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Supporting Information

Synthesis and Functionalization of 3-Bromo-2-(2-chlorovinyl)benzothiophenes as Molecular Tools

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General experimental methods

General Information and Method. All glasswares were oven-dried at 140 °C and all reactions were conducted under an argon atmosphere. Solvents: cyclohexane, ethyl acetate (EtOAc), for chromatography, were technical grade. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR spectroscopy, HRMS and elemental analyses. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ with a Bruker Avance 300. ^{1}H NMR chemical shifts are reported in ppm from an internal standard TMS or of residual chloroform (7.26 ppm). The following abreviation are used: m (multiplet), s (singlet), d (doublet), t (triplet), dd (doublet of doublet), td (triplet of doublet), ddd (doublet of doublet of doublet). ^{13}C chemical shifts are reported in ppm from the central peak of deuteriochloroform (77.14). IR spectra were measured on a Bruker Vector 22 spectrophotometer (neat, cm^{-1}). High-resolution mass spectra were recorded on a Bruker Daltonics micrOTOF-Q instrument. Elemental analyses (C, H) were performed with a Perkin-Elmer 240 analyzer at the microanalyses Service of the Faculty of Pharmacy at Châtenay-Malabry (France) and were within 0.4% of the theorical values otherwise stated. Analytical TLC was performed on Merck precoated silica gel 60 F-254 plates. Merck silica gel 60 (230-400 mesh) was used for column chromatography. The plates were visualized by either UV light (254 nm), or by a solution of phosphomolybdic acid in ethanol.

General Procedure for the Synthesis of (*E*)-Chloroenynes 5a, 5b and 18

To a solution of alkyne (10 mmol) in Et_2O (150 mL) was added successively (E)-1,2-dichloroethylene (8 mL, 100 mmol), $PdCl_2(PPh_3)_2$ (700 mg, 1 mmol), piperidine (2 mL, 20 mmol) and CuI in portions (190 mg, 1 mmol). After complete disappearance of starting material monitored by TLC, the solution was filtered through a pad of celite using EtOAc. The organic layer was washed successively with sat. NH_4Cl, sat. $NaHCO_3$ and HCl (1 M) solutions. After drying over $MgSO_4$ and evaporation in vacuo, the crude residue was purified by silica gel column chromatography.

(*E*)-(2-(4-Chlorobut-3-en-1-yn-1-l)phenyl)(methyl) sulfane (5a)

brown oil, yield 68%, 1.4 g.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 13.5 Hz, 1H), 6.22 (d, *J* = 13.5 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 141.6 (Cq), 132.3 (CH), 130.4 (CH), 129.1 (CH), 124.3

(CH), 124.2 (CH), 120.7 (Cq), 113.8 (CH), 90.7 (Cq), 89.3 (Cq), 15.1 (CH_3). IR (neat): 3069, 2920, 2197, 1687, 1573, 1461, 1431, 1246, 1226, 1165, 1080, 1040, 908, 839, 786, 746, 717, 669 cm^{-1}. HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{11}H_{10}{}^{35}ClS$: 209.0186; found: 209.0195.

(*E*)-3-(4-Chlorobut-3-en-1-yn-1-yl)-2-(methylthio) pyridine (5b)

brown oil, yield 74%, 1.6 g.

^1H NMR (300 MHz, $CDCl_3$) δ = 8.38 (d, *J* = 4.8 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 6.94 (dd, *J* = 7.5 Hz, *J* = 4.8 Hz, 1H), 6.71 (d, *J* = 13.8 Hz, 1H), 6.21 (d, *J* = 13.8 Hz, 1H), 2.56 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 161.8 (Cq), 148.4 (CH), 138.6 (CH), 131.5 (CH), 118.3 (CH), 117.2 (Cq), 113.5 (CH), 93.1 (Cq), 87.1 (Cq), 13.2 (CH_3). IR (neat): 2926, 2853, 1756, 1587, 1565, 1547, 1385, 1244, 1227, 1137, 1096, 1061, 1029, 915, 848, 794, 774, 741, 664 cm^{-1}. HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{10}H_9{}^{35}ClNS$: 210.0139; found: 210.0137.

(*E*)-(2-(4-chlorobut-3-en-1-yn-1-yl)phenyl)(methyl) selane (18)

brown oil, yield 76%, 1.9 g.

^1H NMR (300 MHz, $CDCl_3$) δ = 7.27 (d, *J* = 7.5 Hz, 1H), 7.19 - 7.13 (m, 2H), 7.06 – 6.99 (m, 1H), 6.58 (d, *J* = 13.5 Hz, 1H), 6.11 (d, *J* = 13.5 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 136.4 (Cq), 132.3 (CH), 130.6 (CH), 129.2 (CH), 127.6 (CH), 125.3 (CH), 123.1 (Cq), 113.7 (CH), 90.3 (Cq), 89.9 (Cq), 6.2 (CH_3). IR (neat): 3069, 2928, 1732, 1588, 1509, 1458, 1424, 1277, 1243, 1223, 1161, 1063, 1030, 913, 844, 791, 749, 714, 656 cm^{-1}. HRMS (APCI): *m/z* $[M+H]^+$ calcd for $C_{11}H_{10}{}^{37}ClSe$: 256.9628,; found: 256.9635.

Procedure for the Synthesis of (*Z*)-5a

To a solution of alkyne (10 mmol) in Et_2O (150 mL) was added successively (Z)-1,2-dichloroethylene (8 mL, 100 mmol), $PdCl_2(PPh_3)_2$ (700 mg, 1 mmol), *n*-$BuNH_2$ (2 mL, 20 mmol) and CuI in portions (190 mg, 1 mmol). After complete disappearance of starting material monitored by TLC, the solution was filtered through a pad of celite using EtOAc. The organic layer was washed successively with sat. NH_4Cl, sat. $NaHCO_3$ and HCl (1 M) solutions. After drying over $MgSO_4$ and evaporation in vacuo, the crude residue was purified by silica gel column chromatography.

(*Z*)-(2-(4-Chlorobut-3-en-1-yn-1-yl)phenyl)(methyl) sulfane (5a)

brown oil, yield 56%, 1.2 g.

^1H NMR (300 MHz, $CDCl_3$) δ = 7.46 (d, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.8

Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.47 (d, *J* = 7.5 Hz, 1H), 6.16 (d, *J* = 7.5 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 141.8 (Cq), 132.7 (CH), 129.2 (CH), 128.6 (CH), 124.3 (2 CH), 120.9 (Cq), 112.0 (CH), 94.7 (Cq), 89.6 (Cq), 15.2 (CH_3). IR (neat): 3083, 2920, 2197, 1618, 1590, 1575, 1462, 1434, 1333, 1279, 1242, 1074, 1039, 966, 808, 750, 720, 671, 634 cm^{-1}. HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{11}H_{10}{}^{35}ClS$: 209.0186; found: 209.0192.

Procedure for the Synthesis of Dichloroenyne 5c

Triethylamine (40 mL) was added to a stirred mixture of alkyne (3.0 g, 20.2mmol), 2-bromo-1,1-dichloroethylene (5.7 g, 32.3 mmol), $PdCl_2(PPh_3)_2$ (60 mg, 0.085mmol), CuI (27 mg, 0.14mmol) and PPh_3 (53 mg, 0.2 mmol) under argon atmosphere. The mixture was heated under reflux for 4 h. The precipitated ammonium salt was filtered off, the solvent was evaporated and water (75 mL) was added to the residue. The mixture was extracted with Et_2O (3 x 50 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography.

(2-(4,4-Dichlorobut-3-en-1-yn-1-yl)phenyl)(methyl) sulfane (5c)

yellow oil, yield 71%, 3.5 g.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.43 (d, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.25 (s, 1H), 2.49 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 142.0 (Cq), 132.7 (CH), 131.9 (Cq), 129.5 (CH), 124.4 (CH), 124.3 (CH), 120.5 (Cq), 111.0 (CH), 95.1 (Cq), 89.5 (Cq), 15.2 (CH_3). IR (neat): 3029, 2920, 2198, 1591, 1573, 1462, 1434, 1291, 1264, 1243, 1164, 1131, 1079, 1041, 1016, 955, 922, 819, 748, 719, 672, 655 cm^{-1}. HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{11}H_9{}^{35}Cl_2S$: 242.9797; found: 242.9802.

General Procedure for the Synthesis of (*E*)-6a, (*Z*)-6a, (*E*)-9, (*E*)-6b, 6c and (*E*)-19

To a solution of chloroenyne substrate in CH_2Cl_2 (1 mmol) was added MPHT (1.2 equiv), and the resulting solution was stirred at room temperature until disappearance of the starting material (as judged by TLC). The reaction mixture was next treated with a saturated $Na_2S_2O_3$ solution. The organic layer was washed with 10 % HCl solution (3 x 10 ml) and dried with $MgSO_4$. Removal of the solvent yield a crude product, which was purified by silica gel chromatography.

(*E*)-3-Bromo-2-(2-chlorovinyl)benzo[b]thiophene 6a[1]

yellow solid, mp 97.8 - 98.3 °C, yield 88%, 240.1 mg.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.81 - 7.73 (m, 2H), 7.48 - 7.39 (m, 2H), 7.26 (d, *J* = 13.5 Hz,

1H), 6.76 (d, *J* = 13.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.2 (Cq), 136.4 (Cq), 133.0 (Cq), 126.4 (CH), 126.0 (CH), 125.4 (CH), 123.4 (CH), 122.3 (2 CH), 108.7 (Cq). IR (neat): 3055, 1704, 1601, 1504, 1454, 1432, 1320, 1302, 1254, 1229, 1199, 1157, 1015, 920, 866, 786, 760, 746, 719 cm^{-1}. Anal. Calcd. for $C_{10}H_6BrClS$: C 43.90%, H 2.21%. Found C 43.58%, H 2.31%.

(*Z*)-3-Bromo-2-(2-chlorovinyl)benzo[b]thiophene 6a

yellow solid, mp 70.9 -71.8 °C, yield 85%, 232.5 mg.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.87 - 7.80 (m, 2H), 7.48 - 7.40 (m, 2H), 7.26 (d, *J* = 7.8 Hz, 1H), 6.44 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.5 (Cq), 136.8 (Cq), 131.9 (Cq), 126.3 (CH), 125.3 (CH), 123.4 (CH), 122.7 (CH), 122.3 (CH), 119.8 (CH), 111.2 (Cq). IR (neat): 3076, 3055, 3024, 2924, 2851, 1940, 1908, 1819, 1787, 1733, 1641, 1607, 1556, 1483, 1453, 1431, 1338, 1307, 1260, 1242, 1147, 1018, 922, 867, 807, 767, 749, 721, 638 cm^{-1}. Anal. Calcd. for $C_{10}H_6BrClS$: C 43.90%, H 2.21%. Found C 43.63%, H 2.16%.

(*E*)-1-(4-(2-(3-Bromobenzo[b]thiophen-2-yl)vinyl) phenyl)ethanone (9)

yellow solid, mp 163.0 - 163.4 °C, yield 73%, 260.8 mg.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 8.1 Hz, 2H), 7.80 - 7.73 (m, 2H), 7.63 - 7.55 (m, 3H), 7.45 - 7.35 (m, 2H), 7.07 (d, *J* = 15.9 Hz, 1H), 2.61 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.4 (Cq), 141.0 (Cq), 138.8 (Cq), 136.8 (Cq), 136.7 (Cq), 136.6 (Cq), 131.2 (CH), 129.0 (2 CH), 126.9 (2 CH), 126.5 (CH), 125.5 (CH), 123.4 (CH), 123.2 (CH), 122.4 (CH), 110.0 (Cq), 26.7 (CH_3). IR (neat): 1679, 1598, 1560, 1433, 1407, 1356, 1300, 1272, 1255, 1020, 961, 938, 923, 856, 812, 778, 753 cm^{-1}. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{14}OS^{79}Br$: 356.9949; found: 356.9955.

3-Bromo-2-(2,2-dichlorovinyl)benzo[b]thiophene (6c)

white solid, mp 113.1 - 113.5 °C, yield 80%, 246.4 mg.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.85 - 7.78 (m, 2H), 7.49 - 7.41 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.1 (Cq), 137.0 (Cq), 131.1 (Cq), 126.7 (CH), 125.6 (CH), 123.6 (CH), 123.2 (Cq), 122.6 (CH), 122.4 (CH), 111.4 (Cq). IR (neat): 3030, 1747, 1621, 1481, 1452, 1426, 1368, 1325, 1306, 1252, 1220, 1210, 1184, 1086, 1059, 1047, 1034, 1016, 928, 913, 846, 810, 751, 734, 721, 680, 644 cm^{-1}. Anal. Calcd. for $C_{10}H_5BrCl_2S$: C 38.99%, H 1.64%. Found C 39.20%, H 1.64%.

(*E*)-3-Bromo-2-(2-chlorovinyl)thieno[2,3-b]pyridine (6b)

light yellow solid, mp 131.9 - 132.4 °C, yield 65%, 178.5 mg.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.56 (d, *J* = 4.5 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.36 (dd, *J* = 8.1 Hz, *J* = 4.5 Hz, 1H), 7.21 (d, J = 13.5 Hz, 1H), 6.81 (d, J = 13.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 158.3 (Cq), 148.4 (CH), 133.8 (Cq), 132.6 (Cq), 130.8 (CH), 125.9 (CH), 124.0 (CH), 120.8 (CH), 106.0 (Cq). IR (neat): 3048, 2957, 2923, 1733, 1723, 1603, 1552, 1376, 1317, 1277, 1232, 1196, 966, 885, 791, 765, 672 cm^{-1}. HRMS (APCI): m/z $[M+H]^+$ calcd for $C_9H_6{}^{79}Br^{35}ClNS$: 273.9087; found: 273.9086.

(*E*)-3-Bromo-2-(2-chlorovinyl)benzo[b]selenophene 19

white solid, mp 87.7 - 87.9 °C, yield 93%, 298.1 mg.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.38 - 7.27 (m, 2H), 6.62 (d, *J* = 13.5 Hz, 1H). ^{13}C NMR (75 MHz, CDCl3) δ = 140.2 (Cq), 136.8 (Cq), 134.6 (Cq), 128.5 (CH), 126.8 (CH), 125.9 (CH), 125.8 (CH), 125.4 (CH), 123.2 (CH), 110.8 (Cq). IR (neat): 3044, 1941, 1787, 1724, 1702, 1601, 1508, 1460, 1431, 1310, 1291, 1248, 1226, 1158, 1028, 938, 914, 865, 844, 788, 749, 712 cm^{-1}. Anal. Calcd. for $C_{10}H_6BrClSe$: C 37.48%, H 1.89%. Found C 37.41%, H 1.91%.

General Procedure for the Synthesis of (*E*)-8a-g, (*Z*)-8a, (*Z*)-8b, 15

To a mixture of 3-bromobenzo[b]thiophene (1 mmol) in toluene (12 mL) and MeOH (6 mL) was successively added the desired boronic acid (1.3 mmol), K_2CO_3 (276.4 mg, 2 mmol), and [PdCl(dmba)(IMes)] (70.2 mg, 0.1 mmol). The reaction mixture was heated at 90 °C under vigorous stirring and monitored by TLC until complete disappearance of starting material. The solvent was evaporated in vacuo and water (10 mL) was added. After extraction with EtOAc (3 x 10 mL), the combined organic layers were dried with $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was purified by column chromatography to afford the expected product.

(*E*)-1-(4-(2-(2-Chlorovinyl)benzo[b]thiophen-3-yl) phenyl)ethanone (8a)

yellow solid, mp 148.7 - 149.3 °C, yield 90%, 281.6 mg.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.11 (d, *J* = 7.8 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.53 - 7.48 (m, 3H), 7.40 - 7.28 (m, 2H), 6.90 (d, *J* = 13.5 Hz, 1H), 6.67 (d, *J* = 13.5 Hz, 1H), 2.68 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.7 (Cq), 139.3 (Cq), 139.1 (Cq), 137.9 (Cq), 136.5 (Cq), 134.9 (2 Cq), 130.6 (2 CH), 128.8 (2 CH), 126.1 (CH), 125.8 (CH), 125.0 (CH), 123.1 (CH), 122.4 (CH),

121.3 (CH), 26.8 (CH_3). IR (neat): 3057, 1820, 1734, 1680, 1604, 1564, 1551, 1522, 1492, 1457, 1431, 1403, 1356, 1305, 1285, 1264, 1235, 1209, 1182, 1159, 1131, 1112, 1071, 1018, 958, 924, 906, 877, 837, 790, 763, 732, 679, 657, 645, 626 cm^{-1}. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{14}OS^{35}Cl$: 313.0454; found: 313.0458.

(*E*)-2-(2-Chlorovinyl)-3-(4-methoxyphenyl)benzo [b]thiophene (8b)

Yellow solid, mp 93.3 - 93.6 °C, yield 74%, 222.6 mg.

^1H NMR (300 MHz, $CDCl_3$) δ = 7.79 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.39 - 7.28 (m, 4H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 13.5 Hz, 1H), 6.64 (d, *J* = 13.5 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.5 (Cq), 140.1 (Cq), 137.9 (Cq), 136.1 (Cq), 133.7 (Cq), 131.5 (2 CH), 126.8 (CH), 126.4 (Cq), 125.6 (CH), 124.7 (CH), 123.5 (CH), 122.3 (CH), 120.1 (CH), 114.3 (2 CH), 55.5 (CH_3). IR (neat): 3057, 3000, 2957, 2930, 2906, 2835, 1685, 1610, 1573, 1525, 1494, 1460, 1439, 1413, 1356, 1319, 1305, 1287, 1247, 1210, 1176, 1156, 1130, 1109, 1068, 1034, 1017, 924, 874, 834, 805, 788, 762, 733, 682, 659, 624 cm^{-1}. HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{17}H_{14}{}^{35}ClOS$: 301.0448; found: 301.0451.

(*E*)-2-(2-Chlorovinyl)-3-(4-methoxyphenyl)benzo [b]thiophene (8c)

yellow solid, mp 105.9 - 106.5 °C, yield 88%, 277.0 mg.

^1H NMR (300 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 7.2 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.39 - 7.29 (m, 2H), 7.02 - 6.84 (m, 4H), 6.65 (d, *J* = 13.5 Hz, 1H), 6.07 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 148.0 (Cq), 147.6 (Cq), 140.0 (Cq), 137.8 (Cq), 135.8 (Cq), 134.0 (Cq), 127.8 (Cq), 126.7 (CH), 125.6 (CH), 124.8 (CH), 124.1 (CH), 123.5 (CH), 122.3 (CH), 120.3 (CH), 110.6 (CH), 108.7 (CH), 101.4 (CH_2). IR (neat): 1518, 1501, 1479, 1440, 1425, 1367, 1314, 1272, 1239, 1205, 1117, 1094, 1039, 935, 898, 853, 813, 773, 761, 733 cm^{-1}. HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{17}H_{12}{}^{35}ClO_2S$: 315.0241; found: 315.0240.

(*E*)-4-(2-(2-Chlorovinyl)benzo[b]thiophen-3-yl)phenol (8d)

yellow solid, mp 153.0 - 153.7 °C, yield 59%, 169.2 mg.

^1H NMR (300 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.41 - 7.28 (m, 4H), 7.09 - 6.95 (m, 3H), 6.65 (d, *J* = 13.5 Hz, 1H), 5.33 (br, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 155.5 (Cq), 140.1 (Cq), 137.9 (Cq), 136.0 (Cq), 133.8 (Cq), 131.7 (2 CH), 126.8 (CH), 126.7 (Cq), 125.6 (CH), 124.8 (CH), 123.5 (CH), 122.3 (CH), 120.1 (CH), 115.8 (2 CH). IR (neat): 3058, 1611, 1594, 1525, 1495, 1431, 1350, 1236, 1205, 1172, 1104, 1039, 1018, 908, 874, 837,

817, 761, 732 cm^{-1}. HRMS (ESI): m/z $[M-H]^-$ calcd for $C_{16}H_{10}OS^{35}Cl$: 285.0141; found: 285.0130.

(*E*)-3-(3-Chlorophenyl)-2-(2-chlorovinyl)benzo[b] thiophene (8e)

yellow oil, yield 84%, 256.4 mg.

^1H NMR (300 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 7.8 Hz, 1H), 7.57 - 7.28 (m, 7H), 6.94 (d, *J* = 13.5 Hz, 1H), 6.70 (d, *J* = 13.5 Hz, 1H), 1.47 (cyclohexane). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 139.6 (Cq), 137.9 (Cq), 136.0 (Cq), 134.8 (2 Cq), 134.6 (Cq), 130.2 (CH), 130.1 (CH), 128.6 (CH), 128.3 (CH), 126.2 (CH), 125.8 (CH), 125.0 (CH), 123.2 (CH), 122.3 (CH), 121.1 (CH), 27.0 (cyclohexane). IR (neat): 3058, 1595, 1564, 1517, 1470, 1455, 1432, 1403, 1353, 1317, 1288, 1271, 1234, 1208, 1159, 1132, 1094, 1078, 1019, 998, 953, 925, 894, 875, 846, 809, 785, 846, 809, 785, 760, 731, 713, 693, 650 cm^{-1}. Anal. Calcd. for $C_{16}H_{10}Cl_2S$: C 62.96%, H 3.30%. Found C 62.52%, H 3.37%.

(*E*)-2-(2-Chlorovinyl)-3-(4-vinylphenyl)benzo[b] thiophene (8f)

yellow solid, mp 74.8 - 75.6 °C, yield 75%, 222.6 mg.

^1H NMR (300 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 7.5 Hz, 1H), 7.60 - 7.56 (m, 3H), 7.40 - 7.29 (m, 4H), 6.98 (d, *J* = 13.5 Hz, 1H), 6.83 (dd, *J* = 17.7 Hz, *J* = 10.8 Hz, 1H), 6.66 (d, *J* = 13.5 Hz, 1H), 5.87 (d, *J* = 17.7 Hz, 1H), 5.36 (d, *J* = 10.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 139.8 (Cq), 138.0 (Cq), 137.3 (Cq), 136.4 (CH), 135.9 (Cq), 134.1 (Cq), 133.7 (Cq), 130.5 (2 CH), 126.6 (3 CH), 125.7 (CH), 124.8 (CH), 123.5 (CH), 122.3 (CH), 120.5 (CH), 114.7 (CH_2). IR (neat): 3057, 1710, 1685, 1629, 1606, 1524, 1493, 1456, 1432, 1402, 1354, 1317, 1288, 1271, 1249, 1234, 1209, 1180, 1158, 1131, 1113, 1068, 1034, 1017, 989, 925, 907, 876, 844, 802, 787, 762, 731 cm^{-1}. HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{18}H_{14}{}^{35}ClS$: 297.0499; found: 297.0510.

(*E*)-1-(4-(2-(2-Chlorovinyl)thieno[2,3-b]pyridin-3-yl)phenyl)ethanone (8g)

white solid, mp 166.9 - 167.1 °C, yield 85 %, 267.5 mg.

^1H NMR (300 MHz, $CDCl_3$) δ = 8.55 (d, *J* = 3.9 Hz, 1H), 8.12 (d, *J* = 7.8 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.30 - 7.23 (m, 1H), 6.93 (d, J = 13.5 Hz, 1H), 6.75 (d, *J* = 13.5 Hz, 1H), 2.68 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.5 (Cq), 160.1 (Cq), 147.8 (CH), 138.2 (Cq), 136.9 (Cq), 135.0 (Cq), 133.2 (Cq), 132.3 (Cq), 130.4 (2 CH), 130.3 (CH), 129.0 (2 CH), 125.9 (CH), 123.0 (CH), 120.3 (CH), 26.8 (CH_3). IR (neat): 3056, 1682, 1605, 1552, 1518, 1486, 1424, 1404, 1384, 1357, 1264, 1234, 1211, 1183, 1017, 959, 928, 878, 839, 795, 753, 728 cm^{-1}.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{13}NOS^{35}Cl$: 314.0406; found: 314.0400.

(*Z*)-1-(4-(2-(2-Chlorovinyl)benzo[b]thiophen-3-yl)phenyl)ethanone (8a)

yellow solid, mp 179.1 - 179.8 °C, yield 86%, 240.9 mg.

^{1}H NMR (300 MHz, CDCl3) δ = 8.10 (d, *J* = 8.1 Hz, 2H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.56 - 7.50 (m, 3H), 7.44 - 7.31 (m, 2H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.26 (d, *J* = 8.1 Hz, 1H), 2.68 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.7 (Cq), 140.0 (Cq), 139.9 (Cq), 137.9 (Cq), 137.4 (Cq), 136.6 (Cq), 133.8 (Cq), 130.8 (2 CH), 128.7 (2 CH), 125.7 (CH), 124.8 (CH), 123.1 (CH), 122.7 (CH), 122.3 (CH), 118.6 (CH), 26.8 (CH_3). IR (neat): 1680, 1603, 1426, 1403, 1356, 1332, 1265, 1181, 1160, 1130, 1072, 1017, 958, 931, 908, 859, 823, 766, 729, 660, 643 cm^{-1}. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{14}OS^{35}Cl$: 313.0454; found: 313.0448.

(*Z*)-2-(2-Chlorovinyl)-3-(4-methoxyphenyl)benzo[b] thiophene (8b)

yellow solid, mp 116.5 - 117.2 °C, yield 85%, 255.7 mg.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.88 (d, J = 8.1 Hz, 1H), 7.58 (d, J = 8.1 Hz, 1H), 7.41 - 7.31 (m, 4H), 7.05 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 7.8 Hz, 1H), 6.22 (d, J = 7.8 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.5 (Cq), 139.9 (Cq), 138.7 (Cq), 138.6 (Cq), 132.8 (Cq), 131.7 (2 CH), 127.1 (Cq), 125.5 (CH), 124.5 (CH), 123.5 (CH), 123.3 (CH), 122.2 (CH), 117.4 (CH), 114.2 (2 CH), 55.4 (CH_3). IR (neat): 1743, 1685, 1609, 1521, 1484, 1459, 1362, 1331, 1287, 1245, 1175, 1129, 1108, 1033, 851, 825, 788, 765, 730, 663, 643, 622 cm^{-1}. HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{17}H_{14}^{35}ClOS$: 301.0448; found: 301.0449.

2-(2,2-Dichlorovinyl)-3-(4-methoxyphenyl)benzo[b] thiophene 15

yellow solid, mp 116.6 - 117.0 °C, yield 83%, 278.3 mg.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.42 - 7.30 (m, 4H), 7.08 - 7.02 (m, 3H), 3.91 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.6 (Cq), 139.6 (Cq), 138.8 (Cq), 138.7 (Cq), 131.7 (2 CH), 126.7 (Cq), 125.7 (CH), 124.7 (CH), 123.6 (CH), 123.1 (CH), 122.2 (CH), 120.6 (Cq), 114.4 (2 CH), 55.5 (CH_3), one C not seen. IR (neat): 2835, 1609, 1522, 1484, 1461, 1440, 1359, 1287, 1248, 1212, 1179, 1162, 1108, 1035, 912, 839, 813, 764, 735, 664, 645 cm^{-1}. HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{17}H_{13}OS^{35}Cl_2$: 335.0059; found: 335.0057.

General Procedure for the Synthesis of (*E*)-1ab-ak, (*E*)-11, (*Z*)-1al, (*Z*)-1am

To a mixture of chloroenyne substrate (0.5 mmol) in toluene (6 mL) and MeOH (3 mL) was

successively added the desired boronic acid (0.6 mmol), K_2CO_3 (138.2 mg, 1 mmol) and $Pd(PPh_3)_4$ (28.9 mg, 0.025 mmol). The reaction mixture was heated at 90 °C, under vigorous stirring and monitored by TLC until complete disappearance of starting material. The solvent was evaporated in vacuo and water (10 mL) was added. After extraction with CH_2Cl_2 (3 x 10 mL), the combined organic layer were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude material was purified by column chromatography on silica gel.

(*E*)-1-(4-(2-(3-(4-acetylphenyl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethan-1-one (1aa)

yellow solid, mp 199.5 – 199.7 °C.

^{1}H NMR (300 MHz, DMSO) δ = 8.18 (d, *J* = 8.1 Hz, 2H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.68 – 7.63 (m, 4H), 7.55 – 7.33 (m, 4H), 7.24 (d, *J* = 15.9 Hz, 1H), 2.69 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ = 198.0 (Cq), 197.6 (Cq), 141.0 (Cq), 139.7 (Cq), 138.9 (Cq), 138.7 (Cq), 138.0 (Cq), 136.7 (Cq), 136.5 (Cq), 135.9 (Cq), 131.3 (CH), 131.0 (2 CH), 129.3 (2 CH), 129.2 (2 CH), 127.3 (2 CH), 126.5 (CH), 125.8 (CH), 123.3 (CH), 123.2 (2 CH), 27.3 (CH_3), 27.1 (CH_3). IR (neat): 1678, 1599, 1561, 1456, 1432, 1407, 1357, 1306, 1266, 1223, 1182, 1159, 1112, 1073, 1016, 958, 876, 862, 839, 817, 764, 734, 675, 657, 612 cm^{-1}. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{21}O_2S$: 397.1262; found: 397.1272.

(*E*)-1-(4-(2-(4-Fluorostyryl)benzo[b]thiophen-3-yl) phenyl)ethanone (1ab)

yellow solid, mp 163.4 - 164.1 °C, yield 86%, 160.2 mg.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.14 (d, *J* = 7.8 Hz, 2H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.59 - 7.53 (m, 3H), 7.40 - 7.29 (m, 4H), 7.15 - 6.98 (m, 4H), 2.71 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.8 (Cq), 162.6 (d, *J* = 246.9 Hz, Cq), 140.0 (Cq), 139.9 (Cq), 139.3 (Cq), 138.0 (Cq), 136.4 (Cq), 134.6 (Cq), 132.8 (d, *J* = 3.0 Hz, Cq), 130.8 (3 CH), 128.8 (2 CH), 128.3 (d, *J* = 8.3 Hz, 2 CH), 125.5 (CH), 124.9 (CH), 122.8 (CH), 122.4 (CH), 120.6 (CH), 115.8 (d, *J* = 21.6 Hz, 2 CH), 26.8 (CH_3). ^{19}F NMR (188 MHz, $CDCl_3$): δ = - 111.05. IR (neat): 3060, 1680, 1602, 1564, 1551, 1507, 1491, 1456, 1433, 1403, 1356, 1319, 1304, 1265, 1230, 1214, 1182, 1158, 1112, 1096, 1070, 1016, 951, 933, 907, 875, 854, 816, 778, 763, 731, 684, 656 cm^{-1}. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{14}{}^{35}ClS$: 297.0499; found: 297.0510.

(*E*)-2-(4-Fluorostyryl)-3-(4-methoxyphenyl)benzo[b] thiophene (1ac)

yellow solid, mp 108.2 - 108.9 °C, yield 85%, 153.2 mg.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.41 - 7.30 (m, 6H), 7.20 - 6.96 (m, 6H), 3.91 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.5 (d, *J* = 246.2 Hz, Cq), 159.4 (Cq), 140.8 (Cq), 138.1 (2 Cq), 135.9 (Cq), 133.2 (d, *J* = 2.9 Hz, Cq), 131.7 (2 CH),

129.7 (CH), 128.2 (d, *J* = 7.9 Hz, 2 CH), 127.1 (Cq), 125.3 (CH), 124.6 (CH), 123.2 (CH), 122.3 (CH), 121.5 (CH), 115.8 (d, *J* = 21.7 Hz, 2 CH), 114.2 (2 CH), 55.5 (CH_3). ^{19}F NMR (188 MHz, $CDCl_3$): δ = - 111.66. IR (neat): 2835, 1610, 1528, 1510, 1494, 1460, 1436, 1287, 1248, 1231, 1177, 1157, 1034, 952, 856, 816, 789, 763, 735 cm^{-1}. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{23}H_{18}OFS$: 361.1062; found: 361.1075.

(*E*)-1-(4-(2-(3-(Benzo[d][1,3]dioxol-5-yl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethan-1-one (1ad)

yellow solid, mp 148.3 - 148.7 °C, yield 85%, 169.4 mg.

^1H NMR (300 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 8.1 Hz, 2H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.40 - 7.29 (m, 3H), 7.07 - 6.69 (m, 4H), 6.08 (s, 2H), 2.59 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.5 (Cq), 148.1 (Cq), 147.6 (Cq), 141.6 (Cq), 140.5 (Cq), 138.3 (Cq), 137.9 (Cq), 137.0 (Cq), 136.2 (Cq), 129.7 (CH), 128.9 (2 CH), 128.2 (Cq), 126.7 (2 CH), 125.7 (CH), 124.8 (CH), 124.3 (CH), 124.2 (CH), 123.4 (CH), 122.4 (CH), 110.8 (CH), 108.8 (CH), 101.5 (CH_2), 26.7 (CH_3). IR (neat): 1753, 1679, 1599, 1503, 1482, 1367, 1271, 1237, 1220, 1085, 1038, 957, 916, 865, 816, 765, 735 cm^{-1}. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{19}O_3S$: 399.1055; found: 399.1049.

(*E*)-5-(2-(3,4-Dichlorostyryl)benzo[b]thiophen-3-yl)benzo[d][1,3]dioxole (1ae)

yellow solid, mp 162.2 - 163.1 °C, yield 79%, 168.0 mg.

^1H NMR (300 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 7.2 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.48 (s, 1H), 7.39 - 7.19 (m, 5H), 7.01 - 6.87 (m, 4H), 6.09 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 148.1 (Cq), 147.6 (Cq), 140.6 (Cq), 138.2 (Cq), 137.7 (Cq), 137.1 (2 Cq), 136.7 (Cq), 132.9 (Cq), 131.5 (Cq), 130.7 (CH), 128.4 (CH), 128.2 (CH), 125.7 (CH), 125.6 (CH), 124.8 (CH), 124.2 (CH), 123.4 (CH), 123.3 (CH), 122.3 (CH), 110.7 (CH), 108.8 (CH), 101.5 (CH_2). IR (neat): 1754, 1680, 1552, 1502, 1483, 1439, 1367, 1314, 1236, 1218, 1132, 1093, 1039, 937, 908, 884, 810, 763, 733, 674 cm^{-1}. HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{23}H_{15}{}^{35}Cl_2O_2S$: 425.0164; found: 425.0156.

(*E*)-4-(2-(3,4-Dichlorostyryl)benzo[b]thiophen-3-yl)phenol (1af)

yellow solid, mp 153.3 - 154.0 °C, yield 92%, 182.8 mg.

^1H NMR (300 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.46 (s, 1H), 7.39 - 7.17 (m, 7H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 15.9 Hz, 1H), 5.24 (br, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 155.5 (Cq), 140.6 (Cq), 138.2 (Cq), 137.4 (Cq), 137.2 (Cq), 136.8 (Cq),

132.9 (Cq), 131.9 (2 CH), 131.4 (Cq), 130.6 (CH), 128.3 (CH), 128.2 (CH), 127.1 (Cq), 125.7 (CH), 125.6 (CH), 124.7 (CH), 123.4 (2 CH), 122.4 (CH), 115.8 (2 CH). IR (neat): 1611, 1583, 1552, 1527, 1496, 1471, 1433, 1393, 1355, 1317, 1266, 1219, 1172, 1129, 1101, 1029, 941, 906, 880, 846, 810 cm^{-1}. HRMS (ESI): m/z $[M-H]^-$ calcd for $C_{22}H_{13}OS^{35}Cl_2$: 395.0064; found: 395.0064.

(*E*)-3-(4-Methoxyphenyl)-2-(3-methoxystyryl)benzo [b]thiophene (1ag)

yellow oil, yield 89%, 165.8 mg.

^1H NMR (300 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 8.4 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.44 - 7.24 (m, 6H), 7.12 - 6.97 (m, 5H), 6.84 (d, *J* = 8.1 Hz, 1H), 3.94 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.9 (Cq), 159.4 (Cq), 140.8 (Cq), 138.5 (Cq), 138.1 (2 Cq), 136.0 (Cq), 131.7 (2 CH), 130.8 (CH), 129.7 (CH), 127.1 (Cq), 125.3 (CH), 124.6 (CH), 123.2 (CH), 122.3 (CH), 122.1 (CH), 119.3 (CH), 114.2 (2 CH), 113.4 (CH), 112.3 (CH), 55.5 (CH_3), 55.4 (CH_3). IR (neat): 2834, 1734, 1608, 1597, 1575, 1528, 1498, 1460, 1435, 1347, 1287, 1246, 1209, 1176, 1156, 1108, 1034, 949, 908, 846, 815, 782, 762, 734, 687 cm^{-1}. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{21}O_2S$: 373.1262; found: 373.1254.

(*E*)-3-(4-Methoxyphenyl)-2-(3,4,5-trimethoxystyryl) benzo[b]thiophene (1ah)

yellow solid, mp 167.4 - 167.7 °C, yield 87%, 188.2 mg.

