Supporting Information

Combinatorial Synthesis of Triphenylmethine Library and Their Application in the Development of Surface Enhanced Raman Scattering (SERS) Probes

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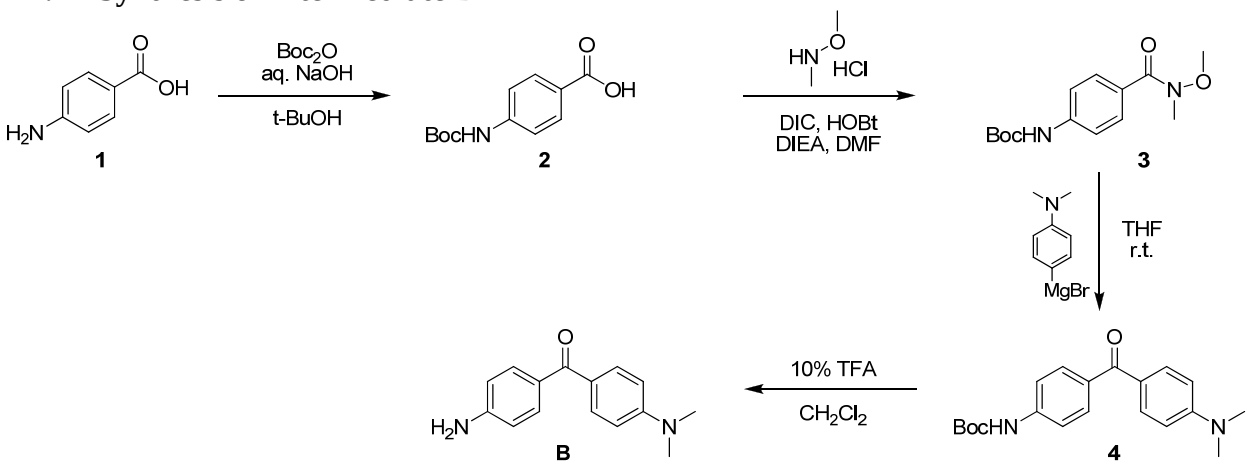
1. Synthesis of Intermediate S1 (B-D)

Synthetic Material and Method

Unless otherwise noted, all the chemicals and solvents were obtained from commercial suppliers (Acros and Aldrich) and used without further purification. 2-Chlorotrityl alcohol resin (1.37 mmol/g) was purchased from BeadTech Inc., Korea. All the Grignard reagents were purchased from Aldrich or Rieke Metals, Inc. All library compounds were identified by LC-MS from Agilent Technology, using a C18 column (20 × 4.0 mm), with 4 minutes elution using a gradient solution of CH_3CN-H_2O (containing 0.1% acetic acid), with UV detector and an electrospray ionization source. NMR spectra were recorded on a Bruker DPX 300 (^{1}H NMR at 300 MHz; ^{13}C NMR at 75 MHz) spectrometer. High-resolution mass spectra were determined on a Finnigem MAT95XL-T instrument. UV-Vis were recorded on HITACHI U-2900 spectrometer. The standard extraction work-up procedure consisted of pouring the reaction mixture into a excess amount of water, extracting with the organic solvent indicated, washing the combined extracts successively with water and brine, drying the extract over anhydrous Na_2SO_4 or $MgSO_4$ and evaporating the solvent.

1-1. Synthesis of Intermediate B



Synthesis of 4-(tert-butoxycarbonylamino)-benzoic acid (**2**)

To a solution of 4-aminobenzoic acid (3.0 g, 21.9 mmol) in t-BuOH (20 mL) and H_2O (20 mL) was added Boc_2O (5.73 g, 26.3 mmol) and NaOH (0.97 g, 24.2 mmol). The reaction mixture was stirred at r.t, for 12 h. The reaction mixture was diluted water and washed with CH_2Cl_2. The aqueous layer was adjusted pH ~ 2 with 2N HCl and extracted with ethyl acetate .The organic layer was dried over Na_2SO_4, and the filtrate was concentrated and purified by silica column chromatography (ethyl acetate / hexane = 1 / 1) (4.64 g, 89%). ^{1}H-NMR (CD_3OD) 7.79 (d, J = 8.7, 2H), 7.48 (d, J = 8.7, 2H), 1.49 (s, 9H). ESI-MS m/z calcd for $C_{12}H_{15}NO_4$: 237.2518 ; found : 235.9861 [M - 1].

Synthesis of tert-butyl 4-[N-methyl-N-methoxyamido]-phenylcarbamate (**3**)

To a solution of **2** (2.0 g, 8.4 mmol) in DMF (15 mL) was added HOBt (2.83 g, 21.1 mmol) and DIC (3.0 mL, 19.4 mmol). After stirring for 15 min, *N,O*-dimethylhydroxylamine hydrochloride (1.64 g, 16.8 mmol) dissolved in DMF (10 mL) and DIPEA (8.2 mL, 46.4 mmol) were added to the solution, then the mixture was stirred at r.t. for 12 h. The reaction mixture was diluted with ethyl acetate and washed with 1N-HCl, $NaHCO_3$, and NaCl aqueous solution, respectively. The organic layer was dried over Na_2SO_4, and the filtrate was concentrated and purified by silica column chromatography (ethyl acetate / hexane = 1 / 1) (1.5 g, 64%). ^{1}H-NMR ($CDCl_3$) 7.67 (d, J = 8.4, 2H), 7.40 (d, J = 8.4, 2H), 3.53 (s, 3H), 3.33 (s, 3H), 1.50 (s, 9H) ppm; ESI-MS m/z calcd for $C_{15}H_{20}N_2O_4$: 280.3196; found 281.1251 [M+1]

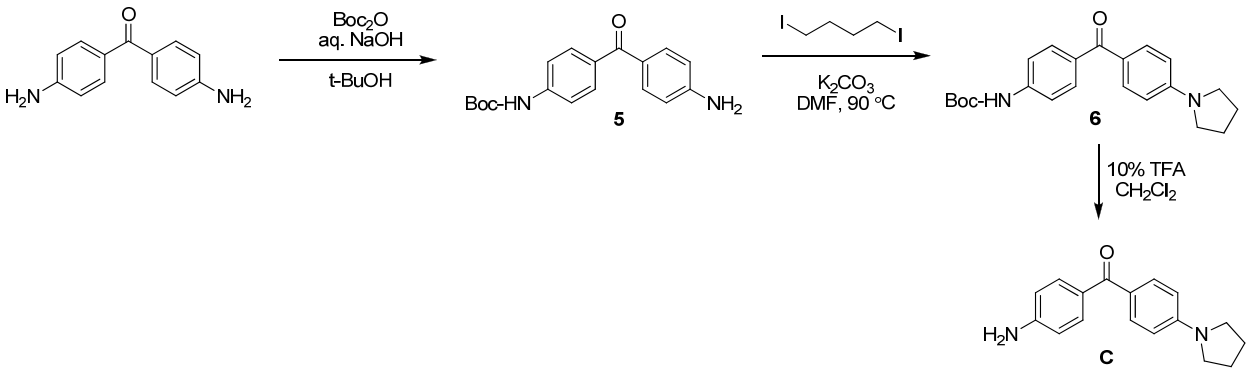
Synthesis of tert-butyl 4-[4'-(dimethylamino)benzoyl]-phenylcarbamate (**4**)

To a solution of **3** (0.56 g, 2.0 mmol) in THF (10 mL) was added (4-(dimethylamino)phenyl) magnesium bromide (16 mL, 8.0 mmol) at 0 ˚C and stirred at r.t. for 12 h. The reaction mixture was diluted with ethyl acetate and washed with 1N-HCl, $NaHCO_3$, and NaCl aqueous solution, respectively. The organic layer was dried over Na_2SO_4, and the filtrate was concentrated and purified by silica column chromatography (ethyl acetate / hexane = 1 / 2) (0.55 g, 81%). ^{1}H-NMR ($CDCl_3$) 7.77 (d, 9.0, 2H), 7.72 (d, J = 8.7, 2H), 7.45 (d, J = 8.7, 2H), 6.67 (d, J = 9.0, 2H), 3.06 (s, 6H), 1.53 (s, 9H) ppm; ESI-MS m/z calcd for $C_{20}H_{24}N_2O_3$: 340.4162; found 341.2371 [M+1].

Synthesis of 4-aminophenyl-[4'-(dimethylamino)phenyl]-methanone (**B**)

The compound **4** (51 mg, 0.15 mmol) was stirred in 10% TFA in dichloromethane (10 mL) at r.t. for 1 h and extracted with ethyl acetate with aqueous $NaHCO_3$. The organic layer was dried over Na_2SO_4, and the filtrate was concentrated to give intermediate **B** (34 mg, 95%). ^{1}H-NMR ($CDCl_3$) 7.76 (d, J = 8.7, 2H), 7.66 (d, J = 8.4, 2H), 6.68 (d, J = 8.7, 2H), 6.67 (d, J = 8.4, 2H), 4.04 (br. s, 1H), 3.06 (s, 6H) ppm; ESI-MS m/z calcd for $C_{15}H_{16}N_2O$: 240. 3004; found 241.2071 [M+1].

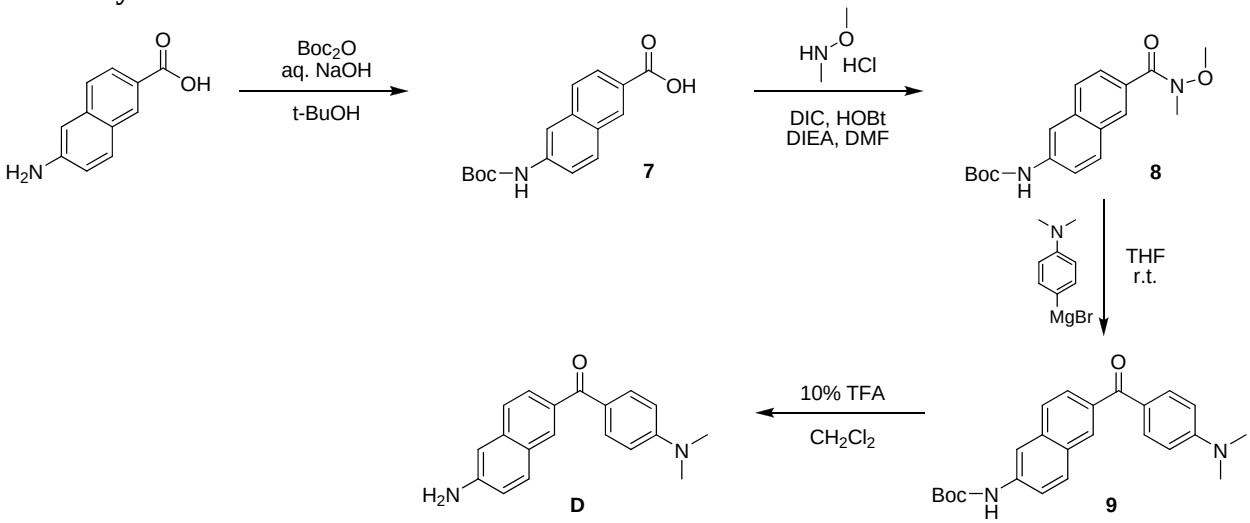
1-2. Synthesis of Intermediate C



4-aminophenyl-[4-(pyrrolidin-1-yl)phenyl]-methanone (**C**)

To a solution of 4,4'-diaminobenzophenone (1.0 g, 4.7 mmol) in t-BuOH (10 mL) and H_2O (10 mL) was added Boc_2O (1.2 g, 5.6 mmol). The reaction mixture was stirred at r.t. for 12 h. The reaction mixture was diluted water and washed with CH_2Cl_2. The aqueous layer was adjusted pH ~ 2 with 2N HCl and extracted with ethyl acetate .The organic layer was dried over Na_2SO_4, and the filtrate was reacted with 1,4-diiodobutane and K_2CO_3 in DMF at 90 ˚C for 12 h. The reaction mixture was diluted with ethyl acetate and washed with 1N-HCl, $NaHCO_3$, and NaCl aqueous solution, respectively. The organic layer was dried over Na_2SO_4, and the filtrate was concentrated. The compound **6** was subsequently stirred in 10% TFA in dichloromethane (10 mL) at r.t. for 1 h and extracted with ethyl acetate with aqueous $NaHCO_3$. The organic layer was dried over Na_2SO_4, and the filtrate was concentrated to give intermediate **C** (overall 250 mg, 20%). ^{1}H-NMR ($CDCl_3$) 7.67 (d, J = 8.7, 2H), 7.56 (d, J = 8.4, 2H), 6.57 (d, J = 8.4, 2H), 6.44 (d, J = 8.7, 2H), 3.26 (m, 4H), 1.93 (m, 4H) ppm; ^{13}C-NMR ($CDCl_3$): 25.54, 47.45, 110.48, 117.20, 131.42, 132.67, 141.23, 142.03, 150.66, 152.22, 160.94 ppm; HRMS (ESI): m/z calcd for $C_{17}H_{18}N_2O$: 266.3376; found 267.3781 [M+1].

1-3. Synthesis of Intermediate D



Synthesis of 6-(tert-butoxycarbonylamino)-2-naphthoic acid (**7**)

To a solution of 6-amino-2-naphthoic acid (200 mg, 1.07 mmol) in t-BuOH (6 mL) and H_2O (6 mL) was added Boc_2O (280 mg, 1.28 mmol) and NaOH (40 mg, 1.0 mmol). The reaction mixture was stirred at r.t. for 12 h. The reaction mixture was diluted water and washed with CH_2Cl_2. The aqueous layer was adjusted pH ~ 2 with 2N HCl and extracted with ethyl acetate .The organic layer was dried over Na_2SO_4, and the filtrate was concentrated and purified by silica column chromatography (ethyl acetate / hexane = 1 / 1) (300 mg, 98%). ^{1}H-NMR (CD_3OD) 8.48 (s, 1H), 8.05 (s, 1H), 7.95 (d, J = 8.4, 1H), 7.86 (d, J = 8.7, 1H), 7.75 (d, J = 8.7, 1H), 7.51 (d, J = 8.8, 1H) 1.53 (s, 9H) ppm; ESI-MS m/z calcd for $C_{16}H_{17}N_2O$: 287.3105; found 288.8273 [M+1].

