Supporting Information

Palladium-Catalyzed Direct C-H Ethoxycarbonylation of 2-Aryl-1,2,3-triazoles and Efficient Synthesis of Suvorexant

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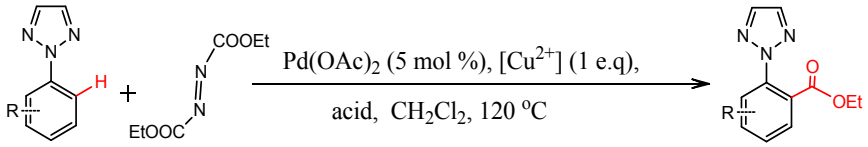
1. General Information

The reagents and solvents were commercially available and used without further purification. All the reactions were monitored by thin-layer chromatography (TLC) and were visualized using UV light. The product purification was done using silica gel column chromatography. Thin layer chromatography (TLC) characterization was performed with precoated silica gel GF254 (0.2mm), while column chromatography characterization was performed with silica gel (100-200mesh).^{1}H and ^{13}C NMR spectra were recorded with tetramethylsilane as the internal standard. ^{1}H NMR spectra were recorded at 400 or 600 MHz and ^{13}C NMR spectra were recorded at 100 or 150 MHz. Infrared (IR) spectra were recorded on a PerkinElmer Spectrum 10.5.0 Fourier transform infrared spectrophotometer. High resolution mass spectroscopy data of the products were collected on a Waters Micromass GCT or a Bruker Apex IV FTMS instrument. Gas chromatography-mass spectrometry is GCMS-QP2010 Plus, SHIMADZU, Japan. Chemical shifts (δ) were reported as parts per million (ppm) downfield from tetramethylsilane and the following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad and all combinations thereof can be explained by their integral parts. Commercial reagent were purchased from Best-reagent (Homepage: http://www.best-reagent.com)and Astatech Chemical Technology Co., Ltd. (Homepage: http://www.astabiochem.com) and Integle (http://www.integle.com). All reagents were directly used without further purification.

The following starting materials: 2-aryl-1,2,3-triazoles were synthesized according to the literature as previously described procedures.[1-3]

2. General Procedure for the Synthesis of 3

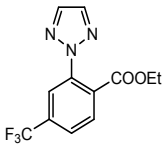


Condition 1 (**3aa** as an example): To a 15ml sealed tube were charged with 2-(3-(trifluoromethyl)phenyl)-2*H*-1,2,3-triazole **1aa** (42.6 mg, 0.2 mmol), diethyl azodicarboxylate 2 (a batch-wise fashion 4 × 0.2 mmol/ 1.5 h), $Pd(OAc)_2$ (2.2 mg, 5% mol), $Cu(CF_3SO_3)_2$ (72 mg, 0.2 mmol), CF_3SO_3H (3.5ul, 0.04 mmol) and DCM (2 ml) at room temperature in air, and the system was sealed with a Teflon cap. The mixture was stirred at 120 °C for 6 h, and then cooled down to ambient temperature. The volatiles were removed under reduced pressure and the analytically pure product 3aa was obtained by flash chromatography of silica gel (gradient of Petroleum ether/EtOAc) with 82% yield;

Condition 2 (**3fa** as an example): To a 15ml sealed tube were charged with 2-(3-(trifluoromethyl)phenyl)-2*H*-1,2,3-triazole **1fa** (32 mg, 0.2 mmol), diethyl azodicarboxylate 2 (a batch-wise fashion (4 × 0.2 mmol/ 2 h), $Pd(OAc)_2$ (2.2 mg, 5% mol), $Cu(CF_3COO)_2$ (51.3 mg, 0.2 mmol), HCOOH (13 ul, 0.4 mmol) and DCM (2 ml) at room temperature in air, and the system was sealed with a Teflon cap. The mixture was stirred at 120 °C for 15 h, and then cooled down to ambient temperature. The volatiles were removed under reduced pressure and the analytically pure product 3fa was obtained by flash chromatography of silica gel (gradient of Petroleum ether/EtOAc) with 76% yield;

3. Spectroscopic Characterization Data of Products 3

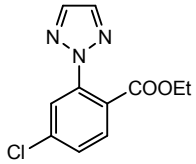
3aa 2-(2*H*-1,2,3-triazol-2-yl)-4-(trifluoromethyl)benzoate



3aa

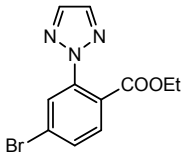
Yellow oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 1.7 Hz, 1H), 7.87- 7.84 (m, 3H), 7.73 (dd, *J* = 8.0, 1.7 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.1, 137.9, 136.2, 133.3 (q, *J* = 34 Hz), 130.4, 130.1, 124.8 (q, *J* = 272 Hz), 120.7 (q, *J* = 3.0 Hz), 62.0, 13.8; IR (cm^{-1}): 3007, 298, 2936, 2903, 1729, 1513, 1468, 1448, 1407, 1362, 1316, 1273, 1261, 1234, 1173, 1127, 1076, 1049, 1016, 962, 952, 897, 862, 825, 764, 749, 714, 652; HRMS (ESI) Calcd. for $C_{12}H_{10}F_3N_3O_2$ $[M+Na]^+$ 308.0623, found 308.0622.

3ab 4-chloro-2-(2*H*-1,2,3-triazol-2-yl)benzoate



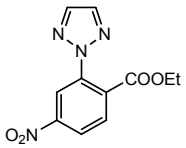
Yellow oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84-7.82 (m, 3H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.47 (dd, *J* = 8.3, 2.0 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.1, 135.9, 135.8, 131.1, 128.5, 125.6, 124.5, 124.4, 61.7, 13.9; IR (cm^{-1}): 2955, 2980，2939, 1725, 1600, 1577, 1494, 1432, 1406, 1366, 1285, 1261, 1231, 1111, 1098, 1069, 1048, 1018, 961, 952, 876, 857, 823, 801, 772, 736, 704, 655; HRMS (ESI) Calcd. for $C_{11}H_{10}ClN_3O_2$ $[M+Na]^+$ 274.0359, found 274.0353.

3ac 4-bromo-2-(2*H*-1,2,3-triazol-2-yl)benzoate



oil, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87-7.81 (m, 3H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.46 (dd, *J* = 8.4, 2.1 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.1, 137.5, 136.0, 131.5, 131.1, 128.5, 125.7, 124.5, 61.7, 13.9; IR (cm^{-1}):2985, 2932, 2904, 2846, 1724, 1600, 1577, 1494, 1465, 1431, 1406, 1366, 1275, 1260, 1231, 1156, 1132, 1110, 1098, 1069, 1048, 1016, 961, 951, 875, 857, 823, 765, 749, 704, 656; HRMS (ESI) Calcd. for $C_{11}H_{10}BrN_3O_2$ $[M+Na]^+$ 317.9854, found 317.9853.

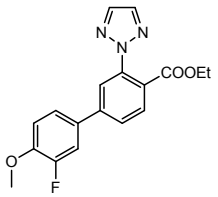
3ad 4-nitro-2-(2*H*-1,2,3-triazol-2-yl)benzoate



Yellow oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.79 (d, *J* = 2.2 Hz, 1H), 8.30 (dd, *J* = 8.4, 2.2 Hz,

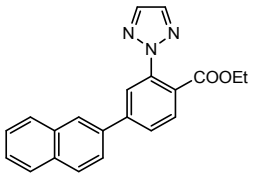
1H), 7.89 (s, 2H), 7.87 (d, *J* = 8.5 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.7, 149.1, 138.1, 136.6, 131.9, 130.7, 122.4, 118.5, 62.3, 13.8; IR (cm^{-1}): 3002, 2987, 1729, 1531, 1495, 1441, 1405, 1349, 1261, 1275, 1231, 1107, 1065, 1045, 1014, 961, 951, 891, 829, 764, 750, 667; HRMS (ESI) Calcd. for $C_{11}H_{10}N_4O_4$ [M+Na]$^+$ 285.0600, found 285.0602.

3ae 3'-fluoro-4'-methoxy-3-(2*H*-1,2,3-triazol-2-yl)-[1,1'-biphenyl]-4-carboxylate



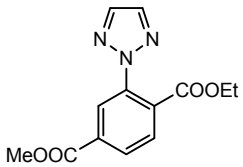
oil, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 1.7 Hz, 1H), 7.90 – 7.84 (m, 3H), 7.65 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.05 (t, *J* = 8.5 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.94 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.5, 152.0 (d, *J* = 148 Hz), 148.0, 143.4, 138.9, 135.6, 131.7 (d, *J* = 10 Hz), 130.8, 126.4, 125.8, 123.0 (d, *J* = 20 Hz), 114.9, 114.8, 113.7; IR (cm^{-1}):2975, 2923, 2846, 1720, 1613, 1564, 1527, 1499, 1463, 1408, 1367, 1274, 1262, 1174, 1134, 1112, 1045, 1019, 961, 914, 872, 810, 762, 749, 702; HRMS (ESI) Calcd. for $C_{16}H_{18}FN_3O_3$[M+Na]$^+$ 364.1073, found 364.1072.

