Supplementary Information

Double-decked Molecular Crescents

Li Lin,[a] Jiaxin Zhang,[a] Xiangxiang Wu,[a] Guoxing Liang,[a] Lan He*[a] and Bing Gong*[ab]

[a] *College of Chemistry, Beijing Normal University, Beijing 100875, China. and State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China Tel: (+86) 10 5880 2076; E-mail: helan1961@hotmail.com.*

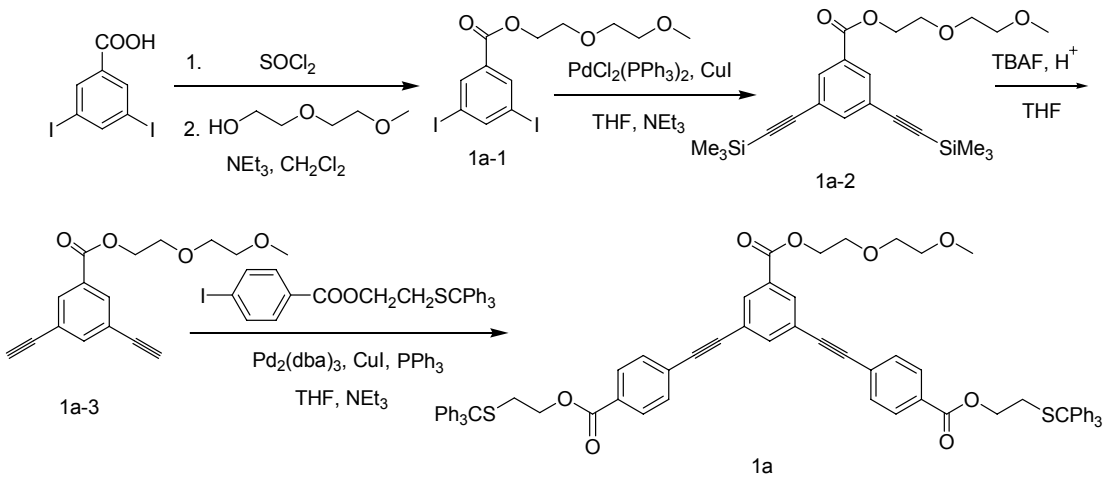
[b] *Department of Chemistry, University at Buffalo, State University of New York, Buffalo, NY 14260, USA. Fax: (+1) 716 645 6963; Tel: (+1) 716 645 4307; E-mail: E-mail: bgong@buffalo.edu*

Contents:

I. Synthetic Procedures

General. Chemicals were purchased from commercial sources and used as received. Reactions requiring an inert gas were all under nitrogen. Silica gel for analytical thin layer chromatography (TLC) and column chromatography (200~300 mesh) were purchased from Qingdao Haiyang Chemical Co., Ltd & Spegial Silica Gel Factory. The ^{1}H NMR spectra were recorded at 400 or 500 MHz and ^{13}C NMR spectra were measured at 100 or 125 MHz on a Bruker AV400 spectrometer at ambient temperature using $CDCl_3$ as solvent (purchased from Beijing Chongxi High-Tech Incubator Co.,Ltd). Chemical shifts are reported in parts per million downfield from TMS (tetramethylsilane). Coupling constant in ^{1}H NMR are expressed in Hertz. Melting points were measured on a microscope hot stage melting point apparatus and are uncorrected.

Synthesis of 1a



2-(2-methoxyethoxy)ethyl-3,5-diiodobenzoate(1a-1). To a 100 mL round-bottomed flask was added 3,5-diiodobenzoic acid (3.47 g, 10 mmol) $SOCl_2$ (25 mL). The resulting suspension liquid was heated to reflux for 5 h. After removing the redundant $SOCl_2$ in vacuo to give a yellow solid. To a dried, ice-cooled flask containing NEt_3 (1.4 mL) 2-(2-methoxyethoxy)ethanol (1.8 mL, 15 mmol) was added the solution of the above solid in CH_2Cl_2 (15 mL). The mixture was stirred for 7 h at rt, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (R_f = 0.2, petroleum ether/ethyl acetate = 15/1) to give the desired product (3.5 g, 74%) as a pale-yellow solid. mp: 52.9-54.8 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) ™ 8.33 (s, 2H), 8.23 (s, 1H), 4.49 (t, J = 4.7 Hz, 2H), 3.83 (t, J = 4.7 Hz, 2H), 3.70 (t, J = 4.5 Hz, 2H), 3.58 (t, J = 4.5 Hz, 2H), 3.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) ™163.69, 149.48, 137.80, 133.28, 94.37, 71.91, 70.58,

69.16, 64.58, 64.44, 59.14. MS: m/z (EI): 476.89 (M^+).

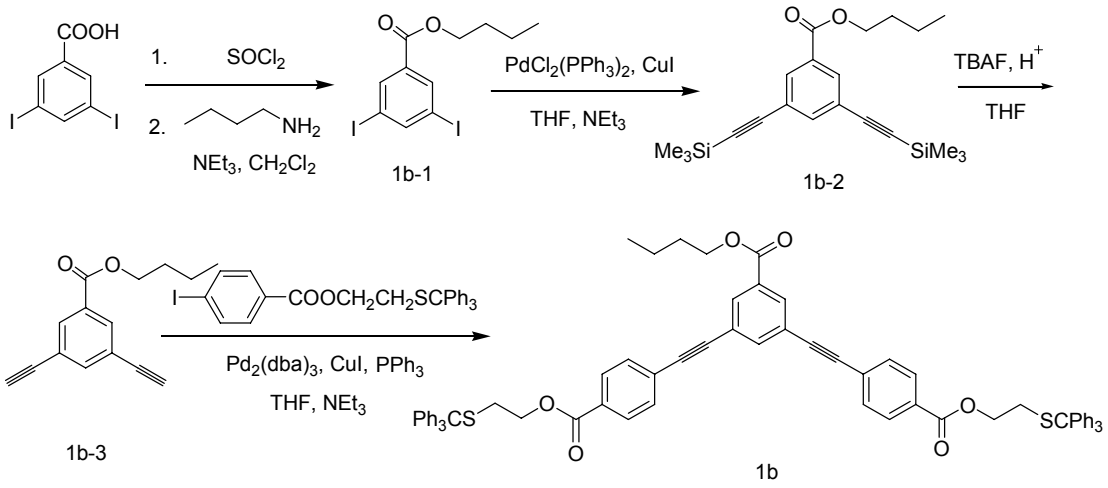
2-(2-methoxyethoxy)ethyl-3,5-bis(2-(trimethylsilyl)ethynyl)benzoate(1a-2). To a flask was added 1a-1 (0. 952 g, 2 mmol), $Pd(PPh_3)_2Cl_2$ (0.07 g, 0.1 mmol), CuI (0.02 g, 0.1 mmol), then degassed. THF (30 ml) and NEt_3 (10 ml) were injected into the flask via syringe, then trimethylsilylethylene (0.71 mL, 5 mmol) was injected into the solution. The mixture was stirred over night at rt. The crude mixture was filtered through a silica gel plug and concentrated in vacuo. The concentrate was purified by column chromatography (R_f= 0.4, petroleum ether/ethyl acetate = 20/1) to give the desired product (0.6 g, 72%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 2H), 7.75 (s, 1H), 4.51 (t, J = 4.6 Hz, 2H), 3.86 (t, J = 4.6 Hz, 2H), 3.72 (t, J = 4.5 Hz, 2H), 3.60 (t, J = 4.5 Hz, 2H), 3.42 (s, 3H), 0.28 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.17, 139.13, 132.94, 130.53, 123.86, 102.96, 96.15, 71.92, 70.56, 69.15, 64.41, 59.11, -0.18. MS: m/z(EI): 416.29 (M^+).

2-(2-methoxyethoxy)ethyl 3,5-diethynylbenzoate(1a-3). To a solution of 2-(2-methoxyethoxy)ethyl-3,5-bis(2-(trimethylsilyl)ethynyl)benzoate (0.6 g, 1.44 mmol) in THF (20 mL) was slow added a solution of tetrabutylammonium fluoride (1.127 g, 1.127 mmol) in THF (5 mL) at rt. The solution was stirred for 1 h, and the solvent was removed in vacuo to leave a brown residue. The residue was purified by column chromatography (R_f = 0.2, petroleum ether/ethyl acetate = 5/1) to give the desired product (0.24 g, 62%) as a white solid. mp: 80.1-81.0 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 2H), 7.77 (s, 1H), 4.51 (t, J = 4.7 Hz, 2H), 3.85 (t, J = 4.7 Hz, 2H), 3.70 (t, J = 4.4 Hz, 2H), 3.58 (t, J = 4.4 Hz, 2H), 3.40 (s, 3H), 3.16 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.94, 139.37, 133.33, 130.83, 122.99, 81.60, 78.95, 71.91, 70.58, 69.09, 64.55, 59.08. MS : m/z(EI): 272.69 (M^+).

Semi-cycle (1a). To a dried, N_2 purged flask containing 2-(2-methoxyethoxy)ethyl 3,5-diethynylbenzoate (0.136 g, 0.5 mmol), 2-(tritylthio) ethyl 4-iodobenzoate (0.55 g, 1 mmol), $Pd_2(dba)_3$ (0.046 g, 0.025 mmol), CuI (0.02 g, 0.05 mmol), PPh_3 (0.033 g, 0.125 mmol) was added THF(30 mL) and NEt_3 (10 mL) via syringe. The solution was stirred at rt for 12 h. The mixture was poured into water, extracted with ethyl acetate, washed with saturated solution of NH_4Cl, brine and water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (silica, petroleum ether/ethyl acetate = 5/1) to obtain the desired product (0.33 g, 59%) as a yellow solid. mp: 66.9-67.1 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 1.5 Hz, 2H), 8.01 (d, J = 8.4 Hz, 4H), 7.90 (t, J = 1.5 Hz, 1H), 7.60 (d, J = 8.4 Hz, 4H), 7.45 (d, J = 7.9 Hz, 12H), 7.30 (t, J = 7.9 Hz, 12H), 7.23 (t, J = 7.2 Hz, 6H), 4.54 (t, J = 4.1 Hz, 2H), 4.12 (t, J = 6.4 Hz, 4H), 3.87 (t, J = 4.5 Hz, 2H), 3.72 (t, J = 4.0 Hz, 2H), 3.59 (t, J = 4.6 Hz, 2H), 3.40 (s, 3H), 2.62 (t, J = 6.5 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.53, 165.09, 144.63, 138.46, 132.79, 131.64,

131.09, 129.92, 129.71, 129.61, 128.00, 127.33, 126.84, 123.77, 90.31, 90.23, 71.98, 70.62, 69.19, 66.98, 64.58, 63.46, 59.12, 31.05. MS: m/z (MALDI-TOF) : 1116.1[M^+], 1139.5[M^++Na].

Synthesis of **1b**



3,5-diiodo-benzoic acid butyl ester(1b-1). To a 100 mL round-bottomed flask was added 3,5-diiodobenzoic acid (3.47 g, 10 mmol) $SOCl_2$ (25 mL). The resulting suspension liquid was heated to reflux for 5 h. After removing the redundant $SOCl_2$ in vacuo to give a yellow solid. To a dried, ice-cooled flask containing NEt_3 (2.0 mL, 15 mmol) butan-1-ol (1.4 mL,15 mmol) was added the solution of the above solid in CH_2Cl_2 (15 mL). The mixture was stirred for 7 h at rt, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (R_f = 0.3, petroleum ether/ethyl acetate = 50/1) to give the desired product (3 g, 69.6%) as a white solid. mp:46.9-47.8 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 2H), 8.23 (s, 1H), 4.32 (t, J = 6.7 Hz, 2H), 1.84 – 1.66 (m, 2H), 1.51 – 1.37 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.12, 149.31, 137.69, 134.03, 94.56, 65.77, 31.18, 18.98, 13.80. MS : m/z(EI): 430.3 (M^+).

3,5-bis-trimethylsilanylethynyl-benzoic acid butyl ester(1b-2). To a flask was added 3,5-diiodo-benzoic acid butyl ester (2.4 g, 5.57 mmol), $Pd(PPh_3)_2Cl_2$ (0.2 g, 0.279 mmol), CuI (0.1 g, 0.557 mmol), then degassed. THF (60 ml) and NEt_3 (20 ml) were injected into the flask via syringe, then trimethylsilylethylene (2.37 mL, 16.7 mmol) was injected into the solution. The mixture was stirred over night at rt. The crude mixture was filtered through a silica gel plug and concentrated in vacuo. The black solide was purified by column chromatography (R_f = 0.5, petroleum ether/ethyl acetate = 60/1) to give the desired product (1.65 g, 80.1%) as a yellow solid. mp:50.5-53.1 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 2H), 7.69 (s, 1H), 4.32 (t, J = 6.7 Hz, 2H),

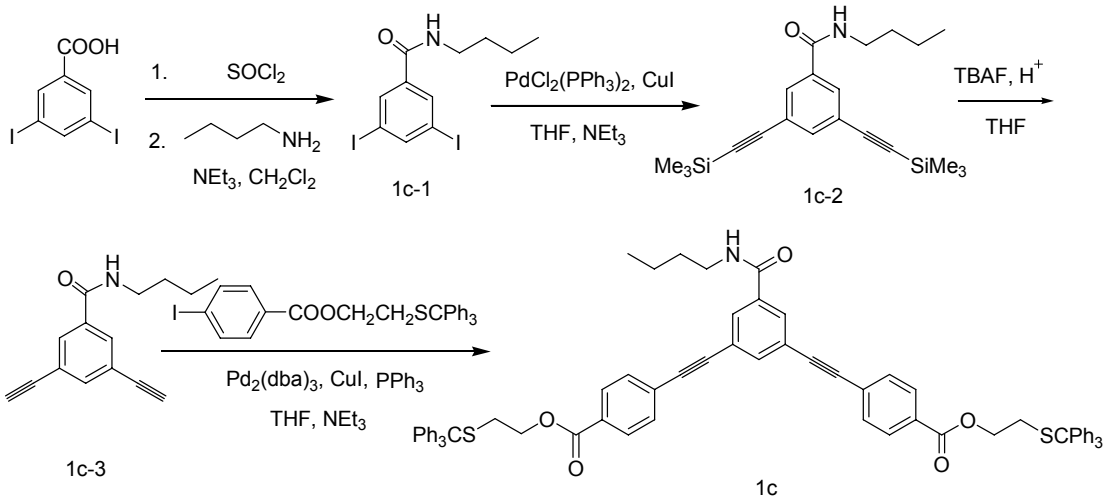
1.86 – 1.68 (m, 2H), 1.56 – 1.38 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H), 0.25 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.40, 139.10, 132.89, 131.37, 124.03, 103.01, 96.02, 65.65, 30.83, 19.48, 13.99, 0.24. MS : m/z(EI): 370.2 (M^+).

3,5-diethynyl-benzoic acid butyl ester(1b-3). To a solution of 3,5-bis-trimethylsilanylethynyl-benzoic acid butyl ester (2.5 g, 6.7 mmol) in THF (50 mL) was slow added a solution of tetrabutylammonium fluoride (5.29 g, 20 mmol) in THF (20 mL) at rt. The solution was stirred for 1 h, and the solvent was removed in vacuo to leave a brown residue. The residue was purified by column chromatography (R_f = 0.3, petroleum ether/ethyl acetate = 20/1) to give the desired product (1.32 g, 85%) as a white solid. mp:106.8-107.3 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 2H), 7.76 (s, 1H), 4.33 (t, J = 6.6 Hz, 2H), 3.14 (s, 2H), 1.81 – 1.68 (m, 2H), 1.47 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.19, 139.24, 132.70, 131.21, 123.16, 81.57, 79.02, 65.24, 30.66, 19.54, 13.29. MS : m/z(ESI): 225.9 (M^+).

Semi-cycle(1b). To a dried, N_2 purged flask containing 3,5-diethynyl-benzoic acid butyl ester (0.452 g, 2 mmol), 2-(tritylthio) ethyl 4-iodobenzoate (2.2 g, 4 mmol), $Pd_2(dba)_3$ (0.091 g, 0.1 mmol), CuI (0.038 g, 0.2 mmol), PPh_3 (0.13 g, 0.5 mmol) was added THF(90 mL) and NEt_3 (30 mL) via syringe. The solution was stirred at rt for 12 h. The mixture was poured into water, extracted with ethyl acetate, washed with saturated solution of NH_4Cl, brine and water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (silica, petroleum ether/ethyl acetate = 5/1) to obtain the desired product (1.55 g, 72.4 %) as a white solid. mp: 69.6-70.5 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 1.4 Hz, 2H), 8.01 (d, J = 8.4 Hz, 4H), 7.89 (s, 1H), 7.60 (d, J = 8.4 Hz, 4H), 7.44 (d, J = 7.5 Hz, 12H), 7.29 (t, J = 7.4 Hz, 12H), 7.23 (t, J = 7.2 Hz, 6H), 4.37 (t, J = 6.6 Hz, 2H), 4.12 (t, J = 6.5 Hz, 4H), 2.78 – 2.53 (m, 4H), 1.85 – 1.74 (m, 2H), 1.48 (d, J = 7.3 Hz, 2H), 1.05 – 0.94 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.09, 165.73, 144.47, 131.45, 129.34, 128.02, 126.48, 123.93, 67.06, 63.71, 45.80, 31.20, 30.67, 13.79. MS : m/z (MALDI-TOF) : 1093.5[M^++Na].

Synthesis of 1c



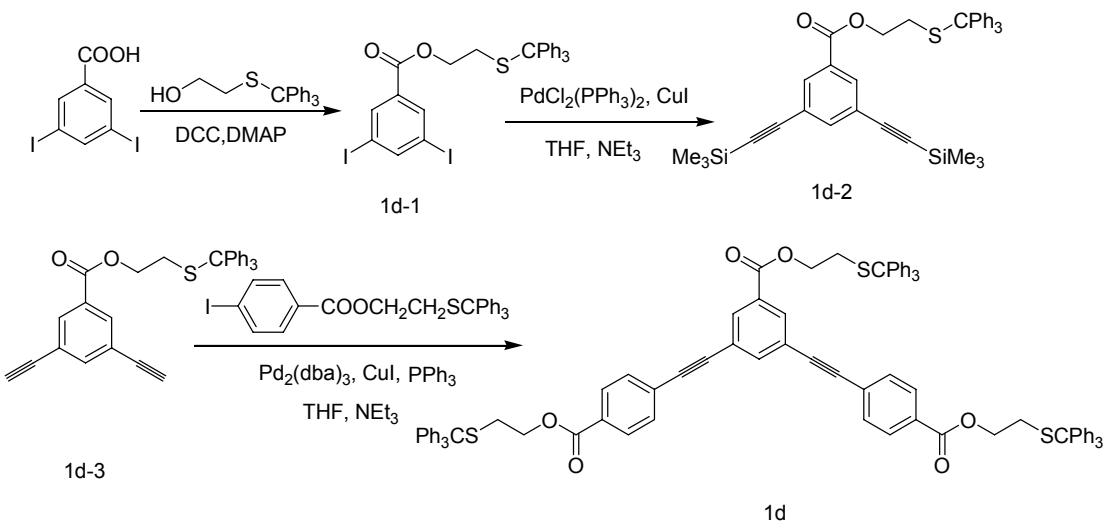
N-Butyl-3,5-diiodobenzamide(1c-1). To a 100 mL round-bottomed flask was added 3,5-diiodobenzoic acid (3.47 g, 10 mmol) $SOCl_2$ (20 mL). The resulting suspension liquid was heated to reflux for 5 h. After removing the redundant $SOCl_2$ in vacuo to give a yellow solid. To a dried, ice-cooled flask containing NEt_3 (2.8 mL, 20 mmol) butylamine (1.5 mL 15 mmol) was added the solution of the above solid in CH_2Cl_2 (15 mL). The mixture was stirred for 7 h at rt, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (R_f = 0.3, petroleum ether/ethyl acetate = 5/1) to give the desired product (3.4 g, 79.2%) as a white solid. mp:131.2-132.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.02 (s, 2H), 6.09 (s, 1H), 3.43 (dd, J = 13.1 Hz, 7.1, 2H), 1.59 (m, 2H), 1.40 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.50, 147.69, 138.21, 135.21, 94.81, 40.08, 31.60, 20.13, 13.76;. MS : m/z(ESI): 429.8 (M^+).

N-Butyl-3,5-bis-trimethylsilanylethynyl-benzamide(1c-2). To a flask was added N-Butyl-3,5-diiodobenzamide (4.29 g, 10 mmol), $Pd(PPh_3)_2Cl_2$ (0.35 g, 0.5 mmol), CuI (0.19 g, 1 mmol), then degassed. THF (45 ml) and NEt_3 (15 ml) were injected into the flask via syringe, then trimethylsilylethylene (4.3 mL, 30 mmol) was injected into the solution. The mixture was stirred over night at rt. The crude mixture was filtered through a silica gel plug and concentrated in vacuo. The solid was purified by column chromatography (R_f = 0.4, petroleum ether/ethyl acetate = 10/1) to give the desired product (2.66 g, 72%) as a white solid. mp:145.2-146.5 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 2H), 7.67 (s, 1H), 6.03 (s, 1H), 3.45 (dd, J = 12.8 Hz, 6.4 Hz, 2H), 1.60 (m, 2H), 1.42 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H), 0.25 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.07, 137.75, 135.43, 130.19, 124.16, 103.29, 96.41, 40.11, 31.88, 20.31, 13.94, 0.17; MS : m/z(ESI): 370.1 (M^+).

N-Butyl-3,5-diethynyl-benzamide(1c-3). To a solution of N-Butyl-3,5-bis-trimethylsilanylethynyl-benzamide (0.69 g, 1.6 mmol) in THF (20 mL) was slow added a solution of tetrabutylammonium fluoride (1.76 g, 4.8 mmol) in THF (10 mL) at rt. The solution was stirred for 1 h, and the solvent was removed in vacuo to leave a brown residue. The solide was purified by column chromatography (R_f= 0.3, petroleum ether/ethyl acetate = 5/1) to give the desired product (0.27 g, 75%) as a white solid. mp:120.1-121.6 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 2H), 7.70 (s, 1H), 6.03 (s, 1H), 3.45 (dd, J = 13.2 Hz, 6.5 Hz, 2H), 3.14 (s, 2H), 1.60 (m, 2H), 1.42 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.69, 137.87, 135.61, 130.65, 123.17, 81.77, 78.92, 39.99, 31.69, 20.15, 13.74; MS : m/z(ESI): 226.0 (M^+).

Semi-cycle(1c). To a dried, N_2 purged flask containing N-Butyl-3,5-diethynyl-benzamide (0.45 g, 2 mmol), 2-(tritylthio) ethyl 4-iodobenzoate (2.2 g, 4 mmol), $Pd_2(dba)_3$ (0.0914 g, 0.1 mmol), CuI (0.038 g, 0.2 mmol), PPh_3 (0.13 g, 0.5 mmol) was added THF(90 mL) and NEt_3 (30 mL) via syringe. The solution was stirred at rt for 12 h. The mixture was poured into water, extracted with ethyl acetate, washed with saturated solution of NH_4Cl, brine and water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (R_f = 0.2, petroleum ether/ethyl acetate = 3/1) to obtain the desired product (1.54 g, 72 %) as a yellow solid. mp: 99.0-100.4 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 4H), 7.90 (d, J = 1.4 Hz, 2H), 7.83 (s, 1H), 7.58 (d, J = 8.4 Hz, 4H), 7.44 (d, J = 7.8 Hz, 12H), 7.29 (t, J = 7.5 Hz, 12H), 7.23 (t, J = 7.2 Hz, 6H), 6.11 (t, J = 5.5 Hz, 1H), 4.12 (t, J = 6.5 Hz, 4H), 3.49 (3.49 (dd, J = 13.0 Hz, 7.0 Hz, 2H), 2.62 (t, J = 6.5 Hz, 4H), 1.64 (m, 2H), 1.44 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.78, 165.52, 144.62, 136.92, 135.75, 131.63, 130.07, 129.91, 129.72, 129.61, 128.01, 127.30, 126.84, 123.86, 90.41, 90.26, 66.97, 63.46, 40.03, 31.72, 31.02, 20.17, 13.78; MS : m/z (MALDI-TOF) : 1092.7[M^++Na].

Synthesis of 1d



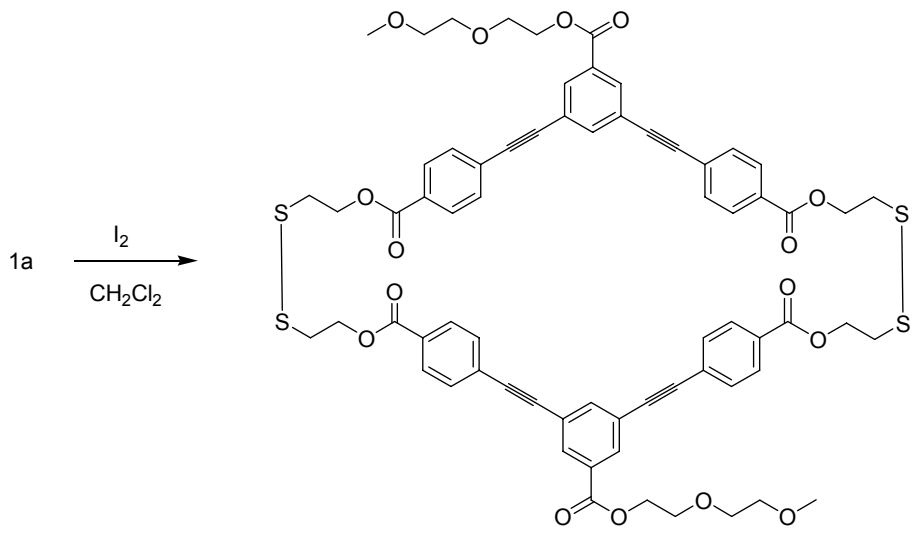
2-(tritylthio)ethyl 3,5-diiodobenzoate(1d-1). A solution of the 3,5-diiodobenzoic acid (3.74 g, 10mmol), DCC (3.09 g,15 mmol), and DMAP (1.83 g, 15 mmol) in THF (40 mL) was stirred for 1 h at rt, to which was added 2-(tritylthio)ethanol (3.2 g,10 mmol). The reaction was stirred for 48 h at rt, filtered, and concentrated to give a white solid, which was purified by column chromatography (silica, petroleum ether/ chloroform = 3/1) to provide the desired product (4.8 g, 71.0%) as a white solid. mp:172.1-174.0 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 1.3 Hz, 2H), 8.22 (s, 1H), 7.44 (d, J = 7.7 Hz, 6H), 7.30 (t, J = 7.5 Hz, 6H), 7.23 (t, J = 7.2 Hz, 3H), 4.06 (t, J = 6.6 Hz, 2H), 2.60 (t, J = 6.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.32, 149.29, 144.45, 137.72, 133.11, 129.54, 128.03, 126.86, 94.37, 66.97, 63.89, 30.72; MS : m/z (MALDI-TOF) : 699.1[M^++Na].

2-(tritylthio)ethyl 3,5-bis(2-(trimethylsilyl)ethynyl)benzoate(1d-2). The compound was synthesized by a procedure similar to that used for 1a-2 to yield a black solide. The solide was purified by column chromatography (R_f = 0.3, petroleum ether/ chloroform = 7/1) to give the desired product (0.5 g, 81.2%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 1.4 Hz, 2H), 7.55 (s, 1H), 7.26 (d, J = 7.7 Hz, 6H), 7.10 (t, J = 7.6 Hz, 6H), 7.02 (m, 3H), 3.91 (t, J = 6.5 Hz, 2H), 2.41 (t, J = 6.5 Hz, 2H), 0.07 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.91, 144.68, 139.32, 130.57, 129.72, 128.17, 126.99, 124.03, 103.12, 96.39, 67.08, 63.64, 31.05. MS: m/z (EI):386.4(M^+-3Ph).

2-(tritylthio)ethyl-3,5-diethynylbenzoate(1d-3). The compound was synthesized by a procedure similar to that used for 1a-3 to yield a brown solide. The residue was purified by column chromatography (R_f= 0.4, petroleum ether/ chloroform = 3/1) to give the desired product (1.302 g, 80.0%) as a white solid. mp: 162.2-162.9 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 1.3 Hz, 2H), 7.76 (s, 1H), 7.44 (d, J = 7.6 Hz, 6H), 7.30 (t, J = 7.6 Hz, 6H), 7.22 (t, J = 7.2 Hz, 3H), 4.09 (t, J = 6.6 Hz, 2H), 3.14 (s, 2H), 2.60 (t, J = 6.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.56, 144.51,

139.41, 133.27, 130.68, 129.56, 128.01, 126.84, 122.99, 81.58, 78.99, 66.97, 63.69, 30.81. MS : m/z (MALDI-TOF) : 495.1[M^++Na].

