

Supporting Information

Dianthracene-Cyclen Conjugate: The First Equal-Equivalent Responding Fluorescent Chemosensor for Pb²⁺ in Aqueous Solution

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1. The determination of the fluorescence quantum yield

The fluorescence quantum yield (Q) is defined as the ratio of the number of photons emitted and the number of photons of the excitation light absorbed while the fluorescent substance absorbed photons. People usually use ratio method for the determination of the fluorescence quantum yield.

$$Q_x = Q_r \left(\frac{A_r(\lambda_r)}{A_x(\lambda_x)} \right) \left(\frac{I(\lambda_r)}{I(\lambda_x)} \right) \left(\frac{n_x^2}{n_r^2} \right) \left(\frac{D_x}{D_r} \right)$$

In this equations $I(a)$ is the relative intensity of the exciting light at wavelength a , n is the average refractive index of the solution to the luminescence, D is the integrated area under the corrected emission spectrum, and $A(a)$ is the absorbance of the solution at the exciting wavelength a . Subscripts x and r refer to the unknown and reference solutions, respectively.^[1,2]

In this paper, we use the same wavelength (365nm) to excite the sample and the standard sample, the two samples were dissolved in the same solvent (H₂O) then the middle two formulas of the equations are 1, so we only need to determine the absorbance (365nm) and the emission spectra of peak area integration. We use fluoresce in 1 N NaOH as reference, $Q_r = 0.85$. The result of the calculation is the fluorescence quantum yield increase from 4.9% to 13.8% after **A1** complex with the lead ions.

[1] E. Tamanini, K. Flavin, M. Motevalli, S. Piperno, L. A. Gheber, M. H. Todd and M. Watkinson, *Inorg. Chem.*, 2009, **49**, 3789-3800.

[2] J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **76**, 994.

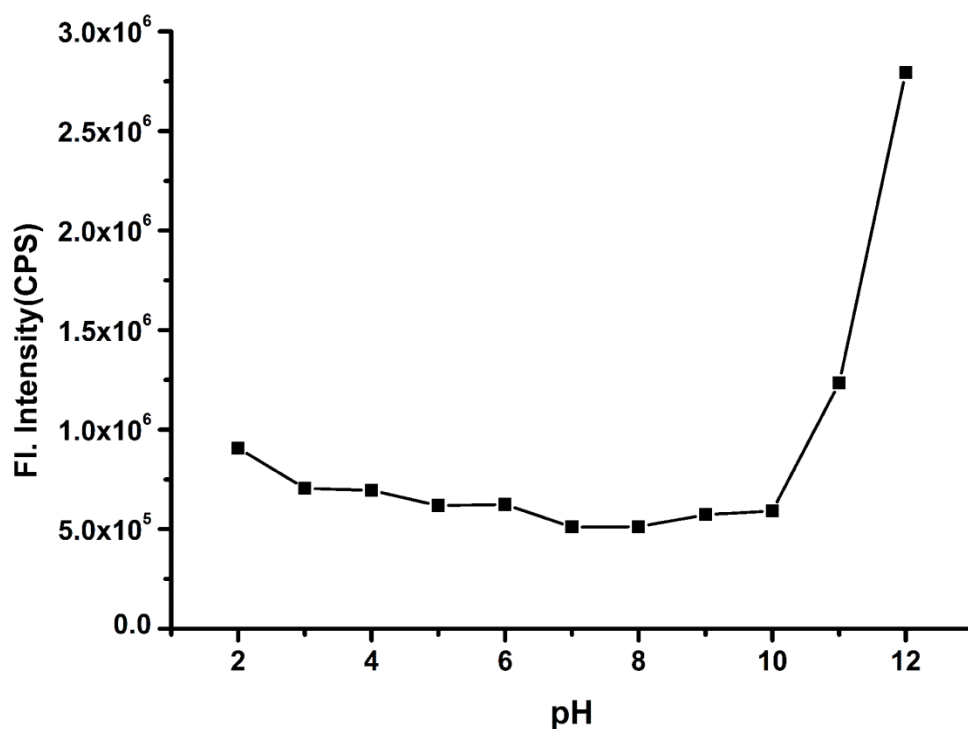


Figure S1. Effect of pH on the fluorescence intensity at 365 nm of **A1** (10 μ M) in buffer solution. The pH of solution was adjusted by aqueous solution of NaOH (1 M) and HCl (1 M).



Figure S2. The color change of **A1** (20 μ M) in HEPES (50 mM, pH = 7.4) under a UV lamp (365 nm) by addition of 2 equiv. different metal ions (from left to right: no metal ion, Pb^{2+} , Cu^{2+} , Hg^{2+} , Zn^{2+} , Mn^{2+} , Ag^+ , Fe^{3+} , Fe^{2+} , Ca^{2+} , Na^+ , Co^{2+} , K^+ , Li^+ , Cr^{3+} , Mg^{2+} , Al^{3+} , Ba^{2+} , Ni^{2+} , Cd^{2+}).

