Electronic Supplementary Material (ESI) for Analyst.

Supporting information

Triphenylcyclopropenylium mass tag: synthesis and application to ultrasensitive LC/MS assay of amines

Artyom P. Topolyan,[a] Dina A. Strizhevskaya,[a] Maria A. Belyaeva,[a] Vladimir A. Brylev,[a] Alexey V. Ustinov,[a,b] Andrey A. Formanovsky,[a] Vladimir A. Korshun[a,c]

[a] Shemyakin-Ovchinnikov Institute of Bioorganic Chemistry, 117997 Moscow, Russian Federation;

[b] Lumiprobe Corp., Hallandale Beach, FL 33009, USA

[c] Gause Institute of New Antibiotics, 119021 Moscow, Russian Federation

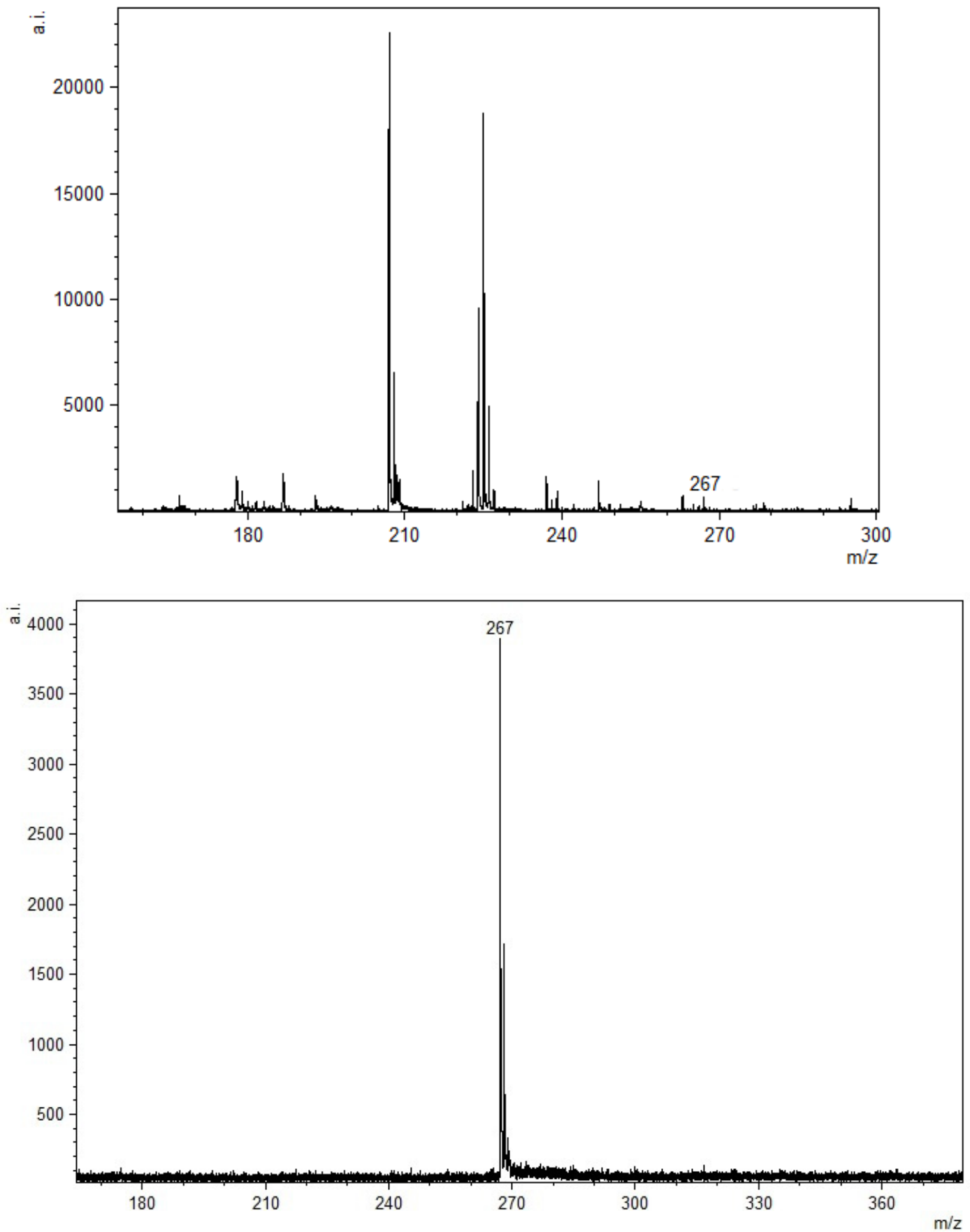
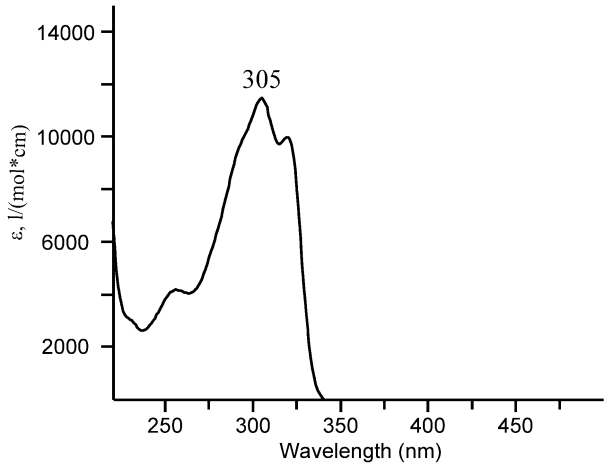
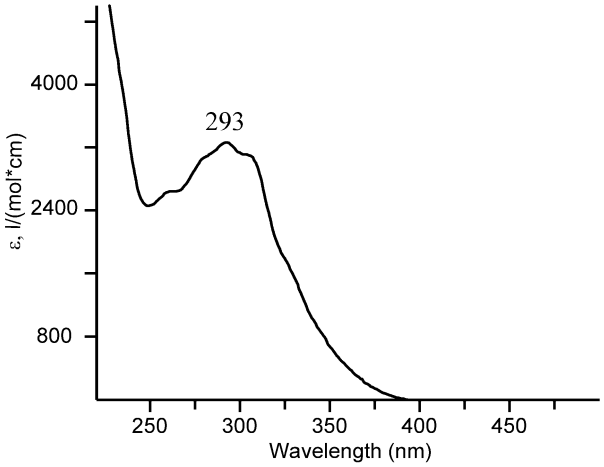


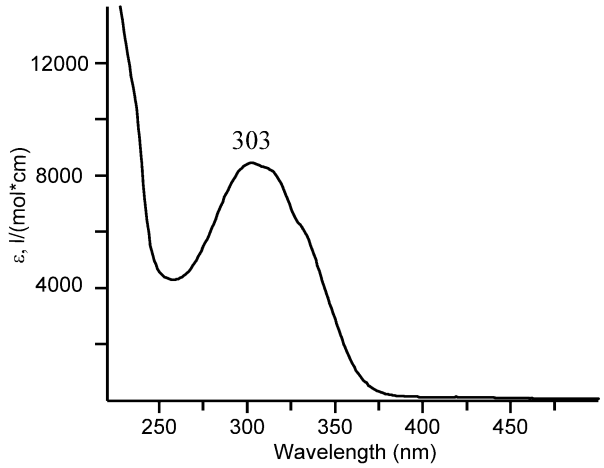
Figure S1. Mass spectra of **1·BF_4**. $1 \cdot 10^{-11}$ mole per sample spot in MALDI, CHCA matrix (top panel). $1 \cdot 10^{-9}$ mole per sample spot in LDI (bottom panel).



Compound **1** ($0.1 \cdot 10^{-4}$ M in MeCN)

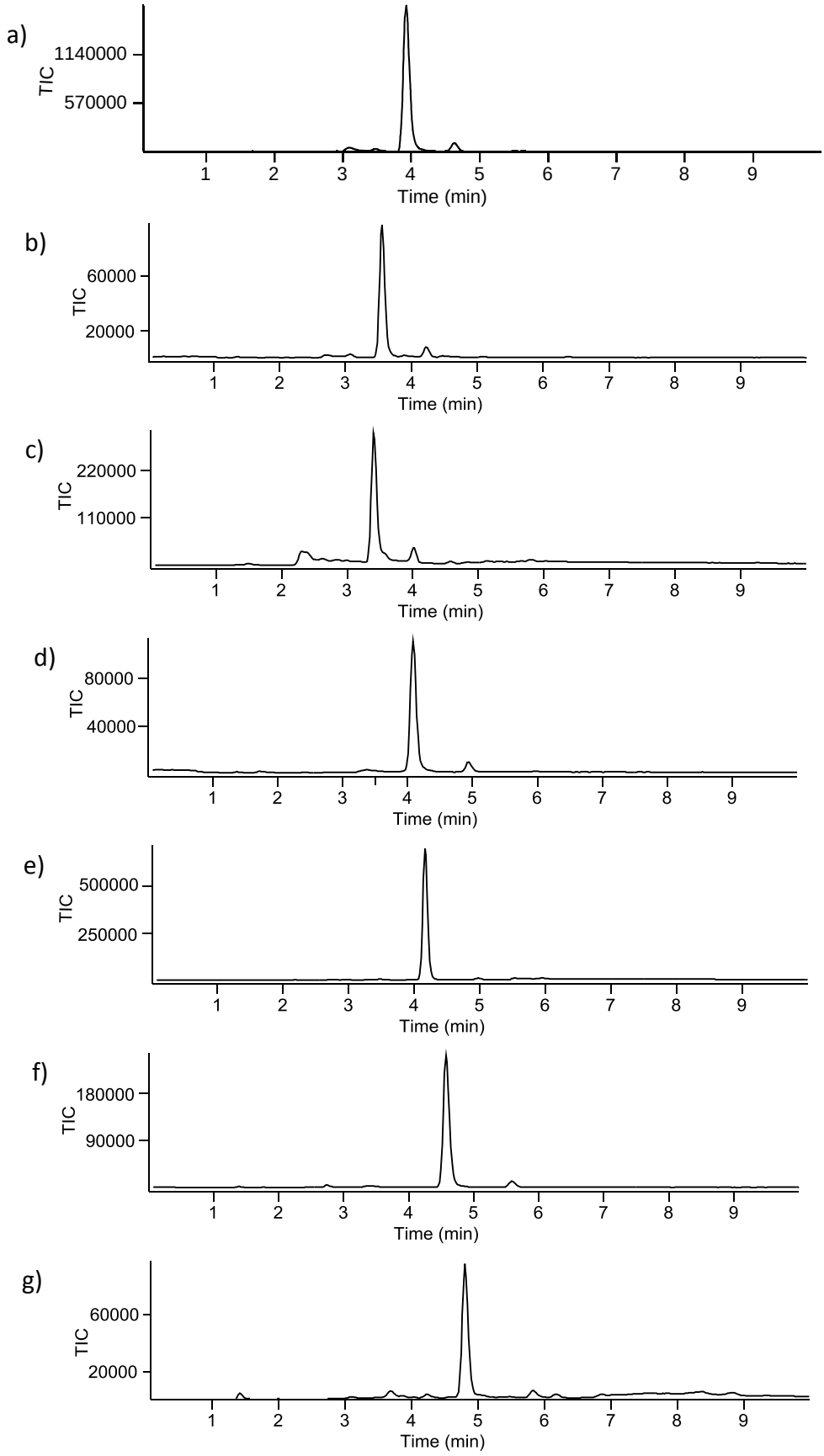


Compound **4a** ($0.9 \cdot 10^{-4}$ M, MeCN)



Compound **4i** ($0.5 \cdot 10^{-4}$M in MeCN)

Figure S2. UV spectra of selected compounds.


a)
TIC
1140000
570000
1 2 3 4 5 6 7 8 9
Time (min)
b)
TIC
60000
20000
1 2 3 4 5 6 7 8 9
Time (min)
c)
TIC
220000
110000
1 2 3 4 5 6 7 8 9
Time (min)
d)
TIC
80000
40000
1 2 3 4 5 6 7 8 9
Time (min)
e)
TIC
500000
250000
1 2 3 4 5 6 7 8 9
Time (min)
f)
TIC
180000
90000
1 2 3 4 5 6 7 8 9
Time (min)
g)
TIC
60000
20000
1 2 3 4 5 6 7 8 9
Time (min)

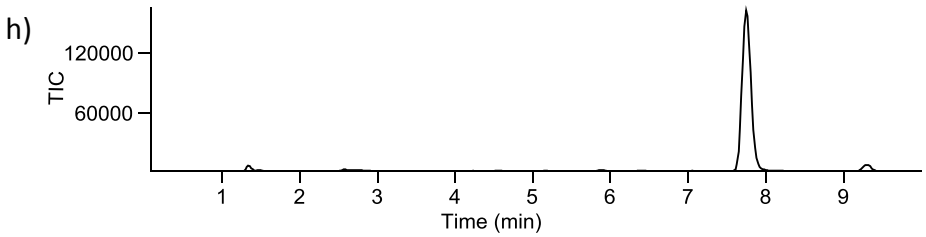


Figure S3. Single-ion mode (m/z = 267) HPLC/ESI-MS analysis of amides **8** prepared in situ by quenching of MeCN solution of **7** (a) by an excess of ammonia (b), $HO(CH_2)_4NH_2$ (c), isopropylamine (d), benzylamine (e), pyrrolidine (f), 1-pentylamine (g), 1-decylanine (h); ca. 4 pmol of **8** per sample.