Semi-cycle(1d). The compound was synthesized by a procedure similar to that used for 1a to yield a white solide.The crude product was purified by column chromatography (R_f = 0.4, petroleum ether/ chloroform = 1/1) to obtain the desired product (0.39 g, 57.8%) as a yellow solid. mp: 90.9-92.3 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 1.5 Hz, 2H), 8.01 (d, J = 8.4 Hz, 4H), 7.89 (t, J = 1.5 Hz, 1H), 7.60 (d, J = 8.4 Hz, 4H), 7.45 (m, 18H), 7.30 (m, 18H), 7.22 (m, 9H), 4.13 (m, 6H), 2.63 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.53, 164.71, 144.58, 144.53, 132.71, 131.64, 130.89, 129.86, 129.70, 129.58, 128.03, 128.00, 127.27, 126.87, 126.83, 123.73, 90.28, 90.26, 66.99, 66.93, 63.74, 63.44, 31.00. MS : m/z (MALDI-TOF) : 1339.6[M^++Na].



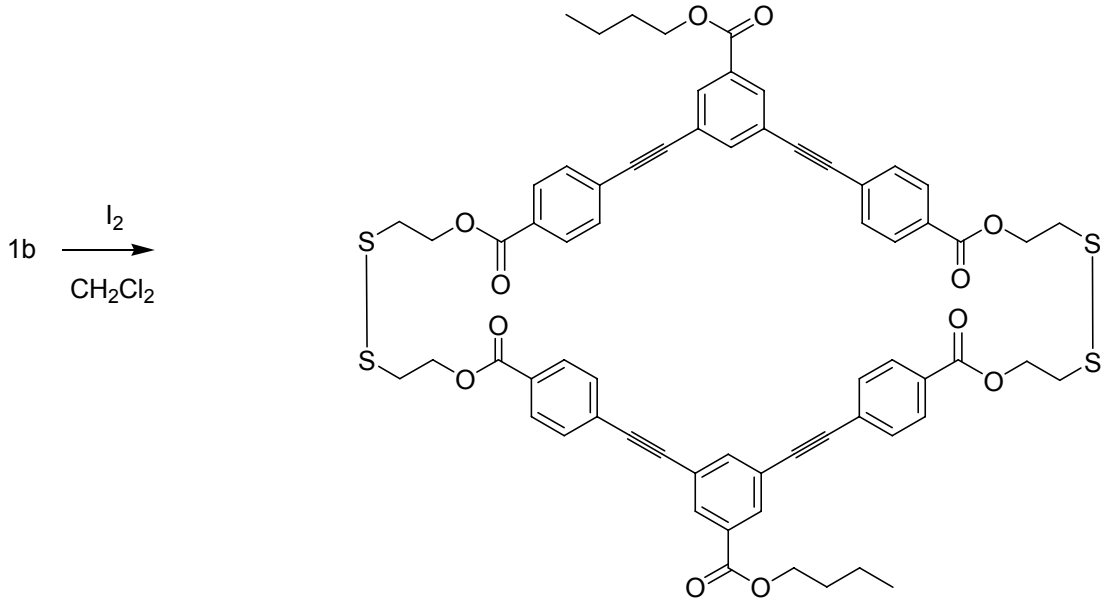
2a

Synthesis of **2a**

Macrocycle(2a). I_2 (0.076 g, 0.3 mmol) was added to a solution of semi-cycle (0.33 g, 0.3 mmol) in CH_2Cl_2 (100 mL) in portion over half an hour. The mixture was stirred at rt for 4 h and then quenched with 10% aqueous sodium thiosulfate (20 mL). The mixture was washed with brine, dried by Na_2SO_4, and concentrated in vacuo to provide a pale-yellow solid. Purification by column chromatography (R_f = 0.3, chloroform/ethyl acetate = 20/1) to give the desired product (0.079 g, 42%) as a white solid. mp:175.5-176.8 ^oC. ^1H NMR (400MHz, $CDCl_3$) δ 8.01 (d, J = 1.6 Hz, 4H), 7.91 (d, J = 8.5 Hz, 8H), 7.68 (t, J = 1.6 Hz, 2H), 7.47 (d, J = 8.5 Hz, 8H), 4.60 (t, J = 6.0 Hz, 8H), 4.48 (s, 4H), 3.86 (s, 4H), 3.71 (s, 4H), 3.60 (s, 4H), 3.39 (s,6H), 3.12 (t, J = 5.9 Hz, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.59, 164.82, 138.26, 132.66, 131.69, 130.88, 129.59, 129.51, 127.48, 123.55, 90.47, 90.11, 77.35, 77.03, 76.71, 71.99, 70.60, 69.16, 64.53, 63.08, 59.11, 38.01. MS : m/z

(MALDI-TOF) : 1283.1[M^++Na].

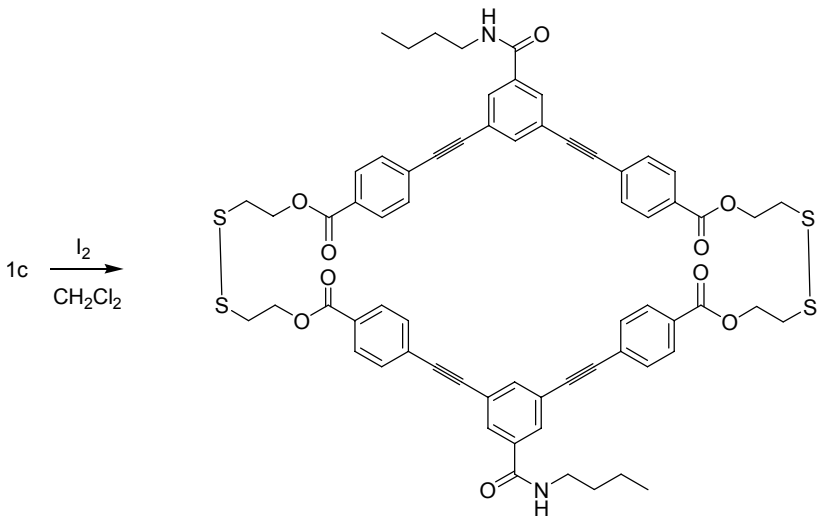
Synthesis of 2b



2b

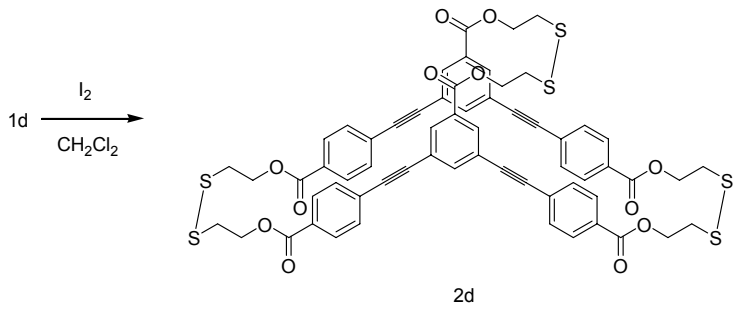
Macrocycle(2b). I_2 (0.38 g, 1.49 mmol) was added to a solution of semi-cycle (1.60 g, 1.49 mmol) in CH_2Cl_2 (200 mL) in portion over half an hour. The mixture was stirred at rt for 4 h and then quenched with 10% aqueous sodium thiosulfate (30 mL). The mixture was washed with brine, dried by Na_2SO_4, and concentrated in vacuo to provide a pale-yellow solid. Purification by column chromatography (silica, chloroform/ethyl acetate = 50/1) to give the desired product (0.39 g, 45.0%) as a white solid. mp: 200.9-203.2 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 4H), 7.91 (d, J = 8.4 Hz, 8H), 7.66 (s, 2H), 7.47 (d, J = 8.4 Hz, 8H), 4.59 (t, J = 6.4 Hz, 8H), 4.31 (t, J = 6.7 Hz, 4H), 3.12 (t, J = 6.4 Hz, 8H), 1.86 – 1.66 (m, 4H), 1.48 (m, 4H), 1.01 (t, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.60, 164.87, 138.13, 132.51, 131.69, 131.24, 129.58, 129.49, 127.49, 123.50, 90.53, 90.03, 65.43, 63.09, 38.01, 30.75, 19.27, 13.79; MS : m/z (MALDI-TOF) : 1191.5[M^++Na].

Synthesis of 2c



2c

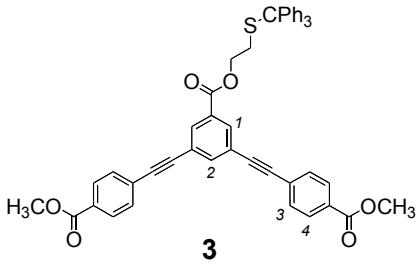
Macrocycle(2c). I_2 (0.12 g, 0.45 mmol) was added to a solution of semi-cycle (0.5 g, 0.45mmol) in CH_2Cl_2 (150 mL) in portion over half an hour. The mixture was stirred at rt for 4 h and then quenched with 10% aqueous sodium thiosulfate (20 mL). The mixture was washed with brine, dried by Na_2SO_4, and concentrated in vacuo to provide a pale-yellow solid. Purification by column chromatography (silica, chloroform/ethyl acetate = 20/1) to give the desired product (0.05 g, 20%) as a white solid. mp: 272.9-275.1 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.1 Hz, 8H), 7.61 (s, 2H), 7.58 (s, 4H), 7.38 (d, J = 8.2 Hz, 8H), 7.05 (t, J = 5.3 Hz, 2H), 4.56 (t, J = 6.5 Hz, 8H), 3.53 (dd, J = 13.0 Hz, 7.0 Hz, 4H), 3.11 (t, J = 6.5 Hz, 8H), 1.72 (m, 4H), 1.50 (m, 4H), 1.03 (t, J = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.65, 165.56, 136.70, 135.72, 131.66, 130.32, 129.52, 129.43, 127.51, 123.49, 90.69, 89.91, 63.11, 40.19, 38.31, 31.70, 20.30, 13.84; MS : m/z (MALDI-TOF) : 1189.6[M^++Na].



2d

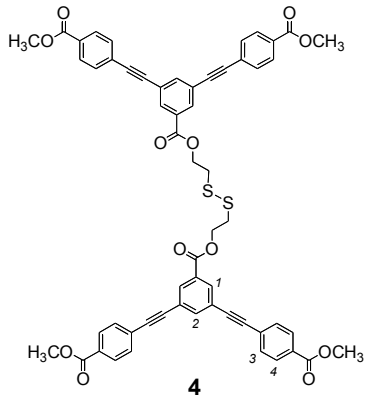
Macrocycle(2d). I_2 (0.5 g, 0.2 mmol) was added to a solution of semi-cycle-1 (1.3 g, 0.1 mmol) in CH_2Cl_2 (20 mL) in portion over half an hour. The mixture was stirred at rt for 4 h and then quenched with 10% aqueous sodium thiosulfate (30 mL). The mixture was washed with brine, dried by Na_2SO_4, and concentrated in vacuo to provide a pale-yellow solid. Purification by column chromatography (silica, chloroform/ethyl acetate = 20/1) to give the desired product (0.23 g, 38.5%)

as a white solid. mp: 263.2-264.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 1.4 Hz, 4H), 7.87 (d, *J* = 8.3 Hz, 8H), 7.61 (t, *J* = 1.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 8H), 4.59 (t, *J* = 6.4 Hz, 12H), 3.16 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.60, 164.66, 138.41, 132.48, 131.69, 130.36, 129.49, 129.37, 127.35, 123.51, 90.32, 90.18, 63.67, 63.20, 38.46, 38.20. MS : m/z (MALDI-TOF) :1197.5[M^++Na].



3

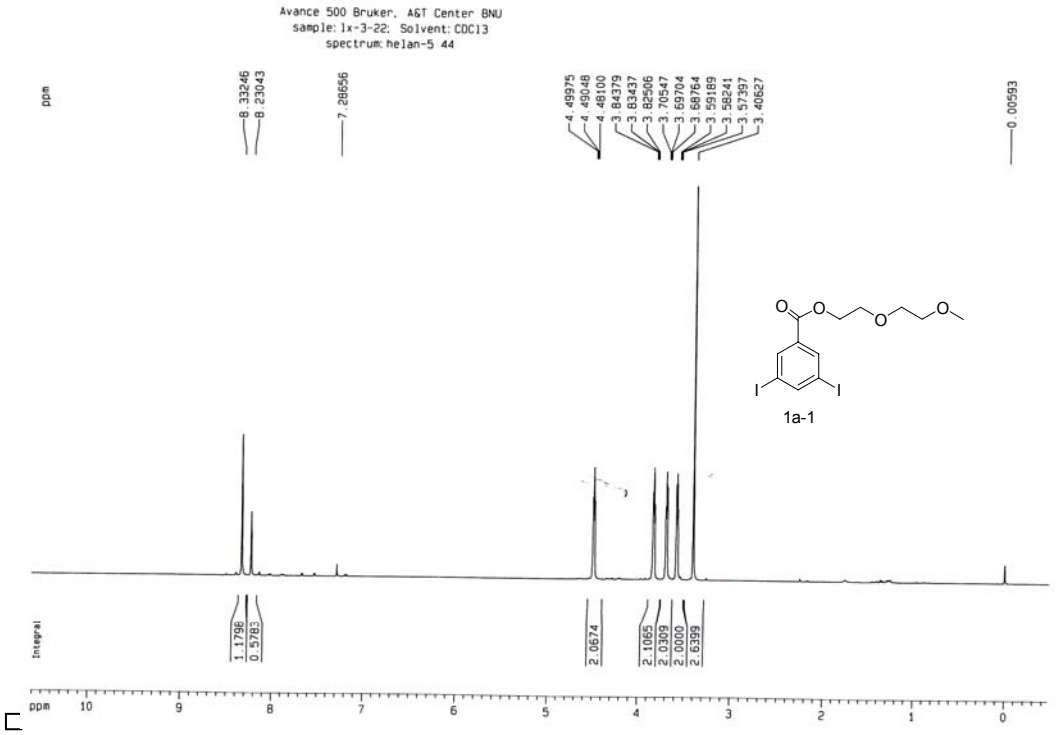
Compound 3. ^{1}H NMR (400 MHz, $CDCl_3$) δ8.14 (d, *J* = 1.6 Hz, 2H), 8.05 (d, *J* = 8.5 Hz, 4H), 7.88 (t, *J* = 1.6 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 4H), 7.45 (m, 6H), 7.31 (t, *J* = 7.6 Hz, 6H), 7.22 (t, *J* = 7.3 Hz, 3H), 4.15 (t, *J* = 6.5 Hz, 2H), 3.94 (s, 6H), 2.64 (t, *J* = 6.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ166.45, 164.71, 144.57, 138.47, 132.71, 130.96, 130.07, 129.63, 128.04, 127.22, 126.88, 123.78, 90.26, 67.03,63.75,52.33,30.

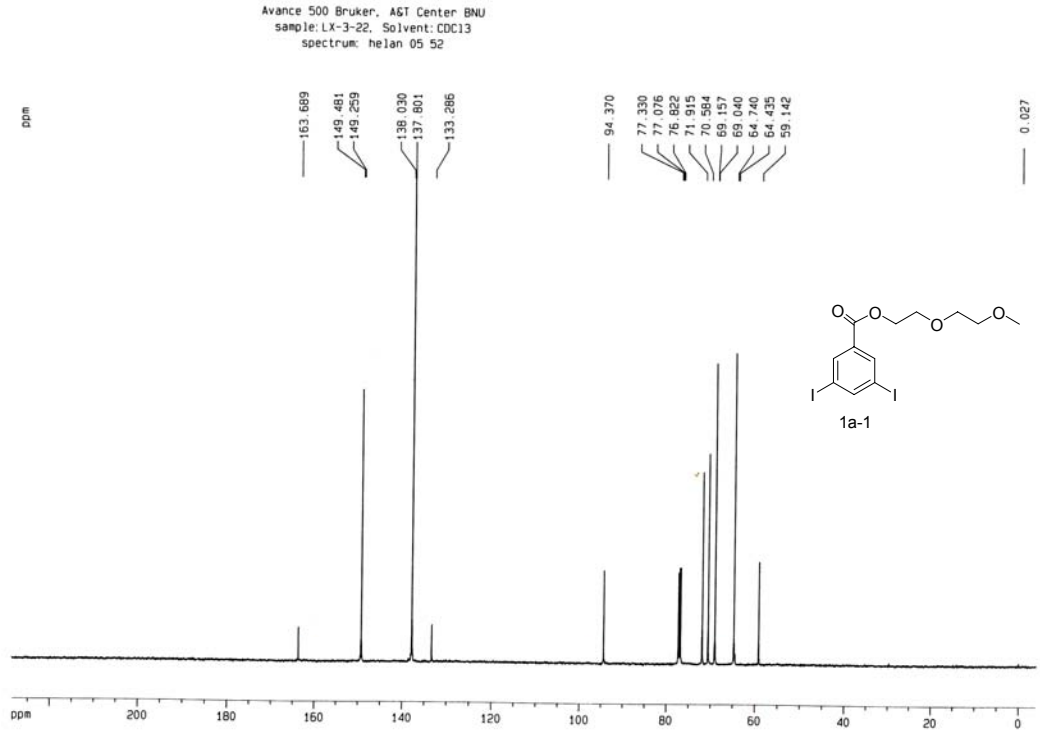


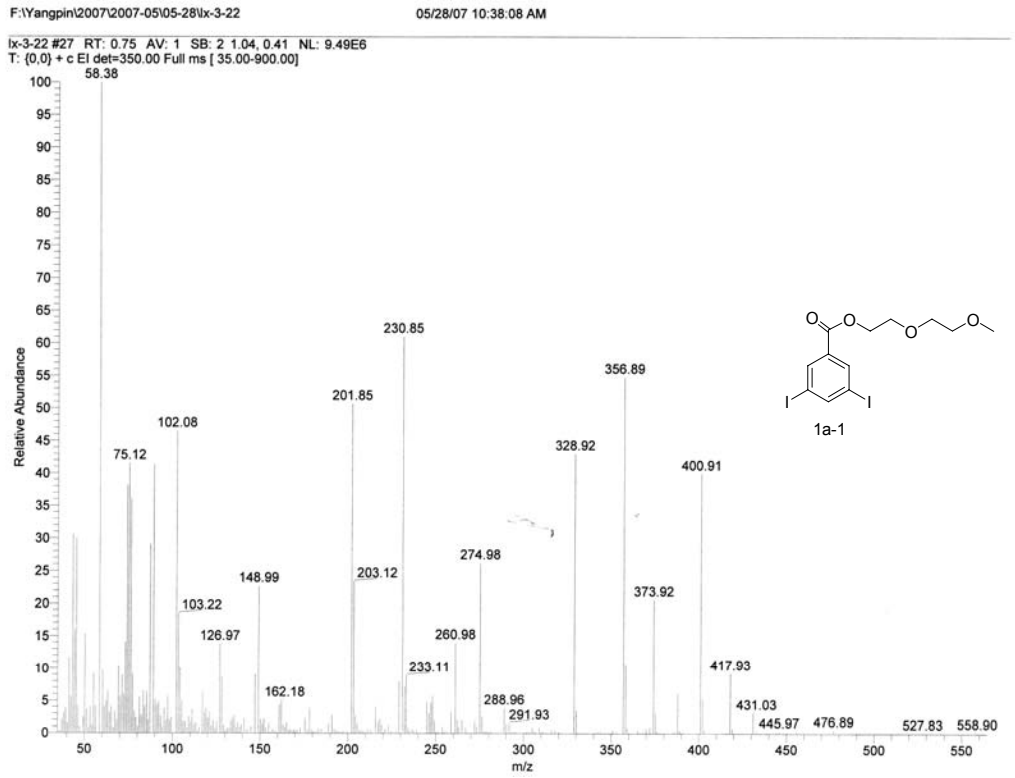
4

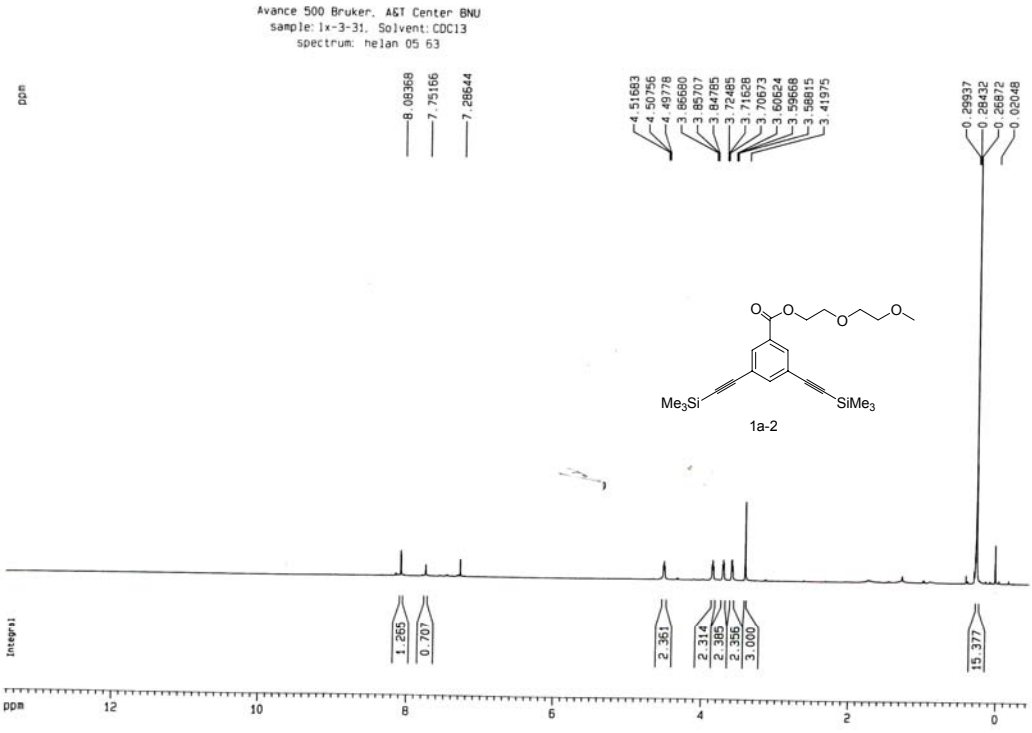
Compound 4. ^{1}H NMR (400 MHz, $CDCl_3$) δ8.15 (d, *J* = 1.6 Hz, 4H), 8.02 (m, 8H), 7.85 (t, *J* = 1.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 8H), 4.65 (t, *J* = 6.5 Hz, 4H), 3.93 (s, 12H), 3.13 (t, *J* = 6.5 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ166.38, 164.81, 138.57, 132.64, 131.63, 130.70, 130.01, 129.57, 127.12, 123.82, 90.29, 90.10, 63.29, 52.29, 52.22, 37.30. MS: m/z (MALDI-TOF): 1017 [M + Na^+].

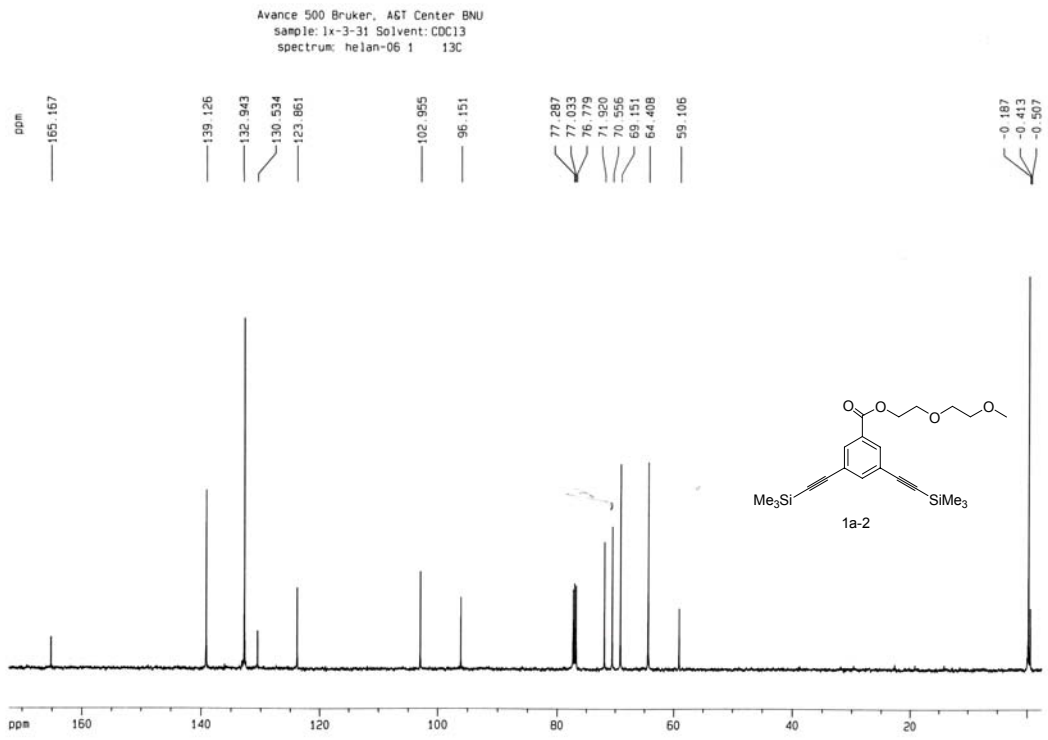
II. NMR and Mass Spectra

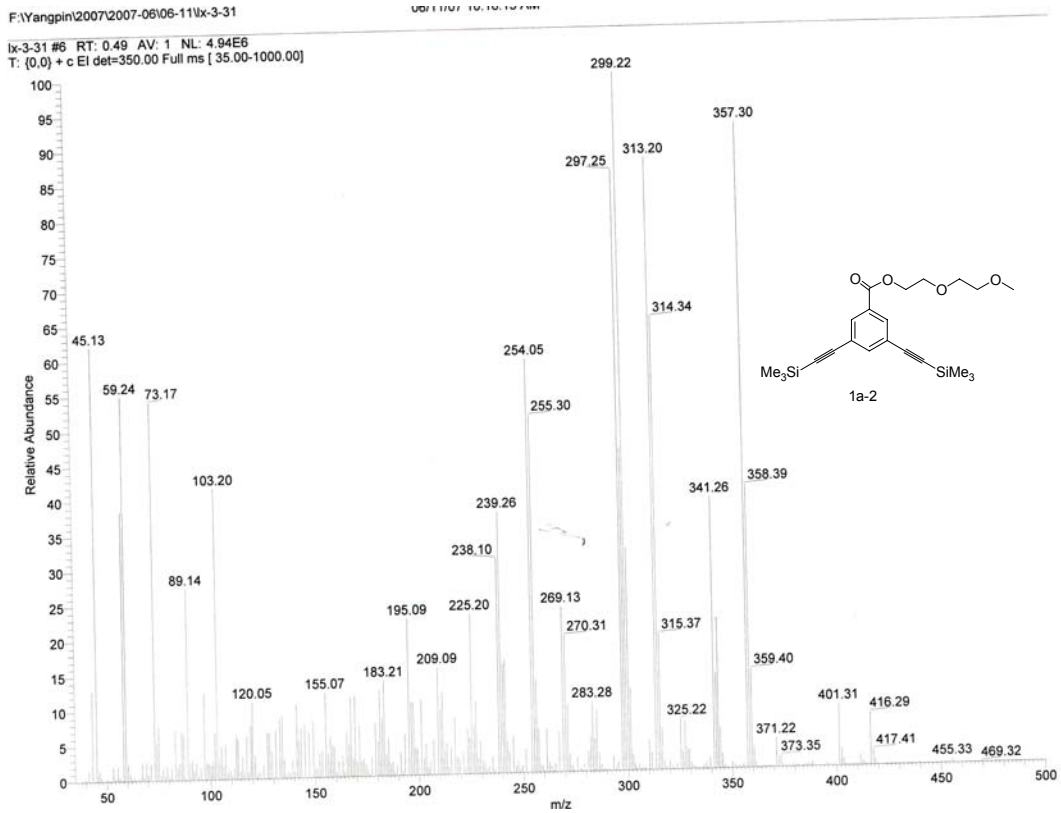

Avance 500 Bruker, A&T Center BNU
sample: lx-3-22; Solvent: CDCl3
spectrum: helan-5 44
ppm
8.33246
8.23043
7.28656
4.49975
4.49048
4.48100
3.84379
3.83437
3.82506
3.70547
3.69704
3.68764
3.59189
3.58241
3.57397
3.40627
0.00593
1a-1
Integral
1.1796
0.5783
2.0674
2.1065
2.0309
2.0000
2.6399
ppm

