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SUPPORTING INFORMATION

Tuning the reaction rates of fluoride probes for detection in aqueous solution

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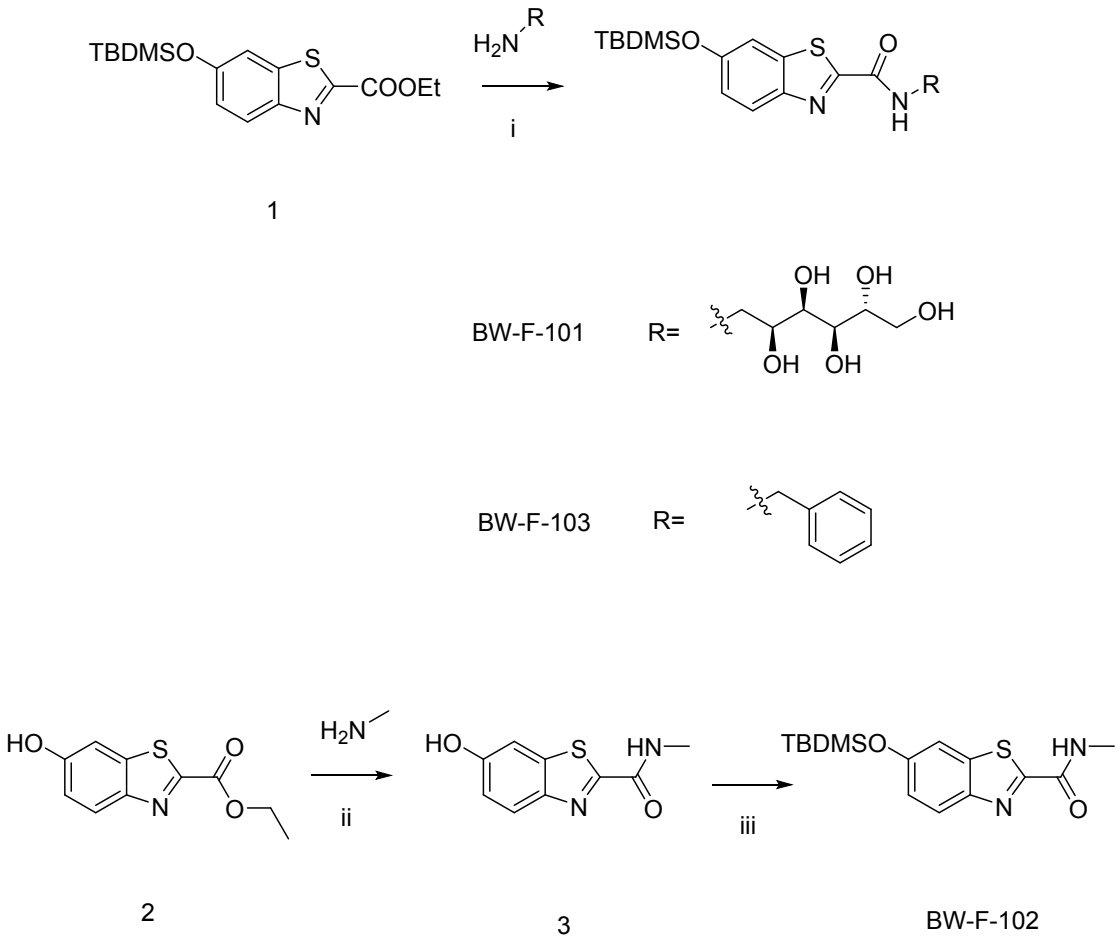
General methods and materials

All chemicals and solvents were of reagent grade and anhydrous solvents were obtained from a SG Water solvent purification system. Column chromatography was carried out on flash silica gel (Sorbent 230–400 mesh). TLC analyses were conducted on silica gel plates (Sorbent Silica G UV254). Mass spectral analyses were performed on an ABI API 3200 (ESI-Triple Quadruple). NMR spectra were recorded at 400 MHz for ^{1}H and 100 MHzfor^{13}C on a Bruker instrument. Chemical shifts (δ values) and coupling constants *(J* values) are given in ppm and hertz, respectively, using solvents as the internal standards. Fluorescence spectra were recorded on a Shimadzu RF-5301PC fluorometer.



Scheme S1. Reagents and conditions: (i) toluene, reflux, 36%, 57% ; (ii) MeOH, 95%; (iii) TBDMSCl, imidazole, DMF, 92%.

Ethyl 6-((*tert*-Butyldimethylsilyl)oxy)benzothiazole-2-carboxylate **(1)** was synthesized following reportedprocedures.[1]Ethyl 6-hydroxybenzothiazole-2-carboxylate **(2)** was synthesized following literature procedures.[2]

6-((*tert*-Butyldimethylsilyl)oxy)-N-((2S,3R,4R,5R)-2,3,4,5,6-pentahydroxyhexyl)benzo[d]thiazole-2-carboxamide (BW-F-101)

A mixture of compound **1** (40 mg, 0.12 mmol) and glucamine (21 mg, 0.12 mmol) in toluene (3 mL) was heated under reflux for 4 h and condensed under reduced pressure. The resulting residue was purified by silica gel flash column chromatography (DCM: MeOH = 12 :1) to afford BW-F-101 as white solid (20 mg, 36 %). ^{1}H NMR (CD_3OD): 0.27 (s, 6H), 1.04 (s, 9H), 3.57-3.52 (m, 1H), 3.68-3.64 (m, 1H), 3.76-3.71 (m, 3H), 3.82-3.79 (m, 1H), 3.86-3.85 (m, 1H), 4.04-4.00 (m,

1H), 7.13 (dd, *J* = 2.4 Hz, *J* = 8.8 Hz, 1H), 7.50 (d, *J* = 2.4 Hz, 1H), 7.98 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (CD_3OD): -5.7, 17.7, 24.6, 42.3, 63.3, 70.1, 71.6, 71.7, 72.3, 111.6, 121.0, 124.6, 138.2, 148.0, 155.1, 160.9, 161.2;HRMS (ESI): m/z calcd for C20H33N2O7SSi $[M+H]^+$: 473.1772, found: 473.1758.FT-IR(cm^{-1}) 3376, 2925, 2854, 1735, 1658, 1553, 1455, 1264, 942, 742. m.p. 143-145 ^oC.

***N*-Benzyl-6-((tert-butyldimethylsilyl)oxy)-1H-indene-2-carboxamide (BW-F-103)**

A mixture of compound **1** (40 mg, 0.12 mmol) and benzylamine (13 mg, 0.12 mmol) in toluene (3 mL) was heated under reflux for 4 h and condensed under reduced pressure. The resulting residue was purified by silica gel flash column chromatography (Hexane: Ethyl acetate = 10:1) to afford BW-F-103 as white solid (27 mg, 57 %). ^{1}H NMR ($CDCl_3$): 0.23 (s, 6H), 0.99 (s, 9H), 4.66 (d, *J* = 6.0 Hz, 2H), 7.03 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 7.37-7.24 (m, 6H), 7.70 (brt, *J* = 5.6 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): -4.2, 18.3, 25.7, 43.9, 112.0, 121.3, 124.8, 127.8, 128.0, 128.8, 137.6, 138.6, 147.9, 155.1, 160.0, 161.5; HRMS (ESI): m/z calcd for C21H27N2O2SSi $[M+H]^+$: 399.1557, found: 399.1539.FT-IR (cm^{-1}) 2925, 2855, 1675, 1527, 1451, 1263, 1214, 938, 839, 738. m.p. 148-150 ^oC.

6-Hydroxy-*N*-methylbenzo[d]thiazole-2-carboxamide (3)

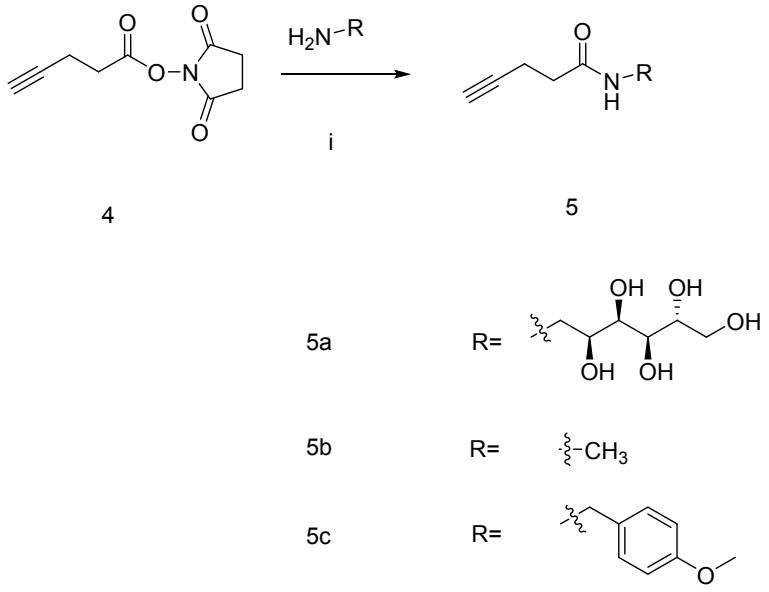
To astirred solution of compound **2** (45 mg, 0.2 mmol) in methanol (1 mL) was added methyl amine aqueous solution (40%, 1 mL) dropwise. The reacting mixture was stirred at r.t. for 0.5 h. After methanol was removed under reduced pressure, the aqueous phase was extracted with EA (1 mL × 3). The combined EA phase was washed with 1 N HCl aqueous solution (1 mL), and then brine (2 mL). After drying over anhydrous Na_2SO_4 and concentration in vacuum, the residue was purified by silica gel flash column chromatography(DCM/MeOH = 15:1) to afford **3** as white solid (40 mg, 95 %). ^{1}H NMR (DMSO-d_6): 2.83 (d, *J* = 4.8 Hz, 3H), 7.08 (dd, *J* = 9.2 Hz, *J* = 2.4 Hz, 1H), 7.46 (d, *J* = 2.0 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 8.93 (br d, *J* = 4.8 Hz, 1H);^{13}C NMR (DMSO-d_6):26.6, 107.3, 117.6, 125.1, 138.3, 146.7, 157.2, 160.6, 161.0; HRMS (ESI): m/z calcd forC9H8N2O2SNa $[M+Na]^+$: 231.0204, found: 231.0212.

6-((*tert*-Butyldimethylsilyl)oxy)-N-methylbenzo[d]thiazole-2-carboxamide (BW-F-102)

To a mixture of compound **3** (40 mg, 0.19 mmol) and imidazole (26 mg, 0.38 mmol) in DMF (1 mL) was added TBDMSCl (57 mg, 0.38 mmol). The reaction mixture was stirred at r.t. for 0.5 h.

Then water (2 mL) was added. The mixture was extracted with EA (2 mL × 3). The combined EA phase was washed with brine (3 mL), and dried over anhydrous Na_2SO_4. After concentrationunder reduced pressure, the residue was purified by silica gel flash column chromatography (Hexane/EA = 10:1) to afford BW-F-102 as white solid (57 mg, 92%). ^{1}H NMR ($CDCl_3$): 0.24 (s, 6H), 1.01 (s, 9H), 3.07 (d, *J* = 5.2 Hz, 3H), 7.05 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 7.35 (d, *J* = 2.4 Hz, 2H), 7.88 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): -4.3, 18.2, 25.6, 26.3, 111.9, 121.1, 124.7, 138.4, 147.8, 154.9, 160.6, 161.6; HRMS (ESI): m/z calcd for C15H22N2O2NaSSi $[M+Na]^+$: 345.1069, found: 345.1074.FT-IR (cm^{-1}) 2924, 2854, 1679, 1548, 1451, 1257, 1215, 941, 876, 740. m.p. 109-111 ^{o}C.

Synthesis and characterizations of BW-F-201, BW-F-202, BW-F-203



Scheme S2. Reagent and conditions: (i) TEA, DCM, rt, 1h, 80-92%.

2,5-dioxopyrrolidin-1-yl pent-4-ynoate **(4)** was synthesized following literature procedures.[3]

***N*-((2S,3R,4R,5R)-2,3,4,5,6-Pentahydroxyhexyl)pent-4-ynamide (5a)**

To a mixture of glucamine (126 mg, 0.75 mmol) and TEA (50 mg, 0.5 mmol) in methanol (10 mL) was added compound **4** (97 mg, 0.5 mmol). The reaction mixture was stirred at room temperature for 1 h and condensed under reduced pressure. The resulting residue was purified by silica gel flash column chromatography (DCM: MeOH = 5:1, 3:1) to afford compound **5a** as colorless oil

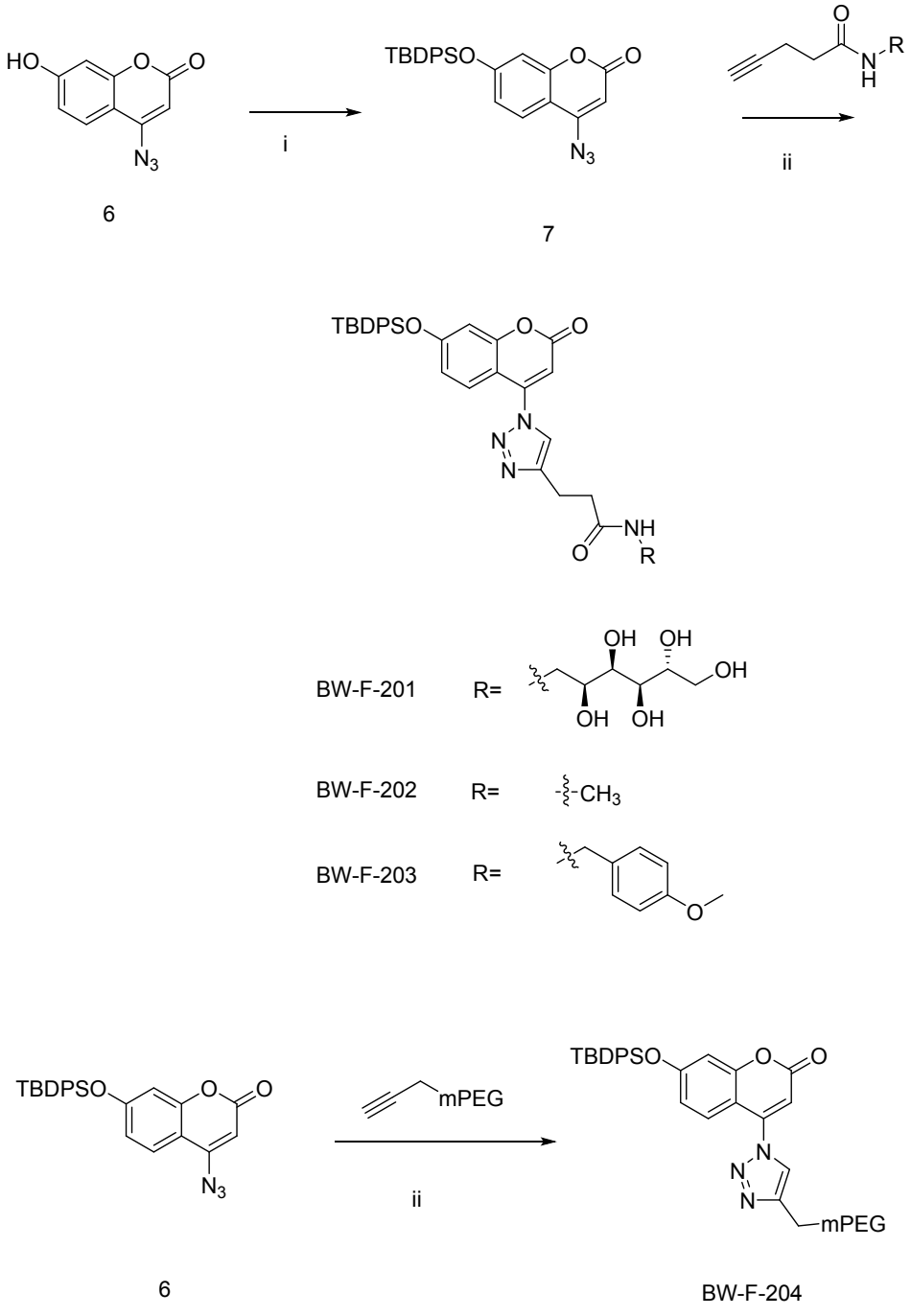
(105 mg, 80%).^{1}H NMR (MeOD): 2.28 (t, *J* = 2.4 Hz, 1H), 2.49-2.40 (m, 4H), 3.26(dd, *J* = 13.6 Hz, *J* = 7.2 Hz, 1H), 3.47 (dd, *J* = 13.6 Hz, *J* = 5.2 Hz, 1H),3.64-3.60 (m, 2H), 3.72-3.67 (m, 1H), 3.84-3.78 (m, 3H);^{13}C NMR (MeOD):14.2, 34.6, 42.0, 63.3, 69.0, 69.7, 71.6, 71.9, 72.4, 82.1, 173.2;HRMS (ESI): m/z calcd for C11H19NO6Na $[M+Na]^{+}$: 284.1110, found: 284.1122.

***N*-Methylpent-4-ynamide (5b)**

To a stirred solution of compound **4** (40 mg, 0.2 mmol) in DCM (2 ml) was added aminomethane (40% aqueous solution, 1mL). The reaction mixture was stirred at room temperature for 1h, and TLC showed the disappearance of compound **4**. Conc. HCl aqueous solution was added dropwise to neutralize the mixture. After separation, the aqueous phase was extracted with DCM (2 mL × 2). The combined DCM phase was washed with saturated $NaHCO_3$ aqueous solution (5 mL), and then brine (5 mL). After drying over anhydrous Na_2SO_4, the DCM solution was concentrated under reduced pressure to afford compound **5b** as white solid (20 mg, 88%).^{1}H NMR ($CDCl_3$): 1.94 (t, *J* = 2.4 Hz, 1H), 2.36 (t, *J* = 6.8 Hz, 2H), 2.46 (dt, *J* = 6.8 Hz, *J* = 2.4 Hz, 2H), 2.75 (d, *J* = 4.8 Hz, 3H), 6.37 (br s, 1H);^{13}C NMR ($CDCl_3$):δ 14.8, 26.3, 35.1, 69.2, 76.7, 77.0, 77.4, 83.0, 171.7;HRMS (ESI): m/z calcd for C6H9NO $[M+H]^{+}$: 112.0757, found: 112.0751.

***N*-(4-Methoxybenzyl)pent-4-ynamide (5c)**

To a stirred solution of (4-methoxyphenyl)methanamine (40 mg, 0.3 mmol) and TEA (20 mg, 0.2 mmol) in DCM (2 mL) was added compound **4** (40 mg, 0.2 mmol). The reaction mixture was stirred at room temperature and monitored by TLC. TLC showed the disappearance of compound **4**after 1 h of reaction. The reaction mixture was washed with 1N HCl aqueous solution (2 mL). The aqueous phase was extracted with DCM (2 mL). The combined DCM phase was washed with saturated $NaHCO_3$ aqueous solution (3 mL), and then brine (3 mL). After drying over anhydrous Na_2SO_4, DCM was removed under reduced pressure to afford compound **5c** as white solid (40 mg, 92%).^{1}H NMR ($CDCl_3$): 1.98 (t, *J* = 2.8 Hz, 1H), 2.41 (t, *J* = 6.4 Hz, 2H), 2.56 (dt, *J* = 6.4 Hz, *J* = 2.8Hz, 2H), 3.79 (s, 3H), 4.39 (d, *J* = 5.6 Hz, 2H), 5.86 (brs, 1H), 6.86 (m, 2H), 7.21 (m, 2H);^{13}C NMR ($CDCl_3$): 14.9, 35.3, 43.2, 55.3, 69.3, 82.9, 114.0, 129.2, 130.1, 159.0, 170.6. HRMS (ESI): m/z calcd for C13H16NO2 $[M+H]^{+}$: 218.1176, found: 218.1173.



Scheme S3. Reagents and conditions: (i) TBDPSCl, imidazole, DMF, rt, 97%; (ii) $CuSO_4 \cdot 5H_2O$, sodium ascorbate, THF: H_2O = 3:1, reflux, 38% - 81%.

