Supporting information

Stereoselective Access to Trisubstituted Fluorinated Alkenyl Thioethers

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1. General information

All reagents and solvents were obtained from commercial suppliers unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) analysis using silica gel plates (60 F254). Compounds were visualized by UV irradiation. Column chromatography was performed on silica gel 60 (230-400 mesh, 0.040-0.063 mm).

^{1}H (300 MHz), ^{13}C (75.5 MHz) and ^{19}F (282 MHz) NMR spectra were recorded on a Bruker spectrometer. For ^{19}F NMR spectra, recycle delay d1 was adjusted to 10 s for accurate integration, and signals were decoupled from ^{1}H. ^{1}H and ^{13}C chemical shifts (δ) are given in parts per million relative to tetramethylsilane (TMS) using the ^{1}H (residual) and ^{13}C chemical shifts of the solvent as secondary standard. α,α,α-trifluorotoluene was used as an internal standard for ^{19}F NMR spectra for the determination of the crude yield of coupling and the ratio of isomers and byproducts. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = doublet of doublets, dt = doublet of triplets.

HRMS Spectra were recorded on a JEOL JMS-GC Mate II apparatus**.**

Cyclic voltammetry (CV) was performed with a Metrohm Autolab PGSTAT101 potentiostat connected to a Nova software interface. CV was performed in a three-electrode cell connected to a Schlenk line under argon at 20 °C with a scan rate of 0.5 $V.s^{-1}$. The working electrode was a steady glassy carbon disk (d = 1 mm), the counter electrode a platinum wire of *ca*. 0.2 cm^2 apparent area. The reference was a saturated calomel electrode (SCE) separated from the solution by a bridge filled with 3 mL of CH_3CN (containing $n$$Bu_4NBF_4$ 0.3 M).

2. Conditions screening

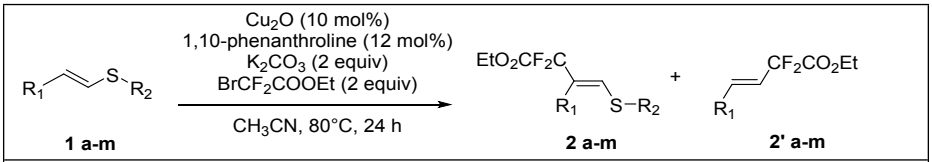
1a **2a**

Entry	Catalyst	Ligand	Base	Solvent	Yield
1	Cu_2O	1,10-phenanthroline	K_2CO_3	CH_3CN	82 % [a]
2[c]	Cu_2O	1,10-phenanthroline	K_2CO_3	CH_3CN	0 %
3[d]	Cu_2O	1,10-phenanthroline	K_2CO_3	CH_3CN	46 % [a]
4[e]	Cu_2O	1,10-phenanthroline	K_2CO_3	CH_3CN	65 % [b]
5[f]	Cu_2O	1,10-phenanthroline	K_2CO_3	CH_3CN	30% [b]
6[g]	Cu_2O	1,10-phenanthroline	K_2CO_3	CH_3CN	24% [b]
7	$Cu(OTf)_2$	1,10-phenanthroline	K_2CO_3	CH_3CN	60 % [a]
8	CuI	1,10-phenanthroline	K_2CO_3	CH_3CN	59 % [a]
9	$Cu(CH_3CN)_4PF_6$	1,10-phenanthroline	K_2CO_3	CH_3CN	70 % [a]
10	-	1,10-phenanthroline	K_2CO_3	CH_3CN	0 %
11	Cu_2O	Neocuproine	K_2CO_3	CH_3CN	0 %
12	Cu_2O	TMEDA	K_2CO_3	CH_3CN	0 %
13	Cu_2O	TMHD	K_2CO_3	CH_3CN	0 %
14	Cu_2O	2,2'-bipyridine	K_2CO_3	CH_3CN	35 % [a]
15	Cu_2O	-	K_2CO_3	CH_3CN	0 %
16	Cu_2O	1,10-phenanthroline	K_2CO_3	DMF	< 5% [b]
17	Cu_2O	1,10-phenanthroline	K_2CO_3	NMP	10 % [b]
18	Cu_2O	1,10-phenanthroline	Cs_2CO_3	CH_3CN	28 % [b]
19	Cu_2O	1,10-phenanthroline	Na_2CO_3	CH_3CN	12 % [b]
20	Cu_2O	1,10-phenanthroline	Et_3N	CH_3CN	< 5 % [b]
21	Cu_2O	1,10-phenanthroline	2,6-lutidine	CH_3CN	0 %
22	Cu_2O	1,10-phenanthroline	nBu$_4$NOAc	CH_3CN	0 %
23	Cu_2O	1,10-phenanthroline	-	CH_3CN	0%
24	$Cu(CH_3CN)_4PF_6$	-	K_2CO_3	CH_3CN	0 %
25	CuI	-	K_2CO_3	CH_3CN	0 %

Standard conditions: 1 mmol **1a**, 2 mmol $BrCF_2CO_2Et$, 2 mmol base, 5 mL solvent, 10 mol% [Cu].

a. Isolated yield
b. ^{19}F NMR yield
c. RT, 40 h
d. 6h instead of 24h
e. Air atmosphere
f. 1.3 equiv of $BrCF_2CO_2Et$
g. 2% Cu_2O

3. Analysis of the regioselectivity of the reaction



1 a-m | 2 a-m | 2' a-m

Substrate	Yield of 2' (%)
1a	10
1b	4
1c	7
1d	12
1e	8
1f	12
1g	9
1h	16
1i	6
1j	7
1k	6
1l	0

4. Preparation of starting vinyl sulfides

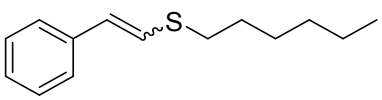
General procedure A for the synthesis of vinyl sulfides 1a to 1l

Vinyl sulfides **1a** to **1l** were synthesized according to a reported procedure[1].

An argon flushed schlenk was charged with KOH (10 mmol) and Cu_2O (0.25 mmol). Then distilled dioxane (2.5 mL) was added, followed by bromostyrene (6 mmol) and then hexanethiol (5 mmol). The schlenk was sealed and heated at 110 °C in a sand bath. After stirring at this temperature for 24 to 72 h, the heterogeneous mixture was cooled to room temperature and diluted with ethyl acetate (100 mL). The resulting solution was filtered through a pad of celite then washed with ethyl acetate (150 mL) and concentrated in vacuo to give the crude material which was then purified by column chromatography (SiO_2, EtOAc in cyclohexane 0 to 5%) to afford the desired product.

The *Z* or *E* configuration of the products was established with the coupling constant of the vinyl protons.

Hexyl(styryl)sulfane (1a)[2] *Z/E* (90:10)

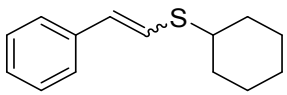


[1] Hsin-Lun Kao, Chin-Fa Lee, *Org. Lett*. **2011**, *13*, 5204-5207

[2] C.-M. Chu, Z. Tu, P. Wu, C.-C. Wang, J.-T. Liu, C.-W. Kuo, Y.-H. Shin, C.-F. Yao, *Tetrahedron*, **2009**, *65*, 3878-3885

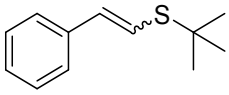
Following the general procedure A, **1a** was synthesized on a 10 mmol scale in 74 % yield. *E isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41-7.18 (m, 5H), 6.77 (d, *J* = 15.6 Hz, 1H), 6.50 (d, *J* = 15.6 Hz, 1H), 2.83 (t, *J* = 7.2 Hz, 2H), 1.81-1.64 (m, 2H), 1.53-1.43 (m, 2H), 1.40-1.30 (m, 4H), 0.97-0.92 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.3, 128.8, 126.8, 126.8, 125.6, 125.5, 32.8, 31.5, 29.6, 28.6, 22.7, 14.2. *Characteristic peaks for the Z isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54-7.52 (m, 2H), 6.47 (d, *J* = 10.9 Hz, 1H), 6.28 (d, *J* = 10.9 Hz, 1H).^{13}C NMR (75 MHz, $CDCl_3$): δ 137.2, 128.3, 127.8, 126.7 (C_{ar}), 125.4 (C_8).

Cyclohexyl(styryl)sulfane (1b)[3] *Z/E* (48:52)



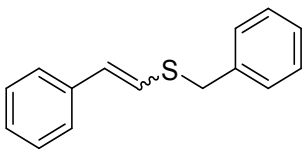
Following the general procedure A, **1b** was synthesized on a 5 mmol scale in 36 % yield. *E isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (d, *J* = 7.2, 1H), 7.38-7.30 (m, 3H), 7.23-7.18 (m, 1H), 6.78 (d, *J* = 15.6 Hz, 1H), 6.58 (d, *J* = 15.6 Hz, 1H), 2.99-2.89 (m, 1H), 2.10-2.06 (m, 2H), 1.84-1.80 (m, 2H, 1.67-1.30 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.3, 128.8, 128.7, 127.0, 125.7, 124.2, 45.5, 33.7, 26.1, 25.8. *Z isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (d, *J* = 7.2, 1H), 7.38-7.30 (m, 3H), 7.23-7.18 (m, 1H), 6.44 (d, *J* = 11.1 Hz, 1H), 6.34 (d, *J* = 11.1 Hz, 1H), 2.99-2.89 (m, 1H), 2.10-2.06 (m, 2H), 1.84-1.80 (m, 2H), 1.67-1.30 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.3, 128.8, 128.3, 126.6, 126.0, 125.2, 47.9, 33.8, 26.1, 25.7. HRMS (EI, m/z) [M] calcd. for $C_{14}H_{18}S$: 218.1129, found: 218,1135.

***Tert*-butyl(styryl)sulfane (1c)**[2] *Z/E* (64:36)



Following the general procedure A, **1c** was synthesized on a 5 mmol scale in 55 % yield. *E isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 (d, *J* = 6.0 Hz, 1H), 7.39-7.29 (m, 3H), 7.25-7.18 (m, 1H), 6.89 (d, *J* = 15.6 Hz, 1H), 6.72 (d, *J* = 15.6 Hz, 1H), 1.42 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.2, 132.2, 128.8, 127.4, 126.0, 122.2, 44.5, 31.2. *Z isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 (d, *J* = 6.0 Hz, 1H), 7.39-7.29 (m, 3H), 7.25-7.18 (m, 1H), 6.50 (d, *J* = 11.4 Hz, 1H), 6.45 (d, *J* = 11.4 Hz, 1H), 1.44 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.3, 128.9, 128.3, 126.7, 125.5, 123.6, 44.6, 30.9. HRMS (EI, m/z) [M] calcd. for $C_{12}H_{16}S$: 192.0973, found: 192,0980.

Benzyl(styryl)sulfane (1d)[4] *Z/E* (20:80)

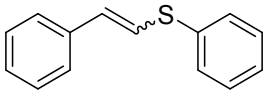


Following the general procedure A, **1d** was synthesized on a 5 mmol scale in 89 % yield. *E isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50-7.22 (m, 10H), 6.75 (d, *J* = 15.6 Hz, 1H), 6.56 (d, *J* = 15.6 Hz, 1H), 4.05 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.4, 137.1, 129.0, 128.8, 128.7, 128.1, 127.5, 127.1,

[3] C. G. Bates, P. Saejueng, M. Q. Doherty, D. Venkataraman, *Org. Lett*. **2004**, *6*, 5005-5008
[4] P. Zhong and X. Huang, *J. Serb. Chem. Soc.*, **2004**, *69*, 175–178

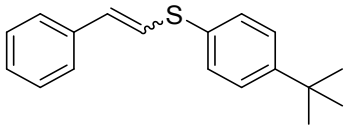
125.7, 124.5, 37.5. Z isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50-7.22 (m, 10H), 6.46 (d, *J* = 10.8 Hz, 1H), 6.29 (d, *J* = 10.8 Hz, 1H), 4.03 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.5, 137.0, 129.1, 128.8, 128.7, 128.4, 127.5, 126.9, 126.1, 126.0, 39.7. HRMS (EI, m/z) [M] calcd. for $C_{15}H_{14}S$: 226.0816, found: 226.0820.

Phenyl(styryl)sulfane (1e)[5] *Z/E* (10:90)



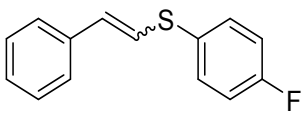
Following the general procedure A, **1e** was synthesized on a 5 mmol scale in 26 % yield. E isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.12 (m, 10H), 6.80 (d, *J* = 15.5 Hz, 1H), 6.65 (d, *J* = 15.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.7, 135.4, 131.9, 130.0, 129.3, 128.8, 127.7, 127.1, 126.2, 123.5. Characteristic peaks for the Z isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48-7.36 (m, 5H), 6.51 (d, *J* = 10.8 Hz, 1H), 6.42 (d, *J* = 10.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 130.2, 128.9, 128.5, 127.4, 127.3. HRMS (EI, m/z) [M] calcd. for $C_{14}H_{12}S$: 212.0660, found: 212.0659.

(4-(tert-butyl)phenyl)(styryl)sulfane (1f) *Z/E* (26:74), white solid.



Following the general procedure A, **1f** was synthesized on a 5 mmol scale in 43 % yield. E isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44-7.08 (m, 9H), 6.79 (d, *J* = 15.6 Hz, 1H), 6.57 (d, *J* = 15.6 Hz, 1H), 1.21 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.5, 136.8, 131.6, 130.8, 130.2, 128.7, 127.5, 126.3, 126.0, 124.5, 34.7, 31.4. Z isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44-7.08 (m, 9H), 6.42 (d, *J* = 10.8 Hz, 1H), 6.37 (d, *J* = 10.8 Hz, 1H), 1.21 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.7, 136.7, 132.8, 130.3, 128.8, 128.4, 127.1, 127.0, 126.6, 126.3, 31.4, 29.8. HRMS (EI, m/z) [M] calcd. for $C_{18}H_{20}S$: 268.1286, found: 268.1282.

(4-Fluorophenyl)(styryl)sulfane (1g)[6] *Z/E* (35:65)

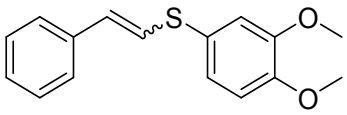


Following the general procedure A, **1g** was synthesized on a 4 mmol scale in 35 % yield. E isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57-7.27 (m, 7H), 7.09 (t, *J* = 9 Hz, 2H), 6.86 (d, *J* = 15.3 Hz, 1H), 6.69 (d, *J* = 15.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.4 (d, J = 245 Hz), 136.5, 132.8 (d, *J* = 8.0 Hz), 131.3, 130.0 (d, *J* = 3 Hz), 128.8, 127.7, 126.1, 124.0, 116.5 (d, *J* = 22 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -114.27. Z isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57-7.27 (m, 7H), 7.09 (t, *J* = 9 Hz, 2H), 6.61 (d,

[5] A. A. Oswald, K. Griesbaum, B. E. Hudson, J. M. Bregman, *J. Am. Chem. Soc*, **1964**, *14*, 2877-2884
[6] Z.-L. Wang, R.-Y. Tang, P.-S. Luo, C.-L. Deng, P. Zhong, J.-H. Li, *Tetrahedron*, **2008**, *64*, 10670-10675

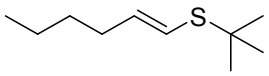
J = 10.8 Hz, 1H), 6.44 (d, *J* = 10.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.5 (d, J = 245 Hz), 136.5, 132.8 (d, *J* = 8.0 Hz), 131.5 (d, *J* = 3 Hz), 128.9, 128.5, 127.3, 127.2, 126.7, 116.4 (d, *J* = 22 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -114.03. HRMS (EI, m/z) [M] calcd. for $C_{15}H_{11}FS$: 230.0565, found: 230.0564.

(3,4-dimethoxyphenyl)(styryl)sulfane (1h) *Z/E* (10:90), pale yellow oil.



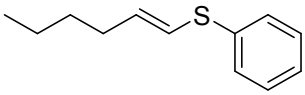
Following the general procedure A, **1h** was synthesized on a 1 mmol scale in 52 % yield. <u>*E isomer:*</u> ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20-7.10 (m, 5H), 6.95 (dd, *J* = 8.4 Hz, *J* = 2.1 Hz, 1H), 6.89 (d, *J* = 2.1 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.75 (d, *J* = 15.6 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 3.77 (s, 3H), 3.78 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$): δ 149.4, 149.1, 136.7, 129.2, 128.7, 127.3, 125.9, 125.4, 124.9, 124.7, 115.0, 111.8, 56.0, 56.0. <u>*Characteristic peaks for the Z isomer:*</u> ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.41 (d, *J* = 10.8 Hz, 1H), 6.34 (d, *J* = 10.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 128.4, 128.1, 127.0, 124.2, 114.6, 111.7. HRMS (EI, m/z) [M] calcd. for $C_{16}H_{16}O_2S$: 272.0871, found: 272.0864.

(E)-*tert*-butyl(hex-1-en-1-yl)sulfane (1i) *Z/E* > (1:99), colorless oil.



Following the general procedure A, **1i** was synthesized on a 2 mmol scale in 46 % yield. <u>*E isomer:*</u> ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.02 (d, *J* = 14.7 Hz, 1H), 5.86 (dt, *J* = 14.7, 6.9 Hz, 1H), 2.08 (dt, *J* = 6.6, 6.6 Hz, 2H), 1.37-1.28 (m, 13H), 0.87 (t, *J* = 7.2, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.1, 119.8, 43.5, 33.0, 31.4, 30.8, 22.2, 13.9.

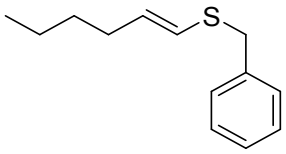
(E)-hex-1-en-1-yl(phenyl)sulfane (1j)[7] *Z/E* > (1:99)



Following the general procedure A, **1j** was synthesized on a 3 mmol scale in 84 % yield. <u>*E isomer:*</u> ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24-7.20 (m, 4H), 7.12-7.07 (m, 1H), 6.06 (d, *J* = 14.9 Hz, 1H), 5.92 (dt, *J* = 14.9, 6.7 Hz, 1H), 2.13-2.06 (m, 2H), 1.41 – 1.05 (m, 4H), 0.84 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.9, 136.8, 129.0, 128.5, 126.1, 120.7, 32.9, 31.3, 22.3, 14.0.

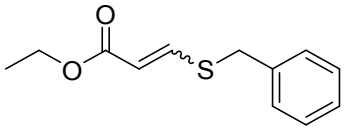
(E)-benzyl(hex-1-en-1-yl)sulfane (1k)[4] *Z/E* > (1:99)

[7] M.-Z. Cai, M.-H. Jiang, H.-G. Li, *J. Chem. Res*. **2006**, *11*, 702-704



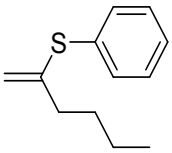
Following the general procedure A, **1k** was synthesized on a 1 mmol scale in 44 % yield. <u>*E isomer:*</u> ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23-7.13 (m, 5H), 5.81 (dt, *J* = 15.0, 1.2 Hz, 1H), 5.58 (dt, *J* = 15.0, 6.9 Hz, 1H), 3.74 (s, 2H), 1.95 (dt, *J* = 6.9, 6.1 Hz, 2H), 1.27-1.13 (m, 4H), 0.78 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.0, 132.7, 128.9, 128.6, 127.1, 122.0, 37.7, 32.9, 31.4, 22.1, 14.0.

Benzyl(2-ethyl carbonovinyl)sulfane (1l)[8] *Z/E* (17:83)



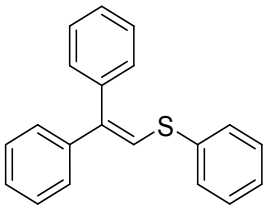
Following the general procedure A, **1l** was synthesized on a 2.5 mmol scale in 58 % yield. <u>*E isomer:*</u> ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (d, *J* = 15.1 Hz, 1H), 7.33 – 7.14 (m, 5H), 5.72 (d, *J* = 15.1 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 2H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.3, 146.0, 135.6, 128.9, 128.8, 127.9, 114.5, 60.3, 36.6, 14.4. <u>*Characteristic peaks for the Z isomer:*</u> ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.97 (d, *J* = 10.2 Hz, 1H), 3.87 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 148.6, 137.3, 113.7, 60.2, 39.5, 14.4. HRMS (EI, m/z) [M] calcd. for $C_{12}H_{14}O_2S$: 222.0715, found: 222.0716.

hex-1-en-2-yl(phenyl)sulfane (1m)[9]



Following a reported procedure[10], **1m** was synthesized on a 6 mmol scale in 27 % yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55-7.49 (m, 2H), 7.43-7.31 (m, 3H), 5.23 (t, *J* = 1.1 Hz, 1 H), 4.96 (s, 1H), 2.38-2.28 (m, 2H), 1.69-1.57 (m, 2H), 1.50-1.32 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.1, 133.3, 133.2, 129.0, 127.7, 112.4 36.3, 30.6, 22.0, 13.9. HRMS (EI, m/z) [M] calcd. for $C_{12}H_{16}S$: 192.0973, found: 192.0964.

(2,2-diphenylvinyl)(phenyl)sulfane (1n)[11]



[8] J. Yang, A. Sabarre, L. R. Fraser, B. O. Patrick, J. A. Love, *J. Org. Chem*, **2009**, *74*, 182-187
[9] V. Fiandanese, G. Marchese, F. Naso, L. Ronzini, *Synthesis*, **1987**, *11*, 1034-1036
[10] V. P. Ananikov, N. V. Orlov, I. P. Beletskaya, *Organometallics*, **2006**, *25*, 1970-1977

Following a reported procedure,[11] **1n** was synthesized on a 6 mmol scale in 47 % yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53-7.23 (m, 15H), 6.90 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.6, 141.3, 139.4, 136.7, 129.9, 129.7, 129.3, 128.5, 128.5, 128.0, 127.4, 127.4, 126.9, 124.3. HRMS (EI, m/z) [M] calcd. for $C_{20}H_{16}S$: 288.0973, found: 288.0979.

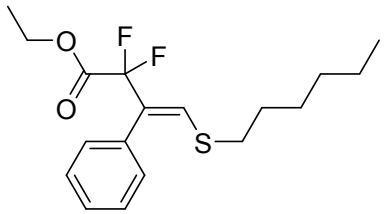
[11] H.-Y. Tu, B.-L. Hu, C.-L. Deng, X.-G. Zhang, *Chem. Commun*. **2015**, *51*, 15558

5. Experimental and characterization of coupling products

General procedure B for the difluoroalkylation

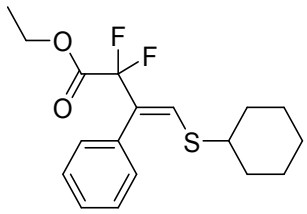
An argon flushed schlenk was charged with the starting vinyl sulfide **1** (1 mmol, 1.0 equiv). Anhydrous acetonitrile (5 mL) was added, then Cu_2O (14.4 mg, 0.1 mmol, 0.10 equiv), 1,10-phenanthroline monohydrate (23.8 mg, 0.12 mmol, 0.12 equiv) and oven-dried potassium carbonate (276.4 mg, 2 mmol, 2 equiv). The mixture was stirred under argon for a few seconds and ethylbromodifluoroacetate (256 µL, 2 mmol, 2 equiv) was added. The Schlenk was sealed and placed in a sand bath at 80 °C, and the mixture was stirred at this temperature for 24 h. The mixture was then cooled to room temperature. Ethyl acetate and water were added; the aqueous layer was separated and extracted with ethyl acetate. The organic layers were gathered, dried over magnesium sulfate and the solvents were evaporated at room temperature. The residue was then purified by column chromatography (SiO_2, EtOAc in cyclohexane 0 to 20%) to afford the corresponding fluorine-containing vinyl sulfide **2**.

Ethyl-2,2-difluoro-4-(hexylthio)-3-phenylbut-3-enoate (2a) *Z/E* (5:95), yellow oil.



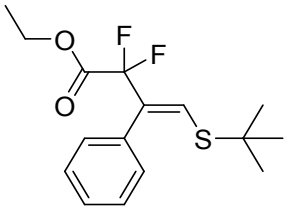
Following the general procedure B, **2a** was synthesized on a 1 mmol scale in 82 % yield. *E isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 – 7.15 (m, 5H), 6.94 (t, *J* = 1.7 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.64 (t, *J* = 7.4 Hz, 2H), 1.62 – 1.45 (m, 2H), 1.36 – 1.13 (m, 6H), 1.05 (t, *J* = 7.2 Hz, 3H), 0.79 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.7 (t, *J* = 35.1 Hz), 135.6 (t, *J* = 9.0 Hz), 133.2, 129.5, 128.6, 128.5, 127.4 (t, *J* = 21.8 Hz), 112.9 (t, *J* = 252.6 Hz), 62.8, 34.6, 31.3, 30.3, 28.1, 22.5, 14.0, 13.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ -100.7. HRMS (EI, m/z) [M] calcd. for $C_{18}H_{24}F_2O_2S$: 342.1465, found: 342.1465. *Characteristic peak for the Z isomer:* ^{19}F NMR (282 MHz, $CDCl_3$): δ -97.6. *Characteristic peak for the major byproduct*: ^{19}F NMR (282 MHz, $CDCl_3$): δ -103.1.

Ethyl-4-(cyclohexylthio)-2,2-difluoro-3-phenylbut-3-enoate (2b) *Z/E* (7:93), yellow oil.



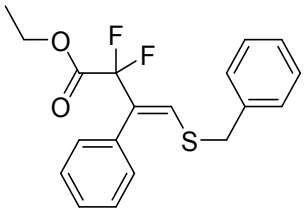
Following the general procedure B, **2b** was synthesized on a 1 mmol scale in 83 % yield. *E isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27-7.17 (m, 5H), 7.02 (t, *J* = 1.8 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 2.86 – 2.74 (m, 1H), 1.89-1.86 (m, 2H), 1.64-1.62 (m, 2H), 1.55 – 1.06 (m, 6H), 1.02 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.6 (t, *J* = 35.4 Hz), 133.7 (t, *J* = 8.9 Hz), 133.3 (t, *J* = 1.6 Hz), 129.4, 128.4, 128.3, 127.1 (t, *J* = 21.3 Hz), 113.0 (t, *J* = 251.3 Hz), 62.7, 46.6, 33.7, 25.8, 25.3, 13.7. ^{19}F NMR (282 MHz, $CDCl_3$): δ -100.4. HRMS (EI, m/z) [M] calcd. for $C_{18}H_{22}F_2O_2S$: 340.1309, found: 340.1319. *Characteristic peak for the E isomer*: ^{19}F NMR (282 MHz, $CDCl_3$): δ -97.3. *Characteristic peak for the major byproduct*: ^{19}F NMR (282 MHz, $CDCl_3$): δ -103.0.

Ethyl-4-(tert-butylthio)-2,2-difluoro-3-phenylbut-3-enoate (2c) *Z/E* (5:95), yellow oil.



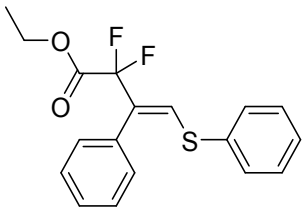
Following the general procedure B, **2c** was synthesized on a 1 mmol scale in 81 % yield. *E isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26-7.18 (m, 5H), 7.11 (t, *J* = 1.9 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 1.29 (s, 9H), 1.05 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.7 (t, *J* = 35.4 Hz), 133.4 (t, *J* = 1.6 Hz), 131.5 (t, *J* = 8.9 Hz), 129.6, 128.5, 128.4, 127.5 (t, *J* = 22.8 Hz), 113.1 (t, *J* = 252.4 Hz), 62.8, 44.7, 31.0, 13.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ -100.4. HRMS (EI, m/z) [M] calcd. for $C_{16}H_{20}F_2O_2S$: 314.1152, found: 314.1152. *Characteristic peak for the Z isomer*: ^{19}F NMR (282 MHz, $CDCl_3$): δ -96.9. *Characteristic peak for the major byproduct*: ^{19}F NMR (282 MHz, $CDCl_3$): δ -103.1.

Ethyl-4-(benzylthio)-2,2-difluoro-3-phenylbut-3-enoate (2d) *Z/E* (6:94), yellow oil.



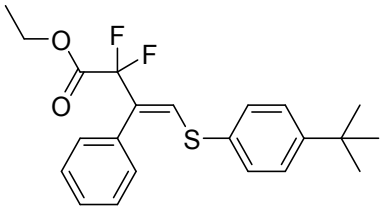
Following the general procedure B, **2d** was synthesized on a 1 mmol scale in 75% yield. *E isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 – 7.15 (m, 10H), 6.94 (t, *J* = 1.9 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 2H), 1.05 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.7, 136.9, 134.2 (t, *J* = 9.0 Hz), 133.1 (t, *J* = 1.6 Hz), 129.6, 129.0, 128.9, 128.8, 128.6, 128.3, 127.7, 112.9 (t, *J* = 252.5 Hz), 63.0, 38.5, 13.9. ^{19}F NMR (282 MHz, $CDCl_3$): -100.8. HRMS (EI, m/z) [M] calcd. for $C_{19}H_{18}F_2O_2S$: 348.0996, found: 348.0995. *Characteristic peak for the Z isomer*: ^{19}F NMR (282 MHz, $CDCl_3$): δ -97.4. *Characteristic peak for the major byproduct*: ^{19}F NMR (282 MHz, $CDCl_3$): δ -103.0.

Ethyl-2,2-difluoro-3-phenyl-4-(phenylthio)but-3-enoate (2e) Z/E (8:92), yellow oil.



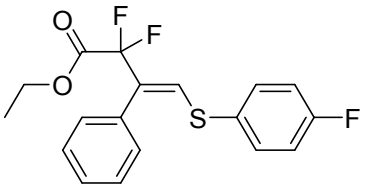
Following the general procedure B, **2e** was synthesized on a 1 mmol scale in 53% yield. *Z isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 – 7.17 (m, 10H), 7.15 (t, *J* = 1.7 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 1.05 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.5 (t, *J* = 35.0 Hz), 134.8 (t, *J* = 9.1 Hz), 134.2, 132.8 (t, *J* = 1.6 Hz), 130.7, 129.6, 129.4, 129.1, 129.0, 128.7, 128.0, 112.9 (t, *J* = 253.1 Hz), 63.0, 13.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ -101.1. HRMS (EI, m/z) [M] calcd. for $C_{18}H_{16}F_2O_2S$: 334.0839, found: 334.0840. *Characteristic peak for the E isomer:* ^{19}F NMR (282 MHz, $CDCl_3$): δ -96.8. *Characteristic peak for the major byproduct:* ^{19}F NMR (282 MHz, $CDCl_3$): δ -103.1.

Ethyl-4-((4-(tert-butyl)phenyl)thio)-2,2-difluoro-3-phenylbut-3-enoate (2f) *Z/E* (9:91), yellow oil.



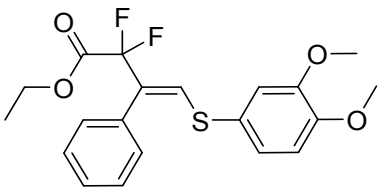
Following the general procedure B, **2f** was synthesized on a 1 mmol scale in 73% yield. *E isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 – 7.21 (m, 9H), 7.13 (t, *J* = 1.8 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 1.20 (s, 9H), 1.04 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.5 (t, *J* = 35.1 Hz), 151.4, 135.7 (t, *J* = 9.0 Hz), 132.9 (t, *J* = 1.6 Hz), 130.9, 130.7, 129.6, 128.9, 128.7, 128.4, 126.5, 112.9 (t, *J* = 255.7 Hz), 63.0, 34.7, 31.3, 13.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ -100.9. HRMS (EI, m/z) [M] calcd. for $C_{22}H_{24}F_2O_2S$: 390.1465, found: 390.1479. *Characteristic peak for the Z isomer:* ^{19}F NMR (282 MHz, $CDCl_3$): δ -96.8. *Characteristic peak for the major byproduct*: ^{19}F NMR (282 MHz, $CDCl_3$): δ -103.1.

Ethyl-2,2-difluoro-4-((4-fluorophenyl)thio)-3-phenylbut-3-enoate (2g) Z/E (8:92), yellow oil.



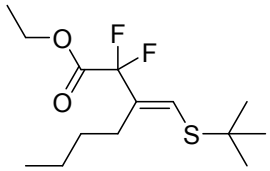
Following the general procedure B, **2g** was synthesized on a 1 mmol scale in 60% yield. *E isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.21 (m, 8H), 7.04 (t, *J* = 1.8 Hz, 1H), 6.92 (t, *J* = 8.6 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 1.04 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.4 (t, *J* = 35.0 Hz), 162.8 (d, *J* = 247.5 Hz), 135.2 (t, *J* = 9.1 Hz), 133.3 (d, *J* = 8.3 Hz), 132.6 (t, *J* = 1.7 Hz), 129.5, 129.3 (d, *J* = 3 Hz), 129.1, 128.9, 128.7, 116.6 (d, *J* = 22.5 Hz), 112.8 (t, *J* = 253.2 Hz), 63.0, 13.8. ^{19}F NMR (282 MHz, $CDCl_3$): -101.2, -112.8. HRMS (EI, m/z) [M] calcd. for $C_{18}H_{15}F_3O_2S$: 352.0745, found: 352.0749.*Characteristic peaks for the Z isomer:* ^{19}F NMR (282 MHz, $CDCl_3$): δ -97.0, -112.7. *Characteristic peak for the major byproduct*: ^{19}F NMR (282 MHz, $CDCl_3$): δ -103.1.

Ethyl-4-((3,4-dimethoxyphenyl)thio)-2,2-difluoro-3-phenylbut-3-enoate (2h) *Z/E* (6:94), yellow oil.



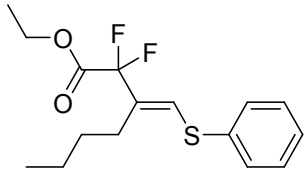
Following the general procedure B, **2h** was synthesized on a 0.25 mmol scale in 41% yield. *E isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36-7.28 (m, 5H), 7.08 (t, *J* = 1.8 Hz, 1H), 6.96 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.87 (d, *J* = 2.1 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 6H), 1.08 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.6, 149.7, 149.4, 136.7 (t, *J* = 9.0 Hz), 132.8, 129.6, 128.9, 128.7, 127.8 (t, *J* = 22.5 Hz), 125.0, 124.8, 115.1, 112.9 (t, *J* = 251.3 Hz), 111.9, 63.0, 56.2, 56.1, 13.9. ^{19}F NMR (282 MHz, $CDCl_3$): δ -101.0. HRMS (EI, m/z) [M] calcd. for $C_{20}H_{20}F_2O_4S$: 394.1050, found: 394.1041. *Characteristic peak for the Z isomer*: ^{19}F NMR (282 MHz, $CDCl_3$): δ -97.1. *Characteristic peak for the major byproduct*: ^{19}F NMR (282 MHz, $CDCl_3$): δ -103.2.

Ethyl-3-((tert-butylthio)methylene)-2,2-difluoroheptanoate (2i) *Z/E* (> 1:99), yellow oil.



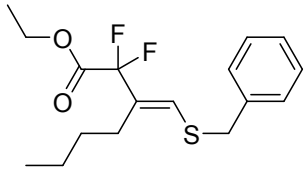
Following the general procedure B **2i** was synthesized on a 1 mmol scale in 81 % yield. *E isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.75 (t, *J* = 2.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.24 – 2.09 (m, 2H), 1.54 – 1.15 (m, 16H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.2 (t, *J* = 35.9 Hz), 128.6 (t, *J* = 21.8 Hz), 128.2 (t, *J* = 9.8 Hz), 114.1 (t, *J* = 251.7 Hz), 62.9, 44.5, 31.1, 30.0, 27.9, 22.9, 14.0, 13.9. ^{19}F NMR (282 MHz, $CDCl_3$): δ -103.5. HRMS (EI, m/z) [M] calcd. for $C_{14}H_{24}F_2O_2S$: 294.1465, found: 294.1461. *Characteristic peak for the major byproduct*: ^{19}F NMR (282 MHz, $CDCl_3$): δ -100.1.