3af 4-(naphthalen-2-yl)-2-(2*H*-1,2,3-triazol-2-yl)benzoate



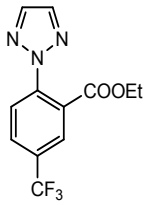
Yellow oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 1.7 Hz, 2H), 7.94 (td, *J* = 8.4, 4.5 Hz, 3H), 7.90 – 7.81 (m, 4H), 7.78 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.54 (td, *J* = 5.6, 5.1, 3.1 Hz, 2H), 4.25 (q, *J* = 7.3 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.6, 144.9, 139.0, 136.0, 135.6, 133.5, 133.1, 130.8, 128.8, 128.4, 127.7, 127.2, 126.6, 126.0, 124.9, 123.5, 61.5, 14.0; IR (cm^{-1}): 2984, 2917, 2848, 1714, 1612, 1502, 1466, 1439, 1410, 1389, 1367, 1298, 1276, 1258, 1193, 1140, 1117, 1075, 1049, 1019, 961, 943, 908, 890, 865, 845, 822, 810, 777, 766, 748, 710, 678, 663, 656, 632, 615;HRMS (ESI) Calcd. for $C_{21}H_{17}N_3O_2$[M+Na]$^+$ 366.1218, found 366.1217.

3ag 4-methyl 2-(2*H*-1,2,3-triazol-2-yl)terephthalate



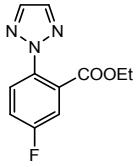
Off white solid, m.p 76-78 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 1.5 Hz, 1H), 8.14 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.85 (s, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.97 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.4, 165.1, 135.9, 133.1, 130.8, 129.9, 129.0, 125.0, 61.9, 52.6, 13.9; IR (cm^{-1}): 3136, 2955, 2918, 2849, 1723, 1617, 1578, 1505, 1439, 1410, 1369, 1355, 1309, 1275, 1257, 1235, 1193, 1174, 1136, 1105, 1076, 1051, 969, 959, 948, 910, 879, 867, 852, 778, 754, 714, 668, 658;HRMS (ESI) Calcd. for $C_{13}H_{13}N_3O_4$[M+Na]$^+$ 298.0804, found 298.0803.

3ba 2-(2*H*-1,2,3-triazol-2-yl)-5-(trifluoromethyl)benzoate



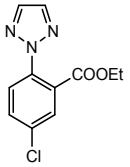
Yellow oil, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.5 Hz, 1H), 7.99 (s, 1H), 7.86 (m, 3H), 4.30 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.1, 140.0, 136.4, 130.3 (q, *J* = 30.0 Hz), 128.3 (q, *J* = 3.0 Hz), 127.1, 124.1 (q, *J* = 270 Hz), 120.5, 62.1, 13.9; IR (cm^{-1}): 2990, 2959, 2916, 2846, 1730, 1621, 1512, 1383, 1333, 1274, 1259, 1173, 1130, 1085, 1065, 1013, 962, 947, 840, 791, 764, 748, 704; HRMS (ESI) Calcd. for $C_{12}H_{10}F_3N_3O_2$ $[M+Na]^+$ 308.0623, found 308.0620.

3bb 5-fluoro-2-(2*H*-1,2,3-triazol-2-yl)benzoate



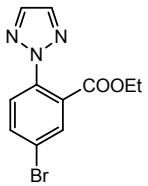
Yellow oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (s, 2H), 7.77-7.74 (m, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.33-7.30 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.3, 162.1 (d, *J* = 167 Hz), 135.6, 129.4, 126.8, 126.7, 118.7(d, *J* = 16 Hz), 117.2 (d, *J* = 10.0 Hz), 61.9, 13.9; IR (cm^{-1}): 2916, 2853, 1728, 1598, 1506, 1430, 1410, 1368, 1280, 1264, 1233, 1203, 1153, 1124, 1099, 1071, 1045, 1018, 962, 954, 896, 859, 829, 776, 732, 702, 635; HRMS (ESI) Calcd. for $C_{11}H_{10}FN_3O_2$ $[M+Na]^+$ 258.0655, found 258.0657.

3bc 5-chloro-2-(2*H*-1,2,3-triazol-2-yl)benzoate



oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (s, 2H), 7.81 – 7.72 (m, 2H), 7.58 (dd, *J* = 8.6, 2.5 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.6, 136.6, 135.8, 134.3, 131.5, 129.9, 126.6, 125.5, 61.9, 13.9; IR (cm^{-1}): 2984, 2930, 1726, 1605, 1495, 1407, 1365, 1294, 1267, 1231, 1139, 1110, 1069, 1043, 1016, 961, 947, 895, 859, 825, 763, 750, 678, 656; HRMS (ESI) Calcd. for $C_{11}H_{10}ClN_3O_2$ $[M+Na]^+$ 274.0359, found 274.0357.

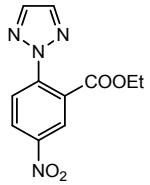
3bd 5-bromo-2-(2*H*-1,2,3-triazol-2-yl)benzoate



Yellow oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (s, 2H), 7.79 – 7.73 (m, 2H), 7.58 (dd, *J* = 8.6,

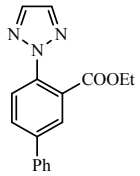
2.4 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.6, 135.7, 134.5, 132.7, 131.5, 129.9, 126.6, 125.5, 61.9, 13.9; IR (cm^{-1}): 3124, 2985, 2955, 2923, 2847, 1720, 1493, 1407, 1366, 1294, 1267, 1230, 1137, 1104, 1068, 1043, 1019, 962, 948, 894, 860, 818, 777, 735, 667; HRMS (ESI) Calcd. for $C_{11}H_{10}BrN_3O_2$ $[M+Na]^+$ 317.9854, found 317.9851.

3be 5-nitro-2-(2*H*-1,2,3-triazol-2-yl)benzoate



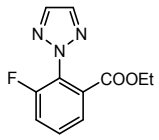
White solid, m.p 144-145 °C, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 2.5 Hz, 1H), 8.45 (dd, *J* = 9.0, 2.5 Hz, 1H), 8.14 (d, *J* = 8.9 Hz, 1H), 7.90 (s, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.3 Hz, 4H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.5, 137.0, 136.9, 127.6, 126.2, 125.3, 125.2, 123.8, 62.4, 13.9; IR (cm^{-1}): 3129, 2920, 1729, 1618, 1585, 1534, 1490, 1469, 1429, 1403, 1375, 1339, 1279, 1261, 1227, 1129, 1115, 1097, 1021, 961, 945, 920, 868, 855, 836, 830, 773, 748, 744, 713, 672, 654; HRMS (ESI) Calcd. for $C_{11}H_{10}N_4O_4$ $[M+Na]^+$ 285.0600, found 285.0593.

3bf 4-(2*H*-1,2,3-triazol-2-yl)-[1,1'-biphenyl]-3-carboxylate



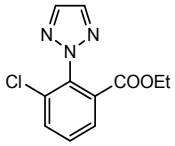
Off white solid, m.p 81-83 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.91 – 7.84 (m, 3H), 7.82 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.0, 141.6, 139.0, 137.2, 135.6, 130.0, 129.0, 128.6, 128.2, 127.8, 127.2, 124.7, 61.6, 14.0; IR (cm^{-1}): 3134, 2987, 2918, 2849, 1714, 1606, 1522, 1487, 1452, 1409, 1366, 1306, 1287, 1248, 1159, 1108, 1070, 1057, 1036, 1014, 899, 835, 781, 762, 732, 688, 676, 661, 654, 617; HRMS (ESI) Calcd. for $C_{17}H_{15}N_3O_2$ $[M+Na]^+$ 316.1062, found 316.1064.

3ca 3-fluoro-2-(2*H*-1,2,3-triazol-2-yl)benzoate



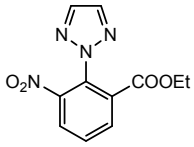
Color less oil, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.91 (s, 2H), 7.49 (t, *J* = 8.0 Hz, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 1.09 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.8, 138.8, 136.9, 135.2, 131.6, 131.1, 130.2, 123.3, 61.7, 13.9; IR (cm^{-1}):2986, 2926, 2846, 1720, 1477, 1211, 1367, 1263, 1198, 1147, 1090, 1016, 962, 952, 821, 763, 732, 702; HRMS (ESI) Calcd. for $C_{11}H_{10}FN_3O_2$ $[M+Na]^+$ 258.0655, found 258.0652.