4-azido-7-hydroxy-2H-chromen-2-one **(6)** was synthesized following literatureprocedures.[4]

4-Azido-7-((*tert*-butyldiphenylsilyl)oxy)-2H-chromen-2-one (7)

4-Azido-7-hydroxy-2H-chromen-2-one (**6**) (203 mg, 1 mmol) and imidazole (136 mg, 2 mmol) were dissolved in 1 mL DMF. TBDPSCl (550 mg, 2 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 1 h. Then ethyl acetate (5 mL) was added and the mixture was washed with water(5 mL). The aqueous phase was extracted with ethyl acetate (5 mL × 2). The combined organic phase was washed with brine (10 mL), and dried over anhydrous Na_2SO_4.After filtration, the filtrate was concentrated under reduced pressure to give the crude product, which was purified by silica gel flash column chromatography (Hexane: Ethyl Acetate = 18: 1) to afford compound **7** as white solid (430 mg, 97%). ^{1}H NMR ($CDCl_3$): 1.12 (s, 9H), 5.91 (s, 1H), 6.68 (d, *J* = 2.4 Hz, 1H), 6.72 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 7.47-7.37 (m, 7H), 7.71-7.69 (m, 4H);^{13}C NMR ($CDCl_3$): 19.4, 26.4, 97.3, 107.6, 108.8, 117.2, 124.2, 128.0, 130.4, 131.5, 135.3, 153.5, 154.9, 160.3, 161.0; HRMS (ESI): m/z calcd for C25H24N3O3Si $[M+H]^+$: 442.1581, found: 442.1564.

3-(1-(7-((*tert*-Butyldiphenylsilyl)oxy)-2-oxo-2H-chromen-4-yl)-1H-1,2,3-triazol-4-yl)-N-((2S,3R,4R,5R)-2,3,4,5,6-pentahydroxyhexyl)propanamide (BW-F-201)

To a mixture of compound **7** (22 mg, 0.05 mmol) and compound **5a** (13 mg, 0.05 mmol) in THF and water (v/v, 3:1, 4 mL) was added $CuSO_4 \cdot 5H_2O$ (2 mg, 0.01 mmol)and sodium ascorbate (4 mg, 0.02 mmol). The resulting mixture was stirred under reflux and monitored by TLC, which showed the reaction completion after 2 h. THF was removed under reduced pressure. The aqueous phase was extracted with ethyl acetate (2 mL × 3). The combined organic phase was washed with brine (5 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (DCM: MeOH = 15: 1)to afford BW-F-201 as white solid (25mg, 71%).^{1}H NMR (MeOD): 1.12 (s, 9H), 2.66 (t, *J* = 7.2 Hz, 2H), 3.10 (t, *J* = 7.2 Hz, 2H), 3.27-3.24 (m, 1H), 3.45-3.40 (m, 1H), 3.62-3.58 (m, 2H), 3.81-3.65 (m, 4H), 6.50 (s, 1H), 6.73 (d, *J* = 2.4 Hz, 1H), 6.83 (dd, *J* = 9.2 Hz, *J* = 2.4 Hz, 1H), 7.51-7.40 (m, 6H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.76-7.72 (m, 4H), 8.26 (s, 1H); ^{13}C NMR (MeOD): 18.8, 20.9, 25.3, 34.5, 42.1, 63.3, 69.9, 71.5, 71.8, 72.3, 106.4, 107.4, 108.4, 117.4, 123.3, 126.6, 127.8, 130.3, 131.3, 135.1, 146.8, 147.2, 155.5, 160.2, 160.7, 173.5; HRMS (ESI): m/z calcd for C36H43N4O9Si $[M+H]^+$: 703.2794, found: 703.2787.FR-IR (cm^{-1}) 2924, 2855, 1732, 1610, 1460, 1266, 741, 706. m.p. 144-146 ^{o}C.

3-(1-(7-((*tert*-Butyldiphenylsilyl)oxy)-2-oxo-2H-chromen-4-yl)-1H-1,2,3-triazol-4-yl)-N-methylpropanamide (BW-F-202)

To a mixture of compound **7** (80 mg, 0.18 mmol) and compound **5b** (20 mg, 0.18 mmol) in THF and water (v/v, 3:1, 8 mL) was added $CuSO_4 \cdot 5H_2O$ (5 mg, 0.02 mmol) and sodium ascorbate (8 mg, 0.04 mmol). The resulting mixture was stirred under reflux and monitored by TLC, which showed the reaction completion after 2 h. THF was removed under reduced pressure. The aqueous phase was extracted with ethyl acetate (4 mL × 3). The combined organic phase was washed with brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (DCM: MeOH = 30:1) to afford BW-F-202 as white solid (70 mg, 70 %). ^{1}H NMR ($CDCl_3$): 1.12 (s, 9H), 2.66 (t, *J* = 7.2 Hz, 2H), 2.76 (d, *J* = 4.8 Hz, 3H), 3.15 (t, *J* = 7.2 Hz, 2H), 5.92 (brs, 1H), 6.31 (s, 1H), 6.78-6.74 (m, 2H), 7.41-7.37 (m, 4H), 7.48-7.43 (m, 2H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.71-7.68 (m, 4H), 7.82 (s, 1H); ^{13}C NMR (MeOD): 18.8, 21.0, 25.1, 25.4, 34.5, 106.2, 107.5, 108.2, 117.3, 123.2, 126.6, 127.8, 130.3, 131.2, 135.1, 146.7, 147.2, 155.5, 160.1, 160.5, 173.5;HRMS (ESI): m/z calcd for C31H33N4O4Si $[M+H]^+$: 553.2266, found: 553.2252.FT-IR (cm^{-1}) 2924, 2854, 1736, 1610, 1456, 1264, 1146, 1002, 822, 739. m.p. 75-77 ^{o}C.

3-(1-(7-((*tert*-Butyldiphenylsilyl)oxy)-2-oxo-2H-chromen-4-yl)-1H-1,2,3-triazol-4-yl)-N-(4-methoxybenzyl)propanamide (BW-F-203)

To a mixture of compound **7** (50 mg, 0.11 mmol) and compound **5c** (24 mg, 0.11 mmol) in THF and water (v/v, 3:1, 4 mL) was added $CuSO_4 \cdot 5H_2O$ (2 mg, 0.01 mmol) and sodium ascorbate (4 mg, 0.02 mmol). The resulting mixture was stirred under reflux and monitored by TLC, which showed the reaction completion after 2 h. THF was removed under reduced pressure. The aqueous phase was extracted with ethyl acetate (2 mL × 3). The combined organic phase was washed with brine (5 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (Hexane: Ethyl Acetate = 2:1) to afford BW-F-203 as white solid (60 mg, 81 %). ^{1}H NMR ($CDCl_3$): 1.12 (s, 9H), 2.66 (t, *J* = 6.8 Hz, 2H), 3.14 (t, *J* = 6.8 Hz, 2H), 3.68 (s, 3H), 4.30 (d, *J*= 6.0 Hz, 2H),6.16 (brt, *J* = 5.6 Hz, 1H), 6.20 (s, 1H), 6.79-6.68 (m, 4H), 7.08 (d,*J* = 8.4 Hz, 2H), 7.41-7.37 (m, 4H), 7.49-7.43 (m, 2H),

7.60 (d,*J* = 8.8 Hz, 1H), 7.75-7.65 (m, 5H); ^{13}C NMR ($CDCl_3$): 19.4, 21.2, 26.3, 35.1, 43.0, 55.1, 105.9, 108.1, 108.1, 113.9, 117.8, 122.6, 126.6, 128.1, 129.0, 130.2, 130.4, 131.3, 135.3, 146.7, 147.3, 155.7, 158.9, 160.3, 160.4, 171.2;HRMS (ESI): m/z calcd for C38H39N4O5Si $[M+H]^+$: 659.2684, found: 659.2655.FT-IR (cm^{-1}) 2923, 2854, 1739, 1611, 1513, 1456, 1289, 1143, 822, 701. m.p. 87-89 ^oC.

BW-F-204

To a mixture of compound **7** (44 mg, 0.1 mmol) and alkyne-mPEG(specification 1000Da, 100 mg, 0.1 mmol) in THF and water (v/v 3:1, 4 mL) was added $CuSO_4 \cdot 5H_2O$ (2 mg, 0.01 mmol) and sodium ascorbate (4 mg, 0.02 mmol). The resulting mixture was stirred under reflux and monitored by TLC, which showed the reaction completion after 2 h. THF was removed under reduced pressure. The aqueous phase was extracted with ethyl acetate (2 mL × 3). The combined organic phase was washed with brine (5 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (DCM: MeOH = 20:1) to afford BW-F-204 as yellowish oil (50 mg, 38 %).^1H NMR ($CDCl_3$): 1.08 (s, 9H), 3.33 (s, 3H), 3.60 (m, 80H), 4.75 (s, 2H), 6.30 (s, 1H), 6.73 (m, 2H), 7-7 (m, 6H), 7-7 (m, 5H), 8 (s, 1H); ^{13}C NMR ($CDCl_3$): 19.4, 26.3, 59.0, 64.4, 70.1, 70.4, 70.5, 71.9, 106.2, 108.1, 108.1, 117.8, 123.6, 126.7, 128.1, 130.4, 131.3, 135.3, 146.2, 146.8, 155.7, 160.2, 160.5;The spectra exhibit multiple peaks becausethe starting material PEG1000comprises polymer chains with different lengths. the signal centering around m/z 1474.6 corresponds to BW-F-204 with 44(MW of one PEG unit (CH_2CH_2O) is 44) repeat units. MS(MALDI): 1342.537, 1386.563, 1430.596, 1474.630, 1518.667, 1562.698, 1606.720, 1650.741.FT-IR (cm^{-1}) 2871, 1739, 1610, 1453, 1348, 1287, 1102, 1002, 732, 701.

Stability studies of probes

Concentration of each probe was 10 uM, concentration of F^- (NaF) was 1mM, solvent is PBS (1X, MeOH 0.5 %, pH = 7.4). For BW-F-204, the final concentration was 14.7ug/mL, and the average MW of BW-F-204 is 1473, so the final concentration of BW-F-204 was about 10 uM.

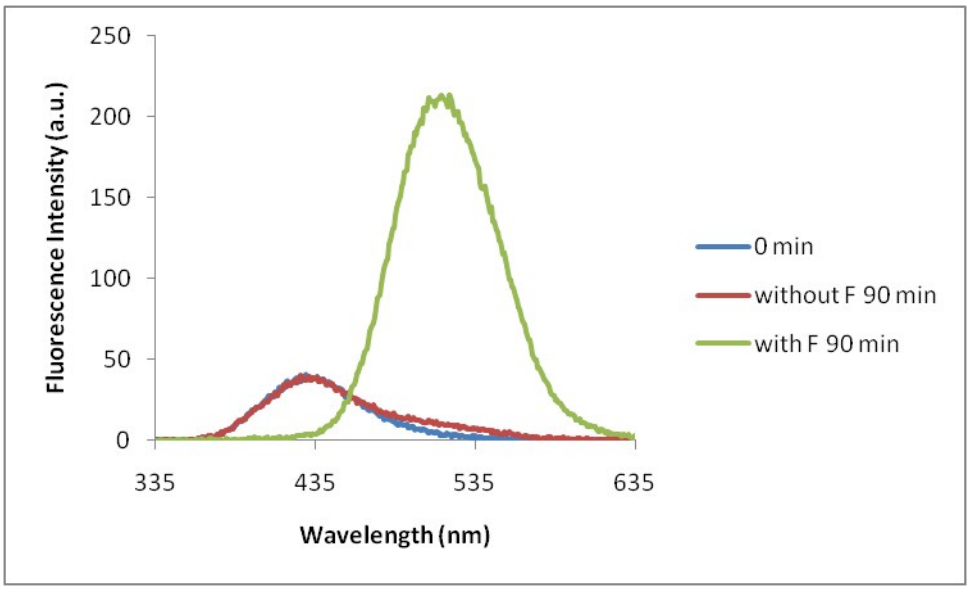


Figure 1 Emission spectra of BW-F-101 λ_{ex}= 325 nm.15 uL stock solution of the probe (final concentration of probe was 10 uM) was added into 2.985 mL PBS (1X, PH = 7.4) with or without 1 mM NaF at room temperature. Spectra were recorded at 0 min and 90 min.

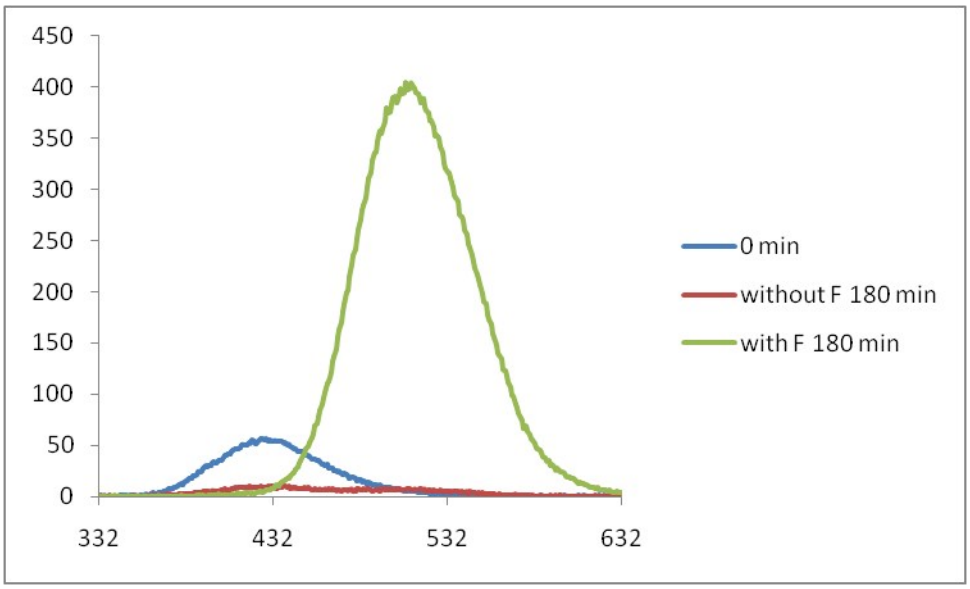


Figure 2 Emission spectra of BW-F-102 λ_{ex}= 322 nm. 15 uL stock solution of the probe (final concentration of probe was 10 uM) was added into 2.985 mL PBS (1X, PH = 7.4) with or without 1 mM NaF at room temperature. Spectra were recorded at 0 min and 180 min.

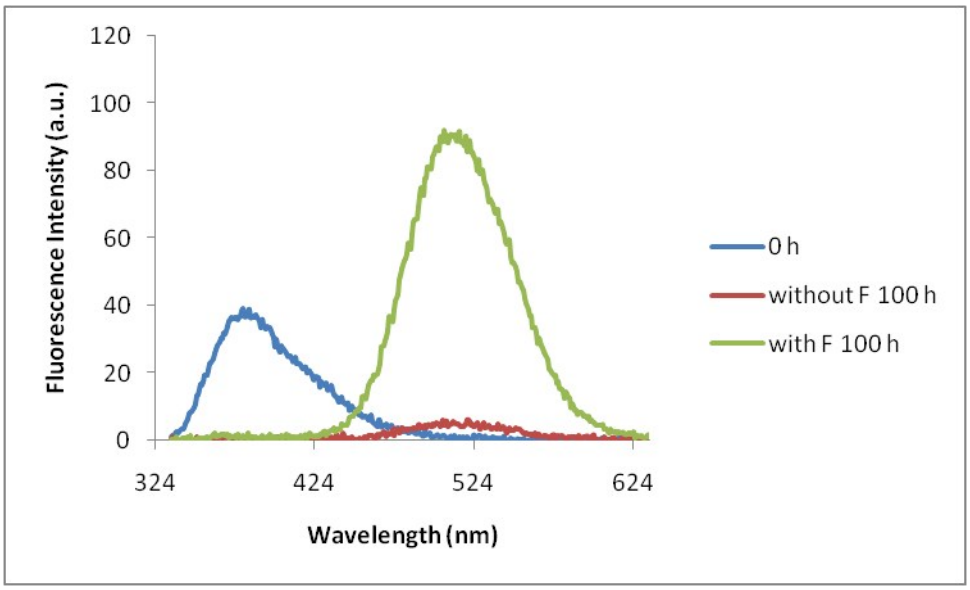


Figure 3 Emission specra of BW-F-103 λ_{ex}= 324 nm. 15 uL stock solution of the probe (final concentration of probe was 10 uM) was added into 2.985 mL PBS (1X, PH = 7.4) with or without 1 mM NaF at room temperature. Spectra were recorded at 0 h and 100 h.

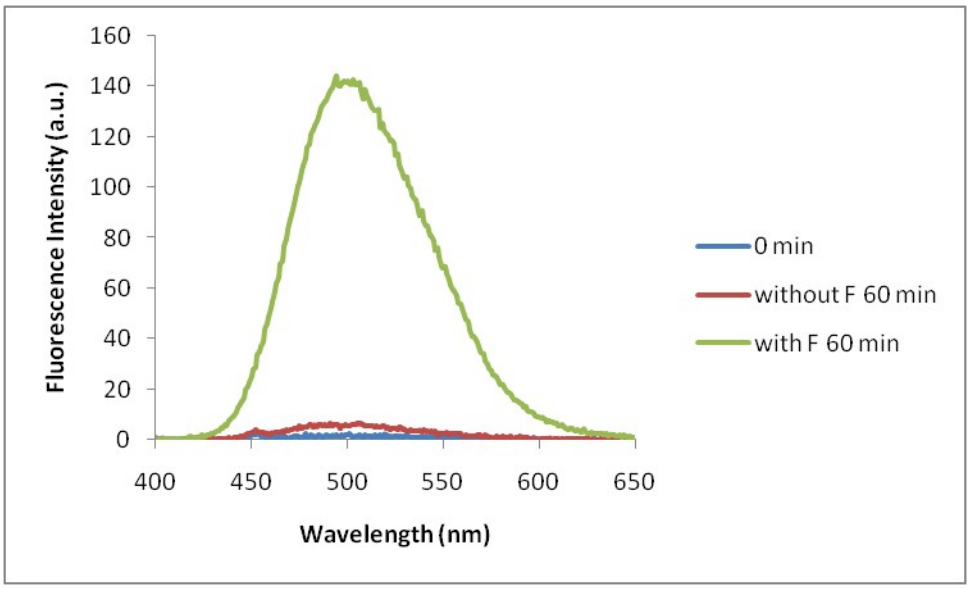


Figure 4Emission spectra of BW-F-201 λ_{ex}= 390 nm. 15 uL stock solution of the probe (final concentration of probe was 10 uM) was added into 2.985 mL PBS (1X, PH = 7.4) with or without 1 mM NaF at room temperature. Spectra were recorded at 0 min and 60 min.

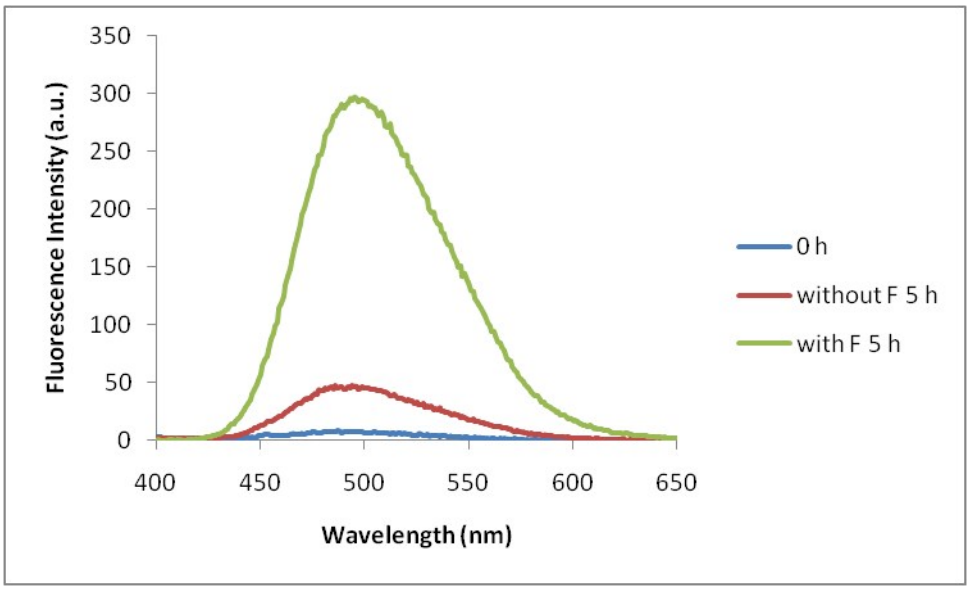


Figure 5 Emission spectra of BW-F-202 λ_{ex} = 390 nm. 15 uL stock solution of the probe (final concentration of probe was 10 uM) was added into 2.985 mL PBS (1X, PH = 7.4) with or without 1 mM NaF at room temperature. Spectra were recorded at 0 h and 5 h.

