	58.6
1443	1.00	38.19	54.13	1.1	40.9	58.0
1467	1.00	34.78	50.50	1.2	40.3	58.5
1635	1.00	382.68	547.06	0.1	41.1	58.8

Rearrangement Reaction Profiles for 22a (343-373 K)

The reaction profile (relative percentage conversion vs time) was plotted using the NMR data above on Excel.

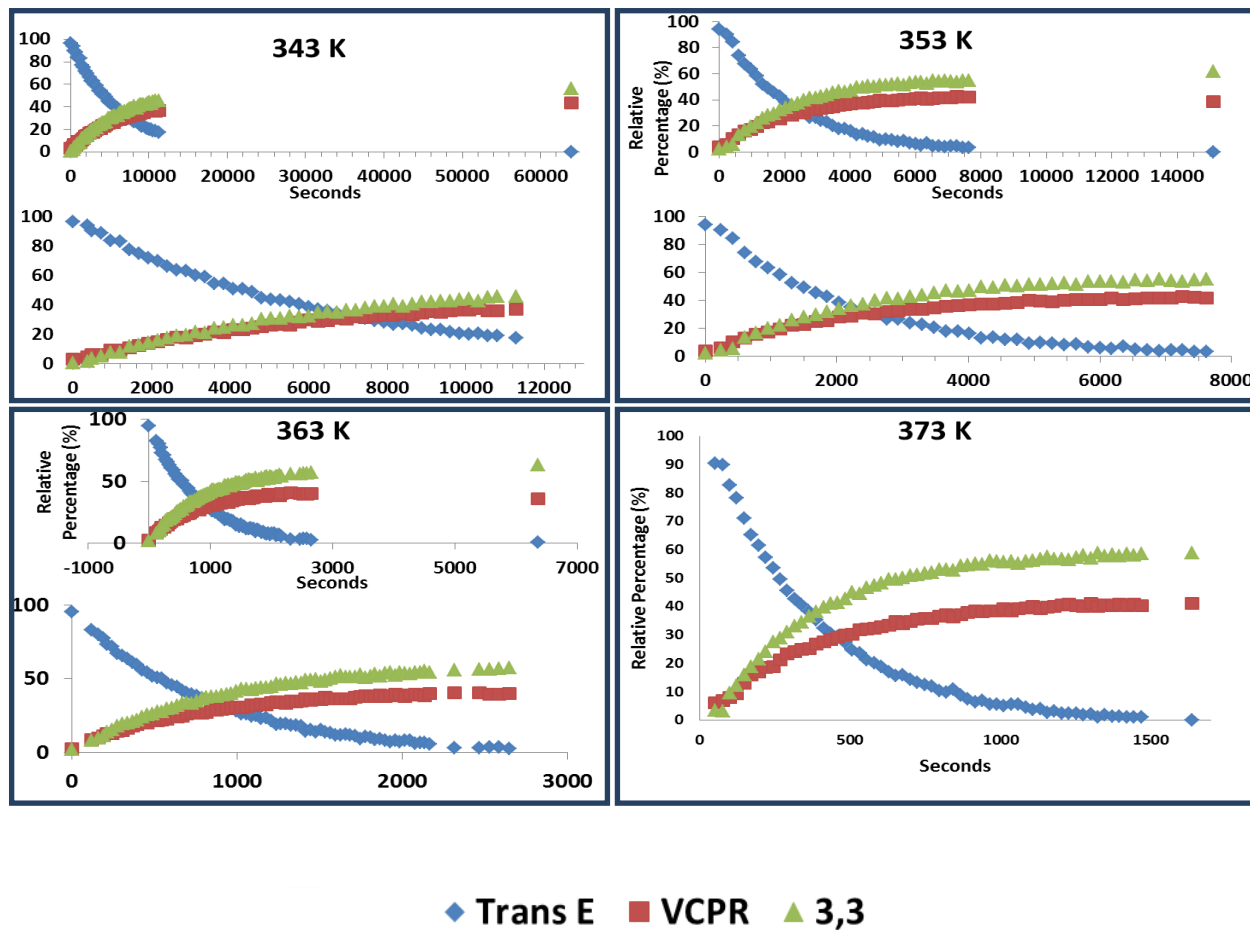


Figure S35: Reaction profiles for the rearrangement of 22a at 343-373 K.

NMR Simulations

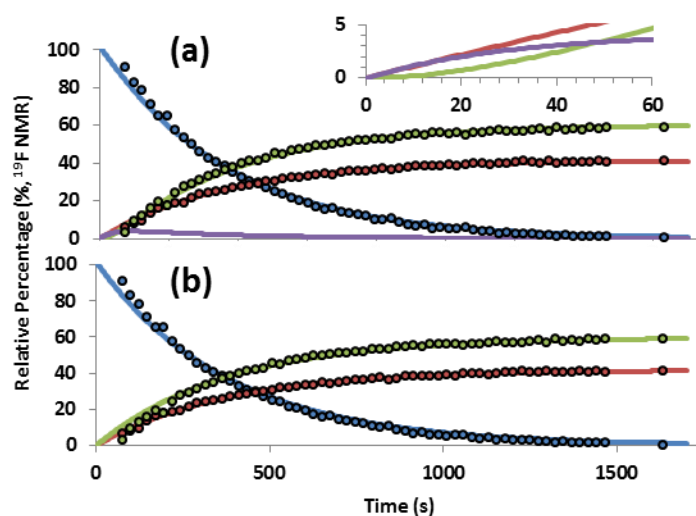
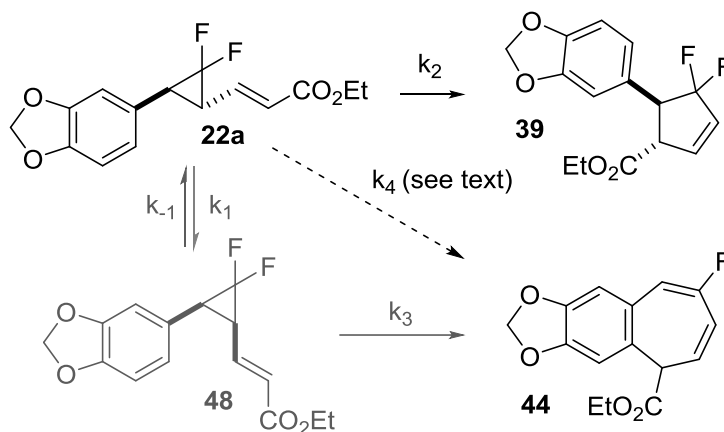


Figure S36: Experimental (points) and simulated (lines) concentration/time profile for thermolysis (373 K) of **22a**; a) simulation Model A takes into account *cis*-**48**; insert shows the first simulated 30 seconds of the rearrangement b) Model B utilising a steady state approximation for *cis*-**48** (blue = *trans*-**22a**, green = **44**, red = **39**, purple = *cis*-**48**).

The experimental concentration/time profile could be simulated successfully as far as experimental end points using numerical integration software^{S37} based on two kinetic models expressed in **Scheme S7**.



Scheme S8: Kinetic models used in the simulation of parallel VCPR and [3,3]-pathways.

Model A used successfully with phenyl **1a**, takes into account the equilibrium set up between *cis*-**48** and *trans*-**22a** due to cyclopropane stereoisomerisation and the subsequent first order rearrangement through to diene **44** and cyclopentene **39**, respectively. Simulated data using this model showed formation of *cis*-**48**, rising to a maximum at about 3% in the

reaction mixture after 30 seconds before slowly decaying (**Figure S36a**). These values are below the lower limit of experimental detection and explain why **48** was not observed. Deconvolution of rate constants predicted that rearrangement of **22a** should be selective for the [3,3]-pathway, with a rate approximately 40 times faster than VCPR (**Table S4**). This does not match experimental findings and may be due to an overestimation in rates involving *cis*-**XX** due to the lack of experimental data points to fit profiles to.

This issue was resolved by treating both rearrangement pathways as first order with respect to *trans*-**22a** (Model B), k_4 represents an overall rate for the conversion of **22a** to **48** and incorporates the cyclopropane stereoisomerisation and [3,3]-rearrangement rates associated with **48**. Again, simulated data showed good correlation with experimental values (**Figure S36b**) and this time the rate constants favoured the [3,3] pathway only slightly (1.5 times faster than VCPR), consistent with experimental conversions of 59% and 41% to diene **44** and cyclopentene **39**, respectively. Furthermore, the much higher rate for VCPR from **22a** ($11.5 \times 10^{-4} \text{ s}^{-1}$) than from phenyl **1a** ($1.6 \times 10^{-4} \text{ s}^{-1}$), matched the predicted differences in calculated activation energies.

Table S4: Rate Constants extracted from reaction simulations.

Rate (10^{-4} s^{-1})	Model	
	A	B
k_2	11.2	11.1
K_1	21.8	-
k_{-1}	153.2	-
k_3	439.4	-
k_4	-	15.8
k_3/k_2	39.2	-
k_4/k_2	-	1.4

Simulation Procedure: The NMR concentration/time data obtained for **22a** (including a measured endpoint) was imported into Berkeley Madonna software^{S37} from text files and simulated using the two methods discussed below:

Model A

```

STARTTIME = 0
STOPTIME=43200
DT = 0.05

A0=100 {start concentration of trans cyclopropane}
Init A=A0
B0=0 {start concentration of cis cyclopropane}
Init B=B0
C0=0 {start concentration of cyclopentene}
Init C=C0
D0=0 {start concentration of benzoheptadiene}
Init D=D0

k1=0.0001 {k1 is isomerisation to cis}
k_1=0.0001 {k_1 is isomerisation to trans}
k2=0.0001 {k2 is the VCPR}
k3=0.0001 {k3 is the 3,3}

d/dt (A)=-k1*A-k2*A+k_1*B
d/dt (B)=-k_1*B-k3*B+k1*A
d/dt (C)=k2*A
d/dt (D)=k3*B

LIMIT A>=0
LIMIT B>=0
LIMIT C>=0
LIMIT D>=0

```

The extracted rate data (343-373 K) from Model A was not consistent with experimental observation of VCPR and [3,3] pathways having similar rates (**Table S5**).

Table S5: Rate data based on Model A.

Temp (K)	$k_1(10^{-4} \text{ s}^{-1})$	$k_{-1}(10^{-4} \text{ s}^{-1})$	$k_2(10^{-4} \text{ s}^{-1})$	$k_3(10^{-4} \text{ s}^{-1})$
343	5.243	440.186	0.734	88.296
353	2.667	0.193	2.028	114.035
363	11.061	165.75	5.466	357.913
373	21.794	153.183	11.246	439.420

Model B

STARTTIME = 0
STOPTIME=43200
DT = 0.05

A0=100 {start concentration of trans cyclopropane}
Init A=A0
C0=0 {start concentration of cyclopentene}
Init C=C0
D0=0 {start concentration of benzoheptadiene}
Init D=D0

k2=0.0001 {k2 is the VCPR}
k4=0.0001 {k3 is the 3,3}

d/dt (A)=- k2*A-k4*A
d/dt (C)=k2*A
d/dt (D)=k4*A

LIMIT A>=0
LIMIT C>=0
LIMIT D>=0

The rate data extracted from **Model B** matched experimental results more closely, giving similar rate values for VCPR and [3,3]-rearrangement pathways (**Table S6**).

Table S6: Rate data extracted from Model B.

Temp (K)	$k_2 (10^{-4} s^{-1})$	$k_4 (10^{-4} s^{-1})$
343	0.7338	0.8725
353	2.0242	2.6320
363	5.4558	7.4840
373	11.0977	15.7878

Arrhenius Plot for Piperonyl 22a

Rate data from **Table S4** was changed into the desired Arrhenius parameters (**Table S7**).

Table S7: Arrhenius Data

Temperature (K)	1/T	$k_2 (10^{-4} \text{ s}^{-1})$	$\ln k_2$	$k_4 (10^{-4} \text{ s}^{-1})$	$\ln k_4$
344.1	0.002906132	0.7338	-9.51986	0.8725	-9.34673
354.2	0.002823264	2.0242	-8.50517	2.632	-8.2426
364.2	0.002745744	5.4558	-7.51366	7.484	-7.19757
374.2	0.002672368	11.0977	-6.8036	15.7878	-6.4511

From Arrhenius equation **1**, a plot of $\ln k_2$ or $\ln k_4$ vs $1/T$ was generated on Excel and a line fitted using the trendline function (**Figure S37**). The equation of the line was calculated using the *LINEST* statistical function and the gradient used to calculate E_a . The errors in the values were estimated by plotting two lines which would result from the maximum errors ($\pm 5\%$) in the outermost points and averaging the gradient to determine the E_a .

$$\ln k = \frac{-E_a}{R} \frac{1}{T} + \ln A \quad (1)$$

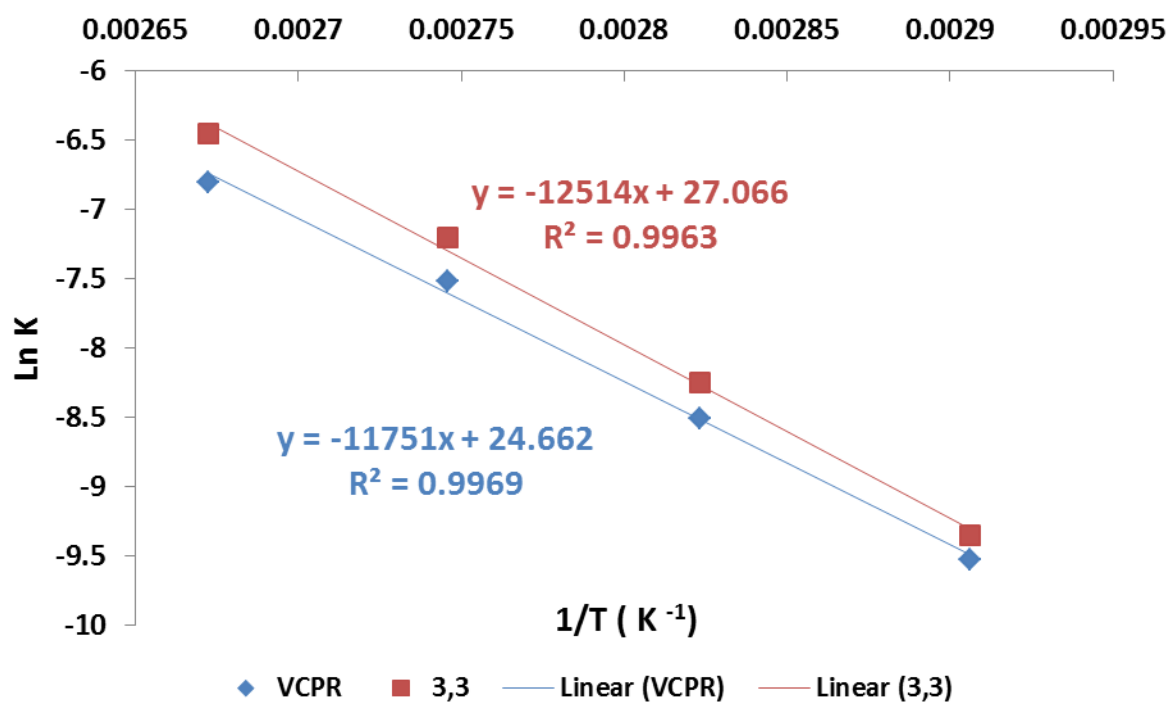


Figure S37: Combined Arrhenius Plots for VCPR and [3,3]-rearrangement of **22a**.

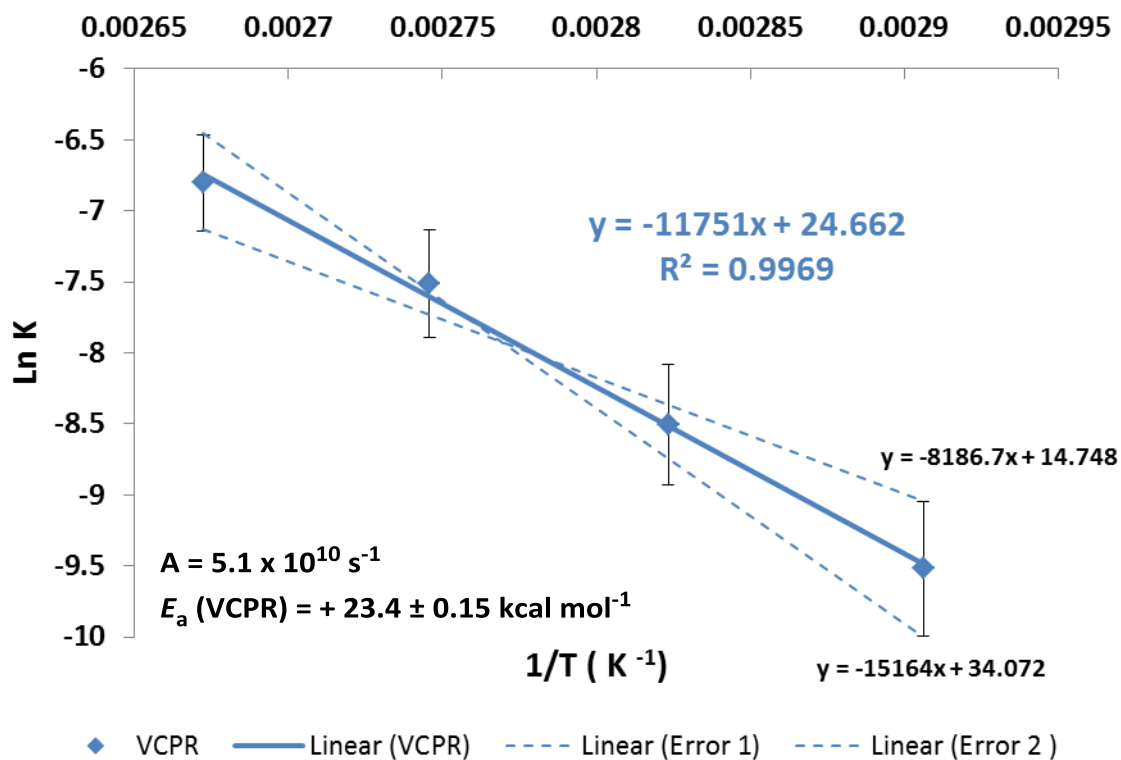


Figure S38: Arrhenius plot for VCPR of **22a** with error estimations.

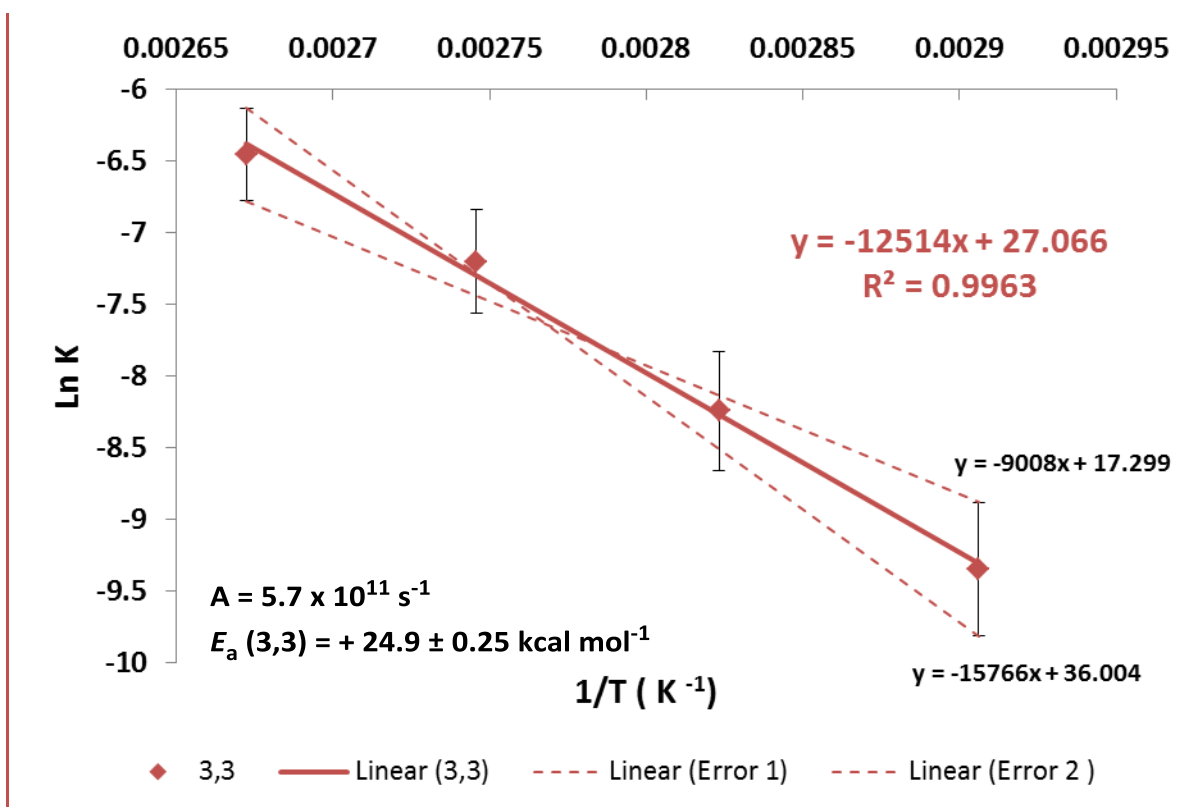


Figure S39: Arrhenius plot for [3,3]-rearrangement of **22a** with error estimations.

Identification the Most Appropriate Method for Electronic Structure Calculations

In order to assess the accuracy of the electronic structure calculations efficiently, all experimental activation energies were recalculated to 298 K using the Arrhenius data and methods described by Maskill.^{S38} We previously reported that for VCPRs, changes to the basis set either had detrimental effects (with UB3LYP, UM06-2X and UB97-D functionals) or gave slightly more accurate values of $\Delta G^\ddagger$ when the diffuse function was introduced (6-31+G*) with the UM05-2X functional. Increasing polarisation and diffuse functions (6-31+G**) gave no improvement in the agreement between experimental and calculated values for a benchmarking set of VCPRs; these trends were also followed for piperonyl **22a** (see S182 for more details). Initial methodology screening was carried out using Spartan'10 software due to the ease of local implementation. All activation energies were then recalculated in Gaussian'09, since the software dealt with the open shell singlet character of the VCPR better giving $\langle S^2 \rangle$ values closer to 0.75, some additional valuable methods were available, and the energies obtained would then be more comparable with the literature. Investigating the barrier height for the rearrangement of VCP **9f** to **TS1f** (models representing piperonyl **22a**), gave results comparable to those observed with phenyl **9j**. The M05-2X functional^{S39} with the 6-31+G* basis set still proved to be the most accurate methodology, with a $\Delta\Delta G^\ddagger = 0.2 \text{ kcal mol}^{-1}$ (**Figure S40**). Truhlar and co-workers reported that the M06-2X functional, with a similar HF-exchange (56% for M05-2X and 58% M06-2X), was slightly more accurate overall in assessing kinetic parameters than M05-2X.^{S40} However in our new system (VCP-**9f**) this was not the case, with a higher (4.5 kcal mol⁻¹) overestimation by the M06-2X functional with the same basis set.

During the review of the manuscript of our previous publication, it was suggested that the different amounts of HF-exchange used in each method could have some role in determining the accuracy of the calculated free energies of activation for the VCPR. The M06 functional, with a lower HF-exchange of 27%, gave the closest agreement with experimental values when the 6-31G* basis set was used ($\Delta\Delta G^\ddagger = 0.7 \text{ kcal mol}^{-1}$). Electronic structure calculations using M05/6-31G* methodology were less accurate ($\Delta\Delta G^\ddagger = 2.6 \text{ kcal mol}^{-1}$), even though this functional has a similar HF-exchange value (28%) to the M06 functional. However, we observed little difference between the M05-2X and M06 functionals when the VCPR barrier heights were calculated with Gaussian'09 for piperonyl **9f**, simple precursor **8a** and phenyl **9j**. Furthermore, for the VCPR of non-fluoro **8b**, M06/6-

31+G* calculations were only within 1.6 kcal mol⁻¹ (underestimate) whereas M05-2X/6-31+G* methods gave $\Delta\Delta G^\ddagger$ values within 0.8 kcal mol⁻¹ (overestimate, see S183 for more details).

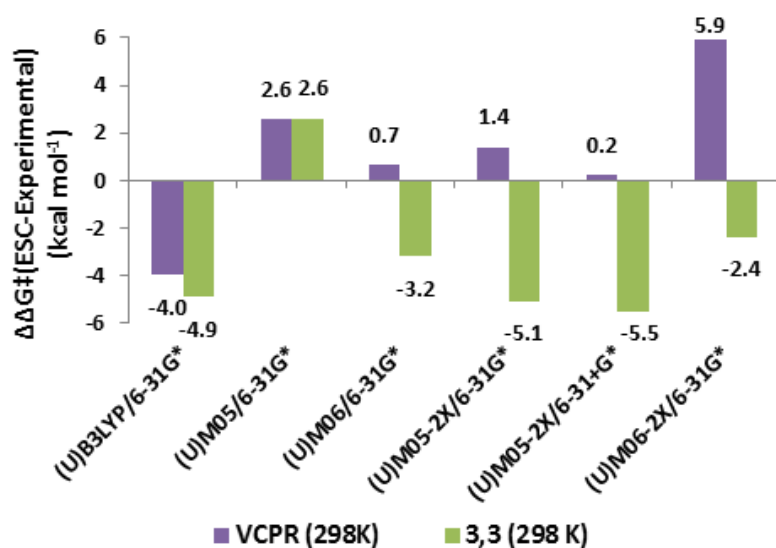


Figure S40: Differences between experimental $\Delta G^\ddagger$ (298 K, re-calculated from activation parameters) and $\Delta G^\ddagger$ from electronic structure calculations (298 K, gas phase, Spartan'10) plotted as $\Delta\Delta G^\ddagger$ ($\Delta G^\ddagger(\text{ESC}) - \Delta G^\ddagger(\text{experimental})$, kcal mol⁻¹) for the VCPR and [3,3]-rearrangement of VCP **9f** and **48**, respectively. Expected error associated with calculated data is ± 0.5 kcal mol⁻¹.

Other DFT methods either underestimated experimental barrier heights when 20% HF-exchange was used (B3LYP), or overestimated (+1.8 kcal mol⁻¹) when a hybrid exchange-correlation was used with 19% HF-exchange at short range and 65% at long range (CAM-B3LYP,⁵⁴¹ (**Figure S41**)). These results suggest that HF-exchange alone does not determine the accuracy of VCPR activation energies.

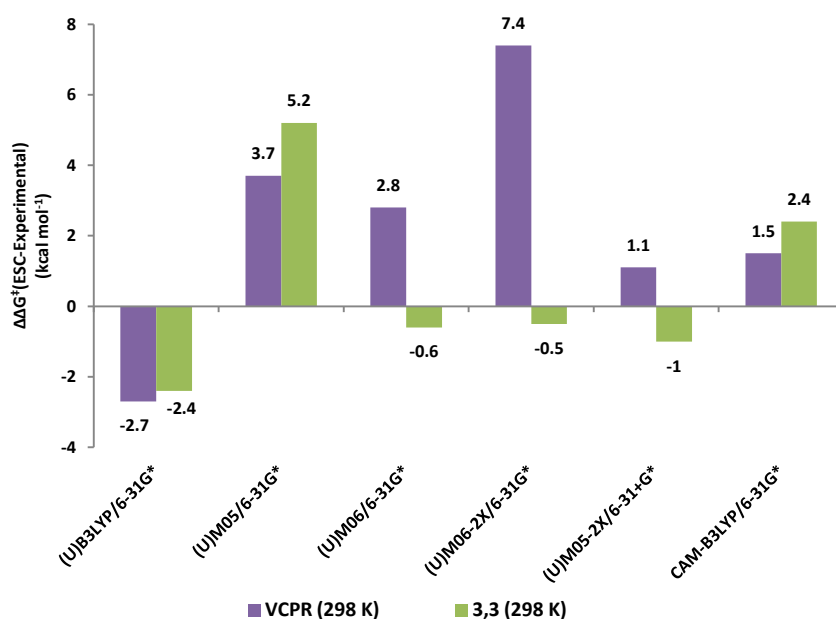


Figure S41: Differences between experimental $\Delta G^\ddagger$ (298 K, re-calculated from activation parameters) and $\Delta G^\ddagger$ from electronic structure calculations (298 K, gas phase, Gaussian'09) plotted as $\Delta\Delta G^\ddagger$ ($\Delta G^\ddagger(\text{ESC}) - \Delta G^\ddagger(\text{experimental})$, kcal mol⁻¹) for the VCPR and [3,3]-rearrangement of VCP **9f** and **48**, respectively. Expected error associated with calculated data is ± 0.5 kcal mol⁻¹.

One difference which was observed between phenyl and piperonyl substituents was the change in dipole moment calculated from precursor to transition state; **9j** showed a slight decrease in calculated polarity during VCPR and [3,3]-rearrangement (change in dipole = -0.39 and -0.22 Debyes, respectively) whereas **9f** showed a slight increase (change in dipole = +1.2 and +0.95 Debyes, respectively, UB3LYP/6-31G*, Gaussian'09, gas phase, 298 K). The calculated activation energies for the two rearrangement pathways from **9f** were assessed using M05-2X/6-31+G* method with different solvation parameters which had varying dielectric constants (range of $\epsilon = 2.37$ -35.7), but only a slight decrease in barrier height for the [3,3]-rearrangement in acetonitrile compared with gas phase was predicted ($\Delta G^\ddagger_{\text{Gas}} - \Delta G^\ddagger_{\text{MeCN}} = -0.9$ kcal mol⁻¹). Maas reported that the experimental rate for the [3,3]-rearrangement of non-fluorinated 1-aryl-2-vinylcyclopropanes was more than 8 times faster in acetonitrile than benzene, but VCPR rates were not affected by reaction solvent.^{S42} VCP **22a** showed no significant change in rearrangement outcome when heated in either [D3]acetonitrile (52% (**44**([3,3]) and 48% (**39**(VCPR)) conversion, determined by ¹⁹F NMR) or [D8]toluene (58% (**44**([3,3]) and 42% (**39**(VCPR)) conversion, determined by ¹⁹F NMR).

Therefore, no solvation methods were applied and all electronic structure calculations were carried out in the gas phase (see S184 for more details).

Previously, only a concerted closed-shell transition state was investigated for the [3,3]-rearrangement of *cis*-**1b**. This was consistent with Özkan and Zora's study^{S43} of the divinylcyclopropane rearrangement; despite running spin-unrestricted calculations, no low energy diradical or triplet intermediates or transition states were found. We used our previously optimised triplet intermediate of ring opened phenyl VCP **9j** as a starting point to search for alternative triplet or open shell singlet pathways for the [3,3]-rearrangement ((U)B3LYP/6-31G* (gas phase, 298 K), Spartan'10). Two triplet transition states connected the alkenoate radical with alternative *ortho*-carbon centred radicals on the aromatic ring; both had uncompetitive calculated activation energies of 53.6 kcal mol⁻¹ and 59.2 kcal mol⁻¹. Only one of these optimised as a diradical, but had a much higher barrier for rearrangement (37.8 kcal mol⁻¹) than the closed shell pathway (27.8 kcal mol⁻¹). For subsequent computational methodology screening, the [3,3]-rearrangement was treated using closed shell methodology (see S187 for more details).

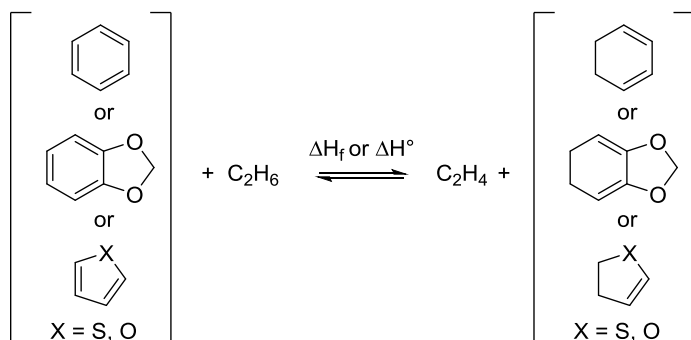
Irrespective of the basis set used, the M05-2X functional was found to be the least accurate of those examined for calculating the free energy of activation of **48** to **TS6a** (6-31G*, $\Delta\Delta G^\ddagger = -5.1$ kcal mol⁻¹ and 6-31+G*, $\Delta\Delta G^\ddagger = -5.5$ kcal mol⁻¹). Instead, the M06-2X/6-31G* combination was found to be the best at predicting barrier height with a $\Delta\Delta G^\ddagger = -2.4$ kcal mol⁻¹ (**Figure S40**). This is opposite to what was observed for the VCPR and gives a strong indication of the functionals' differing abilities in dealing with open shell singlet character or the loss of aromaticity at transition states. The (U)B3LYP/6-31G* method gave a similar underestimation in barrier height for both pathways ($\Delta\Delta G^\ddagger$ values were within error of ± 0.9 kcal mol⁻¹) but (U)M05/6-31G* gave exactly the same overestimate of 2.6 kcal mol⁻¹. If required, these two combinations of functions and basis sets provide a universal method for assessing both rearrangement pathways in Spartan'10.

Electronic structure calculations for VCP **9f** which were carried out in Gaussian'09 dealt with the open shell singlet character of the VCPR better (*S*² value closer to 0.75) than Spartan'10, resulting in more accurate barrier heights; M05/6-31G* was the key exception, with higher $\Delta\Delta G^\ddagger$ values for both VCPR and [3,3]-pathways (+3.7 kcal mol⁻¹ and +5.2 kcal mol⁻¹, respectively). DFT methodology using B3LYP/6-31G* still gave consistent underestimation in barrier height for both pathways; $\Delta\Delta G^\ddagger$ values were within 0.3 kcal mol⁻¹ of each other

(**Figure S41**). Of the Minnesota functionals, the M06-2X/6-31G* method remained the most accurate for the [3,3]-rearrangement ($\Delta\Delta G^\ddagger = -0.5 \text{ kcal mol}^{-1}$) and M05-2X/6-31+G* for the VCPR ($\Delta\Delta G^\ddagger = +1.1 \text{ kcal mol}^{-1}$).

We looked to explore the effectiveness of the B3LYP/6-31G* and M06-2X/6-31G* calculations of barrier heights for divinylcyclopropane^{S11,S44} and heteroarene-vinylcyclopropane rearrangements^{S45} reported in the literature but the reported experimental errors were so big that it made it impossible to distinguish between accurate and inaccurate calculated barriers (see S189 for more details).

An absolutely critical event in the [3,3]-rearrangement is the temporary disruption of aromaticity; the enthalpic consequences of this event must be handled well if any method is to provide realistic free energies of activation. The isodesmic reactions represented in **Scheme S9** were used to assess how well the B3LYP and M06-2X methods dealt with this temporary dearomatisation in the transition state.



Scheme S9: Isodesmic reactions used to model the disruption of aromaticity.

We therefore benchmarked the DFT calculations against well-known thermochemical recipes using these isodesmic reactions. There was little difference between the calculated heats of formation for either T1^{S46} or G3(MP2)^{S47} thermochemical recipes (within computational error of $\pm 0.5 \text{ kcal mol}^{-1}$), but when compared with experimental values,^{S48,S49} T1 was more accurate for ethane and ethylene whereas G3(MP2) was slightly more accurate for aromatic compounds (**Figure S42**).

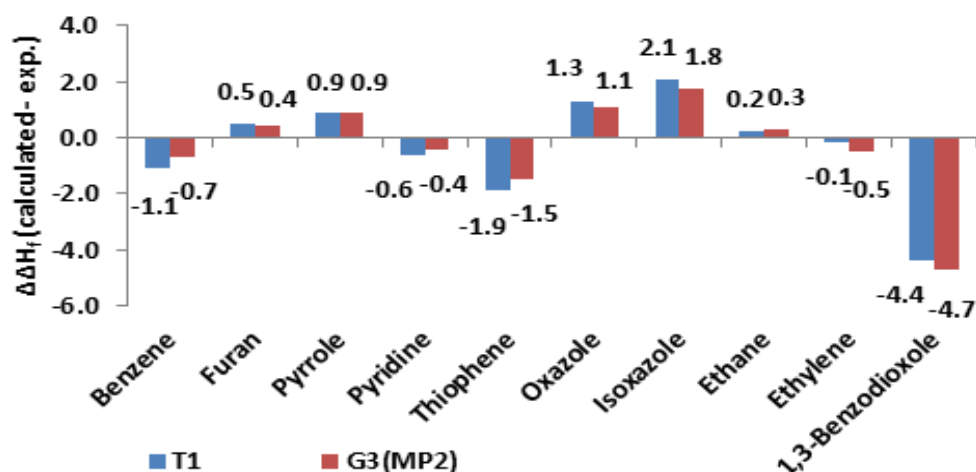


Figure S40: Differences between calculated and experimental heats of formation (Spartan'10, values in kcal mol⁻¹).

The average error associated with the calculated heats of formation for benzene, furan, pyrrole, pyridine, thiophene, oxazole and isoxazole were ± 1.21 kcal mol⁻¹ and ± 0.95 kcal mol⁻¹ for T1 and G3(MP2), respectively. Calculated data for 1,3-benzodioxole had an underestimation greater than 4.0 kcal mol⁻¹ for both methods when compared with experimental values.^{S50}

The G3(MP2) values were used to assess the accuracy of the calculated enthalpy change for the dearomatisation of benzene, benzodioxole, furan and thiophene using either B3LYP/6-31G* or M06-2X/6-31G* methodology (**Figure S43**, see S193, S194 for more details). The B3LYP method had an average overprediction in enthalpy of 5.3 kcal mol⁻¹ for benzene, furan, thiophene and 1,3-benzodioxole, and M06-2X consistently over-estimated the enthalpic cost of dearomatisation, ranging from 3.6 kcal mol⁻¹ to 6.4 kcal mol⁻¹ (total average error of 4.8 kcal mol⁻¹).

This thermochemical analysis suggests that the two most desirable methods for assessing the [3,3]-rearrangement do not deal with the loss of aromaticity at the transition state well. This is important since M06-2X/6-31G* calculations were perceived to be the most accurate, but are likely to over-predict the free energy ($\Delta G^\ddagger$) for rearrangements involving benzene, furan, thiophene and 1,3-benzodioxole.

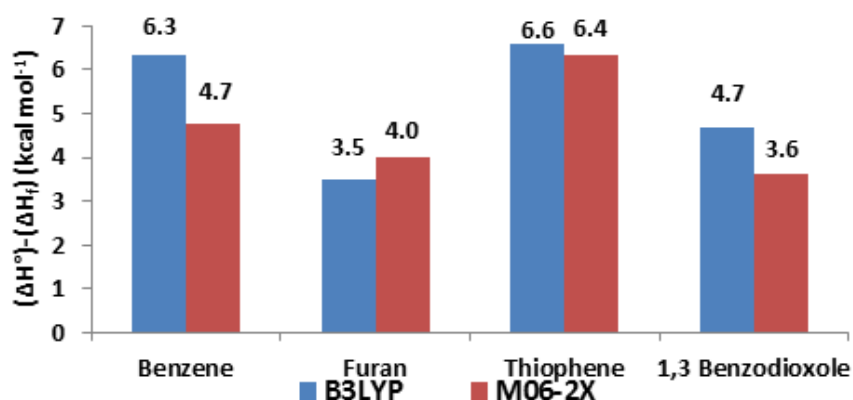


Figure S43: Difference in change in enthalpy (ΔH°) calculated using B3LYP or M06-2X (6-31G*) methods and G3(MP2) heats of formation (ΔH_f) for the isodesmic reactions represented in Scheme 10 (gas phase, 298 K, Spartan'10, units are in kcal mol⁻¹).

Basis Set Effect on 9f VCPR Activation Energies

M05-2X functional was the most accurate method for calculating the free energies of activation for the VCPR of phenyl-**9j** and piperonyl-**9f**. No benefit was found from increased basis sets higher than 6-31+G* for **9f** consistent with our previous studies^{S20} (Table S8 and Figure S44).

Table S8: Basis Set Effect on Accuracy of Calculated VCPR Free Energies of Activation for **9f**

Functional	Basis Set	$\Delta G^\ddagger$ [a]	$\Delta\Delta G^\ddagger$ [b]
M05-2X	6-31G*	29.80	2.80
M05-2X	6-31+G*	28.10	1.10
M05-2X	6-311G*	30.30	3.30
M05-2X	6-311+G**	28.30	1.30

[a] Gaussian'09, gas phase, 298 K. [b] Difference in calculated free energy of activation $\Delta G^\ddagger$ and calculated activation energy (E_a); $\Delta\Delta G^\ddagger = (\Delta G) - (E_a)$. All units are in kcal mol⁻¹.

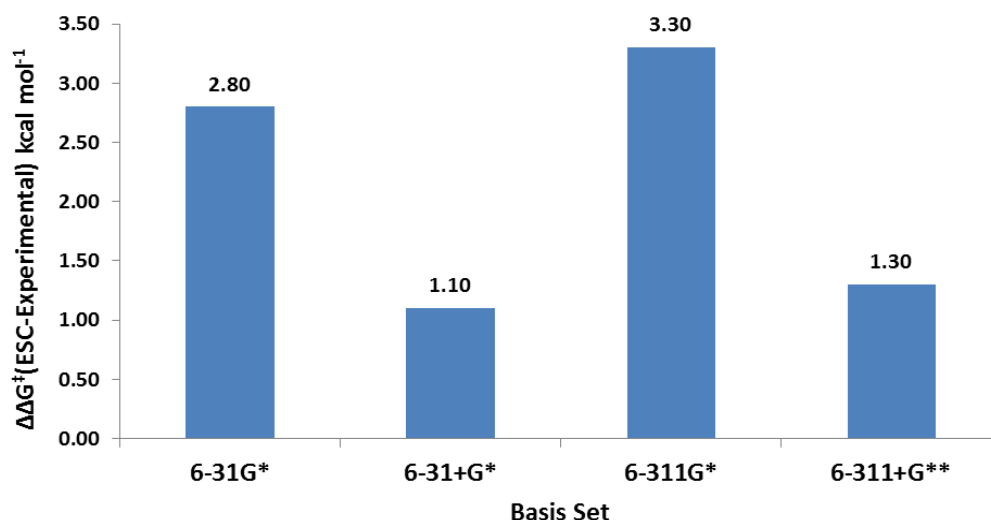


Figure S41: Comparison of $\Delta\Delta G^\ddagger$ values and basis set effects (Gaussian'09, M05-2X, gas phase, 298 K, Energies quoted in kcal mol⁻¹).

Method Screening for VCPR

The calculated activation energies for the VCPR of simple VCP **8b** and difluoro-VCPs, phenyl **9j** and piperonyl **9f**, were assessed showing that the M05-2X/6-31+G* method was the most accurate for all three compounds (**Table S9** and **Figure S45**).

Table S9: Methodology Screening for VCPR

Method	$\Delta\Delta G^\ddagger$ (ESC – Experimental, kcal mol ⁻¹) ^[a]		
	8b ^[b]	9j ^[c]	9f ^[d]
UB3LYP/6-31G*	-2.3	-2	-2.7
UCAM-B3LYP/6-31G*	-	-	1.5
UM05/6-31G*	2.0	3.3	3.7
UM06/6-31G*	1.4	2.4	2.8
UM05-2X/6-31G*	1.6	2.5	2.8
UM05-2X/6-31+G*	0.8	1.2	1.1
UM06/6-31+G*	-1.6	-	-

[a] Gaussian'09, gas phase, 298 K. [b] Experimental activation energy corrected to 298 K from literature data.^{S51} [c] Experimental data reported in previous publication.^{S20} [d] This work.

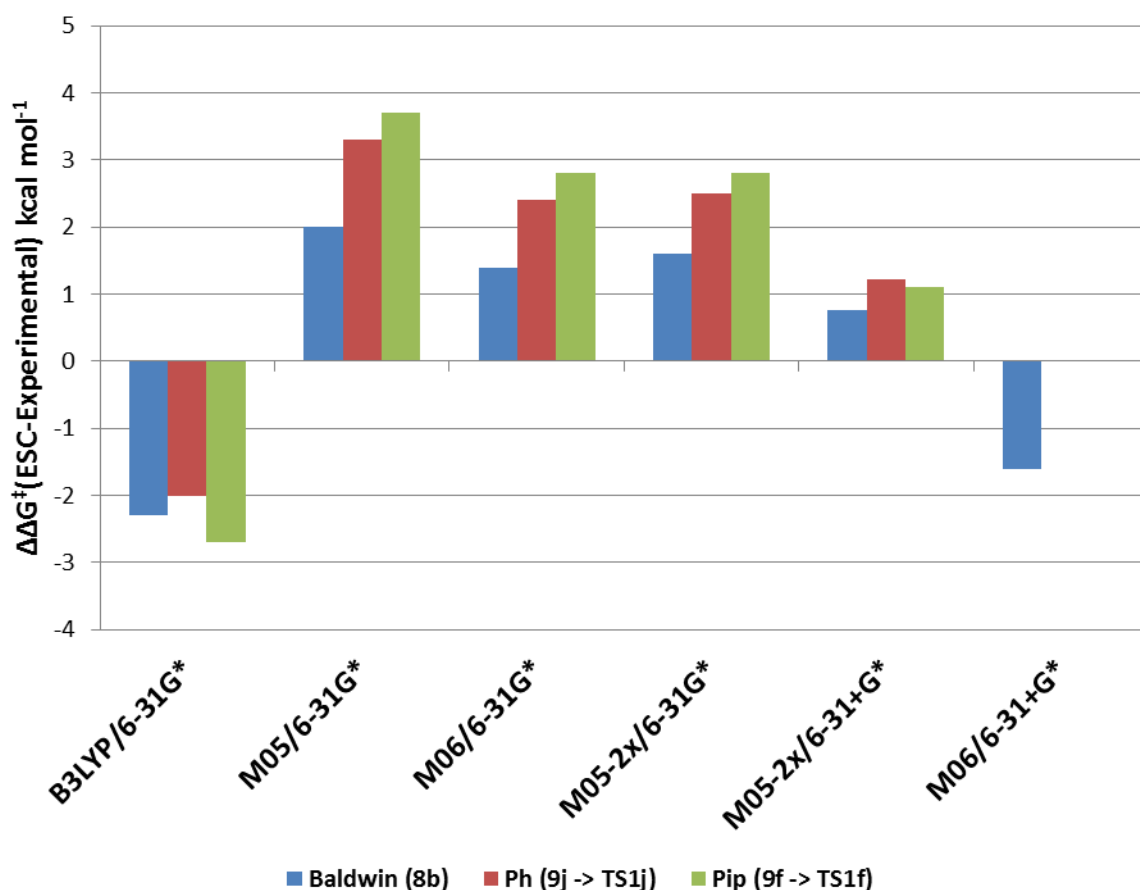


Figure S42: Computational methodology screening for VCPR.

Assessment of Solvent Effects

The difference in dipole between the VCPR and aromatic-vinylcyclopropane rearrangement transition states for the rearrangement of piperonyl-VCP precursors (*trans*-**9f** and *cis*-**9f**, respectively) was used to assess the potential effect solvent would have on electronic structure calculations (**Table S10**).

Table S10: Solvation Effect on VCPR and [3,3]-Rearrangement Dipole Moments

Solvent	Solvent Properties		Difference in Dipole Moment (Debyes) ^[c]	
	Dielectric Constant ^[a]	Dipole Moment (Debyes) ^[b]	9f -> TS1f	48 -> TS6a
Gas Phase (n.a.)	n.a.	n.a.	0.11	0.74
Toluene	2.37	0.36	0.30	0.74
Diphenyl Ether	3.73	1.30	0.63	0.73

1-Pentanol	15.13	1.70	0.50	1.06
Acetonitrile	35.70	3.92	0.53	1.06

[a] Data reported in Gaussian'09 user's reference.^{S52} [b] Data reported by National Institute of Standards and Technology (NIST).^{S53} [c] Gaussian'09, (U)M05-2X/6-31+G*, 298 K, solvation parameterised using Self-Consistent Reaction Field (SCRF)^{S54} using the Conductor-like Polarizable Continuum Model (CPCM).^{S55}

Due to the slightly higher dipole moment for the [3,3]-pathway, more polar solvents (1-pentanol, acetonitrile) gave lower $\Delta G^\ddagger$ values compared with gas phase or less polar solvents (toluene, diphenyl ether); approximately 1.0 kcal mol⁻¹ lower energy barrier (**Table S11** and **Figure S46**).

Table S11: Solvent Effect on Rearrangement Free Energies of Activation ($\Delta G^\ddagger$)

Solvation	$\Delta G^\ddagger$ ((U)M05-2X/6-31+G*, 298 K, Gaussian'09)		
	VCPR	[3,3]	$\Delta\Delta G^\ddagger$ ($\Delta G^\ddagger_{\text{VCPR}} - \Delta G^\ddagger_{[3,3]}$)
Gas Phase	28.1	25.3	2.8
Toluene	28.2	25.5	2.7
Diphenylether	28.3	25.7	2.6
1-Pentanol	28.5	24.4	4.1
Acetonitrile	28.6	24.4	4.2

All units are in kcal mol⁻¹.

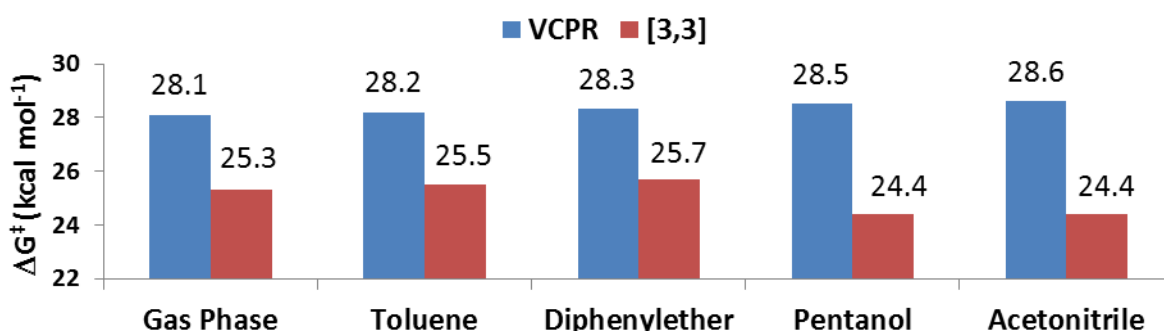
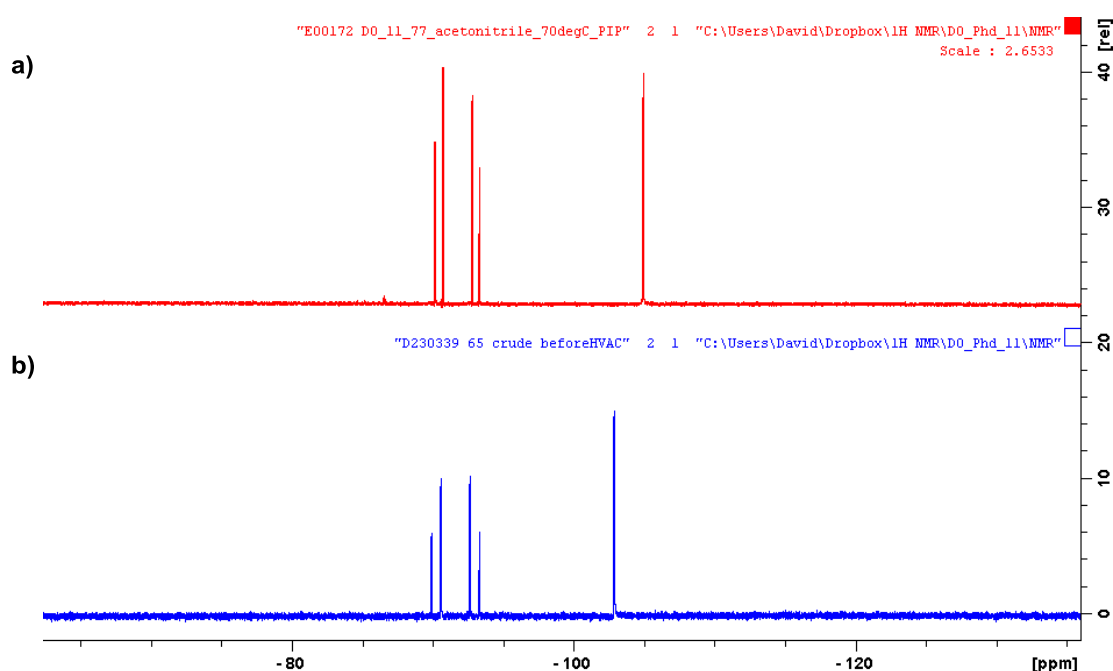


Figure S43: Solvent effect on calculated $\Delta G^\ddagger$ values for the VCPR of **9f** and [3,3]-rearrangement of **48**.

