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Supporting Information

A general approach to spirolactonized Si-rhodamines

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General Methods.

Materials. General chemicals were of the best grade available, supplied by Adamas-beta, Shanghai Chemical Reagent Co., Shanghai Shaoyuan Co. Ltd., Tokyo Chemical Industries (TCI), J&K chemical LTD. and Acros Organics. Unless otherwise stated, all commercial reagents were used without additional purification. All solvents were freshly distilled according to standard procedures prior to use.

Apparatus. All reactions were monitored by thin-layer chromatography (TLC) on gel F254 plates. Flash chromatography was carried out on silica gel (200-300 mesh; Qingdao Ocean Chemicals). The condensation reactions were performed in sealable pressure tubes (Beijing Synthware Glass) behind a blast shield. NMR spectra were recorded on a Bruker AC-300P spectrometer at 300 MHz for ^{1}H NMR and at 75 MHz for ^{13}C NMR or on a Bruker AC-600P spectrometer at 600 MHz for ^{1}H NMR and at 150 MHz for ^{13}C NMR. Δ values are given in ppm relative to tetramethylsilane. Mass spectra (MS) were measured with an API-3000 MS spectrometer using electrospray ionization (ESI). High-resolution mass spectra (HRMS) were recorded on an Aglilent Technologies 6538 UHD Accurate-Mass Q-TOF MS spectrometer using ESI. UV-visible spectra were obtained on a Agilent Cary 100 UV-vis spectrophotometer. Fluorescence spectroscopic studies were performed on a Hitachi F-7000. HPLC analysis was performed on an Diamonsil C18 (4.6 × 250 mm) column (Dikma technologies) using an HPLC system composed of a pump (LC-20AD, Shimadzu) and a detector (SPD-M20A, Shimadzu).

X-ray crystallography. Single crystals of **SiRB** were obtained by slow evaporation of dichloromethane/*n*-hexane solution of **SiRB** at room temperature. The X-ray single crystal diffraction data for **SiRB** were collected on Bruker APEX DUO diffractometers with Mo Kα radiation (λ = 0.71073 Å) at 113 ± 2 K in the ω-2θ scanning mode. The structures were solved by direct methods using the SHELXS-97 program[1] and refined by full-matrix least-squares techniques (SHELXL-97) on F^2.

Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically. CCDC-1011227 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystatllographic Data Ceter via www.ccdc.cam.ac.uk/data_request/cif.

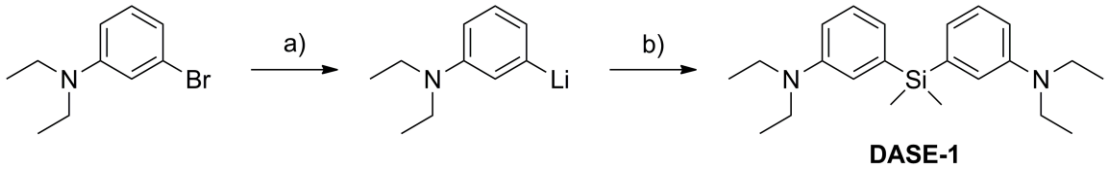
Absorption and fluorescence analysis. Absorption spectra were obtained with 1.0-cm glass cells. Fluorescence emission spectra were obtained with a Xenon lamp and 1.0-cm quartz cells. The fluorescence intensity was measured at 600 nm for **SiRB**s. The excitation and emission slits were set to 5.0 and 5.0 nm, respectively. Relative fluorescence quantum efficiency was obtained by comparing the area under the emission spectrum of the test sample with that of a solution of Cresyl violet in EtOH, which has a quantum efficiency of 0.56[2].

Imaging of bEND3 and HepG2 Cells Incubated with SiRB. bEND3 and HepG2 cells were cultured in culture media (DMEM supplemented with 10% fetal bovine serum, 50 unit/mL of penicillin, and 50 *u*g/mL of streptomycin) in an atmosphere of 5% CO_2 and 95% air at 37 ℃ in a humidified incubator. For fluorescence imaging with **SiRB**, bEND3 and HepG2 cells were seeded in 35-mm glass-bottom culture dishes at a density of 5.0×10^4 cells in culture media. After 24 h, the cells were incubated with 10 μM **SiRB** in culture media for 40 minutes at 37°C. Then the solution of DAPI was added and incubated for another 20 min. Cells were washed three times with PBS (pH = 7.4) and observed under a confocal laser scanning microscope.

Imaging of bEND3 and HepG2 Cells Incubated with Mito-SiRB and rhodamine 123. bEND3 and HepG2 cells were cultured in culture media (DMEM supplemented with 10% fetal bovine serum, 50 unit/mL of penicillin, and 50 *u*g/mL of streptomycin) in an atmosphere of 5% CO_2 and 95% air at 37 ℃ in a humidified incubator. For fluorescence imaging with **Mito-SiRB**, bEND3 and HepG2 cells were seeded in 35-mm glass-bottom culture dishes at a density of 5.0×10^4 cells in culture media.

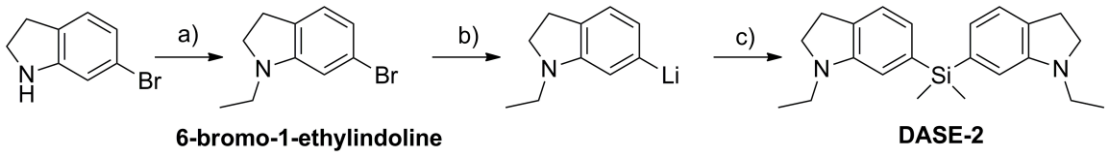
After 24h, the cells were incubated with 10 μM **Mito-SiRB** in culture media for 40 minutes at 37°C. Then 1 μM rhodamine 123 was added and incubated for another 20 min. Cells were washed three times with PBS (pH = 7.4) and observed under a confocal laser scanning microscope.

Synthesis of Intermediates.



Scheme S1. Synthesis of **DASE-1**. Reaction conditions: a) diethyl ether, *n*-BuLi (2.4 M in *n*-hexane), 0 ℃, 2 h; b) diethyl ether, dichlorodimethylsilane, 0 ℃ to RT, overnight.

DASE-1[3]**.** To a 250 mL well-dried flask flushed with argon, 3-bromo-N,N-diethylaniline (6.844 g, 30.0 mmol) and diethyl ether (60 mL) were added. The solution was cooled to 0 ℃, *n*-BuLi (2.4 M in *n*-hexane, 13.1 mL, 31.5 mmol) was added and the reaction mixture was stirred at 0 ℃ for 2 h. Dichlorodimethylsilane (2.2 mL, 18.0 mmol) dissolved in diethyl ether (10 mL) was added dropwise, and the reaction mixture was slowly warmed to room temperature, then stirred overnight. The reaction was quenched with wahter (50 mL) and extracted with diethyl ether (50 mL × 3). The organic layers were combined, washed with brine and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 80 : 1) to afford **DASE-1** (4.362 g, 82% yield) as light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.64 (s, 6H), 1.23 (t, 12H, *J* = 7.2 Hz), 3.43 (q, 8H, *J* = 7.2 Hz), 6.79-7.35 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -2.13, 12.67, 44.45, 112.79, 117.75, 121.47, 128.76, 139.11, 147.10; MS (ESI) calcd. for $C_{22}H_{34}N_2Si$ $[M+H]^+$: 355.26, found: 355.32.



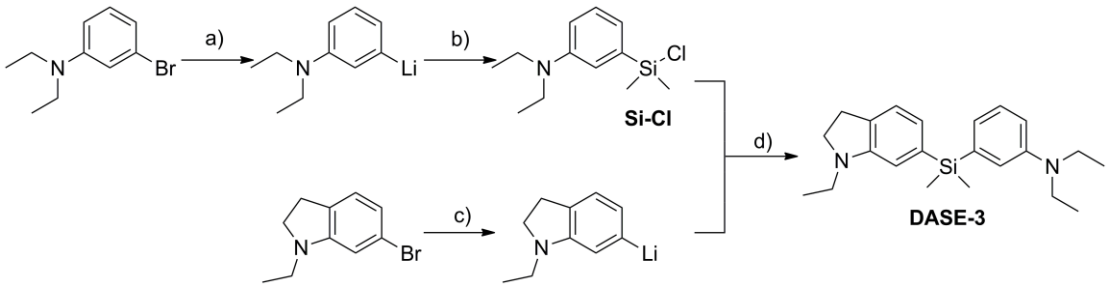
Scheme S2. Synthesis of **DASE-2**. Reaction conditions: a) THF, NaH (60%

dispersion in mineral oil), iodoethane, 0 ℃ to 50 ℃, 12 h; b) diethyl ether, *n*-BuLi (1.6 M in *n*-hexane), 0 ℃, 2 h; c) diethyl ether, dichlorodimethylsilane, 0 ℃ to RT, overnight.

6-bromo-1-ethylindoline. To a solution of 6-bromoindoline hydrochloride (5.863 g, 25.0 mmol) in THF (50 mL) was slowly added NaH (2.00 g, 60% dispersion in mineral oil, 50.0 mmol) at 0 ℃. The mixture was stirred for 1 h at the same temperature. After iodoethane (4.677 g, 30 mmol) was added, the reaction mixture was stirred at room temperature for 6 h and stirred at 50 ℃ for another 6 h. The reaction was quenched with water and extracted with ethyl acetate (30 mL × 3). The organic layers were combined, washed with brine and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether) to give **6-bromo-1-ethylindoline** (5.201 g, 92% yield) as light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, 6H, *J* = 7.2 Hz), 2.88 (t, 2H, *J* = 8.1 Hz), 3.10 (q, 2H, *J* = 7.2 Hz), 3.36 (t, 2H, *J* = 8.4 Hz), 6.53-6.89 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.72, 27.99, 42.57, 52.30, 109.86, 119.71, 121.04, 125.34, 129.26, 153.73; MS (ESI) calcd. for $C_{10}H_{12}BrN$ $[M+H]^+$: 226.02, found: 226.14.

DASE-2. To a 250 mL well-dried flask flushed with argon, **6-bromo-1-ethylindoline** (4.070 g, 18.0 mmol) and diethyl ether (50 mL) were added. After the solution was cooled to 0 ℃, *n*-BuLi (1.6 M in *n*-hexane, 11.8 mL, 18.9 mmol) was added and the reaction mixture was stirred at 0 ℃ for 2 h . Dichlorodimethylsilane (1.3 mL, 10.8 mmol) dissolved in diethyl ether (10 mL) was added dropwise and the reaction mixture was slowly warmed to room temperature, then stirred overnight. The reaction was quenched with water (50 mL) and extracted with diethyl ether (30 mL × 3). The organic layers were combined, washed with brine and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 40 : 1) to give **DASE-2** (2.423 g, 77% yield) as light yellow oil. ^{1}H NMR (300 MHz,

$CDCl_3$) δ 0.49 (s, 6H), 1.16 (t, 6H, *J* = 7.2 Hz), 2.94 (t, 4H, *J* = 8.1 Hz), 3.12 (q, 4H, *J* = 7.2 Hz), 3.30 (t, 4H, *J* = 8.4 Hz), 6.65-7.08 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -1.80, 12.09, 28.57, 43.17, 52.20, 112.39, 124.00, 124.07, 131.64, 137.17, 151.80; MS (ESI) calcd. for $C_{22}H_{30}N_2Si$ $[M+H]^+$: 351.23, found: 351.26.



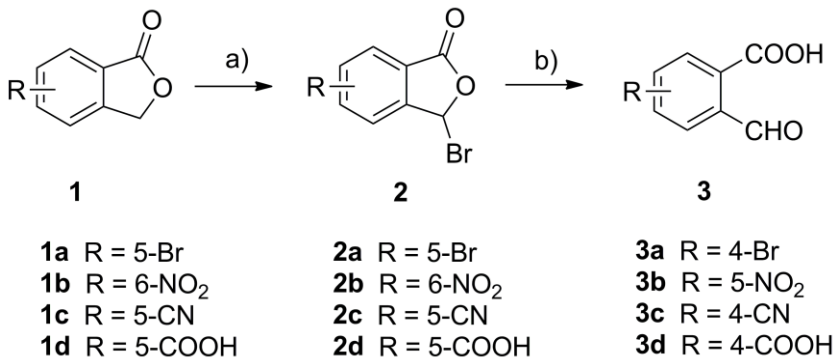
Scheme S3. Synthesis of **DASE-3**. Reaction conditions: a) diethyl ether, *n*-BuLi (1.6 M in *n*-hexane), 0 ℃, 2 h; b) diethyl ether, dichlorodimethylsilane, 0 ℃ to RT, 2 h; c) diethyl ether, *n*-BuLi (1.6 M in *n*-hexane), 0 ℃, 2 h; d) diethyl ether, **Si-Cl**, 0 ℃ to RT, overnight.

Si-Cl. To a 100 mL well-dried flask flushed with argon, 3-bromo-N,N-diethylaniline (2.738 g, 12.0 mmol) and diethyl ether (10 mL) were added. After the solution was cooled to 0 ℃, *n*-BuLi (1.6 M in *n*-hexane, 7.9 mL, 12.0 mmol) was added. After the reaction mixture was stirred at the same temperature for 2 h, the resulting solution was transferred via cannula to a solution of dichlorodimethylsilane (7.3 mL, 60.0 mmol) in diethyl ether (10 mL) at 0 ℃. The reaction was slowly warmed to room temperature and stirred for another 2 h. The solvent and the redundant dichlorodimethylsilane were removed under reduced pressure to give the crude **Si-Cl**, which was used without further purification. Compound **Si-Cl** is sensitive to water and is sealed in the flask.

DASE-3[4]**.** To a 50 mL well-dried flask flushed with argon, **6-bromo-1-ethylindoline** (1.357 g, 6.0 mmol) and diethyl ether (10 mL) were added. After the solution was cooled to 0 ℃, *n*-BuLi (1.6 M in *n*-hexane, 4.0 mL, 6.4 mmol) was added and the reaction mixture was stirred at 0 ℃ for 2 h. This resulting mixture was transferred via cannula into the solution of compound **Si-Cl** in diethyl ether (10 mL) at 0 ℃. The

reaction mixture was slowly warmed to room temperature and stirred overnight. The reaction was quenched with water (30 mL) and extracted with diethyl ether (20 mL × 3). After filtration and removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 40 : 1) to give **DASE-3** (1.116 g, 53% yield) as light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.50 (s, 6H), 1.12 (t, 6H, *J* = 7.2 Hz), 1.16 (t, 3H, *J* = 7.2 Hz), 2.93 (t, 2H, *J* = 8.1 Hz), 3.11 (q, 2H, *J* = 7.2 Hz), 3.30 (t, 2H, *J* = 8.1 Hz), 3.32 (q, 4H, *J* = 7.2 Hz), 6.70-7.23 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -2.01, 12.13, 12.60, 28.56, 43.17, 44.38, 52.22, 112.34, 112.73, 117.72, 121.45, 123.99, 124.02, 128.68, 131.64, 137.00, 139.20, 147.05, 151.84; MS (ESI) calcd. for $C_{22}H_{32}N_2Si$ $[M+H]^+$: 353.60, found: 353.49.

General procedure for synthesis of substituted 2-formylbenzoic acid.



1 **2** **3**

1a R = 5-Br
1b R = 6-NO_2
1c R = 5-CN
1d R = 5-COOH

2a R = 5-Br
2b R = 6-NO_2
2c R = 5-CN
2d R = 5-COOH

3a R = 4-Br
3b R = 5-NO_2
3c R = 4-CN
3d R = 4-COOH

Scheme S4. Synthesis of compounds **3**. Reaction conditions: a) NBS, AIBN, 1,2-dichloroethane, reflux; b) H_2O, reflux.

3a-3d[5]**.** compounds **3a-3d** were prepared following reported method with some modification. To a 250 mL round bottom flask were added substituted phthalide (**1**) (20.0 mmol, 1.0 equiv.), bromosuccinimide (22.0 mmol, 1.1 equiv.), azobisisobutyronitrile (2.0 mmol, 0.1 equiv.) and 1,2-dichloroethane (100 mL). The reaction mixture was stirred and refluxed until the reaction was complete and then kept at –5 ℃ for 2 h. After filtration and removal of the solvent under reduced pressure, water (50 mL) was added and the resulting mixture refluxed for 2 h. The

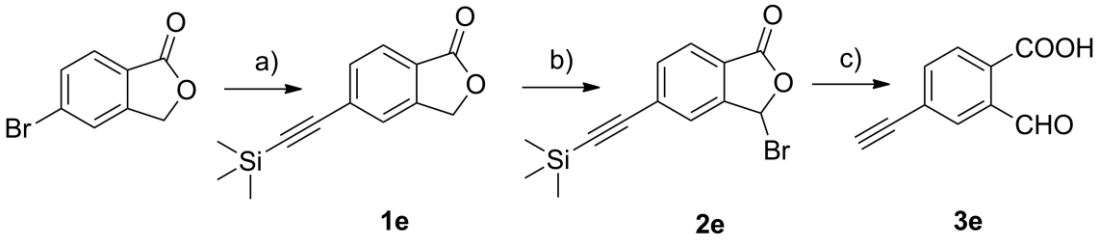
reaction mixture was then cooled to room temperature and kept at 4 ℃ overnight. The precipitate was collected and dried in *vacuo* to give the desired compounds.

3a. White solid (4.524 g, 99% yield); ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.70-7.90 (m, 3H), 7.95 (s, 1H).

