SIMULTANEOUS PROTECTION AND ACTIVATION OF AMINO ACIDS USING PROPARGYL PENTAFLUOROPHENYL CARBONATE

Ramapanicker Ramesh, Sakthidevi Rajasekaran, Rohit Gupta and Srinivasan Chandrasekaran*

Department of Organic Chemistry, Indian Institute of Science

Bangalore-560012, India

SUPPORTING INFORMATION

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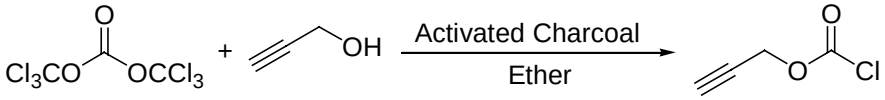
Experimental Procedures

All reactions were performed in oven dry apparatus and were stirred magnetically. Melting points and optical rotation values (recorded at 25 °C) reported are uncorrected. Infrared spectra were recorded using an FT-IR instrument and the frequencies are reported in wave number (cm^{-1}) and intensities of the peaks are denoted as s (strong), w (weak), m (medium). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a 300 MHz, 75 MHz and 282 MHz spectrometer respectively. Chemical shifts are reported in parts per million downfield from the internal reference, tetramethylsilane for ^{1}H and ^{13}C NMR and with trifluoroacetic acid as external reference for ^{19}F NMR. Multiplicity is indicated using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), sb (broad singlet) and db (broad doublet). Coupling constants are reported wherever it is necessary in Hertz (Hz). Mass spectra were recorded on a Q-TOF electrospray instrument. *Note:* The carbon atoms in the pentafluorophenyl ring are not observed in the ^{13}C NMR spectra as clear single lines due to extensive coupling with ^{19}F. So the values corresponding to these peaks are not mentioned.

Preparation of Propargyloxycarbonyl Chloride (PocCl)[5]

To a stirred solution of triphosgene (2.23 g, 7.5 mmol) in dry ether (30 mL), activated charcoal (0.05g) was added and stirred for 1 h at room temperature (28 °C). The solution was cooled to 0 °C and propargyl alcohol (0.9 mL, 15 mmol) in dry ether (10 mL) was added drop wise. The resultant solution was stirred for 12 hours and filtered. The ether layer was concentrated under reduced pressure and the remaining liquid was used for reactions without any further purification.



FT IR (neat): 3303, 2982, 2131, 1771

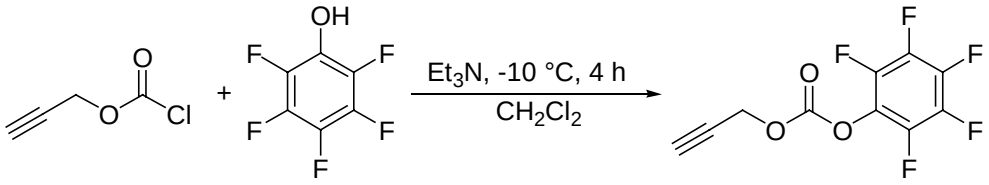
^{1}HNMR (300 MHz, $CDCl_3$): δ 2.6 (t, 1H, J=2.4), 4.7 (d, 2H, *J*=2.4)

^{13}CNMR (75 MHz, $CDCl_3$): δ 150.2, 77.6, 74.9, 58.3

Preparation of Propargyl Pentafluorophenyl Carbonate (PocOPfp, 1)[4]

PocCl (10 mmol) was added to a stirred solution of pentafluorophenol (1.84g, 10 mmol) in dichloromethane (30 mL) at -10 °C. The solution was stirred for 10 min and triethylamine (1.4 mL, 10 mmol) was added dropwise over a period of 15 min. After 4 h

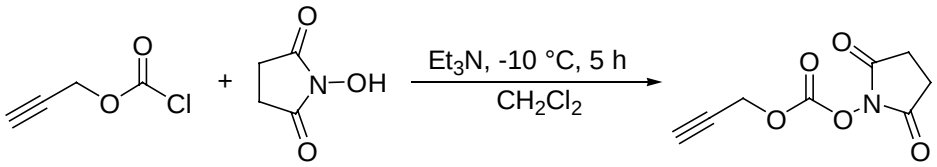
the reaction mixture was diluted with dichloromethane (50 mL) and washed with 0.5N HCl (20 mL), water (2x20 mL) and brine solution (20 mL). The solution containing PocOPfp was dried over anhydrous Na_2SO_4 and was purified by silica gel (100-200 mesh) column chromatography, eluting with 3% solution of ethyl acetate in hexane.



Yield:	98%
Physical state:	White crystalline solid
Melting Point:	65 ºC
FTIR (KBr):	3302 (m), 2134 (w), 1790 (s), 1526 (s)
^{1}H NMR (300 MHz, $CDCl_3$):	δ 4.90 (d, 2H, *J*=2.7), 2.65 (t, 1H, *J*=2.3)
^{13}C NMR (75 MHz, $CDCl_3$):	δ 150.8, 142.9, 139.5, 138.3, 138.3, 136.0, 77.2, 75.3, 57.5

Preparation of Propargyloxycarbonyloxy Succinimide (PocOSu, 7)

PocCl (10 mmol) was added to a stirred solution of *N*-hydroxysuccinimide (1.15 g, 10 mmol) in dichloromethane (30 mL) at -10 °C. The solution was stirred for 10 min and triethylamine (1.4 mL, 10 mmol) was added dropwise over a period of 15 min. After 5 h the reaction mixture was diluted with dichloromethane (50 mL) and washed with 0.5N HCl (20 mL), water (2x20 mL) and brine solution (20 mL). The solution containing PocOSu was dried over anhydrous Na_2SO_4 and was purified by silica gel (100-200 mesh) column chromatography, eluting with 20% solution of ethyl acetate in hexane.



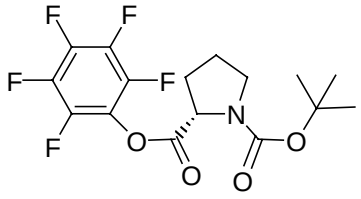
Yield:	92%
Physical state:	White crystalline solid
Melting Point:	107 °C
FTIR (KBr):	3262 (s), 2129 (w), 1814 (s), 1731 (s)

^{1}H NMR (300 MHz, $CDCl_3$):	δ 4.90 (d, *J*=2.1, 2H), 2.85 (s, 4H), 2.66 (t, *J*=2.1, 1H)
^{13}C NMR (75 MHz, $CDCl_3$):	δ 168.3, 151.2, 77.6, 75.0, 58.1, 25.4
High Resolution ESMS (m/z):	Calculated for $C_8H_7NO_5$+Na: 220.0222
	Observed: 220.0218

General Procedure for the Activation of N-Protected Amino Acids as Pentafluorophenyl Esters Using PocOPfp

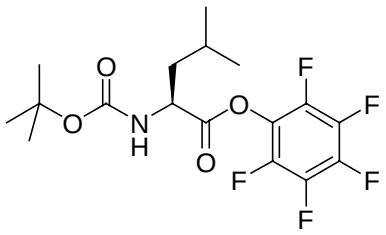
A solution of the *N*-protected amino acid (1 mmol) and PocOPfp (0.292 g, 1.1 mmol) in DMF (2 mL) was cooled to -10 °C. Pyridine (0.88 mL, 1.1 mmol) was added to this solution drop wise while stirring it magnetically. The reaction mixture was stirred for 3 h and was diluted with dichloromethane (30 mL). It is then washed with 0.5N HCl (10 mL), water (2x10 mL) and brine solution (10 mL) and dried over anhydrous Na_2SO_4. The active esters were then purified by silica gel (100-200 mesh) column chromatography eluting with ethyl acetate-hexane mixtures of appropriate concentration (5-20%).

Boc-Pro-OPfp (4a)



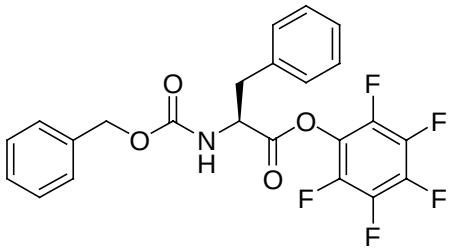
Yield:	88% (Mixture of two rotamers)
Physical State:	Oily Liquid
Optical Rotation:	$[\alpha]_D$ -64.00 (c=1.0, ethanol)
FTIR (Neat):	1797 (s), 1705 (s)
^{1}H NMR (300 MHz, $CDCl_3$):	δ 4.66-4.57 (m, 1H), 3.67-3.41 (m, 2H), 2.51-2.35 (m, 1H), 2.35-2.18 (m, 1H)-2.11-1.91 (m, 2H), 1.47 (d, 9H)
^{13}C NMR (75 MHz, $CDCl_3$):	δ 169.2, 169.0, 80.8, 80.4, 77.4, 77.0, 76.5, 58.5, 58.5, 46.5, 46.3, 31.2, 30.0, 28.2, 28.0, 24.4, 23.4
^{19}F NMR (282 MHz, $CDCl_3$):	δ -40.73 (d, 2F), -45.94 (t, 2F), -50.39 (t, 1F)
High Resolution ESMS (m/z):	Calculated for $C_{16}H_{16}F_5NO_4$+Na: 404.0897
	Observed: 404.0902

Boc-Leu-OPfp (4b)



Yield:	89%
Physical State:	Oily Liquid
Optical Rotation:	$[\alpha]_D$ -13.00 (c=1.0, ethanol)
FTIR (Neat):	3289 (m), 1777 (s), 1710 (s)
^{1}H NMR (300 MHz, $CDCl_3$):	δ 4.90 (d, *J*=2.4, 1H), 4.66-4.59 (m, 1H), 1.87-1.62 (m, 3H), 1.46 (s, 9H), 1.01 (d, *J*=6.0, 6H)
^{13}C NMR (75 MHz, $CDCl_3$):	δ 169.6, 155.2, 80.5, 77.4, 77.0, 76.5, 52.1, 41.1, 28.2, 24.8, 22.7, 21.7
^{19}F NMR (282 MHz, $CDCl_3$):	δ -40.60(d, 2F), -46.02(t, 2F), -50.52 (t, 1F)
High Resolution ESMS (m/z):	Calculated for $C_{17}H_{20}F_5NO_4$+Na: 420.1210
	Observed: 420.1211

Cbz-Phe-OPfp (4c)



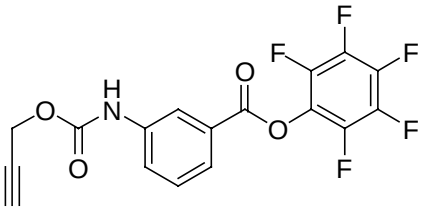
Yield:	85%
Physical State:	White crystalline solid
Melting Point:	96 ˚C
Optical Rotation:	$[\alpha]_D$ +54.00 (c=1.0, ethanol)
FTIR (KBr):	3322 (m), 1791 (s), 1714 (s)

^{1}H NMR (300 MHz, $CDCl_3$):	δ 7.37-7.19 (m, 10H), 5.47 (d, *J*=7.8, 1H), 5.10 (s, 2H), 4.5.06-4.97 (m, 1H), 3.35-3.18 (m, 2H)
^{13}C NMR (75 MHz, $CDCl_3$):	δ 168.0, 155.5, 135.8, 134.5, 129.2, 128.9, 128.5, 128.2, 128.1, 127.5, 67.3, 54.6, 37.7
^{19}F NMR (282 MHz, $CDCl_3$):	δ -40.03 (d, 2F), -45.44 (t, 3F), -50.12 (t, 1F)
High Resolution ESMS:	Calculated for $C_{23}H_{16}F_5NO_4$+Na: 488.0897
	Observed: 488.0900

General Procedure for the Simultaneous Protection and Activation of Amino Acids Using PocOPfp

A solution of the amino acid (1 mmol) and PocOPfp (0.559 g, 2.1 mmol) in DMF (2 mL) was cooled to -10 °C and pyridine (0.177 mL, 2.2 mmol) was added to it dropwise. The reaction mixture was allowed to attain room temperature slowly and was stirred for 3-5 hours. The reaction mixture was then diluted with dichloromethane (30 mL) and washed with 0.5N HCl (10 mL), water (2x10 mL) and brine (10 mL). The resulting solution was dried over Na_2SO_4 and concentrated under vacuum and the products were purified by silica gel (100-200 mesh) column chromatography eluting with ethyl acetate hexane mixtures of appropriate concentration (5-20%).

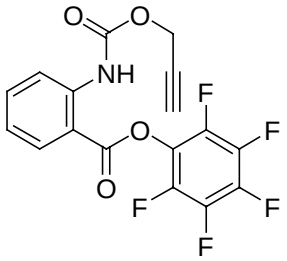
Pentafluorophenyl *m*-(*N*-Poc)aminobenzoate (6a)



Yield:	92%
Physical State:	White crystalline solid
Melting Point:	99 ˚C
FTIR (KBr):	3309 (m), 2130 (w), 1758 (s), 1716 (s)
^{1}H NMR (300 MHz, $CDCl_3$):	δ 8.20 (m, 1H), 7.92-7.89 (m, 1H), 7.81-7.78 (m, 1H), 7.49 (t, *J*=8.1, 1H), 7.12 (s, 1H), 4.80 (d, *J*=2.1, 2H), 2.53 (t, *J*=2.1, 1H)

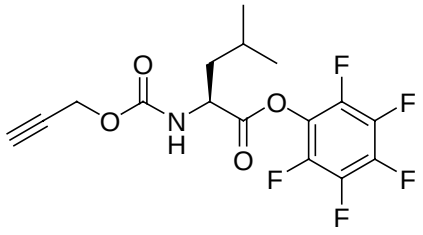
^{13}C NMR (75 MHz, $CDCl_3$):	δ 162.2, 152.4, 138.2, 129.7, 127.7, 125.8, 124.7, 120.5, 77.4, 75.2, 55.0
^{19}F NMR (282 MHz, $CDCl_3$):	δ -40.42 (d, 2F), -45.52 (t, 1F), -50.28 (t, 2F)
High Resolution ESMS (m/z):	Calculated for $C_{17}H_8F_5NO_4$+H: 386.0451
	Observed: 386.0449

Pentafluorophenyl *o*-(*N*-Poc)aminobenzoate (6b)



Yield:	90%
Physical State:	White solid
Melting Point:	125 ˚C
FTIR (KBr):	3280 (m), 2138 (w), 1783 (s), 1722 (s)
^{1}H NMR (300 MHz, $CDCl_3$):	δ 10.02 (s, 1H), 8.55-8.52 (m, 1H), 8.26 (m, 1H), 7.72-7.66 (m, 1H), 7.26-7.15 (m, 1H), 4.78 (d, *J*=2.4, 2H), 2.50 (t, *J*=2.4, 1H)
^{13}C NMR (75 MHz, $CDCl_3$):	δ 164.0, 152.3, 142.5, 136.6, 131.7, 122.3, 119.2, 111.6, 77.4, 75.1, 52.9
^{19}F NMR (282 MHz, $CDCl_3$):	δ -40.63 (d, 2F), -45.49 (t, 1F), -50.31 (t, 2F)
High Resolution ESMS (m/z):	Calculated for $C_{17}H_8F_5NO_4$+Na: 408.0271
	Observed: 408.0275

Poc-Leu-OPfp (6c)



Yield:	82%

Physical State: Gummy solid

Optical Rotation: $[\alpha]_D$ -166.00 (c=1.0, ethanol)

FTIR (Neat): 3318 (m), 2126 (w), 1793 (s), 1718 (s)

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.36 (d, *J*=8.1, 1H), 4.79-4.66 (m, 3H), 2.50 (t, *J*=2.4, 1H), 1.86-1.69 (m, 3H), 1.01 (d, *J*=5.7, 6H)

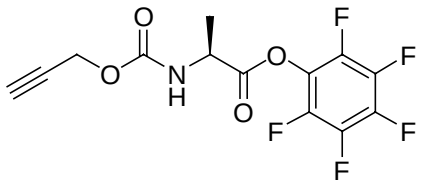
^{13}C NMR (75 MHz, $CDCl_3$): δ 169.2, 155.0, 77.4, 75.0, 53.1, 52.4, 41.1, 24.7, 22.6, 21.5

^{19}F NMR (282 MHz, $CDCl_3$): δ -40.70 (d, 2F), -45.65 (t, 1F), -50.36 (t, 2F)

High Resolution ESMS (m/z): Calculated for $C_{16}H_{14}F_5NO_4$+Na: 402.0741

Observed: 402.0749

Poc-Ala-OPfp (6d)



Yield: 68%

Physical State: Gummy solid

Optical Rotation: $[\alpha]_D$ +11.00 (c=1.0, ethanol)

FTIR (Neat): 3297 (m), 2129 (w), 1781 (s), 1714 (s)

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.41 (d, *J*=7.2, 1H), 4.78-4.66 (m, 3H), 2.50 (t, *J*=2.4, 1H), 1.63 (d, *J*=7.2, 3H)

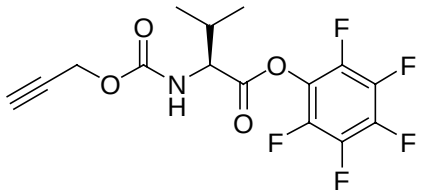
^{13}C NMR (75 MHz, $CDCl_3$): δ 169.2, 154.6, 77.4, 75.0, 53.0, 49.5, 18.2

^{19}F NMR (282 MHz, $CDCl_3$): δ -40.95 (d, 2F), -45.49 (t, 1F), -50.20 (t, 2F)

High Resolution ESMS (m/z): Calculated $C_{13}H_8F_5NO_4$+Na: 360.0271

Observed: 360.0274

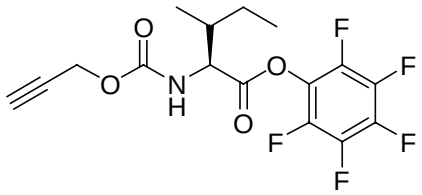
Poc-Val-OPfp (6e)



Yield: 87%

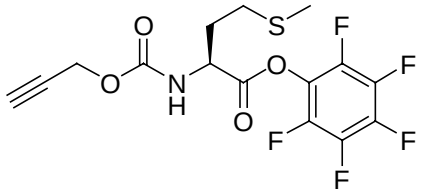
Physical State:	Gummy solid
Optical Rotation:	$[\alpha]_D$ +13.00 (c=1.0, ethanol)
FTIR (Neat):	3313 (m), 2129 (w), 1787 (s), 1720 (s)
^{1}H NMR (300 MHz, $CDCl_3$):	δ 5.43 (d, *J*=9.3, 1H), 4.80-4.64 (m, 3H), 2.51 (t, *J*=2.4, 1H), 2.45-2.35 (m, 1H), 1.10 (d, *J*=6.6, 3H), 1.03 (d, *J*=7.2, 3H)
^{13}C NMR (75 MHz, $CDCl_3$):	δ 168.1, 155.2, 77.4, 75.0, 59.0, 53.1, 31.1, 18.8, 17.1
^{19}F NMR (282 MHz, $CDCl_3$):	δ -40.42 (d, 2F), -45.52 (t, 1F), -50.28 (t, 2F)
High Resolution ESMS (m/z):	Calculated for $C_{15}H_{12}F_5NO_4$+Na: 388.0584 Observed: 388.0591

Poc-Ile-OPfp (6f)



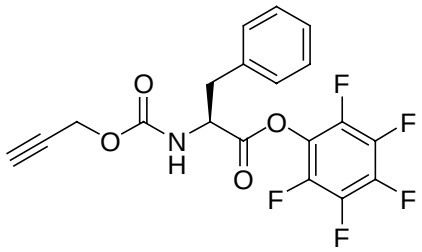
Yield:	84%
Physical State:	Gummy solid
Optical Rotation:	$[\alpha]_D$ +26.00 (c=1.0, ethanol)
FTIR (Neat):	3313 (m), 2130 (w), 1789 (s), 1720 (s)
^{1}H NMR (300 MHz, $CDCl_3$):	δ 5.39 (d, *J*=8.7, 1H), 4.79-4.67 (m, 3H), 2.50 (t, *J*=2.4, 1H), 2.16-2.01 (m, 1H), 1.59-1.48 (m, 1H), 1.36-1.21 (m, 1H), 1.07 (d, *J*=6.9, 3H), 0.99 (t, *J*=7.2, 3H)
^{13}C NMR (75 MHz, $CDCl_3$):	δ 168.1, 155.1, 77.4, 75.0, 58.4, 53.1, 37.8, 24.7, 15.3, 11.4
^{19}F NMR (282 MHz, $CDCl_3$):	δ -40.29 (d, 2F), -45.46 (t, 1F), -50.20 (t, 2F)
High Resolution ESMS (m/z):	Calculated for $C_{16}H_{14}F_5NO_4$+K: 418.0480 Observed: 418.0479

Poc-Met-OPfp (6g)



Yield:	72%
Physical State:	Gummy solid
Optical Rotation:	$[\alpha]_D$ -17.00 (c=1.0, ethanol)
FTIR (Neat):	3286 (m), 2125 (w), 1790 (s), 1718 (s)
^{1}H NMR (300 MHz, $CDCl_3$):	δ 5.69 (d, *J*=7.8, 1H), 4.93-4.99 (m, 1H), 4.80-4.67 (m, 2H), 2.73-2.61 (m, 2H), 2.51 (t, *J*=2.4, 1H), 2.40-2.29 (m, 1H), 2.24-2.14 (m, 4H)
^{13}C NMR (75 MHz, $CDCl_3$):	δ 168.3, 154.9, 77.4, 75.1, 53.2, 53.0, 31.3, 29.6, 15.3
^{19}F NMR (282 MHz, $CDCl_3$):	δ -40.69 (d, 2F), -45.23 (t, 1F), -50.04 (t, 2F)
High Resolution ESMS (m/z):	Calculated for $C_{15}H_{12}F_5NO_4$+Na: 420.0305 Observed: 420.0300

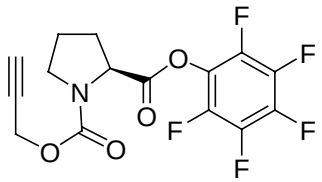
Poc-Phe-OPfp (6h)



Yield:	73%
Physical State:	White Solid
Melting Point:	82 ˚C
Optical Rotation:	$[\alpha]_D$ +12.00 (c=1.0, ethanol)
FTIR (KBr):	3305 (m), 2129 (w), 1793 (s), 1718 (s)
^{1}H NMR (300 MHz, $CDCl_3$):	δ 7.38-7.21 (m, 5H), 5.29 (d, *J*=8.1, 1H), 5.03-4.96 (m, 1H), 4.74-4.62 (m, 2H), 3.37-3.21 (m, 2H), 2.48 (t, *J*=2.4, 1H)

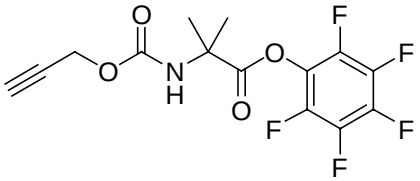
^{13}C NMR (75 MHz, $CDCl_3$):	δ 167.8, 154.6, 134.3, 129.2, 28.9, 127.6, 77.4, 75.0, 54.6, 53.1, 37.7
^{19}F NMR (282 MHz, $CDCl_3$):	δ -40.05 (d, 2F), -45.31 (t, 1F), -50.04 (t, 2F)
High Resolution ESMS (m/z):	Calculated for $C_{19}H_{12}F_5NO_4$+H: 414.0764 Observed: 414.0766

Poc-Pro-OPfp (6i)



Yield:	77% (Mixture of two rotamers)
Physical Appearance:	Gummy solid
Optical Rotation:	$[\alpha]_D$ -292 (c=1.0, ethanol)
FTIR (Neat):	3297 (m), 2130 (w), 1783 (s), 1687 (s)
^{1}H NMR (300 MHz, $CDCl_3$):	δ 4.84-4.61 (m, 3H), 3.74-3.45 (m, 2H), 2.55-1.93 (m, 5H)
^{13}C NMR (75 MHz, $CDCl_3$):	δ 177.7, 176.4, 154.8, 153.8, 77.9, 74.8, 74.7, 59.2, 58.6, 53.3, 53.1, 46.9, 46.6, 30.8, 29.4, 24.2, 23.3
^{19}F NMR (282 MHz, $CDCl_3$):	δ -40.93 9 (d), -41.39 (d), -45.78 (t), -46.07 (t), -50.41 (t), -50.62 (t)
High Resolution ESMS (m/z):	Calculated for $C_{15}H_{10}F_5NO_4$+Na: 386.0428 Observed: 386.0438

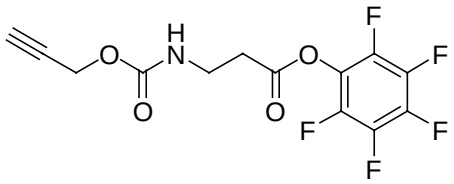
Poc-Aib-OPfp (6j)



Yield:	76%
Physical Appearance:	Gummy Solid
FTIR (Neat):	3313 (m), 2130 (w), 1793 (s), 1718 (s)

