Supporting Information

α-C-H Difluoroalkylation of Alkyl Sulfoxides via Intermolecular Pummerer Reaction

Xin Huang,[1] Weizhao Zhao,[1] Yuchen Liang,[2] Minghui Wang,[1] Yaling Zhan,[1] Yage Zhang,[1] Lichun Kong,[1] Zhi-Xiang Wang[2,*] and Bo Peng[1,*]

[1]Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Zhejiang Normal University, Jinhua 321004, China

[2] School of Chemical Sciences, University of the Chinese Academy of Sciences, Beijing 100049, China

pengbo@zjnu.cn

zxwang@ucas.ac.cn

Table of Contents

Contents

1 General information 2

2 General procedure for the synthesis of starting sulfoxides **1** 2

3 Studies on the influence of reaction parameters..... 10

4 General procedure for reaction of alkyl sulfoxide **1** with enol silyl ethers **2** 11

5 NMR analysis..... 36

6 Density functional theory (DFT) calculations..... 41

7 KIE studies and control experiments 72

8 NMR spectra 76

1 General information

Unless otherwise indicated, all glassware was oven dried before use and all reactions were performed under an atmosphere of Nitrogen. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers. Reaction progress was monitored by thin layer chromatography (TLC) performed on plastic plates coated with silica gel GF254 with 0.2 mm thickness. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using potassium permanganate. Compound isolation was performed on chromatography column using silica gel 60 (160-200 mesh) or Biotage Isolera Prime flash column system. Neat infrared spectra were recorded using a NEXUS670 FT-IR spectrometer. Wavelengths (ν) are reported in cm^{-1}. MS (EI) analysis was performed on Agilent GC-MS instrument. High-resolution mass spectrometry (HRMS) analysis was carried out using a TOF MS instrument with ESI or APCI source. All ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AV-400 or AV-600. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26, methanol δ 3.31), carbon (chloroform δ 77.16, methanol δ 49.00). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet). Coupling constants were reported in Hertz (Hz).

2 General procedure for the synthesis of starting sulfoxides 1

Sulfoxides **1a**, **1d**, **1w**, **1a'**, **1c'**, and enol silyl ether **2b** are commercially available. Sulfoxides **1b**,[1] **1i**,[2] **1j**,[3] **1k**,[4] **1m**,[5] **1r**,[6] **1t**,[7] **1z**,[8] **1b'**,[9] **1d'**,[10] **1h'**,[11] **1i'**,[12] **1j'**,[13] **1k'**,[14] **1l'**[15], **1e'-1g'**[16] and enol silyl ether **2a**,[17] **2c**,[18] **2d**,[19] **2e**[20] are known compounds.

References:

1. Firouzabadi, H.; Iranpoor, N.; Jafari, A. A.; Riazymontazer, E. *Adv. Synth. Catal.* **2006**, *348*, 434.

2. Laudadio, G.; Straathof, N. J. W.; Lanting, M. D. Knoops, B. Hessel, V.; Noël, T. *Green Chem*. **2017**, *19*, 4061.

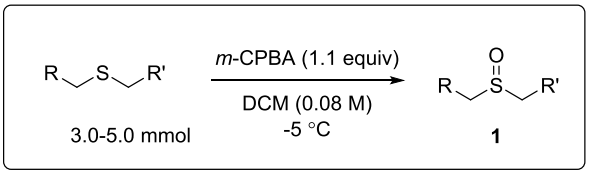
3. Yu, H.; Li, Z.; Bolm, C. *Org. Lett*. **2018**, *20*, 2076

4. Jia, T.-Z.; Bellomo, A.; Baina, K. E.; Dreher, S. D.; Walsh, P. J. *J. Am. Chem. Soc*. **2013**, *135*, 3740.

5. Rioz-Martinez, A.; Kopacz, M.; de Gonzalo, G.; Pazmiño, D. E.; Gotor, V.; Fraaije, M. W. *Org. Biomol. Chem*. **2011**, *9*, 1337.

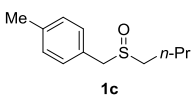
6. Boral, S.; Wang, S.-M.; Wurster, J. A. *U.S. Pat. Appl*. 20120196902, 2012.

7. Choudary, B. M.; Bharathi, B. Reddy, C. V. *J. Chem. Soc. Perkin Trans*. **2002**, *1*, 2069.
8. Imada, Y.; Tonomura, I.; Komiya, N.; Naota, T. *Synlett* **2013**, *24*, 1679.
9. Rani Gogoi, S.; Jyoti Boruah, J.; Sengupta, G.; Saikia, G.; Ahmed, K.; Bania, K. K.; Islam. N. S. *Catal. Sci. Technol*. **2015**, *5*, 595.
10. Cui, H.; Wei, W.; Yang, D.; Zhang, Y.; Zhao, H.; Wang, L.; Wang, H. *Green Chem*. **2017**, *19*, 3520.
11. Ghorbani-Choghamarani, A.; Tahmasbi, B.; Arghand, F.; Faryadi, S. *RSC Adv*. **2015**, *5*, 92174.
12. Javorskis, T.; Bagdziunas, G.; Orentas, E. *Chem. Commun*. **2016**, *52*, 4325.
13. Colas, K.; Mart'n-Montero, R.; Mendoza, A. *Angew. Chem. Int. Ed*. **2017**, *56*, 16042.
14. Hashmat Ali, M.; Bohnert, G. J. *Synthesis* **1998**, *9*, 1238.
15. Johnson, J. A.; Zhang, X.; Reeson, T. C.; Chen, Y.-S.; Zhang, J. *J. Am. Chem. Soc***. 2014**, *45*, 15881.
16. Singh, S. P.; O'Donnell, J. S.; Schwan, A. L. *Org. Biomol. Chem*. **2010**, *8*, 1712.
17. Wu, Y.-B.; Lu, G.-P.; Zhou, B.-J.; Bu, M.-J.; Wan, L.; Cai, C. *Chem. Commun*. **2016**, *52*, 5965.
18. Surya Prakash, G. K.; Hu, J.; Olah, G. A. *J. Fluorine Chem.* **2001**, *112*, 357.
19. Yu, J.-S.; Liu, Y.-L.; Tang, J.; Wang, X.; Zhou, J. *Angew. Chem. Int. Ed.* **2014**, *53*, 9512.
20. Liao, F.-M.; Cao, Z.-Y.; Yu, J.-S.; Zhou, J. *Angew. Chem. Int. Ed.* **2017**, *56*, 2459.



To a solution of sulfide (3.0-5.0 mmol) in DCM (0.08 M) was added a solution of *m*-CPBA (1.1 equiv.) in DCM (0.5 M) at -5 ^{o}C. After the starting sulfide completely consumed, the reaction was quenched with sat. aq. $NaHCO_3$. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtrated and concentrated in vacuo. The obtained residue was purified by column chromatography on silica gel to afford the corresponding sulfoxides **1**.

1-((butylsulfinyl)methyl)-4-methylbenzene (1c):



1c

Following the general procedure, the title compound was prepared from corresponding sulfide (970 mg, 5.0 mmol) and it was obtained as white solid, m.p. 60 – 61 ^{o}C, 703 mg, 67% yield.

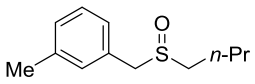
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.17 (s, 4H), 4.00 (d, *J* = 12.9 Hz, 1H), 3.95 (d, *J* = 12.9 Hz, 1H), 2.56 (t, *J* = 7.7 Hz, 2H), 2.32 (s, 3H), 1.77 – 1.68 (m, 2H), 1.49 – 1.37 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 138.2, 129.9, 129.6, 126.7, 57.9, 50.5, 24.4, 22.0, 21.2, 13.7.

IR (neat): 2958, 2869, 2357, 2038, 1513, 1022, 823, 730.

HRMS (ESI-TOF): calculated for $C_{12}H_{18}OSNa([M+Na]^+)$: 233.0971; found: 233.1000.

1-((butylsulfinyl)methyl)-3-methylbenzene (1e):



1e

Following the general procedure, the title compound was prepared from corresponding sulfide (970 mg, 5.0 mmol) and it was obtained as colorless oil, 715 mg, 68% yield.

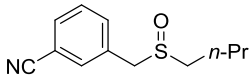
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 – 7.26 (m, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.14 – 7.07 (m, 2H), 4.01 (d, *J* = 12.9 Hz, 1H), 3.96 (d, *J* = 12.8 Hz, 1H), 2.60 (t, *J* = 7.8 Hz, 2H), 2.37 (s, 3H), 1.85 – 1.66 (m, 2H), 1.55 – 1.34 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 138.7, 130.7, 129.8, 129.1, 128.8, 127.0, 58.3, 50.6, 24.4, 22.0, 21.4, 13.7.

IR (neat): 2956, 2927, 1607, 1463, 1028, 790, 702, 437.

HRMS (ESI-TOF): calculated for $C_{12}H_{18}OSNa([M+Na]^+)$: 233.0971; found: 233.0983.

3-((butylsulfinyl)methyl)benzonitrile (1f):



1f

Following the general procedure, the title compound was prepared from corresponding sulfide (1.02 g, 5.0 mmol) and it was obtained as yellow oil, 940 mg, 85% yield.

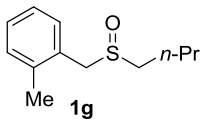
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.7 Hz, 1H), 7.61 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.53 – 7.50 (m, 1H), 4.00 (d, *J* = 13.1 Hz, 1H), 3.94 (d, *J* = 13.1 Hz, 1H), 2.67 – 2.60 (m, 2H), 1.79 – 1.70 (m, 2H), 1.57 – 1.37 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 134.6, 133.4, 132.0, 131.9, 129.7, 118.3, 113.1, 56.8, 51.3, 24.6, 22.0, 13.7.

IR (neat): 2958, 2230, 1481, 1096, 1023, 780

HRMS (ESI-TOF): calculated for $C_{12}H_{15}NOSNa([M+Na]^+)$: 244.0767; found: 244.0771.

1-((butylsulfinyl)methyl)-2-methylbenzene (1g):



1g

Following the general procedure, the title compound was prepared from

corresponding sulfide (970 mg, 5.0 mmol) and it was obtained as white solid, m.p. 37 – 38 °C, 547 mg, 52% yield.

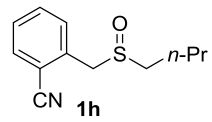
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 – 7.10 (m, 4H), 4.03 (d, *J* = 12.8 Hz, 2H), 3.94 (d, *J* = 12.9 Hz, 1H), 2.67 – 2.59 (m, 2H), 2.39 (s, 3H), 1.80 – 1.66 (m, 2H), 1.48 – 1.34 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 137.3, 131.0, 130.8, 128.8, 128.5, 126.5, 57.0, 51.1, 24.5, 22.0, 19.8, 13.7.

IR (neat): 2957, 2871, 1457, 1077, 768, 743, 726, 447.

HRMS (ESI-TOF): calculated for $C_{12}H_{18}OSNa([M+Na]^+)$: 233.0971; found: 233.0987.

2-((butylsulfinyl)methyl)benzonitrile (1h):



1h

Following the general procedure, the title compound was prepared from corresponding sulfide (615 mg, 3.0 mmol) and it was obtained as white solid, m.p. 63 – 64 °C, 530 mg, 80% yield.

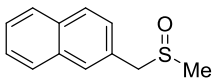
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.59 –7.56 (m, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.43 – 7.40 (m, 1H), 4.20 (d, *J* = 13.2 Hz, 1H), 4.00 (d, *J* = 13.2 Hz, 1H), 2.76 – 2.60 (m, 2H), 1.77 – 1.68 (m, 2H), 1.54 – 1.34 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 134.2, 133.1, 133.1, 131.7, 128.8, 117.5, 113.3, 55.9, 51.7, 24.5, 21.9, 13.6.

IR (neat): 2958, 2857, 2225, 1595, 1464, 1023, 917, 771.

HRMS (ESI-TOF): calculated for $C_{12}H_{15}NOSNa([M+Na]^+)$: 244.0767; found: 244.0775.

methyl(naphthalen-2-ylmethyl)sulfane (1l):



1l

Following the general procedure, the title compound was prepared from corresponding sulfide (940 mg, 5.0 mmol) and it was obtained as white solid, m.p. 130 – 131 °C, 705 mg, 69% yield.

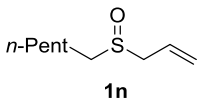
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93 – 7.83 (m, 3H), 7.80 (s, 1H), 7.59 – 7.48 (m, 2H), 7.41 (dd, *J* = 8.4, 1.7 Hz, 1H), 4.23 (d, *J* = 12.9 Hz, 1H), 4.08 (d, *J* = 12.9 Hz, 1H), 2.52 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 133.3, 133.0, 129.4, 128.9, 127.9, 127.8, 127.4, 127.1, 126.6, 126.5, 60.5, 37.3.

IR (neat): 3055, 2904, 2268, 1980, 1597, 1025, 817, 749.

HRMS (ESI-TOF): calculated for $C_{12}H_{12}OSNa([M+Na]^+)$: 227.0501; found: 227.0496.

allyl(hexyl)sulfane (1n):



1n

Following the general procedure, the title compound was prepared from corresponding sulfide (790 mg, 5.0 mmol) and it was obtained as colorless oil, 253 mg, 29% yield.

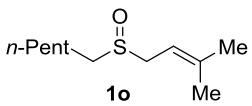
^{1}H NMR (600 MHz, $CDCl_3$): δ 5.93 – 5.85 (m, 1H), 5.49 – 5.33 (m, 2H), 3.52 – 3.40 (m, 2H), 2.74 – 2.63 (m, 2H), 1.85 – 1.67 (m, 2H), 1.53 – 1.36 (m, 2H), 1.36 – 1.25 (m, 4H), 0.95 – 0.81 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 125.8, 123.5, 100.0, 55.7, 50.9, 31.4, 28.5, 22.5, 14.0.

IR (neat): 2952, 2922, 1638, 1466, 1074, 988, 921, 579.

HRMS (ESI-TOF): calculated for $C_9H_{18}OSNa([M+Na]^+)$: 197.0971; found: 197.0965.

hexyl(3-methylbut-2-en-1-yl)sulfane (1o):



1o

Following the general procedure, the title compound was prepared from corresponding sulfide (744 mg, 4.0 mmol) and it was obtained as colorless oil, 428 mg, 53% yield.

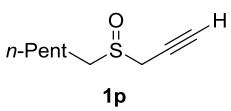
^{1}H NMR (600 MHz, $CDCl_3$): δ 5.26 – 5.16 (m, 1H), 3.50 – 3.38 (m, 2H), 2.65 – 2.61 (m, 2H), 1.79 (s, 3H), 1.77 – 1.72 (m, 2H), 1.71 (s, 3H), 1.49 – 1.35 (m, 2H), 1.30 – 1.27 (m, 4H), 0.90 – 0.85 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 141.6, 111.3, 51.4, 50.9, 31.4, 28.6, 26.0, 22.5, 22.4, 18.6, 14.0.

IR (neat): 2925, 2857, 1451, 1376, 1083, 842, 724

HRMS (ESI-TOF): calculated for $C_{11}H_{22}OSNa([M+Na]^+)$: 225.1284; found: 225.1279.

hexyl(prop-2-yn-1-yl)sulfane (1p):



1p

Following the general procedure, the title compound was prepared from corresponding sulfide (460 mg, 3.0 mmol) and it was obtained as colorless oil, 248 mg, 48% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 3.61 – 3.52 (m, 2H), 2.95 – 2.82 (m, 2H), 2.43 (t, *J* = 2.7 Hz, 1H),

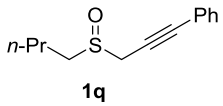
1.87 – 1.70 (m, 2H), 1.54 – 1.40 (m, 2H), 1.38 – 1.28 (m, 4H), 0.90 – 0.87 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 76.3, 72.6, 51.5, 41.8, 31.3, 28.5, 22.4, 22.1, 14.0.

IR (neat): 3212, 2927, 2857, 1458, 1403, 1086, 722, 635,

HRMS (ESI-TOF): calculated for $C_9H_{16}OSNa^+$([M+Na]$^+$): 195.0814; found: 195.0811.

butyl(3-phenylprop-2-yn-1-yl)sulfane (1q):



1q

Following the general procedure, the title compound was prepared from corresponding sulfide (1.02 g, 5.0 mmol) and it was obtained as colorless oil, 364 mg, 33% yield.

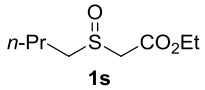
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.47 – 7.42 (m, 2H), 7.37 – 7.31 (m, 3H), 3.82 (d, *J* = 15.9 Hz, 1H), 3.76 (d, *J* = 15.9 Hz, 1H), 3.04 – 2.99 (m, 1H), 2.96 – 2.84 (m, 1H), 1.86 – 1.80 (m, 2H), 1.63 – 1.48 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 131.8, 128.9, 128.4, 122.0, 87.8, 77.7, 51.4, 43.1, 24.2, 22.1, 13.7.

IR (neat): 3063, 2925, 2217, 1673, 1490, 1025, 757, 750.

HRMS (ESI-TOF): calculated for $C_{13}H_{16}OSNa$([M+Na]$^+$): 243.0814; found: 243.0810.

ethyl 2-(butylsulfinyl)acetate (1s):



1s

Following the general procedure, the title compound was prepared from corresponding sulfide (880 mg, 5.0 mmol) and it was obtained as colorless oil, 701 mg, 73% yield.

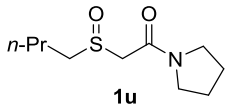
^{1}H NMR (600 MHz, $CDCl_3$): δ 4.20 (q, *J* = 7.1 Hz, 2H), 3.68 – 3.59 (m, 2H), 2.82 (dd, *J* = 8.4, 7.1 Hz, 2H), 1.82 – 1.66 (m, 2H), 1.56 – 1.36 (m, 2H), 1.33 – 1.20 (t, *J* = 7.1 Hz, 3H), 0.94 – 0.91(t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 165.2, 62.1, 55.9, 52.6, 24.3, 21.9, 14.1, 13.6.

IR (neat): 3346, 1723, 1637, 1467, 1371, 1302, 1188, 1018.

HRMS (ESI-TOF): calculated for $C_8H_{16}O_3SNa$([M+Na]$^+$): 215.0712; found: 215.0710.

2-(butylsulfinyl)-1-(pyrrolidin-1-yl)ethan-1-one (1u):



1u

Following the general procedure, the title compound was prepared from corresponding sulfide (603 mg, 3.0 mmol) and it was obtained as colorless oil, 371 mg, 57% yield.

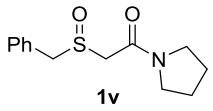
^{1}H NMR (600 MHz, $CDCl_3$): δ 3.81 – 3.62 (m, 2H), 3.61 – 3.34 (m, 4H), 2.99 – 2.93 (m, 1H), 2.91 – 2.76 (m, 1H), 1.96 – 1.91 (m, 2H), 1.87 – 1.83 (m, 2H), 1.77 – 1.71(m, 2H), 1.57 – 1.31 (m, 2H), 1.02 – 0.82 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.7, 56.4, 52.8, 47.5, 46.1, 26.0, 24.5, 24.4, 21.9, 13.7.

IR (neat): 3456, 2956, 2871, 1626, 1436, 1025, 914, 518.

HRMS (ESI-TOF): calculated for $C_{10}H_{19}NO_2SNa([M+Na]^+)$: 240.1029; found: 240.1028.

2-(benzylsulfinyl)-1-(pyrrolidin-1-yl)ethan-1-one (1v):



1v

Following the general procedure, the title compound was prepared from corresponding sulfide (1.17 g, 5.0 mmol) and it was obtained as white solid, m.p. 100 – 101 ^{o}C, 1.13 g, 90% yield.

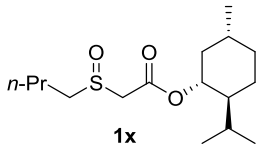
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.44 – 7.28 (m, 5H), 4.41 – 4.32 (m, 1H), 4.16 – 4.06 (m, 1H), 3.56 – 3.54 (m, 2H), 3.51 – 3.47 (m, 2H), 3.46 – 3.31 (m, 2H), 2.00 – 1.91 (m, 2H), 1.89 – 1.83 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.8, 130.6, 129.6, 128.8, 128.4, 57.5, 53.7, 47.4, 46.1, 26.0, 24.4.

IR (neat): 3471, 2965, 1743, 1683, 1433, 1029, 769, 700

HRMS (ESI-TOF): calculated for $C_{13}H_{17}NO_2SNa([M+Na]^+)$: 274.0872; found: 274.0869.

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 2-(butylsulfinyl)acetate (1x):



1x

Following the general procedure, the title compound was prepared from corresponding sulfide (1.14 g, 4.0 mmol) and it was obtained as colorless oil, 1.02 g, 85% yield.

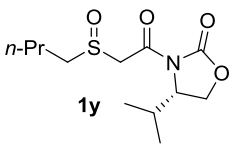
^{1}H NMR (600 MHz, $CDCl_3$):δ 4.82 – 4.67 (m, 1H), 3.76 – 3.57 (m, 2H), 2.92 – 2.75 (m, 2H), 2.06 – 1.93 (m, 1H), 1.93 – 1.72 (m, 3H), 1.67 (d, *J* = 11.5 Hz, 2H), 1.59 – 1.33 (m, 4H), 1.11 – 0.80 (m, 12H), 0.74 (dd, *J* = 6.9, 2.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 164.6, 76.3, 56.34, 56.2, 52.7, 52.5, 46.6, 40.6, 40.5, 33.9, 31.3, 26.0, 24.2, 24.1, 23.0, 21.8, 20.6, 16.0, 15.9, 13.5.

IR (neat): 2954, 2869, 1722, 1456, 1261, 1036, 982, 465.

HRMS (ESI-TOF): calculated for $C_{16}H_{30}O_3SNa([M+Na]^+)$: 325.1808; found: 325.1812.

(4S)-3-(2-(butylsulfinyl)acetyl)-4-isopropyloxazolidin-2-one (1y):



Following the general procedure, the title compound was prepared from corresponding sulfide (777 mg, 3.0 mmol) and it was obtained as white solid, m.p. 88 – 89 °C, 528 mg, 64% yield.

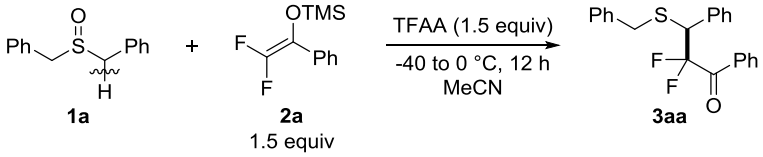
^{1}H NMR (600 MHz, $CDCl_3$):δ 4.54 (d, *J* = 13.6 Hz, 1H), 4.51 – 4.45 (m, 1H), 4.35 – 4.30 (m, 1H), 4.27 – 4.22 (m, 1H), 4.16 (d, *J* = 13.6 Hz, 1H), 2.92 – 2.81 (m, 2H), 2.44 – 2.35 (m, 1H), 1.82 – 1.72 (m, 2H), 1.56 – 1.41 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 164.5, 154.0, 63.8, 58.7, 56.4, 52.9 28.3, 24.4, 21.9, 17.8, 14.6, 13.6.

IR (neat): 2961, 2864, 2160, 1742, 1455, 1026, 950, 825.

HRMS (ESI-TOF): calculated for $C_{12}H_{21}NO_4SNa([M+Na])$: 298.1083; found: 298.1076.

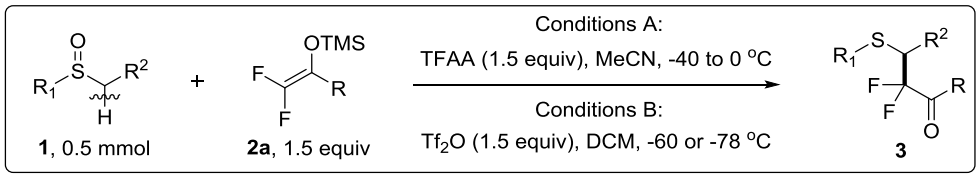
3 Studies on the influence of reaction parameters.



entry	Variation from the "standard" conditions	yield of **3aa**
1	none	94%
1	Tf_2O instead of TFAA	3%
2	TCAA instead of TFAA	89%
3	Ts_2O instead of TFAA	43%
4	Ac_2O instead of TFAA	0%
5	DCM instead of MeCN	41%
6	0 ℃ instead of "-40 to 0 ℃"	83%

To a solution of dibenzyl sulfoxide **1a** (115 mg, 0.5 mmol) and enol silyl ether **2a** (0.75 mmol) in MeCN or DCM (2.5 mL, 0.2 M) was added anhydride (0.75 mmol) under the indicated temperature. After stirring for 5 min, the mixture was warmed to 0 ^{o}C and kept stirring for 12 h. After that, the mixture was passed through a short silica gel column, concentrated under vacuum and purified by flash chromatography on silica gel.

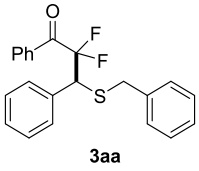
4 General procedure for reaction of alkyl sulfoxide 1 with enol silyl ethers 2



General procedure A: To a solution of alkyl sulfoxide **1** (0.5 mmol) and difluoroenol silyl ether **2** (0.75 mmol, 1.5 equiv) in MeCN (2.5 mL) was added trifluoroacetic anhydride (TFAA, 105 μL, 0.75 mmol) at -40 °C. After stirring for 5 min, the reaction mixture was gradually warmed to 0 °C and kept stirring for 12 h (**3aa-3aq, 3ba-3fa**) or 24 h (**3aa'-3aj'**). After that, the mixture was passed through a short silica gel column and concentrated under vacuum. The obtained residue was further purified by flash chromatography on silica gel affording product **3**.

General procedure B: To a solution of alkyl sulfoxides **1** (0.5 mmol) and difluoroenol silyl ether **2** (0.75 mmol, 1.5 equiv) in DCM (2.5 mL) was added trifluoromethanesulfonic anhydride (Tf_2O, 125 μL, 0.75 mmol) at -78 °C (**3ar**, **3at**, **3av**) or -60 °C (**3as**, **3au**, **3aw-3az**). After stirring for 5 min, the reaction mixture was gradually warmed to 0 °C and kept stirring for 6 h. After that, the mixture was passed through a short silica gel column and concentrated under vacuum. The obtained residue was further purified by flash chromatography on silica gel affording product **3**.

3-(benzylthio)-2,2-difluoro-1,3-diphenylpropan-1-one (3aa):


3aa

Following the general procedure A, the title compound was obtained as light yellow oil, 173 mg, 94% yield. (Rf = 0.30, eluent: PE/EtOAc = 40/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.65 – 7.60 (m, 1H), 7.48 – 7.44 (m, 2H), 7.37 – 5.32 (m, 5H), 7.30 – 7.25 (m, 3H), 7.23 – 7.20 (m, 2H), 4.44 (dd, *J* = 18.7, 13.1 Hz, 1H), 3.73 (dd, *J* = 110.6, 13.2 Hz, 2H).

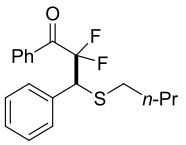
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.5 (t, *J* = 31.7 Hz), 136.6, 134.2, 134.1, 132.9, 130.0, 129.9 (t, *J* = 3.0 Hz), 129.3, 128.7, 128.63, 128.60, 128.5, 127.5, 118.2 (t, *J* = 256.7 Hz), 51.4 (t, *J* = 22.7 Hz), 36.7.

^{19}F NMR (565 MHz, $CDCl_3$): δ -96.9 (d, *J* = 265.6 Hz, 1F), -103.5 (d, *J* = 271.2 Hz, 1F).

IR (neat): 1692, 1448, 1266, 1167, 1058, 918, 695, 683.

HRMS (ESI-TOF): calculated for [$C_{22}H_{18}F_2OSNa$ (M + Na^+)]: 391.0939, found: 391.0938.

3-(butylthio)-2,2-difluoro-1,3-diphenylpropan-1-one (3ab):



3ab

Following the general procedure A, the title compound was obtained as light yellow oil, 159 mg, 95% yield. (Rf = 0.32, eluent: PE/EtOAc = 40/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.9 Hz, 2H), 7.63 – 7.59 (m, 1H), 7.50 – 7.44 (m, 4H), 7.38 – 7.30 (m, 3H), 4.59 (dd, *J* = 20.1, 11.7 Hz, 1H), 2.60 – 2.41 (m, 2H), 1.52 – 1.42 (m, 2H), 1.35 – 1.25 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H).

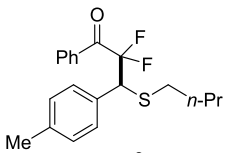
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.2 (t, *J* = 28.7 Hz), 134.9, 134.1, 133.3, 130.0 (t, *J* = 3.0 Hz), 129.9, 128.7, 128.6, 128.5, 119.9 (t, *J* = 259.7 Hz), 52.5 (t, *J* = 22.7 Hz), 32.7, 31.1, 21.8, 13.6.

^{19}F NMR (565 MHz, $CDCl_3$): δ -95.7 (d, *J* = 271.2 Hz, 1F), -105.1 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3062, 2958, 2872, 1701, 1495, 1379, 1077, 859.

HRMS (ESI-TOF): calculated for [$C_{19}H_{20}F_2OSNa$ (M + Na^+)]: 357.1095, found: 357.1110.

3-(butylthio)-2,2-difluoro-1-phenyl-3-(p-tolyl)propan-1-one (3ac):



3ac

Following the general procedure A, the title compound was obtained as light yellow oil, 149.6 mg, 86% yield. (Rf = 0.33, eluent: PE/EtOAc = 40/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.9 Hz, 2H), 7.63 – 7.59 (m, 1H), 7.49 – 7.45 (m, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 4.55 (dd, *J* = 20.1, 11.8 Hz, 1H), 2.54 – 2.44 (m, 2H), 2.34 (s, 3H), 1.48 – 1.42 (m, 2H), 1.32 – 1.26 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H).

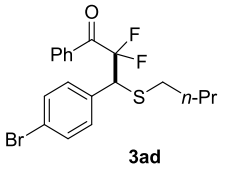
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.3 (t, *J* = 31.7 Hz), 138.3, 134.1, 133.3, 131.7, 130.0 (t, *J* = 3.0 Hz), 129.9, 128.3, 128.7, 118.2 (t, *J* = 259.7 Hz), 52.5 (t, *J* = 22.7 Hz), 32.6, 31.1, 21.8, 21.3, 13.7.

^{19}F NMR (565 MHz, $CDCl_3$): δ -95.8 (d, *J* = 271.2 Hz, 1F), -105.2 (d, *J* = 271.2 Hz, 1F).

IR (neat): 2957, 2872, 2356, 1909, 1701, 1579, 1379, 866.

HRMS (ESI-TOF): calculated for [$C_{20}H_{22}F_2OSNa$ (M + Na^+)]: 371.1252, found: 371.1256.

3-(4-bromophenyl)-3-(butylthio)-2,2-difluoro-1-phenylpropan-1-one (3ad):



3ad

Following the general procedure A, the title compound was obtained as light yellow oil, 186 mg, 90% yield. (Rf = 0.27, eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.65 – 7.61 (m, 1H), 7.51 – 7.45 (m, 4H), 7.35 (d, *J* = 8.3 Hz, 2H), 4.55 (dd, *J* = 20.4, 11.0 Hz, 1H), 2.55 – 2.45 (m, 2H), 1.48 – 1.39 (m, 2H), 1.31 – 1.25 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H).

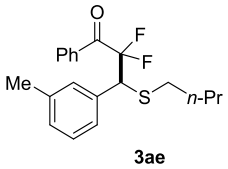
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.8 (t, *J* = 30.2 Hz), 134.3, 134.1, 133.0, 131.7, 131.6, 130.0 (t, *J* = 3.0 Hz), 128.8, 122.6, 117.9 (t, *J* = 259.7 Hz), 51.8 (t, *J* = 22.7 Hz), 32.7, 31.0, 21.8, 13.6.

^{19}F NMR (565 MHz, $CDCl_3$): δ -94.9 (d, *J* = 271.2 Hz, 1F), -105.6 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3062, 2872, 2138, 1579, 1307, 1211, 1001, 867.

HRMS (ESI-TOF): calculated for [$C_{19}H_{19}BrF_2OSNa$ ($M + Na^+$)]: 435.0200, found: 435.0216.

3-(butylthio)-2,2-difluoro-1-phenyl-3-(m-tolyl)propan-1-one (3ae):



3ae

Following the general procedure A, the title compound was obtained as light yellow oil, 149.5 mg, 86% yield. (Rf = 0.31, eluent: PE/EtOAc = 40/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.63 – 7.57 (m, 2H), 7.49 – 7.44 (m, 2H), 7.22 – 7.12 (m, 3H), 4.89 (dd, *J* = 21.0, 11.0 Hz, 1H), 2.61 – 2.46 (m, 2H), 2.37 (s, 3H), 1.49 – 1.39 (m, 2H), 1.32 – 1.25 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H).

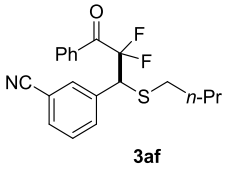
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.6 (t, *J* = 30.2 Hz), 136.9, 134.1, 133.4, 130.5, 130.01 (t, *J* = 3.0 Hz), 130.00, 129.8, 128.7, 128.3, 126.5, 118.8 (t, *J* = 259.7 Hz), 51.8 (t, *J* = 22.7 Hz), 32.7, 31.3, 21.8, 20.0, 13.7.

^{19}F NMR (565 MHz, $CDCl_3$): δ -95.6 (d, *J* = 271.2 Hz, 1F), -103.9 (d, *J* = 271.2 Hz, 1F).

IR (neat): 2957, 2872, 2360, 1580, 1379, 1241, 1001, 831.

HRMS (ESI-TOF): calculated for [$C_{20}H_{22}F_2OSNa$ ($M + Na^+$)]: 371.1252, found: 371.1260.

3-(1-(butylthio)-2,2-difluoro-3-oxo-3-phenylpropyl)benzonitrile (3af):



3af

Following the general procedure A, the title compound was obtained as light yellow oil, 136 mg, 76% yield. (Rf = 0.25, eluent: PE/EtOAc = 20/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.9 Hz, 2H), 7.80 (s, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.66 – 7.57 (m, 2H), 7.52 – 7.44 (m, 3H), 4.60 (dd, *J* =

21.1, 10.0 Hz, 1H), 2.53 – 2.44 (m, 2H), 1.48 – 1.38 (m, 2H), 1.33 – 1.21 (m, 2H), 0.81 (t, *J* = 7.4 Hz, 3H).

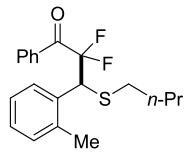
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.3 (t, *J* = 28.7 Hz), 136.9, 134.5, 134.4, 133.5, 132.7, 132.0, 130.0, 129.4, 128.8, 118.5, 117.7 (t, *J* = 259.7 Hz), 112.7, 51.6 (t, *J* = 24.2 Hz), 32.9, 30.9, 21.7, 13.6.

^{19}F NMR (565 MHz, $CDCl_3$): δ -93.6 (d, *J* = 276.9 Hz, 1F), -106.2 (d, *J* = 276.9 Hz, 1F).

IR (neat): 2958, 2871, 2224, 1977, 1579, 1378, 1213, 1000.

HRMS (ESI-TOF): calculated for [$C_{20}H1_9F_2NOSNa$ (M + Na^+)]: 382.1048, found: 383.1062.

3-(butylthio)-2,2-difluoro-1-phenyl-3-(o-tolyl)propan-1-one (3ag):



3ag

Following the general procedure A, the title compound was obtained as light yellow oil, 130.3 mg, 75% yield. (Rf = 0.30, eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.64 – 7.59 (m, 1H), 7.48 (dd, *J* = 8.1, 7.7 Hz, 2H), 7.30 – 7.21 (m, 3H), 7.14 (d, *J* = 7.2 Hz, 1H), 4.57 (dd, *J* = 20.4, 11.5 Hz, 1H), 2.58 – 2.48 (m, 2H), 2.36 (s, 3H), 1.52 – 1.43 (m, 2H), 1.34 – 1.27 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H).

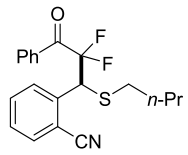
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.2 (t, *J* = 30.2 Hz), 138.2, 134.7, 134.1, 133.3, 130.5, 130.1 (t, *J* = 3.0 Hz), 129.3, 128.7, 128.4, 127.0, 118.2 (t, *J* = 259.7 Hz), 52.4 (t, *J* = 24.2 Hz), 32.7, 31.0, 21.8, 21.5, 13.6.

^{19}F NMR (565 MHz, $CDCl_3$): δ -95.5 (d, *J* = 271.2 Hz, 1F), -105.2 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3062, 3026, 2872, 2337, 2022, 1580, 1001, 858.

HRMS (ESI-TOF): calculated for [$C_{20}H_{22}F_2OSNa$ (M + Na^+)]: 372.1252, found: 372.1265.

2-(1-(butylthio)-2,2-difluoro-3-oxo-3-phenylpropyl)benzonitrile (3ah):



3ah

Following the general procedure A, the title compound was obtained as light yellow oil, 172.1 mg, 96% yield. (Rf = 0.31, eluent: PE/EtOAc = 20/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.8 Hz, 2H), 7.80 (s, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.67 – 7.58 (m, 2H), 7.51 – 7.44 (m, 3H), 4.61 (dd, *J* = 21.1, 10.0 Hz, 1H), 2.60 – 2.42 (m, 2H), 1.49 – 1.39 (m, 2H), 1.32 – 1.24 (m, 2H), 0.81 (t, *J* = 7.4 Hz, 3H).

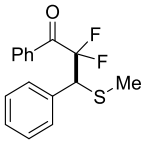
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.3 (t, *J* = 30.2 Hz), 136.9, 134.5, 134.4, 133.5, 132.7, 132.0, 130.1 (t, *J* = 3.0 Hz), 129.4, 128.8, 118.5 (t, *J* = 259.7 Hz), 116.0, 112.7, 51.6 (t, *J* = 24.2 Hz), 32.8, 31.0, 21.7, 13.5.

^{19}F NMR (565 MHz, $CDCl_3$): δ -93.5 (d, *J* = 271.2 Hz, 1F), -106.2 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3063, 2872, 2231, 1700, 1580, 1379, 1001, 830.

HRMS (ESI-TOF): calculated for [$C_{20}H_{19}F_2NOSNa$ (M + Na^+)]: 382.1048, found: 382.1066.

2,2-difluoro-3-(methylthio)-1,3-diphenylpropan-1-one (3ai):



3ai

Following the general procedure A, the title compound was obtained as light yellow oil, 121.2 mg, 83% yield. (Rf = 0.41, eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.9 Hz, 2H), 7.63 – 7.59 (m, 1H), 7.49 – 7.43 (m, 4H), 7.37 – 7.31 (m, 3H), 4.56 (dd, *J* = 19.3, 12.3 Hz, 1H), 2.09 (s, 3H).

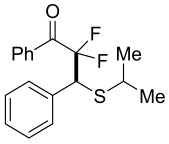
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.0 (t, *J* = 30.2 Hz), 134.2, 134.1, 133.1, 130.0 (t, *J* = 3.0 Hz), 129.9, 128.7, 128.6, 128.5, 118.4 (t, *J* = 259.7 Hz), 53.9 (t, *J* = 24.2 Hz), 16.0.

^{19}F NMR (565 MHz, $CDCl_3$): δ -96.6 (d, *J* = 271.2 Hz, 1F), -104.0 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3062, 2921, 1700, 1579, 1303, 1214, 1077, 1001.

HRMS (ESI-TOF): calculated for [$C_{16}H_{14}F_2OSNa$ (M + Na^+)]: 315.0626, found: 315.0626.

2,2-difluoro-3-(isopropylthio)-1,3-diphenylpropan-1-one (3aj):



3aj

Following the general procedure A, the title compound was obtained as light yellow oil, 92.6 mg, 58% yield. (Rf = 0.44, eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.62 – 7.58 (m, 1H), 7.50 – 7.44 (m, 4H), 7.37 – 7.29 (m, 3H), 4.62 (dd, *J* = 20.6, 11.3 Hz, 1H), 2.92 – 2.84 (m, 1H), 1.17 (dd, *J* = 10.7, 6.7 Hz, 6H).

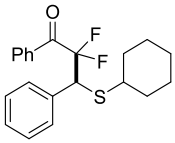
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.5 (t, *J* = 30.2 Hz), 135.4, 134.1, 133.4, 130.1, 130.0 (t, *J* = 3.0 Hz), 128.7, 128.6, 128.5, 118.1 (t, *J* = 259.7 Hz), 51.5 (t, *J* = 24.2 Hz), 36.7, 23.4, 23.0.

^{19}F NMR (565 MHz, $CDCl_3$): δ -95.1 (d, *J* = 271.2 Hz, 1F), -105.6 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3063, 2866, 1696, 1579, 1287, 1076, 1001, 859.

HRMS (ESI-TOF): calculated for [$C_{18}H_{18}F_2OSNa$ (M + Na^+)]: 343.0939, found: 343.0939.

3-(cyclohexylthio)-2,2-difluoro-1,3-diphenylpropan-1-one (3ak):



3ak

Following the general procedure A, the title compound was obtained as light yellow oil, 97 mg, 54% yield. (Rf = 0.41, eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.65 – 7.57 (m, 1H), 7.48 – 7.43 (m, 4H), 7.37 – 7.28 (m, 3H), 4.63 (dd, *J* = 21.2, 11.0 Hz, 1H), 2.71 – 2.56 (m, 1H), 1.88 – 1.76 (m, 2H), 1.70 – 1.62 (m, 2H), 1.56 – 1.50 (m, 1H), 1.30 – 1.17 (m, 5H).

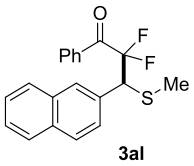
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.6 (t, *J* = 30.2 Hz), 135.7, 134.0, 133.5, 130.0 (t, *J* = 3.0 Hz), 128.8, 128.7, 128.5, 128.4, 118.1 (t, *J* = 259.7 Hz), 50.8 (t, *J* = 24.2 Hz), 45.1, 33.6, 33.0, 25.9, 25.8, 25.7.

^{19}F NMR (565 MHz, $CDCl_3$): δ -94.6 (d, *J* = 271.2 Hz, 1F), -106.1 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3062, 2852, 1598, 1494, 1288, 1077, 857, 770.

HRMS (ESI-TOF): calculated for [$C_{21}H_{22}F_2OSNa$ (M + Na^+)]: 383.1252, found: 383.1265.

2,2-difluoro-3-(methylthio)-3-(naphthalen-2-yl)-1-phenylpropan-1-one (3al):



3al

Following the general procedure A, the title compound was obtained as light yellow oil, 138.7 mg, 81% yield. (Rf = 0.37, eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.8 Hz, 2H), 7.91 – 7.83 (m, 4H), 7.68 – 7.60 (m, 2H), 7.53 – 7.46 (m, 4H), 4.78 (dd, *J* = 19.6, 12.1 Hz, 1H), 2.11 (s, 3H).

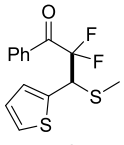
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.8 (t, *J* = 30.2 Hz), 134.2, 133.2, 133.0, 132.9, 131.4, 130.0 (t, *J* = 3.0 Hz), 129.3, 128.7, 128.6, 128.1, 127.7, 127.1, 126.6, 126.5, 118.5 (t, *J* = 259.7 Hz), 54.0 (t, *J* = 24.2 Hz), 15.8.

^{19}F NMR (565 MHz, $CDCl_3$): δ -95.8 (d, *J* = 271.2 Hz, 1F), -103.8 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3060, 2921, 1918, 1578, 1368, 1314, 1001, 869.

HRMS (ESI-TOF): calculated for [$C_{20}H_{16}F_2OSNa$ (M + Na^+)]: 365.0782, found: 365.0790.

2,2-difluoro-3-(methylthio)-1-phenyl-3-(thiophen-2-yl)propan-1-one (3am):



3am

Following the general procedure A, the title compound was obtained as light yellow oil, 92.4 mg, 62% yield. (Rf = 0.40, eluent: PE/EtOAc = 20/1). Note: ^{19}F-NMR

spectra of **3am** show some unknown impurities although many eluent system are tried during flash column separation (PE/EtOAc, PE/Et2O, PE/Acetone, PE/MeOH).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.63 (dd, *J* = 10.6, 4.2 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.32 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.13 (d, *J* = 3.4 Hz, 1H), 6.98 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.90 (dd, *J* = 18.6, 11.9 Hz, 1H), 2.13 (s, 3H).

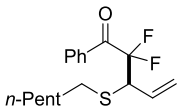
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.6 (t, *J* = 30.2 Hz), 136.3, 134.4, 132.9, 130.0 (t, *J* = 3.0 Hz), 128.8, 128.7, 126.9, 126.7, 117.8 (t, *J* = 259.7 Hz), 48.8 (t, *J* = 24.2 Hz), 15.7.

^{19}F NMR (565 MHz, $CDCl_3$): δ -96.0 (d, *J* = 271.2 Hz, 1F), -104.8 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3072, 2922, 1698, 1579, 1274, 1001, 970, 856.

HRMS (ESI-TOF): calculated for [$C_{14}H_{12}F_2OS_2Na$ ($M + Na^+$)]: 321.0190, found: 321.0193.

2,2-difluoro-3-(hexylthio)-1-phenylpent-4-en-1-one (3an):



3an

Following the general procedure A, the title compound was obtained as light yellow oil, 68 mg, 44% yield. (Rf = 0.35, eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.8 Hz, 2H), 7.65 – 7.61 (m, 1H), 7.53 – 7.47 (m, 2H), 5.96 – 5.86 (m, 1H), 5.36 – 5.28 (m, 2H), 4.02 – 3.85 (m, 1H), 2.61 – 2.46 (m, 2H), 1.55 – 1.45 (m, 2H), 1.34 – 1.17 (m, 6H), 0.86 (t, *J* = 7.1 Hz, 3H).

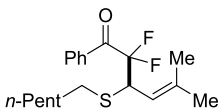
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.6 (t, *J* = 30.2 Hz), 134.3, 133.1, 130.6 (t, *J* = 3.0 Hz), 130.0 (t, *J* = 3.0 Hz), 128.8, 120.5, 118.2 (t, *J* = 259.7 Hz), 51.3 (t, *J* = 24.2 Hz), 31.8, 31.4, 29.1, 28.5, 22.6, 14.1.

^{19}F NMR (565 MHz, $CDCl_3$): δ -96.6 (d, *J* = 271.2 Hz, 1F), -106.4 (d, *J* = 271.2 Hz, 1F).

IR (neat): 2955, 2856, 2341, 1636, 1419, 1378, 1101, 987.

HRMS (ESI-TOF): calculated for [$C_{17}H_{22}F_2OSNa$ ($M + Na^+$)]: 335.1252, found: 335.1252.

2,2-difluoro-3-(hexylthio)-5-methyl-1-phenylhex-4-en-1-one (3ao):



3ao

Following the general procedure, A the title compound was obtained as light yellow oil, 75 mg, 44% yield. (Rf = 0.33, eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.8 Hz, 2H), 7.64 – 7.60 (m, 1H), 7.52 – 7.47 (m, 2H), 5.26 – 5.17 (m, 1H), 4.28 – 4.18 (m, 1H), 2.64 – 2.48 (m, 2H), 1.76 (d, *J* = 0.9 Hz, 3H), 1.62 (d, *J* = 0.9 Hz, 3H), 1.54 – 1.46 (m, 2H), 1.33 – 1.22 (m, 6H), 0.87 (t, *J* = 6.9

Hz, 3H).

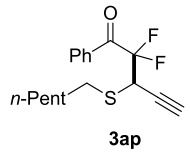
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.9 (t, *J* = 30.2 Hz), 138.9, 134.1, 133.3, 130.0 (t, *J* = 3.0 Hz), 128.8, 118.6 (t, *J* = 259.7 Hz), 117.0, 46.1 (t, *J* = 24.2 Hz), 31.5, 31.4, 26.0, 22.6, 18.4, 14.1.

^{19}F NMR (565 MHz, $CDCl_3$): δ -99.9 (d, *J* = 271.2 Hz, 1F), -104.7 (d, *J* = 271.2 Hz, 1F).

IR (neat): 2956, 2356, 2167, 1580, 1377, 1114, 1001, 778.

HRMS (ESI-TOF): calculated for [$C_{19}H_{26}F_2OSNa$ ($M + Na^+$)]: 363.1565, found: 363.1568.

2,2-difluoro-3-(hexylthio)-1-phenylpent-4-yn-1-one (3ap):



3ap

Following the general procedure A, the title compound was obtained as light yellow oil, 88.4 mg, 57% yield. (Rf = 0.36, eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.7 Hz, 2H), 7.69 - 7.63 (m, 1H), 7.53 – 7.49 (m, 2H), 4.42 – 4.35 (m, 1H), 2.88 – 2.75 (m, 2H), 2.55 (d, *J* = 2.6 Hz, 1H), 1.62 – 1.55 (m, 2H), 1.41 – 1.32 (m, 2H), 1.30 – 1.24 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H).

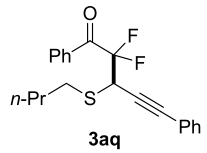
^{13}C NMR (151 MHz, $CDCl_3$): δ 188.6 (t, *J* = 30.2 Hz), 134.6, 132.6, 130.0 (t, *J* = 3.0 Hz), 128.8, 117.0 (t, *J* = 259.7 Hz), 76.0, 75.6, 38.6 (t, *J* = 24.2 Hz), 31.8, 31.5, 29.1, 28.6, 22.6, 14.1.

^{19}F NMR (565 MHz, $CDCl_3$): δ -96.4 (d, *J* = 271.2 Hz, 1F), -105.2 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3304, 2966, 2856, 2125, 1580, 1308, 1001, 876.

HRMS (ESI-TOF): calculated for [$C_{17}H_{20}F_2OSNa$ ($M + Na^+$)]: 333.1095, found: 333.1104.

2,2-difluoro-3-(hexylthio)-1,5-diphenylpent-4-yn-1-one (3aq):



3aq

Following the general procedure A, the title compound was obtained as light yellow oil, 95 mg, 53% yield. (Rf = 0.30, eluent: PE/EtOAc = 40/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11 (d, *J* = 7.7 Hz, 2H), 7.66 – 7.63 (m, 1H), 7.53 – 7.49 (m, 2H), 7.44 – 7.39 (m, 2H), 7.36 – 7.28 (m, 3H), 4.60 (dd, *J* = 15.6, 12.2 Hz, 1H), 2.92 – 2.82 (m, 2H), 1.66 – 1.60 (m, 2H), 1.45 – 1.38 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

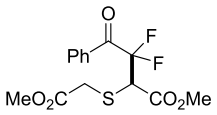
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.1 (t, *J* = 30.2 Hz), 134.5, 132.8, 132.0, 130.0 (t, *J* = 3.0 Hz), 128.9, 128.8, 128.4, 122.2, 117.2 (t, *J* = 259.7 Hz), 117.0, 87.9, 80.7, 39.7 (t, *J* = 24.2 Hz), 31.44, 31.40, 22.1, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$): δ -97.2 (d, *J* = 271.2 Hz, 1F), -104.6 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3061, 2929, 2872, 2228, 1579, 1379, 1001, 883.

HRMS (ESI-TOF): calculated for [$C_{21}H_{20}F_2OS$ (M + Na^+)]: 381.1095, found: 381.1102.

Methyl 2-((2-ethoxy-2-oxoethyl)thio)-3,3-difluoro-4-oxo-4-phenylbutanoate (3ar):



3ar

Following the general procedure B, the title compound was obtained as light yellow oil, 71.4 mg, 43% yield. (Rf = 0.30, eluent: PE/EtOAc = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09 (d, *J* = 7.5 Hz, 2H), 7.69 – 7.63 (m, 1H), 7.53 – 7.49 (m, 2H), 4.45 (dd, *J* = 17.0, 11.5 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.55 (q, *J* = 15.5 Hz, 2H).

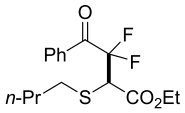
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.1 (t, *J* = 30.2 Hz), 169.8, 167.5, 134.5, 132.8, 130.0 (t, *J* = 3.0 Hz), 128.9, 117.2 (t, *J* = 259.7 Hz), 61.2 (t, *J* = 24.2 Hz), 53.2, 52.8, 34.0.

^{19}F NMR (565 MHz, $CDCl_3$): δ -100.0 (d, *J* = 271.2 Hz, 1F), -102.2 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3012, 2924, 2008, 1735, 1560, 1449, 1054, 842.

The title compound was detected by LC/TOF-MS with ESI and APCI sources, unfortunately the expected MS was not found.

ethyl 2-(butylthio)-3,3-difluoro-4-oxo-4-phenylbutanoate (3as):



3as

Following the general procedure B, the title compound was obtained as light yellow oil, 152 mg, 92% yield. (Rf = 0.25, eluent: PE/EtOAc = 40/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09 (d, J = 7.9 Hz, 2H), 7.67 – 7.61 (m, 1H), 7.53 – 7.47 (m, 2H), 4.28 – 4.20 (m, 2H), 4.16 (dd, *J* = 17.4, 11.9 Hz, 1H), 2.85 – 2.79 (m, 1H), 2.77 – 2.71 (m, 1H), 1.64 – 1.57 (m, 2H), 1.45 – 1.38 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H).

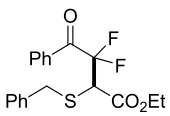
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.1 (t, *J* = 30.2 Hz), 167.7, 134.6, 132.0, 130.3 (t, *J* = 3.0 Hz), 128.8, 116.8 (t, *J* = 259.7 Hz), 62.0, 49.9 (t, *J* = 24.2 Hz), 32.9, 31.3, 21.8, 14.1, 13.7.

^{19}F NMR (565 MHz, $CDCl_3$): δ -100.4 (d, *J* = 271.2 Hz, 1F), -102.3 (d, *J* = 271.2 Hz, 1F).

IR (neat): 2932, 2873, 1698, 1596, 1465, 1097, 1001, 866.

HRMS (ESI-TOF): calculated for [$C_{16}H_{20}F_2O_3SNa$ (M + Na^+)]: 353.0993, found: 353.1004.

ethyl 2-(benzylthio)-3,3-difluoro-4-oxo-4-phenylbutanoate (3at):



3at

Following the general procedure B, the title compound was obtained as light

yellow oil, 83.8 mg, 46% yield. (Rf = 0.30, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09 (d, *J* = 7.9 Hz, 2H), 7.66 (d, *J* = 7.3 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.41 – 7.33 (m, 4H), 7.32 – 7.28 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.11 (dd, *J* = 17.6, 11.5 Hz, 1H), 4.01 (dd, *J* = 32.3, 13.0 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).

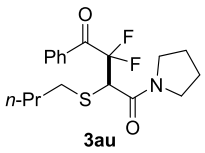
^{13}C NMR (151 MHz, $CDCl_3$): δ 188.8 (t, *J* = 30.2 Hz), 167.4, 136.3, 134.6, 131.9, 130.3 (t, *J* = 3.0 Hz), 129.4, 128.82, 128.77, 127.8, 116.9 (t, *J* = 259.7 Hz), 62.0, 49.1 (t, *J* = 24.2 Hz), 37.1, 14.1.

^{19}F NMR (565 MHz, $CDCl_3$): δ -99.8 (d, *J* = 271.2 Hz, 1F), -102.1 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3063, 2924, 2581, 1735, 1580, 1392, 1324, 1117.

HRMS (ESI-TOF): calculated for [$C_{19}H_{18}F_2O_3SNa$ ($M + Na^+$)]: 387.0837, found: 387.0852.

3-(butylthio)-2,2-difluoro-1-phenyl-4-(pyrrolidin-1-yl)butane-1,4-dione (3au):



3au

Following the general procedure B, the title compound was obtained as light yellow oil, 149 mg, 84% yield. (Rf = 0.23, eluent: PE/EtOAc = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.0 Hz, 2H), 7.62 – 7.58 (m, 1H), 7.50 – 7.44 (m, 2H), 4.29 (dd, *J* = 18.8, 9.9 Hz, 1H), 3.94 – 3.88 (m, 1H), 3.55 – 3.37 (m, 3H), 2.93 – 2.85 (m, 1H), 2.72 – 2.66 (m, 1H), 2.05 – 1.94 (m, 2H), 1.91 – 1.78 (m, 2H), 1.58 – 1.46 (m, 2H), 1.45 – 1.34 (m, 2H), 0.89 (t, *J* = 7.1 Hz, 3H).

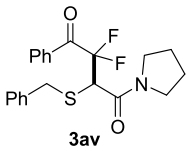
^{13}C NMR (151 MHz, $CDCl_3$): δ 191.2 (t, *J* = 30.2 Hz), 164.6, 134.1, 132.8, 130.3 (t, *J* = 3.0 Hz), 128.6, 117.6 (t, *J* = 259.7 Hz), 49.4 (t, *J* = 24.2 Hz), 46.8, 46.2, 31.5, 31.12, 31.10, 26.3, 24.4, 21.9, 13.7.

^{19}F NMR (565 MHz, $CDCl_3$): δ -97.8 (d, *J* = 271.2 Hz, 1F), -105.8 (d, *J* = 271.2 Hz, 1F).

IR (neat): 2930, 2873, 1598, 1447, 1338, 1227, 1118, 970.

HRMS (ESI-TOF): calculated for [$C_{18}H_{23}F_2NO_2SNa$ ($M + Na^+$)]: 378.1310, found: 378.1324.

3-(benzylthio)-2,2-difluoro-1-phenyl-4-(pyrrolidin-1-yl)butane-1,4-dione (3av):



3av

Following the general procedure B, the title compound was obtained as light yellow oil, 140 mg, 72% yield. (Rf = 0.25, eluent: PE/EtOAc = 3/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.1 Hz, 2H), 7.64 – 7.57 (m, 1H), 7.51 – 7.46 (m, 2H), 7.36 – 7.29 (m, 4H), 7.27 – 7.23 (m, 1H), 4.26 (dd, *J* = 17.9, 10.0 Hz, 1H),

3.97 (dd, *J* = 83.9, 13.4 Hz, 2H), 3.38 – 3.26 (m, 2H), 3.24 – 3.08 (m, 2H), 1.84 – 1.64 (m, 4H).

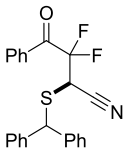
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.1 (t, *J* = 30.2 Hz), 164.2, 137.4, 134.2, 132.7, 130.3 (t, *J* = 3.0 Hz), 129.4, 128.62, 128.61, 127.5, 117.8 (t, *J* = 259.7 Hz), 48.5 (t, *J* = 24.2 Hz), 46.2, 46.0, 35.9, 26.0, 24.2.

^{19}F NMR (565 MHz, $CDCl_3$): δ -97.8 (d, *J* = 271.2 Hz, 1F), -105.8 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3059, 2974, 2363, 1697, 1571, 1088, 879, 836.

HRMS (ESI-TOF): calculated for [$C_{21}H_{21}F_2NO_2SNa$ ($M + Na^+$)]: 412.1153, found: 412.1168.

2-(benzhydrylthio)-3,3-difluoro-4-oxo-4-phenylbutanenitrile (3aw):



3aw

Following the general procedure A, the title compound was obtained as light yellow oil, 106 mg, 54% yield. (Rf = 0.41, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.8 Hz, 2H), 7.66 – 7.62 (m, 1H), 7.55 – 7.47 (m, 6H), 7.41 – 7.37 (m, 4H), 7.35 – 7.31 (m, 2H), 5.15 (dd, *J* = 18.1, 18.1 Hz, 1H).

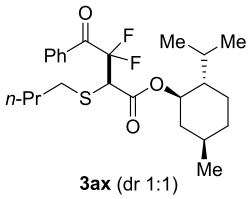
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.0 (t, *J* = 30.2 Hz), 136.4, 134.1, 132.9, 130.2, 129.9 (t, *J* = 3.0 Hz), 129.8, 128.7, 127.6, 119.1 (t, *J* = 259.7 Hz), 55.0 (t, *J* = 24.2 Hz).

^{19}F NMR (565 MHz, $CDCl_3$): δ -97.8 (d, *J* = 271.2 Hz, 1F), -105.8 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3055, 2972, 2231, 2130, 1700, 1581, 1379, 1001, 830.

HRMS (ESI-TOF): calculated for [$C_{23}H_{18}F_2NOS$ ($M + H^+$)]: 394.1072, found: 394.1077

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl2-(butylthio)-3,3-difluoro-4-oxo-4-phenylbutanoate (XX):



3ax (dr 1:1)

Following the general procedure B, the title compound was obtained as the mixture of two diastereoisomers (dr 1:1), light yellow oil, 167 mg, 76% yield. (Rf = 0.32, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.15 – 8.05 (m, 2H), 7.65 – 7.61 (m, 1H), 7.52 – 7.47 (m, 2H), 4.77 – 4.70 (m, 1H), 4.18 – 4.10 (m, 1H), 2.91 – 2.66 (m, 2H), 2.11 – 1.86 (m, 2H), 1.70 – 1.56 (m, 4H), 1.51 – 1.35 (m, 4H), 1.07 – 0.83 (m, 12H), 0.79 – 0.73 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 189.11 (t, *J* = 30.2 Hz), 189.08 (t, *J* = 30.2 Hz), 167.3, 167.2, 134.6, 134.5, 132.1, 132.0, 130.31, 130.25, 128.81, 128.80, 116.9 (t, *J* = 259.7 Hz), 116.8 (t, *J* = 259.7 Hz), 76.12, 76.08, 50.21 (t, *J* = 24.2 Hz), 50.15 (t, *J* = 24.2 Hz), 47.1, 47.0, 40.5, 40.4, 34.3,

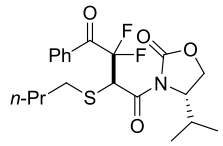
32.9, 31.5, 31.3, 26.1, 25.8, 23.4, 23.1, 22.1, 21.9, 21.8, 20.9, 20.8, 16.2, 15.9, 13.73, 13.70.

^{19}F NMR (565 MHz, $CDCl_3$): δ -100.2 (d, *J* = 271.2 Hz, 1F), -100.7 (d, *J* = 271.2 Hz, 1F), -102.3 (d, *J* = 271.2 Hz, 1F), -102.8 (d, *J* = 271.2 Hz, 1F).

IR (neat): 2928, 2204, 1980, 1731, 1581, 1369, 1078, 847.

HRMS (ESI-TOF): calculated for [$C_{24}H_{34}F_2O_3SNa$ ($M + Na^+$)]: 463.2089, found: 463.2102.

3-(butylthio)-2,2-difluoro-4-((S)-4-isopropyl-2-oxooxazolidin-3-yl)-1-phenylbutane-1,4-dione (3ay):



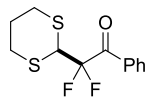
3ay (dr 1:1)

Following the general procedure B, two single diastereoisomers were obtained, total amount 97.1 mg, 47% yield.

Diastereoisomer 1: light yellow oil, 47.5 mg, 23% (Rf = 0.31, eluent: PE/EtOAc = 3/1). **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.12 (d, *J* = 7.6 Hz, 2H), 7.66 – 7.62 (m, 1H), 7.52 – 7.48 (m, 2H), 5.77 (dd, J = 20.7, 9.1 Hz, 1H), 4.47 – 4.41 (m, 1H), 4.36 – 4.32 (m, 1H), 4.30 – 4.27 (m, 1H), 2.99 – 2.77 (m, 2H), 2.48 – 2.31 (m, 1H), 1.63 – 1.50 (m, 2H), 1.44 – 1.37 (dd, *J* = 14.9, 7.5 Hz, 2H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.95 – 0.87 (m, 6H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 188.7, 166.4, 153.7, 134.8, 130.4, 130.2, 128.6, 117.5 (t, *J* = 259.7 Hz), 63.4, 59.1, 47.3 (t, *J* = 24.2 Hz), 32.9, 31.5, 28.4, 21.9, 18.1, 14.6, 13.7. **^{19}F NMR (565 MHz, $CDCl_3$)**: δ -96.9 (d, *J* = 271.2 Hz, 1F), -101.0 (d, *J* = 271.2 Hz, 1F). **IR (neat):** 2962, 2874, 1773, 1580, 1465, 1026, 975, 853. **HRMS (ESI-TOF):** calculated for [$C_{20}H_{25}F_2NO_4SNa$ ($M + Na^+$)]: 436.1365, found: 436.1375

Diastereoisomer 2: light yellow oil, 49.6 mg, 24% (Rf = 0.25, eluent: PE/EtOAc = 3/1). **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.11 (d, *J* = 6.3 Hz, 2H), 7.66 – 7.62 (m, 1H), 7.52 – 7.49 (m, 2H), 5.78 (dd, *J* = 20.7, 9.1 Hz, 1H), 4.54 – 4.52 (m, 1H), 4.40 (t, *J* = 8.6 Hz, 1H), 4.28 (dd, *J* = 9.1, 2.6 Hz, 1H), 2.99 – 2.80 (m, 2H), 2.38 – 2.33 (m, 1H), 1.65 – 1.55 (m, 2H), 1.45 – 1.38 (m, 2H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.93 – 0.89 (m, 6H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 188.8, 166.8, 153.7, 134.9, 130.5, 130.3, 128.9, 119.1 (t, *J* = 259.7 Hz), 63.5, 58.3, 47.5 (m), 32.8, 31.5, 28.5, 22.0, 17.9, 14.9, 13.7. **^{19}F NMR (565 MHz, $CDCl_3$)**: δ -97.1 (d, *J* = 271.2 Hz, 1F), -101.2 (d, *J* = 271.2 Hz, 1F). **IR (neat):** 2962, 2874, 1773, 1580, 1465, 1026, 975, 853. **HRMS (ESI-TOF):** calculated for [$C_{20}H_{25}F_2NO_4SNa$ ($M + Na^+$)]: 436.1365, found: 436.1375

2-(1,3-dithian-2-yl)-2,2-difluoro-1-phenylethan-1-one (3az):



3az

Following the general procedure A, the title compound was obtained as light yellow oil, 99 mg, 72% yield. (Rf = 0.36, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.66 – 7.62 (m, 1H), 7.53 – 7.48 (m, 2H), 4.21 (t, *J* = 16.6 Hz, 1H), 3.26 – 3.08 (m, 2H), 2.54 (d, *J* = 14.0 Hz, 2H), 2.19 – 2.13 (m, 1H), 2.06 – 1.92 (m, 1H).

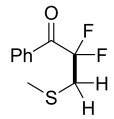
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.7 (t, *J* = 30.2 Hz), 134.3, 133.0, 129.8 (t, *J* = 3.0 Hz), 128.9, 119.7 (t, *J* = 261.2 Hz), 40.4 (t, *J* = 24.2 Hz), 25.6, 24.4.

^{19}F NMR (565 MHz, $CDCl_3$): δ -96.4.

IR (neat): 1701, 1597, 1448, 1174, 1045, 918, 693, 648.

HRMS (ESI-TOF): calculated for [$C_{12}H_{12}F_2OS_2Na$ ($M + Na^+$)]: 297.0190, found: 297.0209.

2,2-difluoro-3-(methylthio)-1-phenylpropan-1-one (3aa'):



3aa'

Following the general procedure A, the title compound was obtained as light yellow oil, 17.2 mg, 16% yield. (Rf = 0.35, eluent: PE/EtOAc = 50/1). ^{19}F-NMR analysis indicated that **3aa'** was obtained in 64% NMR yield. The isolated yield is only 16% is because of the high volatility of the title compound.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11 (d, *J* = 7.6 Hz, 2H), 7.66 – 7.62 (m, 1H), 7.52 – 7.48 (m, 2H), 3.24 (t, *J* = 15.5 Hz, 2H), 2.23 (s, 3H).

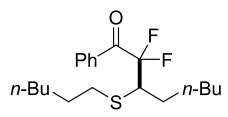
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.1 (t, *J* = 30.2 Hz), 134.5, 132.2, 130.2 (t, *J* = 3.0 Hz), 128.8, 118.9 (t, *J* = 259.7 Hz), 37.2 (t, *J* = 24.2 Hz), 17.6.

^{19}F NMR (565 MHz, $CDCl_3$): δ -97.5.

IR (neat):

HRMS (ESI-TOF): calculated for [$C_{10}H_{10}F_2OSNa$ ($M + Na^+$)]: 239.0313, found: 239.0319.

2,2-difluoro-3-(hexylthio)-1-phenyloctan-1-one (3ab'):



3ab'

Following the general procedure A, the title compound was obtained as light yellow oil, 41 mg, 23% yield. (Rf = 0.35, eluent: PE/EtOAc = 50/1). ^{19}F-NMR analysis indicated that **3ae'** was obtained in 43% NMR yield. The isolated yield is only 23% is because of the high volatility of the title compound.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.66 – 7.62 (m, 1H), 7.52 – 7.48 (m, 2H), 3.27 – 3.17 (m, 1H), 2.57 – 2.43 (m, 2H), 1.93 – 1.85 (m, 1H), 1.83 – 1.67 (m, 1H), 1.59 – 1.39 (m, 4H), 1.38 – 1.17 (m, 10H), 0.93 – 0.83 (m, 6H).

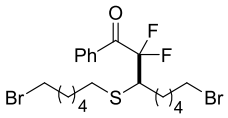
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.6 (t, *J* = 30.2 Hz), 134.1, 133.5, 130.1 (t, *J* = 3.0 Hz), 128.8, 119.5 (t, *J* = 259.7 Hz), 48.4 (t, *J* = 24.2 Hz), 32.4, 31.6, 31.5, 29.4, 28.5, 27.8, 26.5, 22.63, 22.62, 14.14, 14.13.

^{19}F NMR (565 MHz, $CDCl_3$): δ -96.3 (d, *J* = 271.2 Hz, 1F), -107.3 (d, *J* = 271.2 Hz, 1F).

IR (neat): 2926, 1701, 1598, 1448, 1183, 1037, 714, 687.

HRMS (ESI-TOF): calculated for [$C_{20}H_{30}F_2OS$ ($M + H^+$)]: 357.2058, found: 357.2068.

7-bromo-3-((5-bromopentyl)thio)-2,2-difluoro-1-phenylheptan-1-one (3ac'):



3ac'

Following the general procedure A, the title compound was obtained as light yellow oil, 124 mg, 51% yield. (Rf = 0.29, eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.6 Hz, 2H), 7.66 – 7.61 (m, 1H), 7.52 – 7.48 (m, 2H), 3.43 (t, *J* = 6.8 Hz, 2H), 3.38 (t, *J* = 6.8 Hz, 2H), 3.26 – 3.17 (m, 1H), 2.61 – 2.54 (m, 1H), 2.52 – 2.46 (m, 1H), 1.96 – 1.75 (m, 7H), 1.55 – 1.30 (m, 9H).

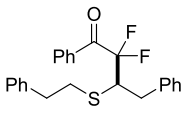
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.6 (t, *J* = 30.2 Hz), 134.2, 133.3, 130.1 (t, *J* = 3.0 Hz), 128.8, 119.5 (t, *J* = 259.7 Hz), 48.3 (t, *J* = 24.2 Hz), 33.8, 32.6, 32.5, 32.3, 32.1, 29.1, 29.0, 27.9, 27.8, 27.7, 25.9.

^{19}F NMR (565 MHz, $CDCl_3$): δ -96.3 (d, *J* = 271.2 Hz, 1F), -107.0 (d, *J* = 271.2 Hz, 1F).

IR (neat): 2930, 1701, 1597, 1448, 1182, 1025, 714, 658.

The title compound was detected by LC/TOF-MS with ESI and APCI sources, unfortunately the expected MS was not found.

2,2-difluoro-3-(phenethylthio)-1,4-diphenylbutan-1-one (3ad'):



3ad'

Following the general procedure A, the title compound was obtained as light yellow oil, 142.7 mg, 72% yield. (Rf = 0.30, eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.66 – 7.62 (m, 1H), 7.52 – 7.48 (m, 2H), 7.36 – 7.31 (m, 4H), 7.29 – 7.26 (m, 1H), 7.23 – 7.19 (m, 2H), 7.18 – 7.14 (m, 1H), 6.94 (d, *J* = 7.2 Hz, 2H), 3.62 – 3.48 (m, 1H), 3.38 (dd, *J* = 14.0, 3.0 Hz, 1H), 2.79 (dd, *J* =

14.0, 11.3 Hz, 1H), 2.51 – 2.39 (m, 4H).

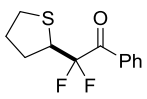
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.3 (t, *J* = 30.2 Hz), 140.1, 138.0, 134.2, 133.4, 130.2 (t, *J* = 3.0 Hz), 129.8, 128.8, 128.6, 128.47, 128.45, 127.0, 126.4, 119.1 (t, *J* = 259.7 Hz), 51.0 (t, *J* = 24.2 Hz), 35.6, 34.8, 34.4.

^{19}F NMR (565 MHz, $CDCl_3$): δ -95.6 (d, *J* = 271.2 Hz, 1F), -107.6 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3027, 1696, 1448, 1183, 1029, 715, 695, 659.

HRMS (ESI-TOF): calculated for [$C_{24}H_{22}F_2OSNa$ (M + Na^+)]: 419.1252, found: 419.1266.

2,2-difluoro-1-phenyl-2-(tetrahydrothiophen-2-yl)ethan-1-one (3ae'):



3ae'

Following the general procedure A, the title compound was obtained as light yellow oil, 11 mg, 9% yield. (Rf = 0.33, eluent: PE/EtOAc = 40/1). ^{19}F-NMR analysis indicated that **3ae'** was obtained in 59% NMR yield. The isolated yield is only 9% is because of the high volatility of the title compound.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.66 – 7.62 (m, 1H), 7.52 – 7.48 (m, 2H), 4.22 – 4.12 (m, 1H), 2.93 – 2.83 (m, 2H), 2.26 – 2.11 (m, 3H), 2.06 – 2.00 (m, 1H).

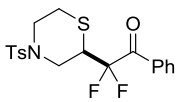
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.5 (t, *J* = 30.2 Hz), 134.5, 133.3, 130.3 (t, *J* = 3.0 Hz), 128.8, 119.0 (t, *J* = 259.7 Hz), 49.3 (t, *J* = 24.2 Hz), 33.1, 31.2, 30.1.

^{19}F NMR (565 MHz, $CDCl_3$): δ -100.8 (d, *J* = 271.2 Hz, 1F), -106.2 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3063, 2872, 2231, 1700, 1580, 1379, 1001, 830.

HRMS (ESI-TOF): calculated for [$C_{12}H_{12}F_2OS$ (M + Na^+)]: 265.0469, found: 265.0484.

2,2-difluoro-1-phenyl-2-(4-tosylthiomorpholin-2-yl)ethan-1-one (3af'):



3af'

Following the general procedure A, the title compound was obtained as light yellow oil, 156.3 mg, 76% yield. (Rf = 0.41, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.9 Hz, 2H), 7.67 – 7.61 (m, 3H), 7.49 (t, J = 7.9 Hz, 2H), 7.51 – 7.47 (m, 2H), 3.72 – 3.57 (m, 3H), 3.39 – 3.30 (m, 2H), 2.96 – 2.89 (m, 1H), 2.67 – 2.57 (m, 1H), 2.41 (s, 3H).

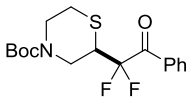
^{13}C NMR (151 MHz, $CDCl_3$): δ 188.3 (t, *J* = 30.2 Hz), 144.1, 134.7, 133.8, 132.0, 130.2, 130.0, 128.8, 127.5, 118.2 (t, *J* = 259.7 Hz), 47.0, 45.8, 40.2 (t, *J* = 24.2 Hz), 26.3, 21.6.

