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SUPPORTING INFORMATION

Substrate-driven selective mono- and bis-couplings of *ortho*-(OTf/I/Br) substituted *gem*-dibromovinylarenes

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1. Experimental

General

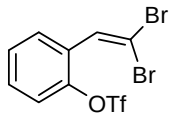
All the coupling experiments were performed in oven-dried Schlenk tubes under N_2 atmosphere conditions. All experiments were conducted with anhydrous solvents.

2. Procedures for the preparation of *ortho-gem*-dibromovinylaryl triflates (1a-1d)

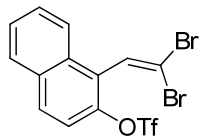
These compounds are prepared from salicylaldehydes using literature known procedure involving 1,1-dibromide preparation followed by its triflate derivatization.[1]

3. Spectral data for *ortho-gem*-dibromovinylaryl triflates (1a-1d)

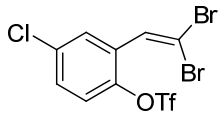
1a.[1] Yellow liquid; R_f = 0.40 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (dd, 1H, J = 7.46 Hz, 1.7 Hz), 7.50 (s, 1H), 7.48-7.39 (m, 2H), 7.33 (dd, 1H, J = 7.92 Hz, 1.48 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.2, 130.6, 130.4, 130.3, 129.4, 128.2, 121.8, 118.6 (q, J = 318.35 Hz), 95.5 ppm. IR (neat, cm^{-1}): 3029, 1425, 1217, 1139, 896, 795. HRMS (EI): calcd for $C_9H_5Br_2F_3O_3S$ $[M]^+$ 407.8278; found 407.8279.



1b.[1] Pale yellow liquid; R_f = 0.38 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98-7.92 (m, 3H), 7.70-7.59 (m, 3H), 7.43 (d, 1H, J = 8.68 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.5, 132.4, 131.1, 130.9, 130.0, 128.5, 128.1, 127.4, 126.6, 125.5, 119.6, 118.6 (q, J = 321.9 Hz), 98.1 ppm. IR (neat, cm^{-1}): 3065, 1585, 1510, 1424, 1216, 1139, 951, 845. HRMS (EI): calcd for $C_{13}H_7Br_2F_3O_3S$ $[M]^+$ 457.8435; found 457.8439.

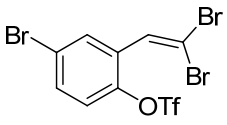


1c.[1] Yellow liquid; R_f = 0.51 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, 1H, J = 2.32 Hz), 7.42-7.39 (m, 2H), 7.27-7.24 (m,



1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.5, 134.0, 130.9, 130.4, 130.2, 129.2, 123.1, 118.5 (q, J = 322.54 Hz), 96.9 ppm. IR (neat, cm^{-1}): 3031, 2855, 1609, 1428, 1219, 871, 619. HRMS (EI): calcd for $C_9H_4Br_2ClF_3O_3S$ $[M]^+$ 441.7889; found 441.7886.

1d. Pale yellow liquid; R_f = 0.51 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, 1H, J = 2.44 Hz), 7.56 (dd, 1H, J = 8.8 Hz, 2.44 Hz), 7.43 (s, 1H), 7.20 (d, 1H, J = 8.8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.1, 133.3, 133.1, 131.2, 129.1, 123.4, 121.7, 118.5 (q, J = 321.9 Hz), 96.9 ppm. IR (neat, cm^{-1}): 3029, 1561, 1468, 1428, 1218, 1138, 869, 616. HRMS (EI): calcd for $C_9H_4Br_3F_3O_3S$ $[M]^+$ 485.7383; found 485.7383.

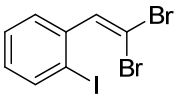


4. Representative synthesis of *ortho-gem*-dibromovinylaryl iodide (2a-2c)

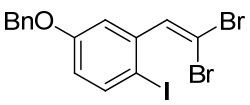
2-Iodoarylaldehydes were converted to the corresponding *gem*-dibromovinyl substrates following the standard procedure.[2]

5. Spectral data for *ortho-gem*-dibromovinylaryl iodides (2a-2c)

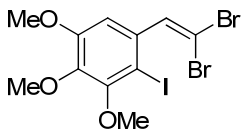
2a. Yellow liquid; R_f = 0.62 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, 1H, J = 7.32 Hz), 7.50 (d, 1H, J = 7.76 Hz), 7.41-7.35 (m, 2H), 7.04 (t, 1H, J = 7.78 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.7, 139.9, 139.0, 129.9, 129.8, 128.0, 98.4, 93.2 ppm. IR (neat, cm^{-1}): 3059, 3011, 2923, 1601, 1457, 1014, 879, 787. HRMS (EI): calcd for $C_8H_5Br_2I$ $[M]^+$ 385.7803; found 385.7801.



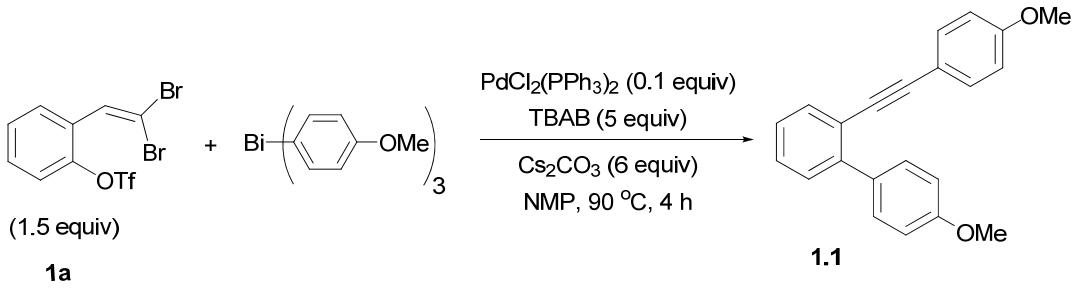
2b. Pale yellow solid; mp 56-58 ^{o}C, R_f = 0.32 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, 1H, J = 8.68 Hz), 7.43-7.32 (m, 6H), 7.14 (d, 1H, J = 2.72 Hz), 6.72 (dd, 1H, J = 8.68 Hz, 2.76 Hz), 5.07 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 140.5, 139.6, 136.3, 128.7, 128.1, 127.6, 127.4, 117.5, 116.6, 93.3, 87.2, 70.3 ppm. IR (neat, cm^{-1}): 3063, 2931, 1583, 1542, 1284, 1226, 1008, 816, 733, 695. HRMS (ESI): calcd for $C_{15}H_{15}Br_2INO$ $[M+NH_4]^+$ 509.8565; found 509.8569.



2c. Colorless solid; mp 72-74 °C, R_f = 0.47 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (s, 1H), 6.96 (s, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.5, 153.2, 142.0, 140.7, 135.0, 109.5, 92.5, 86.5, 61.0, 60.8, 56.2 ppm. IR (neat, cm^{-1}): 2934, 2844, 1554, 1476, 1382, 1330, 1104, 1005, 861. HRMS (EI): calcd for $C_{11}H_{11}Br_2IO_3$ $[M]^+$ 475.8120; found 475.8123.



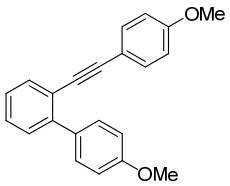
6. Representative procedure for the couplings of *ortho-gem*-dibromovinylaryl triflates *or* iodides



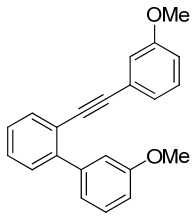
An oven-dried Schlenk tube was charged with **1a** (0.154 g, 0.375 mmol, 1.5 equiv.), Bi(*p*-anisyl)$_3$ (0.133 g, 0.25 mmol, 1 equiv.), $PdCl_2(PPh_3)_2$ (0.018 g, 0.025 mmol, 0.1 equiv.), Cs_2CO_3 (0.49 g, 1.5 mmol, 6 equiv.), TBAB (0.403 g, 1.25 mmol, 5 equiv.), NMP (5 mL) and stirred at 90 °C for 4 h. The reaction mixture was brought to rt and extracted with EtOAc (2 x 25 mL) using a separatory funnel. The organic extract was washed with water (20 mL), brine (10 mL), dried over anhydrous $MgSO_4$ and concentrated. The crude mixture was subjected to column chromatography purification using EtOAc/hexane as eluent. This procedure was followed for the bis-couplings of *gem*-dibromovinylaryl triflates and iodides (**1a**-**1d** and **2a**-**2b**).

7. Spectral data of *ortho*-alkynylbiaryls (1.1-1.18 and 2.1)

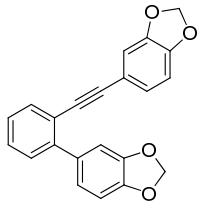
1.1. Brown liquid (0.094 g, 80% (OTf), 0.098 g, 83% (I)); R_f = 0.11 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64-7.60 (m, 3H), 7.41-7.26 (m, 5H), 7.00 (d, 2H, J = 8.72 Hz), 6.83 (d, 2H, J = 8.68 Hz), 3.88 (s, 3H), 3.81 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 159.0, 143.1, 133.1, 132.8, 132.7, 130.5, 129.3, 128.1, 126.6, 121.7, 115.6, 113.9, 113.2, 92.1, 88.2, 55.2, 55.3 ppm. IR (neat, cm^{-1}): 3001, 2933, 2213, 1607, 1511, 1249, 1178, 1001, 831, 761. HRMS (ESI): calcd for $C_{22}H_{19}O_2$ $[M+H]^+$ 315.1385; found 315.1388.



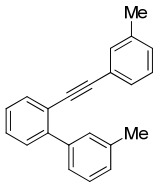
1.2. Yellow liquid (0.062 g, 53% (OTf), 0.066 g, 56% (I)); R_f = 0.22 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (dd, 1H, J = 7.58 Hz, 1.14 Hz), 7.45-7.31 (m, 4H), 7.25-7.17 (m, 3H), 6.95-6.92 (m, 2H), 6.86-6.82 (m, 2H), 3.82 (s, 3H), 3.77 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 159.1, 143.8, 141.9, 132.8, 129.4, 129.3, 128.9, 128.5, 127.1, 124.4, 123.8, 121.9, 121.4, 115.9, 114.9, 114.7, 113.3, 92.4, 89.2, 55.2, 55.1 ppm. IR (neat, cm^{-1}): 3062, 2937, 2834, 1603, 1580, 1465, 1321, 1222, 1043, 856, 784, 759. HRMS (EI): calcd for $C_{22}H_{18}O_2$ $[M]^+$ 314.1307; found 314.1300.



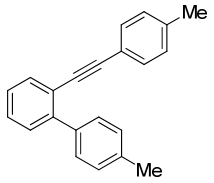
1.3. Brown liquid (0.052 g, 41% (OTf), 0.064 g, 50% (I)); R_f = 0.15 (Hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59 (d, 1H, J = 6.85 Hz), 7.38-7.33 (m, 2H), 7.29 (td, 1H, J = 7.15 Hz, 1.7 Hz), 7.18 (d, 1H, J = 1.7 Hz), 7.12 (dd, 1H, J = 8 Hz, 1.75 Hz), 6.92-6.89 (m, 2H), 6.82 (d, 1H, J = 1.15 Hz), 6.75 (d, 1H, J = 8.05 Hz), 6.02 (s, 2H), 5.96 (s, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.8, 147.4, 147.2, 147.0, 143.2, 134.6, 132.7, 129.3, 128.3, 126.8, 126.0, 123.0, 121.6, 116.7, 111.3, 110.0, 108.4, 107.8, 101.2, 101.1, 92.4, 87.8 ppm. IR (neat, cm^{-1}): 3062, 2893, 2778, 2206, 1604, 1475, 1339, 1242, 1039, 929, 811, 759. HRMS (APCI): calcd for $C_{22}H_{15}O_4$ $[M+H]^+$ 343.0970; found 343.0975.



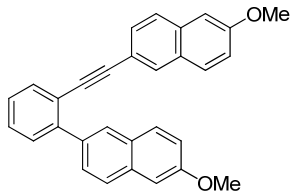
1.4. Pale yellow liquid (0.072 g, 68% (OTf), 0.077 g, 73% (I)); R_f = 0.49 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (dd, 1H, J = 7.36 Hz, 0.92 Hz), 7.51-7.30 (m, 6H), 7.23-7.09 (m, 5H), 2.44 (s, 3H), 2.32 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.9, 140.4, 137.9, 137.3, 132.8, 131.9, 130.1, 129.4, 128.9, 128.4, 128.2, 128.1, 127.8, 126.9, 126.5, 123.3, 121.6, 92.4, 89.1, 21.6, 21.2 ppm. IR (neat, cm^{-1}): 3029, 2922, 2856, 1602, 1487, 1441, 1261, 1092, 1039, 784, 757. HRMS (EI): calcd for $C_{22}H_{18}$ $[M]^+$ 282.1409; found 282.1408.



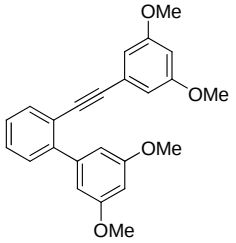
1.5. Yellow solid (0.074 g, 70% (OTf), 0.077 g, 73% (I)); mp 58-60 °C, R_f = 0.62 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63-7.57 (m, 3H), 7.42-7.34 (m, 2H), 7.32-7.24 (m, 5H), 7.10 (d, 2H, J = 7.76 Hz), 2.42 (s, 3H), 2.34 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6, 138.2, 137.6, 137.1, 132.8, 131.2, 129.4, 129.2, 129.0, 128.6, 128.3, 126.7, 121.6, 120.4, 92.3, 88.8, 21.5, 21.2 ppm. IR (neat, cm^{-1}): 3024, 2920, 1510, 1476, 816, 757. HRMS (EI): calcd for $C_{22}H_{18}$ $[M]^+$ 282.1409; found 282.1401.



1.6. Brown solid (0.079 g, 51% (OTf), 0.102 g, 66% (I)); mp 114-116 °C, R_f = 0.49 (EtOAc/hexane, 1:19). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1H), 7.85-7.82 (m, 3H), 7.72-7.70 (m, 2H), 7.60-7.54 (m, 3H), 7.44 (td, 1H, J = 7.56 Hz, 1.37 Hz), 7.36 (td, 1H, J = 7.33 Hz, 1.39 Hz), 7.30 (dd, 1H, J = 8.48 Hz, 1.6 Hz), 7.23-7.18 (m, 2H), 7.12 (dd, 1H, J = 8.94 Hz, 2.54 Hz), 7.06 (d, 1H, J = 2.76 Hz), 3.98 (s, 3H), 3.91 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2, 157.9, 143.7, 135.9, 134.0, 133.9, 132.9, 131.0, 129.8, 129.7, 129.3, 128.7, 128.5, 128.4, 128.3, 128.2, 126.9, 126.7, 126.2, 121.9, 119.3, 118.9, 118.3, 105.7, 105.6, 93.0, 89.3, 55.4, 55.3 ppm. IR (neat, cm^{-1}): 3057, 2958, 2205, 1603, 1486, 1389, 1263, 1164, 1031, 853, 756. HRMS (ESI): calcd for $C_{30}H_{23}O_2$ $[M+H]^+$ 415.1698; found 415.1692.

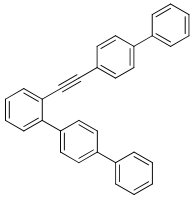


1.7. Brown liquid (0.070 g, 50% (OTf), 0.094 g, 67% (I)); R_f = 0.31 (EtOAc/hexane, 1:19). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (dd, 1H, J = 7.56 Hz, 1.6 Hz), 7.46-7.31 (m, 3H), 6.83 (d, 2H, J = 2.28 Hz), 6.51-6.50 (m, 3H), 6.42 (t, 1H, J = 2.28 Hz), 3.81 (s, 6H), 3.77 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.4, 160.3, 143.9, 142.5, 132.8, 129.3,

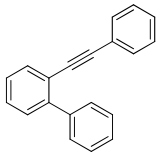


128.5, 127.2, 124.7, 121.3, 108.9, 107.5, 101.9, 99.9, 92.7, 88.9, 55.4, 55.3 ppm. IR (neat, cm^{-1}): 3000, 2937, 2837, 1591, 1420, 1205, 1156, 1064, 836, 761. HRMS (ESI): calcd for $C_{24}H_{23}O_4$ $[M+H]^+$ 375.1596; found 375.1598.

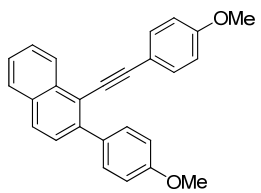
1.8. Brown solid (0.068 g, 45% (OTf), 0.101 g, 66% (I)); mp 110-112 °C, R_f = 0.30 (Hexane). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, 1H, J = 7.76 Hz), 7.74-7.69 (m, 5H), 7.59-7.36 (m, 16H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.4, 140.9, 140.8, 140.6, 140.3, 140.2, 139.5, 133.0, 131.7, 129.8, 129.4, 128.8, 128.6, 127.6, 127.3, 127.1, 127.0, 126.6, 122.3, 121.5, 92.3, 90.1 ppm. IR (neat, cm^{-1}): 3057, 3029, 1599, 1487, 1263, 1007, 840, 760, 696. HRMS (ESI): calcd for $C_{32}H_{23}$ $[M+H]^+$ 407.1800; found 407.1808.



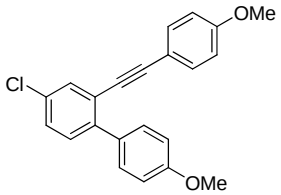
1.9.[3] Brown liquid (0.052 g, 54% (OTf), 0.059 g, 62% (I)); R_f = 0.62 (Hexane). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.69-7.66 (m, 3H), 7.49-7.39 (m, 5H), 7.38-7.28 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.9, 140.5, 132.8, 131.3, 129.5, 129.4, 128.5, 128.2, 128.1, 127.9, 127.4, 127.0, 123.4, 121.6, 92.2, 89.4 ppm. IR (neat, cm^{-1}): 3058, 1598, 1491, 755. HRMS (EI): calcd for $C_{20}H_{14}$ $[M]^+$ 254.1096; found 254.1090.



1.10. Brown liquid (0.096 g, 70%); R_f = 0.39 (EtOAc/hexane, 1:19). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.57 (d, 1H, J = 8.72 Hz), 7.86 (t, 2H, J = 8.94 Hz), 7.76-7.74 (m, 2H), 7.64-7.60 (m, 1H), 7.56-7.51 (m, 2H), 7.44-7.41 (m, 2H), 7.04 (d, 2H, J = 9.16 Hz), 6.88 (d, 2H, J = 9.16 Hz), 3.90 (s, 3H), 3.83 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 159.1, 141.6, 133.7, 133.6, 132.8, 132.0, 131.0, 128.1, 128.0, 127.6, 127.0, 126.7, 126.1, 118.4, 115.9, 114.0, 113.3, 97.6, 86.3, 55.4, 55.3 ppm. IR (neat, cm^{-1}): 3054, 3001, 2835, 2203, 1606, 1510, 1248, 1178, 1030, 818, 751. HRMS (APCI): calcd for $C_{26}H_{21}O_2$ $[M+H]^+$ 365.1542; found 365.1549.

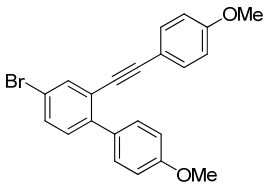


1.11. Yellow liquid (0.095 g, 73%); R_f = 0.15 (Hexane). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.59-7.58 (m, 3H), 7.31-7.29 (m, 4H), 6.99 (d, 2H, J = 8.6 Hz), 6.83 (d, 2H, J = 8.6 Hz), 3.87 (s, 3H), 3.81 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.8, 159.3, 141.5, 132.9, 132.3, 132.1, 132.0, 130.4, 128.2, 123.3, 115.1, 114.1, 114.0, 113.4, 93.2, 87.1,

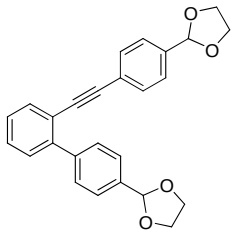


55.3 ppm. IR (neat, cm^{-1}): 3001, 2933, 2216, 1607, 1510, 1290, 1250, 1177, 1034, 819. HRMS (ESI): calcd for $C_{23}H_{18}ClO_4$ $[M+HCO_2]^-$ 393.0894; found 393.0891.

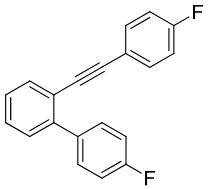
1.12. Yellow liquid (0.110 g, 75%); R_f = 0.09 (Hexane). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.74 (d, 1H, J = 1.75 Hz), 7.58 (d, 2H, J = 8.6 Hz), 7.45 (dd, 1H, J = 8.3 Hz, 2 Hz), 7.29 (d, 2H, J = 8.55 Hz), 7.25-7.23 (m, 1H), 6.98 (d, 2H, J = 8.6 Hz), 6.83 (d, 2H, J = 8.6 Hz), 3.87 (s, 3H), 3.80 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.8, 159.3, 141.9, 135.0, 132.9, 132.0, 131.1, 130.7, 130.3, 123.7, 120.2, 115.1, 114.0, 113.4, 93.4, 86.9, 55.3, 55.2 ppm. IR (neat, cm^{-1}): 2932, 2835, 2212, 1606, 1510, 1464, 1290, 1250, 1177, 1034, 832. HRMS (ESI): calcd for $C_{22}H_{18}BrO_2$ $[M+H]^+$ 393.0490; found 393.0493.



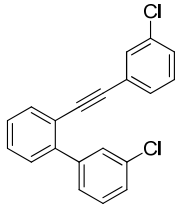
1.13. Yellow liquid (0.073 g, 49%); R_f = 0.11 (EtOAc/hexane, 1:19). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.70-7.64 (m, 3H), 7.57 (d, 2H, J = 8.24 Hz), 7.40 (d, 4H, J = 8.24 Hz), 7.34 (d, 3H, J = 8.68 Hz), 5.91 (s, 1H), 5.80 (s, 1H), 4.19-4.01 (m, 8H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.4, 141.4, 137.8, 137.1, 132.9, 131.4, 129.5, 129.4, 128.6, 127.2, 126.3, 126.0, 124.2, 121.4, 103.6, 103.3, 92.0, 89.7, 65.3, 65.2 ppm. IR (neat, cm^{-1}): 2952, 2884, 2213, 1700, 1601, 1386, 1208, 1080, 830, 761. HRMS (ESI): calcd for $C_{26}H_{23}O_4$ $[M+H]^+$ 399.1596; found 399.1596. *Note: This compound is susceptible for decomposition under the laboratory conditions.*



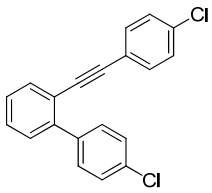
1.14. Pale yellow solid (0.060 g, 55%); mp 70-72 ^oC, R_f = 0.49 (Hexane). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.64-7.60 (m, 3H), 7.41-7.29 (m, 5H), 7.15 (t, 2H, J = 8.72 Hz), 7.00 (t, 2H, J = 8.92 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.4 (d, J = 245.04 Hz), 142.8, 136.5, 133.2 (d, J = 7.63 Hz), 132.8, 130.9 (d, J = 8.58 Hz), 129.4, 128.6, 127.2, 121.4, 119.4, 119.3, 115.6 (d, J = 21.93 Hz), 114.8 (d, J = 20.97 Hz), 91.3, 88.7 ppm. IR (neat, cm^{-1}): 3059, 2925, 1601, 1508, 1232, 1157, 835, 799, 759. HRMS (EI): calcd for $C_{20}H_{12}F_2$ $[M]^+$ 290.0907; found 290.0906.



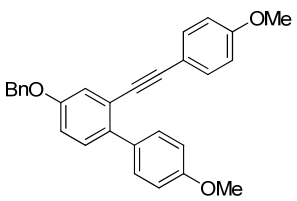
1.15. Pale yellow solid (0.062 g, 51%); mp 72-74 °C, R_f = 0.57 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69-7.68 (m, 1H), 7.64-7.62 (m, 1H), 7.50-7.48 (m, 1H), 7.42-7.33 (m, 6H), 7.28-7.22 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.4, 142.0, 134.1, 133.7, 133.0, 131.2, 129.6, 129.5, 129.5, 129.3, 129.2, 128.9, 128.5, 127.6, 127.5, 124.8, 121.1, 91.3, 89.9 ppm. IR (neat, cm^{-1}): 3062, 1591, 1475, 1405, 1080, 884, 783, 757. HRMS (EI): calcd for $C_{20}H_{12}Cl_2$ $[M]^+$ 322.0316; found 322.0314.



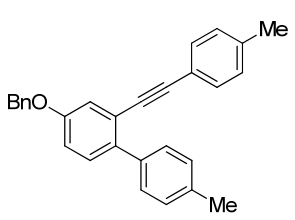
1.16. Pale yellow solid (0.074 g, 61%); mp 104-106 °C, R_f = 0.67 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, 1H, J = 7.32 Hz), 7.57 (d, 2H, J = 8.68 Hz), 7.43-7.32 (m, 5H), 7.29-7.23 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.6, 138.9, 134.3, 133.6, 132.9, 132.5, 130.6, 129.3, 128.8, 128.7, 128.1, 127.4, 121.6, 121.1, 91.4, 89.9 ppm. IR (neat, cm^{-1}): 3056, 2923, 1591, 1489, 1088, 1011, 827, 755. HRMS (ESI): calcd for $C_{20}H_{12}Cl_2$ $[M]^+$ 322.0316; found 322.0312.



1.17. Yellow solid (0.115 g, 73%); mp 74-76 °C, R_f = 0.32 (EtOAc/hexane, 1:19). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, 2H, J = 8.68 Hz), 7.48-7.30 (m, 8H), 7.24 (d, 1H, J = 2.28 Hz), 7.01-6.97 (m, 3H), 6.84 (d, 2H, J = 8.68 Hz), 5.12 (s, 2H), 3.87 (s, 3H), 3.81 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 158.7, 157.3, 136.8, 136.3, 132.8, 130.4, 128.6, 128.0, 127.5, 122.5, 117.9, 115.8, 115.5, 113.9, 113.2, 92.0, 88.2, 70.1, 55.3, 55.2 ppm. IR (neat, cm^{-1}): 3033, 2934, 2206, 1599, 1511, 1248, 1031, 832. HRMS (ESI): calcd for $C_{29}H_{25}O_3$ $[M+H]^+$ 421.1804; found 421.1803.

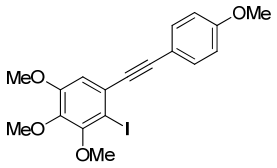


1.18. Yellow solid (0.102 g, 70%); mp 100-102 °C, R_f = 0.67 (EtOAc/hexane, 1:19). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, 2H, J = 8.24 Hz), 7.47-7.30 (m, 6H), 7.26-7.22 (m, 5H), 7.09 (d, 2H, J = 7.8 Hz), 7.00 (dd, 1H, J = 8.26 Hz, 2.74 Hz), 5.11 (s, 2H), 2.40 (s, 3H), 2.33 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5, 138.3, 137.3, 136.8, 136.7, 136.7, 131.3, 130.6, 129.2, 129.0, 128.6, 128.5, 128.0, 127.5, 122.5, 120.3, 118.1, 115.9, 92.1, 88.9, 70.2, 21.5, 21.2 ppm. IR (neat, cm^{-1}): 3029, 2919, 1599, 1489, 1310, 1103, 1029, 814, 737. HRMS



(APCI): calcd for $C_{29}H_{25}O$ $[M+H]^+$ 389.1905; found 389.1904.

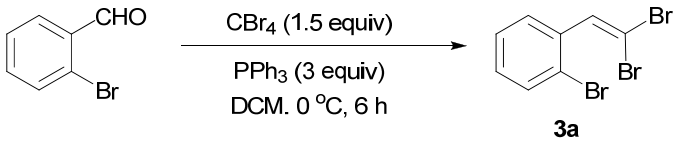
8. Spectral data for *ortho*-alkynylaryl iodide (2.1)



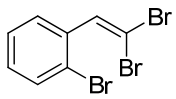
2.1. Colorless solid (0.084 g, 53%); mp 160-162 ^oC, R_f = 0.28 (EtOAc/hexane, 1:19). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, 2H, J = 9.2 Hz), 6.93 (s, 1H), 6.89 (d, 2H, J = 9.2 Hz), 3.89-3.87 (m, 9H), 3.87 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.9, 153.7, 153.6, 142.6, 133.0, 125.2, 115.1, 114.1, 111.6, 92.3, 90.5, 89.4, 61.1, 60.8, 56.2, 55.3 ppm. IR (neat, cm^{-1}): 2999, 2935, 2209, 1605, 1511, 1358, 1249, 1105, 1004, 832. HRMS (ESI): calcd for $C_{18}H_{18}IO_4$ $[M+H]^+$ 425.0250; found 425.0258.

9. Synthesis of *gem*-dibromovinylaryl bromide (3a and 3b)

2-Bromoarylaldehydes were converted to the corresponding *gem*-dibromovinyl substrates following the standard procedure.[2]

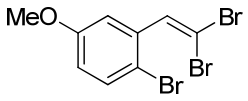


10. Spectral data of *gem*-dibromovinylaryl bromides (3a and 3b)

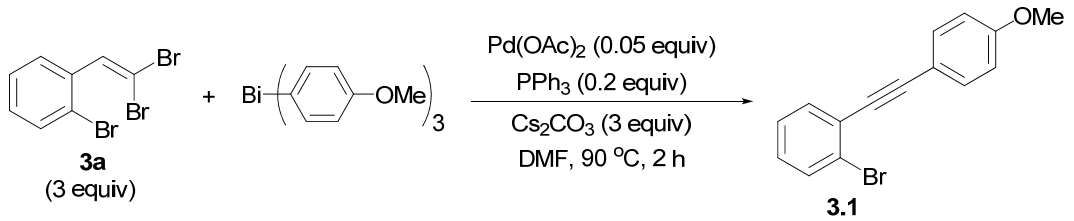


3a.[4] Yellow liquid; R_f = 0.59 (Hexane). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, 2H, J = 8.24 Hz), 7.51 (s, 1H), 7.33 (td, 1H, J = 7.67 Hz, 1.06 Hz), 7.21 (td, 1H, J = 7.78 Hz, 1.51 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.7, 136.1, 132.6, 130.4, 129.9, 127.2, 123.1, 92.9 ppm. IR (neat, cm^{-1}): 3065, 3020, 1922, 1605, 1463, 1026, 881, 790. HRMS (APCI): calcd for $C_8H_5Br_3$ $[M]^+$ 337.7941; found 337.7946.

3b. Pale yellow solid; mp 40-42 °C, R_f = 0.48 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49-7.45 (m, 2H), 7.16 (d, 1H, J = 2.72 Hz), 6.78 (dd, 1H, J = 8.92 Hz, 3 Hz), 3.81 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 136.6, 133.2, 116.0, 115.7, 113.5, 92.9, 55.6 ppm. IR (neat, cm^{-1}): 2961, 2832, 1589, 1462, 1283, 1237, 1018, 869, 807. HRMS (EI): calcd for $C_9H_7Br_3O$ $[M]^+$ 367.8047; found 367.8046.



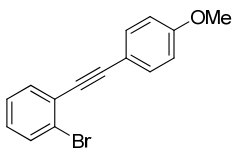
11. Representative cross-coupling procedure for the preparation of compound 3.1



To an oven-dried Schlenk tube, added **3a** (0.128 g, 0.375 mmol, 3 equiv.), Bi(*p*-anisyl)$_3$ (0.067 g, 0.125 mmol, 1 equiv.), $Pd(OAc)_2$ (0.002 g, 0.00625 mmol, 0.05 equiv.), PPh_3 (0.007 mg, 0.025 mmol, 0.20 equiv.) , Cs_2CO_3 (0.122 g, 0.375 mmol, 3 equiv.) in DMF (3 mL) and stirred at 90 °C for 2 h. The reaction mixture was brought to rt and extracted with EtOAc (2 x 20 mL), washed with H_2O (20 mL), brine (10 mL), dried over anhydrous $MgSO_4$ and concentrated. The crude so obtained was purified by silica gel column chromatography using EtOAc/hexane as eluent to obtain **3.1**. This procedure was followed for the preparation of compounds **3.2**-**3.9**. Isolated yields were calculated by considering 0.375 mmol of product as 100% yield.

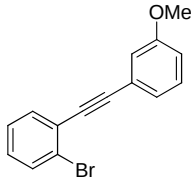
12. Spectral data for *ortho*-alkynylaryl bromide (3.1-3.9)

3.1.[5] Pale brown solid (0.089 g, 83%); mp 76-78 °C, R_f = 0.59 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (dd, 1H, J = 8.24 Hz, 1.36 Hz), 7.55-7.51 (m, 3H), 7.30-7.28 (m, 1H), 7.15 (td, 1H, J = 7.79 Hz, 1.53 Hz), 6.89 (m, 2H), 3.83 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 133.2, 133.0, 132.4, 129.0, 127.0, 125.7, 125.4, 115.0, 114.0, 94.0, 86.8, 55.3 ppm. IR (flim, cm^{-1}): 3015, 2966, 2839, 2218, 1604, 1510, 1291, 1251, 1024, 837, 758. HRMS

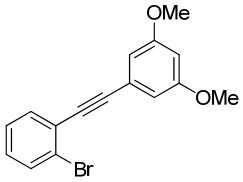


(APCI): calcd for $C_{15}H_{11}BrO$ $[M]^+$ 285.9993; found 285.9995.

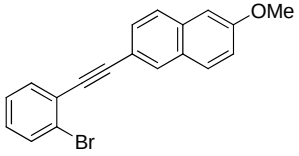
3.2.[6] Yellow liquid (0.068 g, 63%); R_f = 0.30 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, 1H, J = 6.88 Hz), 7.54 (dd, 1H, J = 7.8 Hz, 1.84 Hz), 7.30-7.09 (m, 5H), 6.92-6.89 (m, 1H), 3.82 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.4, 133.2, 132.4, 129.4, 129.4, 127.0, 125.7, 125.3, 124.3, 123.9, 116.4, 115.3, 93.8, 87.8, 55.3 ppm. IR (flim, cm^{-1}): 3065, 2936, 2834, 2211, 1598, 1467, 1283, 1232, 1044, 752, 685. HRMS (ESI): calcd for $C_{15}H_{12}BrO$ $[M+H]^+$ 287.0072; found 287.0078.



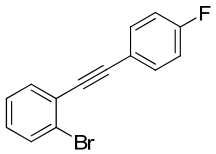
3.3. Pale brown liquid (0.083 g, 70%); R_f = 0.18 (Hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62 (d, 1H, J = 8 Hz), 7.55 (dd, 1H, J = 8.02 Hz, 1.72 Hz), 7.29 (t, 1H, J = 7.45 Hz), 7.18 (td, 1H, J = 7.73 Hz, 1.73 Hz), 6.74 (d, 2H, J = 2.25 Hz), 6.49 (t, 1H, J = 2.3 Hz), 3.81 (s, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.6, 133.3, 132.4, 129.4, 127.0, 125.7, 125.3, 124.2, 109.5, 102.2, 93.9, 87.5, 55.5 ppm. IR (neat, cm^{-1}): 3000, 2936, 2216, 1589, 1420, 1205, 1156, 1064, 753. HRMS (APCI): calcd for $C_{16}H_{13}BrO_2$ $[M]^+$ 316.0099; found 316.0093.



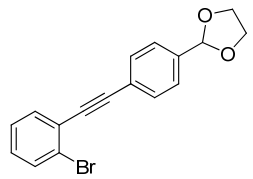
3.4.[6] Brown solid (0.088 g, 70%); 90-94 ^{o}C, R_f = 0.42 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (s, 1H), 7.72 (t, 2H, J = 7.74 Hz), 7.65-7.58 (m, 3H), 7.31 (td, 1H, J = 7.56 Hz, 1.37 Hz), 7.20-7.12 (m, 3H), 3.94 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4, 134.4, 133.2, 132.4, 131.5, 129.4, 129.2, 128.9, 128.4, 127.0, 126.8, 125.6, 119.5, 117.8, 105.8, 94.6, 87.7, 55.3 ppm. IR (neat, cm^{-1}): 3059, 2961, 2839, 2211, 1603, 1465, 1212, 1165, 1027, 853, 752. HRMS (APCI): calcd for $C_{19}H_{14}BrO$ $[M+H]^+$ 337.0228; found 337.0227.



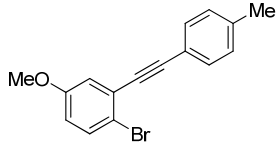
3.5.[7] Pale yellow solid (0.070 g, 68%); mp 56-58 ^{o}C, R_f = 0.54 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61-7.53 (m, 4H), 7.29-7.02 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.7 ($J_{C\text{-}F}$ = 248 Hz), 133.6 ($J_{C\text{-}F}$ = 8.35 Hz), 133.1, 132.4, 129.4, 127.0, 125.6, 125.2, 119.0 ($J_{C\text{-}F}$ = 3.59 Hz), 115.7 ($J_{C\text{-}F}$ = 21.46 Hz), 92.8, 87.7 ppm. IR (neat, cm^{-1}): 3064, 2222, 1601, 1155, 1027, 834, 752. HRMS (APCI): calcd for $C_{14}H_8BrF$ $[M]^+$ 273.9793; found 273.9799.



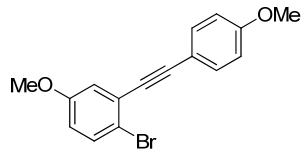
3.6. Yellow liquid (0.081 g, 66%); R_f = 0.33 (EtOAc/hexane, 1:19). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.63-7.59 (m, 3H), 7.56 (dd, 1H, *J* = 7.45 Hz, 1.7 Hz), 7.48 (d, 2H, *J* = 8 Hz), 7.29 (td, 1H, *J* = 7.74 Hz, 1.13 Hz), 7.18 (td, 1H, *J* = 7.73 Hz, 1.72 Hz), 5.84 (s, 1H), 4.14-4.04 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.4, 133.3, 132.5, 131.7, 129.4, 127.0, 126.5, 125.7, 125.3, 123.7, 103.3, 93.6, 88.5, 65.3 ppm. IR (neat, cm^{-1}): 2951, 2884, 2219, 1611, 1512, 1466, 1384, 1218, 1080, 942, 753. HRMS (ESI): calcd for $C_{17}H_{14}BrO_2$ $[M+H]^+$ 329.0177; found 329.0170.



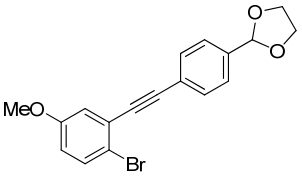
3.7. Yellow liquid (0.079 g, 70%); R_f = 0.68 (EtOAc/hexane, 1:19). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49-7.46 (m, 3H), 7.17 (d, 2H, *J* = 7.8 Hz), 7.08 (d, 1H, *J* = 3.2 Hz), 6.75 (dd, 1H, *J* = 8.92 Hz, 2.96 Hz), 3.81 (s, 3H), 2.38 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4, 138.9, 133.0, 131.6, 129.1, 126.1, 119.7, 117.6, 116.3, 116.2, 93.9, 87.5, 55.5, 21.5 ppm. IR (neat, cm^{-1}): 2935, 2835, 2212, 1587, 1511, 1463, 1229, 1018, 815. HRMS (APCI): calcd for $C_{16}H_{13}BrO$ $[M]^+$ 300.0150; found 300.0159.



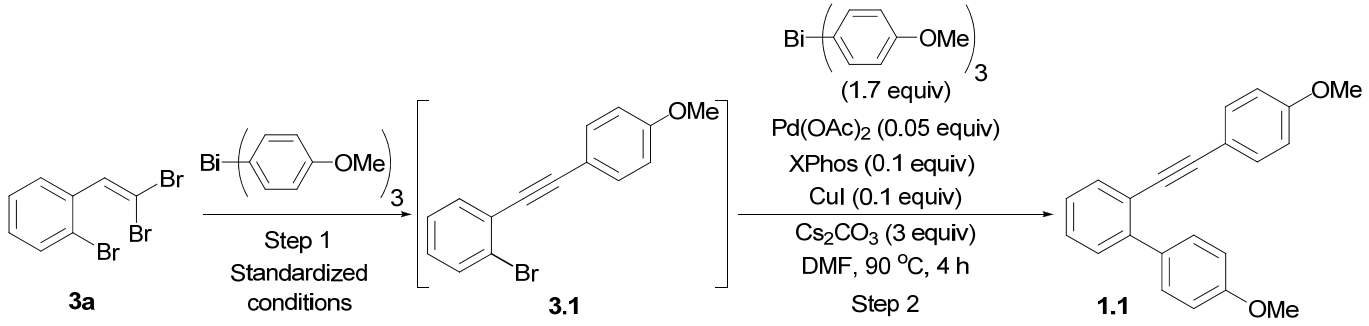
3.8. Yellow liquid (0.089 g, 75%); R_f = 0.44 (EtOAc/hexane, 1:19). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, 2H, *J* = 9.16 Hz), 7.46 (d, 1H, *J* = 8.52 Hz), 7.07 (d, 1H, *J* = 3.04 Hz), 6.89 (d, 2H, *J* = 9.2 Hz), 6.74 (dd, 1H, *J* = 9.16 Hz, 3.04 Hz), 3.83 (s, 3H), 3.80 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 158.4, 133.2, 132.9, 127.7, 126.1, 117.4, 116.1, 114.8, 114.0, 93.8, 86.9, 55.5, 55.3 ppm. IR (flim, cm^{-1}): 3003, 2959, 2835, 2211, 1586, 1511, 1248, 1018, 831. HRMS (ESI): calcd for $C_{16}H_{14}BrO_2$ $[M+H]^+$ 317.0177; found 317.0176.



3.9. Yellow liquid (0.070 g, 52%); R_f = 0.26 (EtOAc/hexane, 1:19). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, 2H, *J* = 8.24 Hz), 7.49-7.46 (m, 3H), 7.08 (d, 1H, *J* = 2.76 Hz), 6.76 (dd, 1H, *J* = 8.94 Hz, 2.98 Hz), 5.83 (s, 1H), 4.14-4.02 (m, 4H), 3.80 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4, 138.4, 133.0, 131.7, 126.5, 125.7, 123.6, 117.7, 116.6, 116.3, 103.2, 93.3, 88.5, 65.3, 55.5 ppm. IR (neat, cm^{-1}): 2960, 2886, 1586, 1464, 1393, 1230, 1081, 1018, 941, 821. HRMS (ESI): calcd for $C_{18}H_{16}BrO_3$ $[M+H]^+$ 359.0283; found 359.0283.

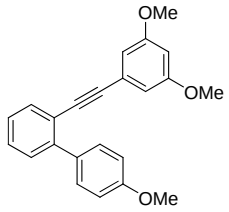


13. Representative cross-coupling procedure for the preparation of 1.1

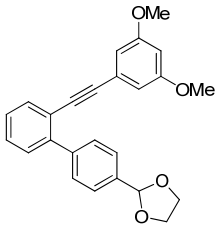


In an oven-dried Schlenk tube, added **3a** (0.128 g, 0.375 mmol, 3 equiv.), Bi(*p*-anisyl)$_3$ (0.067 g, 0.125 mmol, 1 equiv.), Pd(OAc)$_2$ (0.002 g, 0.00625 mmol, 0.05 equiv.), PPh$_3$ (0.007 mg, 0.025 mmol, 0.20 equiv.), Cs$_2$CO$_3$ (0.122 g, 0.375 mmol, 3 equiv.) in DMF (3 mL) and stirred at 90 ^{o}C for 2 h for the completion of Step 1. Then the reaction mixture was brought to rt and was added Bi(*p*-anisyl)$_3$ (0.113 g, 0.212 mmol, 1.7 equiv.), Pd(OAc)$_2$ (0.002 g, 0.00625 mmol, 0.05 equiv.), XPhos (0.006 g, 0.0125 mmol, 0.1 equiv.), Cs$_2$CO$_3$ (0.122 g, 0.375 mmol, 3 equiv.), CuI (0.003 g, 0.0125 mmol, 0.1 equiv.), DMF (3 mL) under nitrogen atmosphere. This combined mixture was stirred at 90 ^{o}C for 4 h. After completion, product mixture was extracted with EtOAc (2 x 25 mL), washed with H$_2$O (20 mL), brine (10 mL), dried over anhydrous MgSO$_4$ and concentrated. The crude was purified by silica gel column chromatography to obtain **1.1**. This procedure was followed for the preparation of different *ortho*-alkynylbiaryls (**1.2**, **1.13-1.14** and **4.1-4.2**). Isolated yields were calculated by considering 0.375 mmol of product as 100% yield.

14. Spectral data of *ortho*-alkynylbiaryls (4.1 and 4.2)

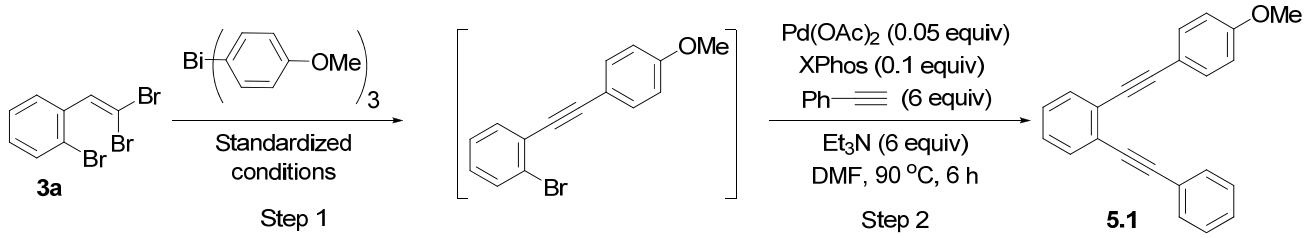


4.1. Yellow liquid (0.072 g, 56%); R_f = 0.35 (EtOAc/hexane, 1:19). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63-7.60 (m, 3H), 7.42-7.36 (m, 2H), 7.32-7.28 (m, 1H), 6.99 (d, 2H, J = 8.72 Hz), 6.51 (d, 2H, J = 2.28 Hz), 6.42 (t, 1H, J = 2.28 Hz), 3.86 (s, 3H), 3.77 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.4, 159.1, 143.6, 133.0, 132.8, 130.5, 129.3, 128.6, 126.6, 124.7, 121.2, 113.3, 109.0, 101.6, 92.1, 89.2, 55.4, 55.3 ppm. IR (neat, cm^{-1}): 2935, 2837, 1586, 1515, 1296, 1245, 1035, 830, 758. HRMS (ESI): calcd for $C_{23}H_{21}O_3$ $[M+H]^+$ 345.1491; found 345.1498.



4.2. Yellow gel (0.072 g, 50%); R_f = 0.25 (EtOAc/hexane, 1:19). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, 2H, J = 8.24 Hz), 7.64 (d, 1H, J = 7.32 Hz), 7.57 (d, 2H, J = 8.24 Hz), 7.41-7.32 (m, 3H), 6.48 (d, 2H, J = 2.28 Hz), 6.41 (t, 1H, J = 2.28 Hz), 5.87 (s, 1H), 4.17-4.04 (m, 4H), 3.76 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.4, 143.5, 141.4, 137.0, 132.7, 129.5, 128.6, 127.2, 126.0, 124.6, 121.4, 108.9, 103.6, 101.9, 92.4, 88.9, 65.3, 55.4 ppm. IR (neat, cm^{-1}): 2960, 2838, 1701, 1588, 1454, 1206, 1156, 1063, 832, 760. HRMS (ESI): calcd for $C_{25}H_{23}O_4$ $[M+H]^+$ 387.1596; found 387.1591.

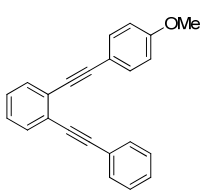
15. Representative procedure for the preparation of compound 5.1



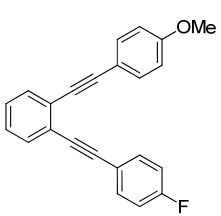
To an oven-dried Schlenk tube was added **3a** (0.128 g, 0.375 mmol, 3 equiv.), Bi(*p*-anisyl)$_3$ (0.067 g, 0.125 mmol, 1 equiv.), $Pd(OAc)_2$ (0.002 g, 0.00625 mmol, 0.05 equiv.), PPh_3 (0.007 g, 0.025 mmol, 0.2 equiv.), Cs_2CO_3 (0.122 g, 0.375 mmol, 3 equiv.) DMF (3 mL) and stirred at 90 ^oC for 2 h. After the Step 1, the reaction mixture was cooled to rt and added Et_3N (0.076 g, 0.75 mmol, 6 equiv.), phenyl acetylene (0.077 g, 0.75 mmol, 6 equiv.), $Pd(OAc)_2$ (0.002 g, 0.00625 mmol, 0.05 equiv.), XPhos (0.006 g, 0.0125 mmol, 0.1 equiv.), DMF (3 mL) under nitrogen atmosphere conditions for Step 2 and the combined mixture was stirred at 90 ^oC for 6 h. The product mixture worked up as given above.

16. Spectral data of 5.1-5.3

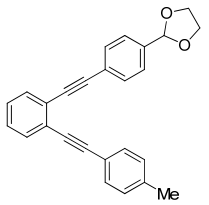
5.1.[8] Brown liquid (0.070 g, 61%); R_f = 0.32 (Hexane). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.59-7.50 (m, 6H), 7.36-7.28 (m, 5H), 6.87 (d, 2H, J = 9.16 Hz), 3.83 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 133.1, 131.7, 131.6, 131.5, 128.3, 128.0, 127.6, 126.1, 125.5, 123.3, 115.4, 114.0, 93.7, 93.4, 88.4, 87.0, 55.3 ppm. IR (neat, cm^{-1}): 3057, 2933, 2836, 2213, 1605, 1510, 1249, 1029, 831, 755. HRMS (APCI): calcd for $C_{23}H_{17}O$ $[M+H]^+$ 309.1279; found 309.1273.



5.2.[9] Brown liquid (0.083 g, 68%); R_f = 0.36 (Hexane). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.56-7.52 (m, 4H), 7.49 (d, 2H, J = 9.16 Hz), 7.31-7.28 (m, 2H), 7.04 (t, 2H, J = 8.70 Hz), 6.88 (d, 2H, J = 8.68 Hz), 3.84 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6 (d, J = 247.89 Hz), 159.8, 133.5 (d, J = 8.58 Hz), 131.7, 131.6, 128.0, 127.7, 126.2, 125.4, 119.5, 119.4, 115.7 (d, J = 21.93 Hz), 115.3, 114.0, 93.7, 92.3, 88.1, 87.0, 55.3 ppm. IR (neat, cm^{-1}): 3058, 2837, 2213, 1605, 1510, 1288, 1249, 1031, 832, 756. HRMS (ESI): calcd for $C_{23}H_{16}FO$ $[M+H]^+$ 327.1185; found 327.1183.

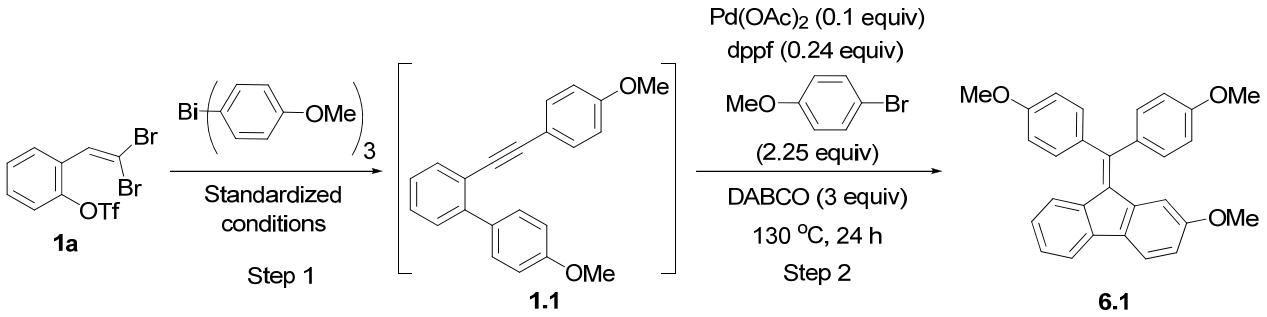


5.3. Brown liquid (0.060 g, 44%); R_f = 0.22 (EtOAc/hexane, 1:19). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.60-7.54 (m, 4H), 7.46 (d, 4H, J = 8.72 Hz), 7.31-7.29 (m, 2H), 7.16 (d, 2H, J = 7.8 Hz), 5.83 (s, 1H), 4.16-4.03 (m, 4H), 2.38 (s, 3H) ppm. ^{13}C



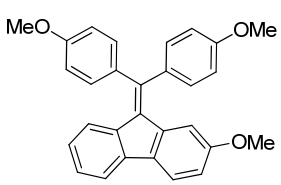
NMR (100 MHz, $CDCl_3$): δ = 138.6, 137.9, 131.8, 131.6, 131.5, 129.2, 128.1, 127.8, 126.5, 126.1, 125.5, 124.2, 120.1, 103.3, 93.9, 93.2, 88.9, 87.6, 65.3, 21.5 ppm. IR (neat, cm^{-1}): 2953, 2885, 2213, 1718, 1616, 1511, 1218, 1080, 1019, 816, 757. HRMS (ESI): calcd for $C_{26}H_{21}O_2$ $[M+H]^+$ 365.1542; found 365.1544.

17. Representative procedure for the preparation of compound 6.1



To an oven-dried Schlenk tube, added with *gem*-dibromophenyl triflate **1a** (0.154 g, 0.375 mmol, 1.5 equiv.), Bi(*p*-anisyl)$_3$ (0.133 g, 0.25 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (0.018 g, 0.025 mmol, 0.1 equiv.), Cs_2CO_3 (0.49 g, 1.5 mmol, 6 equiv.), TBAB (0.403 g, 1.25 mmol, 5 equiv.), NMP (5 mL) and stirred at 90 ^oC for 4 h. After completion of Step 1, added 4-bromoanisole (0.105 g, 0.562 mmol, 2.25 equiv.), $Pd(OAc)_2$ (0.0056 g, 0.025 mmol, 0.1 equiv.), dppf (0.033 g, 0.06 mmol, 0.24 equiv.), DABCO (0.084 g, 0.75 mmol, 3 equiv.) and stirred at 130 ^oC for 24 h for Step 2. Workup was done as described above to isolate the product.

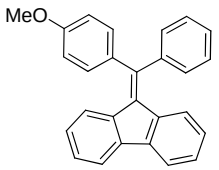
18. Spectral data of products (6.1-6.3)



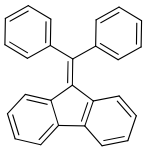
6.1. Yellow solid (0.075 g, 48% (OTf), 0.085 g, 54% (I)); mp 166-168 ^oC, R_f = 0.31 (EtOAc/hexane, 1:19). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.61-7.57 (m, 2H), 7.31-7.28 (m, 4H), 7.19 (td, 1H, J = 7.56 Hz, 0.92 Hz), 6.94 (t, 4H, 8.48 Hz), 6.91-6.87 (m, 1H), 6.82-6.77 (m, 2H), 6.34 (d, 1H, J = 2.76 Hz), 3.88 (s, 3H), 3.85 (s, 3H), 3.50 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 159.8, 158.5, 145.5, 140.6, 140.3, 138.8, 135.4, 135.3, 133.5, 133.4,

131.8, 127.2, 125.1, 124.4, 119.8, 118.4, 114.3, 114.1, 114.0, 109.3, 55.4, 55.3, 54.9 ppm. IR (flim, cm^{-1}): 3002, 2954, 2835, 1603, 1507, 1246, 1172, 1031, 830. HRMS (ESI): calcd for $C_{29}H_{25}O_3$ $[M+H]^+$ 421.1804; found 421.1808.

6.2.[10] Yellow solid (0.063 g, 47%); mp 180-182 °C, R_f = 0.23 (Hexane). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.72-7.69 (m, 2H), 7.42-7.35 (m, 4H), 7.30 (d, 2H, J = 9.16 Hz), 7.27-7.21 (m, 3H), 6.99-6.90 (m, 4H), 6.83 (d, 1H, J = 7.8 Hz), 6.61 (d, 1H, J = 8.24 Hz), 3.88 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 145.5, 143.2, 140.3, 138.9, 135.3, 133.8, 131.5, 130.0, 128.7, 128.2, 127.4, 127.3, 126.3, 126.2, 124.8, 124.7, 119.2, 114.1, 55.3 ppm. IR (neat, cm^{-1}): 3015, 2961, 2836, 1602, 1506, 1288, 1248, 1030, 785, 734. HRMS (APCI): calcd for $C_{27}H_{21}O$ $[M+H]^+$ 361.1592; found 361.1599.



6.3.[11] Colorless solid (0.036 g, 29% (OTf), 0.056 g, 45% (I)); mp 228-230 °C. R_f = 0.40 (Hexane). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, 2H, J = 7.32 Hz), 7.43-7.36 (m, 9H), 7.25-7.21 (m, 3H), 6.92 (t, 2H, J = 7.56 Hz), 6.62 (d, 2H, J = 7.32 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.5, 143.0, 140.5, 138.7, 134.2, 129.7, 128.8, 128.2, 127.6, 126.4, 124.9, 119.2 ppm. IR (neat, cm^{-1}): 3054, 1593, 1487, 1445, 734, 702. HRMS (APCI): calcd for $C_{26}H_{18}$ $[M]^+$ 330.1409; found 330.1400.



