Supporting information

Trifluoromethylthiolation of Allylsilanes and Silyl Enol Ethers with Trifluoromethanesulfonyl Hypervalent Iodonium Ylide under Copper Catalysis

Sadayuki Arimori, Masahiro Takada and Norio Shibata*

Department of Frontier Materials, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466-8555, Japan.

Tel: (+81) 52-735-7543, Fax: (+81) 52-735-5442
E-mail: nozshiba@nitech.ac.jp

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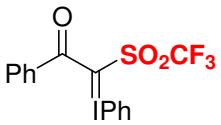
1. General information.

All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred via syringe and were introduced into the reaction vessels through a rubber septum. All solvents were purified by standard method. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel (60-F254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or $KMnO_4$ in water/heat. All of the reaction products were purified by preparative thin-layer plates(PLC) carried out on 2.0 mm Merck silica gel (60-F254) or Column chromatography. Column chromatography was carried out on a column packed with silica gel 60N spherical neutral size 63-210 mm. The ^1H NMR (300 MHz) and ^{19}F NMR (282 MHz) spectra (with Hexafluorobenzene (δ ppm -162.2) as an internal standard) as for solution in $CDCl_3$ were recorded on a Varian Mercury 300. ^{13}C NMR (150.9 MHz) spectra for solution in $CDCl_3$ was recorded on a BRUKER 600 UltraShield^{TR}. Chemical shifts (δ) are expressed in ppm downfield from internal TMS or C_6F_6. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra were recorded on a SHIMADZU GCMS-QP5050A (EI-MS) and SHIMAZU LCMS-2010EV(ESI-MS and APCI-MS). Infrared spectra were recorded on JASCO FT/IR-200 or a JASCO FT/IR-4100 spectrometer.

Preparation of the $^+SCF_3$ reagent 2, Allylsilanes 3 and Silyl Enol Ethers 4

The $^+SCF_3$ reagent **2**[1)], allylsilanes **3**[2)] and silyl enol ethers **4**[3)] were prepared according to the referential procedure.



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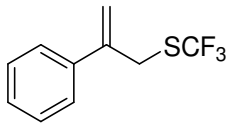
Reference: (1) Yang, Y. -D.; Azuma, A.; Tokunaga, E.; Yamasaki, M.; Shiro, M.; Shibata, N. *J. Am. Chem. Soc.* **2013**, *135*, 8782. (2) Liu, J.; Chu, L.; Qing, F. -L. *Org. Lett.* **2013**,*15,* 894. (3) Miguélez, J.; Boto, A.; Marín, R.; Díaz, M. *Eur. J. Med. Chem.* **2013**, *66*, 540.

2. General Procedure for Trifluromethylthiolation of Allylsilanes and Silyl Enol Ethers with Trifluoromethanesulfonyl Hypervalent Iodonium Yielde ($^{+}SCF_3$ reagent).

A mixture of allylsilanes **3** / silyl enol ether **4** (0.25 mmol), CuF_2 (0.05 mmol), the $^{+}SCF_3$ reagent **2** (0.5 mmol) and *N*, *N*-dimethyl acetamide or *N*-Methyl-2-pyrrolidone (1.25 mL) at room temperature was stirring for 10 h. The resulting mixture was added 1N-HClaq (0.5 mL), extracted by ethyl acetate, and the combined organic phase was washed with water (1.0 mL) for 2 times, with brine for once and then dried over magnesium sulfate. The solvent was removed by rotary evaporation to give a crude product. The crude product was purified by preparative thin-layer plates (PLC) or a column chromatography with hexane and ethyl acetate to give target products (**5a-o**, **6a-j**).

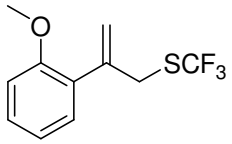
3. Products Spectra data.

(2-Phenylallyl)(trifluoromethyl)sulfane (5a)



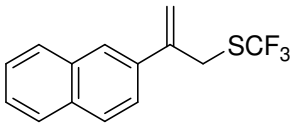
^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 4.00 (s, 2H), 5.40 (s, 1H), 5.53 (s, 1H), 7.31 - 7.43 (m, 5H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -42.0 (s, 3F). MS (EI, m/z) 218 (M^{+}). Colorless oil (41.0 mg, 75%). The product was identified by comparison of the spectral data with the reported data. Reference: Liu, J.; Chu, L.; Qing, F. -L. *Org. Lett.* **2013**, *15,* 894.

(2-(2-Methoxylphenyl)allyl)(trifluoromethyl)sulfane (5b)



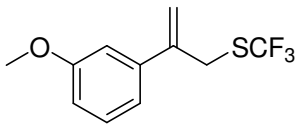
^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 3.83 (s, 3H), 4.04 (s, 2H), 5.24 (s, 1H), 5.39 (s, 1H), 6.88 (d, J = 8.4 Hz, 1H), 6.92 - 6.97 (m, 1H), 7.20 (dd, J = 7.2 Hz, 1.8 Hz, 1H), 7.31 - 7.33 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -41.9 (s, 3F). ^{13}C NMR (150.9 MHz, $CDCl_3$): 35.3, 55.3, 110.6, 118.5, 120.8, 127.8, 129.5, 130.8 (q, J = 306.3Hz), 130.9, 143.3, 156.5. IR (neat) v 3079, 2948, 1600, 1490, 1240, 1113, 915, 753 cm^{-1}. MS (EI, m/z) 248 (M^+). HRMS (EI, m/z) Anal. Calcd for $C_{11}H_{11}F_3OS$ 248.0483, found [M^+] 248.0490. Colorless oil (44.1 mg, 70%).

(2-(Naphthalen-2-yl)allyl)(trifluoromethyl)sulfane (5c)



^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 4.12 (s, 2H), 5.50 (s, 1H), 5.67 (s, 1H), 7.48 - 7.50 (m, 2H), 7.56 (d, J = 7.2 Hz, 1H), 7.78 - 7.85 (m, 4H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -41.9 (s, 3F). MS (EI, m/z) 268 (M^+). White solid (55.4 mg, 82%). The product was identified by comparison of the spectral data with the reported data. Reference: Liu, J.; Chu, L.; Qing, F. -L. *Org. Lett*. **2013**, *15,* 894.

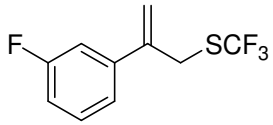
(2-(3-Methoxylphenyl)allyl)(trifluoromethyl)sulfane (5d)



^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 3.83 (s, 3H), 3.98 (s, 2H), 5.40 (s, 1H), 5.52 (s, 1H), 6.87 (d, J = 8.1 Hz, 1H), 6.94 - 6.98 (m, 1H), 7.0 (d, J = 8.1Hz, 1H), 7.25 - 7.31 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -41.9 (s, 3F). MS (EI, m/z) 248 (M^+). Colorless oil (35.9 mg, 58%). The product was identified by comparison of the

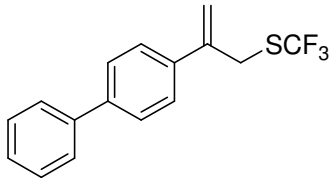
spectral data with the reported data. Reference: Liu, J.; Chu, L.; Qing, F. -L. *Org. Lett*. **2013**, *15,* 894.

(2-(3-Fluorophenyl)allyl)(trifluoromethyl)sulfane (5e)



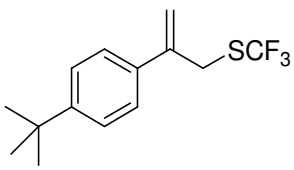
^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 3.97 (s, 2H), 5.45 (s, 1H), 5.55 (s, 1H), 7.06 (t, J = 8.4 Hz, 1H), 7.11 (d, J = 10.2 Hz, 1H), 7.17 - 7.20 (m, 1H), 7.33 - 7.36 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -41.9 (s, 3F), -113.2 (d, J = 5.9 Hz, 1F). MS (EI, m/z) 236 (M^+). Colorless oil (26.7 mg, 45%). The product was identified by comparison of the spectral data with the reported data. Reference: Liu, J.; Chu, L.; Qing, F. -L. *Org. Lett*. **2013**, *15,* 894.

(2-(Biphenyl-4-yl)allyl)(trifluoromethyl)sulfane (5f)



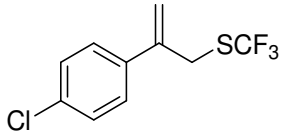
^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 4.04 (s, 2H), 5.43 (s, 1H), 5.60 (s, 1H), 7.37 (d, J = 6.3 Hz, 1H), 7.44-7.52 (m, 4H), 7.55 - 7.65 (m, 4H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -42.0 (s, 3F). MS (EI, m/z) 294 (M^+). White solid (48.1 mg, 65%). The product was identified by comparison of the spectral data with the reported data. Reference: Liu, J.; Chu, L.; Qing, F. -L. *Org. Lett*. **2013**, *15,* 894.

(2-(4-*tert*-Butylphenyl)allyl)(trifluoromethyl)sulfane (5g)



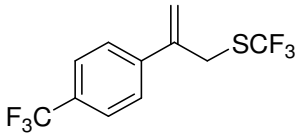
^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 1.33 (s, 9H), 4.00 (s, 2H), 5.36 (s, 1H), 5.53 (s, 1H), 7.38 (brs, 4H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -42.1 (s, 3F). MS (EI, m/z) 274 (M^+). Colorless oil (48.7 mg, 71%). The product was identified by comparison of the spectral data with the reported data. Reference: Liu, J.; Chu, L.; Qing, F. -L. *Org. Lett*. **2013**, *15,* 894.

(2-(4-Chlorophenyl)allyl)(trifluoromethyl)sulfane (5h)



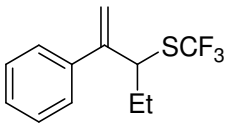
^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 3.97 (s, 2H), 5.42 (s, 1H), 5.50 (s, 1H), 7.30 - 7.35 (m, 4H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -41.9 (s, 3F). MS (EI, m/z) 252 (M^+). Colorless oil (51.2 mg, 81%). The product was identified by comparison of the spectral data with the reported data. Reference: Liu, J.; Chu, L.; Qing, F. -L. *Org. Lett*. **2013**, *15,* 894.

(2-(4-Trifluoromethylphenyl)allyl)(trifluoromethyl)sulfane (5i)



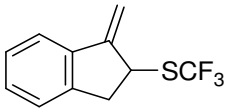
^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 4.01 (s, 2H), 5.51 (s, 1H), 5.59 (s, 1H), 7.51 (d, J = 8.1 Hz, 2H), 7.63 (d, J = 8.1 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -41.9 (s, 3F), -63.2 (s, 3F). MS (EI, m/z) 286 (M^+). Colorless oil (29.3 mg, 41%). The product was identified by comparison of the spectral data with the reported data. Reference: Liu, J.; Chu, L.; Qing, F. -L. *Org. Lett*. **2013**, *15,* 894.

(2-Phenylpent-1-en-3-yl)(trifluoromethyl)sulfane (5j)



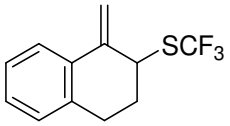
^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 0.99 (t, J = 7.2 Hz, 3H), 1.89 - 1.91 (m, 2H), 4.14 (t, J = 7.2 Hz, 1H), 5.40 (s, 1H), 5.43 (s, 1H), 7.34 - 7.39 (m, 5H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -40.5 (s, 3F). MS (EI, m/z) 246 (M^+). Colorless oil (19.9 mg, 32%). The product was identified by comparison of the spectral data with the reported data. Reference: Liu, J.; Chu, L.; Qing, F. -L. *Org. Lett*. **2013**, *15,* 894.

(1-Methyleneindane-2-yl)(trifluoromethyl)sulfane (5k)



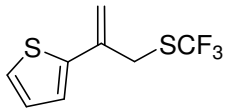
^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 3.29 (dd, J = 17.4 Hz, 3.3 Hz, 1H), 3.61 (dd, J = 17.4 Hz, 7.8 Hz, 1H), 4.61 - 4.64 (m, 1H), 5.38 (d, J = 2.4 Hz, 1H), 5.71 (d, J = 2.1 Hz, 1H), 7.25 - 7.27 (m, 3H), 7.48 - 7.51 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -40.6 (s, 3F). ^{13}C NMR (150.9 MHz, $CDCl_3$): 40.8, 45.4 (d, J = 1.5Hz), 107.6, 121.0, 125.2, 127.3, 129.9, 130.9 (q, J = 306.3Hz), 138.5, 142.6, 147.8. IR (neat) v 3071, 2916, 1639, 1473, 1152, 1114, 887, 777 cm^{-1}. MS (EI, m/z) 230 (M^+). HRMS (EI, m/z) Anal. Calcd for $C_{11}H_9F_3S$ 230.0377, found [M^+] 230.0356. Colorless oil (40.3 mg, 70%).

(1-Methylene-1,2,3,4-tetrahydronaphthalene-2-yl)(trifluoromethyl)sulfane (5l)



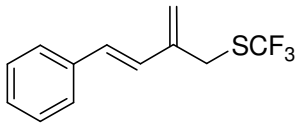
^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 2.25 - 2.28 (m, 2H), 2.83 - 2.89 (m, 1H), 3.08 - 3.17 (m, 1H), 4.50 (s, 1H), 5.29 (s, 1H), 5.66 (s, 1H), 7.12 - 7.24 (m, 3H), 7.61 (d, J = 7.2 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -39.7 (s, 3F). MS (EI, m/z) 244 (M^+). Colorless oil (23.1 mg, 38%). The product was identified by comparison of the spectral data with the reported data. Reference: Liu, J.; Chu, L.; Qing, F. -L. *Org. Lett*. **2013**, *15,* 894.

(2-(Thiophene-2-yl)allyl)(trifluoromethyl)sulfane (5m)



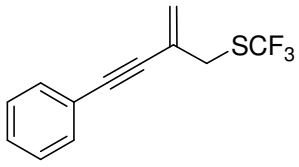
^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 3.95 (s, 2H), 5.29 (s, 1H), 5.58 (d, J = 3.6Hz, 1H), 6.99 - 7.04 (m, 1H), 7.08 - 7.09 (m, 1H), 7.24 (t, J = 1.2Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -42.1 (s, 3F). ^{13}C NMR (150.9 MHz, $CDCl_3$): 34.4 (d, J = 3.0Hz), 115.5. 124.4, 125.3, 127.6, 130.6 (q, J = 306.3Hz), 135.6, 142.1. IR (neat) v 3079, 2954, 1618, 1437, 1152, 1112, 851, 700 cm^{-1}. MS (EI, m/z) 224 (M^+). HRMS (EI, m/z) Anal. Calcd for $C_8H_7F_3S2$ 223.9941, found [M^+] 223.9938. Yellow oil (44.7 mg, 79%).

(*E*)-(2-Methylene-4-phenylbut-3-enyl)(trifluoromethyl)sulfane (5n)



^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 3.85 (s, 2H), 5.37 (s, 2H), 6.61 (d, J = 16.5 Hz, 1H), 6.78 (d, J = 16.5 Hz, 1H), 7.24 - 7.29 (m, 1H), 7.34 (t, J = 7.5 Hz, 2H), 7.43 - 7.46 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -42.3 (s, 3F). MS (EI, m/z) 244 (M^+). Colorless oil (43.9 mg, 72%). The product was identified by comparison of the spectral data with the reported data. Reference: Liu, J.; Chu, L.; Qing, F. -L. *Org. Lett*. **2013**, *15,* 894.

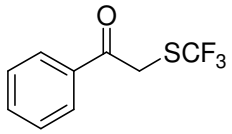
(2-Methylene-4-phenylbut-3-ynyl)(trifluoromethyl)sulfane (5o)



^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 3.70 (s, 2H), 5.59 (s, 1H), 5.61 (s, 1H), 7.34 (brs, 3H), 7.47 (brs, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -41.7 (s, 3F). MS (EI, m/z)

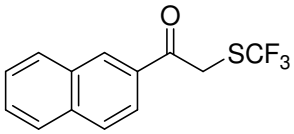
242 (M^+). Colorless oil (9.10 mg, 15%). The product was identified by comparison of the spectral data with the reported data. Reference: Liu, J.; Chu, L.; Qing, F. -L. *Org. Lett*. **2013**, *15,* 894.

1-Pheny-2-((trifluoromethyl)thio)ethanone (6a)



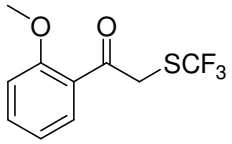
^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 4.53 (s, 2H), 7.51 (t, J=7.6 Hz, 2H), 7.64 (t, J=8.1 Hz, 1H), 7.94 - 7.98 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -41.9 (s, 3F). MS (ESI, m/z) 243 $(M+Na)^+$. Yellow oil (19.3 mg, 35%). The product was identified by comparison of the spectral data with the reported data. Reference: Huang, Y.; He, X.; Lin, X.; Rong, M.; Weng, Z. *Org. Lett.* **2014**, *16*, 3284.

1-(Naphthalen-2-yl)-2-((trifluoromethyl)thio)ethanone (6b)



^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 4.67 (s, 2H), 7.57 - 7.68 (m, 2H), 7.89 - 8.01 (m, 4H), 8.46 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -41.8 (s, 3F). MS (ESI, m/z) 287 $(M+NH_4)^+$. Yellow solid (28.8 mg, 42%). The product was identified by comparison of the spectral data with the reported data. Reference: Huang, Y.; He, X.; Lin, X.; Rong, M.; Weng, Z. *Org. Lett.* **2014**, *16*, 3284.

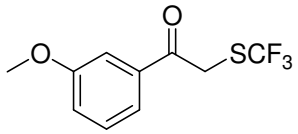
1-(2-Methoxyphenyl)-2-((trifluoroethyl)thio)ethanone (6c)



^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 3.96 (s, 3H), 4.43 (s, 2H), 7.01 (d, J = 8.4 Hz, 1H), 7.06 (t, J = 8.1 Hz, 1H), 7.54 (m, 1H), 7.88 (m, 1H). ^{19}F NMR (282 MHz,

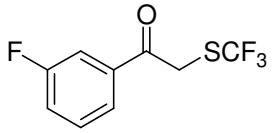
$CDCl_3$): δ ppm -42.1 (s, 3F). MS (ESI, m/z) 273 $(M+Na)^+$. Yellow solid (17.6 mg, 28%). The product was identified by comparison of the spectral data with the reported data. Reference: Huang, Y.; He, X.; Lin, X.; Rong, M.; Weng, Z. *Org. Lett.* **2014**, *16*, 3284.

1-(3-Methoxyphenyl)-2-((trifluoroethyl)thio)ethanone (6d)



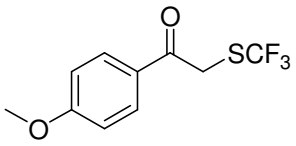
^1H NMR (300 MHz, $CDCl_3$): δ ppm 3.86 (s, 3H), 4.47 (s, 2H), 7.17 (dd, J = 7.8, 2.4 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.47 – 7.52 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -41.8 (s, 3F). MS (ESI, m/z) 273 $(M+Na)^+$. Yellow oil (18.8 mg, 30%). The product was identified by comparison of the spectral data with the reported data. Reference: Huang, Y.; He, X.; Lin, X.; Rong, M.; Weng, Z. *Org. Lett.* **2014**, *16*, 3284.