^{19}F NMR (565 MHz, $CDCl_3$): δ -97.7 (d, *J* = 282.5 Hz, 1F), -104.8 (d, *J* = 282.5 Hz, 1F).

IR (neat): 1696, 1596, 1449, 1338, 1155, 1045, 712, 547.

HRMS (ESI-TOF): calculated for [$C_{19}H_{19}F_2NO_3S_2Na$ (M + Na^+)]: 434.0667, found: 434.0689.

tert-butyl 2-(1,1-difluoro-2-oxo-2-phenylethyl)thiomorpholine-4-carboxylate (3ag'):



3ag'

Following the general procedure A, the title compound was obtained as light yellow oil, 100 mg, 56% yield. (Rf = 0.62, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ) δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.63 (d, *J* = 5.8 Hz, 1H), 7.50 (d, *J* = 6.8 Hz, 2H), 4.60 – 3.90 (m, 2H), 3.75 – 3.20 (m, 3H), 3.05 – 2.85 (m, 1H), 2.40 – 2.30 (m, 1H), 1.39 (s, 9H).

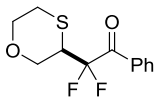
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.1 (t, *J* = 30.2 Hz), 154.2, 134.5, 132.5, 130.2, 128.8, 117.6 (t, *J* = 259.7 Hz), 80.4, 44.6, 44.2, 37.5 (t, *J* = 24.2 Hz), 28.3, 24.8.

^{19}F NMR (565 MHz, $CDCl_3$): δ -95.7 (d, *J* = 282.5 Hz, 1F), -104.9 (d, *J* = 282.5 Hz, 1F).

IR (neat): 3006, 2854, 1702, 1579, 1206, 965, 825, 771.

HRMS (ESI-TOF): calculated for [$C_{17}H_{21}F_2NO_3SNa$ (M + Na^+)]: 380.1102, found: 380.1121.

2,2-difluoro-2-(1,4-oxathian-3-yl)-1-phenylethan-1-one (3ah'):



3ah'

Following the general procedure A, the title compound was obtained as light yellow oil, 71.2 mg, 55% yield. (Rf = 0.30, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.5 Hz, 2H), 7.68 – 7.63 (m, 1H), 7.54 – 7.49 (m, 2H), 4.39 (dd, *J* = 12.6, 3.7 Hz, 1H), 4.09 – 4.03 (m, 2H), 3.85 – 3.79 (m, 1H), 3.43 – 3.35 (m, 1H), 3.07 – 3.00 (m, 1H), 2.36 (d, *J* = 13.7 Hz, 1H).

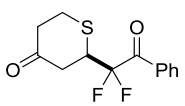
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.2 (t, *J* = 30.2 Hz), 134.5, 132.5, 130.2, 128.8, 119.2 (t, *J* = 259.7 Hz), 68.2, 66.3, 37.6 (t, *J* = 24.2 Hz), 25.0.

^{19}F NMR (565 MHz, $CDCl_3$): δ -95.9 (d, *J* = 282.5 Hz, 1F), -104.6 (d, *J* = 282.5 Hz, 1F).

IR (neat): 1697, 1596, 1448, 1183, 1097, 1039, 875, 686.

HRMS (ESI-TOF): calculated for [$C_{12}H_{12}F_2O_2SNa$ (M + Na^+)]: 281.0418, found: 281.0434.

2-(1,1-difluoro-2-oxo-2-phenylethyl)tetrahydro-4H-thiopyran-4-one (3ai'):



3ai'

Following the general procedure A, the title compound was obtained as light yellow oil, 82.4 mg, 61% yield. (Rf = 0.54, eluent: PE/EtOAc = 20/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.6 Hz, 2H), 7.69 – 7.61 (m, 1H), 7.55 – 7.46 (m, 2H), 4.10 – 3.98 (m, 1H), 3.26 – 3.18 (m, 1H), 2.99 (dd, *J* = 15.0, 5.3 Hz, 1H), 2.90 – 2.78 (m, 2H), 2.77 – 2.67 (m, 2H).

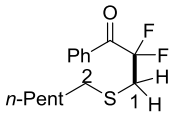
^{13}C NMR (151 MHz, $CDCl_3$): δ 205.6, 188.4 (t, *J* = 30.2 Hz), 134.7, 132.3, 130.1 (t, *J* = 3.0 Hz), 128.9, 119.0 (t, *J* = 261.2 Hz), 43.5 (t, *J* = 24.2 Hz), 42.3, 40.0, 26.8.

^{19}F NMR (565 MHz, $CDCl_3$): δ -95.0 (d, *J* = 276.9 Hz, 1F), -106.3 (d, *J* = 276.9 Hz, 1F).

IR (neat): 3373, 2850, 1718, 1596, 1336, 1109, 847, 791.

HRMS (ESI-TOF): calculated for [$C_{13}H_{12}F_2O_2SNa$ ($M + Na^+$)]: 293.0418, found: 293.0432.

2,2-difluoro-3-(heptylthio)-1-phenylpropan-1-one (3aj'):



3aj' (C1/C2 55/45)

Following the general procedure A, the title compound was obtained as light yellow oil, 64.5 mg, 43% yield. (Rf = 0.30, eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.22 – 8.04 (m, 2H), 7.66 – 7.60 (m, 1H), 7.52 – 7.48 (m, 2H), 3.25 (t, *J* = 15.6 Hz, 1H), 2.63 (t, *J* = 7.4 Hz, 1H), 2.06 (s, 1.62H), 1.94 – 1.85 (m, 0.65H), 1.73 – 1.67 (m, 0.74H), 1.67 – 1.53 (m, 3.31H), 1.39 – 1.22 (m, 4H), 0.93 – 0.86 (m, 3H).

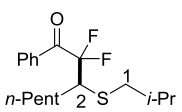
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.4 (t, *J* = 30.2 Hz), 189.2 (t, *J* = 30.2 Hz), 134.5, 134.1, 130.2 (t, *J* = 3.0 Hz), 129.9 (t, *J* = 3.0 Hz), 128.8, 128.7, 120.3, 117.9 (t, *J* = 259.7 Hz), 48.6, 35.0 (t, *J* = 25.7 Hz), 33.8, 31.5, 31.4, 31.3, 29.4, 28.5, 26.4, 26.3, 22.64, 22.61, 14.3, 14.2.

^{19}F NMR (565 MHz, $CDCl_3$): δ -95.2 (d, *J* = 271.2 Hz, 1F, C2), -97.6 (s, 2F, C1), -107.9 (d, *J* = 271.2 Hz, 1F, C2).

IR (neat): 2922, 1698, 1597, 1449, 1137, 1060, 863, 684.

The title compound was detected by LC/TOF-MS with ESI and APCI sources, unfortunately the expected MS was not found.

2,2-difluoro-3-(hexylthio)-4-methyl-1-phenylpentan-1-one (3ak'):



3ak' (C1/C2 25/75)

Following the general procedure A, the title compound was obtained as light yellow oil, 65.8 mg, 40% yield. (Rf = 0.30, eluent: PE/EtOAc = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.7 Hz, 2H), 7.63 – 7.60 (m, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 3.28 – 3.16 (m, 1H), 2.48 – 2.43 (m, 1H), 2.36 – 2.32 (m, 1H), 1.91 – 1.86 (m, 0.76H), 1.75 – 1.66 (m, 1.56H), 1.63 – 1.53 (m, 1.11H), 1.51 – 1.39 (m, 1.33H), 1.40 –

1.27 (m, 3.79H), 1.14 (d, *J* = 6.7 Hz, 0.79H), 1.05 (d, *J* = 6.6 Hz, 0.81H), 0.94 – 0.84 (m, 7.70H).

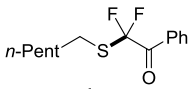
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.6 (t, *J* = 30.2 Hz), 134.1, 134.0, 133.5, 130.1, 130.0 (t, *J* = 3.0 Hz), 128.8, 128.7, 120.0, 119.5 (t, *J* = 259.7 Hz), 54.6, 48.7 (t, *J* = 25.7 Hz), 41.4, 34.7, 31.6, 31.5, 29.8, 29.4, 28.6, 28.5, 27.8, 27.6, 22.6, 22.2, 21.9, 21.8, 18.6, 14.2.

^{19}F NMR (565 MHz, $CDCl_3$): δ -93.9 (d, *J* = 271.2 Hz, 1F, C1), -96.3 (d, *J* = 271.2 Hz, 1F, C2), -106.4 (d, *J* = 271.2 Hz, 1F, C1), -107.3 (d, *J* = 271.2 Hz, 1F, C2)

IR (neat): 2953, 2932, 2858, 1703, 1596, 1578, 1468, 1447, 1263, 1037, 1031, 921.

The title compound was detected by LC/TOF-MS with ESI and APCI sources, unfortunately the expected MS was not found.

2,2-difluoro-2-(hexylthio)-1-phenylethan-1-one (4):



4

Following the general procedure A, the title compound was obtained as light yellow oil, 85.7 mg, 63% yield. (Rf = 0.56, eluent: PE/EtOAc = 20/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14 (d, *J* = 7.6 Hz, 2H), 7.68 – 7.62 (m, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 2.89 (t, *J* = 7.4 Hz, 2H), 1.77 – 1.61 (m, 2H), 1.44 – 1.35 (m, 2H), 1.33 – 1.27 (m, 4H), 0.88 (t, *J* = 6.3 Hz, 3H).

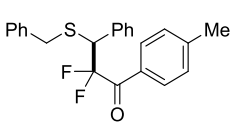
^{13}C NMR (151 MHz, $CDCl_3$): δ 185.4 (t, *J* = 28.9 Hz), 134.7, 131.2, 130.7, 128.8, 124.6 (t, *J* = 288.4 Hz), 31.3, 29.7, 29.1, 28.5, 22.6, 14.1.

^{19}F NMR (565 MHz, $CDCl_3$): δ -79.1 (s, 2F).

IR (neat): 2962, 2929, 2861, 1701, 1596, 1581, 1453, 1278, 1129, 888, 831.

The title compound was detected by LC/TOF-MS with ESI and APCI sources, unfortunately the expected MS was not found.

3-(benzylthio)-2,2-difluoro-3-phenyl-1-(p-tolyl)propan-1-one (3ba):



3ba

Following the general procedure A, the title compound was obtained as light yellow oil, 147.1 mg, 77% yield. (Rf = 0.35, eluent: PE/EtOAc = 40/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.31 (m, 5H), 7.29 – 7.20 (m, 7H), 4.44 (dd, *J* = 18.7, 13.1 Hz, 1H), 3.73 (dd, *J* = 114.0, 13.2 Hz, 2H), 2.45 (s, 3H)

^{13}C NMR (151 MHz, $CDCl_3$): δ 188.9 (t, *J* = 31.7 Hz), 136.6, 134.3, 130.3, 130.1 (t, *J* = 3.0 Hz),

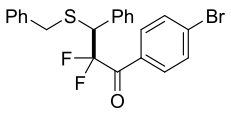
129.9, 129.4, 129.3, 128.59, 128.57, 128.5, 127.4, 118.3 (t, *J* = 256.7 Hz), 51.5 (t, *J* = 22.7 Hz), 36.6, 21.9.

^{19}F NMR (565 MHz, $CDCl_3$): δ -96.9 (d, *J* = 265.6 Hz, 1F), -103.5 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3033, 2951, 1691, 1605, 1494, 1454, 1272, 1364, 1055, 710, 693.

HRMS (ESI-TOF): calculated for [$C_{23}H_{20}F_2OSNa$ (M + Na^+)]: 405.1095, found: 405.1092.

3-(benzylthio)-1-(4-bromophenyl)-2,2-difluoro-3-phenylpropan-1-one (3ca):



3ca

Following the general procedure A, the title compound was obtained as light yellow oil, 111.7 mg, 50% yield. (Rf = 0.33, eluent: PE/EtOAc = 40/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 7.9 Hz, 2H), 7.37 – 7.31 (m, 5H), 7.27 – 7.23 (m, 3H), 7.21 – 7.18 (m, 2H), 4.44 (dd, *J* = 18.7, 13.1 Hz, 1H), 3.73 (dd, *J* = 114.0, 13.2 Hz, 2H).

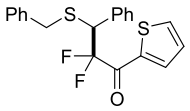
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.7 (t, *J* = 31.7 Hz), 148.8, 136.6, 133.6, 132.9, 130.0, 129.3, 128.7 (t, *J* = 3.0 Hz), 128.60, 128.59, 128.5, 127.5, 118.3 (t, *J* = 256.7 Hz), 51.3 (t, *J* = 22.7 Hz), 36.7.

^{19}F NMR (565 MHz, $CDCl_3$): δ -95.4 (d, *J* = 265.6 Hz, 1F), -104.2 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3027, 1687, 1448, 1265, 1167, 1058, 918, 695, 683.

HRMS (ESI-TOF): calculated for [$C_{22}H_{17}BrF_2OSNa$ (M + Na^+)]: 469.0044, found: 469.0052.

3-(benzylthio)-2,2-difluoro-3-phenyl-1-(thiophen-2-yl)propan-1-one (3da):



3da

Following the general procedure A, the title compound was obtained as light yellow oil, 106.7 mg, 57% yield. (Rf = 0.26, eluent: PE/EtOAc = 40/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88 (d, *J* = 2.9 Hz, 1H), 7.78 (d, *J* = 4.9, 1H), 7.36 – 7.27 (m, 8H), 7.25 – 7.21 (m, 2H), 7.15 – 7.13 (m, 1H), 4.41 (dd, *J* = 19.2, 12.8 Hz, 1H), 3.82 (d, *J* = 13.2 Hz, 1H), 3.65 (d, *J* = 13.2 Hz, 1H).

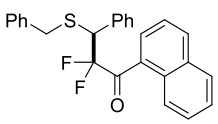
^{13}C NMR (151 MHz, $CDCl_3$): δ 182.5 (t, *J* = 31.7 Hz), 138.9, 136.6, 136.5, 135.9, 134.2, 129.9, 129.3, 128.8, 128.63, 128.60, 128.59, 118.1 (t, *J* = 256.7 Hz), 51.3 (t, *J* = 22.7 Hz), 36.7.

^{19}F NMR (565 MHz, $CDCl_3$): δ -98.1 (d, *J* = 265.6 Hz, 1F), -105.5 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3101, 1662, 1514, 1493, 1409, 1166, 1049, 692.

HRMS (ESI-TOF): calculated for [$C_{20}H_{16}F_2OS_2Na$ ($M + Na^+$)]: 397.0503, found: 397.0501.

3-(benzylthio)-2,2-difluoro-1-(naphthalen-1-yl)-3-phenylpropan-1-one (3ea):



3ea

Following the general procedure A, the title compound was obtained as light yellow oil, 148.4 mg, 71% yield. (Rf = 0.30, eluent: PE/EtOAc = 40/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.12 – 8.08 (m, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.93 – 7.84 (m, 2H), 7.58 – 7.55 (m, 2H), 7.47 – 7.45 (m, 1H), 7.39 – 7.32 (m, 5H), 7.26 – 7.22 (m, 3H), 7.16 – 7.12 (m, 2H), 4.56 (dd, *J* = 20.3, 11.7 Hz, 1H), 3.80 (d, *J* = 13.4 Hz, 1H), 3.61 (d, *J* = 13.2 Hz, 1H).

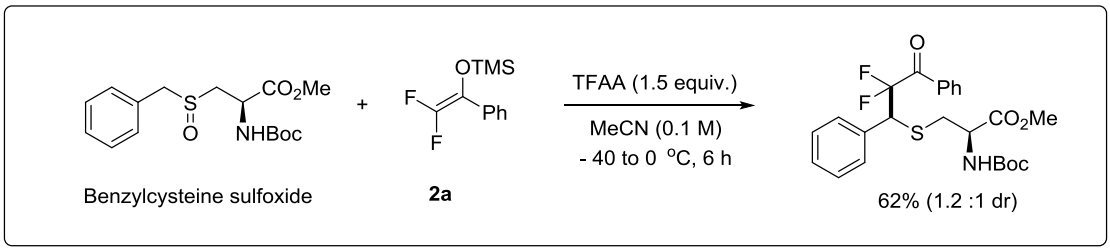
^{13}C NMR (151 MHz, $CDCl_3$): δ 193.0 (t, *J* = 31.7 Hz), 136.4, 134.2, 133.9, 133.5, 131.1, 130.8, 130.1, 129.2, 129.1, 128.7, 128.59, 128.58, 128.57, 128.1, 127.5, 127.1, 126.7, 125.4, 124.1, 117.6 (t, *J* = 256.7 Hz), 51.3 (t, *J* = 22.7 Hz), 36.7.

^{19}F NMR (565 MHz, $CDCl_3$): δ -95.3 (d, *J* = 265.6 Hz, 1F), -104.8 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3060, 1701, 1593, 1508, 1493, 1175, 1054, 775, 694.

HRMS (ESI-TOF): calculated for [$C_{26}H_{20}F_2OSNa$ ($M + Na^+$)]: 441.1095, found: 441.1090.

methyl N-(tert-butoxycarbonyl)-S-(2,2-difluoro-3-oxo-1,3-diphenylpropyl)-L-cysteinate (5a):



To a mixture of Benzylcysteine sulfoxide (171 mg, 0.5 mmol) and difluoroenol silyl ether **2a** (171 mg, 0.75 mmol) in MeCN (5.0 mL) was added trifluoroacetic anhydride (105 μL, 0.75 mmol) at -40 °C. After stirring for 5 min, the reaction mixture was gradually warmed to 0 °C and kept stirring for 6 h. After that, the mixture was passed through a short silica gel column and concentrated under vacuum. The obtained residue was further purified by flash chromatography on silica gel affording product **5a** as a mixture of two diastereoisomers (1.2:1 dr) in 62% yield, 148.5 mg.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.99 – 7.94 (m, 2H), 7.64 – 7.58 (m, 1H), 7.49 – 7.43 (m, 2H), 7.41 – 7.37 (m, 2H), 7.35 – 7.28 (m, 3H), 5.32 (d, *J* = 7.7 Hz, 0.47H), 5.13 (d, *J* = 7.8 Hz, 0.47H), 4.80 – 4.65 (m, 1H), 4.51 (d, *J* = 5.5 Hz, 1H), 3.70 (s, 1.61), 3.63 (s, 1.35), 3.10 – 3.05 (m, 0.56H), 3.02 – 2.90 (m, 1.47H), 1.45 (s, 4H), 1.42 (s, 5H).

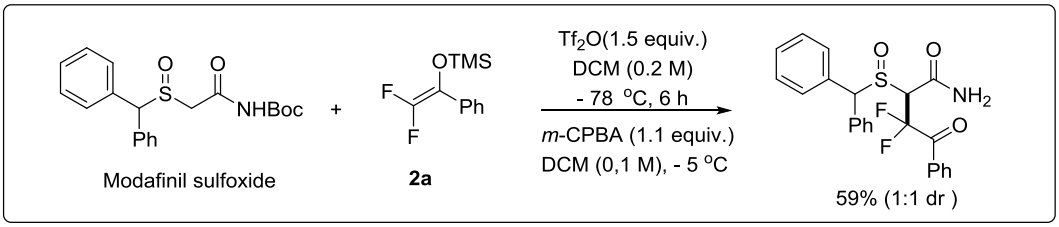
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.6 (t, *J* = 30.2 Hz), 189.5 (t, *J* = 30.2 Hz), 171.2, 171.1, 155.2, 155.1, 134.3, 134.2, 132.9, 132.8, 130.1, 130.0, 128.8, 128.7, 118.0 (t, *J* = 259.7 Hz), 117.9 (t, *J* = 259.7 Hz), 80.4, 80.3, 53.3 (t, *J* = 27.2 Hz), 53.1 (t, *J* = 27.2 Hz), 52.8, 52.7, 35.5, 34.8, 28.4, 28.3.

^{19}F NMR (565 MHz, $CDCl_3$): δ -97.8 (dd, *J* = 276.9 Hz), -98.1 (d, *J* = 276.9 Hz), -103.3 (d, *J* = 276.9 Hz).

IR (neat): 2977, 1741, 1700, 1597, 1498, 1448, 1241, 1159, 1125, 1009, 853, 817.

HRMS (ESI-TOF): calculated for [$C_{24}H_{28}F_2NO_5S(M + H^+)$]: 480.1651, found: 480.1663.

2-(benzhydrylsulfinyl)-3,3-difluoro-4-oxo-4-phenylbutanamide (5b):



To a mixture of Modafinil sulfoxide (186.5 mg, 0.5 mmol) and difluoroenol silyl ether **2a** (171 mg, 0.75 mmol) in DCM (2.5 mL) was added trifluoromethanesulfonic anhydride (125 μL, 0.75 mmol) at -78 °C. After stirring for 6 h, the mixture was passed through a short silica gel column and concentrated under vacuum. The obtained residue was dissolved in DCM (5.0 mL) and a solution of *m*-CPBA (95 mg, 0.55 mmol) in DCM (3 mL) was added slowly at -5 °C. After the sulfide completely consumed, the reaction was quenched with sat. aq. $NaHCO_3$. The organic layer was separated, and the aqueous layer was extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4, filtrated and concentrated in vacuo. The obtained residue was then purified by column chromatography on silica gel affording the title compound **5b** as the mixture of two diastereoisomers (1:1 dr) in 59% yield, 126 mg.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54 – 7.44 (m, 4H), 7.42 – 7.26 (m, 11H), 4.85 – 4.75 (m, 1H), 4.70 – 4.55 (m, 1H).

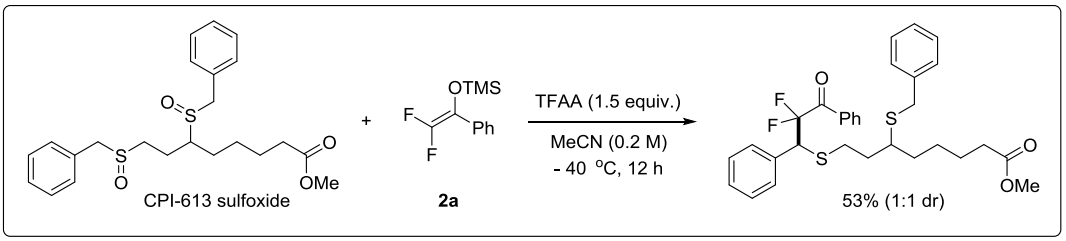
^{13}C NMR (151 MHz, $CDCl_3$): δ 137.7, 137.6, 137.4, 137.3, 136.5, 129.8, 128.9, 128.8, 128.6, 128.4, 128.2, 127.6, 127.4, 124.5, 117.9 (t, *J* = 252.2 Hz), 73.9 (m), 54.7 (t, *J* = 22.7 Hz).

^{19}F NMR (565 MHz, $CDCl_3$): δ -97.7 - -102.9 (m)

IR (neat): 3051, 2919, 2844, 2222, 1631, 1442, 1125, 1040, 860, 748, 688.

HRMS (ESI-TOF): calculated for [$C_{23}H_{20}F_2NO_3S$(M + H^+)]: 428.1126, found: 428.1119.

methyl N-(tert-butoxycarbonyl)-S-(2,2-difluoro-3-oxo-1,3-diphenylpropyl)-L-cysteinate (5c):



To a mixture of CPI-613 sulfoxide (217 mg, 0.5 mmol) and difluoroenol silyl ether **2a** (171 mg, 0.75 mmol) in MeCN (2.5 mL) was added trifluoroacetic anhydride (105 μL, 0.75 mmol) at -40 °C. After stirring for 12 h, the mixture was passed through a short silica gel column and concentrated under vacuum. The obtained residue was further purified by flash chromatography on silica gel affording product **5c** as the mixture of two diastereoisomers (1:1 dr) in 53% yield, 147 mg. Note: The other sulfoxide group was probably reducted to sulfide by the excess difluoroenol silyl ether.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.15 (d, *J* = 7.3 Hz, 0.86H), 8.03 (d, *J* = 7.8 Hz, 1.17H), 7.65 – 7.60 (m, 1H), 7.55 – 7.45 (m, 5H), 7.41 – 7.19 (m, 7H), 4.61 (dd, *J* = 20.4, 11.4 Hz, 1H), 3.76 – 3.56 (m, 5H), 3.13 – 2.79 (m, 0.41H), 2.75 – 2.44 (m, 2.49H), 2.41 – 2.12 (m, 2H), 1.82 – 1.08 (m, 8H).

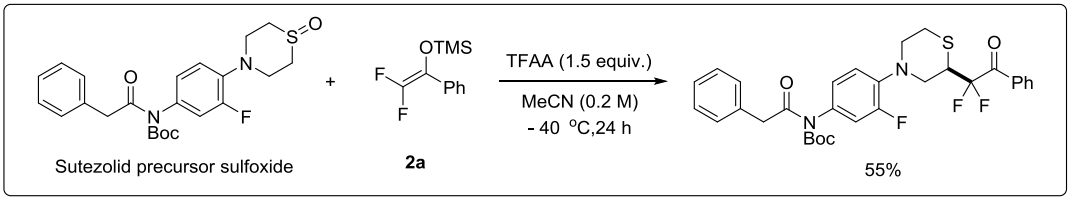
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.97 (t, *J* = 30.2 Hz), 189.92 (t, *J* = 30.2 Hz), 174.1, 138.6, 138.5, 138.4, 134.8, 134.7, 134.6, 134.2, 133.8, 133.0, 130.6, 130.2, 130.0, 129.9, 129.89, 128.9, 128.8, 128.6, 128.5, 127.1, 127.0, 118.0 (t, *J* = 259.7 Hz), 117.8 (t, *J* = 259.7 Hz), 52.4 (t, *J* = 27.2 Hz), 51.6, 44.0, 43.9, 39.7, 38.5, 38.3, 35.1, 34.5, 34.4, 33.93, 33.91, 30.5, 30.0, 26.2, 26.1, 26.0, 24.7, 24.6.

^{19}F NMR (565 MHz, $CDCl_3$): δ -97.8 (d, *J* = 271.2 Hz), -98.3 (d, *J* = 271.2 Hz,), -103.3 (d, *J* = 271.2 Hz).

IR (neat): 3072, 2952, 1697, 1596, 1448, 1230, 1183, 1124, 1010, 809, 711.

HRMS (ESI-TOF): calculated for [$C_{31}H_{35}F_2O_3S_2$(M + H^+)]: 557.1990, found: 557.1997.

tert-butyl (4-(2-(1,1-difluoro-2-oxo-2-phenylethyl)thiomorpholino)-3-fluorophenyl)(2-pheny lacetyl)carbamate (5d):



To a mixture of Sutezolid precursor sulfoxide (223 mg, 0.5 mmol) and difluoroenol silyl ether **2a** (171 mg, 0.75 mmol) in MeCN (5.0 mL) was added trifluoroacetic anhydride (105 μL, 0.75 mmol) at -20 ^{o}C. After stirring for 12 h, the mixture was passed through a short silica gel column and concentrated under vacuum. The obtained residue was further purified by flash chromatography on silica gel affording product **5d** in 55% yield, 160.3 mg.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14 (d, *J* = 7.8 Hz, 2H), 7.67 (dd, *J* = 7.8, 7.4 Hz, 1H), 7.53 (t, *J* = 7.8, 7.6 Hz, 2H), 7.36 – 7.24 (m, 5H), 7.00 – 6.85 (m, 3H), 5.21 (s, 2H), 3.90 – 3.73 (m, 1H), 3.66 (d, J = 4.8 Hz, 2H), 3.43 – 3.33 (m, 2H), 3.15 – 2.95 (m, 1H), 2.87 – 2.70 (m, 1H), 1.44 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 189.0 (t, *J* = 30.2 Hz), 156.0 (d, *J* = 249.2 Hz), 153.0, 151.5, 139.9, 135.4, 134.6, 133.4, 132.4, 130.2, 128.9, 128.6, 128.4, 128.0, 124.4, 120.4, 118.0 (t, *J* = 259.7 Hz), 116.8, 83.9, 68.5, 52.3, 51.4, 41.2 (t, *J* = 27.2 Hz), 27.9, 26.9.

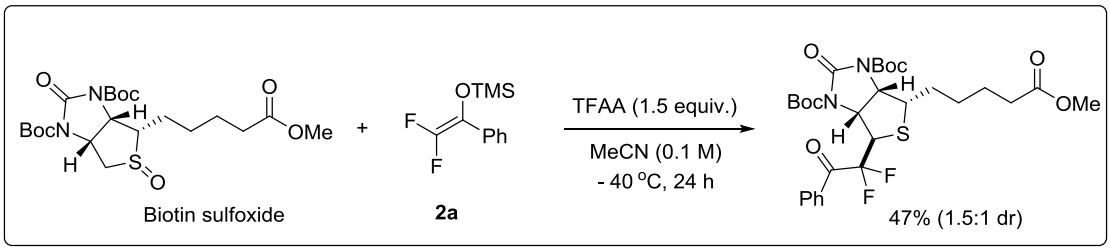
^{19}F NMR (565 MHz, $CDCl_3$): δ -95.8 (dd, *J* = 276.9 Hz), -105.6 (dd, *J* = 276.9 Hz).

IR (neat): 3026, 2982, 1628, 1561, 1498, 1408, 1245, 1206, 1118, 760.

HRMS (ESI-TOF): calculated for [$C_{31}H_{32}F_3N_2O_4S$(M + H^+)]: 585.2029, found: 585.2033.

di-tert-butyl

(3aR,6S,6aS)-4-(1,1-difluoro-2-oxo-2-phenylethyl)-6-(5-methoxy-5-oxopentyl)-2-oxotetrahyd ro-1H-thieno[3,4-d]imidazole-1,3(2H)-dicarboxylate (5e):



To a mixture of Biotin sulfoxide (237 mg, 0.5 mmol) and difluoroenol silyl ether **2a** (171 mg, 0.75

mmol) in MeCN (5.0 mL) was added trifluoroacetic anhydride (105 μL, 0.75 mmol) at -40 °C. After stirring for 24 h, the mixture was passed through a short silica gel column and concentrated under vacuum. The obtained residue was further purified by flash chromatography on silica gel affording product **5e** as the mixture of two diastereoisomers (1.5:1 dr) in 47% yield, 144 mg.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.18 (d, *J* = 7.4 Hz, 0.79H), 8.04 (d, *J* = 7.8 Hz, 1.17H), 7.69 – 7.60 (m, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 6.52 (s, 1H), 5.08 (d, *J* = 7.9 Hz, 0.55H), 4.93 (d, *J* = 7.1 Hz, 0.54H), 4.77 (s, 0.63H), 4.28 (dd, *J* = 27.5, 5.5 Hz, 0.57H), 3.82 – 3.66 (m, 1H), 3.63 (s, 1.2H), 3.62 (s, 1.67H), 2.32 – 2.20 (m, 2H), 1.64 – 1.43 (m, 22.43H), 1.32 – 1.20 (m, 1.69H).

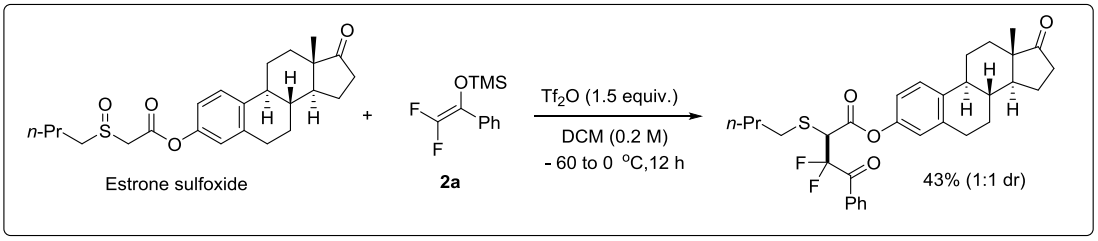
^{13}C NMR (151 MHz, $CDCl_3$): δ 188.0 (t, *J* = 30.2 Hz), 186.0 (t, *J* = 30.2 Hz), 174.0, 155.6, 150.5, 149.9, 149.6, 149.0, 148.3, 135.2, 134.7, 132.2, 132.1, 130.7, 130.1, 128.9, 128.8, 118.9 (t, *J* = 259.7 Hz), 115.0 (t, *J* = 259.7 Hz), 84.9, 84.6, 84.3, 84.2, 61.2, 60.4, 59.5, 54.1, 53.2, 52.9 (t, *J* = 27.2 Hz), 51.7, 33.71, 33.70, 30.5, 29.3, 28.9, 28.1, 28.0, 27.9, 27.8, 26.7, 24.8, 24.2.

^{19}F NMR (565 MHz, $CDCl_3$): δ -95.7 (d, *J* = 276.9 Hz, 1F), -96.9 (d, *J* = 276.9 Hz, 1F), -104.9 (d, *J* = 276.9 Hz, 1F), -105.5 (d, *J* = 276.9 Hz, 1F).

IR (neat): 3026, 2982, 1628, 1561, 1498, 1408, 1245, 1206, 1118, 760.

HRMS (ESI-TOF): calculated for [$C_{29}H_{39}F_2N_2O_8S$(M + H^+)]: 613.2390, found: 613.2377.

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl (S)-2-(butylthio)-3,3-difluoro-4-oxo-4-phenylbutanoate (5f):



To a mixture of Estrone sulfoxide (208 mg, 0.5 mmol) and difluoroenol silyl ether **2a** (171 mg, 0.75 mmol) in DCM (2.5 mL) was added trifluoromethanesulfonic anhydride (125 μL, 0.75 mmol) at -60 °C. After stirring for 5 min, the reaction mixture was gradually warmed to 0 °C and kept stirring for 12 h. After that, the mixture was passed through a short silica gel column and concentrated under vacuum. The obtained residue was further purified by flash chromatography on silica gel affording product **5f** as the mixture of two diastereoisomers (1:1 dr) in 43% yield, 119 mg.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13 (d, *J* = 7.8 Hz, 2H), 7.65 (dd, *J* = 7.8, 7.4 Hz, 1H), 7.51 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 1H), 6.95 – 6.90 (m, 1H), 6.88 (s, 1H), 4.34 (dd, *J* = 18.0, 11.1 Hz, 1H), 2.98 – 2.81 (m, 4H), 2.50 (dd, *J* = 19.1, 8.7 Hz, 1H), 2.44 – 2.35 (m, 1H), 2.30 – 2.24 (m, 1H), 2.18 – 2.10 (m, 1H), 2.09 – 1.90 (m, 3H), 1.73 – 1.38 (m, 10H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.90 (s, 3H).

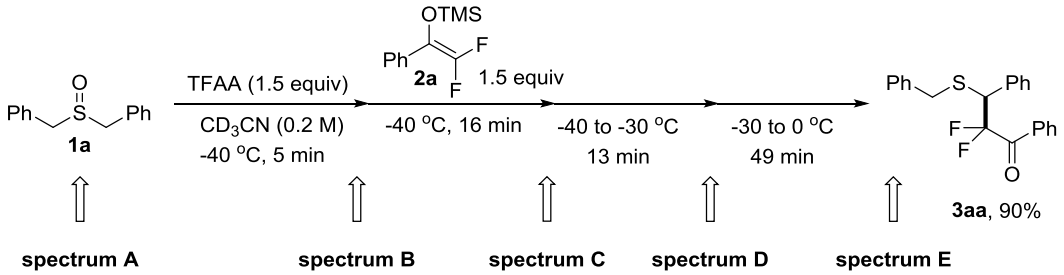
^{13}C NMR (151 MHz, $CDCl_3$): δ 188.8 (t, *J* = 30.2 Hz), 166.5, 148.2, 138.2, 137.9, 134.8, 130.3, 128.8, 126.6, 121.3, 118.5, 116.7 (t, *J* = 259.7 Hz), 50.4, 49.7 (t, *J* = 27.2 Hz), 48.0, 44.2, 38.0, 35.9, 33.0, 31.6, 31.3, 29.4, 26.3, 25.8, 21.8, 21.6, 13.9, 13.7.

^{19}F NMR (565 MHz, $CDCl_3$): δ -99.88 (d, *J* = 276.9 Hz, 1F), -100.41 (d, *J* = 276.9 Hz, 1F), -102.31 (d, *J* = 276.9 Hz, 1F), -102.84 (d, *J* = 276.9 Hz, 1F).

IR (neat): 3012, 2982, 1628, 1561, 1498, 1408, 1245, 1206, 1118, 760.

HRMS (ESI-TOF): calculated for [$C_{32}H_{37}F_2O_4S(M + H^+)$]: 555.2375, found: 555.2377.

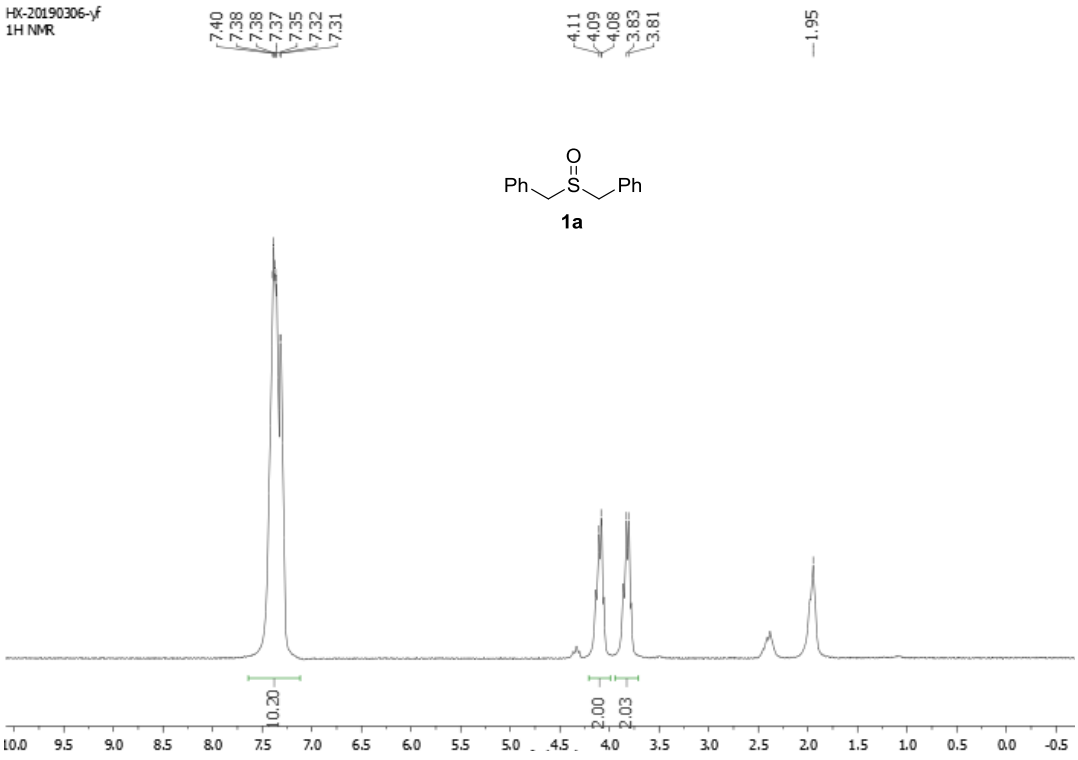
5 NMR analysis.



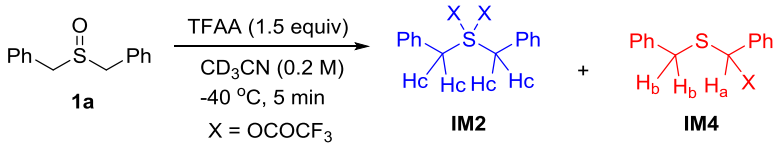
To a solution of dibenzyl sulfoxide **1a** (0.1 mmol in 0.5 mL of CD_3CN) in NMR tube was added trifluoroacetic anhydride TFAA (21 μL, 0.15 mmol) at – 40 °C. After shaking for 5 min, the reaction mixture was brought for NMR analysis (**spectrum B**, 600 MHz, temperature of NMR was -40 °C). After addition of difluoroenol silyl ether **2a** (34 mg, 0.15 mmol) in cooling bath (-40 °C), the tube was quickly inserted into NMR again. The whole reaction process was then monitored. With the temperature gradually increased, **spectra C**, **D**, **E** were obtained at -40, -30 and 0 °C, respectively.

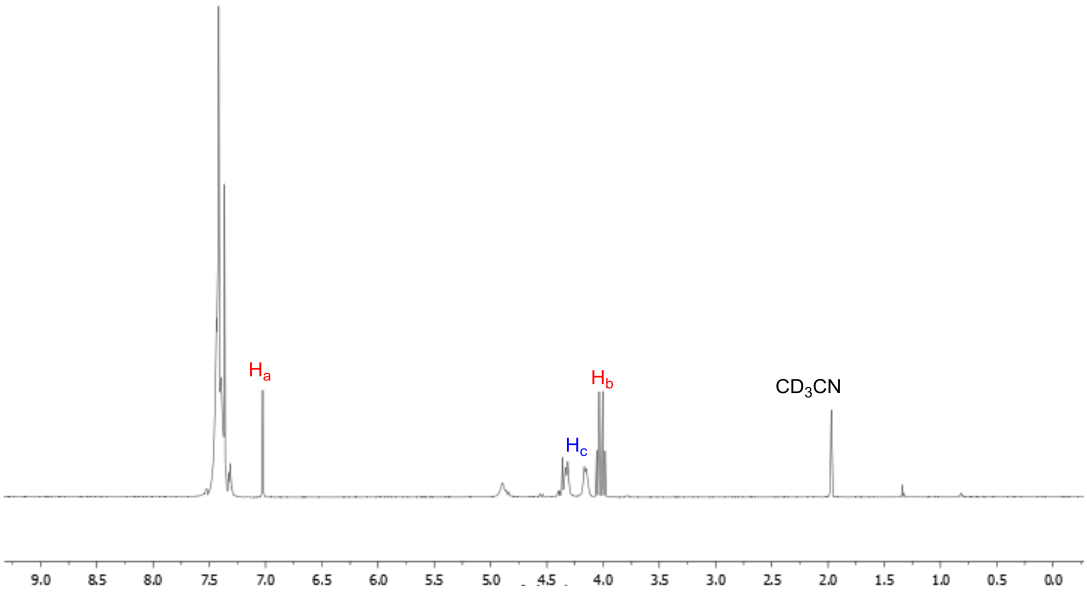
Note: To better understand the reaction process, unlike the general procedure, sulfoxide **1a** was treated with Tf_2O prior to the addition of **2a**. Both procedures gave similar yields of product **3aa**. The ^{19}F-NMR analysis of intermediates were also carried out, however the given NMR spectrums were too complicated to be analyzed.

NMR spectrum A

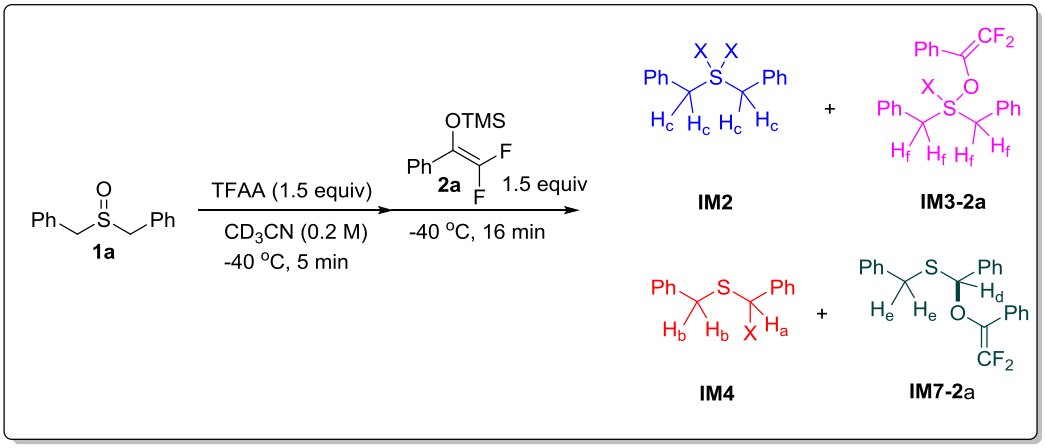


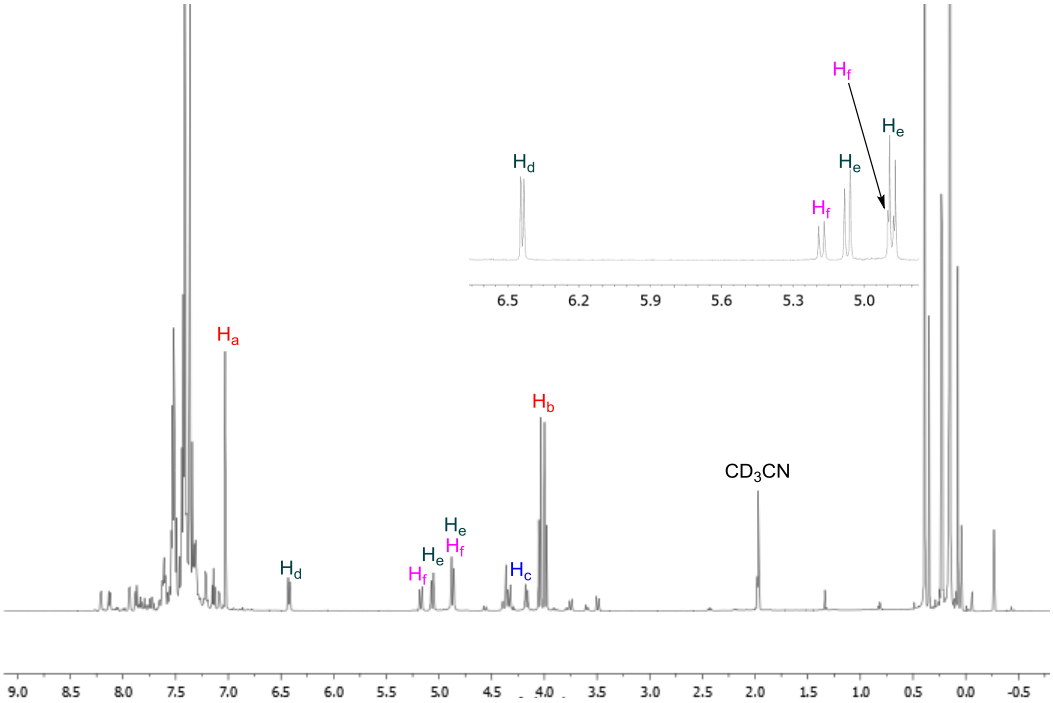
NMR spectrum B





NMR spectrum C

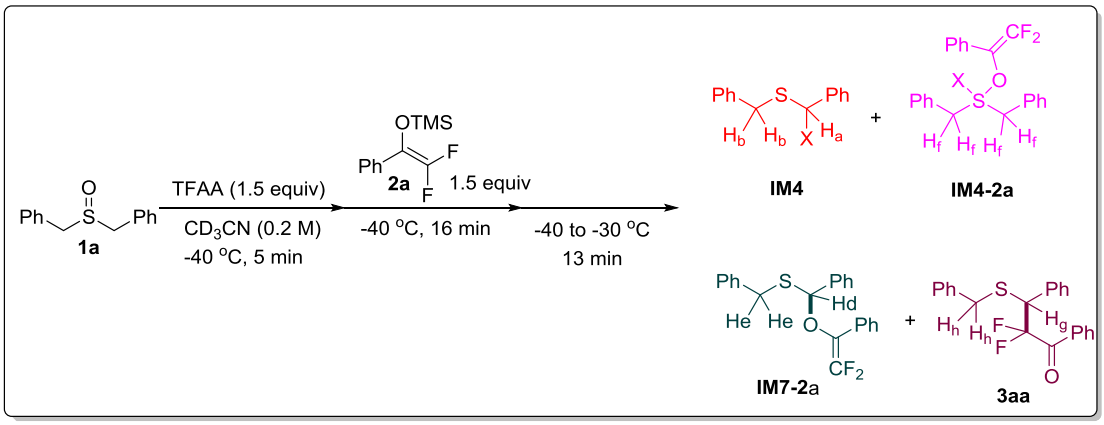


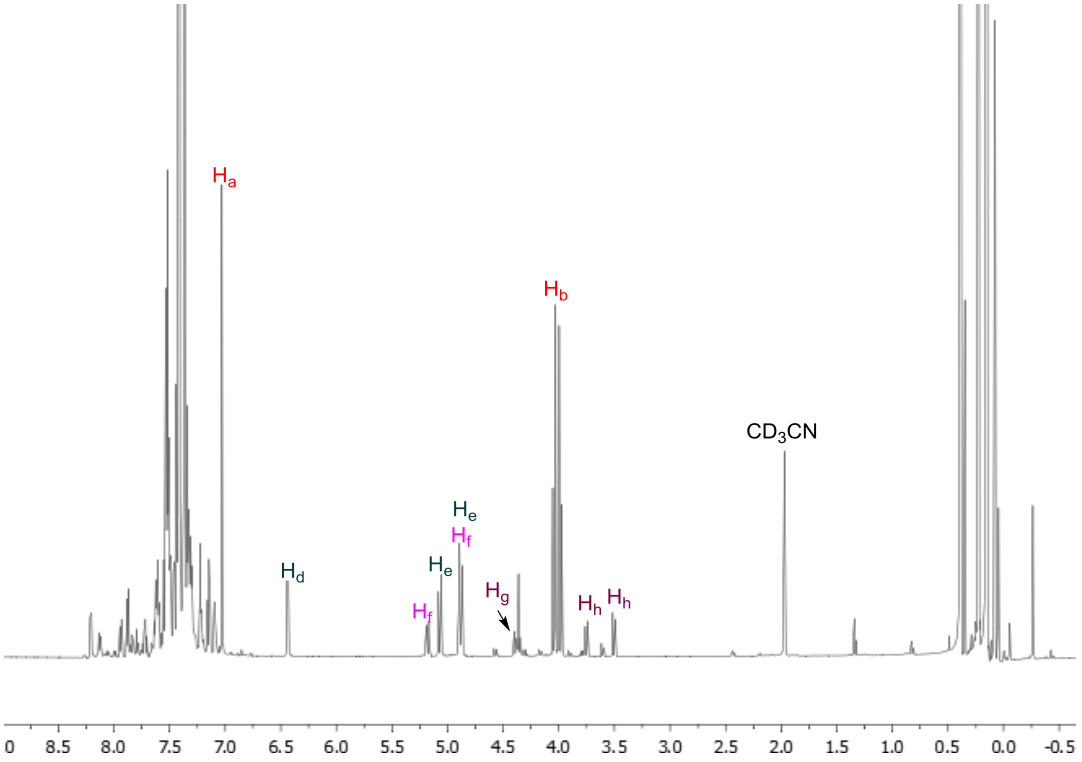


The structure of intermediate **IM3-2a** was proposed on the basis of reported literature (*Tetrahedron Lett*. **1984**, *25*, 4681) and NMR analysis. A similar oxygen-attacked imtermediate was studied in our recent work on the [3,3]-rearrangement reaction of aryliodane with difluoroenol silyl ether (*Angew. Chem. Int. Ed*. **2019**, *58*, 5956).

The structure of intermediate **IM7-2a** was proposed on the basis of DFT calculation and NMR analysis.

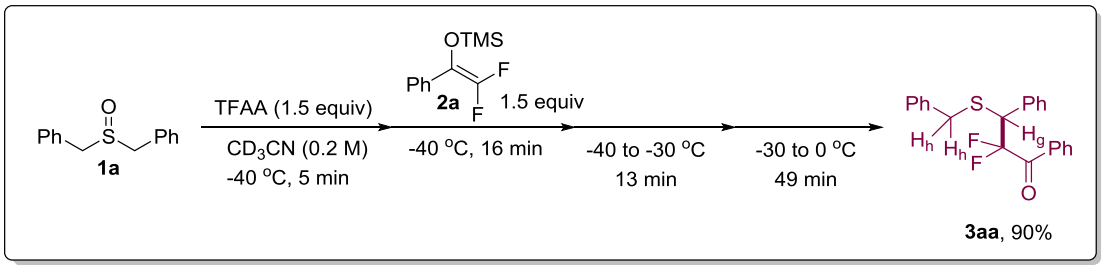
NMR spectrum D

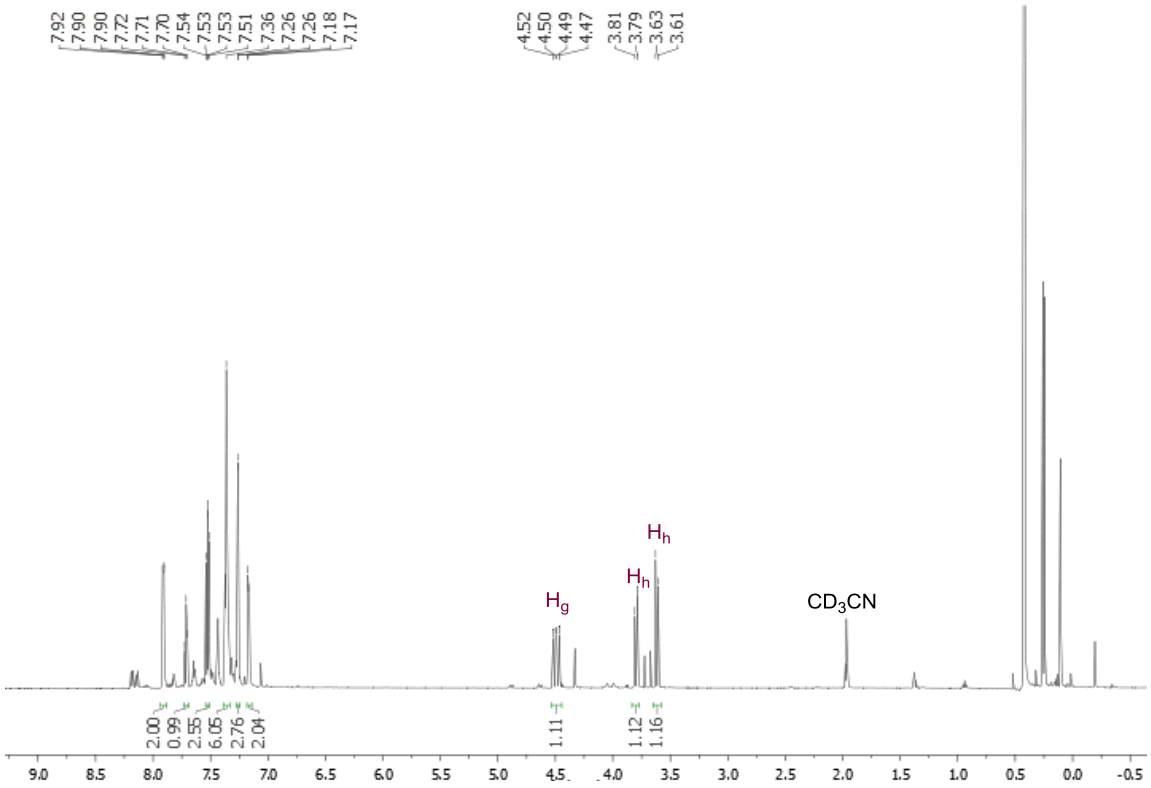




Note: According to NMR intergrations, it was found that intermediate **IM4** would completely convert to the desired product **3aa**, while **IM4-2a** and **IM7-2a** were not stable and decomposed to unknown byproducts with the increasing temperature.

NMR spectrum E





6 Density functional theory (DFT) calculations

Computational Details

All structures were optimized at M062X[1] /6-31G(d,p) with solvent effects accounted by the SMD[2] solvent model, using the experimental solvent (acetonitrile). Harmonic frequency analysis calculations were subsequently performed to verify the optimized geometries to be minima (no imaginary frequency) or transition states (TSs, having unique one imaginary frequency). The energies were then improved by M062X/6-311++G(d,p)//M062X/6-31(d,p) single-point calculations with solvent effects accounted by the SMD solvent model, using the experimental solvent (acetonitrile). The refined energies were then corrected to enthalpies and free energies at experimental temperature (233.15K) and 1 atm, using the M062X/6-31G(d,p) harmonic frequencies. In addition, considering the overestimation of entropic contributions by the ideal gas phase model implemented in Gaussian program, a correction of $RTln(V^T)$[=R*233.15*ln(22.4*233.15/273.15)=1.37 kcal mol^{-1}] to the calculated free energies of all species was applied to adjust 1atm to 1M standard-state concentration.[3] Atomic partial charge were calculated at the M062X(SMD)/6-311++G(d,p)//M062X(SMD) /6-31G(d,p) level according to the natural bond orbital (NBO) method.[4] Total energies and Cartesian coordinates of all optimized structures are given below in this Supporting Information. All standard DFT calculations were carried out using Gaussian 09 program.[5]

References

[1] (a) Y. Zhao and D. G. Truhlar, Theor. Chem. Acc., 2008, 120,215–241; (b) Y. Zhao and D. G. Truhlar, Acc. Chem. Res.,2008, 41, 157–167; (c) R. Valero, R. Costa,I. D. P. R. Moreira, D. G. Truhlar and F. Illas, J. Chem.Phys., 2008, 128, 114103.

[2] A. V. Marenich, C. J. Cramer, D. G. Truhlar, J. Phys. Chem. B 2009, 113, 6378−6396.

[3] C. J. Cramer, *Essentials of Computational Chemistry: Theories and Models*, 2nd ed.; John Wiley & Sons, Ltd: New York, **2004**, pp 378−379; c) L. Vigara, M. Z. Ertem, N. Planas, F. Bozoglian, N. Leidel, H. Dau, M. Haumann, L. Gagliardi, C. J. Cramer, A. Llobet, *Chem. Sci.* **2012**, *3*, 2576-2586.

[4] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem.Rev.* **1988,** *88*, 899-926. c) A. E. Reed, R. B. Weinstock, F. Weinhold, J. Chem. Phys. **1985,** *83*, 735-746. d) J. P. Foster, F. Weinhold *J. Am. Chem. Soc.* **1980,** *102*, 7211-7218

[5] Gaussian 09, Revision A.01, 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, T. Keith, 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, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

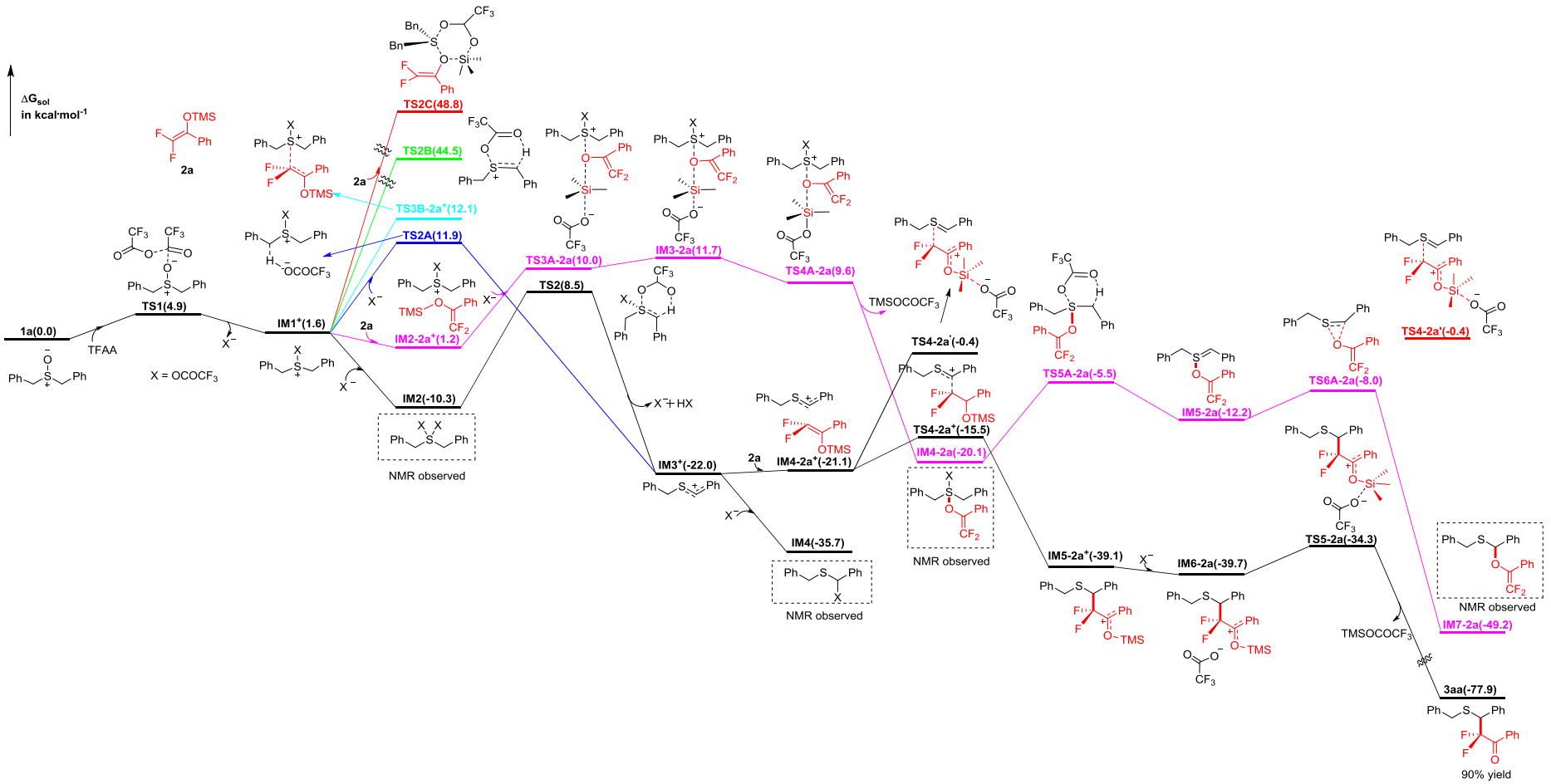


Fig. S1. Free energy profile for the reaction of **1a** with **2a**, along with relative free energies in kcal mol^{-1}. The pathway in pink color lead to the byproduct **IM7-2a** which was observed at NMR (See Section 5). **IM7-2a** was not stable and decomposed with the increasing temperature.

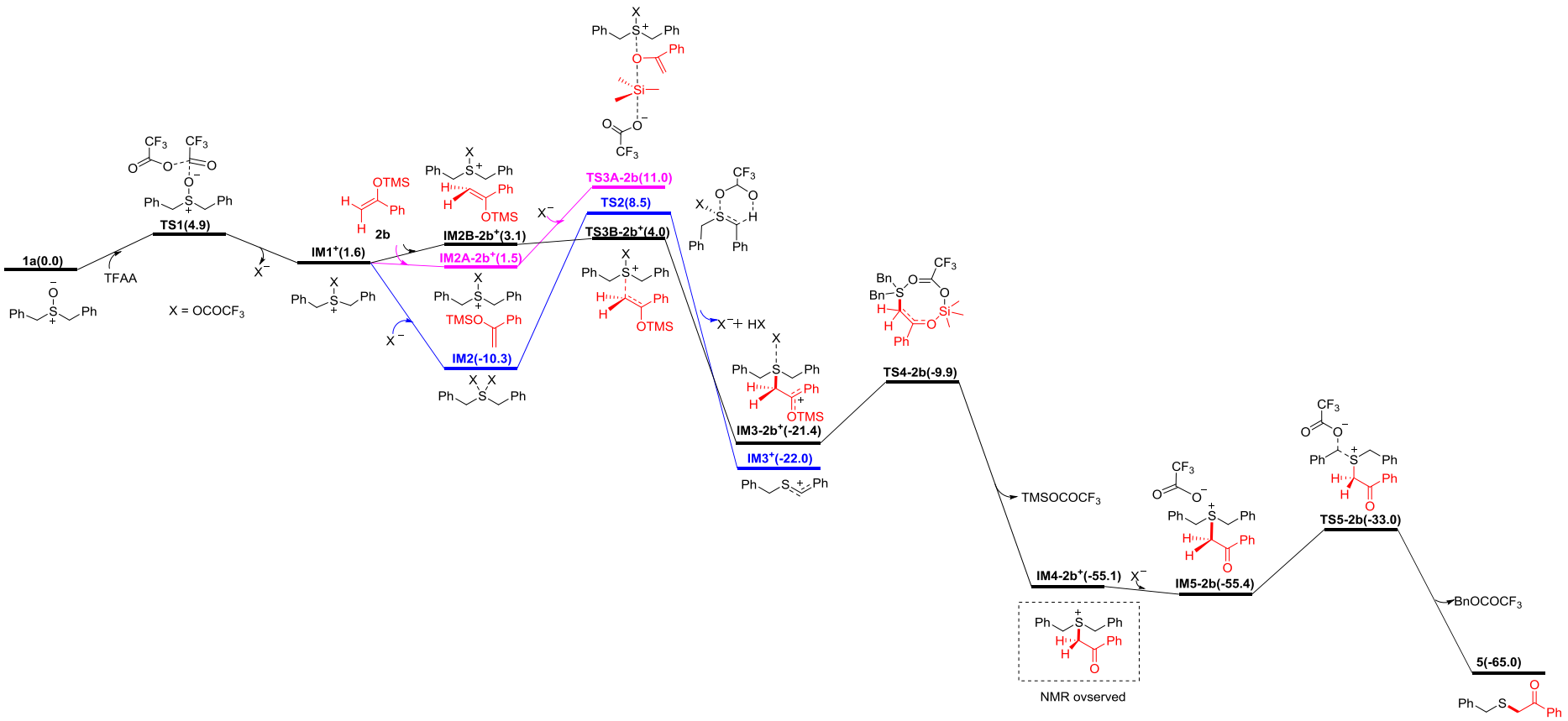


Fig. S2. Free energy profile for the reaction of **1a** with **2b**, along with relative free energies in kcal mol^{-1}.

Cartesian Coordinates (in Å), SCF Energies, and Free Energies (in a.u.) at 233.15 K and 1 atm for the Optimized Structures

BSI=6-31G(d,p)

BSII=6-311++G(d,p)

1a

M062X/BSI SCF energy: -1015.013729 a.u.

M062X/BSII SCF energy in solution: -1015.207973 a.u.

M062X/BSII free energy in solution: -1014.995267 a.u.

S	0.000008	0.164149	-0.016992
O	-0.000178	-1.311577	-0.350674
C	-1.361877	0.429748	1.178976
C	1.361874	0.429310	1.179045
C	-2.678672	0.220116	0.492734
C	-3.211321	-1.067035	0.371455
C	-4.412311	-1.270957	-0.303514
C	-5.088753	-0.191238	-0.869361
C	-4.558844	1.093563	-0.759720
C	-3.357767	1.297131	-0.084972
C	2.678690	0.219846	0.492780
C	3.211171	-1.067307	0.370849
C	4.412175	-1.271041	-0.304170
C	5.088795	-0.191127	-0.869403
C	4.559052	1.093702	-0.759097
C	3.357976	1.297072	-0.084322
H	-1.203480	-0.287488	1.990264
H	-1.253811	1.449669	1.560469
H	-2.679865	-1.906145	0.811148
H	-4.820967	-2.273281	-0.387877
H	-6.026850	-0.350346	-1.392147
H	-5.080975	1.937836	-1.199472
H	-2.942758	2.298175	0.002312
H	1.253883	1.449095	1.560917
H	1.203407	-0.288199	1.990081
H	2.679571	-1.906590	0.810048
H	4.820688	-2.273381	-0.389024
H	6.026887	-0.350075	-1.392243
H	5.081359	1.938139	-1.198330
H	2.943074	2.298125	0.003436

TFAA

M062X/BSI SCF energy: -976.804709 a.u.

M062X/BSII SCF energy in solution: -977.136137 a.u.

M062X/BSII free energy in solution: -977.11092 a.u.

O	-1.380519	1.897752	0.000158
O	1.380510	1.897753	-0.000205
O	-0.000003	0.065182	0.000293
C	2.306371	-0.340106	-0.000025
C	-2.306369	-0.340112	-0.000020
F	3.492175	0.246081	-0.000364
F	2.194559	-1.110123	-1.080244
F	2.194975	-1.109599	1.080637
F	-2.194771	-1.109629	-1.080637
F	-3.492175	0.246075	0.000087
F	-2.194748	-1.110095	1.080248
C	1.197271	0.726786	-0.000037
C	-1.197277	0.726785	0.000165

2a

M062X/BSI SCF energy: -991.733775 a.u.

M062X/BSII SCF energy in solution: -991.965444 a.u.

M062X/BSII free energy in solution: -991.770098 a.u.

C	0.254682	2.028379	-0.313498
C	-0.020679	0.731639	-0.458353
F	1.451838	2.549191	-0.524134
F	-0.611241	2.967766	0.029744
C	-1.351334	0.126123	-0.241784
C	-1.638989	-1.083507	-0.886815
C	-2.316479	0.695587	0.600347
C	-2.872144	-1.702901	-0.707255
H	-0.889238	-1.532215	-1.530412
C	-3.547924	0.071609	0.774657
H	-2.102214	1.615469	1.132532
C	-3.832546	-1.126758	0.121768
H	-3.082131	-2.637803	-1.217736
H	-4.284553	0.520096	1.434112
H	-4.793871	-1.610421	0.263747
O	0.982798	-0.079922	-0.914601

Si	1.995164	-0.878984	0.199586
C	2.983026	0.397708	1.141978
H	3.659222	-0.104735	1.842957
H	3.589665	1.015752	0.473708
H	2.334663	1.057070	1.728353
C	0.948468	-1.883898	1.379854
H	0.392340	-2.671980	0.862763
H	1.593765	-2.360354	2.126630
H	0.229881	-1.255793	1.917208
C	3.075211	-1.953814	-0.873260
H	3.730945	-2.579132	-0.258652
H	2.467550	-2.616272	-1.497890
H	3.706165	-1.348144	-1.531044

2b

M062X/BSI SCF energy: -793.332279 a.u.

M062X/BSII SCF energy in solution: -793.491136 a.u.

M062X/BSII free energy in solution: -793.280443 a.u.

C	0.185281	2.422065	-0.640749
C	-0.016467	1.100308	-0.634064
C	-1.311919	0.440346	-0.318641
C	-1.534674	-0.876200	-0.738461
C	-2.319295	1.101979	0.396581
C	-2.743518	-1.512131	-0.465946
H	-0.755587	-1.395904	-1.286299
C	-3.525958	0.465076	0.666961
H	-2.152225	2.110880	0.761475
C	-3.744066	-0.843251	0.235133
H	-2.902605	-2.532006	-0.802780
H	-4.295844	0.988424	1.225595
H	-4.685368	-1.339338	0.450426
O	0.985914	0.234052	-0.983052
Si	2.089730	-0.333583	0.174381
C	3.340768	1.010733	0.527529
H	4.111502	0.643478	1.214175
H	3.836391	1.341428	-0.390874
H	2.869655	1.882487	0.993559
C	1.160647	-0.789997	1.733983
H	0.450777	-1.604446	1.558346
H	1.865018	-1.116435	2.507045
H	0.604708	0.066005	2.132009
C	2.880271	-1.818229	-0.631916
H	3.641081	-2.256981	0.022064
H	2.133971	-2.590338	-0.845302
H	3.364839	-1.543595	-1.574307
H	-0.617569	3.117996	-0.430441
H	1.161286	2.821889	-0.894069

CF_3COO^-

M062X/BSI SCF energy: -526.144045 a.u.

M062X/BSII SCF energy in solution: -526.350597 a.u.

M062X/BSII free energy in solution: -526.345334 a.u.

O	1.506973	-1.142410	0.000028
O	1.577617	1.129182	0.000052
C	-0.516206	0.015985	0.000050
F	-1.063335	1.243256	0.001186
F	-1.014569	-0.625623	1.078945
F	-1.014306	-0.623448	-1.080304
C	1.041736	0.010375	0.000105

CF_3COOH

M062X/BSI SCF energy: -526.609593 a.u.

M062X/BSII SCF energy in solution: -526.792937 a.u.

M062X/BSII free energy in solution: -526.775676 a.u.

O	-1.438830	-1.242628	0.001247
O	-1.661202	0.971753	-0.001471
C	0.578887	0.007271	0.000237
F	0.947220	1.293566	0.050998
F	1.086065	-0.534013	-1.104088
F	1.095285	-0.621918	1.051548
C	-0.955809	-0.146631	0.001366
H	-1.095343	1.764439	0.006067

$CF_3COOTMS$

M062X/BSI SCF energy: -935.231625 a.u.

M062X/BSII SCF energy in solution: -935.471168 a.u.

M062X/BSII free energy in solution: -935.369569 a.u.

Si	1.869731	-0.075884	0.000001
C	2.216200	0.874070	1.563023
H	1.906339	0.300576	2.442391
H	3.290574	1.067560	1.651541
H	1.694371	1.834483	1.574831
C	2.646785	-1.763770	-0.000005
H	2.352643	-2.333660	-0.886639
H	3.738665	-1.682469	-0.000083
H	2.352766	-2.333621	0.886694
C	2.216026	0.873980	-1.563113
H	3.290401	1.067375	-1.651823
H	1.905974	0.300473	-2.442405
H	1.694278	1.834438	-1.574885
O	0.162644	-0.470930	0.000099
O	-0.605735	1.655385	-0.000018
C	-2.161767	-0.173092	0.000013
F	-3.106133	0.760870	0.000011
F	-2.324506	-0.941751	1.080488
F	-2.324451	-0.941704	-1.080509
C	-0.760864	0.461287	0.000049

CF_3COOBn

M062X/BSI SCF energy: -796.862563 a.u.

M062X/BSII SCF energy in solution: -797.108448 a.u.

M062X/BSII free energy in solution: -796.98696 a.u.

O	-0.950444	1.591046	0.014717
C	0.472513	0.006557	1.703261
C	1.638284	-0.026447	0.753002
C	2.203419	1.157832	0.277790
C	3.281995	1.116207	-0.603434
C	3.792454	-0.110784	-1.022062
C	3.226545	-1.297491	-0.555469
C	2.154530	-1.254857	0.331026
H	0.317413	1.004804	2.117655
H	1.794247	2.110987	0.600495
H	3.719889	2.041115	-0.965791
H	4.632625	-0.143625	-1.708945
H	3.624606	-2.254277	-0.878818
H	1.716148	-2.177061	0.704396
O	-0.752533	-0.416884	1.042908
C	-2.580155	-0.137450	-0.381328
F	-2.275643	-1.224950	-1.094091
F	-3.170404	0.743753	-1.179650
F	-3.445272	-0.497164	0.570307
C	-1.314689	0.470484	0.245337
H	0.591387	-0.714290	2.512187

3aa

M062X/BSI SCF energy: -1521.825383 a.u.

M062X/BSII SCF energy in solution: -1522.163253 a.u.

M062X/BSII free energy in solution: -1521.855209 a.u.

S	-0.167539	-0.898488	-1.213801
C	0.198534	0.135746	0.253812
C	0.847211	-2.371865	-0.807535
C	1.356652	1.093942	0.083066
C	2.283972	1.237199	1.117023
C	3.361036	2.111199	0.981181
C	3.507528	2.862372	-0.182845
C	2.571681	2.737840	-1.209658
C	1.502192	1.857462	-1.078289
C	2.266399	-2.038760	-0.431216
C	3.132561	-1.426588	-1.344552
C	4.425781	-1.082558	-0.966454
C	4.873379	-1.350942	0.329250
C	4.021376	-1.968020	1.240024
C	2.721201	-2.306091	0.860651
H	0.395952	-0.541430	1.091491
H	2.169250	0.648376	2.023696
H	4.086461	2.202133	1.784010
H	4.347455	3.541628	-0.291221
H	2.678432	3.322730	-2.118123
H	0.786037	1.747735	-1.887254
H	0.354276	-2.922200	-0.002796
H	0.802960	-2.979522	-1.716072
H	2.780587	-1.203599	-2.349123
H	5.087550	-0.602174	-1.680936
H	5.882417	-1.078422	0.623026
H	4.361232	-2.181325	2.248998
H	2.051133	-2.778297	1.574932
C	-1.079506	0.875407	0.626227
C	-2.225300	-0.080771	1.037686

F	-0.831546	1.660151	1.711294
F	-1.448282	1.721478	-0.374212
C	-3.538144	-0.112034	0.338269
C	-4.627647	-0.576024	1.088213
C	-3.721450	0.245167	-1.003841
C	-5.888719	-0.661114	0.513170
H	-4.469853	-0.857710	2.124380
C	-4.984307	0.140164	-1.579318
H	-2.889219	0.583988	-1.607877
C	-6.067273	-0.303276	-0.823224
H	-6.731380	-1.006876	1.103032
H	-5.121468	0.406829	-2.622150
H	-7.051344	-0.374204	-1.276245
O	-1.993044	-0.762157	2.014434

3bb

M062X/BSI SCF energy: -1053.154765 a.u.