Synthesis of tert-butyl 6-[N-methyl-N-methoxyamido)-naphthalen-2-ylcarbamate (**8**)

To a solution of **7** (300 mg, 1.04 mmol) in DMF (5 mL) was added HOBt (351 mg, 2.6 mmol) and DIC (0.37 mL, 2.4 mmol). After stirring for 15 min, *N,O*-dimethylhydroxylamine hydrochloride (203 mg, 2.09 mmol) dissolved in DMF (5 mL) and DIPEA (1.1 mL, 5.74 mmol) were added to the solution, then the mixture was stirred at r.t. for 12 h. The reaction mixture was diluted with ethyl acetate and washed with 1N-HCl, $NaHCO_3$, and NaCl aqueous solution, respectively. The organic layer was dried over Na_2SO_4, and the filtrate was concentrated and purified by silica column chromatography (ethyl acetate / hexane = 1 / 1) (300 mg, 87%). ^{1}H-NMR ($CDCl_3$) 8.14 (s, 1H), 8.05 (s, 1H), 7.76 (m, 2H), 7.37 (d, J = 8.4, 1H), 6.87 (s, 1H), 3.56 (s, 3H), 3.40 (s, 3H), 1.55 (s, 9H) ppm; ESI-MS m/z calcd for $C_{18}H_{22}N_2O_4$: 330.3783; found 331.1728 [M+1].

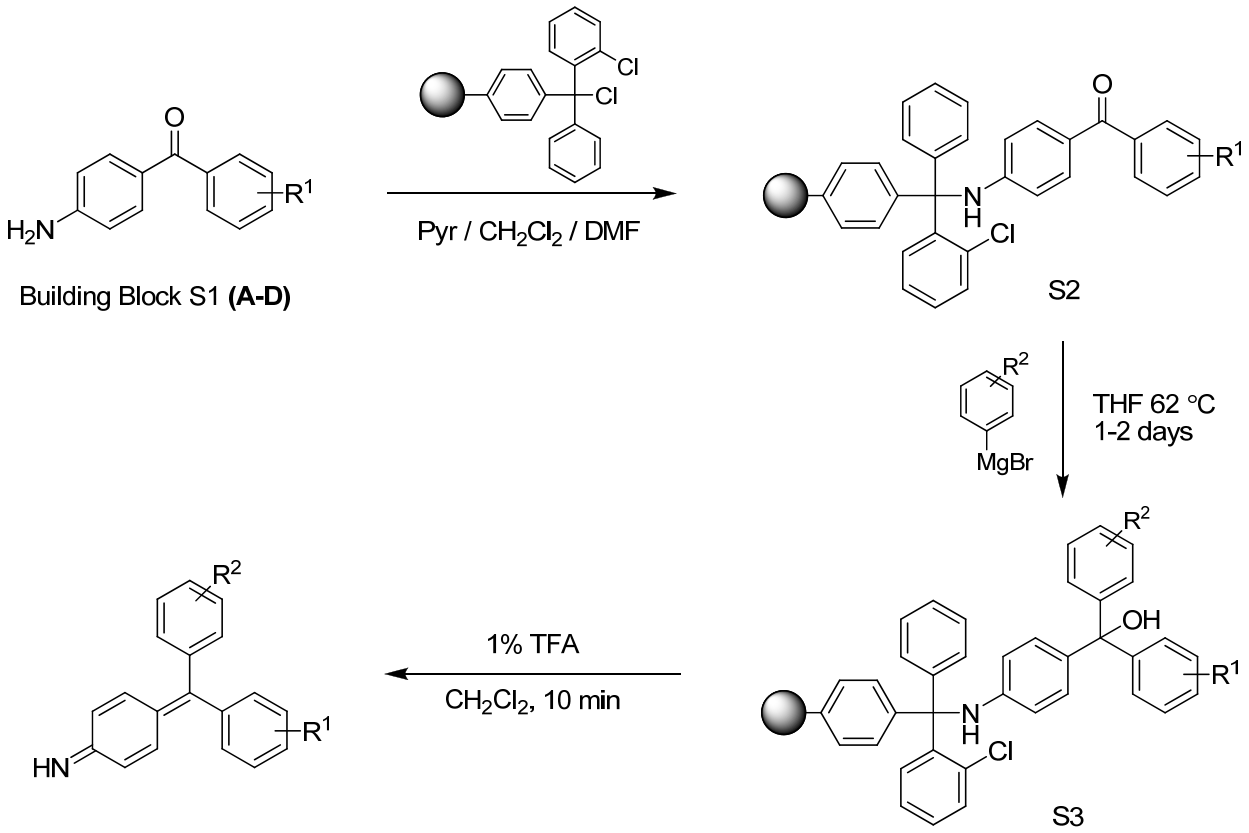
Synthesis of tert-butyl 6-[4-(dimethylamino)benzoyl]-naphthalen-2-ylcarbamate (**9**)

To a solution of **8** (280 mg, 0.85 mmol) in THF (8 mL) was added (4-(dimethylamino)phenyl) magnesium bromide (6.8 mL, 3.4 mmol) at 0 ˚C and stirred for 12 h. The reaction mixture was diluted with ethyl acetate and washed with 1N-HCl, $NaHCO_3$, and NaCl aqueous solution, respectively. The organic layer was dried over Na_2SO_4, and the filtrate was concentrated and purified by silica column chromatography (ethyl acetate / hexane = 1 / 2) (70 mg, 21%). ^{1}H-NMR ($CDCl_3$) 8.14 (s, 1H), 8.07 (s, 1H), 7.83 (m, 3H), 7.39 (d, J = 6.0, 1H), 6.83 (s, 1H), 6.70 (d, J = 9.0, 2H) 3.08 (s, 6H), 1.56 (s, 9H) ppm; ESI-MS m/z calcd for $C_{24}H_{26}N_2O_3$: 390.4748; found 391.6231 [M+1].

Synthesis of 6-aminonaphthalen-2-yl-[4-(dimethylamino)phenyl]-methanone (**D**)

The compound **9** (70 mg, 0.18 mmol) was stirred in 10% TFA in dichloromethane (10 mL) at r.t. for 1 h and extracted with ethyl acetate with aqueous $NaHCO_3$. The organic layer was dried over Na_2SO_4, and the filtrate was concentrated to give intermediate **D** (50 mg, 96%). ^{1}H-NMR (CD_3OD) 8.02 (s, 1H), 7.59-7.78 (m, 5H), 7.00-7.07 (m, 2H), 6.80 (m, 3H), 3.09 (s, 6H) ppm; ESI-MS m/z calcd for $C_{19}H_{18}N_2O$: 290.3590; found 291.1821 [M+1].

2. Library Synthesis on Solid Support



Preparation of 2-chlorotrityl chloride from 2-chlorotrityl alcohol resin:
2-Chlorotrityl alcohol resin (500 mg 1.37 mmol/g) was suspended in dichloromethane (5 mL) for 10 min. Thionyl chloride (150 μL, 2.06 mmol) was added and the resin solution was shaken for 2 hours at room temperature. The resin was filtered and washed with dichloromethane and acetonitrile then dried.

General procedure for loading A-D to solid resin:
Each compound (**A-D**) (0.411 mmol) was dissolved in dichloromethane (5 mL) with 20 mL vial, if not soluble, DMF was added (1-2 mL). The solution was added to 2-chlorotrityl chloride resin (0.274 mmol) suspended in dichloromethane (1 mL), and pyridine (4.1 mmol) was added. After stirring for 4 hrs, the resin was filtered through 3 mL cartridge and washed with DMF (X5), methanol (X10), and dichloromethane (X10), and dried.

General procedure of Grignard reaction and cleavage from the resin.
For each reaction, a resin (10 mg) was suspended in freshly distilled THF (0.1 mL) in a 4 mL glass vial. Each Grignard reagent (0.5 M in THF) (1.5 mL) was added and capped tightly with TFE lined cap, and heated at 62 ˚C on standard heat-block for 1-2 days. The resin was filtered through 1 mL cartridge and washed with dichloromethane (×5), DMF (×5), methanol (×5), and dichloromethane (×5). The resin was dried and treated with 1% TFA in dichloromethane (1.5 mL) for 15 min. The solution was drained to the 4 mL vial, and dried using Speed Vacuum.

3. Raman Microscope

The experiments were carried out using Renishaw InVia Raman (UK) microscope system having an excitation laser at 633 nm. The laser intensity at the sample after passing through the objective lens was about 6.2 mW. System is connected with Leica microscope and laser light was coupled through a 50 X objective lens, which was used to excite the sample and also to collect the return Raman signal. The system uses a Peltier cooled CCD detector to collect all the Raman signals.

The WiRE 3.0 software package (provided with the Renishaw system) was employed for instrument control and data acquisition. Stoke shifted Raman spectra were collected in the wave number range of 400–2000 cm^{-1} with a spectral resolution of about 1 cm^{-1}. The exposure time of 10 s was chosen for each measurement. Prior to measurement, the instrument was calibrated with the Raman signal from a silicon standard centered at 520 cm^{-1}.

4. SERS Measurement

2 μL of the dye solution (10 μM stock solution deionized water) was mixed with 18 μL of Au colloid (2.6 x 10^{10} particles/mL, BBInternational, UK) in water to get an 1 μM effective concentration of the dye. 20 μl of the dye-Au colloid mixture solution is pipette out to a clean glass slide and covered with a cover slip and kept under microscope objective lens for Raman measurement. The average intensities were obtained by three individual measurements of each sample..

5. Thiolated PEG encapsulation

A freshly prepared reporter solutions with various concentrations (viz., 5, 10, 20, 30 μM) was rapidly mixed with gold colloid at a ratio 1:9 (reporter / colloid) volume ratio. This molar ratio of reporter molecules was optimized by maximum SERS intensities and minimum colloidal aggregation. Finally we optimized at 10 μM of dye concentration. After 5 min incubation, thiolated PEG (PEG-SH, M.W $_{PEG}$: 5000 dalton, RAPP Polymere GmbH) solution (100 μM) was added around 10 to 20 fold excess in order to get maximum surface coverage. After overnight incubation, the excess PEG-SH was removed by three round of centrifugation (8000 rpm for 3 mints) and re-suspended with water. (Ref. no. 4 in the manuscript)

6. SERS intensity, Absorbance, Purity, and Mass data Table for the Library Compounds

code	SERS Intensity (counts)[a]	Abs (nm)[b]	Purity[c]	Mass (calc)[d]	Mass (found)[e]
A-2	1764	572	90%	316.2	316.2
A-3	0	550	97%	303.2	303.2
A-7	3894	580	97%	323.2	323.3
A-8	6549	562	93%	319.1	319.3
A-9	0	570	83%	349.2	349.4
A-11	126863	578	96%	373.2	373.3
A-13	0	566	95%	353.2	353.1
A-15	0	572	95%	273.1	273.2

A-16	0	570	97%	301.2	301.2
A-17	0	586	94%	303.2	303.2
A-18	0	562	92%	317.1	317.1
A-19	0	576	86%	291.1	291.2
A-20	0	570	88%	307.1	307.1
A-23	0	562	95%	287.1	287.2
A-25	0	560	97%	331.2	331.2
A-27	0	574	92%	305.1	305.1
A-28	0	574	90%	279.1	279.1
A-29	1878	566	96%	315.2	315.2
B-1	0	596	93%	319.2	319.4
B-2	129997	586	92%	344.2	344.4
B-3	2626	586	98%	331.2	331.3
B-4	104281	586	83%	393.2	393.4
B-7	157517	600	95%	351.2	351.4
B-8	99667	600	96%	347.2	347.3
B-9	25196	600	91%	377.2	377.3
B-11	97303	602	99%	401.2	401.4
B-13	0	600	96%	381.2	381.1
B-15	0	596	93%	301.2	301.2
B-16	48933	588	94%	329.2	329.2
B-17	0	600	93%	331.2	331.2
B-18	11169	586	91%	345.2	345.2
B-23	99523	586	96%	315.2	315.2
B-25	0	588	93%	359.2	359.2
C-1	27572	596	91%	345.2	345.2
C-2	32254	596	91%	370.2	370.2
C-3	139373	584	90%	357.2	357.2
C-4	55437	598	94%	419.2	419.2
C-7	126862	598	90%	377.2	377.2
C-8	8805	602	94%	373.2	373.2
C-9	137243	600	91%	403.2	403.2
C-13	69210	596	95%	407.2	407.2
C-16	89703	596	93%	355.2	355.2
C-17	29557	602	94%	357.2	357.2
C-19	3048	602	88%	345.2	345.2
C-20	92382	602	87%	361.2	361.1
C-23	52236	586	86%	341.2	341.2
C-25	0	596	95%	385.2	385.2
C-27	3676	596	91%	359.2	359.2
C-28	1529	602	95%	333.1	333.2
C-29	68516	596	97%	369.2	369.2
D-2	92117	614	100%	394.2	394.2
D-9	9113	608	97%	427.2	427.2
CV	65977	590			

(a) SERS spectra were obtained from excitation at 633 nm with laser power of 6.2 mW. (b) All absorption data was obtained by SpectraMax Plus384 absorbance plate reader in 50 μM. (c) Purity data was calculated on the basis of the integration in the LCMS trace at 550 nm. (d) Mass was calculated as (M^+), and (e) found in ESI-MS *m/e*.