1-(3-Fluorophenyl)-2-(trifluoromethylthio)ethanone (6e)



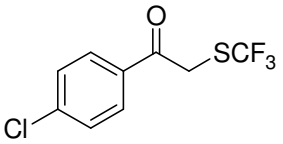
^1H NMR (300 MHz, $CDCl_3$): δ ppm 4.48 (s, 2H), 7.36 (s, 1H), 7.51 (d, J = 6.0 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 7.5 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -111.1 (s, 1F), -41.9 (s, 3F). ^{13}C NMR (150.9 MHz, $CDCl_3$): 38.2, 115.2 (d, J = 22.6 Hz), 121.4 (d, J = 21.1 Hz), 124.2 (d, J = 3.0 Hz), 130.5 (q, J = 306.3 Hz), 136.6 (d, J = 6.0 Hz), 162.1, 163.7, 190.9 (d, J = 3.0 Hz). IR (neat) v 3369, 3079, 2924, 1817, 1688, 1592, 1108, 760, 678 cm^{-1}. MS (ESI, m/z) 271 $(M+CH_3OH)^+$. HRMS (EI, m/z) Anal. Calcd for $C_9H_6OF_4S$ 238.0075, found $[M^+]$ 230.0092. Yellow oil (22.4 mg, 38%).

1-(4-Methoxyphenyl)-2-((trifluoroethyl)thio)ethanone (6f)



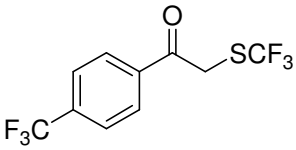
^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 3.89 (s, 3H), 4.48 (s, 2H), 6.98 (d, J = 9.0 Hz, 2H), 7.93 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -41.9 (s, 3F). MS (ESI, m/z) 273 $(M+Na)^+$. Yellow oil (15.6 mg, 25%). The product was identified by comparison of the spectral data with the reported data. Reference: Huang, Y.; He, X.; Lin, X.; Rong, M.; Weng, Z. *Org. Lett.* **2014**, *16*, 3284.

1-(4-Chlorophenyl)-2-((trifluoromethyl)thio)ethanone (6g)



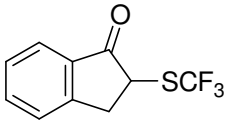
^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 4.47 (s, 2H), 7.49 (d, J = 8.1 Hz, 2H), 7.90 (d, J = 8.1 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -41.9 (s, 3F). MS (ESI, m/z) 287 $(M+NH_4)^+$. Yellow solid (32.9 mg, 52%). The product was identified by comparison of the spectral data with the reported data. Reference: Huang, Y.; He, X.; Lin, X.; Rong, M.; Weng, Z. *Org. Lett.* **2014**, *16*, 3284.

1-(4-(Trifluoromethyl)phenyl)-2-(trifluoromethylthio)ethanone (6h)



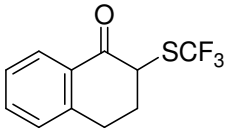
^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 4.50 (s, 2H), 7.79 (d, J = 8.1 Hz, 2H), 8.07 (d, J = 8.1 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -63.8 (s, 3F), -41.9 (s, 3F). MS (ESI, m/z) 304 $(M+NH_4)^+$. Yellow solid (16.9 mg, 23%). The product was identified by comparison of the spectral data with the reported data. Reference: Huang, Y.; He, X.; Li, H.; Weng, Z. *Eur. J. Org. Chem.* **2014**, *33*, 7324.

2,3-Dihydro-2-(trifluoromethylthio)inden-1-one (6i)



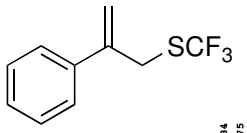
^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 3.37 (d, J = 17.4 Hz, 1H), 3.80 (dd, J = 17.4, 8.1 Hz, 1H), 4.24 (m, 1H), 7.46 (dd, J = 16.2, 7.5 Hz, 2H), 7.67 (d, J = 7.2 Hz, 1H), 7.83 (d, J = 7.5 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -40.0 (s, 3F). ^{13}C NMR (150.9 MHz, $CDCl_3$): 36.3, 47.4, 124.8, 126.4, 128.3, 130.6 (q, J = 306.3 Hz), 134.5, 136.0, 151.7, 199.2. IR (neat) v 3369, 3079, 2924, 1817, 1688, 1592, 1108, 760, 678 cm^{-1}. MS (ESI, m/z) 272 $(M+CH_3CN)^+$. HRMS (EI, m/z) Anal. Calcd for $C_{10}H_7OF_3S$ 232.0170, found [M+] 232.0168. Yellow oil (20.7 mg, 36%). The product was identified by comparison of the spectral data with the reported data. Reference: Alazet, S.; Zimmer, L.; Billard, T. *Chem. Eur. J.* **2014**, *20*, 8589.

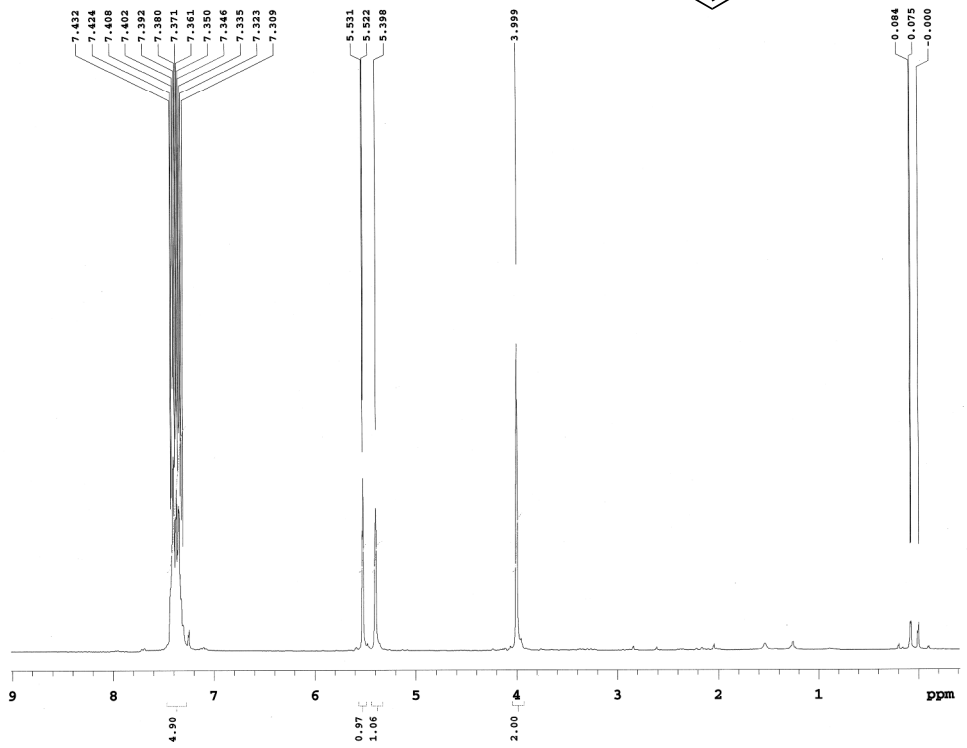
2-((Trifluoromethyl)sulfanyl)-3,4-dihydronaphthalen-1(2*H*)-one (6j)

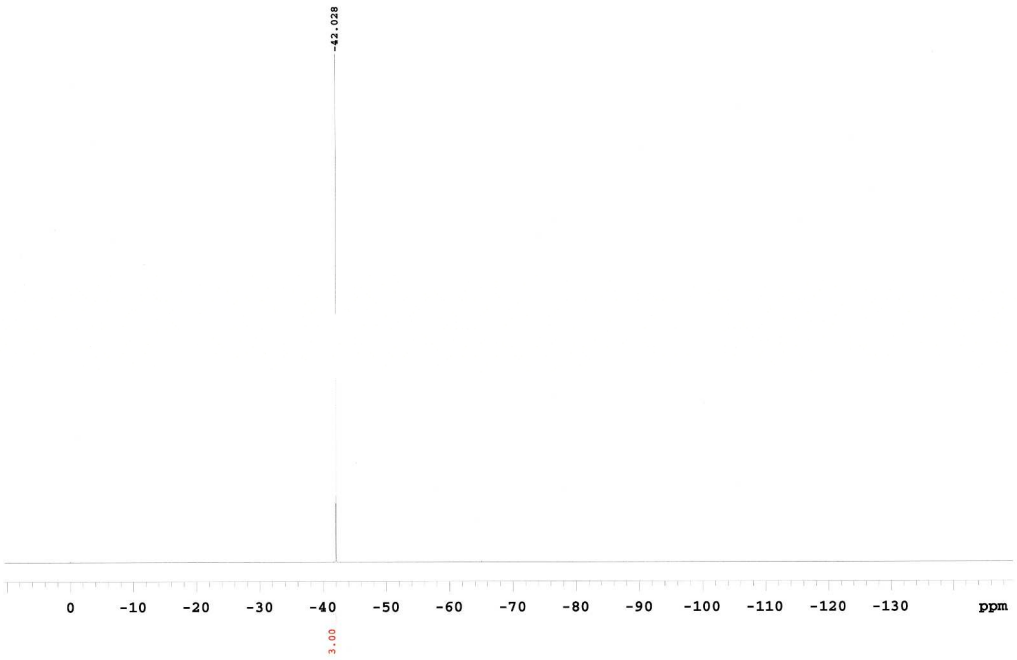


^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 2.33 - 2.46 (m, 1H), 2.66 - 2.75 (m, 1H), 3.13 (t, J = 6.0 Hz, 2H), 4.36 (dd, J = 10.8, 4.5 Hz, 1H), 7.27 (d, J = 6.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.50 – 7.56 (m, 1H), 8.05 (d, J = 7.8 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -39.2 (s, 3F). MS (ESI, m/z) 246 $(M)^+$. Colorless oil (13.3 mg, 22%). The product was identified by comparison of the spectral data with the reported data. Reference: Alazet, S.; Zimmer, L.; Billard, T. *Chem. Eur. J.* **2014**, *20*, 8589.

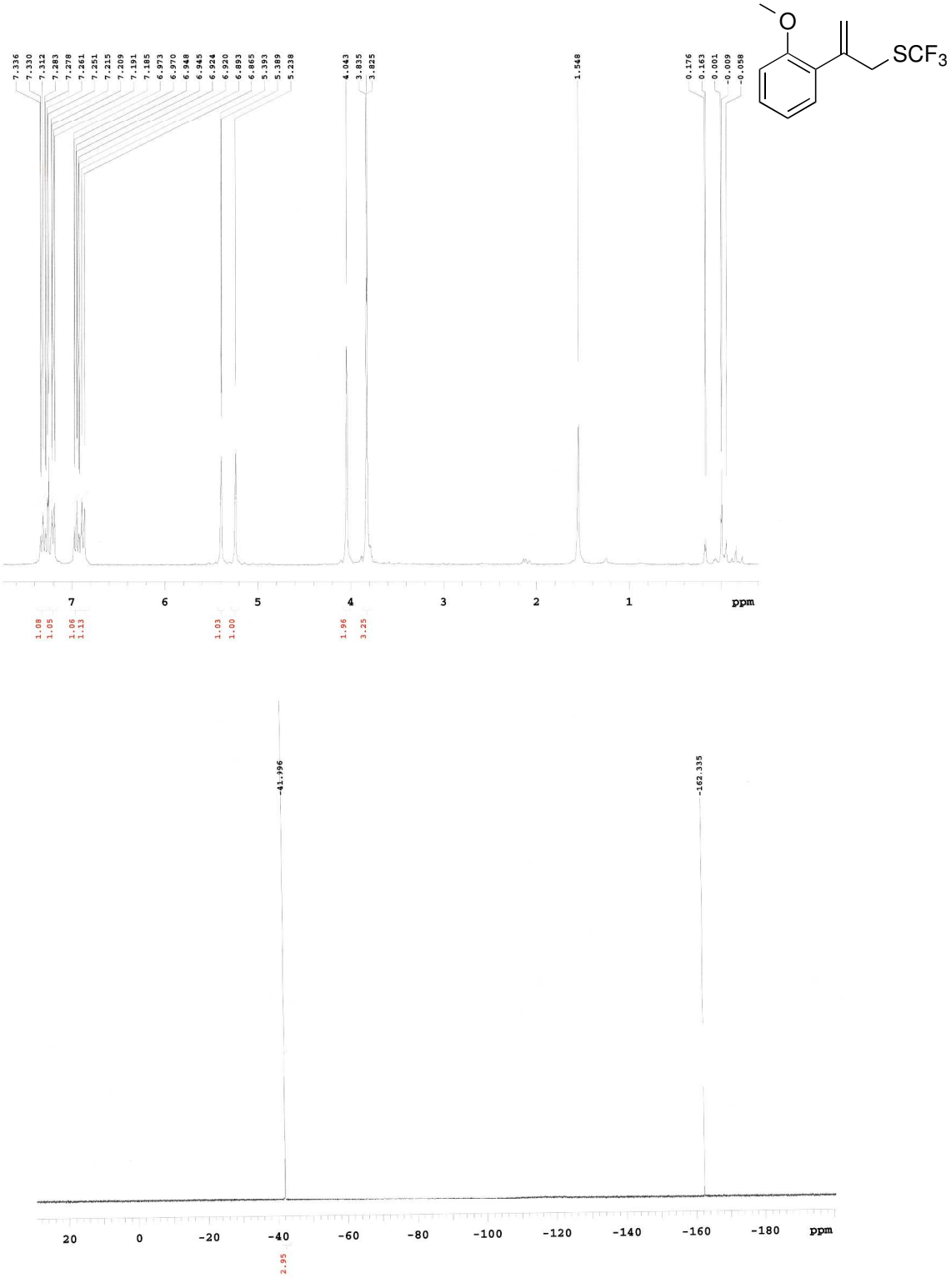
^{1}H NMR spectrum and ^{19}F NMR spectrum of (5a)

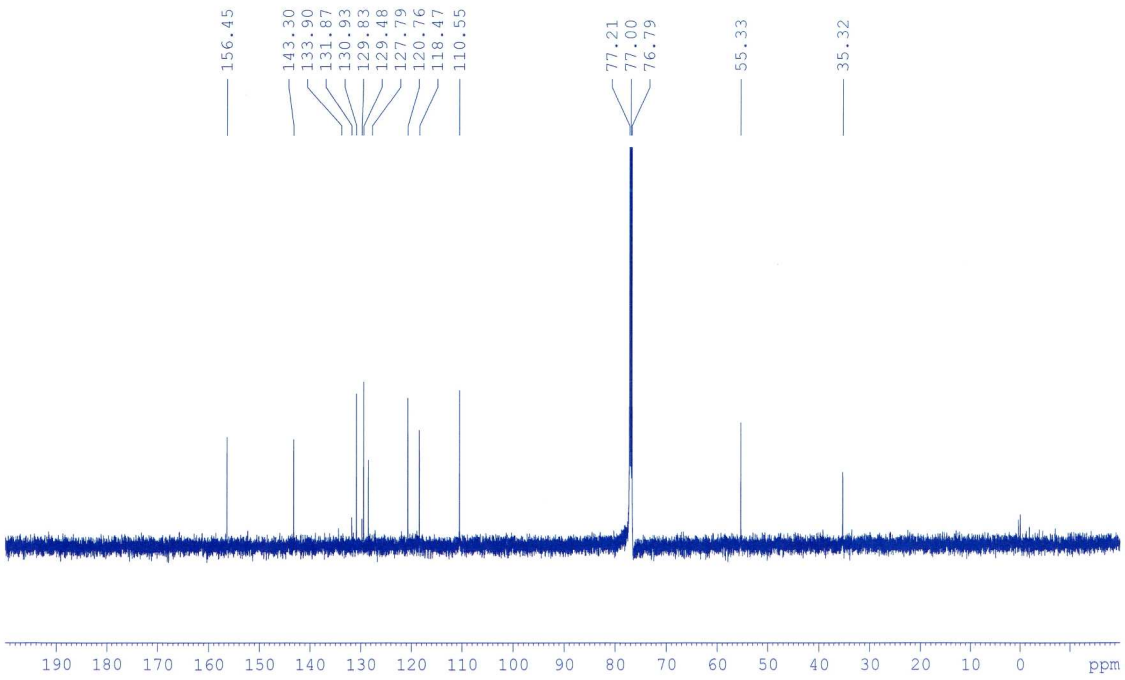




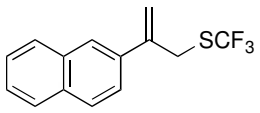


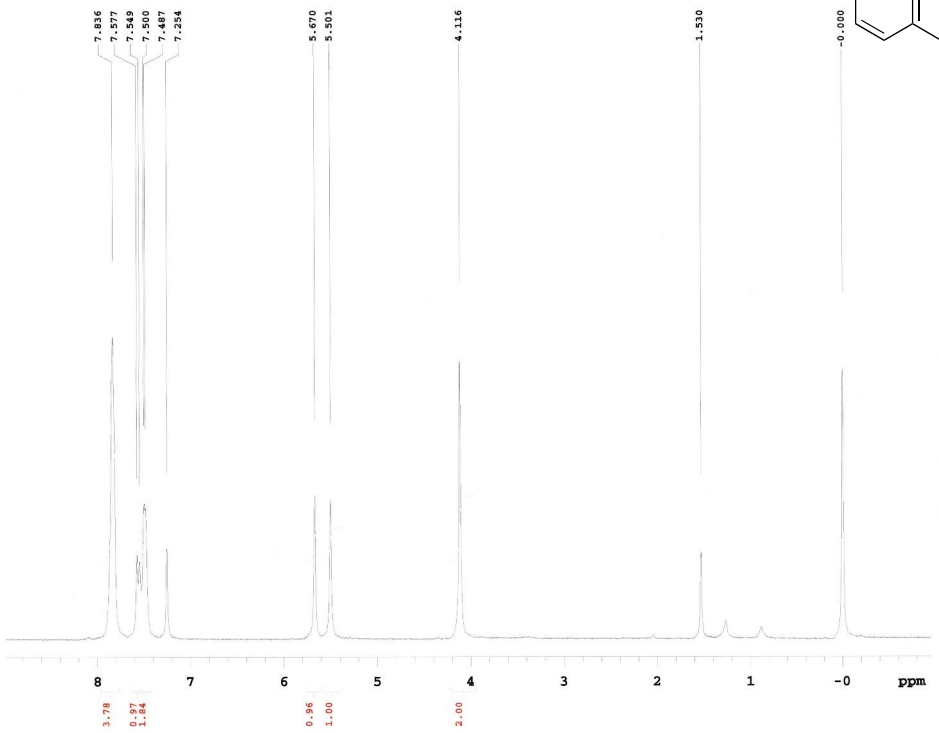
^{1}H NMR spectrum, ^{19}F NMR spectrum and ^{13}C NMR spectrum of (5b)