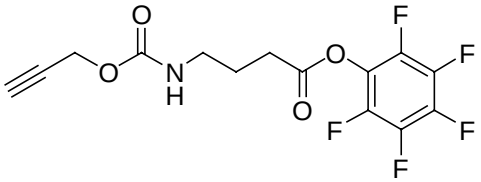
^{1}H NMR (300 MHz, $CDCl_3$):	δ 5.48 (s, 1H), 4.72 (d, *J*=2.4, 2H), 2.48 (t, *J*=2.4, 1H), 1.71 (s, 6H)
^{13}C NMR (75 MHz, $CDCl_3$):	δ 170.3, 154.0, 77.2, 74.9, 56.8, 52.8, 25.1
^{19}F NMR (282 MHz, $CDCl_3$):	δ -40. 98 (d, 2F), -46.12 (t, 1F), -50. 70 (t, 2F)
High Resolution ESMS (m/z):	Calculated for $C_{14}H_{10}F_5NO_4$+H: 352.0608 Observed: 352.0599

Poc-(β)Ala-OPfp (6k)



Yield:	60%
Physical Appearance:	Gummy solid
FTIR (Neat):	3311 (m), 2130 (w), 1787 (s), 1714 (s)
^{1}H NMR (300 MHz, $CDCl_3$):	δ 5.36 (sb, 1H), 4.70 (d, *J*=2.4, 2H), 3.61 (q, *J*=6.3, 2H), 2.96 (t, J=6.3, 2H), 2.49 (t, J=2.4, 1H)
^{13}C NMR (75 MHz, $CDCl_3$):	δ 168.2, 155.4, 77.9, 74.7, 52.6, 36.3, 33.6
^{19}F NMR (282 MHz, $CDCl_3$):	δ -40. 98 (d, 2F), -45.91 (t, 1F), -50. 43 (t, 2F)
High Resolution ESMS (m/z):	Calculated for $C_{13}H_8F_5NO_4$+Na: 360.0271 Observed: 360.0283

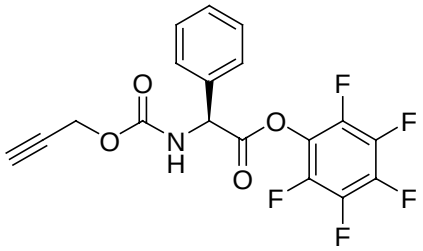
Poc-Gaba-OPfp (6l)



Yield:	68%
Physical State:	White solid
Melting Point:	71 ˚C

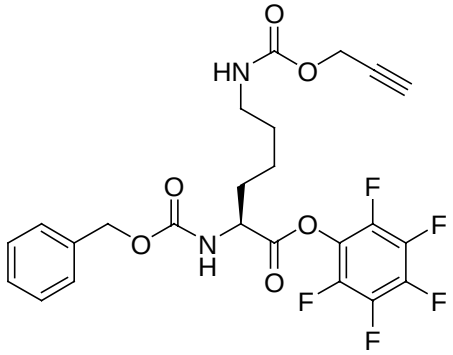
FTIR (KBr):	3309 (m), 2129 (w), 1789 (s), 1710 (s)
^{1}H NMR (300 MHz, $CDCl_3$):	δ 5.08 (s, 1H), 4.69 (d, *J*=2.4, 2H), 3.33 (q, *J*=6.6, 2H), 2.75 (t, *J*=7.5, 2H), 2.48 (t, *J*=2.4, 1H), 2.04-1.95 (m, 2H)
^{13}C NMR (75 MHz, $CDCl_3$):	δ 169.0, 155.6, 78.0, 74.6, 52.5, 40.0, 30.4, 24.9
^{19}F NMR (282 MHz, $CDCl_3$):	δ -41.19 (d, 2F), -46.31 (t, 2F), -50.68 (t, 1F)
High Resolution ESMS (m/z):	Calculated for $C_{14}H_{10}F_5NO_4$+H: 352.0608
	Observed: 352.0608

Poc-Phg-OPfp (6m)



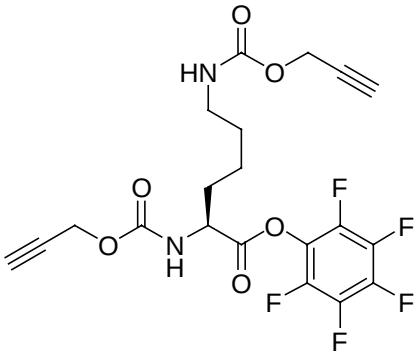
Yield:	75%
Physical State:	Gummy solid
Optical Rotation:	$[\alpha]_D$ +13.00 (c=1.0, ethanol)
FTIR (KBr):	3321 (m), 2124 (w), 1795 (s), 1714 (s)
^{1}H NMR (300 MHz, $CDCl_3$):	δ 7.46-7.42 (m, 5H), 5.84 (db, *J*=6.9, 1H), 5.72 (d, *J*=6.9, 1H), 4.72 (d, *J*=2.1, 2H), 2.48 (t, *J*=2.1, 1H)
^{13}C NMR (75 MHz, $CDCl_3$):	δ 167.2, 154.4, 134.2, 129.4, 129.3, 127.4, 77.5, 75.1, 57.9, 53.2
^{19}F NMR (282 MHz, $CDCl_3$):	δ -40.08 (d, 2F), -45.33 (t, 2F), -50.10 (t, 1F)
High Resolution ESMS (m/z):	Calculated for $C_{18}H_{10}F_5NO_4$+H: 422.0428
	Observed: 422.0435

Cbz-Lys(Poc)-OPfp (6n)



Yield:	76%
Physical Appearance:	Gummy solid
Optical Rotation:	$[\alpha]_D$ -110.00 (c=1.0, ethanol)
FTIR (Neat):	3299 (m), 2127 (w), 1791 (s), 1706 (s)
^{1}H NMR (300 MHz, $CDCl_3$):	δ 7.35-7.26 (m, 5H), 5.57 (d, *J*=6.6, 1H), 5.14 (s, 2H), 4.94 (sb, 1H), 4.73-4.63 (m, 3H), 3.25-3.15 (m, 2H), 2.44 (s, 1H), 2.06-1.84 (m, 2H), 1.61-1.46 (m, 4H)
^{13}C NMR (75 MHz, $CDCl_3$):	δ 168.7, 155.9, 155.7, 135.8, 128.5, 128.2, 128.1, 78.1, 74.5, 67.3, 53.5, 52.4, 40.2, 31.4, 29.2, 29.1
^{19}F NMR (282 MHz, $CDCl_3$):	δ -40.68 (d, 2F), -45.52 (t, 1F), -50.18 (t, 2F)
High Resolution ESMS (m/z):	Calculated for $C_{24}H_{21}F_5N_2O_6$+Na: 551.1218
	Observed: 551.1223

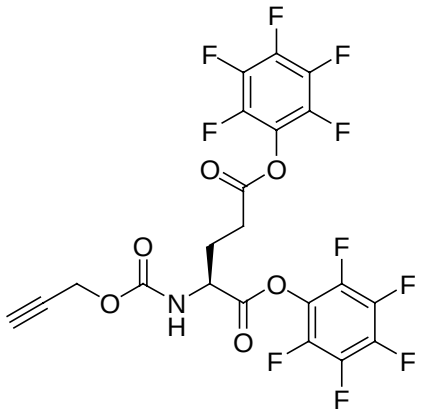
Poc-Lys(Poc)-OPfp (6o)



Yield:	57%
Physical Appearance:	Gummy solid
Optical Rotation:	$[\alpha]_D$ -10.00 (c=1.0, ethanol)

FTIR (Neat):	3295 (m), 2129 (w), 1793 (s), 1712 (s)
^{1}H NMR (300 MHz, $CDCl_3$):	δ 5.71 (db, *J*=7.2, 1H), 5.00 (sb, 1H), 4.73-4.68 (m, 5H), 3.31-3.15 (m, 2H), 2.52-2.47 (two triplets, 2H), 2.05-1.91 (m, 2H), 1.645-1.51 (m, 4H)
^{13}C NMR (75 MHz, $CDCl_3$):	δ 168.5, 155.8, 155.0, 78.1, 77.6, 75.0, 74.6, 53.6, 53.0, 52.5, 40.1, 31.3, 29.2, 21.8
^{19}F NMR (282 MHz, $CDCl_3$):	δ -40.74 (d, 2F), -45.45 (t, 1F), -50.18 (t, 2F)
High Resolution ESMS (m/z):	Calculated for $C_{20}H_{17}F_5N_2O_6$+Na: 499.0905 Observed: 499.0911

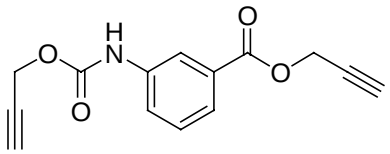
Poc-Glu(Pfp)-OPfp (6p)



Yield:	62%
Physical Appearance:	Gummy solid
Optical Rotation:	$[\alpha]_D$ -21.00 (c=1.0, ethanol)
FTIR (Neat):	3301 (m), 2133 (w), 1791 (s), 1716 (s)
^{1}H NMR (300 MHz, $CDCl_3$):	δ 5.44 (db, *J*=8.4, 1H), 4.91-4.90 (m, 1H), 4.77-4.75 (m, 2H), 3.01-2.83 (m, 2H), 2.65-2.50 (m, 2H), 2.38-2.25 (m, 2H)
^{13}C NMR (75 MHz, $CDCl_3$):	δ 168.3, 167.8, 155.0, 75.9, 75.2, 55.7, 53.38, 53.0, 29.1, 27.1
^{19}F NMR (282 MHz, $CDCl_3$):	δ -40.73 (d, 2F), -40.99 (d, 2F), -44.80 (t, 1F), -45.81 (t, 1F), -49.75 (t, 2F), -50.36 (t, 2F)
High Resolution ESMS (m/z):	Calculated for $C_{21}H_9F_{10}NO_6$+Na: 584.0168

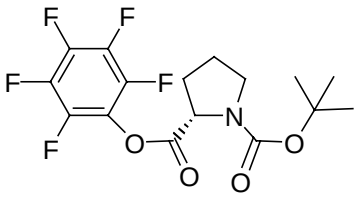
Observed: 584.0159

Propargyl *m*-(*N*-Poc)aminobenzoate (10)

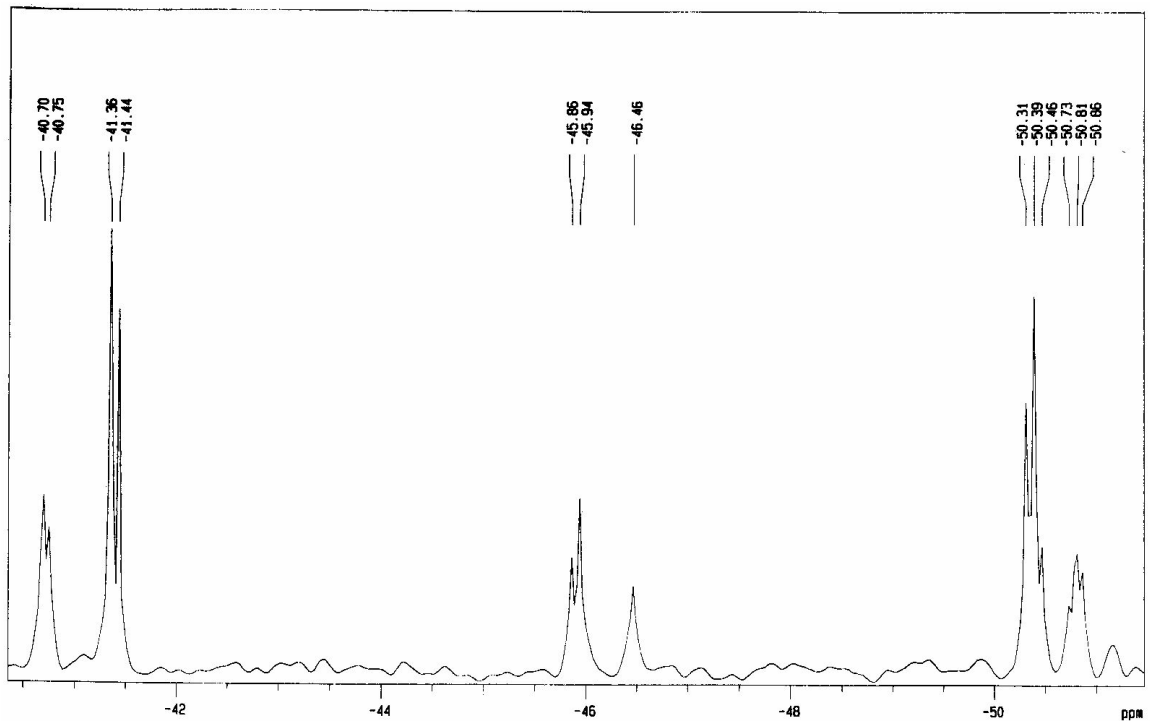


Physical Appearance:	White solid
Melting Point:	146 ˚C
FTIR (KBr):	3338 (m), 2129 (w), 1723 (s), 1704 (s)
^{1}H NMR (300 MHz, $CDCl_3$):	δ 9.35 (sb, 1H), 8.19-8.17 (m, 1H), 7.78-7.69 (m, 2H), 7.38-7.33 (m, 1H), 4.90 (d, *J*=2.7, 2H), 4.78 (d, *J*=2.7, 2H), 2.61-2.58 (m, 2H)
^{13}C NMR (75 MHz, $CDCl_3$):	δ 165.0, 152.5, 138.6, 129.4, 128.4, 123.7, 123.1, 119.2, 77.6, 77.2, 74.8, 74.6, 51.9
High Resolution ESMS (m/z):	Calculated for $C_{14}H_{11}NO_4$+Na: 280.0586 Observed: 280.0593

Compound 4a

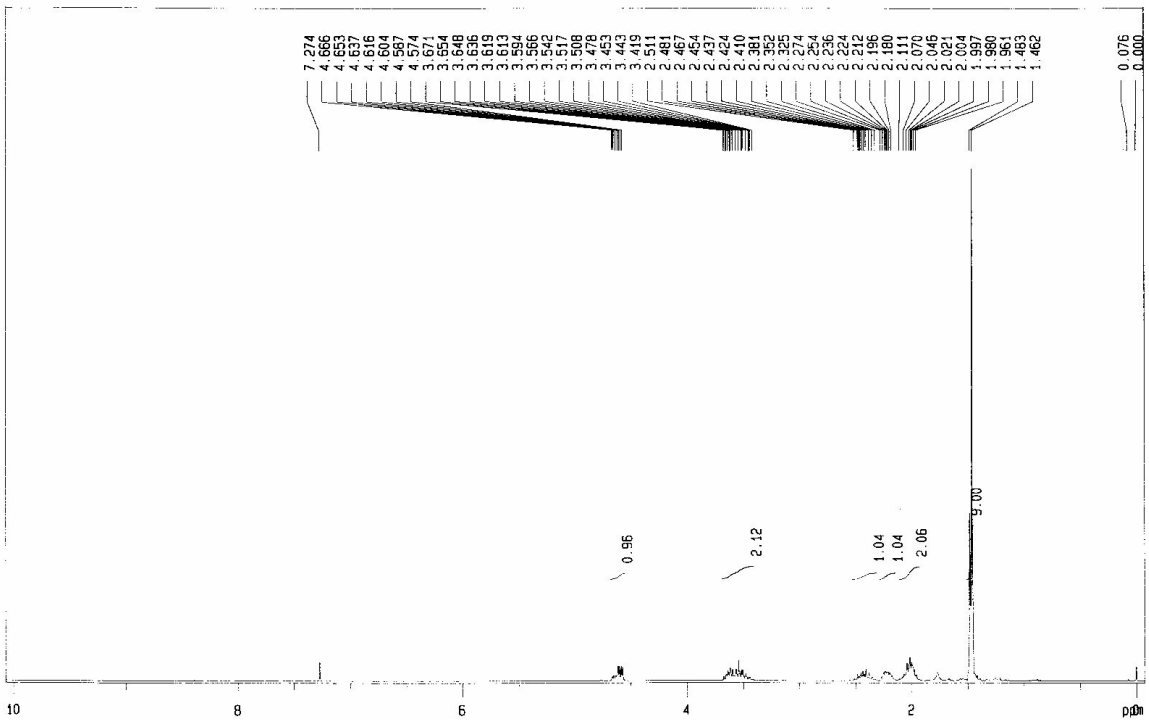


^{19}F NMR (282 MHz, $CDCl_3$)

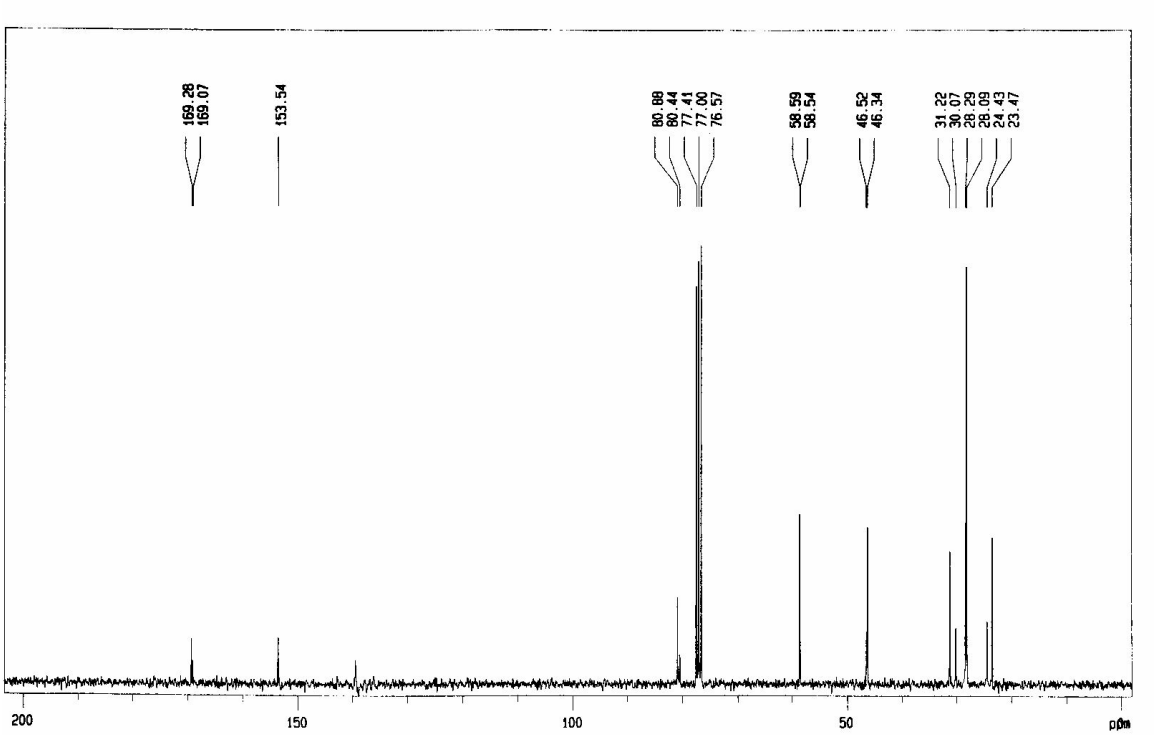


Compound 4a

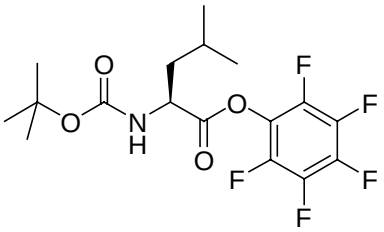
^{1}H NMR (300 MHz, $CDCl_3$)



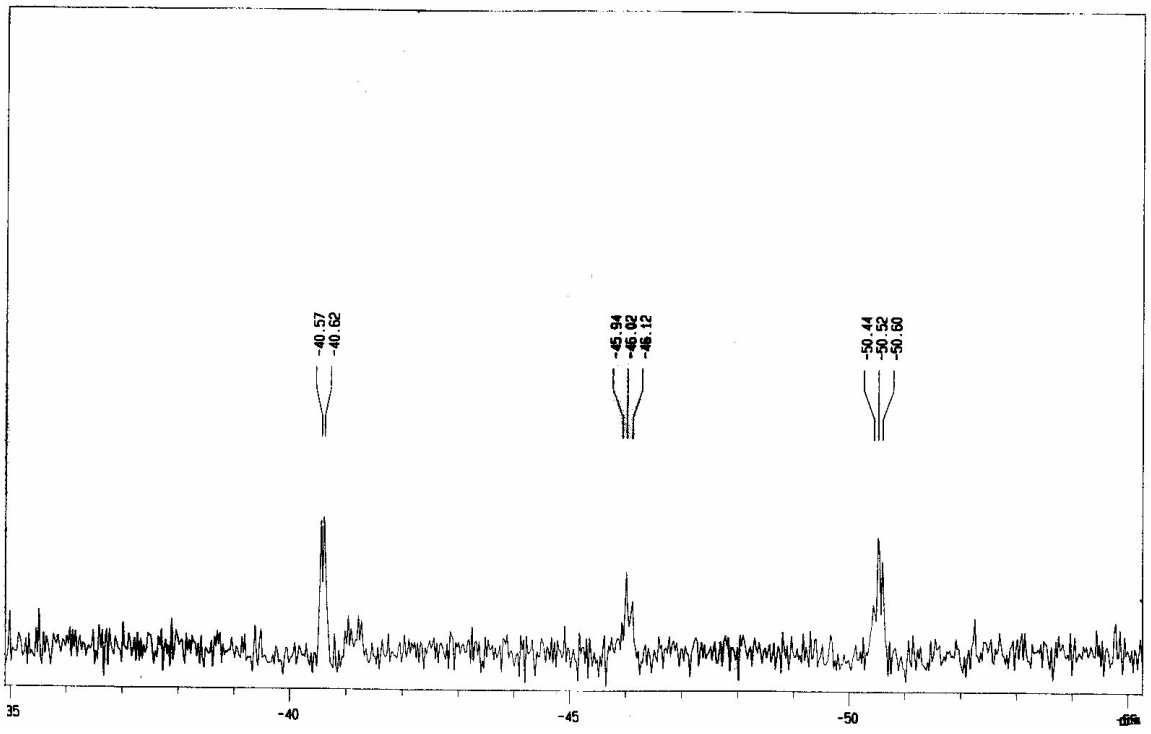
^{13}C NMR (75 MHz, $CDCl_3$)



Compound 4b

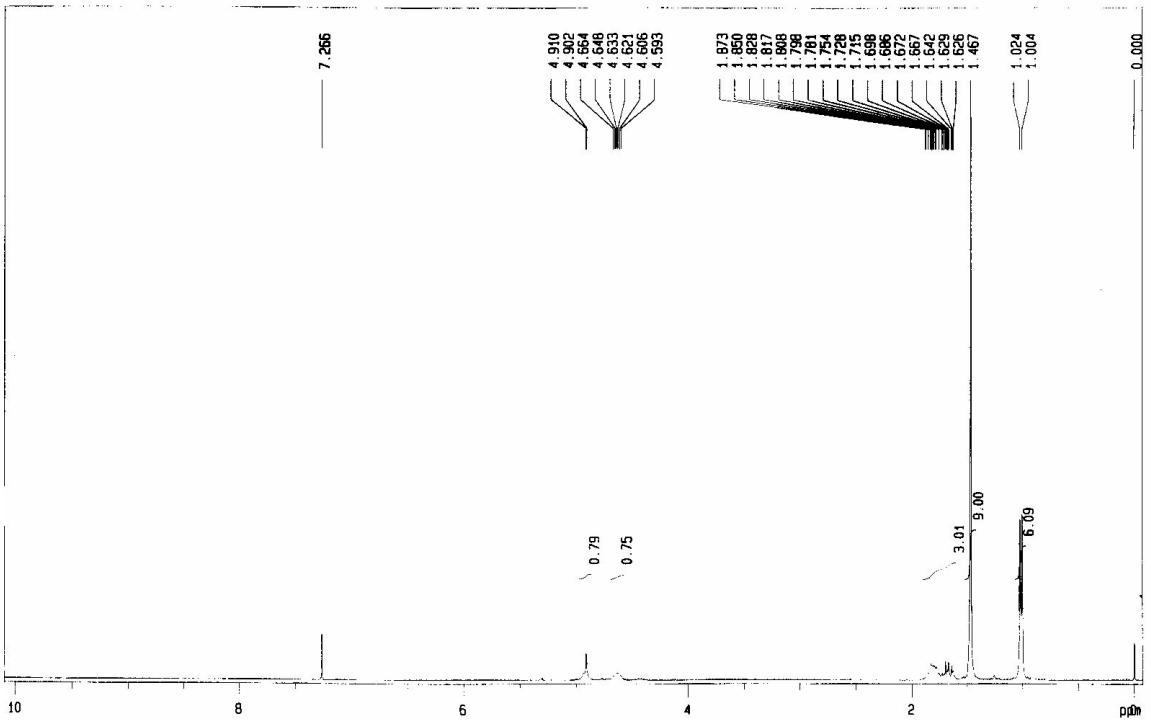


^{19}F NMR (282 MHz, $CDCl_3$)

