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Visible-light-mediated C2-amination of thiophenes by using DDQ as organophotocatalyst

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Supporting Information

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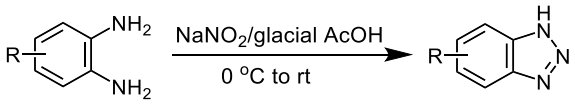
1. General Considerations

All manipulations were carried out by using standard Schlenk techniques. Unless otherwise stated, analytical grade solvents and commercially available reagents were used to conduct the reactions. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum ether (bp. 60−90 ˚C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum ether to the ethyl acetate. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR and HRMS. The known compounds were characterized by ^{1}H NMR and ^{13}C NMR. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. The chemical shifts (δ) were given in part per million relative to internal tetramethyl silane (TMS, 0 ppm for ^{1}H), $CDCl_3$ (77.3 ppm for ^{13}C)or DMSO (2.5 ppm for ^{1}H), DMSO (39.5 ppm for ^{13}C). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument and accurate masses were reported for the molecular ion + Hydrogen (M+H).

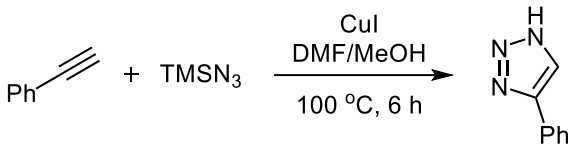
2. Experimental Procedures

2.1 Preparation of substituted nitrobenzotriazoles 1c-1i[1]



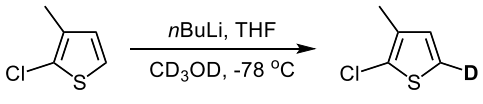
1,2-phenylenediamine derivatives (0.5g, 3.26 mmol) was dissolved in a mixture of 0.45 mL of glacial acetic acid and 1.2 mL of water and cooled to 4 °C. A solution of sodium nitrite (0.26g, 3.76 mmol) in 1 mL of water was added. The reaction temperature rose to 50 °C. Then reaction mixture was allowed to reach room temperature and stirred at this temperature for 12 h. The mixture was cooled to 0 °C for 1 h and filtered. The residue was filtered, washed with water, and dried to provide substituted nitrobenzotriazole **2a-2i**.

2.2 Preparation of 4-Phenyl-1H-1,2,3-triazole 2k[2]



An oven-dried vial was equipped with a magnetic stir bar and charged with CuI (95 mg, 0.5 mmol). The vial was sealed with a screw-cap septum, and then evacuated and backfilled with argon. $TMSN_3$ (2.0 mL, 1.2 mmol) and phenylacetylene (1.1 mL ,10 mmol) were added via syringe, followed by addition of DMF/MeOH (4:1, 10 mL). The reaction mixture was stirred at 100 °C for 6 h. The reaction mixture was cooled to room temperature, diluted with EtOAc, washed with 30% aqueous NH_4OH, dried over $MgSO_4$, concentrated in vacuo and purified via flash chromatography (Hexanes/EtOAc, 1:1) to provide the title compound **1r**.

2.3. Preparation of 1m-D[3]



Preparation of 5-deutero-2-chloro-3-methylthiophene (**1m-D**): A stirred solution of 2-chloro-3-methylthiophene **1m** (10 mmol) in dry THF (10 mL) under nitrogen was cooled to –78 °C and 12 mmol nBuLi in hexane was added dropwise. CD_3OD (1.0 mL) was added to the reaction system after reacting for 1 h. The suspension was extracted with water extracted with dichloromethane three times. The combined organic layers were dried over anhydrous

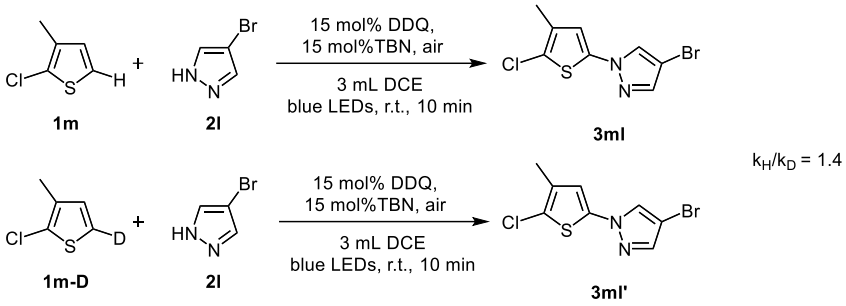
Na_2SO_4 and evaporated in vacuum to provide the title compound **1m-D**.

2.4 General procedure for visible-light-mediated C2-amination of thiophenes by using DDQ as photocatalyst

A solution of the thiophene derivatives **1** (1.0 mmol), the pyrazole derivatives **2** (0.5 mmol), DDQ (15 mol%) and tert-butyl nitrite (15 mol%) in DCE (3 mL) stirred under air atmosphere and irradiation of 3W blue LEDs for 4 h. After completion of the reaction, the products was detected by GC-MS. The solvent was removed under reduced pressure by an aspirator, then the pure product was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 30:1) to afford **3** and **4**.

3. Mechanism Studies

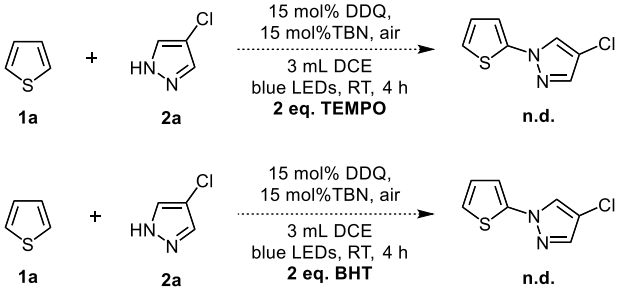
3.1 Kinetic isotope effects of the reaction



Scheme S1. Kinetic isotope effects

A solution of 4-chloro-1H-pyrazole **2l** (0.5 mmol), photocatalyst (15 mol%), tert-butyl nitrite (15 mol%), thiophene **1m** and **1m-D** (1.0 mmol) in DCE (3 mL), stirred under air atmosphere respectively and irradiation of 3W blue LEDs for 10 minutes. After completion of the reaction, the reaction was monitored by TLC and GC. The products **3ml** and **3ml'** could be obtained in a ratio of 1.4, which means k_H/k_D = 1.4. This result indicated that the C-H bond cleavage of aromatic ring might not be involved in the rate-determined step of the reaction.

3.2 Radical-inhibiting experiments

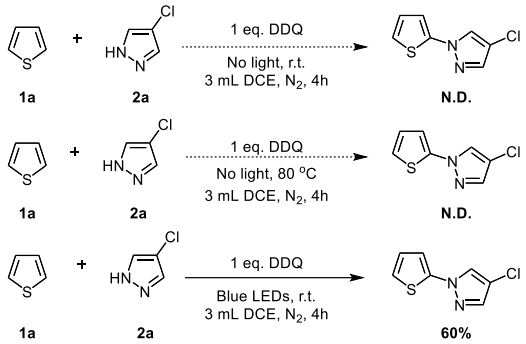


Scheme S2. Radical-inhibiting experiments

A solution of thiophene **1a** (1.0 mmol), 4-chloro-1H-pyrazole **2a** (0.5 mmol), photocatalyst (15 mol%)，tert-butyl nitrite (15 mol%) and TEMPO or BHT (1.0 mmol) in DCE (3 mL) stirred under air atmosphere and irradiation of 3W blue LEDs for 4 h. After completion of the reaction, the reaction was monitored by TLC and GC. And both of the desired product **3a** haven't been detected, implying that this transformation may be involved a radical process.

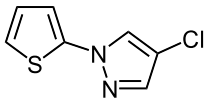
3.3 Control experiments

A solution of thiophene **1a** (1.0 mmol), 4-chloro-1H-pyrazole **2a** (0.5 mmol), photocatalyst (15 mol%) and tert-butyl nitrite (15 mol%) in DCE (3 mL) stirred under air atmosphere and irradiation of 3W blue LEDs for 4 h. After completion of the reaction, the reaction was monitored by TLC and GC.



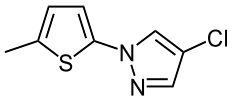
Scheme S 3. Control Experiments

Characterization of Products



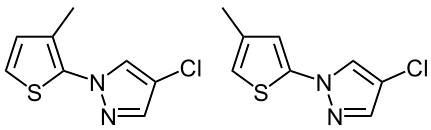
3a

4-Chloro-1-(thiophen-2-yl)-1H-pyrazole (**3a**); 76.2 mg (yield: 81%, 0.5 mmol scale), yellow solid (mp. 44- 46 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1.0H), 7.61 (s, 1.0H), 7.07 (d, *J* = 5.2 Hz, 1.0H), 7.02 - 7.01 (m, 1.0H), 6.97 - 6.94 (m, 1.0H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 139.4, 126.0, 125.9, 120.7, 114.5, 112.3. IR (film); 3110, 1685, 1564, 1525, 1466, 1379, 1329, 1219, 1008, 970, 923, 845, 694, 603 cm^{-1}. HRMS (ESI) calcd for $C_7H_6ClN_2S$, $[M+H]^+$, 184.9935, found 184.9932.



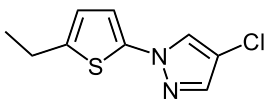
3b

4-Chloro-1-(5-methylthiophen-2-yl)-1H-pyrazole (**3b**); 72.5 mg (yield: 72%, 0.5 mmol scale), white solid (mp. 74- 78 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 0.8 Hz, 1.0H), 7.55 (s, 1.0H), 6.78 (d, *J* = 3.6 Hz, 1.0H), 6.58 - 6.56 (m, 1.0H), 2.45 (s, 3.0H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 139.1, 135.5, 125.9, 123.6, 114.8, 112.0, 15.3. IR (film); 3111, 3085, 1732, 1523, 1413, 1379, 1339, 1256, 1045, 962, 916, 839, 802, 735, 642, 599, 514 cm^{-1}. HRMS (ESI) calcd for $C_8H_8ClN_2S$, $[M+H]^+$, 199.0091, found 199.0090.



3c **3c'**

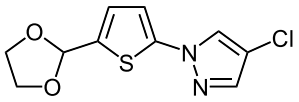
4-Chloro-1-(3-methylthiophen-2-yl)-1H-pyrazole (**3c**) and 4-Chloro-1-(4-methylthiophen-2-yl)-1H-pyrazole (**3c'**), isomer (6:1 based on NMR); 79.5 mg (yield: 80%, 0.5 mmol scale), yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 0.15H), 7.63 (d, *J* = 5.6 Hz, 2.0H), 7.55 (s, 0.15H), 7.09 (d, *J* = 5.2 Hz, 1.0H), 6.82 (d, *J* = 1.6 Hz, 0.15H), 6.80 (d, *J* = 5.6 Hz, 1.0H), 6.62 (s, 0.15H), 2.23 (s, 0.5H), 2.20 (s, 3.1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 139.4, 139.2, 136.5, 135.8, 130.4, 128.9, 128.8, 125.7, 121.7, 116.7, 115.5, 112.1, 111.4, 16.1, 13.2. IR (film); 3112, 2955, 2919, 1676, 1578, 1460, 1390, 1330, 1267, 1089, 1016, 968, 924, 800, 714, 604 cm^{-1}. HRMS (ESI) calcd for $C_8H_8ClN_2S$, $[M+H]^+$, 199.0091, found 199.0089.



3d

4-Chloro-1-(5-ethylthiophen-2-yl)-1H-pyrazole (**3d**); 41.3 mg (yield: 39%, 0.5 mmol scale), colorless liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.65 (s, 1.0H), 7.80 (s, 1.0H), 7.11 (d, *J* = 4.0 Hz, 1.0H), 6.73 (d, *J* = 3.6 Hz, 1.0H), 2.72 (q, *J* = 7.2, 2.0H), 1.18 (t, *J* = 7.6 Hz, 3.0H). ^{13}C NMR

(101 MHz, DMSO) δ 142.0, 139.7, 138.9, 126.8, 122.6, 114.3, 110.9, 22.7, 15.8. IR (film); 3123, 2966, 2930, 1680, 1567, 1502, 1416, 1381, 1333, 1212, 969, 913, 841, 803, 711, 607 cm^{-1}. HRMS (ESI) calcd for $C_9H_{10}ClN_2S$, $[M+H]^+$, 213.0248, found 213.0247.



3e

1-(5-(1, 3-Dioxolan-2-yl)thiophen-2-yl)-4-chloro-1H-pyrazole (**3e**); GC-yield: 48%, 0.5 mmol scale, white solid (mp. 88- 89 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.68 (s, 1H), 7.79 (s, 1H), 7.16 (d, *J* = 4.0 Hz, 1H), 7.08 (d, *J* = 4.0 Hz, 1H), 5.94 (s, 1H), 4.05 – 3.80 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ 143.0, 139.5, 136.4, 127.0, 126.2, 113.6, 111.5, 99.2, 64.9. IR (film); 3117, 2884, 1720, 1569, 1528, 1507, 1333, 1218, 1067, 1011, 961, 887, 837, 805, 610 cm^{-1}. HRMS (ESI) calcd for $C_{10}H_{10}ClN_2O_2S$, $[M+H]^+$, 257.0146, found 257.0147.

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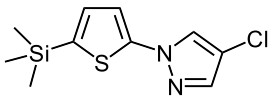
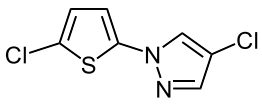


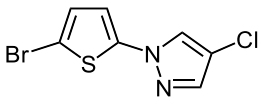
3f

4-Chloro-1-(5-(trimethylsilyl)thiophen-2-yl)-1H-pyrazole (**3f**); 97.8 mg (yield: 76%, 0.5 mmol scale), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1.0H), 7.58 (s, 1.0H), 7.05 – 7.04 (m, 2.0H), 0.32 (s, 9.0H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 139.5, 135.6, 132.9, 125.8, 115.8, 112.4, -0.3. IR (film); 3127, 2953, 2853, 1676, 1553, 1519, 1463, 1379, 1335, 1251, 1210, 1145, 1067, 1007, 977, 914, 843, 793, 755, 628, 599, 515 cm^{-1}. HRMS (ESI) calcd for $C_{10}H_{13}ClN_2SSi$, $[M+H]^+$, 257.0330, found 257.0332.



3g

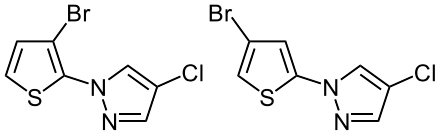
4-Chloro-1-(5-chlorothiophen-2-yl)-1H-pyrazole (**3g**); 89.2 mg (yield: 81%, 0.5 mmol scale), yellow solid (mp. 95- 96 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1.0H), 7.56 (s, 1.0H), 6.80 - 6.69 (m, 2.0H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 139.6, 125.8, 125.4, 124.9, 113.2, 112.8. IR (film); 3107, 3033, 1693, 1566, 1523, 1480, 1407, 1379, 1336, 1213, 1145, 1069, 989, 971, 916, 845, 817, 787, 639, 603 cm^{-1}. HRMS (ESI) calcd for $C_7H_5Cl_2N_2S$, $[M+H]^+$, 218.9545, found 218.9547.



3h

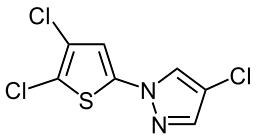
1-(5-Bromothiophen-2-yl)-4-chloro-1H-pyrazole (**3h**); 59.2 mg (yield: 42%, 0.5 mmol scale), white solid (mp. 92- 93 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1.0H), 7.57 (s, 1.0H), 6.91 (d, *J* = 4.0 Hz, 1.0H), 6.74 (d, *J* = 4.0 Hz, 1.0H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 139.7, 128.6, 125.5, 114.2, 112.8, 107.9. IR (film); 3108, 3030, 1631, 1560, 1519, 1473, 1404, 1379, 1336,

1143, 1062, 1012, 969, 907, 845, 813, 785, 639, 602, 481 cm^{-1}. HRMS (ESI) calcd for $C_7H_5BrClN_2S$, $[M+H]^+$, 262.9040, found 262.9039.



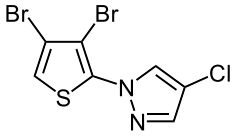
3i **3i'**

1-(3-Bromothiophen-2-yl)-4-chloro-1H-pyrazole(**3i**) and 1-(4-Bromothiophen-2-yl)-4-chloro-1H-pyrazole (**3i'**), isomer (5:1 based on NMR); 85.6mg (yield: 65%, 0.5 mmol scale), yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1.0H), 7.76 (s, 0.2H), 7.65 (s, 1.0H), 7.59 (s, 0.2H), 7.17 (d, *J* = 6.0 Hz, 1.0H), 6.97 (d, *J* = 1.2 Hz, 0.2H), 6.95 (d, *J* = 6.0 Hz, 0.9H), 6.92 (d, *J* = 1.6 Hz, 0.2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.0, 137.3, 129.5, 128.2, 125.6, 125.1, 122.5, 117.6, 116.6, 115.9, 113.1, 112.2, 108.6, 101.4. IR (film); 3109, 2955, 2921, 1691, 1560, 1516, 1462, 1382, 1331, 1234, 1180, 1082, 1005, 968, 918, 867, 793, 703, 642, 602 cm^{-1}. HRMS (ESI) calcd for $C_7H_5BrClN_2S$, $[M+H]^+$, 262.9040, found 262.9041.



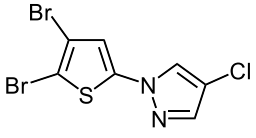
3j

4-Chloro-1-(4, 5-dichlorothiophen-2-yl)-1H-pyrazole (**3j**); 98.2 mg (yield: 78%, 0.5 mmol scale), white solid (mp. 113- 114 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.57 (s, 1H), 6.75 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 138.8, 125.1, 122.6, 119.9, 113.5, 112.9. IR (film); 3126, 3092, 2915, 2849, 1564, 1381, 1352, 1157, 1036, 970, 920, 849, 799, 641, 595, 504 cm^{-1}. HRMS (ESI) calcd for $C_7H_4Cl_3N_2S$, $[M+H]^+$, 252.9155, found 252.9155.



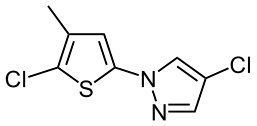
3k

4-Chloro-1-(3, 4-dibromothiophen-2-yl)-1H-pyrazole (**3k**); 71.8 mg (yield: 42%, 0.5 mmol scale), yellow solid (mp. 97- 98 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1.0H), 7.66 (s, 1.0H), 7.26 (s, 1.0H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 138.1, 127.7, 119.3, 113.1, 112.6, 104.6. IR (film); 3147, 3114, 2922, 2848, 1699, 1555, 1513, 1454, 1386, 1339, 1303, 1218, 1186, 1014, 967, 887, 851, 790, 728, 636, 598 cm^{-1}. HRMS (ESI) calcd for $C_7H_4Br_2ClN_2S$, $[M+H]^+$, 340.8145, found 340.8145.



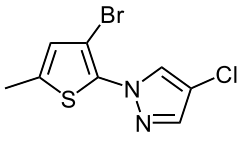
3l

4-Chloro-1-(4, 5-dibromothiophen-2-yl)-1H-pyrazole (**3l**); 73.0 mg (yield: 43%, 0.5 mmol scale), white solid (mp. 124- 125 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1.0H), 7.58 (s, 1.0H), 6.81 (s, 1.0H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 140.2, 125.2, 116.0, 113.5, 112.6, 106.5. IR (film); 3126, 3087, 1558, 1378, 1342, 1141, 982, 914, 849, 799, 639, 595, 500 cm^{-1}. HRMS (ESI) calcd for $C_7H_4Br_2ClN_2S$, $[M+H]^+$, 340.8145, found 340.8142.



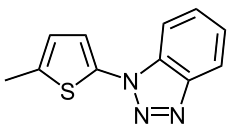
3m

4-Chloro-1-(5-chloro-4-methylthiophen-2-yl)-1H-pyrazole (**3m**); 110.9 mg (yield: 95%, 0.5 mmol scale), white solid (mp. 78- 79 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1.0H), 7.54 (s, 1.0H), 6.66 (s, 1.0H), 2.16 (s, 3.0H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 138.3, 133.3, 125.3, 120.3, 115.5, 112.6, 13.7. IR (film); 3126, 3061, 2958, 2925, 1696, 1581, 1531, 1499, 1410, 1380, 1336, 1241, 1209, 1144, 1052, 1011, 969, 896, 843, 805, 642, 601, 506 cm^{-1}. HRMS (ESI) calcd for $C_8H_7Cl_2N_2S$, $[M+H]^+$, 232.9702, found 232.9701.



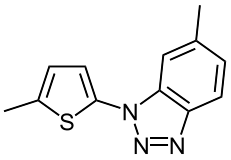
3n

1-(3-Bromo-5-methylthiophen-2-yl)-4-chloro-1H-pyrazole (**3n**); 66.6 mg (yield: 48%, 0.5 mmol scale), yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1.0H), 7.62 (s, 1.0H), 6.62 (s, 1.0H), 2.46 (s, 3.0H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 137.2, 134.2, 128.3, 127.0, 111.8, 101.1, 15.5. IR (film); 3144, 2955, 2916, 2854, 1682, 1637, 1567, 1507, 1442, 1401, 1383, 1330, 1235, 1185, 1141, 1008, 964, 920, 849, 816, 790, 648, 601, 524 cm^{-1}. HRMS (ESI) calcd for $C_8H_7BrClN_2S$, $[M+H]^+$, 276.9196, found 276.9196.

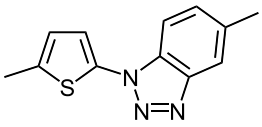


4a

1-(5-Methylthiophen-2-yl)-1H-benzo[d][1,2,3]triazole (**4a**); 62.3 mg (yield: 58%, 0.5 mmol scale), white solid (mp. 72- 75 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.8 Hz, 1.0H), 7.71 (d, *J* = 11.2 Hz, 1.0 H), 7.57 - 7.53 (m, 1.0H), 7.45 - 7.41 (m, 1.0H), 7.17 - 7.15 (m, 1.0H), 6.80 - 6.78 (m, 1.0H), 2.56 (s, 3.0H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 138.4, 134.3, 132.8, 128.5, 124.5, 124.1, 120.2, 120.1, 110.2, 15.5. IR (film); 3099, 3073, 2963, 2913, 2851, 1750, 1608, 1563, 1510, 1445, 1378, 1277, 1251, 1180, 1135, 1067, 1005, 955, 802, 736, 506 cm^{-1}. HRMS (ESI) calcd for $C_{11}H_{10}N_3S$, $[M+H]^+$, 216.0590, found 216.0586.