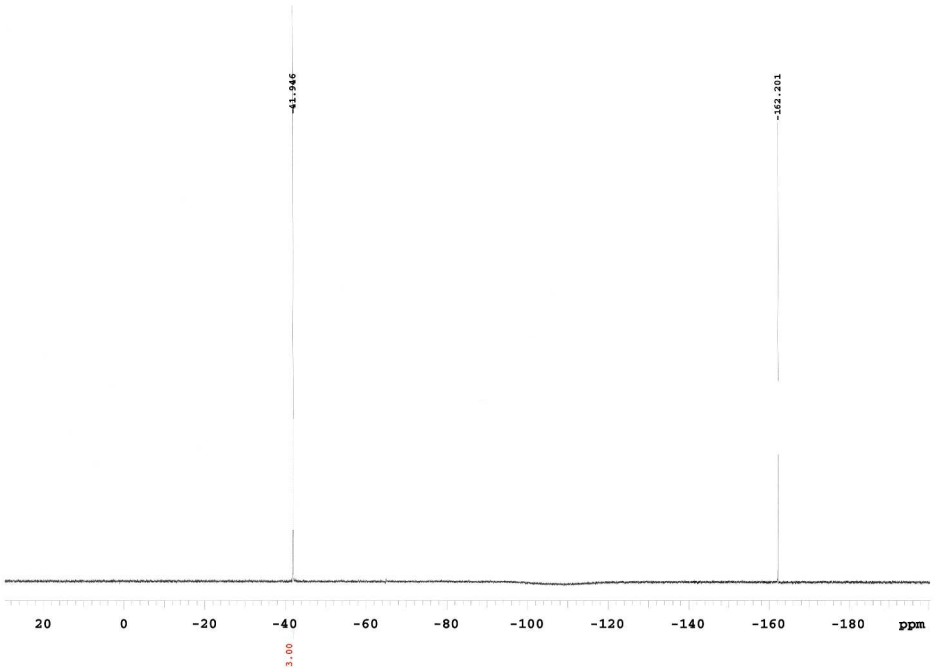




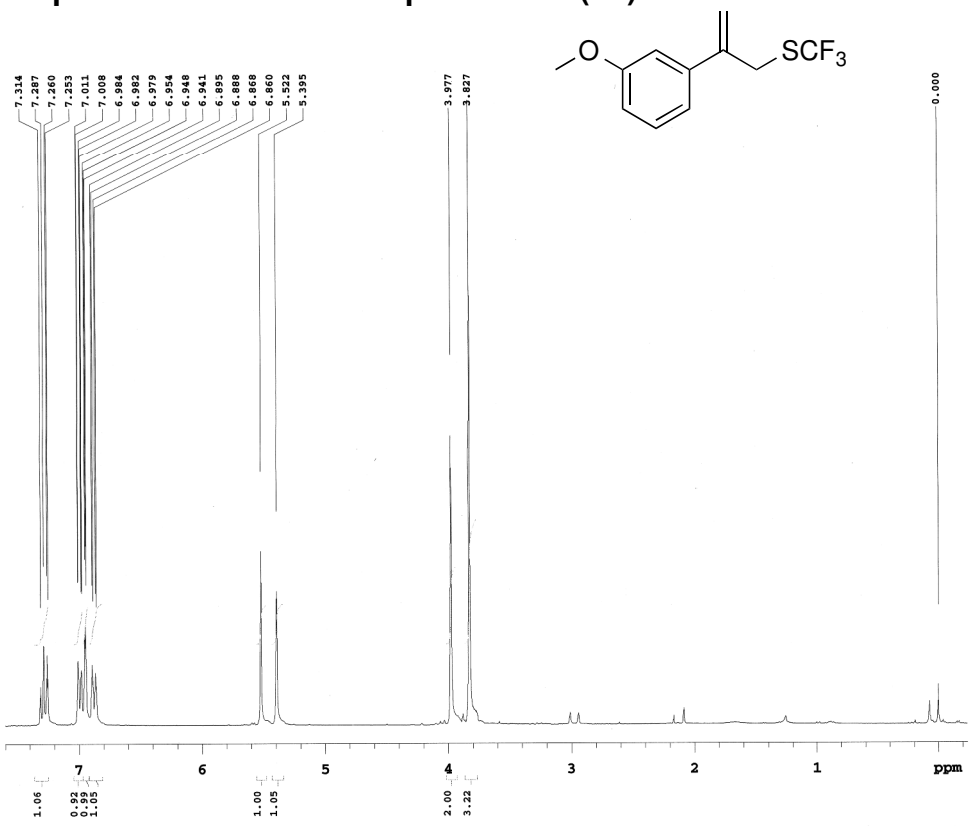
^{1}H NMR spectrum and ^{19}F NMR spectrum of (5c)

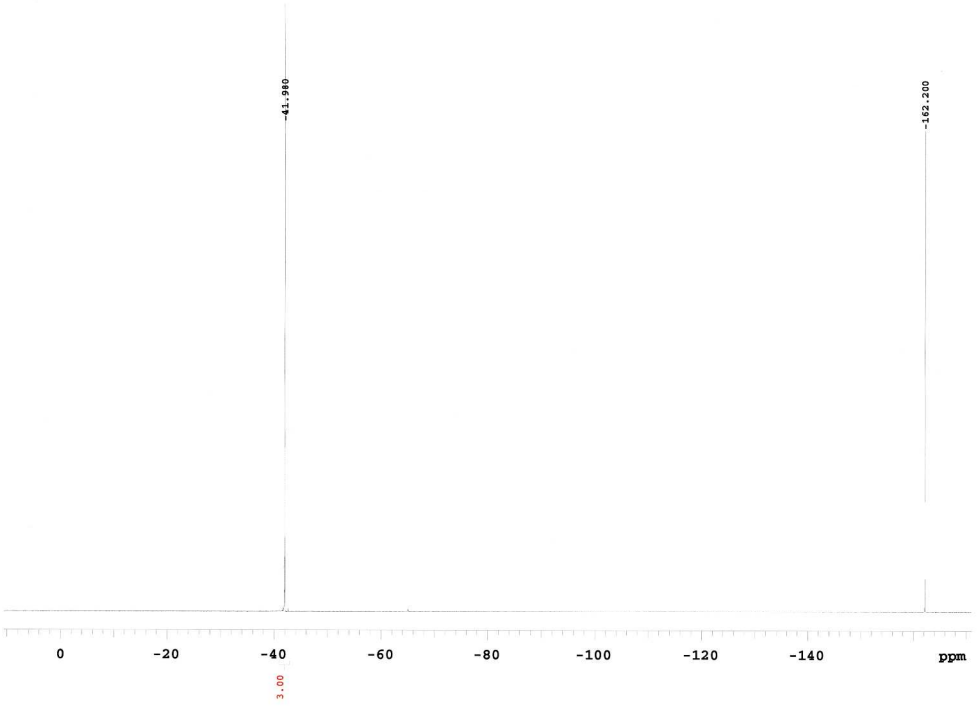




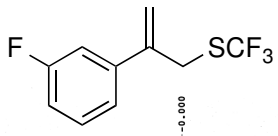


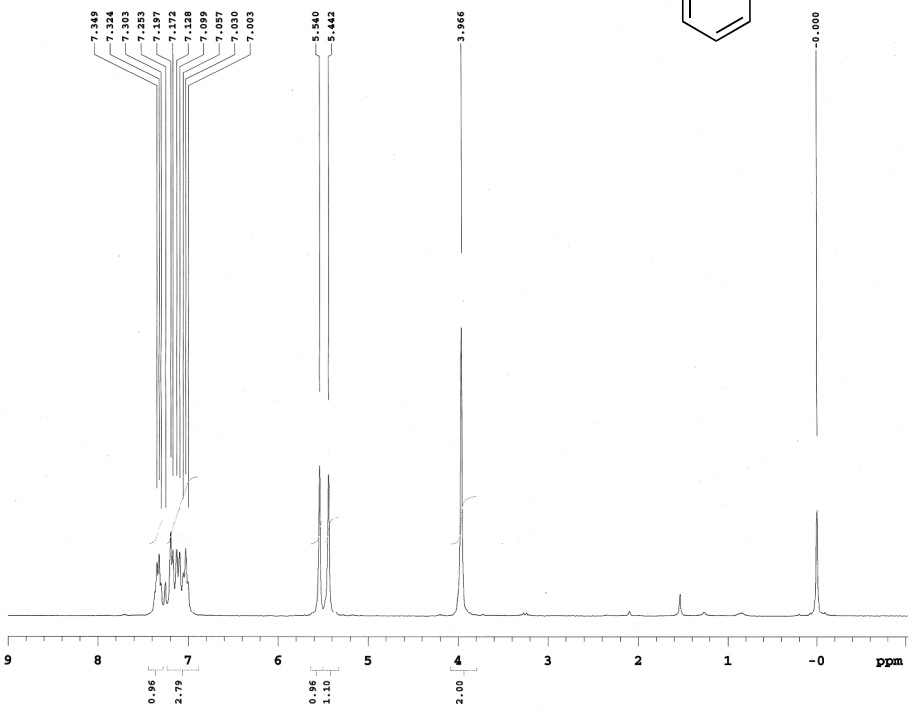
^{1}H NMR spectrum and ^{19}F NMR spectrum of (5d)

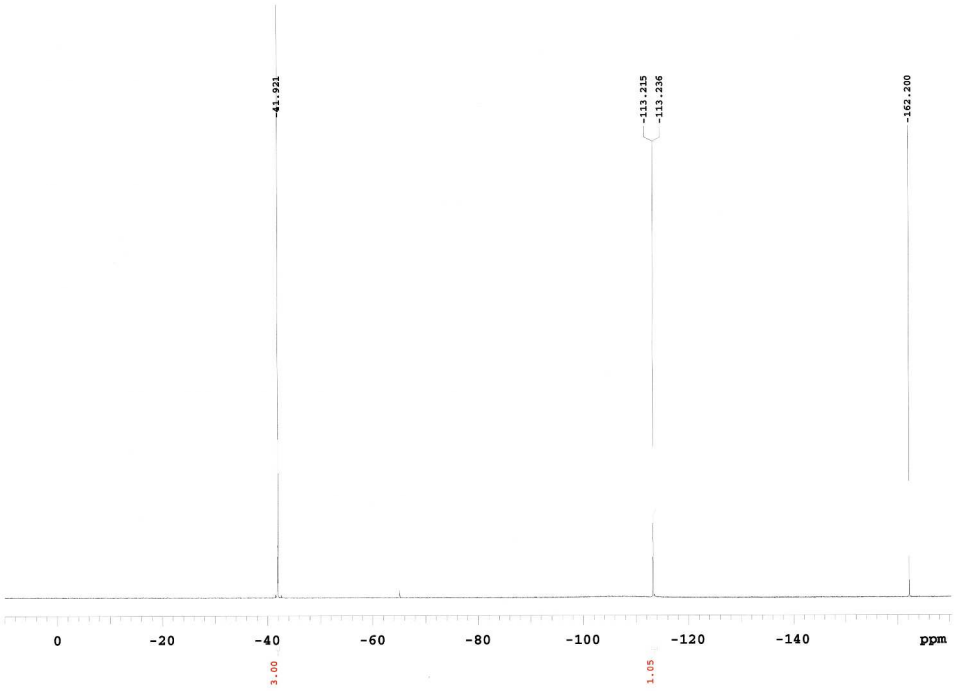




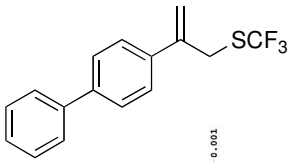
^{1}H NMR spectrum and ^{19}F NMR spectrum of (5e)

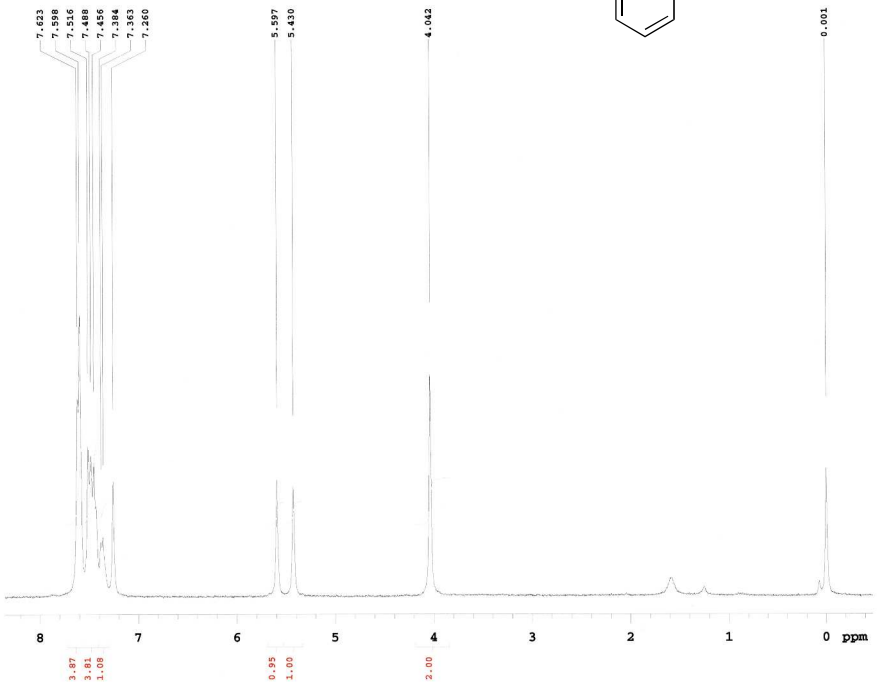


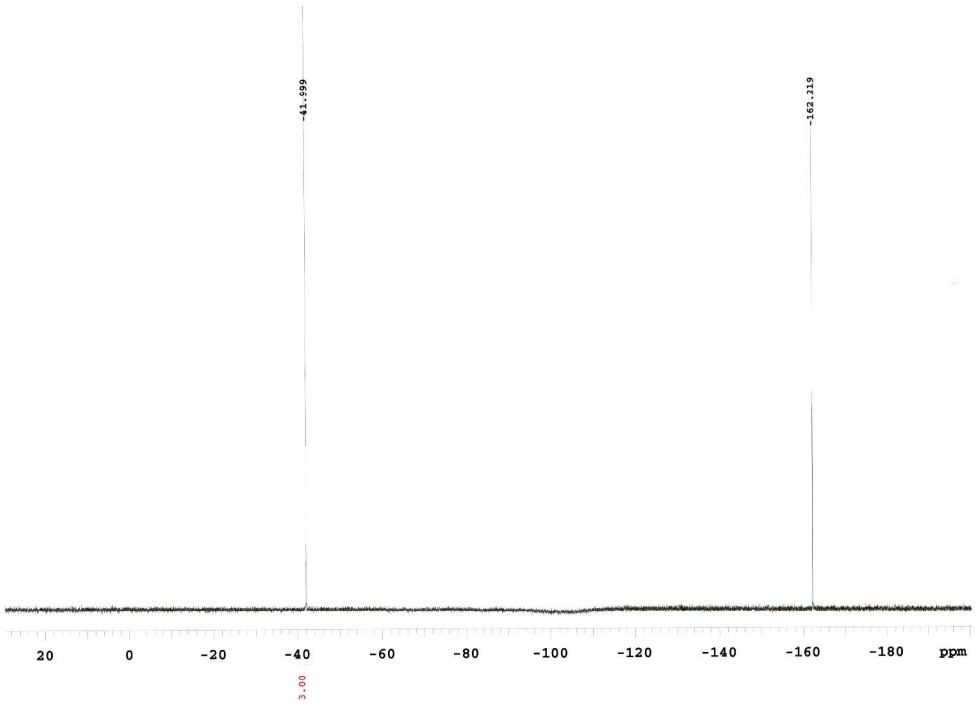




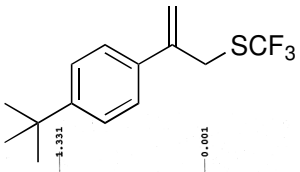
^{1}H NMR spectrum and ^{19}F NMR spectrum of (5f)

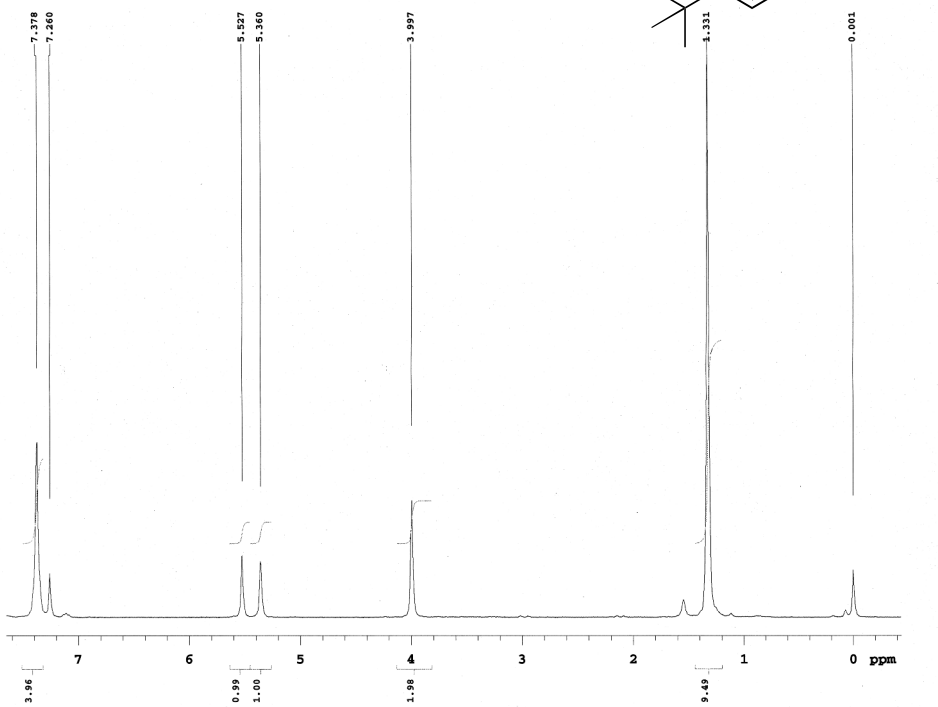


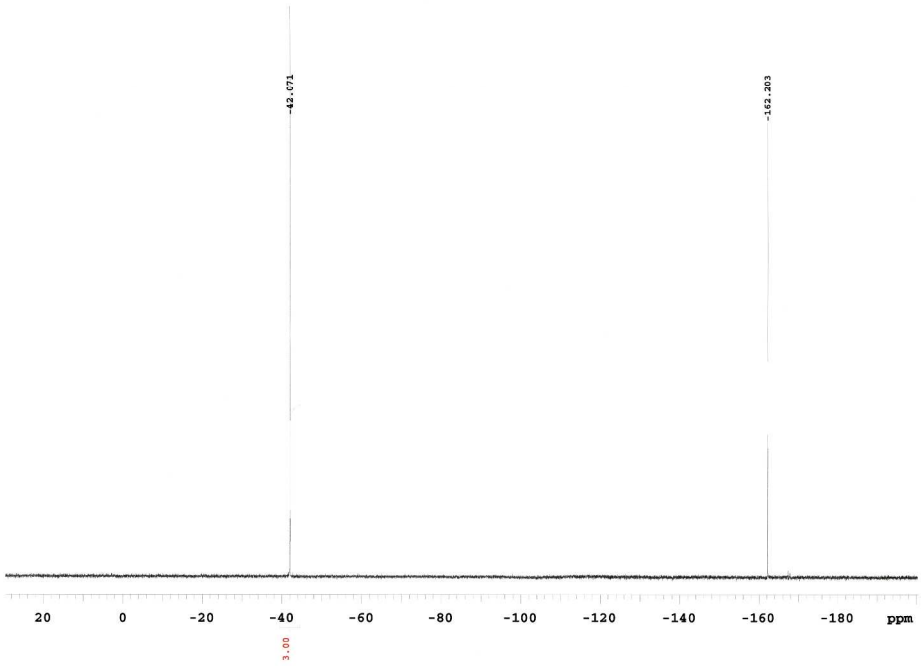




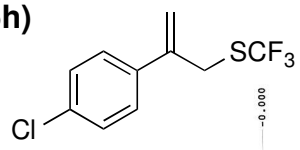
^{1}H NMR spectrum and ^{19}F NMR spectrum of (5g)