The effect of solvent was also investigated experimentally: A solution of piperonyl-**22a** (19.3 mg, 0.33 mmol) in 0.44 M [D3]acetonitrile (0.75 mL) or [D8]toluene (0.75 mL) was heated in an oil bath at 70 °C for 17 hours. Crude ¹⁹F NMR analysis of the resulting mixture was used to determine relative conversion of rearrangement products (**Table S12**), showing little difference in reaction selectivity between solvents (**Figure S47**).

Table S12: Solvent Effect on Thermal Rearrangement of **22a**.

Solvent	Average ¹⁹ F NMR Integration		Relative Percentage (%) ^[a]	
	VCPR (39)	[3,3] (44)	VCPR (39)	[3,3] (44)
[D3]acetonitrile	0.9584	1.0281	48	52
[D6]toluene	0.9744	1.3721	42	58

[a] Assumed NMR integration error of ± 5 %.**Figure S44:** Crude ¹⁹F NMR for thermal rearrangement of **22a** in a) [D3]acetonitrile and b) [D6]toluene.

Investigations into Alternative [3,3]-Diradical/Triplet Pathways

Attempts to use transition state **S-TS5** as a starting point to investigate triplet or diradicaloid possibilities failed when all calculations resulted in closed shell compounds ($S^2 = 0$). Instead, our previously reported *transoid* triplet intermediate **S21** was used as a starting point with atom constraints set up between alkenoate carbon and aryl C5 or C2, giving rise to *transoid* and *cisoid* structures, respectively (**Figure S42**). Molecules were manipulated in Spartan'10

to bring reaction centres within approx. 3.0 Å. Energy profiles were examined by bringing the reaction centres closer together along the constraint (3.073 Å to 1.073 Å, over 15 steps) using low level molecular mechanics (UAM1, multiplicity = 3, no MIX keyword used). Higher energy species with imaginary frequencies were examined without constraints and afforded three triplet transition states for the [3,3]-rearrangement, *transoid* **S-TS6** and *cisoid* **S-TS7a** and **S-TS7b**. These were further optimised using (U)B3LYP/6-31G* methodology with the $\langle S^2 \rangle$ values used to determine multiplicity of the transition state; values of 0 = closed shell, close to 0.75 = diradical and 2.0 = triplet. For triplet calculations the multiplicity was set to 3 and diradical calculations required the additional keyword MIX. For the *transoid* system (**STS-7a**) all three multiplicities gave much higher free energies of activation ($\Delta G^\ddagger = 37.8$ -53.6 kcal mol⁻¹) with respect to the previously optimised closed-shell **S-TS5** ($\Delta G^\ddagger = 27.8$ kcal mol⁻¹). Only a triplet transition state optimised from *cisoid* **S-TS7a** ($\Delta G^\ddagger = 59.2$ kcal mol⁻¹). Alternative *cisoid* **S-TS7b** optimised as a closed shell transition state ($\Delta G^\ddagger = 25.7$ kcal mol⁻¹), the diradical calculations resulted a similar closed shell transition state ($\langle S^2 \rangle = 0$). This newly found closed-shell **S-TS7b** and **S-TS5** were further optimised in Gaussian'09 and gave the same $\Delta G^\ddagger$ value of 23.9 kcal mol⁻¹. These investigations confirmed that the *cisoid*-closed shell **S-TS5** is the lowest energy pathway for aromatic-vinylcyclopropane rearrangements.

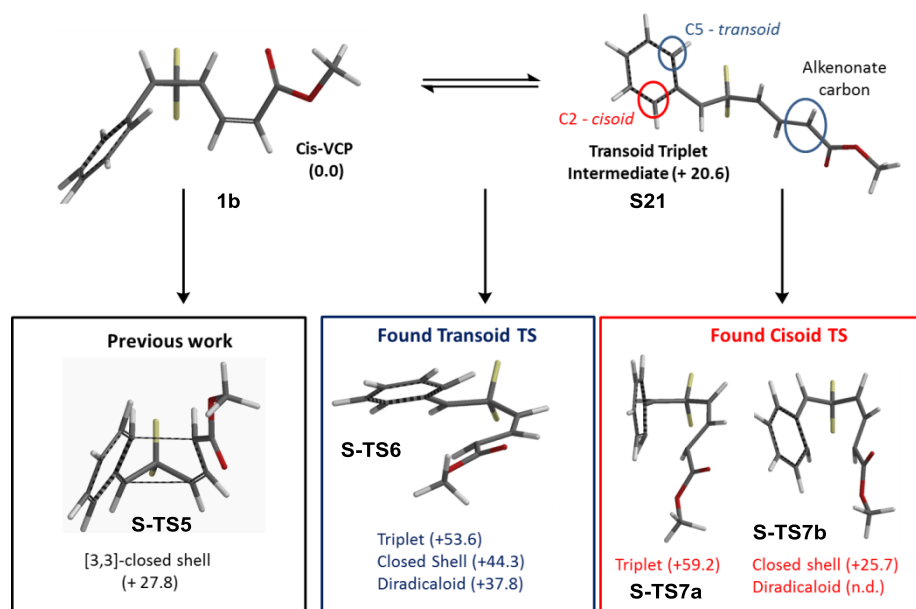


Figure S45: Closed-shell, diradical and triplet transition states for [3,3]-rearrangement (units in kcal mol⁻¹).

Arrhenius Plot for divinyl-difluorocyclopropane **S3**

The kinetic data reported by Erbes and Boland^{S11} for the rearrangement of divinyl-**S3** was altered into Arrhenius parameters in Excel (**Table S13**) and plotted as described above. The resulting Arrhenius plot (**Figure S49**) and errors (**Figure S50**) gave an experimental E_a value for the divinylcyclopropane rearrangements as (24.0 ± 0.17) kcal mol⁻¹; within error of reported value of 23.8 kcal mol⁻¹. The pre-exponential factor (A) was calculated as 7.4×10^{16} s⁻¹. These values were used to recalculate the activation energy at 298 K.

Table S13: Kinetic Data used to generate Arrhenius Plot in **Figure S49**.

T (K)	1/T	k (x 10 ⁻⁵) s ⁻¹	ln k
298	0.003356	0.75	-0.2877
313	0.003195	4.94	1.5974
323	0.003096	14.9	2.7014
333	0.003003	47.8	3.8670
343	0.002915	152.0	5.0239

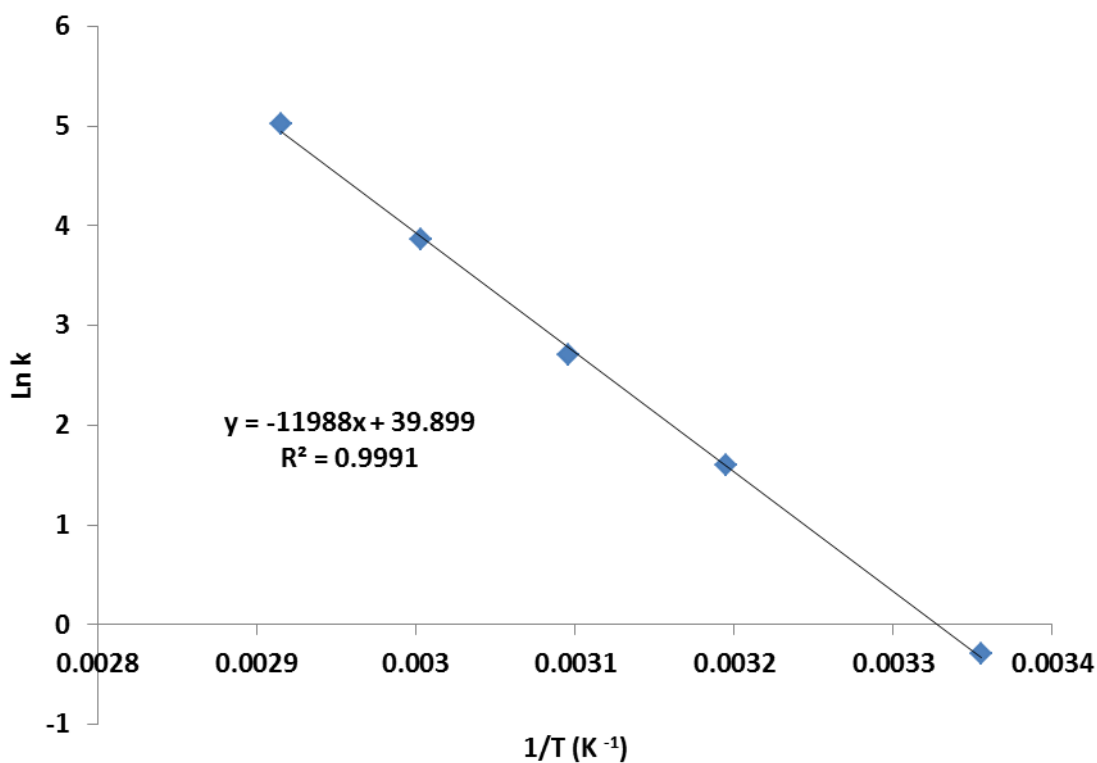


Figure S46: Arrhenius plot from literature kinetic data for the [3,3]-rearrangement of **S3**.

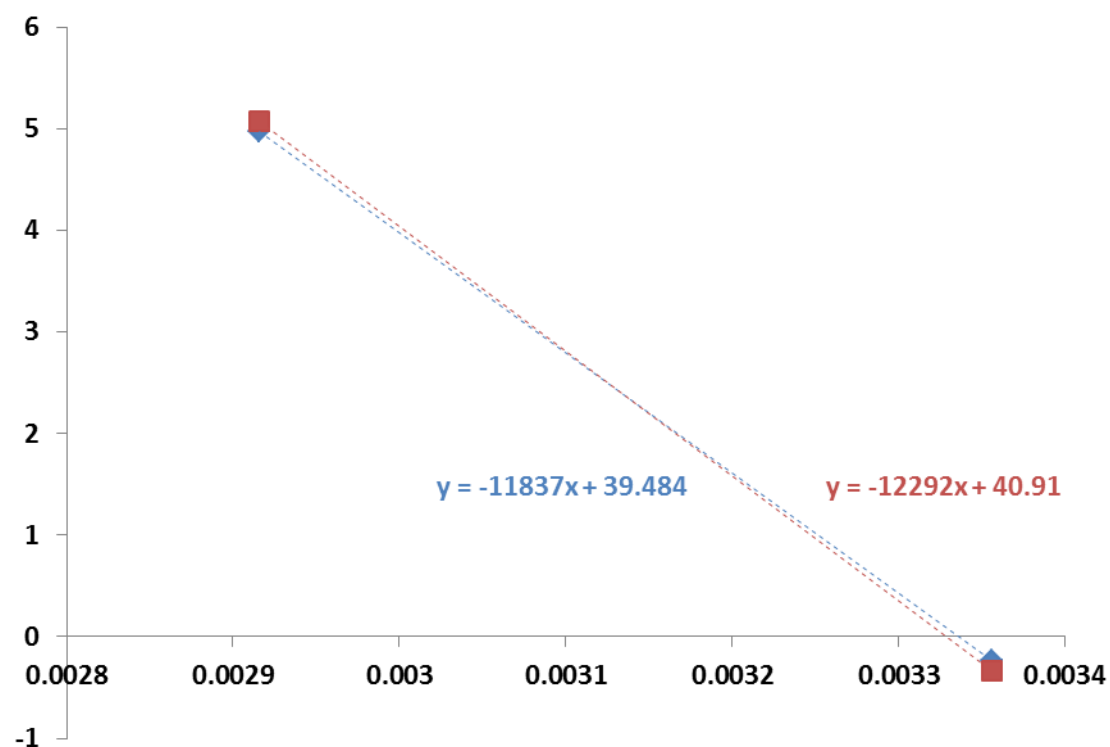


Figure S50: Error associated with Arrhenius plot in **Figure S49**.

[3,3]-Sigmatropic Computational Methodology Screening

We looked to explore the effectiveness of the B3LYP/6-31G* and M06-2X/6-31G* calculations of barrier heights ($\Delta G^\ddagger_{\text{B3LYP}}$ and $\Delta G^\ddagger_{\text{M062X}}$, respectively) for divinylcyclopropane^{S11,44,45} and heteroaromatic-vinylcyclopropane rearrangements^{S46} reported in the literature (**Figure S51**).

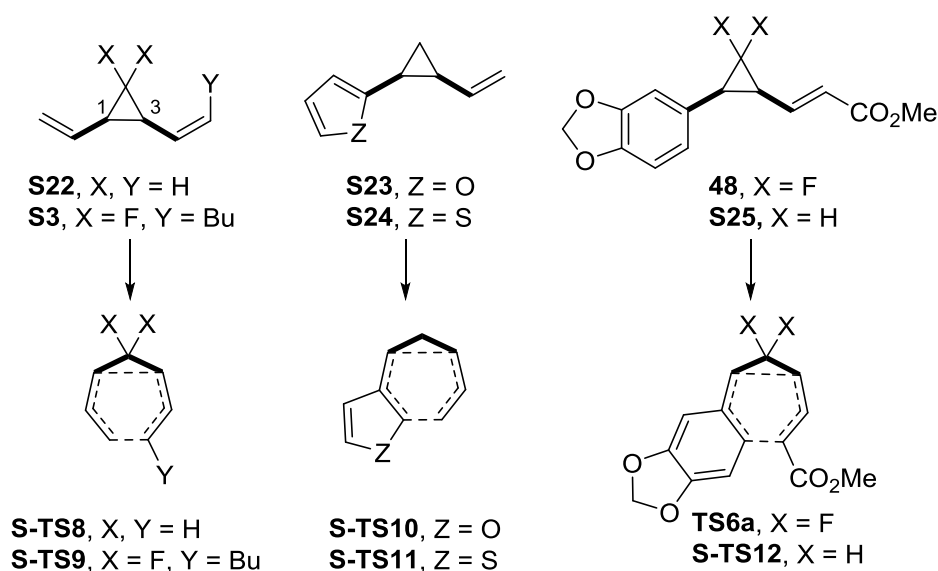


Figure S51: [3,3]-precursors and their corresponding transition states examined with electronic structure calculations.

Little difference was observed for the calculated $\Delta G^\ddagger$ values for the divinylcyclopropane rearrangement of di-VCP **S22** and fluorinated **S3** using the DFT method ($\Delta G^\ddagger_{\text{B3LYP}}$ difference of $0.4 \text{ kcal mol}^{-1}$) but the Minnesota method gave a $\Delta G^\ddagger_{\text{M06-2X}}$ difference of $4.6 \text{ kcal mol}^{-1}$ between systems (**Table S14**). The latter was more consistent with the distal bond of *gem*-difluorocyclopropane being weaker than the corresponding non-fluorinated system.^{S56}

Due to the disruption of aromaticity in **S-TS10** and **S-TS11**, the aromatic-vinylcyclopropane rearrangement of furyl-**S23** and thiophenyl-**S24** showed higher $\Delta G^\ddagger$ values of approximately $4.0 \text{ kcal mol}^{-1}$ (B3LYP) or $10.0 \text{ kcal mol}^{-1}$ (M06-2X) than **S22**; this was less significant for piperonyl **48** ($2.8 \text{ kcal mol}^{-1}$ (B3LYP) and $6.1 \text{ kcal mol}^{-1}$ (M06-2X)). In our system, the difluorocyclopropyl ring has a beneficial effect on the [3,3]-rearrangement, with $\Delta G^\ddagger$ values approximately 8 kcal mol^{-1} lower than the corresponding non-fluorinated **S25** ($\Delta \Delta G^\ddagger_{\text{B3LYP}} = 31.8 \text{ kcal mol}^{-1}$ and $\Delta \Delta G^\ddagger_{\text{M06-2X}} = 33.2 \text{ kcal mol}^{-1}$).

Table S14: Barriers for [3,3]-rearrangement from electronic structure calculations (ESC) and recalculated experimental Arrhenius data.

Computational Methodology	Barriers for [3,3]-Rearrangement ($\Delta G^\ddagger$, kcal mol ⁻¹ , gas phase, 298 K)					
	S22 -> S-TS8	S3 -> S-TS9	S23-> S-TS10	S24 -> S-TS11	48 -> TS6a	S25 -> S-TS12
B3LYP/6-31G*	21.1	21.6	26.1	26.2	23.9	31.8
M06-2X/6-31G*	23.5	19.2	29.7	29.8	25.6	33.2
Experimental ^[a]	21.0	17.6	25.7	27.0	26.3	n.d.
(error)	(± 3.8)	(± 5.9)	(± 3.0)	(± 2.6)	(± 1.9)	

[a] All experimental values were recalculated to 298 K to allow comparison with ESC. Arrhenius determination of kinetic data for substrate **S3** provided an experimental $\Delta G^\ddagger$ which was recalculated to 298 K using methods described by Maskill.^{S38} Calculated values of $\Delta S^\ddagger$ and $\Delta H^\ddagger$ were used for precursors **S23** and **S24** to recalculated $\Delta G^\ddagger$ values to 298 K.

It was promising that the majority of calculated free energies of activation were within experimental error, but the size of the errors made it difficult to assess the most accurate method for the [3,3]-rearrangement fully (**Figure S52**). The B3LYP/6-31G* was the most accurate for the divinylcyclopropane rearrangement with a $\Delta\Delta G^\ddagger$ value of +0.1 kcal mol⁻¹, comparable with Özkan and Zoras' DFT studies ($\Delta\Delta G^\ddagger = -0.3$ kcal mol⁻¹).^{S43} In contrast, the M06-2X/6-31G* calculations gave the best results with difluoro-**S3** ($\Delta\Delta G^\ddagger = +1.6$ kcal mol⁻¹) but the extremely large error associated the experimental free energy of activation (± 5.9 kcal mol⁻¹) made it difficult for an effective comparison between methods.

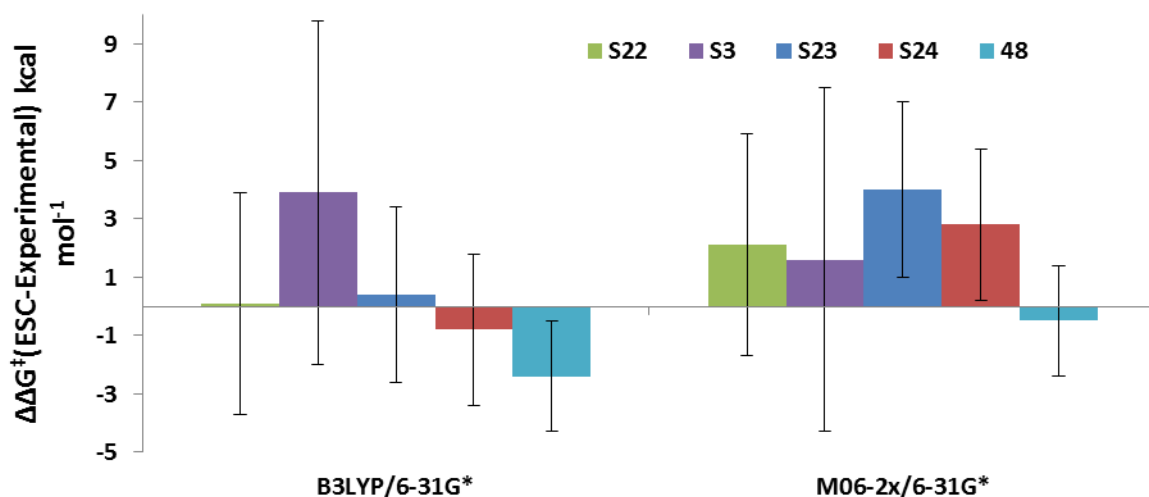


Figure S52: Differences between experimental $\Delta G^\ddagger$ (298 K) and $\Delta G^\ddagger$ from electronic structure calculations (298 K), plotted as $\Delta\Delta G^\ddagger$ ($\Delta G^\ddagger$ (ESC) - $\Delta G^\ddagger$ (experimental), Gaussian'09, kcal mol⁻¹). Expected error associated with calculated data is ± 0.5 kcal mol⁻¹. Error bars represent error associated with experimental data (see **Table S12** for values).

For the aromatic-vinylcyclopropane rearrangement, the closest agreement with experimental values was observed with B3LYP/6-31G* for heteroaromatic substituents **S23** and **S24** ($\Delta\Delta G^\ddagger$ values were within 0.8 kcal mol⁻¹) but M06-2X/6-31G* was favoured for piperonyl **48** ($\Delta\Delta G^\ddagger$ values were within 0.7 kcal mol⁻¹).

Error Associated with T1 and G3(MP2) Calculations

All aromatics examined experimental were built *de novo* on Spartan'10 and minimised using low level molecular mechanics then the heat of formation calculated using the T1 and G3(MP2) thermochemical recipe. The calculated heat of formation (ΔH_f° , **Table 13**) were compared with experimental values to determine the error associated with the calculations (**Figure S53**).

Table S15: Experimental and Calculated Heats of Formation

Compound	Heat of Formation (ΔH_f° , 298 K, kcal mol ⁻¹)				
	Experimental ^[a]	T1	$\Delta\Delta H_f^\circ$ ^[b]	G3(MP2)	$\Delta\Delta H_f^\circ$ ^[b]
Benzene	19.8	18.7	-1.1	19.1	-0.7
1,3-Benzodioxane	-34.1 ^[c]	-38.5	-4.4	-38.8	-4.7
Furan	-8.2	-7.7	0.5	-7.8	0.4
Pyrrole	25.9	26.8	0.9	26.7	0.8
Pyridine	33.6	33.0	-0.6	33.2	-0.4
Thiophene	27.5 ^[d]	25.6	-1.9	26.0	-1.5
Oxazole	-3.7	-2.4	1.3	-2.6	1.1
Isoxazole	18.8	20.9	2.1	20.5	1.8
Ethane	-20.2	-20.0	0.2	-19.9	0.3
Ethylene	12.5	12.4	-0.1	12.0	-0.5

[a] All values reported by Domalski unless otherwise stated.^{S48} [b] $\Delta\Delta H_f^\circ = (\Delta H_f^\circ \text{ calculated}) - (\Delta H_f^\circ \text{ experimental})$. [c] Value reported by Cohen.^{S50} [d] Value reported by Hubbard and co-workers.^{S49}

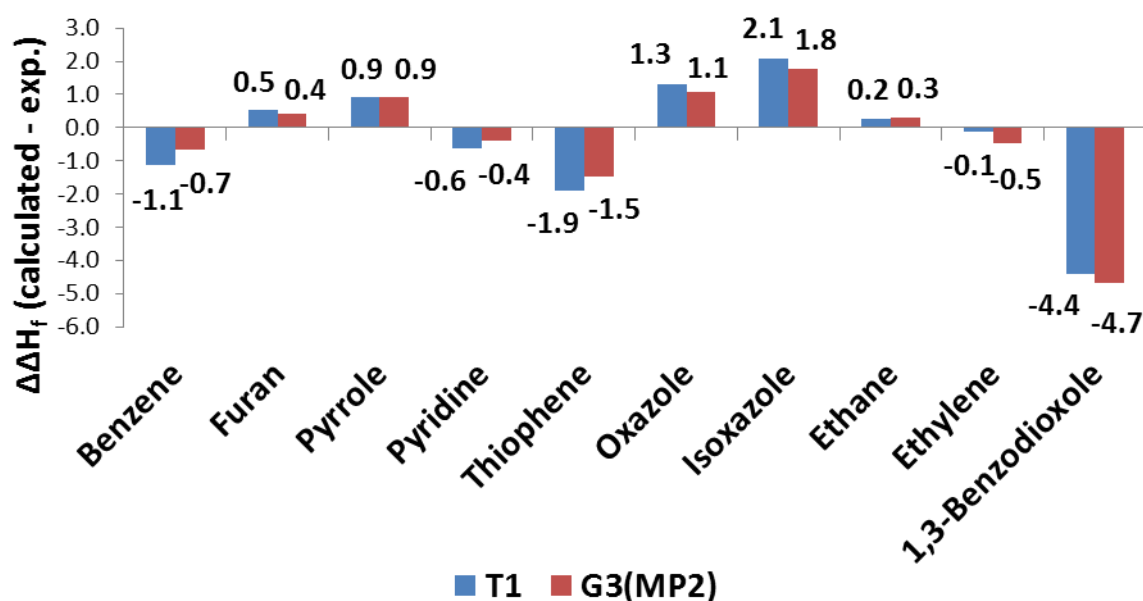


Figure S47: Difference in calculated and experimental heats of formation.

Raw Data for Isodesmic Reactions

The enthalpic change (ΔH° , B3LYP/6-31G* and M06-2X/6-31G*) and heat of formation (ΔH_f , T1 and G3(MP2)) for the isodesmic reactions depicted in **Scheme 10** were calculated on Spartan'10 using the method described above.

Raw data for benzene, 1,3-benzodioxole, furan and thiophene are displayed in **Tables S16-S19**.

Table S16: Raw energy values based on isodesmic reaction with benzene.

Method	benzene	Ethane	Total	reduced	Ethene	Total	ΔH_f or ΔH°
T1 (kJ mol ⁻¹)	78.22	-83.67	-5.45	106.59	51.70	158.29	163.74
G3(MP2) (kJ mol ⁻¹)	80.017	-83.366	-3.35	106.35	50.35	156.71	160.054
B3LYP (a.u.)	-232.14	-79.75	-311.89	-233.29	-78.53	-311.82	0.071055
M062x (a.u.)	-232.03	-79.72	-311.75	-233.17	-78.50	-311.68	0.069946

Table S17: Raw energy values based on isodesmic reaction with 1,3-benzodioxole.

Method	benzodioxole	Ethane	Total	reduced	Ethene	Total	ΔH_f or ΔH°
T1 (kJ mol ⁻¹)	-161.11	-83.67	-244.78	-136.07	51.70	-84.37	160.41
G3(MP2) (kJ mol ⁻¹)	-162.45	-83.37	-245.82	-138.56	50.35	-88.21	157.609
B3LYP (a.u.)	-420.65	-79.75	-500.40	-421.81	-78.53	-500.34	0.0675978
M062x (a.u.)	-420.48	-79.69	-500.17	-421.63	-78.48	-500.11	0.0659189

Table S18: Raw energy values based on isodesmic reaction with thiophene.

Method	thiophene	Ethane	Total	reduced	Ethene	Total	ΔH_f or ΔH°
T1 (kJ mol ⁻¹)	107.11	-83.67	51.70	76.24	51.70	127.94	76.24
G3(MP2) (kJ mol ⁻¹)	108.91	-83.37	50.35	79.29	50.35	129.64	79.285
B3LYP (a.u.)	-552.93	-79.75	-632.68	-554.11	-78.53	-632.64	0.040688
M062x (a.u.)	-552.82	-79.72	-632.54	-553.99	-78.51	-632.50	0.041781

Table S19: Raw energy values based on isodesmic reaction with furan.

Method	furan	Ethane	Total	reduced	Ethene	Total	ΔH_f or ΔH°
T1 (kJ mol ⁻¹)	-32.24	-83.67	-115.91	-73.30	51.70	-21.60	94.31
G3(MP2) (kJ mol ⁻¹)	-32.73	-83.37	-116.10	-73.96	50.35	-23.61	92.486
B3LYP (a.u.)	-229.95	-79.75	-309.70	-231.12	-78.53	-309.68	0.0408578
M062x (a.u.)	-229.85	-79.72	-309.57	-231.02	-78.51	-309.52	0.0430657

All raw values were converted into kcal mol⁻¹ for comparison (**Table S20**). Differences between ΔH_f and ΔH° values were used to assess how well the DFT and Minnesota functionals dealt with the loss of aromaticity in the isodesmic reaction (**Figures S50 and S51**).

Table S20: Compiled Heats of Formation (ΔH_f) and Enthalpies (ΔH°) for Isodesmic Reaction (all energies are in kcal mol⁻¹).

	Method	benzene	furan	thiophene	1,3-benzodioxole
ΔH_f	T1	39.1	38.3	22.5	18.2
	G3(MP2)	38.3	37.7	22.1	18.9
ΔH°	B3LYP	44.6	42.4	25.6	25.5
	M062X	43.0	41.3	26.1	25.3

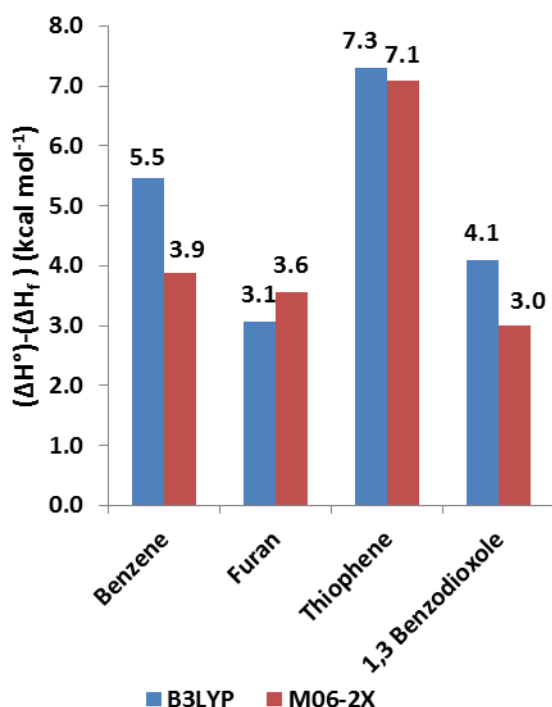


Figure S48: T1 differences between calculated ΔH° and ΔH_f .

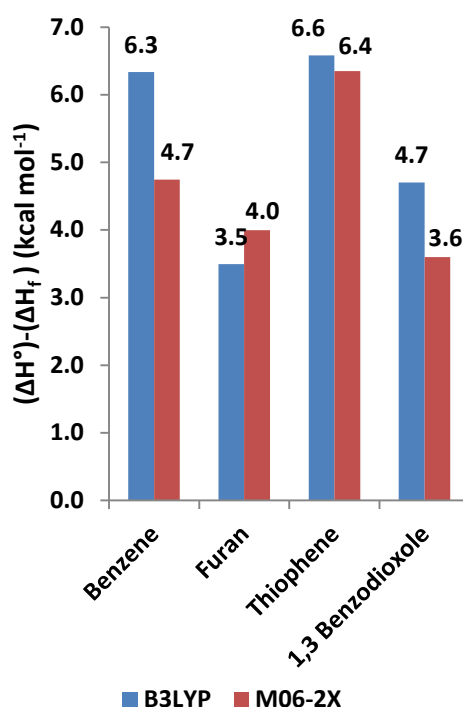


Figure S55: G3(MP2) differences between calculated ΔH° and ΔH_f .

Free Energy Values for Computational Predictions

Table S21: Calculated free energies of activation ($\Delta G^\ddagger$) for VCPR and [3,3]-rearrangement.

VCP	Calculated $\Delta G^\ddagger$ (Gaussian'09, gas phase, 298 K, kcal mol ⁻¹)							
	(U)B3LYP ^[a]		Corrected		UM052X ^[b]	M062X ^[a]	Corrected	
	VCPR	[3,3]	VCPR ^[c]	[3,3] ^[d]	VCPR	[3,3]	VCPR ^[e]	[3,3] ^[f]
1a	26.6	27.8	29.3	30.2	29.8	29.5	28.6	30.0
47	35.1	35.5	37.8	37.9	38.1	36.5	36.9	37.0
22a	24.3	23.9	27.0	26.3	28.1	27.0	26.9	27.8
20a	30.6	33.9	33.3	36.3	32.7	35.0	31.5	35.5
23a	22.1	17.5	24.8	19.9	25.7	20.7	24.5	21.2
25a	25.3	24.2	28.0	26.6	32.7	26.1	26.7	26.6
27a	22.5	21.8	25.2	24.2	26.2	24.2	25.0	24.7
27a	26.3	32.6	29.0	35.0	30.4	33.0	29.2	33.5
24a	22.5	18.5	25.2	20.9	26.0	21.2	24.8	21.7
26a	25.7	25.0	28.4	27.4	29.2	27.5	28.0	28.0
19a	26.2	33.3	28.9	35.7	28.0	35.6	27.6	36.1
21a	24.7	27.9	27.4	30.3	28.8	30.8	27.6	31.3
21b	29.7	32.7	32.4	35.1	34.0	36.7	32.8	37.2

[a] Using 6-31G* basis set. [b] Using 6-31+G* basis set. [c] $\Delta G^\ddagger + 2.7$ kcal mol⁻¹ (UB3LYP/6-31G*) [d] Calculated $\Delta G^\ddagger + 2.4$ kcal mol⁻¹ (B3LYP/6-31G*) [e] Calculated $\Delta G^\ddagger - 1.2$ kcal mol⁻¹ (UM05-2X/6-31+G*) [f] Calculated $\Delta G^\ddagger + 0.5$ kcal mol⁻¹ (M06-2X/6-31G*). All intermediates and transition states are for conformationally simpler Me ester.

VCPR Temperature Predictions

Table S22 represents the data used to generate temperature prediction graphs for M05-2x/6-31+G* and B3LYP/6-31+G* methods (**Figure 12** and **Figure S56**, respectively).

Table S22: Temperature and $\Delta G^\ddagger$ data for prediction graphs.

VCP	Opt. Reaction Temp.		VCPR $\Delta G^\ddagger$	
	°C	K	B3LYP/6-31G*	M05-2X/6-31+G*
22a	70	343	27.0	26.9
21a	90	363	27.4	27.6
19a	95	368	28.9	28.0
1a	100	373	29.3	28.6
21b	160	433	32.4	32.8
47	220	493	37.8	36.9

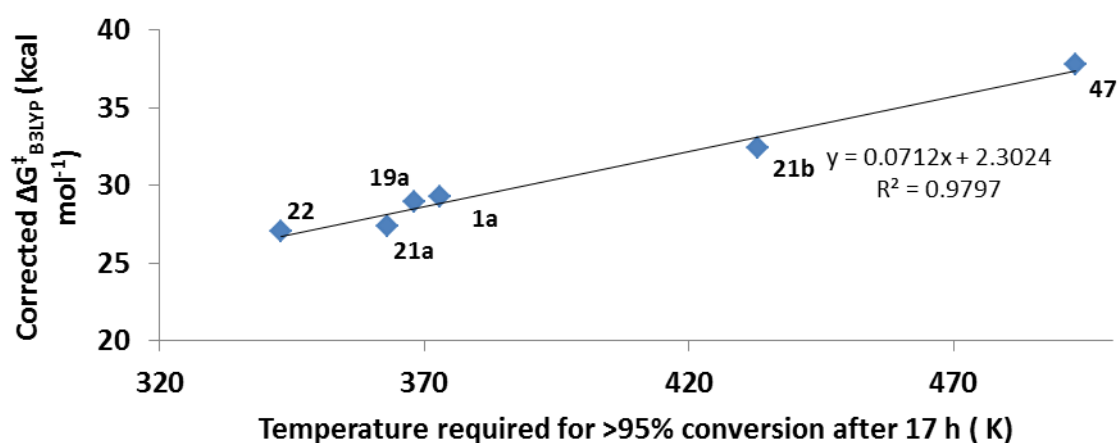


Figure S56: Trend between corrected $\Delta G^\ddagger$ values for VCPR (UB3LYP/6-31G*) and rearrangement temperature.

References

- (S1) Waser, J.; Gaspar, B.; Nambu, H.; Carreira, E. M. *J. Am. Chem. Soc.* **2006**, *128*, 11693.
- (S2) Lohre, C.; Fröhlich, R.; Glorius, F. *Synthesis* **2008**, 2221.
- (S3) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.
- (S4) Fischer, E. O.; Maasböl, A. *Angew. Chem. Int. Ed.* **1964**, *3*, 580.
- (S5) Agirbas, H.; Jackson, R. A. *J. Chem. Soc., Perkin Trans. 2* **1983**, 739.
- (S6) Jiang, X.; Ji, G. *J. Org. Chem.* **1992**, *57*, 6051.
- (S7) Dust, J. M.; Arnold, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 1221.
- (S8) Creary, X. *Acc. Chem. Res.* **2006**, *39*, 761.
- (S9) Zipse, H. In *Radicals in Synthesis I*; Gansäuer, A., Ed.; Springer Berlin Heidelberg: **2006**; Vol. 263, p 163.
- (S10) Henry, D. J.; Parkinson, C. J.; Mayer, P. M.; Radom, L. *J. Phys. Chem. A* **2001**, *105*, 6750.
- (S11) Erbes, P.; Boland, W. *Helv. Chim. Acta* **1992**, *75*, 766.
- (S12) Creary, X.; Wolf, A.; Miller, K. *Org. Lett.* **1999**, *1*, 1615.
- (S13) Schneider, T. F.; Werz, D. B. *Org. Lett.* **2011**, *13*, 1848.
- (S14) Schneider, T. F.; Kaschel, J.; Werz, D. B. *Angew. Chem. Int. Ed.* **2014**, *53*, 5504.
- (S15) Bruno, I.; Cole, J.; Lommerse, J. M.; Rowland, R. S.; Taylor, R.; Verdonk, M. *J. Comput. Aided Mol. Des.* **1997**, *11*, 525.
- (S16) Lebel, H.; Davi, M. *Adv. Synth. Catal.* **2008**, *350*, 2352.
- (S17) Iwasaki, M.; Kobayashi, Y.; Li, J. P.; Matsuzaka, H.; Ishii, Y.; Hidai, M. *J. Org. Chem.* **1991**, *56*, 1922.
- (S18) Acharya, A.; Eickhoff, J. A.; Jeffrey, C. S. *Synthesis* **2013**, *45*, 1825.
- (S19) Arimitsu, S.; Hammond, G. B. *J. Org. Chem.* **2007**, *72*, 8559.
- (S20) Orr, D.; Percy, J. M.; Tuttle, T.; Kennedy, A. R.; Harrison, Z. A. *Chem. Eur. J.* **2014**, *20*, 14305.
- (S21) Charette, A. B.; Juteau, H.; Lebel, H.; Molinaro, C. *J. Am. Chem. Soc.* **1998**, *120*, 11943.
- (S22) Dolbier Jr, W. R.; Tian, F.; Duan, J.-X.; Li, A.-R.; Ait-Mohand, S.; Bautista, O.; Buathong, S.; Marshall Baker, J.; Crawford, J.; Anselme, P.; Cai, X. H.; Modzelewska, A.; Koroniak, H.; Battiste, M. A.; Chen, Q.-Y. *J. Fluorine Chem.* **2004**, *125*, 459.
- (S23) Wang, F.; Luo, T.; Hu, J.; Wang, Y.; Krishnan, H. S.; Jog, P. V.; Ganesh, S. K.; Prakash, G. K. S.; Olah, G. A. *Angew. Chem. Int. Ed.* **2011**, *50*, 7153.
- (S24) Oshiro, K.; Morimoto, Y.; Amii, H. *Synthesis* **2010**, *12*, 2080.
- (S25) Eusterwiemann, S.; Martinez, H.; Dolbier, W. R. *J. Org. Chem.* **2012**, *77*, 5461.
- (S26) Chen, Q.; Wu, S. *J. Org. Chem.* **1989**, *54*, 3023.
- (S27) Aono, T.; Sasagawa, H.; Fuchibe, K.; Ichikawa, J. *Org. Lett.* **2015**, *17*, 5736.
- (S28) Tian, F.; Kruger, V.; Bautista, O.; Duan, J.-X.; Li, A.-R.; Dolbier Jr, W. R.; Chen, Q.-Y. *Org. Lett.* **2000**, *2*, 563.
- (S29) Hagooly, Y.; Cohen, O.; Rozen, S. *Tetrahedron Lett.* **2009**, *50*, 392.
- (S30) Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555.
- (S31) Fuchibe, K.; Koseki, Y.; Aono, T.; Sasagawa, H.; Ichikawa, J. *J. Fluorine Chem.* **2012**, *133*, 52.
- (S32) Thomason, C. S.; Dolbier, W. R. *J. Org. Chem.* **2013**, *78*, 8904.
- (S33) Thomason, C. S.; Wang, L.; Dolbier, W. R. *J. Fluorine Chem.* **2014**, *168*, 34.
- (S34) Li, L.; Wang, F.; Ni, C.; Hu, J. *Angew. Chem. Int. Ed.* **2013**, *52*, 12390.
- (S35) Deng, X.-Y.; Lin, J.-H.; Zheng, J.; Xiao, J.-C. *Chem. Commun.* **2015**, *51*, 8805.

- (S36) Zhou, J.; Campbell-Conroy, E. L.; Silina, A.; Uy, J.; Pierre, F.; Hurley, D. J.; Hilgraf, N.; Frieman, B. A.; DeNinno, M. P. *J. Org. Chem.* **2015**, *80*, 70.
- (S37) Zahnley, T.; Macey, R.; Oster, G. Berkeley Madonna; 8.3.18 ed.; University of California at Berkeley: Berkeley, California, **2010**.
- (S38) Maskill, H., *The Physical Basis of Organic Chemistry*, OUP, Oxford, **1985**, Chapter 6, 242.
- (S39) Zhao, Y. ; Schultz, N. E.; Truhlar, D. G. *J. Chem. Phys.*, **2005**, *123*, 161103.
- (S40) Zhao, Y. ; Truhlar, D. G. *Theor. Chem. Acc.*, **2008**, *120*, 215.
- (S41) Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.*, **2004**, *393*, 51. It is clear that the extent of HF exchange does have an effect on the sign of difference between experimental and calculated values; a wider set of systems would have to be examined before the levels of accuracy of (U)B3LYP and CAM-B3LYP could be assessed more fairly. We proceeded with (U)B3LYP because of the similarity of outcomes between the open-shell singlet and {3,3}-rearrangement pathways; they are more alike than those for for CAM-B3LYP.
- (S42) Maas, G. *Chem. Ber.*, **1979**, *112*, 3241.
- (S43) Özkan, I.; Zora, M. *J. Org. Chem.*, **2003**, *68*, 9635.
- (S44) Brown, J. M.; Golding, B. T.; Stofko, J. J. *J. Chem. Soc., Chem. Commun.*, **1973**, 319.
- (S45) Maas, G.; Hummel, C. *Chem. Ber.*, **1980**, *113*, 3679.
- (S46) Ohlinger, W. S.; Klunzinger, P. E. ; Deppmeier, B. J.; Hehre, W. J. *J. Phys. Chem. A*, **2009**, *113*, 2165.
- (S47) Curtiss, L. A. ; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.*, **1993**, *98*, 1293.
- (S48) Domalski, E. S. *J. Phys. Chem. Ref. Data*, **1972**, *1*, 221.
- (S49) Hubbard, W. N.; Scott, D. W.; Frow, F. R.; Waddington, G. *J. Am. Chem. Soc.*, **1955**, *77*, 5855.
- (S50) Cohen, N. J. *Phys. Chem. Ref. Data*, 1996, *25*, 1411-1481.
- (S51) Lewis, D. K.; Charney, D. J.; Kalra, B. L.; Plate, A.-M.; Woodard, M. H.; Cianciosi, S. J.; Baldwin, J. E. *J. Phys. Chem. A* **1997**, *101*, 4097.
- (S52) http://www.gaussian.com/g_tech/g_ur/k_scrf.htm, Accessed on 9th Nov. 2015.
- (S53) Nelson, R. D., Lide, D. R., Maryott, A. A., & United States. National Bureau of Standards. (1967). Selected values of electric dipole moments for molecules in the gas phase. Washington, D.C.: U.S. Dept. of Commerce, National Bureau of Standards. (<http://www.nist.gov/data/nsrds/NSRDS-NBS-10.pdf>, Accessed 9th Nov. 2015).
- (S54) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999.
- (S55) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669.
- (S56) Dolbier, W. R. *Acc. Chem. Res.* **1981**, *14*, 195.

Cartesian Coordinates

Cartesian Coordinates used in electronic structure calculations – Spartan'10 structures
(Gaussian'09 energy values provided if obtained). All energies are in a.u..

