Supporting Information:

Photo-isomerization of Spiropyran for driving a Molecular Shuttle

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Table of contents:

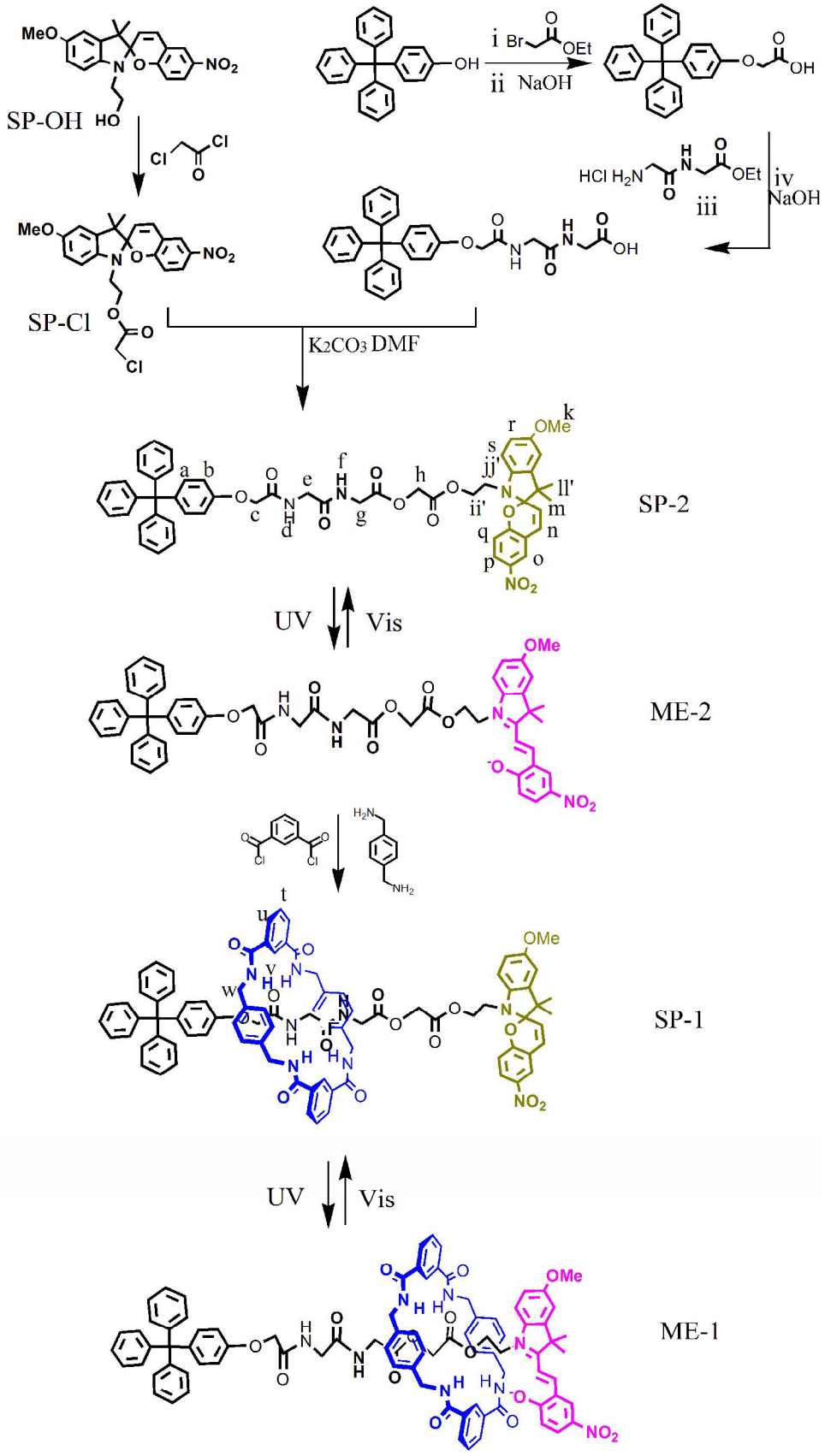
§1. Materials.

Unless stated otherwise, all reagents and anhydrous solvents were purchased for Aldrich Chemicals and used without further purification.

§2. Measurements

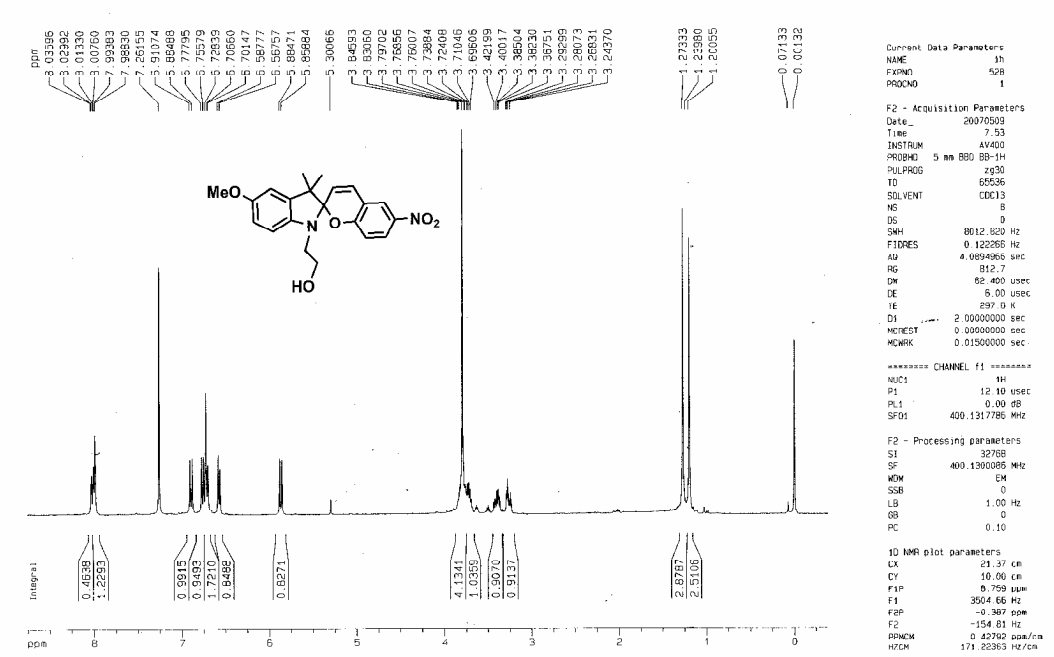
Columnchromatography (CC): SiO_2 (200−300 meshes). TLC glass plates coated with SiO_2 F254 were visualized by UV light. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 400 or 600 instruments, at a constant temperature of 25°C. Chemical shifts are reported in parts per million from low to high field and referenced to TMS. MALDI-TOF mass spectrometric measurements were performed on Bruker Biflex III MALDI-TOF. UV/ vis spectra were measured on a Hitachi U-3010 spectrometer. Fluorescence excitation and emission spectra were recorded using a Hitachi F-4500 FL fluorimeter at a constant temperature of 25°C.