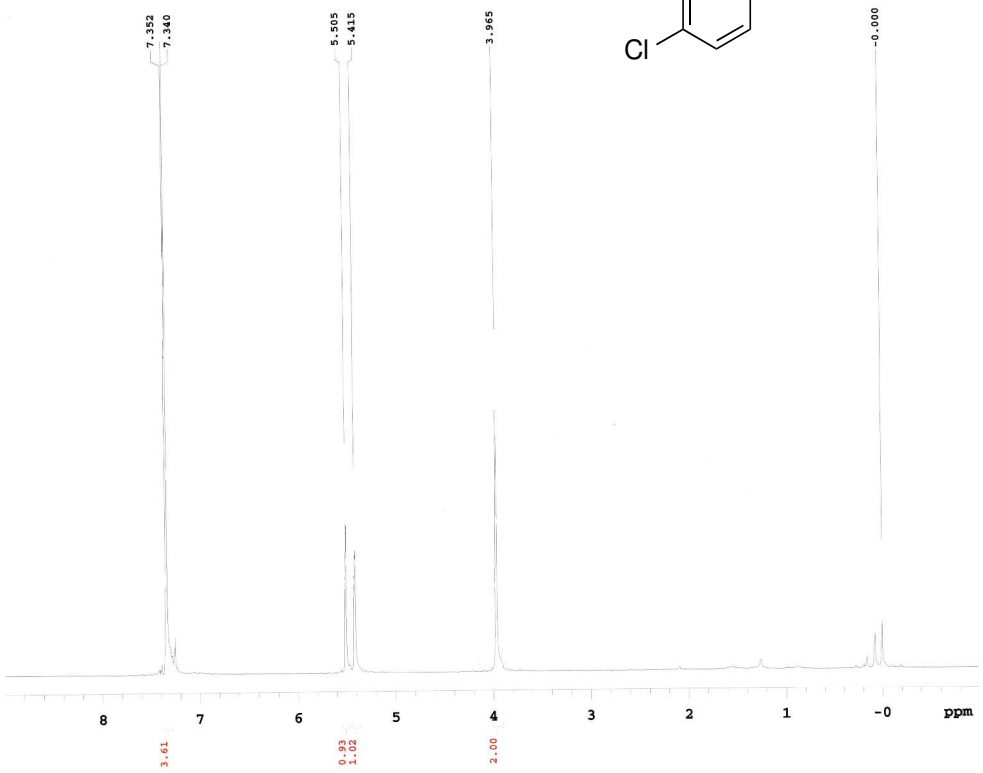


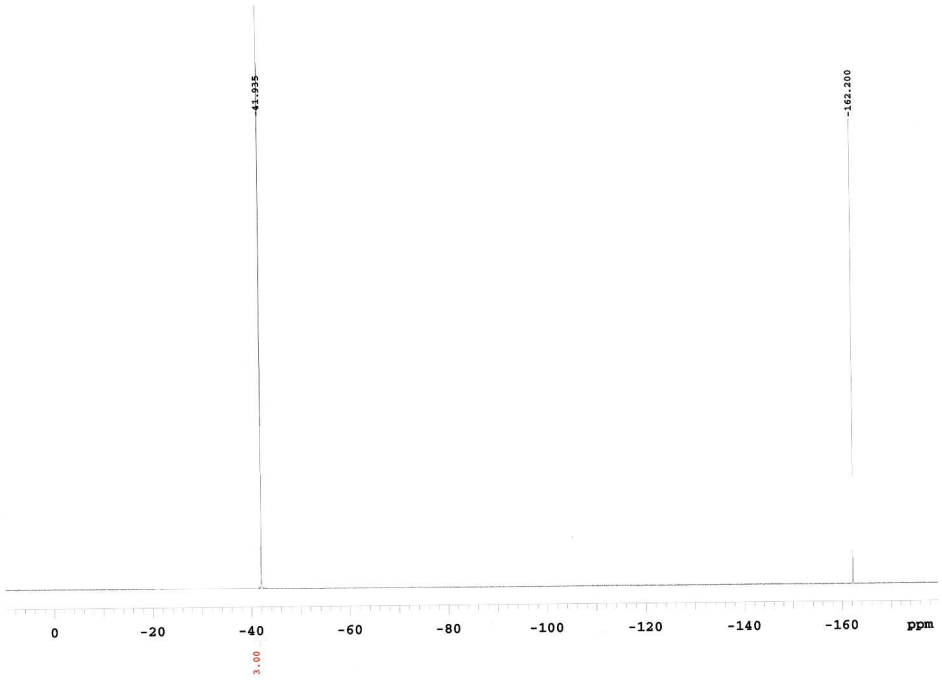




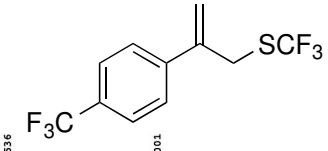
^{1}H NMR spectrum and ^{19}F NMR spectrum of (5h)

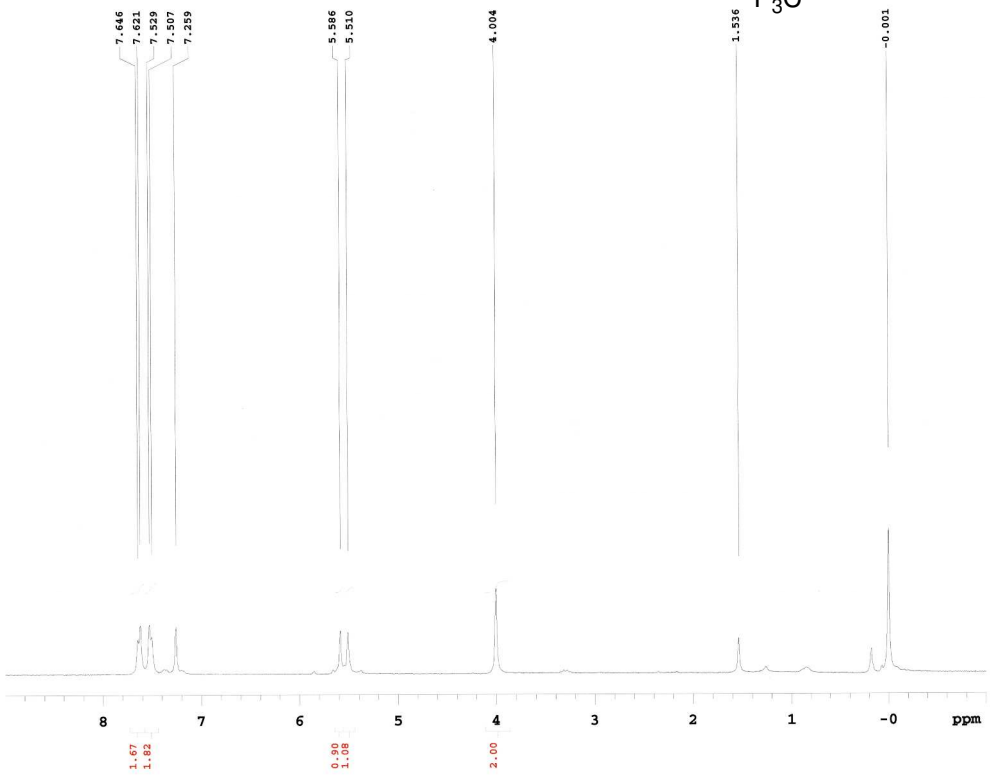


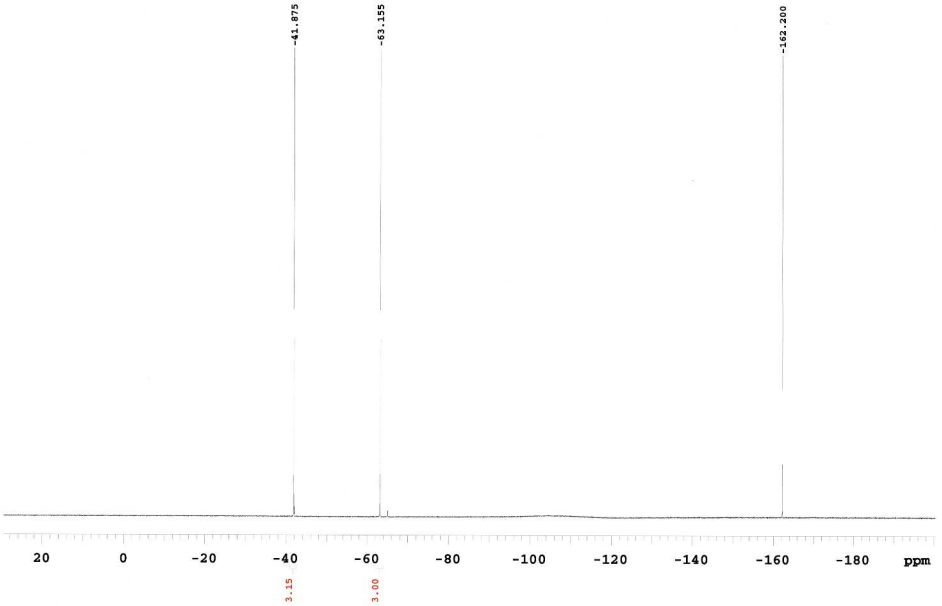




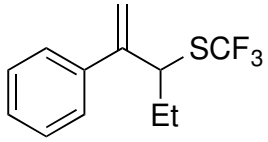
^{1}H NMR spectrum and ^{19}F NMR spectrum of (5i)

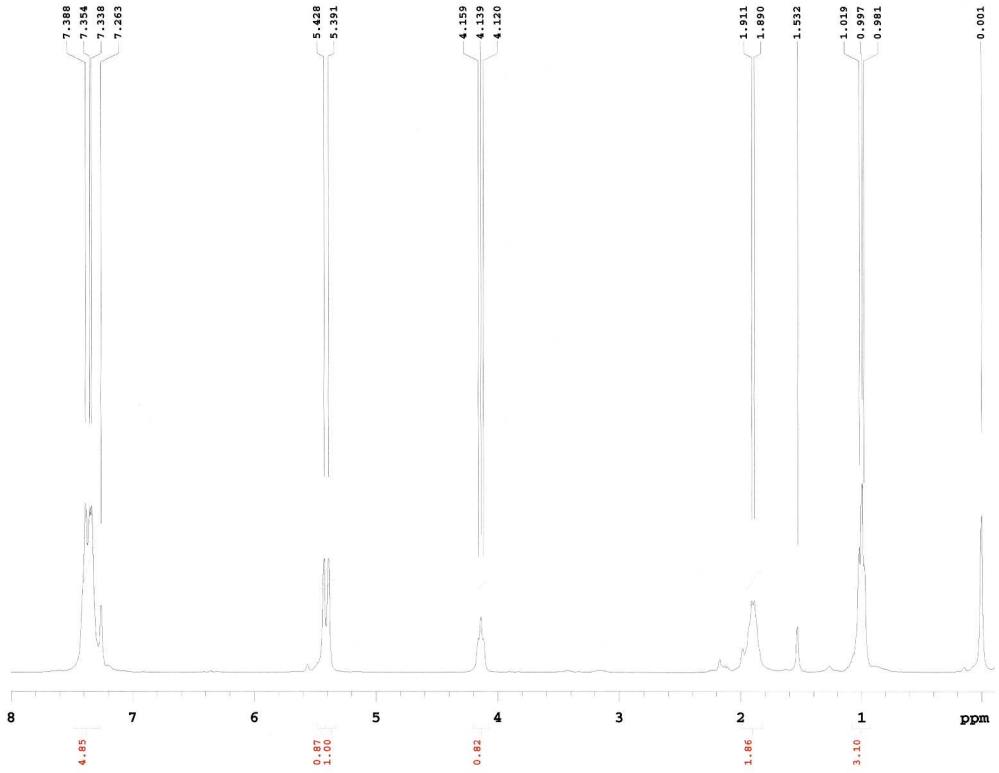


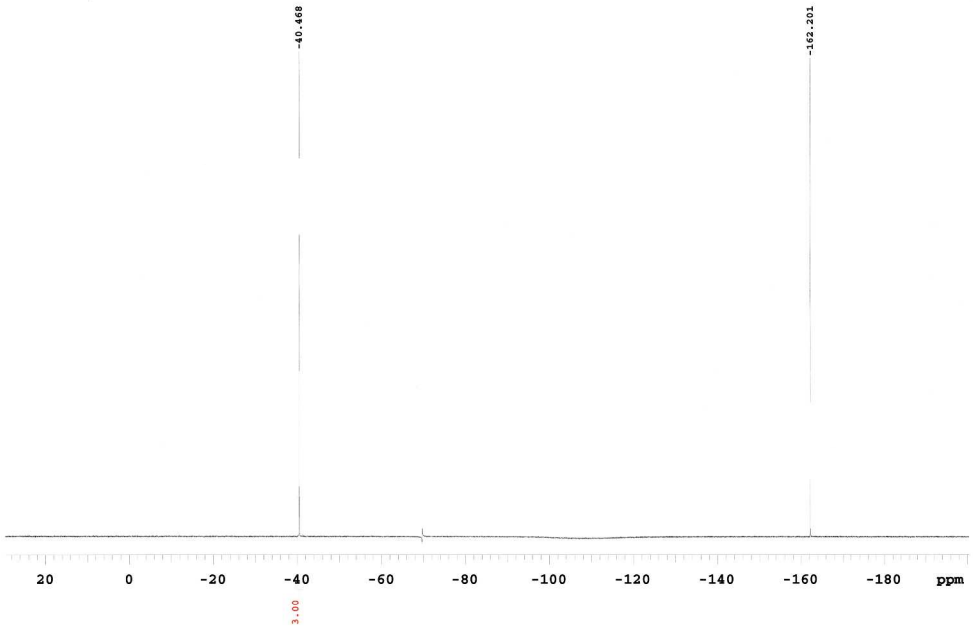




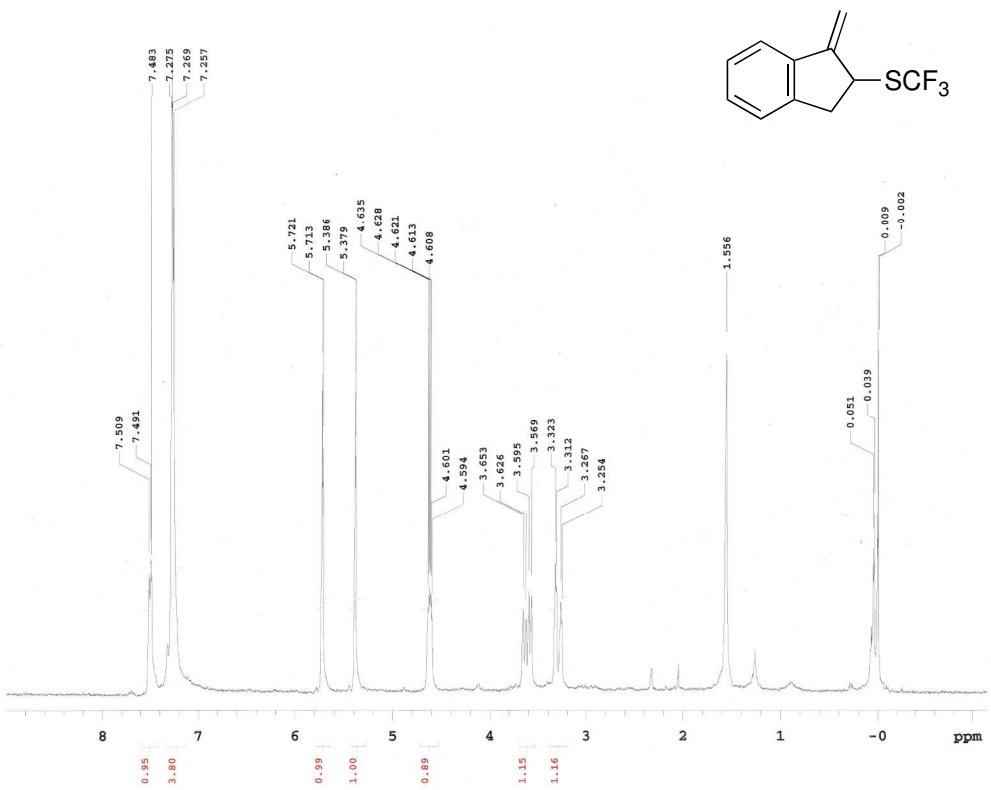
^{1}H NMR spectrum and ^{19}F NMR spectrum of (5j)