Triage: Cyclopropane Substitution

Pyyrole SM (9a)

G = -830.0446014 a.u.

vi = none

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
-----			-----	-----	-----
1	C	C1	1.7222269	1.2445885	-0.9729440
2	C	C2	0.6041819	1.6925847	-0.1197857
3	C	C3	0.9304149	0.1385579	-0.3669379
4	H	H3	-0.2634018	2.0265621	-0.6880495
5	H	H6	1.3972895	-0.3352988	0.4928236
6	C	C10	0.0096991	-0.6684673	-1.1704285
7	H	H11	-0.3761963	-0.2280125	-2.0883867
8	C	C11	-0.4005248	-1.9064327	-0.8511647
9	H	H12	-0.0564018	-2.4218961	0.0407895
10	C	C12	-1.3494274	-2.6233645	-1.7272019
11	O	O1	-1.8337068	-2.1932897	-2.7572939
12	O	O2	-1.6283020	-3.8532978	-1.2286266
13	C	C13	-2.5405183	-4.6357388	-2.0122175
14	H	H5	-3.4923969	-4.1115587	-2.1331000
15	H	H13	-2.6804404	-5.5652310	-1.4591559
16	H	H14	-2.1218863	-4.8377263	-3.0022856
17	F	F1	1.6247087	1.4521976	-2.3073350
18	F	F2	3.0024035	1.4205751	-0.5768409
19	C	C4	0.7970878	2.2851547	1.2148360
20	C	C5	1.8863411	2.8913793	1.8170170
21	C	C6	1.4964665	3.2807468	3.1275918
22	C	C7	0.1816452	2.9031882	3.2976489
23	H	H1	2.8510224	3.0395555	1.3549197
24	H	H8	2.1102781	3.7860042	3.8606918
25	H	H9	-0.4878149	3.0144079	4.1384141
26	N	N1	-0.2348714	2.3028757	2.1350296
27	H	H2	-1.1478764	1.9019360	1.9819925

Pyyrole TS2 (TS1aa)

G = -830.419263

vi = i78

S² = 0.457

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
-----			-----	-----	-----
1	C	C	-0.9297737	2.5748429	0.6568401

2	C	C2	-1.9194433	1.6312626	0.6608880
3	C	C3	-1.6411990	0.2517920	0.7737971
4	C	C4	0.4710368	2.1238864	0.5119996
5	C	C5	0.6265790	1.0214606	-0.4882548
6	H	H	-1.1171696	3.6410222	0.7171927
7	H	H7	-2.9595671	1.9256767	0.5328070
8	H	H8	-0.7662823	-0.1029137	1.3009722
9	H	H12	-0.1240240	0.9537771	-1.2623941
10	F	F1	1.2877910	3.1931977	0.1719855
11	F	F2	1.0287529	1.6979289	1.7555366
12	C	C11	-2.6538475	-0.7310434	0.3954601
13	O	O1	-3.7440986	-0.4774870	-0.0947453
14	O	O2	-2.2384745	-2.0004546	0.6602510
15	C	C12	-3.1717980	-3.0280382	0.3079669
16	H	H1	-4.1123292	-2.9029289	0.8523623
17	H	H9	-2.6929097	-3.9684920	0.5846646
18	H	H10	-3.3842153	-3.0079672	-0.7652038
19	C	C1	1.8411946	0.3622857	-0.6905360
20	C	C6	2.2631551	-0.4716555	-1.7562523
21	C	C7	3.5614344	-0.9103603	-1.4767628
22	C	C8	3.9309200	-0.3557429	-0.2484364
23	H	H3	1.6666996	-0.7030954	-2.6285180
24	H	H5	4.1791181	-1.5561366	-2.0853420
25	H	H11	4.8492544	-0.4533396	0.3134152
26	N	N1	2.9011554	0.3967289	0.2113611
27	H	H6	2.8480404	0.8957936	1.0889455

pyyrole_higher_energyTS2 (TS1ab)

G = -830.414696

iv = i86

S^2 = 0.5102

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C	-0.6158183	2.7256632	0.6820107
2	C C2	-1.5971922	2.1028680	-0.0343527
3	C C3	-1.6947996	0.6924256	-0.0975346
4	C C4	0.4992112	1.9015225	1.2220471
5	C C5	0.9748909	0.8813229	0.2312319
6	H H	-0.5893481	3.7953210	0.8584969
7	H H7	-2.3084203	2.6842247	-0.6185155
8	H H8	-1.3530473	0.0711430	0.7187428
9	H H12	0.8034239	1.1175807	-0.8108546
10	F F1	1.5520191	2.7254997	1.5953164
11	F F2	0.1389744	1.2638429	2.4199903
12	C C11	-2.4700560	0.0560454	-1.1581920
13	O O1	-3.0479337	0.6343226	-2.0667899
14	O O2	-2.4755496	-1.3002263	-1.0228217
15	C C12	-3.2164866	-2.0059029	-2.0242332
16	H H1	-4.2783074	-1.7449992	-1.9780600
17	H H9	-3.0760518	-3.0653510	-1.8034635
18	H H10	-2.8431902	-1.7687789	-3.0250429
19	C C1	1.9005424	-0.1117304	0.5589328

20	C	C6	2.3766330	-0.5907480	1.8048456
21	C	C7	3.2738964	-1.6361421	1.5563537
22	C	C8	3.3447797	-1.8097260	0.1746747
23	H	H3	2.0712456	-0.1937930	2.7607488
24	H	H5	3.8158363	-2.2172635	2.2895826
25	H	H11	3.9124580	-2.5151602	-0.4157203
26	N	N1	2.5264033	-0.8948515	-0.4121237
27	H	H6	2.3758869	-0.7971094	-1.4052698

Furan trans-SM (9b)

Spartan'10: G = -850.314059 vi = none

Gaussian'09: B3LYP/6-31G*, G = -850.319618 vi = none

Gaussian'09: M05-2X/6-31G*, G = -850.262612, vi = none

		Cartesian Coordinates (Angstroms)		
Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	1.5992207	1.3955614	-0.9776466
2	C C2	0.5194974	1.8052430	-0.0580500
3	C C3	0.8775038	0.2658666	-0.3303277
4	H H3	-0.4002896	2.1204185	-0.5444083
5	H H6	1.4087112	-0.1989848	0.4965651
6	C C10	-0.0692639	-0.5633929	-1.0807464
7	H H11	-0.5451553	-0.1204950	-1.9541452
8	C C11	-0.3946896	-1.8258644	-0.7635527
9	H H12	0.0391353	-2.3439339	0.0867471
10	C C12	-1.3721319	-2.5700978	-1.5853767
11	O O1	-1.9604997	-2.1384533	-2.5585899
12	O O2	-1.5371983	-3.8286142	-1.1099537
13	C C13	-2.4677534	-4.6398049	-1.8414309
14	H H5	-3.4717553	-4.2079556	-1.7983632
15	H H13	-2.4506879	-5.6161272	-1.3558111
16	H H14	-2.1651118	-4.7245612	-2.8886582
17	F F1	1.4275165	1.6056448	-2.3021574
18	F F2	2.8925579	1.6160802	-0.6434690
19	C C4	0.7705242	2.3994701	1.2599089
20	C C5	1.8869409	2.7841676	1.9494628
21	C C6	1.4335592	3.2644071	3.2204022
22	C C7	0.0786439	3.1404409	3.2120022
23	H H1	2.9039660	2.7376631	1.5907183
24	H H8	2.0403843	3.6562081	4.0247172
25	H H9	-0.6983851	3.3741271	3.9236340
26	O O3	-0.3452394	2.6129866	2.0285292

Furan TS2 (TS1bb)

Spartan'10: G = -850.28681, vi = i125, S^2 = 0.5808

Gaussian'09: B3LYP/6-31G*, G = -850.284463, vi = i137, S^2 = 0.57

Gaussian'09: M05-2X/6-31G*, G = -850.221609, vi = i163, S^2 = 0.75

		Cartesian Coordinates (Angstroms)		
Atom		X	Y	Z
-----		-----	-----	-----

1	C	C	-0.8561031	2.7015691	0.3283079
2	C	C2	-1.8381630	1.8024358	0.0383813
3	C	C3	-1.6444484	0.4102119	0.2272503
4	C	C4	0.5072269	2.1790487	0.6288748
5	C	C5	0.8856784	1.0394530	-0.2712286
6	H	H	-0.9995893	3.7763684	0.3174435
7	H	H7	-2.7826728	2.1292823	-0.3926797
8	H	H8	-1.0099284	0.0361089	1.0187846
9	H	H12	0.4705459	1.0412851	-1.2696769
10	F	F1	1.4360242	3.2007638	0.5162551
11	F	F2	0.6134274	1.7738239	1.9674583
12	C	C11	-2.4989795	-0.5525386	-0.4685442
13	O	O1	-3.3684446	-0.2715912	-1.2784601
14	O	O2	-2.2061722	-1.8278254	-0.1011751
15	C	C12	-2.9862758	-2.8407750	-0.7484711
16	H	H1	-4.0493679	-2.7126694	-0.5253266
17	H	H9	-2.6237993	-3.7896870	-0.3511872
18	H	H10	-2.8484901	-2.8009163	-1.8330240
19	C	C1	2.0038465	0.2433660	-0.0273076
20	C	C6	2.8291747	0.0348828	1.0837613
21	C	C7	3.7855008	-0.9333375	0.7106043
22	C	C8	3.4978427	-1.2782298	-0.5873676
23	H	H3	2.7222504	0.5366346	2.0329496
24	H	H5	4.5837052	-1.3373896	1.3175395
25	H	H11	3.9437590	-1.9756074	-1.2810134
26	O	O3	2.4334523	-0.5846670	-1.0521485

furan_higher_energyTS2 (TS1ba)

G = -850.277257

iv = i117

S^2 = 0.600

Cartesian Coordinates (Angstroms)

Atom	X	Y	Z

1 C C	-0.9502546	2.6495991	0.6501376
2 C C2	-1.8908863	1.6636452	0.6340407
3 C C3	-1.5252413	0.2997528	0.7679050
4 C C4	0.4866883	2.2452973	0.5815975
5 C C5	0.6994623	1.1466886	-0.4230640
6 H H	-1.1843317	3.7083129	0.6705550
7 H H7	-2.9410498	1.8946944	0.4667669
8 H H8	-0.6672285	0.0082292	1.3580427
9 H H12	0.0014180	1.1086166	-1.2480338
10 F F1	1.2635235	3.3417125	0.2455922
11 F F2	0.9578758	1.8500449	1.8288746
12 C C11	-2.4336857	-0.7569674	0.3243831
13 O O1	-3.5074436	-0.5836509	-0.2312859
14 O O2	-1.9309470	-1.9884494	0.6061859
15 C C12	-2.7538814	-3.0880991	0.1987920
16 H H1	-3.7287557	-3.0463091	0.6926392
17 H H9	-2.2124283	-3.9867342	0.4969680

18	H	H10	-2.9090023	-3.0753115	-0.8840734
19	C	C1	1.8920642	0.4419550	-0.5879881
20	C	C6	2.3133656	-0.4200912	-1.6085995
21	C	C7	3.5834925	-0.9104235	-1.2387796
22	C	C8	3.8752209	-0.3326880	-0.0273526
23	H	H3	1.7534328	-0.6493108	-2.5047380
24	H	H5	4.2111886	-1.5983851	-1.7876640
25	H	H11	4.7235775	-0.4012302	0.6371705
26	O	O3	2.8738262	0.4791018	0.3819280

para-Pyridine-N-oxide SM (9c)

G = -943.714388

vi = none

Cartesian Coordinates (Angstroms)					
Atom			X	Y	Z

1	C	C1	1.3089641	1.2878086	-1.4497207
2	C	C2	0.3057078	1.5125208	-0.3822889
3	C	C3	0.7951372	0.0499645	-0.8058908
4	H	H3	-0.6826092	1.7431318	-0.7723904
5	H	H6	1.4675209	-0.4016004	-0.0798213
6	C	C10	-0.1475861	-0.8399612	-1.4924370
7	H	H11	-0.7435160	-0.4144786	-2.2979791
8	C	C11	-0.3306841	-2.1327832	-1.1854696
9	H	H12	0.2308402	-2.6289737	-0.3990166
10	C	C12	-1.3267131	-2.9400203	-1.9226782
11	O	O1	-2.0384947	-2.5410180	-2.8245489
12	O	O2	-1.3530146	-4.2104131	-1.4542092
13	C	C13	-2.2945397	-5.0801688	-2.1008460
14	H	H5	-3.3109551	-4.6904395	-1.9982644
15	H	H13	-2.1988666	-6.0424089	-1.5969908
16	H	H14	-2.0596651	-5.1776157	-3.1644068
17	F	F1	0.9485834	1.5578329	-2.7241156
18	F	F2	2.6047735	1.6327810	-1.2590384
19	C	C4	0.5748704	2.0527265	0.9723227
20	N	N1	0.9519961	3.0708098	3.5869269
21	C	C6	-0.4849677	2.5780627	1.7269249
22	C	C7	1.8381277	2.0634026	1.5880374
23	C	C8	2.0043379	2.5628860	2.8639135
24	C	C9	-0.2895778	3.0730703	3.0006694
25	H	H2	-1.4913534	2.6050752	1.3191932
26	H	H1	2.7153381	1.6911372	1.0725650
27	H	H4	2.9491794	2.6021993	3.3891100
28	H	H7	-1.0668534	3.4896658	3.6269169
29	O	O3	1.1240199	3.5268064	4.7635328

para-pyridine-N-oxide TS2 (TS1c)

G = -943.680817

vi= i173

S^2 = 0.6244

Cartesian Coordinates (Angstroms)				
Atom	X	Y	Z	

1	C	C	-0.7442934	2.9911665	-0.6529612
2	C	C2	-1.8633238	2.2189125	-0.6559668
3	C	C3	-1.8768379	0.9614702	0.0125223
4	C	C4	0.5056189	2.3730776	-0.1201484
5	C	C5	0.6538498	0.9460111	-0.5710700
6	H	H	-0.6970805	4.0005318	-1.0464526
7	H	H7	-2.7503323	2.5120346	-1.2138959
8	H	H8	-1.3399625	0.8184490	0.9404952
9	H	H12	0.2045073	0.7258017	-1.5310947
10	F	F1	1.6088236	3.1107358	-0.5101945
11	F	F2	0.5285161	2.4437114	1.2816101
12	C	C1	1.6190072	0.0436571	-0.0843508
13	N	N1	3.5077418	-1.8693317	0.8212471
14	C	C7	1.8384409	-1.1962806	-0.7581019
15	C	C8	2.4134554	0.2521798	1.0854579
16	C	C9	3.3234735	-0.6801557	1.5006845
17	C	C10	2.7505123	-2.1100167	-0.3093180
18	H	H2	1.2716721	-1.4303514	-1.6542811
19	H	H6	2.3060988	1.1634289	1.6585467
20	H	H5	3.9580480	-0.5786565	2.3711521
21	H	H3	2.9607491	-3.0624405	-0.7773622
22	C	C11	-2.8422352	-0.0682516	-0.3784039
23	O	O1	-3.6244498	0.0175318	-1.3119035
24	O	O2	-2.7589742	-1.1547562	0.4310049
25	C	C12	-3.6624428	-2.2222009	0.1130110
26	H	H1	-4.7003788	-1.8921776	0.2148756
27	H	H9	-3.4417473	-3.0160126	0.8275249
28	H	H10	-3.5038444	-2.5707545	-0.9116447
29	O	O3	4.3553882	-2.7273136	1.2290179

2-thiophene SM (9d)

Spartan'10: G = -1173.29592, vi = none

Gaussian'09: B3LYP/6-31G*, G = -1173.30199, vi = none

Gaussian'09: M05-2X/6-31G*, G = -1173.23053, vi = none

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
-----			-----	-----	-----
1	C	C1	1.6447102	1.2814457	-0.9375890
2	C	C2	0.5212287	1.7458593	-0.0943692
3	C	C3	0.8411195	0.1957362	-0.3104794
4	H	H3	-0.3426689	2.0754370	-0.6688474
5	H	H6	1.3040248	-0.2653453	0.5585792
6	C	C10	-0.0785972	-0.6272681	-1.1025299
7	H	H11	-0.4640952	-0.2034661	-2.0283529
8	C	C11	-0.4802431	-1.8616494	-0.7637583
9	H	H12	-0.1388546	-2.3582980	0.1397290
10	C	C12	-1.4198937	-2.6011787	-1.6329982
11	O	O1	-1.8957629	-2.1937891	-2.6757460
12	O	O2	-1.6963244	-3.8212538	-1.1117456
13	C	C13	-2.6006195	-4.6235892	-1.8848499
14	H	H5	-3.5553537	-4.1076858	-2.0178802

15	H	H13	-2.7364164	-5.5439176	-1.3157681
16	H	H14	-2.1767881	-4.8399854	-2.8695951
17	F	F1	1.5518602	1.4680768	-2.2742731
18	F	F2	2.9262425	1.4561124	-0.5411711
19	C	C4	0.7023730	2.3602625	1.2372566
20	C	C5	1.8035834	2.9777018	1.7761645
21	C	C6	1.5918459	3.4496041	3.1064879
22	C	C7	0.3333226	3.1878326	3.5700286
23	H	H1	2.7340315	3.0937873	1.2348702
24	H	H8	2.3477142	3.9664063	3.6878268
25	H	H9	-0.0945008	3.4371092	4.5318277
26	S	S1	-0.6219377	2.3520552	2.3871829

2-thiophene TS2 (TS1da)

Spartan'10: G = -1173.261131, vi = i131, S² = 0.5683

Gaussian'09: B3LYP/6-31G*, G = -1173.266174, vi = i334, S² = 0.58

Gaussian'09: M05-2X/6-31G*, G = -1173.189048, vi = i147, S² = 0.76

Cartesian Coordinates (Angstroms)

Atom	X	Y	Z

1 C C	-0.7210256	-0.3769473	-2.7513915
2 C C2	-1.6633130	-0.7878751	-1.8574746
3 C C3	-1.6425208	-0.3469323	-0.5084804
4 C C4	0.4568673	0.3730574	-2.2301141
5 C C5	0.9604340	-0.2059585	-0.9352110
6 H H	-0.7617934	-0.5913906	-3.8136378
7 H H7	-2.4261631	-1.5096041	-2.1435472
8 H H8	-1.2822483	0.6385526	-0.2471795
9 H H12	0.7937751	-1.2673813	-0.8066724
10 F F1	1.4705438	0.3718068	-3.1716569
11 F F2	0.1531733	1.7304276	-2.0604202
12 C C11	-2.3398484	-1.1152447	0.5241681
13 O O1	-2.9346804	-2.1662237	0.3423726
14 O O2	-2.2429288	-0.5139217	1.7384721
15 C C12	-2.8807106	-1.2132354	2.8149511
16 H H1	-3.9557208	-1.3034663	2.6345635
17 H H9	-2.6914657	-0.6153949	3.7074120
18 H H10	-2.4588123	-2.2161999	2.9276998
19 C C1	1.9188089	0.4334481	-0.1364692
20 C C6	2.3884821	1.7569630	-0.1691832
21 C C7	3.3512113	2.0350217	0.8188765
22 C C8	3.6266421	0.9527961	1.6286792
23 H H3	2.0271893	2.4727681	-0.8952321
24 H H5	3.8264599	3.0018556	0.9428367
25 H H11	4.3129625	0.9081502	2.4642703
26 S S1	2.7146815	-0.4450712	1.1823680

2_thiophene_higher_energyTS2 (TS1db)

G = -1173.26196

iv = i122

S² = 0.601

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C	-0.9278013	0.7602316	-2.6901911
2	C C2	-1.8672172	0.7618182	-1.7032288
3	C C3	-1.5086288	0.8413210	-0.3336491
4	C C4	0.5043701	0.6104751	-2.3065949
5	C C5	0.7012026	-0.3701149	-1.1866012
6	H H	-1.1656141	0.8285247	-3.7460605
7	H H7	-2.9232110	0.6526694	-1.9433104
8	H H8	-0.6295369	1.3839016	-0.0131775
9	H H12	0.0016210	-1.1964024	-1.1568814
10	F F1	1.2424323	0.2099791	-3.4085654
11	F F2	1.0677132	1.8421132	-1.9497644
12	C C11	-2.4546584	0.4124461	0.6970248
13	O O1	-3.5602301	-0.0629061	0.4887400
14	O O2	-1.9502468	0.6069819	1.9438422
15	C C12	-2.8142156	0.2091798	3.0160398
16	H H1	-3.7451809	0.7831206	2.9953433
17	H H9	-2.2589454	0.4135549	3.9324871
18	H H10	-3.0572818	-0.8549834	2.9429923
19	C C1	1.8878436	-0.5154771	-0.4587369
20	C C6	2.2076707	-1.5955701	0.3831959
21	C C7	3.4563134	-1.4720247	1.0164381
22	C C8	4.1089268	-0.3048071	0.6769360
23	H H3	1.5361313	-2.4380247	0.5102434
24	H H5	3.8686245	-2.2100946	1.6953957
25	H H11	5.0800204	0.0300601	1.0180010
26	S S1	3.1998985	0.6740277	-0.4199186

pyrrole_N_Boc - SM (9e)

G = -1176.15618

iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	2.7535104	0.5329447	-2.5439534
2	C C2	1.9022163	0.9879434	-1.4270432
3	C C3	1.8744042	-0.5181088	-1.9545018
4	H H3	1.0240211	1.5436471	-1.7384084
5	H H6	2.3889501	-1.2127350	-1.2950455
6	C C10	0.6922396	-1.0140414	-2.6636953
7	H H11	0.2033785	-0.3375816	-3.3618949
8	C C11	0.1738953	-2.2418222	-2.5067290
9	H H12	0.6086345	-2.9725220	-1.8307627
10	C C12	-1.0270908	-2.6493021	-3.2620710
11	O O1	-1.6401087	-1.9646035	-4.0590672
12	O O2	-1.3777460	-3.9235125	-2.9510128
13	C C13	-2.5355171	-4.4200730	-3.6359457
14	H H5	-3.4124388	-3.8079976	-3.4065128
15	H H13	-2.6754402	-5.4400731	-3.2758182
16	H H14	-2.3762980	-4.4132677	-4.7179344

17	F	F1	2.4675232	0.9968779	-3.7830902
18	F	F2	4.0957545	0.4116881	-2.4057509
19	C	C4	2.4334821	1.2902387	-0.0860095
20	C	C5	3.7232841	1.5276603	0.3230500
21	C	C6	3.7171782	1.7451030	1.7362044
22	C	C7	2.4272226	1.6350730	2.1677360
23	H	H1	4.5820521	1.5408932	-0.3309699
24	H	H8	4.5748523	1.9620229	2.3583141
25	H	H9	1.9875509	1.7354041	3.1455720
26	N	N1	1.6202058	1.3551326	1.0643105
27	C	C8	0.2226284	1.1991010	1.0943728
28	O	O3	-0.2133437	1.2468479	2.3591224
29	C	C9	-1.6575265	1.1251508	2.6728774
30	C	C14	-2.4290862	2.2782238	2.0251443
31	H	H4	-2.0009948	3.2405094	2.3261956
32	H	H15	-3.4707766	2.2507602	2.3630633
33	H	H16	-2.4136606	2.2073436	0.9367034
34	C	C15	-1.6721970	1.2482366	4.1979027
35	H	H7	-1.2663801	2.2142387	4.5152625
36	H	H17	-1.0770148	0.4526265	4.6573822
37	H	H18	-2.7006075	1.1669068	4.5639643
38	C	C16	-2.1679553	-0.2495484	2.2317861
39	H	H10	-2.1369785	-0.3572100	1.1464935
40	H	H19	-3.2033431	-0.3743943	2.5670994
41	H	H20	-1.5664571	-1.0443221	2.6862017
42	O	O4	-0.4520227	1.0465409	0.0974583

pyrrole_N_boc_TS2 (TS1e)

G = -1176.11077

iv = i75

S^2 = 0.7190

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C	-2.2966442	2.5038283	-0.7522378
2	C C2	-3.2202595	1.5004654	-0.6686955
3	C C3	-2.8998157	0.1253002	-0.6486436
4	C C4	-0.8707789	2.2304137	-1.0897300
5	C C5	-0.6665939	1.0255474	-1.9622623
6	H H	-2.5642692	3.5472360	-0.6166446
7	H H7	-4.2782632	1.7570888	-0.6453204
8	H H8	-1.9495060	-0.2386669	-0.2794002
9	H H12	-1.3323635	1.0127471	-2.8182339
10	F F1	-0.3734540	3.3374628	-1.7833582
11	F F2	-0.0802355	2.1913624	0.0547077
12	C C11	-3.9457174	-0.8595544	-0.9329093
13	O O1	-5.1044351	-0.6039567	-1.2244142
14	O O2	-3.4698166	-2.1283518	-0.8295764
15	C C12	-4.4254535	-3.1600249	-1.0993711
16	H H1	-5.2735717	-3.0933775	-0.4117197
17	H H9	-3.8909565	-4.1003850	-0.9574250
18	H H10	-4.7998331	-3.0837324	-2.1247538
19	C C1	0.5248792	0.2999435	-2.1256533

20	C	C6	1.0440565	-0.2010755	-3.3344732
21	C	C7	2.3342710	-0.7117037	-3.0941433
22	C	C8	2.5993629	-0.5513321	-1.7497834
23	H	H3	0.5450331	-0.1125159	-4.2904793
24	H	H5	3.0099156	-1.1422242	-3.8205963
25	H	H11	3.4492929	-0.8463660	-1.1545859
26	N	N1	1.5064027	0.0499485	-1.1450145
27	C	C9	1.2605679	-0.0765626	0.2545129
28	O	O3	2.3872856	0.1841217	0.9151857
29	C	C10	2.4358210	0.1211324	2.3991176
30	C	C13	1.4208616	1.1040404	2.9897361
31	H	H13	1.5380529	2.0922187	2.5332578
32	H	H14	0.3958318	0.7679561	2.8300664
33	H	H15	1.5985712	1.1988611	4.0666651
34	C	C14	3.8672117	0.5723141	2.6929274
35	H	H4	4.0324401	1.5918928	2.3313039
36	H	H16	4.5916532	-0.0899223	2.2080669
37	H	H17	4.0478971	0.5521972	3.7724520
38	C	C15	2.2028363	-1.3203461	2.8572202
39	H	H6	1.1937030	-1.6568408	2.6118931
40	H	H18	2.9281275	-1.9949784	2.3889698
41	H	H19	2.3344957	-1.3817917	3.9430077
42	O	O4	0.1933966	-0.4123696	0.7103349

Spartan'10: G = -1041.02196, iv = none

Gaussian'09: B3LYP/6-31G*, G = -1041.030057, iv = none

Gaussian'09: M05-2X/6-31G*, G = -1040.961182, iv = none

Atom			Cartesian Coordinates (Angstroms)		
			X	Y	Z
-----			-----	-----	-----
1	H	H1	0.3173526	1.8117346	-0.4860782
2	C	C1	0.0796698	1.9703530	0.5619833
3	C	C4	-0.5139337	2.3341161	3.2187058
4	C	C2	0.2084874	0.9017002	1.4568499
5	C	C6	-0.3484961	3.2417645	0.9790992
6	C	C5	-0.6383061	3.3915793	2.3211549
7	C	C3	-0.0958245	1.0796197	2.8250814
8	H	H6	-0.4515198	4.0668061	0.2827391
9	H	H3	-0.0162481	0.2654692	3.5352692
10	C	C7	0.7180325	-0.4153577	0.9594682
11	C	C8	0.1449534	-1.7162582	1.3582272
12	C	C9	-0.1583847	-1.2780583	-0.0372637
13	H	H2	1.7827390	-0.4632471	0.7318922
14	H	H9	-1.1646025	-0.8901221	-0.1771914
15	F	F1	-0.8678092	-1.7730911	2.2531620
16	F	F2	0.9806161	-2.7644429	1.5466580
17	C	C10	0.4727736	-1.9279483	-1.1918646
18	H	H8	1.4598095	-2.3639054	-1.0472524
19	C	C11	-0.0808889	-2.0200610	-2.4103728
20	H	H10	-1.0656251	-1.6194806	-2.6329824
21	C	C12	0.6434521	-2.6904227	-3.5104695
22	O	O1	1.7572372	-3.1745849	-3.4406949

23	O	O2	-0.1053900	-2.6999901	-4.6407824
24	C	C13	0.5090769	-3.3295069	-5.7742877
25	H	H7	-0.2243694	-3.2656527	-6.5788836
26	H	H11	0.7479377	-4.3733616	-5.5532355
27	H	H12	1.4297941	-2.8084978	-6.0514828
28	O	O3	-0.8886457	2.7475398	4.4747810
29	C	C14	-1.1176431	4.1571614	4.3678767
30	H	H13	-0.3195540	4.6995025	4.8933865
31	H	H14	-2.0979599	4.3997452	4.7885223
32	O	O4	-1.0967313	4.5068976	2.9779849

Spartan'10: G = -1040.98527, iv = i123, S^2 = 0.4875

Gaussian'09: B3LYP/6-31G*, G = -1040.991312, iv = i123 S^2 = 0.49

Gaussian'09: M05-2X/6-31G*, G = -1040.916448, iv = i154, S^2 = 0.70

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C	-1.9415125	2.8459054	-0.1145085
2	C C2	-2.8968928	1.8980800	0.1045137
3	C C3	-2.5560611	0.6313994	0.6442402
4	C C4	-0.5213291	2.4249366	0.0232476
5	C C5	-0.2785848	1.0938538	-0.6265670
6	H H	-2.1537181	3.8659395	-0.4147181
7	H H7	-3.9327982	2.0688843	-0.1819285
8	H H8	-1.7420745	0.5235062	1.3476045
9	H H12	-0.9914780	0.8153500	-1.3903371
10	F F1	0.3209903	3.3806811	-0.5228531
11	F F2	-0.1367627	2.3813647	1.3763306
12	C C1	0.9674345	0.4091213	-0.6132428
13	C C6	3.3393187	-1.0419376	-0.7024803
14	C C7	1.1304562	-0.7070957	-1.4805967
15	C C8	2.0508659	0.7887275	0.2442712
16	C C9	3.2035145	0.0544406	0.1585045
17	C C10	2.3096788	-1.4497963	-1.5357170
18	H H2	0.3006140	-0.9867083	-2.1230616
19	H H6	1.9583437	1.6244971	0.9238368
20	H H3	2.4233575	-2.3001809	-2.1987607
21	C C11	-3.4612854	-0.5051960	0.4740267
22	O O1	-4.5012178	-0.4946765	-0.1664901
23	O O2	-3.0011475	-1.6060197	1.1264093
24	C C12	-3.8252873	-2.7716733	1.0064332
25	H H1	-4.8175953	-2.5900216	1.4297484
26	H H9	-3.3098968	-3.5550517	1.5638819
27	H H10	-3.9401814	-3.0590914	-0.0429790
28	C C16	5.2862127	-0.7515467	0.3636972
29	H H16	5.6638544	-1.3654739	1.1871797
30	H H17	6.1072607	-0.2495450	-0.1631722
31	O O3	4.5775514	-1.5919137	-0.5642076
32	O O4	4.3683699	0.2192409	0.8676951

Vinyl_SM (9g)

G = -698.896923

iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	1.9355502	1.7969259	-0.3459348
2	C C2	0.8307819	2.1575483	0.5704414
3	C C3	1.1920029	0.6392453	0.2183687
4	H H3	-0.0759566	2.5122382	0.0862674
5	H H6	1.6963533	0.1125771	1.0252585
6	C C10	0.2552858	-0.1365557	-0.6009850
7	H H11	-0.1543285	0.3425355	-1.4885605
8	C C11	-0.1335964	-1.3913708	-0.3282800
9	H H12	0.2329983	-1.9394131	0.5347714
10	C C12	-1.0945064	-2.0825309	-1.2131158
11	O O1	-1.5953320	-1.6208579	-2.2209946
12	O O2	-1.3607729	-3.3286259	-0.7502454
13	C C13	-2.2872051	-4.0875934	-1.5403591
14	H H5	-3.2430000	-3.5630588	-1.6222382
15	H H13	-2.4121995	-5.0357462	-1.0162391
16	H H14	-1.8896012	-4.2541816	-2.5455875
17	F F1	1.8126274	2.0764637	-1.6634147
18	F F2	3.2135469	1.9930861	0.0537993
19	C C4	1.0896415	2.6534012	1.9367450
20	H H2	2.0583814	2.3967857	2.3621727
21	C C5	0.2219098	3.3789314	2.6464829
22	H H1	0.4602017	3.7221319	3.6487135
23	H H4	-0.7527828	3.6580640	2.2529337

Vinyl_TS2 LHS (TS1g)

G = -698.857875

iv = i198

S^2 = 0.6714

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C	0.1652595	2.6452115	-0.3143155
2	C C2	-0.9584813	1.8809569	-0.3019228
3	C C3	-0.9637138	0.5905294	0.2988038
4	C C4	1.4504042	2.0089192	0.1090996
5	C C5	1.5736222	0.5798217	-0.3410965
6	H H	0.1907607	3.6766667	-0.6489816
7	H H7	-1.8694255	2.2159214	-0.7940528
8	H H8	-0.3786445	0.3846912	1.1849748
9	H H12	1.1669910	0.3487995	-1.3194338
10	F F1	2.5134097	2.7425610	-0.3921617
11	F F2	1.6046460	2.0673940	1.4925765
12	C C11	-1.9729073	-0.3973458	-0.0922705
13	O O1	-2.8112126	-0.2389039	-0.9652907

14	O	O2	-1.8623287	-1.5331343	0.6422082
15	C	C12	-2.8063532	-2.5626474	0.3167219
16	H	H1	-3.8302743	-2.2111786	0.4741522
17	H	H9	-2.5784639	-3.3924022	0.9872065
18	H	H10	-2.6972065	-2.8709552	-0.7274202
19	C	C1	2.4851927	-0.3044672	0.2691289
20	H	H3	2.9377797	0.0188533	1.2042950
21	C	C6	2.7966479	-1.5403617	-0.2250625
22	H	H2	3.4848028	-2.2007601	0.2926869
23	H	H4	2.3594953	-1.9081690	-1.1498455

3-thiophene_SM (9h)

G = -1173.29649

iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
1	C C1	1.4442820	1.5404046	-1.0097879
2	C C2	0.3927582	1.8764466	-0.0237970
3	C C3	0.8288766	0.3719452	-0.3204143
4	H H3	-0.5607177	2.1328018	-0.4786628
5	H H6	1.4362987	-0.0670530	0.4676500
6	C C10	-0.1107572	-0.5159186	-1.0134407
7	H H11	-0.6603421	-0.1039428	-1.8581155
8	C C11	-0.3435135	-1.7926382	-0.6731372
9	H H12	0.1711044	-2.2773250	0.1516008
10	C C12	-1.3258436	-2.5989270	-1.4276396
11	O O1	-1.9984877	-2.2113527	-2.3641198
12	O O2	-1.3897156	-3.8597859	-0.9339553
13	C C13	-2.3181495	-4.7285856	-1.5989953
14	H H5	-3.3350508	-4.3325827	-1.5279792
15	H H13	-2.2432837	-5.6872218	-1.0845376
16	H H14	-2.0553539	-4.8368853	-2.6549552
17	F F1	1.1825558	1.7359006	-2.3226269
18	F F2	2.7405856	1.8349551	-0.7532548
19	C C4	0.6386102	2.4940989	1.3012228
20	C C5	1.8650771	2.4391855	2.0495963
21	C C6	1.7847172	3.0813387	3.2512183
22	S S1	0.2168841	3.7791875	3.5053528
23	C C8	-0.3357356	3.1901481	1.9737064
24	H H1	2.7672056	1.9564327	1.6953535
25	H H8	2.5584428	3.1962145	3.9983072
26	H H15	-1.3504474	3.3831587	1.6514110

2-thiophene TS2 alt (TS1h)

G = -1173.25727

iv = i114

S^2 = 0.5844

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
--	------	---	---	---

1	C	C	-0.3331252	2.7439182	-0.5242953
2	C	C2	-1.4517833	1.9650401	-0.5727216
3	C	C3	-1.5103739	0.7180630	0.0976444
4	C	C4	0.9029740	2.1508129	0.0594263
5	C	C5	1.1146943	0.7374396	-0.3968356
6	H	H	-0.2825728	3.7530236	-0.9182330
7	H	H7	-2.3112866	2.2592107	-1.1717697
8	H	H8	-0.9585452	0.5456332	1.0118178
9	H	H12	0.6711376	0.4815216	-1.3498593
10	F	F1	2.0021802	2.9255137	-0.2725910
11	F	F2	0.8715525	2.1990947	1.4621430
12	C	C11	-2.5122966	-0.2777141	-0.2889431
13	O	O1	-3.3033639	-0.1635621	-1.2119161
14	O	O2	-2.4575935	-1.3702203	0.5160657
15	C	C12	-3.3994409	-2.4043657	0.2026418
16	H	H1	-4.4248487	-2.0408846	0.3169501
17	H	H9	-3.1984520	-3.2090659	0.9108671
18	H	H10	-3.2635384	-2.7531014	-0.8251504
19	C	C1	2.1319687	-0.1093191	0.1123631
20	C	C6	2.5032706	-1.3622827	-0.5148334
21	C	C7	3.4928028	-2.0212654	0.1397115
22	S	S1	4.0211354	-1.1473099	1.5576573
23	C	C9	2.8912283	0.1141277	1.2640703
24	H	H3	2.0309517	-1.7285710	-1.4201138
25	H	H5	3.9542148	-2.9658622	-0.1152083
26	H	H14	2.8191103	0.9601255	1.9311122

2-thiazole SM (9i)

G = -1189.35451

iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C1	1.4013058	1.6826903	-0.9862793
2	C C2	0.3481207	1.9349898	0.0400251
3	C C3	0.8159698	0.4777131	-0.3397660
4	H H6	1.4365614	0.0346426	0.4351354
5	C C10	-0.1119487	-0.4004681	-1.0663144
6	H H11	-0.6646054	0.0283623	-1.9004368
7	C C11	-0.3216483	-1.6902861	-0.7672656
8	H H12	0.1965106	-2.1904600	0.0457575
9	C C12	-1.2854305	-2.4901029	-1.5544828
10	O O1	-1.9512959	-2.0857909	-2.4883978
11	O O2	-1.3389844	-3.7630262	-1.0940432
12	C C13	-2.2476632	-4.6264585	-1.7931289
13	H H5	-3.2687791	-4.2396457	-1.7340227
14	H H13	-2.1742931	-5.5940744	-1.2957037
15	H H14	-1.9635389	-4.7121801	-2.8456385
16	F F1	1.0897515	1.9454442	-2.2761353
17	F F2	2.6798604	2.0163755	-0.7391868
18	C C4	0.6871187	2.4484393	1.3825995
19	N N1	1.5569002	1.9082761	2.1889631

20	C	C7	0.9016926	3.7544921	3.4403495
21	H	H9	0.8278894	4.4632764	4.2532685
22	S	S1	-0.0542307	3.9215840	2.0031029
23	H	H3	-0.6141778	2.2362664	-0.3652607
24	C	C6	1.6824389	2.6395753	3.3463609
25	H	H7	2.3724759	2.3003654	4.1105000

2-thiazole TS2 (TS1ia)

G = -1189.31604

iv = i158

S^2 = 0.6401

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
1	C C	-0.8624600	0.6458233	-2.6809721
2	C C2	-1.7945142	0.6484678	-1.6885283
3	C C3	-1.4196477	0.7346465	-0.3224604
4	C C4	0.5731559	0.5015687	-2.2988314
5	C C5	0.7688284	-0.4679819	-1.1699536
6	H H	-1.1050971	0.7031453	-3.7364239
7	H H7	-2.8520204	0.5322726	-1.9168489
8	H H8	-0.5487926	1.2963848	-0.0125430
9	H H12	0.1063398	-1.3231256	-1.1382335
10	F F1	1.3102300	0.0940487	-3.3953137
11	F F2	1.1248412	1.7403949	-1.9531783
12	C C11	-2.3513200	0.2959998	0.7223360
13	O O1	-3.4476576	-0.2001740	0.5203581
14	O O2	-1.8421206	0.5130008	1.9592936
15	C C12	-2.6828069	0.0961690	3.0445494
16	H H1	-3.6349998	0.6336831	3.0225873
17	H H9	-2.1283804	0.3339141	3.9529242
18	H H10	-2.8823985	-0.9775536	2.9854094
19	C C1	1.9504425	-0.5849422	-0.4186831
20	N N1	2.1984549	-1.6348782	0.3707388
21	C C8	4.1034809	-0.3580502	0.7303876
22	H H11	5.0684951	-0.0693435	1.1245010
23	S S1	3.2435322	0.6444020	-0.3730350
24	C C7	3.3860264	-1.5066663	1.0000569
25	H H4	3.7183885	-2.2912055	1.6718630

thiazole_higher_energyTS2 (TS1ib)

G = -1189.31128

iv = i172

S^2 = 0.6211

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
1	C C	-0.9124198	0.5660171	-2.6688343
2	C C2	-1.8409100	0.5476441	-1.6746237
3	C C3	-1.4526669	0.6770132	-0.3132767

4	C	C4	0.5318908	0.5151246	-2.2727045
5	C	C5	0.7450768	-0.4716982	-1.1503779
6	H	H	-1.1557524	0.5780877	-3.7256670
7	H	H7	-2.8933373	0.3752347	-1.8897007
8	H	H8	-0.6112304	1.2936434	-0.0270815
9	H	H12	0.0711162	-1.3178375	-1.1388929
10	F	F1	1.2984462	0.1460785	-3.3609117
11	F	F2	0.9821656	1.7714234	-1.9150056
12	C	C11	-2.3479460	0.2107881	0.7509096
13	O	O1	-3.4172720	-0.3501472	0.5736335
14	O	O2	-1.8381305	0.4805843	1.9781156
15	C	C12	-2.6495697	0.0533101	3.0811159
16	H	H1	-3.6204748	0.5563684	3.0622352
17	H	H9	-2.0932806	0.3274638	3.9780292
18	H	H10	-2.8124816	-1.0275786	3.0439963
19	C	C1	1.9449539	-0.5742326	-0.4236465
20	N	N1	2.9420037	0.3050315	-0.3933605
21	C	C8	3.7444018	-1.3024687	1.0843730
22	H	H11	4.4074900	-1.7902521	1.7856196
23	S	S1	2.2310906	-1.9904853	0.6387774
24	C	C7	3.9330111	-0.1008447	0.4304792
25	H	H4	4.8138256	0.5217320	0.5467991

Ph LHS SM (control compound) (9j)

Spartan'10: G = -852.507737, iv = none

Gaussian'09: B3LYP/6-31G*, G = -852.513911, iv = none

Gaussian'09: M05-2X/6-31G*, G = -852.454583, iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z

1	H H1	-0.7342992	2.1292350	-0.6038797
2	C C1	-0.6896550	2.5456381	0.3996721
3	C C4	-0.5788215	3.6046272	2.9736287
4	C C2	0.1528229	1.9539030	1.3524642
5	C C6	-1.4665871	3.6544153	0.7292205
6	C C5	-1.4135141	4.1868572	2.0197807
7	C C3	0.2019187	2.4950669	2.6438137
8	H H6	-2.1142921	4.1021150	-0.0198156
9	H H5	-2.0191435	5.0512131	2.2786045
10	H H3	0.8466623	2.0454541	3.3913082
11	H H4	-0.5318796	4.0135924	3.9793780
12	C C7	1.0044769	0.7904903	0.9510633
13	C C8	1.3092637	-0.3611739	1.8231770
14	C C9	0.3451828	-0.6317107	0.7160262
15	H H9	-0.6950119	-0.6814867	1.0296629
16	F F1	0.8550859	-0.4026367	3.0973066
17	F F2	2.5471373	-0.9057421	1.7618348
18	C C10	0.7256057	-1.4333489	-0.4525928
19	H H8	1.7776668	-1.4516307	-0.7317858
20	C C11	-0.1366627	-2.1405728	-1.1983779
21	H H10	-1.1996782	-2.1775237	-0.9780074
22	C C12	0.3401656	-2.9115132	-2.3652549
23	O O1	1.4898785	-2.9767628	-2.7568938

24	O	O2	-0.6913356	-3.5547476	-2.9657551
25	C	C13	-0.3365797	-4.3399461	-4.1129601
26	H	H7	0.3705291	-5.1270044	-3.8365732
27	H	H11	0.1186948	-3.7122448	-4.8840365
28	H	H12	-1.2707537	-4.7727264	-4.4725849
29	H	H2	1.7931229	1.0081637	0.2315763

Ph_LHS_TS2 (TS1j)

Spartan'10: G = -852.467491, iv = i124, S^2 = 0.5609

Gaussian'09: B3LYP/6-31G*, G = -852.471539, iv = i139, S^2 = 0.72

Gaussian'09: M05-2X/6-31G*, G = -852.407064, iv = i150 S^2 = 0.73

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
1	C C	-0.7938224	2.9281295	-0.4973567
2	C C2	-1.9169588	2.1548519	-0.5208385
3	C C3	-1.9447433	0.8899069	0.1188859
4	C C4	0.4554569	2.3058113	0.0257641
5	C C5	0.6396500	0.9126099	-0.5034969
6	H H	-0.7489920	3.9452945	-0.8705278
7	H H7	-2.7990824	2.4628835	-1.0784486
8	H H8	-1.3634344	0.6999835	1.0109197
9	H H12	0.1318702	0.7046588	-1.4362973
10	F F1	1.5526349	3.0842611	-0.3012959
11	F F2	0.4548498	2.2993475	1.4302410
12	C C1	1.6981159	0.0337646	-0.1244960
13	C C6	3.7528699	-1.7843479	0.5356695
14	C C7	1.9221078	-1.1367612	-0.8981062
15	C C8	2.5370955	0.2579721	1.0002180
16	C C9	3.5497938	-0.6376134	1.3129267
17	C C10	2.9311417	-2.0302287	-0.5711578
18	H H2	1.2868288	-1.3240531	-1.7604162
19	H H6	2.3799547	1.1370129	1.6122318
20	H H5	4.1864329	-0.4470045	2.1726196
21	H H3	3.0852933	-2.9185318	-1.1775979
22	H H4	4.5447429	-2.4828045	0.7915831
23	C C11	-2.9550719	-0.1019472	-0.2577349
24	O O1	-3.7794569	0.0322524	-1.1481949
25	O O2	-2.8655294	-1.2148241	0.5148987
26	C C12	-3.8127241	-2.2457971	0.2059573
27	H H1	-4.8355106	-1.8867747	0.3524122
28	H H9	-3.5920855	-3.0635919	0.8932747
29	H H10	-3.7014272	-2.5744602	-0.8316365

bis_Ph_SM (9k)

G = -1083.47906

iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
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1	C	C1	2.1401892	-0.0956954	-0.5030615
2	C	C2	1.0084305	0.6541421	0.1013241
3	C	C3	1.0969993	-0.9312616	0.1653649
4	H	H6	1.3824353	-1.3078350	1.1445602
5	C	C4	1.2610998	1.3842374	1.3998916
6	C	C5	1.6621778	2.8368121	3.7687618
7	C	C6	0.5771414	1.0383205	2.5708181
8	C	C7	2.1514488	2.4655458	1.4290384
9	C	C8	2.3510230	3.1865204	2.6055784
10	C	C9	0.7744797	1.7603828	3.7486637
11	H	H4	-0.1128299	0.1982990	2.5605250
12	H	H7	2.6904649	2.7407226	0.5268287
13	H	H8	3.0475027	4.0206999	2.6144128
14	H	H9	0.2348075	1.4804399	4.6494368
15	C	C10	0.1997949	-1.7833133	-0.6270916
16	H	H11	-0.0529765	-1.4603042	-1.6341065
17	C	C11	-0.3192736	-2.9411307	-0.1905993
18	H	H12	-0.1109823	-3.3375552	0.7992122
19	C	C12	-1.2026816	-3.7385484	-1.0670984
20	O	O1	-1.5445314	-3.4423954	-2.1960226
21	O	O2	-1.5992964	-4.8756654	-0.4422651
22	C	C13	-2.4590919	-5.7243013	-1.2159658
23	H	H5	-3.3938217	-5.2092327	-1.4552872
24	H	H13	-2.6519025	-6.5966411	-0.5904149
25	H	H14	-1.9711465	-6.0186838	-2.1489851
26	F	F1	2.2560587	-0.1617158	-1.8507333
27	F	F2	3.3716170	-0.0205447	0.0501528
28	H	H16	1.8186444	3.3988195	4.6855521
29	C	C14	-0.0221504	1.2954522	-0.7972292
30	C	C15	-1.9532314	2.5840539	-2.3773674
31	C	C16	-1.3881705	1.1209839	-0.5374988
32	C	C17	0.3650011	2.1252734	-1.8574405
33	C	C18	-0.5955412	2.7651048	-2.6420020
34	C	C19	-2.3475632	1.7589318	-1.3221684
35	H	H2	-1.7000848	0.4771947	0.2803560
36	H	H1	1.4189827	2.2629083	-2.0781994
37	H	H3	-0.2800252	3.4018179	-3.4642146
38	H	H10	-3.4028383	1.6083512	-1.1113529
39	H	H15	-2.7001597	3.0798098	-2.9913732

bis_Ph_TS2 (TS1k)

G = -1083.43796

iv = i170

S^2 = 0.5387

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z

1	C C	-0.4905029	2.9644064	0.2699805
2	C C2	-1.6739456	2.3000484	0.1811172
3	C C3	-1.8234284	0.9930522	0.7115034
4	C C4	0.7007691	2.2204344	0.7848070
5	C C5	0.8020209	0.7758907	0.2922367
6	H H	-0.3628539	4.0113164	0.0158601

7	H	H7	-2.5148493	2.7325649	-0.3574474
8	H	H8	-1.3254011	0.6920489	1.6207777
9	F	F1	1.8636038	2.8958172	0.4238450
10	F	F2	0.7094526	2.2676910	2.1728991
11	C	C1	1.4274022	-0.2471139	1.1415429
12	C	C6	2.6632180	-2.2619875	2.7066499
13	C	C7	2.3919579	-1.1262335	0.5910474
14	C	C8	1.1150697	-0.4092438	2.5134199
15	C	C9	1.7196106	-1.4031744	3.2752391
16	C	C10	2.9998396	-2.1130276	1.3598395
17	H	H2	2.6831985	-1.0061205	-0.4461451
18	H	H6	0.3847455	0.2361774	2.9804870
19	H	H5	1.4477300	-1.5099628	4.3216431
20	H	H3	3.7451214	-2.7611627	0.9068595
21	H	H4	3.1324323	-3.0357165	3.3080647
22	C	C11	-2.8669953	0.1051841	0.2041829
23	O	O1	-3.6526536	0.3696869	-0.6919707
24	O	O2	-2.8577312	-1.0884394	0.8590324
25	C	C12	-3.8453877	-2.0292641	0.4217172
26	H	H1	-4.8524776	-1.6265121	0.5631762
27	H	H9	-3.6987149	-2.9175849	1.0380379
28	H	H10	-3.7106018	-2.2706167	-0.6369425
29	C	C13	0.7059762	0.5609448	-1.1515914
30	C	C14	0.4088753	0.1093913	-3.9293928
31	C	C15	0.9236744	1.5965010	-2.0893611
32	C	C16	0.3436510	-0.7135608	-1.6564080
33	C	C17	0.1940066	-0.9325095	-3.0176990
34	C	C18	0.7744233	1.3681896	-3.4571869
35	H	H11	1.2584263	2.5672437	-1.7492165
36	H	H12	0.1380548	-1.5165279	-0.9558351
37	H	H13	-0.1056006	-1.9144923	-3.3740211
38	H	H14	0.9565966	2.1808425	-4.1552514
39	H	H15	0.2912871	-0.0641812	-4.9954973

alkynyl_LHS_SM (9I)

G = -697.662199

iv = none

Cartesian Coordinates (Angstroms)					
Atom		X	Y	Z	
-----		-----	-----	-----	
1	C C1	2.0424676	1.9684931	-0.1391170	
2	C C2	0.8725035	2.4962424	0.6162951	
3	C C3	1.1493632	0.9340715	0.4498497	
4	H H3	0.0609649	2.8669018	-0.0070648	
5	H H6	1.5244582	0.4683830	1.3570881	
6	C C10	0.2426017	0.1419043	-0.3899421	
7	H H11	-0.0646980	0.5667251	-1.3437475	
8	C C11	-0.2303187	-1.0678896	-0.0571690	
9	H H12	0.0360504	-1.5606142	0.8732704	
10	C C12	-1.1469251	-1.7848967	-0.9704422	
11	O O1	-1.5497743	-1.3718325	-2.0409954	
12	O O2	-1.4935214	-2.9877721	-0.4535502	
13	C C13	-2.3834903	-3.7677120	-1.2660675	

14	H	H5	-3.3175284	-3.2268389	-1.4405158
15	H	H13	-2.5682923	-4.6831435	-0.7031171
16	H	H14	-1.9222194	-3.9957741	-2.2309570
17	F	F1	2.0512871	2.1302983	-1.4803672
18	F	F2	3.2825906	2.1200466	0.3600670
19	C	C4	1.0217110	3.0973457	1.9084994
20	H	H1	1.2541083	4.0534359	3.9587574
21	C	C5	1.1386614	3.6026259	2.9992259

alkynyl_LHS_TS2 (TS1I)

G = -697.620962

iv = i184

S² = 0.6758

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
-----			-----	-----	-----
1	C	C	0.4165731	2.5068791	-0.3637114
2	C	C2	-0.6902111	1.7284846	-0.5113690
3	C	C3	-0.7689538	0.4441358	0.0901598
4	C	C4	1.6325214	1.8895419	0.2525525
5	C	C5	1.8367364	0.4685151	-0.2135836
6	H	H	0.4814311	3.5345224	-0.7045805
7	H	H7	-1.5231515	2.0493445	-1.1332736
8	H	H8	-0.2830066	0.2352376	1.0335260
9	H	H12	1.5620280	0.2510525	-1.2394046
10	F	F1	2.7448939	2.6456606	-0.0628903
11	F	F2	1.5608009	1.9131080	1.6360459
12	C	C11	-1.7408621	-0.5420694	-0.3985955
13	O	O1	-2.5033990	-0.3717384	-1.3355925
14	O	O2	-1.6893955	-1.6811234	0.3336227
15	C	C12	-2.6113098	-2.7077900	-0.0591668
16	H	H1	-3.6404973	-2.3981585	0.1488279
17	H	H9	-2.3494573	-3.5814320	0.5392686
18	H	H10	-2.5162890	-2.9258022	-1.1264765
19	C	C1	2.6781292	-0.3978923	0.4613271
20	H	H2	4.0143079	-1.8713020	1.5919161
21	C	C6	3.3891107	-1.1891739	1.0613974

4-pyridine_LHS_SM (9m)

G = -868.554947

iv = none

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
-----			-----	-----	-----
1	C	C1	1.7379906	1.0533701	-1.0125123
2	C	C2	0.5948548	1.5544215	-0.2227780
3	C	C3	0.8612826	0.0062370	-0.4070529
4	H	H3	-0.2344211	1.9188458	-0.8277523
5	H	H6	1.2755361	-0.4729380	0.4771572
6	C	C10	-0.0500743	-0.7951991	-1.2344074

7	H	H11	-0.3979950	-0.3587991	-2.1691355
8	C	C11	-0.4826418	-2.0238238	-0.9158956
9	H	H12	-0.1760631	-2.5312450	-0.0058114
10	C	C12	-1.4082921	-2.7431426	-1.8178865
11	O	O1	-1.8477926	-2.3196153	-2.8698685
12	O	O2	-1.7178395	-3.9617345	-1.3139346
13	C	C13	-2.6120458	-4.7454915	-2.1180937
14	H	H5	-3.5544664	-4.2138221	-2.2744602
15	H	H13	-2.7778343	-5.6670627	-1.5592395
16	H	H14	-2.1631492	-4.9616572	-3.0915960
17	F	F1	1.7223381	1.2232993	-2.3539189
18	F	F2	3.0003533	1.1868913	-0.5460287
19	C	C4	0.7315355	2.1769759	1.1301111
20	N	N1	0.9105237	3.3755852	3.6778867
21	C	C6	-0.1933435	1.8824315	2.1393948
22	C	C7	1.7489586	3.0877968	1.4319480
23	C	C8	1.7909243	3.6507591	2.7088508
24	C	C9	-0.0613028	2.5028302	3.3802346
25	H	H2	-1.0006241	1.1775720	1.9604804
26	H	H1	2.4979879	3.3500452	0.6929301
27	H	H4	2.5765237	4.3602219	2.9639503
28	H	H7	-0.7709234	2.2872482	4.1774282

4-pyridine_LHS_TS2 (TS1m)

