Highly Efficient Two-Step Synthesis of (*Z*)-2-Halo-1-Iodoalkenes from Terminal Alkynes

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Supporting Information

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A. General method

^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.24 and 77.0 ppm, respectively, chloroform is solvent with TMS as the internal standard. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrometer. Mass spectra were recorded on a Shimadzu GCMS-QP5050A spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). Elemental analyses were performed with a Vario EL elemental analyzer. TLC was performed by using commercially prepared 100–400 mesh silica gel plates (GF254) and visualization was effected at 254 nm. All the other chemicals were purchased from Aldrich Chemicals.

B. General procedure for the synthesis of 1-haloalkyne

To the mixture of terminal alkyne (1 mmol), NBS (1.2 mmol) and 10 mL acetone, $AgNO_3$ (5 mol %) was added and the mixture was stirred at room temperature for three hours. After completion the reaciton, the solvent was evaporated and extracted with 10 mL petroleum ether (30-60 ^{o}C), then evaporated the solvent and the residue was the title product.

C. General procedure for the synthesis of (*Z*)-2-halo-1-iodoalkene

The mixture of haloalkyne (1 mmol), KI (1.5 mmol) and 2 mL acetic anhydride were heated at 120 ^{o}C for 6 h. The solution was washed with water and extracted with ethyl acetate (3×15 mL), and the combined extract was dried with anhydrous $MgSO_4$. Solvent was removed, and the residue was separated by column chromatography to give the pure sample.

D. General procedure for the one-pot synthesis of (*Z*)-2-halo-1-iodoalkene

To the mixture of terminal alkyne (1 mmol), NBS (1.2 mmol) and 10 mL acetone, $AgNO_3$ (5 mol %) was added and the mixture was stirred at room temperature for three hours. Then evaporated the solvent and added 2 ml acetic anhydride, and the mixture reacted at 120 ^{o}C for 6 h. The solution was washed with water and extracted with ethyl acetate (3×15 mL), and the combined extract was dried with anhydrous $MgSO_4$. Solvent was removed, and the residue was separated by column chromatography to give the pure sample.

E. General procedure for the Sonogashira reaction of 1-((*Z*)-2-bromo-1-iodovinyl)benzene (2a)

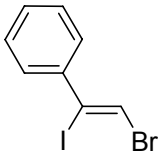
To the mixture of 1-((*Z*)-2-bromo-1-iodovinyl)benzene (**2a**) (1 mmol) and $PdCl_2$ (2 mol %) and water (2 mL), pyrrolidine (20 mol %) was added and the mixture was stirred at 50 ^{o}C for five minutes, phenylacetylene (1.5 mmol) was added, then the mixture was stirred at 50 ^{o}C for 12 h. The solution was extracted with ethyl acetate (3×15 mL), and the combined extract was dried with anhydrous $MgSO_4$. Solvent was removed, and the residue was separated by column chromatography to give the pure

sample.

F. General procedure for the Sonogashira reaction of (Z)-1-bromo-2,4-diphenylbut-1-en-3-yne (3a)

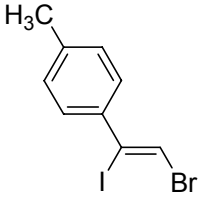
To the mixture of (*Z*)-1-bromo-2,4-Diphenylbut-1-en-3-yne (**3a**) (1 mmol) and $Pd(PPh_3)_2Cl_2$ (5 mol %) and DMF (2 mL), TEA (2 mmol) and CuI (5 mol %) were added successively, stirred for five minutes at the room temperature, 1-ethynyl-4-fluorobenzene (1.5 mmol) were added, then the mixture was stirred at 80 ^oC for 8 h. The solution was extracted with ethyl acetate (3×15 mL), and the combined extract was dried with anhydrous $MgSO_4$. Solvent was removed, and the residue was separated by column chromatography to give the pure sample.

G. Analytical data for 2a-2w and 3a and 4a



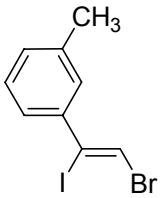
1-((*Z*)-2-bromo-1-iodovinyl)benzene (2a)

IR (KBr): 3051, 1560, 1486, 1441, 1212, 873, 761, 730, 691, 589. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.43 (m, 2H), 7.29-7.31 (m, 3H), 6.99 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.9, 129.0, 128.4, 128.4, 116.1, 111.3. MS (EI) m/z: 76, 102, 181, 308. Anal. Calcd for C_8H_6BrI: C, 31.10; H, 1.96. Found: C, 31.33; H, 1.88.



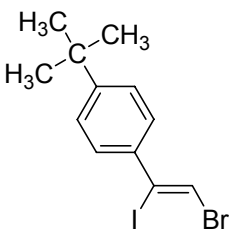
1-((*Z*)-2-bromo-1-iodovinyl)-4-methylbenzene (2b)

IR (KBr): 3045, 2919, 1691, 1606, 1573, 1309, 1265, 880, 773, 731, 531. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.94 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.1, 129.1, 128.3, 127.8, 115.3, 111.5, 21.1. MS (EI) m/z: 63, 89, 116, 197, 322. Anal. Calcd for C_9H_8BrI: C, 33.47; H, 2.50. Found: C, 33.23; H, 2.59.



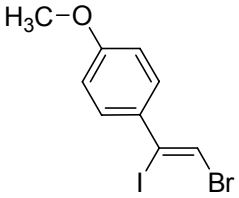
1-((*Z*)-2-bromo-1-iodovinyl)-3-methylbenzene (2c)

IR (KBr): 3045, 2919, 1785, 1691, 1599, 1480, 1213, 938, 768, 724. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.17-7.22 (m, 3H), 7.12 (d, J = 6.8 Hz, 1H), 6.97 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.8, 138.1, 129.8, 129.0, 128.3, 125.5, 115.8, 111.5, 21.2. MS (EI) m/z: 63, 89, 116, 197, 322. Anal. Calcd for C_9H_8BrI: C, 33.47; H, 2.50. Found: C, 33.38; H, 2.55.



1-*tert*-butyl-4-((*Z*)-2-bromo-1-iodovinyl)benzene (2d)

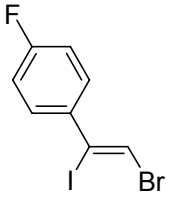
IR (KBr): 3043, 2962, 1786, 1690, 1571, 1465, 1269, 1108, 881. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.8 Hz, 2H), 6.96 (s, 1H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.3, 139.0, 128.1, 125.4, 115.4, 111.5, 34.6, 31.1. MS (EI) m/z: 58, 77, 115, 143, 158, 237, 364. Anal. Calcd for $C_{12}H_{14}BrI$: C, 39.48; H, 3.87. Found: C, 39.21; H, 3.95.



1-((*Z*)-2-bromo-1-iodovinyl)-4-methoxybenzene (2e)

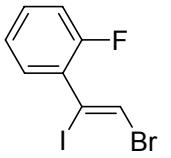
IR (KBr): 3042, 2928, 1602, 1504, 1295, 1252, 1032, 832, 679. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, J = 8.8 Hz, 2H), 6.88 (s, 1H), 6.81 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 134.6, 129.7, 114.6, 113.6, 111.2, 55.3. MS (EI) m/z: 63, 89, 117, 132, 213, 338. Anal. Calcd

for C_9H_8BrIO: C, 31.89; H, 2.38. Found: C, 31.71; H, 2.44.



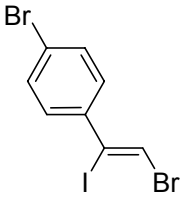
1-((*Z*)-2-bromo-1-iodovinyl)-4-fluorobenzene (2f)

IR (KBr): 3045, 1694, 1597, 1502, 1233, 1159, 878, 805, 619. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.38-7.42 (m, 2H), 6.97-7.01 (m, 2H), 6.94 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 164.1, 161.6, 138.2, 130.1, 130.1, 128.4, 128.4, 116.3, 115.5, 115.2, 109.7. MS (EI) m/z: 74, 94, 120, 201, 326. Anal. Calcd for C_8H_5BrFI: C, 29.39; H, 1.54. Found: C, 29.53; H, 1.48.



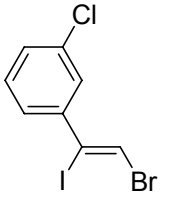
1-((*Z*)-2-bromo-1-iodovinyl)-2-fluorobenzene (2g)

IR (KBr): 3052, 1577, 1483, 1447, 1267, 1230, 1101, 943, 755, 646. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26-7.34 (m, 2H), 7.00-7.13 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =159.9, 157.4, 131.7, 131.1, 131.0, 130.3, 130.2, 124.4, 124.4, 120.1, 120.1, 116.5, 116.3, 100.9. MS (EI) m/z: 74, 94, 120, 199, 326. Anal. Calcd for C_8H_5BrFI: C, 29.39; H, 1.54. Found: C, 29.62; H, 1.46.



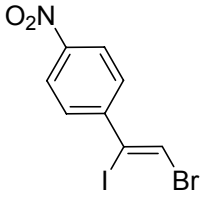
1-bromo-4-((*Z*)-2-bromo-1-iodovinyl)benzene (2h)

IR (KBr): 3044, 1679, 1512, 1391, 1073, 1008, 877, 825, 752, 526. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.43 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.00 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 140.9, 131.6, 129.8, 123.2, 116.8, 109.7. MS (EI) m/z: 51, 75, 101, 182, 261, 388. Anal. Calcd for $C_8H_5Br_2I$: C, 24.77; H, 1.30. Found: C, 24.59; H, 1.38.



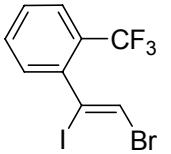
1-((*Z*)-2-bromo-1-iodovinyl)-3-chlorobenzene (2i)

IR (KBr): 3047, 2924, 1587, 1561, 1470, 1407, 1212, 1094, 913, 881, 763, 685. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.40-7.41 (m, 1H), 7.23-7.31 (m, 3H), 7.04 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 143.5, 134.2, 129.6, 129.1, 128.4, 126.6, 117.5, 109.1. MS (EI) m/z: 51, 75, 101, 127, 136, 217, 344. Anal. Calcd for C_8H_5BrClI: C, 27.98; H, 1.47. Found: C, 27.75; H, 1.55.



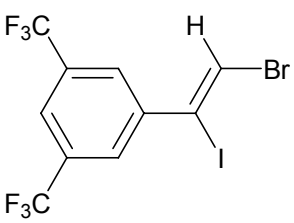
1-((Z)-2-bromo-1-iodovinyl)-4-nitrobenzene (2j)

IR (KBr): 2924, 1584, 1556, 1473, 1415, 1022, 881, 678, 513. δ= 8.16 (d, J = 9.2 Hz, 2H), 7.59 (d, J = 9.2 Hz, 2H), 7.19 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 147.8, 129.3, 123.8, 123.7, 119.8, 108.1. MS (EI) m/z: 51, 75, 101, 117, 182, 226, 353. Anal. Calcd for $C_8H_5BrINO_2$: C, 27.15; H, 1.42; N, 3.96. Found: C, 27.37; H, 1.34; N, 4.07.



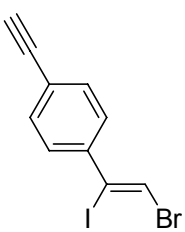
1-((*Z*)-2-bromo-1-iodovinyl)-2-(trifluoromethyl)benzene (2k)

IR (KBr): 3049, 2923, 1585, 1471, 1408, 1132, 921, 880, 765, 683. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.61-7.66 (m, 1H), 7.50-7.58 (m, 1H), 7.36-7.46 (m, 2H), 6.81 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 141.63, 131.90, 131.33, 129.14, 126.61, 126.56, 126.27, 126.21, 125.26, 122.54, 119.19, 102.49. MS (EI) m/z: 75, 120, 151, 170, 231, 251, 376. Anal. Calcd for $C_9H_5BrF_3I$: C, 28.68; H, 1.34. Found: C, 28.45; H, 1.26.



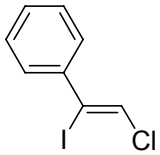
1-((*Z*)-2-bromo-1-iodovinyl)-3,5-bis(trifluoromethyl)benzene (2l)

IR (KBr): 3051, 2925, 1553, 1370, 1280, 1137, 955, 901, 789, 692, 613. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.86 (s, 2H), 7.81 (s, 1H), 7.20 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 143.6, 132.1, 131.8, 131.5, 131.1, 127.9, 127.7, 126.4, 123.7, 122.1, 121.0, 119.5, 118.3, 106.3. MS (EI) m/z: 74, 99, 149, 169, 188, 219, 238, 317, 425, 444. Anal. Calcd for $C_{10}H_4BrF_6I$: C, 26.99; H, 0.91. Found: C, 26.72; H, 0.98.



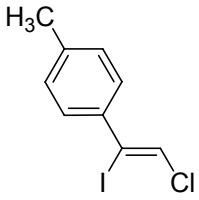
1-((*Z*)-2-bromo-1-iodovinyl)-4-ethynylbenzene (2m)

IR (KBr): 3445, 1649, 1505, 1452, 1214, 1041, 789, 761, 708. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 5.6 Hz, 2H), 7.04 (s, 1H), 2.15 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.5, 132.1, 128.5, 128.4, 117.1, 110.0, 82.8, 78.7. MS (EI) m/z: 74, 126, 205, 332. Anal. Calcd for $C_{10}H_6BrI$: C, 36.07; H, 1.82. Found: C, 36.25; H, 1.77.



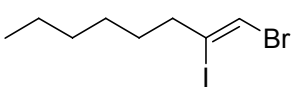
1-((*Z*)-2-chloro-1-iodovinyl)benzene (2n)

IR (KBr): 3050, 1582, 1562, 1485, 1441, 1284, 917, 889, 750, 692, 610. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.44 (m, 2H), 7.31-7.33 (m, 3H), 6.62 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.6, 129.1, 128.6, 128.5, 125.7, 107.3. MS (EI) m/z: 75, 102, 137, 264. Anal. Calcd for C_8H_6ClI: C, 36.33; H, 2.29. Found: C, 36.60; H, 2.21.



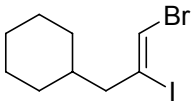
1-((*Z*)-2-chloro-1-iodovinyl)-4-methylbenzene (2o)

IR (KBr): 3045, 2919, 1605, 1577, 1451, 1406, 1213, 1040, 811, 788. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 7.6 Hz, 2H), 6.57 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.1, 137.8, 129.1, 128.4, 124.8, 107.4, 21.1. MS (EI) m/z: 63, 89, 115, 127, 151, 278. Anal. Calcd for C_9H_8ClI: C, 38.81; H, 2.90. Found: C, 38.63; H, 2.97.



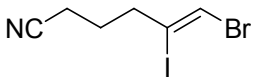
(*Z*)-1-bromo-2-iodooct-1-ene (2p)

IR (KBr): 3045, 2956, 1738, 1591, 1388, 1240, 1042, 771, 728, 636. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.62 (s, 1H), 2.48 (t, J = 7.2 Hz, 2H), 1.48-1.55 (m, 2H), 1.22-1.30 (m, 6H), 0.86 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.7, 112.3, 44.7, 31.3, 29.3, 27.7, 22.4, 14.0. MS (EI) m/z: 67, 81, 109, 119, 246, 316. Anal. Calcd for $C_8H_{14}BrI$: C, 30.31; H, 4.45. Found: C, 30.50; H, 4.39.



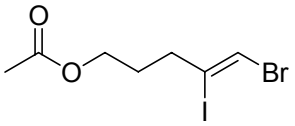
((*Z*)-3-bromo-2-iodoallyl)cyclohexane (2q)

IR (KBr): 3042, 2923, 2848, 1594, 1446, 1272, 1125, 761, 738, 573. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.58 (s, 1H), 2.34 (d, J = 6.4 Hz, 2H), 1.62-1.69 (m, 6H), 1.05-1.28 (m, 3H), 0.79-0.87 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 114.4, 112.5, 52.0, 36.8, 32.1, 26.2, 25.9. MS (EI) m/z: 55, 83, 121, 160, 206, 248, 328. Anal. Calcd for $C_9H_{14}BrI$: C, 32.85; H, 4.29. Found: C, 32.63; H, 4.35.



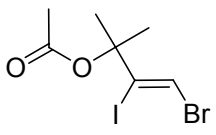
(*Z*)-6-bromo-5-iodohex-5-enenitrile (2r)

IR (KBr): 3043, 2938, 1757, 1591, 1449, 1426, 1230, 778, 725, 566. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.81 (s, 1H), 2.65 (t, J = 6.8 Hz, 2H), 2.31 (t, J = 6.8 Hz, 2H), 1.87-1.90 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 118.68, 114.99, 112.02, 42.65, 24.55, 15.33. MS (EI) m/z: 65, 92, 127, 145, 172, 192, 220, 245, 299. Anal. Calcd for C_6H_7BrIN: C, 24.03; H, 2.35; N, 4.67. Found: C, 24.27; H, 2.29; N, 4.61.



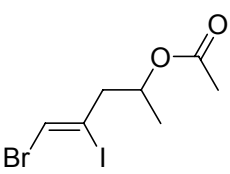
(*Z*)-5-bromo-4-iodopent-4-enyl acetate (2s)

IR (KBr): 3043, 2928, 1592, 1460, 1223, 768, 731. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.70 (s, 1H), 4.02 (t, J = 6.4 Hz, 2H), 2.57 (t, J = 6.8 Hz, 2H), 2.02 (s, 3H), 1.82-1.89 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.8, 113.6, 113.5, 62.3, 41.2, 28.1, 20.8. MS (EI) m/z: 43, 65, 145, 207, 245, 274. Anal. Calcd for $C_7H_{10}BrIO_2$: C, 25.25; H, 3.03. Found: C, 25.48; H, 2.97.



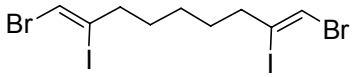
(*Z*)-4-bromo-3-iodo-2-methylbut-3-en-2-yl acetate (2t) or **(2u)**

IR (KBr): 3071, 2985, 2931, 1740, 1582, 1366, 1245, 1137, 1017, 946, 781, 608. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.95 (s, 1H), 2.02 (s, 3H), 1.64 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.3, 122.5, 115.0, 82.9, 26.9, 22.0. MS (EI) m/z: 43, 65, 147, 163, 205, 211, 275. Anal. Calcd for $C_7H_{10}BrIO_2$: C, 25.25; H, 3.03. Found: C, 25.08; H, 3.10.



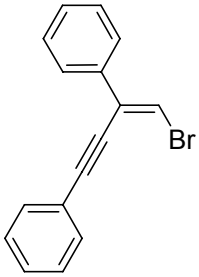
(*Z*)-5-bromo-4-iodopent-4-en-2-yl acetate (2v)

IR (KBr): 2979, 2390, 1737, 1640, 1452, 1240, 1131, 1057, 851, 740. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.73 (s, 1H), 5.09-5.14 (m, 1H), 2.81-2.86 (m, 1H), 2.62-2.67 (m, 1H), 1.98 (s, 3H), 1.21 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 115.5, 108.4, 69.0, 50.4, 21.1, 19.2. MS (EI) m/z: 43, 65, 145, 163, 205, 245, 272, 317, 333. Anal. Calcd for $C_7H_{10}BrIO_2$: C, 25.25; H, 3.03. Found: C, 25.41; H, 2.97.



(1*Z*, 8*Z*)-1,9-dibromo-2,8-diiodonona-1,8-diene (2w)

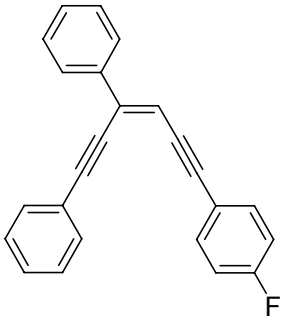
IR (KBr): 3040, 2933, 2855, 1591, 1456, 1425, 1242, 1219, 1089. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.65 (s, 2H), 2.49 (t, J = 6.8 Hz, 4H), 1.50-1.57 (m, 4H), 1.20-1.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.3, 112.8, 44.6, 29.0, 26.6. MS (EI) m/z: 53, 79, 91, 119, 159, 199, 245, 280, 325, 406, 534. Anal. Calcd for $C_9H_{12}Br_2I_2$: C, 20.25; H, 2.27. Found: C, 20.12; H, 2.31.



(*Z*)-1-bromo-2,4-diphenylbut-1-en-3-yne (3a)

IR (KBr): 3060, 2926, 1767, 1672, 1597, 1491, 1446, 1262, 1025, 756. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56-7.61 (m, 4H), 7.33-7.38 (m, 6H), 7.01 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.01, 131.94, 128.99, 128.82, 128.74, 128.53, 126.45, 121.84, 173.15, 98.03, 86.75, 81.87.

MS (EI) m/z: 77, 101, 126, 150, 176, 202, 284. Anal. Calcd for $C_{16}H_{11}Br$: C, 67.87; H, 3.92. Found: C, 67.54; H, 3.99.

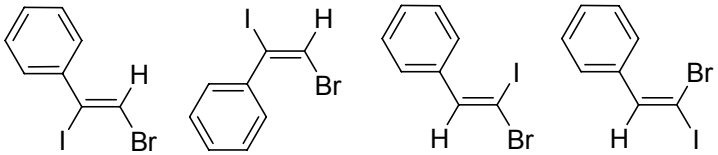


1-((*Z*)-6-(4-fluorophenyl)-3-phenylhexa-3-en-1,5-diynyl)benzene (4a)

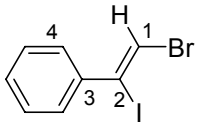
IR (KBr): 3061, 1673, 1610, 1573, 1487, 1449, 1262, 1220, 1104, 799, 756. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71-7.73 (m, 2H), 7.56-7.59 (m, 2H), 7.47-7.50 (m, 2H), 7.32-7.41 (m, 6H), 6.99-7.04 (m, 2H), 6.53 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.9, 161.5, 136.7, 133.5, 133.5, 131.7, 128.9, 128.8, 128.6, 128.5, 126.1, 123.1, 119.6, 119.6, 115.9, 115.6, 113.4, 98.4, 97.3, 88.7, 87.6. MS (EI) m/z: 77, 105, 160, 191, 244, 247, 300, 322. Anal. Calcd for $C_{24}H_{15}F$: C, 89.42; H, 4.69. Found: C, 89.64; H, 4.61.

H. The structure analysis of the products.

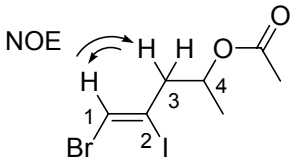
Take the **2a** for example: according to the procedure, the product have four kinds of possible structures, **2a**, **2a-1**, **2a-2** and **2a-3**. The **2a-1**,[1] **2a-2** and **2a-3**[2] are known compounds. In the ^{13}C NMR of **2a-1**, δ = 80.75 (= C-I), 107.14 (= CHBr); In the ^{13}C NMR of **2a-2**, δ = 53.3 (= CBrI), 128.0 (= CH); In the ^{13}C NMR of **2a-3**, δ = 49.9 (= CBrI), 128.3 (= CH); In the ^{13}C NMR of the product, δ =111.3, 116.1. Hence, **2a** is the rational structure.



2a **2a-1** **2a-2** **2a-3**



The HMBC spectra of **2a** also indicates that the vinyl hydrogen has the interactions with the 2-C and 3-C, no interactions with the 4-C, the result proves that the hydrogen atom is on the 1-C.



According to NOE spectra of **2v**, irradiation of the vinyl hydrogen singlet (δ 6.73) produced an enhancement with the hydrogen atom on the 3-C, indicating a cis-relationship between vinyl hydrogen and alkyl group.

The regioselectivity of **2v** was confirmed by HMBC spectra. The HMBC spectra indicates that the vinyl hydrogen has the interactions with the 2-C and 3-C, no interactions with the 4-C, the result proves that the hydrogen atom is on the 1-C.