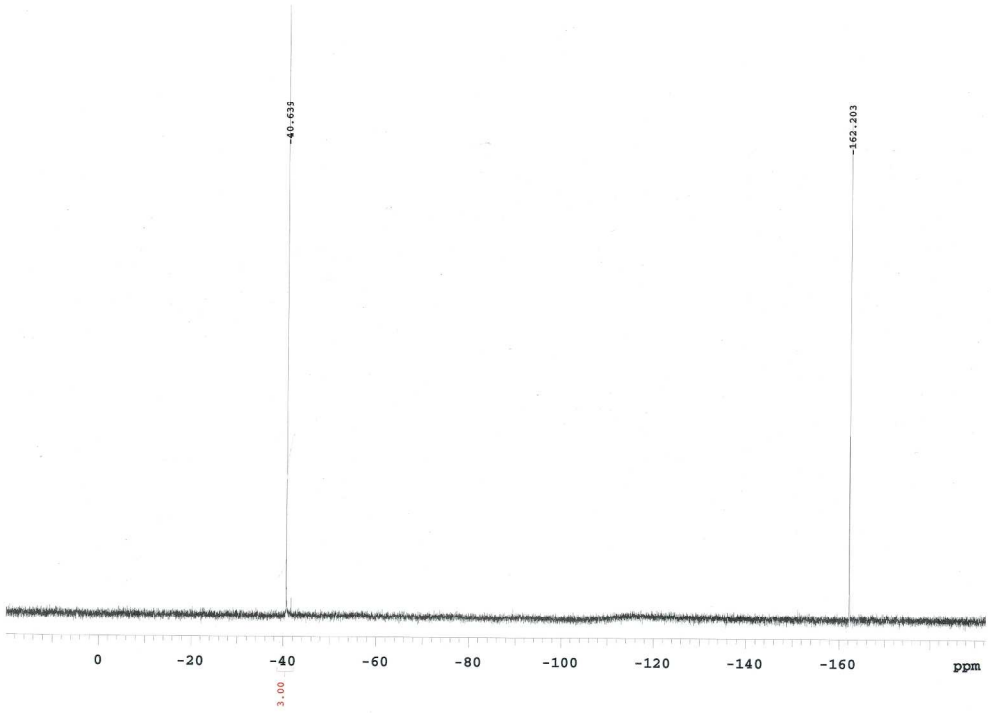


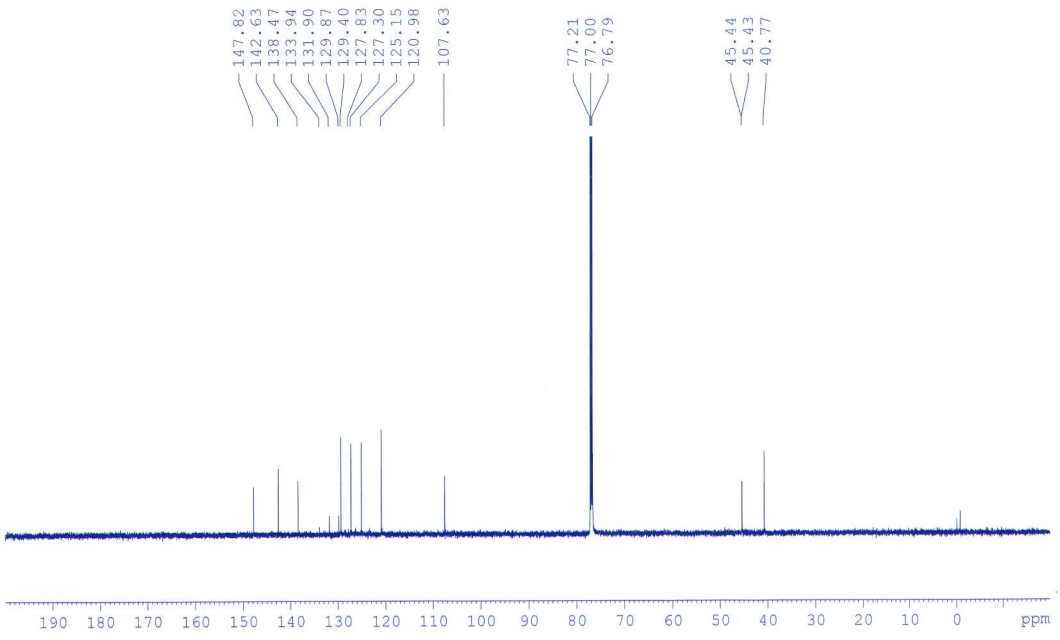




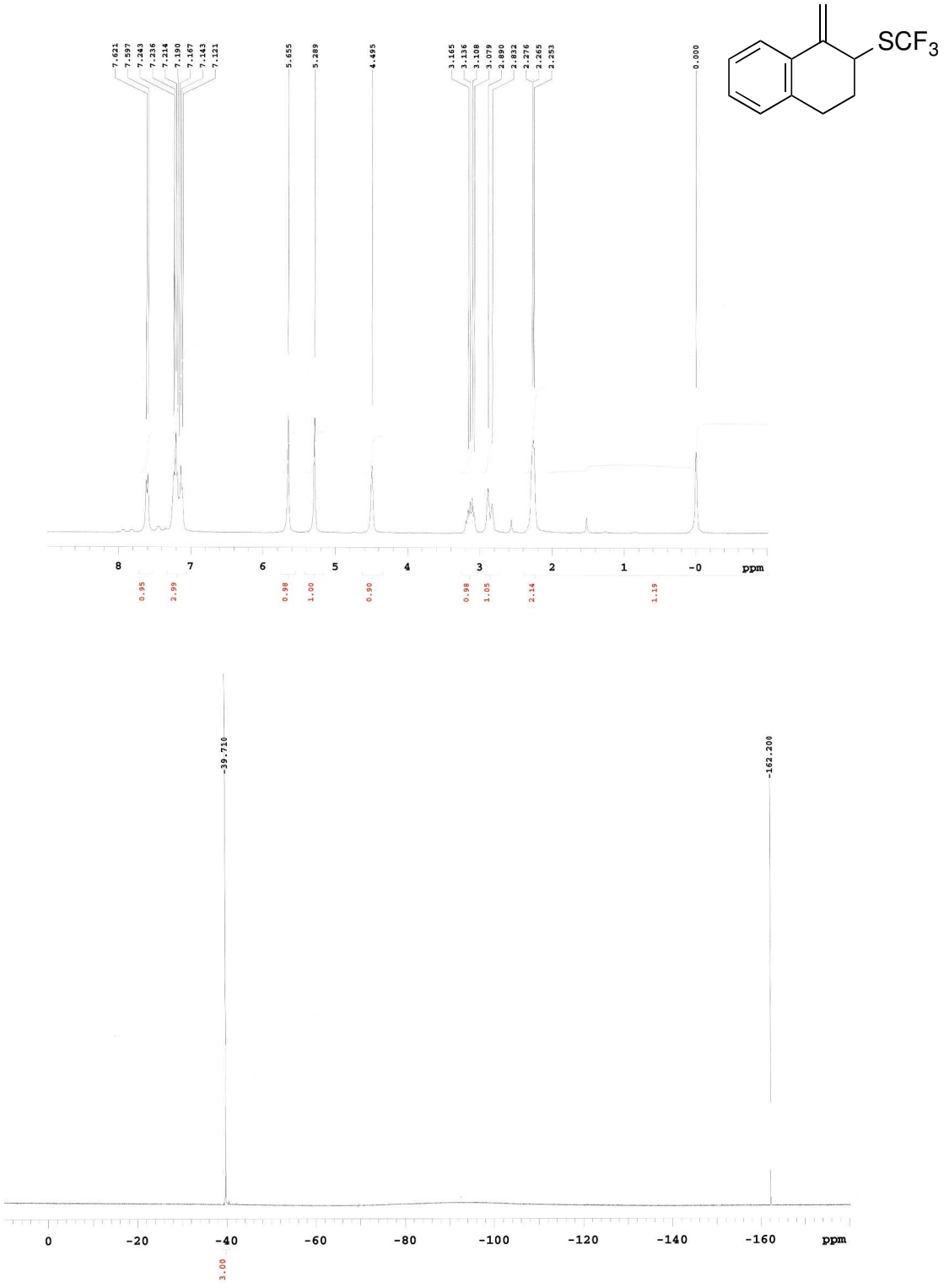
^{1}H NMR spectrum, ^{19}F NMR and ^{13}C NMR spectrum of (5k)



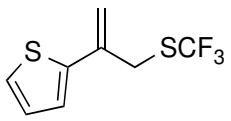

-40.635
-162.203
0
-20
-40
-60
-80
-100
-120
-140
-160
ppm
3.00

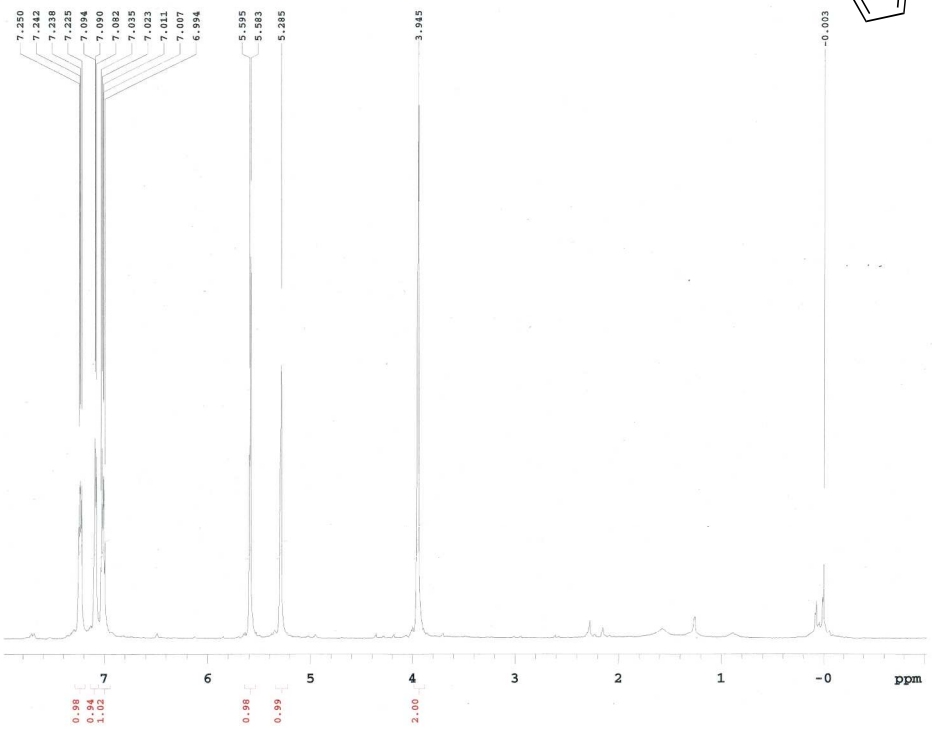

147.82
142.63
138.47
133.94
131.90
129.87
129.40
127.83
127.30
125.15
120.98
107.63
77.21
77.00
76.79
45.44
45.43
40.77
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

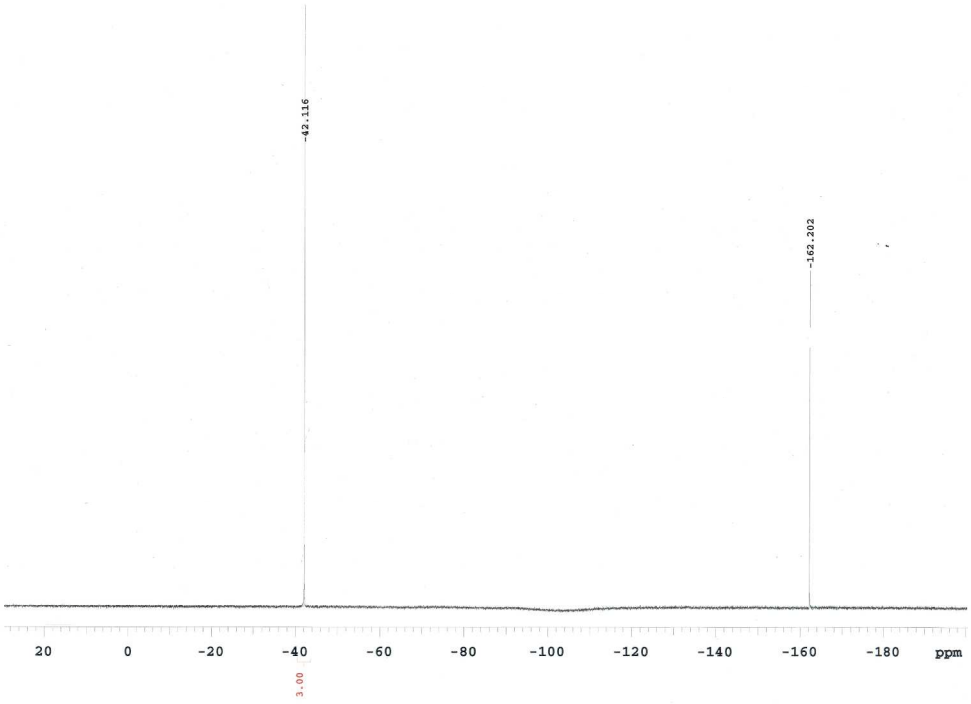
^{1}H NMR spectrum and ^{19}F NMR spectrum of (5l)

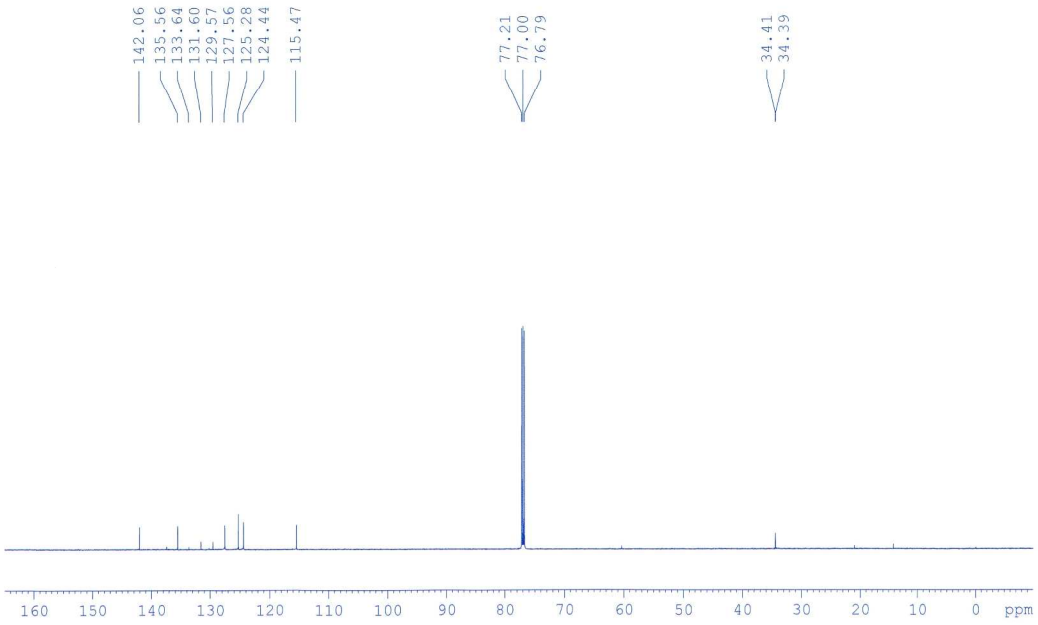


^{1}H NMR spectrum, ^{19}F NMR and ^{13}C NMR spectrum of (5m)