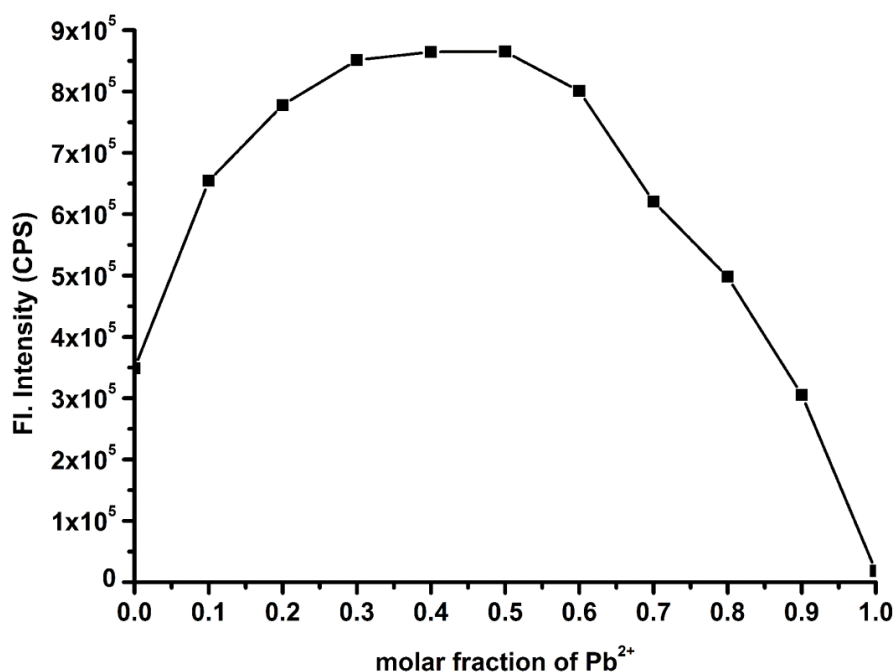


Figure S3. Job's plot of A1 and Pb²⁺. The total concentration of A1 and Pb²⁺ were kept at 10 μM in HEPES (50 mM, pH = 7.4). (λ_{ex} = 365 nm, λ_{em} = 415 nm).

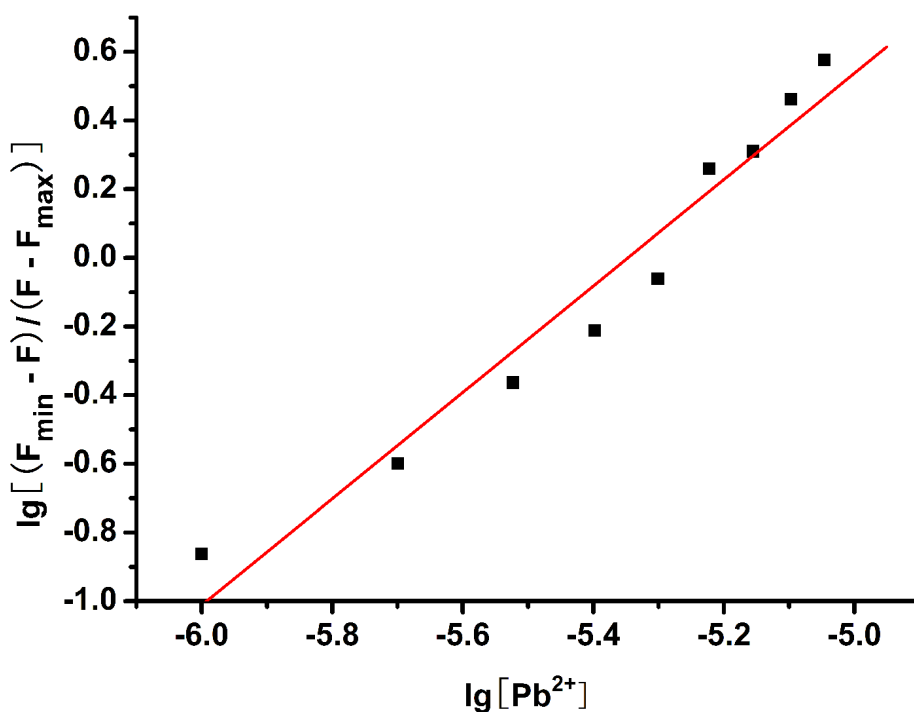


Figure S4. Fluorescence intensity of A1 at 365 nm as a function of lg[Pb²⁺] (1 -10 μM) in the condition of the Pb²⁺ titration. (r = 0.977)