7. ^{1}H-NMR, ^{13}C-NMR, HRMS (ESI), and UV-Vis data of re-synthesized TM Compounds

B2: ^{1}H-NMR ($CDCl_3$) 10.74 (s, 2H, NH_2^+), 8.8.31 (d, J = 8.7 Hz, 4H), 7.09 (d, J = 8.7 Hz, 4H), 6.68 (d, J = 8.7 Hz, 4H), 2.96 (s, 12H); ^{13}C-NMR ($CDCl_3$): 31.18 [$N(CH_3)_2$], 31.81[$N(CH_3)_2$], 109.10, 112.12, 118.79, 125.05, 128.4, 130.71, 135.10, 138.91, 145.47, 150.89, 54.41, 165.00, 176.85 ppm; HRMS (ESI): m/z calcd for $C_{23}H_{26}N_3$: 344.2121; found : 345.2133 [M + H]$^+$; UV (H_2O): λ_{max} (ε): 614 nm (48000 cm^{-1} M^{-1});

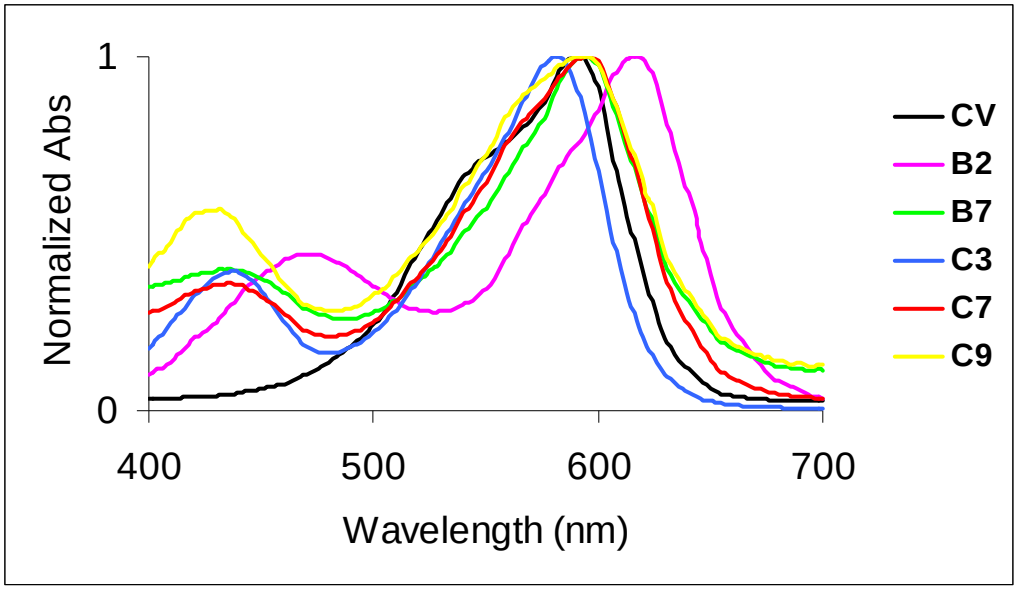
B7: ^{1}H-NMR ($CDCl_3$) 9.07 (s, 2H, NH_2^+), 7.95-7.87 (m, 4H), 7.68-7.59 (m, 3H), 7.26 (d, J = 9 Hz, 2H), 6.76 (d, J = 9 Hz, 2H), 3.21 (s, 6H); ^{13}C-NMR ($CDCl_3$): 38.54 [$N(CH_3)_2$], 110.29, 116.26, 125.10, 125.51, 125.96, 126.15, 127.12, 127.44, 128.29, 130.53, 133.27, 134.26, 135.12, 137.35, 140.53, 153.16, 159.61,174.12 ppm; HRMS (ESI): m/z calcd for $C_{25}H_{23}N_2$: 351.4630 ; found : 352.1895 [M + H]$^+$; UV (H_2O): λ_{max} (ε): 594 nm (38000 cm^{-1} M^{-1});

C3: ^{1}H-NMR ($CDCl_3$) 8.14 (s, 2H, NH_2^+), 7.18-7.25 (m, 6H, aromatic), 7.09 (d, aromatic 2H, J = 8.4 Hz), 6.97 (d, 2H, J = 8.7 Hz, aromatic), 6.62 (d, 2H, J = 9.0 Hz, aromatic), 3.89 (s, 3H), 3.49 (m, 4H), 2.08 (m, 4H); ^{13}C-NMR ($CDCl_3$): 25.85, 48.30, 55.79, 113.09, 114.15, 117.18, 126.47, 127.30, 131.90, 137.58, 139.66, 142.04, 153.30, 160.28, 164.27, 176.35 ppm; HRMS (ESI): m/z calcd for $C_{24}H_{25}N_2O$: 357.1961 ; found : 358.2014 [M + H]$^+$; UV (H_2O): λ_{max} (ε): 580 nm (41600 cm^{-1} M^{-1});

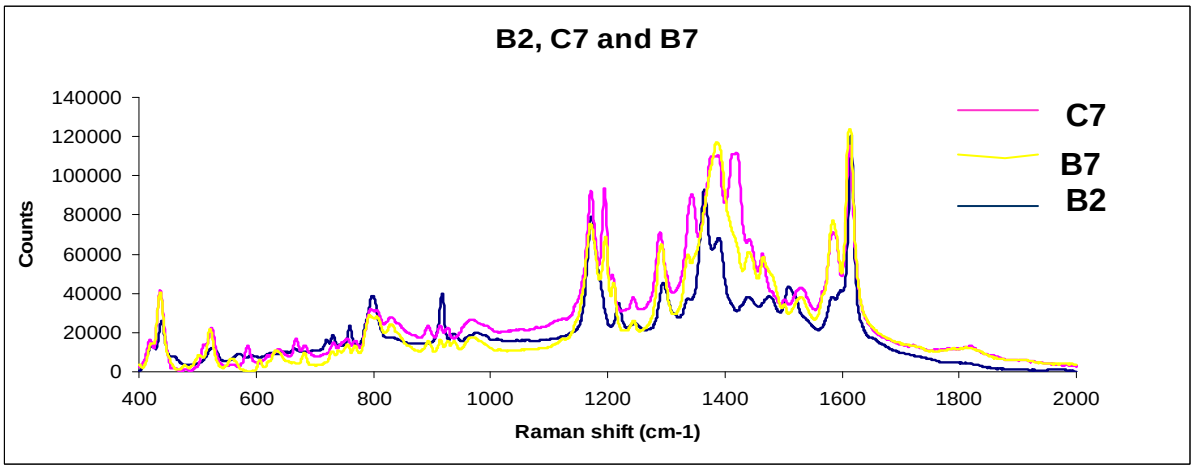
C7: ^{1}H-NMR ($CDCl_3$) 8.58 (s, 2H, NH_2^+), 7.96-7.88 (m, 4H), 7.67-7.60 (m, 3H), 7.31 (d, J = 9Hz, 2H), 6.69 (d, J = 9Hz, 2H), 3.56 (s, 4H), 2.14 (s, 4H); ^{13}C-NMR ($CDCl_3$): 25.47, 48.49, 113.24, 117.82, 127.48, 127.91, 128.06, 128.10, 129.02, 129.37, 130.24, 132.48, 135.22, 136.27, 137.07, 139.91, 142.20, 153.50, 161.24, 176.61 ppm; HRMS (ESI): m/z calcd for $C_{27}H_{25}N_2$: 377.2012 ; found : 378.2047 [M + H]$^+$; UV (H_2O): λ_{max} (ε): 594 nm (59500 cm^{-1} M^{-1});

C9: ^{1}H-NMR ($CDCl_3$) 8.50 (s, 2H, NH_2^+), 7.75-7.68 (m, 2H), 7.51-7.30 (m, 12H), 7.08-7.07 (m, 1H), 6.70 (d, 2H), 3.57 (s, 4H), 2.16 (s, 4H); ^{13}C-NMR ($CDCl_3$): 23.45, 46.31, 110.65, 111.31, 115.35, 125.03, 125.80, 127.22, 130.88, 132.03, 137.51, 138.76, 139.22, 140.29, 154.24, 162.48, 172.26 ppm; HRMS (ESI): m/z calcd for $C_{29}H_{27}N_2$: 403.2169 ; found : 404.2209 [M + H]$^+$; UV (H_2O): λ_{max} (ε): 592 nm (34000 cm^{-1} M^{-1});

8. UV-Vis Spectra of the synthetic TM compounds and CV



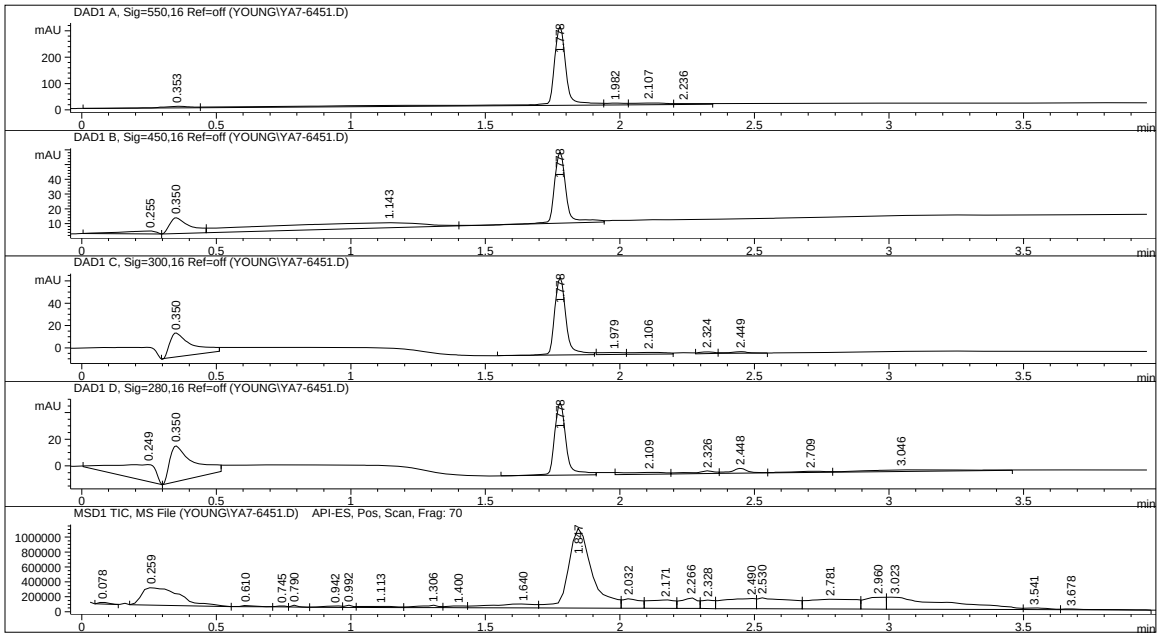
9. SERS spectra of B2, B7, and C7 with some unique identifiable peaks (cm-1).

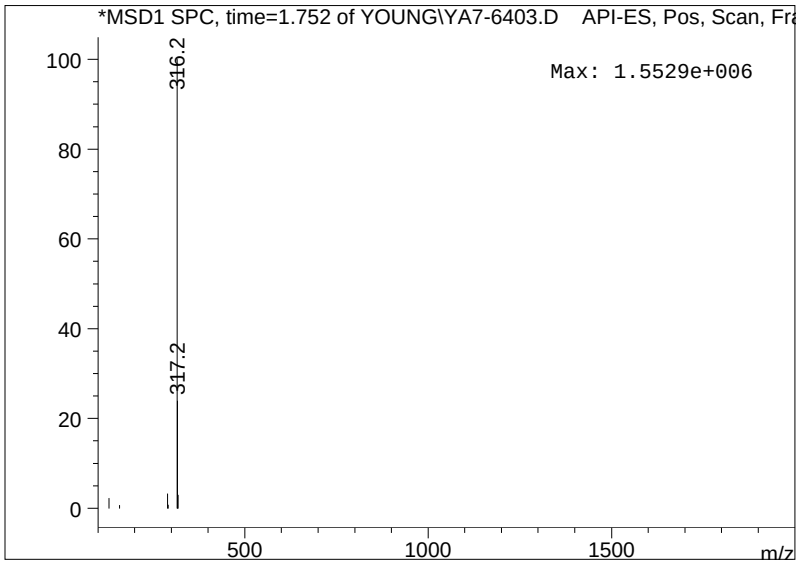


B2	917.43	X	X	X	X
B7	X	1193.47	X	X	1581.43
C7	X	1193.47	1341.33	1411.18	1581.43

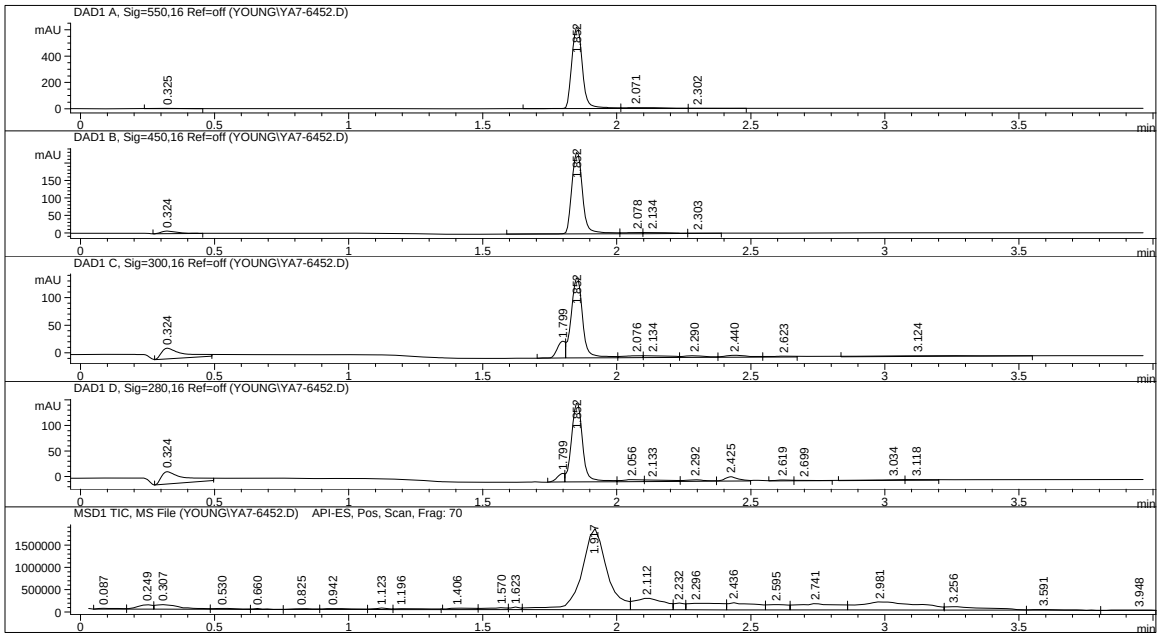
10. LCMS Data of some representative Triphenylmethine library compounds:

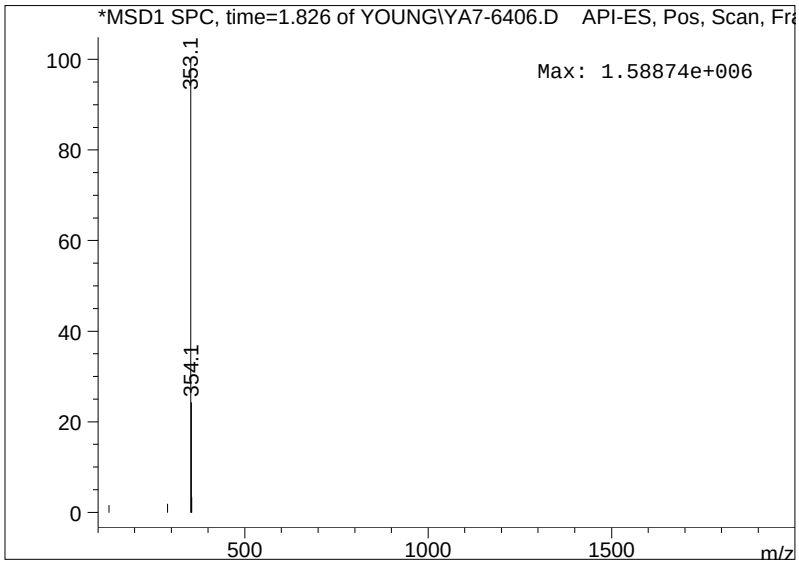
A-2



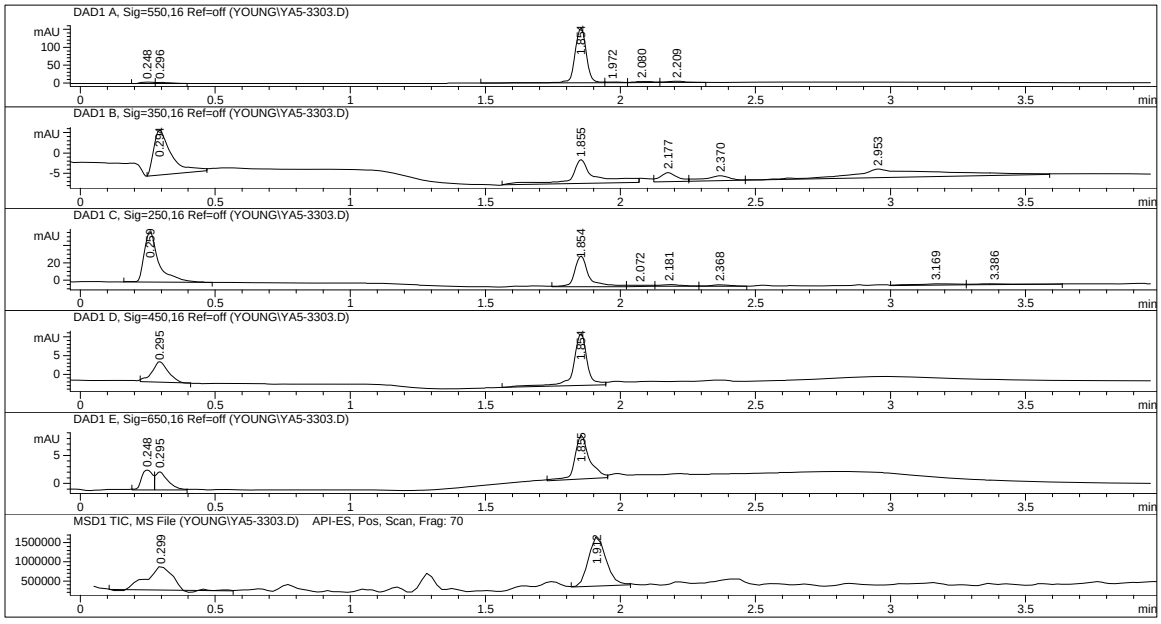

*MSD1 SPC, time=1.752 of YOUNG\YA7-6403.D API-ES, Pos, Scan, Fra
Max: 1.5529e+006
316.2
317.2
100
80
60
40
20
0
500
1000
1500
m/z

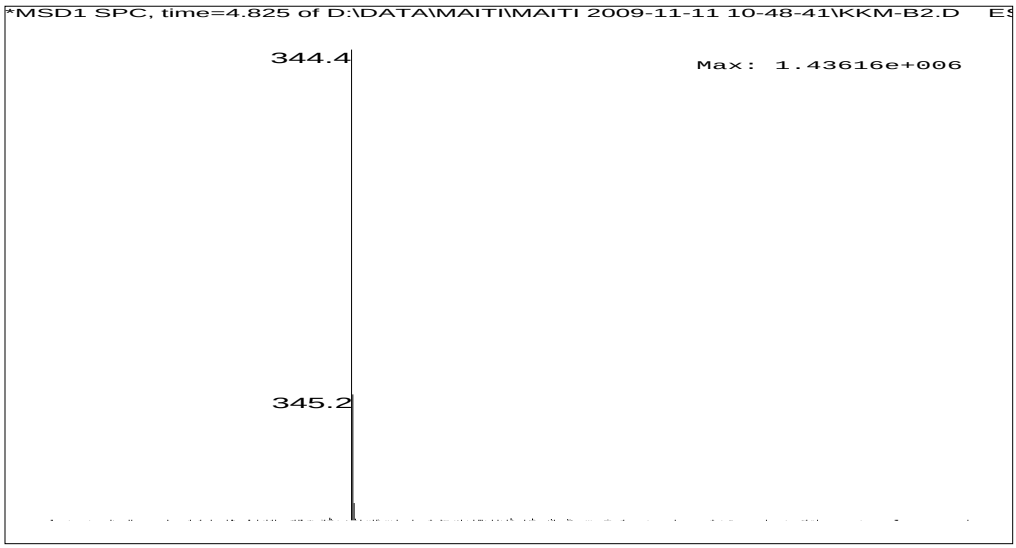
A-13


DAD1 A, Sig=550,16 Ref=off (YOUNG\YA7-6452.D)
DAD1 B, Sig=450,16 Ref=off (YOUNG\YA7-6452.D)
DAD1 C, Sig=300,16 Ref=off (YOUNG\YA7-6452.D)
DAD1 D, Sig=280,16 Ref=off (YOUNG\YA7-6452.D)
MSD1 TIC, MS File (YOUNG\YA7-6452.D) API-ES, Pos, Scan, Frag: 70
mAU
min

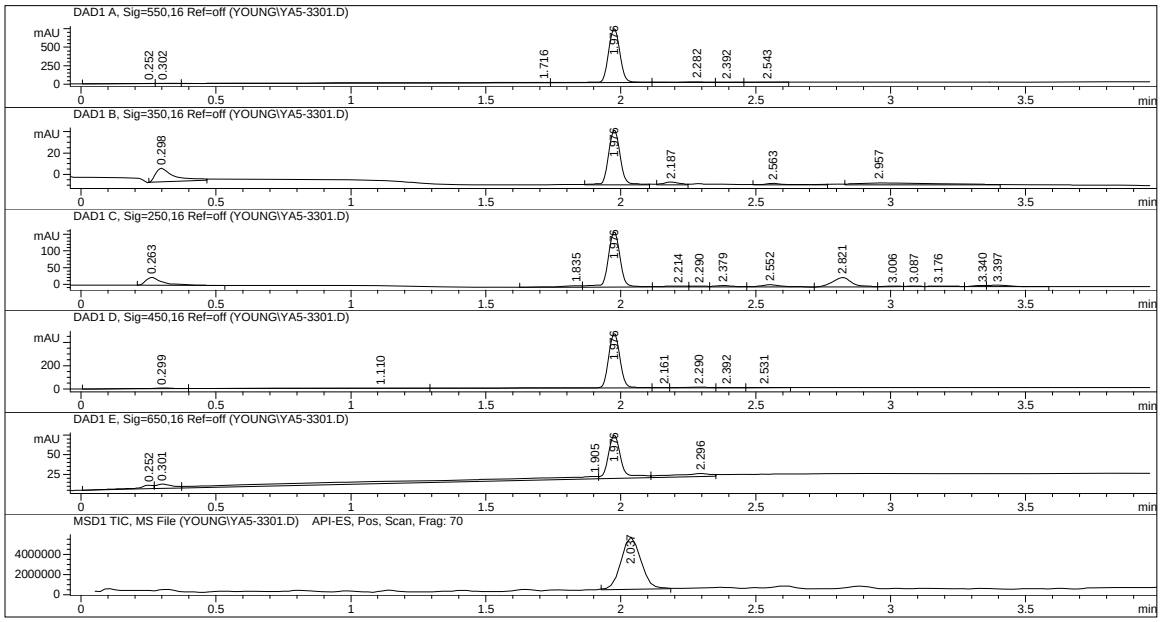

*MSD1 SPC, time=1.826 of YOUNG\YA7-6406.D API-ES, Pos, Scan, Fra
Max: 1.58874e+006
353.1
354.1
100
80
60
40
20
0
500
1000
1500
m/z

B-2

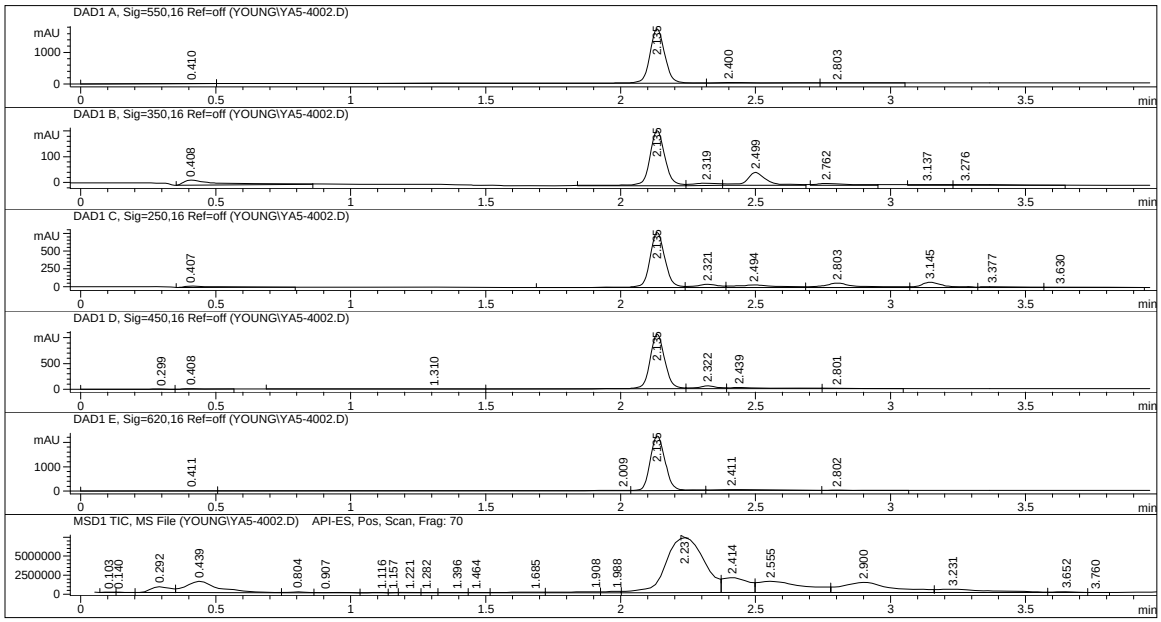

DAD1 A, Sig=550,16 Ref=off (YOUNG\YA5-3303.D)
DAD1 B, Sig=350,16 Ref=off (YOUNG\YA5-3303.D)
DAD1 C, Sig=250,16 Ref=off (YOUNG\YA5-3303.D)
DAD1 D, Sig=450,16 Ref=off (YOUNG\YA5-3303.D)
DAD1 E, Sig=650,16 Ref=off (YOUNG\YA5-3303.D)
MSD1 TIC, MS File (YOUNG\YA5-3303.D) API-ES, Pos, Scan, Frag: 70
mAU
min

