

Design and Synthesis of Fluorinated Amphiphile as ¹⁹F MRI/Fluorescence Dual Imaging Agent through Tuning the Self-assembly

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1. General information

^1H , ^{19}F and ^{13}C NMR spectra were recorded on a 400 MHz. Chemical shifts are in ppm and coupling constants (J) are in Hertz (Hz). ^1H NMR spectra were referenced to tetramethylsilane (d, 0.00 ppm) using CDCl_3 as solvent. ^{13}C NMR spectra were referenced to solvent carbons (77.16 ppm for CDCl_3). ^{19}F NMR spectra were referenced to 2% perfluorobenzene (s, -164.90 ppm) in CDCl_3 . The splitting patterns for ^1H NMR spectra are denoted as follows: s (singlet), d (doublet), q (quartet), m (multiplet). ESI mass was used for compounds below 3,000 Da and MALDI mass was used for compounds above 3,000 Da.

^{19}F MRI experiments were performed on a 9.4 T microimaging system with a 10 mm inner diameter ^{19}F coil (376.4 MHz) for both radiofrequency transmission and reception. The MSME (Multi Slice Multi Echo) pulse sequence was employed for all MRI acquisitions with single average. FOV = 8 x 8 mm², SI = 40.0 mm TR = 2500 ms and TE = 7.6 ms were used. The data collection time was 160 ms.

Unless otherwise indicated, all reagents were obtained from commercial supplier and used without prior purification. DMF, Et_3N , MeOH and THF were dried and freshly distilled prior to use. Flash chromatography was performed on silica gel (200-300 mesh) with either Hexanes/EtOAc as eluents.

2. Relaxation times of amphiphiles

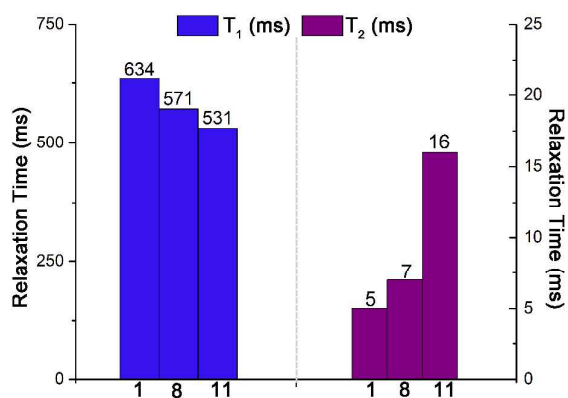


Figure S1. Relaxation times of amphiphiles **1**, **8** and **11**.