M062X/BSII SCF energy in solution: -1053.354131 a.u.

M062X/BSII free energy in solution: -1053.133708 a.u.

S	-0.310038	-1.622639	0.114259
C	-1.368204	-0.645446	1.250164
C	-2.646195	-0.169658	0.616582
C	-2.749664	1.135052	0.125685
C	-3.931545	1.572825	-0.472337
C	-5.019761	0.711163	-0.583257
C	-4.922719	-0.593141	-0.096065
C	-3.742690	-1.030086	0.497201
H	-1.569493	-1.328584	2.079903
H	-0.782612	0.193129	1.636873
H	-1.893706	1.800440	0.209610
H	-4.000834	2.588639	-0.849670
H	-5.941164	1.052747	-1.044949
H	-5.769193	-1.268473	-0.175837
H	-3.666282	-2.046517	0.876262
C	0.166310	-0.314671	-1.066401
C	1.084055	0.670182	-0.377045
C	2.536809	0.348336	-0.213850
C	3.338848	1.278599	0.457523
C	3.112834	-0.827260	-0.708108
C	4.696585	1.040542	0.631164
H	2.880562	2.186161	0.836726
C	4.473295	-1.064862	-0.531828
H	2.513730	-1.568836	-1.226653
C	5.265623	-0.133072	0.135696
H	5.312365	1.767028	1.151891
H	4.913402	-1.979210	-0.916401
H	6.326286	-0.321396	0.271119
O	0.621276	1.701612	0.082381
H	-0.727211	0.213241	-1.407845
H	0.633068	-0.810048	-1.918969

TS1

M062X/BSI SCF energy: -1991.829875 a.u.

M062X/BSII SCF energy in solution: -1992.356068 a.u.

M062X/BSII free energy in solution: -1992.096141 a.u.

S	-0.391444	-1.777271	-0.408518
O	0.201486	-0.292952	-0.088203
C	-1.833810	-1.412182	-1.461087
C	0.872924	-2.188554	-1.657406
C	-3.084876	-1.298287	-0.638849
C	-3.489894	-0.048805	-0.163838
C	-4.647559	0.057827	0.602610
C	-5.394387	-1.079886	0.904560
C	-4.984489	-2.328963	0.439357
C	-3.830432	-2.439282	-0.330820
C	2.223317	-2.193398	-1.001392
C	2.962272	-1.009371	-0.914430
C	4.196058	-1.007525	-0.270588
C	4.696276	-2.184204	0.285270
C	3.960962	-3.365570	0.199388
C	2.724212	-3.370193	-0.438871
H	-1.570905	-0.484134	-1.979895
H	-1.867230	-2.251743	-2.165190
H	-2.892664	0.827342	-0.400612
H	-4.966711	1.029726	0.965625
H	-6.297014	-0.994616	1.501816
H	-5.564935	-3.215605	0.673692
H	-3.508289	-3.409347	-0.701324
H	0.575145	-3.171238	-2.035579
H	0.773102	-1.438409	-2.446957
H	2.564339	-0.092869	-1.340834
H	4.765333	-0.085921	-0.202037

H	5.659275	-2.180391	0.786328
H	4.349887	-4.283011	0.629260
H	2.144600	-4.287347	-0.504678
O	-1.023838	1.731658	-1.662308
O	-0.935280	-0.296453	1.903415
O	-0.755383	1.906551	0.577604
C	1.163485	0.872214	1.735741
C	0.382557	3.433980	-0.860686
F	0.899730	1.698403	2.739045
F	1.863070	1.523191	0.804639
F	1.938465	-0.119821	2.199408
F	0.750134	4.027859	0.276308
F	-0.188860	4.361665	-1.640915
F	1.500420	3.024127	-1.485224
C	-0.125825	0.237328	1.193961
C	-0.568017	2.232312	-0.644044
H	-4.456372	-1.808836	2.181023
H	-2.483629	-2.920441	1.173246
H	1.898398	-2.769386	-1.104375
H	1.503948	-1.321500	-2.085555
H	2.594093	0.859401	-1.571327
H	4.470975	2.065471	-0.488343
H	5.841950	0.932258	1.240399
H	5.340180	-1.410097	1.886237
H	3.466244	-2.620685	0.798114
O	-0.916825	0.580492	1.588693
C	-0.630164	2.371578	-0.038442
F	-1.310884	2.372831	-1.180776
F	0.596171	2.832476	-0.272905
F	-1.237203	3.150365	0.838736
C	-0.540372	0.940172	0.523170
H	-1.013327	-3.215091	-0.850804

IM1^{+}

M062X/BSI SCF energy: -1465.658573 a.u.

M062X/BSII SCF energy in solution: -1465.994703 a.u.

M062X/BSII free energy in solution: -1465.758262 a.u.

S	0.294536	-1.439791	-0.045963
O	0.074695	0.165473	-0.423646
C	-1.091139	-2.135026	-1.017031
C	1.768006	-1.681284	-1.087238
C	-2.349863	-1.530130	-0.467983
C	-2.891704	-0.390647	-1.070246
C	-3.995334	0.236985	-0.496100
C	-4.556063	-0.271653	0.673999
C	-4.018643	-1.411732	1.271024
C	-2.914131	-2.038893	0.704920
C	2.920252	-0.955994	-0.453940
C	3.196351	0.366223	-0.813204
C	4.251232	1.041373	-0.204475
C	5.021253	0.403377	0.766217
C	4.740852	-0.913175	1.130337
C	3.690493	-1.593323	0.522507
H	-0.896959	-1.892578	-2.064913
H	-2.451674	-0.000238	-1.984080
H	-4.414893	1.122095	-0.963346
H	-5.413382	0.220412	1.122191

IM2

M062X/BSI SCF energy: -1991.855107 a.u.

M062X/BSII SCF energy in solution: -1992.380235 a.u.

M062X/BSII free energy in solution: -1992.120442 a.u.

S	-0.299040	0.059096	-0.366653
O	1.350189	-0.806978	-0.444032
C	0.384529	1.415570	-1.429596
C	-0.880057	-1.211964	-1.559430
C	1.616530	2.017316	-0.822375
C	2.880836	1.613369	-1.258960
C	4.026762	2.138563	-0.667320
C	3.913942	3.079311	0.355159
C	2.653761	3.491570	0.786664
C	1.507240	2.959581	0.203675
C	-1.446458	-2.368085	-0.785646
C	-0.617866	-3.425242	-0.398416
C	-1.140339	-4.487402	0.334772
C	-2.488633	-4.495559	0.688583
C	-3.314441	-3.436492	0.313666
C	-2.795529	-2.372703	-0.418676
H	0.584067	0.949831	-2.398133
H	-0.432073	2.130472	-1.524322
H	2.963329	0.872989	-2.049575
H	5.005422	1.813299	-1.006117

H	4.807258	3.491087	0.814558
H	2.563318	4.225663	1.581119
H	0.522067	3.262536	0.546776
H	-1.619885	-0.716117	-2.186388
H	-0.004144	-1.486534	-2.146518
H	0.434538	-3.410418	-0.669062
H	-0.495551	-5.309737	0.628245
H	-2.895627	-5.325691	1.257714
H	-4.363635	-3.439043	0.591986
H	-3.429134	-1.536317	-0.700197
O	-2.098767	0.779234	-0.549359
O	1.910520	-0.079999	1.631943
O	-1.639629	2.310083	1.044005
C	3.387796	-1.539786	0.423817
C	-3.902691	1.999422	0.305077
F	4.042562	-1.177822	-0.683641
F	3.068539	-2.834273	0.303306
F	4.205517	-1.402686	1.461285
F	-4.231201	2.848276	1.274198
F	-4.607714	0.875131	0.472280
F	-4.263888	2.537020	-0.865595
C	2.111927	-0.696546	0.618355
C	-2.390333	1.702895	0.312218

IM2-2a^{+}

M062X/BSI SCF energy: -2457.411496 a.u.

M062X/BSII SCF energy in solution: -2457.977273 a.u.

M062X/BSII free energy in solution: -2457.526906 a.u.

S	0.405995	0.084305	-0.697615
O	2.009745	0.568286	-0.710439
C	-0.070851	1.291694	-1.984074
C	0.614360	-1.511020	-1.598947
C	-0.093697	2.651459	-1.350667
C	1.027309	3.483106	-1.420350
C	1.004428	4.726610	-0.794099
C	-0.127389	5.134886	-0.090146
C	-1.242242	4.300769	-0.011193
C	-1.225032	3.059782	-0.638636
C	1.707419	-2.286645	-0.925518
C	3.024864	-2.144210	-1.372277
C	4.063757	-2.777712	-0.694083
C	3.789474	-3.558074	0.427335
C	2.475426	-3.710284	0.868014
C	1.436206	-3.072745	0.197934
H	0.667988	1.183531	-2.782614
H	1.909395	3.160723	-1.966688
H	1.872368	5.375294	-0.852980
H	-0.140463	6.103999	0.398670
H	-2.123540	4.615650	0.538595
H	-2.086100	2.399418	-0.580854
H	-0.368308	-1.984720	-1.523376
H	0.839481	-1.252572	-2.637070
H	3.234835	-1.531884	-2.244961
H	5.084624	-2.659305	-1.042542
H	4.599156	-4.050344	0.956434
H	2.258216	-4.321518	1.737866
H	0.415638	-3.191527	0.548551
O	2.313569	-0.154605	1.428287
C	4.129547	0.931764	0.226999
F	4.859640	0.713243	1.306543
F	4.039966	2.242454	0.007972
F	4.714682	0.366601	-0.825789
C	2.716899	0.355364	0.434163
H	-1.049910	0.954952	-2.333178
C	-2.039766	-2.403739	0.745501
C	-2.111933	-1.074910	0.693257
C	-2.055861	-0.191777	1.873588
C	-2.775315	1.008025	1.848800
C	-1.278504	-0.508020	2.994611
C	-2.732809	1.872306	2.938784
H	-3.372234	1.258593	0.976218
C	-1.241244	0.359157	4.081763
H	-0.690022	-1.419886	3.006683
C	-1.967488	1.549171	4.058061
H	-3.299401	2.797831	2.914146
H	-0.632906	0.109489	4.945246
H	-1.931980	2.224972	4.906593
O	-2.210874	-0.474564	-0.536574
F	-1.930001	-3.132391	1.838274
F	-2.077248	-3.172984	-0.336506
Si	-3.549296	-0.677394	-1.613897
C	-4.122486	1.048491	-2.026416
H	-3.326080	1.643833	-2.485504
H	-4.949299	0.998522	-2.743893
H	-4.480729	1.579695	-1.138453

C	-2.861178	-1.529819	-3.122268
H	-2.529975	-2.547777	-2.895966
H	-3.623848	-1.588542	-3.906262
H	-2.010464	-0.972401	-3.531000
C	-4.869479	-1.650623	-0.728881
H	-5.780758	-1.645976	-1.337171
H	-4.587149	-2.693320	-0.559211
H	-5.113669	-1.195362	0.236956

IM2B-2b^{+}

M062X/BSI SCF energy: -2259.006261 a.u.

M062X/BSII SCF energy in solution: -2259.500954 a.u.

M062X/BSII free energy in solution: -2259.034169 a.u.

S	0.589581	-0.254844	-0.837259
O	1.706179	-1.365194	-0.219416
C	1.522282	0.126863	-2.378637
C	-0.573359	-1.515720	-1.407688
C	2.849891	0.673625	-1.949456
C	3.952538	-0.181267	-1.865735
C	5.152930	0.283838	-1.332128
C	5.251585	1.600136	-0.885041
C	4.154911	2.457138	-0.979286
C	2.954222	1.995510	-1.509346
C	-1.502976	-2.011446	-0.325774
C	-1.261233	-1.857838	1.038539
C	-2.177494	-2.346119	1.969933
C	-3.327292	-3.003195	1.544385
C	-3.562276	-3.173752	0.179503
C	-2.657586	-2.676150	-0.751370
H	1.592949	-0.809012	-2.938251
H	3.863847	-1.208009	-2.209958
H	6.005972	-0.383563	-1.263702
H	6.184794	1.960517	-0.464021
H	4.232468	3.482913	-0.633384
H	2.090945	2.653872	-1.571155
H	-1.124306	-1.023593	-2.218151
H	0.045575	-2.309587	-1.840311
H	-0.371146	-1.353975	1.407282
H	-1.983968	-2.210260	3.029198
H	-4.038773	-3.382343	2.271031
H	-4.458848	-3.682317	-0.161254
H	-2.849012	-2.791032	-1.814931
O	2.519594	0.202424	1.221291
C	3.508778	-2.011257	1.153937
F	2.835136	-2.936173	1.834412
F	4.463279	-1.510679	1.920010
F	4.054578	-2.584187	0.085301
C	2.541374	-0.885521	0.740587
H	0.891576	0.847950	-2.905495
C	-1.197163	1.978438	-1.542642
C	-1.959507	1.416657	-0.581245
C	-3.262680	0.747125	-0.834185
C	-4.123075	0.491553	0.239865
C	-3.650357	0.357860	-2.123989
C	-5.351611	-0.128723	0.026563
H	-3.823713	0.777489	1.242653
C	-4.876362	-0.263776	-2.332838
H	-2.988847	0.523836	-2.968938
C	-5.732227	-0.508355	-1.258673
H	-6.009246	-0.321700	0.868657
H	-5.161429	-0.564527	-3.336182
H	-6.687629	-0.996925	-1.423038
O	-1.577082	1.386399	0.715813
Si	-1.010649	2.704250	1.642857
C	0.707182	3.232172	1.120724
H	1.147742	3.838646	1.921057
H	1.362592	2.368213	0.967301
H	0.705776	3.840777	0.211471
C	-2.247267	4.087403	1.426458
H	-3.249320	3.772570	1.734736
H	-1.964414	4.958292	2.026822
H	-2.296851	4.406348	0.379907
C	-0.977289	1.992916	3.363733
H	-0.660151	2.746830	4.091521
H	-1.964064	1.625614	3.662651
H	-0.271835	1.156811	3.420224
H	-1.530748	2.019298	-2.572082
H	-0.276240	2.496497	-1.293687

IM2A-2b^{+}

M062X/BSI SCF energy: -22559.00936 a.u.

M062X/BSII SCF energy in solution: -2259.504223 a.u.

M062X/BSII free energy in solution: -2259.036666 a.u.

S	0.293219	-0.102678	-0.582358
O	1.810609	0.602546	-0.694448
C	-0.352327	0.848467	-2.001547
C	0.713534	-1.747918	-1.306498
C	-0.620673	2.251411	-1.545078
C	0.370651	3.229537	-1.661947
C	0.125695	4.520936	-1.203198
C	-1.100784	4.833988	-0.619668
C	-2.087852	3.856371	-0.495971
C	-1.848992	2.565653	-0.957106
C	1.954518	-2.262718	-0.640063
C	3.203747	-1.977109	-1.199463
C	4.367528	-2.367858	-0.541140
C	4.285802	-3.048370	0.672207
C	3.040520	-3.341466	1.227098
C	1.876224	-2.944836	0.577128
H	0.413237	0.770042	-2.778728
H	1.326376	2.980193	-2.114804
H	0.893279	5.281833	-1.300998
H	-1.288034	5.841331	-0.261091
H	-3.043187	4.098736	-0.041094
H	-2.611638	1.796528	-0.866771
H	-0.174931	-2.349875	-1.097518
H	0.832659	-1.586470	-2.381271
H	3.261297	-1.440832	-2.142946
H	5.335005	-2.138984	-0.976465
H	5.192644	-3.350275	1.186664
H	2.976008	-3.872784	2.171135
H	0.903546	-3.152054	1.015855
O	2.269964	0.125144	1.484576
C	3.878070	1.346650	0.129625
F	4.673479	1.295570	1.183989
F	3.594898	2.617260	-0.153380
F	4.495547	0.809541	-0.918808
C	2.569659	0.594434	0.435067
H	-1.251003	0.309886	-2.309867
C	-1.702236	-2.771226	1.196378
C	-1.998946	-1.491943	0.948748
C	-2.116217	-0.433877	1.979988
C	-3.027988	0.611032	1.794037
C	-1.328384	-0.459069	3.137142
C	-3.168484	1.602986	2.760674
H	-3.634307	0.637324	0.893064
C	-1.468642	0.535684	4.100207
H	-0.591165	-1.246407	3.268046
C	-2.389888	1.566652	3.916104
H	-3.886328	2.403523	2.610922
H	-0.849161	0.513341	4.991260
H	-2.495010	2.342564	4.667888
O	-2.207465	-1.029894	-0.333063
Si	-3.422294	-1.654683	-1.380922
C	-4.200795	-0.159880	-2.184123
H	-3.491260	0.427559	-2.775634
H	-4.996801	-0.488166	-2.862262
H	-4.653921	0.500586	-1.437072
C	-2.562372	-2.733343	-2.637802
H	-2.058998	-3.582872	-2.163979
H	-3.287706	-3.133044	-3.355003
H	-1.816056	-2.165784	-3.204578
C	-4.677604	-2.582291	-0.360784
H	-5.554523	-2.791628	-0.983538
H	-4.297019	-3.533795	0.019088
H	-5.010628	-1.982296	0.493307
H	-1.567148	-3.119715	2.213575
H	-1.617387	-3.495147	0.390639

TS2

M062X/BSI SCF energy: -1991.817189 a.u.

M062X/BSII SCF energy in solution: -1992.343726 a.u.

M062X/BSII free energy in solution: -1992.090487 a.u.

S	-0.093327	0.186646	-0.179701
O	-1.824670	0.333498	-0.387867
C	0.354917	-1.166973	-1.123788
C	0.224226	1.600239	-1.284308
C	-0.175487	-2.437800	-0.529287
C	-1.311678	-3.040329	-1.082227
C	-1.843106	-4.196813	-0.517028
C	-1.253590	-4.754988	0.615772
C	-0.125129	-4.157224	1.175255
C	0.415339	-3.008235	0.603450
C	-0.128890	2.884061	-0.591359
C	-1.410902	3.426022	-0.716052
C	-1.730412	4.612988	-0.061528
C	-0.775115	5.257463	0.722398

C	0.502389	4.713885	0.854109
C	0.825354	3.528182	0.201135
H	0.073968	-1.007788	-2.168304
H	1.788096	-1.156644	-1.030077
H	-1.781176	-2.592333	-1.954325
H	-2.723123	-4.656183	-0.956747
H	-1.671219	-5.652754	1.060645
H	0.339274	-4.590133	2.055923
H	1.301305	-2.549552	1.037049
H	1.289570	1.522052	-1.509551
H	-0.367470	1.411601	-2.183728
H	-2.154237	2.917413	-1.323956
H	-2.725067	5.034885	-0.165002
H	-1.025437	6.182988	1.231512
H	1.247761	5.214222	1.464133
H	1.816424	3.093512	0.301518
O	2.651856	0.659705	0.312335
O	-2.179108	-0.751544	1.577748
O	2.971894	-1.213090	-0.901785
C	-4.045518	-0.161988	0.159894
C	4.842589	-0.292504	0.176771
F	-4.245536	-0.894883	-0.936495
F	-4.394483	1.096201	-0.107197
F	-4.812486	-0.627243	1.134969
F	5.562558	-0.172947	-0.945798
F	5.169515	-1.458434	0.745580
F	5.198156	0.688372	1.003359
C	-2.563716	-0.238029	0.569354
C	3.336270	-0.245584	-0.145409

TS3A-2a

M062X/BSI SCF energy: -2983.571163 a.u.

M062X/BSII SCF energy in solution: -2984.331717 a.u.

M062X/BSII free energy in solution: -2983.855954 a.u.

S	1.362893	0.210151	-0.660624
O	2.725620	1.122407	-1.048507
C	0.225066	1.298456	-1.584780
C	1.636628	-1.178075	-1.852128
C	-0.308456	2.393800	-0.707475
C	0.546460	3.351731	-0.150235
C	0.033920	4.333974	0.691813
C	-1.332019	4.372170	0.974491
C	-2.185008	3.427950	0.407626
C	-1.676887	2.436348	-0.429781
C	3.053108	-1.653854	-1.733006
C	4.047729	-1.051294	-2.510170
C	5.382354	-1.410235	-2.337464
C	5.726049	-2.380117	-1.398005
C	4.734566	-2.996137	-0.635366
C	3.402018	-2.631195	-0.797015
H	0.813875	1.648789	-2.438583
H	-0.564257	0.632451	-1.938464
H	1.610000	3.337471	-0.374270
H	0.701850	5.072052	1.124193
H	-1.728353	5.139351	1.632251
H	-3.250161	3.451795	0.616820
H	-2.360975	1.704183	-0.854424
H	0.894137	-1.918574	-1.542116
H	1.395765	-0.778219	-2.840963
H	3.774923	-0.293448	-3.239832
H	6.150503	-0.931087	-2.935854
H	6.766202	-2.659003	-1.261996
H	4.999280	-3.758805	0.089865
H	2.632019	-3.113554	-0.203749
O	-4.964596	-1.199961	-0.667797
O	3.852781	0.256457	0.730737
O	-4.611865	1.019541	-0.990068
C	4.897324	1.941123	-0.672919
C	-6.811559	0.139781	-1.160609
F	4.464949	3.196359	-0.551979
F	5.215029	1.727337	-1.946202
F	5.968864	1.772108	0.082324
F	-7.507328	-0.192667	-0.055357
F	-7.243264	-0.670403	-2.145525
F	-7.177478	1.386111	-1.491453
C	3.789148	0.975189	-0.214395
C	-5.285702	-0.016782	-0.920412
C	0.432514	-2.864835	1.201621
C	-0.033496	-1.619849	1.345711
F	0.235471	-3.584971	0.106050
F	1.155826	-3.545644	2.071346
C	0.201112	-0.759938	2.528173
C	-0.098709	0.605637	2.426949
C	0.708689	-1.247737	3.742750
C	0.123893	1.466244	3.497897

H	-0.527881	0.992070	1.508738
C	0.926964	-0.382625	4.809883
H	0.924445	-2.301133	3.868241
C	0.642975	0.977167	4.693752
H	-0.116118	2.520141	3.392812
H	1.317831	-0.778685	5.741978
H	0.816984	1.646198	5.530536
O	-0.680764	-1.094843	0.258975
Si	-2.430461	-1.345499	-0.009850
C	-2.744091	-3.160893	0.334759
H	-3.823983	-3.331290	0.307061
H	-2.278058	-3.802441	-0.418567
H	-2.378165	-3.466018	1.320684
C	-3.132292	-0.302764	1.380358
H	-2.609025	-0.570582	2.305636
H	-3.013389	0.770233	1.218765
H	-4.193650	-0.519733	1.506145
C	-2.410529	-1.035103	-1.860288
H	-3.163361	-1.688819	-2.306749
H	-2.666156	-0.012779	-2.144977
H	-1.432779	-1.307689	-2.275252

TS2A

M062X/BSI SCF energy: -1991.815387 a.u.

M062X/BSII SCF energy in solution: -1992.34001 a.u.

M062X/BSII free energy in solution: -1992.08502 a.u.

S	-0.825214	-1.508600	-0.301126
O	0.128688	-0.279285	0.420058
C	-2.099807	-0.549867	-0.979152
C	0.267746	-1.798223	-1.752236
C	-3.405575	-0.714751	-0.277137
C	-3.504539	-0.486482	1.100847
C	-4.729953	-0.604747	1.751217
C	-5.877618	-0.926533	1.028743
C	-5.789750	-1.136578	-0.346761
C	-4.561779	-1.038901	-0.995301
C	1.662052	-2.089555	-1.290113
C	2.578924	-1.038174	-1.185202
C	3.846643	-1.274085	-0.655975
C	4.201095	-2.555933	-0.239403
C	3.290985	-3.606637	-0.356106
C	2.021261	-3.374115	-0.875338
H	-1.690161	0.744786	-0.865312
H	-2.119306	-0.730379	-2.056753
H	-2.620050	-0.199413	1.667296
H	-4.789363	-0.430085	2.821071
H	-6.834988	-1.009598	1.533409
H	-6.679171	-1.387106	-0.916856
H	-4.492991	-1.215642	-2.065239
H	-0.209877	-2.638822	-2.264692
H	0.193360	-0.880144	-2.340982
H	2.285087	-0.041143	-1.503972
H	4.554528	-0.455742	-0.566501
H	5.187442	-2.737152	0.176277
H	3.569131	-4.605626	-0.035860
H	1.302427	-4.185892	-0.954884
O	0.461006	1.374763	-1.947368
O	1.170925	-1.728426	1.839718
O	-1.317990	1.919423	-0.666753
C	1.842357	0.596938	1.750258
C	0.511558	3.375743	-0.642776
F	1.122602	1.357217	2.574220
F	2.161518	1.324183	0.679078
F	2.954304	0.222285	2.365786
F	0.474289	3.432473	0.695698
F	-0.139792	4.452753	-1.107237
F	1.785807	3.473887	-1.023347
C	1.026334	-0.650229	1.351212
C	-0.150305	2.080893	-1.158777

TS3B-2a^{+}

M062X/BSI SCF energy: -2457.394497 a.u.

M062X/BSII SCF energy in solution: -2457.960275 a.u.

M062X/BSII free energy in solution: -2457.509416 a.u.

S	-0.552114	0.155435	-0.650239
O	-1.801792	1.392480	-0.167490
C	-1.542513	-0.325588	-2.149780
C	0.460698	1.510137	-1.315416
C	-2.913574	-0.764335	-1.733194
C	-3.975983	0.141608	-1.791804
C	-5.236055	-0.229982	-1.328804
C	-5.439307	-1.510317	-0.816726

C	-4.384407	-2.421271	-0.773433
C	-3.122843	-2.049822	-1.227762
C	1.389905	2.110805	-0.287987
C	1.192808	2.001735	1.088636
C	2.096464	2.592309	1.972734
C	3.187643	3.305962	1.487616
C	3.377155	3.429909	0.110593
C	2.486412	2.830906	-0.772296
H	-1.555539	0.571648	-2.772292
H	-3.809296	1.139406	-2.187565
H	-6.055817	0.480474	-1.368775
H	-6.420398	-1.800307	-0.453958
H	-4.542800	-3.420366	-0.380326
H	-2.296688	-2.754340	-1.186729
H	1.011656	1.093521	-2.165710
H	-0.258891	2.237468	-1.701717
H	0.340362	1.463861	1.497785
H	1.938217	2.494020	3.042012
H	3.889743	3.762515	2.177995
H	4.228912	3.981169	-0.276043
H	2.643250	2.908744	-1.845042
O	-2.688332	-0.054501	1.342934
C	-3.649837	2.134347	1.075228
F	-3.030177	3.078740	1.788034
F	-4.671128	1.668318	1.782090
F	-4.118721	2.695254	-0.039255
C	-2.658516	0.994715	0.763405
H	-0.978593	-1.111380	-2.652008
C	0.972482	-1.541183	-1.213122
C	2.036047	-1.201927	-0.355608
C	3.242506	-0.479656	-0.759980
C	4.120964	-0.079743	0.263277
C	3.566090	-0.200586	-2.100912
C	5.299321	0.581238	-0.048282
H	3.868532	-0.288111	1.297058
C	4.747640	0.465876	-2.398990
H	2.909113	-0.491058	-2.909273
C	5.614655	0.856664	-1.379472
H	5.969167	0.890093	0.747416
H	4.991644	0.680521	-3.433939
H	6.534844	1.379148	-1.621570
O	1.851137	-1.368395	0.921277
Si	1.241851	-2.645456	1.960761
C	-0.573008	-2.352396	2.222525
H	-0.953017	-3.077114	2.951689
H	-0.743734	-1.351354	2.629675
H	-1.160803	-2.451480	1.306914
C	1.697207	-4.262778	1.162519
H	2.745081	-4.251865	0.844654
H	1.582743	-5.069551	1.894814
H	1.073276	-4.498231	0.297295
C	2.218615	-2.309796	3.506951
H	1.896403	-2.975762	4.314265
H	3.288964	-2.468447	3.343945
H	2.069672	-1.278201	3.842462
F	1.150599	-1.646012	-2.532076
F	0.123917	-2.503328	-0.804695

TS2B

M062X/BSI SCF energy: -1465.584628 a.u.

M062X/BSII SCF energy in solution: -1465.920493 a.u.

M062X/BSII free energy in solution: -1465.689872 a.u.

S	0.309462	-1.149388	0.059480
C	1.623344	-0.745946	-0.897782
C	-0.956556	-1.722628	-1.138529
C	2.998436	-0.745131	-0.315665
C	3.343157	-1.448975	0.842022
C	4.643788	-1.387341	1.333673
C	5.612371	-0.638138	0.668697
C	5.275814	0.052423	-0.493941
C	3.973863	0.005700	-0.981803
C	-2.335144	-1.630399	-0.560172
C	-2.817220	-2.636715	0.280103
C	-4.094484	-2.531521	0.823751
C	-4.888893	-1.424226	0.529372
C	-4.408448	-0.419531	-0.309430
C	-3.131404	-0.519781	-0.851905
H	1.498208	-1.028301	-1.948894
H	1.230283	0.558229	-1.095238
H	2.609668	-2.062612	1.358767
H	4.901845	-1.939662	2.231375
H	6.626992	-0.597947	1.051510
H	6.025566	0.634647	-1.019981
H	3.707469	0.553179	-1.882123
H	-0.813715	-1.118469	-2.040324

H	-0.636141	-2.752682	-1.334304
H	-2.194676	-3.499765	0.502845
H	-4.469753	-3.314158	1.474988
H	-5.884721	-1.344431	0.953843
H	-5.026060	0.442249	-0.540705
H	-2.749251	0.260180	-1.505842
O	-0.602931	0.469267	0.403858
O	0.648643	1.661976	-1.044781
C	-0.964202	2.804261	0.345138
F	-0.493829	3.885892	-0.249767
F	-0.813592	2.909737	1.659241
F	-2.257793	2.666875	0.068450
C	-0.217069	1.552489	-0.162118

TS2C

M062X/BSI SCF energy: -2457.333293 a.u.

M062X/BSII SCF energy in solution: -2457.905355 a.u.

M062X/BSII free energy in solution: -2457.45101 a.u.

S	-1.444760	0.328950	-0.159318
O	0.414579	1.219228	-1.869492
C	-2.760413	-0.340846	0.917034
C	-1.601956	-0.770558	-1.654688
C	-4.022027	0.276030	0.366217
C	-4.935480	-0.525377	-0.325135
C	-6.106965	0.030528	-0.830263
C	-6.364214	1.389499	-0.657620
C	-5.452533	2.193317	0.025104
C	-4.282456	1.640727	0.536310
C	-0.810339	-2.036715	-1.671060
C	0.432729	-2.044608	-2.306412
C	1.204215	-3.203725	-2.306339
C	0.729799	-4.354111	-1.679584
C	-0.529499	-4.357559	-1.077504
C	-1.306607	-3.203190	-1.080696
H	-2.782704	-1.427745	0.865363
H	-4.731190	-1.585460	-0.453483
H	-6.817401	-0.597516	-1.357765
H	-7.276815	1.822180	-1.055024
H	-5.653488	3.250560	0.163380
H	-3.577621	2.265294	1.079403
H	-2.682071	-0.951069	-1.647660
H	-1.321429	-0.088693	-2.455003
H	0.785341	-1.139611	-2.793238
H	2.174549	-3.206274	-2.792634
H	1.334133	-5.255619	-1.672324
H	-0.907984	-5.261665	-0.611563
H	-2.292616	-3.204537	-0.622697
O	0.676547	2.480097	-0.020921
C	2.199675	2.777155	-1.797401
F	2.784966	2.010214	-2.726664
F	3.126579	3.071188	-0.877808
F	1.840969	3.926930	-2.390001
C	0.969712	2.080776	-1.168030
H	-2.529822	-0.002780	1.931434
C	0.264695	-2.263763	1.360206
C	0.798037	-1.171466	0.821057
C	2.246105	-0.973381	0.611468
C	2.762105	-0.393437	-0.552883
C	3.114474	-1.316937	1.657215
C	4.125579	-0.135518	-0.654502
H	2.101895	-0.135475	-1.370759
C	4.479450	-1.077358	1.539112
H	2.719650	-1.760595	2.566265
C	4.985334	-0.474460	0.389805
H	4.514491	0.331066	-1.553690
H	5.142631	-1.345313	2.354953
H	6.047897	-0.269070	0.306759
O	-0.012788	0.007241	0.739934
Si	0.469714	1.432092	2.147284
C	-0.990636	2.578756	2.241459
H	-0.662459	3.421209	2.865515
H	-1.299749	2.987704	1.280239
H	-1.833212	2.108388	2.757051
C	0.261515	0.183237	3.524727
H	1.091103	-0.519037	3.630886
H	0.227028	0.783359	4.445031
H	-0.680365	-0.371423	3.467443
C	2.225266	2.044467	2.152707
H	2.821017	1.624792	1.339551
H	2.223150	3.130315	2.031041
H	2.684690	1.775583	3.109365
F	0.930187	-3.371588	1.546233
F	-0.984762	-2.375909	1.737269

TS3A-2b

M062X/BSI SCF energy: -2785.16722 a.u.

M062X/BSII SCF energy in solution: -2785.856228 a.u.

M062X/BSII free energy in solution: -2785.364694 a.u.

S	1.319536	-0.094602	-0.572332
O	2.697365	0.642800	-1.215347
C	0.181080	0.819149	-1.670234
C	1.503930	-1.717397	-1.423744
C	-0.292110	2.088367	-1.022657
C	0.603873	3.122233	-0.730929
C	0.150439	4.277545	-0.101017
C	-1.197204	4.409310	0.234764
C	-2.092093	3.384920	-0.068031
C	-1.643333	2.223701	-0.694226
C	2.882254	-2.238781	-1.147472
C	3.918054	-1.962031	-2.044692
C	5.219573	-2.361248	-1.749648
C	5.486750	-3.041544	-0.563258
C	4.453105	-3.324194	0.329627
C	3.153605	-2.918615	0.042834
H	0.753562	0.968526	-2.591454
H	-0.636451	0.123129	-1.862424
H	1.653102	3.031722	-1.000850
H	0.849374	5.076557	0.124784
H	-1.548230	5.312175	0.724875
H	-3.144466	3.482914	0.181002
H	-2.358657	1.435144	-0.921141
H	0.706881	-2.318662	-0.976821
H	1.311393	-1.535897	-2.484603
H	3.703605	-1.428521	-2.966848
H	6.022183	-2.139842	-2.445814
H	6.501457	-3.350713	-0.332864
H	4.661133	-3.854922	1.253135
H	2.345037	-3.116386	0.742975
O	-4.896877	-1.312617	-0.209666
O	3.882455	0.237748	0.689051
O	-4.626346	0.815847	-0.949312
C	4.897300	1.456392	-1.148787
C	-6.785318	-0.175466	-0.975934
F	4.465200	2.680684	-1.450563
F	5.221449	0.834297	-2.279605
F	5.966097	1.548014	-0.375720
F	-7.495011	-0.316655	0.159819
F	-7.156563	-1.180569	-1.790323
F	-7.188023	0.964711	-1.551682
C	3.788578	0.686229	-0.408071
C	-5.261468	-0.211953	-0.687728
C	0.082483	-2.763508	2.197175
C	-0.089068	-1.491914	1.807646
C	0.451139	-0.323041	2.560445
C	-0.032300	0.965484	2.304408
C	1.478831	-0.477442	3.501426
C	0.476945	2.067697	2.986881
H	-0.808498	1.102604	1.560168
C	1.983218	0.622672	4.186895
H	1.908746	-1.457727	3.681687
C	1.483621	1.900229	3.934961
H	0.082979	3.057222	2.773974
H	2.779863	0.483457	4.911124
H	1.884518	2.758138	4.465865
O	-0.732271	-1.190920	0.635015
Si	-2.494045	-1.446725	0.398734
C	-2.880022	-3.194644	0.966201
H	-3.932341	-3.392196	0.744695
H	-2.276235	-3.935444	0.431270
H	-2.722446	-3.336878	2.039114
C	-3.128095	-0.191641	1.645118
H	-2.496860	-0.215979	2.540592
H	-3.136810	0.828378	1.253225
H	-4.148742	-0.451424	1.931273
C	-2.452888	-1.420351	-1.482273
H	-3.215208	-2.123800	-1.825783
H	-2.695679	-0.451626	-1.924284
H	-1.483969	-1.771292	-1.854802
H	0.573365	-3.008366	3.130984
H	-0.286775	-3.580665	1.588633

TS3B-2b^{+}

M062X/BSI SCF energy: -2259.005251 a.u.

M062X/BSII SCF energy in solution: -2259.500965 a.u.

M062X/BSII free energy in solution: -2259.032717 a.u.

S	0.560380	-0.121713	-0.710252
O	1.724034	-1.319385	-0.139708

C	1.540294	0.221786	-2.252761
C	-0.537799	-1.456699	-1.265737
C	2.901437	0.697570	-1.849430
C	3.965338	-0.207105	-1.799776
C	5.208502	0.204361	-1.324586
C	5.392097	1.521801	-0.908362
C	4.336767	2.431283	-0.975580
C	3.092462	2.021065	-1.443900
C	-1.430716	-1.982455	-0.166778
C	-1.299365	-1.646316	1.179691
C	-2.175284	-2.185359	2.123153
C	-3.175896	-3.067159	1.728708
C	-3.303170	-3.411090	0.382144
C	-2.438181	-2.868670	-0.560979
H	1.560132	-0.724795	-2.797453
H	3.812252	-1.232943	-2.123022
H	6.029649	-0.503970	-1.278774
H	6.359397	1.842901	-0.535104
H	4.482661	3.459343	-0.659926
H	2.265222	2.725747	-1.494760
H	-1.117632	-1.045401	-2.097788
H	0.130185	-2.229650	-1.657846
H	-0.528550	-0.960525	1.524320
H	-2.067867	-1.911344	3.167895
H	-3.856558	-3.483672	2.464338
H	-4.085271	-4.093393	0.063797
H	-2.544764	-3.122709	-1.612551
O	2.630370	0.190019	1.299514
C	3.526857	-2.047808	1.178672
F	2.843421	-2.967176	1.861479
F	4.511065	-1.589275	1.937864
F	4.045938	-2.629287	0.098695
C	2.583767	-0.890880	0.792100
H	0.967007	0.966393	-2.804205
C	-1.098627	1.648573	-1.459893
C	-2.094032	1.346269	-0.567880
C	-3.292169	0.540003	-0.901733
C	-4.170375	0.167478	0.125502
C	-3.569188	0.137890	-2.216626
C	-5.295349	-0.599726	-0.154753
H	-3.958933	0.472197	1.144208
C	-4.692453	-0.634680	-2.490622
H	-2.920456	0.431209	-3.035484
C	-5.557476	-1.006455	-1.462157
H	-5.963439	-0.887304	0.650987
H	-4.896889	-0.939641	-3.511900
H	-6.434499	-1.607471	-1.681523
O	-2.029688	1.698930	0.711248
Si	-1.273059	3.061690	1.449166
C	0.572788	2.810569	1.521879
H	1.006807	3.583862	2.167015
H	0.826697	1.839285	1.956320
H	1.063761	2.887332	0.546556
C	-1.763866	4.564431	0.457794
H	-2.853596	4.652020	0.401947
H	-1.378252	5.469315	0.939381
H	-1.369756	4.534436	-0.562179
C	-2.021352	3.045751	3.151601
H	-1.586241	3.837589	3.769934
H	-3.103391	3.203561	3.109683
H	-1.835579	2.089184	3.650539
H	-1.227144	1.427552	-2.512419
H	-0.349829	2.393204	-1.205188

IM3^{+}

M062X/BSI SCF energy: -939.06194 a.u.

M062X/BSII SCF energy in solution: -939.220655 a.u.

M062X/BSII free energy in solution: -939.022368 a.u.

S	0.051979	0.135345	0.000330
C	-1.348946	-0.757761	0.000098
C	1.349037	-1.179991	0.000240
C	-2.667398	-0.233114	0.000003
C	-3.727064	-1.168401	-0.000104
C	-5.039157	-0.725969	-0.000168
C	-5.301112	0.644516	-0.000143
C	-4.258988	1.582908	-0.000055
C	-2.947638	1.154610	0.000017
C	2.697023	-0.517705	0.000058
C	3.322302	-0.200587	-1.208327
C	4.569326	0.418105	-1.207713
C	5.193950	0.726658	-0.000268
C	4.569543	0.418307	1.207341
C	3.322520	-0.200387	1.208279
H	-1.235540	-1.843779	-0.000035
H	-3.496085	-2.229428	-0.000128

H	-5.855917	-1.438917	-0.000242
H	-6.329376	0.992491	-0.000200
H	-4.485190	2.643181	-0.000050
H	-2.139369	1.881308	0.000073
H	1.183609	-1.780792	0.896611
H	1.183406	-1.780880	-0.896034
H	2.831713	-0.446806	-2.146623
H	5.055215	0.655350	-2.148837
H	6.167780	1.206351	-0.000398
H	5.055602	0.655710	2.148337
H	2.832099	-0.446453	2.146703

IM3-2a

M062X/BSI SCF energy: -2983.575449 a.u.

M062X/BSII SCF energy in solution: -2984.330616 a.u.

M062X/BSII free energy in solution: -2983.85332 a.u.

S	1.279586	0.127858	-0.666213
O	2.721839	0.899301	-1.133261
C	0.272231	1.194759	-1.757443
C	1.494632	-1.398301	-1.690955
C	-0.190829	2.420448	-1.026195
C	0.720569	3.384723	-0.580317
C	0.268505	4.485749	0.140722
C	-1.092236	4.635972	0.411386
C	-2.001539	3.684878	-0.046215
C	-1.553093	2.575647	-0.760715
C	2.886960	-1.930769	-1.525024
C	3.904591	-1.482074	-2.373200
C	5.217974	-1.900088	-2.171715
C	5.518311	-2.774684	-1.129169
C	4.503432	-3.238212	-0.293299
C	3.192537	-2.814992	-0.486291
H	0.922414	1.398053	-2.613887
H	-0.560565	0.566070	-2.073721
H	1.780944	3.278341	-0.794345
H	0.978499	5.228101	0.491048
H	-1.440462	5.496072	0.974841
H	-3.062131	3.797063	0.157929
H	-2.268528	1.829488	-1.099777
H	0.722717	-2.064472	-1.298551
H	1.265939	-1.104890	-2.718933
H	3.666636	-0.798251	-3.183510
H	6.003430	-1.541032	-2.828933
H	6.542152	-3.098535	-0.970614
H	4.733046	-3.926218	0.513838
H	2.405490	-3.180447	0.165383
O	-4.630658	-1.099934	-0.388010
O	3.767755	0.162977	0.749279
O	-4.624100	1.048940	-1.099994
C	4.935816	1.608474	-0.809159
C	-6.655434	-0.203759	-1.120079
F	4.610172	2.901594	-0.771783
F	5.216401	1.283749	-2.068320
F	6.003439	1.406442	-0.055315
F	-7.310447	-0.422950	0.031163
F	-6.892348	-1.254550	-1.918203
F	-7.193994	0.873499	-1.694940
C	3.758015	0.774599	-0.272240
C	-5.144637	-0.029802	-0.859733
C	0.278680	-2.588519	1.458423
C	-0.146488	-1.318240	1.459943
F	0.029921	-3.434974	0.463062
F	1.002769	-3.195679	2.387373
C	0.164632	-0.361335	2.553567
C	-0.010381	1.006872	2.304030
C	0.619569	-0.754710	3.821852
C	0.287347	1.956684	3.276143
H	-0.408128	1.322301	1.345731
C	0.913369	0.198568	4.792177
H	0.734507	-1.803348	4.066216
C	0.756659	1.557520	4.525323
H	0.143444	3.010100	3.054353
H	1.261261	-0.127945	5.767434
H	0.986290	2.295590	5.287462
O	-0.788077	-0.884493	0.346477
Si	-2.703956	-1.100668	0.073683
C	-2.870628	-2.860128	0.729911
H	-3.921921	-3.067173	0.945740
H	-2.527724	-3.593929	-0.006199
H	-2.303104	-3.018912	1.650782
C	-3.066825	0.192352	1.408442
H	-2.522668	-0.083328	2.317700
H	-2.750383	1.201139	1.134962
H	-4.133195	0.223123	1.646844
C	-2.390436	-1.042348	-1.795867

H	-3.104472	-1.730902	-2.259515
H	-2.570554	-0.061701	-2.245412
H	-1.386035	-1.384954	-2.058091

IM3-2b^{+}

M062X/BSI SCF energy: -2259.042435 a.u.

M062X/BSII SCF energy in solution: -2259.545346 a.u.

M062X/BSII free energy in solution: -2459.070325 a.u.

S	0.450947	0.255266	-1.151584
O	2.668896	-1.240884	-1.736101
C	1.426592	1.405369	-2.206191
C	-0.409725	-0.779224	-2.400310
C	2.311991	2.258113	-1.345777
C	3.514618	1.736115	-0.856928
C	4.310967	2.504473	-0.013690
C	3.913082	3.793147	0.345266
C	2.720165	4.317925	-0.147515
C	1.919261	3.551810	-0.993199
C	-1.712320	-1.289597	-1.853837
C	-1.726781	-2.198926	-0.787138
C	-2.941115	-2.642186	-0.273202
C	-4.143381	-2.196610	-0.826960
C	-4.130201	-1.305455	-1.897403
C	-2.916434	-0.846048	-2.405494
H	1.988865	0.720450	-2.842983
H	3.794642	0.719622	-1.121750
H	5.240950	2.095611	0.369483
H	4.535192	4.389658	1.005316
H	2.413291	5.323129	0.123259
H	0.991020	3.959459	-1.386523
H	-0.545026	-0.157539	-3.289481
H	0.327376	-1.565979	-2.579520
H	-0.781170	-2.554014	-0.382746
H	-2.951455	-3.342175	0.556791
H	-5.088847	-2.547587	-0.424767
H	-5.062877	-0.956687	-2.329737
H	-2.901500	-0.141253	-3.232860
O	1.437143	-2.699743	-0.532896
C	3.640216	-2.252771	0.175596
F	3.224587	-2.406106	1.443630
F	4.508021	-1.228510	0.171258
F	4.333350	-3.359808	-0.147513
C	2.453728	-2.039773	-0.800926
H	0.706339	1.980336	-2.793937
C	-0.873253	1.398983	-0.650088
C	-1.740408	0.814048	0.430988
C	-3.175649	0.975591	0.443057
C	-3.914911	0.289822	1.429131
C	-3.841645	1.787654	-0.496645
C	-5.294065	0.410215	1.465779
H	-3.399590	-0.341452	2.145209
C	-5.219971	1.912386	-0.439801
H	-3.295887	2.332585	-1.257926
C	-5.944494	1.219706	0.532744
H	-5.864287	-0.125497	2.216449
H	-5.733663	2.543428	-1.156371
H	-7.025645	1.312792	0.563099
O	-1.204562	0.185248	1.385238
Si	0.175899	-0.094784	2.488096
C	1.685133	0.798616	1.875818
H	2.329720	0.982804	2.744123
H	2.263742	0.218515	1.153958
H	1.448654	1.779213	1.444272
C	-0.511233	0.669273	4.034148
H	-1.438480	0.176316	4.340682
H	0.214071	0.570153	4.848797
H	-0.712961	1.735195	3.889894
C	0.266210	-1.940929	2.503685
H	0.914611	-2.262353	3.326276
H	-0.728438	-2.365759	2.673926
H	0.678309	-2.331129	1.567699
H	-1.435883	1.699739	-1.533314
H	-0.362506	2.277640	-0.228260

IM4-2a^{+}

M062X/BSI SCF energy: -1930.815064 a.u.

M062X/BSII SCF energy in solution: -1931.203505 a.u.

M062X/BSII free energy in solution: -1930.788973 a.u.

S	-1.260542	-1.787460	-0.496118
C	0.195738	-2.130549	0.224486
C	-2.489467	-2.126052	0.833600
C	1.453744	-2.077806	-0.439913

C	2.598574	-2.422569	0.311255
C	3.851416	-2.390725	-0.281216
C	3.971048	-2.005687	-1.616895
C	2.843425	-1.650556	-2.369538
C	1.589899	-1.679742	-1.789993
C	-3.720904	-1.314502	0.534331
C	-4.117752	-0.281691	1.385877
C	-5.233637	0.492727	1.071542
C	-5.947703	0.248941	-0.099651
C	-5.556310	-0.784030	-0.950634
C	-4.451388	-1.567047	-0.631146
H	0.178214	-2.448740	1.267976
H	2.481599	-2.715754	1.350723
H	4.732389	-2.655277	0.293112
H	4.952346	-1.976991	-2.080897
H	2.955729	-1.349755	-3.405365
H	0.716301	-1.404020	-2.373649
H	-2.685033	-3.200531	0.805342
H	-2.033735	-1.855766	1.787566
H	-3.550312	-0.081490	2.289898
H	-5.539227	1.292230	1.739126
H	-6.810451	0.859084	-0.347869
H	-6.113650	-0.983372	-1.860400
H	-4.154282	-2.379487	-1.291081
C	0.086817	0.573649	1.682156
C	0.923837	0.804330	0.662591
F	-1.232003	0.549763	1.521259
F	0.406429	0.392645	2.948349
C	2.395455	0.854639	0.757500
C	3.105453	1.272704	-0.375414
C	3.109455	0.473156	1.905764
C	4.496807	1.314766	-0.361699
H	2.559763	1.547442	-1.271788
C	4.498683	0.522016	1.912623
H	2.590242	0.126609	2.790778
C	5.199100	0.939715	0.781223
H	5.032119	1.637037	-1.249641
H	5.037669	0.223015	2.806216
H	6.284093	0.970055	0.791258
O	0.381788	0.958608	-0.572094
Si	-0.631386	2.251836	-1.058674
C	-0.702755	3.496496	0.331764
H	-1.207842	4.402619	-0.020305
H	-1.255640	3.123670	1.199162
H	0.302125	3.783504	0.659730
C	0.185929	2.963412	-2.578073
H	0.401945	2.180576	-3.312682
H	-0.470375	3.699407	-3.054847
H	1.126210	3.464646	-2.327014
C	-2.310241	1.546631	-1.467988
H	-2.963196	2.341312	-1.846956
H	-2.245861	0.774294	-2.241562
H	-2.788535	1.115438	-0.582558

IM4

M062X/BSI SCF energy: -1465.270814 a.u.

M062X/BSII SCF energy in solution: -1465.613713 a.u.

M062X/BSII free energy in solution: -1465.387361 a.u.

S	0.495520	-1.231671	0.024080
O	-1.045740	0.819765	-0.833942
C	-1.006170	-0.635893	-0.804010
C	1.726230	-0.427356	-1.075108
C	-2.274146	-1.250329	-0.258409
C	-3.322615	-1.473199	-1.154304
C	-4.516794	-2.038727	-0.714331
C	-4.665018	-2.393719	0.624345
C	-3.619186	-2.177787	1.520902
C	-2.428861	-1.603704	1.084482
C	3.095217	-0.607202	-0.478685
C	3.605084	0.345383	0.408395
C	4.860328	0.169919	0.985153
C	5.614915	-0.963428	0.683661
C	5.110140	-1.919296	-0.196249
C	3.854282	-1.742471	-0.773176
H	-0.920799	-0.868260	-1.867262
H	-3.198365	-1.205480	-2.200397
H	-5.325036	-2.207666	-1.418655
H	-5.592996	-2.838713	0.970034
H	-3.731531	-2.452928	2.564828
H	-1.626911	-1.415648	1.791384
H	1.658902	-0.878942	-2.068174
H	1.473623	0.633328	-1.143755
H	3.011772	1.226884	0.640907
H	5.250282	0.917147	1.669464
H	6.593884	-1.099784	1.132786

H	5.694733	-2.802192	-0.435695
H	3.458835	-2.485498	-1.461335
O	-1.254841	1.122494	1.414831
C	-0.856395	2.995530	-0.038848
F	-1.661020	3.414680	-1.015574
F	0.409201	3.156882	-0.446051
F	-1.053392	3.750963	1.033760
C	-1.097539	1.512895	0.293560

IM4-2a

M062X/BSI SCF energy: -2048.359802 a.u.

M062X/BSII SCF energy in solution: -2048.8799 a.u.

M062X/BSII free energy in solution: -2048.536564 a.u.

S	0.118875	-0.083139	-0.908589
O	-1.576267	-1.247499	-0.571802
C	0.556902	-1.420940	-2.076861
C	-1.016139	0.996083	-1.883788
C	1.543017	-2.328839	-1.399429
C	1.114404	-3.194329	-0.386862
C	2.037530	-3.988344	0.286555
C	3.390682	-3.925838	-0.047919
C	3.818892	-3.070077	-1.061028
C	2.897404	-2.268782	-1.732433
C	-2.082443	1.605423	-1.020152
C	-3.383057	1.096810	-1.045364
C	-4.365669	1.641091	-0.222563
C	-4.055641	2.701917	0.627006
C	-2.761011	3.218250	0.650195
C	-1.777858	2.670384	-0.169127
H	-0.378367	-1.916208	-2.331346
H	0.058157	-3.237111	-0.130785
H	1.701571	-4.657242	1.072647
H	4.109108	-4.546136	0.479016
H	4.870594	-3.021724	-1.325527
H	3.226632	-1.587722	-2.512279
H	-0.356015	1.742809	-2.328456
H	-1.434503	0.360086	-2.667041
H	-3.615821	0.258945	-1.695914
H	-5.372167	1.234565	-0.243723
H	-4.820796	3.125715	1.270055
H	-2.515583	4.046925	1.306960
H	-0.766269	3.070329	-0.146459
O	-1.717456	-0.469236	1.554160
C	-3.218548	-2.166032	0.795982
F	-3.704508	-2.153250	2.037270
F	-2.820536	-3.418237	0.523090
F	-4.226317	-1.876170	-0.041686
C	-2.051318	-1.170975	0.619322
H	0.980431	-0.918856	-2.948684
C	1.903774	3.003858	-1.071079
C	1.919487	1.778753	-0.540822
C	2.325755	1.460510	0.843370
C	2.827397	0.181182	1.115072
C	2.196219	2.381489	1.891028
C	3.206117	-0.165871	2.407917
H	2.926250	-0.540084	0.308828
C	2.583999	2.030054	3.180291
H	1.779760	3.365657	1.705320
C	3.089219	0.758047	3.444677
H	3.593455	-1.161690	2.601272
H	2.476611	2.751568	3.984191
H	3.382691	0.486901	4.453889
O	1.591575	0.750785	-1.392075
F	2.295865	4.103308	-0.459114
F	1.530468	3.261921	-2.310753

IM4-2b^{+}

M062X/BSI SCF energy: -1323.835853 a.u.

M062X/BSII SCF energy in solution: -1324.096692 a.u.

M062X/BSII free energy in solution: -1323.759584 a.u.

S	1.142417	-1.312970	0.059900
C	2.649719	-1.248875	-0.984031
C	0.103587	-2.464191	-0.942553
C	3.652974	-0.296775	-0.398622
C	4.399919	-0.655944	0.727885
C	5.326310	0.234399	1.261643
C	5.512126	1.486163	0.674196
C	4.768472	1.847797	-0.446770
C	3.837347	0.959530	-0.980809
C	-1.342834	-2.339938	-0.567148
C	-1.834181	-2.981846	0.572669
C	-3.159995	-2.807061	0.953520

C	-4.003807	-1.990905	0.198337
C	-3.520688	-1.357877	-0.944158
C	-2.192009	-1.531118	-1.327123
H	3.007125	-2.283078	-0.991143
H	4.258920	-1.635070	1.179239
H	5.906992	-0.049295	2.133435
H	6.237866	2.177918	1.089978
H	4.912507	2.819662	-0.907769
H	3.257233	1.233010	-1.858264
H	0.289697	-2.204971	-1.988262
H	0.516233	-3.452157	-0.722000
H	-1.171924	-3.609002	1.164152
H	-3.537300	-3.305455	1.840876
H	-5.037637	-1.853027	0.499450
H	-4.173878	-0.725913	-1.537675
H	-1.812310	-1.040800	-2.220226
H	2.334861	-0.962624	-1.990631
C	0.383960	0.283826	-0.325048
C	-0.766569	0.533369	0.648523
C	-1.718680	1.630286	0.332365
C	-2.885224	1.707743	1.102946
C	-1.488825	2.557593	-0.688942
C	-3.818007	2.704374	0.851549
H	-3.046563	0.972898	1.885091
C	-2.422038	3.562831	-0.929206
H	-0.584614	2.511081	-1.288496
C	-3.584583	3.633886	-0.163757
H	-4.726297	2.759164	1.442654
H	-2.242912	4.289370	-1.714803
H	-4.312693	4.415248	-0.358228
O	-0.871611	-0.148365	1.648188
H	0.075546	0.289931	-1.374137
H	1.161525	1.043957	-0.179944

TS4-2a^{+}

M062X/BSI SCF energy: -1930.809069 a.u.

M062X/BSII SCF energy in solution: -1931.195097 a.u.

M062X/BSII free energy in solution: -1930.780043 a.u.

S	1.106473	-1.852138	0.715840
C	-0.296020	-1.850942	-0.250445
C	2.432896	-2.359606	-0.462938
C	-1.615248	-1.925354	0.359260
C	-2.708167	-2.223898	-0.470583
C	-3.989325	-2.296870	0.063512
C	-4.188588	-2.069146	1.424708
C	-3.107993	-1.759016	2.253531
C	-1.827222	-1.676412	1.726215
C	3.637068	-1.467383	-0.332145
C	4.023696	-0.644458	-1.392200
C	5.115044	0.211508	-1.256909
C	5.823195	0.256581	-0.057988
C	5.449169	-0.571610	1.000073
C	4.366302	-1.435123	0.861010
H	-0.200062	-2.283451	-1.247457
H	-2.538217	-2.396407	-1.530041
H	-4.830797	-2.530720	-0.580352
H	-5.188485	-2.131995	1.842489
H	-3.268060	-1.577277	3.311007
H	-0.993550	-1.430336	2.378077
H	2.668940	-3.393824	-0.201186
H	2.015468	-2.337070	-1.471459
H	3.463957	-0.670258	-2.322616
H	5.407038	0.846237	-2.087720
H	6.666739	0.931098	0.050622
H	6.003301	-0.547069	1.933138
H	4.081580	-2.082238	1.687913
C	-0.094059	0.055086	-1.413032
C	-0.867338	0.759532	-0.511649
F	1.226169	0.153685	-1.359333
F	-0.492337	-0.339988	-2.607634
C	-2.314395	0.924169	-0.606464
C	-3.005964	1.288274	0.560560
C	-3.021061	0.755697	-1.810795
C	-4.383956	1.456321	0.527678
H	-2.456943	1.426920	1.485907
C	-4.396718	0.940051	-1.834720
H	-2.503628	0.497119	-2.725427
C	-5.081230	1.279090	-0.667421
H	-4.916186	1.725206	1.434179
H	-4.936515	0.815447	-2.767445
H	-6.158168	1.413128	-0.690883
O	-0.266665	1.129344	0.606628
Si	0.895104	2.414060	0.795302
C	0.958800	3.309089	-0.837759
H	1.563521	4.216332	-0.732787

H	1.407649	2.699111	-1.627532
H	-0.042172	3.614767	-1.160741
C	0.158283	3.447427	2.155238
H	0.003371	2.849905	3.059284
H	0.823136	4.279125	2.410663
H	-0.806132	3.865721	1.850286
C	2.511695	1.635838	1.277778
H	3.250048	2.416272	1.493801
H	2.402911	1.018239	2.174735
H	2.901886	1.012293	0.468453

TS4A-2a

M062X/BSI SCF energy: -2983.578737 a.u.

M062X/BSII SCF energy in solution: -2984.334588 a.u.

M062X/BSII free energy in solution: -2983.856598 a.u.

S	-1.003025	0.947576	0.423039
O	-1.594458	2.563636	0.161847
C	0.068618	1.430797	1.860721
C	-2.541240	0.491903	1.293204
C	0.966176	2.564523	1.473032
C	0.560357	3.880626	1.717660
C	1.341582	4.946585	1.277263
C	2.536610	4.702311	0.602127
C	2.952039	3.391436	0.373102
C	2.167952	2.324959	0.802610
C	-3.569721	-0.100391	0.368357
C	-3.898767	0.514998	-0.843302
C	-4.840755	-0.065560	-1.687743
C	-5.476858	-1.249177	-1.318047
C	-5.172262	-1.849470	-0.097669
C	-4.215505	-1.281426	0.739570
H	-0.631589	1.699203	2.656716
H	-0.373601	4.066417	2.240975
H	1.016121	5.965440	1.462528
H	3.144503	5.533818	0.259109
H	3.885209	3.191827	-0.144380
H	2.502644	1.311413	0.606848
H	-2.240694	-0.201993	2.079940
H	-2.864184	1.427436	1.760268
H	-3.431772	1.453324	-1.132329
H	-5.080408	0.412217	-2.632263
H	-6.209500	-1.701156	-1.979387
H	-5.665312	-2.771071	0.195725
H	-3.954085	-1.765480	1.677157
O	-0.091115	2.848007	-1.521249
C	-1.698361	4.584052	-1.019684
F	-1.053097	5.313771	-1.916500
F	-1.755044	5.253511	0.129938
F	-2.946694	4.373930	-1.444457
C	-0.992612	3.228991	-0.836831
H	0.573482	0.494480	2.098863
C	-1.187675	-2.394563	2.331206
C	-0.984727	-2.222180	1.019711
C	-1.686759	-3.006951	-0.024286
C	-1.768390	-2.448316	-1.306910
C	-2.278991	-4.253900	0.211387
C	-2.457881	-3.103039	-2.322067
H	-1.287796	-1.493065	-1.498372
C	-2.964055	-4.907879	-0.809920
H	-2.198764	-4.724481	1.184527
C	-3.064957	-4.334175	-2.075831
H	-2.524011	-2.649434	-3.306548
H	-3.417014	-5.875236	-0.614613
H	-3.603236	-4.846484	-2.867090
O	-0.163266	-1.224368	0.625131
Si	1.750711	-1.630506	0.068790
C	1.532944	-0.449206	-1.391024
H	2.286229	0.342410	-1.392828
H	1.711911	-1.054567	-2.288827
H	0.546622	0.001412	-1.492261
C	2.363570	-1.274430	1.822324
H	3.142028	-2.012940	2.045970
H	2.830111	-0.291202	1.927217
H	1.579667	-1.372571	2.574948
C	1.425053	-3.459484	-0.243768
H	2.382481	-3.971788	-0.362677
H	0.888010	-3.934583	0.581701
H	0.840265	-3.620076	-1.154477
O	4.399531	0.192609	-0.108052
O	3.587219	-1.886338	-0.505937
C	5.849371	-1.508094	-0.933119
F	6.359168	-2.330490	-0.001988
F	6.727951	-0.524343	-1.131234
F	5.748199	-2.204996	-2.071298
C	4.480658	-0.969422	-0.469138

F	-2.011040	-3.264934	2.898228
F	-0.634403	-1.616102	3.258463

TS4-2a'

M062X/BSI SCF energy: -2456.944127 a.u.

M062X/BSII SCF energy in solution: -2457.535285 a.u.

M062X/BSII free energy in solution: -2457.099008 a.u.

S	2.739249	0.318221	0.762893
O	-4.494556	0.323204	-0.418650
C	3.207343	-1.264656	0.773988
C	4.176900	1.141815	-0.036187
C	2.431898	-2.336428	1.352352
C	3.021775	-3.609723	1.429609
C	2.327044	-4.672942	1.993700
C	1.038155	-4.479458	2.483175
C	0.434807	-3.221168	2.390966
C	1.114366	-2.159258	1.819491
C	4.150155	2.615133	0.261870
C	3.660367	3.520430	-0.680357
C	3.634013	4.882230	-0.391209
C	4.090696	5.343989	0.839895
C	4.576425	4.442448	1.785815
C	4.605224	3.082878	1.497894
H	4.156048	-1.511221	0.302652
H	4.030321	-3.752873	1.051707
H	2.792191	-5.651487	2.052020
H	0.494839	-5.309460	2.923494
H	-0.580634	-3.075950	2.746026
H	0.601895	-1.211130	1.667625
H	5.069205	0.661649	0.371644
H	4.105831	0.941562	-1.107508
H	3.300012	3.157774	-1.637867
H	3.253293	5.581354	-1.128455
H	4.067919	6.405564	1.064309
H	4.934175	4.799599	2.745985
H	4.984070	2.376876	2.233174
O	-4.656809	1.333468	1.596193
C	-6.633262	0.934402	0.304968
F	-6.890592	1.714838	-0.752511
F	-7.296519	1.422172	1.350460
F	-7.115070	-0.285005	0.037721
C	-5.118315	0.880898	0.573304
C	1.280721	0.979980	-1.339234
C	0.549812	-0.184800	-1.108563
F	0.854089	2.161137	-0.910183
F	2.155155	1.151131	-2.343688
C	1.078269	-1.492788	-1.580986
C	0.276310	-2.617469	-1.331114
C	2.363995	-1.689343	-2.108822
C	0.741223	-3.895324	-1.594288
H	-0.703792	-2.458708	-0.894207
C	2.828596	-2.977648	-2.374125
H	3.012074	-0.846832	-2.321116
C	2.027520	-4.081285	-2.109441
H	0.111420	-4.753428	-1.382046
H	3.825218	-3.112493	-2.783273
H	2.396087	-5.083297	-2.305914
O	-0.415691	-0.162765	-0.279499
Si	-2.678186	0.157174	-0.378530
C	-2.213042	1.972034	-0.319805
H	-3.092585	2.620749	-0.345980
H	-1.646445	2.195741	0.587311
H	-1.573235	2.215921	-1.171595
C	-2.644537	-0.666077	-2.065475
H	-3.067454	-1.675175	-2.005888
H	-3.283846	-0.096632	-2.748036
H	-1.649405	-0.740006	-2.507723
C	-2.540336	-0.935507	1.146865
H	-3.519324	-1.222682	1.538929
H	-1.977313	-1.840884	0.902898
H	-1.997796	-0.410394	1.938694

TS4-2b

M062X/BSI SCF energy: -2259.028458 a.u.

M062X/BSII SCF energy in solution: -2259.528328 a.u.

M062X/BSII free energy in solution: -2259.054906 a.u.

S	0.449233	0.747236	-1.261665
O	1.412421	-2.034371	-1.959143
C	1.359078	2.191036	-1.947098
C	-0.632781	0.328437	-2.689170
C	2.477948	2.564059	-1.020543
C	3.671816	1.837249	-1.052499

C	4.689703	2.128189	-0.150994
C	4.520011	3.147088	0.787213
C	3.335316	3.880091	0.815860
C	2.313188	3.589507	-0.086110
C	-1.932488	-0.286208	-2.257639
C	-1.961212	-1.553368	-1.662007
C	-3.176053	-2.102795	-1.267429
C	-4.365340	-1.400962	-1.473922
C	-4.339344	-0.147228	-2.079585
C	-3.123251	0.413030	-2.465512
H	1.722443	1.823959	-2.911810
H	3.791751	1.031917	-1.773636
H	5.612758	1.557961	-0.176338
H	5.313827	3.371031	1.492834
H	3.204978	4.677086	1.540695
H	1.388045	4.160296	-0.070013
H	-0.785873	1.257638	-3.243796
H	-0.006481	-0.363359	-3.258640
H	-1.027660	-2.084560	-1.499876
H	-3.197744	-3.081600	-0.798115
H	-5.311174	-1.833137	-1.161325
H	-5.262549	0.399377	-2.244631
H	-3.094747	1.395208	-2.930363
O	0.704271	-1.896827	0.167996
C	2.950633	-2.631032	-0.301652
F	3.103104	-2.710012	1.027177
F	3.907266	-1.805531	-0.762563
F	3.199759	-3.846085	-0.806491
C	1.549198	-2.134148	-0.739502
H	0.631490	2.990796	-2.107599
C	-0.698178	1.595189	-0.133764
C	-1.485699	0.602590	0.692849
C	-2.916119	0.748464	0.914061
C	-3.587522	-0.279629	1.603338
C	-3.622539	1.892446	0.502365
C	-4.942920	-0.165489	1.868151
H	-3.039247	-1.163771	1.910977
C	-4.975989	2.003871	0.786515
H	-3.128938	2.704940	-0.017930
C	-5.635763	0.976072	1.461245
H	-5.461114	-0.963020	2.389088
H	-5.519147	2.890887	0.479754
H	-6.696903	1.065736	1.672253
O	-0.890971	-0.347434	1.247418
Si	0.682491	-0.797575	2.087572
C	2.239252	0.092522	1.547110
H	2.968828	-0.029697	2.358138
H	2.708075	-0.227053	0.618993
H	2.036461	1.169462	1.486005
C	0.151744	0.301783	3.551515
H	-0.778096	-0.054322	4.009612
H	0.930038	0.279200	4.324364
H	0.004030	1.349580	3.263156
C	0.550101	-2.510640	2.814483
H	0.762207	-2.480883	3.887506
H	-0.486483	-2.847515	2.694162
H	1.198430	-3.236168	2.326529
H	-1.325272	2.264918	-0.722126
H	-0.068200	2.188326	0.545810

IM5-2a^{+}

M062X/BSI SCF energy: -1930.849925 a.u.

M062X/BSII SCF energy in solution: -1931.234727 a.u.

M062X/BSII free energy in solution: -1930.817604 a.u.

S	-0.655148	1.079427	-1.302997
C	-0.788396	0.130347	0.256087
C	-2.323599	0.745828	-1.983150
C	-1.141140	-1.334448	0.105783
C	-1.810192	-1.955176	1.166559
C	-2.122578	-3.309762	1.104546
C	-1.784290	-4.052864	-0.026470
C	-1.136514	-3.434895	-1.093729
C	-0.813035	-2.081137	-1.027532
C	-3.435803	1.019538	-1.007508
C	-4.216278	-0.034467	-0.527739
C	-5.247890	0.205213	0.380005
C	-5.503612	1.501635	0.818126
C	-4.724473	2.559128	0.346065
C	-3.695928	2.319196	-0.559539
H	-1.555775	0.612388	0.875918
H	-2.083824	-1.371204	2.041380
H	-2.636995	-3.783453	1.934581
H	-2.033905	-5.108079	-0.078125
H	-0.876386	-4.006243	-1.979103
H	-0.297945	-1.605009	-1.857463

H	-2.381014	1.407973	-2.851908
H	-2.362018	-0.286828	-2.337530
H	-4.014489	-1.047004	-0.869377
H	-5.849208	-0.622781	0.742912
H	-6.305435	1.689791	1.525347
H	-4.921380	3.572403	0.682758
H	-3.087636	3.143381	-0.924649
C	0.500514	0.360270	1.066416
C	1.805862	0.015554	0.322868
F	0.571365	1.674416	1.398302
F	0.442001	-0.329856	2.227309
C	2.272836	-1.324149	0.106974
C	3.330548	-1.503409	-0.816608
C	1.728427	-2.441564	0.780090
C	3.814356	-2.771159	-1.071602
H	3.741314	-0.642419	-1.333339
C	2.234638	-3.704922	0.522460
H	0.932268	-2.327696	1.503415
C	3.266308	-3.870718	-0.401928
H	4.613146	-2.912767	-1.790562
H	1.820348	-4.563141	1.039549
H	3.650119	-4.866169	-0.603540
O	2.446836	0.978003	-0.177131
Si	2.901075	2.711236	0.055843
C	3.258927	2.861906	1.870172
H	3.900414	3.735316	2.030326
H	2.351174	2.985738	2.463571
H	3.801140	1.982457	2.232140
C	4.424903	2.731231	-1.001047
H	4.188280	2.472065	-2.037646
H	4.869473	3.731985	-0.995790
H	5.172508	2.025535	-0.626243
C	1.550701	3.789552	-0.609349
H	1.909113	4.825083	-0.560982
H	1.338172	3.561575	-1.657499
H	0.625135	3.719546	-0.035138

IM5-2a

M062X/BSI SCF energy: -1521.714138 a.u.

M062X/BSII SCF energy in solution: -1522.055636 a.u.

M062X/BSII free energy in solution: -1521.750527 a.u.

S	0.757967	-1.041180	-0.048860
C	2.128561	-0.472131	-1.118694
C	-0.490665	-1.103435	-1.089555
C	3.445691	-0.615223	-0.408811
C	4.207333	-1.771130	-0.598365
C	5.433439	-1.919304	0.044877
C	5.904507	-0.911183	0.884066
C	5.145039	0.241434	1.080104
C	3.917394	0.391036	0.438954
C	-1.801710	-1.631683	-0.724829
C	-1.996224	-2.496130	0.366292
C	-3.269188	-2.947380	0.685890
C	-4.370216	-2.548942	-0.075809
C	-4.186413	-1.702492	-1.166874
C	-2.912051	-1.247515	-1.491854
H	2.090529	-1.094449	-2.014284
H	3.838985	-2.551745	-1.259389
H	6.020743	-2.818621	-0.113003
H	6.862202	-1.023261	1.383127
H	5.510401	1.027429	1.734001
H	3.308026	1.275386	0.595426
H	-0.385602	-0.594526	-2.045918
H	-1.147354	-2.822150	0.962006
H	-3.405279	-3.616105	1.530074
H	-5.364318	-2.902445	0.179005
H	-5.037524	-1.390969	-1.764466
H	-2.768279	-0.576296	-2.334313
H	1.899133	0.563479	-1.373945
C	0.547509	2.621840	-0.537243
C	0.046705	1.708848	0.322432
C	-1.420107	1.576980	0.567719
C	-1.808443	0.786897	1.656755
C	-2.420379	2.145193	-0.237180
C	-3.154537	0.573076	1.942798
H	-1.033561	0.332623	2.266126
C	-3.764556	1.933997	0.055260
H	-2.159487	2.737372	-1.105810
C	-4.140769	1.148088	1.144687
H	-3.431842	-0.048247	2.789462
H	-4.523580	2.375202	-0.584142
H	-5.190972	0.977806	1.361187
O	0.875258	0.896189	0.951252
F	-0.126174	3.568586	-1.182368
F	1.853142	2.772950	-0.759535

IM5-2b

M062X/BSI SCF energy: -1850.007659 a.u.

M062X/BSII SCF energy in solution: -1850.46091 a.u.

M062X/BSII free energy in solution: -1850.103227 a.u.