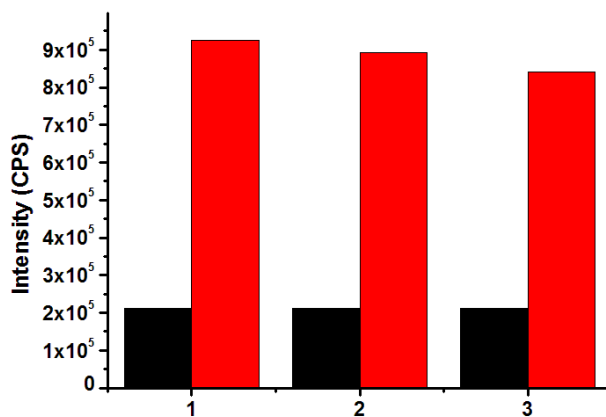


Figure S5 Fluorescent responses of **A1** (10 μM) to Pb^{2+} in the presence of Cu^{2+} and Hg^{2+} (50 mM HEPES, pH = 7.4). 1: 10 μM Pb^{2+} ; 2: 10 μM Pb^{2+} and 1 μM Hg^{2+} ; 3: 10 μM Pb^{2+} and 1 μM Cu^{2+} .

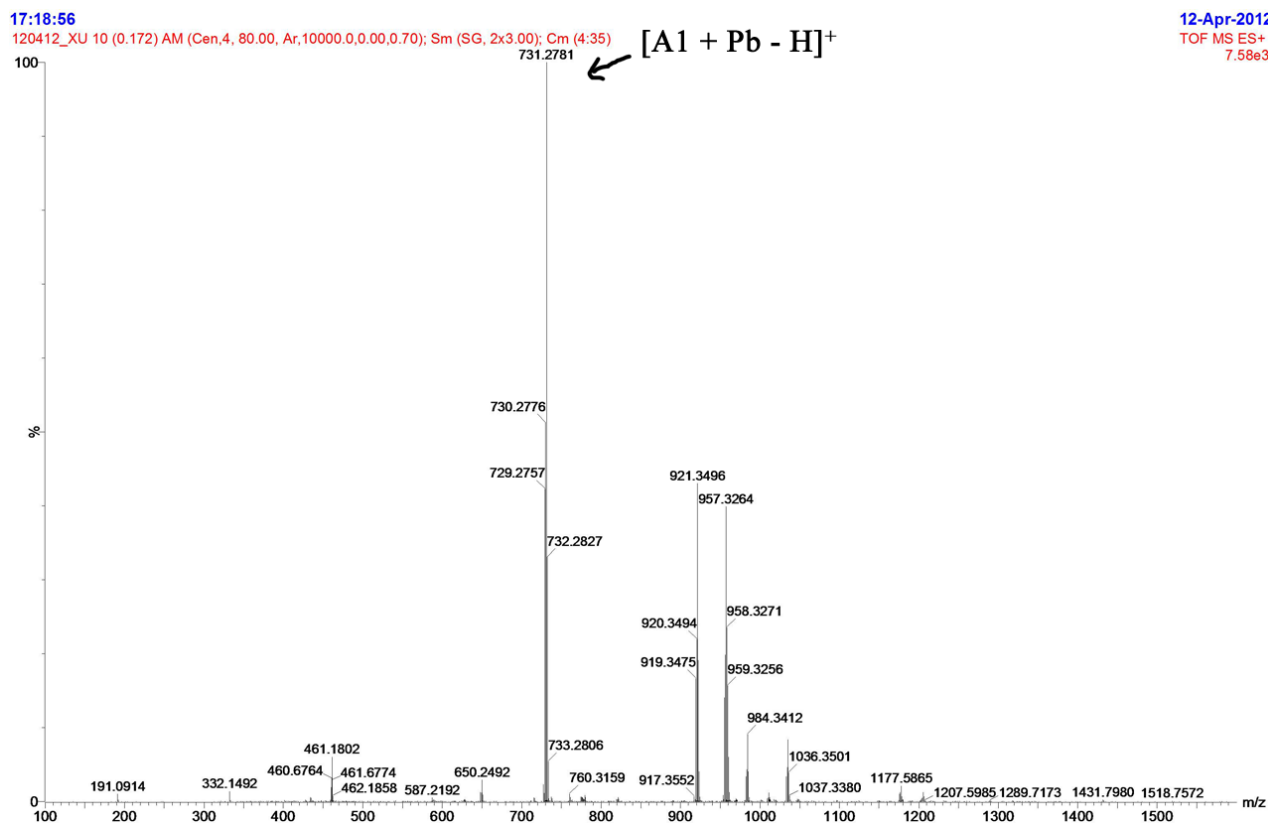


Figure S6. The ESI-TOF mass spectrum of a mixture of **A1** and $\text{Pb}(\text{NO}_3)_2$.