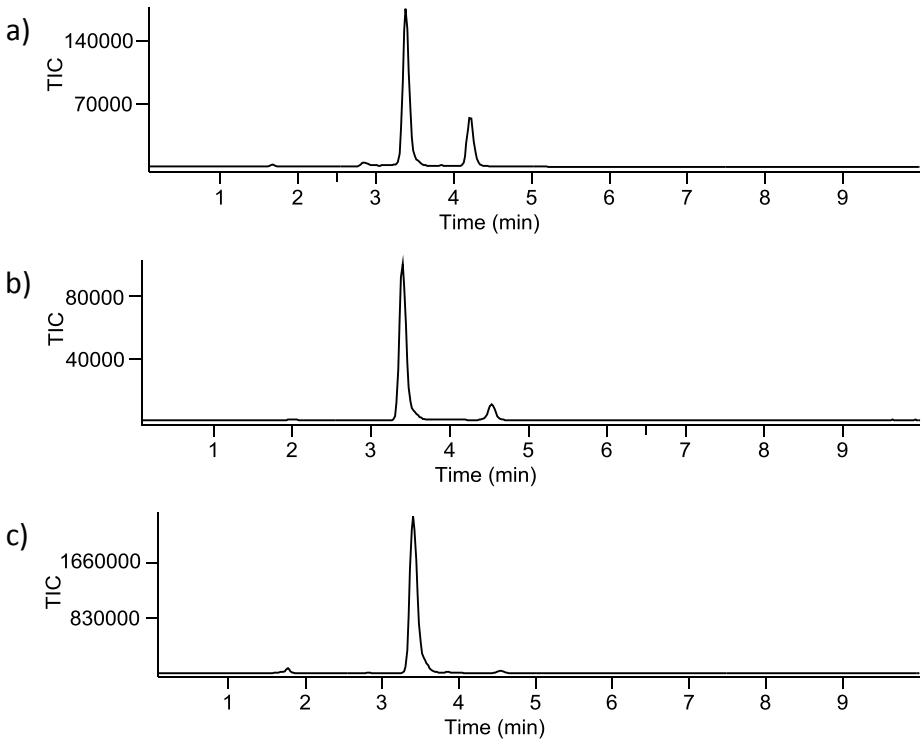
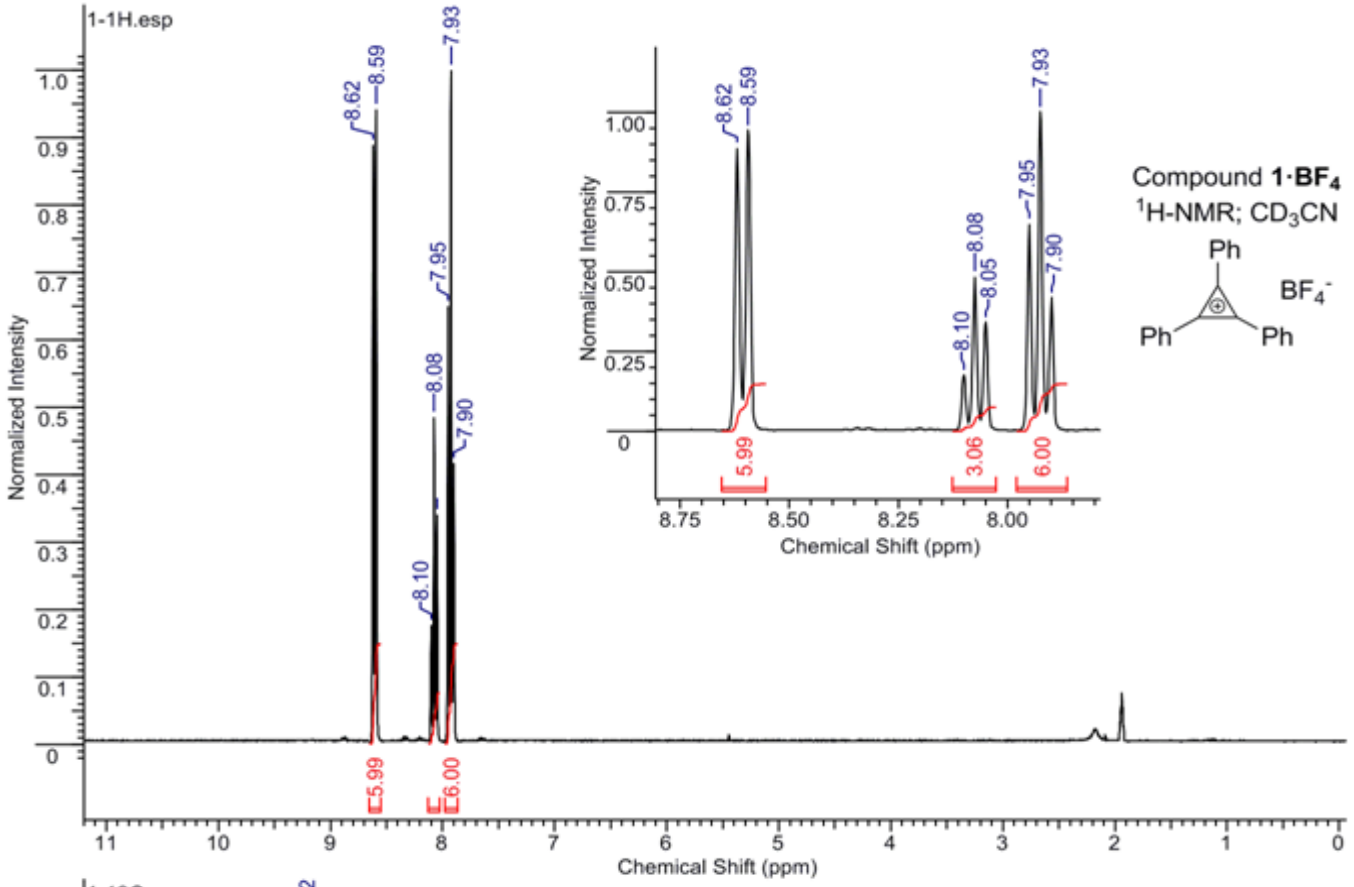
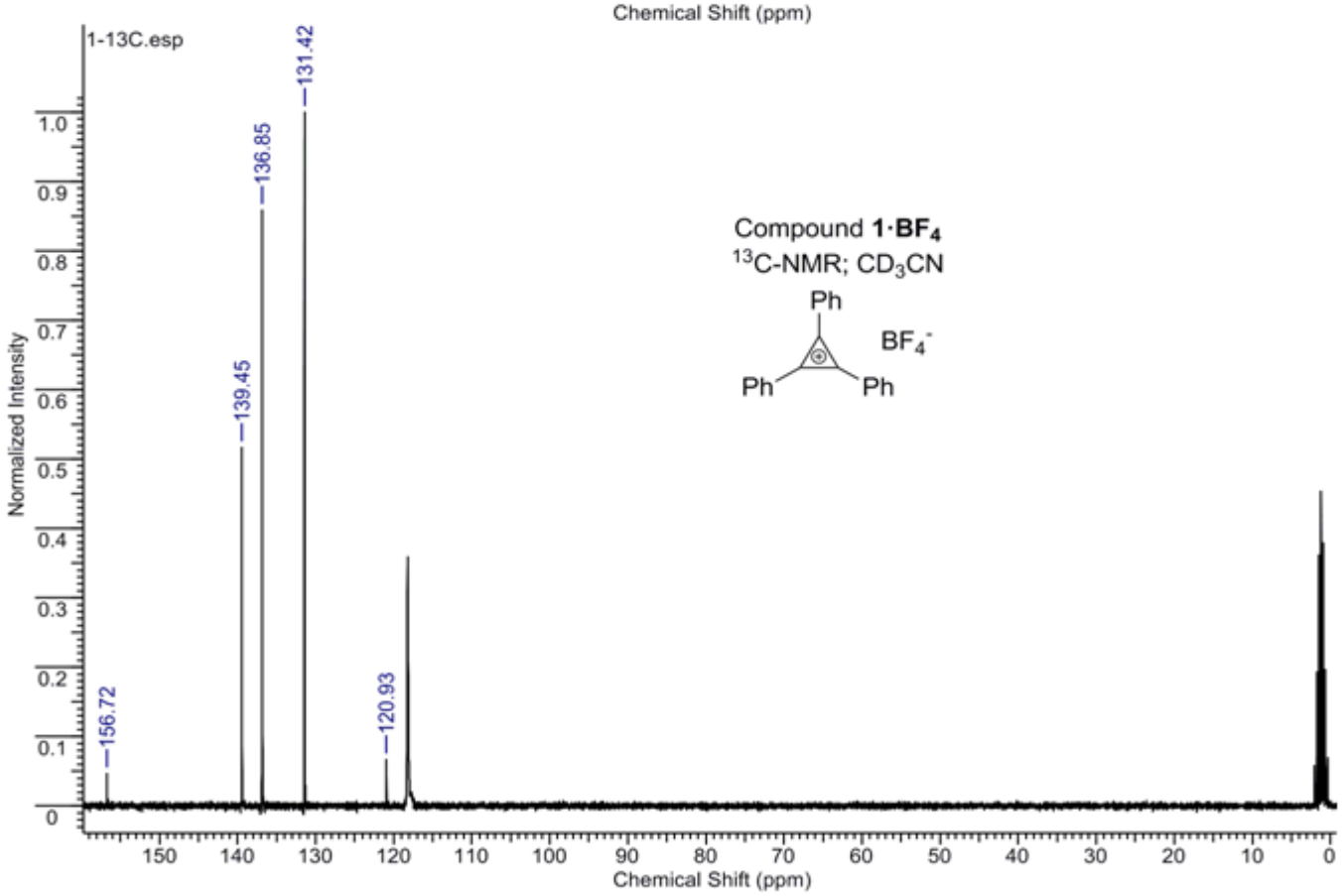


Figure S4. Single-ion mode (m/z = 267) HPLC/ESI-MS profile of pairs of compounds 8, R = $(CH_2)_4OH$ and R = *n*-C_3H_7, 3:1 ratio (a); R = $(CH_2)_4OH$ and R = *n*-C_4H_9, 10:1 ratio (b), 100:1 ratio (c).

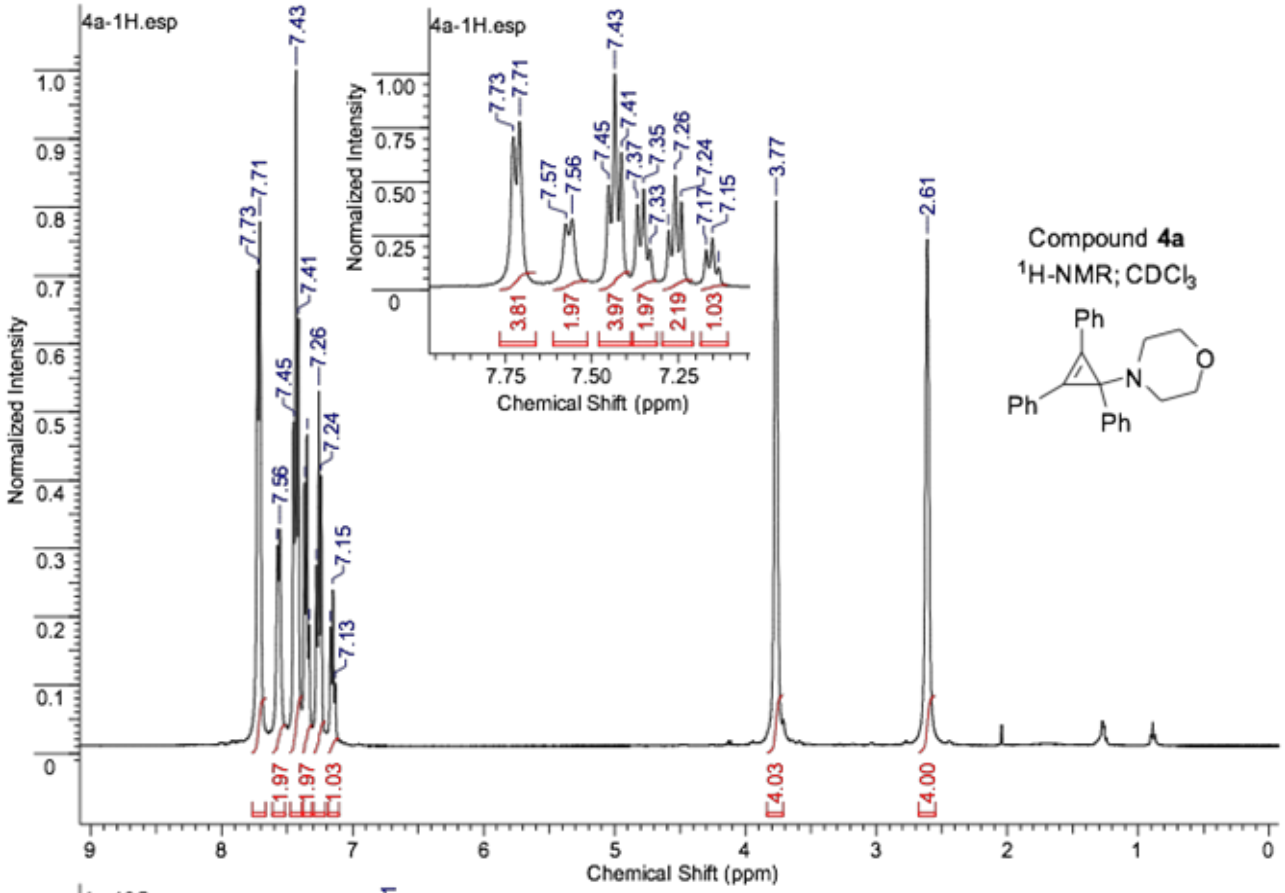
NMR spectra of synthesized compounds

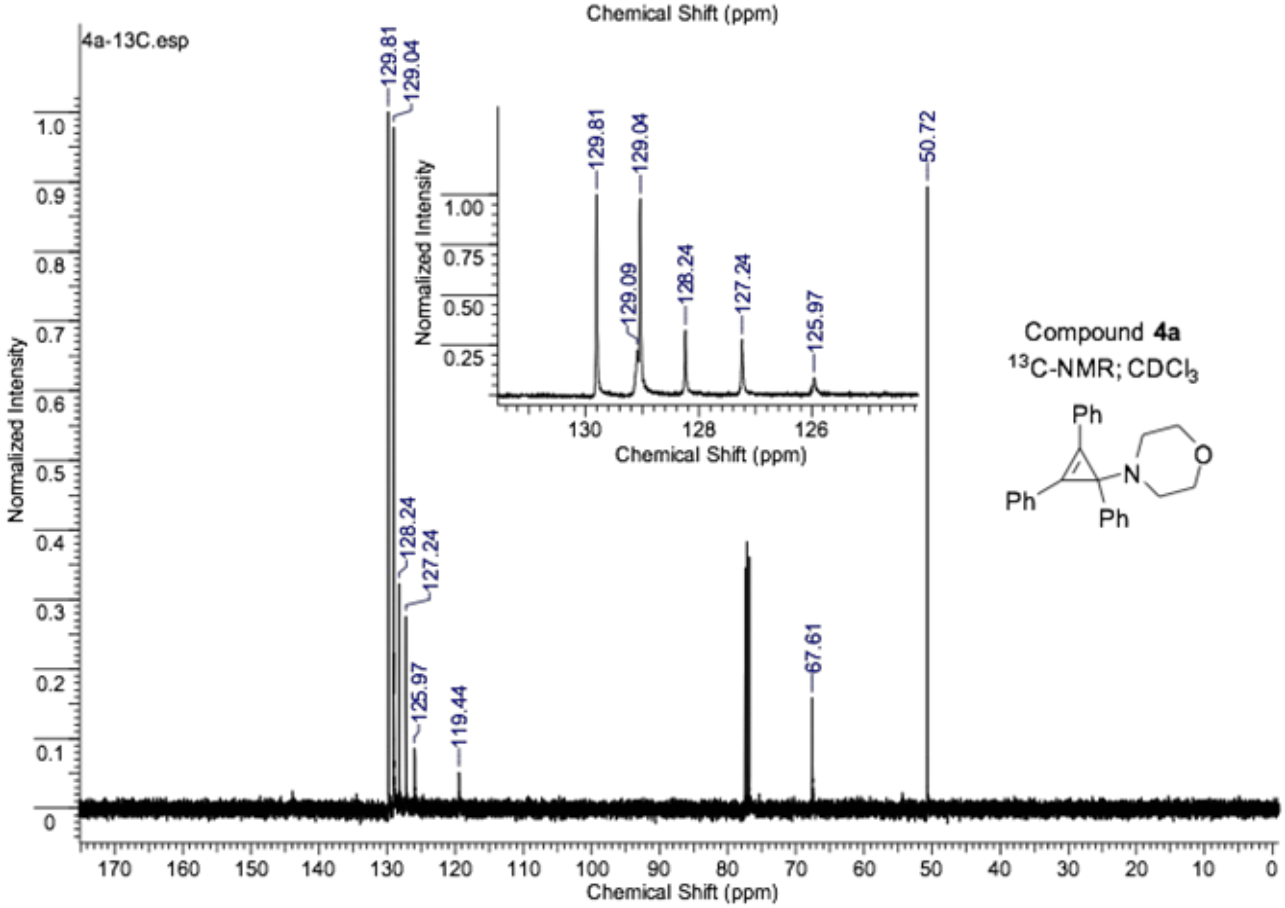
Triphenylcyclopropenylium tetrafluoroborate (**1·BF_4**)



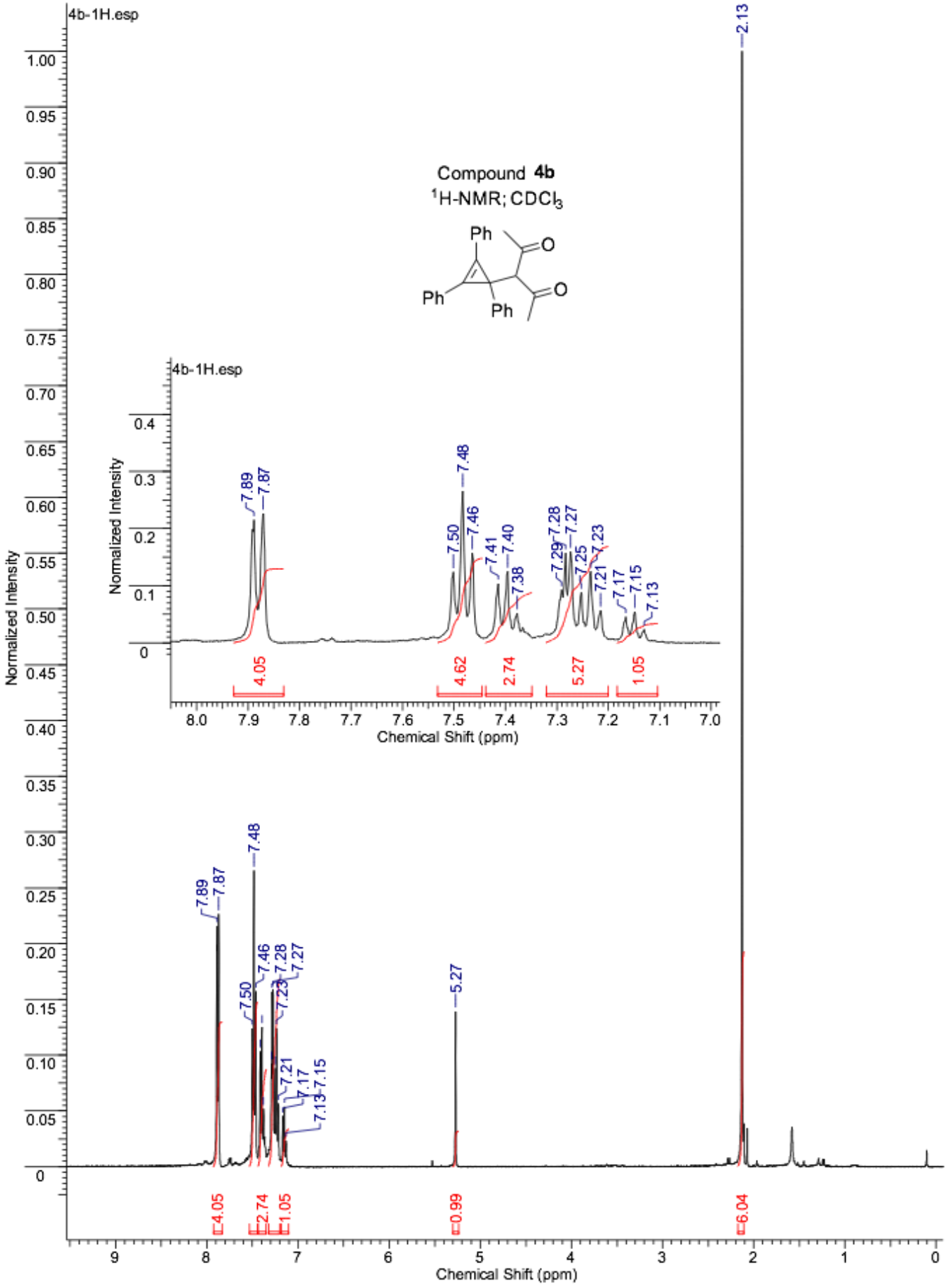


N-(Triphenylcyclopropen-3-yl)morpholine (**4a**)