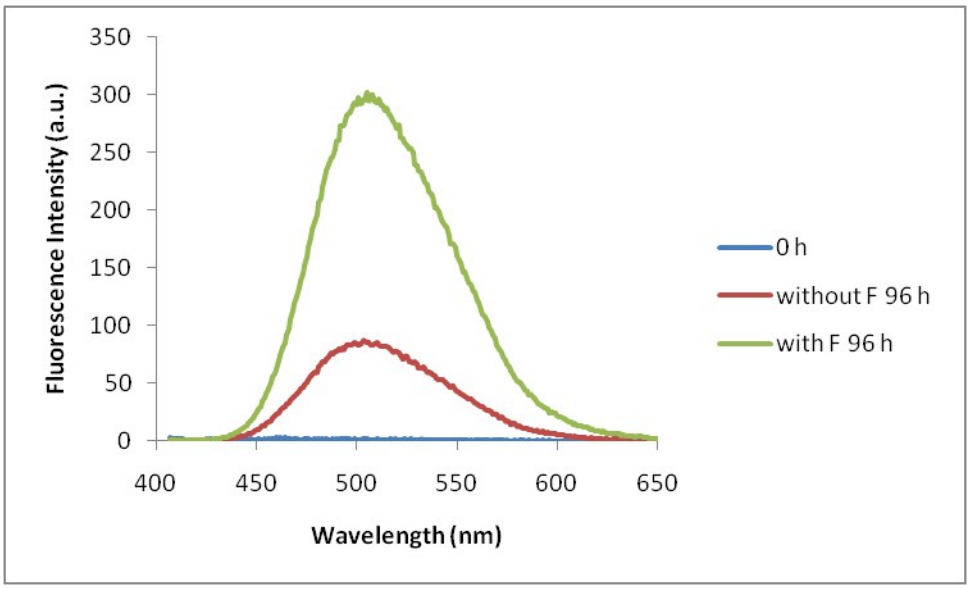


Figure 6 Emission spectra of BW-F-203 λ_{ex} = 397 nm. 15 uL stock solution of the probe (final concentration of probe was 10 uM) was added into 2.985 mL PBS (1X, PH = 7.4) with or without 1 mM NaF at room temperature. Spectra were recorded at 0 h and 96 h.

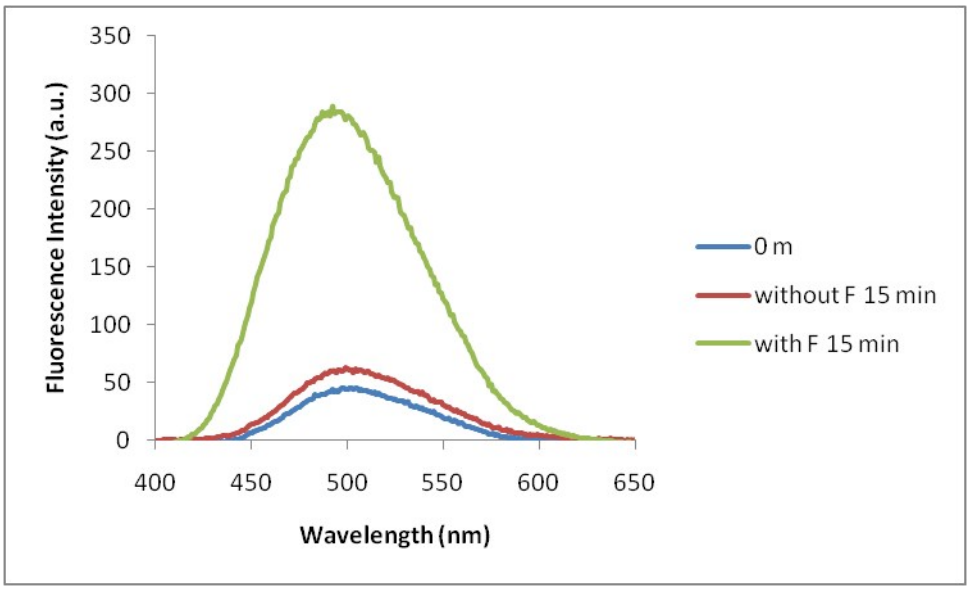


Figure 7 Emission spectra of BW-F-204 λ_{ex} = 390 nm. 15 uL stock solution of the probe (final concentration of probe was 10 uM) was added into 2.985 mL PBS (1X, PH = 7.4) with or without 1 mM NaF at room temperature. Spectra were recorded at 0 min and 15 min.

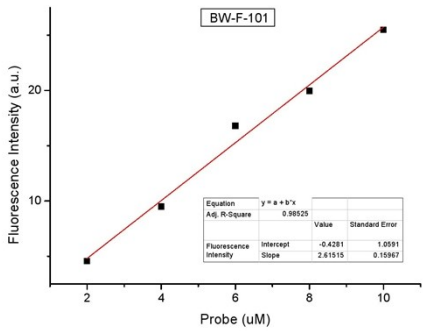
Solubility study of probes

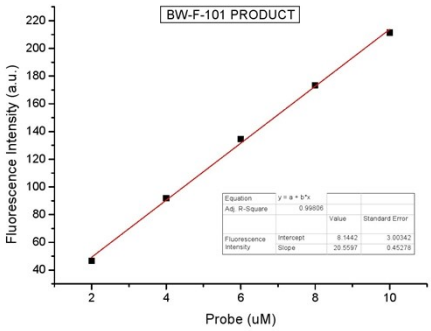
Dissolved the probes in PBS (1X, pH=7.4 0.5% MeOH) at r.t. for 5 min. The fluorescence intensities was recorded (Table S1). The plots (figure S8) show the relationship between the concentration of probes or products with their fluorescence intensities. The results shows the fluorescence intensities of all the probes or product are linearly dependent on their concentrations, which means all these compounds could be fully dissolved in the solution at this condition.

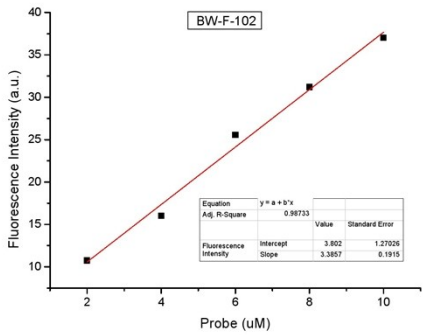
Name	Ex(nm)	Em(nm)	Slit width em (nm)	Slit width ex (nm)
BW-F-101	325	512	3	3
BW-F-101 PRODUCT	325	512	1.5	3
BW-F-102	322	507	3	3
BW-F-102 PRODUCT	322	507	1.5	3
BW-F-103	324	510	3	5

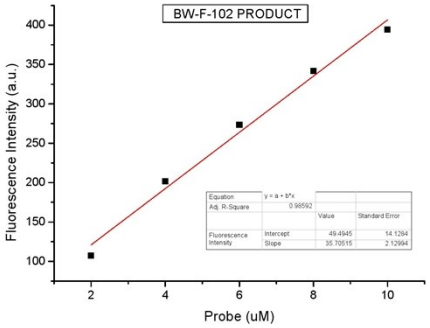
BW-F-103 PRODUCT	324	510	1.5	3
BW-F-201	390	500	5	10
BW-F-201 PRODUCT	390	500	3	3
BW-F-202	390	495	3	5
BW-F-202 PRODUCT	390	495	3	3
BW-F-203	397	503	5	10
BW-F-203 PRODUCT	397	503	3	3
BW-F-204	390	495	5	5
BW-F-204 PRODUCT	390	495	3	3

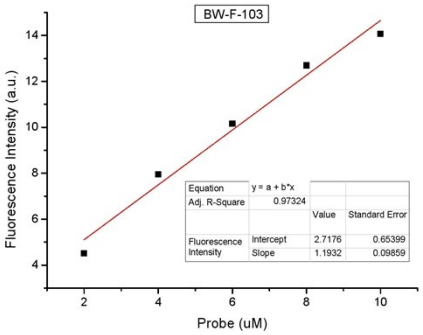
Table 1. The conditions of fluorescence studies.







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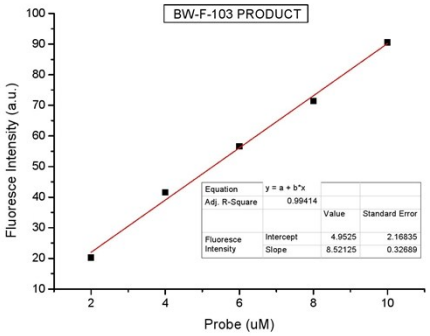
Fluorescence Intensity (a.u.)
Probe (uM)
Equation y = a + b*x
Adj. R-Square 0.97324
Value Standard Error
Fluorescence Intensity Intercept 2.7176 0.65399
Fluorescence Intensity Slope 1.1932 0.09859


BW-F-103 PRODUCT
Fluoresce Intensity (a.u.)
Probe (uM)
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Value Standard Error
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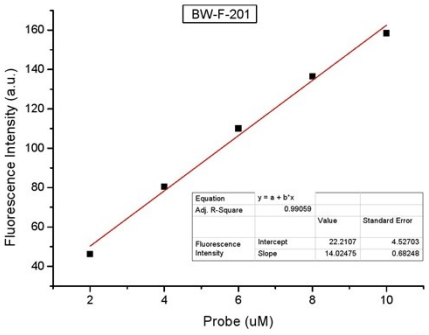
Fluoresce Intensity Slope 8.52125 0.32689


BW-F-201
Fluorescence Intensity (a.u.)
Probe (uM)
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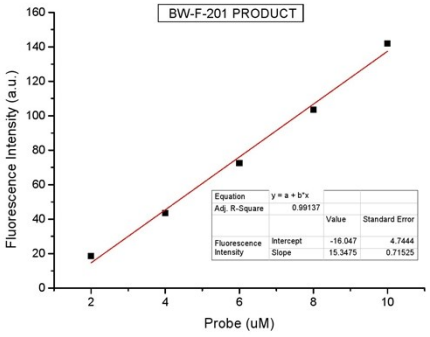
Adj. R-Square 0.99059
Value Standard Error
Fluorescence Intensity Intercept 22.2107 4.52703
Fluorescence Intensity Slope 14.02475 0.68248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Probe (uM)
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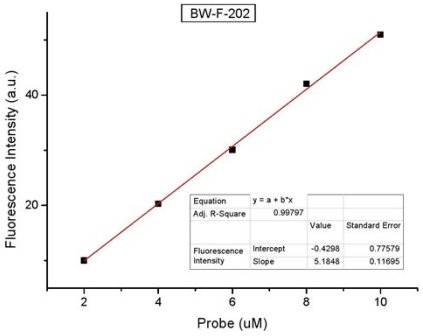
Fluorescence Intensity Slope 15.3475 0.71525


BW-F-202
Fluorescence Intensity (a.u.)
Probe (uM)
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Value Standard Error
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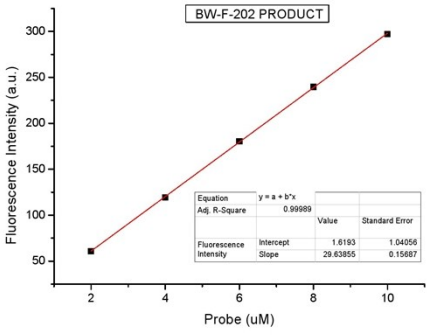
Fluorescence Intensity Slope 5.1848 0.11695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Probe (uM)
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Value Standard Error
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Fluorescence Intensity Slope 29.63855 0.15687

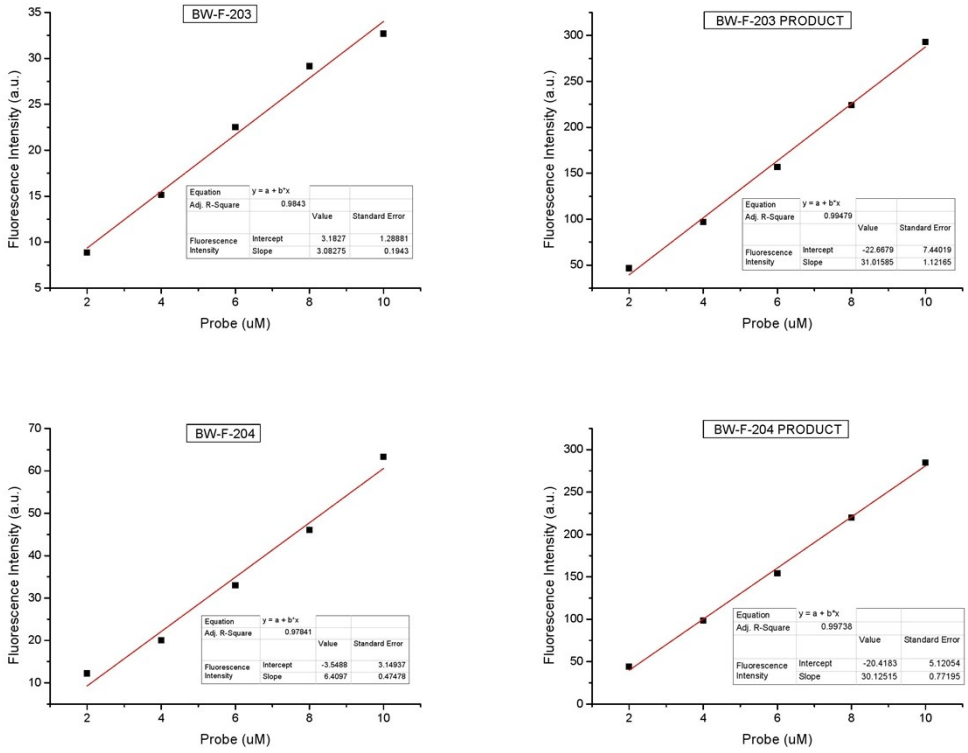


Figure 8. solubility studies of probes

Quantum yield determination

The quantum yields of probes in PBS were calculated using eq. 1

$$\Phi_X = \Phi_{ST}\left(\frac{Grad_X}{Grad_{ST}}\right)\left(\frac{\eta_X^2}{\eta_{ST}^2}\right) \quad (1)$$

Where the subscripts ST and X denote standard and test respectively, Φ is the fluorescence quantum yield, Grad is the gradient from the plot of integrated fluorescence intensity vs absorbance, and η the refractive index of the solvent.

Quinine Sulphate was used as standard for BW-F-101, BW-F-102 and BW-F-103, which has a quantum yield of 0.546 when dissolved in 1N H2SO4

Coumarin 120 was used as standard for BW-F-201, BW-F-202, BW-F-203 and BW-F-204, which has a quantum yield of 0.51 when dissolved in methanol.

1N (0.5M) H2SO4 has a refractive index of 1.346, methanol has a refractive index of 1.327, while the refractive index of PBS is 1.375.

The results are shown in table 2

Probe	BW-F-101	BW-F-102	BW-F-103	BW-F-201	BW-F-202	BW-F-203	BW-F-204
Φ	0.270	0.302	0.260	0.341	0.299	0.261	0.334

Table 2 Quantum yield of probes

Second-order rate constantsdetermination

15 uL stock solution of the probe (2mM in methanol, final concentration of the probeis10 uM) was added into 2.985mL PBS (1X, PH = 7.4), containing 200, 500, and 1000 uM NaF, respectively,at room temperature. The fluorescence changes were recorded. The reaction rate constant, k_{obs}, was calculatedfor each concentration of NaF by fitting the increase in fluorescence intensity versus time using eq.2

$$Y = 1 - \exp(-k_{obs}t) \quad (2)$$

Where Y is fluorescence intensity, t is time in minutes. The pseudo-first-order rate constant, k_{obs}, was then plotted against the concentration of NaF to yield the second-order rate constant using eq.3

$$k_{obs} = k_2[F^-] \quad (3)$$

where k_2 is the second-order rate constant.

The results are shown in table 3

Name	Ex(nm)	Em(nm)	$k_{obs200}(min^{-1})$	$k_{obs500}(min^{-1})$	$k_{obs1000}(min^{-1})$	$k_2(M^{-1}s^{-1})$
BW-F-101	325	512	0.0067	0.0157	0.0326	0.54±0.04
BW-F-102	322	507	0.0072	0.0146	0.0233	0.33±0.02
BW-F-103	324	510	0.0002	0.0004	0.0006	0.0083±0.0005
BW-F-201	390	500	0.0082	0.0179	0.0352	0.56±0.03
BW-F-202	390	495	0.0041	0.0069	0.0097	0.12±0.03
BW-F-203	397	503	0.0002	0.0004	0.0007	0.010±0.002

BW-F-204*	390	495	0.0455	0.1052	0.2075	3.4±0.2

Table 3. Rate constants of probes (n=3 p=0.95). *for the BW-F-204, we used the average MW 1473g/mol to calculate the rate constants

Sensitivity of BW-F-204

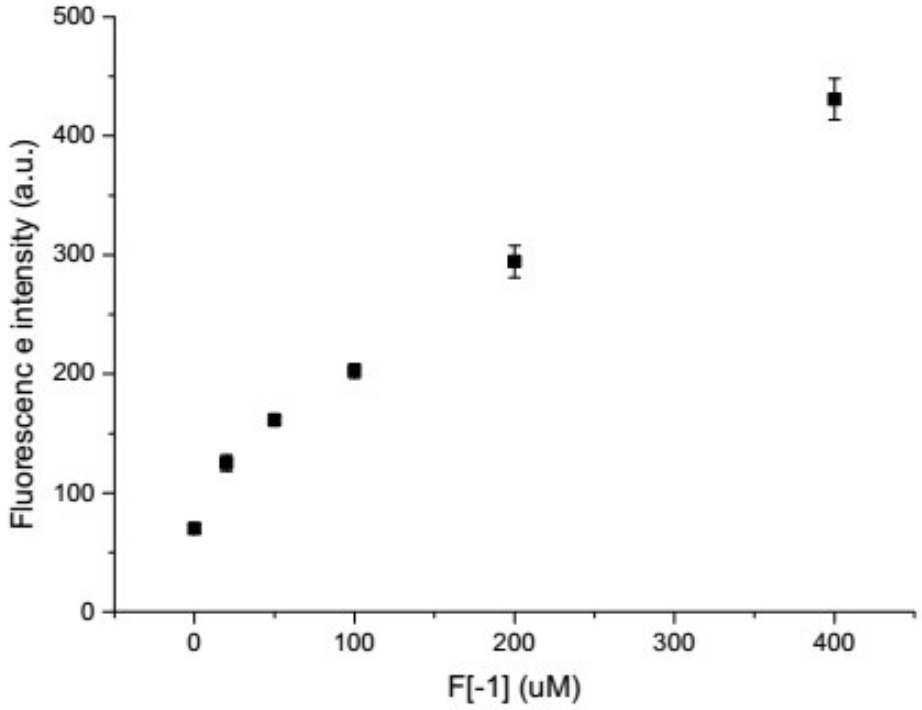


Figure 9. Fluorescence intensity of BW-F-204 in the presence of F^- at various concentrations in PBS.Concentration of probe was 50 uM. F^-(NaF)concentration was 0, 20, 50, 100, 200, and 400 uM. Solvent was pure PBS 1X. Each recordwas obtained 15 min after F^- addition at 25 °C.