Ethyl-2,2-difluoro-3-((phenylthio)methylene)heptanoate (2j) *Z/E* (> 1:99), pale yellow oil.



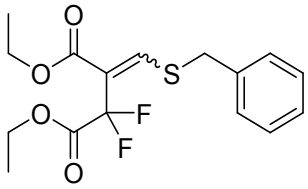
Following the general procedure B **2j** was synthesized on a 1 mmol scale in 81 % yield, *E isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.15 (m, 5H), 6.75 (t, *J* = 1.9 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.22 (m, 2H), 1.48-1.36 (m, 2H), 1.33-1.28 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.9 (t, *J* = 35.6 Hz), 134.4, 131.1 (t, *J* = 10.1 Hz), 130.3, 130.2 (t, *J* = 22.5 Hz), 129.4, 127.7, 113.8 (t, *J* = 252.3 Hz), 63.1, 30.1, 28.0, 22.9, 14.0, 13.9. ^{19}F NMR (282 MHz, $CDCl_3$): δ -103.8. HRMS (EI, m/z) [M] calcd. for $C_{16}H_{20}F_2O_2S$: 314.1152, found: 314.1155. *Characteristic peak for the major byproduct*: ^{19}F NMR (282 MHz, $CDCl_3$): δ -99.7.

Ethyl-3-((benzylthio)methylene)-2,2-difluoroheptanoate (2k) *Z/E* (> 1:99), pale yellow oil.



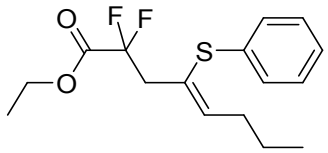
Following the general procedure B, **2k** was synthesized on a 0.5 mmol scale in 71 % yield. *E isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27-7.16 (m, 5H), 6.52 (t, *J* = 2.0 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 2H), 2.15 – 2.05 (m, 2H), 1.33-1.24 (m, 4H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.81 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.0 (t, *J* = 35.6 Hz), 137.2, 131.0 (t, *J* = 10.1 Hz), 129.0 (t, *J* = 18.0 Hz), 128.9, 128.8, 127.6, 113.9 (t, *J* = 251.7 Hz), 63.0, 38.2, 29.8, 28.0 (t, *J* = 1.8 Hz), 22.9, 14.0, 13.9. ^{19}F NMR (282 MHz, $CDCl_3$): δ -103.6. HRMS (EI, m/z) [M] calcd. for $C_{17}H_{22}F_2O_2S$: 314.1309, found: 328.1314. *Characteristic peak for the major byproduct*: ^{19}F NMR (282 MHz, $CDCl_3$): δ -101.0.

Diethyl 3-((benzylthio)methylene)-2,2-difluorosuccinate (2l) *Z/E* (42:58), yellow oil.



Following the general procedure B, **2l** was synthesized on a 1 mmol scale in 20 % yield. *E isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (t, J = 1.4 Hz, 1H), 7.36 – 7.15 (m, 5H), 4.22 (q, *J* = 7.0 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.3 (t, *J* = 33.8 Hz), 163.3 (t, *J* = 3.8 Hz), 152.3 (t, *J* = 8.5 Hz), 136.2, 129.1, 129.1, 128.0, 117.3 (t, *J* = 23.1 Hz), 111.3 (t, *J* = 250.4 Hz), 63.1, 61.4, 40.5, 14.2, 14.0. ^{19}F NMR (282 MHz, $CDCl_3$): δ -101.2. HRMS (EI, m/z) [M] calcd. for $C_{16}H_{18}F_2O_4S$: 344.0894, found: 344.0905. *Z isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (t, J = 2.4 Hz, 1H), 7.33 – 7.22 (m, 5H), 4.24 (q, *J* = 7.0 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.0 (t, *J* = 33.4 Hz), 162.5 (t, *J* = 5.9 Hz), 152.4, 135.8, 129.2, 129.2, 128.2, 118.4 (t, *J* = 24.9 Hz), 113.4 (t, *J* = 250.9 Hz), 63.1, 61.4, 40.4, 14.1, 14.0. ^{19}F NMR (282 MHz, $CDCl_3$): δ -100.0.

Ethyl-2,2-difluoro-4-(phenylthio)oct-4-enoate (2m) *Z/E* (81:19), yellow oil.



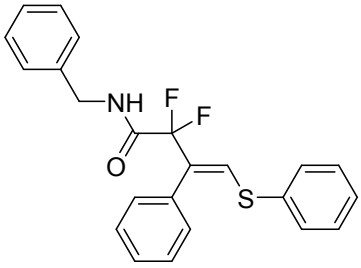
Following the general procedure B (during 12 h to avoid decomposition), **2m** was synthesized on a 1 mmol scale in 55% yield. *Z isomer:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41-7.05 (m, 5H), 6.07 (t, *J* = 7.3 Hz, 1H), 4.24 – 4.15 (m, 2H), 2.98 – 2.75 (m, 2H), 2.35 – 2.20 (m, 2H), 1.47 – 1.29 (m, 2H), 1.28 – 1.07 (m, 3H), 0.91 – 0.77 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$): δ 163.9 (t, *J* = 32.4 Hz), 144.3, 134.6, 129.4, 129.2, 126.5, 123.0 (t, *J* = 5.1 Hz), 115.0 (t, *J* = 252.4 Hz), 62.9, 42.1 (t, *J* = 24.5 Hz), 32.3, 22.3, 13.9, 13.7. ^{19}F NMR (282 MHz, $CDCl_3$): δ -104.1. HRMS (EI, m/z) [M] calcd. for $C_{16}H_{20}F_2O_2S$: 314.1152, found: 314.1151. *Characteristic peak for the E isomer:* ^{19}F NMR (282 MHz, $CDCl_3$): δ -103.5.*Characteristic peaks for the major byproducts:* ^{19}F NMR (282 MHz, $CDCl_3$): δ -92.7, -92.3.

6. Experimental and characterization of post-functionalization products and control experiment

Aminolysis of fluorinated vinyl sulfide (2e)

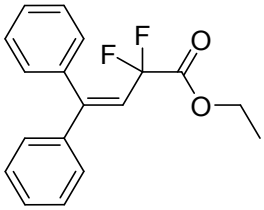
2e (167 mg, 0.5 mmol, 1 equiv) was dissolved in methanol (5 mL) and benzylamine (110 µL, 1 mmol, 2 equiv) was added dropwise at room temperature. After 20 hours, the mixture was diluted with dichloromethane (20 mL) and successively washed with 1N HCl (20 mL), water (20 mL) and brine (20 mL), then dried over magnesium sulfate and evaporated to dryness. The amide **3e** was obtained sufficiently pure as a white solid (178 mg, 90 %).

N-benzyl-2,2-difluoro-3-phenyl-4-(phenylthio)but-3-enamide (3e), *Z/E* (> 1:99), white solid.



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49-7.25 (m, 14H), 7.06-7.00 (m, 2H), 6.55 (br s, 1H), 4.42 (d, J = 5.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.3 (t, J = 30.9 Hz,), 136.7, 135.4 (t, J = 9.2 Hz), 134.2, 133.0 (t, J = 1.6 Hz), 130.8, 129.8, 129.4, 129.0, 128.9, 128.8, 128.5, 127.9, 127.9, 127.7, 114.6 (t, J = 254.3 Hz), 43.6. ^{19}F NMR (282 MHz, $CDCl_3$): δ -102.2. HRMS (EI, m/z) [M] calcd. for $C_{23}H_{19}F_2NOS$: 395.1155, found: 395.1168.

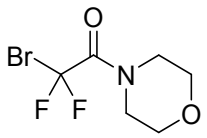
Ethyl 2,2-difluoro-4,4-diphenylbut-3-enoate (2'n)[12]



Following the general procedure B starting from **1n**, **2'n** was synthesized on a 0.6 mmol scale in 30 % yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 – 6.98 (m, 10H), 6.19 (t, J = 11.8 Hz, 1H), 3.82 (q, J = 7.1 Hz, 2H), 1.08 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.6 (t, J = 33.9 Hz), 151.1 (t, J = 9.5 Hz), 140.6, 137.2, 130.0, 129.2, 128.7, 128.5, 128.1, 128.0, 119.6 (t, J = 28.4 Hz), 112.7 (t, J = 245.0 Hz), 62.8, 13.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ -90.9. HRMS (EI, m/z) [M] calcd. for $C_{18}H_{16}F_2O_2$: 302.1118, found: 302.1127.

2-bromo-2,2-difluoro-1-morpholinoethan-1-one

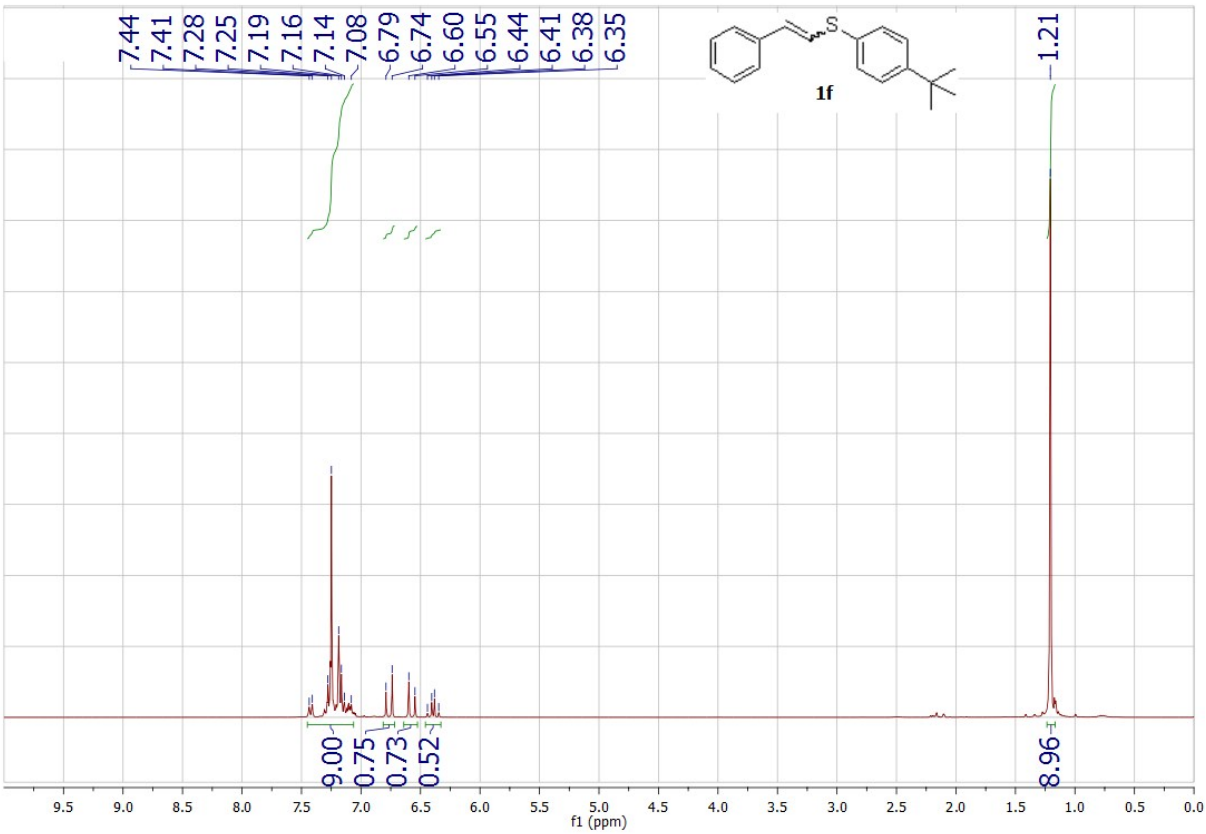
[12] S. Murakami, H. Ishii, T. Fuchigami, *J. Fluorine Chem*. **2004**, *125*, 609-614

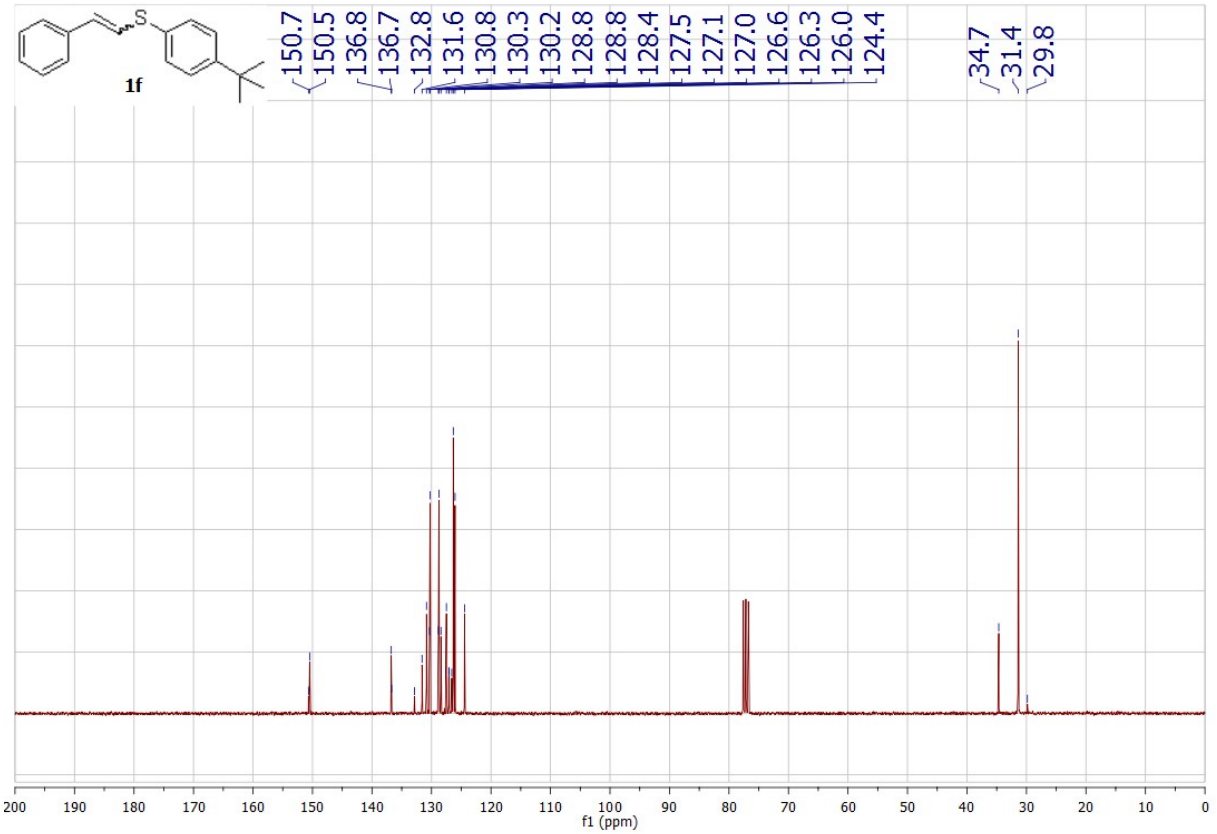


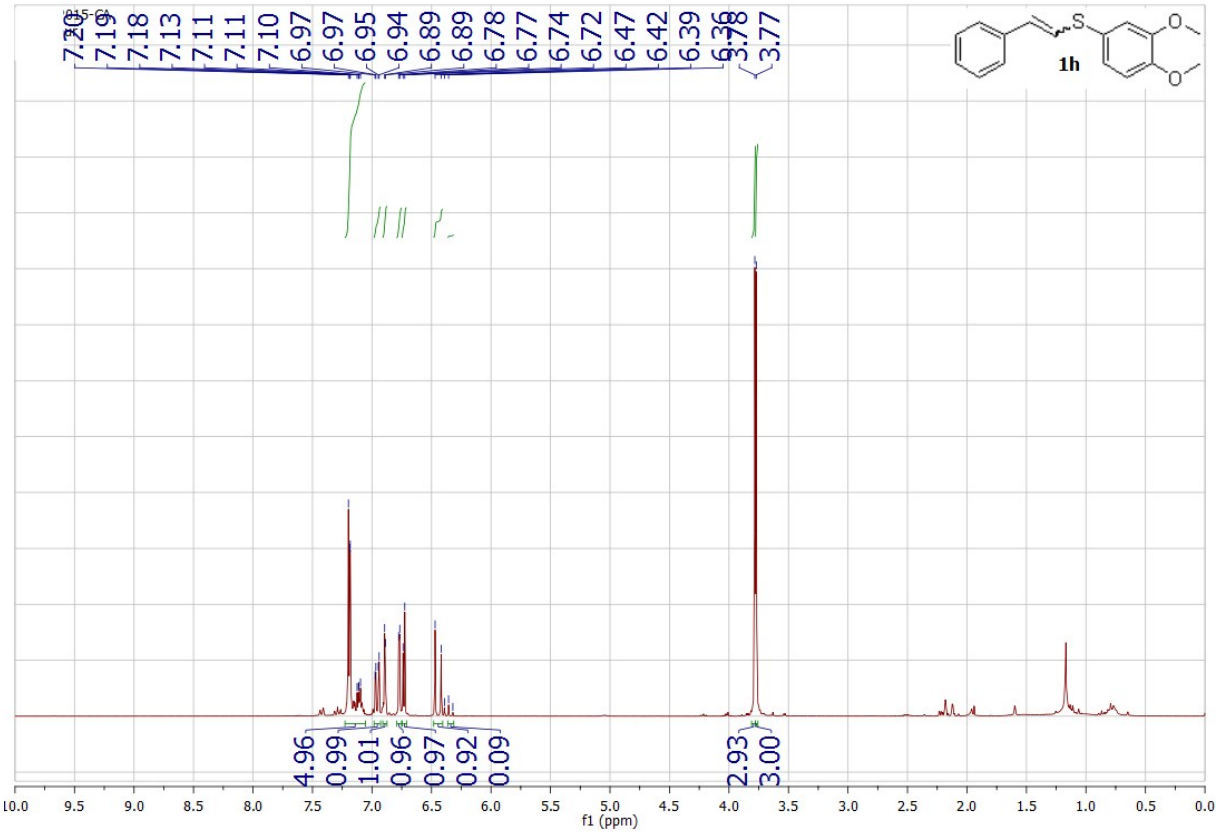
2-bromo-2,2-difluoro-1-morpholinoethan-1-one was synthesized according to a reported procedure.[13]

[13] A. Prieto, R. Melot, D. Bouyssi, N. Monteiro, *ACS Catal.* **2016**, *6*, 1093-1096

7. NMR spectra of the new compounds



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7.18
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7.10
6.97
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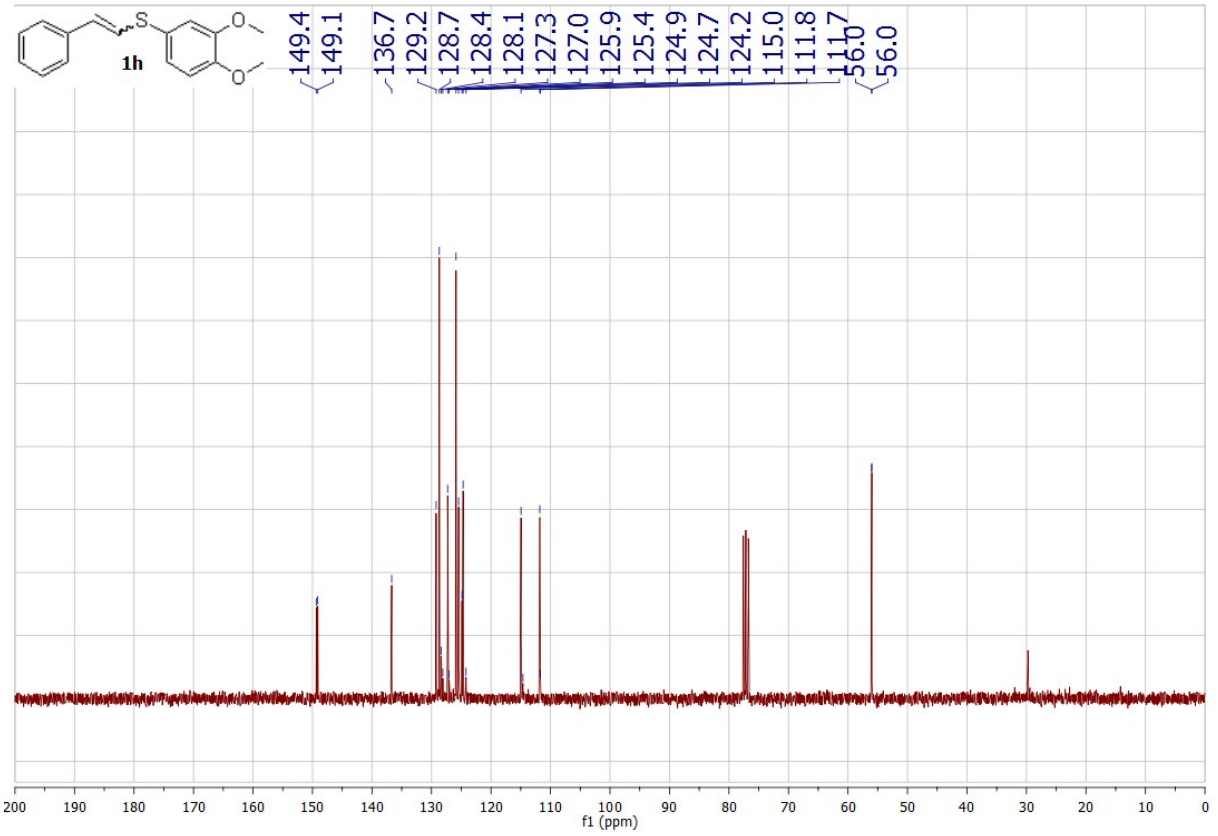
6.95
6.94
6.89
6.89
6.78
6.77
6.74
6.72
6.47
6.42
6.39
6.36
3.78
3.77
1h
4.96
0.99
1.01
0.96
0.97
0.92
0.09
2.93
3.00
f1 (ppm)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128.1
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124.9
124.7
124.2
115.0
111.8
111.7
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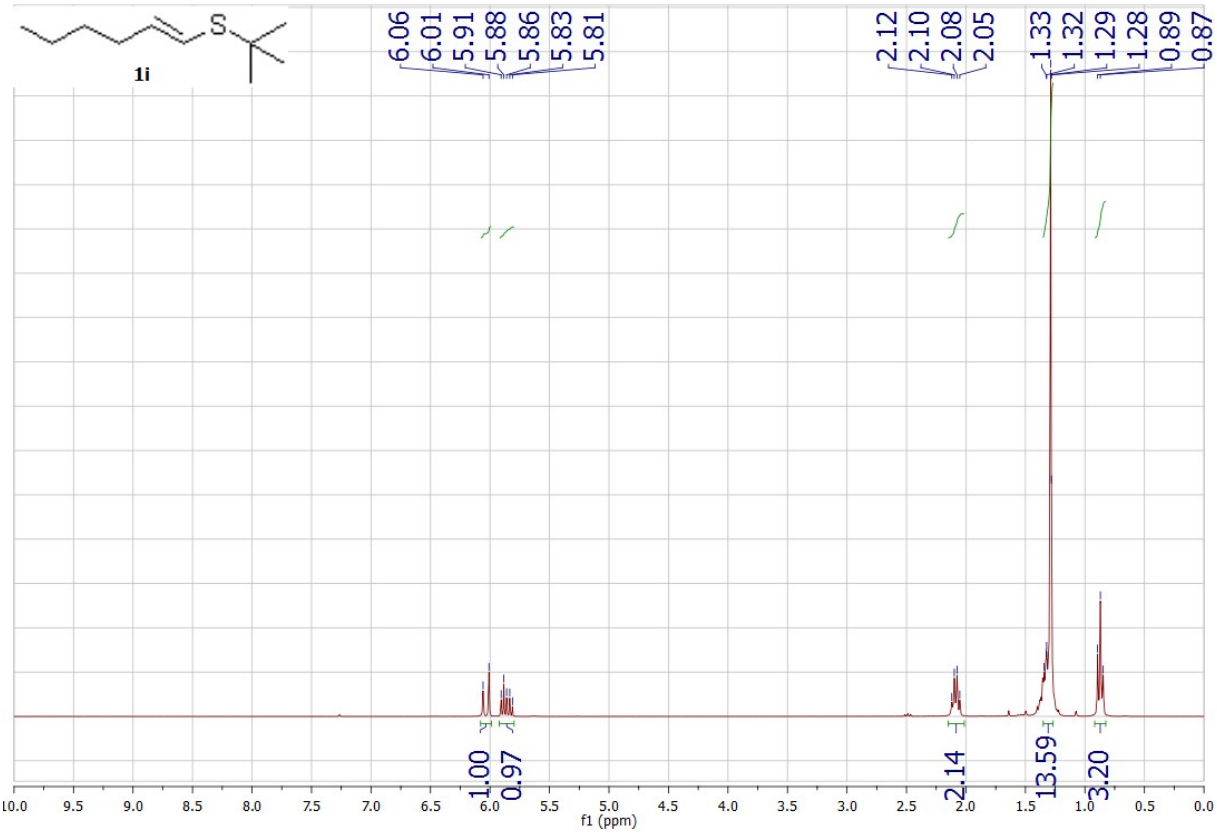
56.0
f1 (ppm)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2.10
2.08
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1.32
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1.28
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0.87
1.00
0.97
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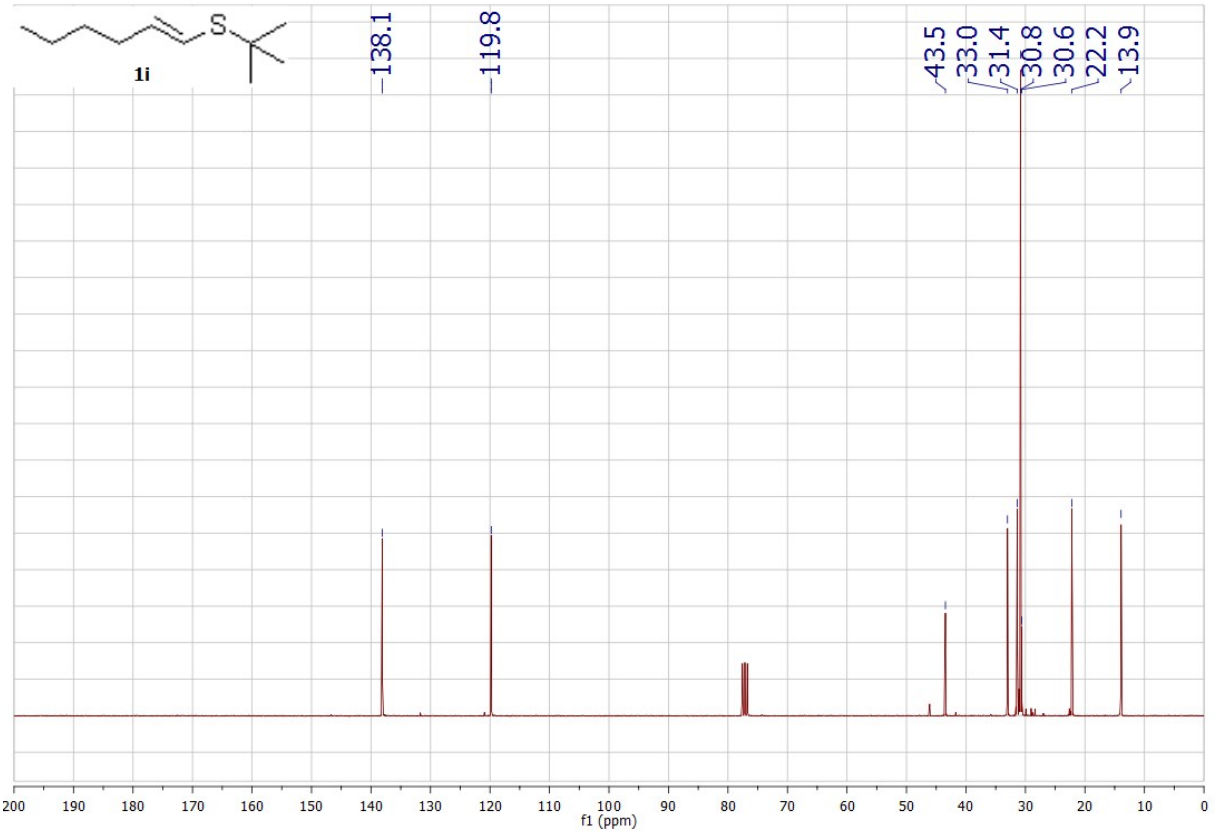
13.59
3.20
f1 (ppm)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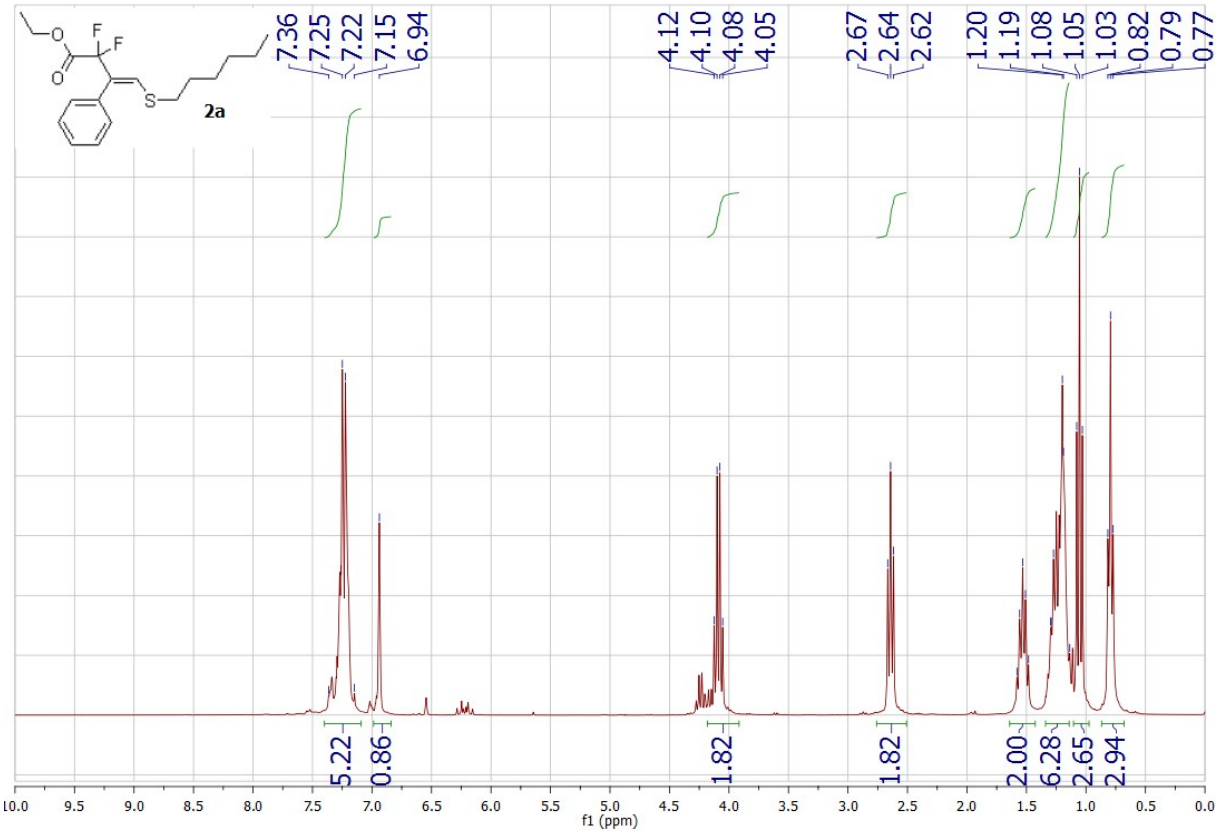
30.6
22.2
13.9
f1 (ppm)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4.08
4.05
2.67
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2.62
1.20
1.19
1.08
1.05
1.03
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5.22
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1.82
1.82
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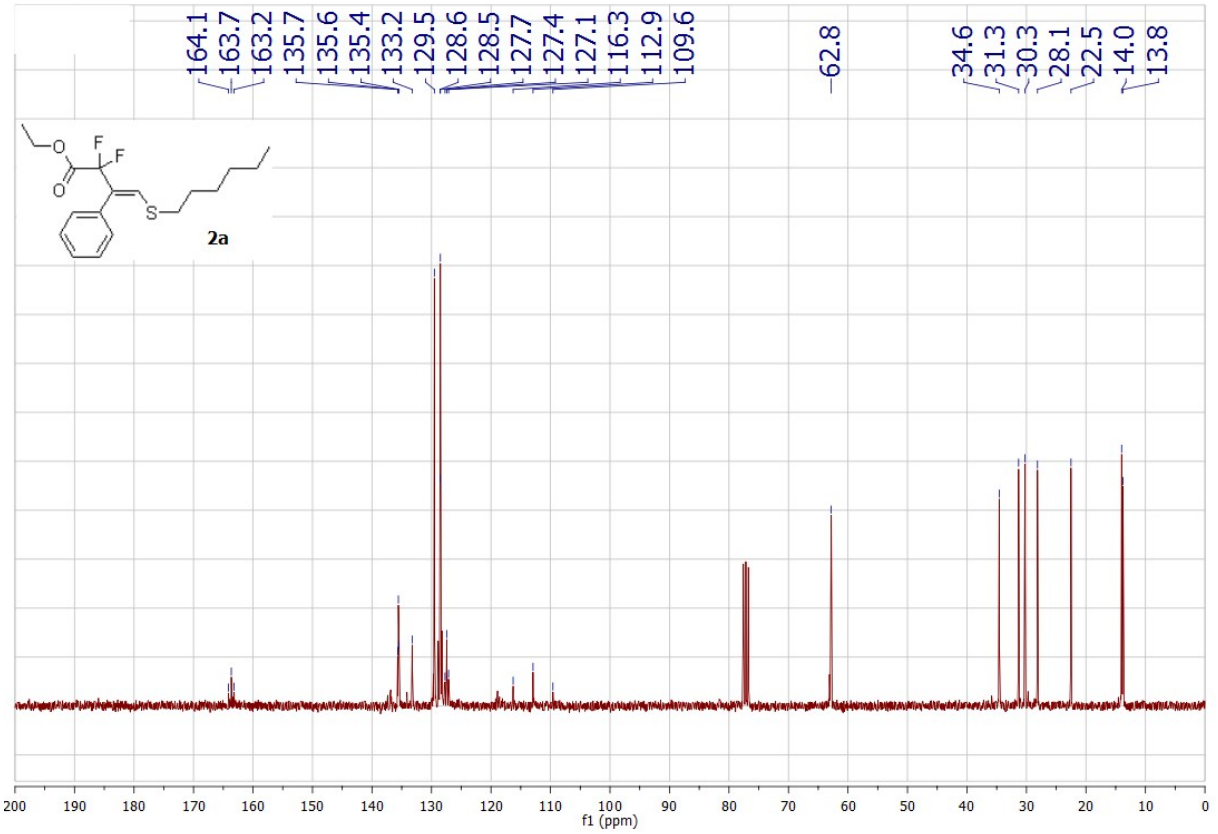
2.65
2.94
f1 (ppm)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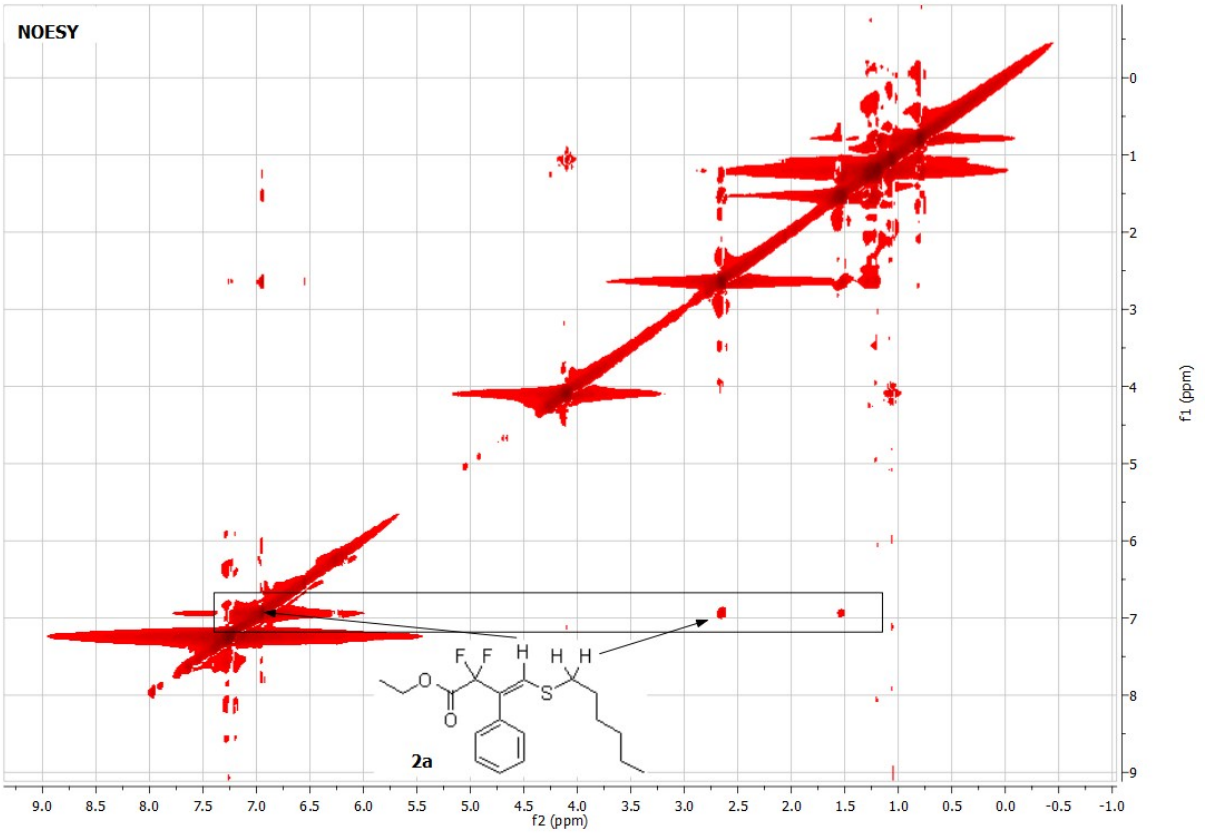
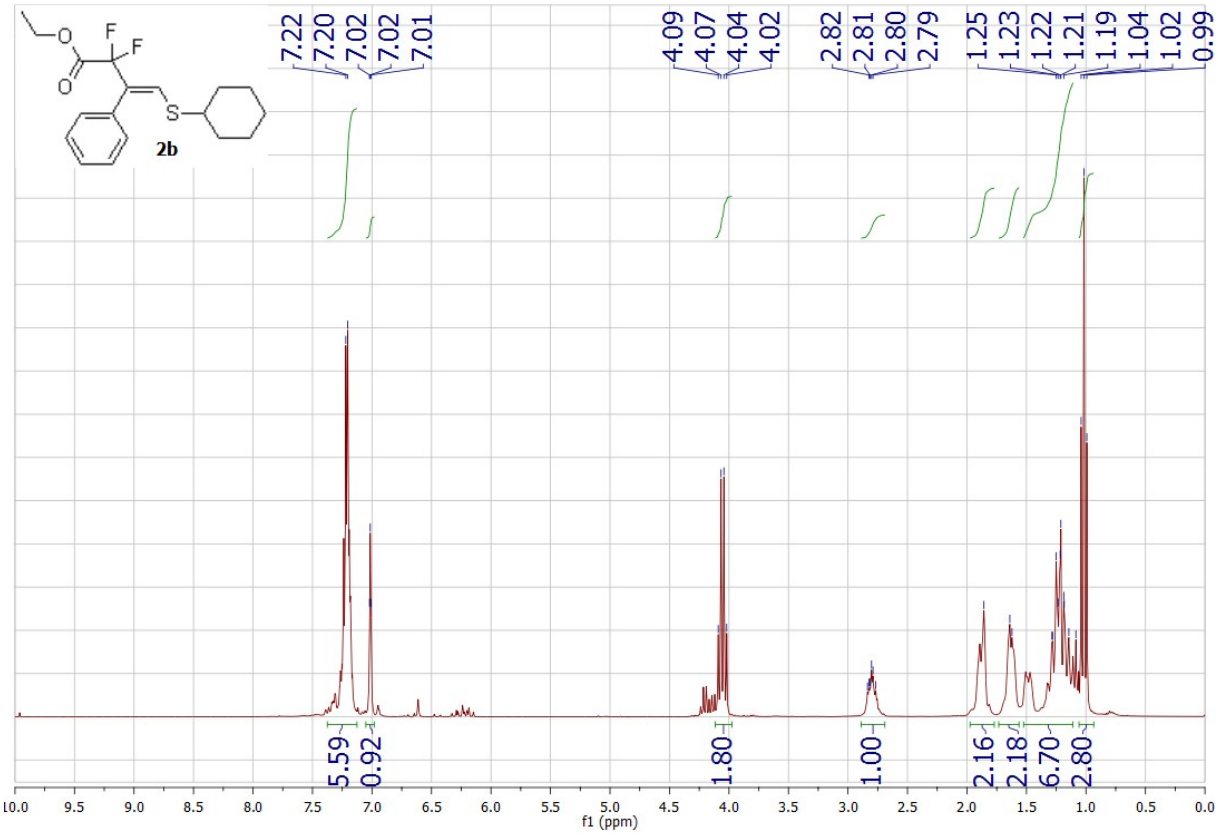
163.2
135.7
135.6
135.4
133.2
129.5
128.6
128.5
127.7
127.4
127.1
116.3
112.9
109.6
62.8
34.6
31.3
30.3
28.1
22.5
14.0
13.8
f1 (ppm)