S	-0.076549	-0.032327	-0.237850
C	-0.668645	-0.230063	1.485980
C	-0.078509	-1.731866	-0.961790
C	-0.842874	1.135787	2.091005
C	-1.928756	1.928741	1.702023
C	-2.101616	3.190912	2.260595
C	-1.194360	3.668831	3.207473
C	-0.111005	2.882737	3.592864
C	0.067549	1.618235	3.033082
C	0.012680	-2.827369	0.051893
C	1.251943	-3.344106	0.440756
C	1.319436	-4.354313	1.398094
C	0.150063	-4.855090	1.967147
C	-1.089166	-4.347199	1.577040
C	-1.158867	-3.335492	0.624253
H	-1.618503	-0.751633	1.376575
H	-2.626955	1.541326	0.963181
H	-2.947229	3.802058	1.960506
H	-1.332880	4.652952	3.644412
H	0.595963	3.252085	4.329021
H	0.909404	0.998915	3.332483
H	-1.010759	-1.733694	-1.529600
H	0.770537	-1.715693	-1.648719
H	2.160724	-2.964042	-0.019809
H	2.284165	-4.753818	1.694586
H	0.204343	-5.644508	2.710513
H	-2.001316	-4.741082	2.014238
H	-2.116547	-2.922295	0.315860
H	0.055736	-0.845045	2.024977
C	1.679766	0.207283	0.136367
C	2.450188	0.475172	-1.145613
C	3.905516	0.756771	-1.032279
C	4.619398	1.016914	-2.208398
C	4.564344	0.764515	0.201881
C	5.981171	1.282490	-2.149415
H	4.092698	1.006472	-3.157188
C	5.929387	1.029068	0.256028
H	4.023668	0.565115	1.121936
C	6.636124	1.287889	-0.916975
H	6.533975	1.485511	-3.060884
H	6.440817	1.034162	1.212905
H	7.700842	1.495224	-0.871849
O	1.873447	0.452259	-2.217328
H	2.068648	-0.669642	0.665677
H	1.741848	1.069612	0.809826
O	-2.874690	-0.500795	-0.396763
O	-2.485884	-0.378877	-2.622871
C	-4.351356	0.767451	-1.693972
F	-5.457311	0.129864	-1.268893
F	-4.592921	1.186729	-2.941894
F	-4.225407	1.870264	-0.927028
C	-3.096847	-0.138489	-1.575876

IM6-2a

M062X/BSI SCF energy: -2457.028177 a.u.

M062X/BSII SCF energy in solution: -2457.603372 a.u.

M062X/BSII free energy in solution: -2457.161629 a.u.

S	-1.012625	-1.848822	-1.266015
C	-0.725404	-0.909922	0.285440
C	-1.708134	-0.520113	-2.308329
C	-1.969739	-0.766140	1.135830
C	-2.503036	0.510457	1.323543
C	-3.682682	0.678546	2.047159
C	-4.325246	-0.426408	2.601173
C	-3.788352	-1.701976	2.424094
C	-2.619644	-1.873709	1.688630
C	-3.066467	-0.002566	-1.895248
C	-4.112077	-0.862877	-1.546833
C	-5.349445	-0.352623	-1.165600
C	-5.561632	1.026887	-1.136996
C	-4.527881	1.888816	-1.493341
C	-3.285338	1.376468	-1.866460
H	-0.365310	0.081411	-0.013378
H	-2.004921	1.360988	0.863288
H	-4.102331	1.672544	2.170645
H	-5.245254	-0.296572	3.162929
H	-4.286371	-2.566243	2.852768
H	-2.219530	-2.871721	1.535128

H	-0.986175	0.299335	-2.335334
H	-1.752305	-0.977185	-3.302902
H	-3.946027	-1.937145	-1.551196
H	-6.149823	-1.031342	-0.885731
H	-6.525731	1.423356	-0.833002
H	-4.682543	2.963538	-1.468640
H	-2.461677	2.044926	-2.099106
C	0.402353	-1.593510	1.064196
C	1.828977	-1.322657	0.533299
F	0.398466	-1.149549	2.348746
F	0.205825	-2.938038	1.137804
C	2.465671	-2.038611	-0.548357
C	3.585185	-1.419615	-1.143979
C	2.028582	-3.296595	-1.008722
C	4.247721	-2.047180	-2.184166
H	3.890173	-0.436468	-0.803502
C	2.714109	-3.921442	-2.039046
H	1.183965	-3.794388	-0.554917
C	3.815124	-3.299483	-2.627816
H	5.096729	-1.564781	-2.655524
H	2.387718	-4.895511	-2.385703
H	4.338536	-3.792339	-3.441188
O	2.484906	-0.433083	1.120565
Si	2.415672	0.972492	2.233345
C	2.900771	0.201459	3.850498
H	3.027591	0.985766	4.604550
H	2.135308	-0.492867	4.207122
H	3.849154	-0.336545	3.761623
C	3.761199	1.991078	1.463371
H	3.584876	2.096942	0.390287
H	3.803543	2.989051	1.910270
H	4.731908	1.507077	1.610131
C	0.746312	1.783056	2.288513
H	0.891844	2.756362	2.774045
H	0.297616	1.971151	1.310329
H	0.044727	1.206840	2.896107
O	-0.372154	2.149820	-0.942698
O	1.561975	0.977138	-1.003957
C	1.628162	3.344476	-1.185331
F	1.696462	3.945486	0.022678
F	1.020890	4.204608	-2.014267
F	2.889117	3.198758	-1.619870
C	0.859616	2.003806	-1.054988

IM7-2a

M062X/BSI SCF energy: -1521.700206 a.u.

M062X/BSII SCF energy in solution: -1522.047032 a.u.

M062X/BSII free energy in solution: -1521.743856 a.u.

S	1.397734	0.893402	0.233078
C	-0.078849	0.984604	-0.832510
C	2.614224	0.427054	-1.055030
C	-1.215702	1.659614	-0.103033
C	-1.976772	2.608633	-0.787498
C	-3.073360	3.209434	-0.173733
C	-3.417875	2.859817	1.130295
C	-2.657679	1.916589	1.821167
C	-1.557730	1.321708	1.209657
C	3.965534	0.249964	-0.418376
C	4.860223	1.321432	-0.356002
C	6.104768	1.169276	0.251322
C	6.464124	-0.057097	0.807364
C	5.573813	-1.128926	0.755274
C	4.330147	-0.975241	0.147376
H	0.189368	1.574102	-1.712515
H	-1.711600	2.870202	-1.808641
H	-3.657830	3.947478	-0.714204
H	-4.275071	3.322838	1.609197
H	-2.923248	1.641544	2.837208
H	-0.978753	0.575072	1.748212
H	2.268583	-0.496408	-1.522717
H	2.640215	1.223007	-1.804328
H	4.577013	2.276684	-0.791394
H	6.794076	2.007385	0.287845
H	7.434607	-0.178204	1.278723
H	5.849454	-2.086485	1.186714
H	3.632880	-1.808189	0.108277
C	-0.122424	-2.205835	-0.148735
C	-0.951244	-1.248444	-0.566728
C	-2.410101	-1.255957	-0.321143
C	-3.246138	-0.618719	-1.245748
C	-2.976175	-1.852527	0.812693
C	-4.621648	-0.581301	-1.041714
H	-2.807648	-0.143500	-2.117413
C	-4.353532	-1.817634	1.008203
H	-2.341650	-2.322827	1.555893

C	-5.181318	-1.181344	0.085191
H	-5.257818	-0.080326	-1.765052
H	-4.779072	-2.276938	1.895096
H	-6.254286	-1.148603	0.245929
O	-0.420436	-0.291524	-1.401735
F	-0.480563	-3.265472	0.551918
F	1.165766	-2.255603	-0.429912

TS5-2a

M062X/BSI SCF energy: -2457.021579 a.u.

M062X/BSII SCF energy in solution: -2457.595846 a.u.

M062X/BSII free energy in solution: -2457.153148 a.u.

S	-0.398661	-1.138942	-1.801956
C	-0.599117	-1.127941	0.020472
C	-1.205503	0.449983	-2.224646
C	-1.887413	-1.754734	0.514643
C	-2.700032	-1.034787	1.391978
C	-3.904915	-1.571529	1.841075
C	-4.301640	-2.839524	1.423733
C	-3.489931	-3.566352	0.552889
C	-2.290700	-3.027177	0.096534
C	-2.595184	0.612875	-1.667340
C	-3.617806	-0.284110	-1.997198
C	-4.889959	-0.133117	-1.456704
C	-5.159252	0.922290	-0.581278
C	-4.150059	1.822690	-0.255915
C	-2.871833	1.667070	-0.795477
H	-0.536550	-0.080957	0.343336
H	-2.401035	-0.037775	1.701012
H	-4.535313	-0.991924	2.508589
H	-5.241682	-3.257908	1.769951
H	-3.795896	-4.553541	0.220749
H	-1.677005	-3.590246	-0.600103
H	-0.551936	1.254917	-1.887413
H	-1.210419	0.447796	-3.319226
H	-3.406139	-1.113044	-2.668504
H	-5.673964	-0.838990	-1.714255
H	-6.151698	1.037290	-0.156275
H	-4.350929	2.646828	0.422008
H	-2.091144	2.378925	-0.540129
C	0.612022	-1.837395	0.621999
C	1.967464	-1.147871	0.351652
F	0.486559	-1.867678	1.976371
F	0.667017	-3.129565	0.218934
C	2.995621	-1.640391	-0.553342
C	4.267896	-1.041997	-0.447803
C	2.774512	-2.643628	-1.517174
C	5.297304	-1.442705	-1.281605
H	4.437242	-0.273967	0.298741
C	3.811400	-3.026606	-2.355404
H	1.805947	-3.110489	-1.632271
C	5.068404	-2.433635	-2.238144
H	6.276363	-0.985677	-1.189706
H	3.638867	-3.791203	-3.104537
H	5.874418	-2.744891	-2.895343
O	2.200167	-0.124287	1.017684
Si	1.642271	1.002562	2.361063
C	2.572633	-0.027515	3.646357
H	2.497834	0.468696	4.621375
H	2.160093	-1.035711	3.754207
H	3.637228	-0.120489	3.405559
C	2.613213	2.591254	2.218860
H	1.959870	3.452539	2.061980
H	3.196829	2.749692	3.131003
H	3.309901	2.533056	1.376483
C	-0.123456	1.007547	2.955387
H	-0.094625	1.393957	3.982889
H	-0.769453	1.646749	2.354103
H	-0.524447	-0.007303	3.010910
O	-0.375983	3.544743	0.969852
O	0.812650	1.731882	0.304982
C	0.666310	3.618170	-1.128141
F	1.524021	4.622163	-0.875180
F	-0.422449	4.159287	-1.696681
F	1.242587	2.828090	-2.043223
C	0.311711	2.886053	0.191116

TS5A-2a

M062X/BSI SCF energy: -2048.332541 a.u.

M062X/BSII SCF energy in solution: -2048.850666 a.u.

M062X/BSII free energy in solution: -2048.51332 a.u.

S	0.389337	-0.610278	-0.026104

O	3.069804	0.562745	-0.314088
C	1.435882	-1.758356	0.927099
C	0.063302	0.615630	1.125242
C	1.774049	-2.964529	0.101431
C	2.855874	-2.918095	-0.782216
C	3.172877	-4.032038	-1.554310
C	2.408435	-5.193501	-1.449265
C	1.324262	-5.239260	-0.574154
C	1.003877	-4.125253	0.198080
C	-0.802829	1.717773	0.600454
C	-0.385001	2.496297	-0.486173
C	-1.210870	3.493553	-0.998562
C	-2.454203	3.740577	-0.418544
C	-2.865387	2.986362	0.680094
C	-2.045910	1.981146	1.184703
H	2.318151	-1.161918	1.168424
H	3.443679	-2.006272	-0.855633
H	4.017455	-3.995266	-2.235119
H	2.658500	-6.063306	-2.048767
H	0.728182	-6.142816	-0.493323
H	0.157872	-4.149101	0.879530
H	-0.237842	0.203368	2.091978
H	1.336037	1.193841	1.301088
H	0.588018	2.316423	-0.940361
H	-0.880543	4.082245	-1.848899
H	-3.099656	4.515787	-0.819598
H	-3.833907	3.169397	1.136058
H	-2.382488	1.367109	2.017000
O	2.335271	1.877365	1.363824
C	4.079832	2.695432	0.009820
F	3.440176	3.623663	-0.719849
F	5.097661	2.235555	-0.717005
F	4.578325	3.301760	1.090229
C	3.090984	1.572443	0.376711
H	0.880375	-2.003006	1.833879
C	-2.307751	-1.628099	1.660205
C	-2.158249	-1.313967	0.370045
C	-3.123052	-0.574538	-0.465272
C	-2.663988	-0.004878	-1.659580
C	-4.458152	-0.374969	-0.085889
C	-3.507929	0.783485	-2.436073
H	-1.643232	-0.176067	-1.986998
C	-5.298236	0.406370	-0.872760
H	-4.849180	-0.824136	0.818732
C	-4.826473	0.998555	-2.042891
H	-3.129398	1.228154	-3.351256
H	-6.329103	0.552921	-0.565704
H	-5.483443	1.615177	-2.647954
O	-0.960878	-1.685889	-0.202123
F	-3.362446	-1.370943	2.398979
F	-1.381552	-2.251449	2.362595

TS5-2b

M062X/BSI SCF energy: -1849.967977 a.u.

M062X/BSII SCF energy in solution: -1850.423094 a.u.

M062X/BSII free energy in solution: -1850.067443 a.u.

S	0.469472	-1.217391	1.443495
C	0.220590	-2.520083	0.184759
C	-1.589755	0.097756	1.082047
C	1.478490	-3.287183	-0.120313
C	1.931268	-4.290615	0.741440
C	3.102982	-4.985830	0.456962
C	3.836595	-4.681781	-0.690086
C	3.392287	-3.681693	-1.551871
C	2.217539	-2.987645	-1.267851
C	-1.229944	0.728603	-0.177701
C	-0.628723	1.996143	-0.183517
C	-0.250475	2.581316	-1.385353
C	-0.479520	1.912110	-2.589417
C	-1.108872	0.667736	-2.594148
C	-1.493531	0.079781	-1.393306
H	-0.555536	-3.166994	0.603436
H	1.359403	-4.527188	1.635351
H	3.443575	-5.767371	1.129108
H	4.749980	-5.225109	-0.911438
H	3.957153	-3.442538	-2.447593
H	1.863973	-2.211451	-1.942874
H	-2.113614	-0.848436	1.096673
H	-1.377270	0.589607	2.020742
H	-0.461102	2.512691	0.757574
H	0.224242	3.557651	-1.385861
H	-0.176104	2.368098	-3.526760
H	-1.305676	0.159664	-3.532569
H	-2.008976	-0.877099	-1.388176
H	-0.168894	-2.039583	-0.717856

C	1.685257	-0.215644	0.558995
C	1.899772	1.087038	1.303375
C	2.793677	2.103993	0.680839
C	2.986590	3.314803	1.355235
C	3.418552	1.884891	-0.551997
C	3.799092	4.297387	0.803434
H	2.492891	3.469871	2.309186
C	4.231495	2.871594	-1.101646
H	3.277032	0.950596	-1.087073
C	4.421986	4.075484	-0.425651
H	3.948313	5.236086	1.327222
H	4.715823	2.701296	-2.057627
H	5.057575	4.842826	-0.856879
O	1.349357	1.283945	2.371854
H	1.327303	-0.024819	-0.459939
H	2.631234	-0.763795	0.489195
O	-4.259494	1.819424	-0.634170
O	-3.470924	0.984974	1.316855
C	-4.958893	-0.336934	0.069827
F	-5.691782	-0.366266	-1.047107
F	-5.790462	-0.548019	1.102671
F	-4.125629	-1.402058	0.022969
C	-4.155384	0.976207	0.247132

TS6A-2a

M062X/BSI SCF energy: -1521.700206 a.u.

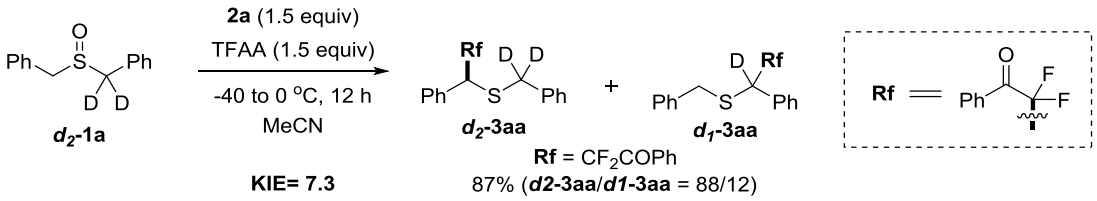
M062X/BSII SCF energy in solution: -1522.047032 a.u.

M062X/BSII free energy in solution: -1521.743856 a.u.

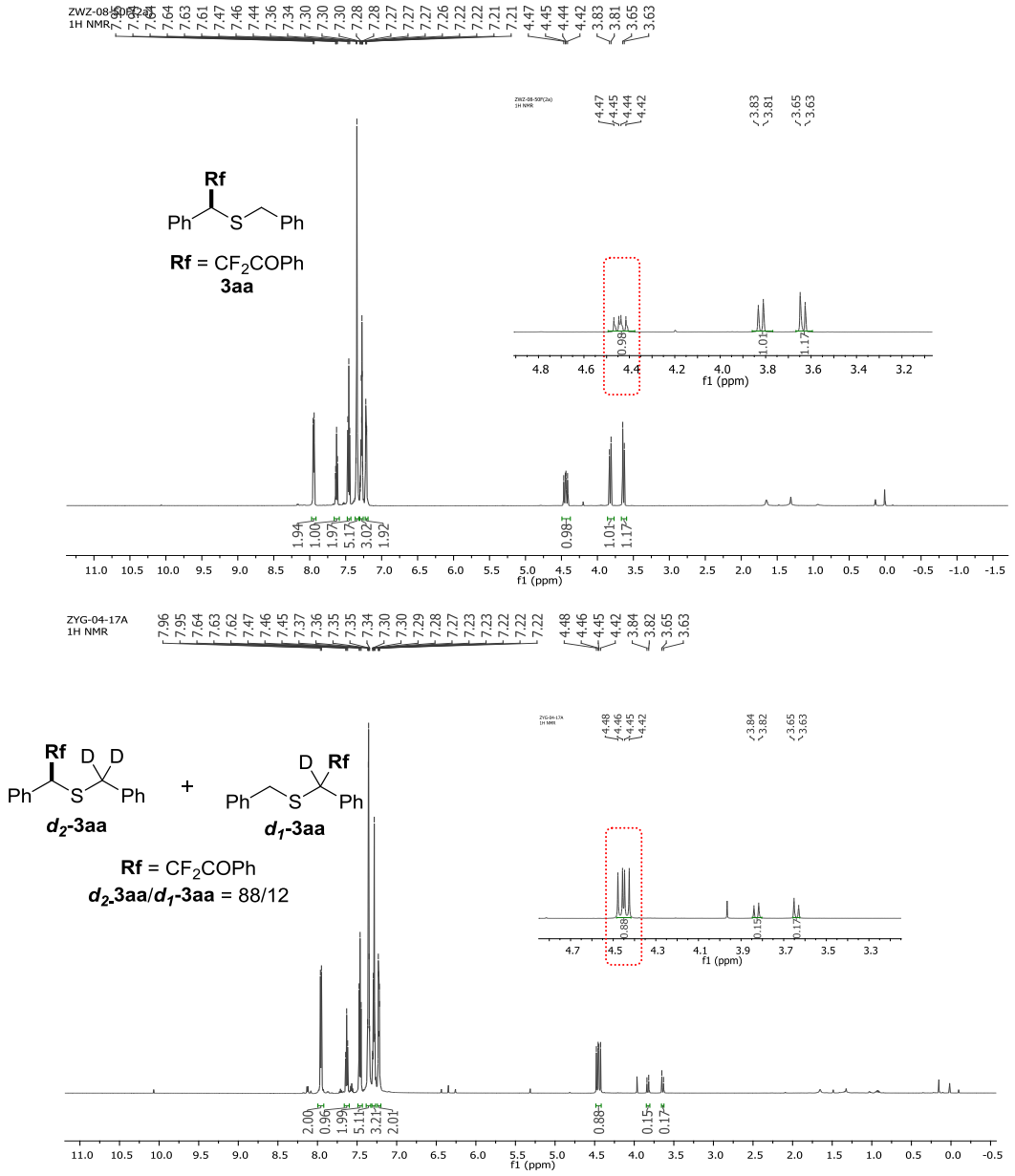
S	-0.158231	-1.905304	-0.297748
C	-1.621207	-2.167438	0.778053
C	1.090602	-2.108320	0.747877
C	-2.855665	-1.790769	0.008381
C	-3.516438	-2.738167	-0.777206
C	-4.650692	-2.378855	-1.501545
C	-5.127437	-1.070123	-1.445206
C	-4.467744	-0.121783	-0.664109
C	-3.330455	-0.477000	0.056705
C	2.480717	-1.988511	0.404345
C	2.919194	-1.606695	-0.881092
C	4.273891	-1.489926	-1.140936
C	5.206353	-1.746245	-0.129579
C	4.783888	-2.120385	1.145499
C	3.427817	-2.239430	1.415647
H	-1.620768	-3.220463	1.067282
H	-3.143259	-3.758711	-0.814730
H	-5.162959	-3.120571	-2.106417
H	-6.012674	-0.790807	-2.008211
H	-4.838781	0.897534	-0.617211
H	-2.800627	0.247224	0.668605
H	0.841471	-2.343839	1.781879
H	2.199720	-1.393360	-1.667353
H	4.610623	-1.193737	-2.128665
H	6.266882	-1.649951	-0.340204
H	5.511312	-2.313662	1.926436
H	3.084611	-2.527408	2.404976
H	-1.452804	-1.508110	1.630011
C	-1.428552	2.414887	1.474159
C	-0.468667	1.680297	0.862484
C	0.516881	2.355443	-0.046327
C	1.696703	1.649206	-0.311702
C	0.331022	3.597073	-0.672173
C	2.672376	2.166154	-1.158571
H	1.824374	0.684582	0.168183
C	1.305582	4.112525	-1.523475
H	-0.580975	4.160088	-0.511548
C	2.481135	3.404404	-1.770147
H	3.581268	1.599717	-1.344891
H	1.140276	5.072151	-2.004959
H	3.235245	3.811040	-2.437102
O	-0.365990	0.400000	1.045059
F	-1.610542	3.745165	1.418183
F	-2.338251	1.878735	2.305253

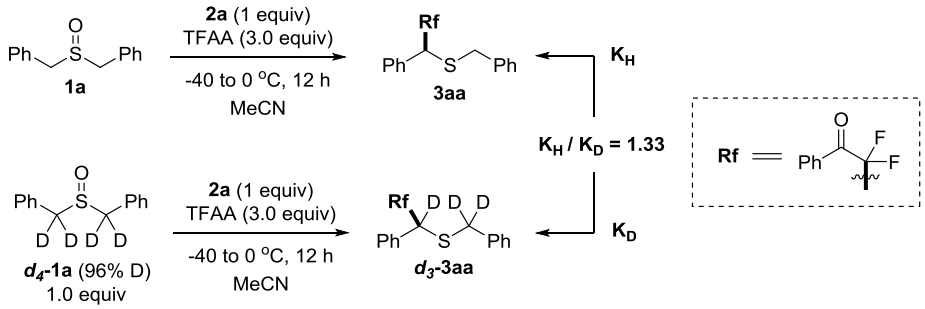
7 KIE studies and control experiments

7.1 KIE studies



To a solution of dibenzyl sulfoxide-d_2 ***d*$_2$-1a** (116 mg, 0.5 mmol) and difluoroenol silyl ether **2a** (171 mg, 0.75 mmol) in MeCN (2.5 mL) was added trifluoroacetic anhydride (105 μL, 0.75 mmol) at -40 °C. After stirring for 5 min, the reaction mixture was gradually warmed to 0 °C and kept stirring for 12 h. After that, the mixture was passed through a short silica gel column and concentrated under vacuum. The obtained residue was further purified by flash chromatography on silica gel affording a mixture of d_2-**3aa** and d_1-**3aa** in 87% yield. The ratio of d_2-**3aa** and d_1-**3aa** (82/12) was determined by ^{1}H NMR as shown blow.





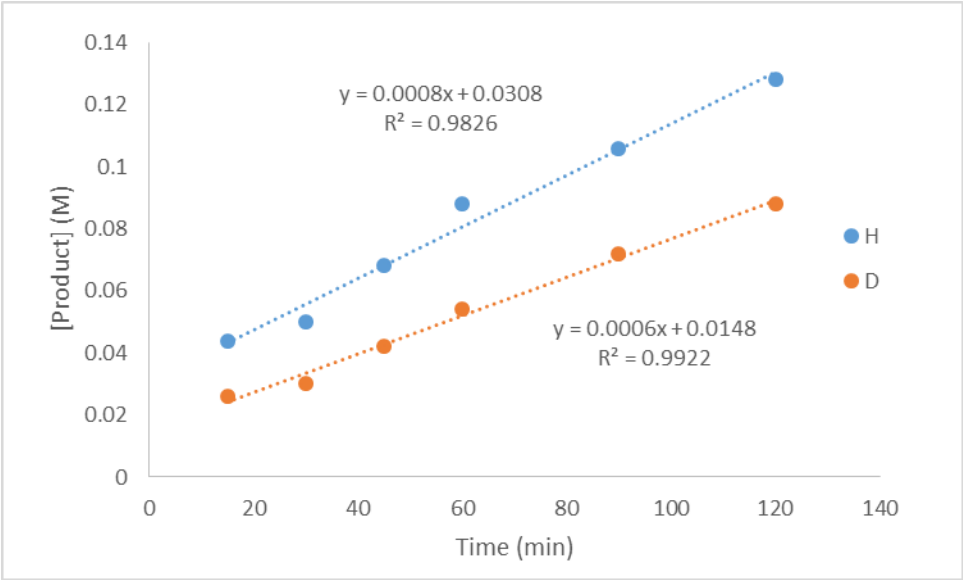
To a mixture of dibenzyl sulfoxide **1a** (115 mg, 0.5 mmol) or dibenzyl sulfoxide-d_4 ***d*$_4$-1a** (117 mg, 0.5 mmol) in MeCN (2.5 mL) was added internal standard trifluorotoluene (73 mg, 0.5 mmol) and trifluoroacetic anhydride (210 μL, 1.5 mmol) at -40 °C. After that, 0.1 mL of reaction mixtures were taken by syringes at the indicated time, and quickly quenched with Et_3N in $CDCl_3$ (0.5 mL, 1 M). The obtained samples were then brought for ^{19}F-NMR analysis. Above experiment was repeated for three times. The resulting data of three experiments was then taken an average for further analysis on Microsoft Excel. The k_H =8.0×10^{-4} min^{-1} and k_D=6.0×10^{-4} min^{-1} were determined by a linear regression model. As the result, the k_H/k_D could be calculated from the equation 8.0×10^{-4}/6.0×10^{-4} = 1.33.

Reaction with 1a

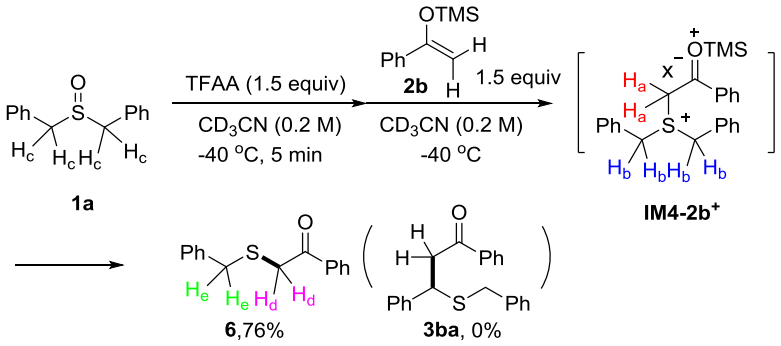
Time (min)	NMR yield (%) 1st trial	NMR yield (%) 2nd trial	NMR yield (%) 3rd trial	NMR yield (%) AVG of 3 trials	[Product] (M)
15	22	25	20	22	0.044
30	26	25	25	25	0.05
45	34	31	37	34	0.068
60	41	44	46	44	0.088
90	51	52	55	53	0.106
120	64	67	62	64	0.128

Reaction with *d*$_4$-1a

Time (min)	NMR yield (%) 1st trial	NMR yield (%) 2nd trial	NMR yield (%) 3rd trial	NMR yield (%) AVG of 3 trials	[Product] (M)
15	14	11	13	13	0.026
30	18	14	13	15	0.03
45	22	20	22	21	0.042
60	24	27	29	27	0.054
90	36	33	40	36	0.072
120	45	42	45	44	0.088



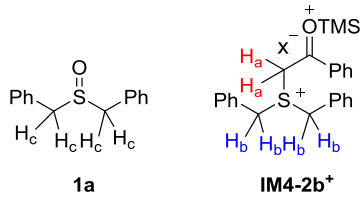
7.2 Control experiments



To a solution of dibenzyl sulfoxide **1a** (0.1 mmol in 0.5 mL of CD_3CN) in NMR tube was added trifluoroacetic anhydride TFAA (21 μL, 0.15 mmol) at – 40 °C. After shaking for 5 min, enol silyl ether **2b** (28 mg, 0.15 mmol) was added, and the resulting tube was quickly inserted into NMR for intermediate determination. After that, the mixture was warmed to 0 °C and then kept at the same temperature for 12 h. During the whole reaction process, no expected product **3ba** was determined. Insteadly, sulfide **6** was obtained in 76% yield. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.65 – 7.60 (m, 1H), 7.48 – 7.44 (m, 2H), 7.49 – 5.32 (m, 4H), 7.30 – 7.27 (m, 1H), 3.79 (s, 2 H), 3.60 (s, 2 H).

The NMR spectra of title compound is consisitant with the data reported in literature (Dias, R. M. P.; Burtoloso, A. C. B. *Org. Lett.* **2016**, *18*, 3034).