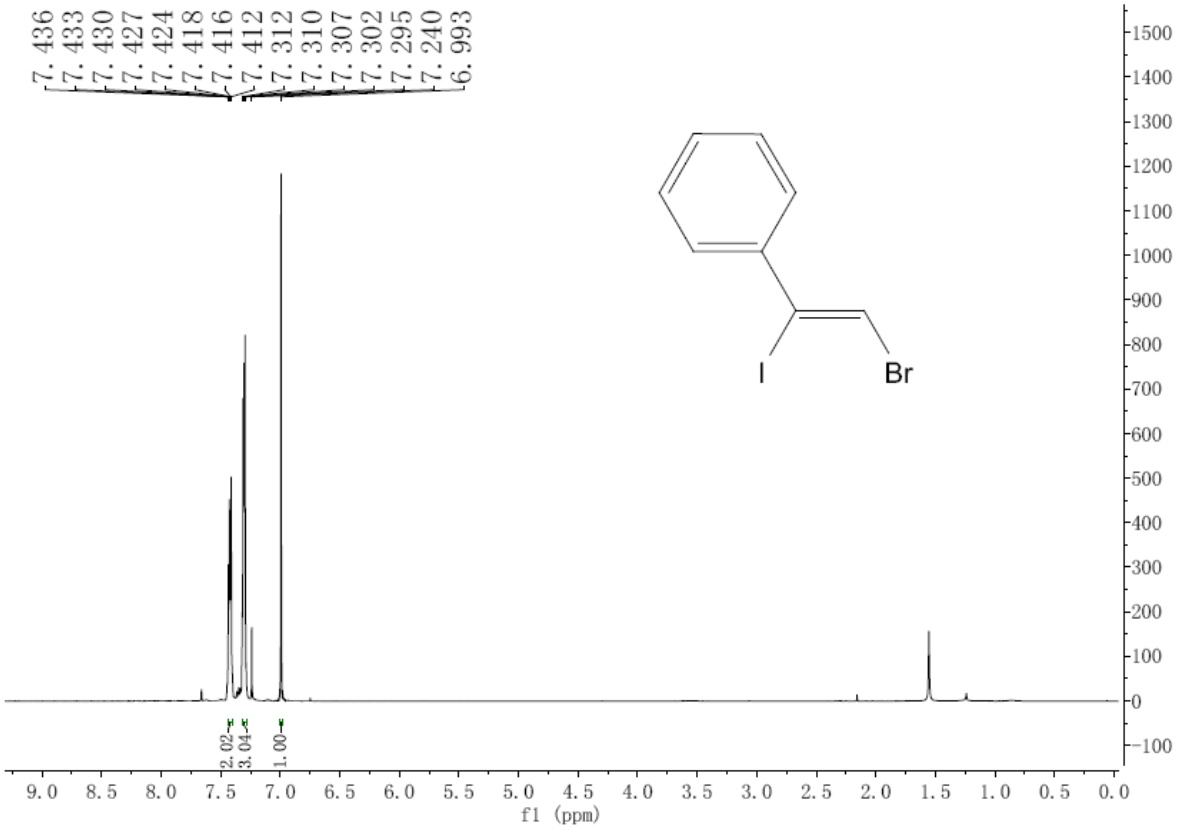
I. Reference

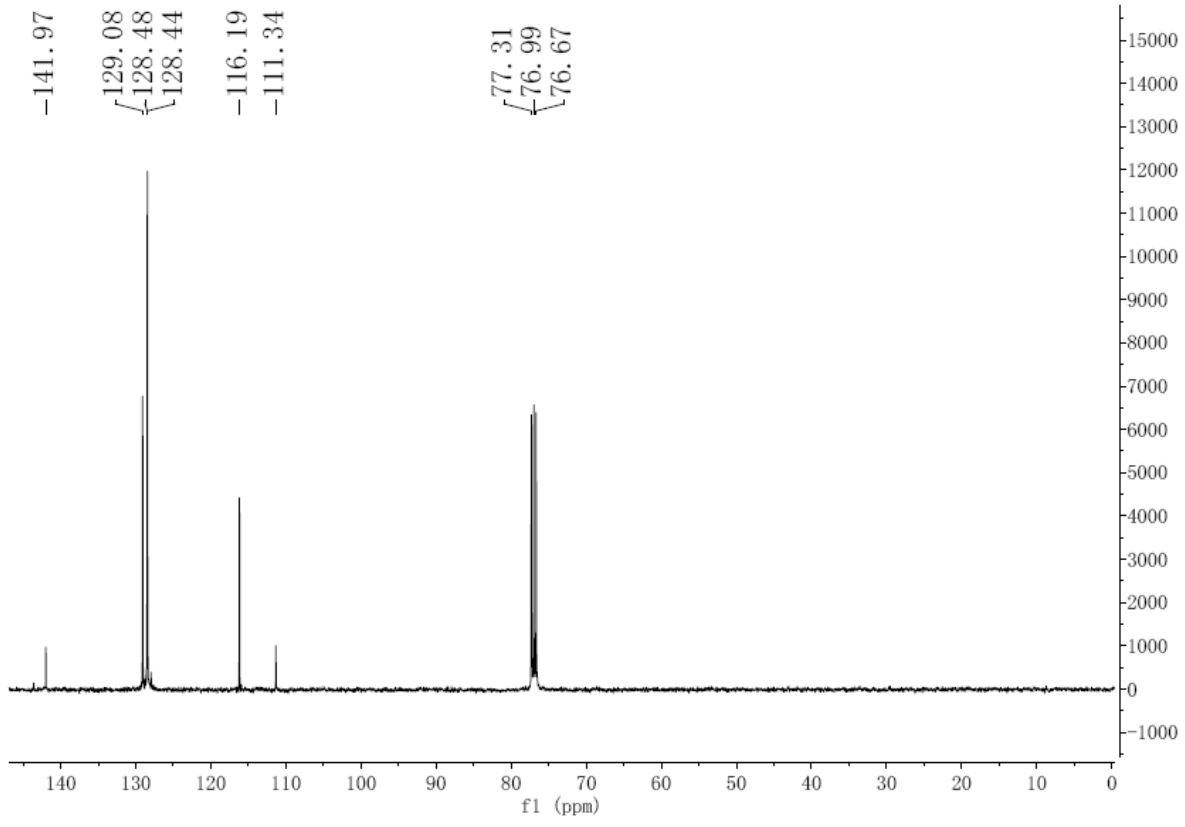
(1) Bortolini, O.; Bottai, M.; Chiappe, C.; Conte, V.; Pieraccini, D. *Green Chem.* **2002**, 621.

(2) Dabdoub, M. J.; Dabdoub, V. B.; Baroni, A. C. M. *J. Am. Chem. Soc.* **2001,** *123,* 9694.

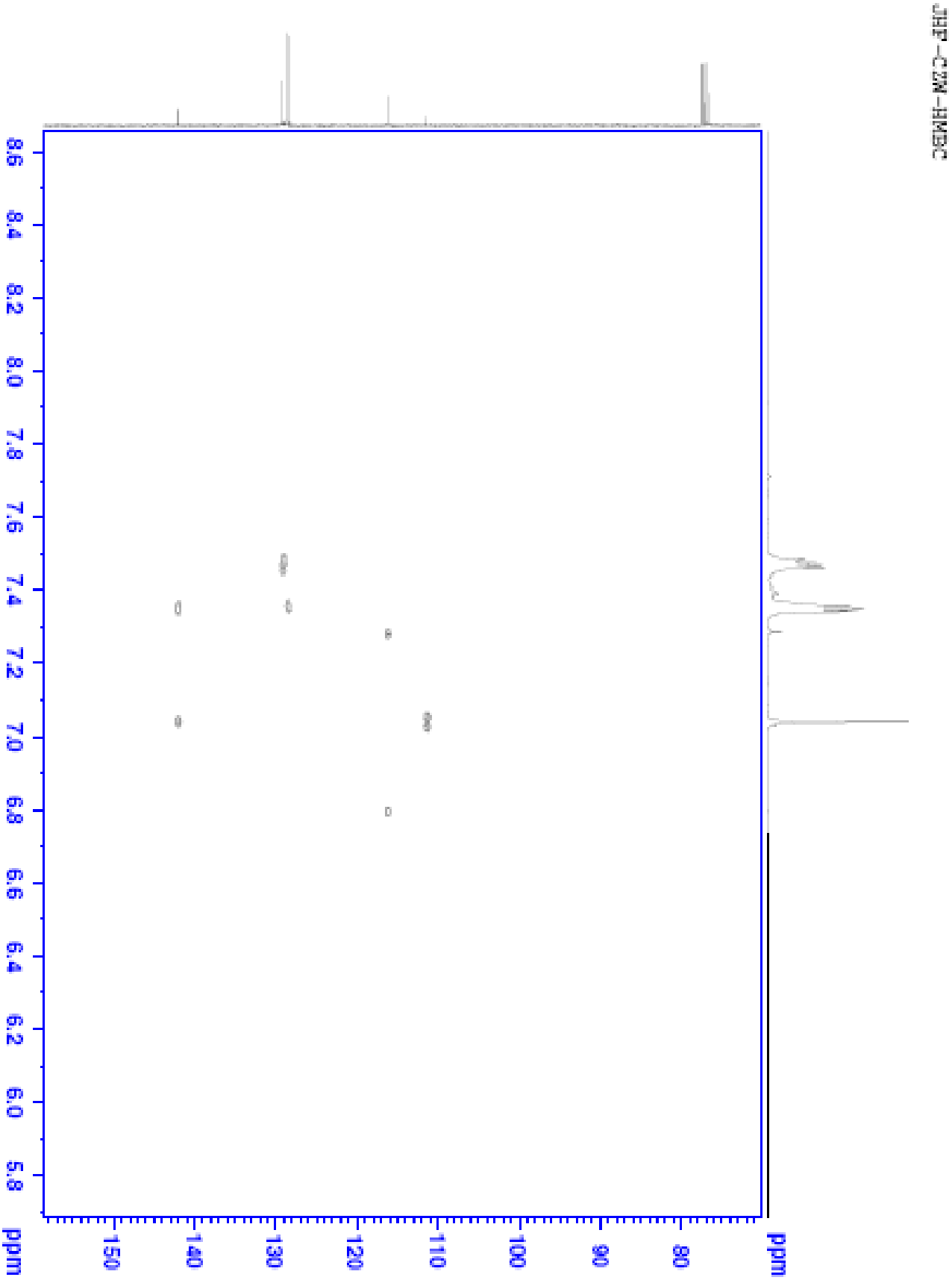
J. NMR Spectra

^{1}H NMR and ^{13}C NMR of 1-((*Z*)-2-bromo-1-iodovinyl)benzene (2a)

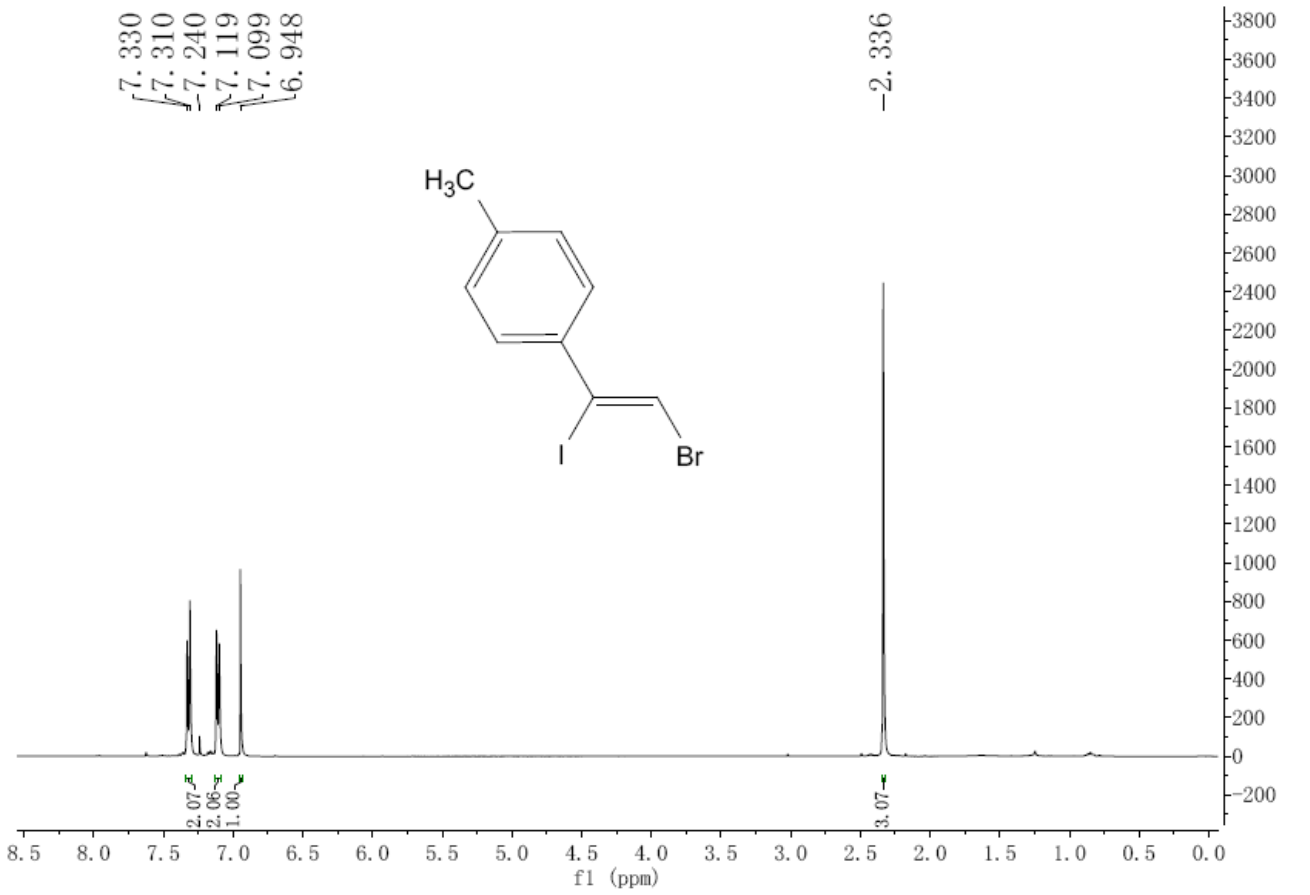


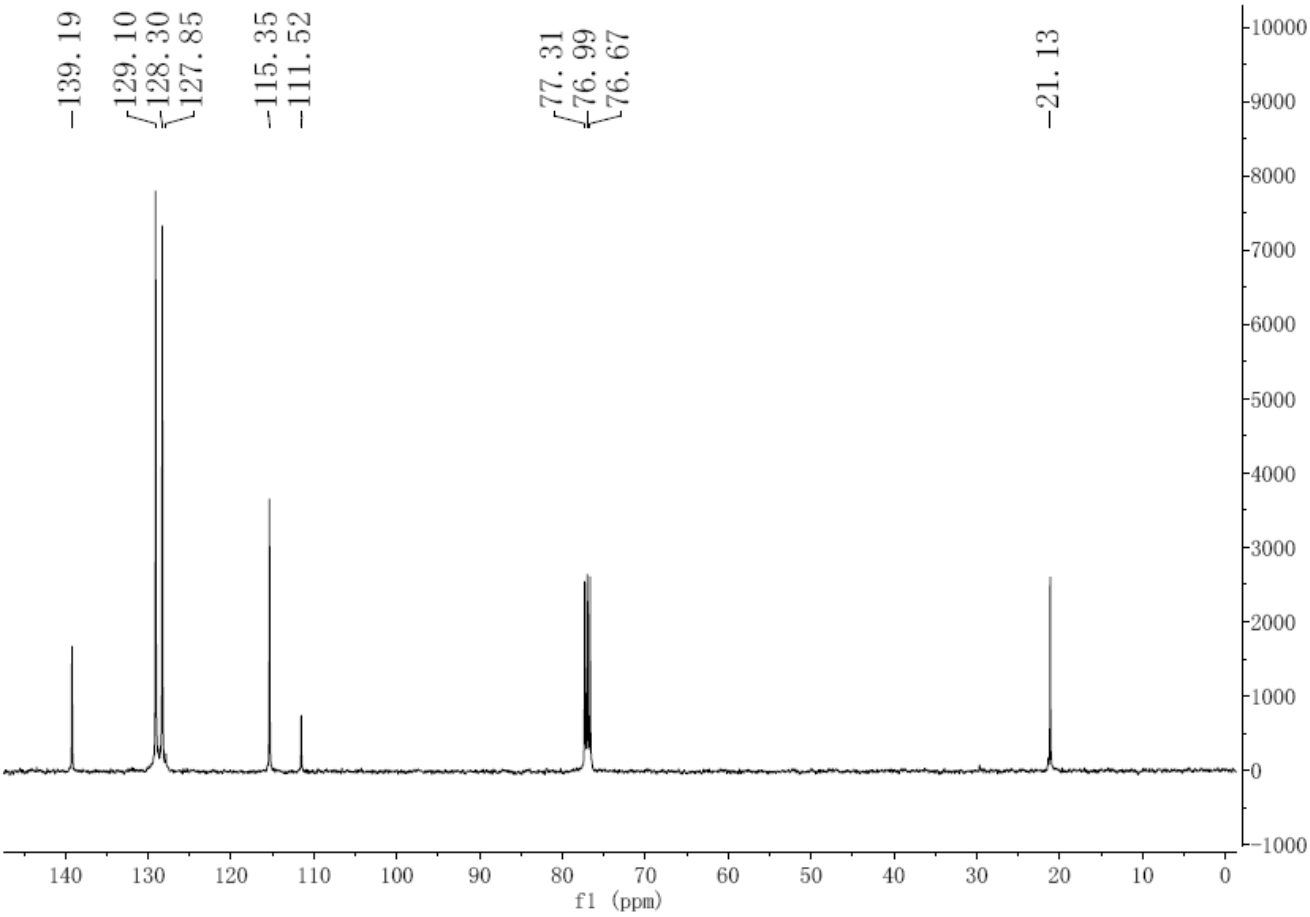


HMBC spectra of 1-((*Z*)-2-bromo-1-iodovinyl)benzene (2a)

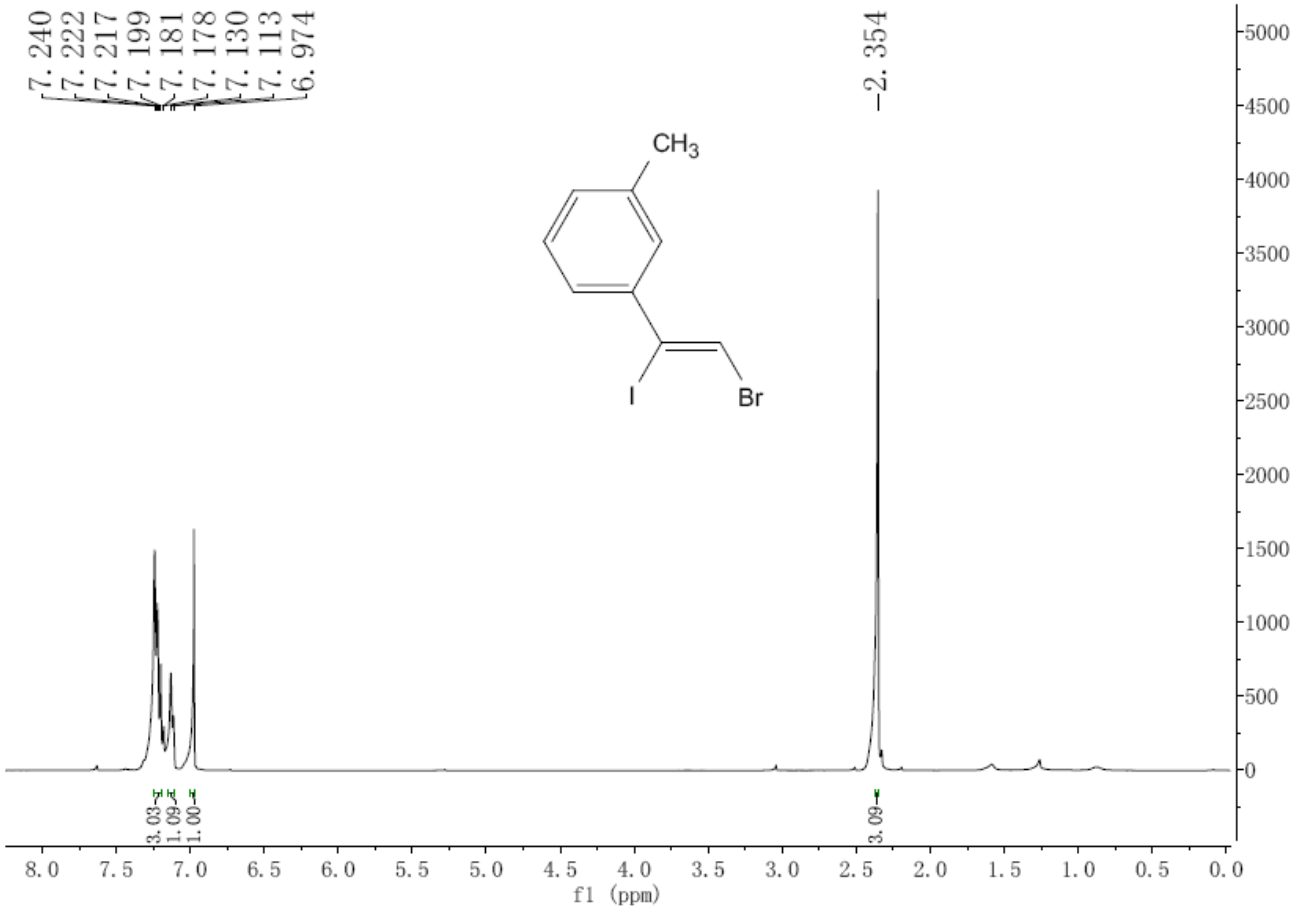


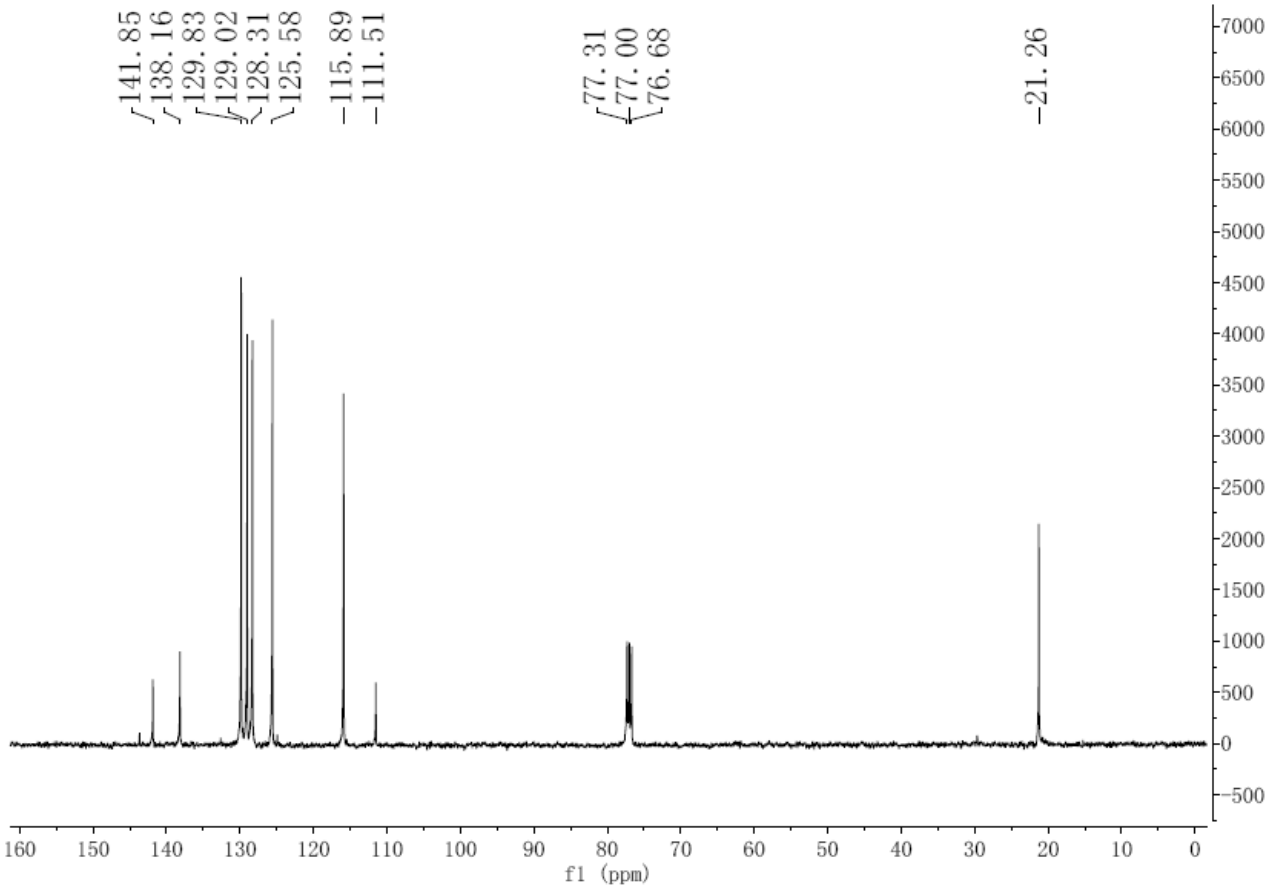
^{1}H NMR and ^{13}C NMR of 1-((*Z*)-2-bromo-1-iodovinyl)-4-methylbenzene (2b)