3b. Light yellow solid (3.284 g, 84% yield); ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.00-8.64 (m, 3H), 8.53 (s, 1H).

3c. White solid (2.646 g, 76% yield); ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.92-8.17 (m, 3H), 8.28 (s, 1H).

3d. White solid (1.012 g, 26% yield); ^{1}H NMR (300 MHz, DMSO-d_6) 6.73-8.19 (m, 3H), 8.13 (s, 1H), 13.62 (s, 1H). The relatively low yield is attributed to the poor solubility of the starting material **2d** in 1,2-dichloroethane. Insoluble compound **2d** was recovered by filtration.



Scheme S5. Synthesis of compound **3e**. Reaction conditions: a) ethynyltrimethylsilane, CuI, $Pd(PPh_3)_4$, TEA, DMF, 65 ℃, 24 h; b) NBS, AIBN, 1,2-dichloroethane, reflux, 12 h; c) K_2CO_3, CH_3OH, 25 ℃, 4 h.

1e. To a 100 mL well-dried flask flushed with argon, 5-bromoisobenzofuran-1(3*H*)-one (10.652 g, 50.0 mmol), ethynyltrimethylsilane (19.644 g, 200.0 mol), copper(I) iodide (2.857 g, 15.0 mol), $Pd(PPh_3)_4$ (2.889 g, 2.5 mmol), triethylamine (6.5 mL, 25 mmol) and DMF (25.0 mL) were added. The reaction mixture was stirred at 65 ℃ for 24 h, then poured into iced water (200 mL)

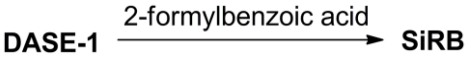
and extracted with ethyl acetate (100 ml × 3). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane : EtOAc = 10 : 1) to give compound **1e** (9.444 g, 82% yield) as white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.29 (s, 9H), 5.31 (s, 2H), 7.59-7.85 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -0.25, 69.31, 99.06, 103.38, 125.19, 25.39, 125.58, 129.20, 132.80, 146.41, 170.38.

2e. To a 500 mL round bottom flask were added 5-((trimethylsilyl)ethynyl)isobenzofuran-1(3H)-one (6.910 g, 30.0 mmol), bromosuccinimide (5.874 g, 33.0 mmol), azobisisobutyronitrile (0.492 g, 3.0 mmol) and 1,2-dichloroethane (150 mL). The reaction mixture was stirred and refluxed for 12 h and then kept at −5 ℃ for 2 h. After filtration and removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane : EtOAc = 15 : 1) to give compound **2e** (4.638 g, 50% yield) as white solid and the recovered material **1e** (2.584 g, 37%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.30 (s, 9H), 7.38 (s, 1H), 7.67-7.89 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -0.31, 73.96, 100.56, 102.72, 123.25, 125.74, 126.73, 130.56, 134.46, 148.84, 166.60.

3e. To a solution of **2e** (1.855 g, 6.0 mmol) in methanol (20 mL) was added anhydrous K_2CO_3 (2.488 g, 18 mmol). The mixture was stirred at 25 ℃ for 4 h. The solvent was removed under reduced pressure and water (50 mL) was added. The clear solution was extracted with dichloromethane (30 mL × 3) and acidified by 2 M hydrochloric acid. The precipitate was collected and washed 3 times by water and dried to give compound **3e** (951 mg, 91% yield) as a light yellow solid. ^{1}H NMR (300 MHz, DMSO-d_6): δ 4.58 (s, 1H), 6.65-7.85 (m, 3H), 8.26 (s, 1H).

Synthesis of SiRBs.

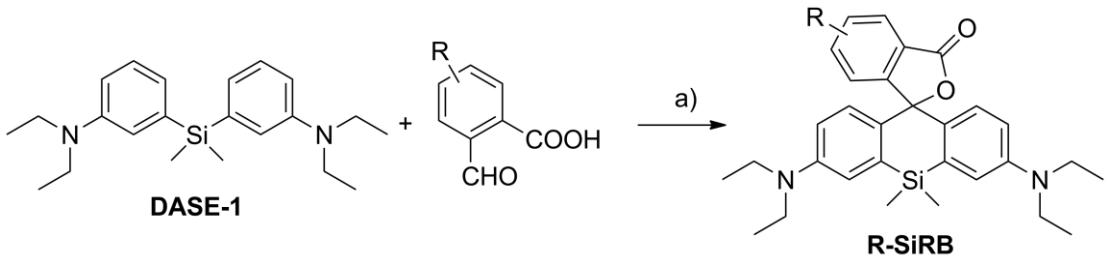
Tables S1. Optimization of the reaction conditions



Entry	Lewis acid	Equiv. of 2-formylbenzoic acid	Temp.	Time	yield[a]
1	-	5	140	8	40
2	$NbCl_5$	5	140	8	31
3	$ZnCl_2$	5	140	8	32
4	$ZnBr_2$	5	140	8	32
5	$AlCl_3$	5	140	8	27
6	$FeCl_3$	5	140	8	39
7	$FeCl_2$	5	140	8	40
8	CuBr	5	140	8	41
9	CuI	5	140	8	39
10	$CuCl_2$	5	140	8	43
11	$CuBr_2$	5	140	8	50
12	$CuBr_2$	3	140	8	44
13	$CuBr_2$	2	140	8	15
14	$CuBr_2$	1	140	8	2
15	$CuBr_2$	5	100	8	10
16	$CuBr_2$	5	120	8	40
17	$CuBr_2$	5	160	8	17
18	$CuBr_2$	5	140	1	37
19	$CuBr_2$	5	140	2	48
20	$CuBr_2$	5	140	5	54

[a] Determined by HPLC. Elution was done with a eluent (85% MeCN; flow rate = 1.0 mL/min). Detection wavelength was 265 nm.

General procedure for synthesis of R-SiRBs.



Scheme S6. Synthesis of **R-SiRBs**. Reaction conditions: a) $CuBr_2$, sealed tube, 140 ℃, 3-8 h.

R-SiRBs. To a 15 mL sealable pressure tube charged with a magnetic stir bar were added the intermediate **DASE-1** (106 mg, 0.3 mmol, 1.0 equiv.), substituted 2-formylbenzoic acid (**3a-3e**, 1.5 mmol, 5.0 equiv.) and copper(II) bromide (7 mg, 0.03 mmol, 0.1 equiv.). The tube was sealed tightly and heated at 140 ℃ for 3-8 h. **[Caution:** To avoid potential danger, all the reaction tubes were placed behind a blast shield.**]** After cooling to room temperature, the reaction mixture was dissolved in 5 mL dichloromethane and purified by column chromatography on silica gel to give the desired compounds.

SiRB. 2-formylbenzoic acid (225 mg) was added and the reaction mixture was stirred for 5 h. The mixture was purified by column chromatography on silica gel (petroleum ether : ethyl acetate : triethylamine = 80 : 1 : 1) to give **SiRB** (75 mg, 52% yield) as a white solid. In scalable synthesis, the reaction mixture was dissolved in dichloromethane and washed with 2M NaOH aqueous solution to remove unreacted 2-formylbenzoic acid and other acid side products. The organic layer was further washed with brine and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel. And the product was further recrystallized from dichloromethane/petroleum ether to give **SiRB** as colorless needle crystals. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.64 (s, 3H), 0.66 (s, 3H), 1.18 (t, 12H, *J* = 7.2 Hz), 3.39 (q, 8H, *J* = 7.2 Hz), 6.50-8.01 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -1.78, 0.44, 12.55,

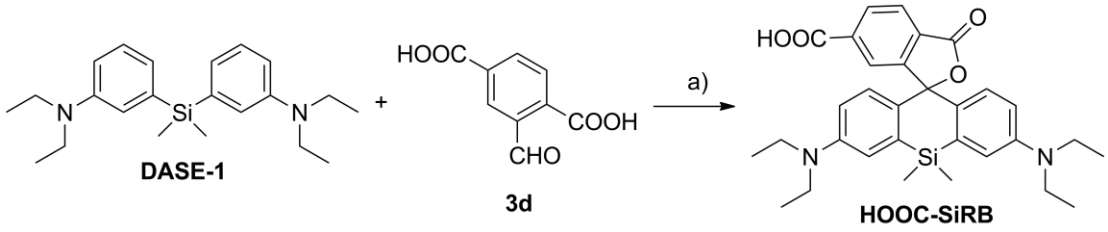
44.28, 92.30, 112.45, 115.94, 124.86, 125.58, 127.48, 128.46, 128.65, 130.79, 133.50, 137.30, 146.58, 154,15, 170.63. HRMS (ESI) calcd. for $C_{30}H_{36}N_2O_2Si$ $[M+H]^+$: 485.2619, found: 485.2623.

Br-SiRB. Compound **3a** (344 mg) was added and the reaction mixture was stirred for 8 h. The mixture was purified by column chromatography on silica gel (petroleum ether : ethyl acetate : triethylamine = 80 : 1 : 1) to give **Br-SiRB** (67 mg, 40% yield) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.59 (s, 3H), 0.63 (s, 3H), 1.17 (t, 12H, *J* = 7.2 Hz), 3.37 (q, 8H, *J* = 7.2 Hz), 6.51-7.83 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -1.36, 0.26, 12.58, 44.30, 91.75, 112.78, 115.82, 125.93, 126.80, 127.79, 128.49, 128.94, 129.87, 132.20, 136.84, 146.67, 156.71, 169.95. HRMS (ESI) calcd. for $C_{30}H_{35}BrN_2O_4Si$ $[M+H]^+$: 563.1724, found: 563.1740, 565.1725.

O_2N-SiRB. Compound **3b** (293 mg) was added and the reaction mixture was stirred for 3 h. The mixture was purified by column chromatography on silica gel (petroleum ether : ethyl acetate : triethylamine = 70 : 1 : 1) to give **O_2N-SiRB** (49 mg, 31% yield) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.59 (s, 3H), 0.63 (s, 3H), 1.16 (t, 12H, *J* = 7.2 Hz), 3.37 (q, 8H, *J* = 7.2 Hz), 6.48-8.80 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ -1.36, 0.18, 12.52, 44.27, 92.56, 112.73, 115.88, 121.31, 125.70, 128.38, 128.52, 128.73, 136.82, 146.84, 148.57, 160.51, 168.49. HRMS (ESI) calcd. for $C_{30}H_{35}N_3O_4Si$ $[M+H]^+$: 530.2470, found: 530.2481.

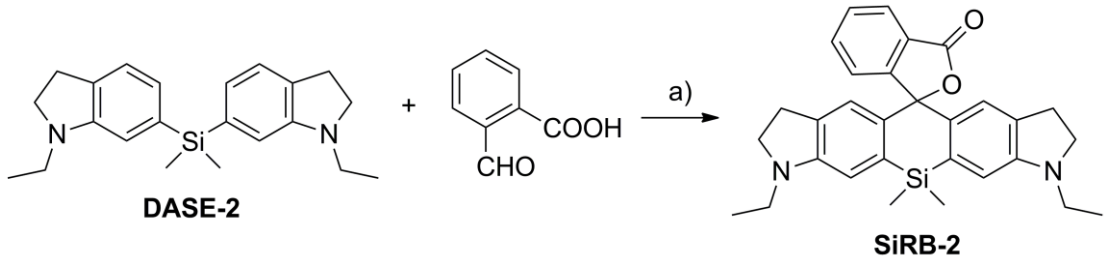
NC-SiRB. Compound **3c** (293 mg) was added and the reaction mixture was stirred for 3 h. The mixture was purified by column chromatography on silica gel (petroleum ether : ethyl acetate : triethylamine = 60 : 1 : 1) to give **NC-SiRB** (50 mg, 31% yield) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.63 (s, 3H), 0.68 (s, 3H), 1.21 (t, 12H, *J* = 6.9 Hz), 3.41 (q, 8H, *J* = 6.9 Hz), 6.50-8.01 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ -1.46, 0.27, 12.54, 44.31, 92.59, 112.68, 115.95, 117.16, 117.77, 126.43, 128.32, 128.65, 129.01, 130.54, 132.22, 137.03, 146.80, 155.29, 168.96. HRMS (ESI) calcd. for $C_{31}H_{35}N_3O_2Si$ $[M+H]^+$: 510.2571, found: 510.2581.

HC≡C-SiRB. Compound **3e** (293 mg) was added and the reaction mixture was stirred for 3 h. The mixture was purified by column chromatography on silica gel (petroleum ether : ethyl acetate : triethylamine = 80 : 1 : 1) to give **HC≡C-SiRB** (24 mg, 16% yield) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.59 (s, 3H), 0.62 (s, 3H), 1.15 (t, 12H, *J* = 7.2 Hz), 3.22 (s, 1H), 3.36 (q, 8H, *J* = 7.2 Hz), 6.48-7.92 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -1.55, 0.30, 12.55, 44.25, 80.57, 82.69, 92.10, 112.60, 115.82, 125.42, 127.14, 127.50, 128.28, 128.48, 130.12, 132.47, 136.98, 146.62, 154.60, 169.94. HRMS (ESI) calcd. for $C_{32}H_{36}N_2O_2Si$ $[M+H]^+$: 509.2619, found: 509.2614.



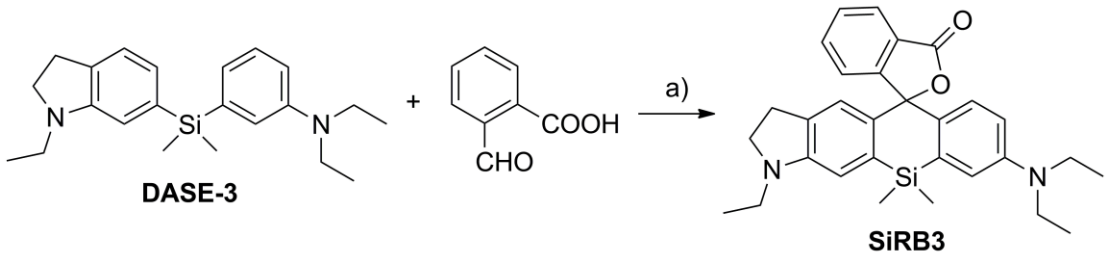
Scheme S7. Synthesis of **HOOC-SiRB**. Reaction conditions: a) $TsOH{\cdot}H_2O$, sealed tube, 140 ℃, 8 h.

HOOC-SiRB. To a 15 mL sealable pressure tube charged with a magnetic stir bar were added the intermediate **DASE-1** (106 mg, 0.3 mmol, 1.0 equiv.), compound **3d** (291 mg, 1.5 mmol, 5.0 equiv.) and *p*-toluenesulfonic acid monohydrate (57 mg, 0.3 mmol, 1.0 equiv.). The tube was sealed tightly and heated at 140 ℃ for 8 h. **[Caution:** To avoid potential danger, the reaction tube was placed behind a blast shield.**]** After cooling to room temperature, the reaction mixture was dissolved in dichloromethane / methanol (5 mL / 5 mL) and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) to give **HOOC-SiRB** (18 mg, 11% yield) as a blue solid. ^{1}H NMR (600 MHz, $CDCl_3$ and CD_3OD) δ 0.55 (s, 3H), 0.60 (s, 3H), 1.11 (t, 12H, *J* = 7.2 Hz), 3.32 (q, 8H, *J* = 7.2 Hz), 6.45-8.20 (m, 9H); ^{13}C NMR (150 MHz, $CDCl_3$ and CD_3OD) δ -1.84, 0.14, 12.37, 44.23, 89.23, 112.62, 116.06, 125.40, 126.24, 128.35, 129.90, 130.17, 130.40, 135.86, 137.22, 146.68, 154.37, 170.48. HRMS (ESI) calcd. for $C_{31}H_{36}N_2O_4Si$ $[M+H]^+$: 529.2517, found: 529.2519.



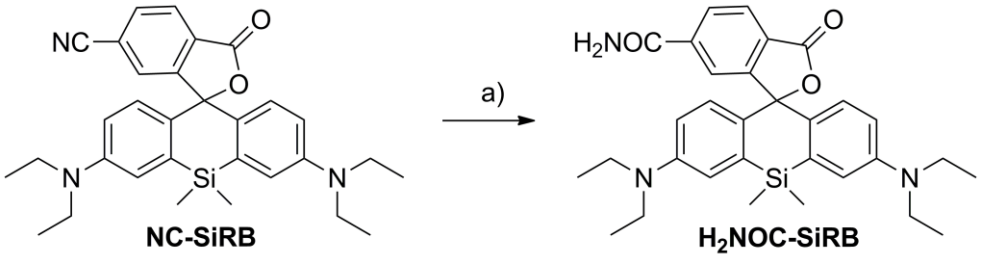
Scheme S8. Synthesis of **SiRB2.** Reaction conditions: a) $CuBr_2$, sealed tube, 140 ℃, 5 h.