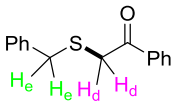
HX-20190306-H
1H NMR



1a

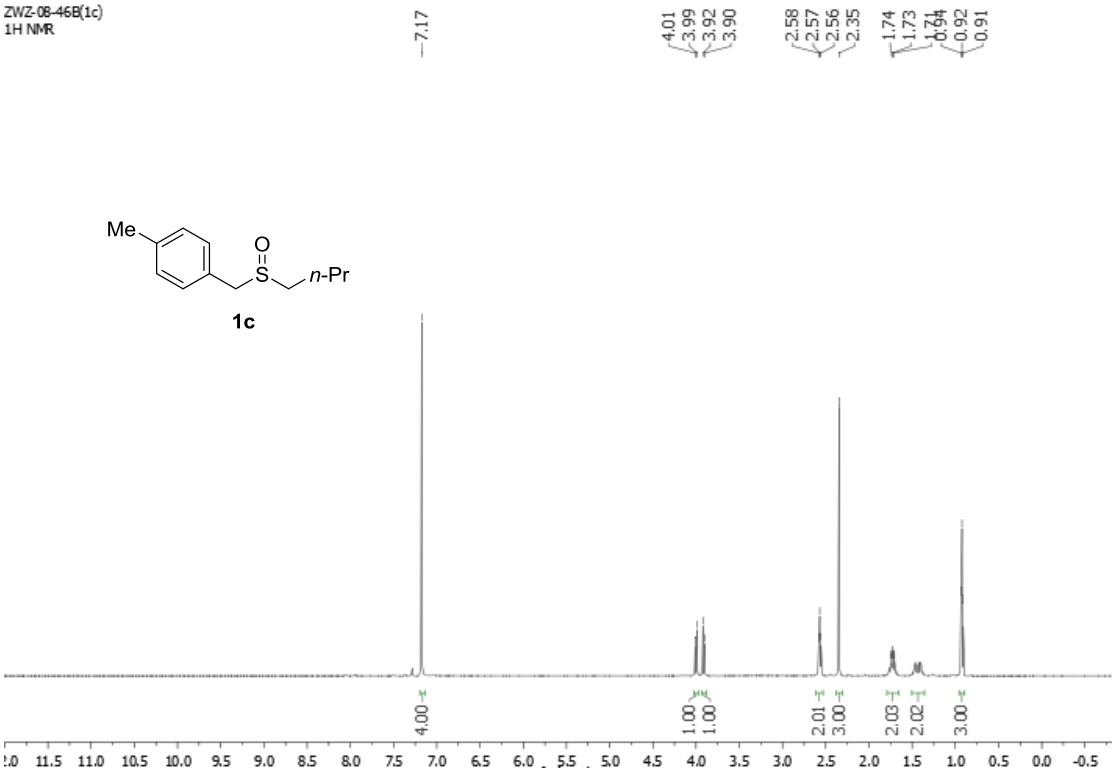
IM4-2b^{+}

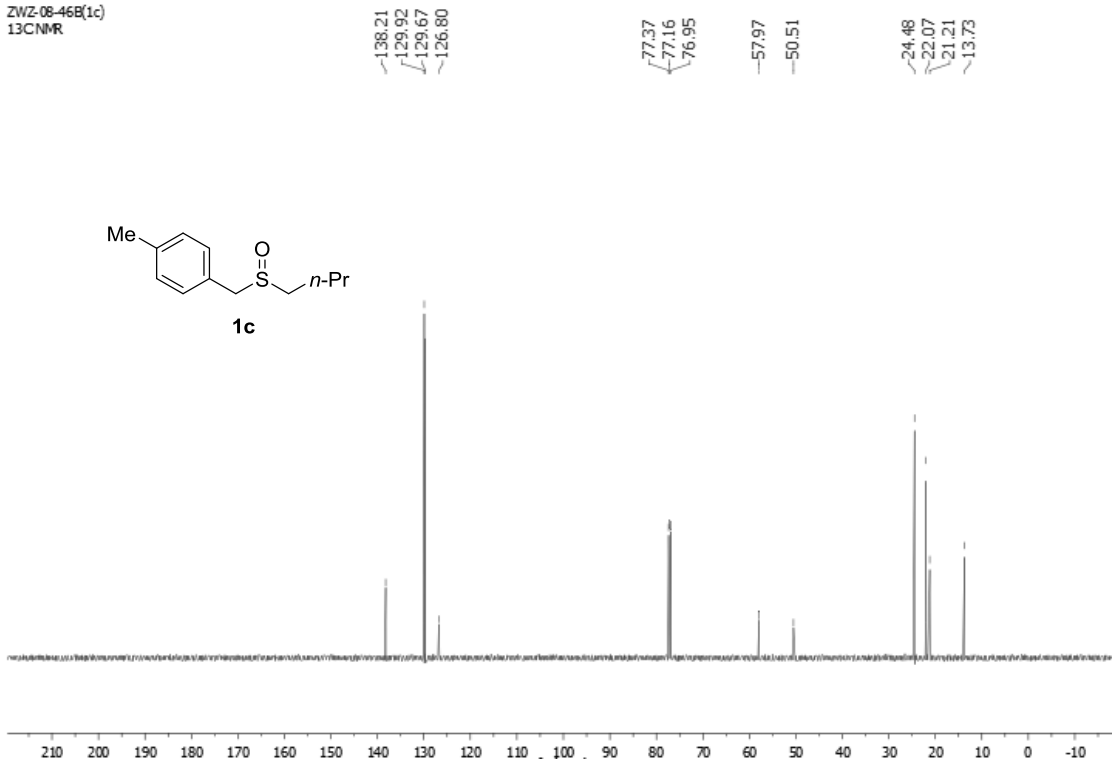
脱干基谱图
1H NMR



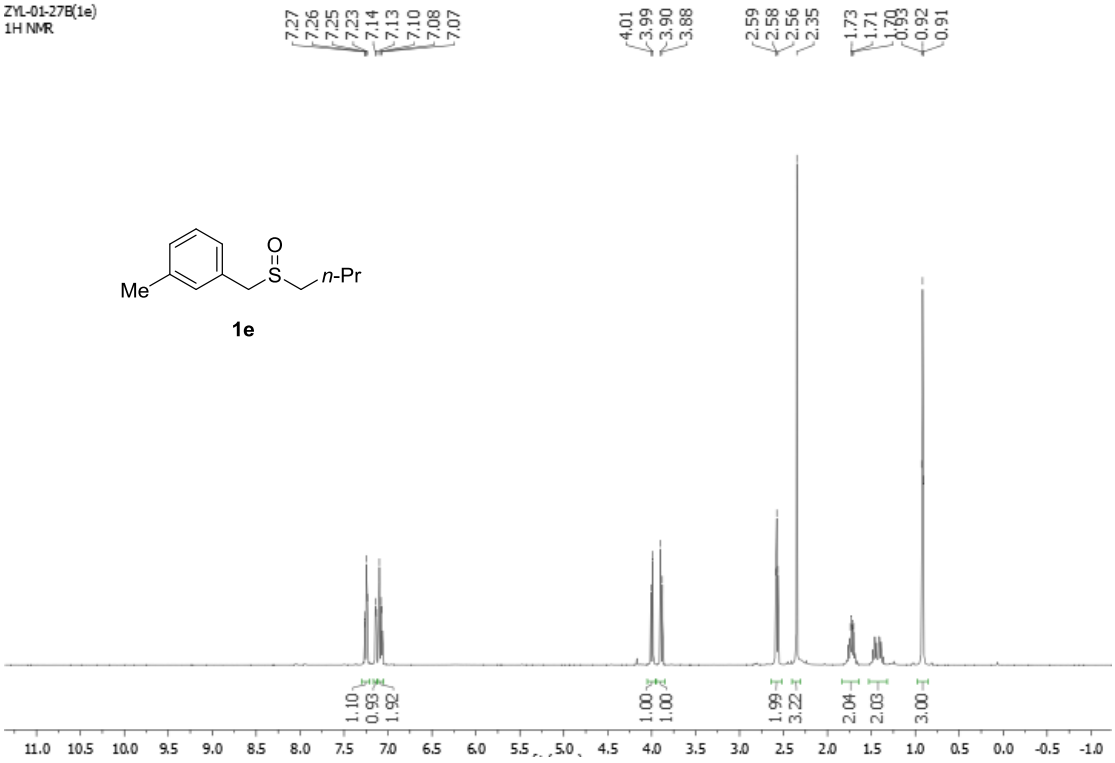
6

8 NMR spectra



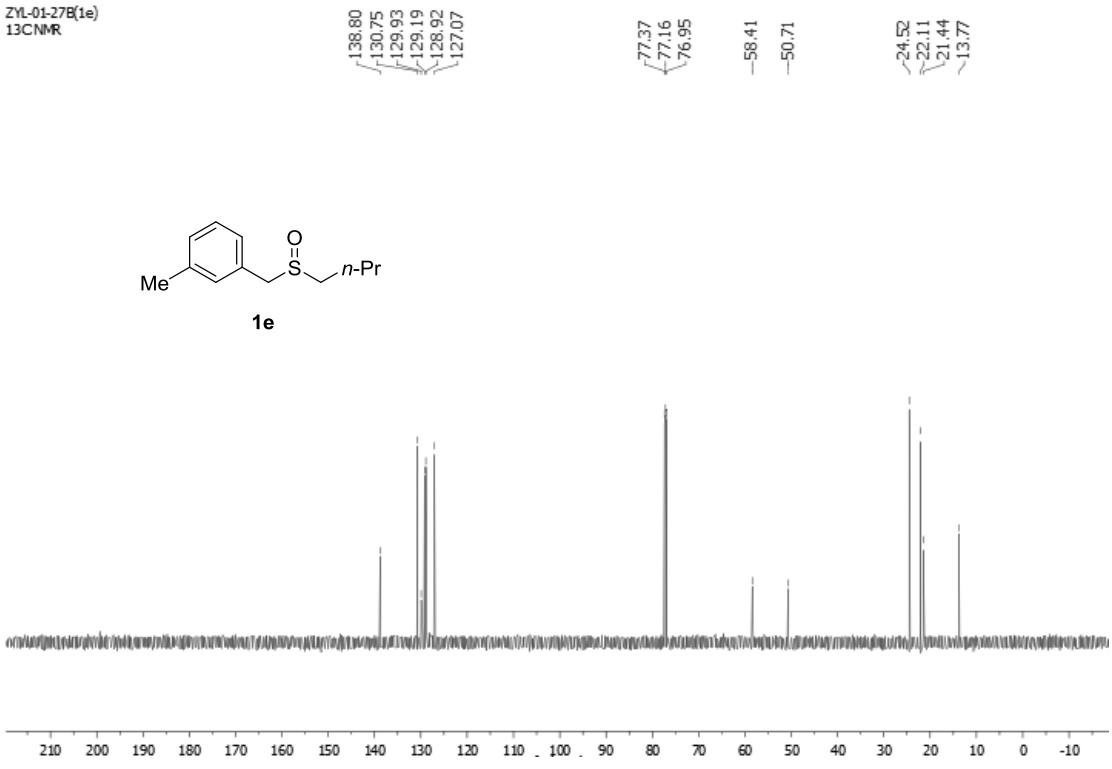


ZYL-01-27B(1e)
1H NMR



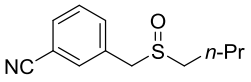
1e

ZYL-01-27B(1e)
13CNMR



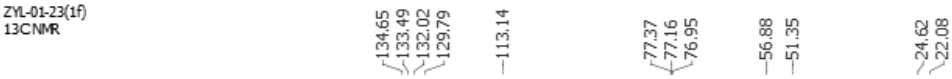
1e

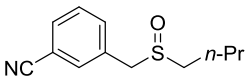
ZYL-01-23(1f)
1H NMR



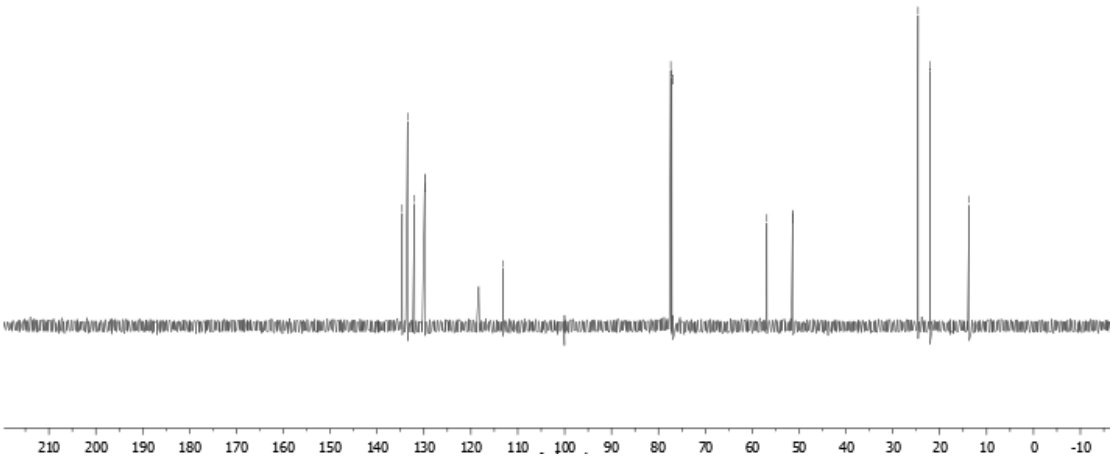
1f

ZYL-01-23(1f)
13CNMR

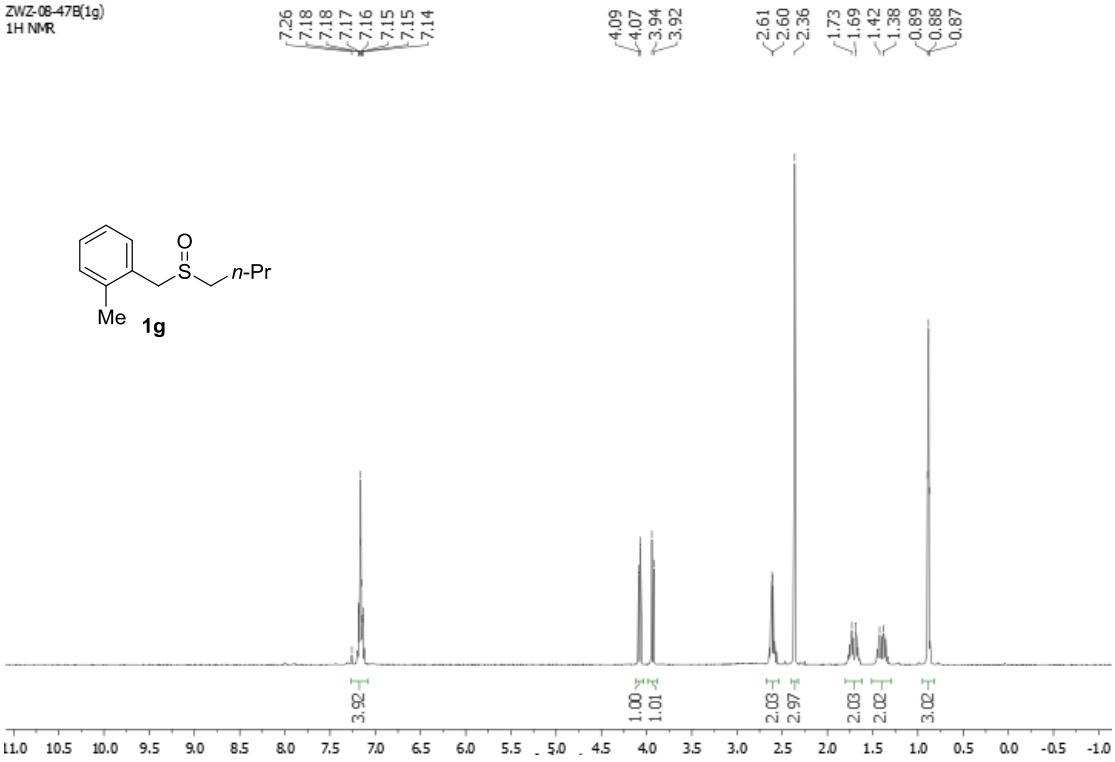




1f

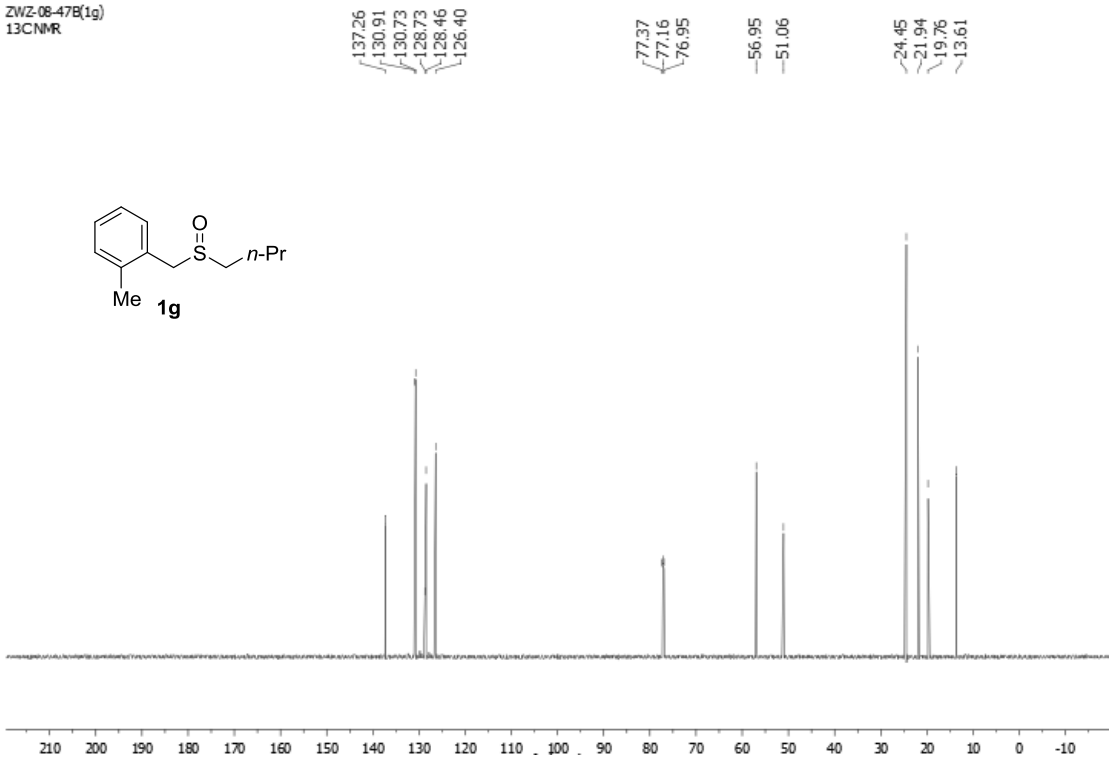


ZWZ-08-47B(1g)
1H NMR



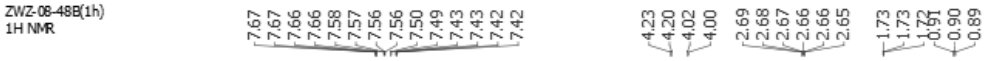
1g

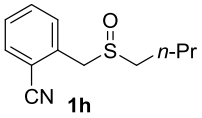
ZWZ-08-47B(1g)
13CNMR



1g

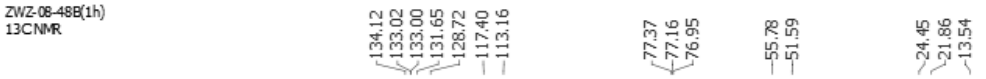
ZWZ-08-48B(1h)
1H NMR

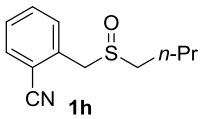




1h

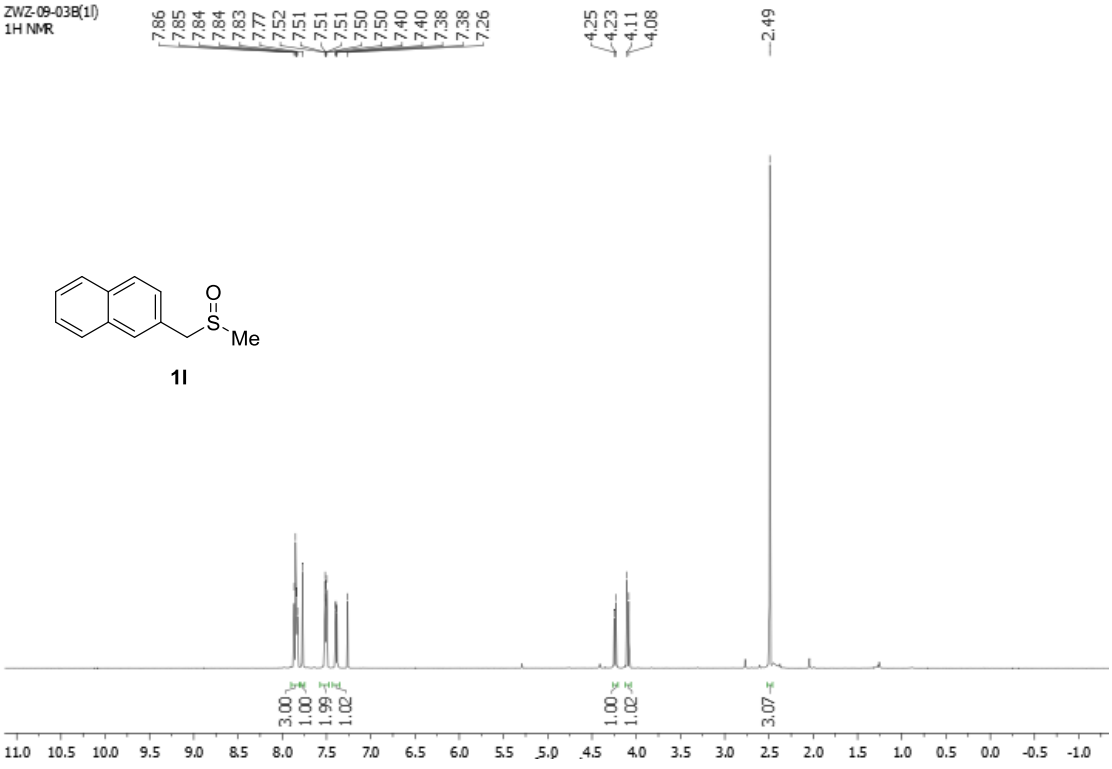
ZWZ-08-48B(1h)
13CNMR





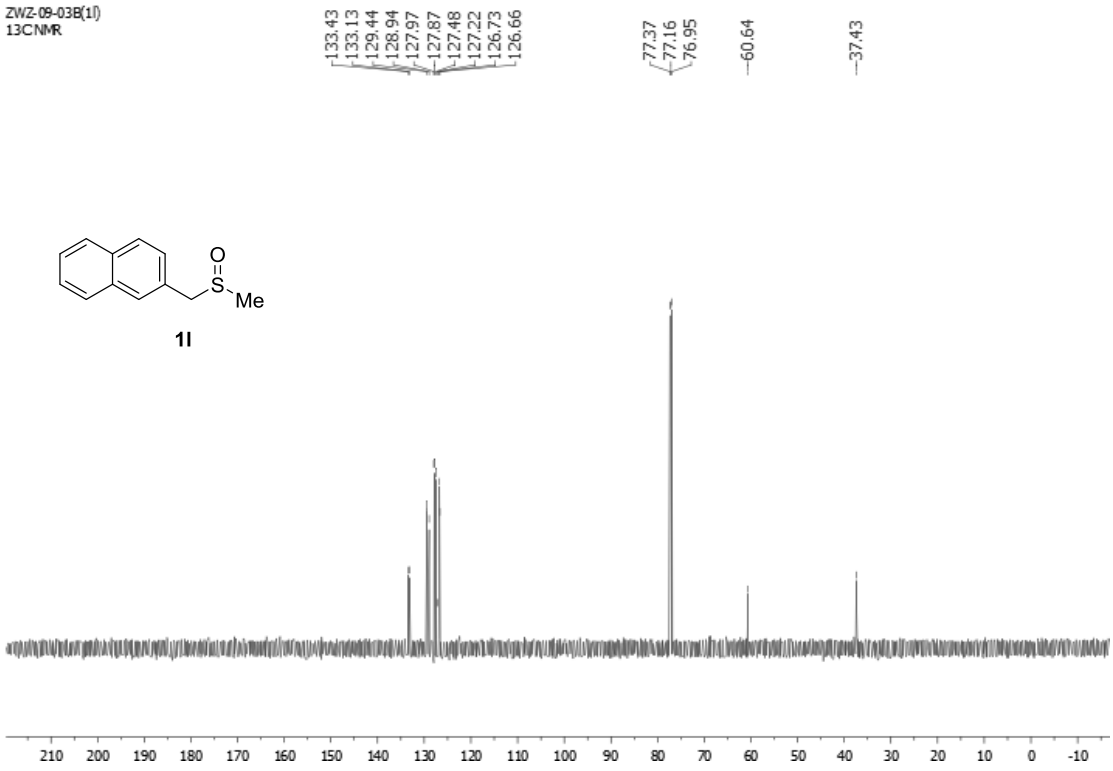
1h

ZWZ-09-03B(1l)
1H NMR



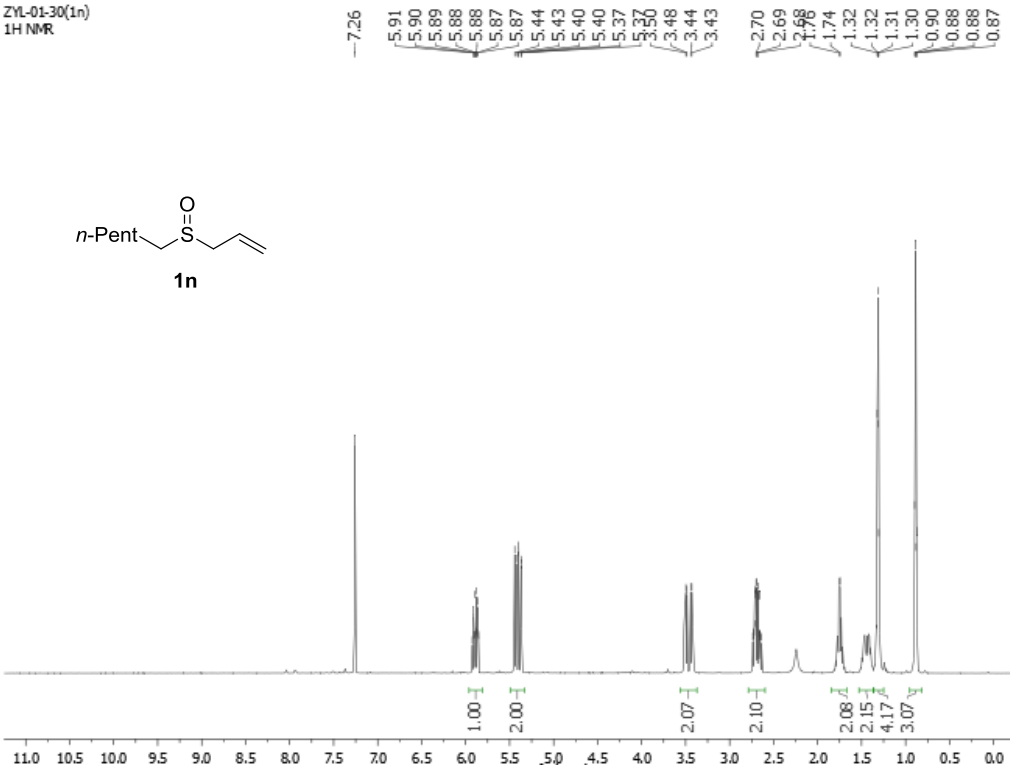
1l

ZWZ-09-03B(1l)
13CNMR



1l

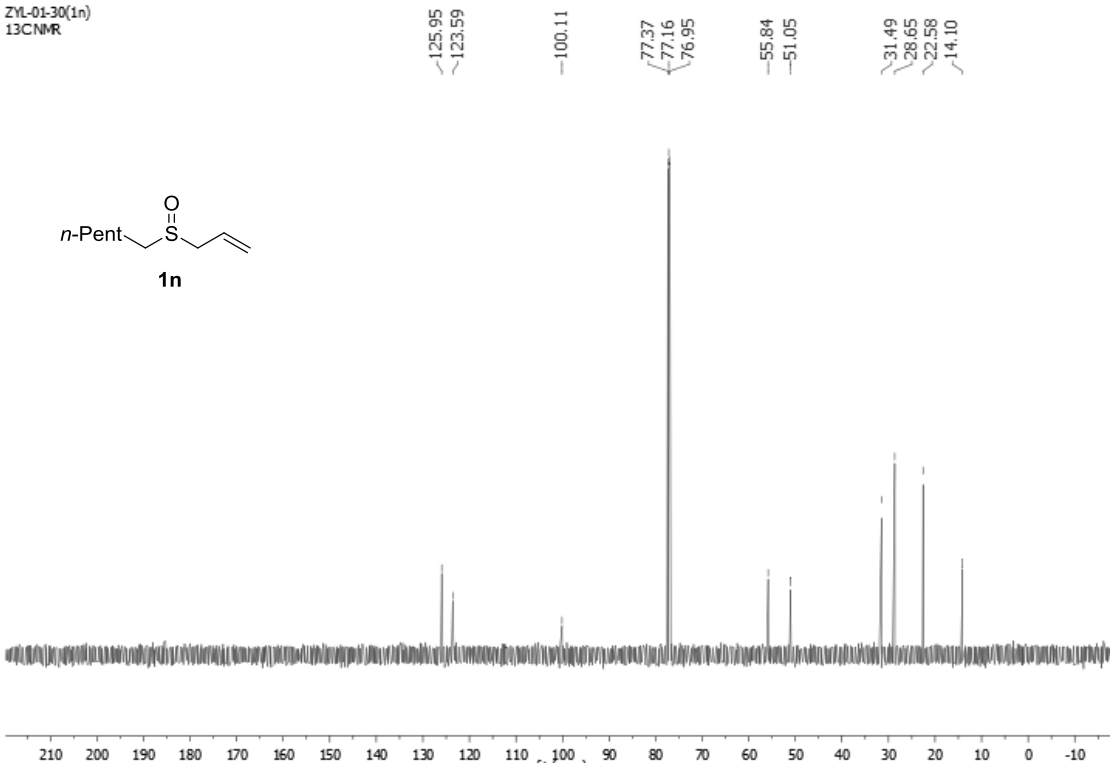
ZYL-01-30(1n)
1H NMR



n-Pent

1n

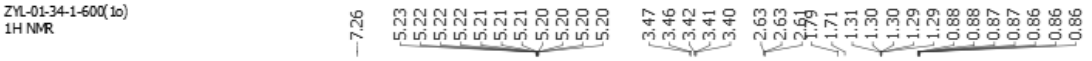
ZYL-01-30(1n)
13CNMR

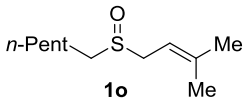


n-Pent

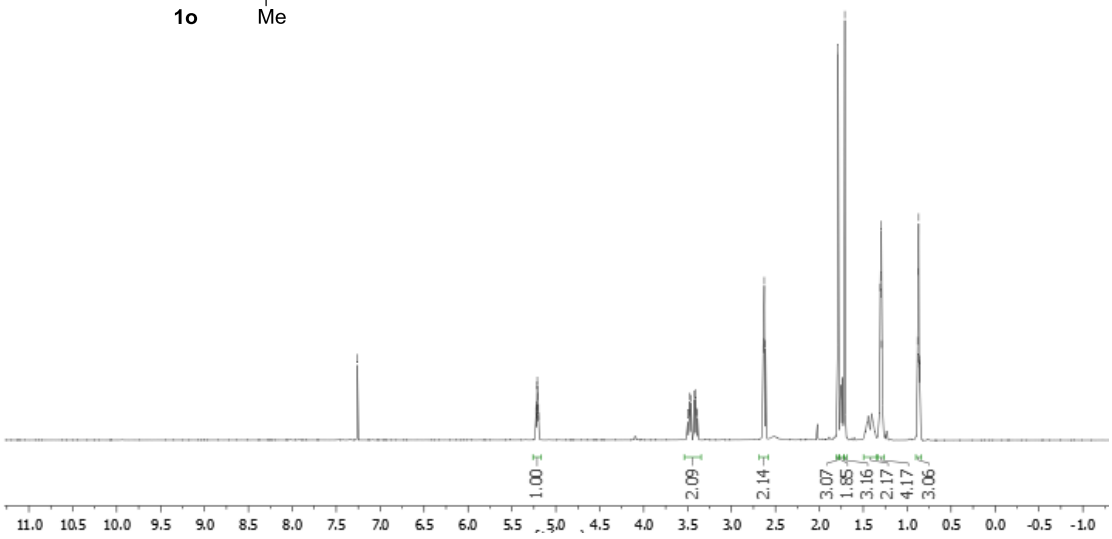
1n

ZYL-01-34-1-600(1o)
1H NMR

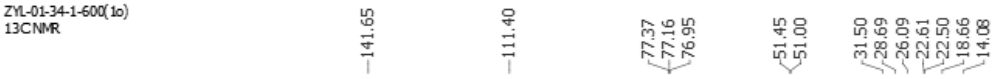


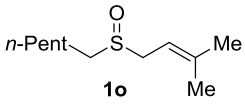


1o

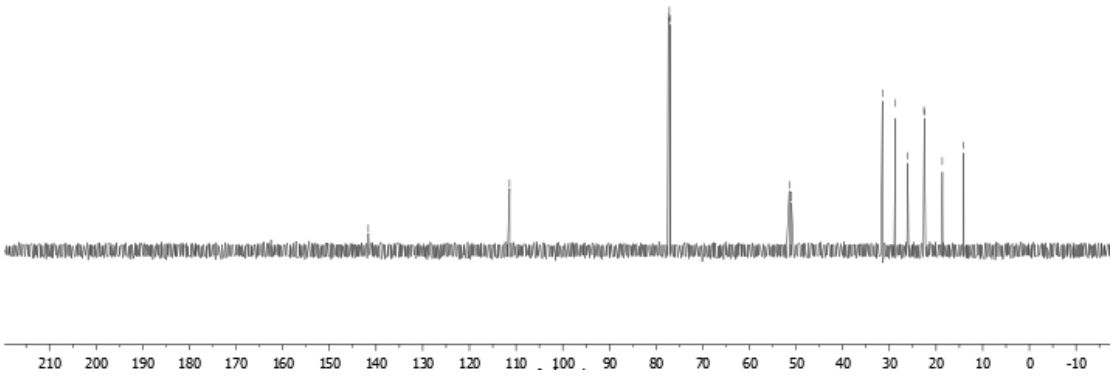


ZYL-01-34-1-600(1o)
13CNMR

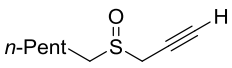




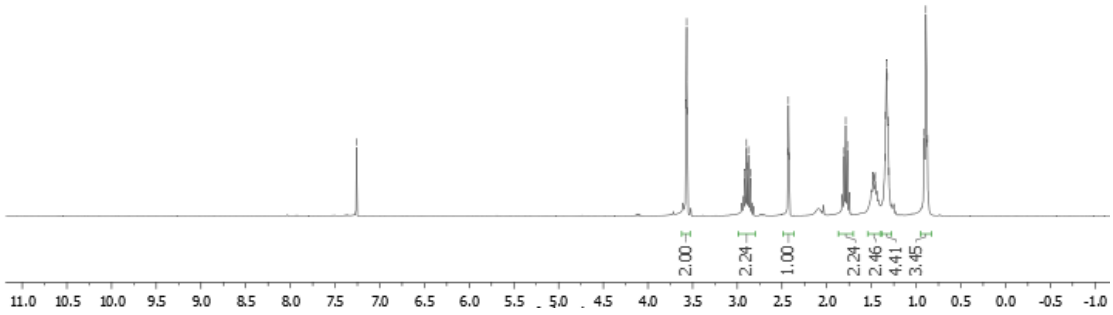
1o



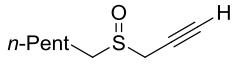
ZYL-01-31(1r)
1H



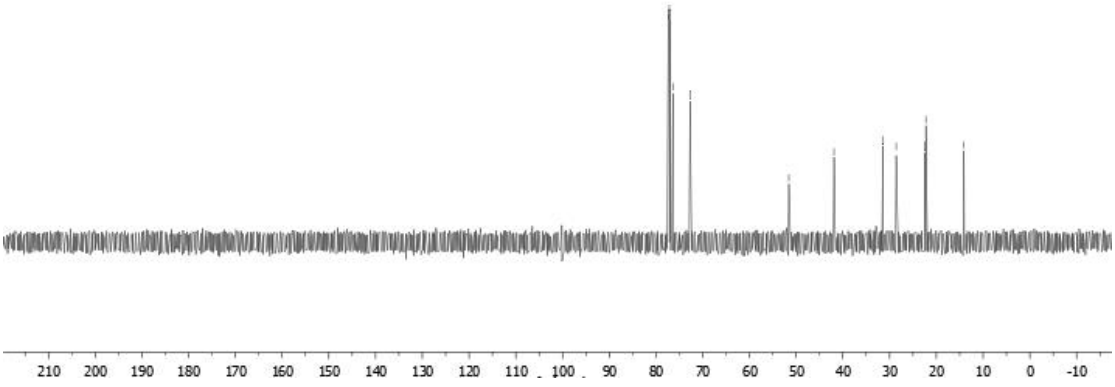
1p

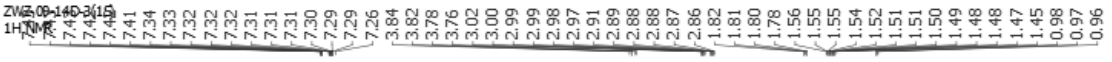


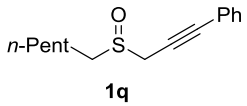
ZYL-01-31(1r)
13CNMR



1p

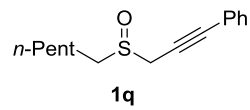




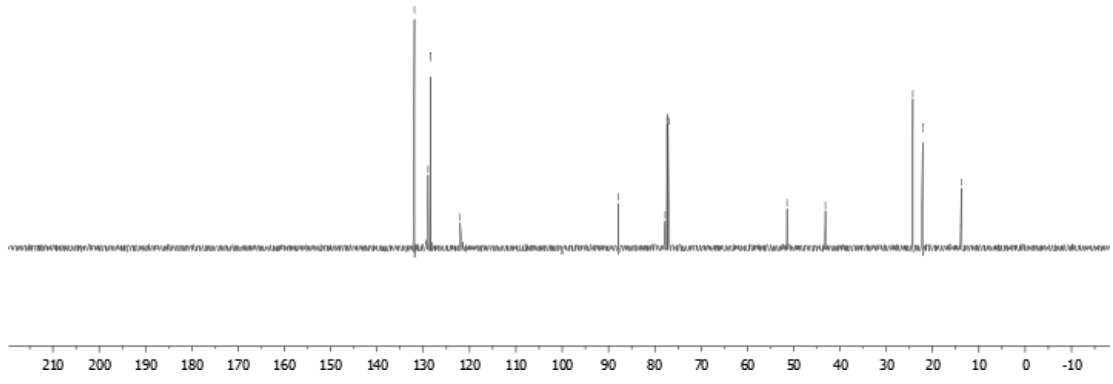


1q

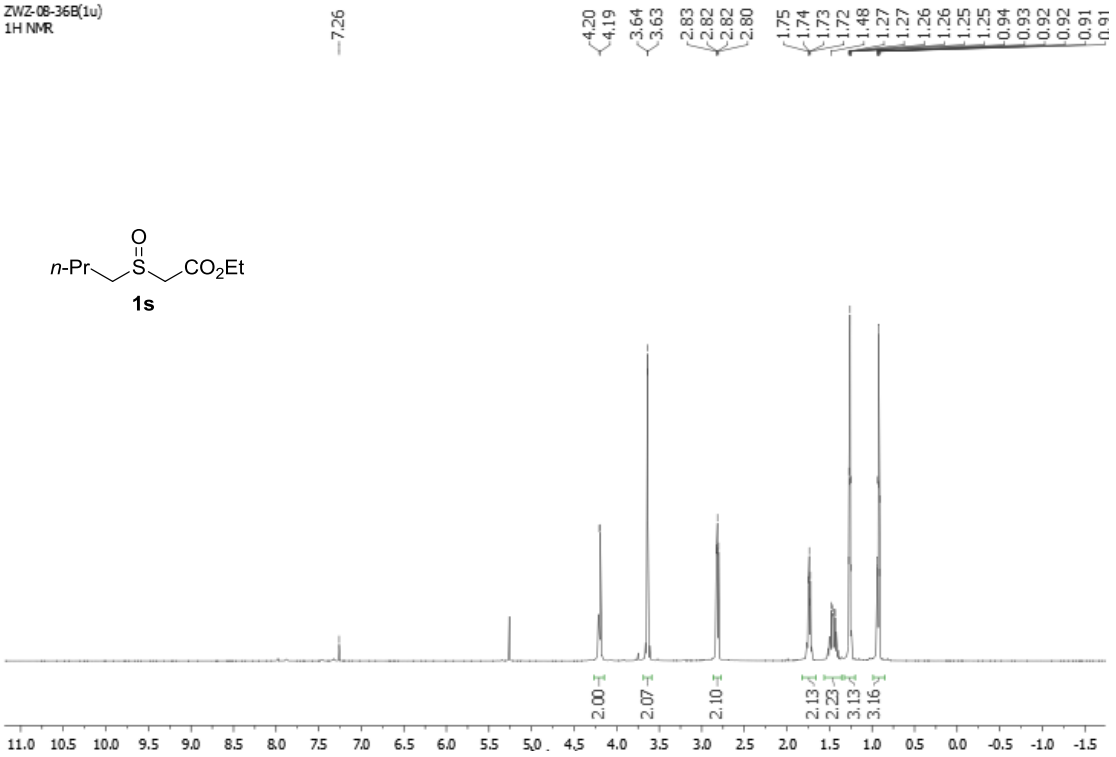
ZWZ-09-14D-3(1S)
13CNMR



1q



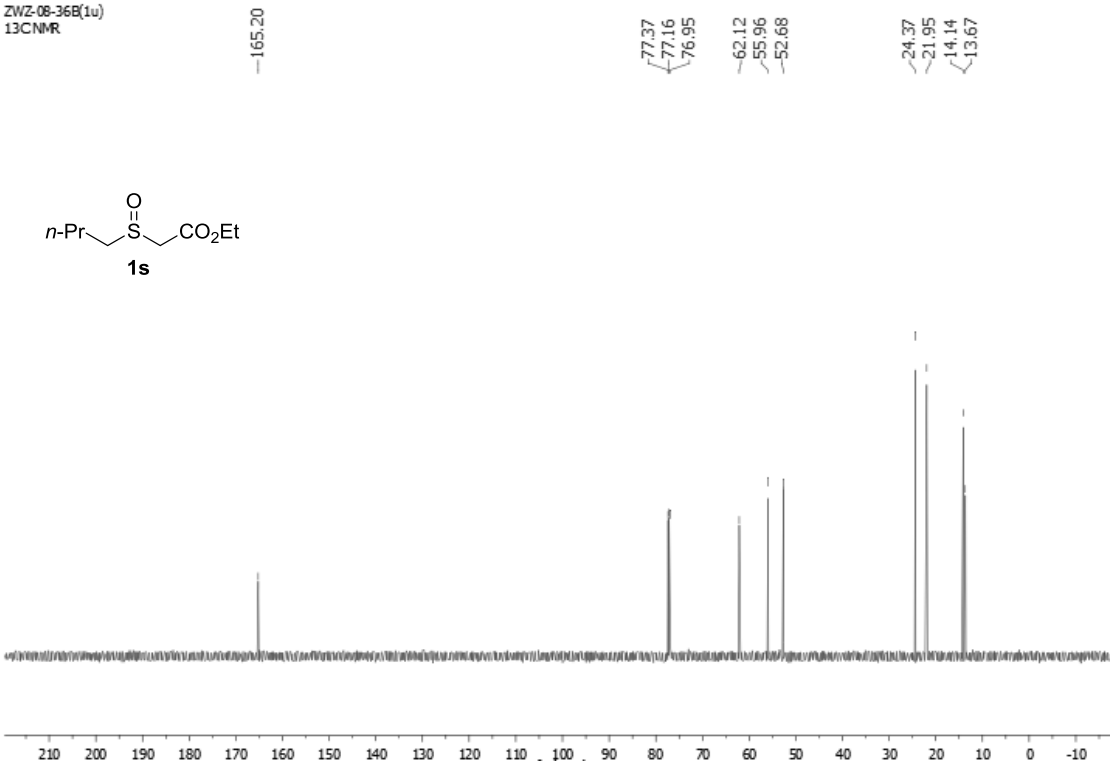
ZWZ-08-36B(1u)
1H NMR



n-Pr, O, S, CO_2Et

1s

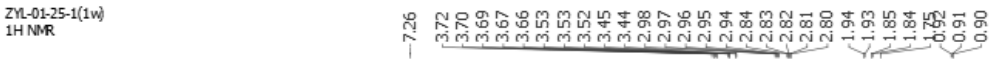
ZWZ-08-36B(1u)
13CNMR

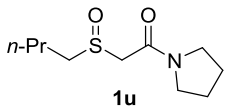


n-Pr, O, S, CO_2Et

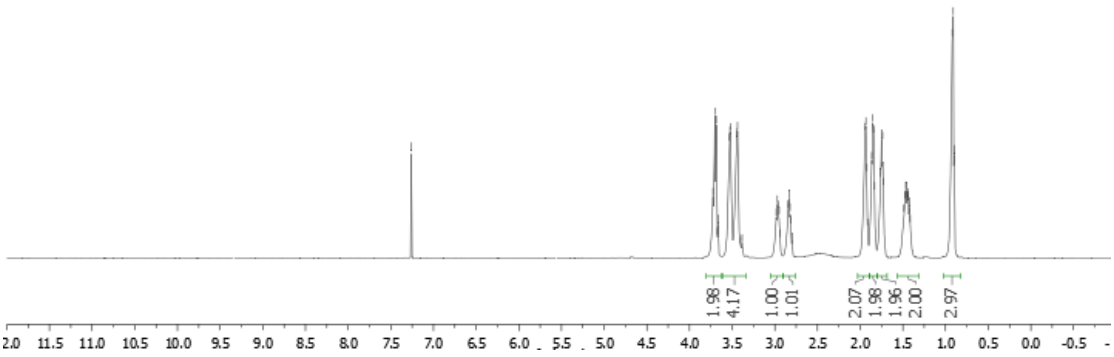
1s

ZYL-01-25-1(1w)
1H NMR

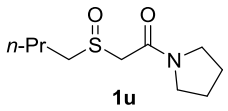




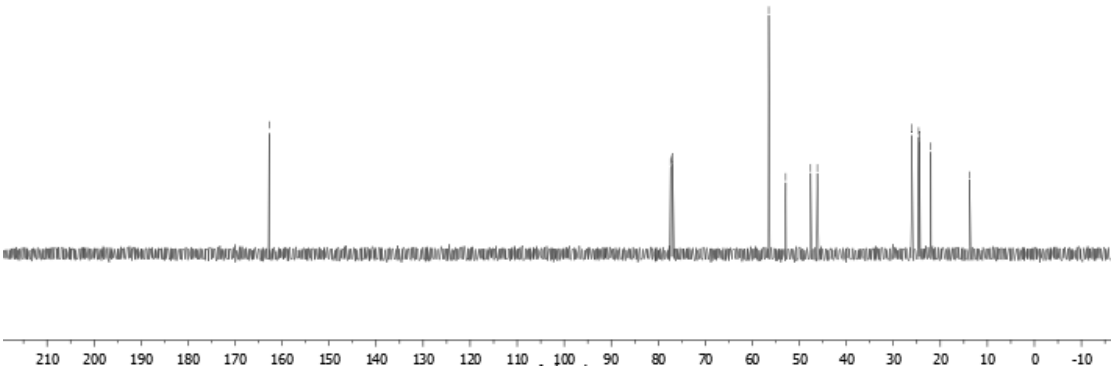
1u



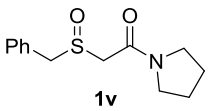
ZYL-01-25-1(1w)
13CNMR



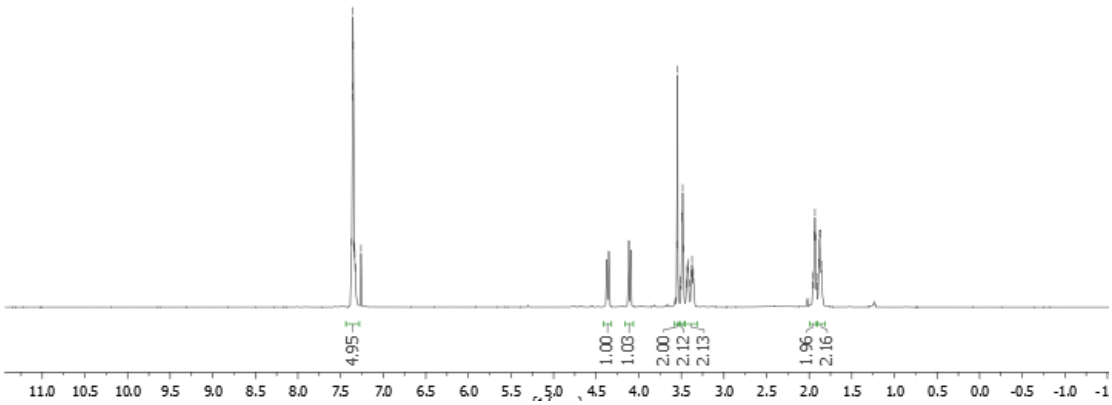
1u



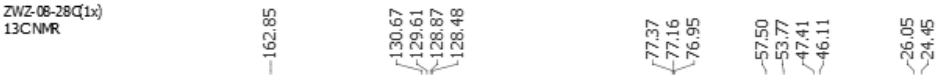
ZWZ-08-28C(1x)
1H NMR

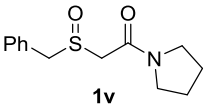


1v

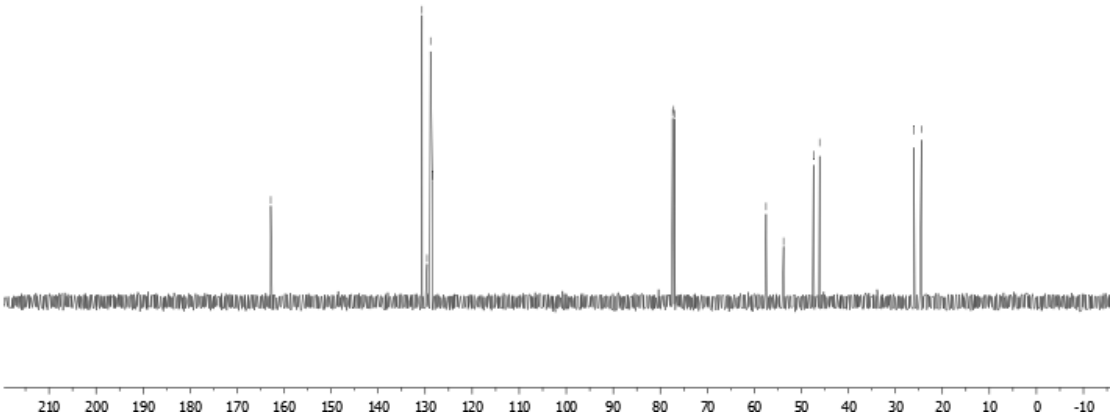


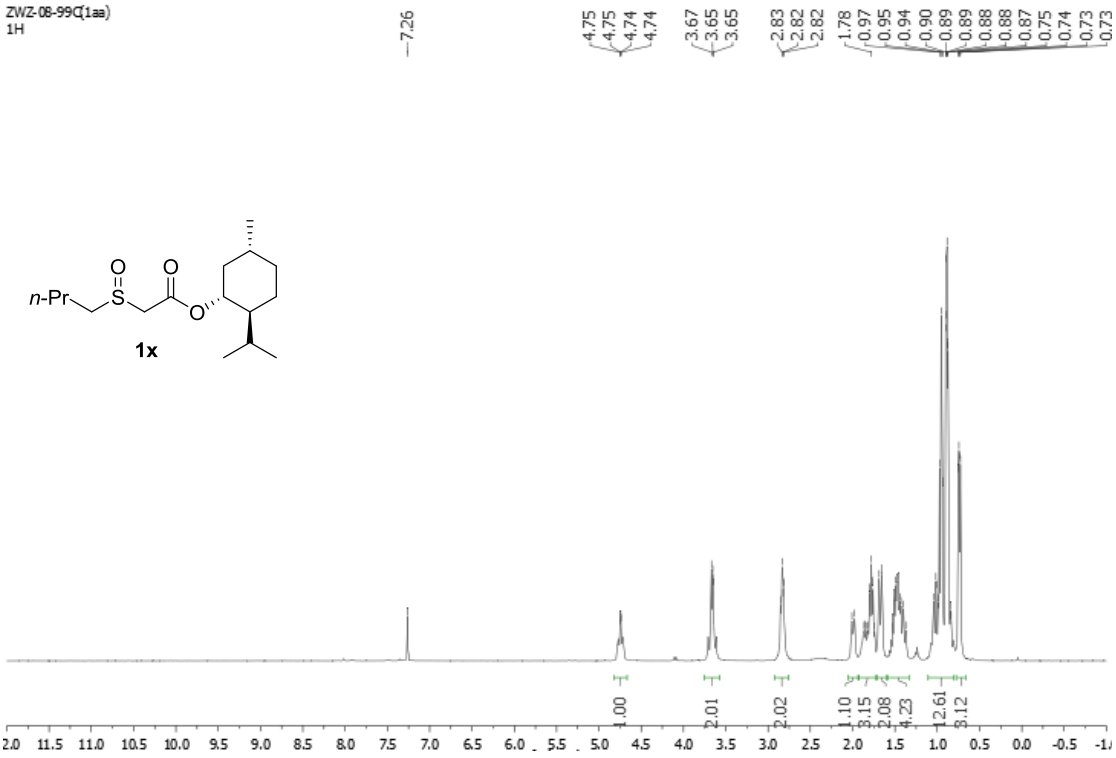
ZWZ-08-28C(1x)
13CNMR

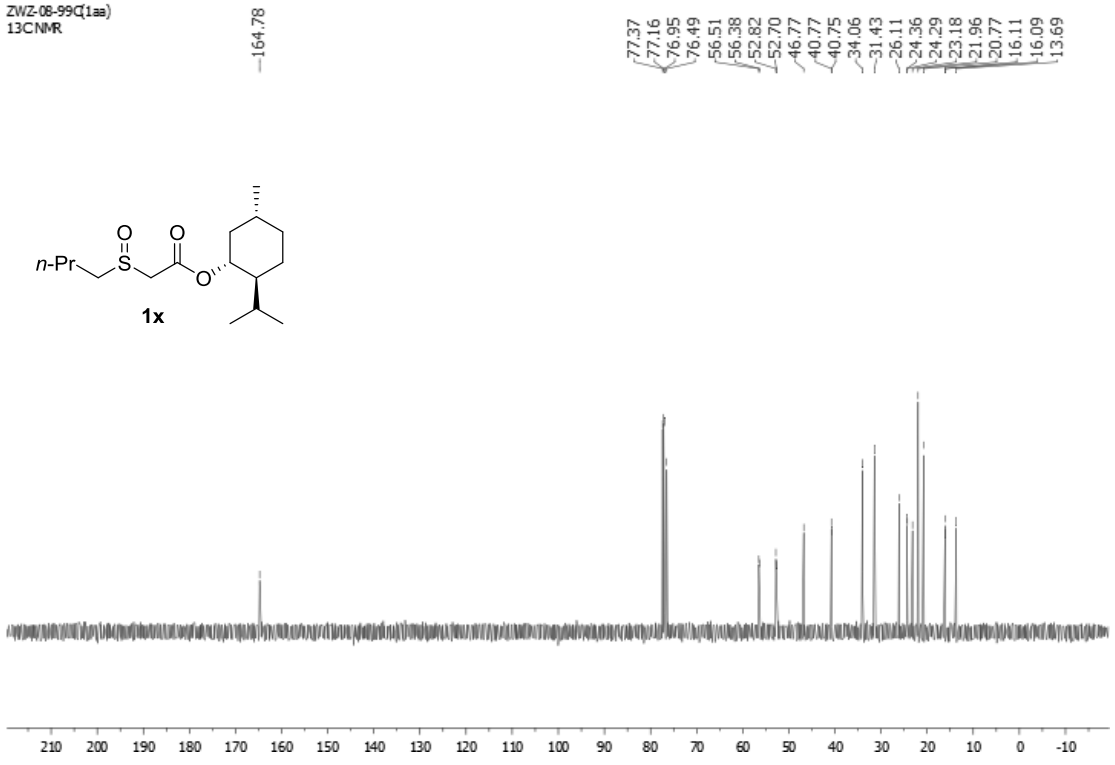




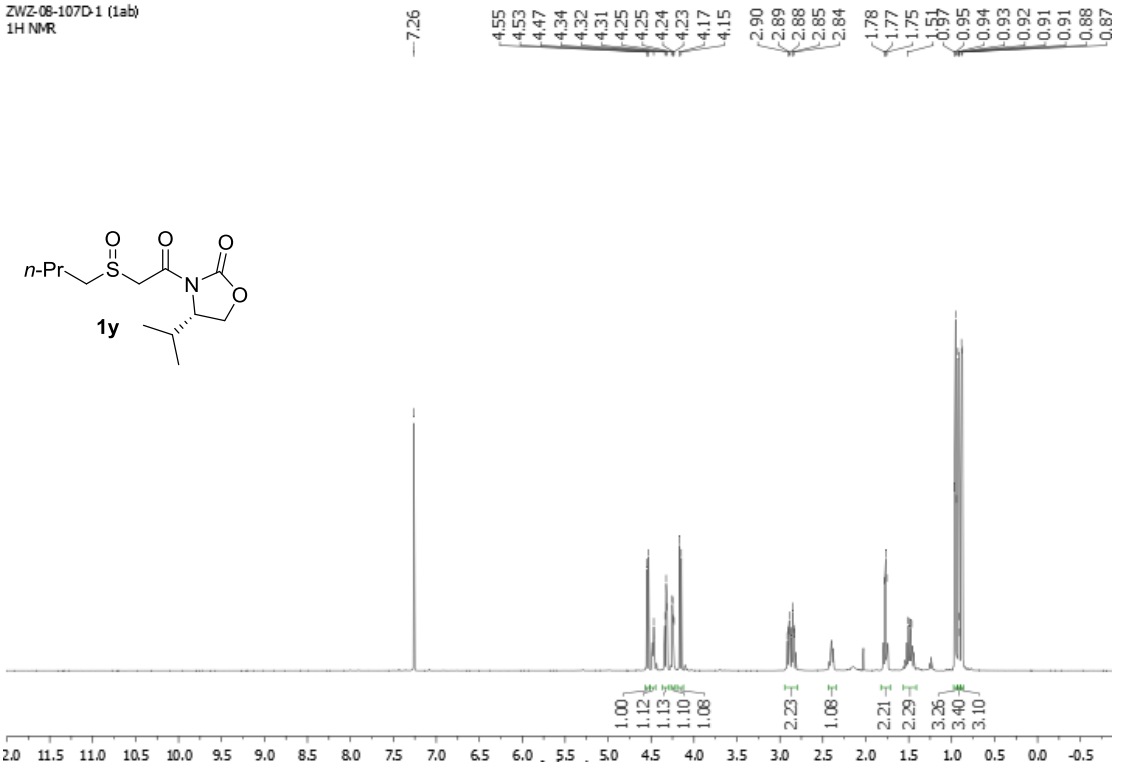
1v



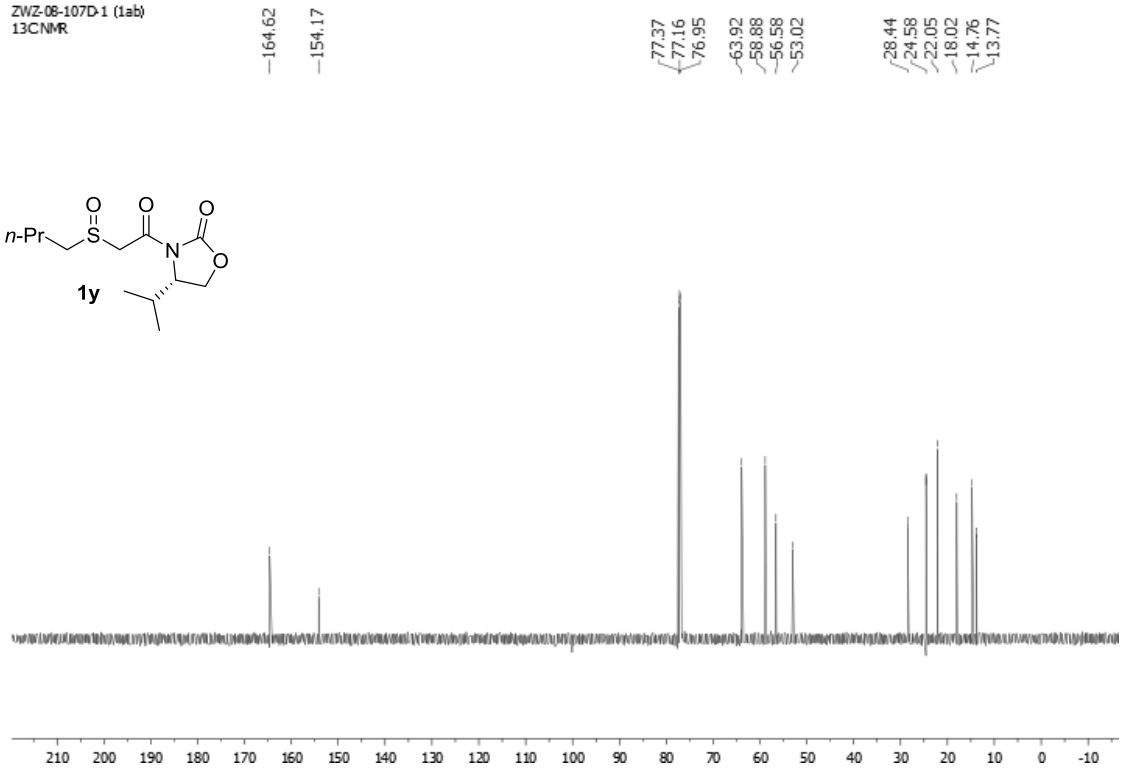

ZWZ-08-99C(1aa)
1H
7.26
4.75
4.75
4.74
4.74
3.67
3.65
3.65
2.83
2.82
2.82
1.78
0.97
0.95
0.94
0.90
0.89
0.89
0.88
0.88
0.87
0.75
0.74
0.73
n-Pr
1x
1.00
2.01
2.02
1.10
3.15
2.08
4.23
12.61
3.12

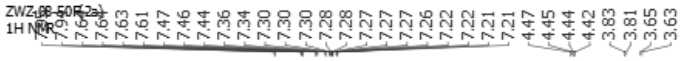

ZWZ-08-99C(1aa)
13CNMR
164.78
77.37
77.16
76.95
76.49
56.51
56.38
52.82
52.70
46.77
40.77
40.75
34.06
31.43
26.11
24.36
24.29
23.18
21.96
20.77
16.11
16.09
13.69
n-Pr
1x

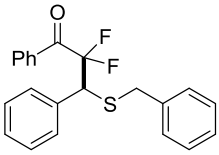
ZWZ-08-107D-1 (1ab)
1H NMR



ZWZ-08-107D-1 (1ab)
13CNMR

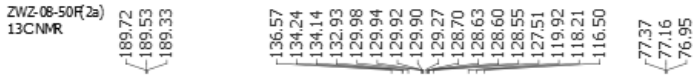


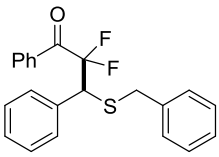

ZWZ-08-50F(2a)
1H NMR
7.64
7.63
7.61
7.47
7.46
7.44
7.36
7.34
7.30
7.30
7.30
7.28
7.28
7.27
7.27
7.27
7.26
7.22
7.21
7.21
4.47
4.45
4.44
4.42
3.83
3.81
3.65
3.63


O
F
Ph
F
S

3aa

1.98
1.00
2.06
5.32
3.13
2.02
1.01
2.25
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5

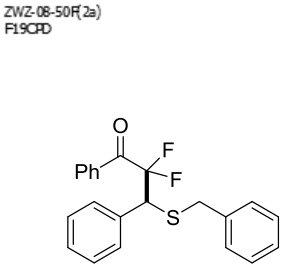

ZWZ-08-50F(2a)
13CNMR
189.72
189.53
189.33
136.57
134.24
134.14
132.93
129.98
129.94
129.92
129.90
129.27
128.70
128.63
128.60
128.55
127.51
119.92
118.21
116.50
77.37
77.16
76.95
51.53
51.38
51.23
36.67


O
F
Ph
F
S

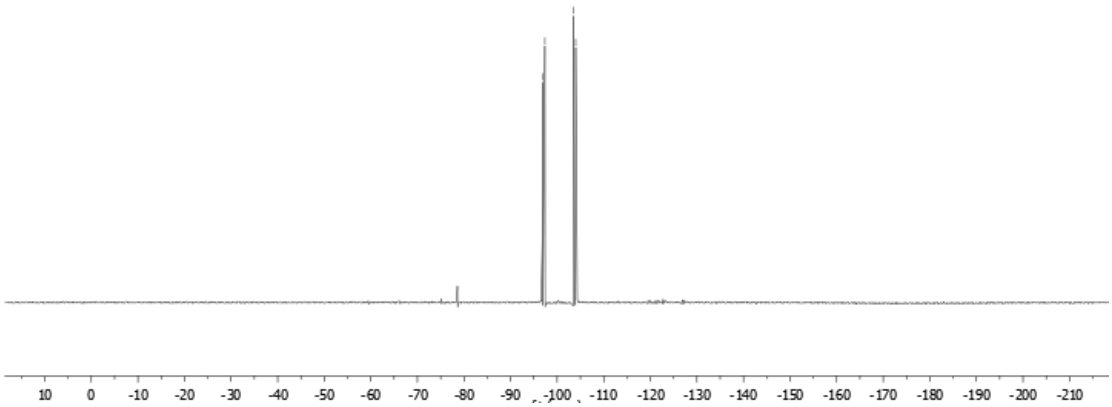
3aa

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

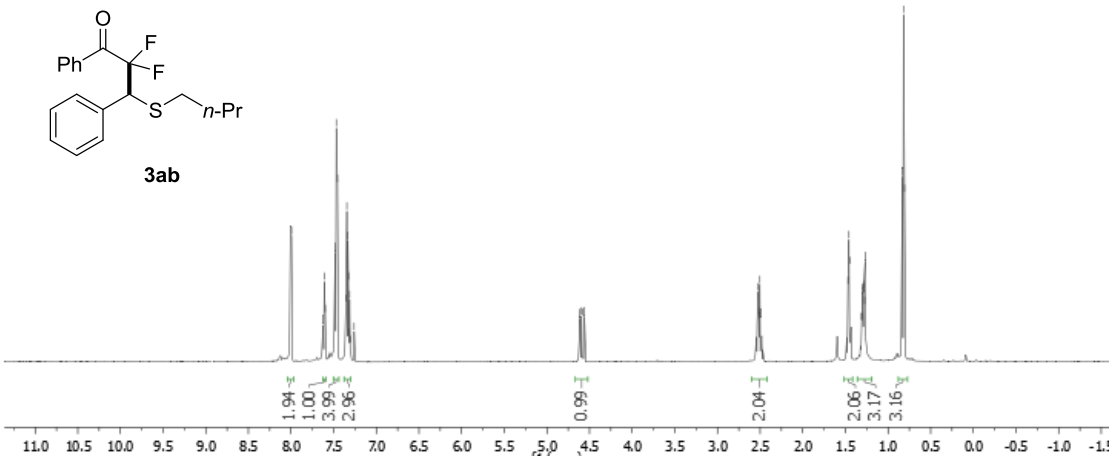
ZWZ-08-50F(2a)
F19CPD



3aa

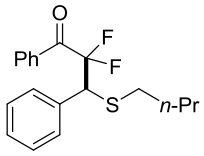


ZWZ-08-31-2(2b)
1H NMR

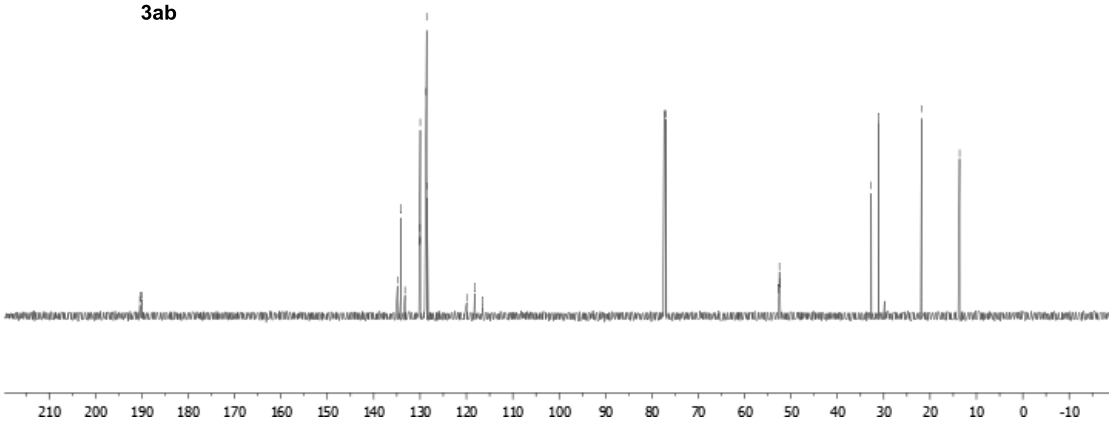


3ab

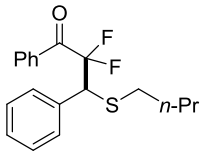
ZWZ-08-31-2(2b)
13CNMR



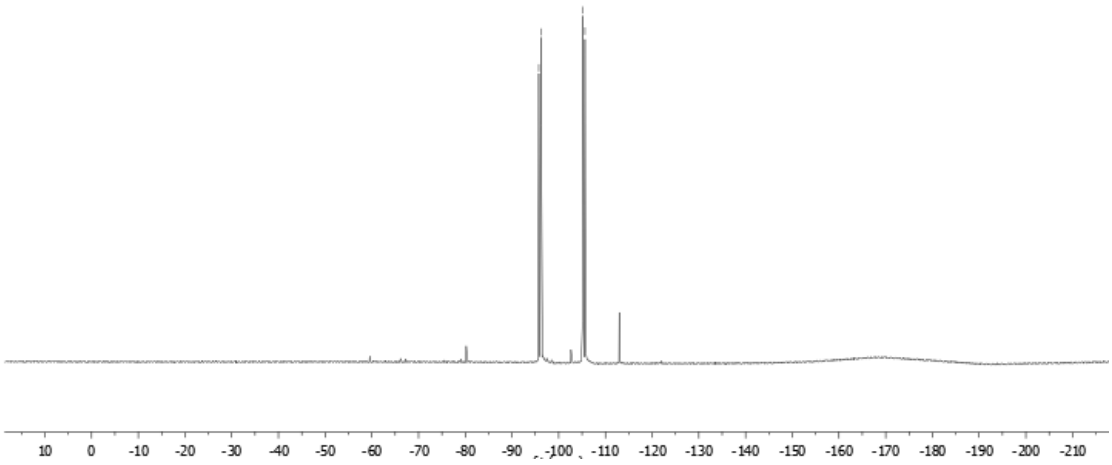
3ab

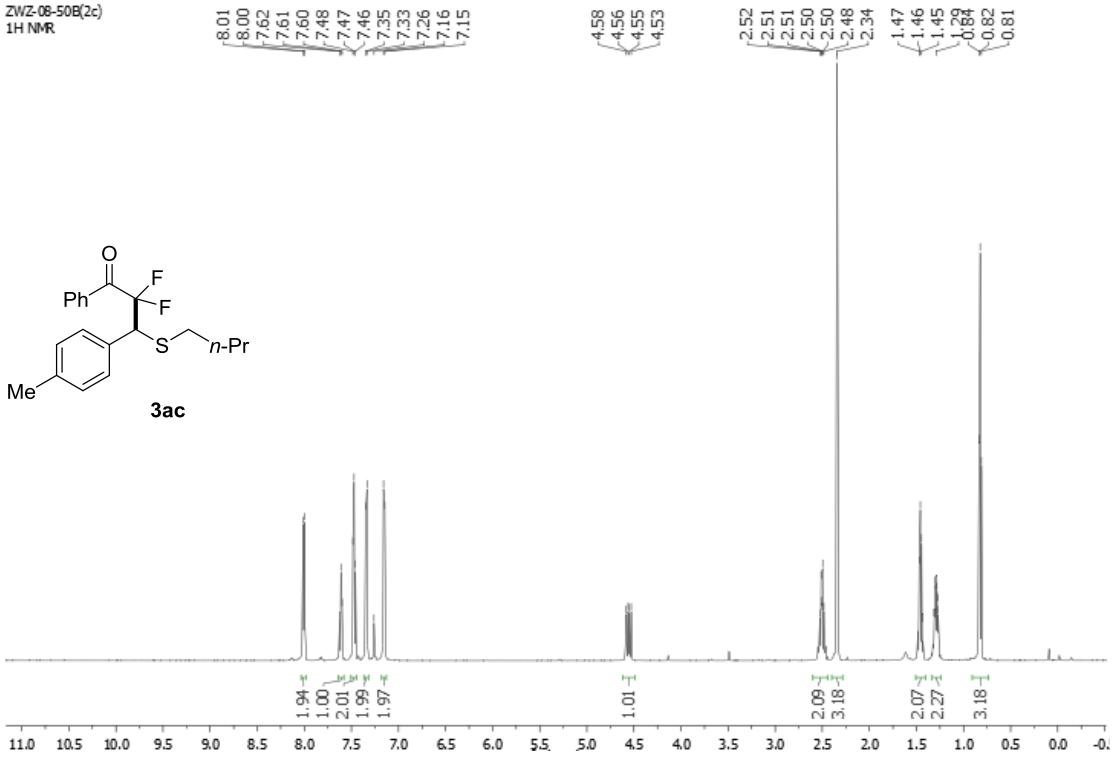


ZWZ-08-31-2(2b)
F19CPD



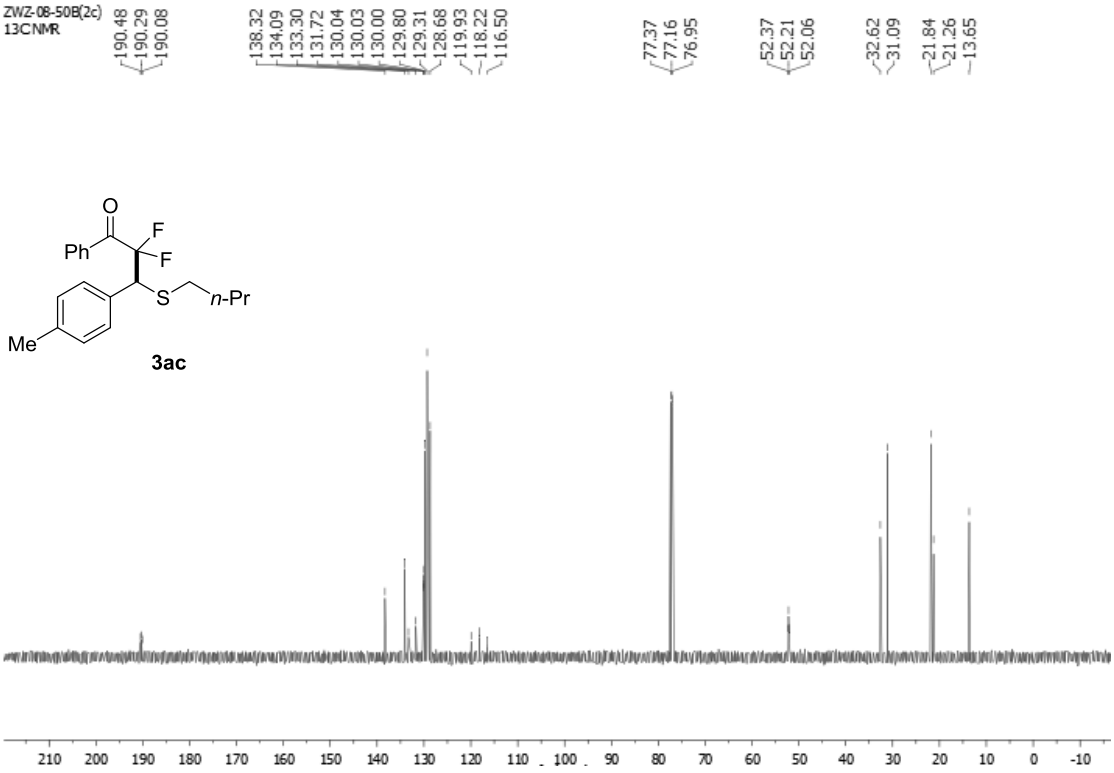
3ab




ZWZ-08-50B(2c)
1H NMR
8.01
8.00
7.62
7.61
7.60
7.48
7.47
7.46
7.35
7.33
7.26
7.16
7.15
4.58
4.56
4.55
4.53
2.52
2.51
2.51
2.50
2.50
2.48
2.34
1.47
1.46
1.45
1.29
0.84
0.82
0.81
1.94
1.00
2.01
1.99
1.97
1.01
2.09
3.18
2.07
2.27
3.18
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

O
F
Ph
F
S
n-Pr
Me

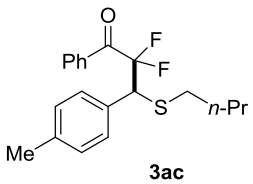
3ac


ZWZ-08-50B(2c)
13CNMR
190.48
190.29
190.08
138.32
134.09
133.30
131.72
130.04
130.03
130.00
129.80
129.31
128.68
119.93
118.22
116.50
77.37
77.16
76.95
52.37
52.21
52.06
32.62
31.09
21.84
21.26
13.65
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

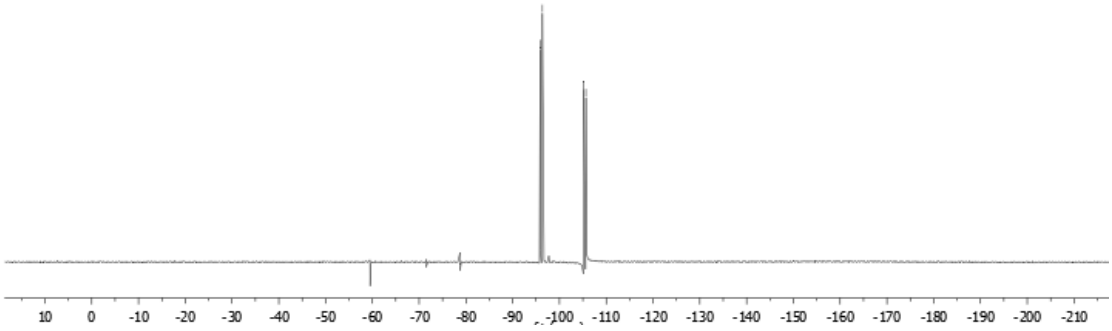
O
F
Ph
F
S
n-Pr
Me

3ac

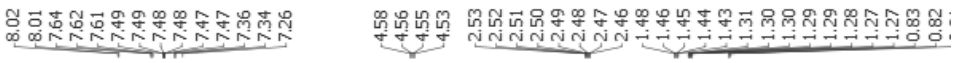
ZWZ-08-50B(2c)
F19CPD

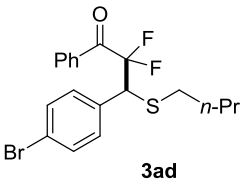


3ac



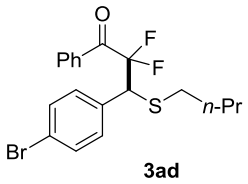
ZWZ-08-50G1(2d)
1H NMR



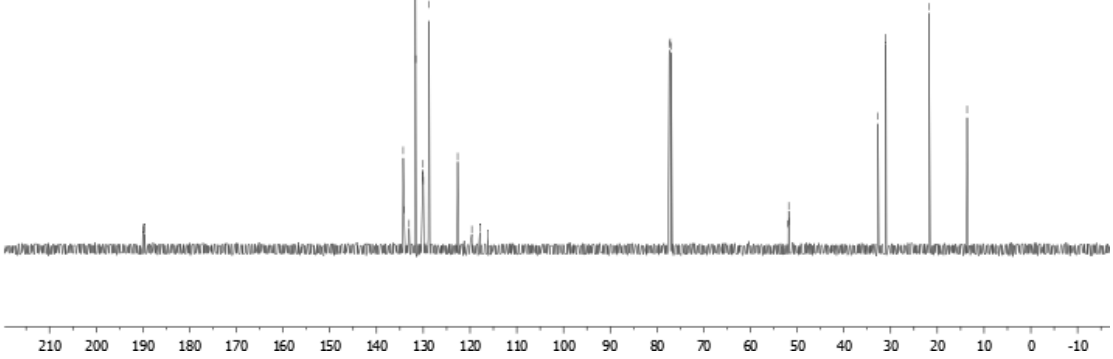


3ad

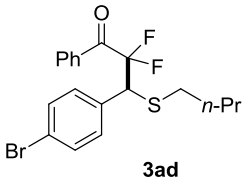
ZWZ-08-50G1(2d)
13CNMR



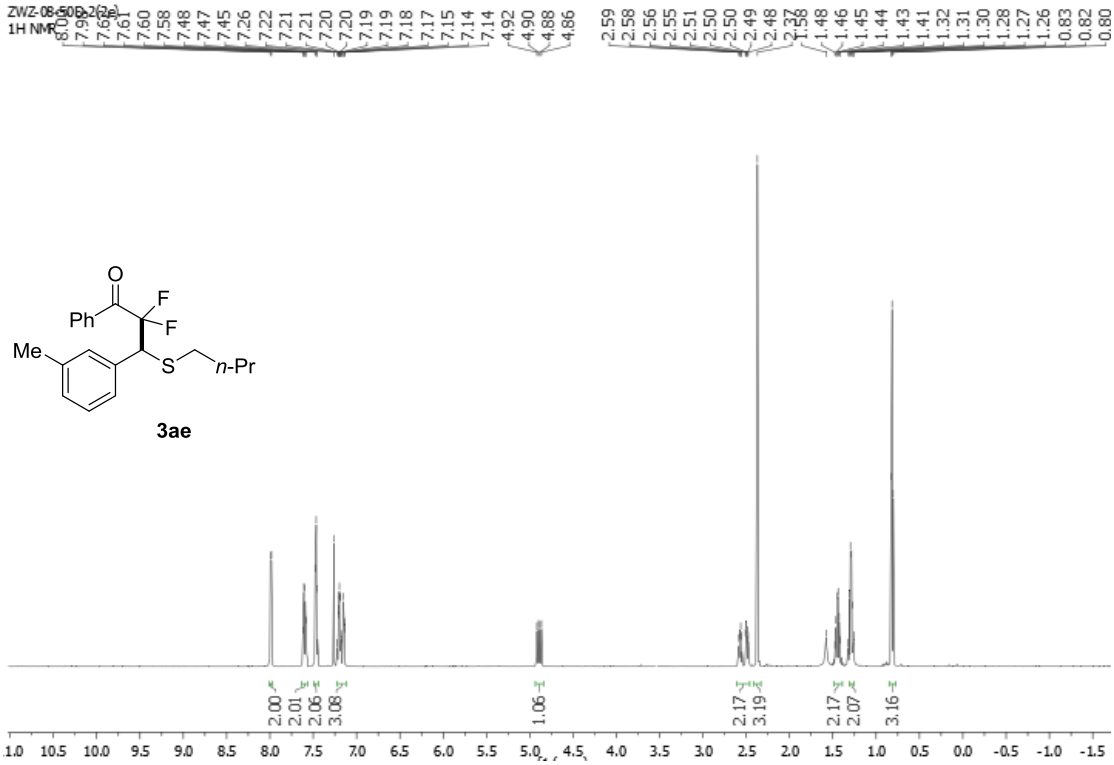
3ad

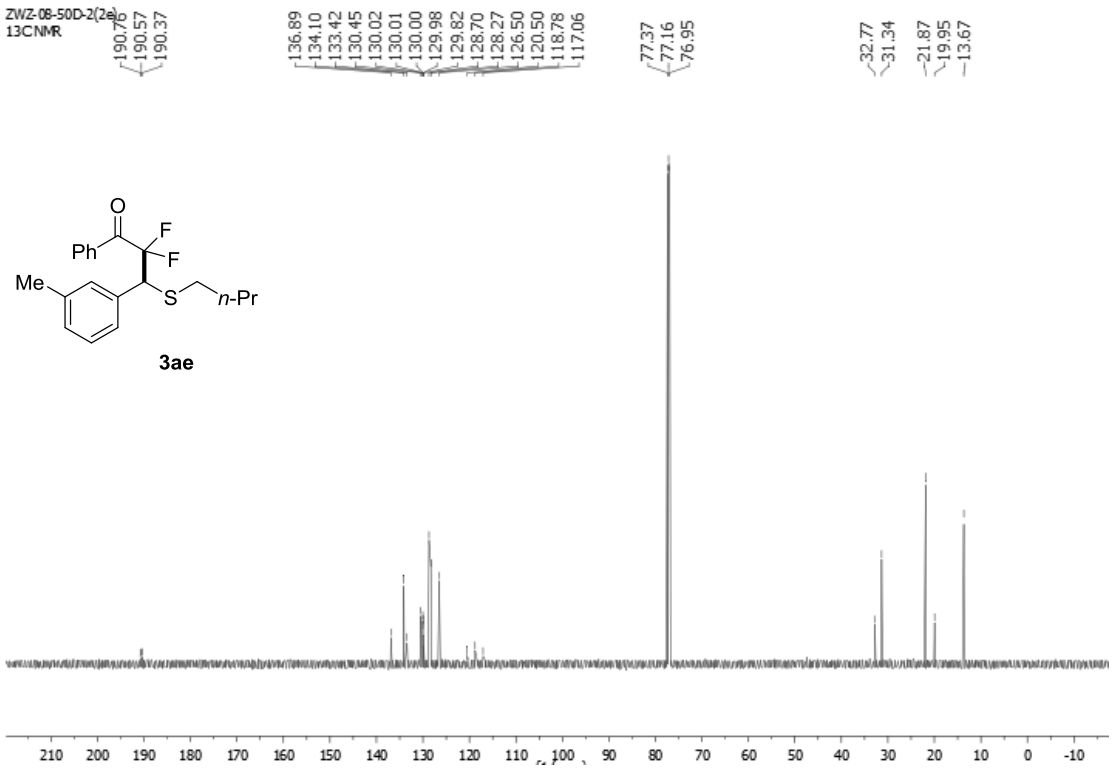


ZWZ-08-50G1(2d)
F19CRD

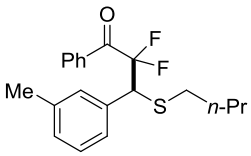


3ad


ZWZ-08-50D-2(2e)
1H NMR
Ph
F
F
Me
S
n-Pr
3ae

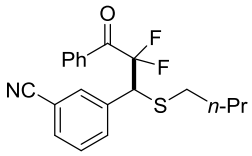

ZWZ-08-50D-2(2e)
13CNMR
Ph
F
F
Me
S
n-Pr
3ae

ZWZ-08-50D-2(2e)
F19CPD

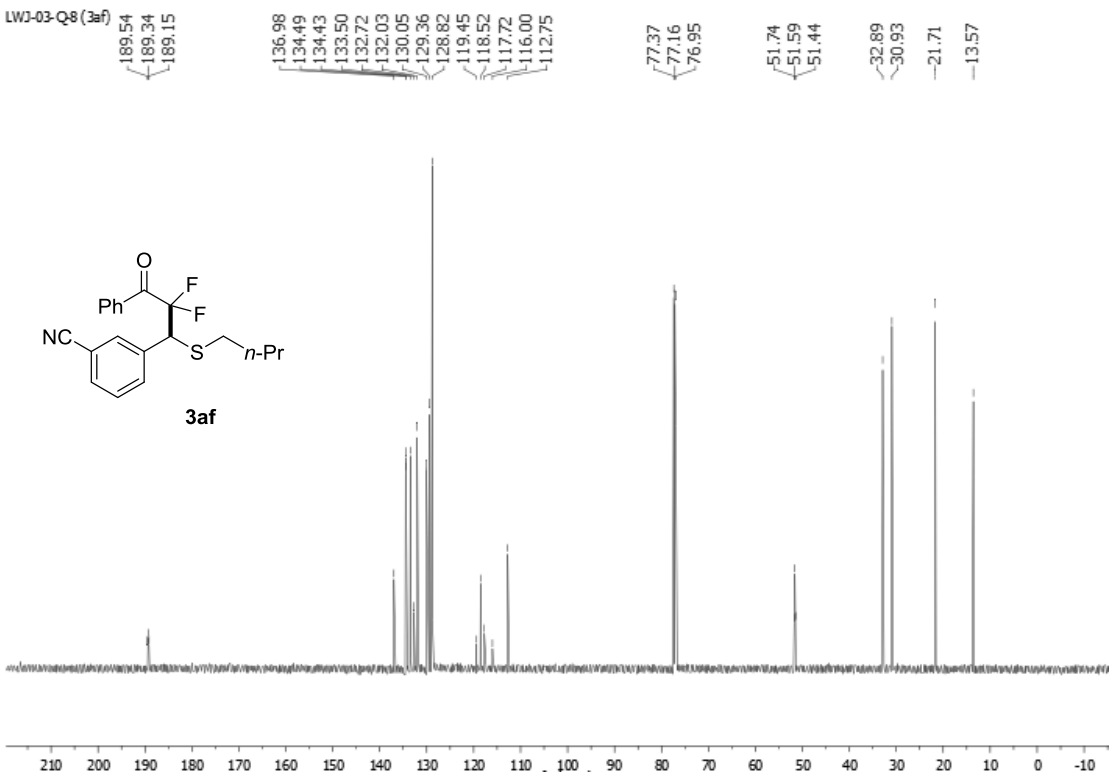


3ae

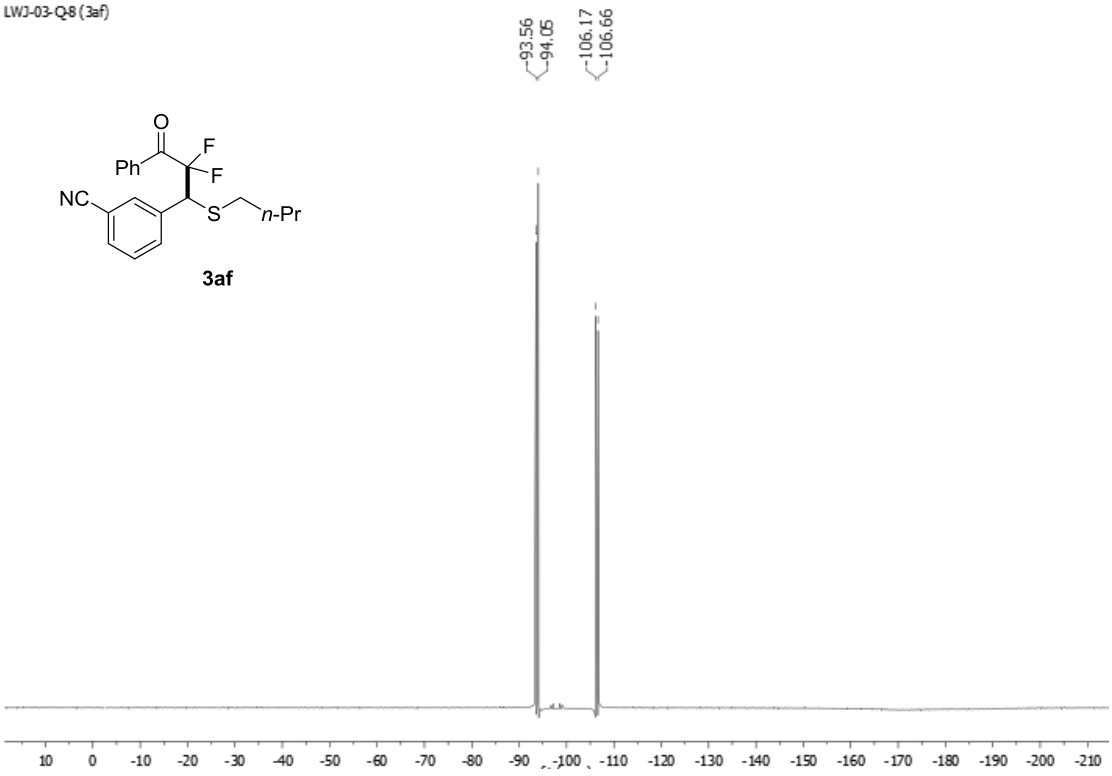
LWJ-03-Q8 (3af)



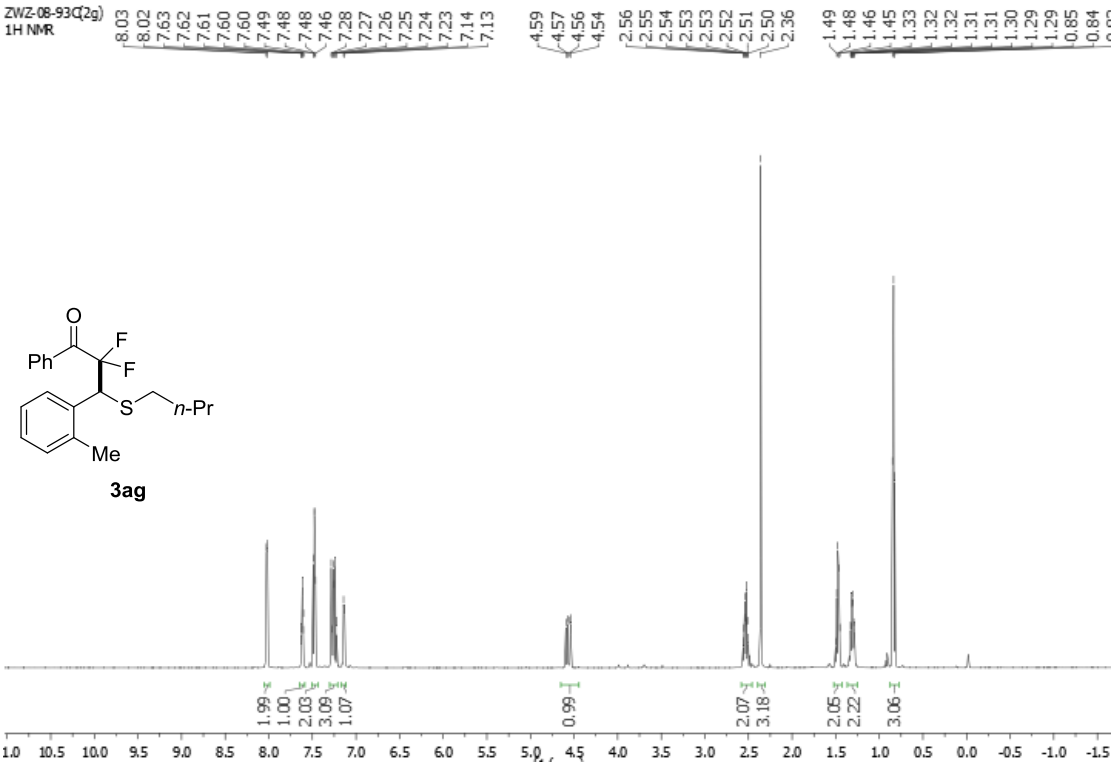
3af

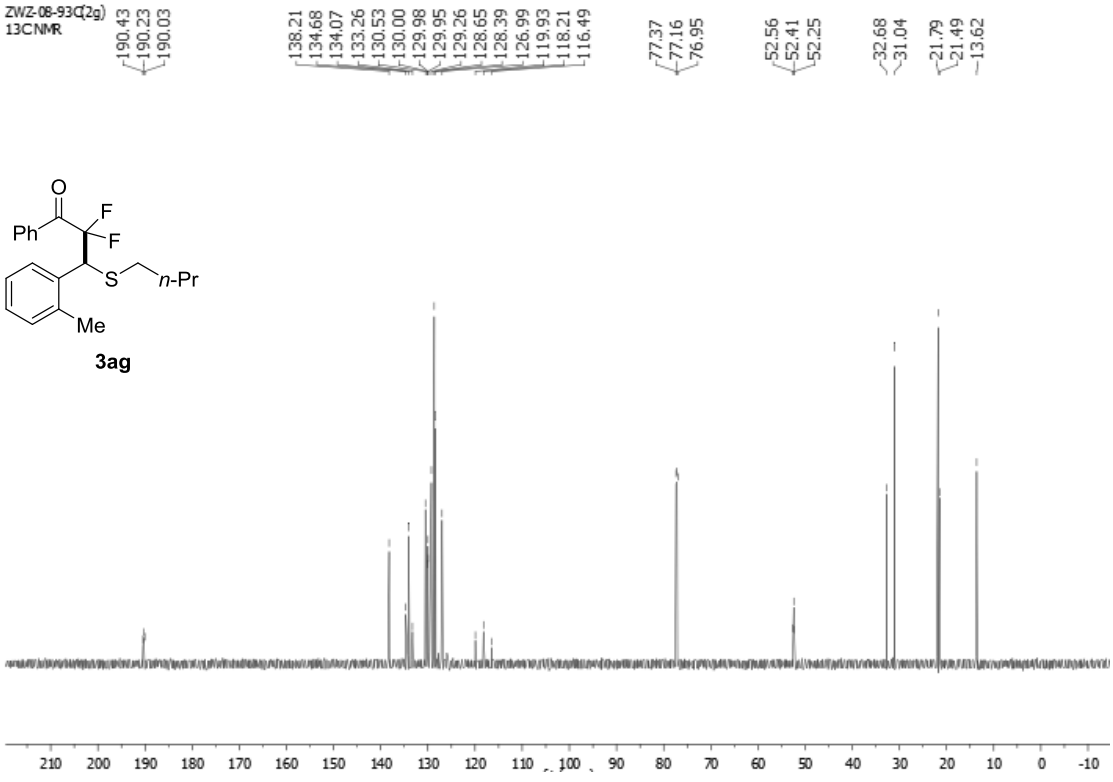

LWJ-03-Q8 (3af)
189.54
189.34
189.15
136.98
134.49
134.43
133.50
132.72
132.03
130.05
129.36
128.82
119.45
118.52
117.72
116.00
112.75
77.37
77.16
76.95
51.74
51.59
51.44
32.89
30.93
21.71
13.57
O
F
Ph
F
NC
S
n-Pr
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

3af

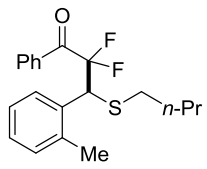

LWJ-03-Q8 (3af)
-93.56
-94.05
-106.17
-106.66
O
F
Ph
F
NC
S
n-Pr
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

3af


ZWZ-08-93C(2g)
1H NMR
8.03
8.02
7.63
7.62
7.61
7.60
7.60
7.49
7.48
7.48
7.46
7.28
7.27
7.26
7.25
7.24
7.23
7.14
7.13
4.59
4.57
4.56
4.54
2.56
2.55
2.54
2.53
2.53
2.52
2.51
2.50
2.36
1.49
1.48
1.46
1.45
1.33
1.32
1.32
1.31
1.31
1.30
1.29
1.29
0.85
0.84
O
F
Ph
F
S
n-Pr
Me
3ag
1.99
1.00
2.03
3.09
1.07
0.99
2.07
3.18
2.05
2.22
3.06
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5

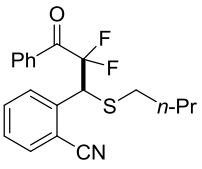

ZWZ-08-93C(2g)
13CNMR
190.43
190.23
190.03
138.21
134.68
134.07
133.26
130.53
130.00
129.98
129.95
129.26
128.65
128.39
126.99
119.93
118.21
116.49
77.37
77.16
76.95
52.56
52.41
52.25
32.68
31.04
21.79
21.49
13.62
O
F
Ph
F
S
n-Pr
Me
3ag
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

ZWZ-08-93C(2g)
F19CPD



3ag

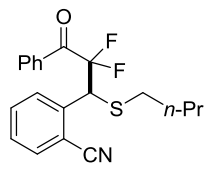
ZWZ-08-83B-1(2h)
1H NMR



3ah

ZWZ-08-83B-1(2h)
13CNMR

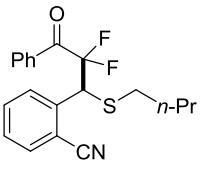
189.51
189.32
189.12
136.97
134.47
134.41
133.48
132.72
132.01
130.04
130.02
130.01
129.99
129.35
128.80
119.44
118.50
117.72
115.99
112.74
77.37
77.16
76.95
51.73
51.58
51.43
32.85
30.91
21.67
13.53



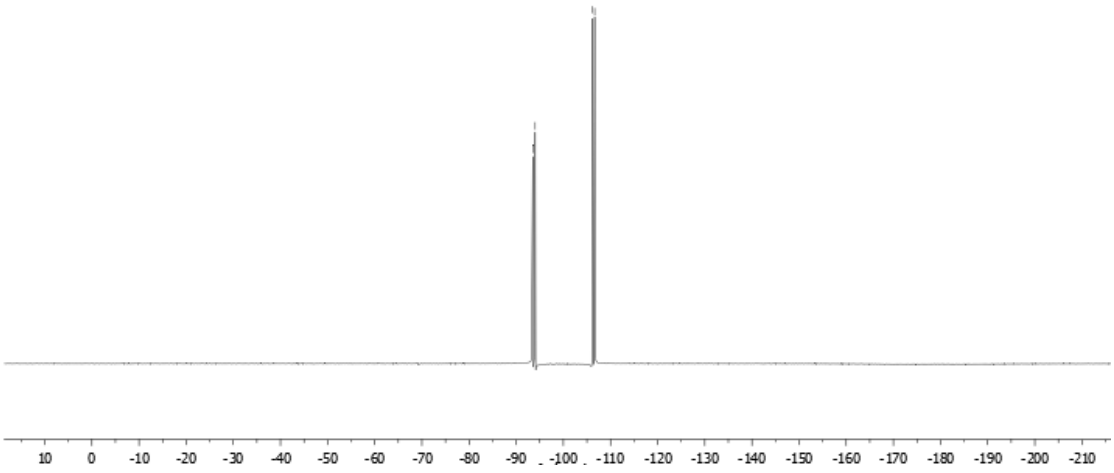
3ah

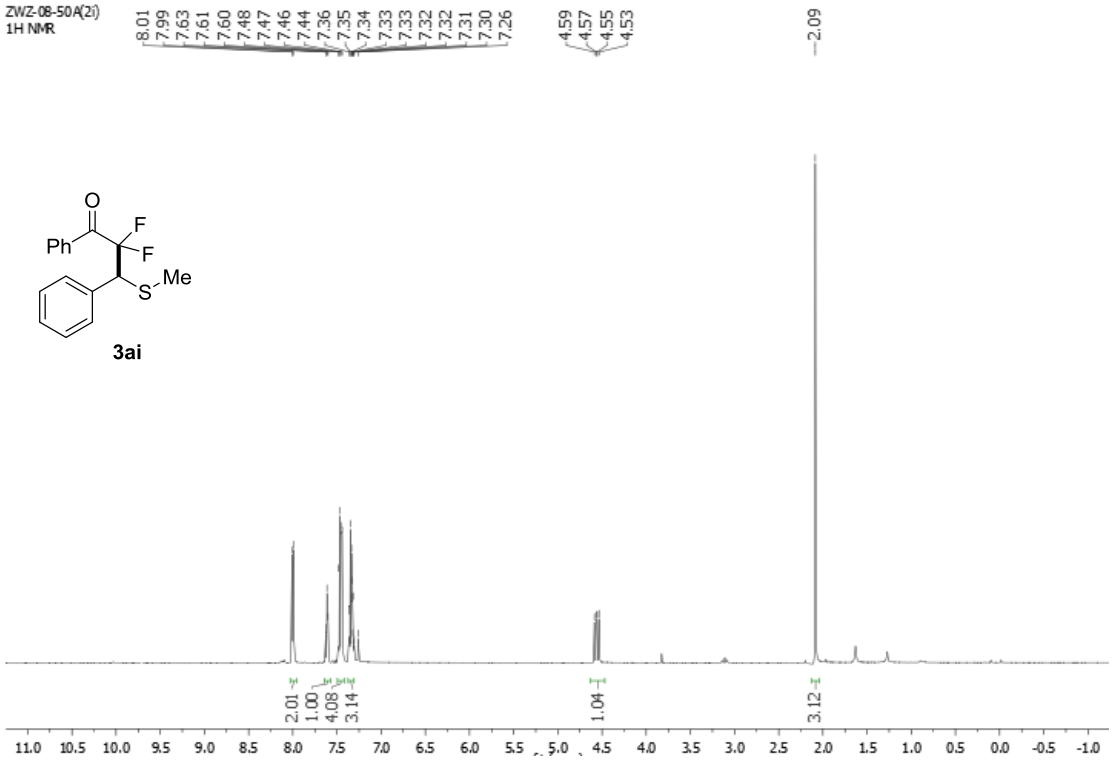
ZWZ-08-83B-1(2h)
F19CPD

93.53
94.02
106.16
106.65

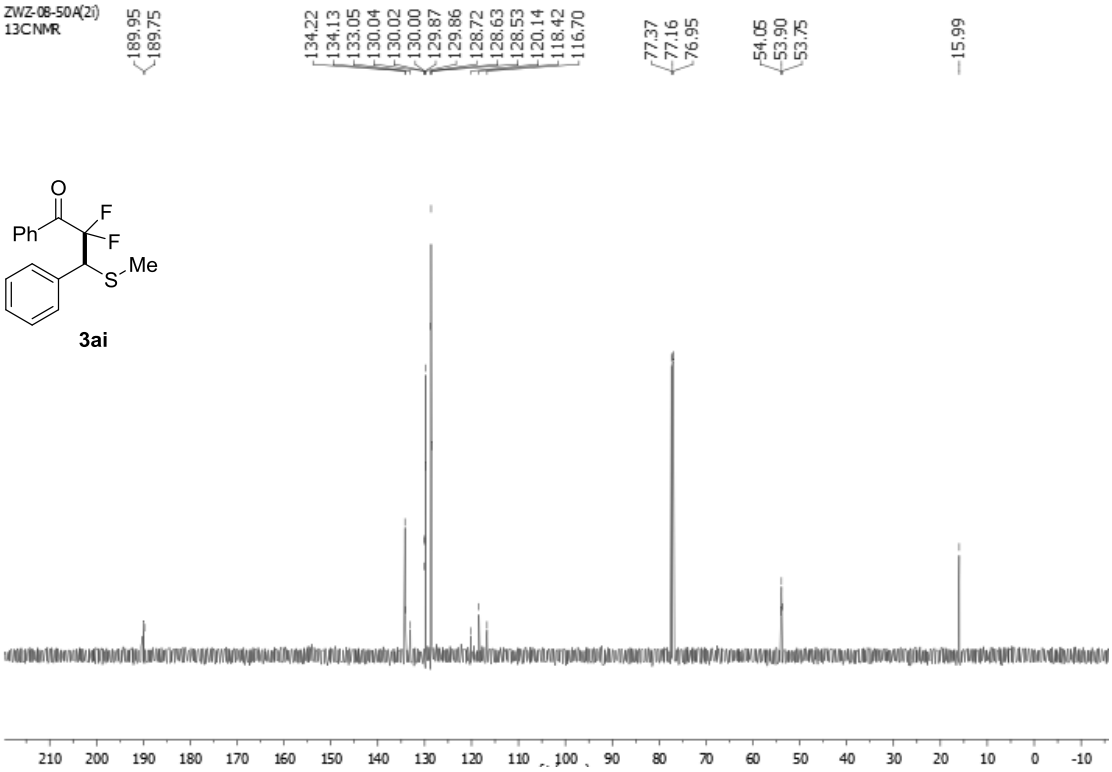


3ah



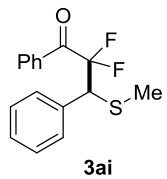

ZWZ-08-50A(2i)
1H NMR
8.01
7.99
7.63
7.61
7.60
7.48
7.47
7.46
7.44
7.36
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.26
4.59
4.57
4.55
4.53
2.09
O
F
Ph
F
S
Me
2.01
1.00
4.08
3.14
1.04
3.12
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

3ai

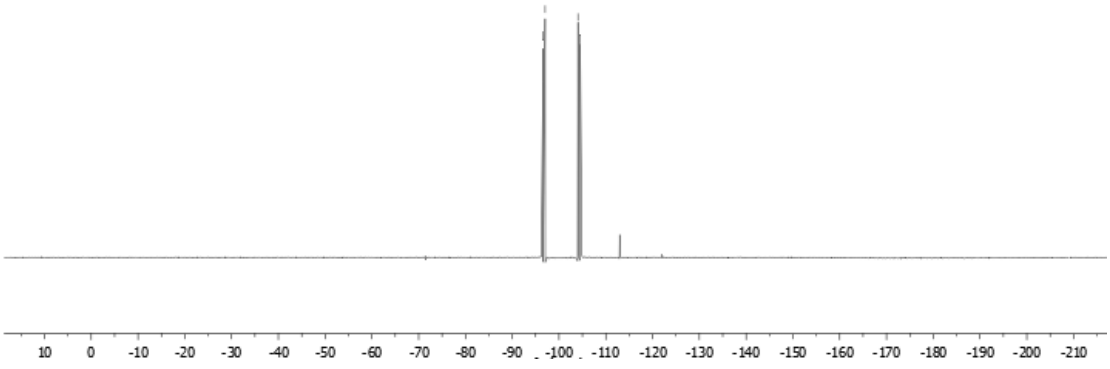

ZWZ-08-50A(2i)
13CNMR
189.95
189.75
134.22
134.13
133.05
130.04
130.02
130.00
129.87
129.86
128.72
128.63
128.53
120.14
118.42
116.70
77.37
77.16
76.95
54.05
53.90
53.75
15.99
O
F
Ph
F
S
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

3ai

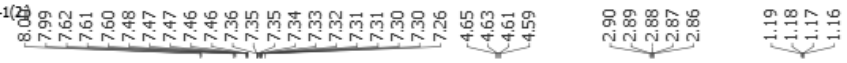
ZWZ-08-50A(2i)
F19CPD

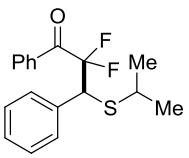


3ai



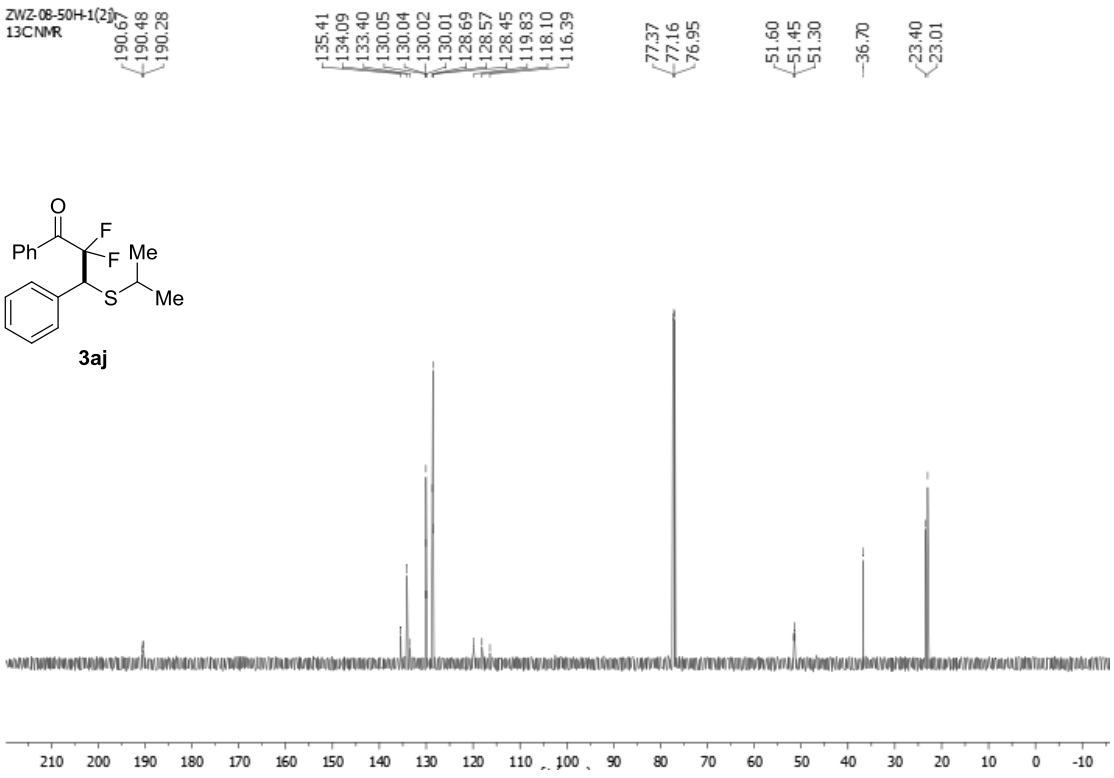
ZWZ-08-50H-1(2i)
1H NMR



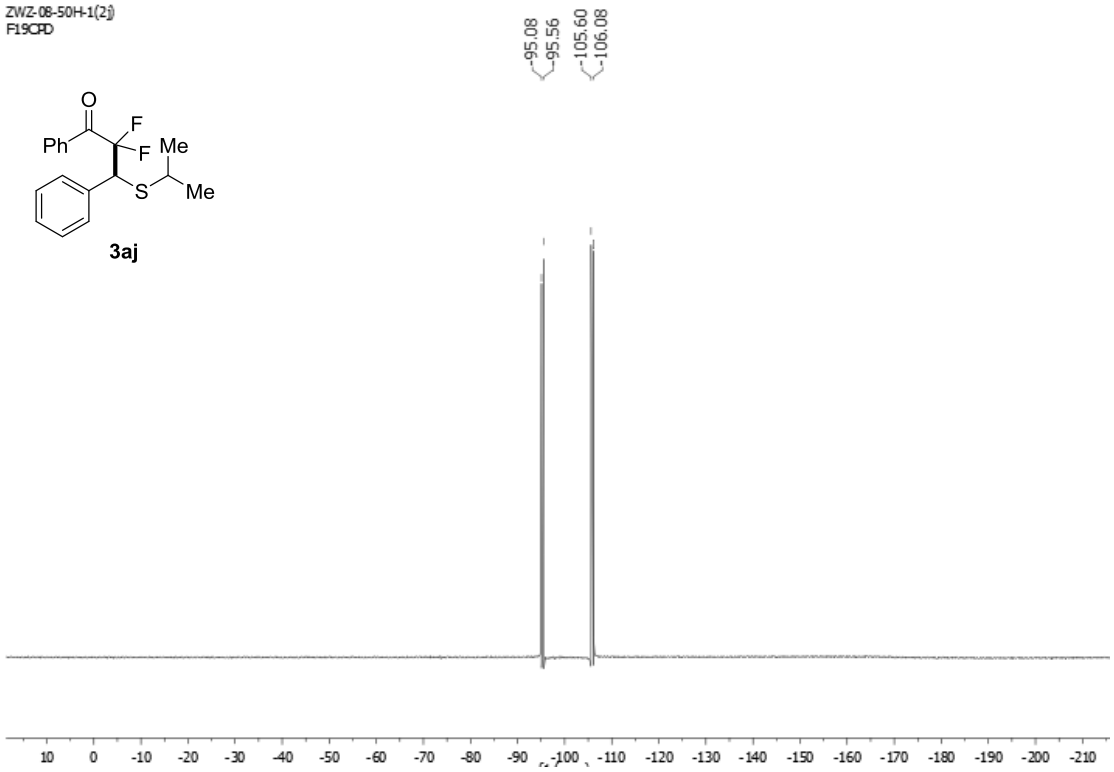


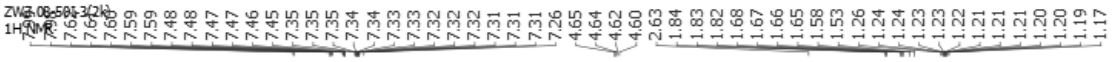
3aj

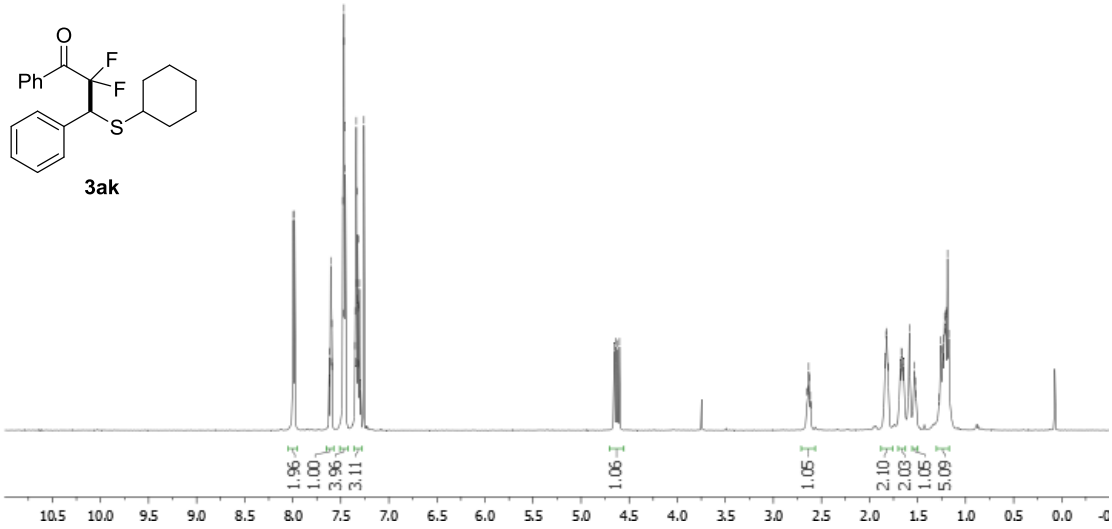
ZWZ-08-50H-1(2j)
13CNMR

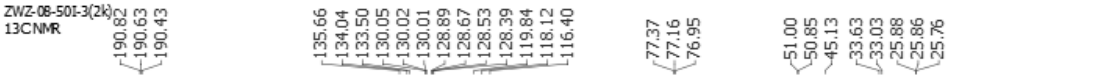


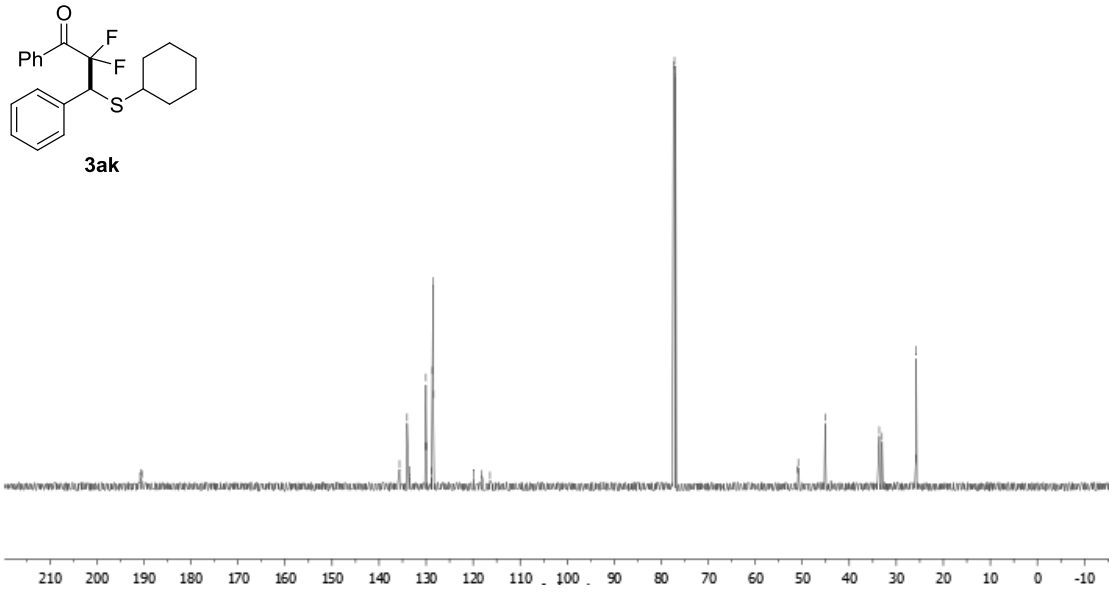
ZWZ-08-50H-1(2j)
F19CPD



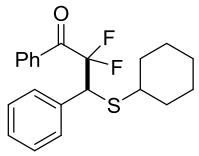



O
F
Ph
F
S
3ak
1.96
1.00
3.96
3.11
1.06
1.05
2.10
2.03
1.05
5.09

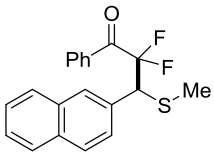



O
F
Ph
F
S
3ak

ZWZ-08-501-3(2k)
F19CPD



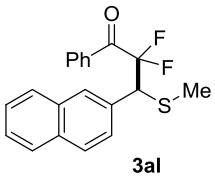
3ak



3al

ZWZ-09-05B(2l)
13CNMR

189.98
189.78
189.58
134.24
133.18
133.01
132.94
131.43
130.05
130.03
130.00
129.26
128.72
128.56
128.13
127.73
127.12
126.60
126.47
120.23
118.51
116.79
77.37
77.16
76.95
54.15
54.00
53.84
15.84