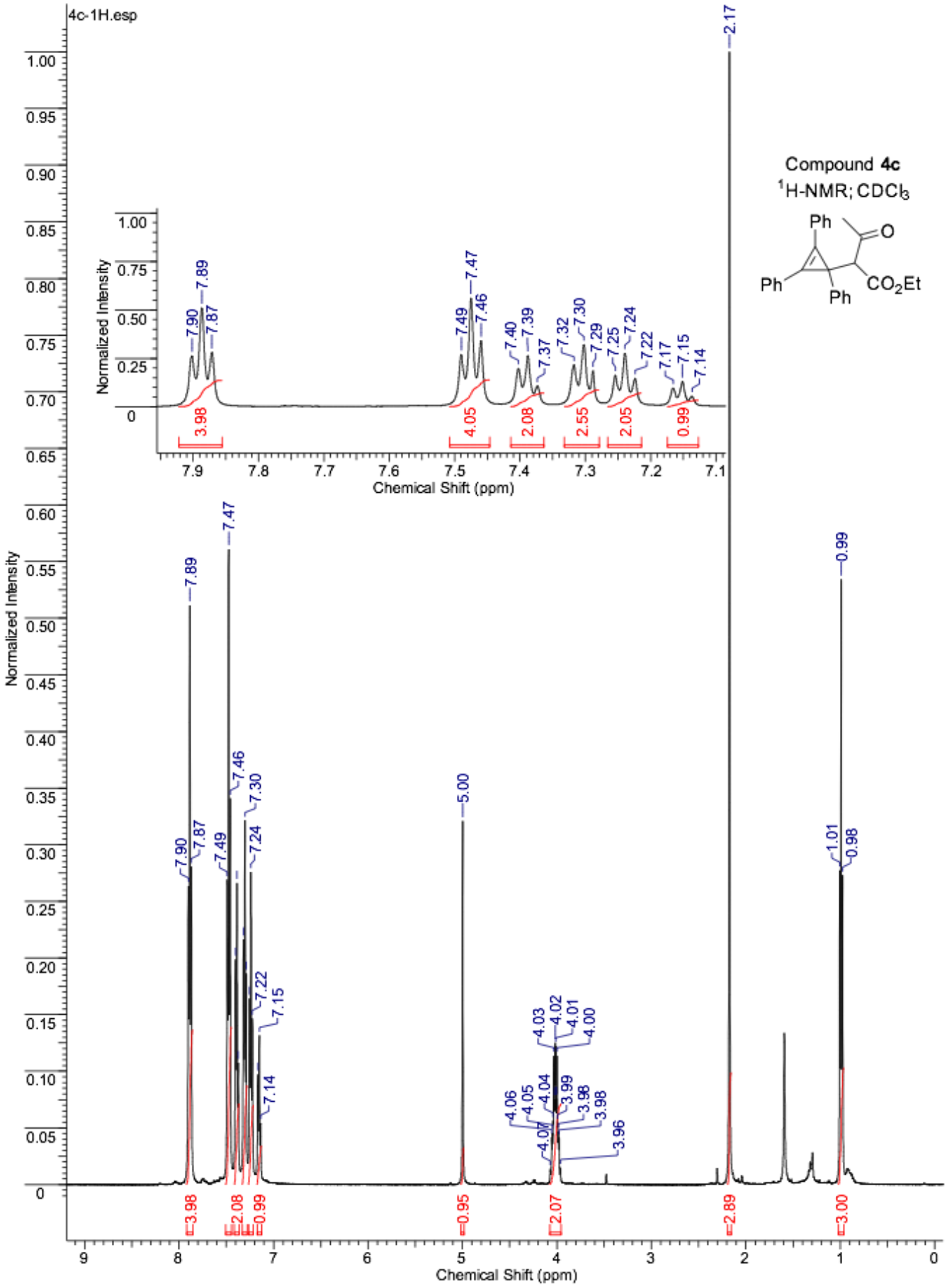




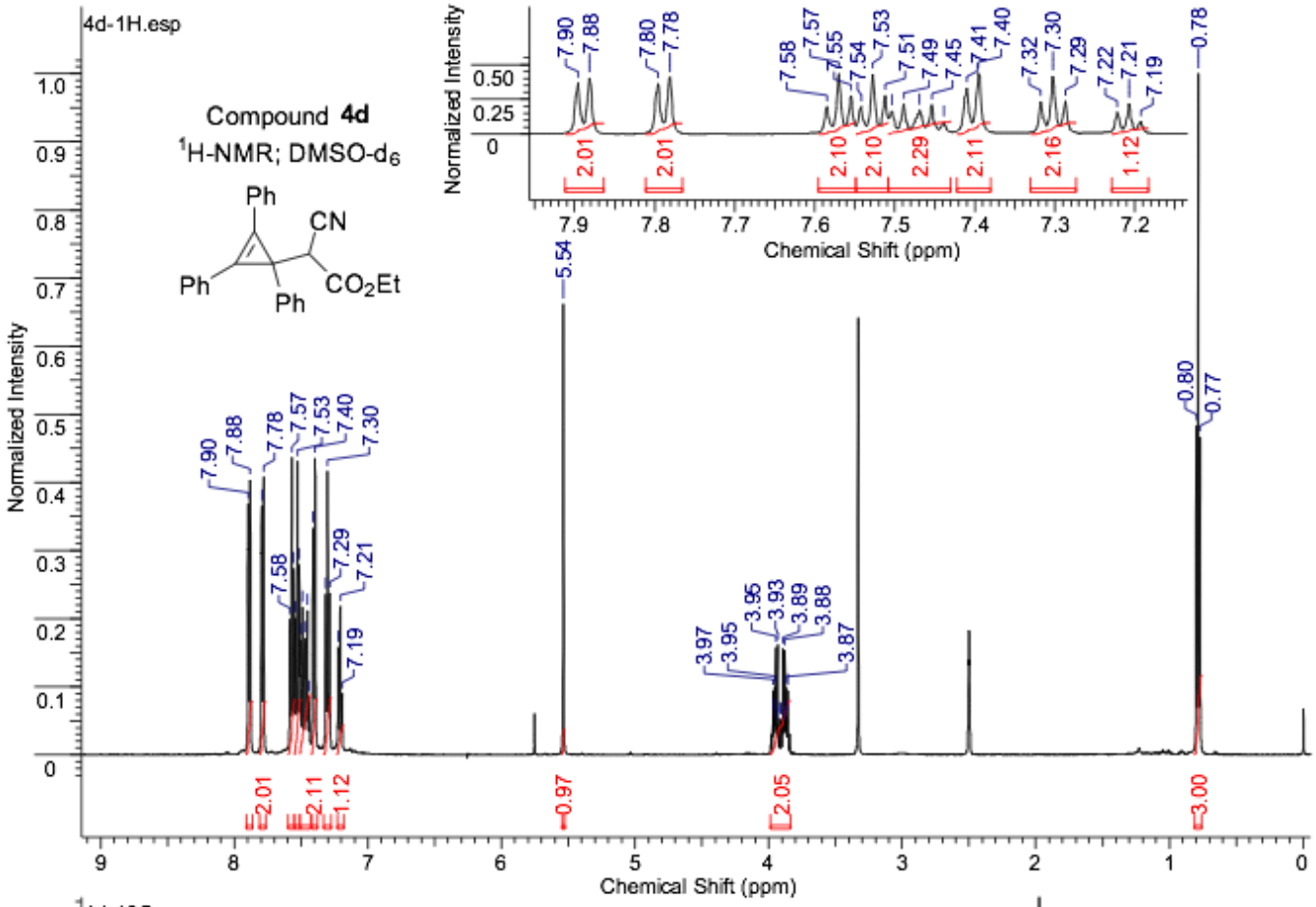
3-(Triphenylcyclopropen-3-yl)-pentane-2,4-dione (**4b**)

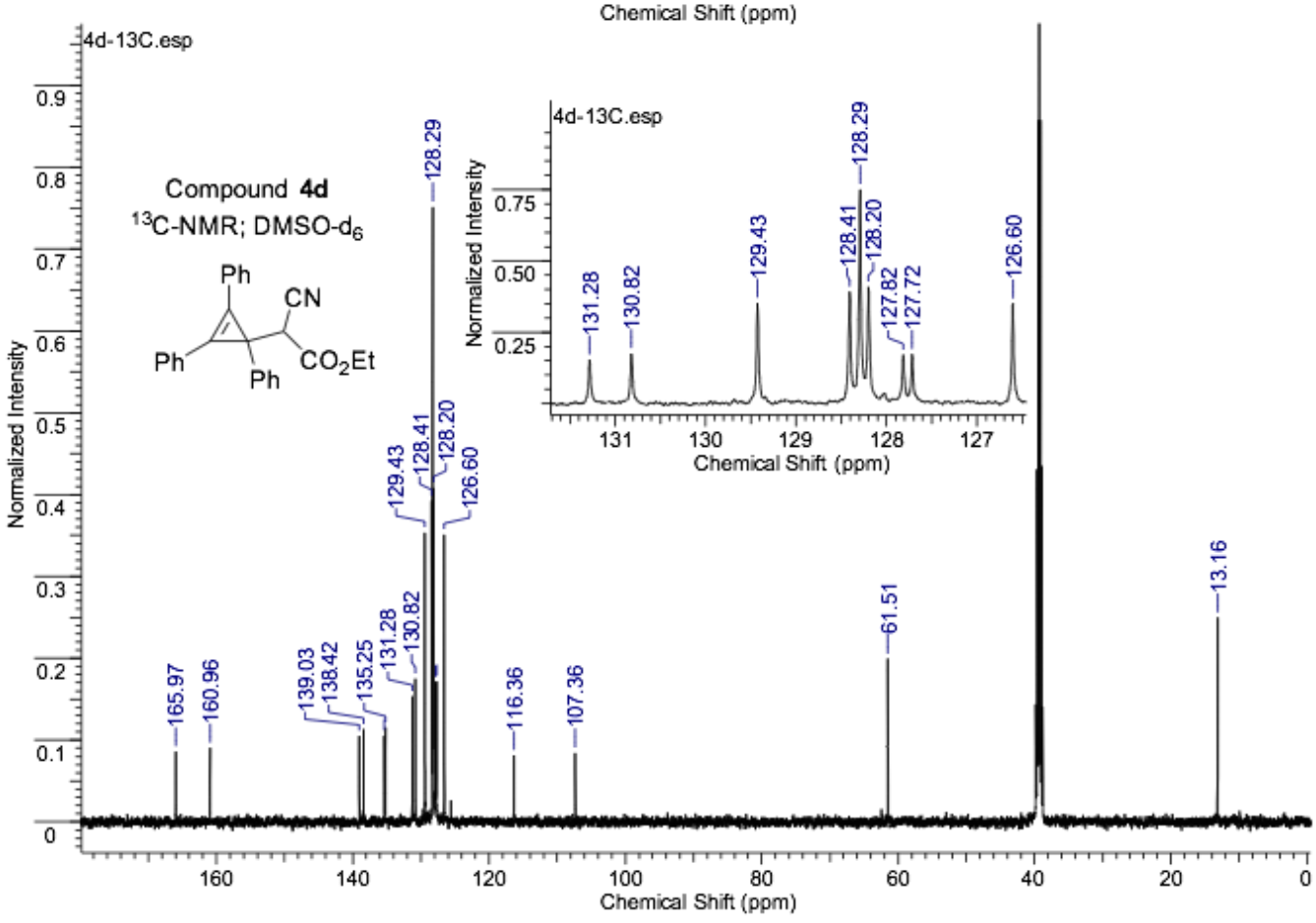


Ethyl 2-(Triphenylcyclopropen-3-yl)acetoacetate (**4c**)