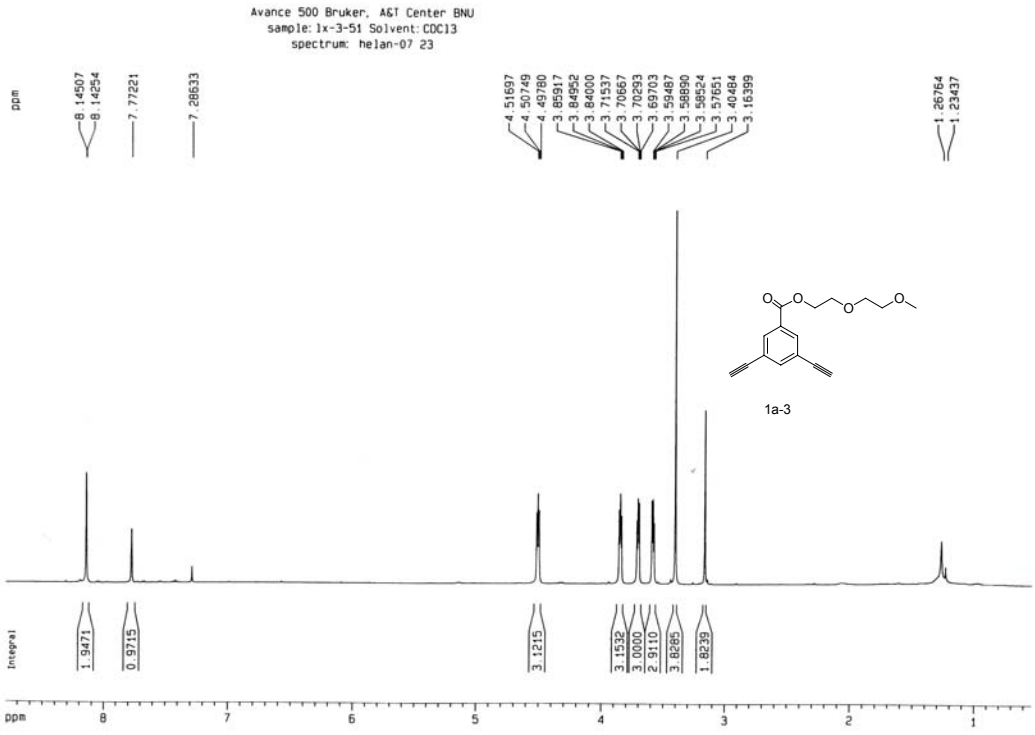

Avance 500 Bruker, A&T Center BNU
sample: LX-3-22; Solvent: CDCl3
spectrum: helan 05 52
ppm
163.689
149.481
149.259
138.030
137.801
133.286
94.370
77.330
77.076
76.822
71.915
70.584
69.157
69.040
64.740
64.435
59.142
0.027
1a-1
ppm

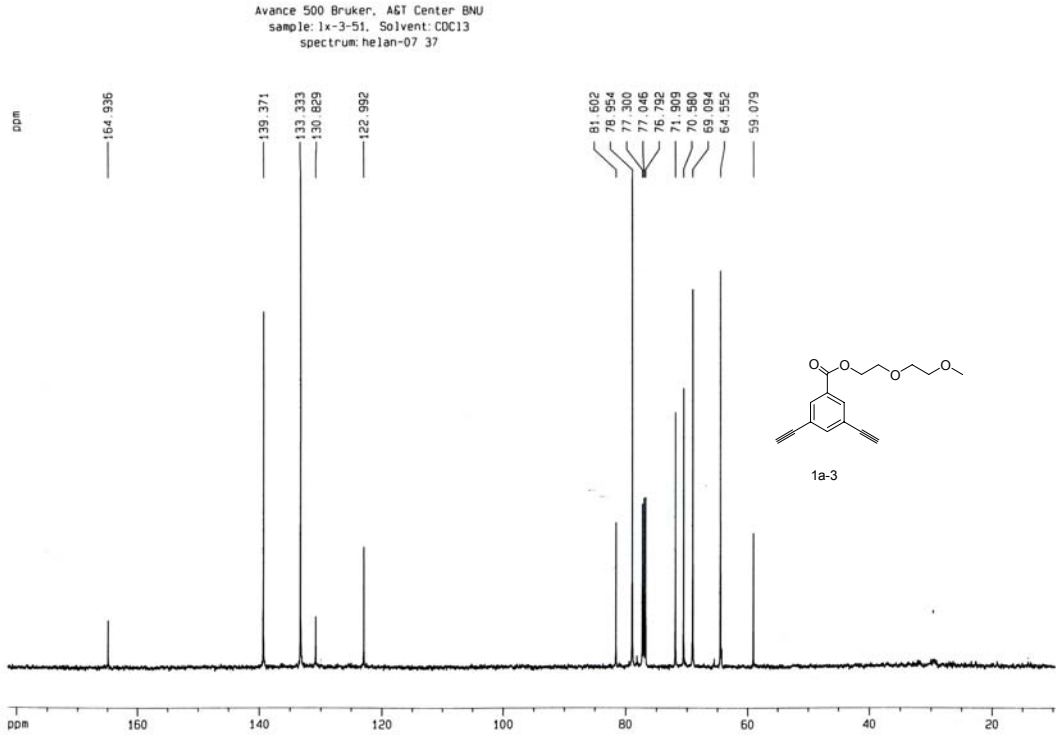

F:\Yangpin\2007\2007-05\05-28\lx-3-22
05/28/07 10:38:08 AM
lx-3-22 #27 RT: 0.75 AV: 1 SB: 2 1.04, 0.41 NL: 9.49E6
T: {0,0} + c EI det=350.00 Full ms [35.00-900.00]
Relative Abundance
m/z
58.38
75.12
102.08
103.22
126.97
148.99
162.18
201.85
203.12
230.85
233.11
260.98
274.98
288.96
291.93
328.92
356.89
373.92
400.91
417.93
431.03
445.97
476.89
527.83
558.90
1a-1

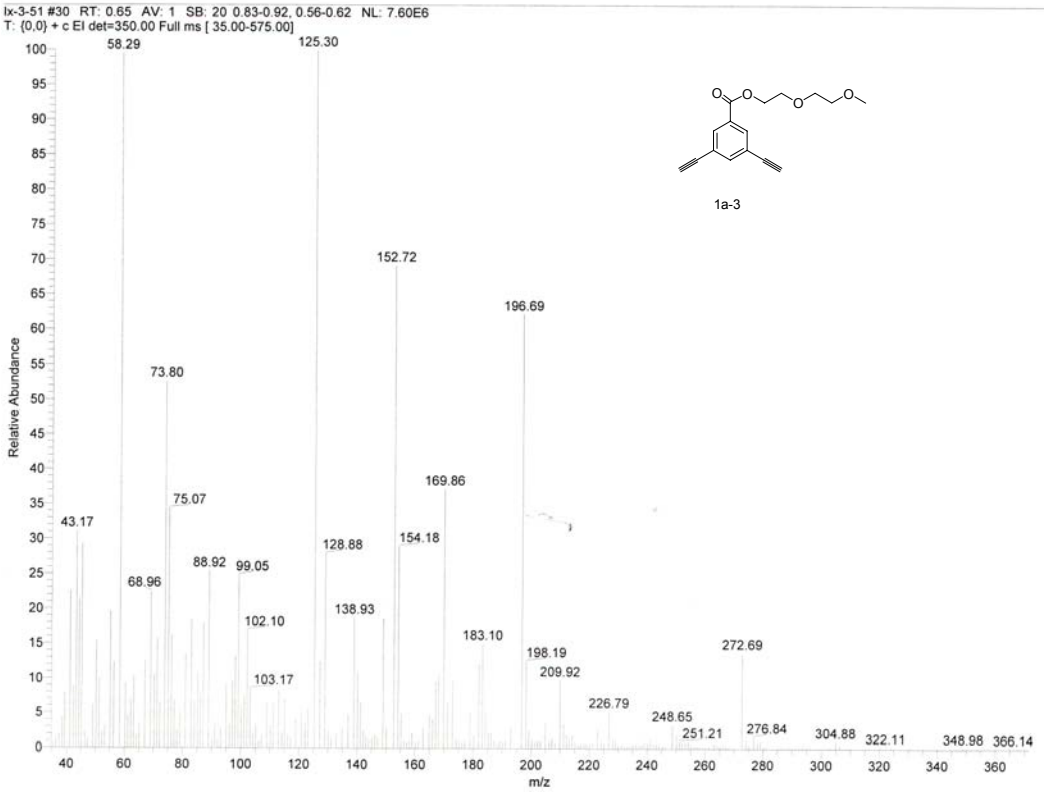

Avance 500 Bruker, A&T Center BNU
sample: lx-3-31, Solvent: CDCl3
spectrum: helan 05 63
ppm
8.08368
7.75166
7.28644
4.51683
4.50756
4.49778
3.86680
3.85707
3.84785
3.72485
3.71628
3.70673
3.60624
3.59668
3.58815
3.41975
0.29937
0.28432
0.26872
0.02048
Me3Si
SiMe3
1a-2
Integral
1.265
0.707
2.361
2.314
2.385
2.356
3.000
15.377


Avance 500 Bruker, A&T Center BNU
sample: lx-3-31 Solvent: CDCl3
spectrum: helan-06 1 13C
ppm
165.167
139.126
132.943
130.534
123.861
102.955
96.151
77.287
77.033
76.779
71.920
70.556
69.151
64.408
59.106
-0.187
-0.413
-0.507
Me3Si
SiMe3
1a-2

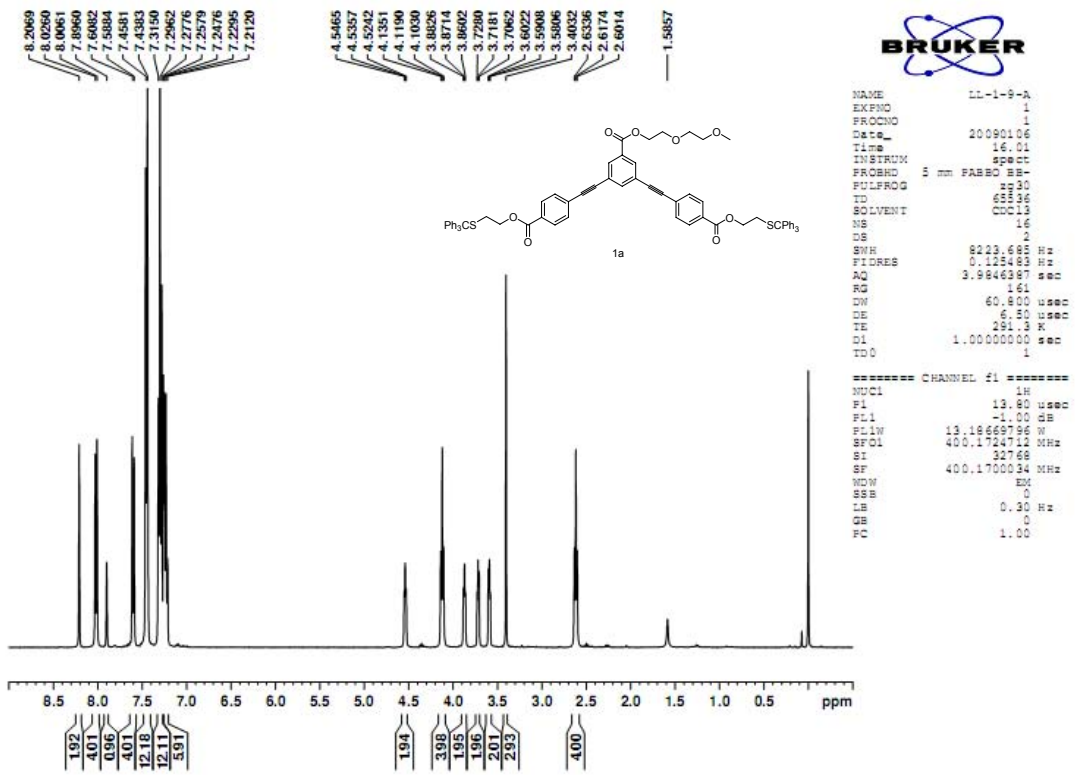

F:\Yangpin\2007\2007-06\06-11\lx-3-31
lx-3-31 #6 RT: 0.49 AV: 1 NL: 4.94E6
T: {0,0} + c EI det=350.00 Full ms [35.00-1000.00]
Relative Abundance
m/z
299.22
357.30
313.20
297.25
314.34
45.13
254.05
59.24
73.17
255.30
103.20
358.39
341.26
239.26
238.10
89.14
269.13
195.09
225.20
270.31
315.37
209.09
359.40
183.21
155.07
120.05
283.28
401.31
416.29
325.22
371.22
373.35
417.41
455.33
469.32
Me3Si
SiMe3
1a-2


Avance 500 Bruker, A&T Center BNU
sample: lx-3-51 Solvent: CDCl3
spectrum: helan-07 23
ppm
8.14507
8.14254
7.77221
7.28633
4.51697
4.50749
4.49780
3.85917
3.84952
3.84000
3.71537
3.70667
3.70293
3.69703
3.59487
3.58890
3.58524
3.57651
3.40484
3.16399
1.26764
1.23437
1a-3
Integral
1.9471
0.9715
3.1215
3.1532
3.0000
2.9110
3.8285
1.8239
ppm

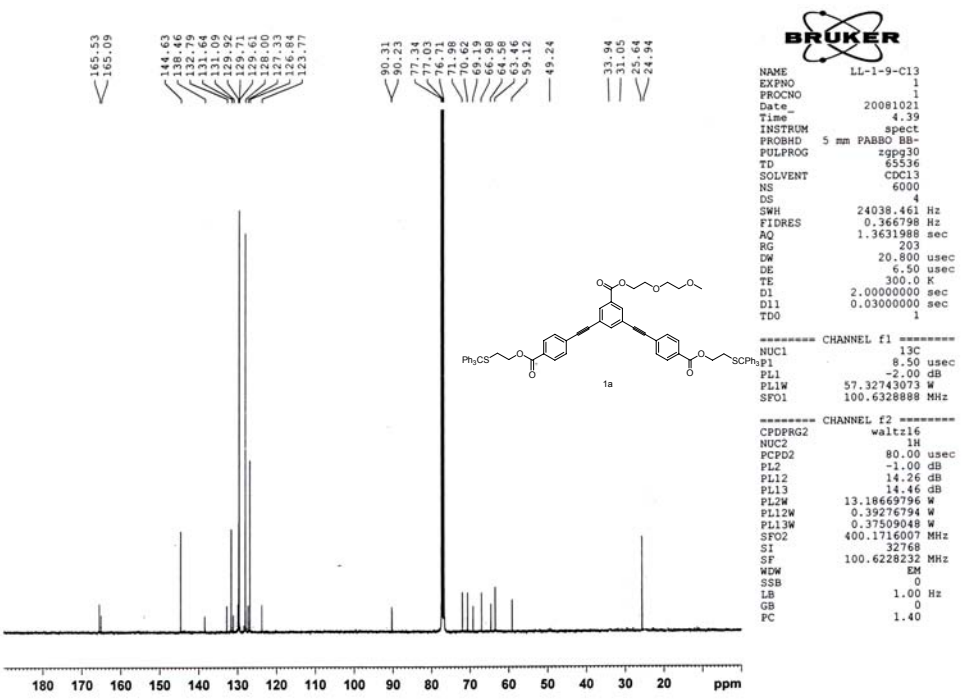

Avance 500 Bruker, A&T Center BNU
sample: lx-3-51, Solvent: CDCl3
spectrum: helan-07 37
ppm
164.936
139.371
133.333
130.829
122.992
81.602
78.954
77.300
77.046
76.792
71.909
70.580
69.094
64.552
59.079
1a-3
ppm

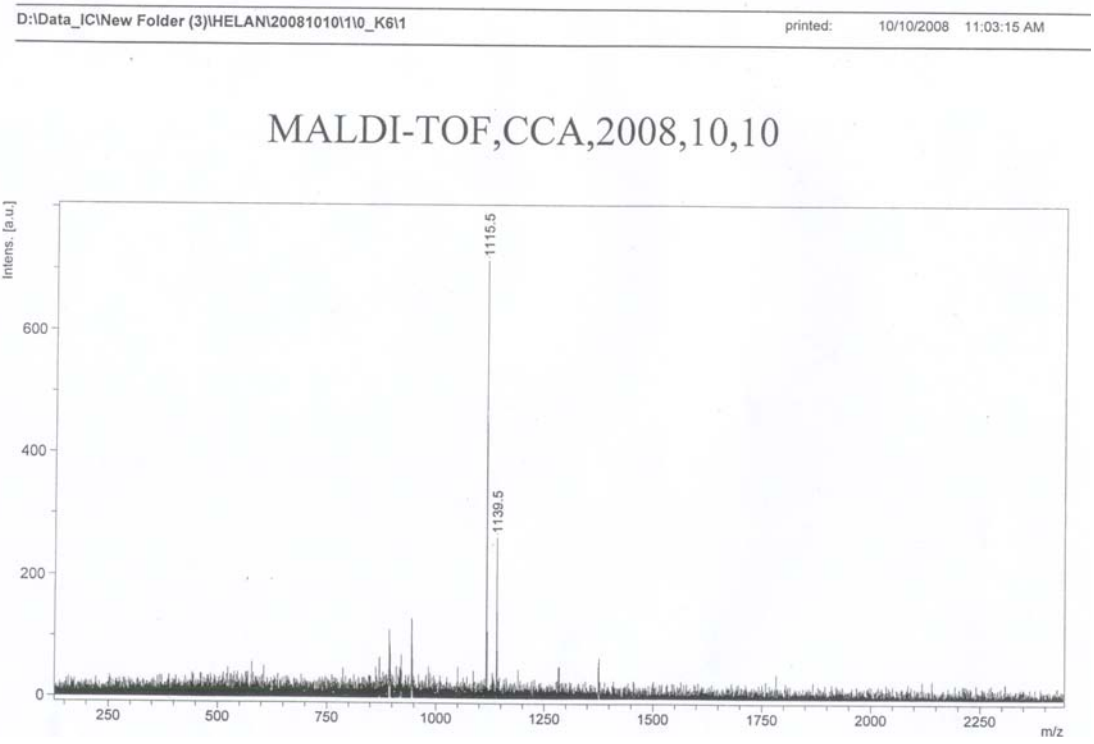

lx-3-51 #30 RT: 0.65 AV: 1 SB: 20 0.83-0.92, 0.56-0.62 NL: 7.60E6
T: {0,0} + c EI det=350.00 Full ms [35.00-575.00]
Relative Abundance
m/z
58.29
125.30
152.72
196.69
73.80
169.86
75.07
43.17
128.88
154.18
88.92
99.05
68.96
138.93
102.10
183.10
198.19
272.69
209.92
103.17
226.79
248.65
251.21
276.84
304.88
322.11
348.98
366.14

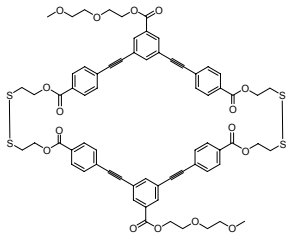
1a-3

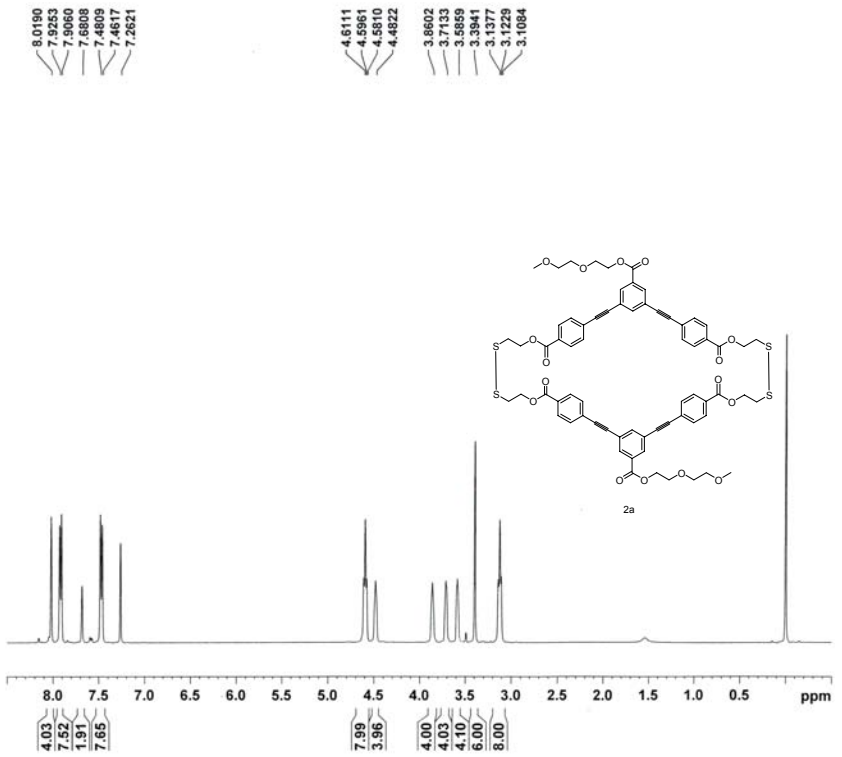

8.2069
8.0260
8.0061
7.8960
7.6082
7.5884
7.4581
7.4383
7.3150
7.2962
7.2776
7.2579
7.2476
7.2295
7.2120
4.5465
4.5357
4.5242
4.1351
4.1190
4.1030
3.8826
3.8714
3.8602
3.7290
3.7181
3.7062
3.6022
3.5908
3.5806
3.4032
2.6336
2.6174
2.6014
1.5857
BRUKER
NAME LL-1-9-A
EXPNO 1
PROCNO 1
Date_ 20090106
Time 16.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 161
DW 60.800 usec
DE 6.50 usec
TE 291.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700034 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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
1.92 4.01 0.96 4.01 2.18 2.11 5.91
1.94 3.98 1.95 1.96 2.01 2.93 4.00

1a


165.53
165.09
144.63
134.46
132.79
131.64
131.09
129.92
129.71
129.61
128.00
127.33
126.84
123.77
90.31
90.23
77.34
77.03
76.71
71.98
70.62
69.19
66.98
64.58
63.46
59.12
49.24
33.94
31.05
25.64
24.94
BRUKER
NAME LL-1-9-C13
EXPNO 1
PROCNO 1
Date_ 20081021
Time_ 4.39
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 6000
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 57.32743073 W
SFO1 100.6328888 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.26 dB
PL13 14.46 dB
PL2W 13.18669796 W
PL12W 0.39276794 W
PL13W 0.37509048 W
SFO2 400.1716007 MHz
SI 32768
SF 100.6228232 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Ph3CS
SCPh3
1a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

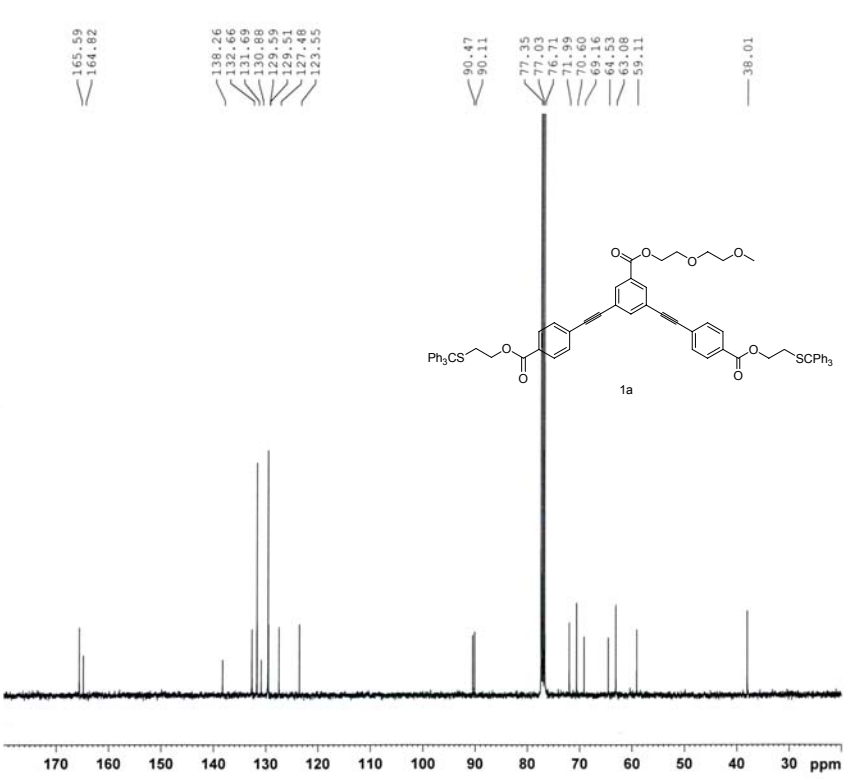

D:\Data_IC\New Folder (3)\HELAN\20081010\1\0_K6\1
printed: 10/10/2008 11:03:15 AM
MALDI-TOF,CCA,2008,10,10
Intens. [a.u.]
1115.5
1139.5
600
400
200
0
250 500 750 1000 1250 1500 1750 2000 2250
m/z


2a



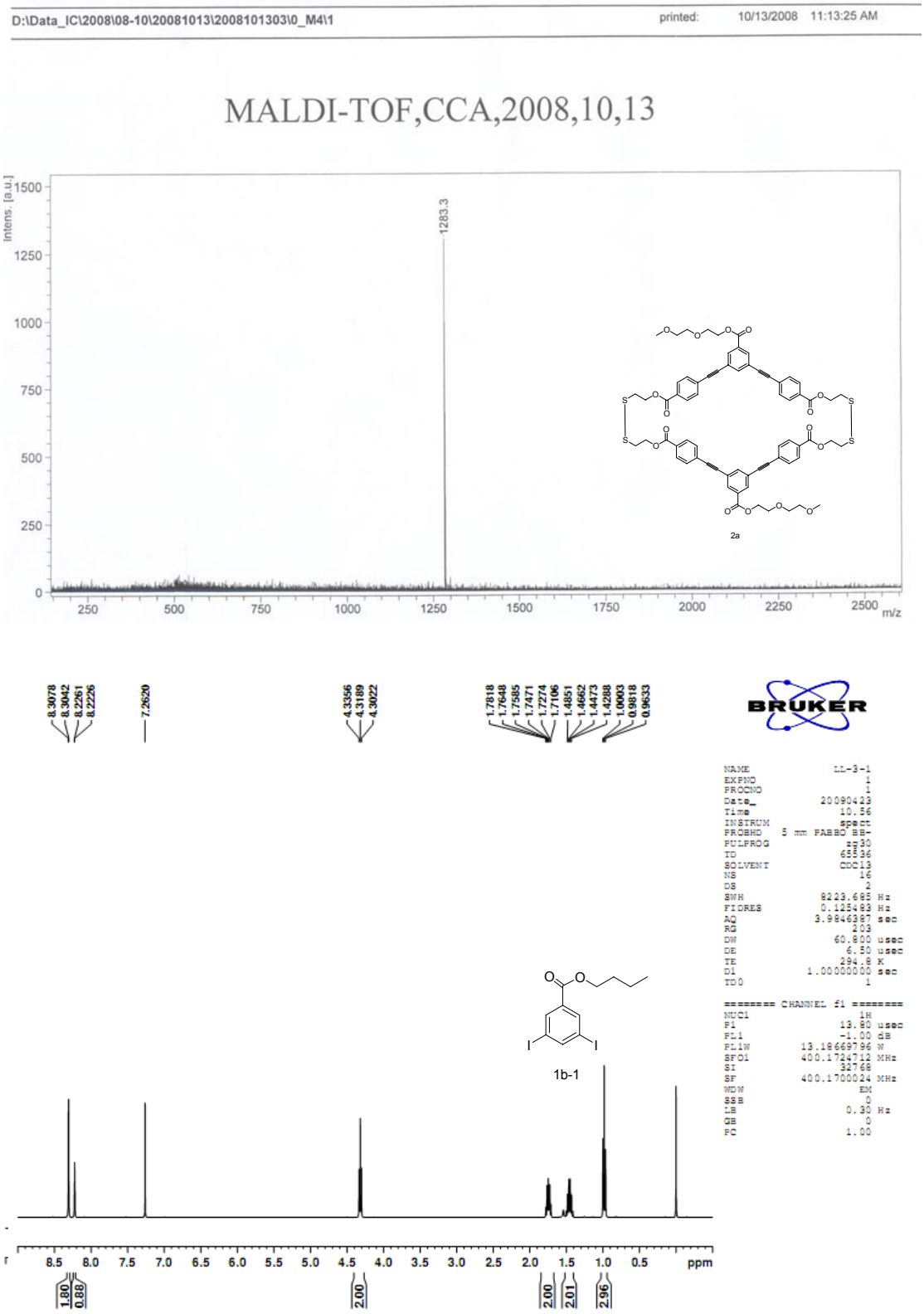
BRUKER

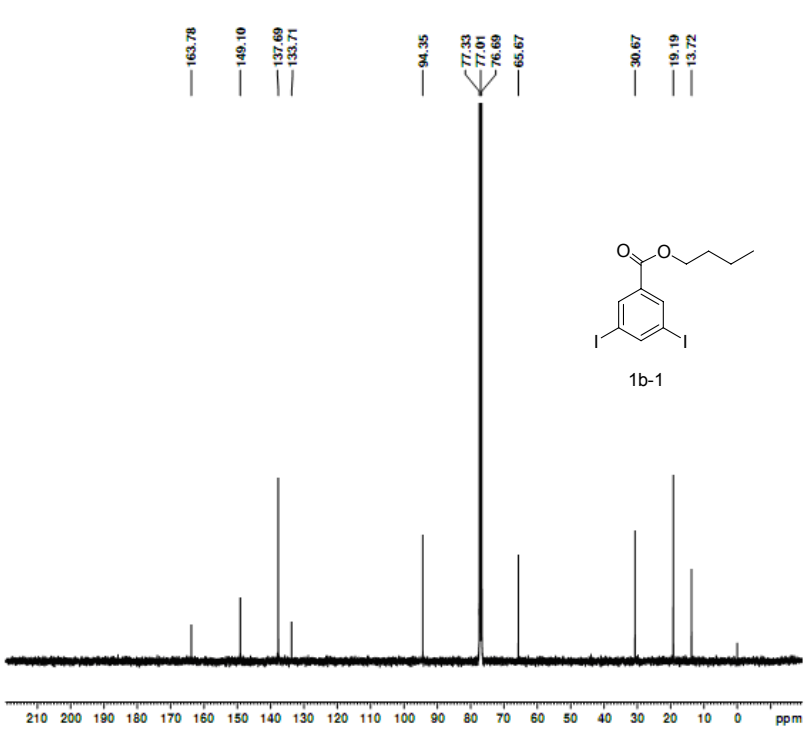
NAME	11-1-10-e
EXPNO	1
PROCNO	1
Date_	20090408
Time	8.36
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDC13
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	203
DW	60.800 usec
DE	6.50 usec
TE	296.8 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	13.80 usec
PL1	-1.00 dB
PL1W	13.18669796 W
SFO1	400.1724712 MHz
SI	32768
SF	400.1700020 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