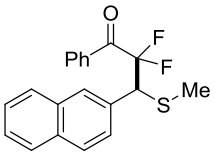


3al

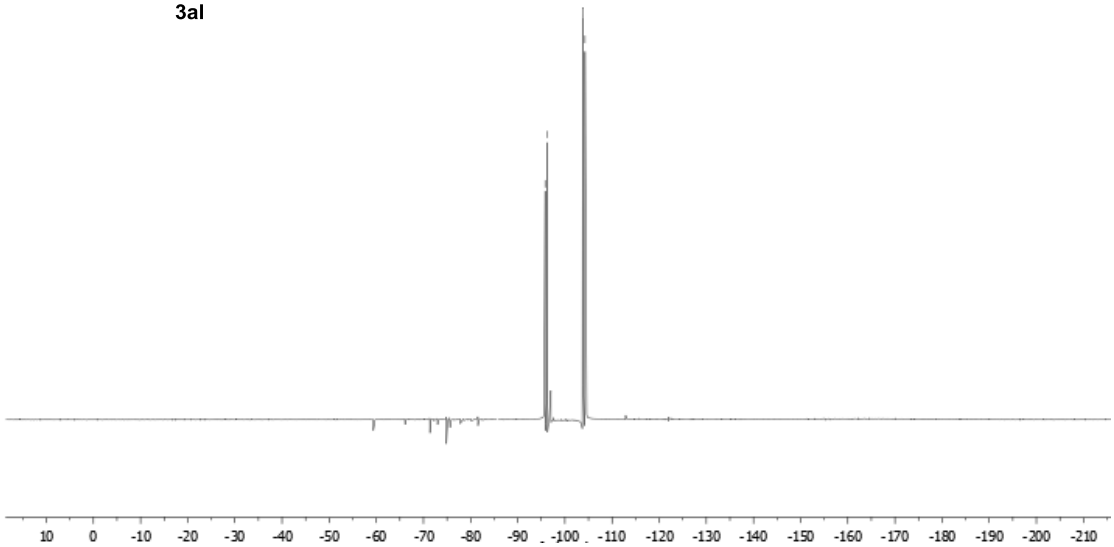
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

ZWZ-09-05B-F
F19CPD

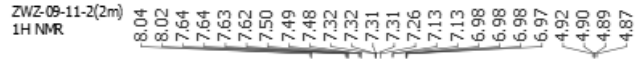
95.81
96.29
103.78
104.27

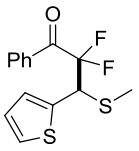


3al



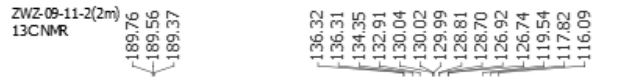
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

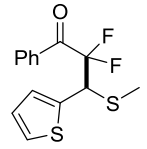

ZWZ-09-11-2(2m)
1H NMR
8.04
8.02
7.64
7.64
7.63
7.62
7.50
7.49
7.48
7.32
7.32
7.31
7.31
7.26
7.13
7.13
6.98
6.98
6.98
6.97
4.92
4.90
4.89
4.87
2.13


O
Ph
F
F
S
S

3am

2.00
1.08
2.22
0.95
0.98
1.06
1.02
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


ZWZ-09-11-2(2m)
13CNMR
189.76
189.56
189.37
136.32
136.31
134.35
132.91
130.04
130.02
129.99
128.81
128.70
126.92
126.74
119.54
117.82
116.09
77.37
77.16
76.95
48.92
48.76
48.60
15.67
15.66

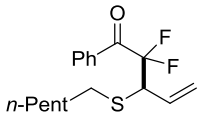

O
Ph
F
F
S
S

3am

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

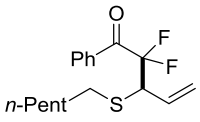
ZWZ-09-11-2-F
F19CPD

3am



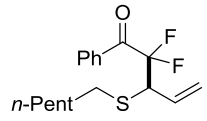
3an

ZWZ-09-18B-1(2n)
13CNMR

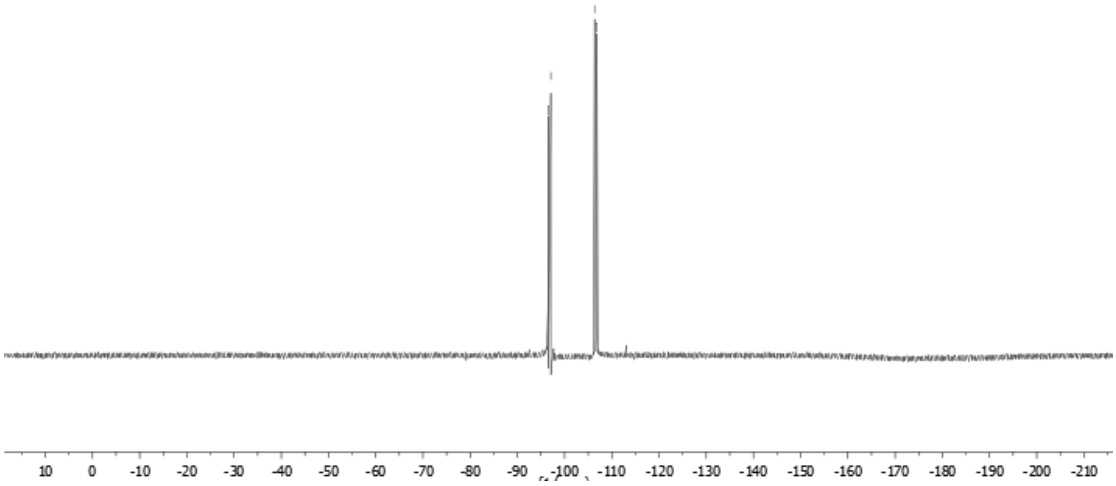


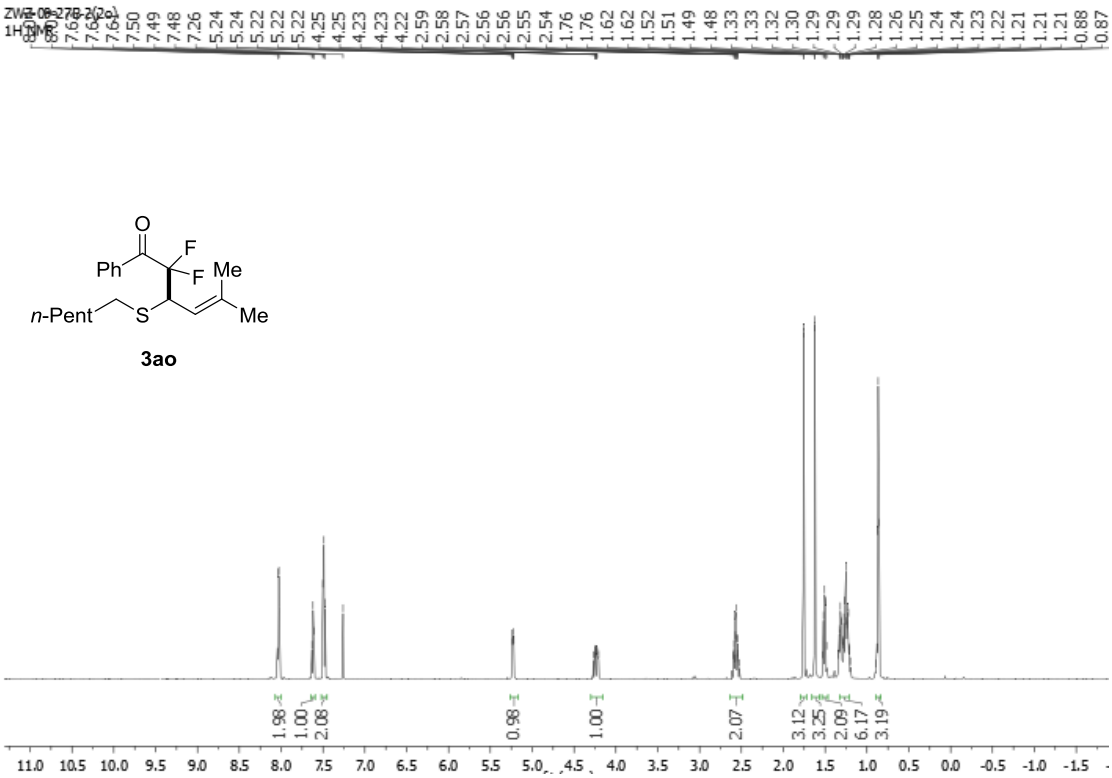
3an

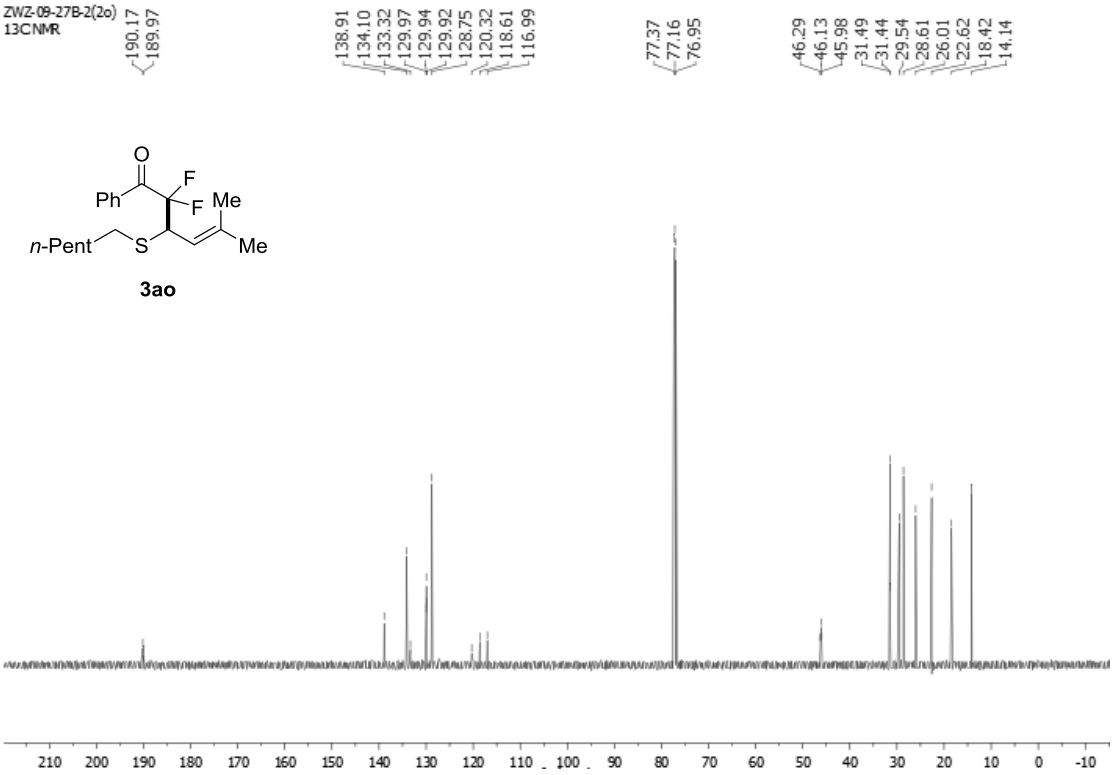
ZWZ-09-18B-1-F
F19CPD



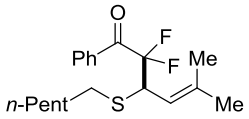
3an



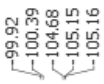

ZWZ-08-27B-2(2o)
1H NMR
8.00
7.63
7.61
7.50
7.49
7.48
7.26
5.24
5.22
5.22
5.22
4.25
4.25
4.23
4.23
4.22
2.59
2.58
2.57
2.56
2.56
2.55
2.54
1.76
1.76
1.62
1.52
1.51
1.49
1.48
1.33
1.32
1.30
1.29
1.29
1.29
1.28
1.26
1.25
1.24
1.24
1.23
1.22
1.21
1.21
1.21
0.88
0.87
O
F
Ph
F
Me
n-Pent
S
Me
3ao
1.98
1.00
2.08
0.98
1.00
2.07
3.12
3.25
2.09
6.17
3.19
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5

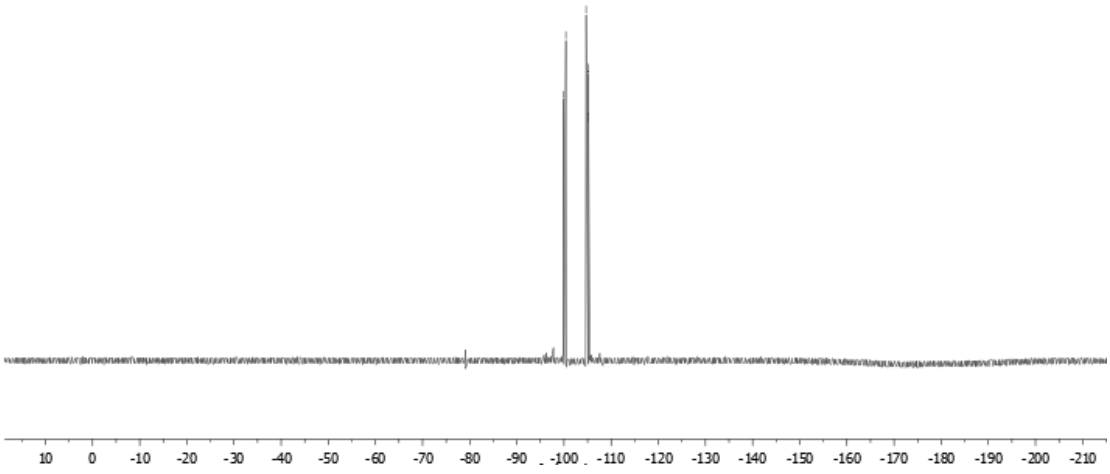

ZWZ-09-27B-2(2o)
13CNMR
190.17
189.97
138.91
134.10
133.32
129.97
129.94
129.92
128.75
120.32
118.61
116.99
77.37
77.16
76.95
46.29
46.13
45.98
31.49
31.44
29.54
28.61
26.01
22.62
18.42
14.14
O
F
Ph
F
Me
n-Pent
S
Me
3ao
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

ZWZ-09-27B-2-F
F19CPD

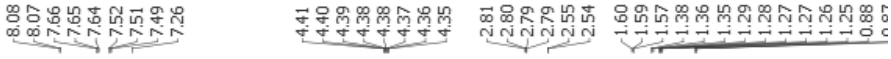


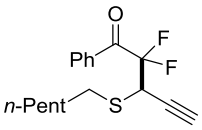
3ao



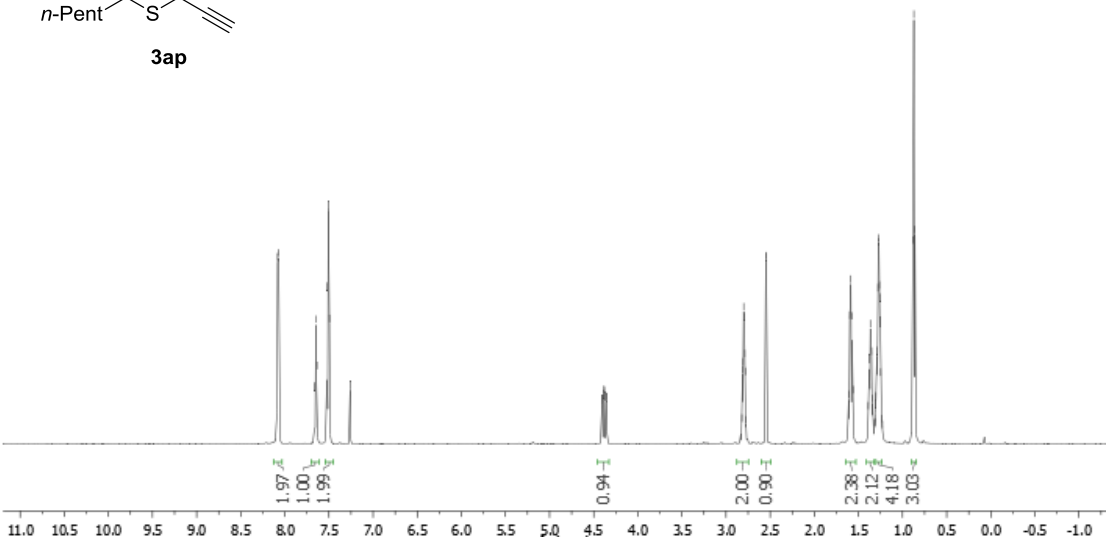


ZWZ-08-98E-2(2r)
1H NMR

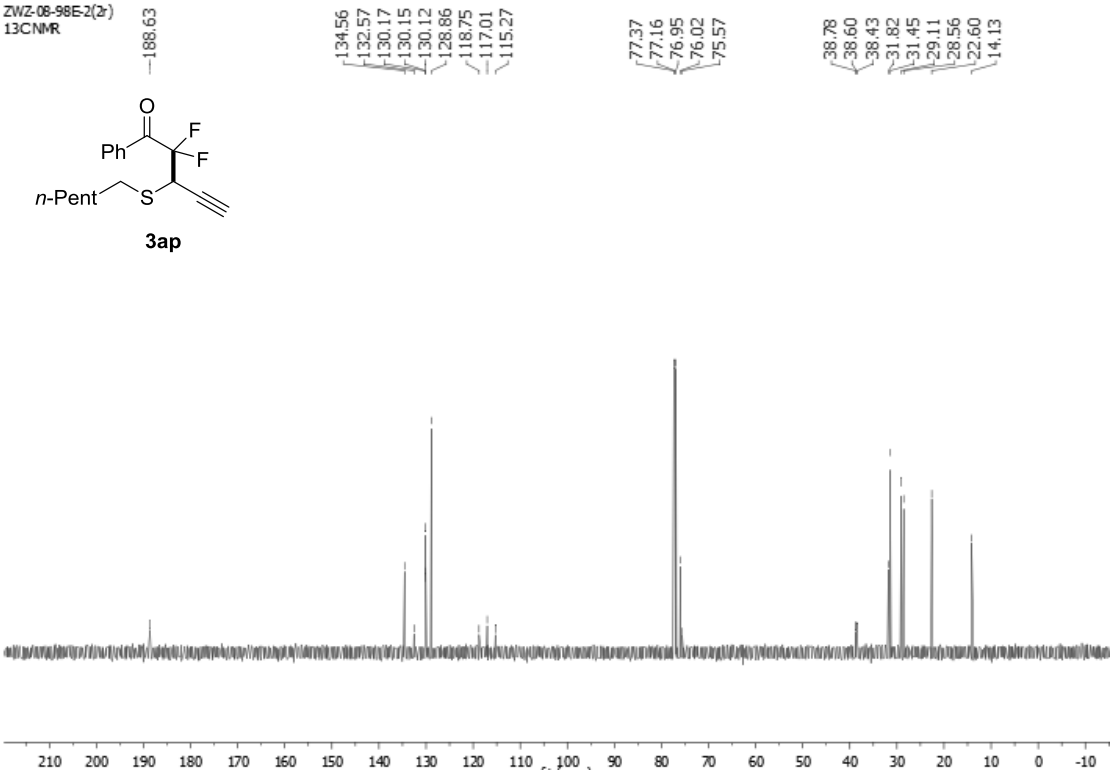




3ap

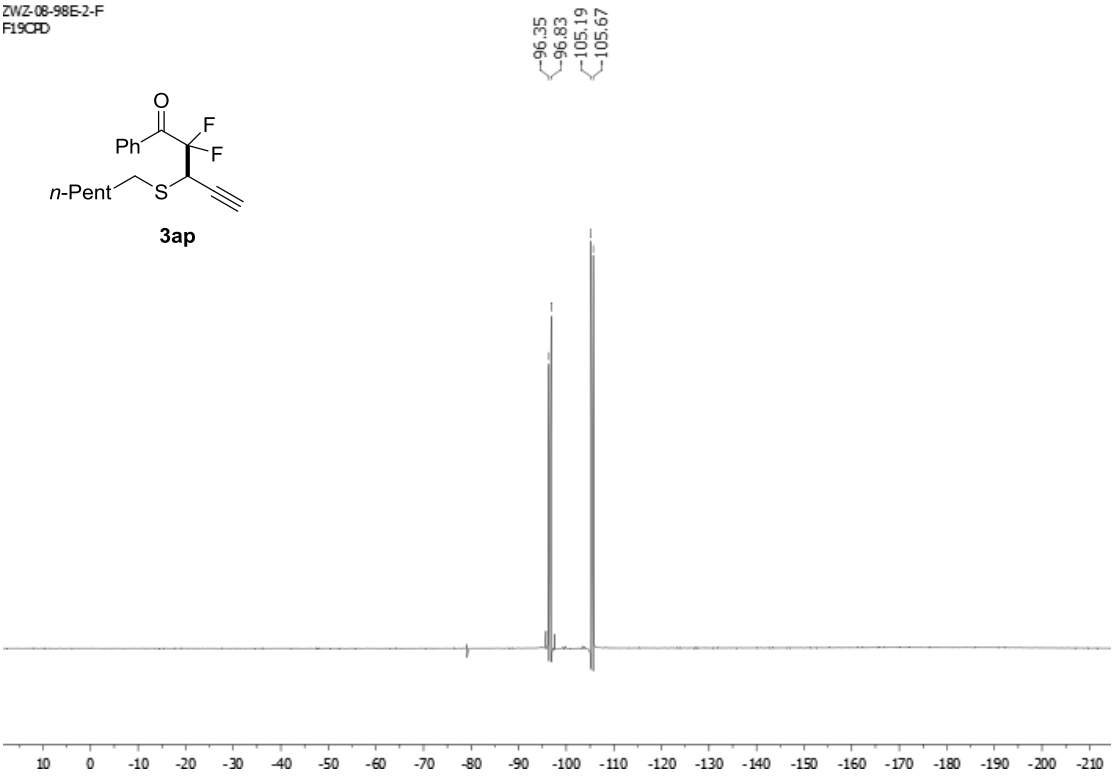


ZWZ-08-98E-2(2r)
13CNMR

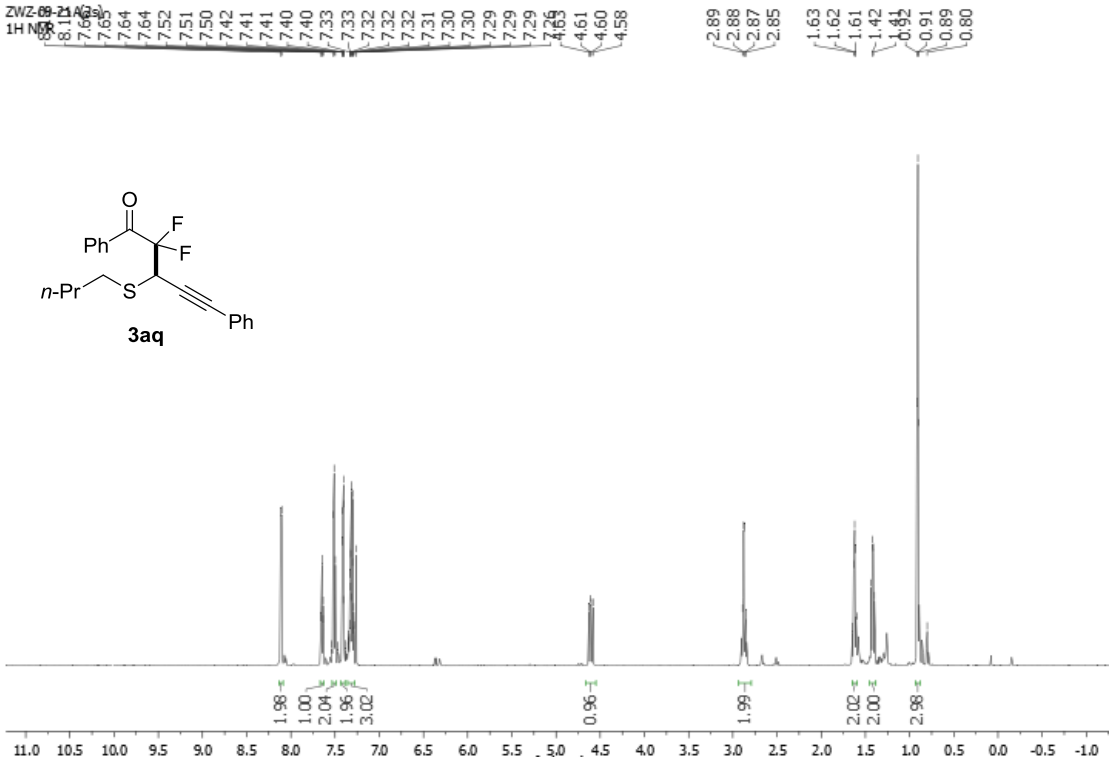


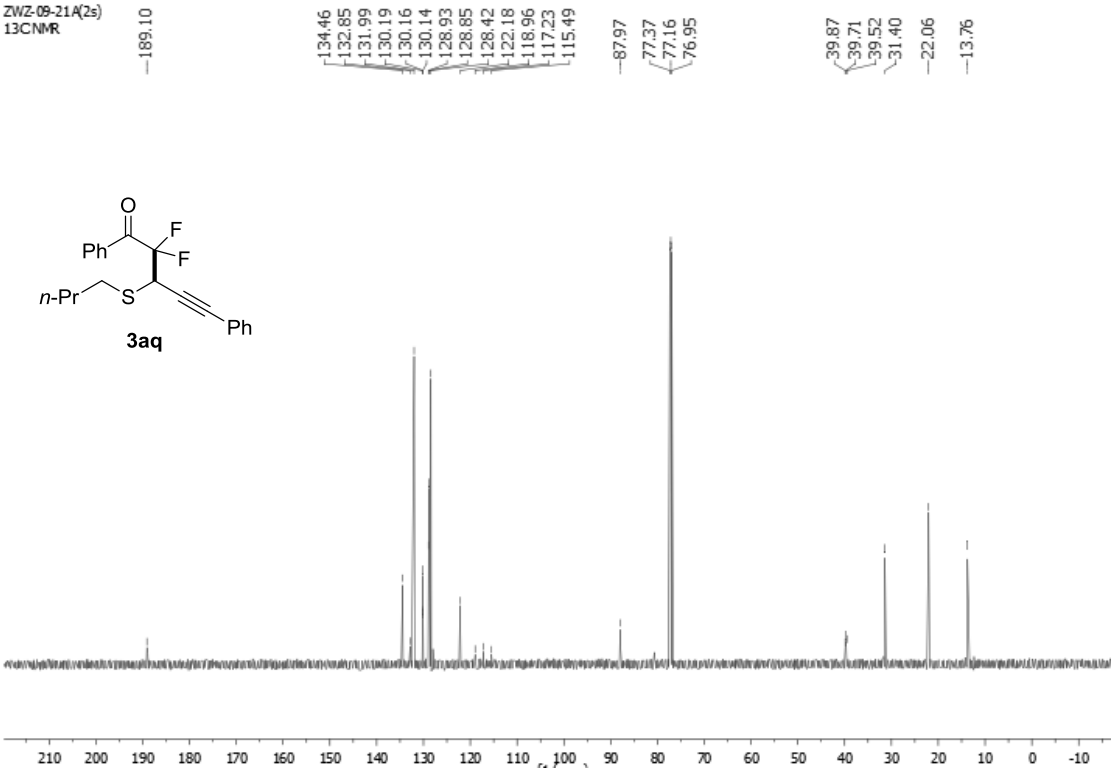
3ap

ZWZ-08-98E-2-F
F19CPD

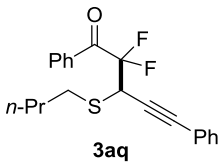


3ap


ZWZ-09-21A(2s)
1H NMR
8.15
7.66
7.65
7.64
7.64
7.52
7.51
7.50
7.42
7.41
7.41
7.40
7.40
7.33
7.33
7.32
7.32
7.32
7.31
7.30
7.30
7.29
7.29
7.29
7.26
4.63
4.61
4.60
4.58
2.89
2.88
2.87
2.85
1.63
1.62
1.61
1.42
1.41
0.92
0.91
0.89
0.80
O
F
Ph
F
n-Pr
S
Ph
3aq
1.98
1.00
2.04
1.96
3.02
0.96
1.99
2.02
2.00
2.98
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

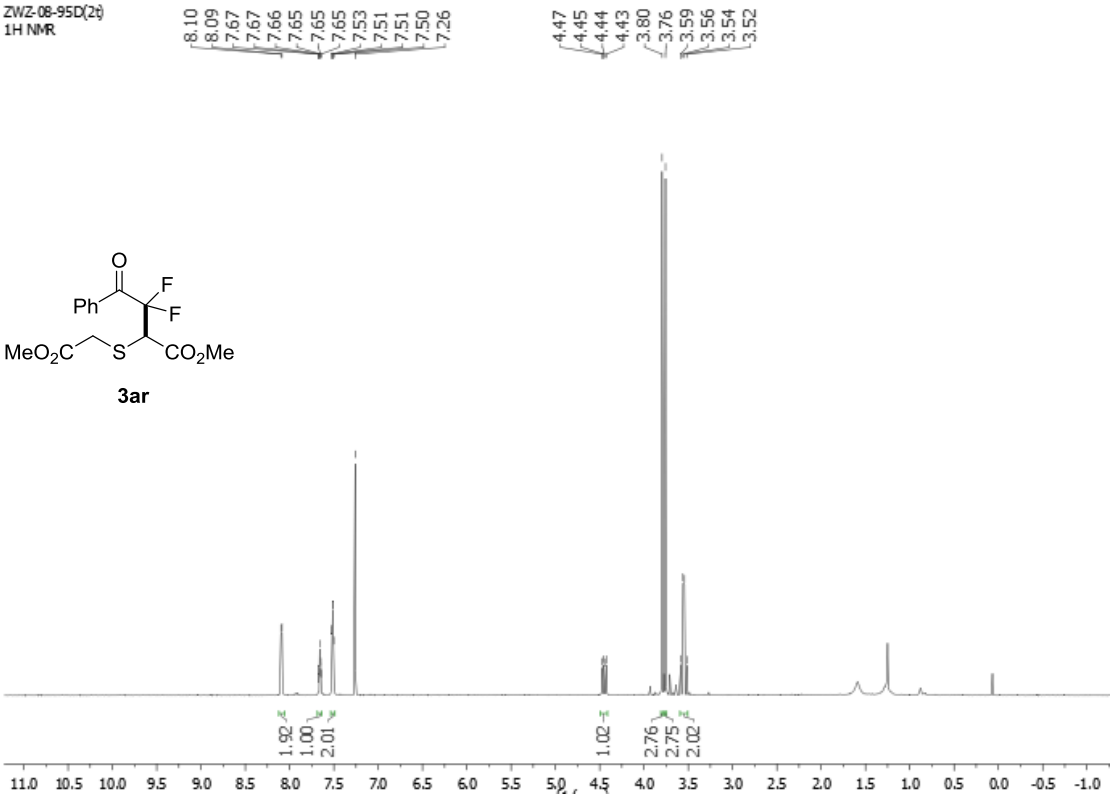

ZWZ-09-21A(2s)
13CNMR
189.10
134.46
132.85
131.99
130.19
130.16
130.14
128.93
128.85
128.42
122.18
118.96
117.23
115.49
87.97
77.37
77.16
76.95
39.87
39.71
39.52
31.40
22.06
13.76
O
F
Ph
F
n-Pr
S
Ph
3aq
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

ZWZ-09-21A-F
F19CPD



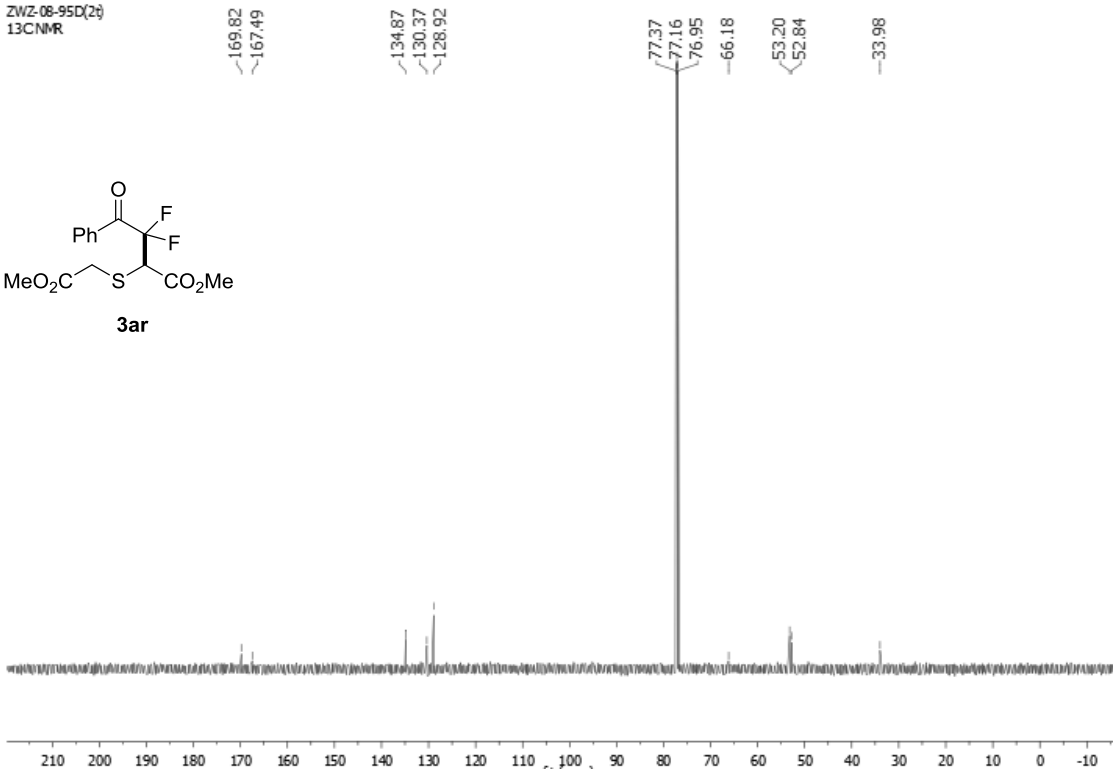
3aq

ZWZ-08-95D(2t)
1H NMR



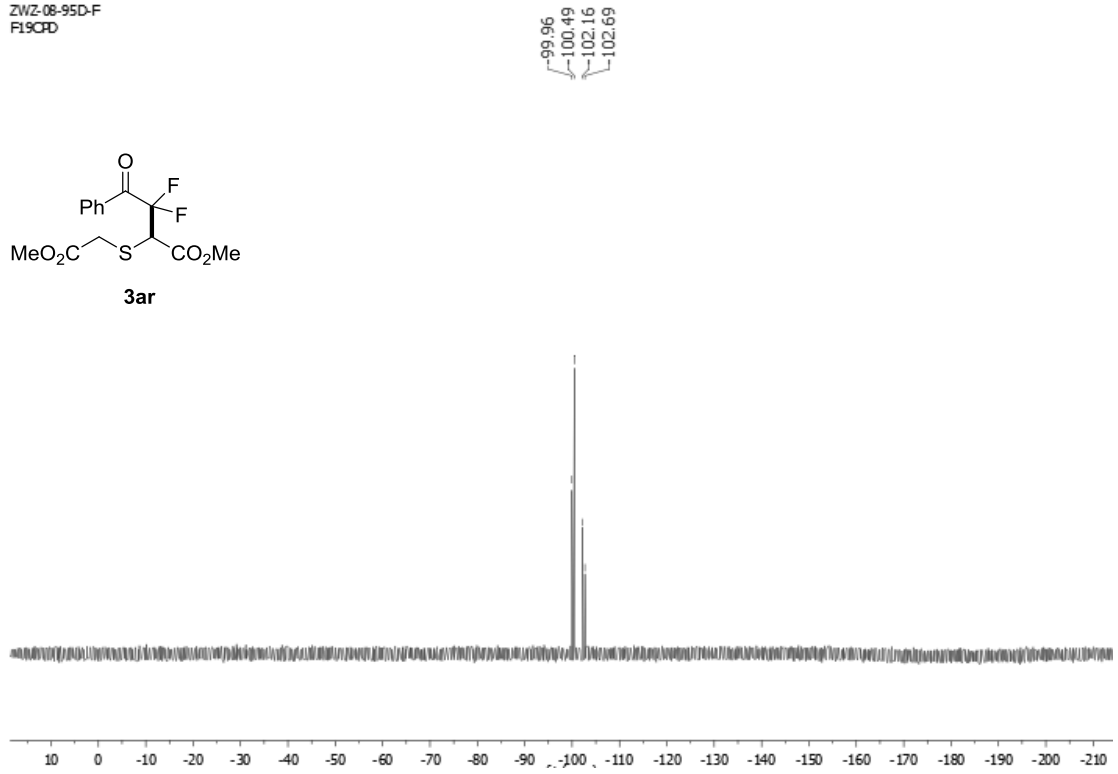
3ar

ZWZ-08-95D(2t)
13CNMR



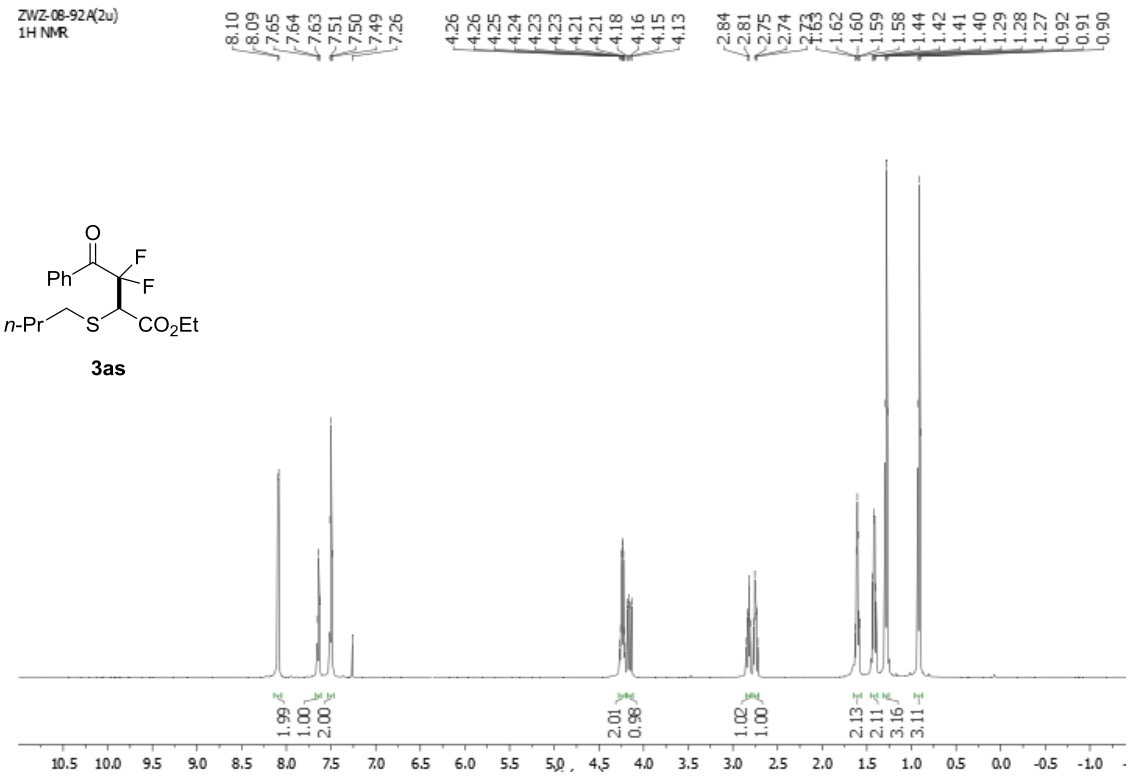
3ar

ZWZ-08-95D-F
F19CPD



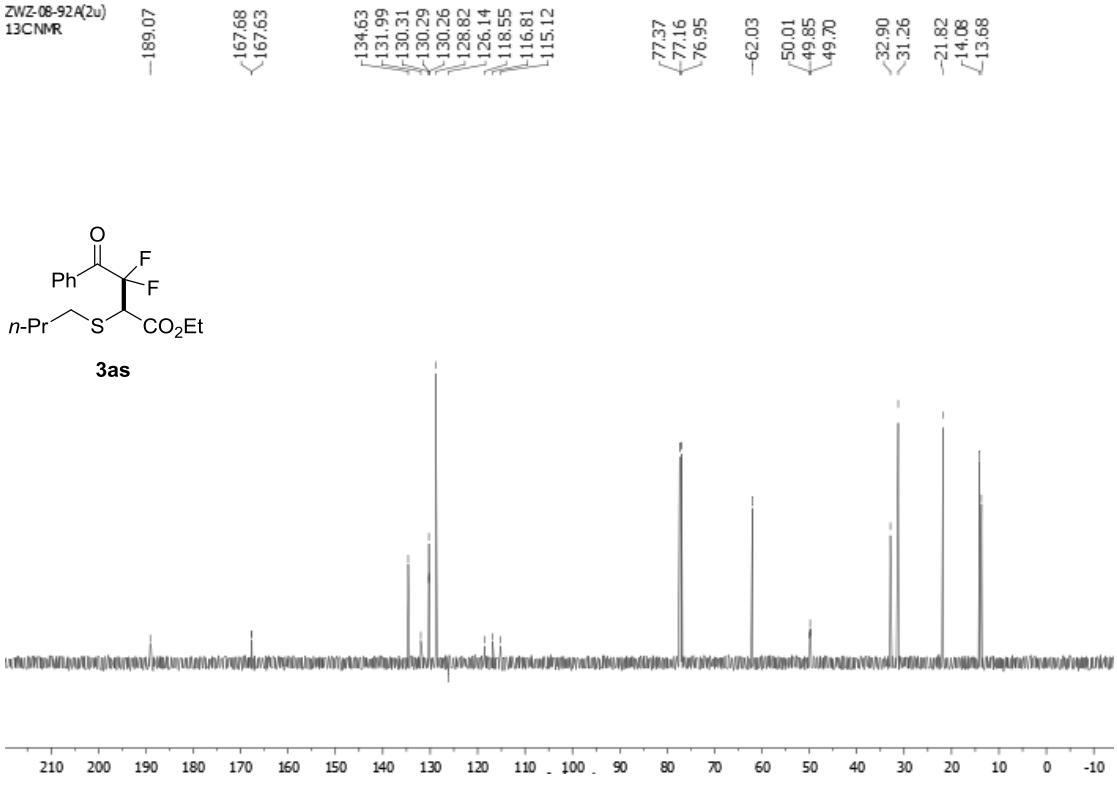
3ar

ZWZ-08-92A(2u)
1H NMR



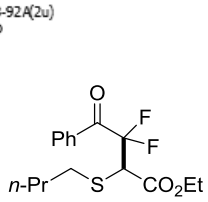
3as

ZWZ-08-92A(2u)
13CNMR



3as

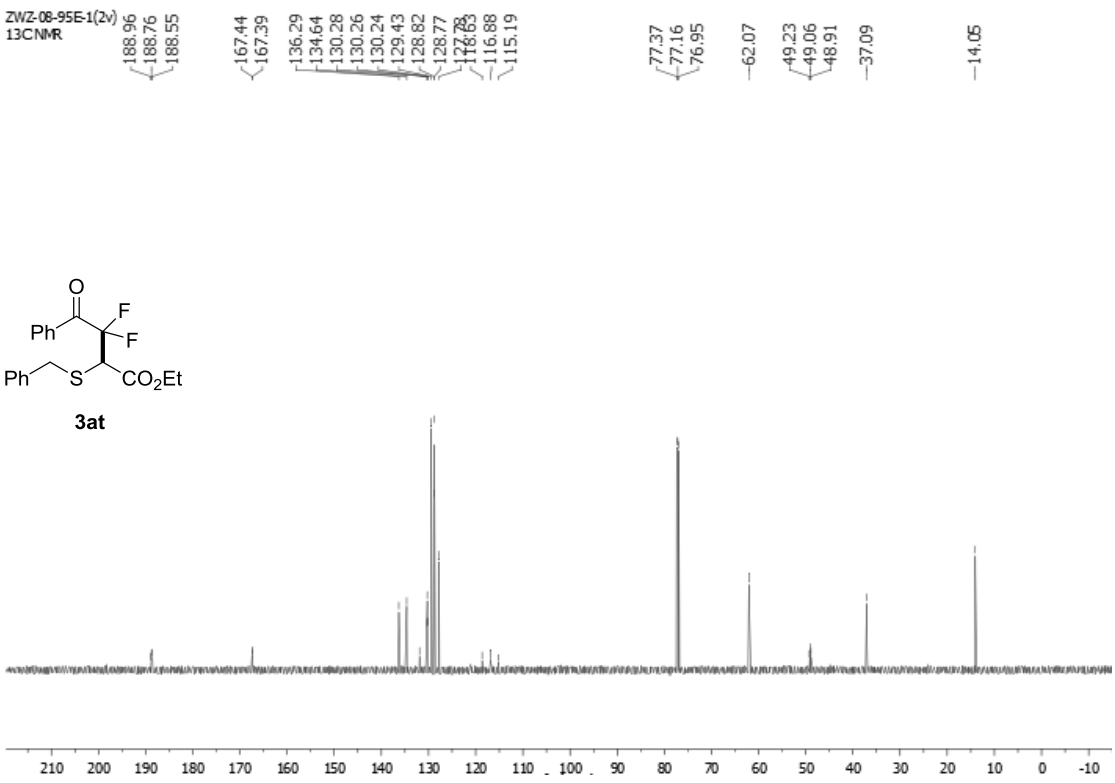
ZWZ-08-92A(2u)
F19CPD

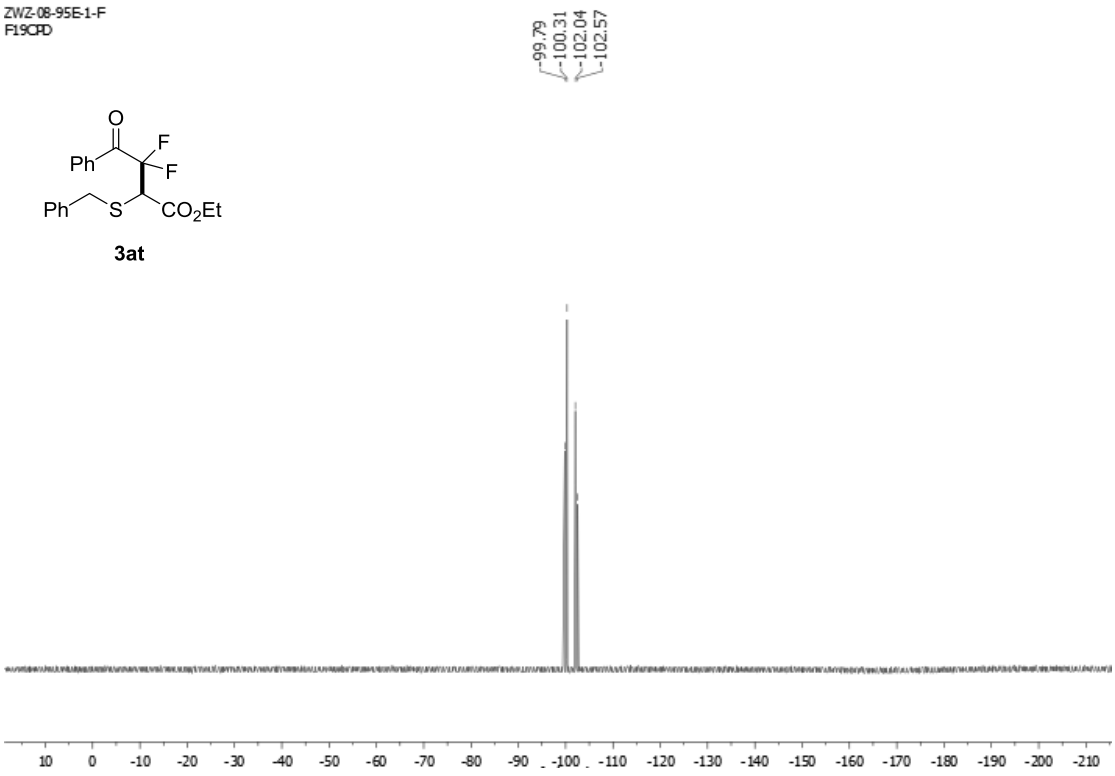


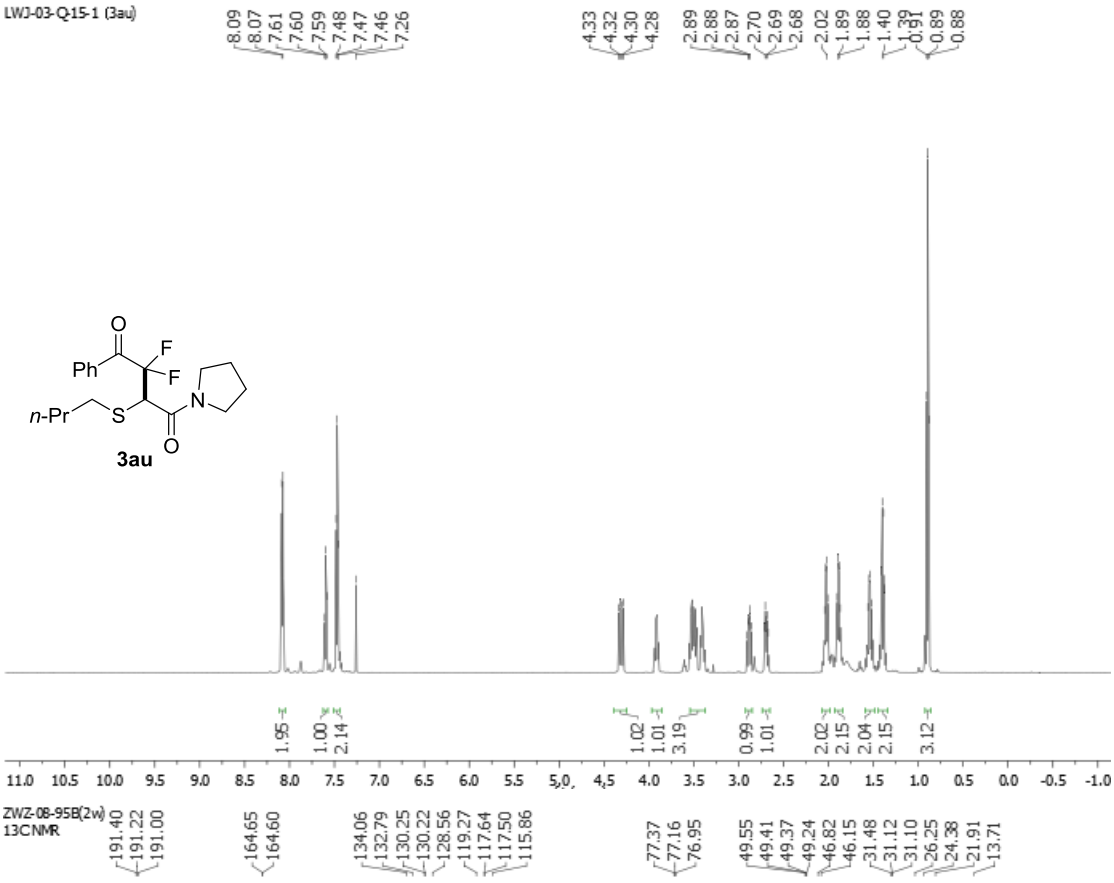
3as

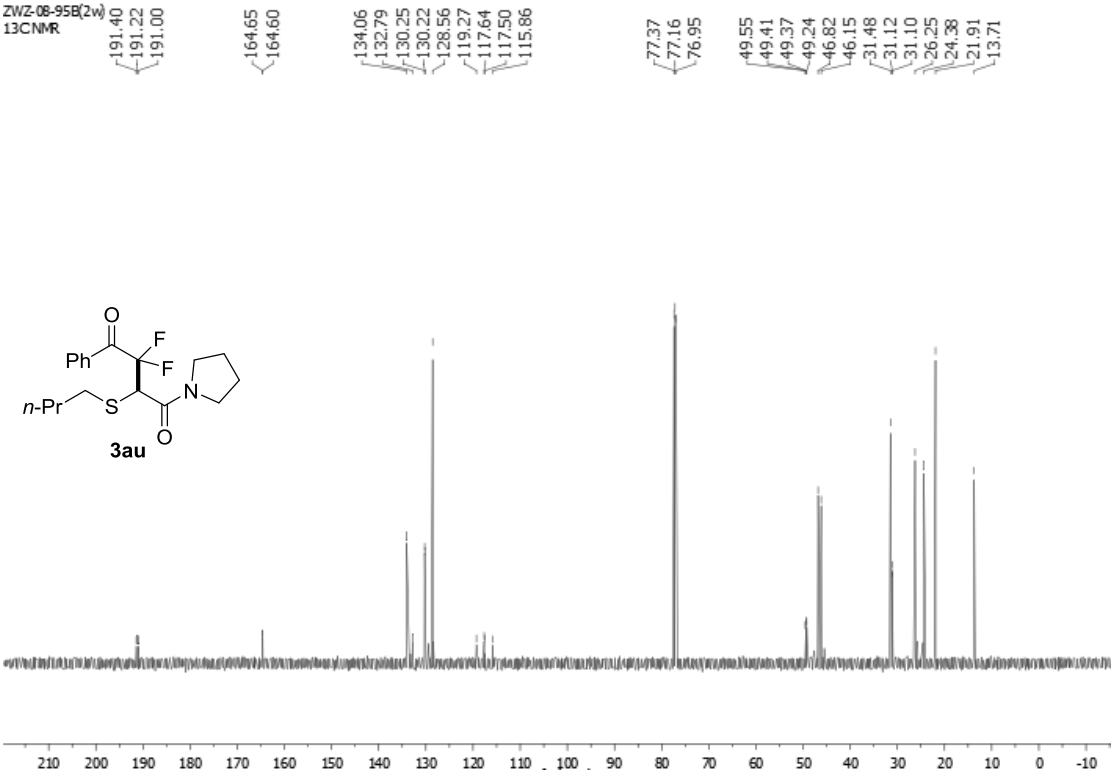
ZWZ-08-95E-1(2v)
1H NMR

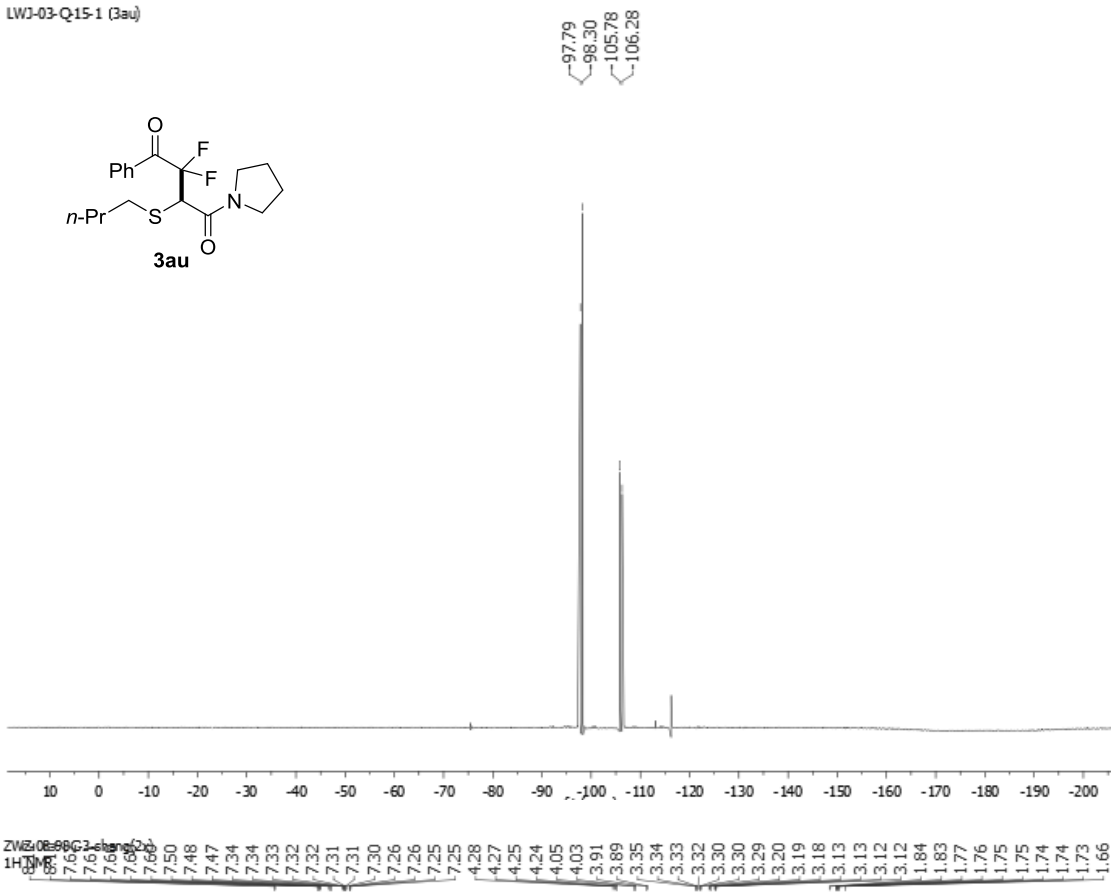
3at

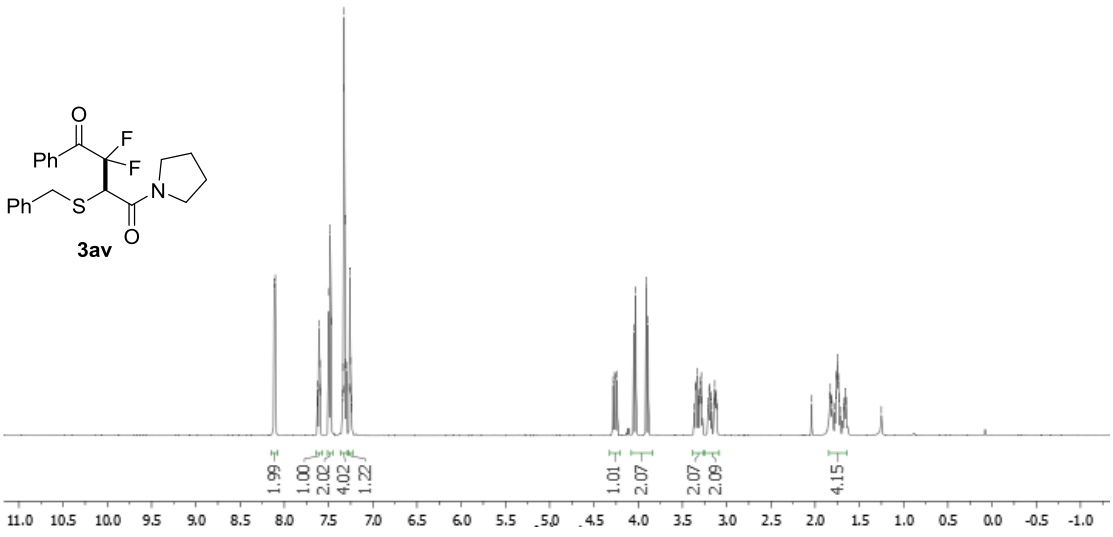

ZWZ-08-95E-1(2v)
13CNMR
188.96
188.76
188.55
167.44
167.39
136.29
134.64
130.28
130.26
130.24
129.43
128.82
128.77
127.28
118.63
116.88
115.19
77.37
77.16
76.95
62.07
49.23
49.06
48.91
37.09
14.05
O
F
Ph
F
Ph
S
CO2Et
3at
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

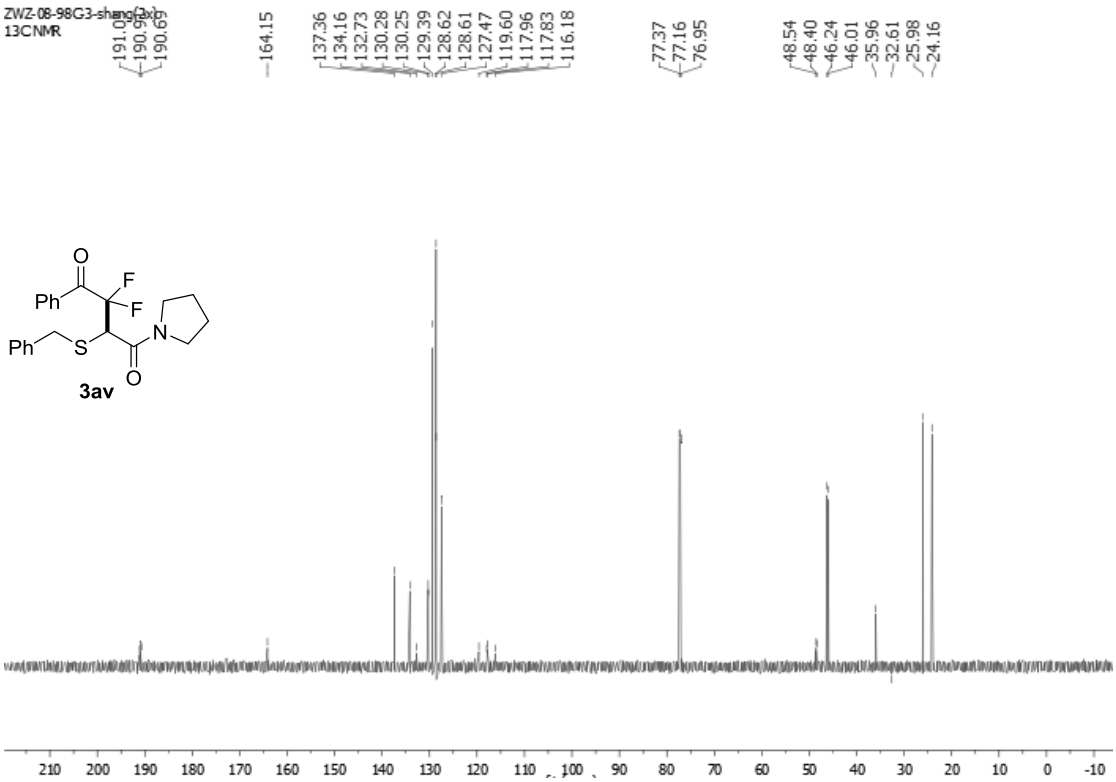

ZWZ-08-95E-1-F
F19CPD
-99.79
-100.31
-102.04
-102.57
O
F
Ph
F
Ph
S
CO2Et
3at
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

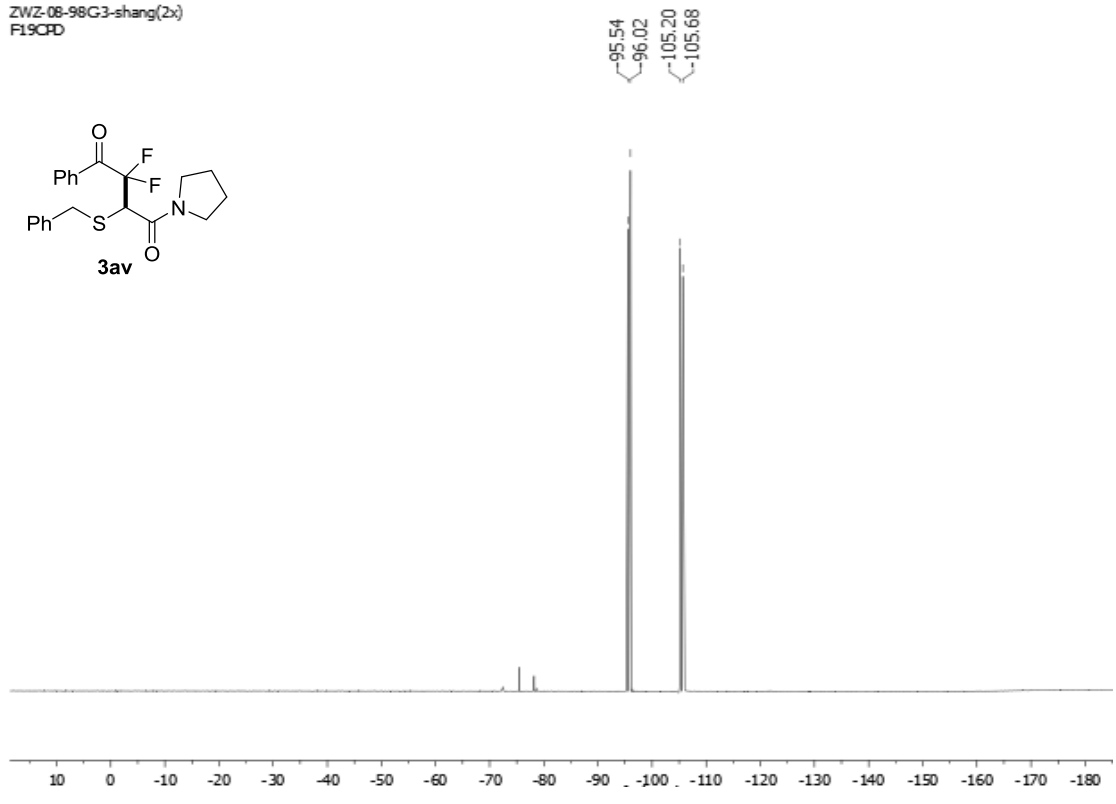

LWJ-03-Q15-1 (3au)
8.09
8.07
7.61
7.60
7.59
7.48
7.47
7.46
7.26
4.33
4.32
4.30
4.28
2.89
2.88
2.87
2.70
2.69
2.68
2.02
1.89
1.88
1.40
1.39
0.91
0.89
0.88
O
Ph
F
F
n-Pr
S
N
O
3au
1.95
1.00
2.14
1.02
1.01
3.19
0.99
1.01
2.02
2.15
2.04
2.15
3.12
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0


ZWZ-08-95B(2w)
13CNMR
191.40
191.22
191.00
164.65
164.60
134.06
132.79
130.25
130.22
128.56
119.27
117.64
117.50
115.86
77.37
77.16
76.95
49.55
49.41
49.37
49.24
46.82
46.15
31.48
31.12
31.10
26.25
24.38
21.91
13.71
O
Ph
F
F
n-Pr
S
N
O
3au
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

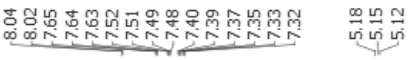

LWJ-03-Q-15-1 (3au)
97.79
98.30
105.78
106.28
O
F
Ph
F
n-Pr
S
N
O
3au
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
1H NMR
7.66 7.61 7.60 7.48 7.47 7.34 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.26 7.26 7.25 7.25 4.28 4.27 4.25 4.24 4.05 4.03 3.91 3.89 3.35 3.34 3.33 3.32 3.30 3.30 3.29 3.20 3.19 3.18 3.13 3.13 3.12 3.12 1.84 1.83 1.77 1.76 1.75 1.75 1.74 1.74 1.73 1.66

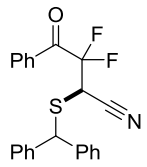

O
F
Ph
F
Ph
S
N
O
3av
1.99
1.00
2.02
4.02
1.22
1.01
2.07
2.07
2.09
4.15
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0


ZWZ-08-98G3-shang(2x)
13CNMR
191.05
190.84
190.69
164.15
137.36
134.16
132.73
130.28
130.25
129.39
128.62
128.61
127.47
119.60
117.96
117.83
116.18
77.37
77.16
76.95
48.54
48.40
46.24
46.01
35.96
32.61
25.98
24.16
O
F
Ph
F
Ph
S
N
O
3av
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


ZWZ-08-98G3-shang(2x)
F19CPD
-95.54
-96.02
-105.20
-105.68
O
F
Ph
F
Ph
S
N
O
3av
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180

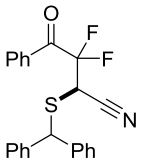
ZYG-03-87(2ay)
1H NMR



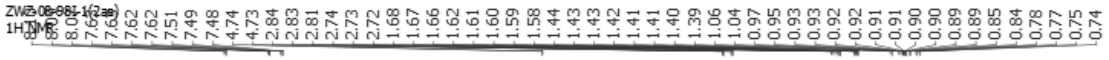


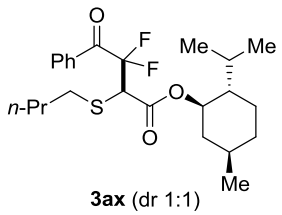
3aw

ZYG-03-87(2ay)
13CNMR

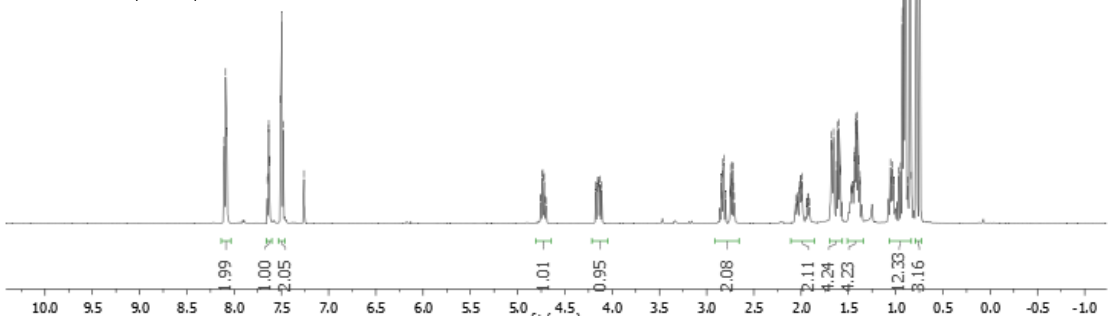


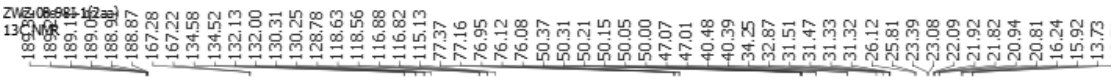
3aw

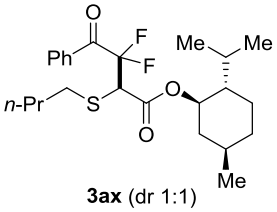




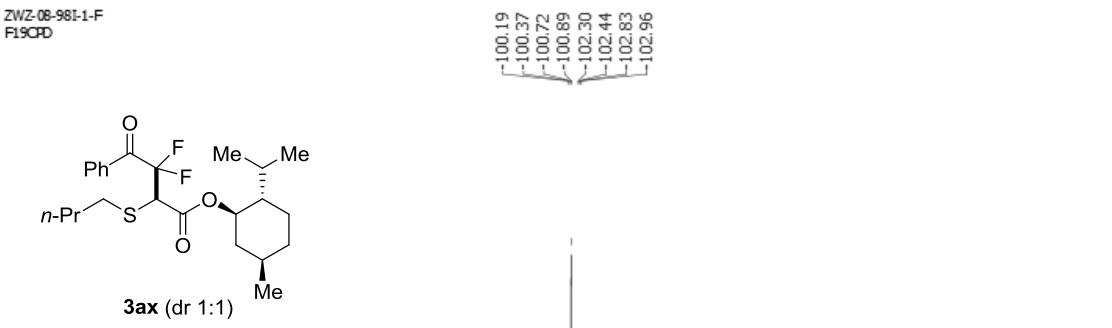
3ax (dr 1:1)



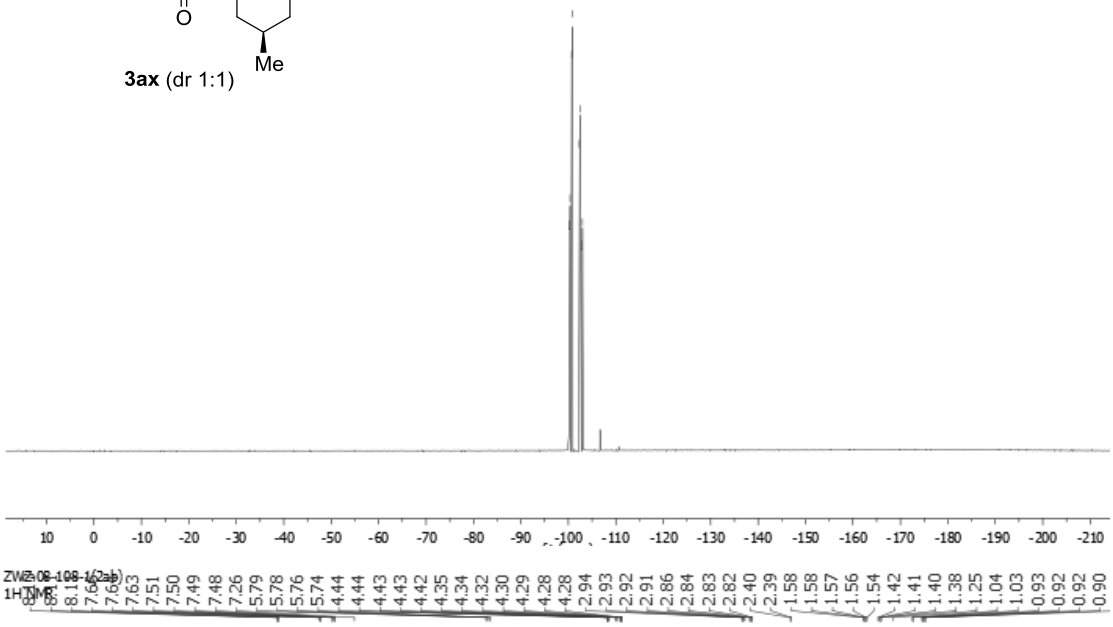


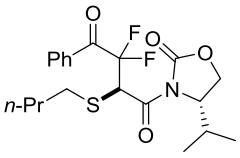


3ax (dr 1:1)



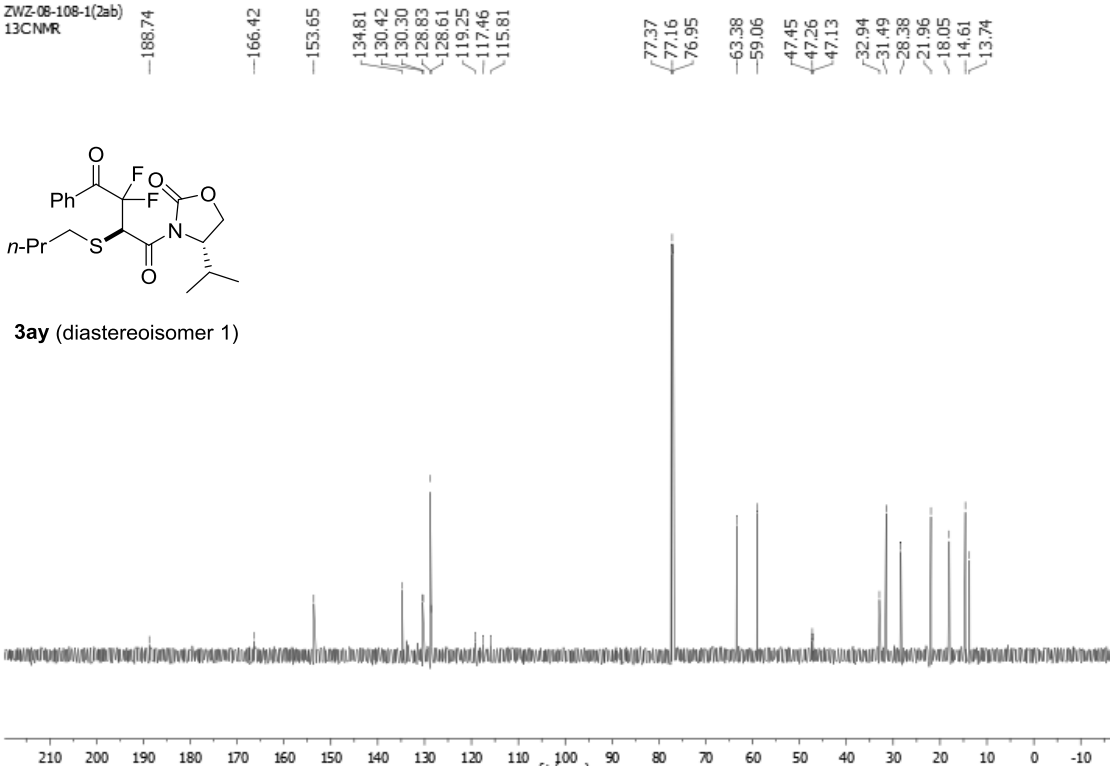
3ax (dr 1:1)