3cd 3-chloro-2-(2*H*-1,2,3-triazol-2-yl)benzoate



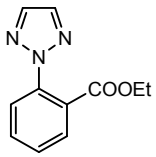
Color less oil, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 7.8 Hz, 1H), 7.91 (s, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 1.09 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.9, 137.3, 135.3, 133.8, 133.7, 131.5, 130.8, 129.5, 61.7, 13.9; IR (cm^{-1}): 3138, 3094, 2996, 2917, 2849, 1703, 1588, 1570, 1478, 1455, 1414, 1395, 1365, 1291, 1274, 1267, 1198, 1158, 1147, 1113, 1095, 1070, 1013, 962, 954, 891, 866, 821, 764, 748; HRMS (ESI) Calcd. for $C_{11}H_{10}ClN_3O_2$ $[M+Na]^+$ 274.0359, found 274.0356.

3ce 3-nitro-2-(2*H*-1,2,3-triazol-2-yl)benzoate



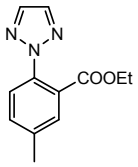
Yellow oil,^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 7.9 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.90 (s, 2H), 7.75 (t, *J* = 8.0 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.9, 150.6, 136.4, 134.5, 132.4, 131.4, 130.3, 127.6, 62.3, 13.8; IR (cm^{-1}): 3091, 3005, 2986, 2914, 2846, 1721, 1612, 1531, 1493, 1465, 1456, 1407, 1370, 1349, 1277, 1267, 1261, 1210, 1147, 1105, 1096, 1018, 962, 954, 870, 832, 826, 765, 749, 724, 707, 656; HRMS (ESI) Calcd. for $C_{11}H_{10}N_4O_4$ $[M+Na]^+$ 285.0600, found 285.0597.

3da 2-(2*H*-1,2,3-triazol-2-yl)benzoate



Yellow oil,^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (s, 2H), 7.80 (ddd, *J* = 8.0, 4.3, 1.3 Hz, 2H), 7.62 (td, *J* = 7.8, 1.5 Hz, 1H), 7.50 (td, *J* = 7.6, 1.2 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.8, 135.5, 135.4, 131.6, 130.0, 128.5, 127.4, 124.4, 61.4, 13.9; IR (cm^{-1}): 2981, 2935, 1722, 1607, 1588, 1498, 1453, 1380, 1366, 1290, 1264, 1233, 1108, 1073, 1050, 1032, 1017, 821, 760, 735, 706, 674, 648; HRMS (ESI) Calcd. for $C_{11}H_{11}N_3O_2$ $[M+Na]^+$ 240.0749, found 240.0747.

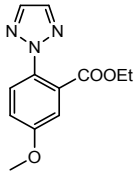
3ea 5-methyl-2-(2*H*-1,2,3-triazol-2-yl)benzoate



Yellow oil, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.81 (s, 2H), 7.69 – 7.57 (m, 2H), 7.41 (d, *J* = 8.1 Hz,

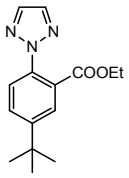
1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.8, 138.8, 136.1, 135.3, 132.2, 130.4, 127.2, 124.4, 61.4, 13.9; IR (cm^{-1}): 2923, 2861, 1723, 1509, 1463, 1410, 1366, 1303, 1285, 1269, 1234, 1201, 1108, 1072, 1044, 1021, 962, 952, 158, 824, 778, 734, 630; HRMS (ESI) Calcd. for $C_{12}H_{13}N_3O_2$ $[M+Na]^+$ 254.0905, found 254.0904.

3eb 5-methoxy-2-(2*H*-1,2,3-triazol-2-yl)benzoate



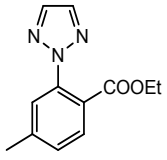
Yellow oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (s, 2H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.33 (d, *J* = 2.9 Hz, 1H), 7.11 (dd, *J* = 8.8, 2.9 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 4H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.2, 159.4, 135.1, 131.9, 128.8, 126.4, 117.4, 114.7, 61.5, 55.8, 13.8; IR (cm^{-1}): 3005, 2984, 2932, 2849, 1723, 1608, 1584, 1507, 1464, 1427, 1411, 1365, 1321, 1290, 1275, 1261, 1228, 1182, 1135, 1108, 1072, 1050, 1022, 962, 953, 860, 820, 764, 749, 633; HRMS (ESI) Calcd. for $C_{12}H_{13}N_3O_3$ $[M+Na]^+$ 270.0855, found 270.0853.

3ec 5-(tert-butyl)-2-(2*H*-1,2,3-triazol-2-yl)benzoate



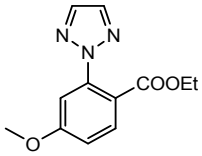
White solid, m.p 106-108 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (s, 2H), 7.80 (d, *J* = 2.2 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.62 (dd, *J* = 8.4, 2.2 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 1.38 (s, 9H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.3, 152.0, 135.3, 135.2, 133.2, 128.7, 126.7, 124.1, 61.4, 31.1, 29.6, 13.9; IR (cm^{-1}): 3121, 2968, 1717, 1610, 1508, 1470, 1412, 1366, 1302, 1270, 1249, 1235, 1160, 1148, 1129, 1113, 1071, 1044, 1020, 961, 953, 913, 861, 849, 836, 781, 755, 734, 682, 661, 636; HRMS (ESI) Calcd. for $C_{15}H_{19}N_3O_2$ $[M+Na]^+$ 296.1375, found296.1377.

3fa 4-methyl-2-(2*H*-1,2,3-triazol-2-yl)benzoate



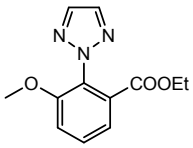
Yellow oil,^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (s, 2H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.56 (s, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 2.46 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.6, 142.7, 135.3, 130.3, 130.2, 129.6, 129.3, 125.4, 124.7, 61.2, 21.2, 13.9; IR (cm^{-1}): 2984, 2921, 2850, 1722, 1615, 1510, 1464, 1410, 1366, 1287, 1262, 1235, 1204, 1157, 1110, 1072, 1050, 1017, 961, 882, 822, 764, 750, 712, 686, 657, 622; HRMS (ESI) Calcd. for $C_{12}H_{13}N_3O_2$ $[M+Na]^+$ 254.0905, found 254.0902.

3fb 4-methoxy-2-(2*H*-1,2,3-triazol-2-yl)benzoate



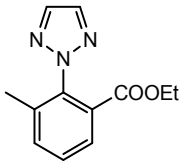
Yellow oil, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.83 (s, 2H), 7.24 (m, 3H), 7.02 (dd, *J* = 8.7, 2.6 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.90 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.1, 162.2, 140.0, 135.4, 132.1, 119.9, 114.7, 110.6, 61.1, 55.8, 14.0; IR (cm^{-1}): 2922, 2847, 1719, 1613, 1586, 1511, 1463, 1453, 1410, 1366, 1263, 1247, 1182, 1153, 1110, 1029, 961, 868, 853, 821, 733, 702, 641, 613; HRMS (ESI) Calcd. for $C_{12}H_{13}N_3O_3$ $[M+Na]^+$ 270.0855, found 270.0851.

3ga 3-methoxy-2-(2*H*-1,2,3-triazol-2-yl)benzoate



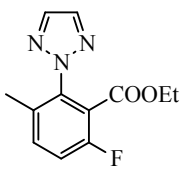
Yellow oil, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (s, 2H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.55 (t, *J* = 8.1 Hz, 1H), 7.26 (d, *J* = 10.5 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 1.08 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.7, 155.7, 134.9, 130.8, 130.7, 128.6, 122.4, 115.7, 61.3, 56.5, 13.9; IR (cm^{-1}):3127, 2984, 2942, 2915, 2844, 1707, 1585, 1491, 1474, 1440, 1414, 1365, 1277, 1192, 1150, 1100, 1057, 1018, 961, 953, 863, 823, 801, 758, 716, 689, 660, 617; HRMS (ESI) Calcd. for $C_{12}H_{13}N_3O_3$ $[M+Na]^+$ 270.0855, found 270.0857.

3gb 3-methyl-2-(2*H*-1,2,3-triazol-2-yl)benzoate



Yellow oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (s, 2H), 7.55 – 7.40 (m, 3H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.09 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.2, 138.6, 136.9, 134.8, 134.5, 129.6, 129.5, 128.7, 61.2, 17.4, 13.9; IR (cm^{-1}): 2981, 2930, 1716, 1590, 1476, 1442, 1412, 1384, 1367, 1287, 1182, 1144, 1102, 1023, 962, 953, 915, 865, 817, 762, 731, 715; HRMS (ESI) Calcd. for $C_{12}H_{13}N_3O_2$ $[M+Na]^+$ 254.0905, found 254.0902.