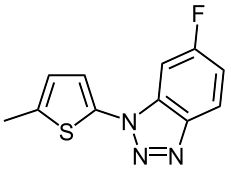


4b

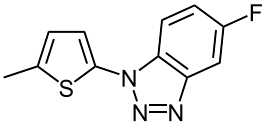


4b'

6-Methyl-1-(5-methylthiophen-2-yl)-1H-benzo[d][1,2,3]triazole(**4b**) and 5-methyl-1-(5-methylthiophen-2-yl)-1H-benzo[d][1,2,3]triazole(**4b'**); isomer (1.3:1 based on NMR); 51.0mg (yield: 45%, 0.5 mmol scale), yellow solid (mp. 68- 72 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 0.8H), 7.84 (s, 1.0H), 7.58 (d, *J* = 8.8 Hz, 1.0H), 7.46 (s, 0.8H), 7.37 - 7.35 (m, 1.0H), 7.24 - 7.22 (m, 0.8H), 7.14 - 7.12 (m, 1.8H), 6.78 - 6.76(m, 1.8H), 2.54 - 2.52 (m, 11.2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 144.4, 139.3, 138.1, 137.9, 134.6, 134.5, 134.4, 133.2, 131.2, 130.5, 126.7, 124.1, 120.1, 119.6, 119.5, 119.0, 109.7, 109.4, 21.9, 21.3, 15.3 (8), 15.3 (6). IR (film); 3096, 2919, 2848, 1617, 1567, 1513, 1445, 1383, 1288, 1253, 1182, 1138, 1070,792, 586, 500 cm^{-1}. HRMS (ESI) calcd for $C_{12}H_{12}N_3S$, $[M+H]^+$, 230.0746, found 230.0744.

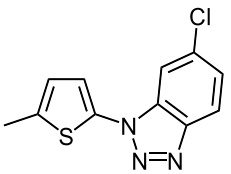


4c

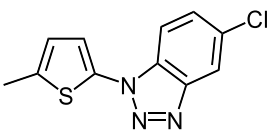


4c'

6-Fluoro-1-(5-methylthiophen-2-yl)-1H-benzo[d][1,2,3]triazole (**4c**) and 5-fluoro-1-(5-methylthiophen-2-yl)-1H-benzo[d][1,2,3]triazole(**4c'**); isomer (1:1 based on NMR); 59.2mg (yield: 51%, 0.5 mmol scale), white solid (mp. 106- 109 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 - 8.05 (m, 0.9H), 7.74 - 7.72 (m, 1.1H), 7.69 - 7.66 (m, 1.1H), 7.37 - 7.32 (m, 2.0H), 7.22 - 7.17 (m, 0.9H), 7.15 (d, *J* = 3.6 Hz, 1.1H), 7.13 (d, *J* = 3.6 Hz, 0.9H), 6.80 - 6.79 (m, 2.0H), 2.56 (3) - 2.56 (0) (m, 6.0H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 161.6, 161.0, 158.6, 146.1, 146.0, 142.6, 138.8, 138.7, 133.8, 133.7, 133.4, 133.3, 129.9, 124.2, 121.7, 121.6, 120.6, 120.5, 118.4, 118.1, 114.6, 114.3, 111.3, 111.2, 104.9, 104.6, 96.4, 96.1, 15.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -110.1, -116.8. IR (film); 3108, 2916, 1738, 1620, 1587, 1567, 1510, 1490, 1442, 1289, 1251, 1177, 1129, 1073, 949, 849, 801, 595, 500 cm^{-1}. HRMS (ESI) calcd for $C_{11}H_9FN_3S$, $[M+H]^+$, 234.0496, found 234.0490.



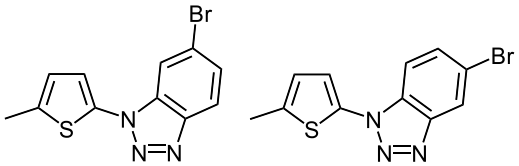
4d



4d'

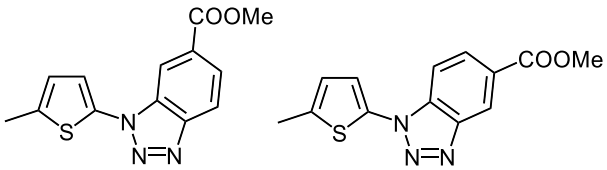
6-Chloro-1-(5-methylthiophen-2-yl)-1H-benzo[d][1,2,3]triazole (**4d**) and 5-chloro-1-(5-methylthiophen-2-yl)-1H-benzo[d][1,2,3]triazole (**4d'**); isomer (1:1 based on NMR); 69.0mg (yield: 55%, 0.5 mmol scale), white solid (mp. 94- 96 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1.0H), 8.02 (d, *J* = 8.8 Hz, 1.0H), 7.70 (s, 1.0H), 7.64 (d, *J* = 8.8 Hz, 1.0H), 7.50 (d, *J* = 8.4 Hz, 1.0H), 7.38 (d, *J* = 8.8 Hz, 1.0H), 7.14 (d, *J* = 1.2 Hz, 2.0H), 6.80 - 6.79 (m, 2.0H), 2.56 (s, 6.0H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 144.4, 138.9, 138.8, 135.0, 133.7, 133.5, 133.4, 131.5, 130.3, 129.3, 125.7, 124.2, 124.2, 121.0, 120.8, 120.6, 119.5, 111.2, 110.1, 15.5. IR (film); 3090, 2919, 1608, 1569, 1505, 1469, 1437, 1277, 1215,1064, 958, 917, 852, 799, 722, 586 cm^{-1}. HRMS (ESI) calcd for $C_{11}H_9ClN_3S$, $[M+H]^+$, 250.0200, found 250.0195.



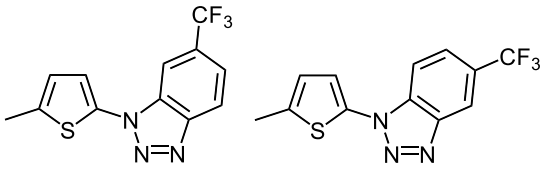
4e **4e'**

6-Bromo-1-(5-methylthiophen-2-yl)-1H-benzo[d][1,2,3]triazole (**4e**) and 5-bromo-1-(5-methylthiophen-2-yl)-1H-benzo[d][1,2,3]triazole (**4e'**); isomer (1:1 based on NMR); 58.0 mg (yield: 40%, 0.5 mmol scale), white solid (mp. 77- 80 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1.0H), 7.96 (d, *J* = 8.8 Hz, 1.0H), 7.87 (s, 1.0H), 7.64 - 7.57 (m, 2.0H), 7.53 - 7.50 (m, 1.0H), 7.14 (d, *J* = 3.6 Hz, 2.0H), 6.80 - 6.78 (m, 2.0H), 2.56 - 2.55 (m, 6.0H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 144.6, 138.9, 138.8, 133.8, 133.6, 133. 5, 131.8, 131.7, 128.2, 124.2 (0), 124.2 (8), 122.9, 122.7, 121.2, 120.9, 120.6, 117.7, 113.2, 111.5, 15.5 (7), 15.5 (6). IR (film); 3090, 2922, 2854, 1726, 1607, 1560, 1501, 1457, 1437, 1277, 1212, 1177, 1059, 946, 908, 855, 801, 707, 586, 427cm^{-1}. HRMS (ESI) calcd for $C_{11}H_9BrN_3S$, $[M+H]^+$, 293.9695, found 293.9689.



4f **4f'**

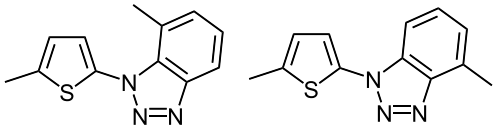
Methyl 1-(5-methylthiophen-2-yl)-1H-benzo[d][1,2,3]triazole-6-carboxylate (**4f**) and methyl 1-(5-methylthiophen-2-yl)-1H-benzo[d][1,2,3]triazole-5-carboxylate (**4f'**); isomer (2:1 based on NMR); 47.6mg (yield: 35%, 0.5 mmol scale), white solid (mp. 96- 98 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 0.5H), 8.43 (s, 1.0H), 8.25 - 8.23 (m, 0.5H), 8.14 - 8.13 (m, 1.1H), 8.11 - 8.08 (m, 0.9H), 7.73 (d, *J* = 8.4 Hz, 0.6H), 7.22 (d, *J* = 3.6 Hz, 1.0H), 7.19 (d, *J* = 3.6 Hz, 0.5H), 6.85 - 6.82 (m, 1.1H), 6.82 - 6.80 (m, 0.5H), 4.00 - 3.99 (7) (m, 5.0H), 2.59 - 2.57 (m, 4.9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2 (1), 166.2 (7), 147.8, 145.6, 139.1, 139.0, 134.9, 133.6, 133.5, 132.7, 130.2, 129.3, 126.9, 125.2, 124.3, 124.2, 122.9, 121.0, 120.9, 120.1, 112.8, 110.1, 52.6, 52.5, 15.5 (8), 15.5 (6). IR (film); 3087, 2952, 2919, 2851, 1720, 1619, 1561, 1440, 1289, 1253, 1221, 1088, 1047, 979, 802, 769, 746, 503 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{12}N_3O_2S$, $[M+H]^+$, 274.0645, found 274.0647.



4g **4g'**

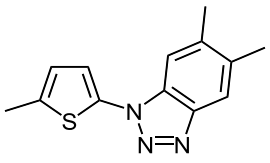
1-(5-Methylthiophen-2-yl)-6-(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (**3n**) and 1-(5-methylthiophen-2-yl)-5-(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (**3n'**); isomer (2:1 based on

NMR); 72.2mg (yield: 51%, 0.5 mmol scale), white solid (mp. 53- 54 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1.0H), 8.24 (d, *J* = 8.8 Hz, 2.0H), 8.02 (s, 2.0H), 7.84 - 7.78 (m, 2.2H), 7.68 (d, *J* = 8.8 Hz, 2.0H), 7.21 - 7.19 (m, 3H), 6.88 - 6.81 (m, 3H), 2.59 - 2.58 (m, 9.0H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 145.1, 139.5, 139.3, 134.3 (9), 133.3 (4), 133.1, 132.4, 131.1, 130.8, 130.5, 130.2, 128.6, 128.3, 127.8, 127.6, 127.4, 127.2, 127.1, 126.8, 126.7, 125.2, 125.2 (7), 125.2 (5), 125.1 (2), 125.1 (0), 124.4, 124.3, 122.5, 122.4, 121.5, 121.3 (1), 121.3 (7), 121.2, 119.7, 118.5 (0), 118.5 (6), 118.4 (2), 118.4 (7), 111.3, 108.6, 108.5 (4), 108.5 (0), 108.5 (5), 15.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -110.1, -116.8. IR (film); 2955, 2922, 2854, 1741, 1629, 1564, 1502, 1445, 1318, 1280, 1215, 1168, 1132, 1059, 952, 819, 684 cm^{-1}. HRMS (ESI) calcd for $C_{12}H_9F_3N_3S$, $[M+H]^+$, 284.0464, found 284.0466.



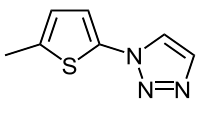
4h **4h'**

7-Methyl-1-(5-methylthiophen-2-yl)-1H-benzo[d][1,2,3]triazole (**4h**) and 5-methyl-1-(5-methylthiophen-2-yl)-1H-benzo[d][1,2,3]triazole (**4h'**); isomer (1.7:1 based on NMR); 46.4 mg (yield: 41%, 0.5 mmol scale), yellow solid (mp. 55- 57 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 0.6H), 7.52 (d, *J* = 8.2 Hz, 1.0H), 7.45 - 7.41 (m, 1.1H), 7.31 – 7.23 (m,1.5H), 7.20 – 7.18 (m, 1.0H), 7.15 (d, *J* = 4.0 Hz, 1.0H), 7.08 (d, *J* = 3.6 Hz, 0.6H), 6.79 – 6.77 (m, 1.6H), 2.84 (s, 3.0H), 2.57 – 2.55 (m, 4.8H), 2.31 (s, 1.9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 145.5, 141.5, 138.3, 134.6, 134.2, 133.9, 132.8, 131.2, 129.6, 128.5, 127.7, 124.5, 124.4, 124.1, 123.6, 121.6, 120.2, 117.9, 107.5, 17.4, 16.7, 15.8, 15.5. IR (film); 3111, 2913, 2851, 1608, 1561, 1511, 1454, 1383, 1280, 1248, 1171, 1070, 1038, 796, 751, 500 cm^{-1}. HRMS (ESI) calcd for $C_{12}H_{12}N_3S$, $[M+H]^+$, 230.0746, found 230.0744.



4i

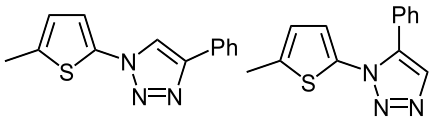
5,6-Dimethyl-1-(5-methylthiophen-2-yl)-1H-benzo[d][1,2,3]triazole (**4i**); 37.7mg (yield: 50%, 0.5 mmol scale), yellow solid (mp. 120- 122 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1.1H), 7.45 (s, 1.0H), 7.12 (d, *J* = 3.6 Hz, 1.0H), 6.77 (d, *J* = 4.8 Hz, 1.0H), 2.55 (s, 3.0H), 2.42 (s, 3.0H), 2.41 (s, 3.0H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 139.0, 137.9, 134.7, 134.3, 131.8, 124.0, 119.7, 119.2, 109.7, 20.9, 20.3, 15.4. IR (film); 3093, 3061, 2969, 2913, 2854, 1614, 1567, 1507, 1451, 1375, 1342, 1298, 1242, 1100, 1067, 1002, 946, 893, 808, 495 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{14}N_3S$, $[M+H]^+$, 244.0903, found 244.0898.



4j

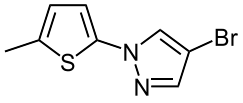
1-(5-Methylthiophen-2-yl)-1H-1,2,3-triazole (**4j**); 27.2mg (yield: 33%, 0.5 mmol scale), white

solid (mp. 59- 61 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 1.2 Hz, 1.0H), 7.78 (d, *J* = 1.2 Hz, 1.0H), 7.02 (d, *J* = 3.6 Hz, 1.0H), 6.68 (d, *J* = 3.6 Hz, 1.0H), 2.51 (s, 3.0H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 135.3, 134.0, 123.9, 122.9, 118.2, 15.3. IR (film); 3128, 2928, 2860, 1720, 1567, 1502, 1463, 1430, 1327, 1242, 1218, 1159, 1085, 1035, 926, 793, 503 cm^{-1}. HRMS (ESI) calcd for $C_7H_8N_3S$, $[M+H]^+$, 166.0433, found 166.0432.



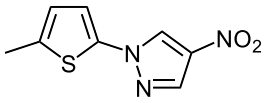
4k **4k'**

1-(5-Methylthiophen-2-yl)-4-phenyl-1H-1,2,3-triazole (**4k**) and 1-(5-methylthiophen-2-yl)-5-phenyl-1H-1,2,3-triazole (**4k'**); isomer (1.3:1 based on NMR); 64.8 mg (yield: 54%, 0.5 mmol scale), white solid (mp. 132- 136 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.20 (s, 1.0H), 8.11 (s, 0.8H), 7.93 - 7.90 (m, 2.0H), 7.51 - 7.47 (m, 3.0H), 7.47 – 7.38 (m, 2.4H), 7.34 (d, *J* = 2.7 Hz, 1.0H), 6.99 (d, *J* = 3.6 Hz, 0.8H), 6.87 - 6.86 (m, 1.0H), 6.80 - 6.79 (m, 0.8H), 2.49 (m, 3.0H), 2.45 (m, 2.4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.2, 140.2, 138.8, 137.0, 134.9, 133.0, 132.9, 129.9, 129.7, 129.1, 128.9, 128.7, 128.5, 128.4, 125.9, 125.4, 124.6, 124.6, 120.2, 118.0, 15.1, 15.0. IR (film); 3129, 3061, 2919, 2845, 1744, 1569, 1513, 1478, 1451, 1419, 1233, 1035, 935, 808, 763, 689, 485 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{12}N_3S$, $[M+H]^+$, 242.0746, found 242.0749.



4l

4-Bromo-1-(5-methylthiophen-2-yl)-1H-pyrazole (**4l**); 81.4mg (yield: 67%, 0.5 mmol scale), white solid (mp. 75- 78 °C).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1.0H), 7.58 (s, 1.0H), 6.79 (d, *J* = 3.6 Hz, 1.0H), 6.58 - 6.57 (m, 1.0H), 2.45 (s, 3.0H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 139.9, 135.5, 128.0, 123.6, 114.8, 95.2, 15.3. IR (film); 3120, 2913, 2851, 1717, 1682, 1572, 1520, 1496, 1434, 1412, 1375, 1330, 1212, 1159, 1132, 1044, 1005, 946, 916, 843, 793, 645, 598, 506 cm^{-1}. HRMS (ESI) calcd for $C_8H_8BrN_2S$, $[M+H]^+$, 242.9586, found 242.9578.



4m

1-(5-Methylthiophen-2-yl)-4-nitro-1H-pyrazole (**4m**); 45.1mg (yield: 43%, 0.5 mmol scale), yellow solid (mp. 118- 119 °C).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1.0H), 8.19 (s, 1.0H), 6.98 (d, *J* = 3.2 Hz, 1.0H), 6.67 - 6.66 (m, 1.0H), 2.50 (s, 3.0H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 137.8, 136.8, 136.5, 126.3, 124.1, 117.0, 15.4. IR (film); 3135, 2916, 2848, 1560, 1528, 1501, 1407, 1216, 1248, 1191, 1153, 1064, 1000, 908, 881, 813, 780, 746, 589, 562, 497 cm^{-1}. HRMS (ESI) calcd for $C_8H_8N_3O_2S$, $[M+H]^+$, 210.0332, found 210.0339.

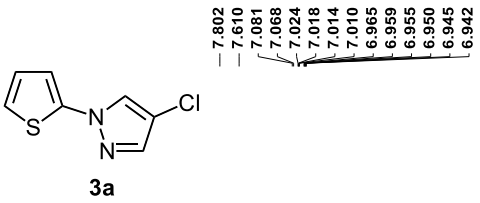
Reference

(1) Damschroder, R. E.; Peterson, W. D. *Org. Synth.* **1940**, *20*, 16

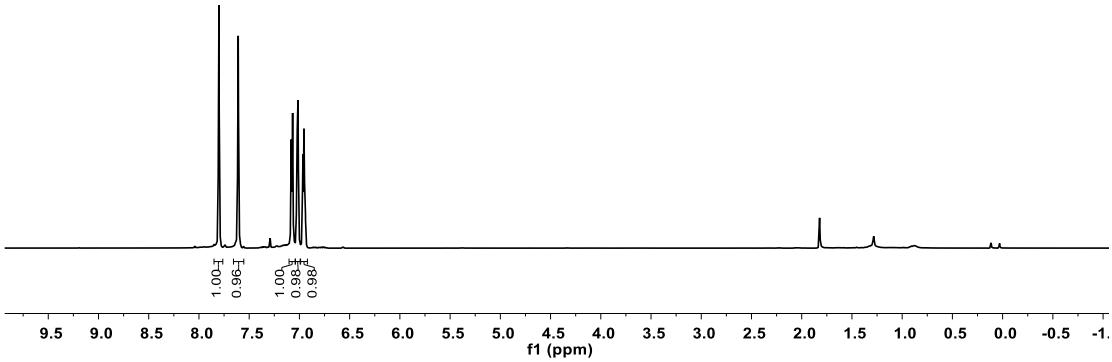
(2) Ueda, S.; Su, M.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2011**, *50*, 8944

(3) Chen, X.; Huang, X; He, Q.; Xie, Y.; Yang, C. *Chem. Commun*. **2014**, *50*, 3996