Compound Cytotoxicity

MB-231 (ATCC® HTB-26™) cells were maintained in DMEM (Dulbecco's Modified Eagle's Medium) supplemented with 10% fetal bovine serum (MidSci; S01520HI) and 1% penicillin-streptomycin (Sigma-Aldrich; P4333) at 37 °C with 5% CO_2. The cells were seeded into 96-well plate one day before the cytotoxicity experiment. Different concentrations of BW-F-204 (1.56 M, 3.13 M, 6.25 M, 12.5 M, 25 M) was added into the cell culture media and incubated for 24 hours at 37 °C. The cell viability was measured by crystal violet assay. Basically, after incubation with compound BW-F-204, the cells were washed with PBS and fixed by 4 % paraformaldehyde in PBS for 30 minutes at room temperature. The cells were then stained with 0.05% crystal violet (Sigma-Aldrich; CO775) for 10 minutes and washed with ddH_2O for two times. Thereafter, the well plate was air-dry and 100 μL of 33% acetic acid was added in each well. The absorbance at 570 nm was measured by a PerkinElmer 1420 Multilabel Counter.

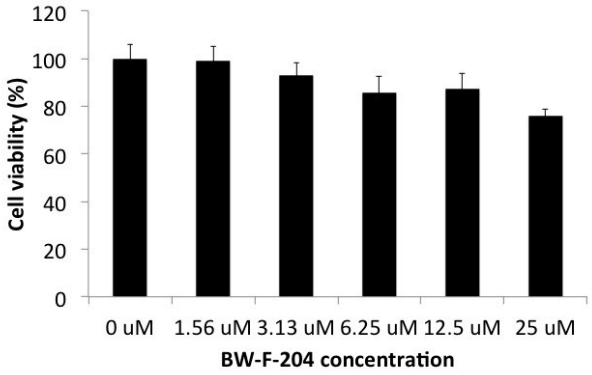


Figure 10. MB-231 cell viability under different BW-F-204 concentrations.

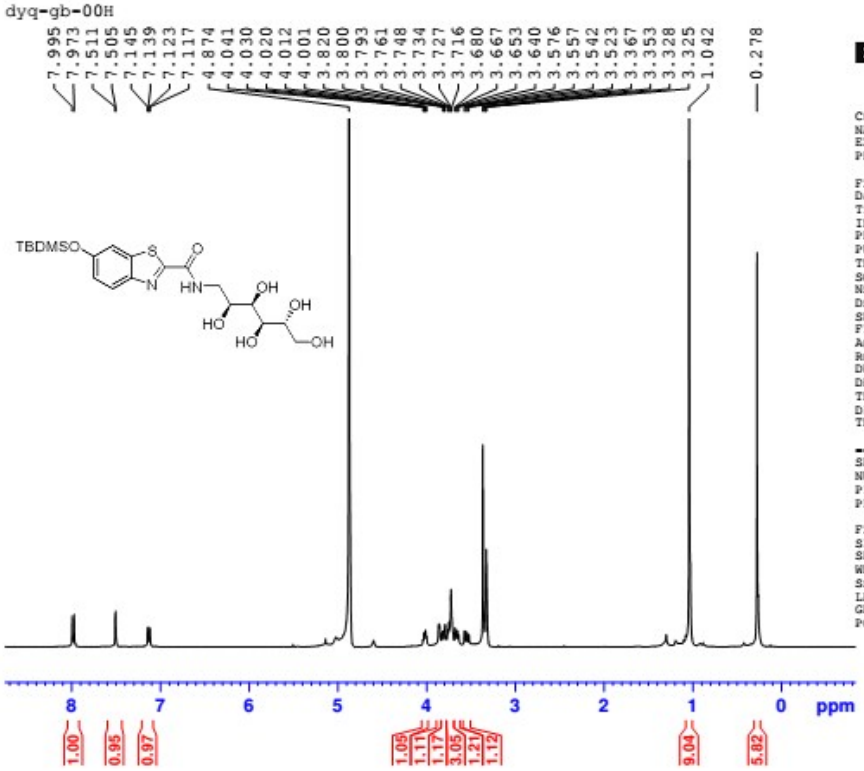
Fluorescent cell imaging

MB-231 (ATCC® HTB-26™) cells were maintained in DMEM (Dulbecco's Modified Eagle's Medium) supplemented with 10% fetal bovine serum (MidSci; S01520HI) and 1% penicillin-streptomycin (Sigma-Aldrich; P4333) at 37 ° C with 5% CO_2. One day before the imaging, the cells were seeded onto coverslips (VWR; 48366 067) put in the 6-well plate (NUNC; 140675). Different concentrations (0 □M, 20 □M, 100 □M) of NaF were added into the cell culture and

incubated with cells for half an hour at 37 ° C. The cell culture supernatant was then removed. Thereafter, 10 □M of the probe BW-F-204 was dissolved in the DMEM and incubated with the cells for half an hour at 37 ° C. The supernatant was then removed and the cells was washed with phosphate-buffered saline (Corning; 21-030-CV) followed by incubation with 4% paraformaldehyde in PBS for 30 minutes at room temperature. The coverslips that contain the fixed cells were mounted onto the glass slides using the ProLong®mounting media (Invitrogen; PL36934). The cell images were obtained using a Zeiss fluorescent microscope under the FITC channel (excitation: 488 nm; emission: 512 nm).

1. B. Ke, W. Chen, N. Ni, Y. Cheng, C. Dai, H. Dinh and B. Wang, *Chem Commun (Camb)*, 2013, **49**, 2494-2496.
2. G. Meroni., M. Rajabi., P. Ciana., A. Maggi. and E. Santaniello., *ARKIVOC*, 2010, 53-60.
3. E. D. Funder, A. B. Jensen, T. Torring, A. L. Kodal, A. R. Azcargorta and K. V. Gothelf, *J Org Chem*, 2012, **77**, 3134-3142.
4. W. Zhang, Z. Li, M. Zhou, F. Wu, X. Hou, H. Luo, H. Liu, X. Han, G. Yan, Z. Ding and R. Li, *Bioorg Med Chem Lett*, 2014, **24**, 799-807.

NMR spectra



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RG                          101
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DE                      6.50 usec
TE                      298.0 K
D1                    1.00000000 sec
TD0                           1

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P1                       13.55 usec
PLW1                16.00000000 W

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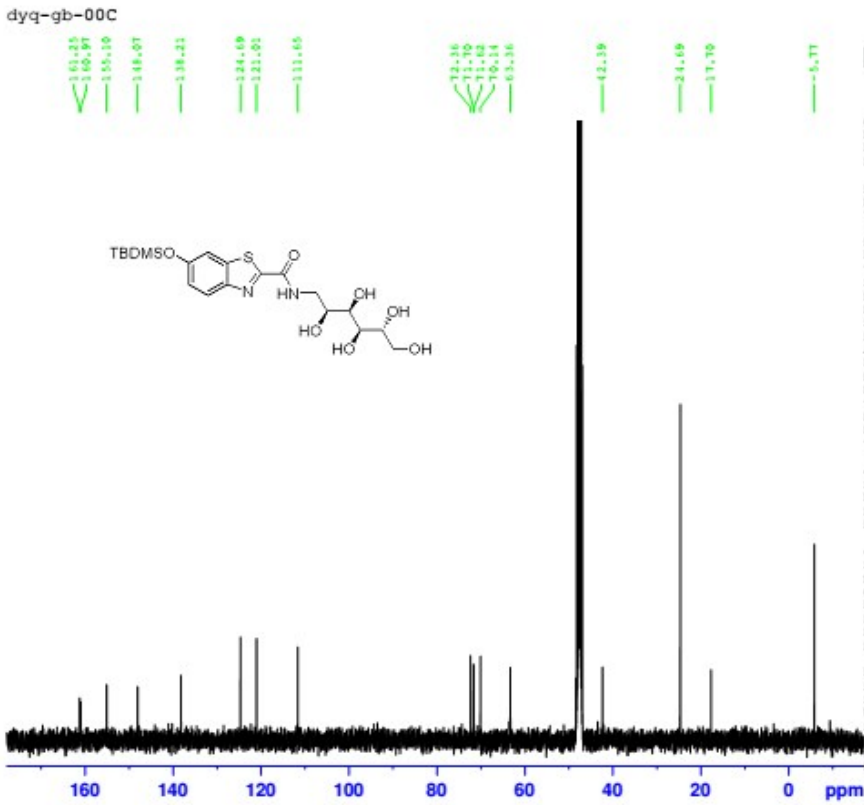

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DE                      6.50 usec
TE                      298.4 K
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NUC2                        1H
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PCPD2                    90.00 usec
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PLW12                0.36267000 W
PLW13                0.29376000 W

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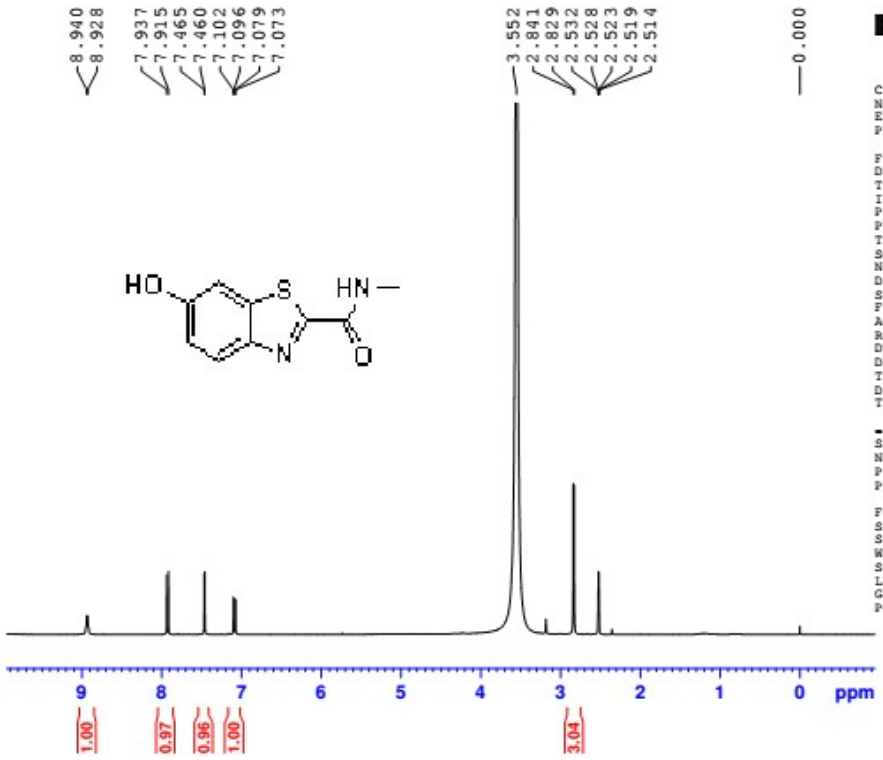
dyq-gd-1 1H



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FIDRES               0.122266 Hz
AQ                4.0894465 sec
RG                      32
DW                  62.400 usec
DE                   6.50 usec
TE                  298.0 K
D1                1.00000000 sec
TD0                      1

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NUC1                    1H
P1                   13.55 usec
PLW1           16.00000000 W

F2 - Processing parameters
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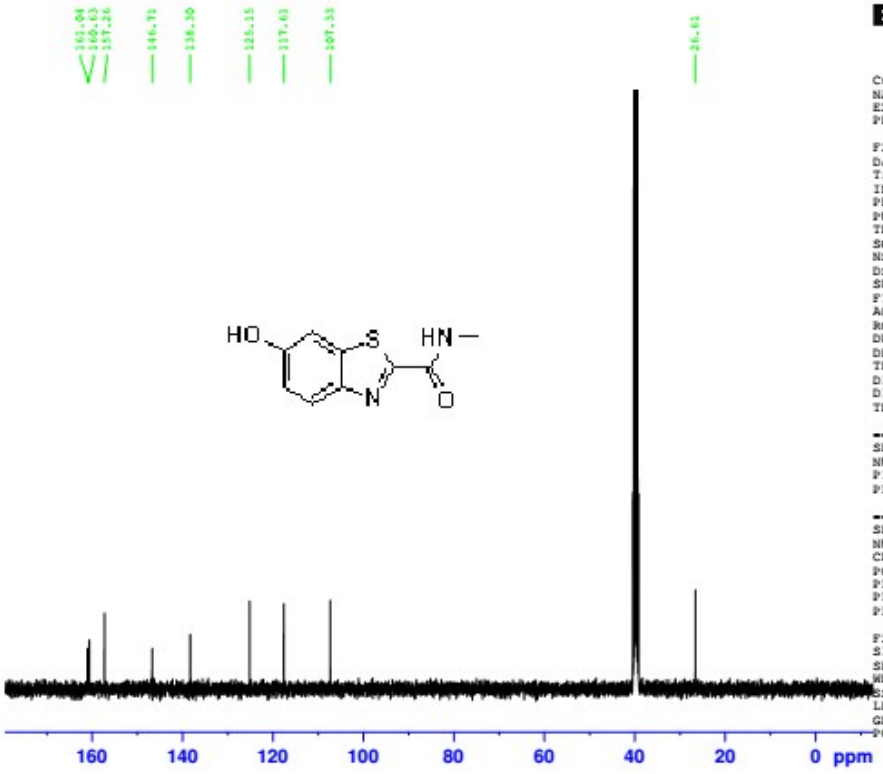

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RG                     203
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DE                   6.50 usec
TE                  298.0 K
D1                2.00000000 sec
D11               0.03000000 sec
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NUC1                    13C
P1                    9.00 usec
PLW1           62.00000000 W

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PCPD2                90.00 usec
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PLW13           0.29376000 W

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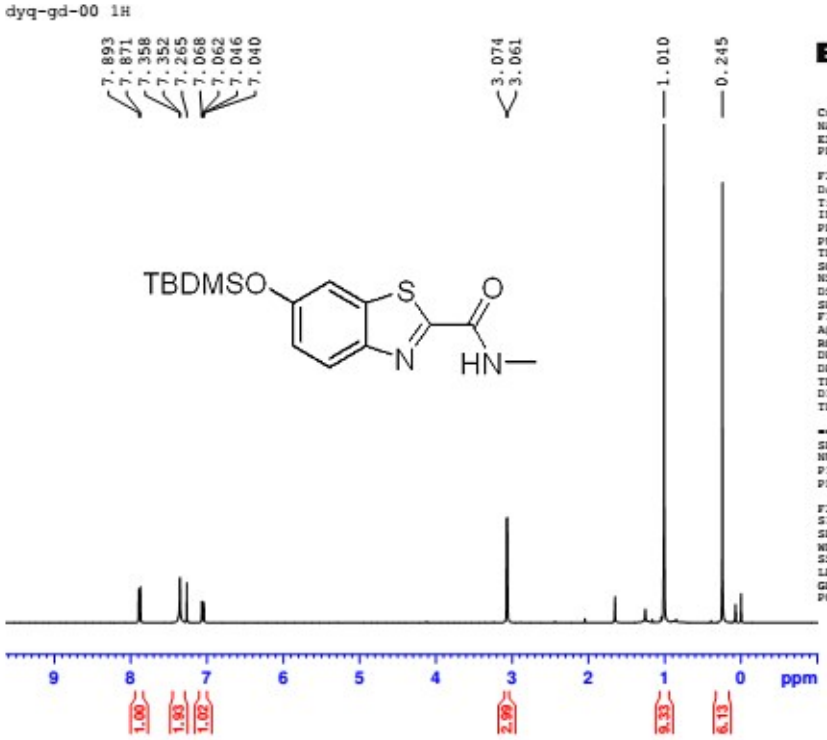

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DE                     6.50 usec
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D1                  1.00000000 sec
TD0                           1

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P1                       13.55 usec
PLW1             16.00000000 W

F2 - Processing parameters
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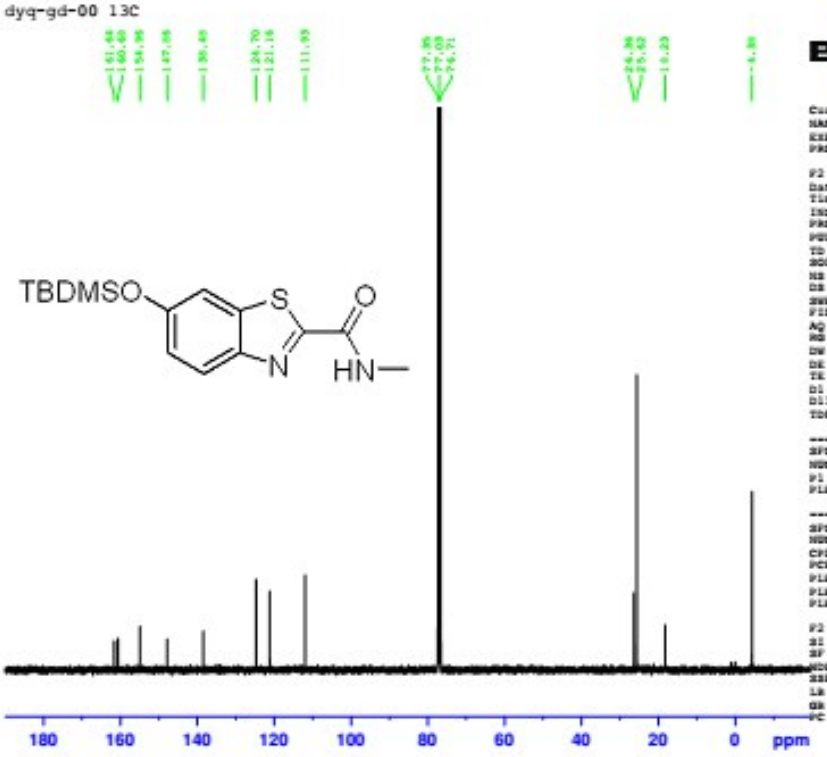
dyq-gd-00 13C



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TD0                           1

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NUC1                       13C
P1                        9.00 usec
PLW1             63.00000000 W

======== CHANNEL f2 ========
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NUC2                        1H
CPDPRG[2              waltz16
PCPD2                    90.00 usec
PLW2             16.00000000 W
PLW12             0.36247000 W
PLW13             0.29376000 W