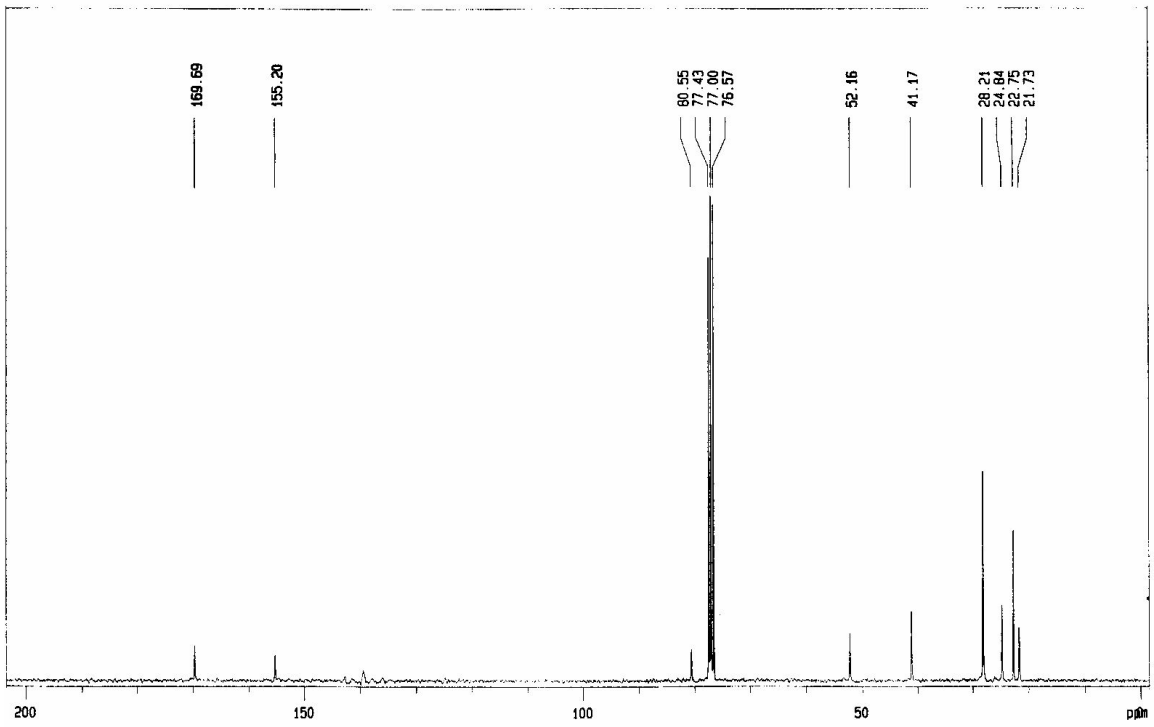


Compound 4b

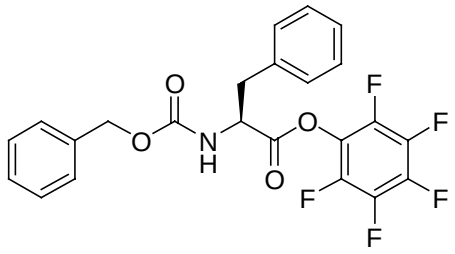
^{1}H NMR (300 MHz, $CDCl_3$)



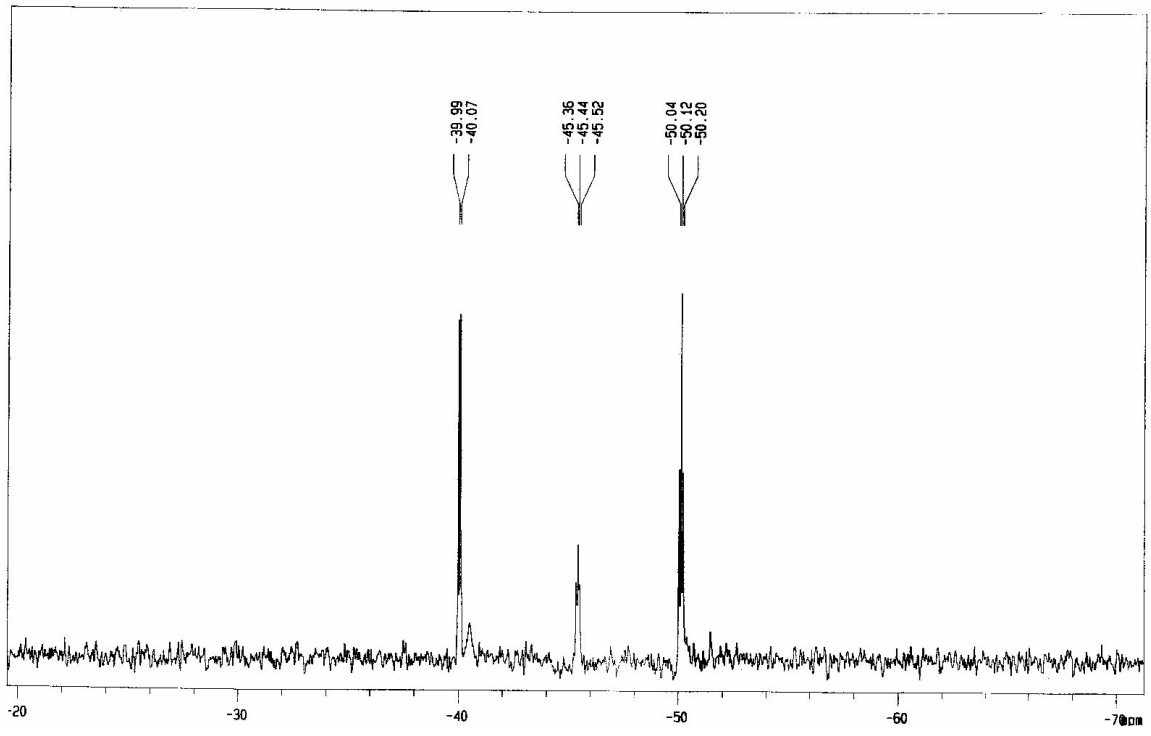
^{13}C NMR (75 MHz, $CDCl_3$)



Compound 4c

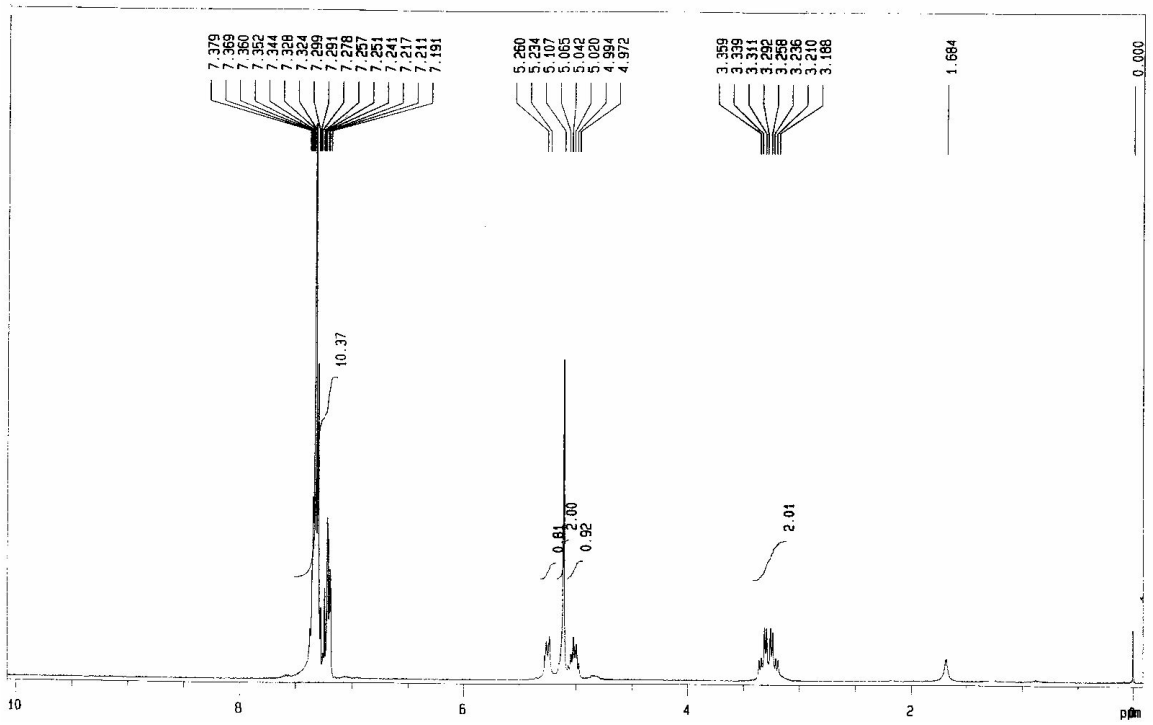


^{19}F NMR (282 MHz, $CDCl_3$)

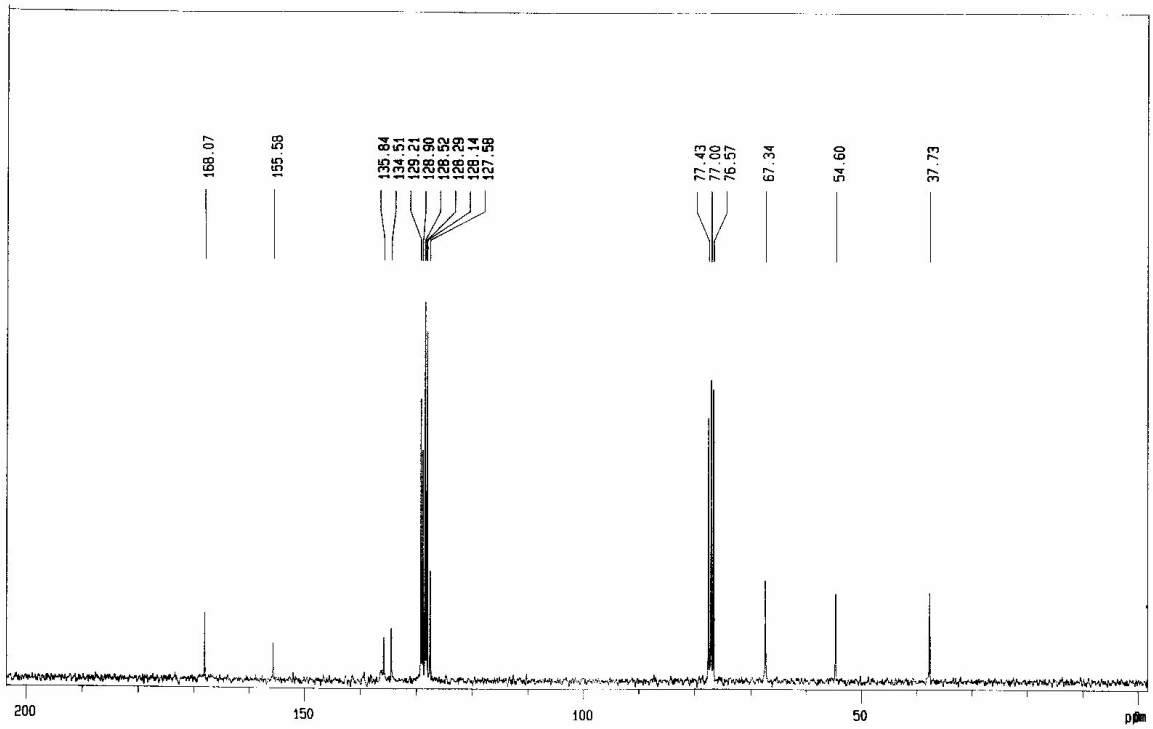


Compound 4c

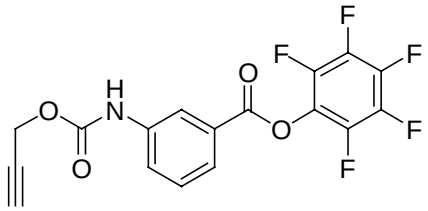
^{1}H NMR (300 MHz, $CDCl_3$)



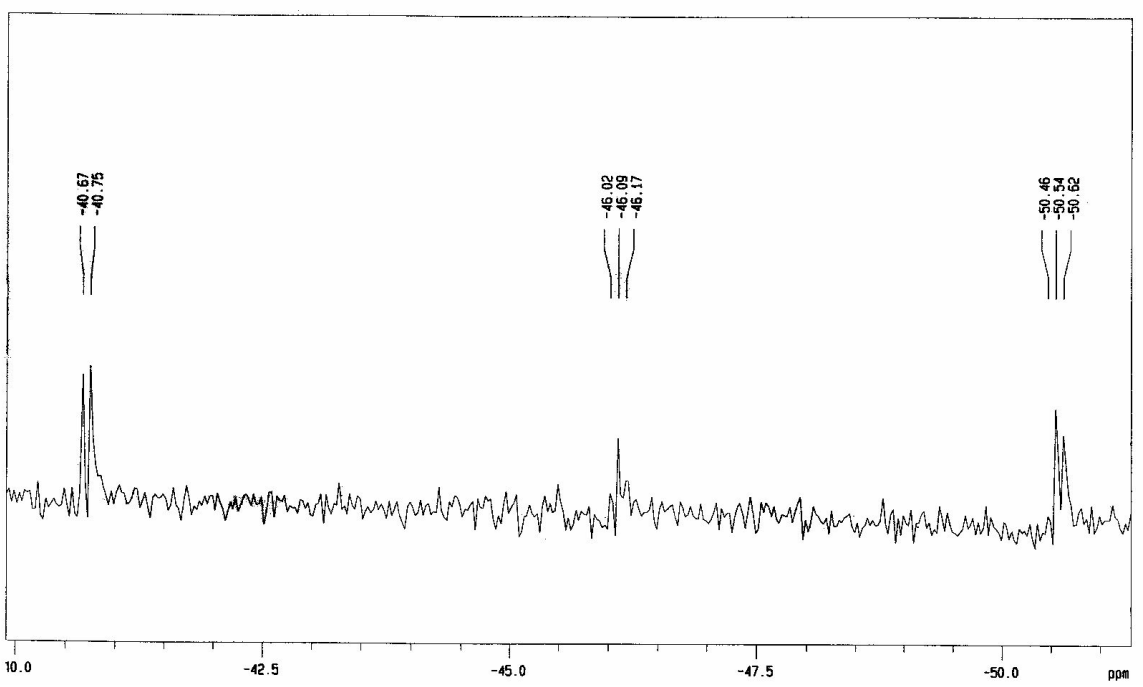
^{13}C NMR (75 MHz, $CDCl_3$)



Compound 6a

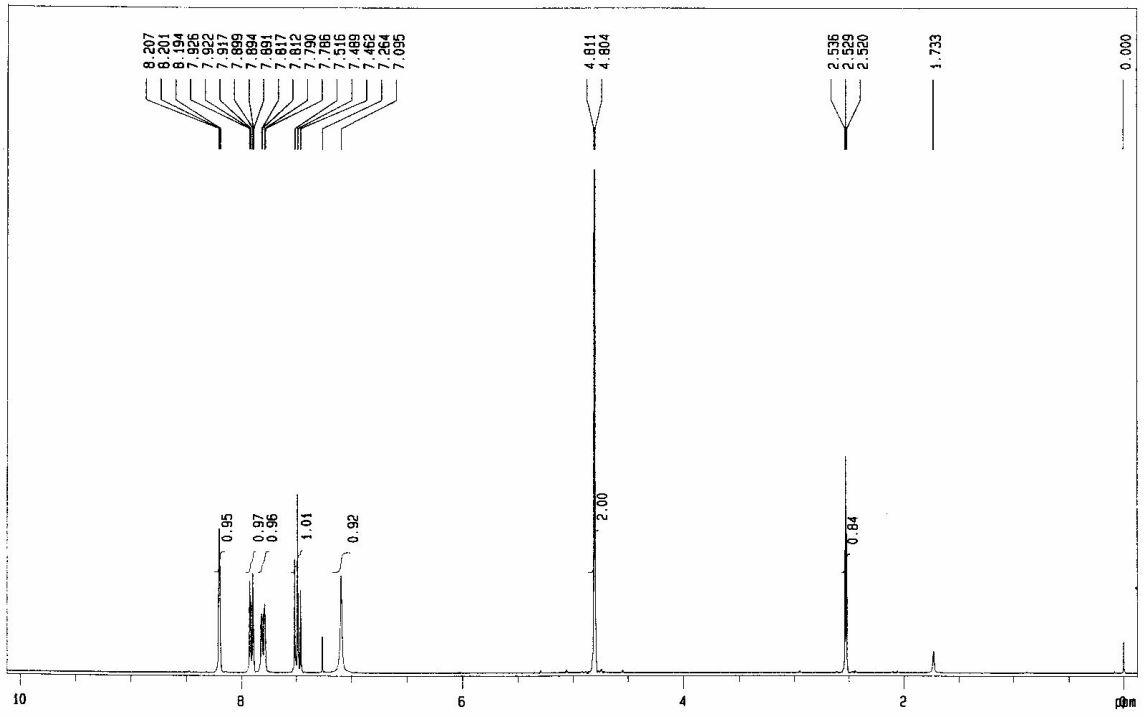


^{19}F NMR (282 MHz, $CDCl_3$)

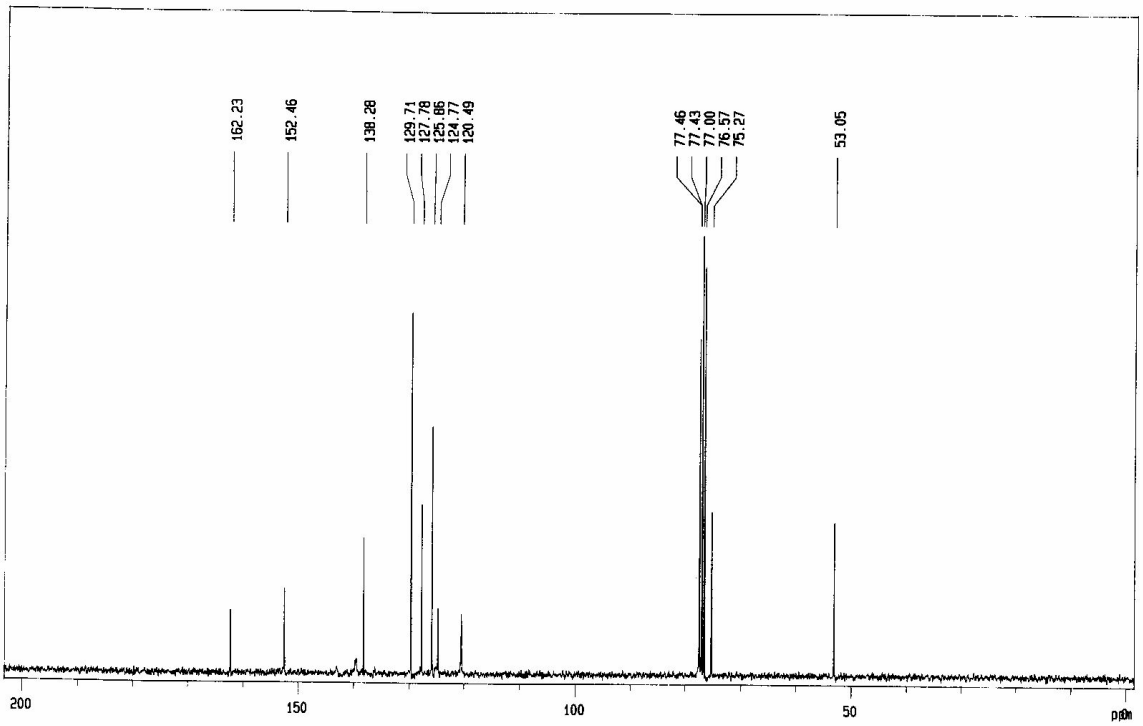


Compound 6a

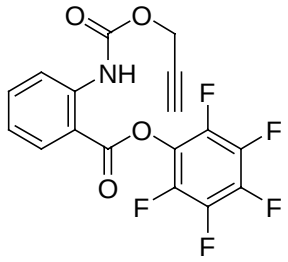
^{1}H NMR (300 MHz, $CDCl_3$)



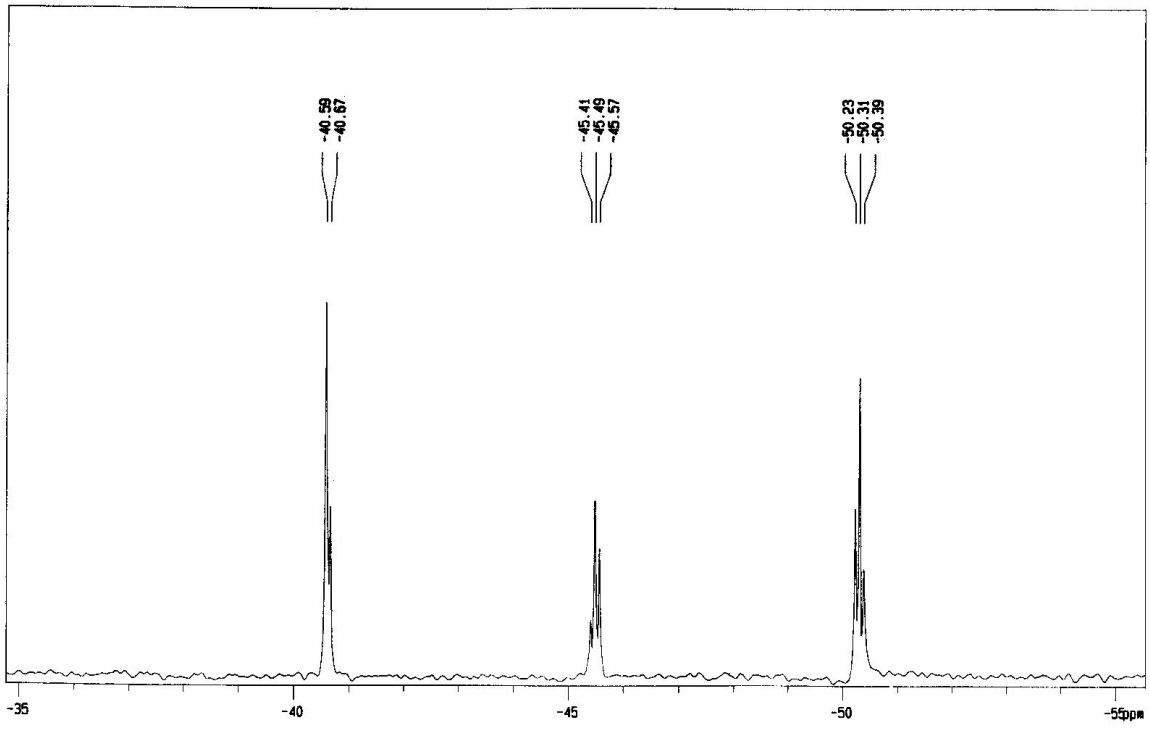
^{13}C NMR (75 MHz, $CDCl_3$)



Compound 6b

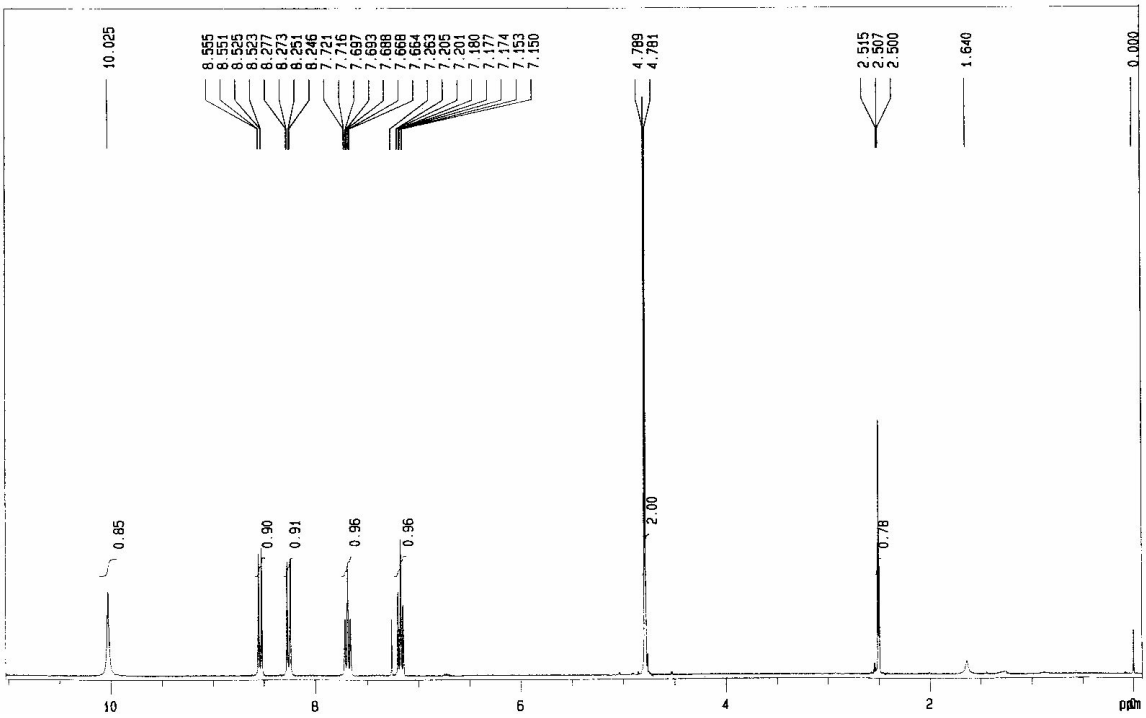


^{19}F NMR (282 MHz, $CDCl_3$)