3. Fluorescence images of amphiphiles

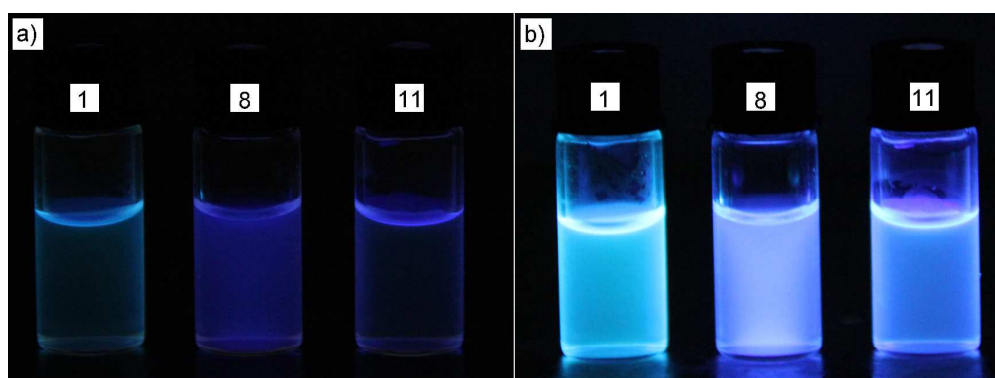
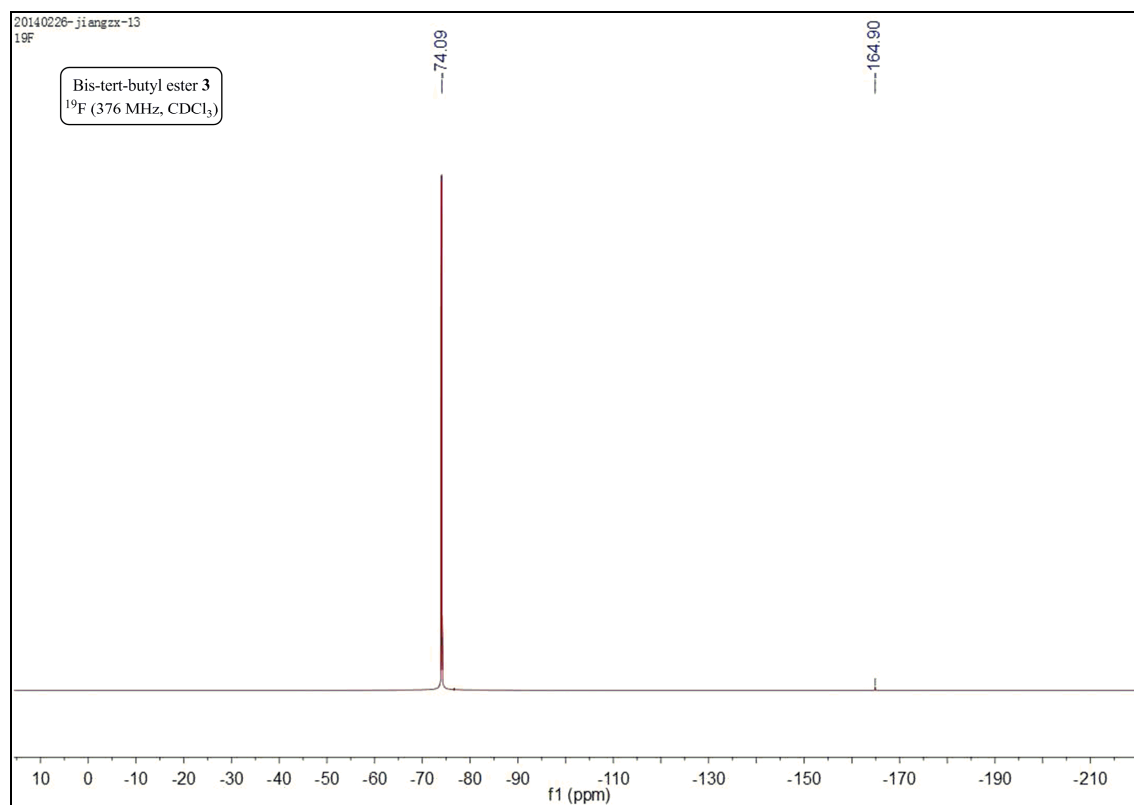
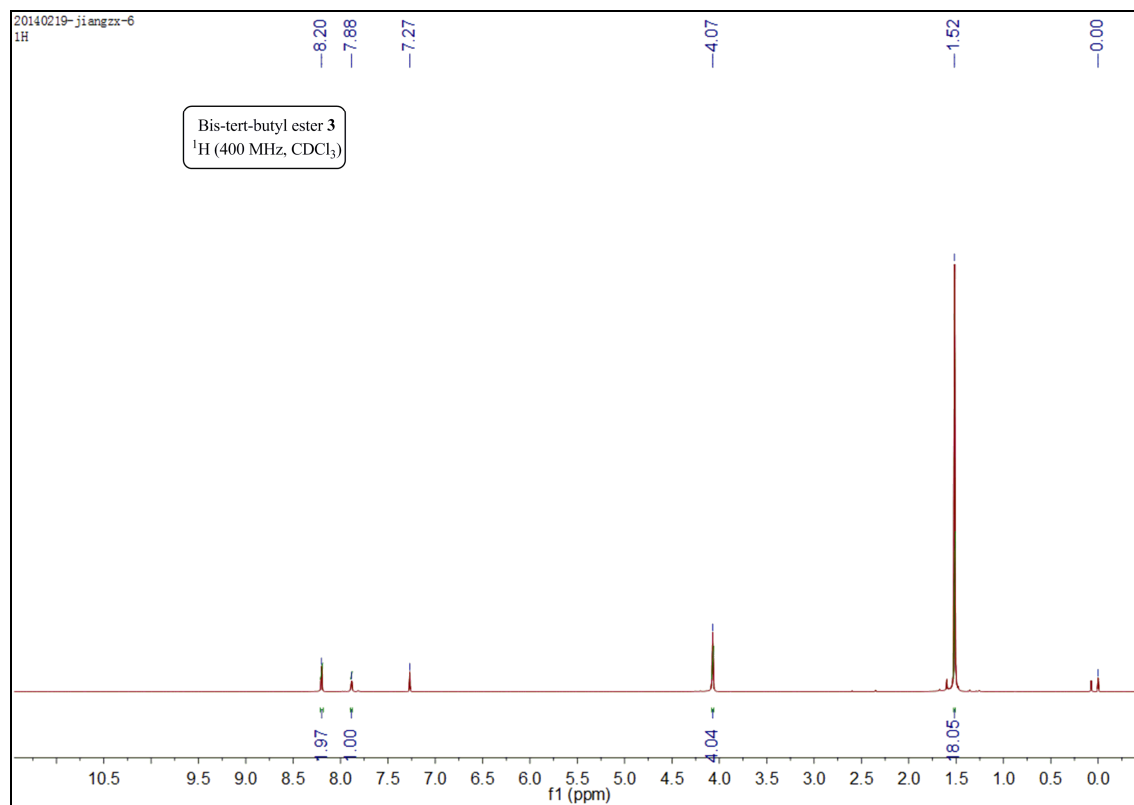
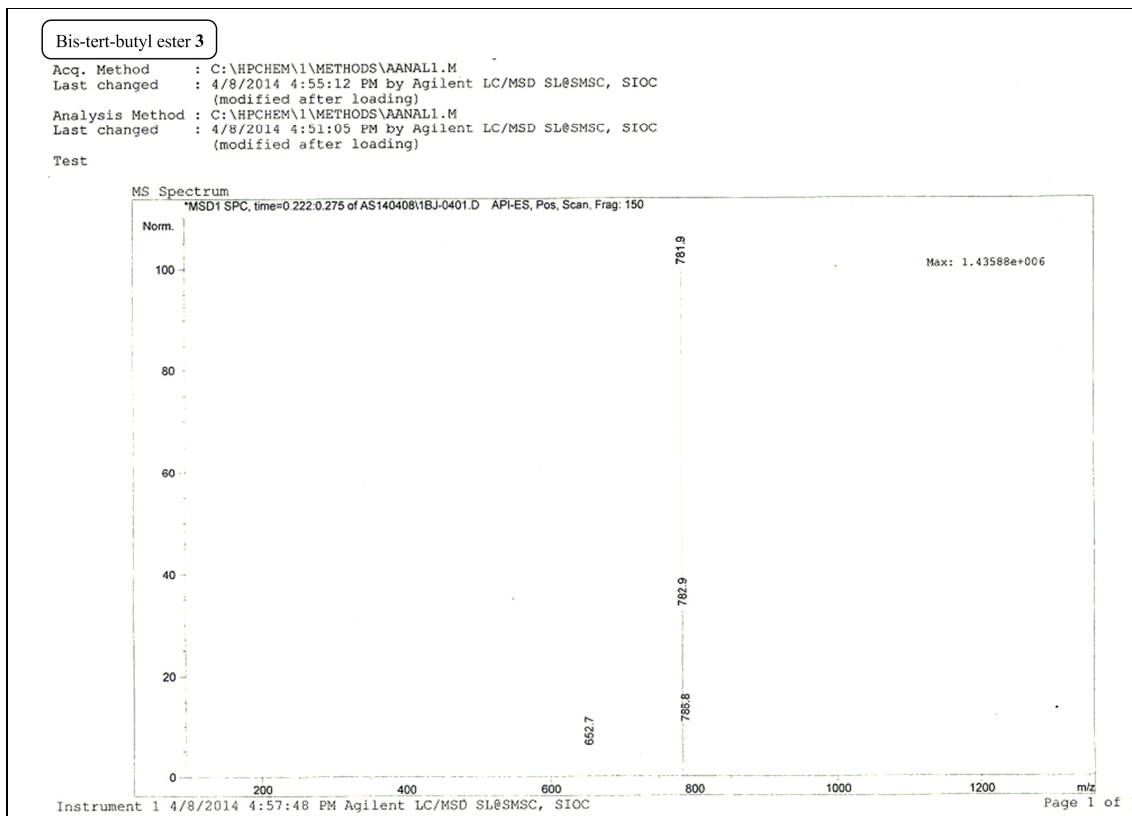
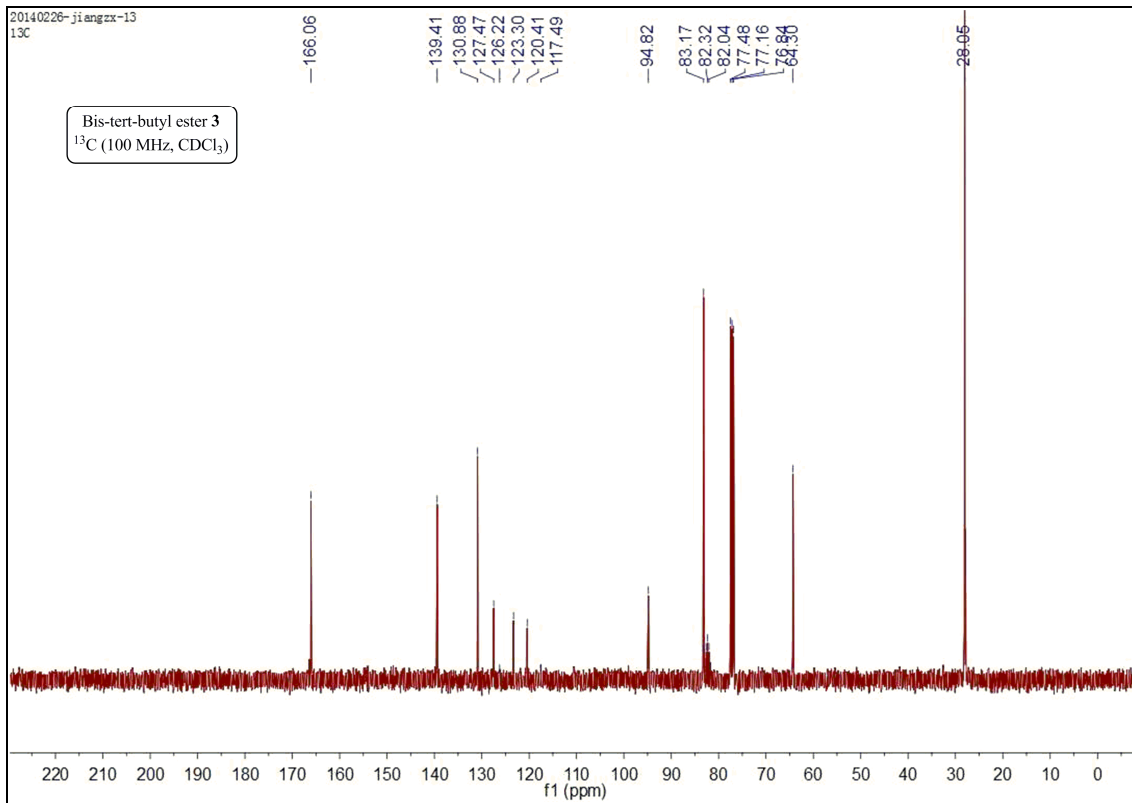


Figure S2. Fluorescence images of amphiphiles **1**, **8** and **11** (4.2 mM in H₂O; excitation wavelength at 254 nm (a) and 365 nm (b)).