SiRB-2. To a 15 mL sealable pressure tube charged with a magnetic stir bar were added the intermediate **DASE-2** (175 mg, 0.5 mmol, 1.0 equiv.), 2-formylbenzoic acid (375 mg, 2.5 mmol, 5.0 equiv.) and copper(II) bromide (11 mg, 0.05 mmol, 0.1 equiv.). The tube was sealed tightly and heated at 140 ℃ for 5 h. **[Caution:** To avoid potential danger, the reaction tube was placed behind a blast shield.**]** After cooling to room temperature, the reaction mixture was dissolved in 10 mL dichloromethane and purified by column chromatography on silica gel (petroleum ether : ethyl acetate : triethylamine = 70 : 1 : 1) to give **SiRB-2** (38 mg, 16% yield) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.54 (s, 3H), 0.58 (s, 3H), 1.18 (t, 12H, *J* = 7.2 Hz), 2.70-2.88 (m, 4H), 3.18 (q, 4H, *J* = 7.2 Hz), 3.29 (t, 4H, *J* = 8.4 Hz), 6.63-7.96 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ -0.39, 0.06, 12.04, 28.37, 42.67, 51.70, 92.06, 109.97, 123.47, 123.83, 125.49, 125.77, 128.37, 132.54, 133.03, 133.95, 134.07, 151.37, 156.39, 171.46. HRMS (ESI) calcd. for $C_{30}H_{32}N_2O_2Si$ $[M+H]^+$: 481.2306, found: 481.2307.



Scheme S9. Synthesis of **SiRB-3**. Reaction conditions: a) $CuBr_2$, sealed tube, 140 ℃, 5 h.

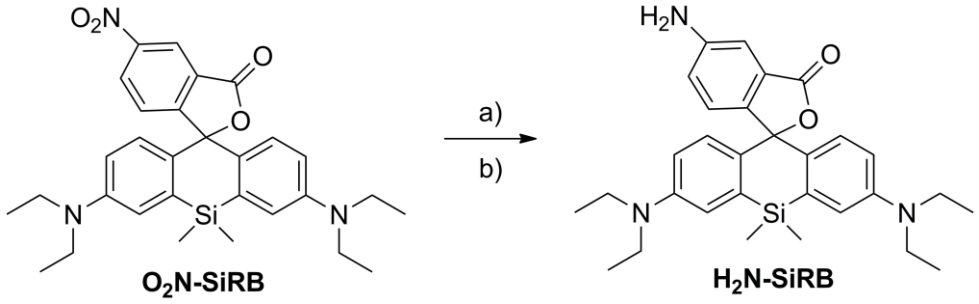
SiRB-3. To a 15 mL sealable pressure tube charged with a magnetc stir bar were added the intermediate **DASE-3** (176 mg, 0.5 mmol, 1.0 equiv.), 2-formylbenzoic acid (375 mg, 2.5 mmol, 5.0 equiv.) and copper(II) bromide (11 mg, 0.05 mmol, 0.1 equiv.). The tube was sealed tightly and heated at 140 ℃ for 5 h. **[Caution:** To avoid potential danger, the reaction tube was placed behind a blast shield.**]** After cooling to room temperature, the reaction mixture was dissolved in 10 mL dichloromethane and purified by column chromatography on silica gel (petroleum ether : ethyl acetate : triethylamine = 70 : 1 : 1) to give **SiRB-3** (75 mg, 31% yield) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.57 (s, 3H), 0.61 (s, 3H), 1.14 (t, 6H, *J* = 7.2 Hz), 1.19 (t, 3H, *J* = 7.2 Hz), 2.78 (t, 2H, *J* = 7.8 Hz), 3.19 (q, 2H, *J* = 7.2 Hz), 3.29 (t, 2H, *J* = 8.1 Hz), 3.35 (q, 4H, *J* = 6.9 Hz), 6.51-7.97 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ -1.08, 0.26, 12.03, 12.52, 28.38, 42.68, 44.26, 51.73, 92.16, 110.32, 112.74, 115.59, 123.58, 124.35, 125.53, 126.63, 128.47, 130.63, 132.28, 133.18, 133.81, 134.78, 136.66, 146.33, 146.55, 151.47, 155.25, 171.00. HRMS (ESI) calcd. for $C_{30}H_{34}N_2O_2Si$ $[M+H]^+$: 483.2462, found: 483.2461.



Scheme S9. Synthesis of **H_2NOC-SiR**. Reaction conditions: a) K_2CO_3, H_2O_2, DMSO, 60 ℃, 1 h.

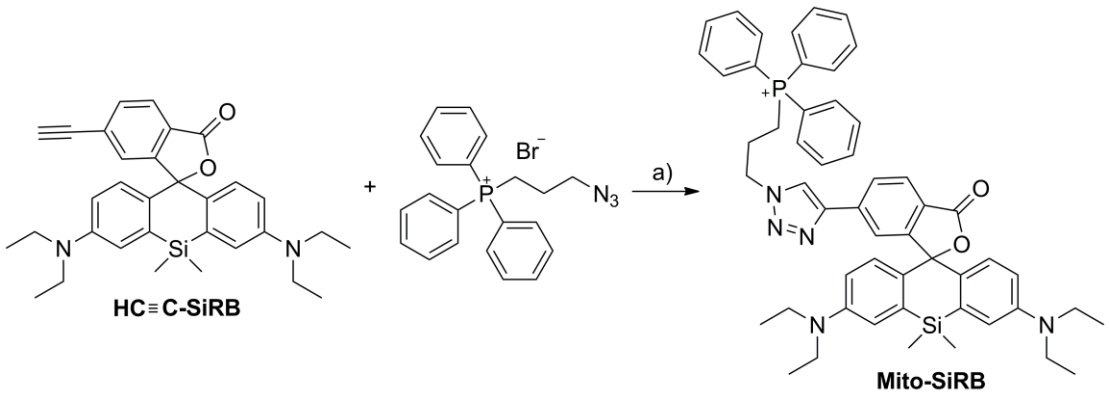
H_2NOC-SiRB[6]**.** To a solution of **NC-SiRB** (51 mg, 0.10 mmol) and potassium carbonate (17 mg, 0.12 mmol) in DMSO (5 mL) was added hydrogen peroxide (200 μL, 30% aqueous solution). The reaction mixture was stirred and heated at 60 ℃ for 1 h, then poured into iced water (25 mL) and extracted with dichloromethane (15 mL × 3). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent under reduced pressure, the

residue was purified by column chromatography on silica gel (petroleum ether : ethyl acetate : trimethyamine = 100 : 10 : 1) to provide **H_2NOC-SiRB** (35 mg, 67% yield) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.58 (s, 3H), 0.63 (s, 3H), 1.15 (t, 12H, *J* = 6.9 Hz), 3.35 (q, 8H, *J* = 6.9 Hz), 6.46-8.01 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -1.52, 0.30, 12.54, 44.25, 92.55, 112.67, 115.83, 123.55, 125.85, 127.93, 128.55, 129.83, 130.01, 137.06, 138.40, 146.68, 155.15, 168.09, 169.81. HRMS (ESI) calcd. for $C_{31}H_{37}N_3O_3Si$ $[M+H]^+$: 528.2677, found: 528.2676.



Scheme S10 . Synthesis of **H_2N-SiRB**. a) H_2, 10% Pd/C, methanol/dichloromethane, RT, 4 h; b) methanol/dichloromethane, chloranil, RT, 10 min.

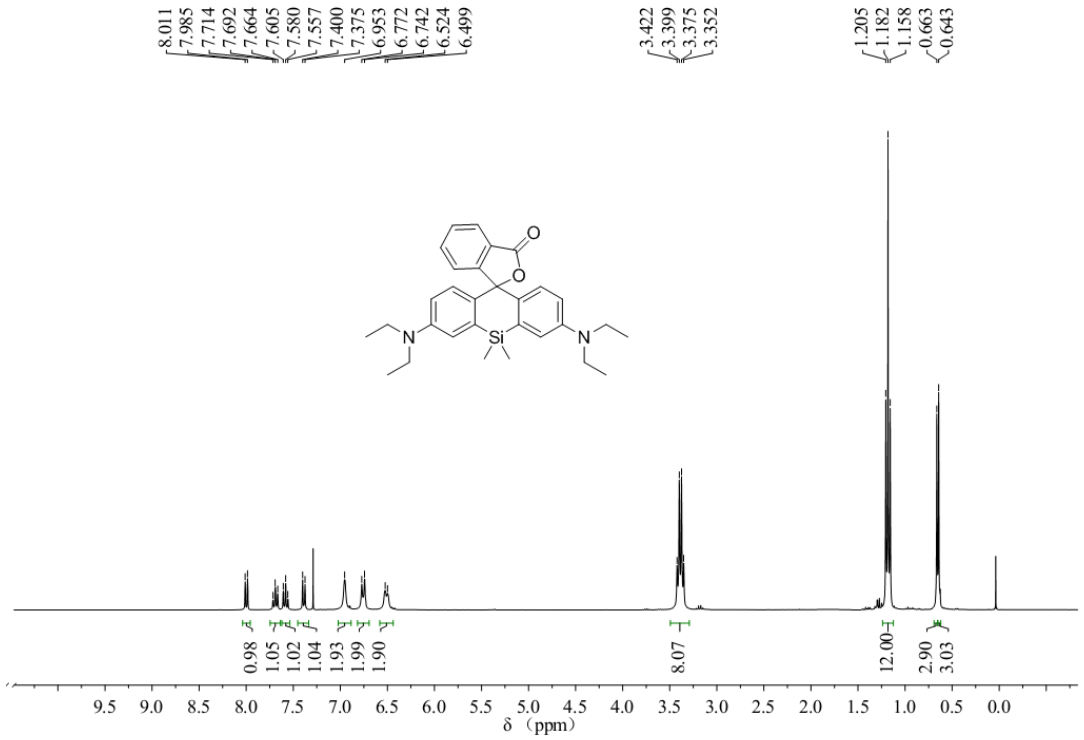
H_2N-SiRB[7]**.** To a solution of **O_2N-SiRB** (106 mg, 0.20 mmol) in methanol/ dichloromethane (15 mL/10 mL), 10% Pd/C (50 mg) was added. The reaction mixture was stirred under a H_2 atmosphere for 4 h at room temperature. After the reaction mixture was filtered through Celite, chloranil (68 mg, 0.3 mmol) was added into the filtrate. The mixture was stirred for 10 min at room temperature. After filtration and removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether : ethyl acetate : trimethyamine = 100 : 10 : 1) to give **H_2N-SiRB** (79 mg, 79% yield) as light yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.60 (s, 6H), 1.14 (t, 12H, *J* = 6.9 Hz), 3.35 (q, 8H, *J* = 6.9 Hz), 3.97 (s, 2H), 6.44-7.25 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -2.18, 0.58, 12.56, 44.26, 92.46, 109.53, 112.22, 116.06, 121.11, 125.72, 128.46, 129.24, 131.62, 137.75, 143.44, 146.52, 147.21, 170.70. HRMS (ESI) calcd. for $C_{30}H_{35}N_3O_2Si$ $[M+H]^+$: 500.2728, found: 500.2712.

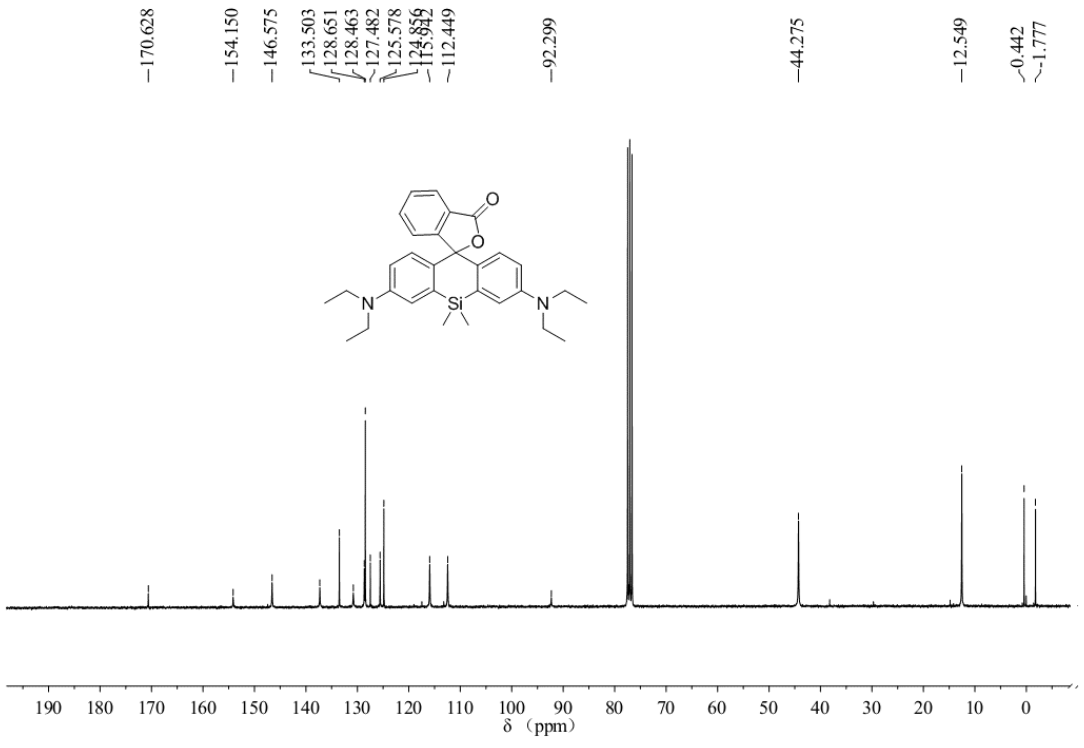


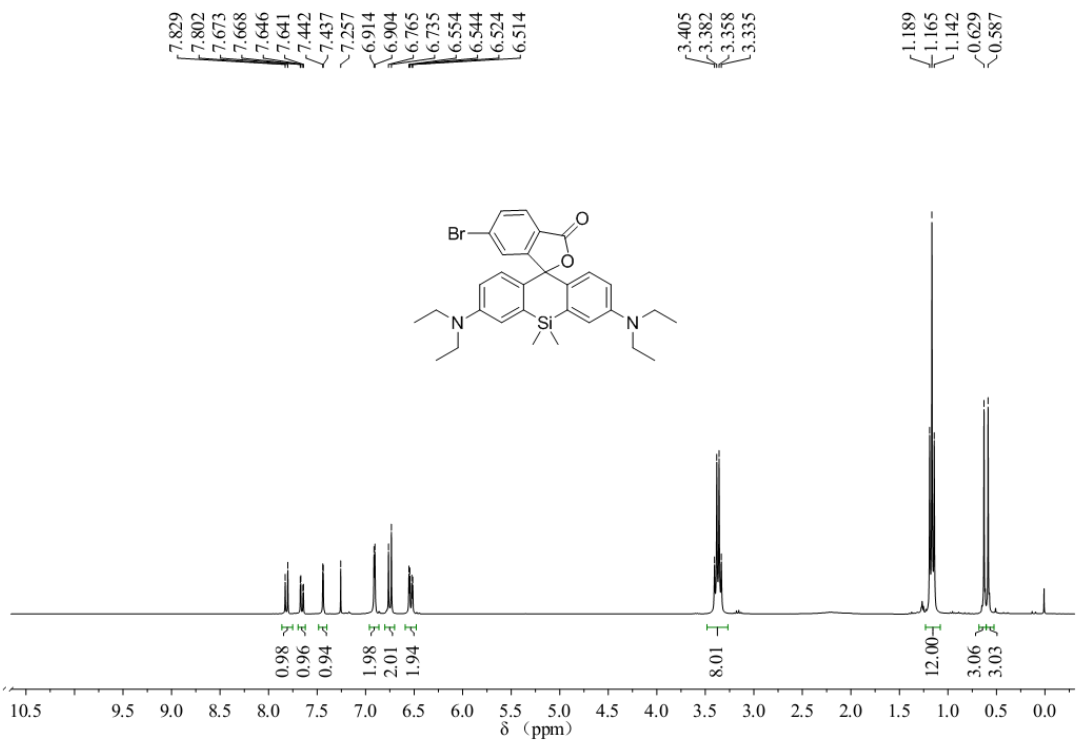
Scheme S11. Synthesis of **Mito-SiRB**. Reaction conditions: a) THF, $CuSO_4 \cdot 5H_2O$, sodium ascorbate, RT, 24 h.

Mito-SiRB. To a 10 mL reaction tube flushed with argon were added **HC≡C-SiRB** (20 mg, 0.039 mmol), (3-azidopropyl)triphenylphosphonium bromide (15 mg, 0.035 mmol) and THF (2 mL). $CuSO_4 \cdot 5H_2O$ (3 mg, 0.01 mmol) and sodium ascorbate (4.0 mg, 0.02 mmol) dissolved in H_2O (0.8 mL) were added into the reaction mixture. After stirred at room temperature for 24 h, the solvent was removed under reduced pressure. Water (10 mL) was added and the mixture was extracted with dichloromethane (15 mL × 3). The organic layers were combined, washed with brine and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (dichloromethane : methanol= 20 : 1) to give **Mito-SiRB** (20 mg, 61% yield) as a light green solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.58 (s, 3H), 0.66 (s, 3H), 1.14 (t, 12H, J = 6.9 Hz), 2.02 (s, 1H), 2.33-2.40 (m, 2H), 3.34 (q, 8H, J = 6.9 Hz), 3.87-3.97 (m, 2H), 5.02-5.06 (m, 2H), 6.47-8.68 (m, 25H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -1.36, 0.31, 12.56, 19.29, 20.00, 23.40, 44.29, 49.08, 49.38, 92.13, 112.87, 117.20, 118.34, 121.24, 124.02, 125.92, 126.24, 126.53, 128.65, 130.50, 130.67, 133.52, 133.65, 135.17, 135.21, 136.18, 136.81, 146.19, 146.49, 155.66, 170.66. HRMS (ESI) calcd. for $C_{53}H_{57}N_5O_2PSi^+$ $[M]^+$:854.4014, found: 854.4019.