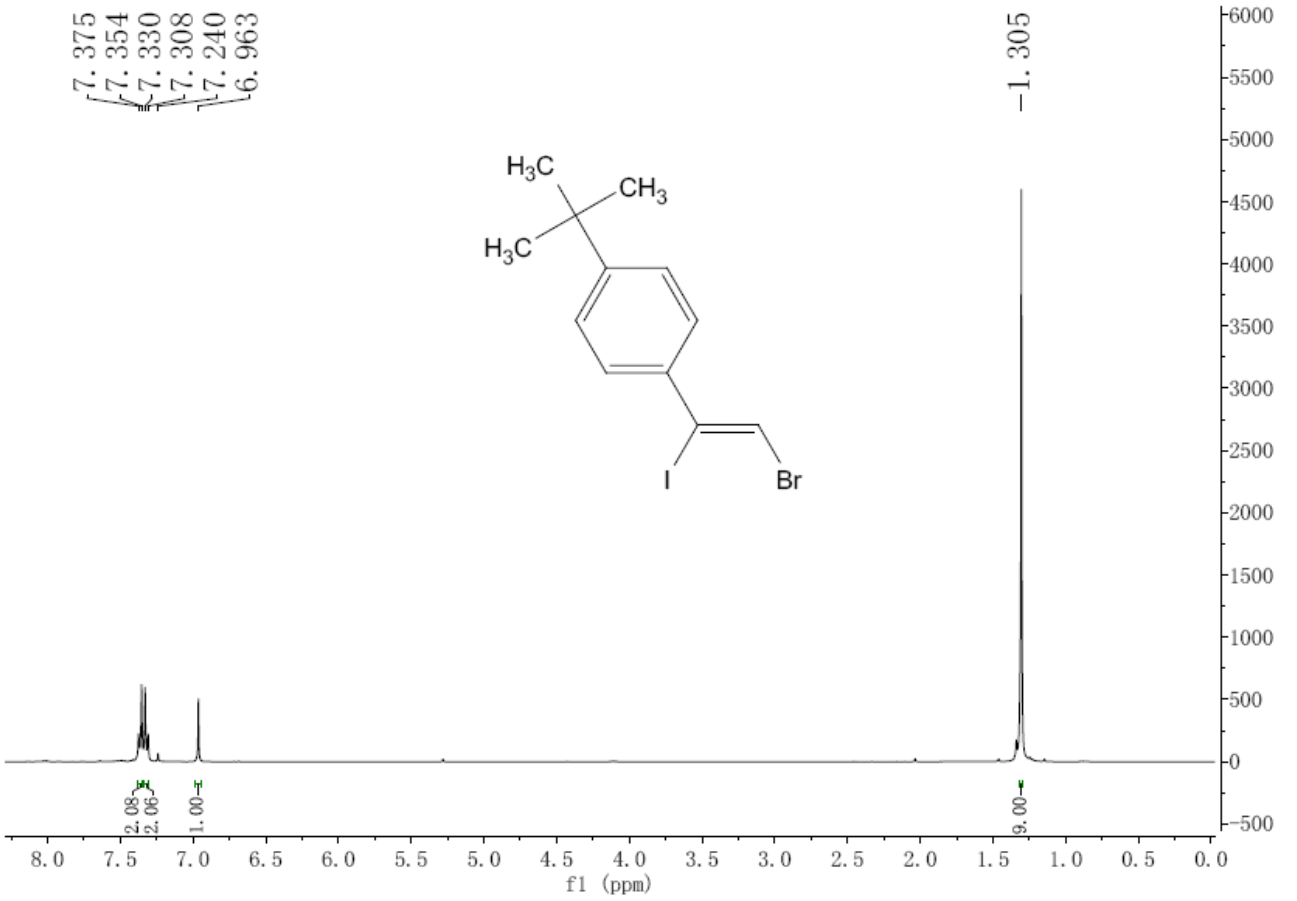


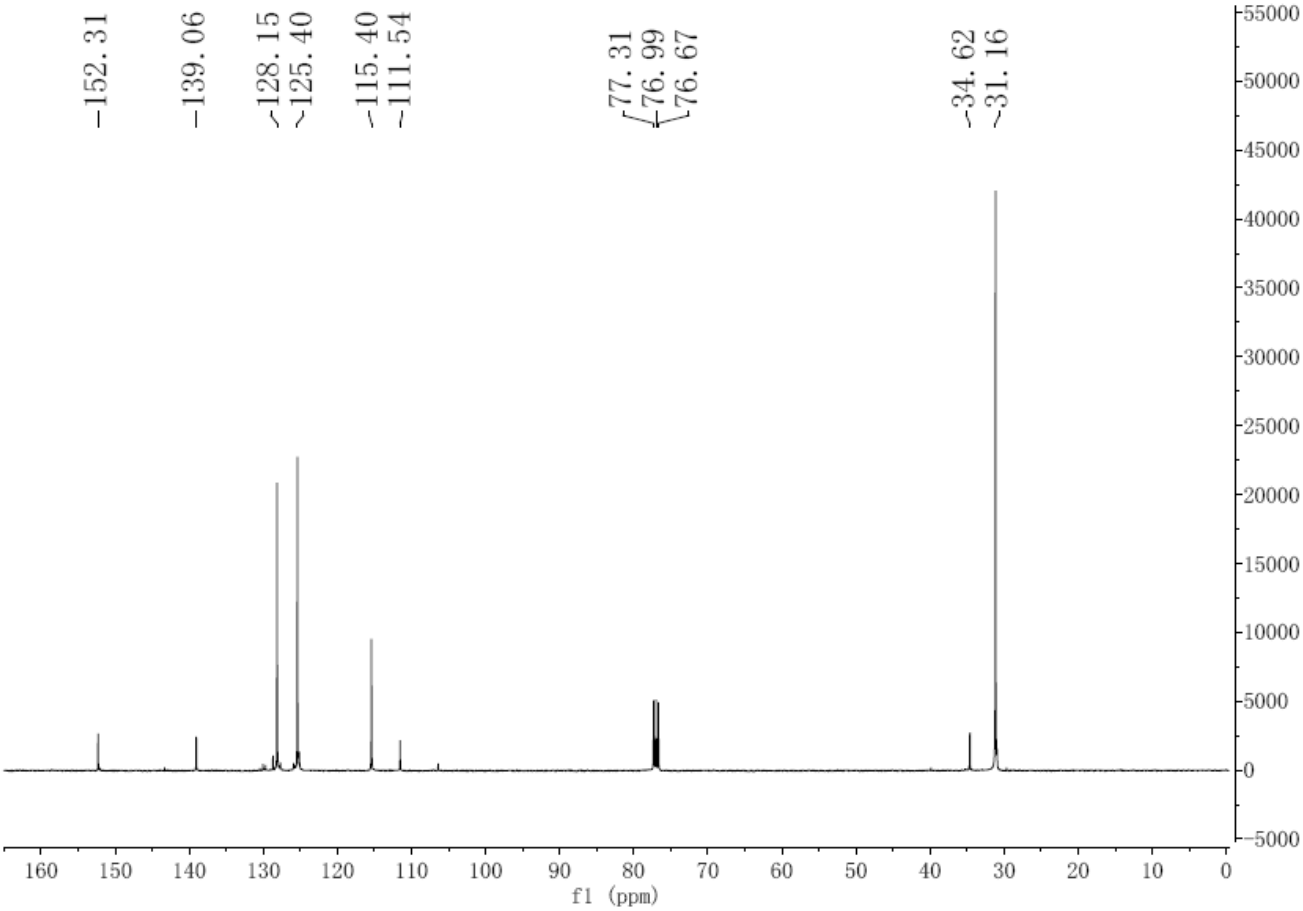
^{1}H NMR and ^{13}C NMR of 1-((*Z*)-2-bromo-1-iodovinyl)-3-methylbenzene (2c)



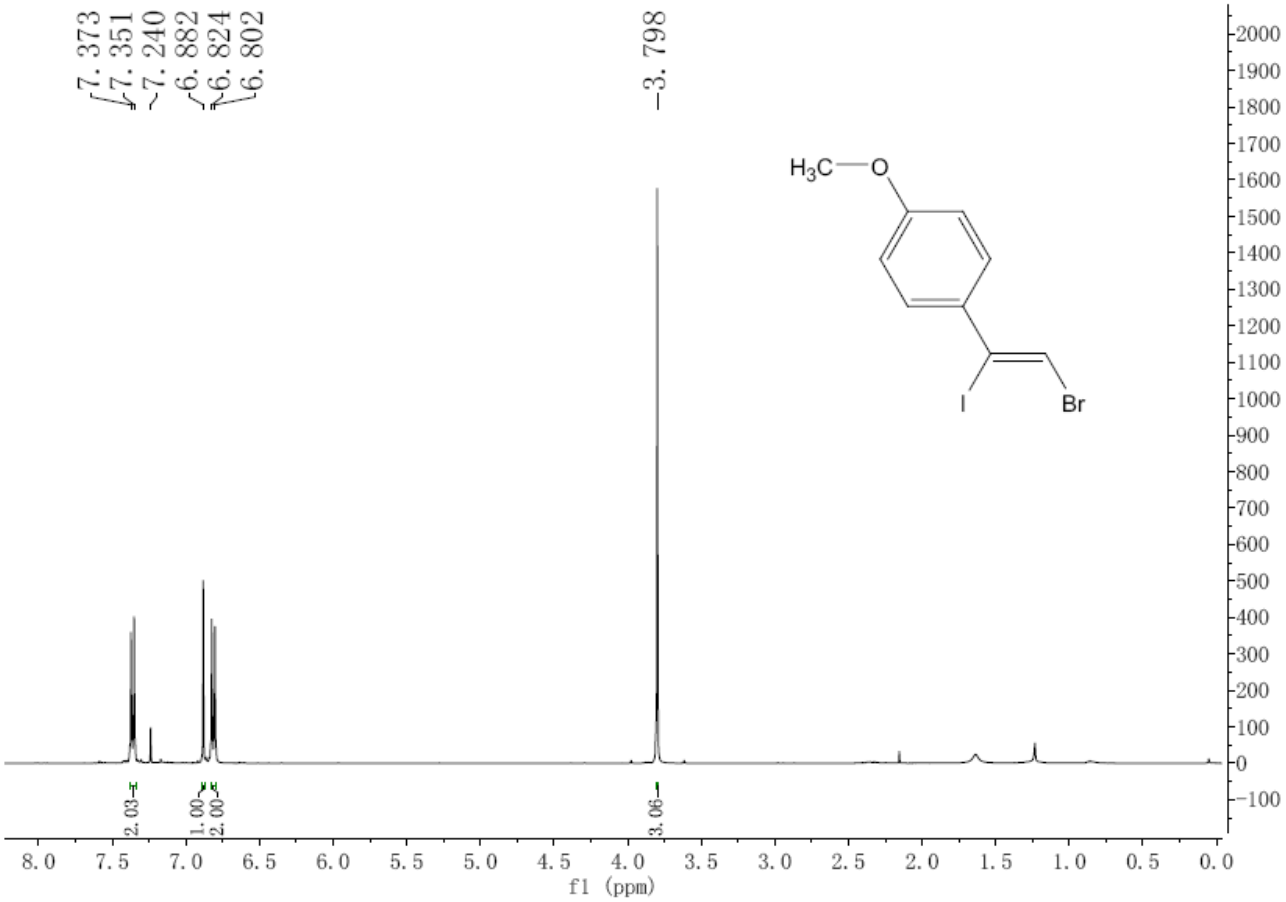


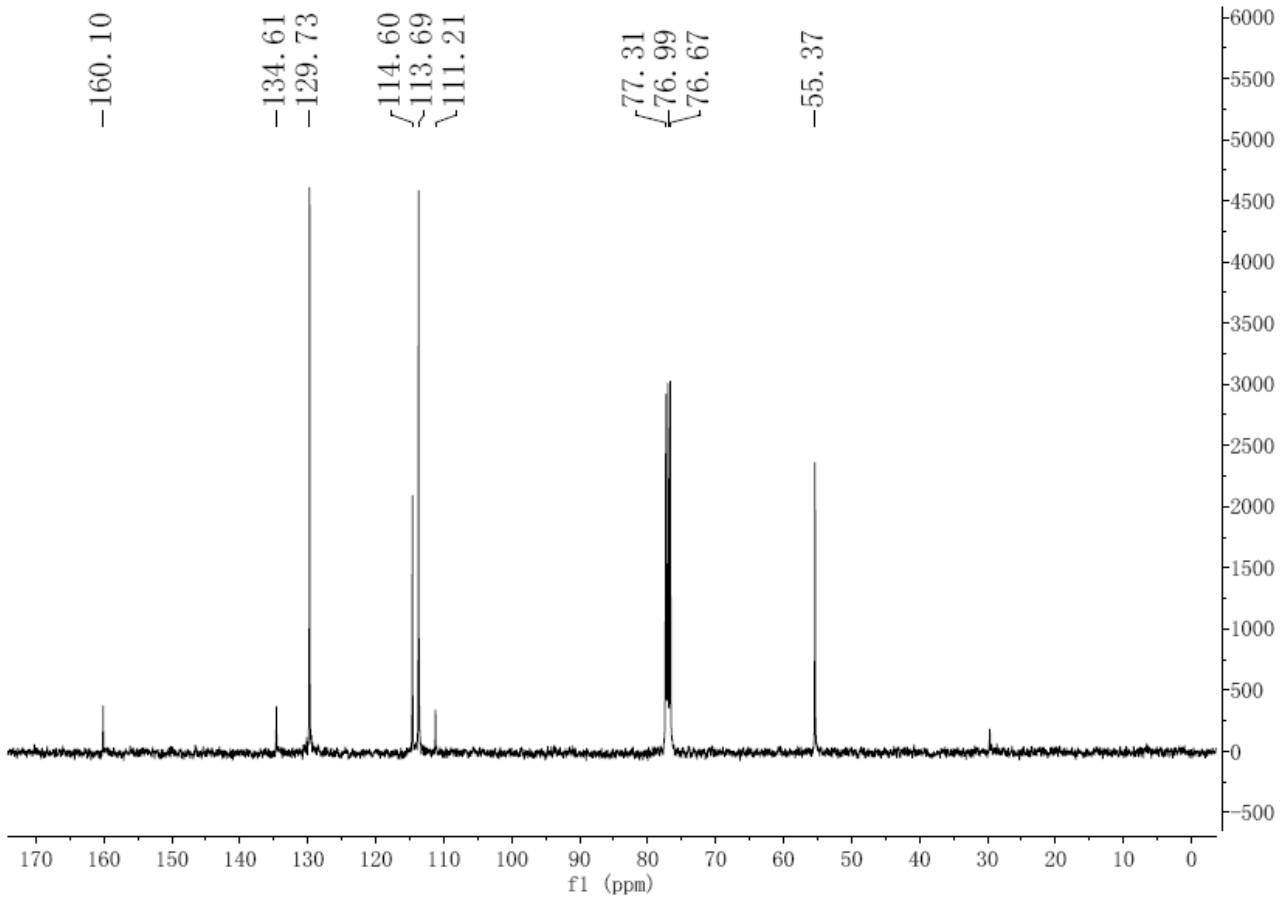
^{1}H NMR and ^{13}C NMR of 1-*tert*-butyl-4-((*Z*)-2-bromo-1-iodovinyl)benzene (2d)



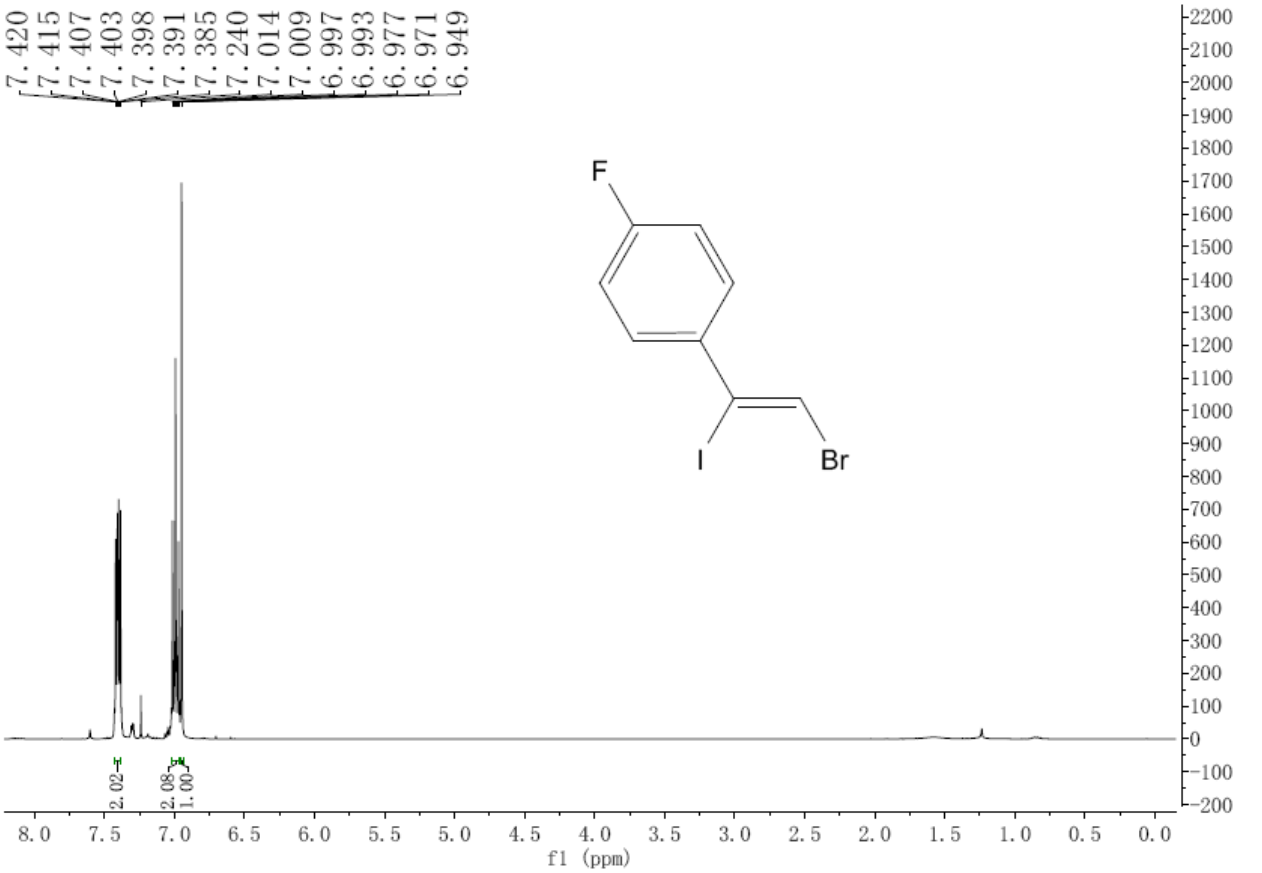


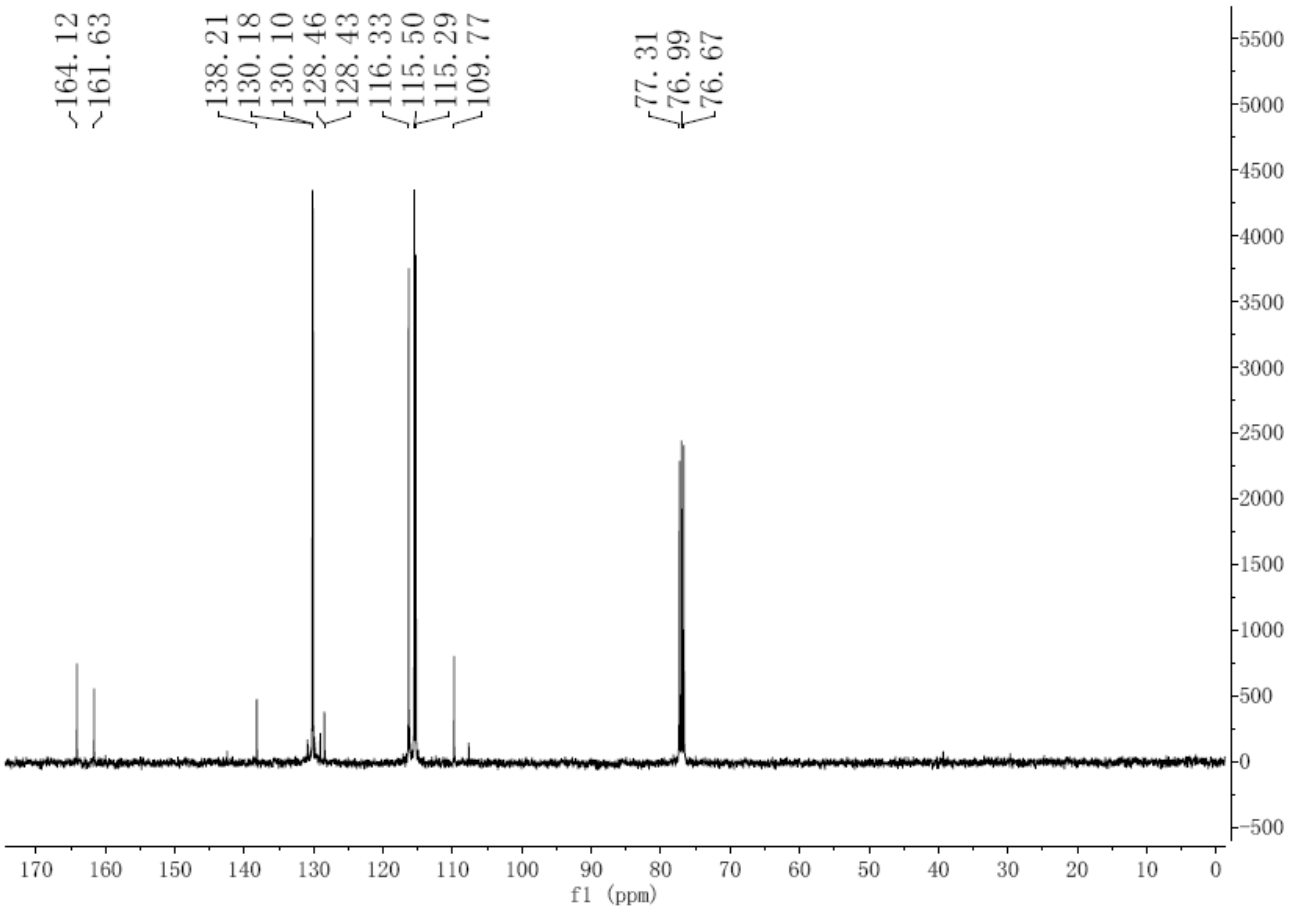
^{1}H NMR and ^{13}C NMR of 1-((*Z*)-2-bromo-1-iodovinyl)-4-methoxybenzene (2e)



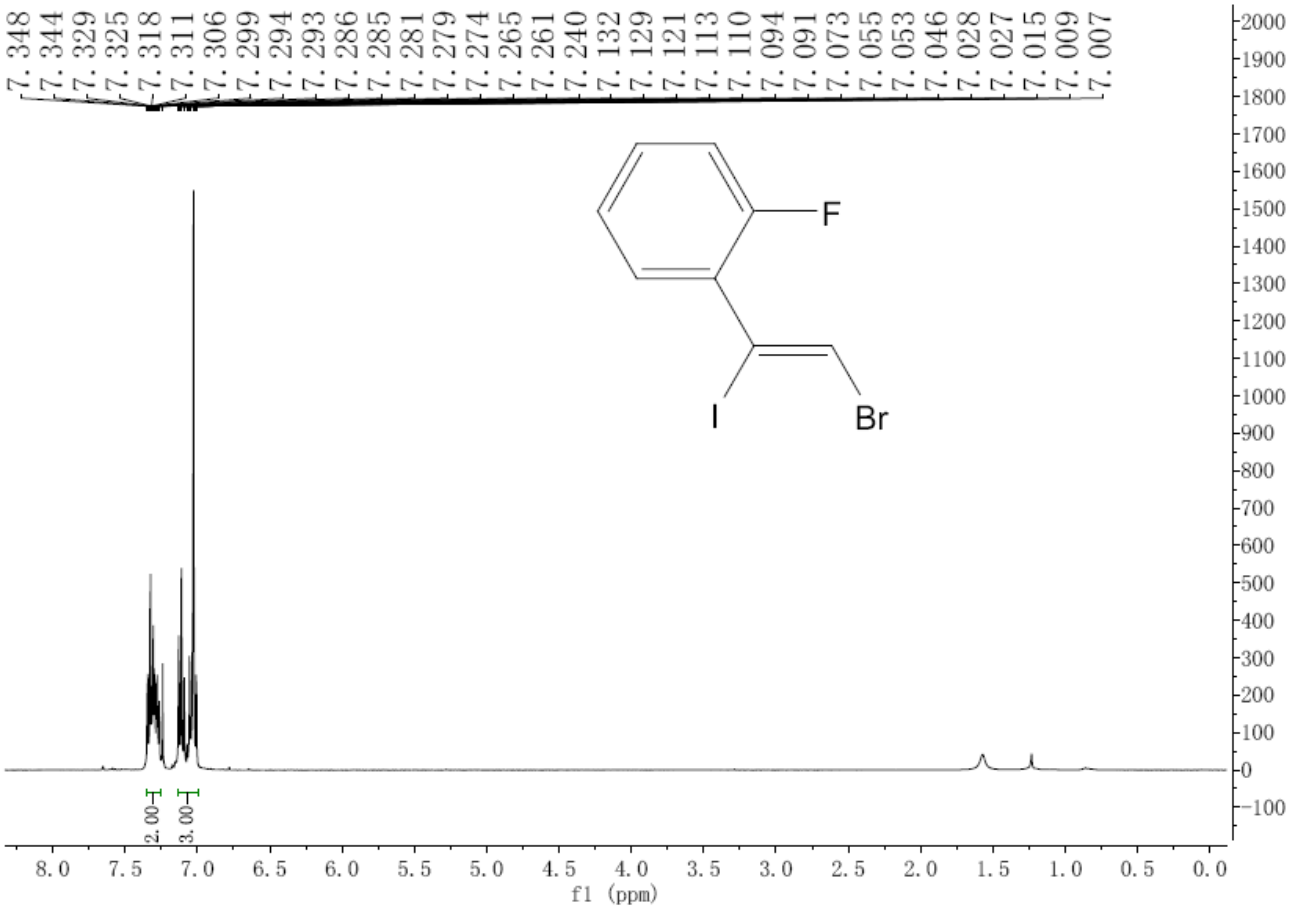


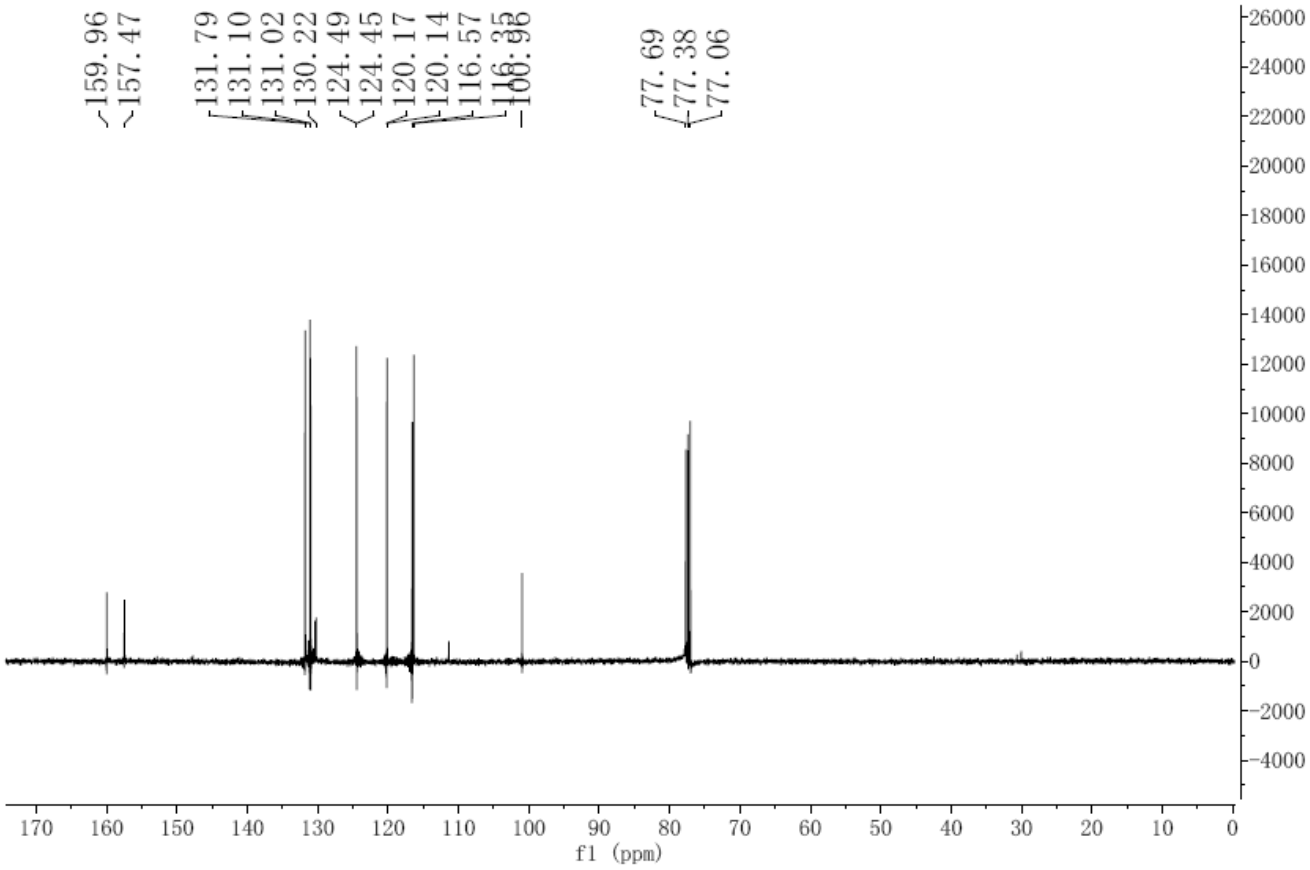
^{1}H NMR and ^{13}C NMR of 1-((*Z*)-2-bromo-1-iodovinyl)-4-fluorobenzene (2f)