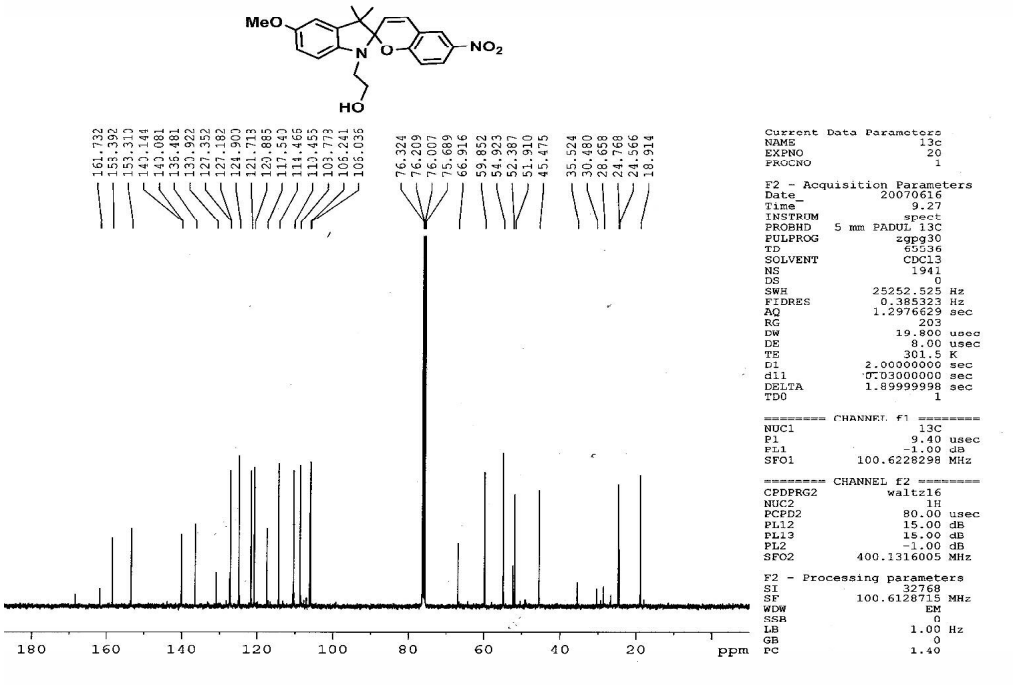
§3. Synthesis Route



§4. Synthesis and characterization data of all compounds

SPN-OH A solution of *6-methoxy-3a,4,4-trimethyloxazolidino[3,2-a]indoline* (932mg, 4 mmol) and 2-hydroxy-5-nitrobenzaldhyde (735mg, 4.4 mmol) in alcohol (15mL) was heated for 3h under reflux and nitrogen. After cooling down to room temperature, the mixture was filtered. The residual purple solid was washed with EtOH (10×3) and dried to afford **ME** (1.2g, 81%). ^{1}H NMR($CDCl_3$) δ 8.007(m, 2H), 6.898(d, 1H, *J*=10.344 Hz), 6.756(m, 3H), 6.577(d, 1H, *J*=8.08Hz), 5.872(d, 1H, *J*=10.35 Hz), 3.79(s, 3H), 3.84-3.69 (m, 2H), 3.40(m, 1H), 3.28(m, 1H), 1.27(s, 3H), 1.239(s, 3H). ^{13}C NMR($CDCl_3$) δ 158.39, 153.31, 140.08, 136.48, 130.92, 127.18, 124.90, 121.718, 120.88, 117.54, 114.466, 110.455, 108.778, 106.24, 106.03, 66.91, 59.85, 54.93, 52.39, 51.91, 45.475, 24.768, 24.566, 18.914. MS (EI): 381(M^+)





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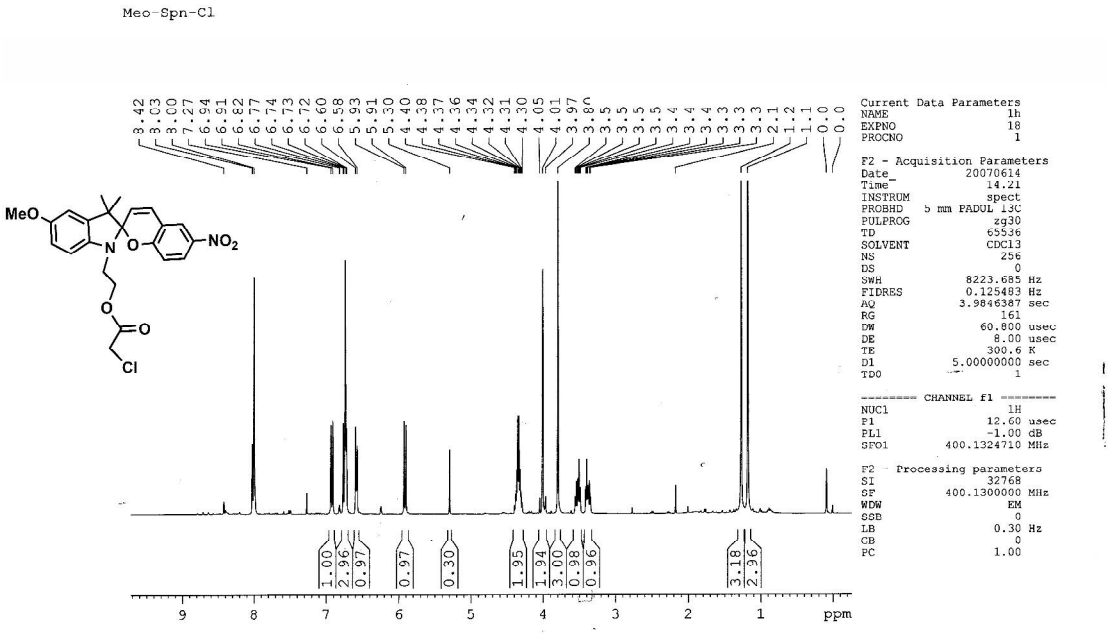
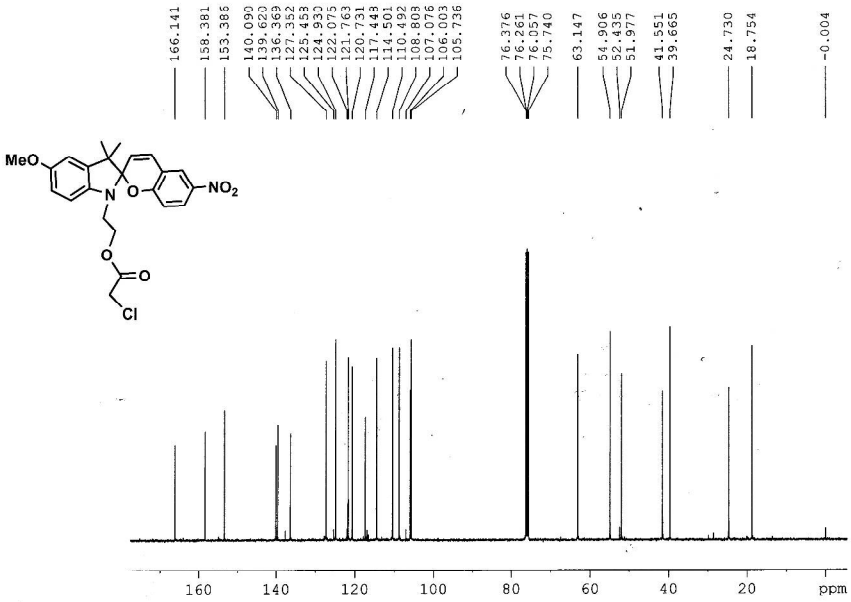
SPN-Cl

2-chloroacetyl chloride (0.67g, 6mmol) was added to a solution of SPN-OH (1g, 2.6mmol) and Et_3N (1mL) in $CHCl_3$ at 0^oC. Then the mixture was stirred at room temperature for 8h and washed with distilled water (3×50mL). The collected organic layers were dried over $NaSO_4$, and the chloroform was removed in vacuum to gain the product **SPN-Cl** (0.892g, 75%) after the purification by flash chromatograph (CH_2Cl_2: hexane, 1/1, v/v). ^1H NMR($CDCl_3$) δ 8.03 (m, 2H), 6.93(d, 1H, *J*=12Hz), 6.74(m, 3H), 6.59(d, 1H, *J*=8Hz), 5.92(d, 1H, *J*=8Hz), 4.3(m, 2H), 4.05(s, 2H), 3.80(s, 3H), 3.5 (m, 1H), 3.4 (m, 1H), 1.2 (s, 3H), 1.1 (s, 3H). ^{13}C NMR($CDCl_3$) δ 166.14, 158.38, 153.38, 140.09, 139.62, 136.37, 127.35, 124.93, 121.76, 120.73, 117.45, 114.50, 110.49, 108.81, 106.003, 105.736, 63.147, 54.91, 51.97, 41.55, 39.66, 24.73, 18.75. MS (EI): 458.1.