G = -868.512852

iv = i151

S² = 0.5934

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C	0.3070064	2.7970608	-0.9446703
2	C C2	-0.8702346	2.2484882	-1.3570235
3	C C3	-1.4285757	1.1354692	-0.6765308
4	C C4	1.0819644	2.0509262	0.0900012
5	C C5	1.1037370	0.5761160	-0.1992953
6	H H	0.7280987	3.7102181	-1.3504719
7	H H7	-1.3808928	2.6113983	-2.2462561
8	H H8	-1.2991936	1.0085770	0.3895858
9	H H12	0.9892222	0.3102938	-1.2422746
10	F F1	2.3744958	2.5344481	0.1628290
11	F F2	0.5526452	2.2904937	1.3649280
12	C C1	1.6724039	-0.4116988	0.6680910
13	N N1	2.7702392	-2.4577611	2.2998445
14	C C7	1.9062917	-1.7183103	0.1748682
15	C C8	2.0121818	-0.1793825	2.0237279
16	C C9	2.5517642	-1.2197246	2.7707856
17	C C10	2.4457148	-2.6822852	1.0166428
18	H H2	1.6680436	-1.9635620	-0.8566372
19	H H6	1.8552203	0.7934610	2.4703350
20	H H5	2.8223384	-1.0542993	3.8121624
21	H H3	2.6310239	-3.6892368	0.6468259
22	C C11	-2.4292836	0.2928172	-1.3442906
23	O O1	-2.7867842	0.4153052	-2.5041783
24	O O2	-2.9178859	-0.6490733	-0.5024576
25	C C12	-3.9064488	-1.5218351	-1.0694465
26	H H1	-4.7684266	-0.9486601	-1.4213600
27	H H9	-4.1964768	-2.1977280	-0.2648775
28	H H10	-3.4881892	-2.0815155	-1.9108571

2-pyridine_SM (9n)

G = -868.560284

iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	2.1000029	0.5055043	-0.6965333
2	C C2	0.9184896	1.2927387	-0.2508197
3	C C3	0.9201405	-0.2843109	-0.2566169
4	H H3	0.3655689	1.7584852	-1.0628600
5	H H6	1.0020918	-0.6850727	0.7505895
6	C C10	0.0820217	-1.0040781	-1.2242092
7	H H11	0.0715084	-0.6434600	-2.2512806
8	C C11	-0.6680193	-2.0749420	-0.9252445

9	H	H12	-0.7026792	-2.4985163	0.0742806
10	C	C12	-1.4832540	-2.7315458	-1.9687958
11	O	O1	-1.5706412	-2.3850279	-3.1315743
12	O	O2	-2.1432411	-3.7999312	-1.4572169
13	C	C13	-2.9636894	-4.5145889	-2.3923749
14	H	H5	-3.7374900	-3.8605552	-2.8038684
15	H	H13	-3.4129366	-5.3306347	-1.8252458
16	H	H14	-2.3588262	-4.9055369	-3.2152852
17	F	F1	2.4062756	0.5330426	-2.0166253
18	F	F2	3.2294763	0.4892063	0.0356387
19	C	C4	0.8835237	2.0151828	1.0526041
20	C	C5	0.4862175	4.0200942	2.3217539
21	C	C6	1.2149747	1.9755476	3.3252197
22	C	C7	0.8534596	3.3152944	3.4674928
23	C	C9	0.5011632	3.3634083	1.0942391
24	H	H1	0.1920557	5.0644380	2.3820080
25	H	H10	1.5038450	1.3864459	4.1940646
26	H	H7	0.8566146	3.7858904	4.4457855
27	H	H4	0.2238540	3.8813328	0.1805933
28	N	N1	1.2294931	1.3315891	2.1542812

2-pyridine_LHS_TS2 (TS1n)

G = -868.515403

iv = i143

S^2 = 0.6016

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z

1	C C	-1.3374758	2.5356748	-1.0093448
2	C C2	-2.2782936	1.6088466	-0.6708224
3	C C3	-1.9635131	0.5397633	0.2053482
4	C C4	0.0726353	2.2614527	-0.6057535
5	C C5	0.4434383	0.8277131	-0.8440428
6	H H	-1.5466778	3.4307520	-1.5847047
7	H H7	-3.2738083	1.6322947	-1.1088727
8	H H8	-1.2360491	0.6601069	0.9961678
9	H H12	-0.1008181	0.3085738	-1.6207575
10	F F1	0.9380644	3.0934627	-1.2933938
11	F F2	0.2717235	2.6027654	0.7419510
12	C C11	-2.8012772	-0.6650313	0.2258161
13	O O1	-3.7626787	-0.8645502	-0.4984173
14	O O2	-2.3748274	-1.5432864	1.1655528
15	C C12	-3.1247583	-2.7633846	1.2453564
16	H H1	-4.1702767	-2.5577539	1.4924223
17	H H9	-2.6510838	-3.3472613	2.0353189
18	H H10	-3.0865709	-3.3018428	0.2938812
19	C C1	1.6820642	0.2233836	-0.4512118
20	C C6	3.0429579	-1.6244868	-0.6922048
21	C C7	3.7697283	0.1398279	0.7639039
22	C C8	4.0071794	-1.1069262	0.1855604
23	C C9	2.5956014	0.8152813	0.4550249
24	H H6	3.1965203	-2.5964725	-1.1593318
25	H H2	4.4882175	0.5785235	1.4508757

26	H	H11	2.3721687	1.7800871	0.8912999
27	H	H15	4.9094911	-1.6702421	0.4031932
28	N	N1	1.9183188	-0.9972714	-1.0128147

mestial_LHS_SM (9o)

G = -931.084973

iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C1	0.1004469	2.2220900	0.6645602
2	C C4	0.6179998	2.7845380	3.3602783
3	C C2	0.4412212	1.1795836	1.5534176
4	C C6	-0.0085121	3.5271508	1.1593174
5	C C5	0.2335058	3.8095278	2.5001810
6	C C3	0.7356289	1.4666546	2.9061109
7	H H6	-0.2769598	4.3290486	0.4757904
8	C C7	0.5808699	-0.2319649	1.0555541
9	C C8	-0.1705426	-1.3846140	1.6029641
10	C C9	-0.5552311	-0.9555791	0.2298027
11	H H2	1.5767018	-0.5169806	0.7105993
12	H H9	-1.4941709	-0.4095453	0.1875632
13	F F1	-1.0798392	-1.2110464	2.5911733
14	F F2	0.4777548	-2.5599177	1.7786826
15	C C10	-0.1959880	-1.7500721	-0.9518852
16	H H8	0.6860607	-2.3846041	-0.8834668
17	C C11	-0.8754358	-1.7385575	-2.1084376
18	H H10	-1.7676427	-1.1355409	-2.2504491
19	C C12	-0.4247943	-2.5601502	-3.2515758
20	O O1	0.5476472	-3.2903961	-3.2670891
21	O O2	-1.2497147	-2.3917060	-4.3140848
22	C C13	-0.9012200	-3.1455892	-5.4840422
23	H H7	-1.6573250	-2.8967817	-6.2294611
24	H H11	-0.9114799	-4.2176582	-5.2686542
25	H H12	0.0948902	-2.8669536	-5.8391450
26	H H13	0.8410760	3.0050004	4.4012792
27	H H14	0.1448661	4.8280735	2.8688423
28	C C14	1.2027439	0.3953000	3.8685409
29	H H3	2.0048709	-0.2166351	3.4392861
30	H H4	0.3904854	-0.2853752	4.1410036
31	H H5	1.5858001	0.8469728	4.7884605
32	C C15	-0.1261934	1.9824906	-0.8125576
33	H H1	0.6219677	1.3088903	-1.2428746
34	H H15	-0.0814835	2.9275316	-1.3626110
35	H H16	-1.1080042	1.5368148	-1.0170736

mestial_LHS_TS2 (TS1o)

G = -931.03943

iv = i163

S² = 0.4019

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C	-0.9096073	2.9999154	-0.6912791
2	C C2	-2.0360516	2.2377163	-0.7378677
3	C C3	-2.1135924	1.0215839	-0.0058768
4	C C4	0.2750223	2.4204254	0.0037197
5	C C5	0.4715012	0.9822567	-0.3974421
6	H H	-0.8218177	3.9896965	-1.1255369
7	H H7	-2.8733542	2.5030118	-1.3800533
8	H H8	-1.6394225	0.9189243	0.9604468
9	H H12	-0.0225180	0.7726982	-1.3310704
10	F F1	1.4016049	3.1758374	-0.2977579
11	F F2	0.1212585	2.5546778	1.3887792
12	C C1	1.4217506	-0.0048547	0.0215955
13	C C6	3.1264852	-2.1716909	0.6879449
14	C C7	1.3363574	-1.2694638	-0.6749484
15	C C8	2.4113891	0.1340256	1.0593259
16	C C9	3.2330401	-0.9551468	1.3562590
17	C C10	2.1784890	-2.3184261	-0.3231740
18	H H5	3.9816581	-0.8398030	2.1353523
19	H H3	2.0933610	-3.2653645	-0.8495429
20	H H4	3.7819432	-2.9982625	0.9491787
21	C C11	-3.1018826	0.0086805	-0.3848636
22	O O1	-3.8836344	0.0960370	-1.3186036
23	O O2	-3.0497525	-1.0689426	0.4432732
24	C C12	-3.9932816	-2.1074128	0.1491285
25	H H1	-5.0179906	-1.7422433	0.2652941
26	H H9	-3.7880318	-2.9023816	0.8670705
27	H H10	-3.8644584	-2.4699381	-0.8747308
28	C C13	0.3217102	-1.5138343	-1.7672206
29	H H2	0.4539469	-0.8378948	-2.6220265
30	H H11	-0.7036854	-1.3781792	-1.4022584
31	H H13	0.4101087	-2.5361182	-2.1452878
32	C C14	2.6522116	1.3956379	1.8523865
33	H H6	3.5569560	1.2846271	2.4567706
34	H H14	1.8176205	1.6153149	2.5241571
35	H H15	2.7726663	2.2688901	1.2088587

CN_LHS_SM (9p)

G = -713.768678

iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	2.1105281	2.1676364	0.0607816
2	C C2	0.9282908	2.6973176	0.8055329
3	C C3	1.2084693	1.1411205	0.6469596
4	H H3	0.1174426	3.0867177	0.1951720
5	H H6	1.5781365	0.6749817	1.5564852
6	C C10	0.2994338	0.3482683	-0.1952820
7	H H11	-0.0074648	0.7713752	-1.1498698
8	C C11	-0.1680119	-0.8609948	0.1413430
9	H H12	0.0980057	-1.3501675	1.0737703
10	C C12	-1.0836522	-1.5834987	-0.7736110
11	O O1	-1.4813821	-1.1690509	-1.8448390
12	O O2	-1.4294060	-2.7821559	-0.2538465
13	C C13	-2.3207190	-3.5670072	-1.0628304
14	H H5	-3.2547926	-3.0265207	-1.2372134
15	H H13	-2.5037297	-4.4796588	-0.4953127
16	H H14	-1.8592968	-3.7978324	-2.0267518
17	F F1	2.1283668	2.3361226	-1.2752149
18	F F2	3.3385408	2.3297532	0.5788564
19	C C4	1.0853552	3.2951414	2.1015202
20	N N1	1.2158852	3.7684526	3.1543505

CN_TS2_LHS (TS1p)

G = -713.721964

iv = i155

S^2 = 0.7284

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C	0.6241679	2.4031406	-0.2738745
2	C C2	-0.4805786	1.6202633	-0.4326921
3	C C3	-0.5716376	0.3395870	0.1665526
4	C C4	1.8411921	1.7973544	0.3558040
5	C C5	2.0667465	0.3810862	-0.1131399
6	H H	0.6878658	3.4299286	-0.6174105
7	H H7	-1.3048091	1.9405880	-1.0662309
8	H H8	-0.0794007	0.1167471	1.1042300
9	H H12	1.8288848	0.1377578	-1.1414734
10	F F1	2.9471866	2.5617131	0.0595204
11	F F2	1.7442745	1.8038173	1.7346643
12	C C11	-1.5489598	-0.6406201	-0.3373632
13	O O1	-2.2846036	-0.4580160	-1.2919570
14	O O2	-1.5247731	-1.7723946	0.3978188
15	C C12	-2.4409557	-2.7978593	-0.0199103
16	H H1	-3.4727192	-2.4461302	0.0688983

17	H	H9	-2.2617445	-3.6389979	0.6500185
18	H	H10	-2.2500442	-3.0821967	-1.0583823
19	C	C1	2.9068816	-0.4760555	0.6003823
20	N	N1	3.5730261	-1.2197129	1.2145449

bis_Me_SM (9q)

G = -700.111308

iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
1	C C1	2.0731041	1.4329992	-0.0574773
2	C C2	0.9105710	2.0532084	0.6154089
3	C C3	1.0819624	0.4757247	0.5293786
4	H H6	1.3885151	0.0266553	1.4718288
5	C C10	0.2298959	-0.3588462	-0.3263205
6	H H11	-0.0043230	-0.0017723	-1.3264940
7	C C11	-0.2750917	-1.5474524	0.0392841
8	H H12	-0.0818387	-1.9863458	1.0138698
9	C C12	-1.1201020	-2.3171720	-0.8962823
10	O O1	-1.4474721	-1.9684929	-2.0150925
11	O O2	-1.5010940	-3.4947810	-0.3414644
12	C C13	-2.3270747	-4.3210829	-1.1737455
13	H H5	-3.2622960	-3.8090614	-1.4171567
14	H H13	-2.5237829	-5.2216600	-0.5908583
15	H H14	-1.8096520	-4.5700095	-2.1043086
16	F F1	2.1749089	1.5080913	-1.4073872
17	F F2	3.3089790	1.5151021	0.4929244
18	C C4	1.1196354	2.6538467	1.9943286
19	H H2	1.3688246	3.7187737	1.9119609
20	H H1	1.9340872	2.1627737	2.5336219
21	H H4	0.2046912	2.5670947	2.5917509
22	C C5	-0.1555183	2.7305982	-0.2274199
23	H H3	0.0607406	3.8027064	-0.3054149
24	H H7	-1.1418916	2.6190904	0.2369124
25	H H8	-0.2057783	2.3300117	-1.2418472

bis_Me_TS2 (TS1q)

G = -700.060667

iv = i100

S^2 = 0.7900

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
1	C C	0.1237299	2.3869725	-0.1597606
2	C C2	-1.0083310	1.6232422	-0.1860150
3	C C3	-1.0802427	0.3424862	0.4046702
4	C C4	1.4031081	1.8012226	0.3541250
5	C C5	1.6811928	0.3858892	-0.0908040
6	H H	0.1467319	3.4180567	-0.4968980

7	H	H7	-1.8932190	1.9779903	-0.7108761
8	H	H8	-0.4412332	0.0606467	1.2306433
9	F	F1	2.4620626	2.6105992	-0.0533107
10	F	F2	1.4223842	1.8616800	1.7422396
11	C	C11	-2.1665313	-0.5719112	0.0454378
12	O	O1	-3.0467581	-0.3398684	-0.7678811
13	O	O2	-2.0779041	-1.7366836	0.7382398
14	C	C12	-3.0991150	-2.6990411	0.4427816
15	H	H1	-4.0897223	-2.2910524	0.6629351
16	H	H9	-2.8872352	-3.5573064	1.0817029
17	H	H10	-3.0645781	-2.9878448	-0.6119782
18	C	C1	2.5335867	-0.4762974	0.7855487
19	H	H2	3.6034920	-0.2525135	0.6302659
20	H	H3	2.3934697	-1.5349386	0.5393255
21	H	H4	2.3220170	-0.3237354	1.8460327
22	C	C6	1.6772984	0.1237909	-1.5629317
23	H	H5	2.6195015	0.4789808	-2.0145781
24	H	H6	0.8634720	0.6478645	-2.0733145
25	H	H11	1.6028234	-0.9482291	-1.7756002

spiro_Cy_SM (9r)

G = -816.783222

iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z

1	C C7	0.8338418	0.2700360	1.6681000
2	C C8	1.3019352	-1.0963801	1.9585323
3	C C9	0.1199460	-1.0099642	1.0427021
4	H H9	-0.8364595	-1.2368433	1.5094591
5	F F1	1.1361577	-1.6278679	3.1952081
6	F F2	2.4865374	-1.5127188	1.4443376
7	C C10	0.2327149	-1.3458225	-0.3817849
8	H H8	1.2117319	-1.2760414	-0.8494771
9	C C11	-0.7940576	-1.7382254	-1.1529121
10	H H10	-1.8033911	-1.8477723	-0.7663437
11	C C12	-0.5809612	-2.0369866	-2.5837731
12	O O1	0.4763905	-1.9589756	-3.1808004
13	C C1	0.0253239	1.0203924	2.7196751
14	C C3	1.6510379	1.1890916	0.7694728
15	C C5	-0.0685140	3.0189961	1.1530655
16	C C4	0.7469214	2.2428305	0.1069988
17	C C6	-0.8763674	2.0762243	2.0588939
18	H H6	2.4012181	1.6924191	1.3970295
19	H H1	0.6167925	3.6165654	1.7724597
20	H H3	0.0654169	1.7409366	-0.5935039
21	H H4	-1.6452781	1.5663157	1.4610916
22	H H13	-0.5610714	0.3219513	3.3257121
23	H H14	2.2108182	0.6259676	0.0173195
24	H H15	-0.7402863	3.7301518	0.6567296
25	H H16	1.3571245	2.9335692	-0.4875397
26	H H17	-1.4061865	2.6472244	2.8313489
27	H H19	0.7275683	1.5149340	3.4072191

28	O	O2	-1.7431661	-2.4142474	-3.1732278
29	C	C2	-1.6457089	-2.7183003	-4.5716870
30	H	H2	-0.9410616	-3.5372764	-4.7398430
31	H	H5	-1.3079479	-1.8430298	-5.1339370
32	H	H7	-2.6510199	-3.0071538	-4.8805256

spiro_Cy_TS2 (TS1r)

G = -816.731056

iv = i97

S^2 = 0.7478

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
1	C C	-0.9106382	0.1385209	-2.4198357
2	C C2	-2.0066762	0.0588373	-1.6096145
3	C C3	-2.0468213	0.6448966	-0.3245854
4	C C4	0.3617085	0.7027390	-1.8766115
5	C C5	0.7101923	0.2673726	-0.4763650
6	H H	-0.9127853	-0.1936752	-3.4526047
7	H H7	-2.8809086	-0.5071742	-1.9252811
8	H H8	-1.4417739	1.5058868	-0.0739070
9	F F1	1.4122950	0.3522255	-2.7348973
10	F F2	0.3253288	2.0931194	-1.9280441
11	C C11	-3.0625295	0.2215394	0.6410615
12	O O1	-3.9253566	-0.6174316	0.4373100
13	O O2	-2.9288840	0.8840187	1.8196481
14	C C12	-3.8809944	0.5254657	2.8300970
15	H H1	-4.8911736	0.8195024	2.5290081
16	H H9	-3.5784079	1.0691925	3.7260809
17	H H10	-3.8678857	-0.5531413	3.0093056
18	C C1	0.7278114	-1.1969004	-0.1483625
19	C C6	3.1970845	-0.9642782	0.4242527
20	C C7	1.6949869	1.0935451	0.2973150
21	C C8	3.1336164	0.5342591	0.0967162
22	C C10	2.1569301	-1.7667288	-0.3710193
23	H H6	3.0191287	-1.1074851	1.5005324
24	H H2	1.4469283	1.0280261	1.3671402
25	H H3	3.4328635	0.7002145	-0.9452832
26	H H4	2.3923188	-1.7226277	-1.4412872
27	H H5	-0.0026178	-1.7533951	-0.7426260
28	H H12	4.2045241	-1.3485397	0.2199300
29	H H13	1.6477085	2.1463858	0.0092794
30	H H14	3.8312146	1.0989149	0.7277639
31	H H16	2.1753025	-2.8235721	-0.0765909
32	H H17	0.4675095	-1.3297124	0.9114743

Me_LHS_SM (9s)

G = -660.822287

iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	2.0231665	1.8219797	-0.1009084
2	C C2	0.8591224	2.3957932	0.5973220
3	C C3	1.0653756	0.8373953	0.4948820
4	H H3	0.0828452	2.7793574	-0.0623670
5	H H6	1.4065548	0.3683184	1.4155768
6	C C10	0.1794920	0.0384012	-0.3610723
7	H H11	-0.1057450	0.4597875	-1.3234845
8	C C11	-0.3015600	-1.1721524	-0.0405860
9	H H12	-0.0568987	-1.6648328	0.8959144
10	C C12	-1.1930632	-1.8907679	-0.9742955
11	O O1	-1.5745636	-1.4815698	-2.0545686
12	O O2	-1.5477945	-3.0970966	-0.4663047
13	C C13	-2.4130947	-3.8792491	-1.3015377
14	H H5	-3.3460342	-3.3437464	-1.4979605
15	H H13	-2.6068929	-4.7973238	-0.7456777
16	H H14	-1.9280348	-4.1029442	-2.2558562
17	F F1	2.1083142	1.9187173	-1.4481460
18	F F2	3.2560764	1.9357782	0.4474883
19	C C4	0.9961342	3.0828046	1.9380245
20	H H2	1.1842622	4.1541589	1.8037964
21	H H1	1.8310465	2.6675779	2.5100867
22	H H4	0.0812917	2.9696133	2.5296743

Me_LHS_TS2 (TS1s)

G = -660.768319

iv = i131

S^2 = 0.6779

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C	0.3085323	2.3948690	-0.3713510
2	C C2	-0.8130753	1.6163945	-0.4309390
3	C C3	-0.8733321	0.3534257	0.2006025
4	C C4	1.5557584	1.7871013	0.1739419
5	C C5	1.7883266	0.4037325	-0.3426420
6	H H	0.3500821	3.4137669	-0.7408256
7	H H7	-1.6791382	1.9321921	-1.0087759
8	H H8	-0.2831662	0.1347899	1.0804898
9	H H12	1.3603866	0.1697550	-1.3099371
10	F F1	2.6477364	2.5869476	-0.1376405
11	F F2	1.5407328	1.7597005	1.5709135
12	C C11	-1.9181127	-0.6061449	-0.1751014
13	O O1	-2.7455039	-0.4375735	-1.0556302
14	O O2	-1.8572819	-1.7243077	0.5904331

15	C	C12	-2.8504334	-2.7170042	0.2970293
16	H	H1	-3.8548958	-2.3160435	0.4598089
17	H	H9	-2.6521582	-3.5419732	0.9820799
18	H	H10	-2.7687977	-3.0501926	-0.7414680
19	C	C1	2.9503630	-0.3851851	0.1507666
20	H	H2	3.8623132	-0.1334861	-0.4167327
21	H	H3	2.7802482	-1.4597707	0.0183974
22	H	H4	3.1514158	-0.1809937	1.2065809

Cyclohexane_LHS_SM (9t)

G = -856.068176

iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C1	1.8132546	-0.1254555	-1.2431369
2	C C2	0.6689606	0.5838044	-0.6484235
3	C C3	0.7976203	-0.9827691	-0.5514934
4	H H6	1.0980521	-1.3510941	0.4276266
5	C C10	-0.0974759	-1.8420595	-1.3358473
6	H H11	-0.3637252	-1.5051304	-2.3363689
7	C C11	-0.6038909	-3.0121600	-0.9186998
8	H H12	-0.3800074	-3.4297584	0.0586900
9	C C12	-1.4888097	-3.7946546	-1.8059083
10	O O1	-1.8576938	-3.4646708	-2.9173734
11	O O2	-1.8499558	-4.9621632	-1.2174127
12	C C13	-2.7011198	-5.8031835	-2.0087260
13	H H5	-3.6432313	-5.2952692	-2.2332015
14	H H13	-2.8796215	-6.6930651	-1.4039693
15	H H14	-2.2120140	-6.0690561	-2.9498777
16	F F1	1.9300157	-0.2036574	-2.5895176
17	F F2	3.0420992	0.0008356	-0.6833144
18	H H27	-0.0787439	0.9222028	-1.3654762
19	C C4	0.8320289	1.4467615	0.5901217
20	C C5	1.5341502	3.7458363	1.4385367
21	C C6	-0.3191983	2.4784660	2.6147853
22	C C7	0.2214645	3.8631329	2.2267911
23	C C8	-0.4816357	1.5709344	1.3856840
24	C C9	1.3760635	2.8396635	0.2090836
25	H H1	2.3145050	3.3312512	2.0936405
26	H H10	0.3738144	2.0058396	3.3264914
27	H H7	-0.5259304	4.3824974	1.6086663
28	H H2	-1.2592787	1.9886008	0.7282212
29	H H3	0.6841610	3.3106055	-0.5056947
30	H H4	1.5795893	0.9671361	1.2389613
31	H H8	1.8840046	4.7383857	1.1281029
32	H H9	-1.2801993	2.5756065	3.1353638
33	H H15	0.3682606	4.4789489	3.1231632
34	H H16	-0.8321850	0.5758432	1.6887860
35	H H17	2.3366723	2.7277945	-0.3082738

Cyclohexane_LHS_TS2 (TS1t)

G = -856.014022

iv = i85

S² = 0.6959

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C	-1.1459943	3.1420549	-0.3807845
2	C C2	-2.3123754	2.4309537	-0.4431040
3	C C3	-2.4581901	1.1834592	0.2011743
4	C C4	0.0639459	2.4728074	0.1785269
5	C C5	0.2378422	1.0780749	-0.3265326
6	H H	-1.0443228	4.1549539	-0.7551947
7	H H7	-3.1534524	2.7964908	-1.0285193
8	H H8	-1.8743492	0.9306885	1.0759075
9	H H12	-0.1990978	0.8539743	-1.2939466
10	F F1	1.1937126	3.2292701	-0.1245203
11	F F2	0.0351417	2.4568309	1.5756810
12	C C11	-3.5671769	0.2930240	-0.1557100
13	O O1	-4.3893255	0.5049005	-1.0319125
14	O O2	-3.5758169	-0.8171822	0.6256282
15	C C12	-4.6388617	-1.7415579	0.3566904
16	H H1	-5.6111052	-1.2696221	0.5252804
17	H H9	-4.4906418	-2.5695469	1.0508394
18	H H10	-4.5931794	-2.0931125	-0.6779004
19	C C1	1.3281238	0.2014565	0.1880883
20	C C6	2.0361646	-2.2017771	0.6649187
21	C C7	3.7606359	-0.5154607	-0.1164017
22	C C8	3.3347840	-1.9902941	-0.1272322
23	C C9	2.6408840	0.4018975	-0.6276467
24	C C10	0.9096345	-1.2879287	0.1613144
25	H H6	2.2214743	-1.9930558	1.7287106
26	H H2	4.0288647	-0.2203249	0.9085850
27	H H3	3.1802209	-2.3140483	-1.1672855
28	H H11	2.4375610	0.1804705	-1.6856019
29	H H4	0.6471647	-1.5634168	-0.8713829
30	H H5	1.5382216	0.4850275	1.2284702
31	H H13	1.7187659	-3.2504677	0.6040024
32	H H14	4.6613020	-0.3721416	-0.7272798
33	H H15	4.1354506	-2.6202288	0.2804987
34	H H16	2.9425636	1.4522243	-0.5736873
35	H H17	0.0014311	-1.4283938	0.7603263

Nosub_SM (9u)

G = -621.530722

iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	2.2693226	2.2659885	0.0864734
2	C C2	1.1197603	2.9740186	0.6698508
3	C C3	1.2450634	1.4144417	0.7701306
4	H H6	1.5344577	1.0450348	1.7510014
5	C C10	0.3425391	0.5632196	-0.0173407
6	H H11	0.0778347	0.9032775	-1.0171279
7	C C11	-0.1726064	-0.6001362	0.4056053
8	H H12	0.0465146	-1.0118713	1.3865594
9	C C12	-1.0708885	-1.3795287	-0.4724605
10	O O1	-1.4275210	-1.0602966	-1.5906800
11	O O2	-1.4615842	-2.5255858	0.1371570
12	C C13	-2.3404688	-3.3567339	-0.6346471
13	H H5	-3.2668138	-2.8246330	-0.8690111
14	H H13	-2.5467023	-4.2262388	-0.0095105
15	H H14	-1.8609645	-3.6579635	-1.5697553
16	F F1	2.3857290	2.1922397	-1.2587838
17	F F2	3.4912239	2.3878929	0.6511892
18	H H19	1.2698913	3.5329598	1.5878548
19	H H27	0.3652130	3.3639145	-0.0065050

Nosub_TS2 (TS1u)

G = -621.573778, iv = i192, S^2 = 0.7541

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C	0.7946670	2.3077343	-0.3275513
2	C C2	-0.3207882	1.5191922	-0.3512372
3	C C3	-0.3471353	0.2472733	0.2644960
4	C C4	2.0777544	1.7153433	0.1641641
5	C C5	2.2929621	0.3245173	-0.3214240
6	H H	0.8063598	3.3332337	-0.6810900
7	H H7	-1.2132158	1.8362782	-0.8866403
8	H H8	0.2852294	0.0174445	1.1119224
9	H H12	1.9390721	0.0455178	-1.3051098
10	F F1	3.1381612	2.5196024	-0.2259812
11	F F2	2.1241288	1.7200433	1.5552521
12	C C11	-1.3975823	-0.7187094	-0.0857327
13	O O1	-2.2725753	-0.5339239	-0.9149029
14	O O2	-1.2755861	-1.8575817	0.6374555
15	C C12	-2.2574039	-2.8663948	0.3575224
16	H H1	-3.2646088	-2.4873954	0.5511549
17	H H9	-2.0236528	-3.6957507	1.0256294
18	H H10	-2.1949143	-3.1843250	-0.6871621
19	H H14	3.1091280	-0.2420994	0.1192347

Traige: Alkene Substitution

CN_E_RHS_SM (10a)

Spartan'10: G = -716.912803, iv = none

Gaussian'09: B3LYP/6-31G*, G = -716.917313, iv = none

Gaussian'09: M05-2X/6-31G*, G = -716.875782, iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
1	C C1	1.2099133	-0.0977419	-1.6065770
2	C C2	0.0590977	0.4469622	-0.8600824
3	C C3	0.2832058	-1.1118198	-1.0155466
4	H H3	-0.7357640	0.8262827	-1.5022389
5	H H6	0.6520854	-1.5923392	-0.1124772
6	C C4	0.1766691	1.0873485	0.4884279
7	C C5	0.3166115	2.3312581	2.9990340
8	C C6	-0.7584871	0.7817166	1.4871255
9	C C7	1.1837058	2.0222044	0.7609151
10	C C8	1.2518592	2.6400825	2.0107107
11	C C9	-0.6903124	1.3999595	2.7345575
12	H H4	-1.5401211	0.0543296	1.2818457
13	H H7	1.9166062	2.2596338	-0.0034322
14	H H8	2.0386332	3.3621794	2.2112263
15	H H9	-1.4215208	1.1546333	3.5000254
16	H H10	0.3715235	2.8128553	3.9715426
17	C C10	-0.6131026	-1.9007668	-1.8689807
18	H H11	-0.9056200	-1.4587226	-2.8188340
19	C C11	-1.0781109	-3.1203258	-1.5398247
20	H H12	-0.7980410	-3.5941554	-0.6016563
21	F F1	1.2349442	0.0471189	-2.9525554
22	F F2	2.4623054	0.0002929	-1.1107415
23	C C12	-1.9519651	-3.8639691	-2.3870171
24	N N1	-2.6641154	-4.4870174	-3.0654468

CN_E_RHS_TS2 (TS2a)

Spartan'10: G = -716.875779, iv = i139, S^2 = 0.5463

Gaussian'09: B3LYP/6-31G*, G = -716.878006, iv = i142, S^2 = 0.71

Gaussian'09: M05-2X/6-31G*, G = -716.822858, iv = i163, S^2 = 0.87

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
1	C C	-2.0151459	2.2303766	-0.0973687
2	C C2	-2.9431550	1.3505820	0.3674799
3	C C3	-2.5398690	0.1873772	1.0918623
4	C C4	-0.5821229	1.8287807	-0.0075954
5	C C5	-0.3850858	0.4037320	-0.4380687
6	H H	-2.2614819	3.1842132	-0.5498818
7	H H7	-4.0012889	1.4983995	0.1605929
8	H H8	-1.6636352	0.2188718	1.7271340
9	H H12	-1.1535598	0.0087404	-1.0894109

10	F	F1	0.2022057	2.6699625	-0.7739606
11	F	F2	-0.1019806	2.0131870	1.2992351
12	C	C1	0.8586417	-0.2923927	-0.3976390
13	C	C6	3.2581461	-1.7749134	-0.3738577
14	C	C7	0.9563986	-1.5448774	-1.0627802
15	C	C8	2.0071669	0.1905469	0.2877517
16	C	C9	3.1855331	-0.5420531	0.2868369
17	C	C10	2.1357579	-2.2738553	-1.0474285
18	H	H2	0.0850569	-1.9299378	-1.5868042
19	H	H6	1.9565916	1.1379754	0.8093028
20	H	H5	4.0568926	-0.1560074	0.8089601
21	H	H3	2.1878759	-3.2298883	-1.5607497
22	H	H4	4.1834916	-2.3440671	-0.3629747
23	C	C11	-3.3726726	-0.9440476	1.2101815
24	N	N1	-4.0537612	-1.8907052	1.2991830

Weinreb_Amide_RHS_SM (10b)

Spartan'10: G = -947.067954, iv = none

Gaussian'09: B3LYP/6-31G*, G = -947.076299, iv = none

Gaussian'09: M05-2X/6-31G*, G = -947.020971, iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C1	-1.4670215	-1.8630042	-0.2979475
2	C C2	-1.7954595	-0.7553857	0.6210089
3	C C3	-0.5077807	-0.7195424	-0.3017992
4	H H3	-1.5563263	-0.9723070	1.6617199
5	H H6	-0.6081401	-0.0550275	-1.1571230
6	C C4	-2.9022014	0.2271570	0.4004430
7	C C5	-4.9645210	2.1066034	0.0780893
8	C C6	-2.7137389	1.5659107	0.7746769
9	C C7	-4.1376207	-0.1588032	-0.1355554
10	C C8	-5.1610036	0.7773159	-0.2962337
11	C C9	-3.7364277	2.4990068	0.6162029
12	H H4	-1.7569553	1.8733261	1.1900092
13	H H7	-4.2953475	-1.1902837	-0.4317271
14	H H8	-6.1137281	0.4635579	-0.7144940
15	H H9	-3.5747818	3.5324214	0.9112700
16	H H10	-5.7625886	2.8333963	-0.0472600
17	C C10	0.8266066	-0.8336070	0.2998313
18	H H11	0.9617074	-1.5572226	1.1015221
19	C C11	1.8856003	-0.0975559	-0.0705567
20	H H12	1.8128700	0.6439152	-0.8574601
21	C C12	3.1819019	-0.2851643	0.6277332
22	O O1	3.3361624	-1.0633959	1.5655795
23	N N1	4.2673549	0.4261932	0.1278718
24	C C13	5.4661468	0.6116434	0.9286587
25	H H5	5.5681329	-0.2635093	1.5695692
26	H H13	5.3895370	1.5154256	1.5463922
27	H H14	6.3395043	0.6949450	0.2750625
28	F F1	-1.0729595	-3.0457522	0.2301305
29	F F2	-2.2134450	-2.0857404	-1.4061244
30	O O2	3.9800488	1.5460992	-0.6824481

31	C	C14	4.4328597	1.3118606	-2.0186236
32	H	H2	4.2195193	2.2375591	-2.5596953
33	H	H1	3.8943077	0.4753809	-2.4795787
34	H	H15	5.5107114	1.1111478	-2.0471366

Weinreb_amide_RHS_TS2 (TS2b)

Spartan'10: G = -947.029070, iv = i127, S² = 0.5635

Gaussian'09: B3LYP/6-31G*, G = -947.034526, iv = i142, S² = 0.55

Gaussian'09: M05-2X/6-31G*, G = -716.829881, iv = i163, S² = 0.87

Cartesian Coordinates (Angstroms)

Atom	X	Y	Z
1 C C	-0.3708103	3.2467077	-0.7831259
2 C C2	-1.5345291	2.5375201	-0.8136579
3 C C3	-1.6370972	1.2810981	-0.1615410
4 C C4	0.8362767	2.5577318	-0.2460828
5 C C5	0.9440416	1.1547946	-0.7683250
6 H H	-0.2640747	4.2559235	-1.1654640
7 H H7	-2.3928187	2.8872876	-1.3828514
8 H H8	-1.0886985	1.0873996	0.7477209
9 H H12	0.4333421	0.9712623	-1.7046199
10 F F1	1.9794635	3.2721405	-0.5629116
11 F F2	0.8234439	2.5560476	1.1595635
12 C C1	1.9584378	0.2243082	-0.3835976
13 C C6	3.9199424	-1.6910241	0.2942364
14 C C7	2.1243885	-0.9626358	-1.1474145
15 C C8	2.8072229	0.4142519	0.7398366
16 C C9	3.7737304	-0.5287123	1.0609754
17 C C10	3.0871008	-1.9039211	-0.8110489
18 H H2	1.4847797	-1.1228519	-2.0121957
19 H H6	2.6945236	1.3061860	1.3428490
20 H H5	4.4196154	-0.3619704	1.9188608
21 H H3	3.1977030	-2.8027072	-1.4116446
22 H H4	4.6764064	-2.4256027	0.5560373
23 C C11	-2.7109407	0.3574663	-0.5597123
24 O O1	-3.4753177	0.5889965	-1.4986722
25 N N1	-2.7996676	-0.8457652	0.1359310
26 O O2	-2.1985384	-0.8783023	1.4133387
27 C C12	-4.0180133	-1.6373118	0.0779455
28 H H9	-3.7798796	-2.6879591	0.2658295
29 H H10	-4.4370453	-1.5272446	-0.9217100
30 H H11	-4.7482652	-1.2934599	0.8216190
31 C C13	-1.1294124	-1.8306027	1.4283861
32 H H1	-0.7534186	-1.8191473	2.4549569
33 H H13	-0.3318626	-1.5429230	0.7352616
34 H H14	-1.4900290	-2.8369809	1.1812269

AllylAlcohol_RHS_E_SM (10c)

G = -739.155508

iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	0.2555785	2.1890182	0.4890142
2	C C4	-0.0090838	2.6009899	3.2310042
3	C C2	0.3676012	1.0972270	1.3622191
4	C C6	0.0168255	3.4717008	0.9799304
5	C C5	-0.1172528	3.6810733	2.3545178
6	C C3	0.2336460	1.3170931	2.7394558
7	H H6	-0.0667795	4.3074216	0.2899720
8	C C7	0.6624323	-0.2635615	0.8118213
9	C C8	0.0034628	-1.4998679	1.2885984
10	C C9	-0.4096150	-1.0224052	-0.0598878
11	H H2	1.6825928	-0.4228790	0.4619987
12	H H9	-1.3779573	-0.5256805	-0.0738933
13	F F1	-0.8920404	-1.4510192	2.3058011
14	F F2	0.7442514	-2.6307156	1.3926437
15	C C10	-0.0144213	-1.7308339	-1.2938316
16	C C11	-0.7356426	-1.7174309	-2.4181920
17	H H10	-1.6777015	-1.1702959	-2.4622000
18	H H13	-0.1140383	2.7552384	4.3017809
19	H H14	-0.3054297	4.6800810	2.7388050
20	H H17	0.3109915	0.4797849	3.4253868
21	H H3	0.3540560	2.0251906	-0.5814957
22	H H12	0.9182520	-2.2882847	-1.2718986
23	C C12	-0.3541539	-2.4248015	-3.6850703
24	H H1	-0.3431852	-1.6949674	-4.5151730
25	H H4	-1.1372756	-3.1636898	-3.9344604
26	O O1	0.9111033	-3.0494862	-3.5340332
27	H H5	1.0937834	-3.5488993	-4.3428135

allylalcOHol_RHS_E_TS2 (TS2c)

G = -739.115497

iv = i149

S^2 = 0.5638

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C	-0.9916180	2.5756204	-0.6751842
2	C C2	-2.1559361	1.8593542	-0.5635713
3	C C3	-2.2167936	0.7019090	0.2369574
4	C C4	0.2411986	1.9532219	-0.1246117
5	C C5	0.3251911	0.5046037	-0.4913438
6	H H	-0.9166136	3.5396422	-1.1658984
7	H H8	-1.5833461	0.6228962	1.1114011
8	H H12	-0.2252742	0.2257674	-1.3802903
9	F F1	1.3654598	2.6372691	-0.5628246

10	F	F2	0.2941675	2.1103313	1.2790261
11	C	C1	1.3651672	-0.3820207	-0.0641299
12	C	C6	3.3555405	-2.2306219	0.7196571
13	C	C7	1.5116549	-1.6321336	-0.7209743
14	C	C8	2.2515829	-0.0921458	1.0071926
15	C	C9	3.2304789	-1.0033181	1.3810741
16	C	C10	2.4878426	-2.5398509	-0.3345601
17	H	H2	0.8427593	-1.8714578	-1.5445940
18	H	H6	2.1571432	0.8506500	1.5309215
19	H	H5	3.9032527	-0.7590580	2.1991517
20	H	H3	2.5795329	-3.4894655	-0.8552001
21	H	H4	4.1215079	-2.9392671	1.0226611
22	H	H14	-3.0327146	2.1343550	-1.1457768
23	C	C11	-3.3073964	-0.3132689	0.1297800
24	H	H1	-4.0085898	-0.1780739	0.9764311
25	H	H7	-2.8726158	-1.3209940	0.2537061
26	O	O1	-3.9795164	-0.1834506	-1.1147506
27	H	H9	-4.7420651	-0.7804935	-1.1042495

Me_RHS_E_SM (10d)

G = -663.957928
iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C1	0.4009824	2.0386001	0.3731448
2	C C4	-0.0441784	2.4200530	3.0959599
3	C C2	0.3917446	0.9285029	1.2304266
4	C C6	0.1932558	3.3240719	0.8705544
5	C C5	-0.0312215	3.5181574	2.2355956
6	C C3	0.1679087	1.1329872	2.5983758
7	H H6	0.2045607	4.1739084	0.1930297
8	C C7	0.6594677	-0.4356104	0.6749485
9	C C8	-0.0604812	-1.6558925	1.1030610
10	C C9	-0.3990780	-1.1480238	-0.2537758
11	H H2	1.6880637	-0.6259657	0.3677942
12	H H9	-1.3489336	-0.6193858	-0.3044273
13	F F1	-0.9952085	-1.5969659	2.0833357
14	F F2	0.6411994	-2.8117864	1.2177540
15	C C10	0.0217734	-1.8588060	-1.4791923
16	C C11	-0.6265763	-1.7904779	-2.6471827
17	H H10	-1.5257926	-1.1758116	-2.7142843
18	H H13	-0.2193715	2.5626497	4.1591164
19	H H14	-0.1950732	4.5194536	2.6249715
20	H H17	0.1518618	0.2821452	3.2714201
21	H H3	0.5698026	1.8869875	-0.6903161
22	H H12	0.9179436	-2.4736188	-1.3967510
23	C C12	-0.2172187	-2.5078523	-3.9001855
24	H H1	0.6855317	-3.1076787	-3.7429439
25	H H4	-0.0183799	-1.8012469	-4.7175624
26	H H5	-1.0125826	-3.1783942	-4.2528668

Me_RHS_E_TS2 (TS2d)

G = -663.917301

iv = i184

S² = 0.5585

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C	-0.9151383	2.6513547	-0.7786512
2	C C2	-2.1077249	1.9853535	-0.8954940
3	C C3	-2.3582101	0.7899579	-0.1888719
4	C C4	0.1849905	1.9441886	-0.0714278
5	C C5	0.2556601	0.5076570	-0.4856083
6	H H	-0.7255362	3.6365584	-1.1899678
7	H H8	-1.8833208	0.6491853	0.7747308
8	H H12	-0.1358502	0.3017099	-1.4732521
9	F F1	1.3945439	2.5835277	-0.3012456
10	F F2	0.0234202	2.0493885	1.3265275
11	C C1	1.1528036	-0.4591358	0.0724220
12	C C6	2.8706507	-2.4587781	1.0962271
13	C C7	1.3491309	-1.6865482	-0.6134791
14	C C8	1.8458027	-0.2716662	1.2975662
15	C C9	2.6926693	-1.2560728	1.7896820
16	C C10	2.1907439	-2.6682562	-0.1092948
17	H H2	0.8298147	-1.8495212	-1.5553695
18	H H6	1.7092330	0.6511676	1.8469904
19	H H5	3.2177380	-1.0883929	2.7266783
20	H H3	2.3247423	-3.5980963	-0.6560184
21	H H4	3.5316207	-3.2251805	1.4915181
22	H H14	-2.8650800	2.3500191	-1.5911246
23	C C11	-3.4330427	-0.1819377	-0.5617517
24	H H1	-3.0292397	-1.2005583	-0.6427918
25	H H7	-3.9040764	0.0698443	-1.5176679
26	H H9	-4.2163453	-0.2257684	0.2096742

nosub_RHS_SM (10e)

G = -624.665083

iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	H H1	-0.7768006	1.0388829	-1.6047737
2	C C1	-0.7173554	1.4647263	-0.6059672
3	C C4	-0.5698059	2.5451006	1.9567121
4	C C2	0.1393784	0.8803837	0.3387670
5	C C6	-1.4888334	2.5770693	-0.2751774
6	C C5	-1.4173630	3.1205023	1.0098283
7	C C3	0.2059673	1.4328222	1.6246422
8	H H6	-2.1470385	3.0188171	-1.0187338
9	H H5	-2.0187004	3.9875695	1.2699744
10	H H3	0.8604990	0.9879185	2.3665809

11	H	H4	-0.5091567	2.9619231	2.9586068
12	C	C7	0.9869728	-0.2859276	-0.0643017
13	C	C8	1.2810050	-1.4418712	0.8111093
14	C	C9	0.3385846	-1.7037254	-0.3110794
15	H	H9	-0.7064157	-1.7584663	-0.0129154
16	F	F1	0.8141422	-1.4814324	2.0827236
17	F	F2	2.5240203	-1.9833723	0.7679361
18	C	C10	0.7298449	-2.5175481	-1.4803324
19	H	H8	1.7922604	-2.5300748	-1.7195707
20	C	C11	-0.1267143	-3.2164337	-2.2292022
21	H	H10	-1.1933096	-3.2345539	-2.0164315
22	H	H2	1.7888044	-0.0620621	-0.7678205
23	H	H13	0.2100143	-3.8002475	-3.0805750

nosub_RHS_TS2 (TS2e)

G = -624.623111

iv = i300

S^2 = 0.5749

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C	-1.7874470	2.4421631	-0.5045635
2	C C2	-2.9103076	1.6546177	-0.5179662
3	C C3	-2.9306507	0.4028033	0.1255955
4	C C4	-0.5366945	1.8213362	0.0097436
5	C C5	-0.3654349	0.4249353	-0.5081575
6	H H	-1.7528806	3.4631134	-0.8681306
7	H H7	-3.7853806	1.9730485	-1.0847020
8	H H8	-2.3409283	0.2191327	1.0131394
9	H H12	-0.8595597	0.2241621	-1.4499067
10	F F1	0.5605938	2.5993423	-0.3282603
11	F F2	-0.5231132	1.8293521	1.4181294
12	C C1	0.6996512	-0.4548601	-0.1310145
13	C C6	2.7580381	-2.2748292	0.5294732
14	C C7	0.9343812	-1.6177403	-0.9109320
15	C C8	1.5307144	-0.2392681	1.0000659
16	C C9	2.5445757	-1.1348745	1.3131165
17	C C10	1.9442125	-2.5118766	-0.5846335
18	H H2	0.3072605	-1.8002019	-1.7805825
19	H H6	1.3680550	0.6346591	1.6181396
20	H H5	3.1740740	-0.9480413	2.1792411
21	H H3	2.1048388	-3.3940255	-1.1988995
22	H H4	3.5500534	-2.9732849	0.7852097
23	H H11	-3.6840514	-0.3396633	-0.1241046

AllylAlcohol_RHS_Z_SM (10f)

G = -739.152680

iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	0.0851050	1.6761281	0.3841732
2	C C4	0.9694170	2.3216998	2.9514251
3	C C2	0.7293453	0.7021926	1.1574226
4	C C6	-0.1117169	2.9621284	0.8898064
5	C C5	0.3298641	3.2887861	2.1730192
6	C C3	1.1666918	1.0368216	2.4462655
7	H H6	-0.6130479	3.7100865	0.2806242
8	C C7	0.9817207	-0.6701300	0.6123821
9	C C8	0.3001452	-1.8728140	1.1463146
10	C C9	-0.1309859	-1.4173229	-0.2025879
11	H H2	1.9948860	-0.8646646	0.2592903
12	H H9	-1.0772748	-0.8910040	-0.2262031
13	F F1	-0.5547505	-1.7599330	2.1893523
14	F F2	1.0125521	-3.0239942	1.2656796
15	C C10	0.2344924	-2.1846184	-1.4139185
16	C C11	-0.2989358	-2.0996594	-2.6390618
17	H H10	0.1029440	-2.7637087	-3.4044095
18	H H13	1.3107232	2.5658500	3.9540720
19	H H14	0.1735724	4.2899330	2.5661627
20	H H17	1.6597545	0.2828651	3.0547075
21	H H3	-0.2702189	1.4158108	-0.6094971
22	H H12	1.0420510	-2.9017490	-1.2741580
23	C C12	-1.4035451	-1.2271609	-3.1634237
24	H H1	-2.2789188	-1.8620928	-3.3906656
25	H H4	-1.0748721	-0.8007048	-4.1272752
26	O O1	-1.7595442	-0.1917930	-2.2533476
27	H H5	-2.5194536	0.2790478	-2.6261489

Allylalcohol_RHS_Z_TS2 (TS2f)

G = -739.107323

iv = i244

S^2 = 0.6641

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C	-2.1259931	2.0740105	-0.1662080
2	C C2	-2.5424791	1.5174060	1.0086412
3	C C15	-1.8016030	0.6027220	1.8031781
4	C C4	-0.9168276	1.5576179	-0.8649583
5	C C13	-0.7384488	0.0873205	-0.6639539
6	H H	-2.6797738	2.8649364	-0.6622078
7	H H8	-2.3837208	-0.0497596	2.4558284
8	H H12	-1.6672560	-0.4609286	-0.5726305
9	F F1	-1.0227259	1.8395517	-2.2240077

10	F	F2	0.2272279	2.2801359	-0.4820522
11	C	C1	0.4300140	-0.6726015	-0.9764675
12	C	C6	2.6656667	-2.3058208	-1.5618602
13	C	C7	0.3417808	-2.0913285	-0.9412475
14	C	C8	1.6894536	-0.1010288	-1.3069829
15	C	C9	2.7777544	-0.9110292	-1.6028171
16	C	C10	1.4388181	-2.8908837	-1.2260127
17	H	H2	-0.6111088	-2.5494343	-0.6868931
18	H	H6	1.7894984	0.9759755	-1.3396011
19	H	H5	3.7265815	-0.4526459	-1.8683576
20	H	H3	1.3419452	-3.9726504	-1.1924436
21	H	H4	3.5248236	-2.9305226	-1.7894764
22	H	H14	-3.5589411	1.7394595	1.3403955
23	C	C11	-0.3624922	0.6962153	2.2256699
24	H	H1	0.1722012	1.4506196	1.6412898
25	H	H7	0.1431767	-0.2710079	2.0799692
26	O	O1	-0.3830862	1.0317742	3.6228611
27	H	H9	0.5255144	0.9418970	3.9503449

Me_Z_RHS_SM (10g)