NOESY
f2 (ppm)
f1 (ppm)
2a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4.07
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4.02
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2.80
2.79
1.25
1.23
1.22
1.21
1.19
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1.02
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0.92
1.80
1.00
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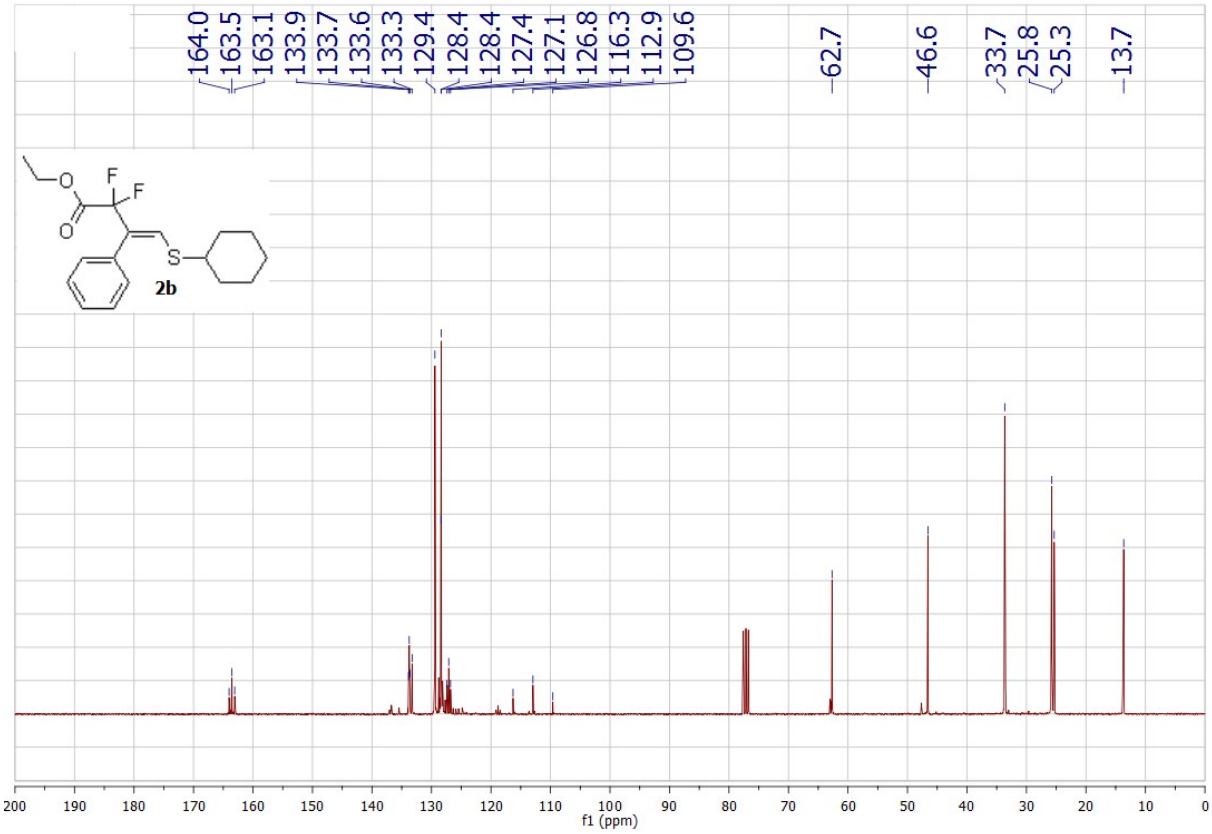
f1 (ppm)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127.4
127.1
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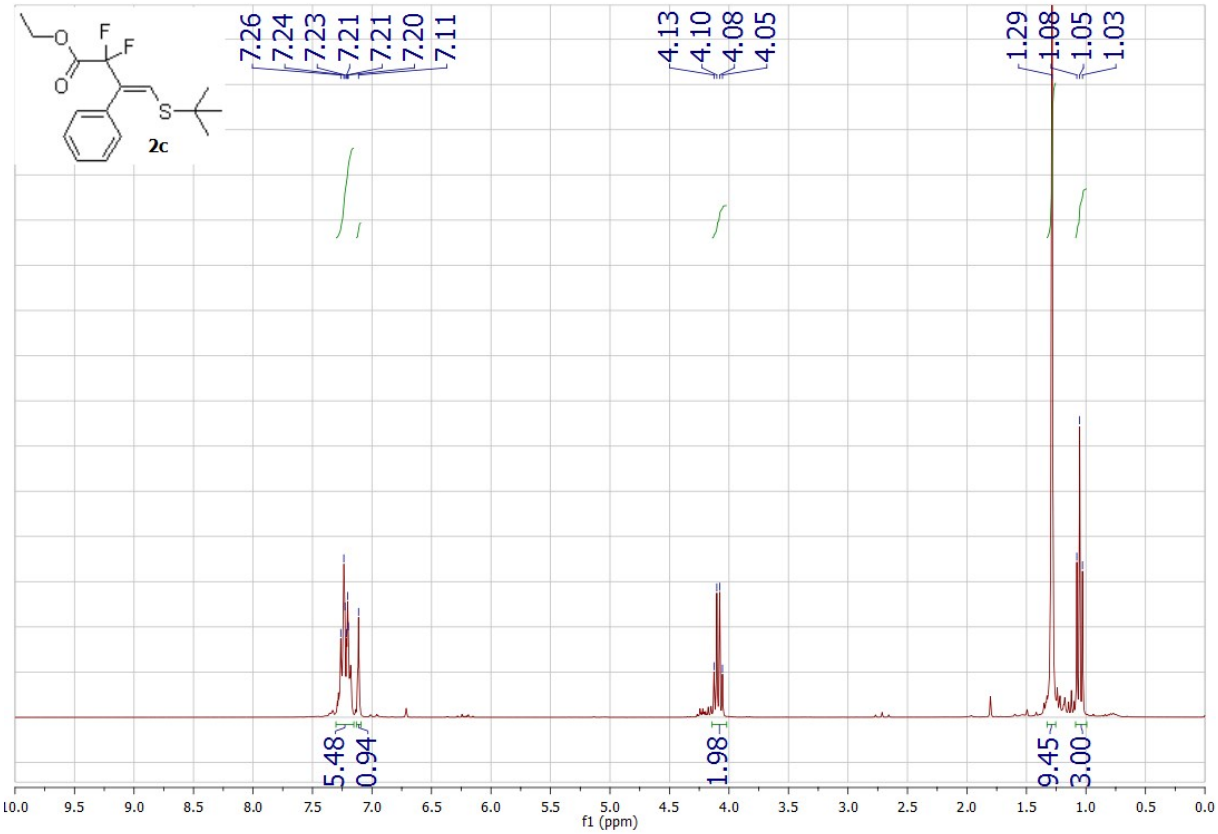
25.8
25.3
13.7
2b
f1 (ppm)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4.08
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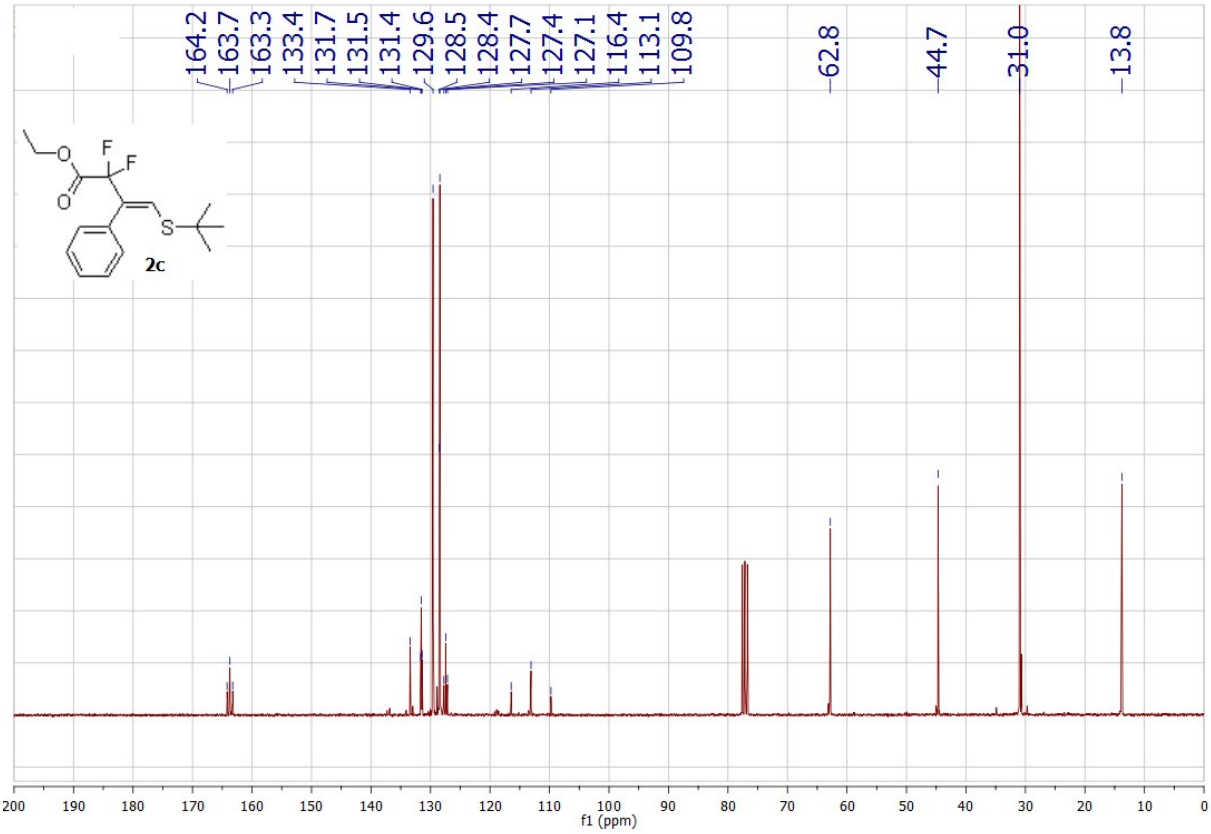
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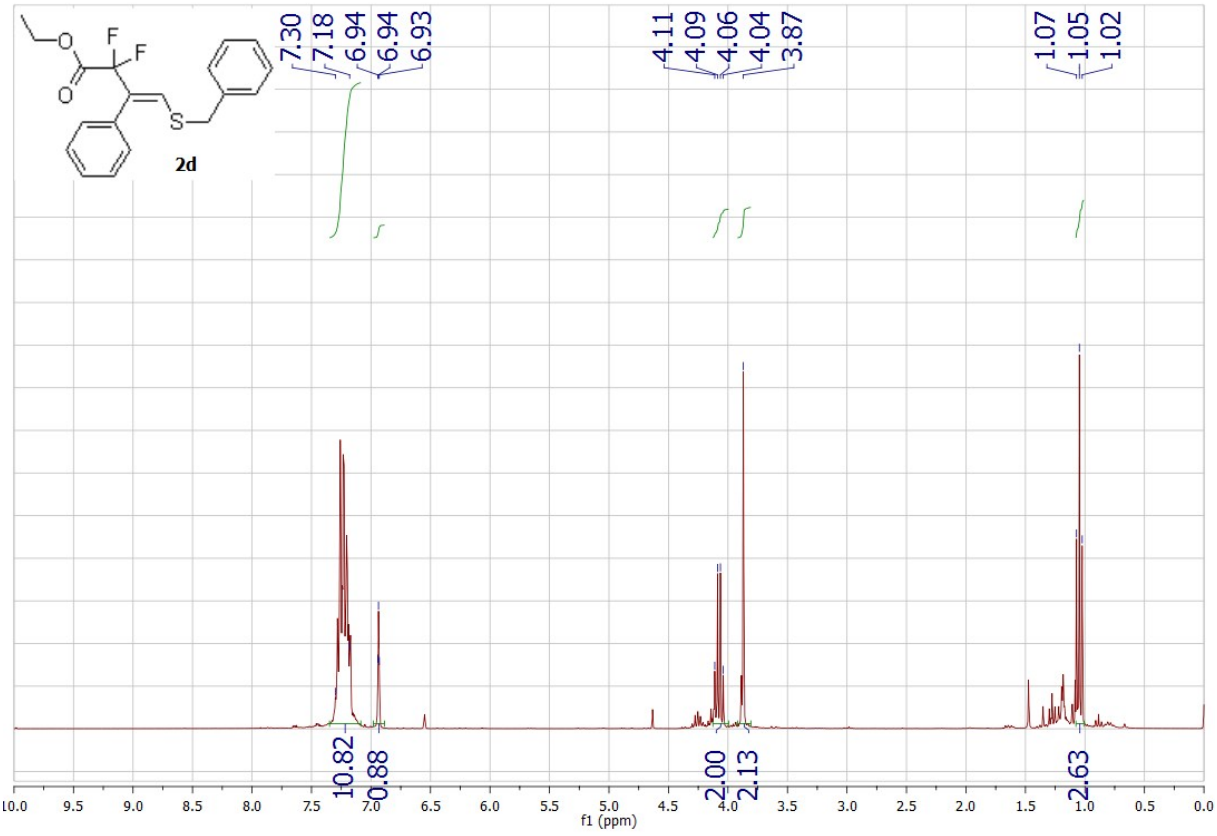
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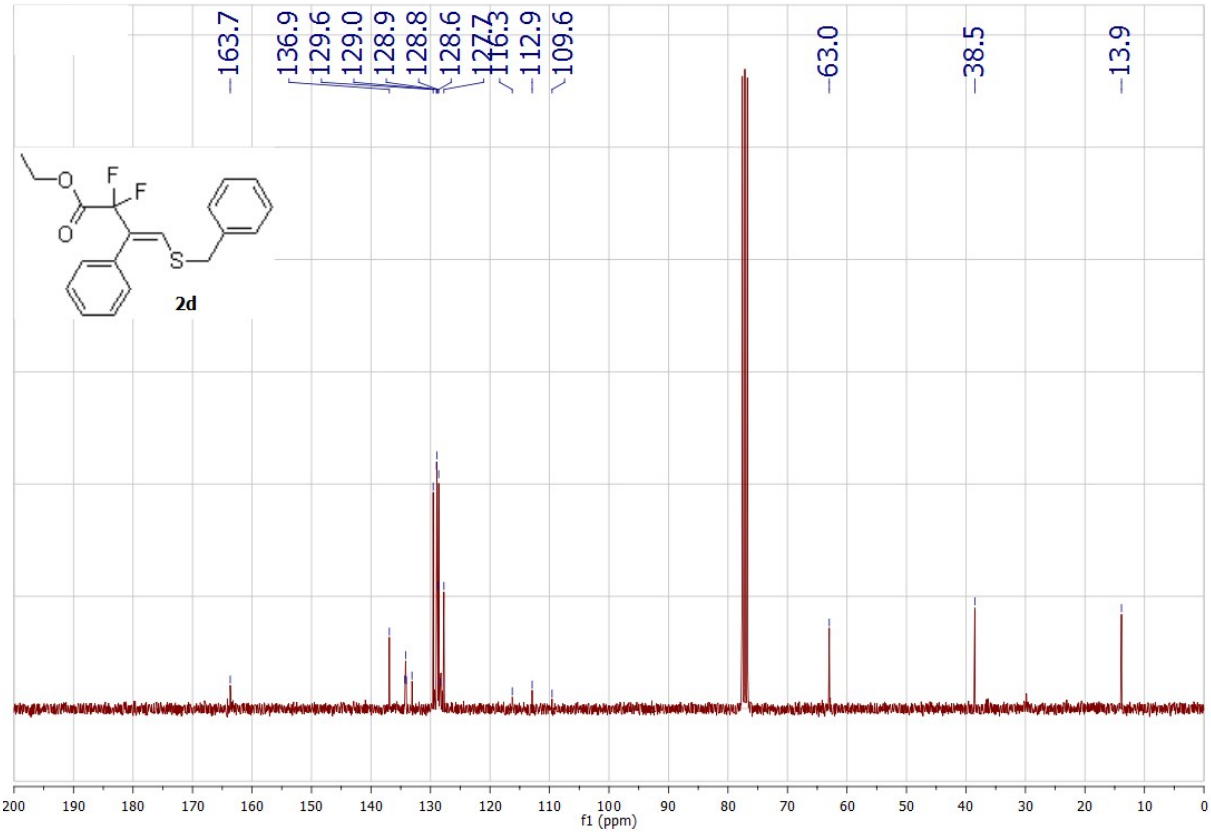
f1 (ppm)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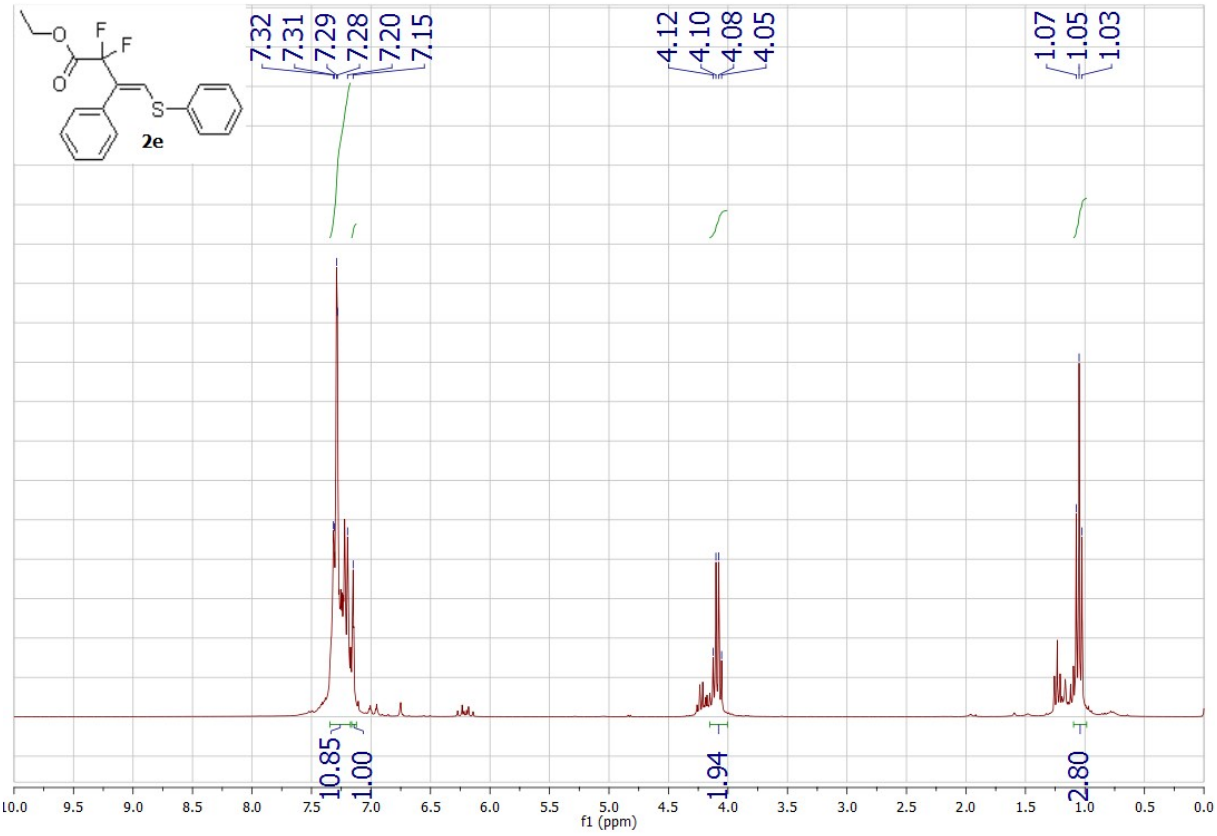
f1 (ppm)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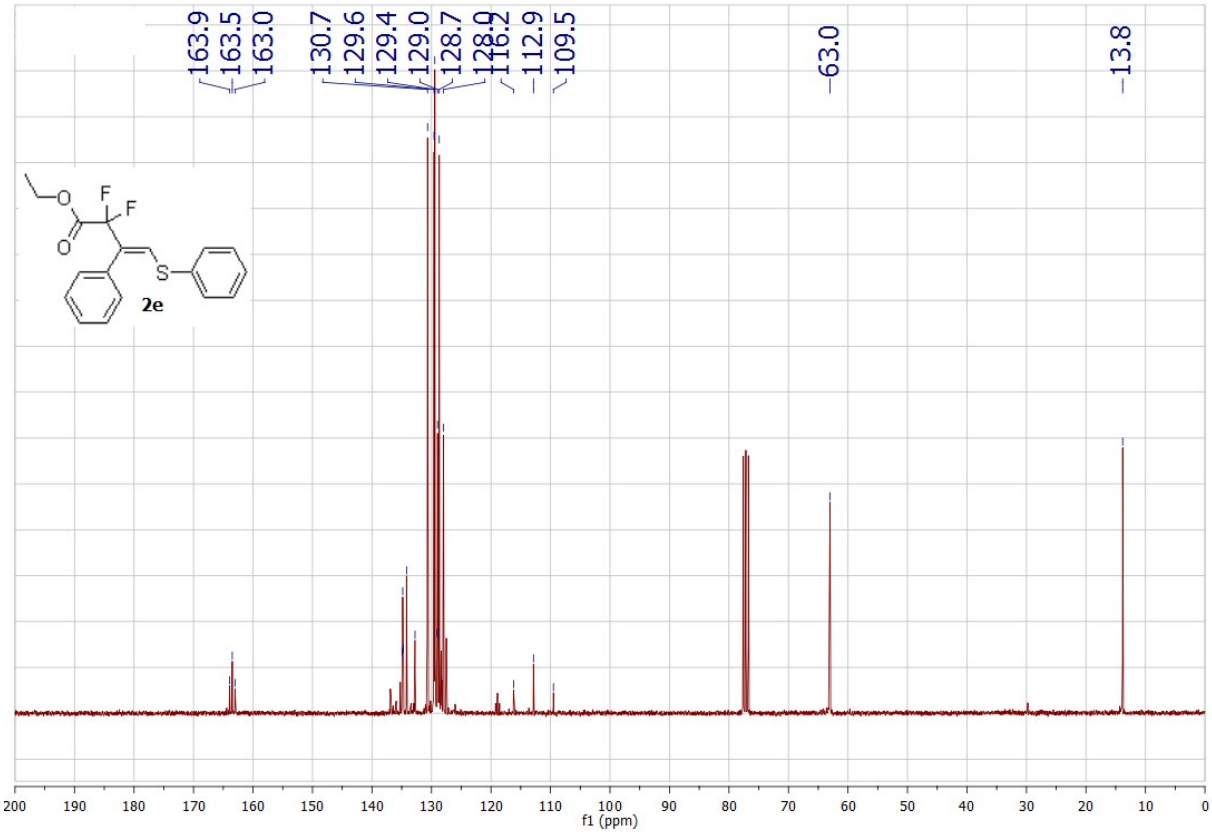
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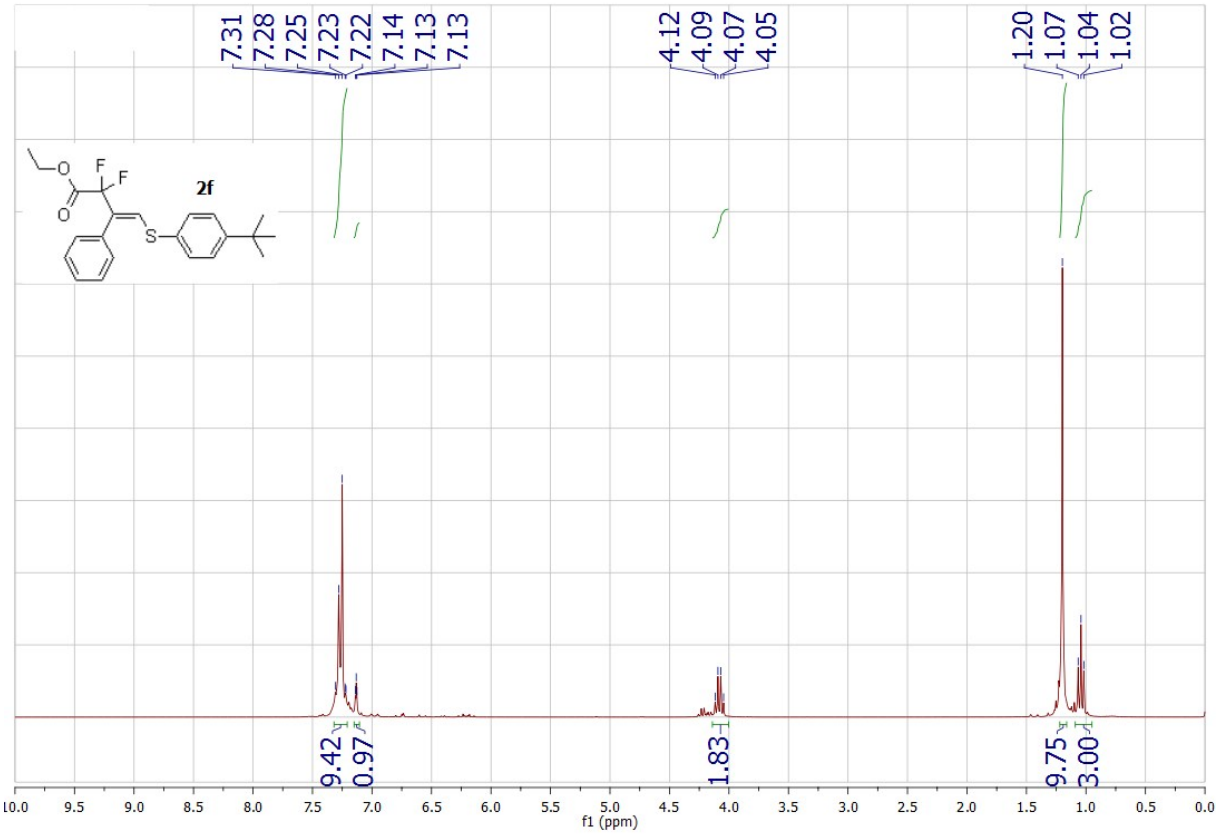
2e
f1 (ppm)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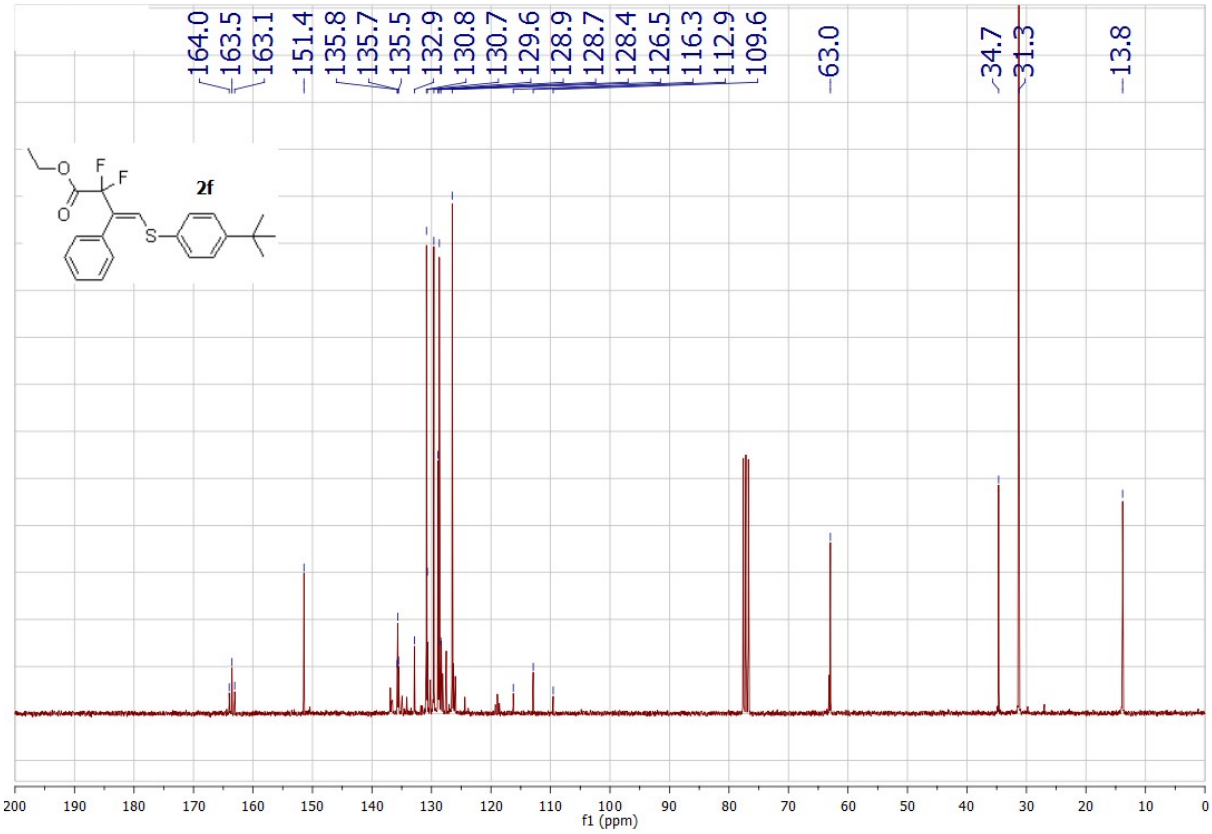
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109.6
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31.3
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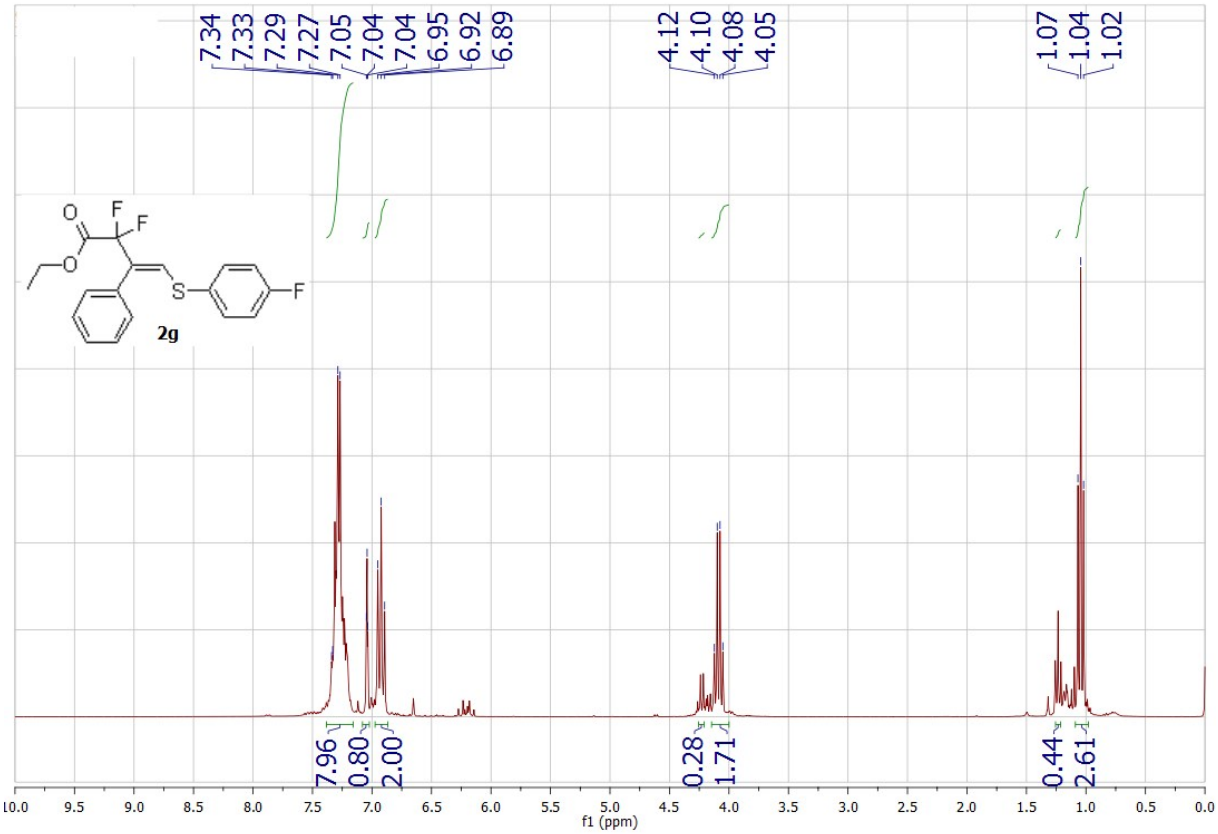
2f
f1 (ppm)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4.05
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1.71
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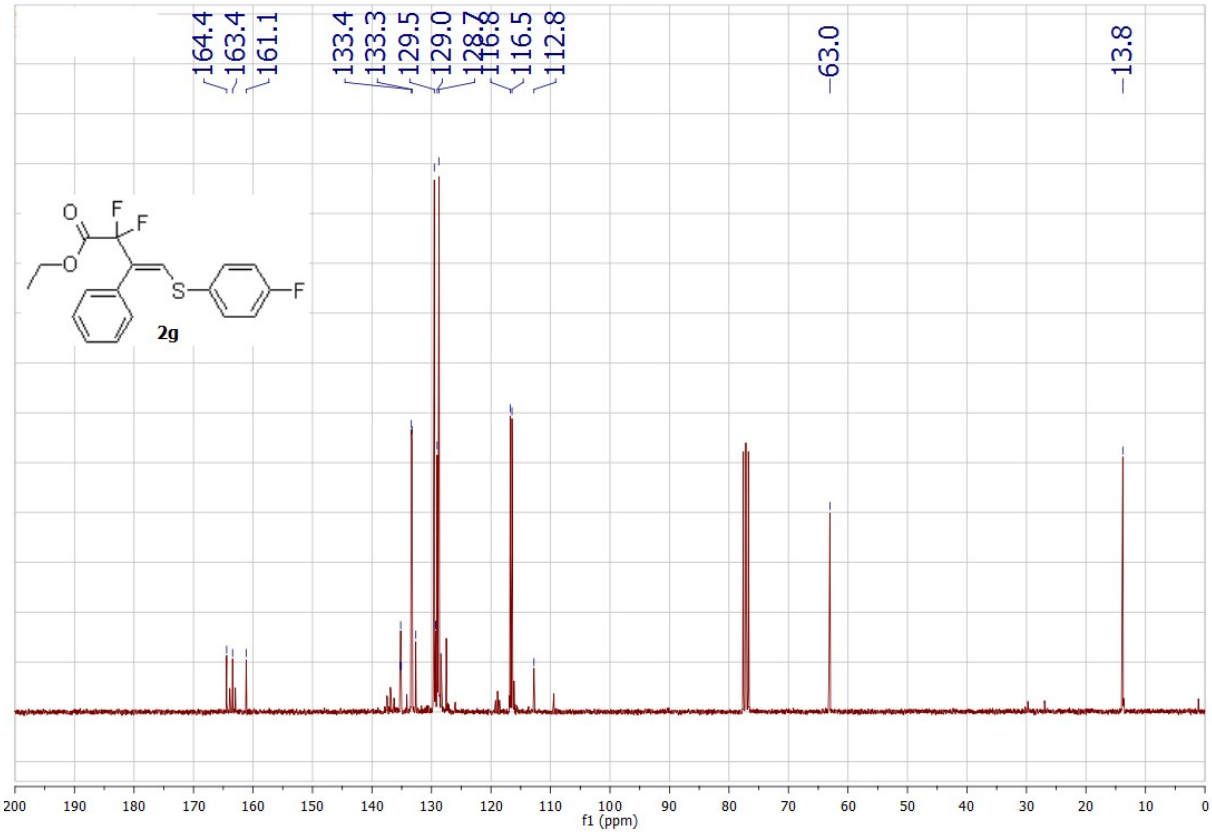
f1 (ppm)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112.8
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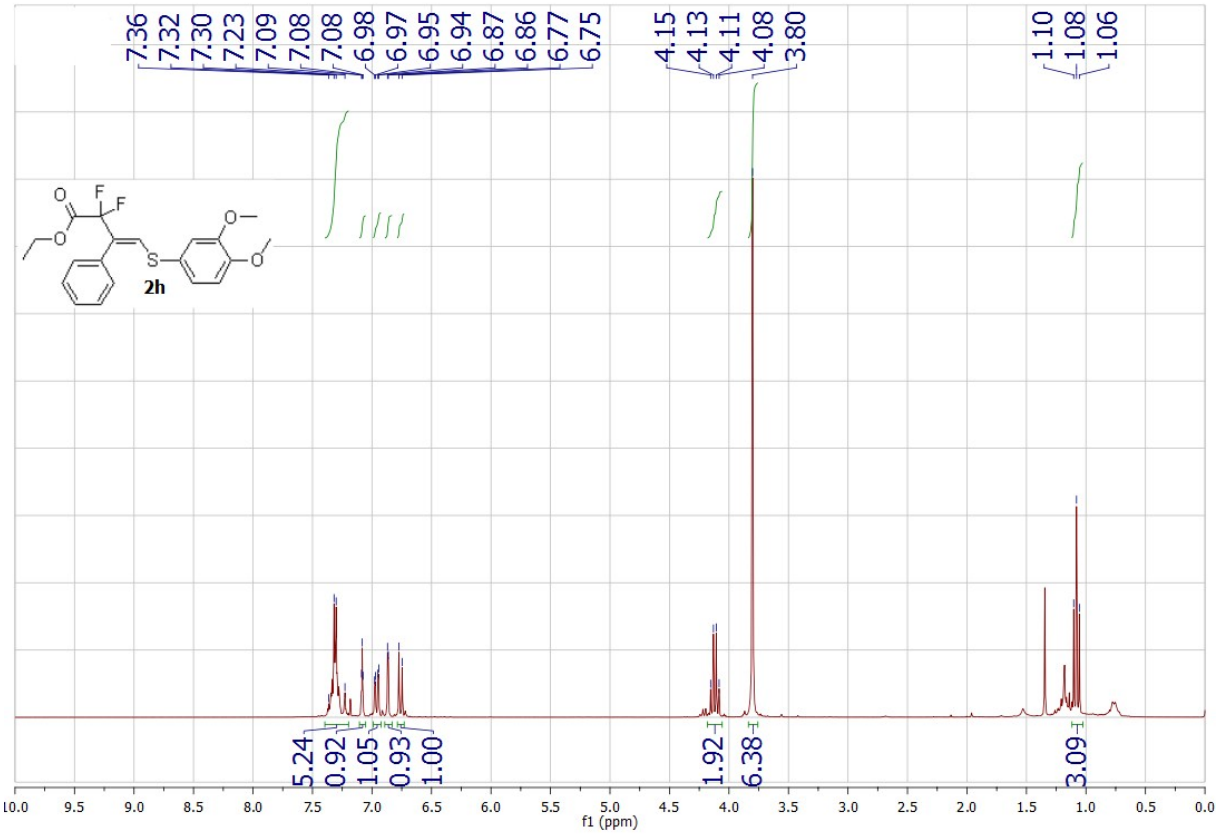