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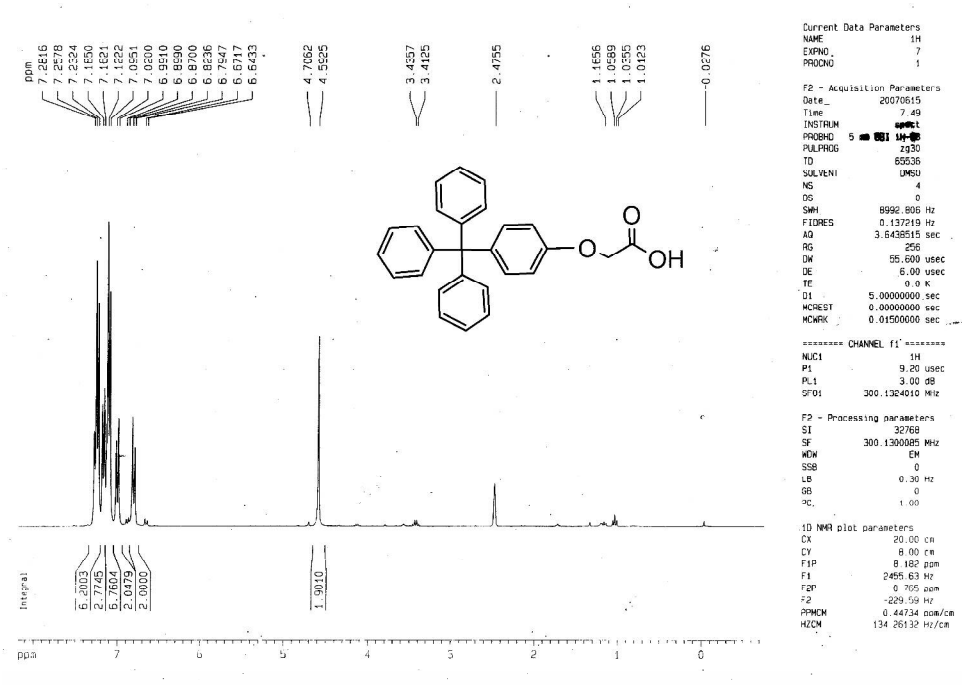
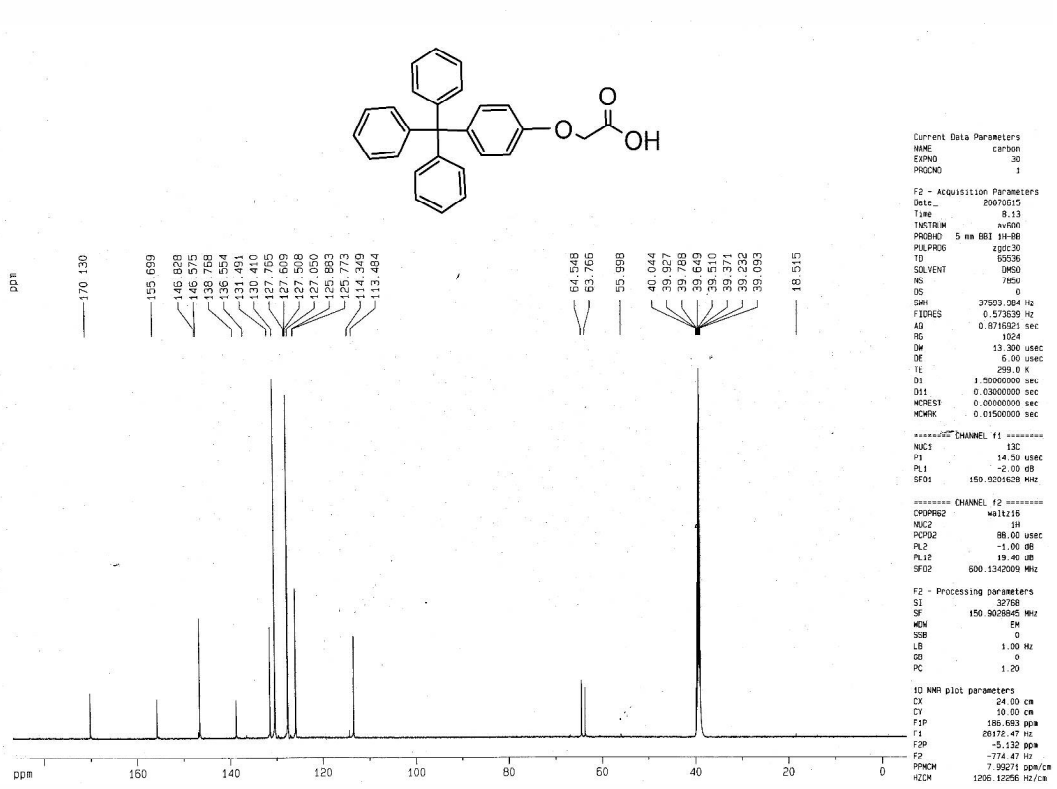
2-(4-tritylphenoxy)acetic acid (2)

A mixture of 4-tritylphenol (3.36g, 10mmol) and ethyl 2-bromoacetate (1.67g, 10mmol) were dissolved in 250 mL dry acetone and refluxed for 6 hours in the presence of K_2CO_3 (4.14 g, 30mmol) under nitrogen. The mixture was filtered and the solvent was evaporated. The crude product was dissolved in CH_2Cl_2 and washed three times with distilled water. The organic solvent was then evaporated off to give a pale solid, which was used directly in the following step without further purification. To the ethanol solution of this pale solid, 10ml 50% NaOH aqueous solution was added at room temperature. The mixture was stirred for 10 hours followed by the addition of excess hydrochloric acid. Much white appreciate formed with the addition of hydrochloric acid, then it was filtered and washed with distilled water and CH_2Cl_2 for several times to give the white solid (2.1g, 53%). MS (EI): 393(M^+). ^{1}H NMR(DMSO-D_6) δ7.258 (m, 6H), 7.18-7.09(9H), 7.005(d, 2H, *J*=9Hz), 6.801(d, 2H, *J*=9Hz), 4.59(s, 2H). ^{13}C NMR(DMSO-D_6) δ170.13，155.699，146.575，138.768，131.491，130.41，127.609，125.773，113.486, 64.548, 63.766.

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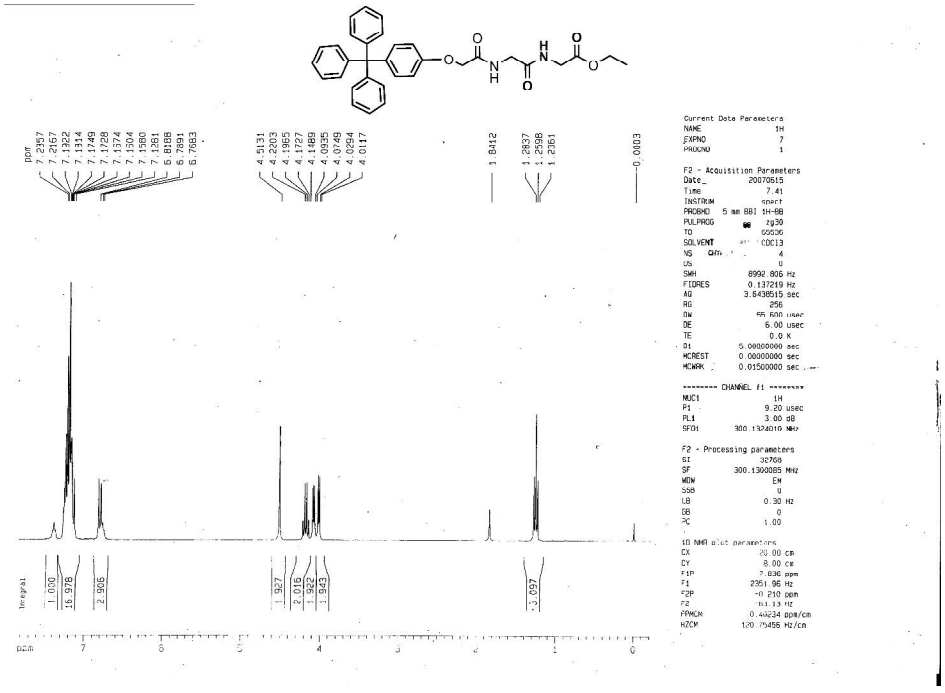
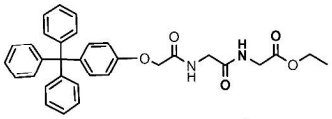
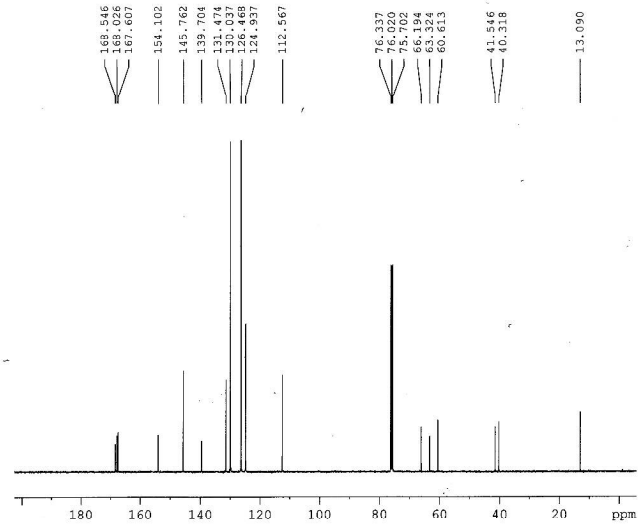
ethyl 2-(2-(2-(4-tritylphenoxy)acetamido)acetamido)acetate (3)