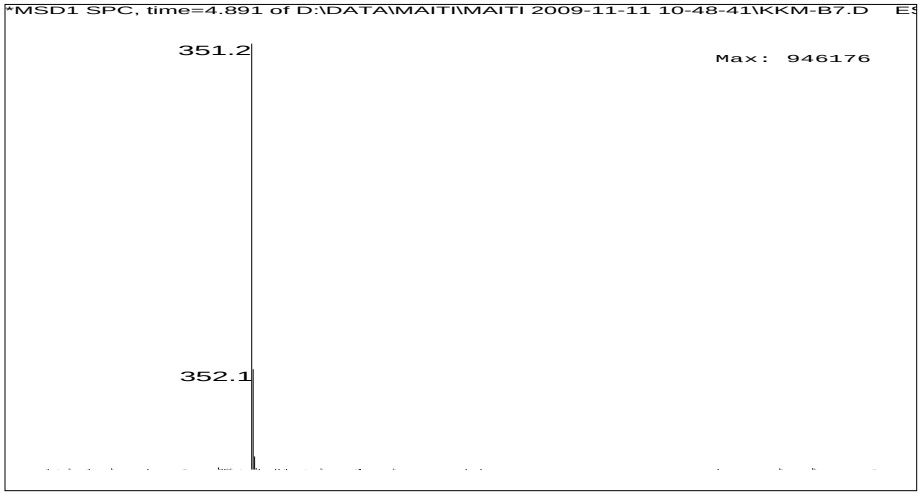

*MSD1 SPC, time=4.825 of D:\DATA\MAITI\MAITI 2009-11-11 10-48-41\KKM-B2.D
344.4
Max: 1.43616e+006
345.2

B-4

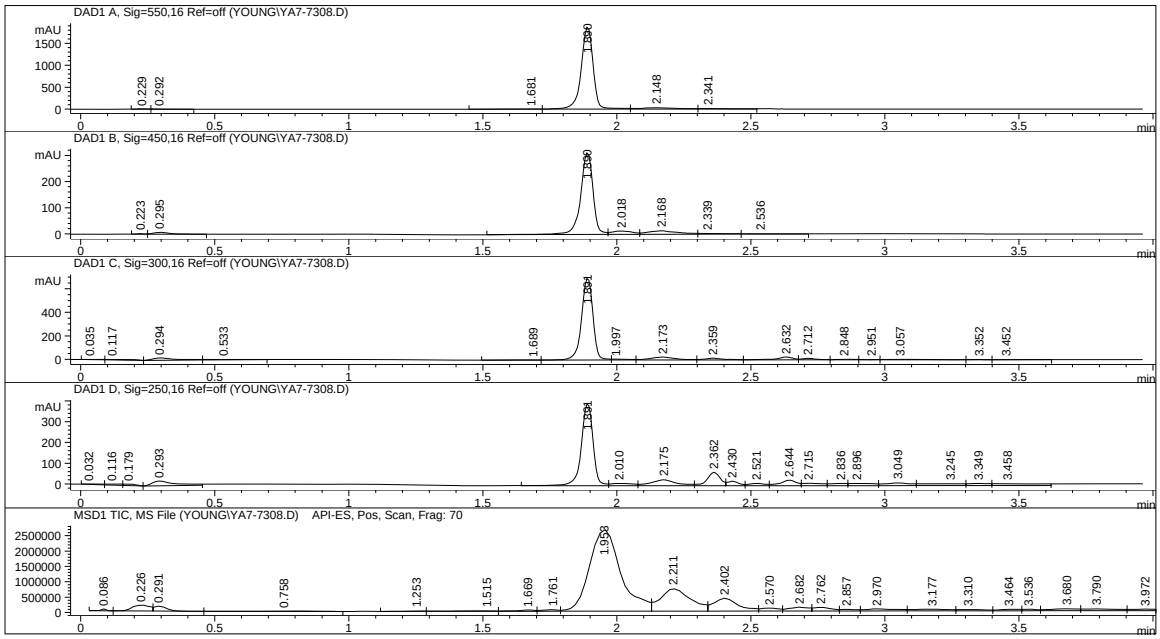

DAD1 A, Sig=550,16 Ref=off (YOUNG\YA5-3301.D)
DAD1 B, Sig=350,16 Ref=off (YOUNG\YA5-3301.D)
DAD1 C, Sig=250,16 Ref=off (YOUNG\YA5-3301.D)
DAD1 D, Sig=450,16 Ref=off (YOUNG\YA5-3301.D)
DAD1 E, Sig=650,16 Ref=off (YOUNG\YA5-3301.D)
MSD1 TIC, MS File (YOUNG\YA5-3301.D) API-ES, Pos, Scan, Frag: 70
mAU
min

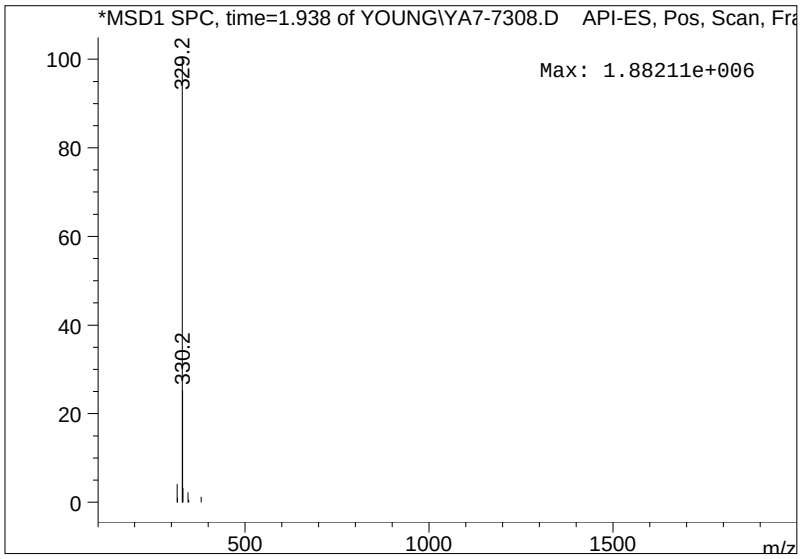
B-7


DAD1 A, Sig=550,16 Ref=off (YOUNG\YA5-4002.D)
mAU
0.410
2.135
2.400
2.803
DAD1 B, Sig=350,16 Ref=off (YOUNG\YA5-4002.D)
0.408
2.135
2.319
2.499
2.762
3.137
3.276
DAD1 C, Sig=250,16 Ref=off (YOUNG\YA5-4002.D)
0.407
2.135
2.321
2.494
2.803
3.145
3.377
3.630
DAD1 D, Sig=450,16 Ref=off (YOUNG\YA5-4002.D)
0.299
0.408
1.310
2.135
2.322
2.439
2.801
DAD1 E, Sig=620,16 Ref=off (YOUNG\YA5-4002.D)
0.411
2.009
2.135
2.411
2.802
MSD1 TIC, MS File (YOUNG\YA5-4002.D) API-ES, Pos, Scan, Frag: 70
0.103
0.140
0.292
0.439
0.804
0.907
1.116
1.157
1.221
1.282
1.396
1.464
1.685
1.908
1.988
2.23
2.414
2.555
2.900
3.231
3.652
3.760
min

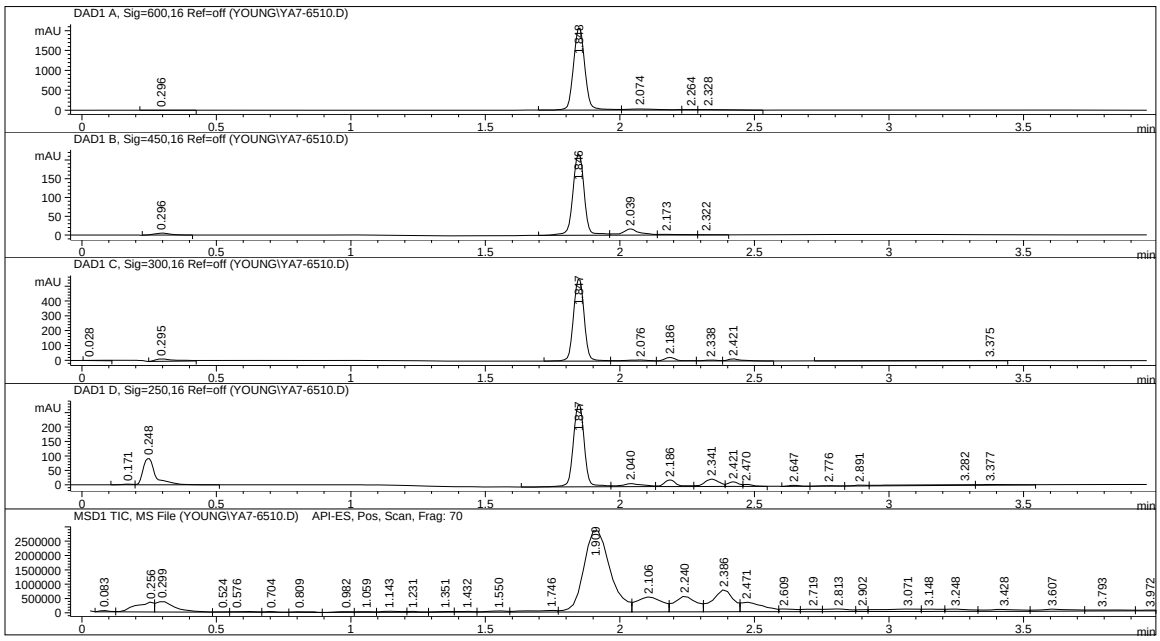

*MSD1 SPC, time=4.891 of D:\DATA\MAITI\MAITI 2009-11-11 10-48-41\KKM-B7.D
351.2
Max: 946176
352.1

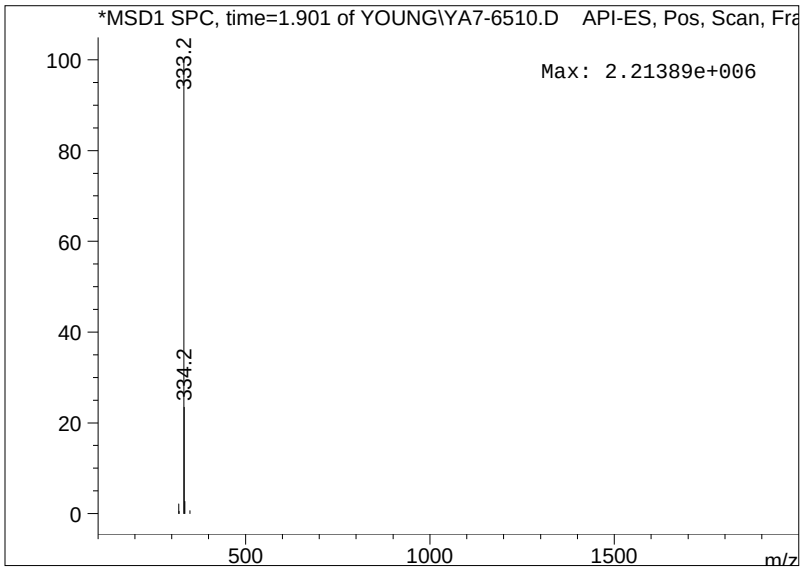
B-16


DAD1 A, Sig=550,16 Ref=off (YOUNG\YA7-7308.D)
mAU
1500
1000
500
0
0.229
0.292
1.681
1.890
2.148
2.341
0
0.5
1
1.5
2
2.5
3
3.5
min
DAD1 B, Sig=450,16 Ref=off (YOUNG\YA7-7308.D)
mAU
200
100
0
0.223
0.295
1.890
2.018
2.168
2.339
2.536
DAD1 C, Sig=300,16 Ref=off (YOUNG\YA7-7308.D)
mAU
400
200
0
0.035
0.117
0.294
0.533
1.689
1.894
1.997
2.173
2.359
2.632
2.712
2.848
2.951
3.057
3.352
3.452
DAD1 D, Sig=250,16 Ref=off (YOUNG\YA7-7308.D)
mAU
300
200
100
0
0.032
0.116
0.179
0.293
1.894
2.010
2.175
2.362
2.430
2.521
2.644
2.715
2.836
2.896
3.049
3.245
3.349
3.458
MSD1 TIC, MS File (YOUNG\YA7-7308.D) API-ES, Pos, Scan, Frag: 70
2500000
2000000
1500000
1000000
500000
0
0.086
0.226
0.291
0.758
1.253
1.515
1.669
1.761
1.938
2.211
2.402
2.570
2.682
2.762
2.857
2.970
3.177
3.310
3.464
3.536
3.680
3.790
3.972

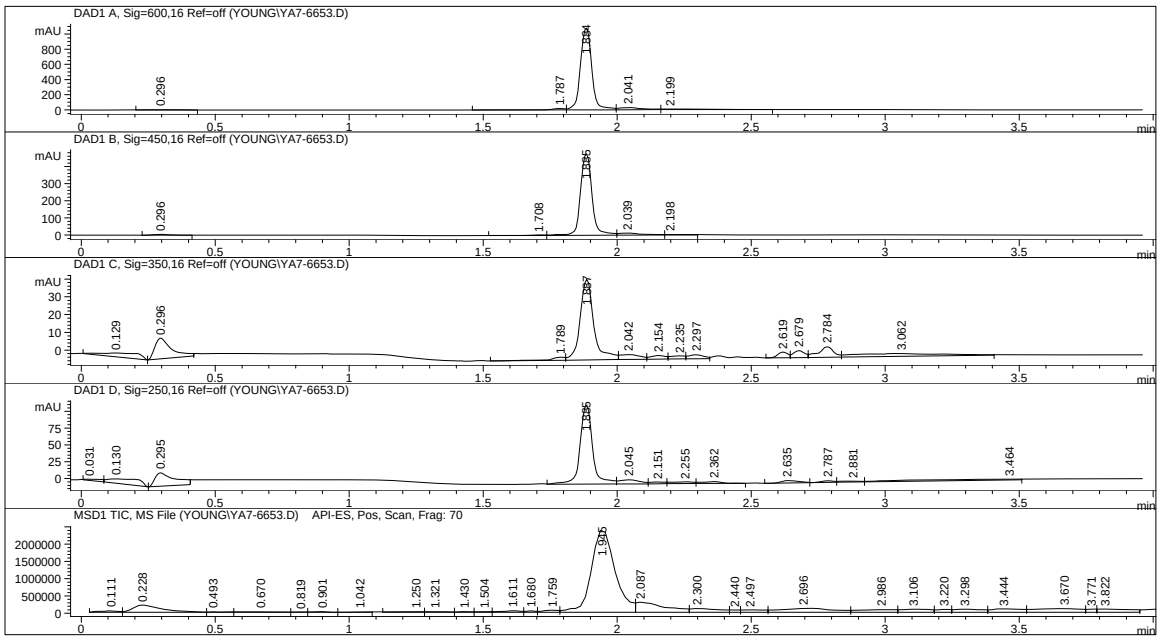

*MSD1 SPC, time=1.938 of YOUNG\YA7-7308.D API-ES, Pos, Scan, Fra
Max: 1.88211e+006
100
80
60
40
20
0
329.2
330.2
500
1000
1500
m/z