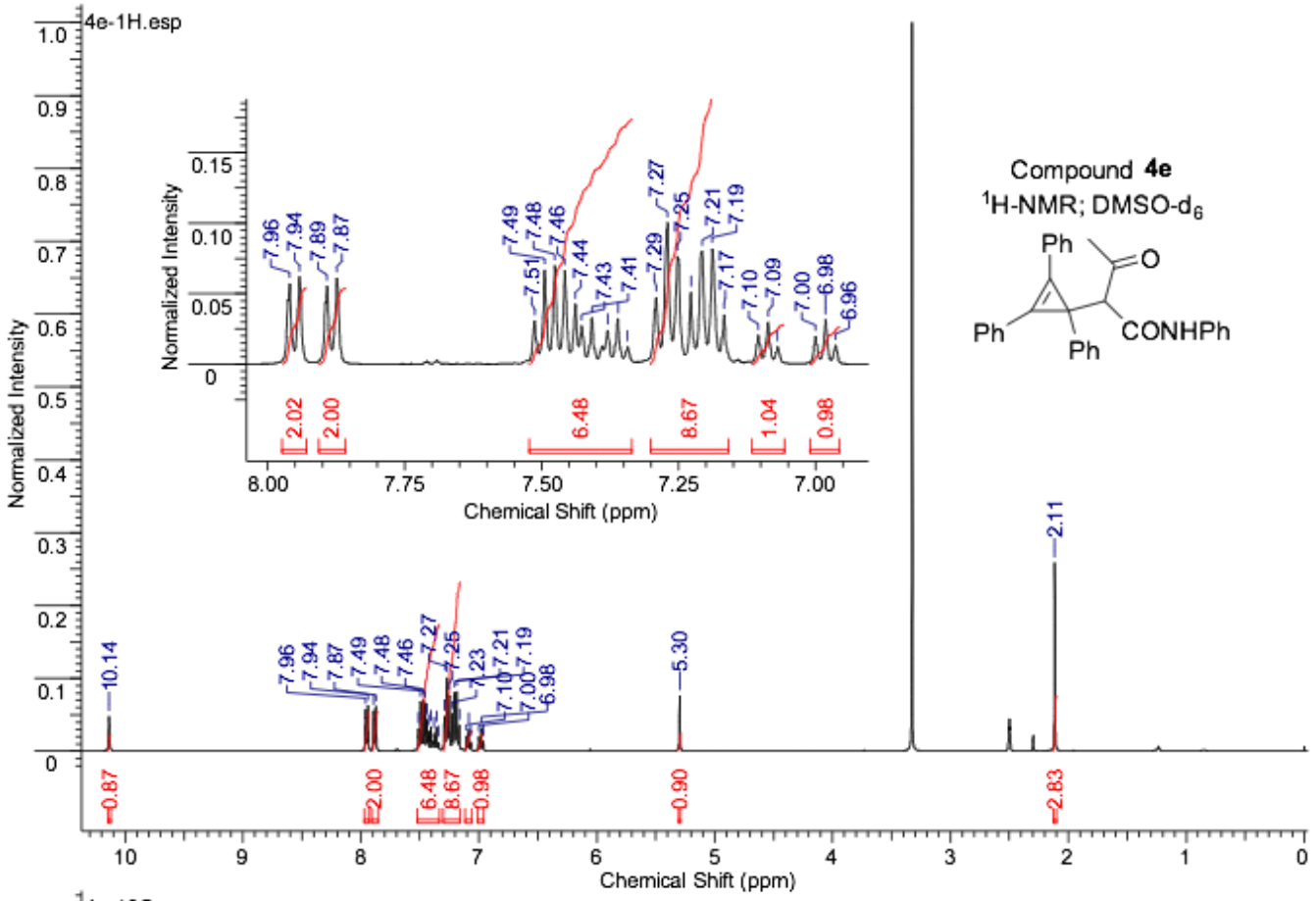


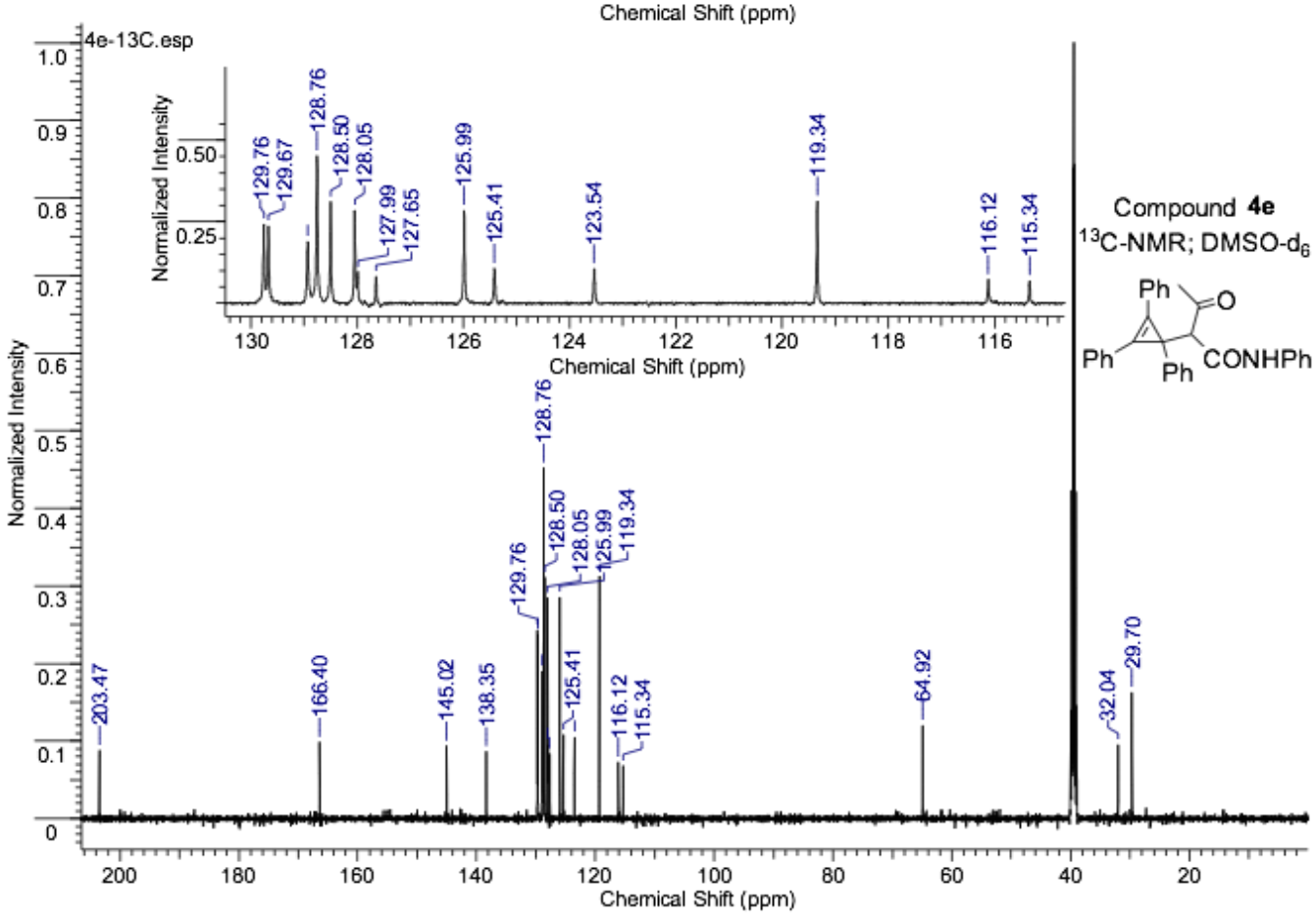
Ethyl 2-(Triphenylcyclopropen-3-yl)cyanoacetate **(4d)**



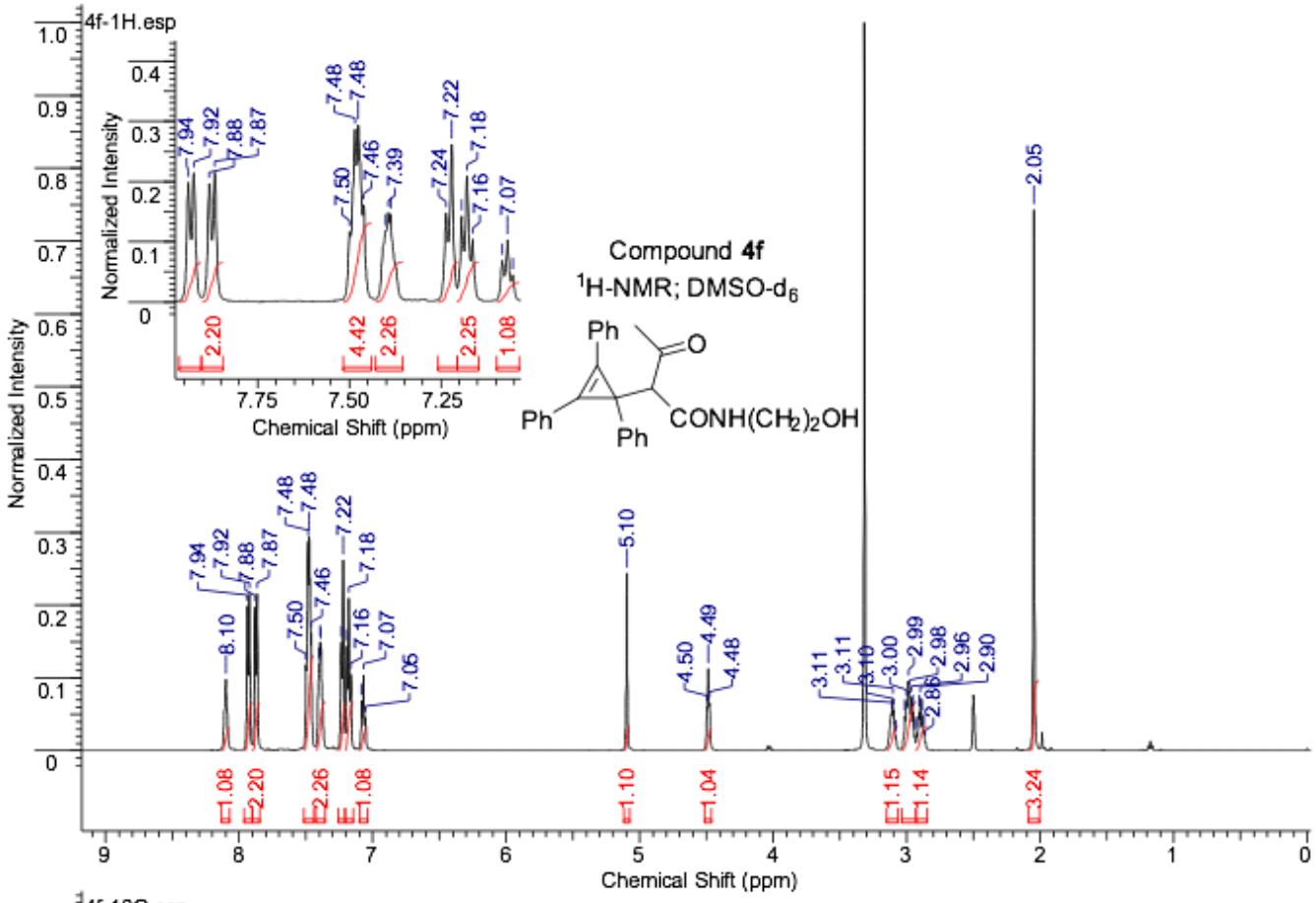


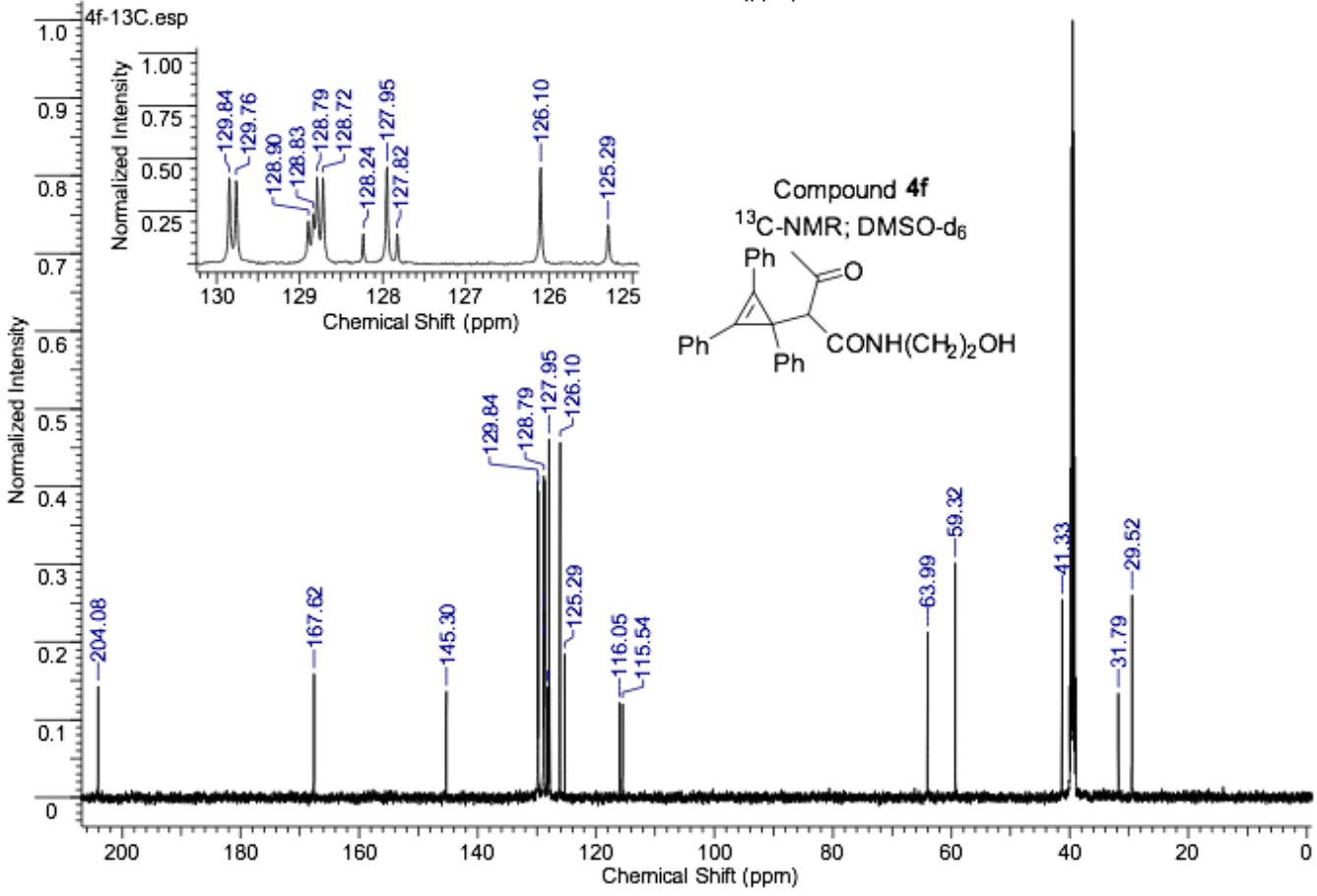
N-Phenyl-2-(triphenylcyclopropen-3-yl)acetoacetamide (**4e**)



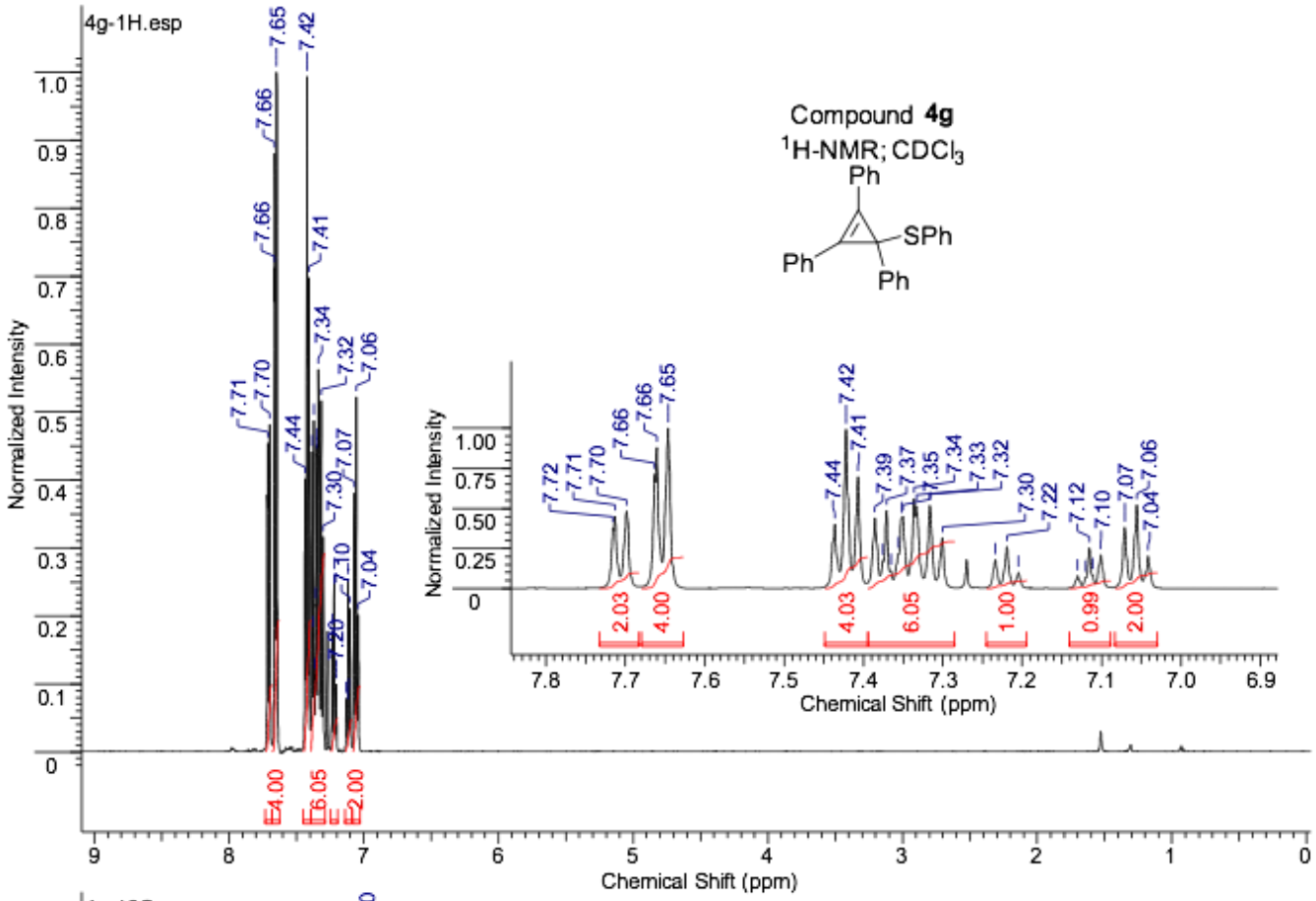


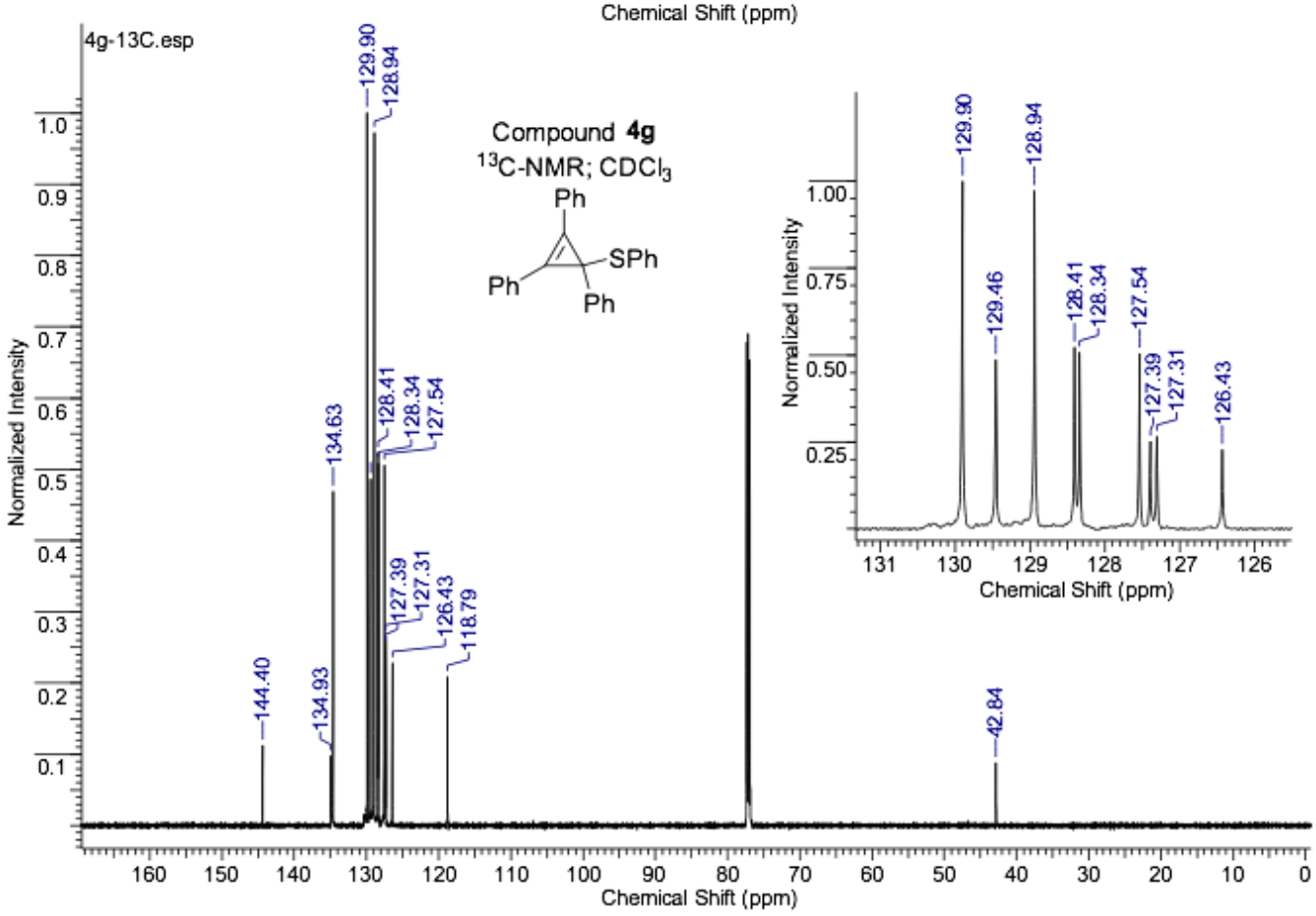
N-(2-Hydroxyethyl)-2-(triphenylcyclopropen-3-yl)acetoacetamide (**4f**)