4. Copies of ^1H NMR, ^{19}F NMR, ^{13}C NMR, MS and HRMS spectra of compounds





Bis-tert-butyl ester 3



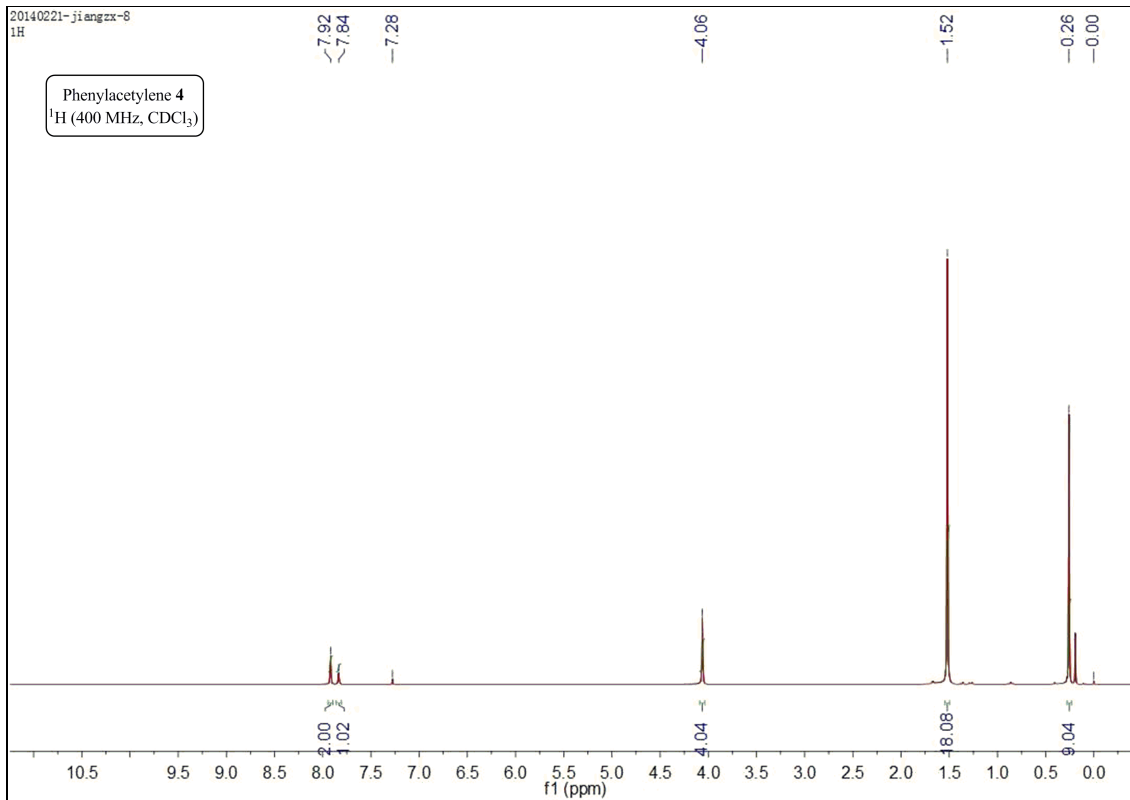
Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS

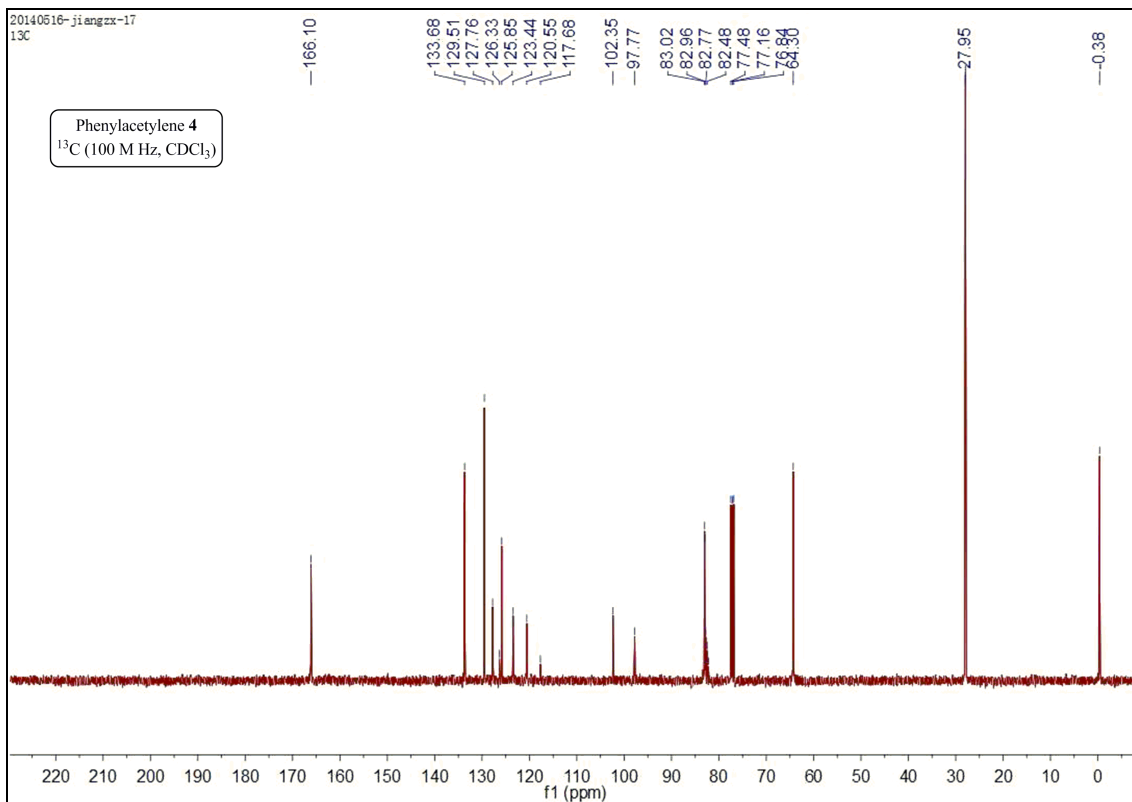
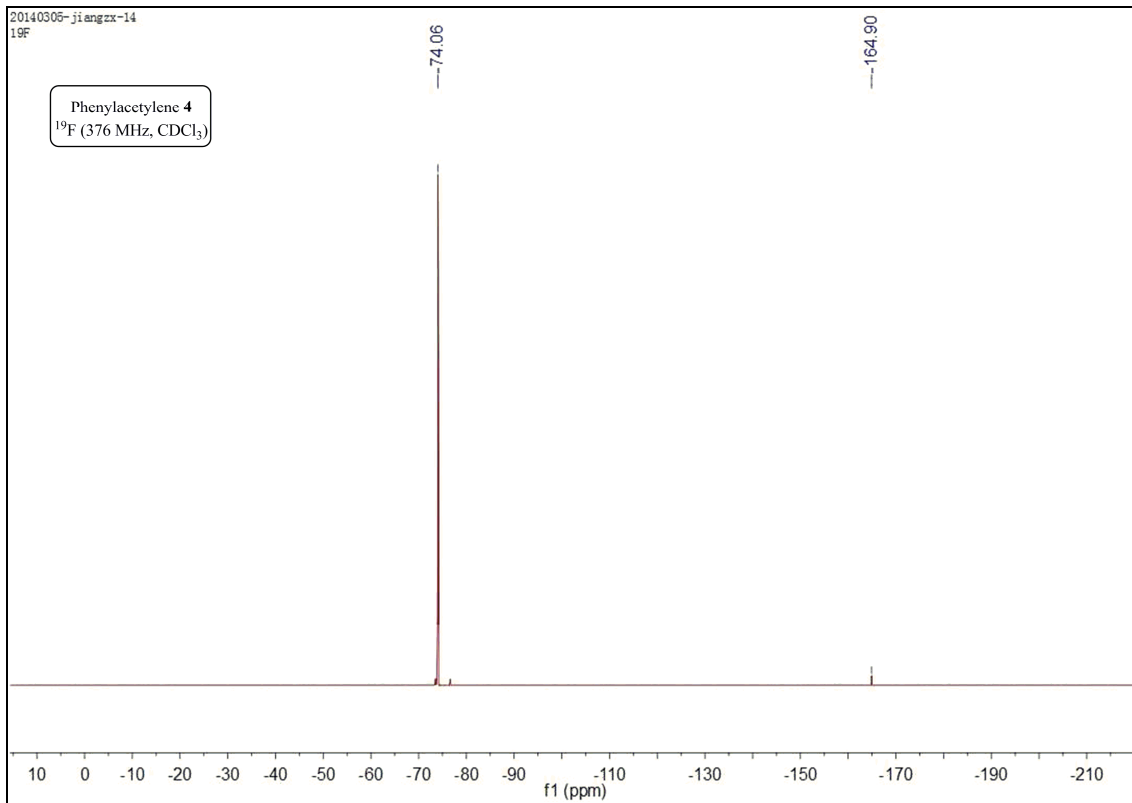
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Acquisition Date 4/19/2014 1:59:42 PM
Operator: zjf
Ionization Mode ESI-Positive
Ion Mass (Measured) 787.0395

Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e ⁻
C 23 H 25 F 9 I 1 N 2 O 10	0.134	787.0405	1.29	1.29	1.02	7.50	ok	even
C 24 H 25 F 8 I 1 N 2 Na 1 O 9	0.139	787.0369	-3.22	-3.22	-2.53	8.50	ok	even
C 23 H 27 F 10 I 1 Na 1 O 9	0.150	787.0432	4.80	4.80	3.78	4.50	ok	even
C 24 H 25 F 12 I 1 Na 1 O 6	0.155	787.0396	0.24	0.24	0.19	5.50	ok	even
C 24 H 23 F 11 I 1 N 2 O 7	0.160	787.0369	-3.27	-3.27	-2.57	8.50	ok	even

20140221-jiangzx-8
1H

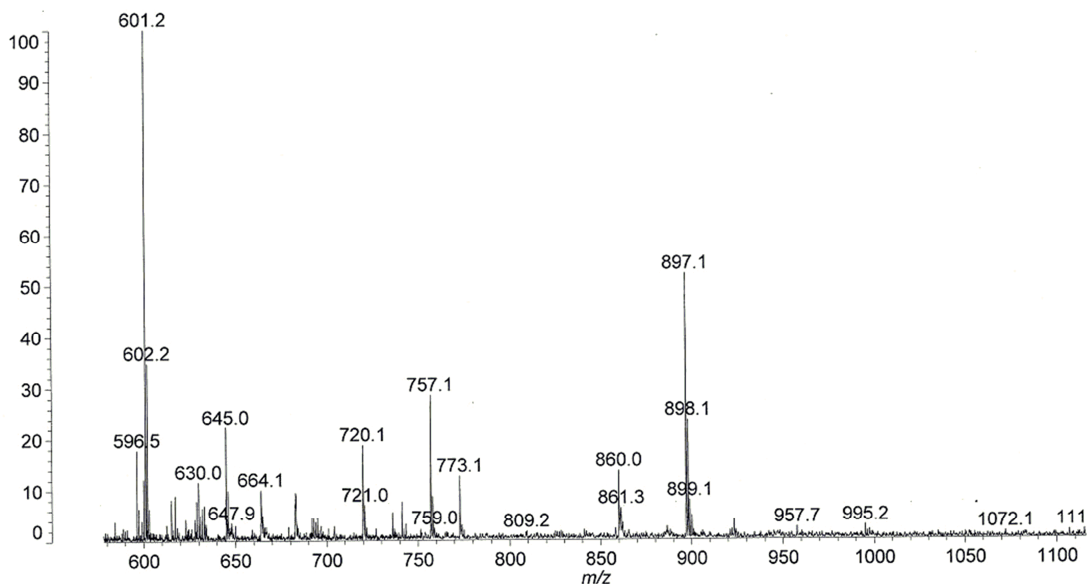
Phenylacetylene 4
¹H (400 MHz, CDCl₃)





Phenylacetylene 4

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 Shimadzu Biotech Axima Performance 2.8.4.20081127: Mode Reflectron, Power: 84, Blanked, P.Ext. @ 739 (bin 56)
 %Int. 56 mV[sum= 2063 mV] Profiles 24-60 Smooth Av 5 -Baseline 80



Phenylacetylene 4

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:

Target m/z = 757.1848 ± 0.003
 Charge = +1

Possible Elements:

Element:	Exact Mass:	Min:	Max:
C	12.000000	0	100
H	1.007825	0	100
O	15.994915	0	7
F	18.998403	10	14
Si	27.976927	0	1
Na	22.989770	0	1