To a stirred solution of compound **2** (1.56 g, 4 mmol), ethyl 2-(2-aminoacetamido)acetate hydrochloride (784m g, 4 mmol) and DMAP (576mg, 4.5 mmol) in anhydrous CH_2Cl_2 (200 mL) cooled on an ice bath was added EDCI·HCl (955mg, 5 mmol). After 12 h the solution was washed with a saturated solution of citric acid (3x80 mL) and H_2O (3x50 mL) and the organic layer dried over anhydrous Na_2SO_4, filtered and the filtrate reduced in volume to obtain a white solid. Purification was accomplished by column chromatography on silica with CH_2Cl_2/CH_3OH (50/1, v/v) to give **3** (1.71 g, 80%). ^{1}H NMR ($CDCl_3$): δ 7.37 (broad, 1H), 7.23-7.12 (m, 17H), 6.789 (d, 2H, *J*=8.9Hz), 4.51 (s, 2H), 4.18(q, 2H, *J*=7.14Hz), 4.08 (d, 2H, *J*=5.58Hz), 4.02(d, 2H, *J*=5.31Hz), 1.25(t, 3H, *J*=7.16Hz). ^{13}C NMR ($CDCl_3$): δ 168.54, 168.02, 167.6, 154.1, 145.76, 139.7, 131.47, 131.04, 126.468, 124.94, 112.56, 66.19, 63.32, 60.61, 41.54, 40.32, 13.09. MS (EI): 536.





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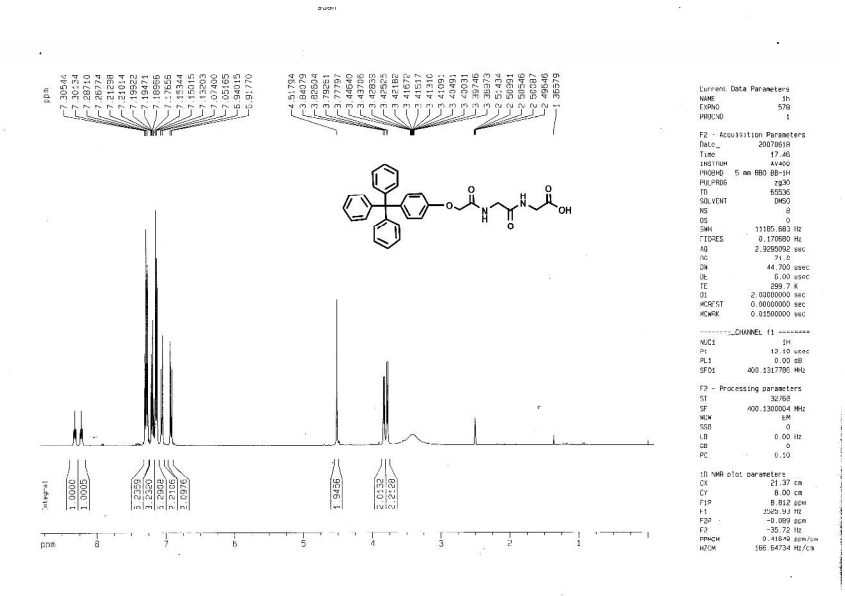
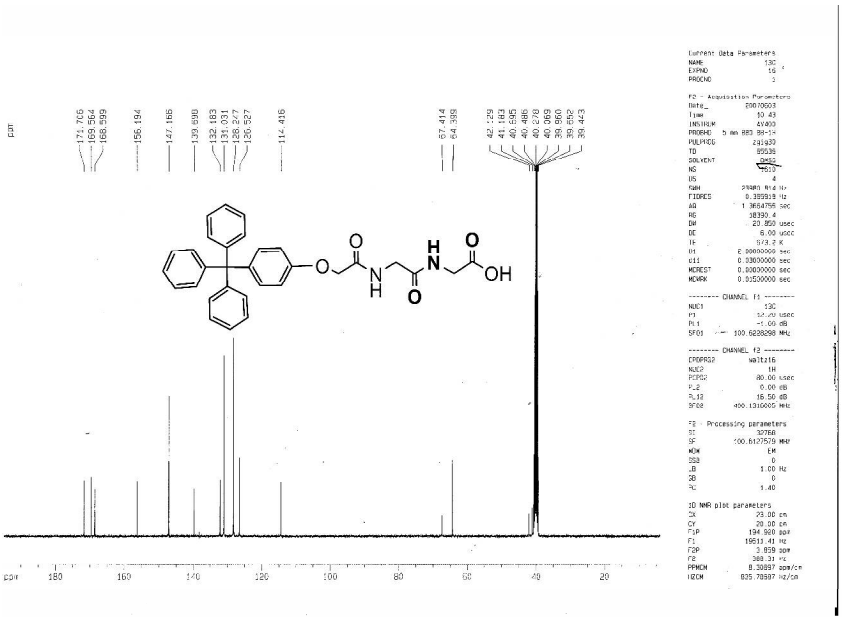
2-(2-(2-(4-tritylphenoxy)acetamido)acetamido)acetic acid (4)

In a 50-mL flask, compound **3** (1.07g, 2mmol) was dissolved in 100 mL of EtOH/THF (1:1, v:v). NaOH aquous solution (5mL, 2mol/L) was carefully added under stirring. The reaction mixture was stirred for 12 h at room temperature. Then, the solvent was removed under reduced pressure, and the residue was redissolved in distilled water. HCl aquous solution (10mL, 2mol/L) was carefully added under stirring. The reaction mixture was filtered and washed with distilled water for several times. 975 mg (96%) product was obtained as a white solid after dehydration. ^{1}HNMR (DMSO-D_6): δ 8.32(t, 1H, *J*=5.9Hz), 8.22(t, 1H, *J*=5.9Hz), 7.31-7.28(m, 6H), 7.26-7.13(m 9H), 7.06(d, 2H, *J*=8.9Hz), 6.93(d, 2H, *J*=8.9Hz), 4.52(s, 2H), 3.83(d, 2H, *J*=5.9Hz), 3.78(d, 2H, *J*=5.9Hz). ^{13}C NMR (DMSO-D_6): δ 171.706, 169.564, 168.599, 156.19, 147.17, 139.69, 132.18, 131.03, 128.25, 126.53, 114.41, 67.414, 64.399, 42.129, 41.18. MS (EI): 507(M^+).