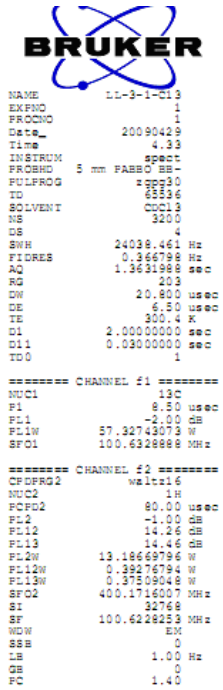


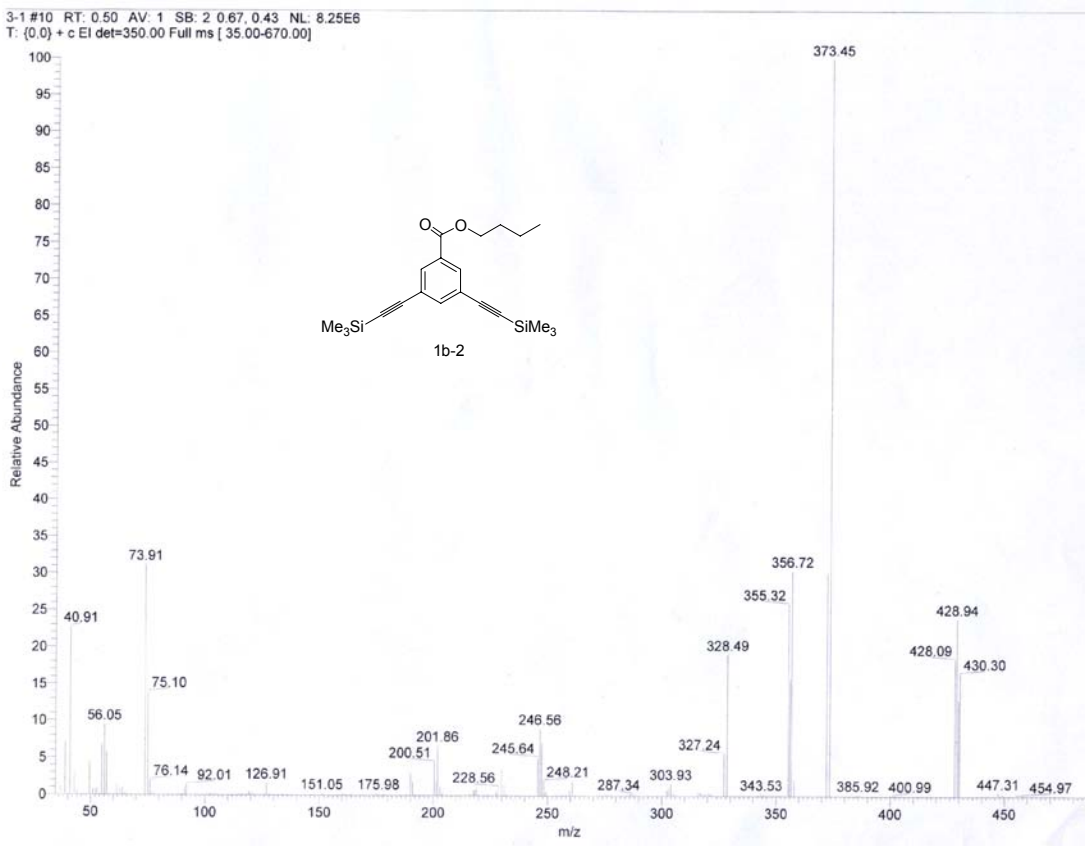
BRUKER

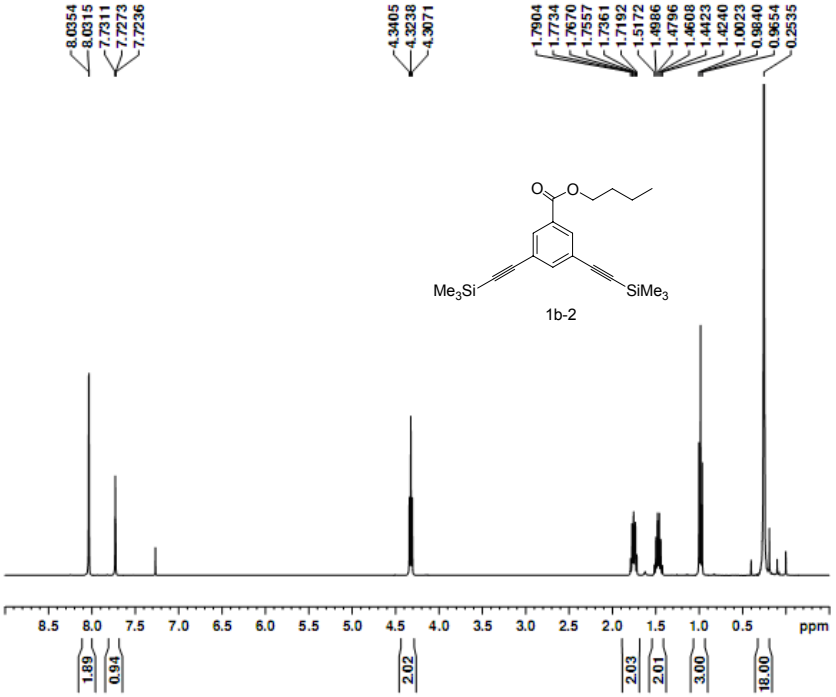
NAME	LL-1-10-C13
EXPNO	1
PROCNO	1
Date_	20081020
Time	22.49
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDC13
NS	1061
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	300.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6328888 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.26 dB
PL13	14.46 dB
PL2W	13.18669796 W
PL12W	0.39276794 W
PL13W	0.37509048 W
SFO2	400.1716007 MHz
SI	32768
SF	100.6228225 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

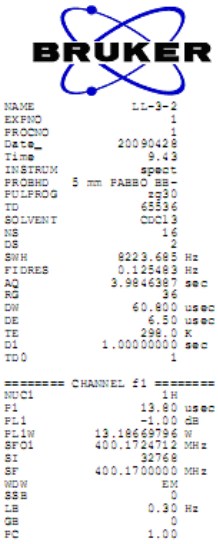

D:\Data_IC\2008\08-10\20081013\20081013303\0_M4\1
printed: 10/13/2008 11:13:25 AM
MALDI-TOF,CCA,2008,10,13
Intens. [a.u.]
1283.3
m/z
2a
8.3078
8.3042
8.2261
8.2226
7.2620
4.3356
4.3189
4.3022
1.7818
1.7648
1.7585
1.7471
1.7274
1.7106
1.4851
1.4662
1.4473
1.4288
1.0003
0.9818
0.9633
BRUKER
NAME LL-3-1
EXPNO 1
PROCNO 1
Date_ 20090423
Time 10.56
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846987 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 294.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700024 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1b-1
ppm
1.80
0.88
2.00
2.00
2.01
2.96


163.78
149.10
137.69
133.71
94.35
77.33
77.01
76.69
65.67
30.67
19.19
13.72
O
O
I
I
1b-1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

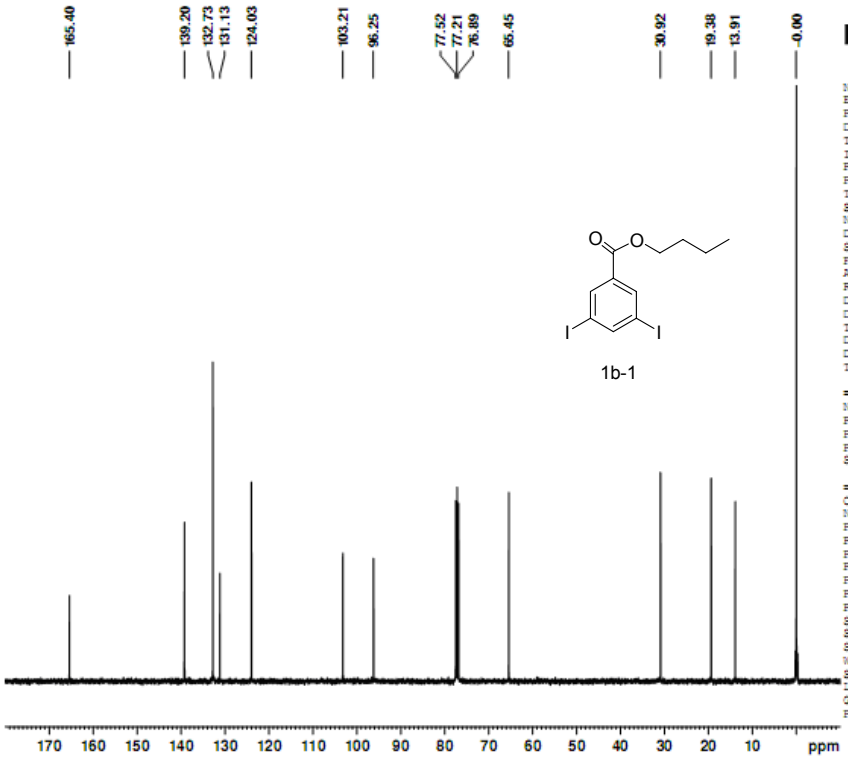

BRUKER
NAME LL-3-1-C13
EXPNO 1
PROCNO 1
Date_ 20090429
Time 4.33
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3200
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 300.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 57.32743073 W
SFO1 100.6328888 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.26 dB
PL13 14.46 dB
PL2W 13.18669796 W
PL12W 0.39276794 W
PL13W 0.37509048 W
SFO2 400.1716007 MHz
SI 32768
SF 100.6228253 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


3-1 #10 RT: 0.50 AV: 1 SB: 2 0.67, 0.43 NL: 8.25E6
T: {0,0} + c EI det=350.00 Full ms [35.00-670.00]
Relative Abundance
m/z
O
O
Me3Si
SiMe3
1b-2
373.45
356.72
355.32
328.49
428.94
428.09
430.30
73.91
40.91
75.10
56.05
246.56
245.64
201.86
200.51
327.24
76.14
92.01
126.91
151.05
175.98
228.56
248.21
287.34
303.93
343.53
385.92
400.99
447.31
454.97

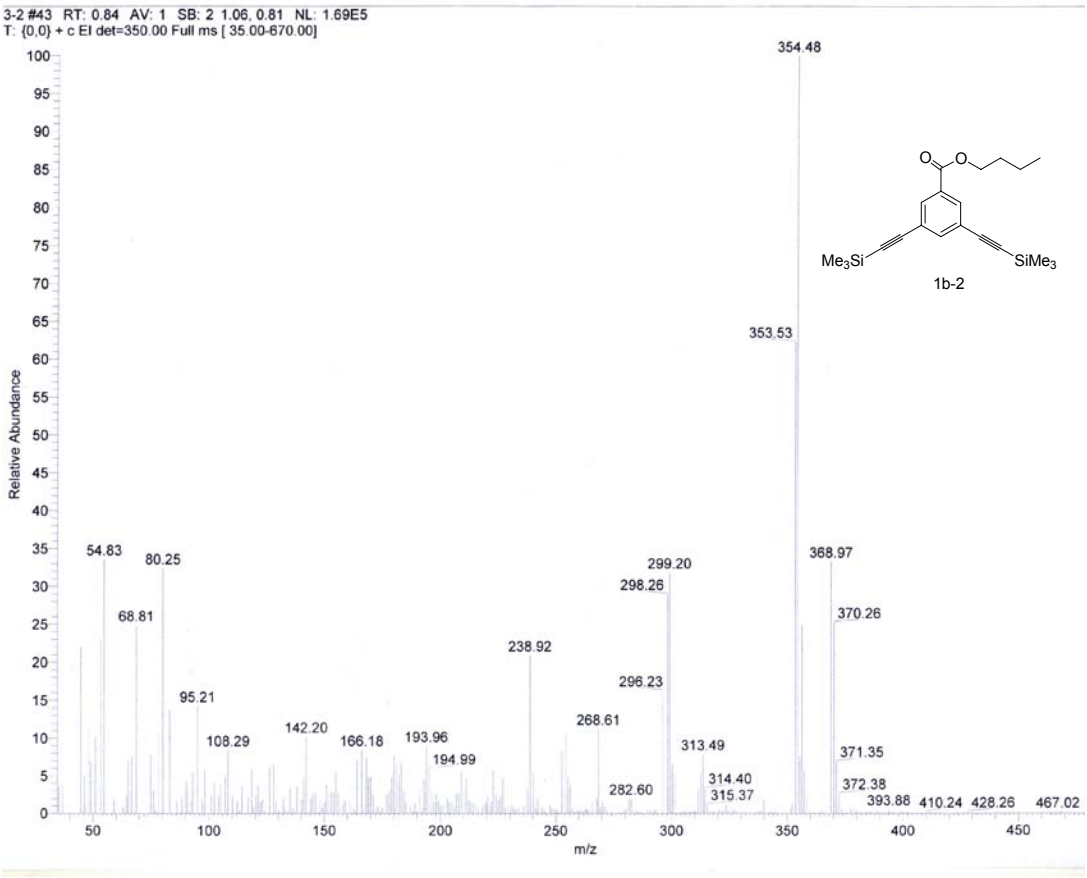


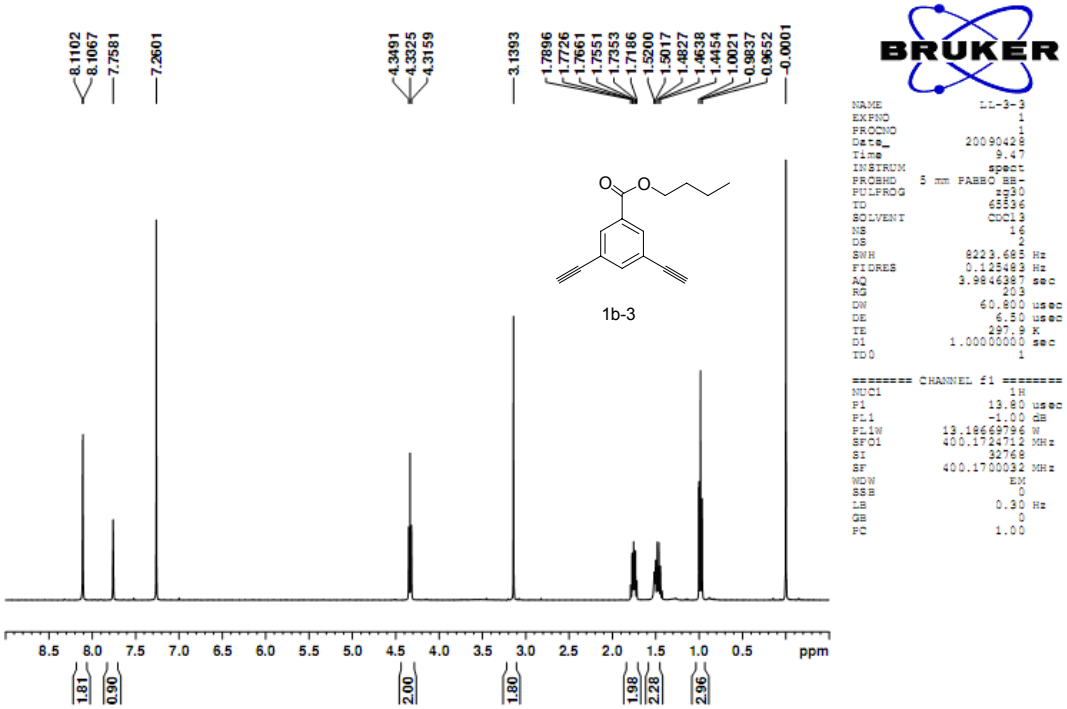


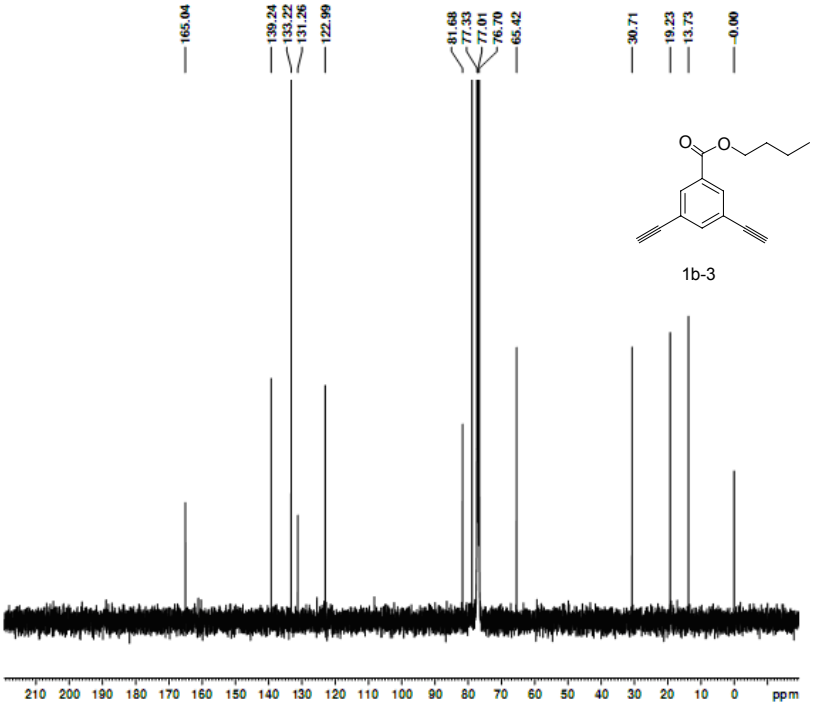

```
NAME                LL-3-2
EXPNO                    1
PROCNO                   1
Date_             20090428
Time                  9.43
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      16
DS                       2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                      26
DW                60.800 usec
DE                 6.50 usec
TE                298.0 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                 13.80 usec
PL1                -1.00 dB
PL1W        13.18669796 W
SFO1        400.1724712 MHz
SI                   32768
SF          400.1700000 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 1.00
```

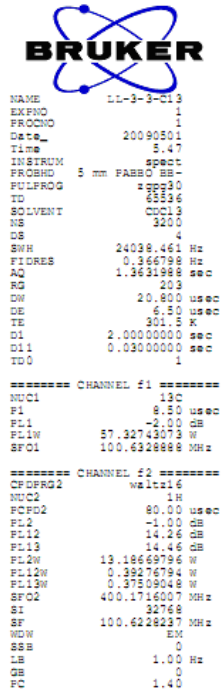


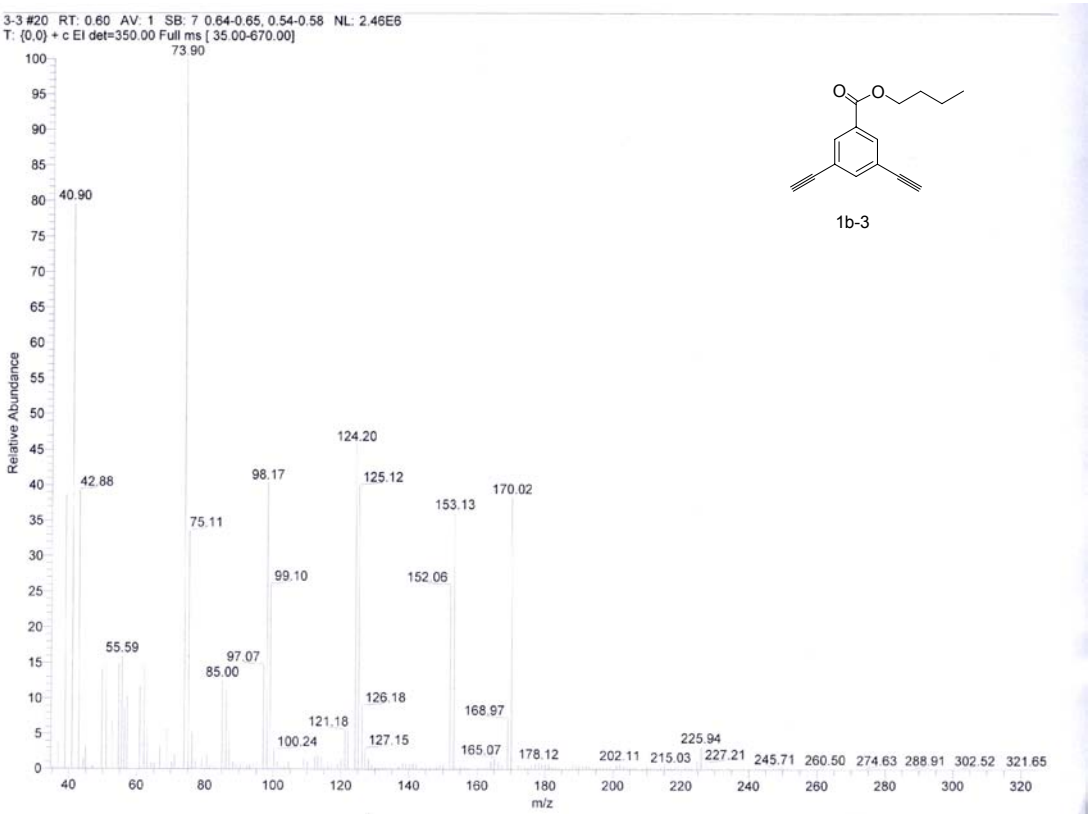

```
NAME             LL-3-2-C13
EXPNO                    1
PROCNO                   1
Date_             20090505
Time                 16.20
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     136
DS                       4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                     203
DW                20.800 usec
DE                 6.50 usec
TE                300.7 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W        57.32743073 W
SFO1        100.6328888 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               14.26 dB
PL13               14.46 dB
PL2W        13.18669796 W
PL12W        0.39276794 W
PL13W        0.37509048 W
SFO2        400.1716007 MHz
SI                   32768
SF          100.6228060 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 1.40
```

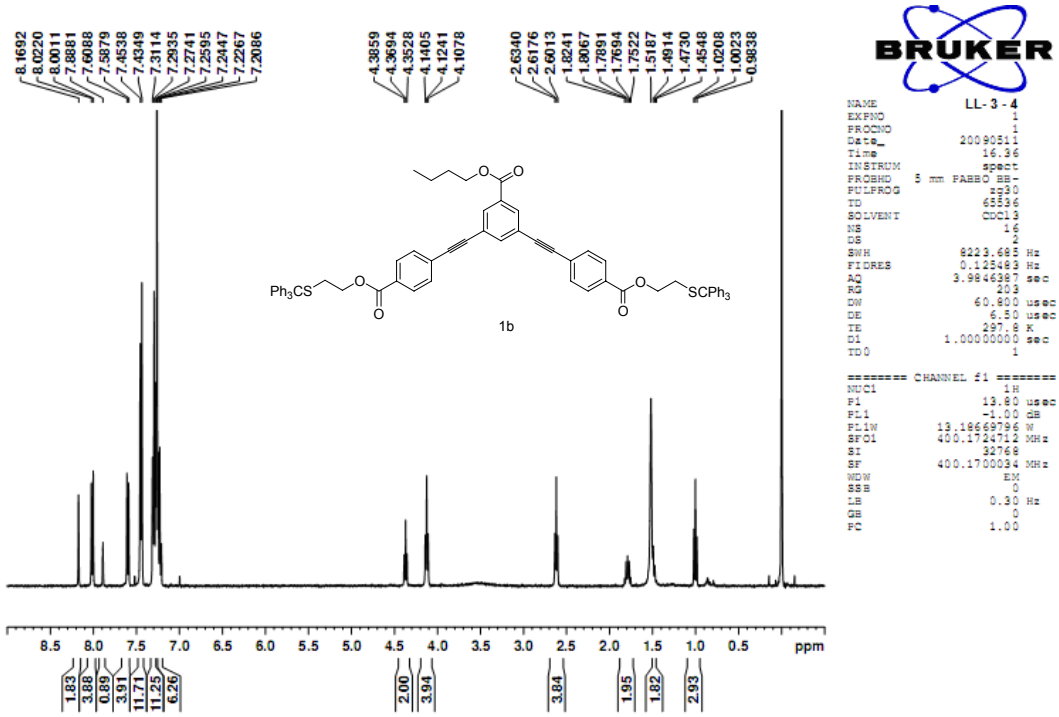

3-2 #43 RT: 0.84 AV: 1 SB: 2 1.06, 0.81 NL: 1.69E5
T: {0,0} + c EI det=350.00 Full ms [35.00-670.00]
Relative Abundance
m/z
354.48
353.53
368.97
370.26
371.35
372.38
299.20
298.26
296.23
238.92
54.83
80.25
68.81
95.21
108.29
142.20
166.18
193.96
194.99
268.61
282.60
313.49
314.40
315.37
393.88
410.24
428.26
467.02
Me3Si
SiMe3
1b-2


8.1102
8.1067
7.7581
7.2601
4.3491
4.3325
4.3159
3.1393
1.7896
1.7726
1.7661
1.7551
1.7353
1.7186
1.5200
1.5017
1.4827
1.4638
1.4454
1.0021
0.9837
0.9652
-0.0001
1.81
0.90
2.00
1.80
1.98
2.28
2.96
ppm
1b-3
BRUKER
NAME LL-3-3
EXPNO 1
PROCNO 1
Date_ 20090428
Time 9.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 297.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PLW 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700032 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

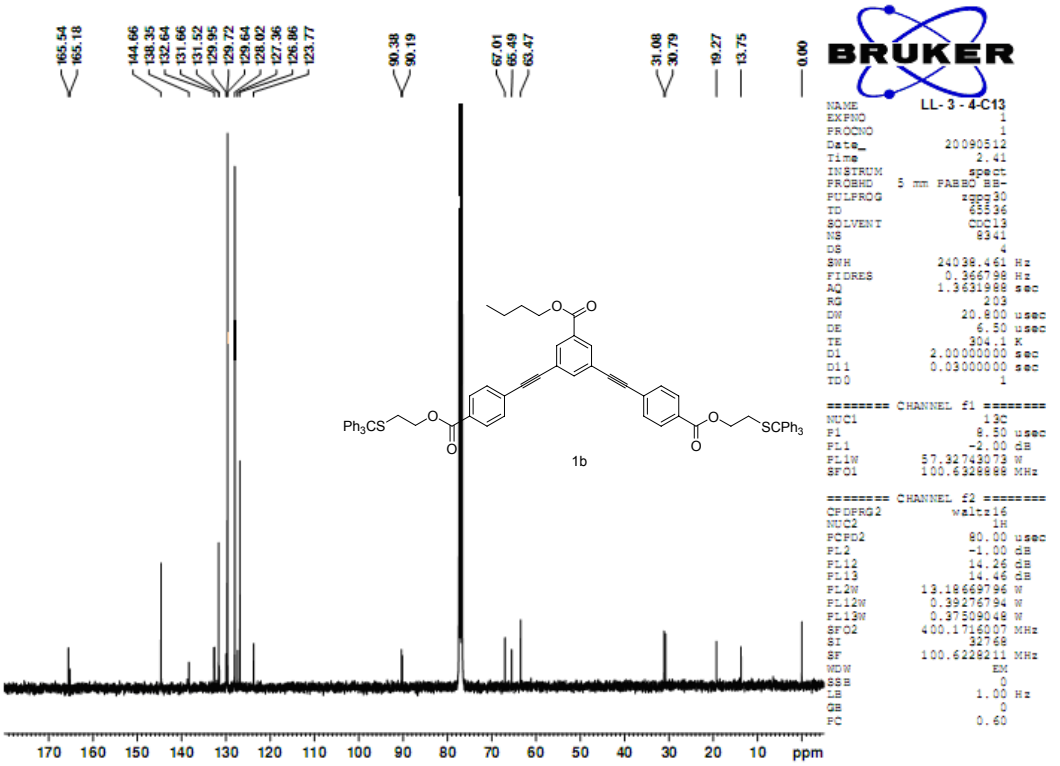

165.04
139.24
133.22
131.26
122.99
81.68
77.33
77.01
76.70
65.42
30.71
19.23
13.73
-0.00
O
O
1b-3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