F2 - Processing parameters
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SF                100.6152830 MHz
WDW                        EM
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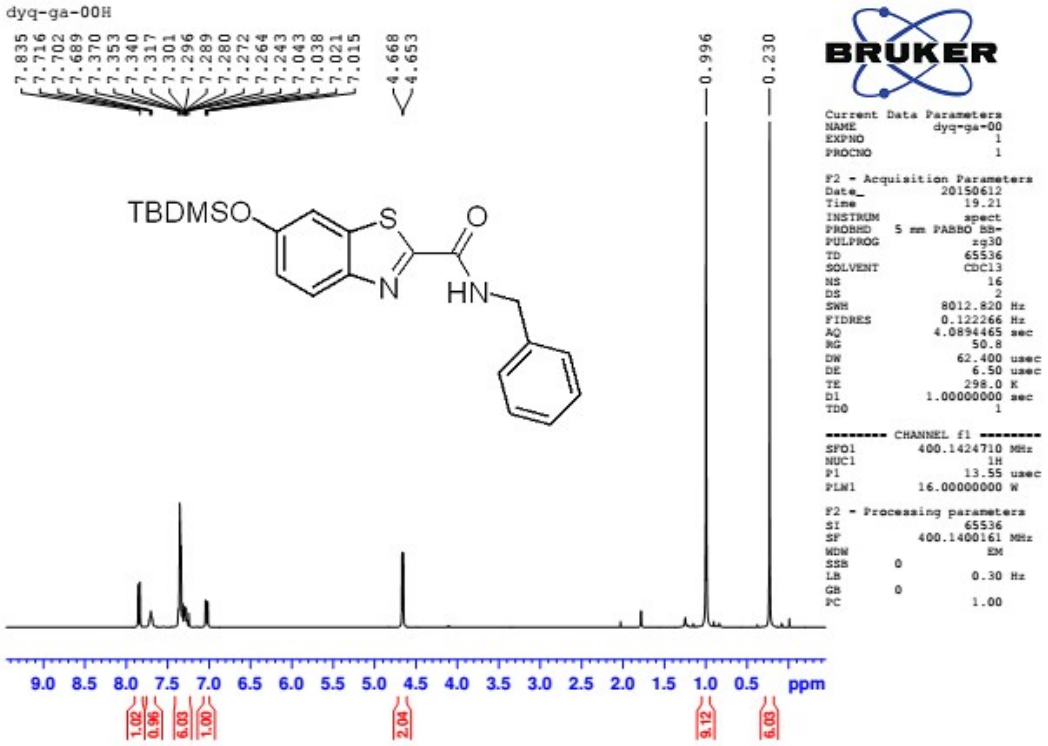
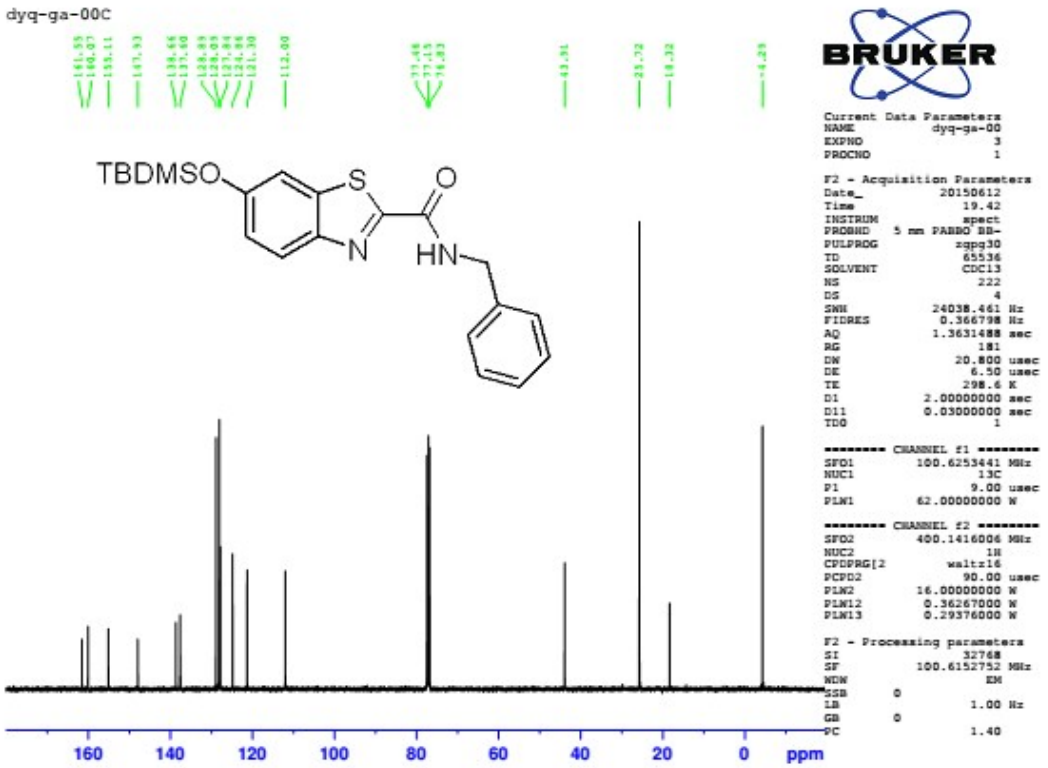
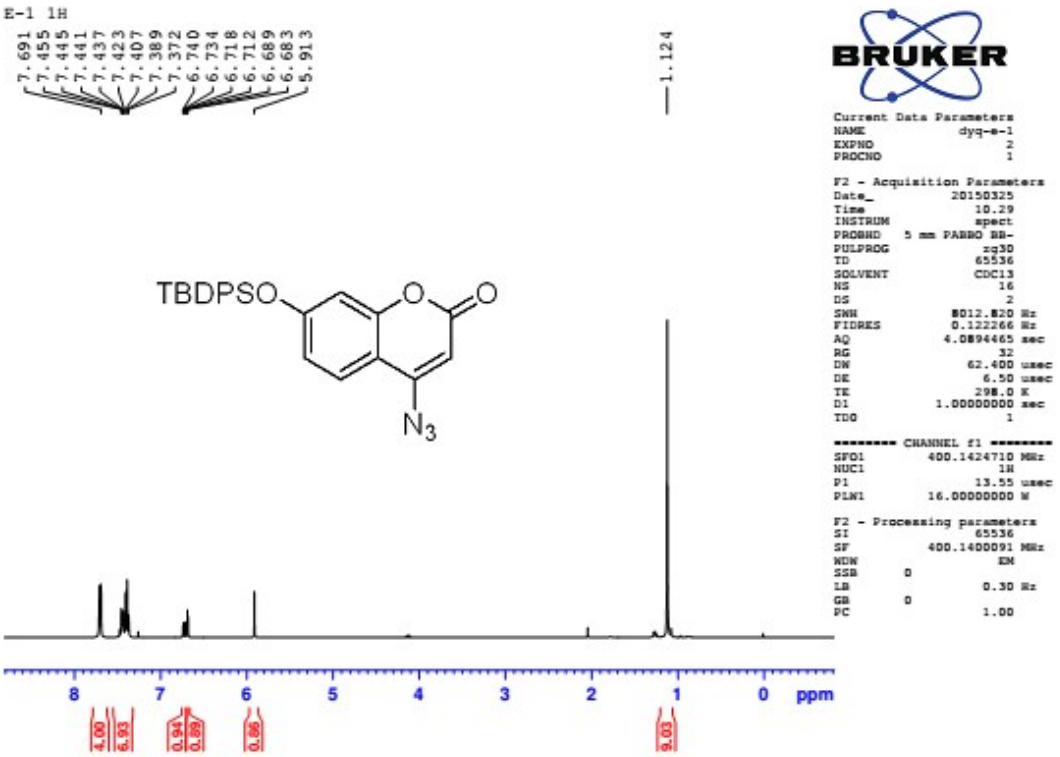
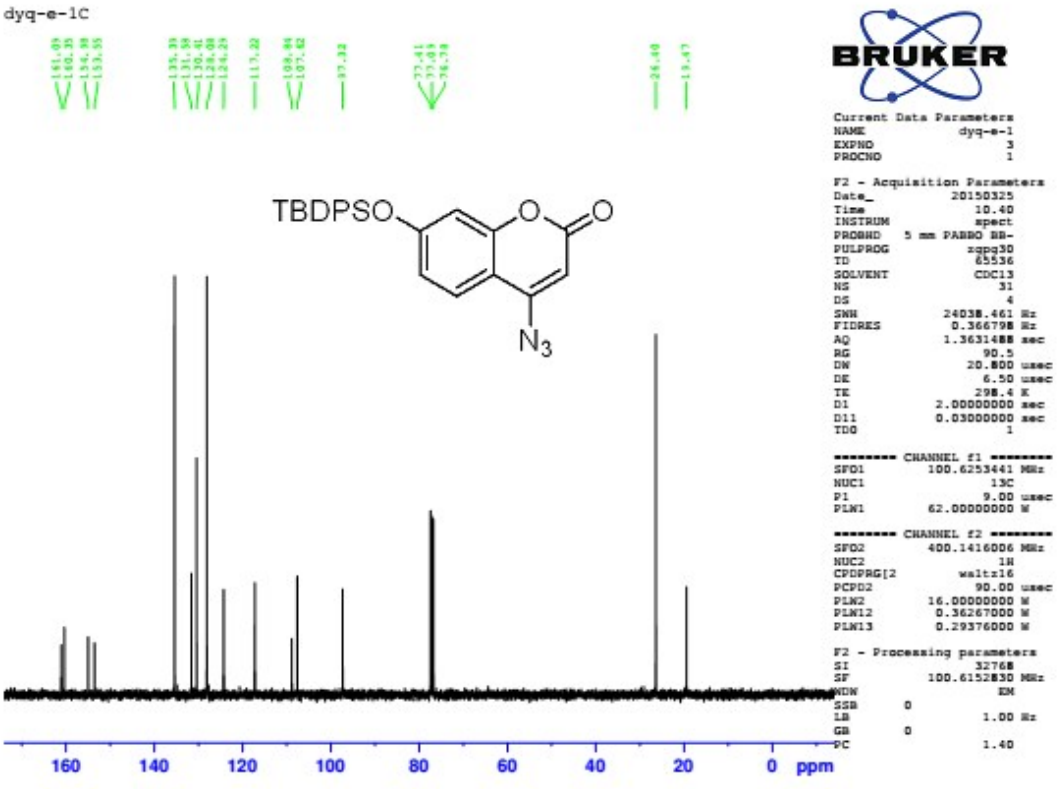
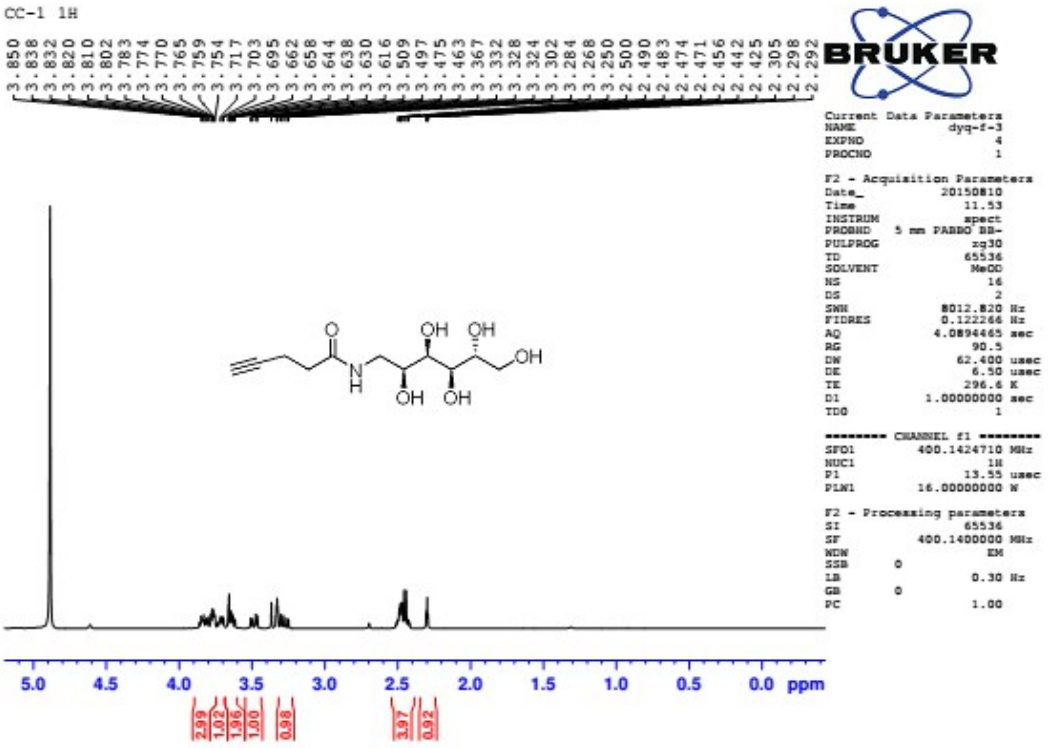
GB           0
PC                        1.40
```

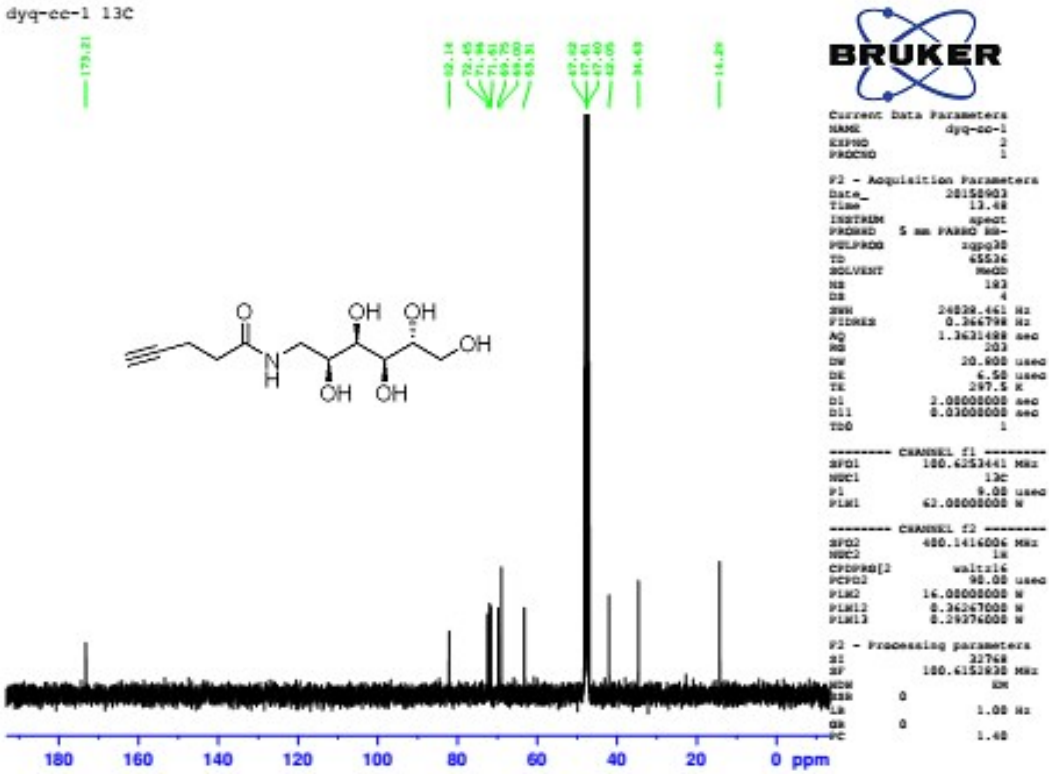

dyq-ga-00H
7.835
7.716
7.702
7.689
7.370
7.353
7.340
7.317
7.301
7.296
7.289
7.280
7.272
7.264
7.243
7.043
7.038
7.021
7.015
4.668
4.653
0.996
0.230
TBDMSO
S
O
N
HN
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.02
0.96
6.03
1.00
2.04
9.12
6.03
BRUKER
Current Data Parameters
NAME dyq-ga-00
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150612
Time 19.21
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 50.8
DW 62.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1424710 MHz
NUC1 1H
P1 13.55 usec
PLW1 16.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1400161 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


dyq-ga-00C
161.55
160.07
153.11
147.93
138.66
135.60
128.83
128.03
127.84
124.86
121.30
112.00
77.48
77.15
76.83
43.51
25.72
18.32
-4.23
TBDMSO
S
O
N
HN
160 140 120 100 80 60 40 20 0 ppm
BRUKER
Current Data Parameters
NAME dyq-ga-00
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150612
Time 19.42
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 222
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 181
DW 20.800 usec
DE 6.50 usec
TE 298.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6253441 MHz
NUC1 13C
P1 9.00 usec
PLW1 62.00000000 W
======== CHANNEL f2 ========
SFO2 400.1416006 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 16.00000000 W
PLW12 0.36267000 W
PLW13 0.29376000 W
F2 - Processing parameters
SI 32768
SF 100.6152752 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

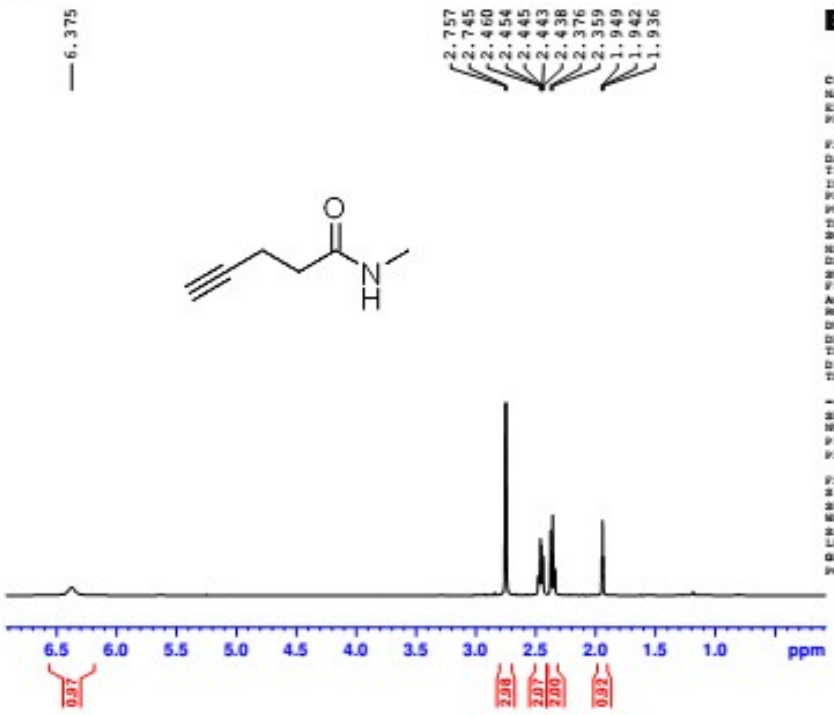

E-1 1H
7.691
7.455
7.445
7.441
7.437
7.423
7.407
7.389
7.372
6.740
6.734
6.718
6.712
6.689
6.683
5.913
1.124
TBDPSO
O
O
N3
8
7
6
5
4
3
2
1
0
ppm
4.00
6.93
0.94
0.89
0.86
9.03
BRUKER
Current Data Parameters
NAME dyq-e-1
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150325
Time 10.29
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 32
DW 62.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1424710 MHz
NUC1 1H
P1 13.55 usec
PLW1 16.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1400091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


dyq-e-1C
151.09
160.35
154.39
153.55
135.39
131.59
130.41
128.04
124.29
117.22
108.84
107.82
97.32
77.41
77.05
76.78
26.40
13.47
TBDPSO
O
O
N3
160
140
120
100
80
60
40
20
0
ppm
BRUKER
Current Data Parameters
NAME dyq-e-1
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150325
Time 10.40
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 31
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 90.5
DW 20.800 usec
DE 6.50 usec
TE 298.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6253441 MHz
NUC1 13C
P1 9.00 usec
PLW1 62.00000000 W
======== CHANNEL f2 ========
SFO2 400.1416006 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 16.00000000 W
PLW12 0.36267000 W
PLW13 0.29376000 W
F2 - Processing parameters
SI 32768
SF 100.6152830 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


CC-1 1H
3.850 3.838 3.832 3.820 3.810 3.802 3.783 3.774 3.770 3.765 3.759 3.754 3.717 3.703 3.695 3.662 3.658 3.644 3.638 3.630 3.616 3.509 3.497 3.475 3.463 3.367 3.332 3.328 3.324 3.302 3.284 3.268 3.250 2.500 2.490 2.483 2.474 2.471 2.456 2.442 2.425 2.305 2.298 2.292
O
OH OH
OH
N
H
OH OH
5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.99 1.02 1.36 1.00 0.98 3.97 0.92
BRUKER
Current Data Parameters
NAME dyq-f-3
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150810
Time 11.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 90.5
DW 62.400 usec
DE 6.50 usec
TE 296.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1424710 MHz
NUC1 1H
P1 13.55 usec
PLW1 16.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1400000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


dyq-cc-1 13C
179.21
92.14 72.45 71.67 71.20 69.60 63.91
57.02 57.60 57.05 42.05 34.43 14.29
O
OH OH
OH
N
H
OH OH
180 160 140 120 100 80 60 40 20 0 ppm
BRUKER
Current Data Parameters
NAME dyq-cc-1
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150903
Time 13.48
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 193
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 297.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6253441 MHz
NUC1 13C
P1 9.00 usec
PLW1 62.00000000 W
======== CHANNEL f2 ========
SFO2 400.1416006 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 98.00 usec
PLW2 16.00000000 W
PLW12 0.36247000 W
PLW13 0.29376000 W
F2 - Processing parameters
SI 32768
SF 100.6152830 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

dyq-cd-1H



BRUKER

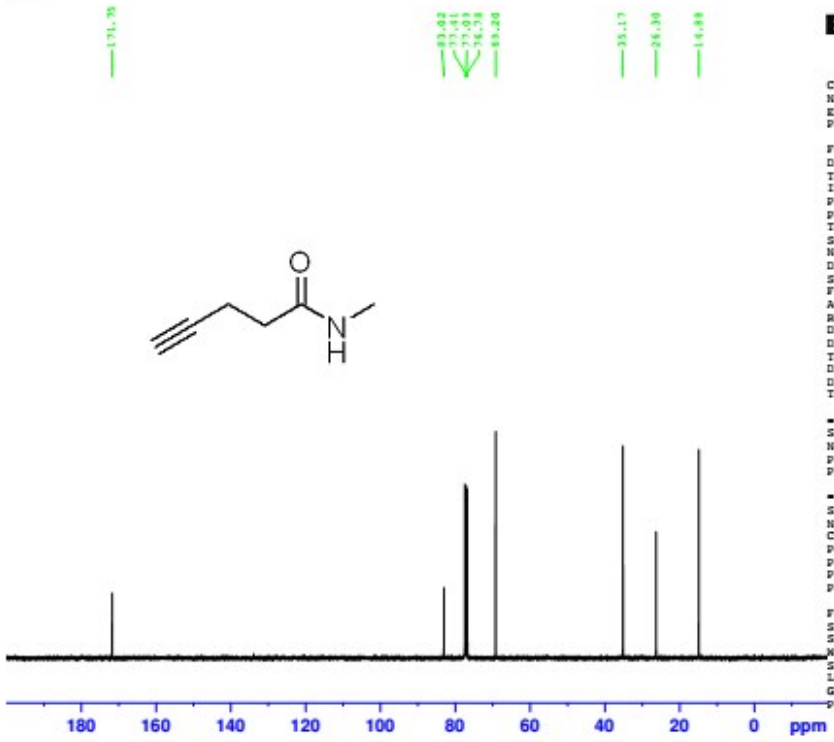
```
Current Data Parameters
NAME                  dyq-cd-1
EXPNO                        5
PROCNO                       1