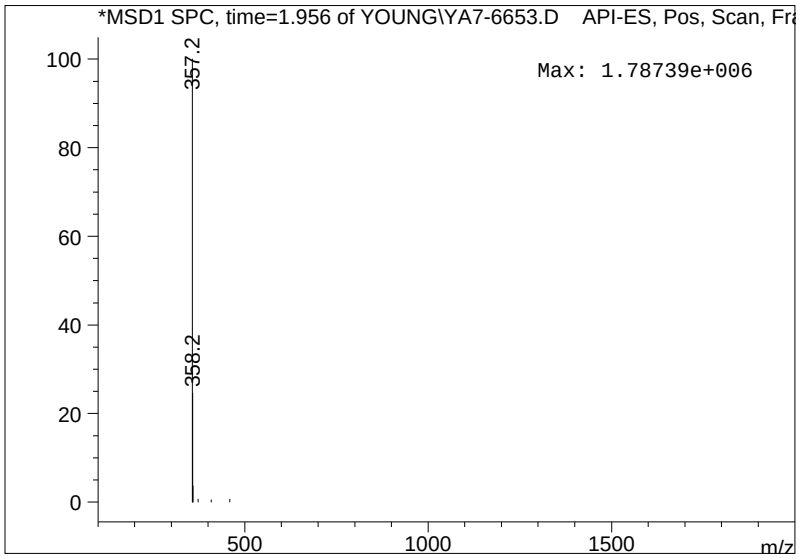
B-25


DAD1 A, Sig=600,16 Ref=off (YOUNG\YA7-6510.D)
mAU
1500
1000
500
0
0.296
1.848
2.074
2.264
2.328
0
0.5
1
1.5
2
2.5
3
3.5
min
DAD1 B, Sig=450,16 Ref=off (YOUNG\YA7-6510.D)
mAU
150
100
50
0
0.296
1.846
2.039
2.173
2.322
DAD1 C, Sig=300,16 Ref=off (YOUNG\YA7-6510.D)
mAU
400
300
200
100
0
0.028
0.295
1.847
2.076
2.186
2.338
2.421
3.375
DAD1 D, Sig=250,16 Ref=off (YOUNG\YA7-6510.D)
mAU
200
150
100
50
0
0.171
0.248
1.847
2.040
2.186
2.341
2.421
2.470
2.647
2.776
2.891
3.282
3.377
MSD1 TIC, MS File (YOUNG\YA7-6510.D) API-ES, Pos, Scan, Frag: 70
2500000
2000000
1500000
1000000
500000
0
0.083
0.256
0.299
0.524
0.576
0.704
0.809
0.982
1.059
1.143
1.231
1.351
1.432
1.550
1.746
1.909
2.106
2.240
2.386
2.471
2.609
2.719
2.813
2.902
3.071
3.148
3.248
3.428
3.607
3.793
3.972

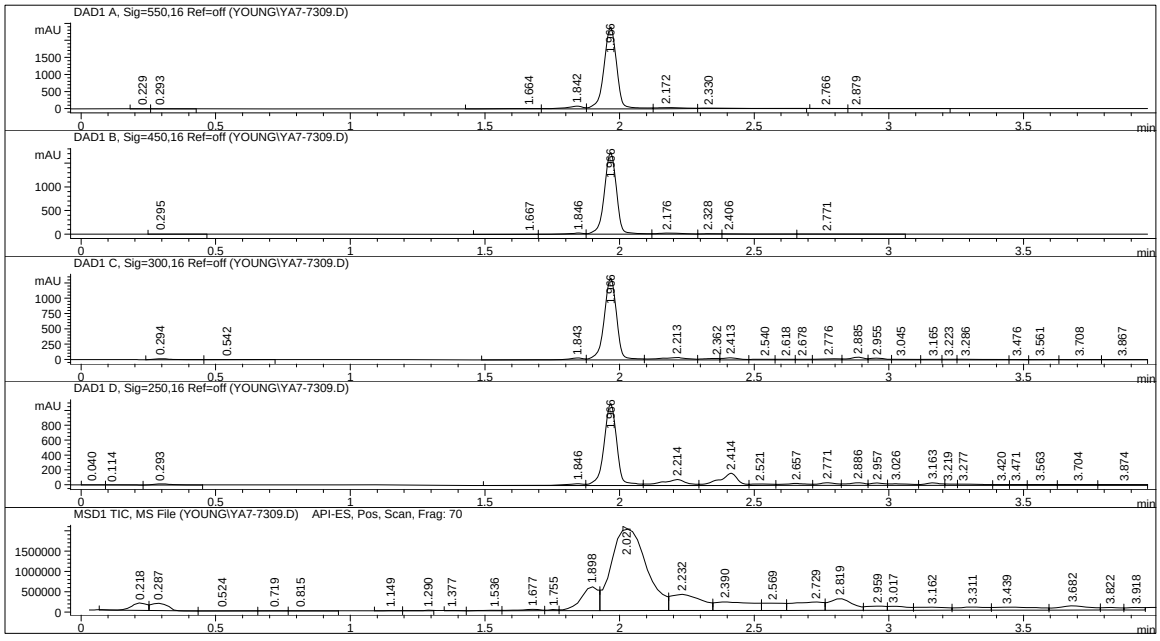

*MSD1 SPC, time=1.901 of YOUNG\YA7-6510.D API-ES, Pos, Scan, Fra
Max: 2.21389e+006
333.2
334.2
m/z

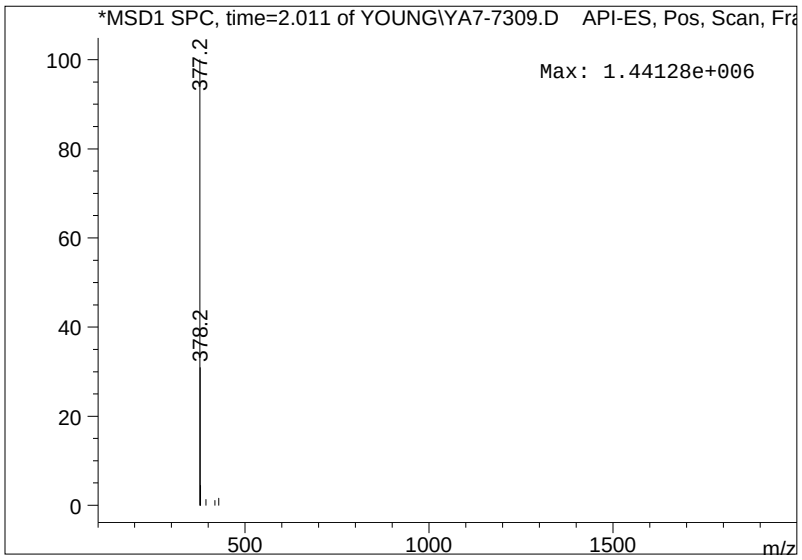
C-3


DAD1 A, Sig=600,16 Ref=off (YOUNG\YA7-6653.D)
DAD1 B, Sig=450,16 Ref=off (YOUNG\YA7-6653.D)
DAD1 C, Sig=350,16 Ref=off (YOUNG\YA7-6653.D)
DAD1 D, Sig=250,16 Ref=off (YOUNG\YA7-6653.D)
MSD1 TIC, MS File (YOUNG\YA7-6653.D) API-ES, Pos, Scan, Frag: 70
mAU
min

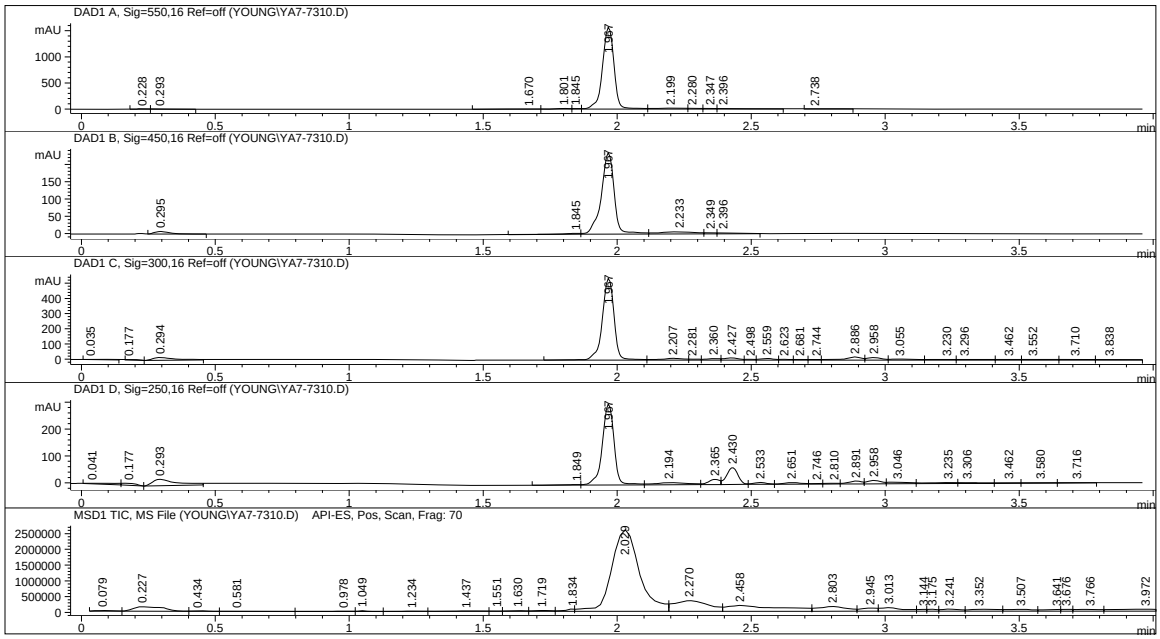

*MSD1 SPC, time=1.956 of YOUNG\YA7-6653.D API-ES, Pos, Scan, Fra
Max: 1.78739e+006
357.2
358.2
m/z

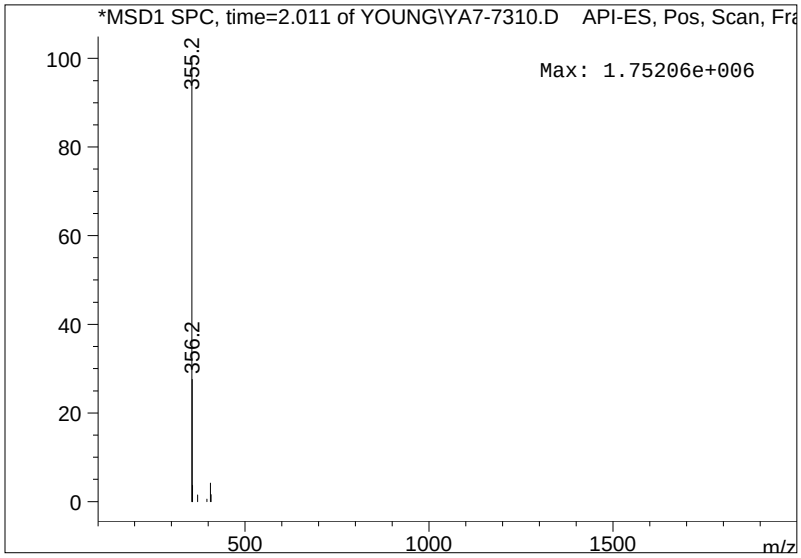
C-7


DAD1 A, Sig=550,16 Ref=off (YOUNG\YA7-7309.D)
DAD1 B, Sig=450,16 Ref=off (YOUNG\YA7-7309.D)
DAD1 C, Sig=300,16 Ref=off (YOUNG\YA7-7309.D)
DAD1 D, Sig=250,16 Ref=off (YOUNG\YA7-7309.D)
MSD1 TIC, MS File (YOUNG\YA7-7309.D) API-ES, Pos, Scan, Frag: 70
mAU
min

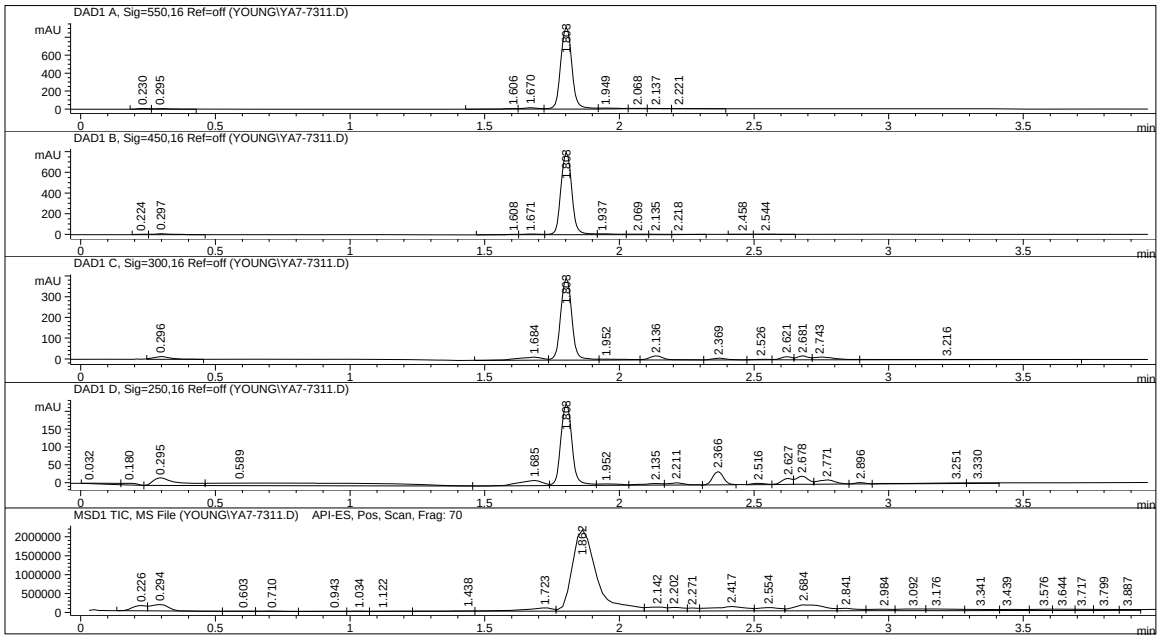

*MSD1 SPC, time=2.011 of YOUNG\YA7-7309.D API-ES, Pos, Scan, Fra
Max: 1.44128e+006
377.2
378.2
100
80
60
40
20
0
500
1000
1500
m/z