BRUKER
NAME LL-3-3-C13
EXPNO 1
PROCNO 1
Date_ 20090501
Time 5.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 320
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 301.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 57.32743073 W
SFO1 100.6328888 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.26 dB
PL13 14.46 dB
PL2W 13.18669796 W
PL12W 0.39276794 W
PL13W 0.37509048 W
SFO2 400.1716007 MHz
SI 32768
SF 100.6228237 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

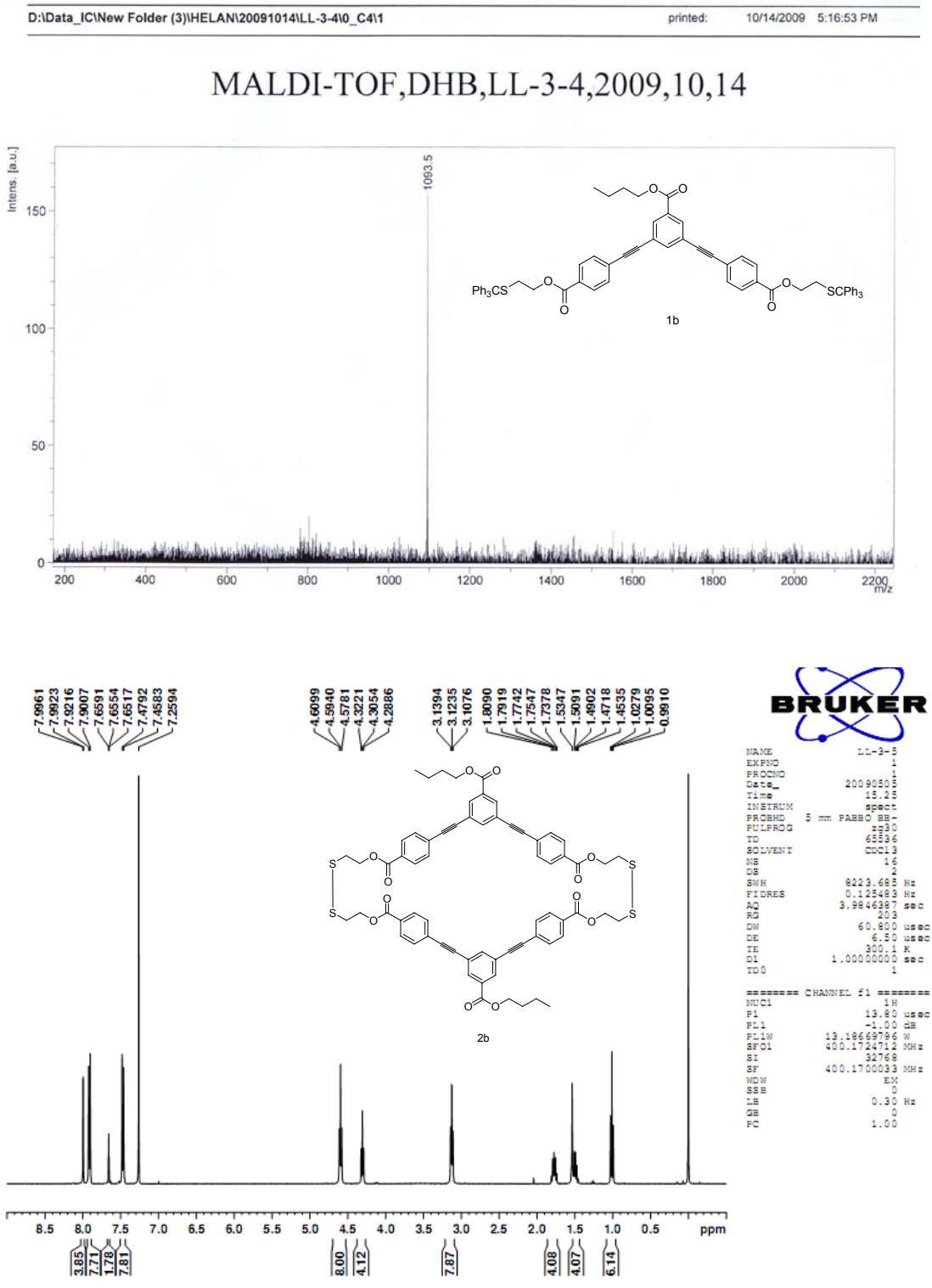

3-3 #20 RT: 0.60 AV: 1 SB: 7 0.64-0.65, 0.54-0.58 NL: 2.46E6
T: {0,0} + c EI det=350.00 Full ms [35.00-670.00]
Relative Abundance
m/z
73.90
40.90
42.88
75.11
98.17
124.20
125.12
153.13
170.02
99.10
152.06
55.59
97.07
85.00
126.18
121.18
168.97
100.24
127.15
165.07
178.12
202.11
215.03
225.94
227.21
245.71
260.50
274.63
288.91
302.52
321.65
O
O
1b-3

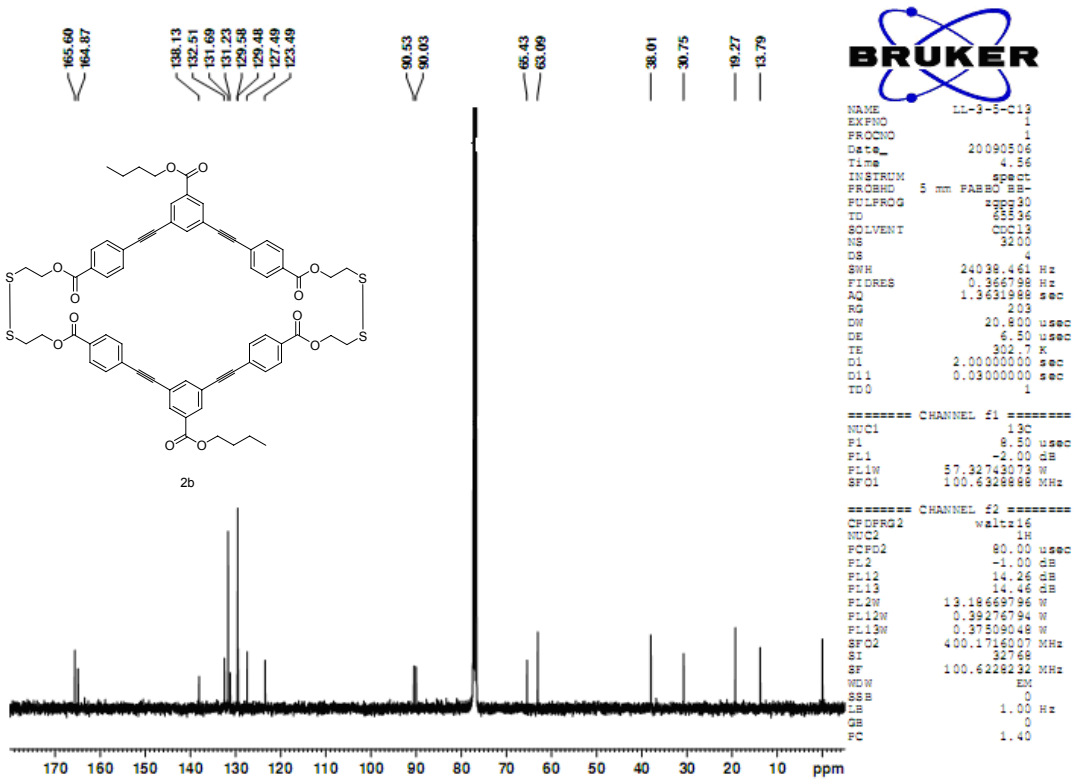


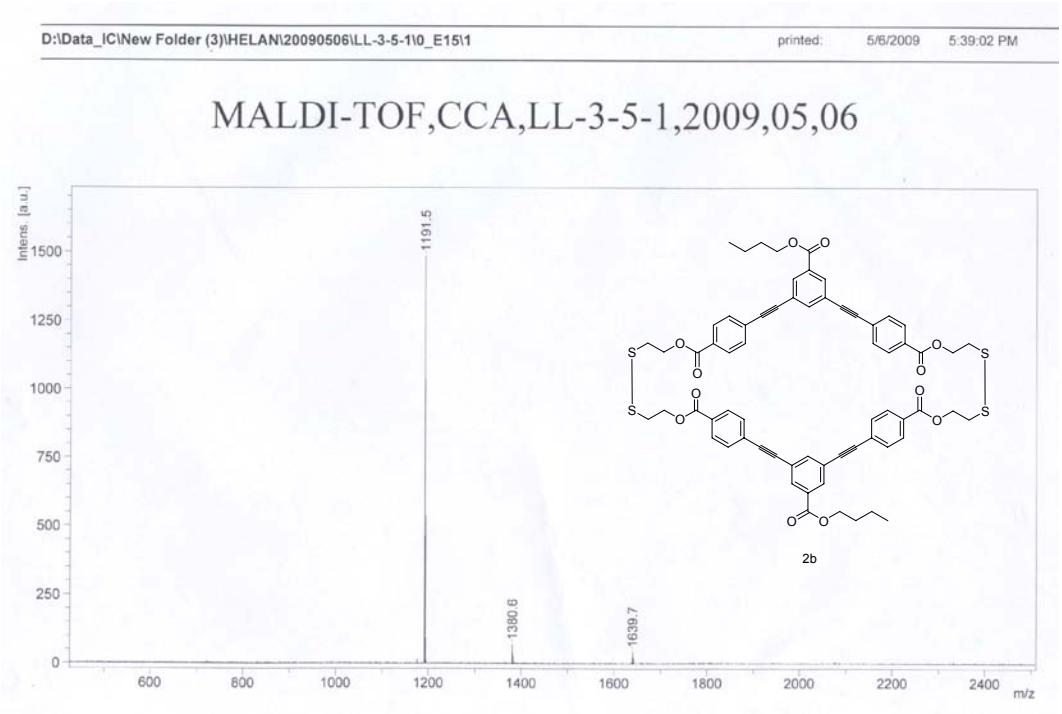

```
NAME                LL-3-4
EXPNO                    1
PROCNO                   1
Date_             20090511
Time                 16.36
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                 655360
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                     203
DW                  60.800 usec
DE                   6.50 usec
TE                  297.8 K
D1                1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                  13.80 usec
PL1                 -1.00 dB
PL1W          13.18669796 W
SFO1          400.1724712 MHz
SI                   32768
SF            400.1700034 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

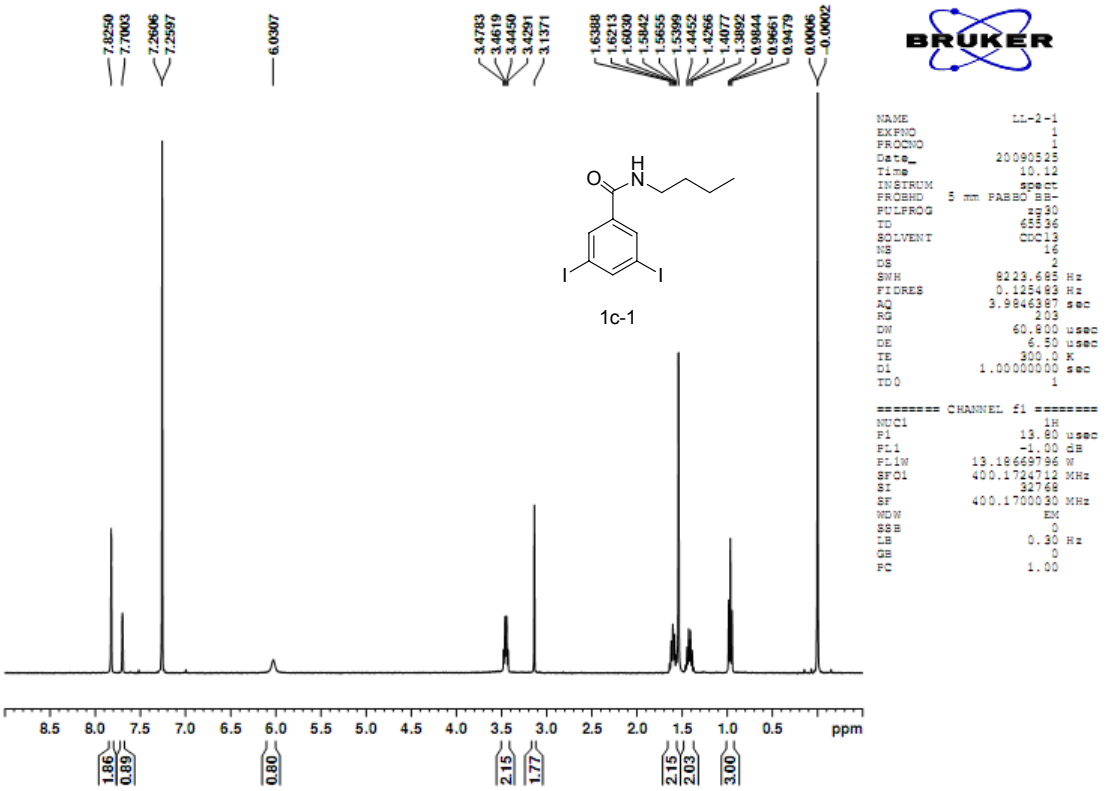



```
NAME              LL-3-4-C13
EXPNO                    1
PROCNO                   1
Date_             20090512
Time                  2.41
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                 655360
SOLVENT              CDCl3
NS                    9341
DS                       4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                     203
DW                  20.800 usec
DE                   6.50 usec
TE                  304.1 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          57.32743073 W
SFO1          100.6328888 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                 -1.00 dB
PL12                14.26 dB
PL13                14.46 dB
PL2W          13.18669796 W
PL12W         0.39276794 W
PL13W         0.37509048 W
SFO2          400.1716007 MHz
SI                   32768
SF            100.6228211 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    0.60
```

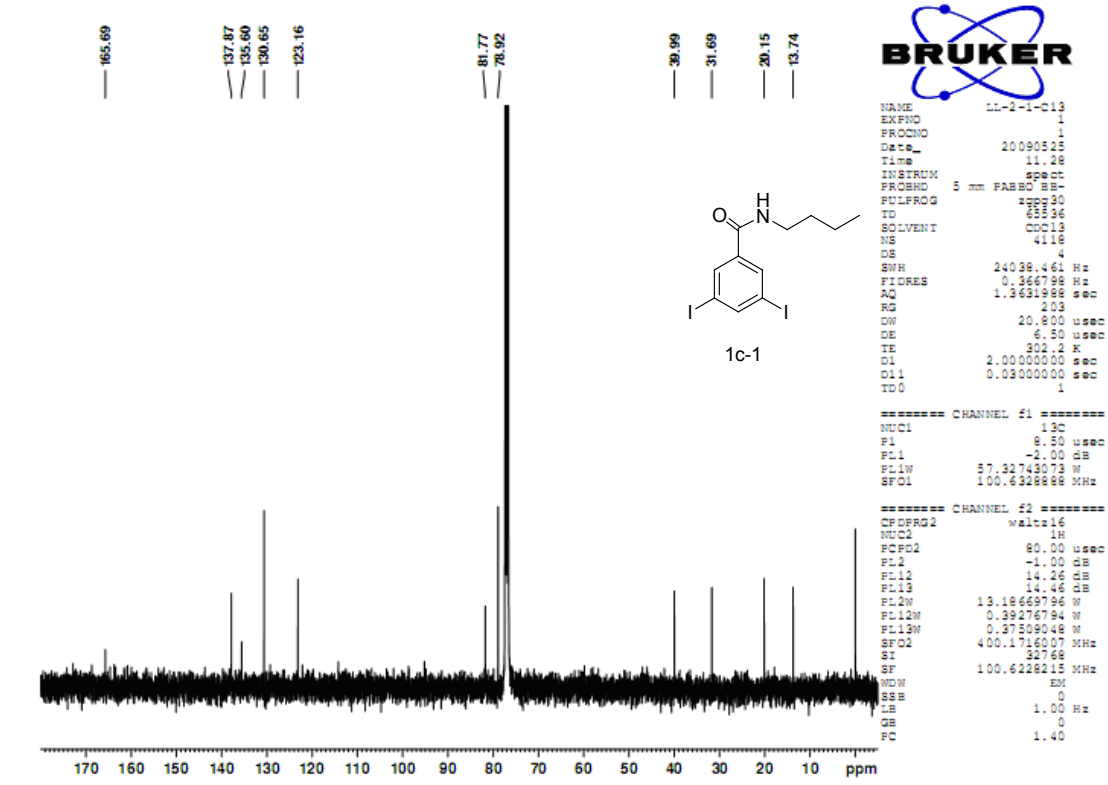

D:\Data_IC\New Folder (3)\HELAN\20091014\LL-3-4\0_C4\1
printed: 10/14/2009 5:16:53 PM
MALDI-TOF,DHB,LL-3-4,2009,10,14
Intens. [a.u.]
1093.5
m/z
1b
2b
BRUKER
NAME LL-3-5
EXPNO 1
PROCNO 1
Date_ 20090505
Time 15.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9844387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 300.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700033 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm


165.60
164.87
138.13
132.51
131.69
131.23
129.58
129.48
127.49
123.49
90.53
90.03
65.43
63.09
38.01
30.75
19.27
13.79
2b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
BRUKER
NAME LL-3-5-C13
EXPNO 1
PROCNO 1
Date_ 20090506
Time 4.56
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3200
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 302.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 57.32743073 W
SFO1 100.6328888 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.26 dB
PL13 14.46 dB
PL2W 13.18669796 W
PL12W 0.39276794 W
PL13W 0.37509048 W
SFO2 400.1716007 MHz
SI 32768
SF 100.6228232 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

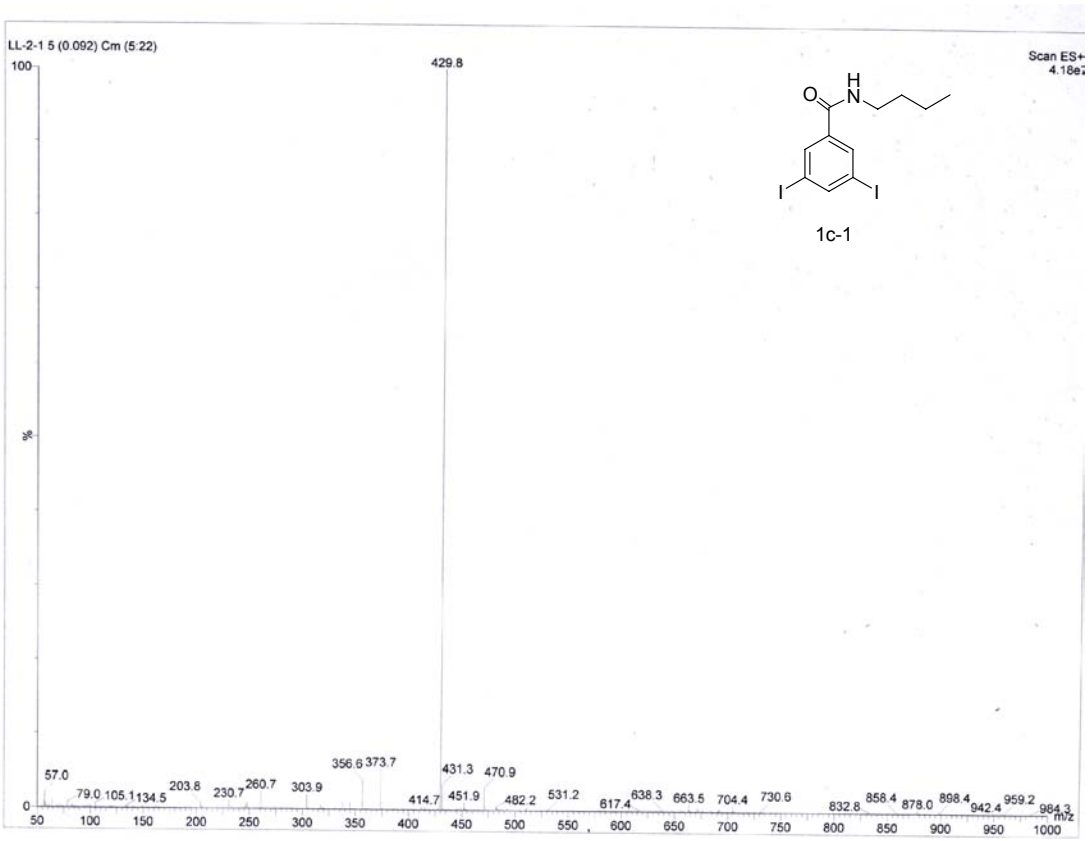

D:\Data_IC\New Folder (3)\HELAN\20090506\LL-3-5-1\0_E15\1
printed: 5/6/2009 5:39:02 PM
MALDI-TOF,CCA,LL-3-5-1,2009,05,06
Intens. [a.u.]
1500
1250
1000
750
500
250
0
1191.5
1380.6
1639.7
600 800 1000 1200 1400 1600 1800 2000 2200 2400 m/z
2b



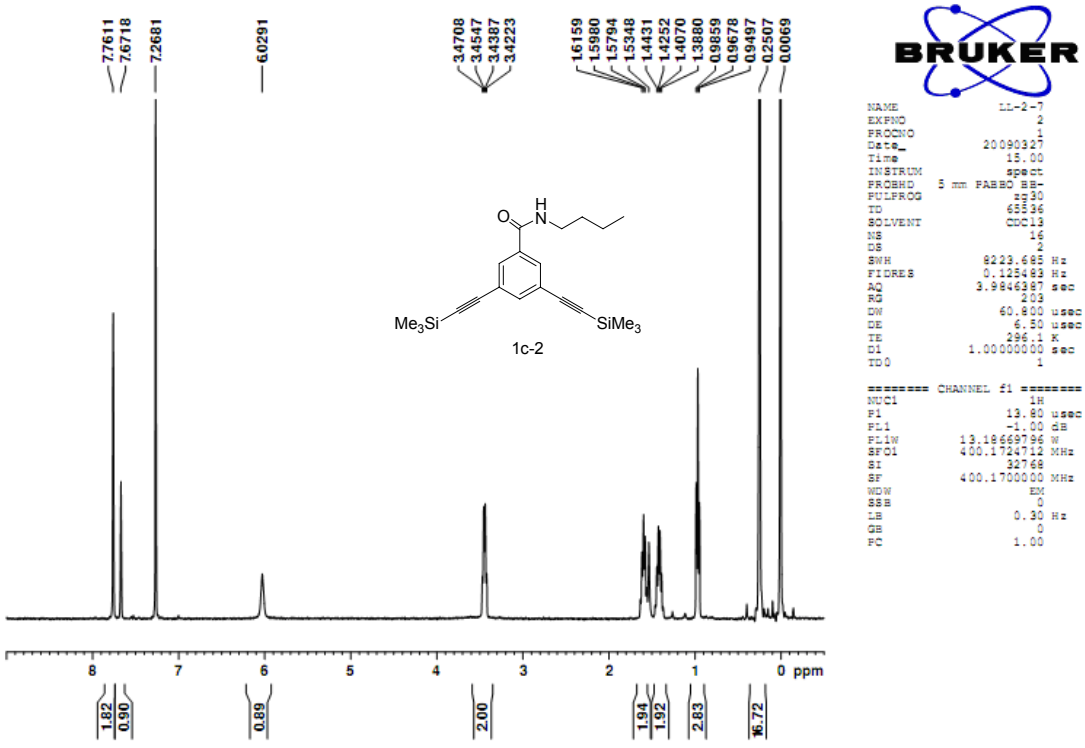

```
NAME                LL-2-1
EXPNO                    1
PROCNO                   1
Date_             20090525
Time                 10.12
INSTRUM              spect
PROBHD     5 mm PABBO BB-
PULPROG              zg30
TD                 655536
SOLVENT             CDCl3
NS                      16
DS                       2
SWH              8223.685 Hz
FIDRES           0.125463 Hz
AQ               3.9846367 sec
RG                     203
DW                60.800 usec
DE                 6.50 usec
TE                 300.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                 13.60 usec
PL1                -1.00 dB
PL1W        13.18669796 W
SFO1       400.1724712 MHz
SI                   32768
SF         400.1700030 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 1.00
```