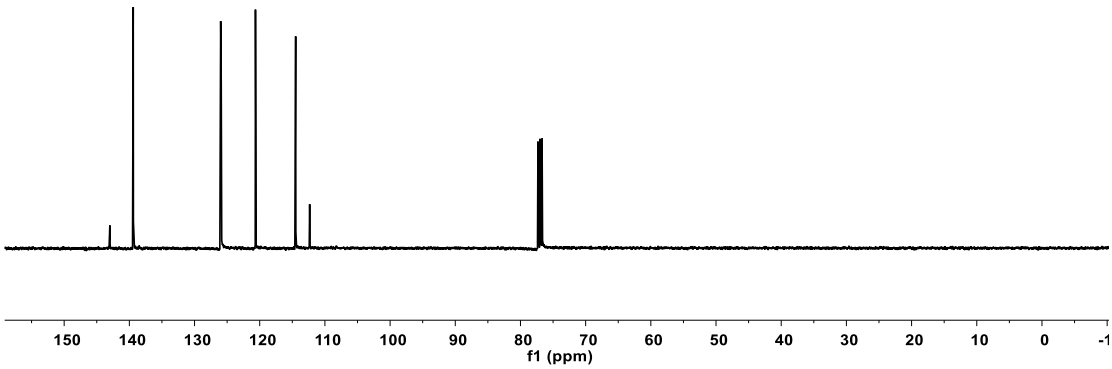
NMR Spectra of Products

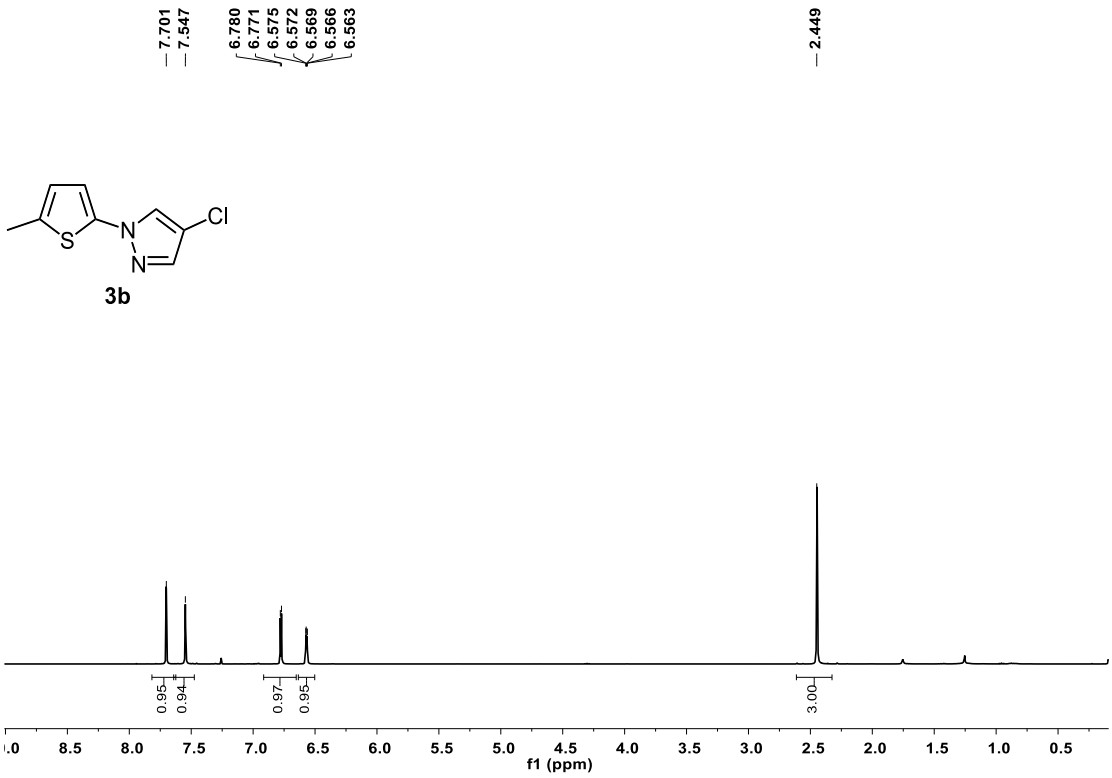


3a



3a

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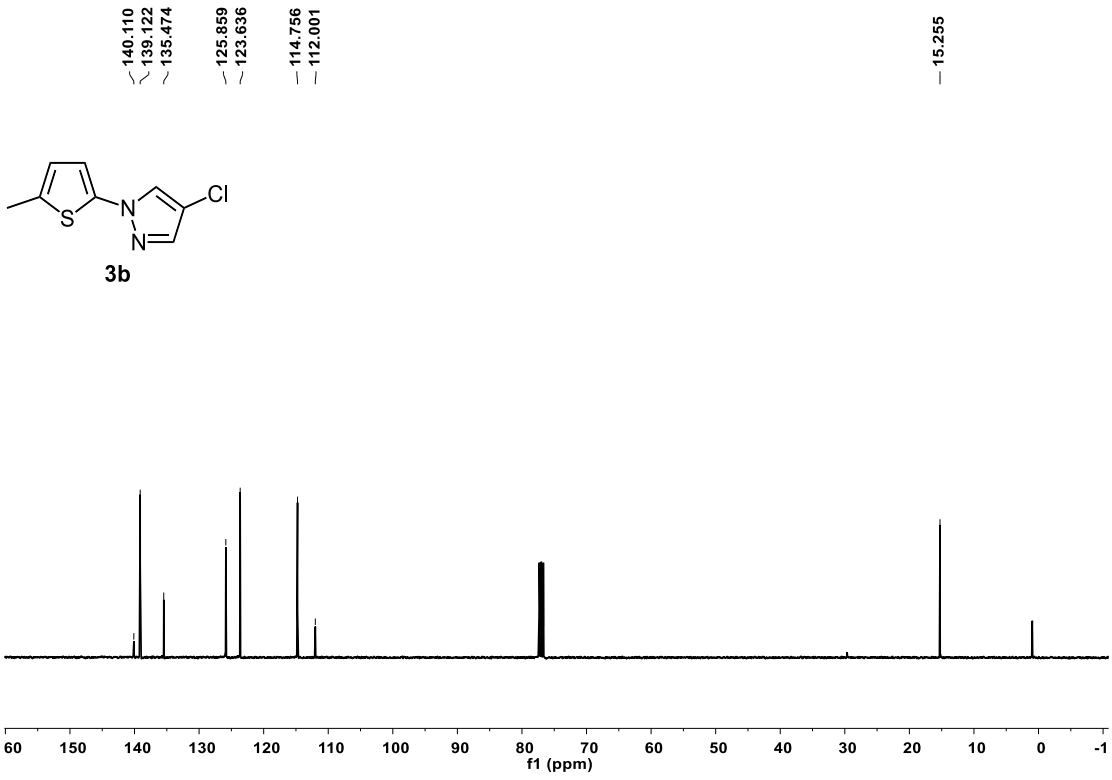
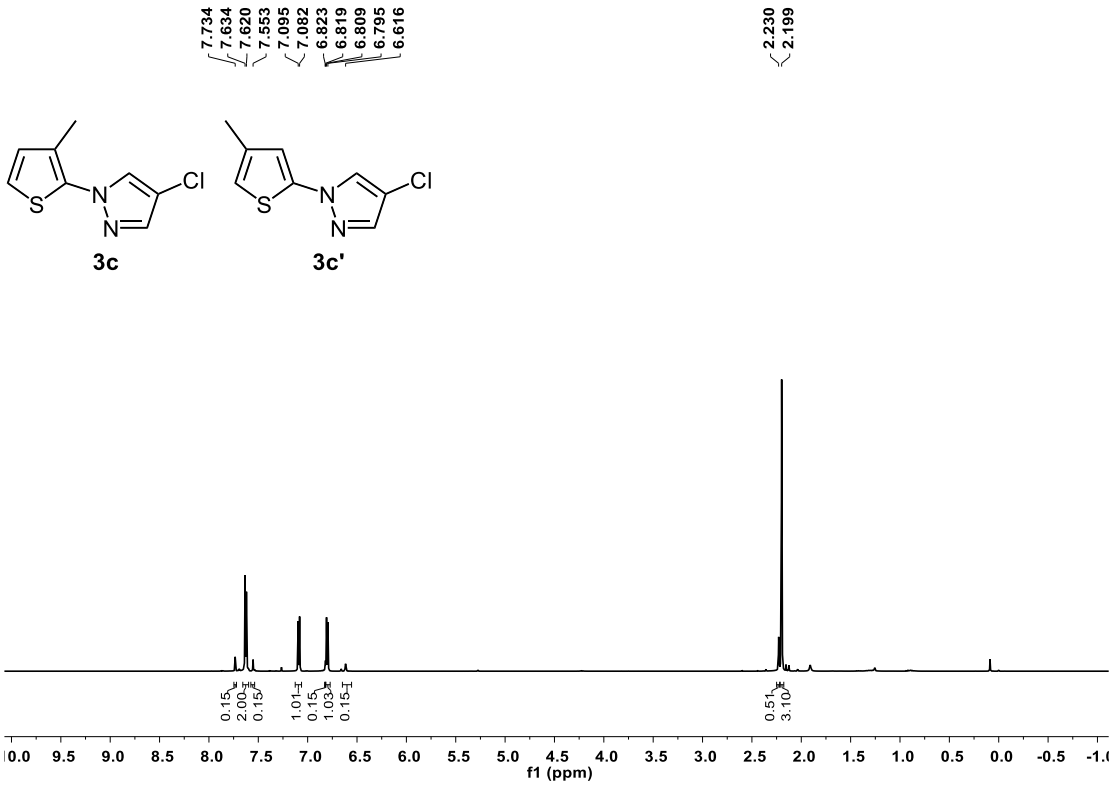
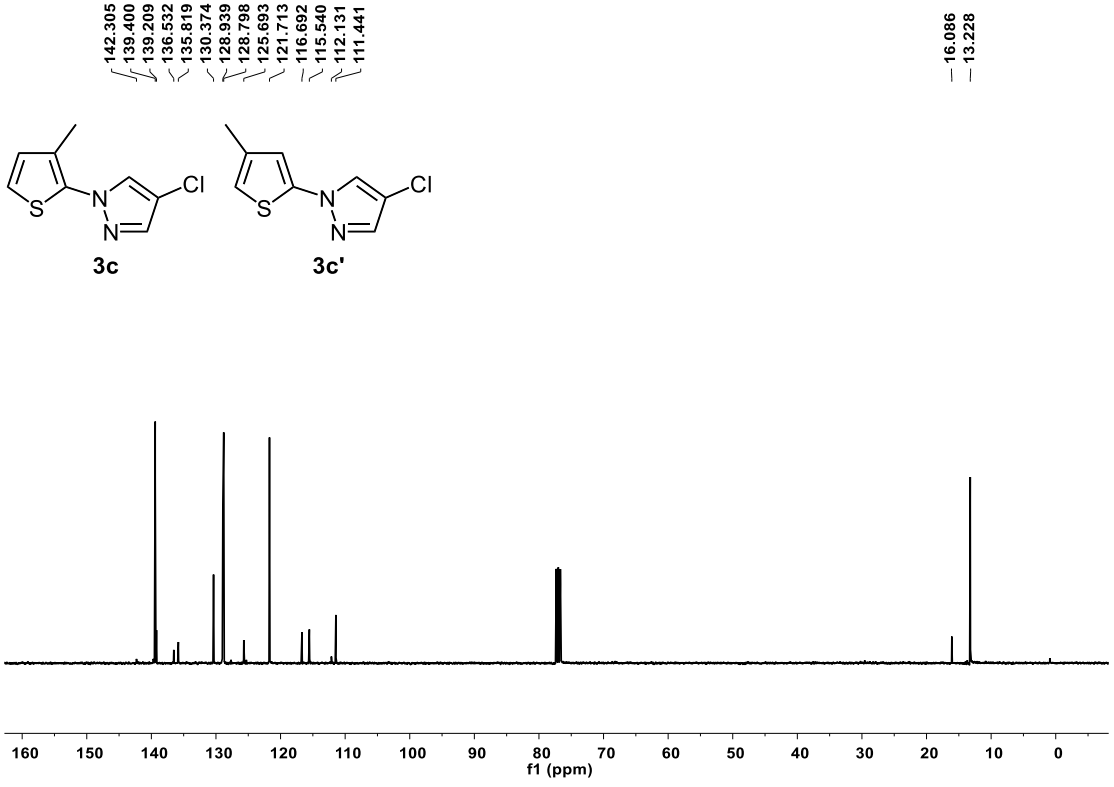
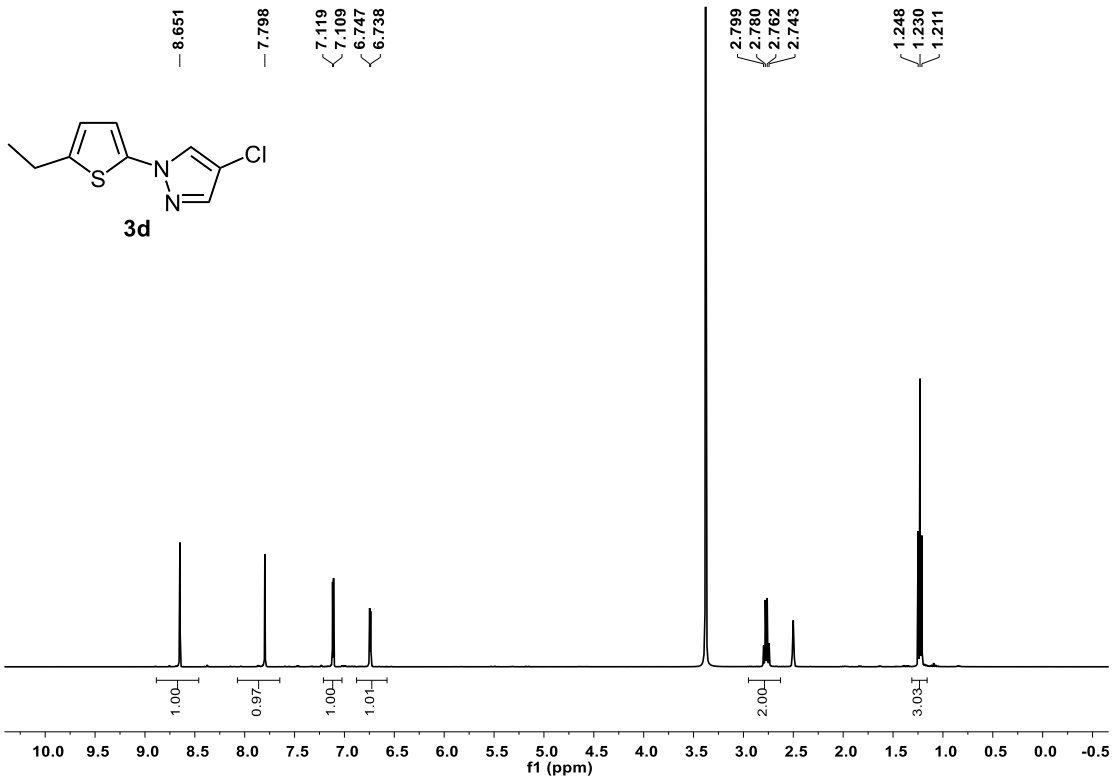
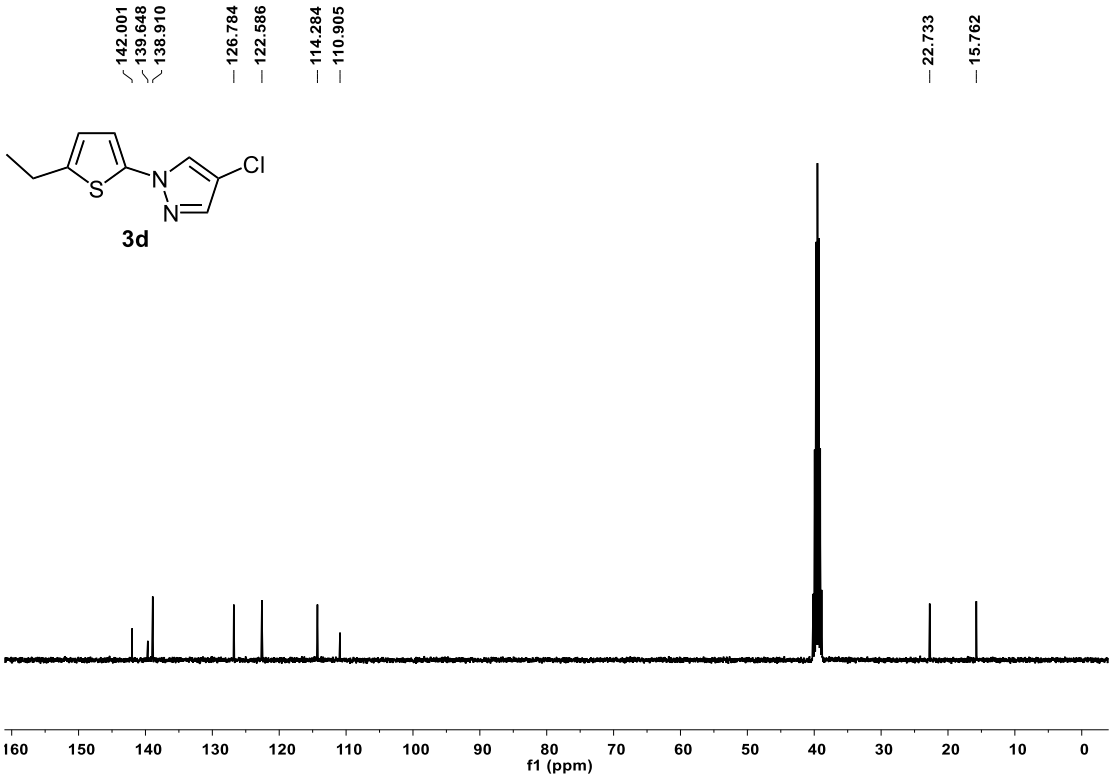
7.547
6.780
6.771
6.575
6.572
6.569
6.566
6.563
2.449
Cl
S
N
N
3b
0.95
0.94
0.97
0.95
3.00
f1 (ppm)

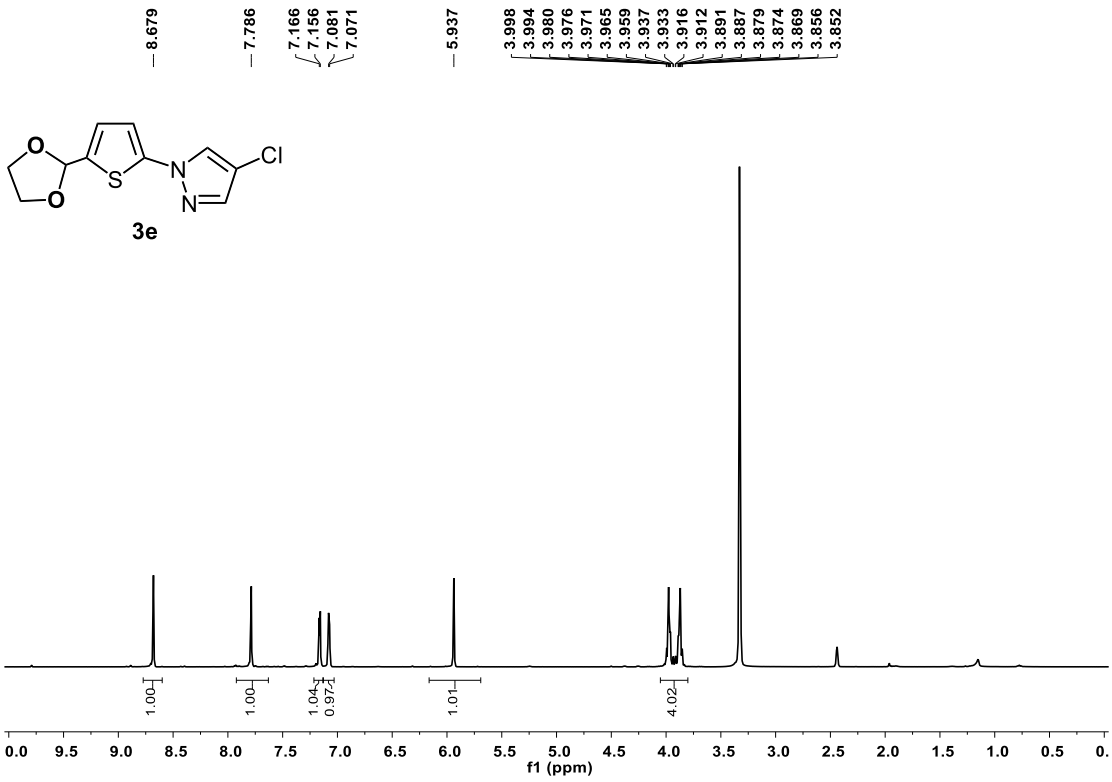

140.110
139.122
135.474
125.859
123.636
114.756
112.001
15.255
Cl
S
N
N
3b
f1 (ppm)

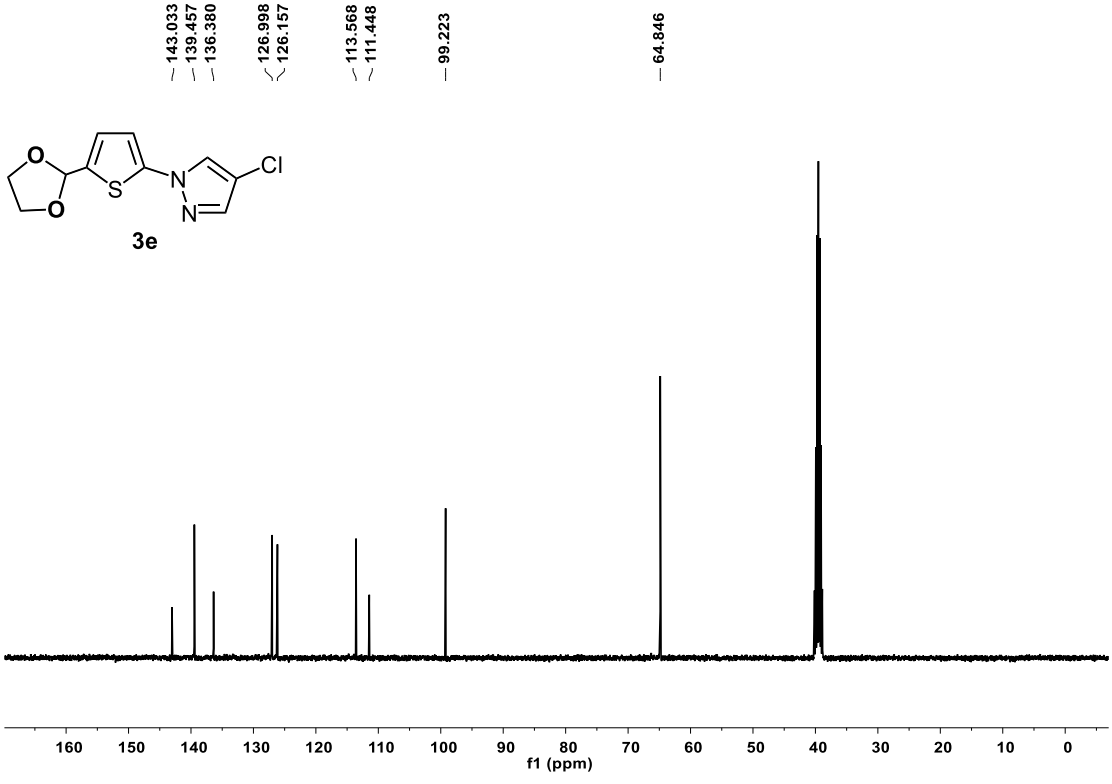

7.734
7.634
7.620
7.553
7.095
7.082
6.823
6.819
6.809
6.795
6.616
2.230
2.199
Cl
S
N
N
3c
3c'
0.15
2.00
0.15
1.01
0.15
1.03
0.15
0.51
3.10
f1 (ppm)

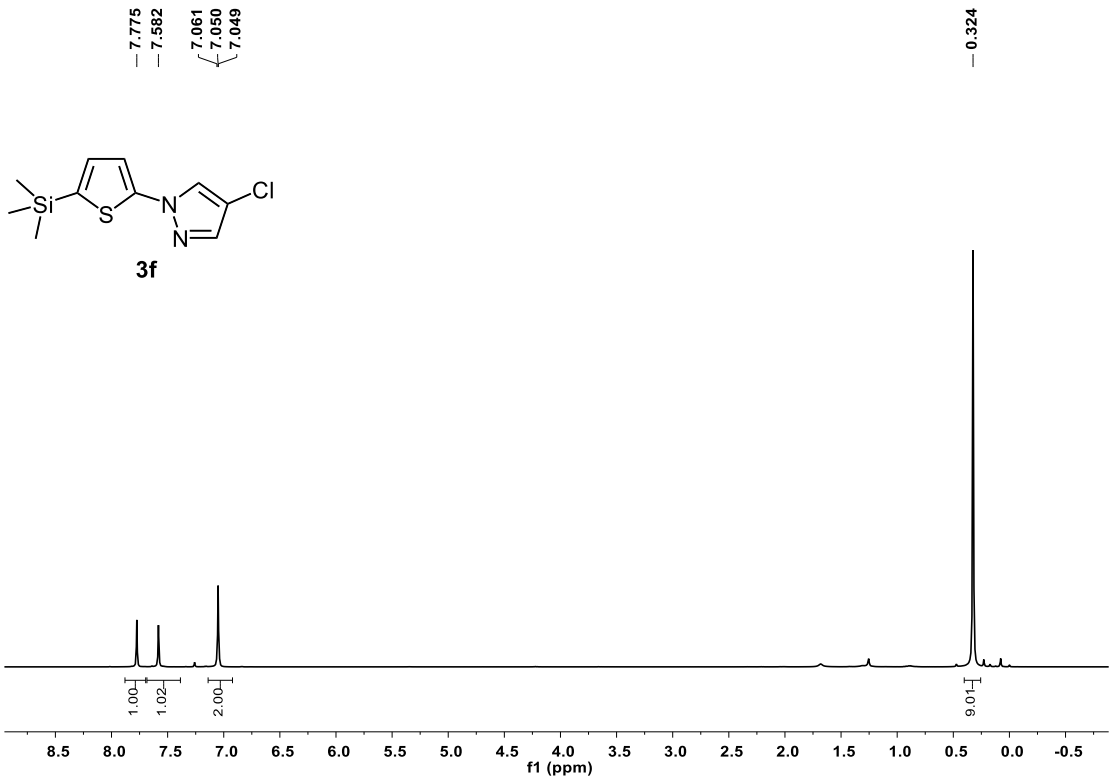

142.305
139.400
139.209
136.532
135.819
130.374
128.939
128.798
125.693
121.713
116.692
115.540
112.131
111.441
16.086
13.228
Cl
S
N
N
3c
3c'
f1 (ppm)