^{1}H NMR, ^{13}C NMR and HRMS Spectra.



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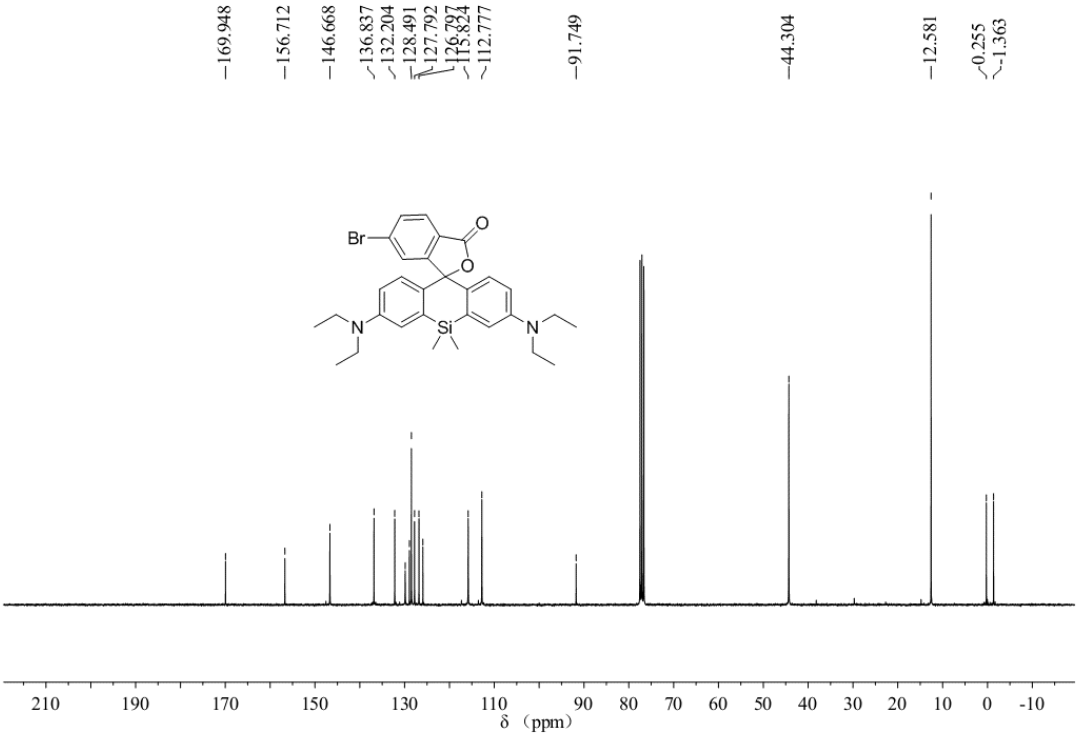
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δ（ppm）

Qualitative Analysis Report

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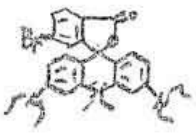

User Spectra

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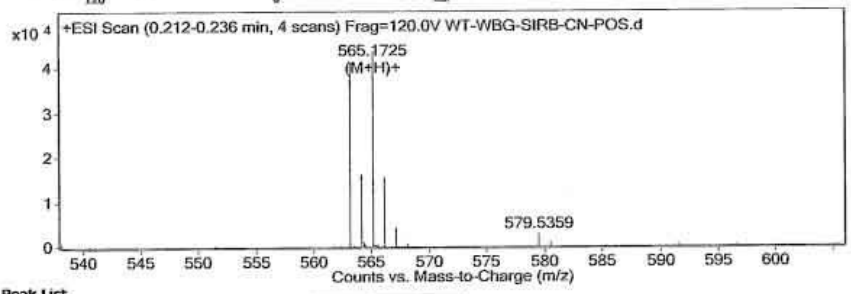

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564.1772	1	16339	C30 H36 Br N2 O2 Si	(M+H)+
565.1725	1	43490	C30 H36 Br N2 O2 Si	(M+H)+
566.175	1	15451	C30 H36 Br N2 O2 Si	(M+H)+

Formula Calculator Element Limits

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H	0	400
N	0	6
O	0	10
Si	0	1
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Formula Calculator Results

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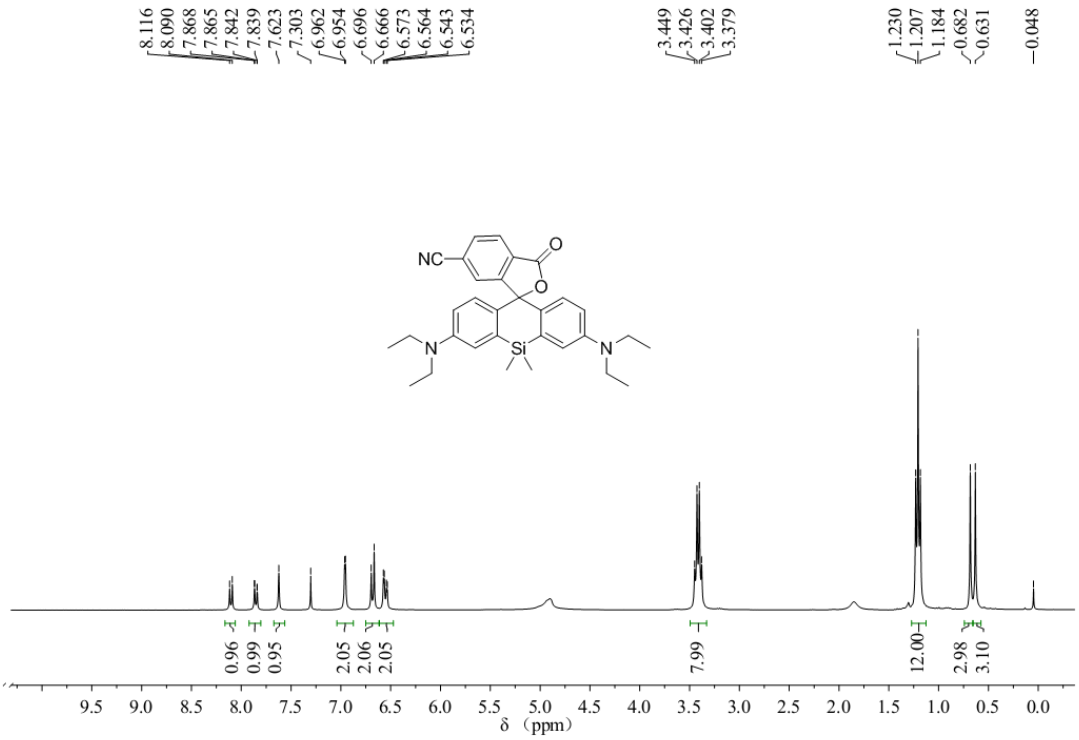
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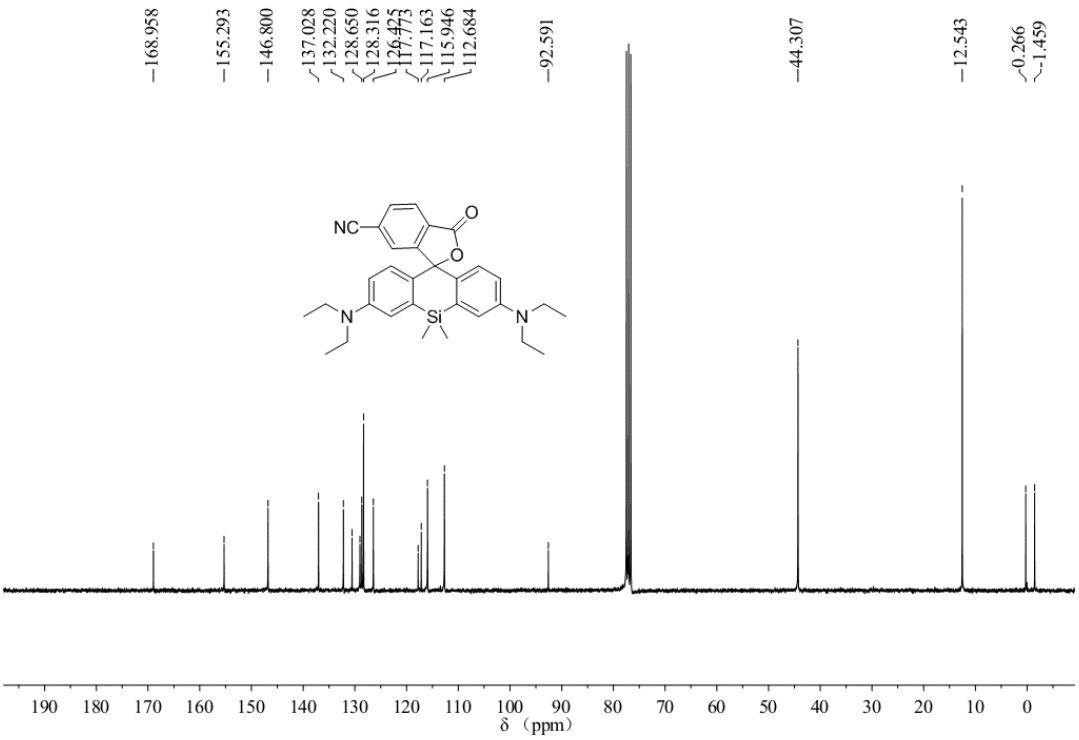
δ（ppm）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Qualitative Analysis Report

CN

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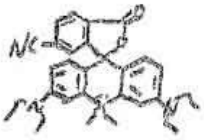

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
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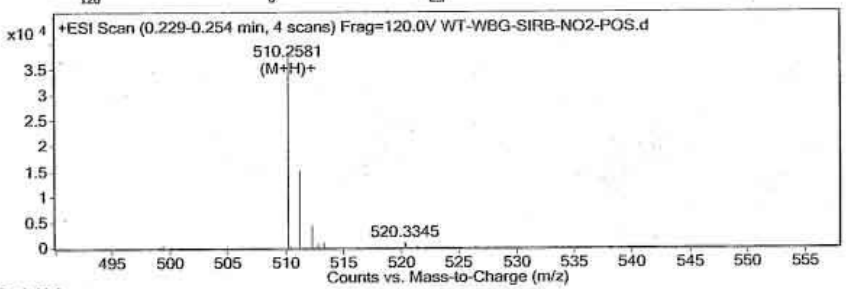

Peak List

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302.3054	1	4873		
413.3783	1	6128		
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511.2608	1	15088	C31 H36 N3 O2 Si	(M+H)+

Formula Calculator Element Limits

Element	Min	Max
C	3	200
H	0	400
N	0	6
O	0	10
Si	0	1

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
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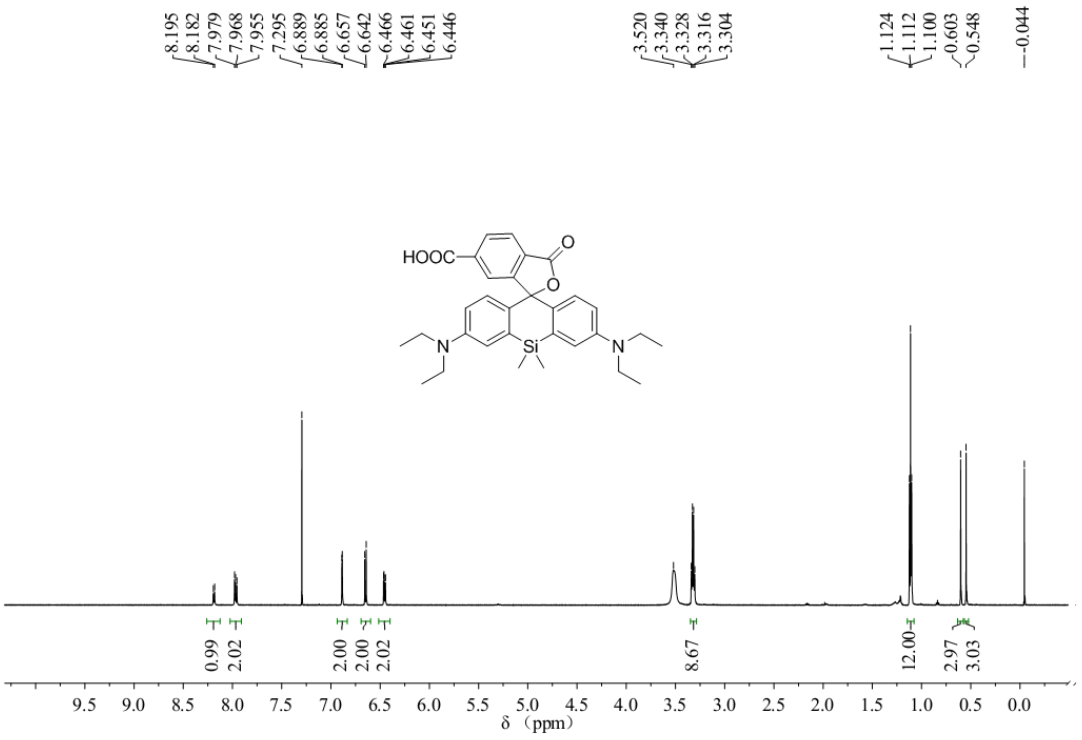
--- End Of Report ---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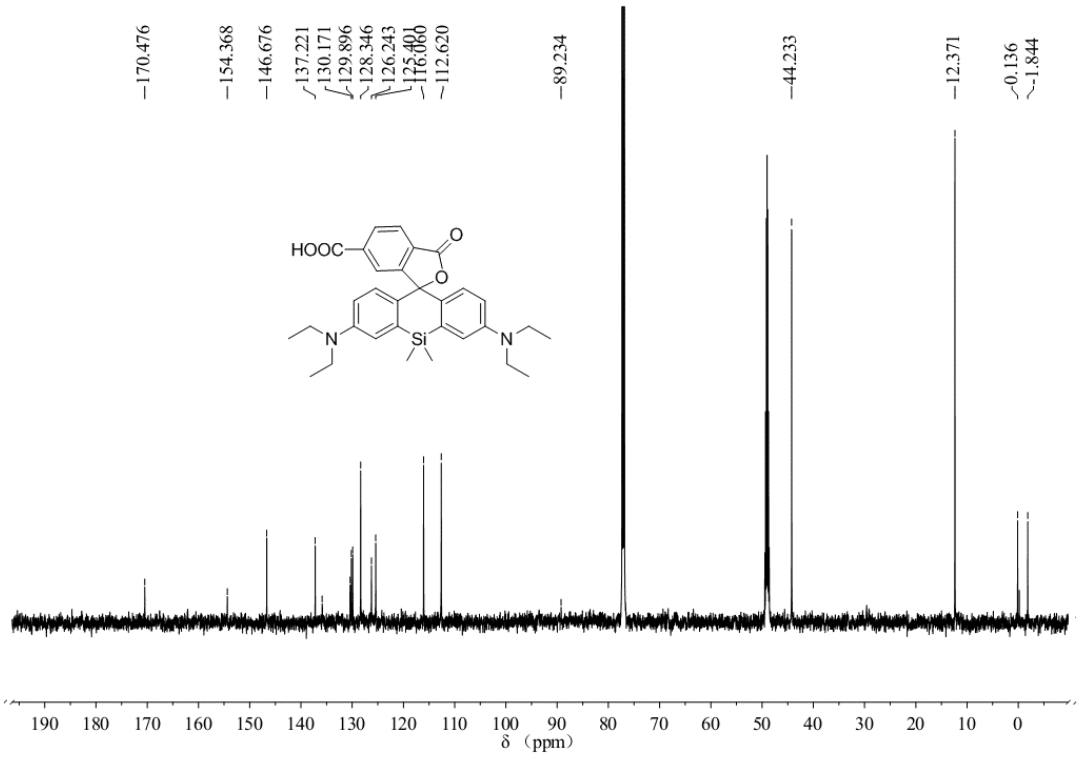
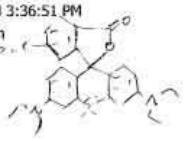
-0.044
HOOC
O
O
N
Si
N
0.99
2.02
2.00
2.00
2.02
8.67
12.00
2.97
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ（ppm）


170.476
154.368
146.676
137.221
130.171
129.896
128.346
126.243
125.401
116.060
112.620
89.234
44.233
12.371
0.136
-1.844
HOOC
O
O
N
Si
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ（ppm）

Qualitative Analysis Report

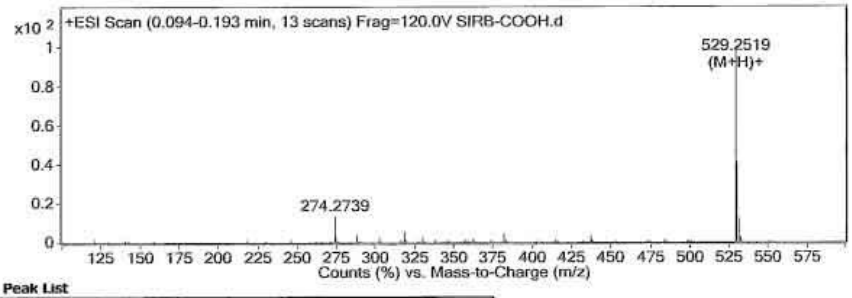
Data Filename	SIRB-COOH.d	**Sample Name**	SIRB-COOH
Sample Type	Sample	**Position**	P1-E3
Instrument Name	Instrument 1	**User Name**	
Acq Method	TEST-POS.m	**Acquired Time**	6/4/2013 3:36:51 PM
IRM Calibration Status	Some Ions Missed	**DA Method**	ERROR.m
Comment			