```
NAME             LL-2-1-C13
EXPNO                    1
PROCNO                   1
Date_             20090525
Time                 11.26
INSTRUM              spect
PROBHD     5 mm PABBO BB-
PULPROG          zgpg30
TD                 655536
SOLVENT             CDCl3
NS                    4116
DS                       4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                     203
DW                20.800 usec
DE                 6.50 usec
TE                 302.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                  13C
P1                 8.50 usec
PL1                -2.00 dB
PL1W        57.32743073 W
SFO1       100.6328898 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               14.26 dB
PL13               14.46 dB
PL2W        13.18669796 W
PL12W        0.39276794 W
PL13W        0.37509048 W
SFO2       400.1716007 MHz
SI                   32768
SF         100.6228215 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 1.40
```



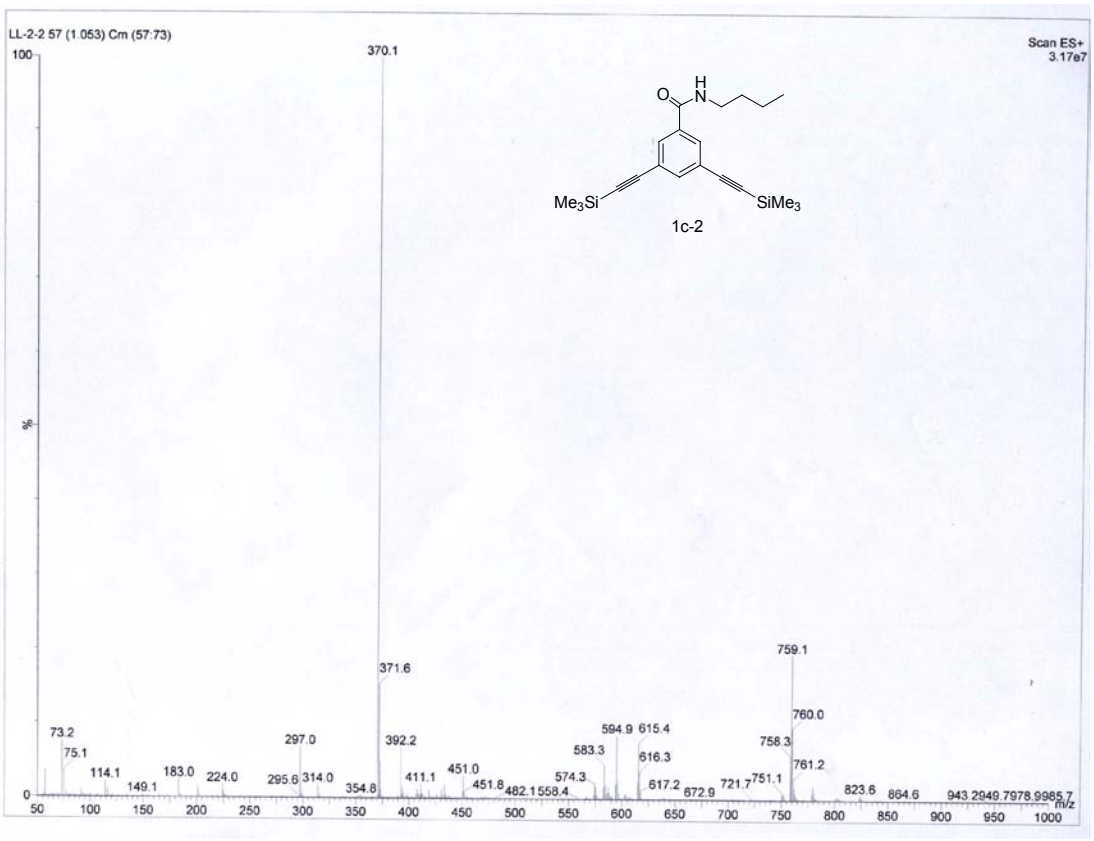
1c-1

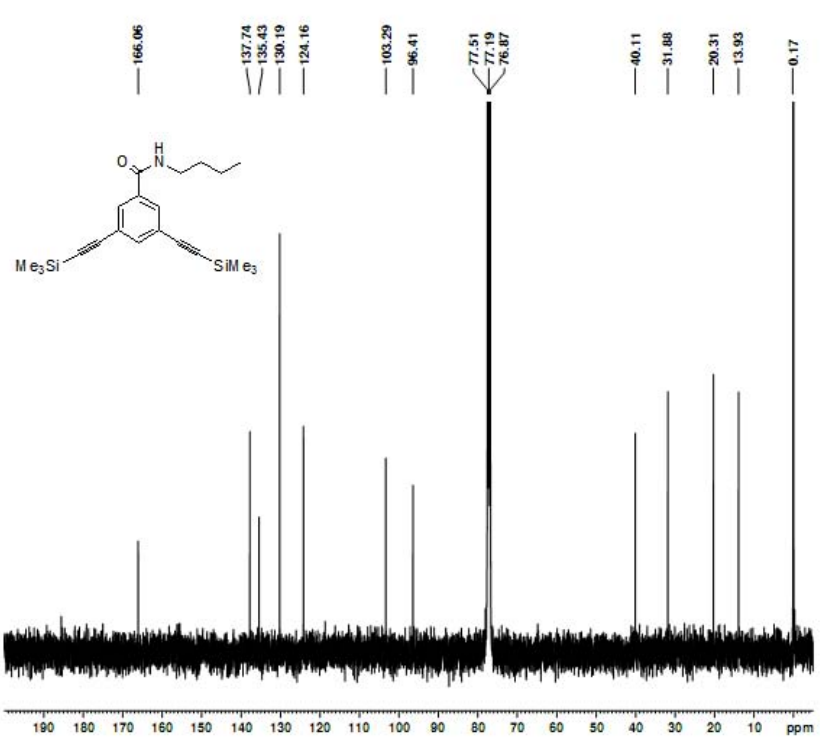


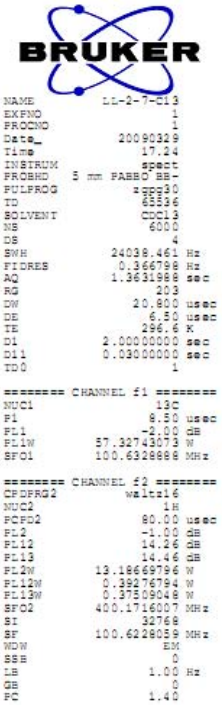
1c-2

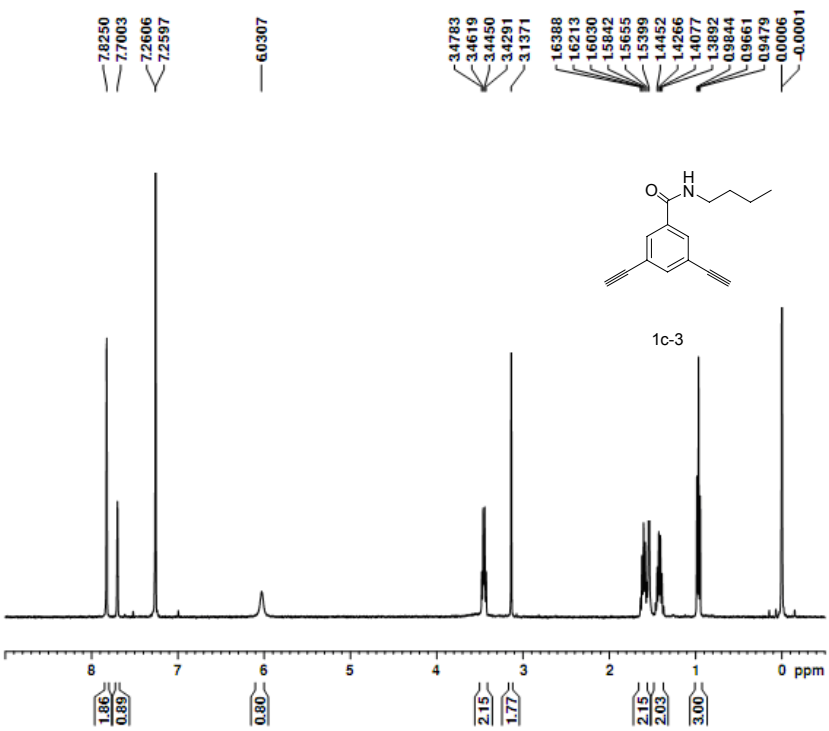
BRUKER

NAME	LL-2-7
EXPNO	2
PROCNO	1
Date_	20090327
Time	15.00
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846287 sec
RG	203
DW	60.800 usec
DE	6.50 usec
TE	296.1 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	13.80 usec
PL1	-1.00 dB
PL1W	13.18669796 W
SFO1	400.1724712 MHz
SI	32768
SF	400.1700000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

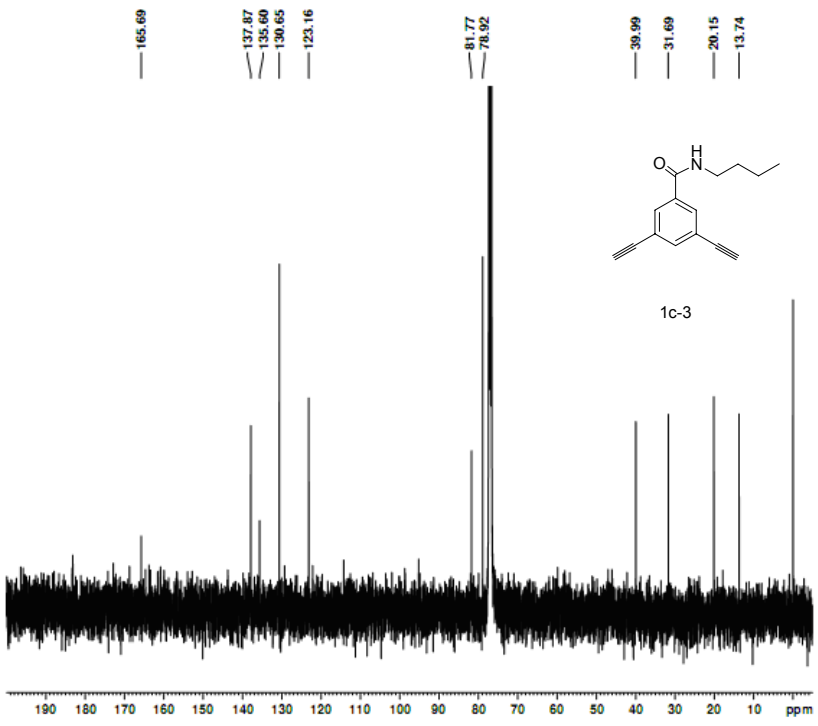

LL-2-2 57 (1.053) Cm (57:73)
Scan ES+
3.17e7
100
%
0
370.1
371.6
759.1
760.0
73.2
75.1
114.1
149.1
183.0
224.0
297.0
295.6
314.0
354.8
392.2
411.1
451.0
451.8
482.1
558.4
574.3
583.3
594.9
615.4
616.3
617.2
672.9
721.7
751.1
758.3
761.2
823.6
864.6
943.2
949.7
978.9
985.7
m/z
50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
Me3Si
SiMe3
1c-2


166.06
137.74
135.43
130.19
124.16
103.29
96.41
77.51
77.19
76.87
40.11
31.88
20.31
13.93
0.17
Me3Si
SiMe3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

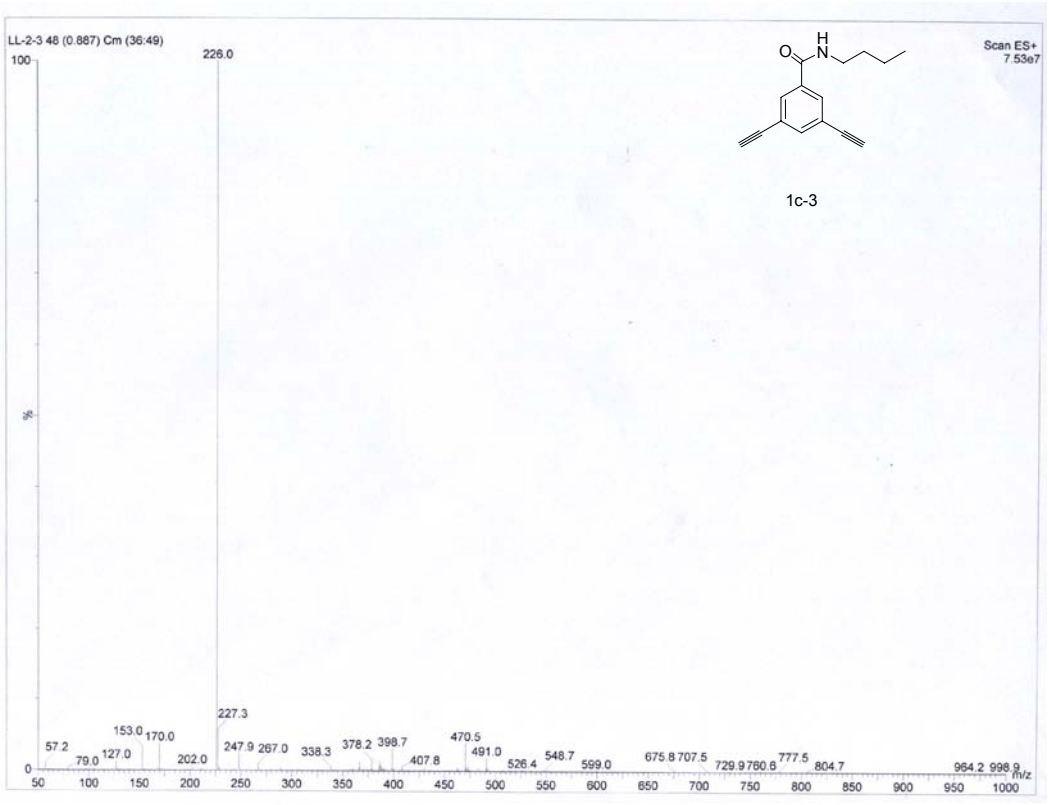

BRUKER
NAME LL-2-7-C13
EXPNO 1
PROCNO 1
Date_ 20090329
Time 17.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 6000
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 296.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 57.32743073 W
SFO1 100.6328888 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.46 dB
PL13 14.46 dB
PL2W 13.18669796 W
PL12W 0.39276794 W
PL13W 0.37509048 W
SFO2 400.1716007 MHz
SI 32768
SF 100.6228059 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

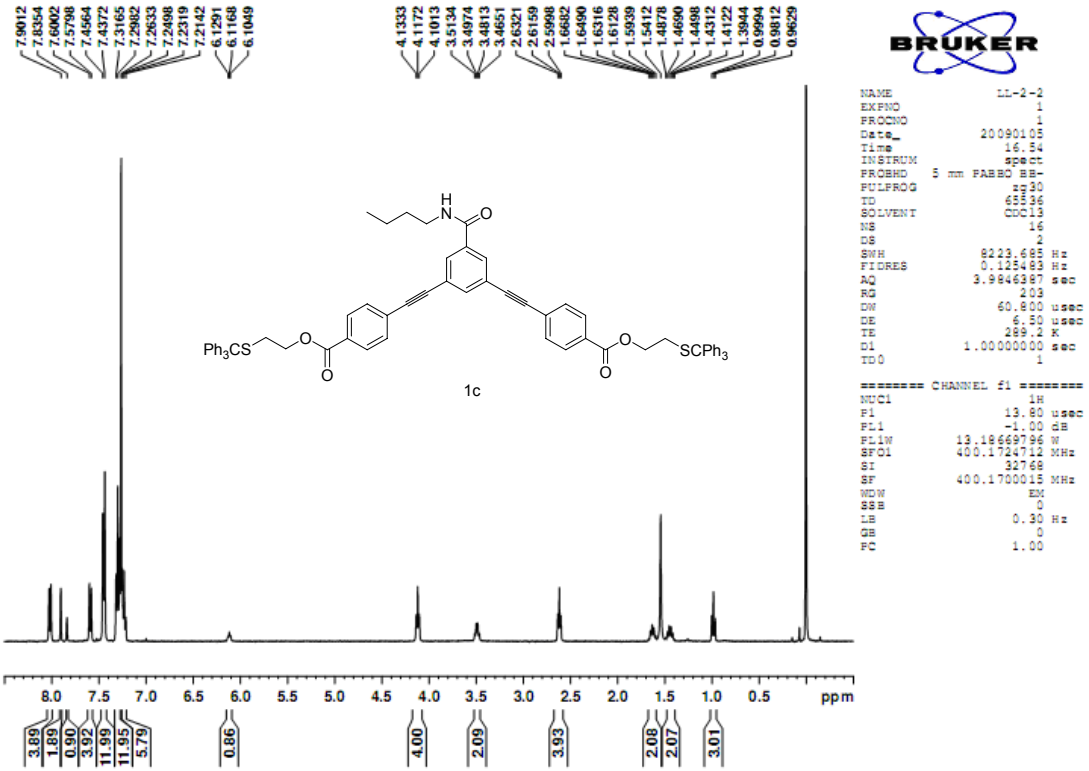


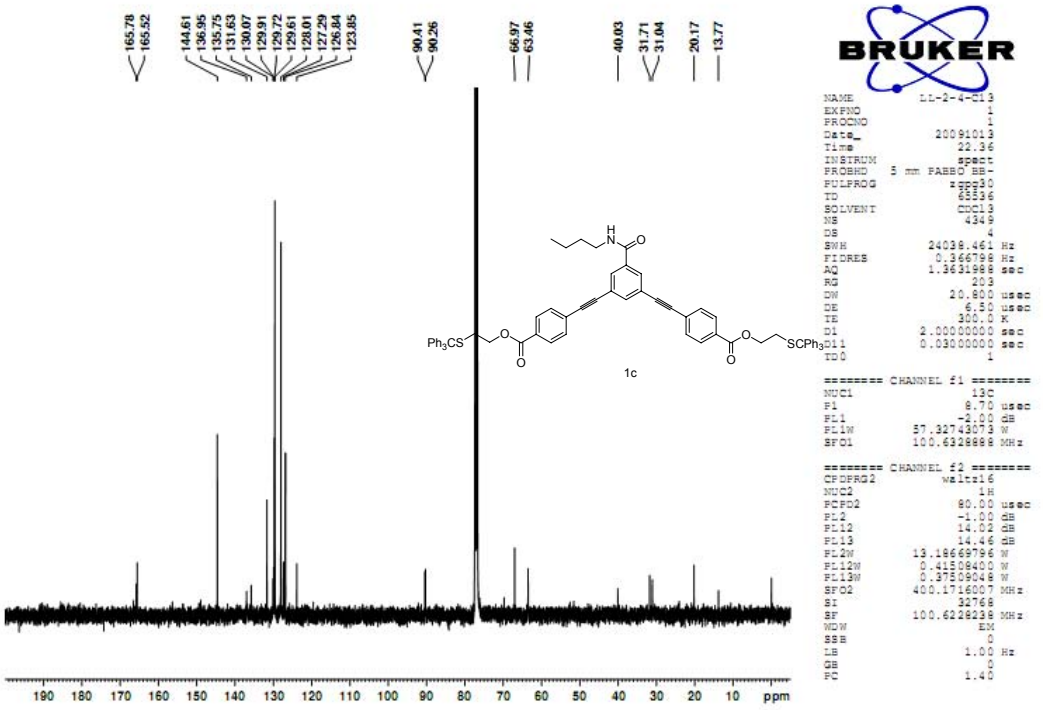

```
NAME                LL-2-1
EXPNO                    1
PROCNO                   1
Date_           20090525
Time                10.12
INSTRUM              spect
PROBHD     5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                      16
DS                       2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                     203
DW                60.800 usec
DE                 6.50 usec
TE                300.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                 13.80 usec
PL1                -1.00 dB
PL1W        13.18669796 W
SFO1        400.1724712 MHz
SI                 32768
SF          400.1700030 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```

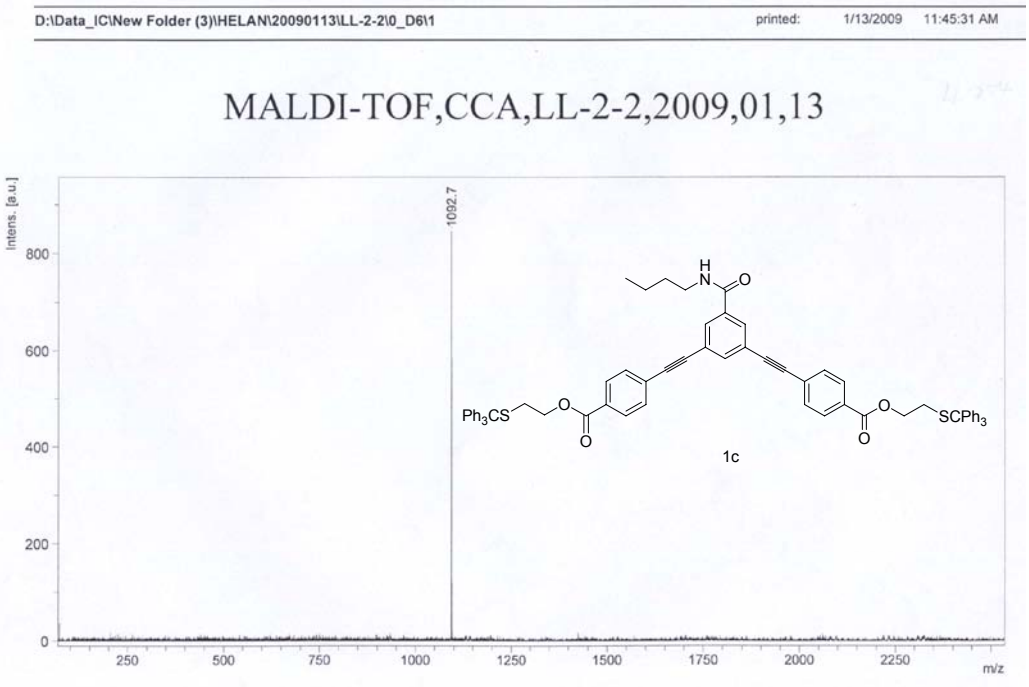


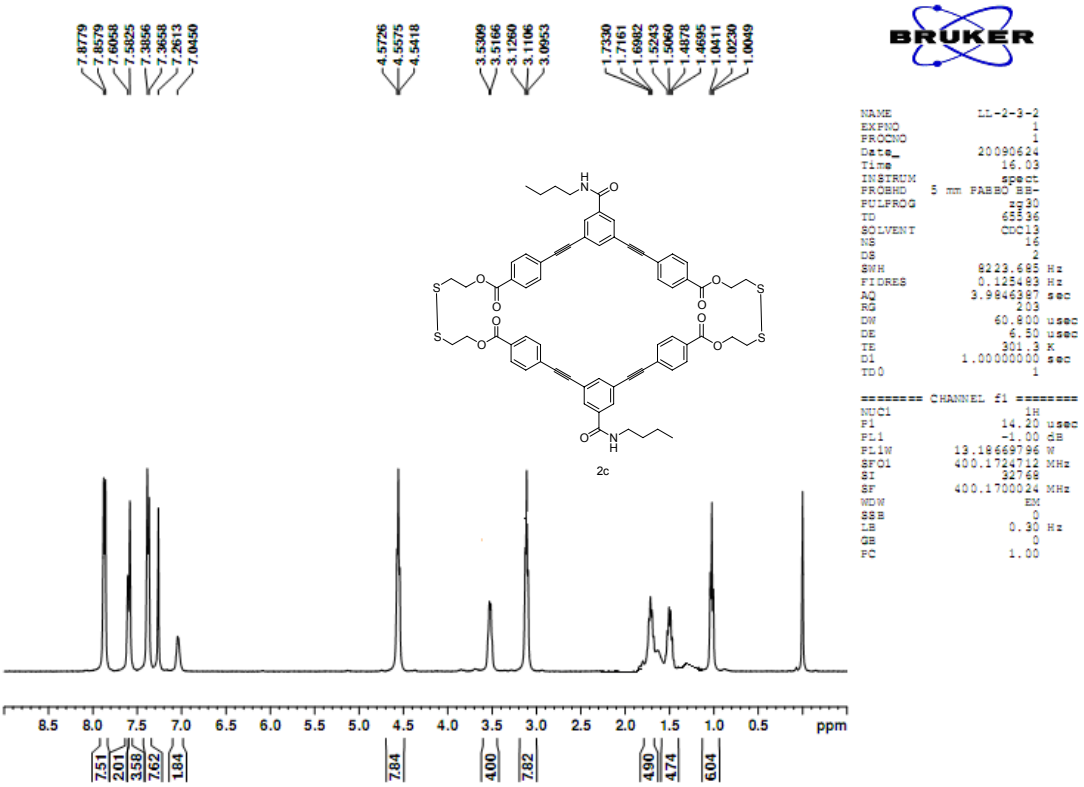

```
NAME              LL-2-1-C13
EXPNO                    1
PROCNO                   1
Date_           20090525
Time                11.28
INSTRUM              spect
PROBHD     5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   4116
DS                       4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                     203
DW                20.800 usec
DE                 6.50 usec
TE                302.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                  8.50 usec
PL1                -2.00 dB
PL1W        57.32743073 W
SFO1        100.6328888 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               14.26 dB
PL13               14.46 dB
PL2W        13.18669796 W
PL12W        0.39276794 W
PL13W        0.37509048 W
SFO2        400.1716007 MHz
SI                 32768
SF          100.6228215 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```


LL-2-3 48 (0.887) Cm (36:49)
Scan ES+
7.53e7
226.0
227.3
1c-3
%
m/z

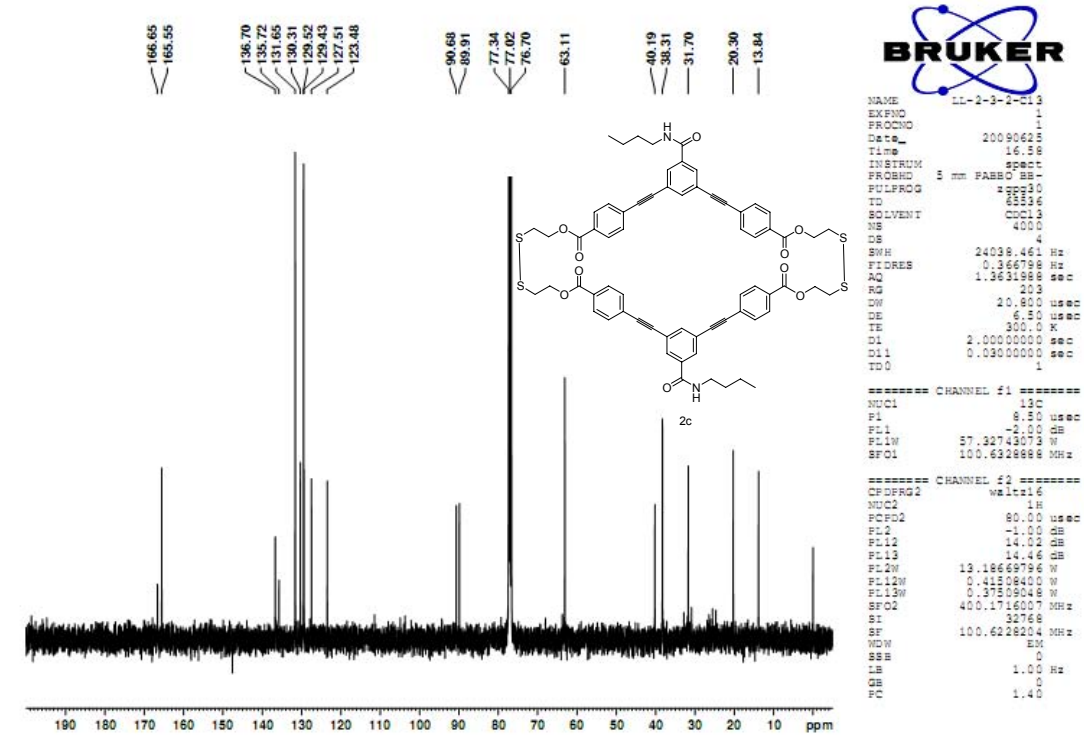

BRUKER
1c
ppm


165.78
165.52
144.61
136.95
135.75
131.63
130.07
129.91
129.72
129.61
128.01
127.29
126.84
123.85
90.41
90.26
66.97
63.46
40.03
31.71
31.04
20.17
13.77
BRUKER
1c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

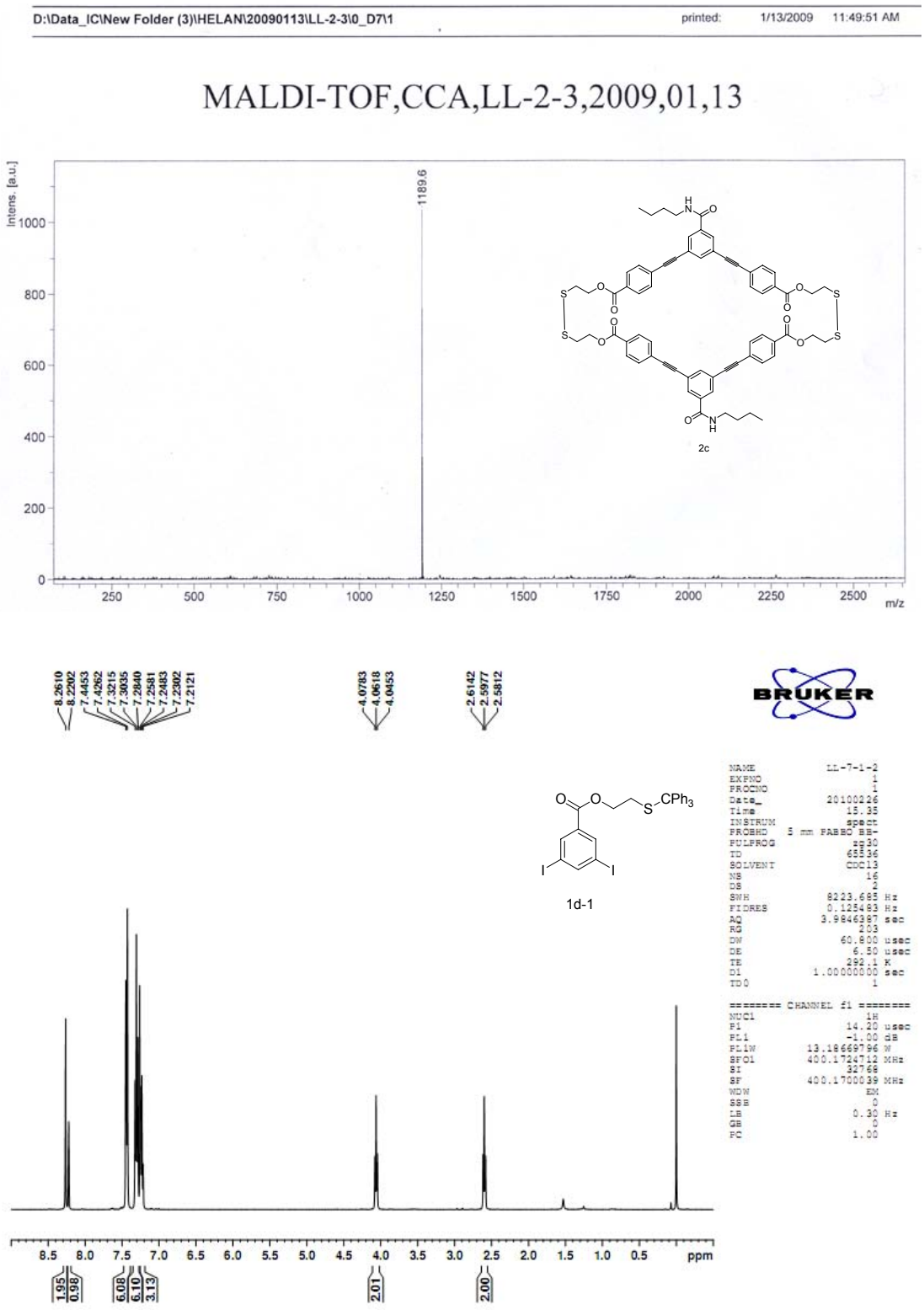

D:\Data_IC\New Folder (3)\HELAN\20090113\LL-2-2\0_D6\1
printed: 1/13/2009 11:45:31 AM
MALDI-TOF,CCA,LL-2-2,2009,01,13
Intens. [a.u.]
1092.7
1c
m/z

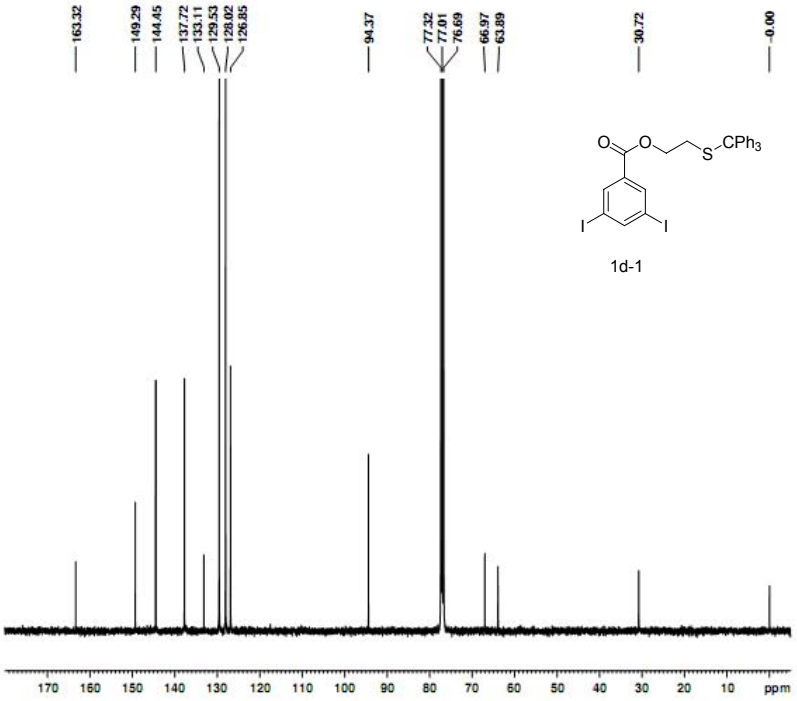