G = -664.955651
iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C1	0.6876844	1.8059308	0.2717546
2	C C4	0.2332772	2.1619593	2.9962718
3	C C2	0.6402783	0.6845481	1.1130431
4	C C6	0.5129610	3.0897137	0.7856787
5	C C5	0.2839789	3.2711096	2.1517316
6	C C3	0.4122952	0.8762936	2.4822057
7	H H6	0.5541235	3.9482377	0.1204040
8	C C7	0.8758488	-0.6774199	0.5386953
9	C C8	0.1402163	-1.8910747	0.9564978
10	C C9	-0.2033816	-1.3607236	-0.3908768
11	H H2	1.8972229	-0.8817126	0.2169921
12	H H9	-1.1441406	-0.8177792	-0.4139133
13	F F1	-0.7876269	-1.8294679	1.9434392
14	F F2	0.8237780	-3.0590947	1.0536399
15	C C10	0.2126043	-2.0669876	-1.6213846
16	C C11	-0.3788681	-2.0009782	-2.8219581
17	H H13	0.0549811	2.2947349	4.0601739
18	H H14	0.1465586	4.2711907	2.5541931
19	H H17	0.3680571	0.0172382	3.1433062
20	H H3	0.8611049	1.6644457	-0.7923559
21	H H5	0.0623687	-2.5931285	-3.6236434
22	H H12	1.0901639	-2.7021730	-1.5132039
23	C C12	-1.5928016	-1.2066712	-3.2116891
24	H H1	-1.3569106	-0.5121795	-4.0294335
25	H H4	-2.0052938	-0.6196340	-2.3862491
26	H H7	-2.3884795	-1.8663773	-3.5833190

Me_Z_RHS_TS2 (TS2g)

G = -663.908400

iv = i271

S² = 0.7108

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C	-1.5504450	2.4776641	-0.6191524
2	C C2	-2.6238280	1.6386294	-0.6718734
3	C C3	-2.6681504	0.3067540	-0.1672499
4	C C4	-0.2008042	1.9546502	-0.2616217
5	C C5	0.0096776	0.5600419	-0.7584830
6	H H	-1.6142070	3.5236503	-0.9017007
7	H H12	-0.4798152	0.3547298	-1.7024576
8	F F1	0.7668653	2.7997959	-0.7985427
9	F F2	0.0214425	2.0575976	1.1224109
10	C C1	1.0293103	-0.3495120	-0.3479285
11	C C6	2.9841249	-2.2674036	0.3711957
12	C C7	1.2144525	-1.5409105	-1.1033773
13	C C8	1.8610609	-0.1597168	0.7899370
14	C C9	2.8220179	-1.1026679	1.1298415
15	C C10	2.1707081	-2.4804807	-0.7487619
16	H H2	0.5883137	-1.7070611	-1.9770387
17	H H6	1.7452761	0.7351629	1.3868514
18	H H5	3.4518718	-0.9319488	1.9991310
19	H H3	2.2898196	-3.3812381	-1.3451807
20	H H4	3.7347479	-3.0020007	0.6493852
21	H H7	-3.3665500	-0.3611418	-0.6760890
22	H H14	-3.5119600	1.9904034	-1.2035033
23	C C11	-2.2362635	-0.1744225	1.1888731
24	H H1	-1.5813535	0.5328307	1.6967027
25	H H8	-1.7263941	-1.1446348	1.1324948
26	H H9	-3.1299182	-0.3287709	1.8161379

CN_Z_RHS_SM (10h)

Spartan'10: G = -716.912699, iv = none

Gaussian'09: B3LYP/6-31G*, G = -716.917609, iv = none

Gaussian'09: M05-2X/6-31G*, G = -716.877091, iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	0.8179847	0.4610398	-1.8635220
2	C C2	-0.3416567	0.4689995	-0.9506254
3	C C3	0.4045255	-0.8718587	-1.3259301
4	H H3	-1.2995784	0.5872061	-1.4573460
5	H H6	1.0320986	-1.2635388	-0.5294869
6	C C4	-0.2651222	0.9957873	0.4498269
7	C C5	-0.1980338	2.0131451	3.0630712
8	C C6	-0.7499435	0.2341961	1.5211498
9	C C7	0.2576765	2.2709732	0.7012935

10	C	C8	0.2898950	2.7763162	2.0014705
11	C	C9	-0.7179257	0.7399927	2.8203014
12	H	H4	-1.1462860	-0.7610274	1.3358170
13	H	H7	0.6466198	2.8635872	-0.1213348
14	H	H8	0.7007166	3.7655608	2.1843421
15	H	H9	-1.0945771	0.1378479	3.6425950
16	H	H10	-0.1699119	2.4064027	4.0757033
17	C	C10	-0.2505385	-1.8537494	-2.1986835
18	H	H11	-0.7665948	-1.4637915	-3.0729015
19	C	C11	-0.2592490	-3.1874688	-2.0083162
20	H	H12	-0.7683717	-3.8396237	-2.7121403
21	F	F1	1.9994365	0.9831711	-1.4741208
22	F	F2	0.6103896	0.7185857	-3.1784391
23	C	C12	0.3781323	-3.8268640	-0.9027312
24	N	N1	0.8903143	-4.3548891	0.0000069

CN_Z_RHS_TS2 (TS2h)

Spartan'10: G = -716.865358, iv = i141, S² = 0.6948

Gaussian'09: B3LYP/6-31G*, G = -716.870285, iv = i165, S² = 0.71

Gaussian'09: M05-2X/6-31G*, G = -716.822858, iv = i157, S² = 0.87

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C	-1.6959458	2.4322037	-0.5853651
2	C C2	-2.8320034	1.6728406	-0.5751580
3	C C3	-2.9807398	0.3998630	0.0375008
4	C C4	-0.4175204	1.8559479	-0.1169702
5	C C5	-0.2444133	0.4520397	-0.6140125
6	H H	-1.6942970	3.4655487	-0.9128003
7	H H7	-3.6967941	2.0395279	-1.1290636
8	H H12	-0.8219802	0.2020451	-1.4936243
9	F F1	0.6514990	2.6240699	-0.5853241
10	F F2	-0.2852804	1.9416445	1.2749634
11	C C1	0.8219841	-0.4094148	-0.2537761
12	C C6	2.8634354	-2.2330723	0.4205645
13	C C7	1.0618240	-1.5728641	-1.0405546
14	C C8	1.6432015	-0.1977193	0.8914358
15	C C9	2.6488791	-1.0981051	1.2106711
16	C C10	2.0650588	-2.4670966	-0.7082571
17	H H2	0.4437234	-1.7493459	-1.9171956
18	H H6	1.4717272	0.6691657	1.5142291
19	H H5	3.2624894	-0.9291043	2.0913627
20	H H3	2.2336450	-3.3494409	-1.3192103
21	H H4	3.6455019	-2.9392286	0.6860434
22	H H9	-3.8222598	-0.2064568	-0.3046222
23	C C11	-2.3987703	-0.0760801	1.2324707
24	N N1	-1.9229643	-0.5269678	2.1966924

Me_CO2Et_RHS_SM (10i)

Spartan'10, G = -891.796469, iv = none

Gaussian'09: B3LYP/6-31G*, G = -891.805001, iv = none

Gaussian'09: M05-2X/6-31G*, G = -891.739337, iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	H H1	1.0446575	2.2529926	0.3038655
2	C C1	0.6803316	2.4282900	1.3133353
3	C C4	-0.2625032	2.8772000	3.8951227
4	C C2	0.2451012	1.3409889	2.0855825
5	C C6	0.6461051	3.7238963	1.8257449
6	C C5	0.1726455	3.9521526	3.1200901
7	C C3	-0.2258138	1.5785692	3.3836570
8	H H6	0.9875777	4.5551942	1.2146256
9	H H5	0.1441892	4.9618900	3.5207809
10	H H3	-0.5693807	0.7480578	3.9909839
11	H H4	-0.6314050	3.0461543	4.9033250
12	C C7	0.3355870	-0.0422941	1.5220763
13	C C8	-0.6565510	-1.1087543	1.7646985
14	C C9	-0.6767509	-0.5166698	0.3952902
15	H H2	1.3441159	-0.4219058	1.3611400
16	H H9	-1.4879302	0.1870095	0.2353990
17	F F1	-1.7181082	-0.8976478	2.5784862
18	F F2	-0.2105188	-2.3788247	1.9208703
19	C C10	-0.1732717	-1.2781974	-0.7575398
20	H H8	0.5383231	-2.0645695	-0.5233232
21	C C11	-0.5062844	-1.0987494	-2.0513345
22	C C12	0.0974987	-1.9667538	-3.1024499
23	O O1	-0.1662135	-1.8665359	-4.2864012
24	O O2	0.9733092	-2.8843421	-2.6229824
25	C C13	1.5644962	-3.7388047	-3.6115307
26	H H7	2.2118431	-4.4205317	-3.0585095
27	H H11	2.1468352	-3.1535082	-4.3286787
28	H H12	0.7938764	-4.2943522	-4.1526963
29	C C14	-1.4727345	-0.0764040	-2.5904011
30	H H10	-0.9791214	0.5663472	-3.3277598
31	H H13	-1.8904669	0.5564653	-1.8044602
32	H H14	-2.2994382	-0.5663625	-3.1170062

Me_CO2Et_RHS_TS2 (TS2i)

Spartan'10: G = -891.751323, iv = i100, S² = 0.7421

Gaussian'09: B3LYP/6-31G*, G = -891.756292, iv = i92, S² = 0.75

Gaussian'09: M05-2X/6-31G*, G = -891.68717, iv = i70, S² = 0.91

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C	-0.7492316	2.8416276	-0.6069933
2	C C2	-1.8256500	2.0339074	-0.4681444
3	C C3	-1.8311064	0.7379227	0.1677036
4	C C4	0.6373249	2.3487772	-0.3422518
5	C C5	0.8153452	0.9098674	-0.7192309
6	H H	-0.8360057	3.8517814	-0.9954873
7	H H7	-2.7673212	2.3486960	-0.9174200
8	H H12	0.2552825	0.6281755	-1.6035435
9	F F1	1.5256631	3.1226515	-1.0794369
10	F F2	1.0038965	2.6003383	0.9844375
11	C C1	1.8685020	0.0389292	-0.3180248
12	C C6	3.9090872	-1.7988735	0.3628609
13	C C7	2.0633196	-1.1621470	-1.0576450
14	C C8	2.7324120	0.2773956	0.7875127
15	C C9	3.7319599	-0.6297908	1.1116369
16	C C10	3.0667499	-2.0588718	-0.7258170
17	H H2	1.4142271	-1.3625323	-1.9066413
18	H H6	2.6102043	1.1790719	1.3722462
19	H H5	4.3820658	-0.4266731	1.9585224
20	H H3	3.2014201	-2.9617152	-1.3153402
21	H H4	4.6952357	-2.5015952	0.6247043
22	C C11	-2.7852724	-0.2244240	-0.4164488
23	O O1	-3.3895750	-0.0539514	-1.4651962
24	O O2	-2.9290712	-1.3403758	0.3432352
25	C C12	-3.8551082	-2.3092594	-0.1659952
26	H H1	-4.8430391	-1.8615727	-0.3058310
27	H H9	-3.8935191	-3.1006354	0.5838020
28	H H10	-3.5102835	-2.7061803	-1.1254549
29	C C13	-1.2696131	0.4568753	1.5383462
30	H H8	-0.6997947	-0.4782820	1.5628785
31	H H11	-2.0971278	0.3325175	2.2523740
32	H H13	-0.6309769	1.2683454	1.8846422

Other Synthesised VCP Precursors

Me Furan SM Trans (S9a)

G = -697.705753

iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C7	0.1406689	-0.9956178	0.5964871
2	C C8	1.3872171	-1.1047379	1.3823601
3	C C9	0.4327958	-0.0392131	1.8146329
4	H H2	-0.5882604	-1.7749922	0.8259152
5	H H9	0.7063655	0.9810075	1.5644678
6	F F1	2.5620693	-0.7294608	0.8469569
7	F F2	1.5578818	-2.1889554	2.1726557
8	C C10	-0.3889264	-0.2021742	3.0432596
9	H H12	-0.6630748	-1.2485563	3.2963319
10	O O1	-0.7568556	0.7285319	3.7269647
11	C C1	0.1434540	-0.4465200	-0.7726300
12	O O2	0.9128662	-1.1269062	-1.6855271
13	C C3	0.7601324	-0.4932891	-2.8790145
14	C C4	-0.0823992	0.5655587	-2.7531779
15	C C5	-0.4971161	0.6019962	-1.3757939
16	H H6	1.3135119	-0.9125578	-3.7057550
17	H H8	-0.3834437	1.2479830	-3.5367193
18	C C2	-1.4470105	1.5859241	-0.7584351
19	H H1	-1.0728967	2.6131767	-0.8500036
20	H H3	-1.6130408	1.3840237	0.3032771
21	H H4	-2.4239387	1.5547792	-1.2562526

Me Furan SM cis (S9b)

G = -697.706140

iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C7	0.7390908	0.3844384	-1.0657176
2	C C8	1.6688781	-0.7588474	-0.9599335
3	C C9	2.1938189	0.5450926	-0.4611973
4	H H9	2.9086128	1.0603466	-1.0954608
5	F F1	2.1952401	-1.2833724	-2.0859645
6	F F2	1.4154475	-1.7446922	-0.0696108
7	C C10	2.3730149	0.7819041	0.9998585
8	H H12	1.6535859	0.2669332	1.6659712
9	O O1	3.2535027	1.4874759	1.4429023
10	C C1	-0.4487462	0.5029065	-0.1991059
11	O O2	-0.6162882	1.7157256	0.4288353
12	C C3	-1.7758070	1.6365772	1.1365563
13	C C4	-2.3502310	0.4161752	0.9749909
14	C C5	-1.4901531	-0.3344543	0.0984126

15	H	H6	-2.0449353	2.5206780	1.6946725
16	H	H8	-3.2754549	0.0746172	1.4194284
17	C	C2	-1.7172756	-1.7403138	-0.3741531
18	H	H1	-1.6172550	-2.4576887	0.4494956
19	H	H3	-1.0063412	-2.0322880	-1.1511297
20	H	H4	-2.7278852	-1.8545588	-0.7834508
21	H	H5	0.6691809	0.8133453	-2.0653994

Me Furan [3,3]-TS (TS3)

G = -697.672991

iv = i309

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
1	C C1	-0.9655277	-0.1281625	0.5395914
2	C C2	0.3919177	0.1289556	0.9945501
3	C C5	0.2274272	0.8396342	-1.9004649
4	H H7	0.1609263	1.7533491	-2.5101504
5	O O1	-0.8684853	0.4606492	-1.3383232
6	C C3	1.4773684	0.2600752	-1.8088386
7	C C4	1.6018603	-0.1920409	0.4785488
8	C C11	1.8373657	-0.8215650	-0.8598650
9	H H2	2.3096381	0.7303558	-2.3220689
10	H H10	2.4830843	0.2571453	0.9257838
11	F F1	1.1678797	-2.0112550	-1.0464222
12	F F2	3.1739584	-1.1193241	-0.9750310
13	O O3	0.3647330	1.1247164	1.9796098
14	C C8	-0.9295091	1.5043356	2.1026746
15	H H12	-1.1124427	2.2748555	2.8394582
16	C C7	-1.7628534	0.8250046	1.2825503
17	H H11	-2.8371378	0.9257828	1.2236656
18	C C9	-1.5565897	-1.4572627	0.1605722
19	H H3	-0.8663429	-2.0669327	-0.4148454
20	H H4	-2.4636009	-1.2919639	-0.4275625
21	H H9	-1.8336694	-1.9963523	1.0765677

Me Furan VCPR Ts (use NODISS keyword) (TS4)

G = -697.665879

iv = i234

S^2 = 0.29

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
1	C C	-1.4362337	2.2538247	-1.3566871
2	C C2	-2.5135153	1.5219083	-1.8423498
3	C C4	-0.5217870	1.5210494	-0.4698253
4	C C5	-0.3577867	0.0914781	-0.9001564
5	H H	-1.2556072	3.2975305	-1.5802847
6	H H12	-0.6239173	-0.1605270	-1.9144912
7	F F1	0.7415242	2.1148315	-0.4410394
8	F F2	-0.9294237	1.5682960	0.8718760

9	H	H14	-3.1555660	1.9765040	-2.6177622
10	O	O1	-2.7358741	0.3260619	-1.4868078
11	C	C1	0.3479232	-0.8708234	-0.1989309
12	O	O2	0.4898193	-2.0924328	-0.8613604
13	C	C6	1.1870195	-2.9027068	-0.0585477
14	C	C7	1.5357917	-2.2711910	1.1116651
15	C	C8	1.0070982	-0.9638114	1.0508234
16	H	H5	1.3664614	-3.9011673	-0.4315501
17	H	H7	2.1094802	-2.6960812	1.9238066
18	C	C3	1.1627819	0.0895214	2.0983756
19	H	H2	1.9011221	-0.2221925	2.8422719
20	H	H3	0.2090776	0.2796994	2.6039992
21	H	H4	1.4716117	1.0402281	1.6569753

Non-Fluoro-SM trans (47a)

Spartan'10: G = -654.027526, iv = none

Gaussian'09: B3LYP/6-31G*, G = -654.032624 , iv = none

Gaussian'09: M05-2X/6-31G*, G = -653.968582, iv = none

Cartesian Coordinates (Angstroms)					
Atom		X	Y	Z	
-----		-----	-----	-----	-----
1	H H1	2.4558148	1.9664977	1.3490937	
2	C C1	1.5137206	2.2423943	1.8174568	
3	C C4	-0.8907964	2.9604966	3.0162407	
4	C C2	0.4921939	1.2865397	1.9171313	
5	C C6	1.3395373	3.5362157	2.3087436	
6	C C5	0.1349941	3.9019932	2.9103722	
7	C C3	-0.7135294	1.6673011	2.5267193	
8	H H6	2.1472528	4.2581074	2.2200627	
9	H H5	-0.0036711	4.9091323	3.2937697	
10	H H3	-1.5254456	0.9506187	2.6227930	
11	H H4	-1.8335371	3.2322952	3.4841012	
12	C C7	0.7180306	-0.0812305	1.3680533	
13	C C8	0.0127924	-1.3021650	1.8856731	
14	C C9	-0.3721006	-0.7724019	0.5197991	
15	H H2	1.7317359	-0.2449302	1.0093980	
16	H H9	-1.3118509	-0.2275742	0.4625525	
17	C C10	0.0192075	-1.4923450	-0.6960636	
18	H H8	0.9411453	-2.0733622	-0.6593643	
19	C C11	-0.6623738	-1.4863038	-1.8532113	
20	H H10	-1.5889776	-0.9328562	-1.9759883	
21	C C12	-0.1648266	-2.2407264	-3.0192128	
22	O O1	0.8483886	-2.9142415	-3.0597069	
23	O O2	-0.9984269	-2.0894137	-4.0801680	
24	C C13	-0.6046241	-2.7846876	-5.2704153	
25	H H7	-1.3671695	-2.5496443	-6.0140814	
26	H H11	-0.5623012	-3.8628738	-5.0915100	
27	H H12	0.3786244	-2.4463030	-5.6097971	
28	H H13	-0.7063055	-1.1776952	2.6905673	
29	H H14	0.5724986	-2.2328375	1.9269918	

Non-Fluoro-SM cis (47b)

Spartan'10: G = -654.024790, iv = none

Gaussian'09: B3LYP/6-31G*, -654.030414, iv = none

Gaussian'09: M06-2X/6-31G*, -653.744967, iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	H H1	-0.2542662	2.2915662	-0.5021848
2	C C1	0.7344812	2.1645972	-0.0684421
3	C C4	3.2703973	1.8162921	1.0317255
4	C C2	0.8557636	1.5844524	1.2029998
5	C C6	1.8639337	2.5634010	-0.7812665
6	C C5	3.1369438	2.3904917	-0.2325234
7	C C3	2.1367416	1.4171786	1.7429408
8	H H6	1.7515622	3.0044603	-1.7682719
9	H H5	4.0179587	2.6984646	-0.7892128
10	H H3	2.2450075	0.9756370	2.7302087
11	H H4	4.2566489	1.6773723	1.4669251
12	C C7	-0.3721506	1.2032446	1.9764382
13	C C8	-0.4452043	-0.0400410	2.8065827
14	C C9	-1.2889387	0.0486890	1.5393170
15	H H9	-2.3527386	0.2234564	1.6844538
16	C C10	-0.9508286	-0.7867763	0.3807042
17	H H8	0.1013634	-1.0033740	0.2018760
18	C C11	-1.8446828	-1.3043687	-0.4777387
19	H H10	-2.9127551	-1.1332973	-0.3753246
20	C C12	-1.4011137	-2.1362181	-1.6124187
21	O O1	-0.2530060	-2.4438418	-1.8737535
22	O O2	-2.4635381	-2.5336285	-2.3607591
23	C C13	-2.1367419	-3.3489422	-3.4935561
24	H H7	-1.6065193	-4.2521592	-3.1792809
25	H H11	-1.5049799	-2.7981740	-4.1966114
26	H H12	-3.0903901	-3.6047972	-3.9573000
27	H H13	-0.9306797	2.0551654	2.3645298
28	H H2	-0.9651543	-0.0097442	3.7598570
29	H H14	0.4028861	-0.7191062	2.7800860

non-fluoro-VCPR TS trans (TS5a)

Spartan'10: -653.972598, iv = i236, S² = 0.7146

Gaussian'09: B3LYP/6-31G*, G = -653.976701, iv = i246, S² = 0.73

Gaussian'09: M05-2X/6-31+G*, G = -653.90781, iv = i262, S² = 0.84

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C	-0.8222470	3.0250060	-0.4539541
2	C C2	-1.9052459	2.2106773	-0.3804376
3	C C3	-1.7973923	0.8903636	0.1578220
4	C C4	0.5337323	2.4619301	-0.0897511
5	C C5	0.6885928	1.0683410	-0.6550086
6	H H	-0.9020935	4.0478346	-0.8109030

7	H	H7	-2.8638439	2.5116103	-0.7984342
8	H	H8	-1.1422527	0.6749249	0.9926968
9	H	H12	0.2525740	0.9082878	-1.6370826
10	C	C1	1.6275974	0.0969890	-0.1977950
11	C	C6	3.4438317	-1.9011993	0.6552119
12	C	C7	1.7957586	-1.1120289	-0.9276113
13	C	C8	2.4099294	0.2652341	0.9762530
14	C	C9	3.2978055	-0.7199932	1.3906673
15	C	C10	2.6850935	-2.0892635	-0.5080156
16	H	H2	1.2071244	-1.2629430	-1.8294584
17	H	H6	2.3250788	1.1801860	1.5546033
18	H	H5	3.8876218	-0.5662147	2.2907224
19	H	H3	2.7948555	-3.0029020	-1.0863701
20	H	H4	4.1438640	-2.6655275	0.9811905
21	C	C11	-2.7745767	-0.1316268	-0.2028367
22	O	O1	-3.6664012	-0.0019144	-1.0287858
23	O	O2	-2.5783681	-1.2815095	0.5006099
24	C	C12	-3.4934341	-2.3395480	0.1952483
25	H	H1	-4.5241878	-2.0317324	0.3947253
26	H	H9	-3.2103695	-3.1704373	0.8431085
27	H	H10	-3.4145251	-2.6308234	-0.8566405
28	H	H11	1.3311852	3.1187271	-0.4745862
29	H	H13	0.6702929	2.4475518	1.0048117

non-fluoro-VCPR TS cis (TS5b)

Spartan'10:
G = -654.971681,
iv = i237,
S^2 = 0.7337

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
-----			-----	-----	-----
1	C	C	0.2453010	2.5048609	1.2953703
2	C	C2	-0.8039811	1.7101068	1.6249380
3	C	C3	-0.6682026	0.3122649	1.8687047
4	C	C4	1.6121357	1.9196713	0.9916982
5	C	C5	1.5785997	0.5091379	0.4474431
6	H	H	0.1262525	3.5838445	1.2259920
7	H	H7	-1.8111301	2.1230173	1.6485146
8	H	H8	0.1915083	-0.0898749	2.3880552
9	C	C11	-1.8097139	-0.5797378	1.6968693
10	O	O1	-2.9124260	-0.2548200	1.2832605
11	O	O2	-1.5012132	-1.8571654	2.0611001
12	C	C12	-2.5659716	-2.8020317	1.9057740
13	H	H1	-3.4406680	-2.5021625	2.4904006
14	H	H9	-2.1715884	-3.7530990	2.2671430
15	H	H10	-2.8605324	-2.8857106	0.8549572
16	H	H11	2.1336028	2.5856755	0.2877626
17	H	H13	2.2259734	1.9238677	1.9062310
18	H	H16	2.0380922	-0.2751250	1.0425867
19	C	C1	1.2934012	0.1999010	-0.9135336
20	C	C6	0.6974007	-0.4795327	-3.5935287
21	C	C7	0.8119491	1.1739275	-1.8285683

22	C	C8	1.4690232	-1.1260625	-1.3953192
23	C	C9	1.1765396	-1.4563796	-2.7094170
24	C	C10	0.5172298	0.8326852	-3.1429608
25	H	H2	0.6605875	2.1940342	-1.4909004
26	H	H6	1.8339548	-1.8874860	-0.7099350
27	H	H5	1.3199579	-2.4769201	-3.0548471
28	H	H3	0.1450793	1.5932011	-3.8244866
29	H	H4	0.4688384	-0.7400881	-4.6233044

non fluoro VCP- [3,3] TS (S-TS13)

Spartan'10 G = -653.971614, iv = i403

Gaussian'09: B3LYP/6-31G*, -653.973922, iv = i403

Gaussian'09: M06-2X/6-31G*, -653.686835, iv = i400

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C1	-0.0894029	-0.6486226	0.8616396
2	H H3	-0.2343972	-1.7199948	0.7606184
3	C C2	1.2368519	-0.2540877	1.3416020
4	C C5	1.2386251	-0.1502183	-1.6576682
5	H H7	1.3283122	0.7889579	-2.1995328
6	C C6	-0.0737839	-0.5112904	-1.2033351
7	H H6	-0.3526574	-1.5564982	-1.2871950
8	C C7	1.3398635	0.9153519	2.1770254
9	H H4	2.3328995	1.2425020	2.4775117
10	C C8	0.2341933	1.6054176	2.5757404
11	H H9	0.3352882	2.4889856	3.1999974
12	C C9	-1.0757048	1.1624901	2.1900805
13	H H11	-1.9457203	1.6985261	2.5607054
14	C C10	-1.2329787	0.0613238	1.4049207
15	H H12	-2.2246786	-0.2981886	1.1479309
16	C C3	2.3703942	-0.8199918	-1.2934753
17	C C4	2.3739013	-0.8979018	0.8956232
18	C C11	2.3917636	-1.8913224	-0.2310380
19	H H2	3.3360345	-0.4478167	-1.6272447
20	H H10	3.3402224	-0.5319360	1.2370583
21	C C12	-1.1691115	0.4082697	-1.6053860
22	O O1	-1.0412943	1.5755153	-1.9183351
23	O O2	-2.3775113	-0.2147373	-1.5535430
24	C C13	-3.5017889	0.6153777	-1.8776802
25	H H1	-3.4106571	1.0103859	-2.8931257
26	H H5	-3.5750941	1.4536613	-1.1791992
27	H H8	-4.3774856	-0.0300456	-1.7958804
28	H H13	3.3004002	-2.4970704	-0.2515753
29	H H14	1.5235165	-2.5570425	-0.2562403

piperonyl cis SM (48)

Spartan'10: G = -1041.02078, iv = none

Gaussian'09: B3LYP/6-31G* G = -1041.028189, iv = none

Gaussian'09: M06-2X/6-31G* G = -1040.629122, iv = none

Cartesian Coordinates (Angstroms)				
Atom		X	Y	Z
-----		-----	-----	-----
1 C	C1	3.0423844	-0.2086799	0.8498853
2 C	C2	1.9712958	0.6511022	1.3910393
3 C	C3	1.8273286	-0.9333291	1.3301227
4 H	H6	1.9311472	-1.4268921	2.2931801
5 C	C10	0.9105989	-1.5575832	0.3680707
6 H	H11	0.8299722	-1.1099408	-0.6198009
7 C	C11	0.1704137	-2.6453405	0.6293754
8 H	H12	0.1962986	-3.1500943	1.5910290
9 C	C12	-0.7183097	-3.2114163	-0.4070501
10 O	O1	-0.8667601	-2.7810948	-1.5347917
11 O	O2	-1.3693752	-4.3033018	0.0663863
12 C	C13	-2.2558576	-4.9350251	-0.8680243
13 H	H5	-3.0221314	-4.2329708	-1.2081799
14 H	H13	-2.7091715	-5.7665514	-0.3271395
15 H	H14	-1.7017856	-5.2994578	-1.7376918
16 F	F1	3.3167039	-0.2109170	-0.4764377
17 F	F2	4.1926516	-0.3416594	1.5506246
18 C	C4	1.1090415	1.5624446	0.5757094
19 C	C5	0.8036928	3.1156355	-1.2954926
20 C	C6	-0.9956292	2.6403948	0.2548302
21 C	C7	-0.4946950	3.2982780	-0.8682452
22 C	C9	1.6034720	2.2303373	-0.5494306
23 H	H1	1.1902327	3.6322954	-2.1670758
24 H	H4	2.6255347	2.0574505	-0.8640583
25 C	C8	-0.2261551	1.7713216	0.9962538
26 H	H2	2.1680653	0.9832609	2.4097456
27 H	H3	-0.6311615	1.2628101	1.8648840
28 O	O3	-2.2980178	3.0223465	0.4704360
29 O	O4	-1.4650229	4.1142322	-1.3960229
30 C	C14	-2.6615555	3.8075867	-0.6710824
31 H	H7	-3.1330517	4.7362777	-0.3381130
32 H	H10	-3.3401538	3.2284802	-1.3129356

piperonyl [3,3]-TS - actual product (TS6a)

Spartan'10: G = -1040.98573, iv = i345

Gaussian'09: B3LYP/6-31G* G = -1040.990095, iv = i346

Gaussian'09: M06-2X/6-31G* G = -1040.586048, iv = i403

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	0.0299913	-0.9765097	0.5447855
2	H H3	-0.0919916	-2.0411956	0.4137142
3	C C2	1.3614143	-0.5751782	1.0108108
4	C C5	1.3636871	-0.5111860	-2.0543037
5	H H7	1.4537369	0.4091006	-2.6287065
6	C C6	0.0517463	-0.8483121	-1.5978248
7	H H6	-0.2395078	-1.8891689	-1.6318160
8	C C7	1.4922535	0.5993397	1.8477715
9	H H4	2.4728296	0.9436762	2.1581912
10	C C8	0.3628135	1.2572276	2.2002409
11	C C9	-0.9392342	0.8221317	1.8038003
12	C C10	-1.1381880	-0.2826499	1.0474906
13	H H12	-2.1309181	-0.6337514	0.7940555
14	C C3	2.5066100	-1.1683158	-1.7020673
15	C C4	2.5020439	-1.2262617	0.5869547
16	C C11	2.5903161	-2.1494753	-0.5812988
17	H H2	3.4711995	-0.8224478	-2.0616157
18	H H10	3.4706018	-0.8816310	0.9385686
19	C C12	-1.0242132	0.1017440	-1.9670565
20	O O1	-0.8665404	1.2683970	-2.2727871
21	O O2	-2.2473210	-0.4856953	-1.8957493
22	C C13	-3.3538526	0.3761447	-2.2020706
23	H H1	-3.2688036	0.7645485	-3.2204452
24	H H5	-3.3906132	1.2179722	-1.5049668
25	H H8	-4.2456265	-0.2439745	-2.1027276
26	F F1	1.6195434	-3.1315895	-0.6096091
27	F F2	3.8003624	-2.7946598	-0.5875743
28	O O3	-1.8708063	1.6633345	2.3447234
29	O O4	0.2406542	2.3885294	2.9577602
30	C C14	-1.1582213	2.6450504	3.1015459
31	H H9	-1.3866334	3.6423907	2.7120647
32	H H13	-1.4373328	2.5624154	4.1581412

piperonyl [3,3] -TS - alternative regioisomer (TS6b)

Spartan'10: G = -1040.97722

iv = i380

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	0.2385885	-0.7298865	0.7224743
2	H H3	0.0276832	-1.7842292	0.6037600
3	C C2	1.5951995	-0.4027051	1.2177965
4	C C5	1.4721330	-0.1108453	-1.8181119
5	H H7	1.5045379	0.8562664	-2.3158420
6	C C6	0.1974816	-0.5696510	-1.3534490
7	H H6	0.0086455	-1.6282209	-1.4642294
8	C C7	1.7716717	0.6741291	2.1666199
9	H H4	2.7859233	0.9105927	2.4746075
10	C C8	0.7251018	1.4116844	2.6504553
11	H H9	0.8673343	2.2246265	3.3541622
12	C C9	-0.5691163	1.0800378	2.1831251
13	C C10	-0.7933501	0.0582918	1.3159113
14	C C3	2.6474765	-0.7549716	-1.5599684
15	C C4	2.7220531	-1.0155180	0.7105452
16	C C11	2.7866601	-1.8315684	-0.5349616
17	H H2	3.5910266	-0.3508489	-1.9139038
18	H H10	3.6972904	-0.7160370	1.0845140
19	C C12	-0.9732522	0.2802463	-1.6932325
20	O O1	-0.9832406	1.4969908	-1.6931776
21	O O2	-2.0514151	-0.4793664	-1.9984359
22	C C13	-3.2456076	0.2469918	-2.3140927
23	H H1	-3.0876808	0.8904759	-3.1847093
24	H H5	-3.5544741	0.8660227	-1.4670107
25	H H8	-4.0017662	-0.5095511	-2.5281664
26	F F1	1.8295525	-2.8240916	-0.6069984
27	F F2	4.0040881	-2.4515217	-0.6373763
28	O O3	-2.1500850	-0.1133524	1.1274261
29	O O4	-1.7631087	1.6229029	2.6040112
30	C C14	-2.7287256	1.0660126	1.7046521
31	H H12	-2.9406554	1.7919193	0.9059492
32	H H14	-3.6299698	0.7951741	2.2576566

Isodesmic Compounds (Energies can be found in Table S16-S19)

Ethane

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	0.0000001	0.0000000	0.7637754
2	H H2	1.0121266	-0.0000001	1.1565569
3	H H3	-0.5060633	-0.8765272	1.1565570
4	H H4	-0.5060631	0.8765274	1.1565570
5	C C2	-0.0000001	0.0000000	-0.7637754
6	H H1	0.5060631	-0.8765274	-1.1565570
7	H H5	0.5060633	0.8765272	-1.1565570
8	H H6	-1.0121266	0.0000001	-1.1565569

Ethene

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	0.0000000	0.0000000	0.6585346
2	H H2	0.0000000	0.9144843	1.2256492
3	H H3	0.0000000	-0.9144843	1.2256492
4	C C2	0.0000000	0.0000000	-0.6585346
5	H H1	0.0000000	-0.9144843	-1.2256492
6	H H4	0.0000000	0.9144843	-1.2256492

Benzene

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	H H1	0.0000000	0.0000000	-2.4836029
2	C C1	0.0000000	-0.0000001	-1.3965320
3	C C4	0.0000000	-0.0000001	1.3965320
4	C C2	0.0000000	-1.2095560	-0.6982739
5	C C6	0.0000000	1.2095560	-0.6982740
6	C C5	0.0000000	1.2095560	0.6982740
7	C C3	0.0000000	-1.2095560	0.6982739
8	H H2	0.0000000	-2.1508686	-1.2419479
9	H H6	0.0000000	2.1508686	-1.2419480
10	H H5	0.0000000	2.1508686	1.2419480
11	H H3	0.0000000	-2.1508686	1.2419480
12	H H4	0.0000000	-0.0000001	2.4836029

Benzene - reduced

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	H H1	1.0881541	-0.5985062	-2.1761678
2	C C1	0.6434959	-0.2310204	-1.2671432
3	C C3	0.4539005	1.3985299	0.5292146
4	C C5	-0.6486740	-0.7877853	0.8245360
5	C C4	-0.3680277	0.6386557	1.2368443
6	C C6	-0.5413287	-0.9731704	-0.6936467
7	C C2	1.0859599	0.8801419	-0.6985849
8	H H10	0.0680039	-1.4397351	1.3250990
9	H H7	-0.8121612	1.0069181	2.1458111
10	H H11	-1.4473510	-0.6014106	-1.1733836
11	H H3	1.9051309	1.4317046	-1.1264837
12	H H5	0.6856329	2.4020851	0.8415236
13	H H9	-1.6321903	-1.0961221	1.1650105
14	H H12	-0.4805450	-2.0302851	-0.9326293

Furan

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	O O1	0.0506086	-0.4485978	-1.2845127
2	C C2	1.0978809	-0.0928593	-0.5216394
3	C C3	0.6907284	0.3010616	0.6916180
4	C C4	-0.7447007	0.1773514	0.6782675
5	C C5	-1.0559874	-0.2784870	-0.5416720
6	H H3	2.0606797	-0.1735618	-0.9770217
7	H H5	1.3099502	0.6364801	1.4975195
8	H H7	-1.4269491	0.4006048	1.4720643
9	H H9	-1.9822107	-0.5219919	-1.0146236

Furan - reduced

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	O O1	0.2823937	-0.4458870	-1.3684354
2	C C2	1.2687481	0.0829888	-0.6101449
3	C C3	0.9192139	0.4245706	0.6106088
4	C C4	-0.5396163	0.0842859	0.8071793
5	C C5	-0.9272401	-0.3714167	-0.6179478
6	H H3	2.2210539	0.1535510	-1.0962173
7	H H5	1.5638401	0.8469238	1.3544034
8	H H7	-1.1345112	0.9320998	1.1315137
9	H H8	-0.6786505	-0.7048947	1.5411980
10	H H9	-1.5783534	0.3422369	-1.1071110
11	H H10	-1.3968781	-1.3444585	-0.6450469

thiophene

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	S S1	0.1167444	-0.7253040	-1.5997346
2	C C2	1.2671448	-0.1588718	-0.4449549
3	C C3	0.6707684	0.3240820	0.6597454
4	C C4	-0.7621015	0.2433484	0.5917821
5	C C5	-1.1936835	-0.2975247	-0.5616759
6	H H3	2.3162648	-0.2167911	-0.6518827
7	H H5	1.2070897	0.7252313	1.4987648
8	H H7	-1.4167593	0.5773933	1.3743115
9	H H9	-2.2054677	-0.4715633	-0.8663556

thiophene -reduced

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	S S1	0.2381818	-0.1586916	-1.8476764
2	C C2	1.4343914	0.1554841	-0.5805729
3	C C3	0.9357534	0.2978303	0.6304529
4	C C4	-0.5698240	0.2147878	0.7144893
5	C C5	-1.0420275	-0.4756587	-0.5772318
6	H H3	2.4697948	0.2300008	-0.8513928
7	H H5	1.5396600	0.5097448	1.4940703
8	H H7	-0.9878734	1.2166165	0.7920098
9	H H8	-0.9060149	-0.3384097	1.5853369
10	H H9	-1.9954398	-0.1062750	-0.9266186
11	H H10	-1.1166018	-1.5454293	-0.4328669

piperonyl

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	H H1	-2.4890973	0.0000000	0.7605630
2	C C1	-1.4155844	0.0000000	0.7735268
3	C C4	1.4155844	0.0000000	0.7735268
4	C C2	-0.6905232	0.0000000	-0.3841316
5	C C6	-0.6899151	0.0000000	1.9718652
6	C C5	0.6899151	0.0000000	1.9718652
7	C C3	0.6905232	0.0000000	-0.3841316
8	H H6	-1.2223019	0.0000000	2.9054279
9	H H5	1.2223019	0.0000000	2.9054279
10	H H4	2.4890973	0.0000000	0.7605630
11	O O1	-1.1369414	0.0000000	-1.6665113
12	O O2	1.1369414	0.0000000	-1.6665113
13	C C7	0.0000000	0.0000000	-2.4974534
14	H H3	0.0000000	-0.8891458	-3.1120134
15	H H8	0.0000000	0.8891458	-3.1120134

piperonyl reduced

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	H H1	-2.5329374	0.0000000	0.4013201
2	C C1	-1.4590576	0.0000000	0.4432548
3	C C3	0.7815602	0.0000000	1.7990097
4	C C5	0.7299606	0.0000000	-0.6478620
5	C C4	1.4590576	0.0000000	0.4432548
6	C C6	-0.7299606	0.0000000	-0.6478620
7	C C2	-0.7815602	0.0000000	1.7990097
8	H H6	1.1341868	0.8637486	2.3556278
9	H H7	2.5329374	0.0000000	0.4013201
10	H H3	-1.1341868	-0.8637486	2.3556278
11	H H5	1.1341868	-0.8637486	2.3556278
12	H H4	-1.1341868	0.8637486	2.3556278
13	O O1	1.1332016	0.0000000	-1.9415502
14	O O2	-1.1332016	0.0000000	-1.9415502
15	C C7	0.0000000	0.0000000	-2.7666606
16	H H12	0.0000000	0.8882923	-3.3820978
17	H H13	0.0000000	-0.8882923	-3.3820978

pyrrole

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	-0.4449852	1.0284683	0.3679170
2	H H2	-0.8752591	1.9155106	0.8102523
3	C C2	0.0893702	0.8040222	-0.8825847
4	H H4	0.1681822	1.5338806	-1.6771450
5	N N1	-0.3576710	-0.1471977	1.0761889
6	H H3	-0.6730776	-0.2771132	2.0246473
7	C C3	0.2239280	-1.1194084	0.2961859
8	H H6	0.3804864	-2.1188340	0.6759902
9	C C4	0.5125838	-0.5560907	-0.9280150
10	H H5	0.9764424	-1.0632377	-1.7634369

pyridine

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	H H1	0.0000000	-0.0000007	-2.2824770
2	C C1	0.0000000	-0.0000003	-1.1955420
3	N N1	0.0000000	0.0000004	1.6106501
4	C C2	0.0000000	-1.1985966	-0.4833139
5	C C6	0.0000000	1.1985963	-0.4833146
6	C C5	0.0000000	1.1422376	0.9115526
7	C C3	0.0000000	-1.1422371	0.9115532
8	H H2	0.0000000	-2.1577589	-0.9929579
9	H H6	0.0000000	2.1577583	-0.9929590

10	H	H5	0.0000000	2.0597701	1.4984036
11	H	H3	0.0000000	-2.0597693	1.4984048

oxazole

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
1	N N1	-0.2423485	-1.0732650	-0.6256410
2	C C2	0.9713989	-0.7097296	-0.3615412
3	C C5	-1.0233183	-0.0579885	-0.0804509
4	H H4	1.8940387	-1.2145675	-0.6086099
5	H H10	-2.1019922	-0.0783051	-0.1413901
6	O O1	1.0812771	0.4623778	0.3144037
7	C C1	-0.2161812	0.8710022	0.4885116
8	H H2	-0.3628746	1.8004756	1.0147178

isoxazole

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
1	N N1	-1.3579729	-0.3166155	0.6680020
2	O O1	-0.9688970	-1.0478468	-0.4596005
3	C C1	-0.3749555	0.5260090	0.8839956
4	H H3	-0.4490582	1.2097088	1.7205650
5	C C2	0.2337272	-0.6094549	-0.8719390
6	H H4	0.6405663	-1.1029212	-1.7432137
7	C C3	0.6770494	0.3923385	-0.0660168
8	H H5	1.5995407	0.9487822	-0.1317926

Remaining Species for Computational Prediction

Ph cis SM (1b)

Spartan'10: G = -852.505870, iv = none

Gaussian'09: B3LYP/6-31G*, G = -852.511692, iv = none

Gaussian'09: M06-2X/6-31G*, G = -852.17197, iv = none

		Cartesian Coordinates (Angstroms)		
Atom		X	Y	Z
-----		-----	-----	-----
1 H	H1	-0.2566781	2.1773309	-0.5418559
2 C	C1	0.7326203	2.1016848	-0.0979338
3 C	C4	3.2705797	1.8884782	1.0330952
4 C	C2	0.8683703	1.5838354	1.1975351
5 C	C6	1.8530942	2.5100396	-0.8195723
6 C	C5	3.1260344	2.4054202	-0.2547015
7 C	C3	2.1488322	1.4797692	1.7561690
8 H	H6	1.7326412	2.9064500	-1.8241942
9 H	H5	3.9999792	2.7221862	-0.8173662
10 H	H3	2.2673570	1.0735024	2.7558601
11 H	H4	4.2579709	1.8001634	1.4782035
12 C	C7	-0.3508853	1.2086657	1.9816477
13 C	C8	-0.4570777	-0.0224345	2.7885630
14 C	C9	-1.2947057	0.0093460	1.5504614
15 H	H9	-2.3531250	0.1988810	1.7111959
16 F	F1	-1.0722914	0.0238570	3.9930383
17 F	F2	0.5874286	-0.8816675	2.8417710
18 C	C10	-0.9504897	-0.8346112	0.3975477
19 H	H8	0.0925116	-1.1108468	0.2613425
20 C	C11	-1.8431113	-1.2883794	-0.4950921
21 H	H10	-2.9028398	-1.0588657	-0.4270965
22 C	C12	-1.4068747	-2.1361501	-1.6249384
23 O	O1	-0.2668900	-2.4927457	-1.8526699
24 O	O2	-2.4647872	-2.4769771	-2.4025691
25 C	C13	-2.1481186	-3.3039233	-3.5313814
26 H	H7	-1.6796913	-4.2367585	-3.2058806
27 H	H11	-1.4645918	-2.7848208	-4.2092518
28 H	H12	-3.0995277	-3.5034504	-4.0257970
29 H	H13	-0.9257341	2.0420210	2.3838702

Ph [3,3] - TS

Spartan'10: G = -852.464912, iv = i379

Gaussian'09: B3LYP/6-31G*, G = -852.467339, iv = i380

Gaussian'09: M06-2X/6-31G*, G = -852.124968, iv = i450

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1 C	C1	-0.1088780	-0.6432231	0.8863613
2 H	H3	-0.2589437	-1.7075866	0.7739837

3	C	C2	1.2220184	-0.2597465	1.3621125
4	C	C5	1.2048982	-0.1785670	-1.6827749
5	H	H7	1.2844671	0.7425621	-2.2565575
6	C	C6	-0.1033175	-0.5238935	-1.2142480
7	H	H6	-0.3862752	-1.5665343	-1.2643495
8	C	C7	1.3310470	0.9008674	2.2111675
9	H	H4	2.3241582	1.2134430	2.5246042
10	C	C8	0.2299951	1.6063232	2.5951180
11	H	H9	0.3384265	2.4867706	3.2225007
12	C	C9	-1.0815962	1.1903990	2.1893254
13	H	H11	-1.9465638	1.7409931	2.5492119
14	C	C10	-1.2449905	0.0914736	1.4014086
15	H	H12	-2.2377005	-0.2546742	1.1316479
16	C	C3	2.3539553	-0.8303083	-1.3422934
17	C	C4	2.3677107	-0.9013675	0.9378646
18	C	C11	2.4527866	-1.8220421	-0.2319275
19	H	H2	3.3133015	-0.4772245	-1.7088463
20	H	H10	3.3345269	-0.5601096	1.2979552
21	C	C12	-1.1878915	0.4137056	-1.6091269
22	O	O1	-1.0362810	1.5742628	-1.9352174
23	O	O2	-2.4035180	-0.1866668	-1.5458552
24	C	C13	-3.5160485	0.6557767	-1.8841186
25	H	H1	-3.4156713	1.0343754	-2.9050867
26	H	H5	-3.5773554	1.5046847	-1.1970147
27	H	H8	-4.4003348	0.0232509	-1.7948402
28	F	F1	1.4839922	-2.8045753	-0.2568552
29	F	F2	3.6640819	-2.4623688	-0.2541494

furan cis SM (cis-9b)

Spartan'10: G = -850.312391, iv = none

Gaussian'09: B3LYP/6-31G*, G = -850.318011, iv = none

Gaussian'09: M06-2X/6-31G*, G = -849.99051, iv = none

Cartesian Coordinates (Angstroms)

Atom	X	Y	Z

1 C C1	2.4512641	1.3354068	0.2415934
2 C C2	1.3356127	1.7987431	1.0906077
3 C C3	1.6498298	0.2431782	0.8642397
4 H H6	2.1119688	-0.2326259	1.7254883
5 C C10	0.7489355	-0.5847449	0.0548152
6 H H11	0.2835022	-0.1279728	-0.8156985
7 C C11	0.4611098	-1.8668181	0.3233625
8 H H12	0.8845279	-2.3941822	1.1733777
9 C C12	-0.4570930	-2.6247006	-0.5533210
10 O O1	-1.0187351	-2.1938951	-1.5421198
11 O O2	-0.5986966	-3.8979997	-0.1092677
12 C C13	-1.4696957	-4.7237084	-0.8953584
13 H H5	-2.4872360	-4.3224924	-0.8919402
14 H H13	-1.4449165	-5.7075124	-0.4253723
15 H H14	-1.1173309	-4.7811726	-1.9288566
16 F F1	2.3876458	1.5065515	-1.1002996
17 F F2	3.7188171	1.5340913	0.6670521

18	C	C4	0.1324177	2.4429016	0.5472554
19	C	C5	-0.2167458	2.9711565	-0.6638453
20	C	C6	-1.5600181	3.4501561	-0.5266274
21	C	C7	-1.9288519	3.1814347	0.7548266
22	H	H1	0.4101903	3.0158134	-1.5416556
23	H	H8	-2.1620993	3.9312406	-1.2845736
24	H	H9	-2.8285917	3.3542179	1.3254461
25	O	O3	-0.9144789	2.5658491	1.4256099
26	H	H2	1.6286680	2.1270843	2.0852611

Furan 3,3 TS

Spartan'10: G = -850.287883, iv = none

Gaussian'09: B3LYP/6-31G*, G = -850.290209, iv = i284

Gaussian'09: M06-2X/6-31G*, G = -849.957473, iv = i332

			Cartesian Coordinates (Angstroms)		
Atom			X	Y	Z
-----			-----	-----	-----
1	C	C1	-0.0686022	-0.6391635	1.1400999
2	H	H3	-0.3649563	-1.6315030	0.8437269
3	C	C2	1.2811173	-0.3378544	1.5213062
4	C	C5	1.1576922	0.3153033	-1.4749842
5	H	H7	1.1552839	1.3253536	-1.8803005
6	C	C6	-0.0969354	-0.2147826	-1.0919058
7	H	H6	-0.2642143	-1.2768469	-1.1819185
8	C	C3	2.3686760	-0.2873355	-1.2439468
9	C	C4	2.4762418	-0.7290840	0.9905851
10	C	C11	2.5722832	-1.4377316	-0.3188344
11	H	H2	3.2891460	0.2053055	-1.5429394
12	H	H10	3.4002144	-0.3149572	1.3784504
13	C	C12	-1.2884862	0.6414637	-1.2503270
14	O	O1	-1.2818295	1.8382432	-1.4710164
15	O	O2	-2.4318212	-0.0765206	-1.0850122
16	C	C13	-3.6464005	0.6748159	-1.2190799
17	H	H1	-3.7181560	1.1183212	-2.2162060
18	H	H5	-3.6912395	1.4756892	-0.4752773
19	H	H8	-4.4538401	-0.0415801	-1.0609347
20	F	F1	1.6519208	-2.4545275	-0.4594124
21	F	F2	3.8126397	-1.9929923	-0.4799666
22	O	O3	1.2640133	0.6728156	2.4716370
23	C	C8	-0.0472362	0.9682551	2.7083964
24	H	H12	-0.2145705	1.7366318	3.4495822
25	C	C7	-0.8906130	0.2167166	1.9638239
26	H	H11	-1.9703284	0.2459645	1.9844542

cis 2-thiophene (cis-9d)