F2 - Acquisition Parameters
Date_              20150923
Time                    14.08
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                          16
DS                           2
SWH                9812.928 Hz
FIDRES             0.149754 Hz
AQ                 4.6894445 sec
RG                          32
DW                    62.400 usec
DE                     6.50 usec
TE                    298.0 K
D1                 1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1             400.1424718 MHz
NUC1                       1H
P1                      13.55 usec
PLW1              16.00000000 W

F2 - Processing parameters
SI                       65536
SF               400.1400091 MHz
WDW                         EM
SSB          0
LB                       0.30 Hz
GB           0
PC                       1.00
```

dyq-cd-1C



BRUKER

```
Current Data Parameters
NAME                  dyq-cd-1
EXPNO                        2
PROCNO                       1

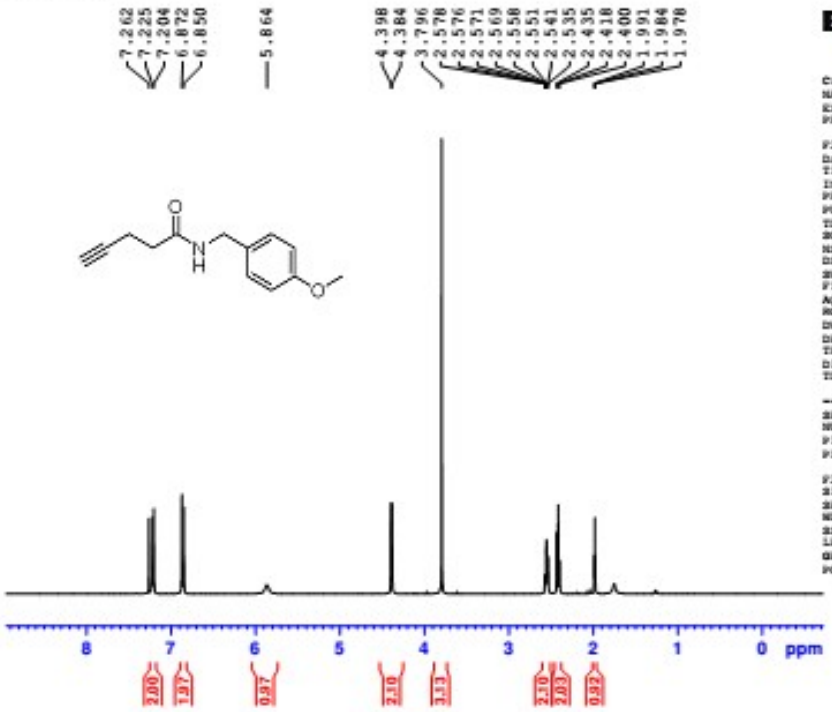
F2 - Acquisition Parameters
Date_              20150820
Time                    14.45
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                     65536
SOLVENT                CDCl3
NS                         117
DS                           4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                         203
DW                   20.800 usec
DE                     6.50 usec
TE                    297.8 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1             100.6253441 MHz
NUC1                       13C
P1                       9.00 usec
PLW1              62.00000000 W

======== CHANNEL f2 ========
SFO2             400.1416006 MHz
NUC2                       1H
CPDPRG[2              waltz16
PCPD2                   90.00 usec
PLW2              16.00000000 W
PLW12              0.36267000 W
PLW13              0.29376000 W

F2 - Processing parameters
SI                       32768
SF               100.6152830 MHz
WDW                         EM
SSB          0
LB                       1.00 Hz
GB           0
PC                       1.40
```

dyq-c-104H



BRUKER

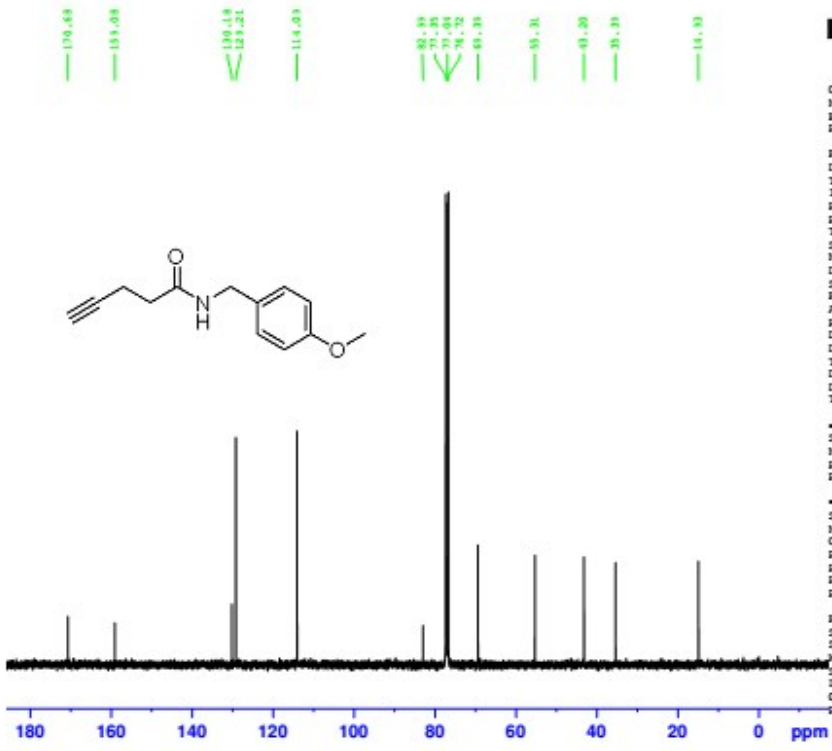
```
Current Data Parameters
NAME                 dyq-c-104
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_               20150213
Time                     14.23
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  9812.926 Hz
FIDRES               0.122366 Hz
AQ                   4.0894465 sec
RG                         161
DW                      62.400 usec
DE                       6.50 usec
TE                     298.0 K
D1                   1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1            400.1424718 MHz
NUC1                     1H
P1                      13.55 usec
PLW1           16.00000000 W

F2 - Processing parameters
SI                       65536
SF                  400.1400095 MHz
WDW                         EM
SSB                  0
LB                       0.30 Hz
GB                   0
PC                       1.00
```

dyq-c-104C



BRUKER

```
Current Data Parameters
NAME                 dyq-c-104
EXPNO                        2
PROCNO                       1

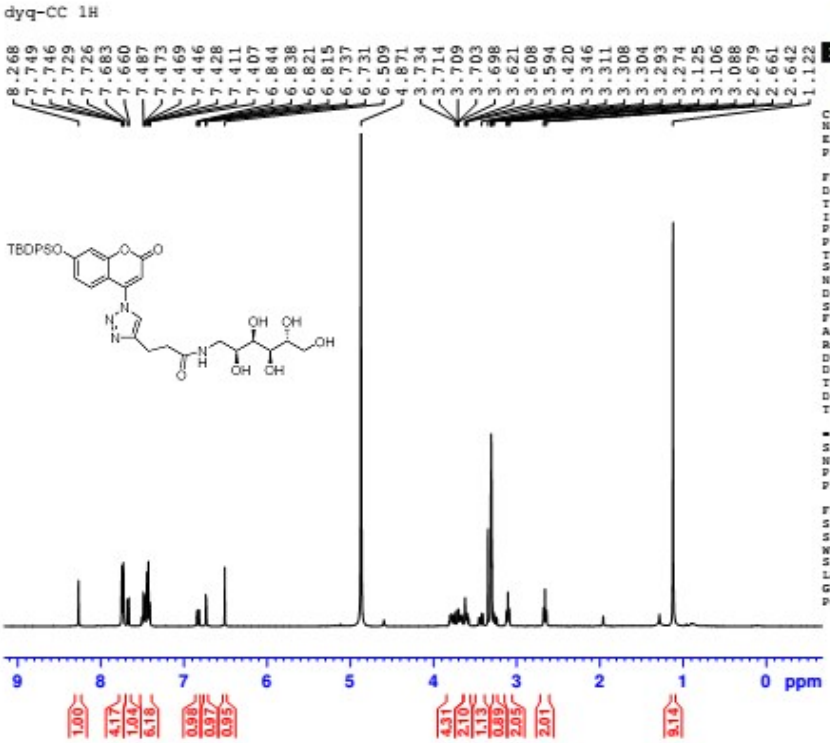
F2 - Acquisition Parameters
Date_               20150622
Time                     17.23
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zgpg30
TD                      65536
SOLVENT                  CDCl3
NS                         270
DS                           4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631488 sec
RG                         161
DW                      20.800 usec
DE                       6.50 usec
TE                     298.0 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1            100.6253441 MHz
NUC1                     13C
P1                       9.00 usec
PLW1           62.00000000 W

======== CHANNEL f2 ========
SFO2            400.1416006 MHz
NUC2                     1H
CPDPRG[2              waltz16
PCPD2                   90.00 usec
PLW2           16.00000000 W
PLW12           0.36267000 W
PLW13           0.29376000 W

F2 - Processing parameters
SI                       32768
SF                  100.6152830 MHz
WDW                         EM
SSB                  0
LB                       1.00 Hz
GB                   0
PC                       1.40
```

dyq-CC 1H



BRUKER

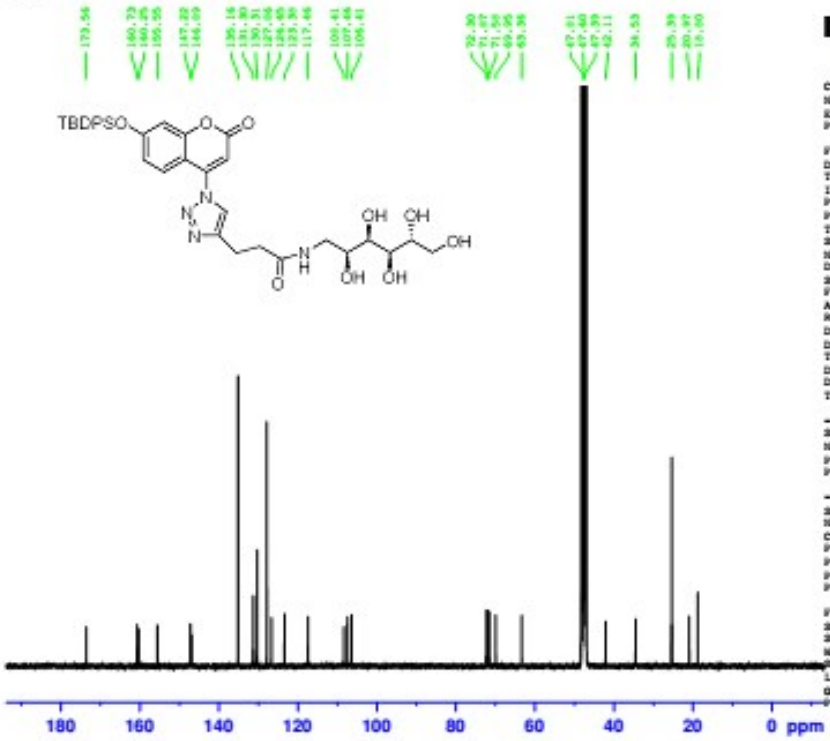
```
Current Data Parameters
NAME                  dyq-f-4
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_              20150803
Time                   11.52
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT                MeOD
NS                       64
DS                        2
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                 4.0894465 sec
RG                      144
DW                   62.400 usec
DE                    6.50 usec
TE                   296.2 K
D1                 1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1               400.1424710 MHz
NUC1                       1H
P1                    13.55 usec
PLW1              16.00000000 W

F2 - Processing parameters
SI                    65536
SF                 400.1400084 MHz
WDW                       EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```

dyq-f-4 13C



BRUKER

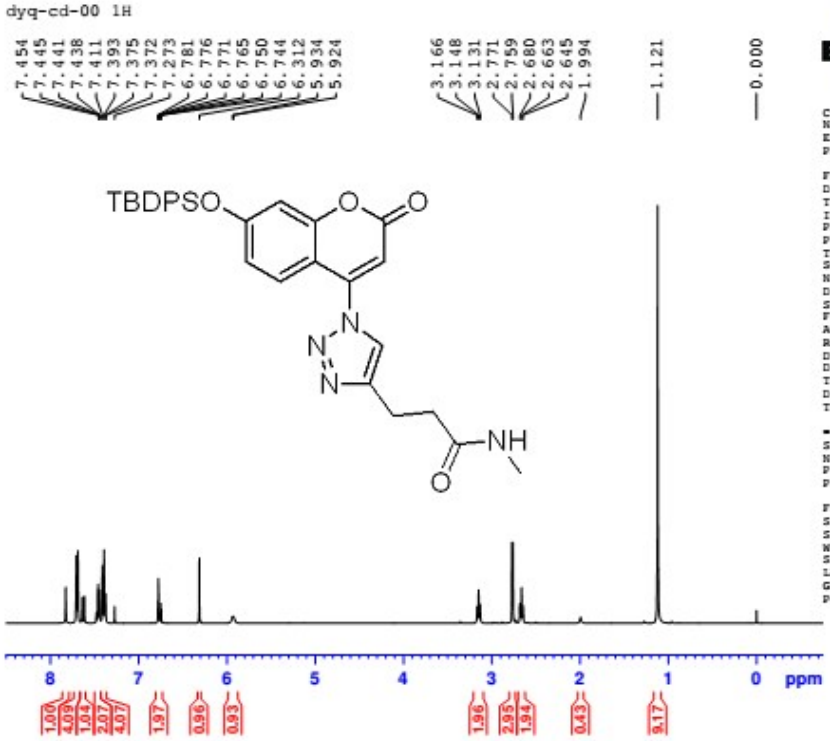
```
Current Data Parameters
NAME              dyq-f-4 13C
EXPNO                       3
PROCNO                      3

F2 - Acquisition Parameters
Date_              20150803
Time                   21.37
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT                MeOD
NS                     12232
DS                        0
SWH                24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                      203
DW                   20.800 usec
DE                    6.50 usec
TE                   296.8 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1               100.6253441 MHz
NUC1                       13C
P1                     9.00 usec
PLW1              62.08000000 W

======== CHANNEL f2 ========
SFO2               400.1416006 MHz
NUC2                       1H
CPDPRG[2          waltz16
PCPD2                 98.00 usec
PLW2              16.08000000 W
PLW12              0.36267000 W
PLW13              0.29376000 W

F2 - Processing parameters
SI                    32768
SF                 100.6152830 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```



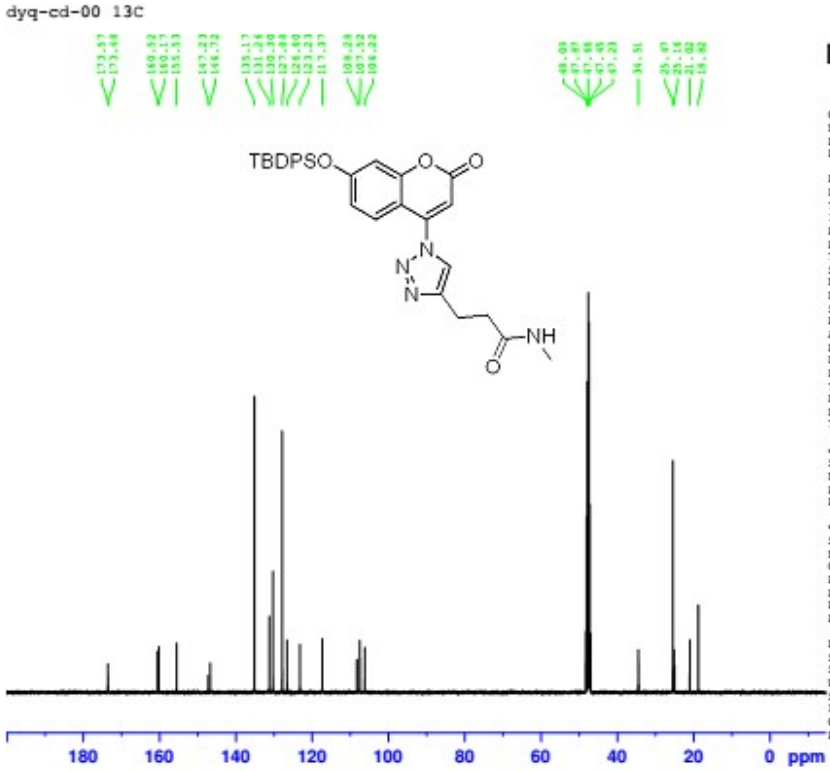
BRUKER

```
Current Data Parameters
NAME      dyq-cd-00 0925
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_          20150925
Time              18.57
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           8012.820 Hz
FIDRES        0.122266 Hz
AQ            4.0894465 sec
RG                71.8
DW               62.400 usec
DE                6.50 usec
TE              296.0 K
D1            1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1         400.1424710 MHz
NUC1                 1H
P1                13.55 usec
PLW1         16.00000000 W

F2 - Processing parameters
SI               65536
SF          400.1400043 MHz
WDW                 EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```