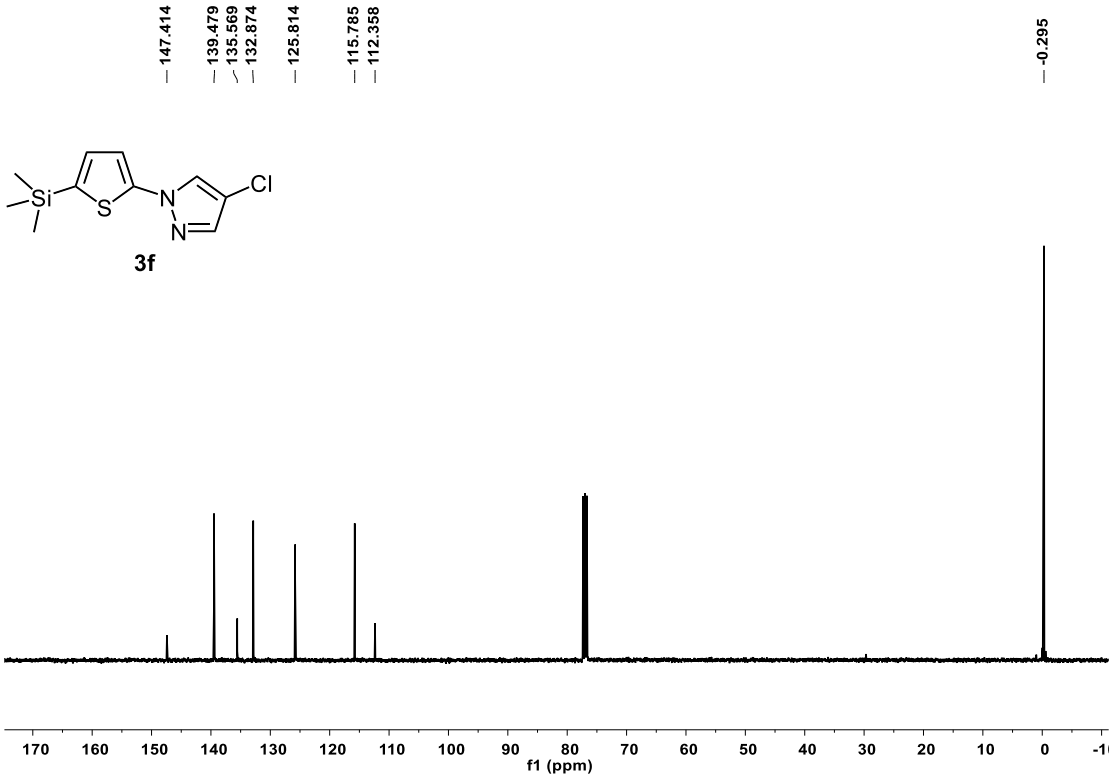

8.651
7.798
7.119
7.109
6.747
6.738
2.799
2.780
2.762
2.743
1.248
1.230
1.211
Cl
S
N
N
3d
1.00
0.97
1.00
1.01
2.00
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

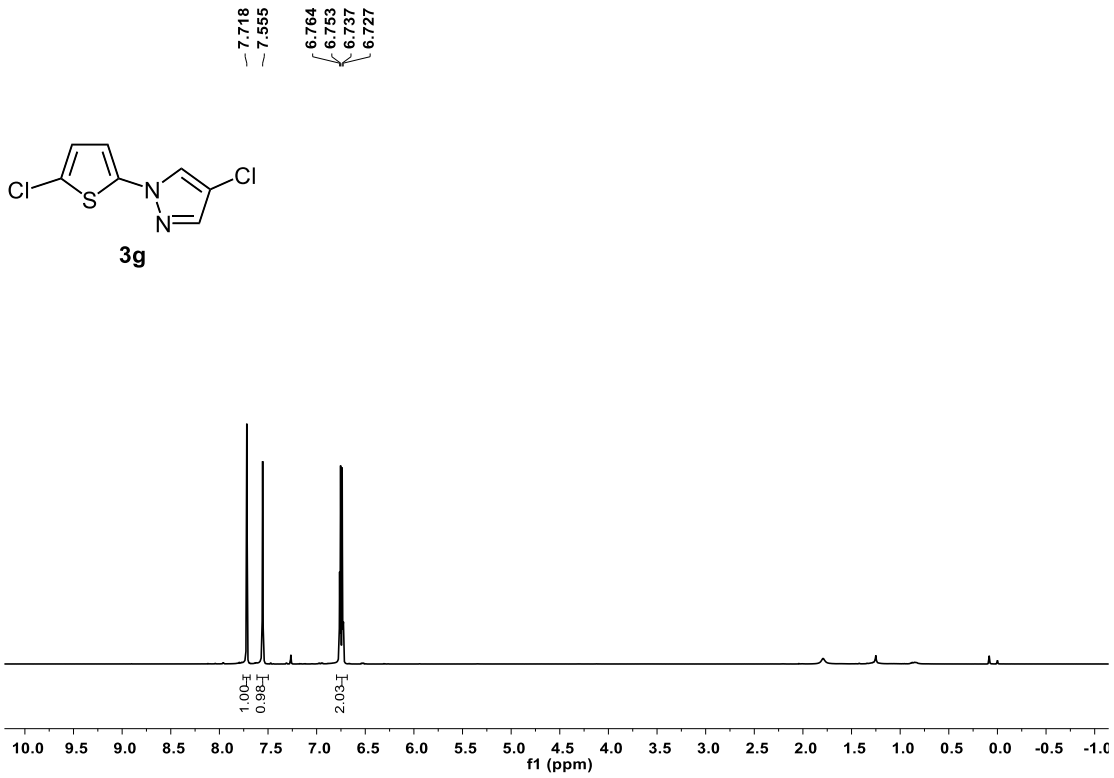

142.001
139.648
138.910
126.784
122.586
114.284
110.905
22.733
15.762
Cl
S
N
N
3d
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

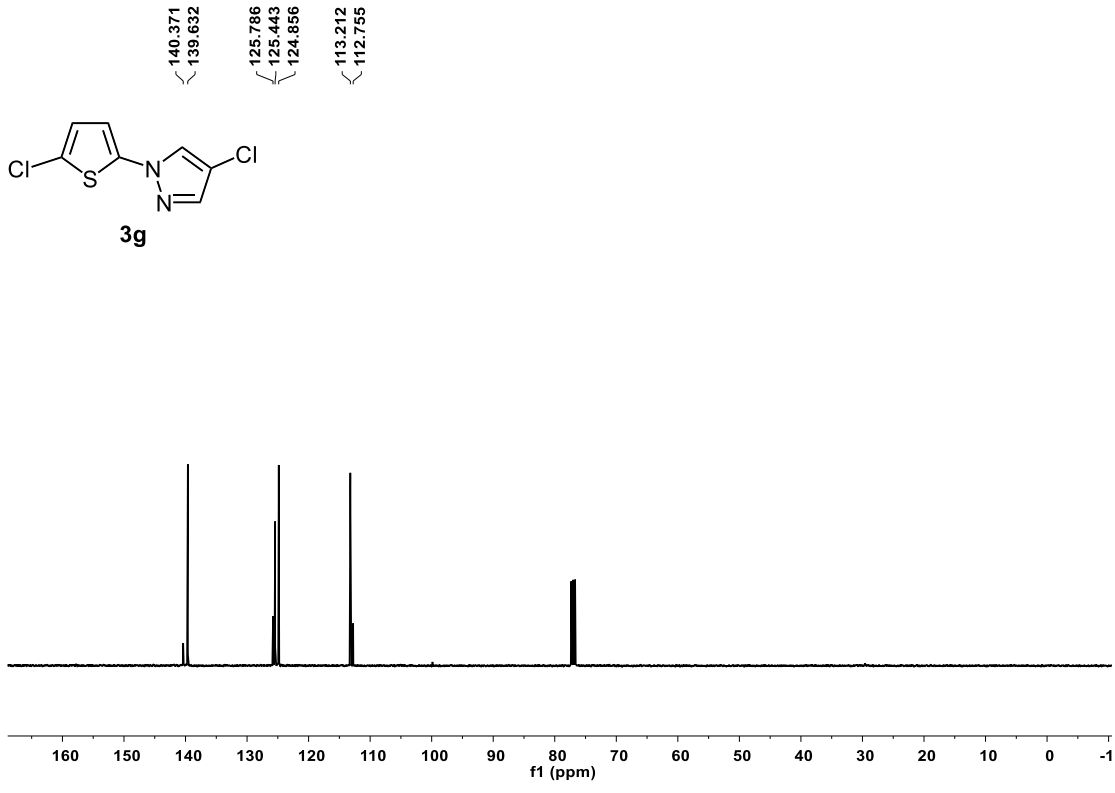

8.679
7.786
7.166
7.156
7.081
7.071
5.937
3.998
3.994
3.980
3.976
3.971
3.965
3.959
3.937
3.933
3.916
3.912
3.891
3.887
3.879
3.874
3.869
3.856
3.852
O
O
S
N
N
Cl
3e
1.00
1.00
1.04
0.97
1.01
4.02
f1 (ppm)

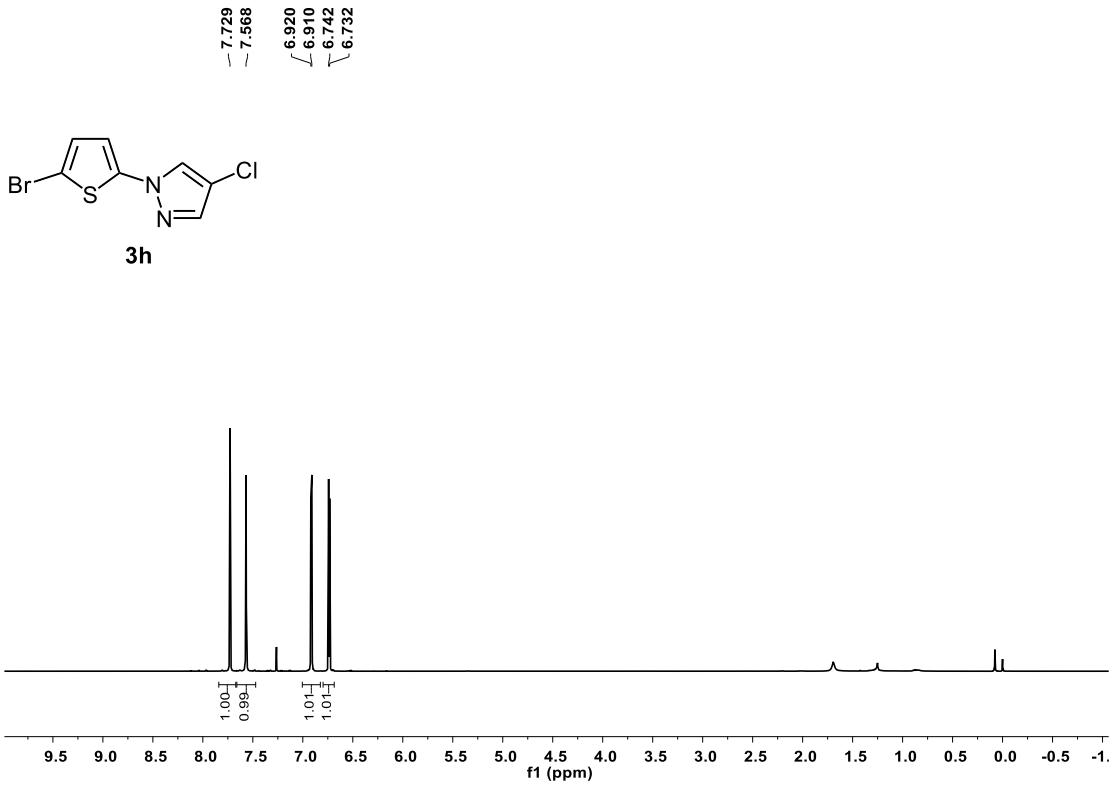

143.033
139.457
136.380
126.998
126.157
113.568
111.448
99.223
64.846
O
O
S
N
N
Cl
3e
f1 (ppm)


7.775
7.582
7.061
7.050
7.049
0.324
Si
S
N
N
Cl
3f
1.00
1.02
2.00
9.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


147.414
139.479
135.569
132.874
125.814
115.785
112.358
-0.295
Si
S
N
N
Cl
3f
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.718
7.555
6.764
6.753
6.737
6.727
Cl
S
N
N
Cl
3g
1.00
0.98
2.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


140.371
139.632
125.786
125.443
124.856
113.212
112.755
Cl
S
N
N
Cl
3g
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.568
6.920
6.910
6.742
6.732
Br
S
N
N
Cl
3h
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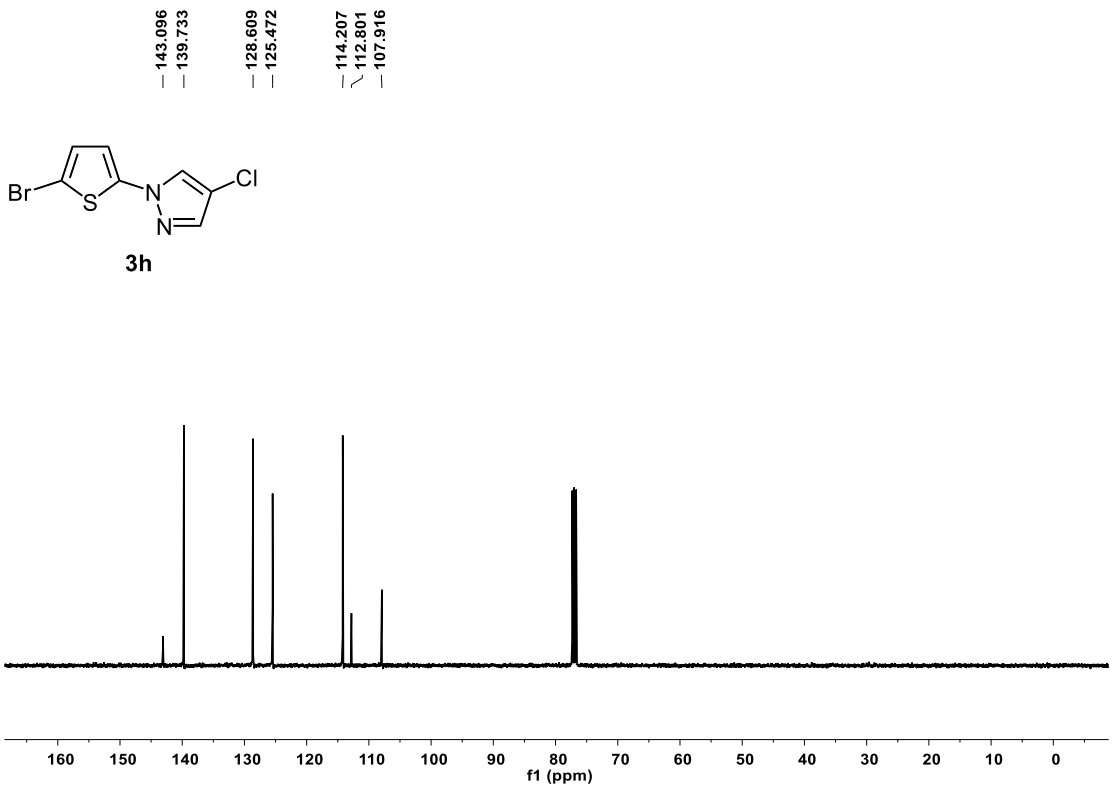
0.99
1.01
1.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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139.733
128.609
125.472
114.207
112.801
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Br
S
N
N
Cl
3h
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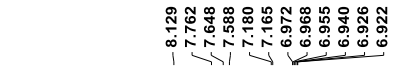
f1 (ppm)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7.165
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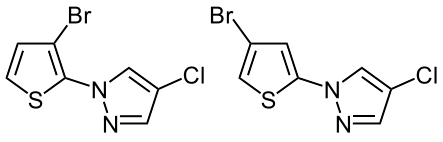
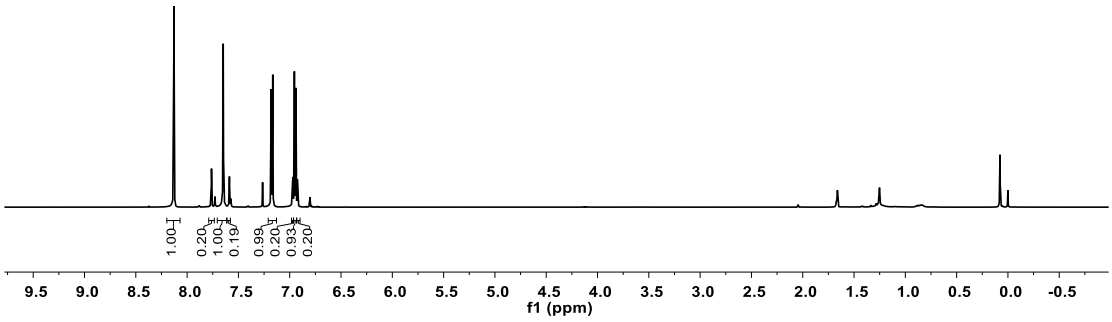
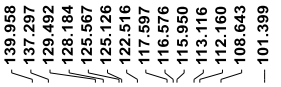
6.968
6.955
6.940
6.926
6.922


Br
Cl
S
N
N
Br
Cl
S
N
N

3i **3i'**


1.00
0.20
1.00
0.19
0.99
0.20
0.93
0.20
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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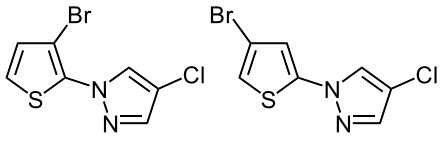
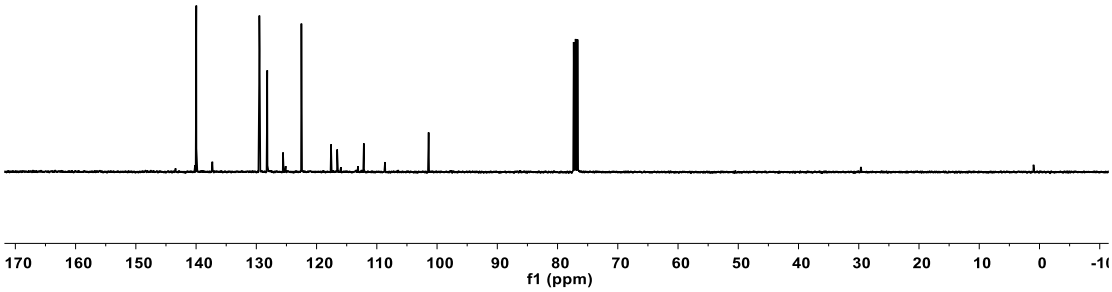
128.184
125.567
125.126
122.516
117.597
116.576
115.950
113.116
112.160
108.643
101.399


Br
Cl
S
N
N
Br
Cl
S
N
N

3i **3i'**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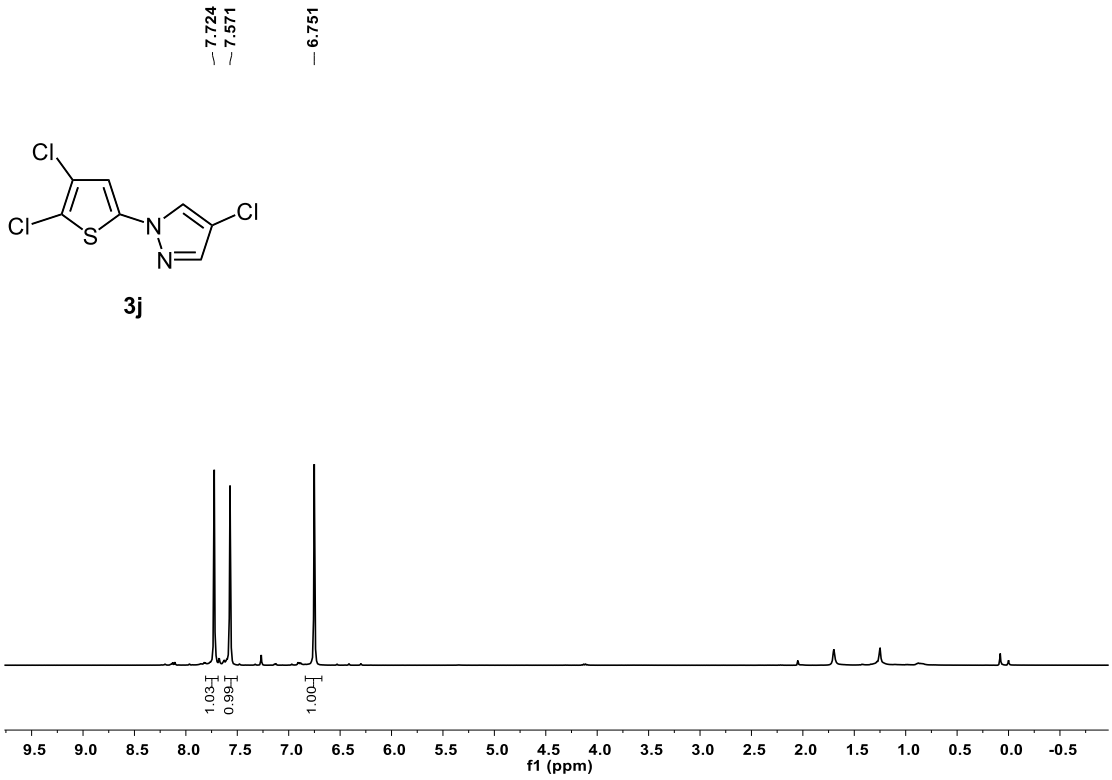
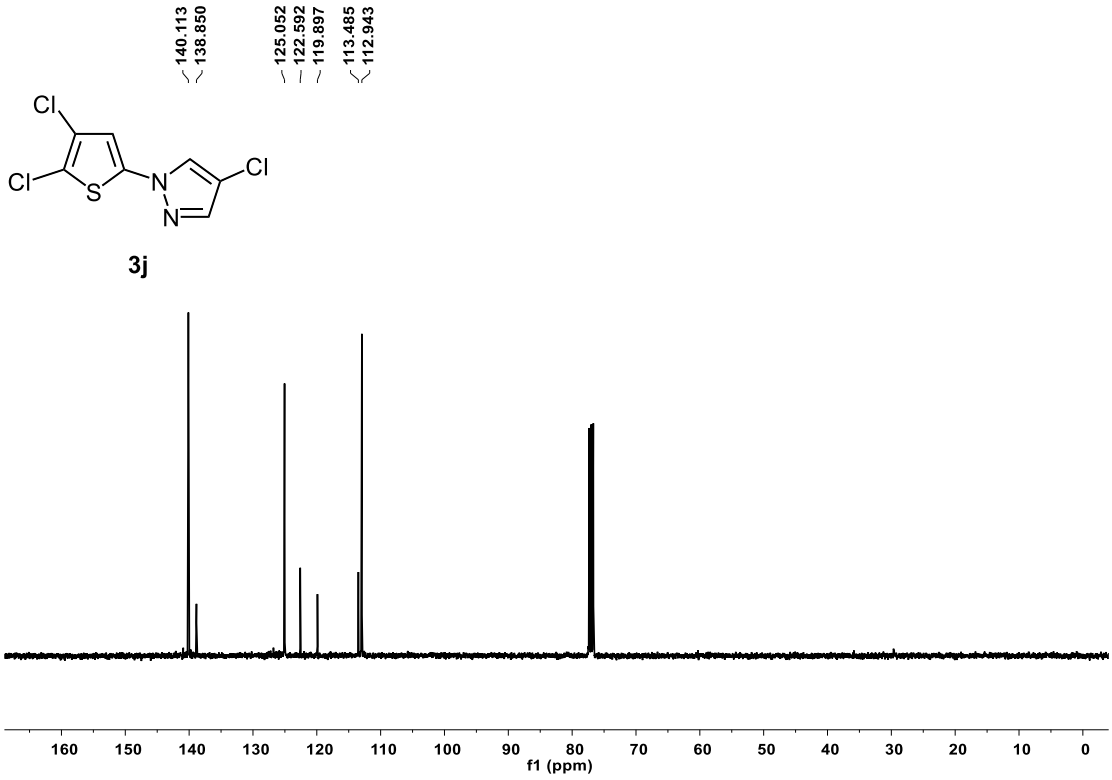
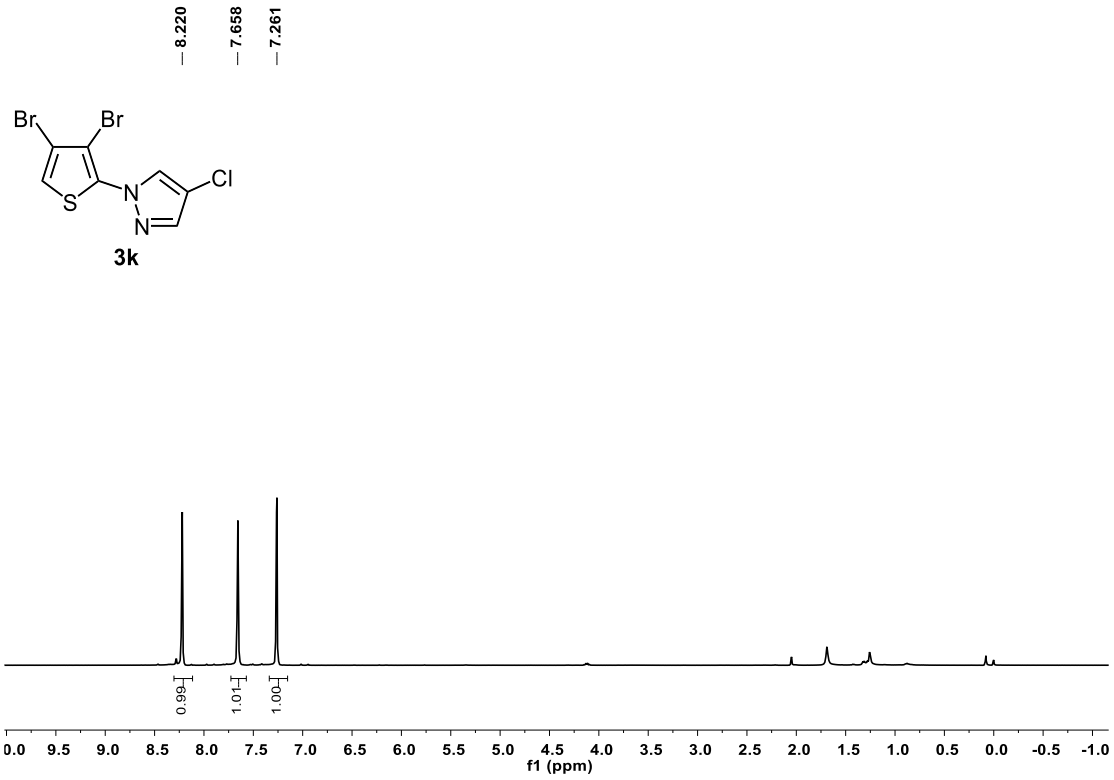
f1 (ppm)