Sample Group **Info.**



User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
120	0	Esi



Peak List

m/z	z	Abund	Formula	Ion
274.2739		204686		
318.3001		80061		
529.2519	1	1502819	C31 H37 N2 O4 Si	(M+H)+
530.2547	1	615729	C31 H37 N2 O4 Si	(M+H)+
531.2556	1	185306	C31 H37 N2 O4 Si	(M+H)+

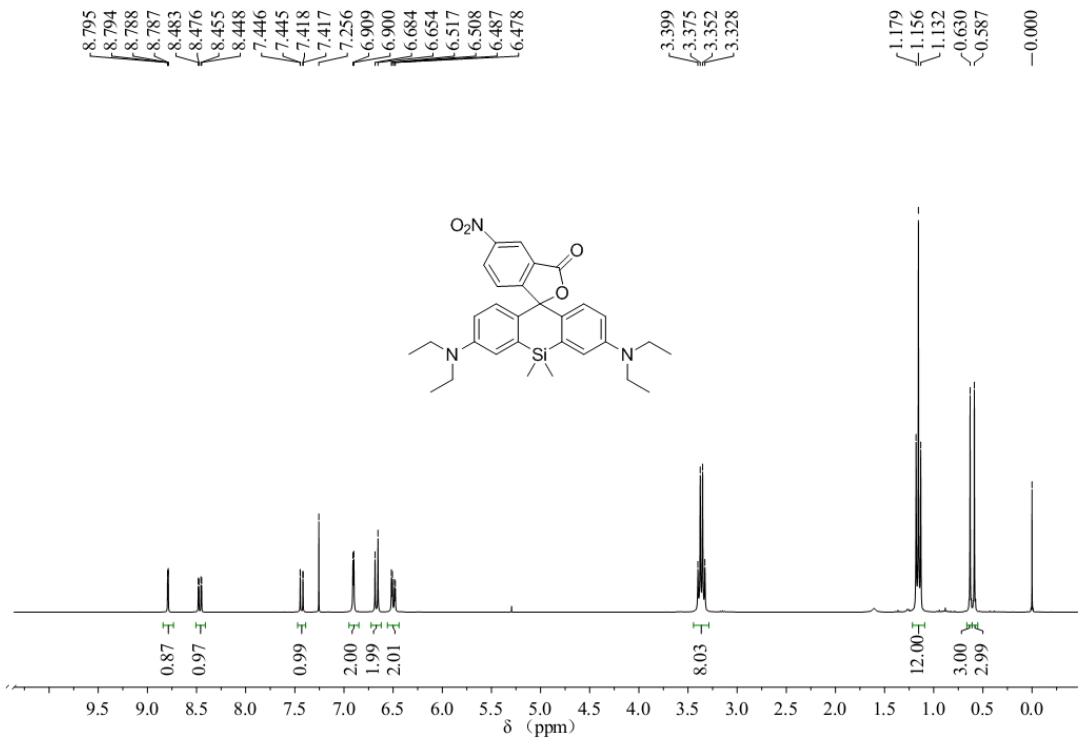
Formula Calculator Element Limits

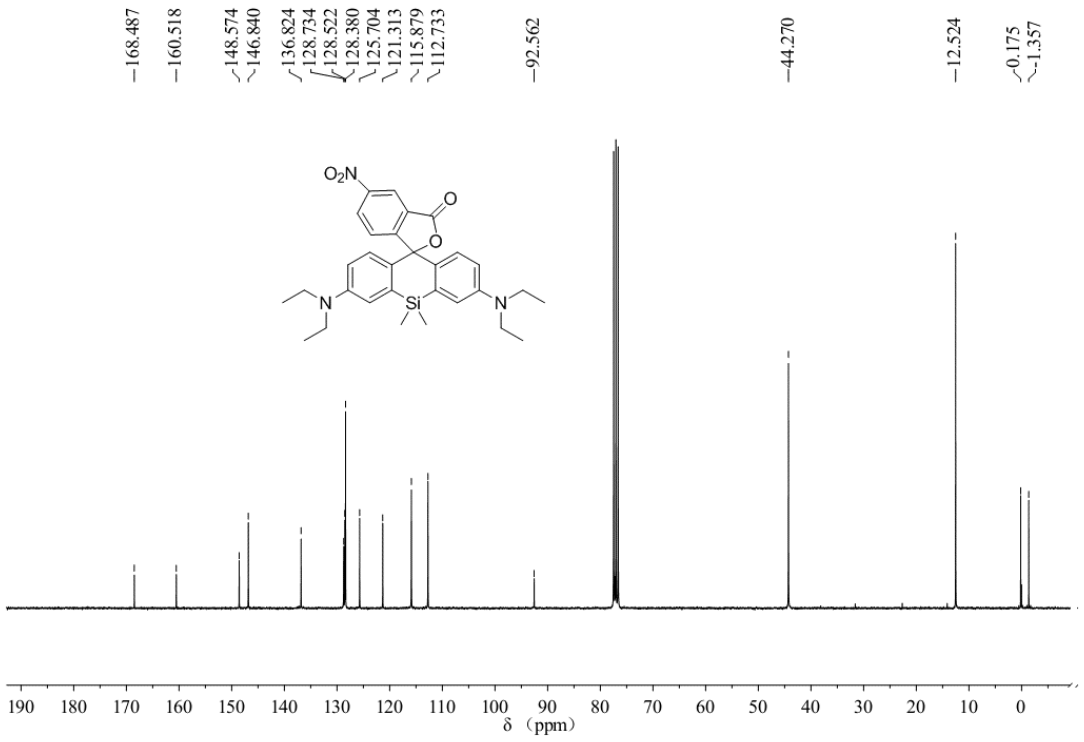
Element	Min	Max
C	3	100
H	0	300
N	0	5
Si	0	5
O	0	5

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C31 H36 N2 O4 Si	TRUE	528.2447	528.2444	-0.43	C31 H37 N2 O4 Si	99.67

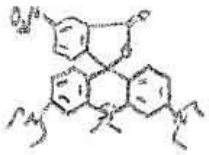
--- End Of Report ---


8.795
8.794
8.788
8.787
8.483
8.476
8.455
8.448
7.446
7.445
7.418
7.417
7.256
6.909
6.900
6.684
6.654
6.517
6.508
6.487
6.478
3.399
3.375
3.352
3.328
1.179
1.156
1.132
0.630
0.587
0.000
O2N
O
O
N
Si
N
0.87
0.97
0.99
2.00
1.99
2.01
8.03
12.00
3.00
2.99
9.5 9.0 8.5 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 0.5 0.0
δ（ppm）


168.487
160.518
148.574
146.840
136.824
128.734
128.522
128.380
125.704
121.313
115.879
112.733
92.562
44.270
12.524
0.175
-1.357
O2N
O
O
N
Si
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ（ppm）

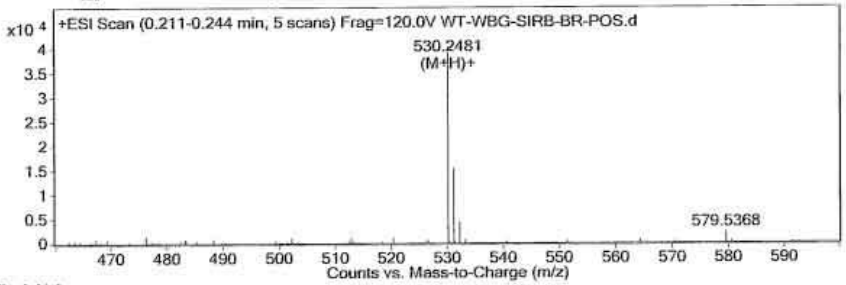
Qualitative Analysis Report

Data Filename	WT-WBG-SIRB-BR-POS.d	**Sample Name**	WT-WBG-SIRB-BR
Sample Type	Sample	**Position**	P1-E3
Instrument Name	Instrument 1	**User Name**	
Acq Method	TEST-POS-01-WL.m	**Acquired Time**	6/25/2013 4:01:14 PM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			



User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
120	0	Esi



Peak List

m/z	z	Abund	Formula	Ion
117.0547		9292		
121.0509		8474		
173.1649		6929		
274.2749		5868		
298.275	1	18946		
300.2899	1	9994		
302.3059	1	6052		
413.3783	1	7746		
530.2481	1	40108	C30 H36 N3 O4 Si	(M+H)+
531.2505	1	15520	C30 H36 N3 O4 Si	(M+H)+

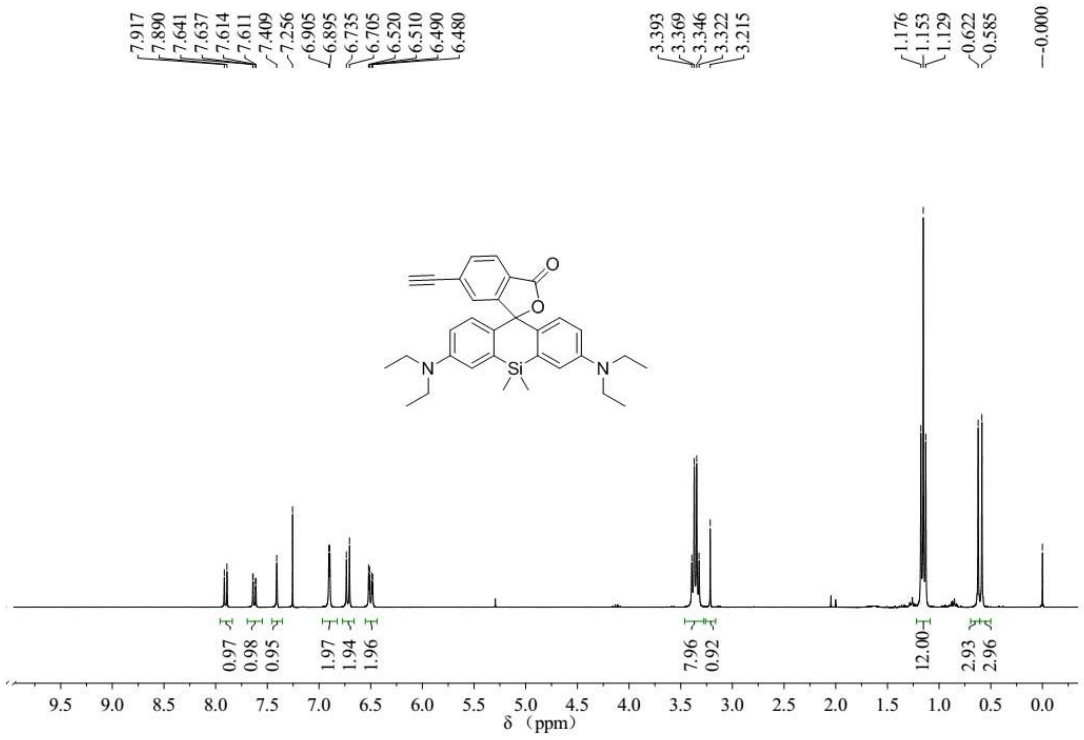
Formula Calculator Element Limits

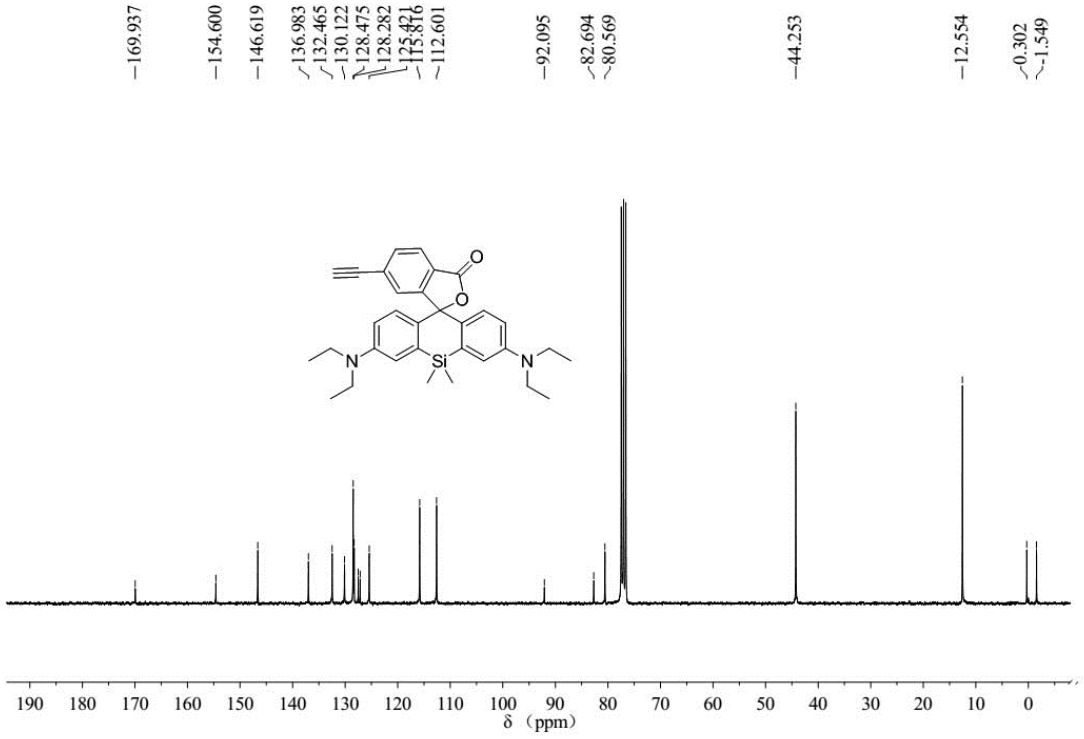
Element	Min	Max
C	3	200
H	0	400
N	0	6
O	0	10
Si	0	1
Br	0	1

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C30 H35 N3 O4 Si	TRUE	529.2408	529.2397	-2.11	C30 H36 N3 O4 Si	97.28

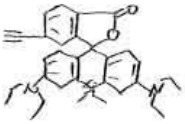
— End Of Report —


7.917
7.890
7.641
7.637
7.614
7.611
7.409
7.256
6.905
6.895
6.735
6.705
6.520
6.510
6.490
6.480
3.393
3.369
3.346
3.322
3.215
1.176
1.153
1.129
0.622
0.585
-0.000
O
O
N
Si
N
0.97
0.98
0.95
1.97
1.94
1.96
7.96
0.92
12.00
2.93
2.96
9.5 9.0 8.5 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 0.5 0.0
δ（ppm）


169.937
154.600
146.619
136.983
132.465
130.122
128.475
128.282
125.421
115.816
112.601
92.095
82.694
80.569
44.253
12.554
0.302
-1.549
O
O
N
Si
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ（ppm）

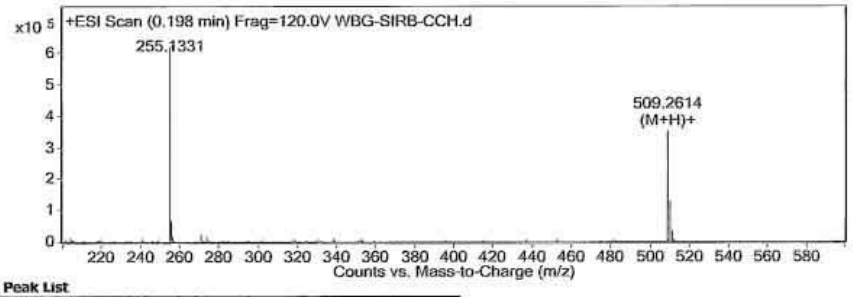
Qualitative Analysis Report

Data Filename	WBG-SIRB-CCH.d	**Sample Name**	WBG-SIRB-CCH
Sample Type	Sample	**Position**	P1-B9
Instrument Name	Instrument 1	**User Name**	
Acq Method	TEST-POS-01-WL.m	**Acquired Time**	4/8/2014 11:14:52 AM
IRM Calibration Status	Success	**DA Method**	1.m
Comment			



User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
120	0	Esi



Peak List

m/z	z	Abund	Formula	Ion
121.0509		118073		
125.9863		47384		
255.1331	2	620043		
255.6365	2	223524		
256.1367	2	68071		
509.2614	1	351208	C32 H37 N2 O2 Si	(M+H)+
510.2647	1	128673	C32 H37 N2 O2 Si	(M+H)+
511.266	1	32778	C32 H37 N2 O2 Si	(M+H)+