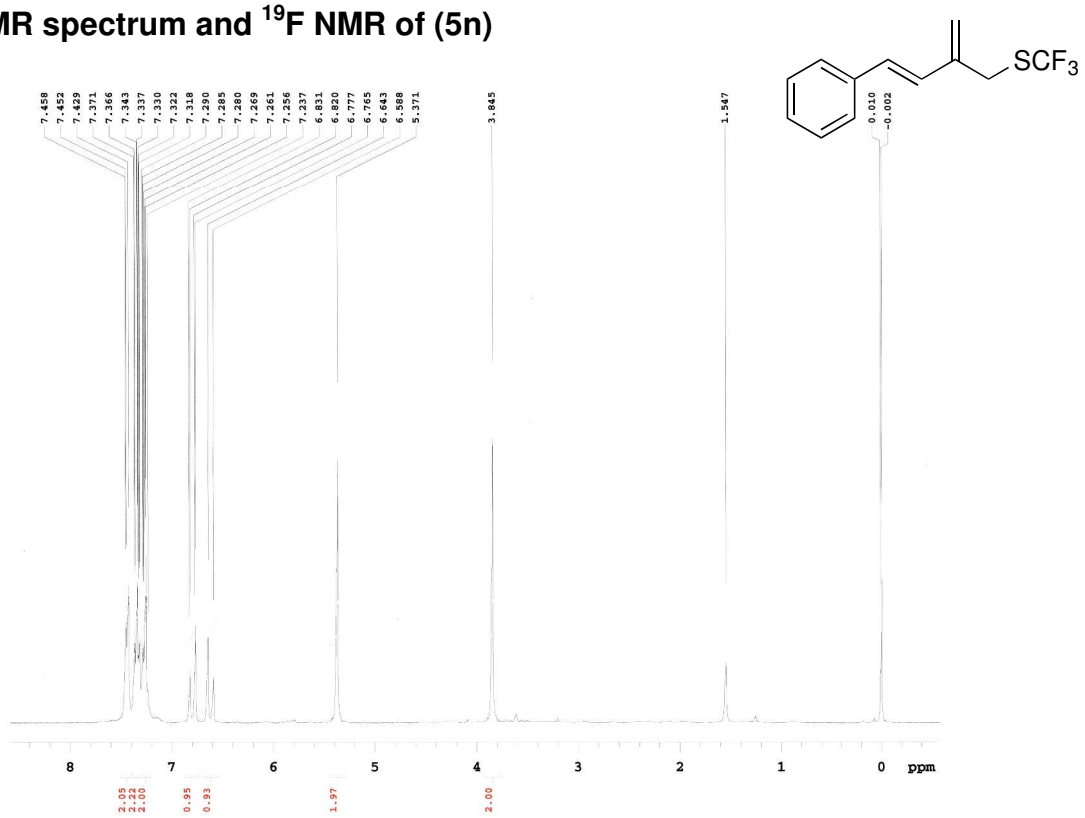


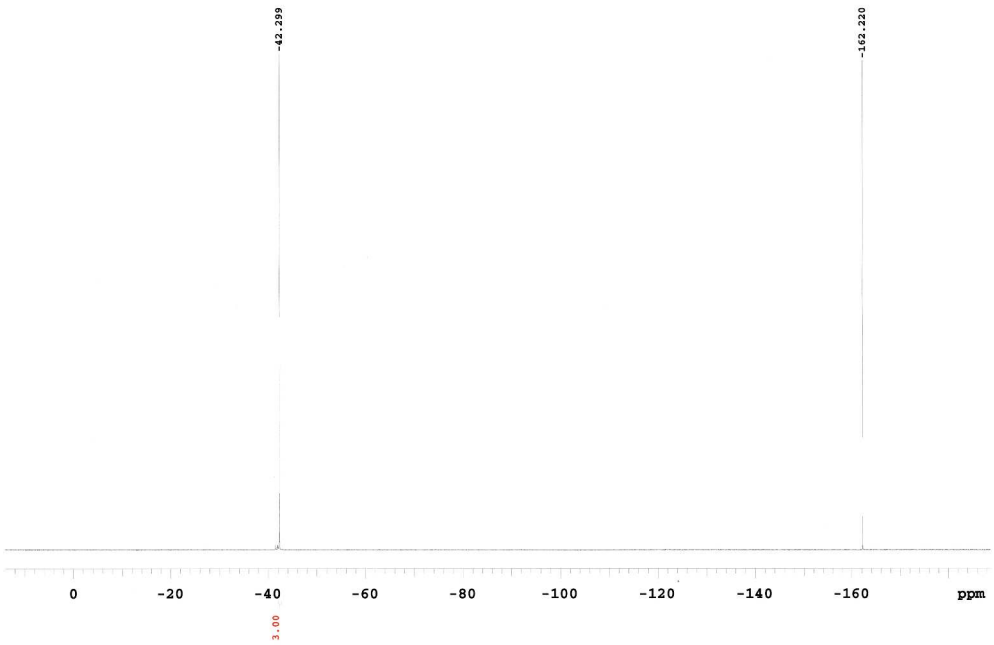




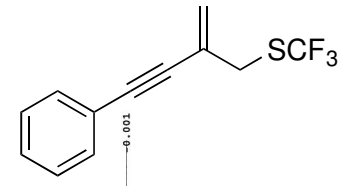


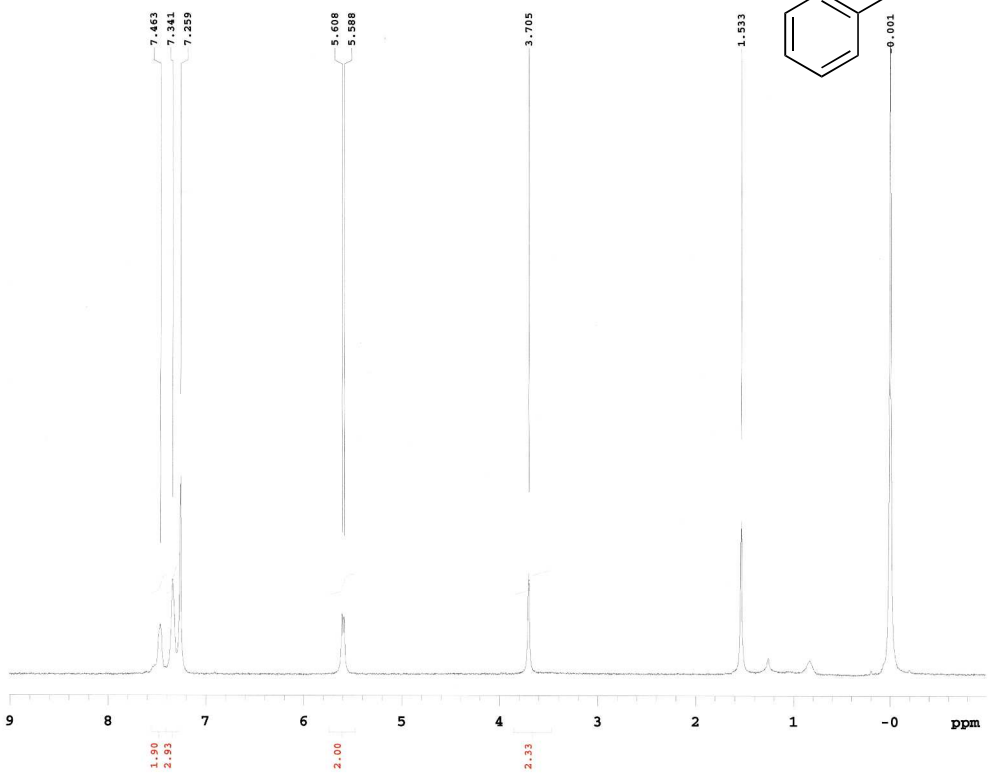
^{1}H NMR spectrum and ^{19}F NMR of (5n)

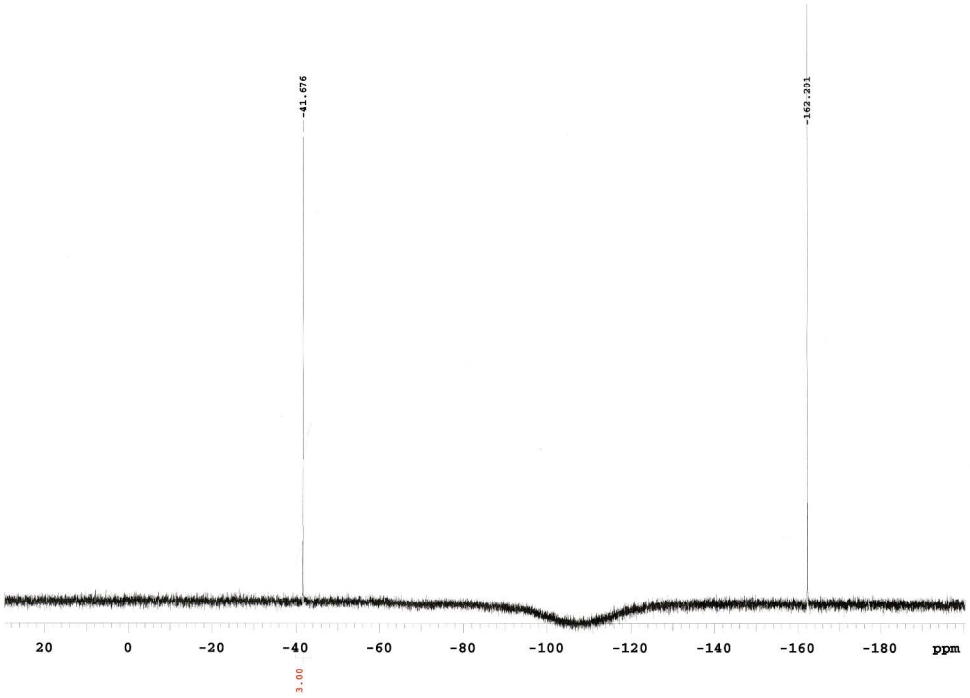




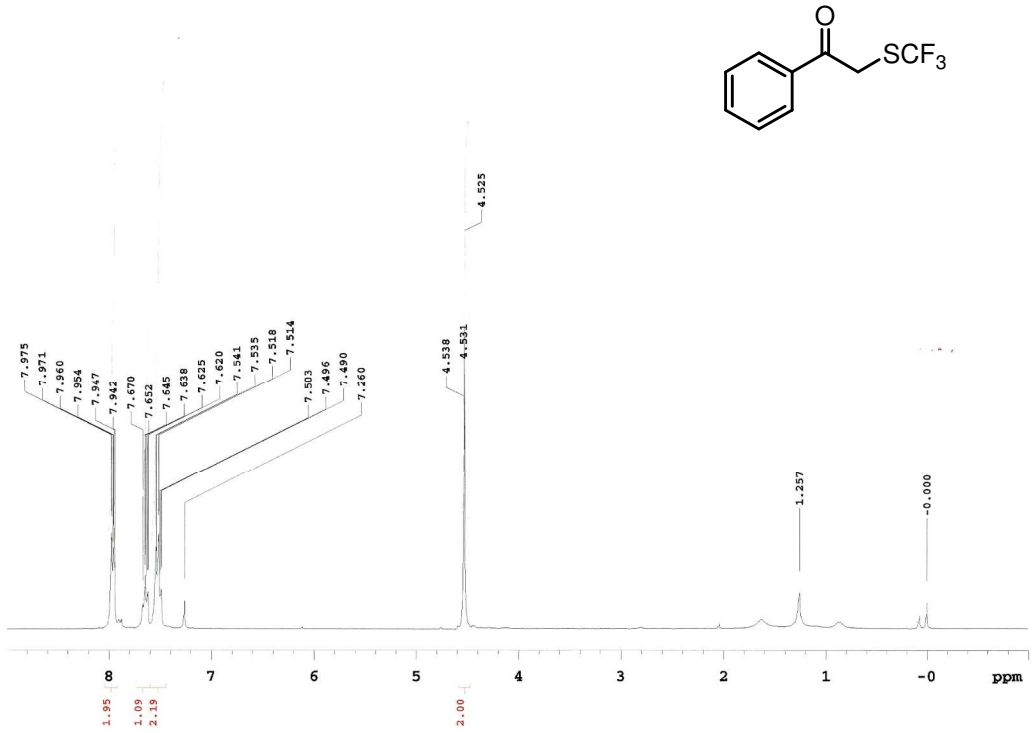
^{1}H NMR spectrum and ^{19}F NMR spectrum of (5o)

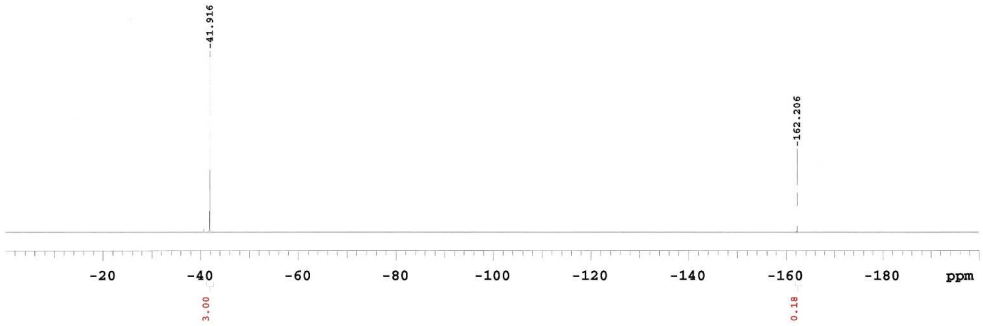




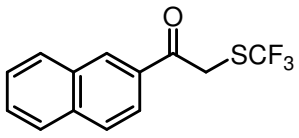


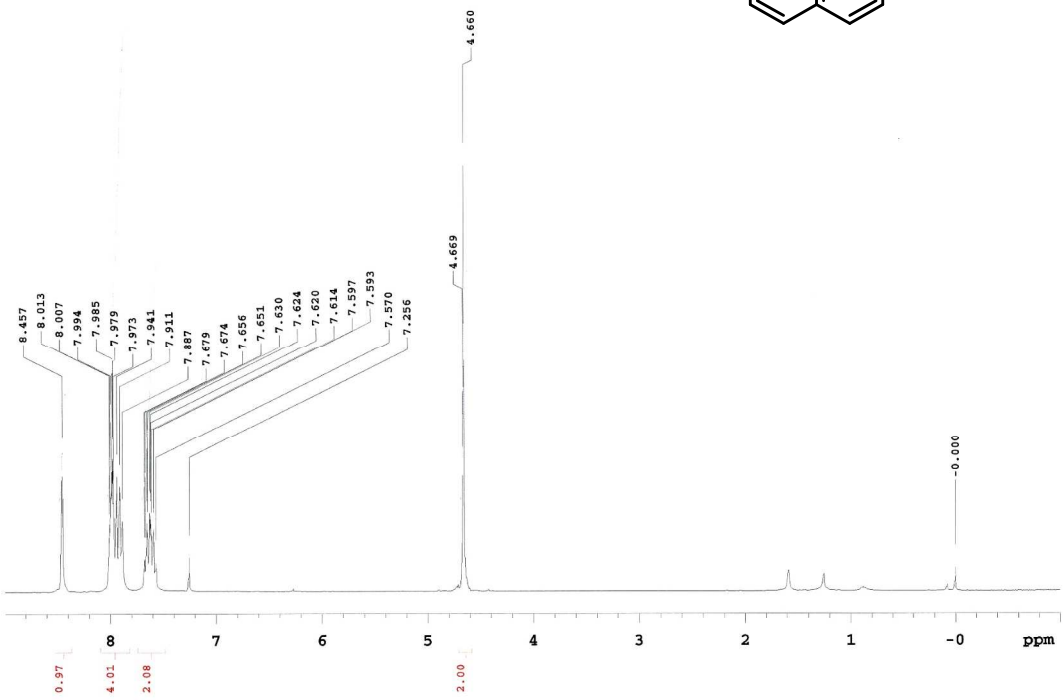
^{1}H NMR spectrum and ^{19}F NMR spectrum of (6a)

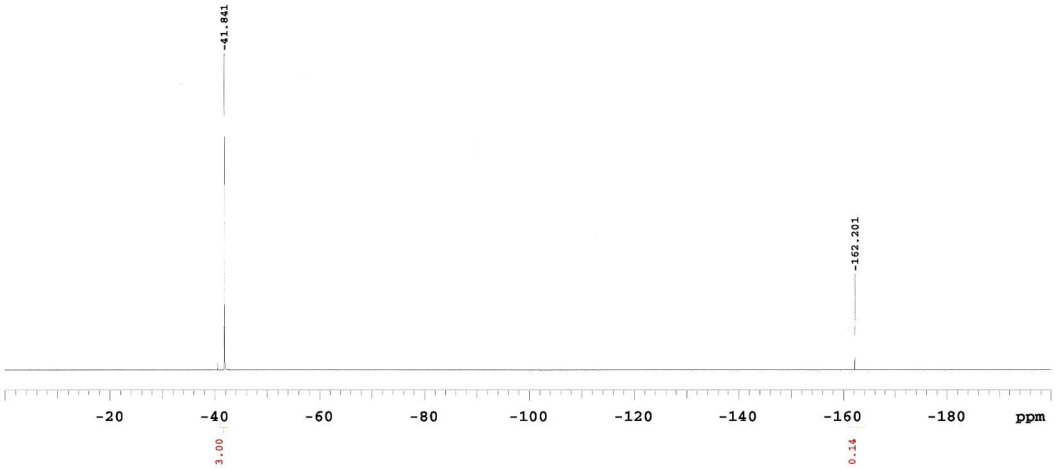




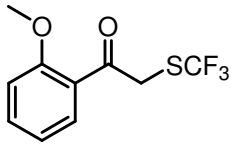
^{1}H NMR spectrum and ^{19}F NMR spectrum of (6b)

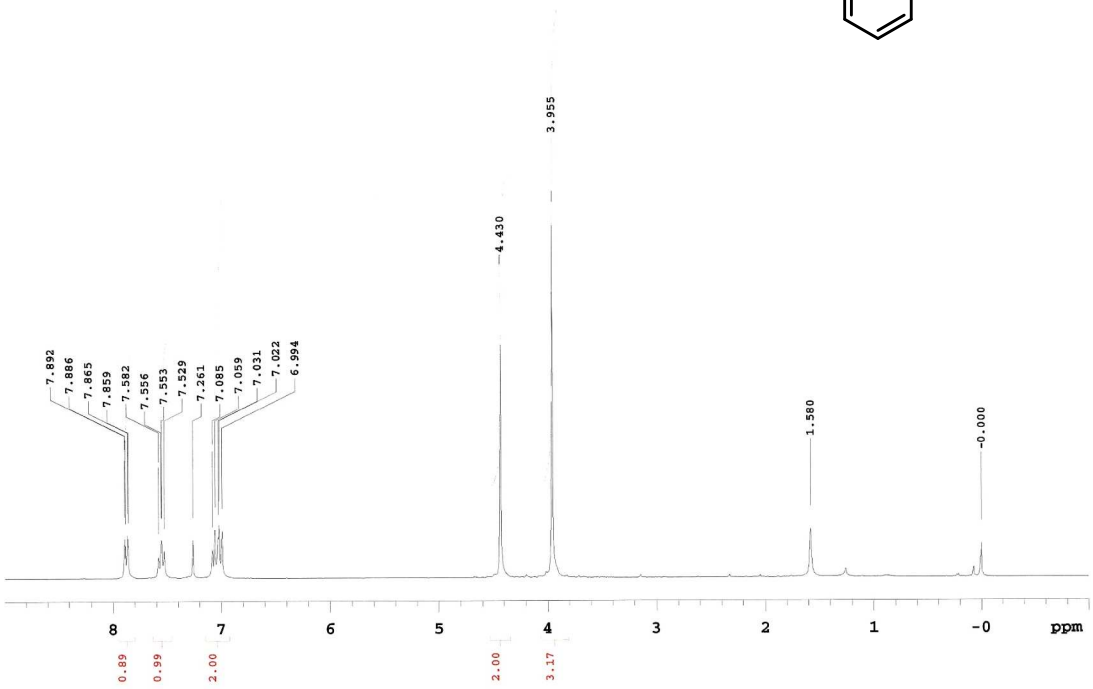


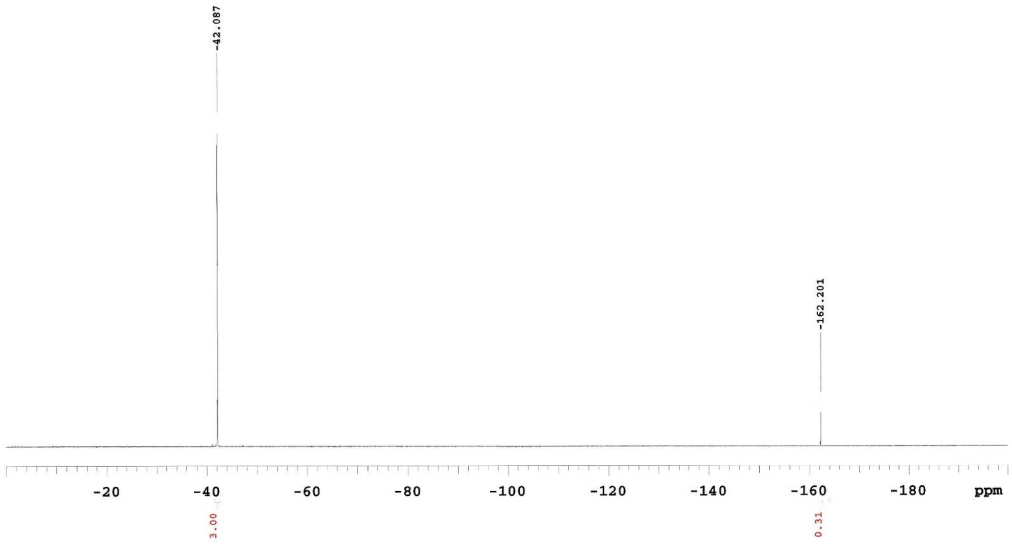




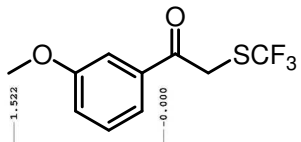
^{1}H NMR spectrum and ^{19}F NMR spectrum of (6c)