Spartan'10: G = -1173.29413, iv = none
Gaussian'09: B3LYP/6-31G*, G = -1173.266174, iv = none
Gaussian'09: M06-2X/6-31G*, G = -1172.963766, iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1 C	C1	2.5255454	1.2442007	0.3046356
2 C	C2	1.4092065	1.7127642	1.1546039
3 C	C3	1.7042303	0.1577513	0.9110483
4 H	H6	2.1492153	-0.3384332	1.7698751
5 C	C10	0.7967803	-0.6445570	0.0819703
6 H	H11	0.4006088	-0.1915052	-0.8237508
7 C	C11	0.4227832	-1.8986507	0.3752741
8 H	H12	0.7706948	-2.4181631	1.2634495
9 C	C12	-0.4986782	-2.6301292	-0.5203969
10 O	O1	-0.9591428	-2.2123635	-1.5654584
11 O	O2	-0.7784609	-3.8584840	-0.0190998
12 C	C13	-1.6709491	-4.6513349	-0.8149407
13 H	H5	-2.6213165	-4.1310089	-0.9613722
14 H	H13	-1.8205664	-5.5759300	-0.2562606
15 H	H14	-1.2297810	-4.8612060	-1.7934949
16 F	F1	2.4811110	1.4238483	-1.0366860
17 F	F2	3.7919029	1.4207600	0.7448429
18 C	C4	0.1974389	2.3794114	0.6317526
19 C	C5	-0.0206193	2.9993977	-0.5735478
20 C	C6	-1.3376590	3.5345359	-0.7029058
21 C	C7	-2.1103877	3.3194067	0.4031767
22 H	H1	0.7391033	3.0735412	-1.3415374
23 H	H8	-1.6890187	4.0596242	-1.5843589
24 H	H9	-3.1355766	3.6182392	0.5758638
25 S	S1	-1.2434068	2.4495722	1.6278462
26 H	H2	1.7269422	2.0187127	2.1494713

cis 2-thiophene TS

Spartan'10: G = -1173.26802, iv = i300
Gaussian'09: B3LYP/6-31G*, G = -1173.27068, iv = i292
Gaussian'09: M06-2X/6-31G*, G = -1172.930053, iv = i355

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1 C	C1	0.0363919	-0.6432743	1.1516885
2 H	H3	-0.1761859	-1.6591940	0.8567293
3 C	C2	1.3874465	-0.2999837	1.5137127
4 C	C5	1.1733536	0.2907682	-1.4934262
5 H	H7	1.1752585	1.2953169	-1.9124989
6 C	C6	-0.0790655	-0.2116921	-1.0622572
7 H	H6	-0.2724851	-1.2692479	-1.1547817

8	C	C3	2.3786214	-0.3339823	-1.3002843
9	C	C4	2.5468282	-0.7424851	0.9329581
10	C	C11	2.5890941	-1.4767566	-0.3677304
11	H	H2	3.2976792	0.1349339	-1.6388706
12	H	H10	3.5118299	-0.3750983	1.2683835
13	C	C12	-1.2579048	0.6675101	-1.2124209
14	O	O1	-1.2307474	1.8606375	-1.4478607
15	O	O2	-2.4125233	-0.0273033	-1.0305440
16	C	C13	-3.6139604	0.7468960	-1.1609657
17	H	H1	-3.6960384	1.1636488	-2.1688630
18	H	H5	-3.6249968	1.5685421	-0.4391052
19	H	H8	-4.4331588	0.0529329	-0.9673123
20	F	F1	1.6536572	-2.4833370	-0.4711193
21	F	F2	3.8170567	-2.0516754	-0.5559142
22	S	S2	1.3849854	1.0245650	2.7059169
23	C	C8	-0.3631965	1.0161350	2.7583118
24	H	H12	-0.8724305	1.6934226	3.4324691
25	C	C7	-0.9252665	0.1083666	1.9231062
26	H	H11	-1.9942427	-0.0496457	1.8406781

alpha Me cis SM (*cis*-10i)

Spartan'10: G = -891.794682, iv = none

Gaussian'09: B3LYP/6-31G*, G = -891.802283, iv = none

Gaussian'09: M06-2X/6-31G*, G = -891.443545, iv = none

Cartesian Coordinates (Angstroms)

Atom	X	Y	Z

1 H H1	1.0605970	2.2101135	0.9795402
2 C C1	1.4318218	1.3411226	1.5172655
3 C C4	2.3865025	-0.8862409	2.8887981
4 C C2	0.5185848	0.4461580	2.0944014
5 C C6	2.8045038	1.1268614	1.6258776
6 C C5	3.2865377	0.0103681	2.3130865
7 C C3	1.0111170	-0.6707822	2.7826651
8 H H6	3.4977073	1.8308283	1.1731001
9 H H5	4.3566476	-0.1582550	2.3986995
10 H H3	0.3185399	-1.3740829	3.2324462
11 H H4	2.7523580	-1.7575112	3.4255959
12 C C7	-0.9468513	0.7418941	2.0124806
13 C C8	-2.0024763	-0.2830311	1.8928866
14 C C9	-1.7848029	0.5524054	0.6736209
15 H H9	-2.5331798	1.3236271	0.5234112
16 F F1	-3.1525956	-0.1268753	2.5902310
17 F F2	-1.6724700	-1.5967678	1.8516777
18 C C10	-1.1539931	-0.0304295	-0.5213977
19 H H8	-0.4580820	-0.8435968	-0.3434813
20 C C11	-1.3639456	0.3454763	-1.7988830
21 C C12	-0.6574363	-0.3600092	-2.9068867
22 O O1	-0.8167572	-0.0880527	-4.0826858
23 O O2	0.1855185	-1.3350438	-2.4887181
24 C C13	0.8788792	-2.0320139	-3.5329248
25 H H7	1.5263014	-2.7480706	-3.0254650

26	H	H11	1.4701051	-1.3364892	-4.1346099
27	H	H12	0.1715048	-2.5502677	-4.1865157
28	H	H13	-1.2694853	1.6294198	2.5548831
29	C	C14	-2.2831145	1.4423181	-2.2707235
30	H	H2	-1.7367054	2.1587340	-2.8934231
31	H	H10	-2.7448759	1.9845092	-1.4427544
32	H	H14	-3.0804549	1.0336839	-2.9021983

alpha Me [3,3] - TS

Spartan'10: G = -891.746085, iv = i364

Gaussian'09: B3LYP/6-31G*, G = -891.748315, iv = i353

Gaussian'09: M06-2X/6-31G*, G = -891.387733, iv = i436

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z

1	C C1	-0.0100016	-0.5463738	1.0292330
2	H H3	-0.0273706	-1.6176378	0.8919358
3	C C2	1.2581965	0.0056784	1.4941897
4	C C5	1.2777056	-0.1356812	-1.5540668
5	H H7	1.3712153	0.7638974	-2.1600692
6	C C6	-0.0625493	-0.4626455	-1.1428007
7	C C7	1.2247206	1.2095288	2.2856223
8	H H4	2.1708031	1.6498380	2.5907106
9	C C8	0.0431027	1.7927875	2.6374625
10	H H9	0.0404109	2.7063545	3.2256452
11	C C9	-1.2045022	1.2028254	2.2521706
12	H H11	-2.1324069	1.6587688	2.5871540
13	C C10	-1.2272576	0.0556325	1.5131135
14	H H12	-2.1709460	-0.4165290	1.2572406
15	C C3	2.4490914	-0.7115405	-1.1506657
16	C C4	2.4742416	-0.5391727	1.1292349
17	C C11	2.6692876	-1.5584310	0.0591998
18	H H2	3.3809668	-0.3191597	-1.5489410
19	H H10	3.3945289	-0.0738765	1.4714696
20	C C12	-1.0180917	0.6571089	-1.4359339
21	O O1	-0.7001388	1.8127592	-1.6418218
22	O O2	-2.3096672	0.2444313	-1.4290949
23	C C13	-3.2803384	1.2756347	-1.6612080
24	H H1	-3.1226569	1.7401591	-2.6382425
25	H H5	-3.2131662	2.0462063	-0.8880948
26	H H8	-4.2502372	0.7774966	-1.6258174
27	F F1	1.8593515	-2.6707964	0.1829681
28	F F2	3.9592687	-2.0250141	0.0765105
29	C C14	-0.6043500	-1.8668552	-1.3905727
30	H H6	0.1631754	-2.6169170	-1.2093664
31	H H13	-0.9247594	-1.9509253	-2.4368304
32	H H14	-1.4776266	-2.0875518	-0.7703345

Alpha-Me furan trans intermediate (25a)

Spartan'10: G = -889.603013, iv = none

Gaussian'09: B3LYP/6-31G*, G = -889.610117, iv = none

Gaussian'09: M05-2X/6-31+G*, G = -889.546801, iv = none

		Cartesian Coordinates (Angstroms)		
Atom		X	Y	Z
-----		-----	-----	-----
1 C	C1	1.5534980	1.4511661	-0.8407189
2 C	C2	0.4917211	1.7903833	0.1279921
3 C	C3	0.9244027	0.2753336	-0.1820042
4 H	H3	-0.4628635	2.0583940	-0.3175496
5 H	H6	1.5218784	-0.1559734	0.6148856
6 C	C10	-0.0116118	-0.5872870	-0.9142971
7 H	H11	-0.4795535	-0.1381529	-1.7855085
8 C	C11	-0.3444786	-1.8574102	-0.6079688
9 C	C12	-1.3239442	-2.5939509	-1.4571208
10 O	O1	-1.6466618	-3.7502884	-1.2574843
11 O	O2	-1.8309451	-1.8576180	-2.4768333
12 C	C13	-2.7730240	-2.5429624	-3.3135530
13 H	H5	-2.2981176	-3.3916242	-3.8139591
14 H	H13	-3.1050025	-1.8051376	-4.0450116
15 H	H14	-3.6177249	-2.9086313	-2.7238128
16 F	F1	1.3171784	1.6717582	-2.1548017
17 F	F2	2.8454017	1.7427335	-0.5556694
18 C	C4	0.7592403	2.3888452	1.4405016
19 C	C5	1.8814512	2.7972985	2.1068452
20 C	C6	1.4445417	3.2683479	3.3872879
21 C	C7	0.0927241	3.1158777	3.4074928
22 H	H1	2.8913403	2.7738015	1.7262248
23 H	H8	2.0596539	3.6732968	4.1787556
24 H	H9	-0.6741849	3.3331767	4.1351185
25 O	O3	-0.3444406	2.5796988	2.2324140
26 C	C8	0.1868351	-2.6638126	0.5478402
27 H	H2	0.9275234	-2.1143936	1.1329438
28 H	H4	0.6441148	-3.5929560	0.1908463
29 H	H7	-0.6289523	-2.9599131	1.2171449

alpha Me Furan Cis (cis-25a)

Spartan'10: G = --889.601018, iv = none

Gaussian'09: B3LYP/6-31G*, G = -889.608862, iv = none

Gaussian'09: M06-2X/6-31G*, G = -889.261077, iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1 C	C1	-0.3974741	-2.6219144	-0.7714089
2 C	C2	-0.7247780	-2.2690318	0.6247589

3	C	C3	-1.1395947	-1.3394771	-0.6178839
4	H	H6	-2.1994387	-1.4005129	-0.8440415
5	C	C10	-0.4706465	-0.0488947	-0.8306487
6	H	H11	0.5991262	-0.0217513	-0.6541930
7	C	C11	-1.0889629	1.0876410	-1.2085464
8	C	C12	-0.2992271	2.3444460	-1.3638573
9	O	O1	-0.7798013	3.4150566	-1.6872710
10	O	O2	1.0223717	2.1864956	-1.1093573
11	C	C13	1.8179072	3.3713603	-1.2452303
12	H	H5	1.7452196	3.7714566	-2.2602172
13	H	H13	2.8408053	3.0620862	-1.0270429
14	H	H14	1.4908954	4.1394187	-0.5386698
15	F	F1	0.8932726	-2.5849295	-1.1823553
16	F	F2	-1.0238371	-3.6754609	-1.3426948
17	C	C8	-2.5694172	1.2172905	-1.4795333
18	H	H2	-2.9498456	0.3755506	-2.0671873
19	H	H4	-2.7689453	2.1413464	-2.0245422
20	H	H7	-3.1435270	1.2566239	-0.5445140
21	H	H12	-1.5836150	-2.7932609	1.0376843
22	C	C4	0.2948733	-1.8679838	1.6026016
23	C	C5	1.6595919	-1.9238444	1.6504779
24	C	C6	2.0461629	-1.3645208	2.9116015
25	C	C7	0.8917900	-1.0125971	3.5394103
26	O	O3	-0.1860522	-1.3079138	2.7592418
27	H	H8	2.3055975	-2.3206775	0.8820351
28	H	H10	3.0502738	-1.2492973	3.2950736
29	H	H15	0.6672747	-0.5667041	4.4963103

alpha Me Furan VCPR TS

Spartan'10: G = -889.565926, iv = i88, 0.7630

Gaussian'09: B3LYP/6-31G*, G = -889.569816, iv = i85, S^2 = 0.76

Gaussian'09: M05-2X/6-31+G*, G = -889.502352, iv = i56, S^2 = 0.9266

Cartesian Coordinates (Angstroms)

Atom	X	Y	Z

1 C C	-0.4041129	2.5914948	-0.9599034
2 C C2	-1.4497983	1.7333183	-0.9510775
3 C C3	-1.5151473	0.4795265	-0.2387479
4 C C4	0.9435780	2.2099149	-0.4366464
5 C C5	1.2510123	0.7573553	-0.6097426
6 H H	-0.4729379	3.5694436	-1.4267338
7 H H7	-2.3116161	1.9696306	-1.5753268
8 H H12	0.9287033	0.3061349	-1.5389267
9 F F1	1.8954887	2.9697258	-1.1062616
10 F F2	1.0946380	2.5940510	0.9005045
11 C C11	-2.2979979	-0.5701880	-0.9151502
12 O O1	-2.7696087	-0.4709860	-2.0386564
13 O O2	-2.4406324	-1.6860087	-0.1536856
14 C C12	-3.1718374	-2.7532977	-0.7712530
15 H H1	-4.1968192	-2.4421135	-0.9921350
16 H H9	-3.1665562	-3.5696404	-0.0474465
17 H H10	-2.6905039	-3.0619753	-1.7032552
18 C C1	2.1664149	0.0632262	0.1719121

19	C	C6	2.8457301	0.3285411	1.3714154
20	C	C7	3.6296160	-0.8085007	1.6620184
21	C	C8	3.3922828	-1.7109159	0.6550611
22	H	H3	2.7687563	1.2442339	1.9361133
23	H	H5	4.2858374	-0.9543082	2.5087800
24	H	H11	3.7547219	-2.7086143	0.4573138
25	O	O3	2.5168398	-1.2117084	-0.2505679
26	C	C9	-1.1929891	0.3198419	1.2245581
27	H	H2	-0.6549729	-0.6120974	1.4253217
28	H	H4	-2.1297930	0.2662678	1.7999525
29	H	H6	-0.6082963	1.1576479	1.6025651

alpha Me Furan [3,3] TS

Spartan'10: G = -889.572731, iv = i272

Gaussian'09: B3LYP/6-31G*, G = -889.570319, iv = i247

Gaussian'09: M06-2X/6-31G*, G = -889.219479, iv = i329

Cartesian Coordinates (Angstroms)					
Atom		X	Y	Z	

1	C	C1	-0.0507601	-0.4543224	1.0779417
2	C	C2	1.3285473	-0.1922498	1.4254050
3	C	C5	1.2591109	0.6796953	-1.4833306
4	H	H7	1.2276939	1.7135085	-1.8212804
5	C	C6	0.0194505	0.0856812	-1.1461993
6	H	H6	-0.1045372	-0.9757655	-1.2924427
7	C	C3	2.4871096	0.0990027	-1.2918649
8	C	C4	2.5242029	-0.5775166	0.8877604
9	C	C11	2.7170973	-1.1330789	-0.4856225
10	H	H2	3.3934558	0.6452063	-1.5353547
11	H	H10	3.4272686	-0.1629699	1.3237368
12	C	C12	-1.1932294	0.9112987	-1.2931720
13	O	O1	-1.2210239	2.1234481	-1.3997915
14	O	O2	-2.3211897	0.1474670	-1.2620386
15	C	C13	-3.5513839	0.8747359	-1.3868180
16	H	H1	-3.5914586	1.4020560	-2.3439272
17	H	H5	-3.6540328	1.6057142	-0.5796587
18	H	H8	-4.3426300	0.1260135	-1.3300535
19	F	F1	1.8935485	-2.1879088	-0.8149991
20	F	F2	4.0033845	-1.5811108	-0.6317074
21	O	O3	1.3742344	0.8415684	2.3582190
22	C	C8	0.0889164	1.2342896	2.5778535
23	H	H12	-0.0279724	2.0390440	3.2899567
24	C	C7	-0.7988195	0.5208325	1.8549223
25	H	H11	-1.8752294	0.6180992	1.8757905
26	C	C9	-0.6351157	-1.8391381	0.8793952
27	H	H3	0.0482415	-2.5028530	0.3522604
28	H	H4	-1.5800524	-1.7834940	0.3308222
29	H	H9	-0.8448273	-2.2772530	1.8641973

alpha Me thiophene trans INT

Spartan'10: G = -1212.58519, iv = none

Gaussian'09: B3LYP/6-31G*, G = -1212.592277, iv = none

Gaussian'09: M05-2X/6-31+G*, G = -1212.515989, iv = none

Cartesian Coordinates (Angstroms)				
Atom		X	Y	Z
-----		-----	-----	-----
1 C	C1	1.3238346	1.8053593	-1.0873313
2 C	C2	0.3236245	2.0555461	-0.0261839
3 C	C3	0.7947459	0.5774852	-0.4337566
4 H	H3	-0.6629199	2.2910881	-0.4193521
5 H	H6	1.4671961	0.1447690	0.3006432
6 C	C10	-0.1521435	-0.2998764	-1.1306003
7 H	H11	-0.7086025	0.1470115	-1.9516066
8 C	C11	-0.4132408	-1.5938060	-0.8575352
9 C	C12	-1.4436718	-2.2378082	-1.7276760
10 O	O1	-2.0529892	-1.6948496	-2.6300681
11 O	O2	-1.6367371	-3.5367477	-1.3911883
12 C	C13	-2.6140969	-4.2329163	-2.1782058
13 H	H5	-3.5922056	-3.7524431	-2.0896039
14 H	H13	-2.6456048	-5.2463562	-1.7764506
15 H	H14	-2.3212873	-4.2449945	-3.2316104
16 F	F1	0.9666480	2.0709919	-2.3647945
17 F	F2	2.6255702	2.1330297	-0.9051421
18 C	C4	0.6368519	2.6075189	1.3066015
19 C	C5	1.8186201	3.0845746	1.8198117
20 C	C6	1.7098868	3.5215417	3.1739268
21 C	C7	0.4500156	3.3767994	3.6831748
22 H	H1	2.7336715	3.1321452	1.2437964
23 H	H8	2.5379027	3.9365040	3.7385555
24 H	H9	0.0885315	3.6356113	4.6692928
25 S	S1	-0.6328297	2.6926397	2.5135808
26 C	C8	0.2286312	-2.4216599	0.2250870
27 H	H2	0.9683101	-1.8523869	0.7935081
28 H	H4	0.7256047	-3.3028920	-0.1960225
29 H	H7	-0.5233161	-2.7958786	0.9291498

alpha Me thiophene cis INT

Spartan'10: G = -1212.58342, iv = none

Gaussian'09: B3LYP/6-31G*, G = -1212.590736, iv = none

Gaussian'09: M06-2X/6-31G*, G = -1212.235623, iv = none

Cartesian Coordinates (Angstroms)				
Atom		X	Y	Z
-----		-----	-----	-----
1 C	C1	-0.3940924	-2.6141307	-0.8489641
2 C	C2	-0.6969888	-2.3231410	0.5698131
3 C	C3	-1.1912896	-1.3758097	-0.6243956
4 H	H6	-2.2506758	-1.4802514	-0.8338615
5 C	C10	-0.5785213	-0.0523812	-0.8104740

6	H	H11	0.4985106	-0.0069438	-0.6890946
7	C	C11	-1.2258589	1.0922481	-1.1062525
8	C	C12	-0.4554745	2.3600827	-1.2657540
9	O	O1	-0.9745590	3.4315331	-1.5179732
10	O	O2	0.8816684	2.2138075	-1.1053489
11	C	C13	1.6495322	3.4162353	-1.2480852
12	H	H5	1.5244135	3.8375129	-2.2492658
13	H	H13	2.6864147	3.1213705	-1.0834070
14	H	H14	1.3404552	4.1617108	-0.5102149
15	F	F1	0.8754880	-2.5058601	-1.3074883
16	F	F2	-0.9959479	-3.6751708	-1.4339463
17	C	C8	-2.7101438	1.2581473	-1.3035409
18	H	H2	-3.2576160	0.3225437	-1.1691833
19	H	H4	-2.9256928	1.6449311	-2.3055924
20	H	H7	-3.1088181	1.9955476	-0.5985513
21	H	H12	-1.5180544	-2.9178563	0.9655118
22	C	C4	0.3183431	-1.8915918	1.5540113
23	C	C5	1.6851787	-2.0166016	1.5284367
24	C	C6	2.3232695	-1.4802018	2.6874215
25	C	C7	1.4390497	-0.9528049	3.5858528
26	S	S1	-0.1970221	-1.0952734	3.0276960
27	H	H8	2.2159130	-2.4811604	0.7070238
28	H	H10	3.3963745	-1.4948614	2.8431709
29	H	H15	1.6461442	-0.4916305	4.5424558

alpha Me thiophene VCPR TS

Spartan'10: G = -1212.54641, iv = i83, S^2 = 0.7803

Gaussian'09: B3LYP/6-31G*, G = -1212.551391, iv = i86, S^2 = 0.58

Gaussian'09: M05-2X/6-31+G*, G = -1173.189048, iv = i147, S^2 = 0.76

Cartesian Coordinates (Angstroms)					
Atom		X	Y	Z	

1	C C	-0.4286277	2.7001455	-0.9162575	
2	C C2	-1.4696176	1.8359440	-0.9008575	
3	C C3	-1.5298555	0.5868081	-0.1810509	
4	C C4	0.9236504	2.3299843	-0.3973802	
5	C C5	1.2423567	0.8764220	-0.5519030	
6	H H	-0.5044532	3.6750544	-1.3882538	
7	H H7	-2.3326688	2.0647375	-1.5261167	
8	H H12	0.9100625	0.4291747	-1.4816979	
9	F F1	1.8675989	3.0832268	-1.0833248	
10	F F2	1.0843598	2.7255446	0.9334470	
11	C C11	-2.3012032	-0.4732423	-0.8537228	
12	O O1	-2.7566482	-0.3912181	-1.9855045	
13	O O2	-2.4475340	-1.5807004	-0.0805073	
14	C C12	-3.1677261	-2.6588455	-0.6922473	
15	H H1	-4.1896634	-2.3530341	-0.9335474	
16	H H9	-3.1724031	-3.4633918	0.0441862	
17	H H10	-2.6722572	-2.9815926	-1.6123564	
18	C C1	2.1479112	0.1502133	0.2188714	
19	C C6	2.5984777	-1.1573475	-0.0604199	
20	C C7	3.5003476	-1.6637240	0.8898238	
21	C C8	3.7575592	-0.7702064	1.9093507	

22	H	H3	2.2685549	-1.6969482	-0.9416766
23	H	H5	3.9518922	-2.6480383	0.8325259
24	H	H11	4.4127766	-0.9097496	2.7593308
25	S	S1	2.8858342	0.7148177	1.7306140
26	C	C9	-1.1945736	0.4309267	1.2788112
27	H	H2	-0.6295144	-0.4869083	1.4728387
28	H	H4	-2.1251082	0.3495401	1.8604097
29	H	H6	-0.6295277	1.2824074	1.6566148

alpha Me thiophene 3,3 TS

Spartan'10: G = -1212.54839, iv = i263

Gaussian'09: B3LYP/6-31G*, G = -1173.27068, iv = 292

Gaussian'09: M06-2X/6-31G*, G = -1172.930053, iv = i335

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C1	0.1457678	-0.4810391	1.3189222
2	H H3	0.1130342	-1.5256464	1.0528317
3	C C2	1.4068513	0.1148581	1.6544117
4	C C5	1.1974107	0.2862417	-1.4050061
5	H H7	1.1652146	1.2606365	-1.8906403
6	C C6	-0.0702641	-0.2276530	-1.0040764
7	C C3	2.4511871	-0.1973151	-1.1229512
8	C C4	2.6415093	-0.2034674	1.1489605
9	C C11	2.8414681	-1.1165508	-0.0159610
10	H H2	3.3075510	0.3408363	-1.5206281
11	H H10	3.5263145	0.3521231	1.4426269
12	C C12	-1.1599725	0.7907009	-1.0778121
13	O O1	-0.9961082	1.9873594	-1.2296738
14	O O2	-2.3904437	0.2366229	-0.9236220
15	C C13	-3.4816825	1.1680769	-0.9479221
16	H H1	-3.5329320	1.6767006	-1.9144631
17	H H5	-3.3642256	1.9185182	-0.1616101
18	H H8	-4.3799083	0.5719050	-0.7817891
19	F F1	2.1428866	-2.2998007	0.0822550
20	F F2	4.1653004	-1.4563063	-0.1251042
21	S S1	1.1568384	1.5248199	2.7115962
22	C C8	-0.5628487	1.2204223	2.7615546
23	H H12	-1.1944145	1.8597683	3.3654718
24	C C7	-0.9435487	0.1521811	2.0143278
25	H H11	-1.9682185	-0.1939008	1.9442078
26	C C9	-0.4705883	-1.6687664	-1.2745490
27	H H4	0.3836005	-2.3380882	-1.1976401
28	H H6	-0.8652987	-1.7402301	-2.2972913
29	H H9	-1.2644803	-2.0130071	-0.6064268

Weinreb cis E INT (29a)

Spartan'10: G = -947.065987, iv = none

Gaussian'09: B3LYP/6-31G*, G = -947.073972, iv = none

Gaussian'09: M06-2X/6-31G*, G = -946.691616, iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	-2.3342695	-1.5454125	-1.3511858
2	C C2	-2.7447096	-0.4462149	-0.4551097
3	C C3	-1.4273573	-0.3577660	-1.3337565
4	H H6	-1.5152749	0.2988081	-2.1960640
5	C C4	-2.6988380	-0.5252874	1.0397700
6	C C5	-2.6905013	-0.5938805	3.8467547
7	C C6	-2.2668534	0.5848170	1.7792730
8	C C7	-3.1259504	-1.6709614	1.7235669
9	C C8	-3.1207600	-1.7036023	3.1190950
10	C C9	-2.2629843	0.5521683	3.1726594
11	H H4	-1.9246668	1.4736453	1.2554516
12	H H7	-3.4552808	-2.5399206	1.1631142
13	H H8	-3.4517391	-2.6000725	3.6365206
14	H H9	-1.9215411	1.4191895	3.7317247
15	H H10	-2.6846636	-0.6219162	4.9330309
16	C C10	-0.0989138	-0.4383716	-0.7096473
17	H H11	0.0410455	-1.1351713	0.1130367
18	C C11	0.9532007	0.2940602	-1.1057679
19	H H12	0.8719660	1.0115473	-1.9139824
20	C C12	2.2567329	0.1334208	-0.4136725
21	O O1	2.4230121	-0.6104655	0.5490410
22	N N1	3.3366603	0.8264438	-0.9512772
23	C C13	4.5433780	1.0426835	-0.1707411
24	H H5	4.6505058	0.1942966	0.5044075
25	H H13	4.4740857	1.9710549	0.4103888
26	H H14	5.4103153	1.0977487	-0.8358071
27	F F1	-1.8898330	-2.7129702	-0.8300171
28	F F2	-3.0590584	-1.7918138	-2.4682801
29	O O2	3.0426753	1.9122541	-1.8046925
30	C C14	3.4748363	1.6169464	-3.1354056
31	H H2	3.2608473	2.5197991	-3.7136277
32	H H1	2.9239356	0.7653288	-3.5521093
33	H H15	4.5506512	1.4065694	-3.1695807
34	H H16	-3.5406528	0.1730448	-0.8671103

Weinreb [3,3] TS

Spartan'10: G = -947.017003, iv = i374

Gaussian'09: B3LYP/6-31G*, G = -947.020971, iv = i276

Gaussian'09: M06-2X/6-31G*, G = -946.63488, iv = i451

Cartesian Coordinates (Angstroms)				
Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	-0.2914116	-0.5301221	1.3258970
2	H H3	-0.1490741	-1.5987044	1.2410897
3	C C2	-1.5992406	-0.1288100	1.8498740
4	C C5	-1.7065614	-0.0875395	-1.1823929
5	H H7	-1.7936212	0.8376777	-1.7473401
6	C C6	-0.3866717	-0.4669373	-0.7768860
7	H H6	-0.1859351	-1.5272410	-0.8212505
8	C C7	-1.6684294	1.0558448	2.6685345
9	H H4	-2.6462624	1.3782920	3.0177572
10	C C8	-0.5526258	1.7769196	2.9728796
11	H H9	-0.6332733	2.6798318	3.5717877
12	C C9	0.7381171	1.3485167	2.5196794
13	H H11	1.6188502	1.9132518	2.8122116
14	C C10	0.8642911	0.2210823	1.7668847
15	H H12	1.8503260	-0.1294780	1.4762307
16	C C3	-2.8492911	-0.7208373	-0.7866194
17	C C4	-2.7675325	-0.7699790	1.4889247
18	C C11	-2.9136347	-1.7018603	0.3353786
19	H H2	-3.8192515	-0.3540813	-1.1095863
20	H H10	-3.7145119	-0.4114708	1.8831897
21	C C12	0.6929765	0.4679799	-1.2320579
22	O O1	0.4761184	1.6632645	-1.3886650
23	N N1	1.9294753	-0.0828262	-1.5421181
24	F F1	-1.9577050	-2.6994676	0.2803596
25	F F2	-4.1312168	-2.3293136	0.3714625
26	C C13	2.4761775	-1.3675948	-1.1439412
27	H H1	3.2010075	-1.6879700	-1.8983552
28	H H5	1.6857440	-2.1163524	-1.0894241
29	H H8	2.9888294	-1.3077874	-0.1739330
30	O O2	2.9719230	0.8527016	-1.6718440
31	C C14	3.0387716	1.3529058	-3.0114028
32	H H13	3.1756382	0.5367688	-3.7324742
33	H H14	3.9163757	2.0046060	-3.0220940
34	H H15	2.1416286	1.9287295	-3.2517563

CN E cis (cis-10a)

Spartan'10: G = -716.911798, iv = none

Gaussian'09: B3LYP/6-31G*, G = -716.91601, iv = none

Gaussian'09: M06-2X/6-31G*, G = -716.635411, iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1 C	C1	0.8384972	-0.0293373	-2.2221422
2 C	C2	-0.3885136	0.3527766	-1.4965935
3 C	C3	0.0569712	-1.1649306	-1.6406357
4 H	H3	-1.2259717	0.5801881	-2.1550650
5 C	C4	-0.4016202	1.0552264	-0.1737740
6 C	C5	-0.5390172	2.4067366	2.2840982
7 C	C6	-1.3816954	0.7197947	0.7719740
8 C	C7	0.5083578	2.0774201	0.1262152
9 C	C8	0.4386420	2.7474573	1.3492651
10 C	C9	-1.4511456	1.3901265	1.9918145
11 H	H4	-2.0912052	-0.0732301	0.5488670
12 H	H7	1.2735488	2.3463932	-0.5943289
13 H	H8	1.1521606	3.5368782	1.5694348
14 H	H9	-2.2152386	1.1173901	2.7146395
15 H	H10	-0.5905754	2.9289998	3.2354672
16 C	C10	0.5670599	-1.9031929	-0.4780249
17 H	H11	1.2154473	-1.3671086	0.2095548
18 F	F1	0.8806104	0.1048032	-3.5664402
19 F	F2	2.0528279	0.2561481	-1.6955350
20 H	H2	-0.5309570	-1.7369171	-2.3540265
21 C	C11	0.2694682	-3.1931334	-0.2351451
22 H	H1	-0.3753362	-3.7579873	-0.9051597
23 C	C12	0.7710893	-3.8997362	0.8981439
24 N	N1	1.1665959	-4.4947655	1.8173967

CN E [3,3] TS

Spartan'10: G = -716.870471, iv = i381

Gaussian'09: B3LYP/6-31G*, G = -716.871513, iv = i384

Gaussian'09: M06-2X/6-31G*, G = -716.586383, iv = i459

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1 C	C1	-0.8088086	-0.5052546	0.4670589
2 H	H3	-0.9601465	-1.5672415	0.3333548
3 C	C2	0.5041776	-0.1360068	1.0003515
4 C	C5	0.6094299	0.0070984	-2.0576895
5 H	H7	0.7322234	0.9241156	-2.6299300
6 C	C6	-0.7219691	-0.3378939	-1.6323141
7 H	H6	-0.9883166	-1.3847092	-1.7170743
8 C	C7	0.5845518	1.0116801	1.8701791
9 H	H4	1.5646116	1.3115768	2.2327551
10 C	C8	-0.5278186	1.7231151	2.2079213
11 H	H9	-0.4417853	2.5954906	2.8497921

12	C	C9	-1.8226470	1.3286345	1.7312997
13	H	H11	-2.6973987	1.8905458	2.0459019
14	C	C10	-1.9604833	0.2386595	0.9266856
15	H	H12	-2.9446696	-0.0819697	0.5984315
16	C	C3	1.7357562	-0.6589915	-1.6744165
17	C	C4	1.6614246	-0.7759015	0.6076258
18	C	C11	1.7837623	-1.6715874	-0.5788014
19	H	H2	2.7107493	-0.3107918	-2.0015767
20	H	H10	2.6162454	-0.4503849	1.0114748
21	F	F1	0.8069298	-2.6435541	-0.6632285
22	F	F2	2.9879160	-2.3219049	-0.5697096
23	C	C12	-1.7787176	0.5460953	-2.0362881
24	N	N1	-2.6450171	1.2691801	-2.3218035

CN Z INT (*cis*-10h)

Spartan'10: G = -716.911953, iv = none

Gaussian'09: B3LYP/6-31G*, G = -716.916391, iv = none

Gaussian'09: M06-2X/6-31G*, G = -716.637087, iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C1	-1.3052491	0.6534900	-1.7473256
2	C C2	-1.3174749	-0.1515324	-0.5107186
3	C C3	-0.4276179	-0.5571128	-1.7622719
4	H H3	-2.1888862	-0.7992368	-0.4249284
5	C C4	-0.7118527	0.2902570	0.7861344
6	C C5	0.3586852	1.0479699	3.2694727
7	C C6	-0.0334426	-0.6418633	1.5849899
8	C C7	-0.8476052	1.6066244	1.2466254
9	C C8	-0.3145495	1.9816313	2.4812757
10	C C9	0.4975196	-0.2667018	2.8179120
11	H H4	0.0793366	-1.6643518	1.2335346
12	H H7	-1.3672142	2.3390743	0.6376639
13	H H8	-0.4277317	3.0060297	2.8256598
14	H H9	1.0205771	-1.0003674	3.4254199
15	H H10	0.7729671	1.3412882	4.2302219
16	C C10	1.0319841	-0.4074183	-1.7078640
17	H H11	1.4187922	0.4888395	-1.2314107
18	C C11	1.9199131	-1.2914217	-2.2029974
19	H H12	2.9864701	-1.1004944	-2.1261998
20	F F1	-0.7198674	1.8760887	-1.7499297
21	F F2	-2.3991365	0.6706445	-2.5398610
22	H H2	-0.8069124	-1.4069014	-2.3229696
23	C C12	1.5417345	-2.5090008	-2.8455583
24	N N1	1.2395607	-3.5055343	-3.3668747

CN Z [3,3] TS

Spartan'10: G = -716.863331, iv = none

Gaussian'09: B3LYP/6-31G*, G = -716.864276, iv = i384

Gaussian'09: M06-2X/6-31G*, G = -716.578656, iv = i458

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	-0.8423313	-0.3854496	0.4662477
2	H H3	-0.9858849	-1.4242021	0.2074645
3	C C2	0.4608799	-0.0289211	1.0064344
4	C C5	0.6213220	0.2719571	-2.0300150
5	H H7	0.8147920	1.2431589	-2.4844903
6	C C6	-0.7472213	0.0044337	-1.6969464
7	H H8	-1.4126024	0.8586842	-1.8178538
8	C C7	0.5317204	1.0873507	1.9133168
9	H H4	1.5069625	1.3804196	2.2941124
10	C C8	-0.5896368	1.7785552	2.2738744
11	H H9	-0.5117713	2.6244792	2.9512872
12	C C9	-1.8760834	1.3957891	1.7765733
13	H H11	-2.7567043	1.9402548	2.1060845
14	C C10	-1.9991775	0.3320961	0.9280028
15	H H12	-2.9767536	0.0045472	0.5842892
16	C C3	1.7198049	-0.4566810	-1.6635881
17	C C4	1.6261879	-0.6463821	0.5838551
18	C C11	1.7519420	-1.5222970	-0.6186132
19	H H2	2.7069898	-0.1011847	-1.9440974
20	H H10	2.5791735	-0.3257808	0.9957299
21	F F1	0.7885549	-2.4881404	-0.7296507
22	F F2	2.9645099	-2.1596987	-0.6208029
23	C C12	-1.3931786	-1.2146902	-2.0820448
24	N N1	-1.9814943	-2.1682982	-2.3991697

Literature Predictions

Erbes and Boland trans SM (trans-49)

Gaussian'09: B3LYP/6-31G*, G = -628.208979, iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C1	2.1824440	2.4440161	-0.9529439
2	C C2	0.8731754	3.0361150	-0.5198276
3	C C3	1.0267060	1.5332680	-0.6077047
4	H H6	1.0998863	1.0140289	0.3462317
5	C C10	0.3221516	0.7643655	-1.6561767
6	H H11	0.2760916	1.2185969	-2.6460780
7	C C11	-0.2358471	-0.4350329	-1.4712997
8	H H15	-0.7345043	-0.9617367	-2.2797294
9	C C4	0.7568048	3.6565147	0.8060946
10	C C6	0.0066983	4.7264722	1.1004036
11	H H1	-0.5936315	5.2214553	0.3431933
12	H H13	-0.0211473	5.1271845	2.1088408
13	H H17	1.3404568	3.2048235	1.6081830
14	F F1	3.2781083	2.4714643	-0.1094657
15	F F2	2.4980711	2.5871280	-2.2918194
16	C C5	-0.2048685	-1.1384911	-0.1118337
17	H H3	0.8356307	-1.2967445	0.1939984
18	H H5	-0.7140301	-0.5163774	0.6331126
19	C C7	-0.9161152	-2.4899150	-0.2201975
20	H H4	-0.4069540	-3.1120293	-0.9651436
21	H H7	-1.9566144	-2.3316614	-0.5260294
22	C C8	-0.8851375	-3.1933728	1.1392687
23	H H8	0.1553615	-3.3516268	1.4451012
24	H H10	-1.3942988	-2.5712584	1.8842147
25	C C9	-1.5963850	-4.5447962	1.0309051
26	H H9	-1.0872241	-5.1669111	0.2859594
27	H H12	-2.6368840	-4.3865419	0.7250728
28	H H14	-1.5742096	-5.0483816	2.0041091
29	H H16	0.3062651	3.5394442	-1.2964399

Erbes and Boland cis SM (49)

Gaussian'09: B3LYP/6-31G*, G = -628.207323, iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C1	2.3048106	2.4092042	-0.5864680
2	C C2	1.0108544	3.0286131	-0.1099256
3	C C3	1.1490726	1.4984560	-0.2412288
4	H H6	1.2222529	0.9792168	0.7127076
5	C C10	0.4445181	0.7295535	-1.2897008
6	H H11	0.3984581	1.1837849	-2.2796021
7	C C11	-0.1134805	-0.4698449	-1.1048238
8	H H2	1.0063096	3.3831285	0.9192383

9	H	H15	-0.6121377	-0.9965488	-1.9132536
10	C	C4	0.1658656	3.8275133	-1.0234979
11	C	C6	-0.5814338	4.8690025	-0.6480115
12	H	H1	-0.6234135	5.2003890	0.3875069
13	H	H13	-1.1781026	5.4289125	-1.3622669
14	H	H17	0.1764772	3.5403149	-2.0750644
15	F	F1	3.4004749	2.4366523	0.2570101
16	F	F2	2.6204377	2.5523160	-1.9253435
17	C	C5	-0.0825019	-1.1733032	0.2546422
18	H	H3	0.9579973	-1.3315565	0.5604743
19	H	H5	-0.5916635	-0.5511894	0.9995885
20	C	C7	-0.7937486	-2.5247270	0.1462784
21	H	H4	-0.2845874	-3.1468413	-0.5986678
22	H	H7	-1.8342478	-2.3664734	-0.1595536
23	C	C8	-0.7627709	-3.2281848	1.5057446
24	H	H8	0.2777281	-3.3864388	1.8115770
25	H	H10	-1.2719322	-2.6060704	2.2506905
26	C	C9	-1.4740185	-4.5796082	1.3973810
27	H	H9	-0.9648575	-5.2017231	0.6524352
28	H	H12	-2.5145175	-4.4213540	1.0915487
29	H	H14	-1.4518430	-5.0831936	2.3705850

Erbes and Boland VCPR TS

Gaussian'09: B3LYP/6-31G*, G = -628.163404, iv = i262, S^2 = 0.7753

Cartesian Coordinates (Angstroms)

Atom	X	Y	Z

1 C C	0.1797769	2.4851927	-1.7655285
2 C C2	-0.9439639	1.7209381	-1.7531359
3 C C3	-0.9491965	0.4305106	-1.1524093
4 C C4	1.4649215	1.8489004	-1.3421135
5 C C5	1.5881396	0.4198029	-1.7923096
6 H H	0.2052781	3.5166479	-2.1001947
7 H H7	-1.8549081	2.0559026	-2.2452659
8 H H12	1.1815084	0.1887807	-2.7706469
9 F F1	2.5279271	2.5825422	-1.8433748
10 F F2	1.6191634	1.9073752	0.0413634
11 C C1	2.4997100	-0.4644860	-1.1820841
12 H H3	2.9522971	-0.1411655	-0.2469181
13 C C6	2.8111653	-1.7003805	-1.6762756
14 H H2	3.4993201	-2.3607789	-1.1585262
15 H H4	2.3740126	-2.0681877	-2.6010585
16 H H16	-1.7373684	-0.2135955	-1.5598184
17 C C7	-0.4063762	-0.1645800	0.0803931
18 H H1	0.3309212	0.4487369	0.5844297
19 H H5	0.0334044	-1.1397334	-0.1532436
20 C C8	-1.5525354	-0.3853769	1.0822626
21 H H8	-2.3197989	-1.0295050	0.6341871
22 H H9	-2.0358990	0.5747139	1.3037845
23 C C9	-1.0461147	-1.0194032	2.3778715
24 H H6	-0.2876426	-0.3746243	2.8368189
25 H H10	-0.5660855	-1.9803051	2.1590619
26 C C10	-2.1775044	-1.2408641	3.3689390

27	H	H11	-1.7931010	-1.6945214	4.2878153
28	H	H13	-2.9384534	-1.9088238	2.9528676
29	H	H14	-2.6585977	-0.2937128	3.6331091

Erbes and Boland [3,3] TS

Gaussian'09: B3LYP/6-31G*, G = -628.172483, iv = i284

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C1	-0.7635387	1.2387820	2.6379056
2	H H3	-0.9712143	0.1953323	2.4383484
3	C C2	0.5214959	1.6455185	2.9610528
4	C C5	0.5149436	1.7746469	-0.0281305
5	H H7	0.6413982	2.7611400	-0.4746427
6	C C6	-0.7712610	1.3484632	0.2653336
7	C C3	1.6749619	1.1534769	0.4440985
8	C C4	1.6800959	1.0703481	2.4308735
9	C C11	1.6956791	-0.0067176	1.3906396
10	H H2	2.6396795	1.5699725	0.1427050
11	H H10	2.6460830	1.4328050	2.7921912
12	H H17	-1.6195833	1.9563442	-0.0370334
13	H H1	-1.6149759	1.8093846	2.9985664
14	H H11	0.6397727	2.5236634	3.5908744
15	F F1	0.5830745	-0.8275205	1.3577380
16	F F2	2.8511190	-0.7659216	1.3551840
17	C C7	-1.2869475	-0.1133111	-0.2617409
18	H H5	-2.3310062	0.0417838	-0.5682532
19	H H6	-1.3322165	-0.8273506	0.5612621
20	C C8	-0.4980649	-0.6330584	-1.4586575
21	H H4	0.5484327	-0.7963460	-1.1815678
22	H H8	-0.5024572	0.1240830	-2.2517814
23	C C9	-1.0898539	-1.9387801	-1.9875949
24	H H12	-2.1338189	-1.7826954	-2.2833101
25	H H13	-1.0864397	-2.6963103	-1.1951802
26	C C10	-0.3067223	-2.4618498	-3.1811563
27	H H9	0.7352312	-2.6601956	-2.9103080
28	H H14	-0.3167139	-1.7397327	-4.0038203
29	H H15	-0.7471530	-3.3959545	-3.5435962

Gaich trans VCP SM (50)

Gaussian'09: B3LYP/6-31G*, G = -1145.573154, iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C1	1.6197059	-0.8005199	-2.6549743
2	C C2	0.5016609	-0.3525236	-1.8018160
3	C C3	0.8278940	-1.9065505	-2.0489682
4	H H3	-0.3659227	-0.0185463	-2.3700799
5	H H6	1.2947686	-2.3804072	-1.1892069
6	C C10	-0.0928219	-2.7135757	-2.8524589

7	H	H11	-0.4787172	-2.2731209	-3.7704171
8	C	C11	-0.5030457	-3.9515410	-2.5331951
9	H	H12	-0.1589228	-4.4670044	-1.6412409
10	C	C4	0.6945669	0.2400464	-0.4671944
11	C	C5	1.7838202	0.8462710	0.1349866
12	C	C6	1.3939455	1.2356385	1.4455614
13	C	C7	0.0791243	0.8580797	1.6156185
14	H	H1	2.7485014	0.9944472	-0.3271107
15	N	N1	-0.3373923	0.2577674	0.4529992
16	H	H4	2.6578182	-0.6578100	-2.3337691
17	H	H7	1.5407672	-0.6324651	-3.7351328
18	H	H10	-1.1996851	-4.4813017	-3.1751735
19	C	C8	-0.5815492	1.1320459	2.8351548
20	C	C12	1.4364990	2.1607410	3.6885985
21	C	C13	2.0869119	1.8917182	2.4846385
22	C	C14	0.1140458	1.7824750	3.8598686
23	H	H13	3.1242060	2.1867092	2.3504244
24	H	H14	-0.3886491	1.9853945	4.8031395
25	H	H16	-1.6118828	0.8380517	3.0161146
26	H	H18	1.9693372	2.6622921	4.4922558
27	S	S1	-2.0091027	-0.0544889	0.1539555
28	O	O1	-2.1126963	-0.8254080	-1.0678739
29	O	O2	-2.5459969	-0.5894233	1.3920482
30	C	C9	-2.7561756	1.5265115	-0.1429219
31	H	H2	-2.2740572	1.9858205	-1.0079086
32	H	H5	-2.6400932	2.1531404	0.7424699
33	H	H8	-3.8168623	1.3675366	-0.3483918

Gaich cis VCP SM (cis-50)

Gaussian'09: B3LYP/6-31G*, G = -1145.574428, iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
-----		-----	-----	-----
1	C C1	0.5772912	-2.0168209	-2.6912849
2	C C2	-0.4755920	-1.4227026	-1.8065477
3	C C3	0.1486847	-0.6115404	-2.9341770
4	H H6	-0.5652451	-0.4887302	-3.7446853
5	C C10	1.0297737	0.5175099	-2.6283467
6	H H11	1.8128888	0.3591332	-1.8886099
7	C C11	0.9343620	1.7352010	-3.1859273
8	H H12	0.1886167	1.9741007	-3.9385868
9	C C4	-0.1797073	-1.0976278	-0.3127173
10	C C5	0.8118500	-1.6934701	0.4355737
11	C C6	0.7786294	-1.1265360	1.7382202
12	C C7	-0.2780851	-0.2076168	1.7758048
13	H H1	1.5091388	-2.4445218	0.0876724
14	N N1	-0.8679872	-0.2463571	0.5217833
15	H H4	0.3076245	-2.7846842	-3.4253706
16	H H7	1.5763829	-2.1850111	-2.3024834
17	H H10	1.6182629	2.5265533	-2.8958751
18	C C8	-0.5639331	0.5245644	2.9441336
19	C C12	1.2864664	-0.5905565	4.0494810
20	C C13	1.5661520	-1.3194300	2.8908299

21	C	C14	0.2348618	0.3177570	4.0731321
22	H	H13	2.3878390	-2.0303952	2.8816971
23	H	H14	0.0211906	0.8691525	4.9865939
24	H	H16	-1.3946649	1.2226822	3.0002371
25	H	H18	1.8924320	-0.7413470	4.9396372
26	S	S1	-2.1152702	0.8215448	0.0447368
27	O	O1	-2.5640956	0.3965081	-1.2676831
28	O	O2	-3.0458025	0.8515416	1.1593617
29	C	C9	-1.3897601	2.4303800	-0.1089514
30	H	H2	-0.5860389	2.3920360	-0.8420049
31	H	H5	-1.0075041	2.7484702	0.8619686
32	H	H8	-2.1659855	3.1214365	-0.4444398
33	H	H9	-1.4827759	-1.8012238	-1.9731721

Gaich cis VCPR TS 50

Gaussian'09: B3LYP/6-31G*, G = -1145.512932, iv = i451, S² = 0.7540

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
		-----	-----	-----
1	C C	-3.2306126	2.4446878	0.6697624
2	C C2	-4.2202822	1.5011075	0.6738103
3	C C3	-3.9420378	0.1216369	0.7867193
4	C C4	-1.8298021	1.9937313	0.5249219
5	C C5	-1.6742598	0.8913056	-0.4753325
6	H H	-3.4311433	3.5154477	0.6530915
7	H H7	-5.2604059	1.7955217	0.5457293
8	H H8	-3.0671211	-0.2330688	1.3138945
9	H H12	-2.4248628	0.8236220	-1.2494718
10	C C1	-0.4596443	0.2321306	-0.6776137
11	C C6	-0.2005191	-0.4626763	-1.8531098
12	C C7	1.1697130	-0.8601541	-1.8616532
13	C C8	1.7273980	-0.4742062	-0.6391548
14	H H3	-0.8602812	-0.6009484	-2.7062280
15	N N1	0.6809631	0.0224647	0.0816724
16	H H2	-1.4017182	1.6667809	1.4794185
17	H H4	-1.1848019	2.8381787	0.2564089
18	H H13	-4.7016903	-0.6156509	0.5029046
19	C C9	3.0889678	-0.6561729	-0.3579910
20	C C11	1.9799289	-1.4934810	-2.8204477
21	C C12	3.3318649	-1.6992840	-2.5376187
22	C C13	3.8768732	-1.2773033	-1.3304490
23	H H1	3.5714265	-0.3184691	0.5560382
24	H H14	1.5919290	-1.8166411	-3.7863838
25	H H15	3.9740948	-2.1817240	-3.2767897
26	H H17	4.9426785	-1.4328413	-1.1485794
27	S S1	0.5609192	0.0277857	1.7628150
28	O O1	0.7534589	1.4339937	2.0410944
29	O O2	-0.8212567	-0.4545720	1.8865347
30	C C10	1.7027156	-1.0271505	2.6098716
31	H H5	2.7004349	-0.5918645	2.5708941
32	H H6	1.6764925	-2.0178412	2.1536728
33	H H9	1.3805806	-1.0943451	3.6515687