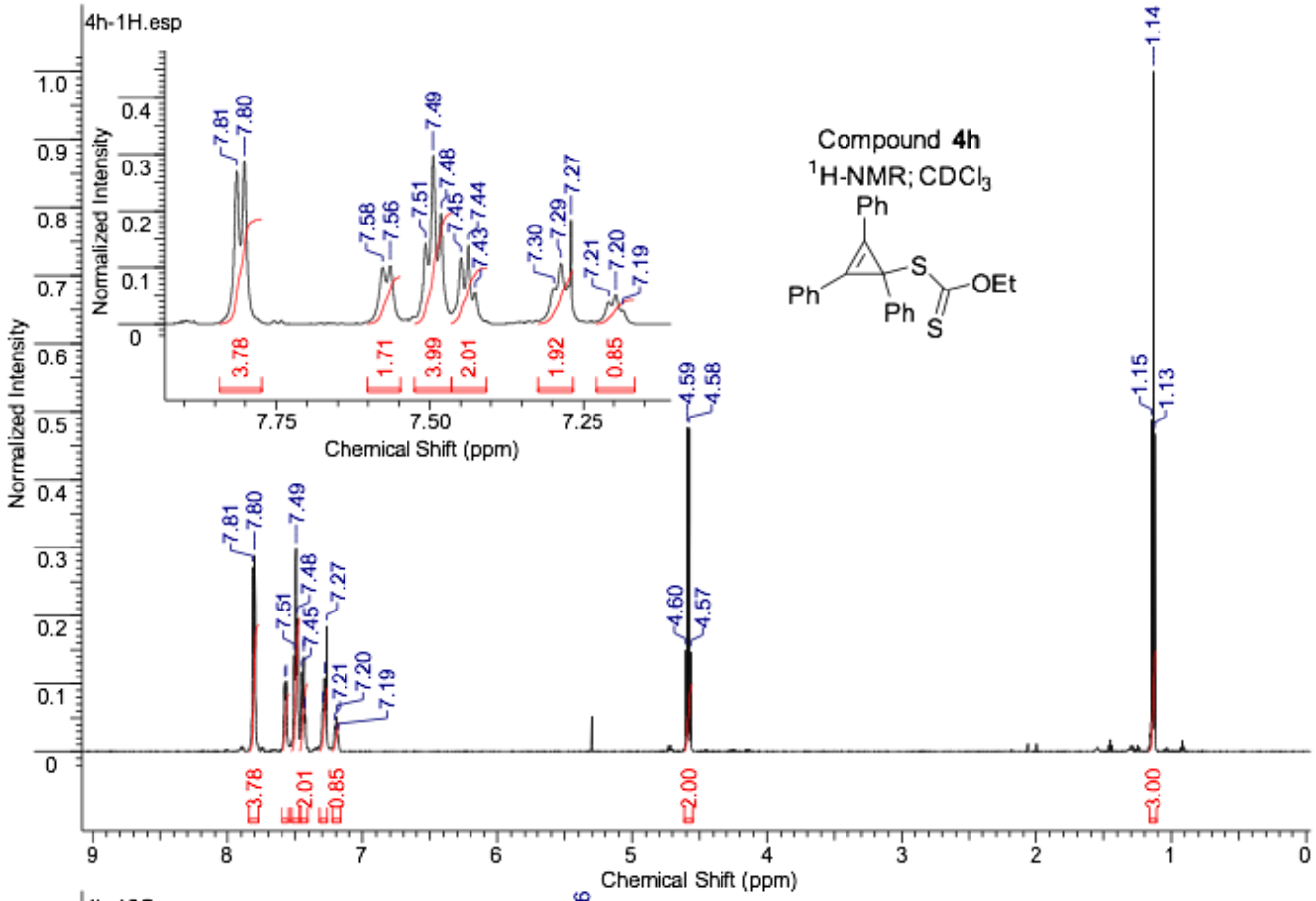


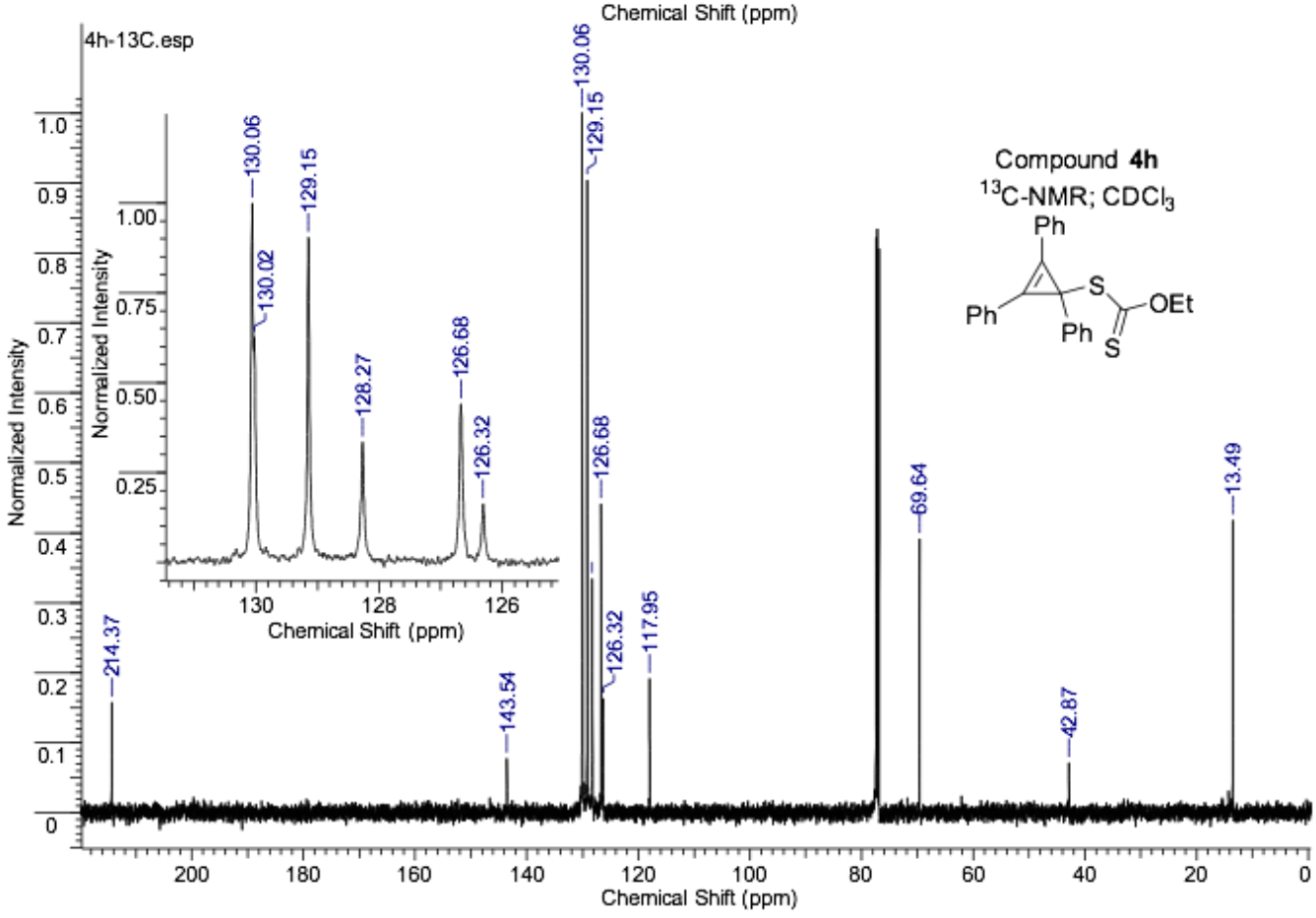
3-(Phenylthio)triphenylcyclopropene (**4g**)



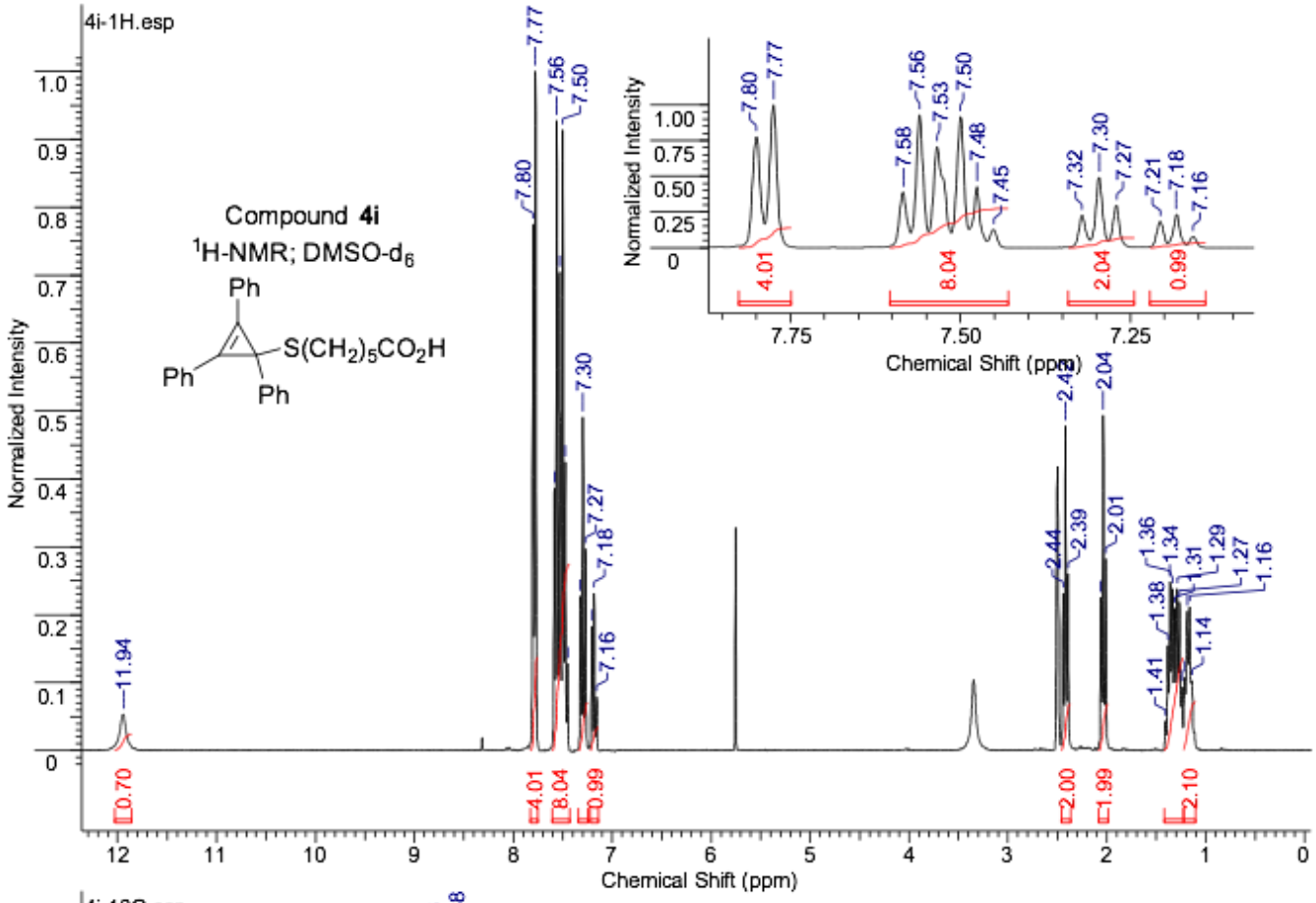


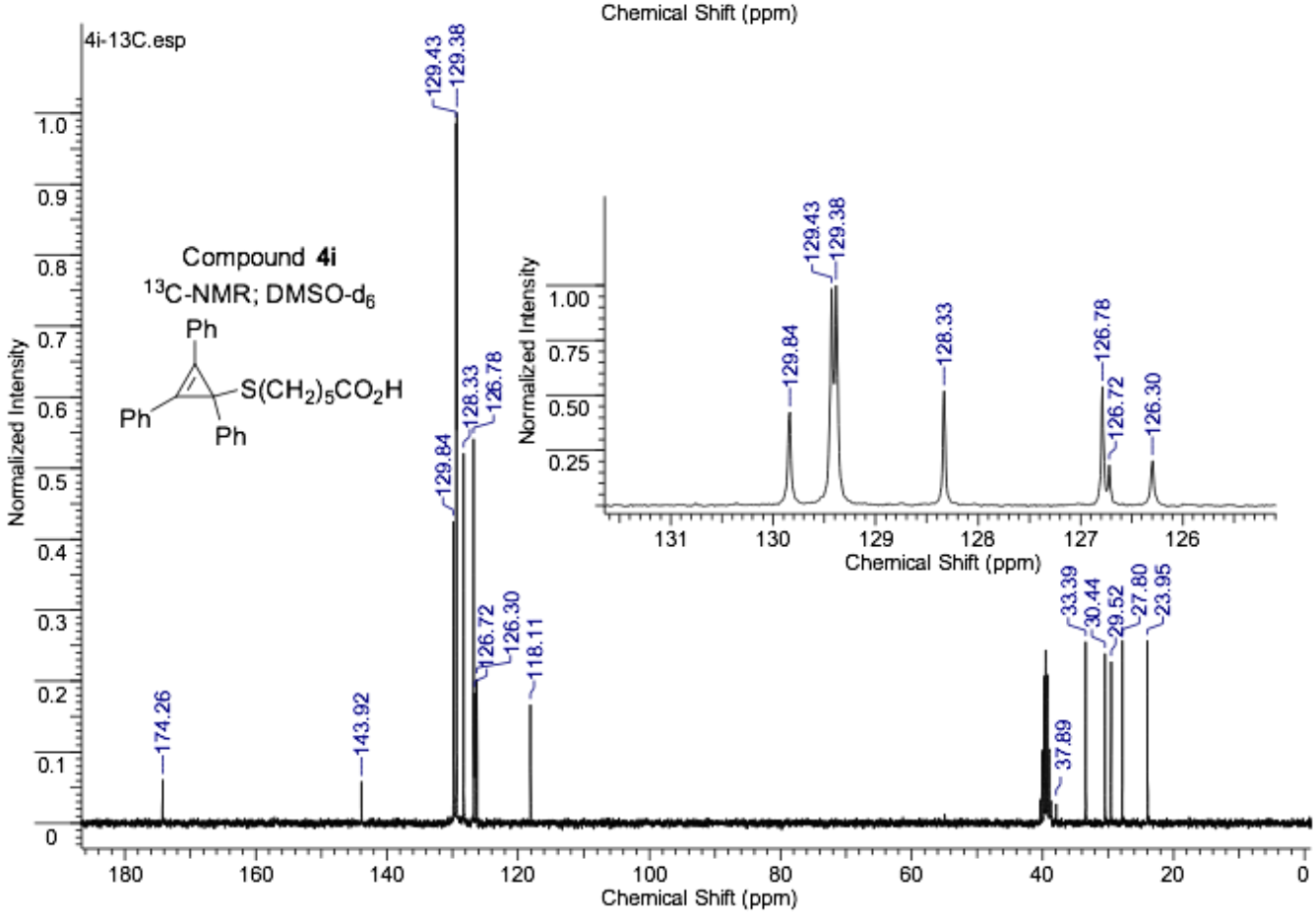
Triphenylcyclopropenyl ethoxyxanthate (**4h**)