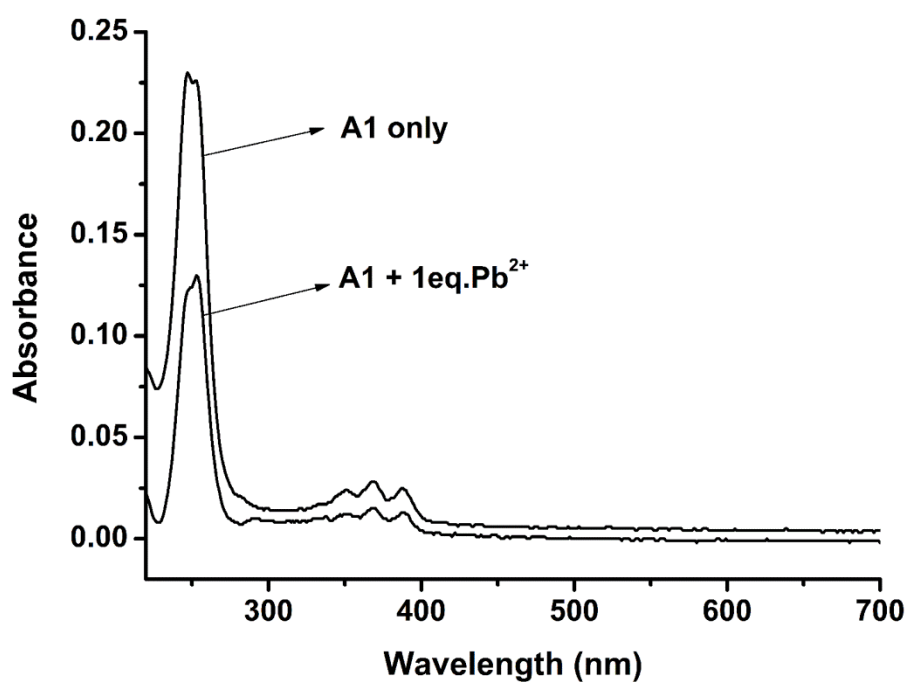


Figure S7. UV-vis spectra of probe **A1** ($1 \mu\text{M}$) in 50mM HEPES (pH=7.4) and followed by Pb^{2+} (1 equiv.).

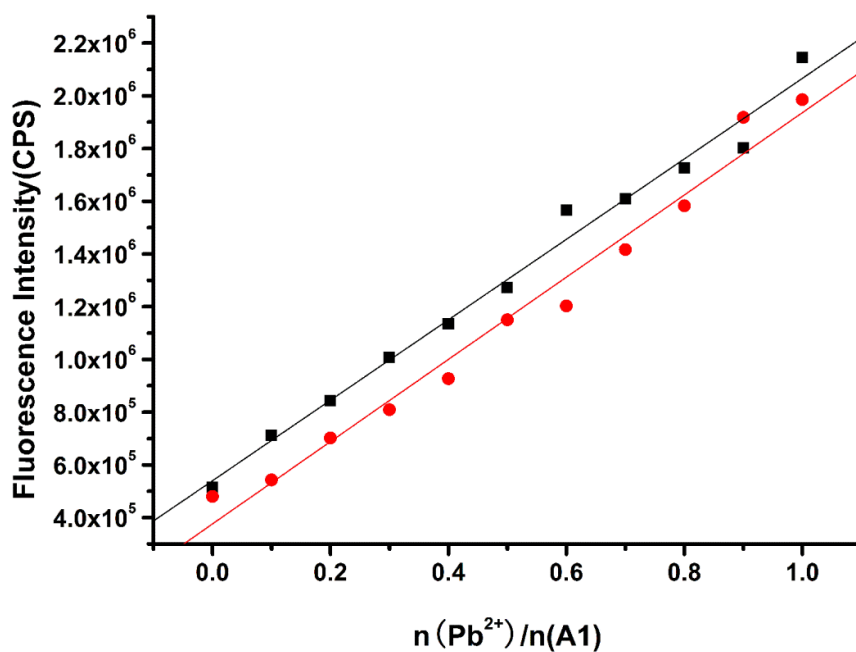
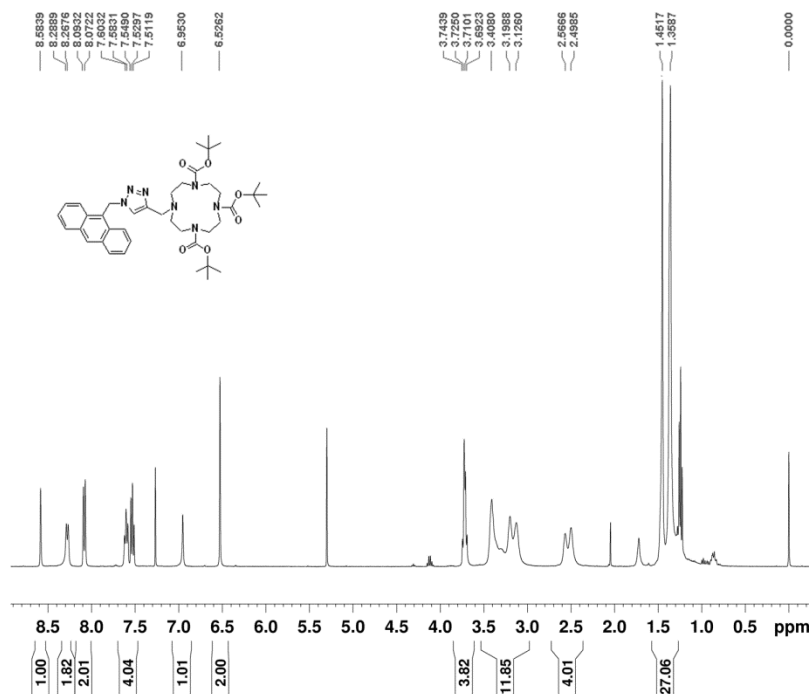