BRUKER

```
Current Data Parameters
NAME      dyq-cd-00 0929
EXPNO                1
PROCNO               1

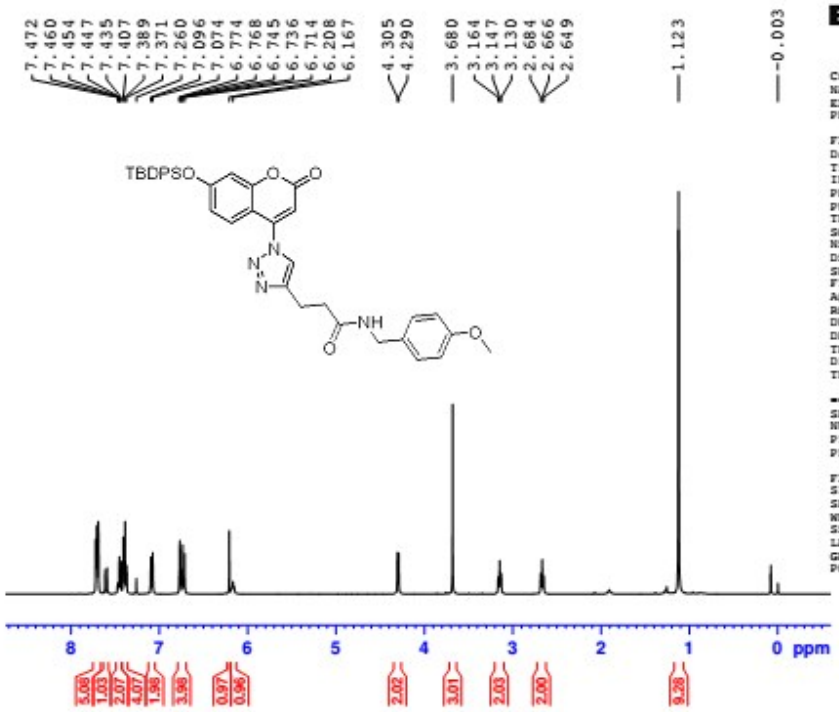
F2 - Acquisition Parameters
Date_          20150929
Time              10.06
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT           MeOD
NS                 193
DS                   4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631488 sec
RG                 203
DW               20.800 usec
DE                6.50 usec
TE              294.8 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1         100.6253441 MHz
NUC1                 13C
P1                9.00 usec
PLW1         62.00000000 W

======== CHANNEL f2 ========
SFO2         400.1416006 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2             90.00 usec
PLW2         16.00000000 W
PLW12         0.36267000 W
PLW13         0.29376000 W

F2 - Processing parameters
SI                32768
SF          100.6152830 MHz
WDW                 EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.40
```

dyq-CA-00 1H



BRUKER

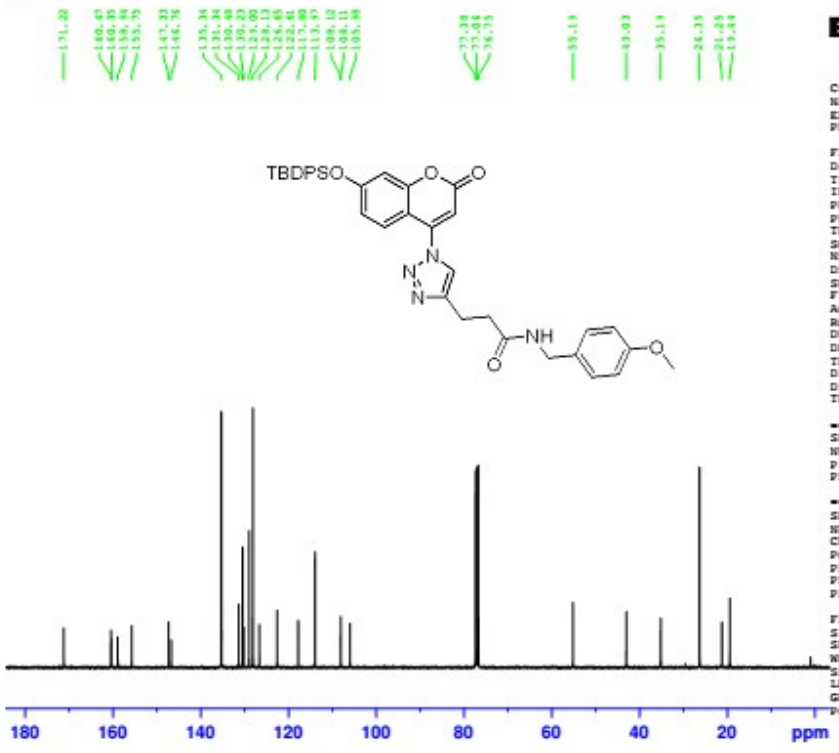
```
Current Data Parameters
NAME            dyq-CA-00
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_           20150919
Time              15.10
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ             4.0894465 sec
RG                   57
DW               62.400 usec
DE                6.50 usec
TE               298.0 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         400.1424710 MHz
NUC1                 1H
P1                13.55 usec
PLW1         16.00000000 W

F2 - Processing parameters
SI                65536
SF           400.1400090 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```

dyq-CA-00 13C



BRUKER

```
Current Data Parameters
NAME            dyq-CA-00
EXPNO                   6
PROCNO                  1

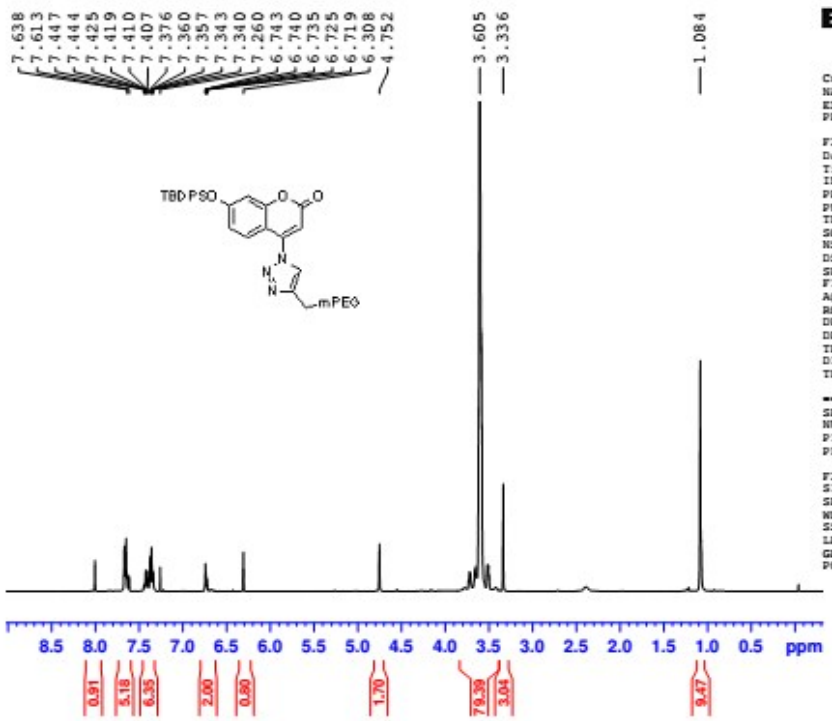
F2 - Acquisition Parameters
Date_           20150919
Time              15.35
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                  500
DS                    4
SWH            24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                 90.5
DW               20.800 usec
DE                6.50 usec
TE               298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         100.6253441 MHz
NUC1                 13C
P1                 9.00 usec
PLW1         62.00000000 W

======== CHANNEL f2 ========
SFO2         400.1416006 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2              90.00 usec
PLW2         16.00000000 W
PLW12         0.36267000 W
PLW13         0.29376000 W

F2 - Processing parameters
SI                32768
SF           100.6152854 MHz
WDW                  EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.40
```

dyq-cb-00 1H



BRUKER

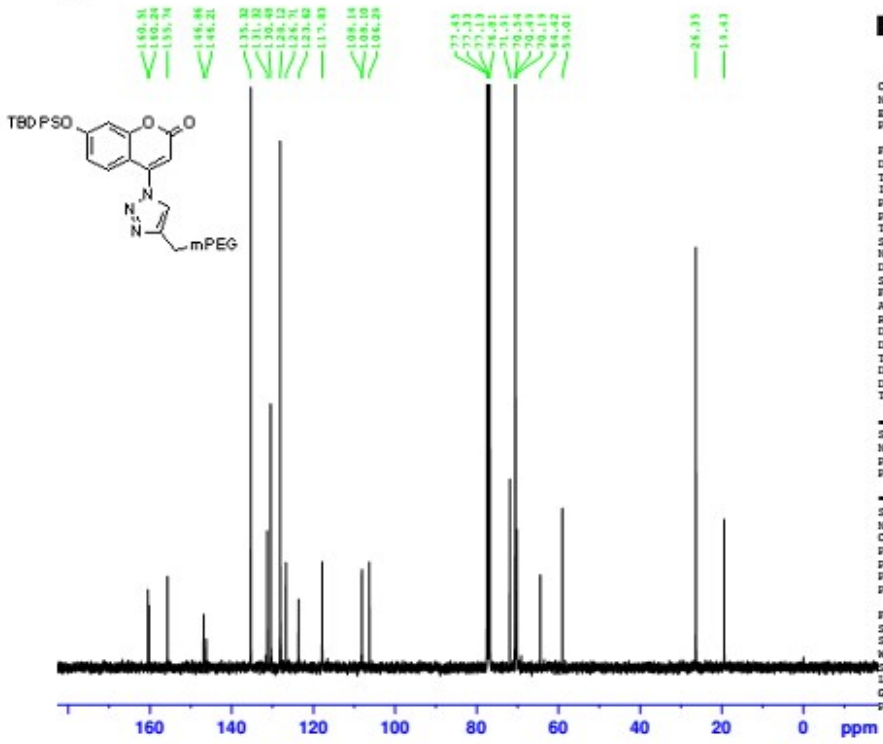
```
Current Data Parameters
NAME                  dyq-cb
EXPNO                      7
PROCNO                     1

F2 - Acquisition Parameters
Date_              20151208
Time                   17.42
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        16
DS                         2
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                 4.0894465 sec
RG                        32
DW                   62.400 usec
DE                    6.50 usec
TE                   298.0 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1          400.1424710 MHz
NUC1                      1H
P1                     13.55 usec
PLW1          16.00000000 W

F2 - Processing parameters
SI                        65536
SF            400.1400092 MHz
WDW                       EM
SSB                    0
LB                     0.30 Hz
GB                     0
PC                     1.00
```

dyq-cb-00 13C



BRUKER

```
Current Data Parameters
NAME                  dyq-cb
EXPNO                      8
PROCNO                     1

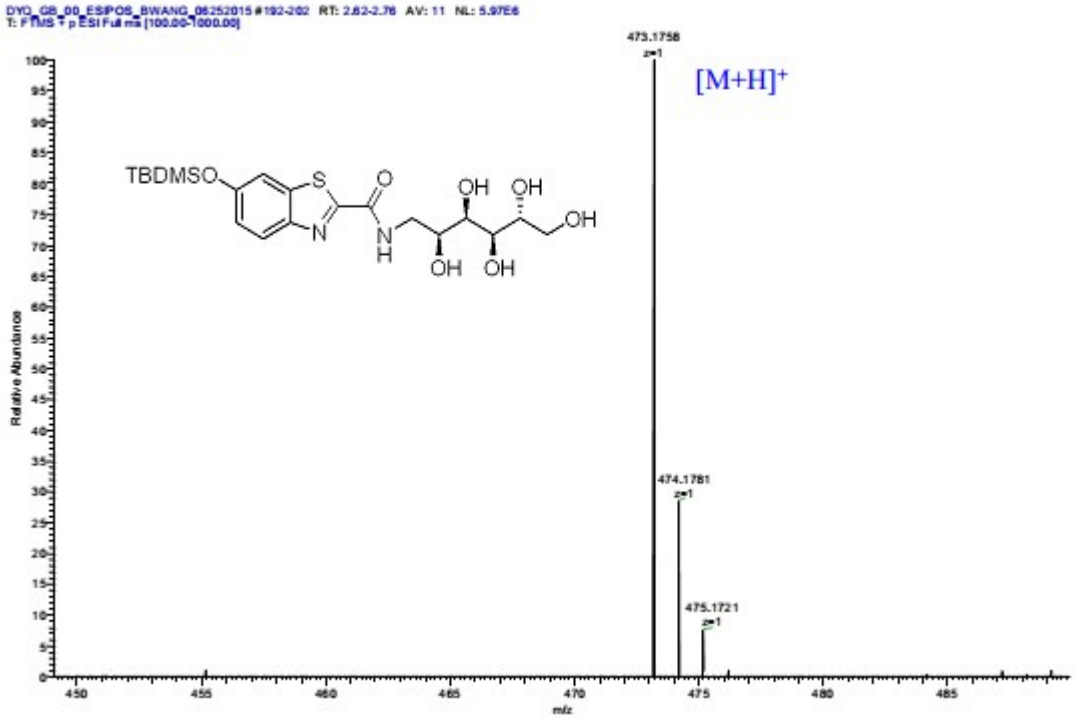
F2 - Acquisition Parameters
Date_              20151208
Time                   17.54
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       501
DS                         4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                       203
DW                   20.800 usec
DE                    6.50 usec
TE                   298.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1

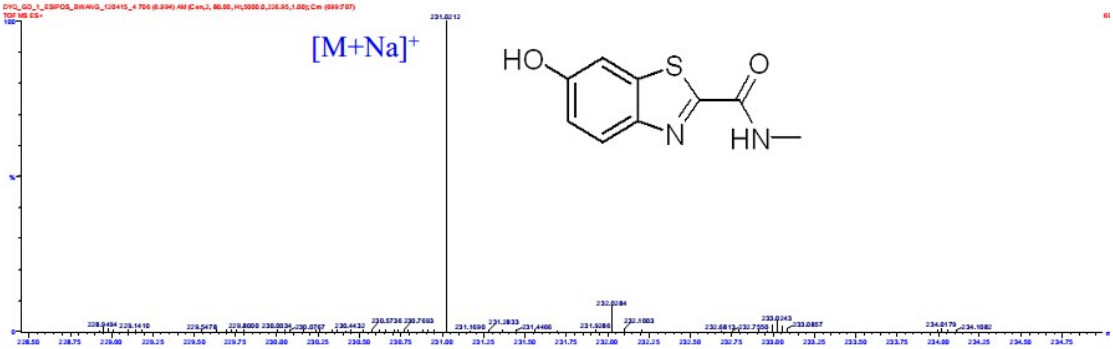
======== CHANNEL f1 ========
SFO1          100.6253441 MHz
NUC1                      13C
P1                     9.00 usec
PLW1          62.00000000 W

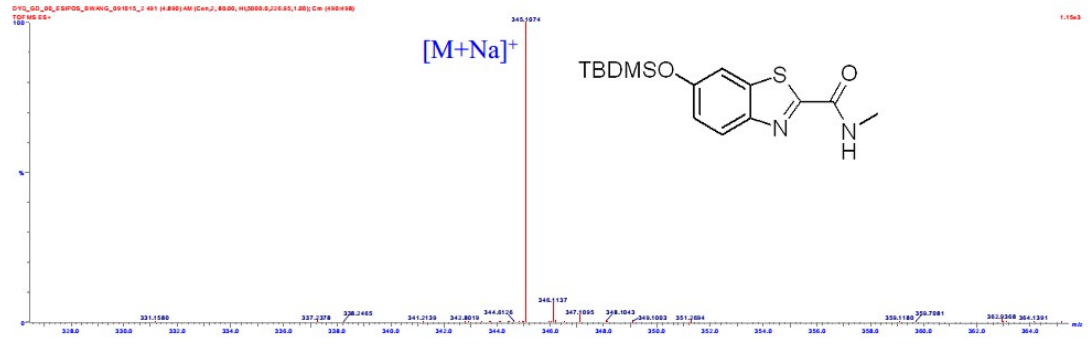
======== CHANNEL f2 ========
SFO2          400.1416006 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2                 90.00 usec
PLW2          16.00000000 W
PLW12          0.36267000 W
PLW13          0.29376000 W