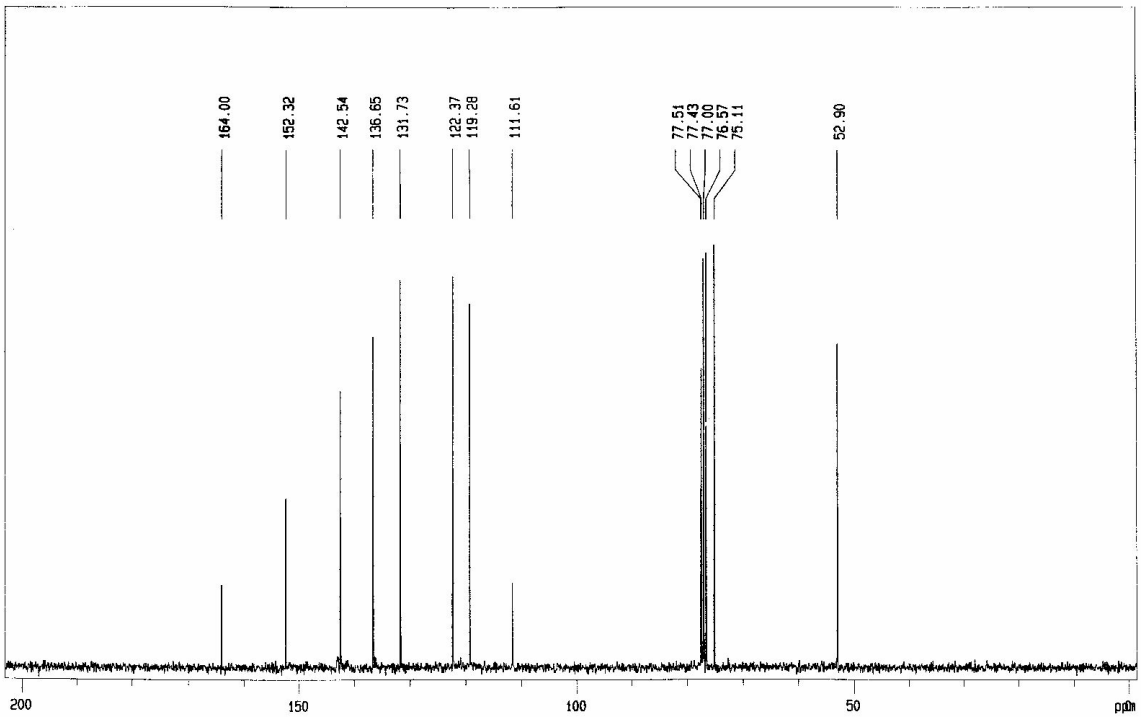


Compound 6b

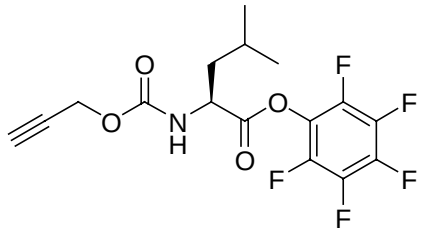
^{1}H NMR (300 MHz, $CDCl_3$)



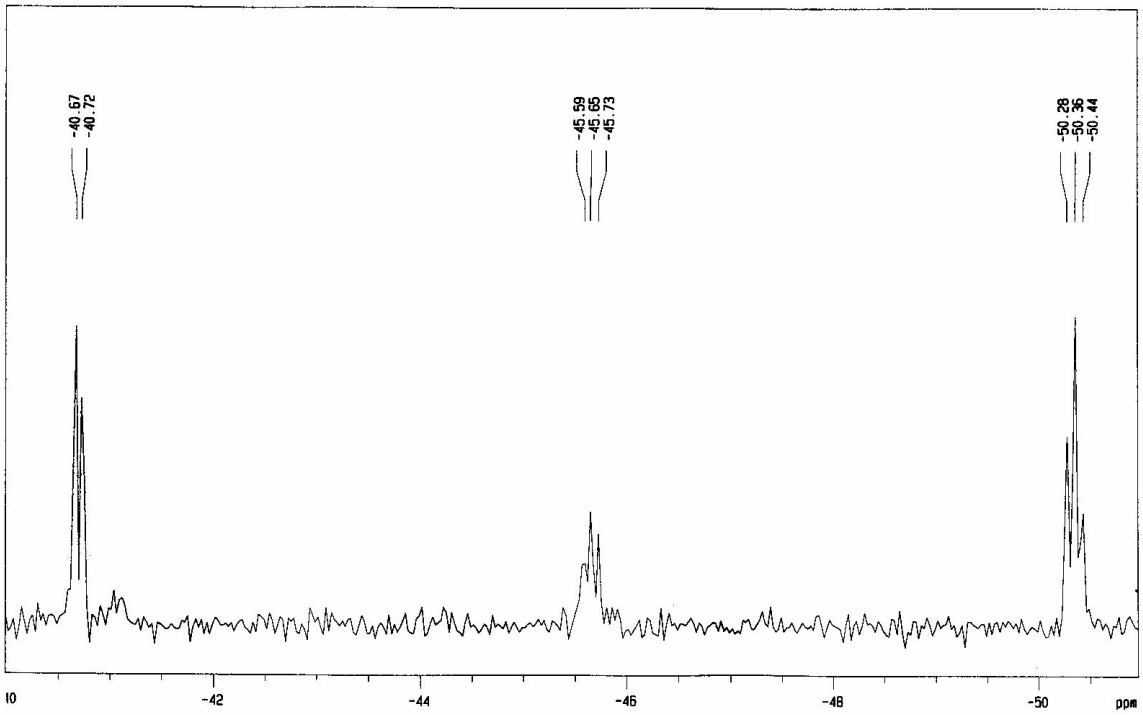
^{13}C NMR (75 MHz, $CDCl_3$)



Compound 6c

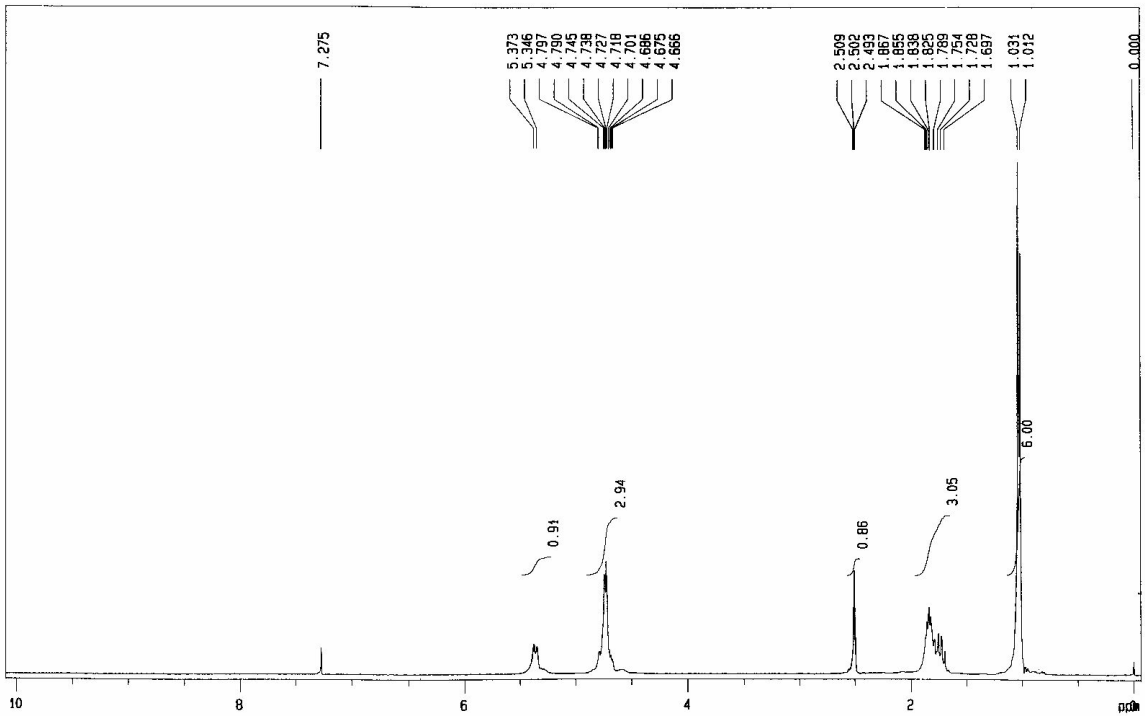


^{19}F NMR (282 MHz, $CDCl_3$)

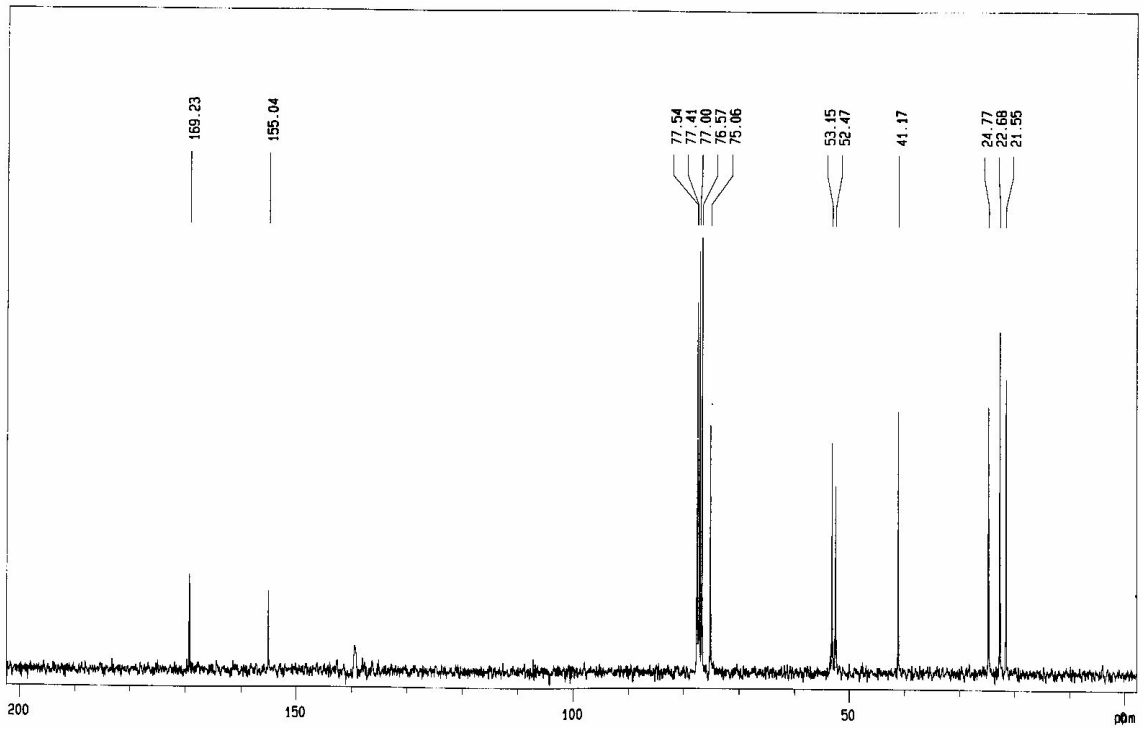


Compound 6c

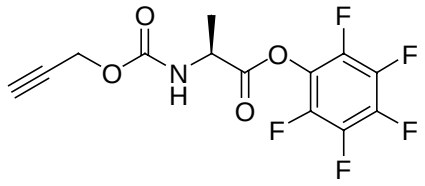
^{1}H NMR (300 MHz, $CDCl_3$)



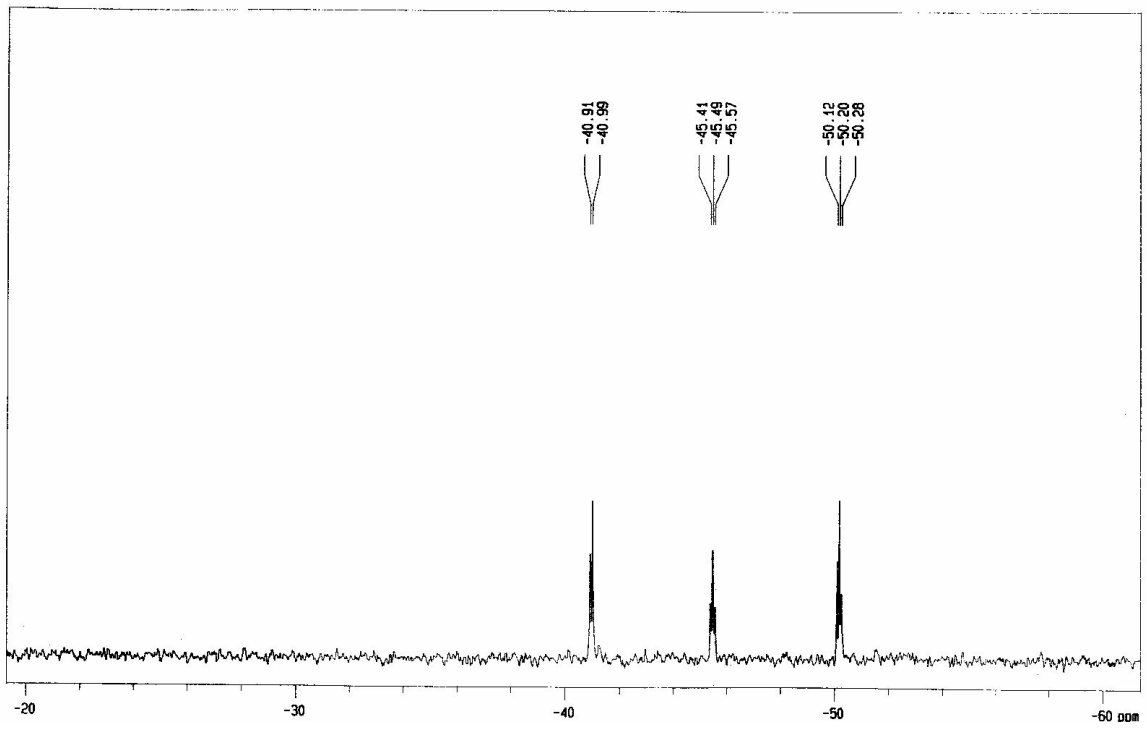
^{13}C NMR (75 MHz, $CDCl_3$)



Compound 6d

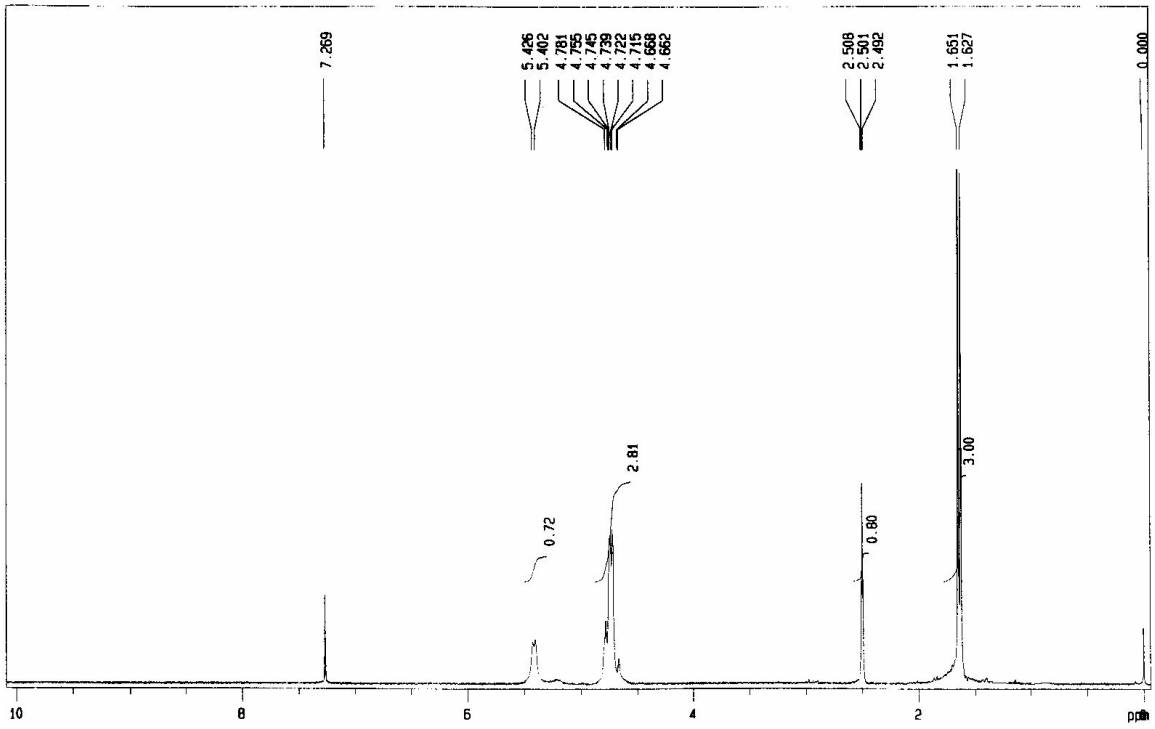


^{19}F NMR (282 MHz, $CDCl_3$)

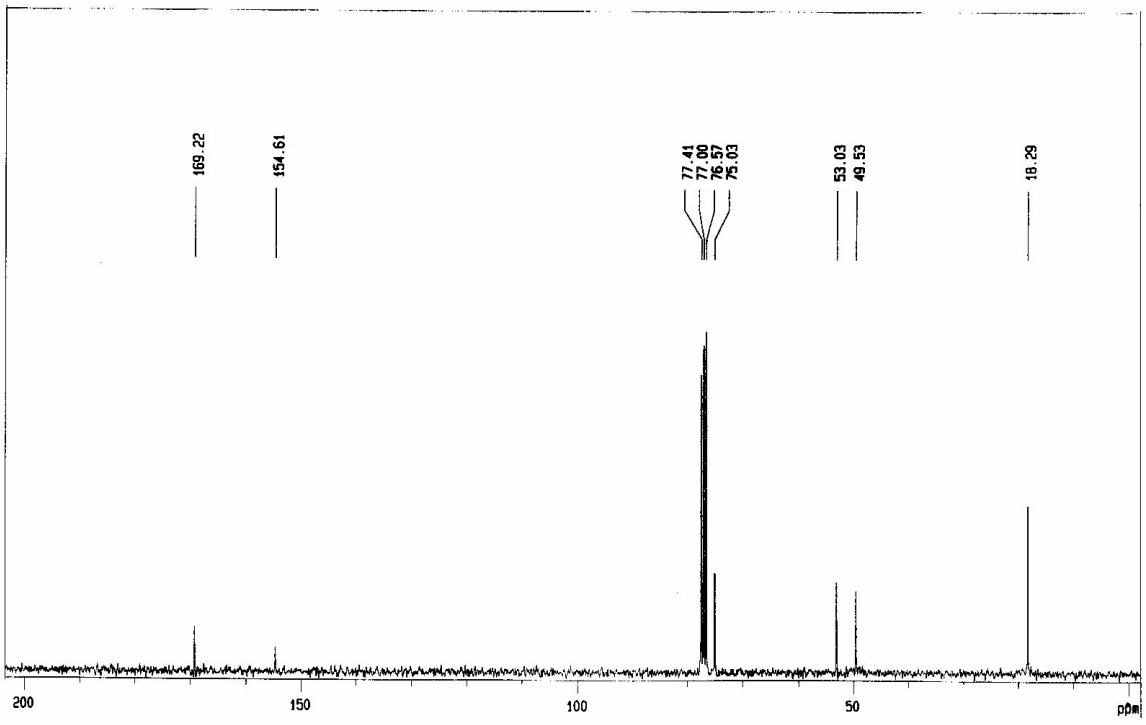


Compound 6d

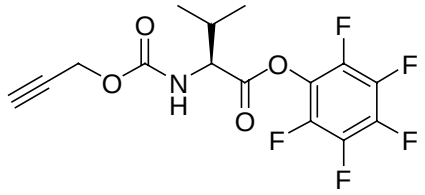
^{1}H NMR (300 MHz, $CDCl_3$)



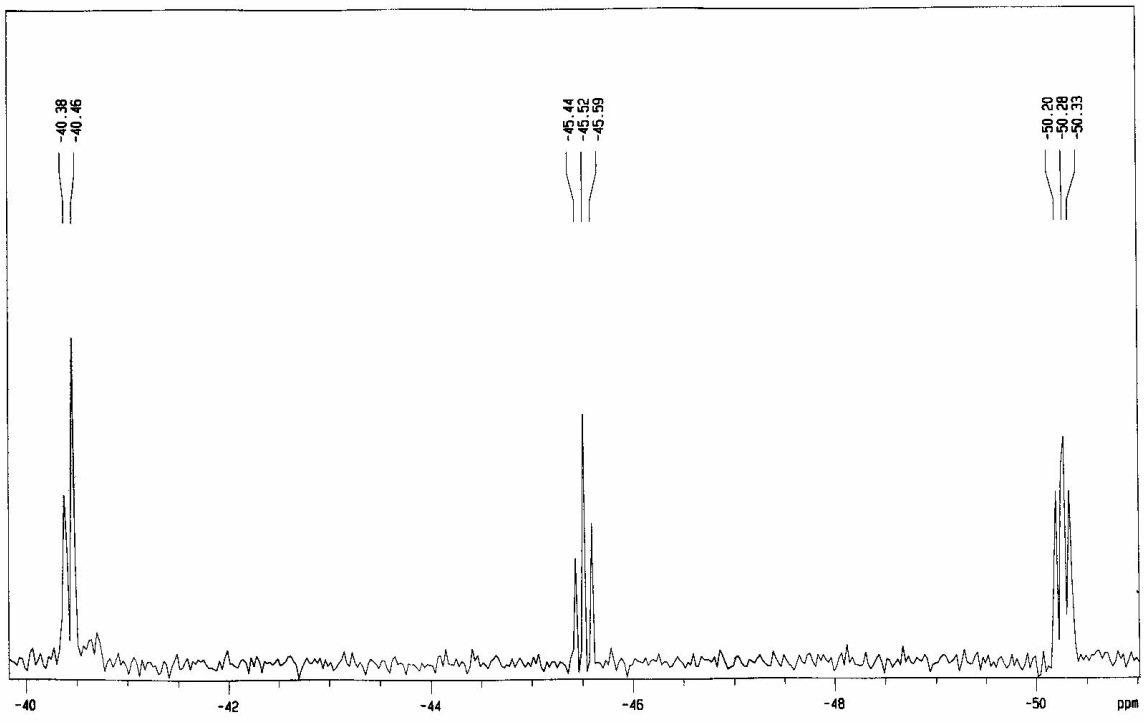
^{13}C NMR (75 MHz, $CDCl_3$)



Compound 6e

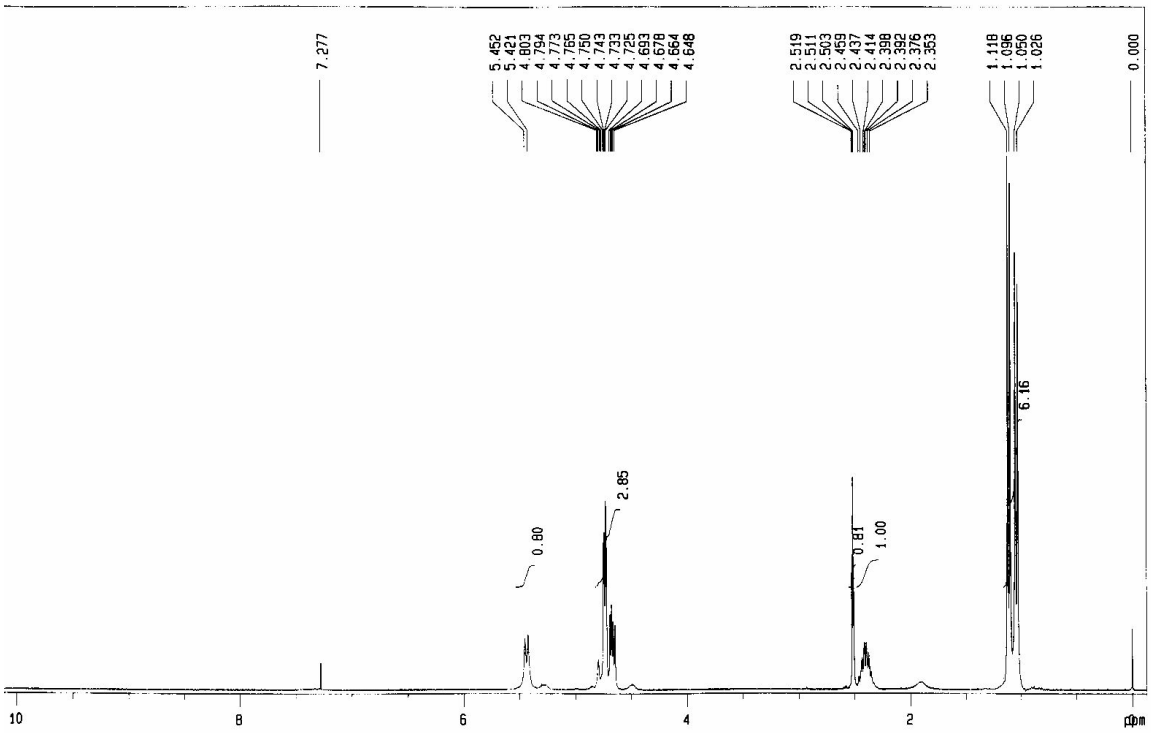


^{19}F NMR (282 MHz, $CDCl_3$)