2g
f1 (ppm)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6.94
6.87
6.86
6.77
6.75
4.15
4.13
4.11
4.08
3.80
1.10
1.08
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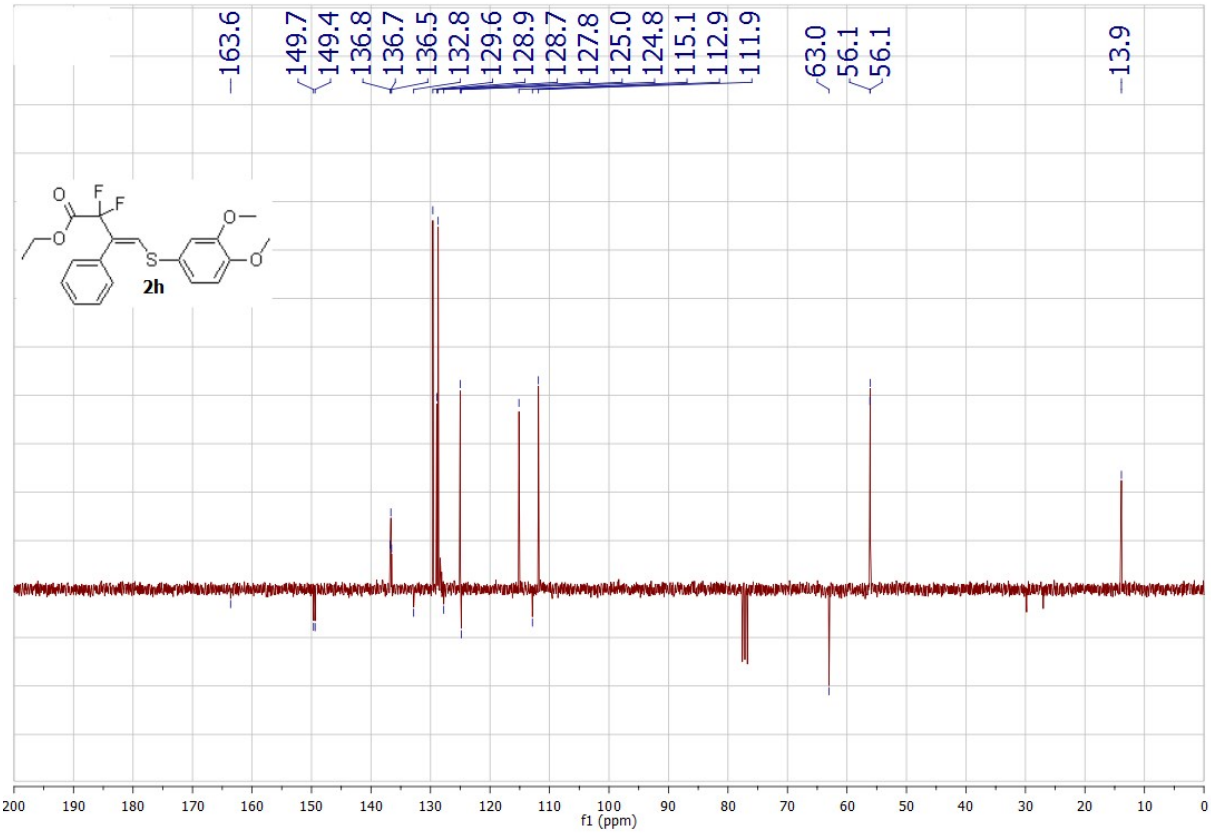
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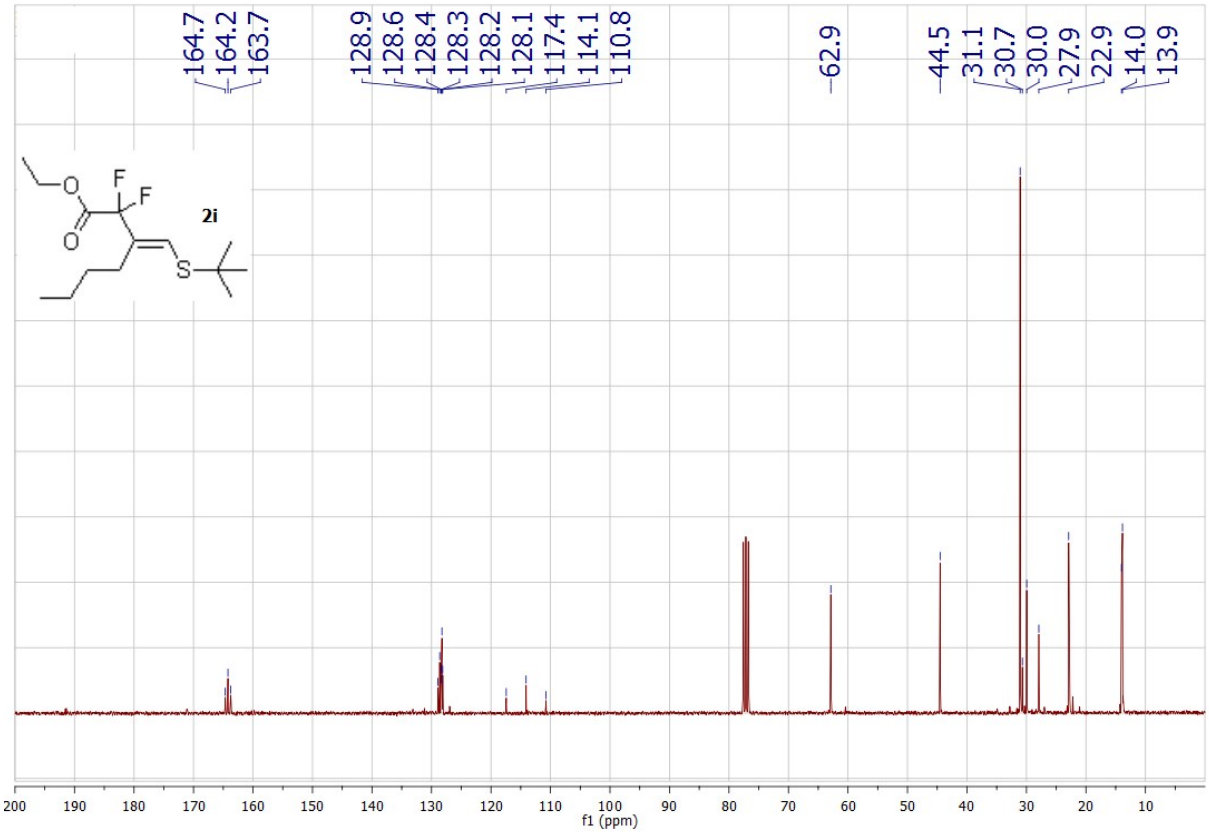
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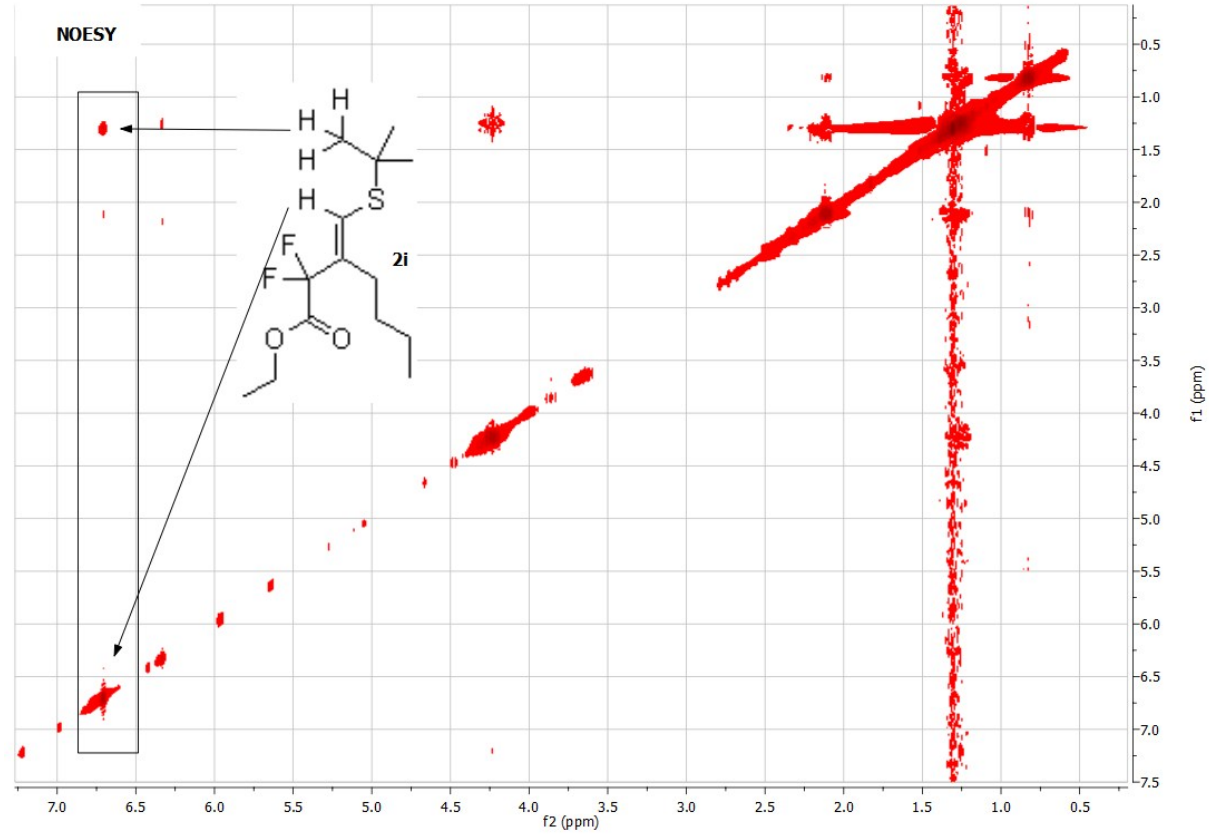
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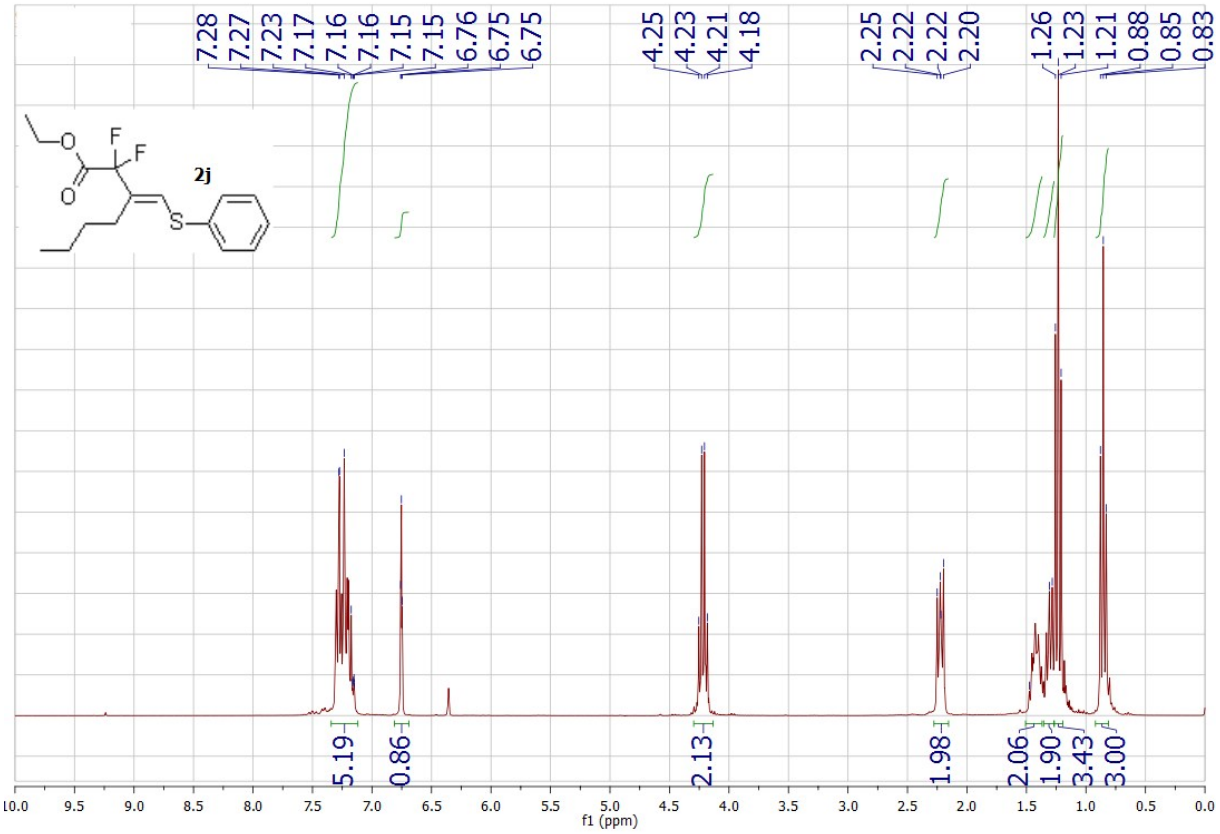
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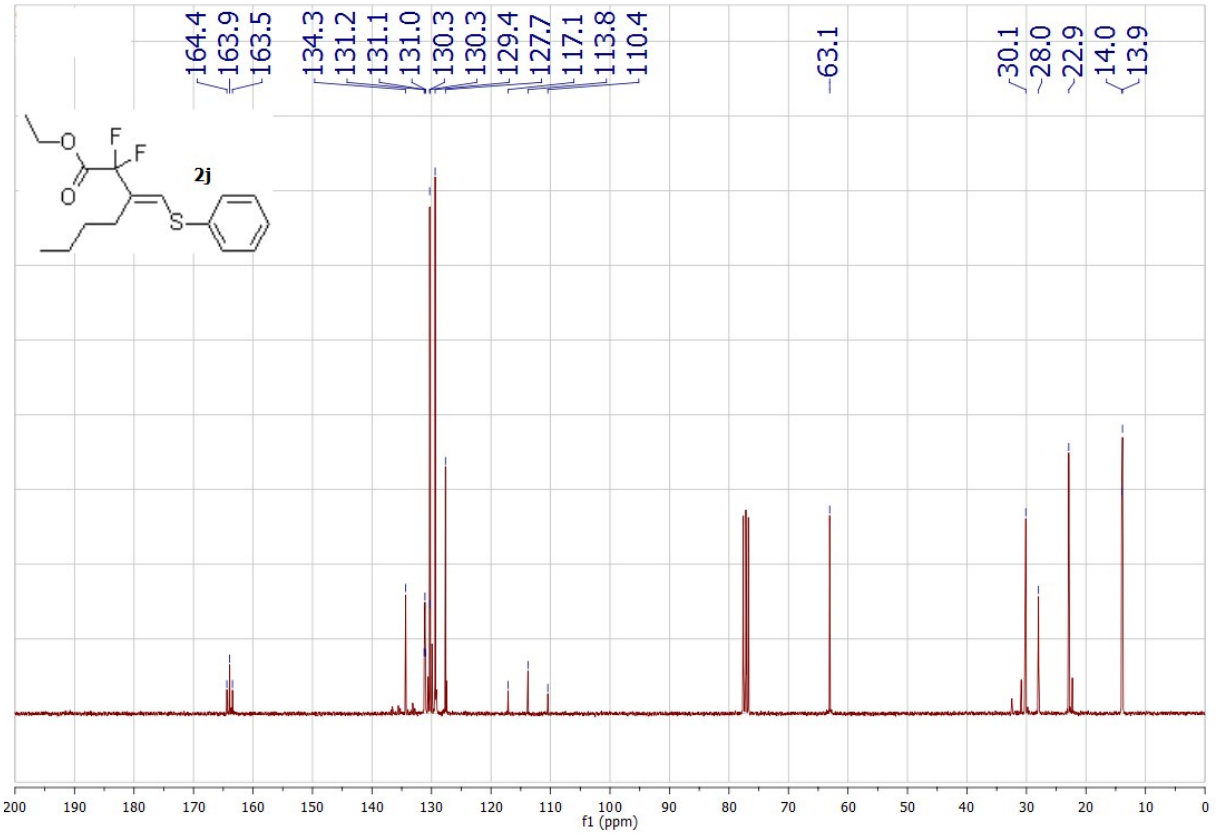
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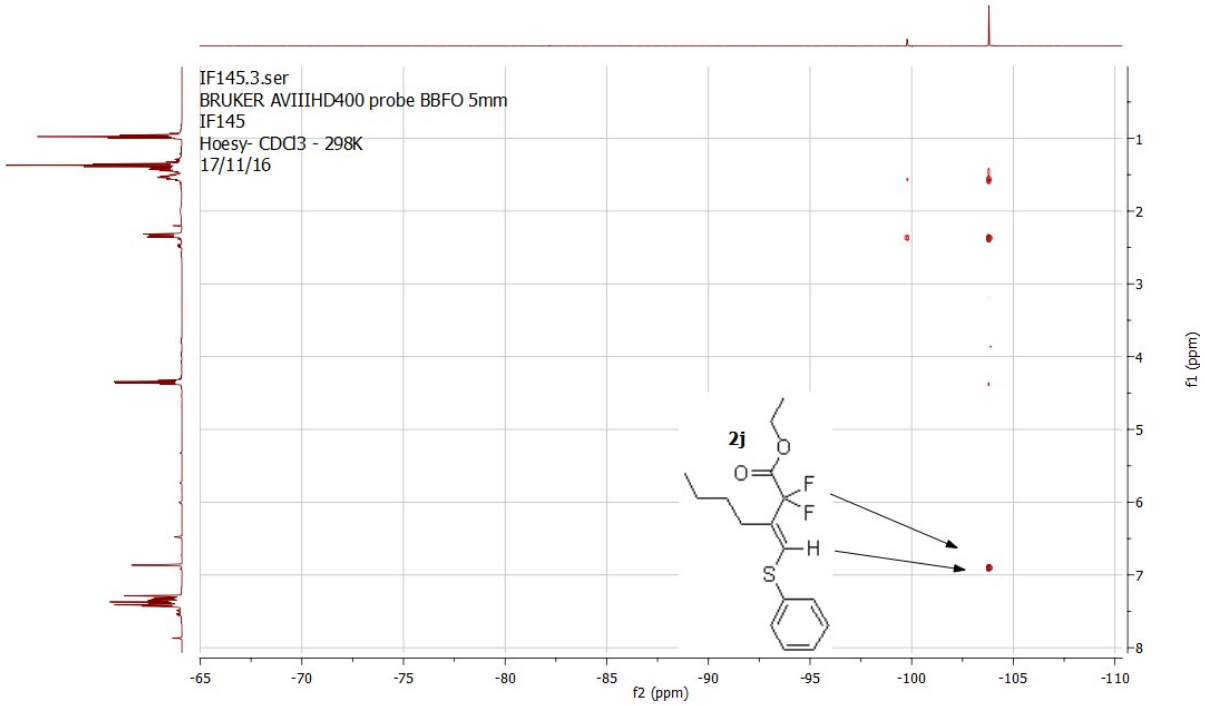
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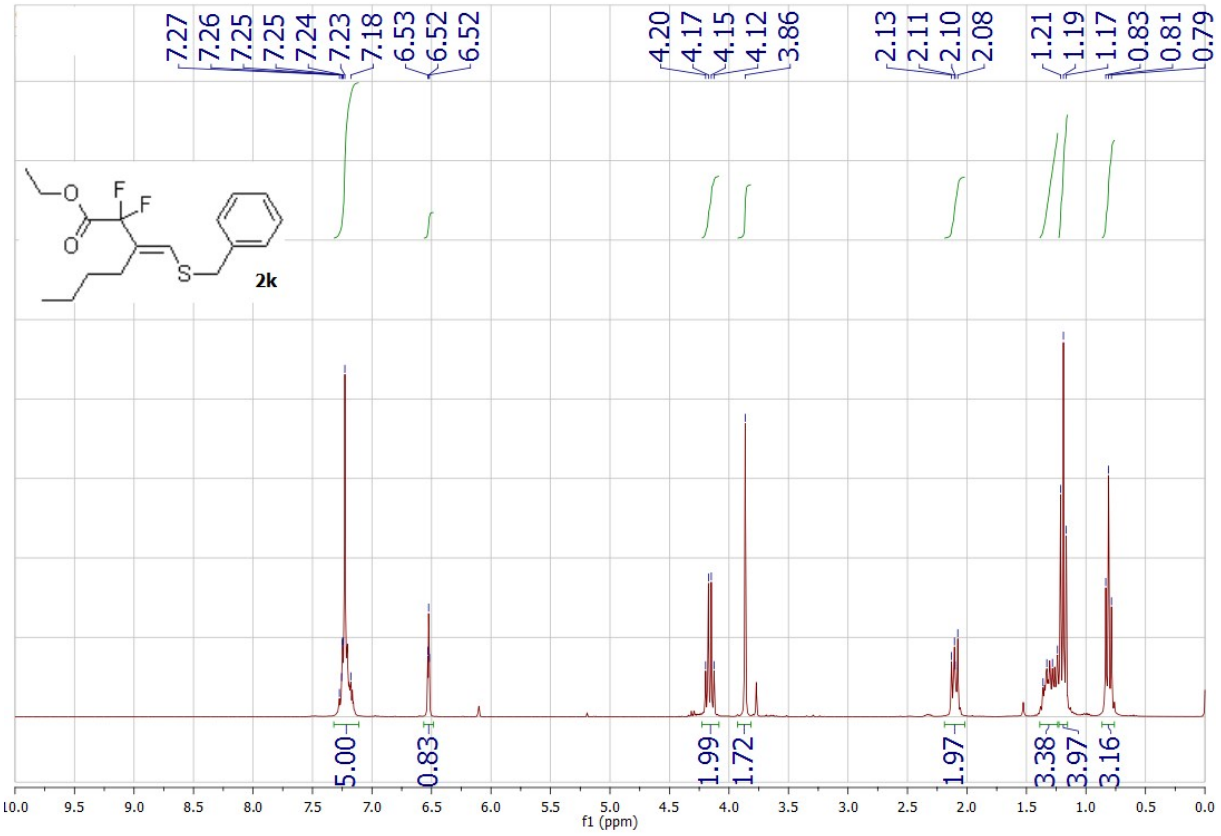
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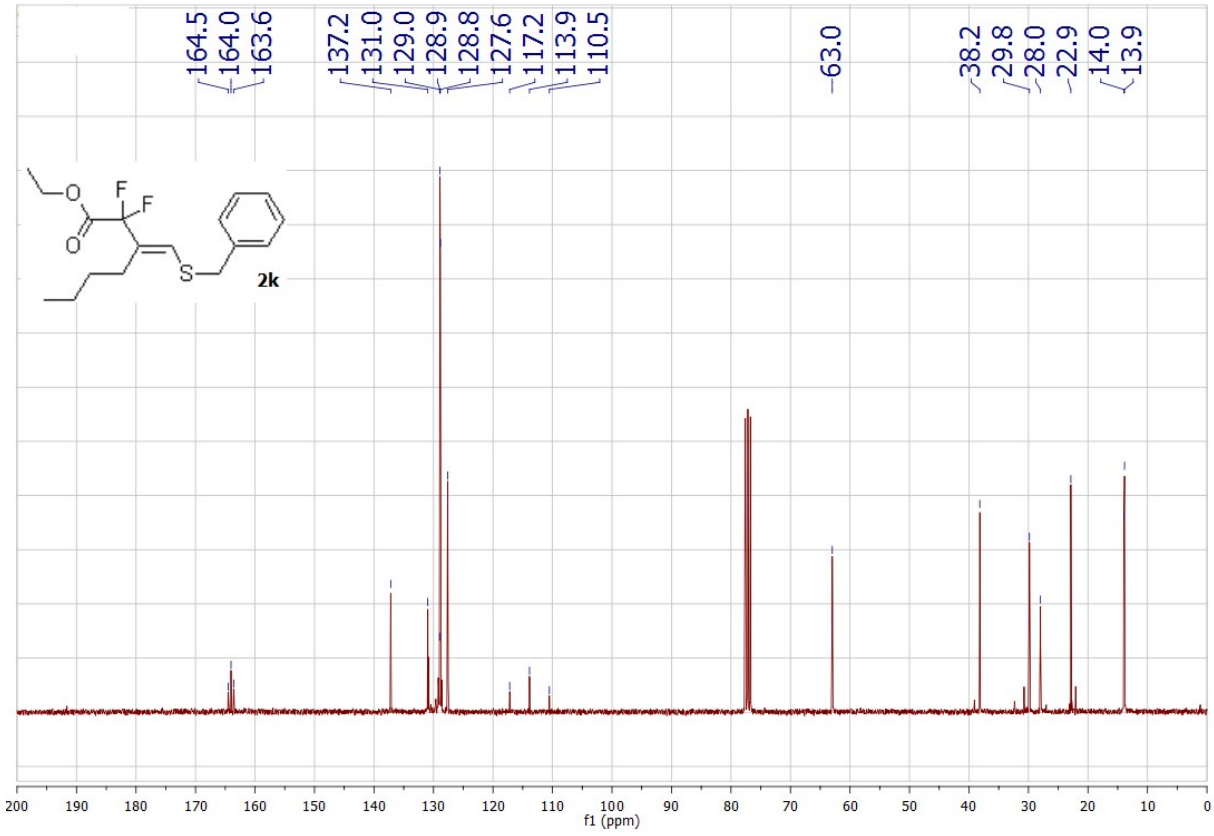
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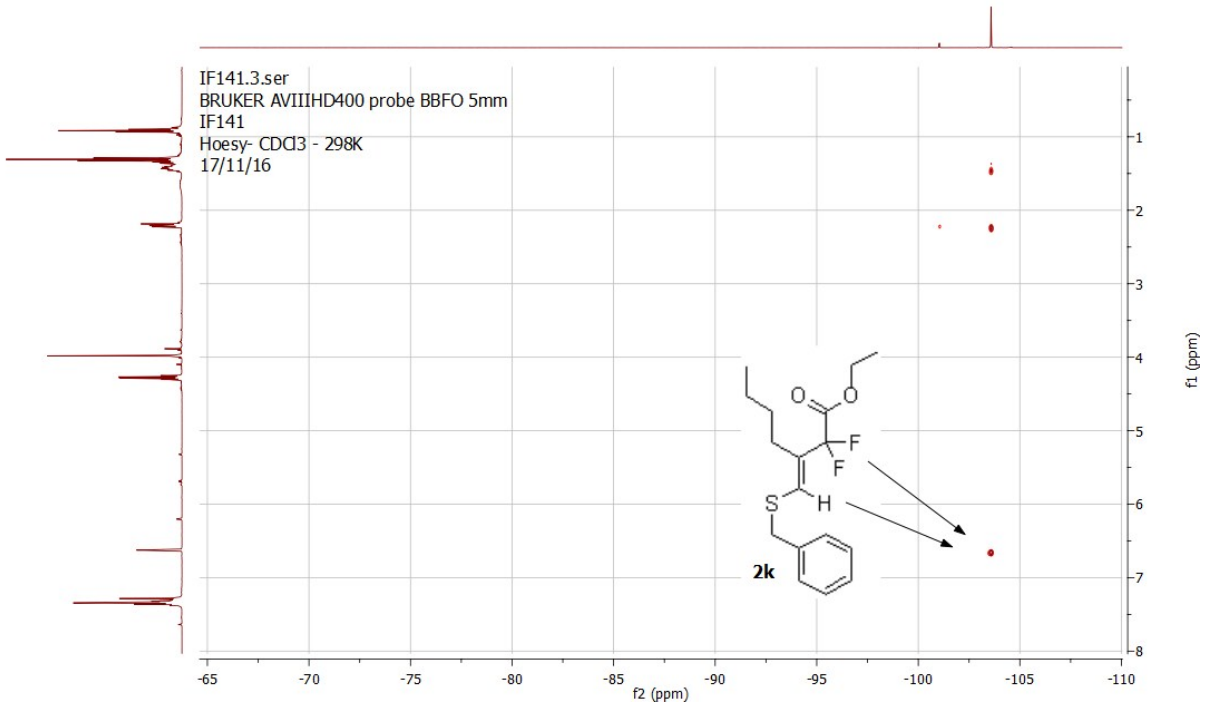
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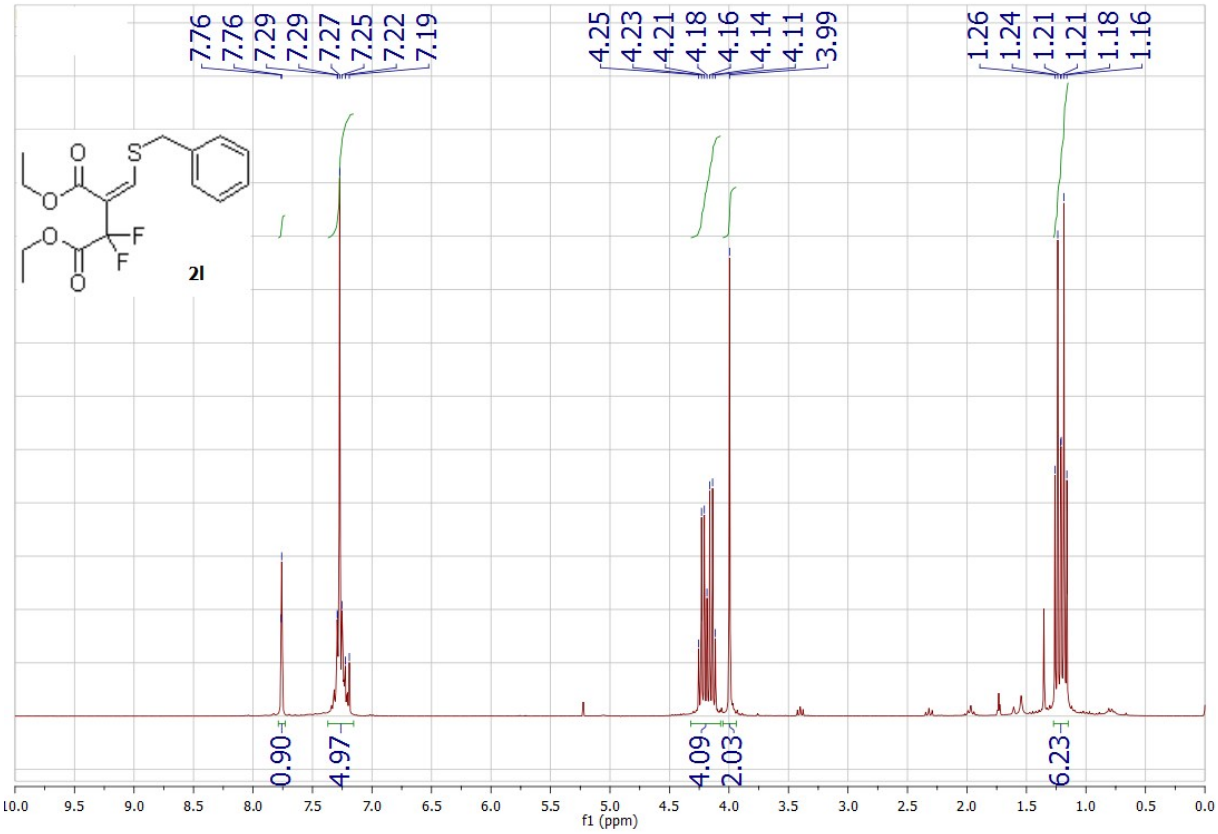
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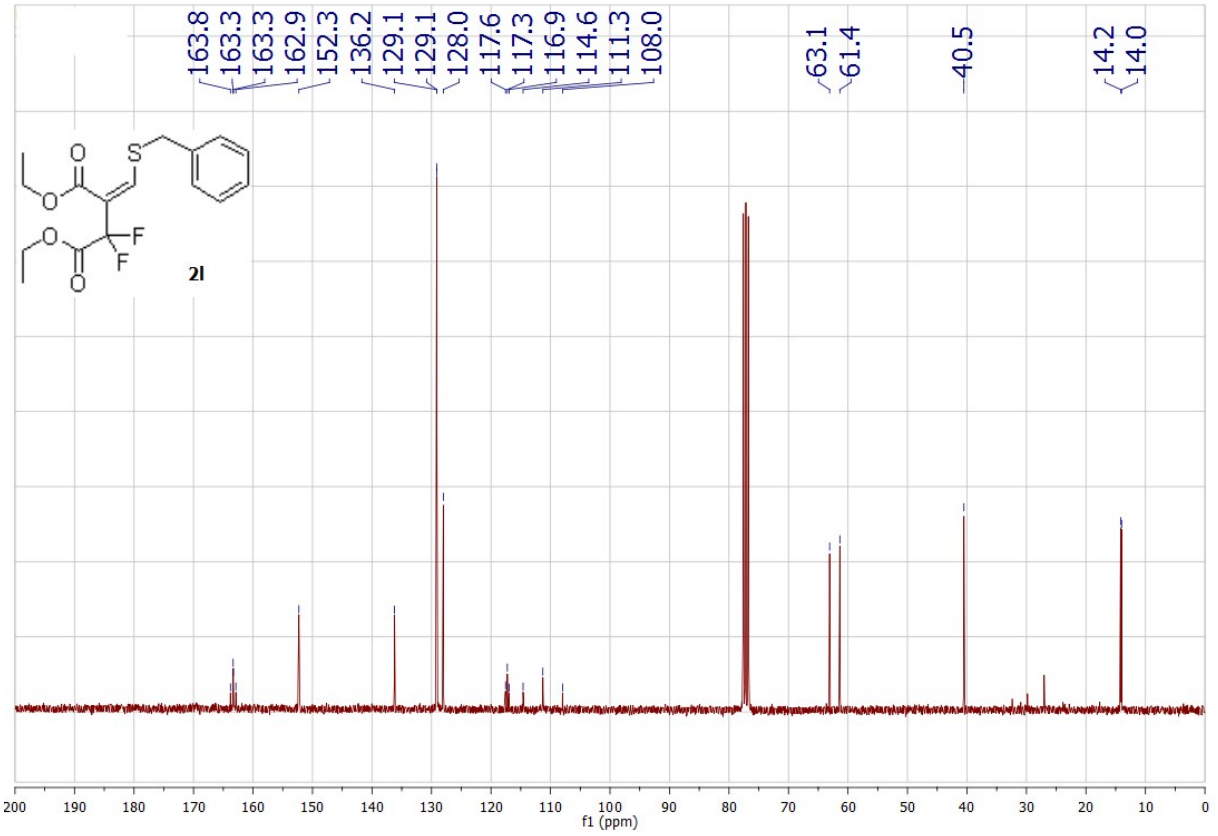
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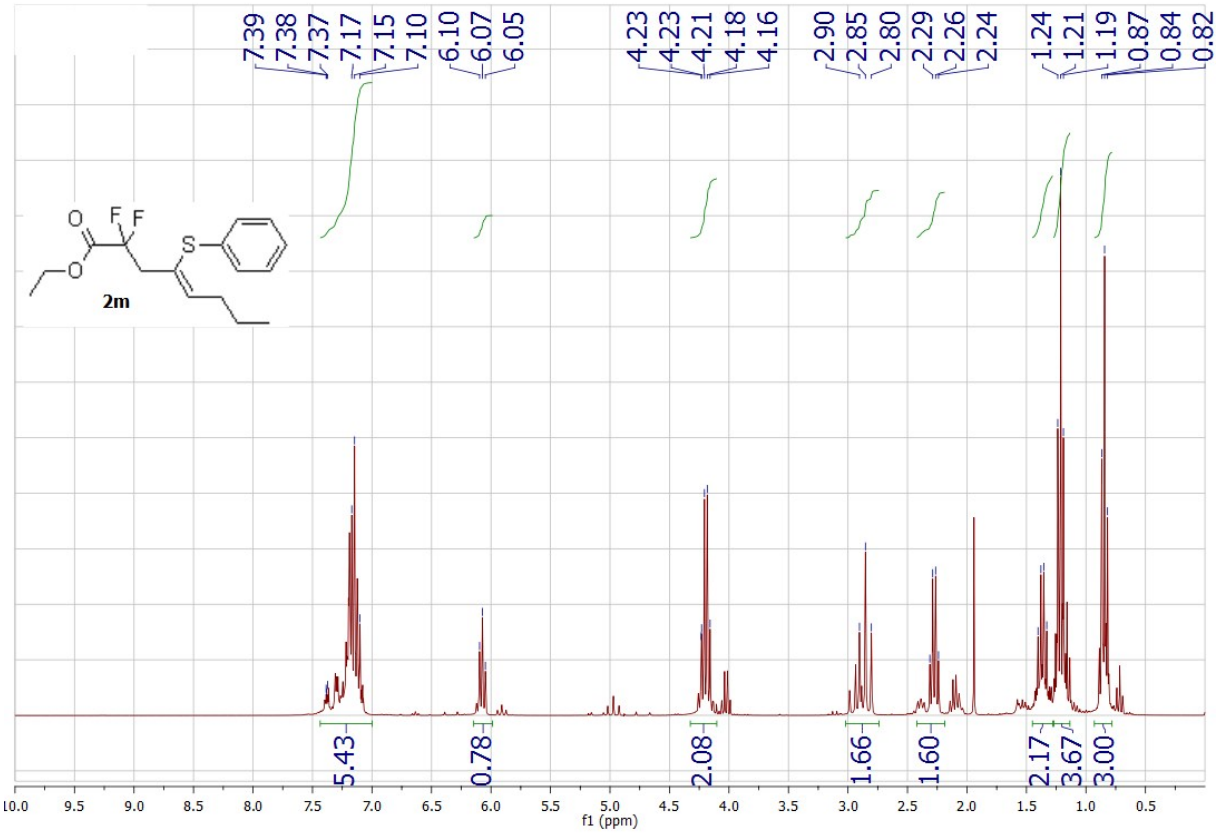
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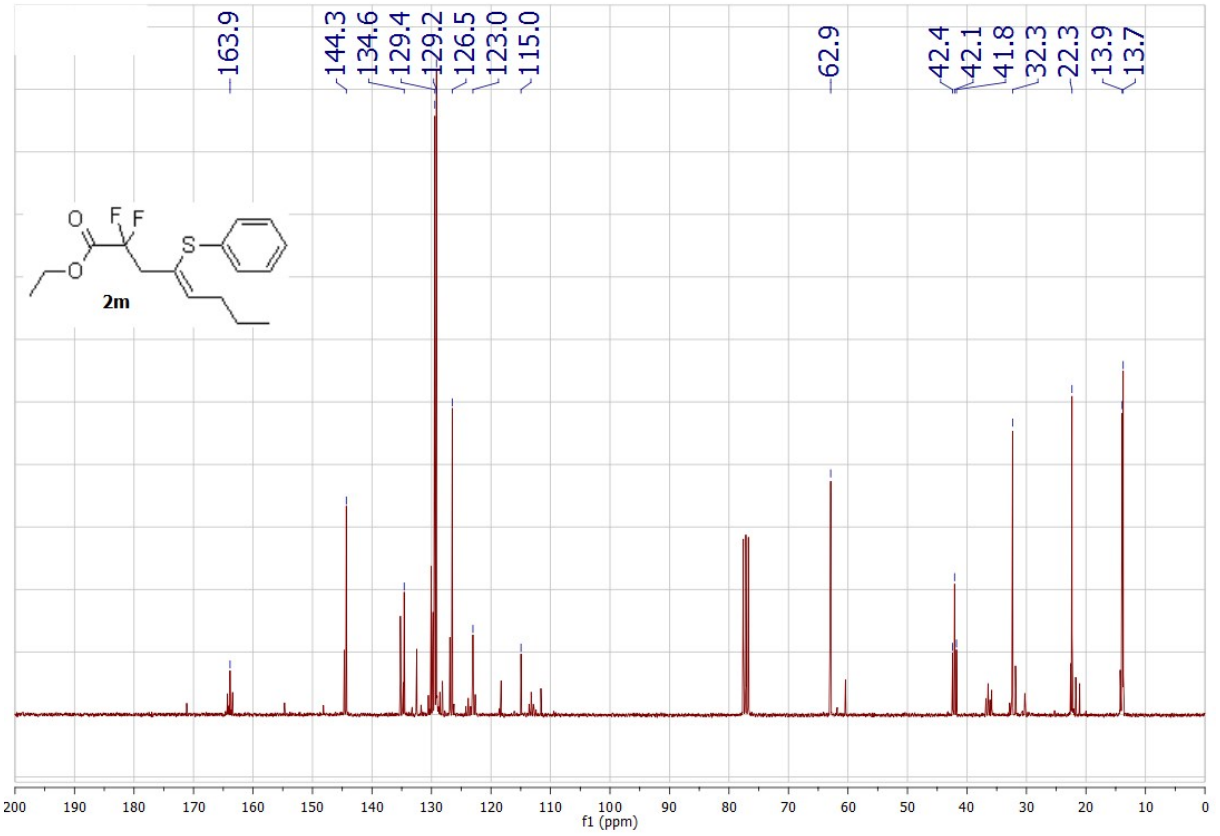
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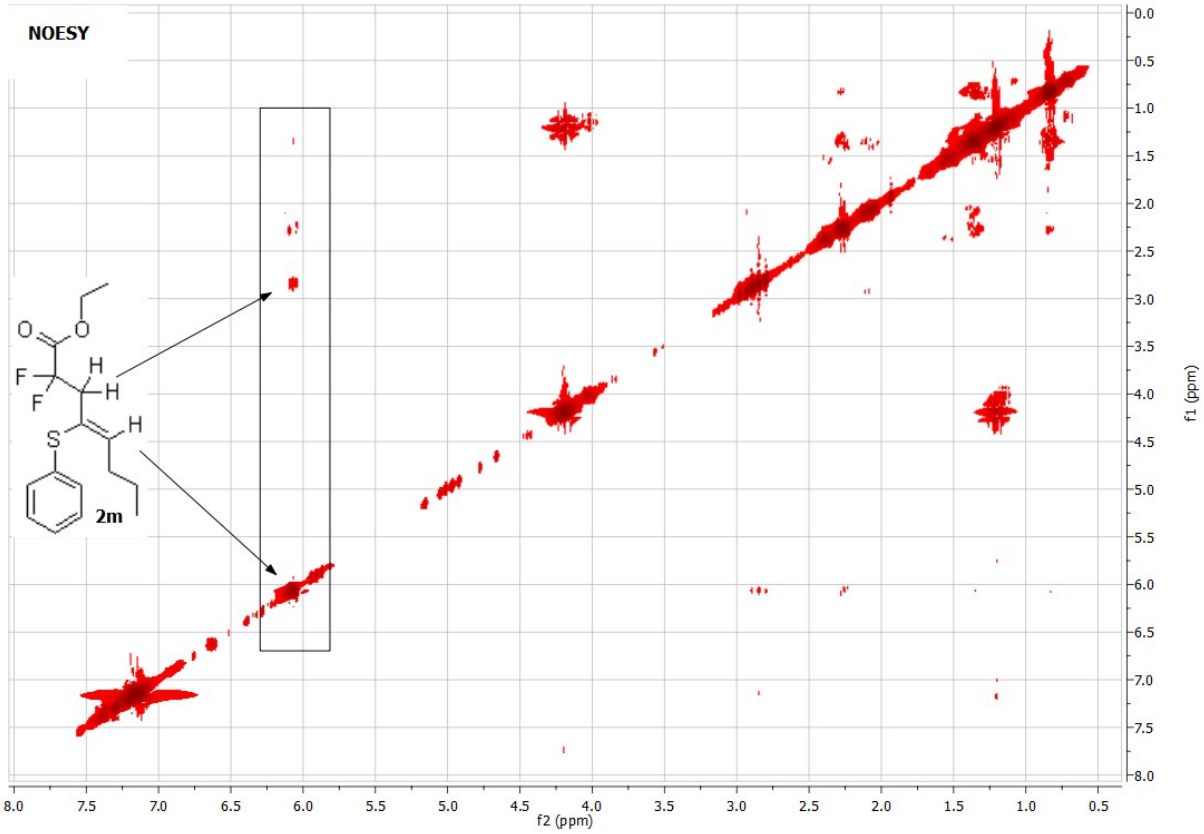
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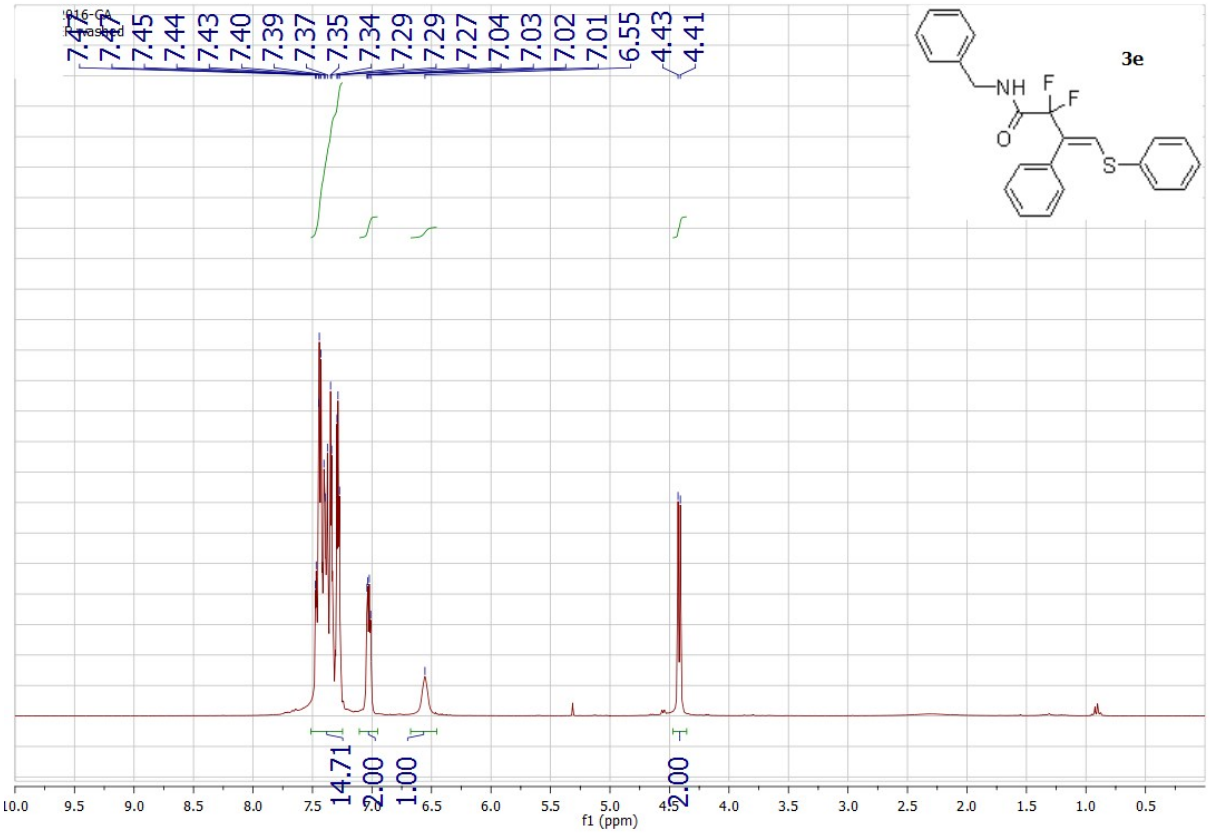
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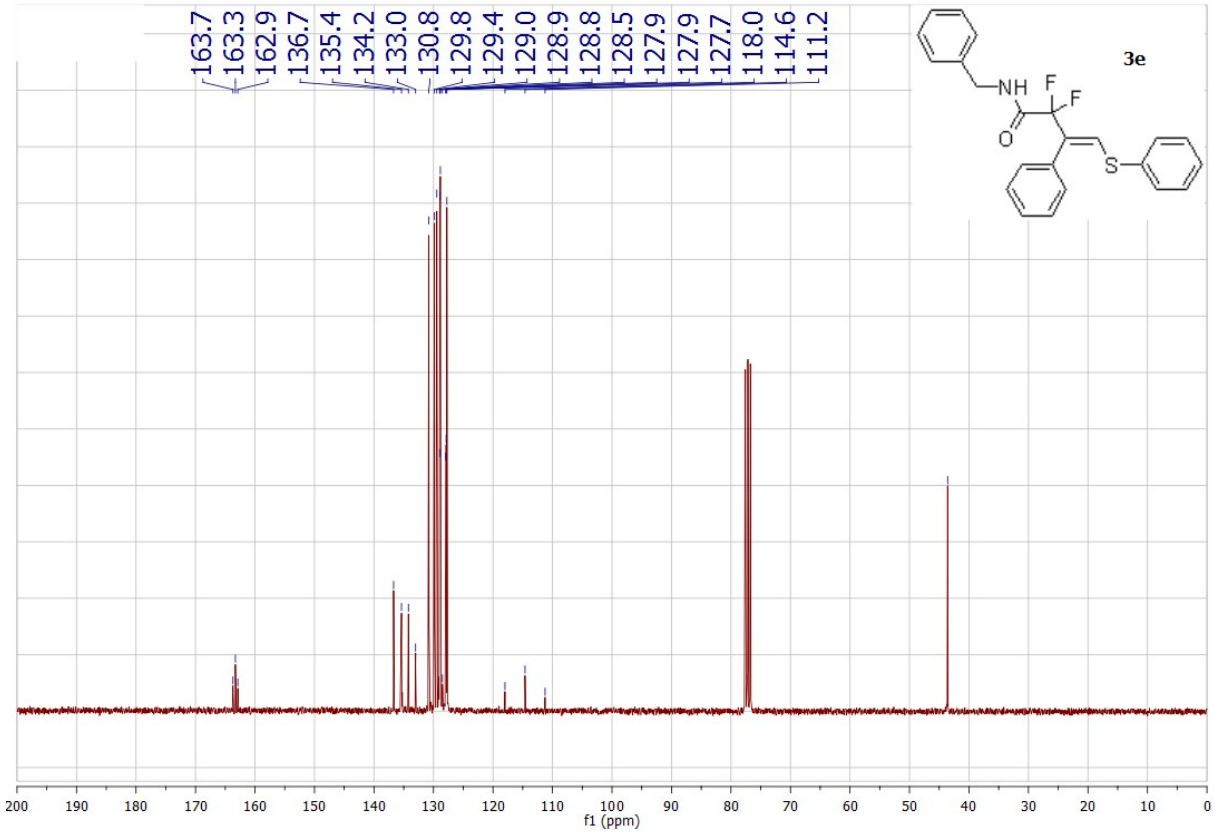
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F
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S
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180
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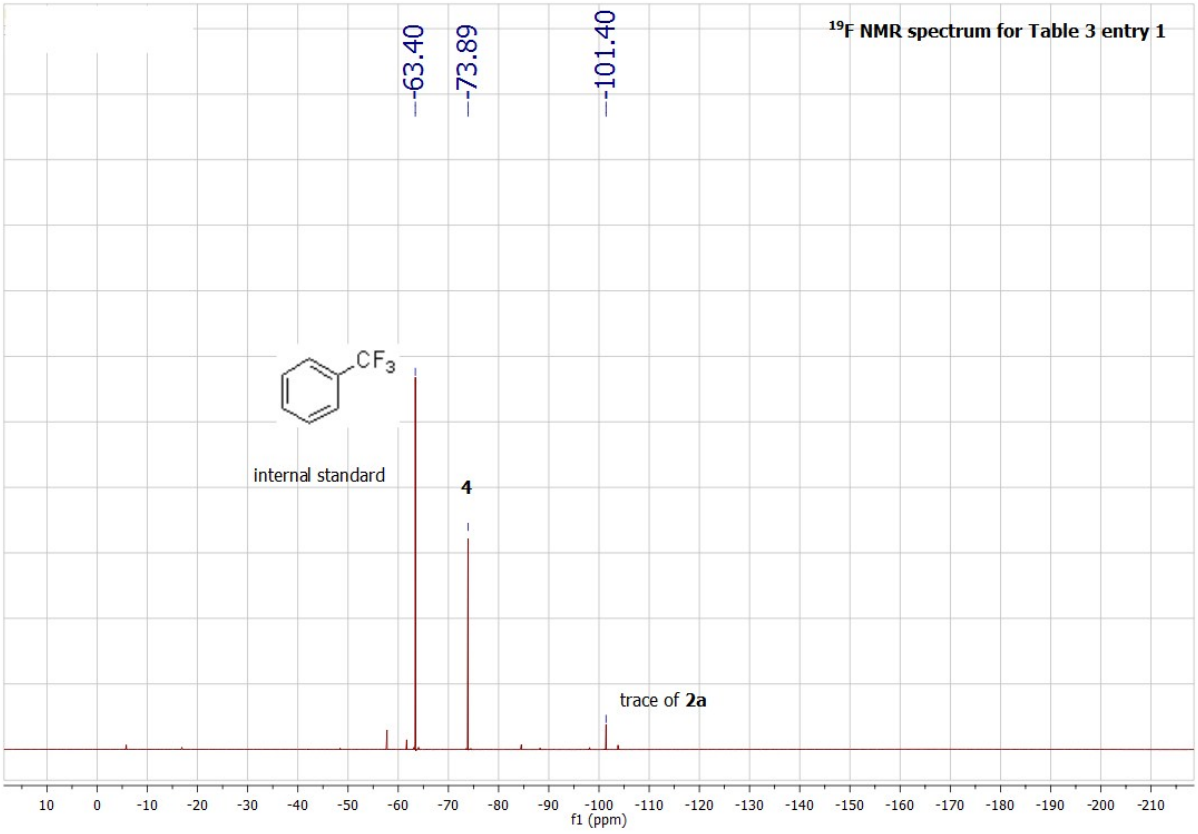
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