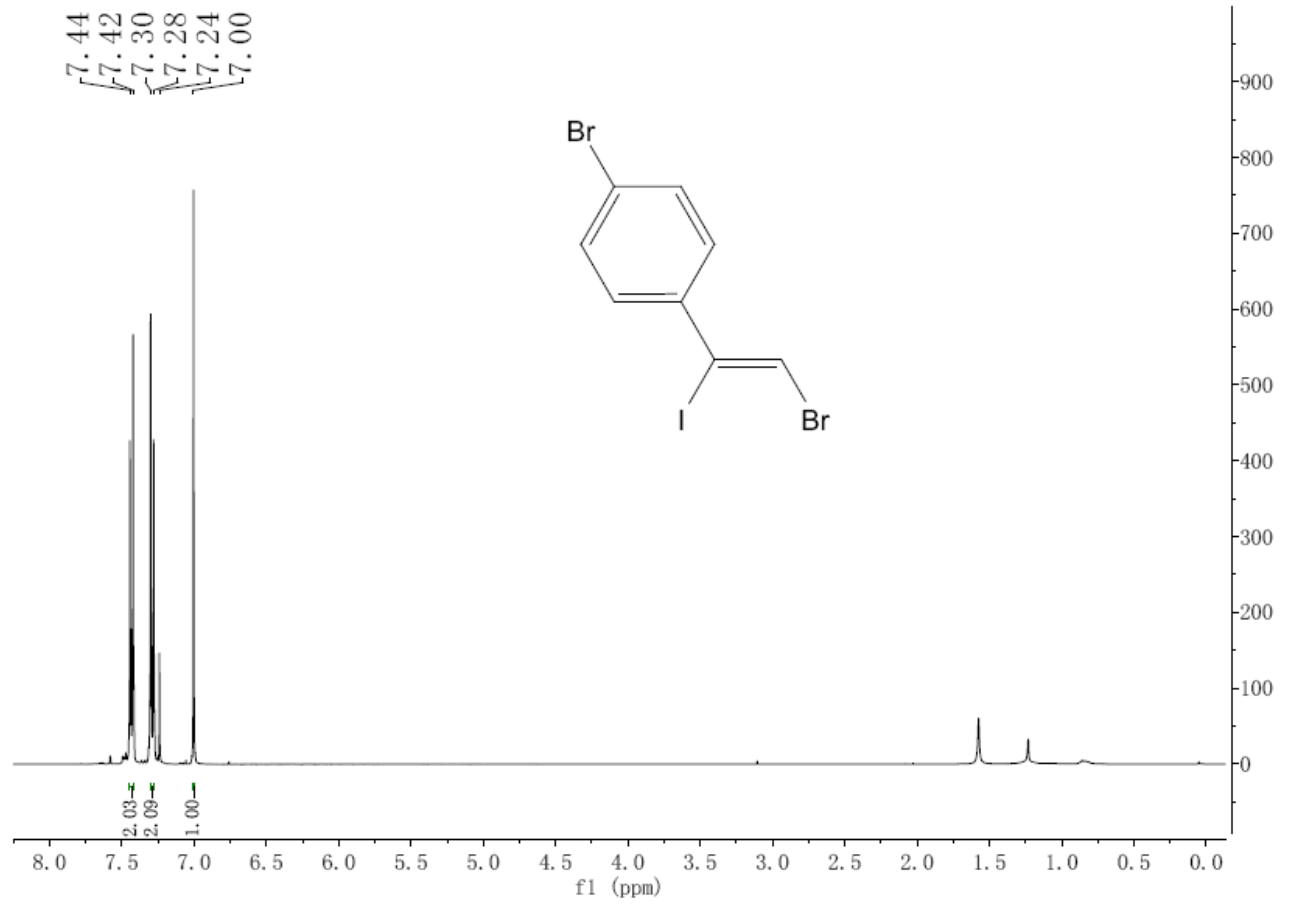


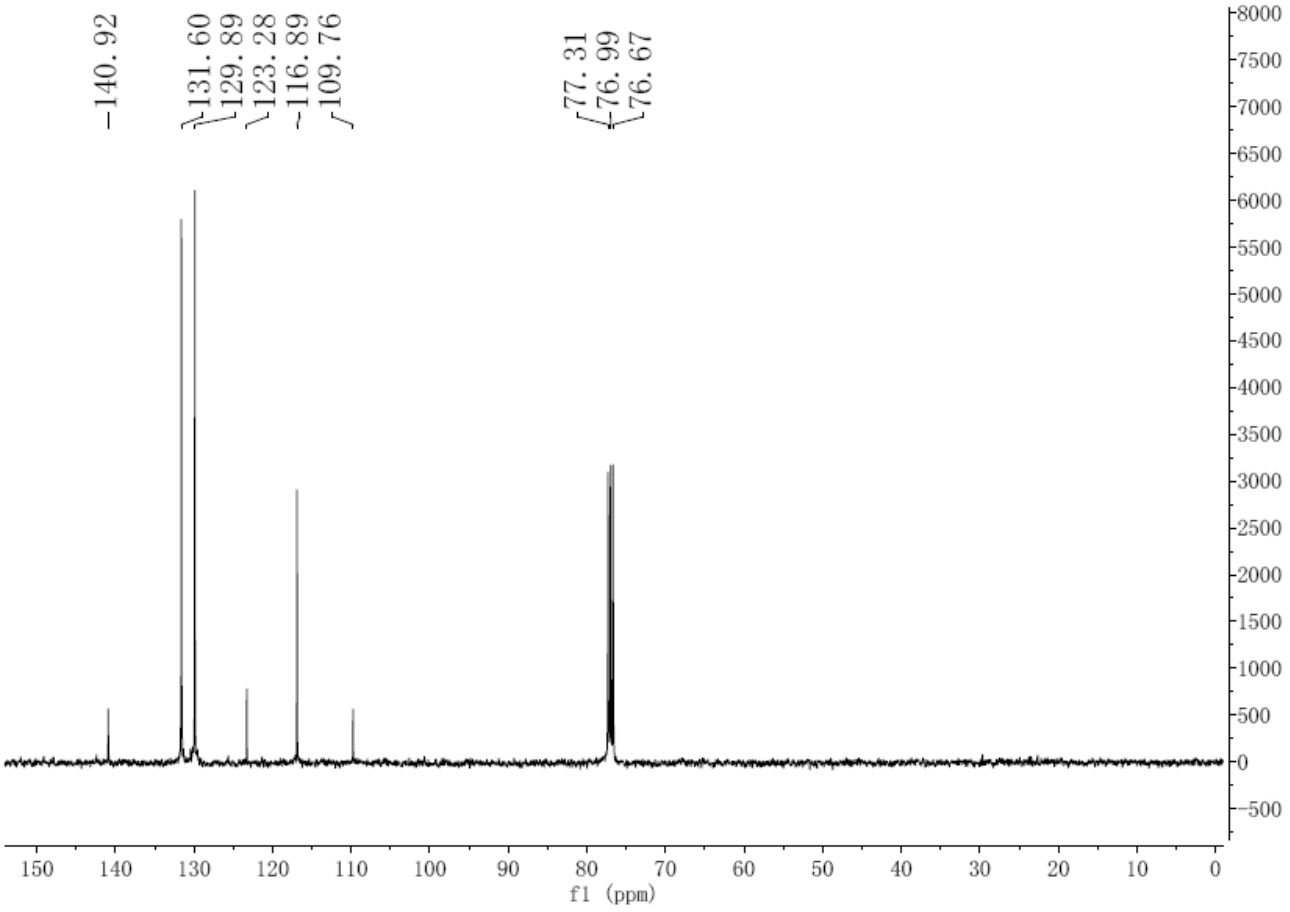
^{1}H NMR and ^{13}C NMR of 1-((*Z*)-2-bromo-1-iodovinyl)-2-fluorobenzene (2g)



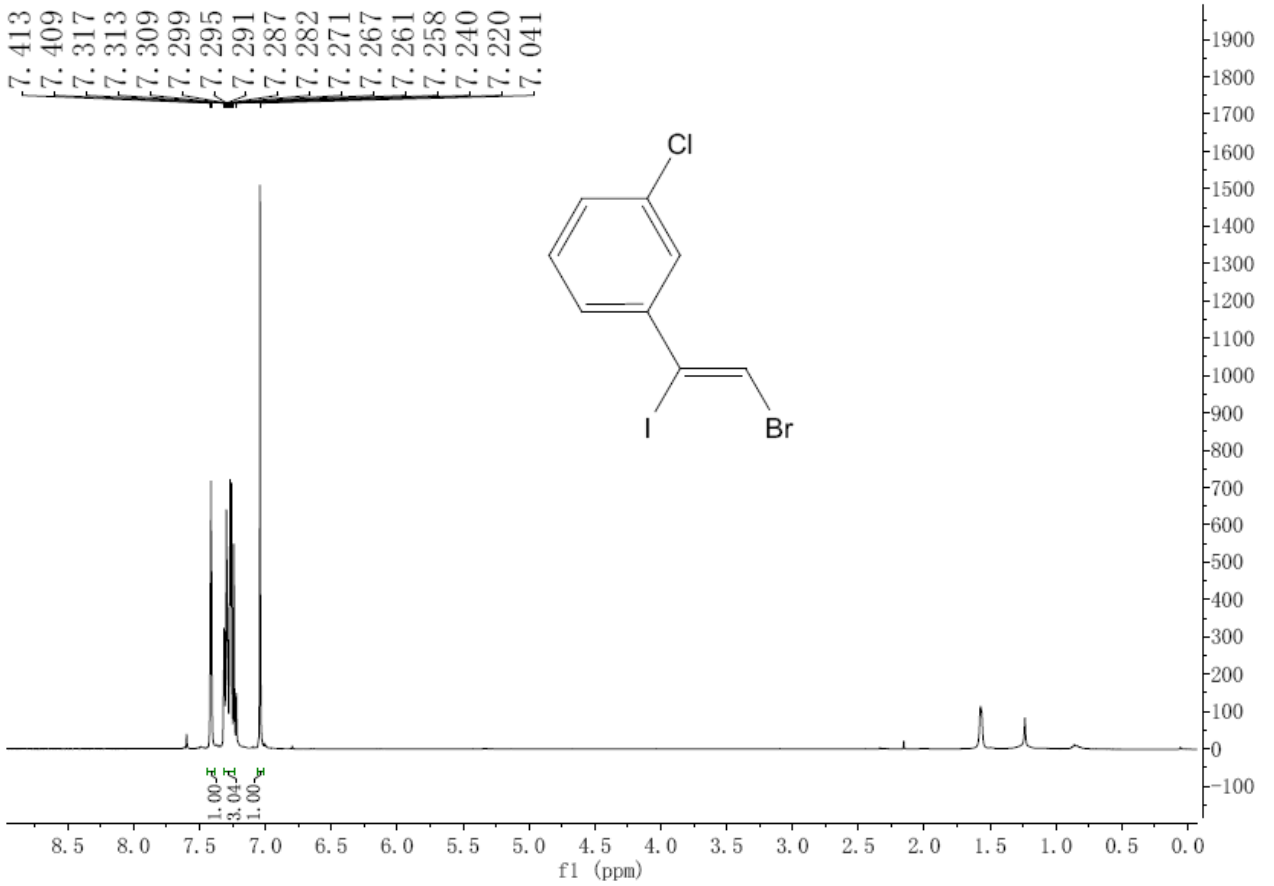


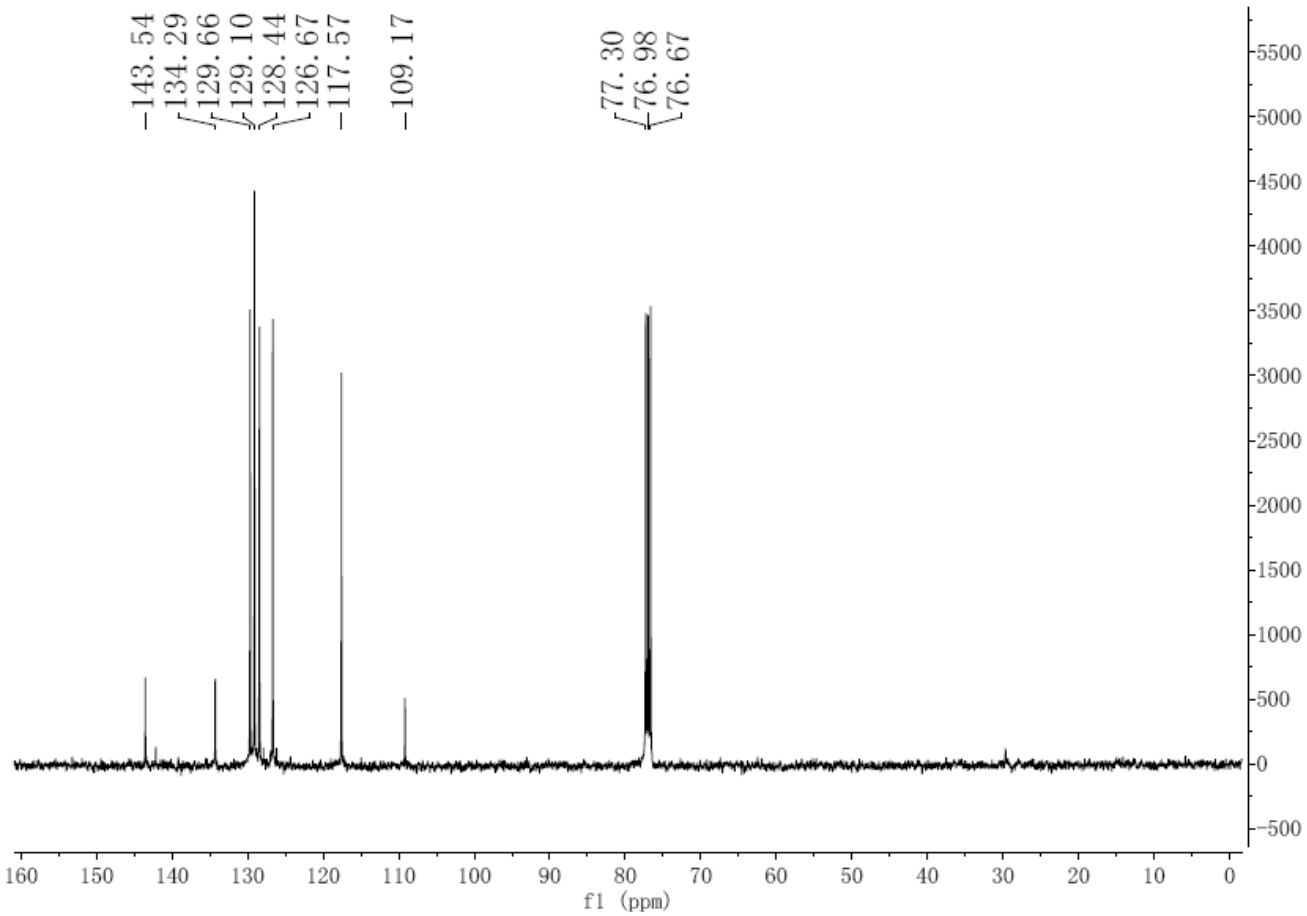
^{1}H NMR and ^{13}C NMR of 1-bromo-4-((*Z*)-2-bromo-1-iodovinyl)benzene (2h)



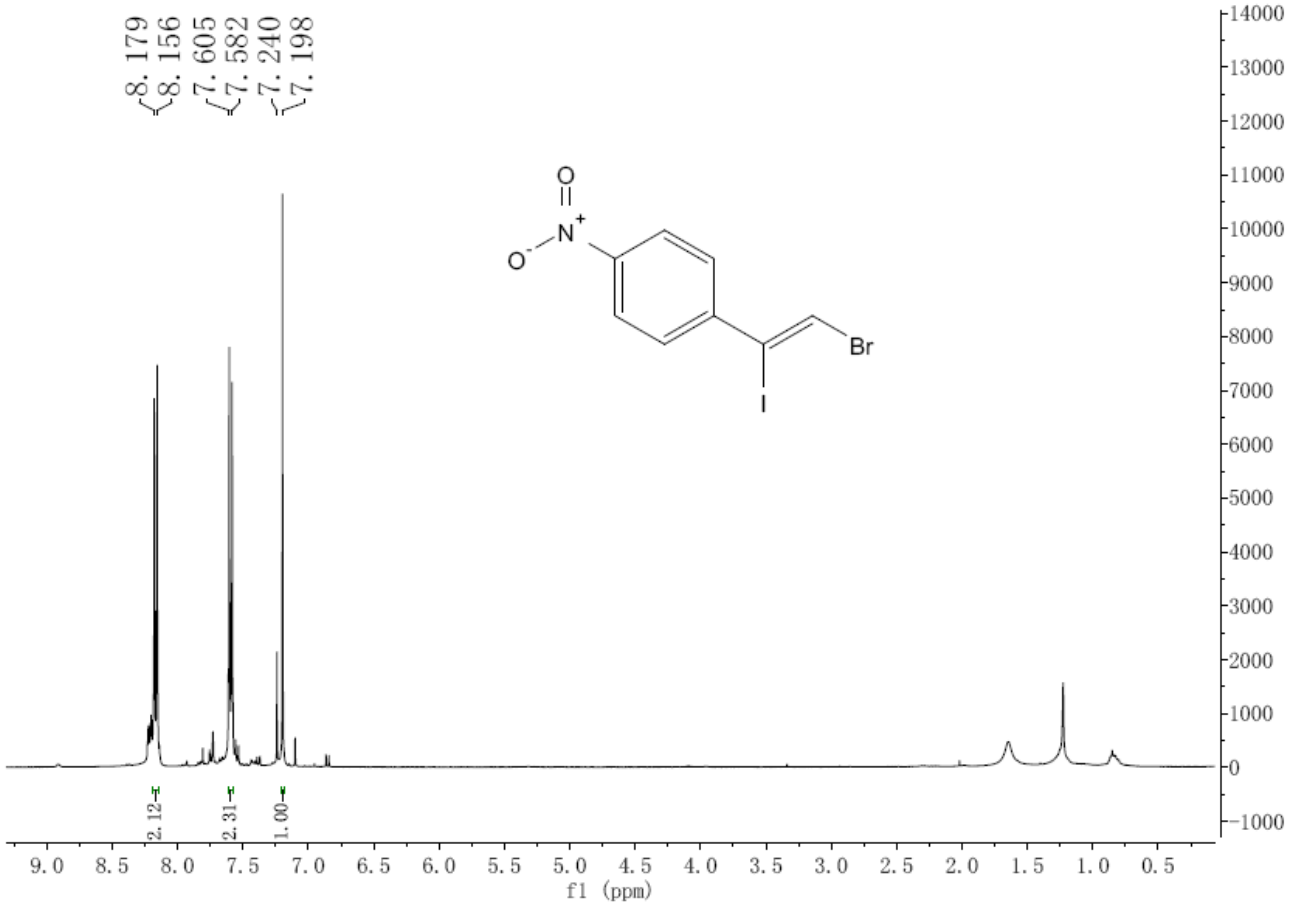


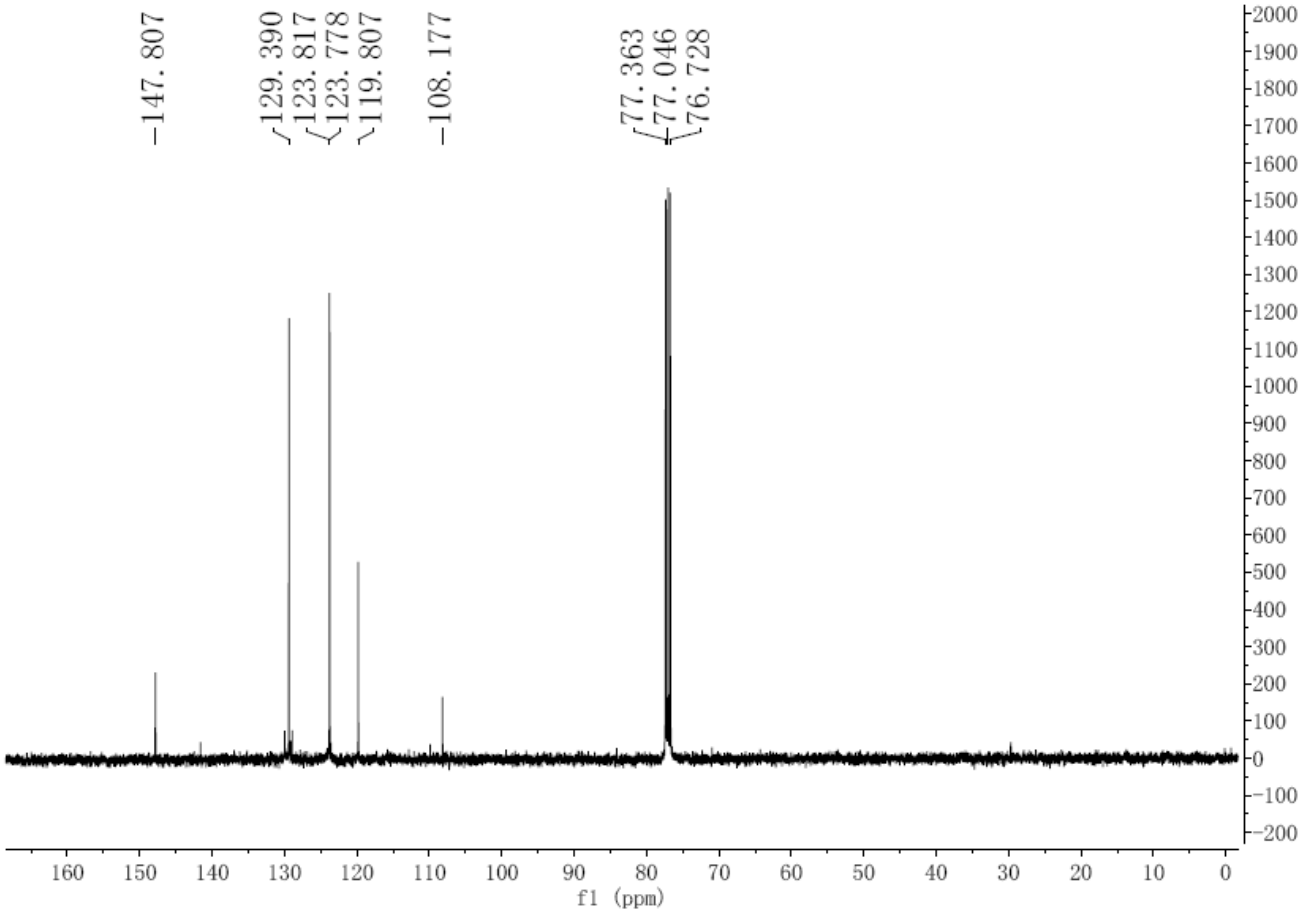
^{1}H NMR and ^{13}C NMR of 1-((*Z*)-2-bromo-1-iodovinyl)-3-chlorobenzene (2i)