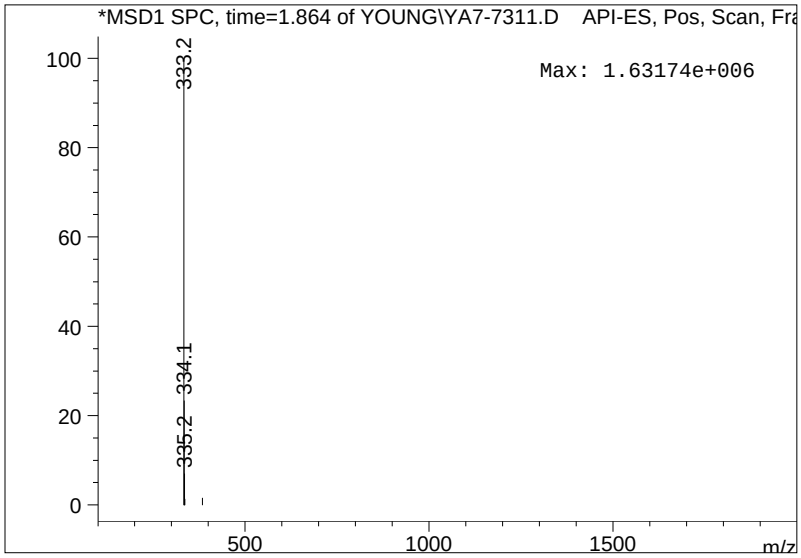
C-16

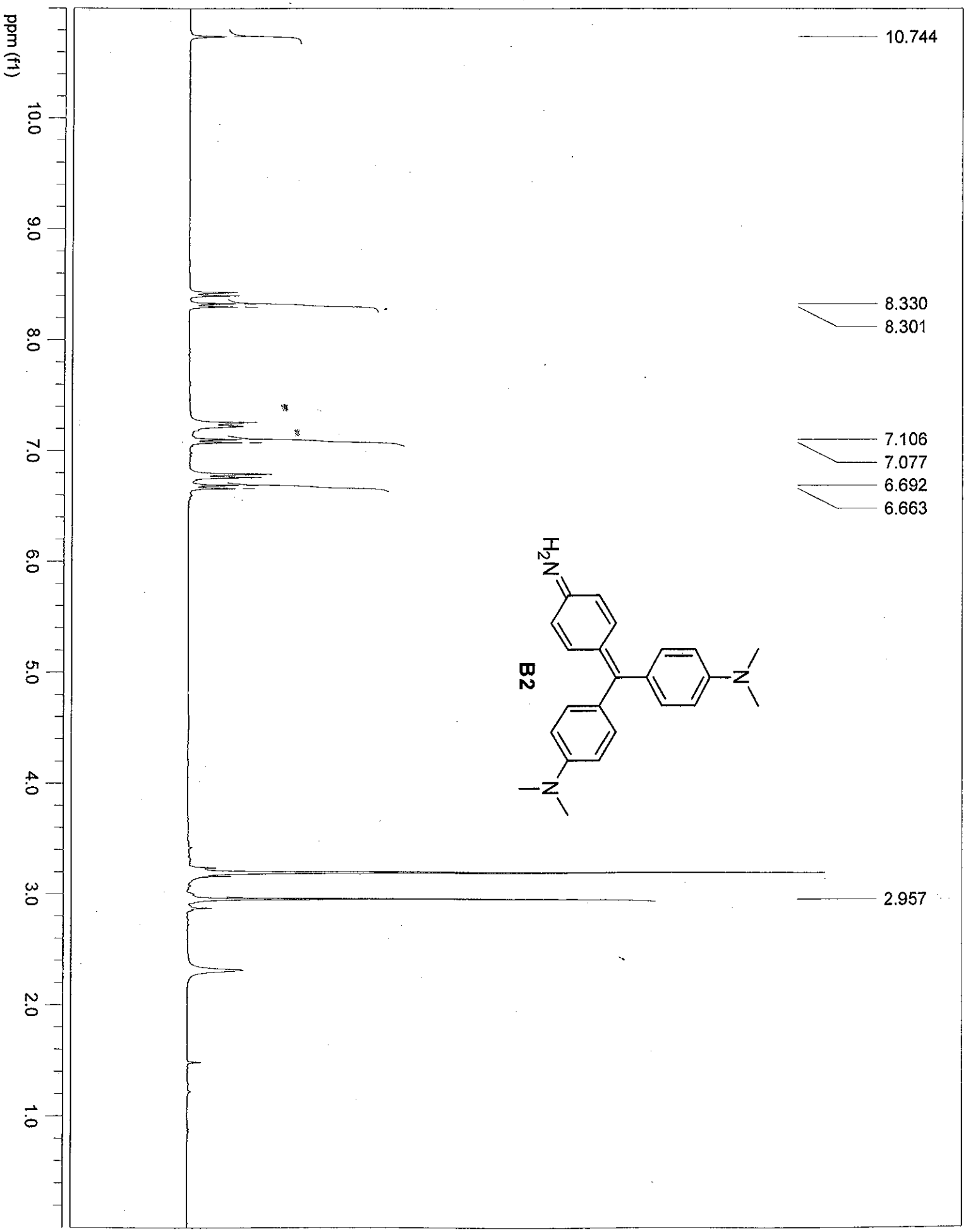

DAD1 A, Sig=550,16 Ref=off (YOUNG\YA7-7310.D)
DAD1 B, Sig=450,16 Ref=off (YOUNG\YA7-7310.D)
DAD1 C, Sig=300,16 Ref=off (YOUNG\YA7-7310.D)
DAD1 D, Sig=250,16 Ref=off (YOUNG\YA7-7310.D)
MSD1 TIC, MS File (YOUNG\YA7-7310.D) API-ES, Pos, Scan, Frag: 70
mAU
min

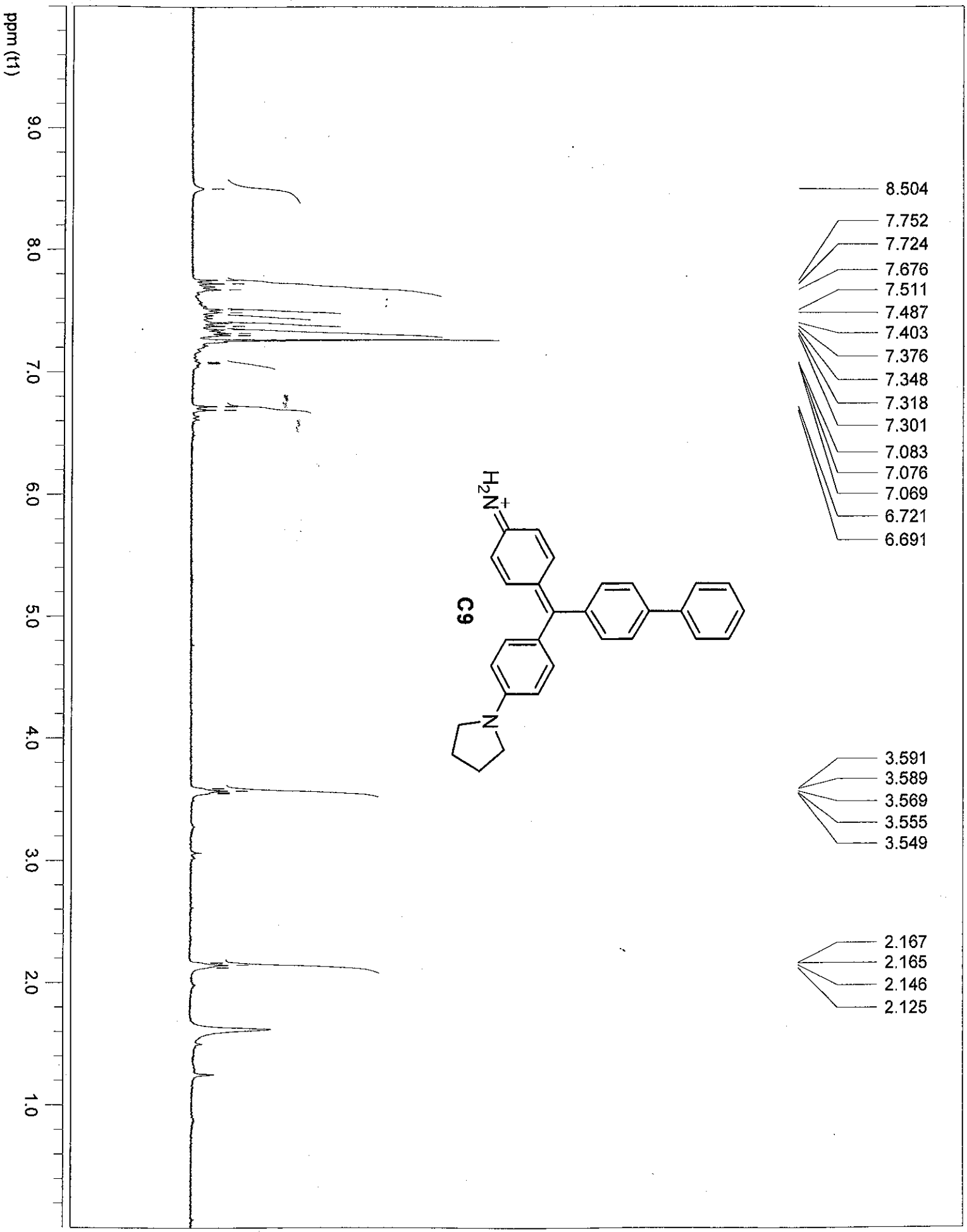

*MSD1 SPC, time=2.011 of YOUNG\YA7-7310.D API-ES, Pos, Scan, Fra
Max: 1.75206e+006
355.2
356.2
m/z