8. Mechanistic experiments

Radical trapping experiments

Experiments described in Table 3 in the presence of TEMPO were conducted according to the general procedure B, with the addition of TEMPO (1 equiv) after the other reagents. The substrate **1a**, the ligand or the base, were omitted according to Table 3. After concentration in vacuo, α,α,α trifluorotoluene was added as internal standard, the mixture was diluted with DCM and analyzed by ^{19}F NMR with a DMSO-d_6 insert.

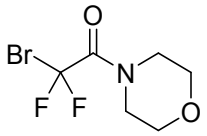
Ethyl 2,2-difluoro-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acetate (4) ^{19}F NMR (282 MHz, DMSO-d_6): δ -73.9. MS (GC/CI-NH3) [M+H$^+$] : 280.13.



Cyclic voltammetry (CV) experiments

CV were performed in CH_3CN containing *n*-Bu_4NBF_4 (0.3 M) at a steady glassy carbon disk electrode (d = 1 mm), at a scan rate of 0.5 V.s^{-1}, at 20 °C, starting from the resting potential

Table S1- Reduction potentials for reactive and unreactive alkylhalides

Entry	Substrate	Reactivity	Measured reduction potential (vs ECS)
1	$BrCF_2CO_2Et$	Yes	-1.50 V
2		No	-1.61 V
3	$BrCH_2CO_2Et$	No	-1.68 V
4	$BrCF_2PO(OEt)_2$	No	-1.97 V

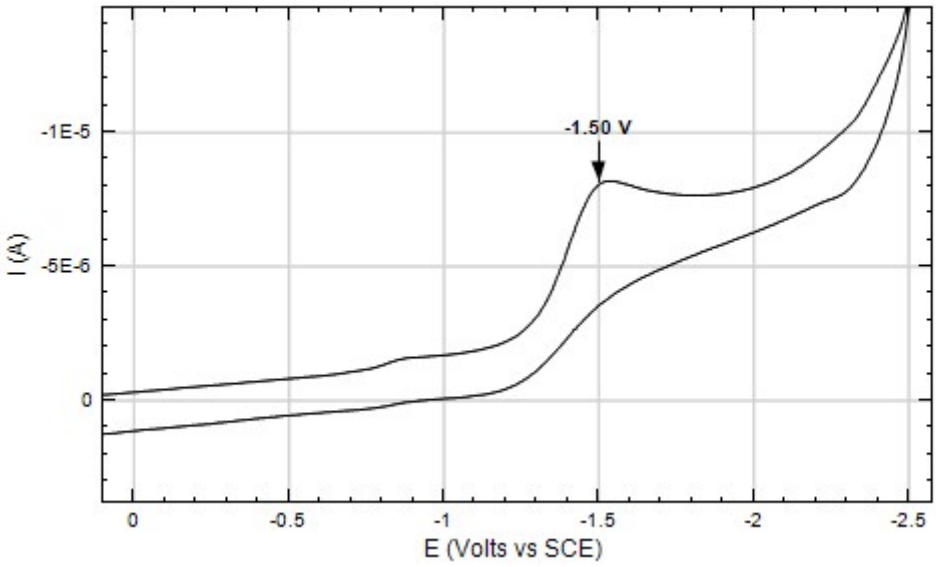


Figure S1 Reduction of $BrCF_2CO_2Et$ (2 mM)

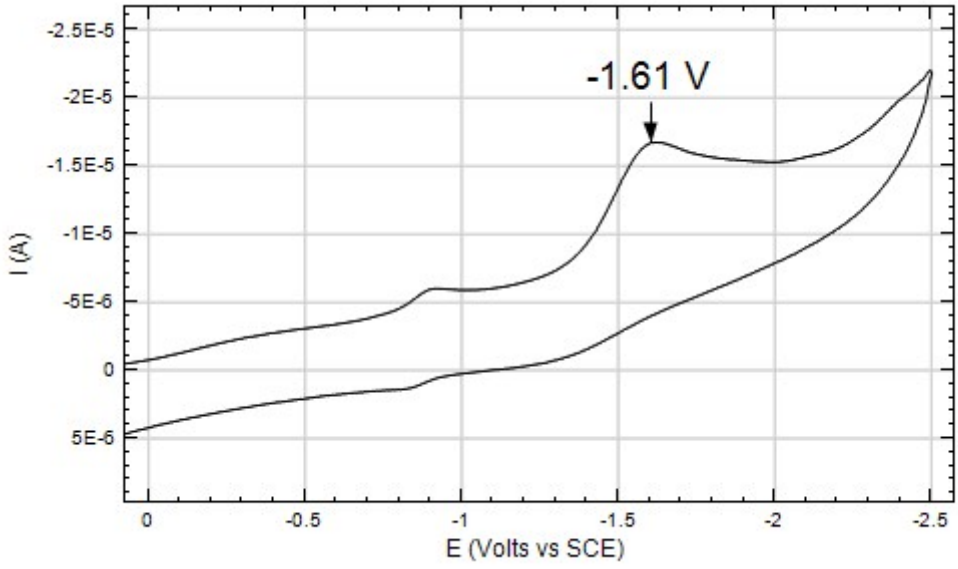


Figure S2 Reduction of 2-bromo-2,2-difluoro-1-morpholinoethan-1-one (2mM)

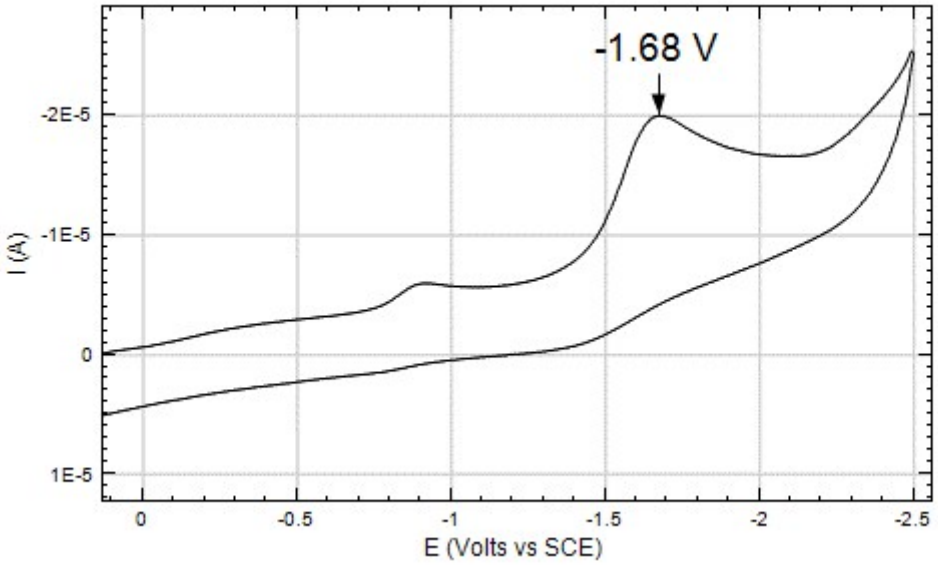


Figure S3 Reduction of $BrCH_2CO_2Et$ (2mM)

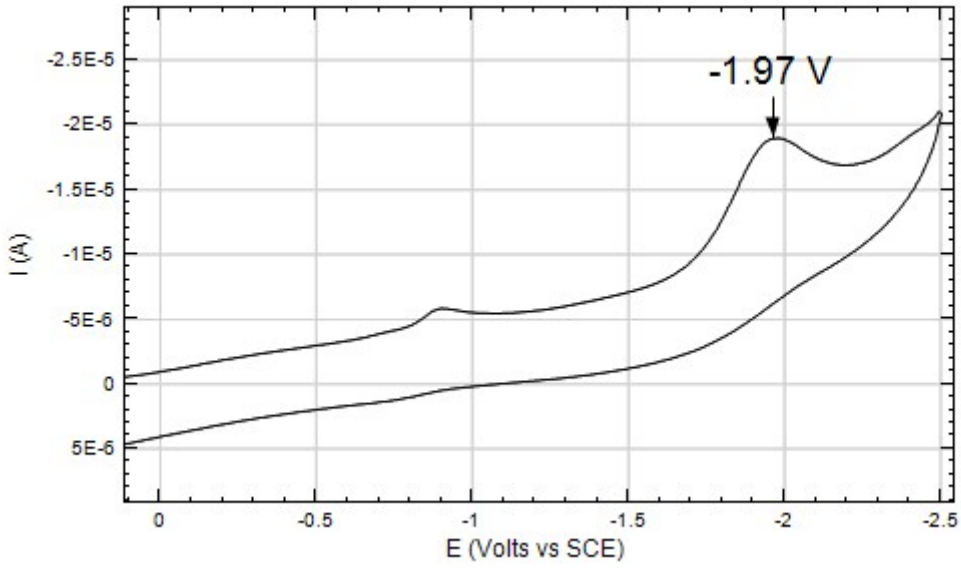
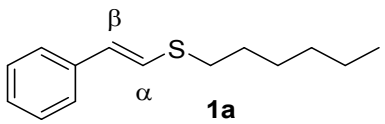


Figure S4 Reduction of $BrCF_2PO(OEt)_2$ (2mM)

Complexation in the presence of copper and base measured by ^{1}H NMR

An oven-dried NMR tube was charged under argon with tetrakis(acetonitrile)copper(I) hexafluorophosphate (9.3 mg, 0.025mmol), phenanthroline monohydrate (5.0 mg, 0.025 mmol), 0.5 mL CD_3CN, and 2 µL 1,2-dichloroethane as an internal standard. Increasing amounts of vinylsulfide 1a in solution in CD_3CN were added and ^{1}H NMR spectra were recorded at 23 °C. The same experiment was then performed with the addition of nBu$_4$NOH (0.025 mmol, 16 µL of a 1.54 M solution in water,).