19. References

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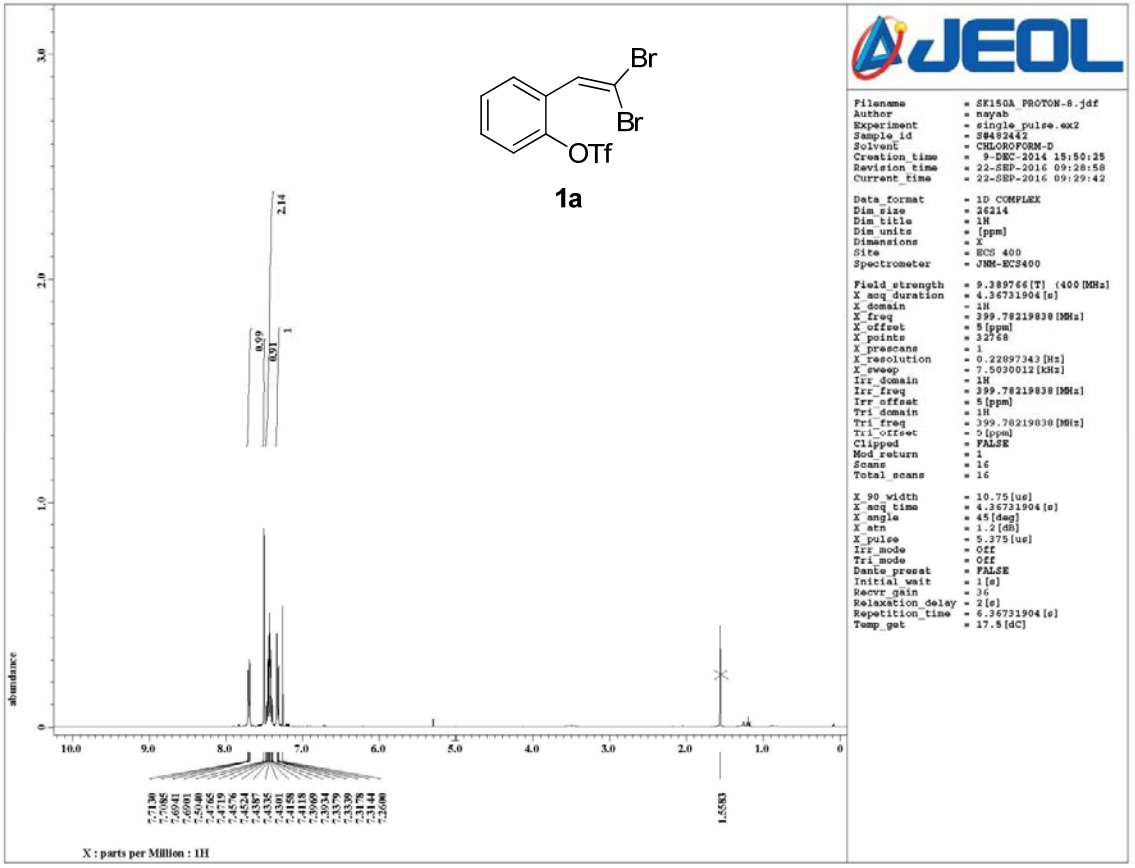
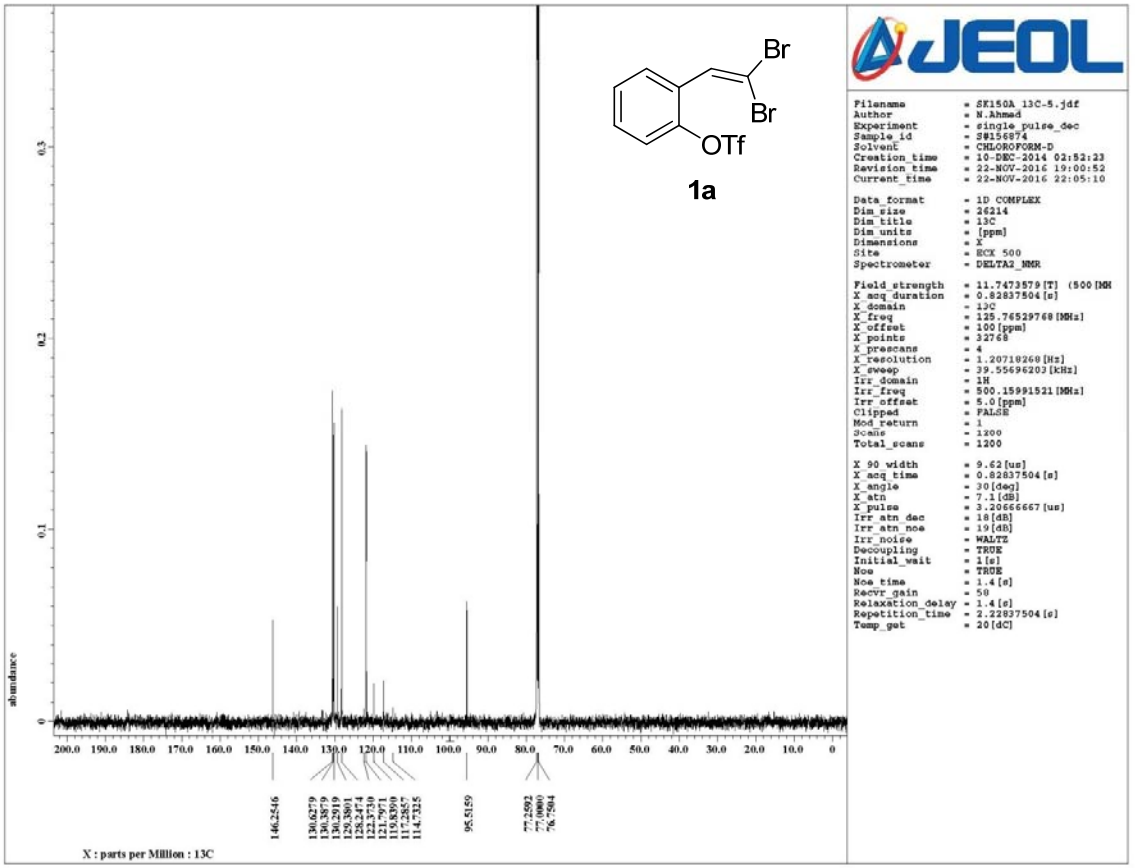
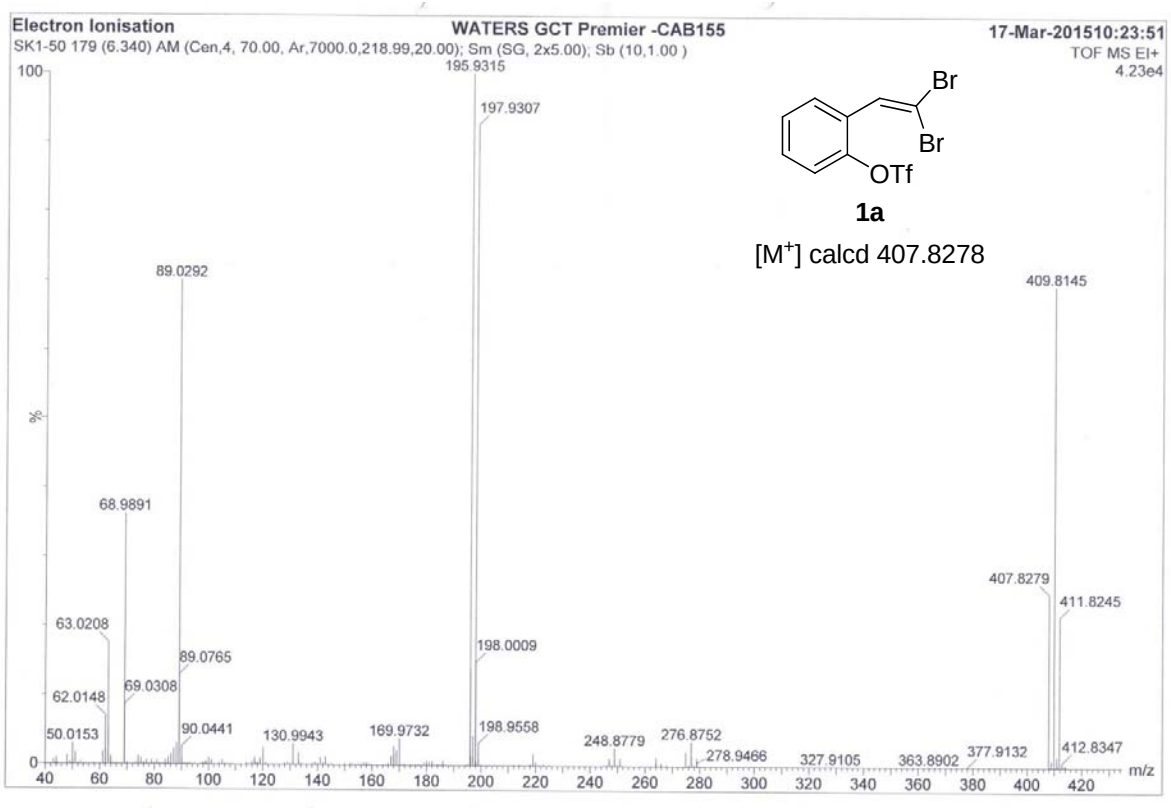
20. ^{1}H, ^{13}C and HRMS spectra



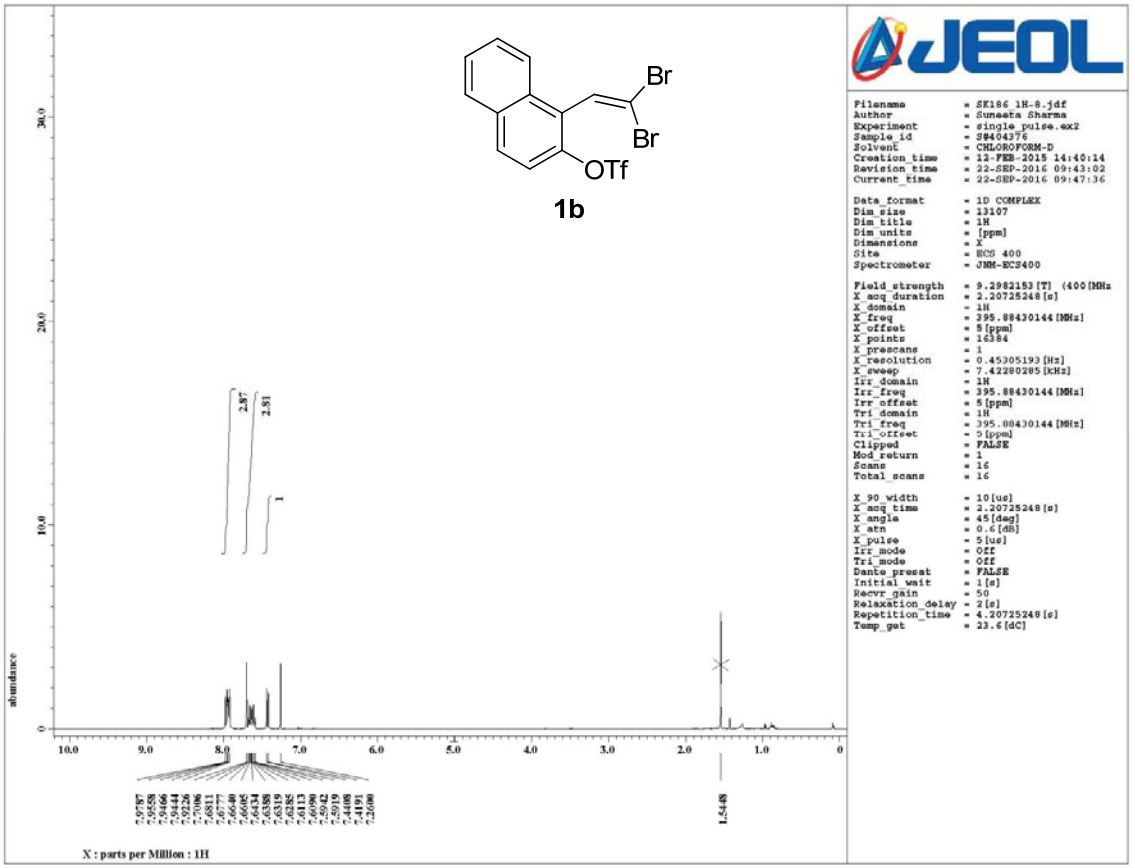
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1a**



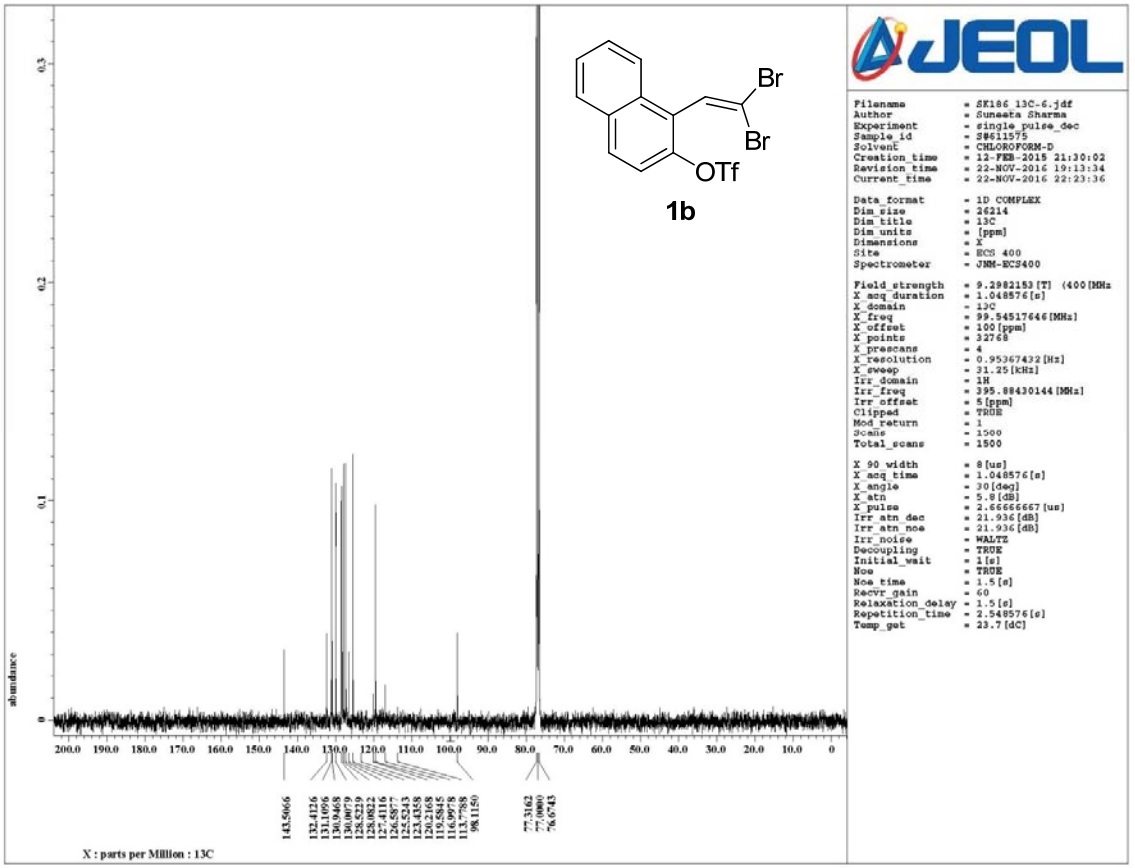
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **1a**



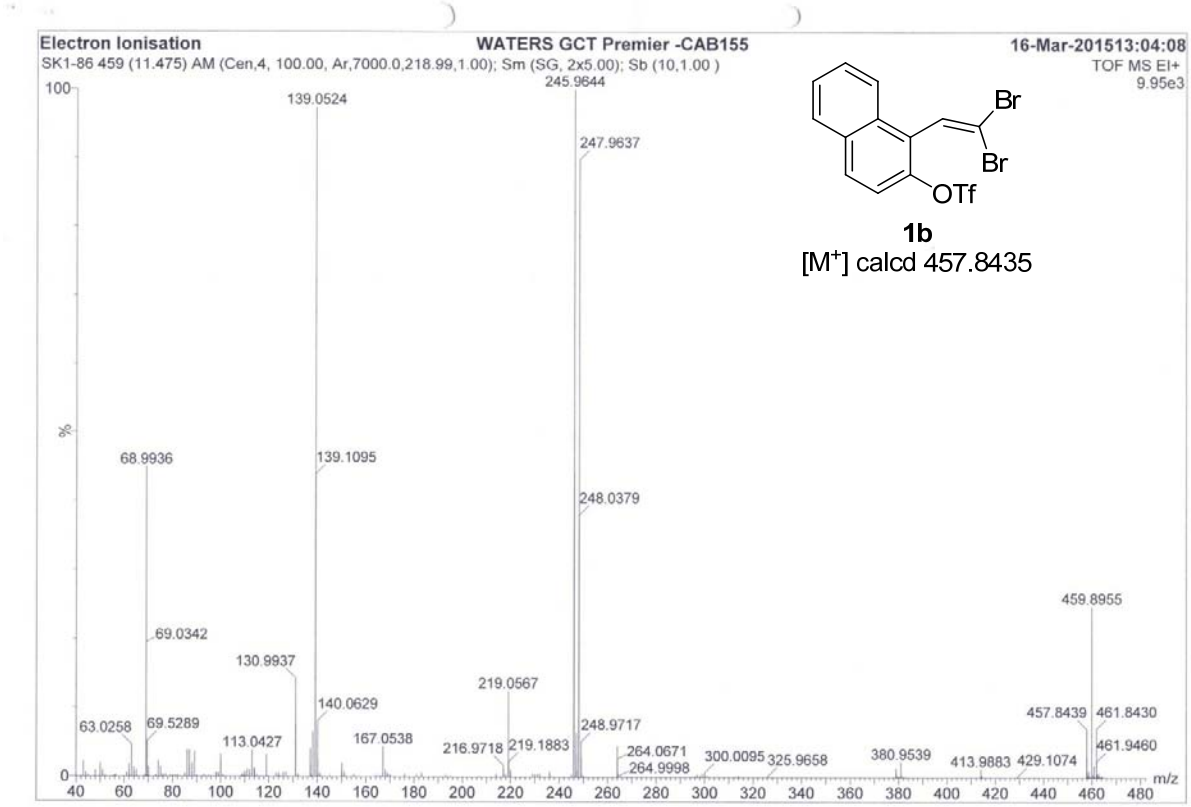
EI (HRMS) spectrum of **1a**



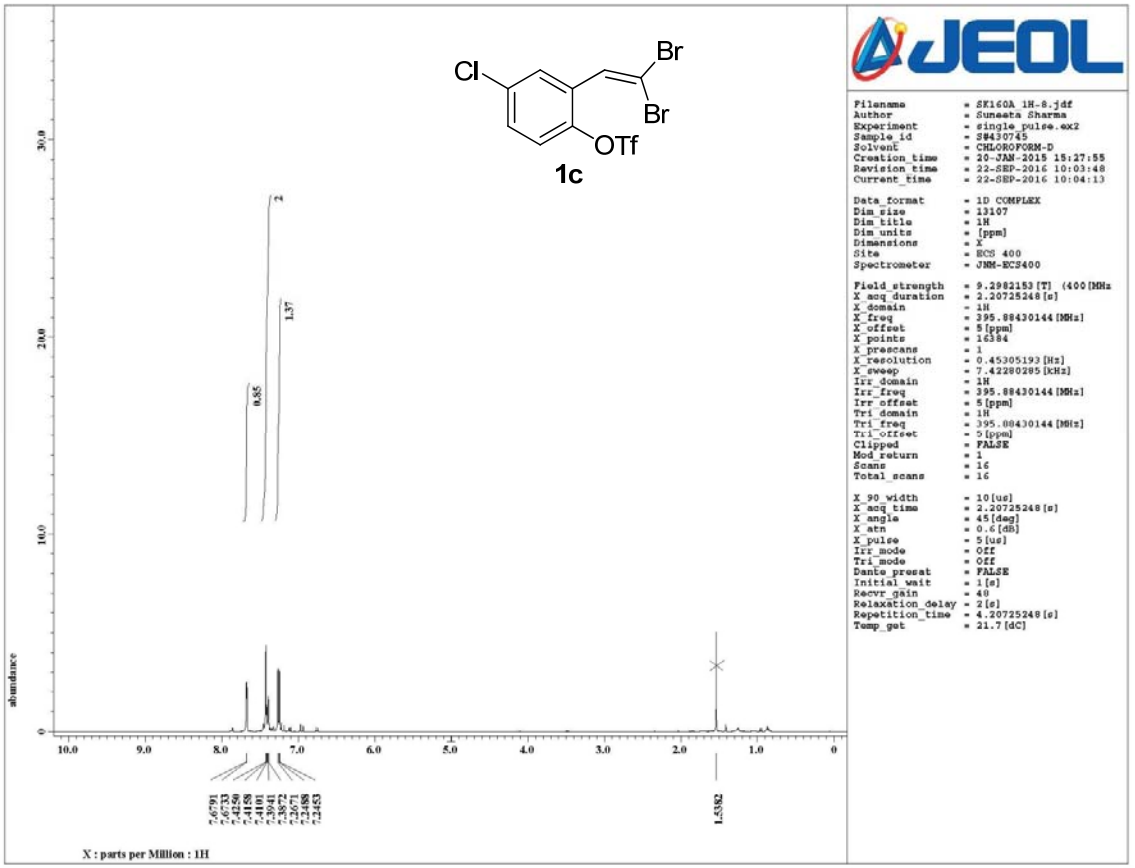
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1b**



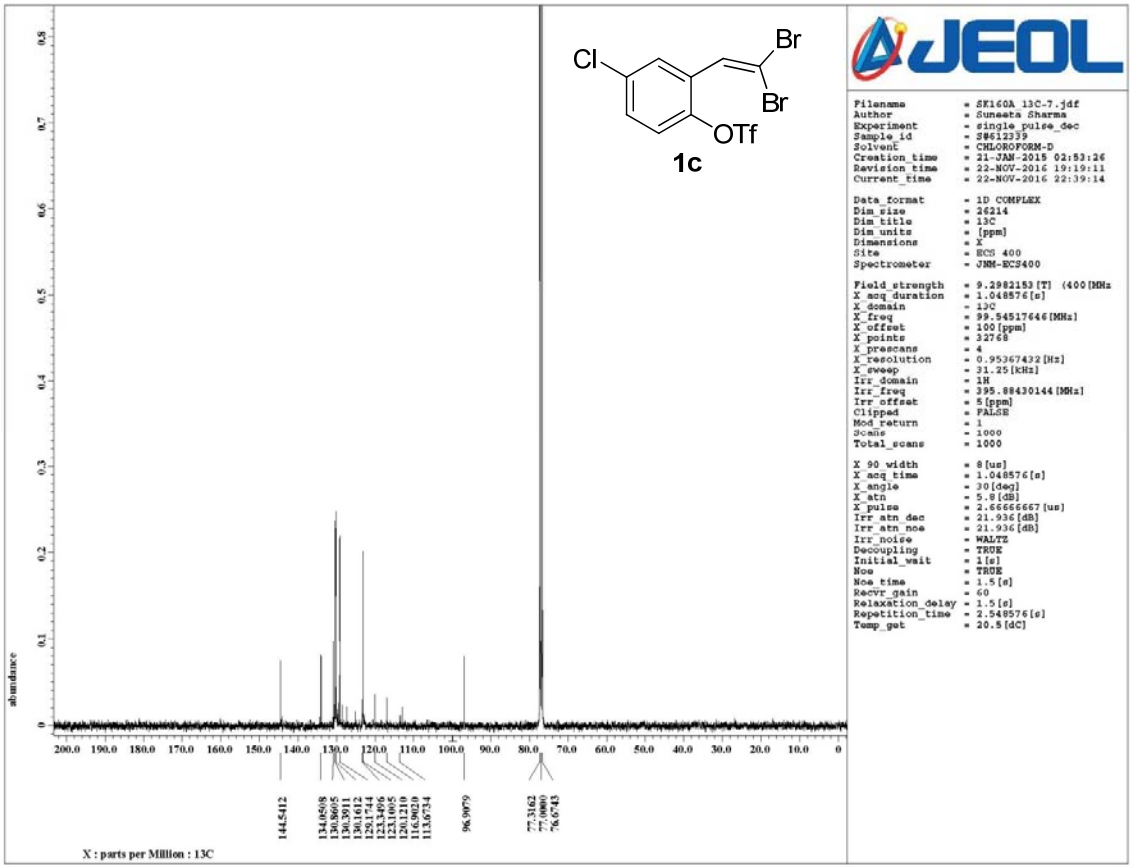
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1b**



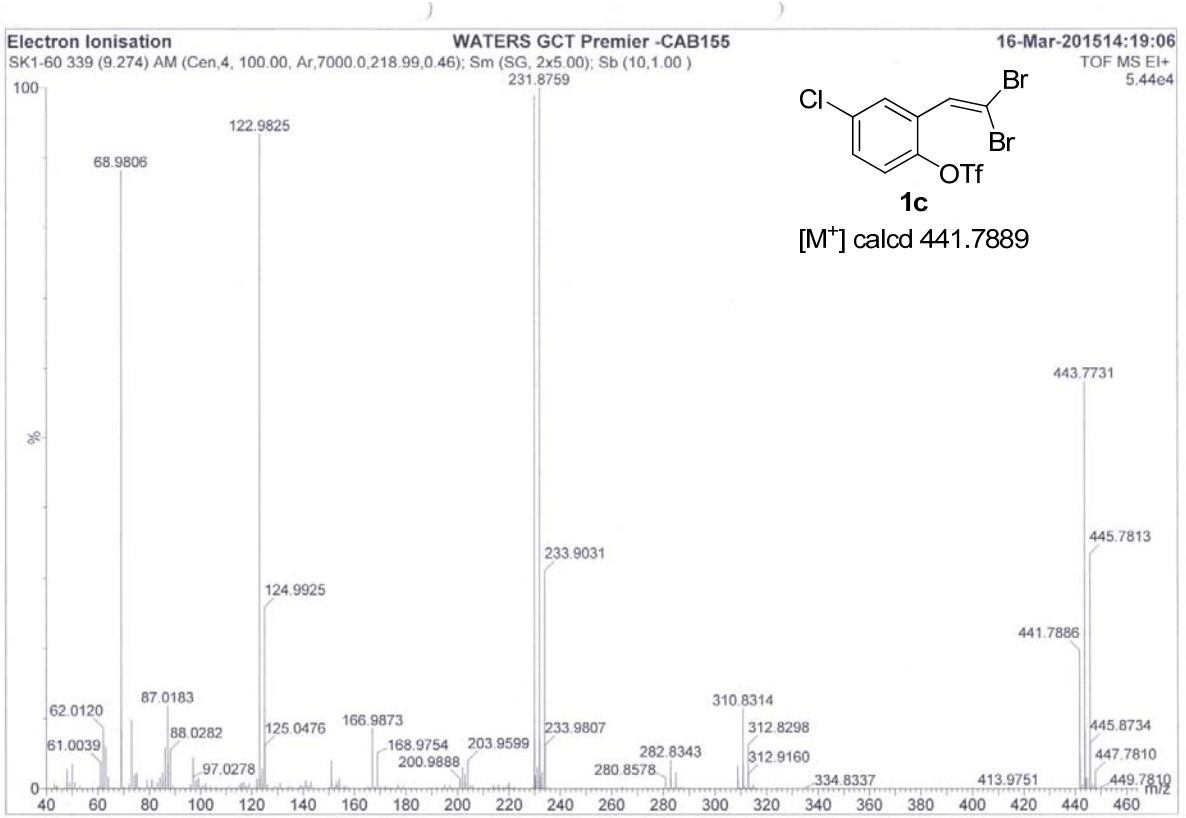
EI (HRMS) spectrum of **1b**



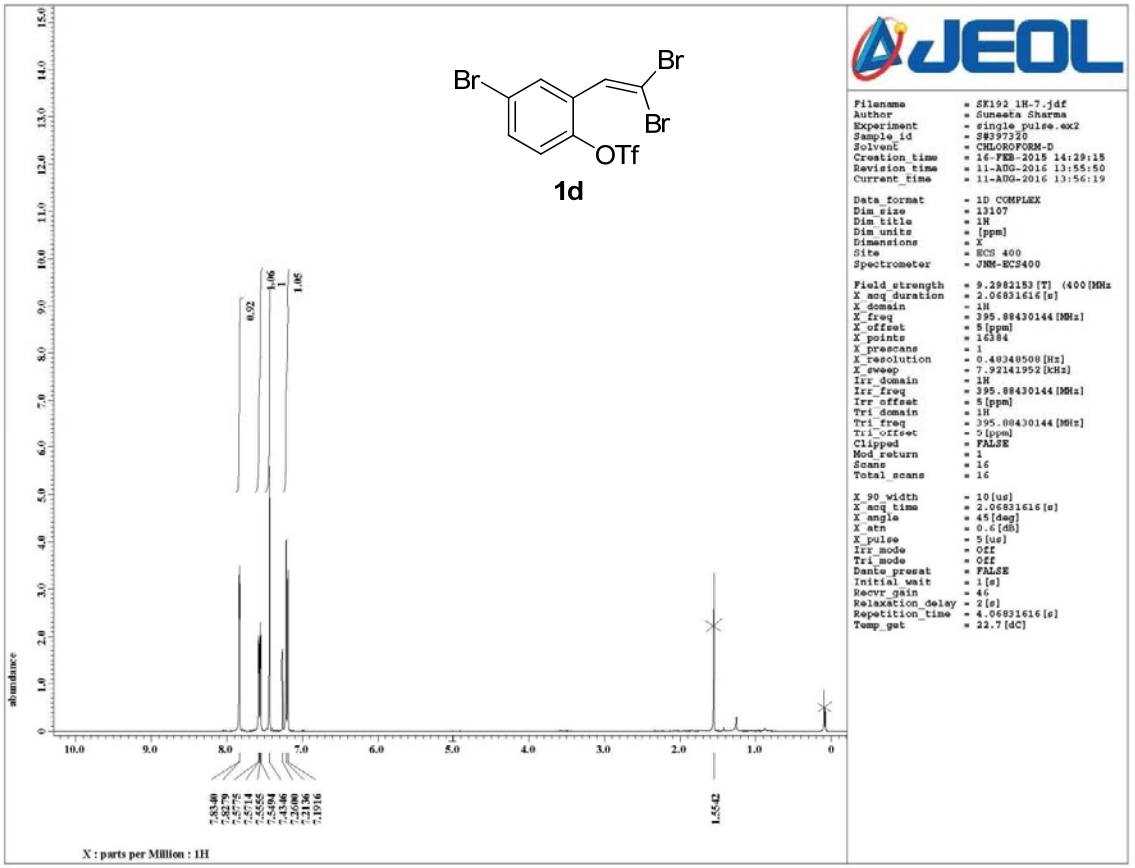
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1c**



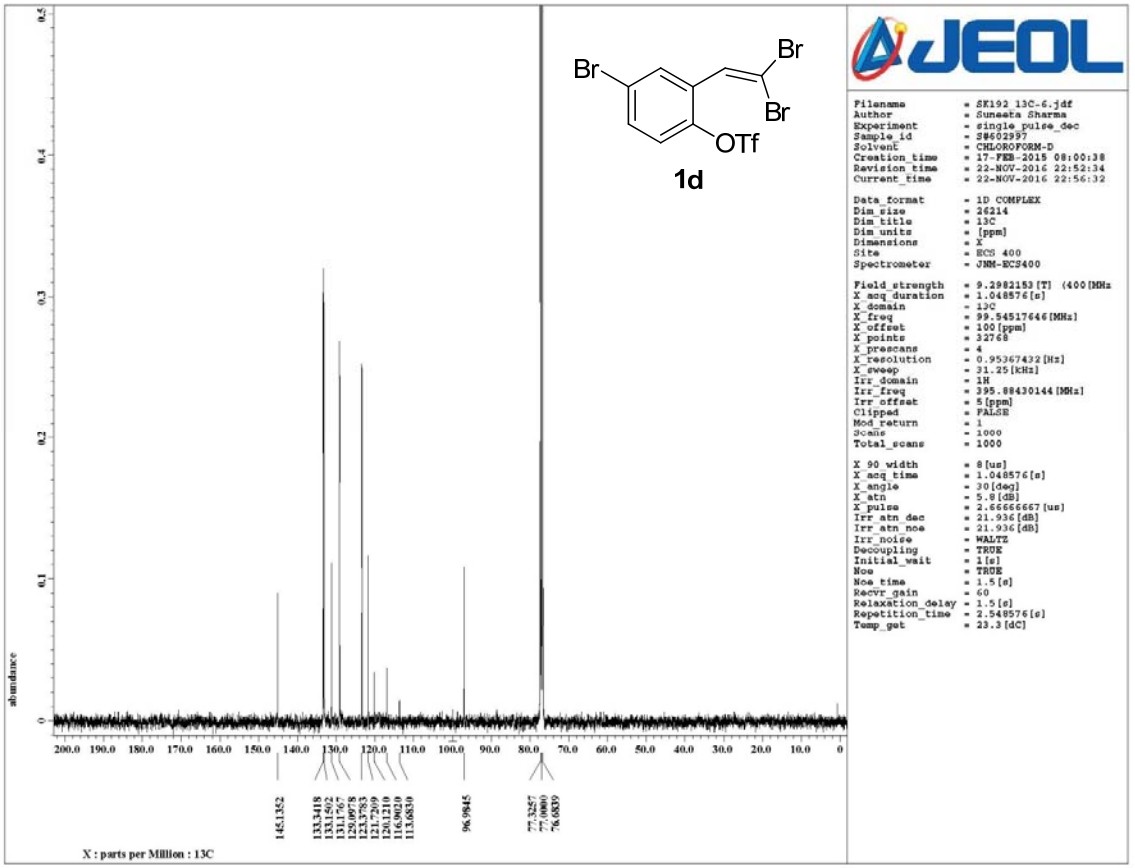
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1c**



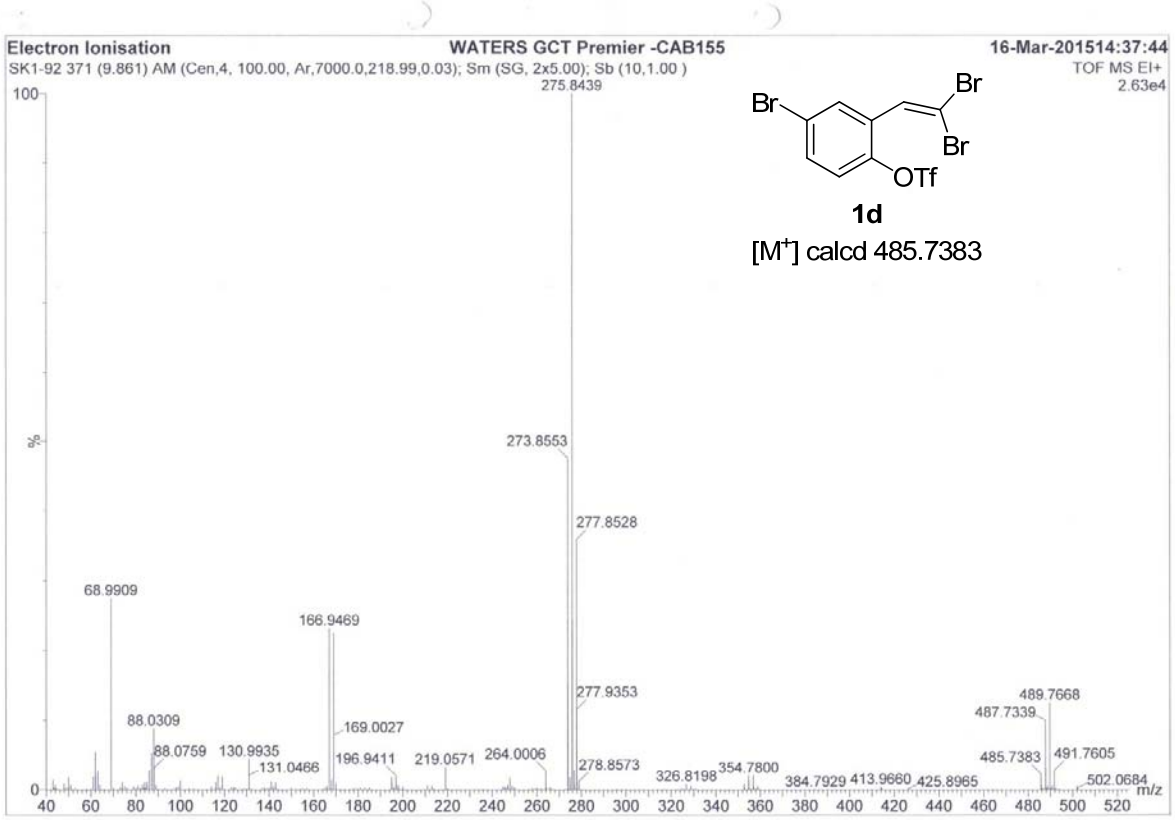
EI (HRMS) spectrum of **1c**



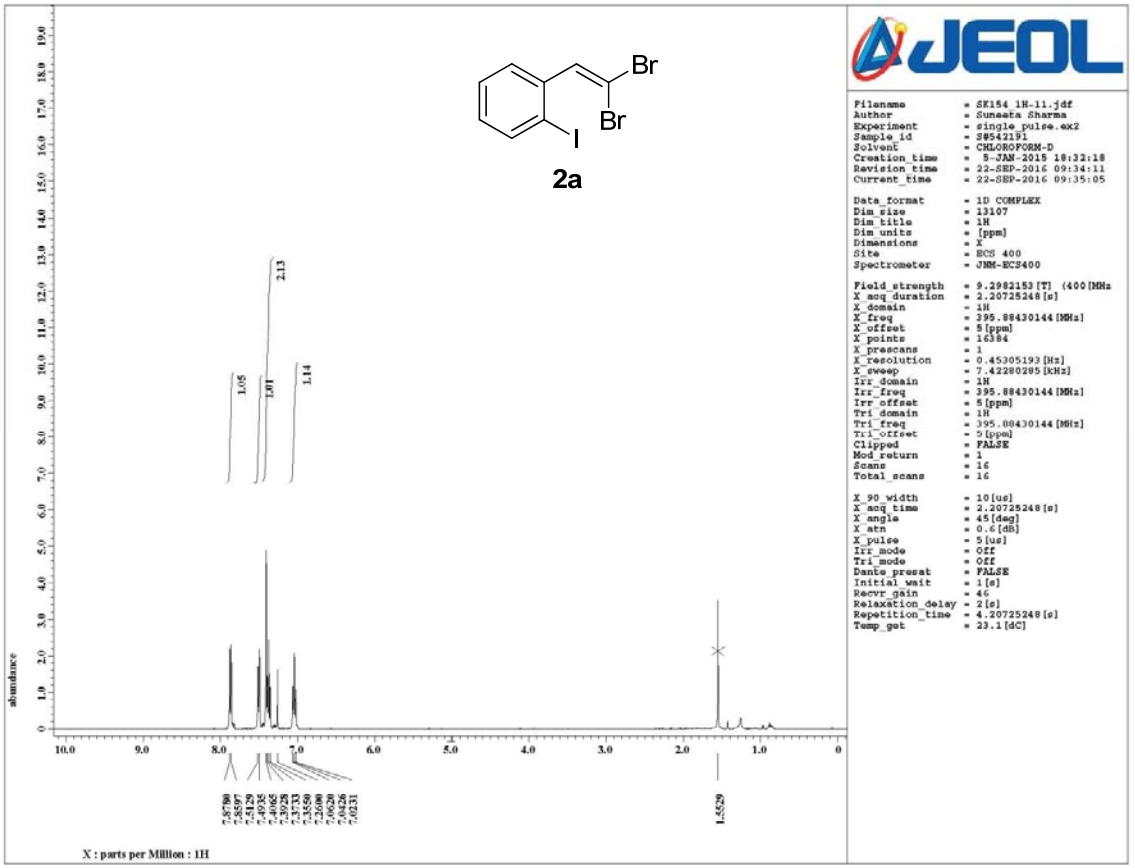
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1d**



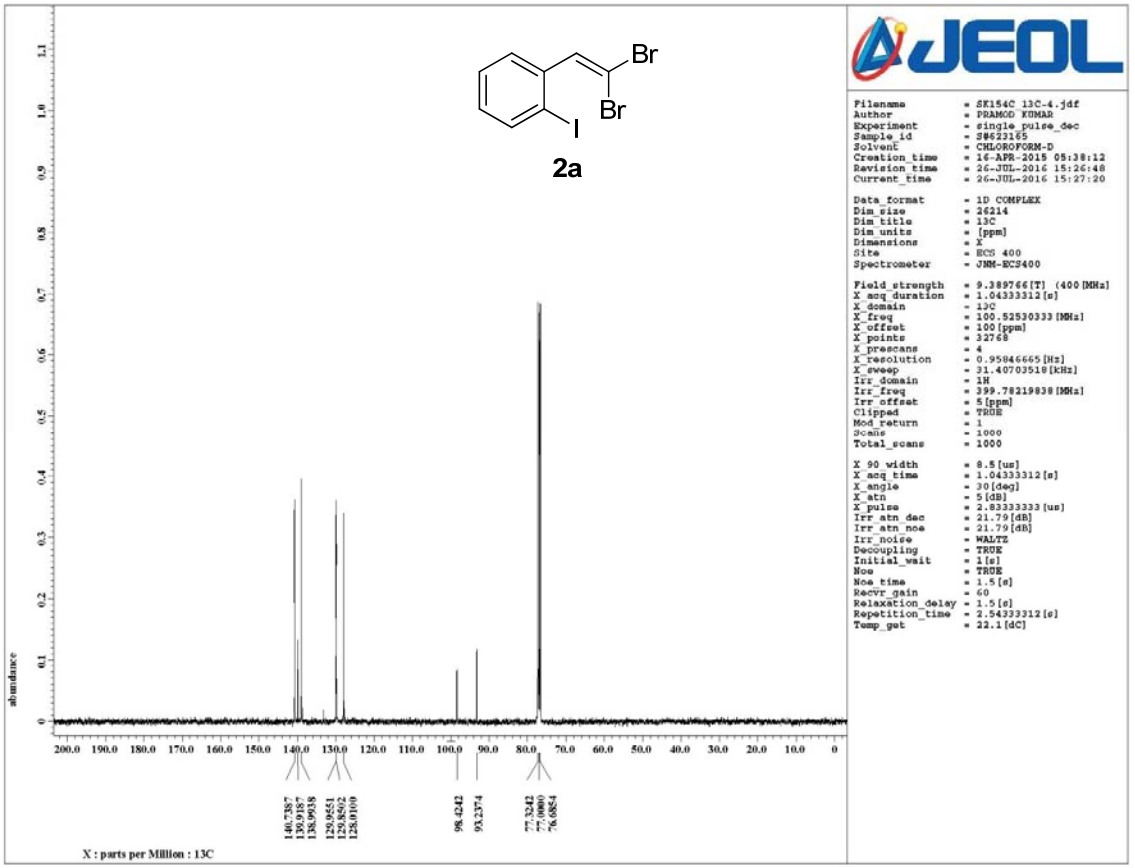
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1d**



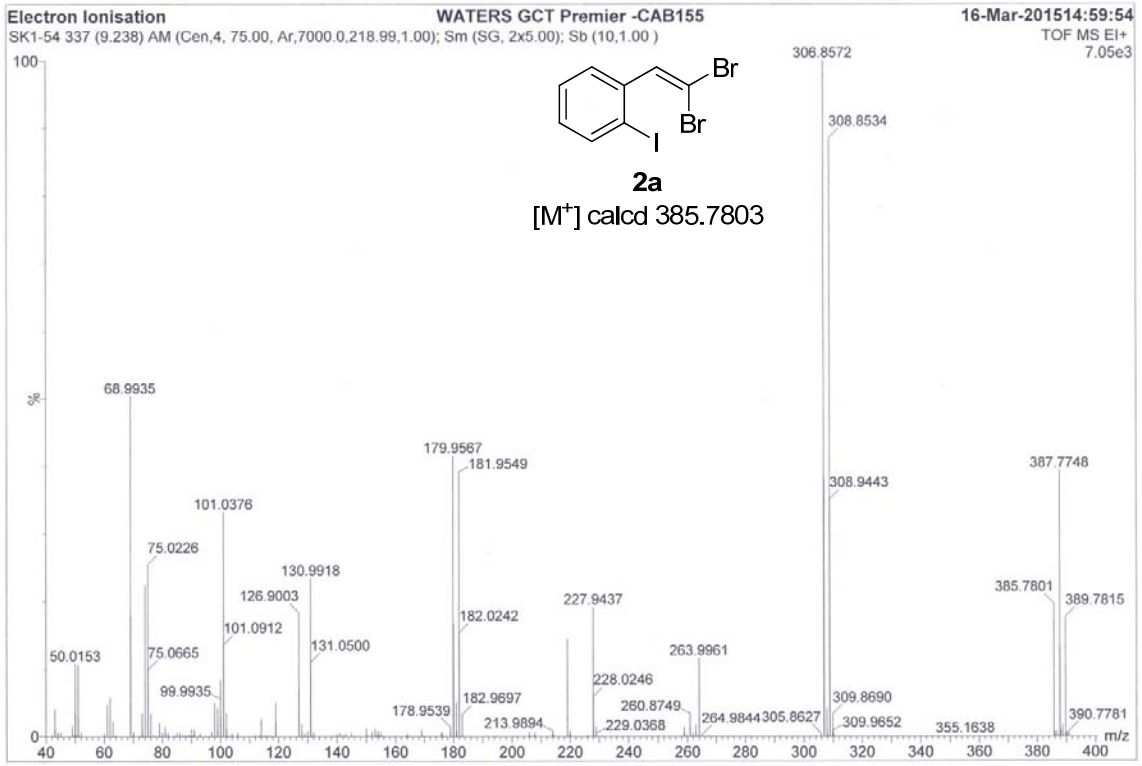
EI (HRMS) spectrum of **1d**



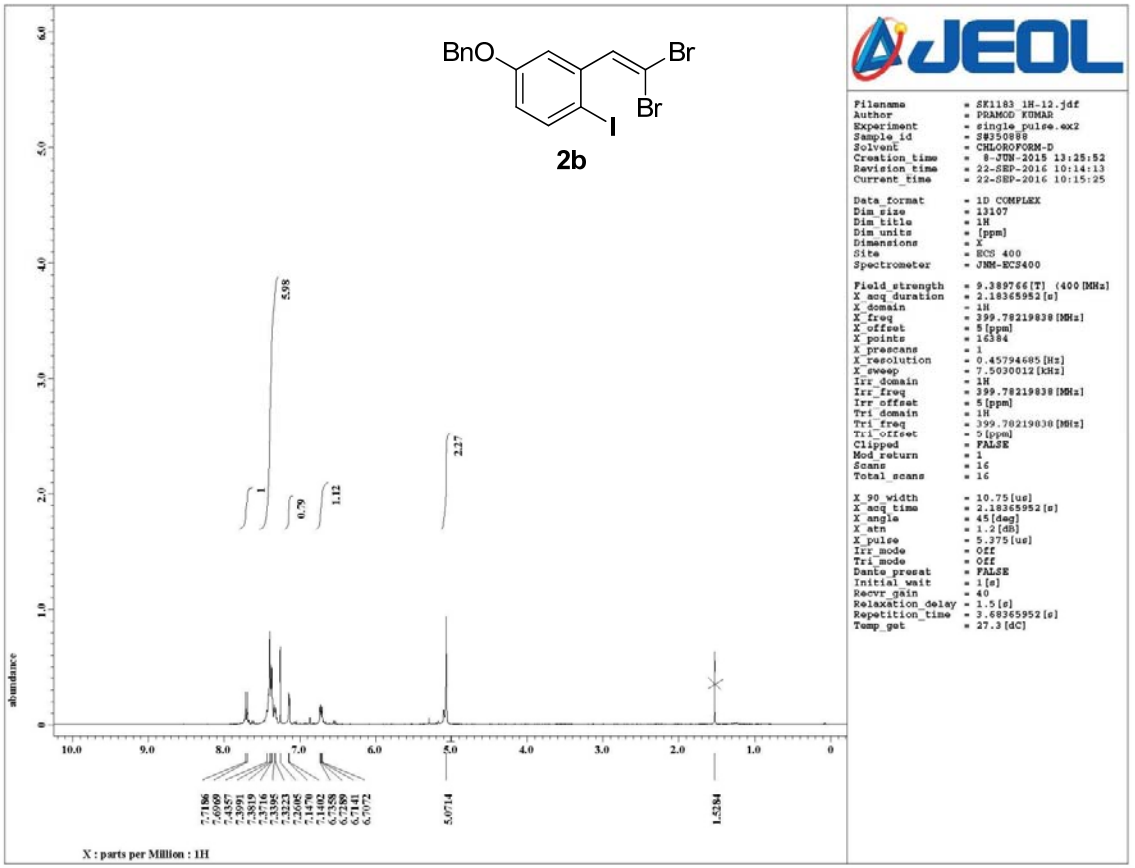
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2a**



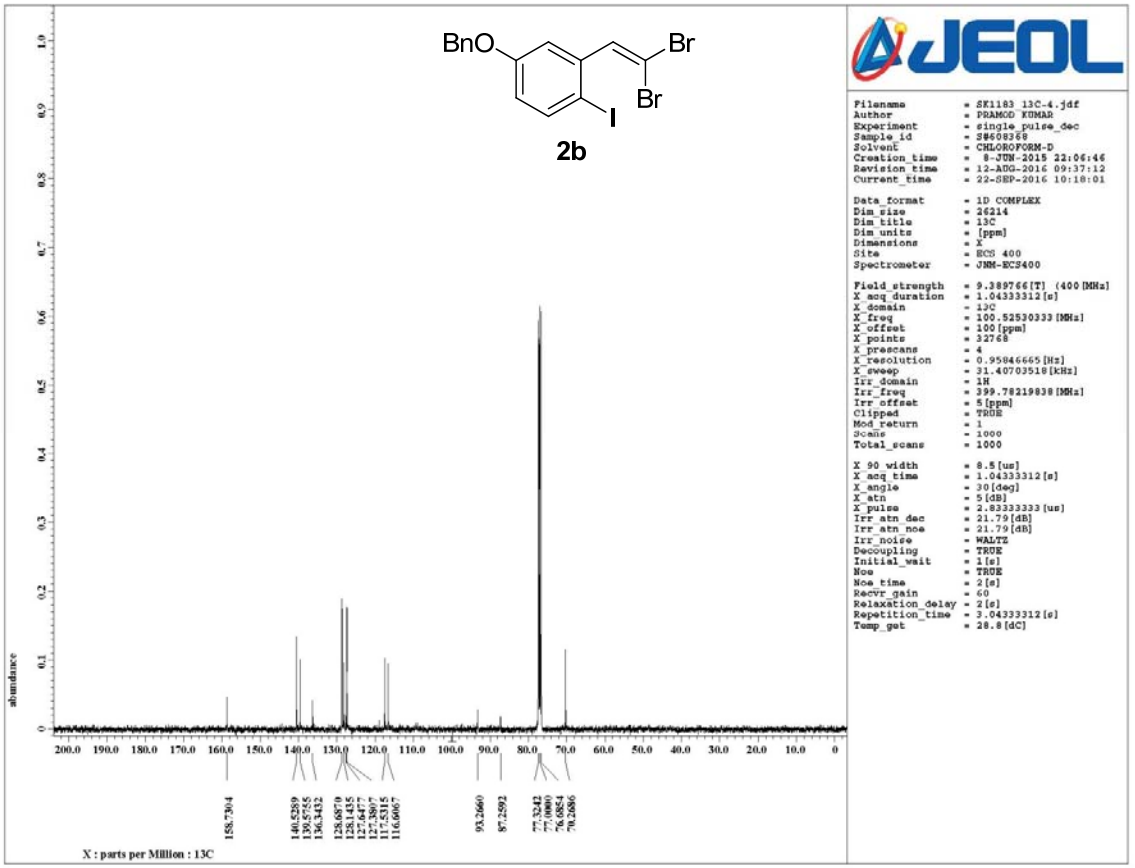
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2a**



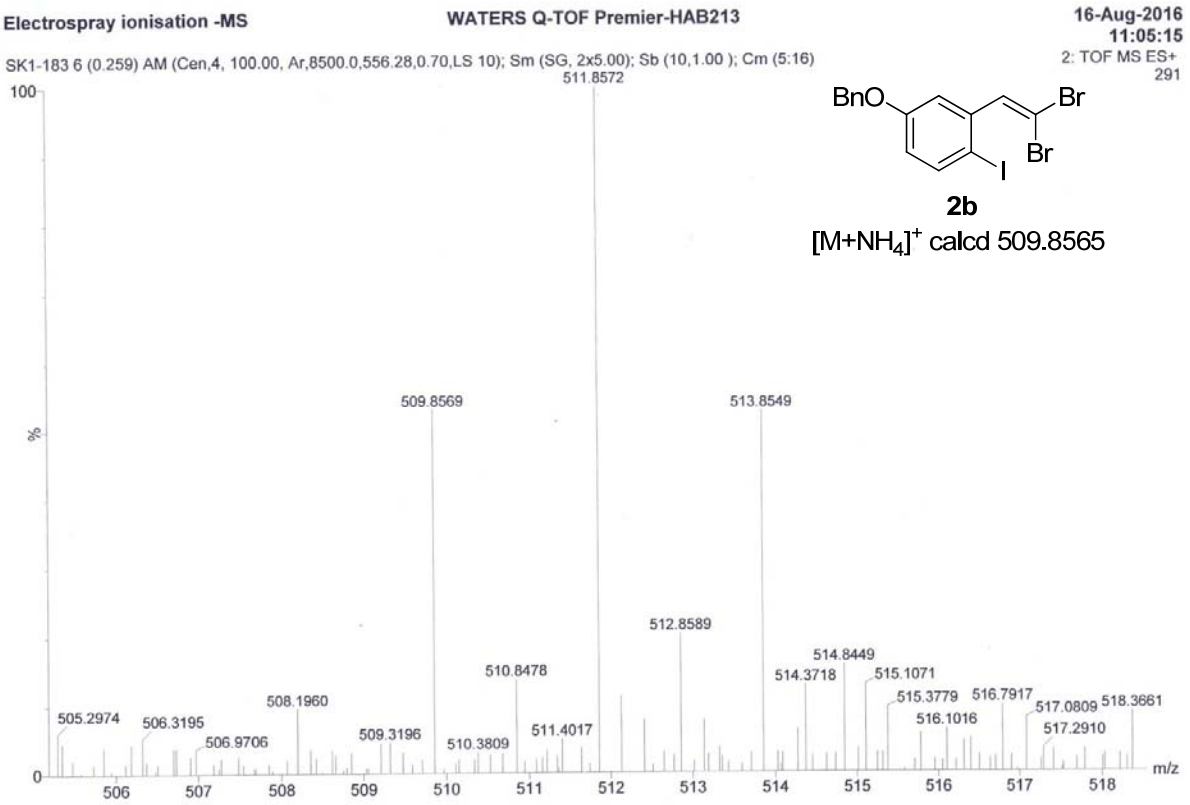
EI (HRMS) spectrum of **2a**



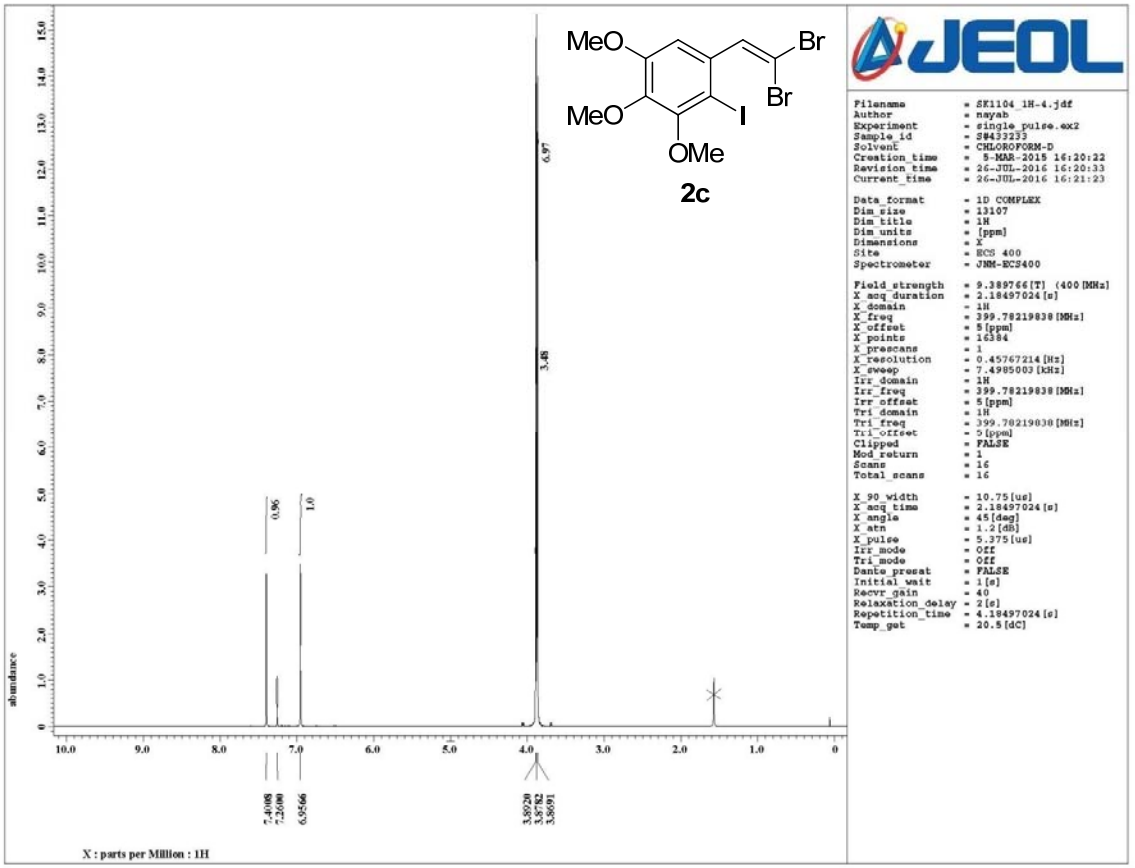
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2b**



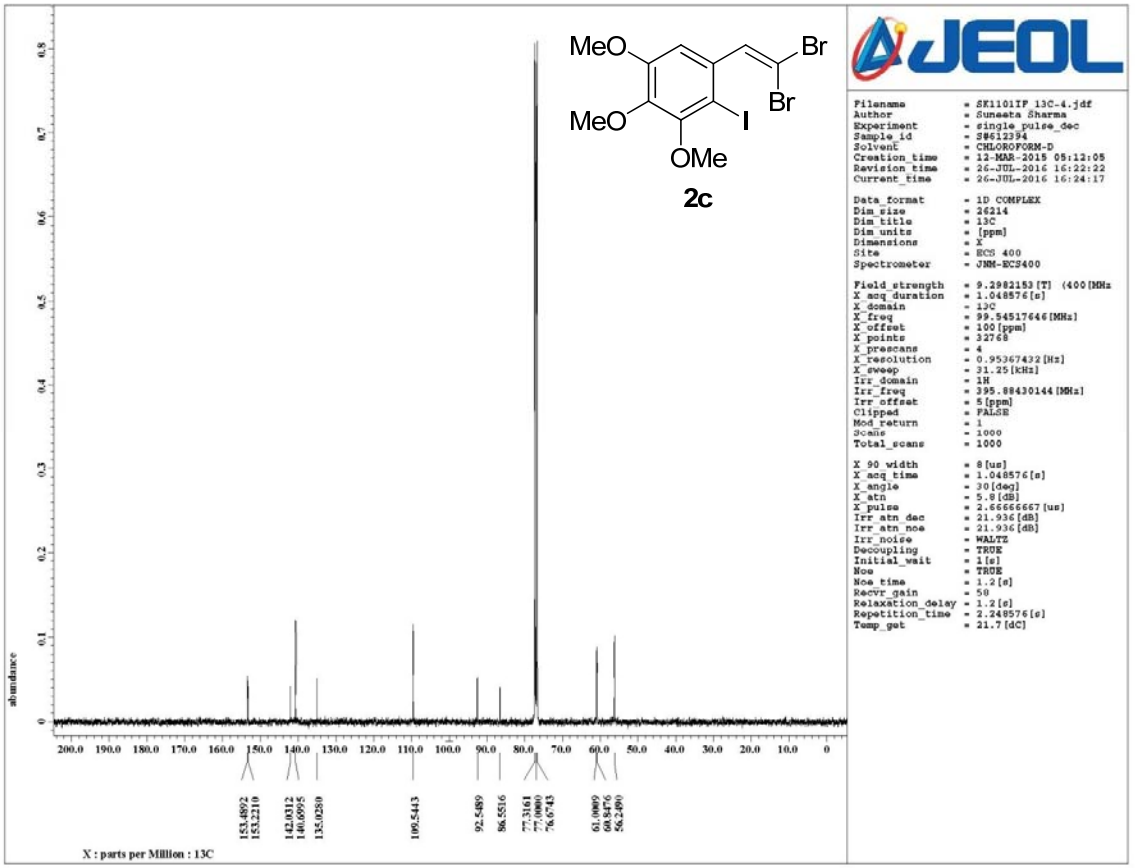
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2b**