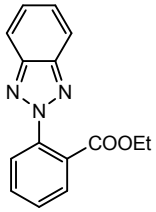
3ha 6-fluoro-3-methyl-2-(2*H*-1,2,3-triazol-2-yl)benzoate



^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (s, 2H), 7.45 – 7.38 (m, 1H), 7.21 (t, *J* = 8.7 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 2.20 (s, 2H), 1.14 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.7,

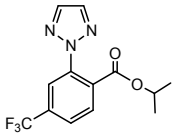
158.2 (d, *J* = 168 Hz), 137.8 (d, *J* = 3.0 Hz), 135.4, 133,7 (d, *J* = 6.0 Hz), 131.1 (d, *J* = 3.0 Hz), 120.1 (d, *J* = 11 Hz), 117.2 (d, *J* = 14 Hz), 61.8, 17.5, 13.9. IR (cm^{-1}): 3005, 2987, 2917, 2846, 1729, 1608, 1487, 1410, 1368, 1297, 1274, 1267, 1214, 1153, 1110, 1026, 961, 932, 881, 819, 764, 749, 716, 619; HRMS (ESI) Calcd. for $C_{12}H_{12}FN_3O_2$ $[M+Na]^+$ 272.0811, found 272.0813.

3ia 2-(2*H*-benzo[d][1,2,3]triazol-2-yl)benzoate



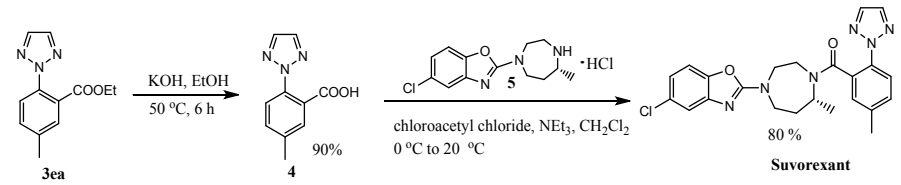
Yellow oil, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.95 (td, *J* = 6.6, 6.2, 2.2 Hz, 2H), 7.89 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.69 (td, *J* = 7.7, 1.6 Hz, 1H), 7.60 (td, *J* = 7.6, 1.3 Hz, 1H), 7.44 (dt, *J* = 6.3, 3.2 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 0.92 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.6, 145.0, 1139.0, 131.8, 130.3, 129.5, 128.5, 127.2, 125.4, 118.4, 61.6, 13.6; IR (cm^{-1}): 2984, 2932, 2853, 1722, 1605, 1565, 1496, 1460, 1441, 1366, 1343, 1294, 1274, 1267, 1261, 1218, 1109, 1066, 1036, 1016, 963, 854, 811, 763, 748, 703, 649, 625; HRMS (ESI) Calcd. for $C_{15}H_{13}N_3O_2$ $[M+Na]^+$ 290.0905, found 290.0903.

3ja 2-(2*H*-1,2,3-triazol-2-yl)-4-(trifluoromethyl)benzoate



Yellow oil, ^1H NMR (600 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 7.86 (s, 2H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 5.19 (m, 1H), 1.22 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.6, 137.8, 136.1, 133.2 (q, *J* = 34 Hz), 130.6, 130.4, 124.3 (q, *J* = 272 Hz), 120.9 (q, *J* = 3.0 Hz), 69.9, 21.5; IR (cm^{-1}): 2985, 2941, 1727, 1512, 1468, 1448, 1407, 1371, 1363, 1316, 1273, 1262, 1235, 1174, 1127, 1100, 1075, 1049, 962, 952, 915, 897, 863, 849, 713, 801, 764, 749, 713, 652; HRMS (ESI) Calcd. for $C_{13}H_{12}F_3N_3O_2$ $[M+Na]^+$ 322.0779, found 322.0777.

4. The Synthesis of suvorexant

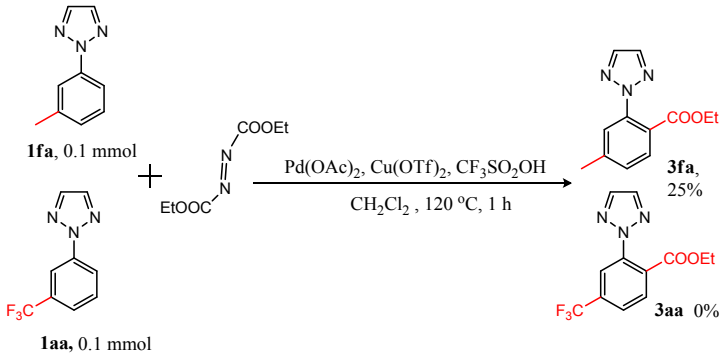


To a round bottom flask charged 4-methyl-2-(2*H*-1,2,3-triazol-2-yl)benzoate (50 mg, 0.22 mmol), KOH (67.2 mg, 1.2 mmol), EtOH (3 ml) and H_2O (0.5 ml), and the system was react at 40 °C for 5 h, and then cooled down to ambient temperature. The pH was adjusted to 1 with 5% HCl, and EtOH was removed under reduced pressure. The residual solvent was extracted with EtOAc (3 x 10 ml), and the solvent was evaporated under reduced pressure. The oily residue was purified by chromatography on a silica gelcolumn (DCM/MeOH) and product 4 was obtained with 90% yield. Suvorexant was synthesised from **4** and **5** according to the literature as previous report. [4, 5]

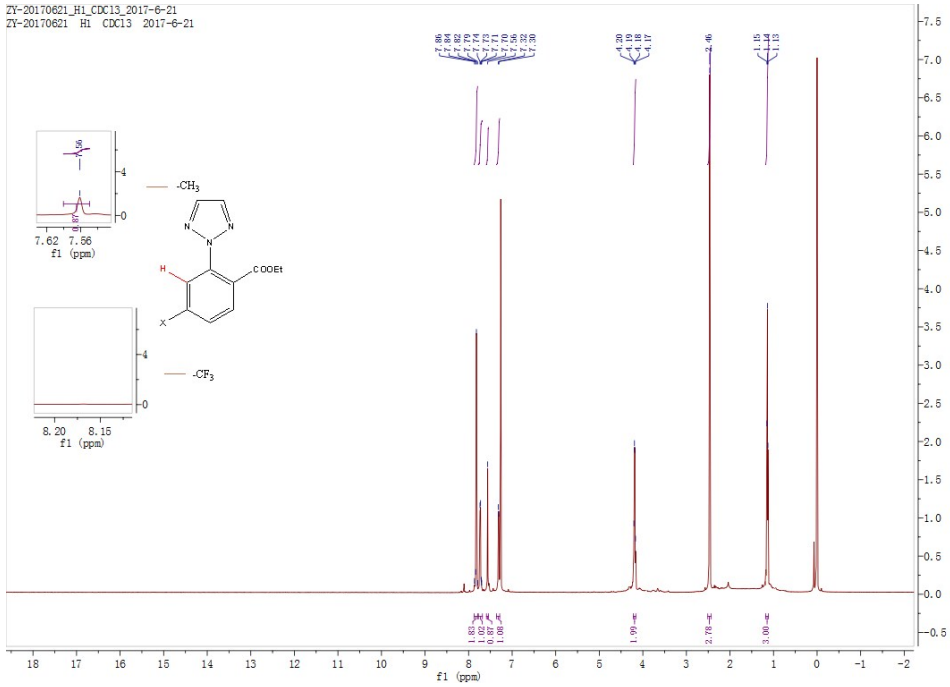
Product 4: 5-methyl-2-(2*H*-1,2,3-triazol-2-yl)benzoic acid: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (s, 2H), 7.76 (d, *J* = 2.0 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.50 – 7.42 (m, 1H), 2.47 (s, 3H). [4, 5]
Suvorexant: 1H NMR (400 MHz, Chloroform-d) δ 7.90−7.75 (m, 3H), 7.68-7.01 (m, 5H), 5.09 – 4.46 (m, 1H), 4.23 - 3.41 (m, 6H), 3.16-2.31 (m, 4H), 2.20 – 2.01 (m, 1H), 1.91 - 1.16 (m, 3H); [4, 5]

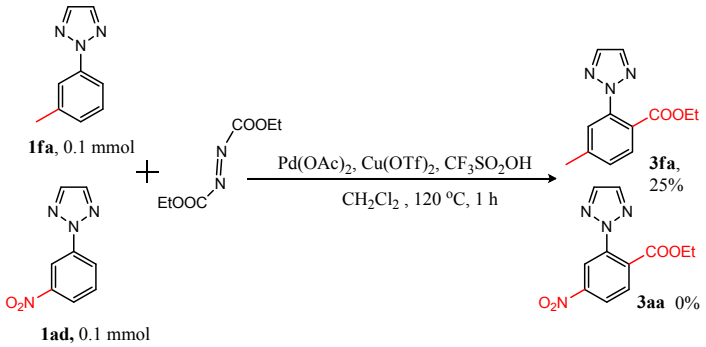
5. Mechanistic studies

5.1 Electronic effects



To a 15ml sealed tube were charged with 2-(m-tolyl)-2*H*-1,2,3-triazole **1fa** (16 mg, 0.1 mmol) and 2-(3-(trifluoromethyl)phenyl)-2*H*-1,2,3-triazole **1aa** (21.3 mg, 0.1 mmol), diethyl azodicarboxylate 2 (0.1 mmol), $Pd(OAc)_2$ (1.12 mg, 5% mol), $Cu(CF_3SO_3)_2$ (36.18 mg, 0.1 mmol), CF_3SO_3H (1.8ul, 0.02 mmol) and DCM (1 ml) at room temperature in air, and the system was sealed with a Teflon cap. The mixture was stirred at 120 °C for 1 h, and then cooled down to ambient temperature. The volatiles were removed under reduced pressure and the analytically pure product was obtained by flash chromatography of silica gel (gradient of Petroleum ether/EtOAc).The product was analyzed by ^{1}H NMR in $CDCl_3$ and only 3fa was obtained.