1a

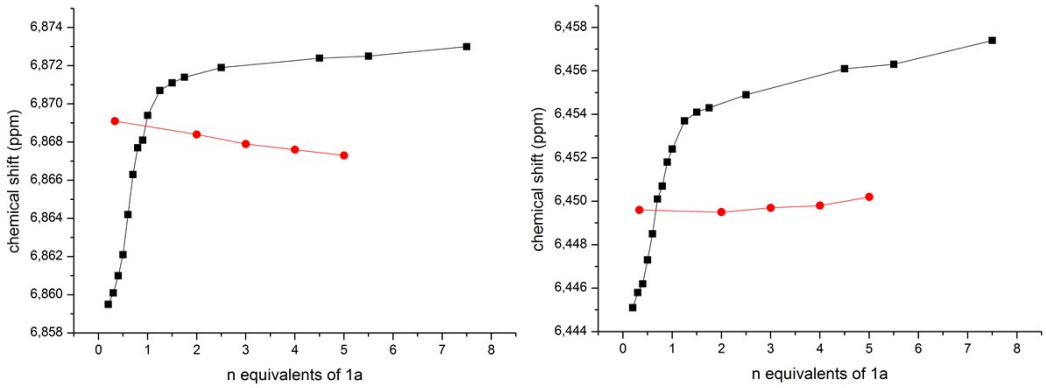


Figure S5 NMR ^{1}H chemical shift of the α (left) and β (right) proton of **1a** as a function of n, equivalents of **1a** added, in the absence (black curve) and presence (red curve) of hydroxide

In the absence of base, the evolution of the chemical shift of both protons shows the complexation of **1a** to copper. In the presence of base, the complexation cannot be evidenced by ^{1}H NMR.

9. Computational details

All calculations were performed using the Gaussian 09 program (Revision A.02).[14] All geometric structures were fully optimized using the B3LYP functional[15] which had been shown to provide good structures and energies for transition metal complexes.[16] Subsequent frequency calculations were performed in order to assess the nature of each intermediate (minimum or transition state). The 6-311+G(d,p)[17] basis sets was used for all main group atoms. Copper atom was described using a double zeta basis set (Lanl2dz[18]) and associated pseudo potential. Bulk solvent effects to model acetonitrile were introduced using a Polarizable Continuum model (PCM)[19]. Selected computed intermediates

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

[15] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37* (2), 785-789; Becke, A. D. **1988**, *38* (6), 3098–3100; Becke, A. D. *J. Chem. Phys.* **1993**, *98* (7), 5648-5652.

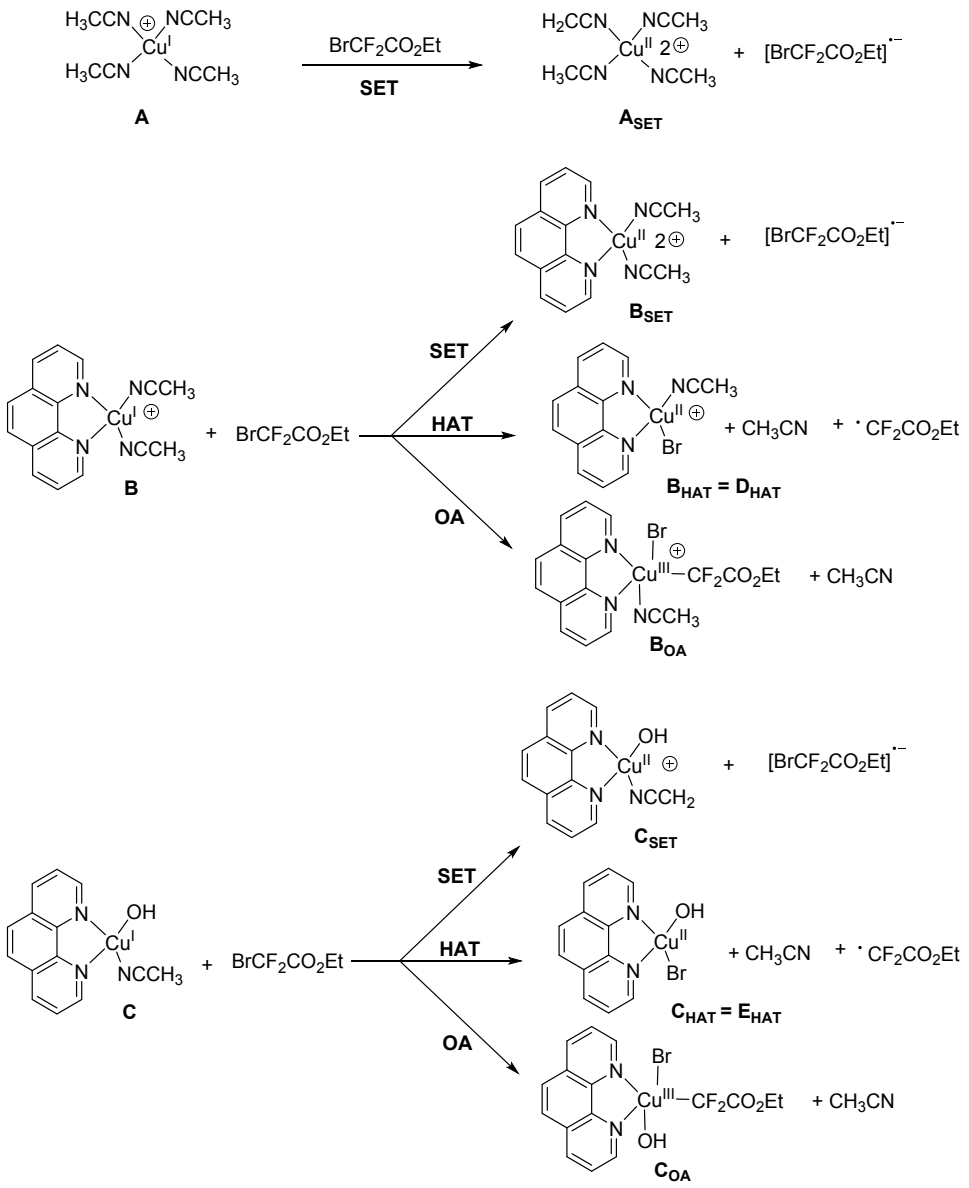
[16] Cramer, C. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2009**, *11* (46), 10757; Sousa, S. F.; Fernandes, P. A.; Ramos, M. J. *J. Phys. Chem. A* **2007**, *111* (42), 10439–10452.

[17] R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650–654

[18] P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270-283; W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284-298; P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299-310.

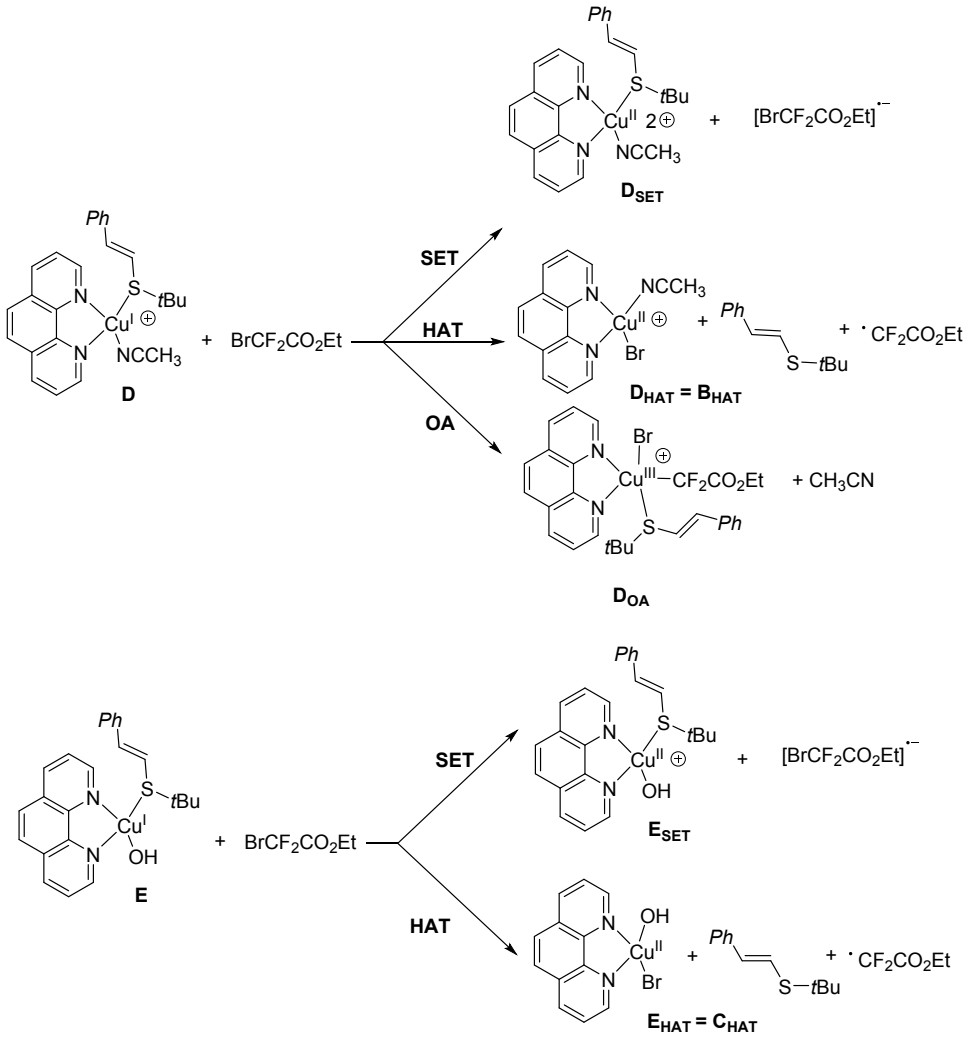
structures are reported below. IRC calculations[20] were used to confirm the minima linked by the transition states. Enthalpies and free energies were calculated for standard conditions at 298.15 K.

Reactions related to energies reported in Table S2 to S4



[19] J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999–3094.

[20] K. Fukui, *Acc. Chem. Res.*, 1981, **14**, 363–368; H. P. Hratchian and H. B. Schlegel, *Theory and Applications of Computational Chemistry: The First 40 Years*, Elsevier: Amsterdam, Eds. C. E. Dykstra, G. Frenking, K. S. Kim, and G. Scuseria., 2005.



	A	B	C	D	E
ΔE SET	55.0	39.2	10.7	38.7	16.0
ΔE HAT	-	29.3	5.2	26.9	4.9
ΔE OA	-	30.3	16.1	27.1	-
ΔE_a OA	-	36.6	37.5	36.9	-

Table S2 - Compared reactivity of different complexes (energies in kcal mol^{-1})

	A	B	C	D	E
ΔG SET	57.1	39.9	10.2	38.1	14.6
ΔG HAT	-	18.6	-5.1	13.5	-8.6
ΔG OA	-	37.9	21.5	34.6	-
ΔG_a OA	-	41.9	40.0	41.7	-

Table S3- Compared reactivity of different complexes (free energies in kcal mol^{-1})

	A	B	C	D	E
ΔH SET	55.2	39.9	11.7	39.1	16.7
ΔH HAT	-	28.4	4.7	25.8	4.1
ΔH OA	-	30.4	16.4	27.2	-
ΔH_a OA	-	35.7	36.5	36.1	-

Table S4 - Compared reactivity of different complexes (enthalpies in kcal.mol^{-1})

Addition of the CF_2CO_2Et radical on 1b

Table S5 – Comparison of the addition of the difluoroacetate radical on **1b** (energies in kcal.mol^{-1})

	Ea addition	ΔE addition
Free substrate -α	+7.29	-20.01
Free substrate -β	+4.68	-16.76
D-β	+ 7.9	-15.48

Table S6 - Comparison of the addition of the difluoroacetate radical on **1b** (free energies in kcal.mol^{-1})

	Ga addition	ΔG addition
Free substrate -α	+20.96	-3.76
Free substrate -β	+18.11	-1.45
D-β	+21.65	+0.62

Table S7 - Comparison of the addition of the difluoroacetate radical on **1b** (enthalpies in kcal.mol^{-1})

	Ha addition	ΔH addition
Free substrate -α	+7.56	-18.34
Free substrate -β	+5.05	-15.02
D-β	+8.18	-13.76

Computed reaction energies for non-reactive alkyl halides

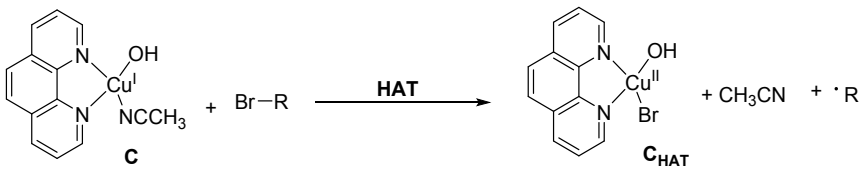
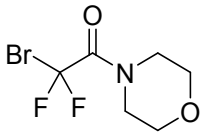
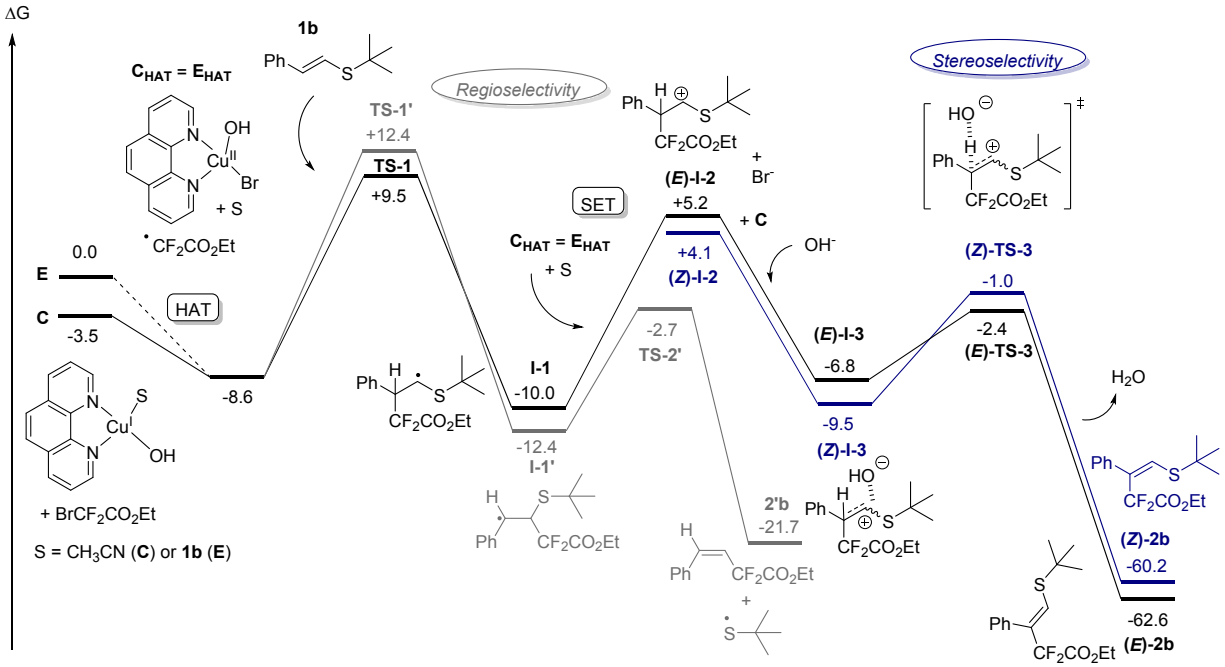


Table S8 - Computed reaction energies for the non-reactive alkyl halides (in kcal.mol^{-1})

Entry	Substrate	ΔE	ΔG	ΔH
1		6.1	-3.8	5.5
2	$BrCH_2CO_2Et$	8.2	-1.7	6.1
3	$BrCF_2PO(OEt)_2$	8.3	-1.5	7.9

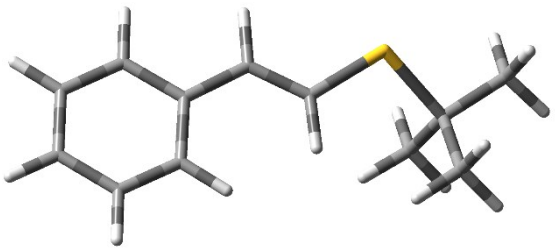


Scheme S1- Computed reaction pathways (free energies in kcal.mol^{-1}). Solid line: initiation with **C**. Dashed line: initiation with **E**. The last part of the reaction path after regeneration of **E** by SET is omitted for clarity. This part is the same as for **C**. Grey: path for the formation of the main byproduct. Blue: path for the formation of the minor stereoisomer.

10. Cartesian coordinates of computed structures

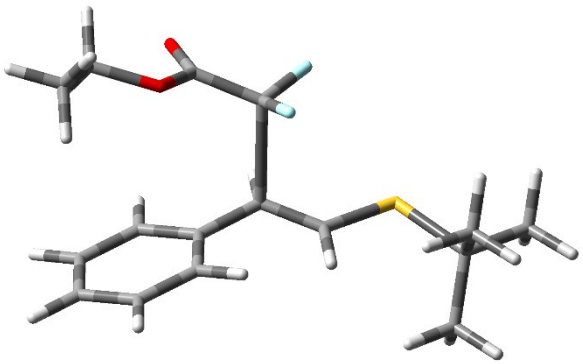
Cartesian coordinates and absolute electronic energies for the intermediates

1b -865.252987953 hartree



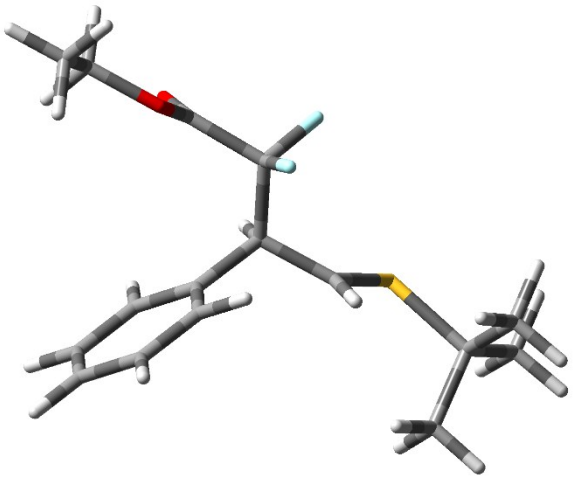
C	-2.54098366	1.24999998	0.00000000
C	-2.26014666	-0.10353702	0.18239700
C	-0.95343366	-0.57032802	0.05808500
C	0.10702834	0.30135098	-0.24800300
C	-0.19628966	1.66257098	-0.44070400
C	-1.50046366	2.12864198	-0.31370900
H	-3.55670566	1.61681298	0.09350400
H	-3.05830166	-0.79780302	0.42080800
H	-0.74494466	-1.62531202	0.20314800
H	0.58862034	2.36241998	-0.70306100
H	-1.70926766	3.18161198	-0.46779000
C	1.46510034	-0.24923202	-0.34511400
H	1.52659234	-1.33438802	-0.30888500
C	2.60434634	0.45298898	-0.46659100
H	2.60182334	1.53753398	-0.47737900
S	4.17245534	-0.31238502	-0.72533900
C	5.40369234	0.90617998	0.01643500
C	6.75825934	0.19936498	-0.13419400
H	6.98928134	-0.00429702	-1.18296900
H	7.54643134	0.84428498	0.26523900
H	6.78101534	-0.74401802	0.41688600
C	5.39986834	2.22017598	-0.77358500
H	4.44041934	2.73799398	-0.70905800
H	6.16084734	2.89160098	-0.36209000
H	5.62955834	2.04803898	-1.82718200
C	5.08075434	1.14370898	1.49538900
H	5.09445534	0.20740498	2.05761800
H	5.82983134	1.81498398	1.92862600
H	4.10076834	1.60821698	1.62547200

Transition state TS-1 -1370.92211005 hartree



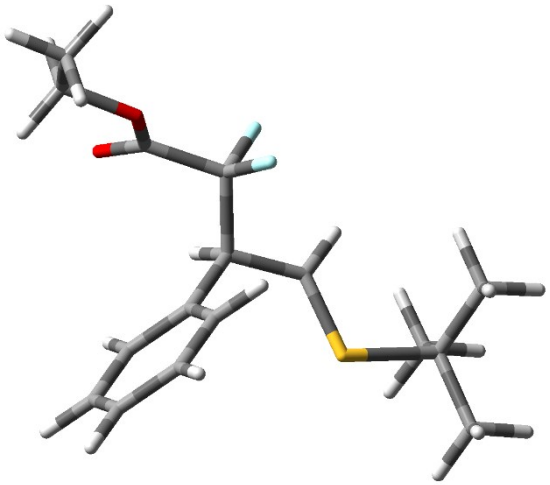
C	-1.35245905	1.12704916	0.00000000
H	-1.49517505	1.73175216	0.88674900
S	-2.75083805	0.28563116	-0.59012500
C	1.00183295	1.94833316	-0.25133400
C	1.97338395	2.22009116	-1.22741800
C	1.12830295	2.56953716	1.00234500
C	3.02772795	3.09394516	-0.96763000
H	1.89543695	1.74802416	-2.20106300
C	2.18073195	3.44256716	1.26085300
H	0.41014395	2.36482416	1.78810000
C	3.13565295	3.71108016	0.27774700
H	3.76272195	3.29259416	-1.73968000
H	2.25978195	3.91084416	2.23567300
H	3.95476195	4.39075516	0.48296400
C	-4.13211405	0.78126416	0.59376400
C	-4.35779805	2.29610016	0.53614800
H	-5.20345605	2.55672716	1.18058400
H	-3.48946005	2.85533016	0.89070700
H	-4.58814605	2.62386516	-0.47967400
C	-3.80528605	0.31288616	2.01602500
H	-4.64487605	0.55836316	2.67434400
H	-3.64832805	-0.76708784	2.05137300
H	-2.91730105	0.80469016	2.41865400
C	-5.35764705	0.03309216	0.04954200
H	-5.20561805	-1.04889384	0.06200200
H	-6.22145405	0.26012616	0.68046500
H	-5.59515305	0.34077216	-0.97171100
C	-0.10826605	1.02802616	-0.58500000
H	-0.05165905	0.57980816	-1.57311200
C	0.64667595	-0.98913684	0.21913200
F	-0.17778605	-1.83965884	-0.41463500
F	0.35641695	-0.97972784	1.53043900
C	2.06940195	-1.13678984	-0.15547100
O	2.41678195	-1.50119284	-1.26350600
O	2.88457795	-0.74178784	0.82555600
C	4.31458695	-0.74252284	0.53316100
H	4.49180795	-0.05152284	-0.29287200
H	4.59722695	-1.74675684	0.21328000
C	5.03833295	-0.32294884	1.79355500
H	6.11425195	-0.31305684	1.60245500
H	4.73674695	0.67896616	2.10611900
H	4.84248495	-1.02158584	2.60990900

Intermediate I-1 -1370.95626543 hartree



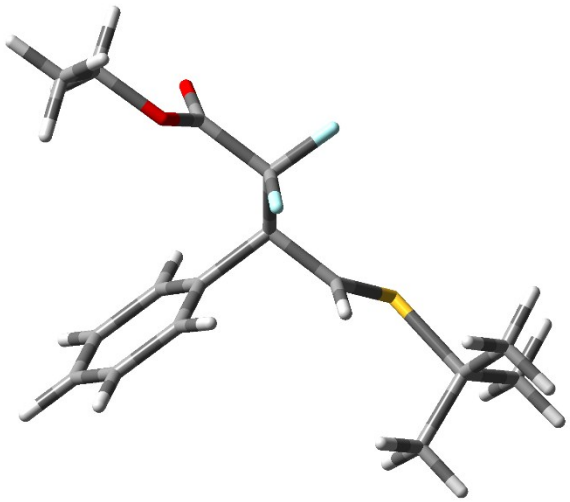
C	-4.05737714	1.74180325	0.00000000
H	-4.19932714	2.01216325	1.03698400
S	-5.40209214	1.18139325	-0.92975100
C	-1.92748114	3.01762225	-0.38833200
C	-1.50127314	3.74188425	-1.50696700
C	-1.67448314	3.53814825	0.88777900
C	-0.83748714	4.95986425	-1.35800000
H	-1.69051314	3.35325025	-2.50190200
C	-1.00888314	4.75291725	1.03733000
H	-1.99361514	2.99552825	1.76930600
C	-0.58843714	5.46857925	-0.08463500
H	-0.51637514	5.50766925	-2.23676000
H	-0.81913314	5.14107125	2.03175100
H	-0.07216114	6.41438925	0.03410200
C	-6.92100414	1.69775325	0.05790000
C	-6.94524914	3.22112125	0.22197700
H	-7.85401214	3.51102925	0.75949000
H	-6.08811114	3.58065725	0.79467300
H	-6.94738814	3.72438025	-0.74739000
C	-6.93338714	0.98730025	1.41622700
H	-7.85303214	1.24869525	1.94991900
H	-6.90515614	-0.09768575	1.29564700
H	-6.09243414	1.28708225	2.04468900
C	-8.09989214	1.22559625	-0.80492700
H	-8.08207214	0.14249025	-0.94945200
H	-9.03683014	1.48370525	-0.30309300
H	-8.09761114	1.70824925	-1.78533400
C	-2.67603814	1.69907925	-0.58533200
H	-2.74584814	1.51642425	-1.66121900
C	-1.86302214	0.49178325	-0.05713400
F	-2.52128514	-0.67414975	-0.38544500
F	-1.78854714	0.50522925	1.31055500
C	-0.45342414	0.38986825	-0.68540900
O	-0.32143814	0.18483125	-1.86898100
O	0.51577986	0.56818525	0.19366100
C	1.89044486	0.52195325	-0.31507500
H	1.99455786	1.31065125	-1.06149700
H	2.03384386	-0.44353375	-0.80167200
C	2.81867086	0.71657025	0.86193300
H	3.85213586	0.68737825	0.50812100
H	2.64868286	1.68196725	1.34287400
H	2.68789186	-0.07598975	1.60164100

Intermediate (*E*)-I-2 -1370.78650000 hartree



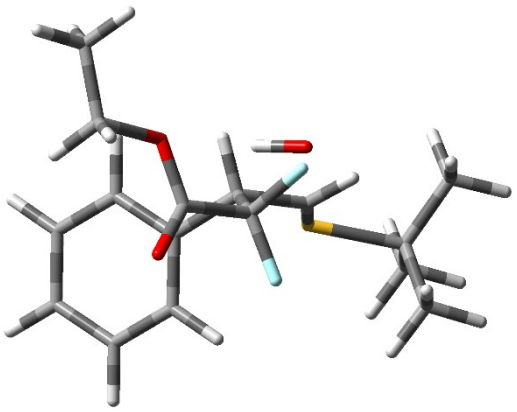
C	2.78688531	0.84016392	0.00000000
H	3.06073031	-0.20640508	0.10739400
S	3.93331331	1.92181192	-0.41323100
C	0.94553031	2.62455092	-0.04383800
C	0.66169331	3.51983392	0.99290900
C	0.83793031	3.05485592	-1.37278000
C	0.27714931	4.82817192	0.70793100
H	0.73918431	3.19564292	2.02467400
C	0.45075731	4.36318992	-1.65363500
H	1.05081831	2.37662992	-2.18992300
C	0.17059531	5.25143892	-0.61586900
H	0.06016831	5.51268592	1.51936300
H	0.36800731	4.68641692	-2.68456800
H	-0.13033569	6.26856392	-0.83841700
C	5.57662431	0.92802392	-0.57430600
C	5.38730831	-0.18535608	-1.60346700
H	6.35352231	-0.68072308	-1.73443100
H	4.67455231	-0.94376708	-1.27593900
H	5.07309031	0.20371792	-2.57317800
C	5.95170431	0.40406592	0.81243800
H	6.93286631	-0.07261508	0.73426900
H	6.02554731	1.20877892	1.54574900
H	5.24821731	-0.34557508	1.17847100
C	6.55566031	1.99966992	-1.06714700
H	6.66293331	2.81702692	-0.35097700
H	7.53470731	1.52986192	-1.18836800
H	6.25792731	2.40948792	-2.03448600
C	1.37012331	1.20543992	0.30193800
H	1.29935131	1.07568792	1.39409600
C	0.42089131	0.10988092	-0.24355900
F	0.82700531	-1.11380408	0.23650800
F	0.49921831	0.03054292	-1.60004300
C	-1.03654069	0.32016392	0.24564500
O	-1.26277969	0.42667492	1.42585200
O	-1.89986469	0.34154392	-0.74368900
C	-3.31817469	0.51501492	-0.39117600
H	-3.40733369	1.45496292	0.15417500
H	-3.59469469	-0.30714008	0.26945700
C	-4.10720669	0.51481192	-1.67947500
H	-5.16664169	0.64244192	-1.44472600
H	-3.79931569	1.33574592	-2.33003800
H	-3.98646769	-0.42884808	-2.21505400

Intermediate (*Z*)-I-2 -1370.78811904 hartree



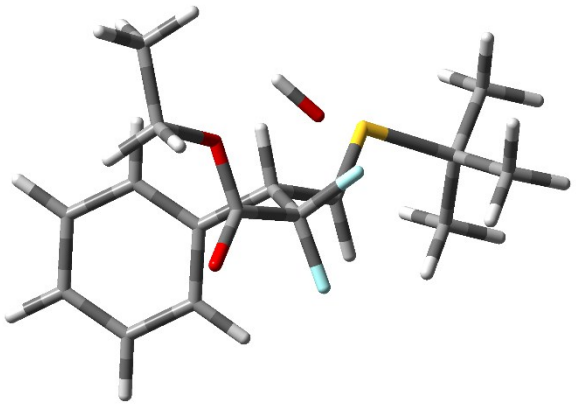
C	4.05737714	0.45081967	0.00000000
H	3.97233814	0.43645967	1.08314200
S	2.70996714	0.38839467	-0.91986400
C	5.86612214	2.02092067	-0.28147200
C	5.94927714	2.92978267	-1.34372900
C	6.14673714	2.44970667	1.02305400
C	6.34197414	4.24339667	-1.10857200
H	5.71805714	2.60712767	-2.35227200
C	6.53794014	3.76734667	1.25118900
H	6.07448614	1.76576667	1.85854100
C	6.63668514	4.66430367	0.18922000
H	6.41824814	4.93679867	-1.93758200
H	6.76178614	4.09047467	2.26072700
H	6.93849314	5.68910367	0.37099200
C	1.20927814	0.38378667	0.28214100
C	1.18554514	1.72346167	1.01938600
H	0.27939214	1.74943967	1.63121100
H	2.04006714	1.84443867	1.68743000
H	1.15142014	2.56862367	0.32994600
C	1.33060914	-0.81280133	1.22509500
H	0.42462114	-0.84526833	1.83661600
H	1.40523814	-1.75542833	0.68061200
H	2.17916714	-0.72600333	1.90558500
C	0.02267214	0.23644167	-0.67693700
H	0.06301214	-0.70154533	-1.23423900
H	-0.89263186	0.23380667	-0.08032300
H	-0.03860386	1.06827967	-1.38162900
C	5.42331514	0.58335567	-0.59074000
H	5.39054214	0.45156967	-1.67245000
C	6.37097914	-0.51084933	-0.06413000
F	5.88722414	-1.73193033	-0.47058900
F	6.38113314	-0.54080033	1.29863800
C	7.79987114	-0.36755733	-0.65049300
O	7.95738614	-0.32057033	-1.84571300
O	8.72372014	-0.32064133	0.28295700
C	10.12030914	-0.19757233	-0.16344000
H	10.19685714	0.71640567	-0.75319500
H	10.33672214	-1.05288833	-0.80411300
C	10.98858614	-0.16430033	1.07249200
H	12.03375014	-0.07186033	0.76762000
H	10.73967314	0.68967667	1.70552200
H	10.88118214	-1.08209733	1.65386000

Intermediate (*E*)-I-3 -1446.78122917 hartree



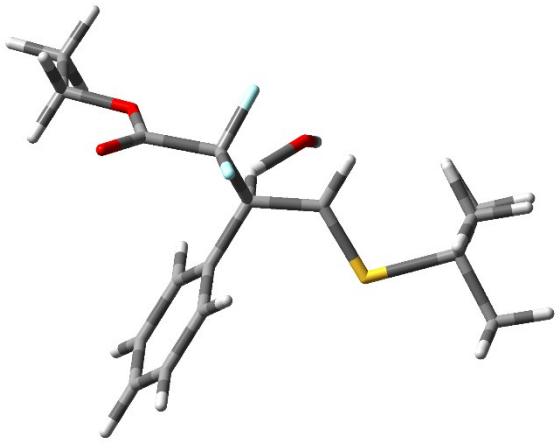
C	-0.09259259	0.06172310	-0.00080800
C	-0.38843059	-0.52834290	1.22646500
C	-0.13766359	-1.88593090	1.42628800
C	0.41565441	-2.66990790	0.40833100
C	0.71370541	-2.06640790	-0.82041500
C	0.45841041	-0.71188790	-1.02317600
H	-0.28815659	1.11603710	-0.16038000
H	-0.81431059	0.06386510	2.02842700
H	-0.37098759	-2.33887890	2.38402100
H	1.14905041	-2.65327490	-1.61930000
H	0.69173441	-0.25987690	-1.98059200
C	0.68373441	-4.14910690	0.66785700
H	0.27684641	-4.38114590	1.65931200
C	2.14129841	-4.56814390	0.61179400
H	2.34045341	-5.62670790	0.73003300
S	3.34911541	-3.50023790	0.86144900
C	4.94190341	-4.42685890	0.39703100
C	6.07564641	-3.41038790	0.58109800
H	6.17365441	-3.11181190	1.62341400
H	7.01111541	-3.87613190	0.25863400
H	5.91749341	-2.51841390	-0.03069100
C	5.14333041	-5.65225390	1.28941700
H	4.35454741	-6.39497190	1.15562500
H	6.08953641	-6.12590690	1.00988400
H	5.19424241	-5.37075690	2.34038000
C	4.80476441	-4.81489590	-1.07953200
H	4.60990641	-3.94442890	-1.71063200
H	5.74952141	-5.26088990	-1.40435100
H	4.00932141	-5.54322390	-1.23858200
O	3.93370141	-3.30735690	2.69310300
H	3.49144241	-2.49200390	2.96577000
C	-0.13863159	-5.05421390	-0.27102100
F	0.00624541	-6.37253690	0.12728700
F	0.32025841	-5.00476490	-1.55530800
C	-1.65763959	-4.74541190	-0.29867800
O	-2.24782959	-4.40993290	-1.29413300
O	-2.17560359	-4.91030690	0.90872100
C	-3.61373259	-4.66927590	1.06116200
H	-4.13731059	-5.32770890	0.36697600
H	-3.80886959	-3.63359690	0.77960500
C	-3.97247559	-4.95166190	2.50224600
H	-5.04218959	-4.77882690	2.64286300
H	-3.75581859	-5.98899590	2.76557800
H	-3.42733759	-4.29222390	3.18063700