^1H NMR (300 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 7.2 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.43 - 7.29 (m, 4H), 7.17 - 6.94 (m, 4H), 6.64 (s, 2H), 3.91 - 3.85 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.4 (Cq), 153.5 (2 Cq), 140.8 (Cq), 138.1 (Cq), 138.0 (Cq), 135.6 (Cq), 132.8 (Cq), 131.7 (2 CH), 131.1 (CH), 127.2 (Cq), 125.2 (CH), 124.6 (CH), 123.2 (CH), 122.3 (CH), 121.2 (CH), 114.2 (2 CH), 104.0 (2 CH), 61.1 (CH_3), 56.4 (2 CH_3), 55.5 (CH_3), one C not seen. IR (neat): 1734, 1610, 1578, 1527, 1506, 1494, 1463, 1453, 1416, 1357, 1335, 1287, 1247, 1234, 1177, 1153, 1126, 1104, 1034, 1005, 942, 908, 845, 812, 788, 764 cm^{-1}. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{26}H_{24}O_4NaS$: 455.1293; found: 455.1302.

(*E*)-4-(2-(3-(4-methoxyphenyl)benzo[b]thiophen-2-yl)vinyl)pyridine (1ai)

yellow oil and solid, yield 75%, 128.8 mg.

^1H NMR (300 MHz, DMSO) δ = 8.51 (d, *J* = 5.7 Hz, 2H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.35 (m, 7H), 7.16 (d, *J* = 8.7 Hz, 2H), 7.08 (d, *J* = 16.2 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ = 159.6 (Cq), 150.6 (2 CH), 143.8 (Cq), 140.1 (Cq), 138.1 (Cq), 137.8 (Cq), 136.8 (Cq), 131.9 (2

CH), 128.7 (CH), 126.5 (CH), 126.0 (Cq), 125.6 (CH), 125.5 (CH), 123.6 (CH), 123.1 (CH), 121.2 (2 CH), 114.9 (2 CH), 55.7 (CH_3). IR (neat): 1593, 1553, 1526, 1501, 1486, 1460, 1415, 1358, 1285, 1247, 1177, 1156, 1109, 1068, 1032, 964, 944, 838, 814, 800, 765, 735 cm^{-1}. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{18}NOS$: 344.1109; found: 344.1106.

(*E*)-1-(4-(2-(2-(benzo[b]thiophen-2-yl)vinyl)benzo[b]thiophen-3-yl)phenyl)ethan-1-one (1aj)

yellow solid, mp 206.9 – 207.2 °C, yield 80%, 164.2 mg.

^1H NMR (300 MHz, DMSO) δ = 8.19 (d, *J* = 7.8 Hz, 2H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.90 – 7.85 (m, 1H), 7.81 – 7.76 (m, 1H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.59 – 7.33 (m, 7H), 7.01 (d, *J* = 15.9 Hz, 1H), 2.69 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ = 198.1 (Cq), 141.8 (Cq), 140.3 (Cq), 139.6 (Cq), 138.9 (Cq), 138.8 (Cq), 138.2 (Cq), 137.9 (Cq), 136.7 (Cq), 135.5 (Cq), 131.0 (2 CH), 129.3 (2 CH), 126.5 (CH), 126.0 (CH), 125.9 (CH), 125.8 (CH), 125.7 (CH), 125.4 (CH), 124.4 (CH), 123.2 (CH), 123.1 (CH), 122.9 (CH), 122.4 (CH), 27.3 (CH_3). IR (neat): 1679, 1602, 1552, 1530, 1455, 1436, 1403, 1356, 1307, 1264, 1213, 1182, 1159, 1111, 1069, 1016, 958, 933, 855, 817, 764, 747, 734, 726 cm^{-1}. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{20}OS_2$: 411.0877; found: 411.0869.

(*E*)-1-(4-(2-(3-(4-Fluorophenyl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethanone (1ak)

yellow solid, mp 144.3 - 144.5 °C, yield 82%, 152.7 mg.

^1H NMR (300 MHz, $CDCl_3$) δ = 7.93 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.57 - 7.24 (m, 10H), 7.08 (d, *J* = 16.9 Hz, 1H), 2.61 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.4 (Cq), 162.7 (d, *J* = 246.2 Hz, Cq), 141.4 (Cq), 140.4 (Cq), 138.3 (Cq), 138.2 (Cq), 136.3 (Cq), 136.2 (Cq), 132.2 (d, *J* = 8.0 Hz, 2 CH), 130.6 (d, *J* = 3.1 Hz, Cq), 130.1 (CH), 129.0 (2 CH), 126.7 (2 CH), 125.8 (CH), 124.9 (CH), 123.8 (CH), 123.2 (CH), 122.4 (CH), 115.9 (d, *J* = 21.4 Hz, 2 CH), 26.7 (CH_3). ^{19}F NMR (188 MHz, $CDCl_3$): δ = - 111.67. IR (neat): 1679, 1599, 1561, 1526, 1492, 1433, 1409, 1358, 1305, 1269, 1258, 1223, 1182, 1158, 1095, 1015, 958, 943, 908, 861, 842, 815, 764 cm^{-1}. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{18}OFS$: 373.1062; found: 373.1067.

(*E*)-1-(4-(4-(2-(methylthio)phenyl)but-1-en-3-yn-1-yl)phenyl)ethanone 11

white solid, mp 80.1 - 80.3 °C, yield 71%, 103.8 mg.

^1H NMR (300 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.18 - 7.06 (m, 3H), 6.57 (d, *J* = 16.2 Hz, 1H), 2.59 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.4 (Cq), 141.8 (Cq), 140.8 (Cq), 140.1 (CH), 136.8 (Cq), 132.5 (CH), 129.1 (CH), 128.9 (2 CH), 126.5 (2 CH), 124.4 (CH), 124.2 (CH), 121.2 (Cq),

111.0 (CH), 95.0 (Cq), 90.9 (Cq), 26.7 (CH_3), 15.2 (CH_3). IR (neat): 1677, 1598, 1560, 1506, 1463, 1433, 1409, 1357, 1308, 1270, 1262, 1241, 1182, 1114, 1076, 1040, 1014, 959, 945, 860, 812, 751 cm^{-1}. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{17}OS$: 293.1000; found: 293.0992.

(*Z*)-1-(4-(2-(4-Methoxystyryl)benzo[b]thiophen-3-yl)phenyl)ethanone (1al)

yellow solid, mp 143.7 - 144.1 °C, yield 89%, 171.1 mg.

^1H NMR (300 MHz, DMSO) δ = 8.11 (d, *J* = 8.1 Hz, 2H), 7.90 - 7.86 (m, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.54 - 7.50 (m, 1H), 7.39- 7.28 (m, 4H), 6.90 (d, *J* = 8.1 Hz, 2H), 6.72 (d, *J* = 12.0 Hz, 1H), 6.47 (d, *J* = 12.0 Hz, 1H), 3.77 (s, 3H), 2.64 (s, 3H), 1.38 (cyclohexane). ^{13}C NMR (75 MHz, DMSO) δ = 198.0 (Cq), 159.6 (Cq), 139.6 (Cq), 139.0 (Cq), 138.4 (Cq), 136.9 (Cq), 136.4 (Cq), 135.5 (Cq), 133.4 (CH), 130.8 (2 CH), 130.7 (2 CH), 129.0 (2 CH), 128.6 (Cq), 125.8 (CH), 125.3 (CH), 123.0 (CH), 122.7 (CH), 121.0 (CH), 114.3 (2 CH), 55.6 (CH_3), 27.3 (CH_3), 26.8 (cyclohexane). IR (neat): 1735, 1680, 1603, 1510, 1457, 1435, 1404, 1356, 1305, 1266, 1245, 1175, 1143, 1110, 1081, 1032, 1018, 951, 907, 875, 850, 819, 764, 728 cm^{-1}. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{21}O_2S$: 385.1262; found: 385.1260.

(*Z*)-1-(4-(2-(3-(4-Methoxyphenyl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethanone (1am)

yellow solid, mp 123.2 – 123.6 °C, yield 83%, 159.6 mg.

^1H NMR (300 MHz, DMSO) δ = 7.94 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 4.8 Hz, 1H), 7.54 - 7.51 (m, 3H), 7.41 - 7.34 (m, 4H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.78 (d, *J* = 12.0 Hz, 1H), 6.65 (d, *J* = 12.0 Hz, 1H), 3.84 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ = 197.8 (Cq), 159.5 (Cq), 141.6 (Cq), 139.0 (Cq), 138.8 (Cq), 137.8 (Cq), 136.4 (Cq), 134.3 (Cq), 131.8 (2 CH), 131.2 (CH), 129.7 (2 CH), 128.8 (2 CH), 126.6 (Cq), 125.9 (CH), 125.1 (CH), 124.6 (CH), 123.1 (CH), 122.9 (CH), 114.7 (2 CH), 55.7 (CH_3), 27.1 (CH3). IR (neat): 1675, 1612, 1595, 1559, 1525, 1503, 1491, 1410, 1357, 1288, 1269, 1246, 1181, 1153, 1108, 1060, 1033, 958, 941, 907, 863, 838, 813, 769, 728 cm^{-1}. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{21}O_2S$: 385.1262; found: 385.1261.

Procedure for the Synthesis of 1ca and 16

In a round-bottomed flask, under an argon atmosphere, containing the chlorovinylic substrate (0.5 mmol) and $Fe(acac)_3$ (0.05 mmol) was added THF (6 mL). The reaction mixture was cooled to -30 °C and EtMgBr (0.75 mmol of typically 1 M solution in THF) was added dropwise (for the synthesis of **18** the quantity of EtMgBr was 1.5 mmol). The red colored solution turned dark brown to black (depending on the Grignard reagent quantity). The reaction mixture was stirred

until the disappearance of starting material as judged by TLC. A 1 M aq HCl solution (5.0 mL) was then added, and the two layers were separated. After extraction using Et_2O (2 × 20 mL), the combined organic layers were washed three times with H_2O, then dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude residue was then purified by silica gel column chromatography.

(*E*)-2-(But-1-en-1-yl)-3-(4-methoxyphenyl) benzo[b]thiophene (1ca)

yellow solid, mp 73.6 - 73.9 °C, yield 84 %, 123.7 mg.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 6.9 Hz, 1H), 7.55 (d, *J* = 6.9 Hz, 1H), 7.40 - 7.29 (m, 4H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 15.6 Hz, 1H), 6.33 - 6.23 (m, 1H), 3.93 (s, 3H), 2.29 - 2.19 (m, 2H), 1.10 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.1 (Cq), 140.9 (Cq), 138.6 (Cq), 137.8 (Cq), 135.7 (CH), 133.5 (Cq), 131.6 (2 CH), 127.4 (Cq), 124.7 (CH), 124.3 (CH), 122.9 (CH), 122.2 (2 CH), 114.1 (2 CH), 55.4 (CH_3), 26.4 (CH_2), 13.6 (CH_3). IR (neat): 1751, 1682, 1610, 1529, 1499, 1458, 1434, 1381, 1356, 1287, 1246, 1206, 1181, 1132, 1107, 1083, 1034, 955, 910, 841, 812, 762, 732 cm^{-1}. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{19}OS$: 295.1157; found: 295.1160.

2-(2-Ethylbut-1-en-1-yl)-3-(4-methoxyphenyl)benzo[b] thiophene (16)

colorless oil, yield 74 %, 119.3 mg.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.83 - 7.80 (m, 1H), 7.59 - 7.55 (m, 1H), 7.37 - 7.28 (m, 4H), 7.02 (d, *J* = 7.8 Hz, 2H), 6.27 (s, 1H), 3.89 (s, 3H), 2.50 (q, *J* = 7.5 Hz, 2H), 2.17 (q, *J* = 7.5 Hz, 2H), 1.12 (t, *J* = 7.5 Hz, 3H), 1.03 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 158.8 (Cq), 148.6 (Cq), 139.7 (Cq), 138.8 (Cq), 136.1 (Cq), 134.2 (Cq), 131.6 (2 CH), 127.9 (Cq), 124.1 (CH), 124.0 (CH), 122.7 (CH), 121.8 (CH), 116.3 (CH), 113.8 (2 CH), 55.3 (CH_3), 30.4 (CH_2), 25.0 (CH_2), 12.9 (2 CH_3). IR (neat): 2965, 1610, 1524, 1492, 1460, 1431, 1352, 1287, 1247, 1176, 1157, 1108, 1069, 1035, 936, 870, 830, 801, 764, 734 cm^{-1}. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{21}OS$: 321.1313; found: 321.1323.

General procedure for the Synthesis of (*E*)-12, (*E*)-13

To a solution of $PdCl_2(PhCN)_2$ (9.6 mg, 0.025 mmol), (*E*)-chlorovinylic substrate (0.5 mmol), CuI (9.5 mg, 0.05 mmol) in 3 mL of piperidine was added the required 1-alkyne (0.6 mmol) in 1 mL of piperidine. The stirring was continued at 60 °C until TLC analysis indicated complete consumption of the chloroenyne. The reaction mixture was hydrolyzed with H_2O (10 mL) and

HCl 0.5M (10 mL) and extracted with diethylether (3 x 10 mL). The organic layers were dried over $MgSO_4$ and the solvent was removed in vacuo. Purification by column chromatography afforded the expected (*E*)-enynes.

(*E*)-3-(4-Methoxyphenyl)-2-(4-(2-(methylthio)phenyl)but-1-en-3-yn-1-yl)benzo[b]thiophene (12)

brown oil, yield 91%, 187.7 mg.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.44 - 7.26 (m, 6H), 7.21 - 7.08 (m, 5H), 6.43 (d, *J* = 15.9 Hz, 1H), 3.93 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.5 (Cq), 141.6 (Cq), 140.5 (Cq), 138.4 (Cq), 137.3 (Cq), 136.9 (Cq), 134.1 (CH), 132.4 (CH), 131.7 (2 CH), 128.9 (CH), 126.7 (Cq), 125.8 (CH), 124.7 (CH), 124.4 (CH), 124.3 (CH), 123.6 (CH), 122.3 (CH), 121.5 (Cq), 114.3 (2 CH), 109.7 (CH), 95.4 (Cq), 90.8 (Cq), 55.5 (CH_3), 15.2 (CH_3). IR (neat): 1680, 1609, 1598, 1576, 1525, 1494, 1462, 1433, 1357, 1320, 1287, 1246, 1209, 1178, 1160, 1130, 1109, 1079, 1035, 936, 908, 844, 814, 765, 751 cm^{-1}. HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{26}H_{21}OS_2$: 413.1028; found: 413.1017.

(*E*)-*N*-(2-(4-(3-(4-Methoxyphenyl)benzo[b]thiophen-2-yl)but-3-en-1-yn-1-yl)phenyl)-*N*,4-dimethyl benzenesulfonamide (13)

yellow solid, mp 80.9 - 81.2 °C, yield 75 %, 206.1 mg.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 8.1 Hz, 1H), 7.61 - 7.57 (m, 3H), 7.42 - 7.27 (m, 8H), 7.17 - 7.08 (m, 4H), 6.89 (d, *J* = 15.9 Hz, 1H), 5.91 (d, *J* = 15.9 Hz, 1H), 3.92 (s, 3H), 3.30 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.7 (Cq), 143.5 (Cq), 142.2 (Cq), 140.4 (Cq), 138.3 (Cq), 137.4 (Cq), 136.5 (Cq), 136.2 (Cq), 133.9 (CH), 133.5 (CH), 131.6 (2 CH), 131.4 (CH), 129.6 (2 CH), 129.1 (CH), 128.0 (CH), 127.8 (2 CH), 126.5 (Cq), 126.0 (CH), 124.8 (CH), 123.7 (CH), 122.6 (Cq), 122.4 (CH), 114.3 (2 CH), 109.3 (CH), 93.8 (Cq), 90.0 (Cq), 55.5 (CH_3), 38.1 (CH_3), 21.6 (CH_3). IR (neat): 1610, 1525, 1495, 1482, 1443, 1348, 1288, 1248, 1210, 1176, 1155, 1109, 1090, 1070, 1036, 938, 910, 891, 867, 845, 815, 765, 732, 710, 696, 676, 650 cm^{-1}. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{33}H_{28}NO_3S_2$: 550.1511; found: 550.1503.

Procedure for the Synthesis of 14

Toluene (3 mL) was added to a mixture of $AuBr_3$ (21.8 mg, 0.05 mmol) and **13** (274.9 mg, 0.5 mmol) at rt and the mixture was warmed immediately to 80 °C. After complete consumption of the starting material, as monitored by TLC, the reaction mixture was cooled to rt and filtered

through a short SiO_2 pad, and the filtrate was concentrated. The residue was purified by silica-gel column chromatography.

(*E*)-2-(2-(3-(4-Methoxyphenyl)benzo[b]thiophen-2-yl)vinyl)-1-methyl-3-tosyl-1*H*-indole (14)

brown solid, mp 169.5 - 169.7 °C, yield 90 %, 247.4 mg.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.29 - 8.25 (m, 1H), 7.92 - 7.84 (m, 3H), 7.74 (d, *J* = 16.5 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.46 - 7.26 (m, 8H), 7.20 - 7.15 (m, 2H), 7.11 - 7.05 (m, 2H), 3.91 (s, 3H), 3.73 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.6 (Cq), 143.1 (Cq), 141.3 (Cq), 140.4 (Cq), 140.3 (Cq), 138.9 (Cq), 138.3 (Cq), 137.7 (Cq), 137.1 (Cq), 131.6 (2 CH), 130.7 (CH), 129.6 (2 CH), 126.6 (Cq), 126.5 (2 CH), 126.1 (CH), 125.2 (Cq), 124.9 (CH), 124.1 (CH), 123.7 (CH), 122.8 (CH), 122.6 (CH), 120.5 (CH), 117.1 (CH), 114.3 (2 CH), 113.5 (Cq), 110.0 (CH), 55.5 (CH_3), 32.4 (CH_3), 21.6 (CH_3). IR (neat): 2957, 1732, 1609, 1531, 1505, 1458, 1437, 1393, 1317, 1287, 1249, 1213, 1179, 1159, 1141, 1109, 1082, 1033, 1017, 976, 909, 843, 811, 765, 737, 724, 705 cm^{-1}. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{33}H_{28}NO_3S_2$: 550.1511; found: 550.1503.

References

(1) D. C. Neckers and F. L. Wagenaar, *J. Org. Chem.*, 1983, **48**, 1725-1732.

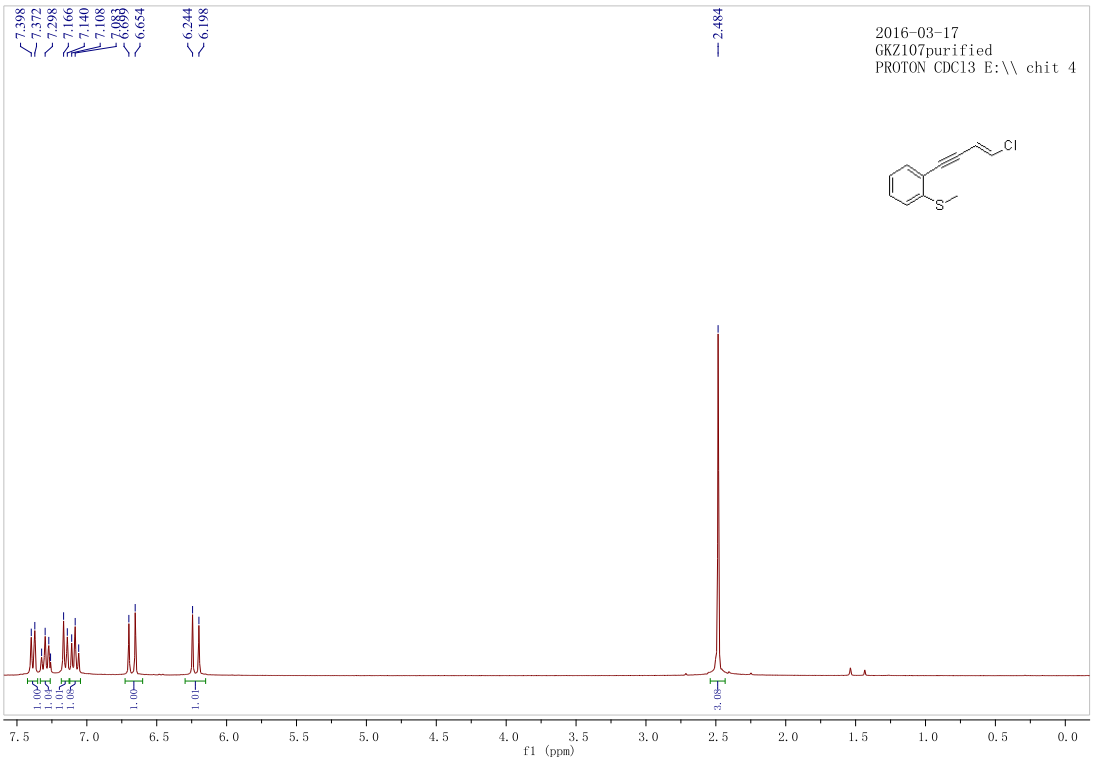

Fig. 1 ^{1}H NMR of (*E*)-(2-(4-chlorobut-3-en-1-yn-1-yl)phenyl)(methyl)sulfane **5a**

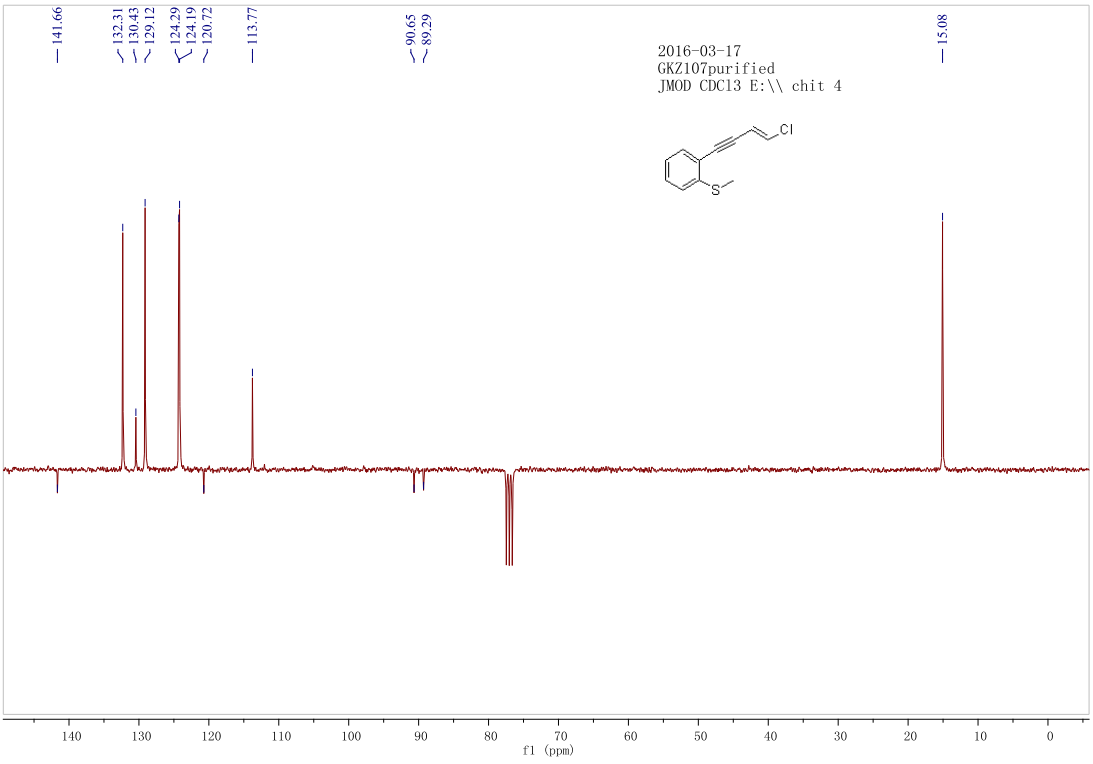

Fig. 2 ^{13}C NMR of (*E*)-(2-(4-chlorobut-3-en-1-yn-1-yl)phenyl)(methyl)sulfane **5a**

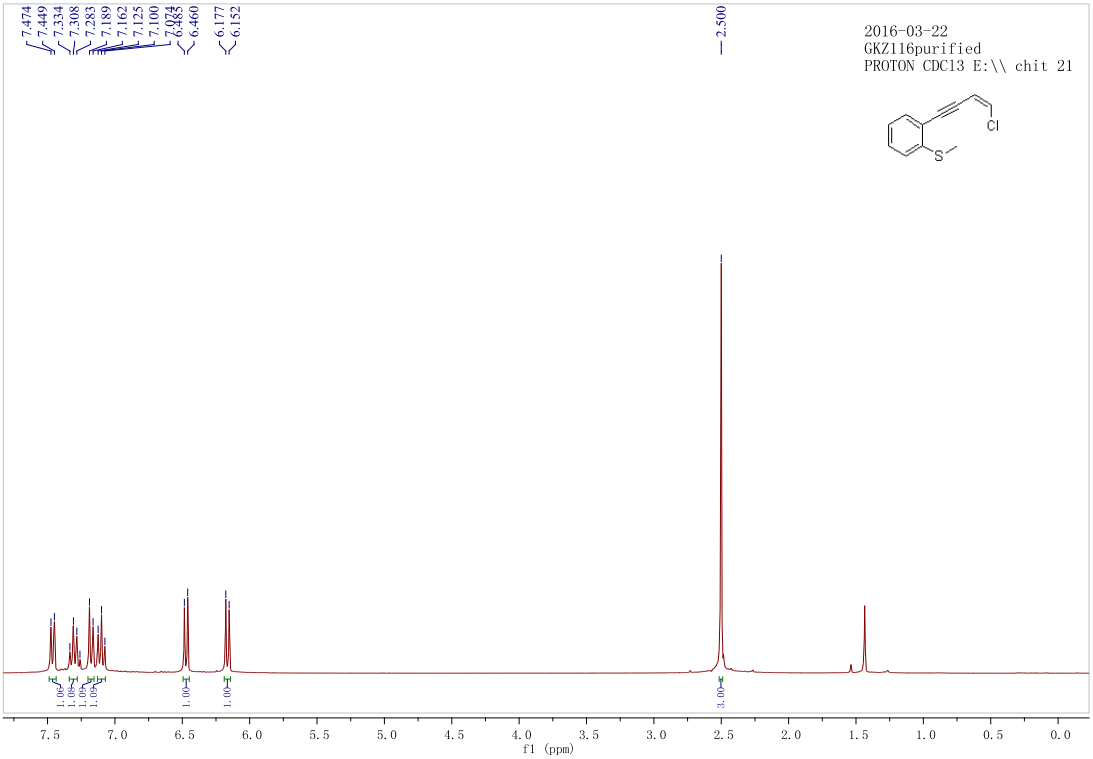

Fig. 3 ^{1}H NMR of (*Z*)-(2-(4-chlorobut-3-en-1-yn-1-yl)phenyl)(methyl)sulfane **5a**

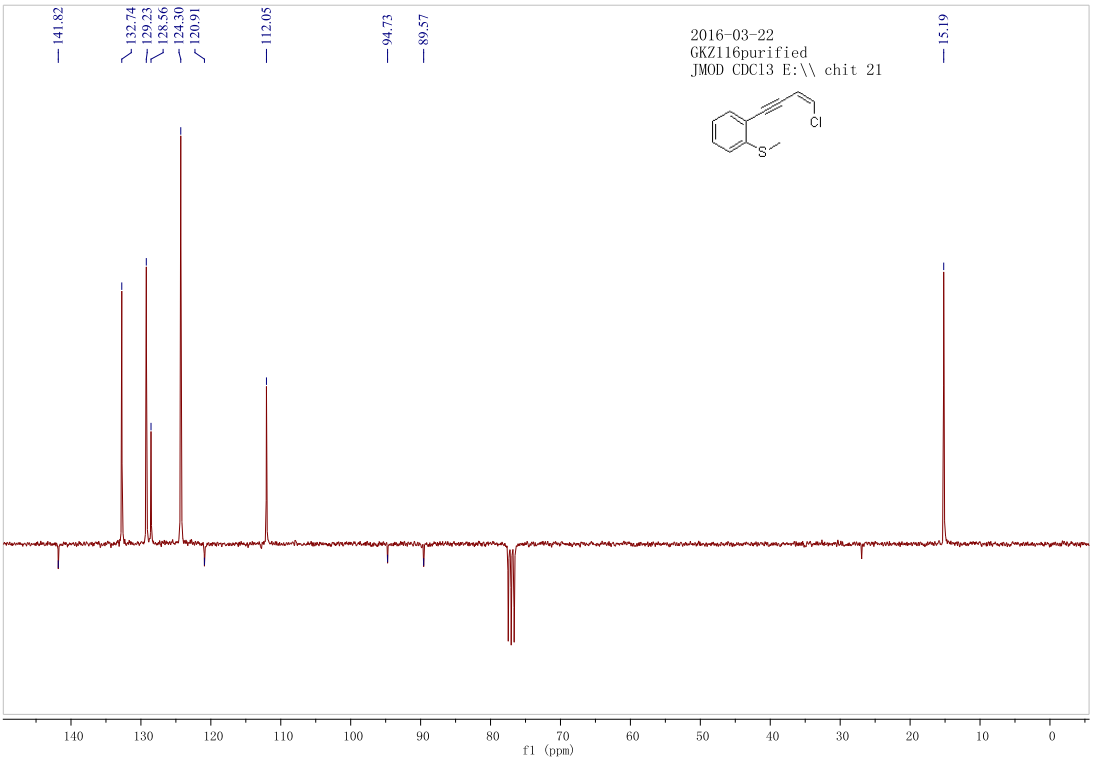

Fig. 4 ^{13}C NMR of (*Z*)-(2-(4-chlorobut-3-en-1-yn-1-yl)phenyl)(methyl)sulfane **5a**

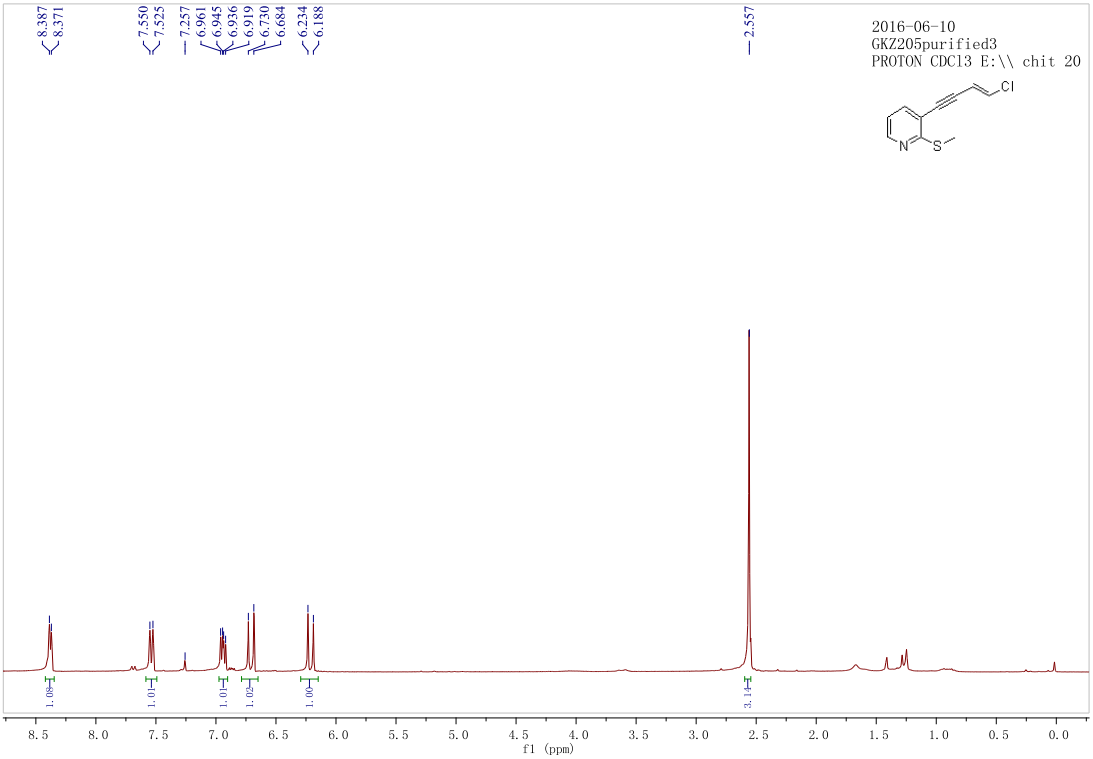

Fig. 5 ^{1}H NMR of (*E*)-3-(4-chlorobut-3-en-1-yn-1-yl)-2-(methylthio)pyridine **5b**

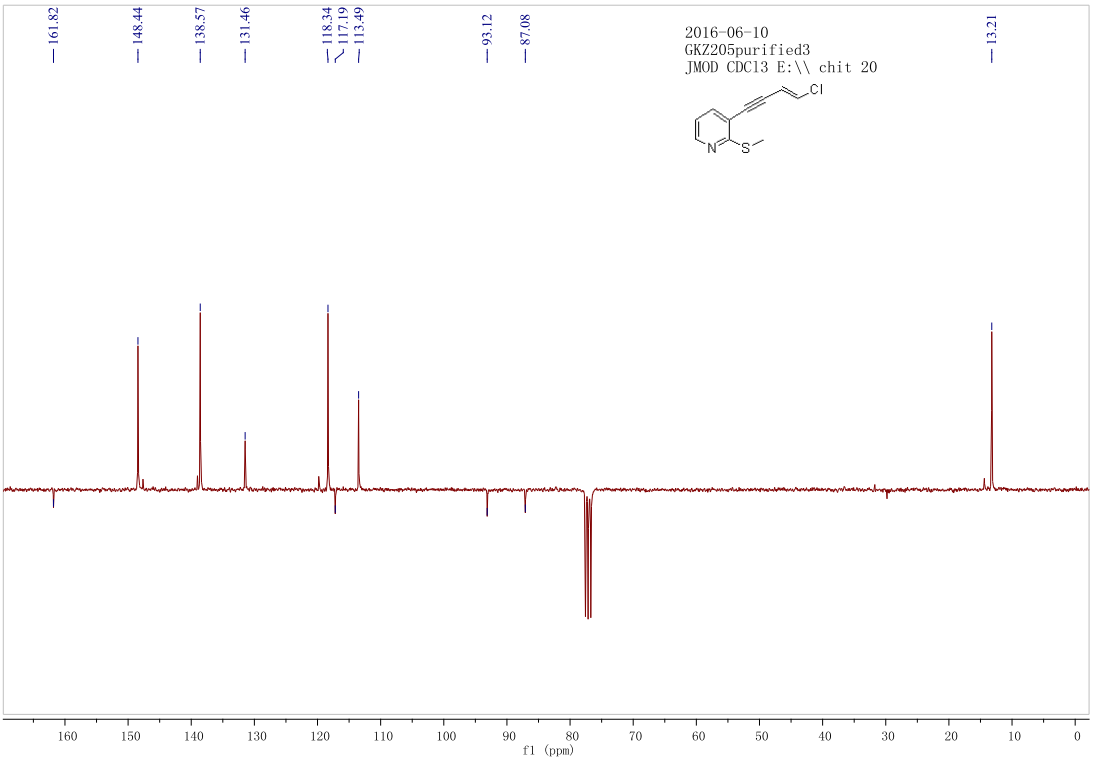

Fig. 6 ^{13}C NMR of (*E*)-3-(4-chlorobut-3-en-1-yn-1-yl)-2-(methylthio)pyridine **5b**