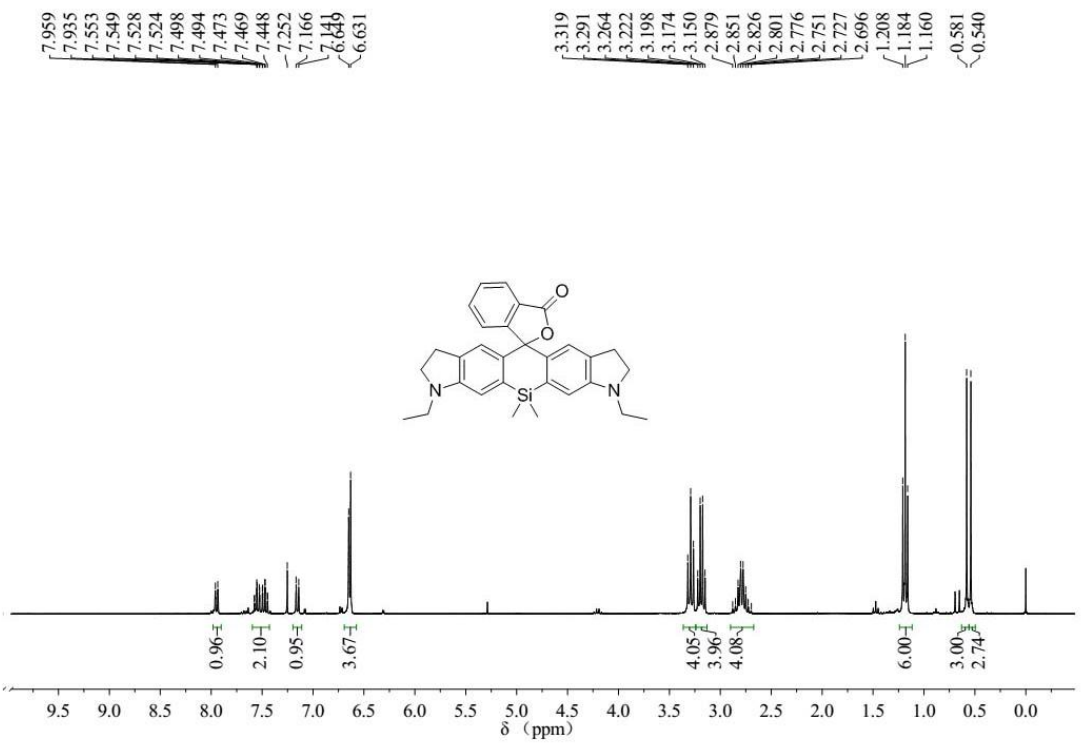
Formula Calculator Element Limits

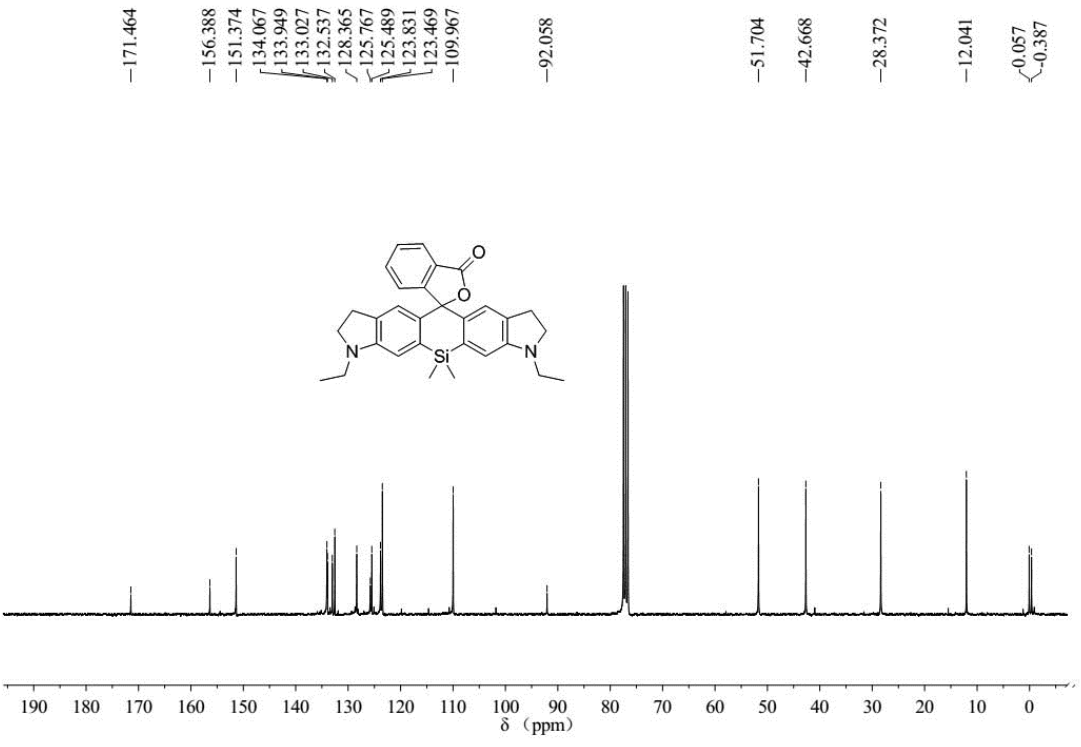
Element	Min	Max
C	3	200
H	0	300
O	1	3
N	1	3
Si	1	2

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C32 H36 N2 O2 Si	TRUE	508.2542	508.2546	0.81	C32 H37 N2 O2 Si	97.43

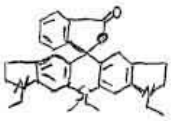
--- End Of Report ---


7.959
7.935
7.553
7.549
7.528
7.524
7.498
7.494
7.473
7.469
7.448
7.252
7.166
7.141
6.649
6.631
3.319
3.291
3.264
3.222
3.198
3.174
3.150
2.879
2.851
2.826
2.801
2.776
2.751
2.727
2.696
1.208
1.184
1.160
0.581
0.540
O
O
N
Si
N
0.96
2.10
0.95
3.67
4.05
3.96
4.08
6.00
3.00
2.74
9.5 9.0 8.5 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 0.5 0.0
δ（ppm）


171.464
156.388
151.374
134.067
133.949
133.027
132.537
128.365
125.767
125.489
123.831
123.469
109.967
92.058
51.704
42.668
28.372
12.041
0.057
-0.387
O
O
N
Si
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ（ppm）

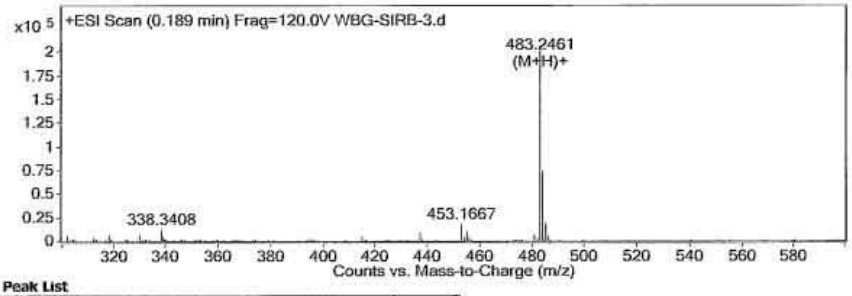
Qualitative Analysis Report

Data Filename	WBG-SIRB-3.d	**Sample Name**	WBG-SIRB-3
Sample Type	Sample	**Position**	P1-B7
Instrument Name	Instrument 1	**User Name**	
Acq Method	TEST-POS-01-WL.m	**Acquired Time**	4/8/2014 11:11:39 AM
IRM Calibration Status	Success	**DA Method**	1.m
Comment			



User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
120	0	Esi



Peak List

m/z	z	Abund	Formula	Ion
118.0656		35057		
121.0509		102382		
125.9862		20058		
242.127	2	79917		
242.6284	2	31704		
271.1877		37105		
453.1667		17425		
483.2461	1	206632	C30 H35 N2 O2 Si	(M+H)+
484.2487	1	73691	C30 H35 N2 O2 Si	(M+H)+
485.2496	1	18963	C30 H35 N2 O2 Si	(M+H)+

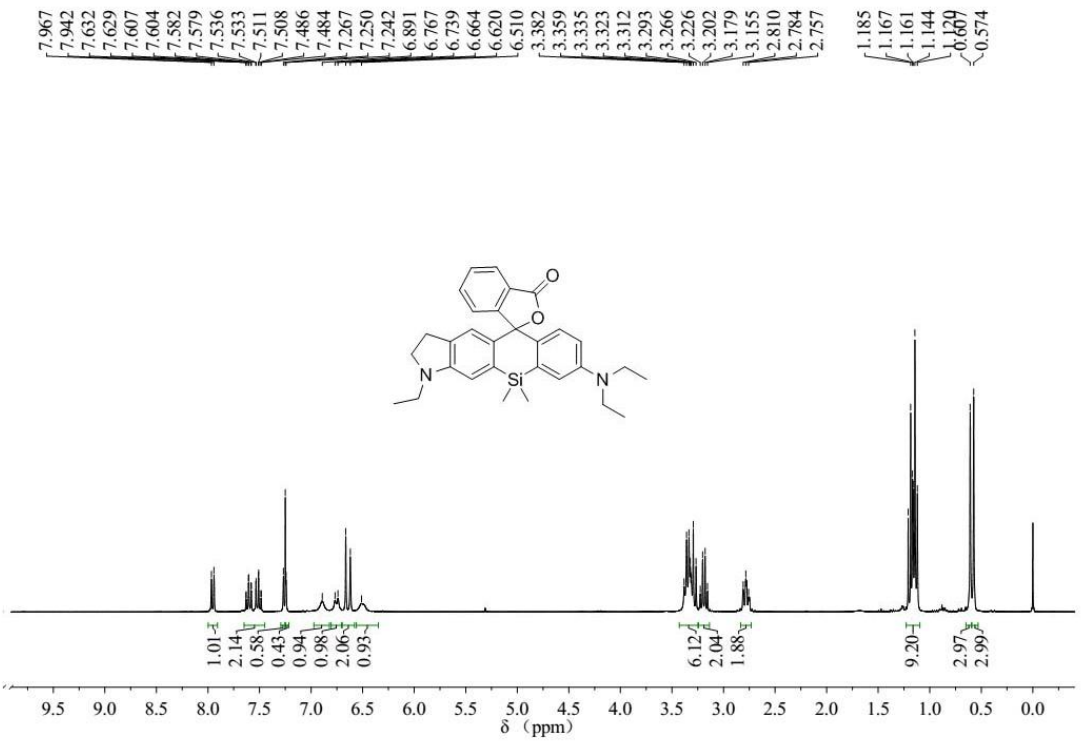
Formula Calculator Element Limits

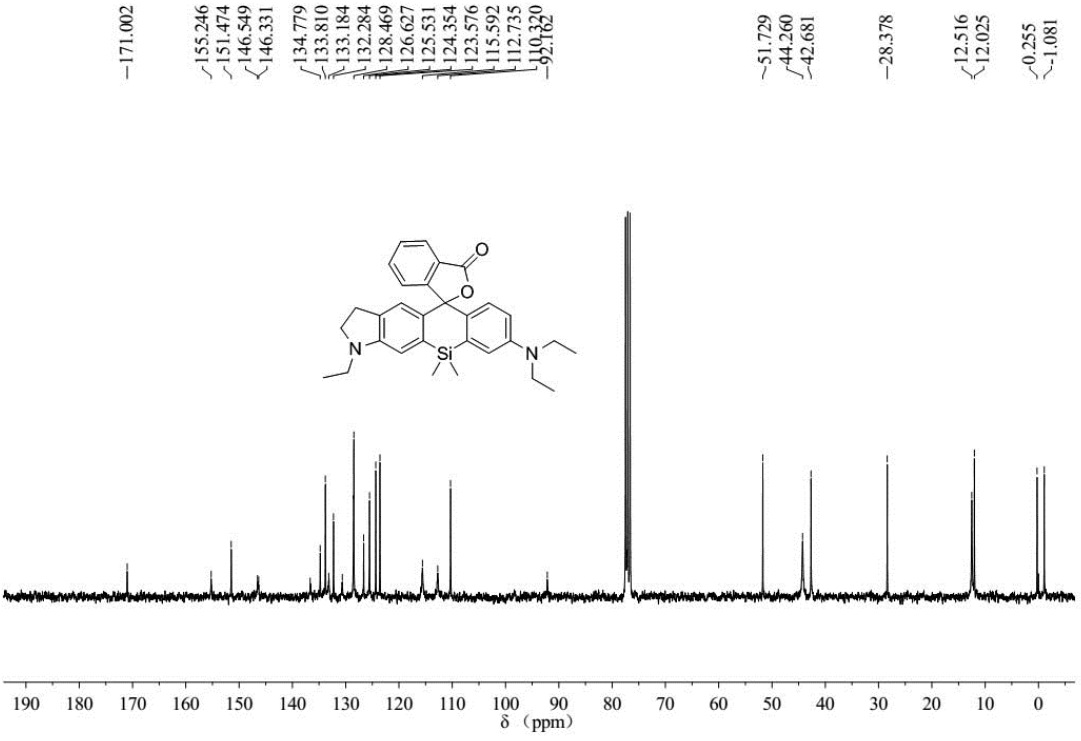
Element	Min	Max
C	3	200
H	0	300
O	1	3
N	1	3
Si	1	2

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C30 H34 N2 O2 Si	TRUE	482.2388	482.239	0.26	C30 H35 N2 O2 Si	98.69

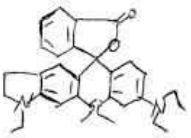
— End Of Report —


7.967
7.942
7.632
7.629
7.607
7.604
7.582
7.579
7.536
7.533
7.511
7.508
7.486
7.484
7.267
7.250
7.242
6.891
6.767
6.739
6.664
6.620
6.510
3.382
3.359
3.335
3.323
3.312
3.293
3.266
3.226
3.202
3.179
3.155
2.810
2.784
2.757
1.185
1.167
1.161
1.144
1.120
0.607
0.574
O
O
N
Si
N
1.01
2.14
0.58
0.43
0.94
0.98
2.06
0.93
6.12
2.04
1.88
9.20
2.97
2.99
9.5 9.0 8.5 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 0.5 0.0
δ（ppm）


171.002
155.246
151.474
146.549
146.331
134.779
133.810
133.184
132.284
128.469
126.627
125.531
124.354
123.576
115.592
112.735
110.320
92.162
51.729
44.260
42.681
28.378
12.516
12.025
0.255
-1.081
O
O
N
Si
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ（ppm）

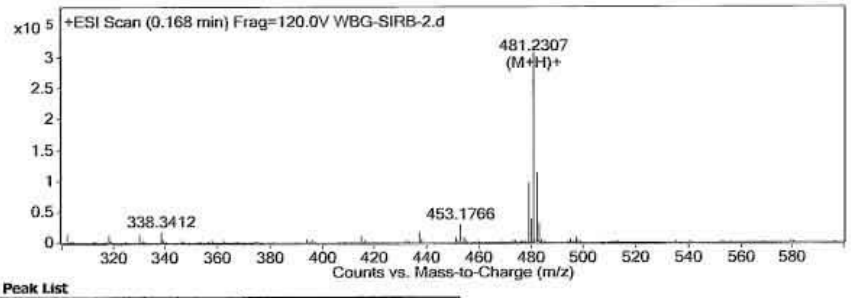
Qualitative Analysis Report

Data Filename	WBG-SIRB-2.d	**Sample Name**	WBG-SIRB-2
Sample Type	Sample	**Position**	P1-B6
Instrument Name	Instrument 1	**User Name**	
Acq Method	TEST-POS-01-WL.m	**Acquired Time**	4/8/2014 11:10:01 AM
IRM Calibration Status	Success	**DA Method**	1.m
Comment			



User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
120	0	Esi



Peak List

m/z	z	Abund	Formula	Ion
121.0509		92170		
271.1875		54260		
274.2739		29918		
437.1941		17338		
453.1766		29929		
479.2157	1	97400		
480.2181	1	37569		
481.2307	1	316926	C30 H33 N2 O2 Si	(M+H)+
482.2342	1	113162	C30 H33 N2 O2 Si	(M+H)+
483.2341	1	30400	C30 H33 N2 O2 Si	(M+H)+