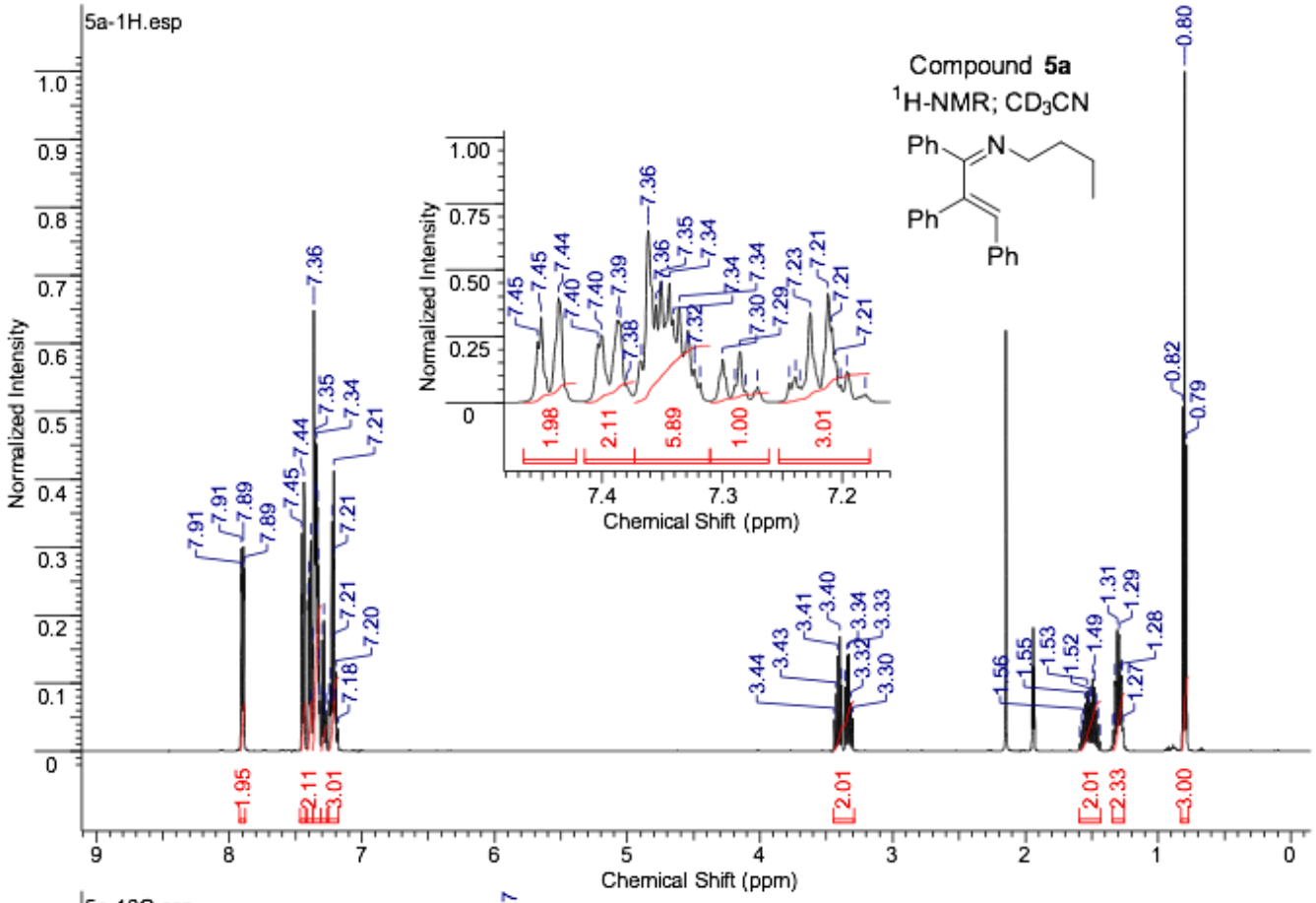


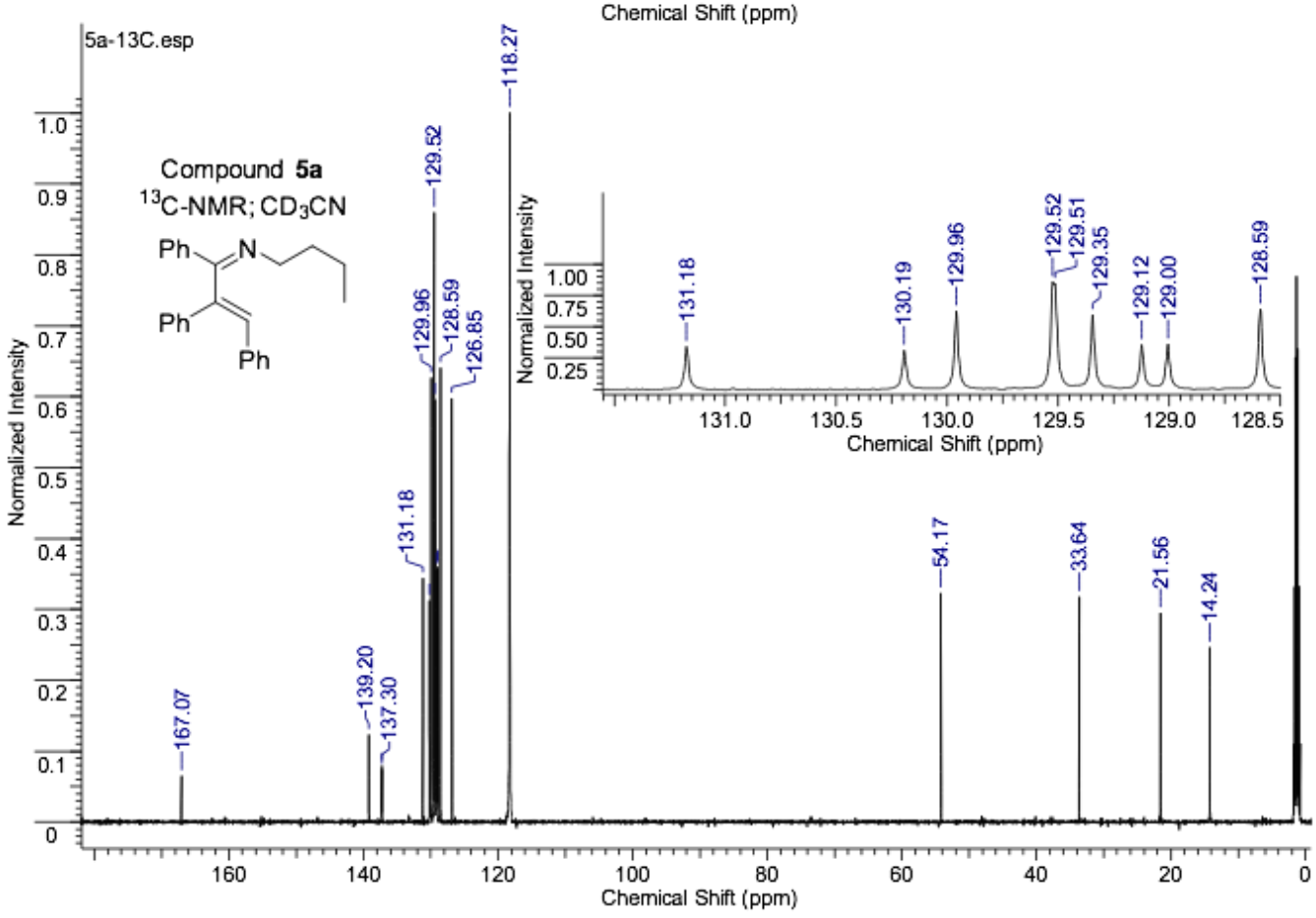
6-(Triphenylcyclopropen-3-ylthio)hexanoic acid (**4i**)



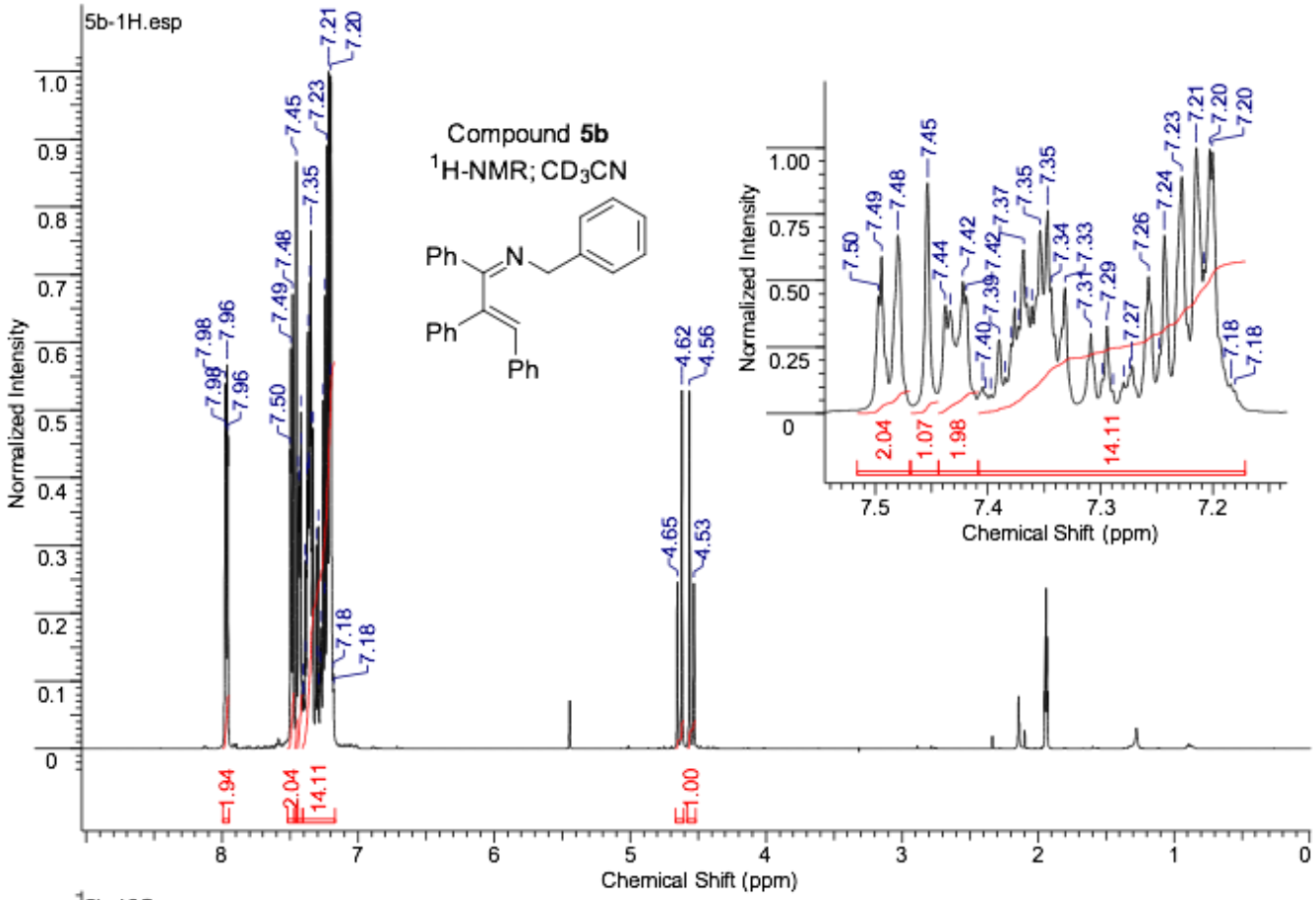


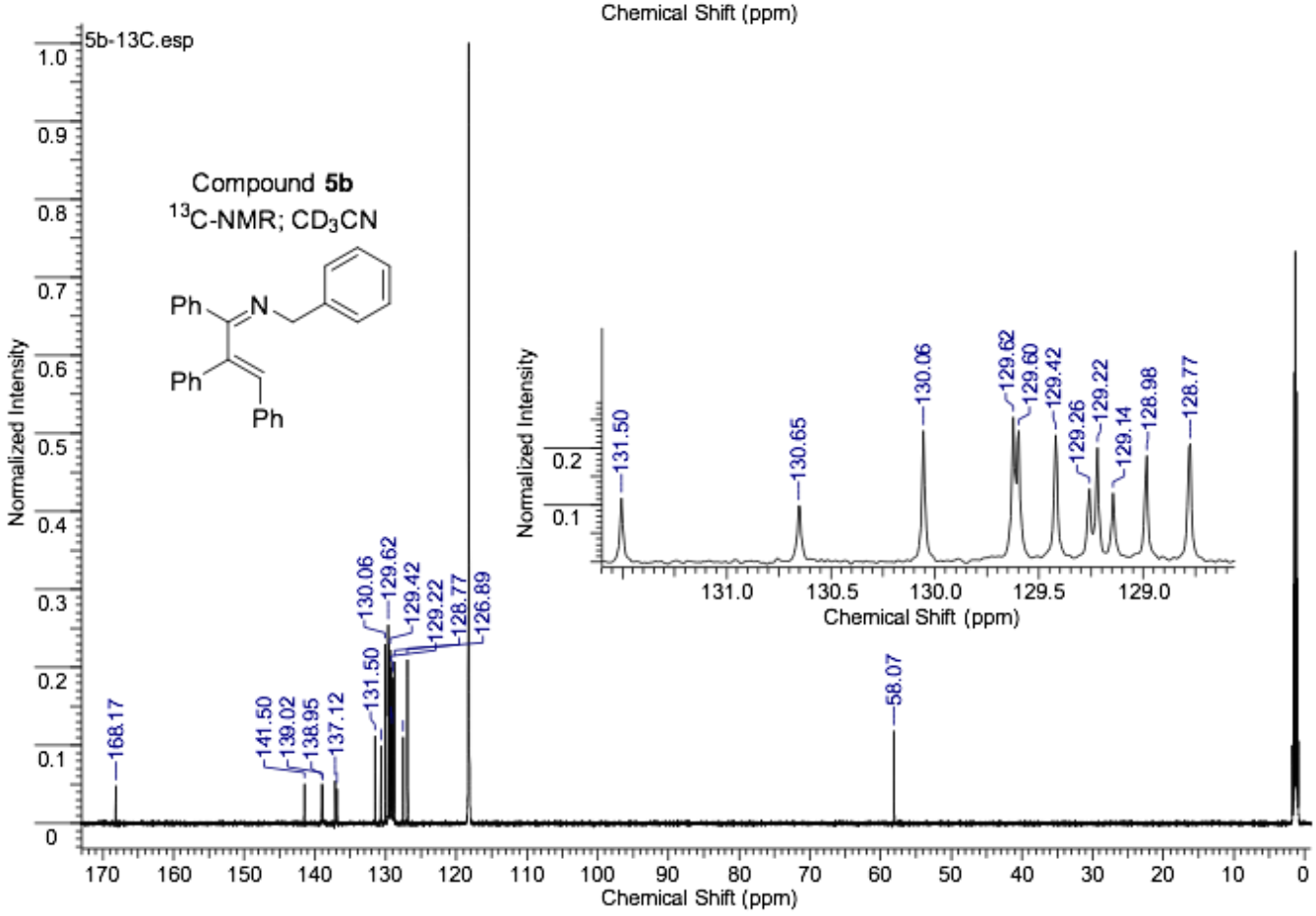
Butyl-[1,2,3-triphenylprop-2(E)-en-1-ylidene]amine (**5a**)