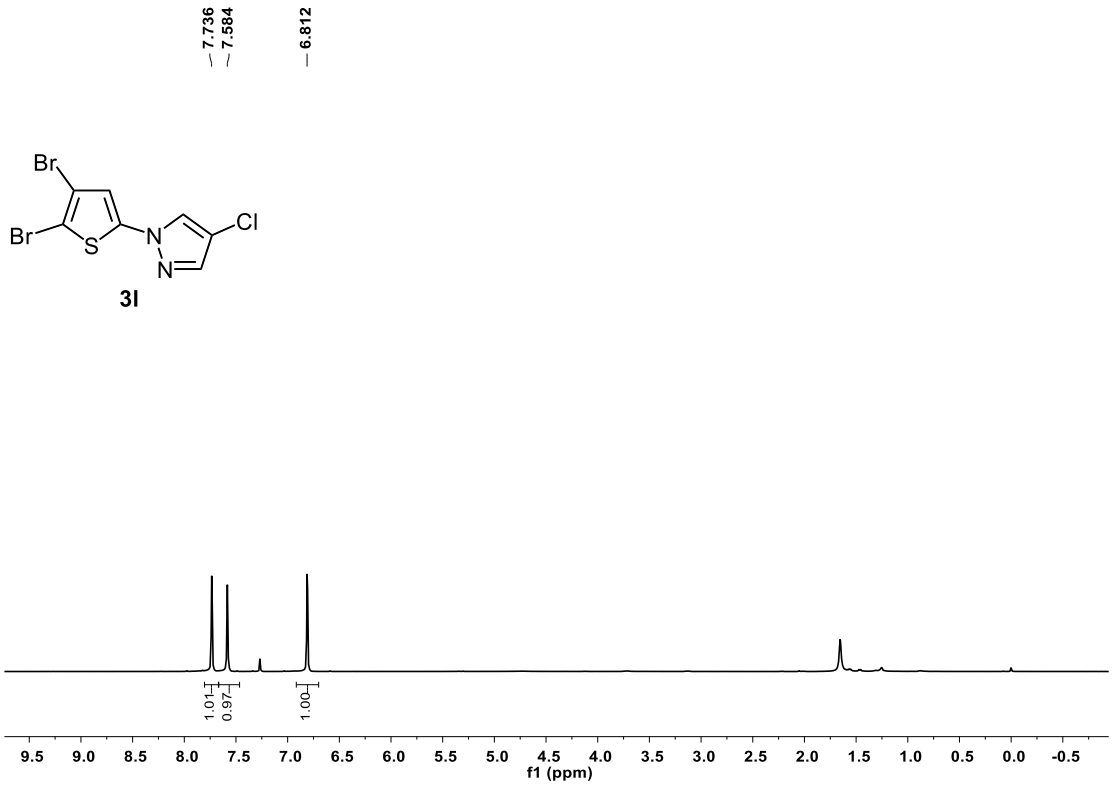

7.724
7.571
6.751
Cl
Cl
S
N
N
Cl
1.03
0.99
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

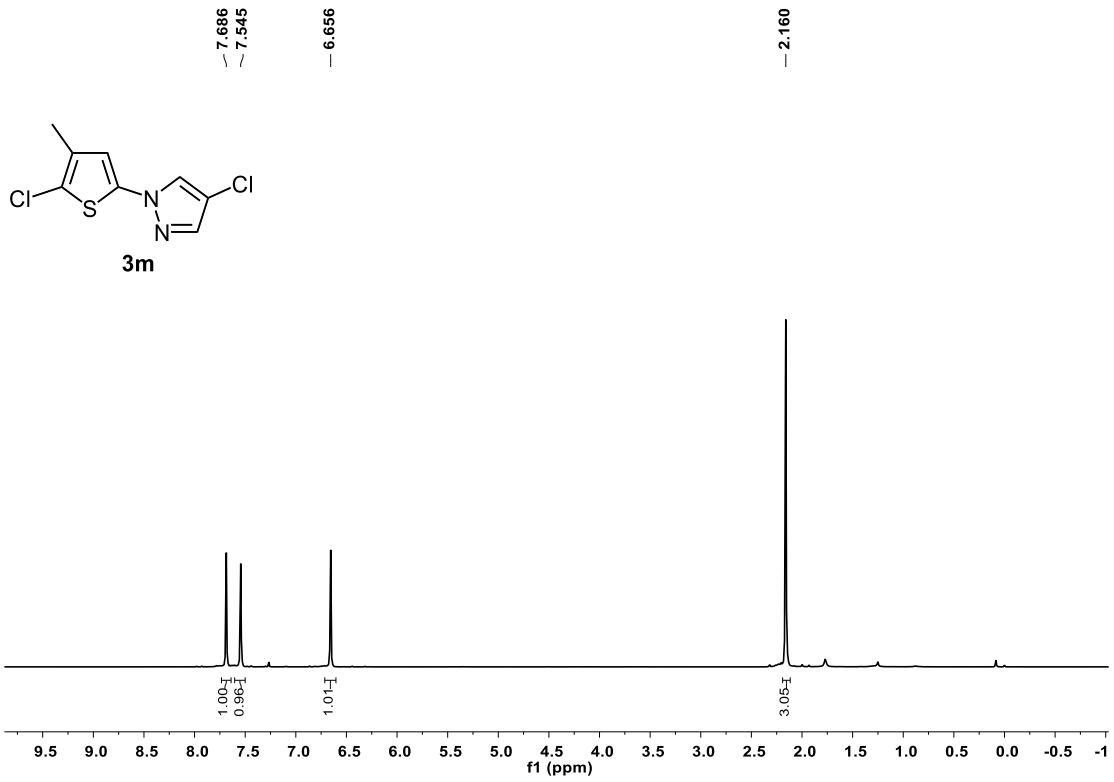
3j


140.113
138.850
125.052
122.592
119.897
113.485
112.943
Cl
Cl
S
N
N
Cl
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3j


8.220
7.658
7.261
Br
Br
Cl
S
N
N
3k
0.99
1.01
1.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
140.271
138.118
127.729
119.310
113.093
112.604
104.594
Br
Br
Cl
S
N
N
3k
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.736
7.584
6.812
Br
Br
S
N
N
Cl
3l
1.01
0.97
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
142.892
140.221
125.155
115.997
113.490
112.567
106.482
Br
Br
S
N
N
Cl
3l
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.686
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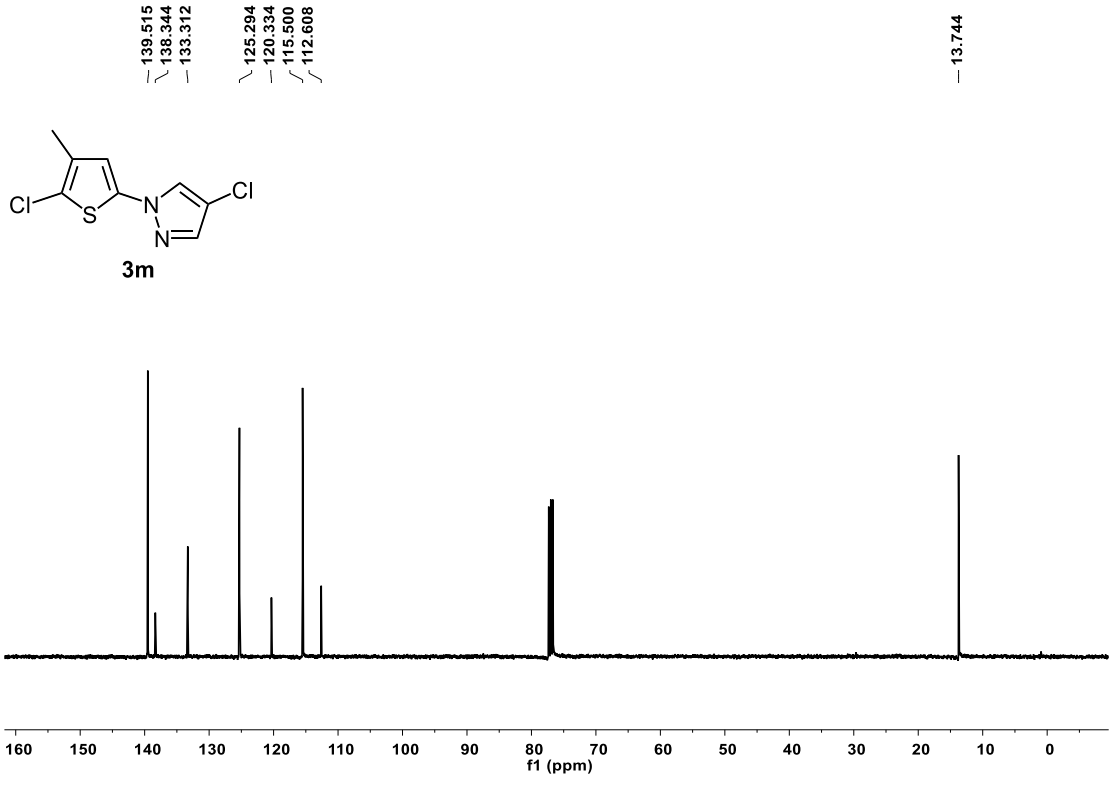
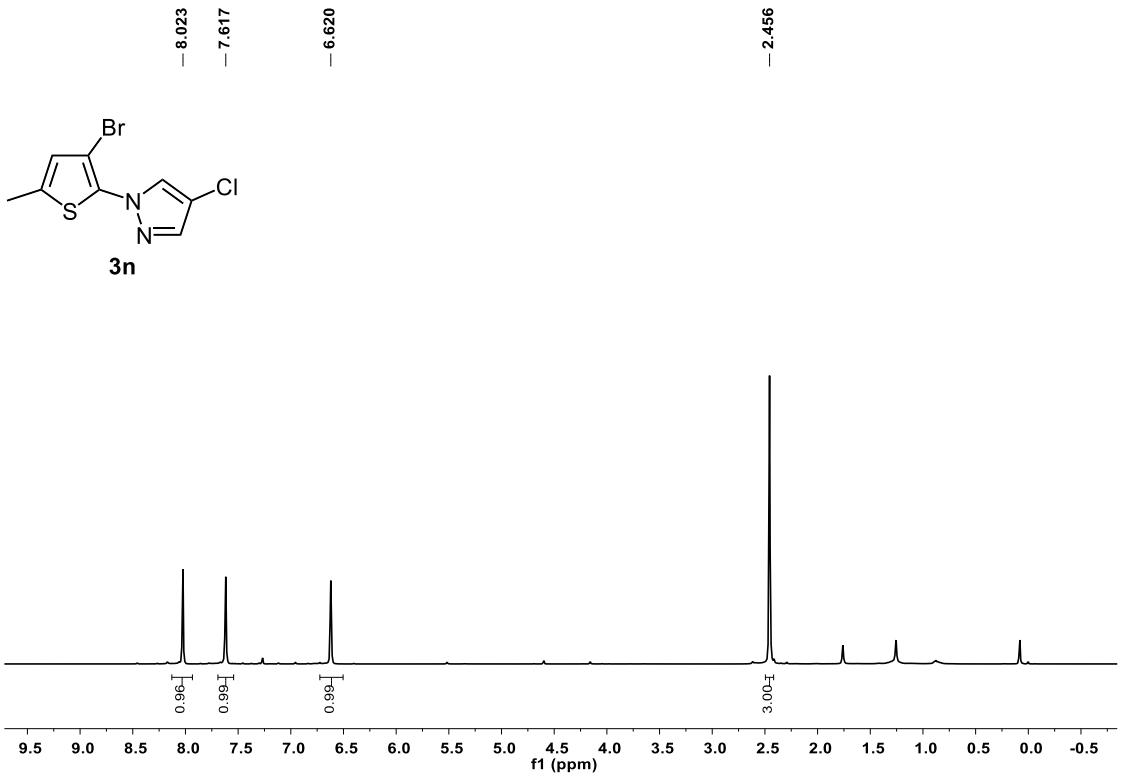
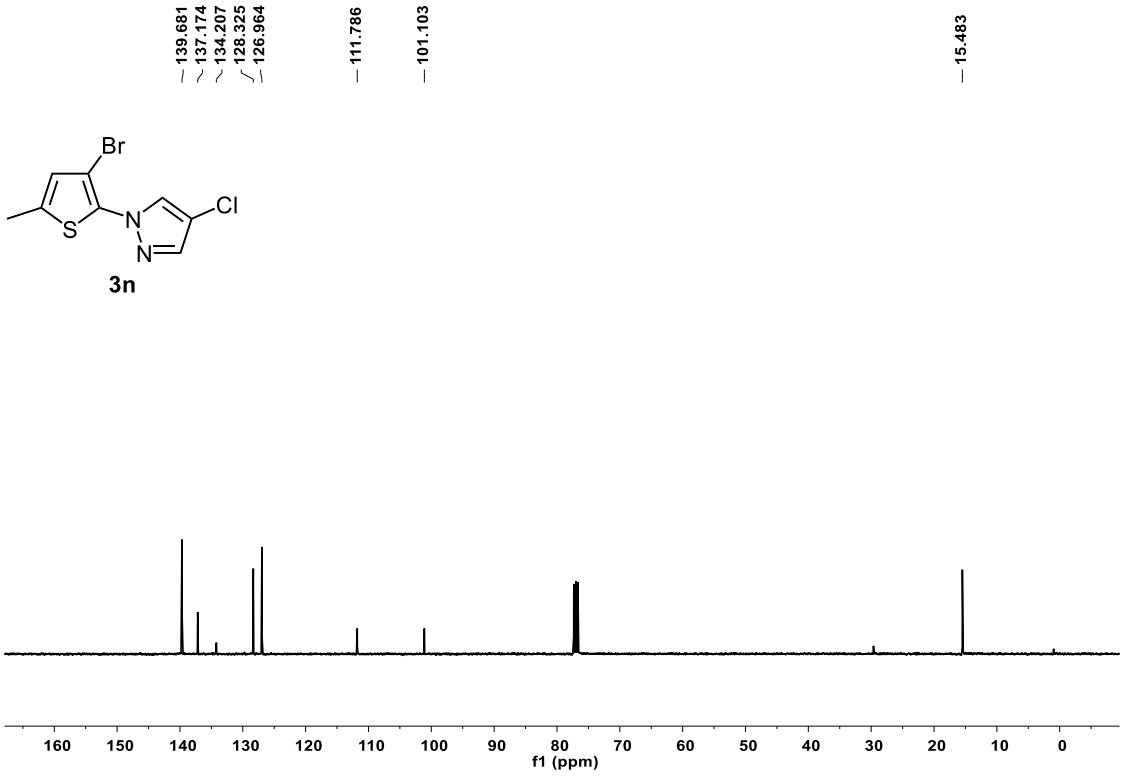
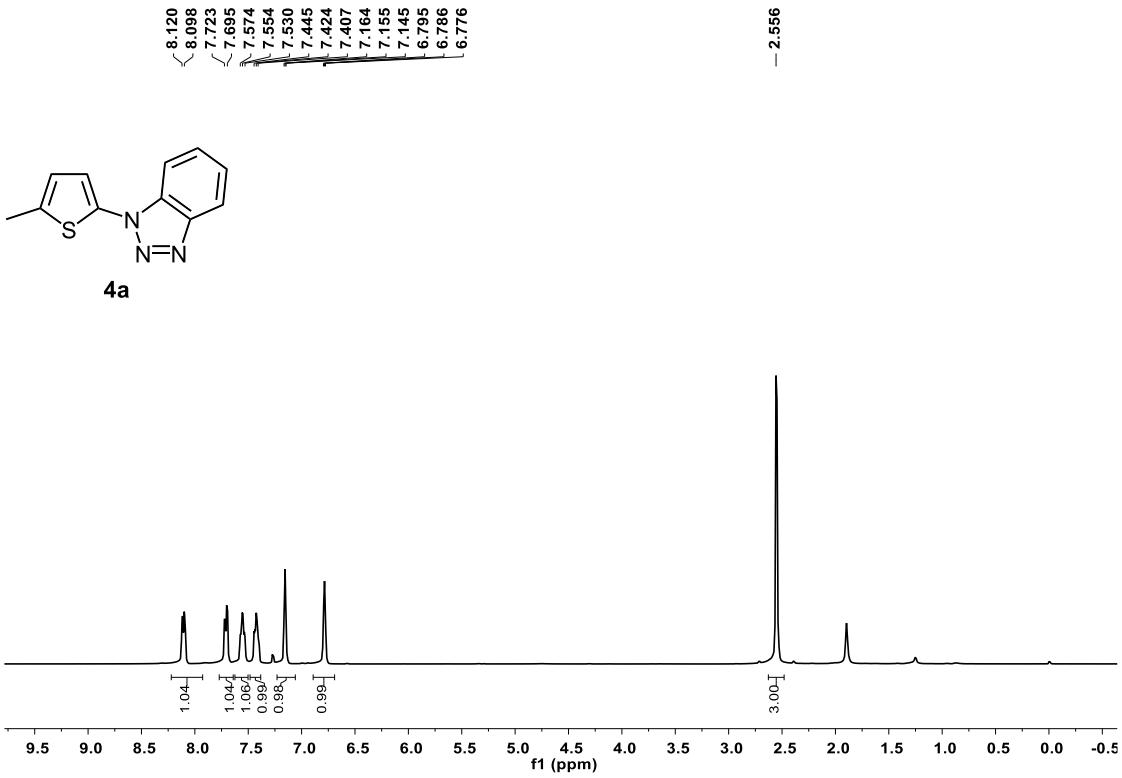
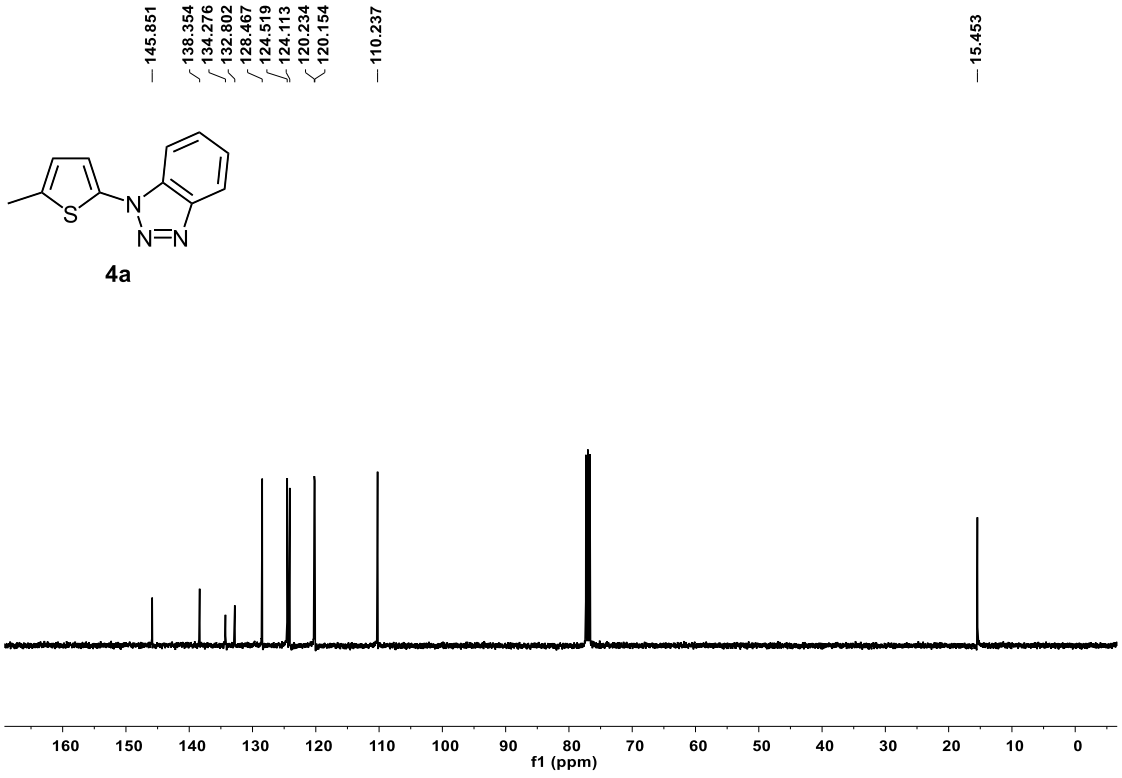
6.656
2.160
Cl
S
N
N
Cl
3m
1.00
0.96
1.01
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