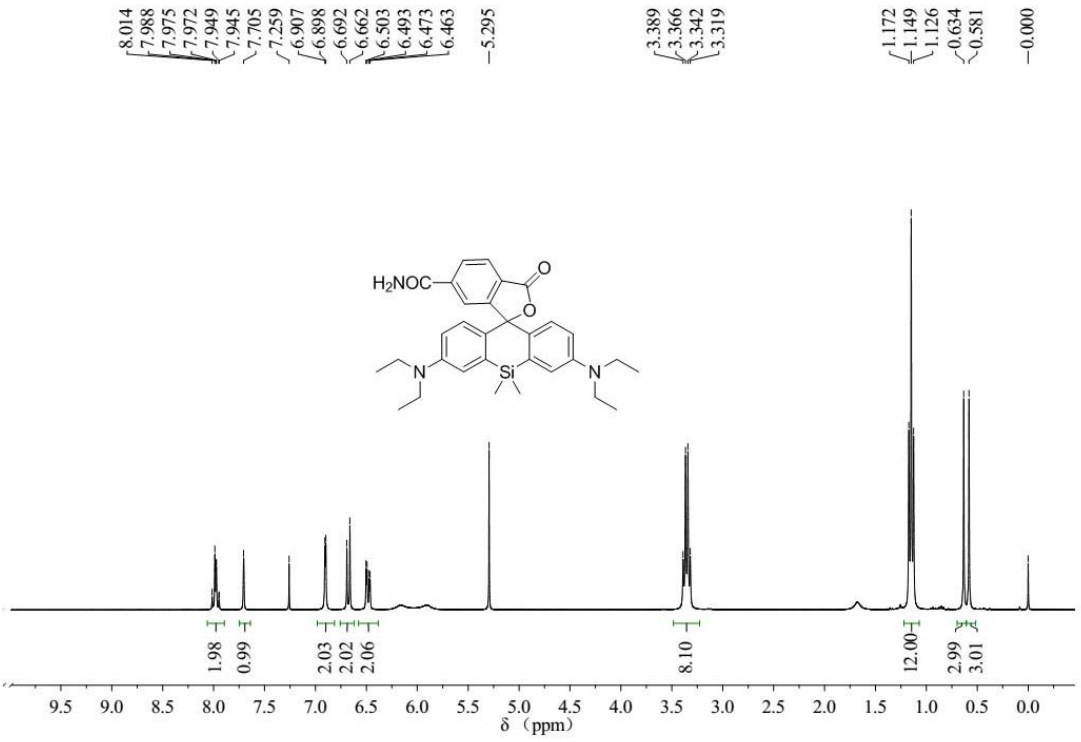
Formula Calculator Element Limits

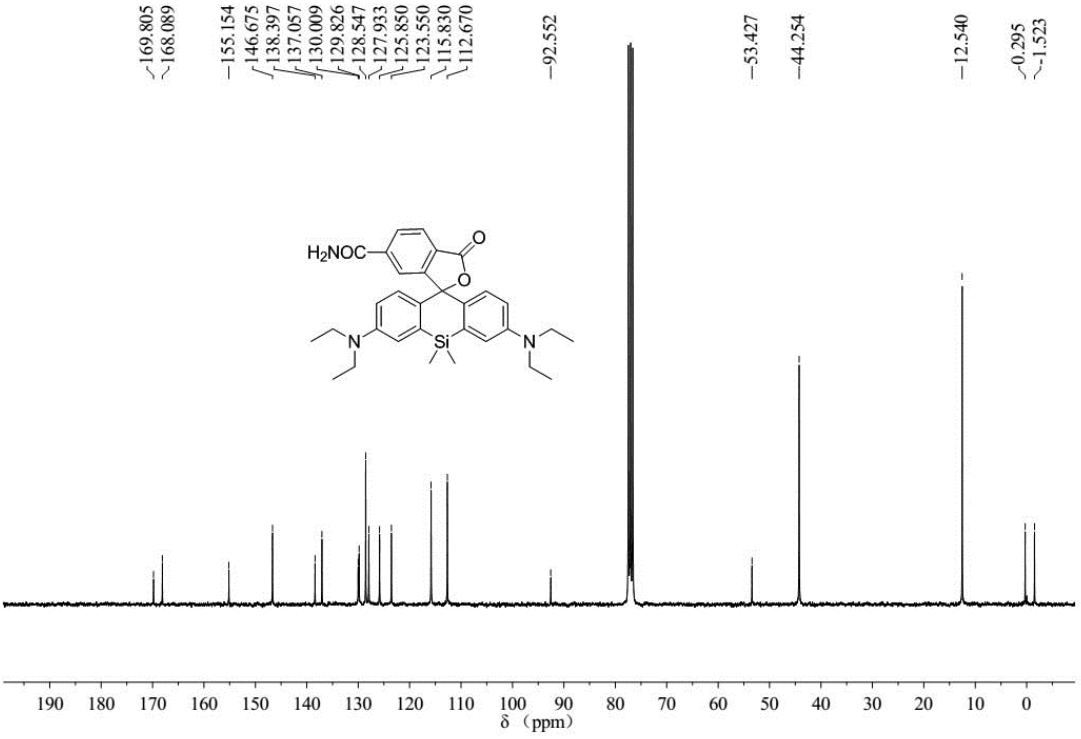
Element	Min	Max
C	3	200
H	0	300
O	1	3
N	1	3
Si	1	2

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C30 H32 N2 O2 Si	TRUE	480.2235	480.2233	-0.41	C30 H33 N2 O2 Si	98.75

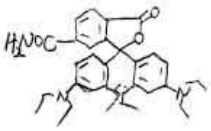
--- End Of Report ---


8.014
7.988
7.975
7.972
7.949
7.945
7.705
7.259
6.907
6.898
6.692
6.662
6.503
6.493
6.473
6.463
5.295
3.389
3.366
3.342
3.319
1.172
1.149
1.126
0.634
0.581
0.000
H2NOC
O
O
N
Si
N
1.98
0.99
2.03
2.02
2.06
8.10
12.00
2.99
3.01
9.5 9.0 8.5 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 0.5 0.0
δ（ppm）


169.805
168.089
155.154
146.675
138.397
137.057
130.009
129.826
128.547
127.933
125.850
123.550
115.830
112.670
92.552
53.427
44.254
12.540
0.295
-1.523
H2NOC
O
O
N
Si
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ（ppm）

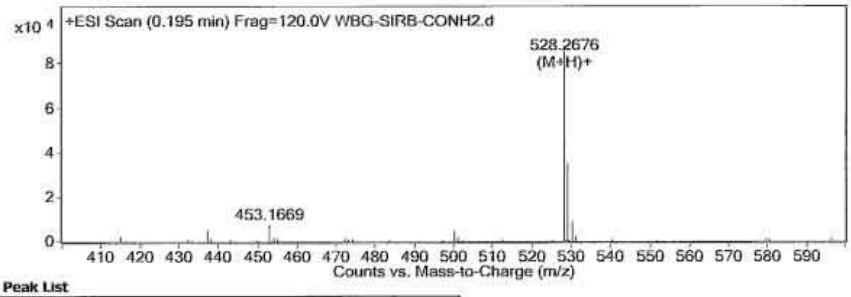
Qualitative Analysis Report

Data Filename	WBG-SIRB-CONH2.d	**Sample Name**	WBG-SIRB-CONH2
Sample Type	Sample	**Position**	P1-B8
Instrument Name	Instrument 1	**User Name**	
Acq Method	TEST-POS-01-WL.m	**Acquired Time**	4/8/2014 11:13:16 AM
IRM Calibration Status	Success	**DA Method**	1.m
Comment			



User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
120	0	Esi



Peak List

m/z	z	Abund	Formula	Ion
84.9597		20573		
121.0509	1	121494		
125.9857		40802		
158.0026		14769		
264.637	2	103477		
265.1382	2	41750		
271.187		32286		
528.2676	1	87712	C31 H38 N3 O3 Si	(M+H)+
529.2693	1	35167	C31 H38 N3 O3 Si	(M+H)+
922.0098		18389		

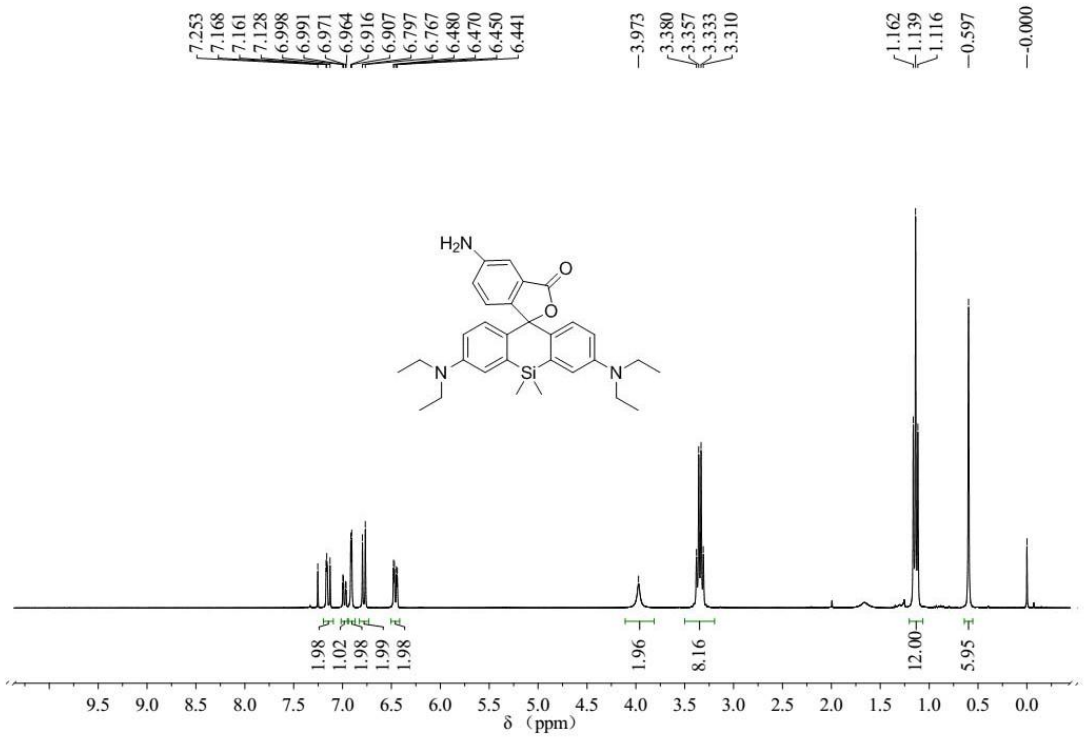
Formula Calculator Element Limits

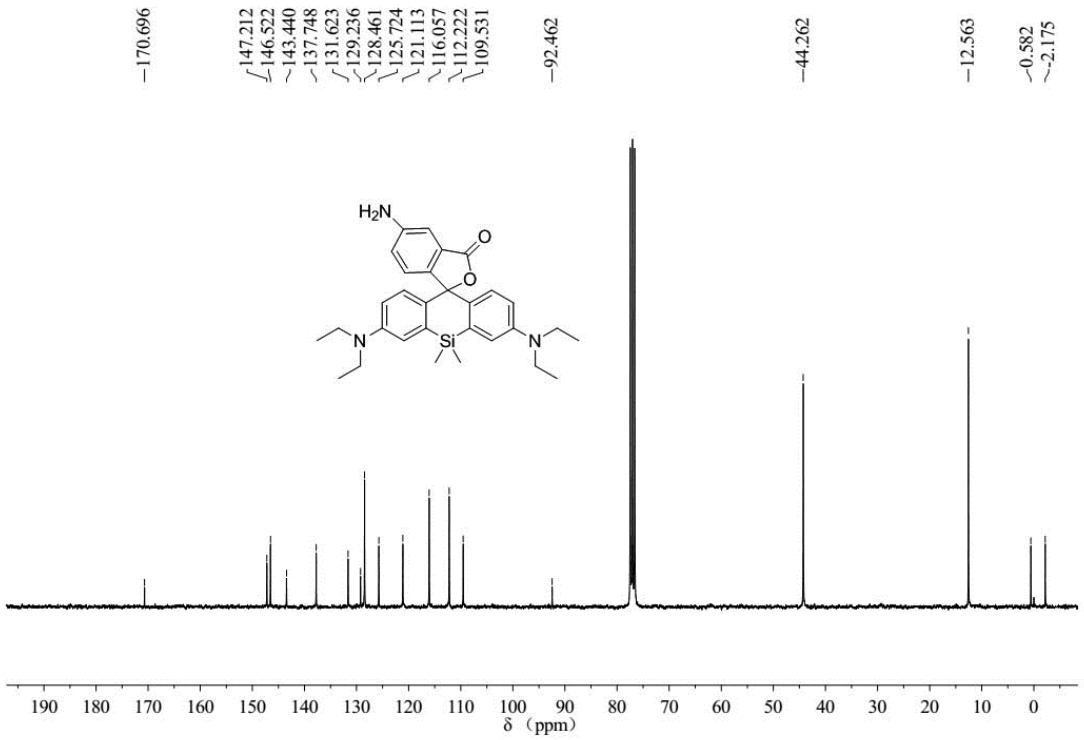
Element	Min	Max
C	3	200
H	0	300
O	1	3
N	1	3
Si	1	2

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C31 H37 N3 O3 Si	TRUE	527.2603	527.2604	0.29	C31 H38 N3 O3 Si	98.99

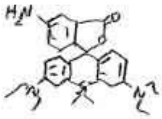
--- End Of Report ---


7.253
7.168
7.161
7.128
6.998
6.991
6.971
6.964
6.916
6.907
6.797
6.767
6.480
6.470
6.450
6.441
3.973
3.380
3.357
3.333
3.310
1.162
1.139
1.116
0.597
0.000
H2N
O
O
N
Si
N
1.98
1.02
1.98
1.99
1.98
1.96
8.16
12.00
5.95
δ (ppm)


170.696
147.212
146.522
143.440
137.748
131.623
129.236
128.461
125.724
121.113
116.057
112.222
109.531
92.462
44.262
12.563
0.582
-2.175
H2N
O
O
N
Si
N
δ (ppm)

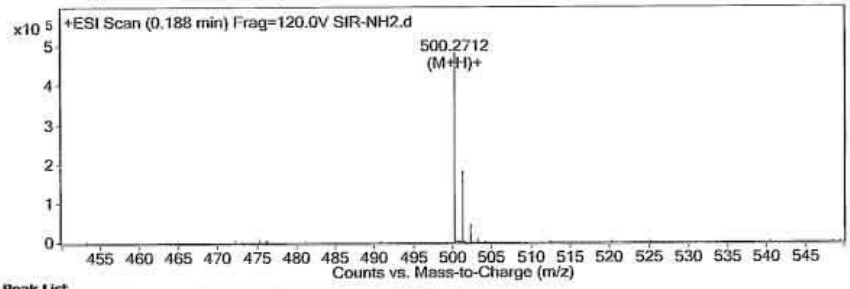
Qualitative Analysis Report

Data Filename	SIR-NH2.d	**Sample Name**	SIR-NH2
Sample Type	Sample	**Position**	P1-B6
Instrument Name	Instrument 1	**User Name**	
Acq Method	TEST-POS-01-WL.m	**Acquired Time**	3/12/2014 5:07:06 PM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			



User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
120	0	Esi



Peak List

m/z	z	Abund	Formula	Ion
121.0509		154346		
250.6402	2	272646		
251.1416	2	94769		
282.279		69039		
338.34	1	1181564		
339.3454	1	261759		
500.2712	1	497652	C30 H38 N3 O2 Si	(M+H)+
501.2755	1	183907	C30 H38 N3 O2 Si	(M+H)+

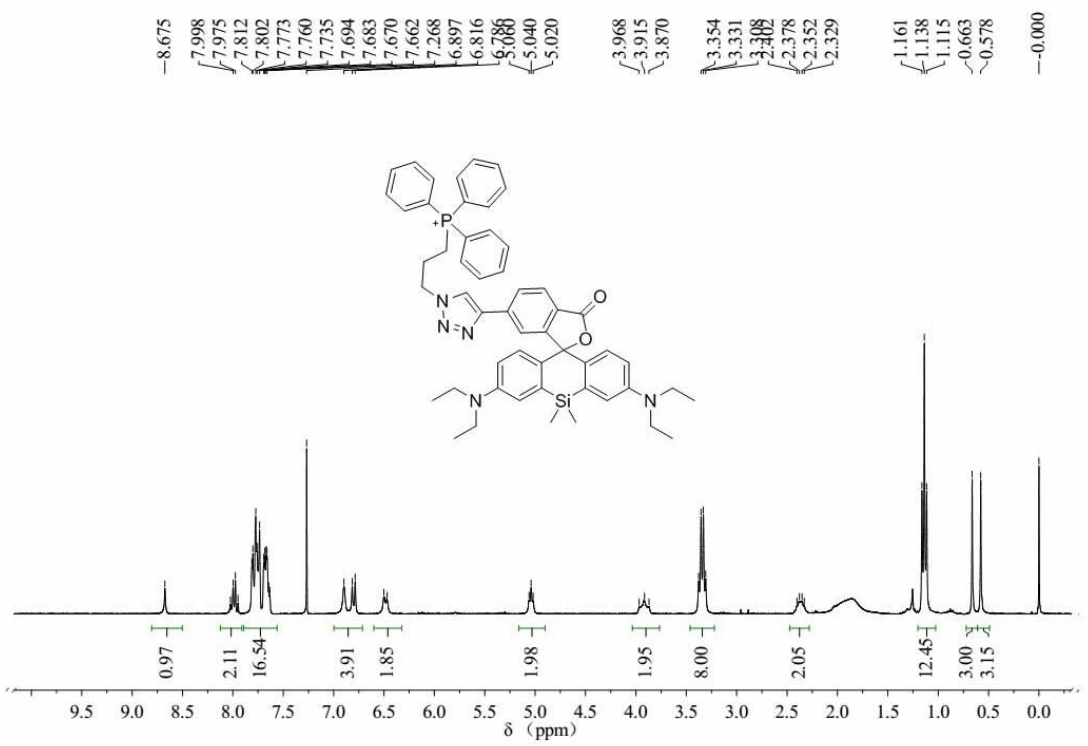
Formula Calculator Element Limits

Element	Min	Max
C	0	60
H	0	120
O	0	30
Cl	0	5
N	0	5
Si	0	1

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C30 H37 N3 O2 Si	TRUE	499.264	499.2655	2.97	C30 H38 N3 O2 Si	92.64