Intermediate (*Z*)-I-3 -1446.78349479 hartree



C	0.91049377	1.74382713	0.00000000
C	0.90684177	0.94526613	1.14218900
C	1.53826677	-0.29855087	1.12739300
C	2.18472677	-0.76028087	-0.02403900
C	2.18554177	0.05095013	-1.16616000
C	1.55174777	1.29187613	-1.15401500
H	0.42047177	2.71076413	0.00831300
H	0.41417677	1.28742113	2.04535600
H	1.53190977	-0.91247787	2.02180800
H	2.68120377	-0.28176787	-2.07030800
H	1.56059377	1.90695413	-2.04680500
C	2.89153477	-2.11662287	0.00087600
H	2.76070477	-2.53842387	1.00054400
C	4.36869577	-2.04217487	-0.31514200
H	4.67535177	-1.56332787	-1.23658600
S	5.45457977	-2.30877487	0.87247100
C	7.12814577	-2.55856887	0.01002800
C	8.14127777	-2.83056887	1.12861500
H	7.84932277	-3.69271087	1.73391800
H	9.10786577	-3.05609487	0.66921800
H	8.25509477	-1.96460887	1.77827500
C	6.96750477	-3.79452487	-0.88248900
H	6.25859277	-3.62338087	-1.69289200
H	7.94202977	-4.02821187	-1.32109300
H	6.63847677	-4.66638287	-0.31174600
C	7.51219877	-1.32000787	-0.80079600
H	7.57764377	-0.43670387	-0.16688300
H	8.49376377	-1.49818887	-1.25066400
H	6.81085277	-1.12529487	-1.61430500
O	6.10079677	-0.74944987	1.77824900
H	5.52651877	-0.70372287	2.55469100
C	2.20213177	-3.13361487	-0.93200400
F	2.73781177	-4.38828687	-0.72522100
F	2.44134477	-2.83663387	-2.24589500
C	0.66792477	-3.25329087	-0.74645400
O	-0.12876323	-3.01359387	-1.61810800
O	0.39222977	-3.65150187	0.48650700
C	-1.02075423	-3.82683587	0.83461100
H	-1.44619923	-4.55615587	0.14404600
H	-1.52095323	-2.86873287	0.68703400
C	-1.08169823	-4.29284587	2.27141900
H	-2.12739523	-4.43163687	2.55637700
H	-0.56303423	-5.24530587	2.39857400
H	-0.63888023	-3.55538687	2.94398400

Transition state (E)-TS-3 -1446.76701863 hartree



C	-5.10245913	1.22950818	0.00000000
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C	-4.21989213	-0.57713782	-1.34187300
C	-4.56072713	0.76646518	-1.19913100
H	-5.36686213	2.27513118	0.10936200
H	-5.72475613	0.69437518	1.99118200
H	-5.12559513	-1.69023682	1.73545500
H	-3.80043313	-0.92534382	-2.27808700
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C	-4.06037513	-2.94586782	-0.40892300
H	-4.22869213	-3.50498982	0.61544400
C	-2.64350013	-3.30808982	-0.45041200
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S	-1.40467513	-2.21919982	-0.19851400
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C	1.29128987	-2.17712582	-0.13607800
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H	2.26367087	-2.67618882	-0.12088400
H	1.27083287	-1.50444282	-0.99668500
C	0.21199987	-4.16532982	0.99962400
H	-0.61700313	-4.87435982	0.99030500
H	1.14896287	-4.73036882	0.99844300
H	0.16258887	-3.59143882	1.92744800
C	0.29822887	-4.02699982	-1.53831200
H	0.23734487	-3.36532882	-2.40441700
H	1.26882987	-4.53124282	-1.56331600
H	-0.46921813	-4.79773582	-1.62930300
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H	-3.27729913	-4.49285082	2.53649600
C	-4.87700313	-3.70008882	-1.45794600
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C	-6.41227813	-3.50204082	-1.33394400
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C	-8.27604913	-3.88031082	0.09870100
H	-8.80077013	-4.38594182	-0.71273600
H	-8.54856513	-2.82403682	0.09093900
C	-8.52750413	-4.53071782	1.43971100
H	-9.59512213	-4.47614082	1.66602900
H	-8.23305813	-5.58206282	1.42792200
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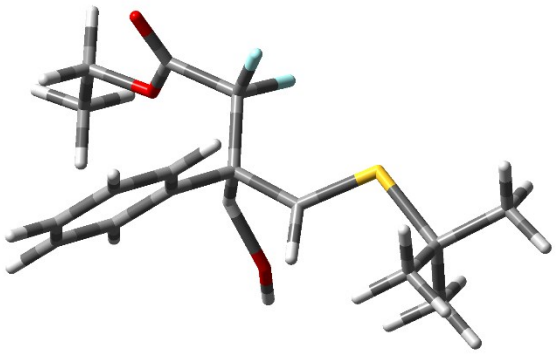
Transition state (Z)-TS-3 -1446.76495085 hartree



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H	-1.53590689	-0.91577451	1.69649700
H	0.67655611	0.23662949	-1.79947100
H	-0.38873489	2.46175849	-1.74291500
C	0.28647111	-1.87663451	-0.08528400
H	0.07861811	-2.39383651	0.93071600
C	1.74354011	-1.80131951	0.07839000
H	2.07272411	-1.06857951	0.80364900
S	2.91191411	-2.65206051	-0.74999200
C	4.57418611	-2.07924551	-0.01251300
C	5.60059711	-2.81252451	-0.88596000
H	5.53077911	-2.51041251	-1.93339300
H	6.60169311	-2.55915251	-0.52780100
H	5.48569811	-3.89700251	-0.82302600
C	4.71040011	-0.56275151	-0.15771500
H	3.98146311	-0.01823651	0.44518300
H	5.70480111	-0.27343951	0.19445500
H	4.61321511	-0.24669451	-1.19795400
C	4.65293411	-2.53570751	1.44514100
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C	-0.25111289	-2.76471551	-1.20178600
F	0.23758611	-4.04932651	-1.07012900
F	0.16661311	-2.33470351	-2.43522100
C	-1.80162289	-2.85670351	-1.24157200
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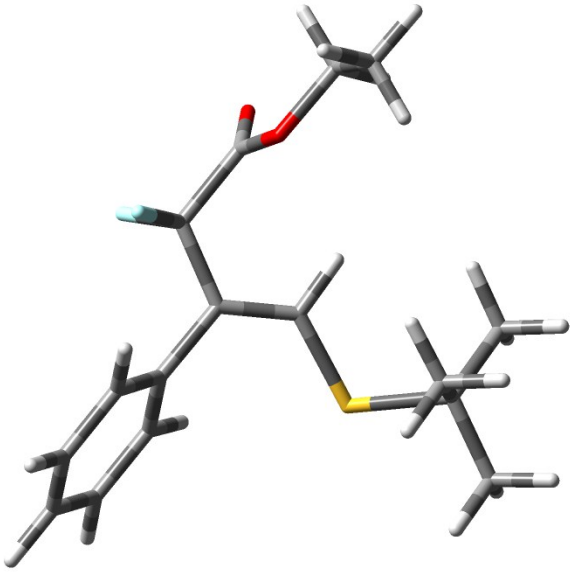
C	-3.96011889	-4.32371651	1.29165500
H	-5.03678089	-4.47029551	1.40709700
H	-3.47832789	-5.30349751	1.29773200
H	-3.59953589	-3.74600951	2.14500100

(E)-2b -1370.38052492 hartree



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C	-0.14827292	1.14922316	-0.59263900
C	0.78864808	1.64130816	-1.51306700
C	2.15139708	1.62822716	-1.21975200
H	3.66227208	1.11767016	0.22789200
H	2.01913208	0.26183416	1.88390800
H	-0.38684192	0.28383716	1.36885100
H	0.46141608	2.04105516	-2.46496400
H	2.85868208	2.01140016	-1.94659500
C	-1.61347992	1.17666916	-0.89038100
C	-2.32381092	2.29660916	-1.12470700
H	-3.39075492	2.23873516	-1.30871100
S	-1.63077192	3.90076216	-1.26646500
C	-2.92801792	5.06787216	-0.54483300
C	-2.25342592	6.44332316	-0.63691300
H	-2.02523192	6.71029016	-1.67187500
H	-2.93359192	7.19996316	-0.23546200
H	-1.32877892	6.47692416	-0.05559500
C	-4.20971092	5.04032616	-1.38421300
H	-4.69696292	4.06310316	-1.36001400
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H	-4.00751192	5.30156716	-2.42488700
C	-3.20644692	4.69349016	0.91434900
H	-2.29223092	4.71702416	1.51110700
H	-3.91430892	5.41069616	1.34312300
H	-3.64788392	3.69770916	0.99846300
C	-2.29872192	-0.16488584	-0.99128900
F	-2.13803692	-0.89623384	0.17456700
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C	-3.81341392	-0.14998884	-1.33405300
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C	-5.99452192	0.15300916	-0.42554100
H	-6.30562892	-0.81525484	-0.81926900
H	-6.23058292	0.92336116	-1.16114400
C	-6.59952192	0.44450316	0.92869700
H	-6.26350192	1.41059016	1.31071200
H	-7.68764492	0.47350716	0.83350900
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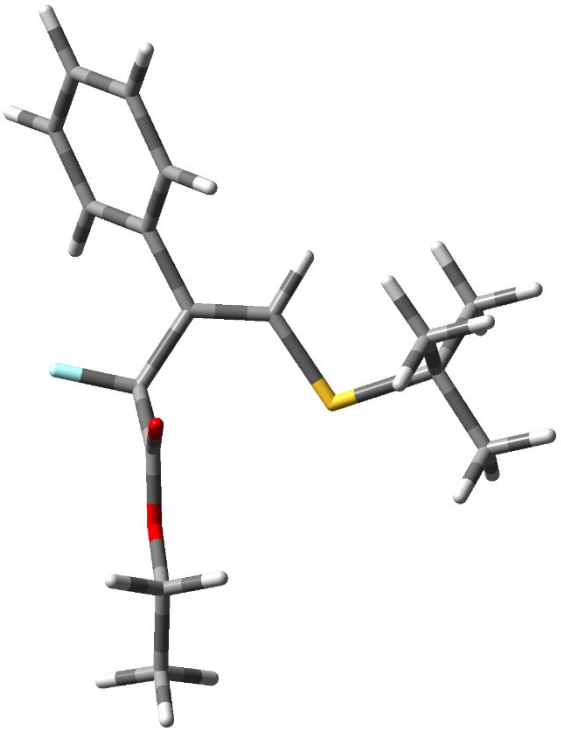
(Z)-2b -1370.37905893 hartree



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C	3.83230279	1.61652668	-0.41810300
C	3.34387479	2.34914768	0.67349000
C	1.97273179	2.49680968	0.87807500
H	-0.00085321	2.01592368	0.16039200
H	0.84211579	0.70889168	-1.77703000
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H	4.04367479	2.79443668	1.37142700
H	1.61573679	3.06562768	1.72928100
C	5.30165579	1.51929168	-0.64899100
C	6.05499279	2.63521868	-0.69777700
H	5.55819179	3.59012168	-0.57181800
S	7.77486679	2.72444868	-1.03518900
C	8.26518779	4.43397768	-0.39868900
C	9.78053679	4.48097068	-0.64223100
H	10.02090479	4.36549168	-1.70201100
H	10.16322479	5.45143268	-0.31387500
H	10.30221579	3.70365068	-0.07886400
C	7.55945879	5.52527368	-1.21026300
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H	7.78399079	5.43553168	-2.27489500
C	7.95334979	4.55276368	1.09628900
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C	5.93520179	0.15954268	-0.83588100
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O	6.92584979	0.04968168	1.36112000
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C	9.17010579	-1.22899832	0.50335000
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C	10.19540579	-1.94212732	-0.34845000
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H	11.01864479	-2.27448432	0.28868300
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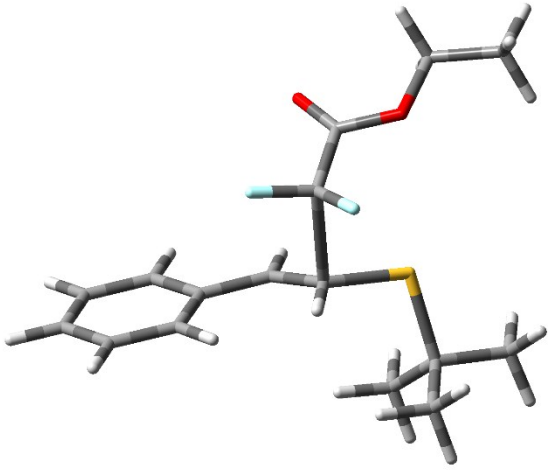
Transition state TS-1' -1370.91794516 hartree



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C	-2.47606647	3.38842519	0.95676100
C	-1.14623347	3.02224819	1.11255900
H	0.66924253	2.40026619	0.12806100
H	-0.34018847	2.45985619	-2.14262800
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H	-3.05593047	3.65051419	1.83277000
H	-0.70870947	3.00113119	2.10418600
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S	-6.96705047	4.84964119	-0.08034000
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C	-7.97920947	7.33455719	-0.32394700
H	-8.78307647	7.01437319	0.34372000
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H	-5.34001347	6.61106819	1.83876400
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H	-5.39521347	8.22470119	-0.82966500
H	-4.57617747	6.66898119	-0.65641600
C	-5.40803647	4.08540219	0.38375900
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C	-6.18958047	2.04470519	1.08100700
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O	-8.31896947	1.68062519	0.19291900
C	-9.23153747	1.22516019	-0.85430100
H	-9.14211447	0.14049119	-0.93236600
H	-8.91195647	1.67086019	-1.79755700
C	-10.62657247	1.65629619	-0.46034800
H	-11.33224547	1.32658319	-1.22678500
H	-10.92189347	1.20994019	0.49153700
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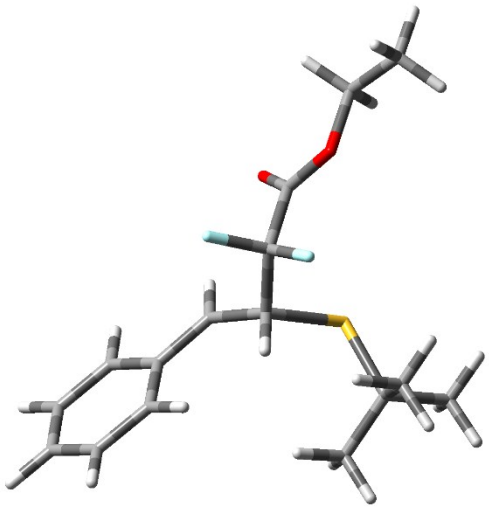
Intermediate I-1’ -1370.96144723 hartree



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H	1.85306935	1.08383718	0.20568200
H	0.85396935	0.20907518	-1.90014100
H	-1.54059165	0.54112018	-2.36787900
H	-1.96053365	2.61564818	1.40549400
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S	-5.11642465	3.85597218	-1.16457000
C	-4.72380365	5.50422018	-0.33606200
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H	-6.46798965	6.37724818	-1.32929900
H	-5.20270665	7.53238518	-0.88877400
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C	-5.34211965	5.58776118	1.06232200
H	-4.90538165	4.86158818	1.75029500
H	-5.15771865	6.58518118	1.47520200
H	-6.42070065	5.42393118	1.02937000
C	-3.20884265	5.73213518	-0.28930500
H	-2.76979065	5.69048218	-1.28806200
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C	-4.33305765	2.54537218	-0.08149100
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F	-6.06693765	2.40309518	1.53407400
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C	-8.80331965	0.71135618	-0.84709600
H	-8.60430065	-0.35087782	-0.99431600
H	-8.75601465	1.21549918	-1.81317900
C	-10.11184465	0.95935918	-0.13197500
H	-10.92948865	0.56282318	-0.73878100
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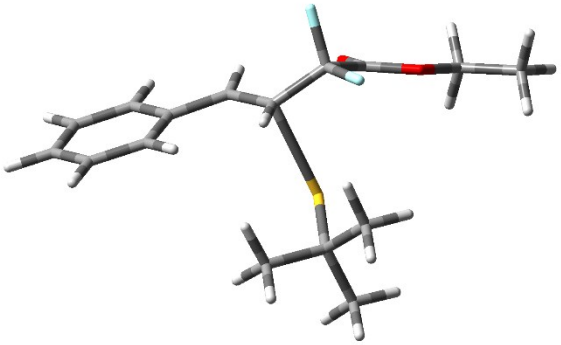
Transition state TS-2' -1370.94482002 hartree



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C	-0.44738860	0.69310662	0.18029906
C	0.23523540	1.62750062	0.98810506
C	1.60704540	1.79883562	0.86749606
H	3.40703440	1.18202362	-0.14682494
H	2.23872440	-0.48117438	-1.57614594
H	-0.20190360	-0.79264938	-1.36517294
H	-0.30458960	2.21210262	1.72249906
H	2.11547040	2.51889362	1.49819606
C	-1.87304160	0.45641162	0.25689206
H	-2.24838260	-0.35845738	-0.35249194
S	-3.51954460	2.93960062	-0.64006394
C	-3.42029660	4.63002762	0.15747906
C	-3.87498760	5.59803662	-0.95281094
H	-4.89513760	5.38487162	-1.28072194
H	-3.85365560	6.62047762	-0.55911694
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C	-4.36562460	4.72653962	1.36107806
H	-4.08069860	4.03086962	2.15237406
H	-4.33086160	5.74065662	1.77456506
H	-5.39620760	4.51039262	1.07160006
C	-1.97802460	4.95019762	0.57004706
H	-1.29383160	4.86447362	-0.27644694
H	-1.92623260	5.97547262	0.95291106
H	-1.62971760	4.28557262	1.36338506
C	-2.79453660	1.18411262	0.97729206
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F	-4.79904360	1.45748562	2.16151806
C	-5.06794160	0.25961862	0.09507806
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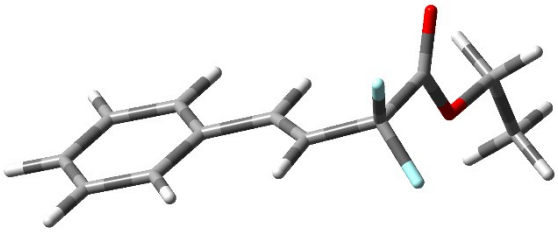
C	-7.27689160	0.32236362	-0.77425894
H	-7.26561560	-0.76012038	-0.90721494
H	-6.93665960	0.79366562	-1.69745994
C	-8.62878260	0.83428262	-0.33174094
H	-9.36764060	0.59918462	-1.10172394
H	-8.94301760	0.36006462	0.60031606
H	-8.61327560	1.91694762	-0.19111094

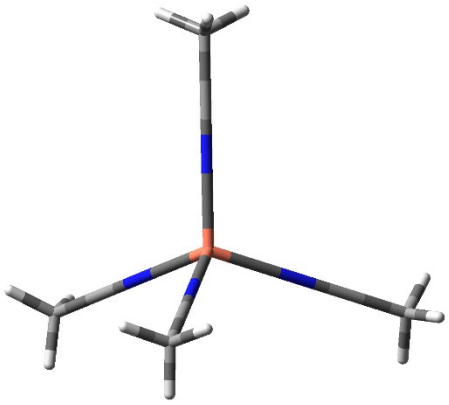
2'b -814.873504490 hartree



C	-3.31938773	1.27049178	-0.04345317
C	-2.44197073	2.18762478	0.53193983
C	-1.08053973	1.90016778	0.59873483
C	-0.57104273	0.69314578	0.09309583
C	-1.46844873	-0.22239222	-0.48437117
C	-2.82647373	0.06491178	-0.55089317
H	-4.37954273	1.48969578	-0.09734117
H	-2.81515173	3.12488178	0.92830283
H	-0.40081873	2.61686278	1.04714283
H	-1.10870573	-1.16322222	-0.88346917
H	-3.50509973	-0.65178422	-0.99899317
C	0.87305927	0.44936578	0.19334483
H	1.42791027	1.25437078	0.66809383
C	1.53867627	-0.63174122	-0.23002917
H	1.04674327	-1.47120422	-0.71071517
C	3.00724427	-0.83008722	-0.08199217
F	3.24665727	-1.96149222	0.67218683
F	3.56625727	-1.11074622	-1.31954817
C	3.80438927	0.33076078	0.56669883
O	4.14132427	0.32193578	1.72401783
O	4.02480627	1.29568478	-0.31044717
C	4.75763827	2.47594578	0.15991383
H	5.72576327	2.13974778	0.53309483
H	4.19370427	2.91108478	0.98617983
C	4.88954027	3.42422678	-1.00979317
H	5.43326027	4.31493678	-0.68584417
H	5.44477427	2.96352778	-1.82939517
H	3.90948127	3.73595978	-1.37661017

Cartesian coordinates for complexes A to E.

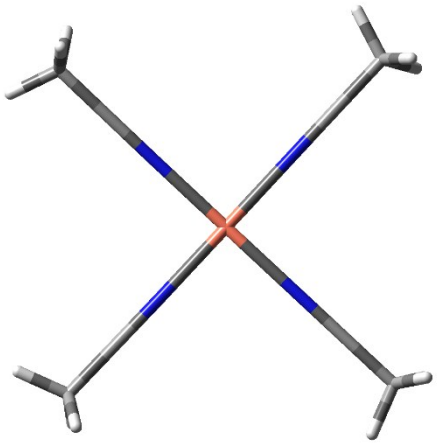
Copper complex A -727.303676588 hartree



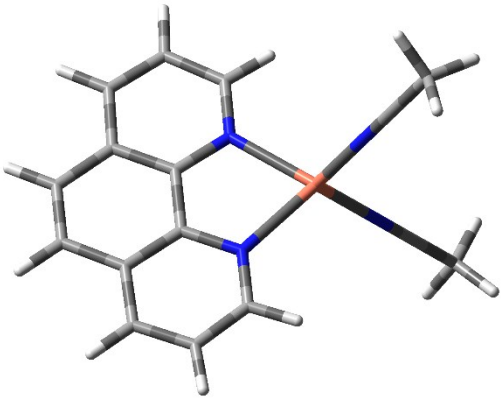
Cu	-2.08167341	2.56972108	0.00000000
N	-3.80505641	3.00221808	-1.04478600
N	-1.35528841	4.28635108	0.88452000
C	-4.76825641	3.24459708	-1.62647200
C	-0.95310841	5.24462108	1.37980500
C	-5.98076341	3.55333108	-2.36025300
H	-6.35162841	2.65484208	-2.85643800
H	-6.74328541	3.92362308	-1.67293500
H	-5.77273741	4.31790308	-3.11083700
C	-0.44703641	6.45349408	2.00161600
H	-0.14413241	6.24290908	3.02881100
H	0.41414159	6.82310208	1.44234200
H	-1.22506541	7.21890608	2.00793000
N	-2.50394841	1.17220408	1.46043000
N	-0.65867741	1.81441808	-1.28494200
C	-2.73562841	0.39185108	2.27450900
C	0.13605959	1.38924308	-2.00075200
C	-3.03048341	-0.59089992	3.29986300
H	-2.99170841	-1.59416192	2.87202500
H	-2.29811841	-0.51605292	4.10565400
H	-4.02835841	-0.41238992	3.70433100
C	1.13980159	0.85290808	-2.90009100
H	0.70063059	0.06795508	-3.51809600
H	1.52024659	1.64664708	-3.54531400
H	1.96564259	0.43399708	-2.32251000

Copper complex A_{SET} -727.074859579 hartree

Cu	0.22908368	0.67729083	0.00000000
N	1.49495368	2.21165583	-0.03200600
N	1.76388068	-0.58887417	0.03412300
C	2.22696368	3.09532283	-0.05594900
C	2.64799668	-1.32058717	0.05846100
C	3.15084568	4.20551983	-0.08654700
H	3.87494868	4.05206183	-0.88878800
H	2.60191068	5.13232883	-0.26165100
H	3.67442968	4.26639483	0.86932500
C	3.76049068	-2.24196117	0.08942000
H	3.38451368	-3.26650517	0.09379500
H	4.38514468	-2.08651217	-0.79214700
H	4.35237268	-2.06710117	0.98983900
N	-1.03920732	-0.85522617	-0.02878000
N	-1.30412032	1.94622083	0.02611000
C	-1.77987132	-1.73176517	-0.05386000
C	-2.18305832	2.68374683	0.05396500
C	-2.71368832	-2.83359217	-0.08761400
H	-2.56338832	-3.46340617	0.79105900
H	-3.73390832	-2.44581017	-0.08877500
H	-2.54591532	-3.42345517	-0.99064600
C	-3.28822832	3.61357083	0.09386200
H	-4.22025532	3.07971383	-0.09963900
H	-3.33259432	4.07944283	1.08016500
H	-3.14242432	4.38372283	-0.66589900

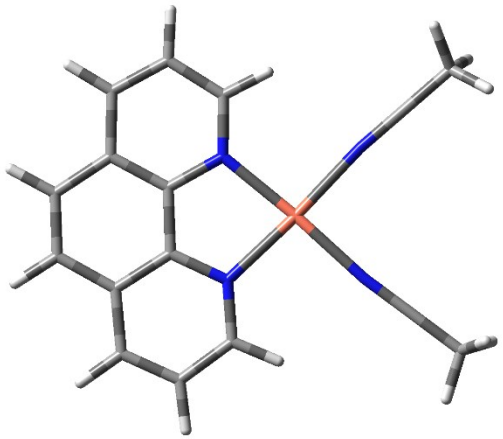


Copper complex B -1033.46573754 hartree



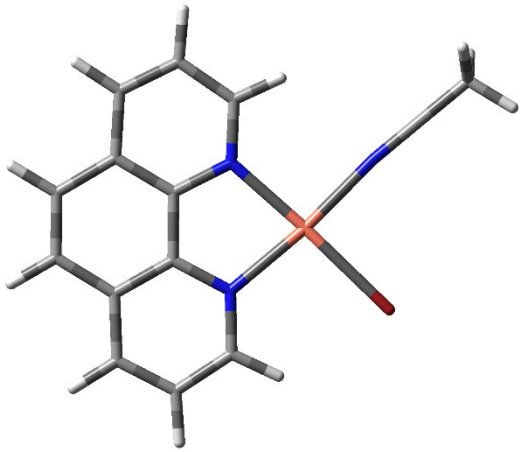
C	0.02049180	1.55737703	0.00000000
C	-1.20076920	0.91901503	0.00103400
C	-1.24715620	-0.49123997	0.00359500
C	-0.01350520	-1.18635197	0.00501400
C	1.19218880	0.78278503	0.00155400
C	-2.47761620	-1.22891597	0.00484200
C	-0.01408820	-2.63309597	0.00771800
C	-1.24830720	-3.32719097	0.00886400
C	-2.47816520	-2.58850697	0.00736400
C	-1.20309720	-4.73748897	0.01151100
H	-2.12781620	-5.30325297	0.01245100
C	0.01763280	-5.37685497	0.01287100
C	1.18997080	-4.60323197	0.01156300
H	-3.41079820	-0.67737197	0.00373500
H	0.09249580	2.63734703	-0.00195700
H	-2.12501520	1.48555003	-0.00009400
H	2.16544580	1.26072603	0.00078200
H	-3.41179020	-3.13929997	0.00830300
H	0.08876180	-6.45688197	0.01489800
H	2.16282280	-5.08199397	0.01259800
N	1.18209080	-0.54446897	0.00399700
N	1.18099480	-3.27597097	0.00907300
Cu	2.83684180	-1.91091997	0.00728500
N	3.96859580	-1.90748497	1.68553500
N	3.97332380	-1.91414697	-1.66730800
C	4.61137680	-1.90465197	2.64099900
C	4.62123080	-1.91612897	-2.61929800
C	5.42186280	-1.90094697	3.84381500
H	4.78539080	-1.75439897	4.71819300
H	5.94666680	-2.85319997	3.93844600
H	6.15358780	-1.09267597	3.79372500
C	5.43837280	-1.91834297	-3.81752900
H	4.95308280	-2.51084697	-4.59504800
H	5.56993280	-0.89607097	-4.17641300
H	6.41657680	-2.34911397	-3.59701700

Copper complex B_{SET} -1033.26206089 hartree



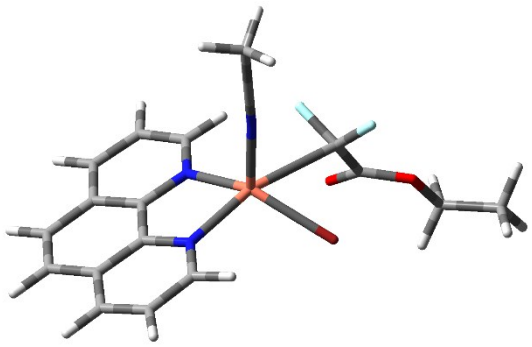
C	0.47008545	0.64102563	0.00000000
C	1.70592445	0.02900963	0.00003100
C	1.78607145	-1.38055337	-0.00069400
C	0.56947745	-2.08934337	-0.00205000
C	-0.69333655	-0.14427937	-0.00100400
C	3.01480445	-2.12202337	-0.00027700
C	0.56937345	-3.51550237	-0.00325500
C	1.78553545	-4.22488837	-0.00237700
C	3.01457945	-3.48400237	-0.00095400
C	1.70468845	-5.63446537	-0.00290600
H	2.61287945	-6.22528937	-0.00174000
C	0.46864145	-6.24615037	-0.00504200
C	-0.69438955	-5.46023937	-0.00654300
H	3.94883945	-1.57333537	0.00070000
H	0.37602545	1.71844863	0.00072000
H	2.61431245	0.61958663	0.00068600
H	-1.67369155	0.31099463	-0.00079100
H	3.94839445	-4.03308937	-0.00062800
H	0.37422845	-7.32354537	-0.00580100
H	-1.67567955	-5.91400037	-0.00896600
N	-0.64022855	-1.47122937	-0.00200500
N	-0.64032455	-4.13337937	-0.00540600
Cu	-2.16130755	-2.80343337	-0.00487100
N	-3.59810555	-1.39163137	-0.00254700
N	-3.60109455	-4.21192337	-0.00001700
C	-4.49460455	-0.67338237	-0.00344900
C	-4.50019955	-4.92693537	0.00152700
C	-5.62138455	0.23168863	-0.00575000
H	-5.33925955	1.16503163	-0.49608200
H	-6.45464555	-0.22543037	-0.54227300
H	-5.92113155	0.43831463	1.02327100
C	-5.62764955	-5.83118137	0.00409400
H	-5.26823955	-6.86160037	0.01148300
H	-6.23572455	-5.65152637	0.89242500
H	-6.23060255	-5.66230737	-0.88981700

Copper complex $B_{HAT} = D_{HAT}$ -3474.8126226 hartree



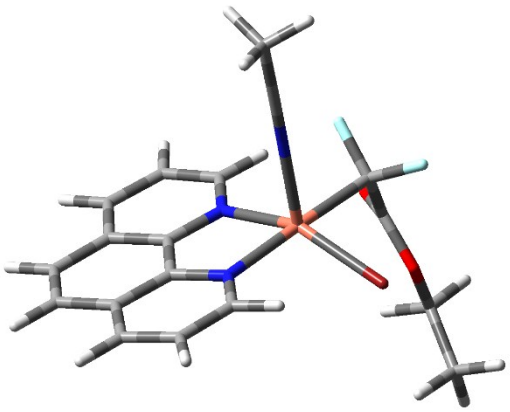
C	-1.45491791	1.22950818	0.00000000
C	-0.18775491	0.68654518	0.00280400
C	-0.03166591	-0.71635182	0.01020400
C	-1.20848291	-1.49304582	0.01417000
C	-2.57089491	0.37753518	0.00471900
C	1.23909109	-1.38165082	0.01401200
C	-1.12586791	-2.92082382	0.02161200
C	0.13489209	-3.55200482	0.02597800
C	1.31824309	-2.74052682	0.02177100
C	0.14949609	-4.96345082	0.03470600
H	1.09621709	-5.49098682	0.03880100
C	-1.04302491	-5.65383682	0.03807200
C	-2.25442391	-4.94458982	0.03235100
H	2.13858209	-0.77784082	0.01082000
H	-1.60835391	2.30024318	-0.00558300
H	0.68851509	1.32415518	-0.00049200
H	-3.57549391	0.77787618	0.00298000
H	2.28203809	-3.23527682	0.02492300
H	-1.06767191	-6.73527882	0.04486100
H	-3.20890091	-5.45375482	0.03385000
N	-2.44937591	-0.94413782	0.01162000
N	-2.29368591	-3.61718882	0.02438200
Cu	-3.92347191	-2.38849782	0.01783600
N	-5.40795891	-1.03116882	0.02921100
C	-6.32836791	-0.34382182	0.03870600
C	-7.48972191	0.51810318	0.05186100
H	-7.54978891	1.03364018	1.01207300
H	-7.40864491	1.25385418	-0.75030800
H	-8.38979891	-0.08201282	-0.09480000
Br	-5.59554991	-4.18171982	-0.00201600

Transition state TS-B_{OA} -3980.46957629 hartree



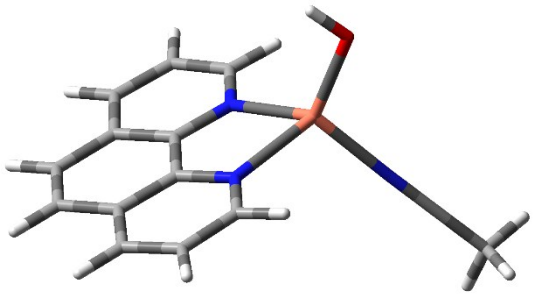
C	0.32786883	2.25409833	0.00000000
C	-0.94024217	2.16732733	-0.52978600
C	-1.29481917	1.03768733	-1.29696300
C	-0.31149617	0.03762433	-1.48086100
C	1.23994983	1.21325633	-0.23636300
C	-2.59245917	0.87330133	-1.88656900
C	-0.63585417	-1.13208667	-2.26003200
C	-1.92259817	-1.26240067	-2.83220200
C	-2.89412317	-0.22844067	-2.62426500
C	-2.18015217	-2.42419367	-3.59122200
H	-3.15453917	-2.56021667	-4.04633200
C	-1.18999517	-3.37048267	-3.74715200
C	0.05823983	-3.15549167	-3.14054200
H	-3.33033117	1.65179233	-1.73182400
H	0.63569983	3.10621833	0.59162500
H	-1.66760017	2.95419133	-0.36646500
H	2.24195083	1.26626233	0.16688000
H	-3.87603317	-0.34370567	-3.06803100
H	-1.35574617	-4.27023467	-4.32499000
H	0.86041783	-3.87754067	-3.24724900
N	0.93782983	0.13591233	-0.95205600
N	0.32249783	-2.07575167	-2.41957000
Cu	2.10692083	-1.58094767	-1.42495500
Br	3.82501483	-2.25756367	-2.94096300
C	4.49965683	-1.00319767	-0.79551400
C	5.17501383	0.09833833	-1.63735900
O	6.37437683	-0.27895867	-2.00930900
O	4.61335683	1.14202533	-1.83753800
C	7.14521483	0.66681033	-2.83771300
H	7.22558683	1.60035733	-2.28086200
H	6.56935883	0.84013233	-3.74754900
C	8.48872283	0.03411233	-3.11019600
H	9.07908183	0.71653033	-3.72637000
H	9.03400083	-0.14750567	-2.18204200
H	8.37881183	-0.90791767	-3.65055800
F	3.84827583	-0.47865367	0.23694500
F	5.23871983	-1.99125567	-0.36531800
N	2.13592783	-2.88982567	0.26069400
C	2.04605783	-3.63703667	1.13101300
C	1.93476383	-4.57586767	2.22979000
H	0.88560383	-4.69875767	2.50378800
H	2.34424983	-5.54243767	1.93156500
H	2.48971883	-4.20069067	3.09130100