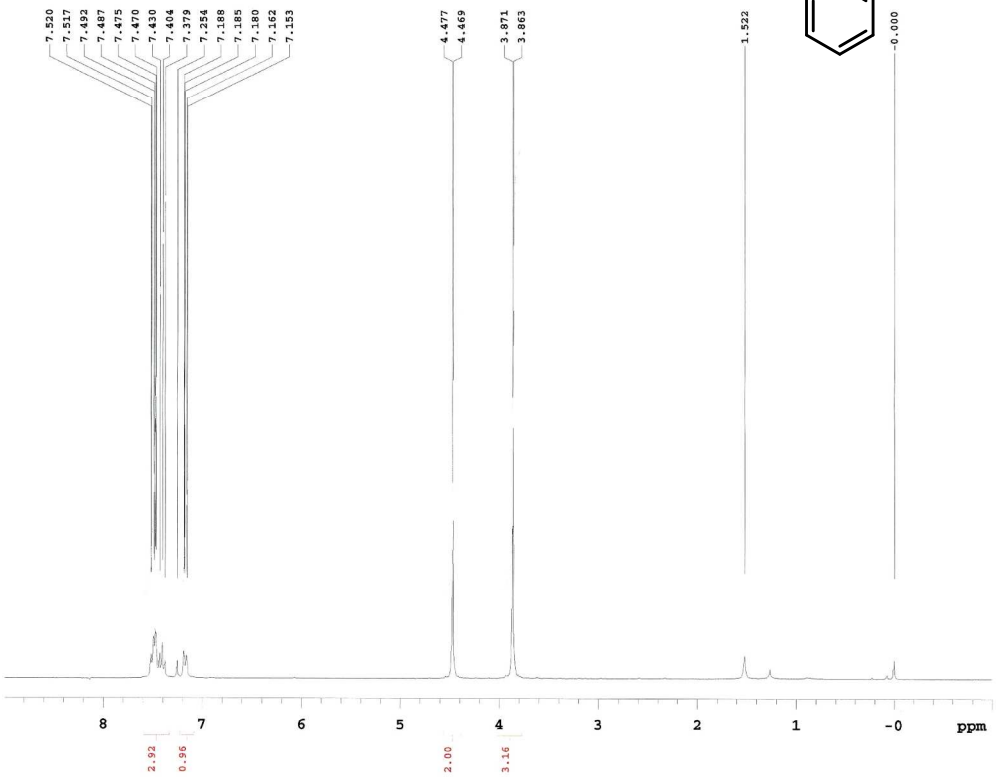


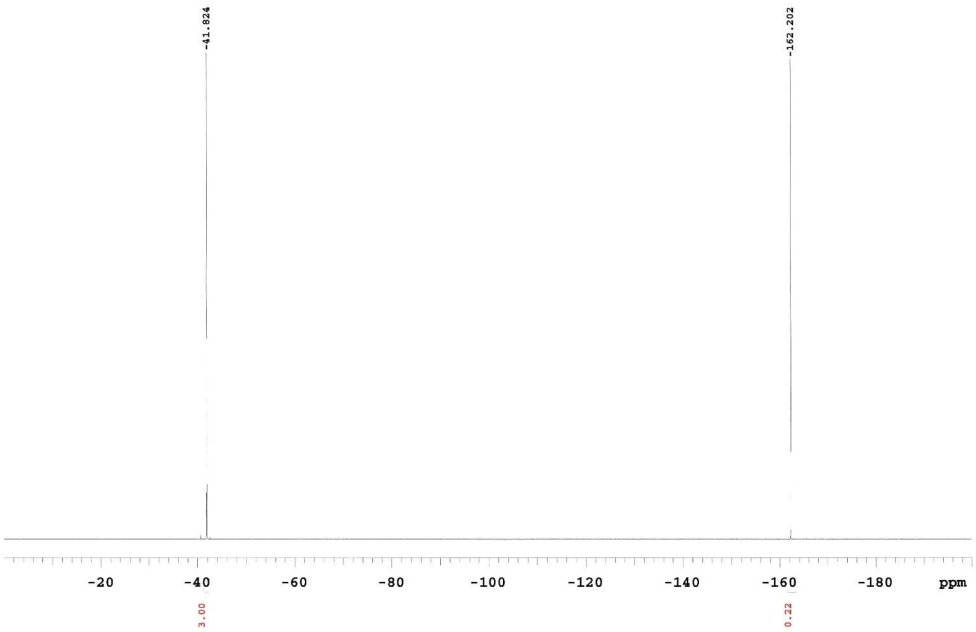




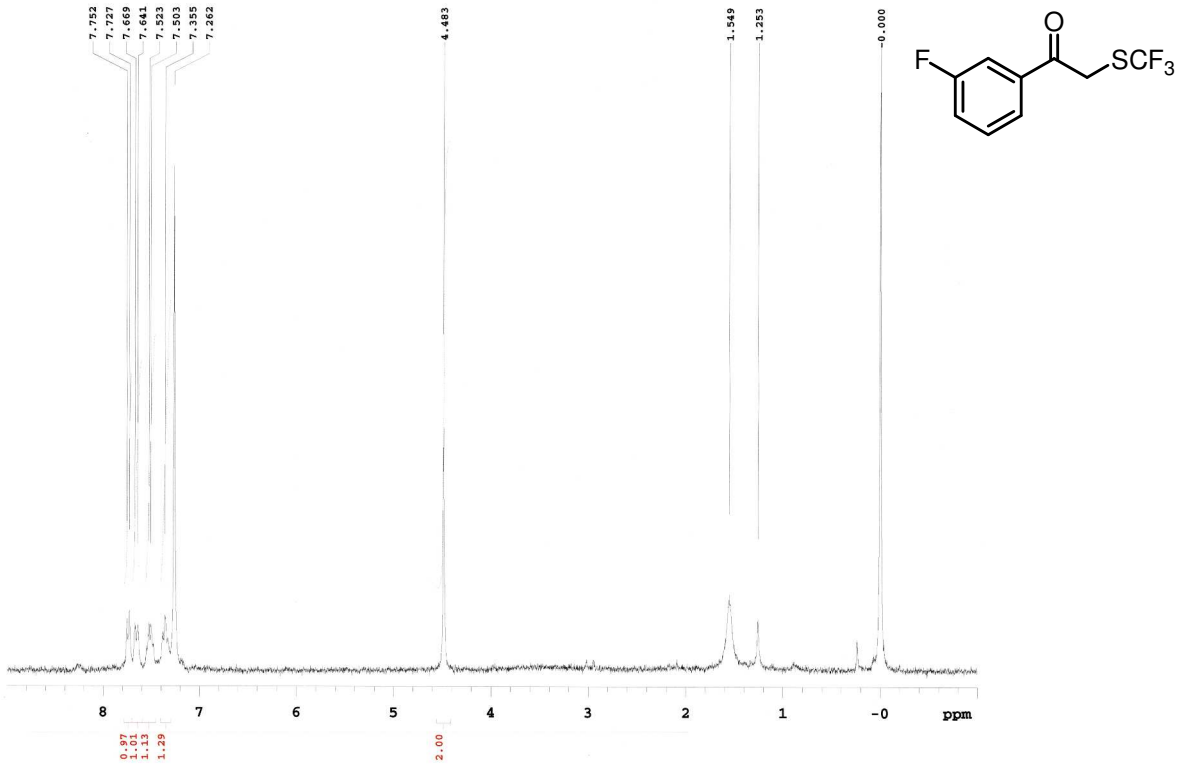
^{1}H NMR spectrum and ^{19}F NMR spectrum of (6d)

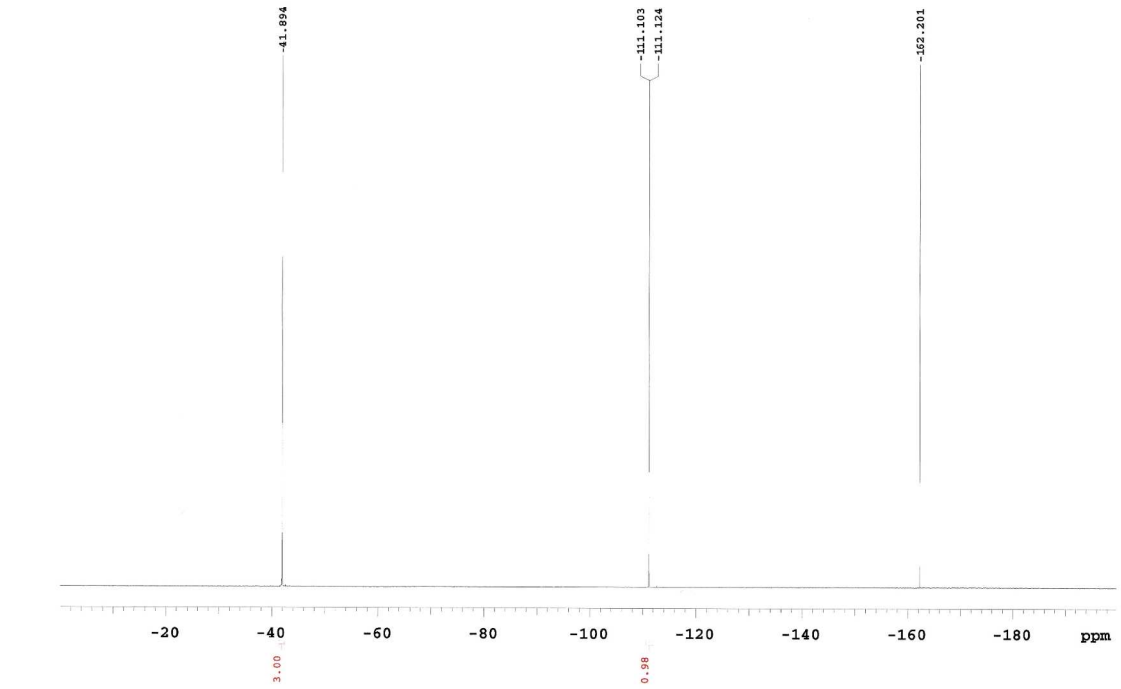






^{1}H NMR spectrum , ^{19}F NMR spectrum and ^{13}C NMR spectrum of (6e)

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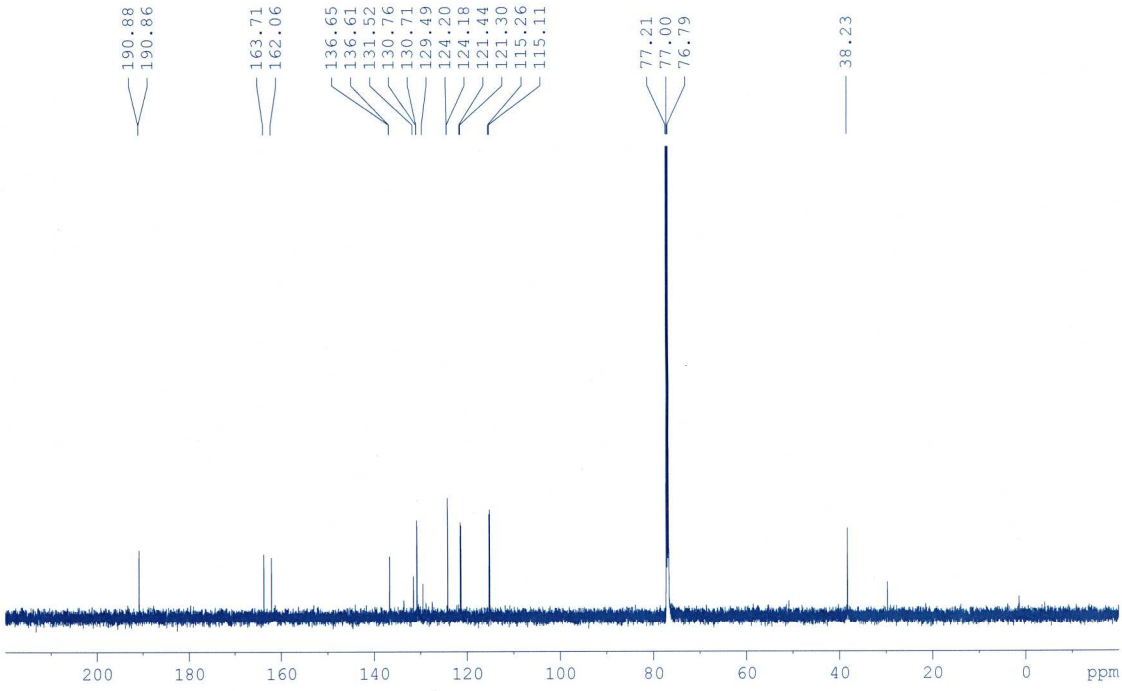
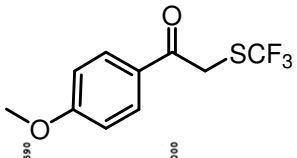
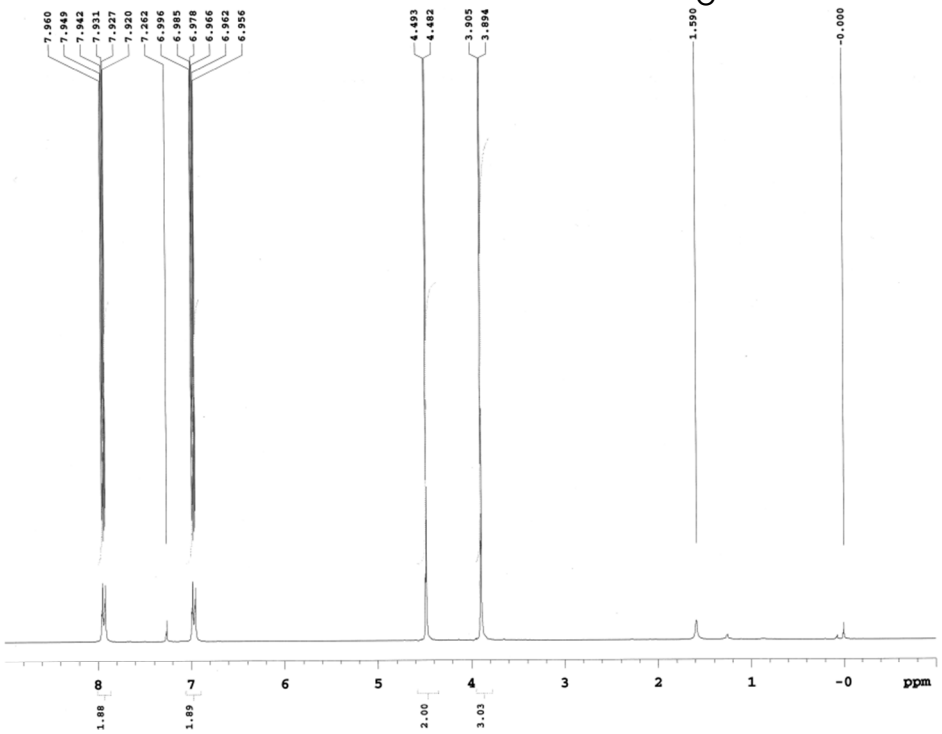
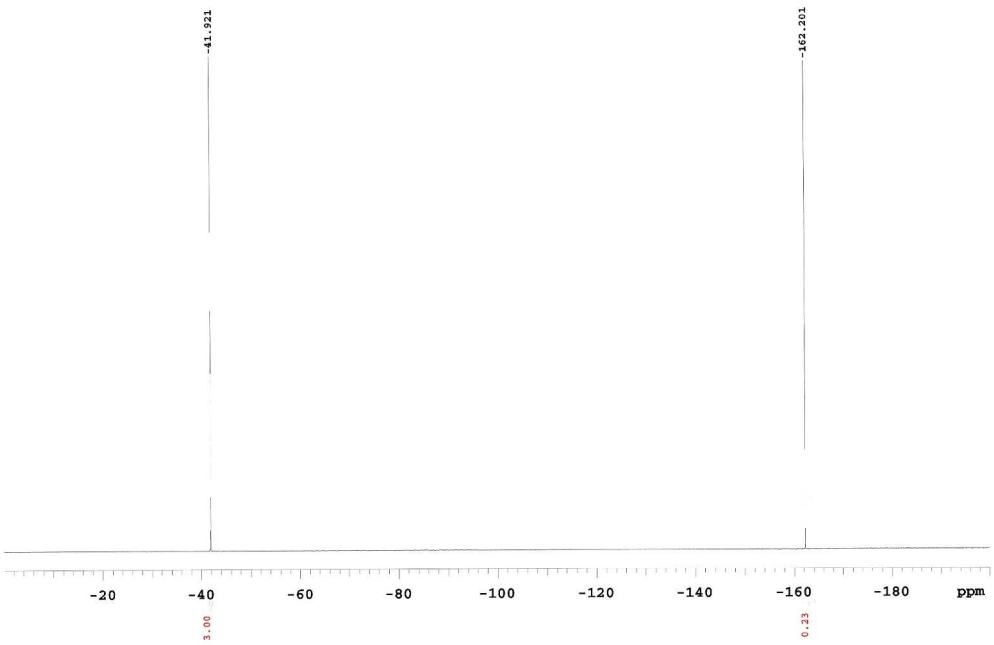
-111.124
-162.201
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
3.00
0.98


190.88
190.86
163.71
162.06
136.65
136.61
131.52
130.76
130.71
129.49
124.20
124.18
121.44
121.30
115.26
115.11
77.21
77.00
76.79
38.23
200
180
160
140
120
100
80
60
40
20
0
ppm

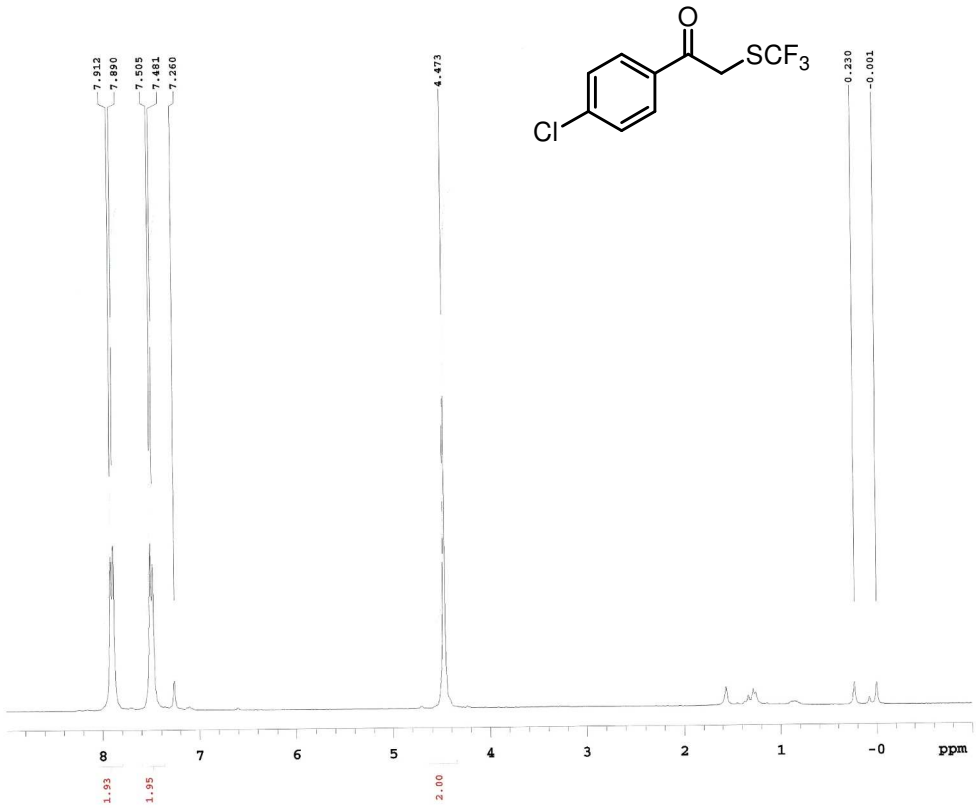
^{1}H NMR spectrum and ^{19}F NMR spectrum of (6f)