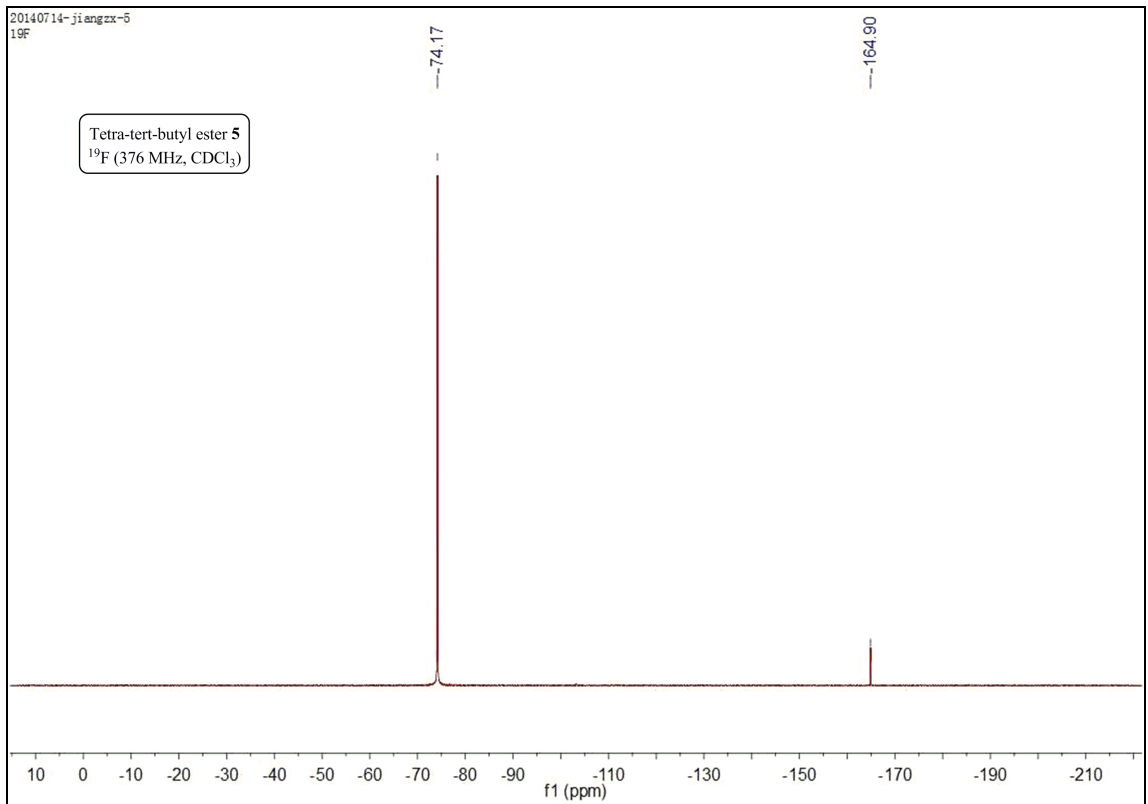
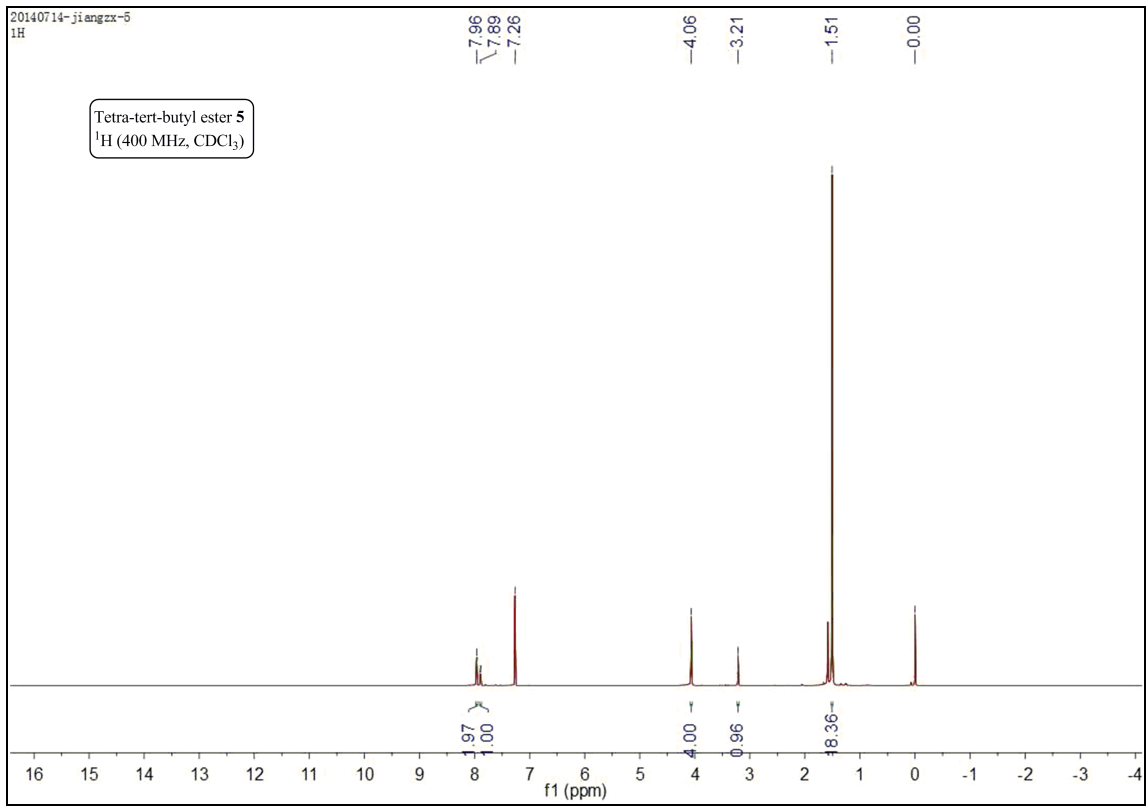
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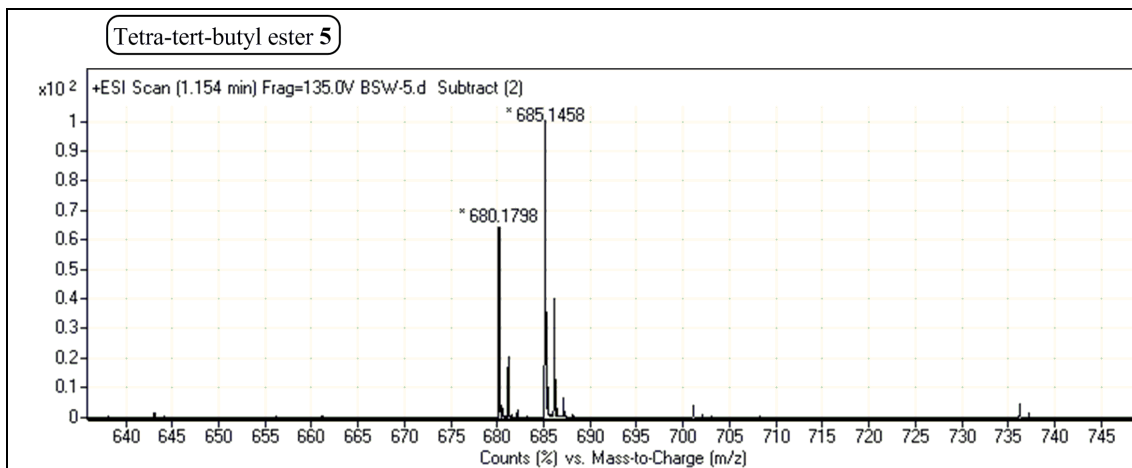
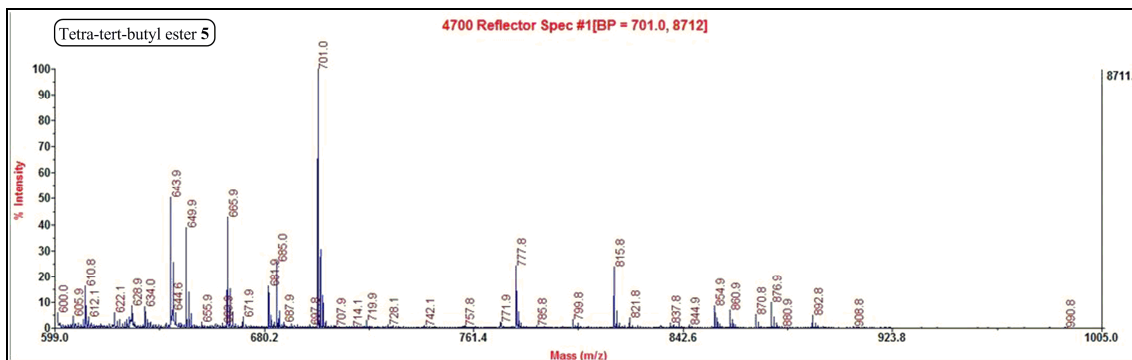
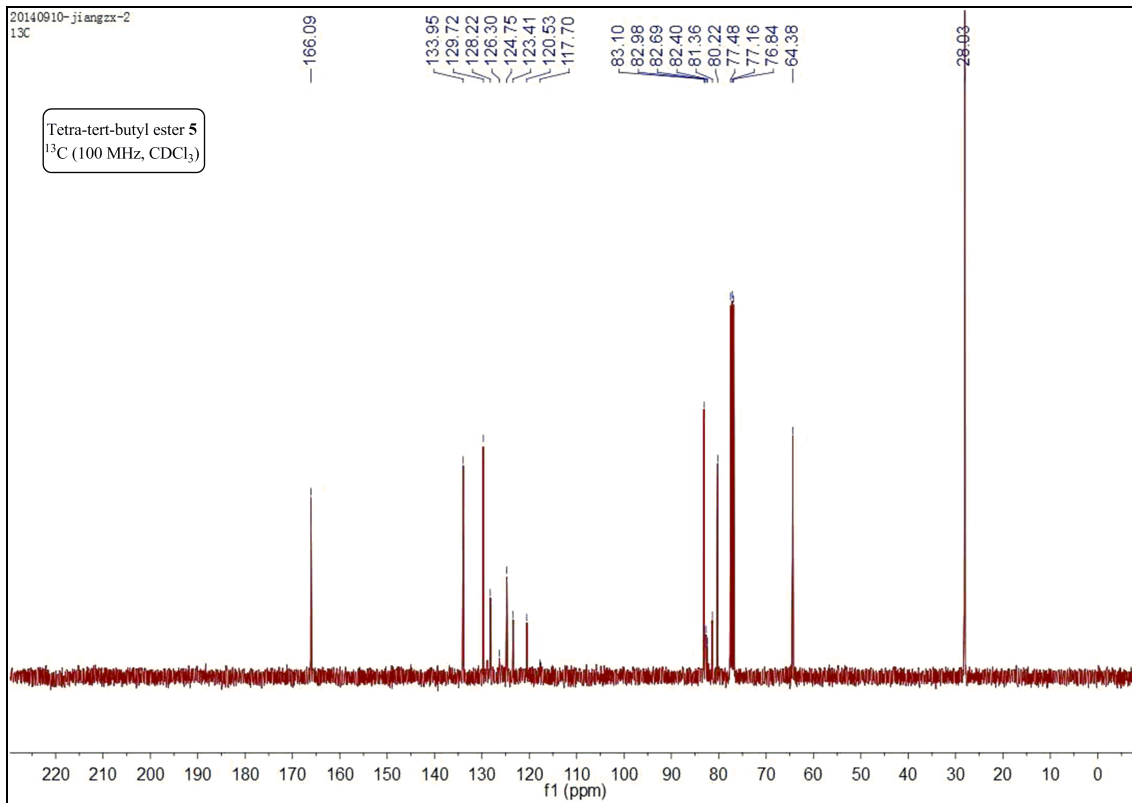
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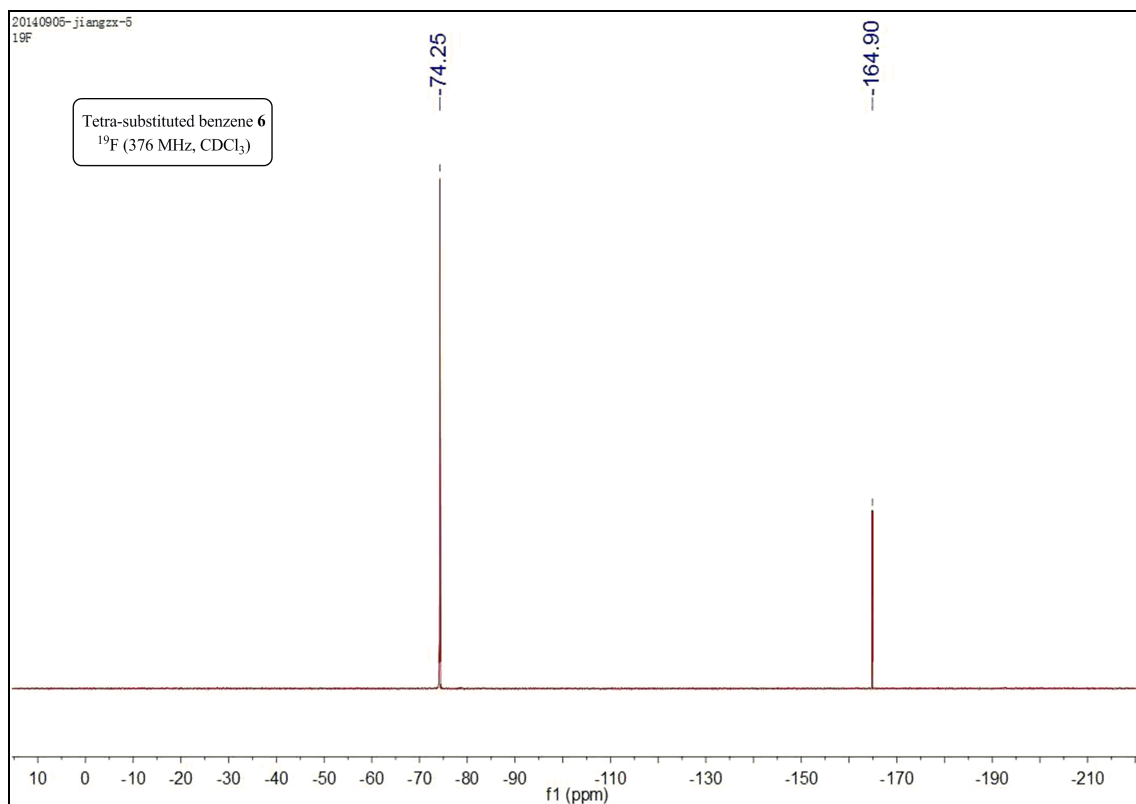