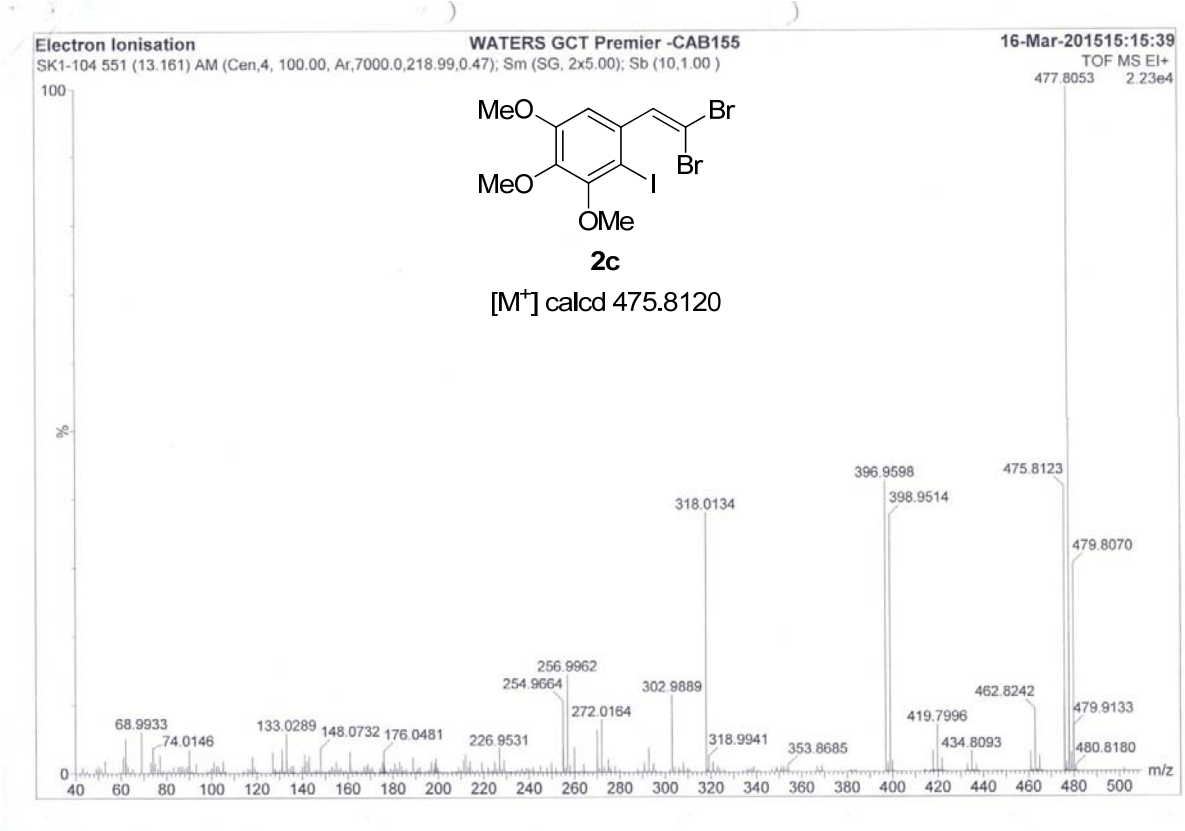
ESI (HRMS) spectrum of **2b**



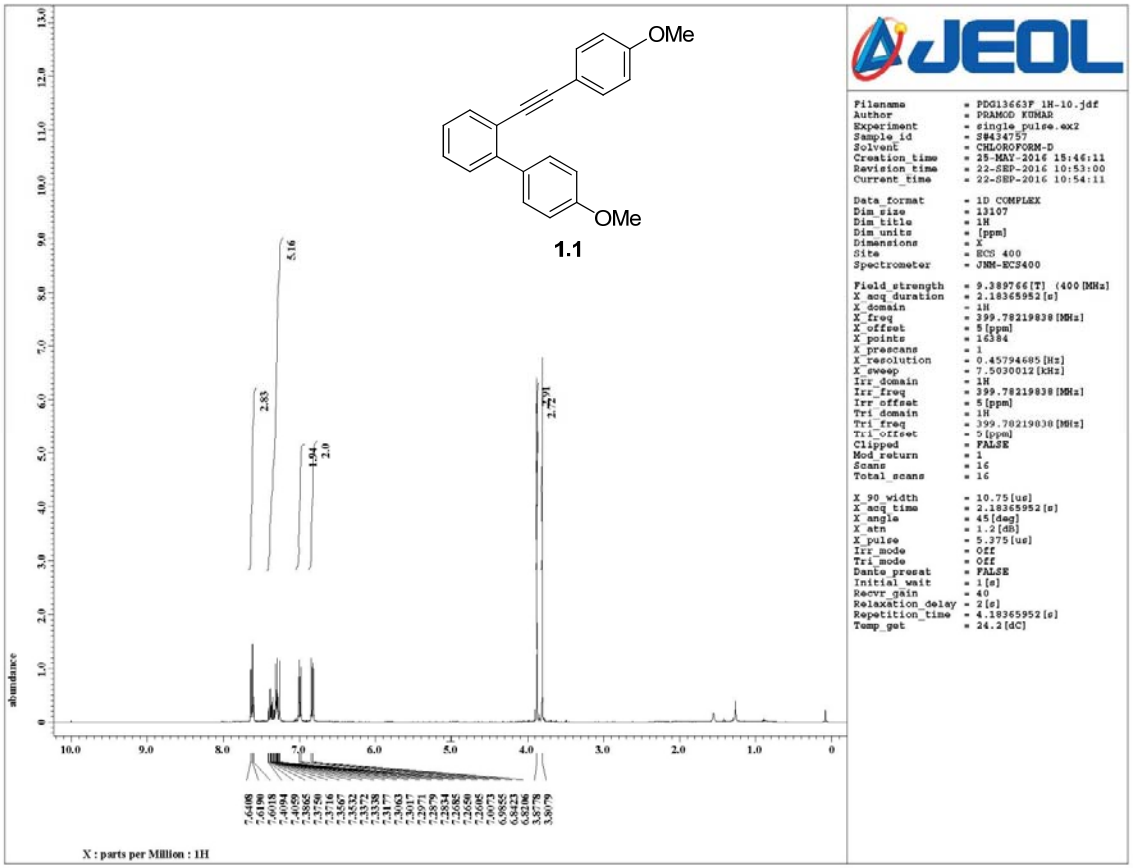
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2c**



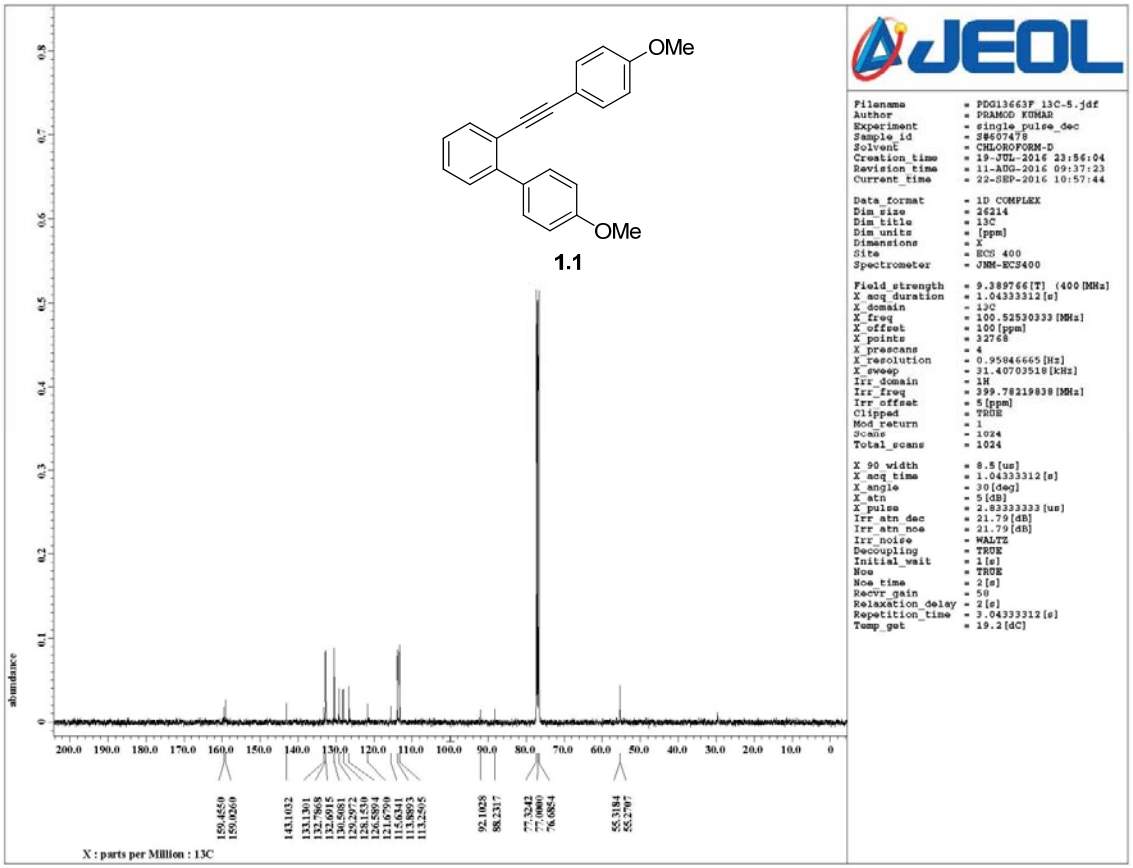
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2c**



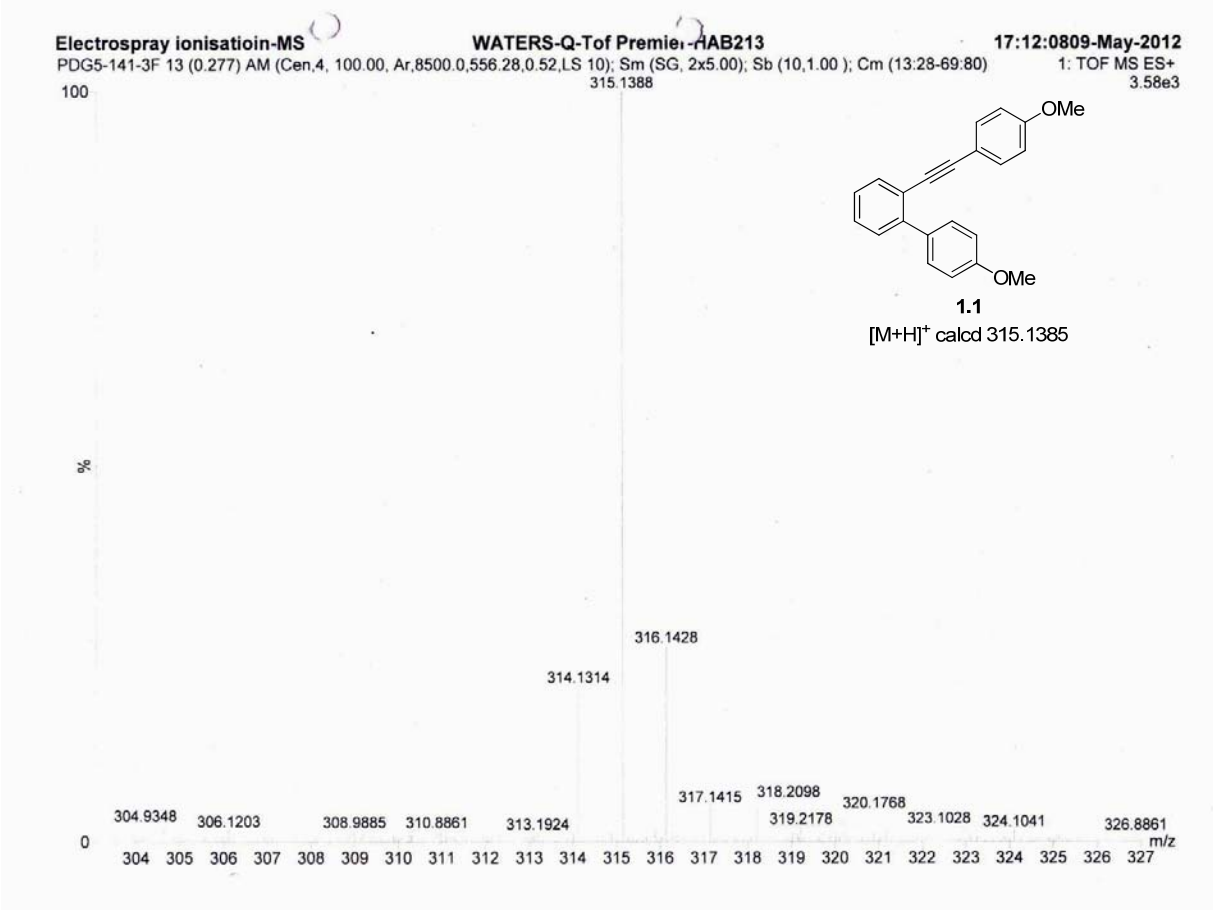
EI (HRMS) spectrum of **2c**



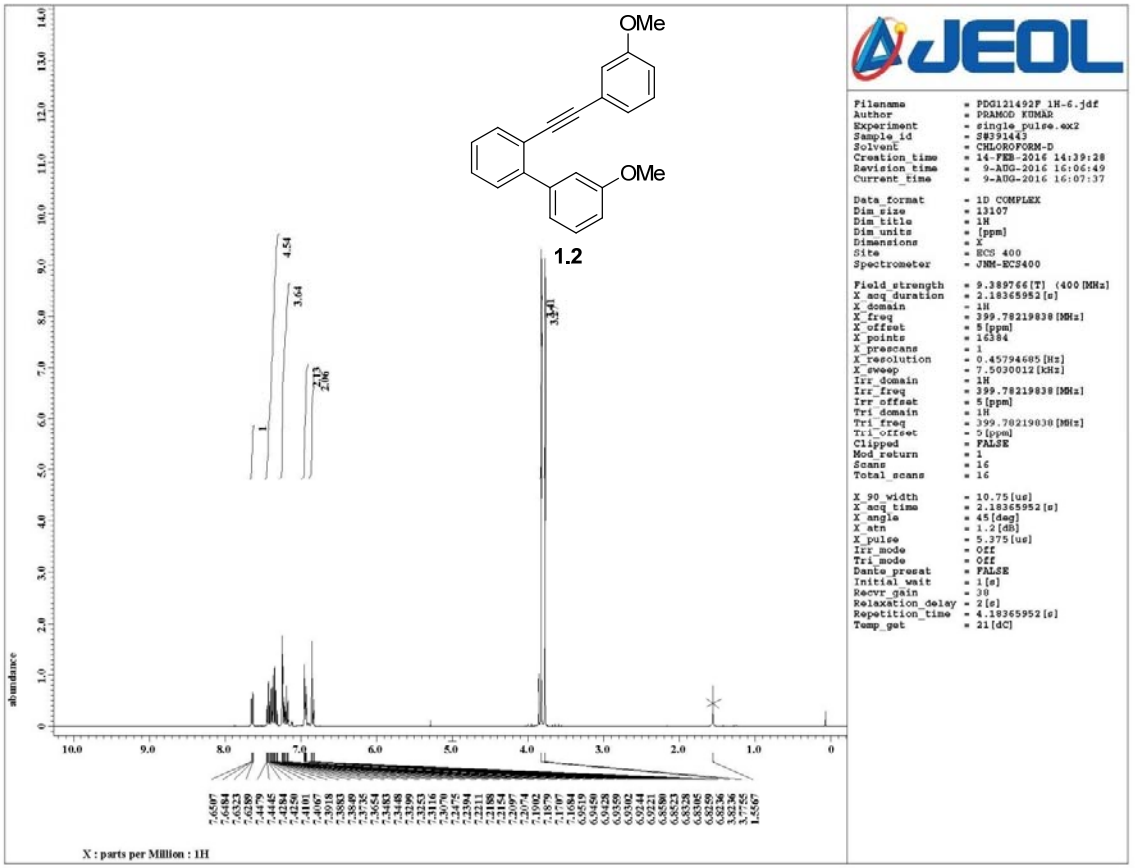
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1.1**



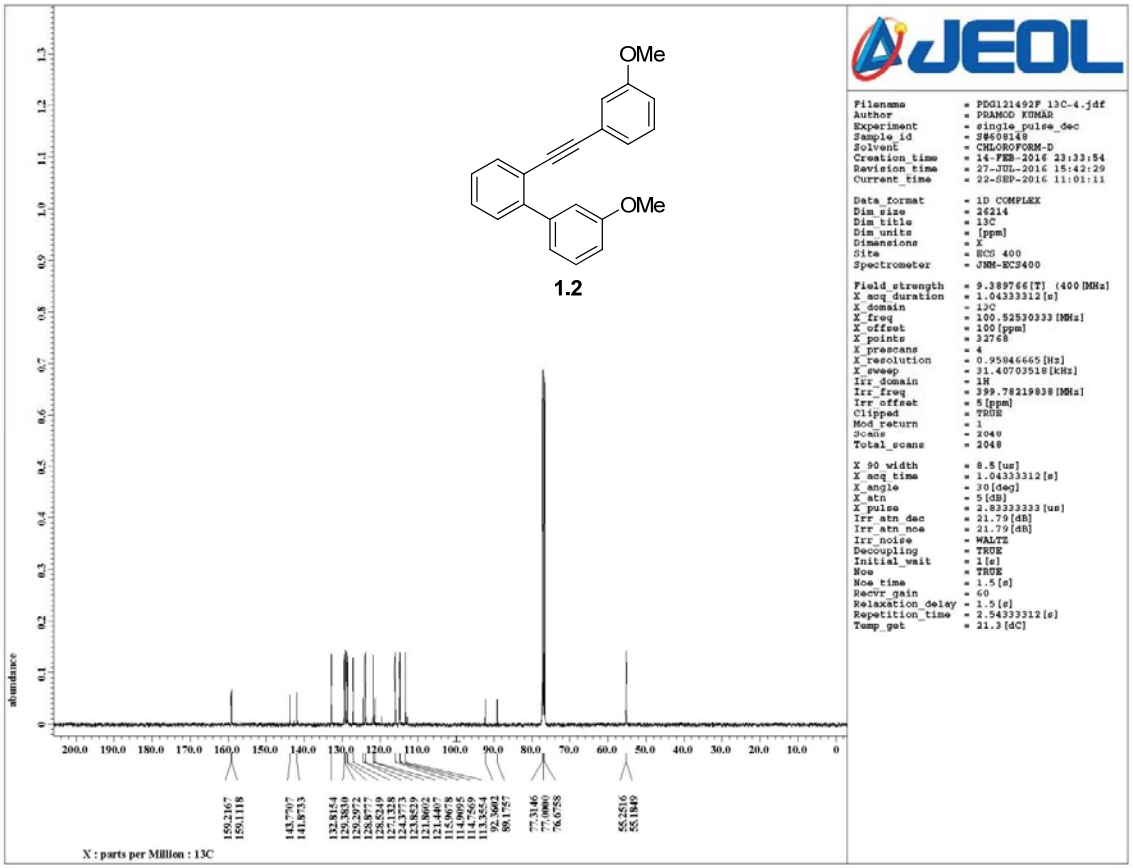
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1.1**



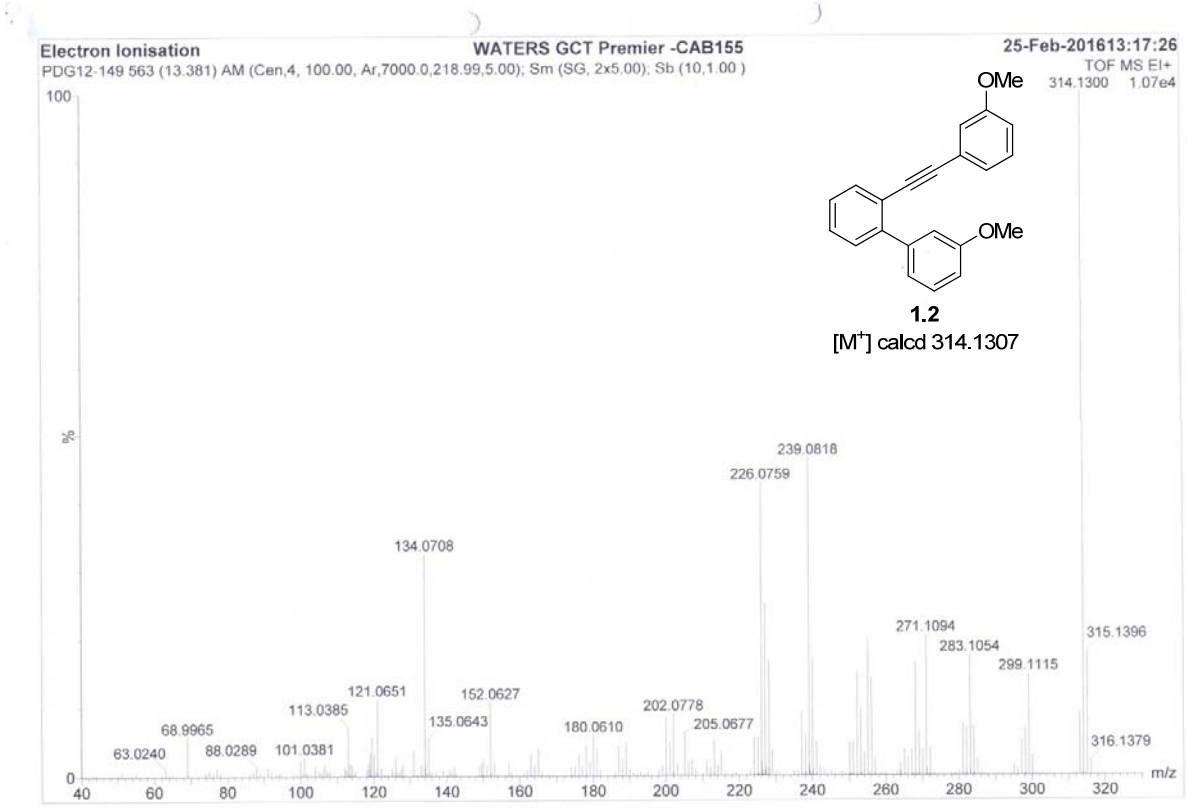
ESI (HRMS) spectrum of **1.1**



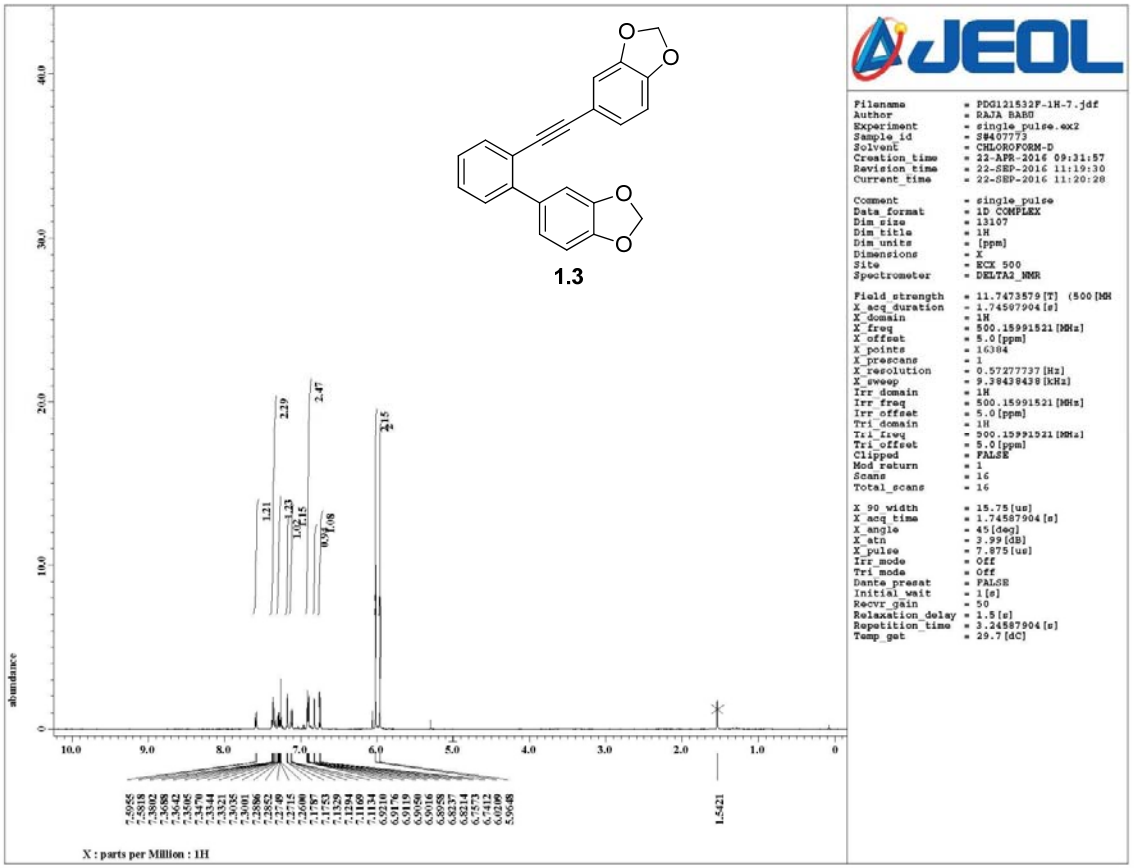
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1.2**



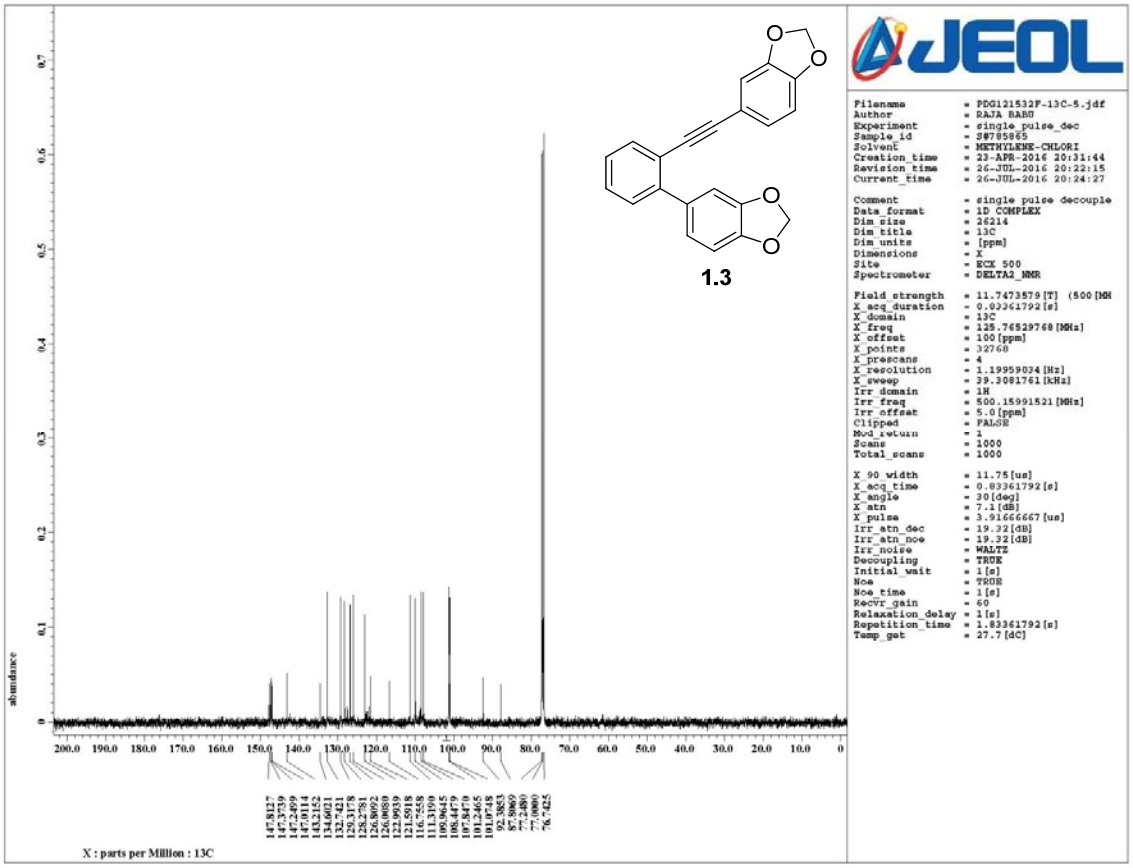
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1.2**



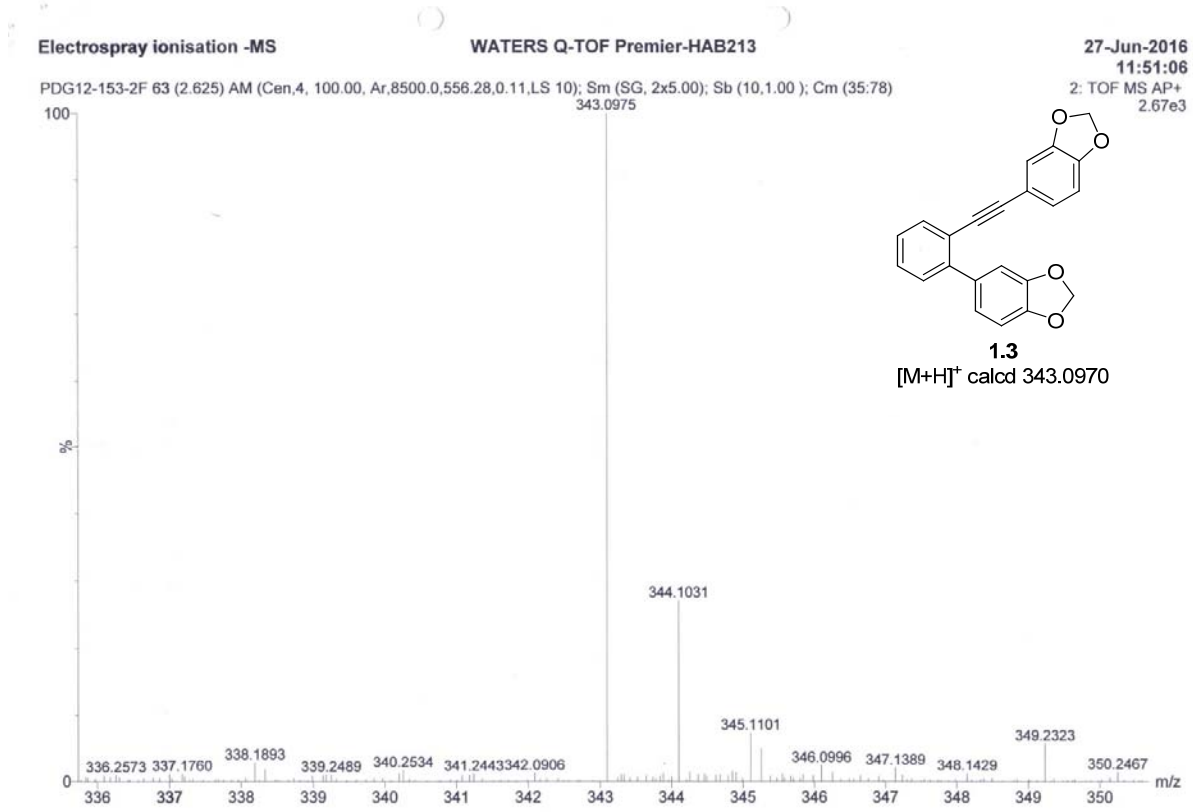
EI (HRMS) spectrum of **1.2**



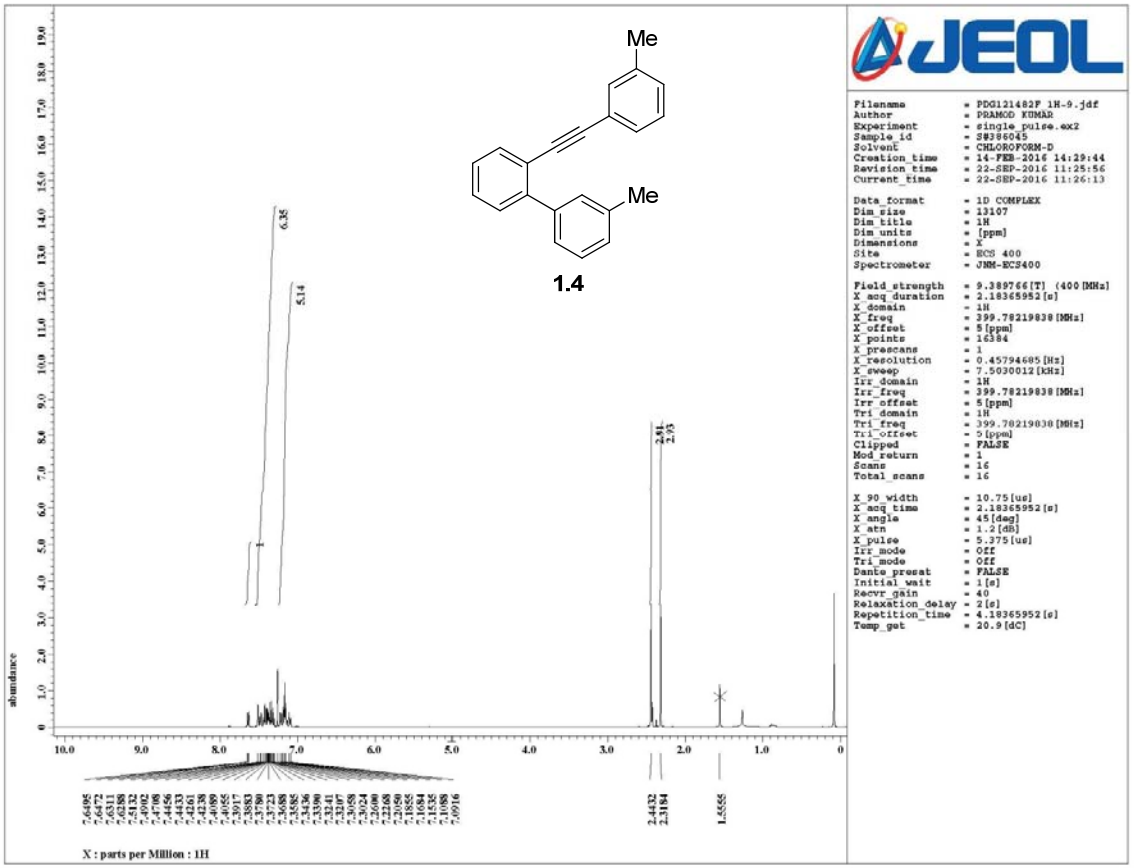
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1.3**



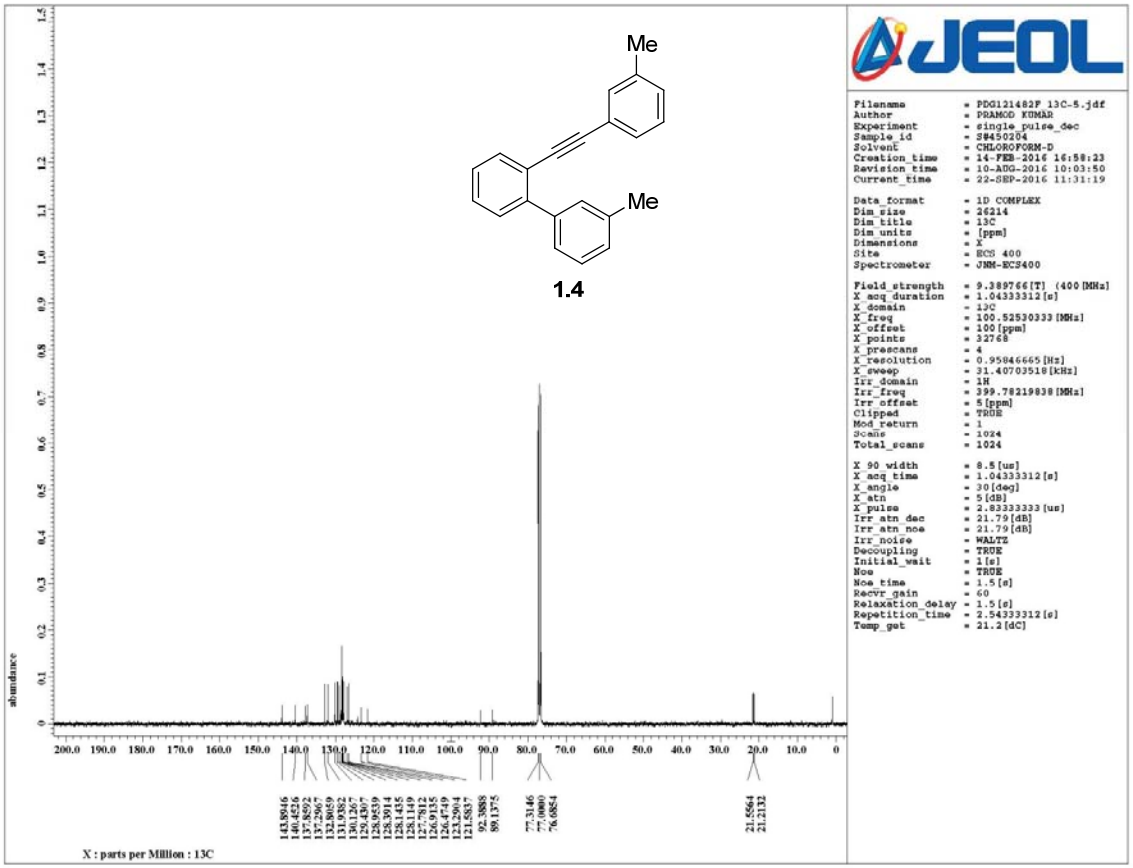
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **1.3**



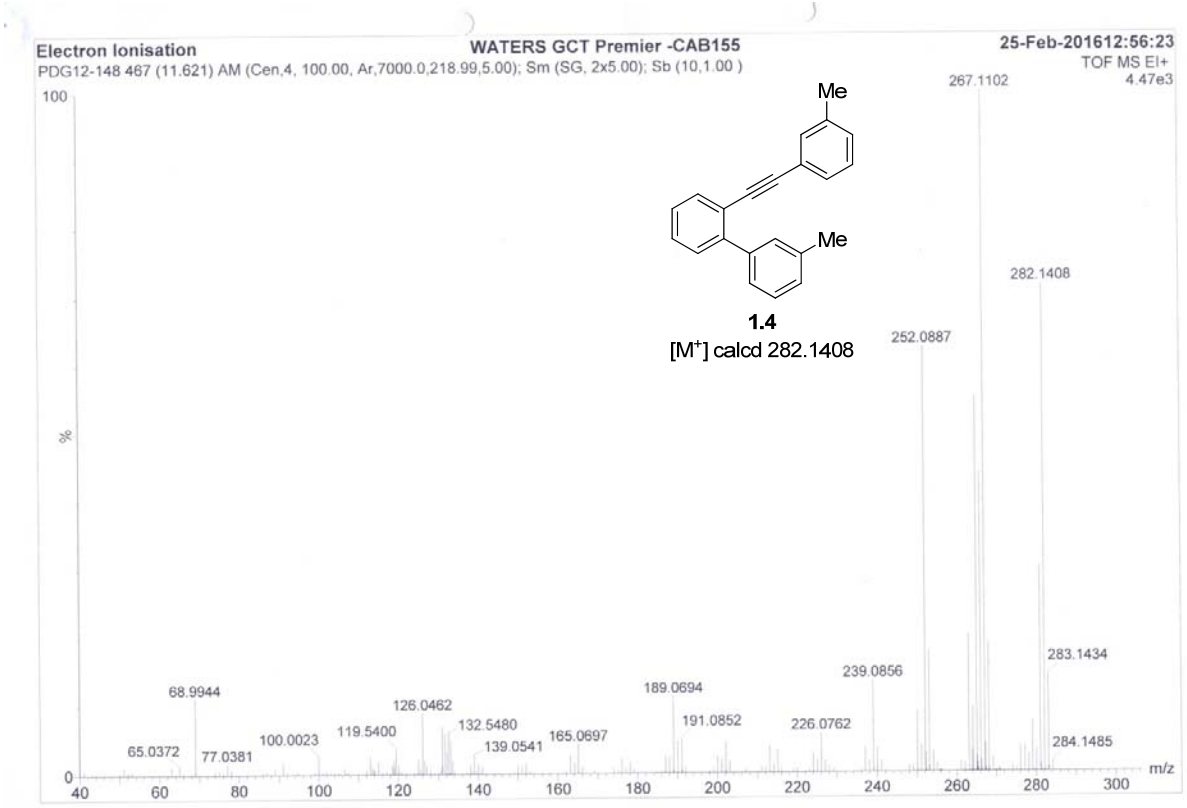
APCI (HRMS) spectrum of **1.3**



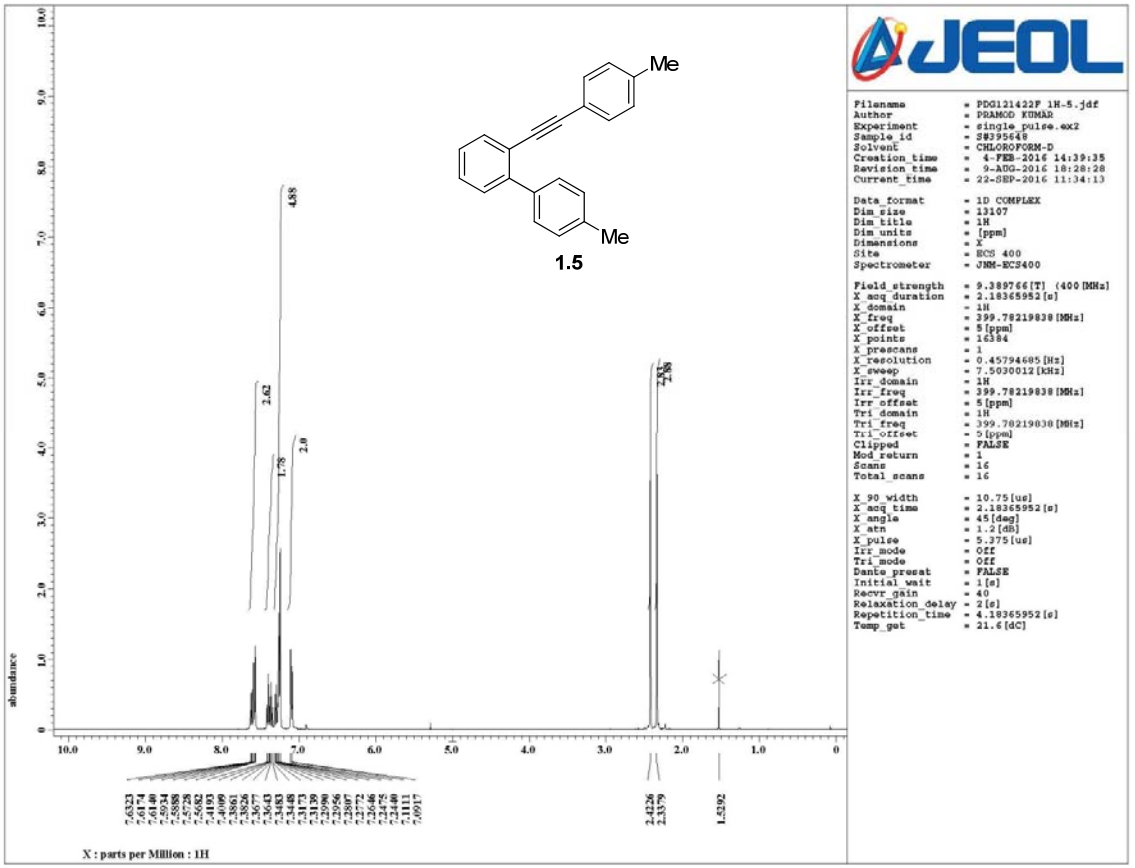
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1.4**



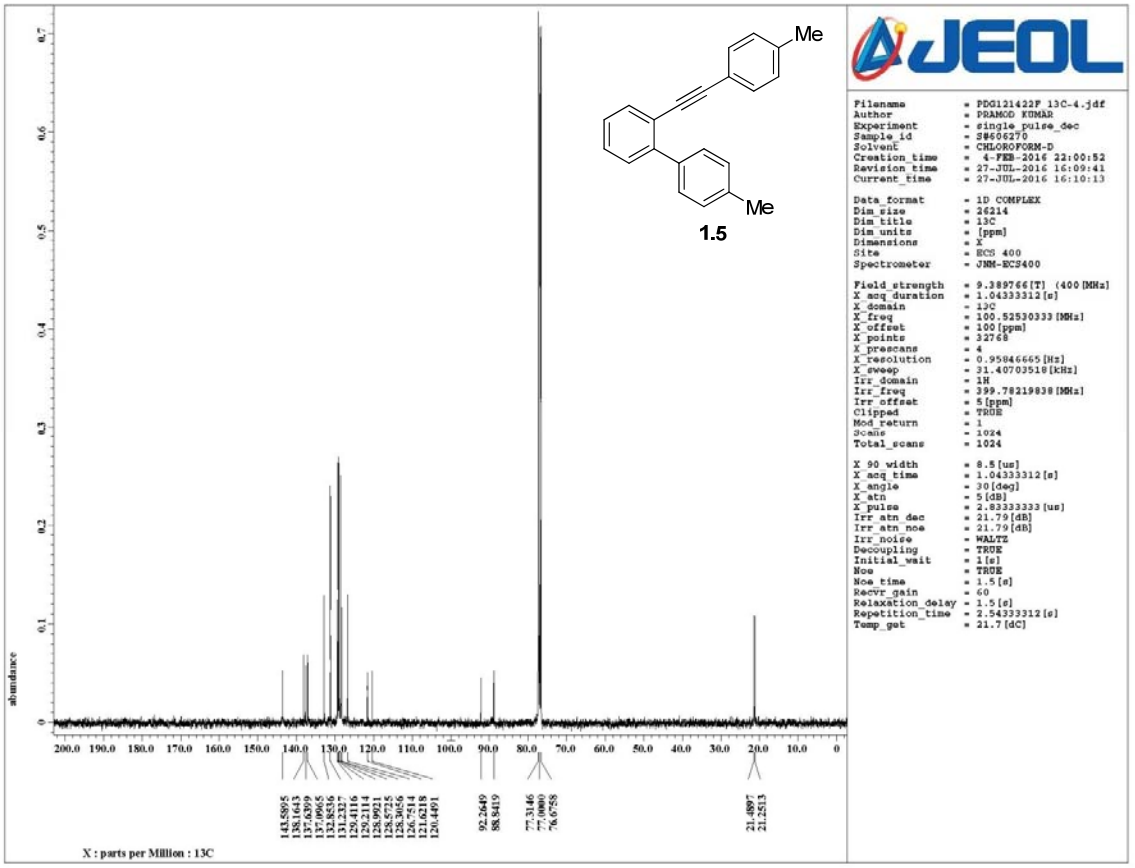
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1.4**



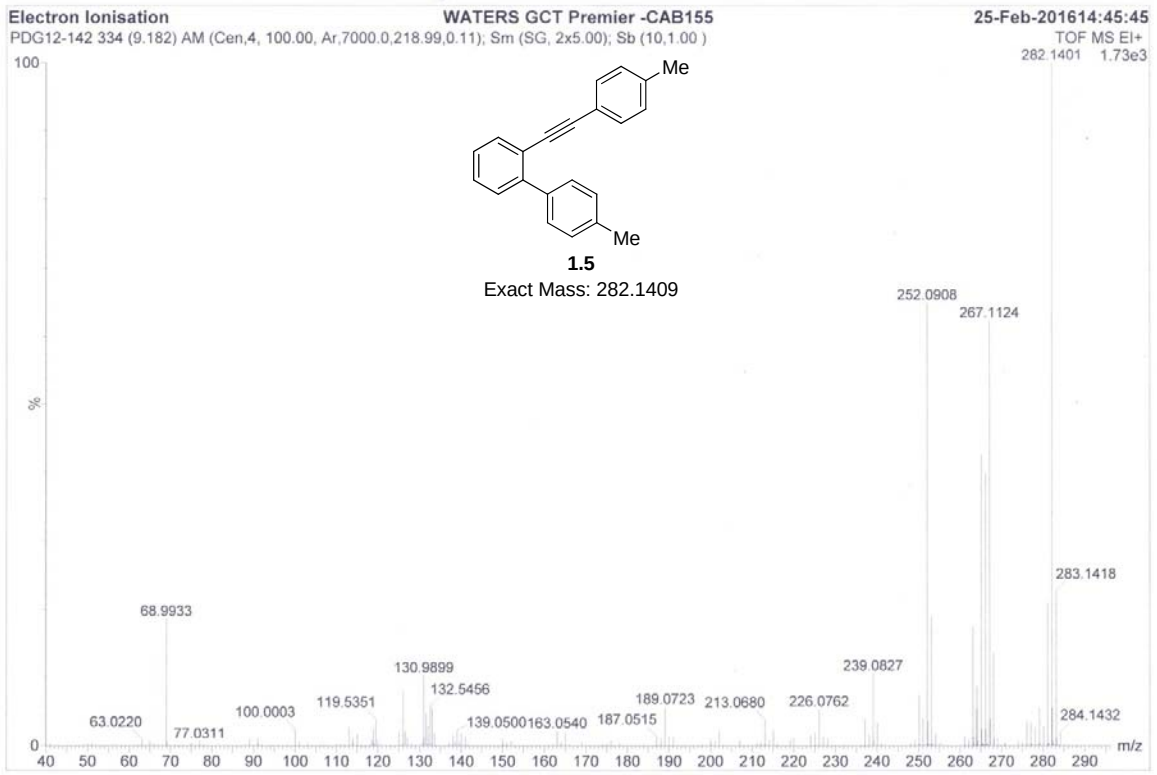
EI (HRMS) spectrum of **1.4**



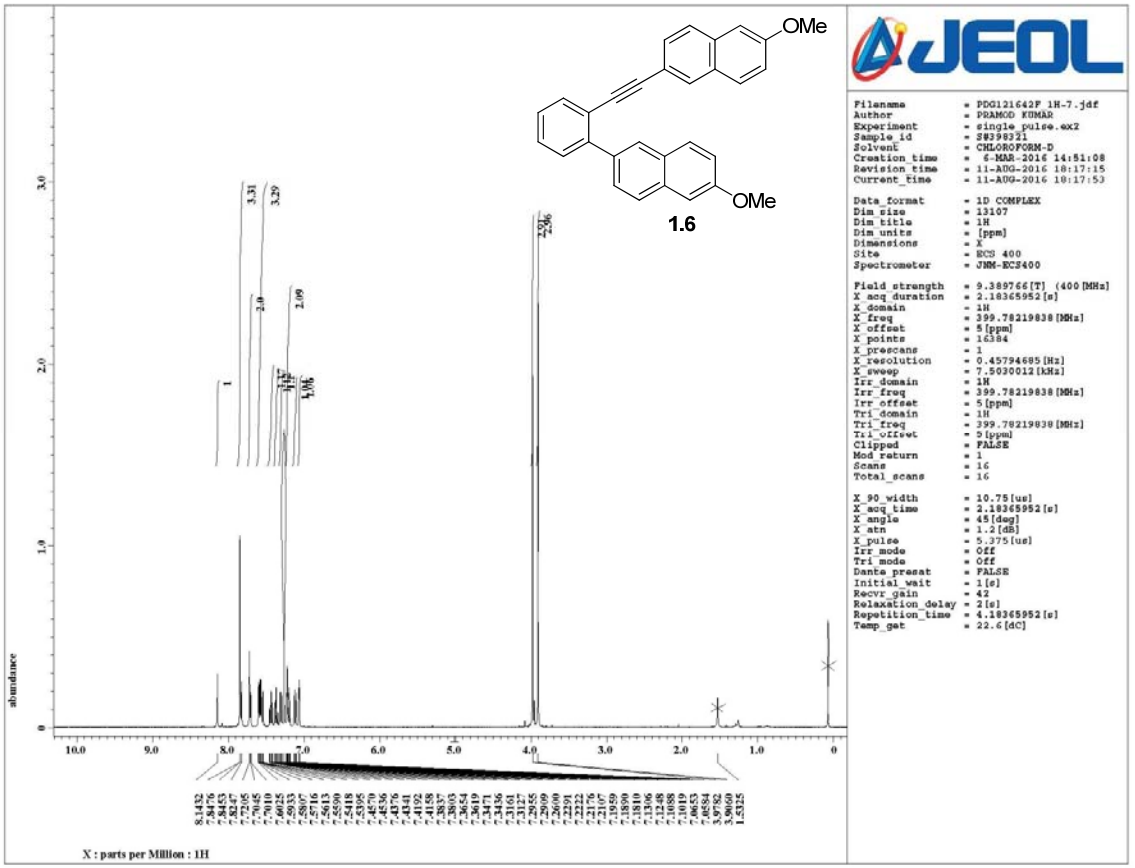
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1.5**



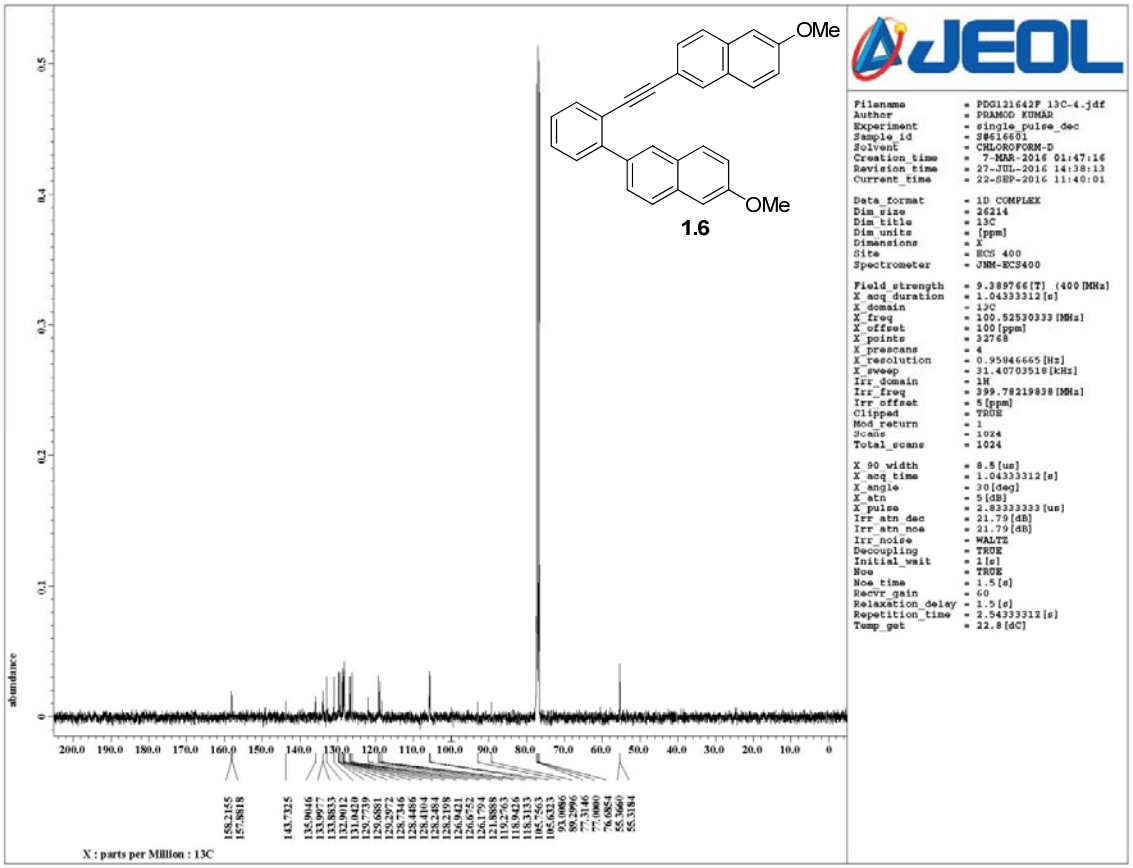
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1.5**



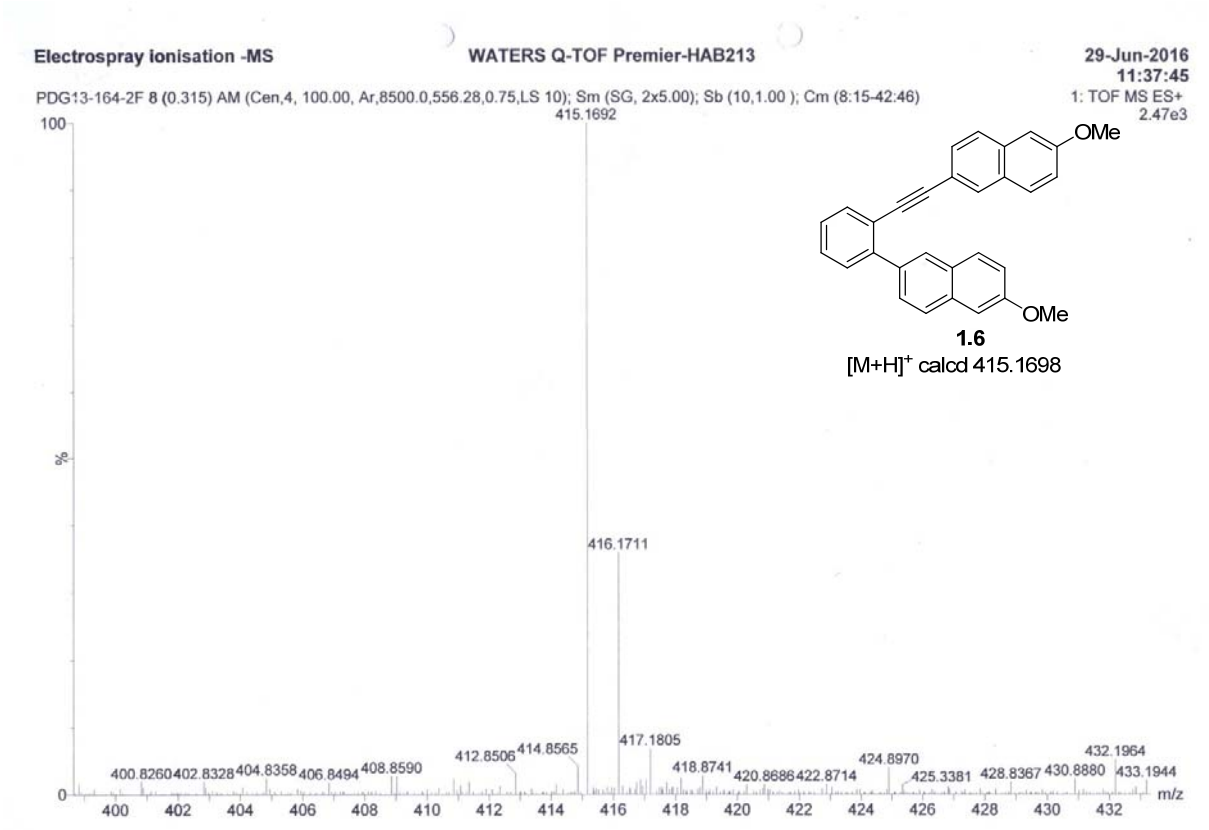
EI (HRMS) spectrum of **1.5**



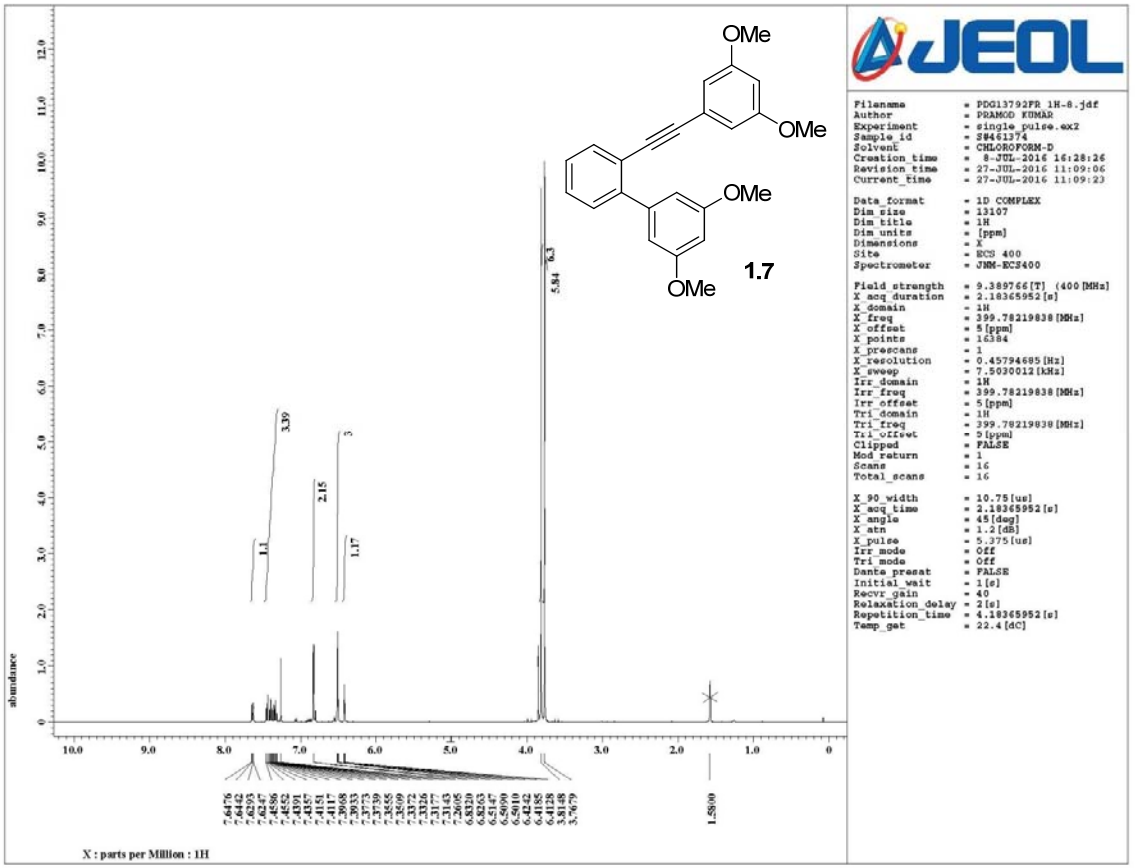
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1.6**