Gaich cis [3,3] TS

Gaussian'09: B3LYP/6-31G*, G = -1145.535705, iv = i388

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	-0.5354495	-0.9954063	-0.6005013
2	H H3	-0.6066520	-2.0631530	-0.7723441
3	C C2	0.7837370	-0.5430534	-0.1823152
4	C C5	0.5332369	-0.1362140	-3.0944368
5	H H7	0.5127026	0.8715480	-3.5066809
6	C C6	-0.6930158	-0.6444662	-2.5707256
7	H H6	-0.9282083	-1.6827987	-2.7742534
8	C C3	1.7525154	-0.7429426	-2.9246180
9	C C4	1.9459117	-1.0599260	-0.7440129
10	C C11	1.9810344	-1.8681167	-1.9859001
11	H H2	2.6585646	-0.2828496	-3.3108351
12	H H10	2.9153312	-0.6781863	-0.4285817
13	C C9	-1.5088898	-0.2812568	0.1619200
14	C C8	-0.8226449	0.6792747	0.7617455
15	N N2	0.5383226	0.6398357	0.6569621
16	H H11	-1.5487914	0.0329326	-2.6707005
17	H H16	1.2454242	-2.6784578	-2.0445588
18	H H17	2.9656358	-2.3250472	-2.1375266
19	C C7	-2.9003677	-0.4601979	0.3202661
20	C C12	-1.5704315	1.6188409	1.5337430
21	C C13	-2.9562851	1.4943808	1.6866126
22	C C14	-3.6226375	0.4435674	1.0905411
23	H H1	-3.4073908	-1.2784191	-0.1831761
24	H H13	-1.0869852	2.4573567	2.0308196
25	H H14	-3.5021339	2.2237180	2.2799495
26	H H18	-4.6966160	0.3318542	1.2055523
27	S S1	1.6919267	1.3908105	1.6402702
28	O O1	2.9810173	1.1549805	1.0178166
29	O O2	1.2241193	2.7472334	1.8558173
30	C C10	1.6640816	0.5328646	3.1908993
31	H H4	2.4112996	0.9875830	3.8445906
32	H H5	1.9092720	-0.5166522	3.0180000
33	H H8	0.6723665	0.6303628	3.6356613

Sustmann VCP INT (51)

Gaussian'09: B3LYP/6-31G*, G = -888.147718, iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	2.3755578	0.2955231	-0.2584893
2	C C2	1.2437991	1.0453606	0.3458963
3	C C3	1.3323679	-0.5400432	0.4099371
4	H H6	1.6293956	-0.9742177	1.3626546
5	C C4	1.4964683	1.7754558	1.6444639
6	C C5	1.8975463	3.2280305	4.0133341

7	C	C6	0.8125100	1.4295389	2.8153903
8	C	C7	2.3868173	2.8567642	1.6736107
9	C	C8	2.5863915	3.5777389	2.8501506
10	C	C9	1.0098482	2.1516013	3.9932360
11	H	H4	0.1036468	0.6053497	2.8103845
12	H	H7	2.9165295	3.1509523	0.7712183
13	H	H8	3.2746411	4.4187474	2.8602973
14	H	H9	0.4670704	1.8787003	4.8943076
15	C	C10	0.4351634	-1.3920948	-0.3825193
16	H	H11	0.2058968	-1.0547255	-1.3920468
17	C	C11	-0.0839051	-2.5499123	0.0539730
18	H	H12	0.1640927	-2.9173582	1.0465816
19	H	H16	2.0497456	3.7930719	4.9286282
20	C	C14	0.2132182	1.6866706	-0.5526569
21	C	C15	-1.7178629	2.9752724	-2.1327952
22	C	C16	-1.1528020	1.5122024	-0.2929265
23	C	C17	0.6003696	2.5164918	-1.6128682
24	C	C18	-0.3601727	3.1563232	-2.3974298
25	C	C19	-2.1121947	2.1501502	-1.0775961
26	H	H2	-1.4740149	0.8847489	0.5348762
27	H	H1	1.6540170	2.6825218	-1.8205484
28	H	H3	-0.0491263	3.8026883	-3.2139870
29	H	H10	-3.1683130	2.0104767	-0.8629331
30	H	H15	-2.4648964	3.4766167	-2.7418699
31	H	H17	3.3513352	0.3428039	0.2164551
32	H	H18	2.4593056	0.2393659	-1.3395042
33	C	C12	-0.9860671	-3.3988915	-0.7362677
34	C	C13	-2.7262649	-5.0860924	-2.1560505
35	C	C20	-1.9629416	-2.8637967	-1.5869450
36	C	C21	-0.9080837	-4.7900142	-0.5908611
37	C	C22	-1.7697516	-5.6296747	-1.3013609
38	C	C23	-2.8248758	-3.7035835	-2.2971076
39	H	H5	-2.0707841	-1.7874104	-1.6994879
40	H	H13	-0.1679214	-5.2335634	0.0711705
41	H	H14	-1.6932297	-6.7074940	-1.1856945
42	H	H19	-3.5754602	-3.2756175	-2.9563243
43	H	H20	-3.3970656	-5.7386774	-2.7082956

Sustmann VCPR TS

Gaussian'09: B3LYP/6-31G*, G = -888.098339, iv = i201, S^2 = 0.6849

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C	-0.0269135	3.0322724	0.3651644
2	C C2	-1.2103563	2.3679144	0.2763010
3	C C3	-1.3598391	1.0609182	0.8066873
4	C C4	1.1643584	2.2883003	0.8799909
5	C C5	1.2656103	0.8437567	0.3874205
6	H H	0.1194959	4.0502385	0.0037539
7	H H7	-2.0512600	2.8004308	-0.2622636
8	H H8	-0.8618118	0.7599148	1.7159615
9	C C1	1.8909915	-0.1792479	1.2367267
10	C C6	3.1268072	-2.1941215	2.8018338

11	C	C7	2.8555473	-1.0583675	0.6862312
12	C	C8	1.5786590	-0.3413779	2.6086037
13	C	C9	2.1831999	-1.3353085	3.3704229
14	C	C10	3.4634290	-2.0451617	1.4550234
15	H	H2	3.2210392	-0.9799177	-0.3384494
16	H	H6	0.8868435	0.2999722	3.1447167
17	H	H5	1.9531260	-1.4530058	4.4328034
18	H	H3	4.2224089	-2.7040790	1.0248655
19	H	H4	3.6127696	-2.9629314	3.4072836
20	C	C13	1.1695655	0.6288107	-1.0564075
21	C	C14	0.8724646	0.1772572	-3.8342089
22	C	C15	1.3872637	1.6643669	-1.9941773
23	C	C16	0.8072404	-0.6456949	-1.5612241
24	C	C17	0.6575959	-0.8646435	-2.9225151
25	C	C18	1.2380126	1.4360556	-3.3620031
26	H	H11	1.8179670	2.6327972	-1.7364651
27	H	H12	0.6492528	-1.5164453	-0.9209106
28	H	H13	0.4119018	-1.8580422	-3.3112913
29	H	H14	1.4735600	2.2149849	-4.0950196
30	H	H15	0.7975208	-0.0117358	-4.9092232
31	H	H16	1.1167981	2.3143977	1.9749587
32	H	H17	2.0788858	2.8248769	0.5980375
33	C	C11	-2.5255896	0.0640594	0.3526260
34	C	C12	-4.4846969	-1.7852412	-0.3841672
35	C	C19	-3.3685840	0.3320269	-0.7365100
36	C	C20	-2.6731429	-1.1355713	1.0686093
37	C	C21	-3.6530577	-2.0555931	0.6977398
38	C	C22	-4.3461298	-0.5980304	-1.0985063
39	H	H1	-3.3329778	1.2302020	-1.3474036
40	H	H9	-2.0583888	-1.3923795	1.9312546
41	H	H10	-3.7896071	-2.9892860	1.2506341
42	H	H18	-5.0219184	-0.4118401	-1.9386429
43	H	H19	-5.2580407	-2.5055313	-0.6682614

Sustmann [3,3] TS

Gaussian'09: B3LYP/6-31G*, G = -888.090641, iv = i385

Cartesian Coordinates (Angstroms)

Atom	X	Y	Z

1 C C1	-1.2158865	-0.8522870	0.6734974
2 H H3	-1.3659523	-1.9166506	0.5611198
3 C C2	0.1150097	-0.4688105	1.1492486
4 C C5	0.0978896	-0.3876310	-1.8956387
5 H H7	0.1774585	0.5334981	-2.4694213
6 C C6	-1.2103261	-0.7329575	-1.4271119
7 H H6	-1.4932838	-1.7755982	-1.4772134
8 C C7	0.2240385	0.6918035	1.9983036
9 H H4	1.2171496	1.0043791	2.3117403
10 C C8	-0.8770135	1.3972592	2.3822541
11 H H9	-0.7685821	2.2777066	3.0096368
12 C C9	-2.1886048	0.9813351	1.9764615
13 H H11	-3.0535724	1.5319291	2.3363479
14 C C10	-2.3519991	-0.1175903	1.1885447

15	H	H12	-3.3447091	-0.4637382	0.9187841
16	C	C3	1.2469468	-1.0393722	-1.5551573
17	C	C4	1.2607021	-1.1104314	0.7250007
18	C	C11	1.3457780	-2.0311061	-0.4447914
19	H	H2	2.2062929	-0.6862884	-1.9217102
20	H	H13	0.5763900	-2.8114049	-0.4645882
21	H	H14	2.3145953	-2.5432517	-0.4625649
22	C	C14	2.6763274	-0.7228923	1.2349276
23	C	C15	5.2516079	-0.0650837	2.1853548
24	C	C16	3.2742115	-1.4487114	2.2797424
25	C	C17	3.4072101	0.3442956	0.6815639
26	C	C18	4.6813961	0.6713438	1.1505058
27	C	C19	4.5482476	-1.1250240	2.7515672
28	H	H10	2.7323243	-2.2771313	2.7313969
29	H	H15	2.9668480	0.9359623	-0.1181157
30	H	H16	5.2249259	1.5026153	0.7094284
31	H	H17	4.9883312	-1.7004903	3.5615061
32	H	H18	6.2423913	0.1887231	2.5524460
33	C	C12	-2.3385948	0.1661957	-1.9295166
34	C	C13	-4.4027784	1.7976193	-2.8176402
35	C	C20	-2.2398596	1.5472552	-1.7738149
36	C	C21	-3.4616944	-0.4095593	-2.5177089
37	C	C22	-4.4965870	0.4116445	-2.9657211
38	C	C23	-3.2759898	2.3659111	-2.2200140
39	H	H1	-1.3679619	1.9698680	-1.2846959
40	H	H5	-3.5283929	-1.4856102	-2.6323173
41	H	H8	-5.3756705	-0.0270590	-3.4301205
42	H	H19	-3.2076139	3.4431710	-2.0960297
43	H	H20	-5.2109992	2.4361639	-3.1654863

Ichikawa VCP INT (52)

Gaussian'09: B3LYP/6-31G*, G = -1108.506583, iv = none

Cartesian Coordinates (Angstroms)

Atom	X	Y	Z

1 C C1	2.2910281	2.0104097	-1.1886598
2 C C2	1.1414659	2.7184398	-0.6052825
3 C C3	1.2667689	1.1588629	-0.5050026
4 C C10	0.3642447	0.3076408	-1.2924739
5 H H11	0.0800168	0.6873774	-2.2712185
6 C C11	-0.1509008	-0.8557149	-0.8695280
7 H H12	0.1025203	-1.2572522	0.1062422
8 C C4	-1.0821648	-1.6724113	-1.6593521
9 C C5	-2.8682629	-3.3006439	-3.0877385
10 C C6	-0.9100064	-1.8836438	-3.0334648
11 C C7	-2.1480908	-2.3047403	-1.0065605
12 C C8	-3.0403695	-3.1103883	-1.7182796
13 C C9	-1.8020244	-2.6901298	-3.7449847
14 H H3	-0.0731336	-1.4334427	-3.5615838
15 H H4	-2.2975245	-2.1679229	0.0620295
16 H H5	-3.8678956	-3.5900222	-1.2022587
17 H H7	-1.6594109	-2.8458606	-4.8111041
18 H H8	-3.5610375	-3.9289132	-3.6413769

19	H	H9	1.3255102	3.3309280	0.2670203
20	H	H10	0.3916141	3.1226335	-1.2753837
21	O	O1	1.7880427	0.6696859	0.7730615
22	Si	Si1	0.9911971	0.9088461	2.2335392
23	C	C12	1.0619693	-0.6762027	3.2549177
24	H	H13	2.1006089	-0.9713172	3.4299155
25	H	H15	0.5540851	-1.4914534	2.7316314
26	H	H16	0.5751629	-0.5302304	4.2235639
27	C	C13	-0.8176967	1.3790454	2.0350855
28	H	H6	-1.2795211	1.5279189	3.0159549
29	H	H17	-1.3734971	0.5922526	1.5178984
30	H	H18	-0.9244139	2.3079912	1.4682959
31	C	C14	1.8461939	2.2653271	3.2230294
32	H	H14	2.8988511	2.0148413	3.3836261
33	H	H19	1.3676965	2.3868878	4.1992625
34	H	H20	1.7962275	3.2212932	2.6945525
35	F	F1	3.5239867	2.1531621	-0.5786402
36	F	F2	2.3887598	1.9467462	-2.5667325

Ichikawa VCPR TS

Gaussian'09: B3LYP/6-31G* using scf=(qcverytight) and
guess=(mix,always,densitymix) in input line, G = -1108.460735, iv =
i109, S^2 = 0.79

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z

1	C C	1.9137391	1.1672811	0.4623618
2	C C2	0.7982840	0.3787391	0.4386759
3	C C3	0.7719369	-0.8931799	1.0544091
4	C C4	3.1968266	0.5748901	0.9540772
5	C C5	3.4120343	-0.8159359	0.4684891
6	H H	1.9254320	2.1927805	0.1088231
7	H H8	1.4043016	-1.1230086	1.9018355
8	H H12	3.0581443	-1.0949354	-0.5151967
9	H H4	4.2350300	-1.3872942	0.9128354
10	O O3	-0.3890101	0.7109659	-0.1542352
11	Si Si1	-0.7786309	2.1508656	-0.9389403
12	C C1	-0.6701825	3.5884769	0.2476550
13	H H7	-1.3026780	3.4129458	1.1232011
14	H H11	-1.0122807	4.5094809	-0.2345161
15	H H13	0.3508105	3.7575846	0.5985019
16	C C6	0.3729825	2.4152865	-2.3902891
17	H H5	0.3692404	1.5399622	-3.0469016
18	H H14	1.4026811	2.5957345	-2.0723966
19	H H15	0.0509264	3.2797206	-2.9791621
20	C C7	-2.5316834	2.0200185	-1.5819238
21	H H6	-3.2343665	1.8577902	-0.7591750
22	H H16	-2.6260887	1.1830513	-2.2802412
23	H H17	-2.8233725	2.9357156	-2.1047400
24	C C8	-0.3347065	-2.0859988	0.8493571
25	C C9	-2.1173226	-4.2323675	0.6236915
26	C C10	-1.3177024	-2.0818909	-0.1502703
27	C C11	-0.2485493	-3.1829850	1.7262542

28	C	C12	-1.1408365	-4.2489898	1.6126115
29	C	C13	-2.2062767	-3.1567098	-0.2549064
30	H	H1	-1.4565368	-1.3088833	-0.8971375
31	H	H9	0.4835660	-3.2459843	2.5313231
32	H	H10	-1.0931269	-5.1014248	2.2961903
33	H	H18	-2.9836290	-3.1763755	-1.0247698
34	H	H19	-2.8191322	-5.0675515	0.5381456
35	F	F1	4.2306300	1.3778540	0.6270610
36	F	F2	3.1095464	0.5543711	2.3093024

Hammett Plot

p_NMe2_SM (S1a)

G = -986.405584

iv = none

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
-----			-----	-----	-----
1	C	C1	1.5584825	0.1025224	-2.3886327
2	C	C2	0.4103350	0.6021148	-1.6087786
3	C	C3	0.6679862	-0.9553396	-1.8292907
4	H	H3	-0.3986704	0.9730780	-2.2377576
5	H	H6	1.0586619	-1.4515965	-0.9442274
6	C	C4	0.5001002	1.1869267	-0.2380093
7	C	C5	0.5732065	2.3190323	2.3824332
8	C	C6	-0.5615688	1.0151570	0.6614430
9	C	C7	1.6000107	1.9356895	0.1982475
10	C	C8	1.6435293	2.4858832	1.4755522
11	C	C9	-0.5345924	1.5585553	1.9391770
12	H	H4	-1.4287926	0.4329341	0.3574701
13	H	H7	2.4449454	2.0864268	-0.4648848
14	H	H8	2.5221955	3.0502945	1.7635900
15	H	H9	-1.3797019	1.3873351	2.5950487
16	C	C10	-0.2340745	-1.7296817	-2.6860464
17	H	H11	-0.5575400	-1.2745917	-3.6205935
18	C	C11	-0.6941664	-2.9563111	-2.3925762
19	H	H12	-0.4109535	-3.4788213	-1.4834960
20	C	C12	-1.6147289	-3.6494885	-3.3153280
21	O	O1	-2.0354075	-3.2116057	-4.3698009
22	O	O2	-1.9500367	-4.8718127	-2.8302762
23	C	C13	-2.8426018	-5.6310552	-3.6570646
24	H	H5	-3.7770573	-5.0862991	-3.8173613
25	H	H13	-3.0270436	-6.5595776	-3.1153547
26	H	H14	-2.3854629	-5.8382771	-4.6289032
27	F	F1	1.5632782	0.3054300	-3.7284662
28	F	F2	2.8228242	0.2003465	-1.9124621
29	N	N1	0.6028731	2.8829986	3.6510640
30	C	C14	1.8395244	3.4710273	4.1367540
31	H	H1	2.1484069	4.3141581	3.5067625
32	H	H10	2.6710701	2.7489363	4.1695523
33	H	H15	1.6805189	3.8558945	5.1459552
34	C	C15	-0.4124265	2.5103263	4.6210870
35	H	H2	-0.2419652	3.0633957	5.5468705

36	H	H16	-0.4061960	1.4336214	4.8563569
37	H	H17	-1.4149619	2.7723735	4.2619463

NMe2_TS2 (S-TS1a)

G = -986.371766

iv = i75

S² = 0.4500

			Cartesian Coordinates (Angstroms)		
Atom			X	Y	Z
-----			-----	-----	-----
1	C	C	-1.7257165	3.6608005	-1.0708224
2	C	C2	-2.8870564	2.9448482	-1.1483783
3	C	C3	-3.0524220	1.7261259	-0.4506724
4	C	C4	-0.5565938	3.0194769	-0.4159069
5	C	C5	-0.3836554	1.5979954	-0.8610707
6	H	H	-1.6022001	4.6557693	-1.4838963
7	H	H7	-3.6991650	3.2728347	-1.7948143
8	H	H8	-2.5315502	1.5364955	0.4779677
9	H	H12	-0.8743979	1.3410869	-1.7900136
10	F	F1	0.5982312	3.7432144	-0.6825366
11	F	F2	-0.6580277	3.0804251	0.9893451
12	C	C1	0.6067414	0.7159363	-0.3745757
13	C	C6	2.5419146	-1.1846315	0.5589313
14	C	C7	0.8259172	-0.5246276	-1.0369708
15	C	C8	1.4021316	0.9650054	0.7809334
16	C	C9	2.3374050	0.0555558	1.2252386
17	C	C10	1.7498539	-1.4449934	-0.5932123
18	H	H2	0.2369406	-0.7532016	-1.9219840
19	H	H6	1.2651172	1.8922670	1.3235701
20	H	H5	2.9141905	0.2991633	2.1095642
21	H	H3	1.8633518	-2.3748420	-1.1375105
22	C	C11	-4.0928551	0.7828418	-0.8453818
23	O	O1	-4.8594126	0.9119027	-1.7888919
24	O	O2	-4.1147561	-0.3020953	-0.0188599
25	C	C12	-5.0906560	-1.2947775	-0.3485181
26	H	H1	-6.1040563	-0.8931400	-0.2514844
27	H	H9	-4.9354454	-2.1081869	0.3623164
28	H	H10	-4.9537390	-1.6503536	-1.3741766
29	N	N1	3.4629040	-2.0964084	1.0116655
30	C	C13	3.6322520	-3.3693753	0.3261360
31	H	H4	4.4017447	-3.9509484	0.8352652
32	H	H13	3.9474534	-3.2280999	-0.7162523
33	H	H14	2.7040599	-3.9568964	0.3266268
34	C	C14	4.2471670	-1.8172132	2.2061765
35	H	H11	4.9151404	-2.6574804	2.3998742
36	H	H15	3.6075847	-1.6789864	3.0885939
37	H	H16	4.8616043	-0.9154872	2.0837247

pNH2_SM (S1b)

G = -907.846024

iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	1.6851610	0.1319418	-1.5815304
2	C C2	0.6384108	0.9359312	-0.9216993
3	C C3	0.6730599	-0.6463225	-0.8066263
4	H H3	-0.1322477	1.2860880	-1.6088658
5	H H6	1.0203339	-0.9992078	0.1615377
6	C C4	0.8805428	1.7764293	0.2902526
7	C C5	1.2586871	3.4160653	2.5710386
8	C C6	-0.0743025	1.8211479	1.3164424
9	C C7	2.0281729	2.5685850	0.4268111
10	C C8	2.2176801	3.3742094	1.5456268
11	C C9	0.1049242	2.6230367	2.4372474
12	H H4	-0.9719102	1.2120028	1.2378336
13	H H7	2.7894641	2.5492299	-0.3465061
14	H H8	3.1164852	3.9816222	1.6268973
15	H H9	-0.6525406	2.6419044	3.2180763
16	C C10	-0.3479446	-1.4519089	-1.4842468
17	H H11	-0.6428478	-1.1489419	-2.4876272
18	C C11	-0.9455504	-2.5303317	-0.9540096
19	H H12	-0.7023801	-2.9010621	0.0376269
20	C C12	-1.9715553	-3.2674690	-1.7192850
21	O O1	-2.3657116	-2.9917879	-2.8367407
22	O O2	-2.4387865	-4.3209899	-1.0030180
23	C C13	-3.4418486	-5.1077992	-1.6601821
24	H H5	-4.2967329	-4.4869973	-1.9414600
25	H H13	-3.7395441	-5.8681781	-0.9370796
26	H H14	-3.0349725	-5.5754868	-2.5614979
27	F F1	1.6792664	0.0435328	-2.9332927
28	F F2	2.9618784	0.1596004	-1.1329688
29	N N1	1.4187425	4.2650383	3.6670814
30	H H2	0.9101470	3.9942771	4.4993782
31	H H1	2.3759190	4.5158404	3.8807859

pNH2_TS2 (S-TS1b)

G = -907.811148

iv = i93

S^2 = 0.4444

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C	-1.0033632	3.1014530	-0.7660046
2	C C2	-2.1485900	2.3610330	-0.8316443
3	C C3	-2.2708494	1.1339810	-0.1359989
4	C C4	0.1839831	2.4738482	-0.1310559
5	C C5	0.3705269	1.0576570	-0.5915524

6	H	H	-0.9033214	4.1003023	-1.1761130
7	H	H7	-2.9780636	2.6709029	-1.4646857
8	H	H8	-1.7499928	0.9640771	0.7962412
9	H	H12	-0.1191565	0.8072066	-1.5228758
10	F	F1	1.3244981	3.2147033	-0.4056469
11	F	F2	0.0981061	2.5204954	1.2754407
12	C	C1	1.3963136	0.1950264	-0.1345531
13	C	C6	3.4137602	-1.6272165	0.7115376
14	C	C7	1.6470497	-1.0214553	-0.8308863
15	C	C8	2.2002934	0.4568797	1.0128273
16	C	C9	3.1820342	-0.4235911	1.4158791
17	C	C10	2.6207714	-1.9087996	-0.4239561
18	H	H2	1.0484108	-1.2537662	-1.7080921
19	H	H6	2.0335083	1.3660344	1.5770487
20	H	H5	3.7873072	-0.1954740	2.2905431
21	H	H3	2.7895711	-2.8287797	-0.9791327
22	C	C11	-3.2961996	0.1690414	-0.5228418
23	O	O1	-4.0604403	0.2788837	-1.4702046
24	O	O2	-3.3086894	-0.9043195	0.3167099
25	C	C12	-4.2820913	-1.9058321	0.0036247
26	H	H1	-5.2961855	-1.5047171	0.0952275
27	H	H9	-4.1241115	-2.7069217	0.7274931
28	H	H10	-4.1449068	-2.2768805	-1.0163953
29	N	N1	4.4201155	-2.4844004	1.0969438
30	H	H4	4.7824353	-2.3941872	2.0359887
31	H	H11	4.3872762	-3.4351844	0.7561341

pOH_SM (S1c)

G = -927.720966

iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C1	1.7176635	0.7049715	-1.2705558
2	C C2	0.5244052	1.2429854	-0.5888208
3	C C3	0.8191476	-0.3143685	-0.6521193
4	H H3	-0.2658900	1.5445537	-1.2763492
5	H H6	1.1813468	-0.7248364	0.2875717
6	C C4	0.5664812	1.9608276	0.7219435
7	C C5	0.5510370	3.3453453	3.1697163
8	C C6	-0.4413795	1.7357997	1.6732258
9	C C7	1.5661187	2.8935809	1.0212313
10	C C8	1.5625457	3.5815466	2.2345678
11	C C9	-0.4569616	2.4159899	2.8847103
12	H H4	-1.2238110	1.0124494	1.4576288
13	H H7	2.3594454	3.0816508	0.3057250
14	H H8	2.3489012	4.3021003	2.4524849
15	H H9	-1.2354174	2.2422225	3.6207104
16	C C10	-0.0256227	-1.1835437	-1.4787692
17	H H11	-0.3308351	-0.8084850	-2.4543328
18	C C11	-0.4506697	-2.4033908	-1.1162162
19	H H12	-0.1849613	-2.8529013	-0.1637986
20	C C12	-1.3099918	-3.1921371	-2.0232351

21	O	O1	-1.7058173	-2.8384995	-3.1178977
22	O	O2	-1.6165460	-4.3919981	-1.4708236
23	C	C13	-2.4504622	-5.2374544	-2.2758548
24	H	H5	-3.4026611	-4.7454437	-2.4925444
25	H	H13	-2.6102318	-6.1404204	-1.6854493
26	H	H14	-1.9556246	-5.4785865	-3.2207919
27	F	F1	1.7827542	0.7845676	-2.6206418
28	F	F2	2.9518510	0.8833571	-0.7438053
29	O	O3	0.4915019	3.9861025	4.3747873
30	H	H15	1.2436836	4.5940145	4.4477026

pOH_TS2 (S-TS1c)

G = -927.683551

iv = i104

S^2 = 0.5058

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C	-0.8343384	3.0005875	-0.7407077
2	C C2	-1.9829047	2.2662349	-0.8020632
3	C C3	-2.1042135	1.0372641	-0.1082562
4	C C4	0.3542186	2.3643336	-0.1116000
5	C C5	0.5256601	0.9448303	-0.5683545
6	H H	-0.7301742	3.9984166	-1.1522788
7	H H7	-2.8147603	2.5799453	-1.4296835
8	H H8	-1.5836454	0.8652785	0.8238757
9	H H12	0.0492697	0.7031459	-1.5090688
10	F F1	1.4973858	3.0949055	-0.3957734
11	F F2	0.2712326	2.4172782	1.2927841
12	C C1	1.5376800	0.0644986	-0.0982657
13	C C6	3.5070141	-1.7720166	0.7576334
14	C C7	1.7747574	-1.1543337	-0.7946901
15	C C8	2.3301349	0.3200217	1.0546892
16	C C9	3.2991461	-0.5778997	1.4669917
17	C C10	2.7337107	-2.0572561	-0.3797899
18	H H2	1.1816258	-1.3754413	-1.6783337
19	H H6	2.1723372	1.2324451	1.6157909
20	H H5	3.8997598	-0.3626211	2.3492904
21	H H3	2.9095243	-2.9851554	-0.9146080
22	C C11	-3.1320862	0.0717056	-0.4974130
23	O O1	-3.8953467	0.1895222	-1.4437008
24	O O2	-3.1415021	-1.0023819	0.3367300
25	C C12	-4.1134268	-2.0068523	0.0224721
26	H H1	-5.1277049	-1.6073436	0.1168668
27	H H9	-3.9514965	-2.8086909	0.7442256
28	H H10	-3.9754656	-2.3741969	-0.9985851
29	O O3	4.4384058	-2.6900073	1.1254616
30	H H4	4.9052025	-2.3762166	1.9163605

pOMe_SM (S1d)

G = -966.999935

iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	1.5684705	0.2206178	-1.7265240
2	C C2	0.3767325	0.7586473	-1.0428449
3	C C3	0.6711354	-0.7986142	-1.1054805
4	H H3	-0.4146782	1.0603301	-1.7291412
5	H H6	1.0361460	-1.2083128	-0.1665828
6	C C4	0.4192798	1.4751382	0.2683520
7	C C5	0.3995578	2.8646981	2.7183402
8	C C6	-0.5826736	1.2374397	1.2250323
9	C C7	1.4069566	2.4176329	0.5652301
10	C C8	1.4062191	3.1116747	1.7788282
11	C C9	-0.5978226	1.9188432	2.4327813
12	H H4	-1.3580613	0.5051265	1.0139794
13	H H7	2.1951714	2.6143151	-0.1540665
14	H H8	2.1883617	3.8356514	1.9764159
15	H H9	-1.3698877	1.7390233	3.1742316
16	C C10	-0.1777455	-1.6675893	-1.9280107
17	H H11	-0.4818819	-1.2951250	-2.9049402
18	C C11	-0.6097880	-2.8832318	-1.5593780
19	H H12	-0.3457029	-3.3298459	-0.6051592
20	C C12	-1.4759922	-3.6705031	-2.4608967
21	O O1	-1.8727548	-3.3192847	-3.5560320
22	O O2	-1.7885307	-4.8663163	-1.9026053
23	C C13	-2.6297513	-5.7098323	-2.7019138
24	H H5	-3.5815062	-5.2147909	-2.9137000
25	H H13	-2.7893392	-6.6115801	-2.1095754
26	H H14	-2.1413615	-5.9538428	-3.6494661
27	F F1	1.6301616	0.2985041	-3.0770919
28	F F2	2.8034684	0.4007019	-1.2029834
29	O O3	0.2963876	3.4834113	3.9292099
30	C C14	1.2722343	4.4550219	4.2726559
31	H H2	2.2778950	4.0167761	4.3222211
32	H H1	0.9909234	4.8256908	5.2598928
33	H H10	1.2783764	5.2896248	3.5592219

pOMe_TS2 (S-TS1d)

G = -966.962804

iv = i120

S² = 0.4627

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C	-1.2853765	-0.9843654	-3.2298744
2	C C2	-2.4478855	-1.0570847	-2.5210862
3	C C3	-2.5969876	-0.3738806	-1.2876998
4	C C4	-0.1215990	-0.3415462	-2.5660629
5	C C5	0.0152474	-0.7873108	-1.1388865
6	H H	-1.1548866	-1.3895044	-4.2272081
7	H H7	-3.2700595	-1.6867161	-2.8552197
8	H H8	-2.0992402	0.5680364	-1.1019723
9	H H12	-0.4471057	-1.7370223	-0.9060560
10	F F1	1.0444644	-0.6188252	-3.2626443
11	F F2	-0.2163996	1.0621237	-2.6311444
12	C C1	1.0108366	-0.3040677	-0.2465697
13	C C6	2.9925752	0.5632996	1.5807666
14	C C7	1.2470701	-0.9924939	0.9779465
15	C C8	1.7997017	0.8480714	-0.5034394
16	C C9	2.7768615	1.2693620	0.3848445
17	C C10	2.2087428	-0.5715467	1.8713489
18	H H2	0.6540083	-1.8744149	1.2063193
19	H H6	1.6379786	1.4053597	-1.4172121
20	H H5	3.3622031	2.1496247	0.1452903
21	H H3	2.3890886	-1.0999616	2.8021740
22	C C11	-3.6490779	-0.7776127	-0.3544587
23	O O1	-4.4312068	-1.7000828	-0.5247839
24	O O2	-3.6601480	0.0151239	0.7508289
25	C C12	-4.6736312	-0.2900381	1.7162525
26	H H1	-5.6501013	0.0616953	1.3679974
27	H H9	-4.3875978	0.2408311	2.6251722
28	H H10	-4.7307654	-1.3660361	1.8947585
29	O O3	3.9193253	0.8926177	2.5124782
30	C C13	4.7696399	2.0076929	2.2673506
31	H H4	5.4324808	2.0698038	3.1316097
32	H H11	4.1950788	2.9381197	2.1803286
33	H H13	5.3667660	1.8607484	1.3588516

pNHCOMe_SM (S1e)

G = -1060.47329

iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	1.1713988	0.1575743	-2.5063816
2	C C2	0.0746468	0.5360569	-1.5940816
3	C C3	0.4551586	-0.9803119	-1.8554379

4	H	H3	-0.8364244	0.8316940	-2.1138577
5	H	H6	0.9977653	-1.4393910	-1.0322157
6	C	C4	0.2848449	1.1340345	-0.2398241
7	C	C5	0.5967967	2.2851907	2.3182726
8	C	C6	-0.5347055	0.7412212	0.8278222
9	C	C7	1.2582649	2.1111000	-0.0000613
10	C	C8	1.4233990	2.6872720	1.2588706
11	C	C9	-0.3842648	1.3064663	2.0872504
12	H	H4	-1.2963958	-0.0181440	0.6698103
13	H	H7	1.9085981	2.4281561	-0.8084713
14	H	H8	2.1795727	3.4397135	1.4311937
15	H	H9	-1.0315881	0.9864734	2.9017992
16	C	C10	-0.4605186	-1.8381581	-2.6155977
17	H	H11	-0.9621526	-1.3995086	-3.4768142
18	C	C11	-0.7271914	-3.1200015	-2.3225197
19	H	H12	-0.2622053	-3.6350699	-1.4868079
20	C	C12	-1.6764426	-3.8919940	-3.1511922
21	O	O1	-2.2963893	-3.4692799	-4.1086108
22	O	O2	-1.7767426	-5.1674604	-2.7017280
23	C	C13	-2.6724119	-6.0064804	-3.4449387
24	H	H5	-3.6915473	-5.6111880	-3.4077610
25	H	H13	-2.6236443	-6.9849591	-2.9658000
26	H	H14	-2.3589465	-6.0737342	-4.4903650
27	F	F1	1.0067983	0.3562810	-3.8353220
28	F	F2	2.4596795	0.3884930	-2.1653710
29	N	N1	0.6944204	2.8088096	3.6232082
30	H	H2	0.0386330	2.4191320	4.2864124
31	C	C14	1.5413221	3.7860268	4.1073753
32	C	C15	1.3137490	4.1357926	5.5722271
33	H	H10	2.2809986	4.3566528	6.0286279
34	H	H15	0.8180166	3.3435332	6.1430953
35	H	H16	0.7007428	5.0424378	5.6345030
36	O	O3	2.3867645	4.3535694	3.4326912

pNHCOMe_TS2 (S-TS1e)

G = -1060.43552

iv = i111

S^2 = 0.5197

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C	-1.6566376	3.6562397	-1.3429537
2	C C2	-2.8091997	2.9353394	-1.4526862
3	C C3	-2.9883888	1.7254383	-0.7364660
4	C C4	-0.5135962	3.0231753	-0.6280485
5	C C5	-0.3433739	1.5860810	-1.0289568
6	H H	-1.5148126	4.6412060	-1.7738071
7	H H7	-3.5988899	3.2442342	-2.1348052
8	H H8	-2.5298791	1.5721052	0.2307956
9	H H12	-0.7556016	1.3301491	-1.9960268
10	F F1	0.6542942	3.7247365	-0.8777820
11	F F2	-0.6747975	3.1267197	0.7632907
12	C C1	0.6022874	0.6913855	-0.4611539

13	C	C6	2.4405540	-1.1914785	0.6027409
14	C	C7	0.8445679	-0.5530769	-1.1050284
15	C	C8	1.3194300	0.9470487	0.7398929
16	C	C9	2.2230487	0.0367430	1.2593855
17	C	C10	1.7360915	-1.4694016	-0.5875130
18	H	H2	0.3128024	-0.7833655	-2.0245305
19	H	H6	1.1551133	1.8812405	1.2618904
20	H	H5	2.7621316	0.2510878	2.1710956
21	H	H3	1.8992264	-2.4146737	-1.1015990
22	C	C11	-4.0012680	0.7610459	-1.1655510
23	O	O1	-4.6951792	0.8583805	-2.1659369
24	O	O2	-4.0858484	-0.2853448	-0.3010219
25	C	C12	-5.0537372	-1.2823288	-0.6490319
26	H	H1	-6.0577532	-0.8501166	-0.6890899
27	H	H9	-4.9935350	-2.0375100	0.1359261
28	H	H10	-4.8235019	-1.7226931	-1.6237780
29	N	N1	3.3253262	-2.1722419	1.0681610
30	H	H11	3.3779714	-3.0037897	0.4949480
31	C	C13	4.1130617	-2.1734547	2.2098966
32	O	O3	4.1640704	-1.2460722	3.0004609
33	C	C14	4.8948472	-3.4621882	2.4184878
34	H	H4	5.0617664	-4.0281969	1.4960790
35	H	H13	4.3512309	-4.1022614	3.1235117
36	H	H14	5.8581785	-3.2141621	2.8692043

pMe_SM (S1f)

G = -891.799548

iv = none

Cartesian Coordinates (Angstroms)

Atom	X	Y	Z
-----	-----	-----	-----
1 C C1	1.3804811	0.7111935	-1.7861492
2 C C2	0.2866776	1.1001233	-0.8747163
3 C C3	0.6545210	-0.4190597	-1.1326506
4 H H3	-0.6218868	1.4031422	-1.3943647
5 H H6	1.1922568	-0.8807027	-0.3076510
6 C C4	0.4999533	1.7001255	0.4795990
7 C C5	0.8180760	2.8514766	3.0485519
8 C C6	-0.3228548	1.3150779	1.5462997
9 C C7	1.4852563	2.6683170	0.7125421
10 C C8	1.6392027	3.2305764	1.9790346
11 C C9	-0.1651259	1.8825139	2.8089096
12 H H4	-1.0877670	0.5590569	1.3853688
13 H H7	2.1401209	2.9749506	-0.0963091
14 H H8	2.4142963	3.9768668	2.1390680
15 H H9	-0.8130135	1.5654741	3.6230621
16 C C10	-0.2649214	-1.2725938	-1.8936981
17 H H11	-0.7636714	-0.8315028	-2.7553215
18 C C11	-0.5361347	-2.5538572	-1.6025425
19 H H12	-0.0747847	-3.0711972	-0.7662466
20 C C12	-1.4852845	-3.3226127	-2.4346723
21 O O1	-2.1001038	-2.8977963	-3.3944603
22 O O2	-1.5911644	-4.5978163	-1.9858790

23	C	C13	-2.4873711	-5.4339559	-2.7316450
24	H	H5	-3.5055214	-5.0358820	-2.6967921
25	H	H13	-2.4426931	-6.4127267	-2.2526976
26	H	H14	-2.1715024	-5.5017247	-3.7763096
27	F	F1	1.2180697	0.9082906	-3.1158431
28	F	F2	2.6714102	0.9320561	-1.4462235
29	C	C14	0.9777194	3.4838681	4.4113072
30	H	H2	2.0336375	3.6363601	4.6612334
31	H	H1	0.5308679	2.8644512	5.1956799
32	H	H10	0.4912538	4.4675073	4.4535157

pMe_TS2 (S-TS1f)

G = -891.760479

iv = i127

S^2 = 0.5260

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z

1	C C	-3.2411448	-1.2102549	-0.6227091
2	C C2	-2.4874199	-2.3441240	-0.6934144
3	C C3	-1.2165378	-2.4161221	-0.0674915
4	C C4	-2.5935456	0.0064873	-0.0586121
5	C C5	-1.1983952	0.1824275	-0.5854099
6	H H	-4.2614524	-1.1355115	-0.9823186
7	H H7	-2.8158369	-3.2012848	-1.2777478
8	H H8	-1.0091756	-1.8761448	0.8464066
9	H H12	-1.0032239	-0.2927791	-1.5377288
10	F F1	-3.3510705	1.1303709	-0.3428770
11	F F2	-2.5823967	-0.0427127	1.3458421
12	C C1	-0.3037842	1.2109320	-0.1706401
13	C C6	1.5609839	3.2326926	0.5674210
14	C C7	0.8735575	1.4472643	-0.9302234
15	C C8	-0.5101283	2.0163608	0.9806499
16	C C9	0.4012146	3.0022437	1.3260025
17	C C10	1.7792142	2.4286188	-0.5661451
18	H H2	1.0593694	0.8395307	-1.8125398
19	H H6	-1.3893384	1.8548016	1.5913664
20	H H5	0.2168835	3.6080511	2.2102775
21	H H3	2.6724990	2.5831353	-1.1672359
22	C C11	-0.2498418	-3.4333873	-0.4866398
23	O O1	-0.4115242	-4.2305043	-1.3975294
24	O O2	0.8750528	-3.3888637	0.2741351
25	C C12	1.8774345	-4.3551328	-0.0657145
26	H H1	1.5029010	-5.3711438	0.0908148
27	H H9	2.7184454	-4.1524296	0.5986839
28	H H10	2.1789390	-4.2503344	-1.1117792
29	C C13	2.5350013	4.3207831	0.9419171
30	H H4	3.5725585	3.9931121	0.8114697
31	H H11	2.4041978	4.6352923	1.9820438
32	H H13	2.3965637	5.2086255	0.3097265

pCl_SM (S1i)

G = -1312.11478

iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	1.0629383	1.4158113	-1.5049339
2	C C2	0.1398042	1.5398942	-0.3527260
3	C C3	0.6951483	0.1310238	-0.8500301
4	H H3	-0.8906327	1.7074024	-0.6573324
5	H H6	1.4579103	-0.2833529	-0.1946151
6	C C4	0.4782137	2.0756827	0.9941942
7	C C5	0.9765783	3.0761558	3.5642872
8	C C6	-0.5657112	2.5572507	1.7980247
9	C C7	1.7836200	2.1102276	1.5110443
10	C C8	2.0351636	2.6052449	2.7889840
11	C C9	-0.3281184	3.0574004	3.0764095
12	H H4	-1.5847155	2.5400634	1.4200373
13	H H7	2.6183172	1.7625201	0.9131847
14	H H8	3.0474087	2.6301134	3.1785618
15	H H9	-1.1452559	3.4269295	3.6864817
16	C C10	-0.2266630	-0.8184726	-1.4845070
17	H H11	-0.9308160	-0.4240651	-2.2149550
18	C C11	-0.2609302	-2.1326999	-1.2185126
19	H H12	0.4155811	-2.5990981	-0.5081290
20	C C12	-1.2386765	-3.0086821	-1.8988252
21	O O1	-2.0799745	-2.6502155	-2.7007146
22	O O2	-1.0788318	-4.2959737	-1.5072398
23	C C13	-1.9833911	-5.2345541	-2.1077452
24	H H5	-3.0166572	-5.0010274	-1.8356089
25	H H13	-1.6960144	-6.2107232	-1.7156897
26	H H14	-1.8922845	-5.2144020	-3.1970391
27	F F1	0.5750157	1.6800851	-2.7386468
28	F F2	2.3408549	1.8533815	-1.4198456
29	Cl C11	1.2921180	3.7040797	5.1758867

pCl_TS2 (S-TS1i)

G = -1312.07449

iv = i128

S^2 = 0.5583

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C	-0.7144027	2.9378750	-0.6746949
2	C C2	-1.8511631	2.1867377	-0.7221207
3	C C3	-1.9368194	0.9513782	-0.0304521
4	C C4	0.4928846	2.3128350	-0.0633652
5	C C5	0.6661820	0.8922119	-0.5199505
6	H H	-0.6282091	3.9366106	-1.0883615
7	H H7	-2.6978162	2.4866973	-1.3362765

8	H	H8	-1.4114849	0.7924321	0.9016563
9	H	H12	0.2049960	0.6564334	-1.4701264
10	F	F1	1.6232164	3.0494124	-0.3706913
11	F	F2	0.4255219	2.3689785	1.3382104
12	C	C1	1.6791377	0.0074726	-0.0450402
13	C	C6	3.6443348	-1.8165463	0.7981102
14	C	C7	1.9135574	-1.2045907	-0.7476448
15	C	C8	2.4683437	0.2617319	1.1090983
16	C	C9	3.4425531	-0.6352618	1.5198311
17	C	C10	2.8790198	-2.1090211	-0.3356613
18	H	H2	1.3216660	-1.4240667	-1.6324540
19	H	H6	2.3093340	1.1715125	1.6741328
20	H	H5	4.0459134	-0.4291387	2.3977672
21	H	H3	3.0491448	-3.0301417	-0.8828047
22	C	C11	-2.9471157	-0.0383071	-0.4165050
23	O	O1	-3.7156678	0.0695285	-1.3586056
24	O	O2	-2.9270737	-1.1113717	0.4138963
25	C	C12	-3.8792252	-2.1384886	0.1055527
26	H	H1	-4.9007242	-1.7588757	0.2013831
27	H	H9	-3.6978636	-2.9334902	0.8297628
28	H	H10	-3.7348658	-2.5053594	-0.9146126
29	Cl	Cl1	4.8766261	-2.9471882	1.3199661

pBr_TS2 (S1j)

G = -3425.80123

iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C1	1.3562471	2.6029050	1.2666918
2	C C4	-0.6298350	2.8110397	3.2079051
3	C C2	0.7185734	1.4376814	1.7172858
4	C C6	1.0156669	3.8582232	1.7679532
5	C C5	0.0187999	3.9511614	2.7362616
6	C C3	-0.2767281	1.5624892	2.6997928
7	H H6	1.5175193	4.7487317	1.4057904
8	C C7	1.1124539	0.1354154	1.1133198
9	C C8	0.9466757	-1.1990873	1.7365377
10	C C9	0.0186687	-0.9076405	0.6097841
11	H H2	1.9701604	0.1879599	0.4468276
12	H H9	-0.9951829	-0.6472929	0.9066102
13	F F1	0.4393115	-1.3158115	2.9860755
14	F F2	1.9255881	-2.1146176	1.5561425
15	C C10	0.1900134	-1.5358200	-0.7050430
16	H H8	1.1912244	-1.8658255	-0.9766831
17	C C11	-0.7967142	-1.7231741	-1.5941015
18	H H10	-1.8237509	-1.4308560	-1.3952506
19	C C12	-0.5098685	-2.3537982	-2.9004189
20	O O1	0.5832979	-2.7182529	-3.2898171
21	O O2	-1.6438204	-2.4791110	-3.6311886
22	C C13	-1.4742752	-3.0839992	-4.9217103
23	H H7	-2.4696650	-3.1096851	-5.3663640
24	H H11	-1.0703997	-4.0951857	-4.8222437

25	H	H12	-0.7925507	-2.4909454	-5.5376410
26	H	H13	-1.4009261	2.8927997	3.9661981
27	H	H3	2.1299839	2.5312127	0.5064749
28	H	H1	-0.7762866	0.6814874	3.0855627
29	Br	Br1	-0.4741812	5.6699962	3.4252475

pBr_TS2 (S-TS1j)

G = -3425.76075

iv = i133

S^2 = 0.5546

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
1	C C	-0.8155237	2.9537288	-0.5005872
2	C C2	-1.9361827	2.1779372	-0.5224954
3	C C3	-1.9545462	0.9087785	0.1112560
4	C C4	0.4367717	2.3287633	0.0126214
5	C C5	0.6140255	0.9352300	-0.5191788
6	H H	-0.7736767	3.9729385	-0.8683150
7	H H7	-2.8226476	2.4857335	-1.0731278
8	H H8	-1.3765984	0.7210921	1.0060768
9	H H12	0.1141262	0.7341125	-1.4577151
10	F F1	1.5334149	3.1042878	-0.3197891
11	F F2	0.4451122	2.3186286	1.4168530
12	C C1	1.6689735	0.0538574	-0.1377762
13	C C6	3.7061034	-1.7621794	0.5299251
14	C C7	1.8972427	-1.1169033	-0.9086001
15	C C8	2.5045807	0.2725334	0.9903035
16	C C9	3.5144744	-0.6203524	1.3151728
17	C C10	2.8992134	-2.0179835	-0.5834434
18	H H2	1.2701520	-1.3074775	-1.7757957
19	H H6	2.3514741	1.1504878	1.6046668
20	H H5	4.1489201	-0.4387045	2.1760502
21	H H3	3.0594091	-2.9063750	-1.1843230
22	C C11	-2.9634732	-0.0861036	-0.2659838
23	O O1	-3.7881729	0.0484362	-1.1556234
24	O O2	-2.8700630	-1.1978847	0.5058995
25	C C12	-3.8159820	-2.2322315	0.2024378
26	H H1	-4.8390917	-1.8783145	0.3588484
27	H H9	-3.5853585	-3.0496220	0.8865239
28	H H10	-3.7123637	-2.5580693	-0.8366212
29	Br Br1	5.0896863	-2.9943441	0.9927401

pCF3_SM (S1k)

G = -1189.54302

iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	1.3905282	0.7055646	-1.7814656
2	C C2	0.2860935	1.0987292	-0.8829945
3	C C3	0.6555983	-0.4194453	-1.1289813
4	H H3	-0.6187309	1.4030623	-1.4078014
5	H H6	1.1862778	-0.8794566	-0.2982996
6	C C4	0.4892453	1.7050214	0.4698021
7	C C5	0.7850619	2.8541838	3.0090151
8	C C6	-0.3390294	1.3145880	1.5311086
9	C C7	1.4671871	2.6831757	0.6967647
10	C C8	1.6144269	3.2544324	1.9584724
11	C C9	-0.1953346	1.8829654	2.7939078
12	H H4	-1.1003497	0.5572787	1.3640782
13	H H7	2.1162669	2.9943651	-0.1141762
14	H H8	2.3696859	4.0159093	2.1260048
15	H H9	-0.8429598	1.5783240	3.6088363
16	C C10	-0.2602967	-1.2750697	-1.8940802
17	H H11	-0.7489088	-0.8381627	-2.7635918
18	C C11	-0.5380935	-2.5527254	-1.5965082
19	H H12	-0.0868739	-3.0667832	-0.7526672
20	C C12	-1.4830539	-3.3227510	-2.4344922
21	O O1	-2.0871486	-2.8970320	-3.4003378
22	O O2	-1.5959496	-4.5945813	-1.9822844
23	C C13	-2.4876238	-5.4324597	-2.7329928
24	H H5	-3.5059636	-5.0348042	-2.7029678
25	H H13	-2.4440293	-6.4107954	-2.2533911
26	H H14	-2.1657269	-5.4996729	-3.7757532
27	F F1	1.2442136	0.8987727	-3.1118325
28	F F2	2.6753105	0.9304317	-1.4225751
29	C C14	0.9962693	3.4407113	4.3786791
30	F F3	2.0580250	2.8770349	5.0005748
31	F F4	1.2410832	4.7691376	4.3188786
32	F F5	-0.0752004	3.2600513	5.1810706

pCF3_TS2 (S-TS1k)