Figure S8. Fluorescence intensity of **A1** at 415 nm as a function of $n(\text{Pb}^{2+})/n(\text{A1})$ in the condition of the Pb^{2+} titration. One of them is in water (black, ■, $r = 0.9934$), another is in calf serum (red, ●, $r = 0.9898$).

¹H-NMR, ¹³C-NMR and HRMS spectra of A1, A2 and intermediates.

LEN-3BOC-HNMR



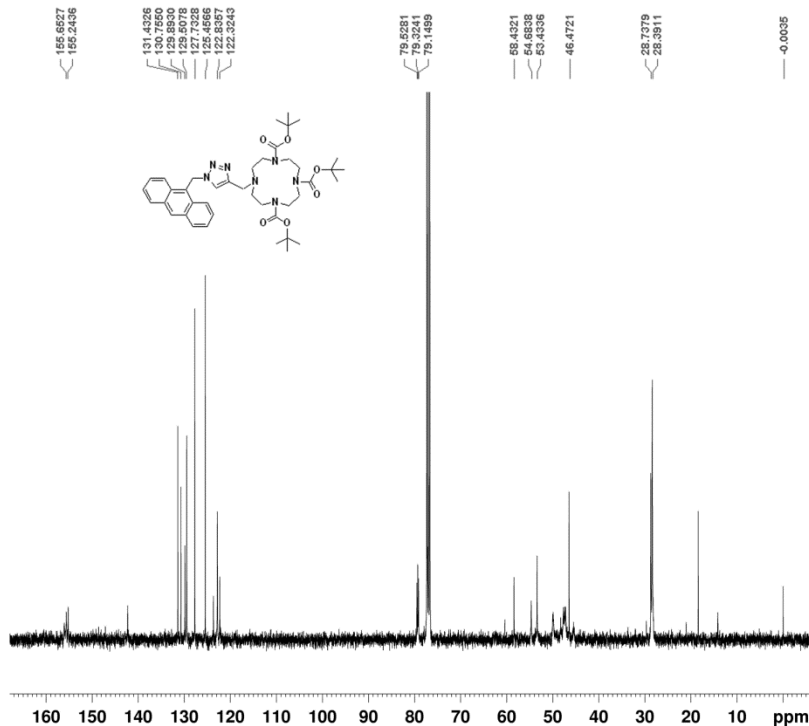
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PROCNO   1
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Time     15.41
INSTRUM  spect
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PULPROG  zg30
TD       65536
SOLVENT  CDCl3
NS       16
DS       2
SWH      8223.685 Hz
FIDRES   0.125483 Hz
AQ       3.9846387 sec
RG       113.18
DW       60.800 usec
DE       8.00 usec
TE       294.6 K
D1       1.00000000 sec
D10      1
    
```

```

===== CHANNEL f1 =====
NUC1     1H
P1       12.60 usec
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LB       0.30 Hz
GB       0
PC       1.00
    