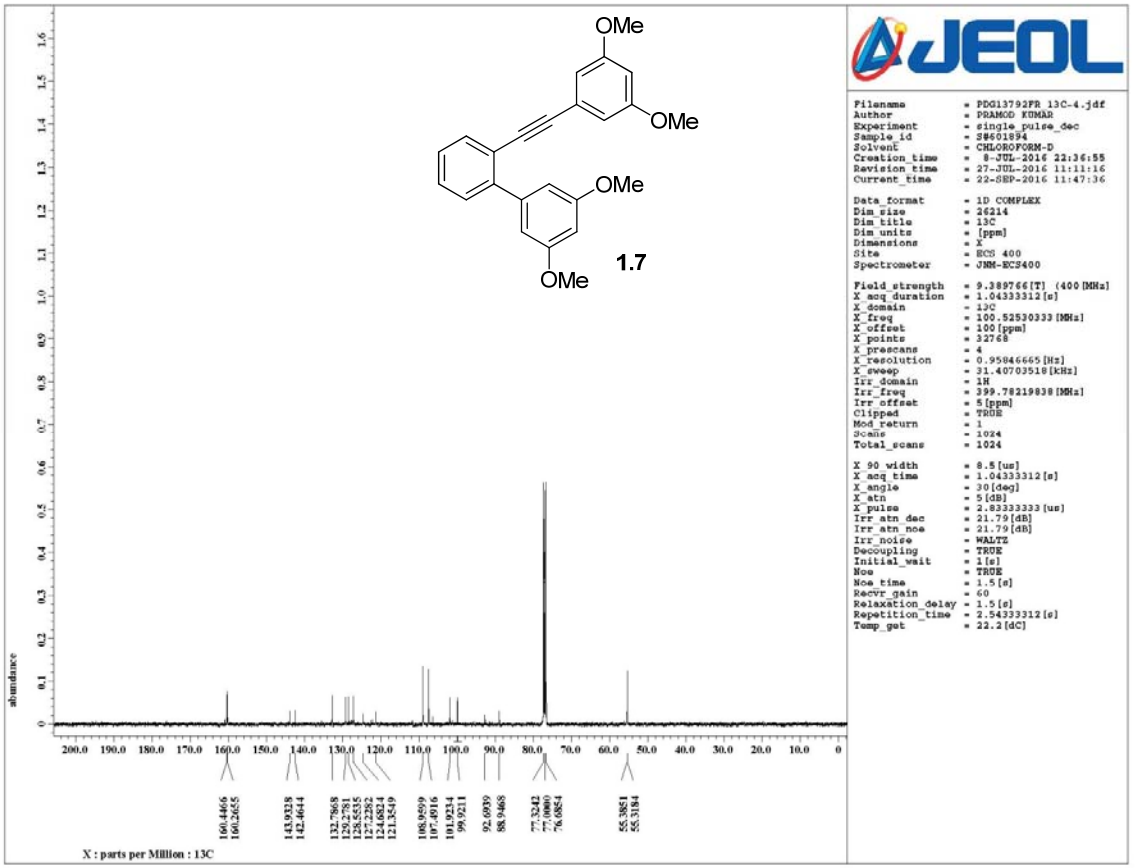
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1.6**



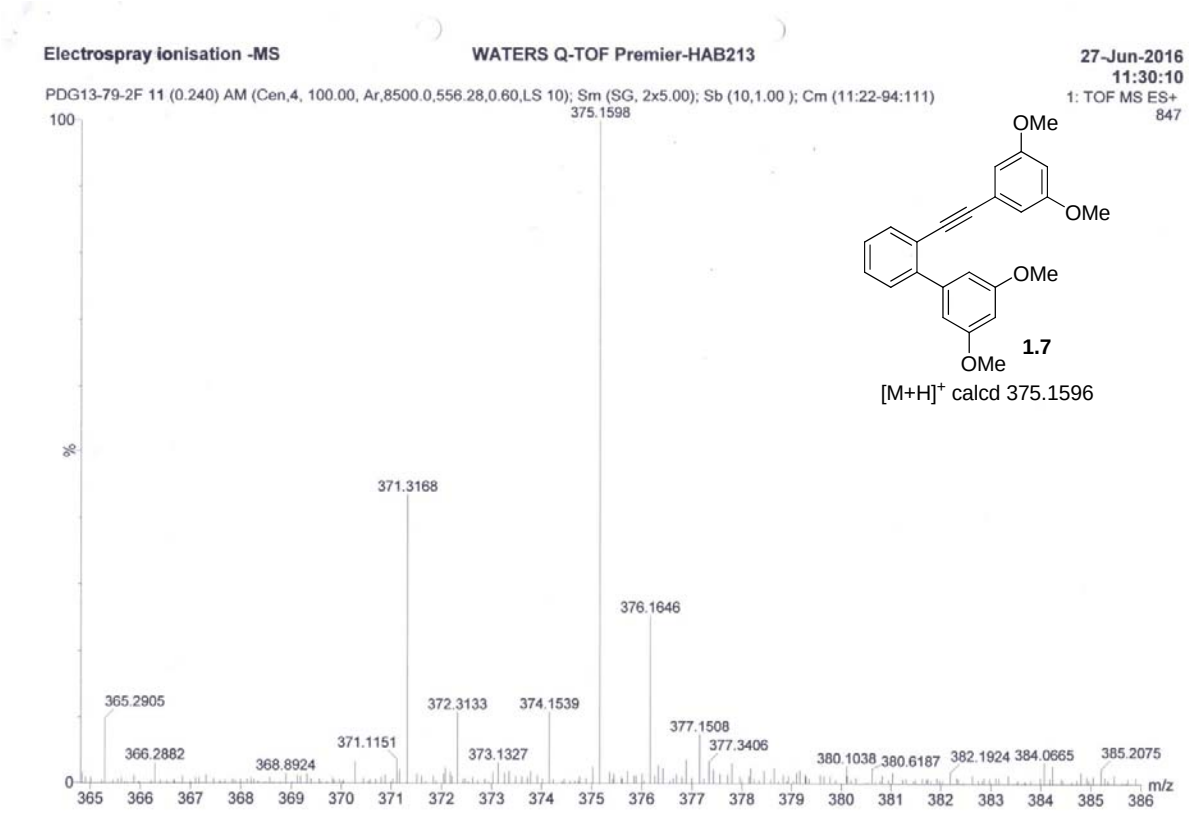
ESI (HRMS) spectrum of **1.6**



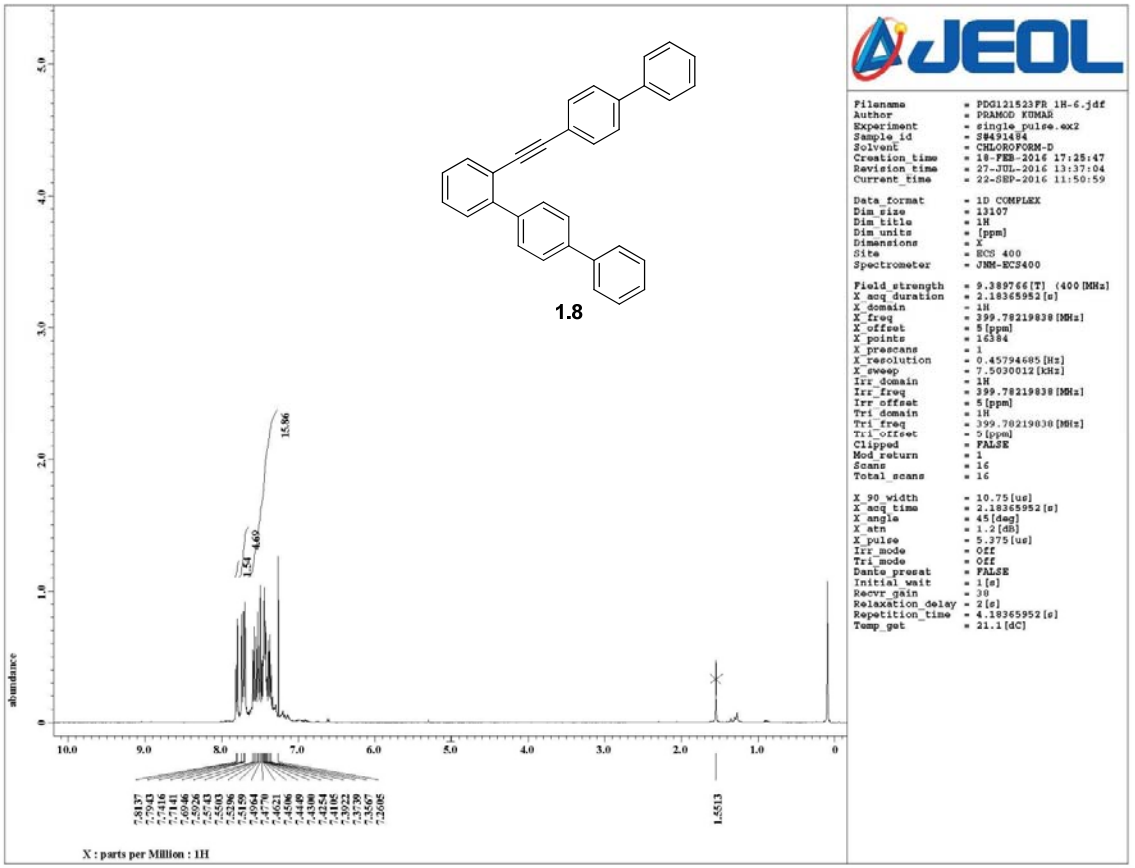
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1.7**



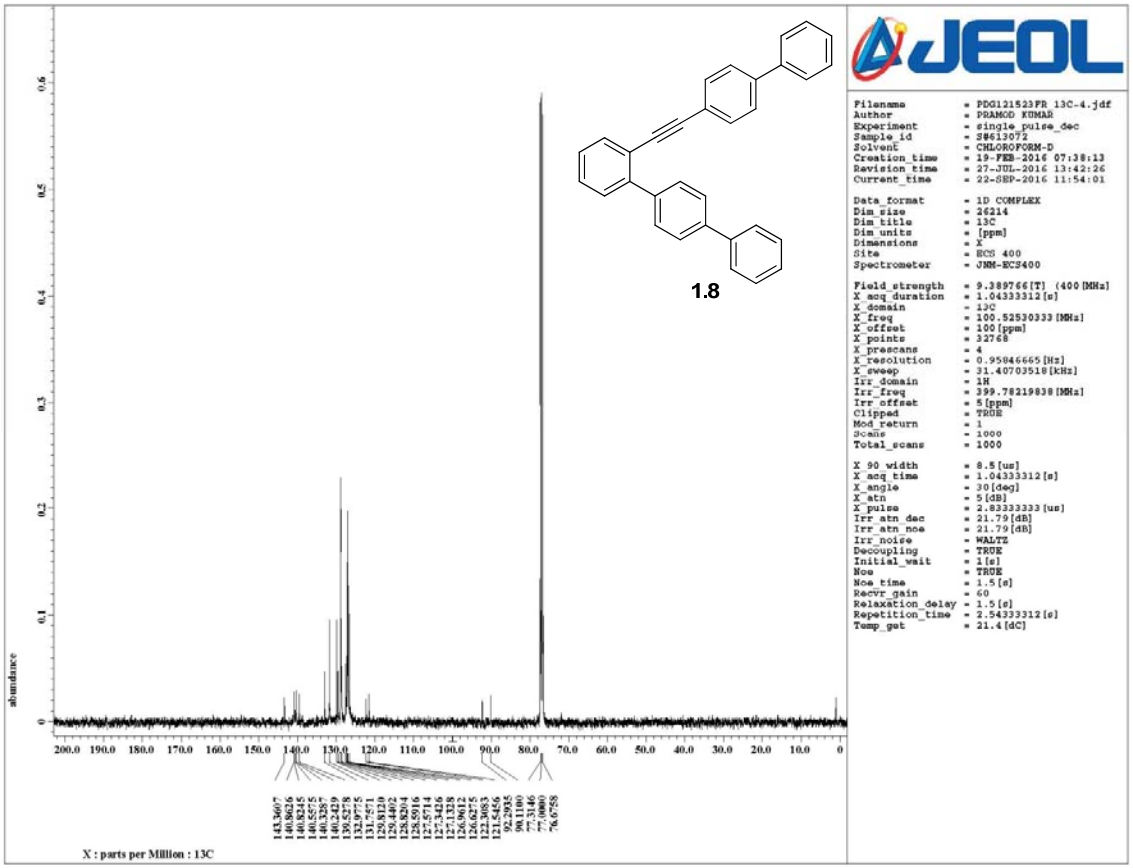
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1.7**



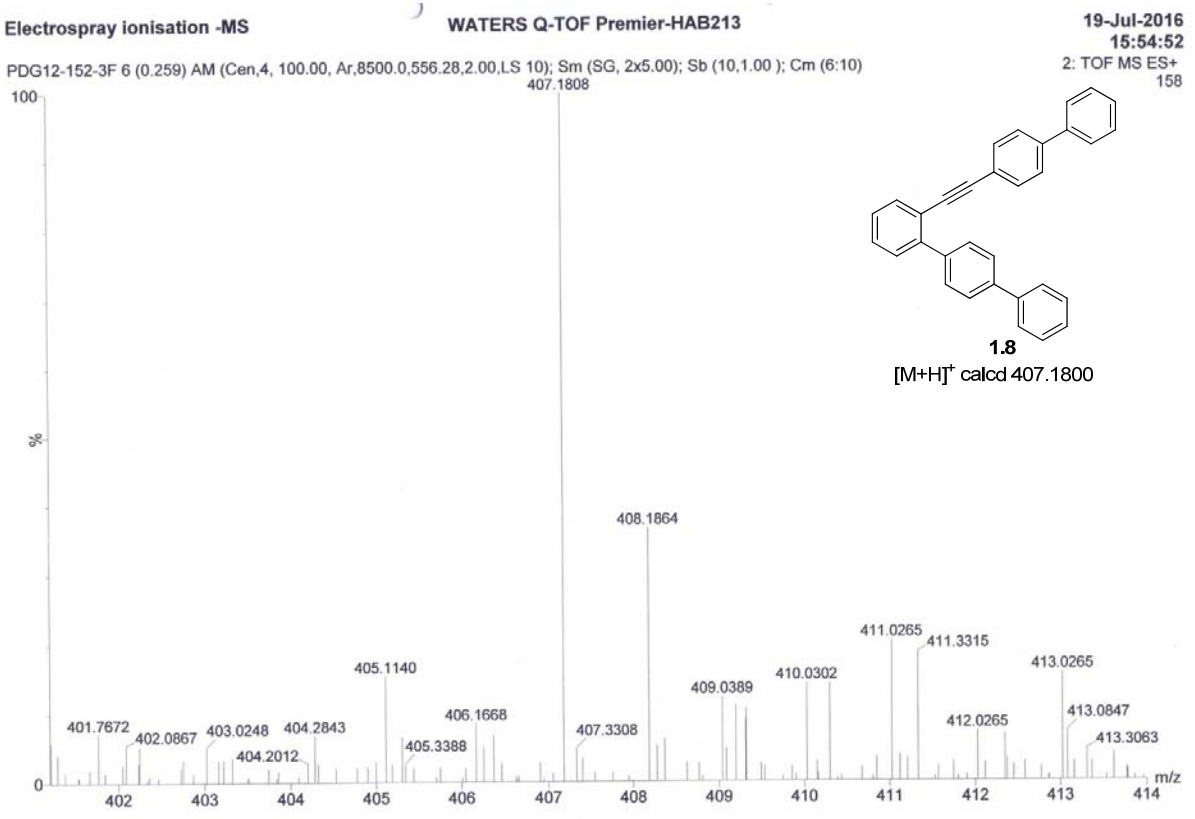
ESI (HRMS) spectrum of **1.7**



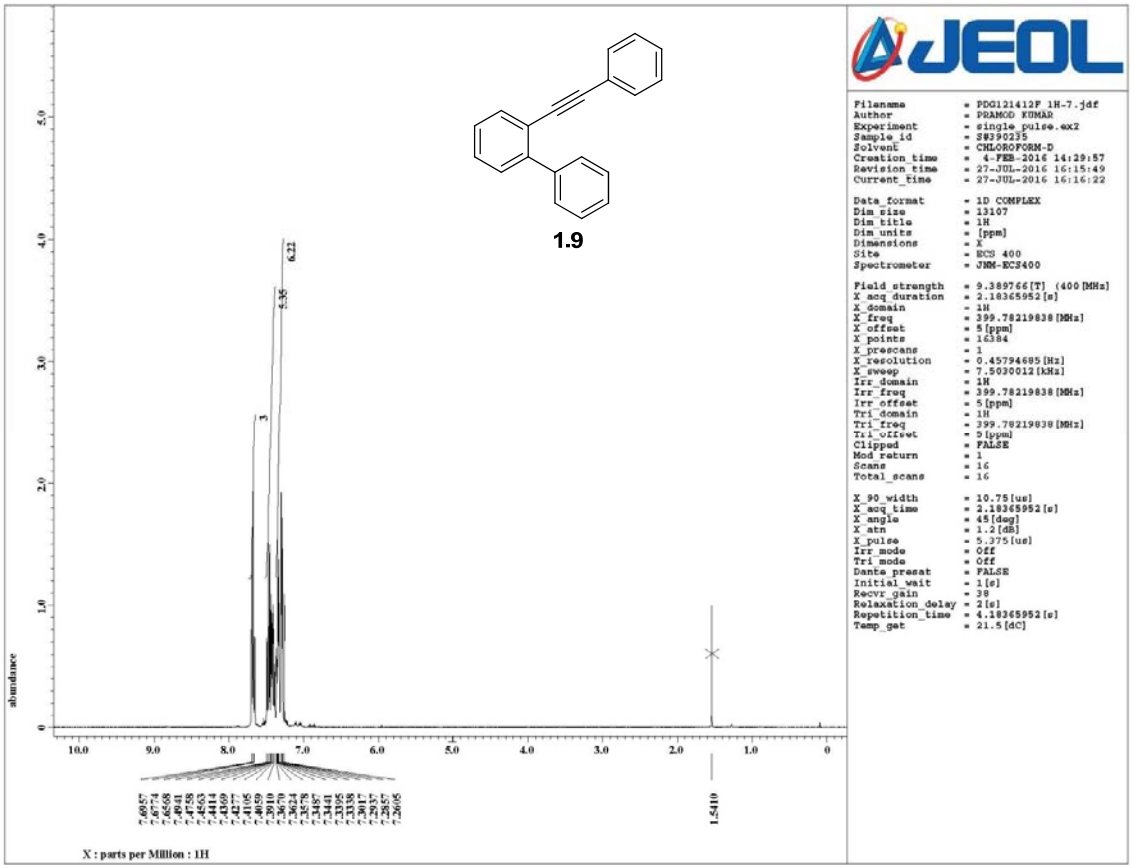
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1.8**



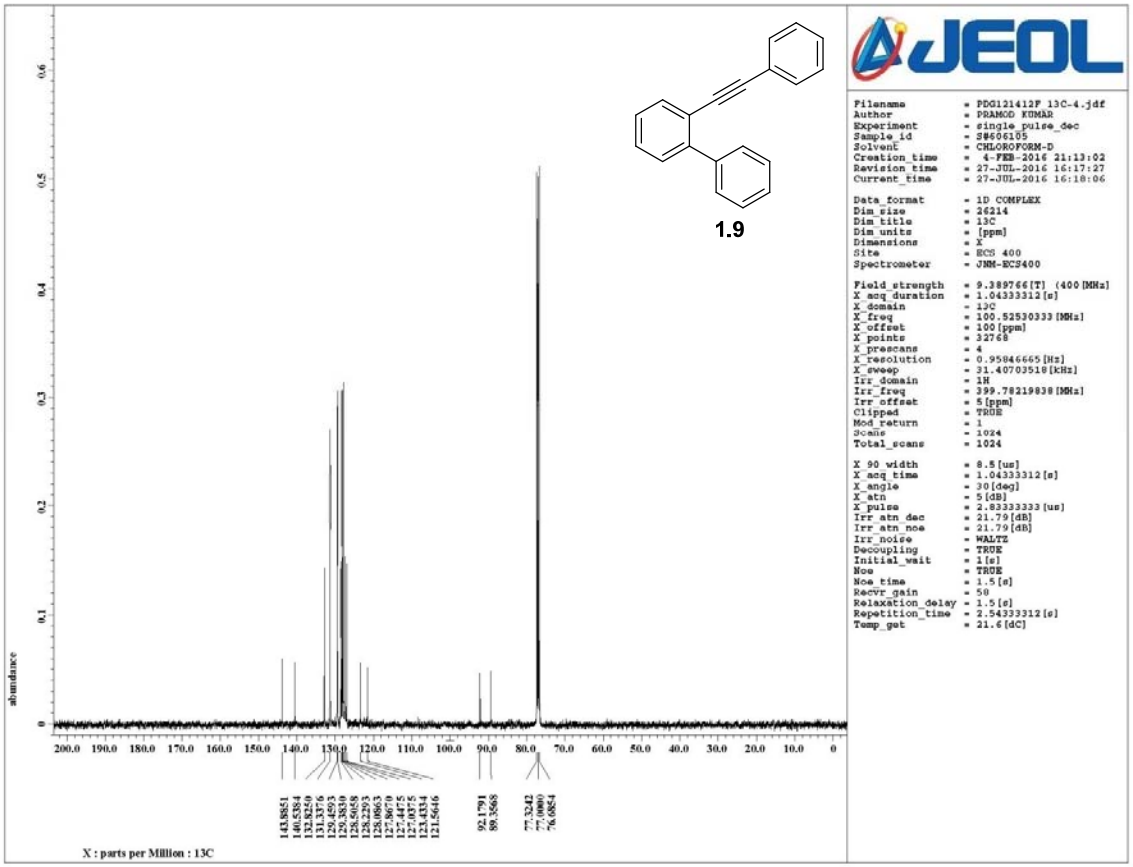
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1.8**



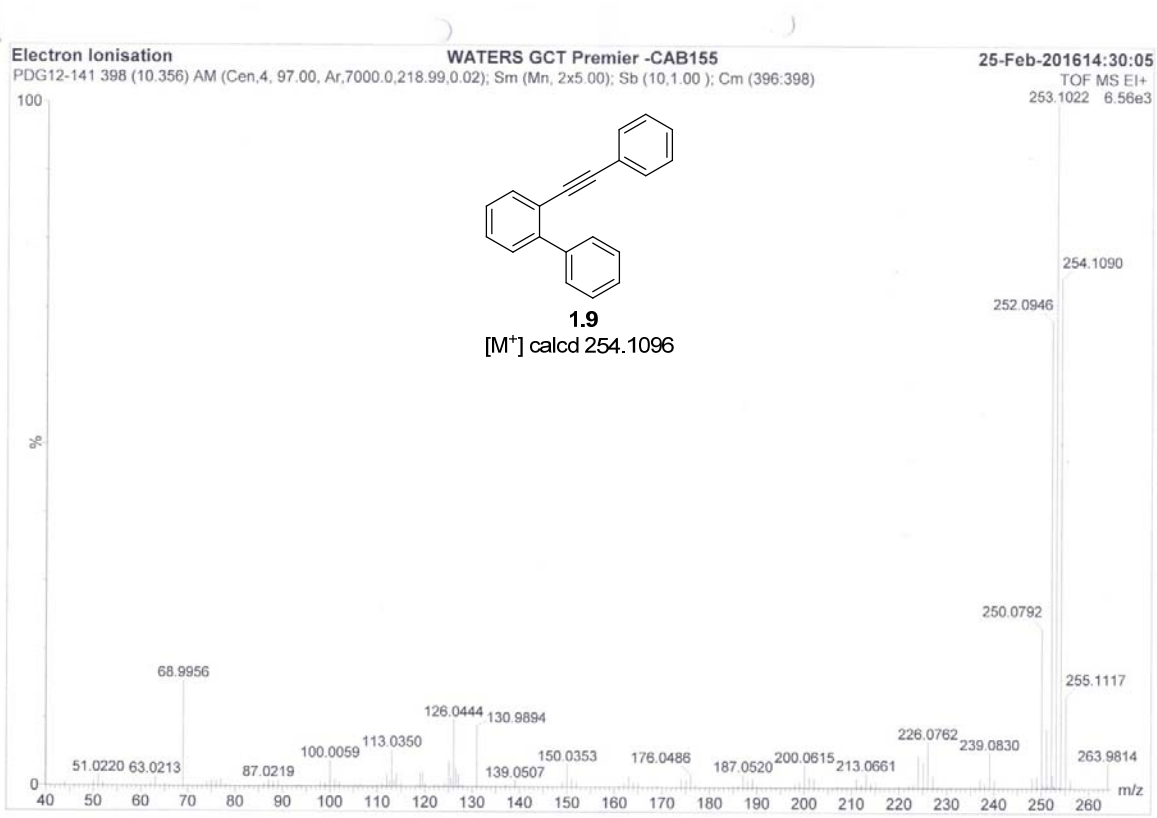
ESI (HRMS) spectrum of **1.8**



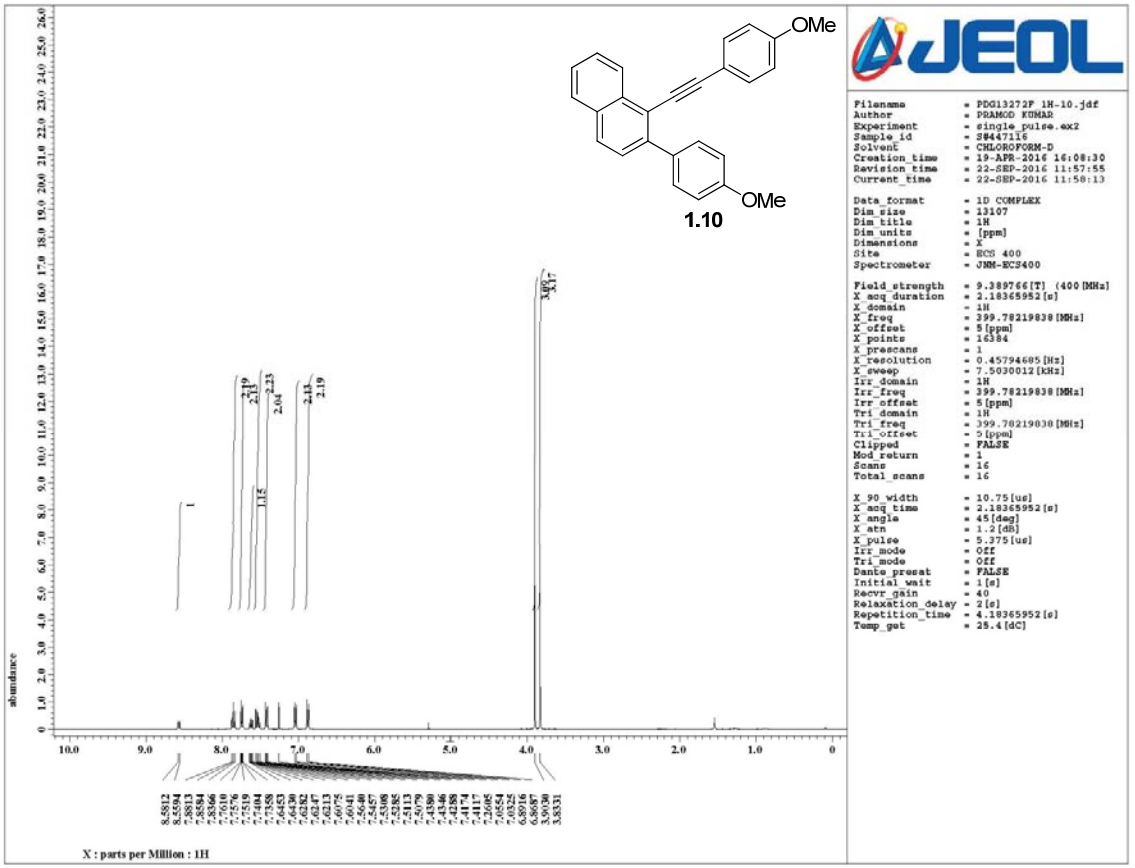
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1.9**



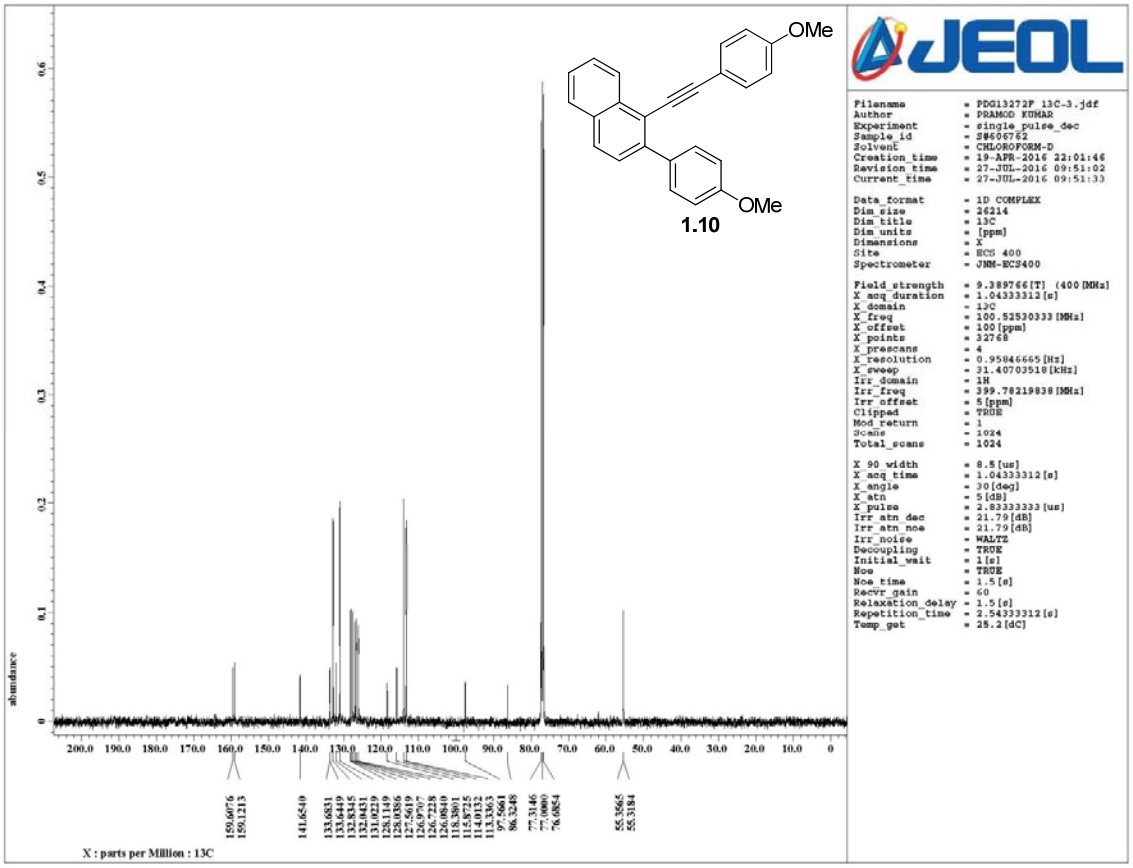
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1.9**



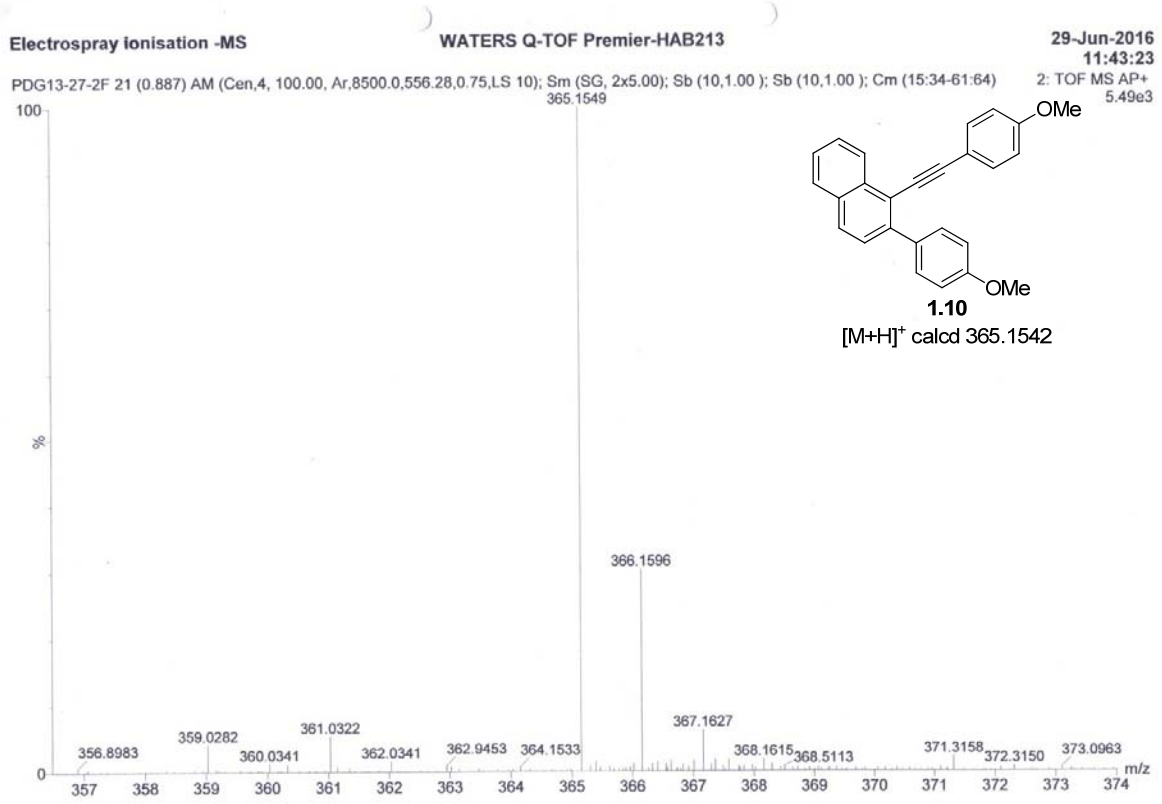
EI (HRMS) spectrum of **1.9**



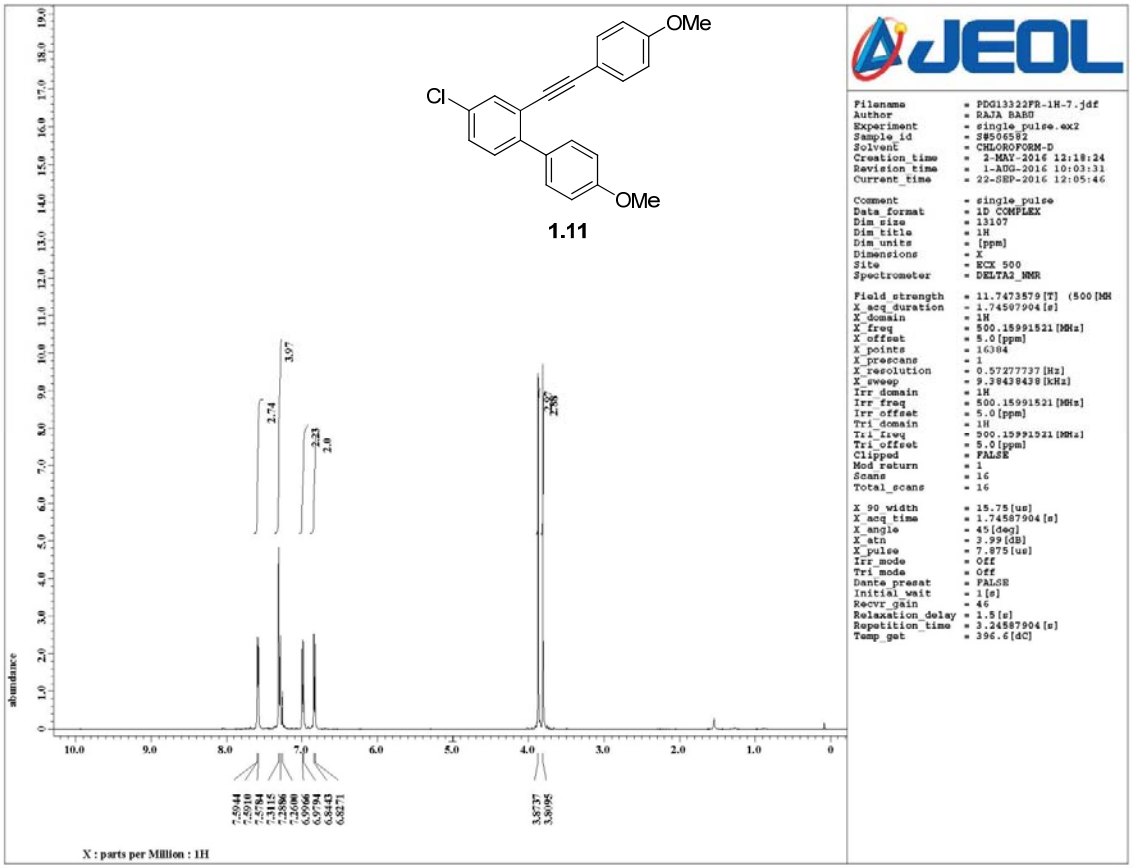
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1.10**



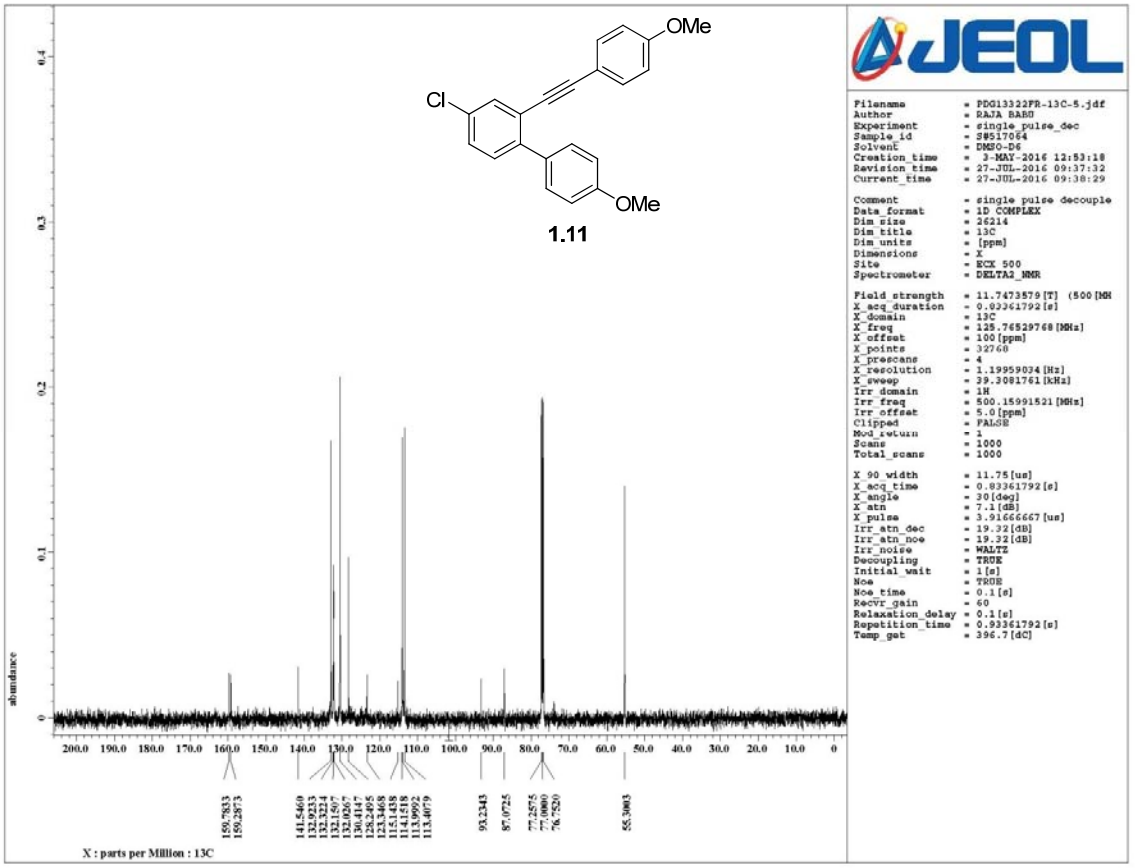
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1.10**



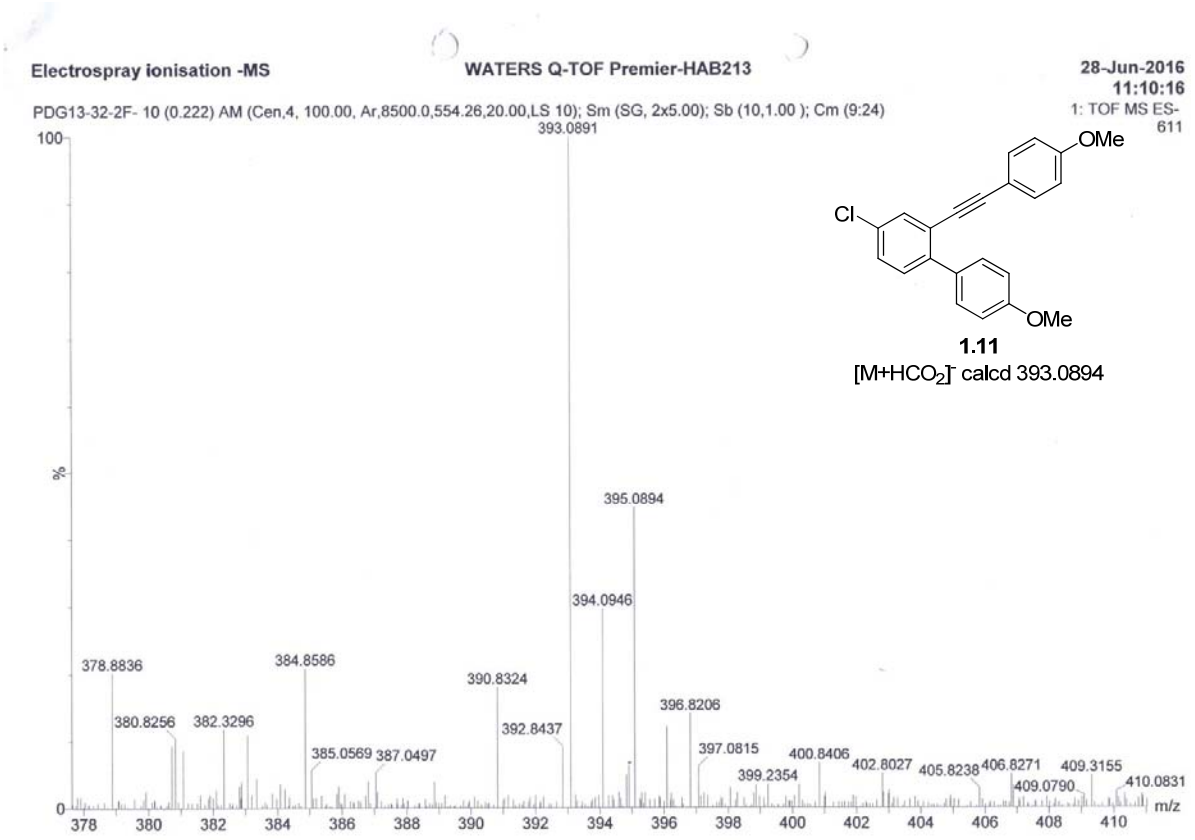
APCI (HRMS) spectrum of **1.10**



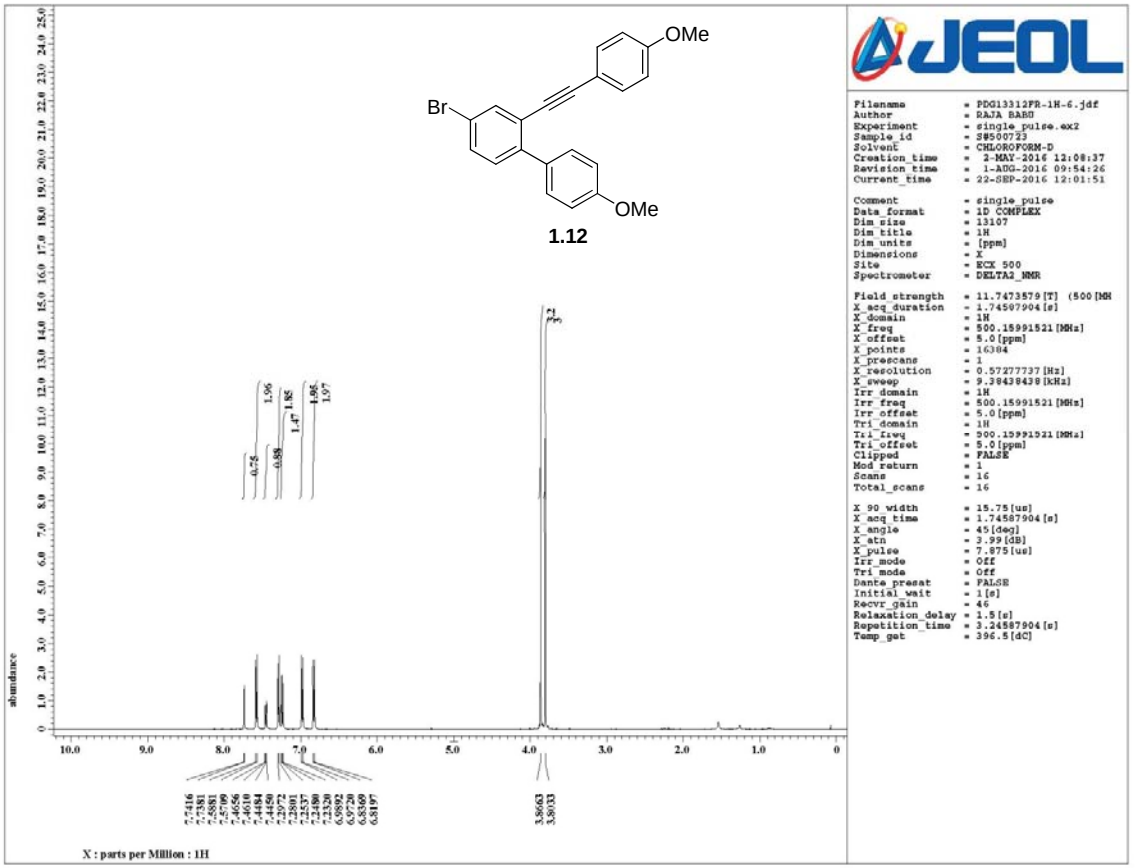
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1.11**



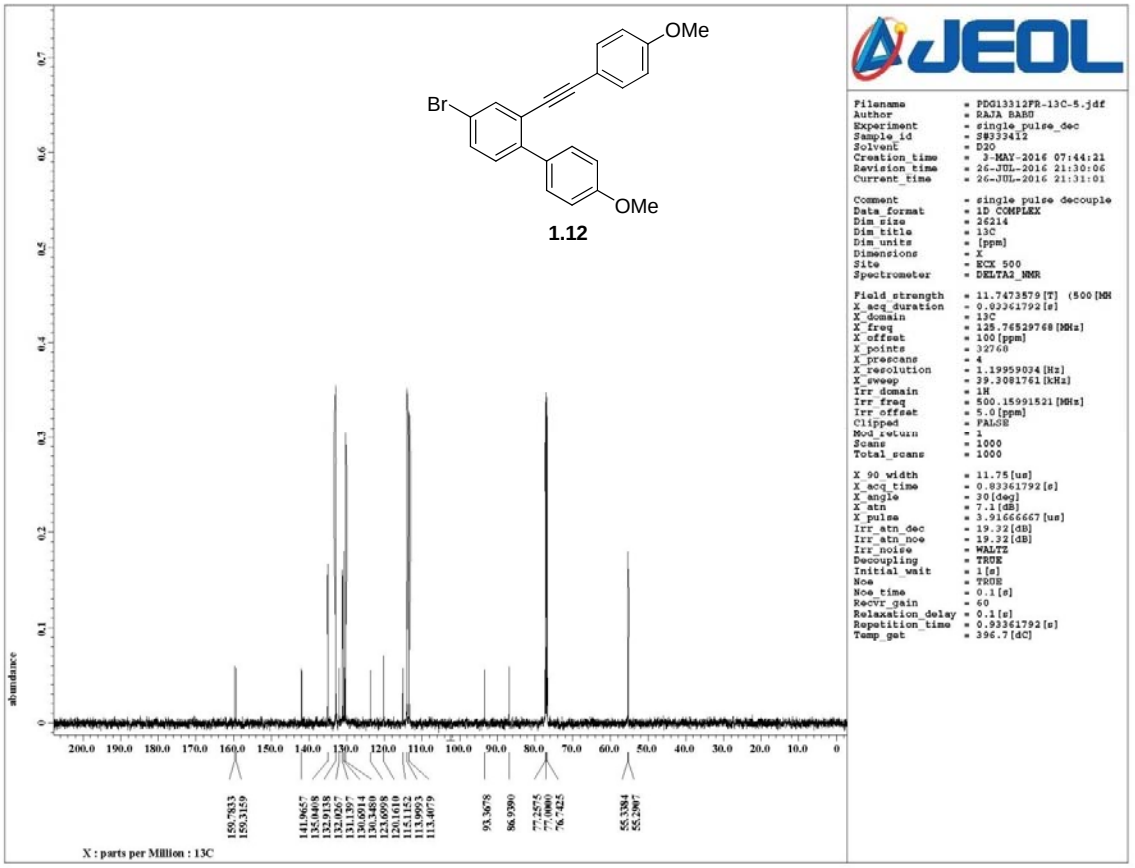
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **1.11**



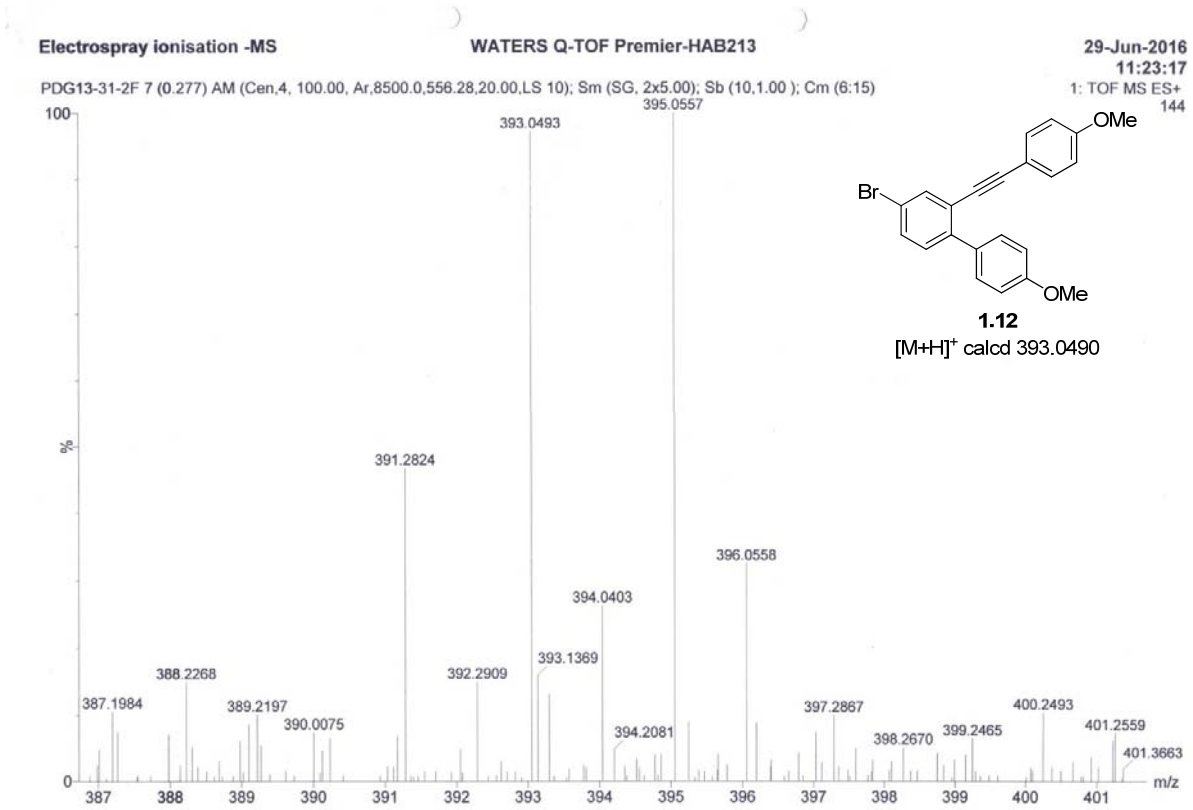
ESI (HRMS) spectrum of **1.11**



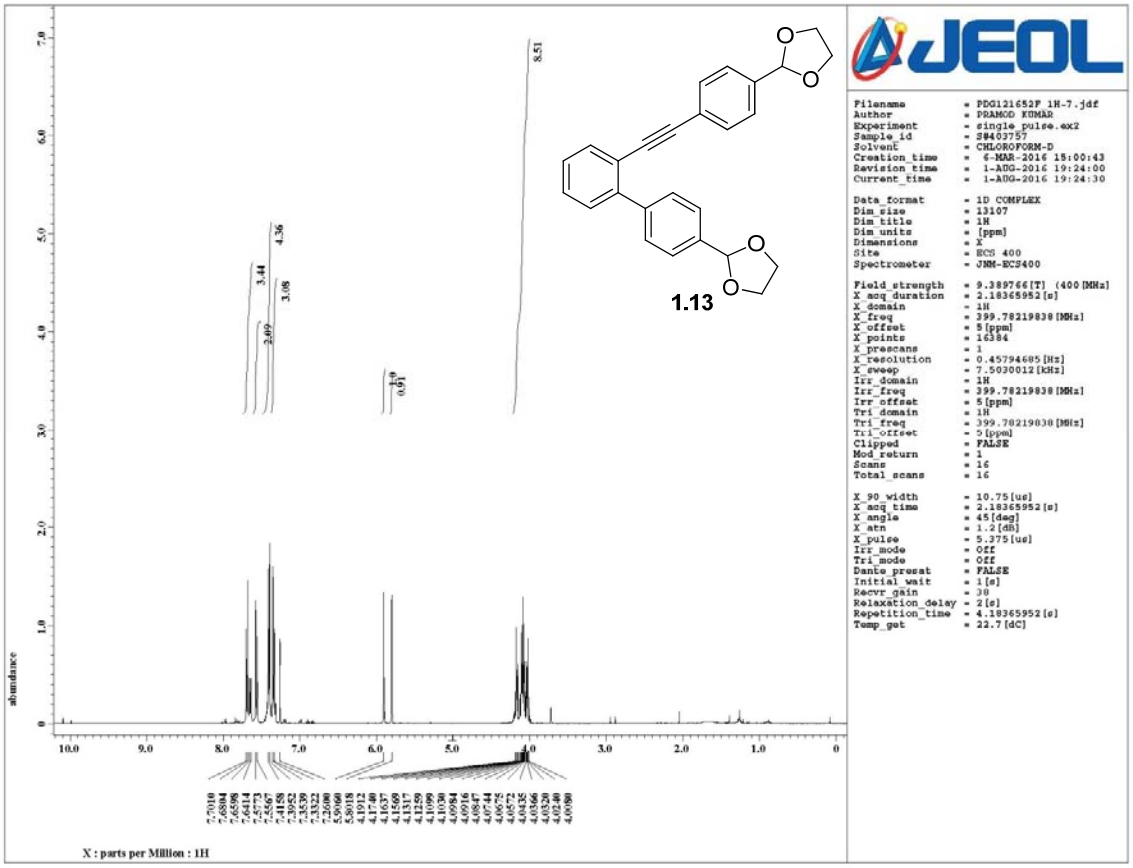
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1.12**