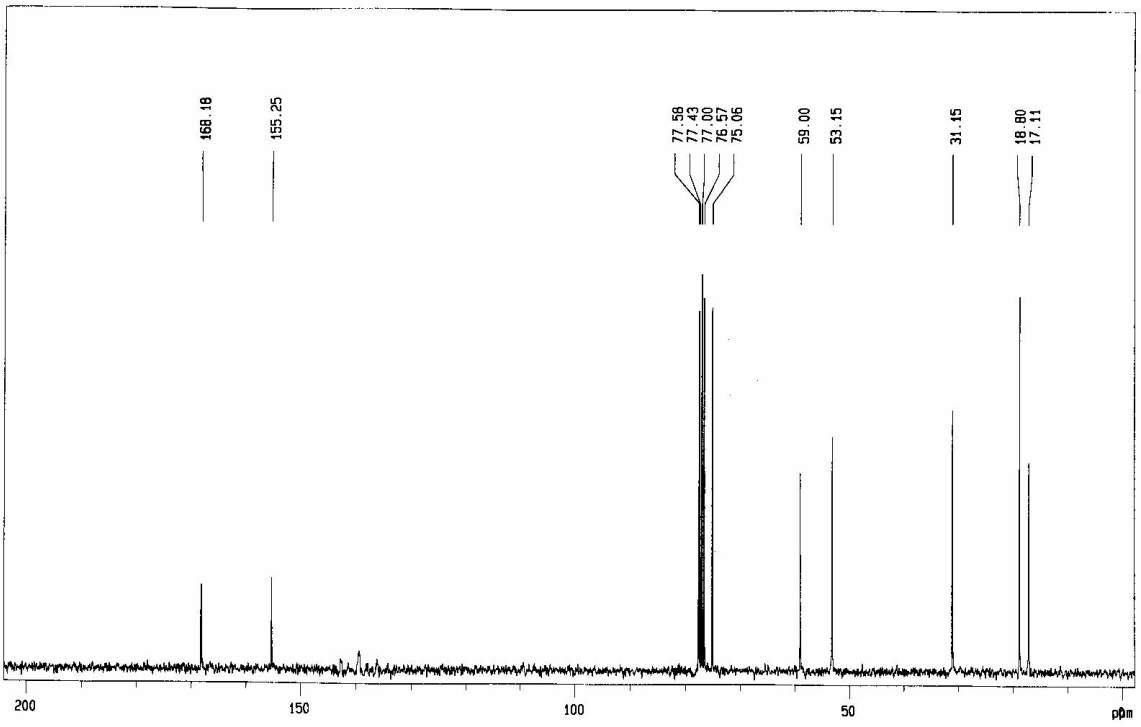


Compound 6e

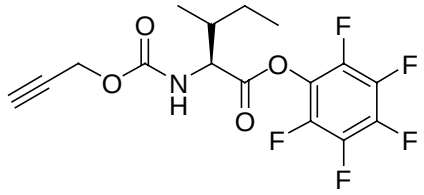
^{1}H NMR (300 MHz, $CDCl_3$)



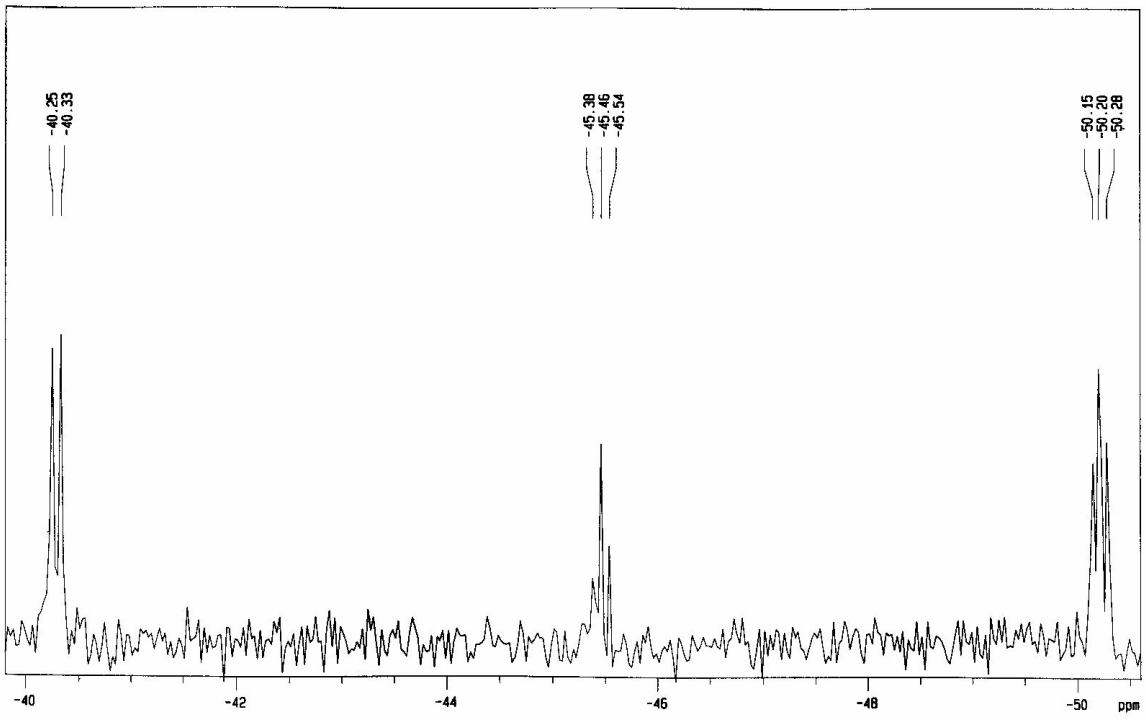
^{13}C NMR (75 MHz, $CDCl_3$)



Compound 6f

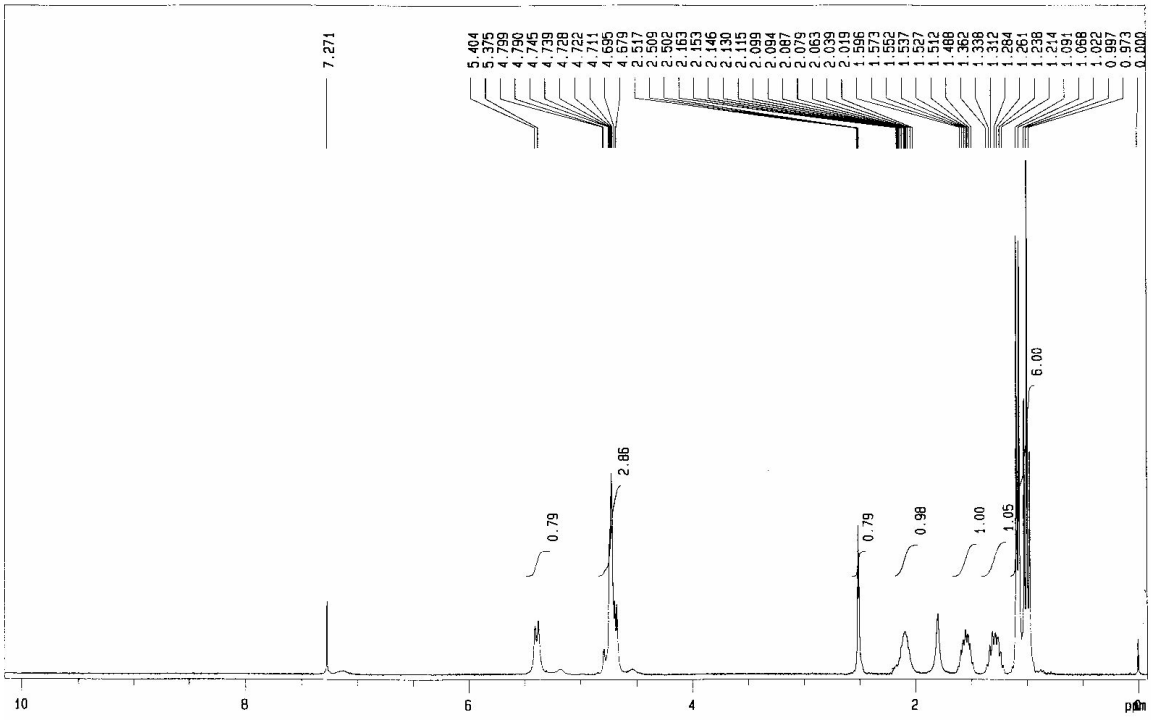


^{19}F NMR (282 MHz, $CDCl_3$)

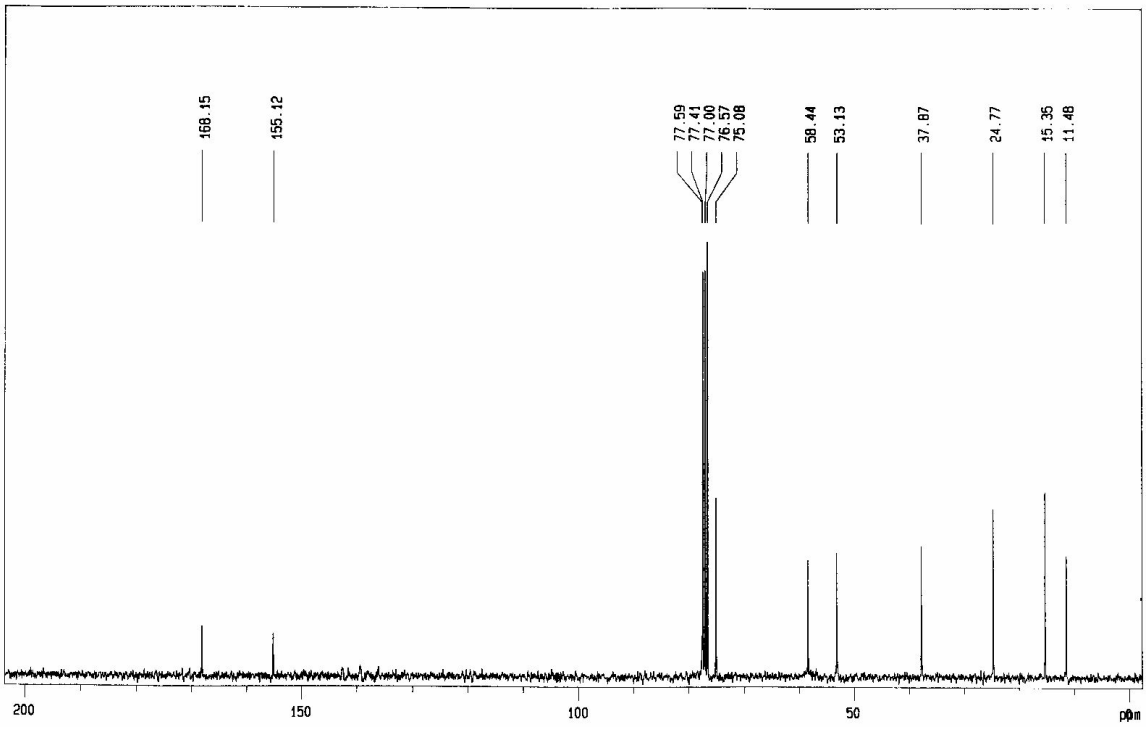


Compound 6f

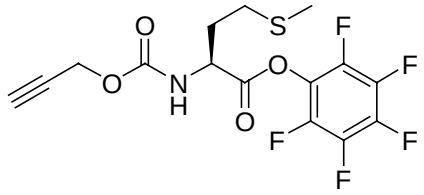
^{1}H NMR (300 MHz, $CDCl_3$)



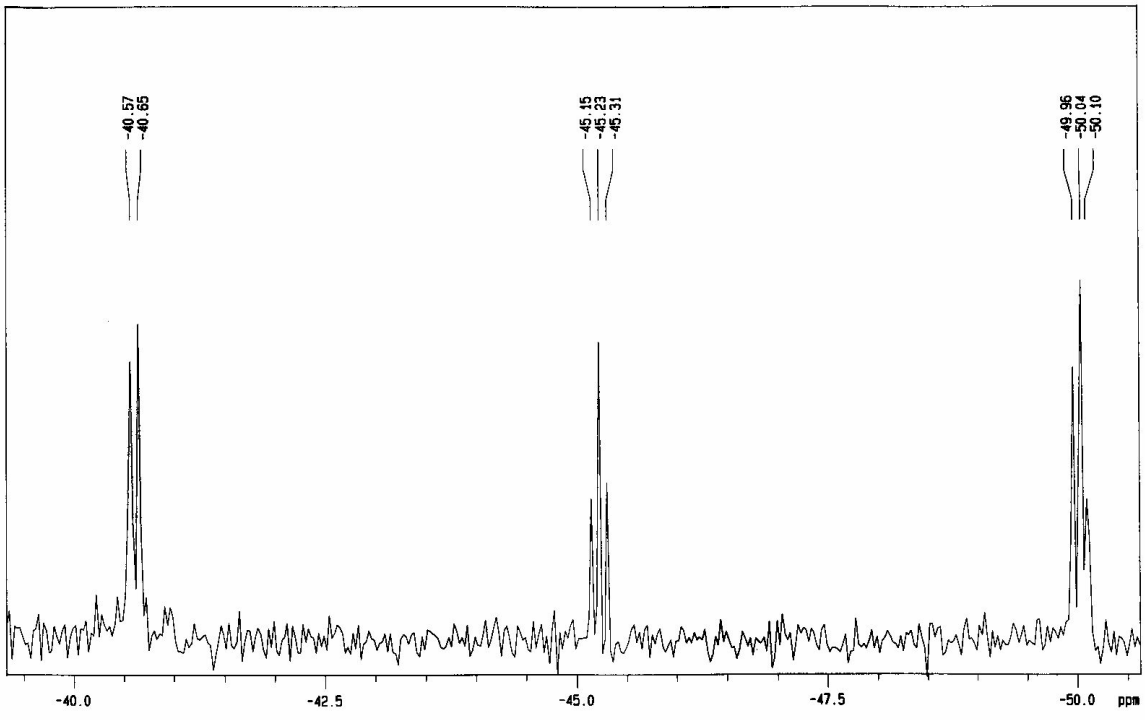
^{13}C NMR (75 MHz, $CDCl_3$)



Compound 6g

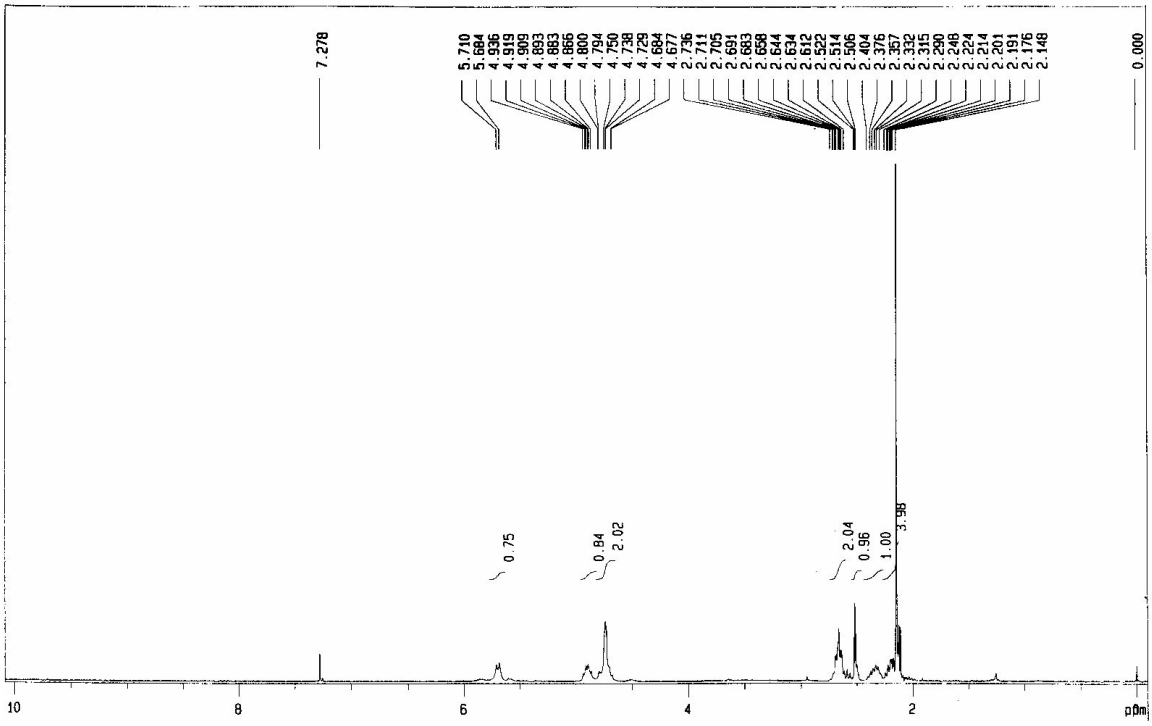


^{19}F NMR (282 MHz, $CDCl_3$)

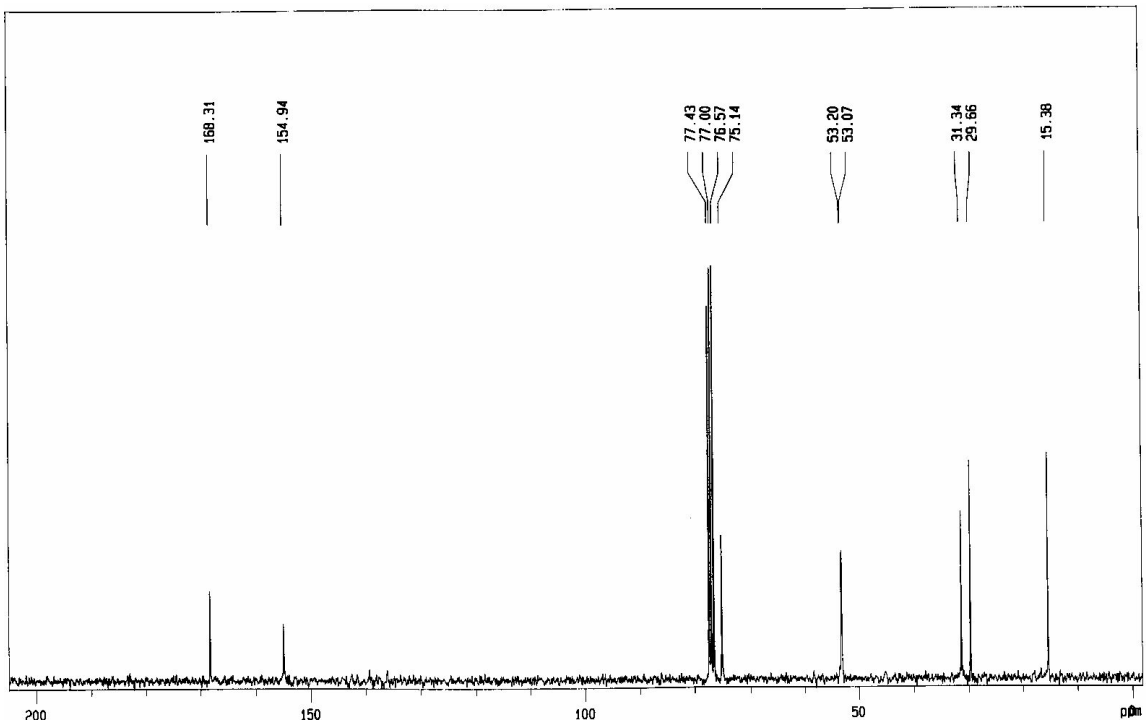


Compound 6g

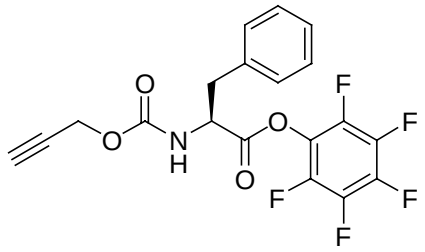
^{1}H NMR (300 MHz, $CDCl_3$)



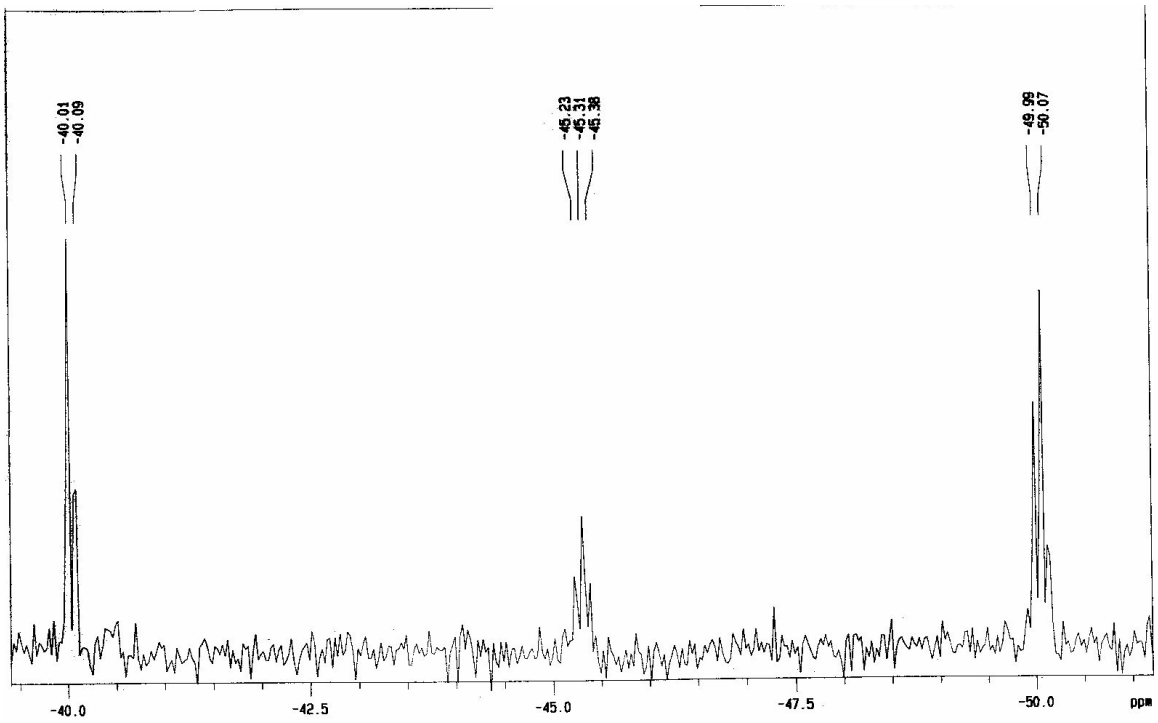
^{13}C NMR (75 MHz, $CDCl_3$)



Compound 6h

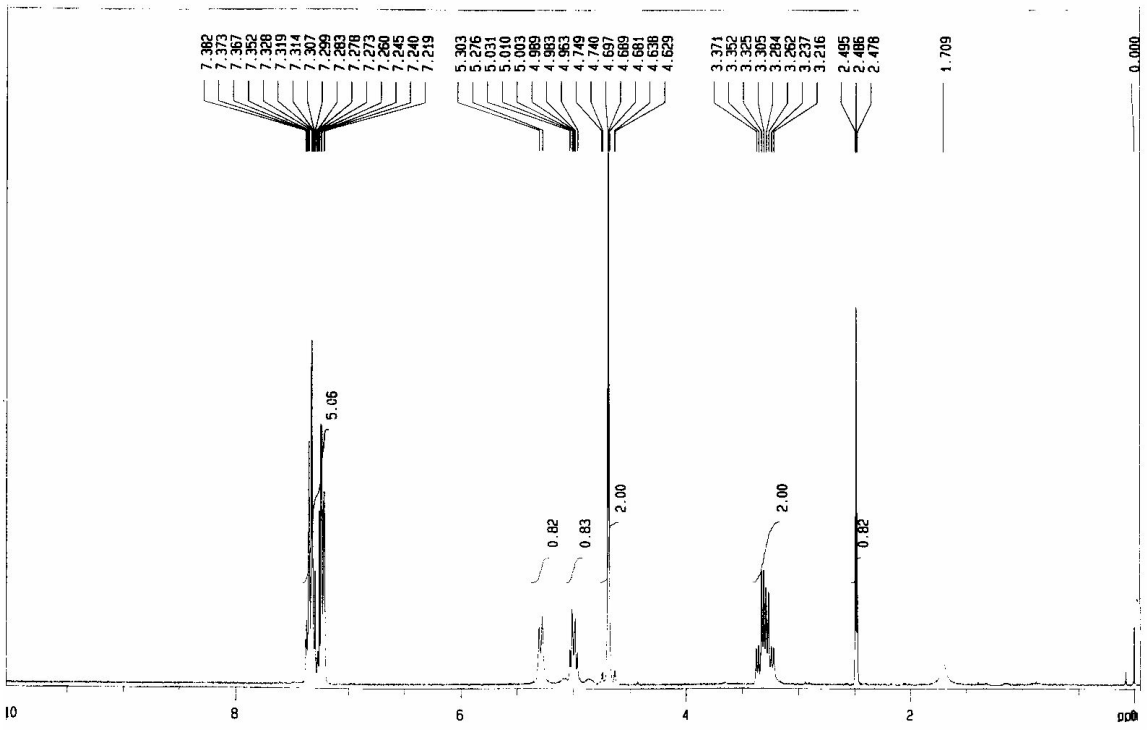


^{19}F NMR (282 MHz, $CDCl_3$)