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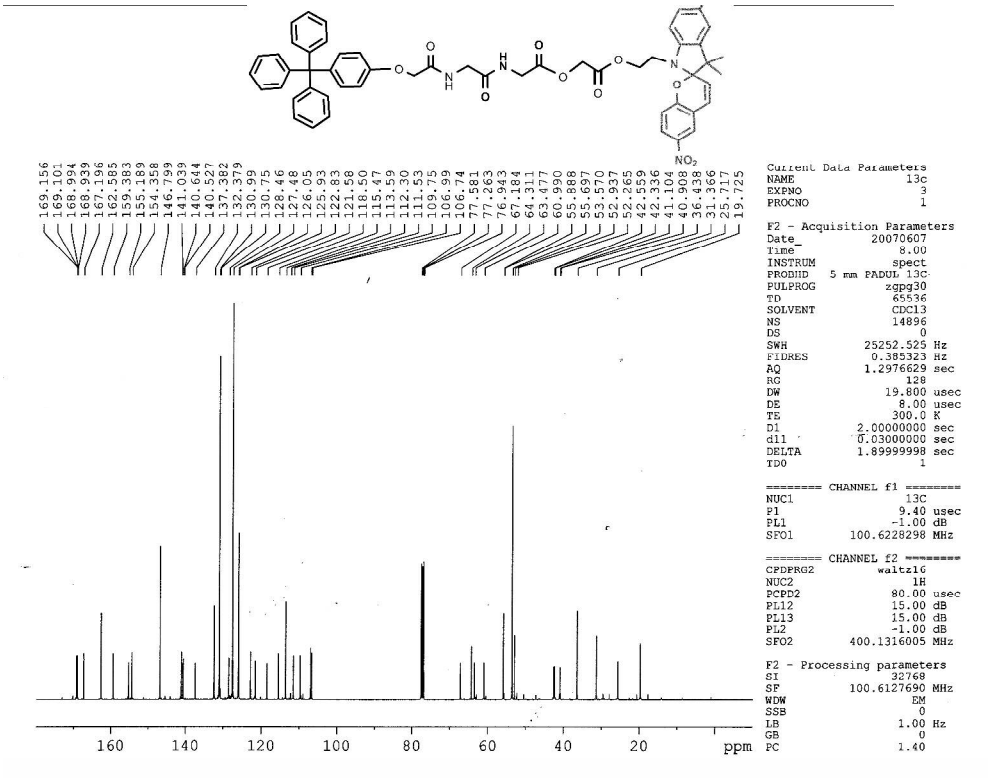
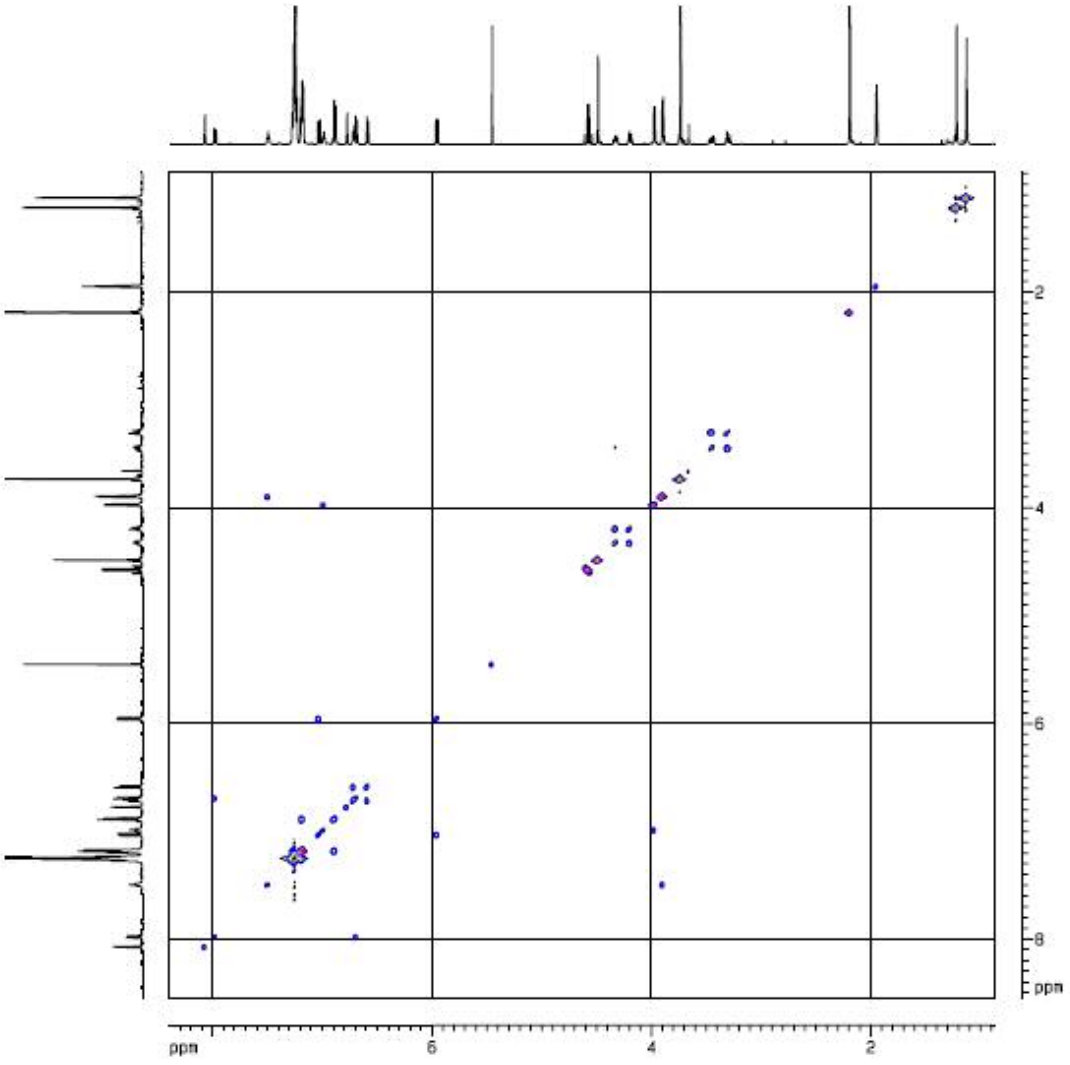
SP-2

To a stirred solution of **4** (508 mg, 1mmol) in DMF was added **SP-Cl** (458mg, 1mmol) and K_2CO_3 (414mg, 3mmol) under nitrogen flux. The mixture was heated to 80^0C and stirred for 8 hours. Then the solvent was distilled under reduced pressure, and the residue was washed with water and dried with Na_2SO_4. Purification was accomplished by column chromatography on silica with CH_2Cl_2/MeOH (50/1, v/V) to give **SP-2** 600mg(65%). ^{1}H NMR (CD_3CN-D_3): δ 8.07(d, 1H, *J*=2.94Hz), 7.98(d×d, 1H, *J*=8.82Hz, J=3.2Hz), 7.49(t, 1H, *J*=5.5Hz), 7.28-7.22(m, 13H), 7.20-7.16(m, 5H), 7.03(d, 1H, *J*=10.2Hz), 6.98(t, 1H, *J*=5.4Hz), 6.88(d, 2H, *J*=9Hz), 6.77(d, 1H, *J*=2.4Hz), 6.72(d×d, 1H, *J*=8.4Hz, *J*=3.2 Hz), 6.69(d, 1H, *J*=9Hz), 6.59(d, 1H, *J*=8.4Hz), 5.95(d, 1H, *J*=10.2Hz), 4.57(q, 2H, *J*=10.2Hz), 4.48(s, 2H), 4.35-4.30(m, 1H), 4.22-4.17(m, 1H), 3.97(d, 2H, *J*=6.6Hz), 3.89 (d, 2H, *J*=6.0Hz), 3.73 (s, 3H), 3.48-3.42(m, 1H), 3.33-3.27(m, 1H), 1.22(s, 3H), 1.12(s, 3H). ^{13}C NMR (CD_3Cl) δ 168.994, 167.196, 162.585, 159.383, 155.189, 154.358, 146.799, 141.039, 140.527, 137.382, 132.379, 130.99, 128.46, 127.48, 126.05, 122.83, 121.58, 118.50, 115.47, 109.75, 106.99, 106.74, 113.59, 111.53, 67.184, 64.311, 63.477, 60.99, 55.888, 53.57, 52.94, 42.559, 42.336, 40.9, 36.438, 31.366, 25.717, 19.725. MS (MALDI-TOF): 930, 953(**SP-2** +Na).