```
NAME                LL-2-3-2
EXPNO                       1
PROCNO                      1
Date_              20090624
Time                   16.03
INSTRUM                spect
PROBHD     5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                      203
DW                 60.800 usec
DE                  6.50 usec
TE                  301.3 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                     14.20 usec
PL1                    -1.00 dB
PL1W            13.18669796 W
SFO1           400.1724712 MHz
SI                      32768
SF             400.1700024 MHz
WDW                        EM
SSB                         0
LB                     0.30 Hz
GB                          0
PC                     1.00
```




```
NAME             LL-2-3-2-C13
EXPNO                       1
PROCNO                      1
Date_              20090625
Time                   16.58
INSTRUM                spect
PROBHD     5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     4000
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631988 sec
RG                      203
DW                 20.800 usec
DE                  6.50 usec
TE                  300.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                     8.50 usec
PL1                    -2.00 dB
PL1W            57.32743073 W
SFO1           100.6328688 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL2                    -1.00 dB
PL12                   14.02 dB
PL13                   14.46 dB
PL2W            13.18669796 W
PL12W           0.41508400 W
PL13W           0.37509048 W
SFO2           400.1716007 MHz
SI                      32768
SF             100.6228204 MHz
WDW                        EM
SSB                         0
LB                     1.00 Hz
GB                          0
PC                     1.40
```


D:\Data_IC\New Folder (3)\HELAN\20090113\LL-2-3\0_D7\1
printed: 1/13/2009 11:49:51 AM
MALDI-TOF,CCA,LL-2-3,2009,01,13
Intens. [a.u.]
1189.6
m/z
2c
8.2610
8.2202
7.4453
7.4262
7.3215
7.3035
7.2940
7.2581
7.2483
7.2302
7.2121
4.0783
4.0618
4.0453
2.6142
2.5977
2.5812
BRUKER
1d-1
NAME LL-7-1-2
EXPNO 1
PROCNO 1
Date_ 20100226
Time 15.35
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846287 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 292.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.20 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700039 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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
1.95
0.98
6.08
6.10
3.13
2.01
2.00

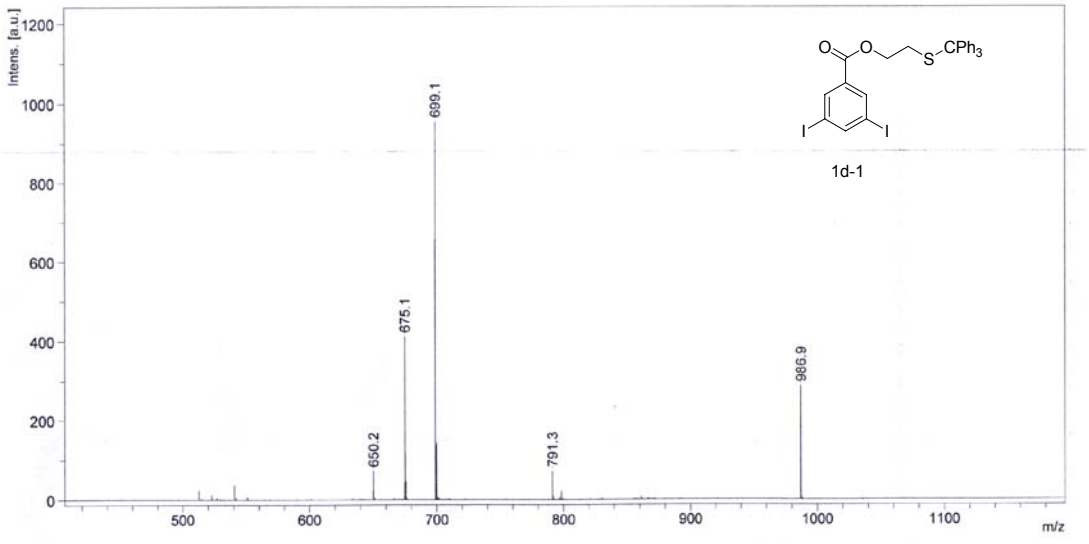


1d-1

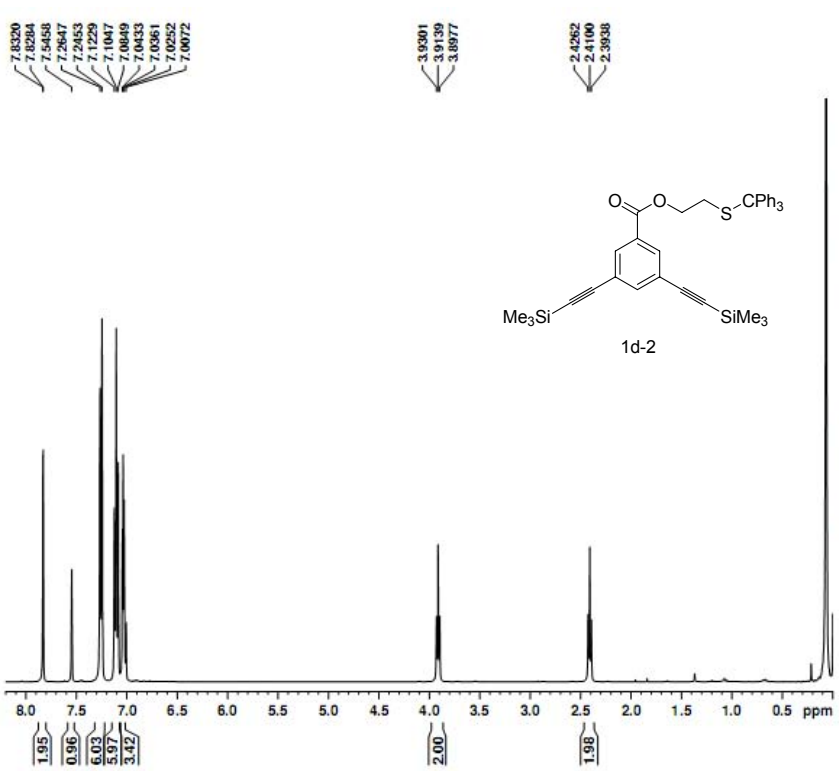

```
NAME                LL-7-1-2-C13
EXPNO                          1
PROCNO                         1
Date_                   20100226
Time                       22.16
INSTRUM                    spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgpg30
TD                         65536
SOLVENT                    CDCl3
NS                          6000
DS                             4
SWH                    24038.461 Hz
FIDRES                 0.366798 Hz
AQ                     1.3631988 sec
RG                           203
DW                        20.800 usec
DE                         6.50 usec
TE                       292.2 K
D1                     2.00000000 sec
D11                    0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         13C
P1                         9.70 usec
PL1                        -2.00 dB
PL1W                57.32743072 W
SFO1               100.6328898 MHz

======== CHANNEL f2 ========
CPDPRG2                  waltz16
NUC2                         1H
PCPD2                     80.00 usec
PL2                        -1.00 dB
PL12                       14.02 dB
PL13                       14.46 dB
PL2W                13.18669796 W
PL12W                0.41508400 W
PL13W                0.37509049 W
SFO2               400.1716007 MHz
SI                         32768
SF                 100.6228293 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40
```

D:\Data_IC\New Folder (3)\HELAN\20100413\LL-7-1\0_G16\1 printed: 4/13/2010 4:51:12 PM

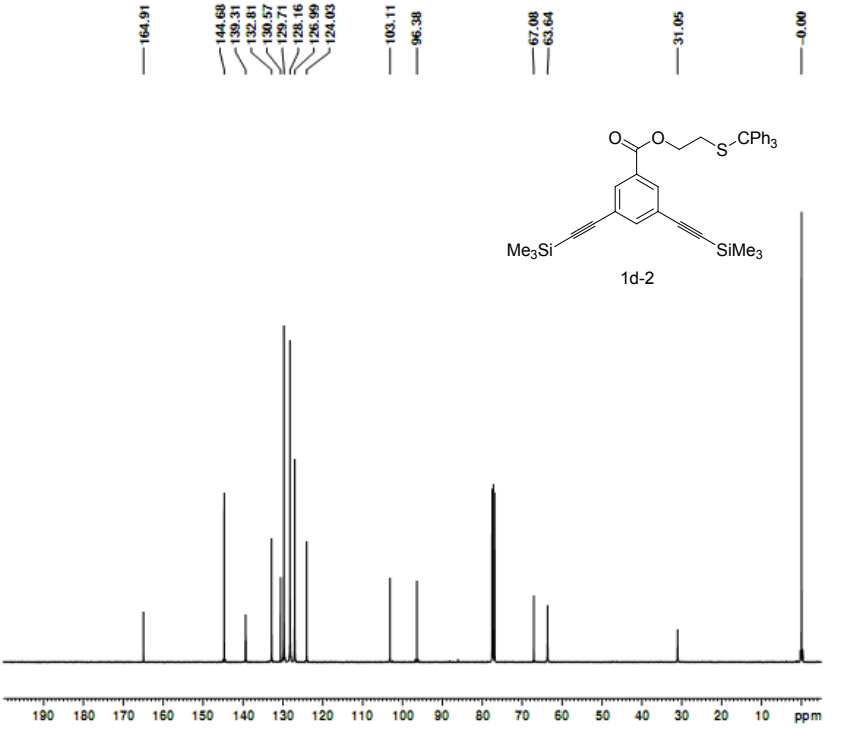
MALDI-TOF,CCA,LL-7-1,2010,04,13



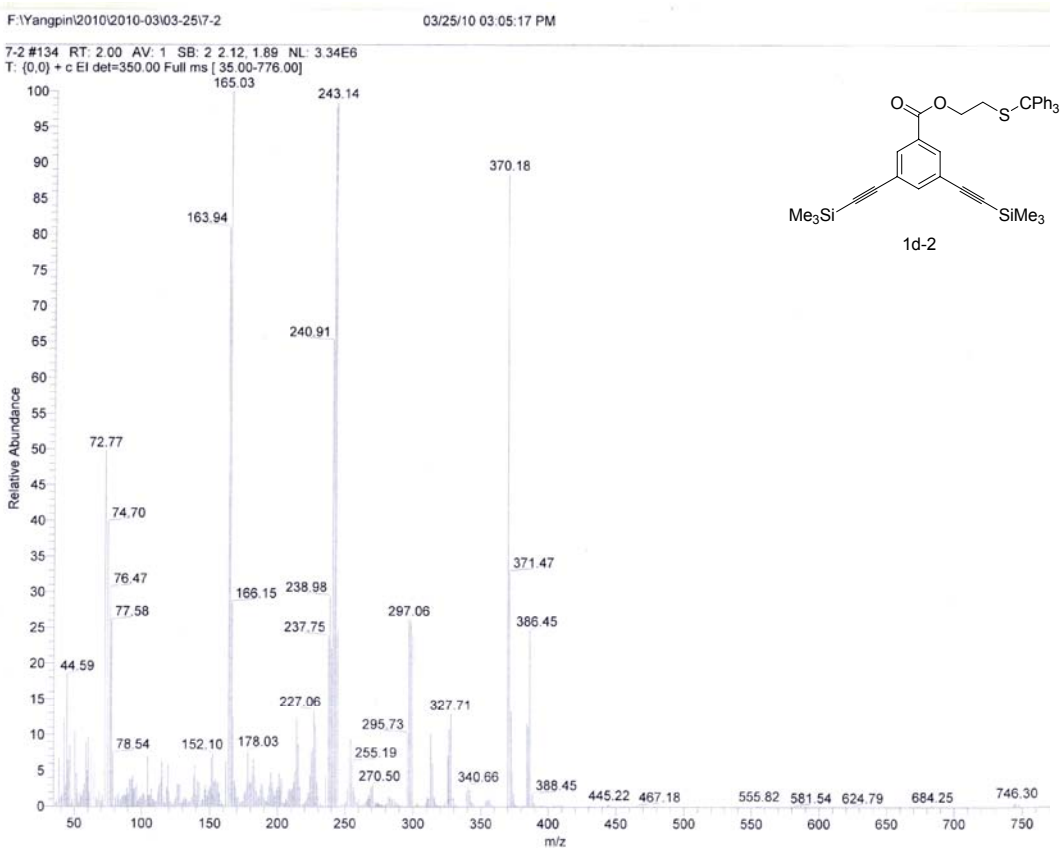
1d-1



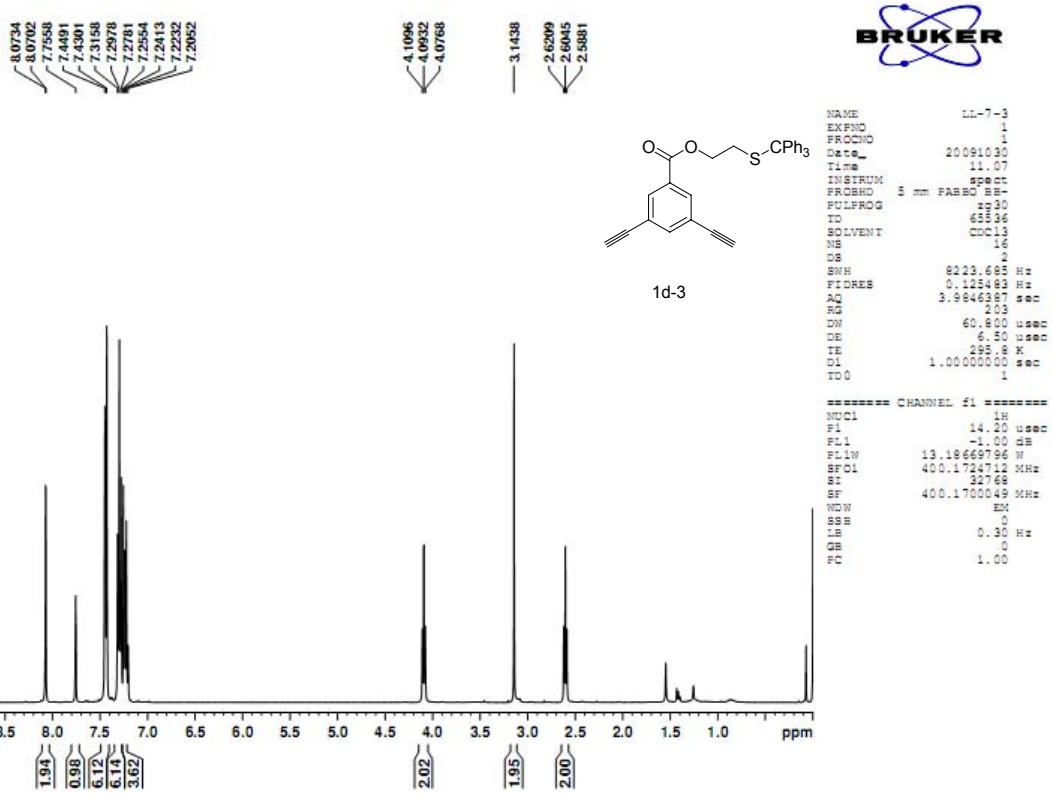

```
NAME                LL-7-2
EXPNO                    1
PROCNO                   1
Date_             20091030
Time                 11.02
INSTRUM              spect
PROBHD     5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                      16
DS                       2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                      36
DW                 60.800 usec
DE                  6.50 usec
TE                294.8 K
D1               1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                 14.20 usec
PL1                -1.00 dB
PL1W            13.18669796 W
SFO1            400.1724712 MHz
SI                   32768
SF              400.1700926 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                  1.00
```



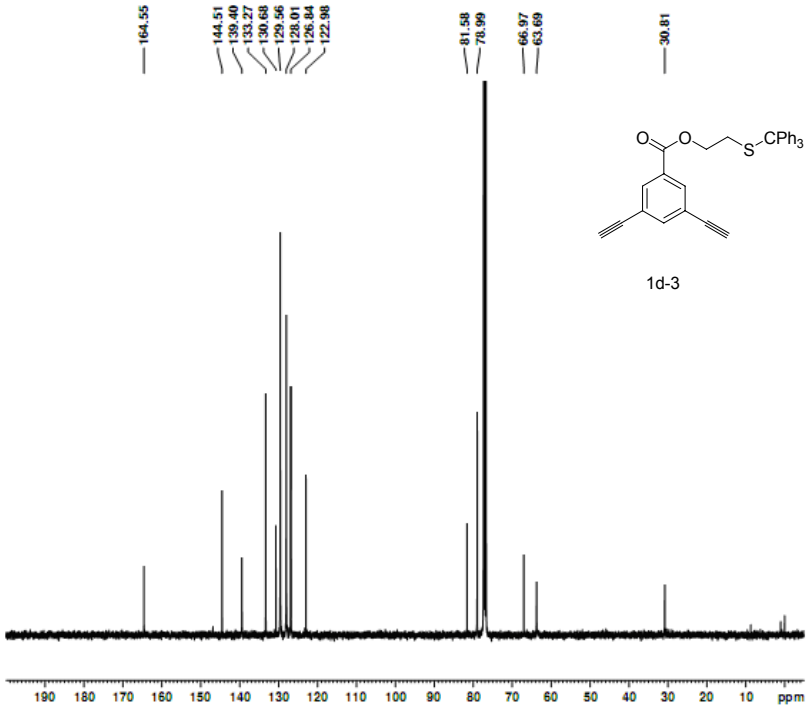

```
NAME             LL-7-2-C13
EXPNO                    1
PROCNO                   1
Date_             20091101
Time                 21.16
INSTRUM              spect
PROBHD     5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    4000
DS                       4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 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 ========
NUC1                   13C
P1                  8.70 usec
PL1                -3.00 dB
PL1W            57.32743073 W
SFO1            100.6328888 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               14.02 dB
PL13               14.46 dB
PL2W            13.18669796 W
PL12W            0.41508400 W
PL13W            0.37509048 W
SFO2            400.1716007 MHz
SI                   32768
SF              100.6228153 MHz
WDW                     EM
SSB                      0
LB                  1.00 Hz
GB                       0
PC                  1.40
```


F:\Yangpin\2010\2010-03\03-25\7-2
03/25/10 03:05:17 PM
7-2 #134 RT: 2.00 AV: 1 SB: 2 2.12, 1.89 NL: 3.34E6
T: {0,0} + c EI det=350.00 Full ms [35.00-776.00]
Relative Abundance
m/z
165.03
243.14
370.18
163.94
240.91
72.77
74.70
76.47
77.58
166.15
238.98
237.75
297.06
371.47
386.45
44.59
227.06
327.71
295.73
78.54
152.10
178.03
255.19
270.50
340.66
388.45
445.22
467.18
555.82
581.54
624.79
684.25
746.30
O
O
S
CPh3
Me3Si
SiMe3

1d-2


8.0734
8.0702
7.7558
7.4491
7.4301
7.3158
7.2978
7.2781
7.2554
7.2413
7.2232
7.2052
4.1096
4.0932
4.0768
3.1438
2.6209
2.6045
2.5881
BRUKER
O
O
S
CPh3
NAME LL-7-3
EXPNO 1
PROCNO 1
Date_ 20091030
Time 11.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 295.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.20 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700049 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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
ppm
1.94
0.98
6.12
6.14
3.62
2.02
1.95
2.00

1d-3



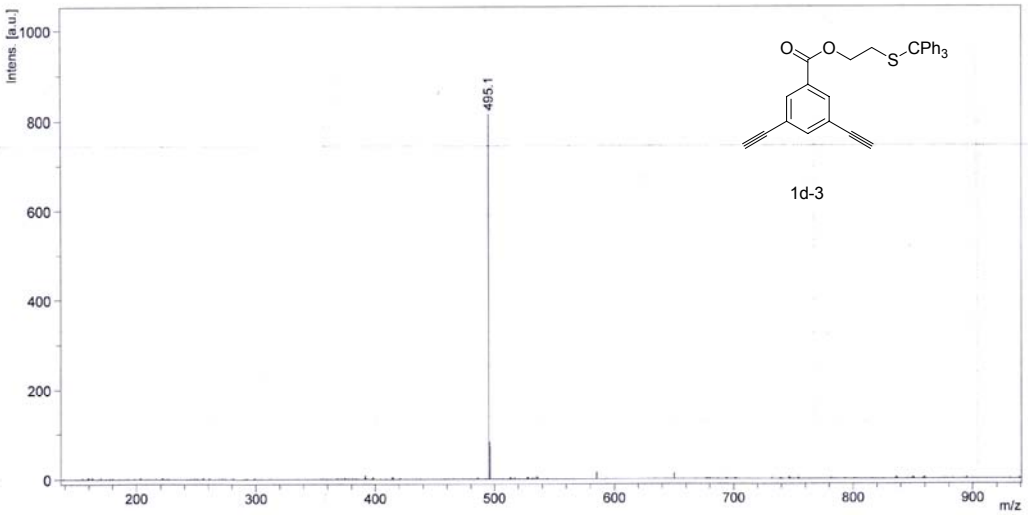
1d-3

BRUKER

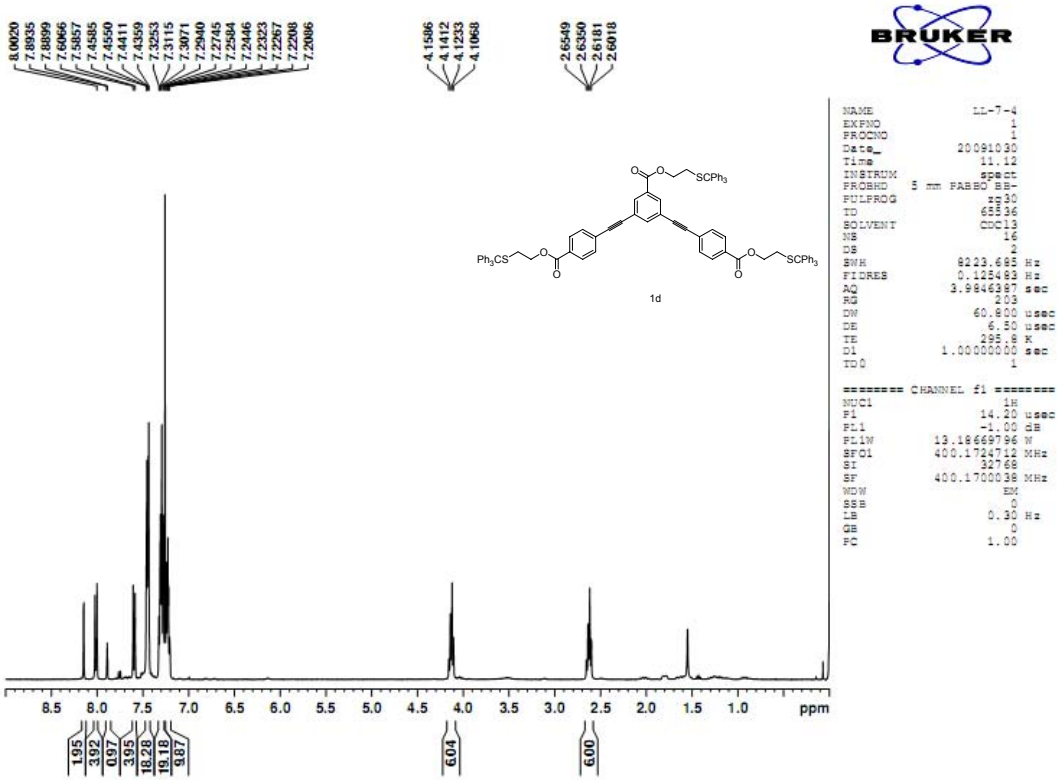
```
NAME                LL-7-3-C13
EXPNO                        1
PROCNO                       1
Date_                 20091101
Time                     13.32
INSTRUM                   spect
PROBHD     5 mm PABBO BB-
PULPROG                zgpg30
TD                        65536
SOLVENT                  CDCl3
NS                        4000
DS                           4
SWH                  24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                         203
DW                       20.800 usec
DE                        6.50 usec
TE                      294.4 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        13C
P1                         9.70 usec
PL1                       -2.00 dB
PL1W             57.32743073 W
SFO1            100.6328888 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                     80.00 usec
PL2                       -1.00 dB
PL12                      14.02 dB
PL13                      14.46 dB
PL2W             13.18669796 W
PL12W             0.41508400 W
PL13W             0.37509048 W
SFO2            400.1716007 MHz
SI                        32768
SF               100.6228274 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```

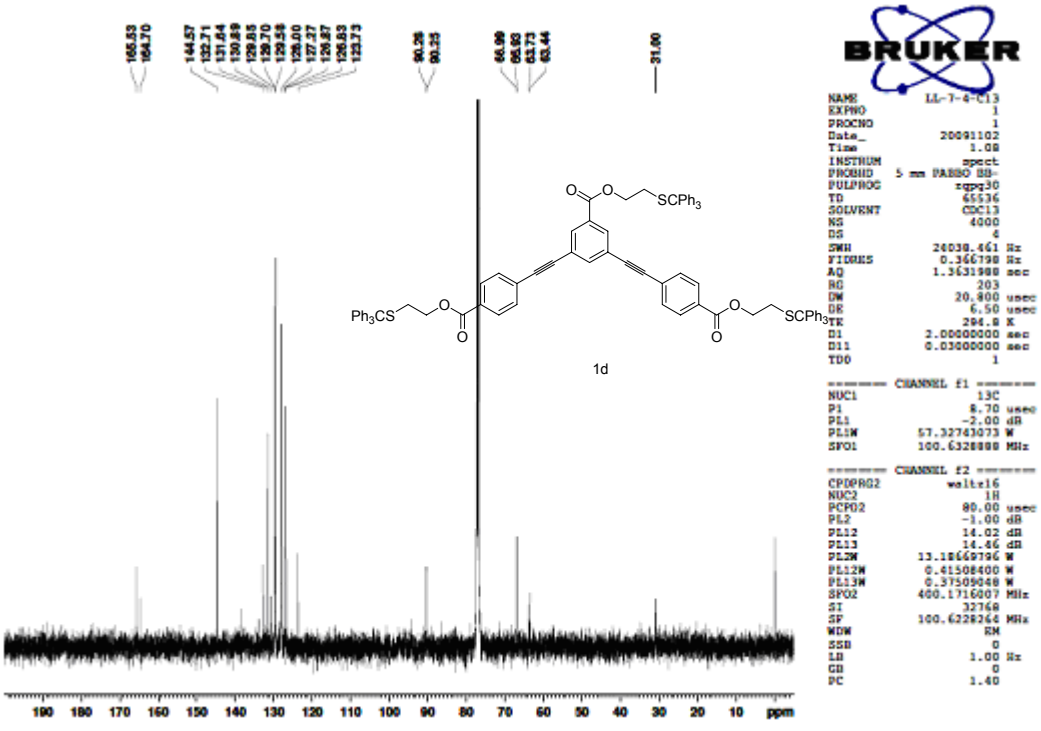
D:\Data_IC\New Folder (3)\HELAN\20100413\LL-7-3\0_G17\1 printed: 4/13/2010 4:52:12 PM

MALDI-TOF,CCA,LL-7-3,2010,04,13



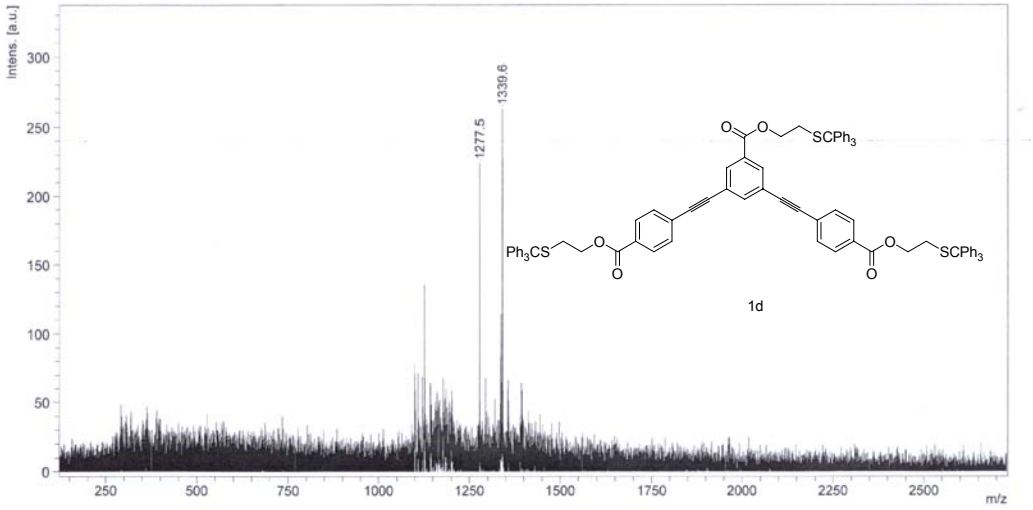
1d-3


8.0020
7.8935
7.8899
7.6066
7.5857
7.4585
7.4550
7.4411
7.4359
7.3253
7.3115
7.3071
7.2940
7.2745
7.2584
7.2446
7.2323
7.2267
7.2208
7.2086
4.1586
4.1412
4.1233
4.1068
2.6549
2.6350
2.6181
2.6018
1d
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 ppm
1.95
3.92
0.97
3.95
18.28
19.18
9.87
6.04
6.00