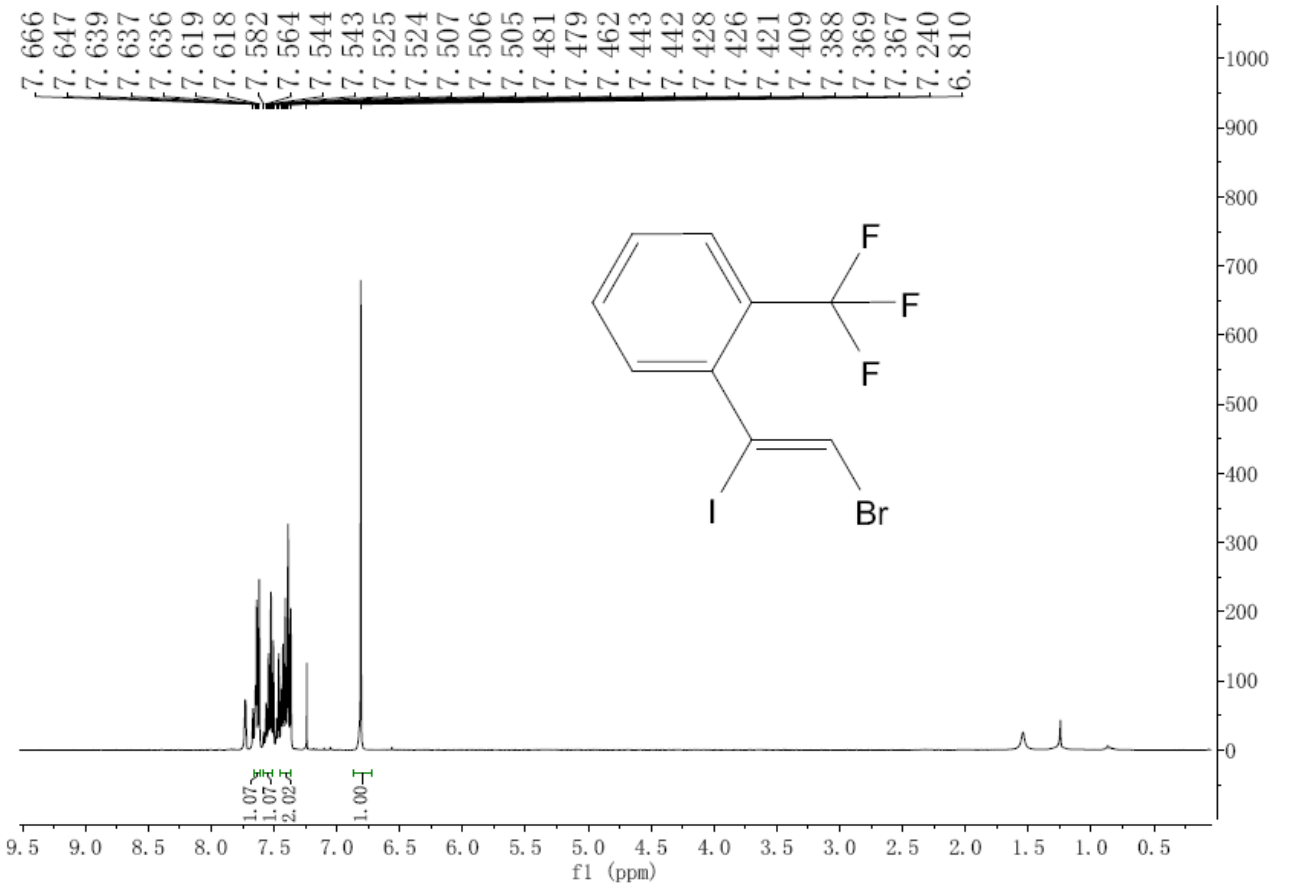


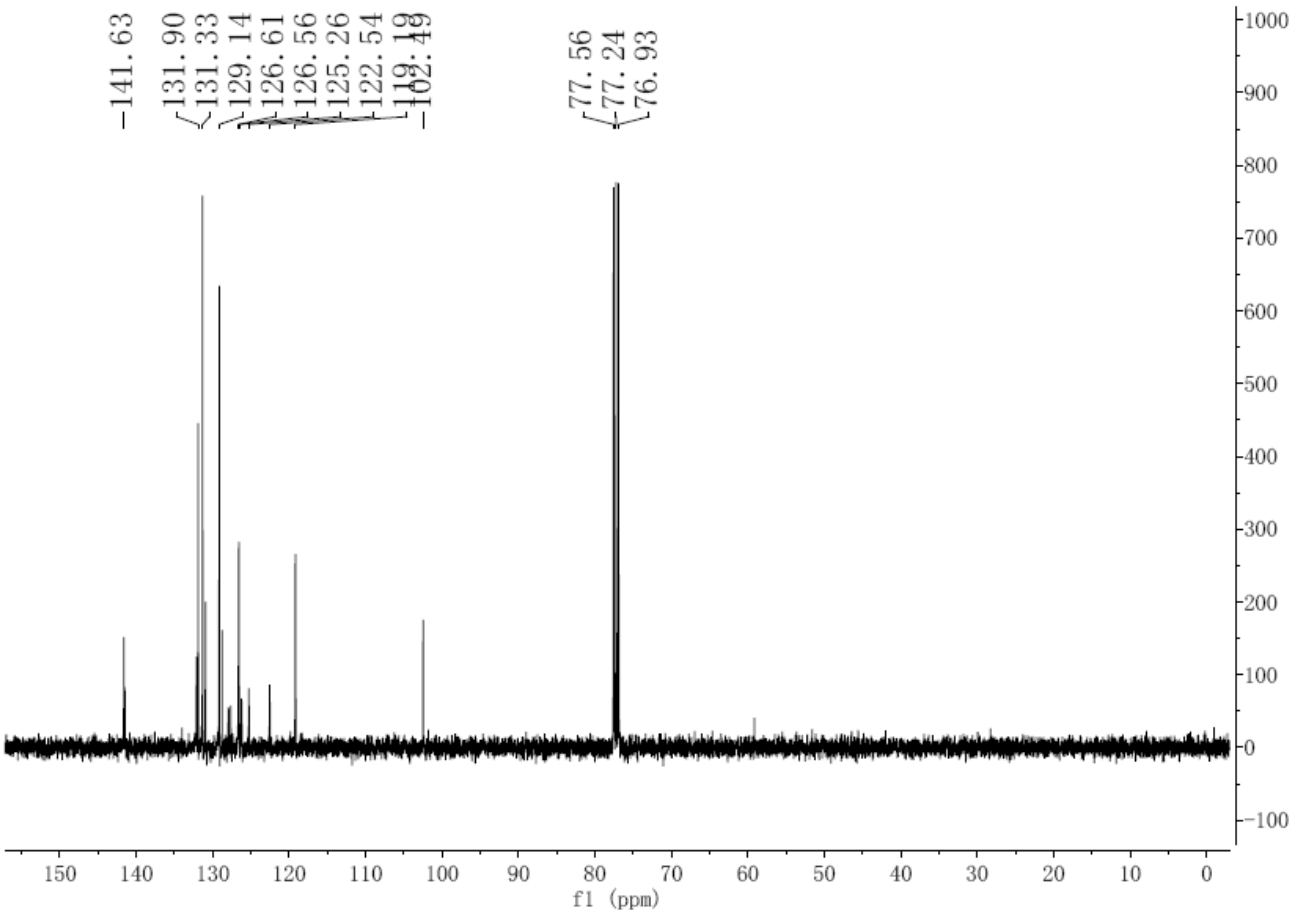
^{1}H NMR and ^{13}C NMR of 1-((Z)-2-bromo-1-iodovinyl)-4-nitrobenzene (2j)



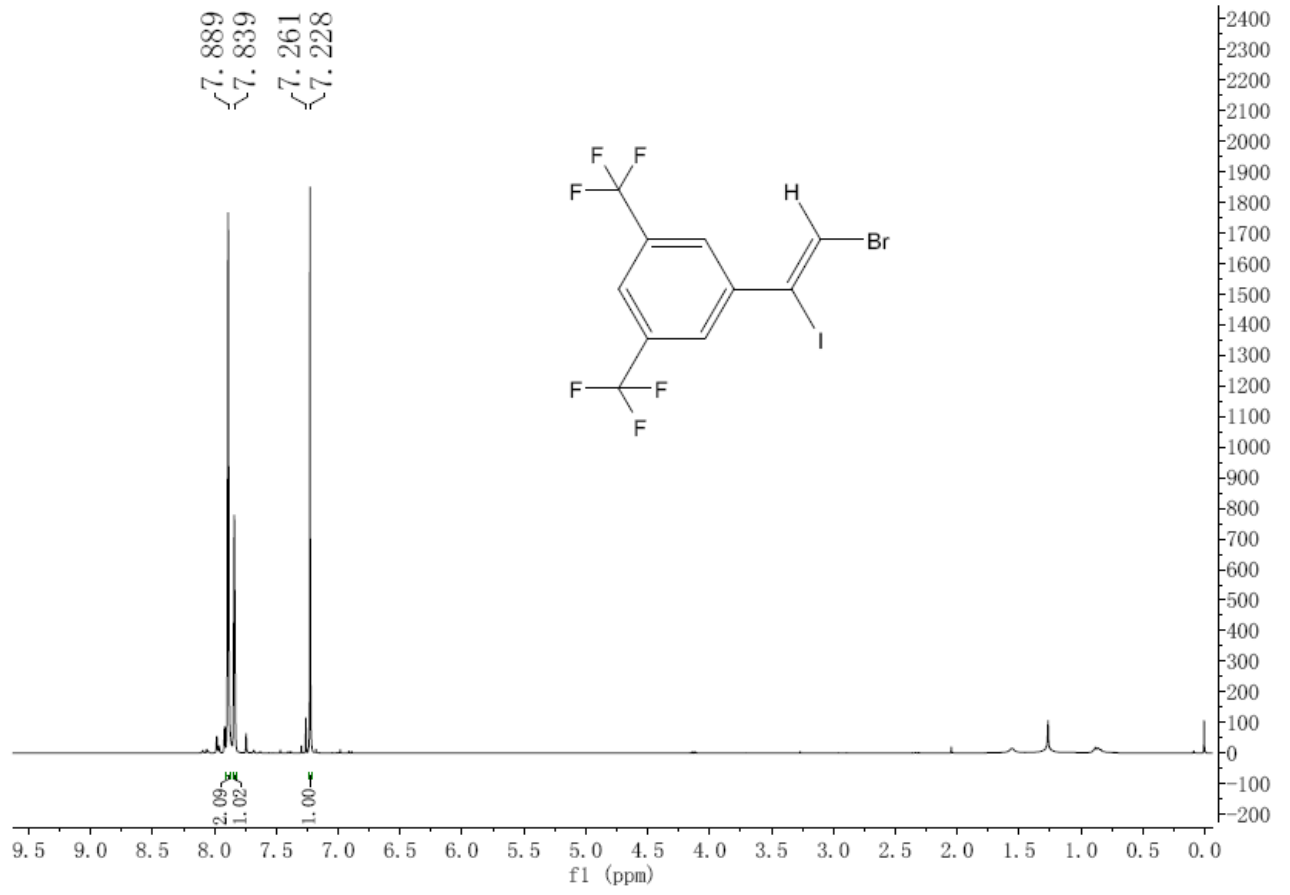


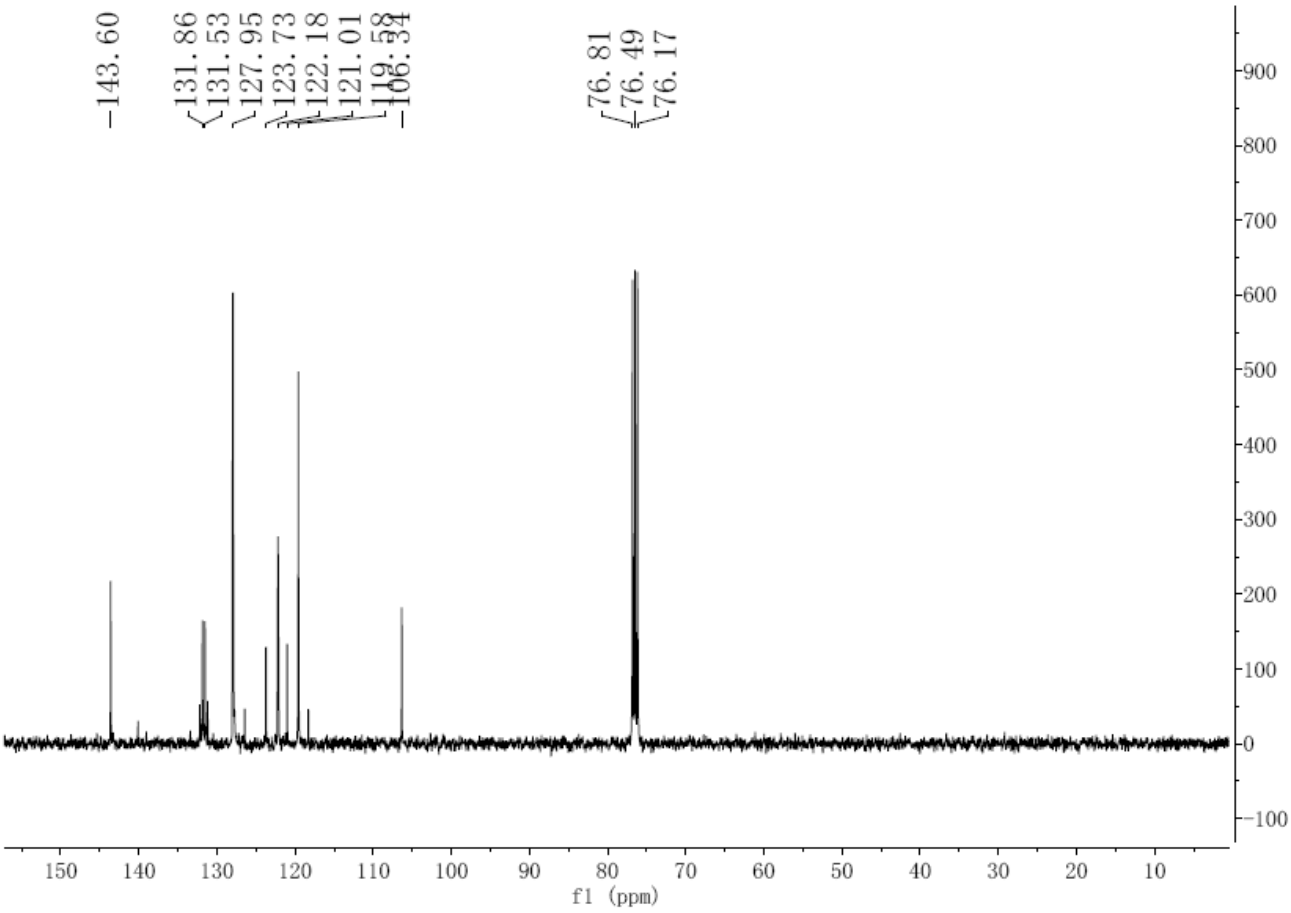
^{1}H NMR and ^{13}C NMR of 1-((*Z*)-2-bromo-1-iodovinyl)-2-(trifluoromethyl)benzene (2k)



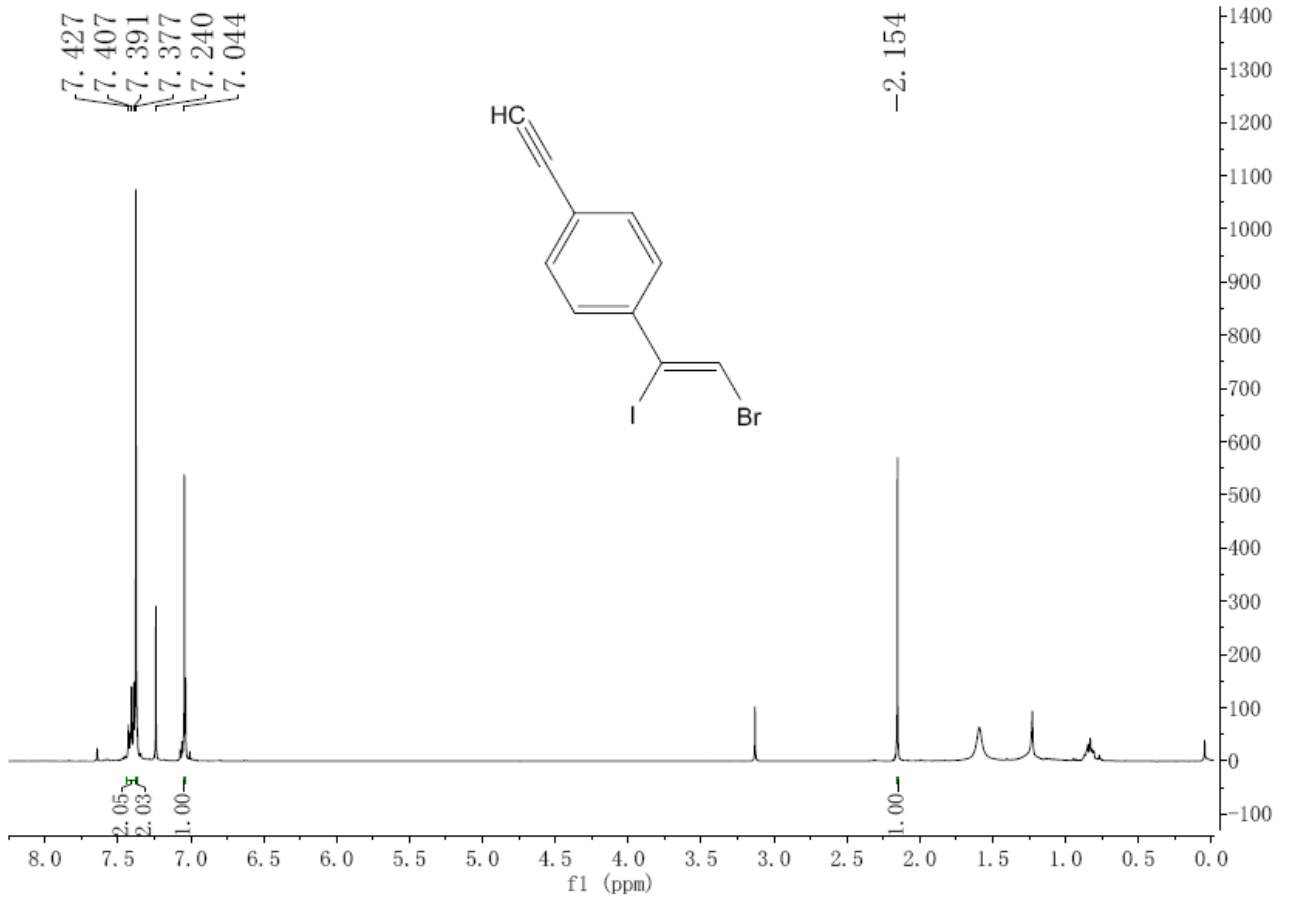


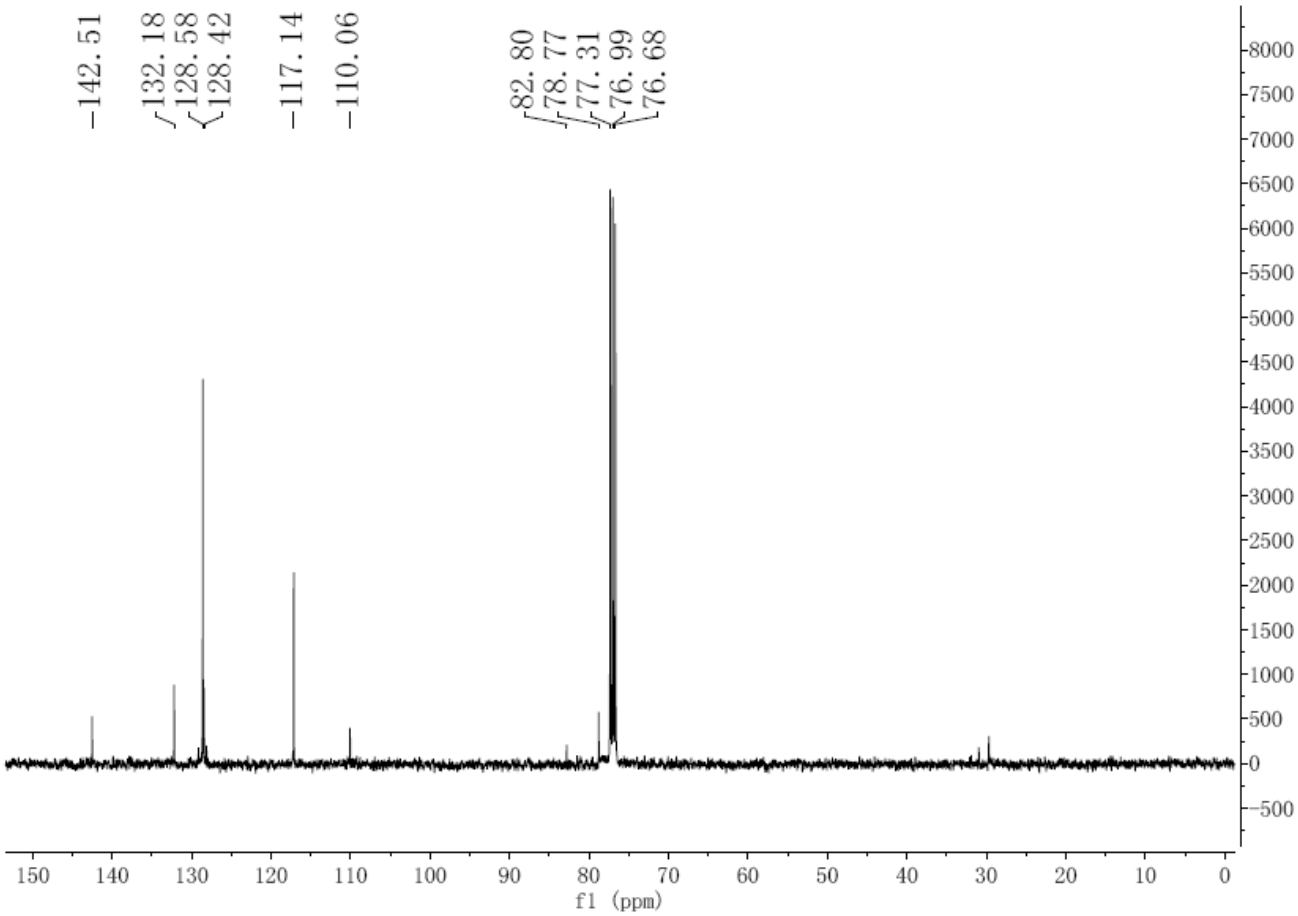
^{1}H NMR and ^{13}C NMR of 1-((*Z*)-2-bromo-1-iodovinyl)-3,5-bis(trifluoromethyl)benzene (2l)



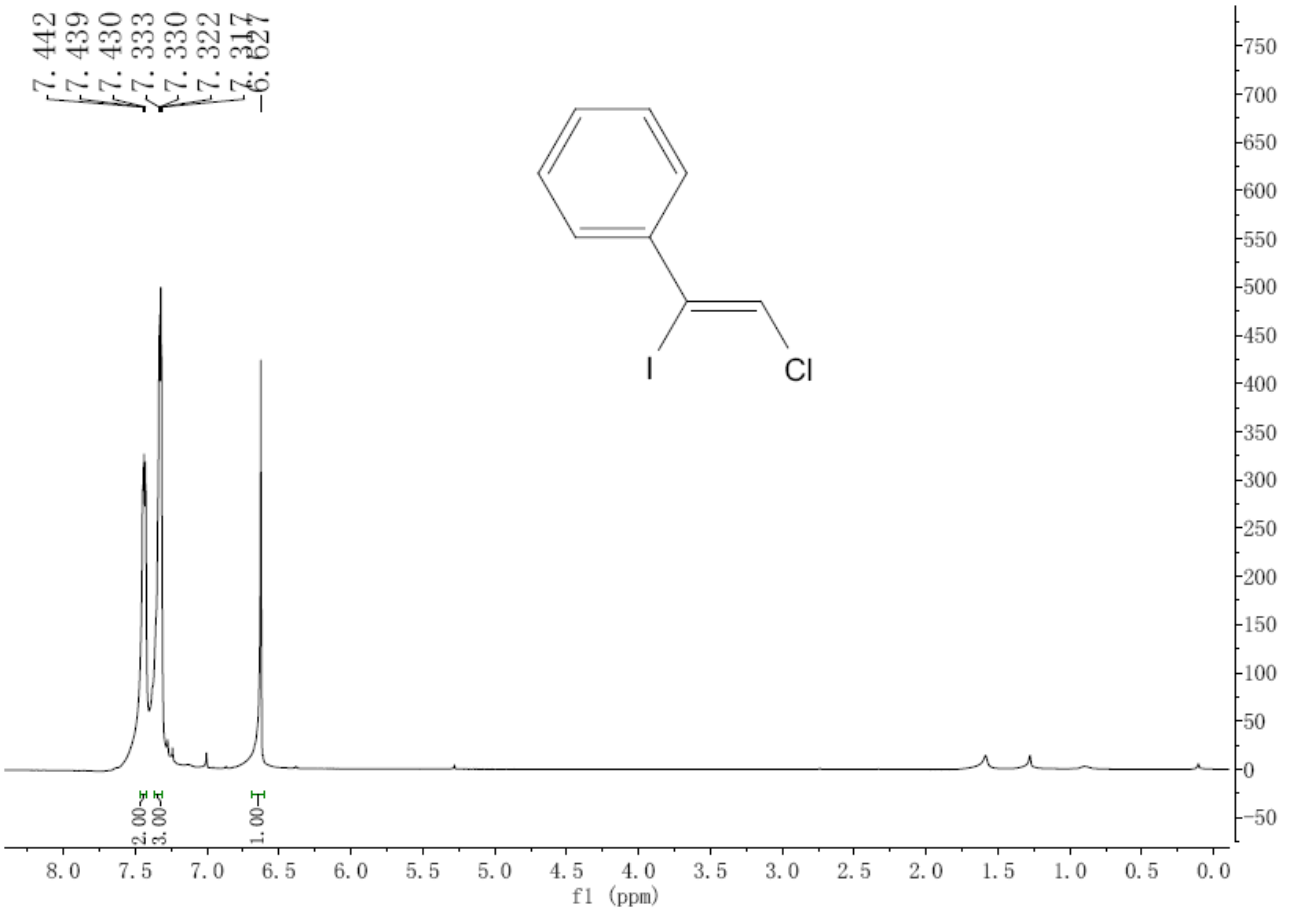


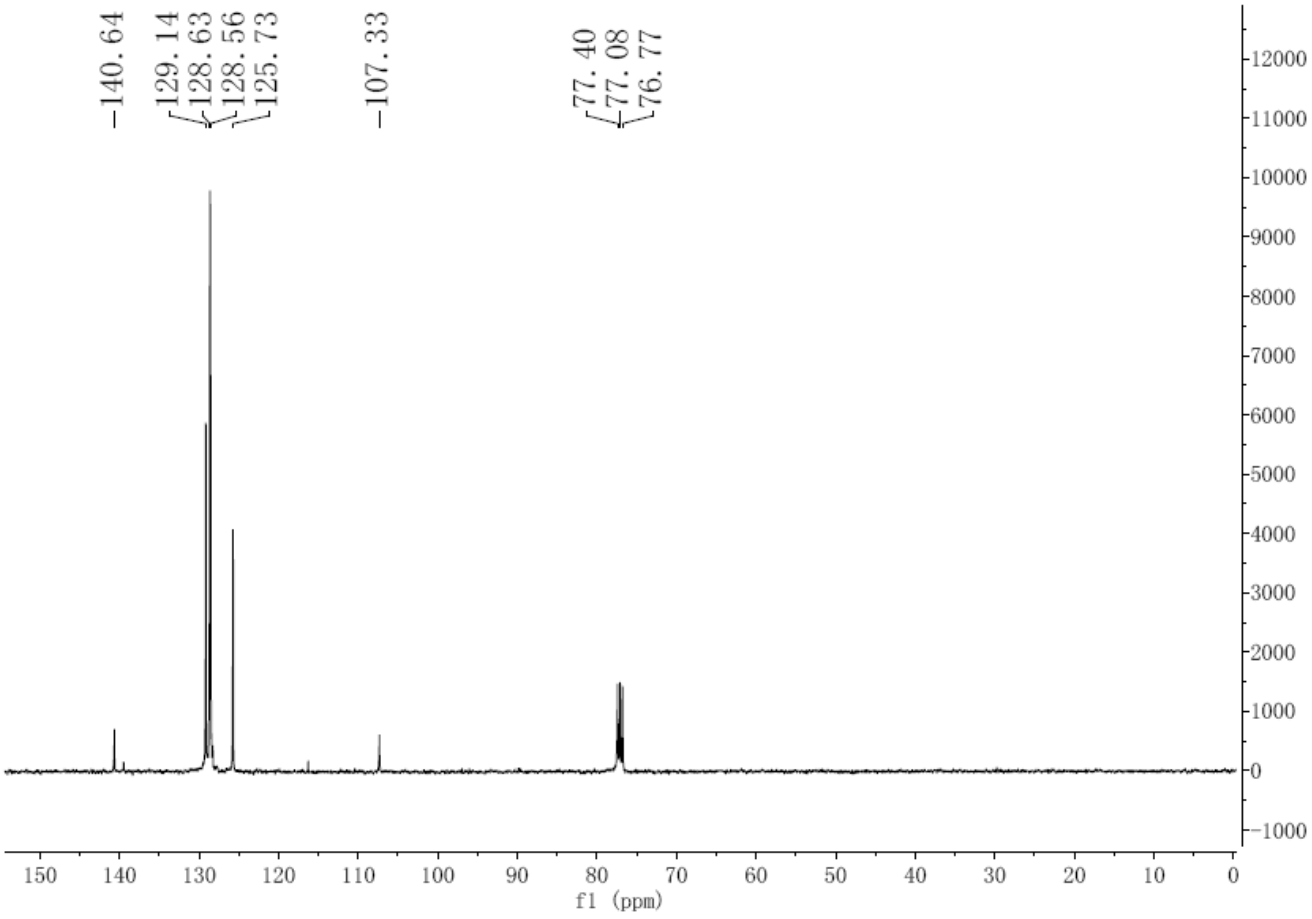
^{1}H NMR and ^{13}C NMR of 1-((*Z*)-2-bromo-1-iodovinyl)-4-ethynylbenzene (2m)