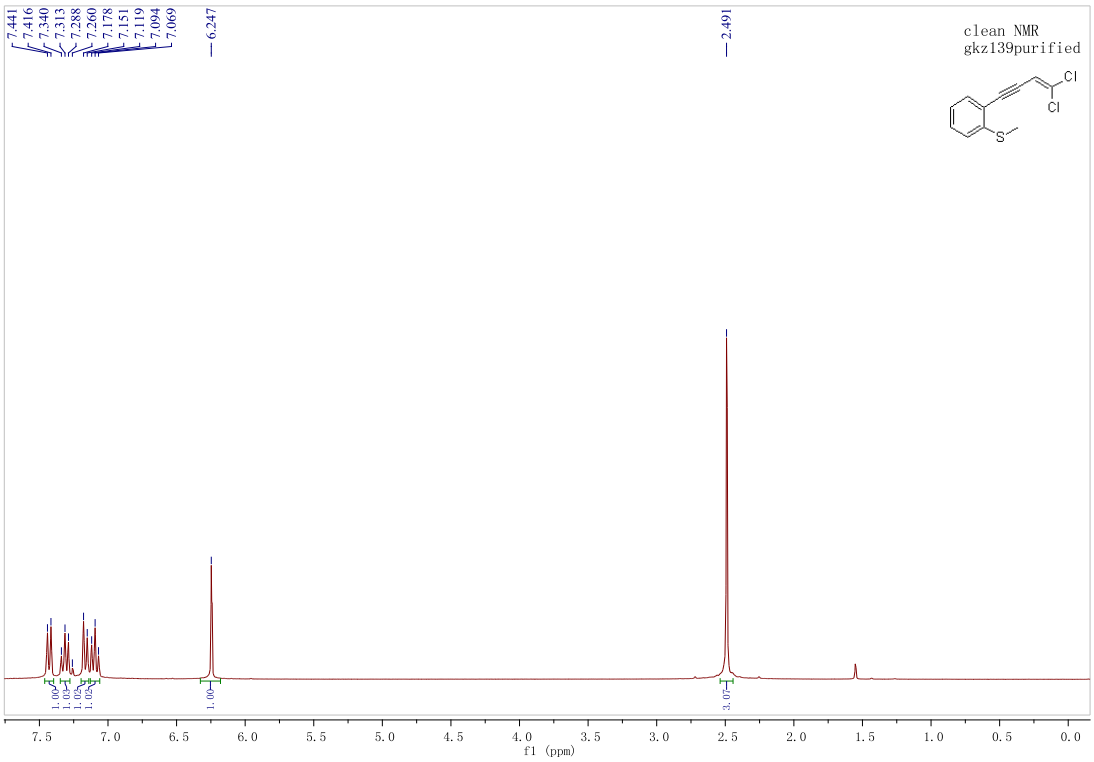

Fig. 7 ^{1}H NMR of (2-(4,4-dichlorobut-3-en-1-yn-1-yl)phenyl)(methyl)sulfane **5c**

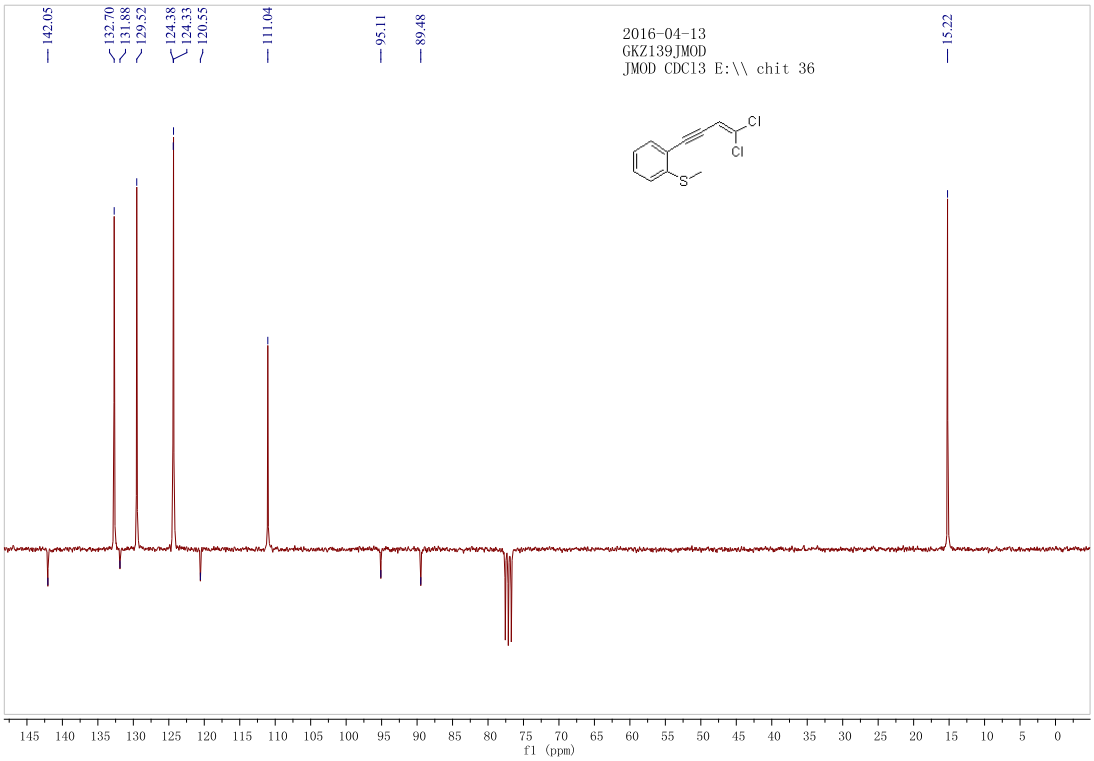

Fig. 8 ^{13}C NMR of (2-(4,4-dichlorobut-3-en-1-yn-1-yl)phenyl)(methyl)sulfane **5c**

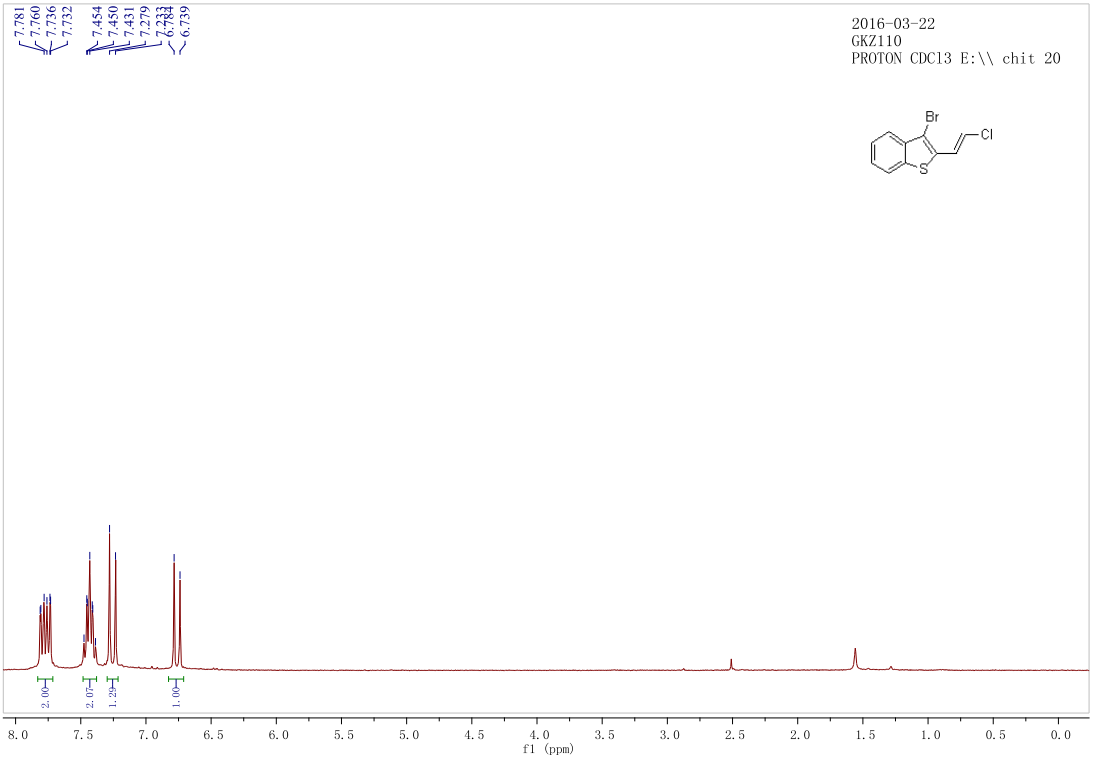

Fig. 9 ^{1}H NMR of (*E*)-3-bromo-2-(2-chlorovinyl)benzo[b]thiophene **6a**

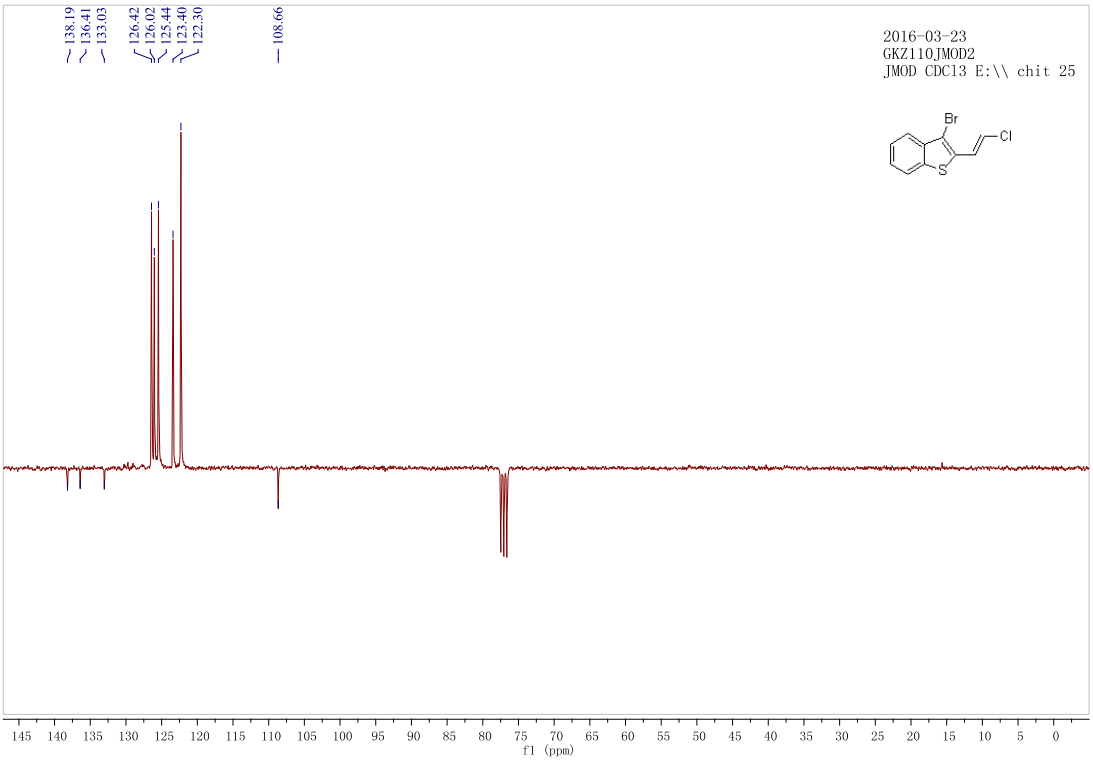

Fig. 10 ^{13}C NMR of (*E*)-3-bromo-2-(2-chlorovinyl)benzo[b]thiophene **6a**

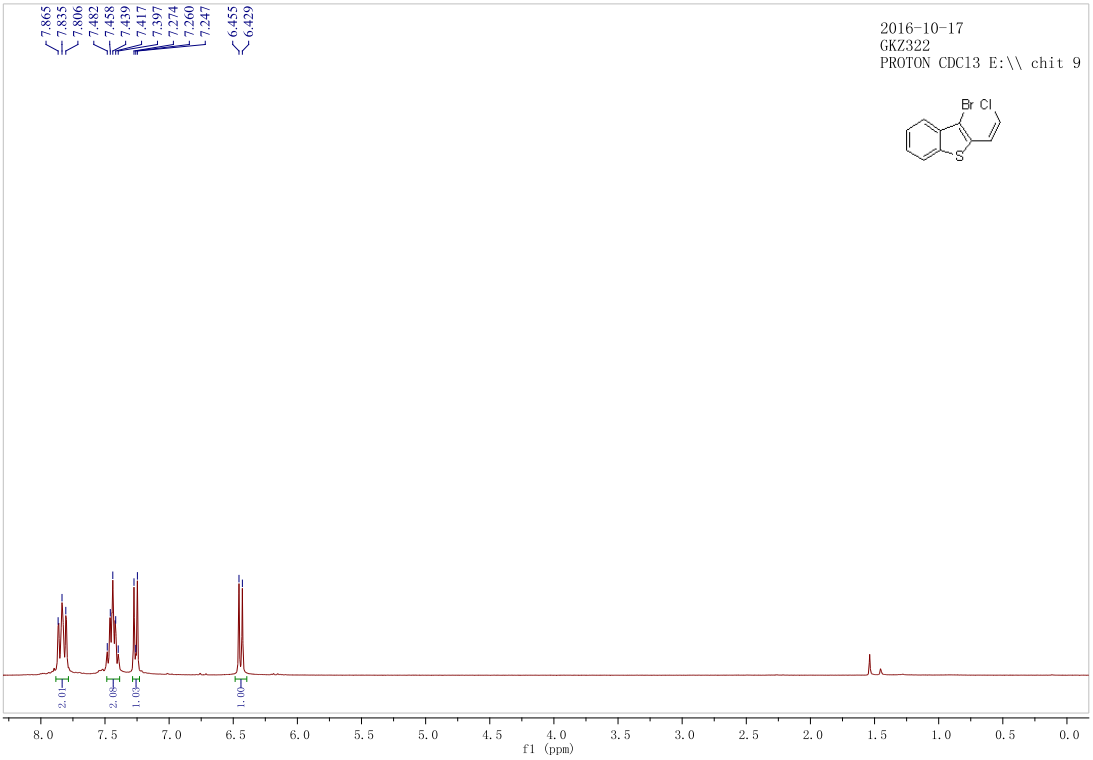

Fig. 11 ^{1}H NMR of (*Z*)-3-bromo-2-(2-chlorovinyl)benzo[b]thiophene **6a**

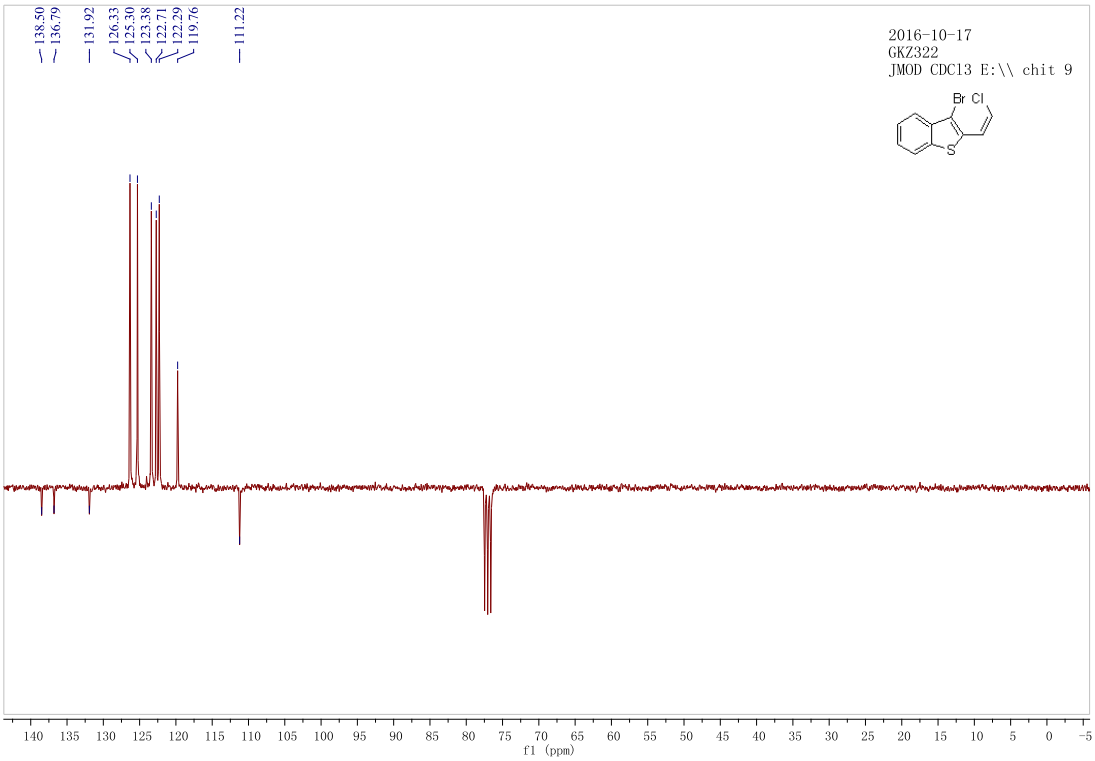

Fig. 12 ^{13}C NMR of (*Z*)-3-bromo-2-(2-chlorovinyl)benzo[b]thiophene **6a**

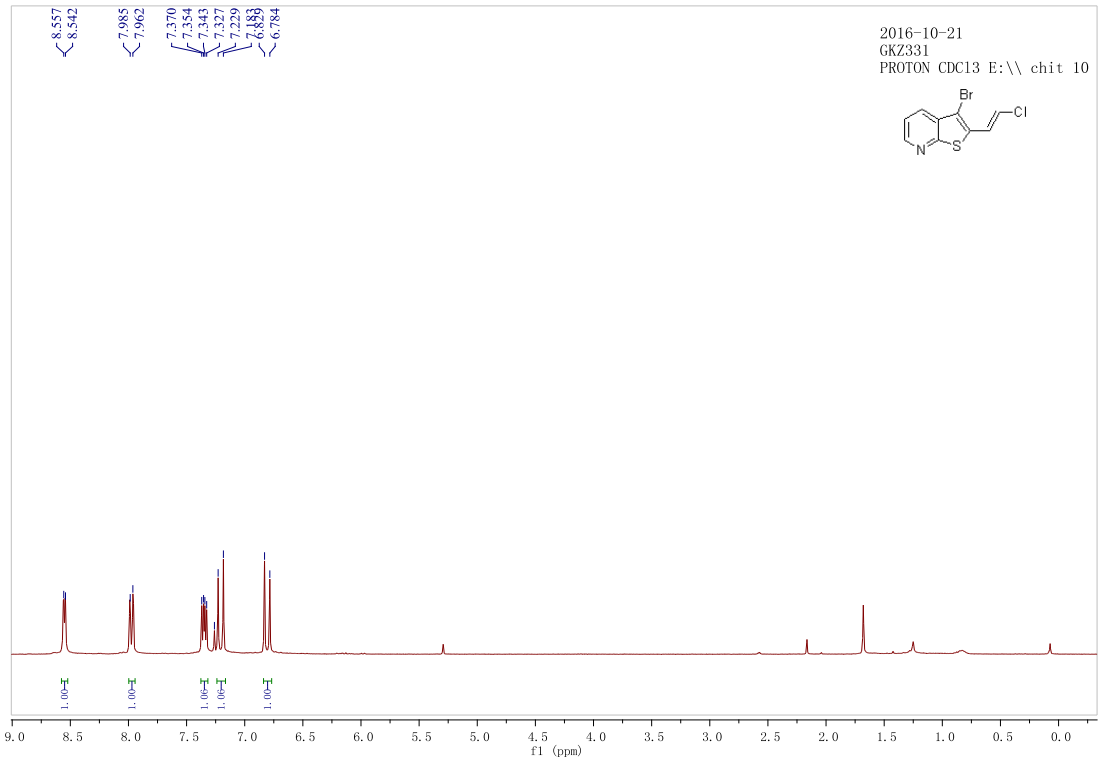

Fig. 13 ^{1}H NMR of (*E*)-3-bromo-2-(2-chlorovinyl)thieno[2,3-b]pyridine **6b**

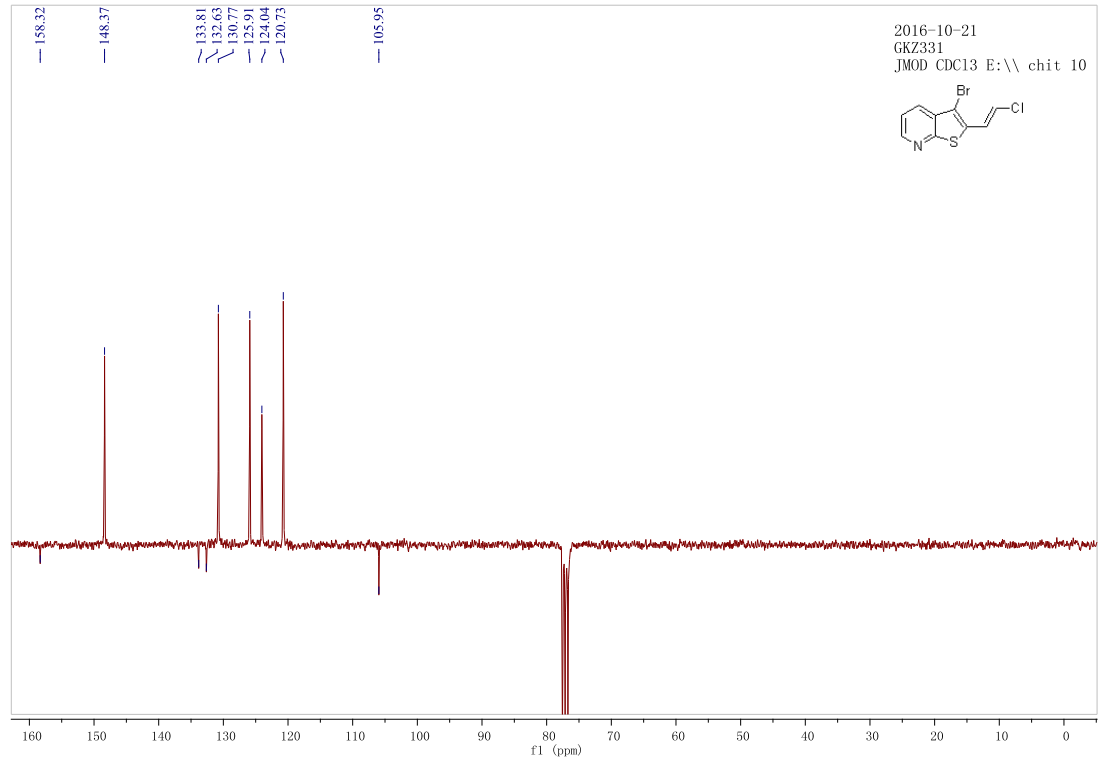

Fig. 14 ^{1}H NMR of (*E*)-3-bromo-2-(2-chlorovinyl)thieno[2,3-b]pyridine **6b**

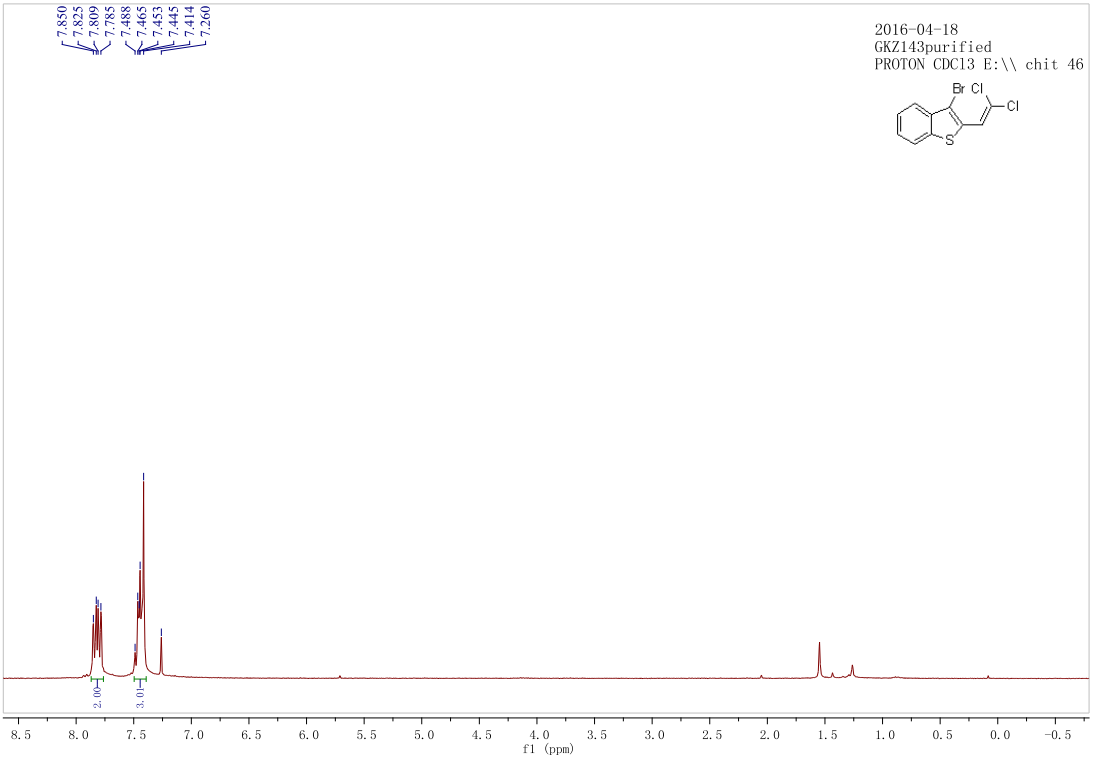

Fig. 15 ^{1}H NMR of 3-bromo-2-(2,2-dichlorovinyl)benzo[b]thiophene **6c**

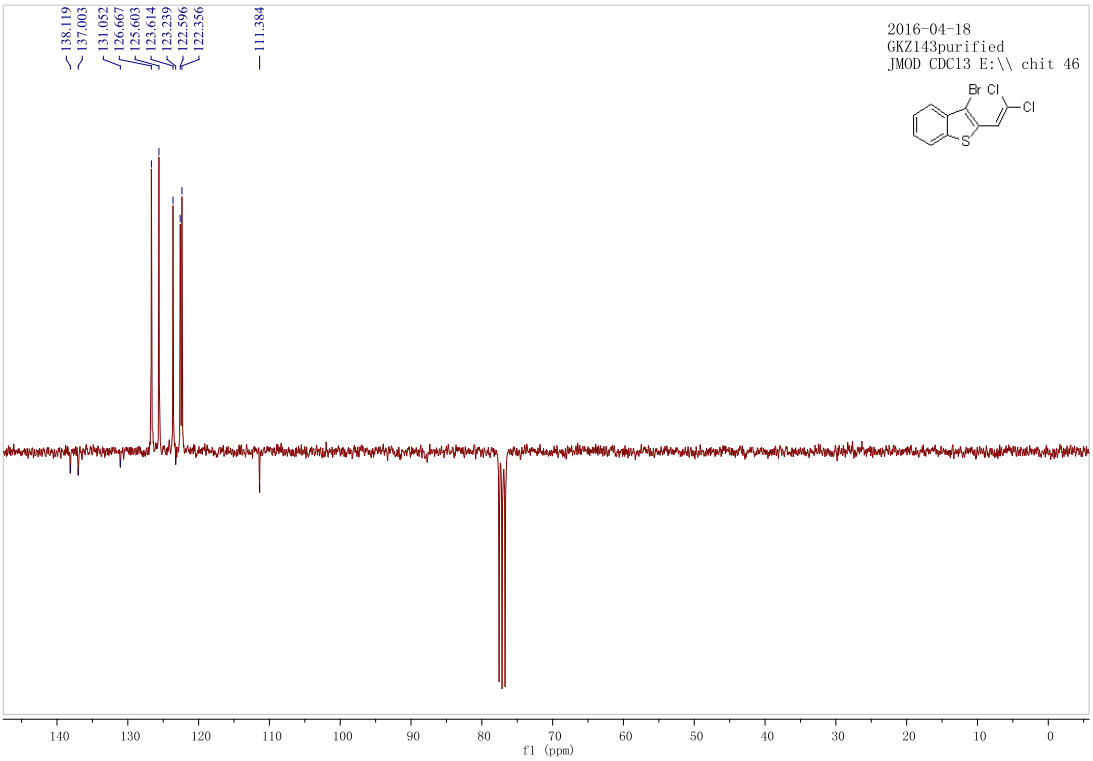

Fig. 16 ^{13}C NMR of 3-bromo-2-(2,2-dichlorovinyl)benzo[b]thiophene **6c**

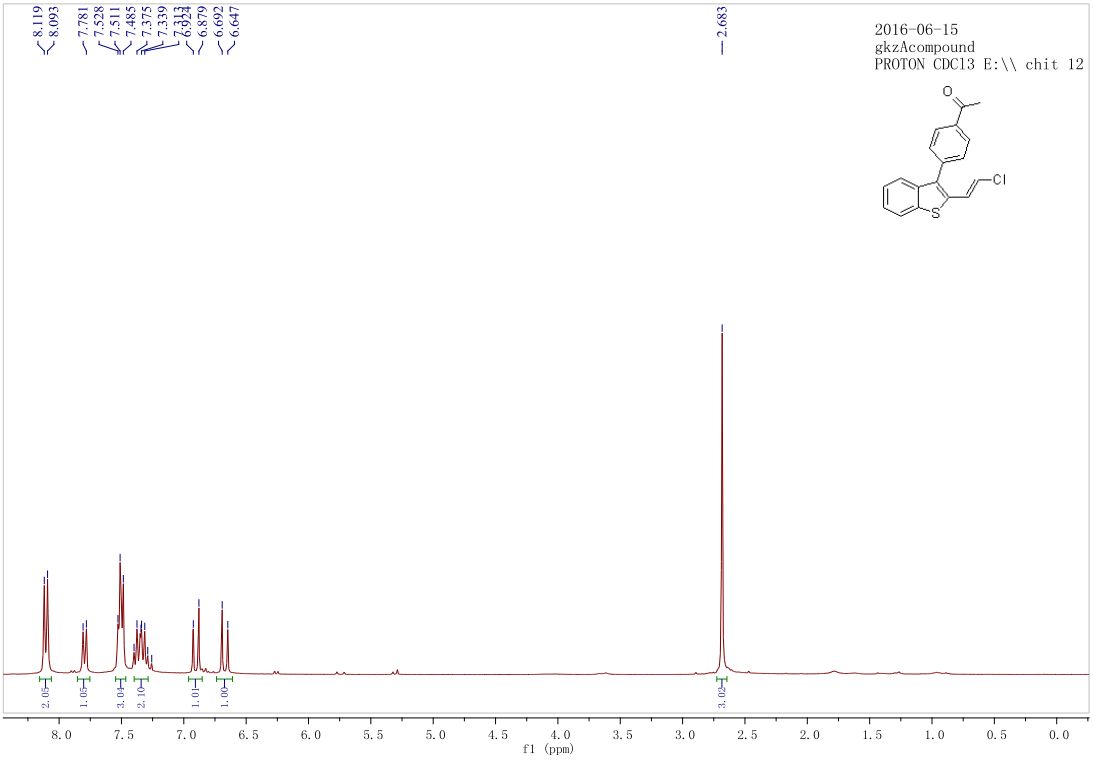

Fig. 17 ^{1}H NMR of (*E*)-1-(4-(2-(2-chlorovinyl)benzo[b]thiophen-3-yl)phenyl)ethanone **8a**

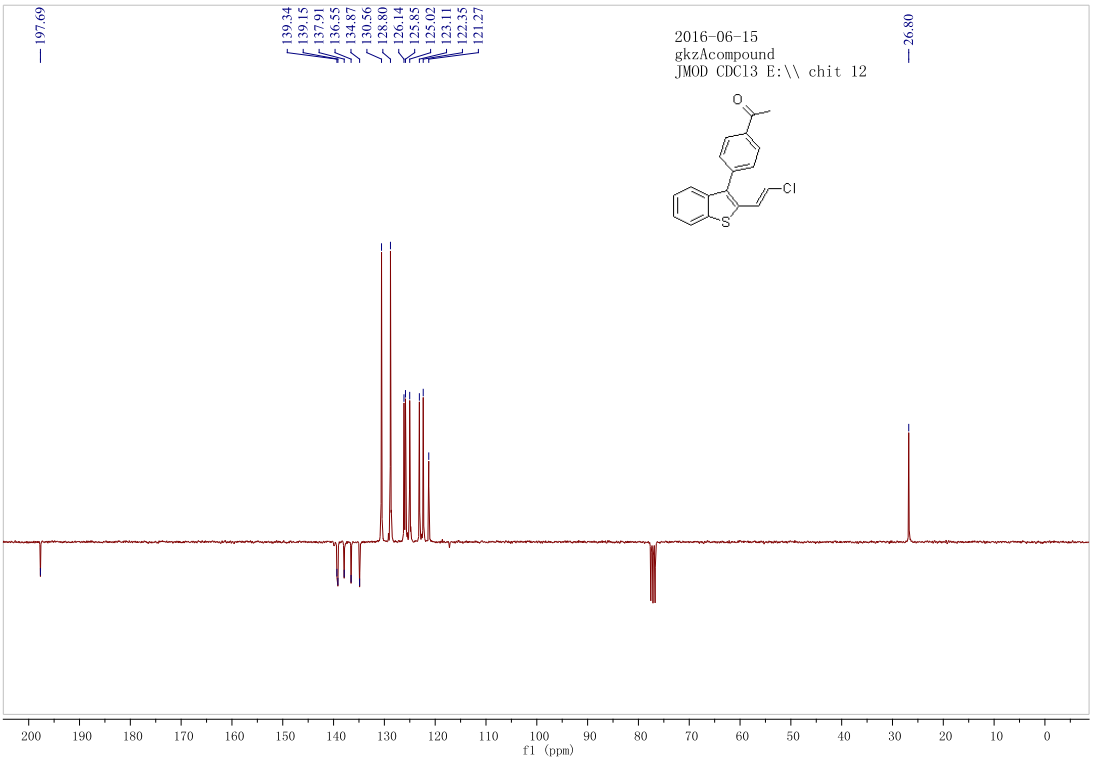

Fig. 18 ^{13}C NMR of (*E*)-1-(4-(2-(2-chlorovinyl)benzo[b]thiophen-3-yl)phenyl)ethanone **8a**

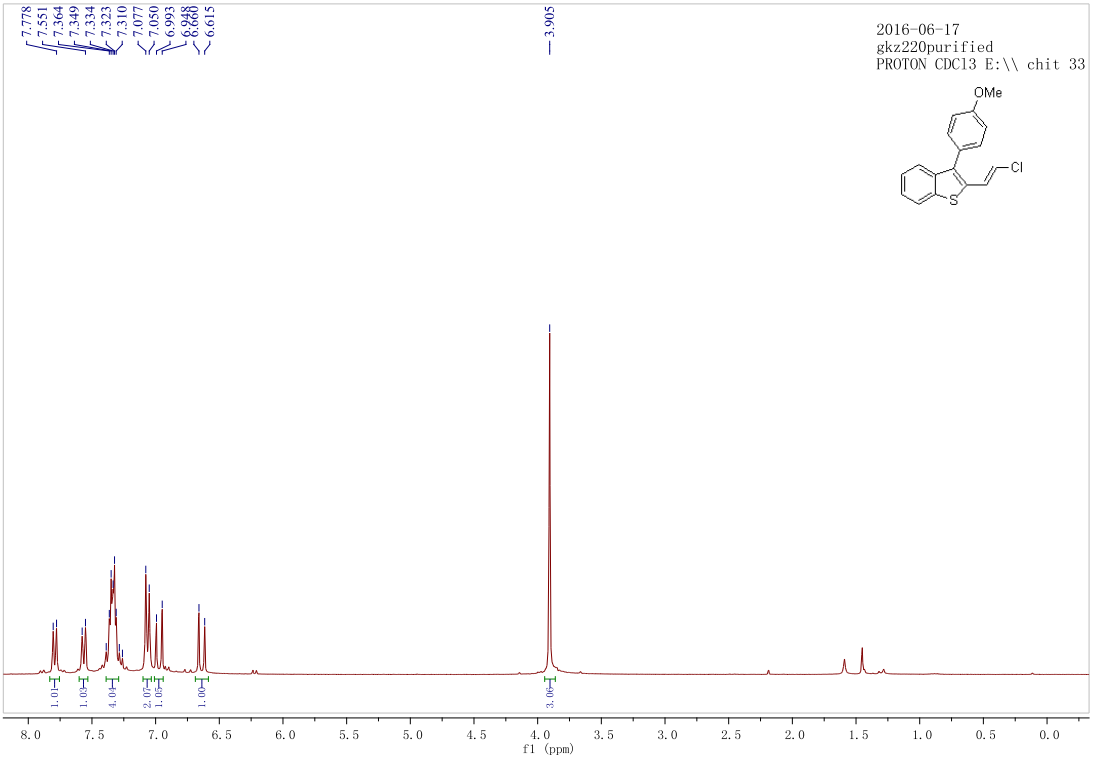

Fig. 19 ^{1}H NMR of (*E*)-2-(2-chlorovinyl)-3-(4-methoxyphenyl)benzo[b]thiophene **8b**