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LEN-3BOC-CNMR



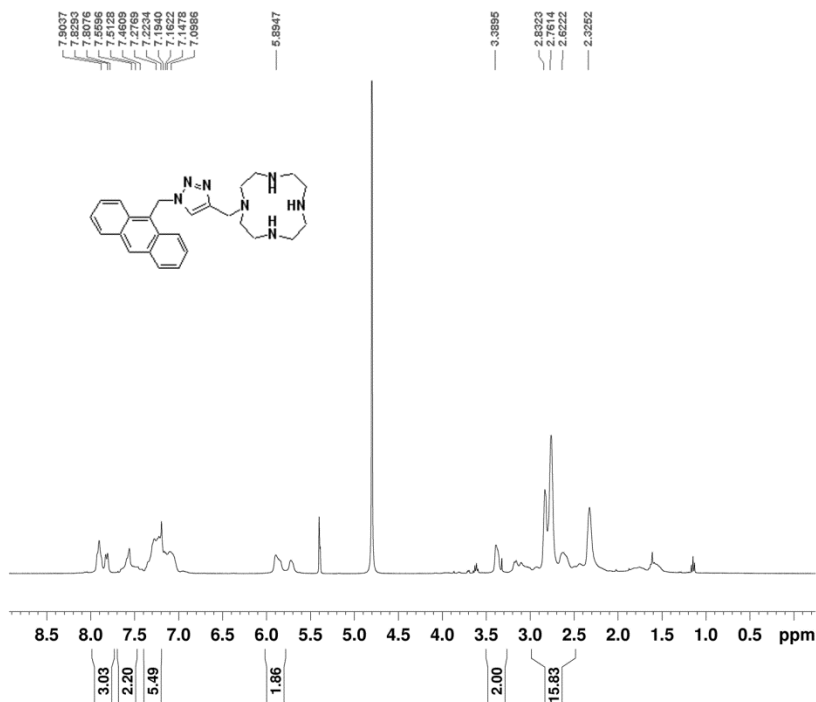
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PULPROG  zgpg30
TD       65536
SOLVENT  CDCl3
NS       2048
DS       4
SWH      24038.461 Hz
FIDRES   0.366798 Hz
AQ       1.3631988 sec
RG       197.41
DW       20.800 usec
DE       8.00 usec
TE       295.6 K
D1       2.00000000 sec
D11      0.03000000 sec
D10      1
    
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```

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LEN-CYC-HNMR



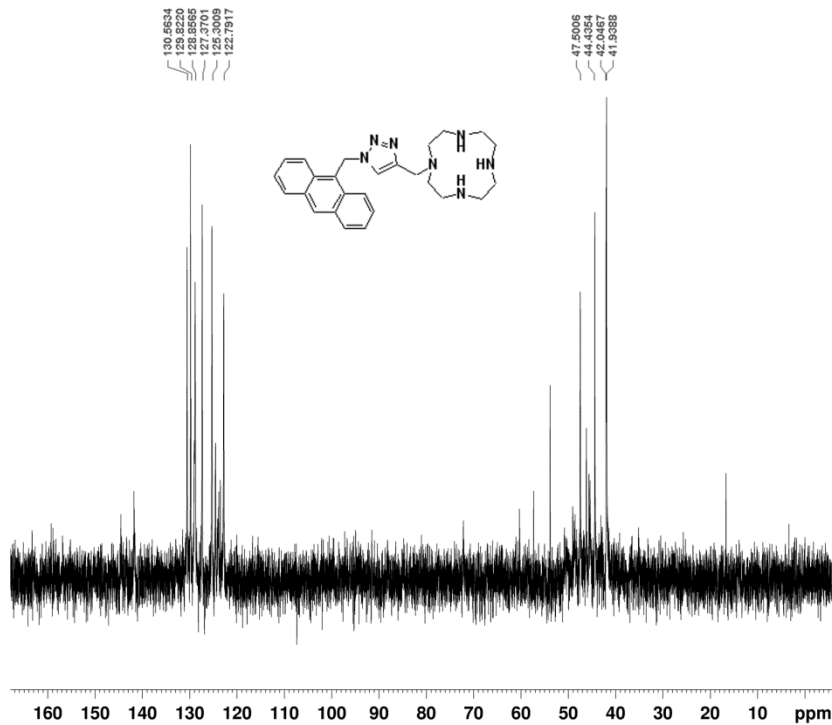
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PULPROG        zg30
TD             65536
SOLVENT        D2O
NS             16
DS             2
SWH            8223.685 Hz
FIDRES         0.125483 Hz
AQ            3.9846387 sec
RG            99.91
DW            60.800 usec
DE            8.00 usec
TE            294.8 K
D1            1.00000000 sec
D10           1
    
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```

===== CHANNEL f1 =====
NUC1           1H
P1            12.60 usec
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LEN-CYC-CNMR