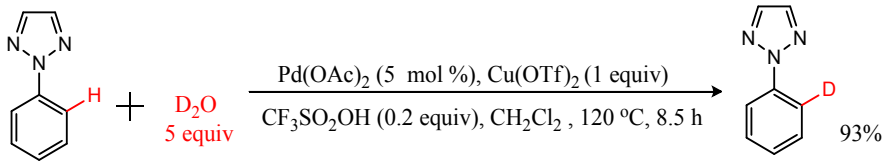




To a 15ml sealed tube were charged with 2-(3-nitrophenyl)-2*H*-1,2,3-triazole **1fa** (16 mg, 0.1 mmol) and 2-(3-(trifluoromethyl)phenyl)-2*H*-1,2,3-triazole **1ad** (19 mg, 0.1 mmol), diethyl azodicarboxylate 2 (0.1 mmol), $Pd(OAc)_2$ (1.12 mg, 5% mol), $Cu(CF_3SO_3)_2$ (36.18 mg, 0.1 mmol), CF_3SO_3H (1.8 ul, 0.02 mmol) and DCM (1 ml) at room temperature in air, and the system was sealed with a Teflon cap. The mixture was stirred at 120 °C for 1 h, and then cooled down to ambient temperature. The volatiles were removed under reduced pressure and the analytically pure product was separated by flash chromatography of silica gel (gradient of Petroleum ether/EtOAc) and only **3fa** was obtained (**3fa** and **3ad** shown different polarity and can be separated).

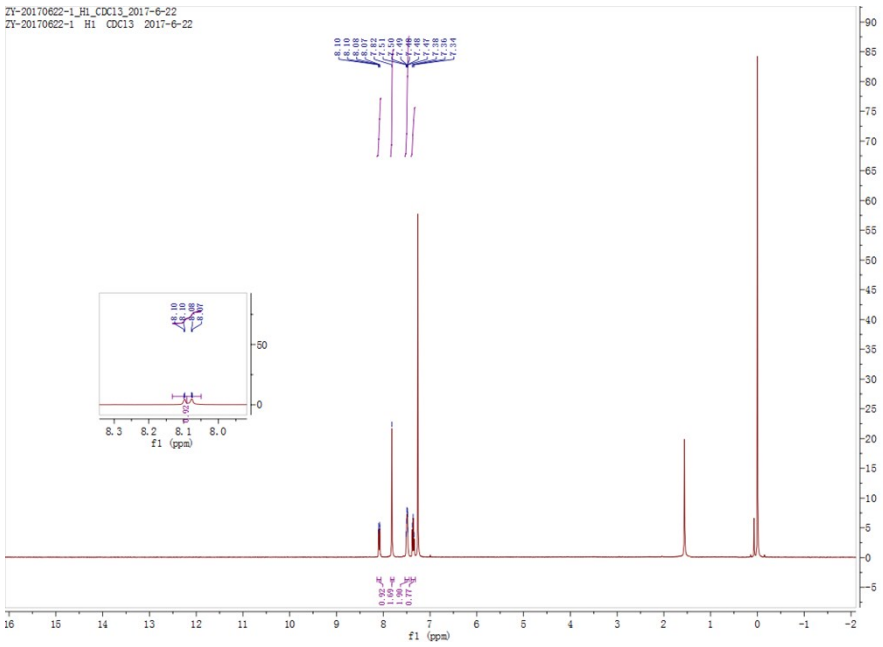
Those results indicated that there is a significant electronic effect on the reaction and an electrophilic C−H activation process may include.

5.2 The reversibility of C–H activation step

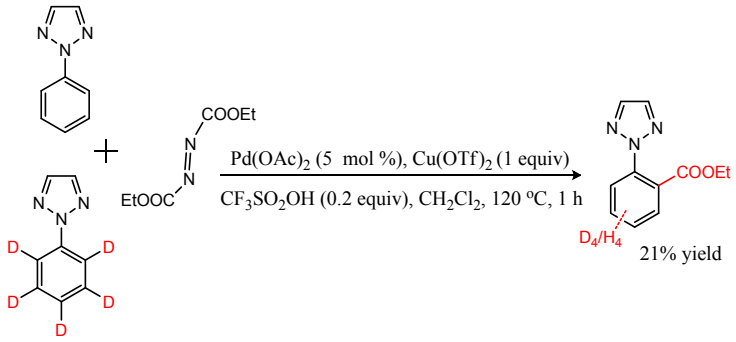


To a 15ml sealed tube were charged with **1da** (15 mg, 0.1 mmol), D_2O (10 mg, 0.5 mmol), $Pd(OAc)_2$ (1.12 mg, 5% mol), $Cu(CF_3SO_3)_2$ (36.18 mg, 0.1 mmol), CF_3SO_3H (1.8ul, 0.02 mmol) and DCM (1 ml) at room temperature in air, and the system was sealed with a Teflon cap. The mixture was stirred at 120 °C for 8.5 h, and then cooled down to ambient temperature. The volatiles were removed under reduced pressure and the analytically pure product was obtained by flash chromatography of silica gel (gradient of Petroleum ether/EtOAc).The product was analyzed by ^1H NMR in $CDCl_3$.

The result determined that 93% H was exchanged by D. This deuterium experiment suggested that the C–H activation step was reversible.

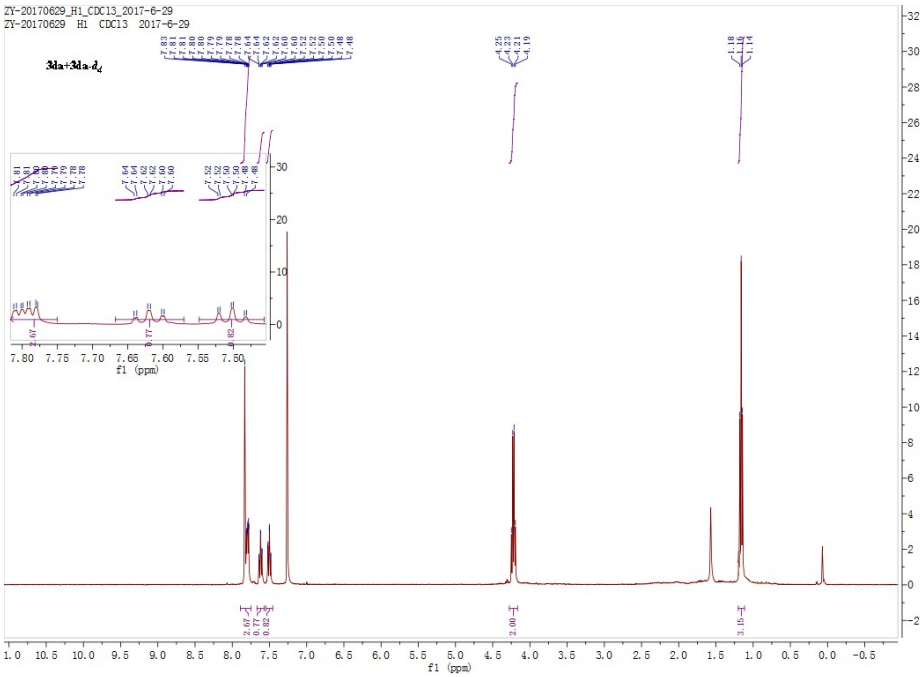


5.3 KIE study

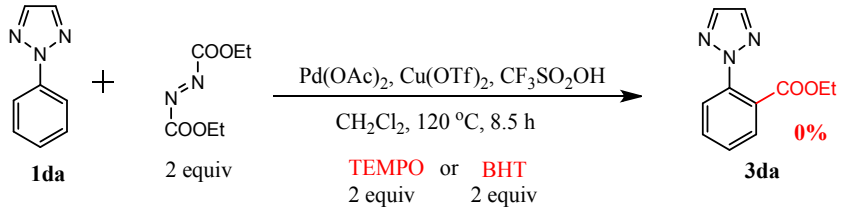


To a 15 ml sealed tube were charged with **1da** (15 mg, 0.1 mmol), **1da-*d*$_5$** 2-phenyl[d5]-2*H*-1,2,3-triazole (15 mg, 0.1 mmol), $Pd(OAc)_2$ (1.12 mg, 5% mol), $Cu(CF_3SO_3)_2$ (36.18 mg, 0.1 mmol), CF_3SO_3H (1.8ul, 0.02 mmol) and DCM (1 ml) at room temperature in air, and the system was sealed with a Teflon cap. The mixture was stirred at 120 °C for 1 h, and then cooled down to ambient temperature. The volatiles were removed under reduced pressure and the analytically pure product was obtained by flash chromatography of silica gel (gradient of Petroleum ether/EtOAc).The product was analyzed by ^1H NMR in $CDCl_3$. ^1H NMR spectra