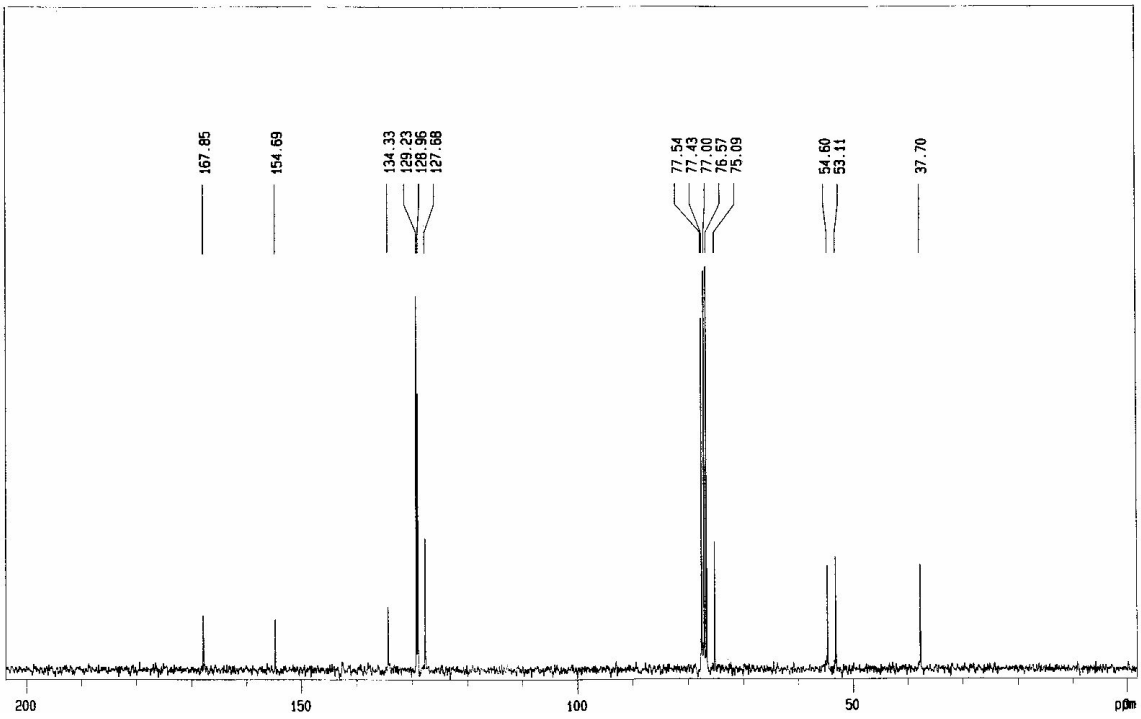


Compound 6h

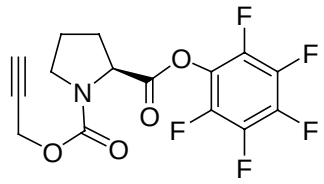
^{1}H NMR (300 MHz, $CDCl_3$)



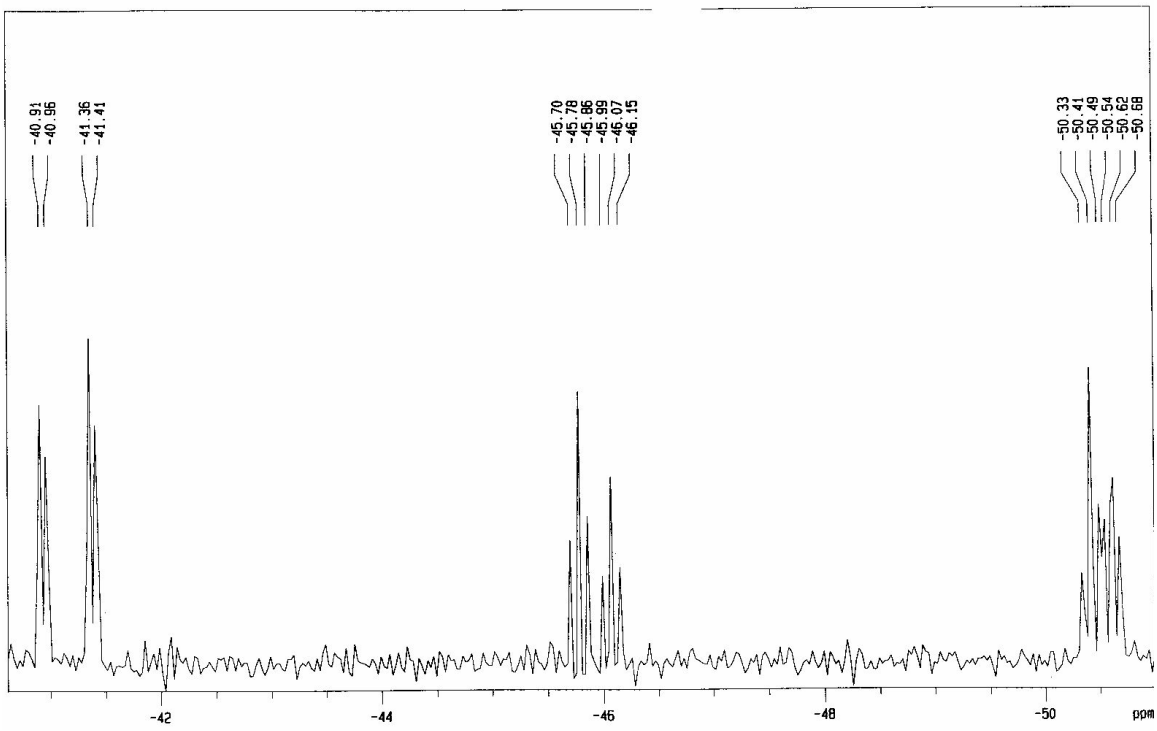
^{13}C NMR (75 MHz, $CDCl_3$)



Compound 6i

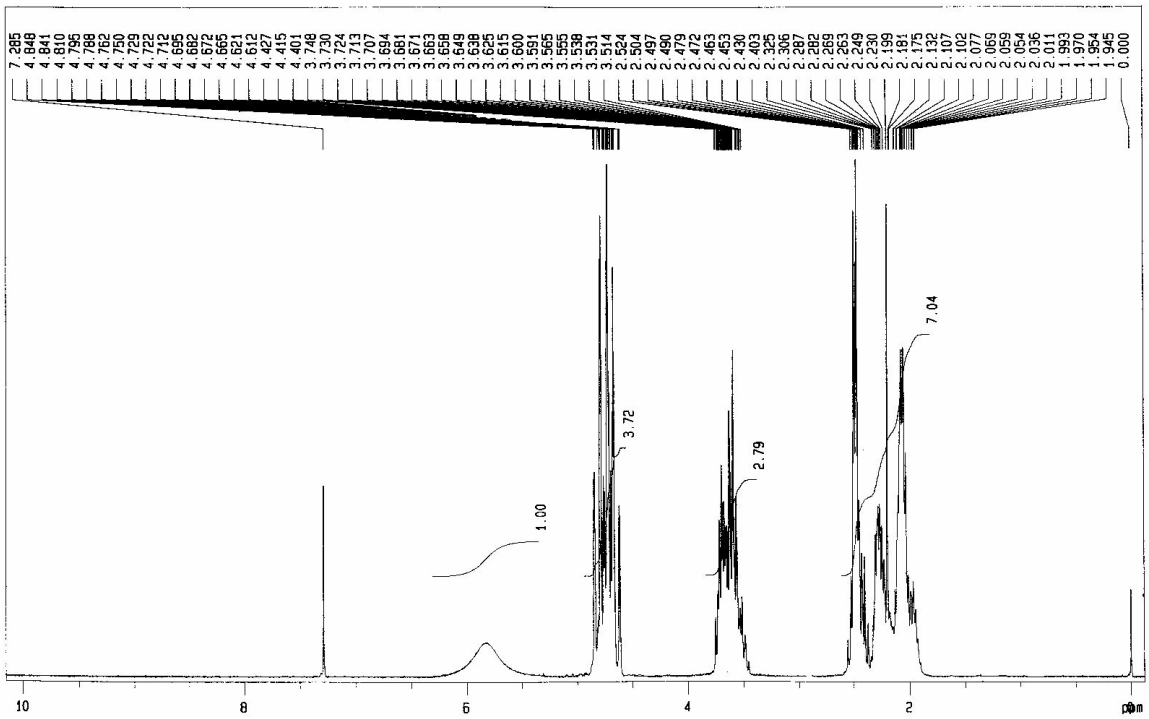


^{19}F NMR (282 MHz, $CDCl_3$)

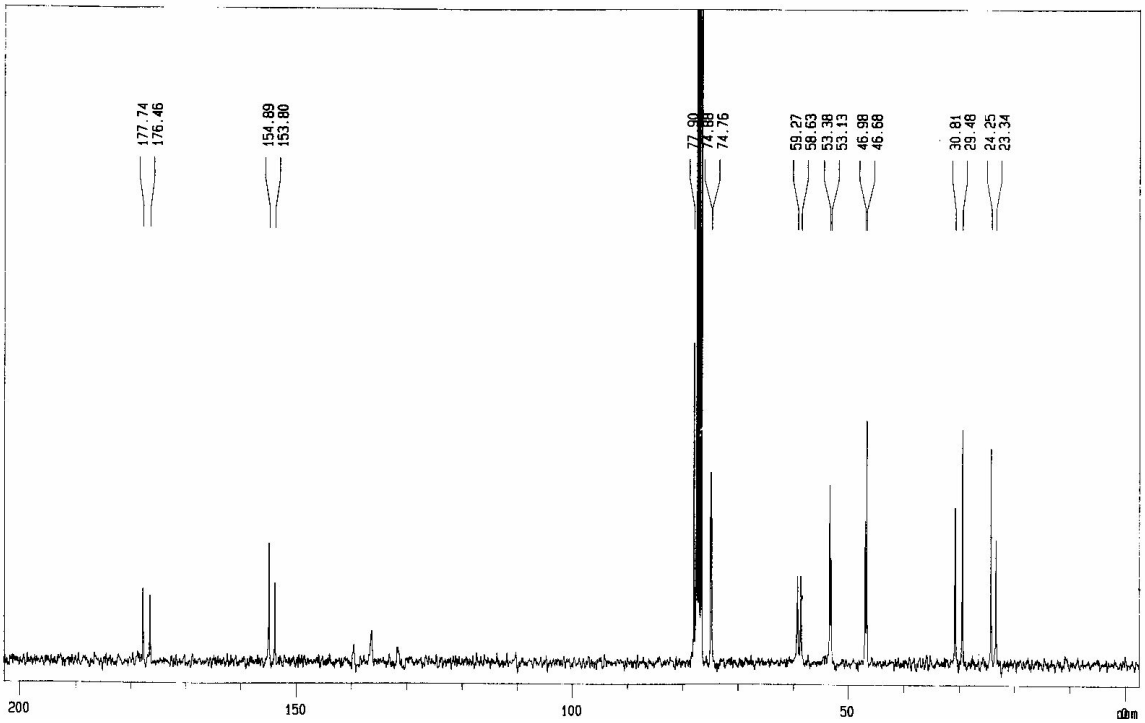


Compound 6i

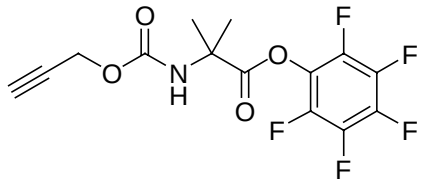
^{1}H NMR (300 MHz, $CDCl_3$)



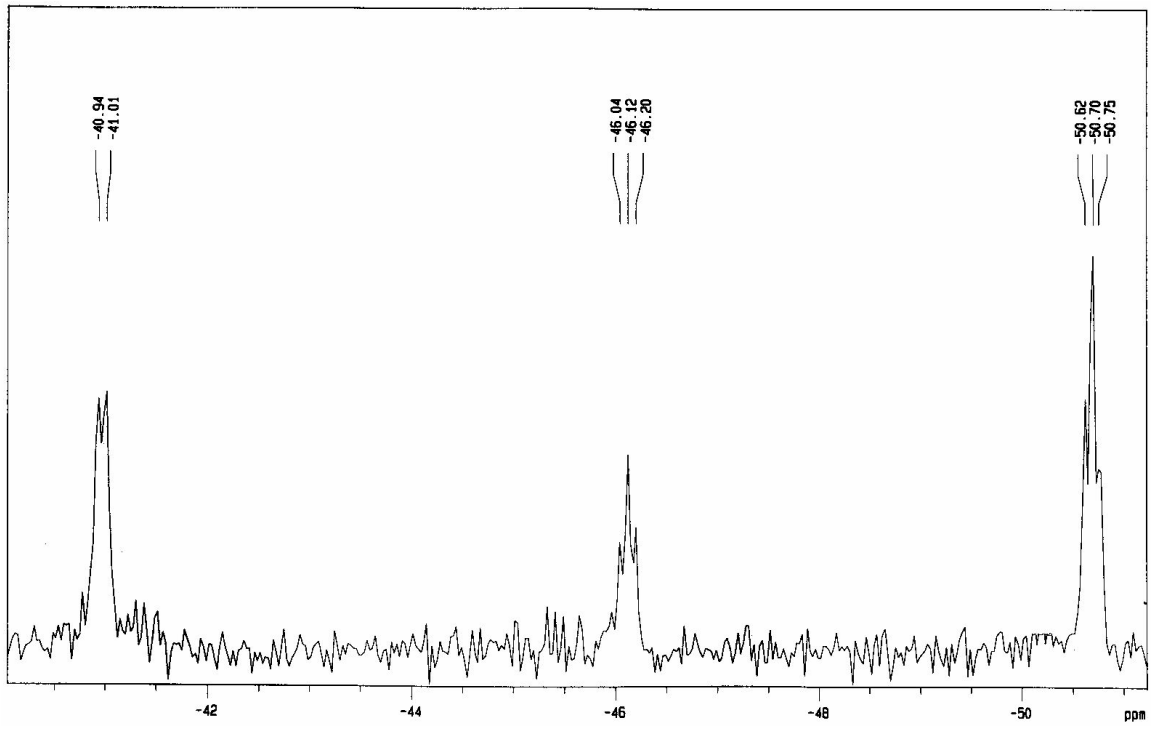
^{13}C NMR (75 MHz, $CDCl_3$)



Compound 6j

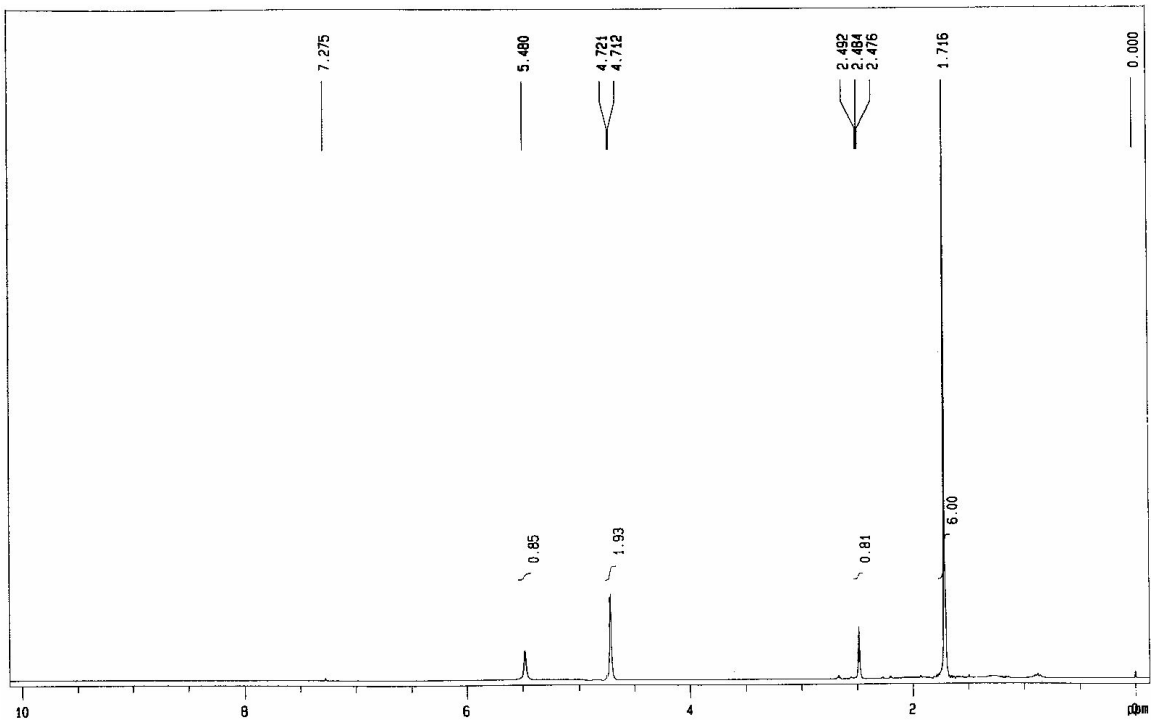


^{19}F NMR (282 MHz, $CDCl_3$)

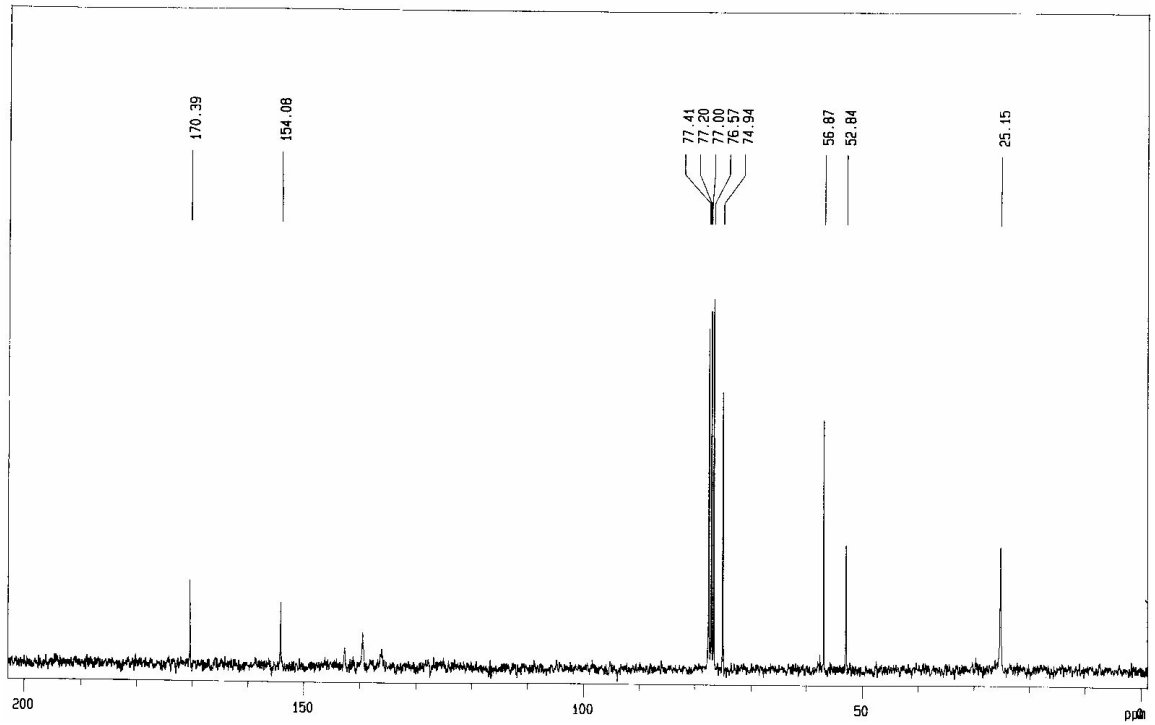


Compound 6j

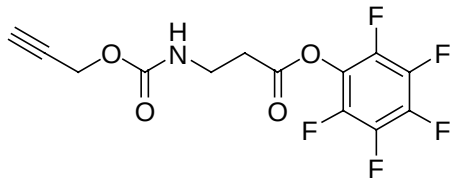
^{1}H NMR (300 MHz, $CDCl_3$)



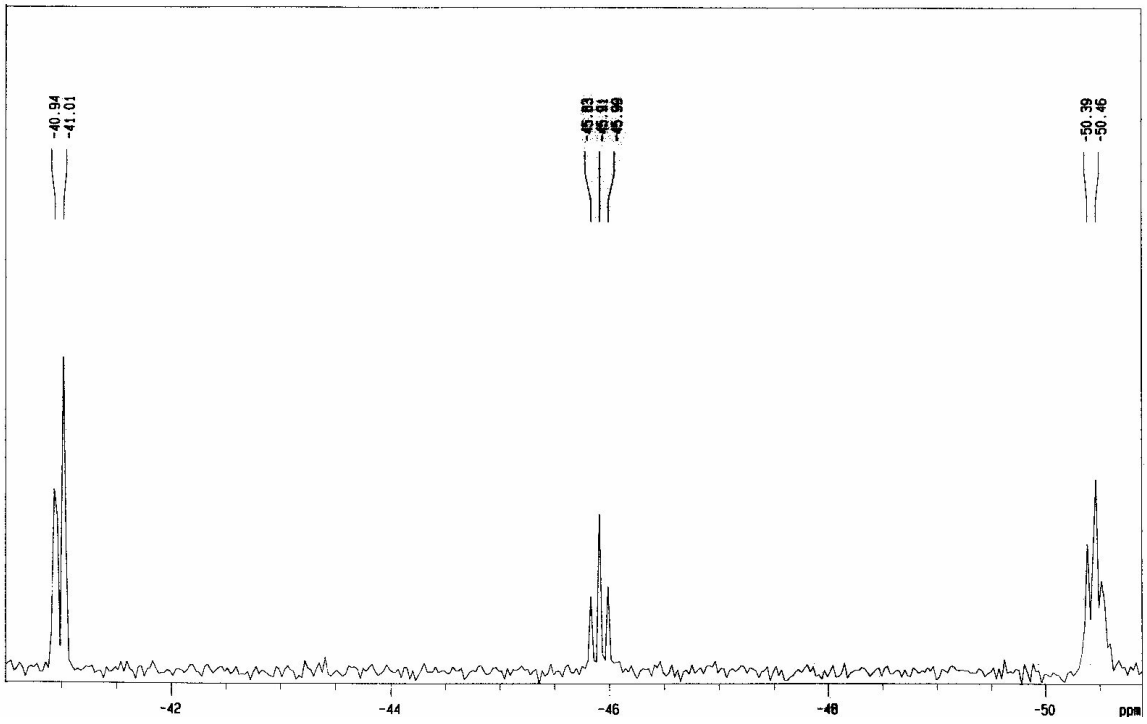
^{13}C NMR (75 Hz, $CDCl_3$)