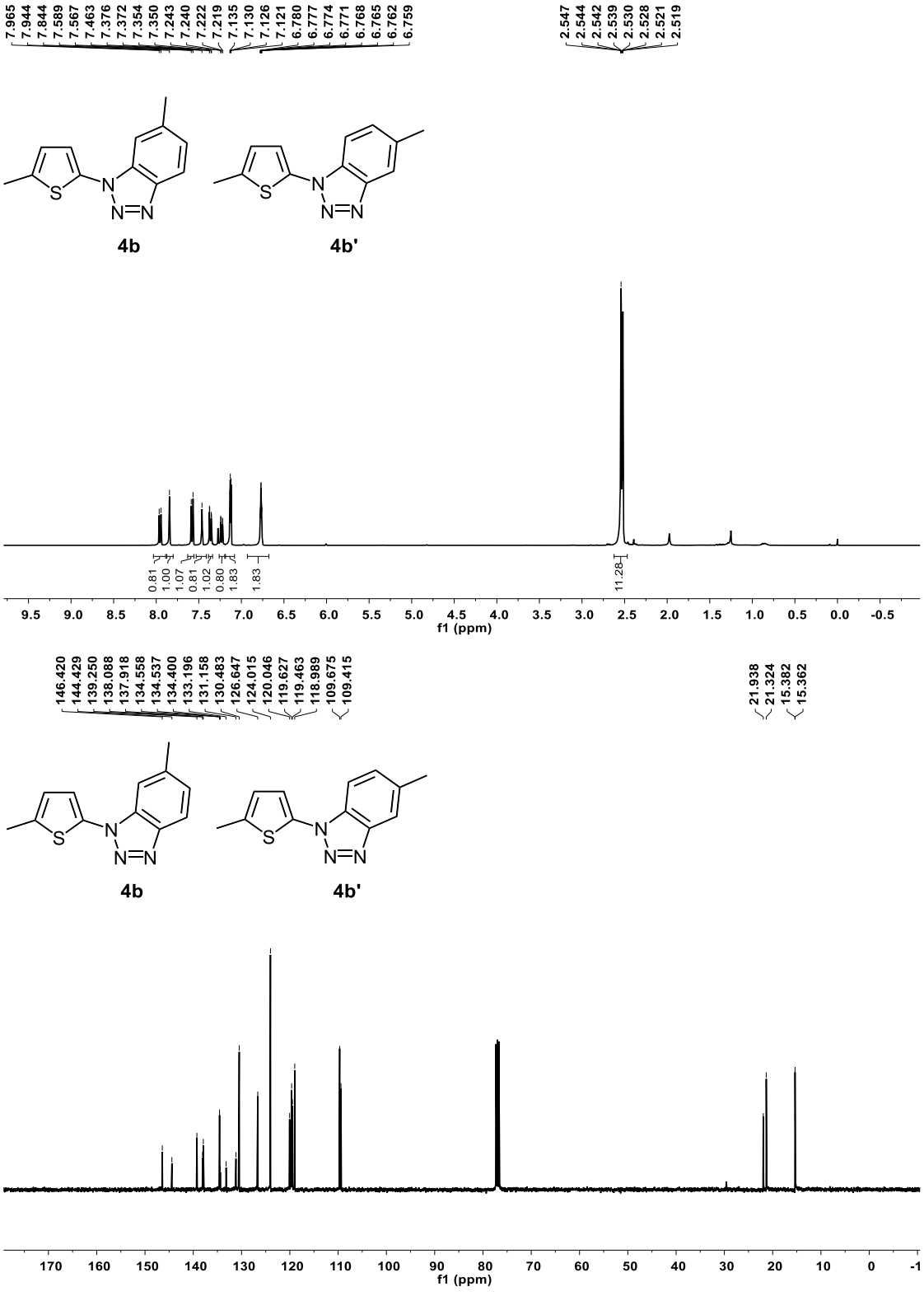

139.515
138.344
133.312
125.294
120.334
115.500
112.608
13.744
Cl
S
N
N
Cl
3m
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

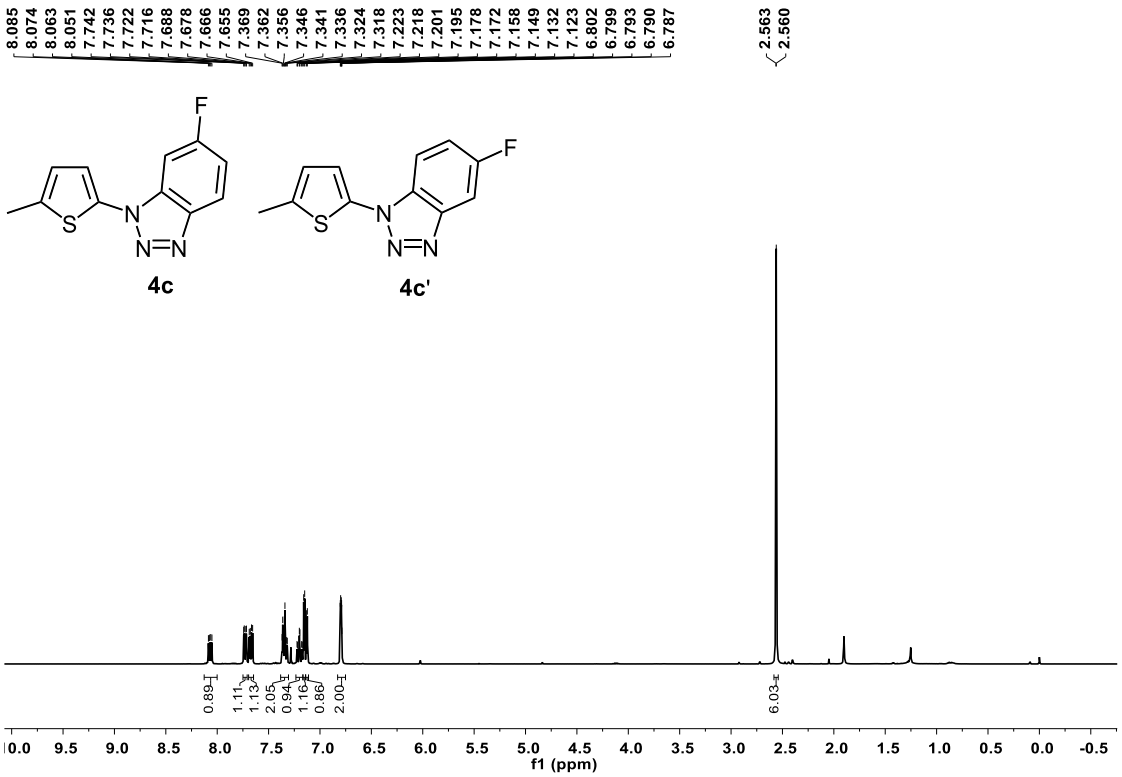

8.023
7.617
6.620
2.456
Br
Cl
S
N
N
3n
0.96
0.99
0.99
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

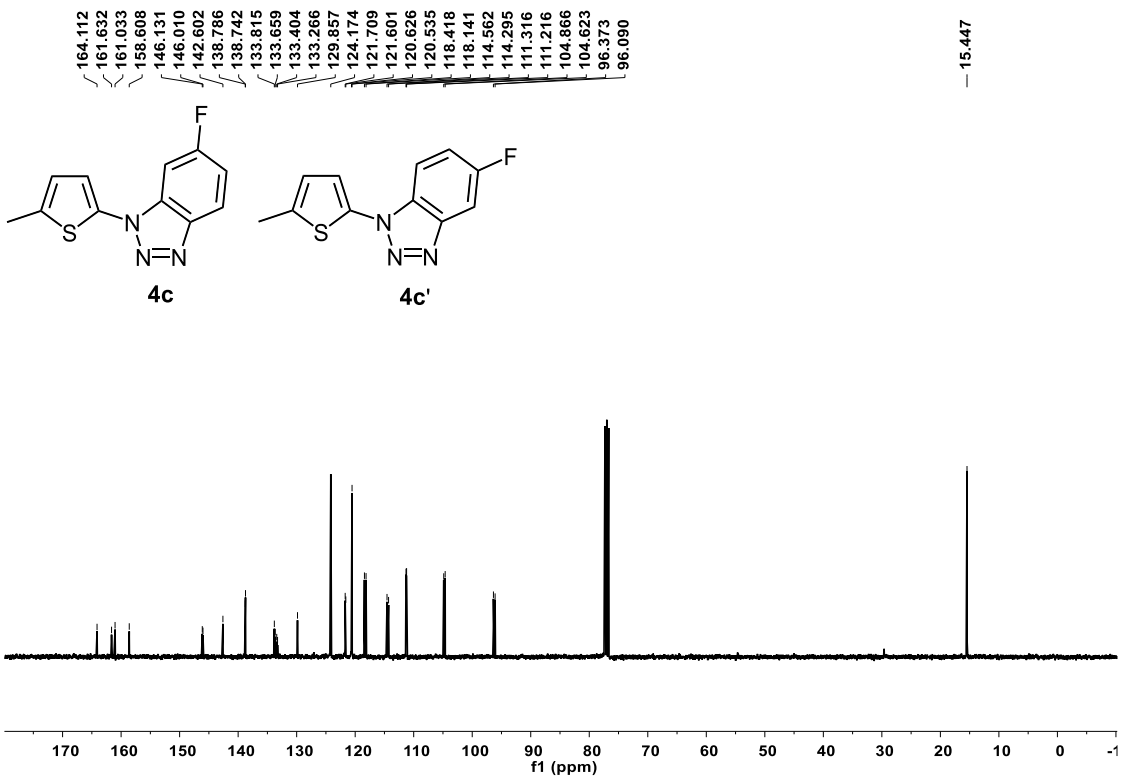

139.681
137.174
134.207
128.325
126.964
111.786
101.103
15.483
Br
Cl
S
N
N
3n
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

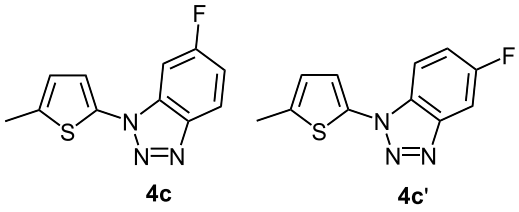

8.120
8.098
7.723
7.695
7.574
7.554
7.530
7.445
7.424
7.407
7.164
7.155
7.145
6.795
6.786
6.776
2.556
4a
1.04
1.04
1.06
0.99
0.98
0.99
3.00
f1 (ppm)


145.851
138.354
134.276
132.802
128.467
124.519
124.113
120.234
120.154
110.237
15.453
4a
f1 (ppm)


7.965
7.944
7.844
7.589
7.567
7.463
7.376
7.372
7.354
7.350
7.243
7.240
7.222
7.219
7.135
7.130
7.126
7.121
6.780
6.777
6.774
6.771
6.768
6.765
6.762
6.759
2.547
2.544
2.542
2.539
2.530
2.528
2.521
2.519
4b
4b'
0.81
1.00
1.07
0.81
1.02
0.80
1.83
1.83
11.28
f1 (ppm)
146.420
144.429
139.250
138.088
137.918
134.558
134.537
134.400
133.196
131.158
130.483
126.647
124.015
120.046
119.627
119.463
118.989
109.675
109.415
21.938
21.324
15.382
15.362
4b
4b'
f1 (ppm)


8.085
8.074
8.063
8.051
7.742
7.736
7.722
7.716
7.688
7.678
7.666
7.655
7.369
7.362
7.356
7.346
7.341
7.336
7.324
7.318
7.223
7.218
7.201
7.195
7.178
7.172
7.158
7.149
7.132
7.123
6.802
6.799
6.793
6.790
6.787
2.563
2.560
F
S
N
N=N
4c
4c'
0.89
1.11
1.13
2.05
0.94
1.16
0.86
2.00
6.03
f1 (ppm)


164.112
161.632
161.033
158.608
146.131
146.010
142.602
138.786
138.742
133.815
133.659
133.404
133.266
129.857
124.174
121.709
121.601
120.626
120.535
118.418
118.141
114.562
114.295
111.316
111.216
104.866
104.623
96.373
96.090
15.447
F
S
N
N=N
4c
4c'
f1 (ppm)

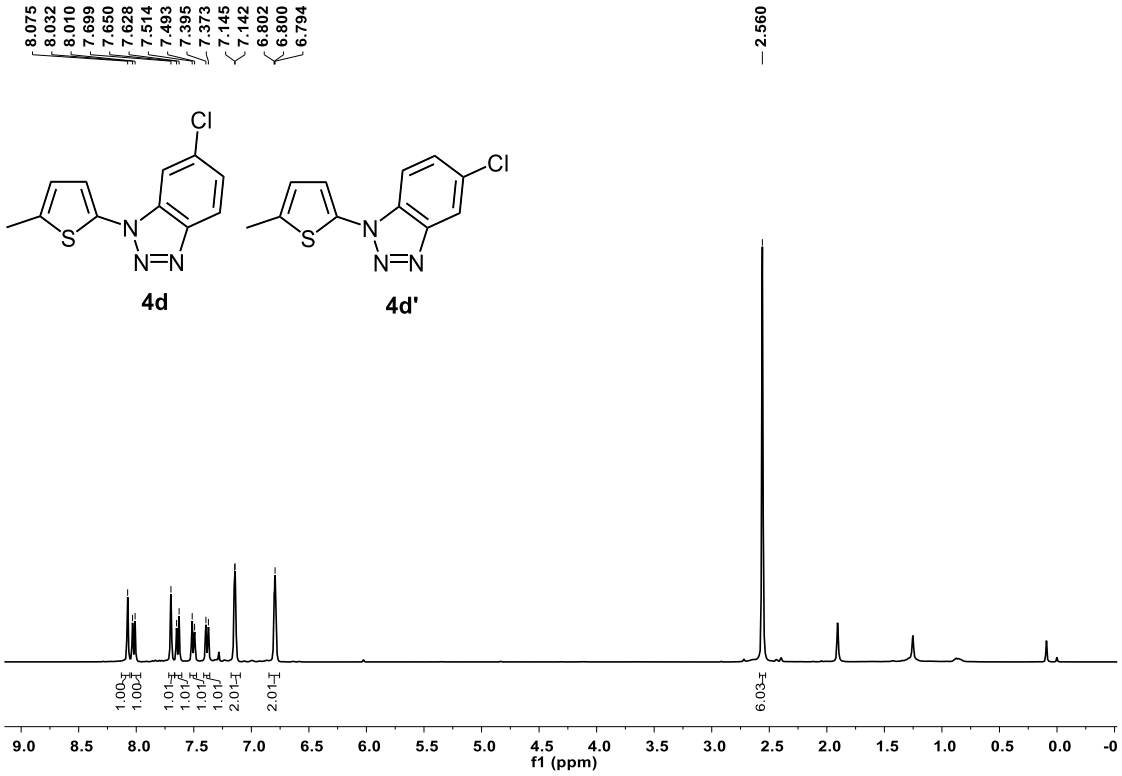

F
S
N
N=N

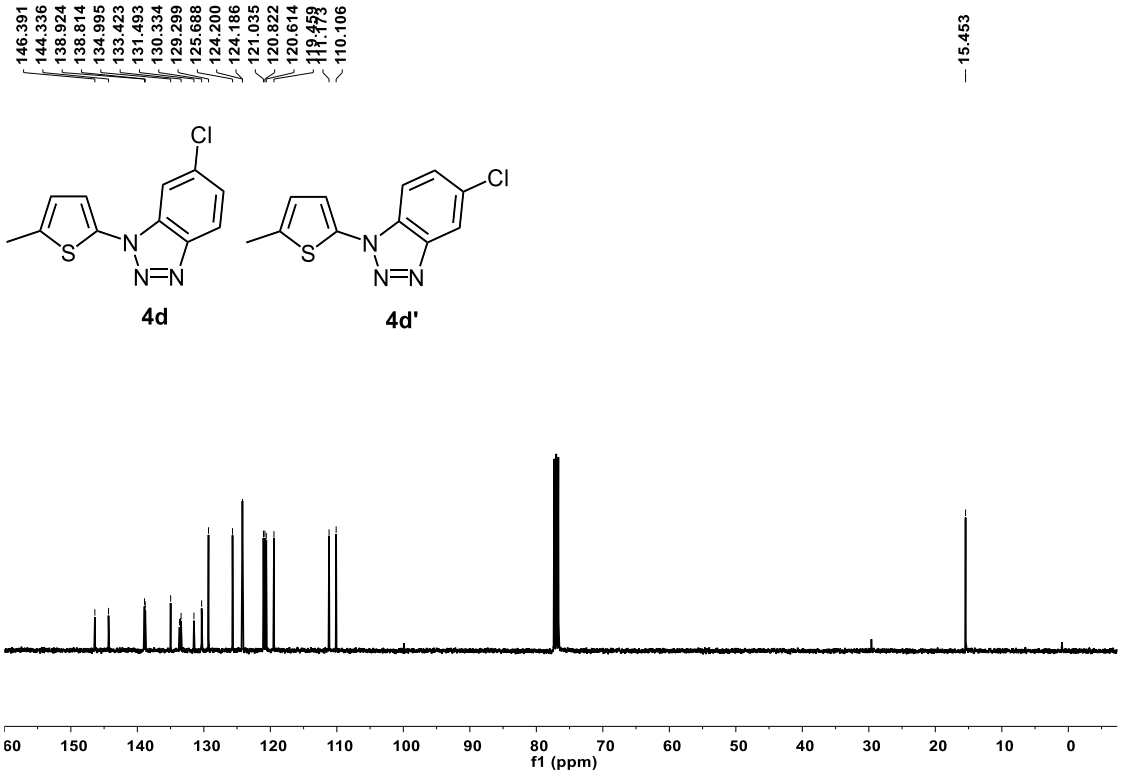
4c

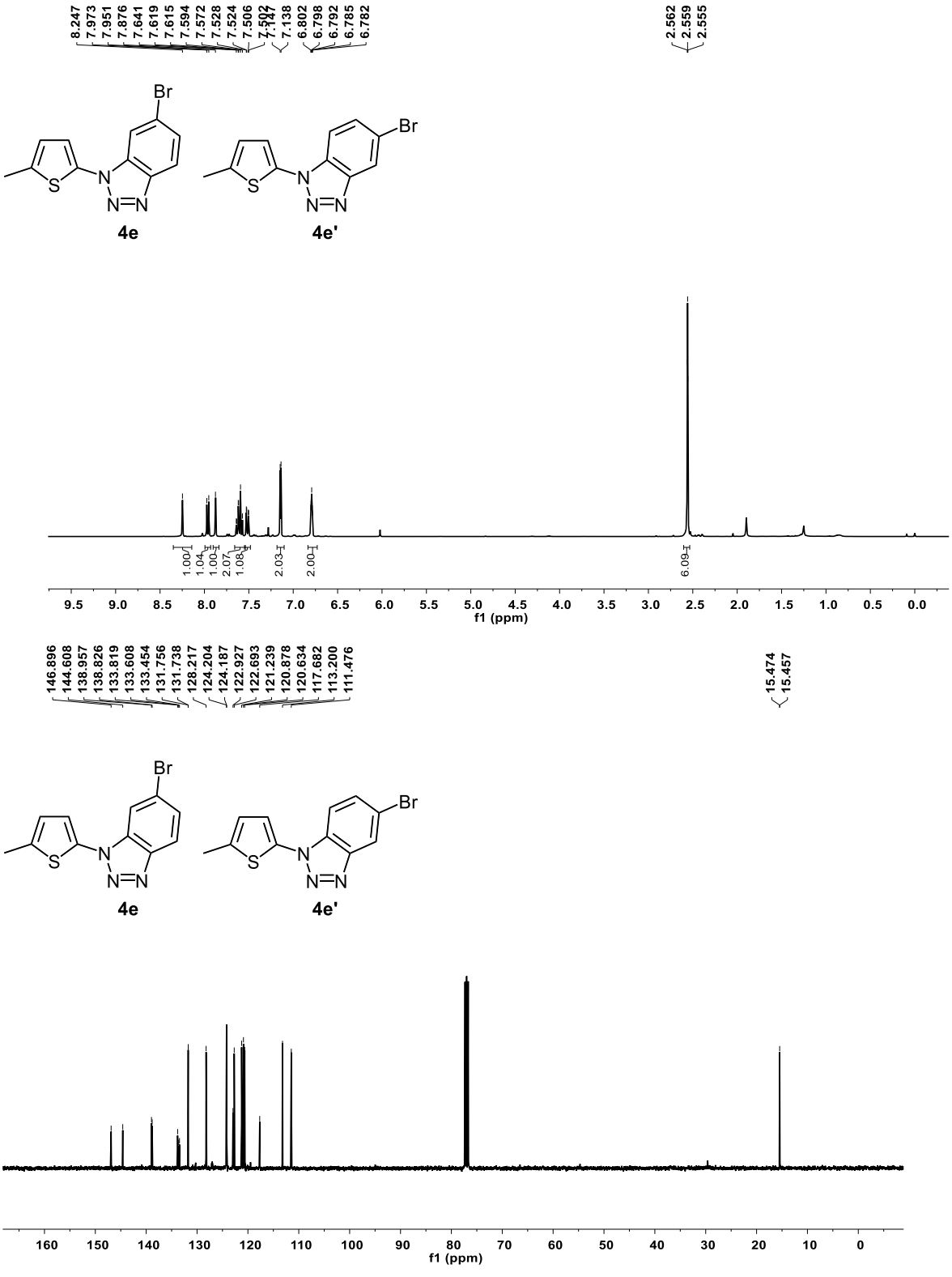
F
S
N
N=N

4c'

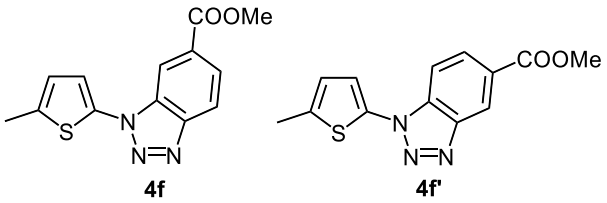
-110.047
-116.839
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.075
8.032
8.010
7.699
7.650
7.628
7.514
7.493
7.395
7.373
7.145
7.142
6.802
6.800
6.794
2.560
Cl
S
N
N=N
4d
4d'
1.00
1.00
1.01
1.01
1.01
1.01
2.01
2.01
6.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