G = -1189.50258

iv = i125

S^2 = 0.6218

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C	-3.2797245	-1.2121588	-0.6934350
2	C C2	-2.5116752	-2.3389138	-0.7257791
3	C C3	-1.2485162	-2.3795873	-0.0840931
4	C C4	-2.6572962	0.0335206	-0.1545598

5	C	C5	-1.2544317	0.2152299	-0.6599795
6	H	H	-4.2960100	-1.1609020	-1.0682988
7	H	H7	-2.8238888	-3.2146668	-1.2915952
8	H	H8	-1.0537595	-1.8003942	0.8086027
9	H	H12	-1.0478156	-0.2542267	-1.6132811
10	F	F1	-3.4240074	1.1344557	-0.4887828
11	F	F2	-2.6735928	0.0180651	1.2469293
12	C	C1	-0.3414879	1.2165497	-0.2128568
13	C	C6	1.5803490	3.1115657	0.6072974
14	C	C7	0.8566129	1.4185644	-0.9486864
15	C	C8	-0.5428462	2.0040522	0.9524360
16	C	C9	0.4027038	2.9375492	1.3464393
17	C	C10	1.8018631	2.3468040	-0.5454231
18	H	H2	1.0317660	0.8247198	-1.8418622
19	H	H6	-1.4418121	1.8672061	1.5393060
20	H	H5	0.2384953	3.5271246	2.2426382
21	H	H3	2.7160970	2.4785463	-1.1145699
22	C	C11	-0.2546706	-3.3889999	-0.4658764
23	O	O1	-0.3981751	-4.2218233	-1.3459778
24	O	O2	0.8666229	-3.2780076	0.2884928
25	C	C12	1.9083338	-4.2149400	-0.0204087
26	H	H1	1.5696190	-5.2398952	0.1571965
27	H	H9	2.7348424	-3.9637807	0.6454817
28	H	H10	2.2139805	-4.1210829	-1.0664875
29	C	C13	2.5837831	4.1520212	1.0246198
30	F	F3	3.8341185	3.8301821	0.6250771
31	F	F4	2.6119925	4.3099328	2.3660114
32	F	F5	2.2985296	5.3632898	0.4914248

pCN_SM (S11)

G = -944.753991

iv = none

Cartesian Coordinates (Angstroms)

Atom	X	Y	Z

1 C C1	1.0319461	1.2778849	-1.6937737
2 C C2	0.0960445	1.4105239	-0.5500448
3 C C3	0.6562833	-0.0010430	-1.0350636
4 H H3	-0.9313648	1.5780907	-0.8640662
5 H H6	1.4120200	-0.4125834	-0.3698562
6 C C4	0.4258318	1.9500567	0.7956994
7 C C5	0.9120884	2.9620527	3.3793517
8 C C6	-0.6242761	2.4441046	1.5866669
9 C C7	1.7293305	1.9753284	1.3219641
10 C C8	1.9710244	2.4727423	2.5969470
11 C C9	-0.3928655	2.9454223	2.8618626
12 H H4	-1.6382702	2.4325100	1.1963269
13 H H7	2.5640968	1.6184703	0.7302804
14 H H8	2.9815089	2.4894410	2.9924417
15 H H9	-1.2149625	3.3233372	3.4609522
16 C C10	-0.2624683	-0.9535721	-1.6712338
17 H H11	-0.9582229	-0.5639595	-2.4121110
18 C C11	-0.3001821	-2.2650782	-1.3947489

19	H	H12	0.3681632	-2.7265686	-0.6734562
20	C	C12	-1.2719021	-3.1459489	-2.0797017
21	O	O1	-2.1015530	-2.7909135	-2.8947798
22	O	O2	-1.1196444	-4.4287818	-1.6745291
23	C	C13	-2.0183944	-5.3721133	-2.2777354
24	H	H5	-3.0547174	-5.1307052	-2.0252943
25	H	H13	-1.7410356	-6.3439496	-1.8683700
26	H	H14	-1.9089291	-5.3660210	-3.3654563
27	F	F1	0.5541761	1.5386864	-2.9307855
28	F	F2	2.3079413	1.7167013	-1.5969534
29	C	C14	1.1623931	3.4751953	4.6940105
30	N	N1	1.3659400	3.8906899	5.7614562

pCN_TS2 (S-TS1)

G = -944.713152

iv = i137

S^2 = 0.6312

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C	-3.1090839	-0.9324188	-0.6288647
2	C C2	-2.3299329	-2.0510375	-0.6568641
3	C C3	-1.0677673	-2.0729066	-0.0120571
4	C C4	-2.4941114	0.3212685	-0.0957804
5	C C5	-1.0923355	0.5099731	-0.6068847
6	H H	-4.1244855	-0.8900055	-1.0067117
7	H H7	-2.6301789	-2.9322518	-1.2195622
8	H H8	-0.8846812	-1.4899310	0.8805992
9	H H12	-0.8991695	0.0591984	-1.5725171
10	F F1	-3.2673527	1.4146714	-0.4344781
11	F F2	-2.5075325	0.3085765	1.3047115
12	C C1	-0.1713863	1.4984922	-0.1545684
13	C C6	1.7710068	3.3804744	0.6695429
14	C C7	1.0077671	1.7263356	-0.9176674
15	C C8	-0.3437069	2.2530012	1.0391001
16	C C9	0.6063549	3.1763799	1.4373984
17	C C10	1.9601638	2.6448086	-0.5183662
18	H H2	1.1573829	1.1623713	-1.8345869
19	H H6	-1.2283877	2.0984419	1.6431480
20	H H5	0.4639545	3.7456288	2.3504729
21	H H3	2.8537470	2.8065734	-1.1128248
22	C C11	-0.0618197	-3.0751446	-0.3826549
23	O O1	-0.1945299	-3.9142076	-1.2579497
24	O O2	1.0527218	-2.9477331	0.3771840
25	C C12	2.1026021	-3.8824063	0.0888101
26	H H1	1.7739496	-4.9044379	0.2965142
27	H H9	2.9289161	-3.6062448	0.7440922
28	H H10	2.4016408	-3.8142906	-0.9604735
29	C C13	2.7594867	4.3219007	1.0961977
30	N N1	3.5667676	5.0849199	1.4450410

pNO2_SM (S1m)

G = -1057.00885

iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	0.9606723	1.1812896	-1.8531310
2	C C2	0.0349246	1.3009843	-0.6988658
3	C C3	0.6076703	-0.1026353	-1.1926552
4	H H3	-0.9977203	1.4565647	-1.0014392
5	H H6	1.3756553	-0.5061260	-0.5366140
6	C C4	0.3728128	1.8414923	0.6438564
7	C C5	0.8678980	2.8424244	3.1975676
8	C C6	-0.6762743	2.3263099	1.4439078
9	C C7	1.6821014	1.8755084	1.1574627
10	C C8	1.9328487	2.3726145	2.4314691
11	C C9	-0.4396627	2.8281044	2.7184806
12	H H4	-1.6930405	2.3069563	1.0617016
13	H H7	2.5138430	1.5262153	0.5574401
14	H H8	2.9367882	2.4057915	2.8364874
15	H H9	-1.2428769	3.2030971	3.3406388
16	C C10	-0.3076445	-1.0649760	-1.8194009
17	H H11	-1.0183375	-0.6823453	-2.5496635
18	C C11	-0.3245048	-2.3775919	-1.5468055
19	H H12	0.3591994	-2.8329974	-0.8361436
20	C C12	-1.2937805	-3.2687425	-2.2226481
21	O O1	-2.1399540	-2.9205701	-3.0234733
22	O O2	-1.1171806	-4.5510993	-1.8270998
23	C C13	-2.0109161	-5.5043847	-2.4224850
24	H H5	-3.0469881	-5.2780942	-2.1555785
25	H H13	-1.7149043	-6.4738903	-2.0208165
26	H H14	-1.9155940	-5.4923632	-3.5114841
27	F F1	0.4660604	1.4392177	-3.0836845
28	F F2	2.2315837	1.6358706	-1.7681280
29	N N1	1.1310496	3.3684380	4.5444891
30	O O3	2.2963591	3.3664470	4.9414150
31	O O4	0.1699121	3.7784903	5.1952003

pNO2_TS2 (S-TS1m)

G = -1056.96757

iv = i146

S^2 = 0.6042

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C	-1.0505402	3.1613109	-0.7618680
2	C C2	-2.1778288	2.3962176	-0.7922475
3	C C3	-2.2302077	1.1537247	-0.1084434
4	C C4	0.1781153	2.5460614	-0.1766937
5	C C5	0.3521525	1.1241184	-0.6346538

6	H	H	-0.9837357	4.1629145	-1.1721862
7	H	H7	-3.0406011	2.6876625	-1.3875016
8	H	H8	-1.6896861	0.9984542	0.8158345
9	H	H12	-0.1009347	0.8923349	-1.5900162
10	F	F1	1.2940308	3.2870577	-0.5132652
11	F	F2	0.1336866	2.6051720	1.2220645
12	C	C1	1.3486363	0.2263447	-0.1484016
13	C	C6	3.2565094	-1.6254149	0.7179857
14	C	C7	1.5537745	-0.9991868	-0.8410035
15	C	C8	2.1409860	0.4810842	1.0053119
16	C	C9	3.0916634	-0.4325935	1.4277239
17	C	C10	2.4929002	-1.9212115	-0.4151085
18	H	H2	0.9577564	-1.2107602	-1.7245399
19	H	H6	2.0011554	1.4019270	1.5562857
20	H	H5	3.7062824	-0.2451737	2.2997809
21	H	H3	2.6528627	-2.8563351	-0.9375804
22	C	C11	-3.2254250	0.1435432	-0.4913149
23	O	O1	-4.0094962	0.2502472	-1.4195601
24	O	O2	-3.1620420	-0.9377572	0.3211888
25	C	C12	-4.0918647	-1.9882898	0.0159936
26	H	H1	-5.1206382	-1.6338762	0.1248956
27	H	H9	-3.8819071	-2.7821657	0.7331040
28	H	H10	-3.9474514	-2.3441567	-1.0078561
29	N	N1	4.2574823	-2.5951503	1.1752864
30	O	O3	4.9390762	-2.2930285	2.1558377
31	O	O4	4.3552888	-3.6530746	0.5509473

Phenolate Computational Attempts

Phenolate Intermediate - before opt (S7)

Cartesian Coordinates (Angstroms)

Atom	X	Y	Z

1 H H1	-1.2586477	1.7626345	-0.6723651
2 C C1	-0.9593205	2.4202187	0.1371390
3 C C4	-0.2979218	4.1741696	2.1509685
4 C C2	0.2137577	2.1675758	0.8567993
5 C C6	-1.7765691	3.5228465	0.4322519
6 C C5	-1.4837140	4.4444830	1.4487606
7 C C3	0.5323914	3.0761858	1.8689170
8 H H6	-2.6812601	3.6767329	-0.1548029
9 H H3	1.4327505	2.9470927	2.4620282
10 H H4	-0.0103865	4.8530754	2.9532110
11 C C7	1.0948251	0.9939612	0.5158621
12 C C8	1.6506051	0.0771063	1.5469454
13 C C9	0.5283833	-0.4138679	0.7043742
14 H H9	-0.4263771	-0.5138067	1.2125096
15 F F1	1.4564273	0.2726912	2.8952971
16 F F2	2.9162592	-0.4510259	1.3985080
17 C C10	0.7675142	-1.4081322	-0.3507062
18 H H8	1.7384715	-1.3585969	-0.8450345
19 C C11	-0.1058439	-2.3552803	-0.7279450
20 H H10	-1.0813320	-2.4452598	-0.2647076
21 C C12	0.2326341	-3.3145459	-1.7973213

22	O	O1	1.2898992	-3.3544446	-2.4044986
23	O	O2	-0.8331080	-4.1340864	-1.9776217
24	C	C13	-0.6385568	-5.1147946	-2.9957679
25	H	H7	0.1956046	-5.7751339	-2.7383907
26	H	H11	-0.4683390	-4.6343656	-3.9644557
27	H	H12	-1.5482733	-5.7177461	-3.0641878
28	H	H2	1.7504441	1.1589466	-0.3355664
29	O	O3	-2.2303178	5.4433666	1.7097995

Phenolate Intermediate - after geometry optimisation (Total Charge = -1) (S8)

Spartan'10: G = -927.192975, iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	H H1	1.2808579	3.0897020	0.6306506
2	C C1	0.7034081	2.9159564	1.5382962
3	C C4	-0.7906655	2.3886376	3.8520824
4	C C2	0.4615034	1.5430458	1.9214290
5	C C6	0.2458640	3.9704274	2.2653526
6	C C5	-0.5409795	3.7856705	3.4865468
7	C C3	-0.3177473	1.3411958	3.1233992
8	H H6	0.4449109	4.9963243	1.9647671
9	H H3	-0.5169180	0.3229192	3.4373228
10	H H4	-1.3749331	2.2249088	4.7547202
11	C C7	0.9940677	0.5293339	1.1434880
12	C C8	0.7754011	-0.9401199	1.1873830
13	C C9	-0.3501997	-1.1906383	0.2744310
14	H H2	1.5802893	0.8142811	0.2724571
15	H H9	-1.3228352	-0.8910906	0.6559472
16	F F1	0.5348639	-1.4046105	2.4809257
17	F F2	1.9329416	-1.5751813	0.7622446
18	C C10	-0.1909201	-1.6214304	-1.0372029
19	H H8	0.8233621	-1.8602679	-1.3499328
20	C C11	-1.1941300	-1.8064516	-1.9796295
21	H H10	-2.2305457	-1.5924159	-1.7330885
22	C C12	-0.9905567	-2.2883093	-3.3131497
23	O O1	-1.8563495	-2.4639529	-4.1707136
24	O O2	0.3441622	-2.5618713	-3.6054491
25	C C13	0.5736672	-3.0254089	-4.9252715
26	H H7	1.6529881	-3.1873279	-5.0035254
27	H H11	0.2512599	-2.2918886	-5.6739473
28	H H12	0.0402419	-3.9627018	-5.1235976
29	O O3	-0.9630088	4.7412646	4.1640642

Phenolate VCPR Transition State - before optimisation (S-TS4)

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
-----			-----	-----	-----
1	C	C	-0.6651935	2.9186490	-0.6746263
2	C	C2	-1.8137598	2.1842964	-0.7359817
3	C	C3	-1.9350686	0.9553256	-0.0421748
4	C	C4	0.5233634	2.2823951	-0.0455186
5	C	C5	0.6948050	0.8628918	-0.5022731
6	H	H	-0.5610292	3.9164781	-1.0861974
7	H	H7	-2.6456154	2.4980068	-1.3636021
8	H	H8	-1.4145005	0.7833400	0.8899571
9	H	H12	0.2184147	0.6212074	-1.4429874
10	F	F1	1.6665307	3.0129670	-0.3296920
11	F	F2	0.4403775	2.3353397	1.3588655
12	C	C1	1.7068249	-0.0174399	-0.0321843
13	C	C6	3.6761591	-1.8539552	0.8237148
14	C	C7	1.9439024	-1.2362722	-0.7286087
15	C	C8	2.4992798	0.2380831	1.1207706
16	C	C9	3.4682911	-0.6598382	1.5330731
17	C	C10	2.9028556	-2.1391946	-0.3137085
18	H	H2	1.3507707	-1.4573798	-1.6122523
19	H	H6	2.3414821	1.1505066	1.6818723
20	H	H5	4.0689047	-0.4445596	2.4153719
21	H	H3	3.0786691	-3.0670939	-0.8485266
22	C	C11	-2.9629413	-0.0102329	-0.4313316
23	O	O1	-3.7262018	0.1075837	-1.3776194
24	O	O2	-2.9723572	-1.0843205	0.4028114
25	C	C12	-3.9442819	-2.0887908	0.0885536
26	H	H1	-4.9585600	-1.6892821	0.1829482
27	H	H9	-3.7823516	-2.8906294	0.8103071
28	H	H10	-3.8063206	-2.4561354	-0.9325037
29	O	O3	4.6075507	-2.7719458	1.1915431

Phenolate VCPR Transition State - after optimisation (Total Charge = -1) (S-TS4)

Spartan'10: G = -927.176731, iv = i107, S^2 = 0.0001

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
-----			-----	-----	-----
1	C	C	-0.7028045	3.1038515	-0.7049473
2	C	C2	-1.8062730	2.3228423	-0.6517956
3	C	C3	-1.7138557	1.0591249	0.0372463
4	C	C4	0.5346220	2.4555659	-0.2063623
5	C	C5	0.5468191	0.9779598	-0.5446132
6	H	H	-0.6564795	4.1166443	-1.0921863
7	H	H7	-2.7285382	2.5909061	-1.1690556
8	H	H8	-1.3345859	1.0349481	1.0507740
9	H	H12	0.1757076	0.8044173	-1.5488622
10	F	F1	1.6590641	3.0695692	-0.7550712
11	F	F2	0.7014846	2.6522265	1.1777744

12	C	C1	1.4400750	0.0208918	-0.0467964
13	C	C6	3.2567048	-2.0801602	0.8438868
14	C	C7	1.6307000	-1.1953743	-0.7939404
15	C	C8	2.1821669	0.1323339	1.1826385
16	C	C9	3.0387980	-0.8459548	1.5968119
17	C	C10	2.4790717	-2.1830413	-0.3899775
18	H	H2	1.0690408	-1.3098361	-1.7214063
19	H	H6	2.0580032	1.0296004	1.7780306
20	H	H5	3.5991611	-0.7413867	2.5237495
21	H	H3	2.6118024	-3.0895804	-0.9767112
22	C	C11	-2.5691403	-0.0267344	-0.3637043
23	O	O1	-3.2566035	-0.0943725	-1.3823008
24	O	O2	-2.5362285	-1.0691777	0.5430958
25	C	C12	-3.2875790	-2.2130706	0.1628205
26	H	H1	-4.3600864	-1.9901305	0.1056993
27	H	H9	-3.1030485	-2.9638402	0.9357245
28	H	H10	-2.9691897	-2.5938533	-0.8138878
29	O	O3	4.0411914	-2.9743692	1.2233663

Cartesian Coordinates for Alkenoates

2-pyridyl

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
-----			-----	-----	-----
1	H	H1	-0.8129841	0.1160651	2.5439774
2	C	C1	-0.4744235	1.0344220	2.0725097
3	C	C4	0.3943767	3.2735988	0.7940912
4	C	C2	-0.0405019	1.0174219	0.7369124
5	C	C6	-0.4631111	2.2371419	2.7754328
6	C	C5	-0.0197364	3.3864943	2.1263621
7	N	N1	0.3892637	2.1317818	0.1089558
8	H	H4	0.7478073	4.1512814	0.2545482
9	C	C7	-0.0462173	-0.2423610	-0.0175247
10	H	H7	-0.3962029	-1.1224421	0.5161015
11	C	C8	0.3475029	-0.3625529	-1.2967223
12	H	H8	0.7005955	0.5006879	-1.8504334
13	C	C9	0.3445492	-1.6289205	-2.0555207
14	O	O1	-0.1019638	-2.6869584	-1.3305635
15	O	O2	0.7050368	-1.7230232	-3.2132418
16	C	C10	-0.1160287	-3.9392129	-2.0292282
17	H	H2	0.8925777	-4.2122539	-2.3520599
18	H	H9	-0.7640376	-3.8835557	-2.9083329
19	H	H10	-0.5000801	-4.6695127	-1.3157786
20	H	H5	-0.7941878	2.2743412	3.8097505
21	H	H14	0.0077656	4.3475572	2.6307644

2-thiazoyl

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	-0.5454436	0.0226715	0.5437647
2	H H2	-1.5032974	0.5360423	0.5852073
3	C C2	0.2303064	0.1838704	-0.5432247
4	H H1	1.1980552	-0.2977856	-0.6521511
5	C C3	-0.2472724	-0.7859274	1.7085530
6	N N1	-1.0663557	-0.8859838	2.7293949
7	C C5	-0.5603522	-1.7087601	3.6968361
8	C C6	0.6653319	-2.2605474	3.4372234
9	S S1	1.2388862	-1.7305197	1.8953617
10	H H8	-1.1365473	-1.8812683	4.5989361
11	H H9	1.2465596	-2.9321230	4.0541349
12	C C7	-0.2190138	1.0410760	-1.6602688
13	O O2	-1.2669478	1.6552306	-1.7114256
14	O O3	0.7078642	1.0543694	-2.6485952
15	C C8	0.3693540	1.8522579	-3.7929022
16	H H3	1.2024448	1.7372158	-4.4868972
17	H H4	0.2476541	2.9011807	-3.5085135
18	H H6	-0.5612263	1.4990010	-4.2454338

piperonyl

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	H H1	-0.3968724	1.5543129	-1.3560687
2	C C1	-0.2192789	1.5267201	-0.2859382
3	C C4	0.2450682	1.4866853	2.5233457
4	C C2	0.0211857	0.2990016	0.3837331
5	C C6	-0.2191316	2.6804777	0.4651621
6	C C5	0.0089855	2.6658740	1.8389725
7	C C3	0.2470043	0.3044367	1.7726828
8	H H3	0.4295927	-0.6324651	2.2881308
9	H H4	0.4213928	1.4824670	3.5934008
10	C C7	0.0240148	-0.9245584	-0.4176954
11	H H7	-0.1664618	-0.7832148	-1.4795257
12	C C8	0.2353728	-2.1861381	0.0068761
13	H H8	0.4339741	-2.4278969	1.0460958
14	C C9	0.2267218	-3.3702372	-0.8687748
15	O O1	-0.0136184	-3.0745762	-2.1734061
16	O O2	0.4168139	-4.5054560	-0.4720569
17	C C10	-0.0228284	-4.2012089	-3.0594418
18	H H2	-0.8102129	-4.9071183	-2.7801998
19	H H9	0.9393850	-4.7202783	-3.0349791
20	H H10	-0.2118046	-3.7914998	-4.0526112
21	O O3	-0.4233879	3.9719759	0.0435385
22	O O4	-0.0403356	3.9417654	2.3335158
23	C C11	-0.3280039	4.7920731	1.2135373
24	H H11	0.4857080	5.5156442	1.0892889
25	H H12	-1.2832833	5.3032144	1.3824176

Ethyl cinnamate

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
-----			-----	-----	-----
1	H	H1	0.8094665	2.1829020	-1.8821796
2	C	C1	0.6152364	2.3709243	-0.8290218
3	C	C4	0.1166399	2.8516511	1.8674978
4	C	C2	0.2366564	1.2981348	-0.0015361
5	C	C6	0.7431351	3.6617944	-0.3205155
6	C	C5	0.4946944	3.9069062	1.0304224
7	C	C3	-0.0111336	1.5636824	1.3593274
8	H	H6	1.0367395	4.4750189	-0.9786682
9	H	H5	0.5939834	4.9120816	1.4309070
10	H	H3	-0.3067116	0.7558034	2.0222448
11	H	H4	-0.0787780	3.0361425	2.9204475
12	C	C7	0.1191615	-0.0348170	-0.5930555
13	C	C8	-0.2237237	-1.1829758	0.0195615
14	H	H2	0.3360990	-0.1044686	-1.6583634
15	H	H7	-0.4614193	-1.2461745	1.0765785
16	C	C10	-0.2891713	-2.4409783	-0.7496115
17	O	O1	-0.0614930	-2.5691224	-1.9382809
18	O	O2	-0.6456391	-3.4745586	0.0550586
19	C	C11	-0.7367231	-4.7496375	-0.5948518
20	H	H8	0.2257049	-5.0290876	-1.0327061
21	H	H11	-1.4897831	-4.7263014	-1.3877804
22	H	H12	-1.0229413	-5.4569196	0.1845253

2-furyl

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
-----			-----	-----	-----
1	C	C1	-0.5861778	-0.0457215	0.4069199
2	H	H2	-1.6046844	0.3335817	0.3597083
3	C	C2	0.2518868	0.2643737	-0.6030869
4	H	H1	1.2811268	-0.0766997	-0.6246977
5	C	C3	-0.2679092	-0.8368358	1.5595421
6	C	C4	-1.0186753	-1.2156629	2.6482011
7	C	C5	-0.1709988	-2.0004238	3.4831726
8	C	C6	1.0370148	-2.0482303	2.8499015
9	O	O1	1.0002162	-1.3521308	1.6850159
10	H	H5	-2.0542990	-0.9572724	2.8216408
11	H	H8	-0.4226338	-2.4661278	4.4255788
12	H	H9	1.9809179	-2.5160889	3.0863099
13	C	C7	-0.2240321	1.0933730	-1.7233965
14	O	O2	-1.3455036	1.5517945	-1.8497766
15	O	O3	0.7672365	1.2943735	-2.6288477
16	C	C8	0.4033583	2.0961908	-3.7604271
17	H	H3	1.2990927	2.1540682	-4.3800789
18	H	H4	0.0919452	3.0950270	-3.4414956
19	H	H6	-0.4178814	1.6324117	-4.3141840

2-thiophenyl

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1 C	C1	-0.4535858	-0.0243428	0.3412620
2 H	H2	-1.4645077	0.3808937	0.3148997
3 C	C2	0.3535076	0.2789904	-0.6953413
4 H	H1	1.3778722	-0.0748932	-0.7661434
5 C	C3	-0.1423379	-0.8297731	1.4961240
6 C	C4	-0.9971067	-1.1209763	2.5413079
7 C	C5	-0.4150242	-1.9414346	3.5445300
8 C	C6	0.8834163	-2.2741323	3.2616380
9 S	S1	1.4183528	-1.5900039	1.7624876
10 H	H5	-2.0159633	-0.7489986	2.5761987
11 H	H8	-0.9355970	-2.2706286	4.4369541
12 H	H9	1.5598762	-2.8829791	3.8468853
13 C	C7	-0.1471378	1.1227217	-1.7944892
14 O	O2	-1.2619570	1.6062332	-1.8750323
15 O	O3	0.8116420	1.3030524	-2.7380140
16 C	C8	0.4213655	2.1165398	-3.8527611
17 H	H3	1.2929905	2.1560024	-4.5071847
18 H	H4	0.1455531	3.1209030	-3.5190446
19 H	H6	-0.4313588	1.6728258	-4.3742764

3-Me-2-furyl

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1 C	C1	-0.1800432	0.0010486	-0.0533776
2 H	H2	-1.1985498	-0.0461630	-0.4326809
3 C	C2	0.6580214	-1.0089582	-0.3634728
4 H	H1	1.6872614	-1.0305690	-0.0223994
5 C	C3	0.1382254	1.1536708	0.7377366
6 C	C4	-0.6125407	2.2423298	1.1165637
7 C	C5	0.2351358	3.0773013	1.9013247
8 C	C6	1.4431494	2.4440302	1.9491312
9 O	O1	1.4063508	1.2791446	1.2530316
10 H	H8	-0.0164993	4.0197075	2.3670287
11 H	H9	2.3870525	2.6804386	2.4169897
12 C	C7	0.1821025	-2.1292679	-1.1924721
13 O	O2	-0.9393690	-2.2556479	-1.6508937
14 O	O3	1.1733711	-3.0347191	-1.3934727
15 C	C8	0.8094929	-4.1662985	-2.1952900
16 H	H3	1.7052273	-4.7859503	-2.2531674
17 H	H4	0.4980798	-3.8473669	-3.1941262
18 H	H6	-0.0117468	-4.7200553	-1.7315109
19 C	C9	-2.0787718	2.4878848	0.7507357
20 H	H5	-2.1312767	3.0980072	-0.1582252
21 H	H7	-2.5773364	3.0137329	1.5730088
22 H	H10	-2.5773364	1.5276999	0.5755379

N-Boc-2-pyrrolyl

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	1.2835003	0.0246371	-0.8176050
2	H H2	0.4573820	0.6022074	-0.4253786
3	C C2	1.6434672	0.2773757	-2.0940092
4	H H1	2.4366695	-0.2564087	-2.6077389
5	C C3	1.9067766	-0.9304564	0.0646007
6	C C4	3.1300951	-1.5680919	-0.0617223
7	C C5	3.3727855	-2.3355217	1.1068869
8	C C6	2.3000683	-2.1602396	1.9417346
9	N N1	1.3927693	-1.3112357	1.3275764
10	H H5	3.7966605	-1.4526068	-0.9059462
11	H H8	4.2415600	-2.9448850	1.3147515
12	H H9	2.0707186	-2.5626340	2.9152865
13	C C7	0.9274185	1.3158813	-2.8498912
14	O O2	0.0024641	1.9983814	-2.4411995
15	O O3	1.4288196	1.4302126	-4.1074914
16	C C8	0.7931884	2.4165788	-4.9300804
17	H H3	1.3037365	2.3698145	-5.8929337
18	H H4	0.8961602	3.4127238	-4.4900456
19	H H6	-0.2711004	2.1941355	-5.0492187
20	C C9	0.1569124	-1.0315429	1.9667199
21	O O1	-0.0304055	-1.3261031	3.1276429
22	O O4	-0.7017898	-0.4573704	1.1277316
23	C C10	-2.0430104	0.0056071	1.5781028
24	C C11	-1.8692816	1.0950983	2.6378016
25	H H7	-1.3961684	0.7013709	3.5394425
26	H H12	-2.8524620	1.4962416	2.9074989
27	H H13	-1.2634745	1.9190589	2.2458376
28	C C12	-2.8591165	-1.1864860	2.0837571
29	H H10	-2.4441450	-1.5982818	3.0048652
30	H H14	-2.8916951	-1.9750289	1.3241647
31	H H15	-3.8873846	-0.8606490	2.2757576
32	C C13	-2.6408231	0.5700264	0.2877880
33	H H11	-2.0110335	1.3598982	-0.1330557
34	H H16	-3.6325881	0.9862970	0.4928455
35	H H17	-2.7466742	-0.2180043	-0.4644761

Baldwin VCP INT (8b)

H	1.442750	0.921698	-1.239800
C	1.174223	1.088619	-0.199764
C	-0.205397	1.594368	0.105723
C	0.151197	0.149790	0.419148
H	2.000646	1.417717	0.424305
H	-0.883108	1.775465	-0.724784
H	-0.338621	2.274416	0.942683
H	0.296804	-0.086999	1.471332
C	-0.430333	-0.944346	-0.387160
H	-0.576162	-0.721840	-1.446325
C	-0.778212	-2.146752	0.078483

H	-1.202504	-2.908299	-0.569397
H	-0.651283	-2.413837	1.125558

Baldwin VCPR TS

C	-0.215191	1.190052	-0.227090
C	-1.349112	0.421866	-0.217252
C	-1.386915	-0.875798	0.339664
C	1.093057	0.583636	0.232001
C	1.230186	-0.836001	-0.253629
H	-0.232714	2.211810	-0.596753
H	-2.244410	0.795796	-0.714968
H	-0.751599	-1.161244	1.168910
H	1.069204	-1.040072	-1.308078
H	1.867359	-1.532357	0.287554
H	1.931023	1.206053	-0.128602
H	1.174797	0.603886	1.332791
H	-2.185686	-1.567628	0.085453

[3,3]-Mechanism Searching

(S-TS6)

[3,3] Transoid Triplet Transition State

Spartan'10: G = -852.420461, iv = i613, S^2 = 2.0177

[3,3] Transoid Diradicaloid

Spartan'10: G = -852.445602, iv = i552, S^2 = 0.6134

[3,3] Transoid Closed Shell

Spartan'10: G = -852.435275, iv = i67

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C	2.3374563	0.3330489	-2.1080915
2	F F	2.4256384	-0.9115264	-2.7529639
3	F F3	3.4032088	1.0617736	-2.6006786
4	C C4	2.5657165	0.1320971	-0.6505621
5	H H	3.5622940	0.3928016	-0.3080310
6	C C6	1.0789034	0.9809830	-2.6058204
7	H H7	1.1643354	1.2641873	-3.6525420
8	C C8	-0.0983823	1.1552714	-1.9821114
9	H H9	-0.9281032	1.5043633	-2.5947118
10	C C10	-0.4496947	0.8566367	-0.5843182
11	H H11	0.0756405	1.4190667	0.1825713
12	C C12	-1.9129894	0.7750143	-0.3343334
13	O O	-2.7518708	0.4856100	-1.1684378
14	O O14	-2.2070567	1.0142512	0.9659606
15	C C15	-3.5943332	0.8855277	1.3115032
16	H H16	-3.9494122	-0.1297150	1.1106489
17	H H17	-4.2020983	1.5907992	0.7377134
18	H H18	-3.6522700	1.1081487	2.3777128
19	C C19	1.6719391	-0.5048293	0.2540782
20	C C20	-0.0900694	-1.7376610	2.1226550
21	C C21	0.3209353	-0.9075669	-0.1755517
22	C C22	2.0237697	-0.6627839	1.5896103
23	C C23	1.1433487	-1.2623996	2.5352652

24	C	C24	-0.4724439	-1.6238969	0.7762227
25	H	H25	0.2363543	-1.2466427	-1.2060124
26	H	H26	3.0008465	-0.3182240	1.9195639
27	H	H27	1.4593765	-1.3631237	3.5690190
28	H	H28	-1.4118475	-2.0562905	0.4427653
29	H	H29	-0.7491923	-2.2349208	2.8288763

S-TS7a

[3,3] Cisoid Triplet Transition State

Spartan'10: G = -852.411611, iv = i538, S² = 2.0397

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
-----			-----	-----	-----
1	C	C	1.6839700	1.4112607	-2.0466638
2	F	F	2.5766738	1.4465241	-3.1009893
3	F	F3	1.4296522	2.7520214	-1.7493923
4	C	C4	2.3582761	0.7947560	-0.8570935
5	H	H	3.2596855	1.2951852	-0.5073202
6	C	C6	0.4237176	0.7233898	-2.4994167
7	H	H7	0.4089928	0.4155717	-3.5405067
8	C	C8	-0.6096278	0.4606696	-1.6793565
9	H	H9	-1.4616330	-0.1043965	-2.0492272
10	C	C10	-0.6553100	0.8631396	-0.2727040
11	H	H11	-0.2399756	1.8467288	-0.0730032
12	C	C12	-1.9414769	0.6218576	0.4290469
13	O	O	-2.8204701	-0.1344267	0.0639202
14	O	O14	-1.9994752	1.3246740	1.5906512
15	C	C15	-3.1948822	1.1333352	2.3624714
16	H	H16	-3.3078673	0.0836187	2.6482809
17	H	H17	-4.0751618	1.4390237	1.7906988
18	H	H18	-3.0761145	1.7608966	3.2465162
19	C	C19	1.7705130	-0.3620541	-0.1613052
20	C	C20	0.4476392	-2.5605370	1.0378059
21	C	C21	2.0701335	-1.6586126	-0.5413184
22	C	C22	0.6974892	-0.1188347	0.7983874
23	C	C23	0.1260122	-1.2833207	1.4447133
24	C	C24	1.4172969	-2.7631849	0.0394031
25	H	H25	2.8258561	-1.8237732	-1.3048759
26	H	H26	0.8222681	0.7481696	1.4468545
27	H	H27	-0.5881718	-1.1257393	2.2476791
28	H	H28	1.6790043	-3.7695293	-0.2736922
29	H	H29	-0.0270143	-3.4164129	1.5104359

S-TS7b

[3,3] Cisoid Closed Shell Transition State
Spartan'10: G = -852.464842, iv = i385

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C	1.8306612	1.5956508	-1.8575741
2	F F	2.6870122	2.1184195	-2.7906786
3	F F3	1.8069515	2.4827641	-0.7996484
4	C C4	2.2410148	0.2100367	-1.4905855
5	H H	2.8205396	-0.2931099	-2.2601120
6	C C6	0.4929078	1.3164800	-2.4574821
7	H H7	0.5094519	1.1703634	-3.5334670
8	C C8	-0.6102237	0.9738261	-1.7309582
9	H H9	-1.4344701	0.4807224	-2.2423811
10	C C10	-0.7132016	1.0783911	-0.3075953
11	H H11	-0.3784892	2.0027709	0.1423622
12	C C12	-1.9631461	0.5379098	0.2891657
13	O O	-2.7047621	-0.2721485	-0.2306949
14	O O14	-2.1783377	1.0574306	1.5250633
15	C C15	-3.3528503	0.5724078	2.1939135
16	H H16	-3.3040250	-0.5128555	2.3185646
17	H H17	-4.2514107	0.8221237	1.6232500
18	H H18	-3.3648593	1.0714663	3.1636692
19	C C19	1.7137344	-0.5284032	-0.4510369
20	C C20	0.5579043	-2.1472863	1.5830749
21	C C21	1.8689793	-1.9623226	-0.4539682
22	C C22	0.8996587	0.0751830	0.6064962
23	C C23	0.3968822	-0.7962414	1.6475472
24	C C24	1.3030441	-2.7412087	0.5104419
25	H H25	2.4373971	-2.4126343	-1.2642251
26	H H26	1.2378510	1.0456992	0.9401489
27	H H27	-0.1236510	-0.3391174	2.4835210
28	H H28	1.4204899	-3.8209299	0.4779126
29	H H29	0.1549463	-2.7853874	2.3652758

[3,3]-Methodology Screening

Divinyl Species VCP INT (S22)

Spartan'10: B3LYP/6-31G*, G = -272.648654, iv = none
Gaussian'09: B3LYP/6-31G*, G = -272.569679, iv = none
M06-2X/6-31G*, G = -272.431421, iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	1.6922994	0.1392844	0.1378774
2	C C2	0.3988567	0.7574908	0.6151673
3	C C3	0.5377290	-0.7716186	0.4834085
4	H H6	0.6119170	-1.2877553	1.4356786
5	C C10	-0.1664634	-1.5377762	-0.5636591
6	H H11	-0.2166977	-1.0847065	-1.5512695

7	C	C11	-0.7243985	-2.7353400	-0.3801304
8	H	H12	-0.7005566	-3.2348517	0.5837612
9	H	H2	0.3943943	1.1086332	1.6424865
10	H	H8	2.5494545	0.1604584	0.8004636
11	H	H9	1.9359198	0.2523124	-0.9131092
12	H	H15	-1.2222093	-3.2567650	-1.1892550
13	C	C4	-0.4449305	1.5535815	-0.2977803
14	C	C6	-1.1908461	2.5945287	0.0754445
15	H	H1	-1.2316971	2.9258508	1.1086497
16	H	H13	-1.7851697	3.1497837	-0.6406867
17	H	H17	-0.4376017	1.2668891	-1.3470473

Divinyl Species [3,3]-TS (S-TS8)

Spartan'10: B3LYP/6-31G*, G = -272.536339, iv = i434

Gaussian'09: B3LYP/6-31G*, G = -272.53598, iv = i419

M06-2X/6-31G*, G = -272.394561, iv = i518

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z

1	C C1	-1.3141431	0.0858792	1.1956138
2	H H3	-1.5218186	-0.9575706	0.9960566
3	C C2	-0.0291084	0.4926157	1.5187609
4	C C5	-0.0356607	0.6217441	-1.4704223
5	H H7	0.0907939	1.6082371	-1.9169345
6	C C6	-1.3218653	0.1955604	-1.1769583
7	H H6	-1.5372630	-0.8597391	-1.0695242
8	C C3	1.1243576	0.0005740	-0.9981933
9	C C4	1.1294915	-0.0825547	0.9885817
10	C C11	1.1450748	-1.1596204	-0.0516523
11	H H2	2.0898886	0.4141807	-1.2762521
12	H H10	2.0959052	0.3084491	1.2937960
13	H H17	-2.1701876	0.8034414	-1.4793252
14	H H21	0.2677384	-1.8068587	-0.0775966
15	H H22	2.0565693	-1.7585354	-0.0796222
16	H H1	-2.1655803	0.6564818	1.5562745
17	H H11	0.0958078	1.4377156	2.0473972

Furan basic alkene INT [3,3] (S23)

Spartan'10: B3LYP/6-31G*, G = -423.988081, iv = none

Gaussian'09: B3LYP/6-31G*, G = -423.990183, iv = none

M06-2X/6-31G*, G = -423.804524, iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z

1	C C1	2.0211098	-0.2019559	-0.2878635
2	C C2	1.0455931	0.5679385	0.5563511
3	C C3	1.1811074	-0.9579600	0.7227411
4	H H6	1.6950687	-1.2655714	1.6311662
5	C C10	0.1137728	-1.8791687	0.2796023
6	H H11	-0.4504758	-1.5718682	-0.6005445

7	C	C11	-0.1862803	-3.0316599	0.8841588
8	H	H12	0.3516805	-3.3717411	1.7665564
9	C	C4	-0.1463955	1.1835360	-0.0514472
10	C	C5	-0.5099529	1.5057073	-1.3288209
11	C	C6	-1.8161123	2.0934018	-1.2526201
12	C	C7	-2.1512630	2.0926024	0.0654157
13	H	H1	0.0865861	1.3586969	-2.2183691
14	H	H8	-2.4149282	2.4695347	-2.0705875
15	H	H9	-3.0151894	2.4311237	0.6170684
16	O	O3	-1.1518294	1.5413520	0.8119593
17	H	H2	1.4658002	1.1388947	1.3828715
18	H	H3	3.0821058	-0.0798072	-0.0895872
19	H	H4	1.7797895	-0.3460992	-1.3375905
20	H	H7	-0.9801871	-3.6769564	0.5195397

Furan basic alkene TS [3,3] (S-TS10)

Spartan'10: B3LYP/6-31G*, G = -423.948929, iv = i375

Gaussian'09: B3LYP/6-31G*, G = -423.94862, iv = i364

M06-2X/6-31G*, G = -423.804524, iv = i501

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z

1	C C1	-1.0283397	-0.4010231	0.7571931
2	H H3	-1.3288846	-1.4018108	0.4822254
3	C C2	0.3149653	-0.0843233	1.1143534
4	C C5	0.1806775	0.5851929	-1.8049434
5	H H7	0.1886549	1.6298365	-2.1155432
6	C C6	-1.0478457	-0.0056010	-1.4914104
7	H H6	-1.1562864	-1.0802117	-1.5818701
8	C C3	1.4061193	-0.0015796	-1.5255067
9	C C4	1.5056262	-0.4561222	0.5381058
10	C C11	1.5647472	-1.2614028	-0.7289562
11	H H2	2.3179841	0.5447544	-1.7517164
12	H H10	2.4243494	-0.0184088	0.9139063
13	O O3	0.3046054	0.9591443	2.0340899
14	C C8	-1.0061254	1.2405430	2.2973044
15	H H12	-1.1694267	2.0232775	3.0244229
16	C C7	-1.8501102	0.4577518	1.5881914
17	H H11	-2.9302458	0.4734522	1.6347546
18	H H8	-1.9647426	0.5515984	-1.6637485
19	H H13	0.7543954	-1.9858727	-0.8430314
20	H H14	2.5198825	-1.7691948	-0.8778209

Thiophene basic alkene INT [3,3] (S24)

Spartan'10: B3LYP/6-31G*, G = -746.970146, iv = none

Gaussian'09: B3LYP/6-31G*, G = -746.972369, iv = none

M06-2X/6-31G*, G = -746.779248, iv = none

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C1	2.0342002	-0.2274222	-0.0893840
2	C C2	1.0083838	0.5175287	0.7205973
3	C C3	1.1438292	-1.0097873	0.8564552
4	H H6	1.6098827	-1.3407959	1.7825414
5	C C10	0.1071938	-1.9243166	0.3331753
6	H H11	-0.4024356	-1.6036092	-0.5748702
7	C C11	-0.2265279	-3.0867859	0.9001834
8	H H12	0.2573181	-3.4399102	1.8085163
9	C C4	-0.1614673	1.1537212	0.0676524
10	C C5	-0.3028157	1.5991983	-1.2219863
11	C C6	-1.5793267	2.1816071	-1.4925050
12	C C7	-2.4031674	2.1789389	-0.4026654
13	H H1	0.4935970	1.5255504	-1.9551030
14	H H8	-1.8643257	2.5889943	-2.4567860
15	H H9	-3.4137035	2.5570230	-0.3227241
16	S S1	-1.6333832	1.4513366	0.9735079
17	H H2	1.3955547	1.0633116	1.5801496
18	H H3	3.0826091	-0.1075179	0.1690450
19	H H4	1.8493969	-0.3496373	-1.1530430
20	H H7	-0.9948125	-3.7274275	0.4772432

Thiophene basic alkene TS [3,3] (S-TS11)

Spartan'10: B3LYP/6-31G*, G = -746.930649, iv = i388

Gaussian'09: B3LYP/6-31G*, G = -746.93057, iv = i390

M06-2X/6-31G*, G = -746.731749, iv = i513

Cartesian Coordinates (Angstroms)

	Atom	X	Y	Z
	-----	-----	-----	-----
1	C C1	-0.9189548	-0.4240114	0.7504790
2	H H3	-1.1147122	-1.4402266	0.4318292
3	C C2	0.4086231	-0.0557975	1.1303085
4	C C5	0.2563491	0.6375349	-1.7780825
5	H H7	0.2835947	1.6895231	-2.0613975
6	C C6	-0.9818885	0.0654255	-1.4649227
7	H H6	-1.1223033	-1.0004326	-1.6017383
8	C C3	1.4714917	0.0183867	-1.5254622
9	C C4	1.5815088	-0.4486707	0.5176155
10	C C11	1.6126170	-1.2567297	-0.7494393
11	H H2	2.3922651	0.5471979	-1.7569661
12	H H10	2.5296780	-0.0491525	0.8658829
13	S S1	0.3554048	1.2920013	2.2966335
14	C C8	-1.3938788	1.2278275	2.3506109
15	H H12	-1.9282369	1.8907785	3.0194038
16	C C7	-1.9142747	0.2946522	1.5169151
17	H H11	-2.9785961	0.0998604	1.4329914
18	H H8	-1.8852902	0.6542682	-1.5999269
19	H H13	0.7880972	-1.9646036	-0.8631282
20	H H14	2.5585060	-1.7778317	-0.9116061

Non-fluoro Pip cis (S25)

Spartan'10: B3LYP/6-31G*, G = -842.539706, iv = none

Gaussian'09: B3LYP/6-31G*, G = -842.546027, iv = none

M06-2X/6-31G*, G = -842.201221, iv = none

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	3.0422011	-0.2059109	0.8333341
2	C C2	1.9462495	0.6301462	1.4123946
3	C C3	1.7915637	-0.9034859	1.3561728
4	H H6	1.8915419	-1.4139110	2.3115219
5	C C10	0.8668632	-1.5315163	0.4062663
6	H H11	0.7192598	-1.0383017	-0.5535636
7	C C11	0.1896422	-2.6696412	0.6288198
8	H H12	0.2760755	-3.2240637	1.5592409
9	C C12	-0.7076642	-3.2212370	-0.4038901
10	O O1	-0.9249719	-2.7396061	-1.5003832
11	O O2	-1.2831356	-4.3747921	0.0257938
12	C C13	-2.1743954	-4.9936572	-0.9108810
13	H H5	-3.0200563	-4.3360514	-1.1326643
14	H H13	-2.5192305	-5.9092198	-0.4284011
15	H H14	-1.6551503	-5.2236293	-1.8455651
16	C C4	1.0978825	1.5520209	0.5894276
17	C C5	0.7952224	3.0268768	-1.3505680
18	C C6	-0.9677564	2.7108075	0.2779478
19	C C7	-0.4784712	3.2893029	-0.8931402
20	C C9	1.5781117	2.1438437	-0.5822917
21	H H1	1.1760331	3.4839111	-2.2574735
22	H H4	2.5895542	1.9257801	-0.9106321
23	C C8	-0.2120485	1.8458768	1.0381704
24	H H2	2.1242673	0.9867590	2.4267254
25	H H3	-0.6104691	1.3989510	1.9432289
26	O O3	-2.2450646	3.1618447	0.5151643
27	O O4	-1.4305404	4.1247672	-1.4279509
28	C C14	-2.6158043	3.8916840	-0.6597057
29	H H7	-3.0544472	4.8499658	-0.3687754
30	H H10	-3.3255377	3.2962697	-1.2517681
31	H H8	3.9619561	-0.3310041	1.3976659
32	H H9	3.1783192	-0.2027794	-0.2442203

Non-fluoro Pip cis [3,3] TS (S-TS12)

Spartan'10: B3LYP/6-31G*, G = -842.491477, iv = i374

Gaussian'09: B3LYP/6-31G*, G = -842.495343, iv = i369

M06-2X/6-31G*, G = -842.148309, iv = i487

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
-----		-----	-----	-----
1	C C1	0.0520814	-0.9917968	0.5259498
2	H H3	-0.0680629	-2.0610640	0.3911571
3	C C2	1.3793483	-0.5890499	1.0005366
4	C C5	1.3946502	-0.4550237	-2.0184814
5	H H7	1.4907740	0.4909212	-2.5477833
6	C C6	0.0803486	-0.8195318	-1.5814762

7	H	H6	-0.2016633	-1.8639056	-1.6606524
8	C	C7	1.5052318	0.5844828	1.8403494
9	H	H4	2.4855943	0.9358776	2.1449348
10	C	C8	0.3724354	1.2214879	2.2165992
11	C	C9	-0.9278742	0.7683988	1.8341607
12	C	C10	-1.1222078	-0.3267477	1.0639775
13	H	H12	-2.1142224	-0.6851961	0.8171351
14	C	C3	2.5223390	-1.1324057	-1.6537495
15	C	C4	2.5117020	-1.2325879	0.5429250
16	C	C11	2.5316142	-2.2105191	-0.5981357
17	H	H2	3.4917592	-0.7607891	-1.9772189
18	H	H10	3.4793786	-0.8679440	0.8810774
19	C	C12	-1.0121538	0.1108352	-1.9457873
20	O	O1	-0.8861163	1.2902719	-2.2159820
21	O	O2	-2.2234775	-0.5100299	-1.9038794
22	C	C13	-3.3475585	0.3342121	-2.1883485
23	H	H1	-3.2619765	0.7689444	-3.1882166
24	H	H5	-3.4161761	1.1444830	-1.4567240
25	H	H8	-4.2243907	-0.3122520	-2.1268798
26	O	O3	-1.8664221	1.5764937	2.4190921
27	O	O4	0.2391522	2.3310099	3.0111647
28	C	C14	-1.1535291	2.6447480	3.0458727
29	H	H9	-1.3334033	3.5774634	2.4962941
30	H	H13	-1.4795959	2.7345598	4.0862811
31	H	H11	3.4385629	-2.8191869	-0.6170676
32	H	H14	1.6638581	-2.8761594	-0.6371249