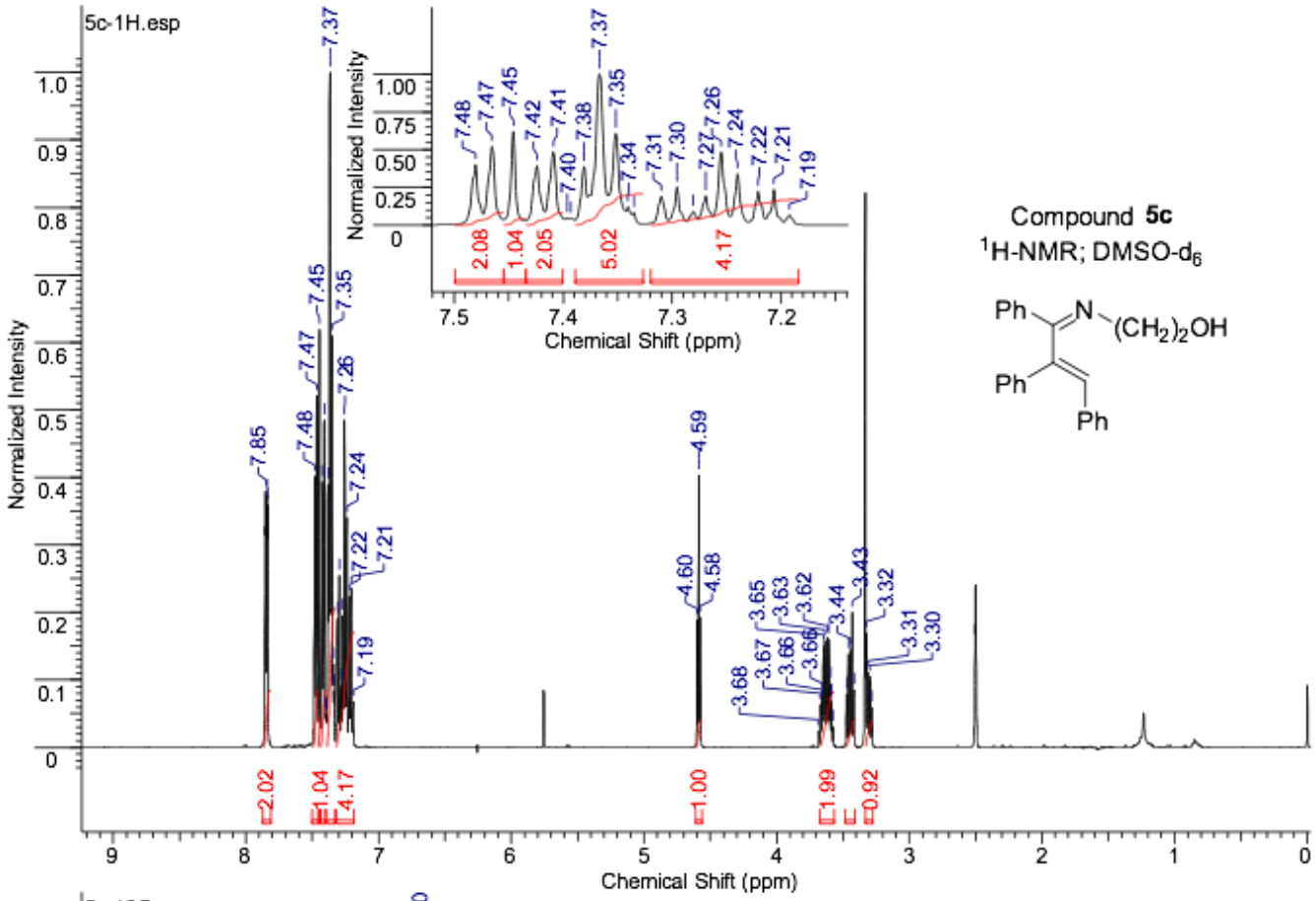


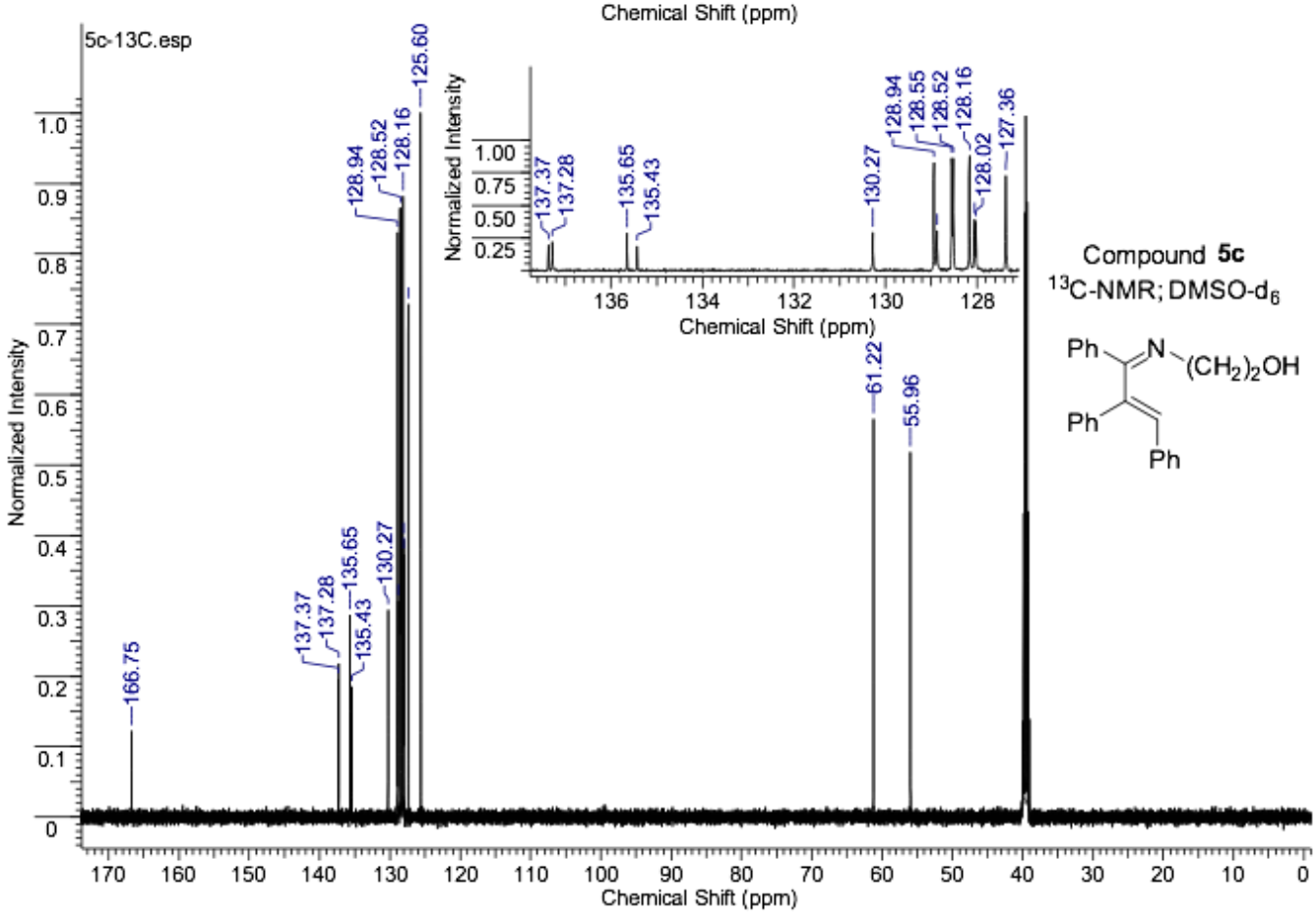
Benzyl-[1,2,3-triphenylprop-2(E)-en-1-ylidene]amine (**5b**)



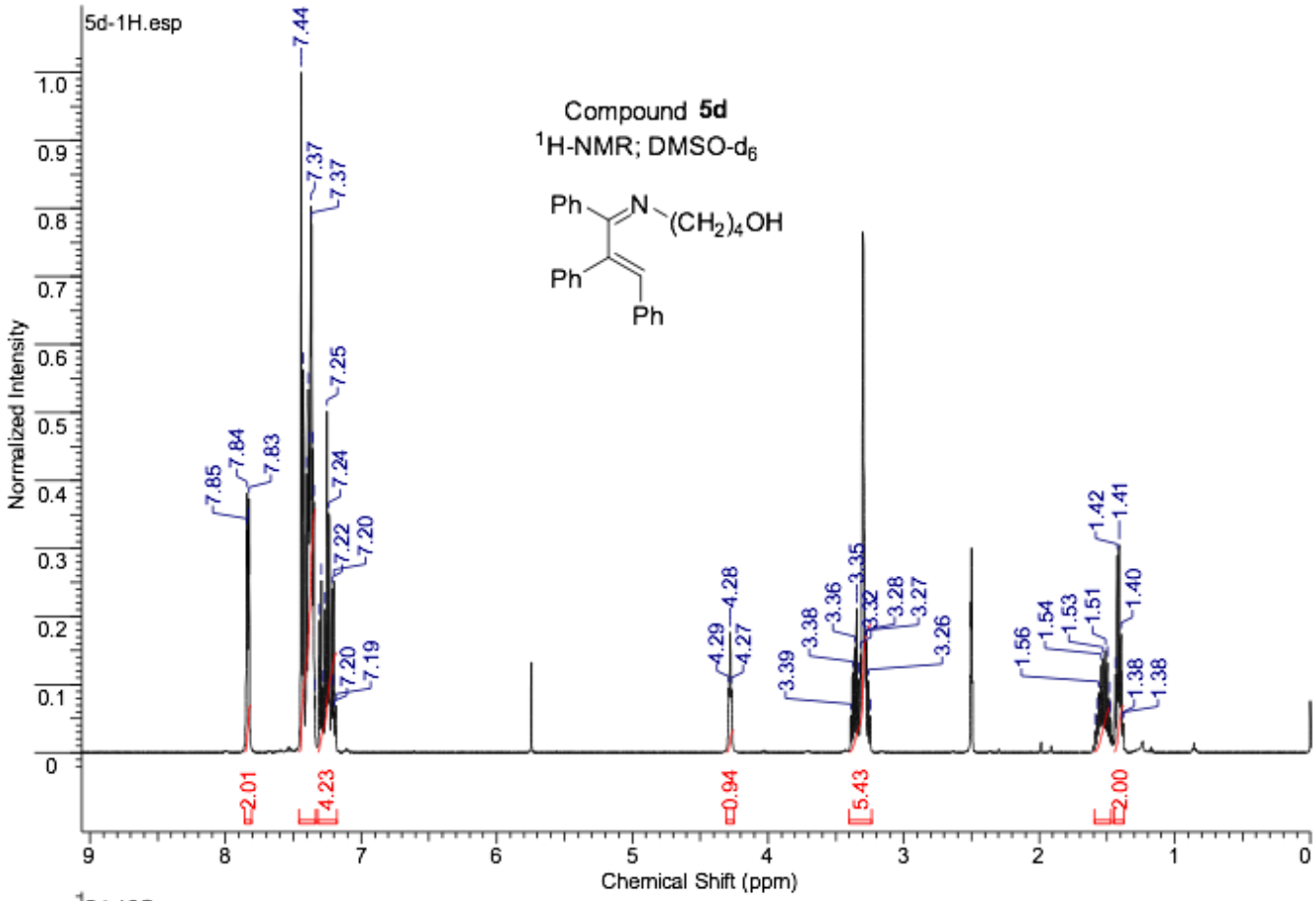


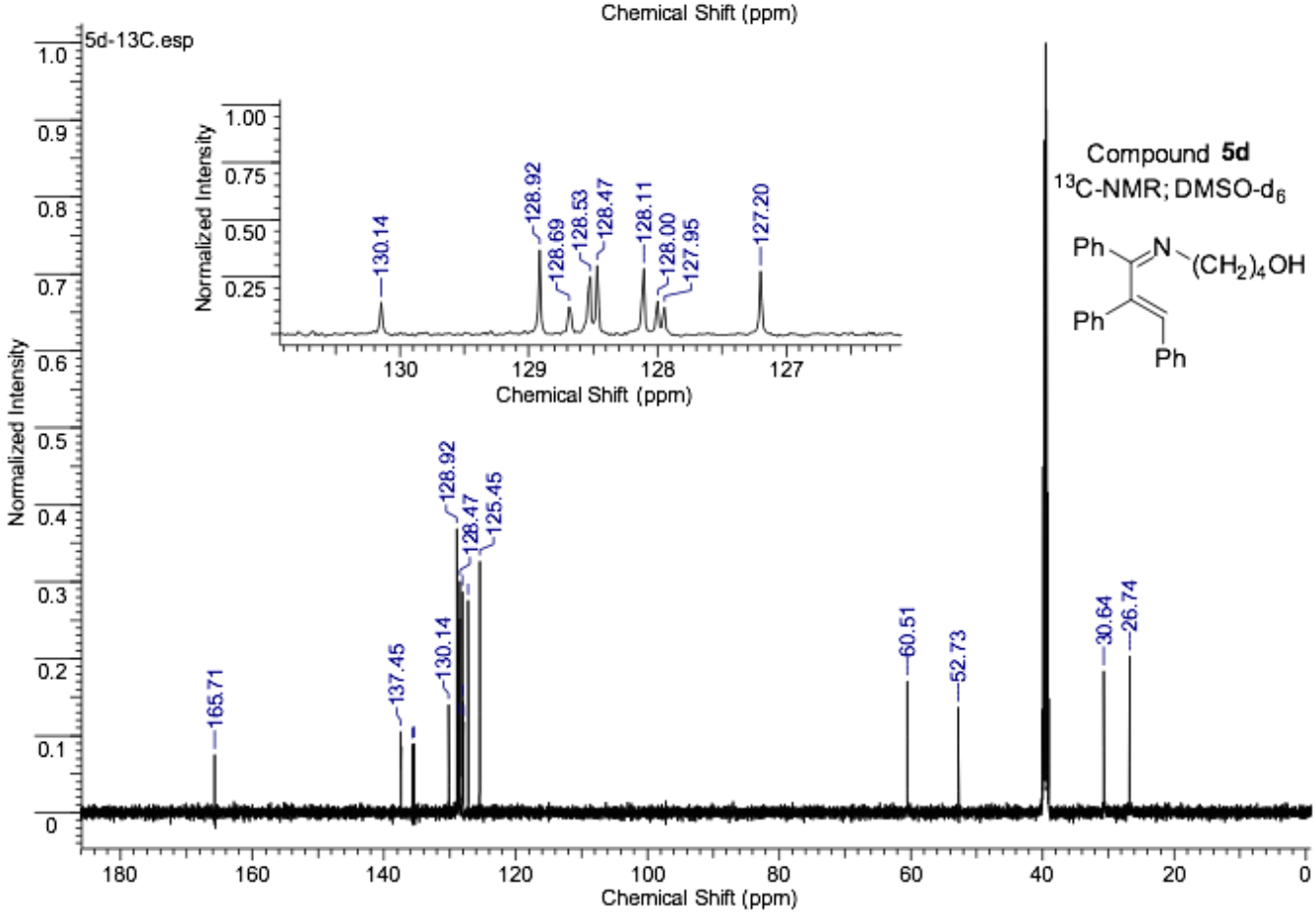
2-Hydroxyethyl-[1,2,3-triphenylprop-2(E)-en-1-ylidene]amine (**5c**)