Compound 6k

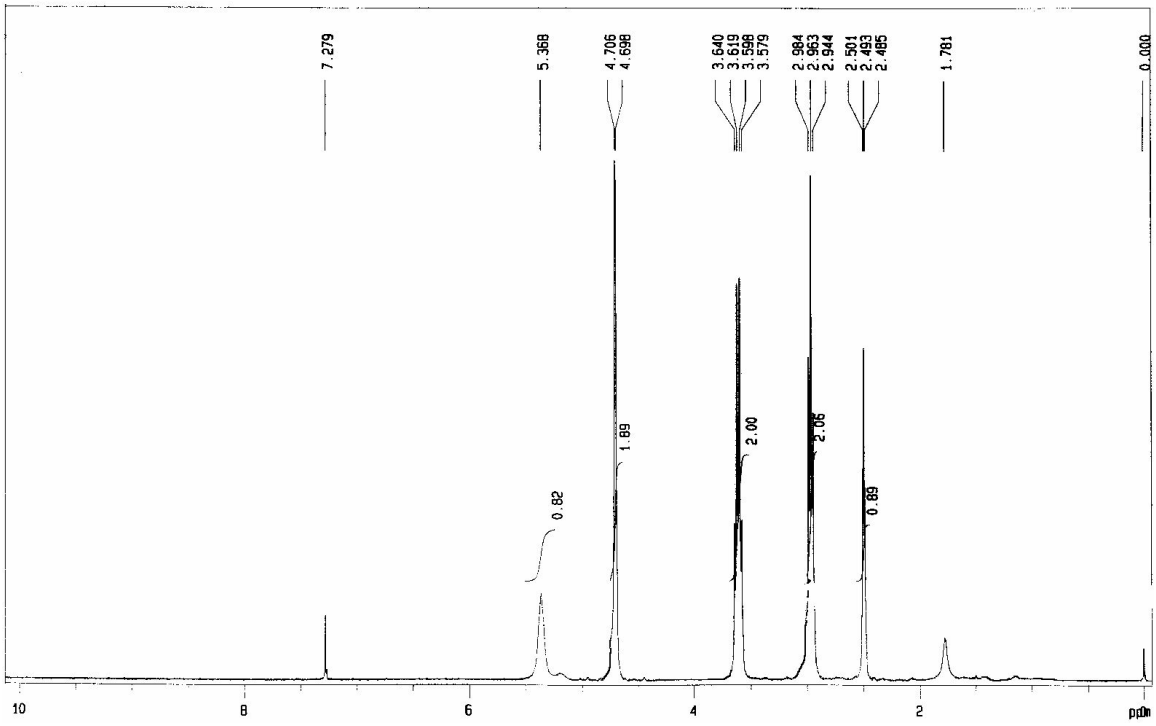


^{19}F NMR (282 MHz, $CDCl_3$)

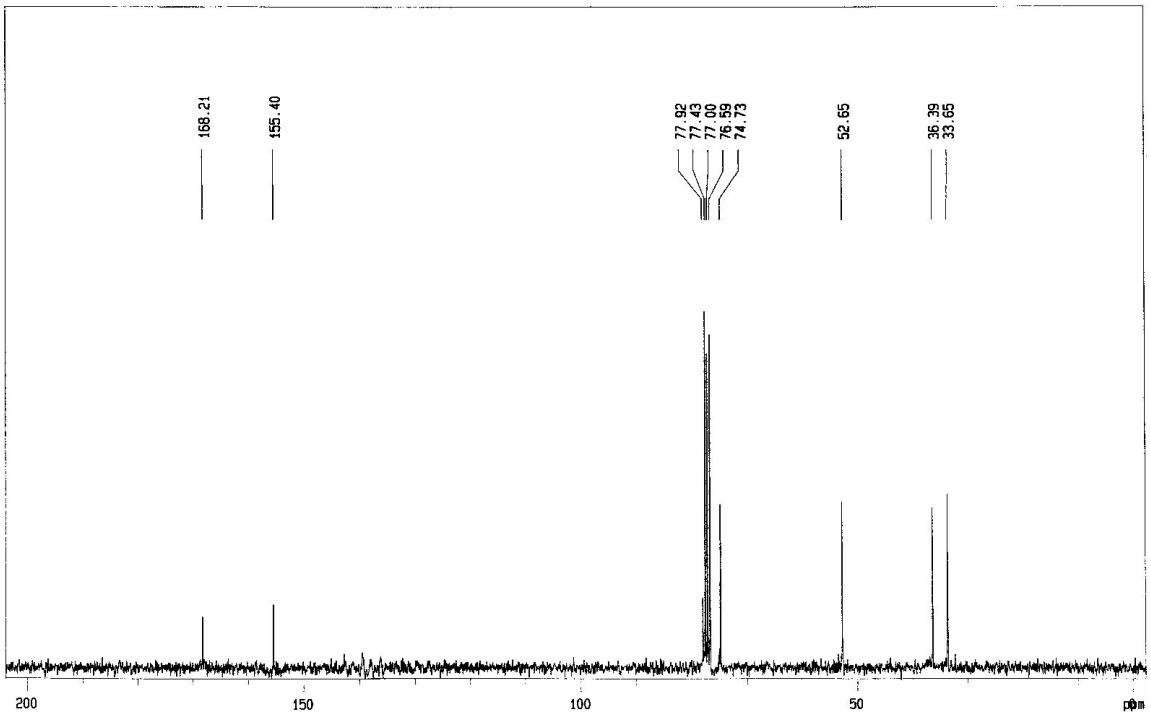


Compound 6k

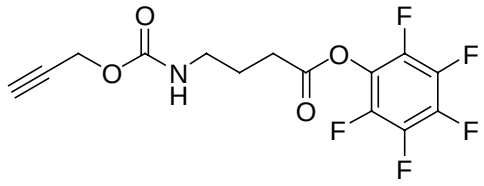
^{1}H NMR (300 MHz, $CDCl_3$)



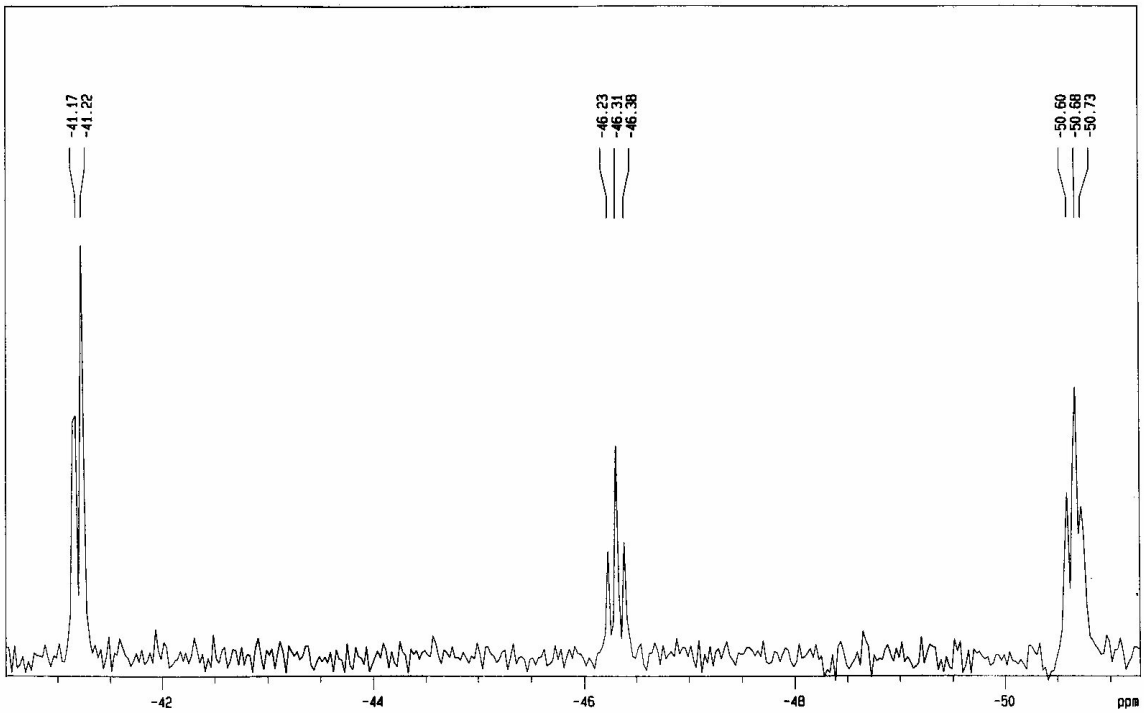
^{13}C NMR (75 MHz, $CDCl_3$)



Compound 6l

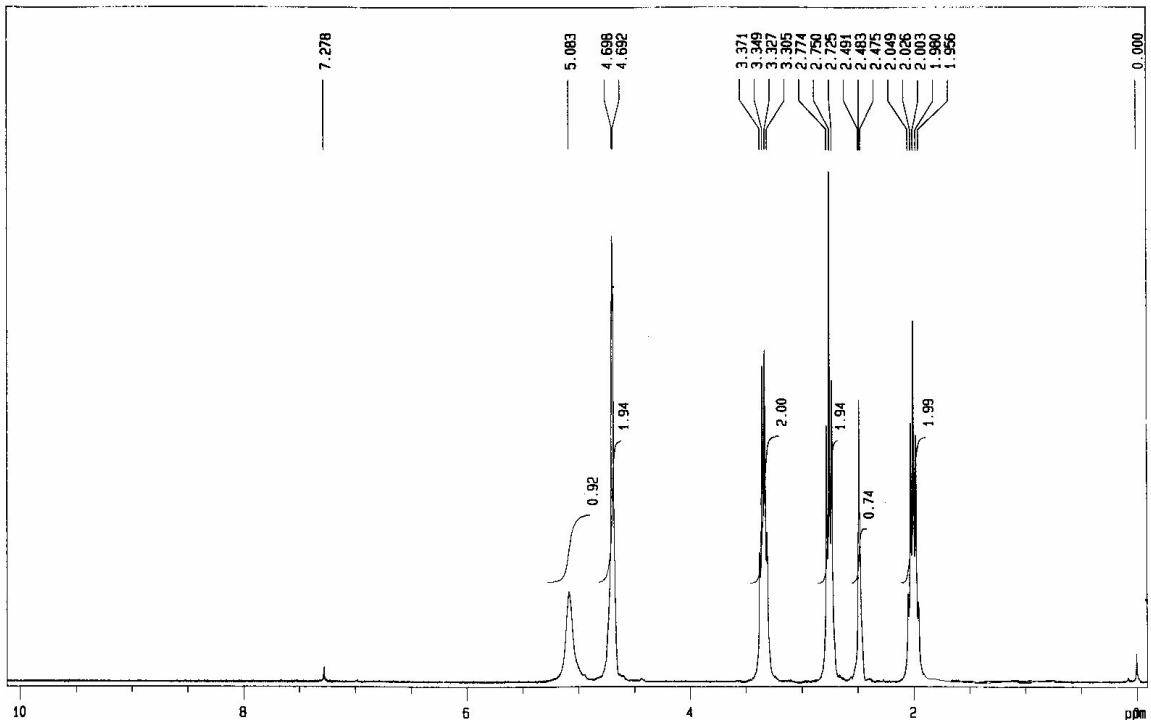


^{19}F NMR (282 MHz, $CDCl_3$)

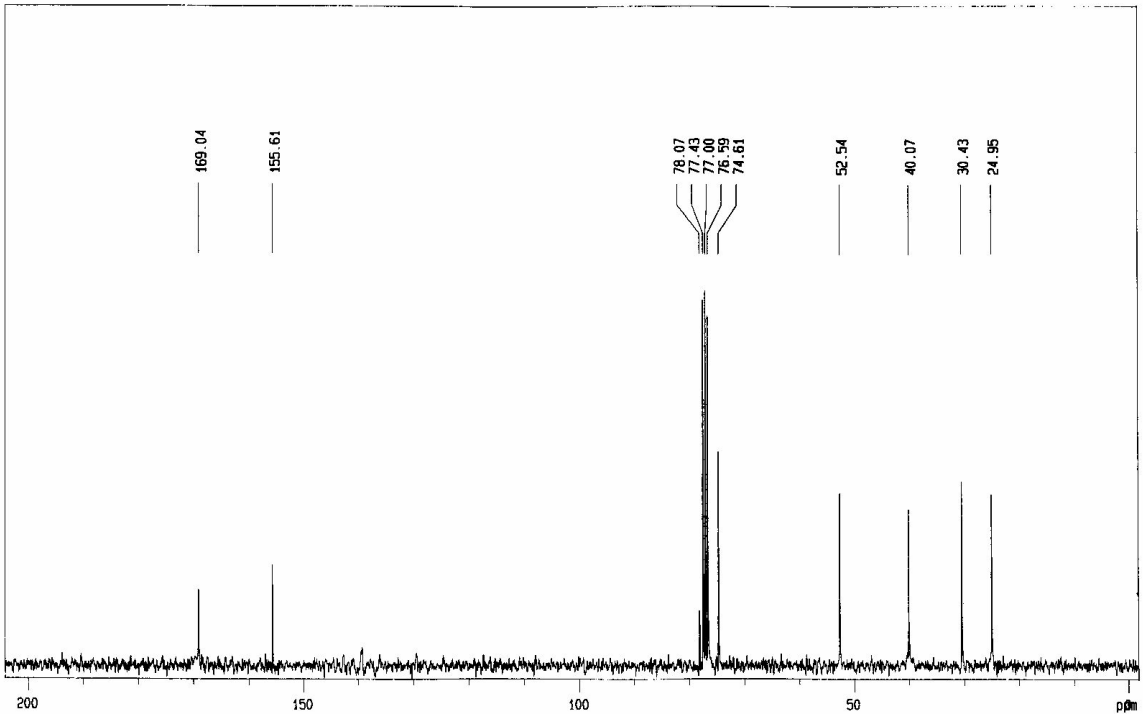


Compound 6l

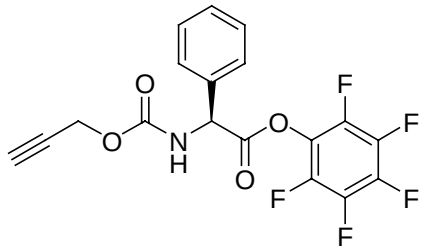
^{1}H NMR (300 MHz, $CDCl_3$)



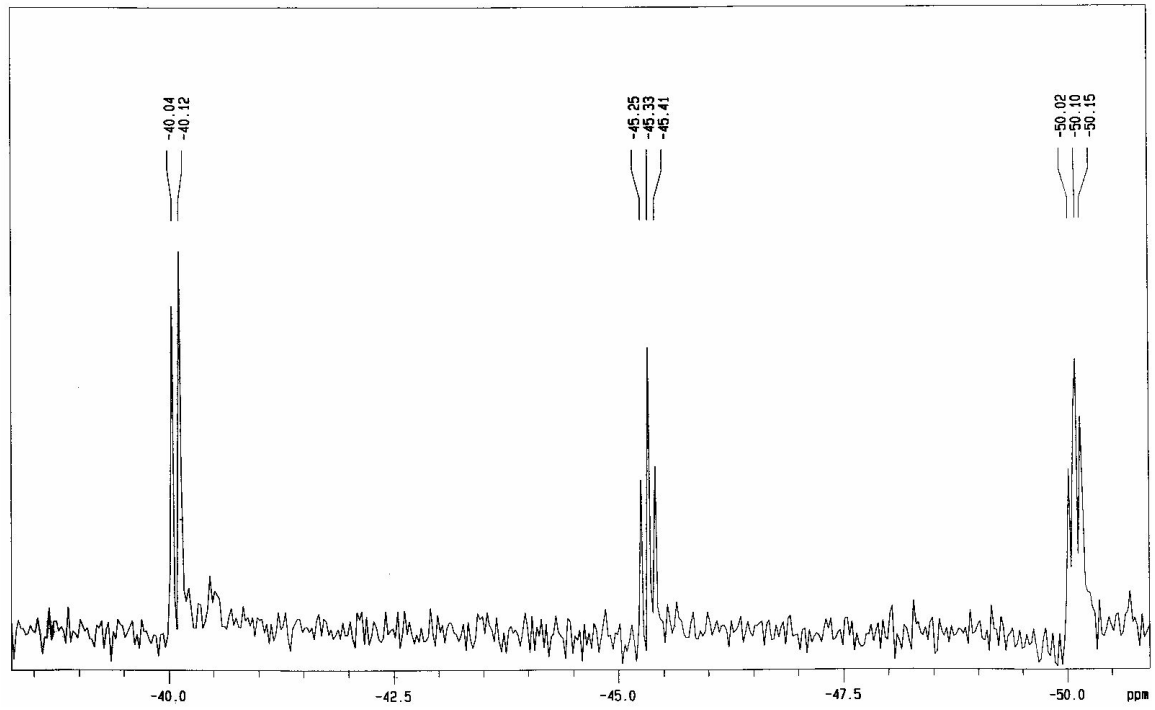
^{13}C NMR (75 MHz, $CDCl_3$)



Compound 6m

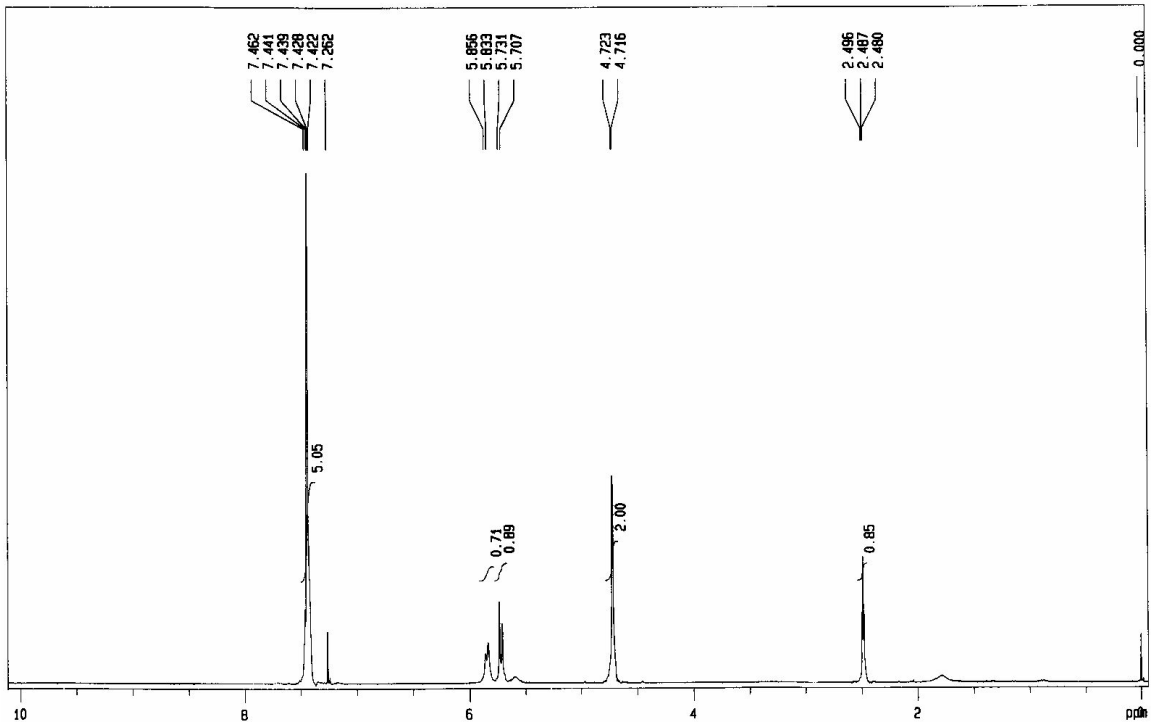


^{19}F NMR (282 MHz, $CDCl_3$)

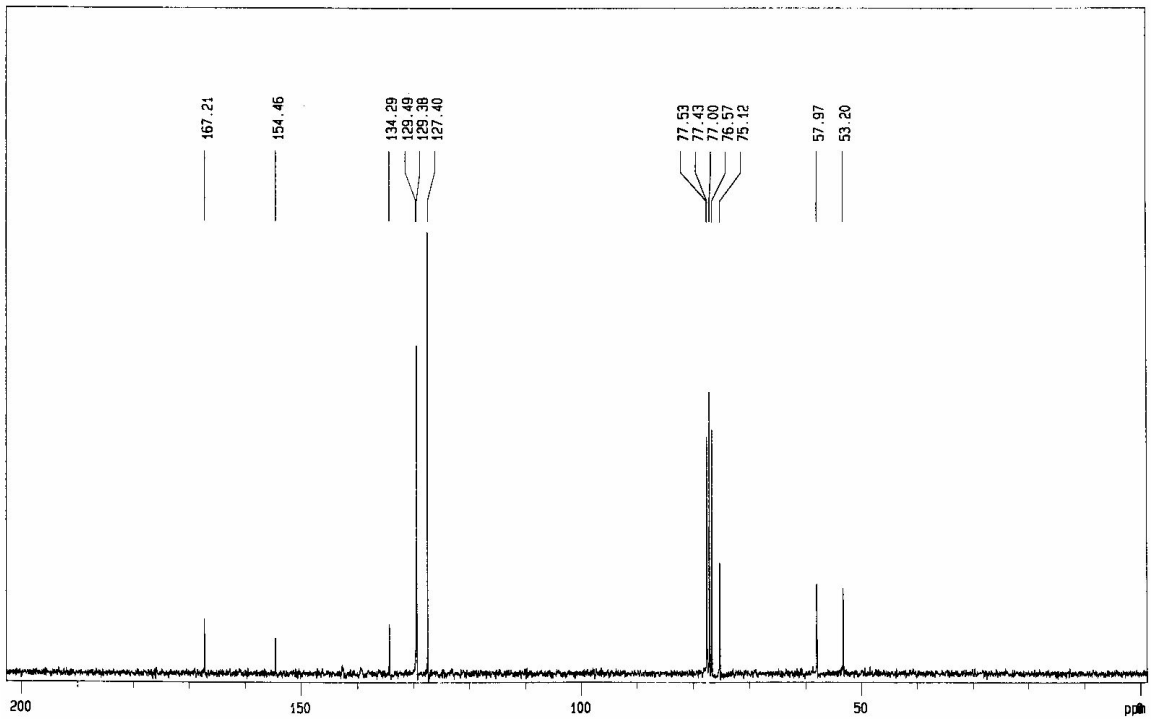


Compound 6m

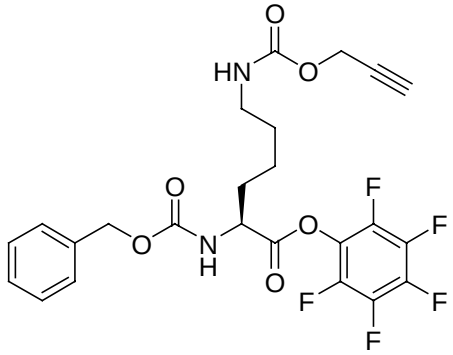
^{1}H NMR (300 MHz, $CDCl_3$)



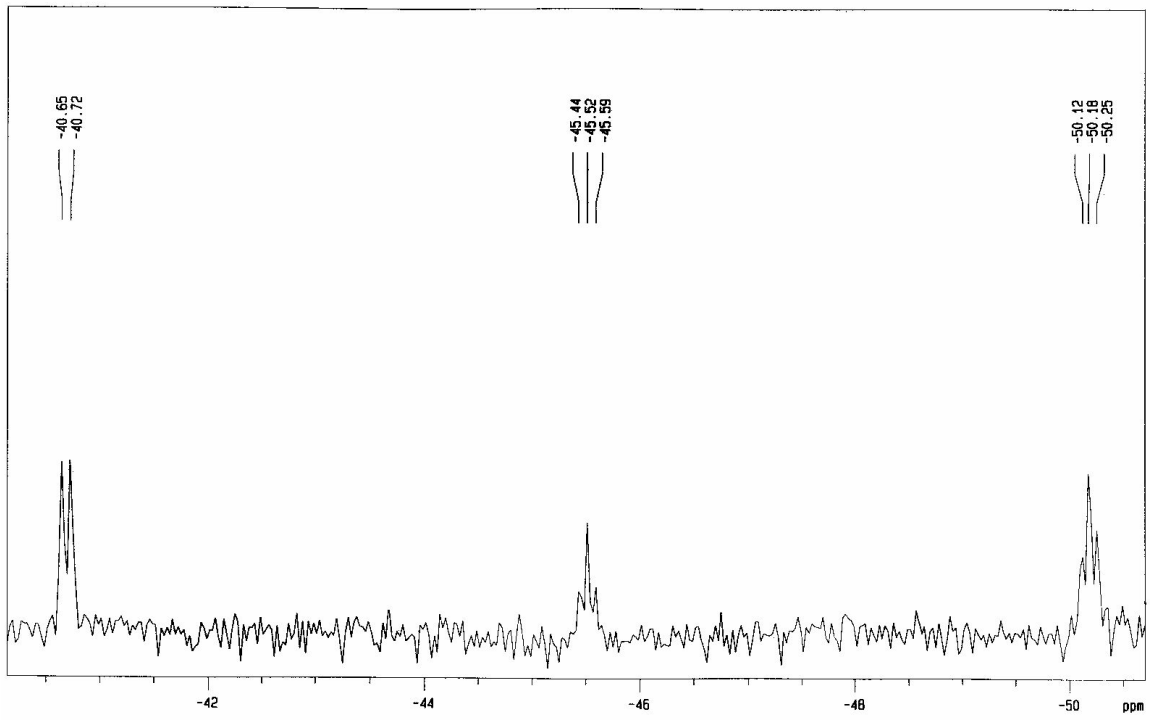
^{13}C NMR (75 MHz, $CDCl_3$)