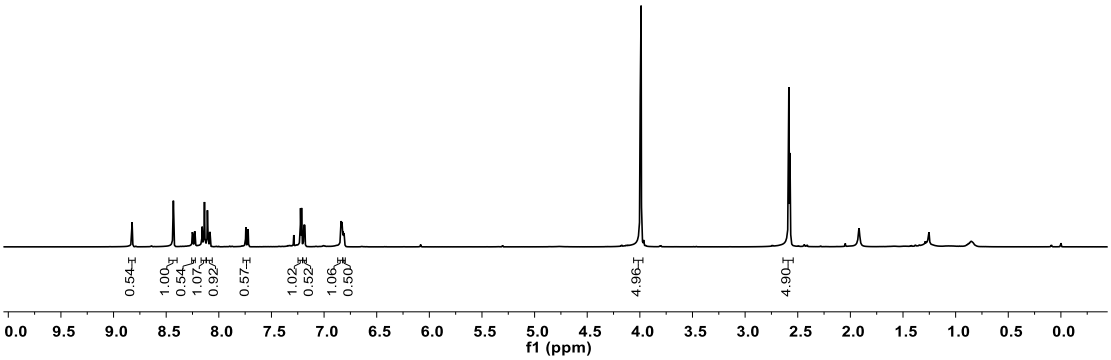

146.391
144.336
138.924
138.814
134.995
133.423
131.493
130.334
129.299
125.688
124.200
124.186
121.035
120.822
120.614
110.106
15.453
Cl
S
N
N=N
4d
4d'
60 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

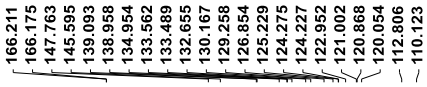

8.247
7.973
7.951
7.876
7.641
7.619
7.615
7.594
7.572
7.528
7.524
7.506
7.138
6.802
6.798
6.792
6.785
6.782
2.562
2.559
2.555
Br
S
N
N=N
4e
4e'
1.00
1.04
1.00
2.07
1.08
2.03
2.00
6.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
146.896
144.608
138.957
138.826
133.819
133.608
133.454
131.756
131.738
128.217
124.204
124.187
122.927
122.693
121.239
120.878
120.634
117.682
113.200
111.476
15.474
15.457
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

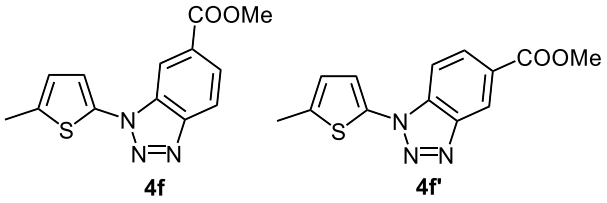

8.824
8.432
8.251
8.248
8.230
8.226
8.159
8.157
8.137
8.135
8.108
8.105
8.087
8.083
7.743
7.722
7.223
7.214
7.192
7.183
6.842
6.839
6.836
6.833
6.830
6.827
6.819
6.816
6.810
6.807
3.997
3.988
2.586
2.583
2.575
2.572


COOMe
COOMe

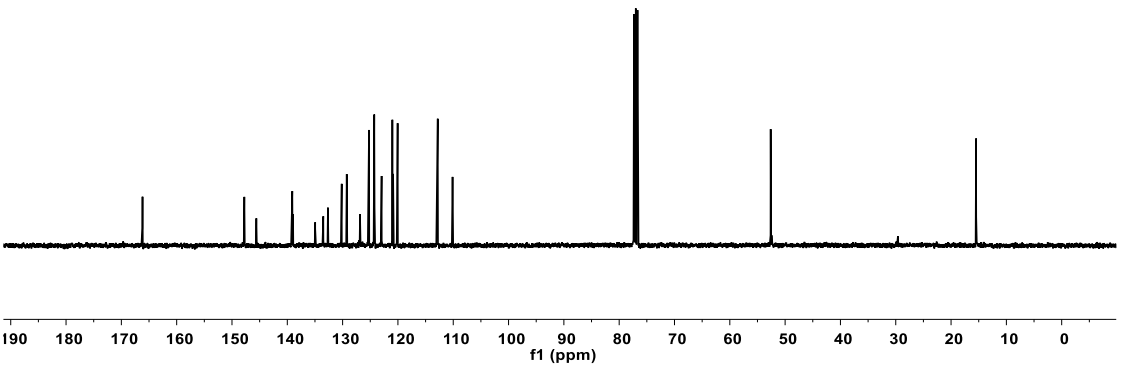
4f **4f'**

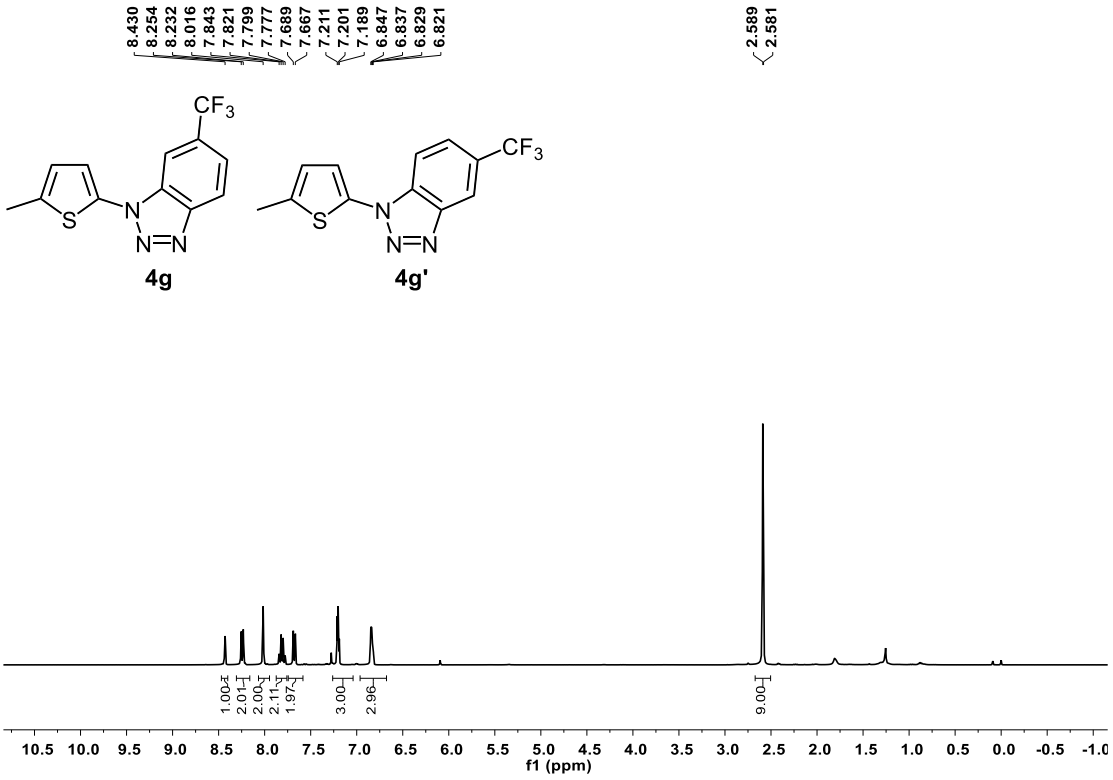

0.54
1.00
0.54
1.07
0.92
0.57
1.02
0.52
1.06
0.50
4.96
4.90
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

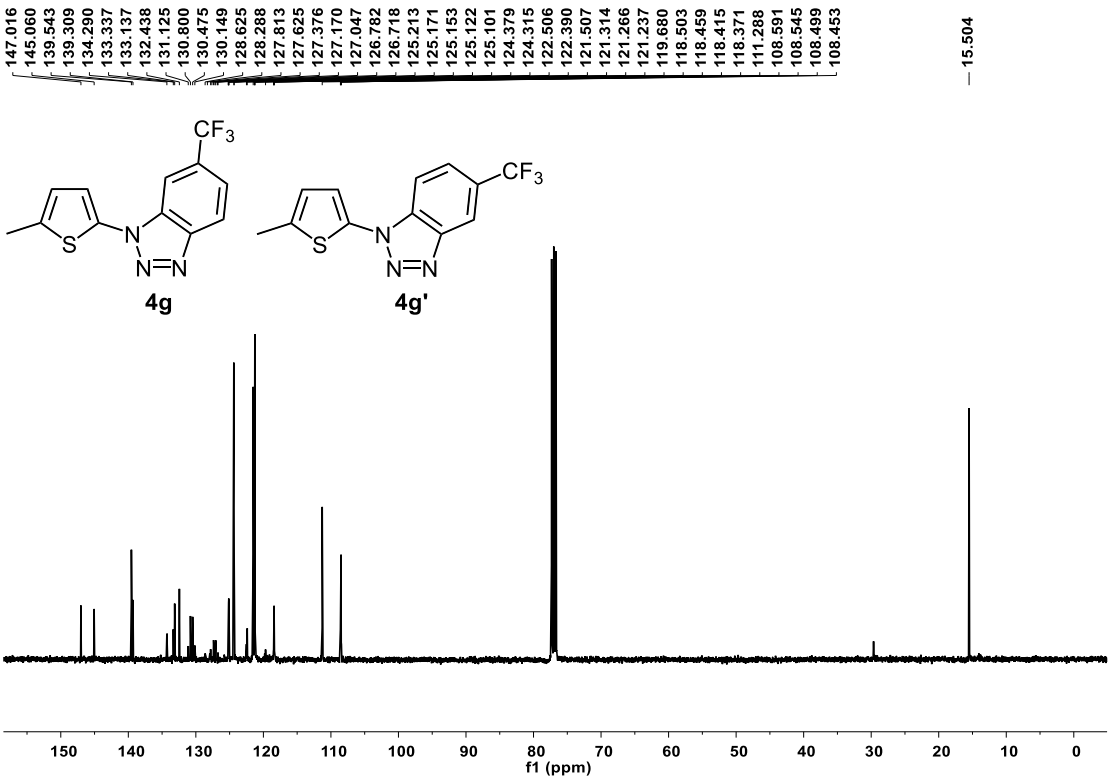

166.211
166.175
147.763
145.595
139.093
138.958
134.954
133.562
133.489
132.655
130.167
129.258
126.854
125.229
124.275
124.227
122.952
121.002
120.868
120.054
112.806
110.123
52.615
52.466
15.480
15.461

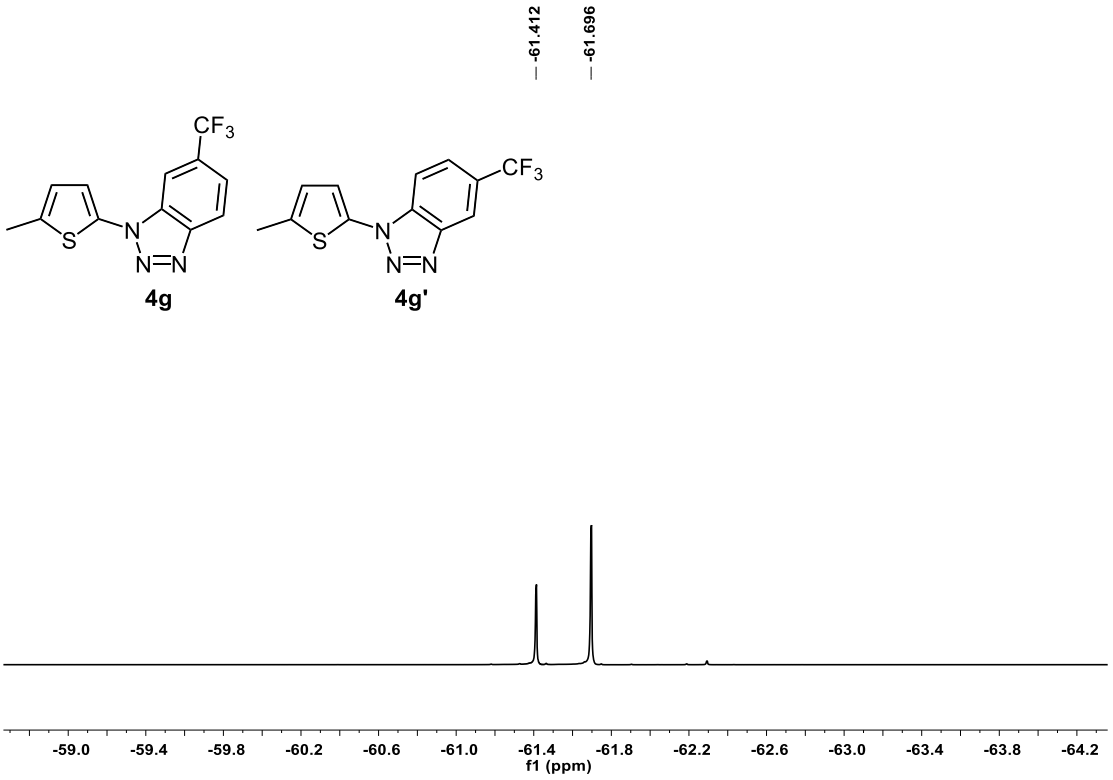

COOMe
COOMe

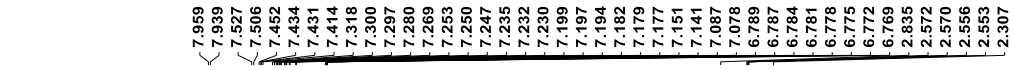
4f **4f'**

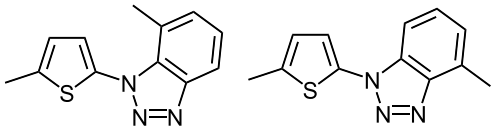

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

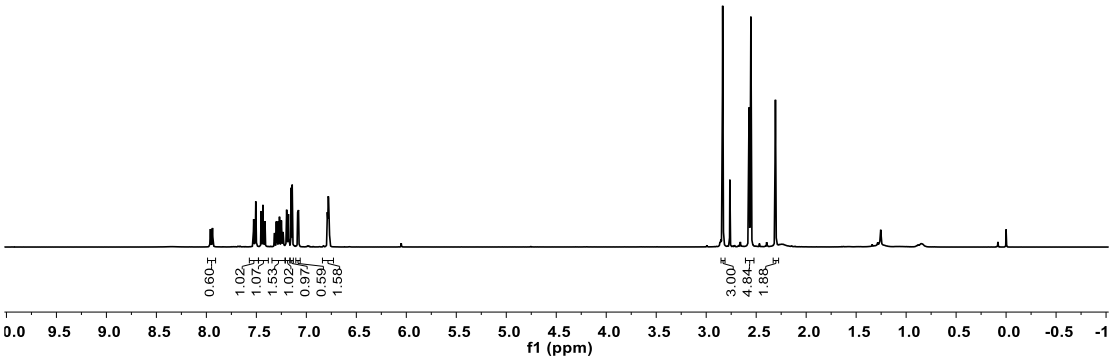

8.430
8.254
8.232
8.016
7.843
7.821
7.799
7.777
7.689
7.667
7.211
7.201
7.189
6.847
6.837
6.829
6.821
2.589
2.581
CF3
S
N
N=N
4g
4g'
1.00
2.01
2.00
2.11
1.97
3.00
2.96
9.00
f1 (ppm)


147.016
145.060
139.543
139.309
134.290
133.337
133.137
132.438
131.125
130.800
130.475
130.149
128.625
128.288
127.813
127.625
127.376
127.170
127.047
126.782
126.718
125.213
125.171
125.153
125.122
125.101
124.379
124.315
122.506
122.390
121.507
121.314
121.266
121.237
119.680
118.503
118.459
118.415
118.371
111.288
108.591
108.545
108.499
108.453
15.504
CF3
S
N
N=N
4g
4g'
f1 (ppm)

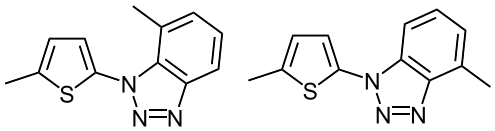

-61.412
-61.696
CF3
S
N
N=N
4g
CF3
S
N
N=N
4g'
-59.0
-59.4
-59.8
-60.2
-60.6
-61.0
-61.4
-61.8
-62.2
-62.6
-63.0
-63.4
-63.8
-64.2
f1 (ppm)


7.959
7.939
7.527
7.506
7.452
7.434
7.431
7.414
7.318
7.300
7.297
7.280
7.269
7.253
7.250
7.247
7.235
7.232
7.230
7.199
7.197
7.194
7.182
7.179
7.177
7.151
7.141
7.087
7.078
6.789
6.787
6.784
6.781
6.778
6.775
6.772
6.769
2.835
2.572
2.570
2.556
2.553
2.307

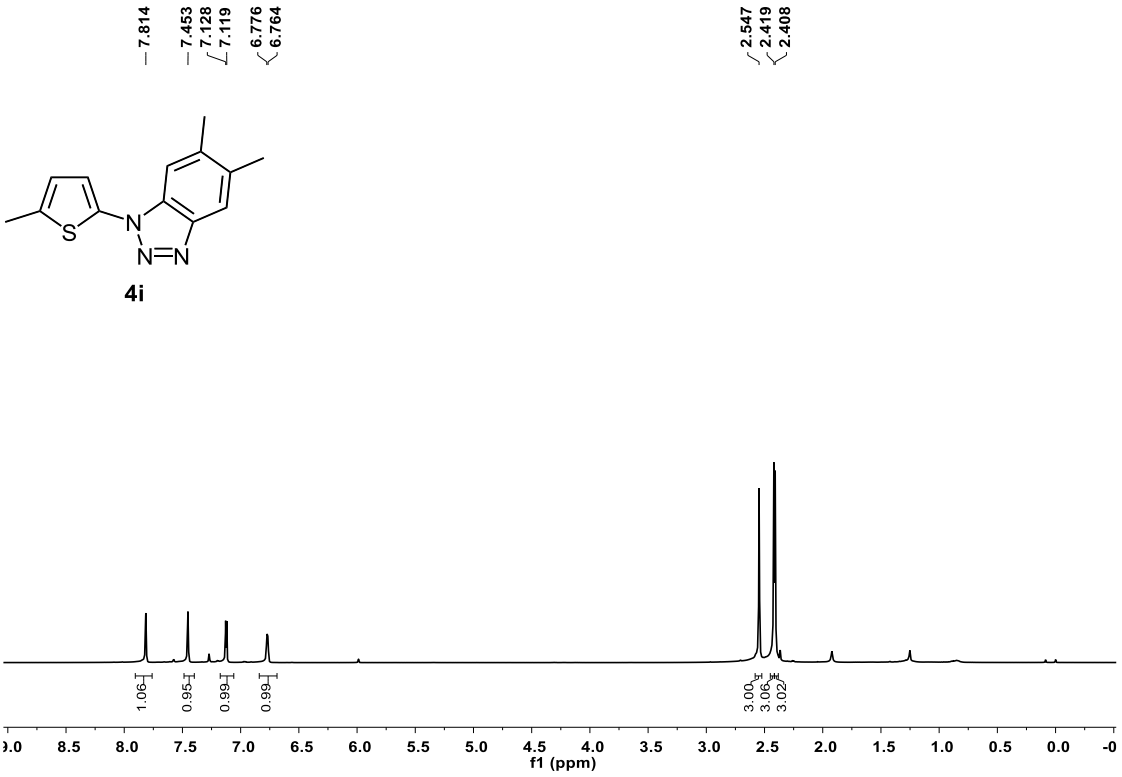

4h
4h'

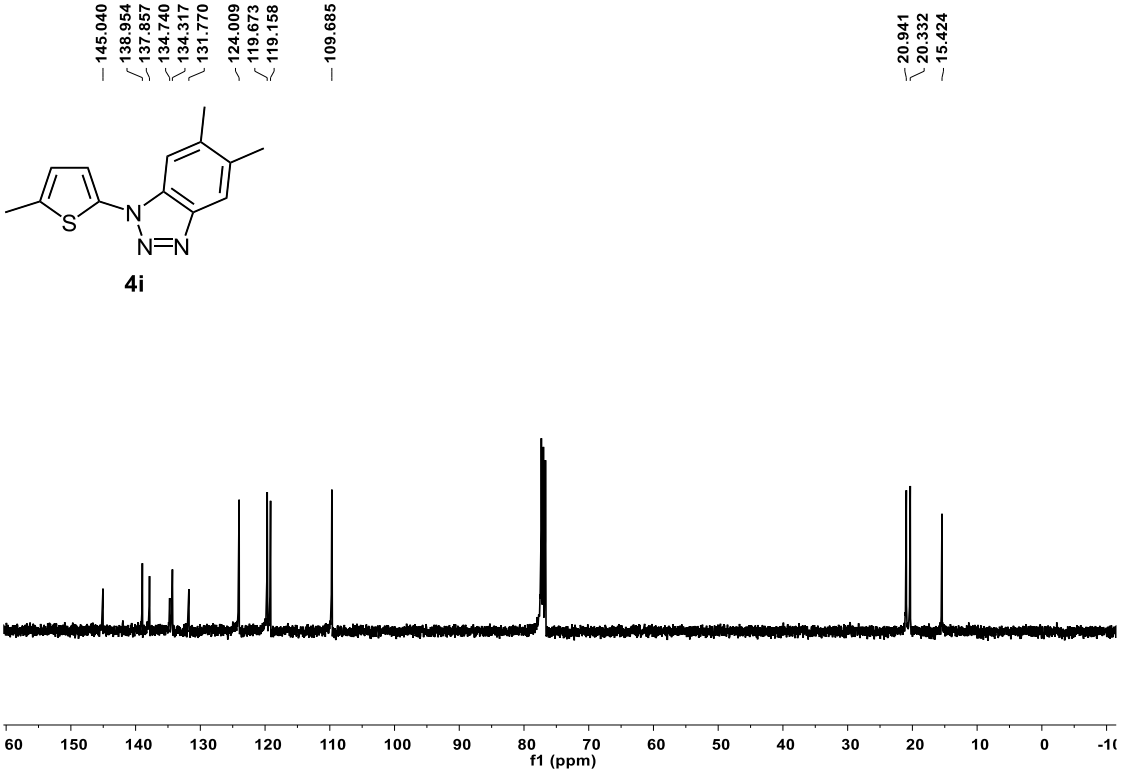

0.60
1.02
1.07
1.53
1.02
0.97
0.59
1.58
3.00
4.84
1.88
f1 (ppm)