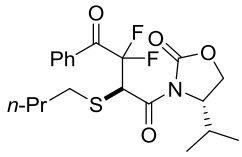
3ay (diastereoisomer 1)

ZWZ-08-108-1(2ab)
13CNMR

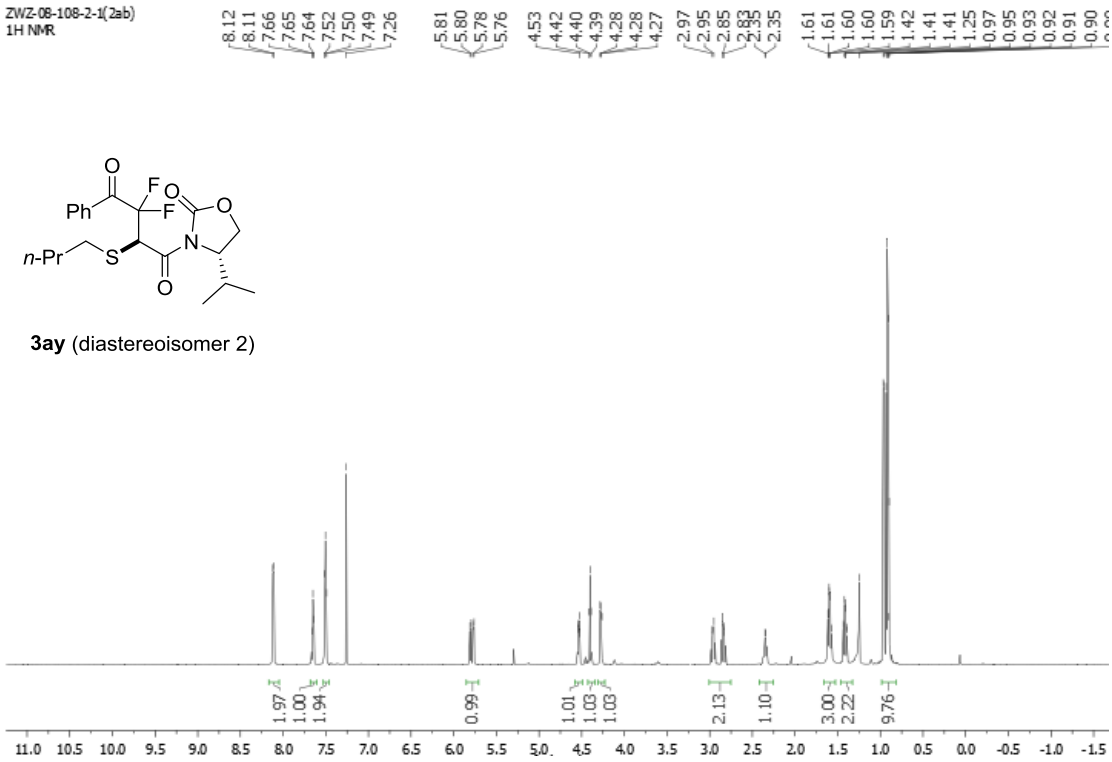


3ay (diastereoisomer 1)

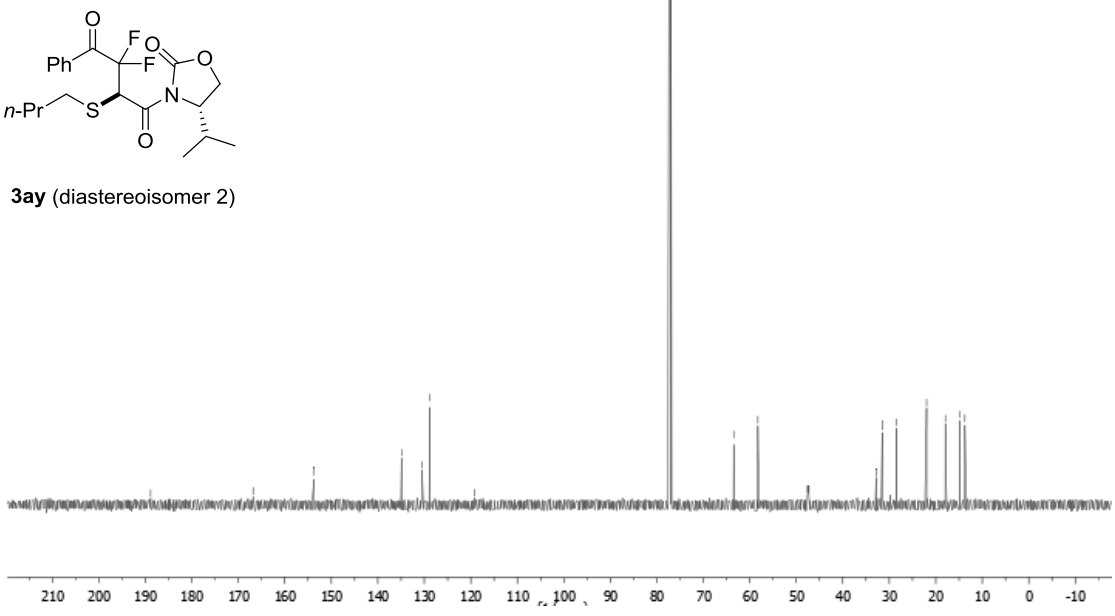
ZWZ-08-108-1-F
F19CRD



3ay (diastereoisomer 1)

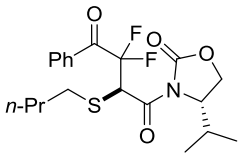


3ay (diastereoisomer 2)

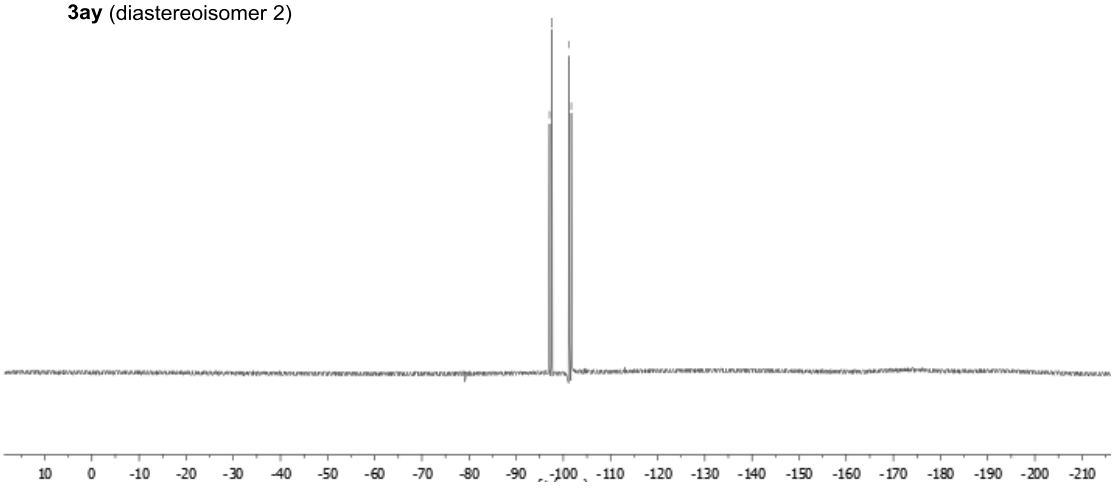


3ay (diastereoisomer 2)

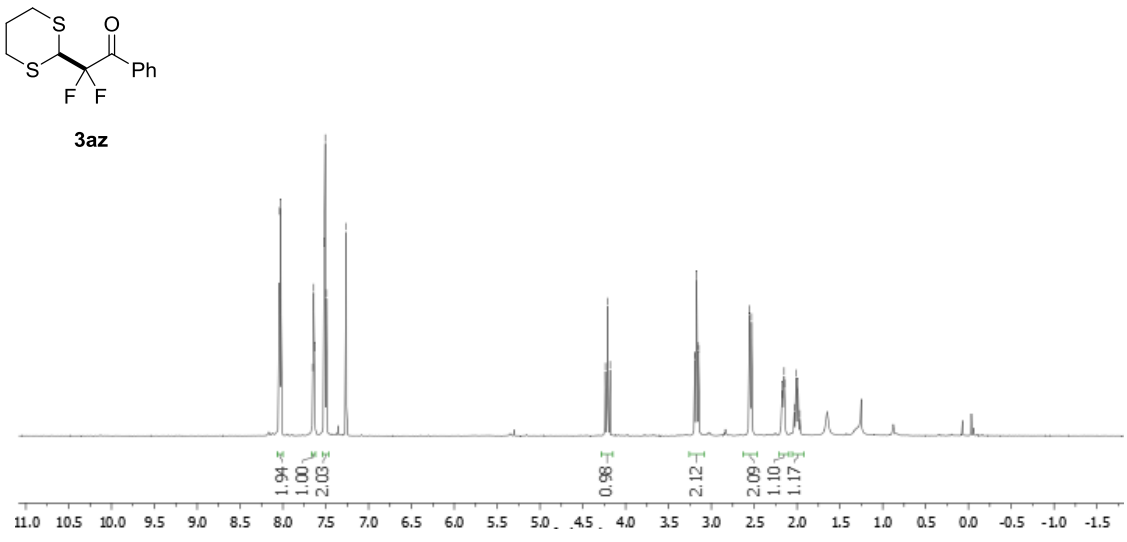
ZWZ-08-108-2-1-F
F19CPD



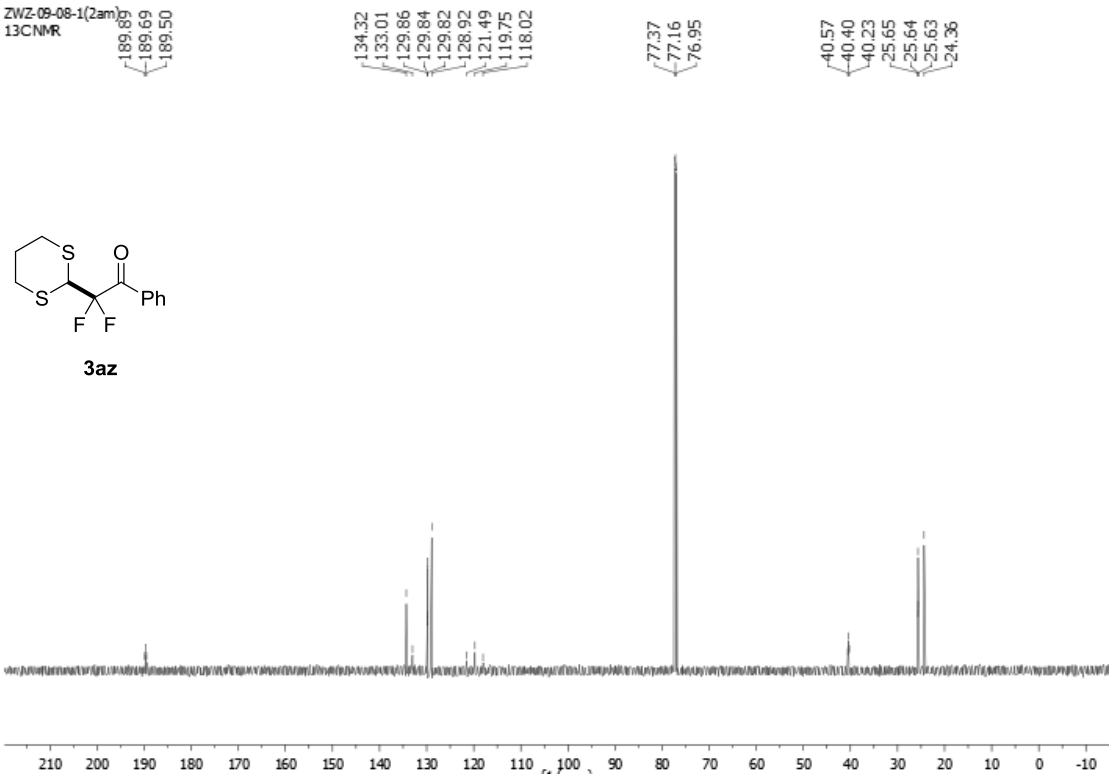
3ay (diastereoisomer 2)



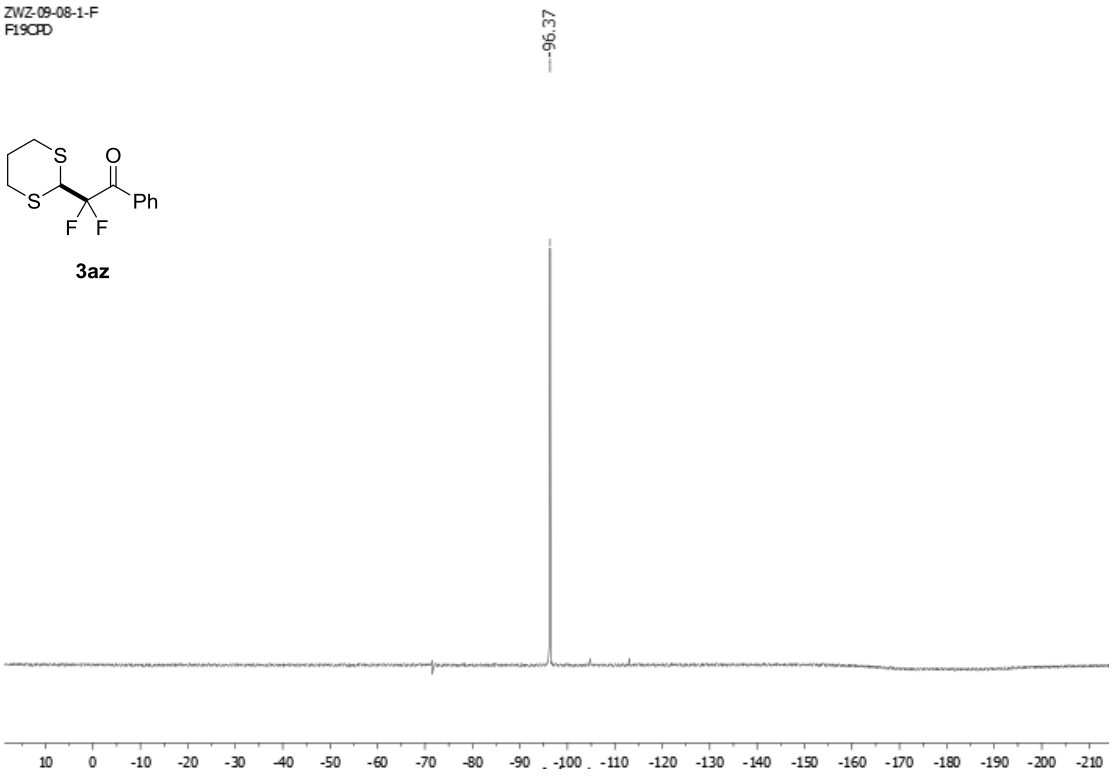
ZWZ-09-08-1(2am)
1H NMR



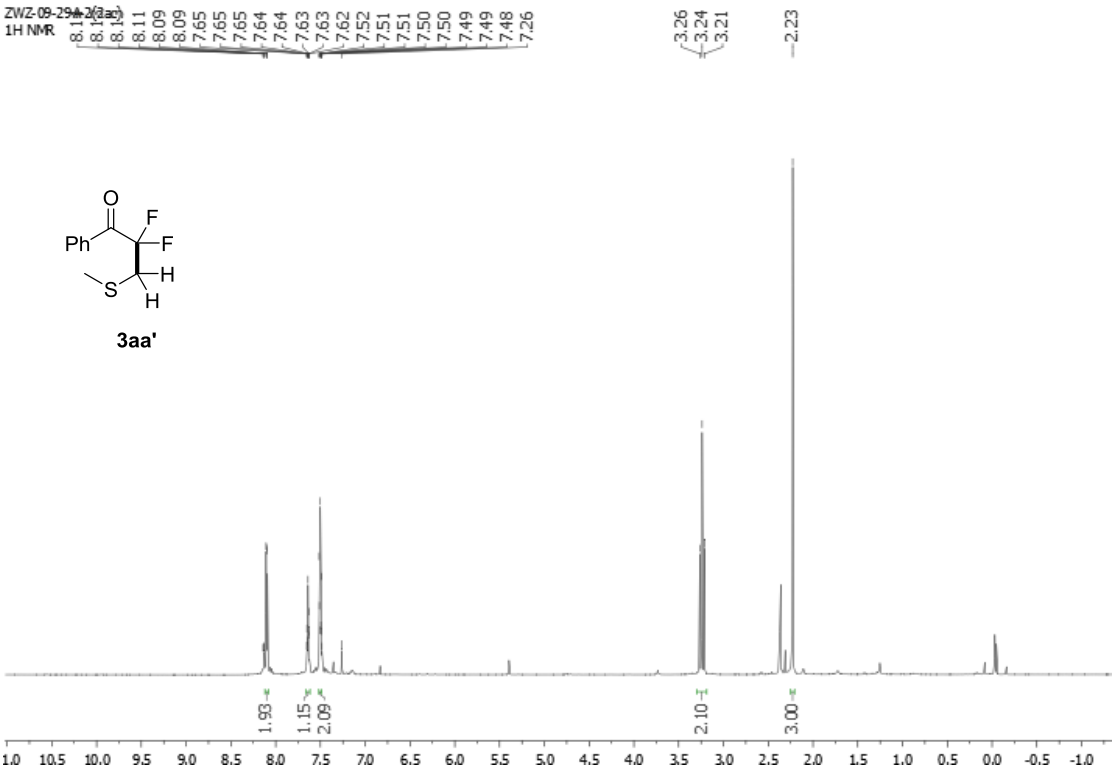
3az


ZWZ-09-08-1(2am)
13CNMR
189.89
189.69
189.50
134.32
133.01
129.86
129.84
129.82
128.92
121.49
119.75
118.02
77.37
77.16
76.95
40.57
40.40
40.23
25.65
25.64
25.63
24.36
S
O
S
Ph
F F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

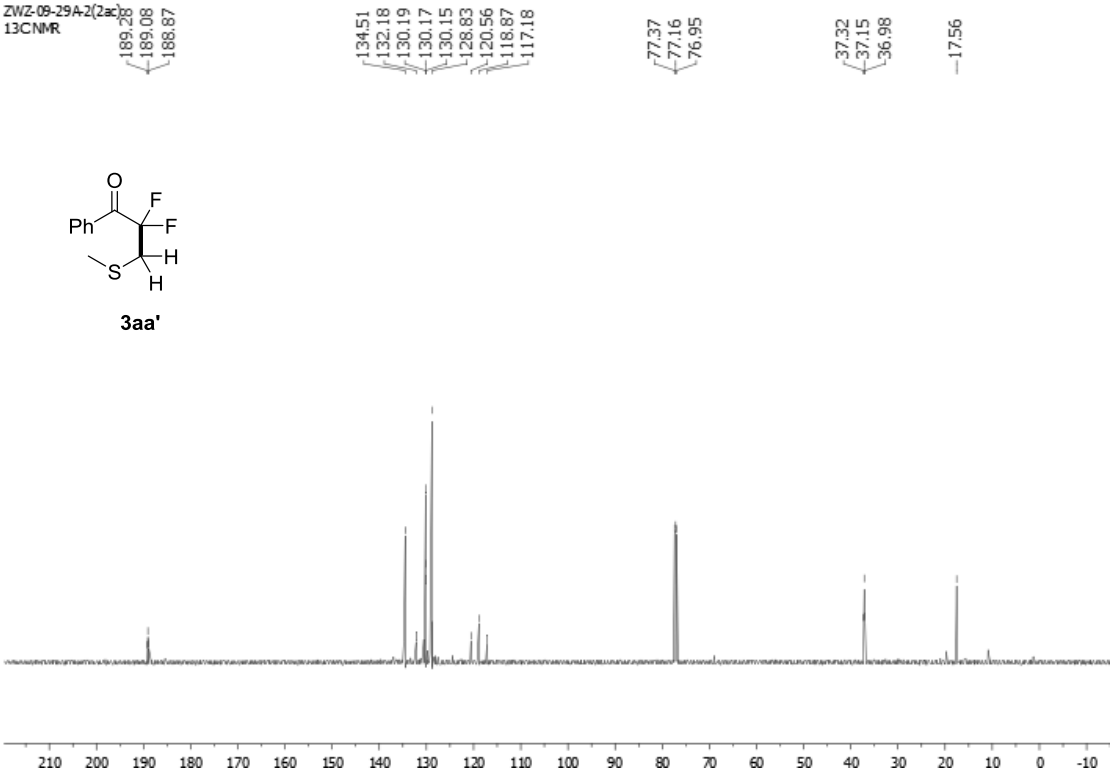
3az


ZWZ-09-08-1-F
F19CPD
-96.37
S
O
S
Ph
F F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

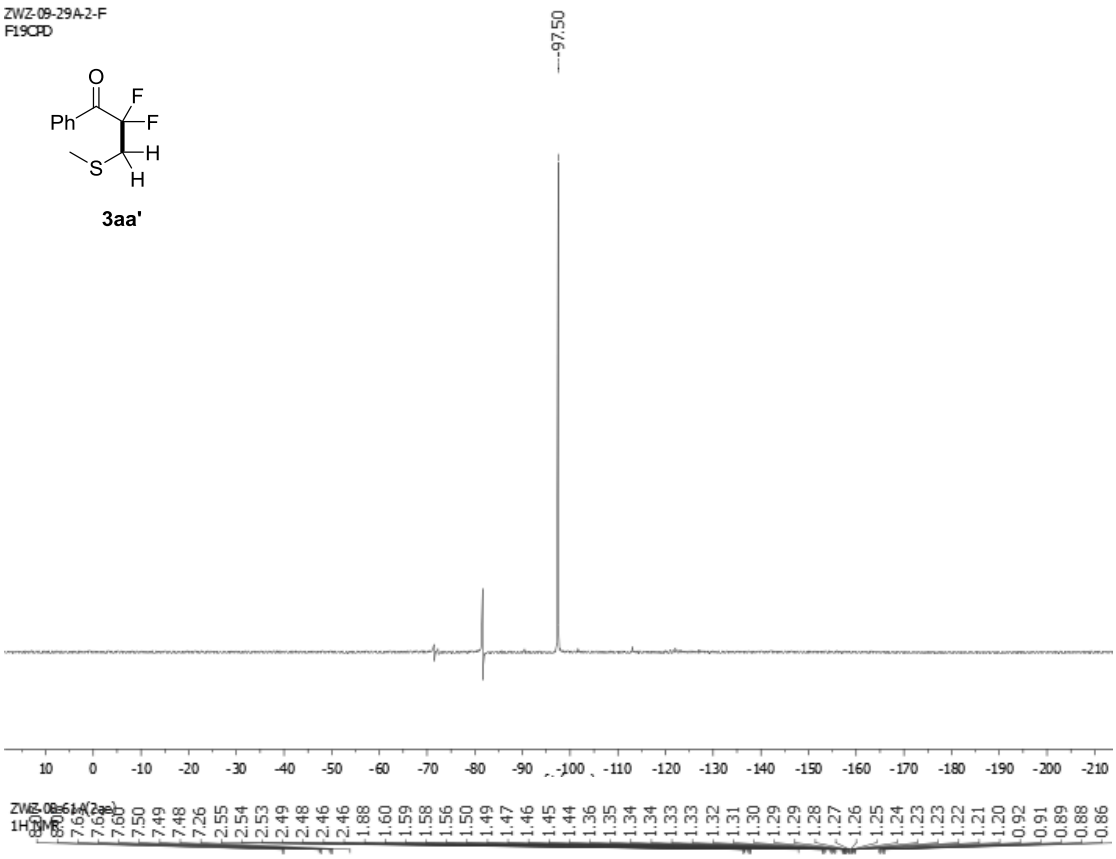
3az

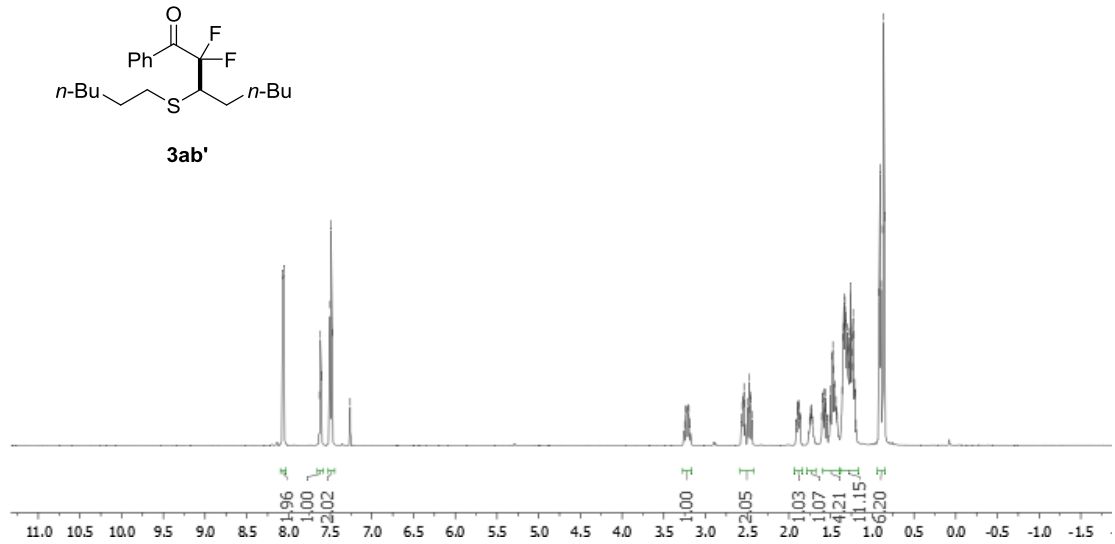

ZWZ-09-29A-2(3aa)
1H NMR
8.11
8.09
8.09
7.65
7.65
7.64
7.64
7.63
7.63
7.62
7.52
7.51
7.51
7.50
7.50
7.49
7.49
7.48
7.26
3.26
3.24
3.21
2.23
O
F
Ph
F
H
S
H
1.93
1.15
2.09
2.10
3.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

3aa'

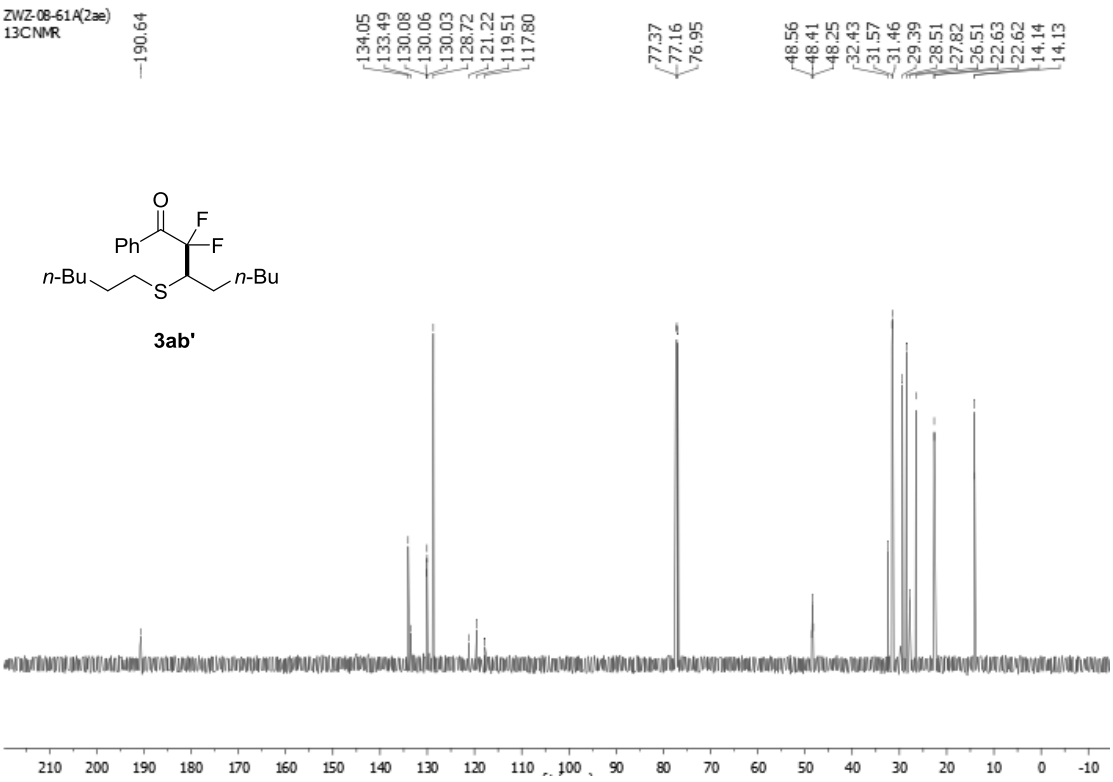

ZWZ-09-29A-2(2aa)
13CNMR
189.28
189.08
188.87
134.51
132.18
130.19
130.17
130.15
128.83
120.56
118.87
117.18
77.37
77.16
76.95
37.32
37.15
36.98
17.56
O
F
Ph
F
H
S
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

3aa'


ZWZ-09-29A-2-F
F19CPD
-97.50
O
F
Ph
F
H
S
H
3aa'
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

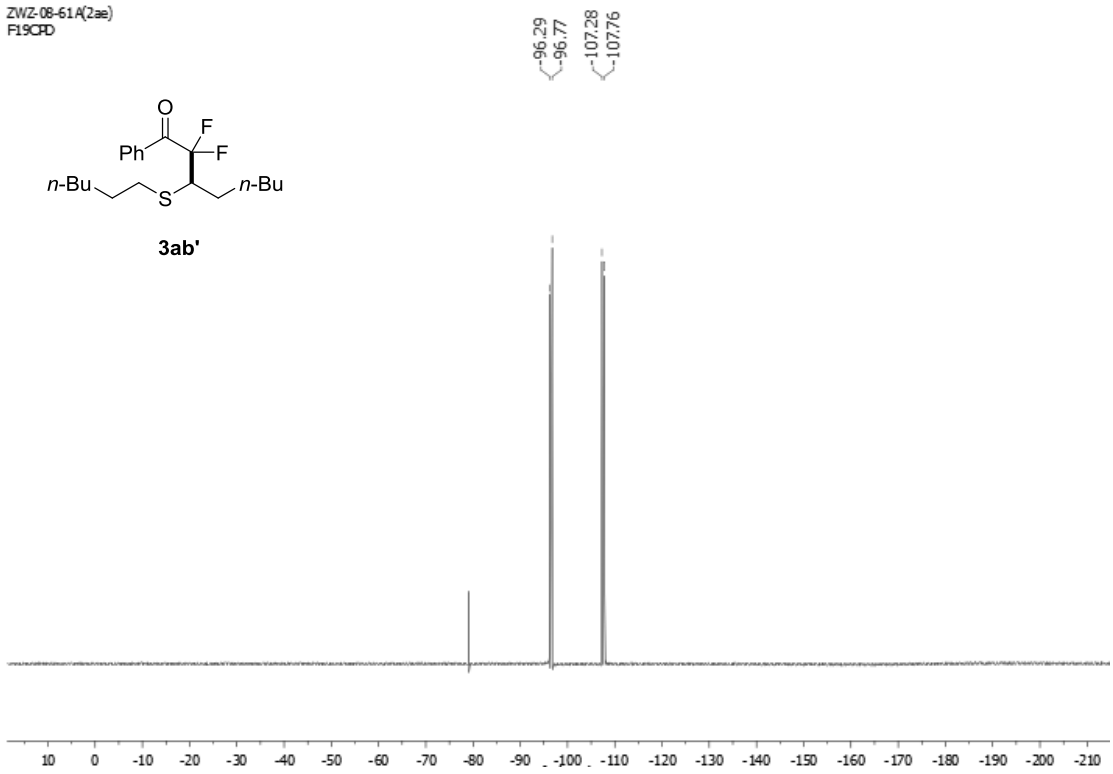

O
F
Ph
F
n-Bu
S
n-Bu
3ab'
1.96
1.00
2.02
1.00
2.05
1.03
1.07
4.21
11.15
6.20
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5

ZWZ-08-61A(2ae)
13CNMR

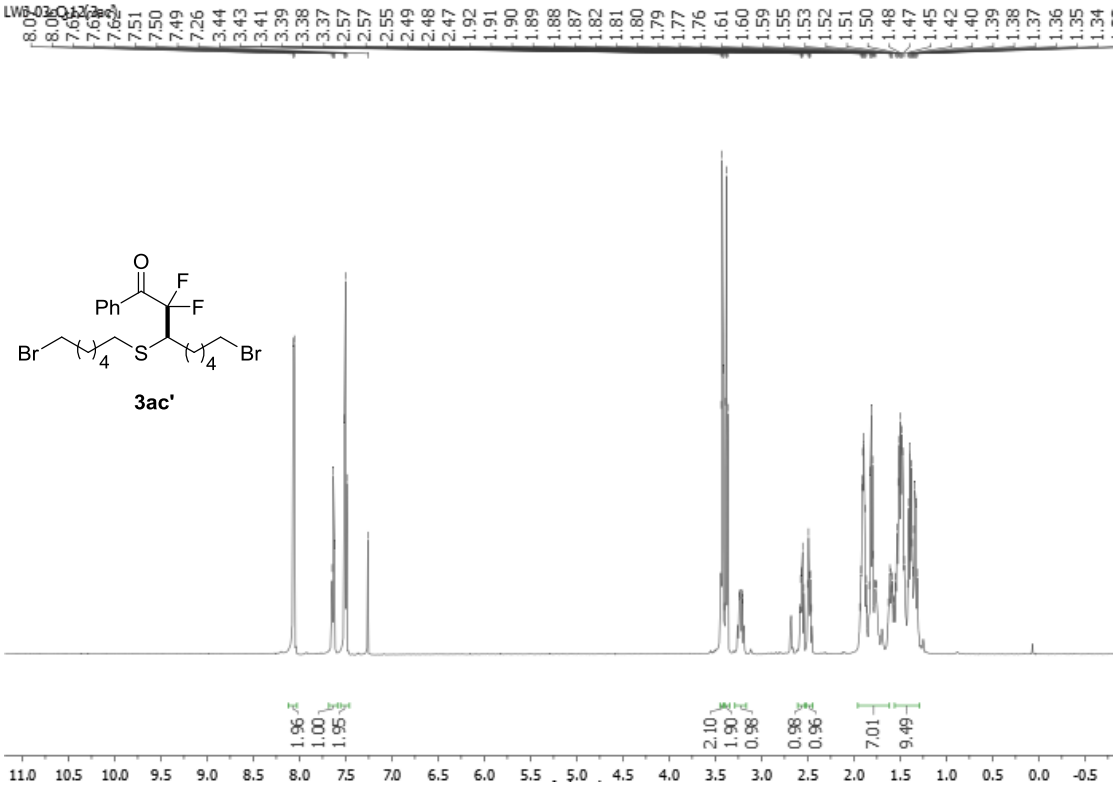


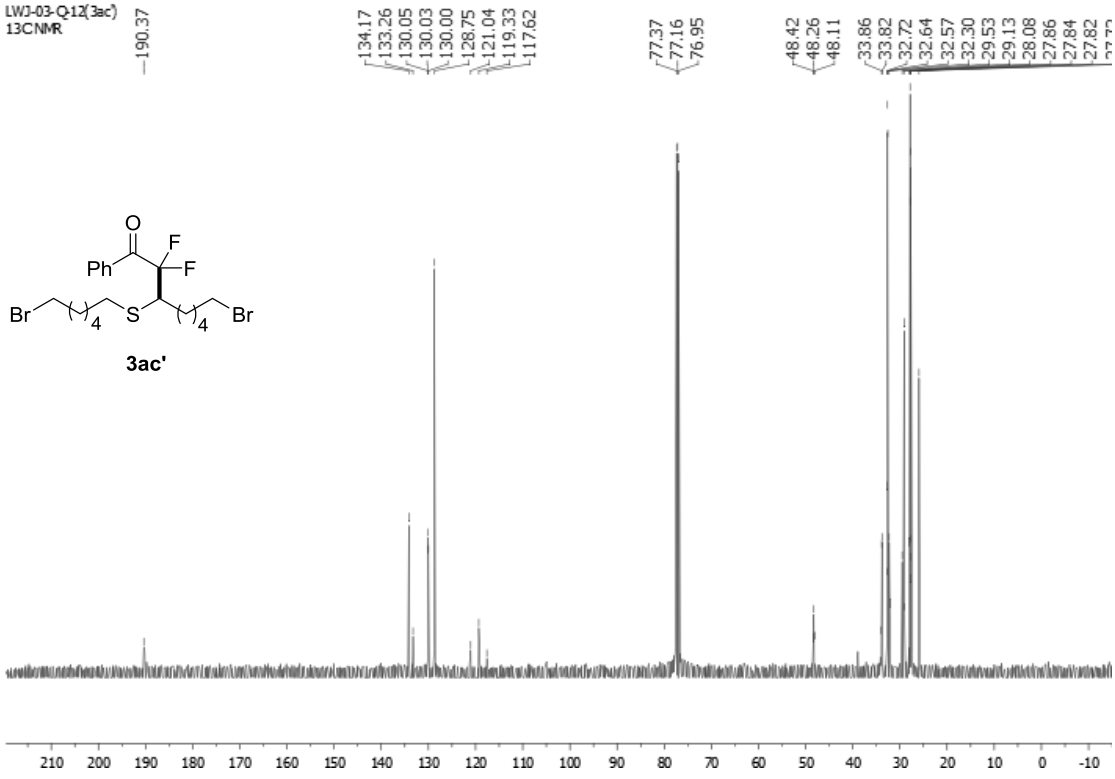
3ab'

ZWZ-08-61A(2ae)
F19CPD

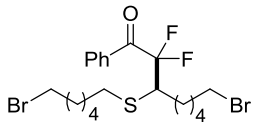


3ab'

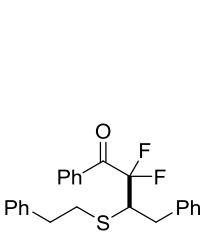

3ac'


LWJ-03-Q-12(3ac')
13CNMR
3ac'

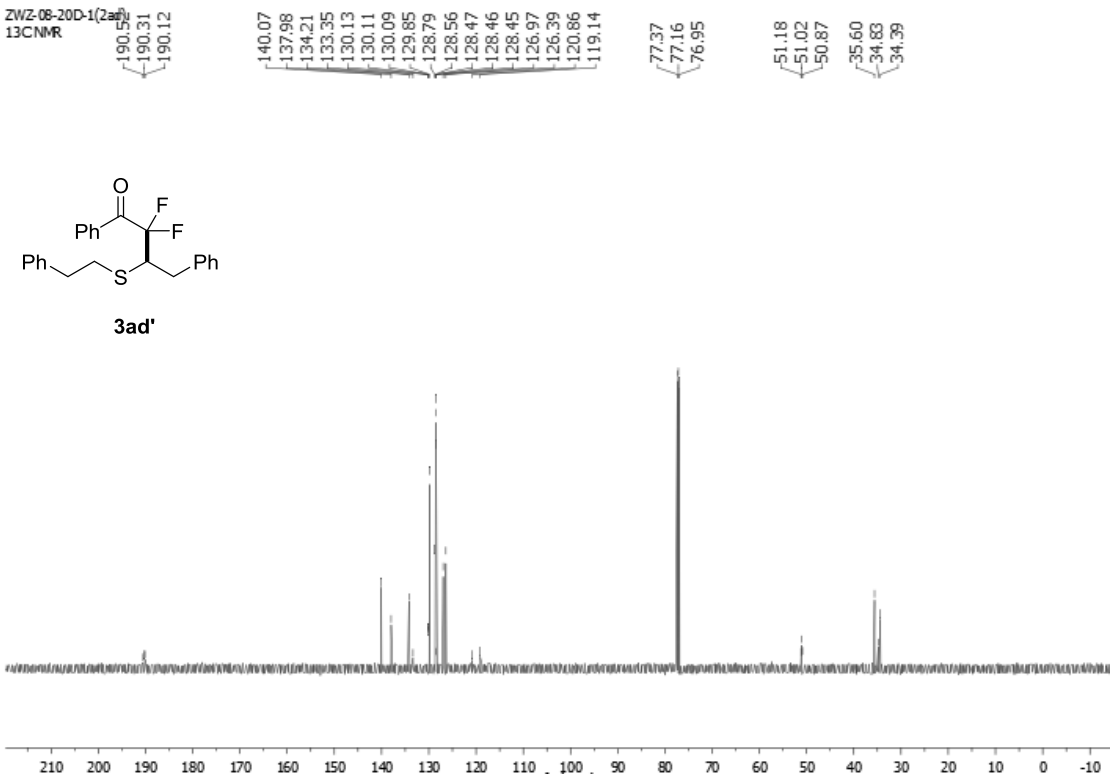
LWJ-03-Q-12(3ac')



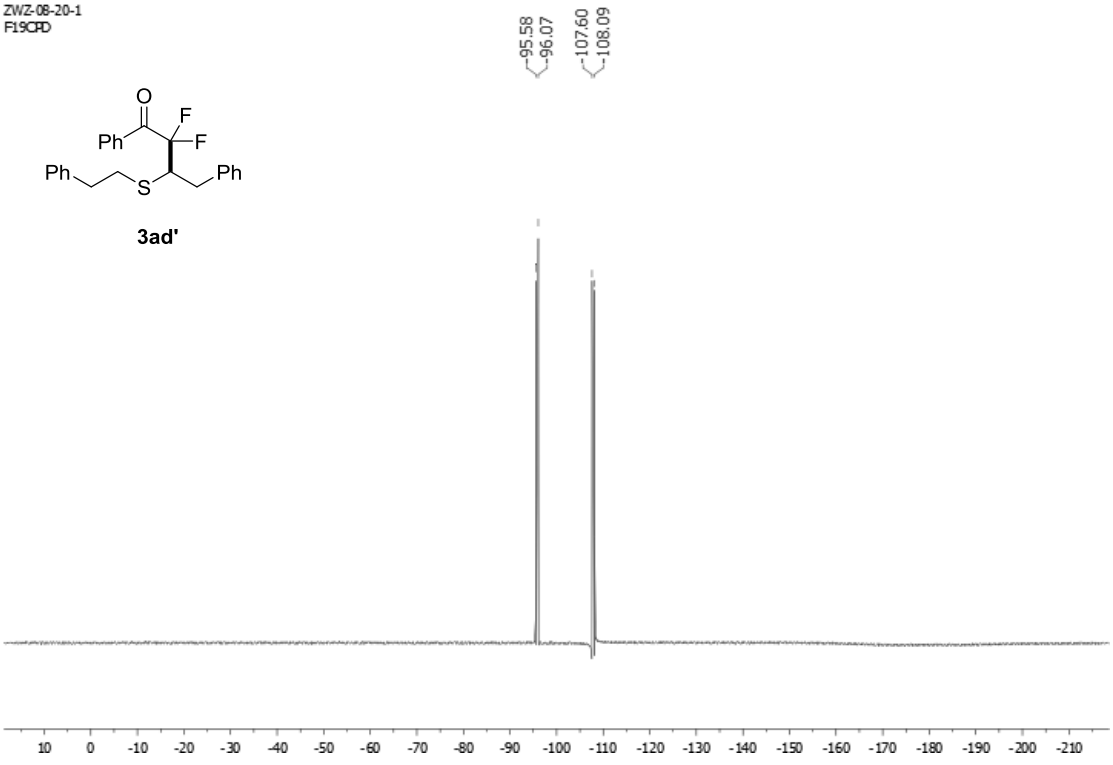
3ac'



3ad'

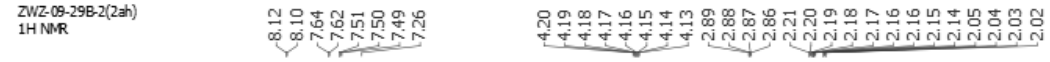

ZWZ-08-20D-1(2ad)
13CNMR
190.52
190.31
190.12
140.07
137.98
134.21
133.35
130.13
130.11
130.09
129.85
128.79
128.56
128.47
128.46
128.45
126.97
126.39
120.86
119.14
77.37
77.16
76.95
51.18
51.02
50.87
35.60
34.83
34.39
O
F
Ph
F
Ph
S
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

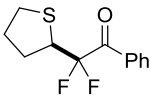
3ad'


ZWZ-08-20-1
F19CPD
-95.58
-96.07
-107.60
-108.09
O
F
Ph
F
Ph
S
Ph
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

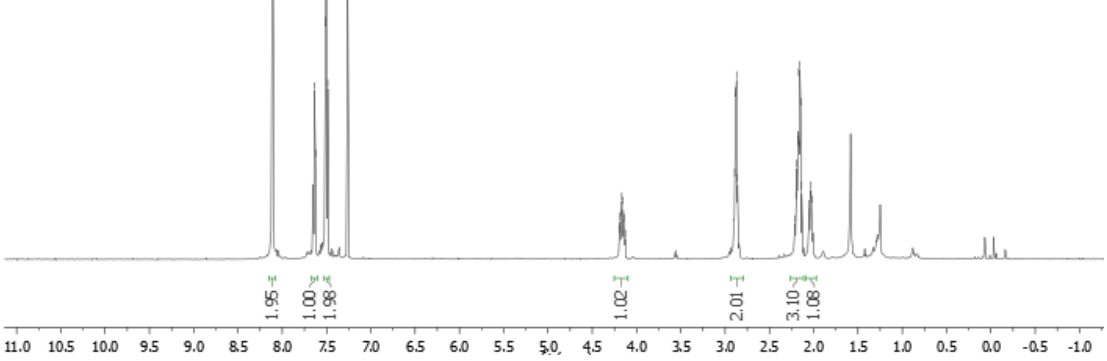
3ad'

ZWZ-09-29B-2(2ah)
1H NMR

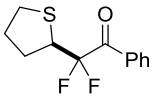




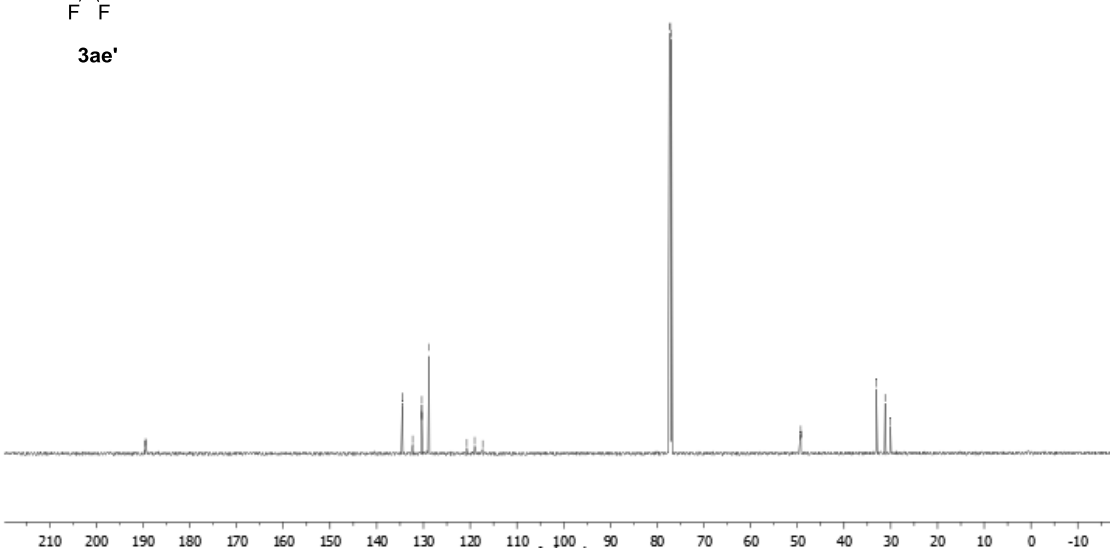
3ae'



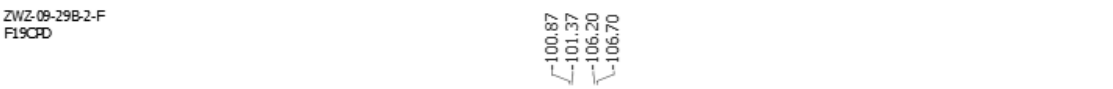
ZWZ-09-29B-2(2ah)
13CNMR

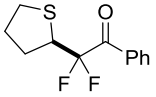


3ae'

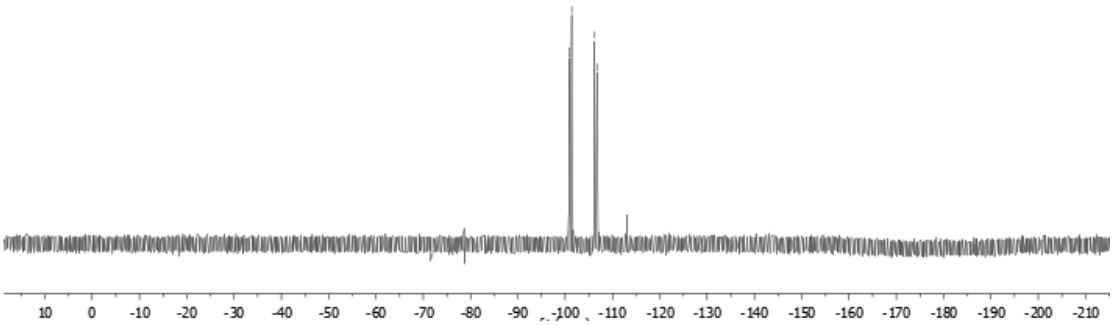


ZWZ-09-29B-2-F
F19CPD

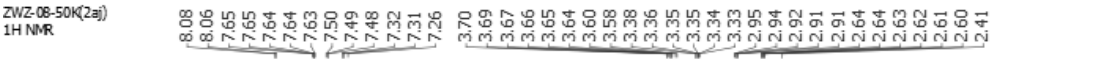


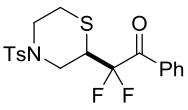


3ae'



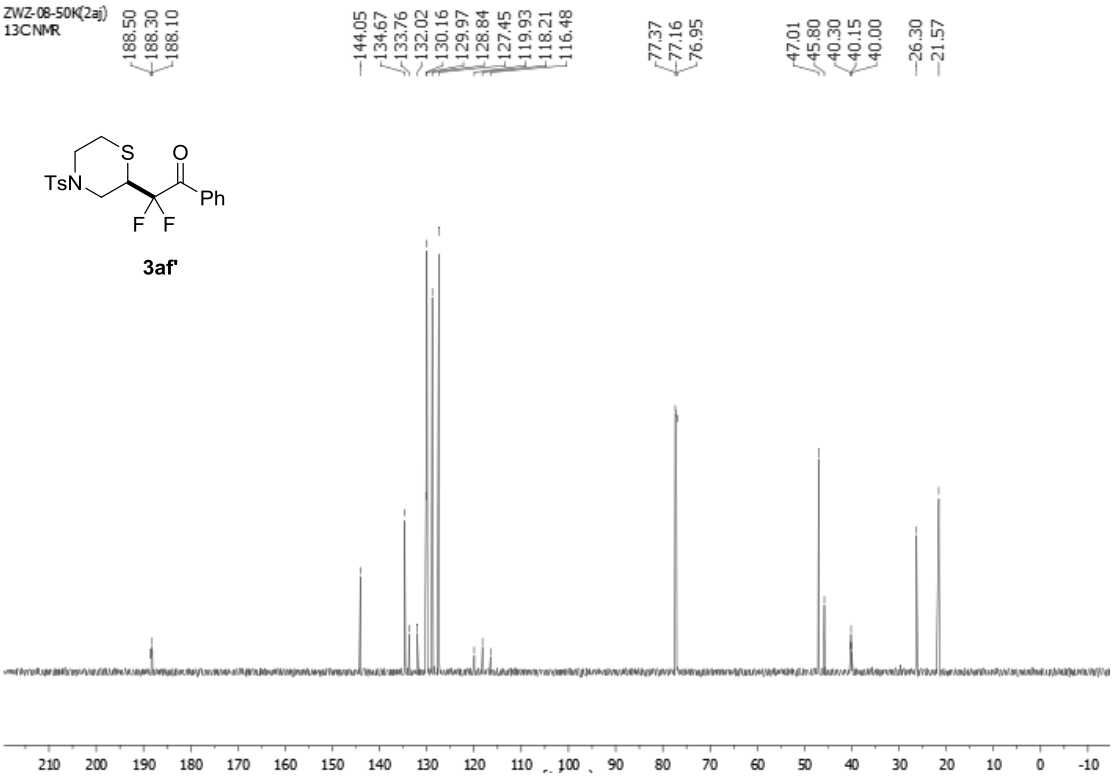
ZWZ-08-50K(2aj)
1H NMR





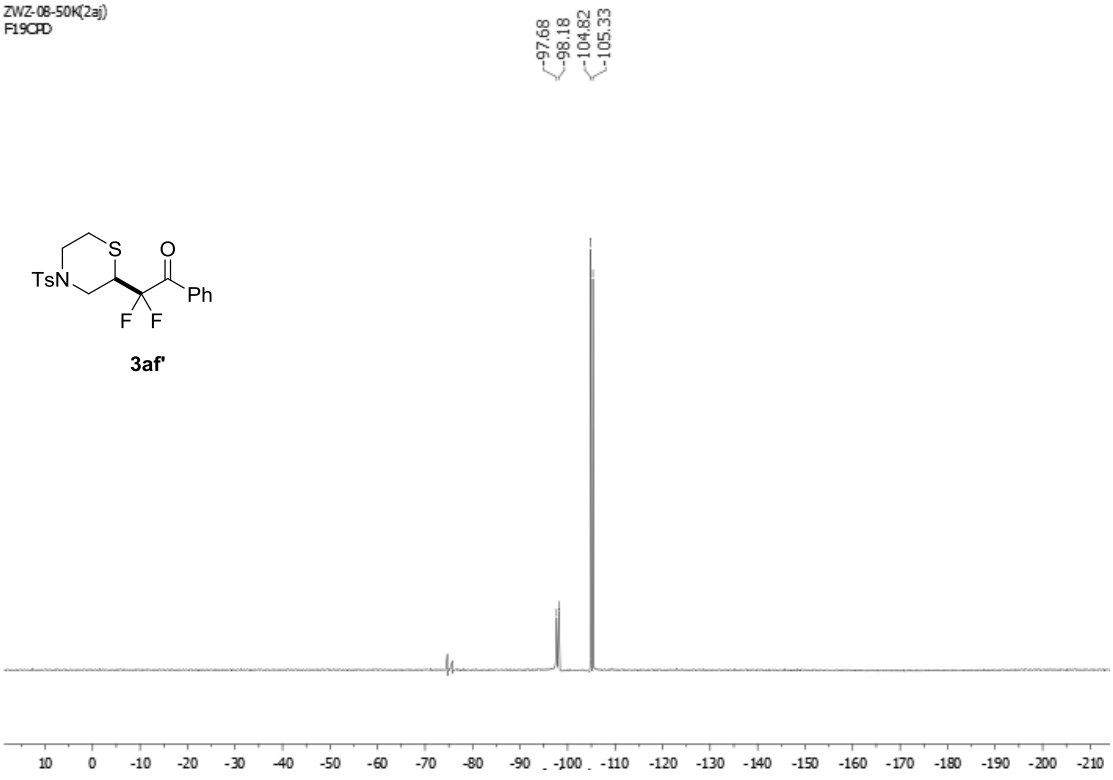
3af'

ZWZ-08-50K(2aj)
13CNMR

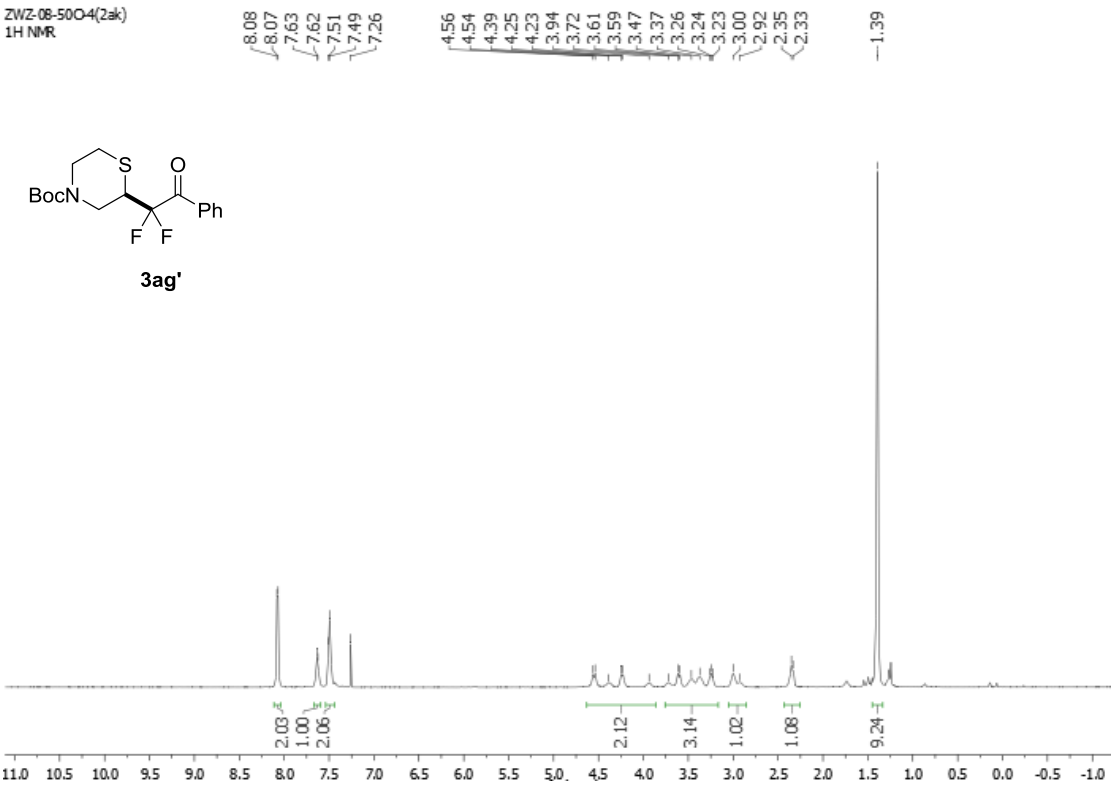


3af'

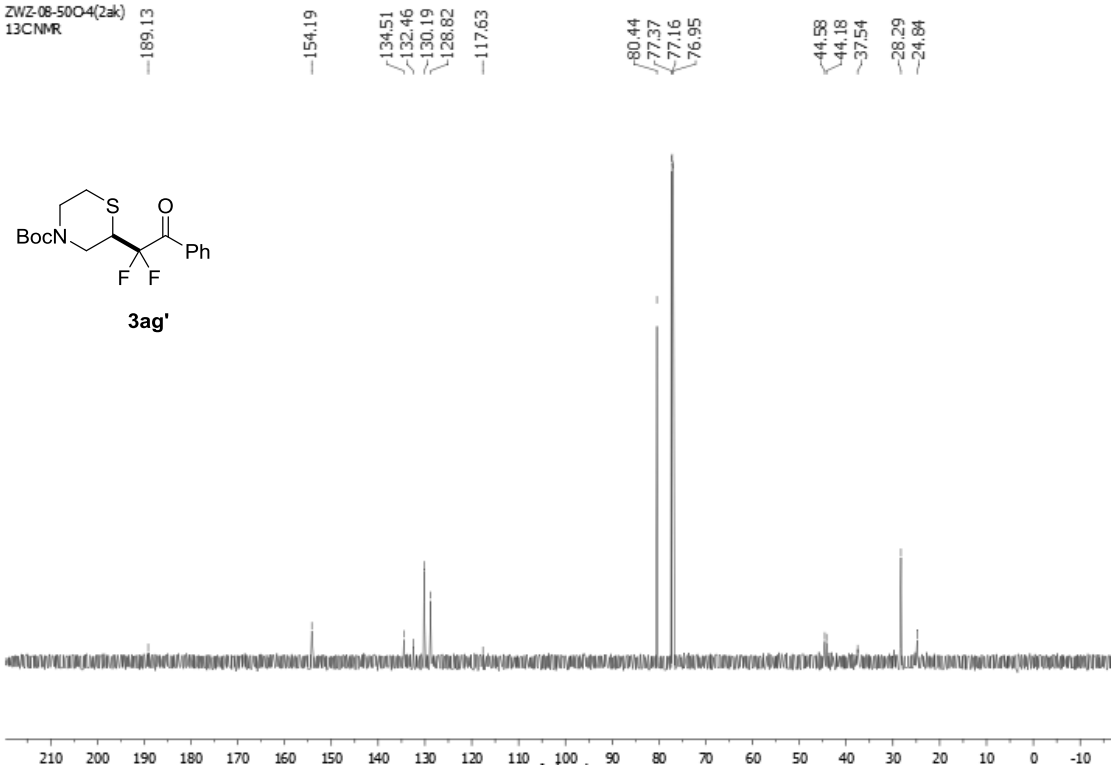
ZWZ-08-50K(2aj)
F19CPD



3af'

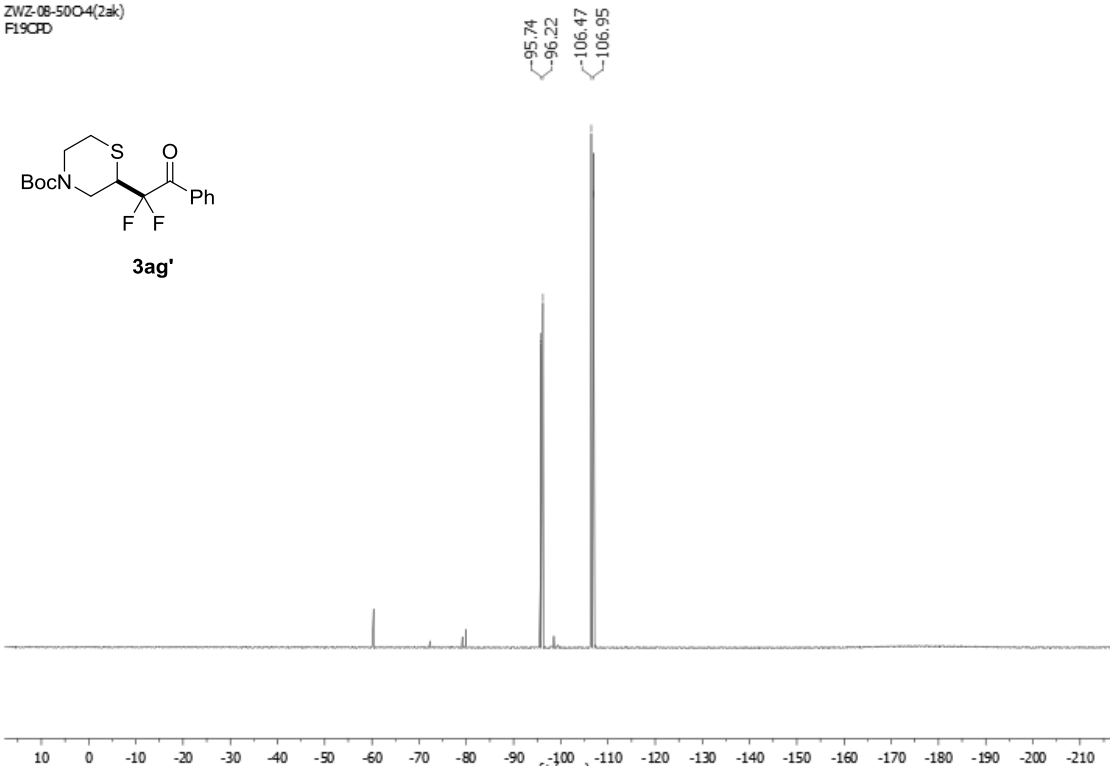

ZWZ-08-50O-4(2ak)
1H NMR
8.08
8.07
7.63
7.62
7.51
7.49
7.26
4.56
4.54
4.39
4.25
4.23
3.94
3.72
3.61
3.59
3.47
3.37
3.26
3.24
3.23
3.00
2.92
2.35
2.33
1.39
BocN
S
O
Ph
F F
2.03
1.00
2.06
2.12
3.14
1.02
1.08
9.24

3ag'


ZWZ-08-50O-4(2ak)
13CNMR
189.13
154.19
134.51
132.46
130.19
128.82
117.63
80.44
77.37
77.16
76.95
44.58
44.18
37.54
28.29
24.84
BocN
S
O
Ph
F F

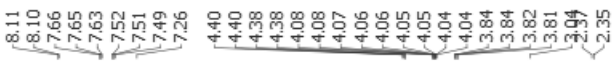
3ag'

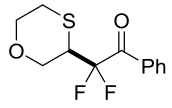
ZWZ-08-50O-4(2ak)
F19CPD



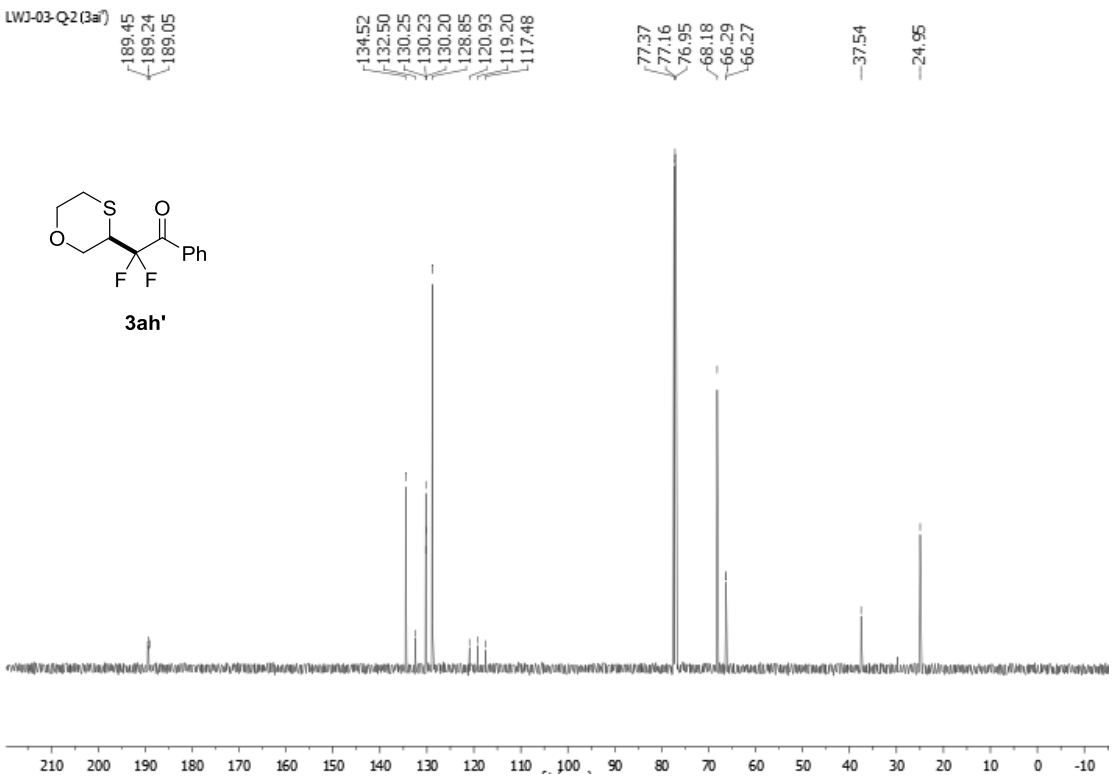
3ag'

LWJ-03-Q2 (3ai')

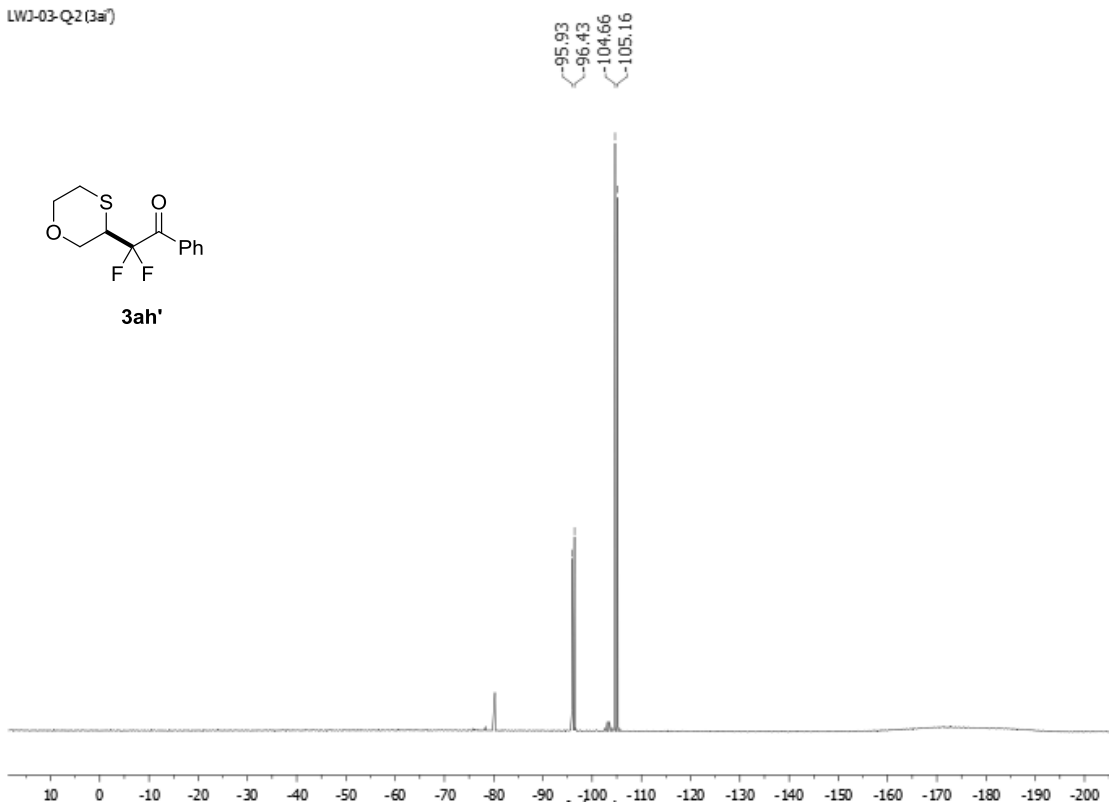




3ah'

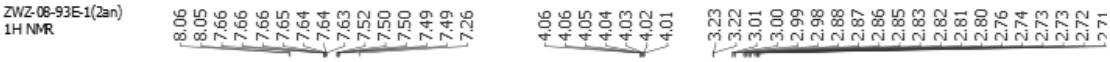

LWJ-03-Q-2 (3ai')
189.45
189.24
189.05
134.52
132.50
130.25
130.23
130.20
128.85
120.93
119.20
117.48
77.37
77.16
76.95
68.18
66.29
66.27
37.54
24.95
S
O
O
Ph
F F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

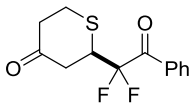
3ah'


LWJ-03-Q-2 (3ai')
-95.93
-96.43
-104.66
-105.16
S
O
O
Ph
F F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

3ah'

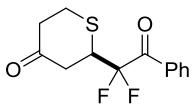
ZWZ-08-93E-1(2an)
1H NMR





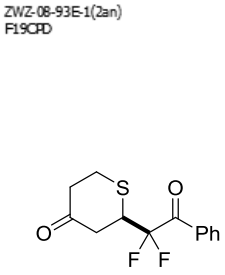
3ai'

ZWZ-08-98E-1(2an)
13CNMR



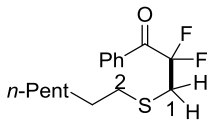
3ai'

ZWZ-08-93E-1(2an)
F19CPD

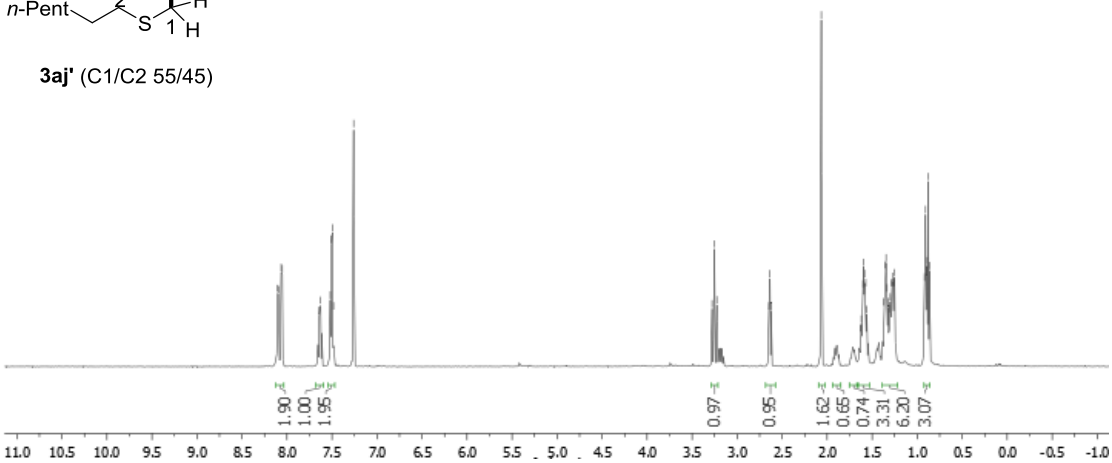


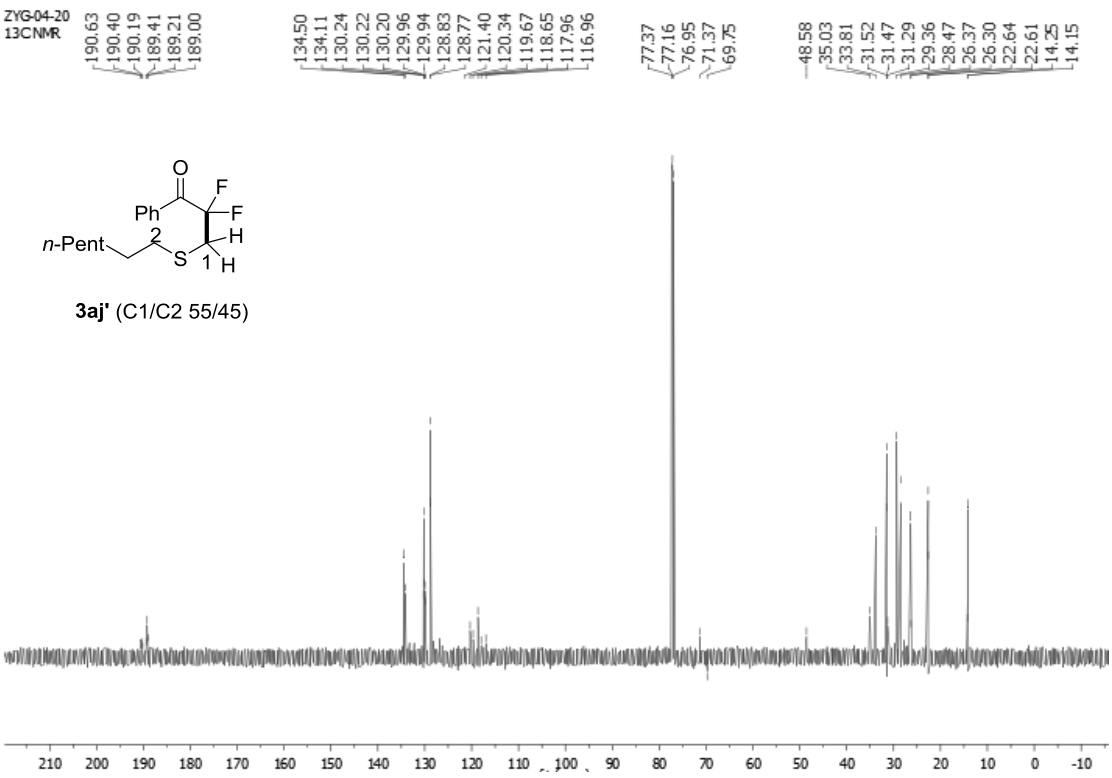
3ai'