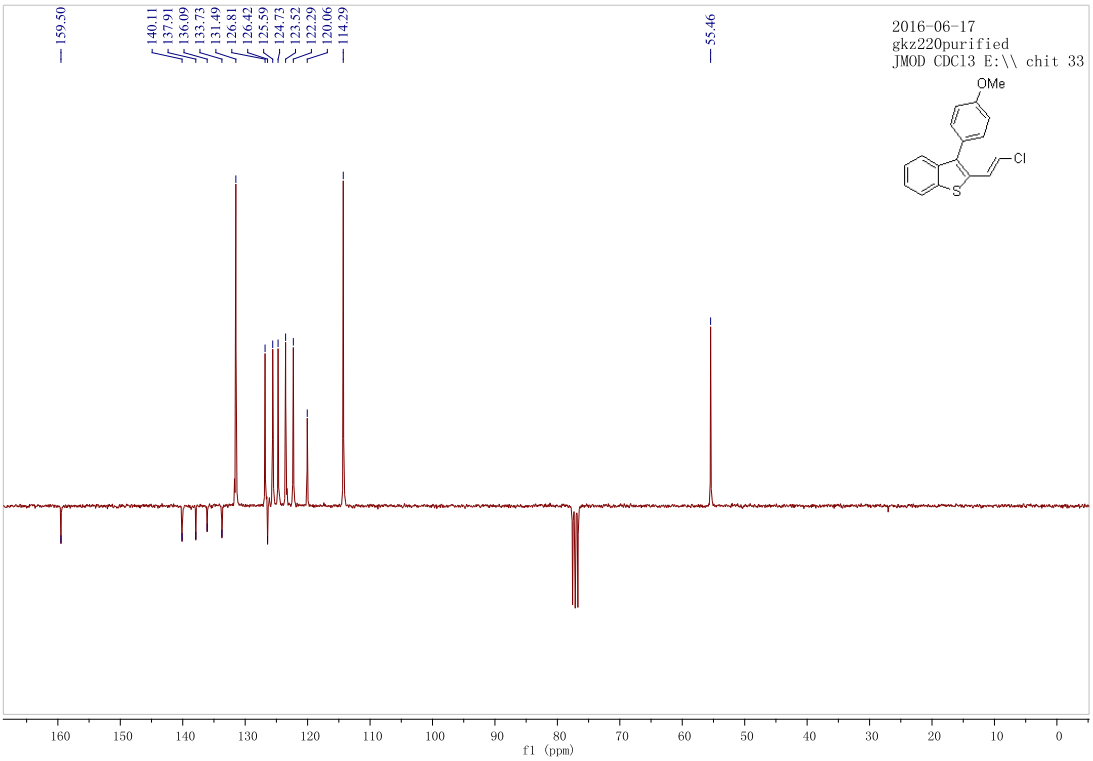

Fig. 20 ^{13}C NMR of (*E*)-2-(2-chlorovinyl)-3-(4-methoxyphenyl)benzo[b]thiophene **8b**

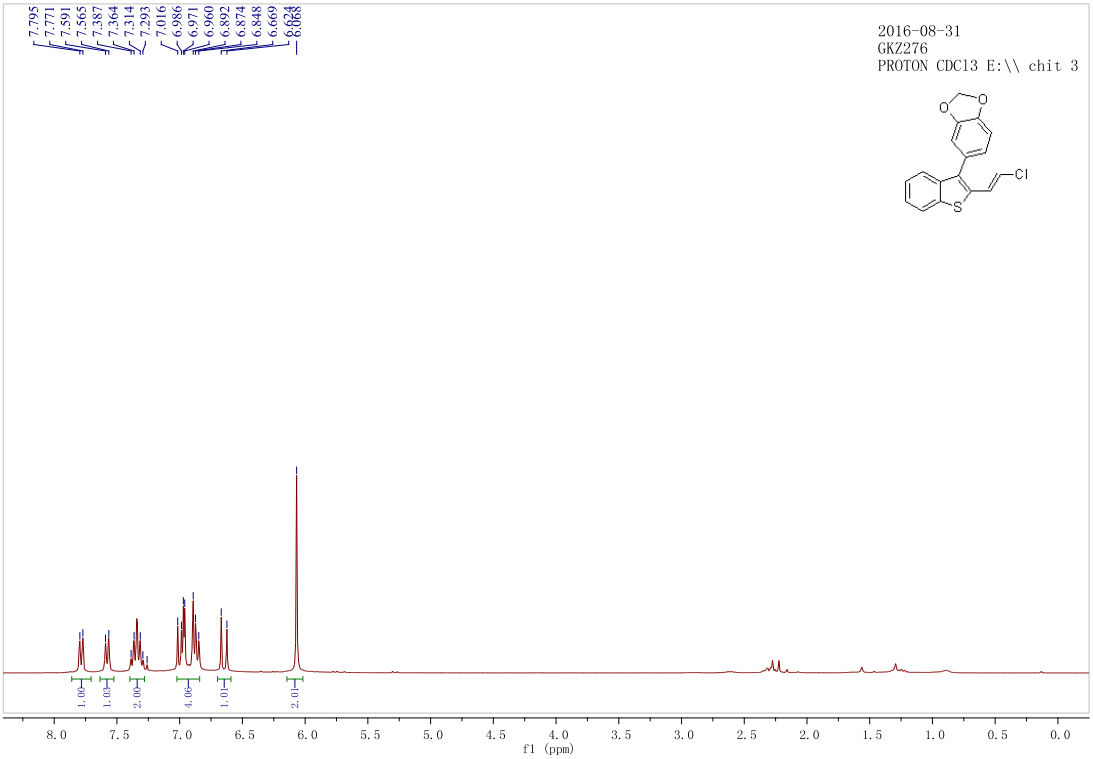

Fig. 21 ^{1}H NMR of (*E*)-5-(2-(2-chlorovinyl)benzo[b]thiophen-3-yl)benzo[d][1,3]dioxole **8c**

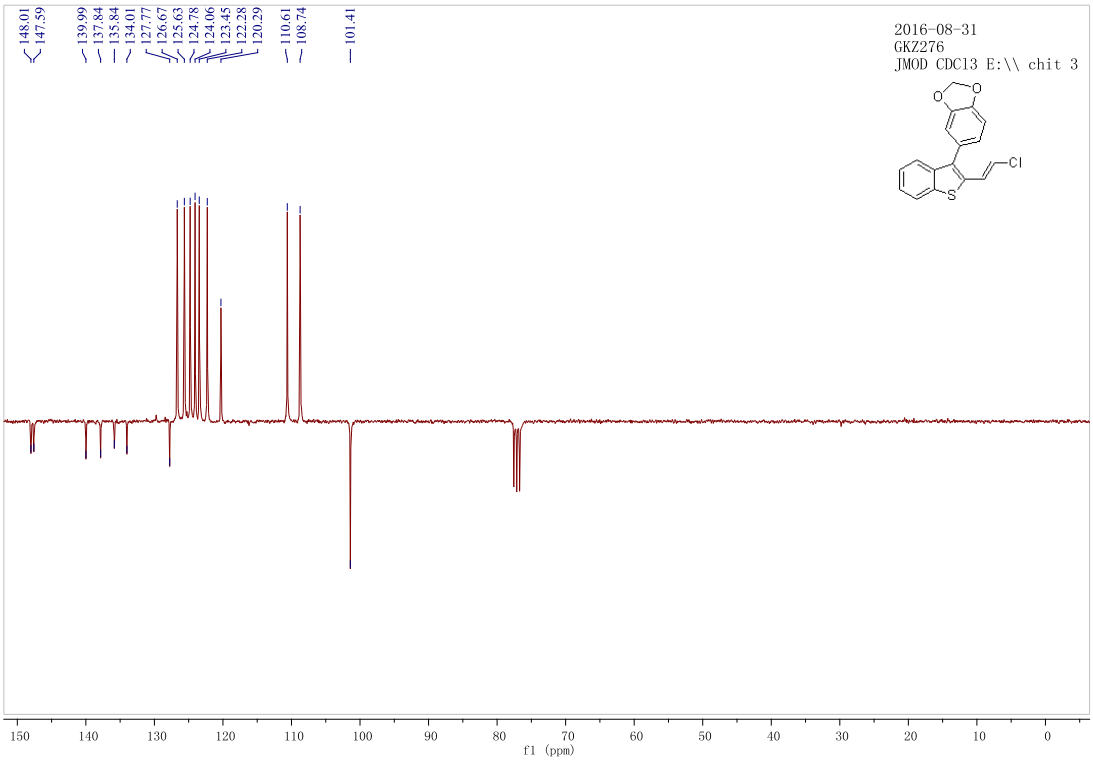

Fig. 22 ^{13}C NMR of (*E*)-5-(2-(2-chlorovinyl)benzo[b]thiophen-3-yl)benzo[d][1,3]dioxole **8c**

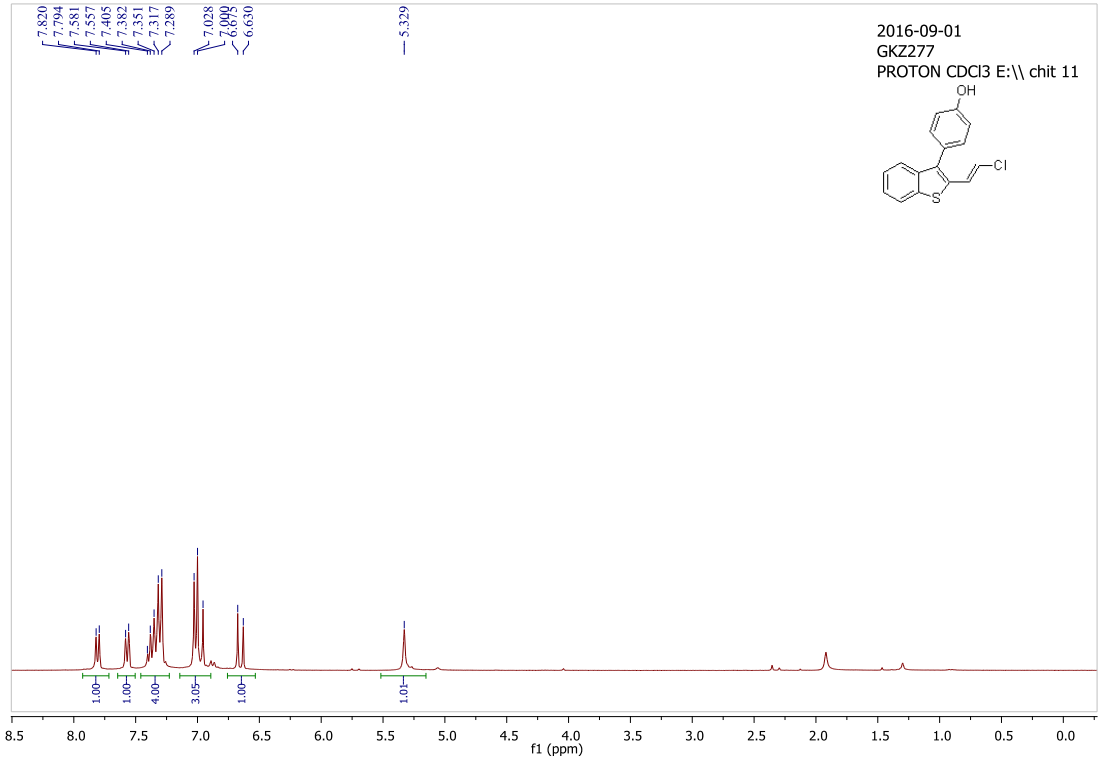

Fig. 23 ^{1}H NMR of (*E*)-4-(2-(2-chlorovinyl)benzo[b]thiophen-3-yl)phenol **8d**

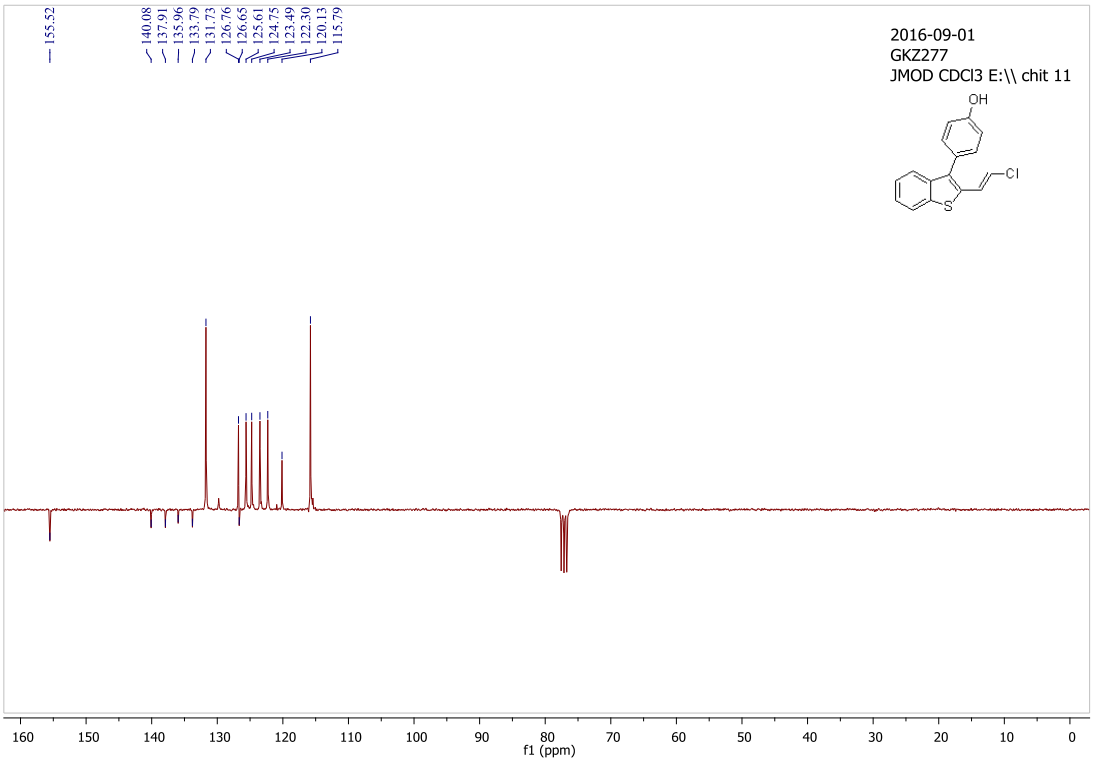

Fig. 24 ^{13}C NMR of (*E*)-4-(2-(2-chlorovinyl)benzo[b]thiophen-3-yl)phenol **8d**

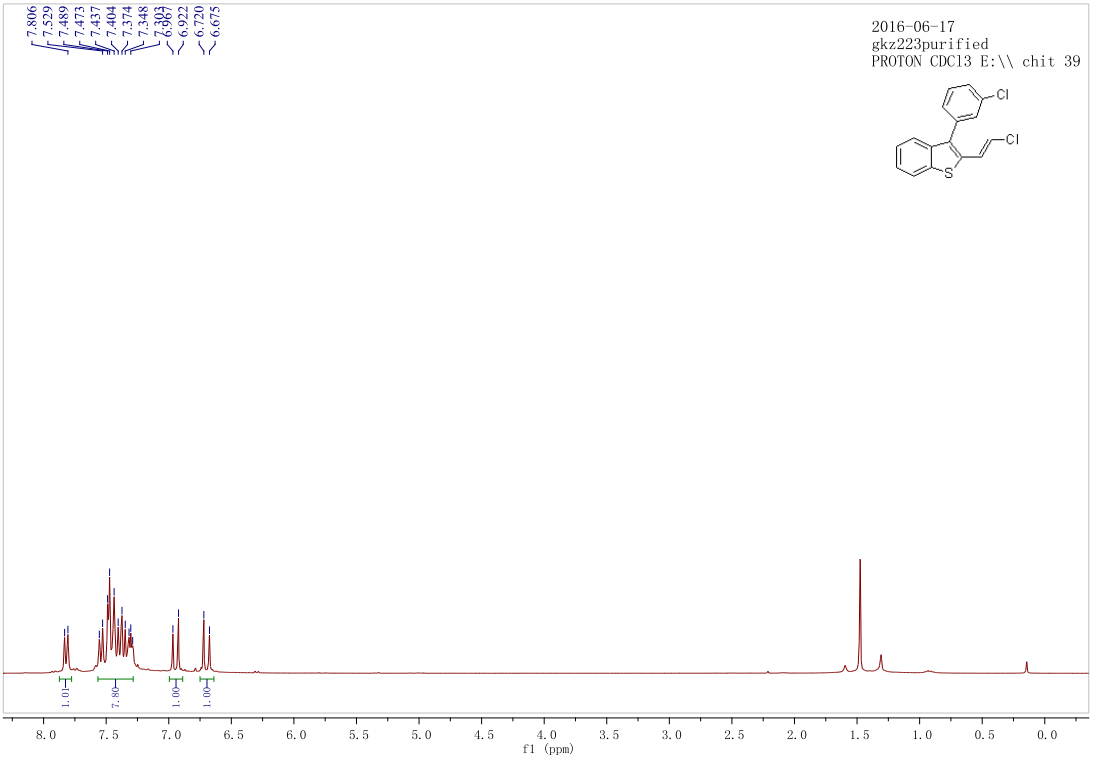

Fig. 25 ^{1}H NMR of (*E*)-3-(3-chlorophenyl)-2-(2-chlorovinyl)benzo[b]thiophene **8e**

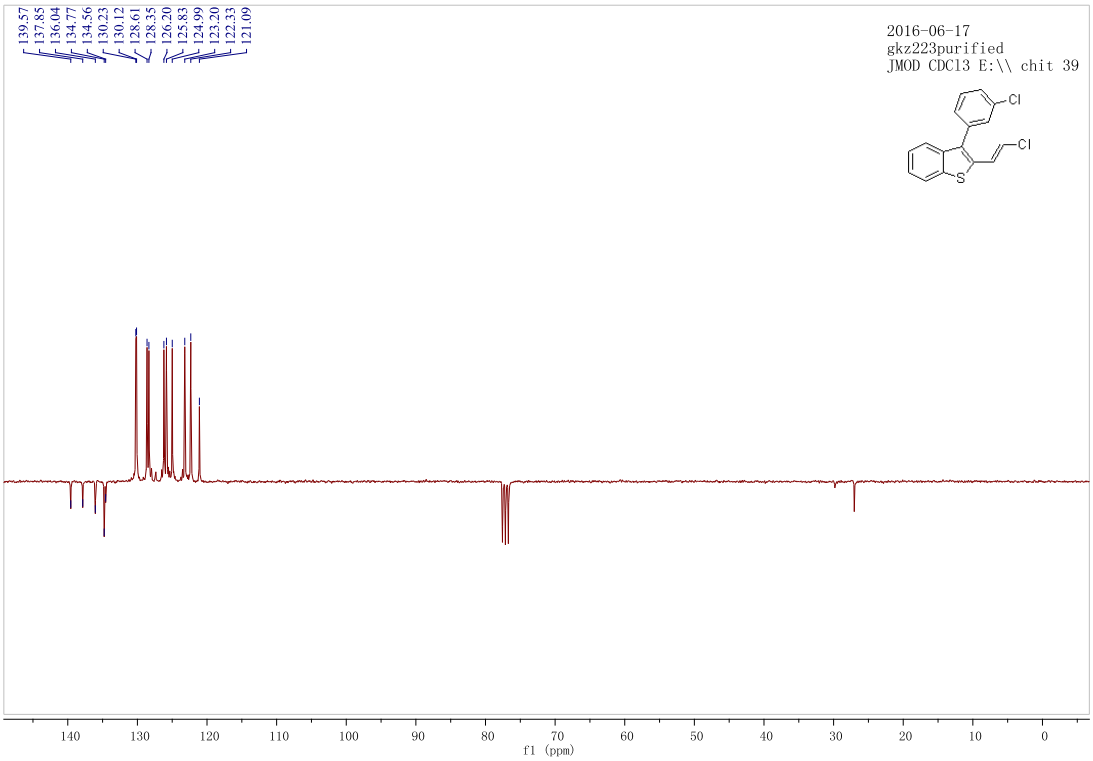

Fig. 26 ^{13}C NMR of (*E*)-3-(3-chlorophenyl)-2-(2-chlorovinyl)benzo[b]thiophene **8e**

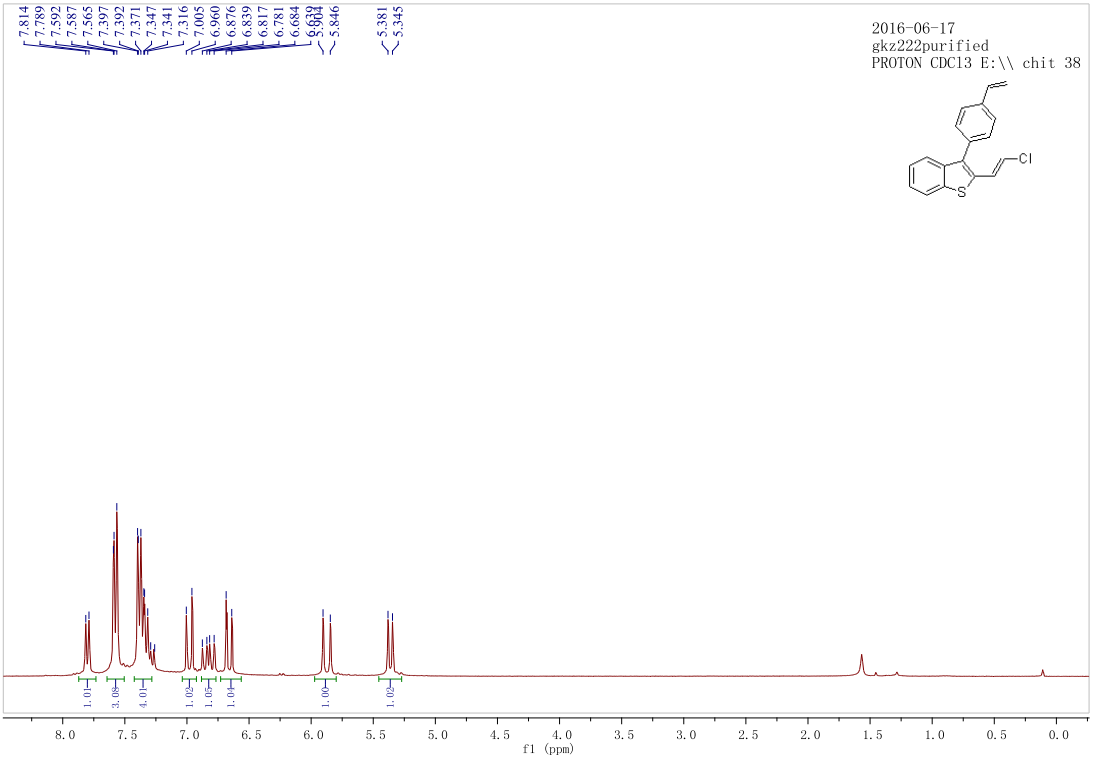

Fig. 27 ^{1}H NMR of (*E*)-2-(2-chlorovinyl)-3-(4-vinylphenyl)benzo[b]thiophene **8f**

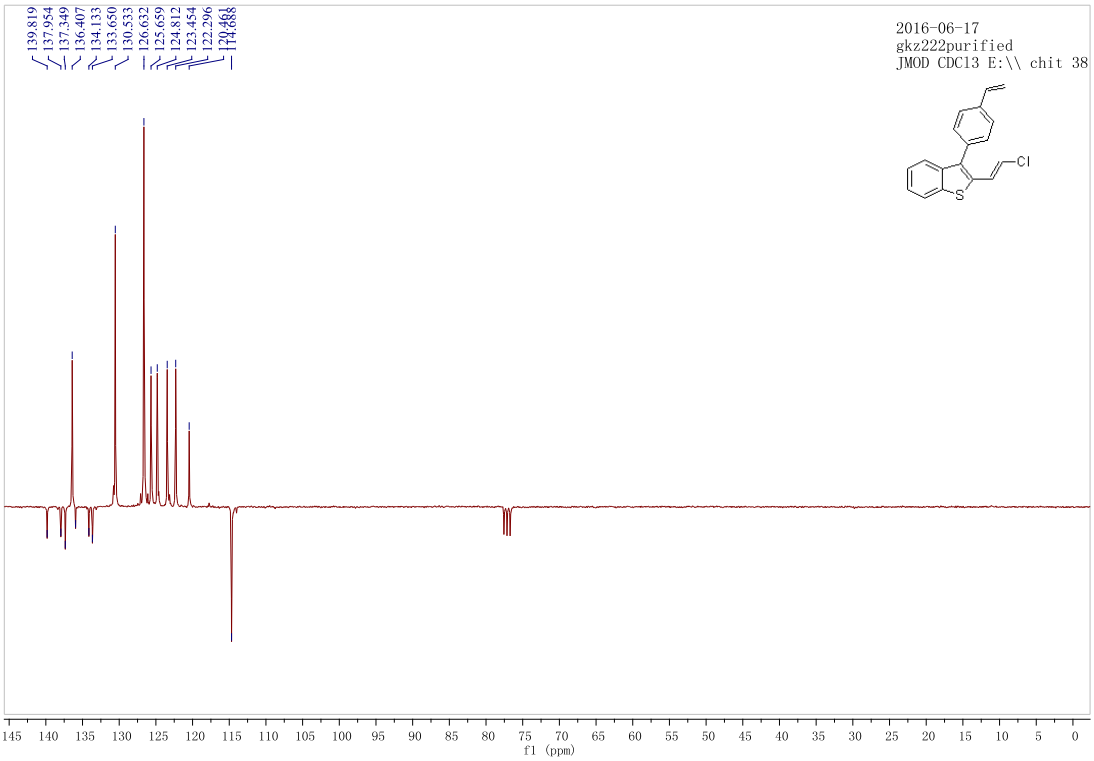

Fig. 28 ^{13}C NMR of (*E*)-2-(2-chlorovinyl)-3-(4-vinylphenyl)benzo[b]thiophene **8f**

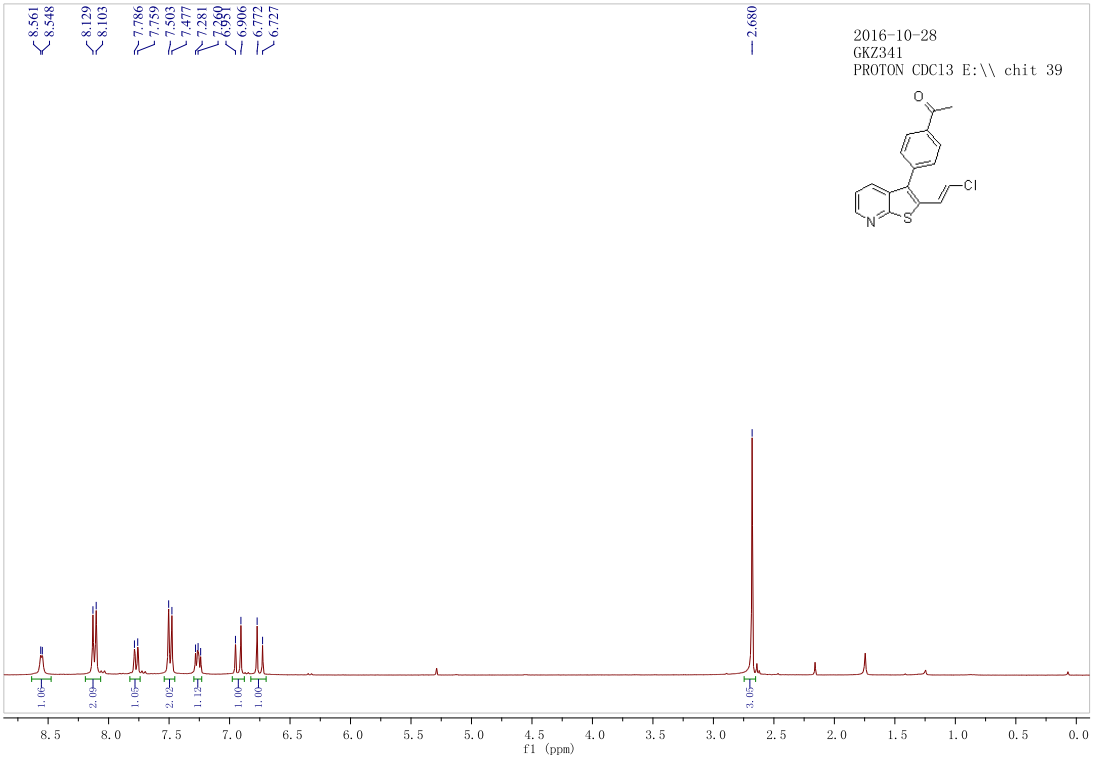

Fig. 29 ^{1}H NMR of (*E*)-1-(4-(2-(2-chlorovinyl)thieno[2,3-b]pyridin-3-yl)phenyl)ethanone **8g**

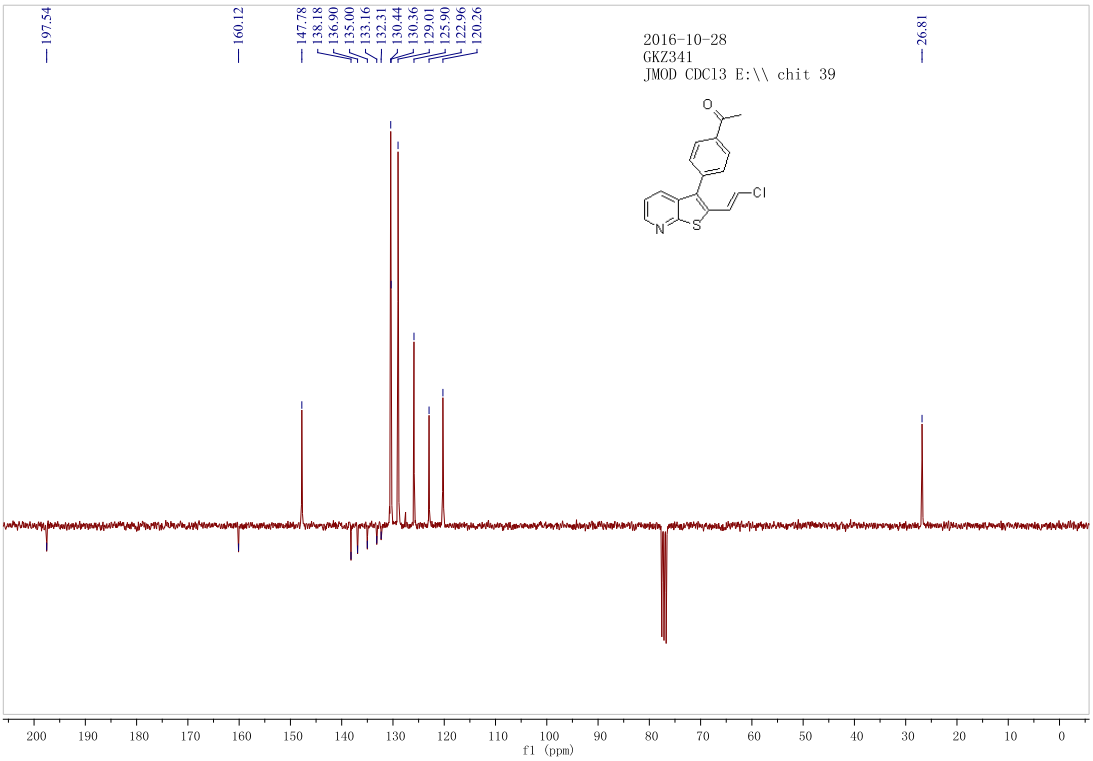

Fig. 30 ^{13}C NMR of (*E*)-1-(4-(2-(2-chlorovinyl)thieno[2,3-b]pyridin-3-yl)phenyl)ethanone **8g**

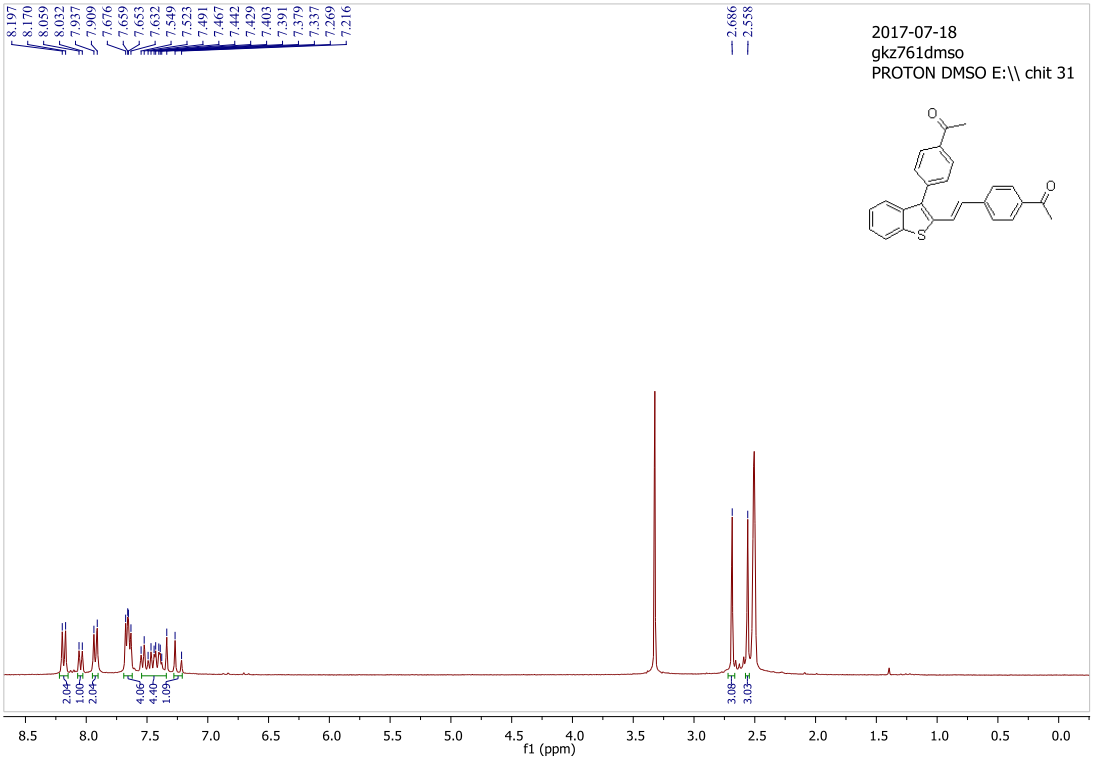

Fig. 31 [1]H NMR of (*E*)-1-(4-(2-(3-(4-acetylphenyl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethan-1-one **1aa**

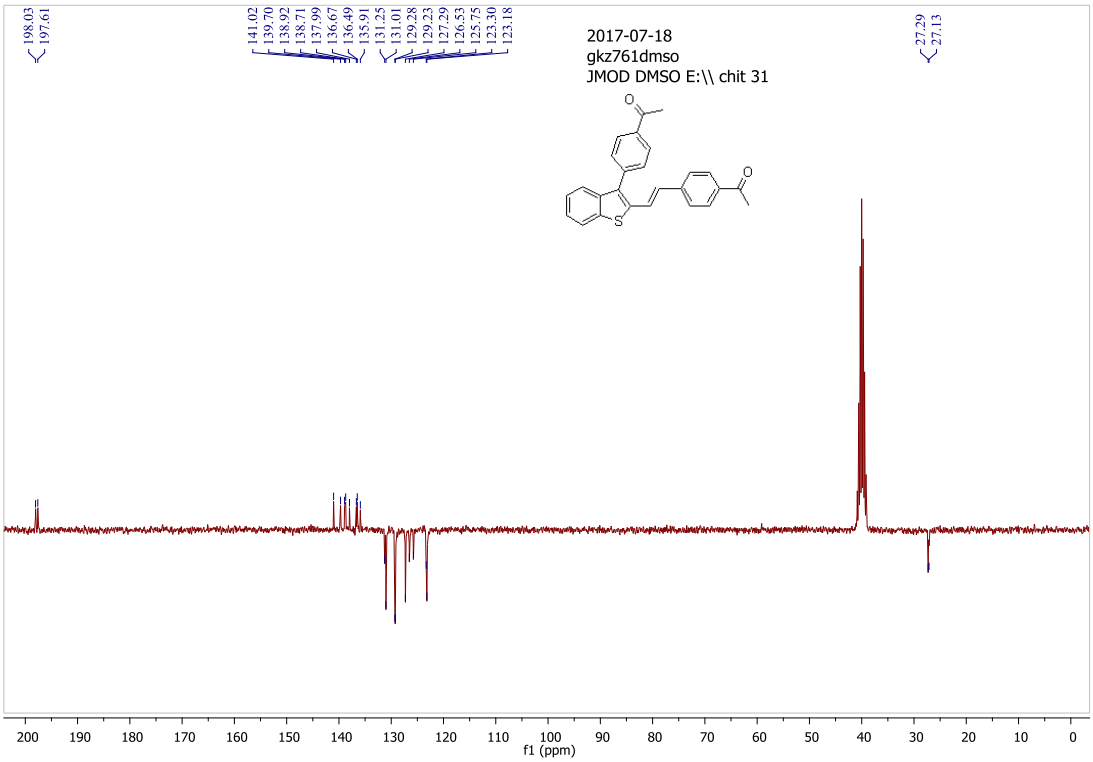

Fig. 32 [13]C NMR of (*E*)-1-(4-(2-(3-(4-acetylphenyl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethan-1-one **1aa**