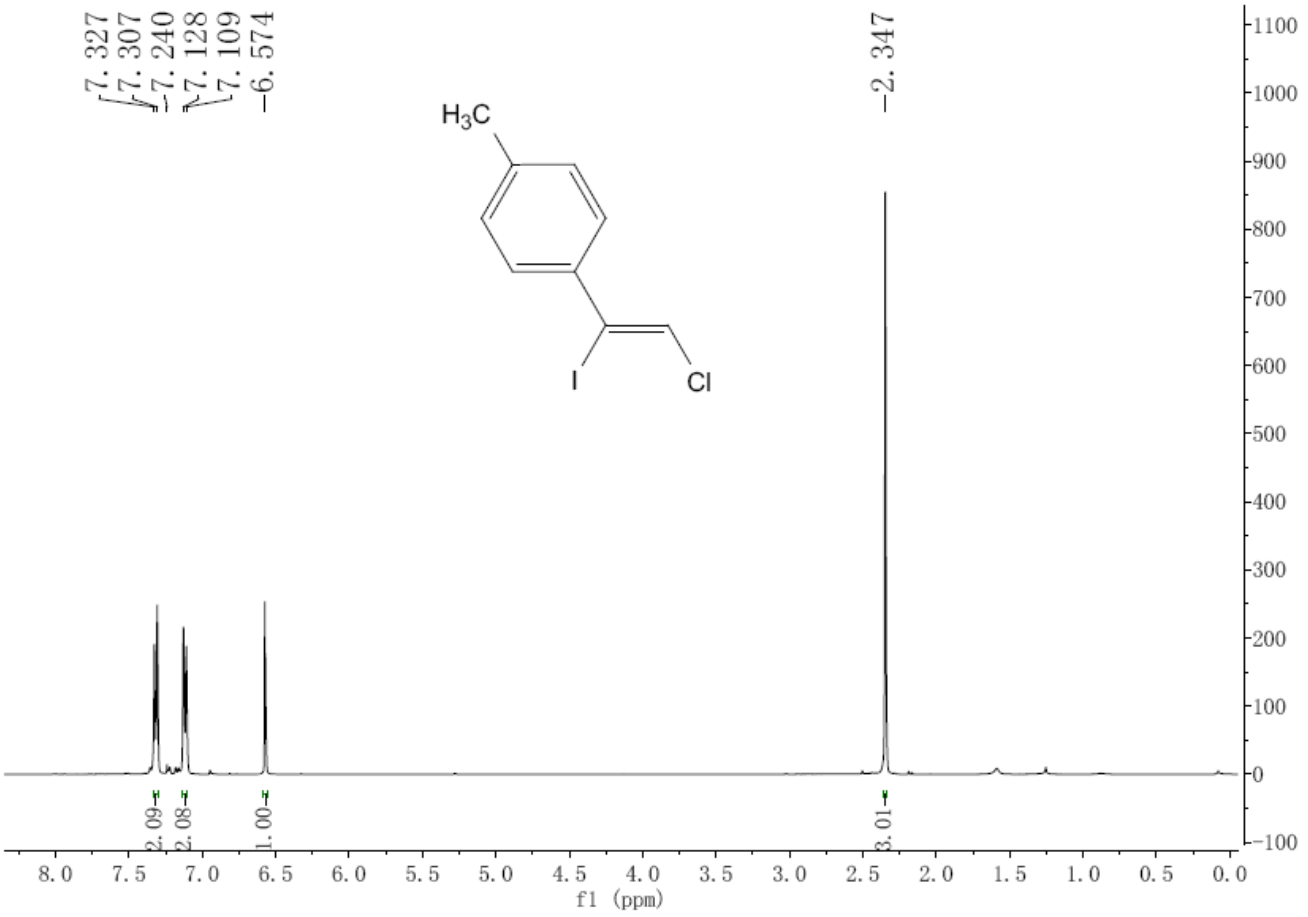


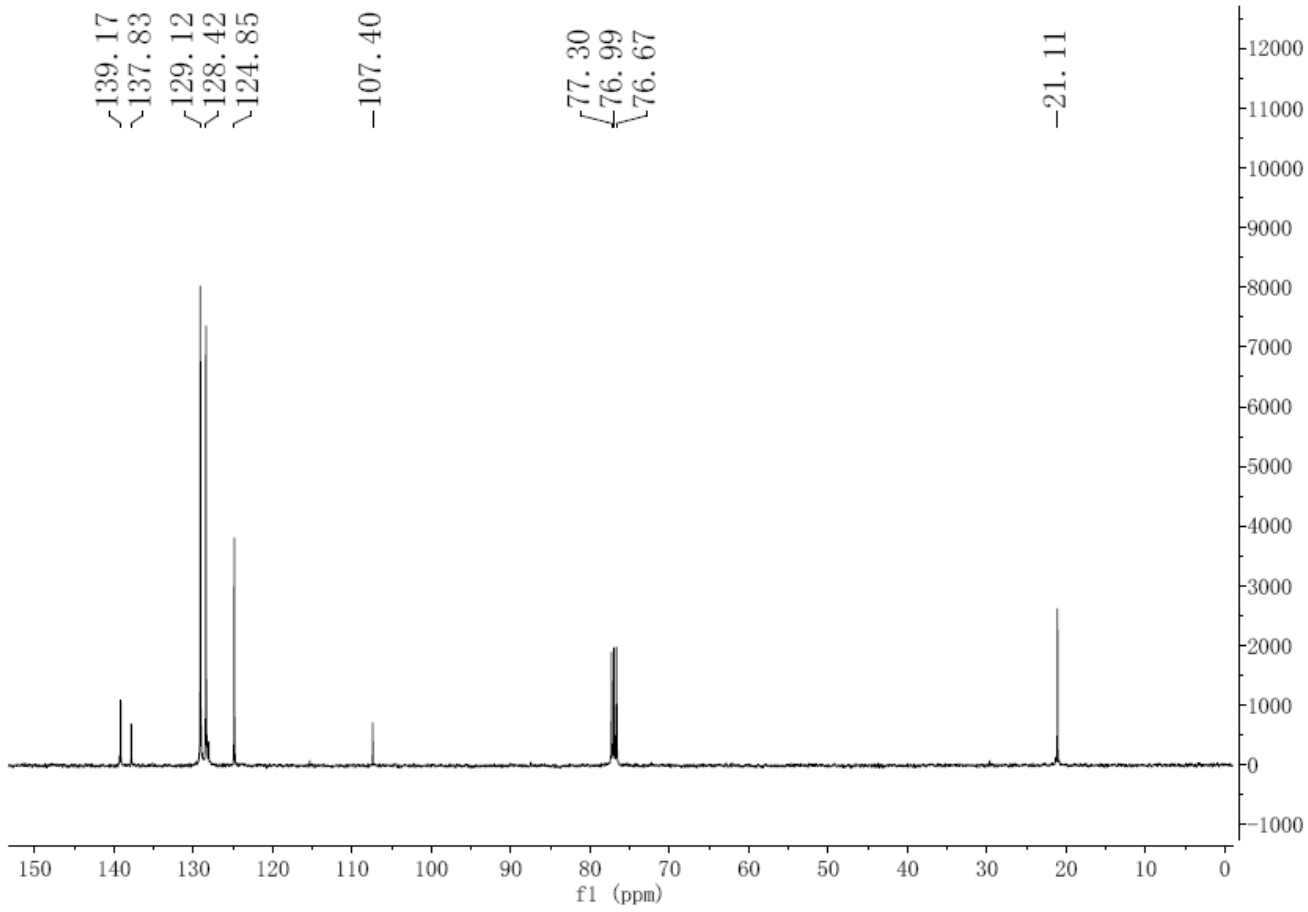
^{1}H NMR and ^{13}C NMR of 1-((*Z*)-2-chloro-1-iodovinyl)benzene (2n)



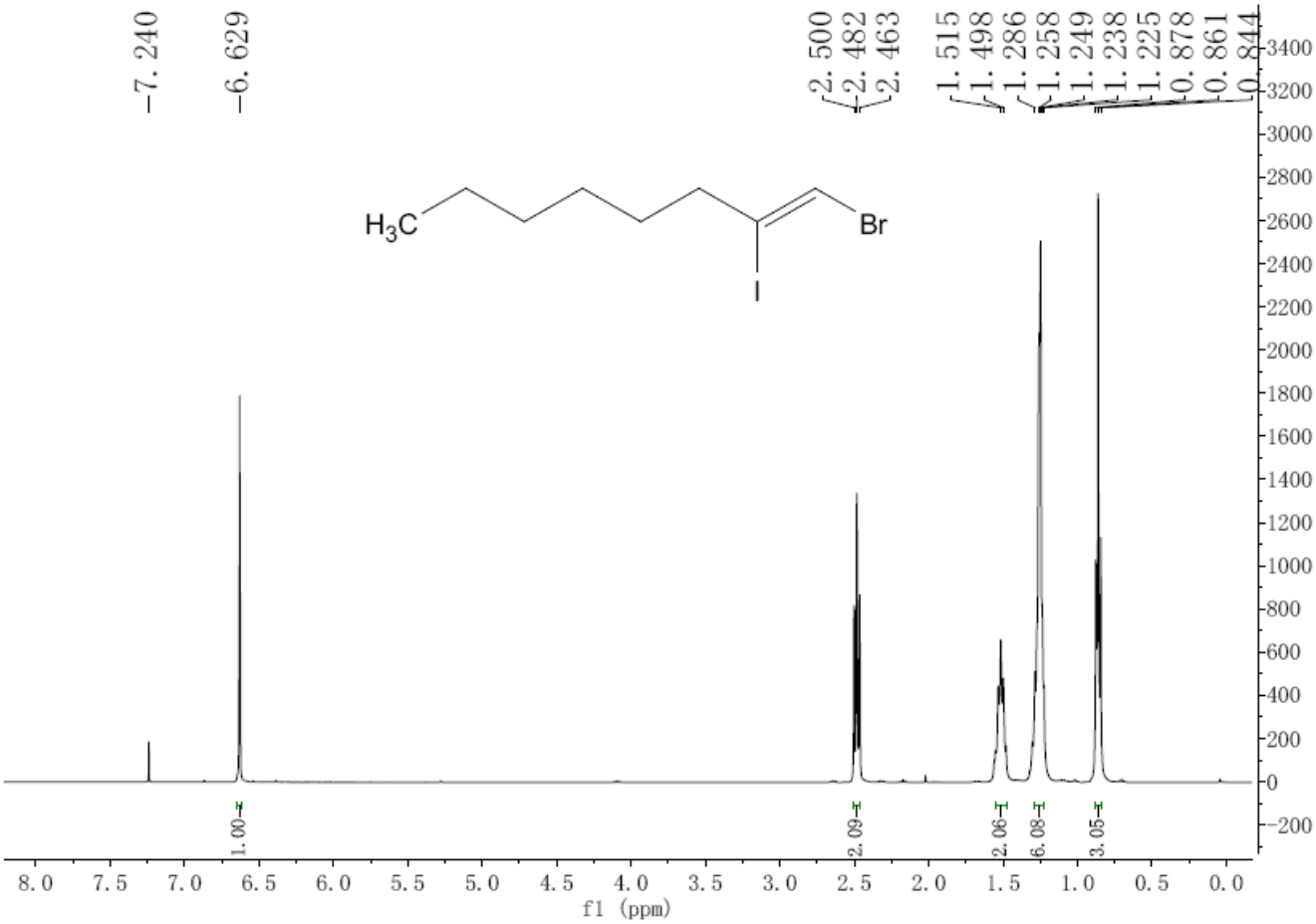


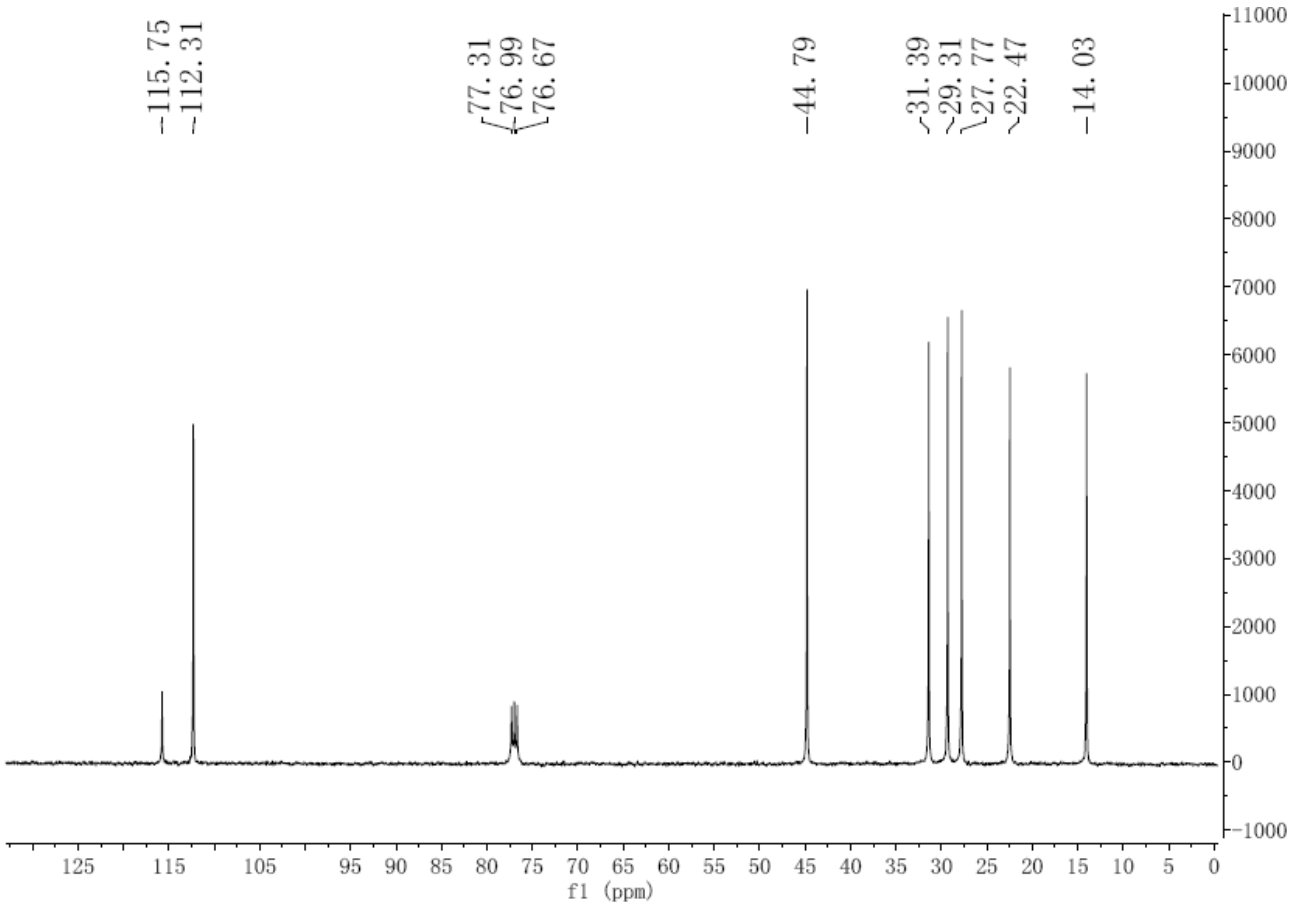
^{1}H NMR and ^{13}C NMR of 1-((*Z*)-2-chloro-1-iodovinyl)-4-methylbenzene (2o)



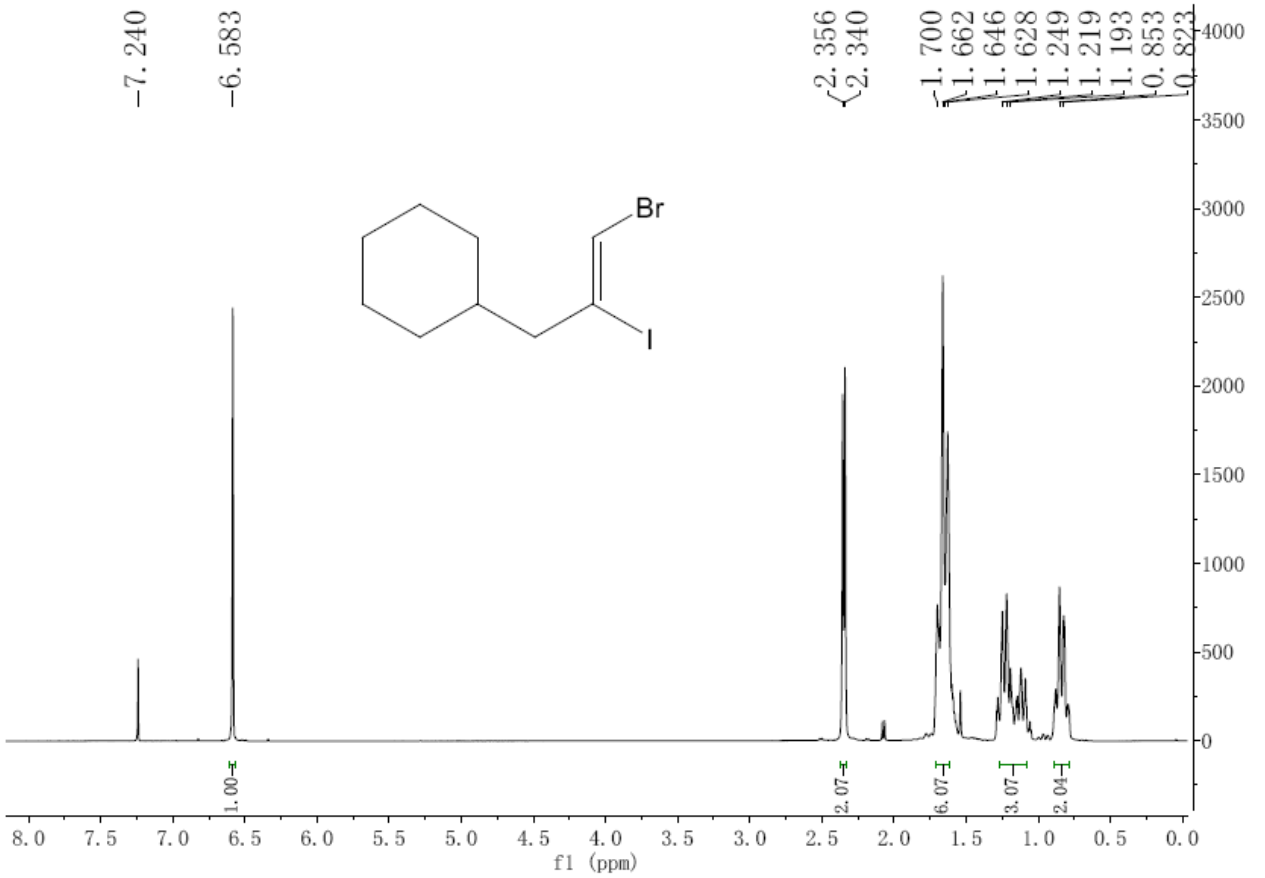


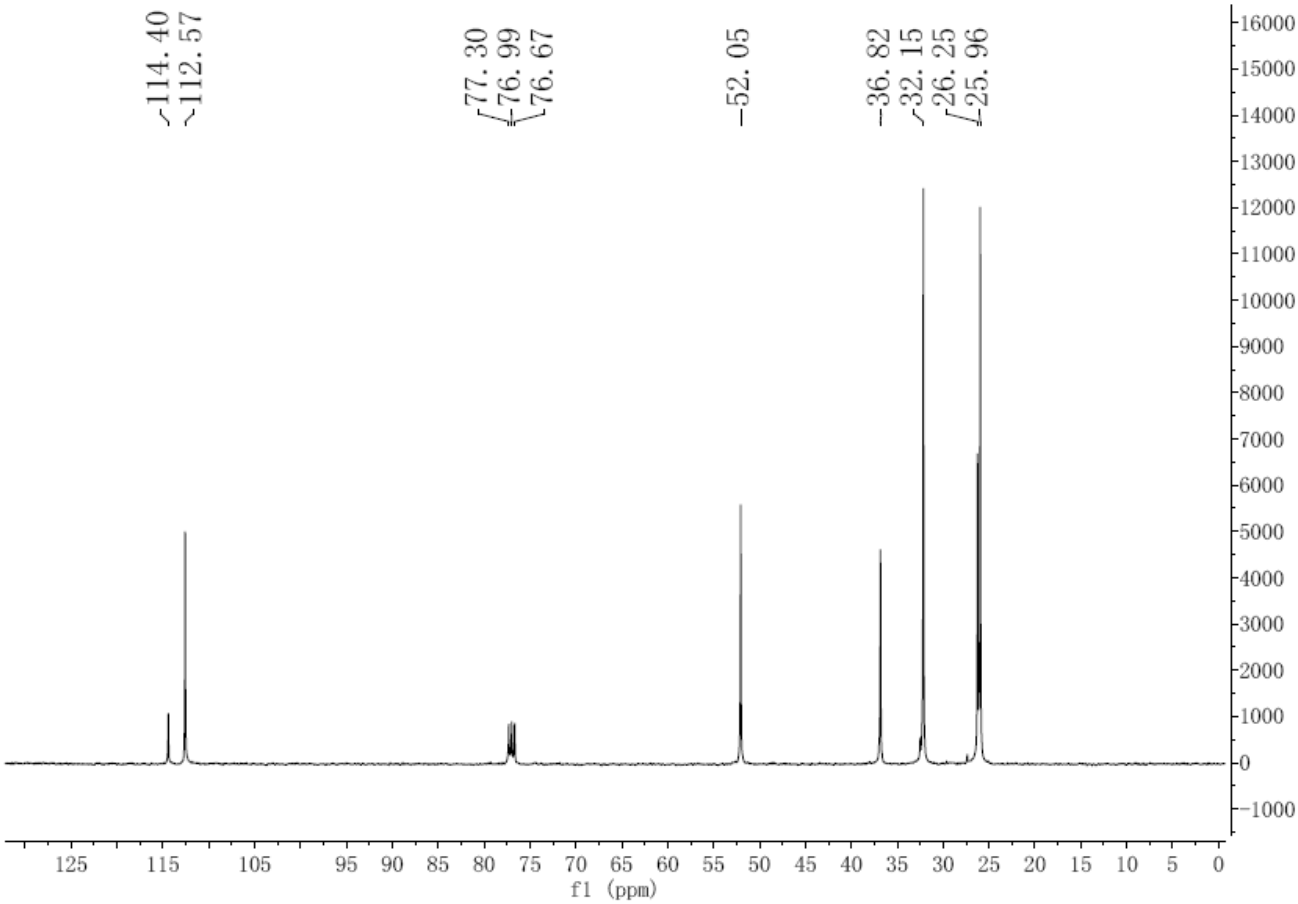
^{1}H NMR and ^{13}C NMR of (*Z*)-1-bromo-2-iodooct-1-ene (2p)