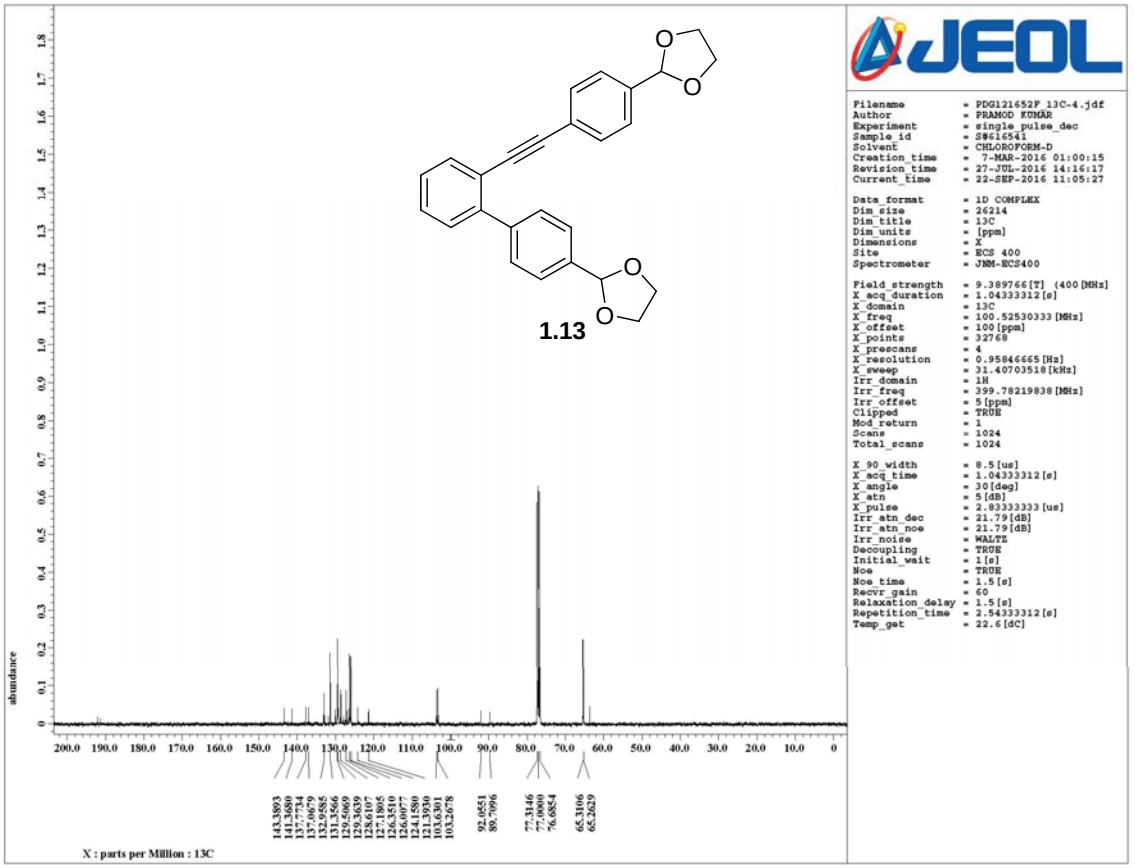
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **1.12**



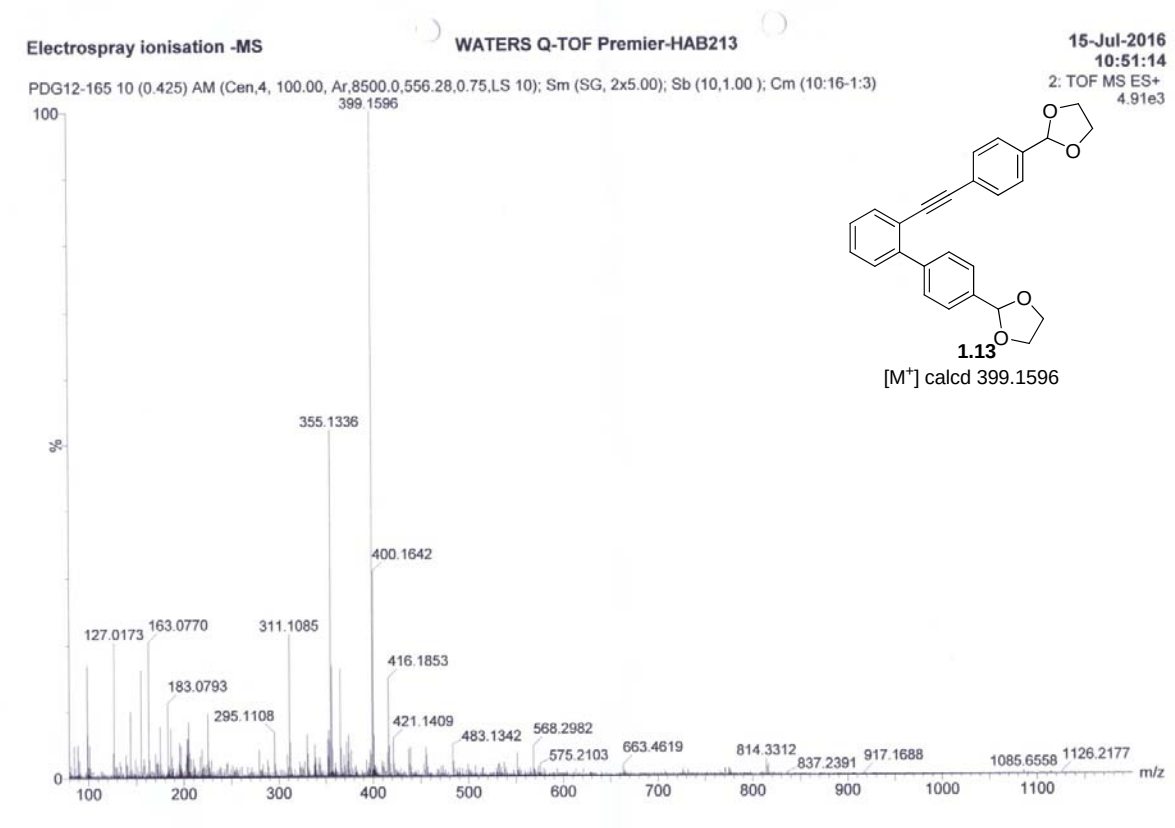
ESI (HRMS) spectrum of **1.12**



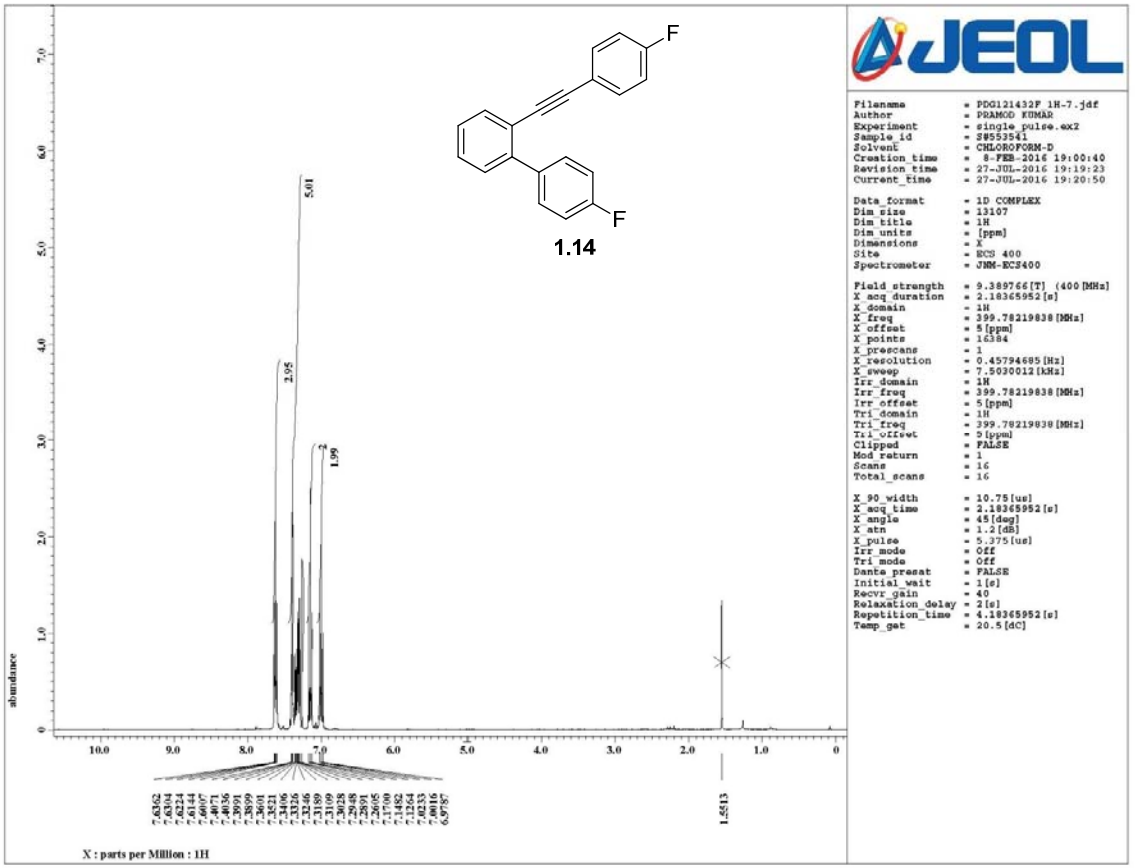
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1.13**



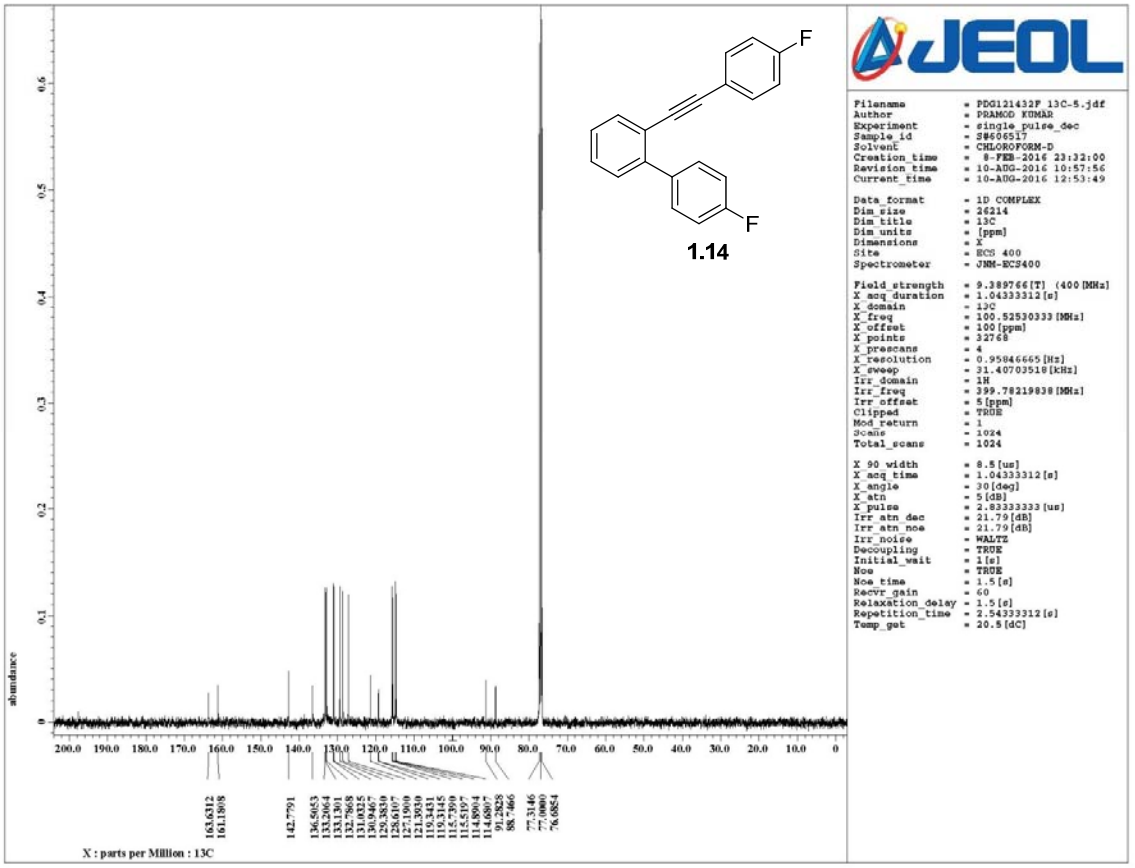
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1.13**



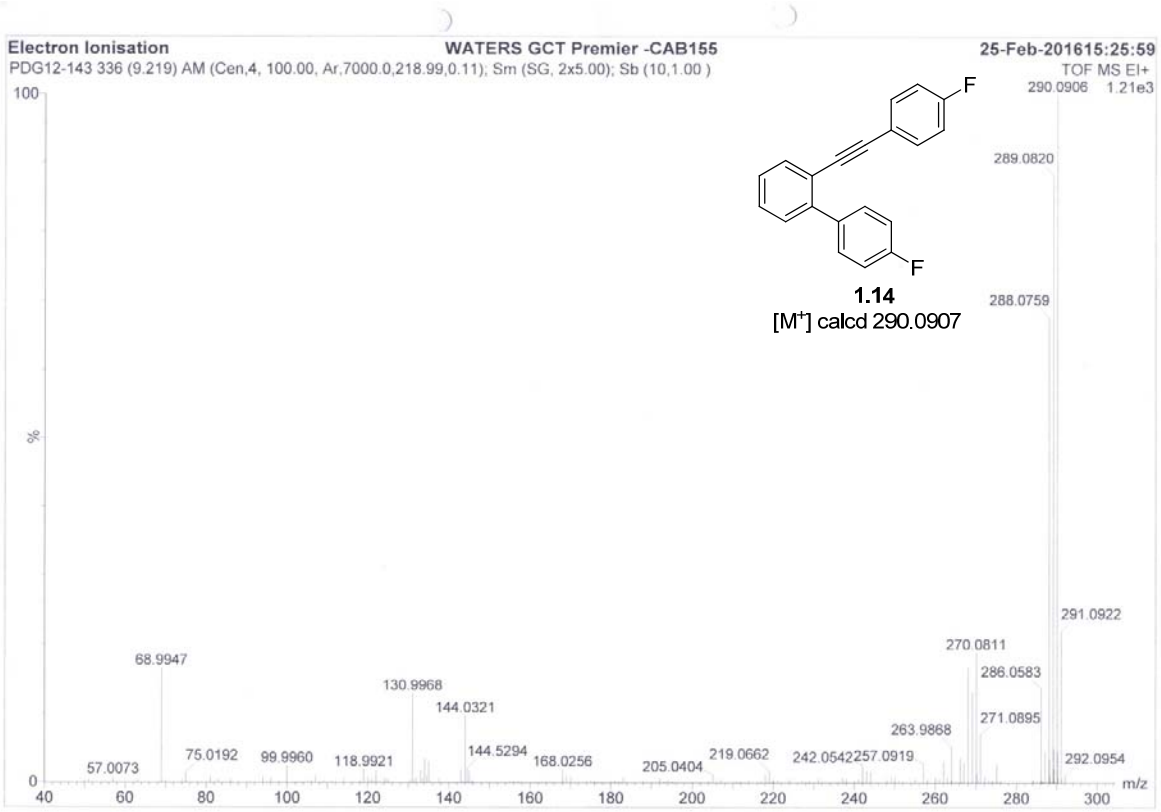
ESI (HRMS) spectrum of **1.13**



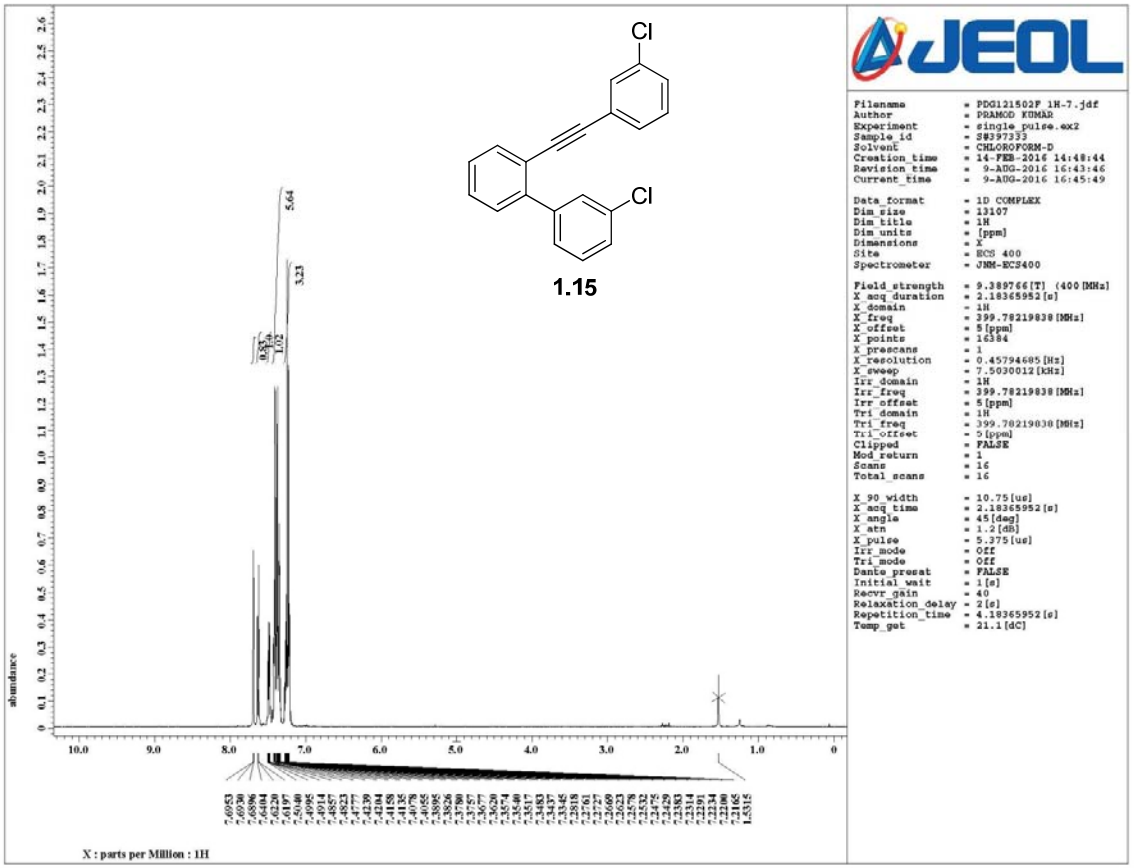
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1.14**



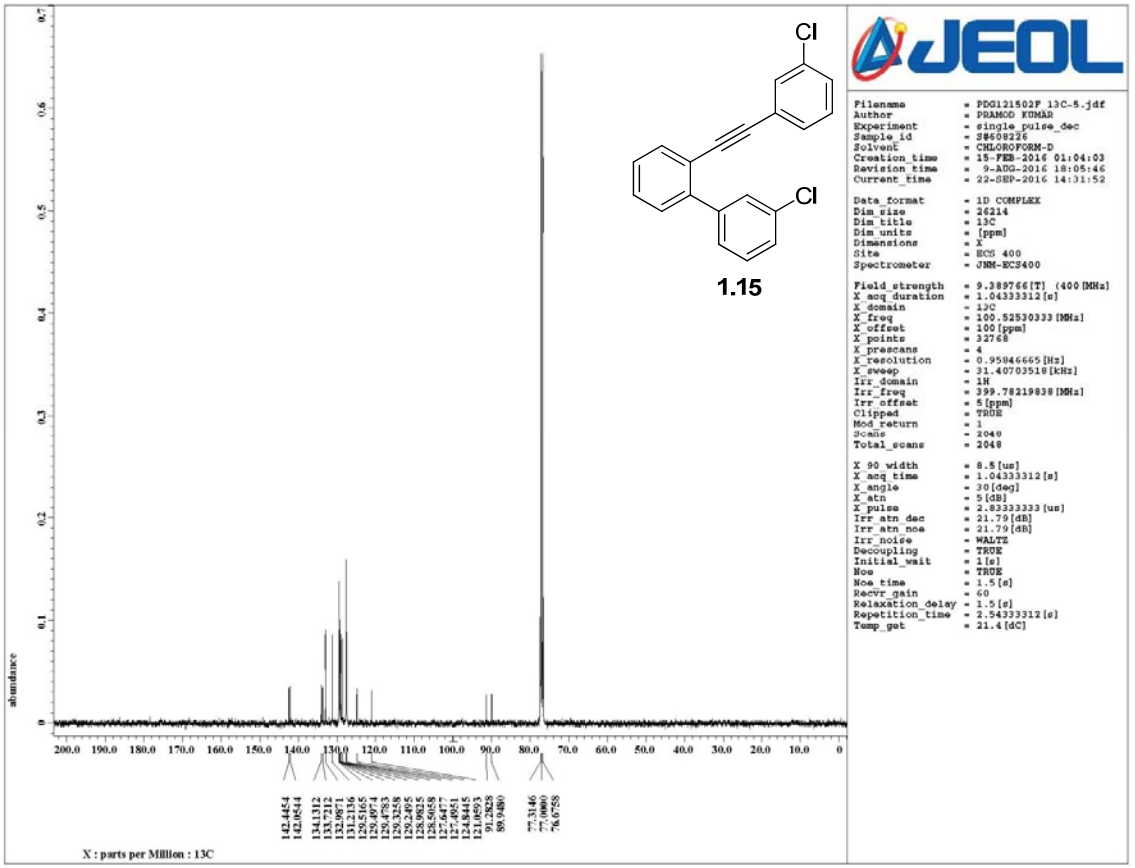
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1.14**



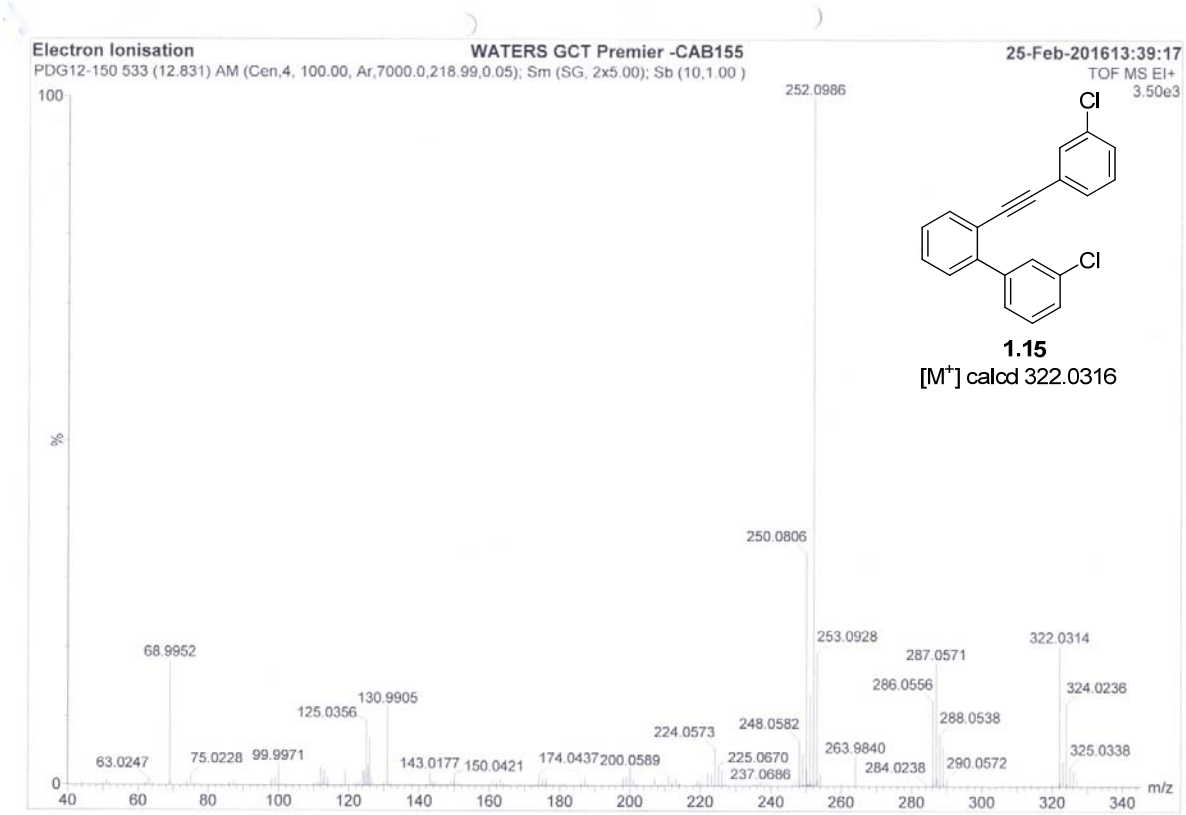
EI (HRMS) spectrum of **1.14**



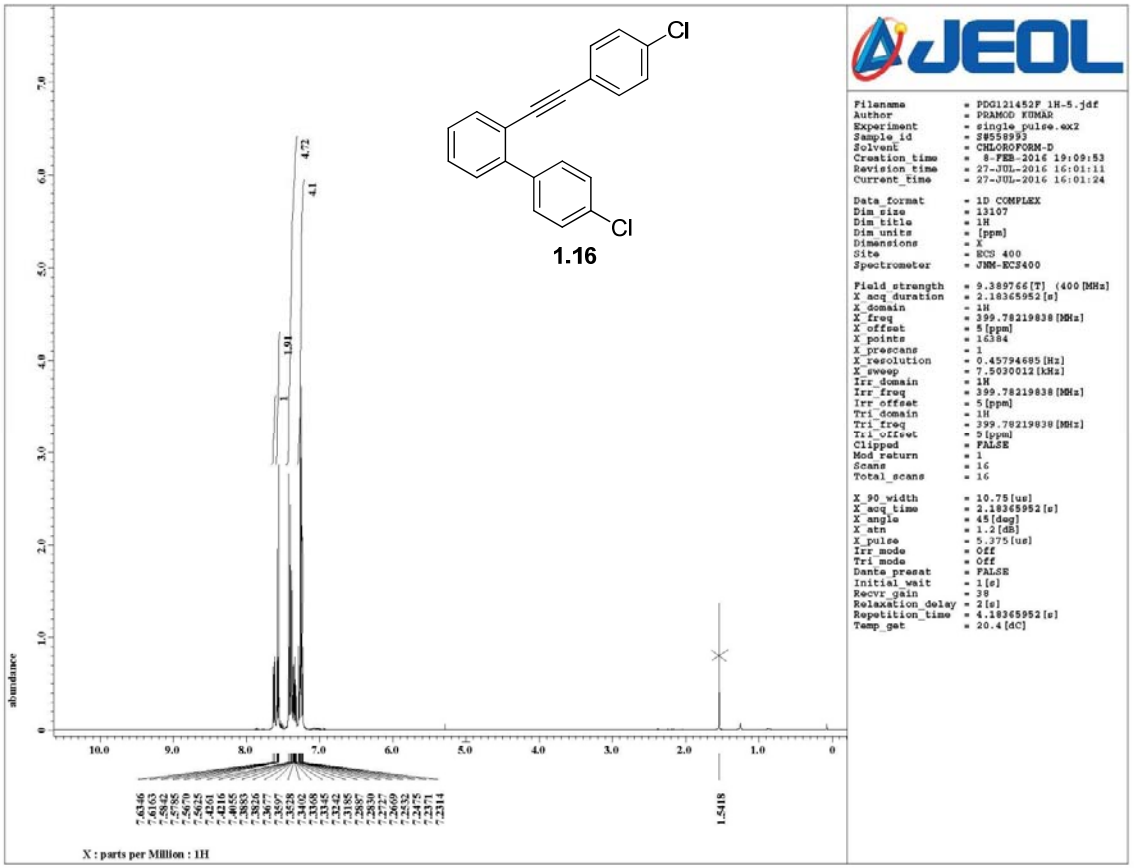
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1.15**



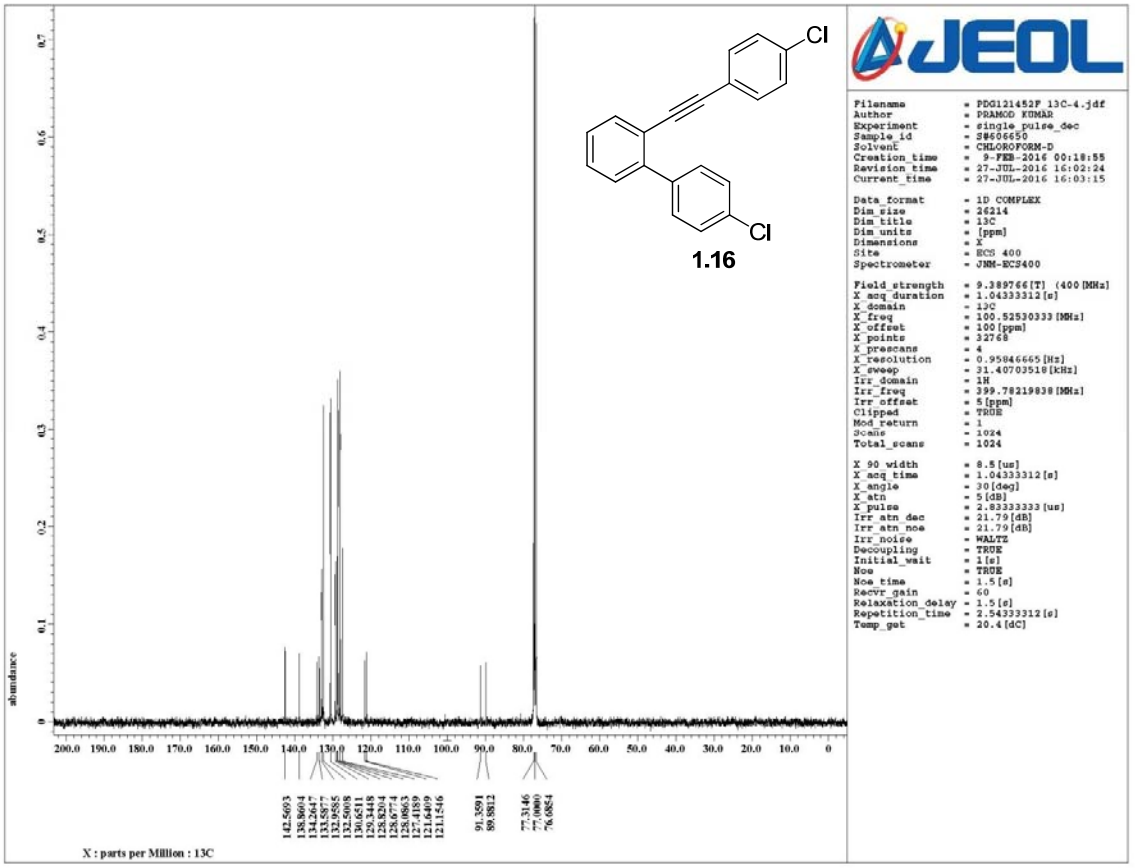
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1.15**



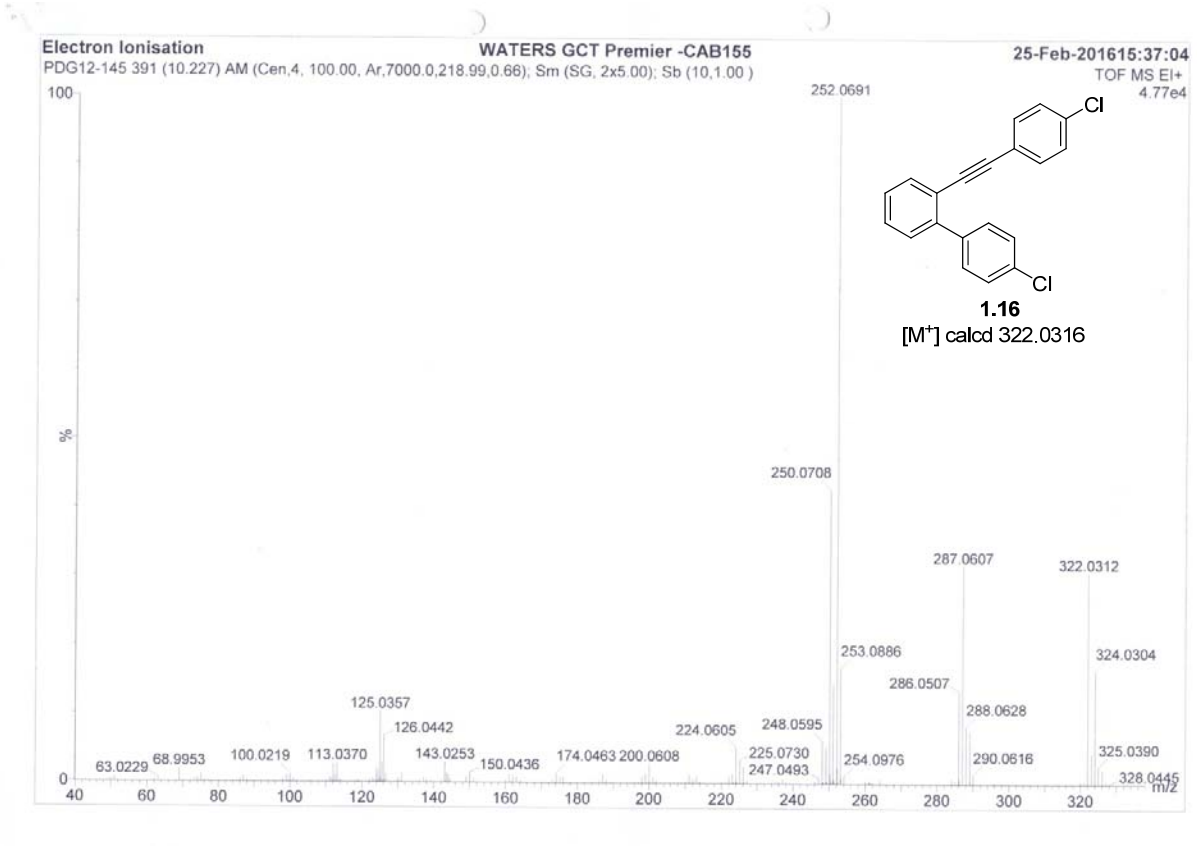
EI (HRMS) spectrum of **1.15**



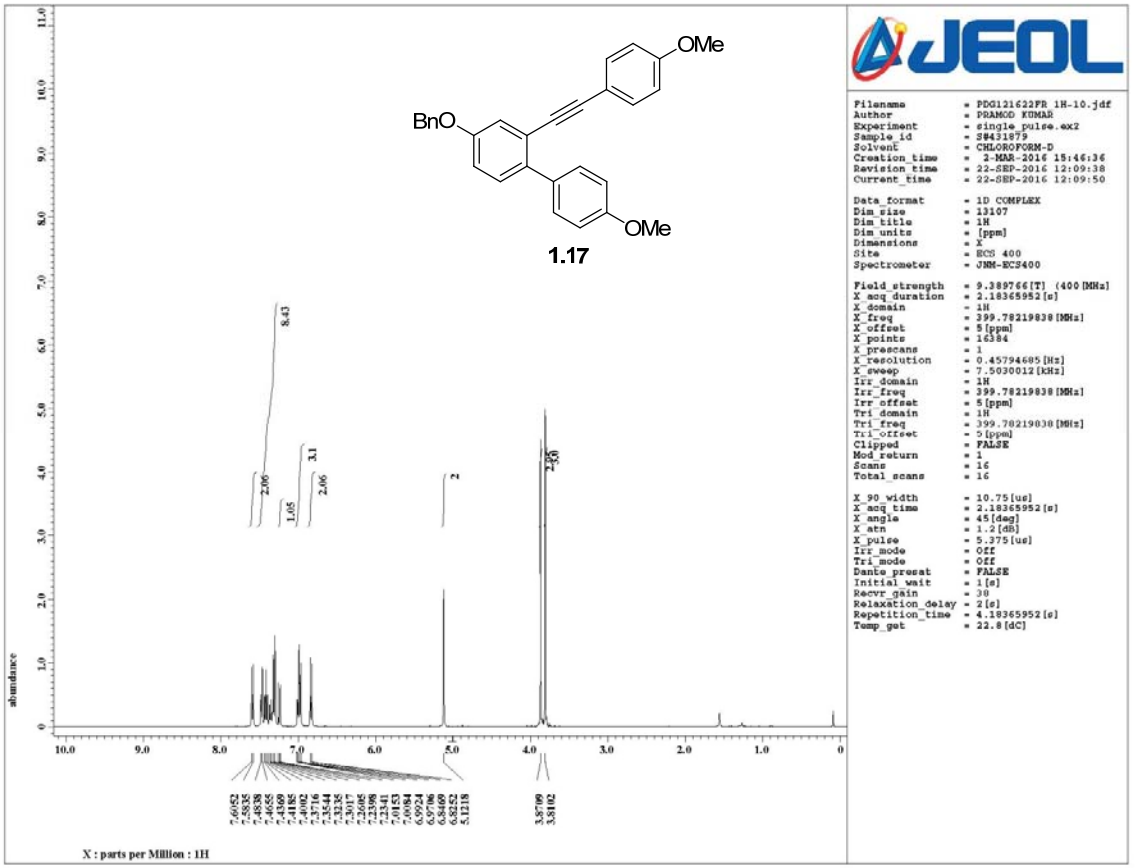
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1.16**



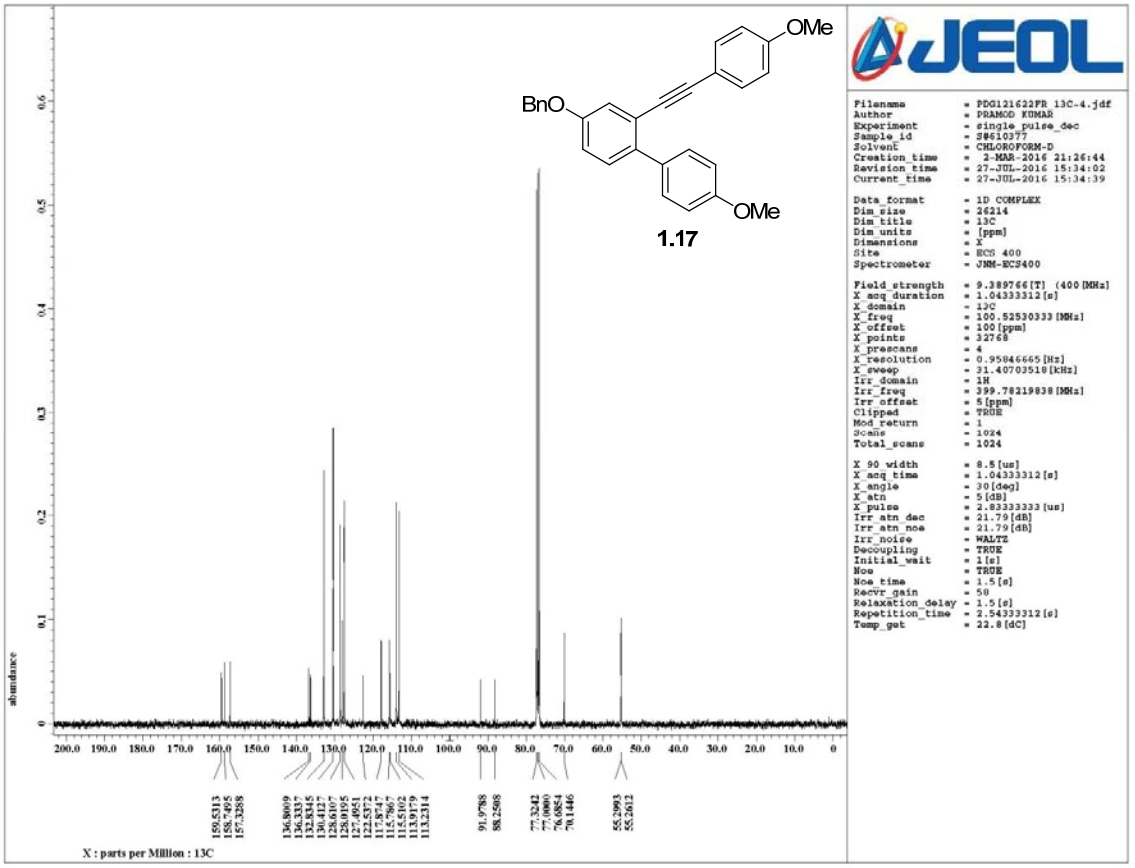
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1.16**



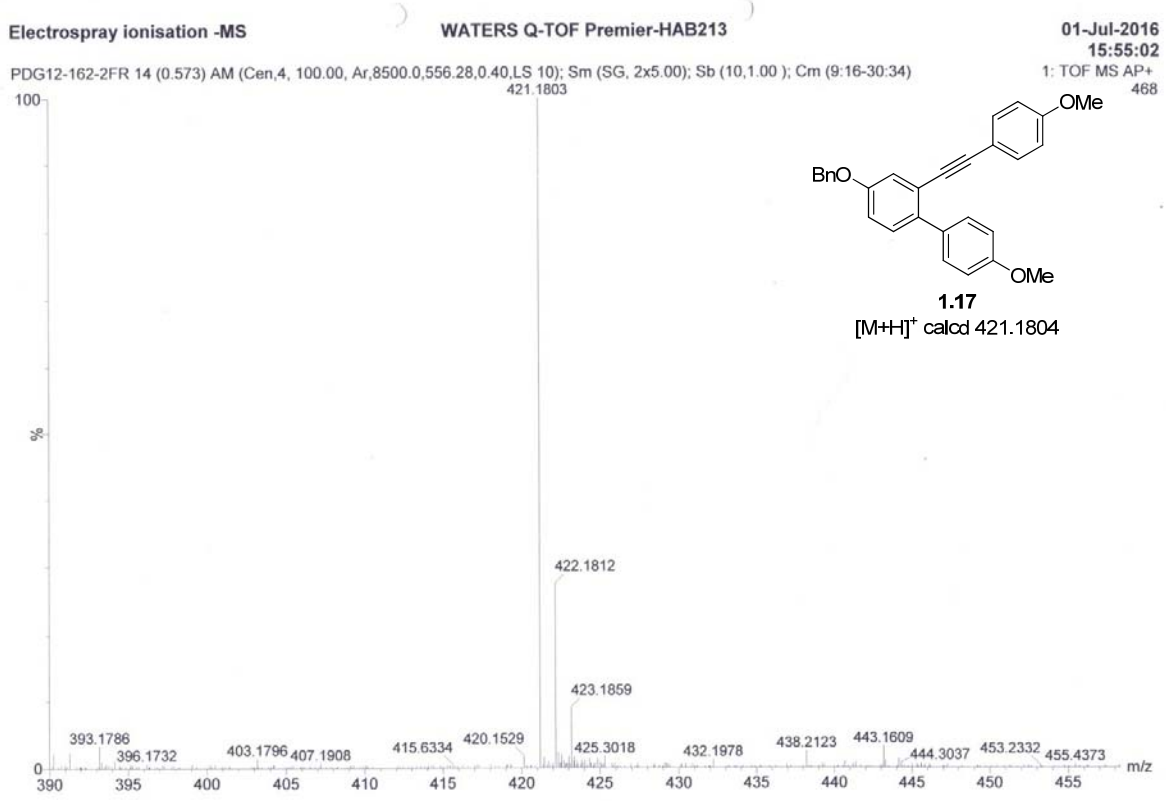
EI (HRMS) spectrum of **1.16**



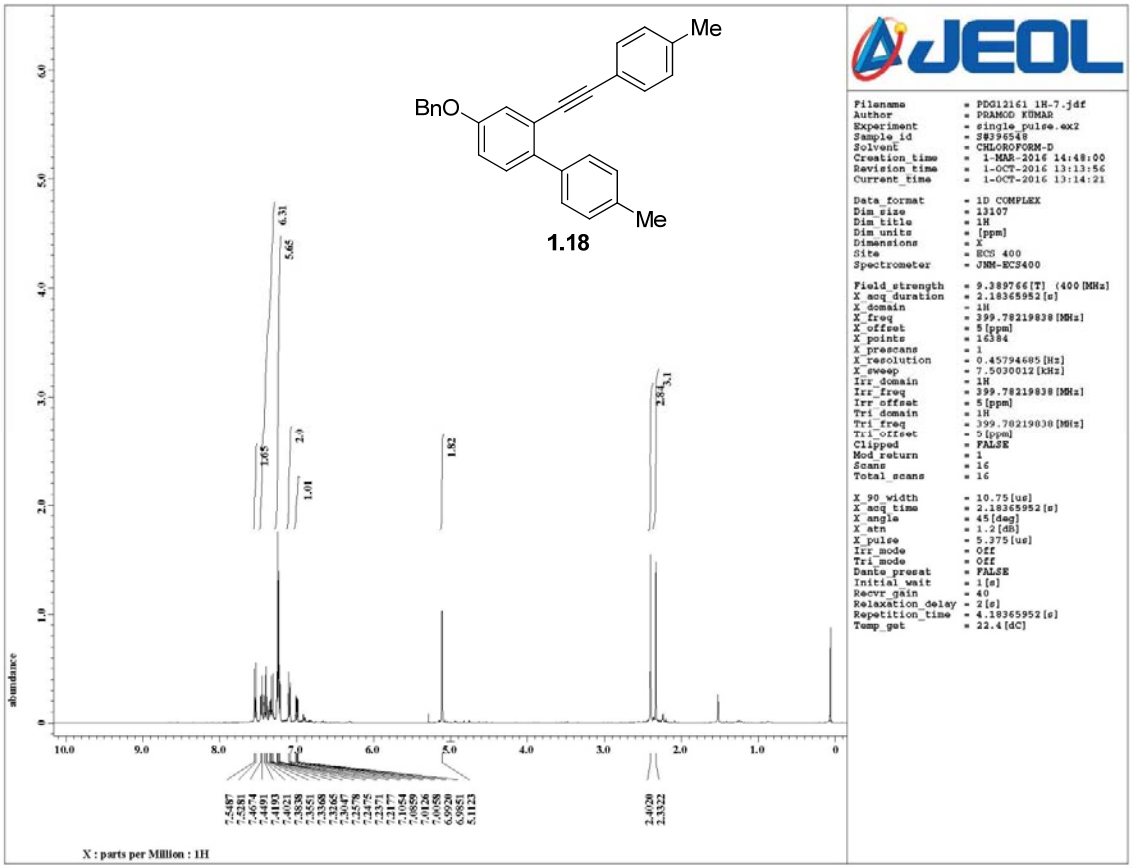
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1.17**



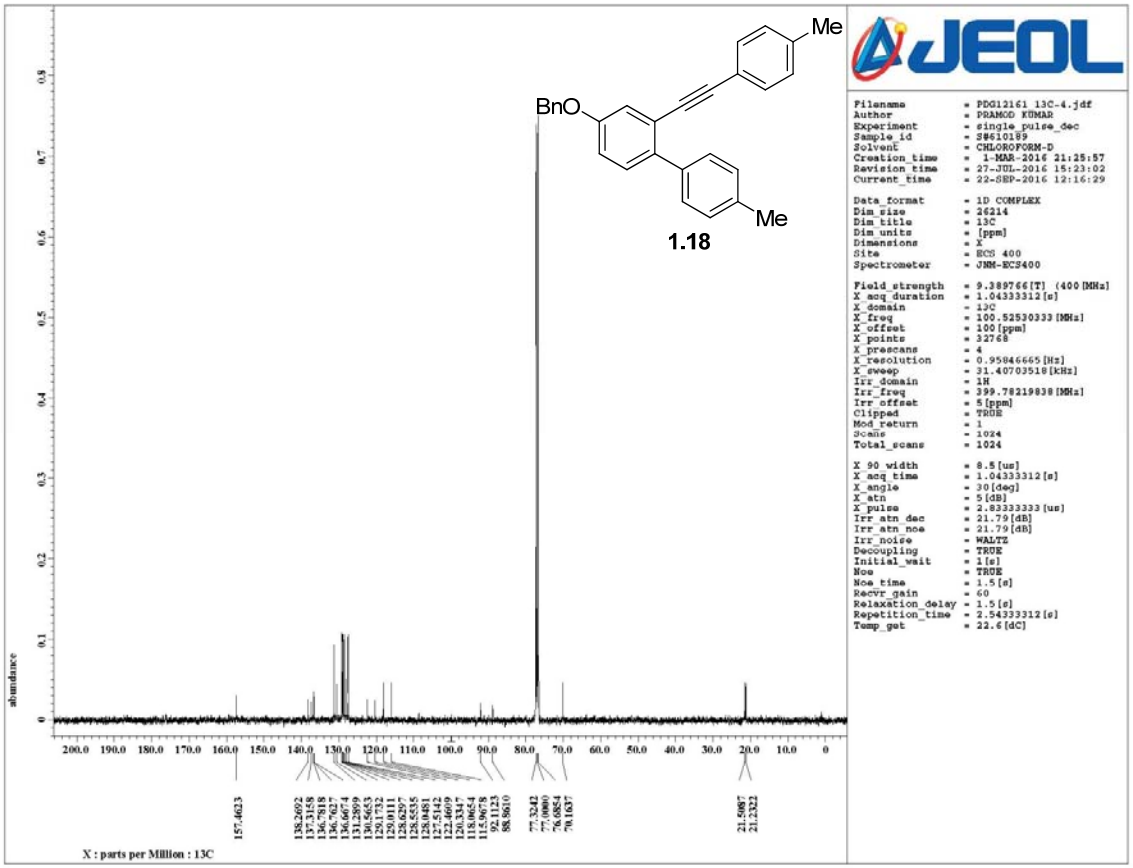
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1.17**



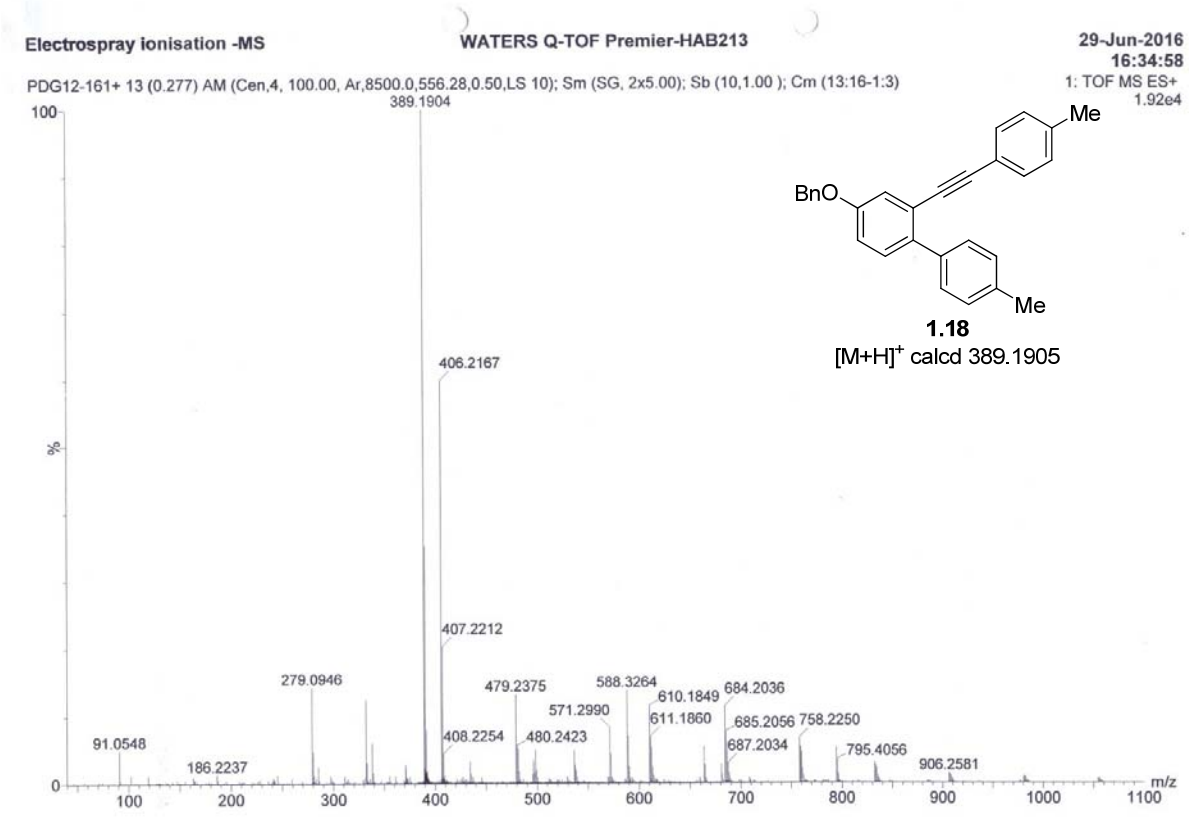
APCI (HRMS) spectrum of **1.17**



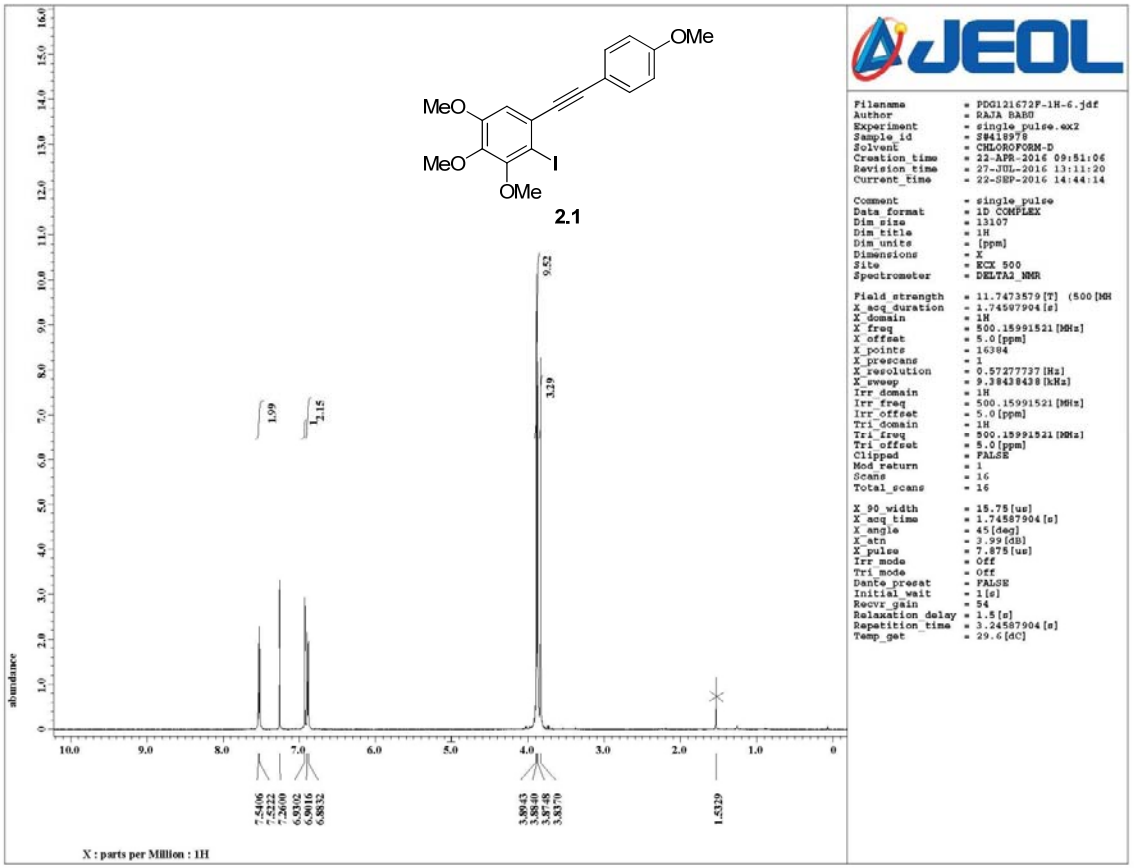
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1.18**



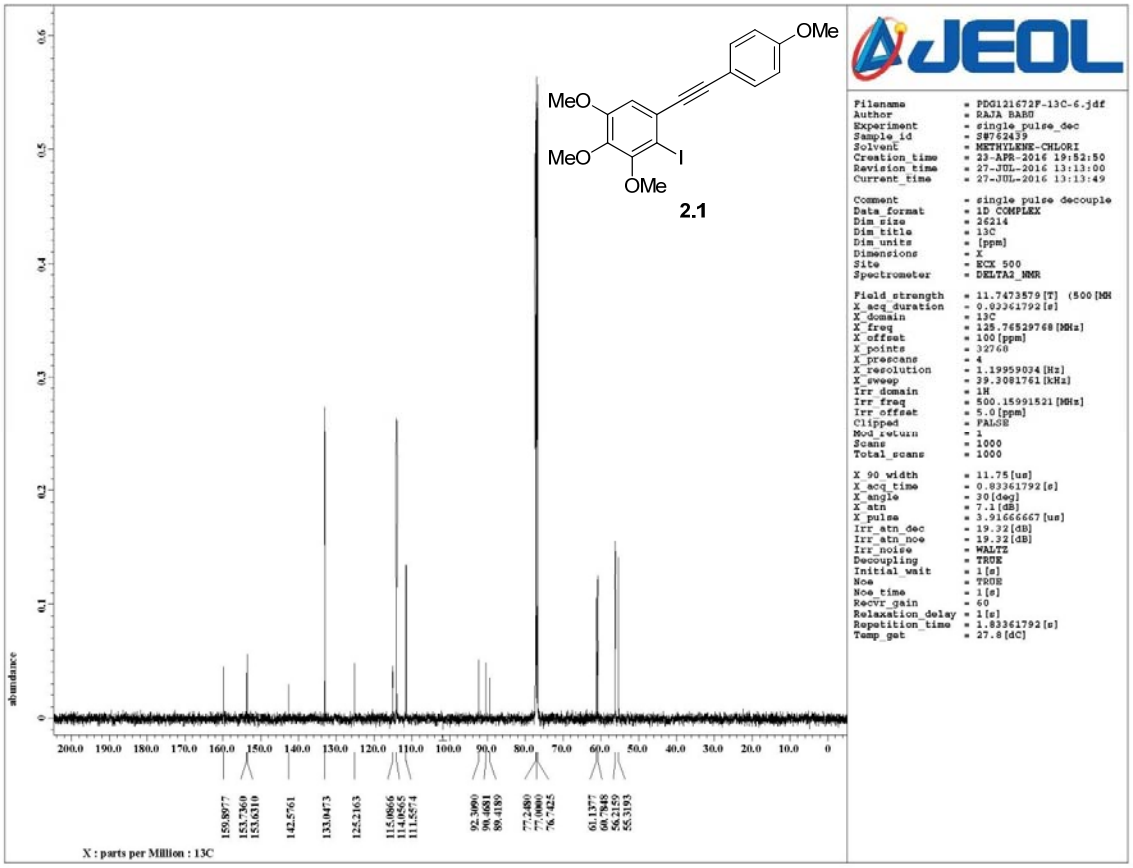
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1.18**