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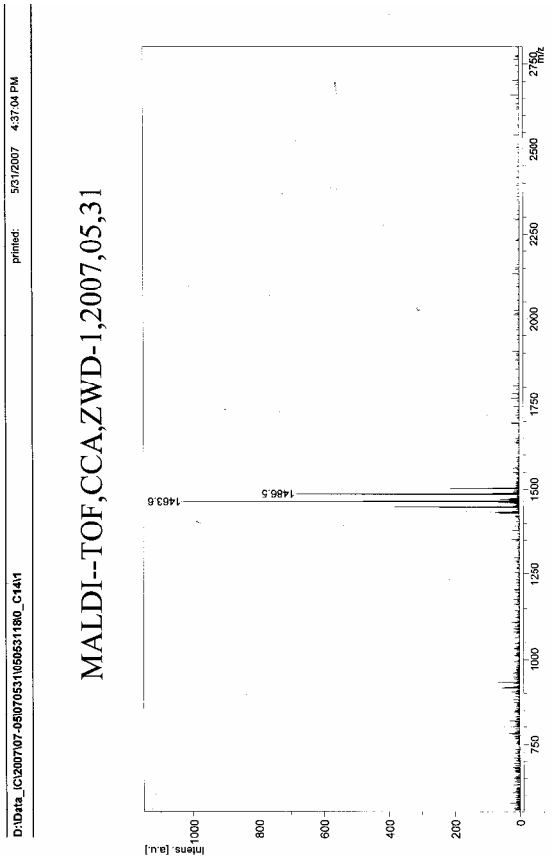
SP-1

To a solution of 0.186 g (0.2mmol) of **SP-2** in 200 mL of CH_2Cl_2 and Et_3N (exc.) were added simultaneously solutions of 0.404 g (2 mmol) of 3,5-pyridinedicarbonyl dichloride in 60 mL of CH_2Cl_2 and 0.272 g (2 mmol) of p-xylylenediamine in 60 mL of CH_2Cl_3 over a period of 2 hrs. The mixture was stirred for 4 hours and then filtrated. The filtrate was concentrated and purified by flash chromatography (silica gel, 5% MeOH in CH_2Cl_2) to obtain 58 mg (20 %) of the title compound as a grey solid.

^{1}HNMR (CD_3CN-D_3): δ 8.385 (s, 2H), 8.028-7.988(m, 5H), 7.953(d×d, 1H, *J*=9Hz, *J*=3Hz), 7.659(m, 4H), 7.518(t, 2H, *J*=7.8), 7.499(t, 1H, *J*=5.4), 7.264(m, 7H), 7.179(m, 10H), 7.143(s, 8H), 6.970(d, 1H, *J*=11.4Hz), 6.938(d, 3H, *J*=9.6Hz), 6.747(d, 1H, *J*=2.4Hz), 6.674(d, 2H, *J*=9Hz), 6.501(d, 1H, *J*=8.4Hz), 6.413(d, 2H, *J*=9.6Hz), 5.875(d, 1H, *J*=11.2Hz), 4.42-4.37(m, 9H), 4.19(m, 1H), 4.09(m, 1H), 4.07(s, 2H), 3.807(d, 2H, *J*=5.4Hz), 3.72(s, 3H),3.389-3.31(m, 1H), 3.235-3.108(m, 1H), 2.817(d, 2H, *J*=4.8Hz), 1.188(3, 3H), 1.08(s, 3H). ^{13}CNMR (CD_3CN) 169.625, 168.923, 169.23, 166.94, 166.64, 159.37, 154.36, 154.14, 146.63, 141.32, 140.98, 140.57, 137.46, 133.91, 131.457, 130.96, 129.036, 127.56, 125.98, 118.37, 106.911, 64.27, 53.45, 52.96, 44.095. MS (MALDI-TOF): 1463.6.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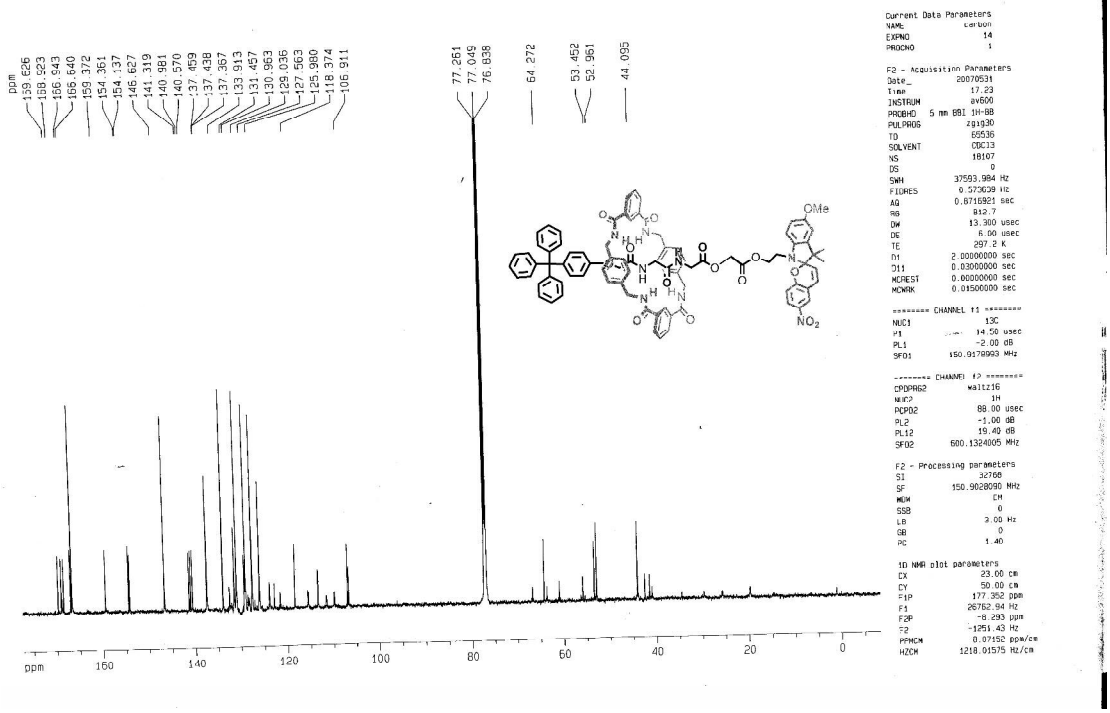
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129.036
127.563
125.980
118.374
106.911
77.261
77.045
76.838
64.272
53.452
52.961
44.095
OMe
NO2
Current Data Parameters
NAME carbon
EXPNO 14
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070531
Time 17.23
INSTRUM av600
PROBHD 5 mm BBI 1H-BB
PULPROG zgig30
TD 65536
SOLVENT CDCl3
NS 18107
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SWH 37593.984 Hz
FIDRES 0.573639 Hz
AQ 0.8716921 sec
RG 812.7
DW 13.300 usec
DE 6.50 usec
TE 297.2 K
D1 2.00000000 sec
D11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
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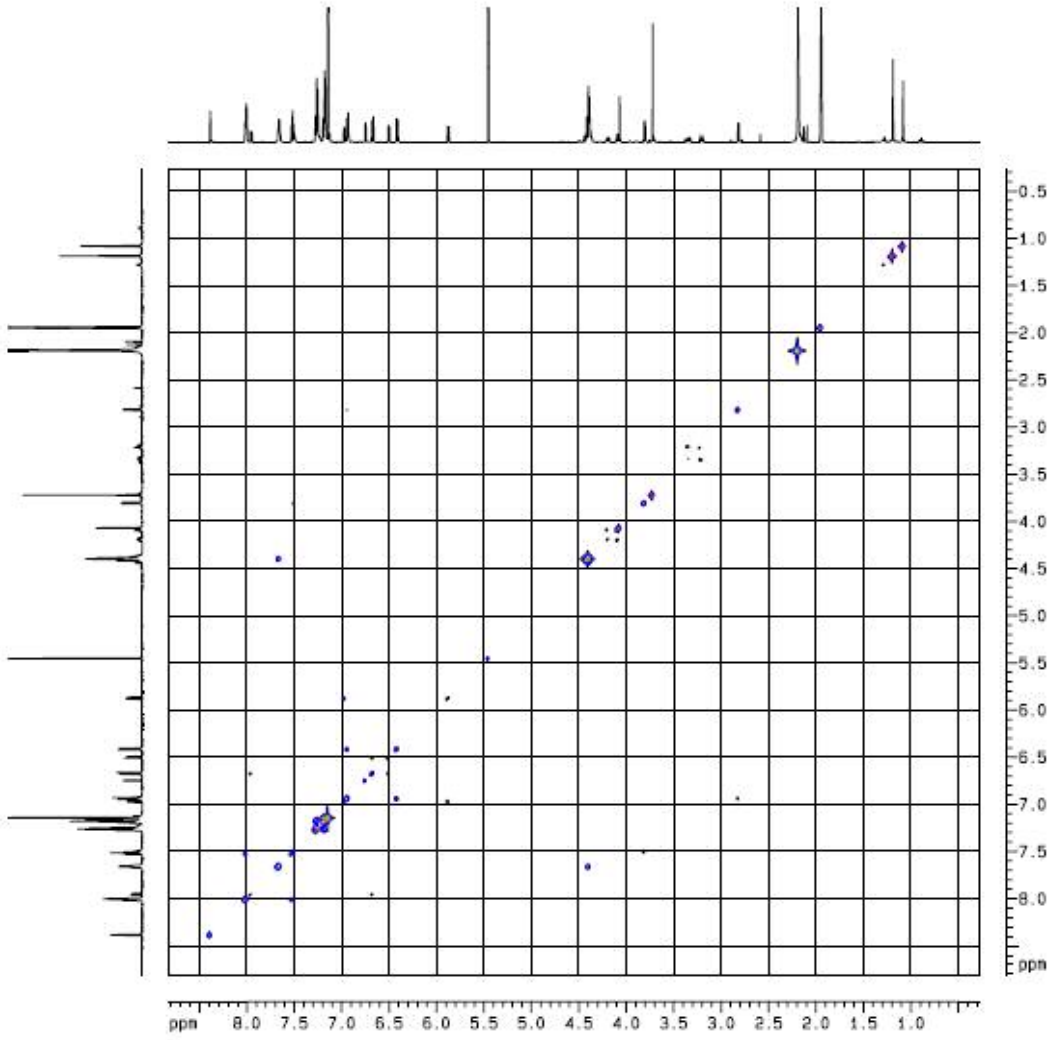
NUC1 13C
P1 14.50 usec
PL1 -2.00 dB
SFO1 150.9179993 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 88.00 usec
PL2 -1.00 dB
PL12 19.40 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 32768
SF 150.9028090 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 23.00 cm
CY 50.00 cm
F1P 177.352 ppm
F1 26762.94 Hz
F2P -8.293 ppm
F2 -1251.43 Hz
PPMCM 0.07152 ppm/cm
HZCM 1218.01575 Hz/cm