--- End Of Report ---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7.998
7.975
7.812
7.802
7.773
7.760
7.735
7.694
7.683
7.670
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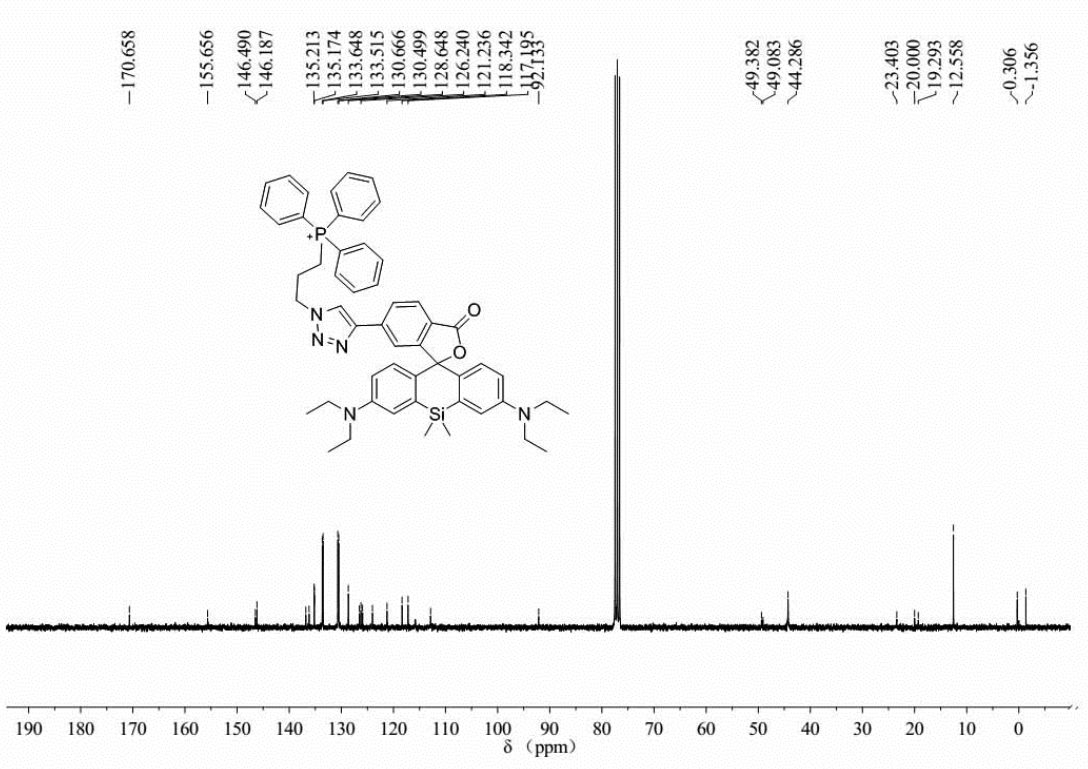
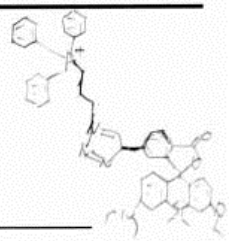
7.268
6.897
6.816
5.040
5.020
3.968
3.915
3.870
3.354
3.331
2.378
2.352
2.329
1.161
1.138
1.115
0.663
0.578
0.000
0.97
2.11
16.54
3.91
1.85
1.98
1.95
8.00
2.05
12.45
3.00
3.15
δ (ppm)


170.658
155.656
146.490
146.187
135.213
135.174
133.648
133.515
130.666
130.499
128.648
126.240
121.236
118.342
117.195
92.133
49.382
49.083
44.286
23.403
20.000
19.293
12.558
0.306
-1.356
δ (ppm)

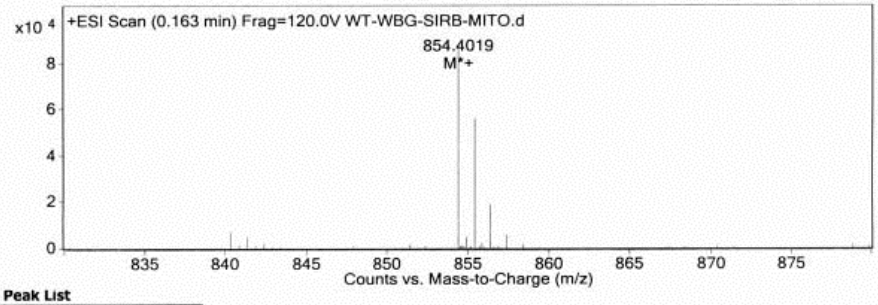
Qualitative Analysis Report

Data Filename	WT-WBG-SIRB-MITO.d	**Sample Name**	WT-WBG-SIRB-MITO
Sample Type	Sample	**Position**	P1-E3
Instrument Name	Instrument 1	**User Name**	
Acq Method	TEST-POS-01-WL.m	**Acquired Time**	6/12/2014 9:52:23 AM
IRM Calibration Status	Success	**DA Method**	ERROR11.m
Comment			



User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
120	0	Esi



Peak List

m/z	z	Abund
274.2743	1	236824
282.2788	1	365886
285.472		346339
285.8077		180527
318.3002		116111
326.1486	2	203641
413.6897	2	166960
427.7034	2	492645
428.2063	2	317553
651.2888	1	189232

Formula Calculator Element Limits

Element	Min	Max
C	0	100
H	0	100
O	0	5
N	0	5
P	0	1
Si	0	1

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C53 H57 N5 O2 P Si	TRUE	854.4024	854.4019	-0.51	C53 H57 N5 O2 P Si	98.77

--- End Of Report ---

X-Ray Crystallography.

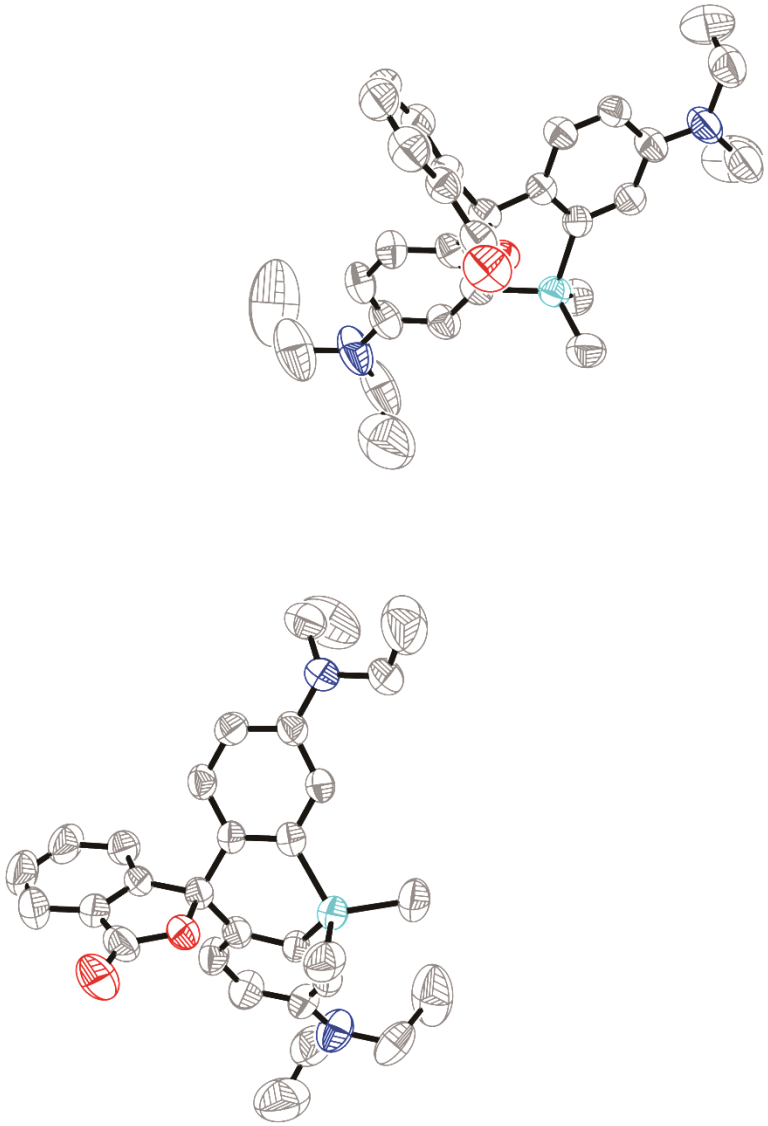


Fig. S1 Single-crystal structure of **SiRB**.

Table S2 Crystal data and structure refinement for a30614a.

Identification code	a30614a
Empirical formula	$C_{30}H_{36}N_2O_2Si$
Formula weight	3877.58
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pna2(1)
Unit cell dimensions	a = 22.481(5) Å α = 90°
	b = 12.174(2) Å β = 90°
	c = 20.069(4) Å γ = 90°
Volume	5492.6(19) $Å^3$
Z, Calculated density	1, 1.172 Mg/m^3
Absorption coefficient	0.114 mm^{-1}
F(000)	2080
Crystal size	0.40 x 0.28 x 0.14 mm
Theta range for data collection	1.81 to 25.02 °
Limiting indices	-20<=h<=26, -14<=k<=14, -23<=l<=23
Reflections collected / unique	21808 / 9615 [$R_{(int)}$ = 0.0526]
Completeness to θ = 25.02	99.8 %
Absorption correction	none
Max. and min. transmission	0.9842 and 0.9559
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9615 / 1 / 644
Goodness-of-fit on F^2	0.849
Final R indices [I>2sigma(I)]	R_1 = 0.0456, wR_2 = 0.0837
R indices (all data)	R_1 = 0.0896, wR_2 = 0.0938
Largest diff. peak and hole	0.269 and -0.206 e. $Å^{-3}$

Absorption and Fluorescence.

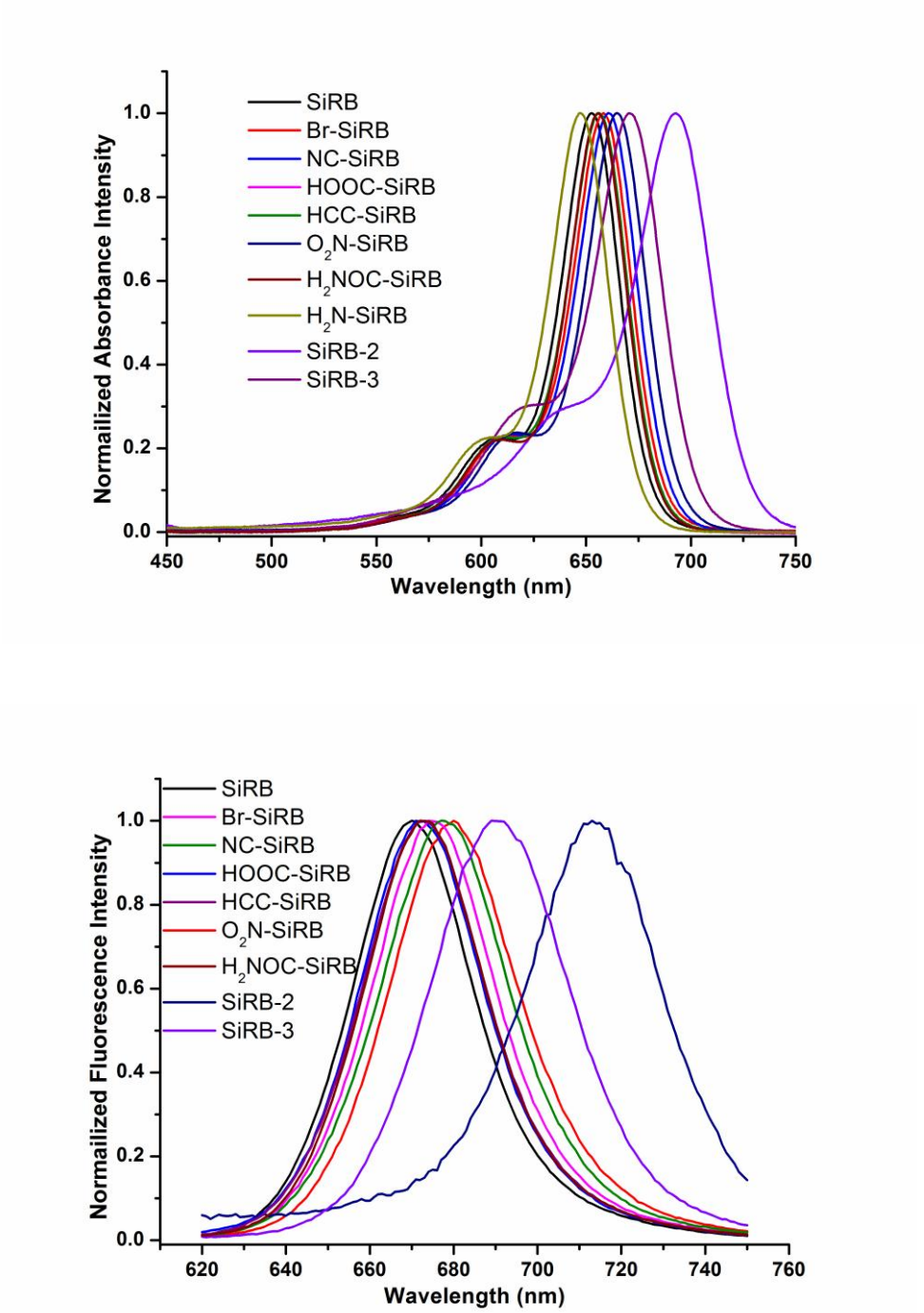


Fig. S2 Absorbance (top) and fluorescence (bottom) spectra of **SiRB**s. Spectra were obtained in EtOH solution containing 0.1 mM HCl.

Tables S3. Spectral properties of **SiRB**s in EtOH solution containing 0.1 mM HCl.

SiRBs	λ_{maxabs} (nm)	ε_{max} ($cm^{-1}M^{-1}$)	λ_{fluor} (nm)	Φ_f (%)
SiRB	652	160000	670	17
SiRB-3	670	120000	689	8
SiRB-2	693	110000	713	2.3
Br-SiRB	658	140000	674	14
NO_2-SiRB	664	160000	680	9
CN-SiRB	661	140000	677	12
COOH-SiRB	656	92000	671	16
HC≡C-SiRB	656	140000	672	16
NH_2-SiRB	647	140000	667	0.4
NH_2OC-SiRB	656	160000	672	15

Fluorescence Imaging

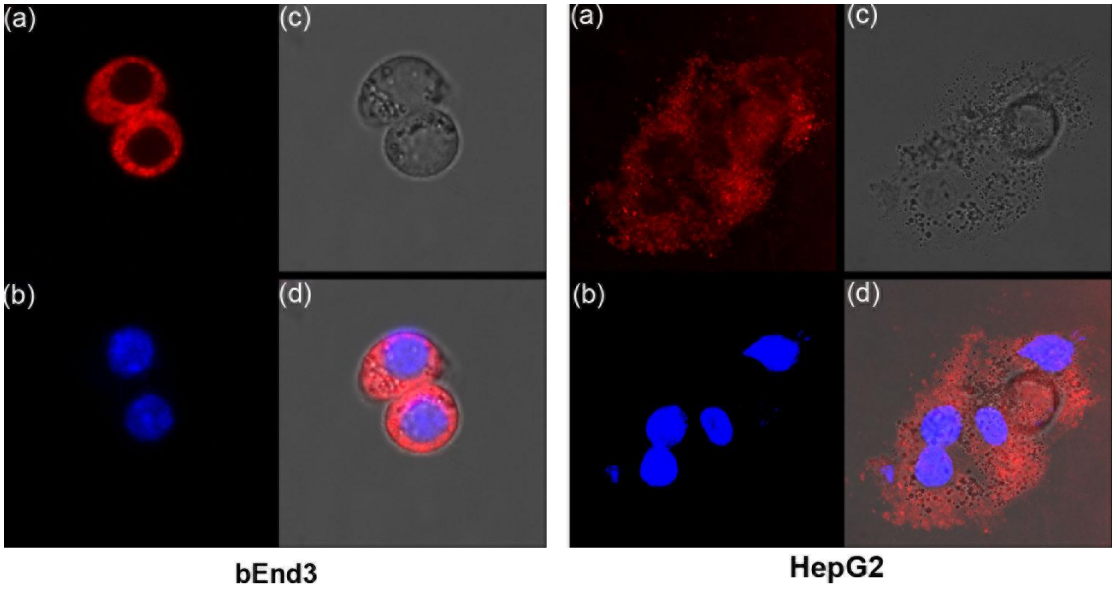


Fig. S3 Fluorescence images of bEnd3 (left) and HepG2 (right) cells co-stained with 10.0 μM **SiRB** and DAPI. (a) Fluorescence microscopic images from **SiRB** (b) Fluorescence microscopic images from DAPI. (c) Microscopic images. (d) Merged fluorescence microscopic images.

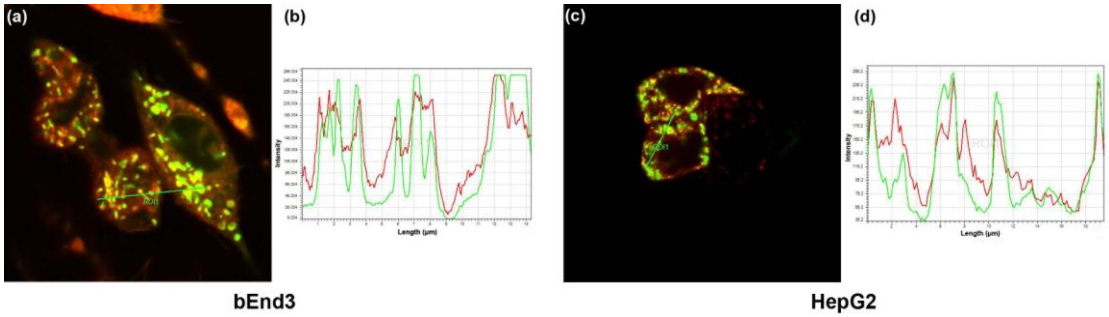


Fig. S4 Fluorescence images of bEnd3 (left) and HepG2 (right) cells co-stained with 10.0 μM **Mito-SiRB** and 50 nM Rhodamine 123. (a) and (c) Merged fluorescence microscopic images. (b) and (d) Intensity profiles of region of interest cross the cells.

References

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S3. D. Frahm, M. Fischer, F. Hoffmann and M. Fröba, *Inorg. Chem.*, 2011, **50**, 11055.

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