Copper complex B_{OA} -3980.4795359 hartree



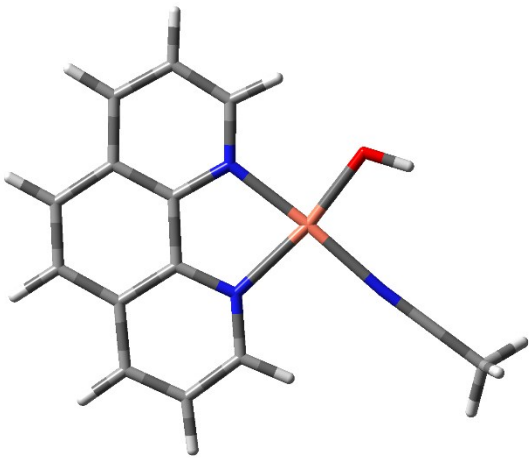
C	-1.88492061	1.06150796	0.00000000
C	-3.12448861	0.99878996	-0.59225100
C	-3.47254761	-0.14322804	-1.34301600
C	-2.51321961	-1.17513004	-1.45092500
C	-0.99078761	-0.00898804	-0.15385200
C	-4.74631461	-0.29601704	-1.98230300
C	-2.83447461	-2.35431304	-2.19518000
C	-4.10082261	-2.48662604	-2.80626700
C	-5.04951761	-1.42037604	-2.68466300
C	-4.36253561	-3.68374304	-3.50634400
H	-5.32301561	-3.82274204	-3.98858400
C	-3.39437461	-4.66100104	-3.56490500
C	-2.15945661	-4.44288004	-2.93475300
H	-5.46676761	0.50727096	-1.88733800
H	-1.57926761	1.91859196	0.58594500
H	-3.83419061	1.81096696	-0.48905800
H	-0.01690061	0.04209196	0.30571300
H	-6.01595261	-1.53214204	-3.16014200
H	-3.56239261	-5.59206004	-4.09012400
H	-1.37211761	-5.18322904	-2.97654700
N	-1.28368561	-1.09817704	-0.86069800
N	-1.88963361	-3.32439804	-2.27494700
Cu	-0.17818761	-2.82777504	-1.25654200
Br	1.18017339	-4.28078504	-2.54899700
C	1.57150939	-2.23992004	-0.29497000
C	2.21548339	-1.02572304	-1.02705400
O	2.74756739	-1.37529504	-2.17292500
O	2.18456939	0.06825096	-0.52267000
C	3.39303439	-0.31205704	-2.96682500
H	4.28527739	0.00554396	-2.42566600
H	2.69079139	0.52204296	-3.02261900
C	3.71524539	-0.89306504	-4.32639700
H	4.13914039	-0.10492004	-4.95598000
H	4.44662839	-1.70285404	-4.25319400
H	2.81036839	-1.26845904	-4.81223800
F	1.08522439	-1.86517204	0.89586000
F	2.45359739	-3.21390304	-0.06707400
N	-0.84170261	-4.06001304	0.53222000
C	-1.19567261	-4.75583104	1.37676000
C	-1.65606761	-5.62411304	2.44237800
H	-0.80197761	-6.10304604	2.92457200
H	-2.20380561	-5.03729404	3.18211100
H	-2.31622361	-6.39158404	2.03254100

Copper complex C -976.63684917 hartree



C	2.02127669	1.38297870	0.00000000
C	3.21141369	0.76892670	-0.32770100
C	3.27972669	-0.63979030	-0.35181500
C	2.10059969	-1.35883730	-0.03367000
C	0.90631369	0.58444670	0.30343000
C	4.47995669	-1.35357230	-0.68130700
C	2.12635869	-2.80528930	-0.04748700
C	3.33032769	-3.47543430	-0.37907600
C	4.50417369	-2.71290830	-0.69444700
C	3.31258369	-4.88591630	-0.38221200
H	4.21504069	-5.43290430	-0.63116100
C	2.14513769	-5.54831730	-0.06713200
C	1.00243969	-4.79630430	0.25158800
H	5.37057169	-0.78340430	-0.92025400
H	1.93240269	2.46156770	0.02847100
H	4.09360869	1.35238870	-0.56602100
H	-0.04020231	1.04381370	0.56802900
H	5.41452769	-3.24604030	-0.94412000
H	2.09479069	-6.62974030	-0.05975800
H	0.07307969	-5.29425130	0.50700800
N	0.93630769	-0.74265030	0.28859700
N	0.98485569	-3.46882930	0.26303400
Cu	-0.67059931	-2.14224230	0.81760600
N	-2.12953431	-2.13905130	-0.61387000
C	-2.98552631	-2.10183530	-1.38534600
C	-4.06464331	-2.05009230	-2.35445500
H	-3.67692431	-2.25262830	-3.35455200
H	-4.82185631	-2.79632930	-2.10759900
H	-4.52385831	-1.05985830	-2.34450900
O	-1.37944331	-2.15642030	2.68979700
H	-0.64552231	-2.14773430	3.31175300

Copper complex C_{SET} -976.478530913 hartree



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C	-0.66763417	2.44220499	0.00651900
C	-1.05342517	0.15733499	0.01042500
C	1.56346183	3.44775299	-0.01165500
C	-1.24275117	3.75401599	0.01240000
C	-0.40392417	4.88675699	0.00648000
C	1.01914083	4.69644599	-0.00650800
C	-1.03364417	6.15024199	0.01491200
H	-0.43144217	7.05126099	0.01063600
C	-2.41075017	6.22253099	0.02935300
C	-3.16460117	5.03770499	0.03418900
H	2.63909283	3.31764299	-0.02080400
H	0.67404583	-1.12749901	-0.00186800
H	2.28709983	0.77297599	-0.01585500
H	-1.79811717	-0.62940401	0.01652100
H	1.65607883	5.57300699	-0.01164900
H	-2.92312017	7.17530399	0.03701300
H	-4.24634217	5.06686299	0.04618800
N	-1.52537117	1.39522399	0.01348300
N	-2.59815617	3.83719799	0.02508700
Cu	-3.48540717	1.96508999	0.02487600
N	-5.39481317	2.66719799	0.00901700
C	-6.50340717	2.96973299	-0.01311100
C	-7.89888417	3.35139799	-0.03860700
H	-7.99143217	4.37711099	-0.39941800
H	-8.44789917	2.68243299	-0.70324400
H	-8.31390217	3.28245799	0.96833200
O	-4.01912617	0.14444599	0.03156000
H	-4.97965817	0.07348499	0.05122200

Copper complex $C_{HAT} = E_{HAT}$ -3418.022008 hartree

C	-1.02459008	0.65573770	0.00000000
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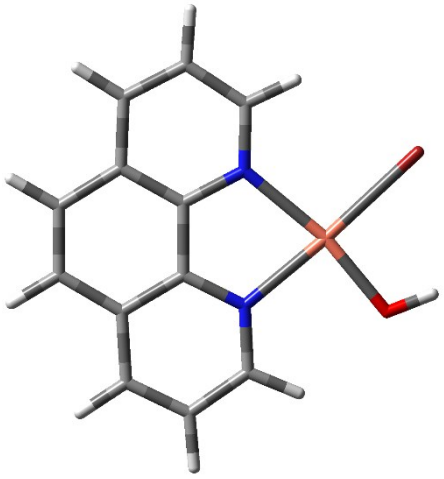
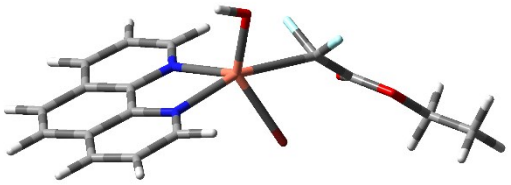
C	-0.45049608	3.00019870	-0.00012200
C	-1.83586508	3.26501070	0.00000200
C	-2.38315708	1.01689570	0.00011300
C	0.46538692	4.10497270	-0.00022500
C	-2.31491708	4.61676070	0.00004300
C	-1.39204008	5.68362470	-0.00002800
C	0.01339892	5.38959670	-0.00017800
C	-1.92194408	6.99192870	0.00006100
H	-1.25132608	7.84346270	0.00002100
C	-3.28907108	7.16830270	0.00020500
C	-4.13148908	6.04399970	0.00024000
H	1.52891492	3.89698570	-0.00033600
H	-0.75336108	-0.39181730	0.00000900
H	0.99299592	1.38706870	-0.00022300
H	-3.18301508	0.28621170	0.00020400
H	0.71260392	6.21755170	-0.00025100
H	-3.72789708	8.15729970	0.00028600
H	-5.20950508	6.14686170	0.00032700
N	-2.76695408	2.28459170	0.00010300
N	-3.66079708	4.80275970	0.00015600
Cu	-4.71604808	2.99668670	0.00016600
O	-5.35399208	1.20569870	0.00012500
H	-6.31717508	1.22905270	0.00008400
Br	-6.99708308	3.97758770	-0.00020500



Transition state TS-C_{OA} -3923.65437839 hartree



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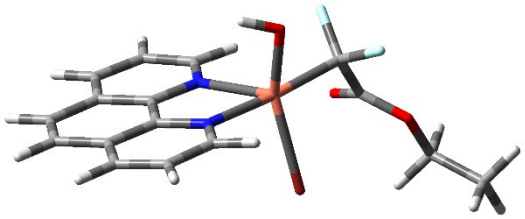
C	1.59561517	-1.78417367	-0.07205500
C	3.09638517	-0.08369667	0.33462900
C	-0.71493383	-1.35393267	-0.82547900
C	1.31096517	-3.20389967	-0.10561400
C	0.02424517	-3.64655967	-0.50164000
C	-0.97924983	-2.68676767	-0.86080300
C	-0.21028183	-5.03773267	-0.52300300
H	-1.18324483	-5.41107667	-0.82196500
C	0.79914617	-5.90367467	-0.16262500
C	2.04161517	-5.37279067	0.21939300
H	-1.47756183	-0.63291567	-1.09692600
H	2.42695817	1.94748333	0.04693600
H	0.13326417	1.23744233	-0.65073000
H	4.09814317	0.19996133	0.63637900
H	-1.95602183	-3.04828567	-1.16126700
H	0.65259717	-6.97600167	-0.16770500
H	2.85447317	-6.02847567	0.51150000
N	2.83386817	-1.38225567	0.30231800
N	2.29108017	-4.07059467	0.24694500
Cu	4.15552617	-3.17366067	0.85709400
Br	5.50941217	-3.37237467	-1.15557600
C	6.55337217	-2.29760667	0.84676900
C	7.69649517	-1.81206667	-0.06907600
O	8.63371417	-2.73053567	-0.17032800
O	7.68016617	-0.71269567	-0.55878900
C	9.77595817	-2.42115467	-1.04099800
H	10.24715217	-1.51448967	-0.66049500
H	9.38261017	-2.22520367	-2.03947600
C	10.70482917	-3.61229467	-1.00861900
H	11.56455317	-3.40765567	-1.65122400
H	11.07044917	-3.79899067	0.00307800
H	10.20647017	-4.51050567	-1.37837900
F	5.97786517	-1.25185767	1.43407700
F	6.92959717	-3.19893567	1.72938400
O	4.27268817	-3.46668767	2.77720900
H	3.40562717	-3.74875167	3.08540700

Copper complex C_{OA} -3923.688398 hartree



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C	-1.01055953	-3.18565329	0.13206700
C	0.51115947	-1.47305029	0.36656600
C	-3.34191953	-2.81316229	-0.57334600
C	-1.29245653	-4.59783329	0.21385500
C	-2.58696653	-5.07583929	-0.10179200
C	-3.60292553	-4.14573329	-0.50176100
C	-2.81556253	-6.46391529	-0.00133100
H	-3.79535053	-6.86193929	-0.23885600
C	-1.79414153	-7.29748629	0.40074400
C	-0.54142753	-6.74281529	0.69703700
H	-4.11567953	-2.11601029	-0.87335700
H	-0.16921653	0.53509471	-0.03319400
H	-2.48592553	-0.20871129	-0.59902700
H	1.52807447	-1.18026029	0.59901300
H	-4.58679953	-4.53028529	-0.74429800
H	-1.93768453	-8.36596729	0.49088700
H	0.28273947	-7.36802429	1.01719300
N	0.24115247	-2.76815829	0.43412400
N	-0.30201653	-5.44082029	0.60158900
Cu	1.52619347	-4.63046729	0.99533800
Br	2.32481947	-5.21968129	-1.22669900
C	3.30050947	-3.83633529	1.56978100
C	4.14370147	-3.25439929	0.41310100
O	5.17472047	-4.02713229	0.13024500
O	3.86854847	-2.19368729	-0.08954900
C	6.01604847	-3.62255729	-0.99864900
H	6.46535447	-2.65792629	-0.75438000
H	5.36494947	-3.50050729	-1.86535100
C	7.05202947	-4.70493829	-1.20423800
H	7.68083847	-4.43983929	-2.05754500
H	7.69438047	-4.81021129	-0.32679700
H	6.57729247	-5.66546929	-1.41371800
F	3.00249147	-2.81994329	2.40484900
F	3.95713447	-4.77966529	2.25832000
O	1.33425947	-4.92343029	2.86242800
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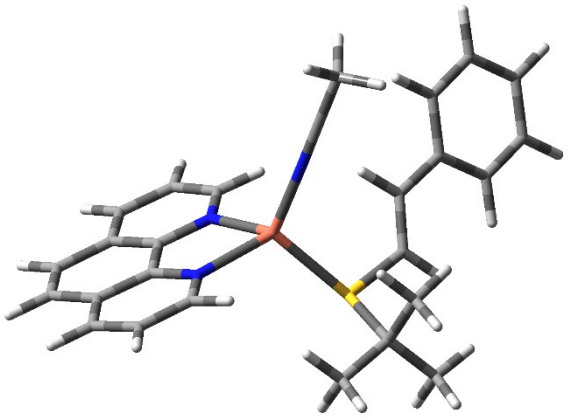
Copper complex D -1765.91013349 hartree



C	-0.76923074	1.90170937	0.00000000
C	-0.02317974	0.85165337	-0.48917900
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C	-2.08719274	-0.36713063	-0.80574200
C	-2.16631174	1.77268537	0.05753900
C	0.03233126	-1.46378263	-1.42321500
C	-2.79334574	-1.56527863	-1.20401300
C	-2.06051174	-2.66878163	-1.70484700
C	-0.63215374	-2.58567963	-1.80767500
C	-2.78743874	-3.81811963	-2.08121900
H	-2.25981074	-4.68149163	-2.47028600
C	-4.15863474	-3.82717763	-1.94676200
C	-4.79828774	-2.68616763	-1.43513700
H	1.11225226	-1.40857563	-1.49823500
H	-0.30194774	2.81837637	0.33584300
H	1.05696926	0.91709937	-0.55333900
H	-2.77444474	2.58513337	0.43880100
H	-0.09178574	-3.44123963	-2.19617400
H	-4.74744374	-4.69185163	-2.22452400
H	-5.87580474	-2.67008963	-1.31703700
N	-2.81071974	0.68108637	-0.33687900
N	-4.14358074	-1.58993963	-1.07321100
Cu	-4.91909674	0.28431237	-0.33646500
C	-12.16334974	-2.11023463	-0.86233500
C	-11.18416374	-2.32356663	0.10660500
C	-9.93547874	-1.71837763	-0.01803600
C	-9.63852274	-0.88443563	-1.10941300
C	-10.63402774	-0.68726463	-2.08364200
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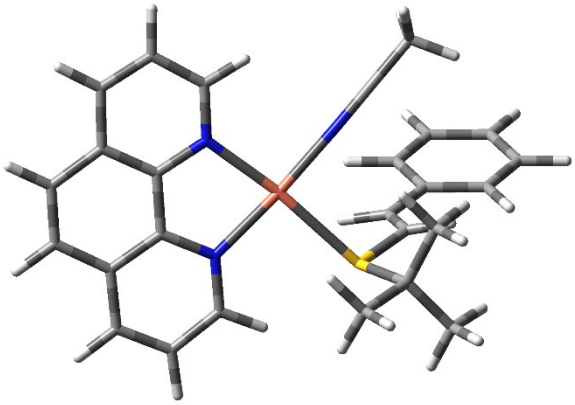
H	-13.13527074	-2.58124263	-0.77051500
H	-11.39050974	-2.96172163	0.95837500
H	-9.17787974	-1.88923963	0.73958300
H	-10.43396974	-0.06822863	-2.95026300
H	-12.63392674	-1.12665063	-2.72045200
C	-8.30913174	-0.26170063	-1.17299800
H	-7.60332874	-0.60113563	-0.41995100
C	-7.90277674	0.66852937	-2.04859200
H	-8.56035374	1.06576937	-2.81292100
S	-6.22258074	1.23258937	-2.16235700
C	-6.37007474	3.12790237	-2.08174700
C	-4.93133974	3.62841037	-2.24451900
H	-4.50010574	3.30799637	-3.19589500
H	-4.93232874	4.72202537	-2.22466400
H	-4.28817174	3.27945237	-1.43474700
C	-7.23856174	3.61040337	-3.24798700
H	-8.27374074	3.27643037	-3.15674100
H	-7.24881174	4.70499537	-3.25081300
H	-6.84276474	3.27248937	-4.20808900
C	-6.95937874	3.54747837	-0.73457800
H	-6.33416474	3.21278737	0.09547800
H	-7.02511774	4.63981137	-0.69539200
H	-7.96547374	3.14572337	-0.59438300
N	-5.76832574	0.36336237	1.48395500
C	-6.24463374	0.38733737	2.53248500
C	-6.84608574	0.42528237	3.85040100
H	-6.07635274	0.60557137	4.60351100
H	-7.58652074	1.22617437	3.89580700
H	-7.33604574	-0.52735163	4.06128200

Copper complex D_{SET} -1765.70731831 hartree



C	-0.22680502	1.78500984	-0.00296904
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C	0.13514298	-0.42943416	1.56824896
C	-1.24065002	1.27909084	0.82407396
C	2.45131898	-0.70821716	0.80307896
C	0.28785698	-1.60363016	2.37513696
C	1.51288798	-2.30425116	2.37851996
C	2.59654698	-1.81980116	1.57423496
C	1.59130998	-3.46090616	3.18410396
H	2.51331698	-4.02950116	3.21634896
C	0.49293998	-3.85552516	3.91718496
C	-0.68564302	-3.09493116	3.85323196
H	3.27235598	-0.34967616	0.19396996
H	-0.42817402	2.65916184	-0.60777604
H	1.80148498	1.53117584	-0.65455204
H	-2.21134902	1.75583284	0.85348796
H	3.53487298	-2.36194016	1.58997196
H	0.51959398	-4.73874516	4.54133096
H	-1.56183902	-3.38276416	4.41906396
N	-1.06785602	0.20922084	1.59271696
N	-0.78207002	-2.00242816	3.10652896
Cu	-2.38365802	-0.69267616	2.88022096
C	-9.56793702	-2.71833916	0.51893896
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C	-7.20658002	-2.37433316	0.15634796
C	-7.20397902	-1.29955416	1.06581196
C	-8.41757902	-0.93935216	1.68501296
C	-9.58432602	-1.64082216	1.41082096
H	-10.48144002	-3.26268016	0.30968096
H	-8.35521802	-3.91388916	-0.80369004
H	-6.28129902	-2.65662116	-0.33672204
H	-8.45578502	-0.09664716	2.36635096
H	-10.51314702	-1.34569516	1.88792896
C	-5.94351102	-0.60373616	1.31305796
H	-5.14314202	-0.83115816	0.61310496
C	-5.69347702	0.24656784	2.32762596
H	-6.42452002	0.48209984	3.09101596
S	-4.14085202	1.05392184	2.48568596
C	-4.35054902	2.23072484	3.97660796
C	-2.98587702	2.91367984	4.12159996
H	-2.68720402	3.42843184	3.20596296
H	-3.06434702	3.66294184	4.91367796
H	-2.20140802	2.21094384	4.40898896
C	-5.42772902	3.24665784	3.57655396
H	-6.40636402	2.78413484	3.43816896
H	-5.51933002	3.97979784	4.38345596
H	-5.15876002	3.77902684	2.66219496
C	-4.72725002	1.46569584	5.24532196
H	-3.95422802	0.75357984	5.53577796
H	-4.83821302	2.19140284	6.05634296
H	-5.67739402	0.93749484	5.15132996
N	-3.62556302	-1.71148216	4.05981696
C	-4.34976202	-2.34023016	4.69304196
C	-5.26193902	-3.12764016	5.49143896
H	-5.56019202	-4.01605716	4.93185596
H	-4.76859202	-3.43008116	6.41689196
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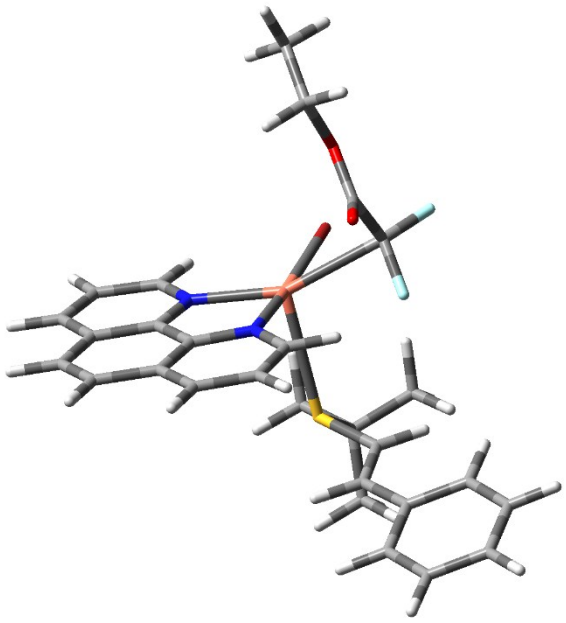
Transition state TS-D_{OA} -4712.91386803 hartree



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C	0.97656189	1.01615755	0.64969300
C	-0.64930711	4.75797955	1.60331200
C	-1.55204411	2.39257155	2.85018800
C	-2.11372811	3.64400355	3.18930100
C	-1.63732011	4.82754855	2.53557900
C	-3.12679911	3.65134255	4.17296900
H	-3.58463211	4.59048255	4.46144800
C	-3.52097911	2.46601355	4.75599400
C	-2.90020511	1.27020755	4.35781100
H	-0.28795011	5.65549655	1.11538200
H	2.29513689	2.02019055	-0.71937500
H	1.35311989	4.27658455	-0.20398000
H	1.36358789	0.03309755	0.42614700
H	-2.07824011	5.78058355	2.80294400
H	-4.29470711	2.43980455	5.51195900
H	-3.18424911	0.31911755	4.79539900
N	-0.00665111	1.08926855	1.54172200
N	-1.94786211	1.23902355	3.43905500
Cu	-0.88197311	-0.39801945	2.65615500
Br	-2.04478511	-2.25447245	3.46909900
C	-0.49757411	-2.44909645	1.38700100
C	-1.13195711	-1.88854445	0.09416600
O	-2.41165311	-2.15672445	0.05167400
O	-0.44614811	-1.33391645	-0.72441800
C	-3.14415711	-1.74326145	-1.16138600
H	-2.67975811	-2.24814145	-2.00858100
H	-3.01179511	-0.66632245	-1.26840700
C	-4.58890811	-2.13684445	-0.97008000
H	-5.15254411	-1.84246945	-1.85856100
H	-4.68944411	-3.21626745	-0.84274900
H	-5.02381311	-1.63252945	-0.10526000
F	0.79531789	-2.19646145	1.50925800
F	-0.67379511	-3.75339345	1.49691200
C	7.17068389	-0.31148145	0.71427600
C	6.85076489	0.96000855	1.18840100
C	5.69528289	1.15418655	1.94203800
C	4.83666689	0.08316255	2.24417900
C	5.16680189	-1.19096145	1.74714100
C	6.32148189	-1.38467745	0.99675800
H	8.06737289	-0.46601245	0.12519900
H	7.49932989	1.80125655	0.97126300
H	5.45387789	2.14622855	2.30926400
H	4.51377889	-2.03482845	1.93679700
H	6.55710889	-2.37464745	0.62243500
C	3.64762489	0.34558155	3.06631000
H	3.42274089	1.39543055	3.23596200
C	2.84701389	-0.57658845	3.62301000
H	3.03852989	-1.63847145	3.51872200
S	1.36041989	-0.13531545	4.47635500
C	1.40210189	-1.20517245	6.03888900
C	0.12063689	-0.82452245	6.79118800
H	-0.77269311	-1.07357345	6.21495500
H	0.08182389	-1.38126645	7.73210800
H	0.09850589	0.24172555	7.02990000

C	1.40373489	-2.69516245	5.68485200
H	2.30543989	-2.98691345	5.14231700
H	1.37856089	-3.28020545	6.61015900
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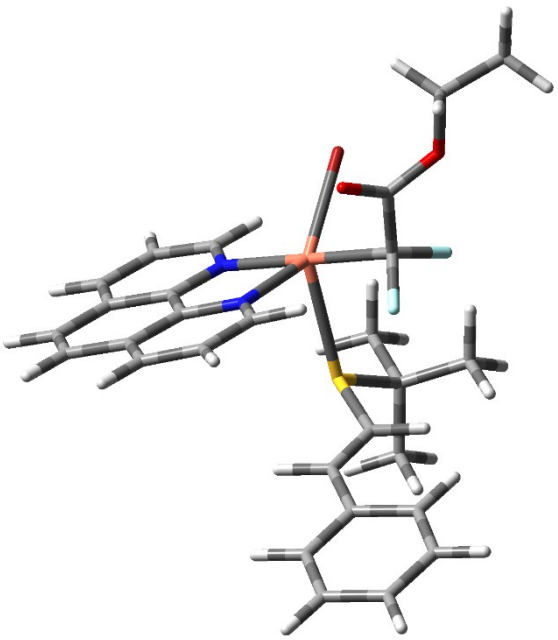
C	2.64267089	-0.82863745	6.85504000
H	2.64036189	0.23186055	7.11654200
H	2.65276589	-1.41016645	7.78288400
H	3.56428789	-1.04843845	6.31159300

Copper complex D_{OA} -4712.9295774 hartree



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C	0.36538045	4.03885270	0.91593400
C	0.46297045	2.63766470	1.02064200
C	1.59583845	1.97191270	0.57038700
H	3.53541545	2.16018070	-0.35211500
H	3.38463545	4.63083970	-0.56401500
H	1.37381045	5.81956270	0.23773100
H	-0.35163355	2.06409670	1.44607700
H	1.65401745	0.89302170	0.65695700
C	-0.79067655	4.79978870	1.38675200
H	-0.79034055	5.85561770	1.12980300
C	-1.82214755	4.31880770	2.10742600
H	-1.87913655	3.28582370	2.42585900
S	-3.19303355	5.34010170	2.51022300
C	-3.67801155	4.80878170	4.27660500
C	-4.90156355	5.66583370	4.61697700
H	-5.75822755	5.41766270	3.98740500
H	-5.18311755	5.46938170	5.65521200
H	-4.68704655	6.73295570	4.52569900
C	-4.01249455	3.31959370	4.35776300
H	-3.16638555	2.68654470	4.08466700
H	-4.27076455	3.08407470	5.39489200
H	-4.86388055	3.06212570	3.72961900
C	-2.49042155	5.16705170	5.17784700
H	-2.24363855	6.22883270	5.11471900
H	-2.76033555	4.94029070	6.21400200
H	-1.60063055	4.58594170	4.92750900
C	-2.01953055	5.85736970	-2.67374200
C	-1.90891255	7.22890670	-2.65171500
C	-2.69087855	7.97081870	-1.74180400
C	-3.55592155	7.25023370	-0.88723600
C	-2.90319355	5.22260870	-1.78632900
C	-2.64886255	9.40180070	-1.65854400
C	-4.38298755	7.96410570	0.04050700
C	-4.32774355	9.37478470	0.09710400

C	-3.43388455	10.07635070	-0.77660200
C	-5.17621055	10.02229970	1.01934800
H	-5.16070155	11.10336170	1.09310900
C	-6.01881655	9.27256870	1.81074600
C	-6.01412655	7.87559270	1.68604100
H	-1.97812955	9.93626970	-2.32073300
H	-1.44102355	5.25444970	-3.36095000
H	-1.23343655	7.74430670	-3.32442300
H	-3.00542755	4.14904570	-1.79797800
H	-3.40067955	11.15790070	-0.72210700
H	-6.68652755	9.73732670	2.52375600
H	-6.67680455	7.26054470	2.28005600
N	-3.64922855	5.89188970	-0.91481900
N	-5.21485455	7.24277470	0.83585600
Cu	-5.05161855	5.22991470	0.56618500
Br	-7.42309655	4.83691470	0.85510400
C	-4.88988855	3.21581070	0.30398200
C	-5.68244355	2.78474870	-0.95491100
O	-6.54350655	1.83191870	-0.67268400
O	-5.44981055	3.27161370	-2.03250700
C	-7.36734155	1.33088870	-1.78317800
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H	-8.86799655	-0.15991830	-2.04249600
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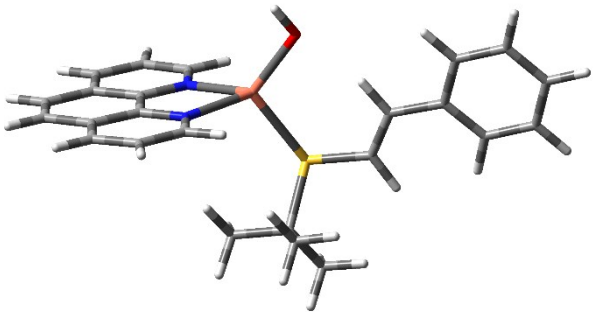
Copper complex E -1709.08450935 hartree



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C	-1.86313499	1.17714949	-0.86549900
C	1.94777401	1.57301249	-2.54473200
C	-0.39465999	1.63334749	-4.14288300
C	0.88953501	1.77236549	-4.72532600
C	2.05554701	1.73918649	-3.88997100
C	0.95585701	1.93713449	-6.12485300
H	1.92085301	2.04816049	-6.60655300
C	-0.21022499	1.95277549	-6.86035400
C	-1.43662599	1.80036949	-6.19278800
H	2.83296501	1.54524149	-1.91945400
H	-0.91578199	0.99138849	1.06235900
H	1.38489401	1.22638349	0.11007200
H	-2.86972499	1.07640349	-0.47442500
H	3.02821901	1.84692149	-4.35642000
H	-0.19676199	2.07618249	-7.93581600
H	-2.36765399	1.80344249	-6.74948600
N	-1.75203599	1.34392549	-2.17841000
N	-1.53375699	1.64425949	-4.87825300
Cu	-3.33077899	1.30066749	-3.66880000
C	-11.03553399	0.74088949	-3.35676100
C	-10.02803499	-0.21883751	-3.27047600
C	-8.69113299	0.15856149	-3.38078000
C	-8.32594299	1.50251849	-3.57551800
C	-9.35670699	2.45653249	-3.66968300
C	-10.69093099	2.08036549	-3.55832600
H	-12.07696199	0.45150549	-3.27394200
H	-10.28159299	-1.26222251	-3.11886900
H	-7.91277799	-0.59378451	-3.31257000
H	-9.11865099	3.50019549	-3.83947600
H	-11.46771899	2.83328949	-3.63471600
C	-6.89507199	1.83131149	-3.66500300
H	-6.21105899	0.98233549	-3.67376300
C	-6.37844799	3.06748749	-3.74062600
H	-6.99398699	3.96007749	-3.72457900
S	-4.65333599	3.36281749	-4.03101100
C	-4.25678399	4.84362049	-2.91567900
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H	-2.52367499	5.30116049	-4.16372400
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H	-2.16626599	4.22413949	-2.79901400
C	-5.05822899	6.06409249	-3.38260500
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H	-5.62864299	4.28803649	-1.31085800
O	-4.51686099	-0.29226951	-3.83589200
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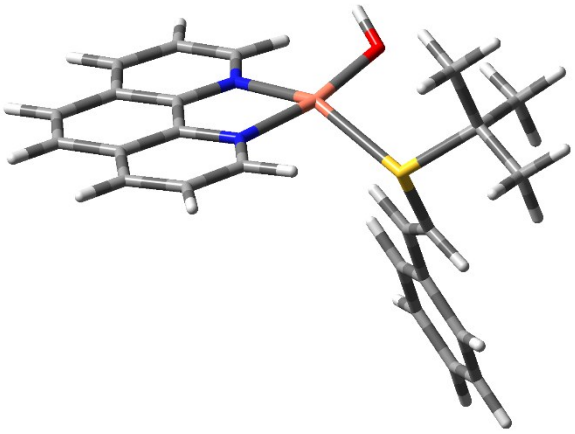
Copper complex E_{SET} -1708.91786692 hartree



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C	3.40322651	3.06308765	1.97209600
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C	1.33238251	4.06450065	1.11681900
C	3.40860051	4.03638465	3.02547000
C	2.38992651	5.01046465	3.09304900
C	1.34735251	4.99726365	2.10784400
C	2.46757151	5.95102365	4.14291100
H	1.70752751	6.71829465	4.23301500
C	3.51219251	5.88527765	5.04024400
C	4.47723951	4.87527965	4.89937100
H	0.53958851	4.05914965	0.37835900
H	3.49244651	0.39510765	-0.75494000
H	1.61894851	2.04587865	-0.73615200
H	5.26258351	0.54921265	0.98010300
H	0.56798051	5.74750865	2.16931600
H	3.60255051	6.59462165	5.85202000
H	5.31022151	4.80106465	5.58715700
N	4.42322251	2.16434365	1.94007800
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Cu	5.72800951	2.41765765	3.51768500
C	11.33889751	7.10718765	1.58211600
C	10.26383351	7.24733465	2.45797300
C	9.41973451	6.16673365	2.70392000
C	9.63427551	4.92444265	2.08379000
C	10.71946951	4.80054165	1.19761500
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H	11.99673251	7.94605265	1.38609600
H	10.08056551	8.19649865	2.94844900
H	8.58378451	6.28117265	3.38581800
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H	12.39217551	5.76538065	0.26586600
C	8.71635151	3.82155365	2.39702700
H	7.87499351	4.09190165	3.02927700
C	8.83301451	2.54858465	1.99450400
H	9.66251151	2.20560865	1.38705700
S	7.60884451	1.30077065	2.29655800
C	8.51792151	-0.04019735	3.30790400
C	7.40279751	-0.98062635	3.77577500
H	6.82926751	-1.37892735	2.93483600
H	7.85628051	-1.82709835	4.29989600
H	6.72343051	-0.47835035	4.46673600
C	9.47580251	-0.75568135	2.34987100
H	10.24599951	-0.08432235	1.96420400
H	9.98305851	-1.55749435	2.89603600
H	8.94443651	-1.20122135	1.50634800
C	9.25562151	0.59109265	4.48634300
H	8.56599051	1.14395865	5.12497200
H	9.72523551	-0.20787635	5.06979400
H	10.04586251	1.26565565	4.14898600
O	6.63881551	2.38475765	5.16118700
H	6.04694351	2.67731765	5.86393700