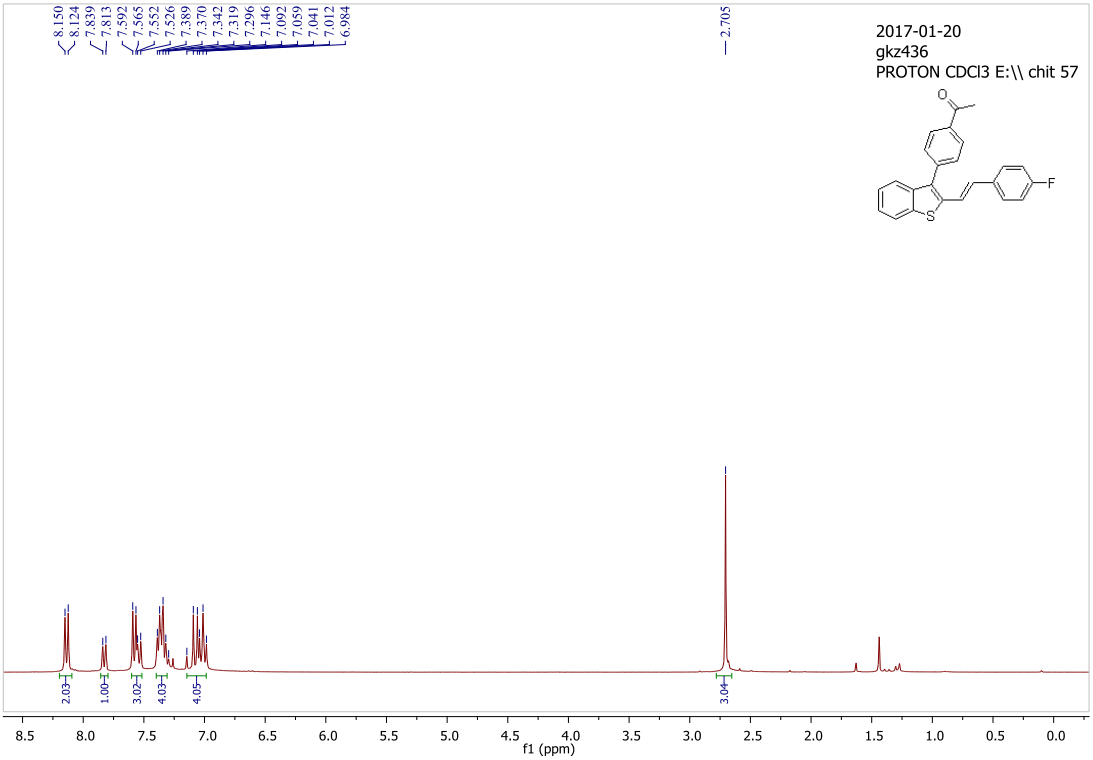

Fig. 33 ^{1}H NMR of (*E*)-1-(4-(2-(4-fluorostyryl)benzo[b]thiophen-3-yl)phenyl)ethanone **1ab**

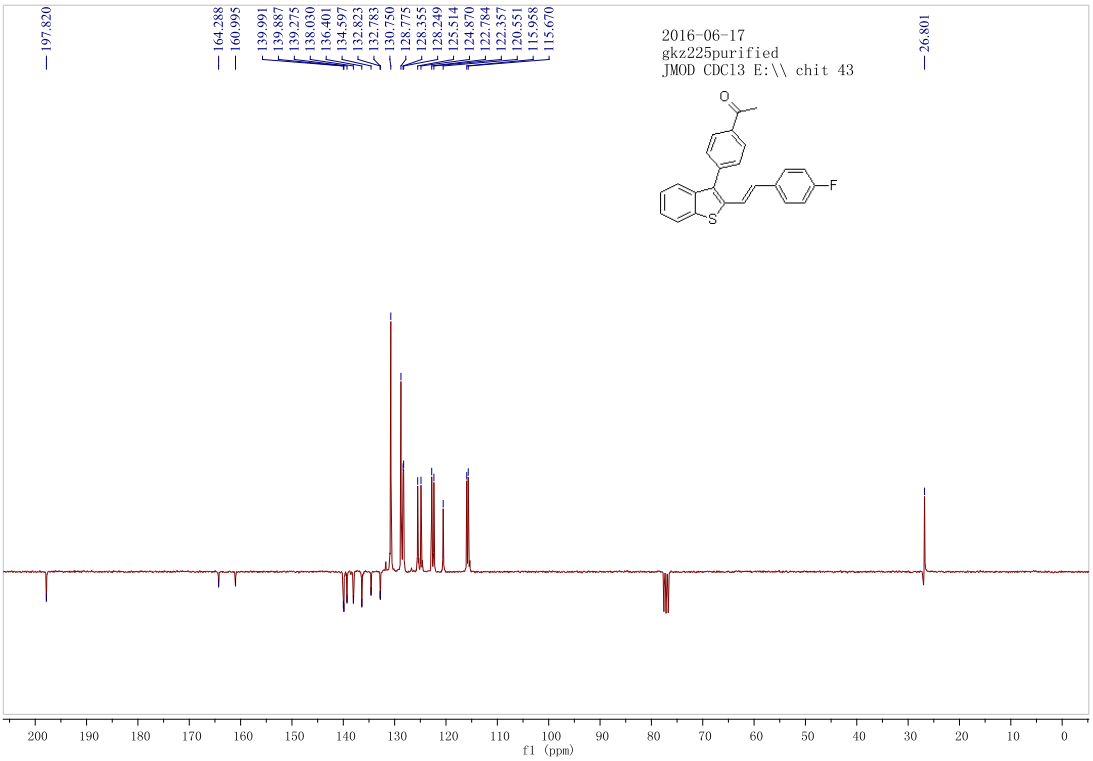

Fig. 34 ^{13}C NMR of (*E*)-1-(4-(2-(4-fluorostyryl)benzo[b]thiophen-3-yl)phenyl)ethanone **1ab**

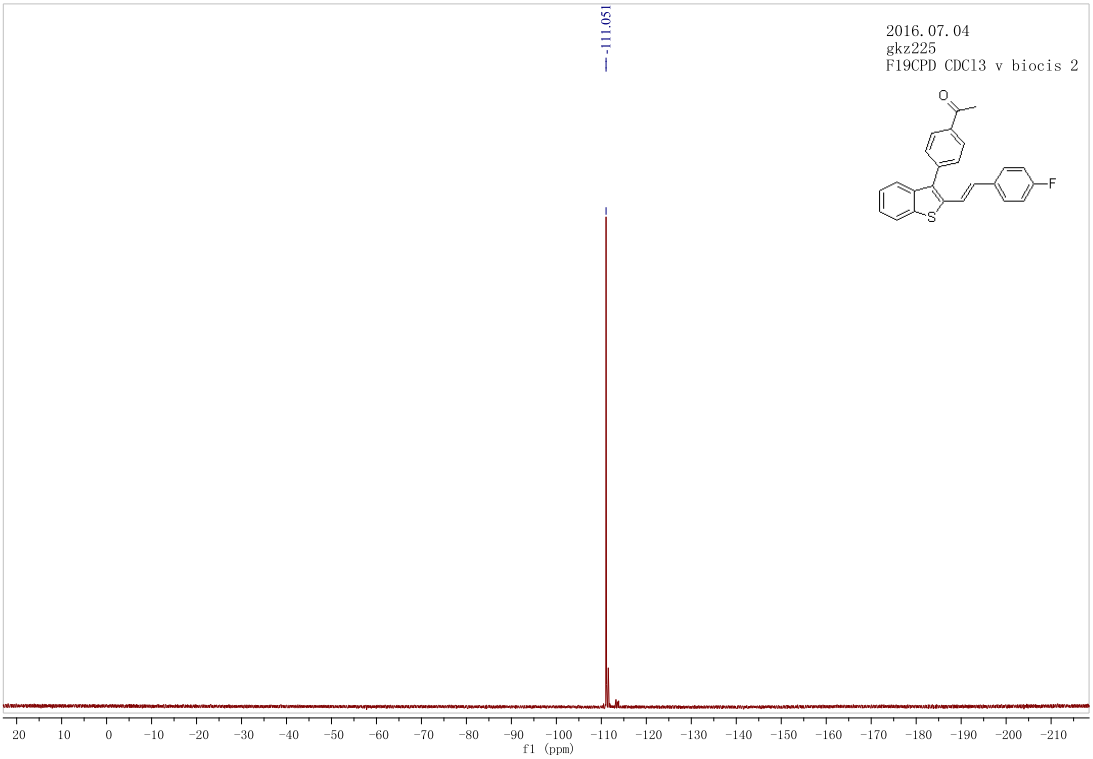

Fig. 35 ^{19}F NMR of (*E*)-1-(4-(2-(4-fluorostyryl)benzo[b]thiophen-3-yl)phenyl)ethanone **1ab**

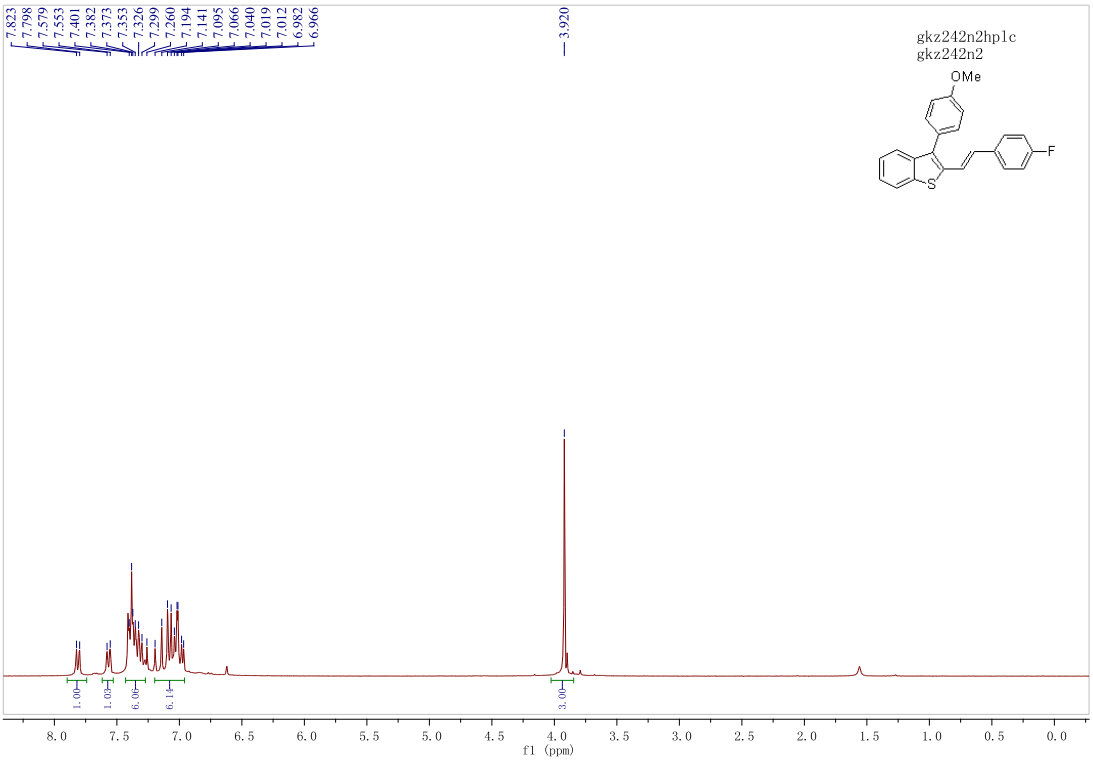

Fig. 36 ^{1}H NMR of (*E*)-2-(4-fluorostyryl)-3-(4-methoxyphenyl)benzo[b]thiophene **1ac**

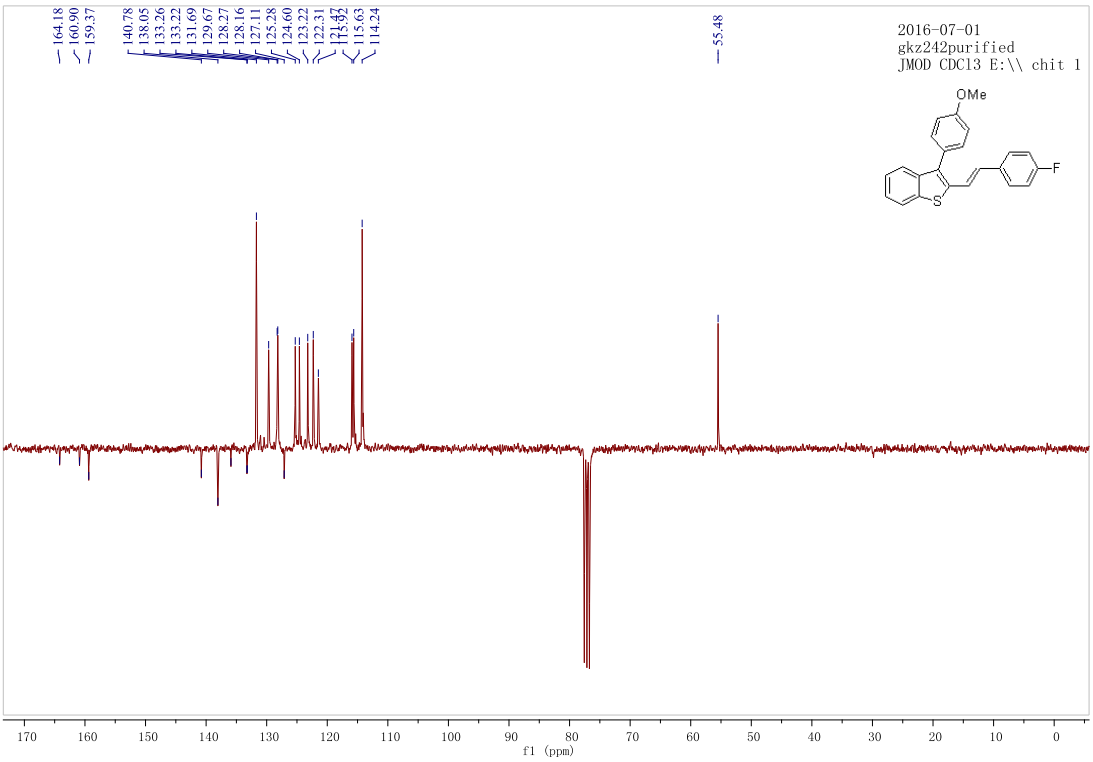

Fig. 37 ^{13}C NMR of (*E*)-2-(4-fluorostyryl)-3-(4-methoxyphenyl)benzo[b]thiophene **1ac**

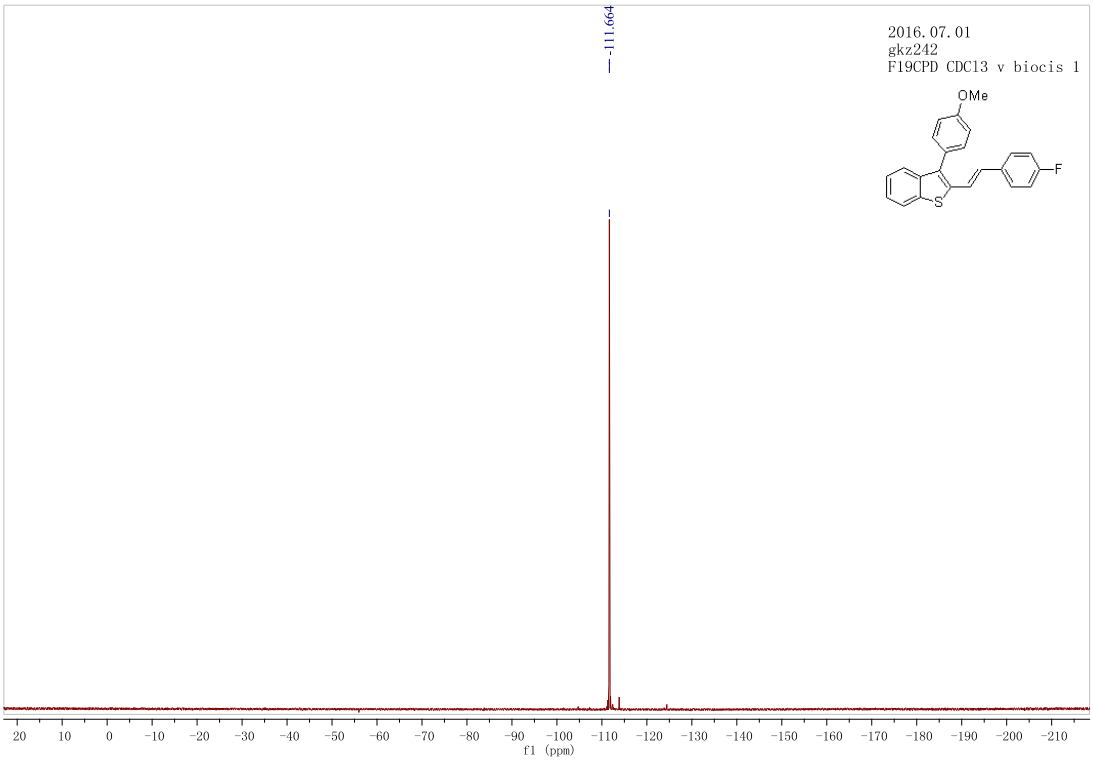

Fig. 38 ^{19}F NMR of (*E*)-2-(4-fluorostyryl)-3-(4-methoxyphenyl)benzo[b]thiophene **1ac**

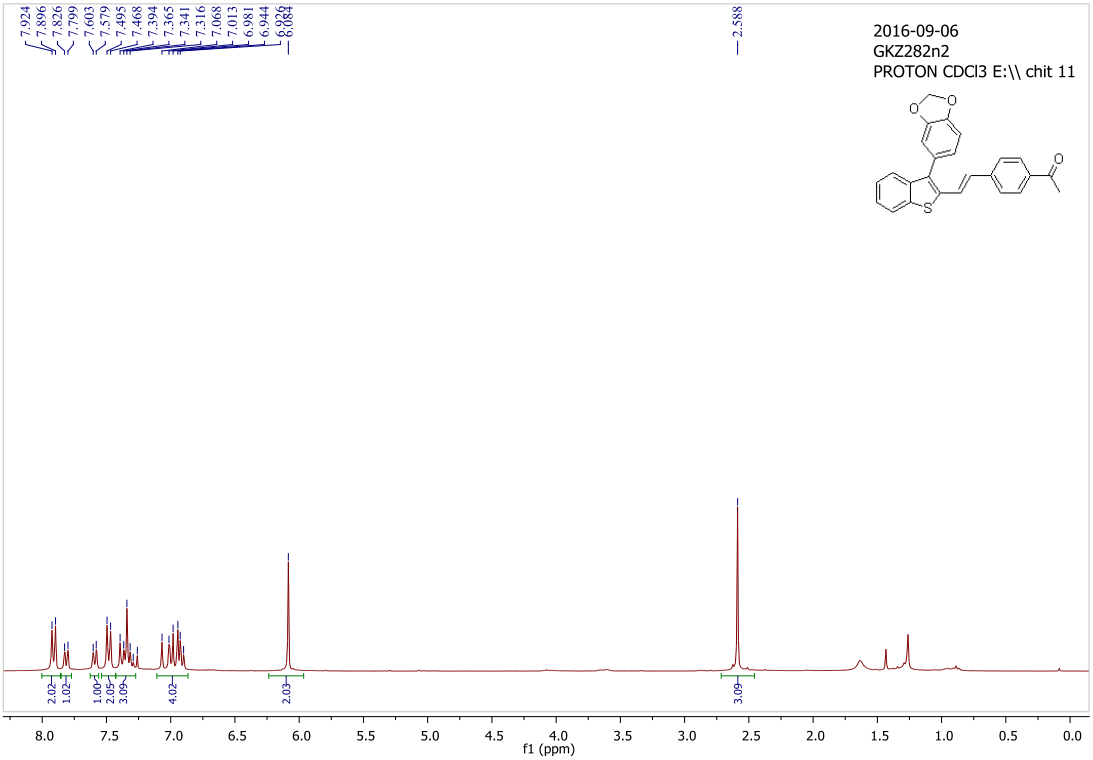

Fig. 39 the ^{1}H NMR of
(*E*)-1-(4-(2-(3-(benzo[d][1,3]dioxol-5-yl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethan-1-one **1ad**

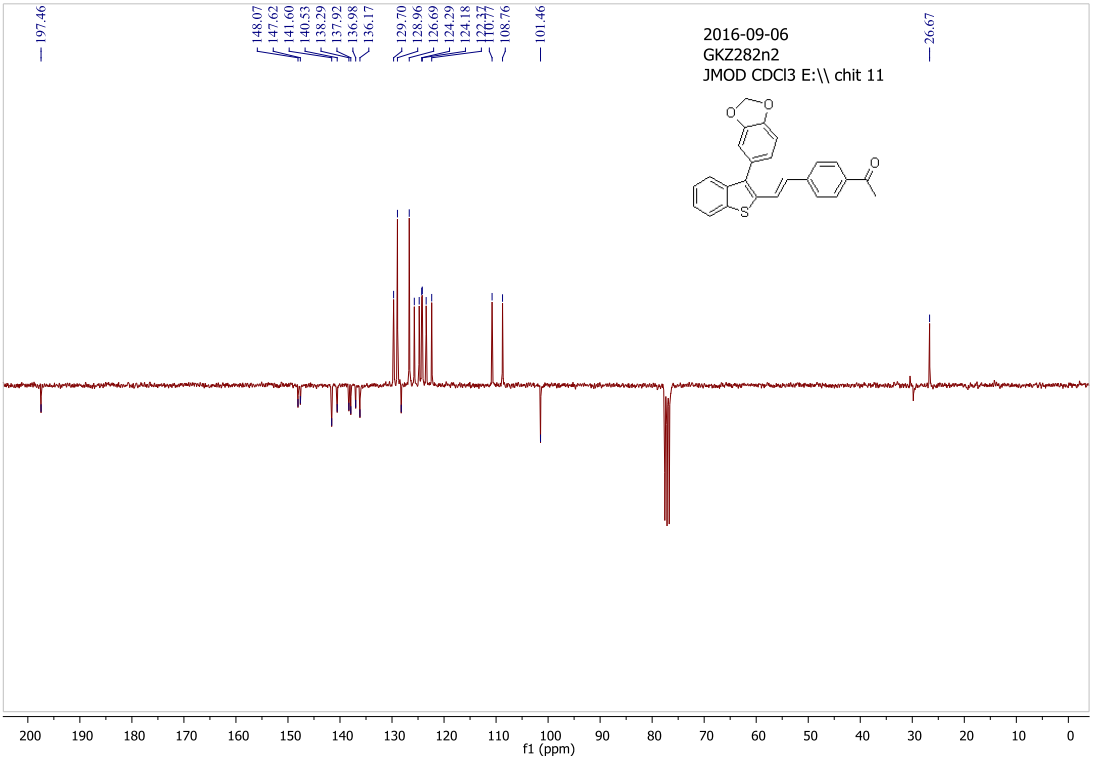

Fig. 40 ^{13}C NMR of
(*E*)-1-(4-(2-(3-(benzo[d][1,3]dioxol-5-yl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethan-1-one **1ad**

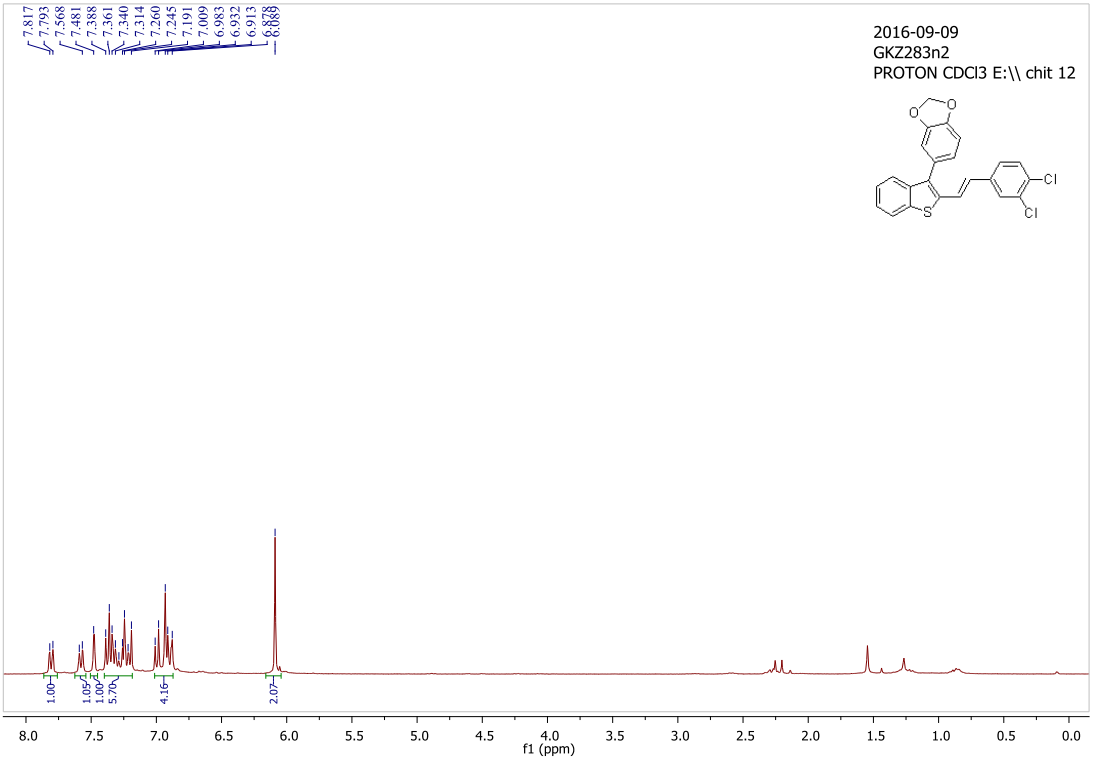

Fig. 41 ^{1}H NMR of (*E*)-5-(2-(3,4-dichlorostyryl)benzo[b]thiophen-3-yl)benzo[d][1,3]dioxole **1ae**

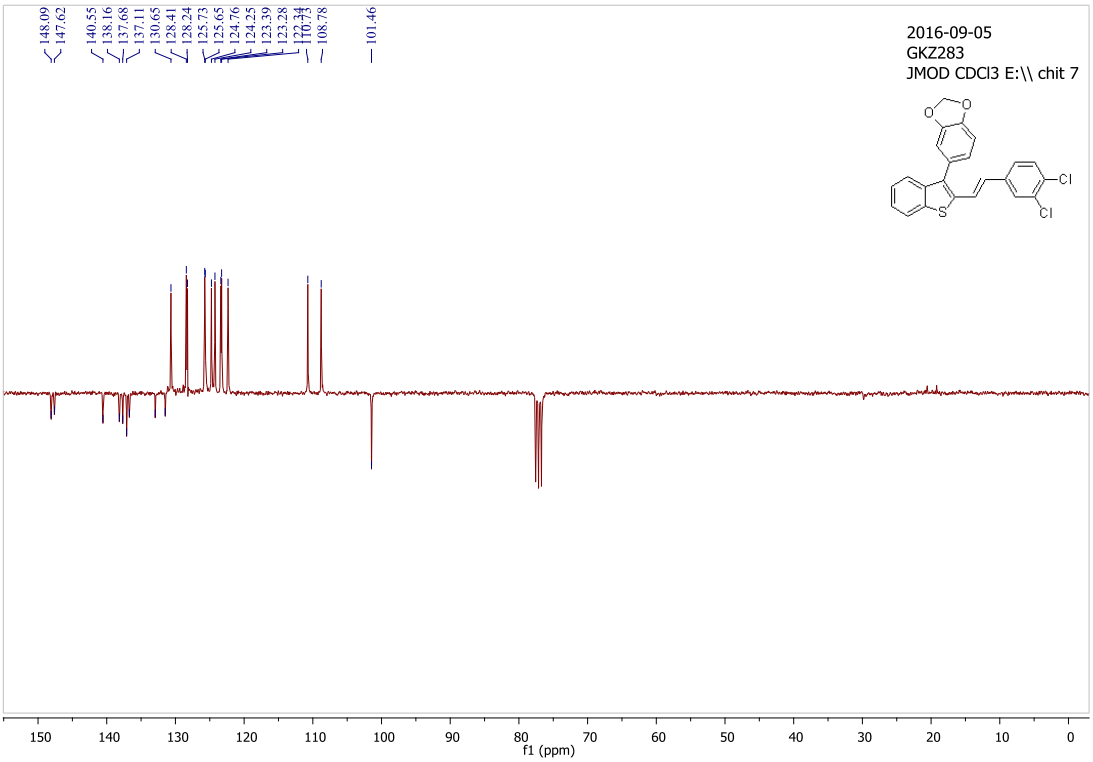

Fig. 42 ^{13}C NMR of (*E*)-5-(2-(3,4-dichlorostyryl)benzo[b]thiophen-3-yl)benzo[d][1,3]dioxole **1ae**

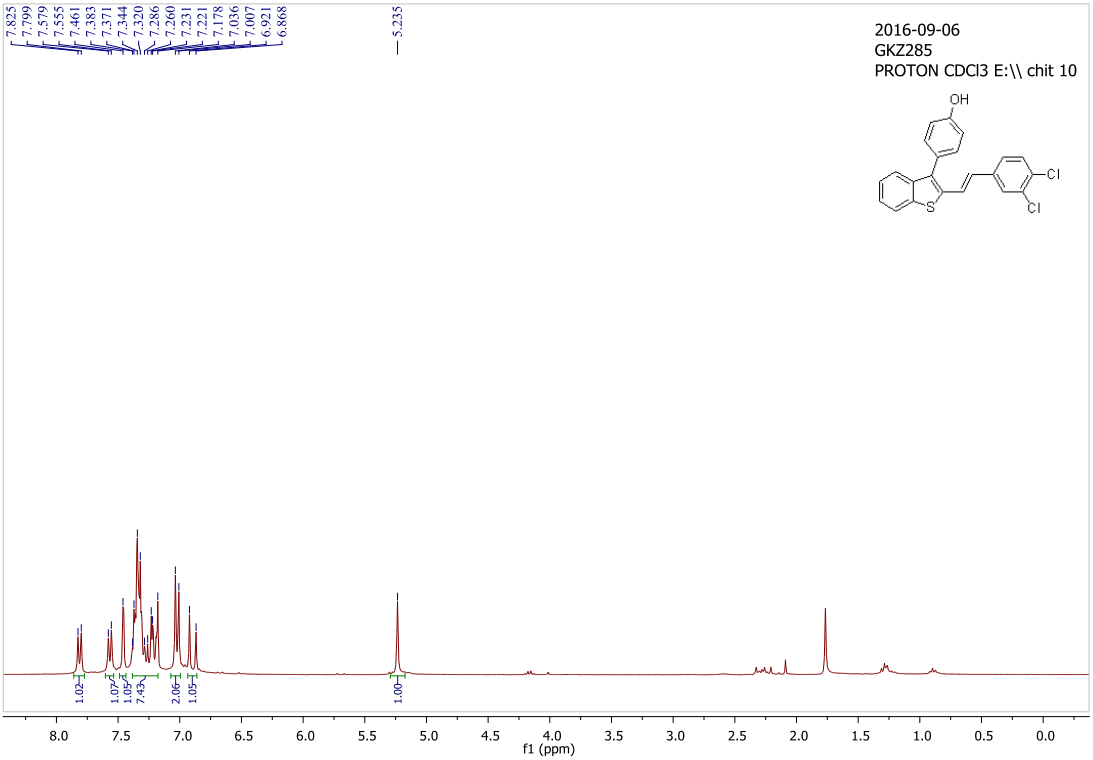

Fig. 43 ^{1}H NMR of (*E*)-4-(2-(3,4-dichlorostyryl)benzo[b]thiophen-3-yl)phenol **1af**

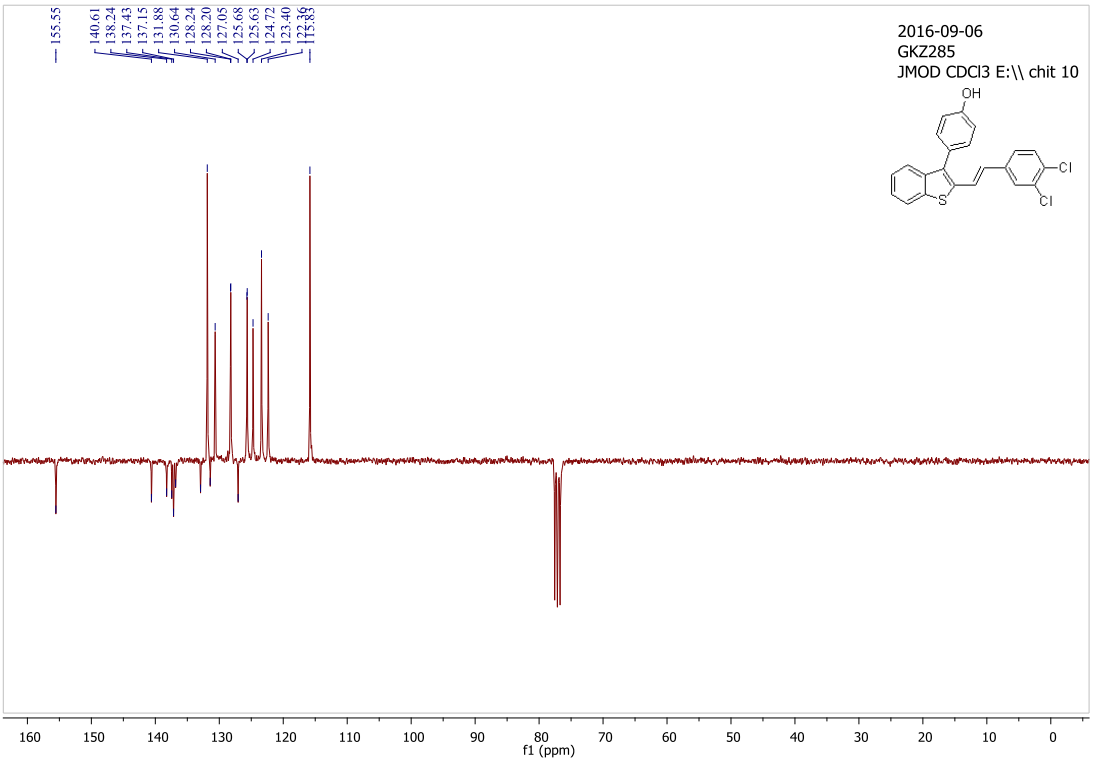

Fig. 44 ^{13}C NMR of (*E*)-4-(2-(3,4-dichlorostyryl)benzo[b]thiophen-3-yl)phenol **1af**

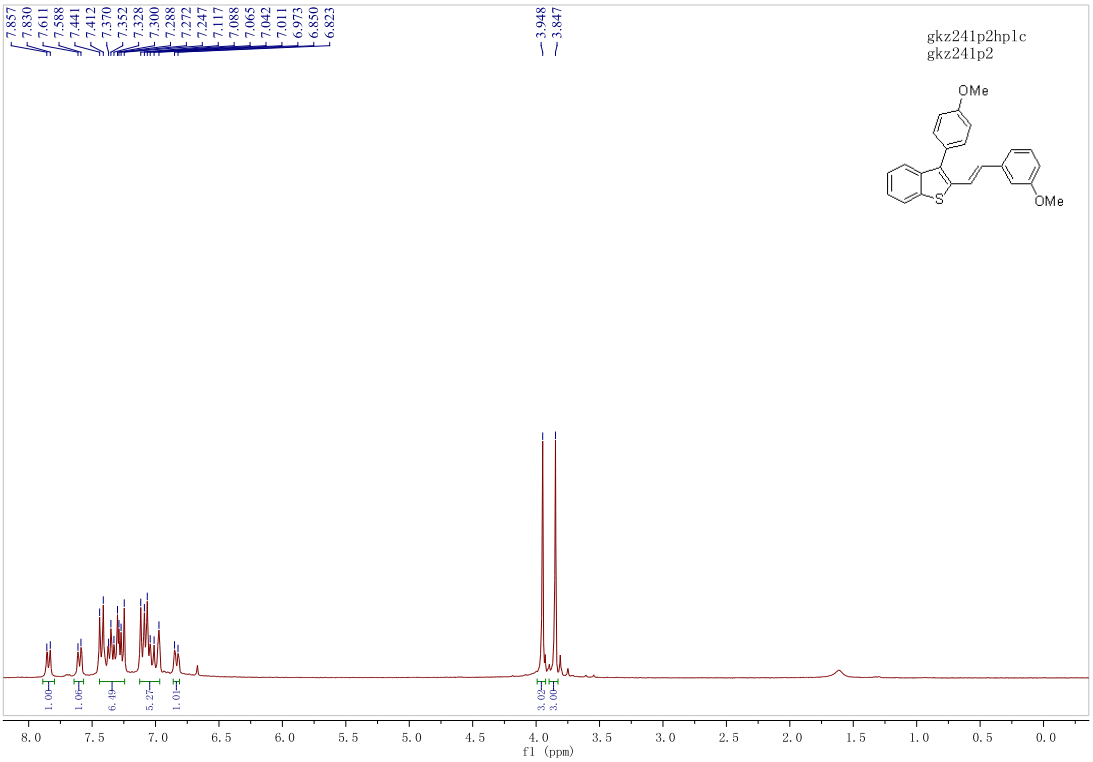

Fig. 45 ^{1}H NMR of (*E*)-3-(4-methoxyphenyl)-2-(3-methoxystyryl)benzo[b]thiophene **1ag**