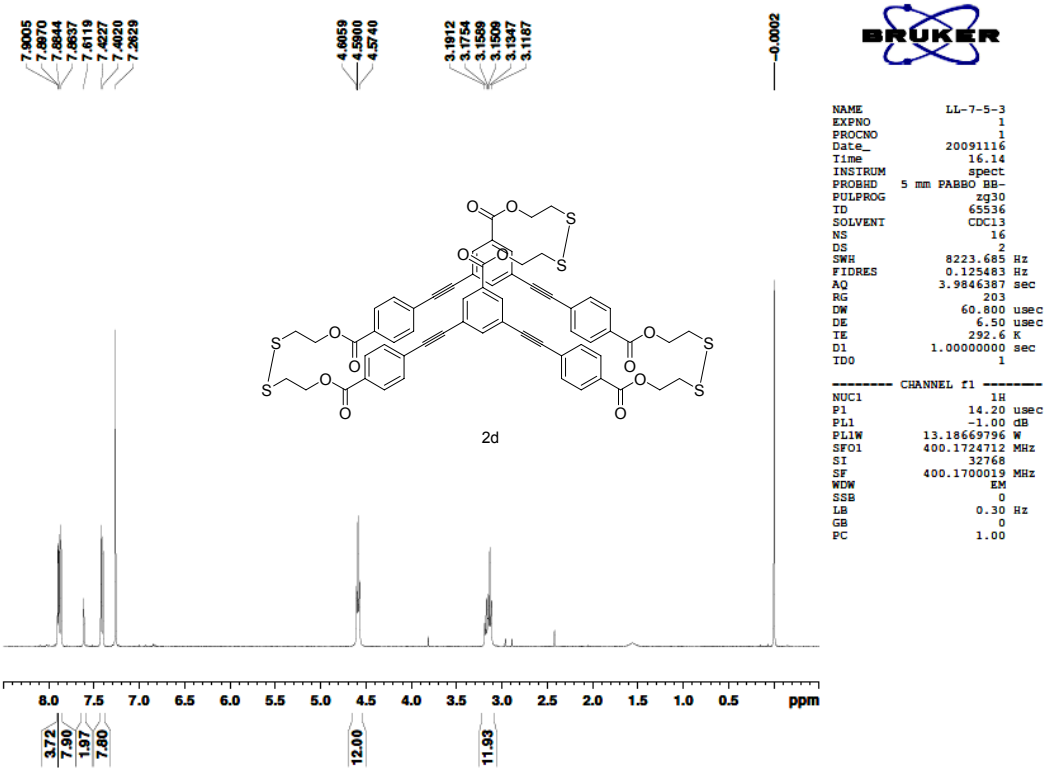

165.53
164.70
144.57
132.71
131.64
130.89
129.85
129.70
129.58
129.00
127.27
126.87
126.63
123.73
90.26
90.25
66.99
66.83
63.73
63.44
31.00
1d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

D:\Data_IC\New Folder (3)\HELAN\20100308\11-7-6\0_C7\1 printed: 3/8/2010 4:15:12 PM

MALDI-TOF,CCA,11-7-6,2010,03,08

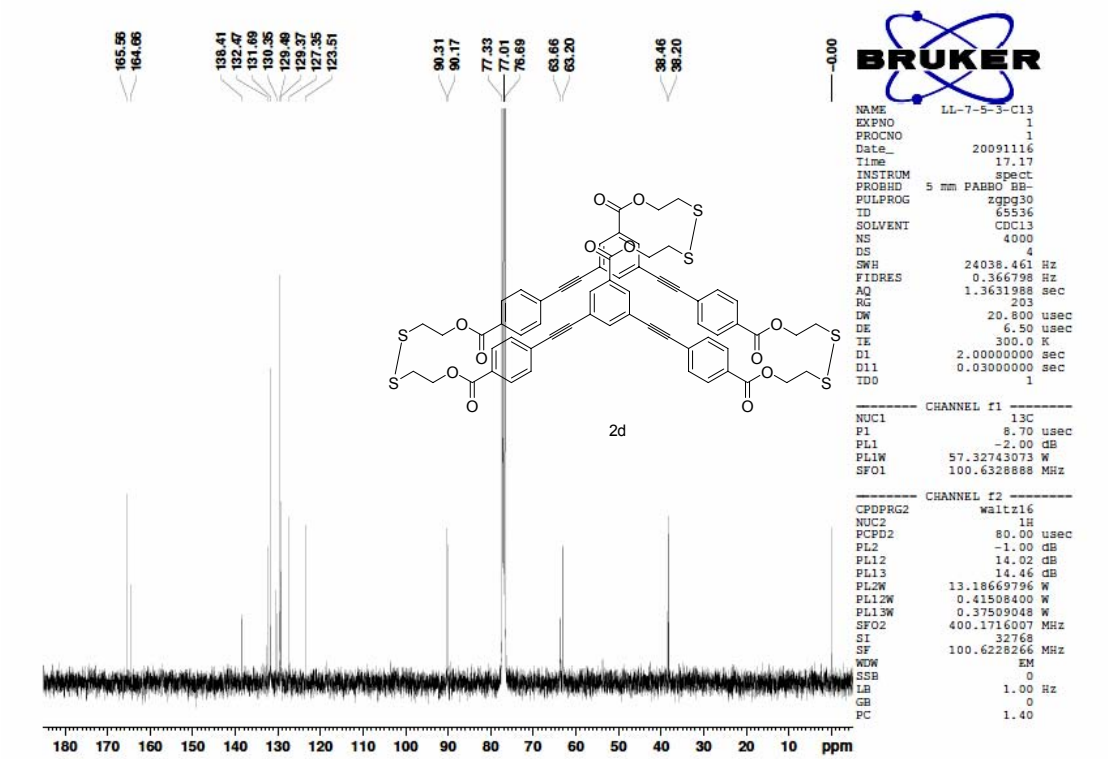


1d



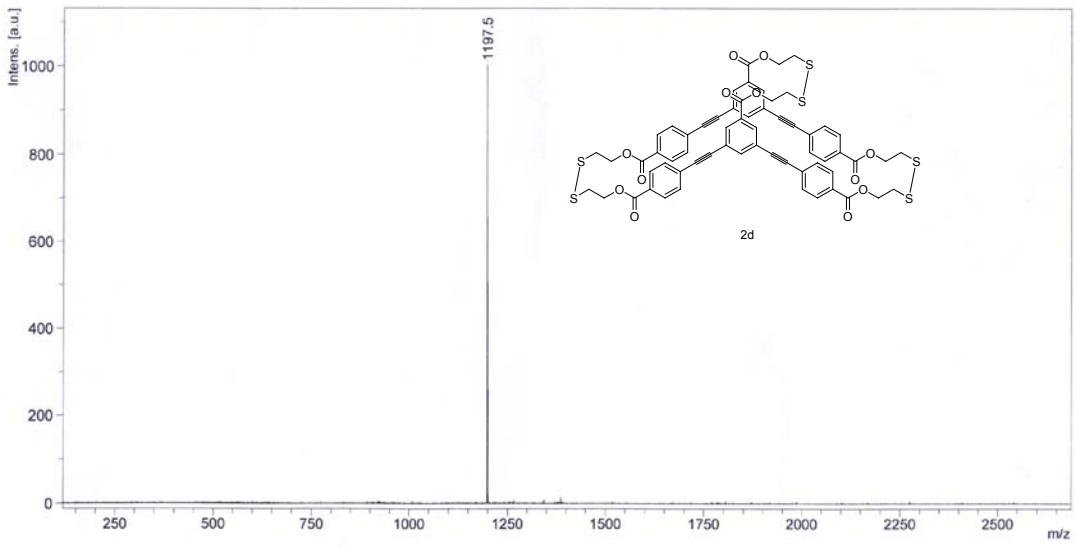
2d

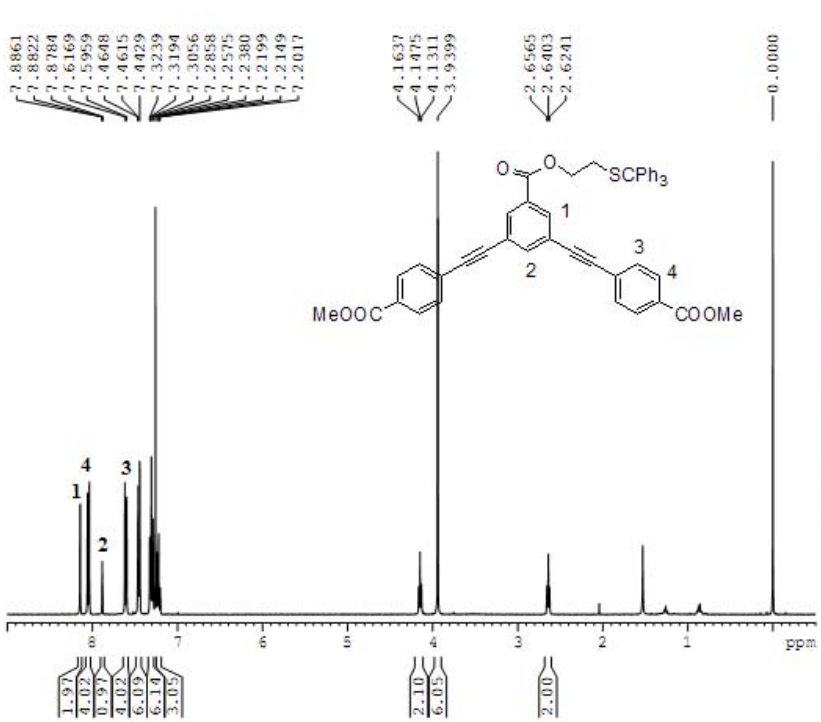
```
NAME            LL-7-5-3
EXPNO                  1
PROCNO                 1
Date_           20091116
Time               16.14
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                   203
DW                60.800 usec
DE                 6.50 usec
TE                292.6 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.20 usec
PL1               -1.00 dB
PL1W        13.18669796 W
SFO1        400.1724712 MHz
SI                 32768
SF          400.1700019 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

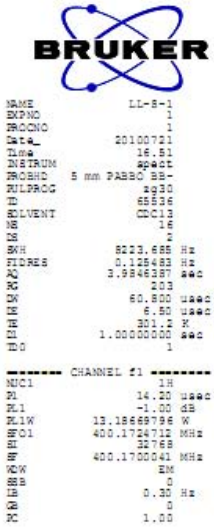


D:\Data_IC\New Folder (3)\HELAN\20091023\LL-7-5\0_P4\1 printed: 10/23/2009 4:01:56 PM

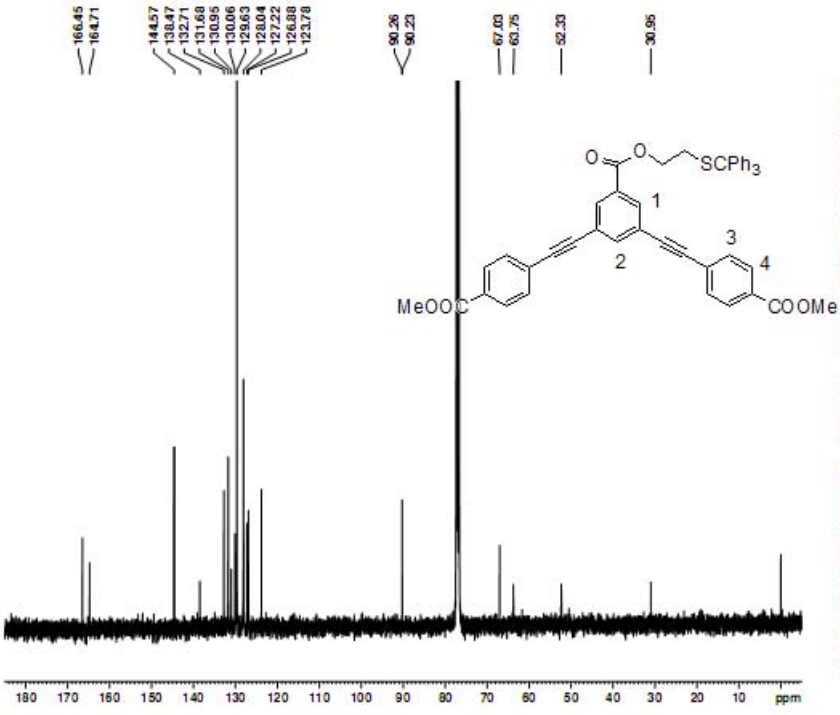
MALDI-TOF,CCA,LL-7-5,2009,10,23

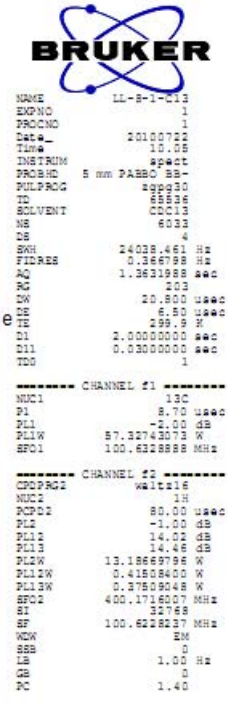



7.8861
7.8822
7.8784
7.6169
7.5959
7.4648
7.4615
7.4429
7.3239
7.3194
7.3056
7.2858
7.2575
7.2380
7.2199
7.2149
7.2017
4.1637
4.1475
4.1311
3.9399
2.6565
2.6403
2.6241
0.0000
SCPh3
MeOOC
COOMe
1.97
4.02
0.97
4.02
6.09
6.14
3.05
2.10
6.05
2.00
ppm

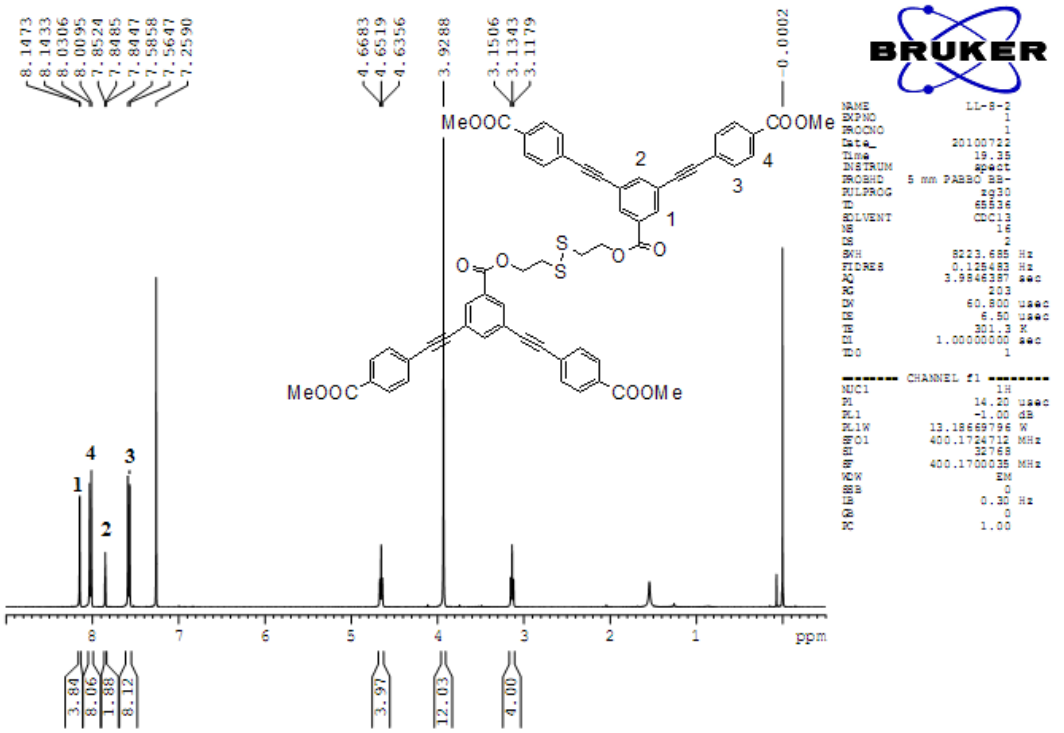

BRUKER
NAME LL-8-1
EXPNO 1
PROCNO 1
Date_ 20100721
Time 16.51
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 301.2 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 14.20 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700041 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

3

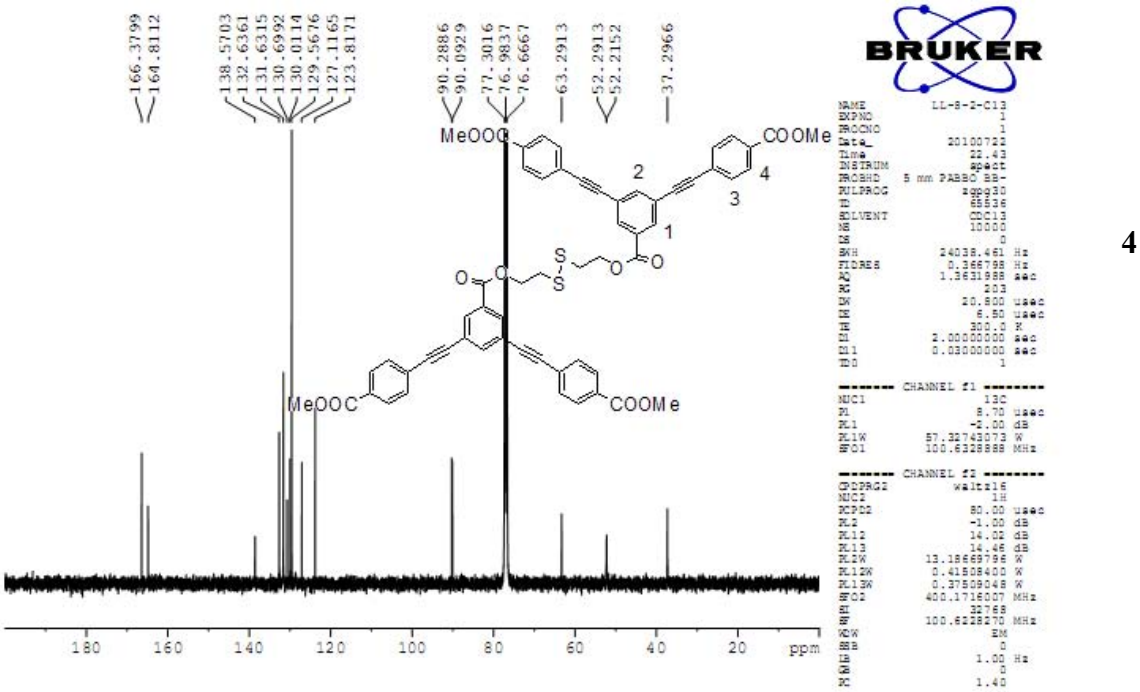

166.45
164.71
144.57
138.47
132.71
131.68
130.95
130.06
129.63
128.04
127.22
126.88
123.78
90.36
90.23
67.03
63.75
52.33
30.95
SCPh3
MeOOC
COOMe
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


BRUKER
NAME LL-8-1-C13
EXPNO 1
PROCNO 1
Date_ 20100722
Time 10.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 6033
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 299.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 8.70 usec
PL1 -2.00 dB
PL1W 57.32743073 W
SFO1 100.6328888 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.02 dB
PL13 14.46 dB
PL2W 13.18669796 W
PL12W 0.41508400 W
PL13W 0.37509048 W
SFO2 400.1716007 MHz
SI 32768
SF 100.6228237 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

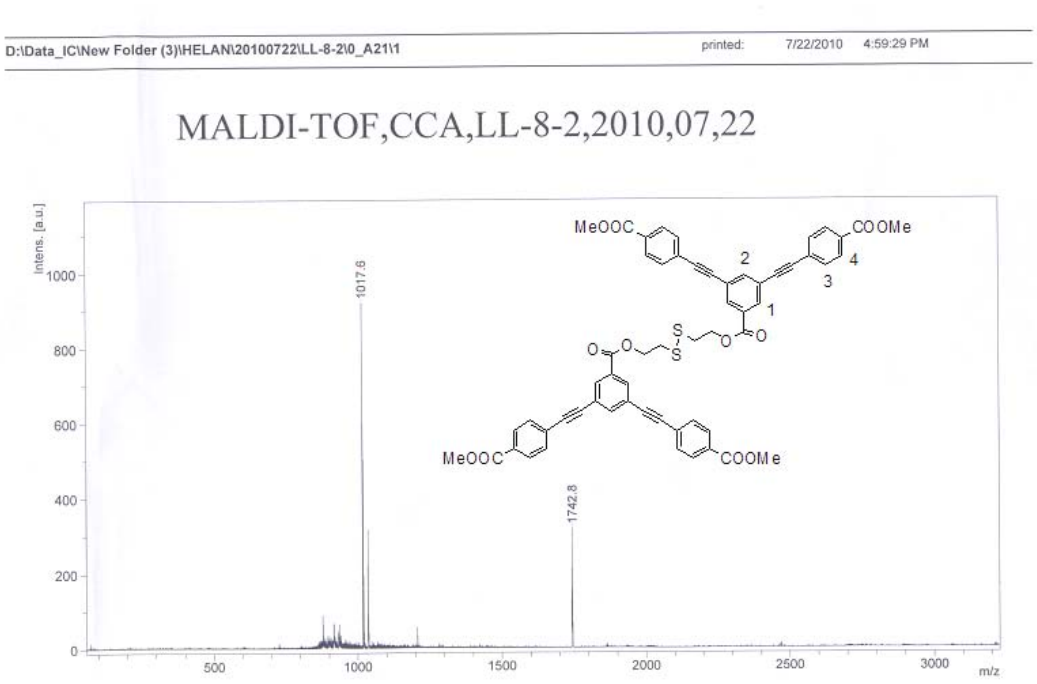
3


8.1473
8.1433
8.0306
8.0095
7.8524
7.8485
7.8447
7.5858
7.5647
7.2590
4.6683
4.6519
4.6356
3.9288
3.1506
3.1343
3.1179
0.0002
MeOOC
COOMe
MeOOC
COOMe
1
2
3
4
3.84
8.06
1.88
8.12
3.97
12.03
4.00
ppm
BRUKER
NAME LL-8-2
EXPNO 1
PROCNO 1
Date_ 20100722
Time 19.35
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 301.3 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 14.20 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700035 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

4

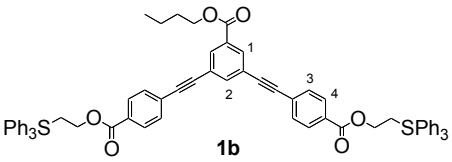

166.3799
164.8112
138.5703
132.6361
131.6315
130.6992
130.0114
129.5676
127.1165
123.8171
90.2886
90.0929
77.3016
76.9837
76.6667
63.2913
52.2913
52.2152
37.2966
MeOOC
COOMe
MeOOC
COOMe
1
2
3
4
ppm
BRUKER
NAME LL-8-2-C13
EXPNO 1
PROCNO 1
Date_ 20100722
Time 22.43
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 10000
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 8.70 usec
PL1 -2.00 dB
PL1W 57.32743073 W
SFO1 100.6328888 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.02 dB
PL13 14.46 dB
PL2W 13.18669796 W
PL12W 0.41508400 W
PL13W 0.37509048 W
SFO2 400.1716007 MHz
SI 32768
SF 100.6228270 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

4

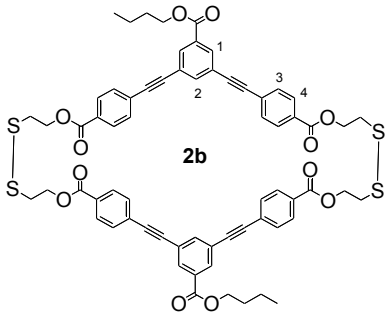

D:\Data_IC\New Folder (3)\HELAN\20100722\LL-8-2\0_A21\1
printed: 7/22/2010 4:59:29 PM
MALDI-TOF,CCA,LL-8-2,2010,07,22
Intens. [a.u.]
1017.6
1742.8
MeOOC
COOMe
m/z

4

III. Summary of NMR (Chemical Shift) Data



1b

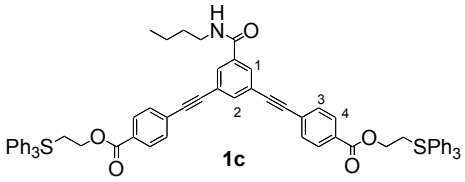


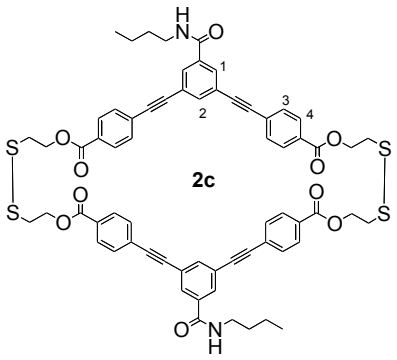
2b

In $CDCl_3$

H	**1b** (40 mM)	**2b** (20 mM)	δ_{1b}-δ_{2b}	**1b** (20 mM)	**2b** (10 mM)	δ_{1b}-δ_{2b} (ppm)
1	8.17	7.99	0.18	8.18	7.99	0.19
2	7.89	7.65	0.24	7.89	7.66	0.23
3	7.60	7.47	0.13	7.60	7.47	0.13
4	8.01	7.91	0.10	8.02	7.91	0.11

H	**1b** (2 mM)	**2b** (1 mM)	δ_{1b}-δ_{2b}	**1b** (0.02 mM)	**2b** (0.01 mM)	δ_{1b}-δ_{2b} (ppm)
1	8.18	7.99	0.19	8.17	7.99	0.18
2	7.89	7.66	0.23	7.88	7.66	0.22
3	7.60	7.47	0.13	7.60	7.47	0.13
4	8.02	7.91	0.11	8.01	7.91	0.10



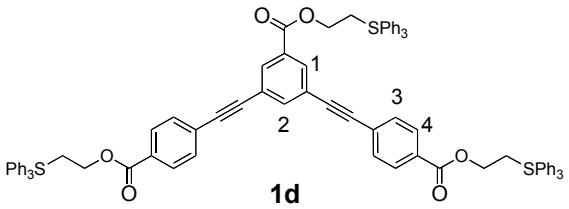


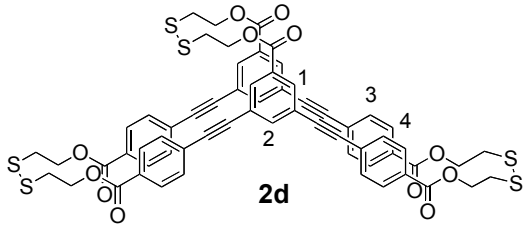
In $CDCl_3$

H	**1c** (2 mM)	**2c** (1 mM)	δ_{1c}-δ_{2c}	**1c** (20 mM)	**2c** (10 mM)	δ_{1c}-δ_{2c} (ppm)
1	7.90	7.58	0.32	7.90	7.58	0.32
2	7.84	7.62	0.22	7.83	7.61	0.22
3	7.59	7.38	0.21	7.58	7.37	0.21
4	8.01	7.87	0.24	8.01	7.87	0.24
NH	6.12	7.09	-0.83	6.16	7.05	-0.89

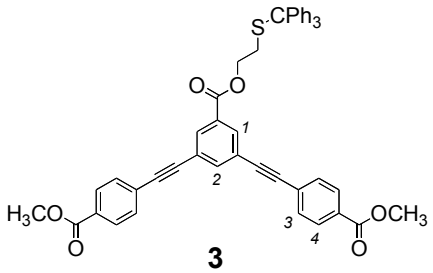
H	**1c** (0.2mM)	**2c** (0.1 mM)	δ_{1c}-δ_{2c}	**1c** (0.02mM)	**2c** (0.01 mM)	δ_{1c}-δ_{2c} (ppm)
1	7.89	7.59	0.30	7.89	7.59	0.30
2	7.83	7.62	0.21	7.83	7.61	0.21
3	7.59	7.38	0.21	7.58	7.38	0.20
4	8.01	7.87	0.14	8.01	7.88	0.13
NH	ND*	ND*	N/A	ND*	ND*	N/A

*Not detectable

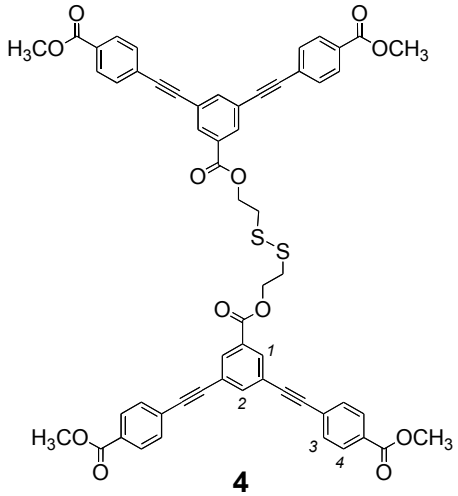




H	**1d** (2 mM)	**2d** (1 mM)	δ_{1d} - δ_{2d} (ppm)
1	8.15	7.90	0.25
2	7.89	7.61	0.28
3	7.60	7.41	0.19
4	8.01	7.87	0.14



3



4

recorded in $CDCl_3$:

H	**3** (8 mM)	**4** (4 mM)	$\delta_3 - \delta_4$ (ppm)
1	8.14	8.15	-0.01
2	7.88	7.85	0.03
3	7.61	7.58	0.03
4	8.05	8.02	0.03