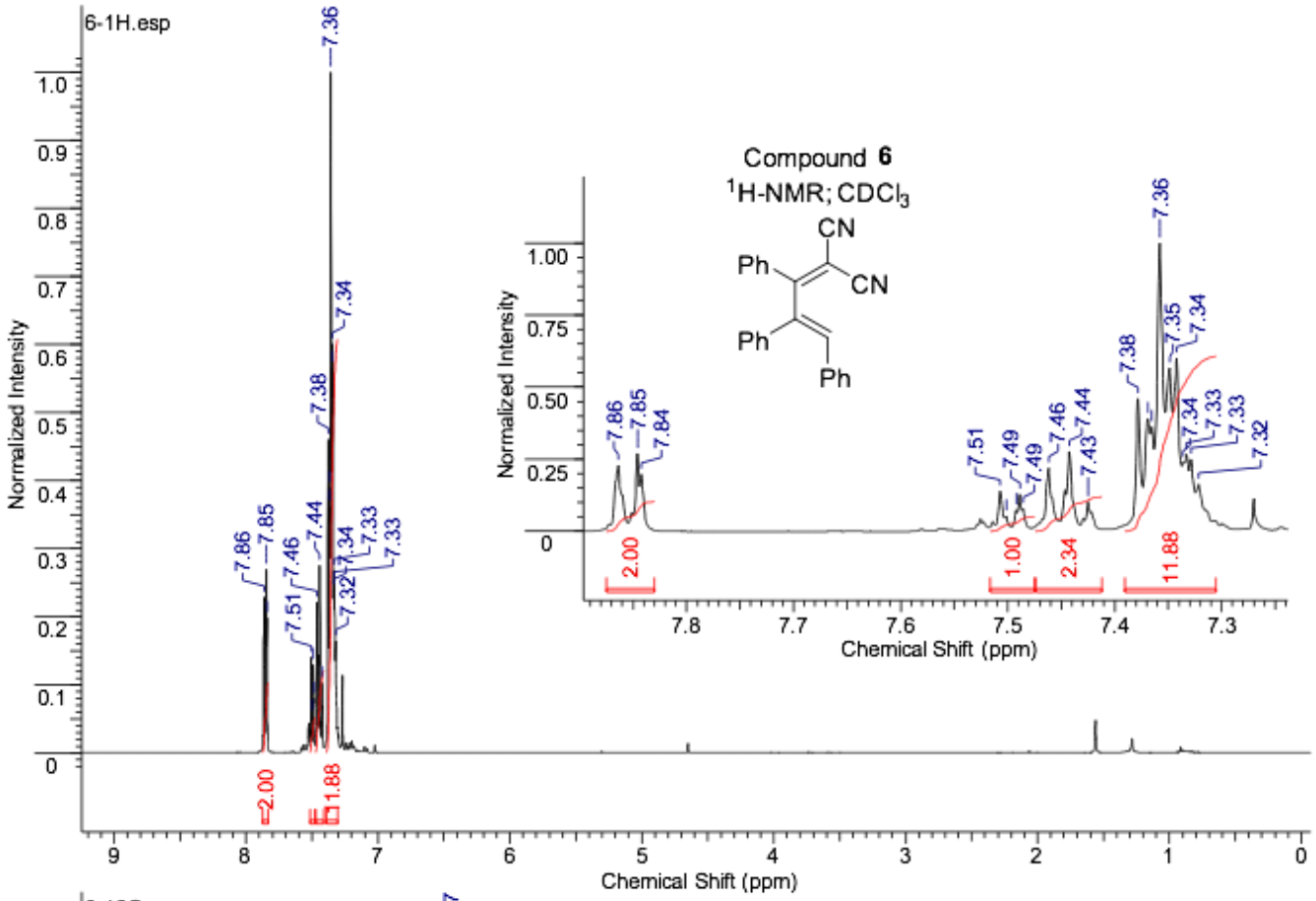


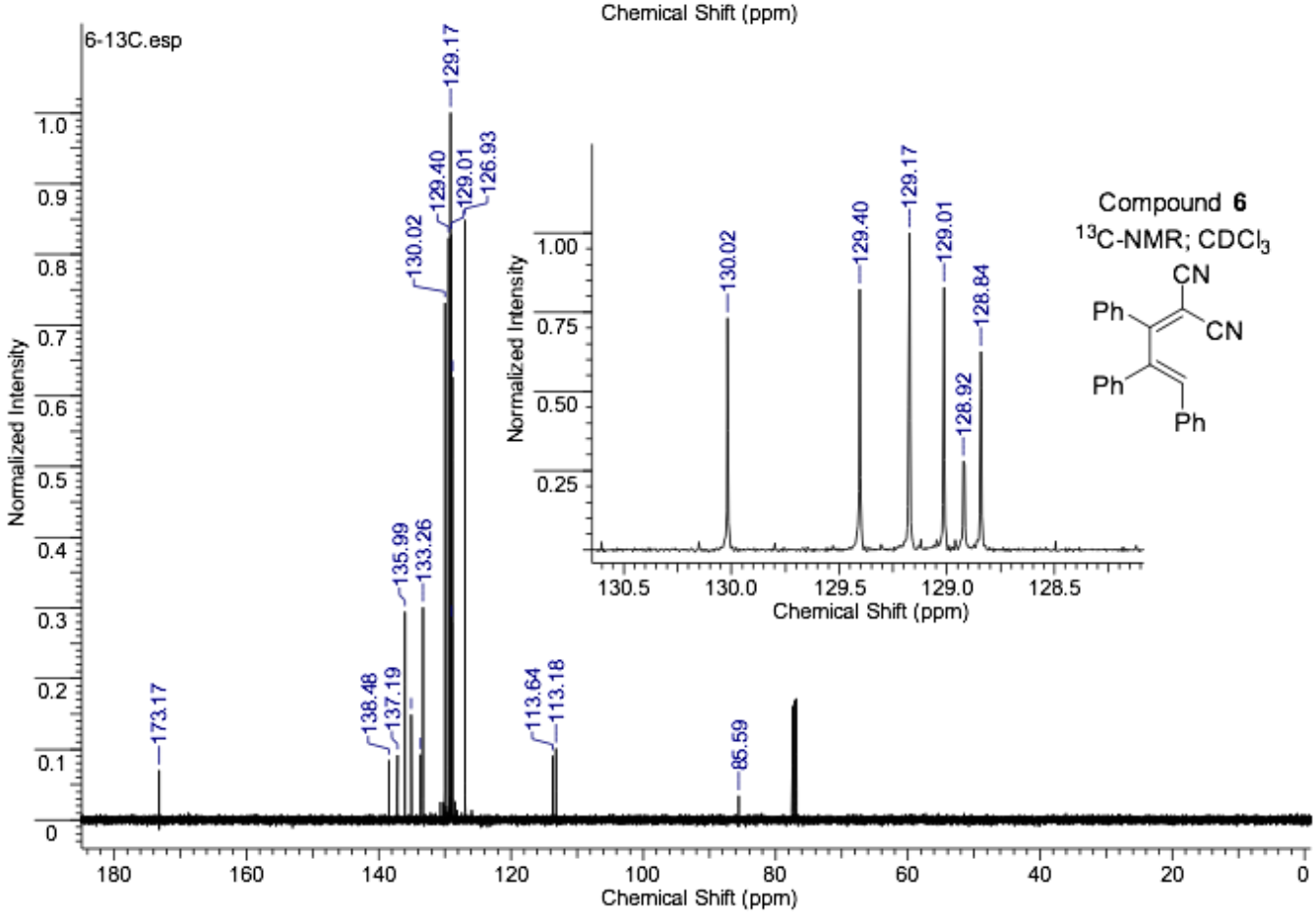
4-Hydroxybutyl-[1,2,3-triphenylprop-2(E)-en-1-ylidene]amine (**5d**)



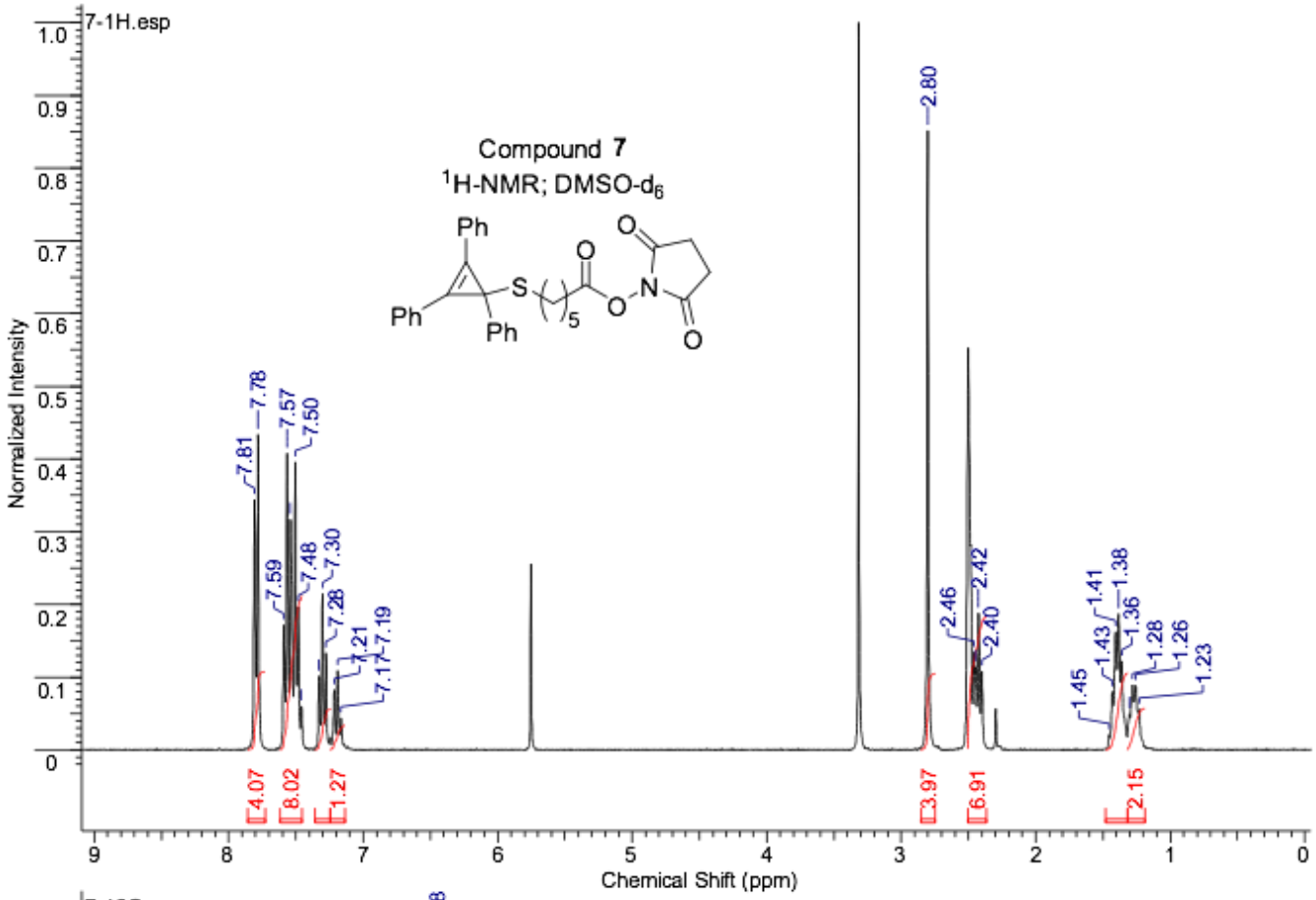


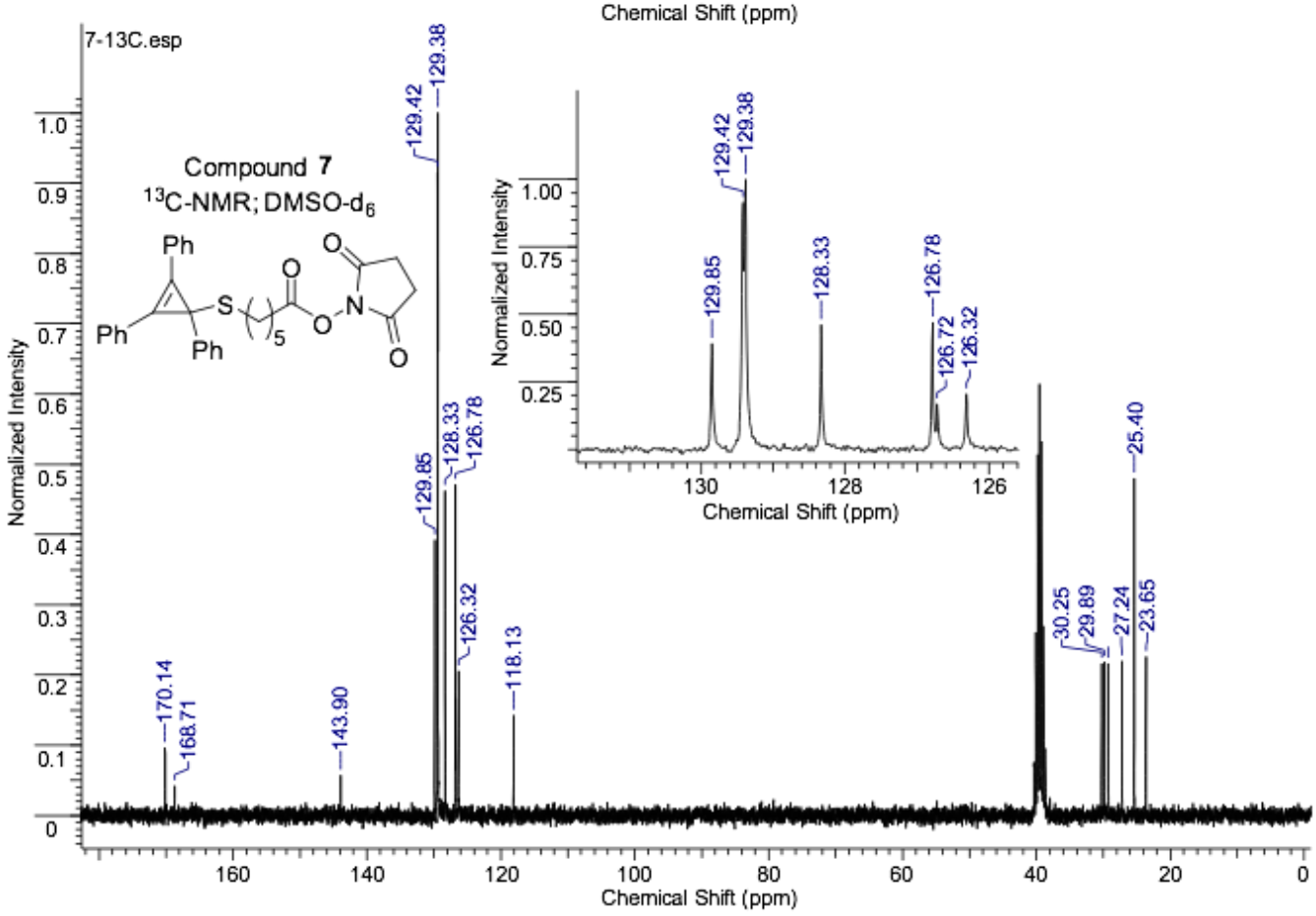
[1,2,3-Triphenylprop-2(E)-en-1-ylidene]malononitrile (**6**)



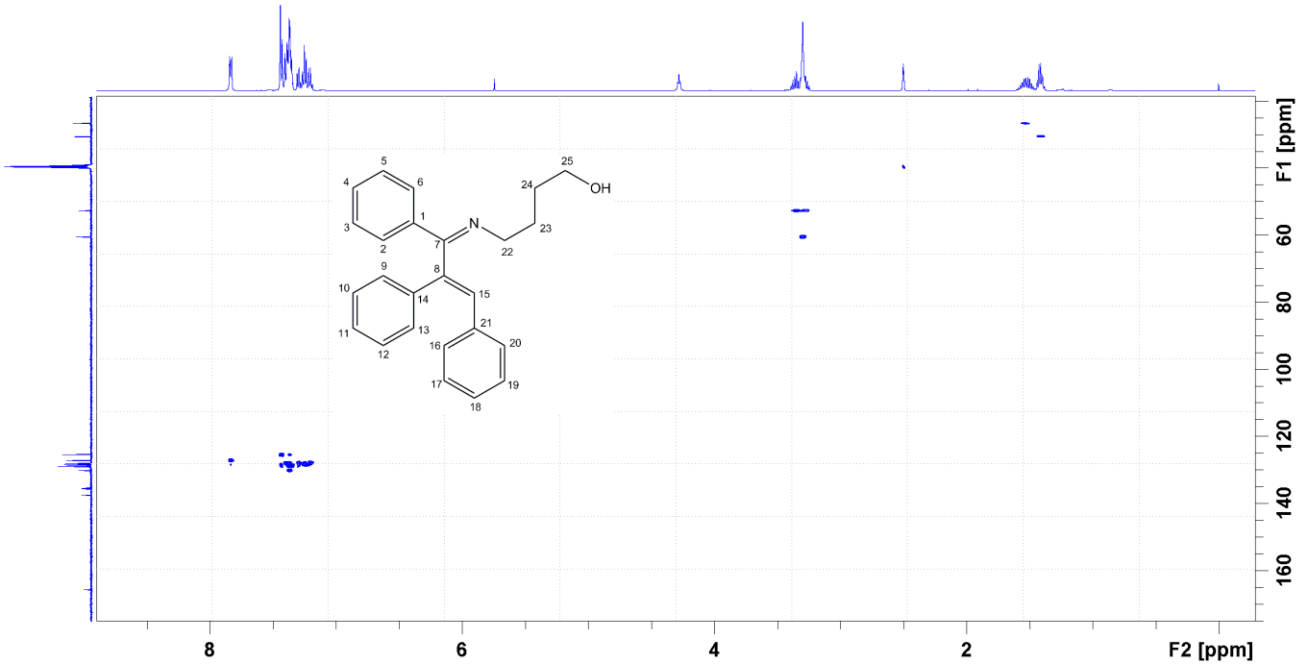


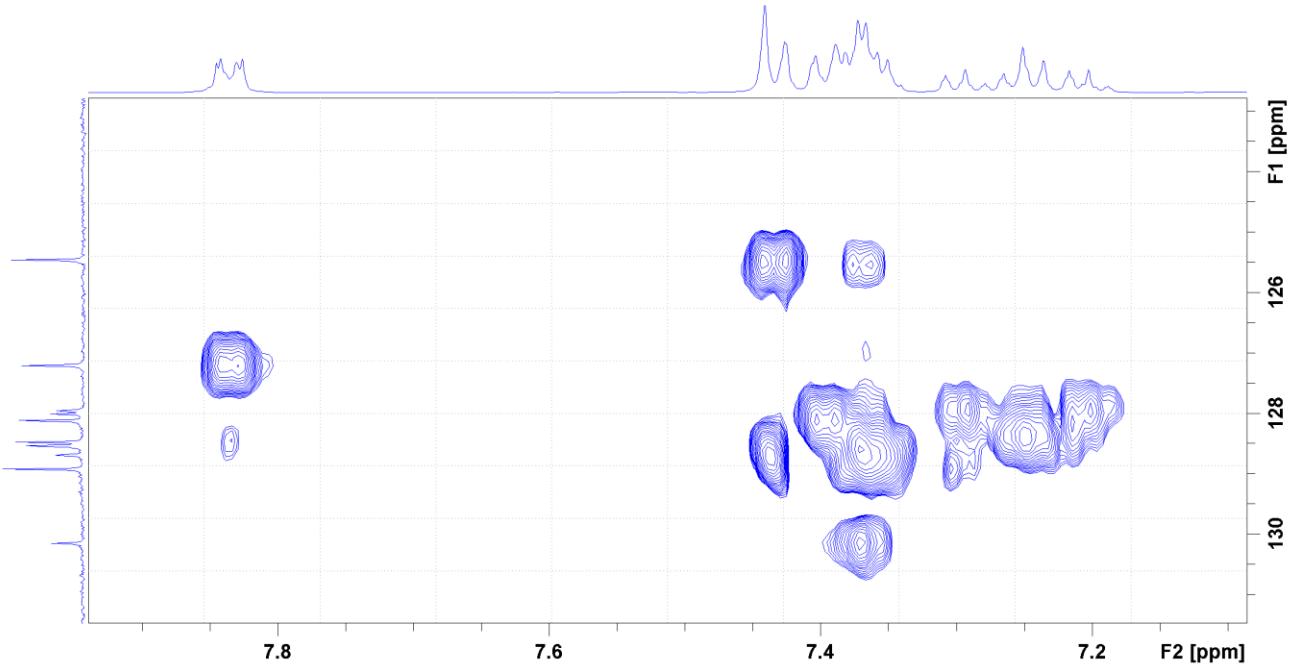
6-(Triphenylcyclopropen-3-ylthio)hexanoic acid, N-oxysuccinimide ester (**7**)





^{1}H-^{13}C HSQC NMR of compound **5d** (DMSO-d_6)





^{1}H-^{13}C HMBC NMR of compound **5d** (DMSO-d_6)