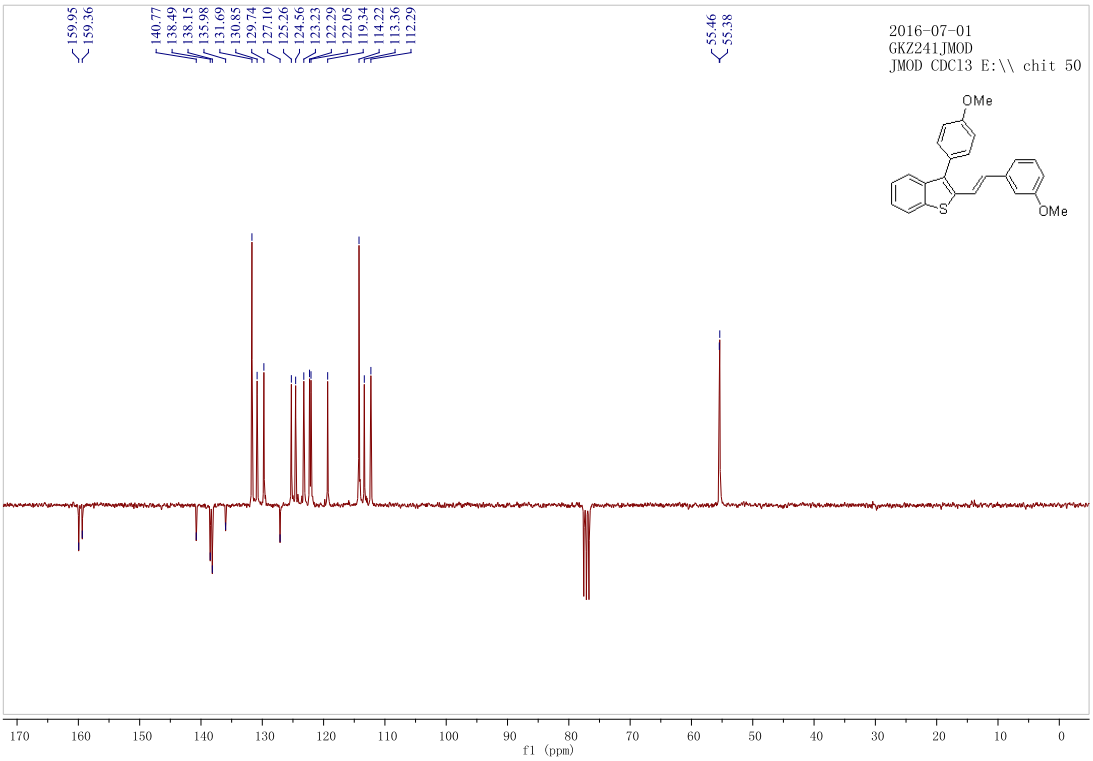

Fig. 46 ^{13}C NMR of (*E*)-3-(4-methoxyphenyl)-2-(3-methoxystyryl)benzo[b]thiophene **1ag**

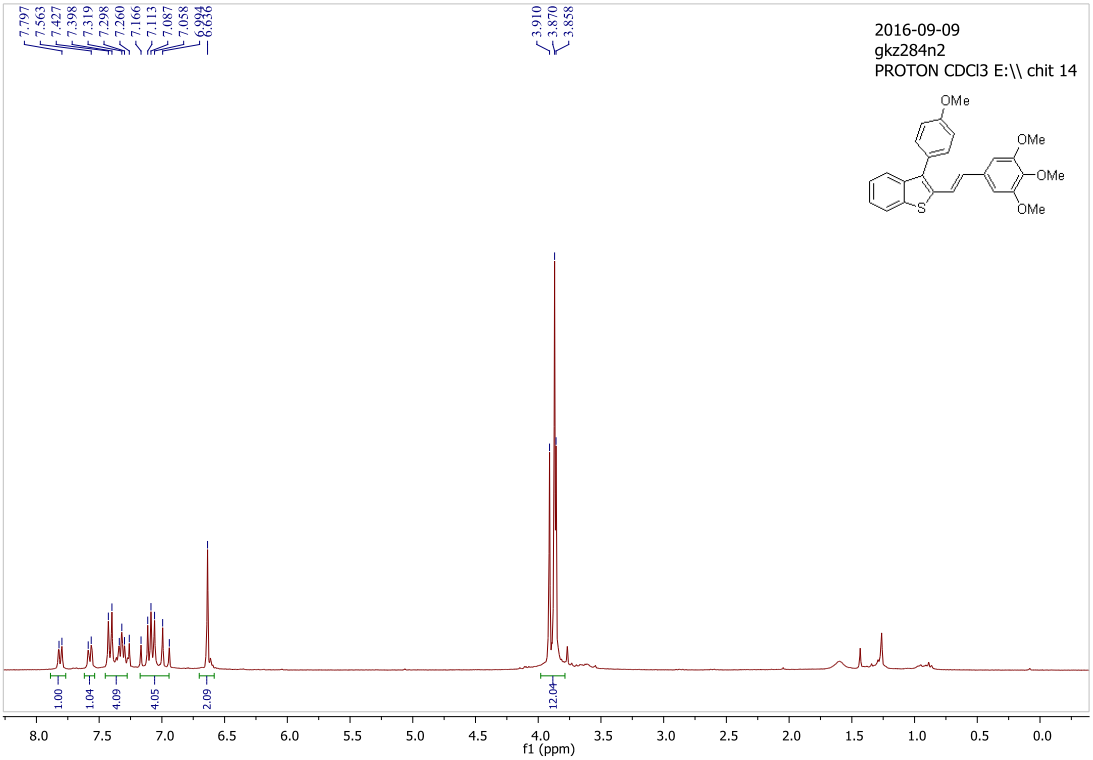

Fig. 47 ^{1}H NMR of (*E*)-3-(4-methoxyphenyl)-2-(3,4,5-trimethoxystyryl)benzo[b]thiophene **1ah**

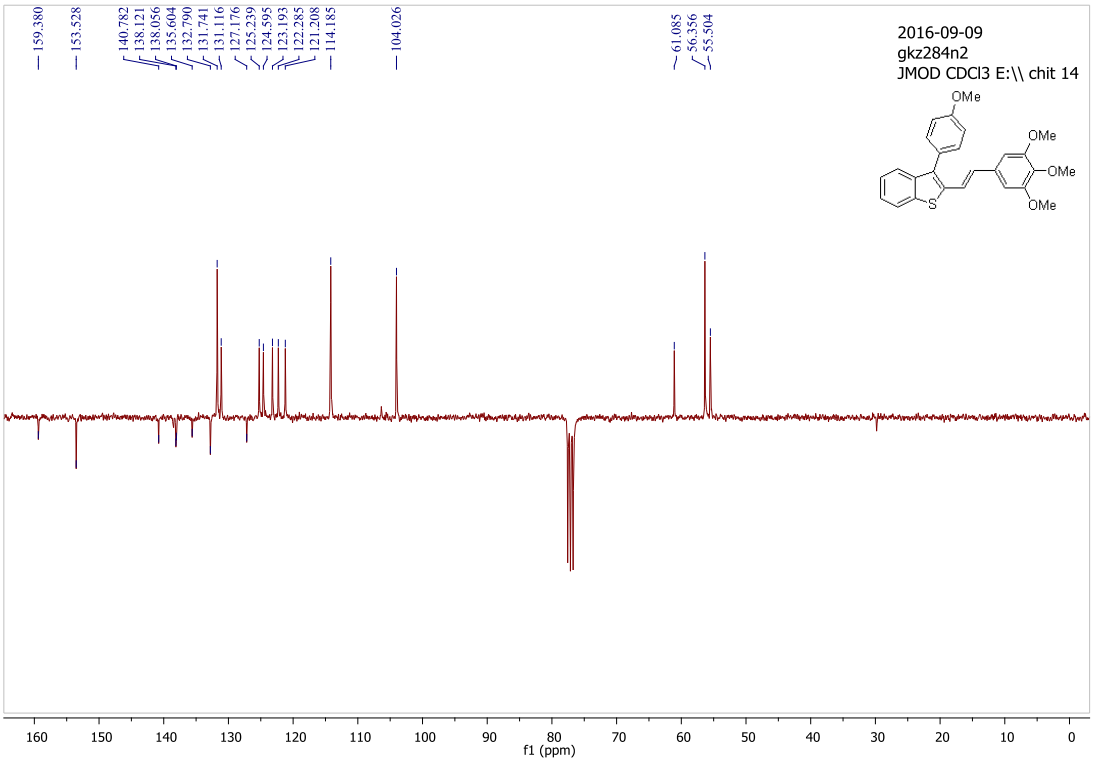

Fig. 48 ^{13}C NMR of (*E*)-3-(4-methoxyphenyl)-2-(3,4,5-trimethoxystyryl)benzo[b]thiophene **1ah**

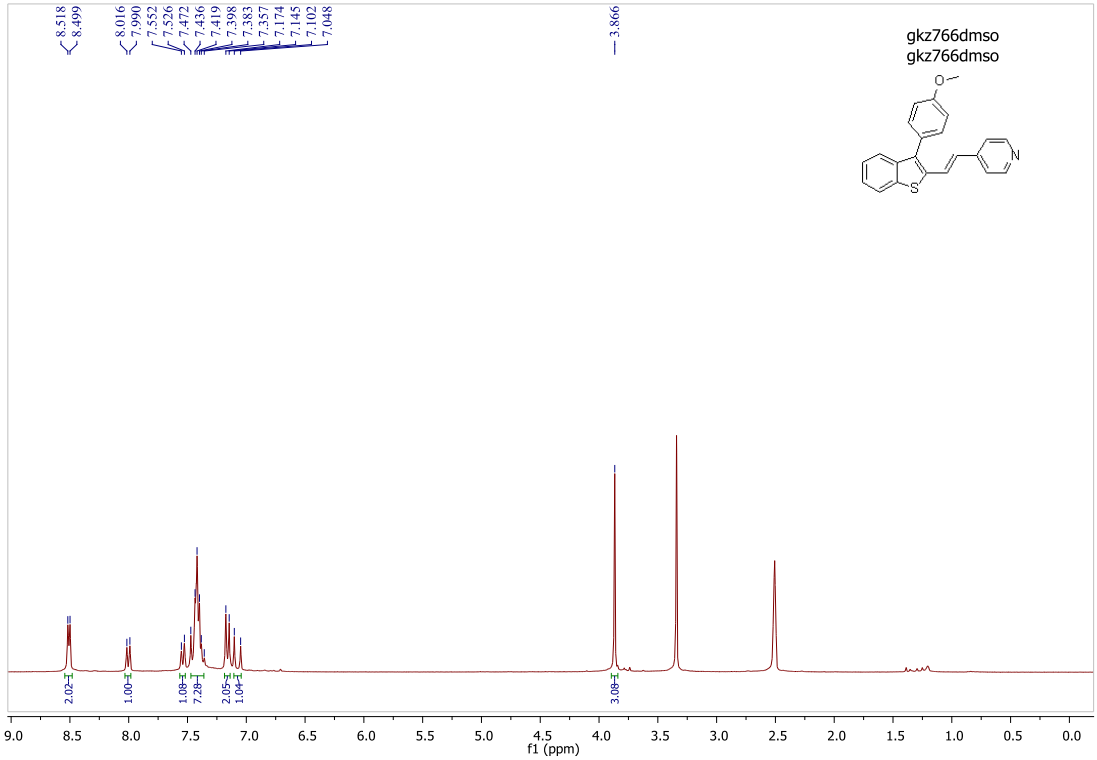

Fig. 49 ^{1}H NMR of (*E*)-4-(2-(3-(4-methoxyphenyl)benzo[b]thiophen-2-yl)vinyl)pyridine **1ai**

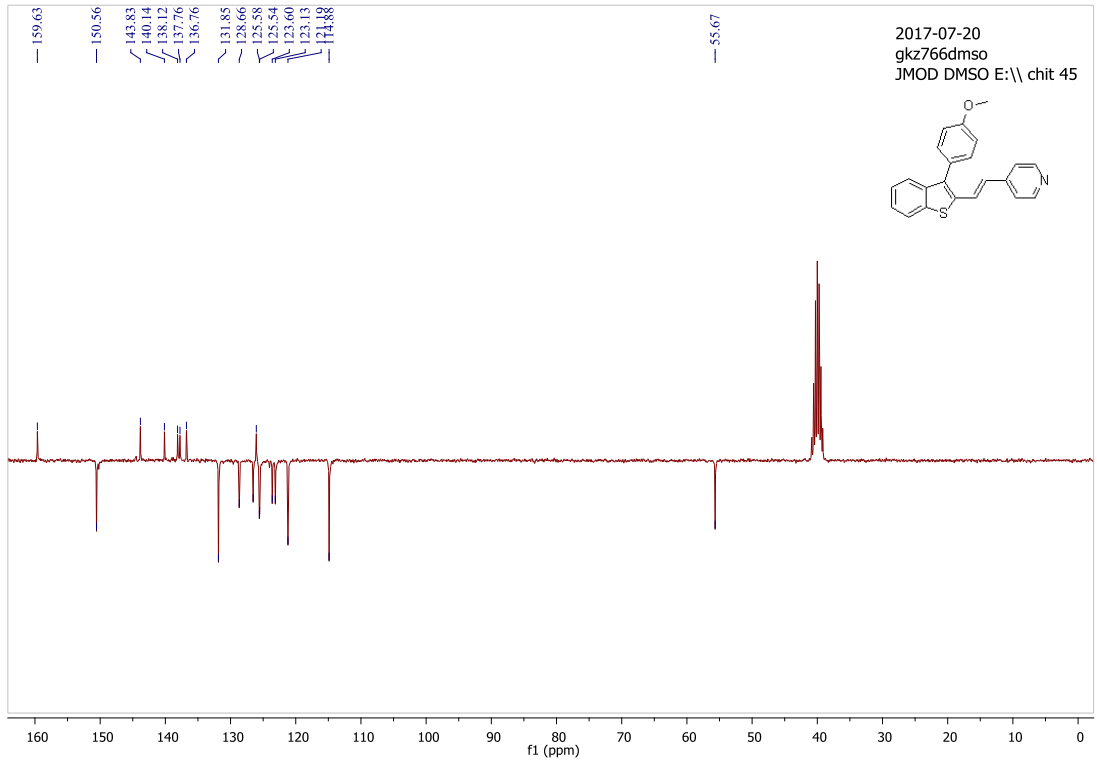

Fig. 50 ^{13}C NMR of (*E*)-4-(2-(3-(4-methoxyphenyl)benzo[b]thiophen-2-yl)vinyl)pyridine **1ai**

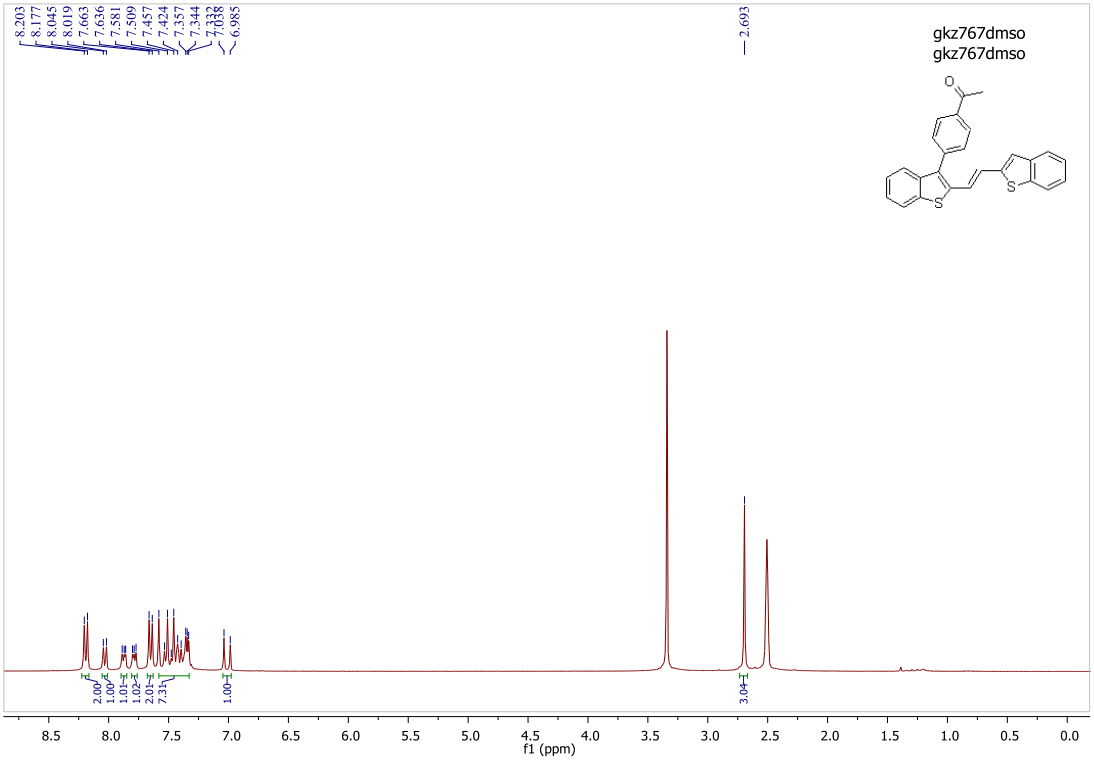

Fig. 51 ^{1}H NMR of (*E*)-1-(4-(2-(2-(benzo[b]thiophen-2-yl)vinyl)benzo[b]thiophen-3-yl)phenyl)ethan-1-one **1aj**

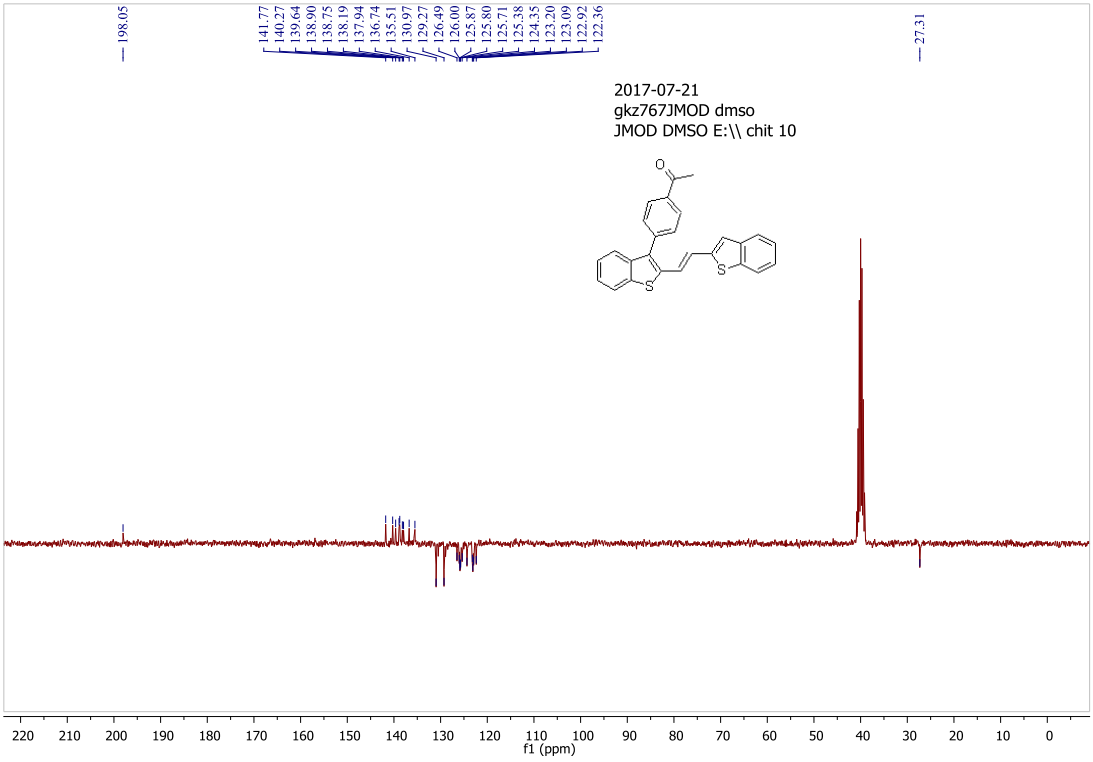

Fig. 52 ^{13}C NMR of
(*E*)-1-(4-(2-(2-(benzo[b]thiophen-2-yl)vinyl)benzo[b]thiophen-3-yl)phenyl)ethan-1-one **1aj**

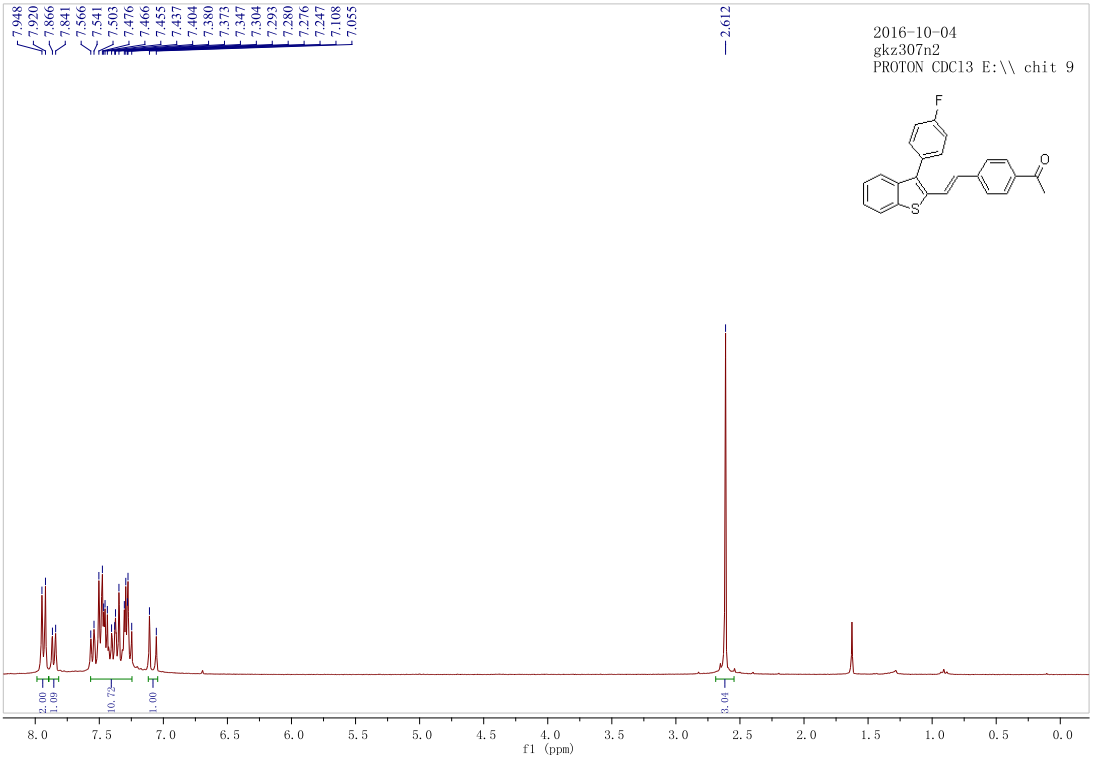

Fig. 53 ^{1}H NMR of (*E*)-1-(4-(2-(3-(4-fluorophenyl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethanone **1ak**

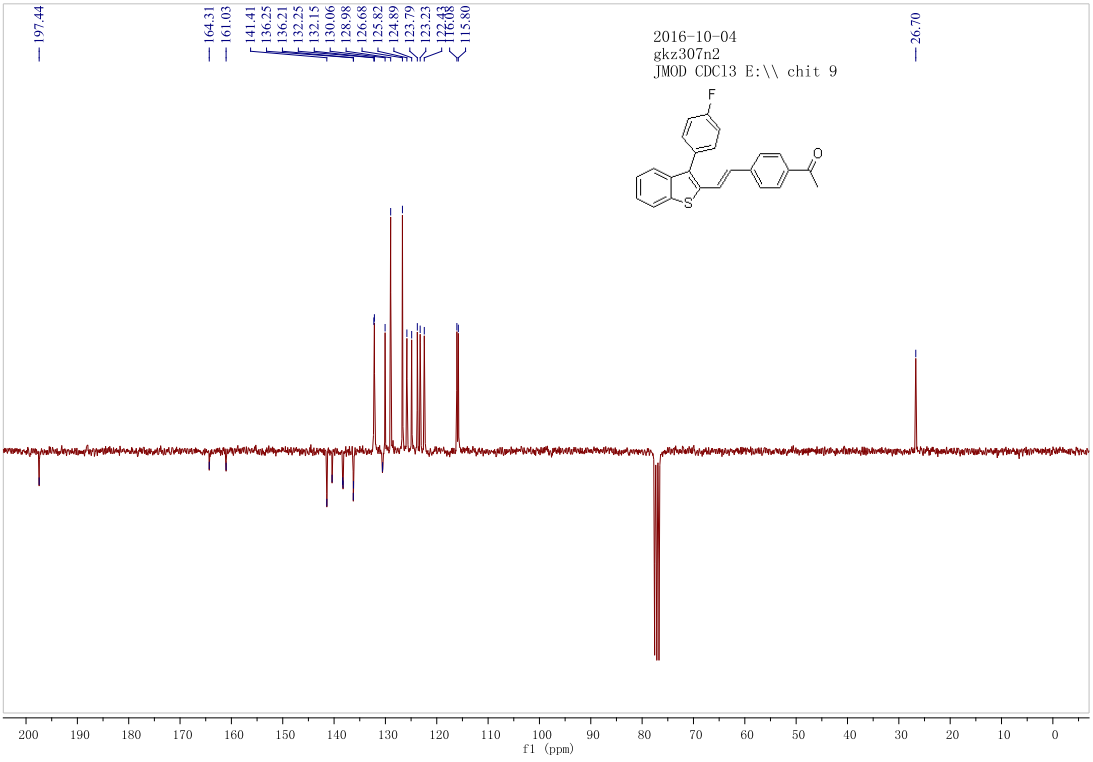

Fig. 54 ^{13}C NMR of (*E*)-1-(4-(2-(3-(4-fluorophenyl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethanone **1ak**

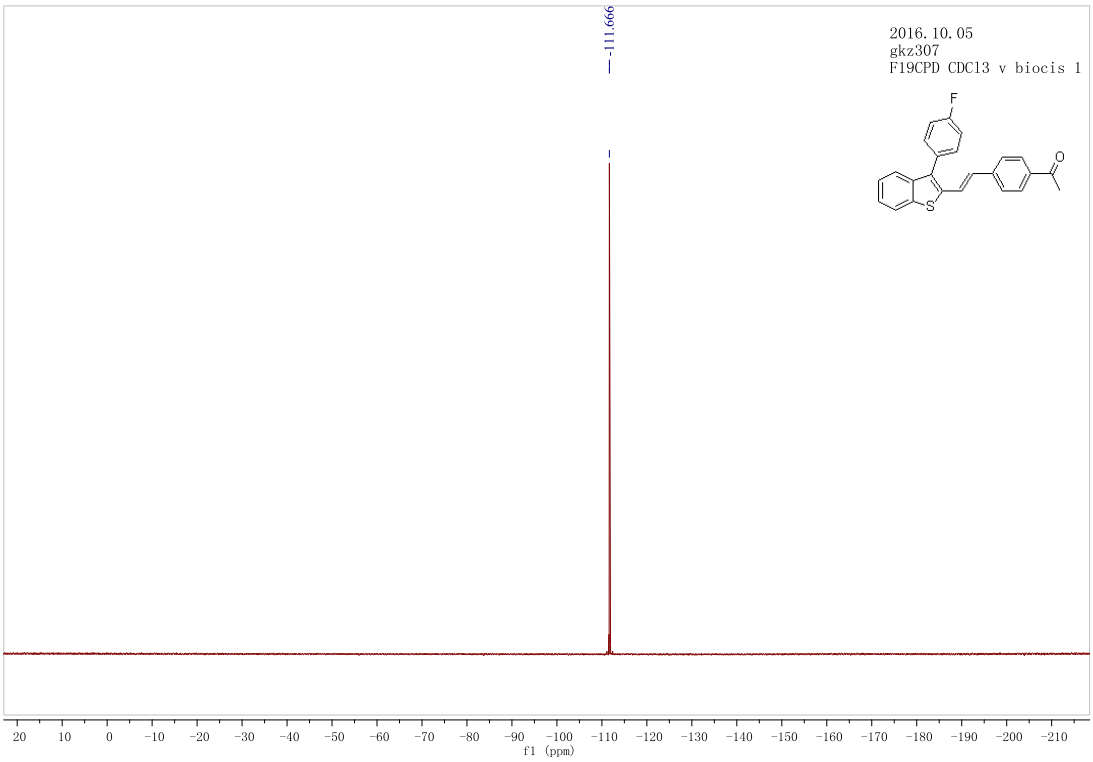

Fig. 55 ^{19}F NMR of (*E*)-1-(4-(2-(3-(4-fluorophenyl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethanone **1ak**

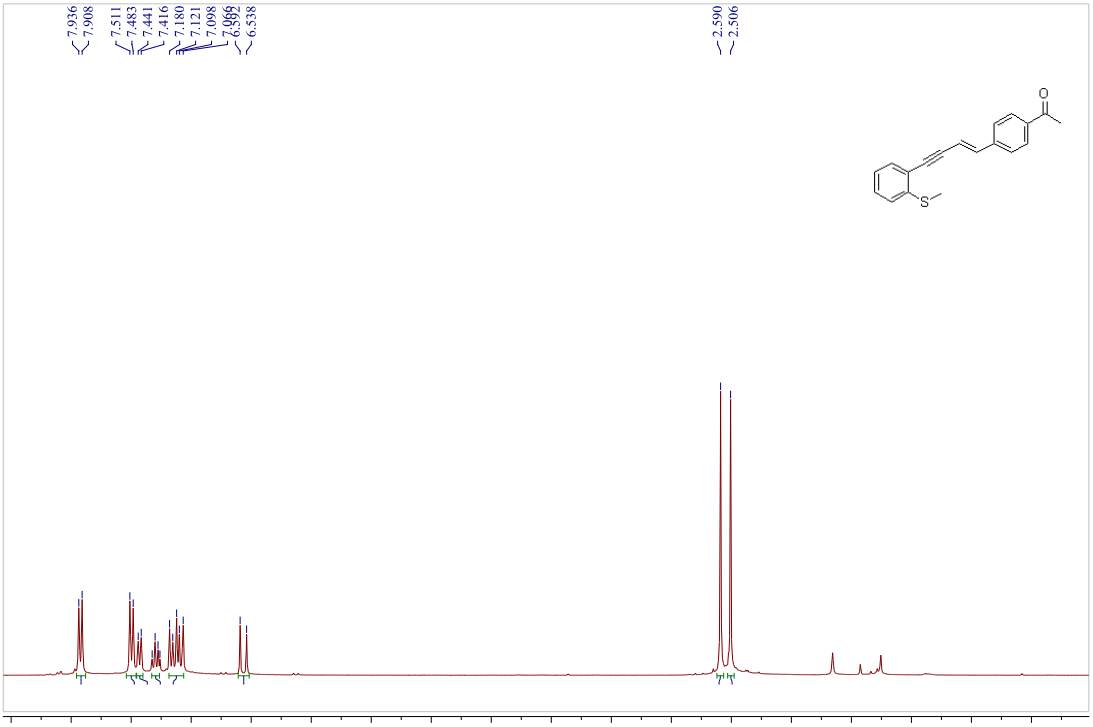

Fig. 56 ^{1}H NMR of (*E*)-1-(4-(4-(2-(methylthio)phenyl)but-1-en-3-yn-1-yl)phenyl)ethanone **11**

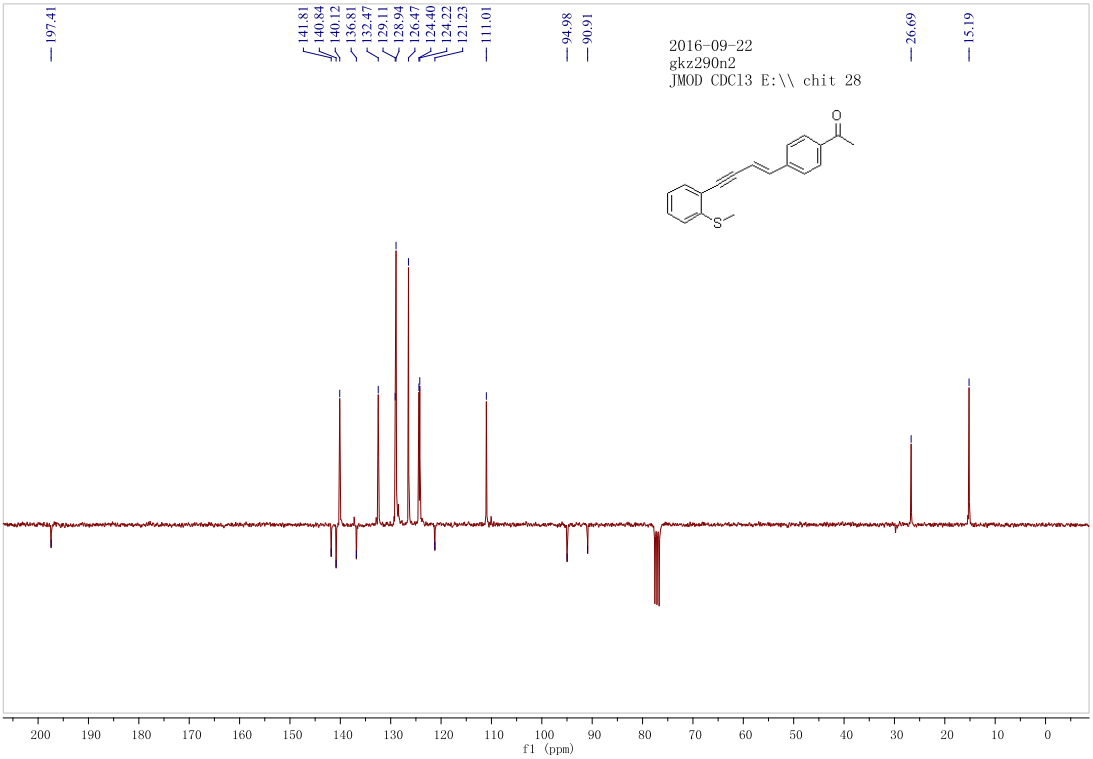

Fig. 57 ^{13}C NMR of (*E*)-1-(4-(4-(2-(methylthio)phenyl)but-1-en-3-yn-1-yl)phenyl)ethanone **11**

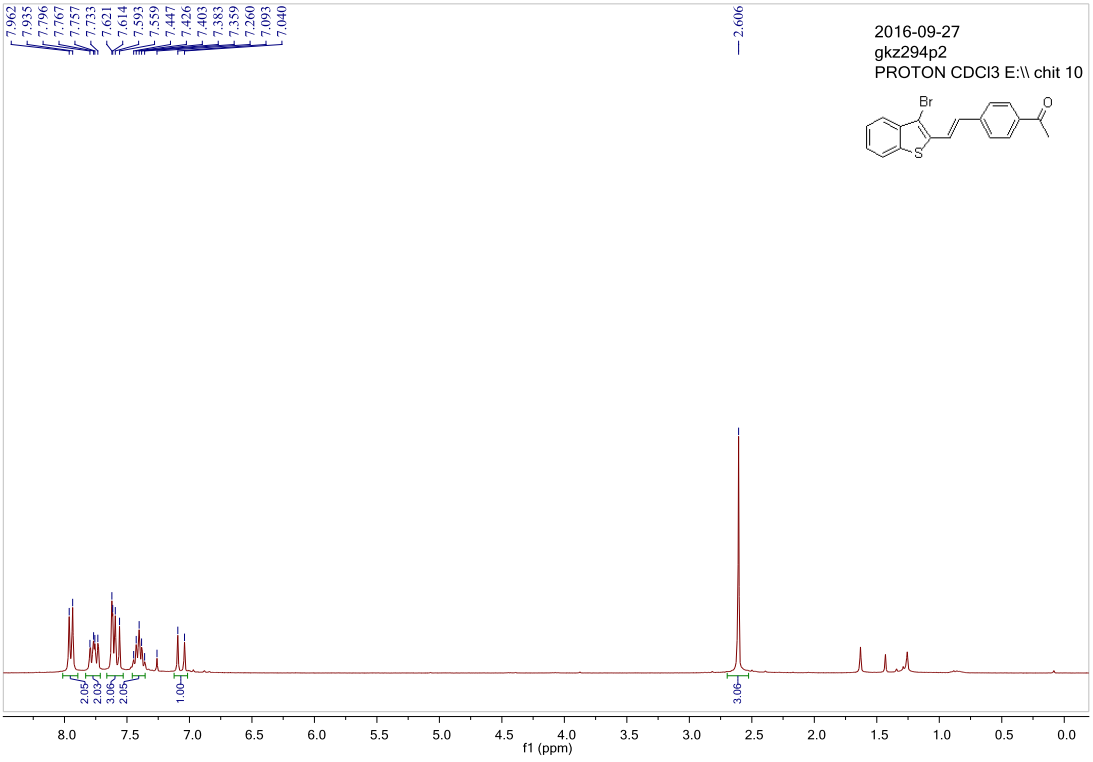

Fig. 58 ^{1}H NMR of (*E*)-1-(4-(2-(3-bromobenzo[b]thiophen-2-yl)vinyl)phenyl)ethanone **9**