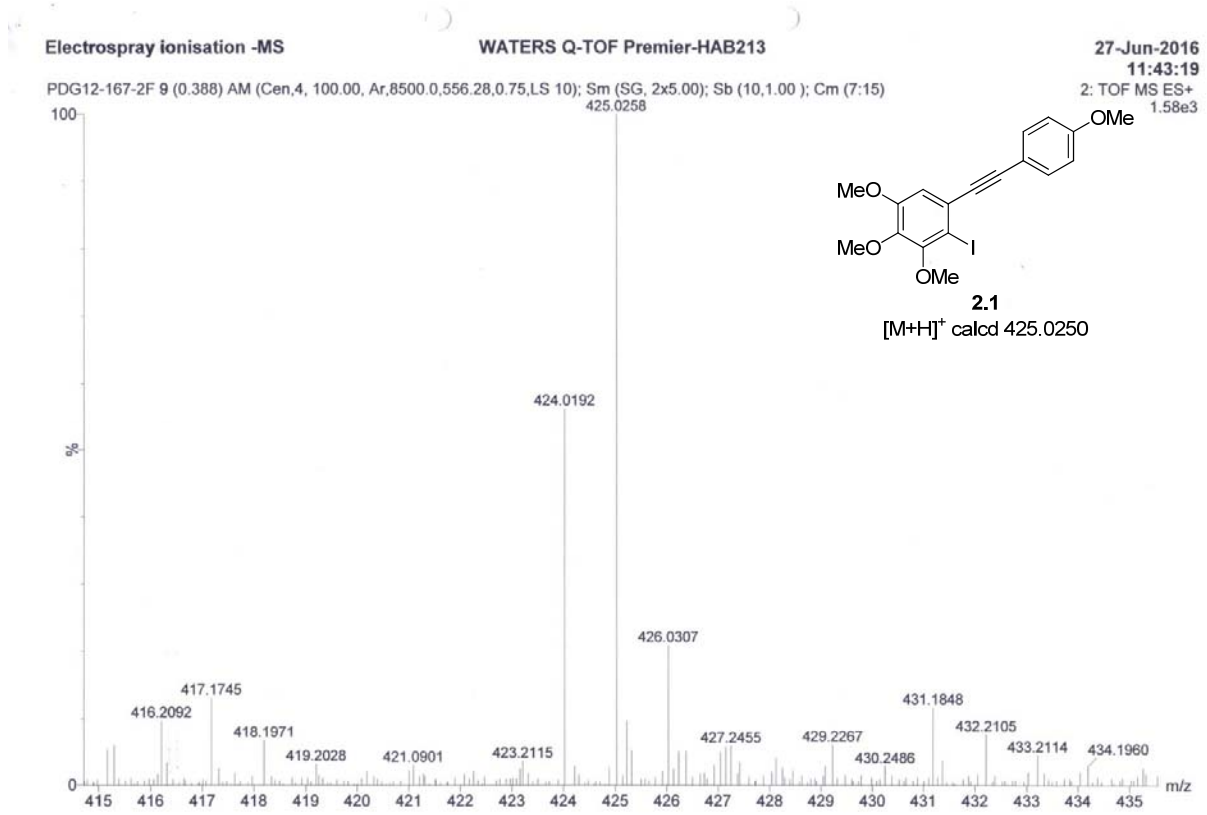
ESI (HRMS) spectrum of **1.18**



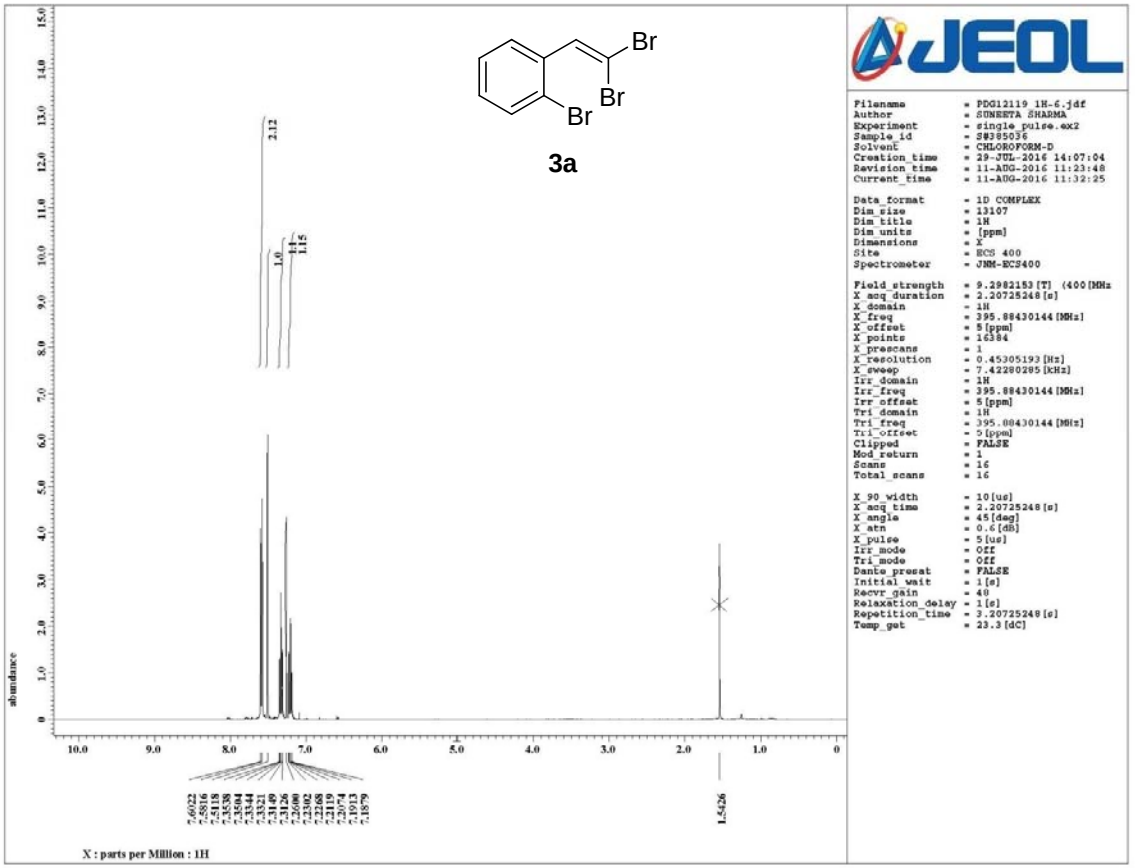
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2.1**



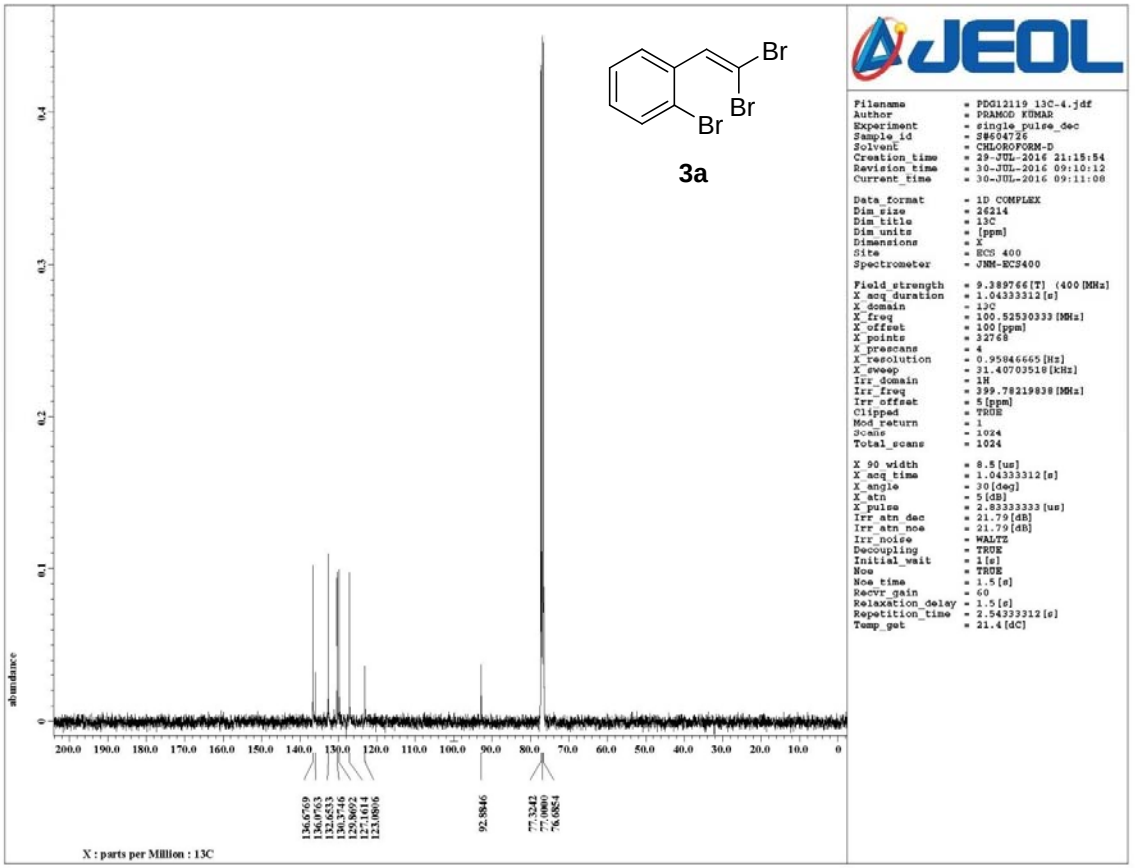
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2.1**



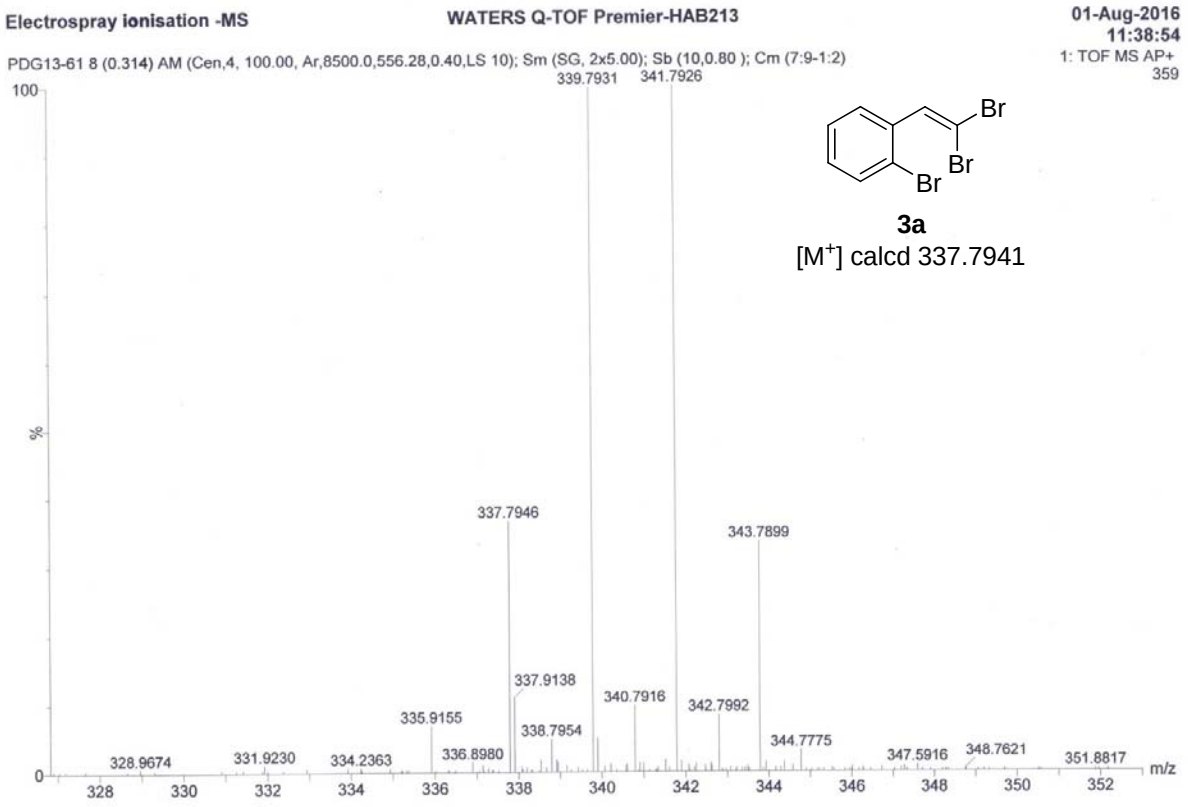
ESI (HRMS) spectrum of **2.1**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a**



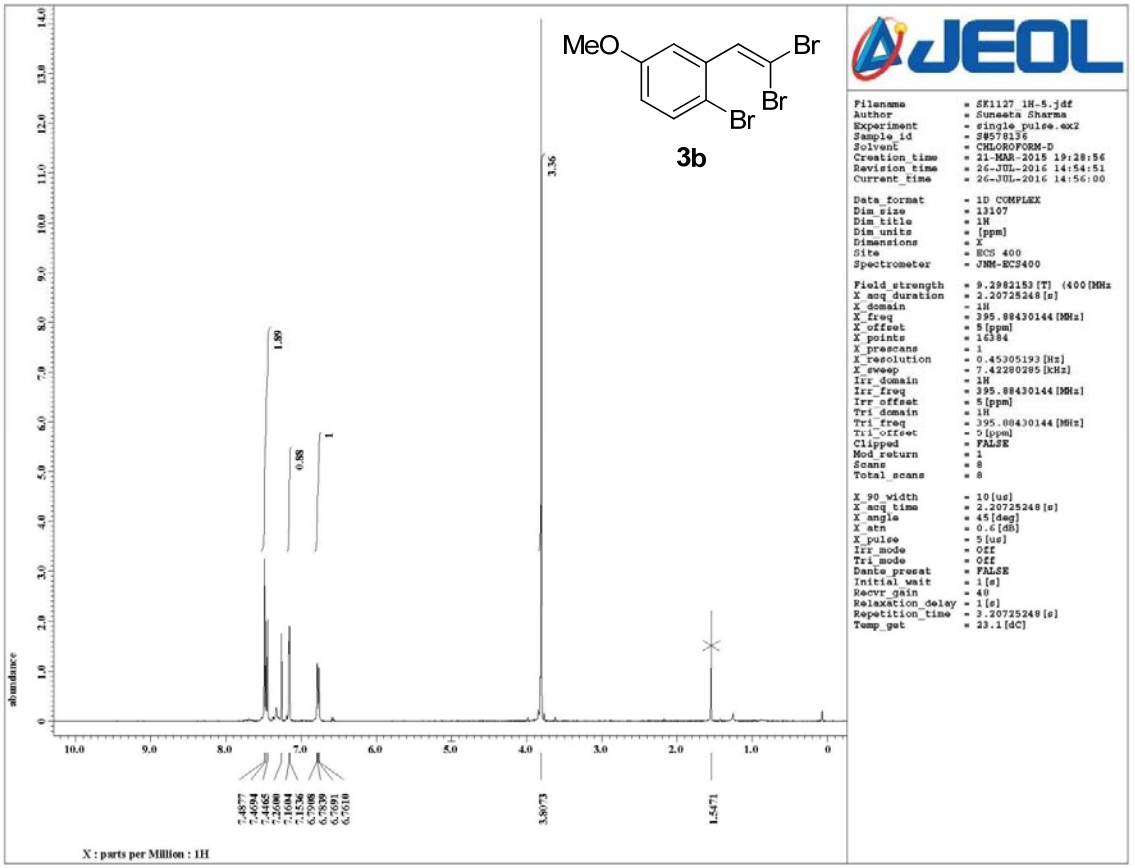
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3a**



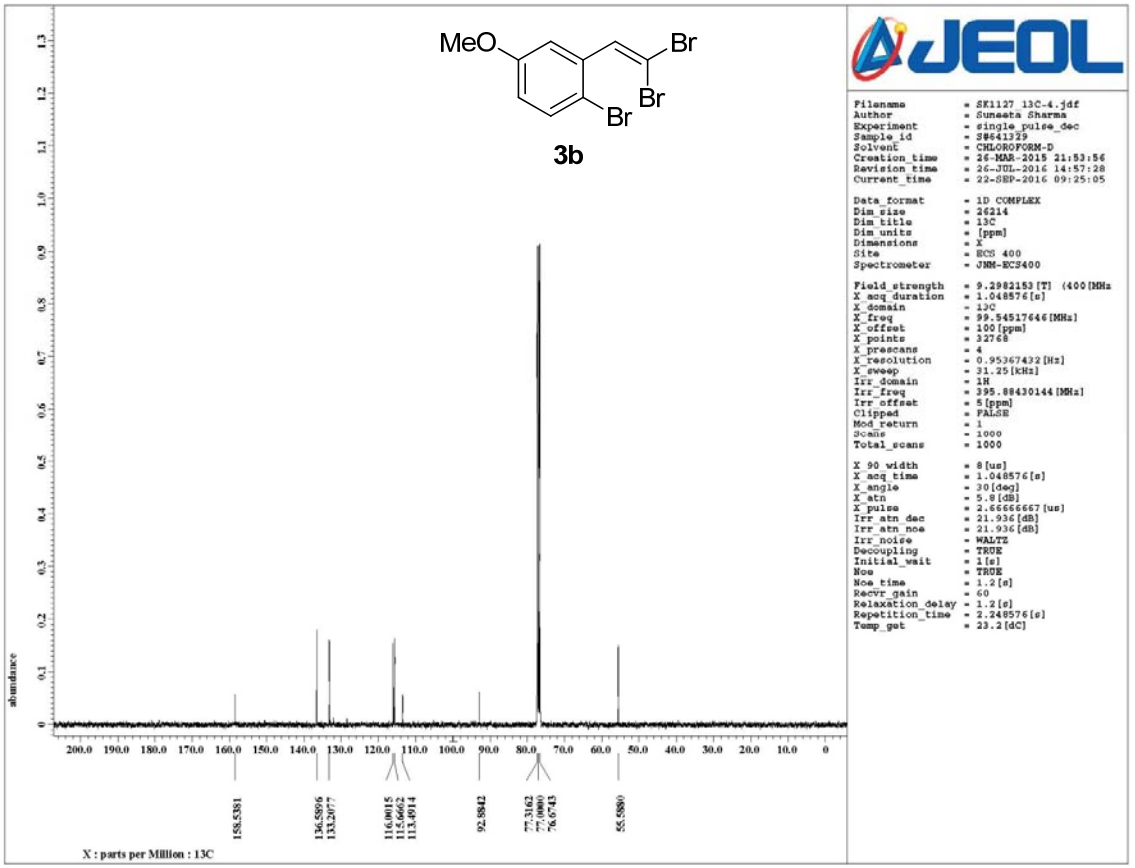
3a

[M^+] calcd 337.7941

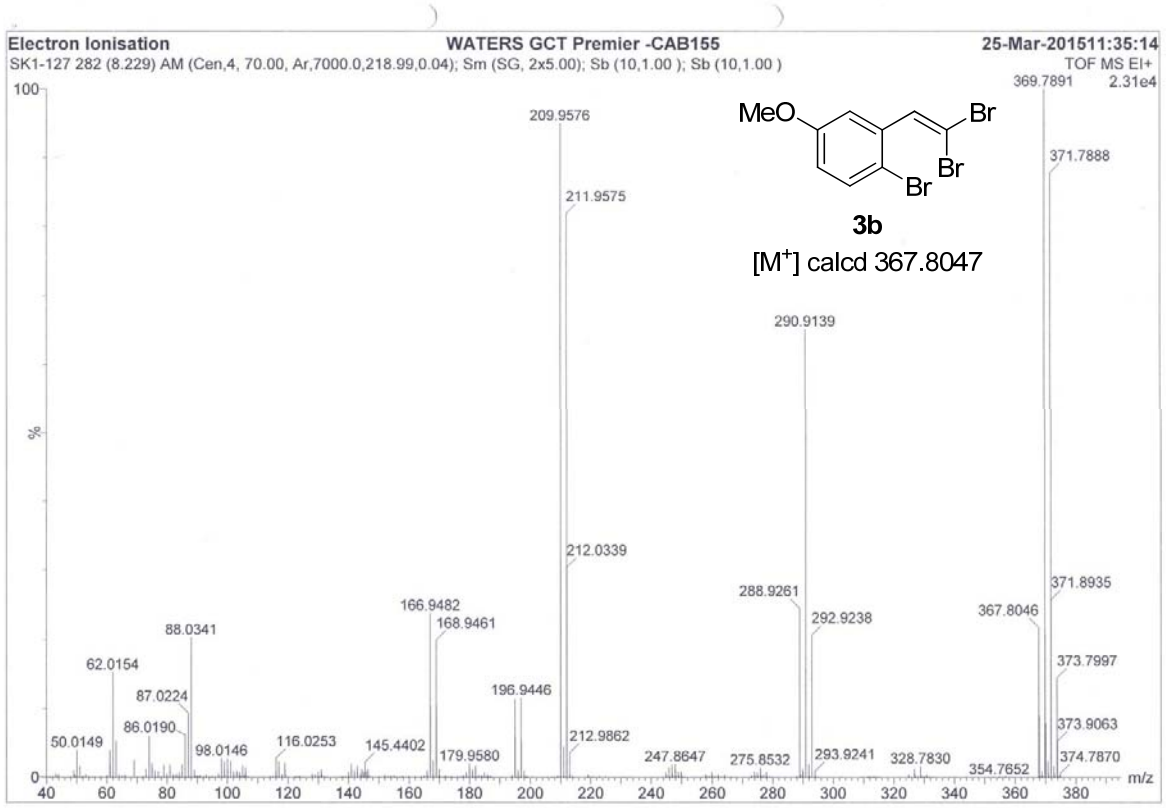
APCI (HRMS) spectrum of **3a**



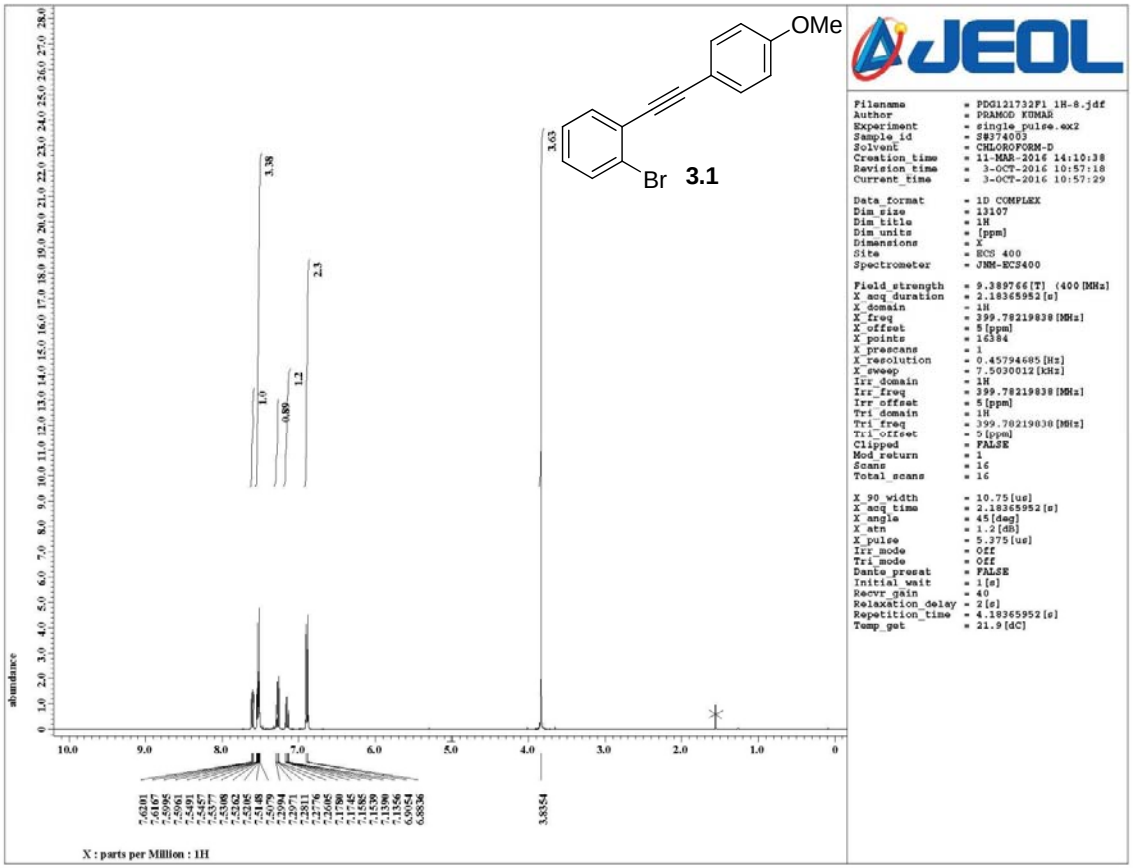
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3b**



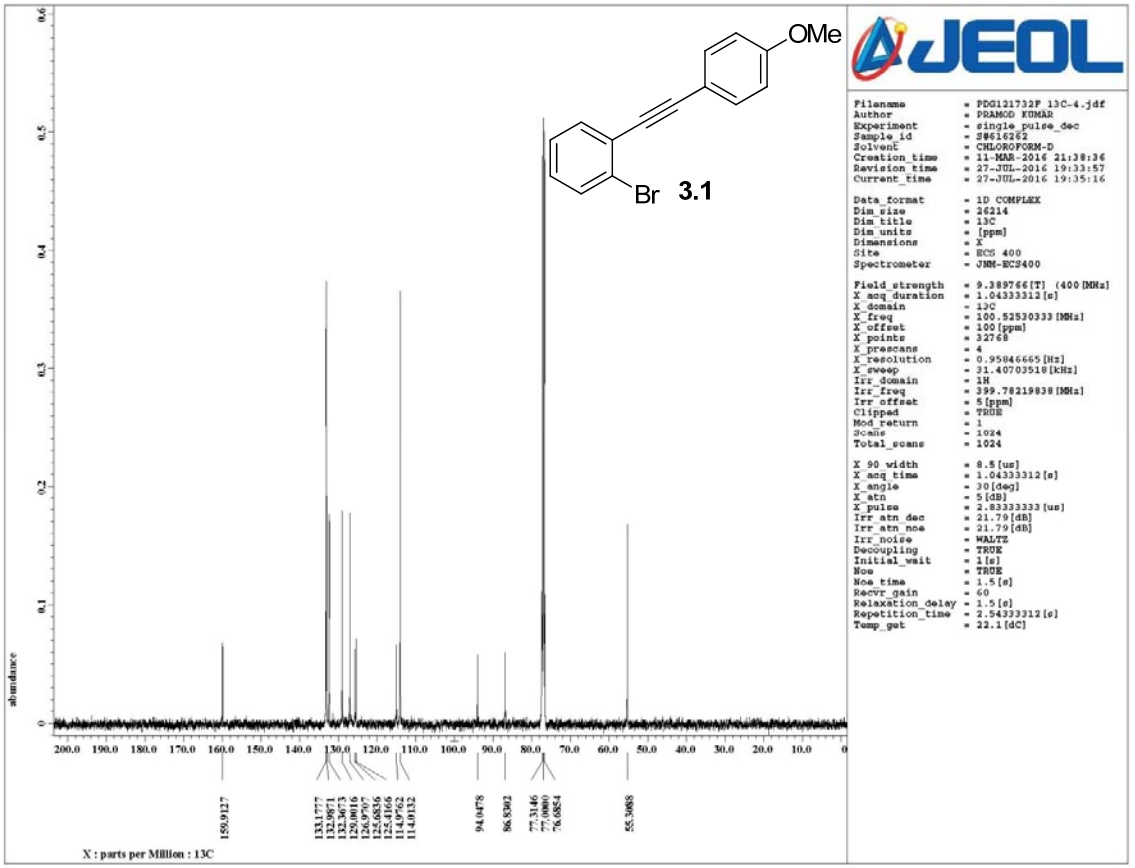
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3b**



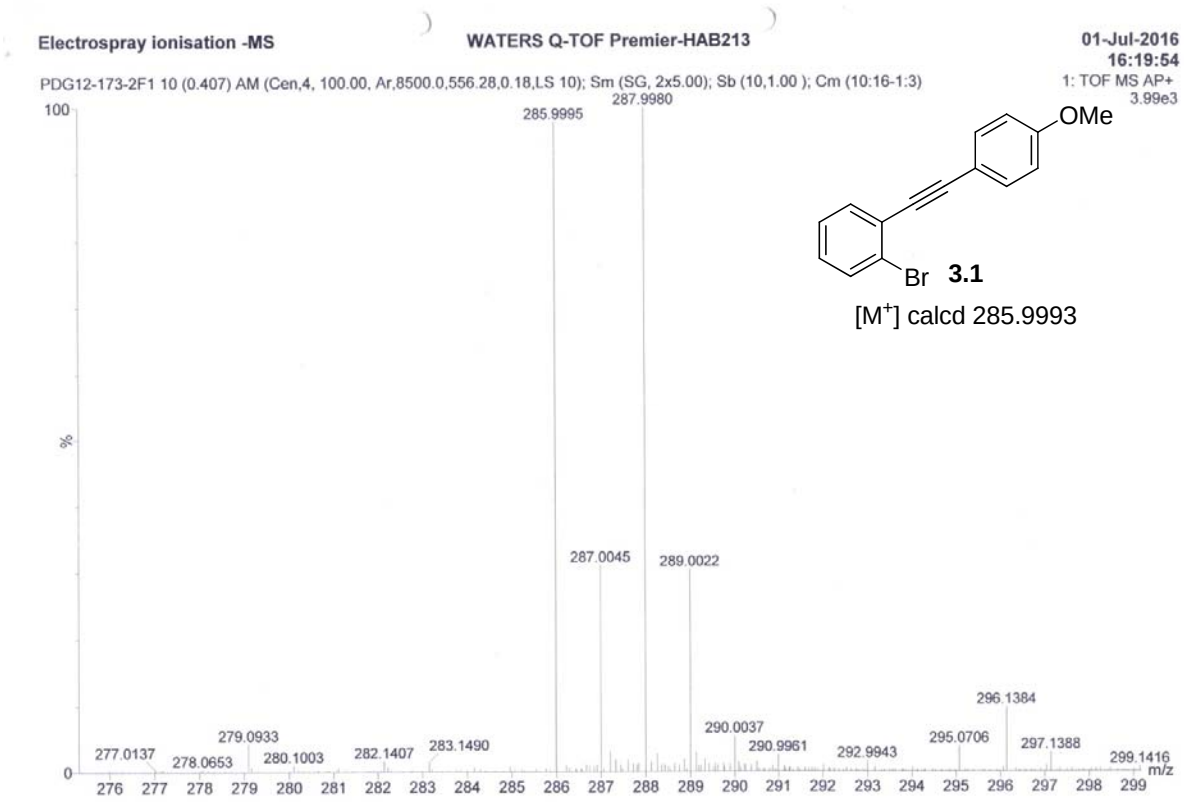
EI (HRMS) spectrum of **3b**



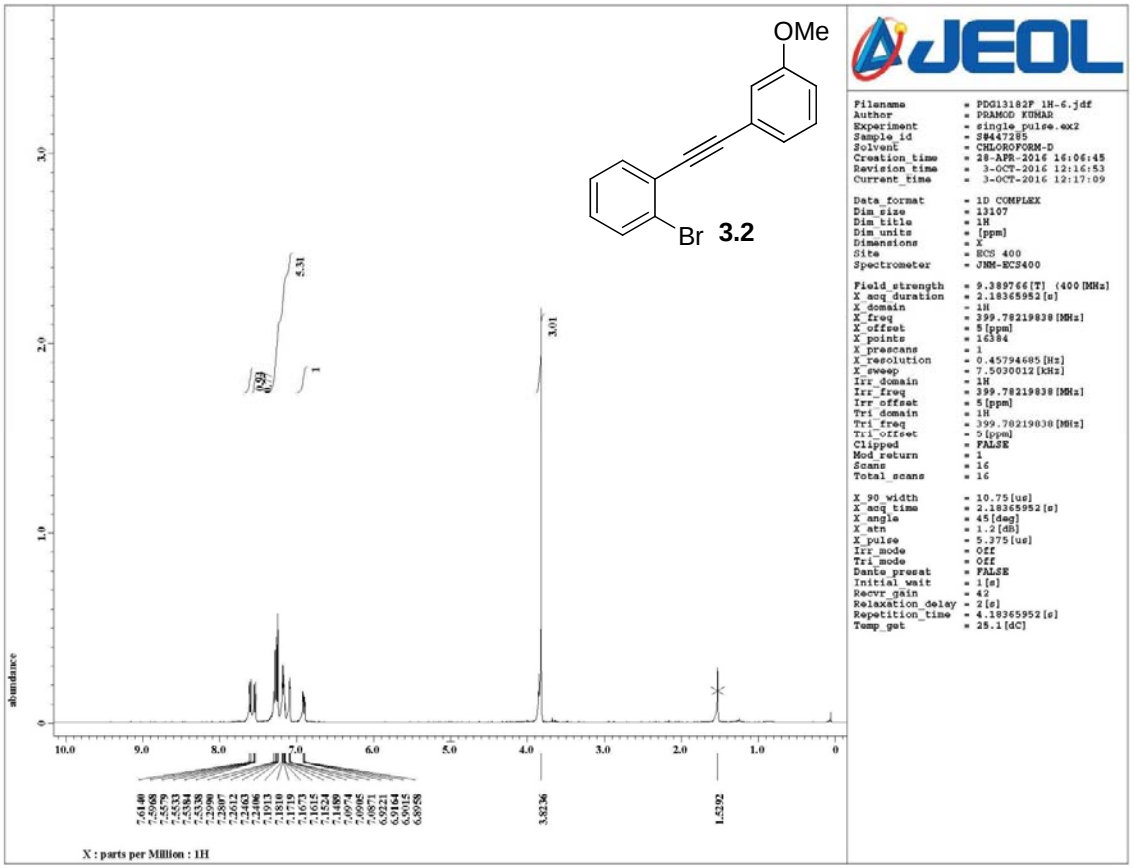
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.1**



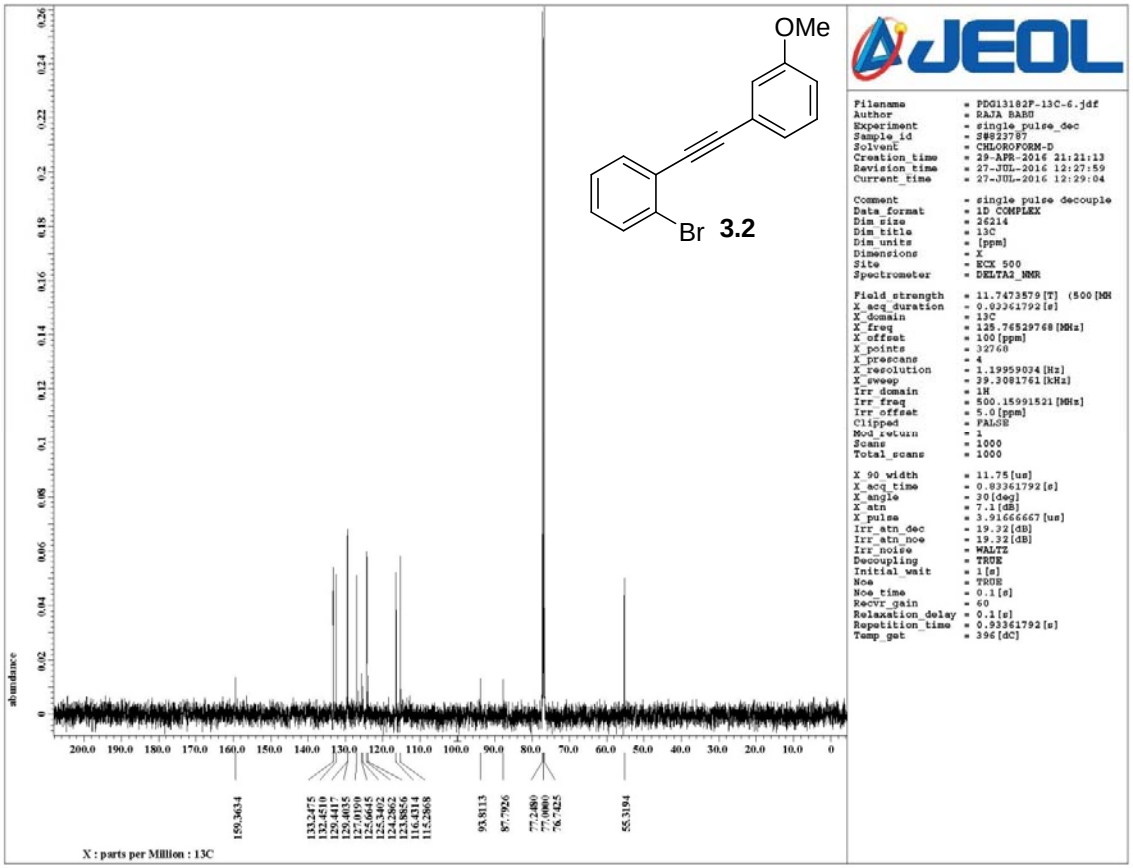
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3.1**



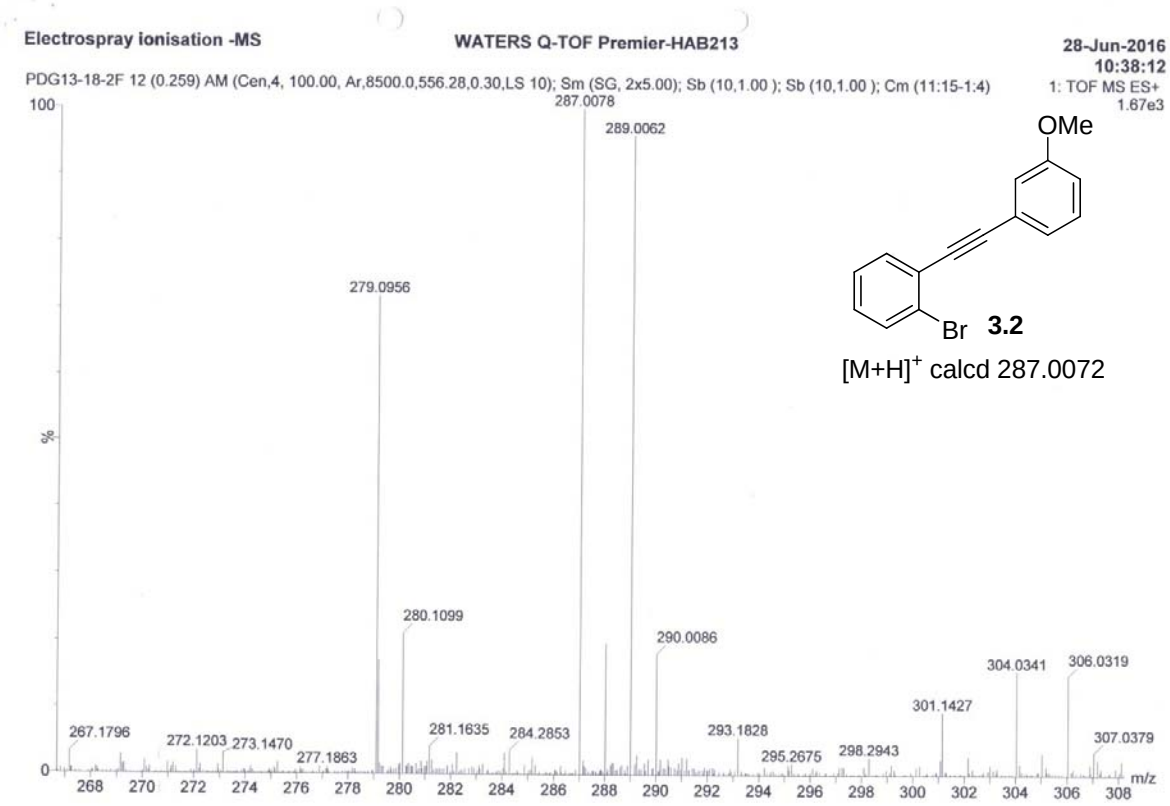
APCI (HRMS) spectrum of **3.1**



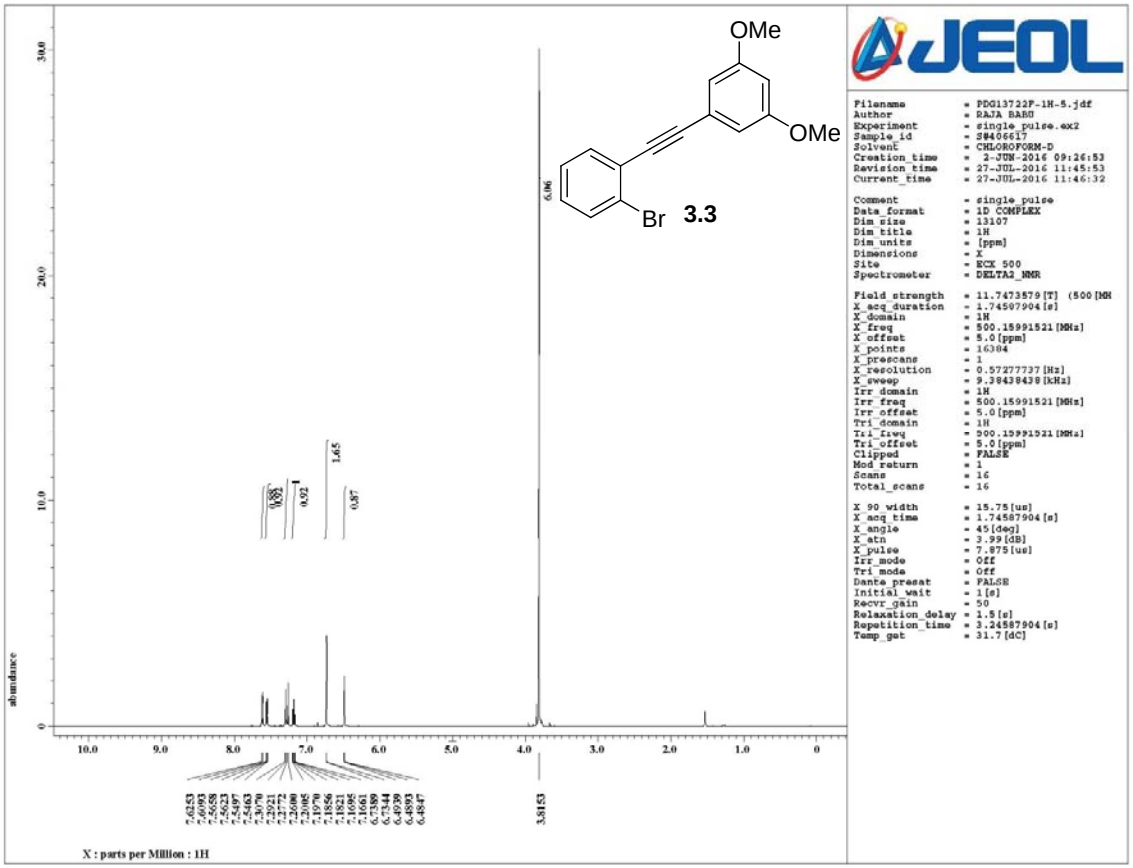
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.2**



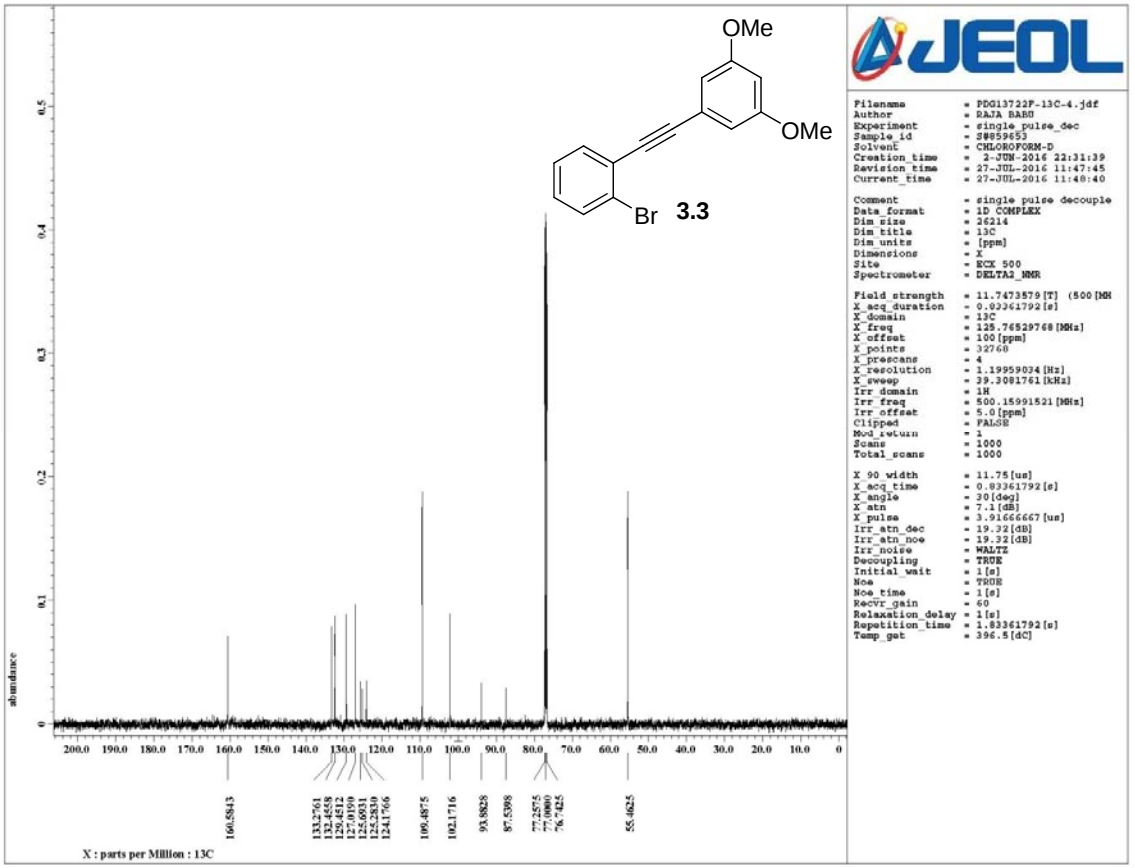
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **3.2**



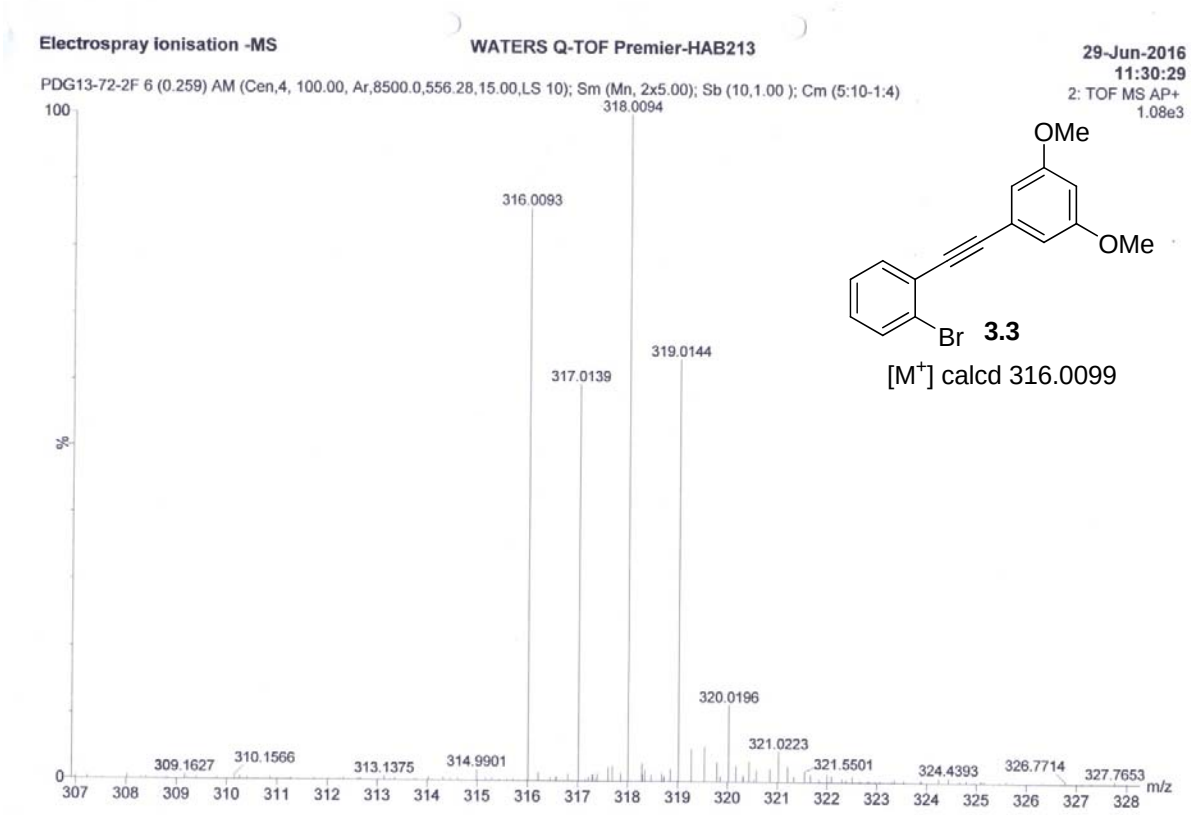
ESI (HRMS) spectrum of **3.2**



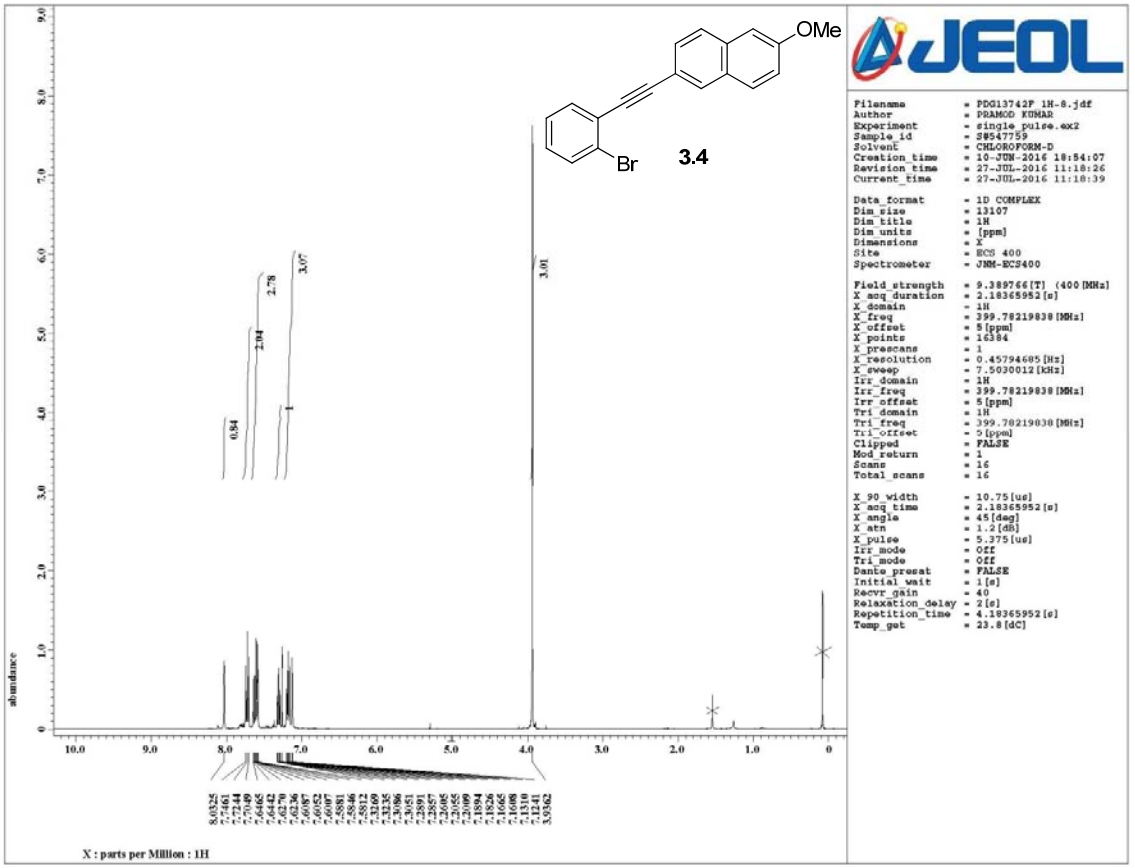
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3.3**



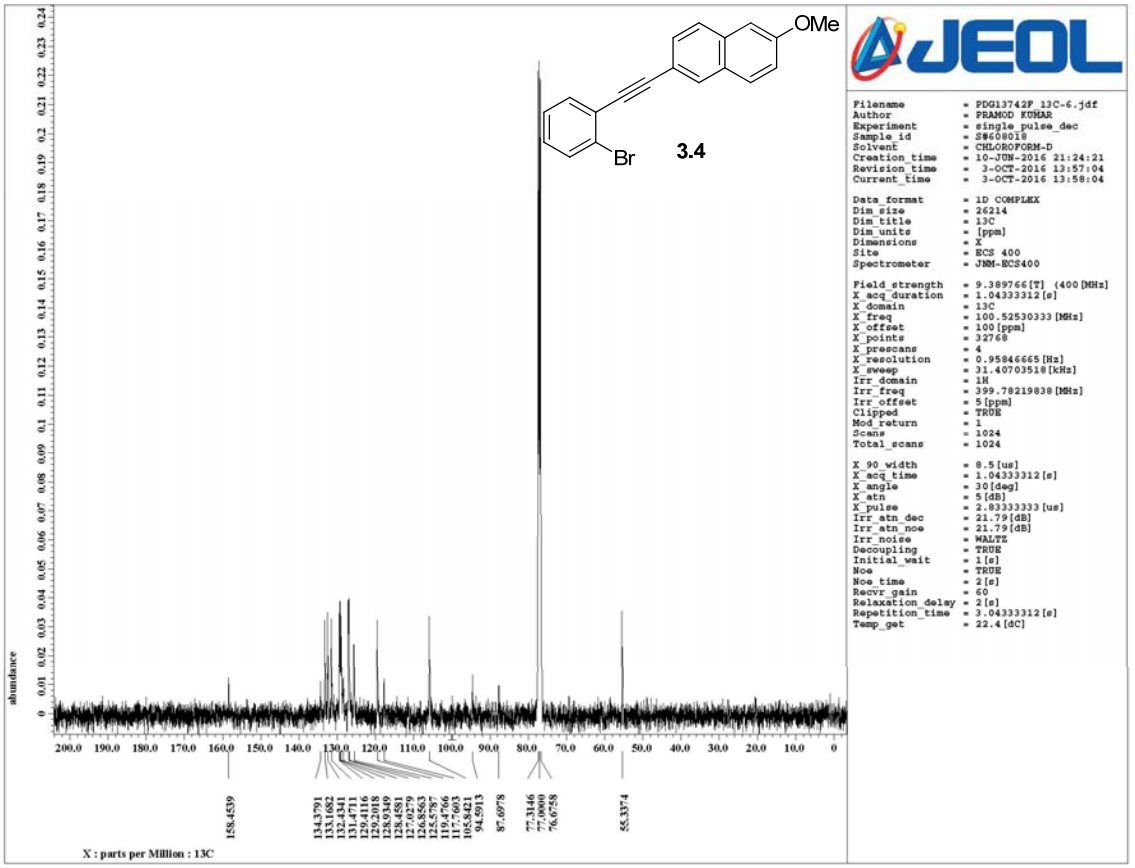
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **3.3**



APCI (HRMS) spectrum of **3.3**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.4**



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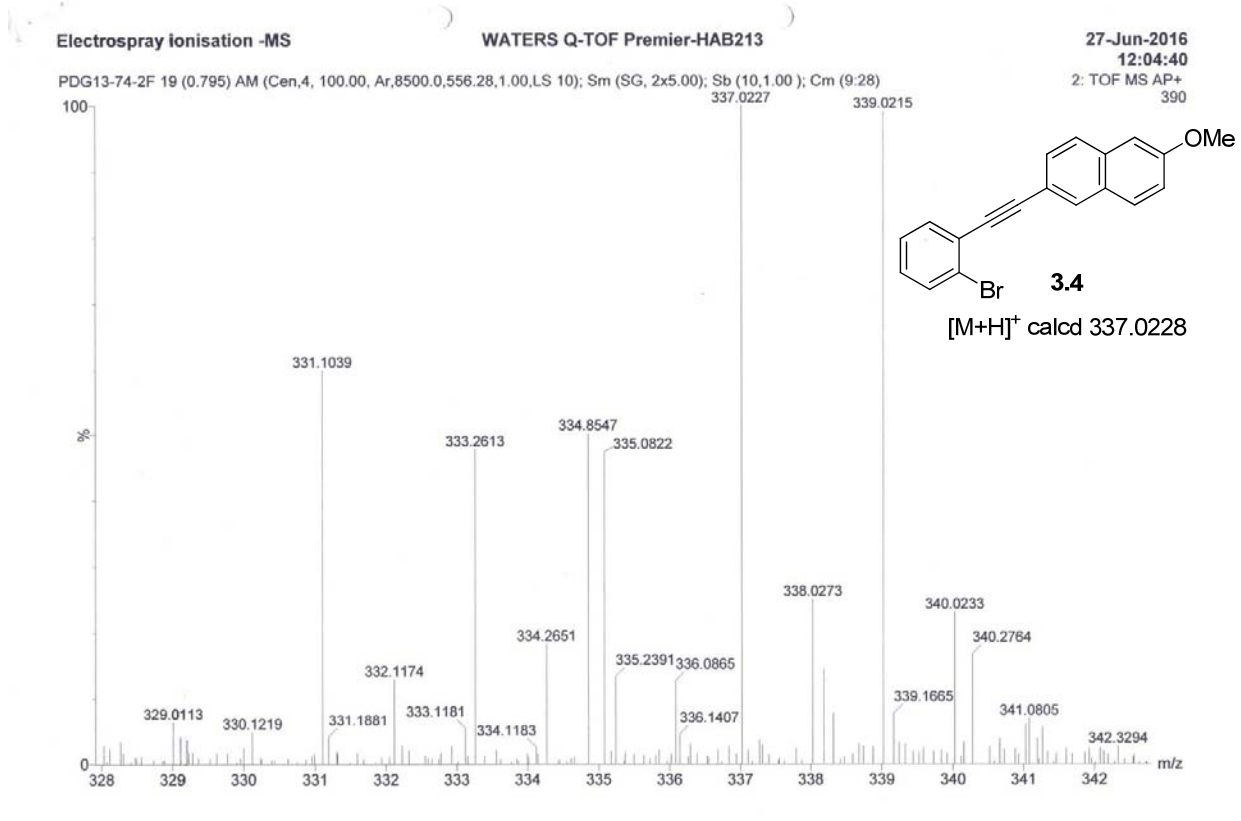
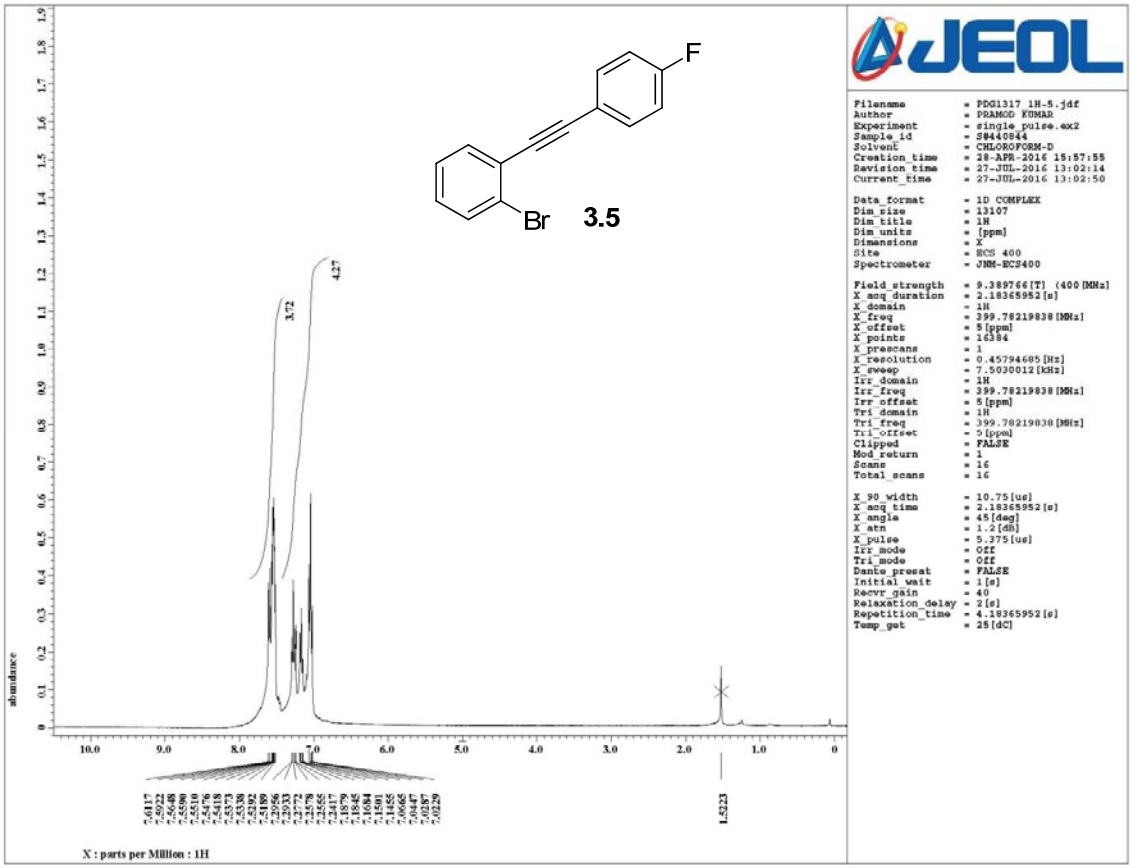
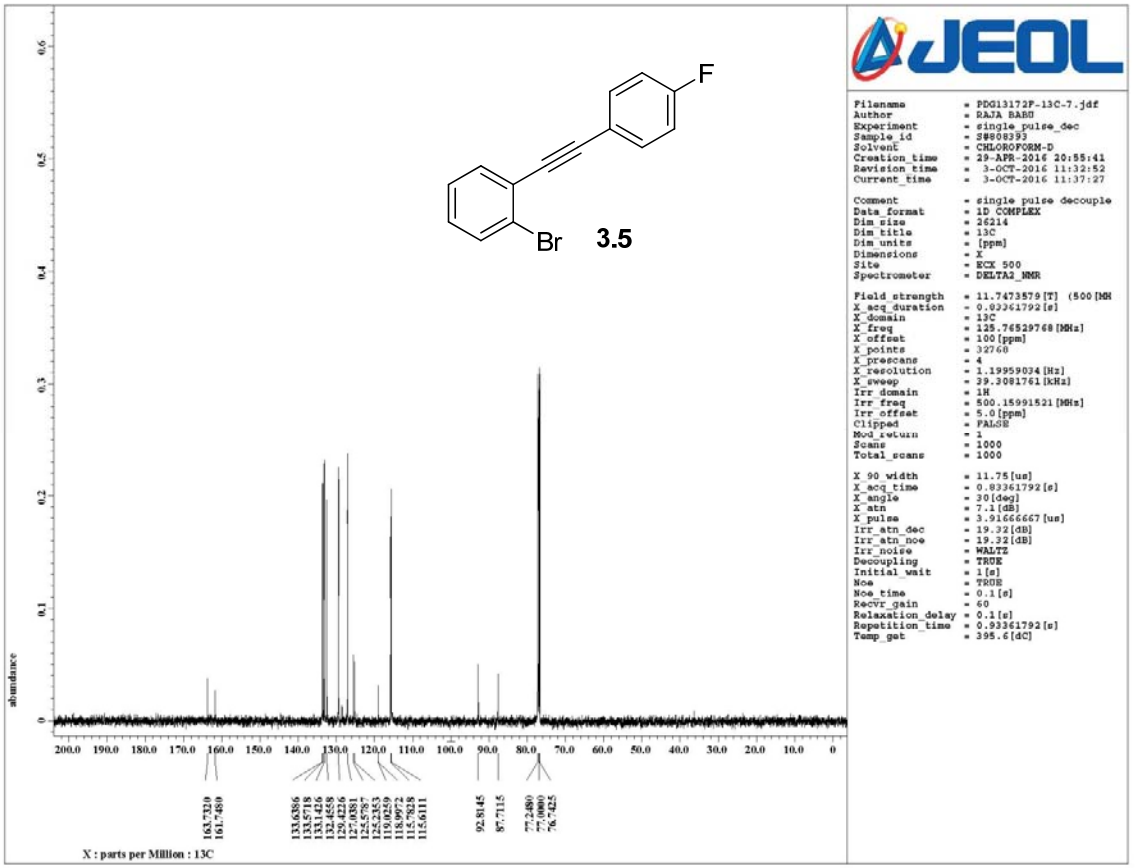
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3.4**