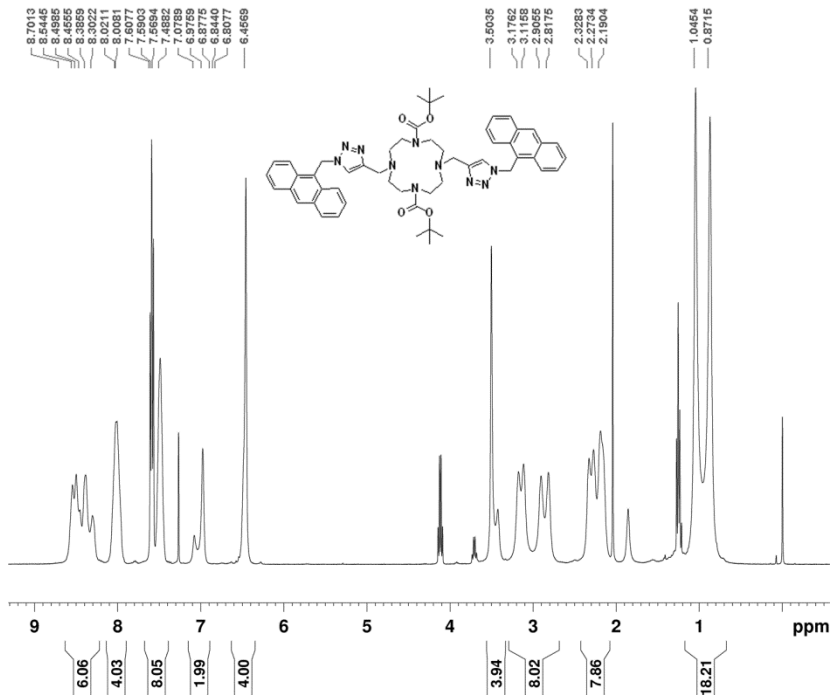
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PROCNO         1
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TD             65536
SOLVENT        D2O
NS            2048
DS             4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG            197.41
DW            20.800 usec
DE            8.00 usec
TE            295.8 K
D1            2.00000000 sec
D11           0.03000000 sec
D10           1
    
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```

===== CHANNEL f1 =====
NUC1           13C
P1            9.60 usec
SI            32768
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WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
    
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ZEN2BOC-HNMR

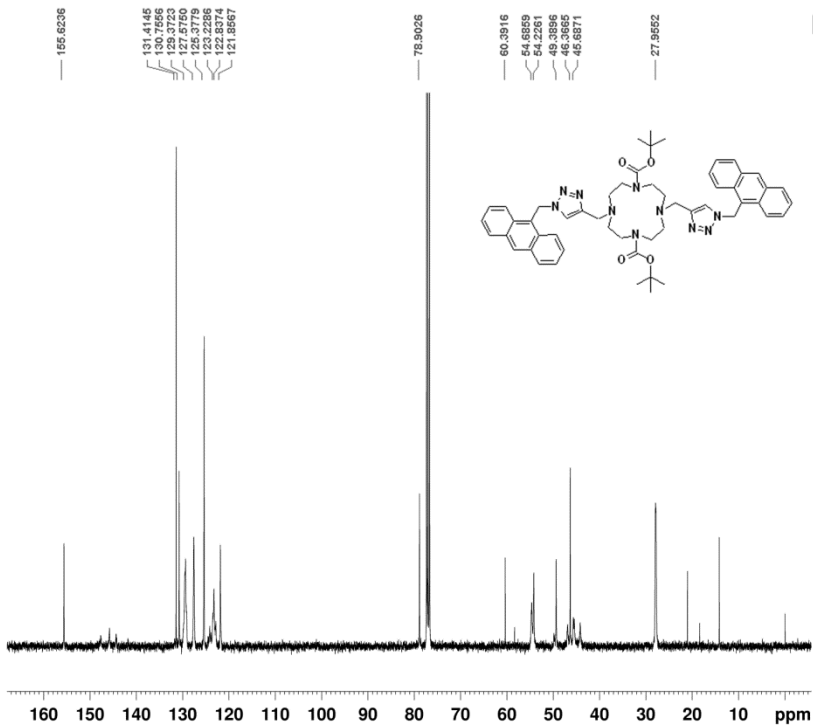


```

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PROCNO   1
Date_    20120503
Time     15.37
INSTRUM  spect
PROBHD   5 mm PABBO BB/
PULPROG  zg30
TD       65536
SOLVENT  CDCl3
NS       16
DS       2
SWH      8223.685 Hz
FIDRES   0.125483 Hz
AQ       3.9846387 sec
RG       71.59
DW       60.800 usec
DE       8.00 usec
TE       294.8 K
D1       1.00000000 sec
TD0      1

----- CHANNEL f1 -----
NUC1     1H
P1       12.60 usec
SI       65536
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LB       0.30 Hz
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PC       1.00
    
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ZEN2BOC-CNMR

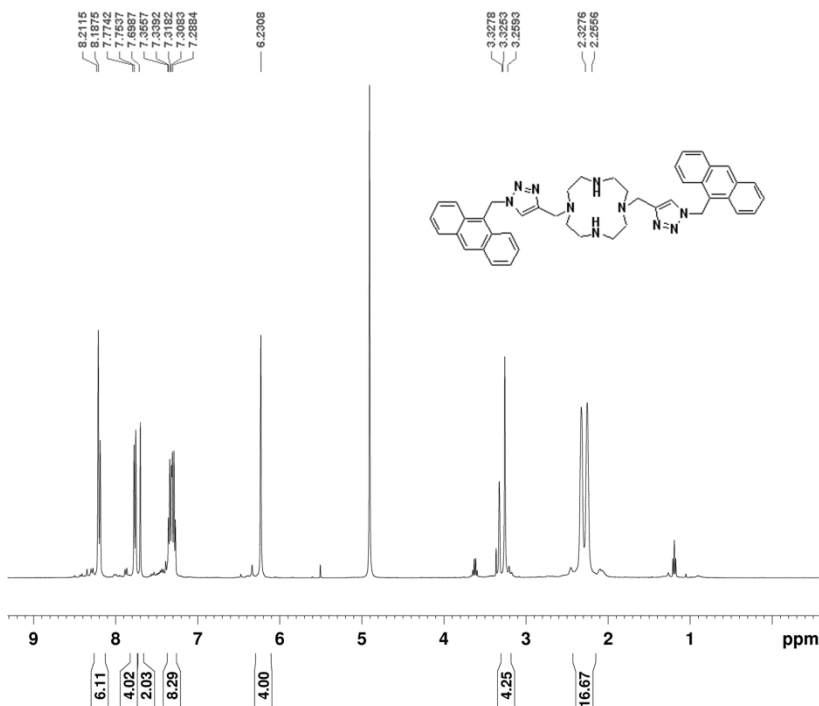