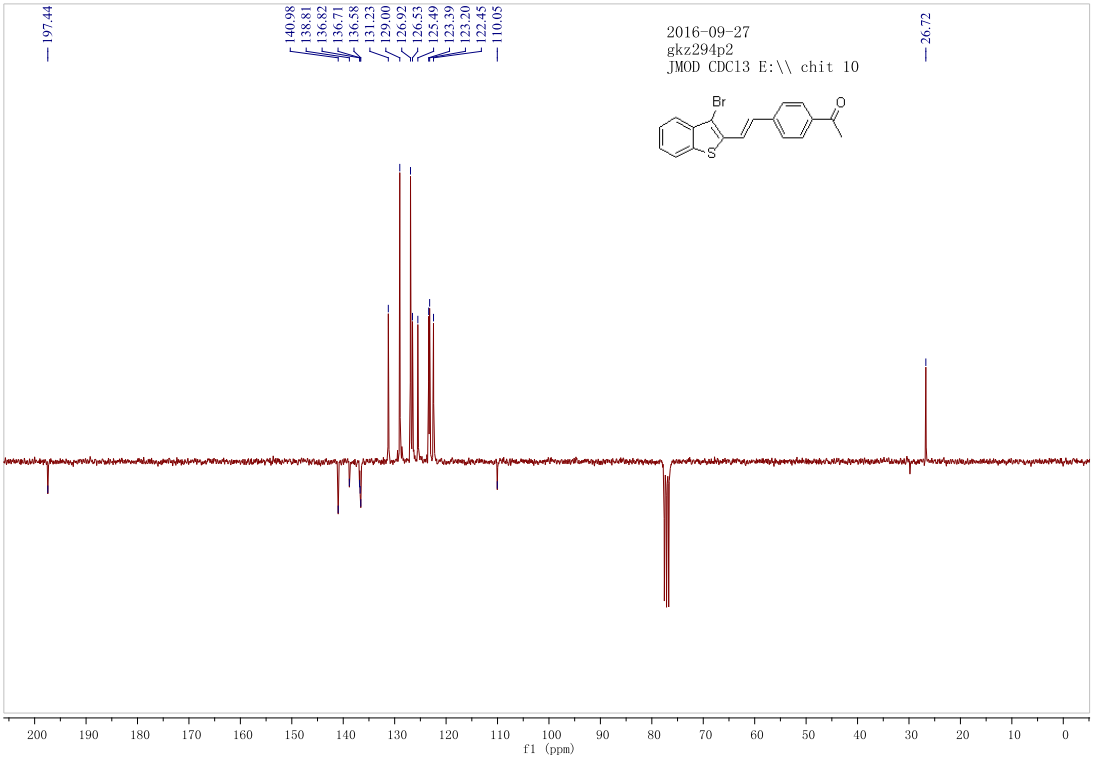

Fig. 59 ^{13}C NMR of (*E*)-1-(4-(2-(3-bromobenzo[b]thiophen-2-yl)vinyl)phenyl)ethanone **9**

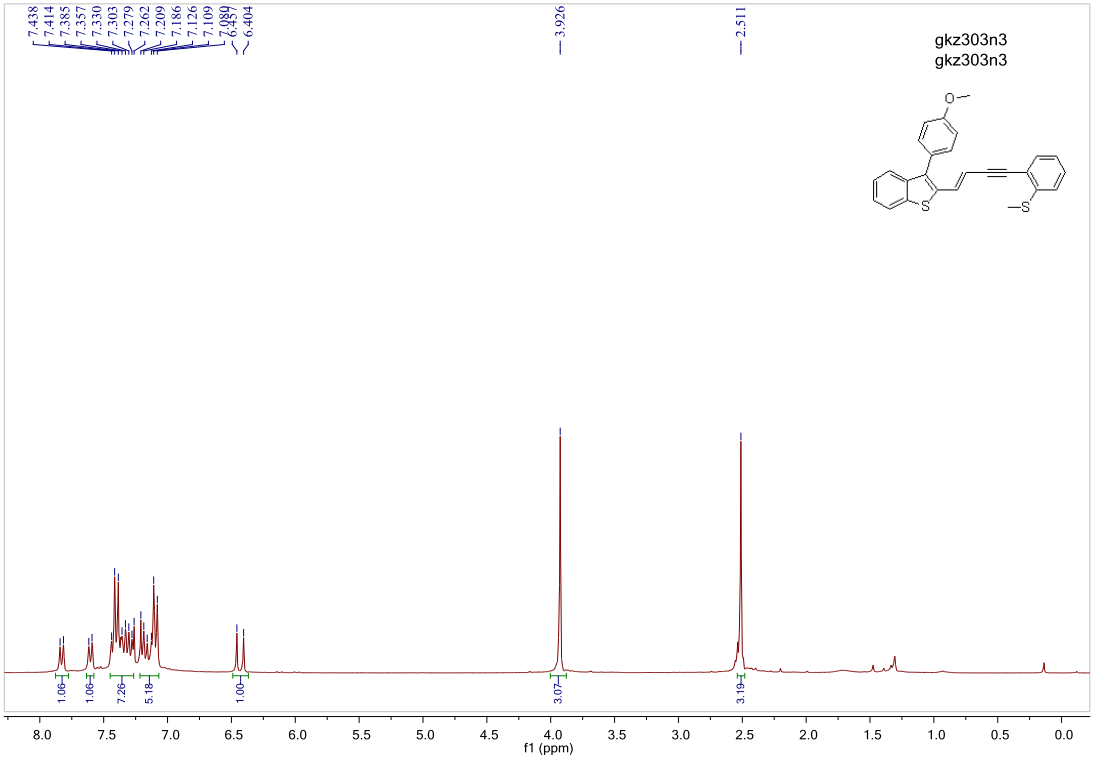

Fig. 60 ^{1}H NMR of (*E*)-3-(4-methoxyphenyl)-2-(4-(2-(methylthio)phenyl)but-1-en-3-yn-1-yl)benzo[b]thiophene **12**

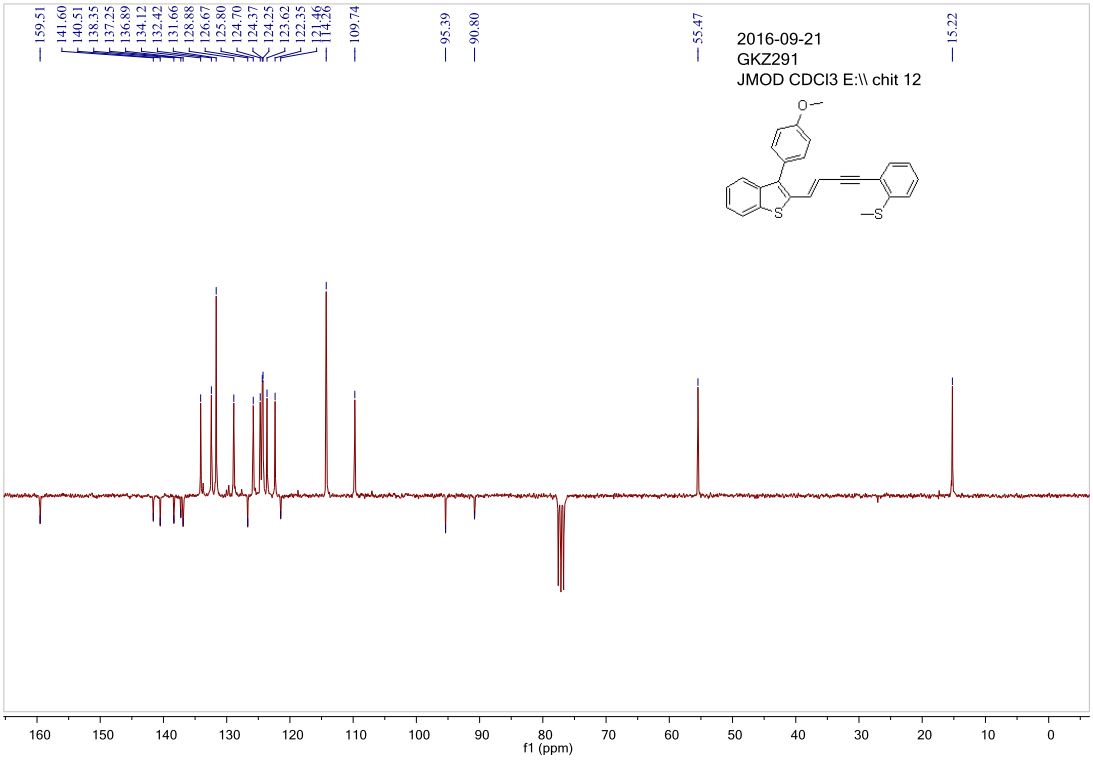

Fig. 61 ^{13}C NMR of (*E*)-3-(4-methoxyphenyl)-2-(4-(2-(methylthio)phenyl)but-1-en-3-yn-1-yl)benzo[b]thiophene **12**

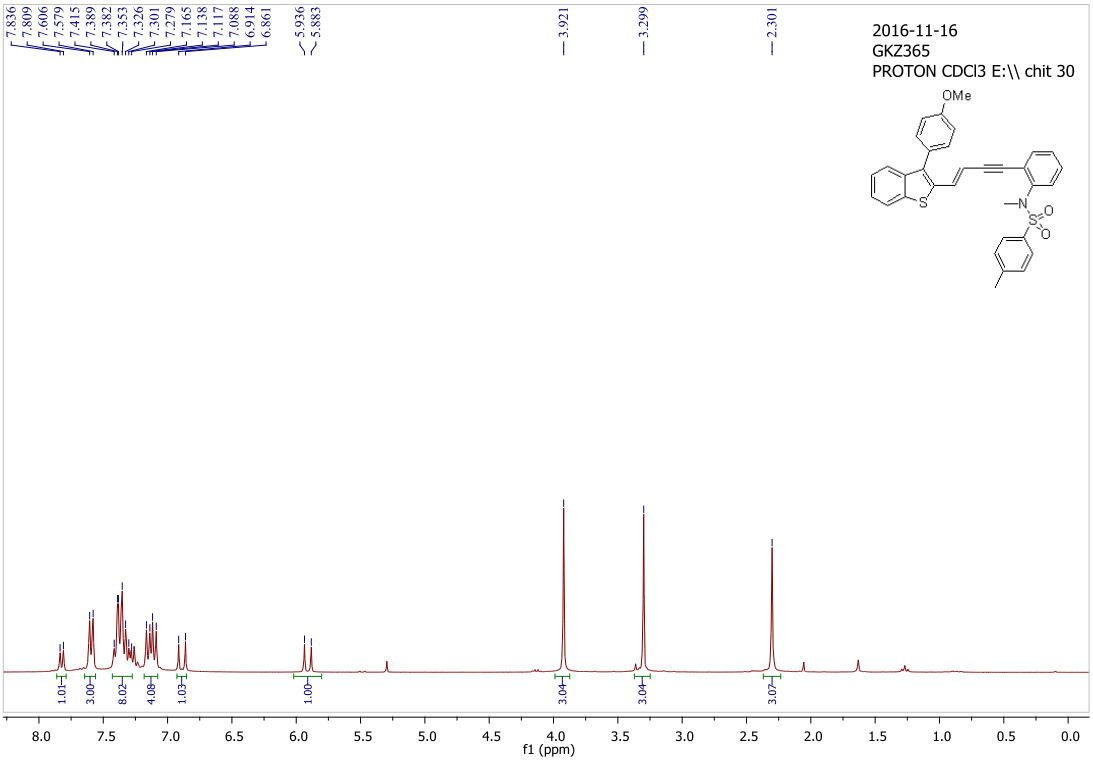

Fig.62 ^{1}H NMR of (*E*)-N-(2-(4-(3-(4-methoxyphenyl)benzo[b]thiophen-2-yl)but-3-en-1-yn-1-yl)phenyl)-N,4-dimethylbenzene sulfonamide **13**

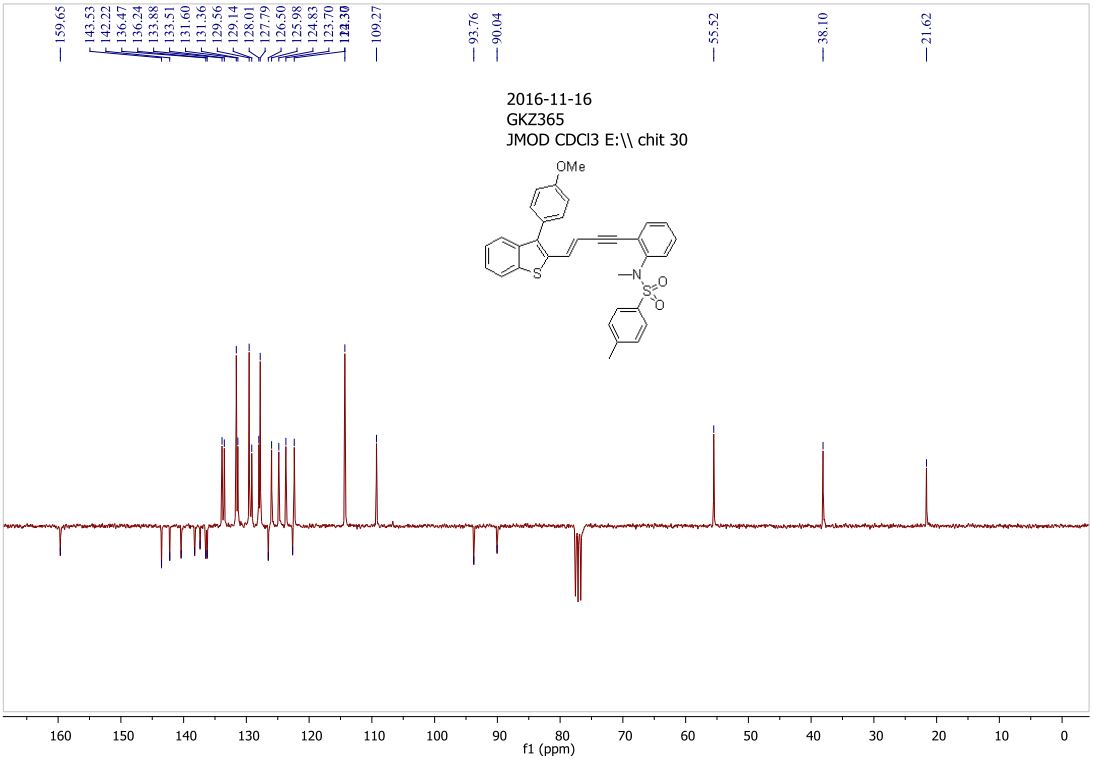

Fig. 63 ^{1}H NMR of (*E*)-N-(2-(4-(3-(4-methoxyphenyl)benzo[b]thiophen-2-yl)but-3-en-1-yn-1-yl)phenyl)-N,4-dimethylbenzenesulfonamide **13**

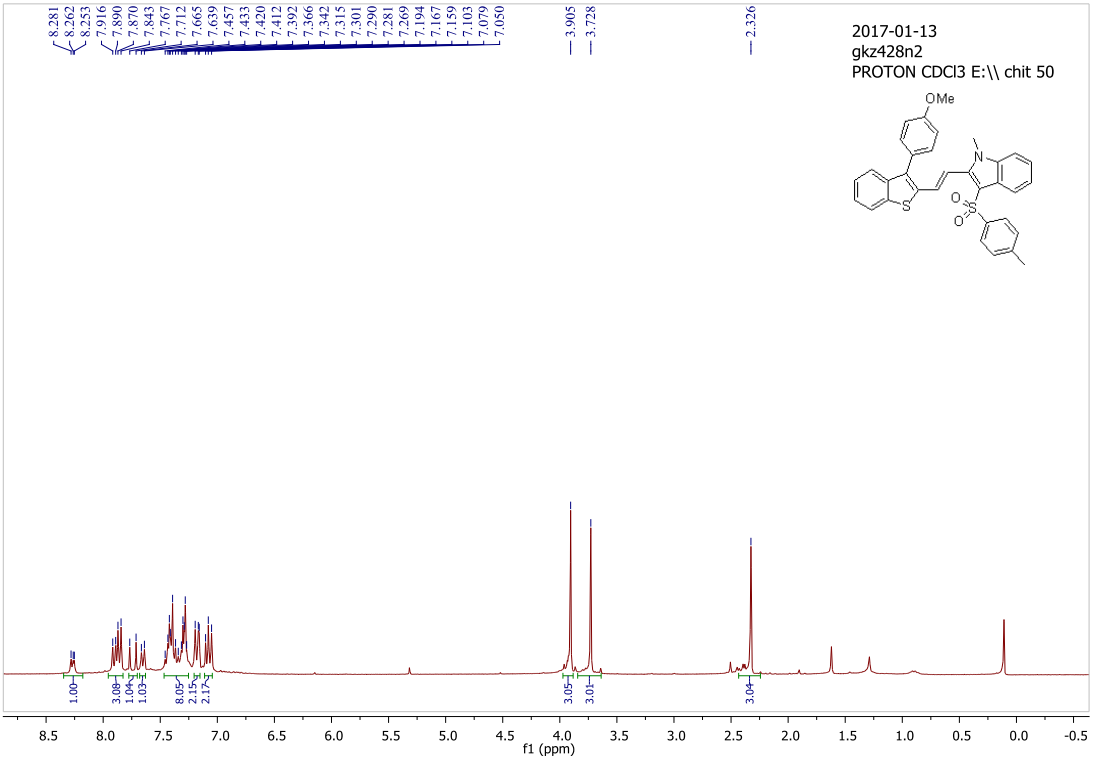

Fig. 64 ^{1}H NMR of (*E*)-2-(2-(3-(4-methoxyphenyl)benzo[b]thiophen-2-yl)vinyl)-1-methyl-3-tosyl-1H-indole **14**

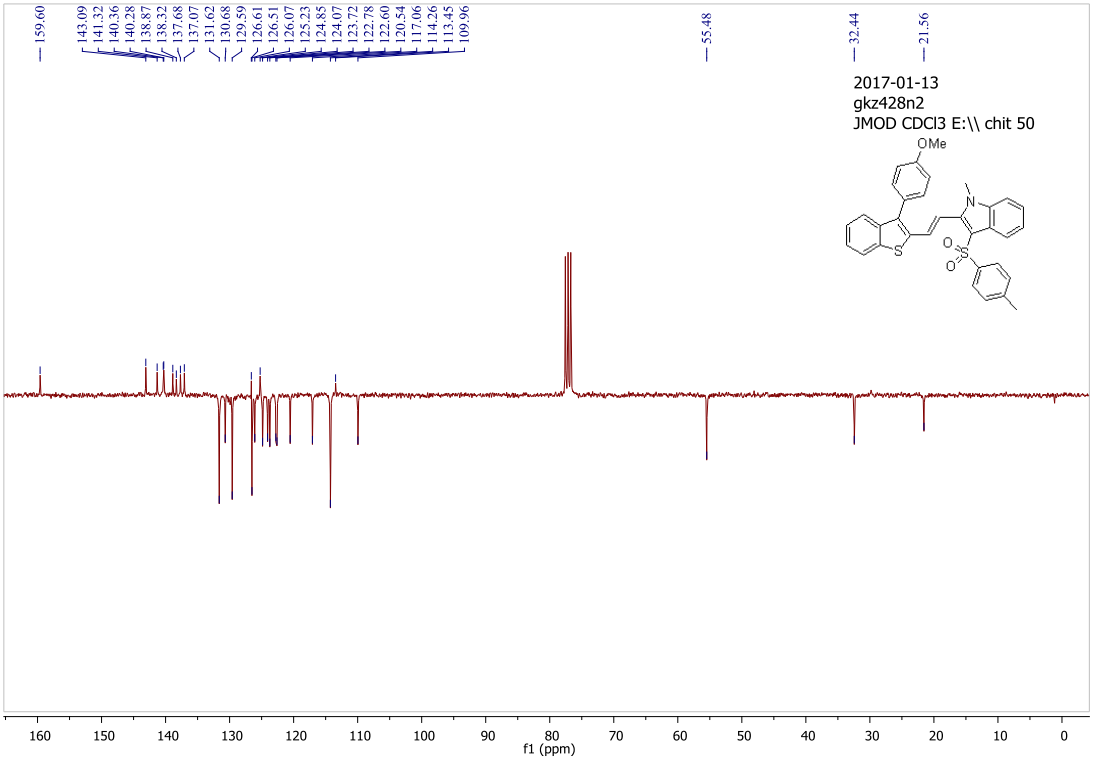

Fig. 65 ^{13}C NMR of (*E*)-2-(2-(3-(4-methoxyphenyl)benzo[b]thiophen-2-yl)vinyl)-1-methyl-3-tosyl-1H-indole **14**

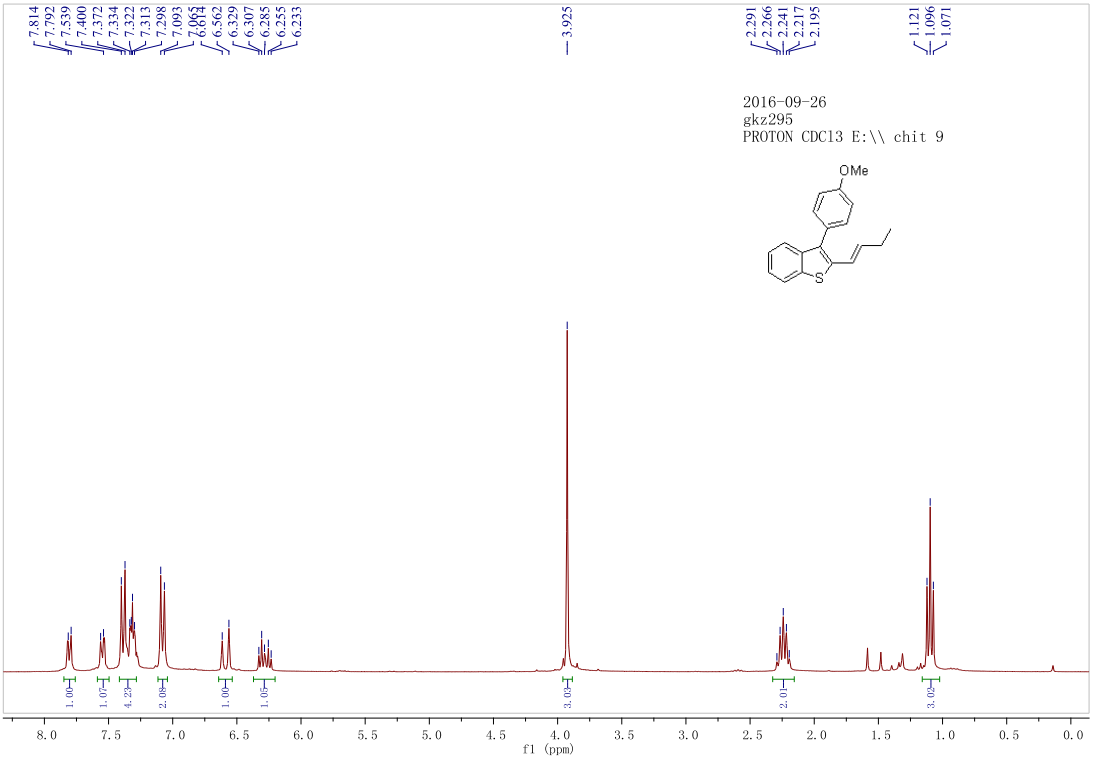

Fig. 66 ^{1}H NMR of (*E*)-2-(but-1-en-1-yl)-3-(4-methoxyphenyl)benzo[b]thiophene **1ca**

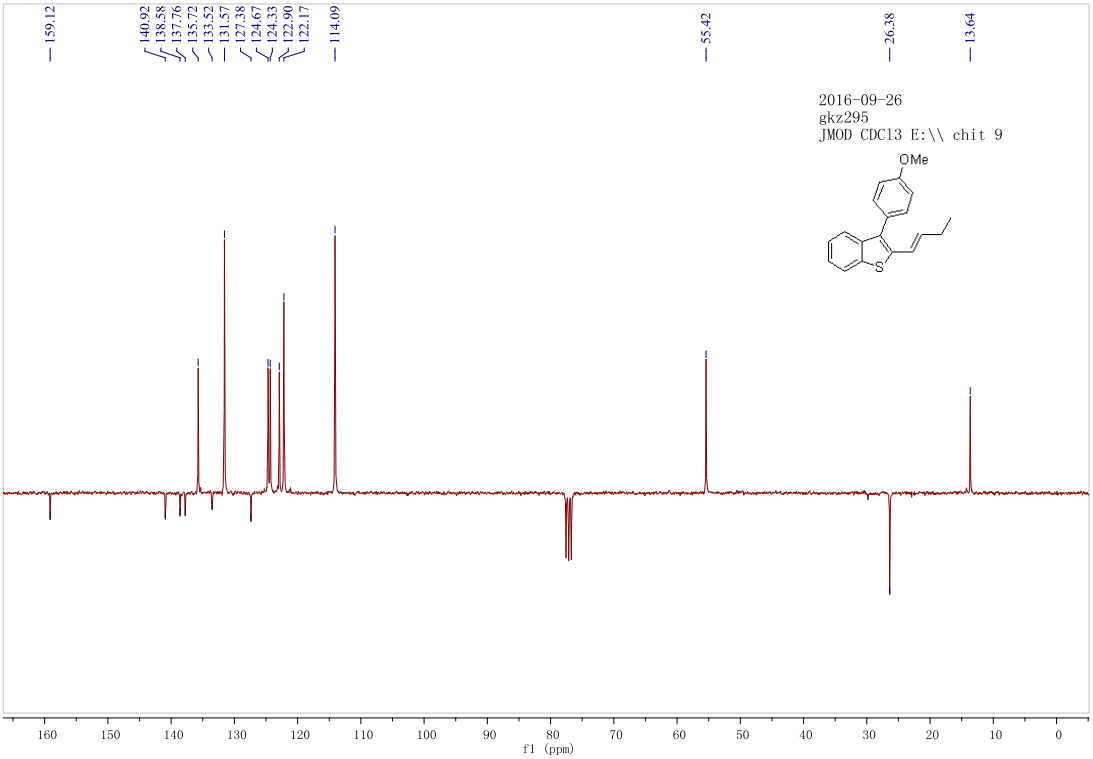

Fig.67 ^{1}H NMR of (*E*)-2-(but-1-en-1-yl)-3-(4-methoxyphenyl)benzo[b]thiophene **1ca**

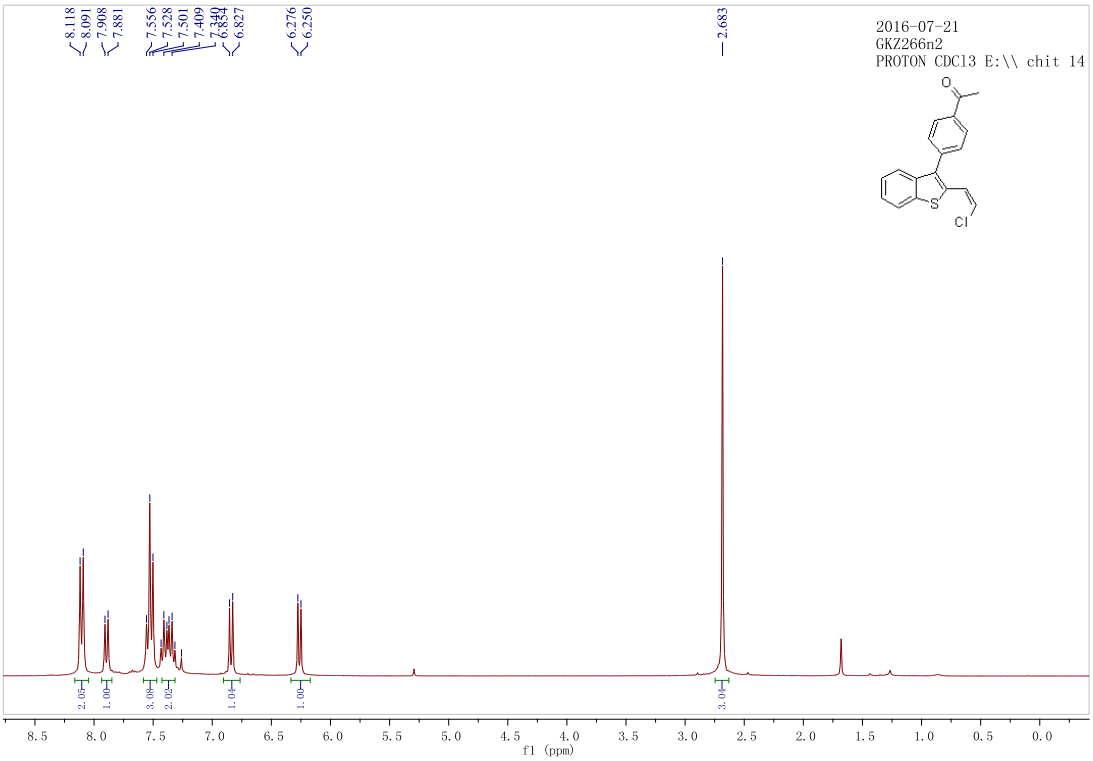

Fig. 68 ^{1}H NMR of (*Z*)-1-(4-(2-(2-chlorovinyl)benzo[b]thiophen-3-yl)phenyl)ethanone **8a**

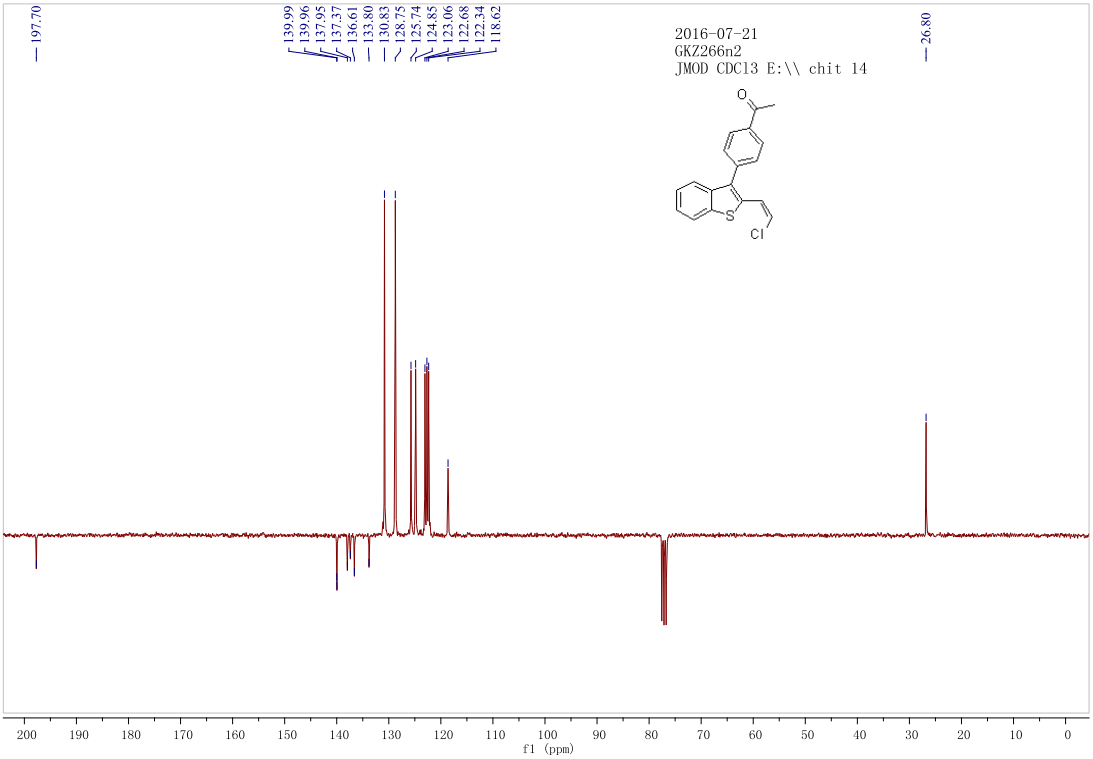

Fig. 69 ^{13}C NMR of (*Z*)-1-(4-(2-(2-chlorovinyl)benzo[b]thiophen-3-yl)phenyl)ethanone **8a**

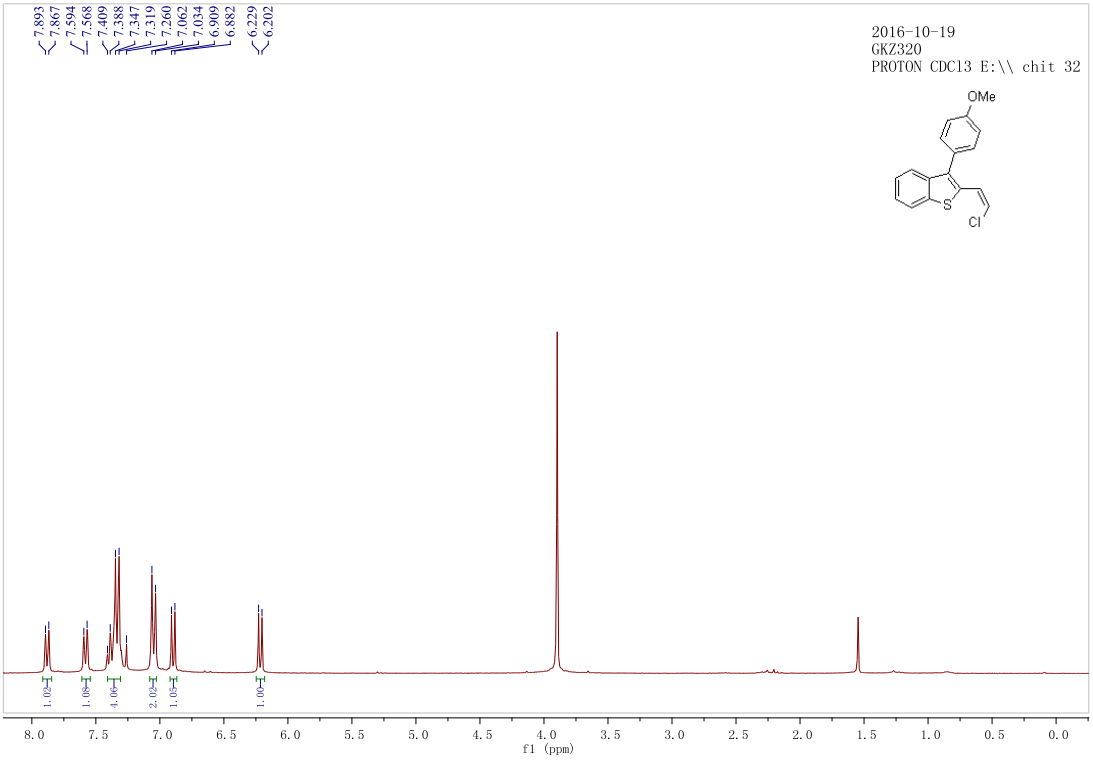

Fig. 70 ^{1}H NMR of (*Z*)-2-(2-chlorovinyl)-3-(4-methoxyphenyl)benzo[b]thiophene **8b**