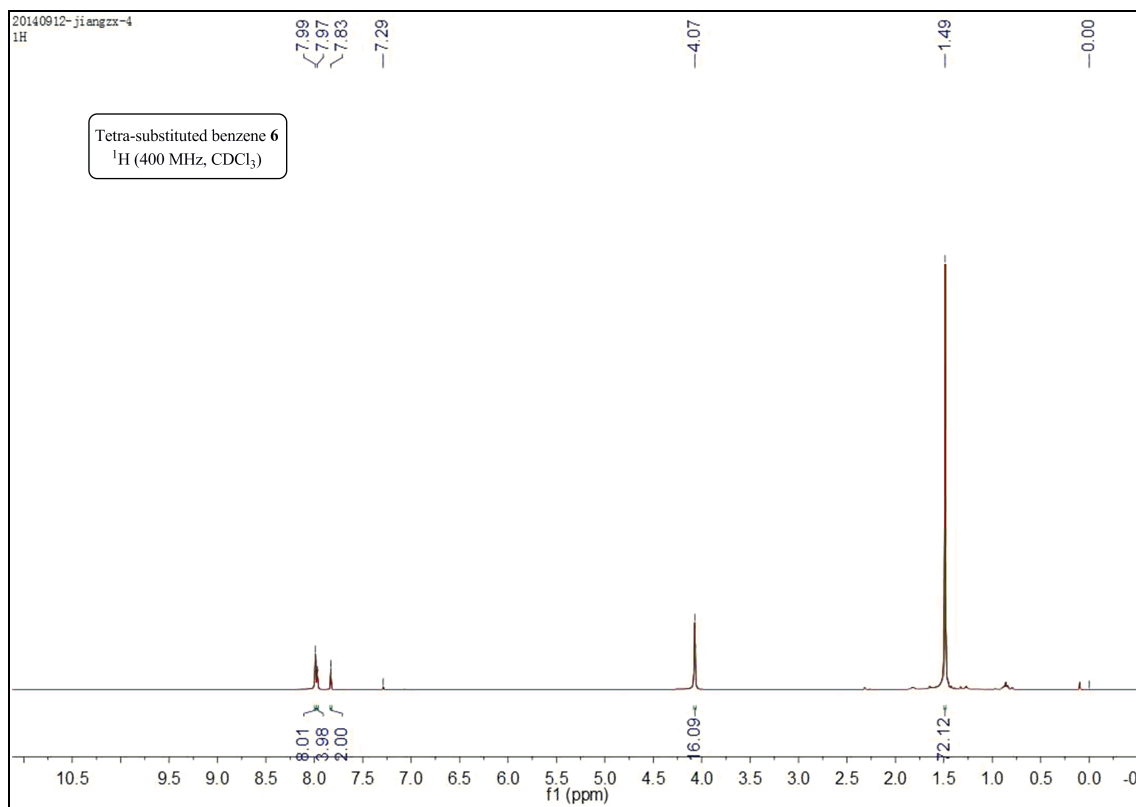
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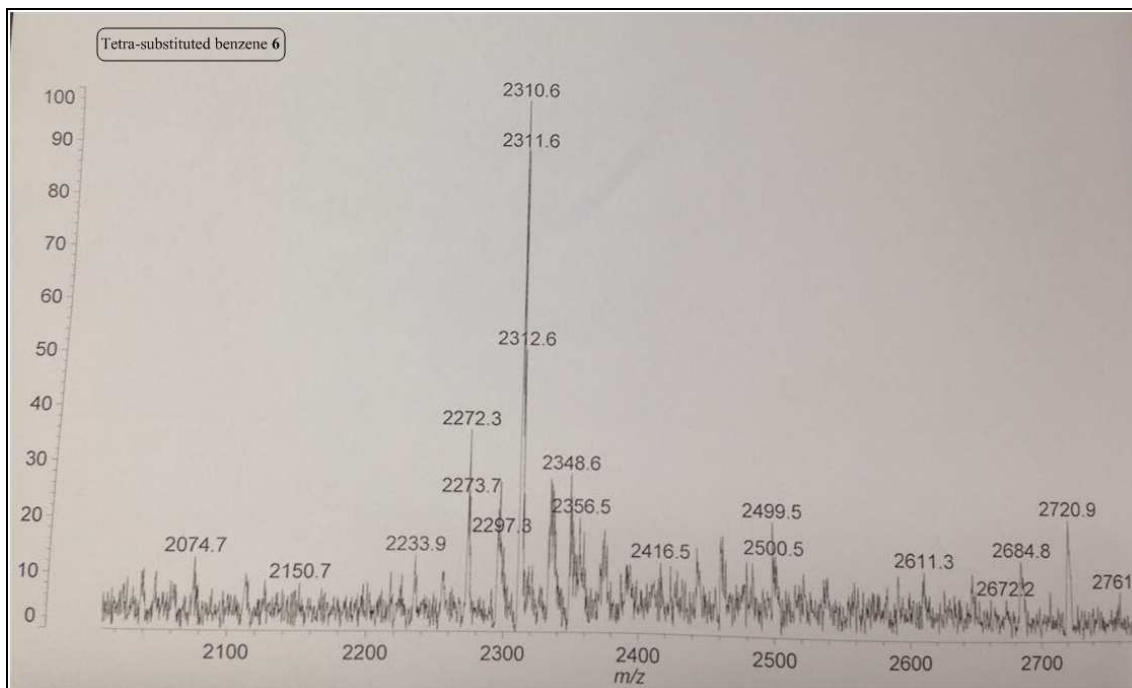
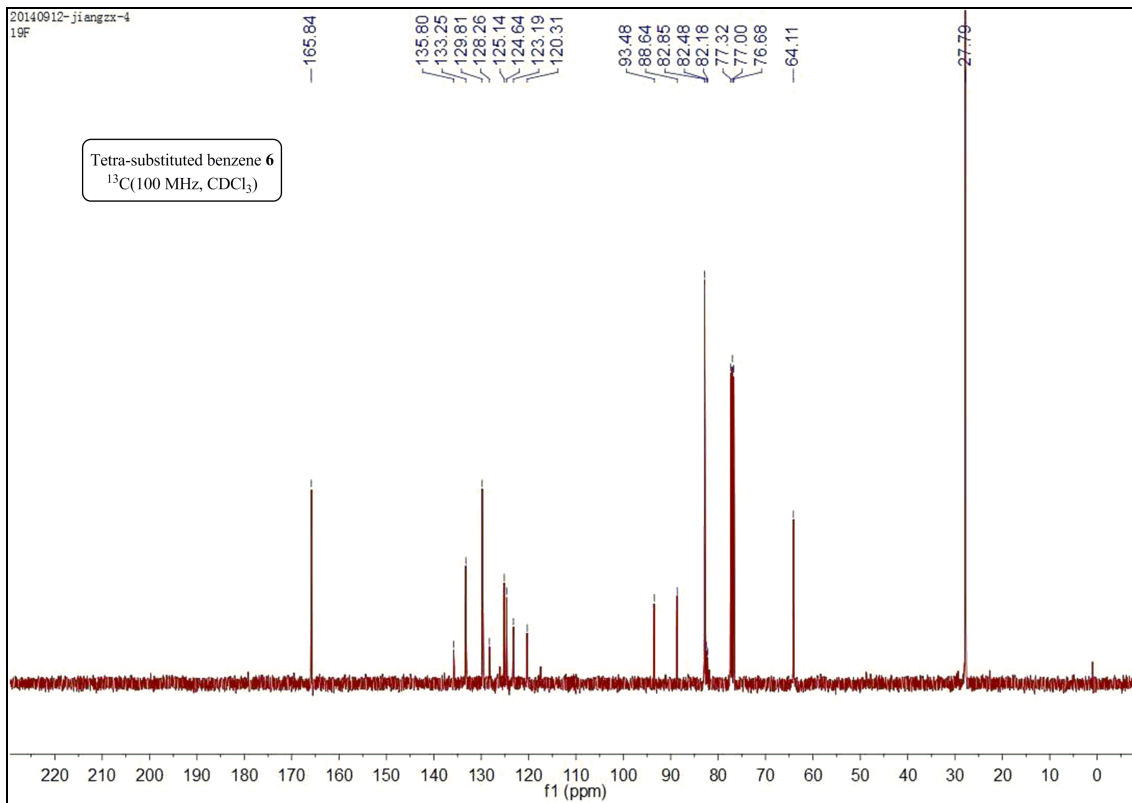
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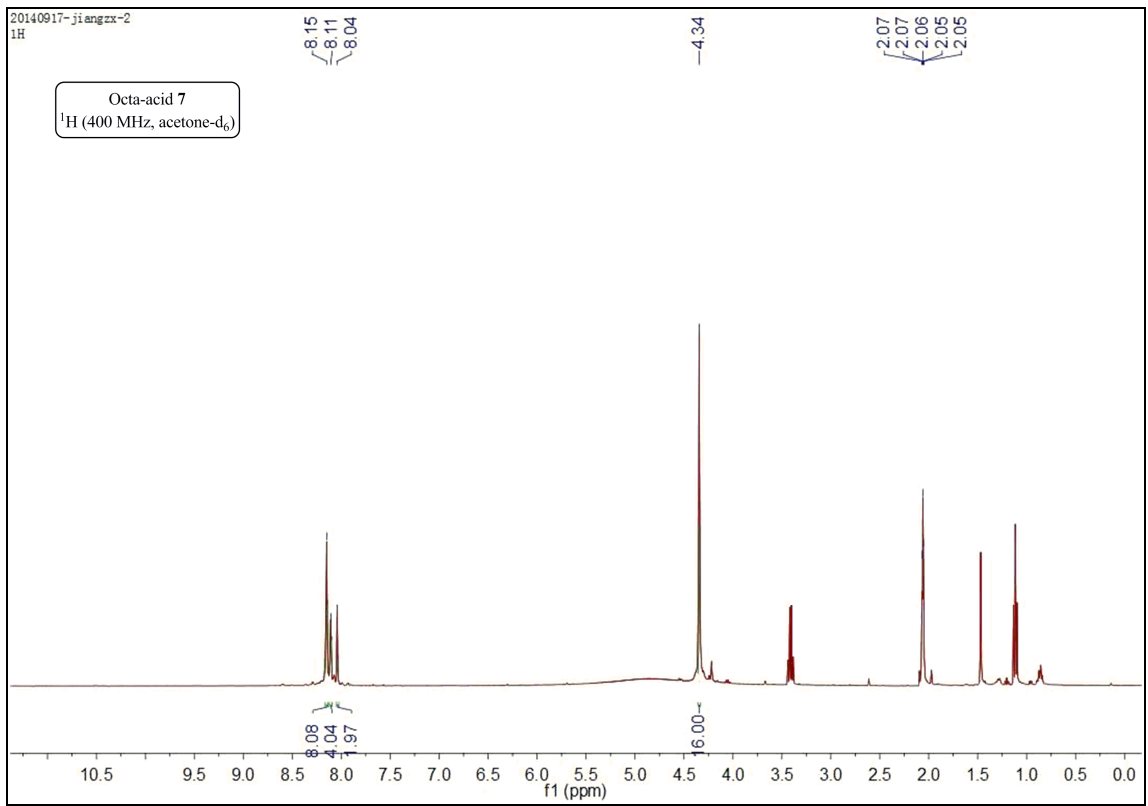
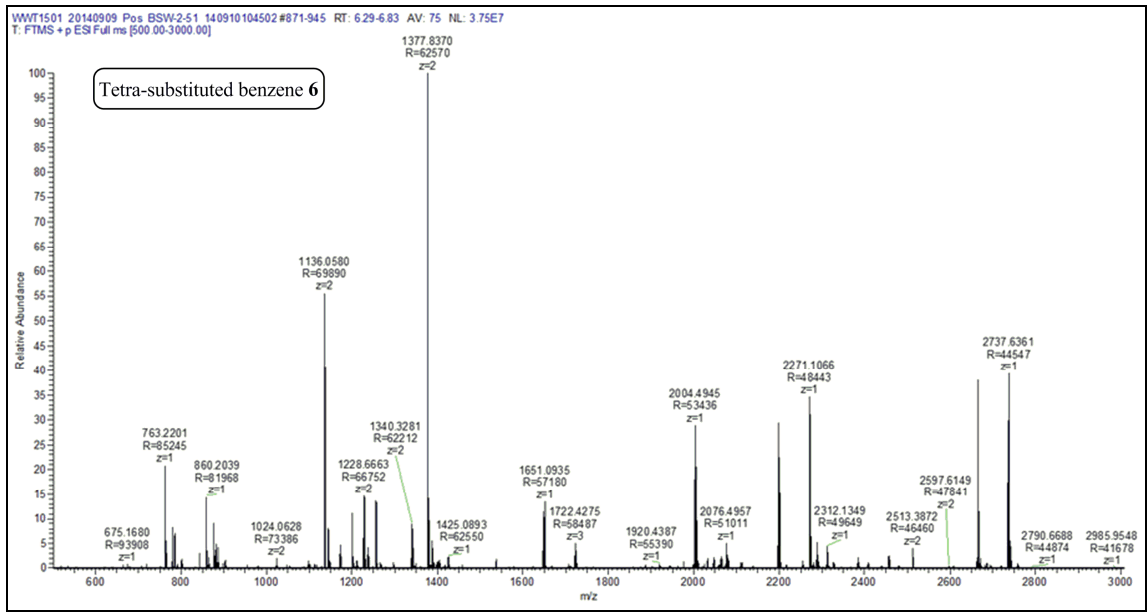
m/z	Delta m/z	DBE	Formula
757.18493	-0.00013	15.5	C ₃₁ H ₃₃ O ₆ F ₁₂ Si ⁺
757.18407	0.00073	14.5	C ₂₉ H ₃₁ O ₇ F ₁₄ ⁺
757.18379	0.00101	19.0	C ₃₄ H ₃₂ O ₅ F ₁₁ Si ⁺
757.18367	0.00113	9.5	C ₂₆ H ₃₅ O ₇ F ₁₃ SiNa ⁺
757.18607	-0.00127	12.0	C ₂₈ H ₃₄ O ₇ F ₁₃ Si ⁺
757.18293	0.00187	18.0	C ₃₂ H ₃₀ O ₆ F ₁₃ ⁺
757.18264	0.00216	22.5	C ₃₇ H ₃₁ O ₄ F ₁₀ Si ⁺
757.18252	0.00228	13.0	C ₂₈ H ₃₄ O ₆ F ₁₂ SiNa ⁺