of the **3da** and **3da-*d*$_4$** determined the intermolecular KIE value equal to 4.5.

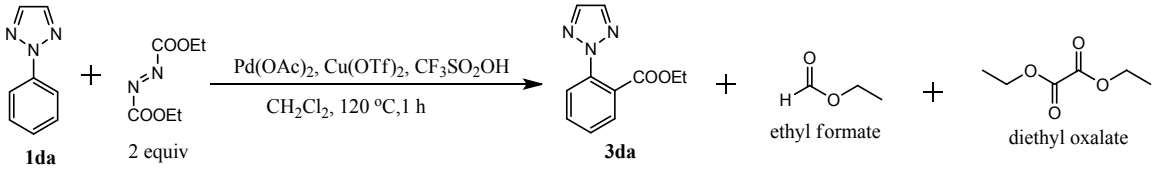


5.4 Control experiments



To a 15ml sealed tube were charged with **1da** (15mg, 0.1 mmol), diethyl azodicarboxylate 2 (0.2 mmol), $Pd(OAc)_2$ (1.12 mg, 5% mol), $Cu(CF_3SO_3)_2$ (36.18 mg, 0.1 mmol), CF_3SO_3H (1.8 ul, 0.02 mmol) and DCM (1 ml) at room temperature in air. Then, TEMPO (31 mg, 0.2 mmol) or BHT (44 mg, 0.2 mmol) was added and the system was sealed with a Teflon cap. The mixture was stirred at 120 °C for 8.5 h, and then cooled down to ambient temperature. The volatiles were analyzed by TLC and not product was detected. It is proposed that a radical pathway of C-H alkoxycarbonylation was involved.

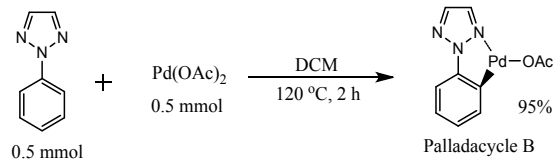
5.5 The by-products detection



When the reaction was carried out under the optimal condition for one hour, the reaction mixture was tested by gas chromatography-mass spectrometry. The by-products ethyl formate

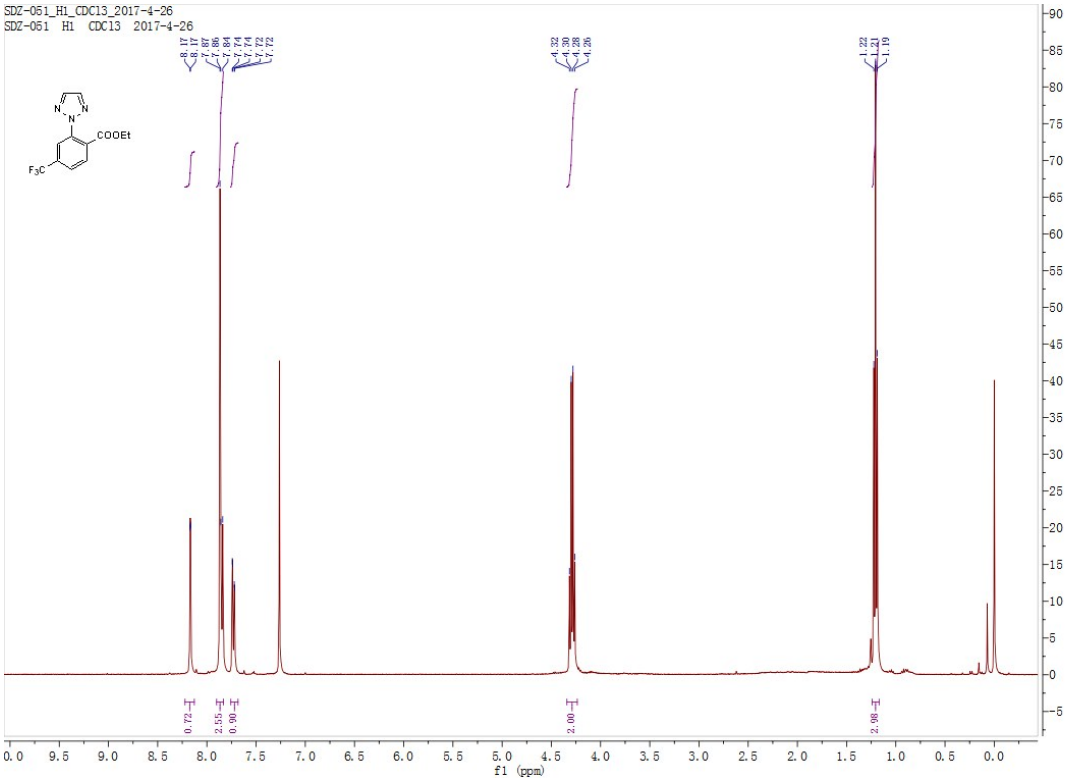
and diethyl oxalate were detected. This result indirectly proves that the radical of ethyl formate is subsistent.