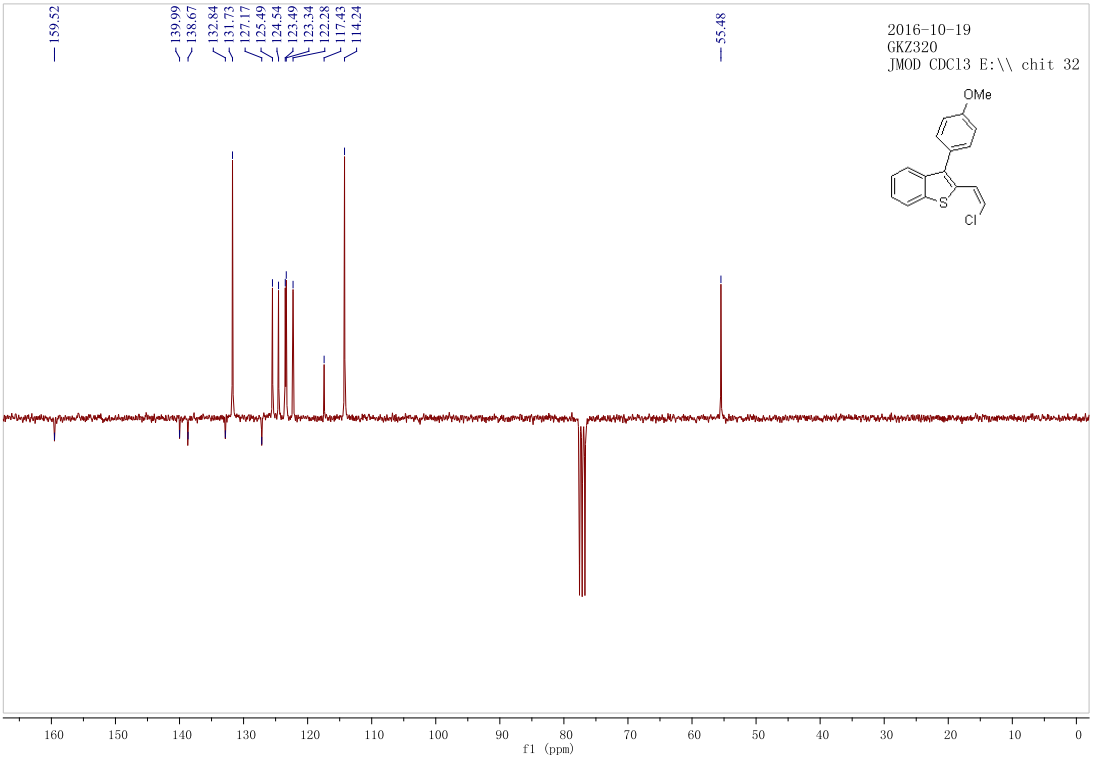

Fig. 71 ^{13}C NMR of (*Z*)-2-(2-chlorovinyl)-3-(4-methoxyphenyl)benzo[b]thiophene **8b**

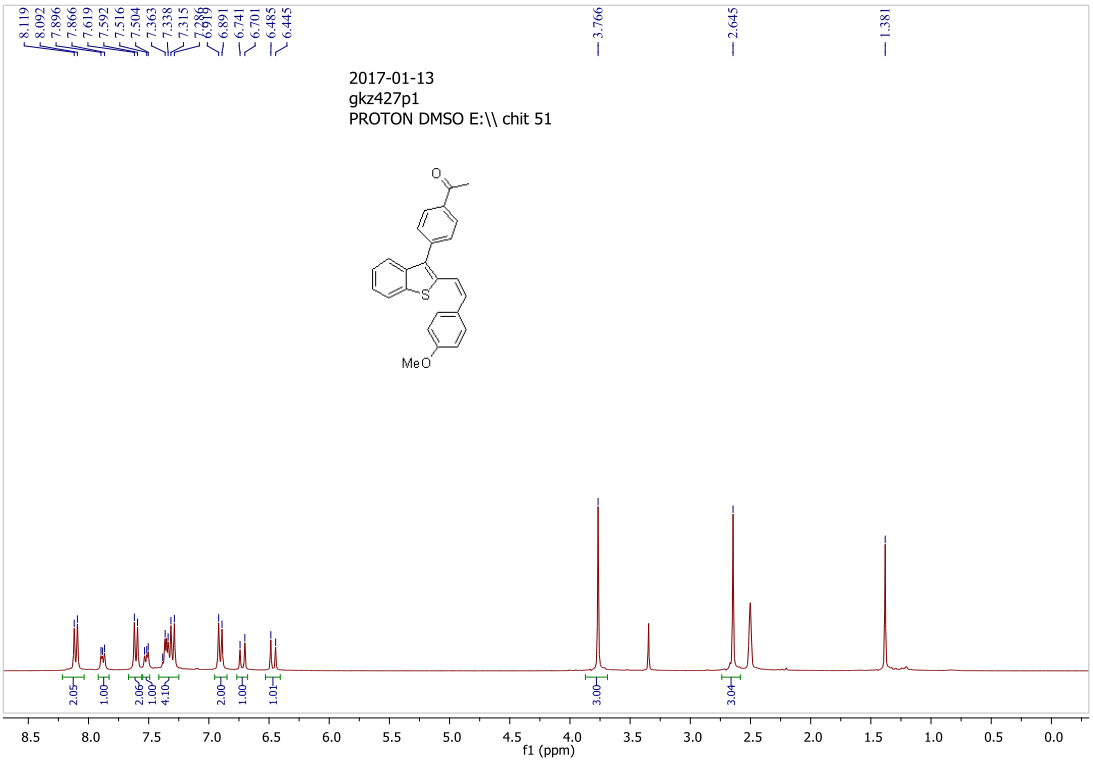

Fig. 72 ^{1}H NMR of (*Z*)-1-(4-(2-(4-methoxystyryl)benzo[b]thiophen-3-yl)phenyl)ethanone **1al**

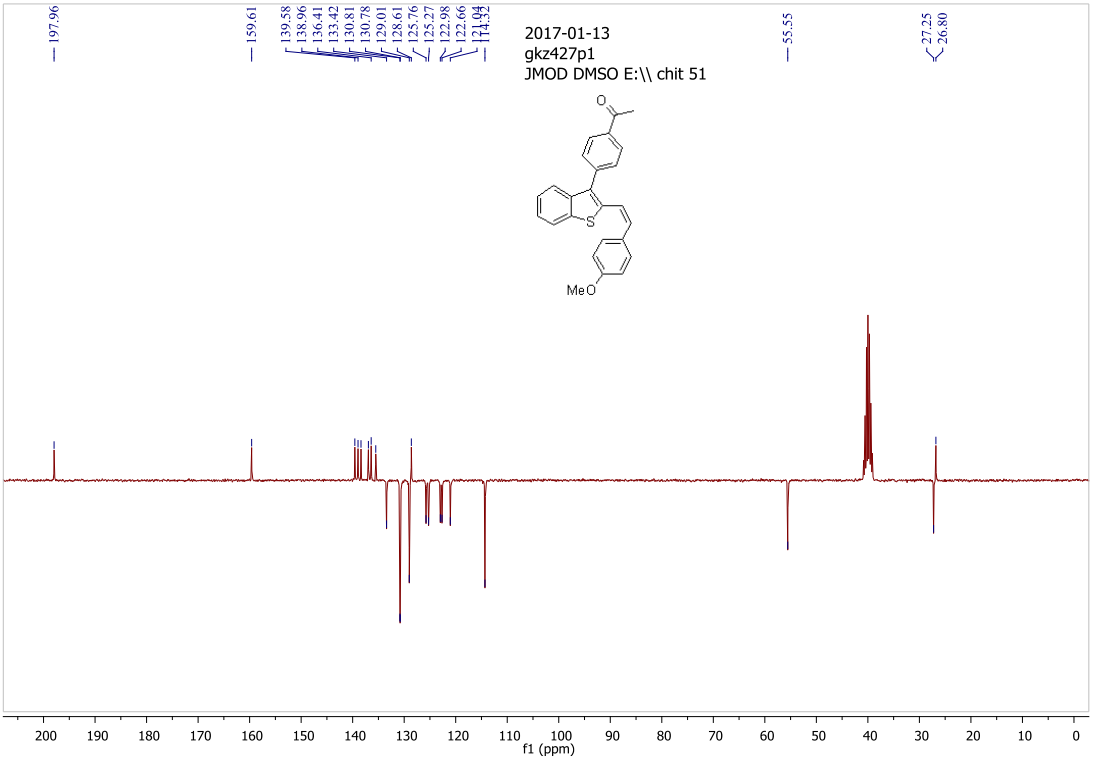

Fig. 73 ^{13}C NMR of (*Z*)-1-(4-(2-(4-methoxystyryl)benzo[b]thiophen-3-yl)phenyl)ethanone **1al**

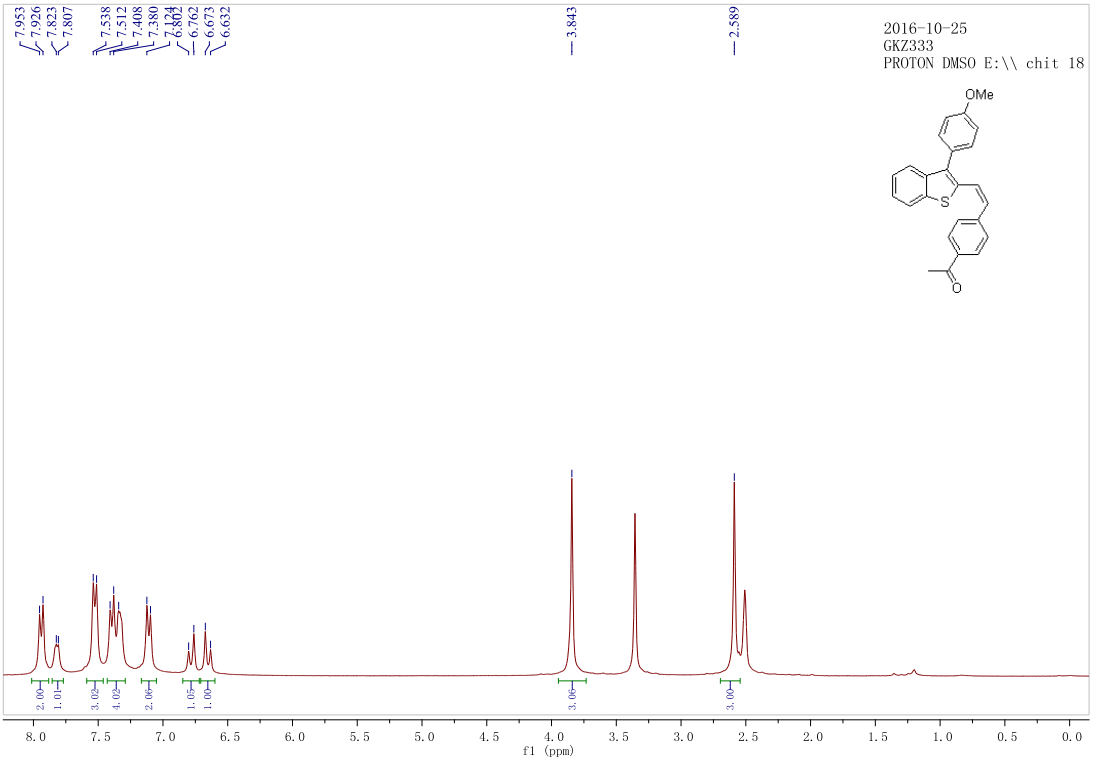

Fig. 74 ^{1}H NMR of (*Z*)-1-(4-(2-(3-(4-methoxyphenyl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethanone **1am**

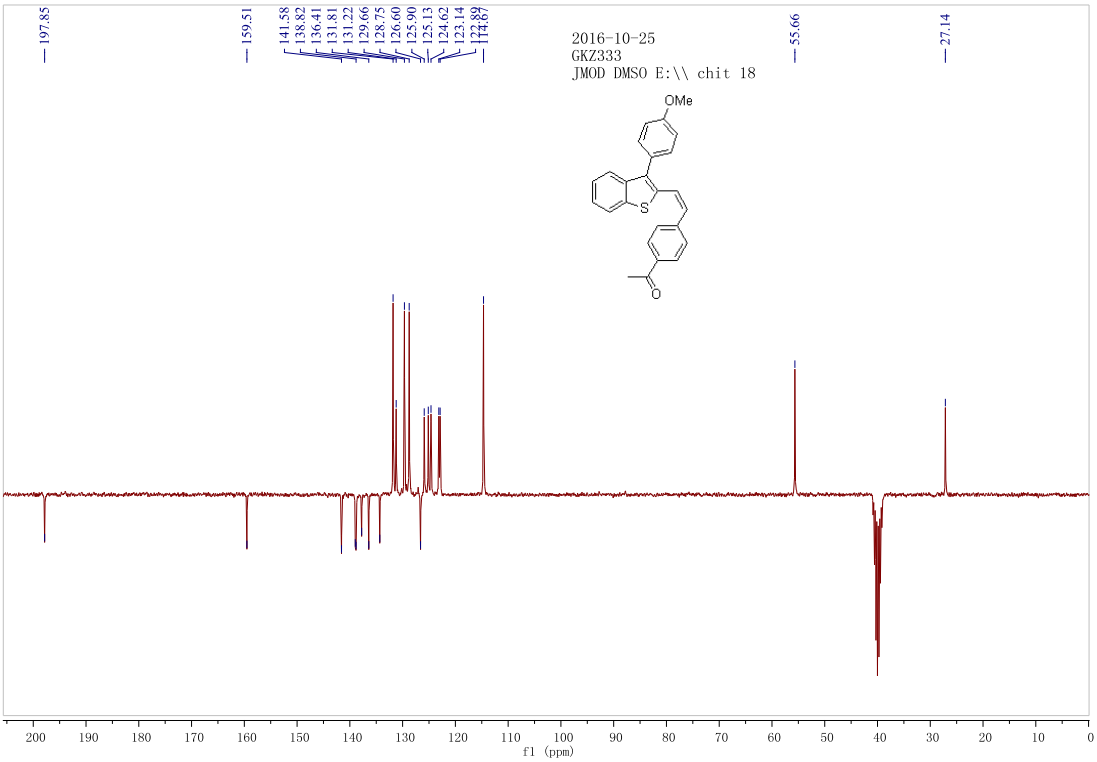

Fig. 75 ^{13}C NMR of (*Z*)-1-(4-(2-(3-(4-methoxyphenyl)benzo[b]thiophen-2-yl)vinyl)phenyl)ethanone **1am**

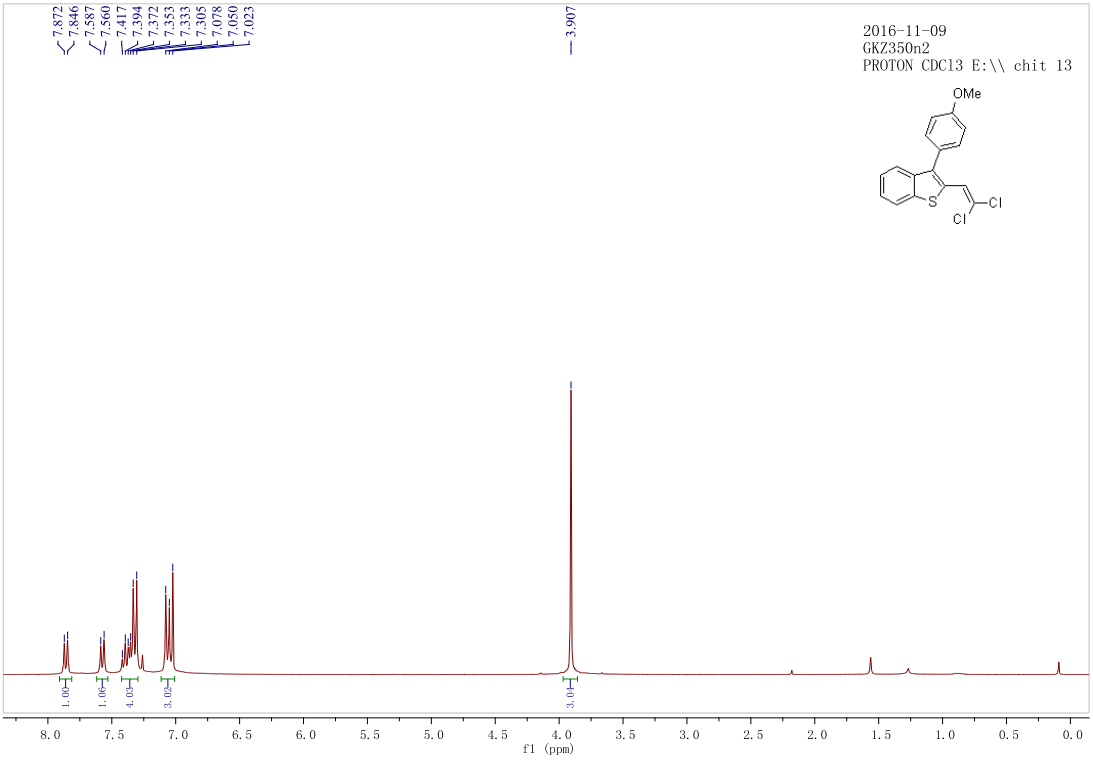

Fig. 76 ^{1}H NMR of 2-(2,2-dichlorovinyl)-3-(4-methoxyphenyl)benzo[b]thiophene **15**

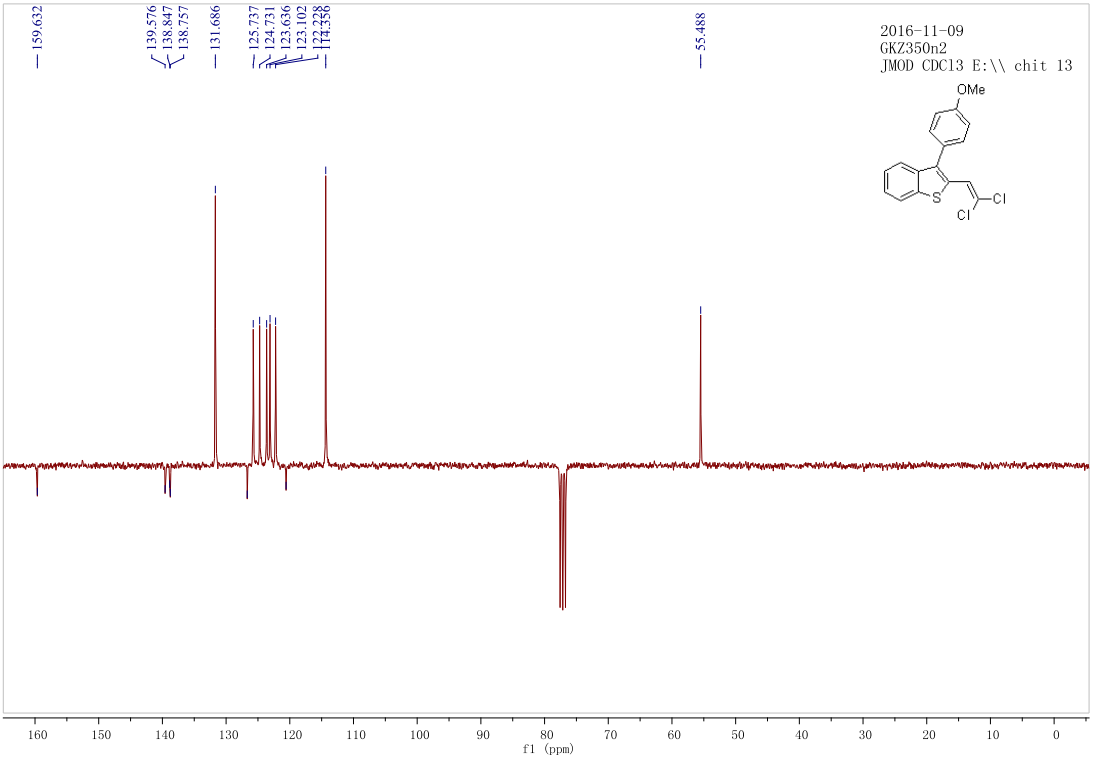

Fig. 77 ^{13}C NMR of 2-(2,2-dichlorovinyl)-3-(4-methoxyphenyl)benzo[b]thiophene **15**

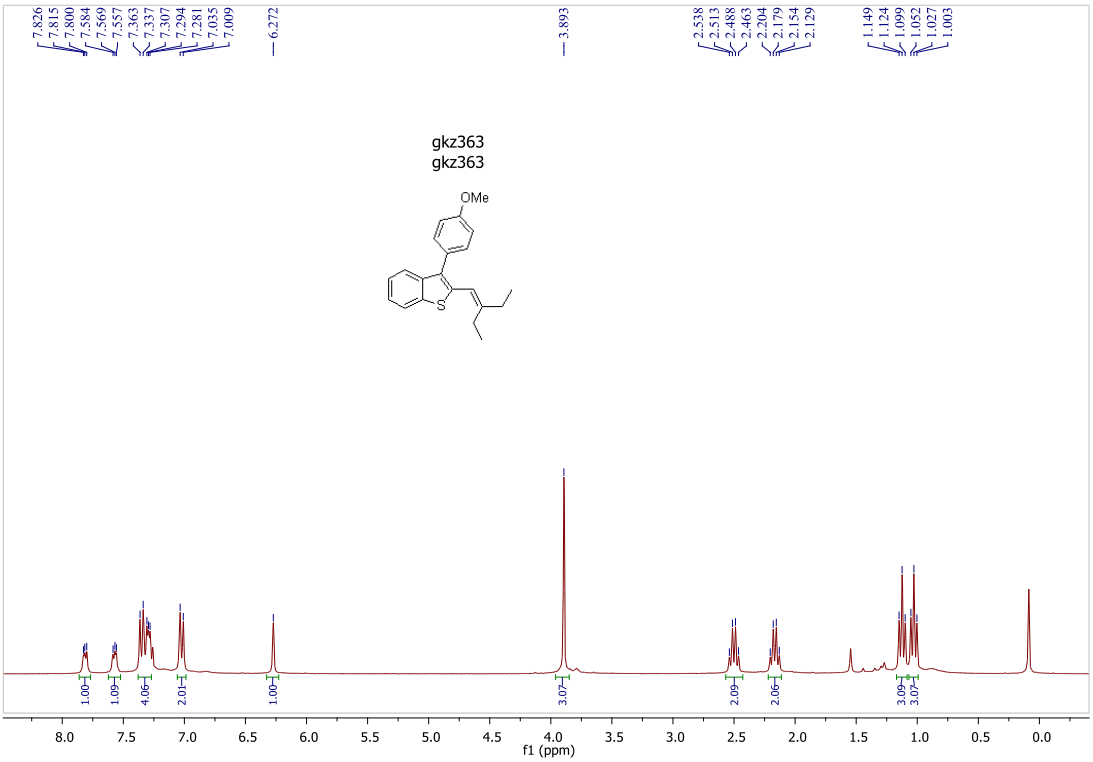

Fig. 78 ^{1}H NMR of 2-(2-ethylbut-1-en-1-yl)-3-(4-methoxyphenyl)benzo[b]thiophene **16**

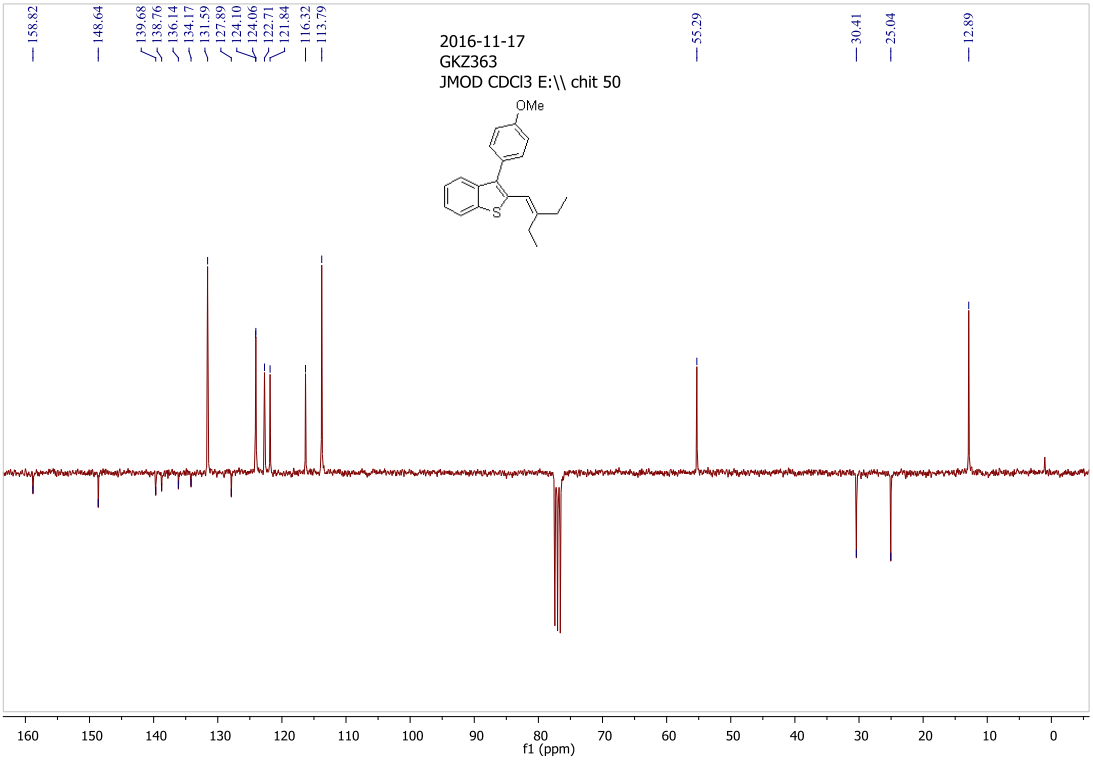

Fig. 79 ^{13}C NMR of 2-(2-ethylbut-1-en-1-yl)-3-(4-methoxyphenyl)benzo[b]thiophene **16**

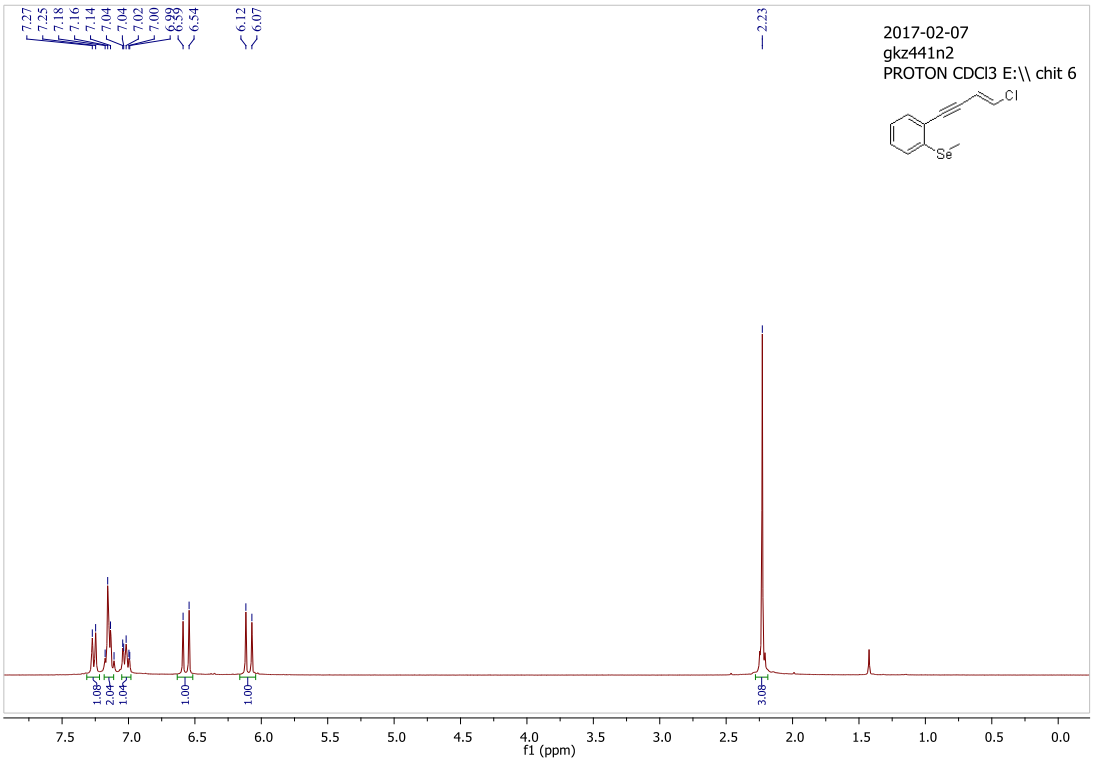

Fig. 80 ^{1}H NMR of (*E*)-(2-(4-chlorobut-3-en-1-yn-1-yl)phenyl)(methyl)selane **18**

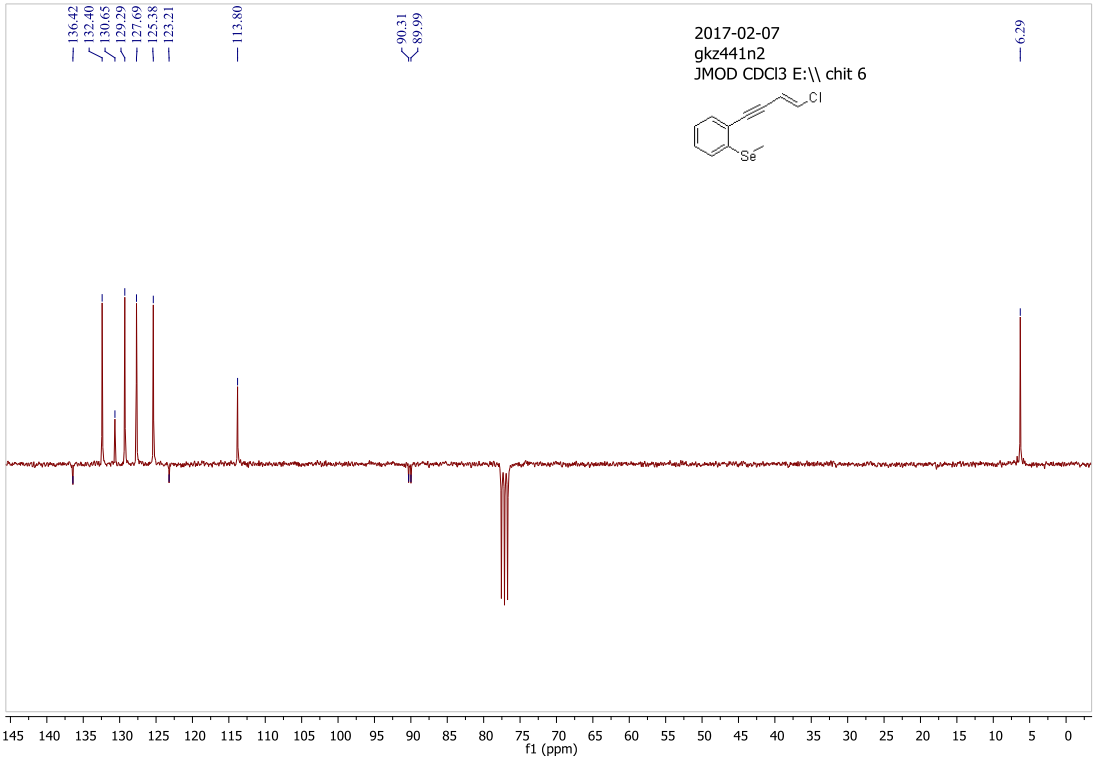

Fig. 81 ^{13}C NMR of (*E*)-(2-(4-chlorobut-3-en-1-yn-1-yl)phenyl)(methyl)selane **18**

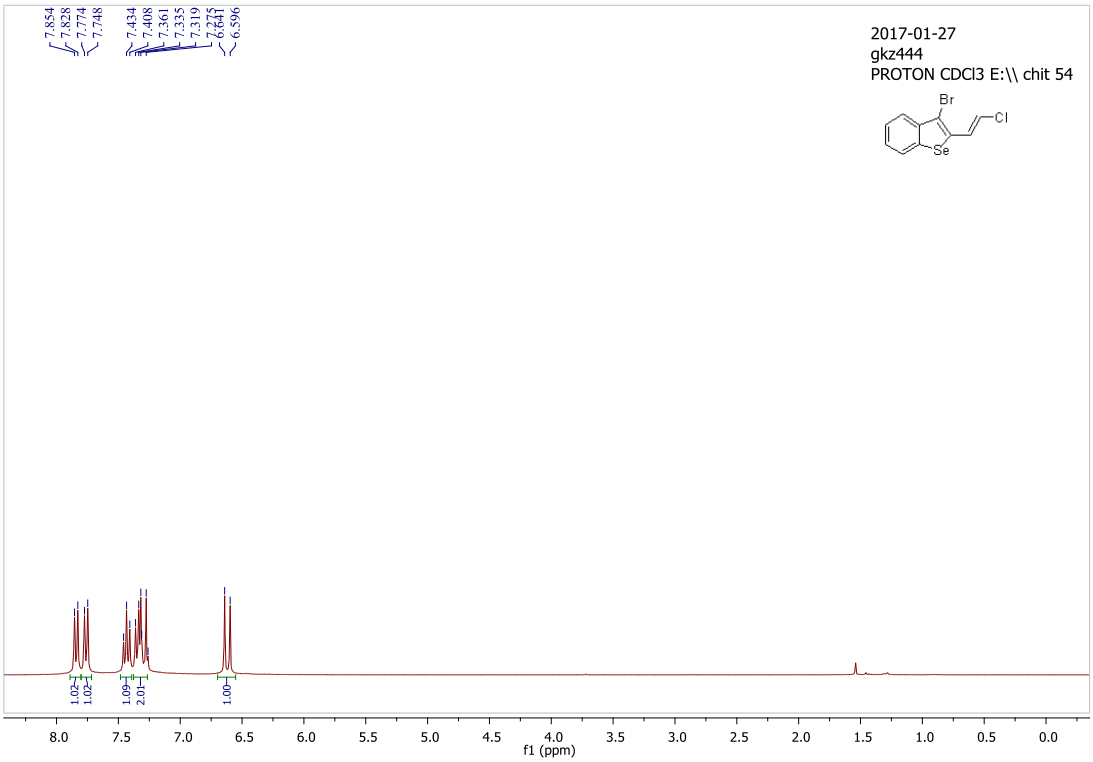

Fig. 82 ^{1}H NMR of (*E*)-3-bromo-2-(2-chlorovinyl)benzo[b]selenophene **19**

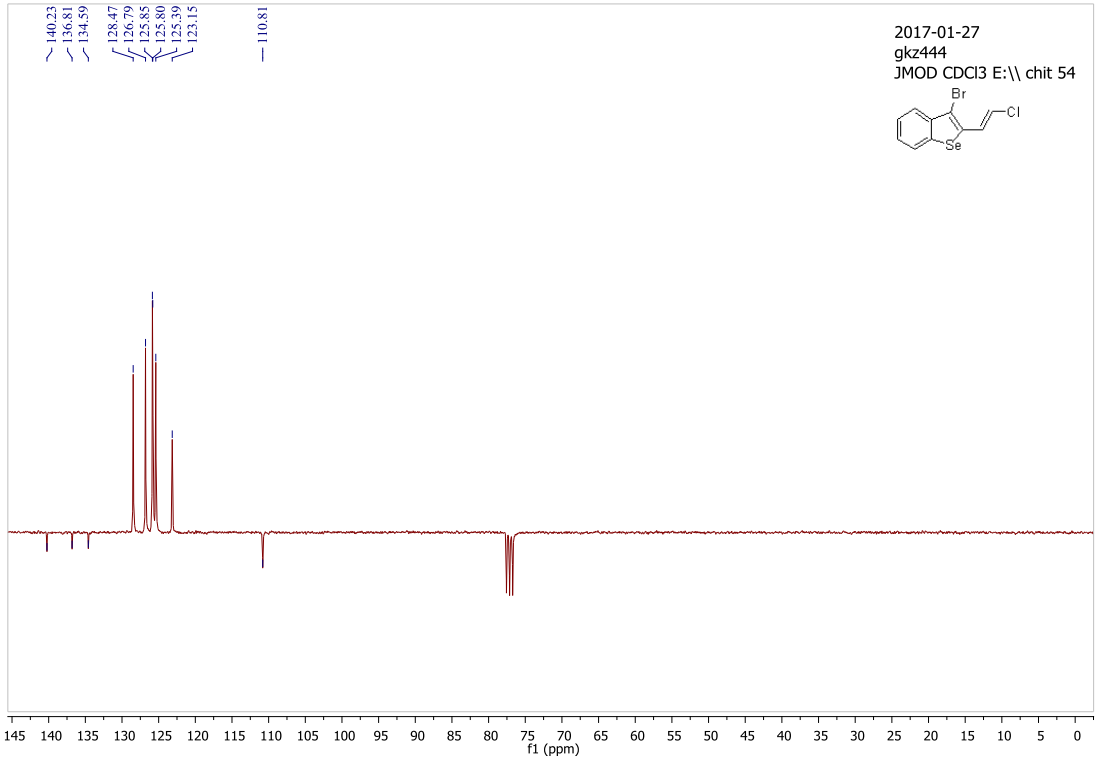

Fig. 83 ^{13}C NMR of (*E*)-3-bromo-2-(2-chlorovinyl)benzo[b]selenophene **29**