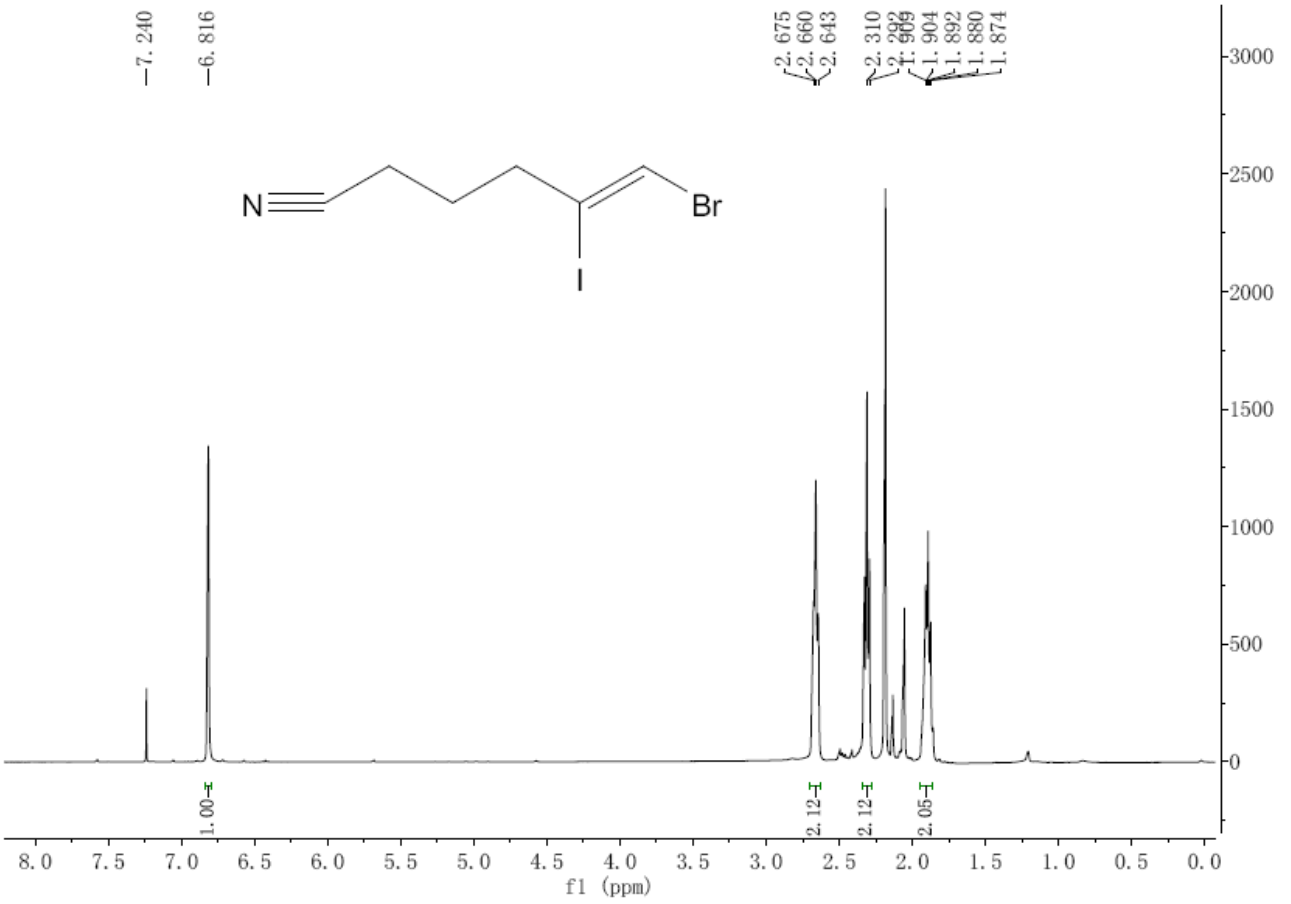


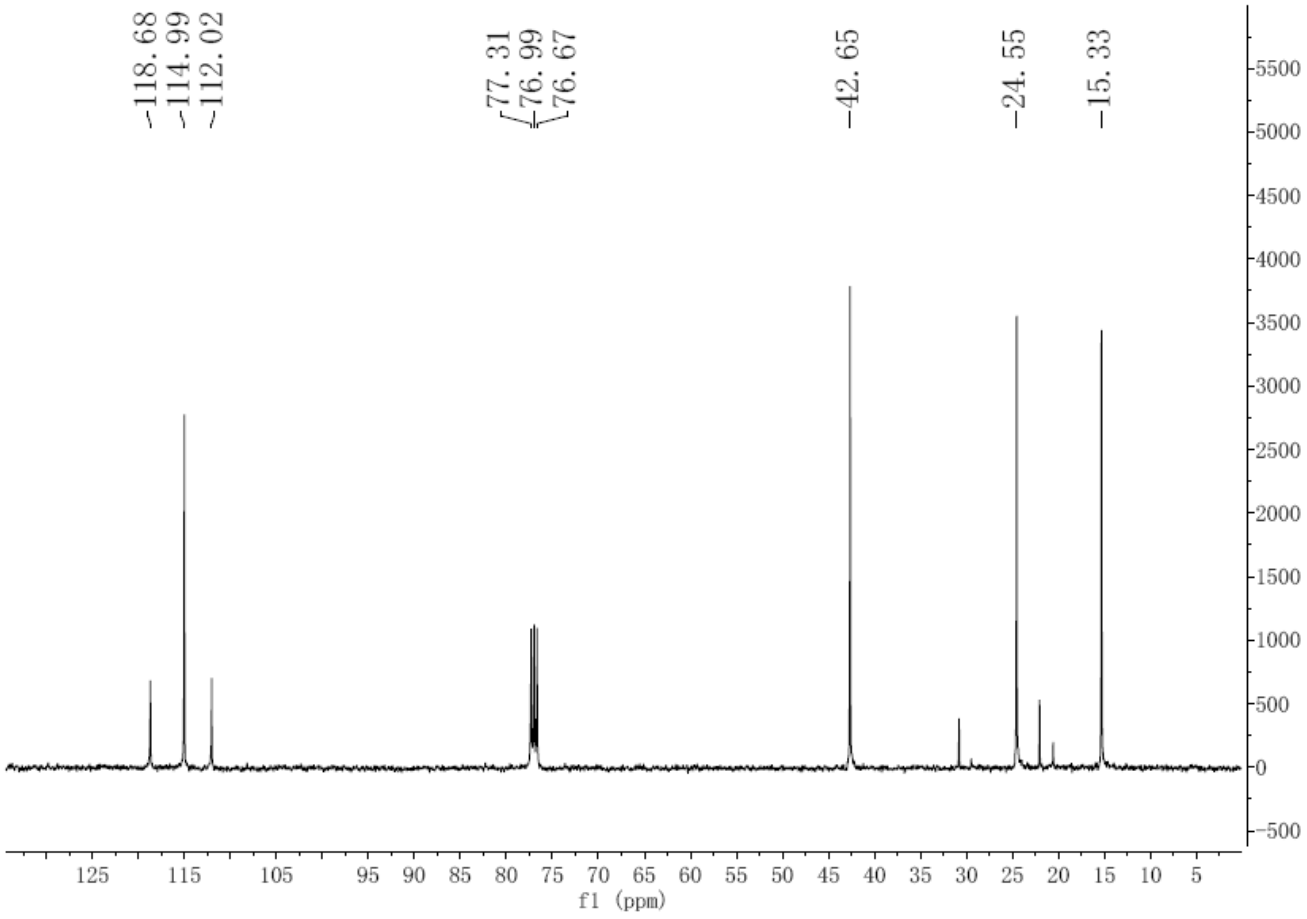
^{1}H NMR and ^{13}C NMR of ((*Z*)-3-bromo-2-iodoallyl)cyclohexane (2q)



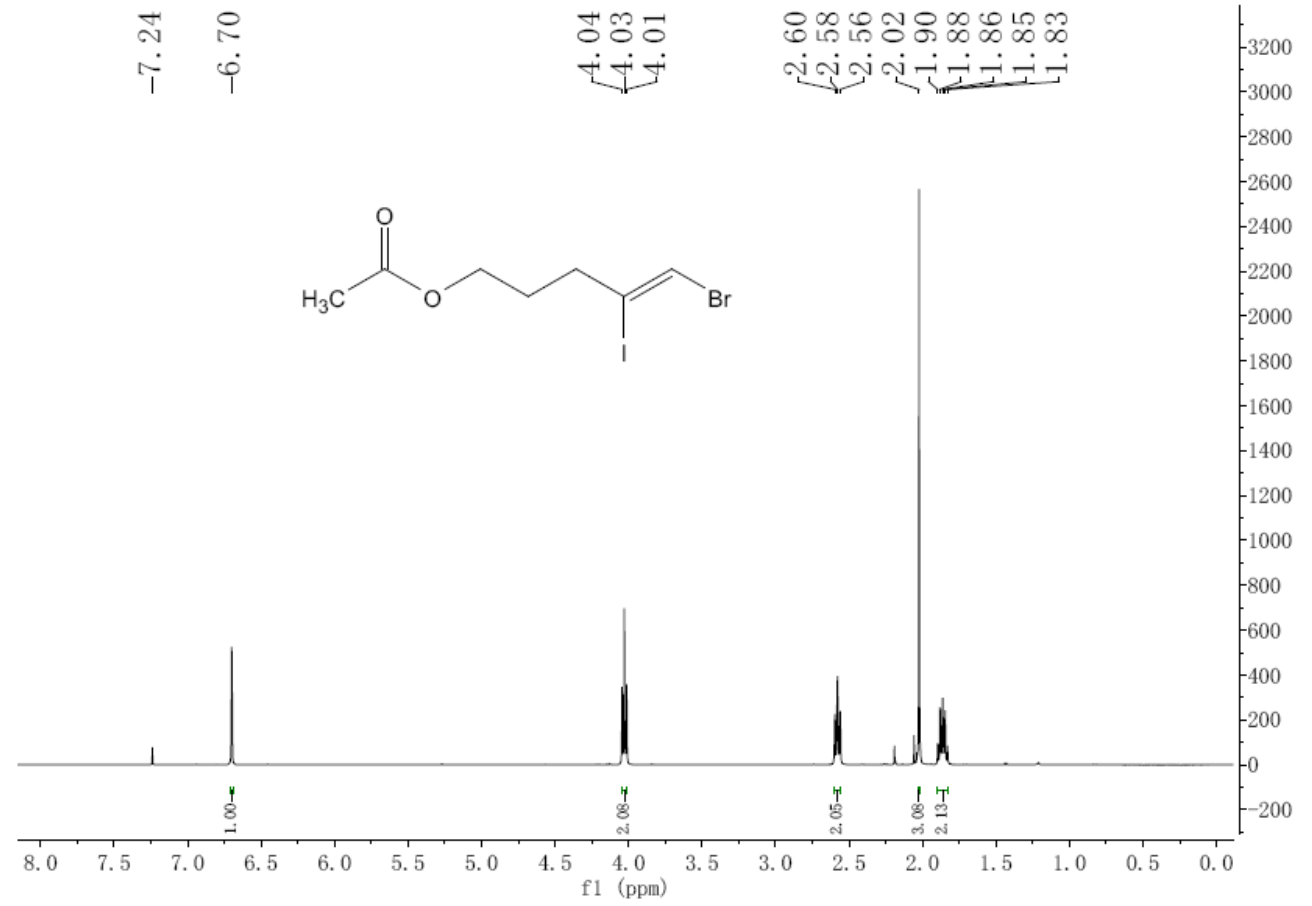


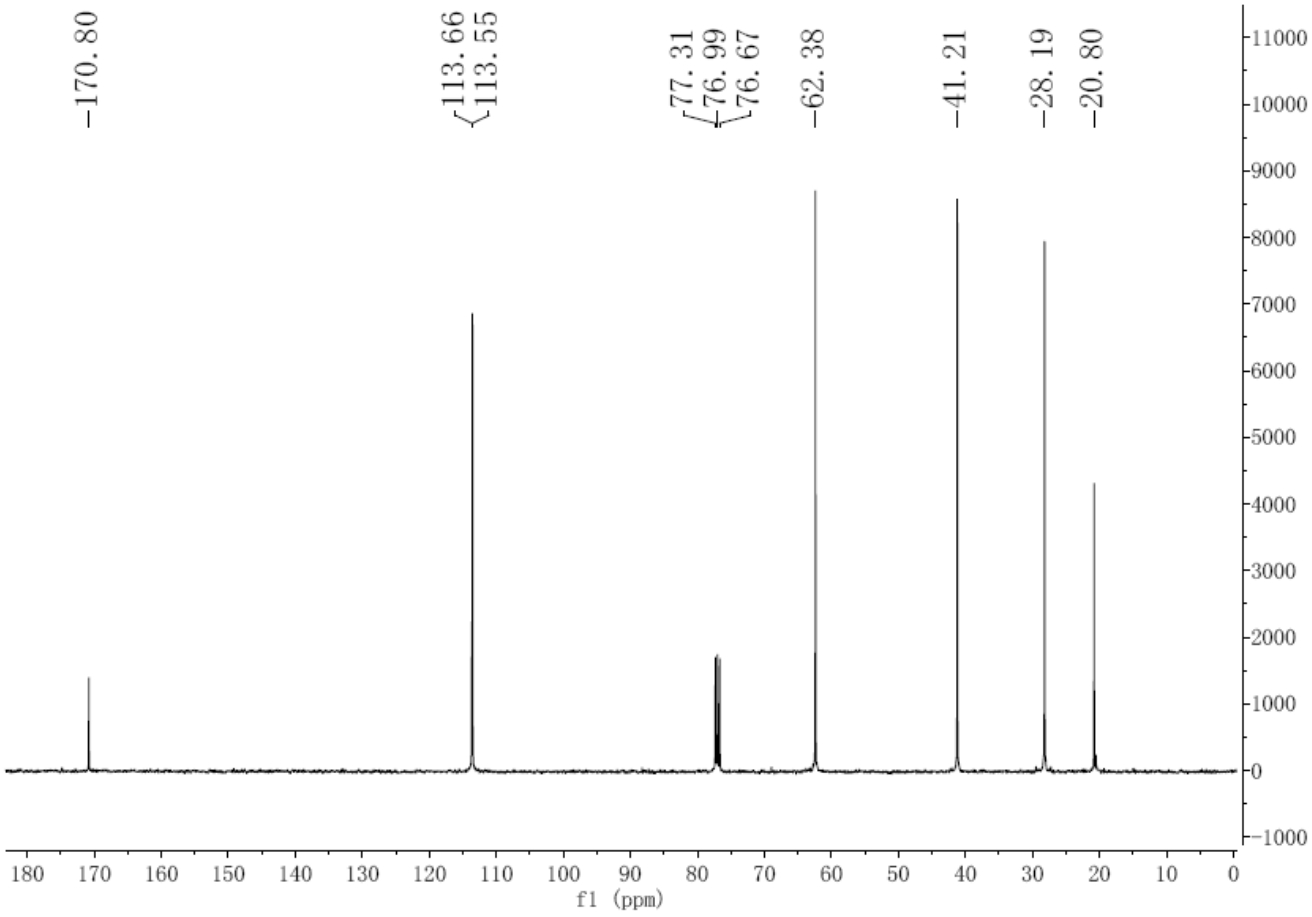
^{1}H NMR and ^{13}C NMR of (*Z*)-6-bromo-5-iodohex-5-enenitrile (2r)



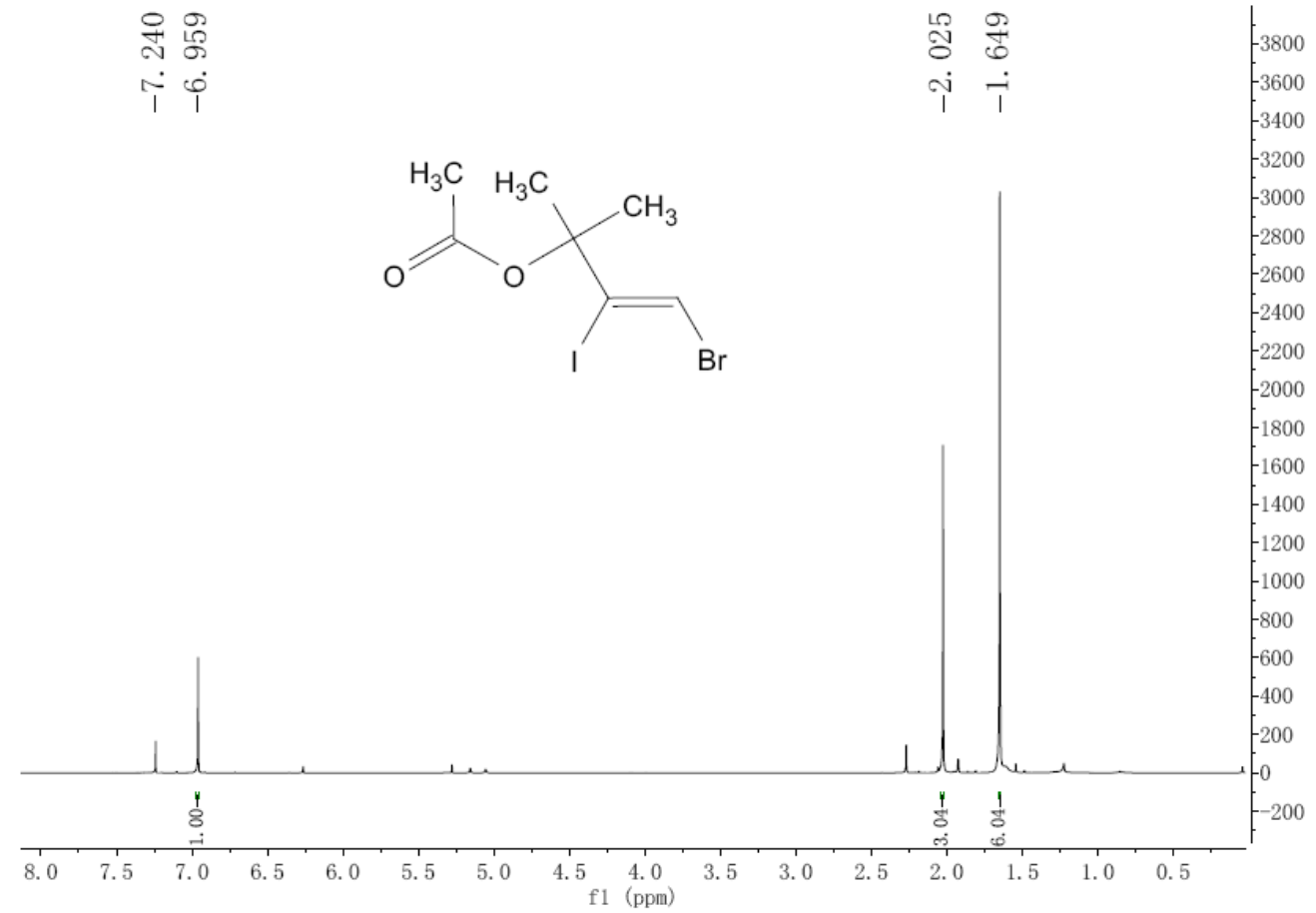


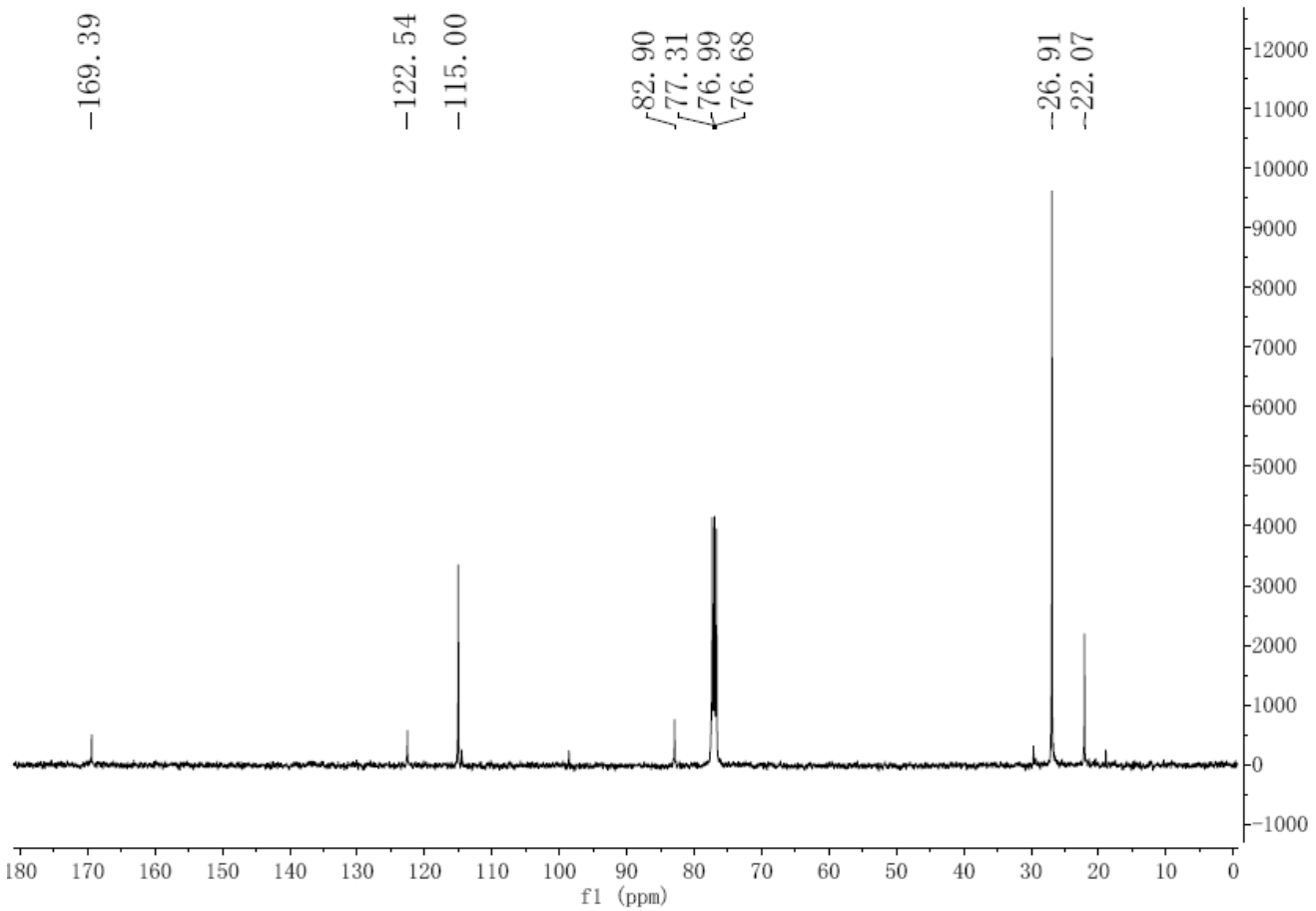
^{1}H NMR and ^{13}C NMR of (*Z*)-5-bromo-4-iodopent-4-enyl acetate (2s)



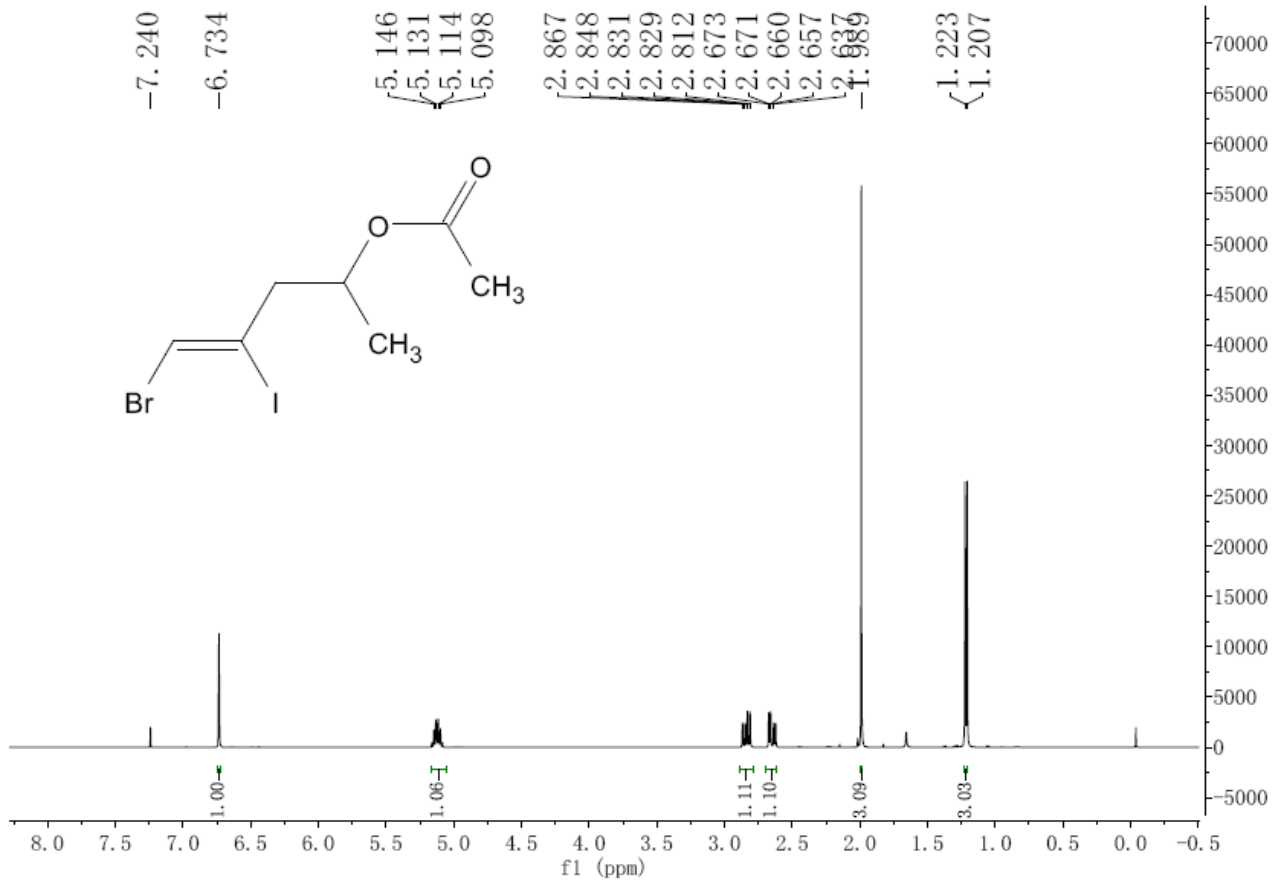


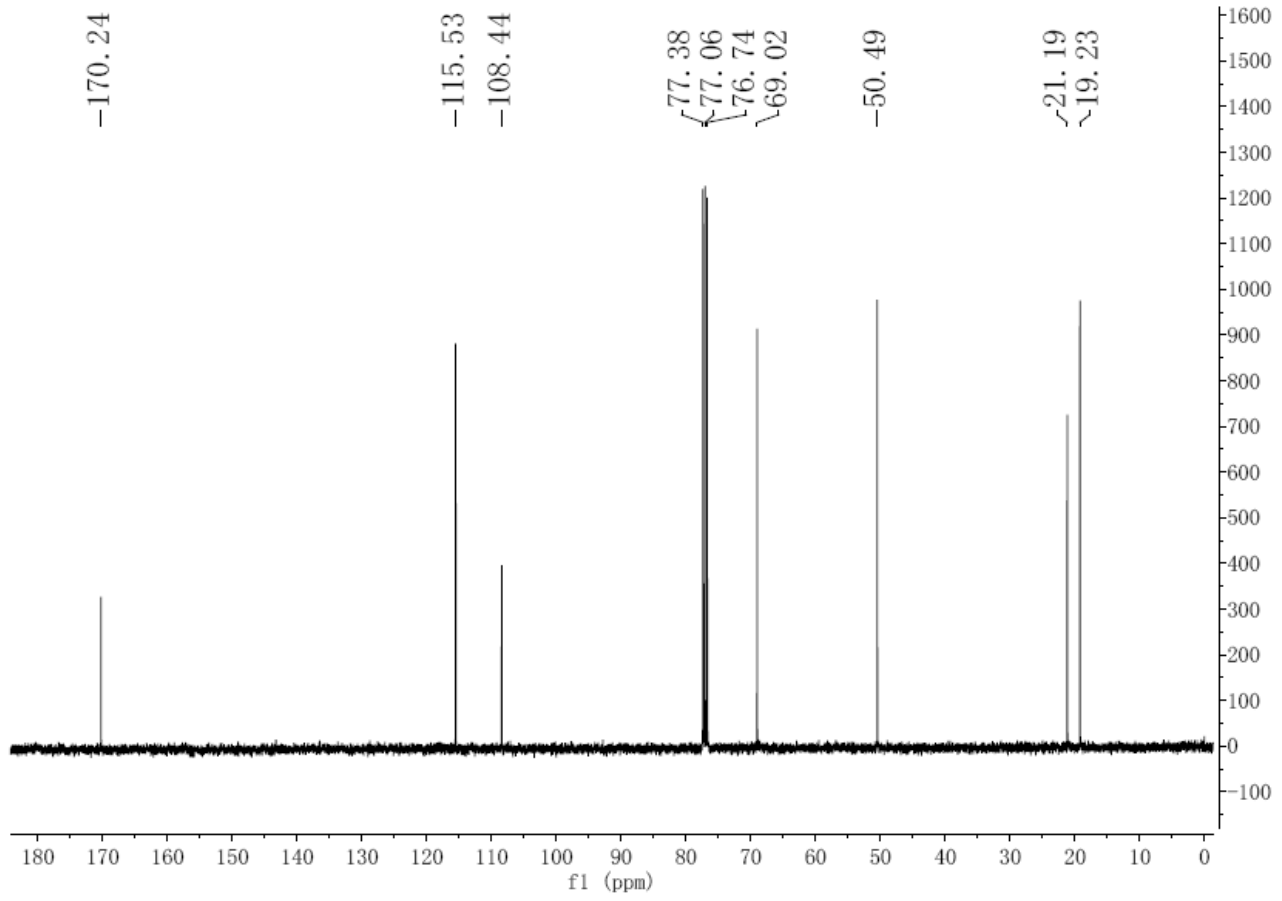
^{1}H NMR and ^{13}C NMR of (*Z*)-4-bromo-3-iodo-2-methylbut-3-en-2-yl acetate (2t) or (2u)