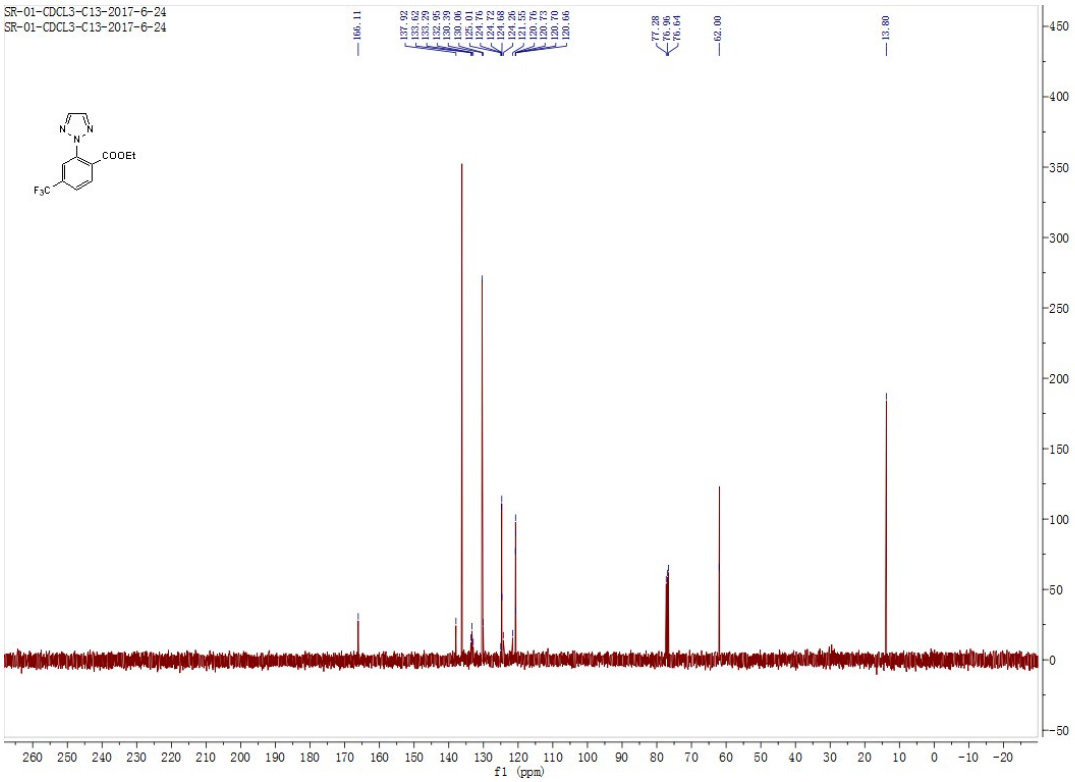
5.6 Formation of Palladacycle B

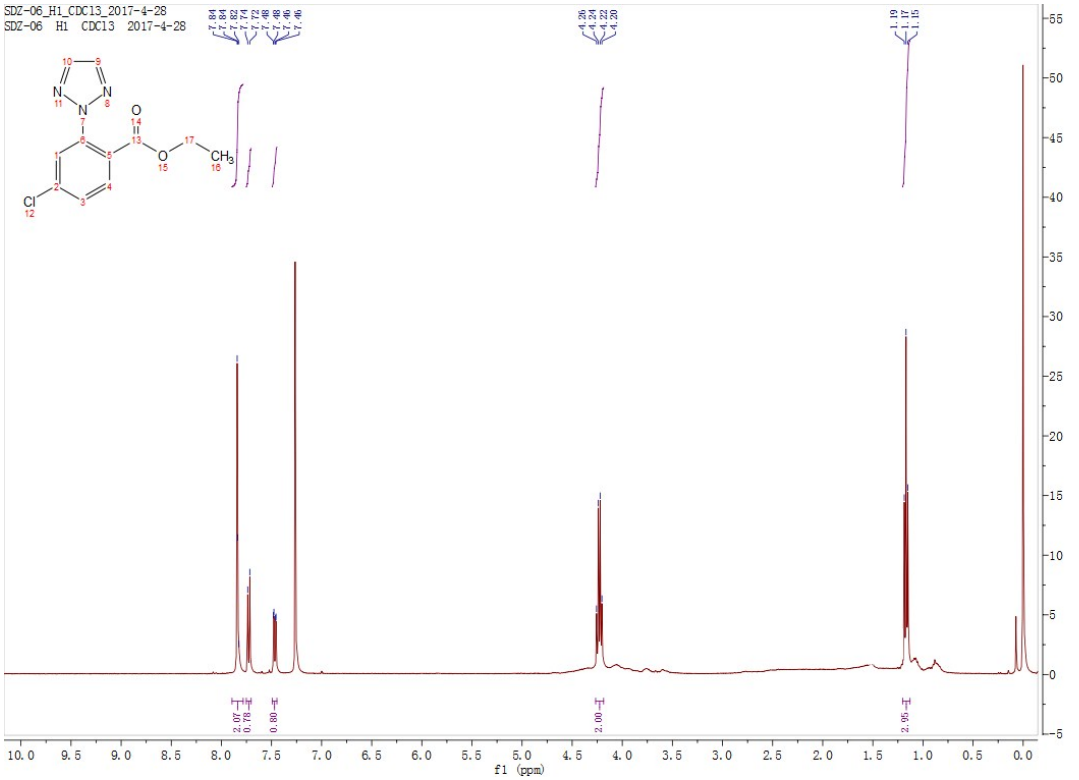


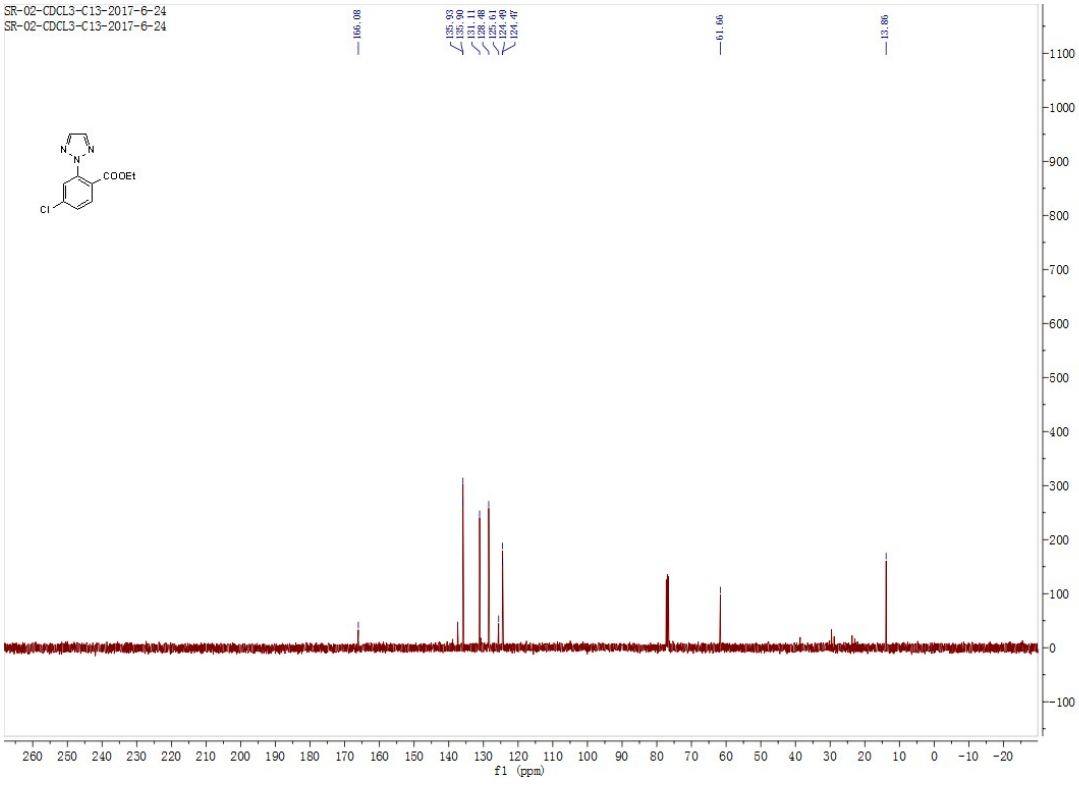
To a mixture 1da (72.6 mg, 0.5 mmol), $Pd(OAc)_2$ (112 mg, 0.5 mmol), and DCM (3 mL) were added to the sealed tube and reaction under 120 °C for 2 hours. Then, cooled to room temperature, and the solid was collected and washed with EtOAc to give intermediate Palladacycle B (147.1 mg, 95% yield) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.11 (d, J = 7.8 Hz, 1H), 7.08 (s, 1H), 7.04 – 6.98 (m, 1H), 6.93 (dd, J = 3.2, 1.9 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.4, 141.0, 134.0, 133.4, 131.7, 129.4, 126.5, 125.1, 113.6, 24.5.