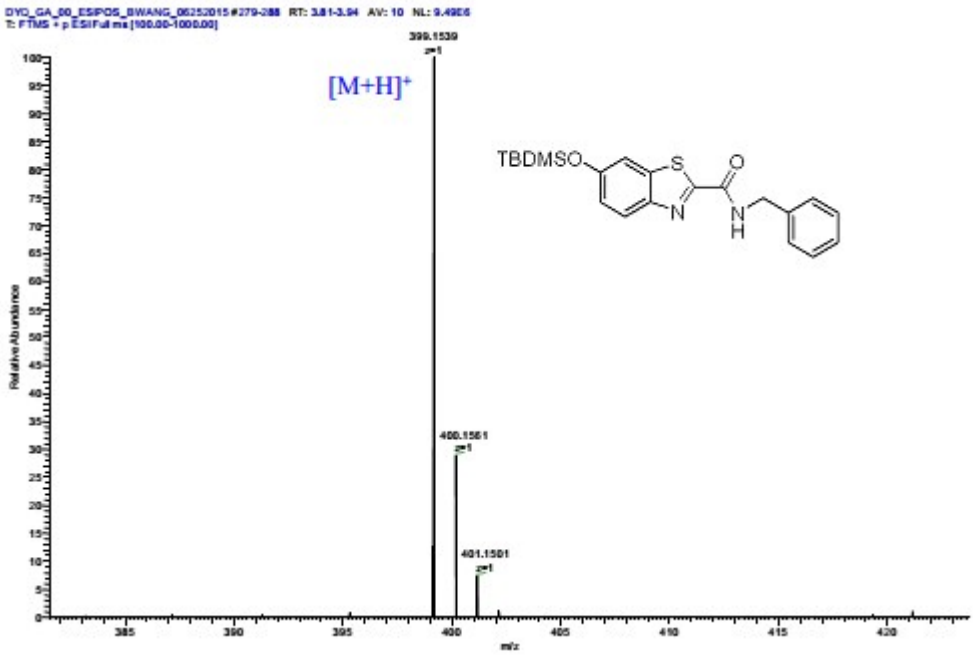
F2 - Processing parameters
SI                        32768
SF            100.6152830 MHz
WDW                       EM
SSB                    0
LB                     1.00 Hz
GB                     0
PC                     1.40
```

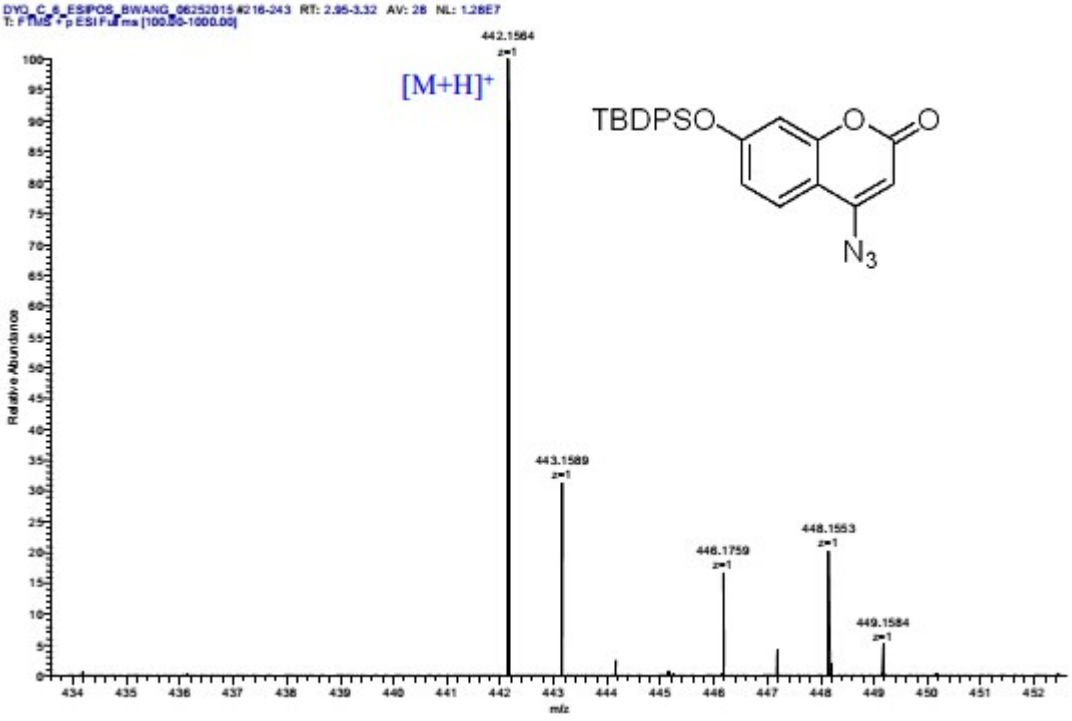
MS spectra

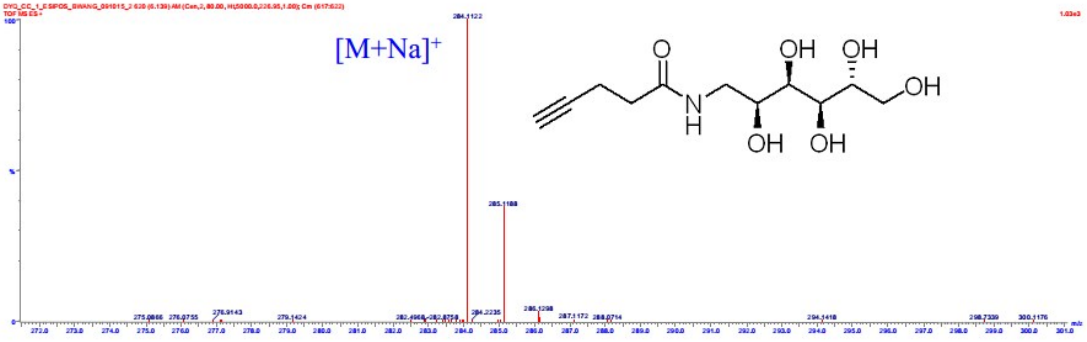

DYQ_GB_00_ESIPOS_BWANG_06252015 #192-202 RT: 2.62-2.76 AV: 11 NL: 5.97E6
T: FTMS + p ESI Full ms [100.00-1000.00]
473.1758
z=1
[M+H]+
TBDMSO
S
O
N
N
H
OH
OH
OH
OH
OH
474.1781
z=1
475.1721
z=1
Relative Abundance
m/z

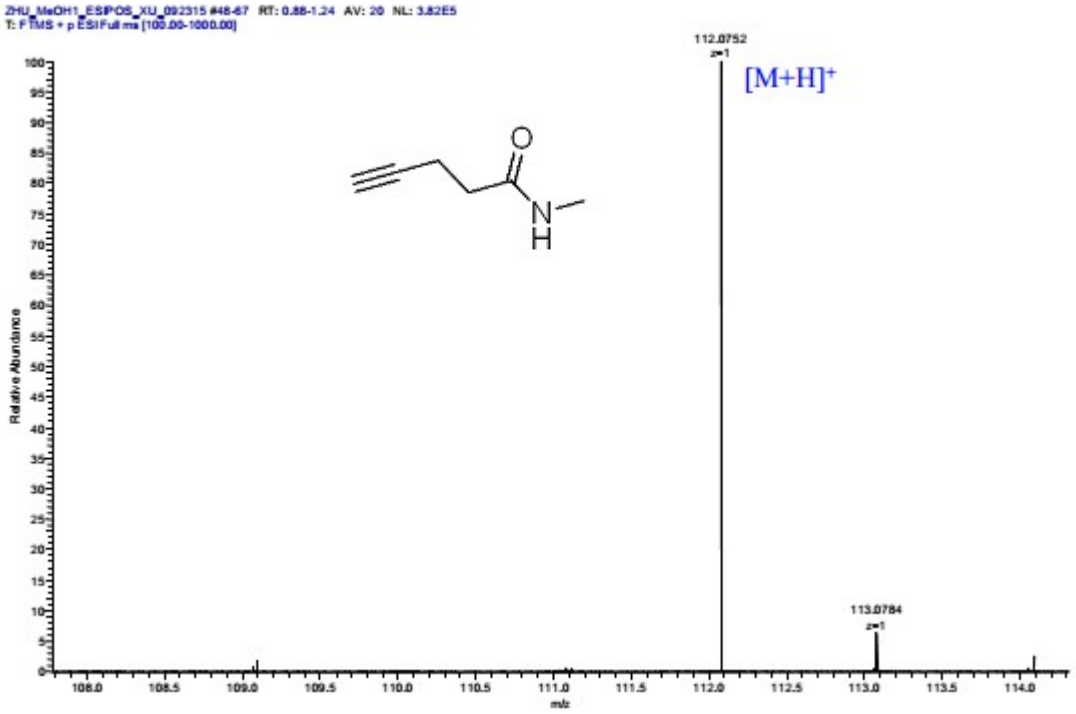

[M+Na]+
HO
S
O
N
HN—

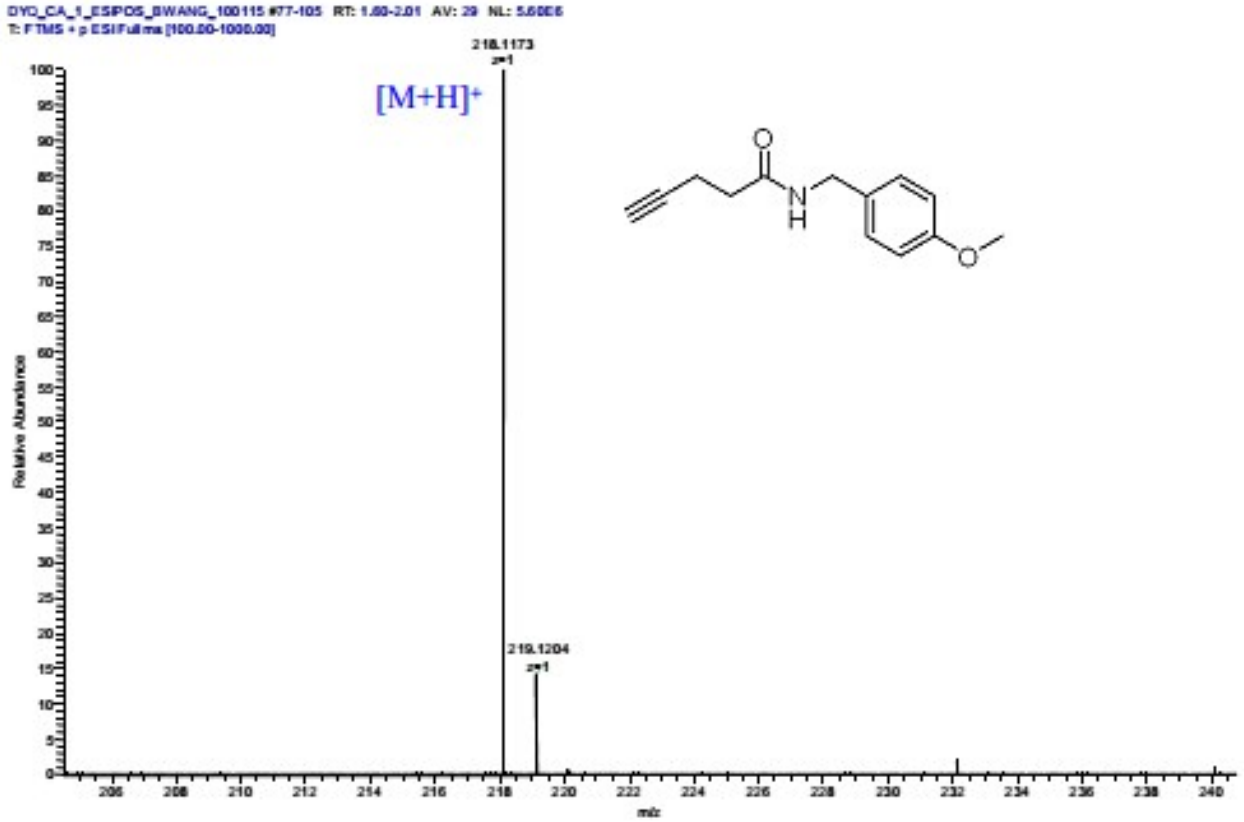

[M+Na]+
TBDMSO
S
O
N
N
H

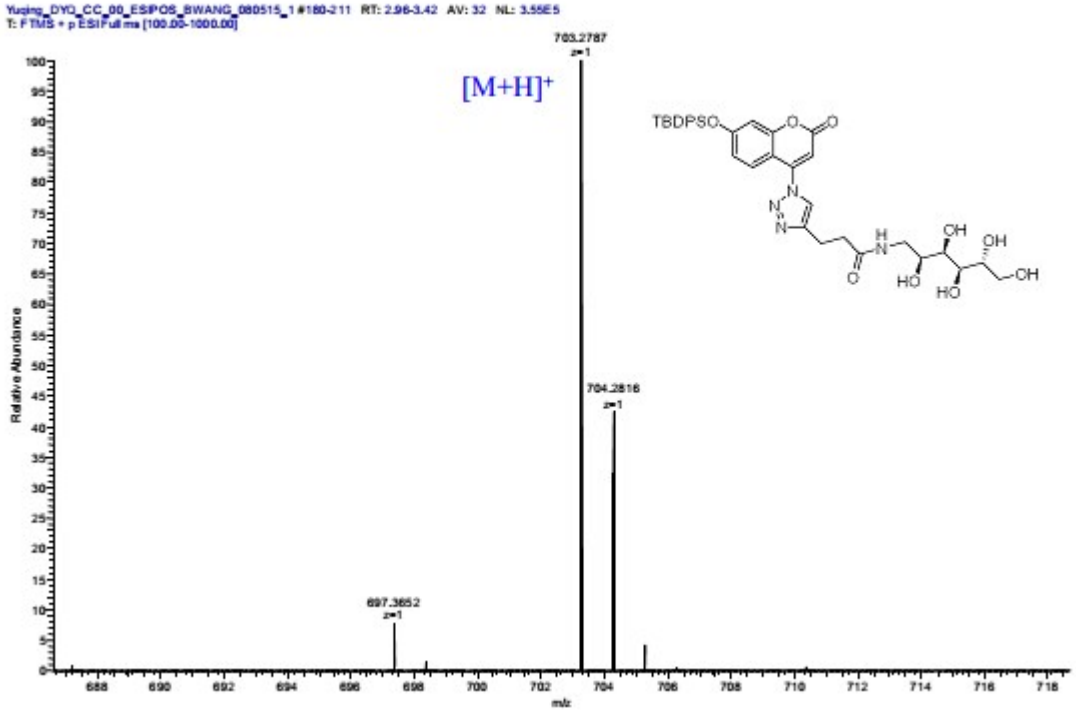

DYD_GA_00_ESIPOS_BWANG_06252015#279-288 RT: 3.81-3.94 AV: 10 NL: 9.49E6
T: FTMS + p ESI Full ms [100.00-1000.00]
399.1539
z=1
[M+H]+
TBDMSO
S
O
N
N
H
400.1561
z=1
401.1591
z=1
Relative Abundance
m/z

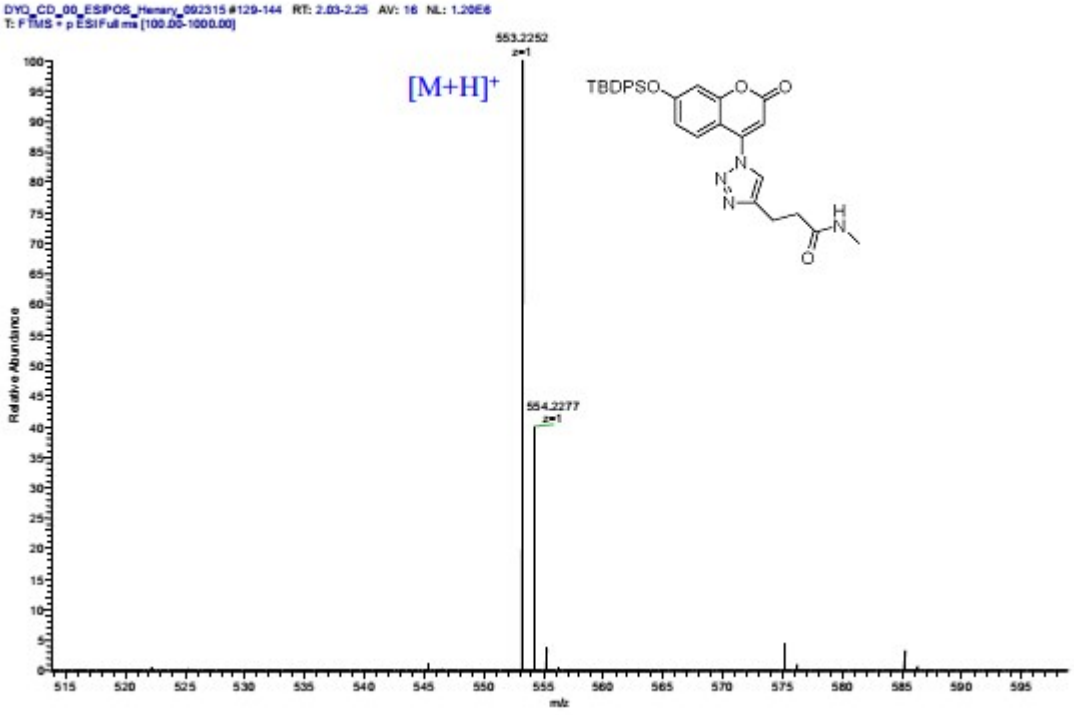

DYD_C_6_ESIPOS_BWANG_06252015#216-243 RT: 2.95-3.32 AV: 28 NL: 1.28E7
T: FTMS + p ESI Full ms [100.00-1000.00]
442.1564
z=1
[M+H]+
TBDPSO
O
O
N3
443.1589
z=1
446.1759
z=1
448.1553
z=1
449.1584
z=1
Relative Abundance
m/z

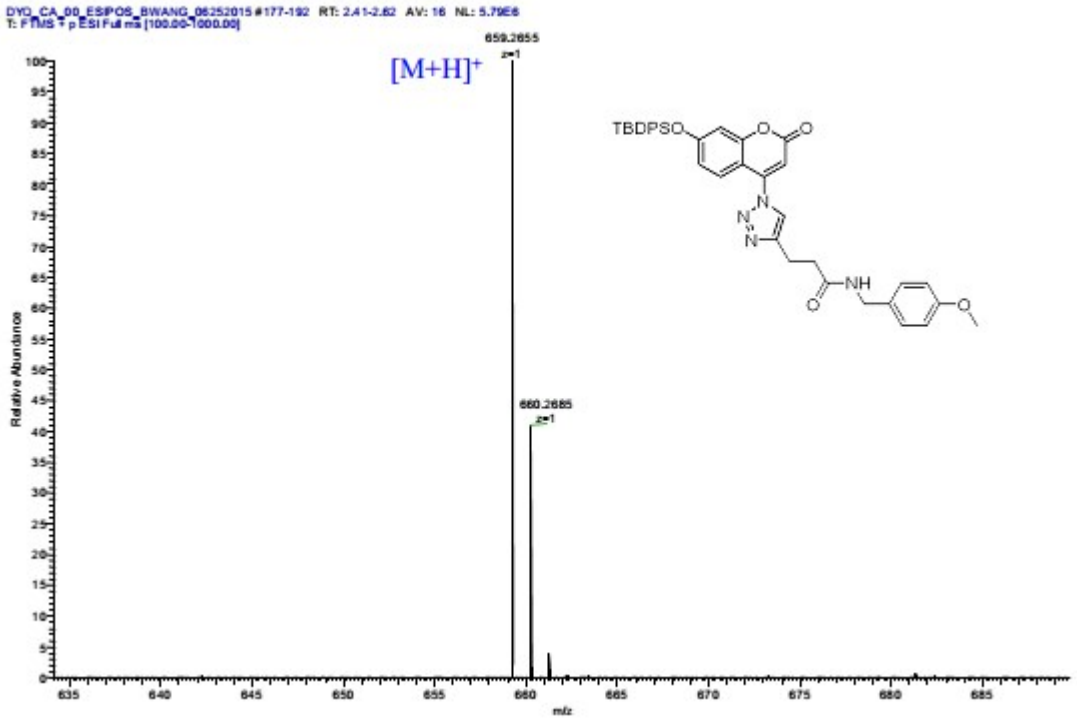

[M+Na]+
O
OH
OH
OH
N
H
OH
OH

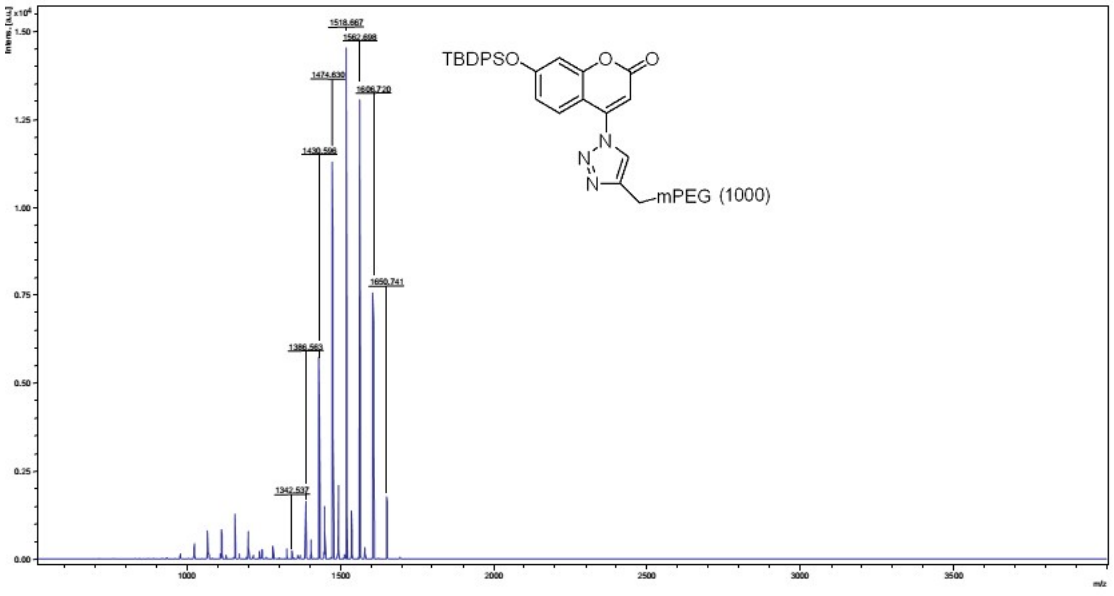

ZHU_MeOH1_ESIPOS_XU_092315 #48-67 RT: 0.88-1.24 AV: 20 NL: 3.82E5
T: FTMS + p ESI Full ms [100.00-1000.00]
112.0752
z=1
[M+H]+
113.0784
z=1
Relative Abundance
m/z

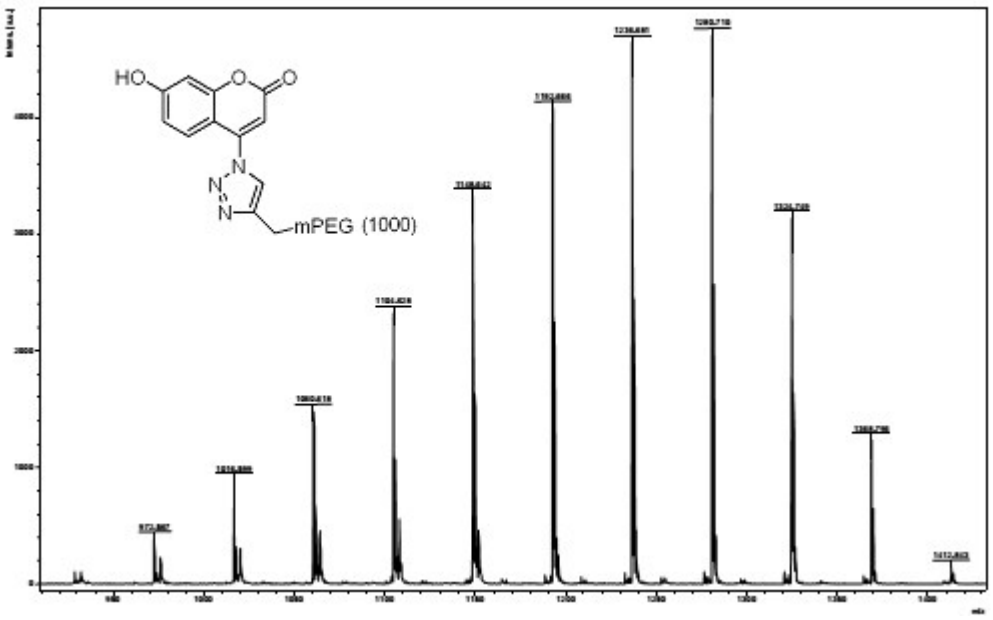

DYQ_CA_1_ESIPOS_BWANG_100115 #77-105 RT: 1.60-2.01 AV: 29 NL: 5.60E6
T: FTMS + p ESI Full ms [100.00-1000.00]
218.1173
z=1
[M+H]+
219.1204
z=1
Relative Abundance
m/z


Yuqing_DYQ_CC_00_ESIPOS_BWANG_080515_1 #180-211 RT: 2.96-3.42 AV: 32 NL: 3.55E5
T: FTMS + p ESI Full ms [100.00-1000.00]
703.2787
z=1
[M+H]+
TBDPSO
704.2816
z=1
697.3652
z=1
Relative Abundance
m/z


DYQ_CD_00_ESIPOS_Henary_092315 #129-144 RT: 2.03-2.25 AV: 16 NL: 1.20E6
T: FTMS + p ESI Full ms [100.00-1000.00]
553.2252
z=1
[M+H]+
TBDPSO
554.2277
z=1
Relative Abundance
m/z


DYO_CA_00_ESIPOS_BWANG_06252015 #177-192 RT: 2.41-2.82 AV: 16 NL: 5.79E6
T: FTMS + p ESI Full ms [100.00-1000.00]
659.2655
z=1
[M+H]+
660.2685
z=1
Relative Abundance
m/z
TBDPSO
NH


1518.667
1562.698
1474.630
1606.720
1430.596
1650.741
1386.563
1342.537
TBDPSO
mPEG (1000)


HO
O
O
N
N
N
mPEG (1000)