ZWZ-08-503-2(2ag)
1H NMR

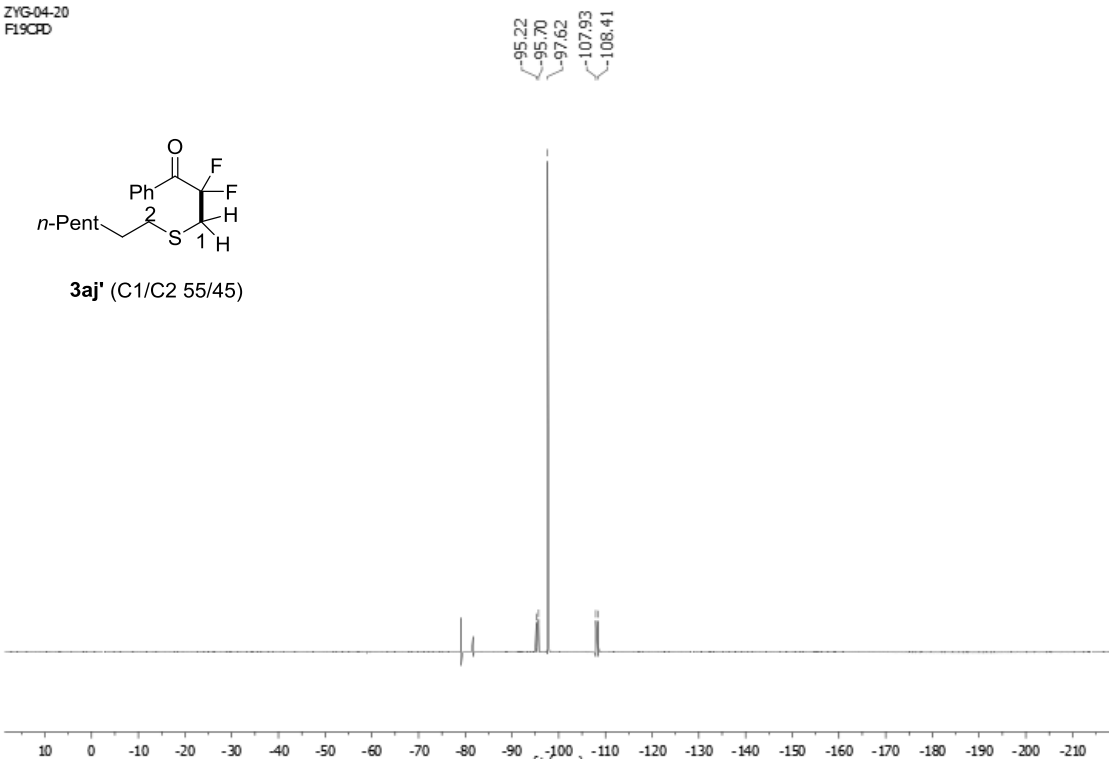


3aj' (C1/C2 55/45)

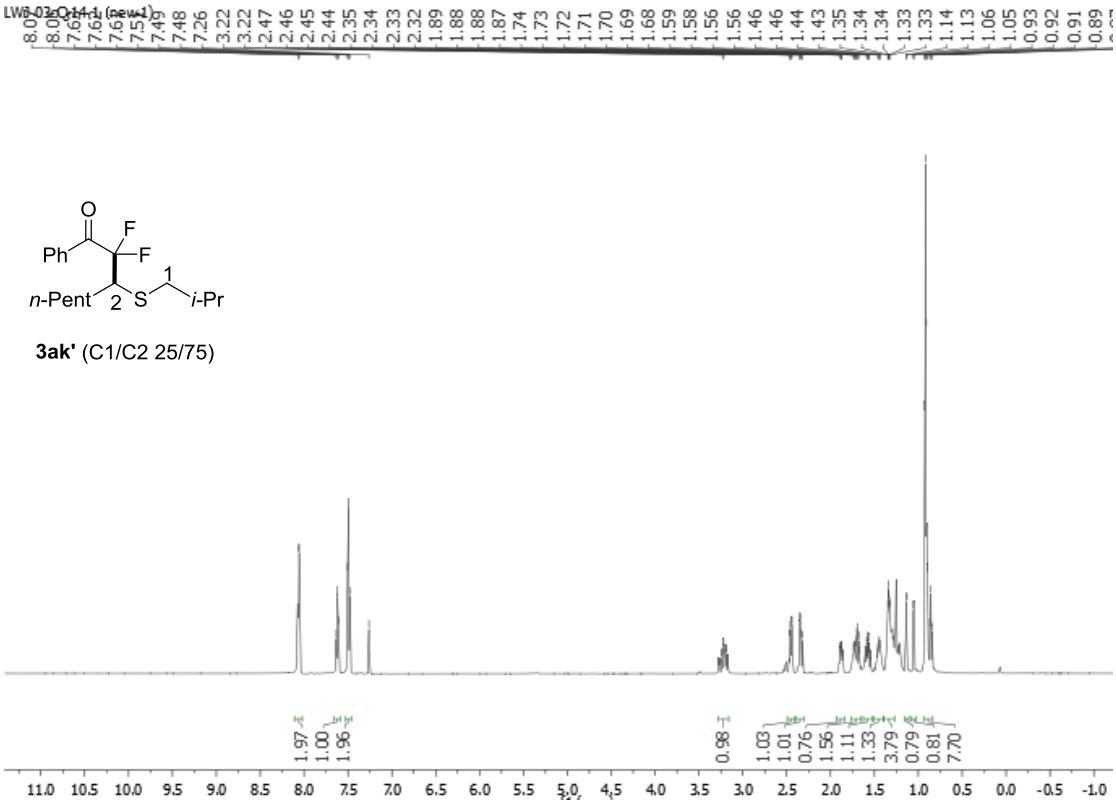




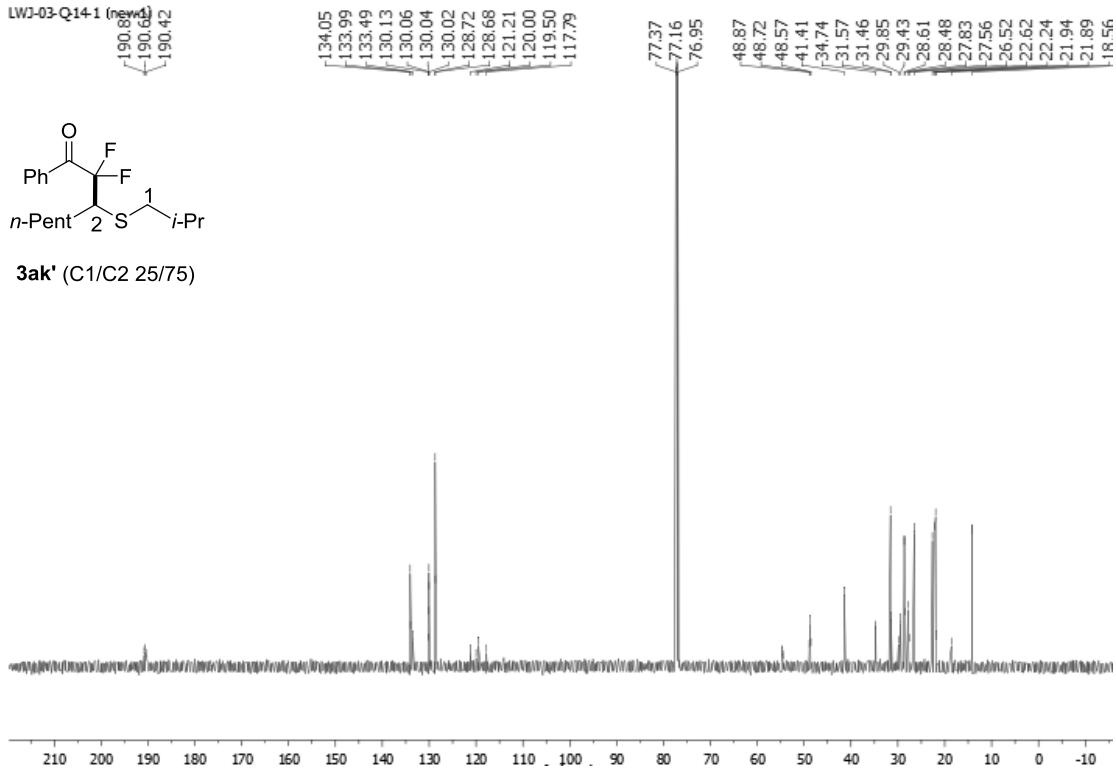
3aj' (C1/C2 55/45)



3aj' (C1/C2 55/45)

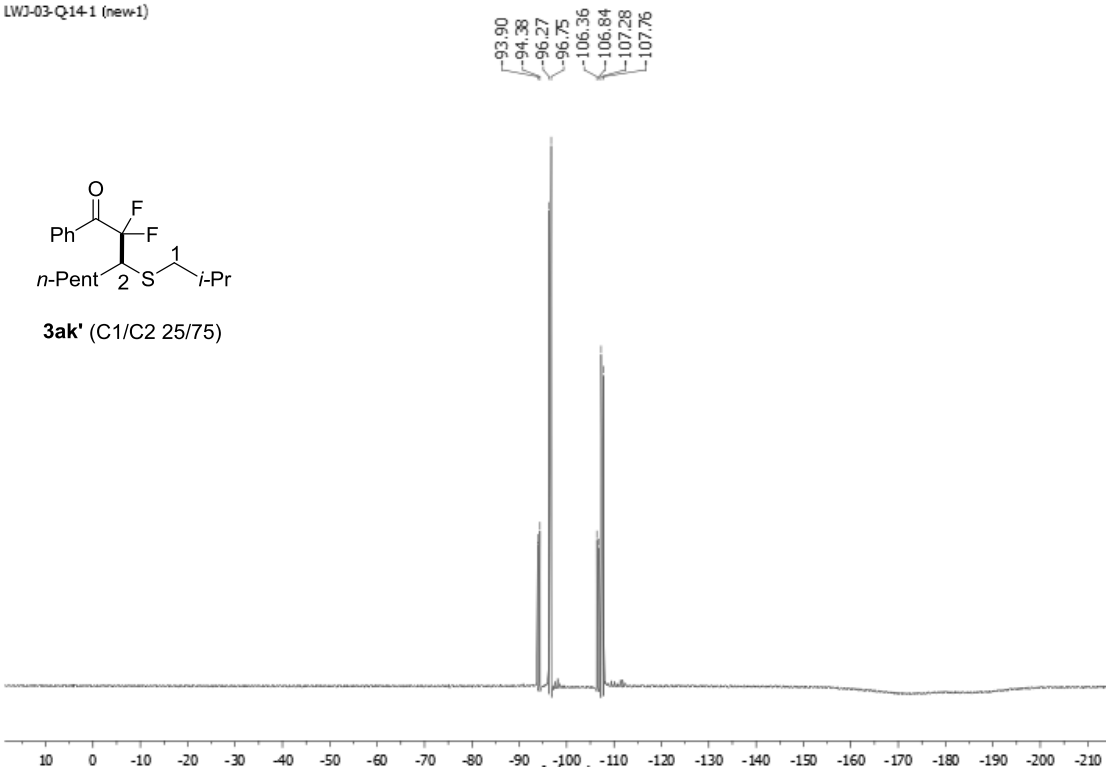


3ak' (C1/C2 25/75)



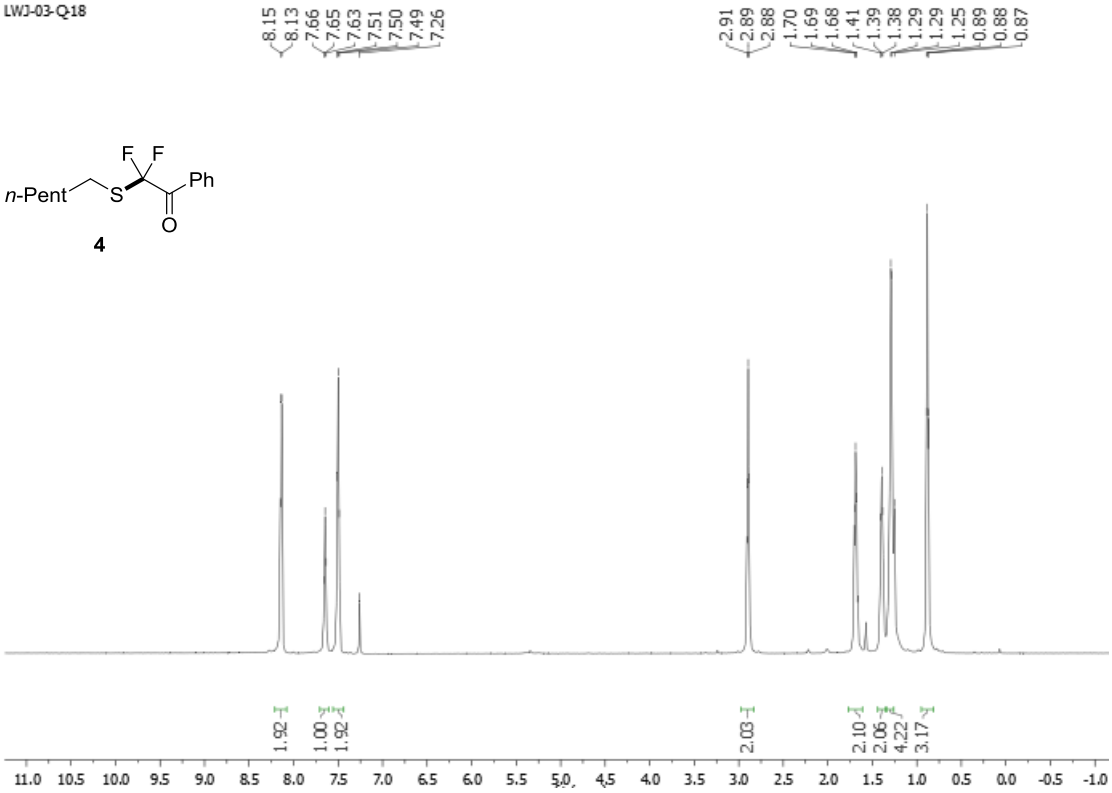
3ak' (C1/C2 25/75)

LWJ-03-Q14-1 (new-1)



3ak' (C1/C2 25/75)

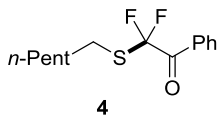
LWJ-03-Q18



4

LWJ-03-Q18

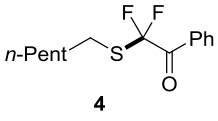
185.72
185.53
185.34
134.74
131.22
130.65
128.78
126.50
124.59
122.68
77.37
77.16
76.95
31.31
29.73
29.09
28.51
22.60
14.13



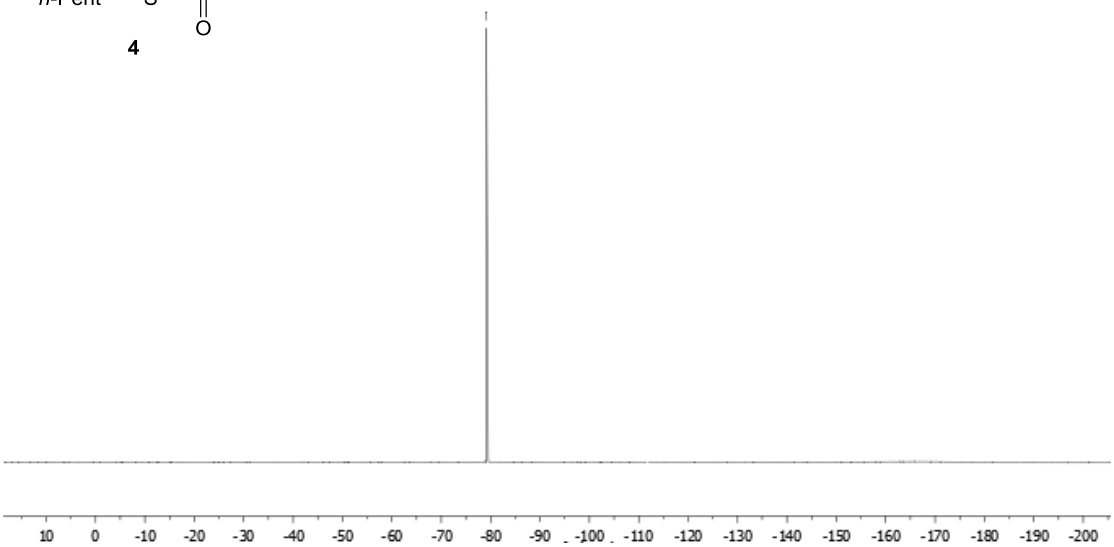
4

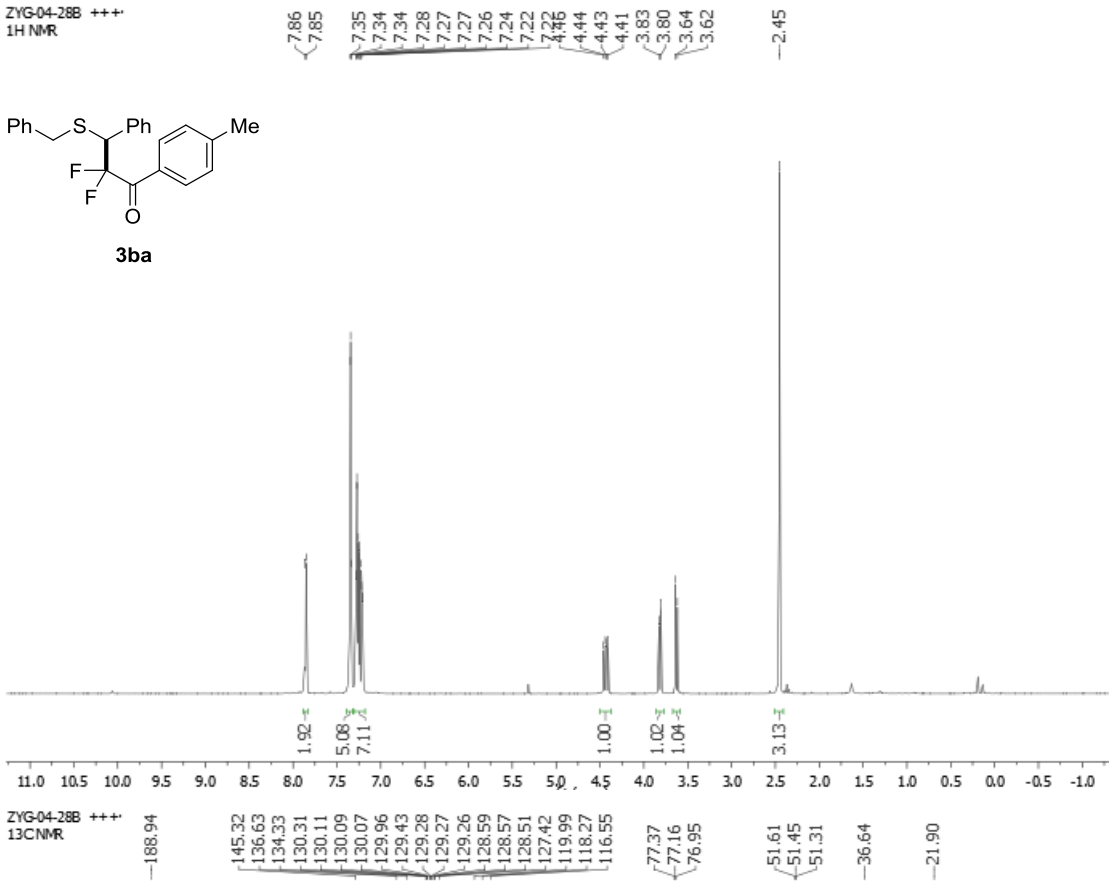
LWJ-03-Q18

-79.13



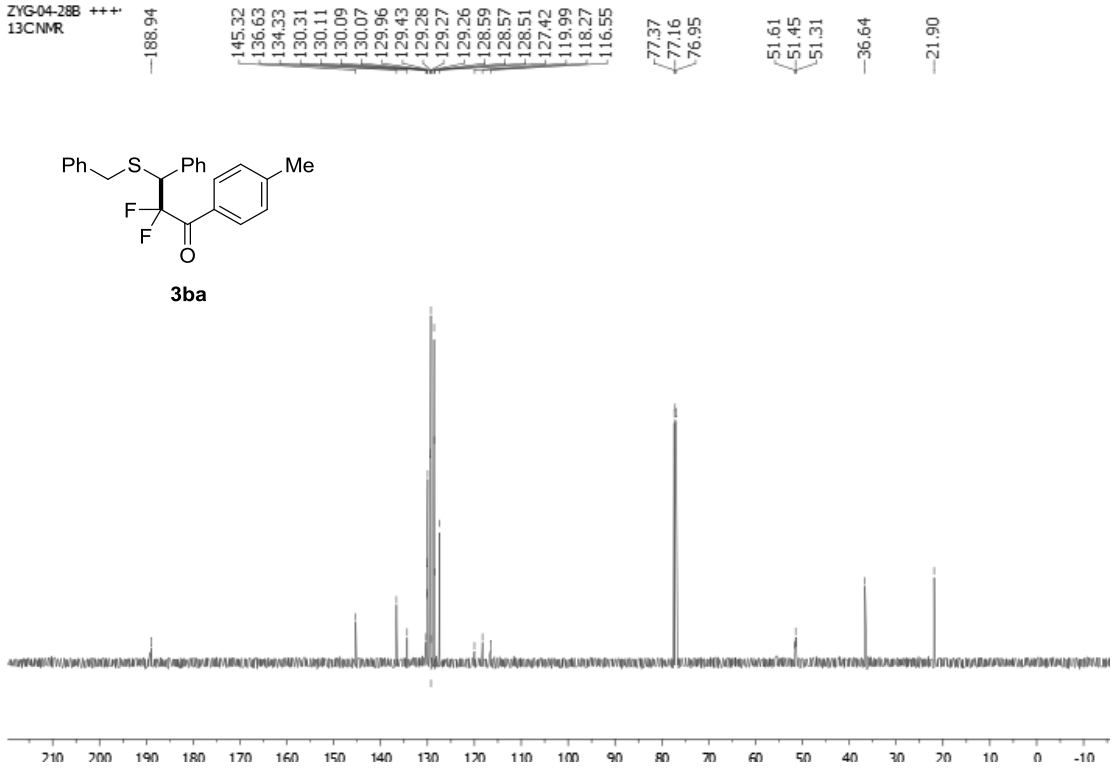
4




ZYG-04-28B +++
1H NMR
7.86
7.85
7.35
7.34
7.34
7.28
7.27
7.27
7.26
7.24
7.22
4.46
4.44
4.43
4.41
3.83
3.80
3.64
3.62
2.45
1.92
5.08
7.11
1.00
1.02
1.04
3.13
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

Ph
S
Ph
Me
F
F
O

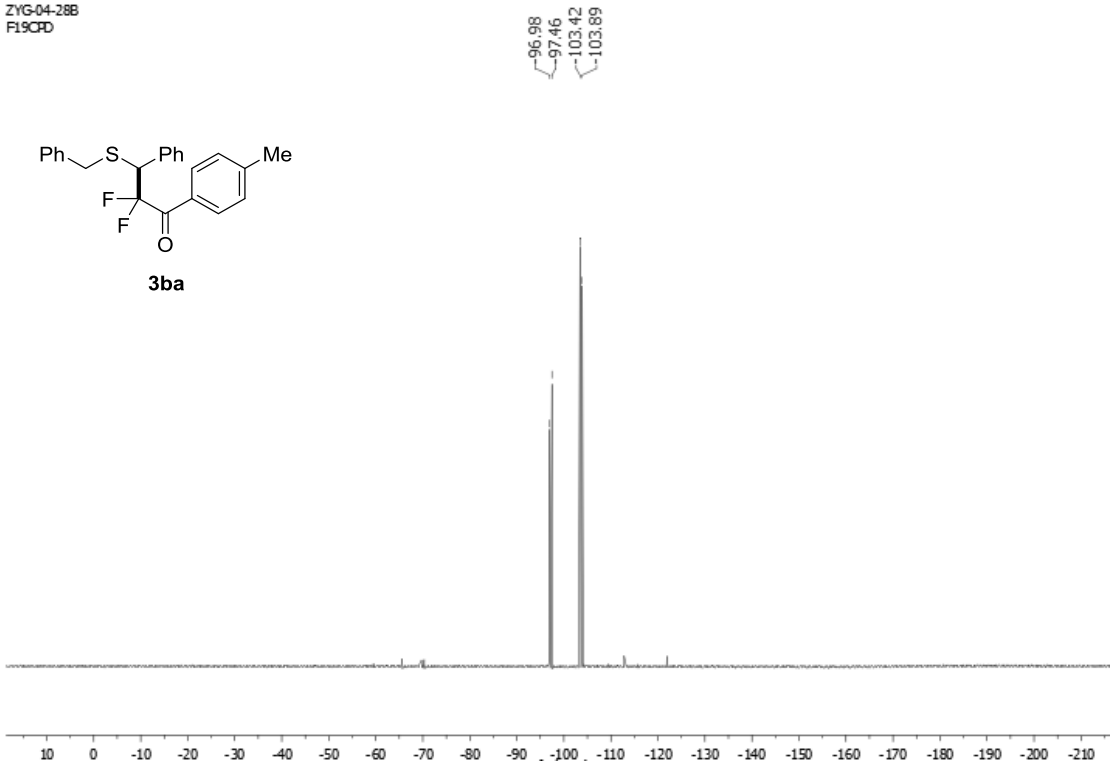
3ba


ZYG-04-28B +++
13C NMR
188.94
145.32
136.63
134.33
130.31
130.11
130.09
130.07
129.96
129.43
129.28
129.27
129.26
128.59
128.57
128.51
127.42
119.99
118.27
116.55
77.37
77.16
76.95
51.61
51.45
51.31
36.64
21.90
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Ph
S
Ph
Me
F
F
O

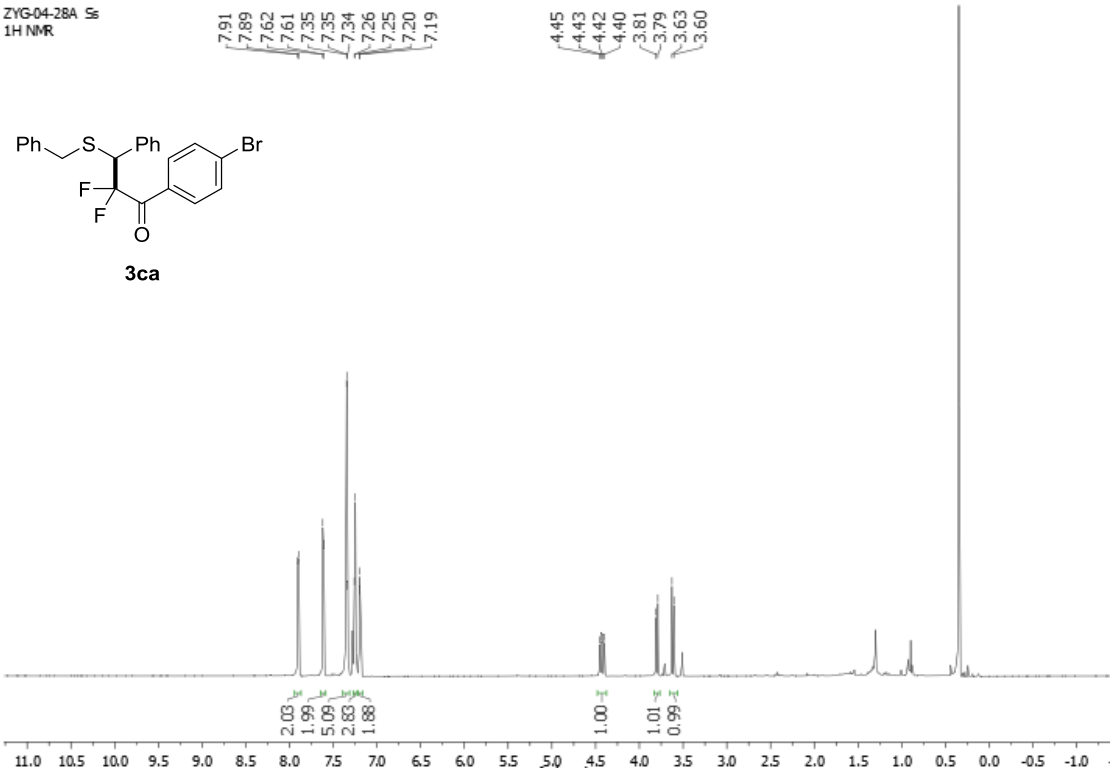
3ba

ZYG-04-28B
F19CRD

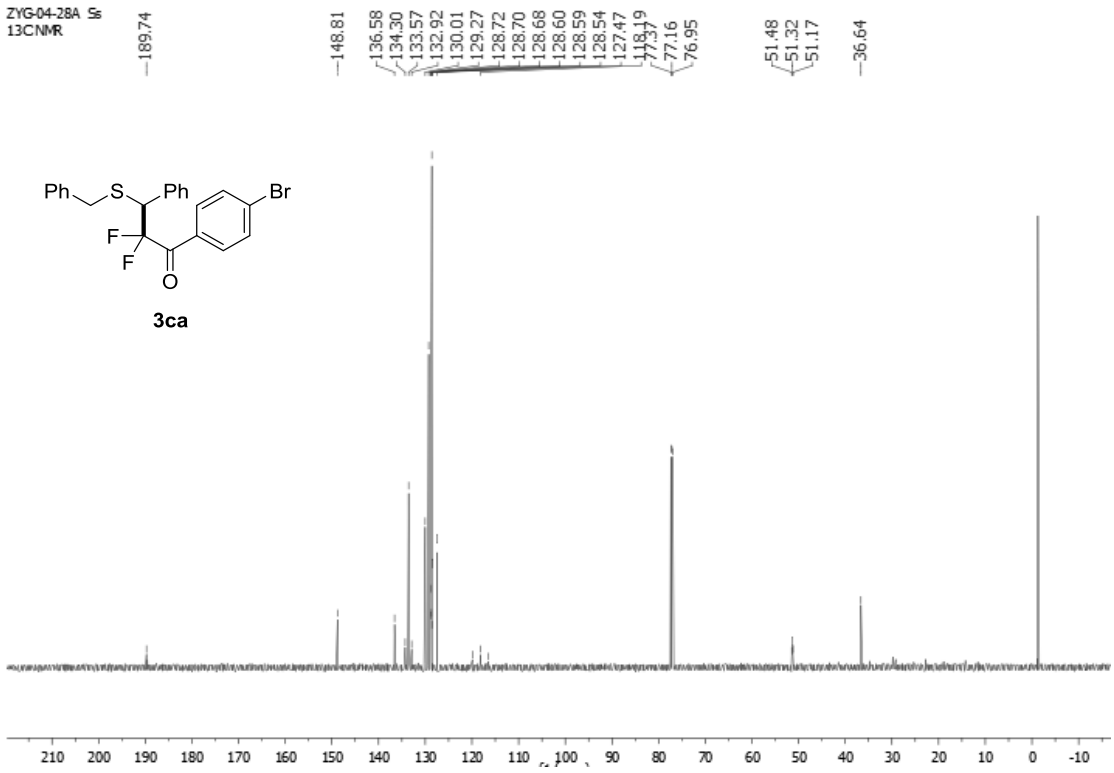


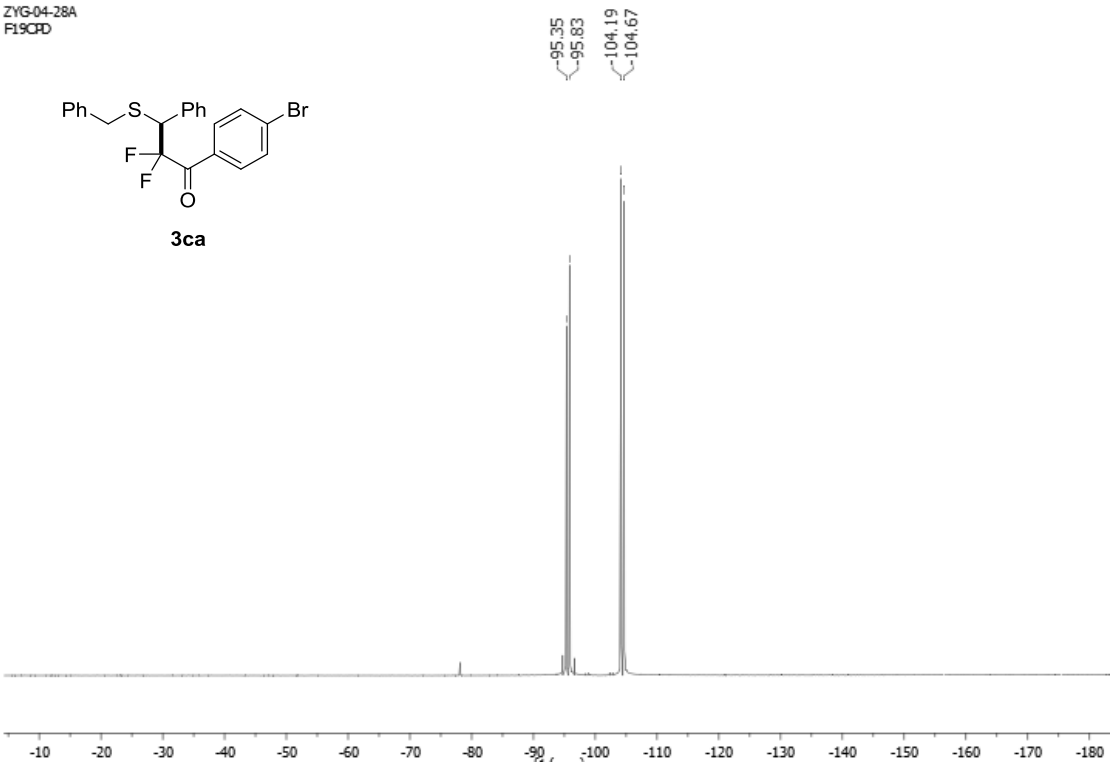
3ba

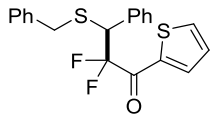
ZYG-04-28A Ss
1H NMR



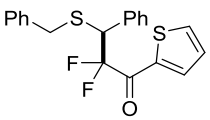
3ca


ZYG-04-28A Ss
13CNMR
189.74
148.81
136.58
134.30
133.57
132.92
130.01
129.27
128.72
128.70
128.68
128.60
128.59
128.54
127.47
118.19
77.37
77.16
76.95
51.48
51.32
51.17
36.64
Ph
S
Ph
Br
F
F
O
3ca
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


ZYG-04-28A
F19CPD
95.35
95.83
104.19
104.67
Ph
S
Ph
Br
F
F
O
3ca
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180

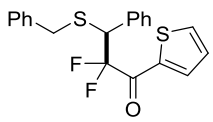


3da

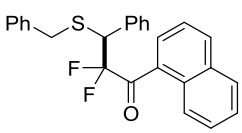


3da

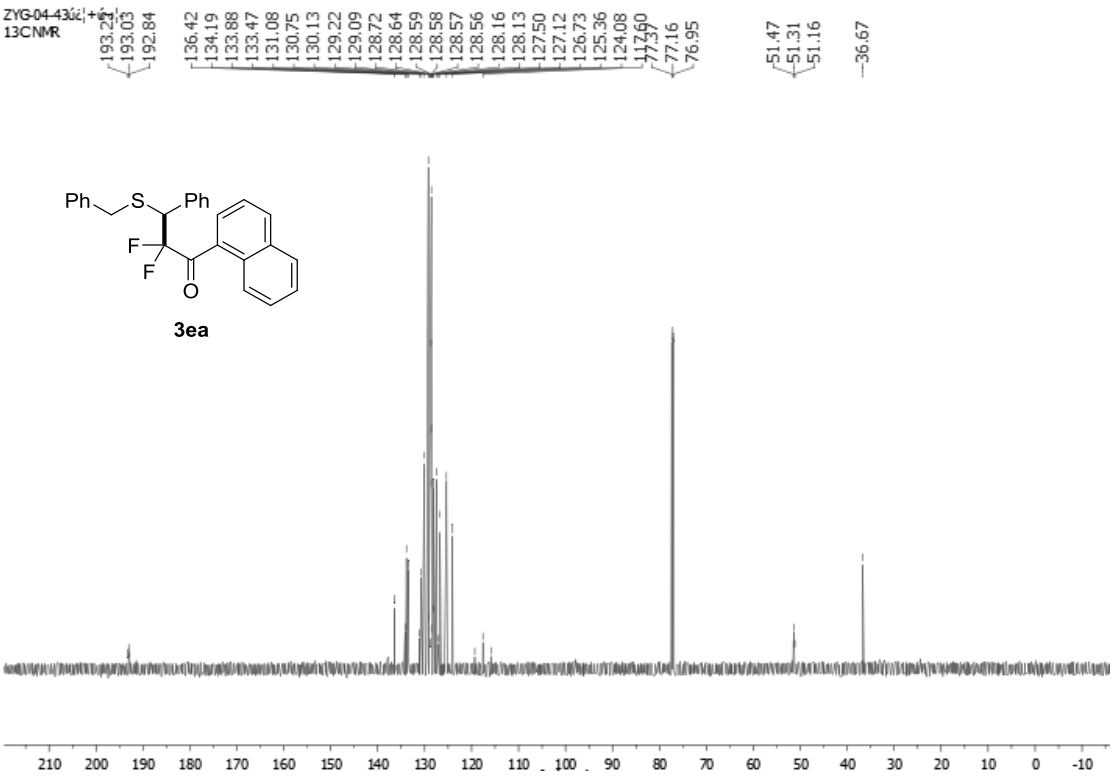
LWJ-03-1-1 (3da)

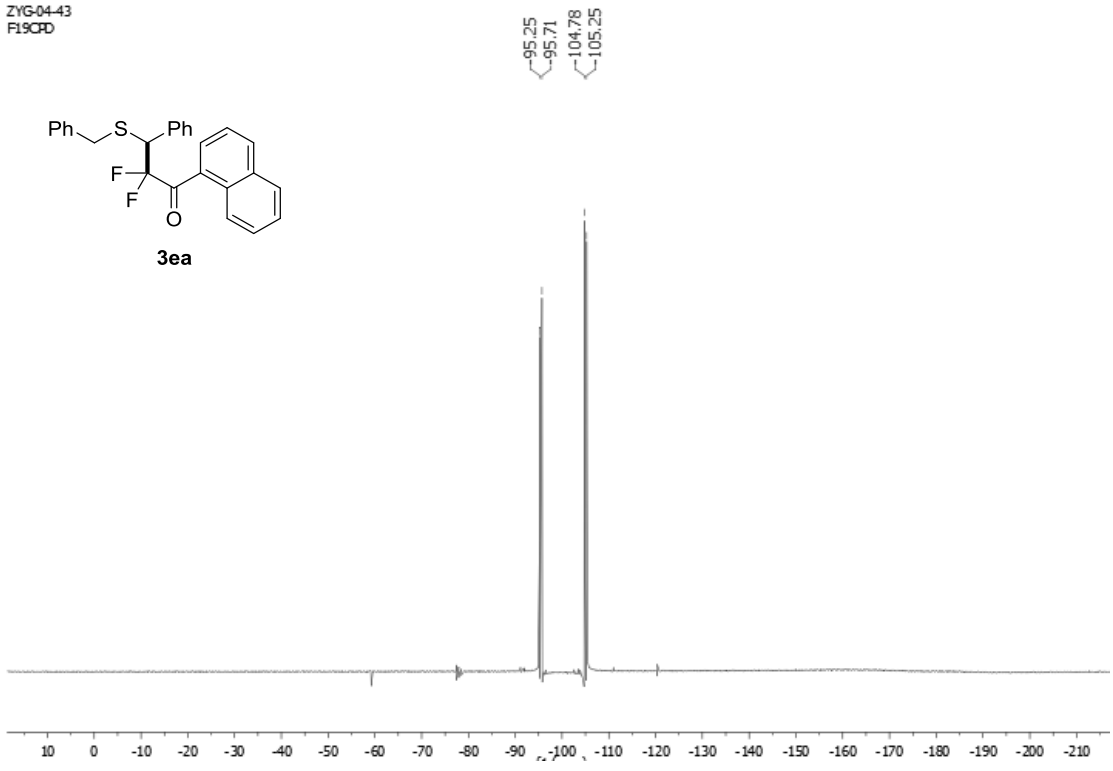


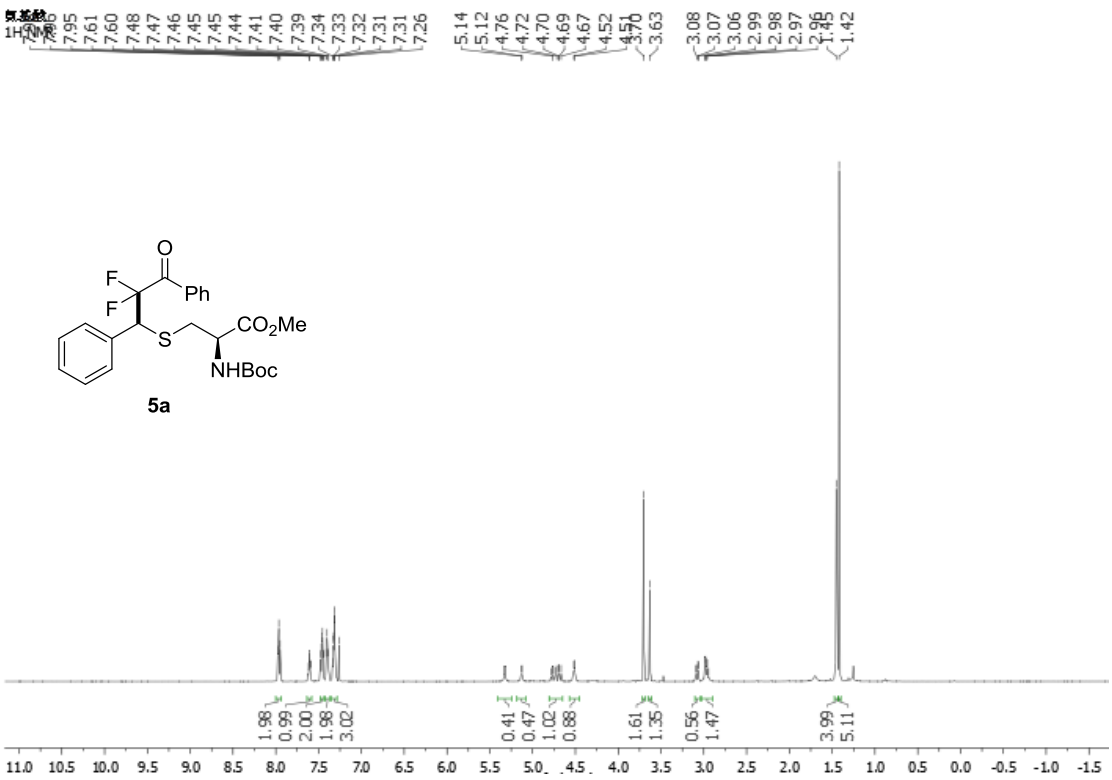
3da

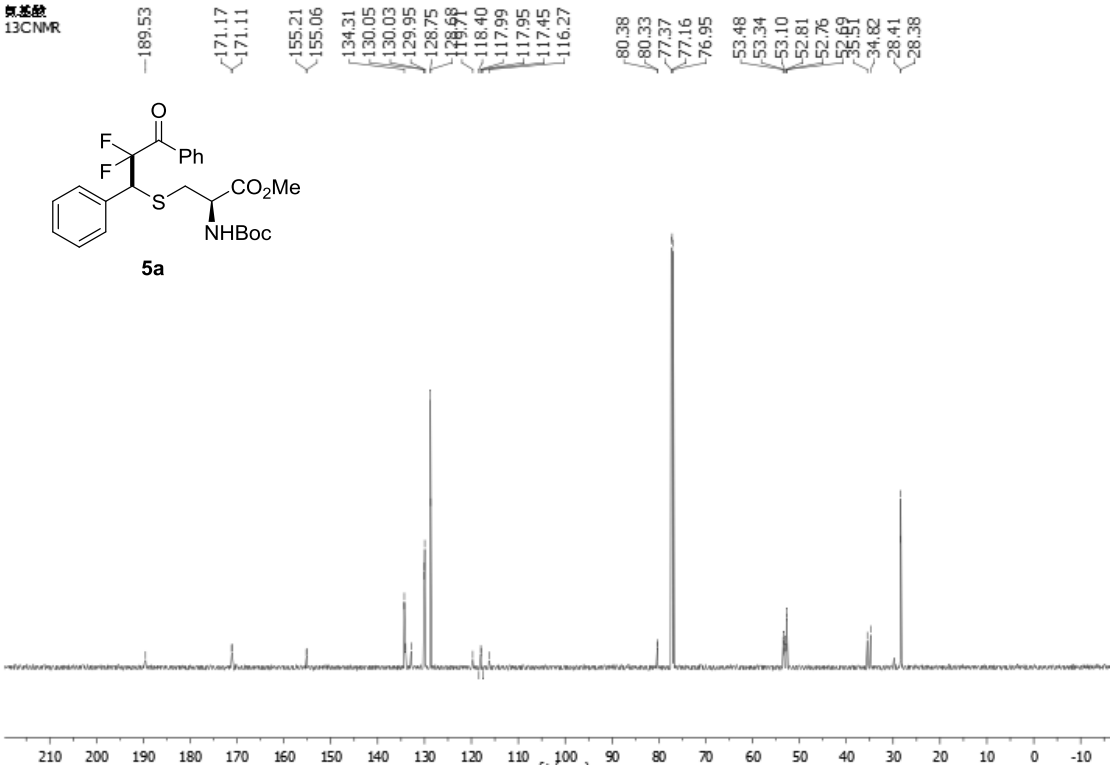


3ea

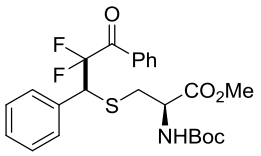

ZYG-04-43
13CNMR
193.03
192.84
136.42
134.19
133.88
133.47
131.08
130.75
130.13
129.22
129.09
128.72
128.64
128.59
128.58
128.57
128.56
128.16
128.13
127.50
127.12
126.73
125.36
124.08
77.16
76.95
51.47
51.31
51.16
36.67
Ph
S
Ph
F
F
O
3ea
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


ZYG-04-43
F19CPD
95.25
95.71
104.78
105.25
Ph
S
Ph
F
F
O
3ea
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210


1H NMR
7.95
7.61
7.60
7.48
7.47
7.46
7.45
7.45
7.44
7.41
7.40
7.39
7.34
7.33
7.32
7.31
7.31
7.26
5.14
5.12
4.76
4.72
4.70
4.69
4.67
4.52
4.51
3.70
3.63
3.08
3.07
3.06
2.99
2.98
2.97
1.45
1.42
O
F
F
Ph
S
CO2Me
NHBoc
5a
1.98
0.99
2.00
1.98
3.02
0.41
0.47
1.02
0.88
1.61
1.35
0.56
1.47
3.99
5.11
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5

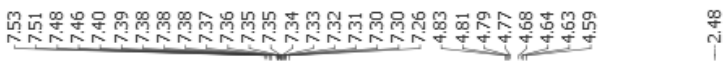

13CNMR
189.53
171.17
171.11
155.21
155.06
134.31
130.05
130.03
129.95
128.75
118.40
117.99
117.95
117.45
116.27
80.38
80.33
77.37
77.16
76.95
53.48
53.34
53.10
52.81
52.76
35.51
34.82
28.41
28.38
O
F
F
Ph
S
CO2Me
NHBoc
5a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

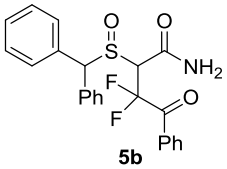
氨基酸
F19CPD



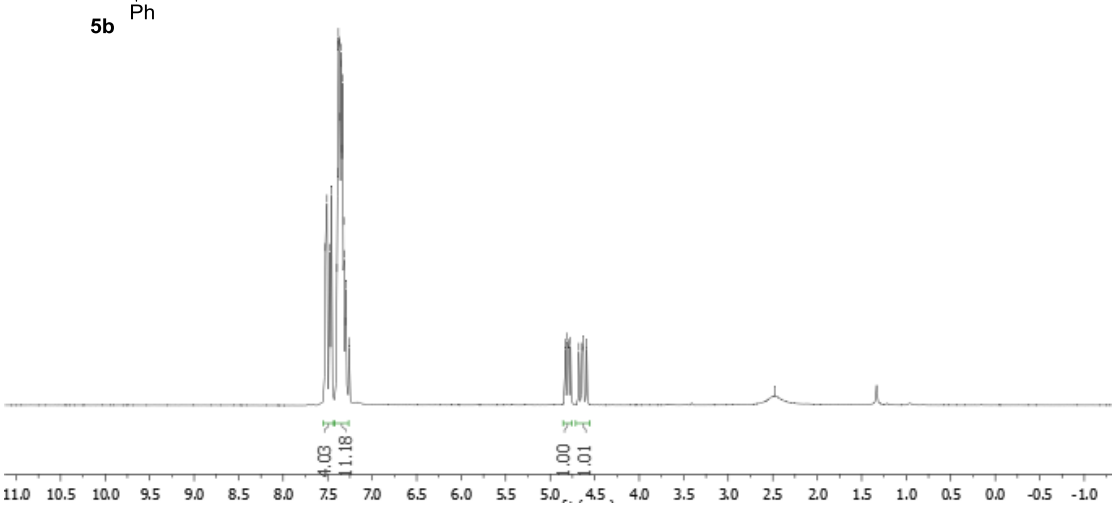
5a

氨基酸
1H



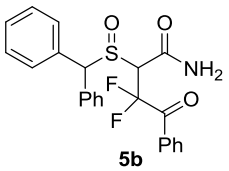


5b

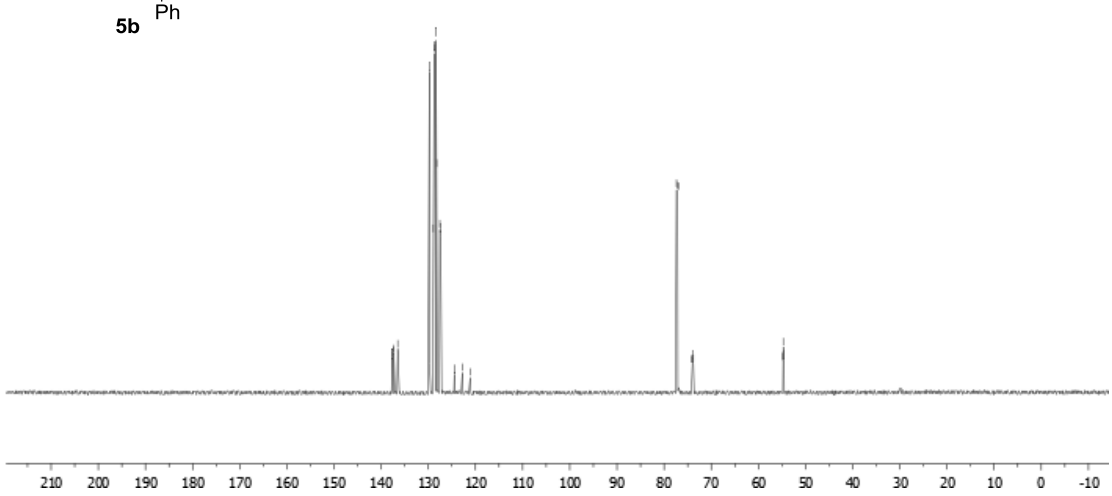


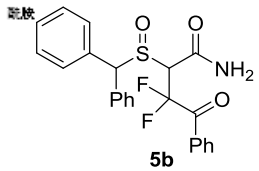
ZYG-04-3-2
13CNMR

137.69
137.65
137.36
137.34
136.49
129.78
128.94
128.76
128.62
128.36
128.22
127.56
127.38
124.48
122.80
121.13
77.37
77.16
76.95
74.15
73.99
73.96
73.79
54.86
54.71
54.56



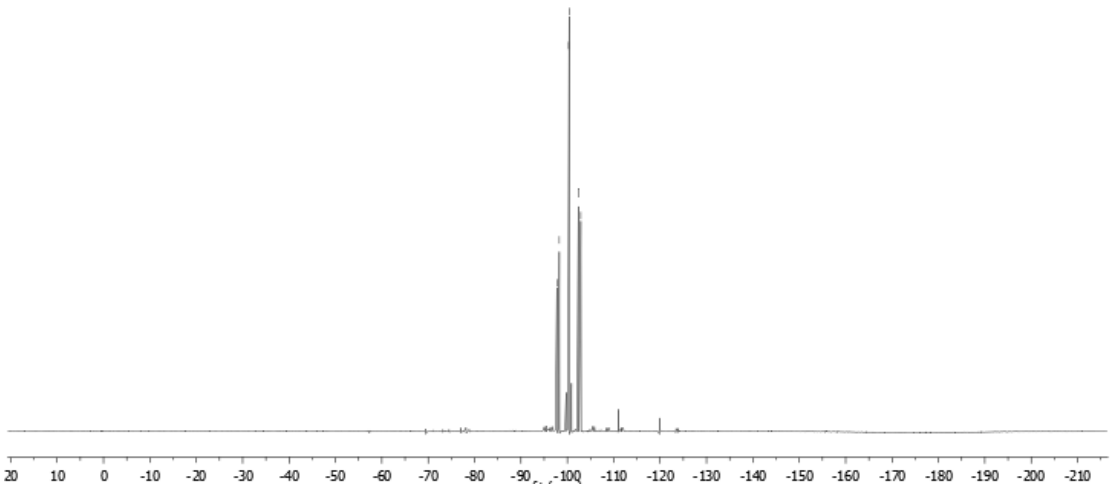
5b

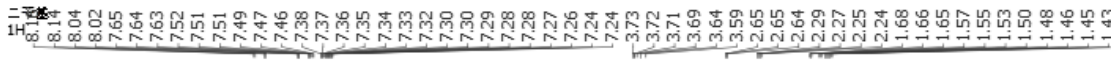


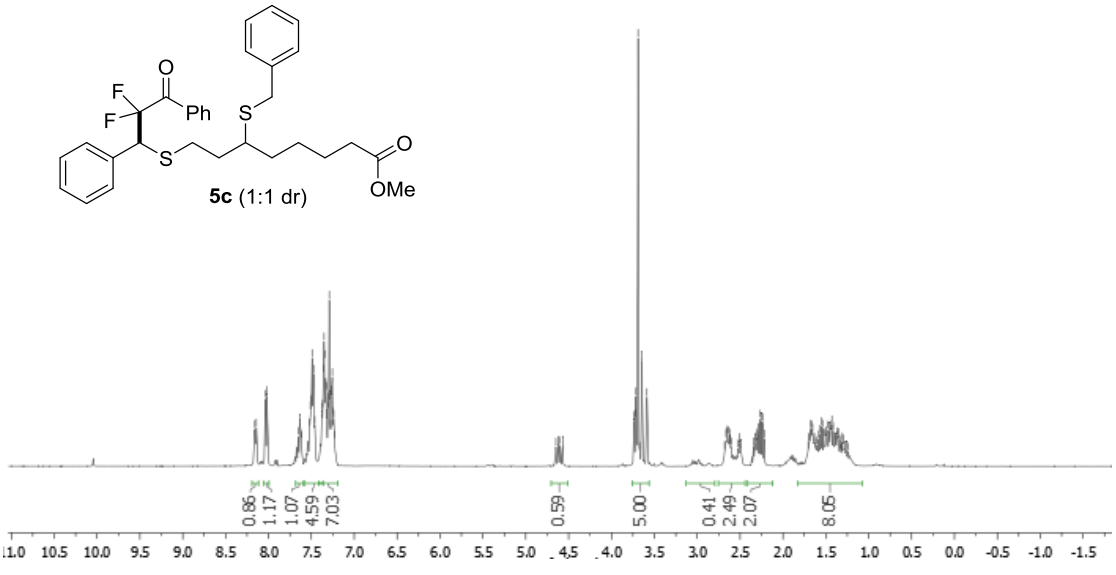


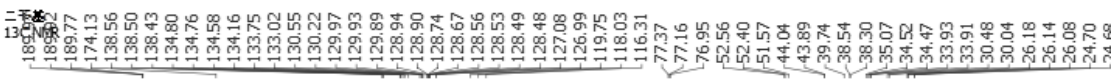
5b

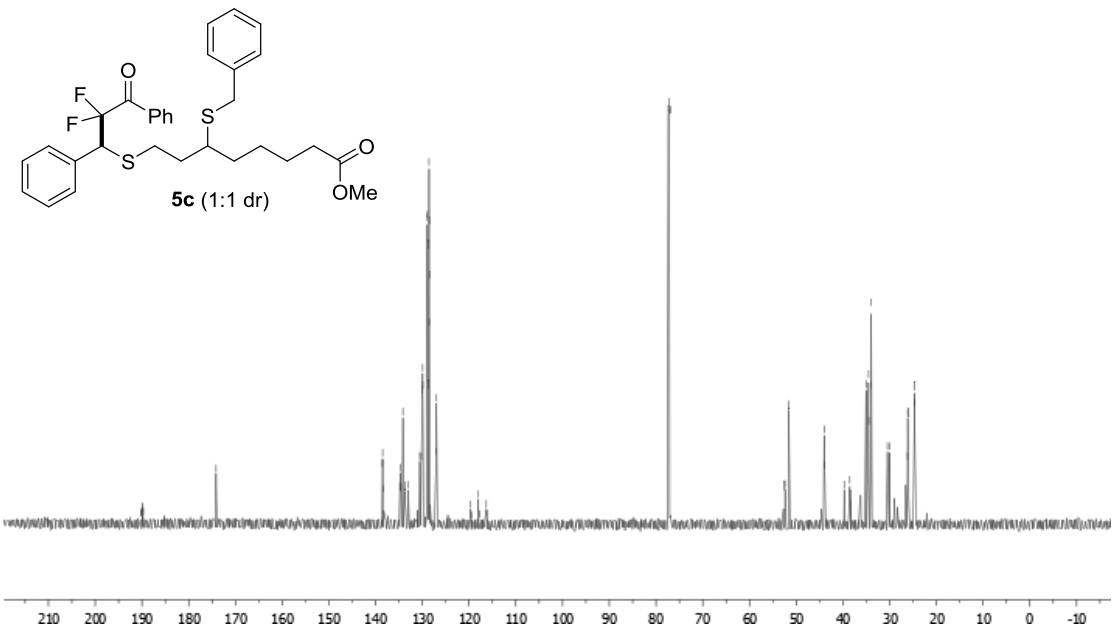
97.74
98.26
100.26
100.38
102.37
102.89



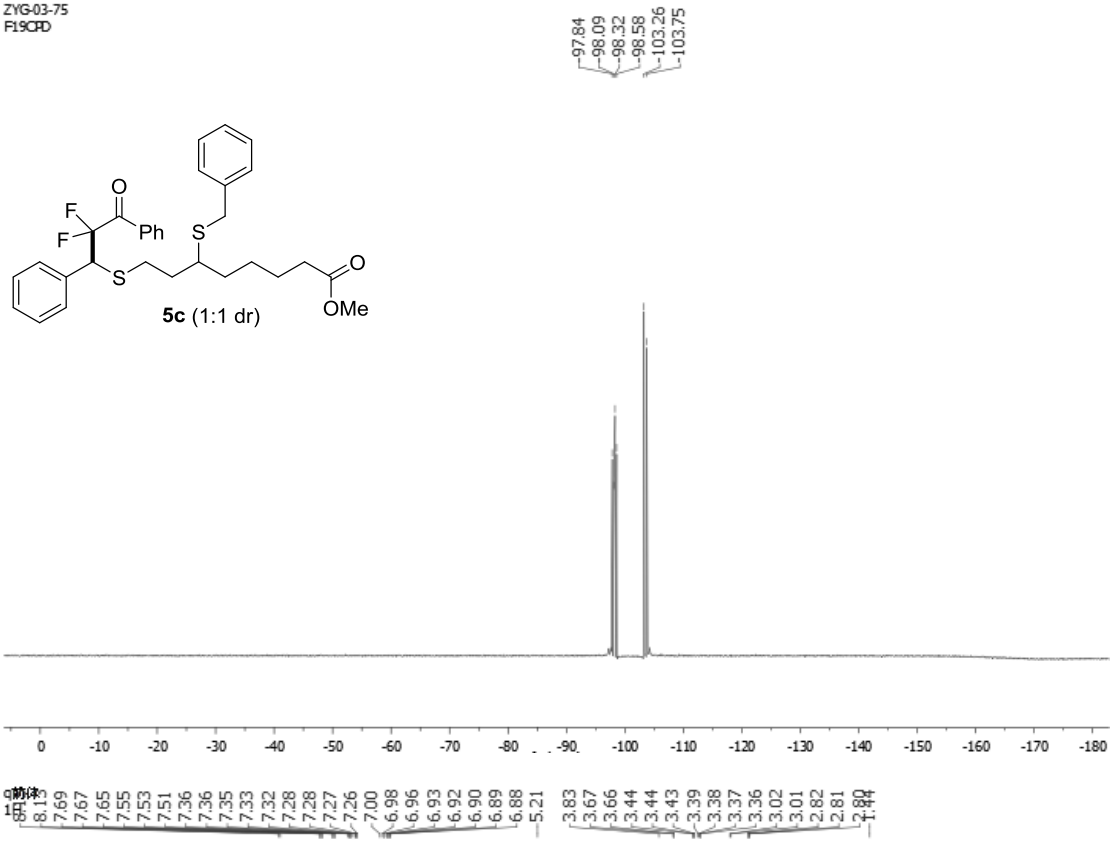



F
F
O
Ph
S
S
O
OMe
5c (1:1 dr)

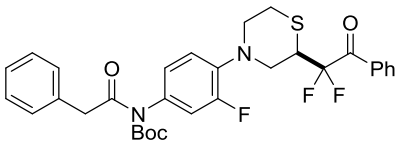



F
F
O
Ph
S
S
O
OMe
5c (1:1 dr)

ZYG-03-75
F19CPD



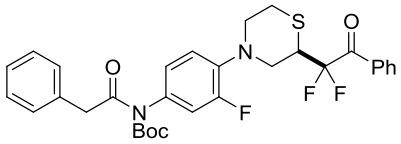
5c (1:1 dr)



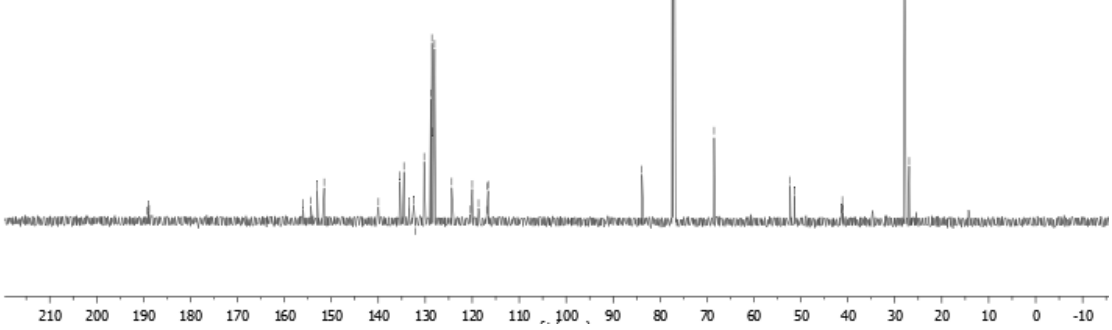
5d

q前体
13CNMR

189.20
189.00
188.80
155.99
154.35
153.01
151.53
139.98
135.39
134.55
132.43
130.24
128.85
128.59
128.40
128.00
124.37
120.00
116.75
116.61
83.85
77.37
77.16
76.95
68.48
52.27
51.35
41.33
41.17
41.02
27.94
26.93

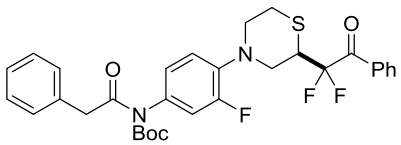


5d

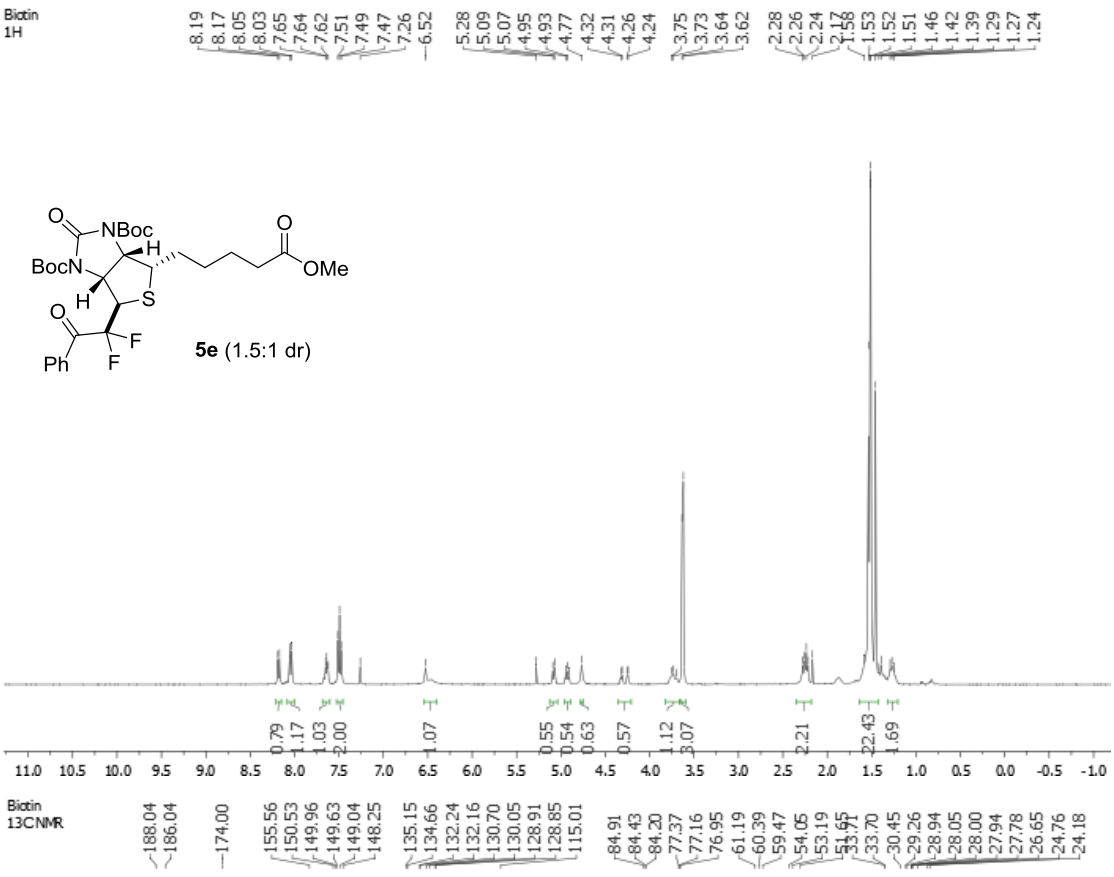


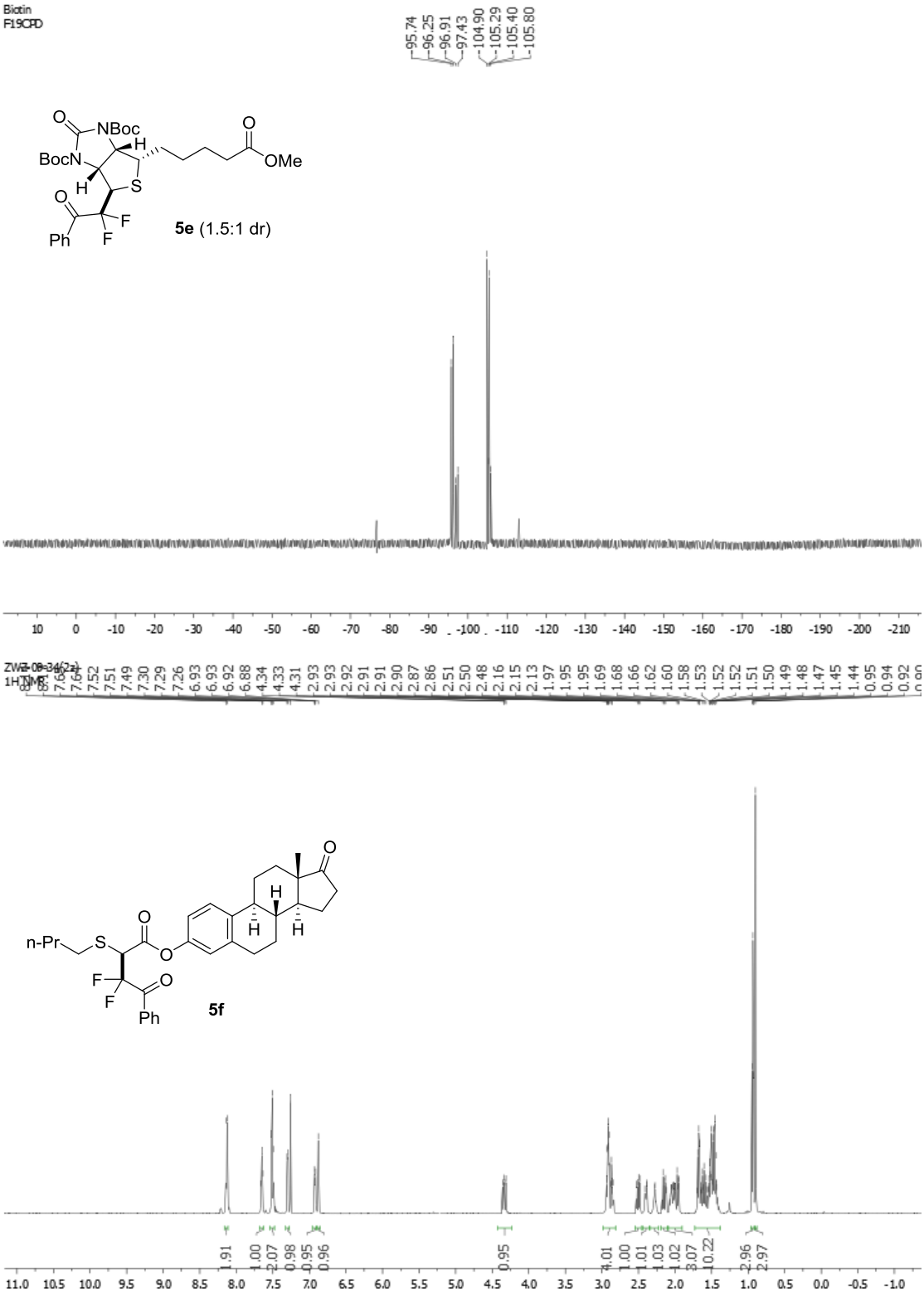
q前体
F19CPD

95.08
95.56
105.60
106.08



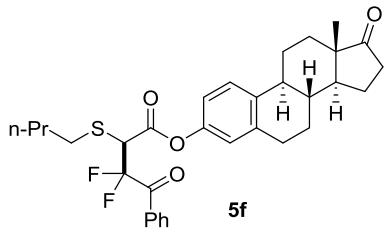
5d


Biotin
1H
8.19
8.17
8.05
8.03
7.65
7.64
7.62
7.51
7.49
7.47
7.26
6.52
5.28
5.09
5.07
4.95
4.93
4.77
4.32
4.31
4.26
4.24
3.75
3.73
3.64
3.62
2.28
2.26
2.24
2.17
1.58
1.53
1.52
1.51
1.46
1.42
1.39
1.29
1.27
1.24
NBoc
BocN
O
OMe
H
S
F
Ph
5e (1.5:1 dr)
0.79
1.17
1.03
2.00
1.07
0.55
0.54
0.63
0.57
1.12
3.07
2.21
22.43
1.69
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
Biotin
13CNMR
188.04
186.04
174.00
155.56
150.53
149.96
149.63
149.04
148.25
135.15
134.66
132.24
132.16
130.70
130.05
128.91
128.85
115.01
84.91
84.43
84.20
77.37
77.16
76.95
61.19
60.39
59.47
54.05
53.19
33.70
30.45
29.26
28.94
28.05
28.00
27.94
27.78
26.65
24.76
24.18
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

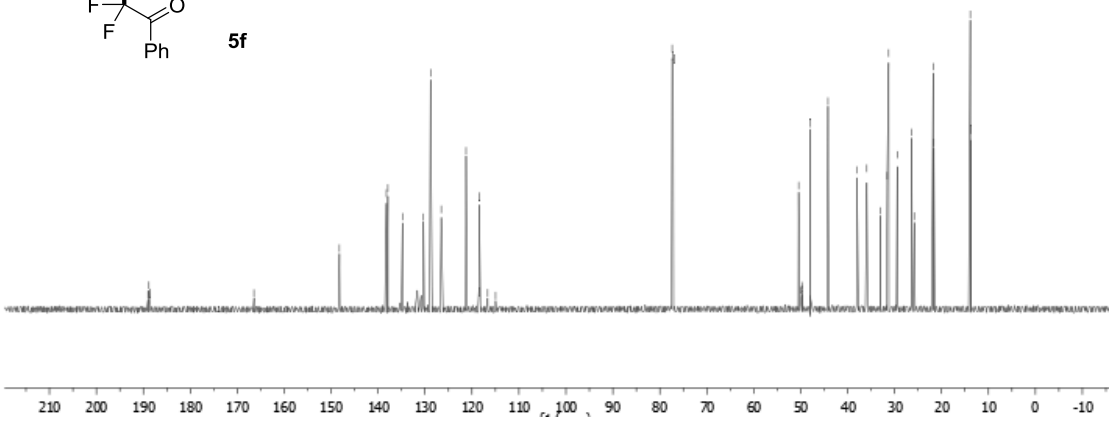

Biotin
F19CPD
-95.74
-96.25
-96.91
-97.43
-104.90
-105.29
-105.40
-105.80
O
NBoc
H
O
BocN
OMe
H
S
O
F
Ph
F
5e (1.5:1 dr)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
1H NMR
7.92 7.90 7.68 7.66 7.52 7.51 7.49 7.30 7.29 7.26 6.93 6.93 6.92 6.88 4.34 4.33 4.31 2.93 2.93 2.92 2.91 2.91 2.90 2.87 2.86 2.51 2.50 2.48 2.16 2.15 2.13 1.97 1.95 1.95 1.69 1.68 1.66 1.62 1.60 1.58 1.53 1.52 1.52 1.51 1.50 1.49 1.48 1.47 1.45 1.44 0.95 0.94 0.92
O
H
H
H
n-Pr
S
O
O
F
O
F
Ph
5f
1.91 1.00 2.07 0.98 0.95 0.96 0.95 4.01 1.00 1.01 1.03 1.02 8.07 10.22 2.96 2.97
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

ZWZ-09-34(2z)
13CNMR

189.01
188.81
188.60
166.45
148.24
138.23
137.92
134.80
130.34
128.83
126.55
121.27
118.46
118.42
116.67
114.98
77.37
77.16
76.95
50.43
49.92
49.74
49.59
48.01
44.18
38.00
35.92
33.01
31.57
31.26
29.44
26.34
25.81
21.79
21.64
13.87
13.68

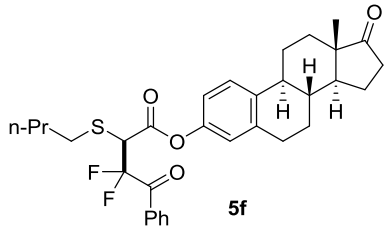


5f



ZWZ-09-34-F
F19CPD

-99.88
-99.89
-100.41
-100.42
-102.31
-102.35
-102.84
-102.89



5f