0.5
1.0
1.5
2.0
2.5
3.0
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5.0
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6.0
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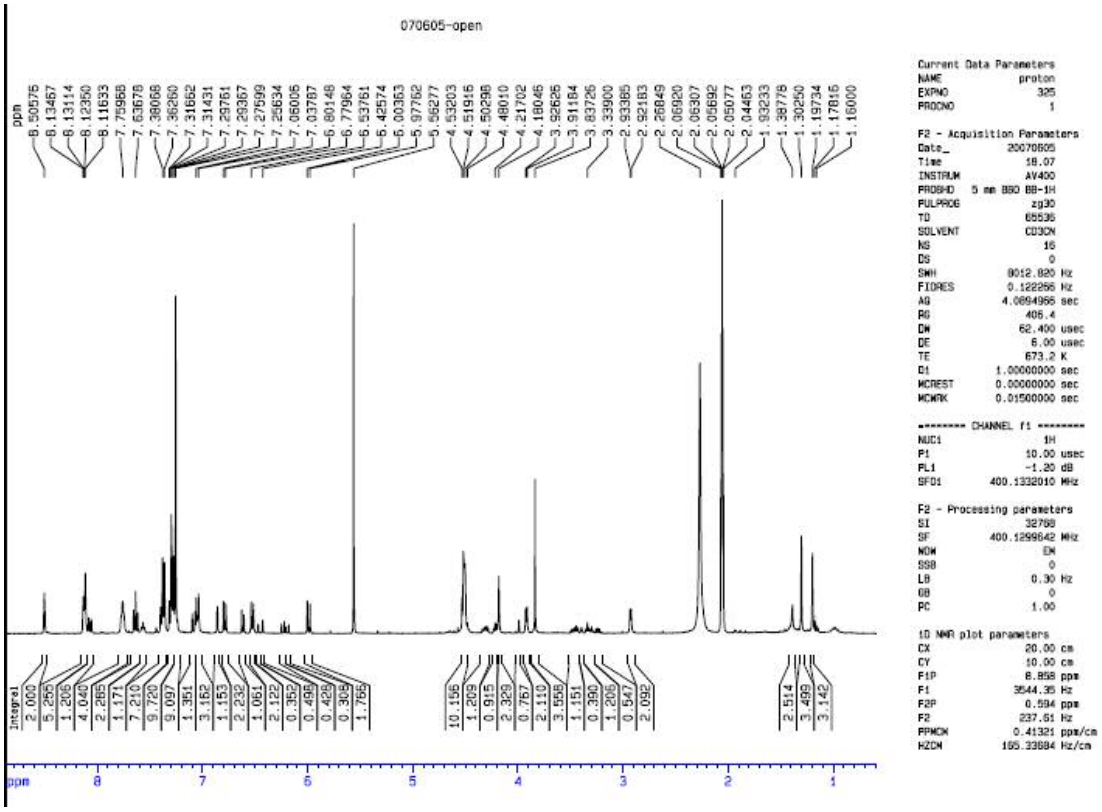
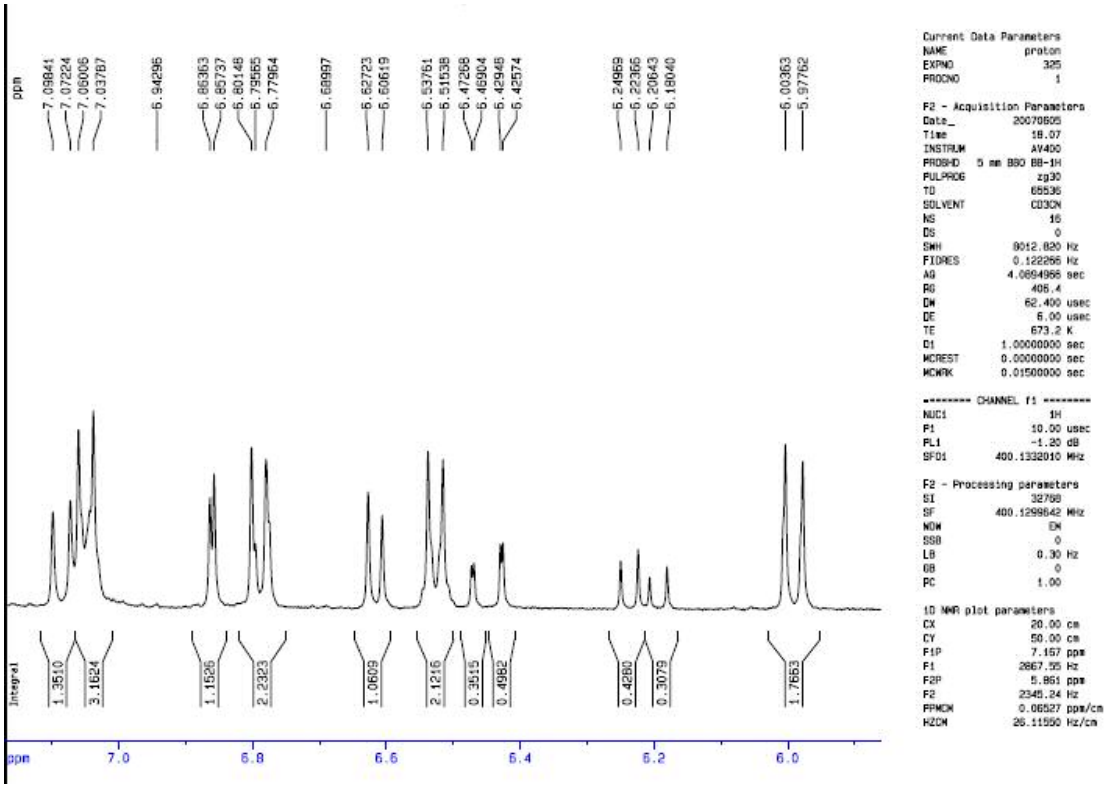
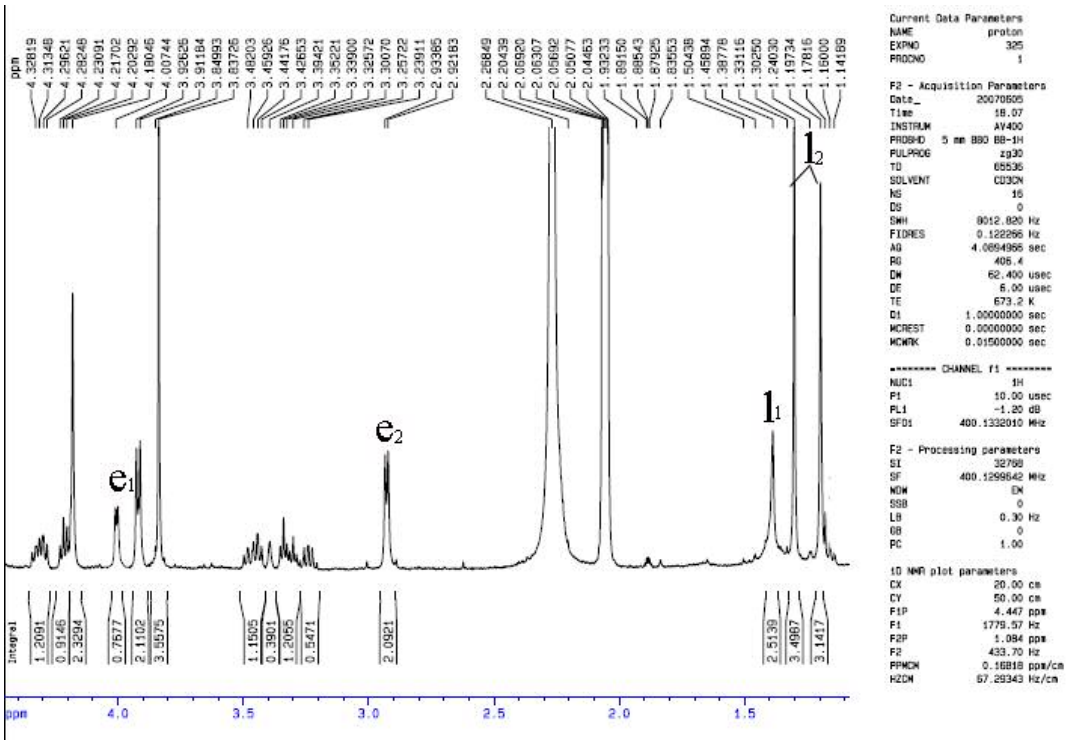
7.0
7.5
8.0
ppm
ppm 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0