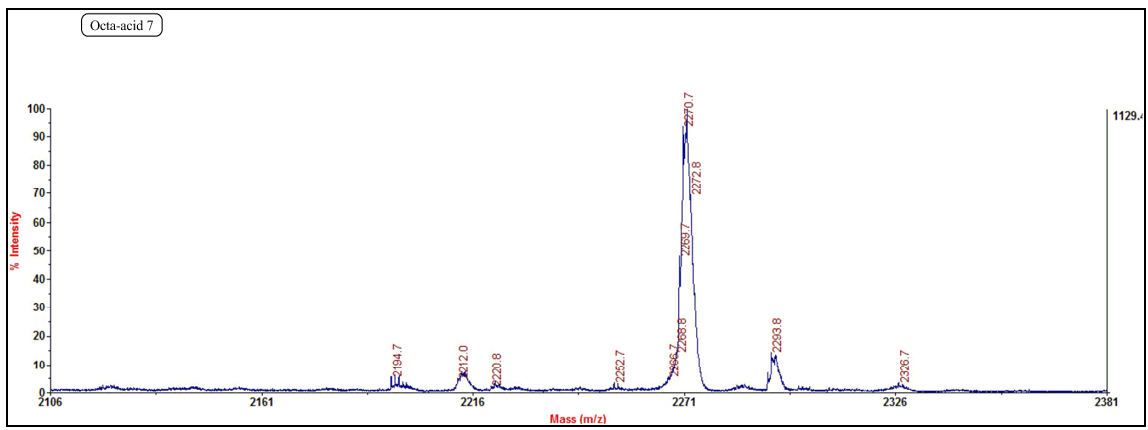
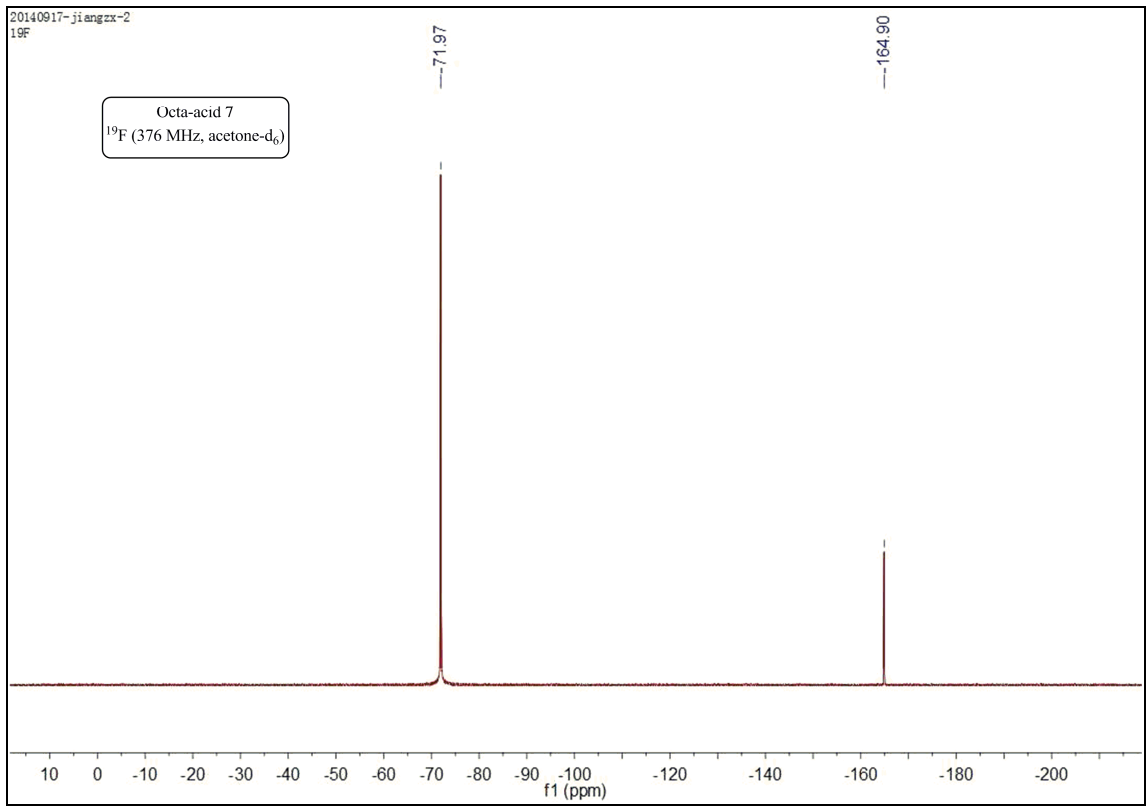












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