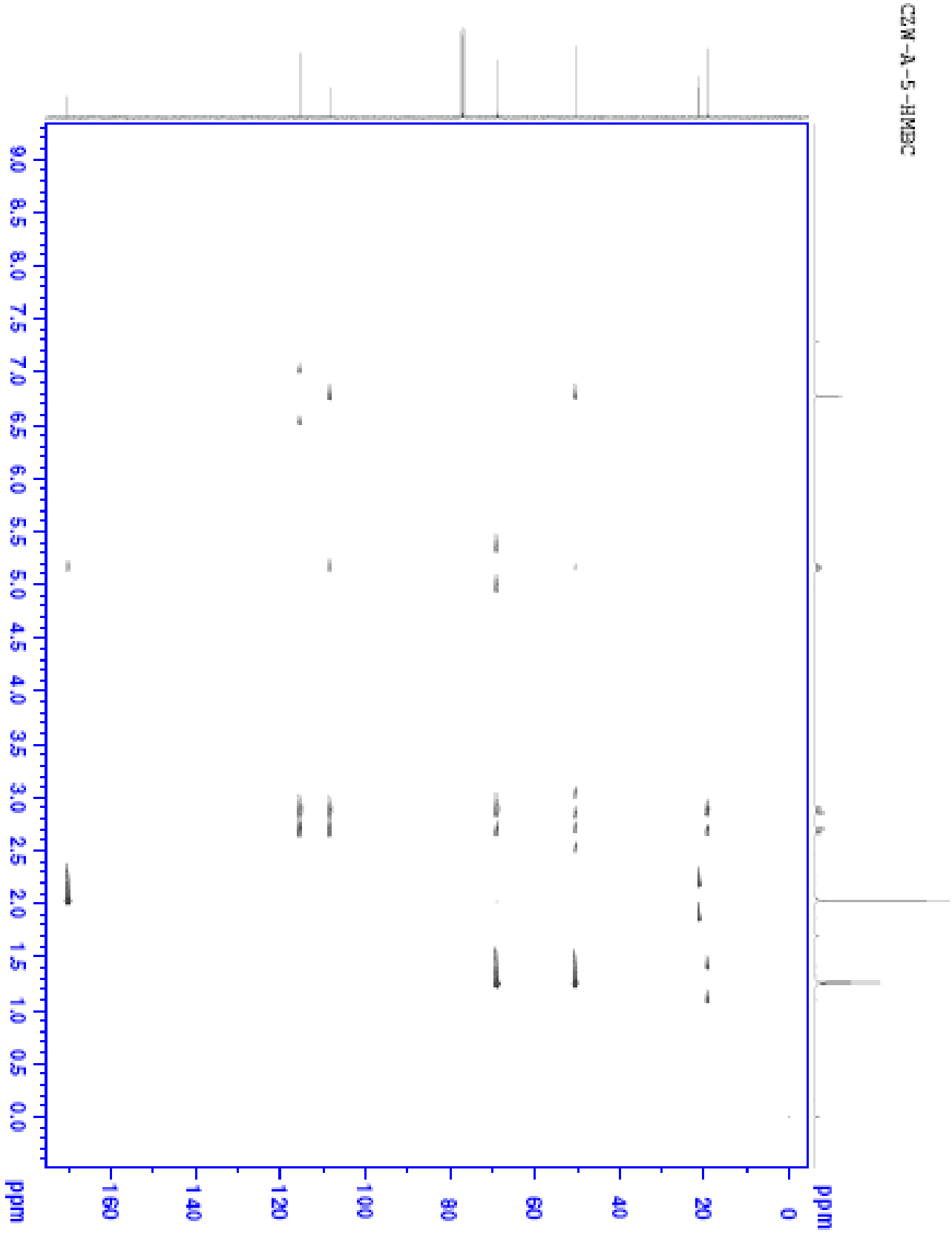


^{1}H NMR and ^{13}C NMR of (Z)-5-bromo-4-iodopent-4-en-2-yl acetate (2v)

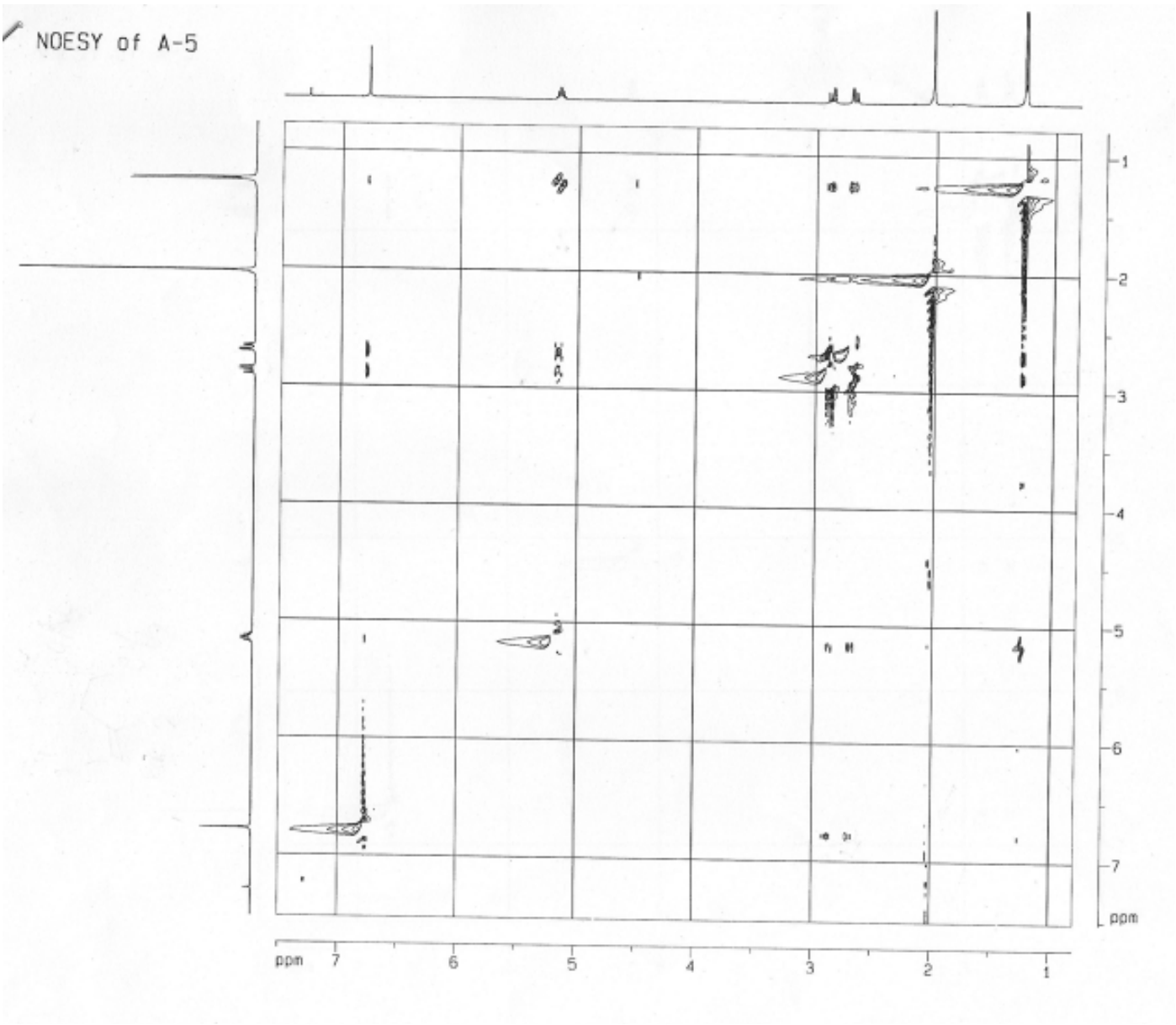




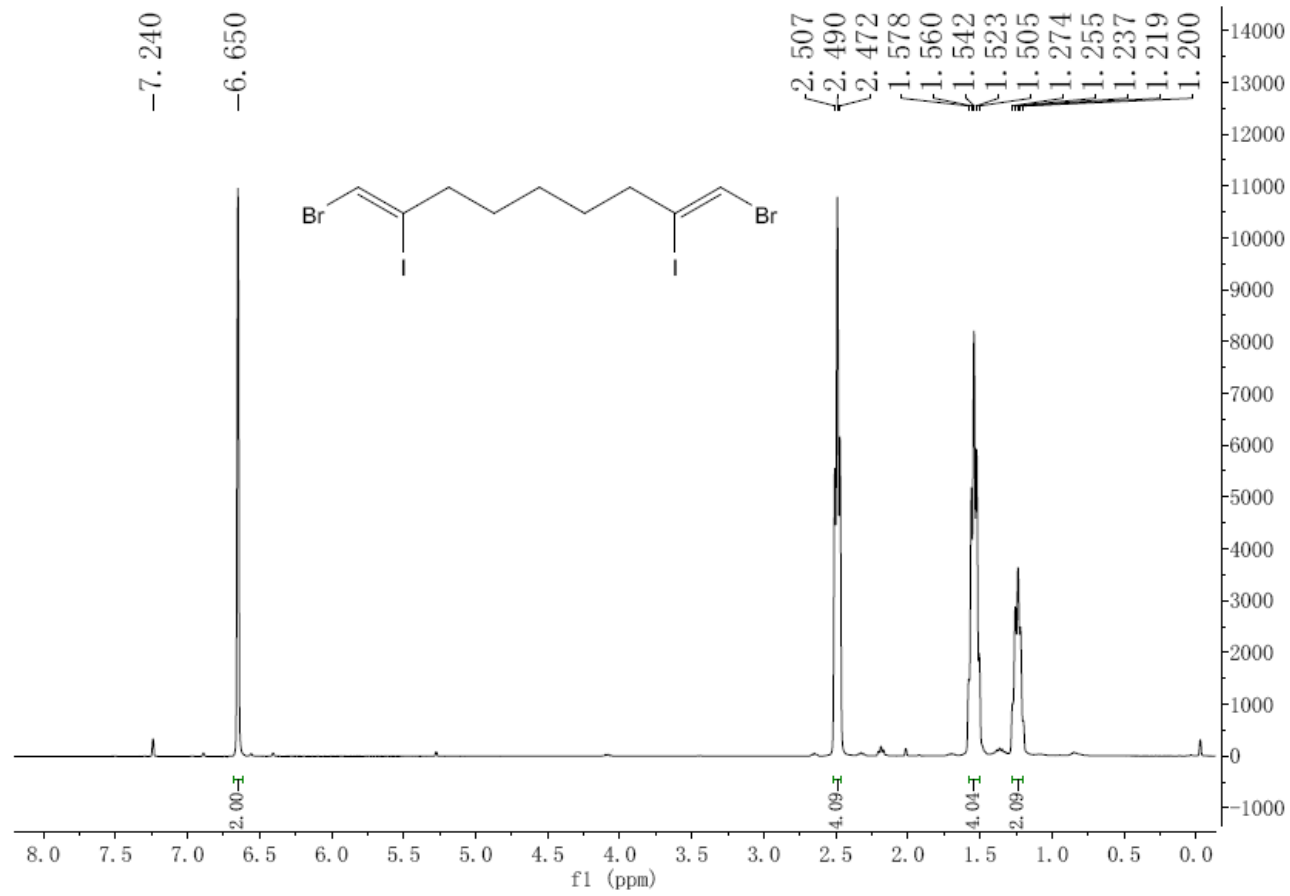
HMBC spectra of (Z)-5-bromo-4-iodopent-4-en-2-yl acetate (2v)

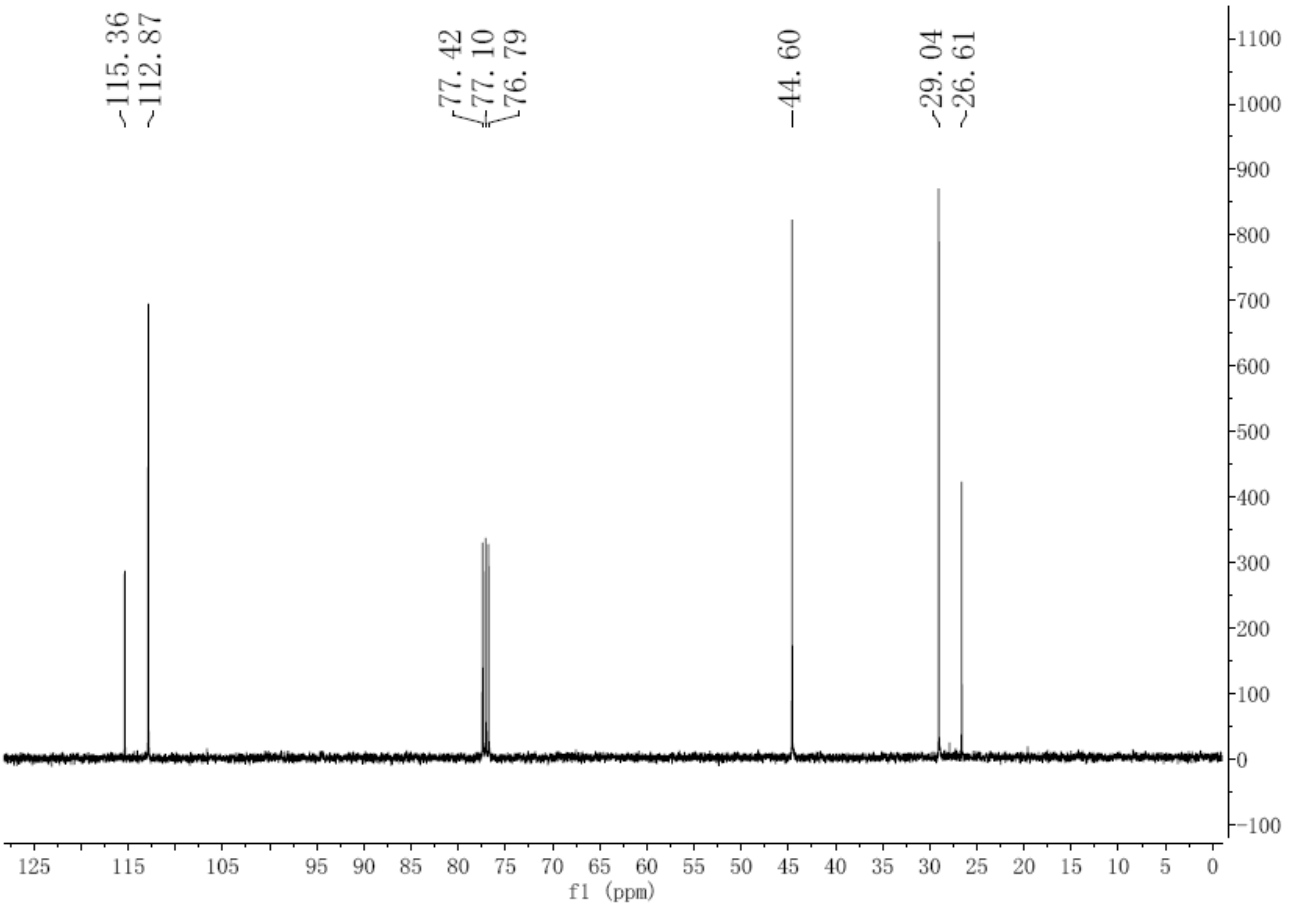


NOE spectra of (Z)-5-bromo-4-iodopent-4-en-2-yl acetate (2v)

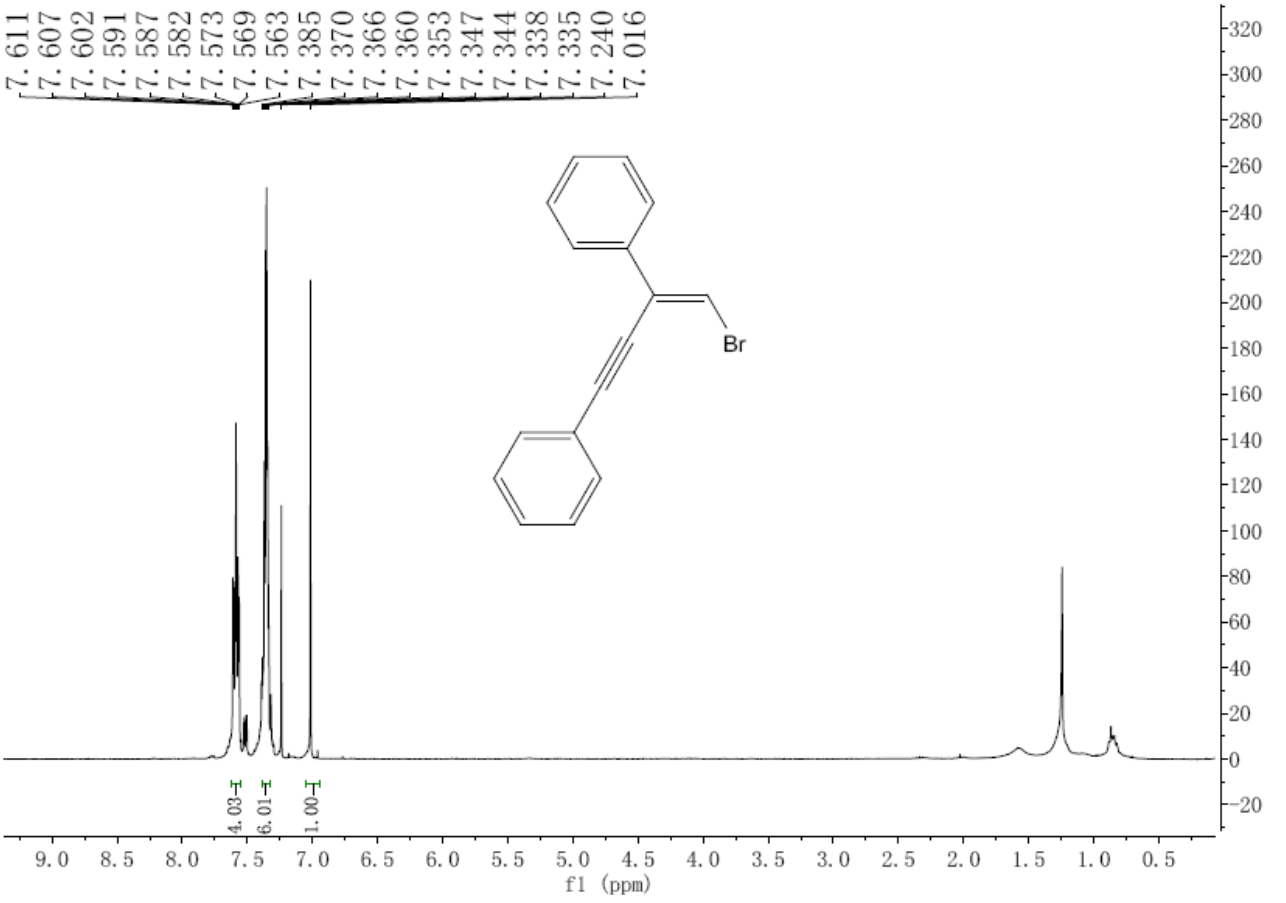


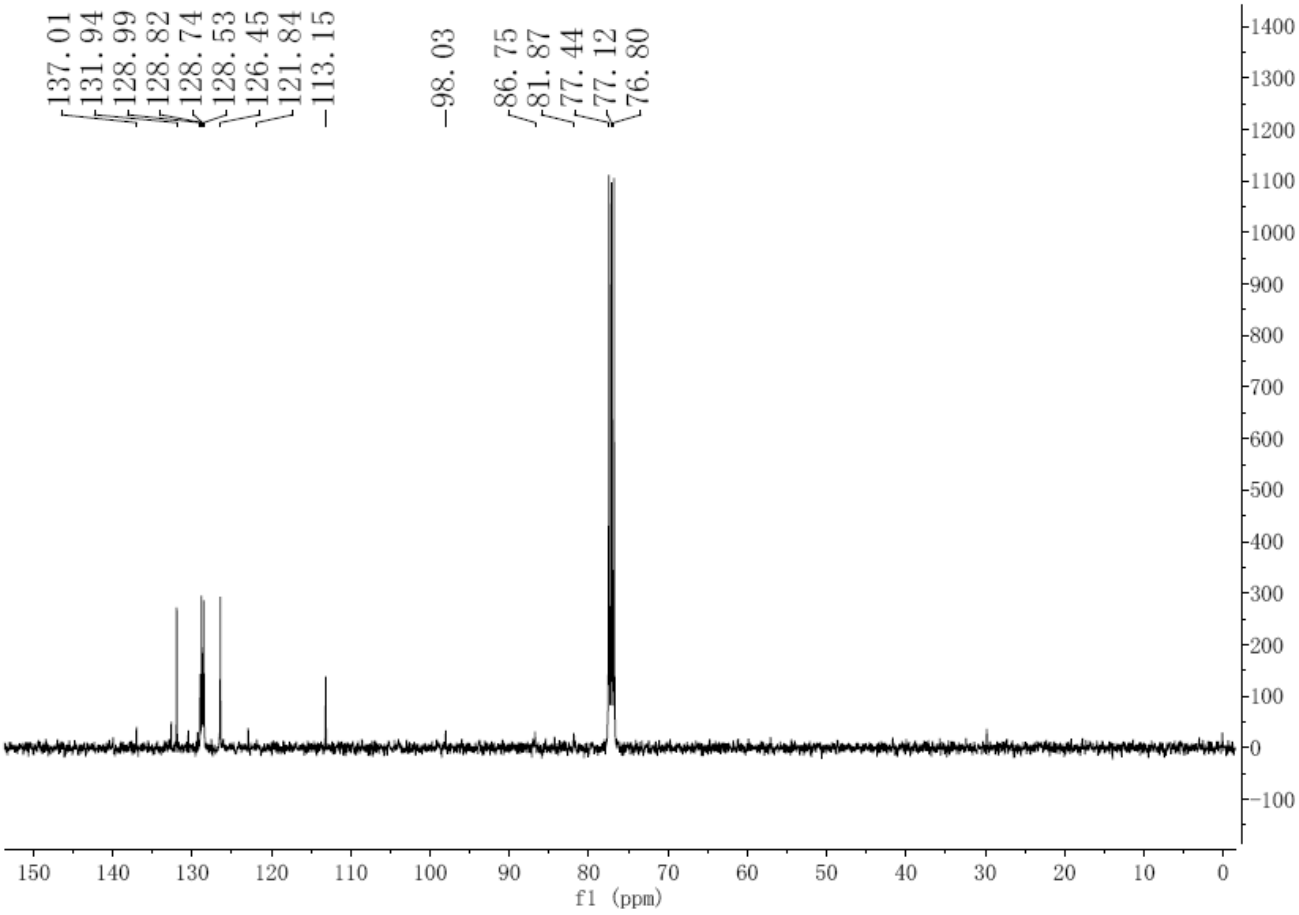
^{1}H NMR and ^{13}C NMR of (1*Z*, 8*Z*)-1,9-dibromo-2,8-diiodonona-1,8-diene (2w)





^{1}H NMR and ^{13}C NMR of (*Z*)-1-bromo-2,4-diphenylbut-1-en-3-yne (3a)





^{1}H NMR and ^{13}C NMR of 1-((*Z*)-6-(4-fluorophenyl)-3-phenylhexa-3-en-1,5-diynyl)benzene (4a)