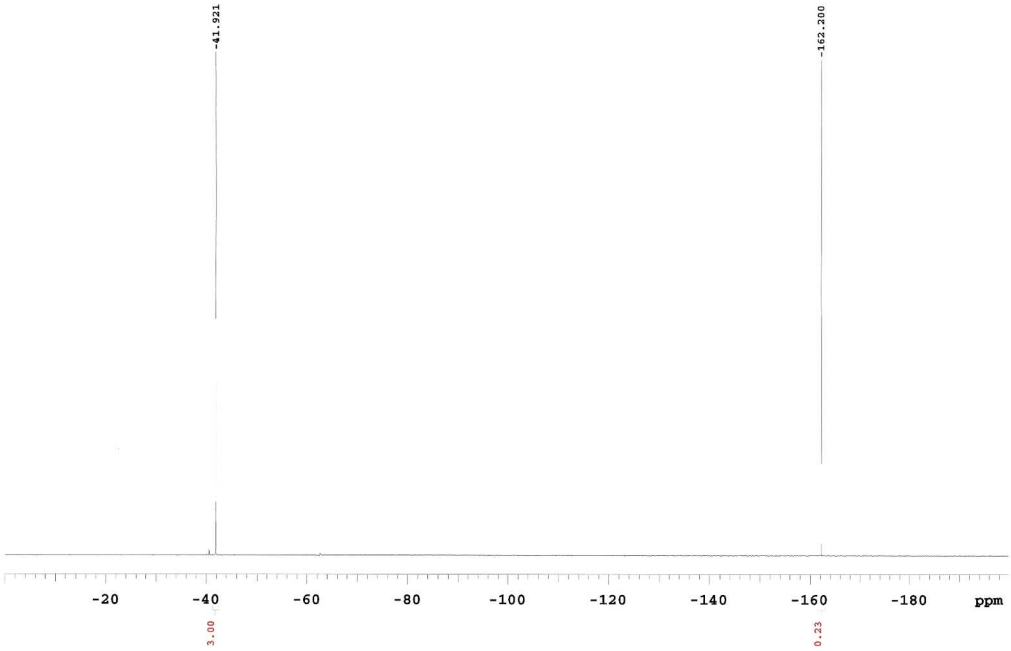




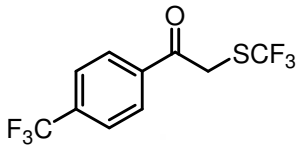


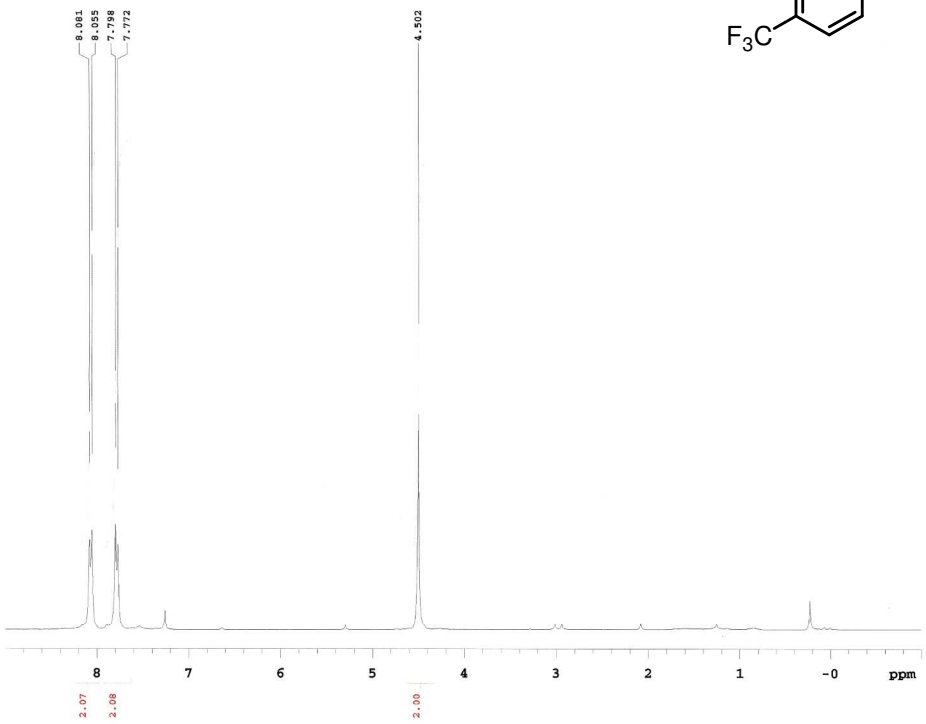
^{1}H NMR spectrum and ^{19}F NMR spectrum of (6g)

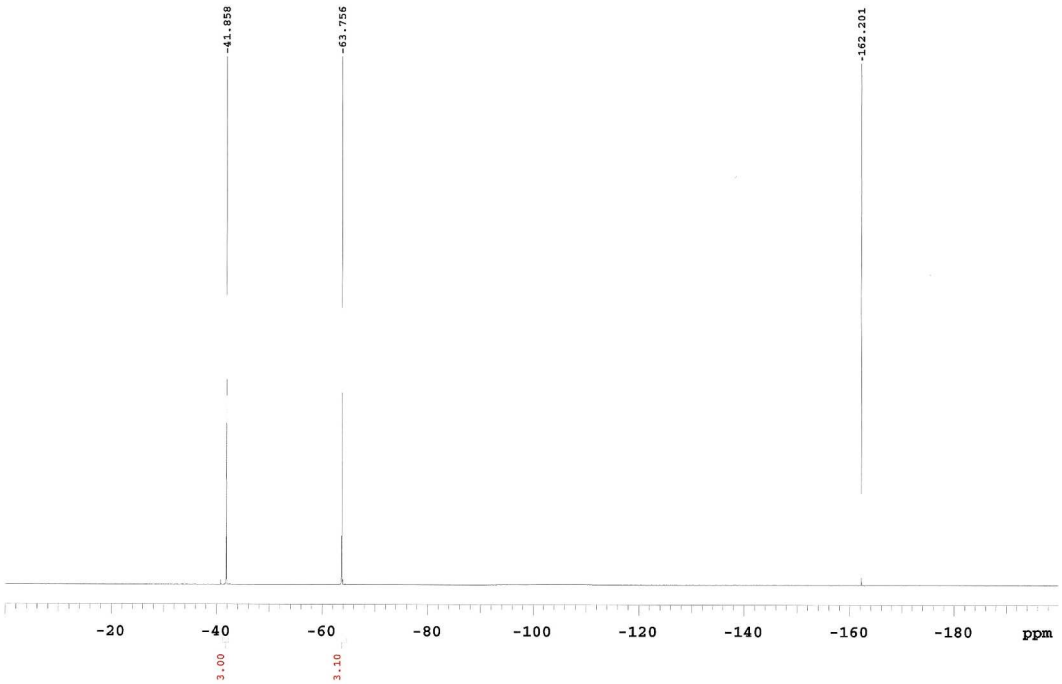




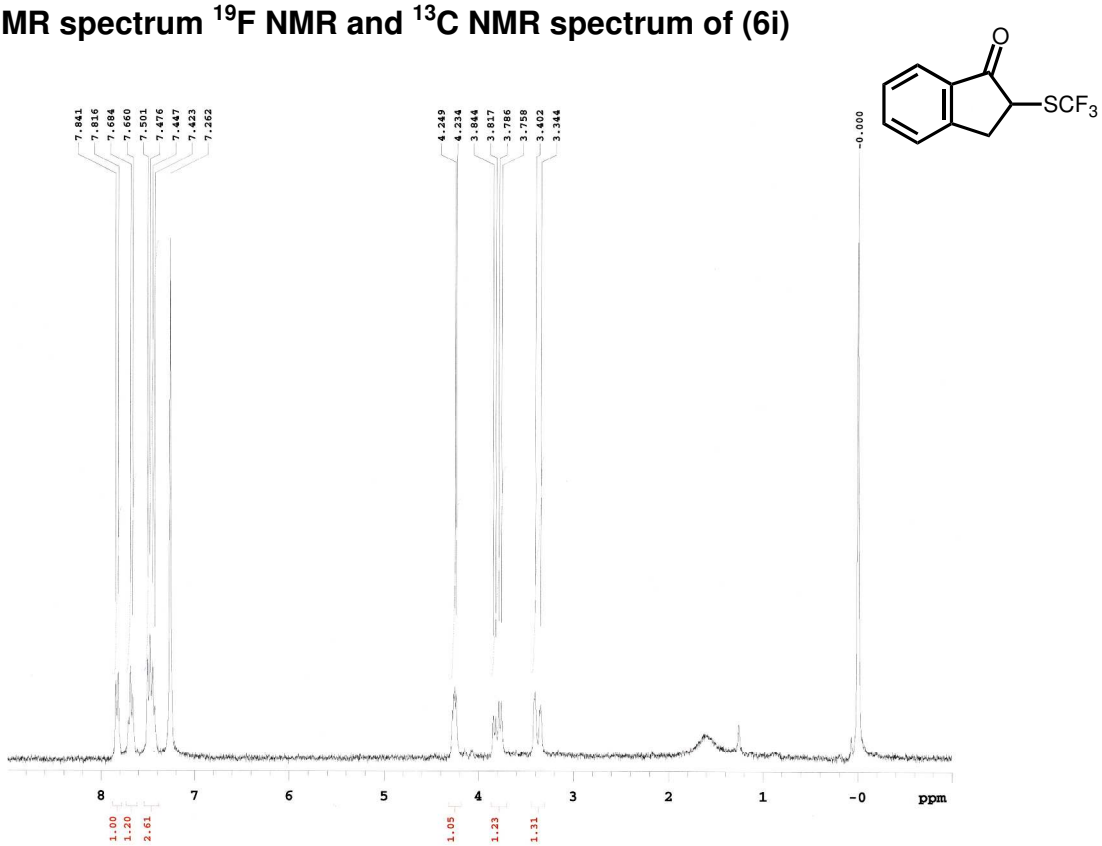
^{1}H NMR spectrum and ^{19}F NMR spectrum of (6h)

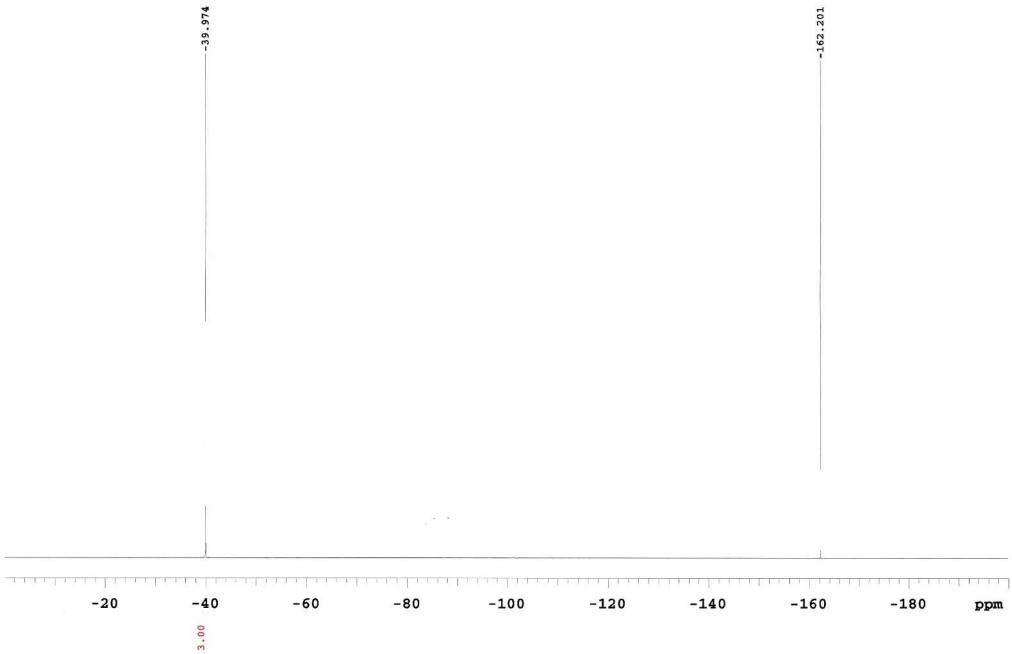


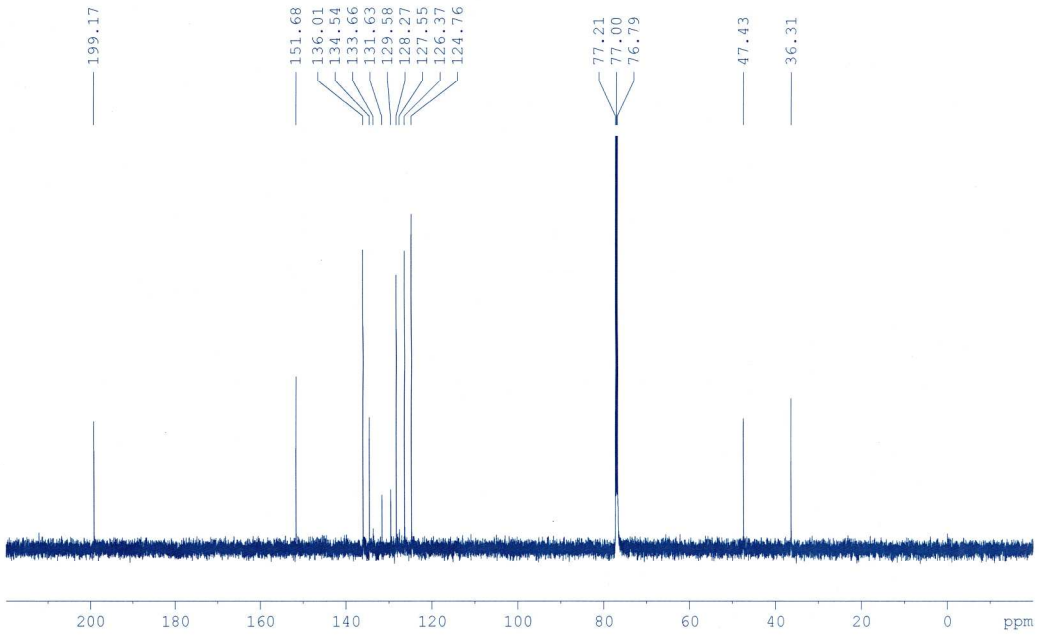




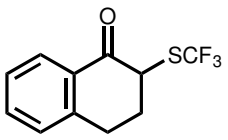
^{1}H NMR spectrum ^{19}F NMR and ^{13}C NMR spectrum of (6i)

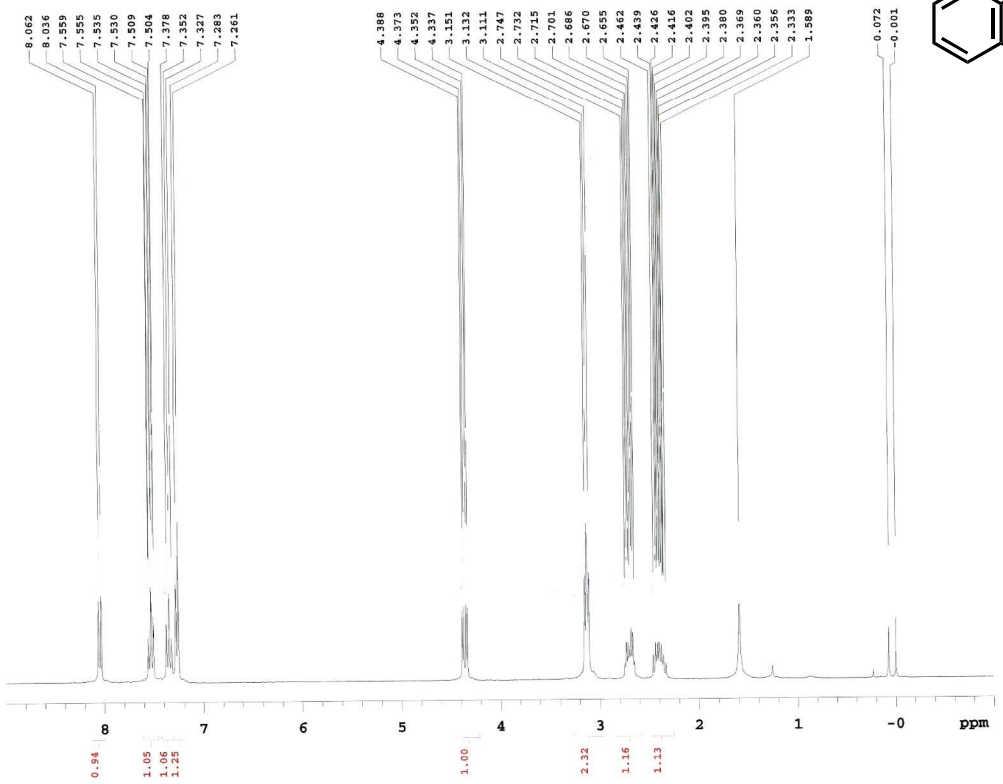


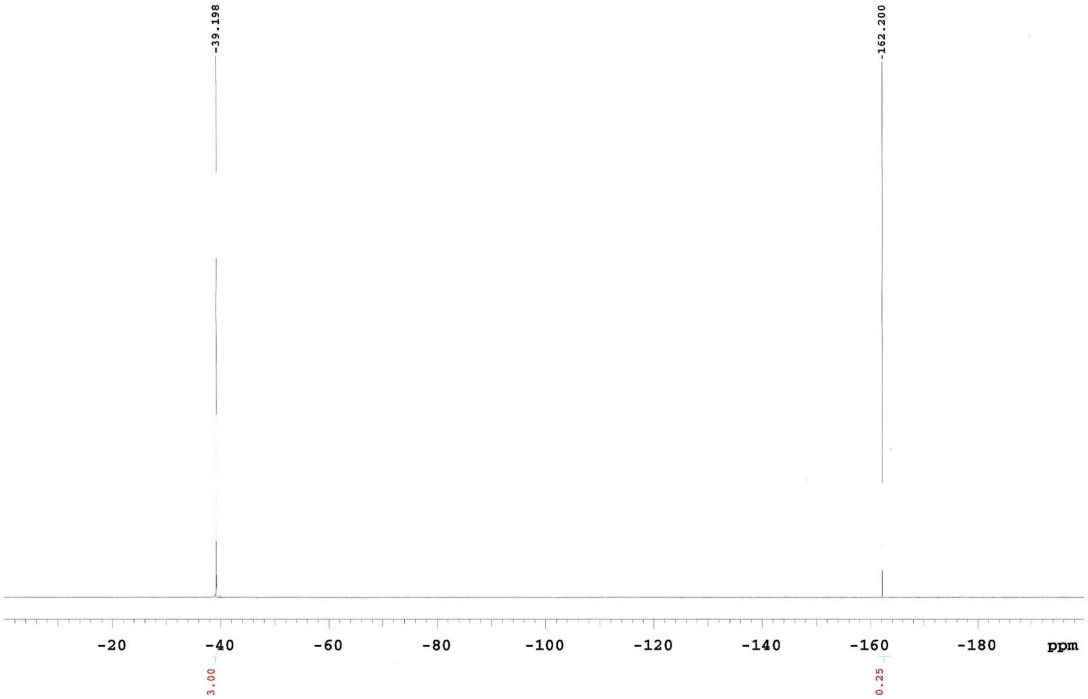




^{1}H NMR spectrum and ^{19}F NMR spectrum of (6j)



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-20
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-60
-80
-100
-120
-140
-160
-180
ppm
3.00
0.25