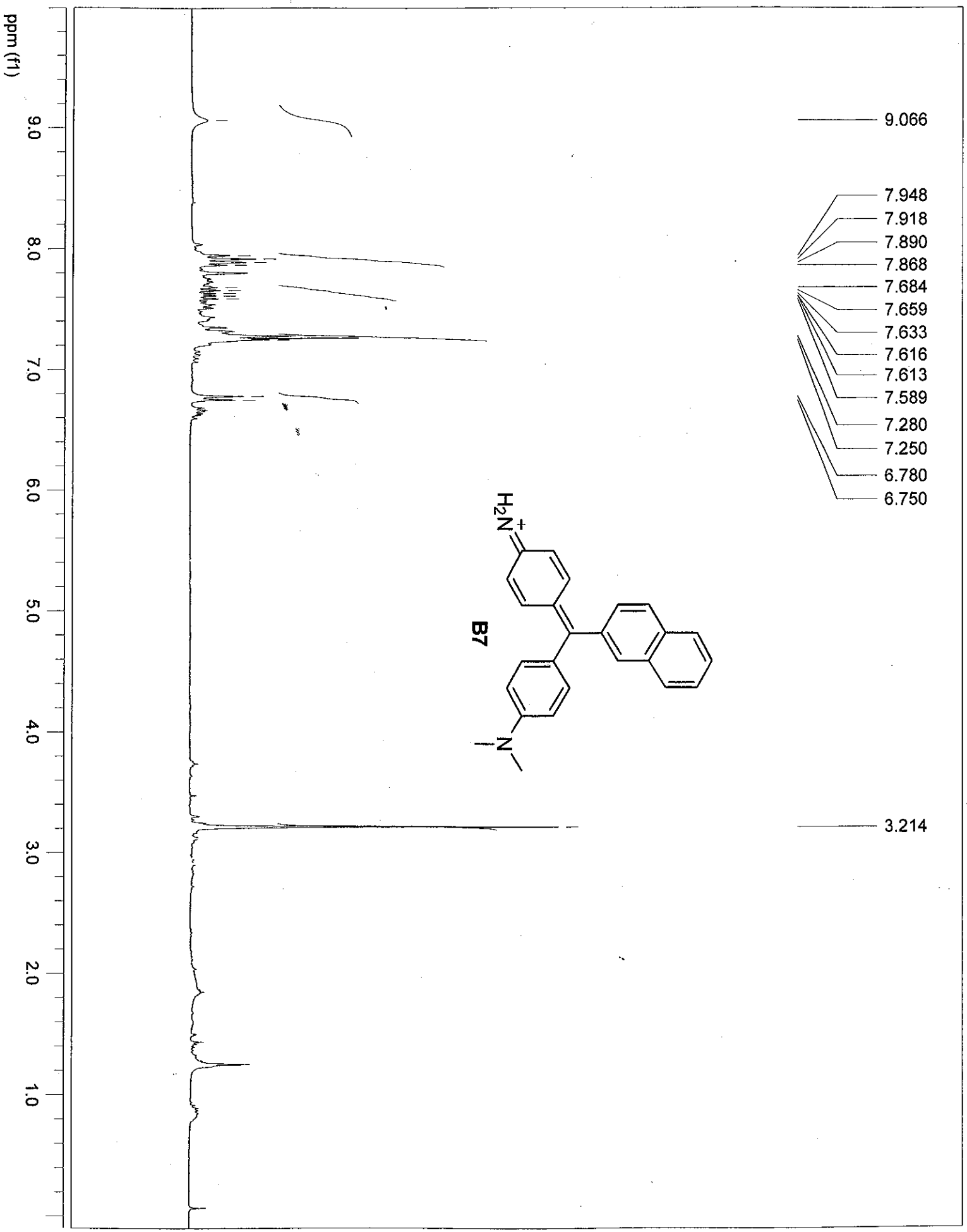
C-28

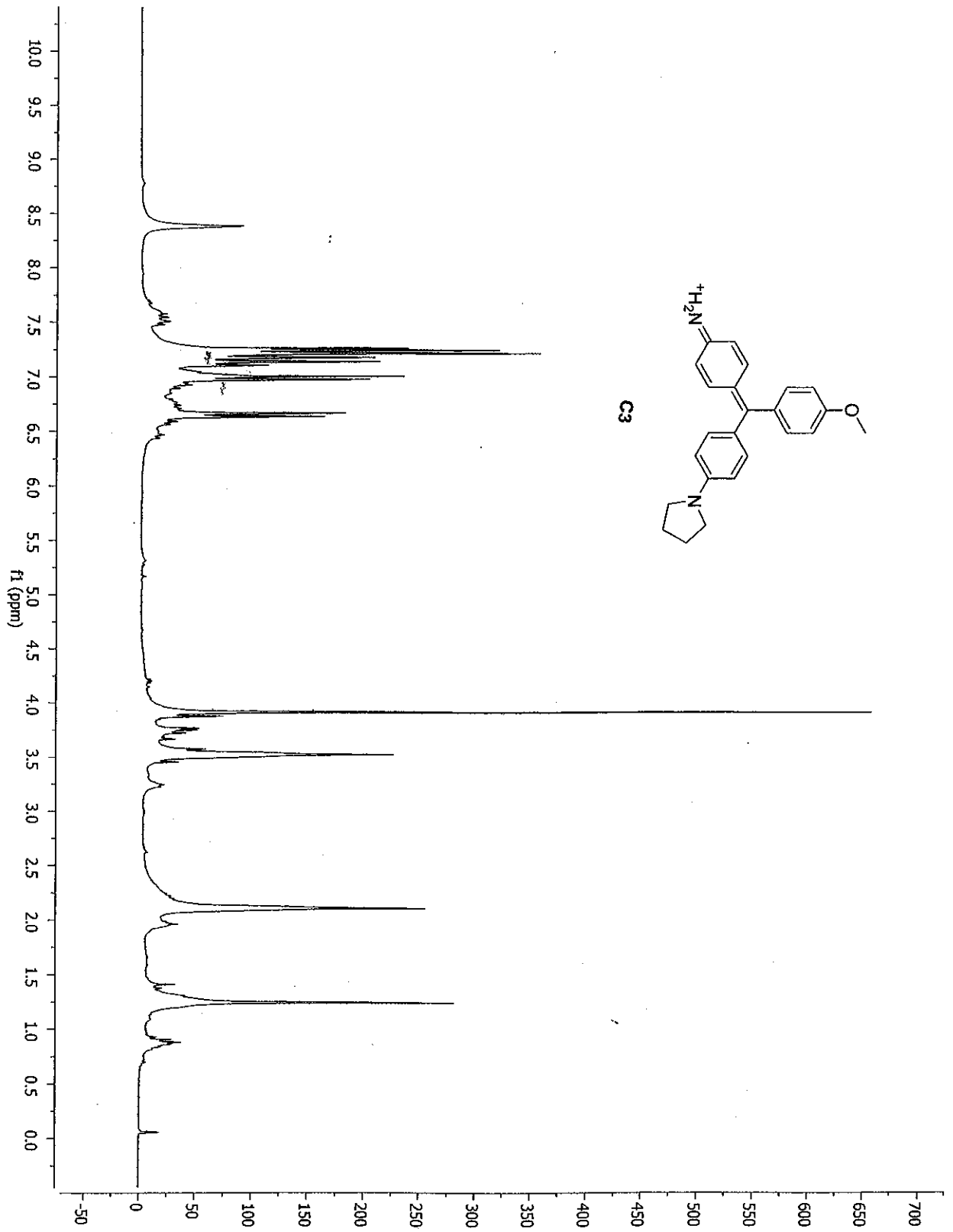

DAD1 A, Sig=550,16 Ref=off (YOUNG\YA7-7311.D)
DAD1 B, Sig=450,16 Ref=off (YOUNG\YA7-7311.D)
DAD1 C, Sig=300,16 Ref=off (YOUNG\YA7-7311.D)
DAD1 D, Sig=250,16 Ref=off (YOUNG\YA7-7311.D)
MSD1 TIC, MS File (YOUNG\YA7-7311.D) API-ES, Pos, Scan, Frag: 70
mAU
min

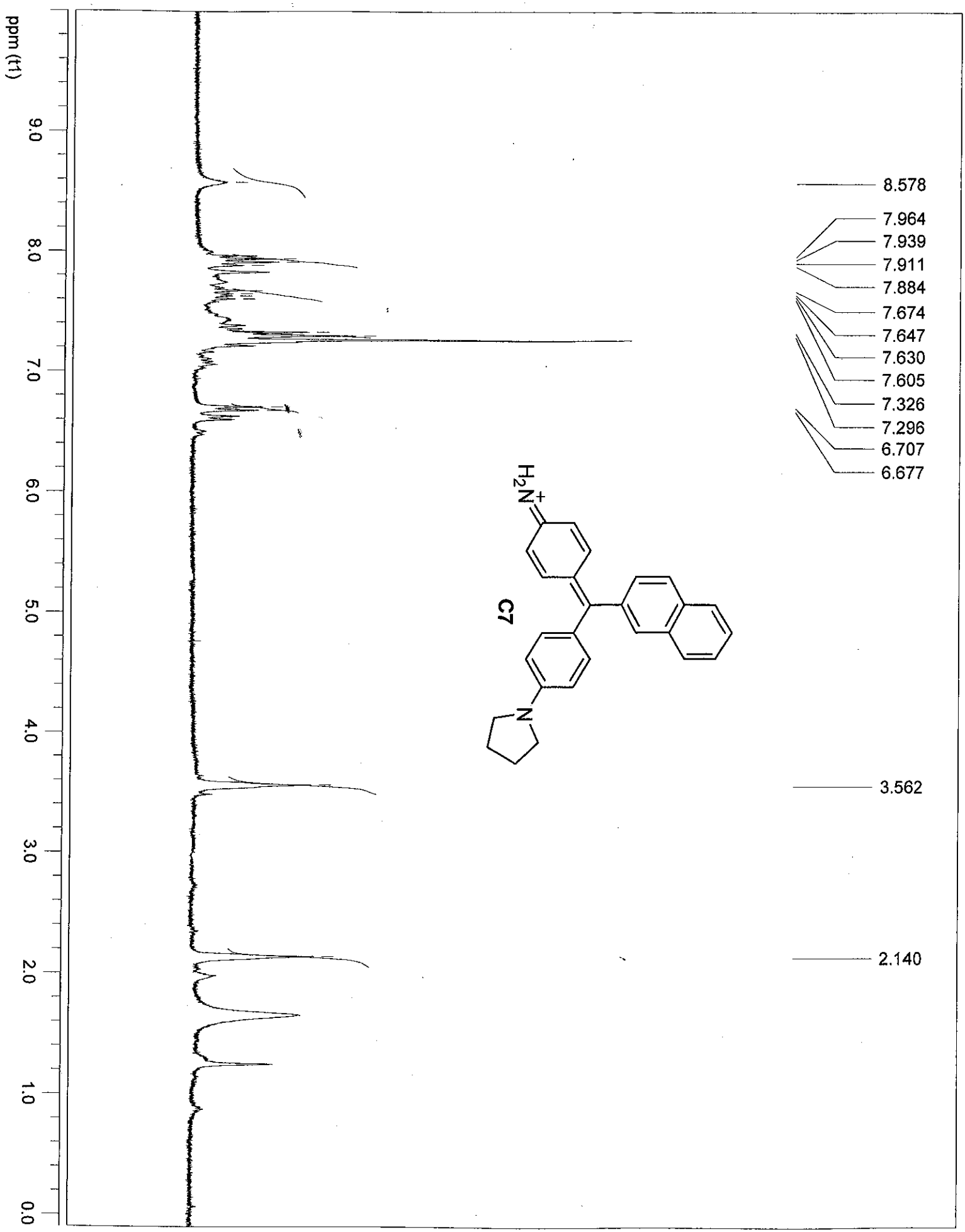

*MSD1 SPC, time=1.864 of YOUNG\YA7-7311.D API-ES, Pos, Scan, Fra
Max: 1.63174e+006
333.2
334.1
335.2
m/z

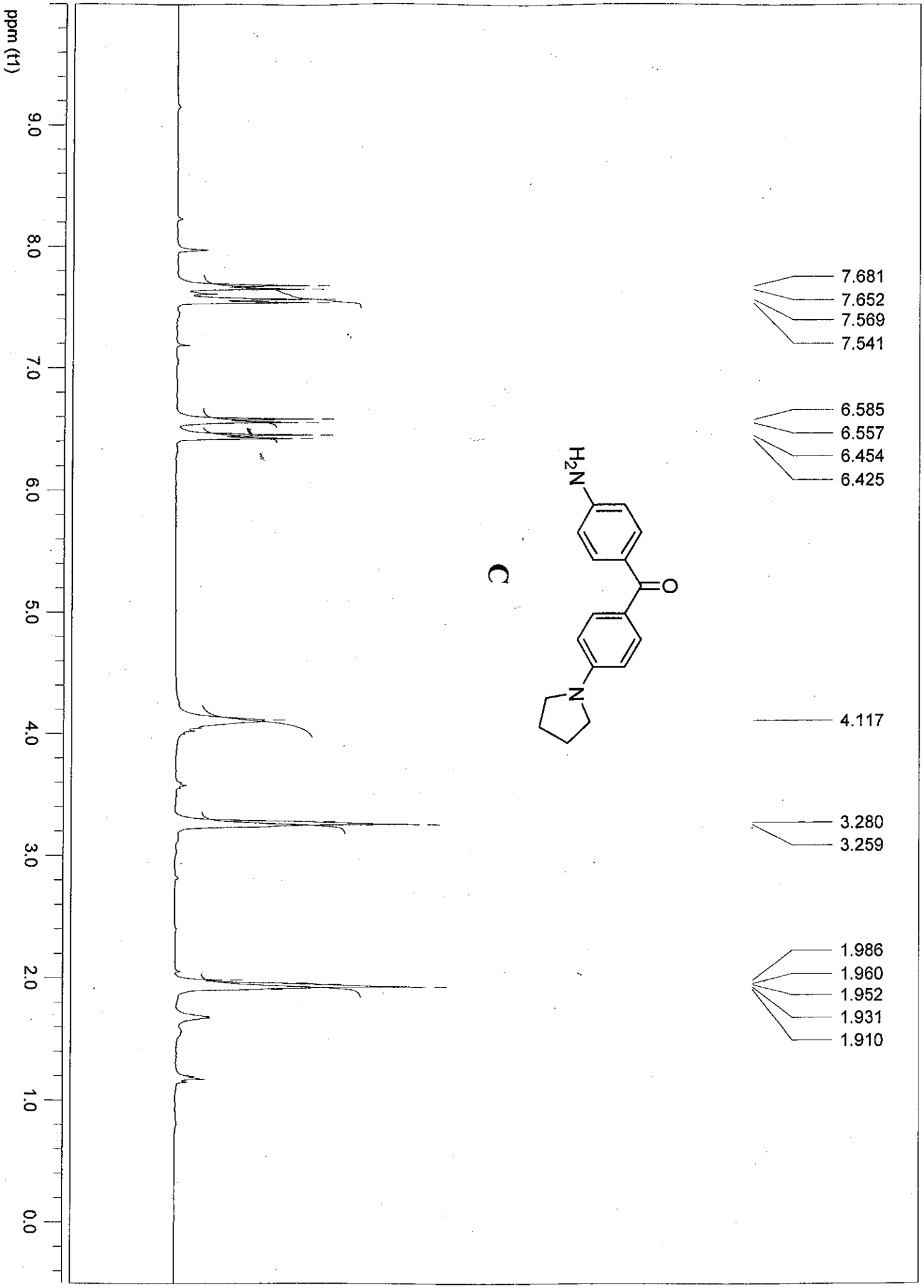

ppm (f1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
10.744
8.330
8.301
7.106
7.077
6.692
6.663
2.957
B2


ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
8.504
7.752
7.724
7.676
7.511
7.487
7.403
7.376
7.348
7.318
7.301
7.083
7.076
7.069
6.721
6.691
3.591
3.589
3.569
3.555
3.549
2.167
2.165
2.146
2.125
C9


ppm (f1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
9.066
7.948
7.918
7.890
7.868
7.684
7.659
7.633
7.616
7.613
7.589
7.280
7.250
6.780
6.750
3.214
B7


C3
f1 (ppm)


ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.578
7.964
7.939
7.911
7.884
7.674
7.647
7.630
7.605
7.326
7.296
6.707
6.677
3.562
2.140
C7


ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.681
7.652
7.569
7.541
6.585
6.557
6.454
6.425
4.117
3.280
3.259
1.986
1.960
1.952
1.931
1.910
H2N
O
N