```

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PROCNO   1
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Time     1.22
INSTRUM  spect
PROBHD   5 mm PABBO BB/
PULPROG  zgpg30
TD       65536
SOLVENT  CDCl3
NS       2048
DS       4
SWH      24038.461 Hz
FIDRES   0.366798 Hz
AQ       1.3631988 sec
RG       197.41
DW       20.800 usec
DE       8.00 usec
TE       295.8 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0      1

----- CHANNEL f1 -----
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P1       9.60 usec
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LB       1.00 Hz
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PC       1.40
    
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ZENCYC-HNMR



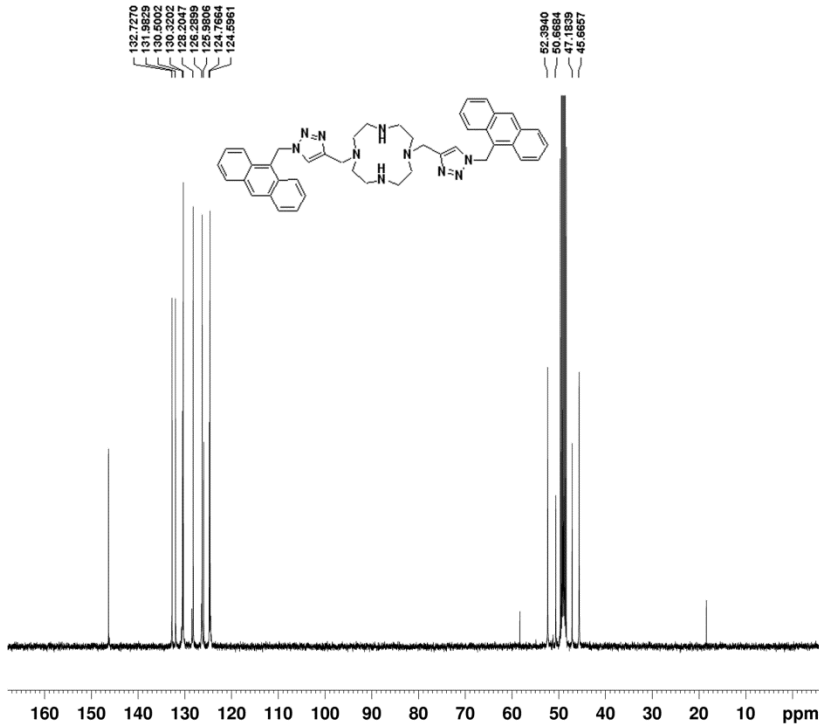
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PROCNO        1
Date_         20120503
Time          15.31
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PULPROG       zg30
TD            65536
SOLVENT       MeOD
NS            16
DS            2
SWH           8223.685 Hz
FIDRES        0.125483 Hz
AQ            3.9846387 sec
RG            71.59
DW            60.800 usec
DE            8.00 usec
TE            294.5 K
D1            1.00000000 sec
D0            1
    
```

```

===== CHANNEL f1 =====
NUC1          1H
P1            12.60 usec
SI            65536
SF            400.1600000 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
    
```

ZENCYC-CNMR



```

NAME          A9i¼Æ×
EXPNO         1
PROCNO        1
Date_         20120503
Time          23.21
INSTRUM       spect
PROBHD        5 mm PABBO BB/
PULPROG       zgpg30
TD            65536
SOLVENT       MeOD
NS            2048
DS            4
SWH           24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631988 sec
RG            197.41
DW            20.800 usec
DE            8.00 usec
TE            295.7 K
D1            2.00000000 sec
D11           0.03000000 sec
D0            1
    
```

```

===== CHANNEL f1 =====
NUC1          13C
P1            9.60 usec
SI            32768
SF            100.6201691 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
    
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