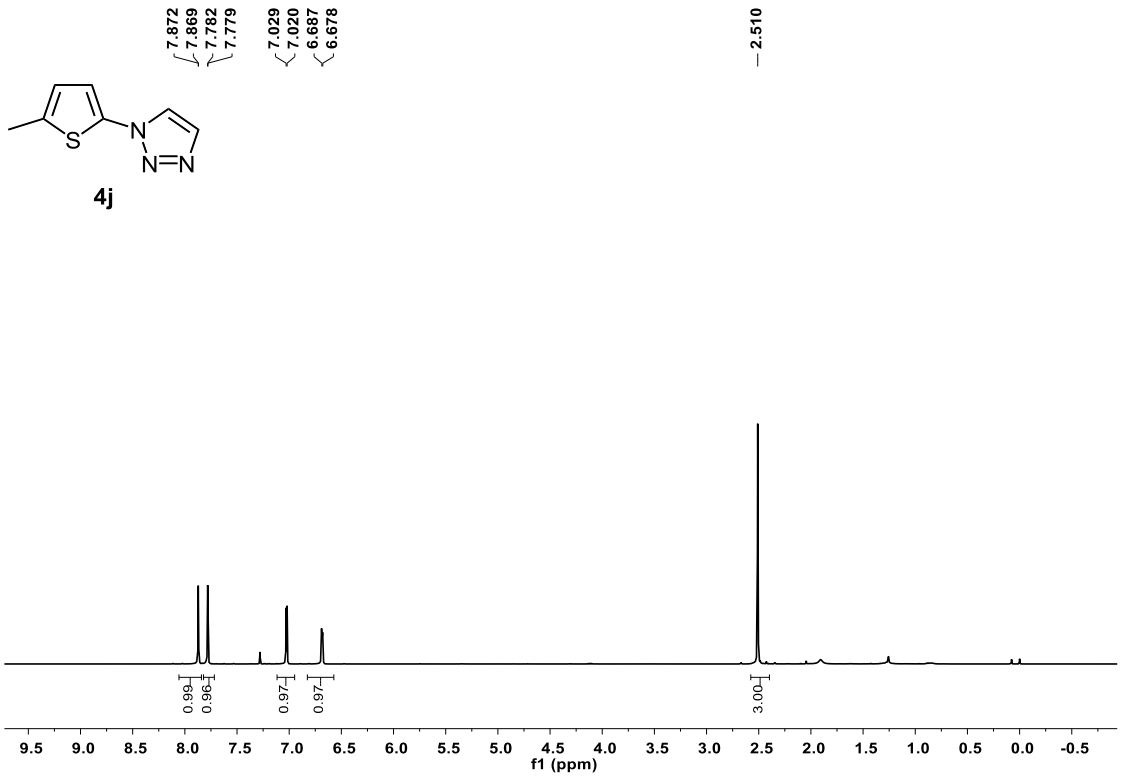

145.777
145.470
141.468
138.276
134.559
132.816
131.193
129.598
128.455
127.667
124.529
124.434
124.095
123.608
121.617
120.239
17.414
16.728
15.777
15.496

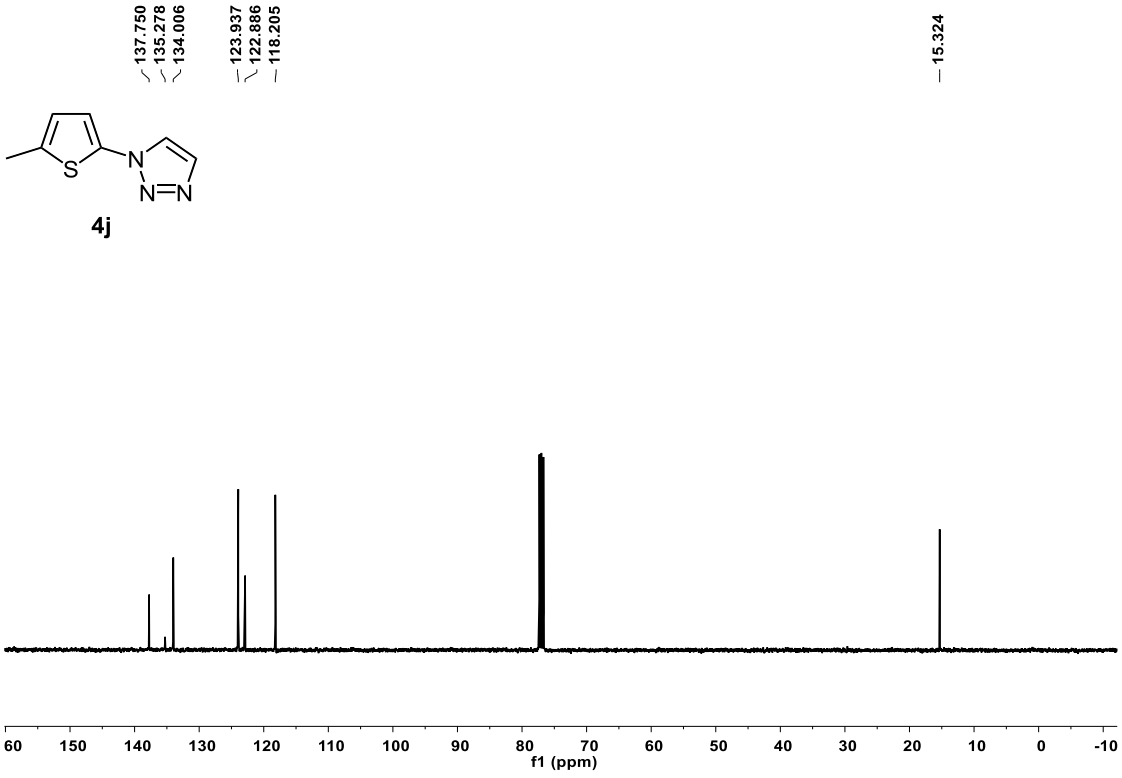

4h
4h'

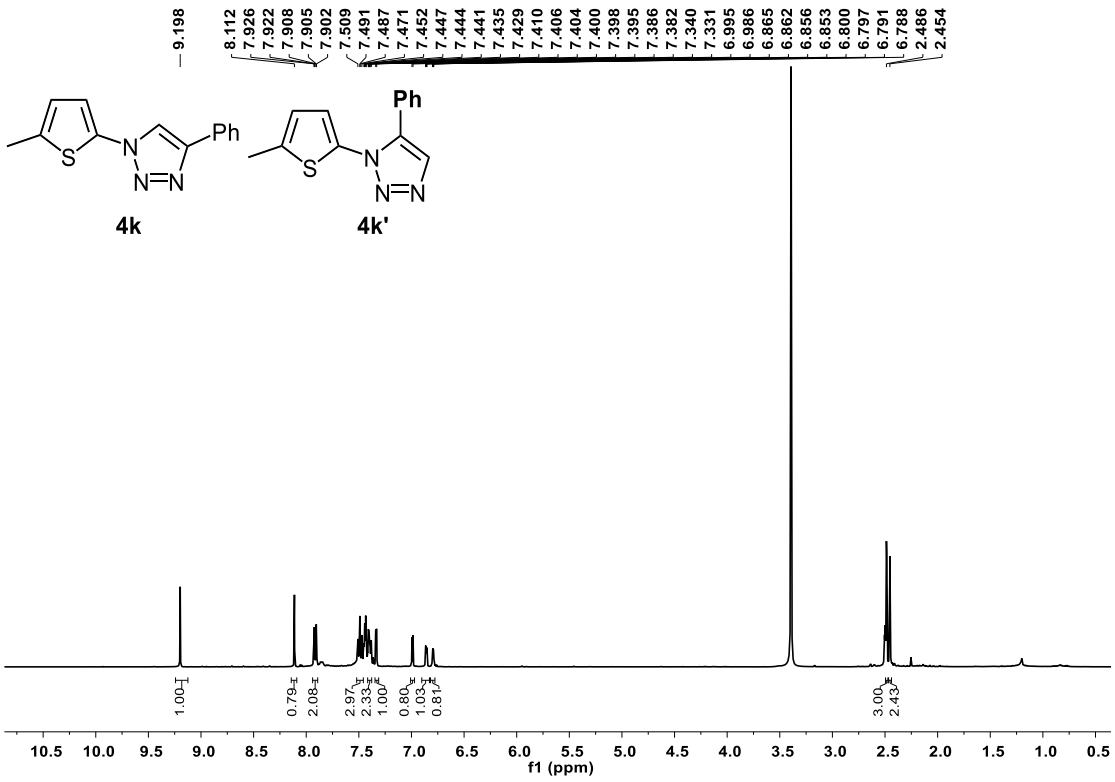
f1 (ppm)

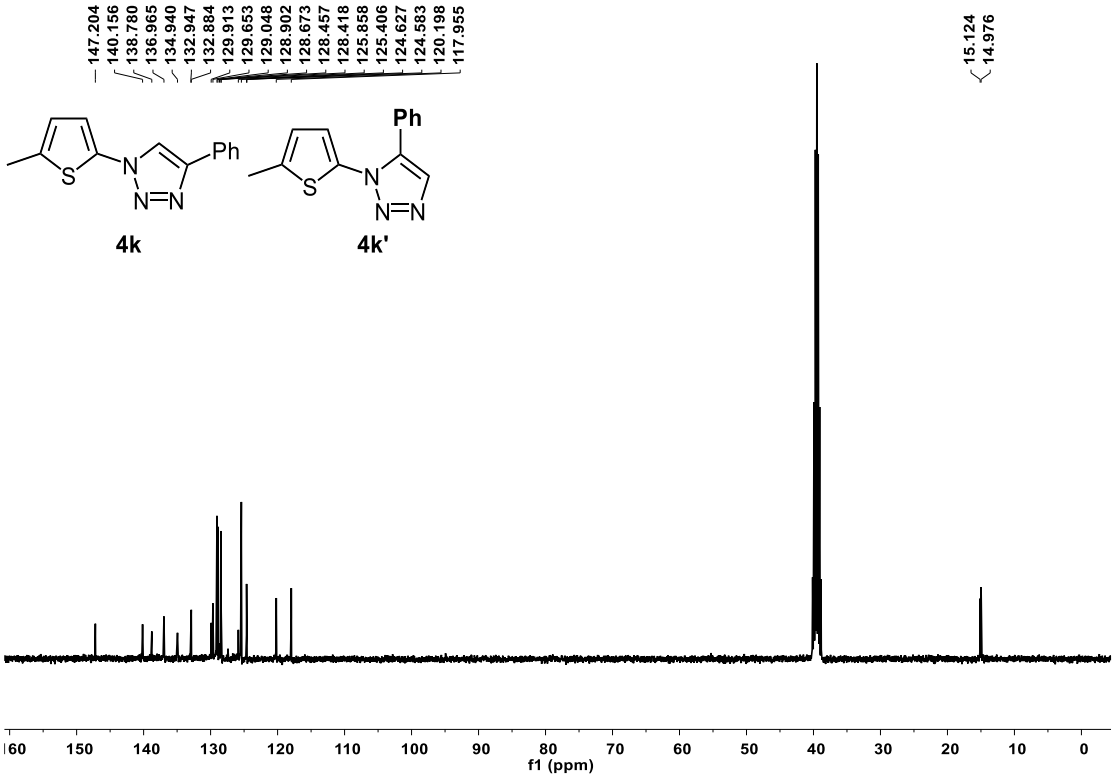

7.814
7.453
7.128
7.119
6.776
6.764
2.547
2.419
2.408
4i
1.06
0.95
0.99
0.99
3.00
3.06
3.02
f1 (ppm)

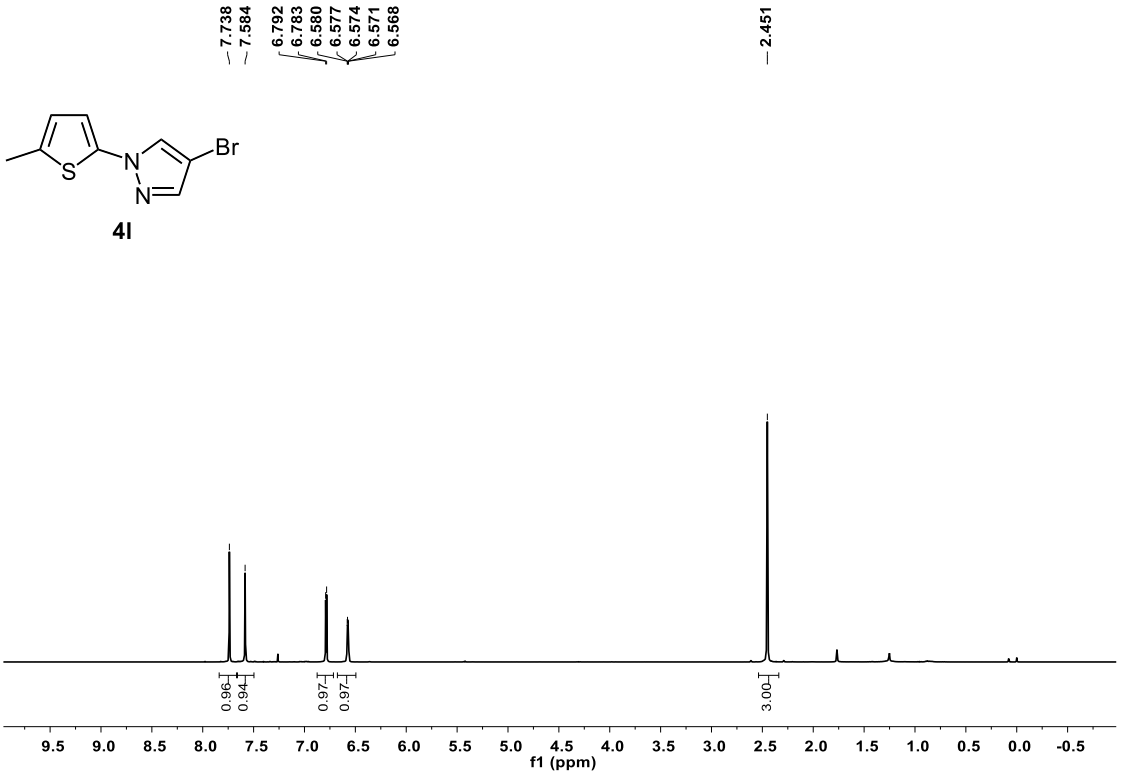

145.040
138.954
137.857
134.740
134.317
131.770
124.009
119.673
119.158
109.685
20.941
20.332
15.424
4i
f1 (ppm)

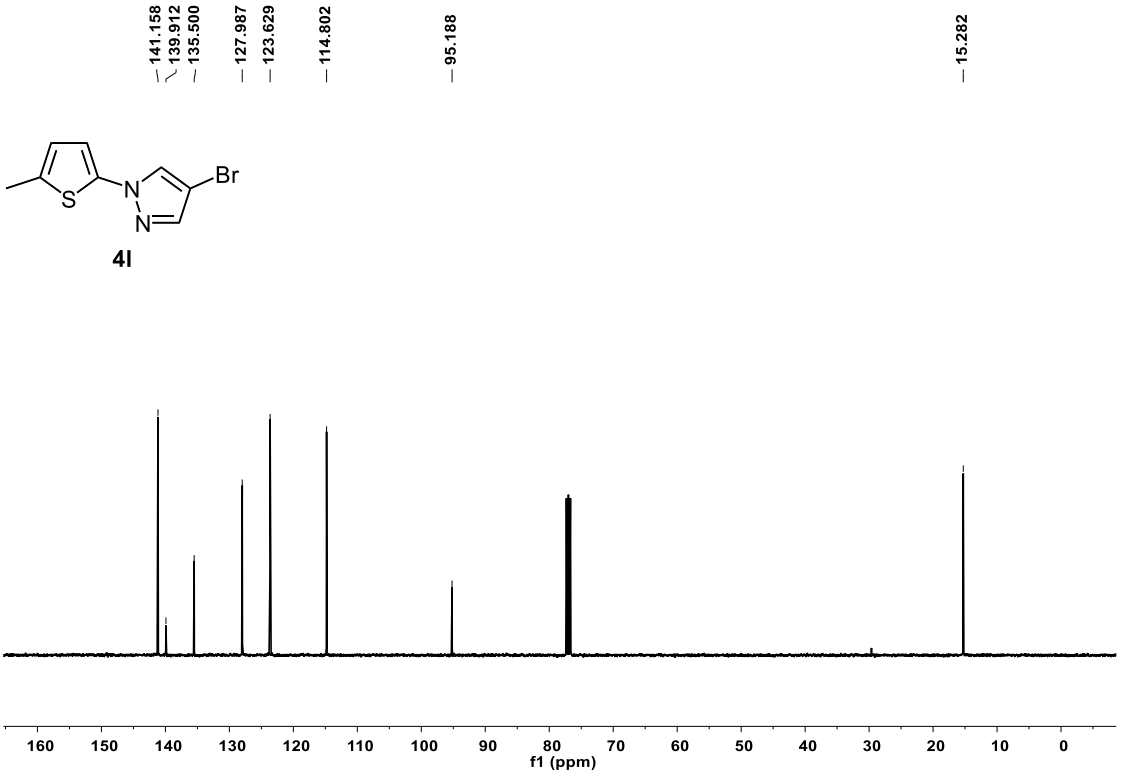

7.872
7.869
7.782
7.779
7.029
7.020
6.687
6.678
2.510
4j
0.99
0.96
0.97
0.97
3.00
f1 (ppm)

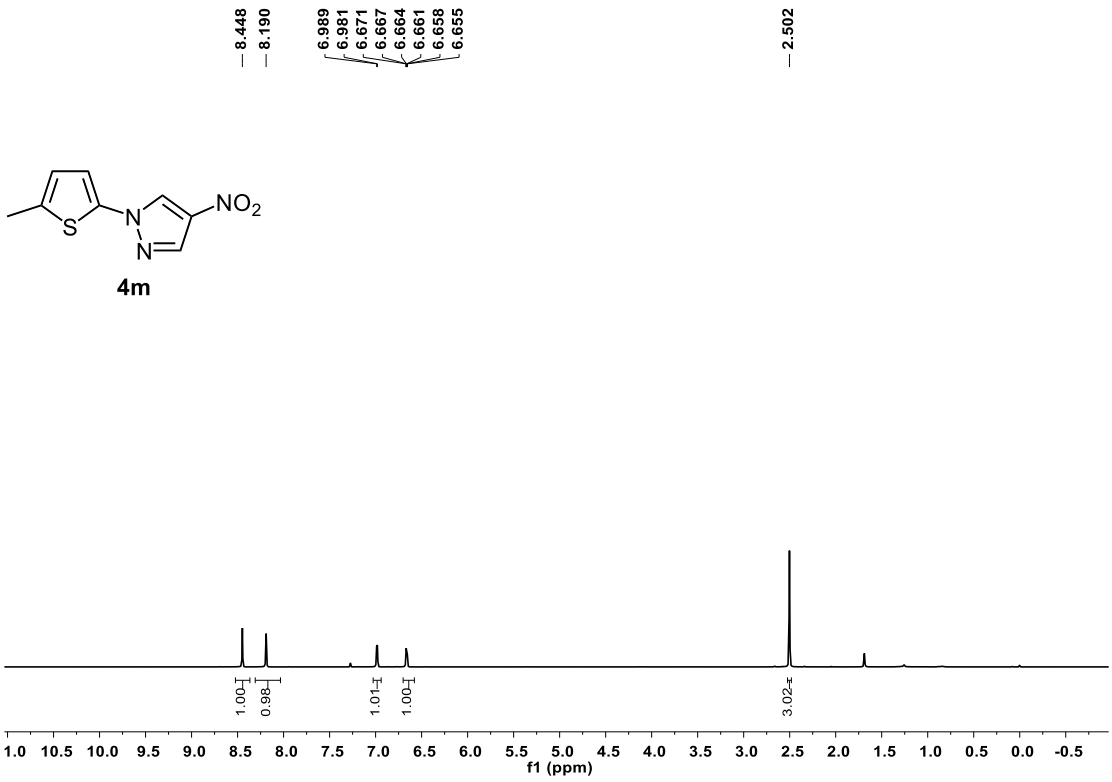

137.750
135.278
134.006
123.937
122.886
118.205
15.324
4j
f1 (ppm)

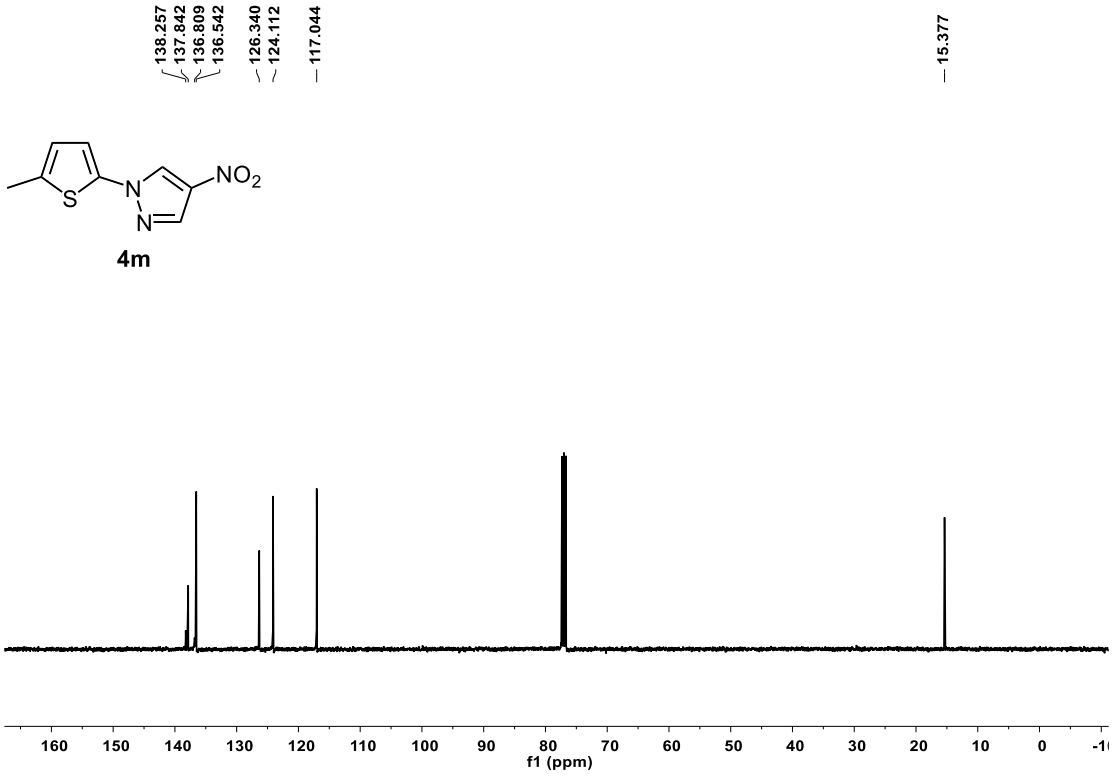

9.198
8.112
7.926
7.922
7.908
7.905
7.902
7.509
7.491
7.487
7.471
7.452
7.447
7.444
7.441
7.435
7.429
7.410
7.406
7.404
7.400
7.398
7.395
7.386
7.382
7.340
7.331
6.995
6.986
6.865
6.862
6.856
6.853
6.800
6.797
6.791
6.788
2.486
2.454
Ph
S
N
N=N
4k
Ph
S
N
N=N
4k'
1.00
0.79
2.08
2.97
2.33
1.00
0.80
1.03
0.81
3.00
2.43
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


147.204
140.156
138.780
136.965
134.940
132.947
132.884
129.913
129.653
129.048
128.902
128.673
128.457
128.418
125.858
125.406
124.627
124.583
120.198
117.955
15.124
14.976
Ph
S
N
N=N
4k
Ph
S
N
N=N
4k'
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.738
7.584
6.792
6.783
6.580
6.577
6.574
6.571
6.568
2.451
Br
S
N
N
4l
0.96
0.94
0.97
0.97
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


141.158
139.912
135.500
127.987
123.629
114.802
95.188
15.282
Br
S
N
N
4l
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.448
8.190
6.989
6.981
6.671
6.667
6.664
6.661
6.658
6.655
2.502
NO2
S
N
N
4m
1.00
0.98
1.01
1.00
3.02
f1 (ppm)


138.257
137.842
136.809
136.542
126.340
124.112
117.044
15.377
NO2
S
N
N
4m
f1 (ppm)