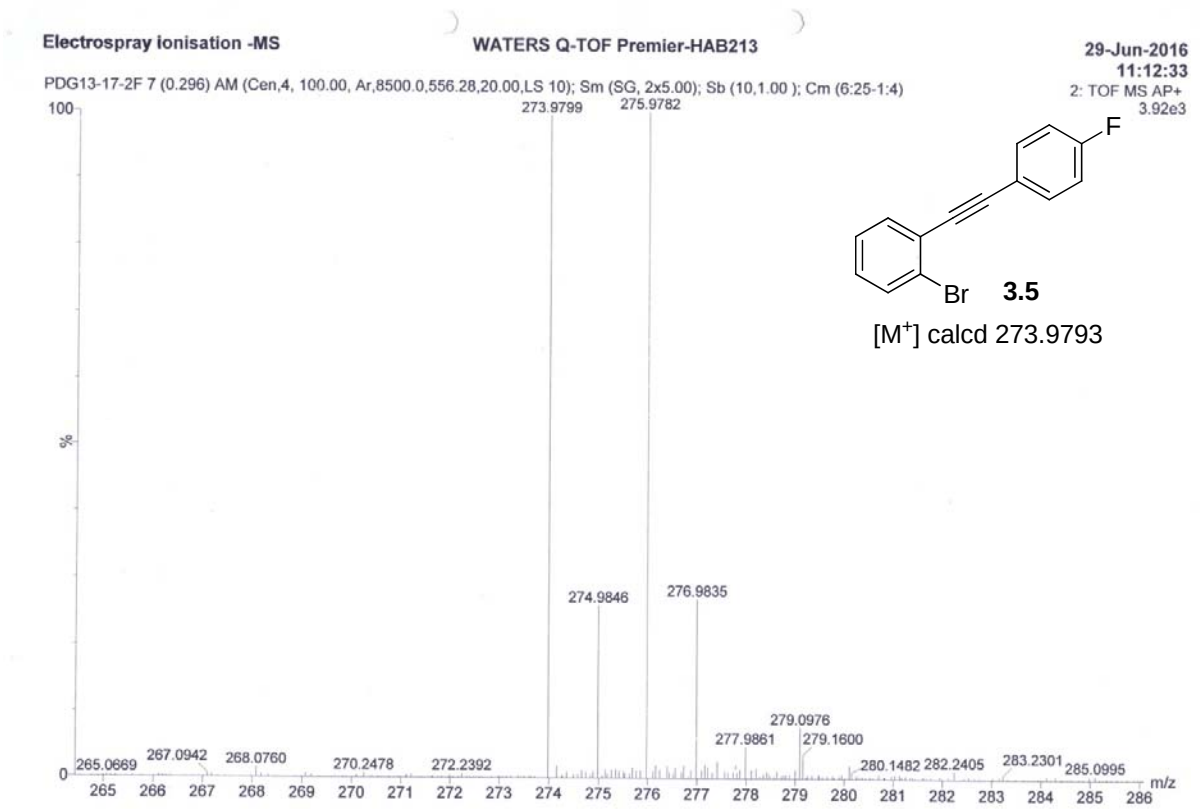
APCI (HRMS) spectrum of **3.4**



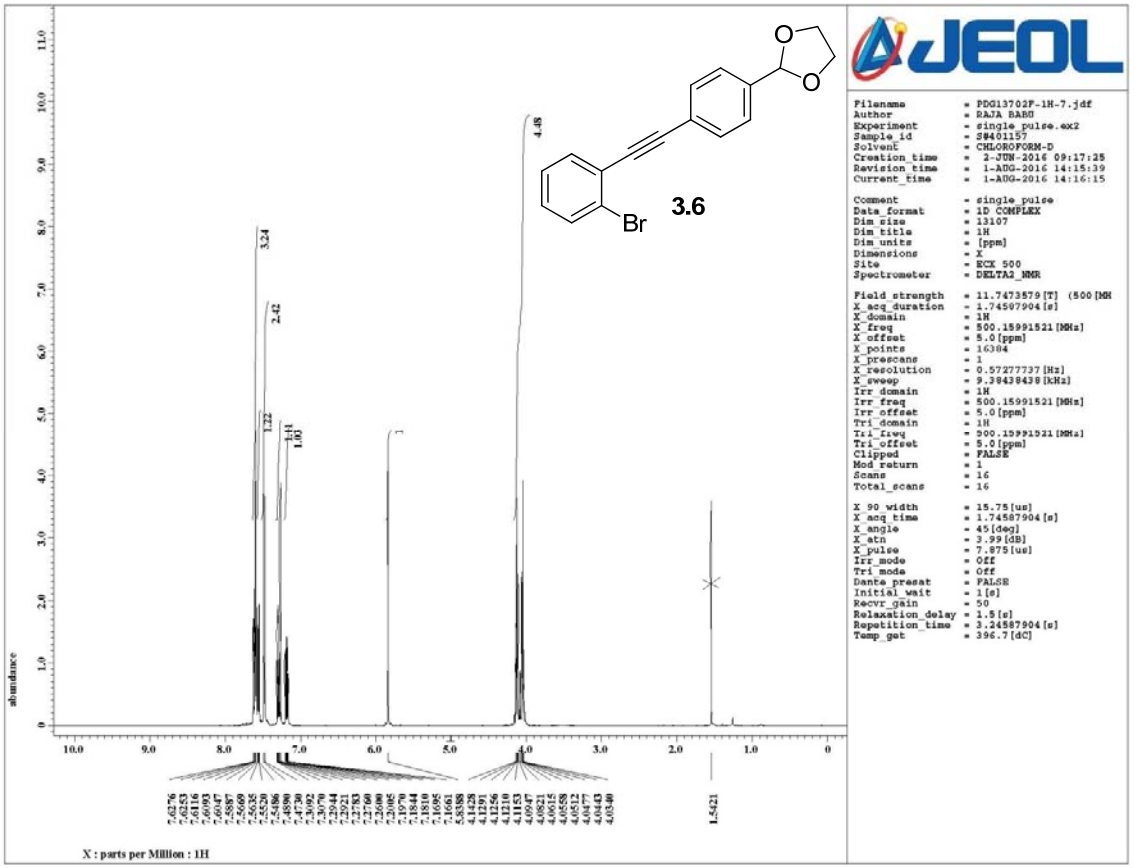
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.5**



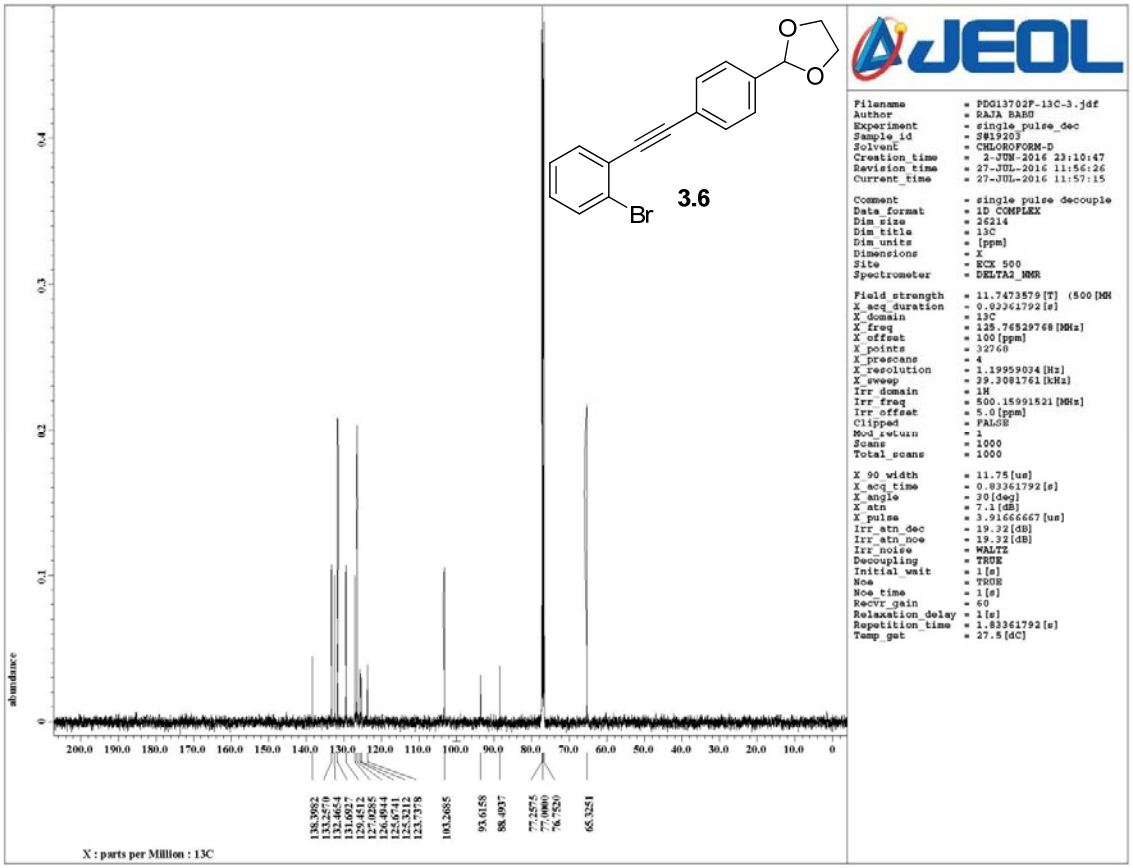
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **3.5**



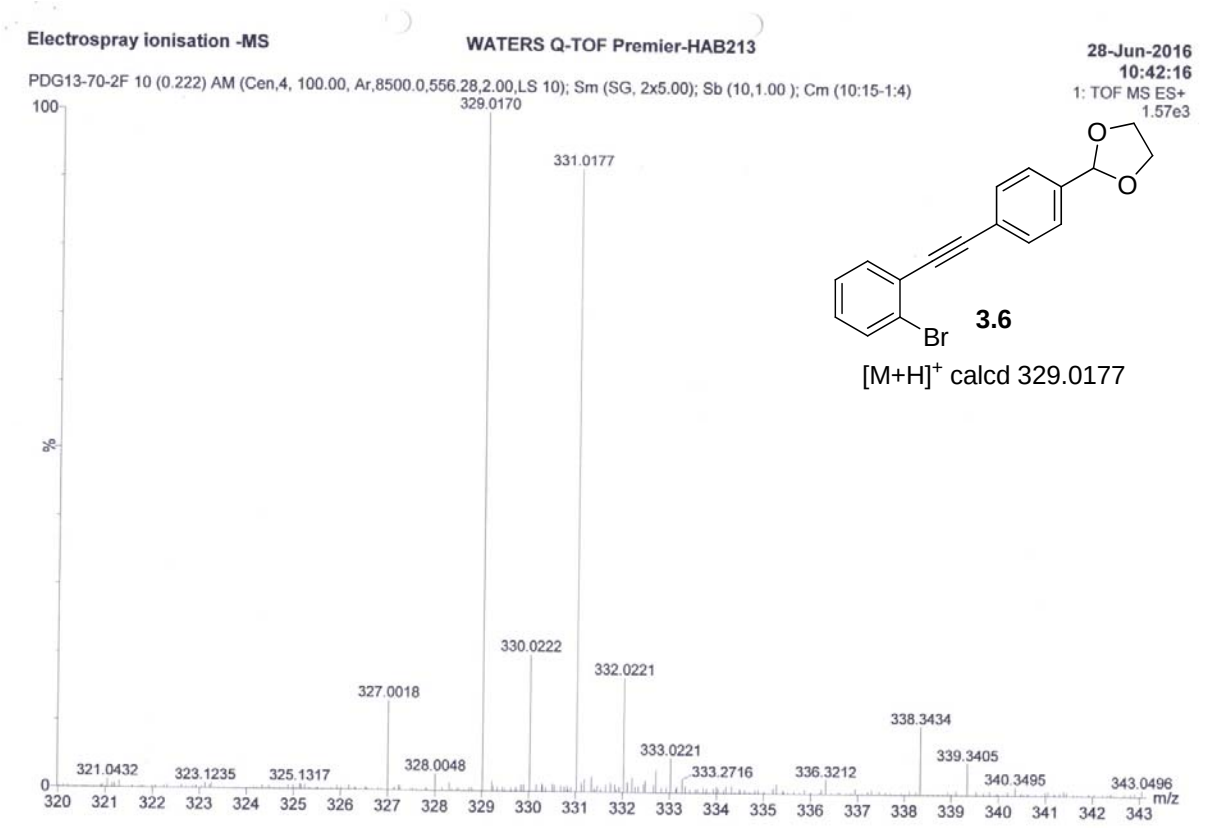
APCI (HRMS) spectrum of **3.5**



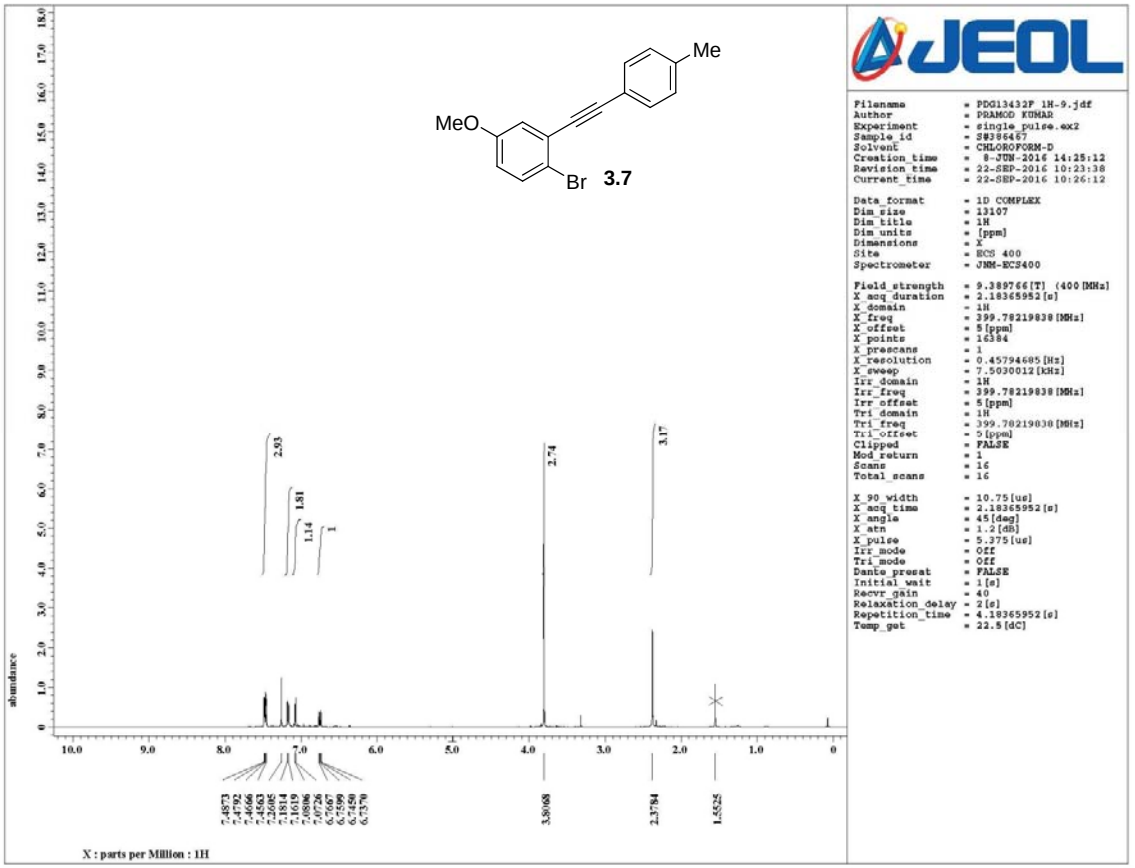
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3.6**



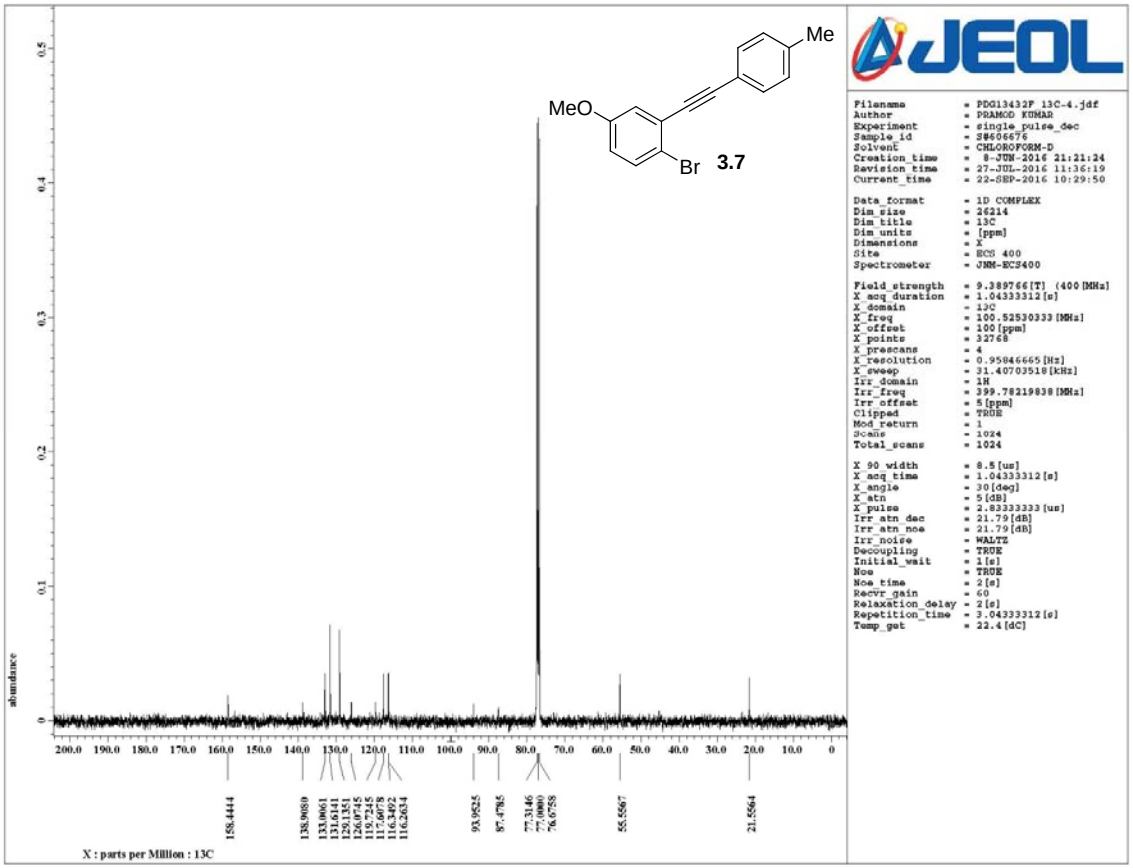
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **3.6**



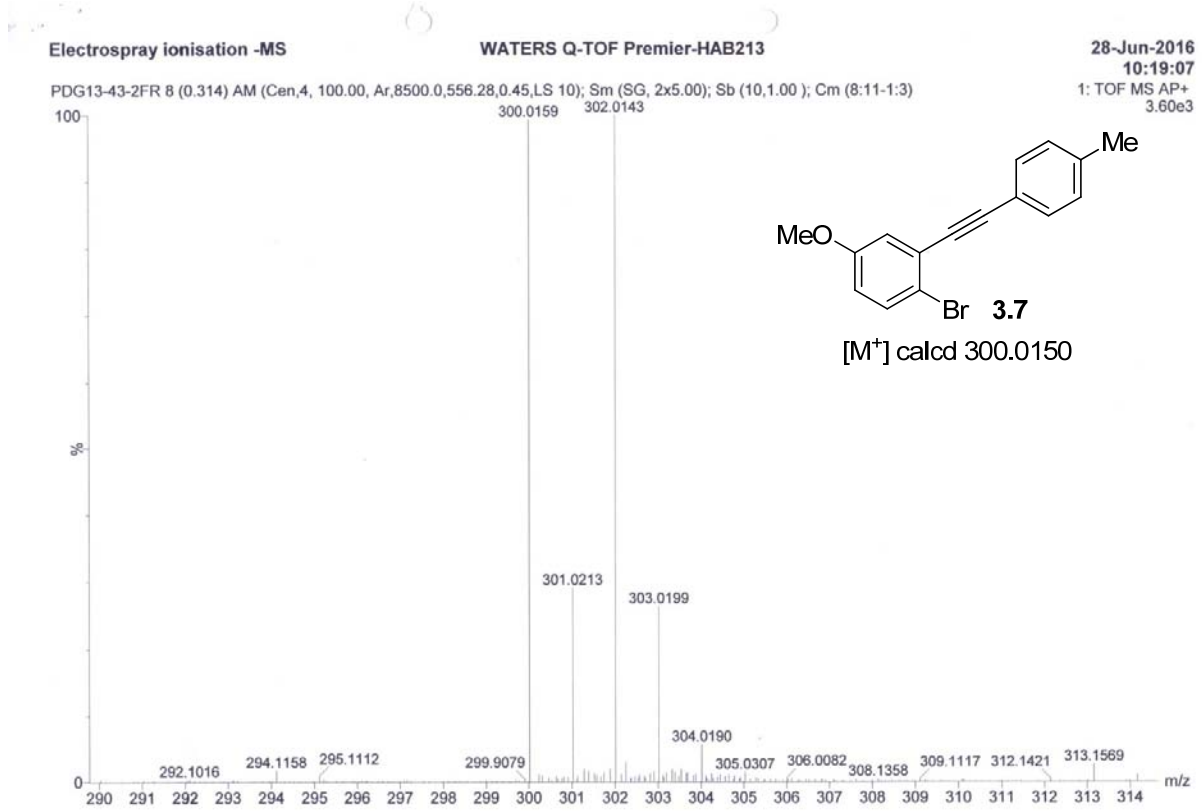
ESI (HRMS) spectrum of **3.6**



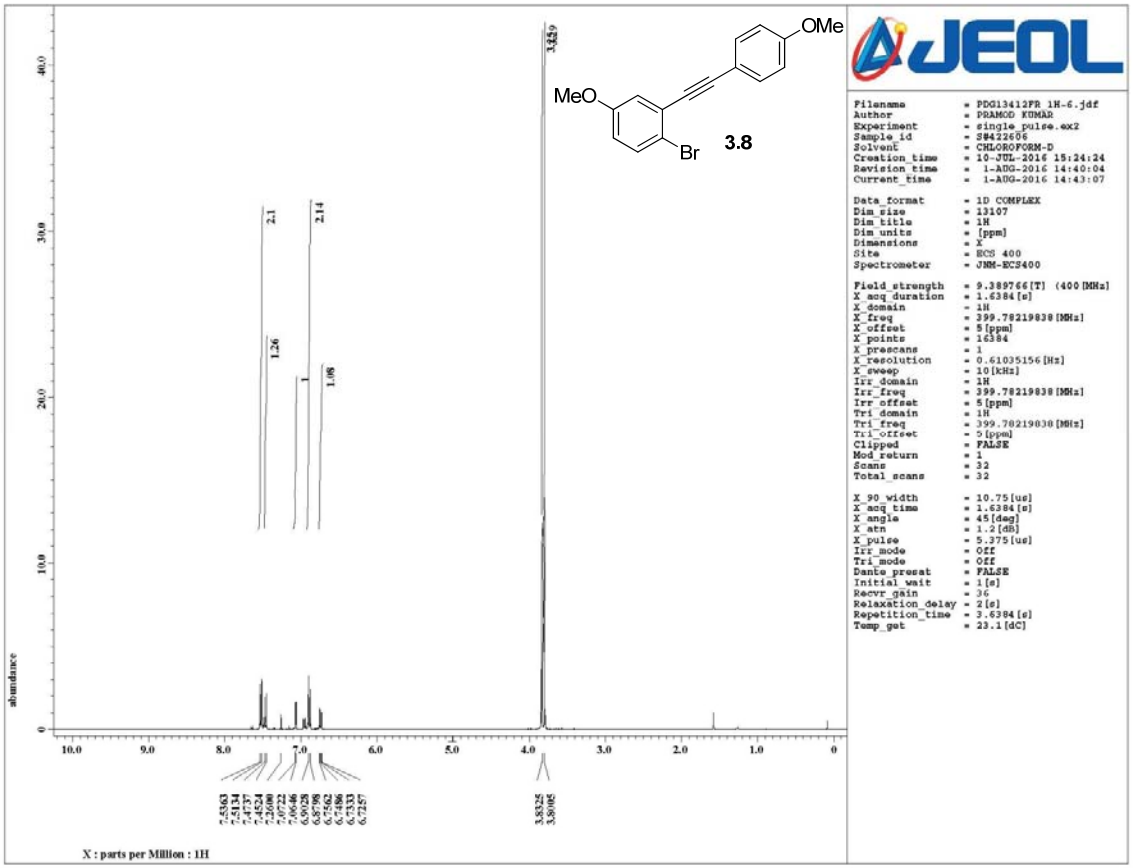
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3.7**



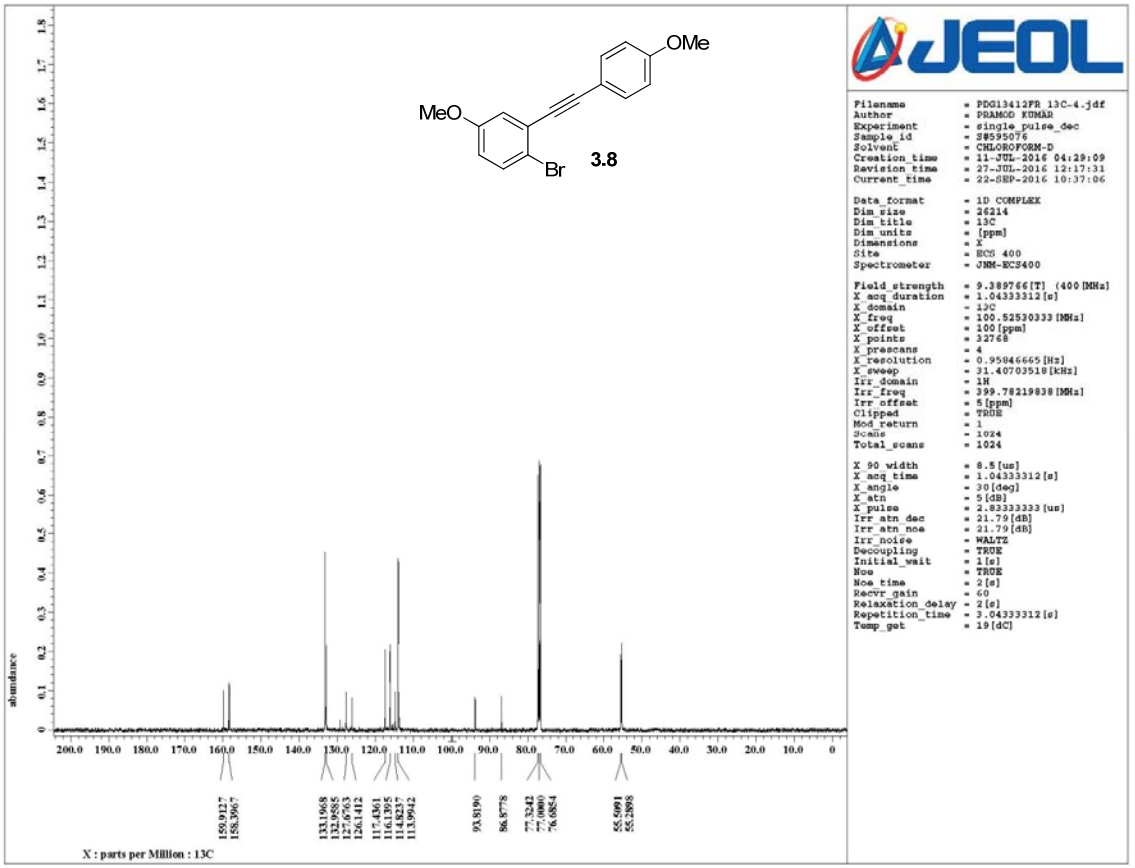
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3.7**



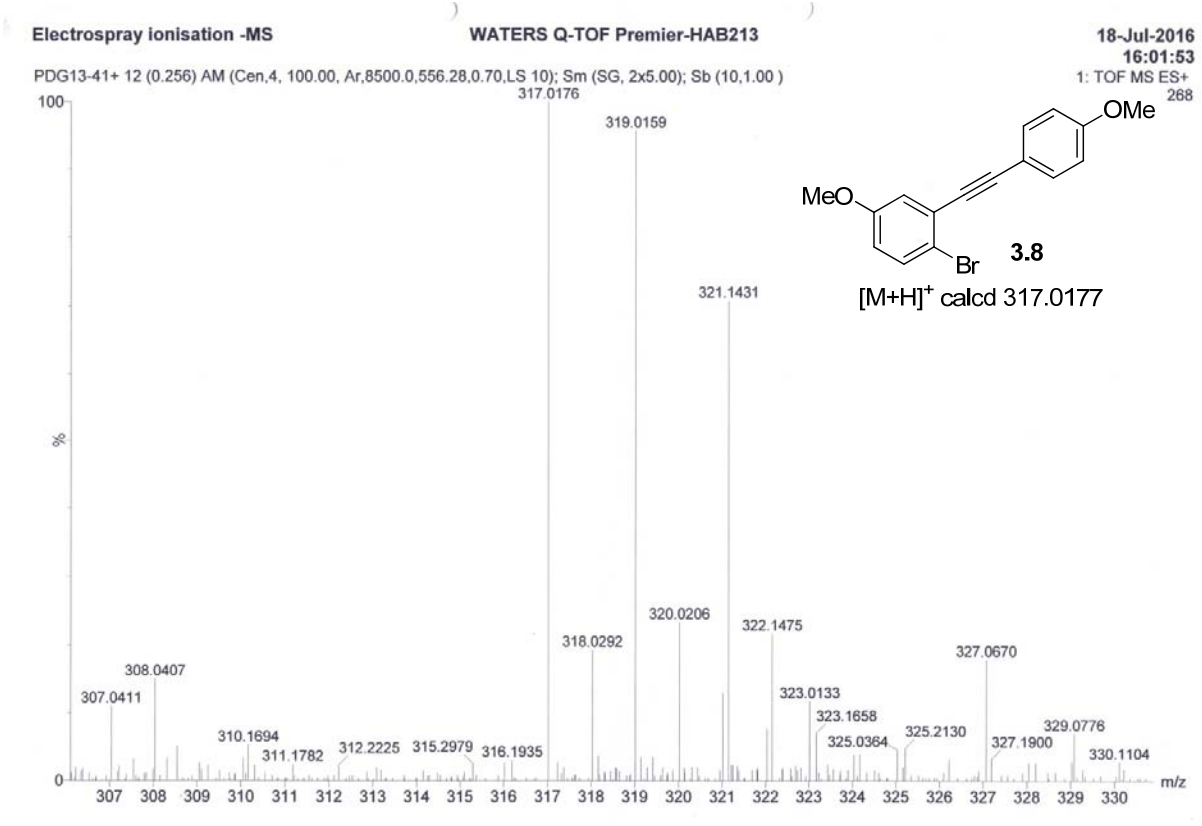
APCI (HRMS) spectrum of **3.7**



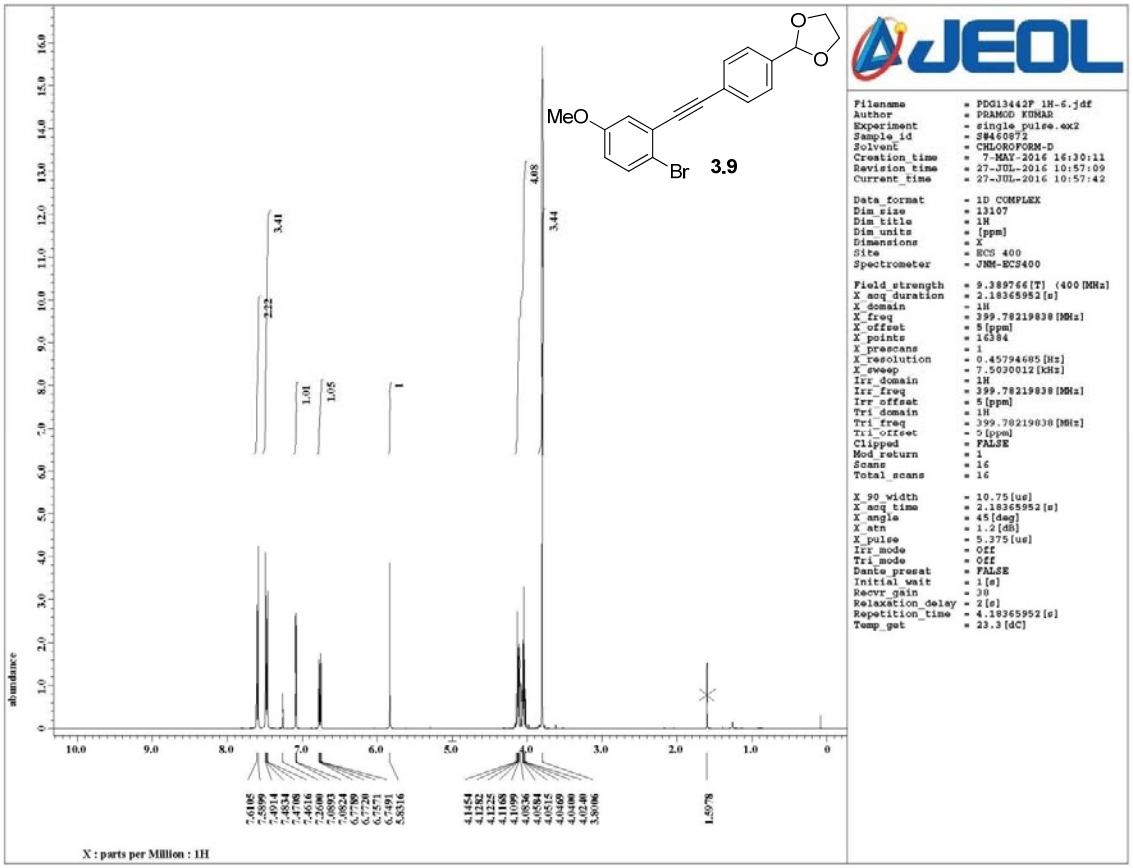
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.8**



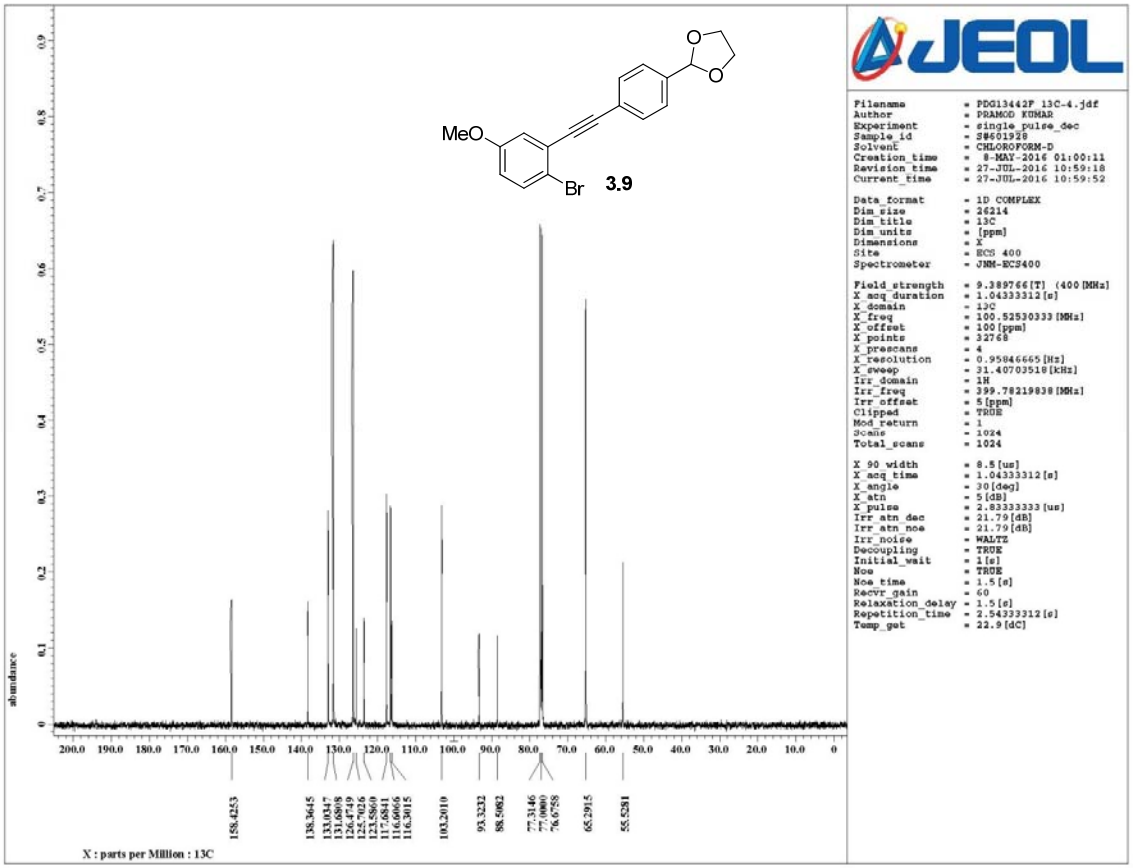
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3.8**



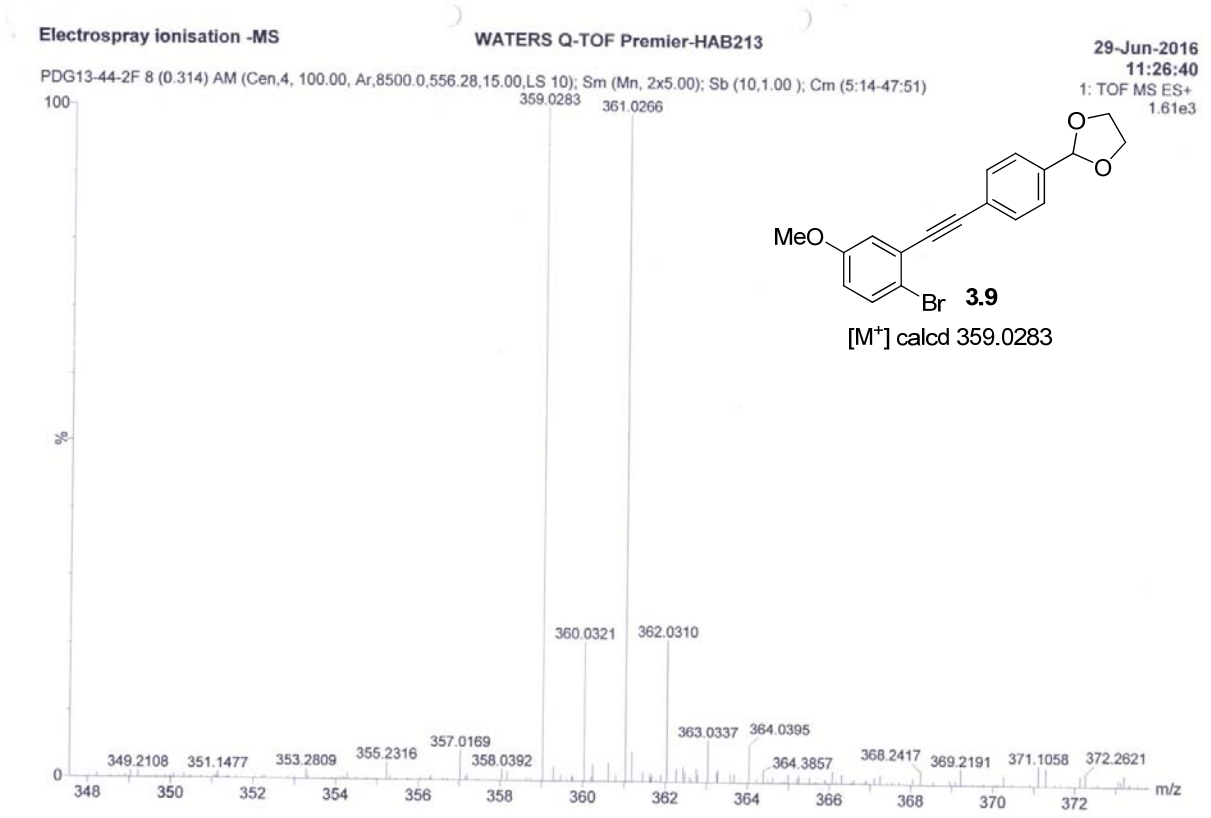
ESI (HRMS) spectrum of **3.8**



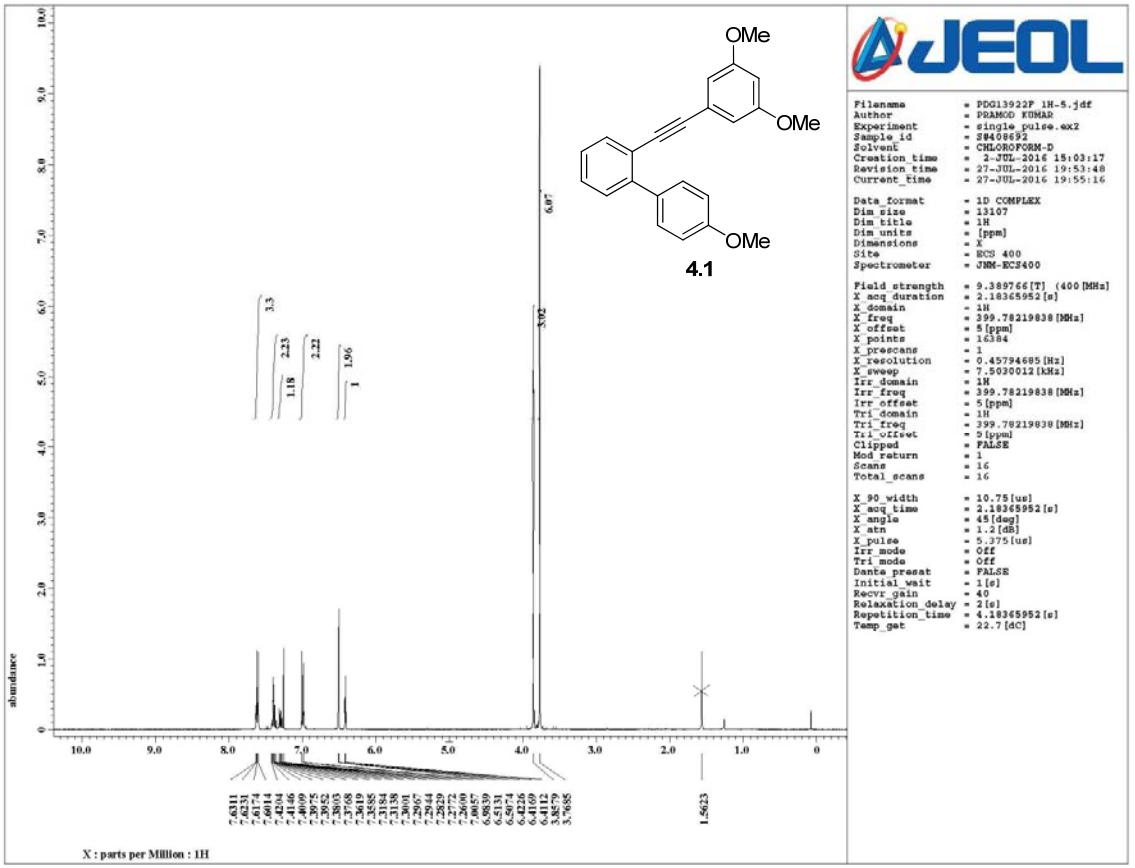
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.9**



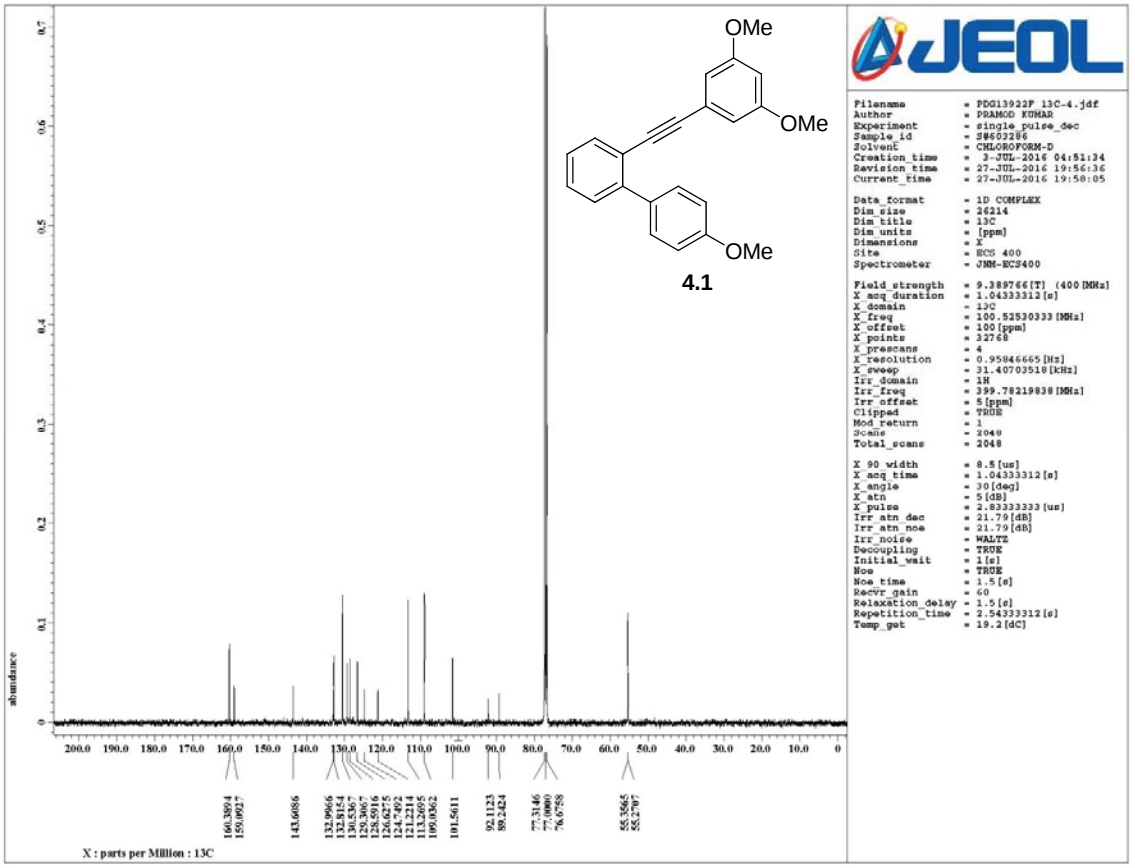
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3.9**



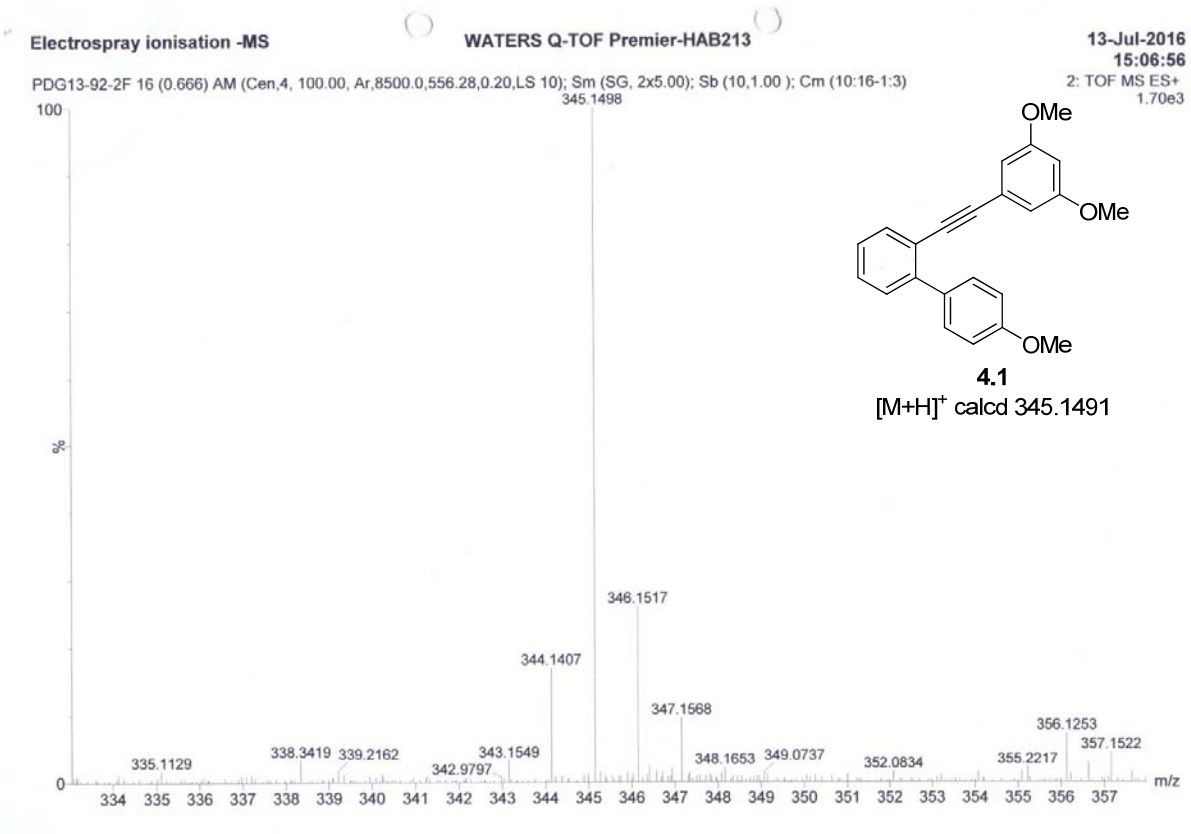
ESI (HRMS) spectrum of **3.9**



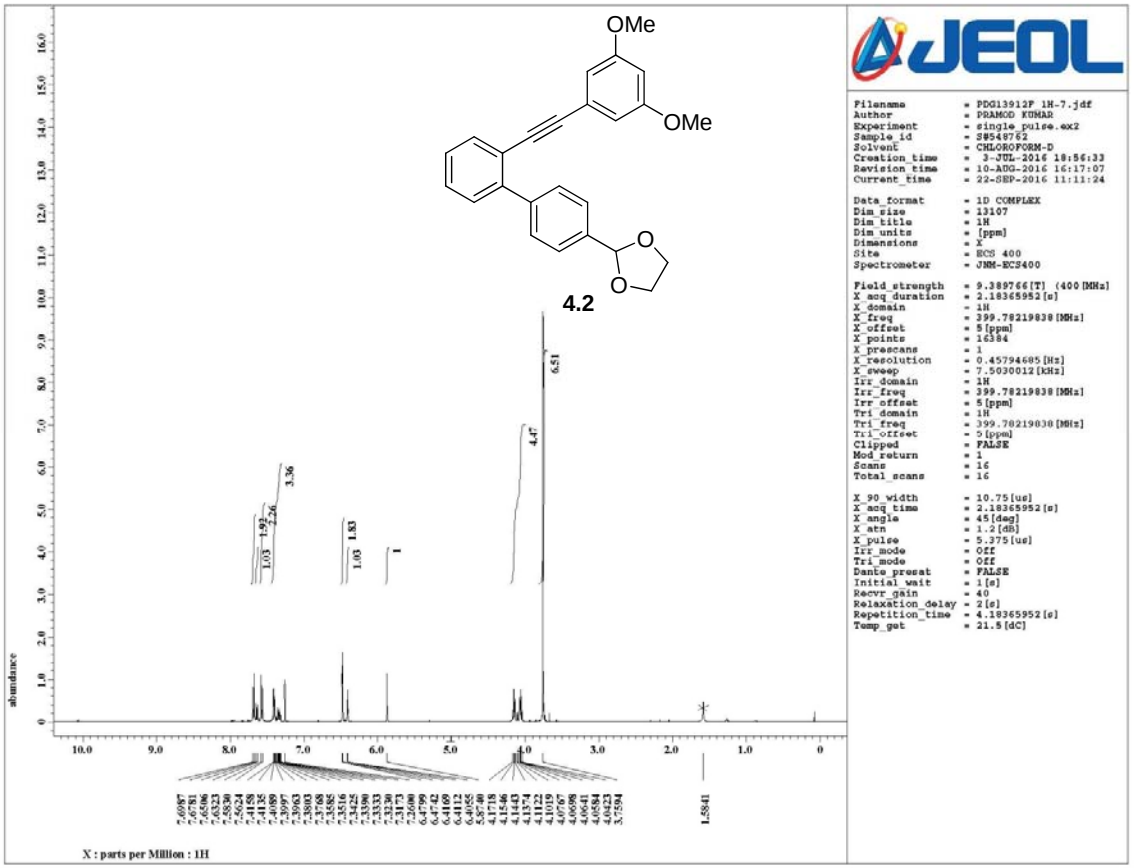
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4.1**



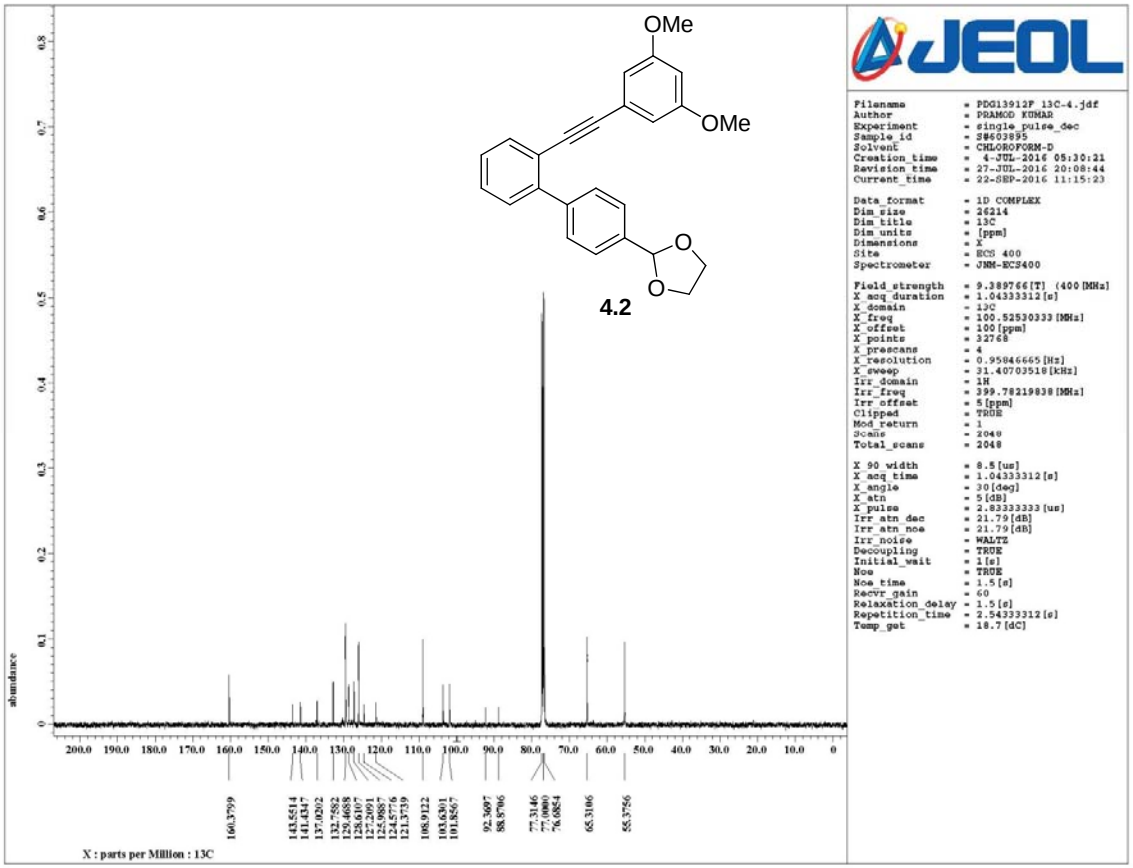
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4.1**



ESI (HRMS) spectrum of **4.1**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4.2**



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Experiment = single_pulse_dec
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Revision_time = 27-JUL-2016 20:08:44
Current_time = 22-SEP-2016 11:15:23