ME-1

ME-1 was gained from the irradiation of **SP-1** with 365nm UV light for 3min at room temperature. The opened structure **ME-1** is just about 26% of the total isomers according to the analysis of this ^{1}H NMR spectrum.



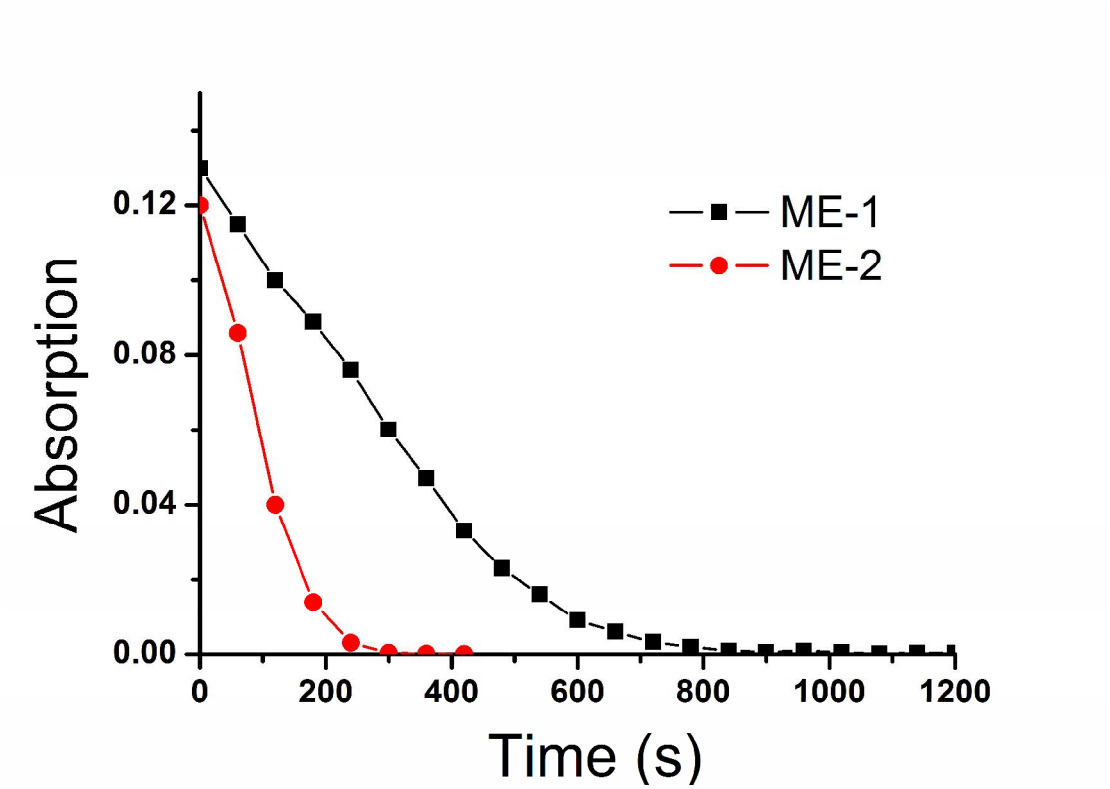




The signals of e_1 and l_1 come from the opened form **ME-1**, while the e_2 and l_2 come from the closed form **SP-1.** e_1/e_2=0.36, l_1/l_2=0.37.

§5. Kinetic Studies

In the dark, the rate of switching from ME to SP is given by equation (1).[1] [ME1] and [ME2] are concentrations of **ME1** and **ME2**, respectively. k_1 and k_2 are rate constants for two isomerization reactions. t_1 and t_2 are reaction times. [ME] is related to the absorption (A), measured at a certain wavelength. The ratio of k_1/k_2 was calculated from the equation (2) which is deduced from equation (1).



The plot of the absorption spectra from **ME-1** and **ME-2** at 569nm against time in the dark. (5×10^{-5} M, CH_3CN, 25 ^{0}C)

$\ln[ME]=-kt+\ln[ME_0]$ (1)

$-kt=\ln[ME]-\ln[ME_0]$

$k_1/k_2=(\ln[ME1]-\ln[ME1_0])/(\ln[ME2]-\ln[ME2_0])\times(t_2/t_1)$ (2)

$k_1/k_2=0.167$

§6. Reference.

(1) F. M. Raymo, S. Giordani *J. Am. Chem. Soc.* **2001,** *123,* 4651-4652.

mol L^{-1}