Compound 6n

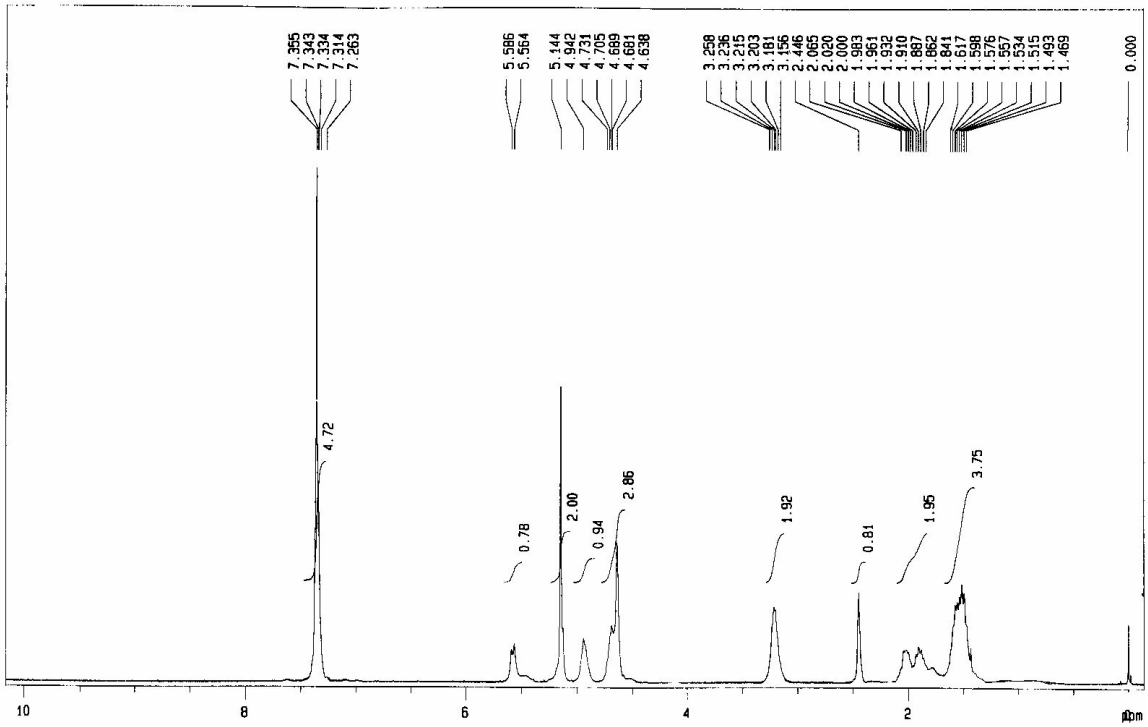


^{19}F NMR (282 MHz, $CDCl_3$)

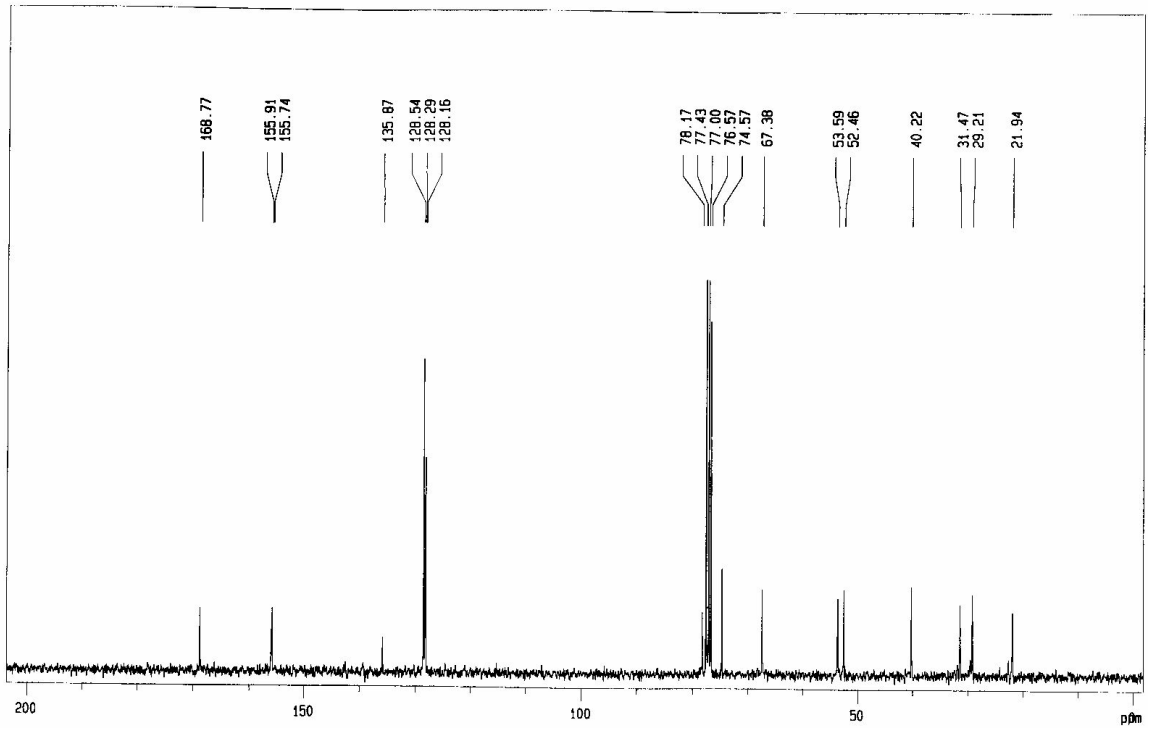


Compound 6n

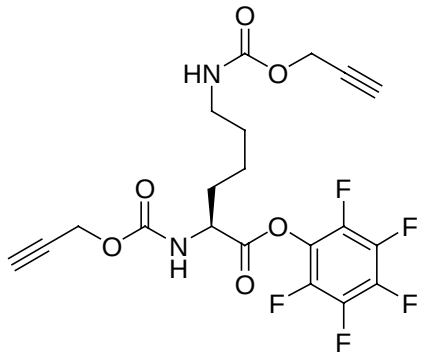
^{1}H NMR (300 MHz, $CDCl_3$)



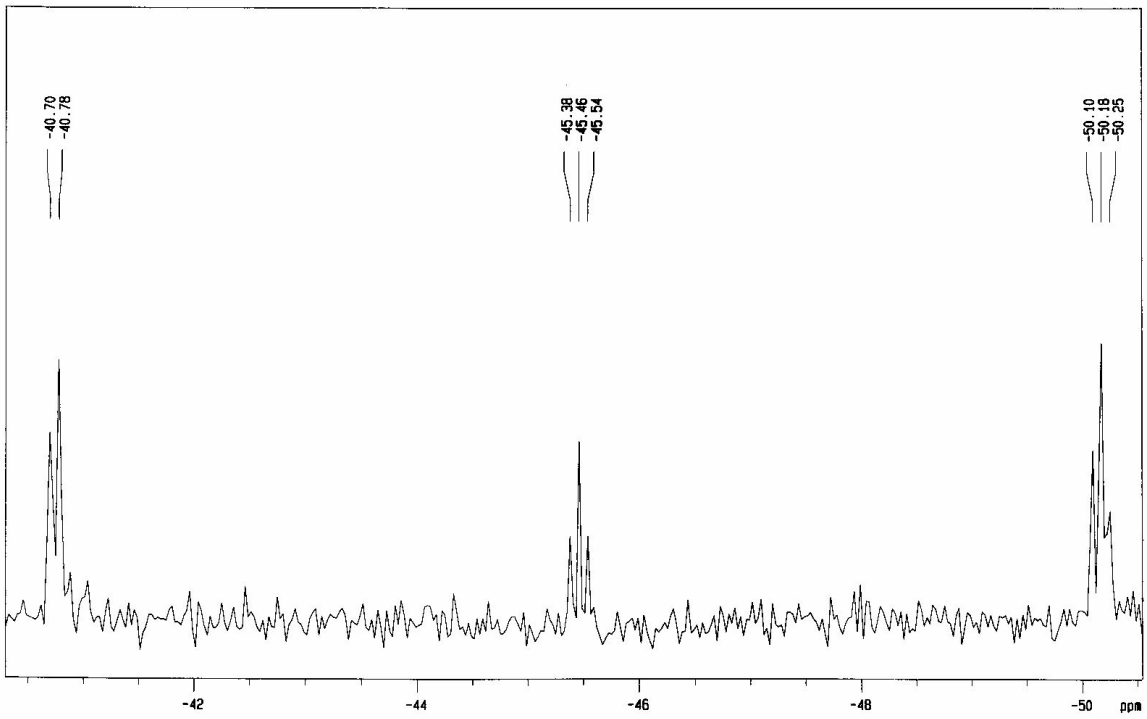
^{13}C NMR (75 MHz, $CDCl_3$)



Compound 6o

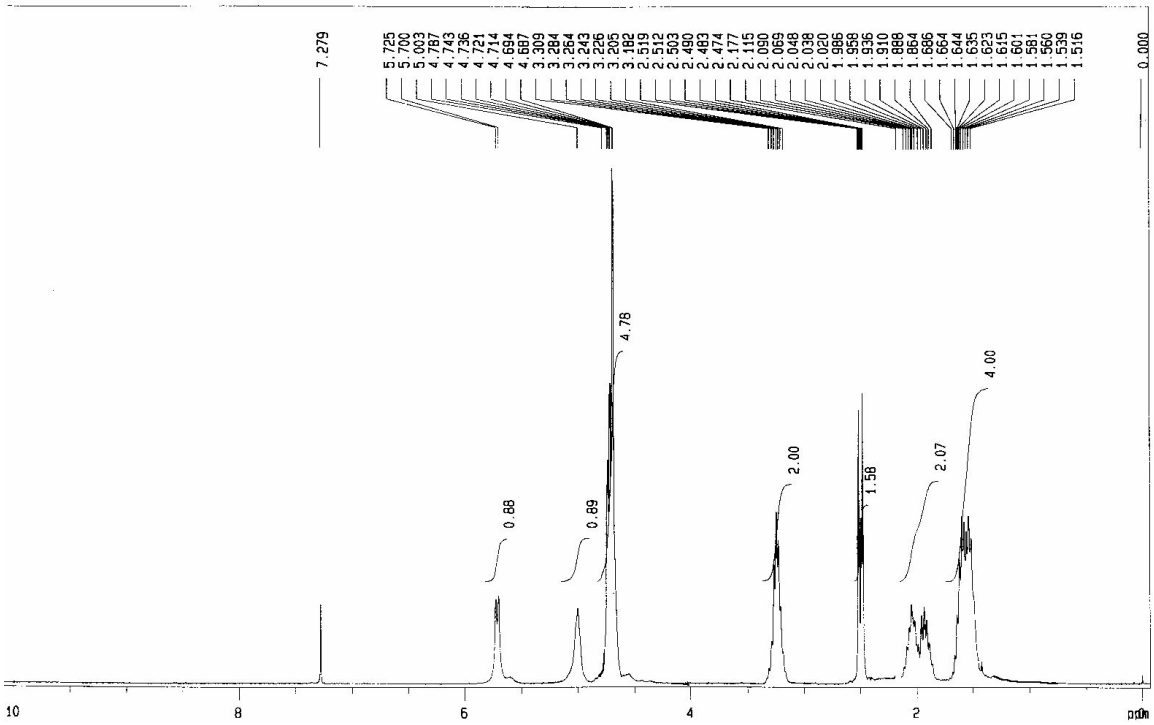


^{19}F NMR (282 MHz, $CDCl_3$)

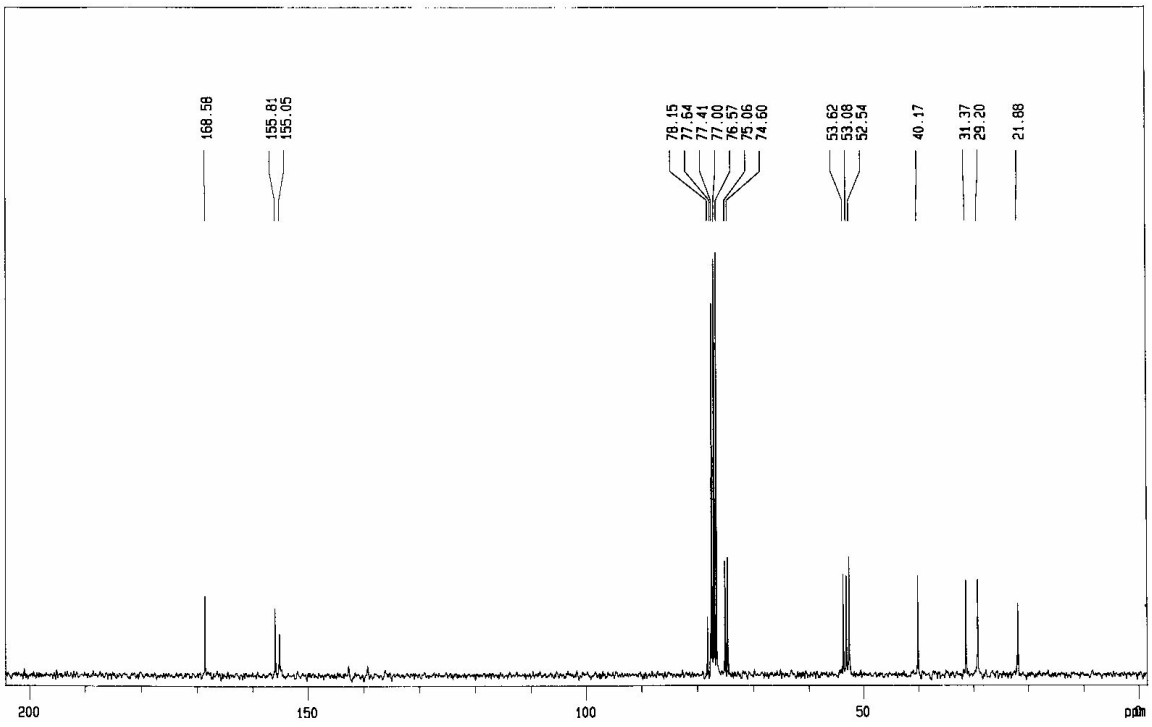


Compound 6o

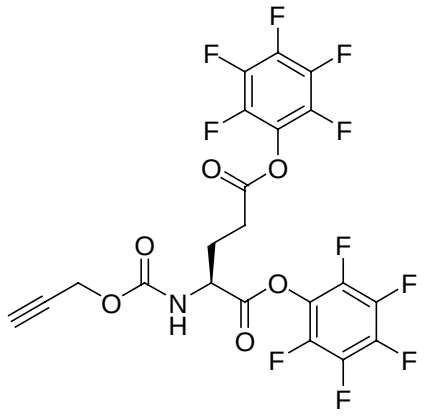
^{1}H NMR (300 MHz, $CDCl_3$)



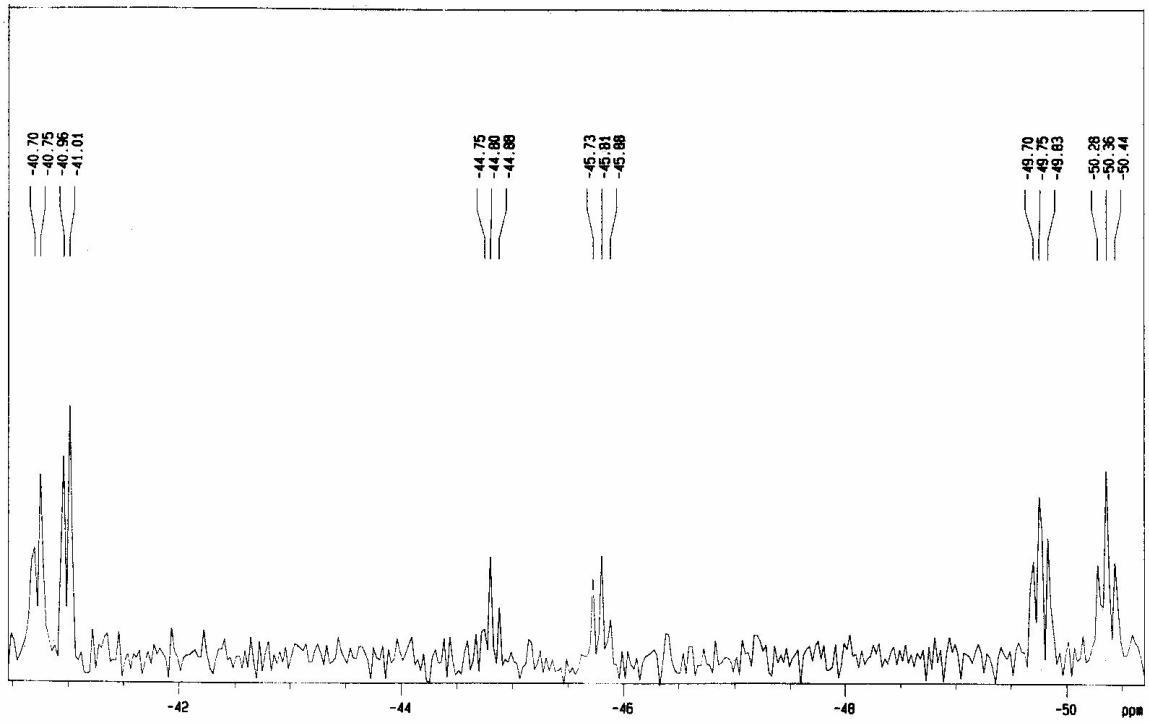
^{13}C NMR (75 MHz, $CDCl_3$)



Compound 6p

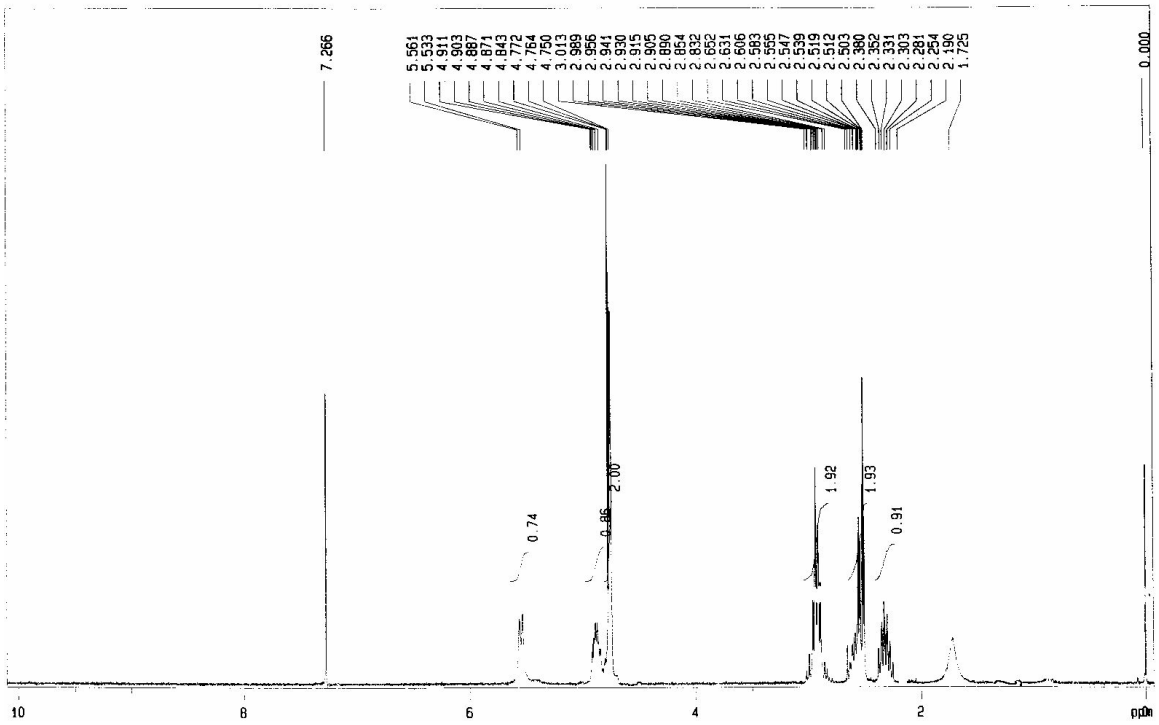


^{19}F NMR (282 MHz, $CDCl_3$)

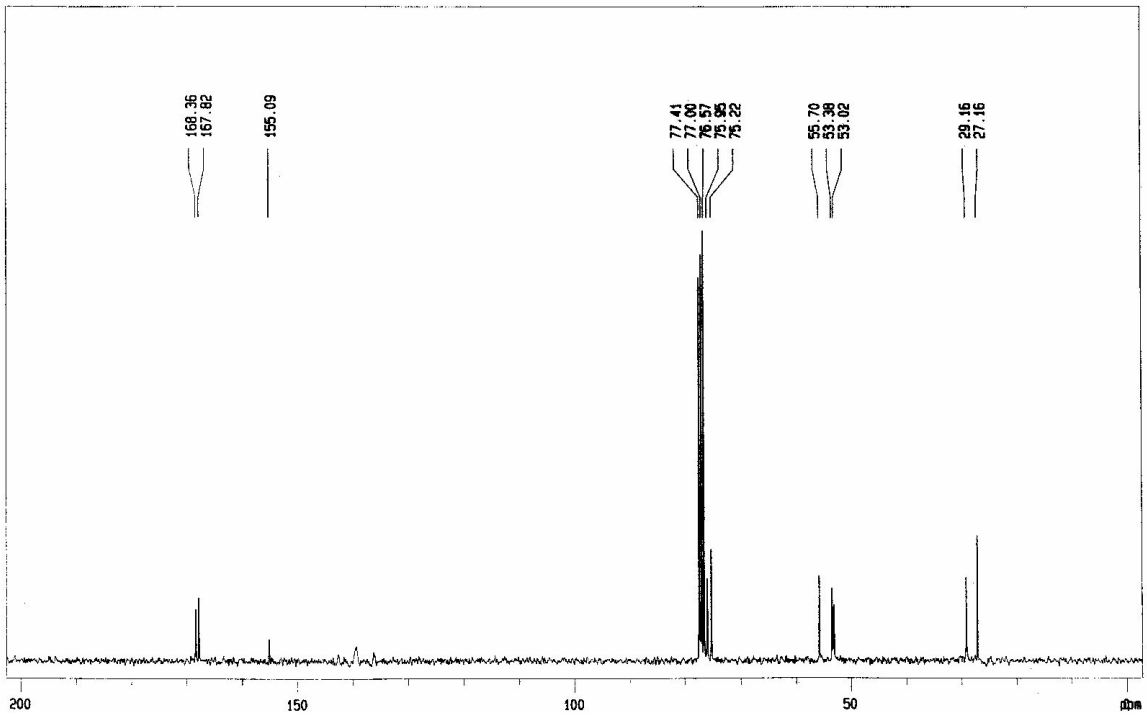


Compound 6p

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

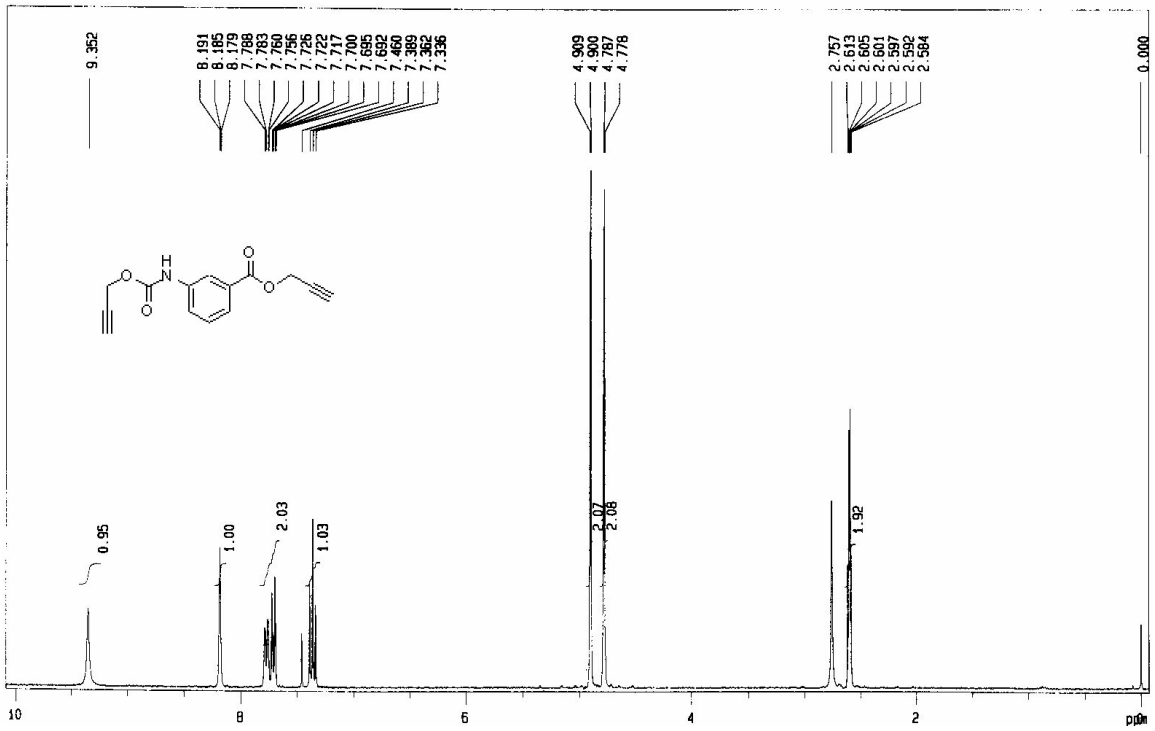


^{13}C NMR (75 MHz, $CDCl_3$)



Compound 10

^{1}H NMR (300 MHz, $CDCl_3/CD_3SOCD_3$)



^{13}C NMR (75 MHz, $CDCl_3/CD_3SOCD_3$)