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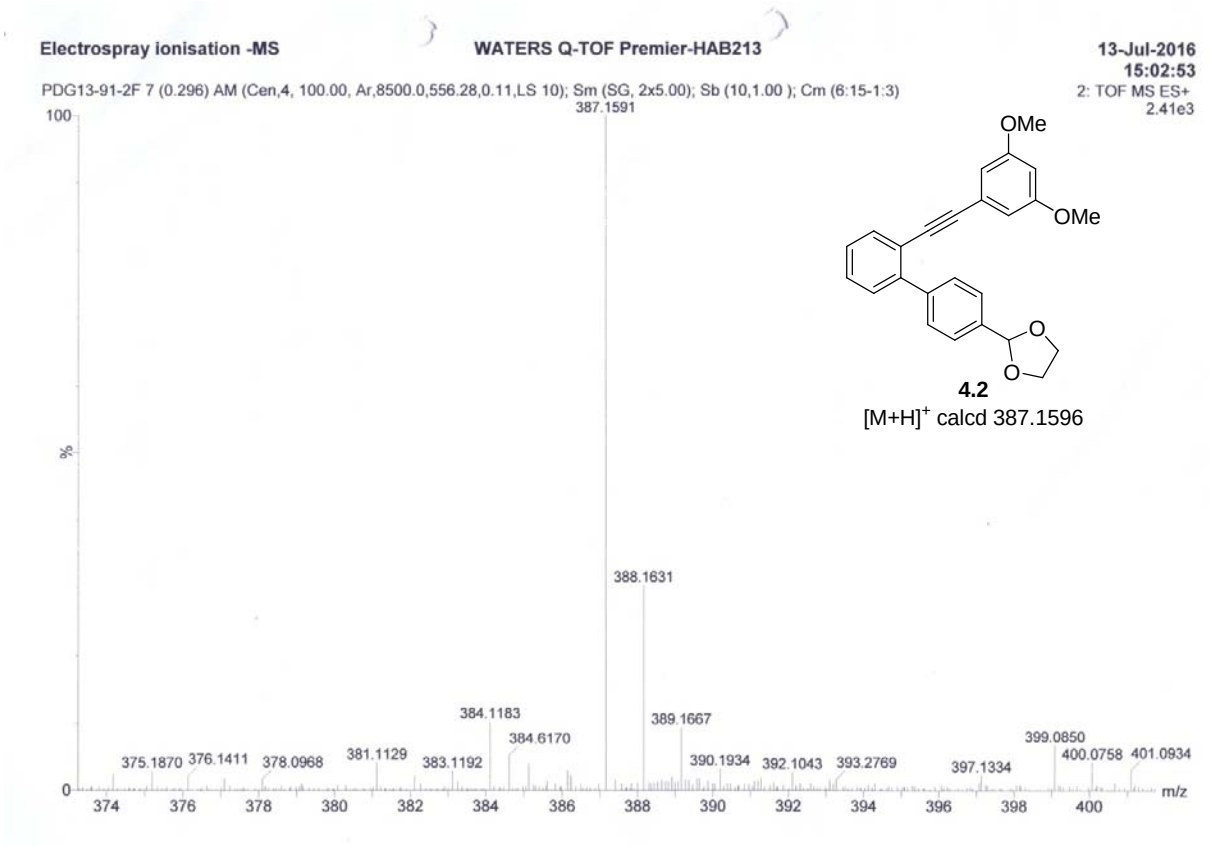
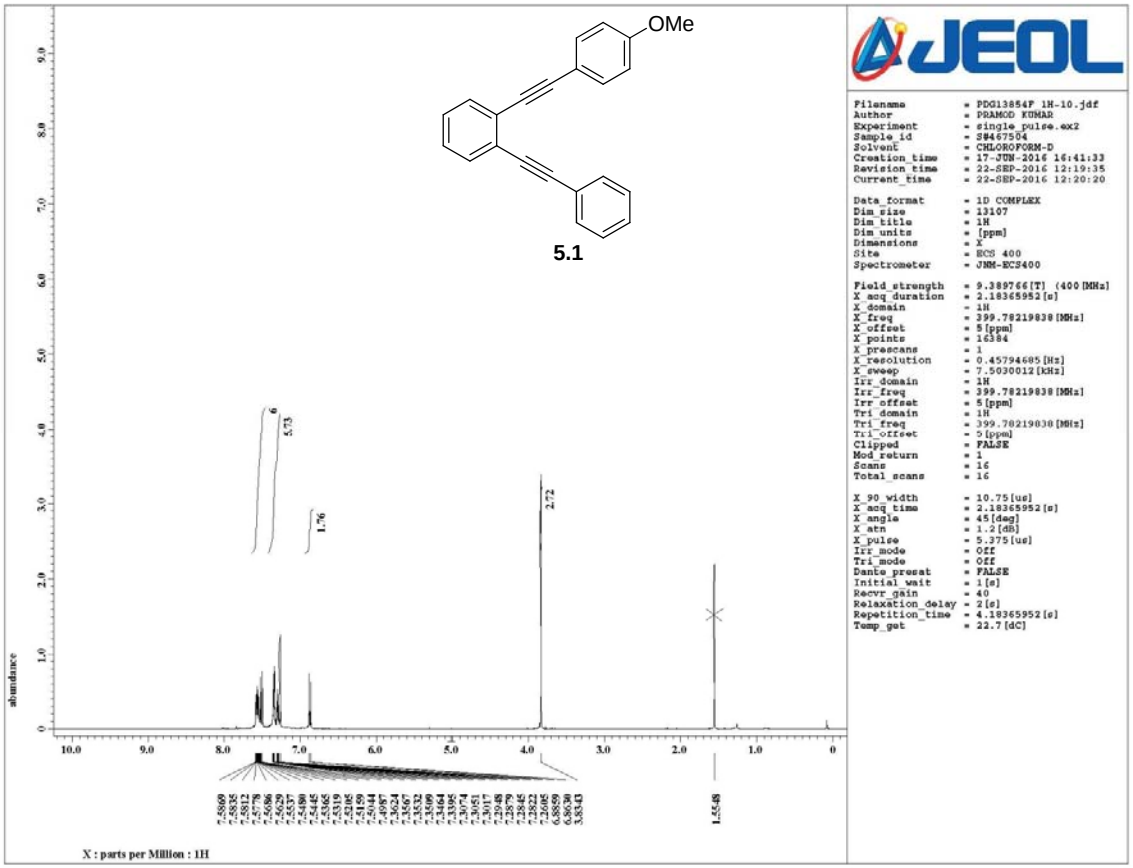
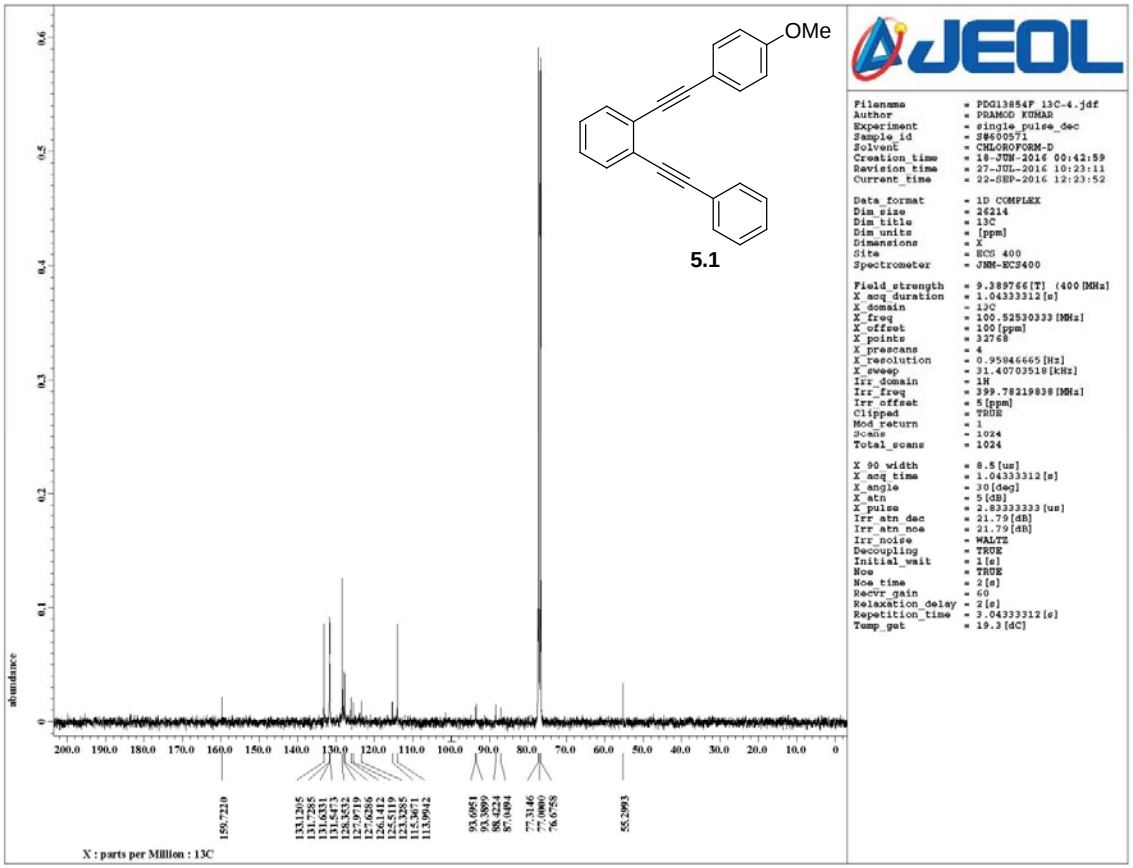
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4.2**



ESI (HRMS) spectrum of **4.2**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5.1**



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X_pulse = 2.83333333[us]
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Irr_atn_noe = 21.79[dB]
Irr_noise = WALTZ
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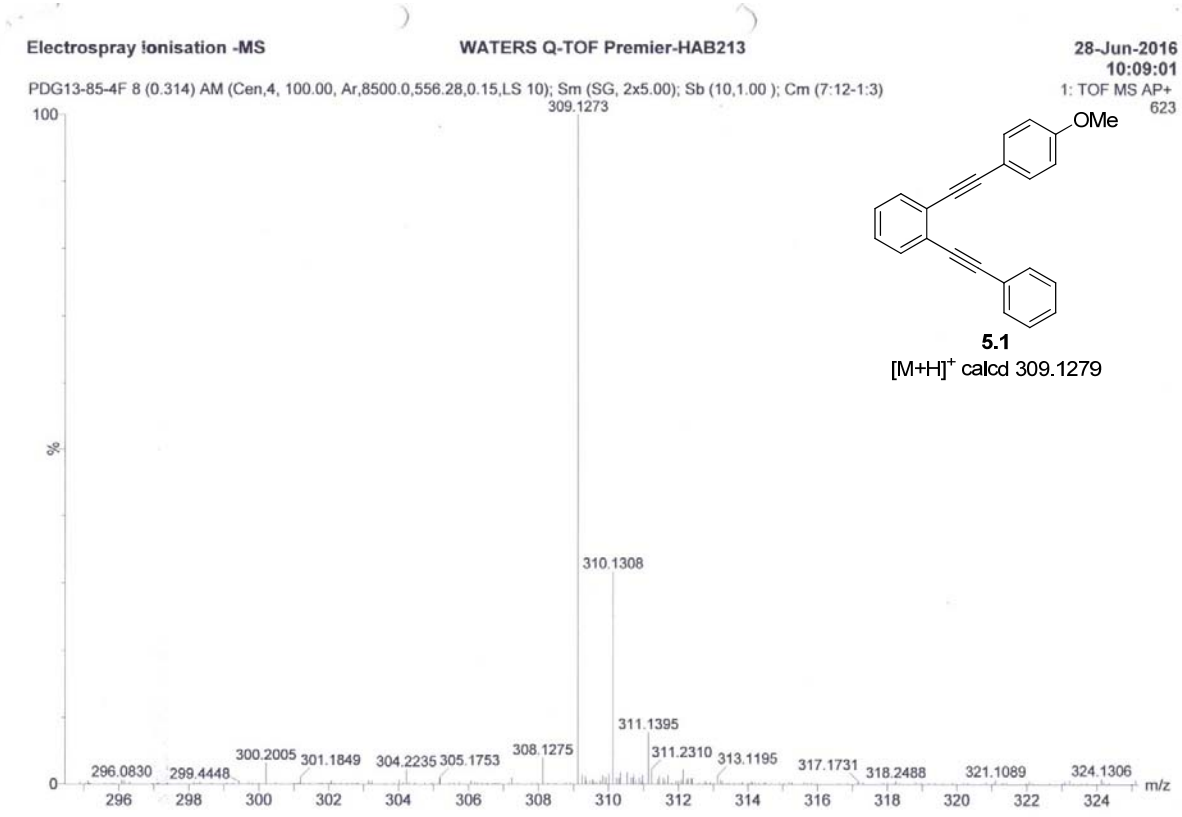
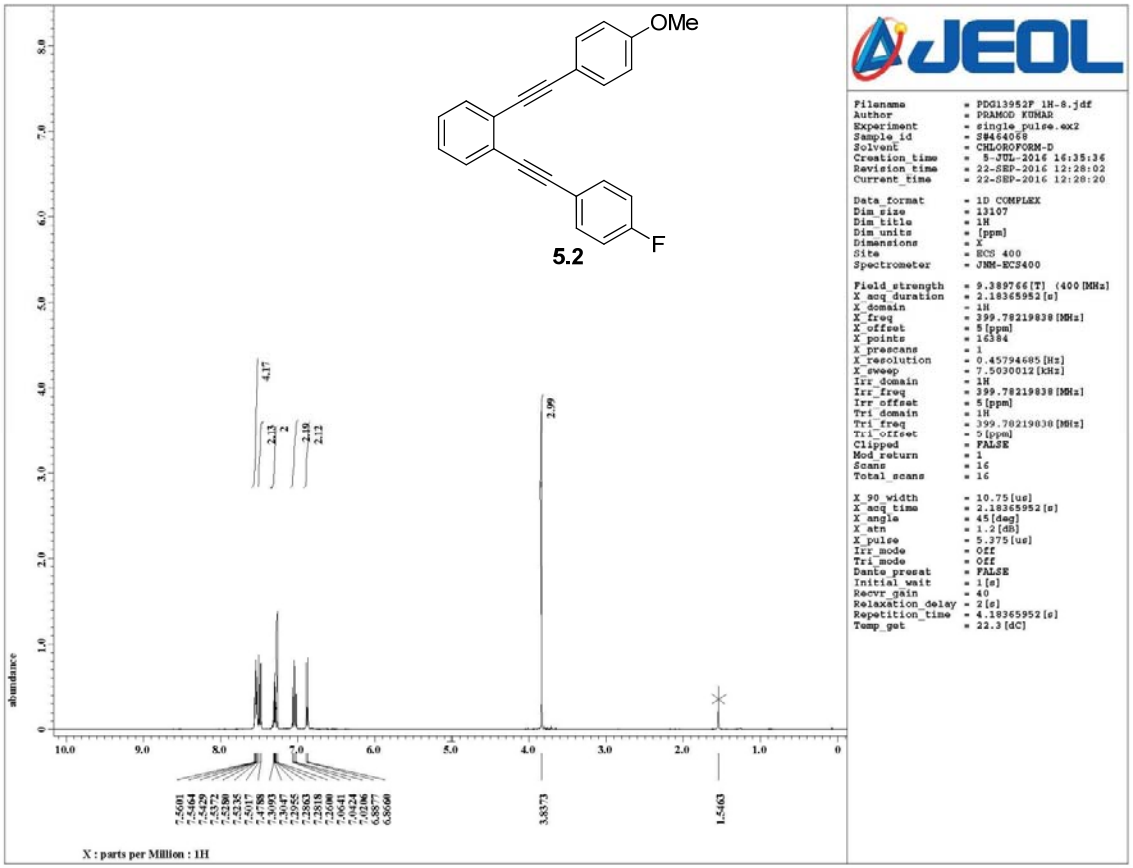
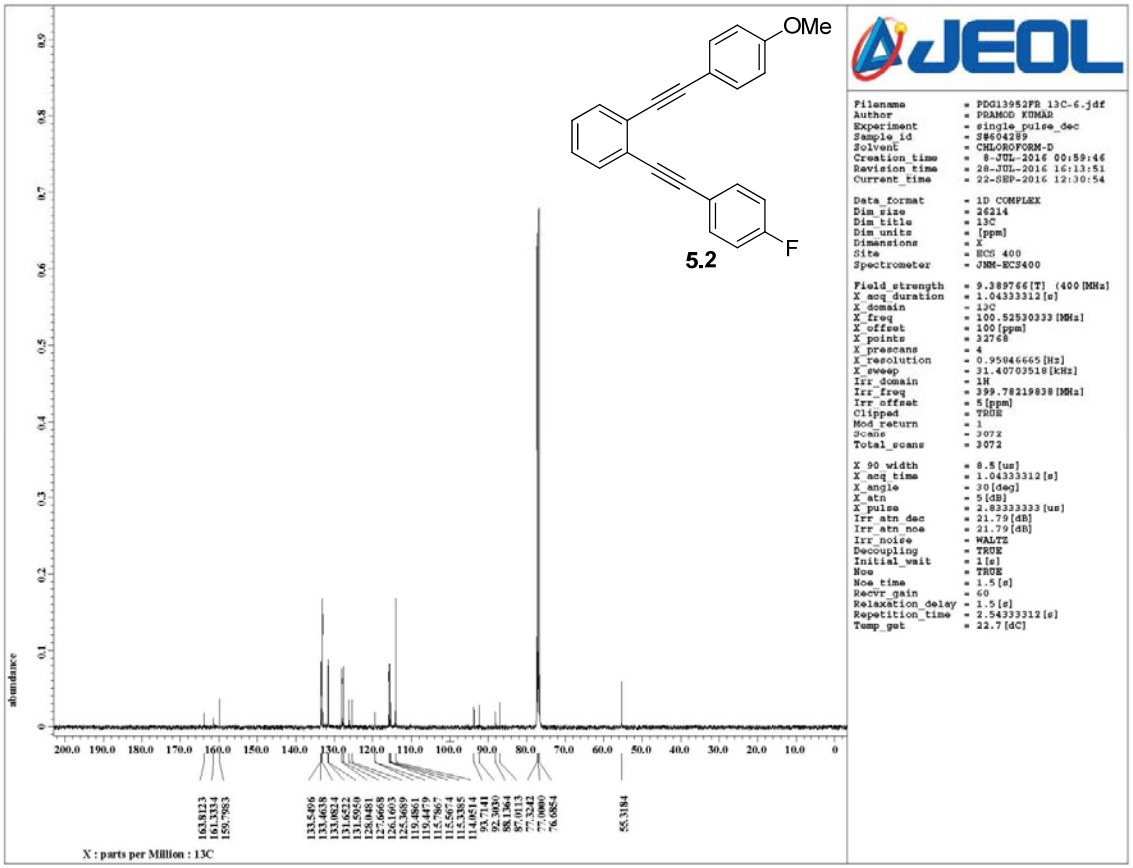
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5.1**



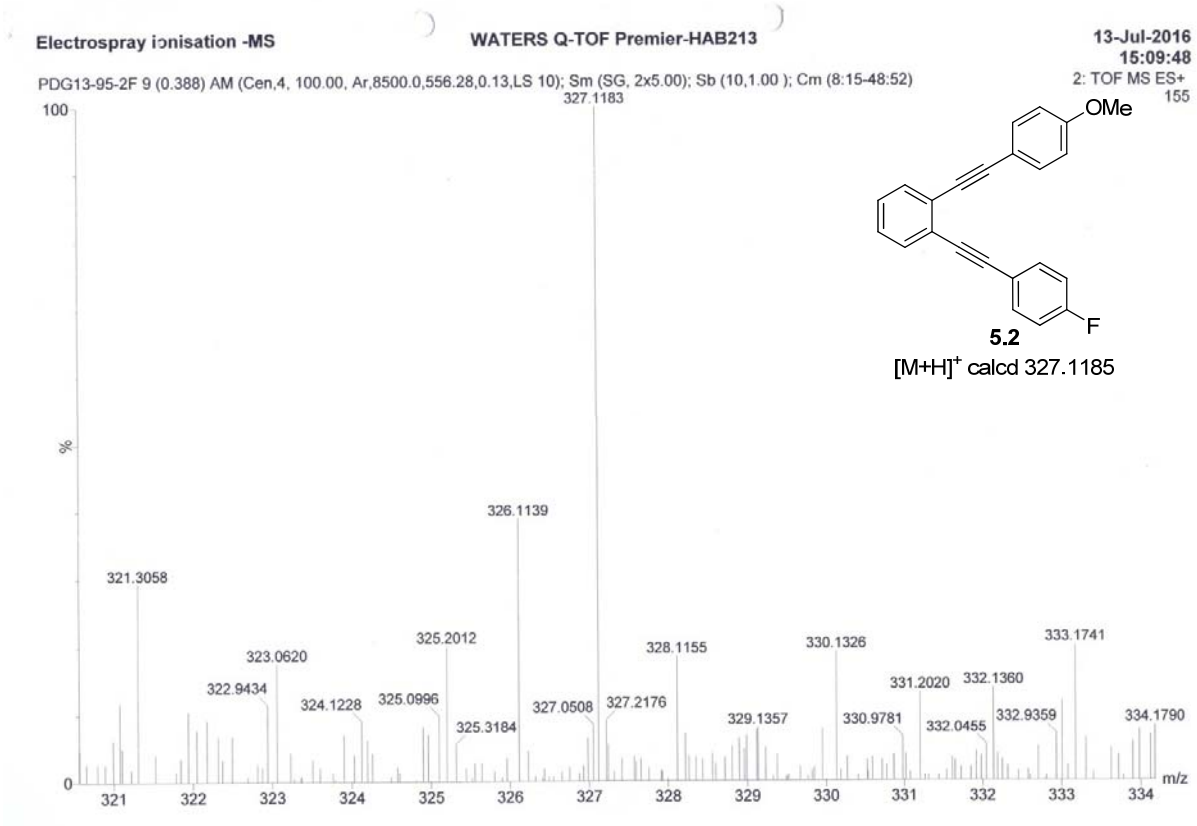
APCI (HRMS) spectrum of **5.1**



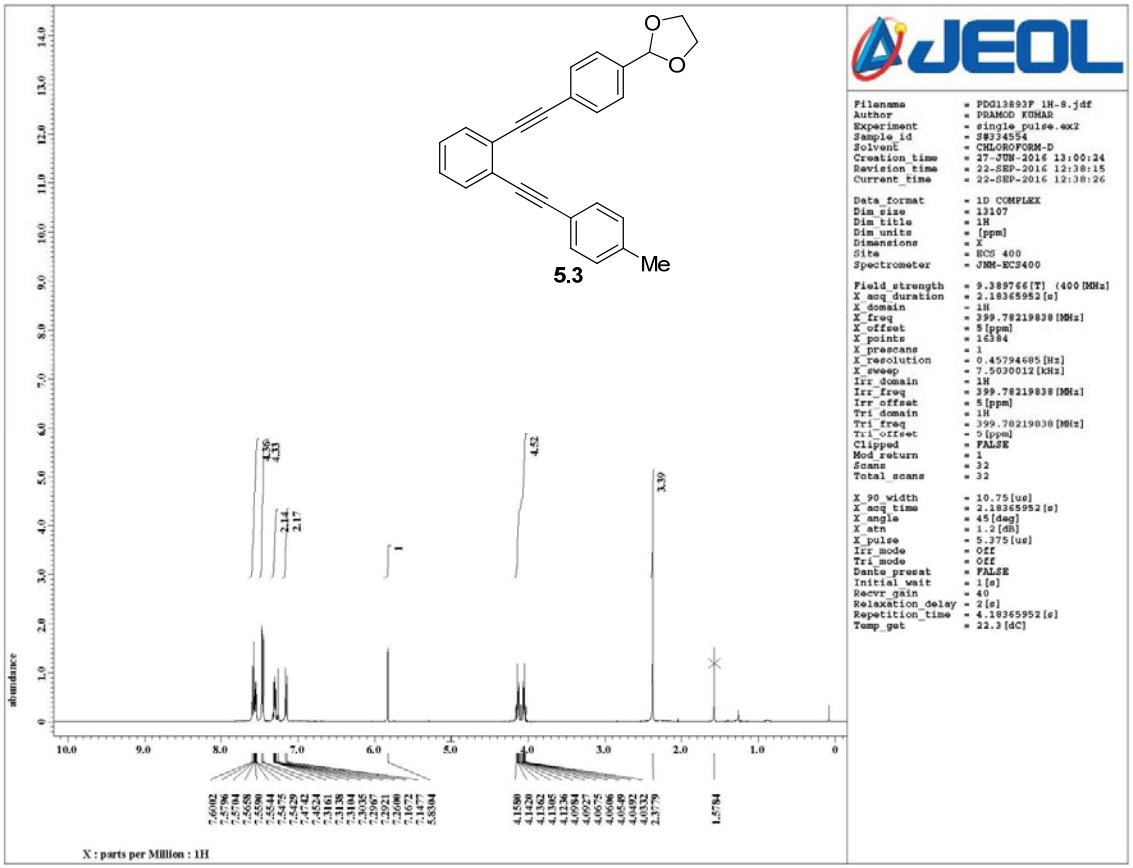
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5.2**



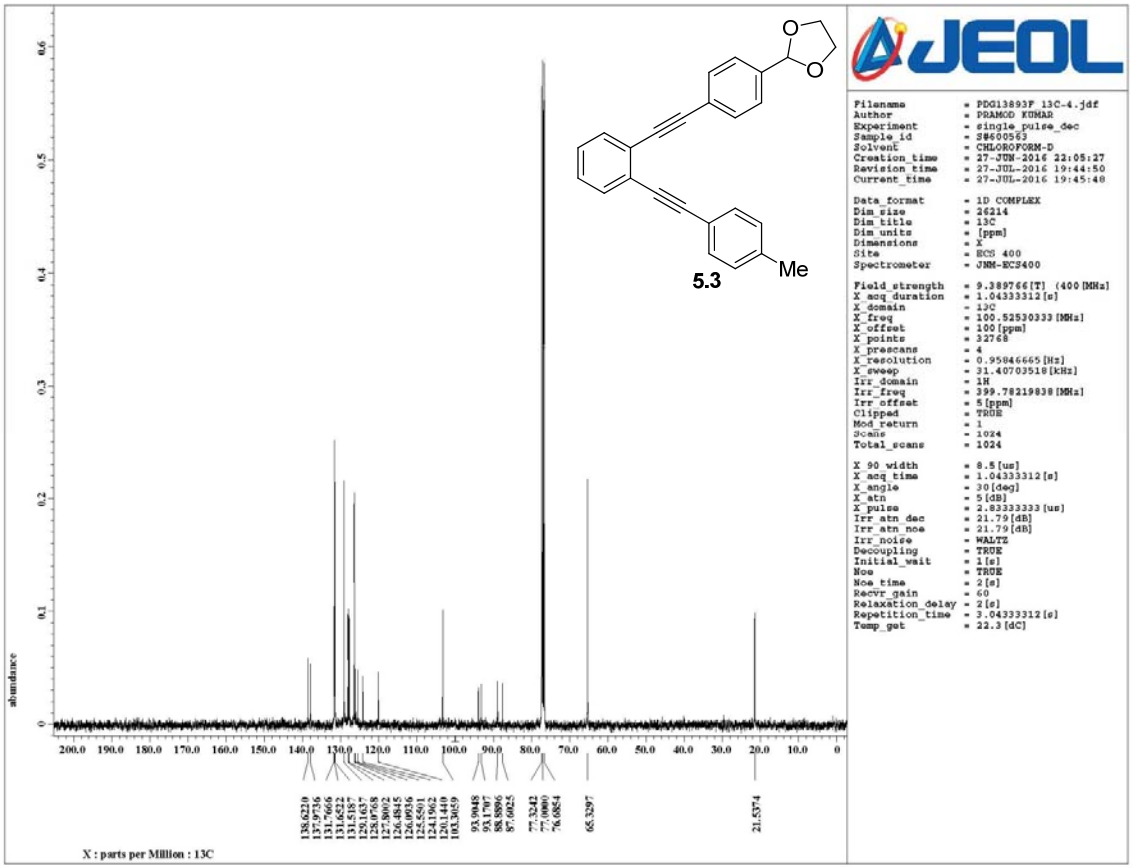
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5.2**



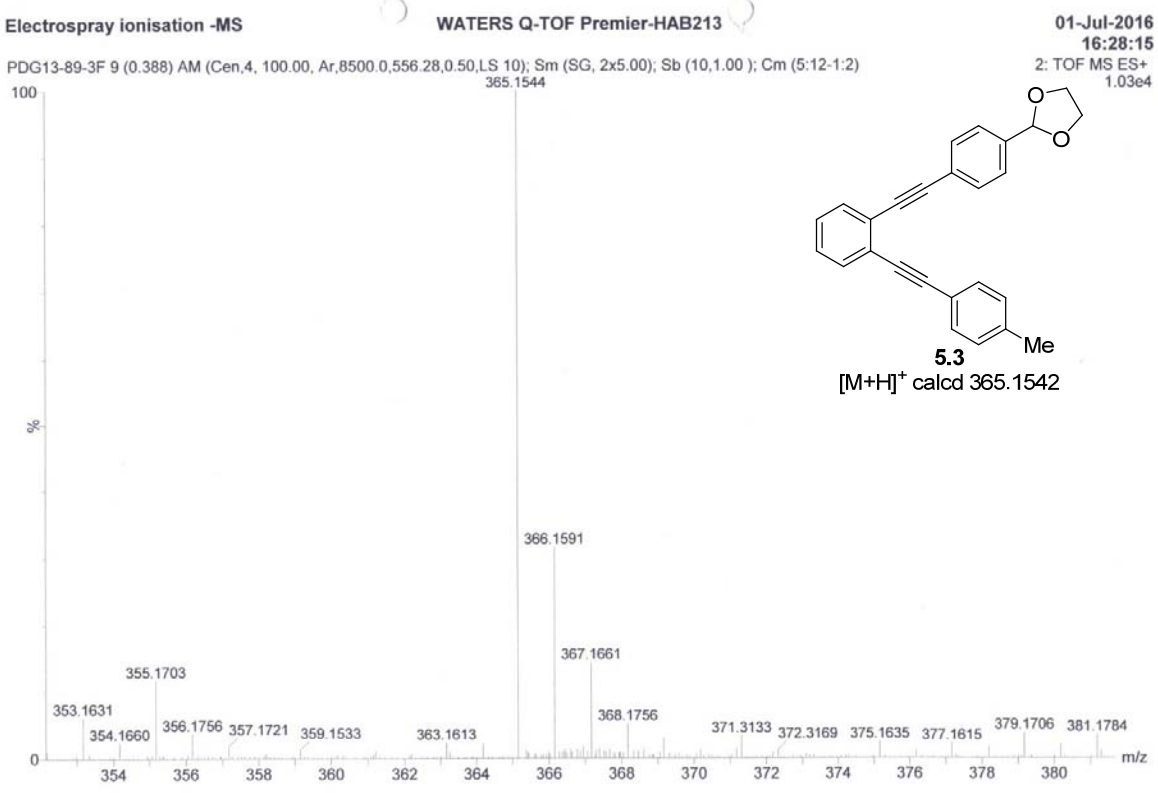
ESI (HRMS) spectrum of **5.2**



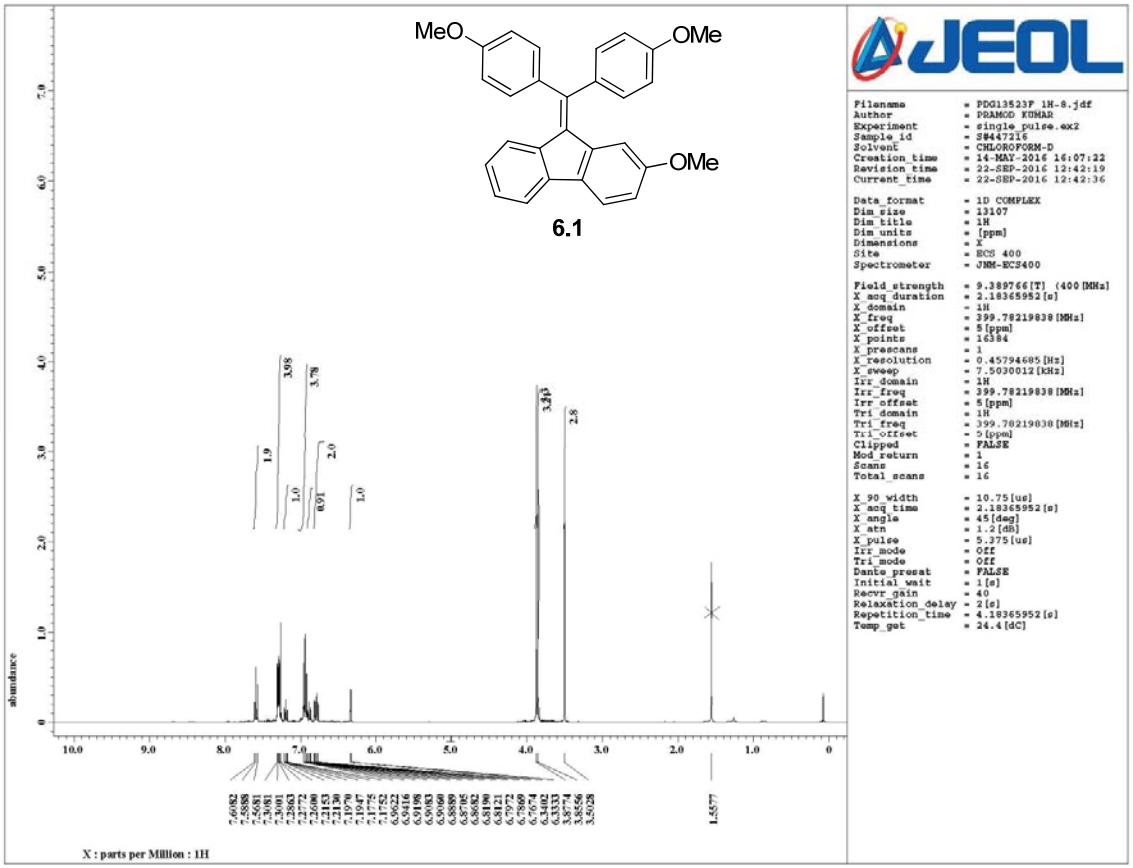
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5.3**



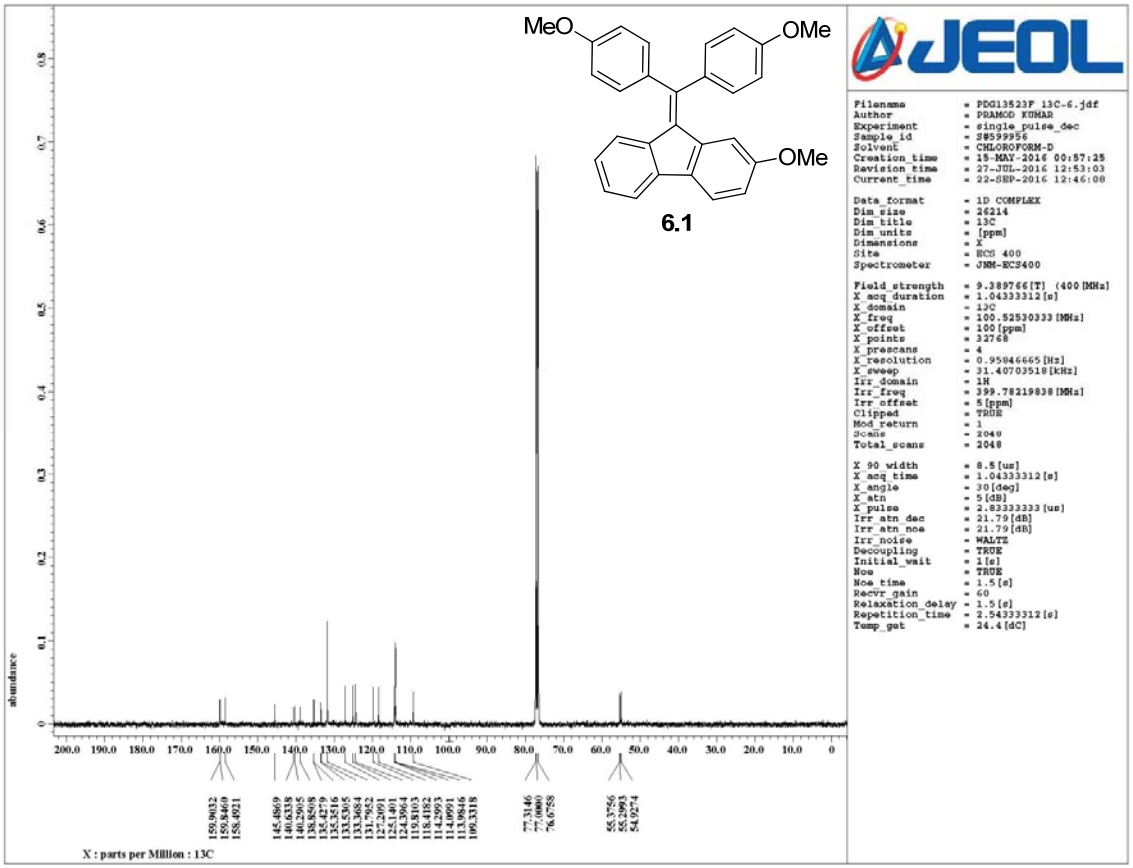
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5.3**



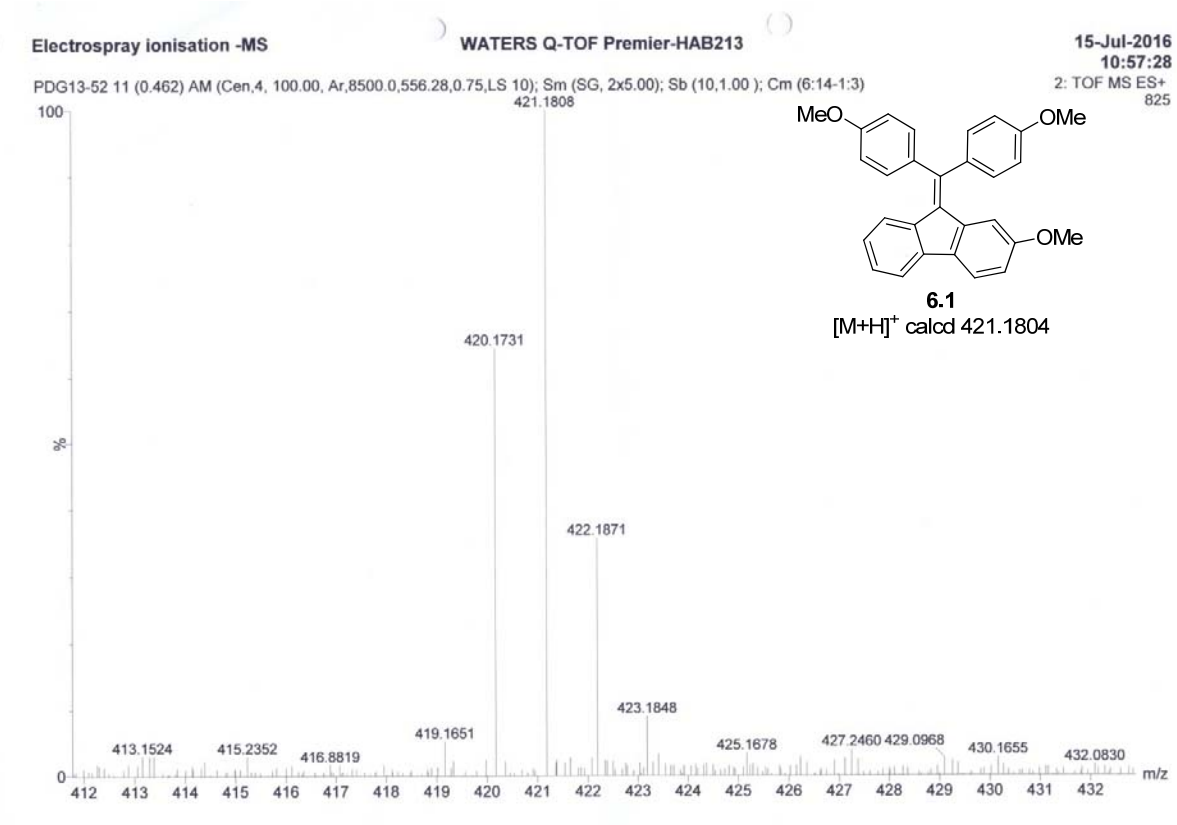
ESI (HRMS) spectrum of **5.3**



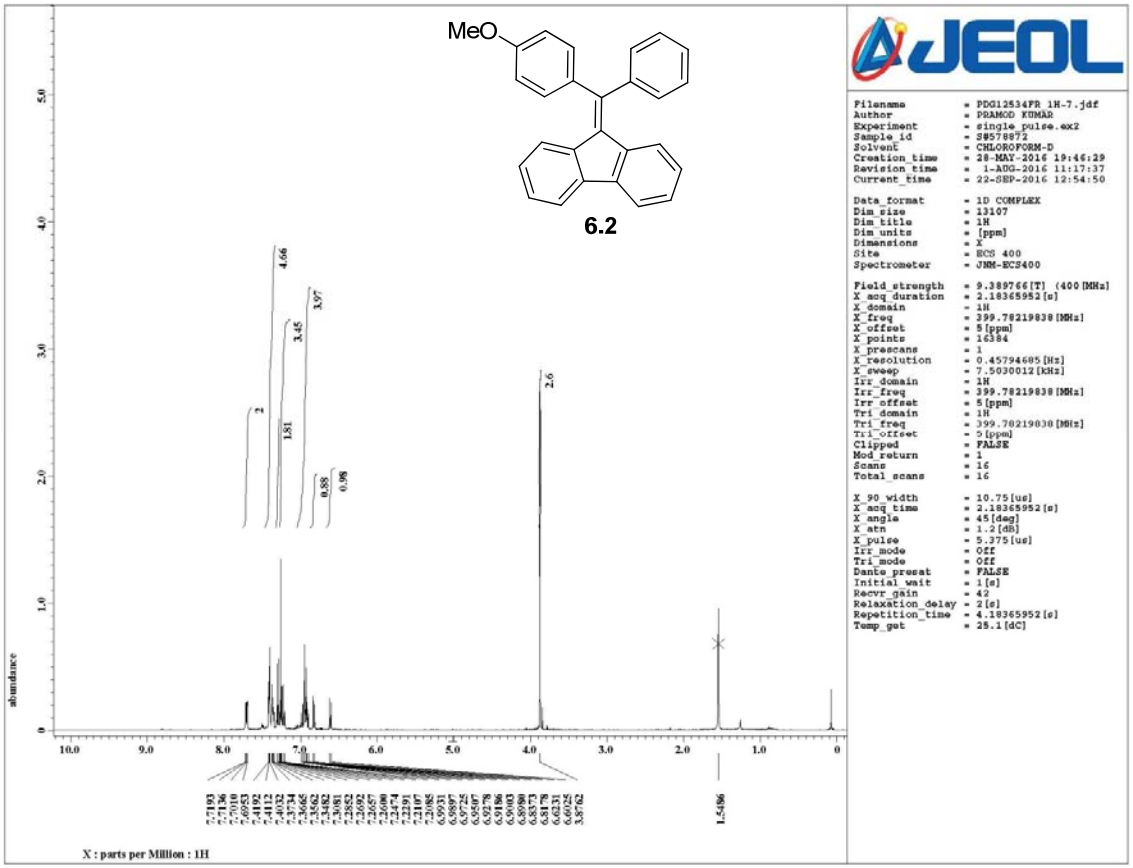
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6.1**



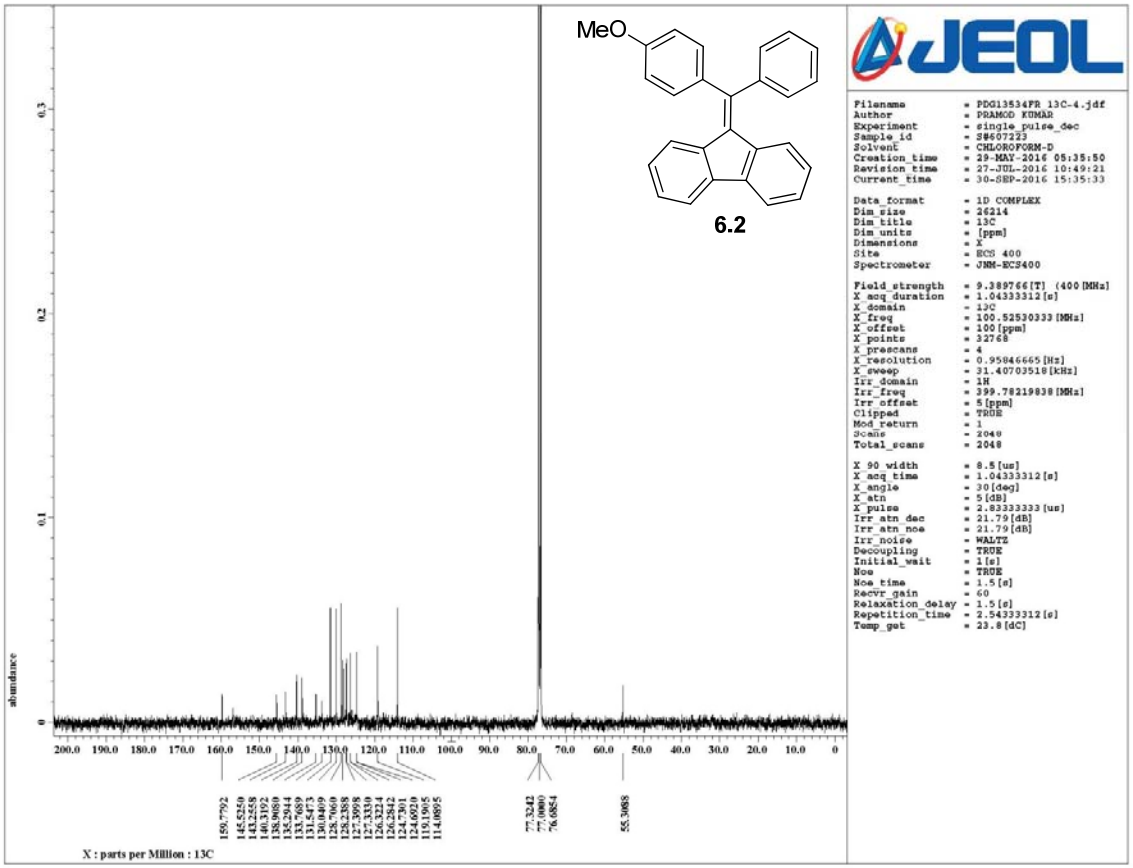
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6.1**



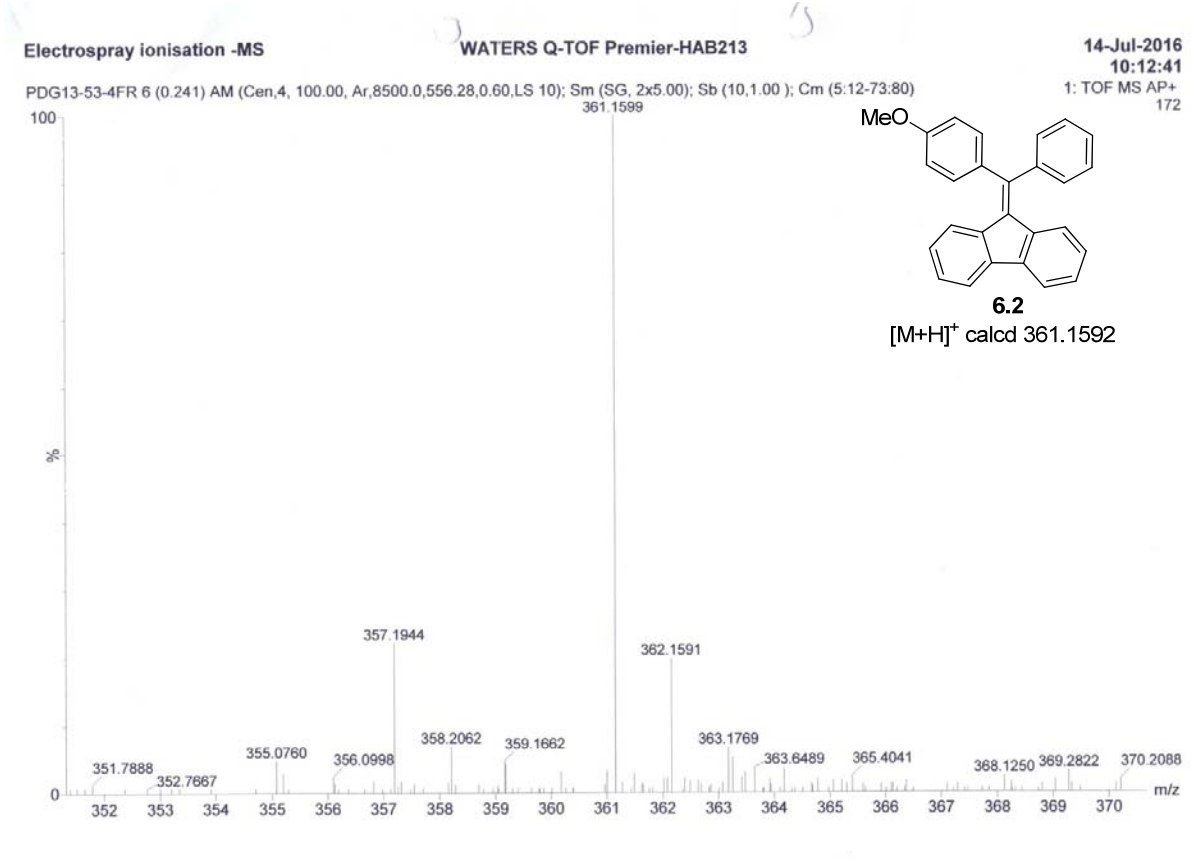
ESI (HRMS) spectrum of **6.1**



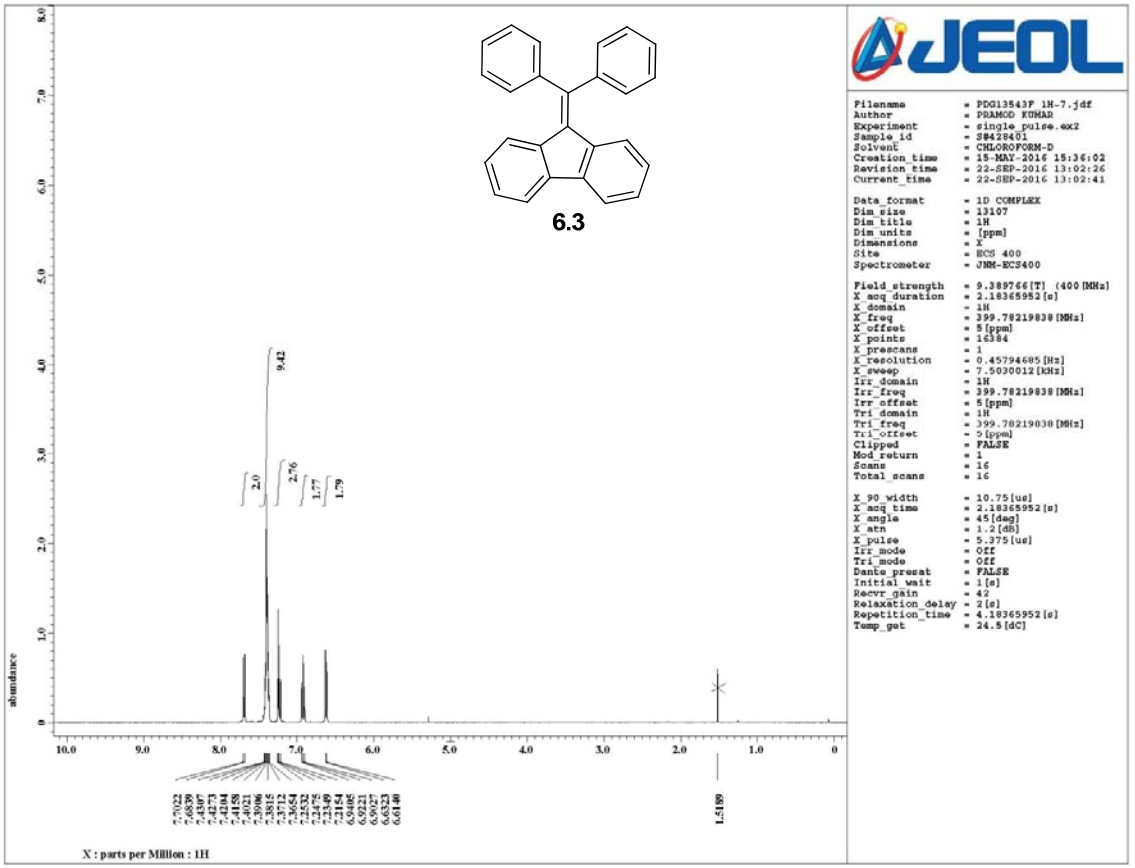
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6.2**



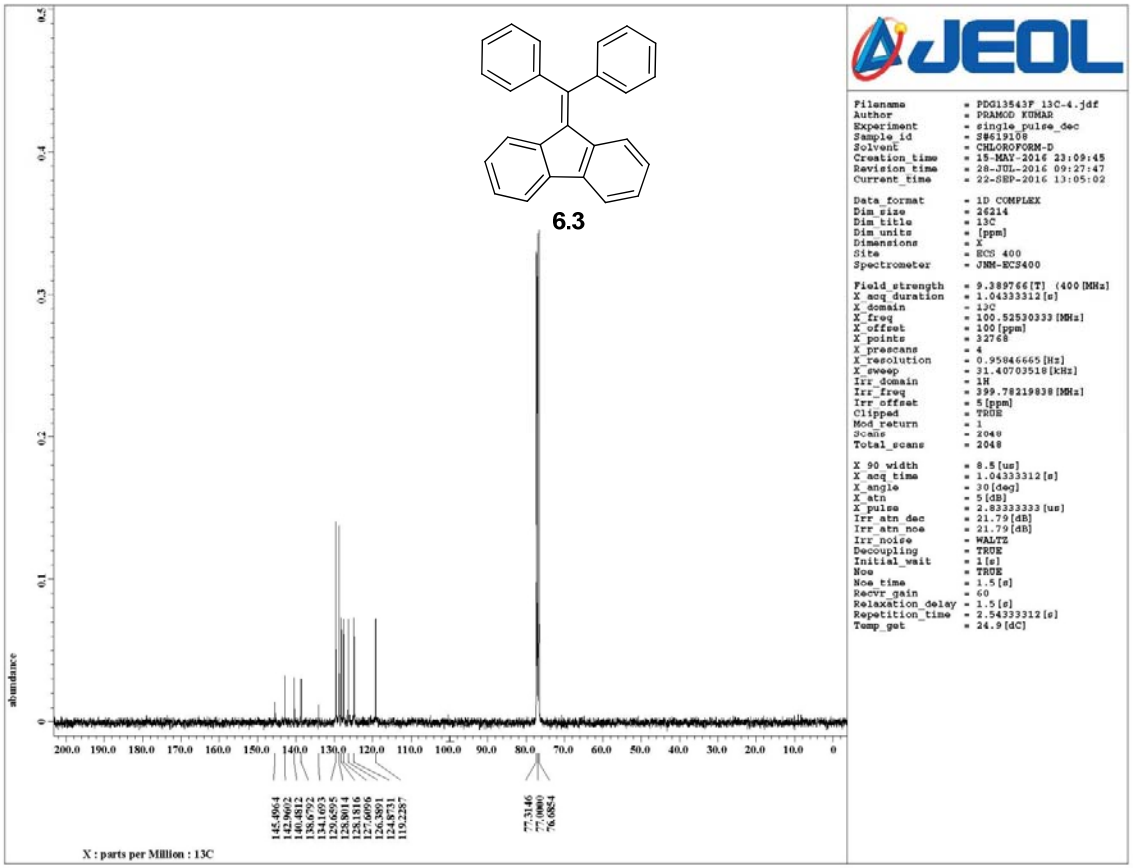
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6.2**



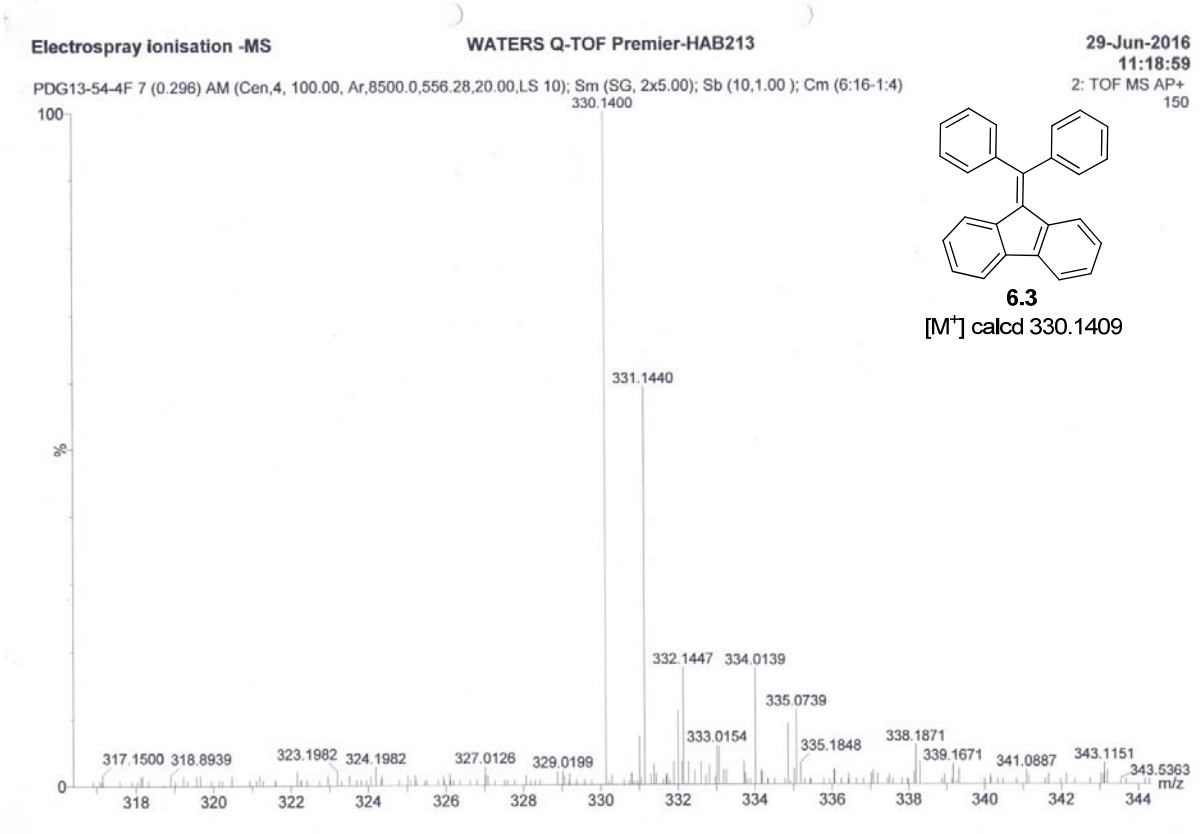
APCI (HRMS) spectrum of **6.2**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6.3**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6.3**



APCI (HRMS) spectrum of **6.3**