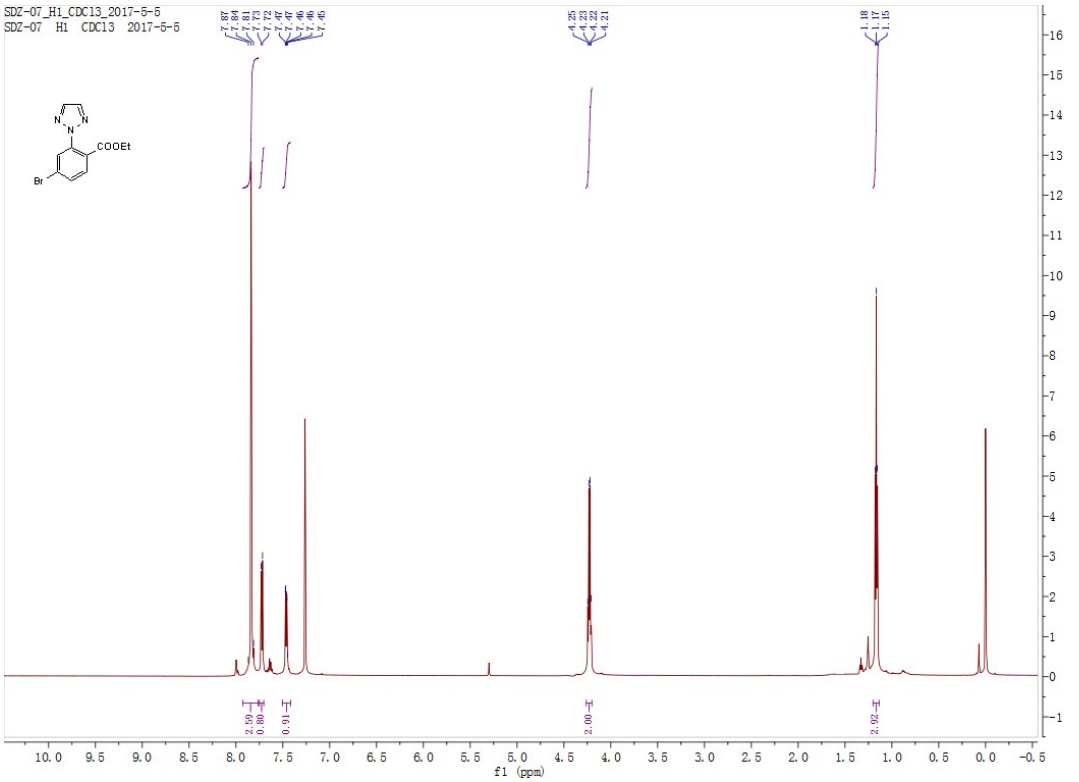
6. "NMR"Spectra

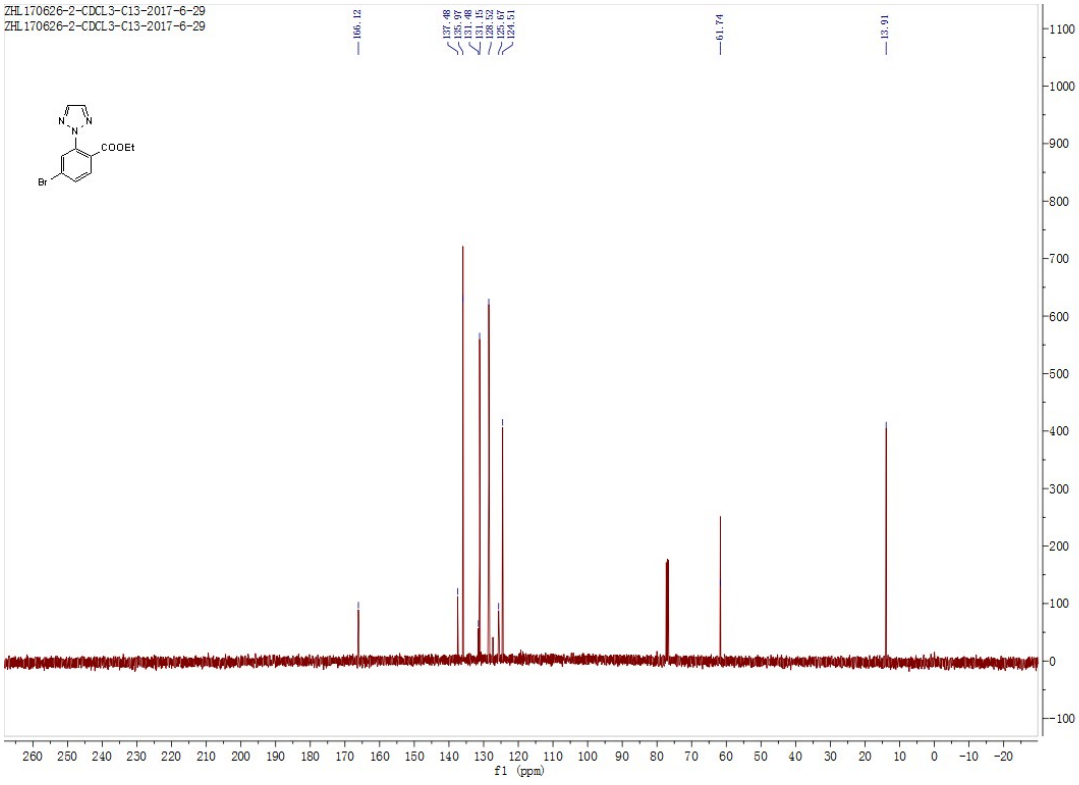


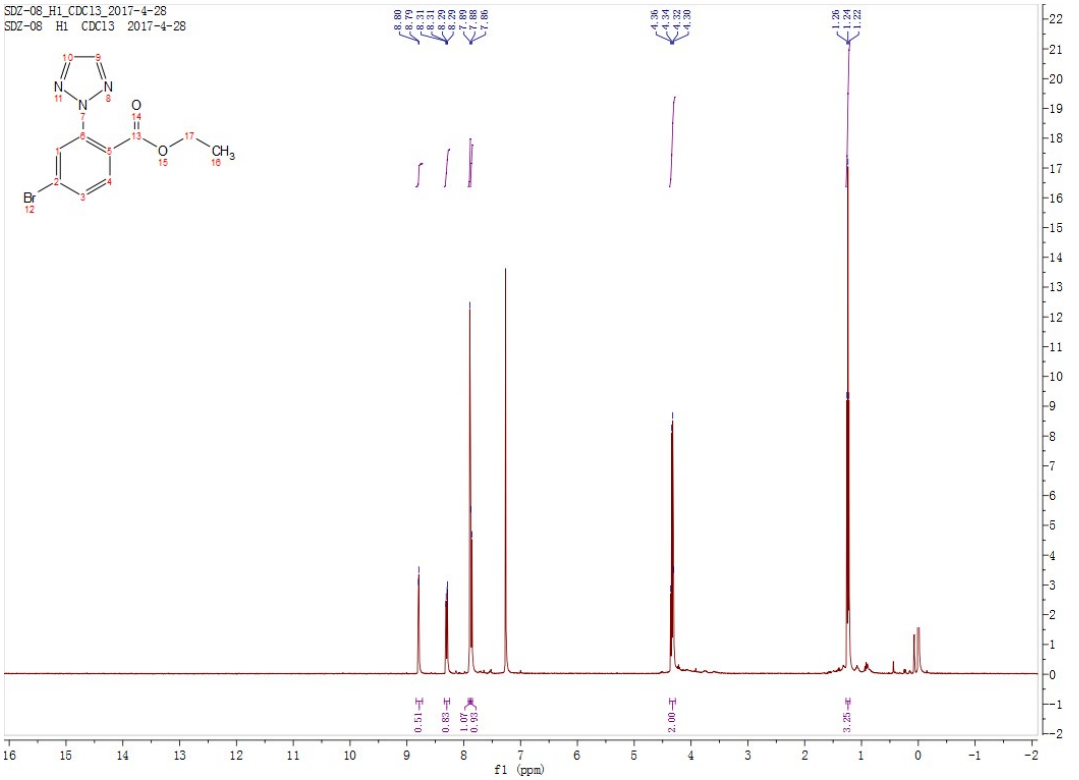


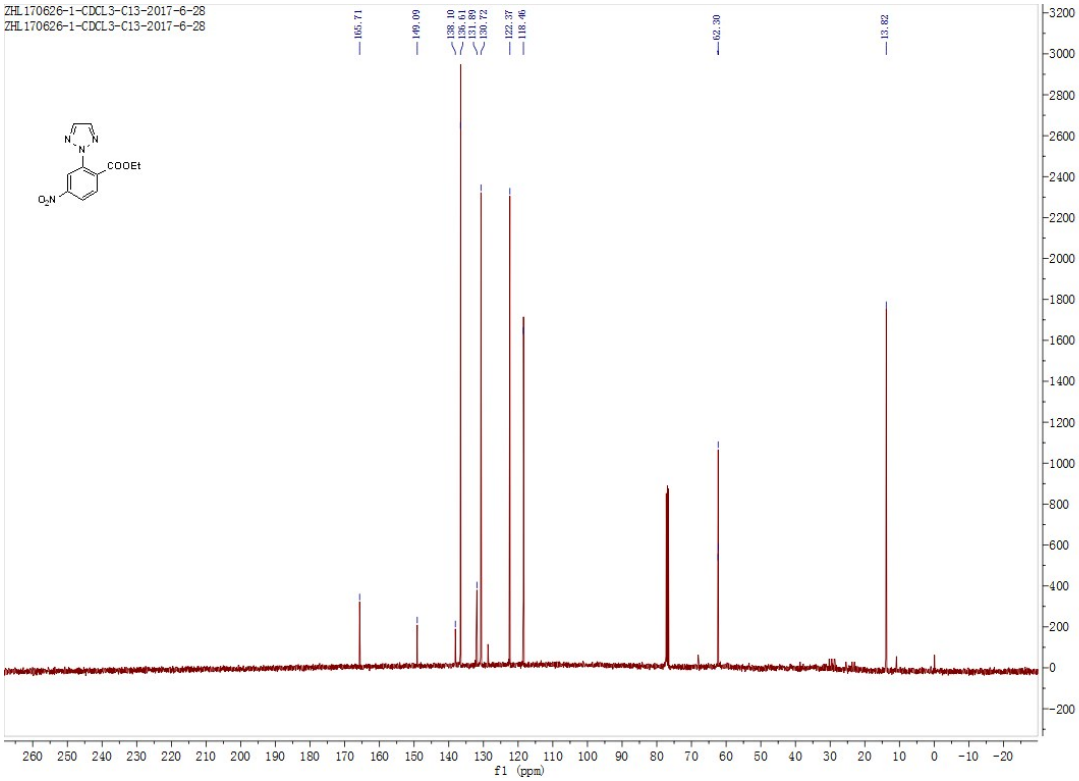

SDZ-06_H1_CDCl3_2017-4-28
SDZ-06 H1 CDCl3 2017-4-28
f1 (ppm)

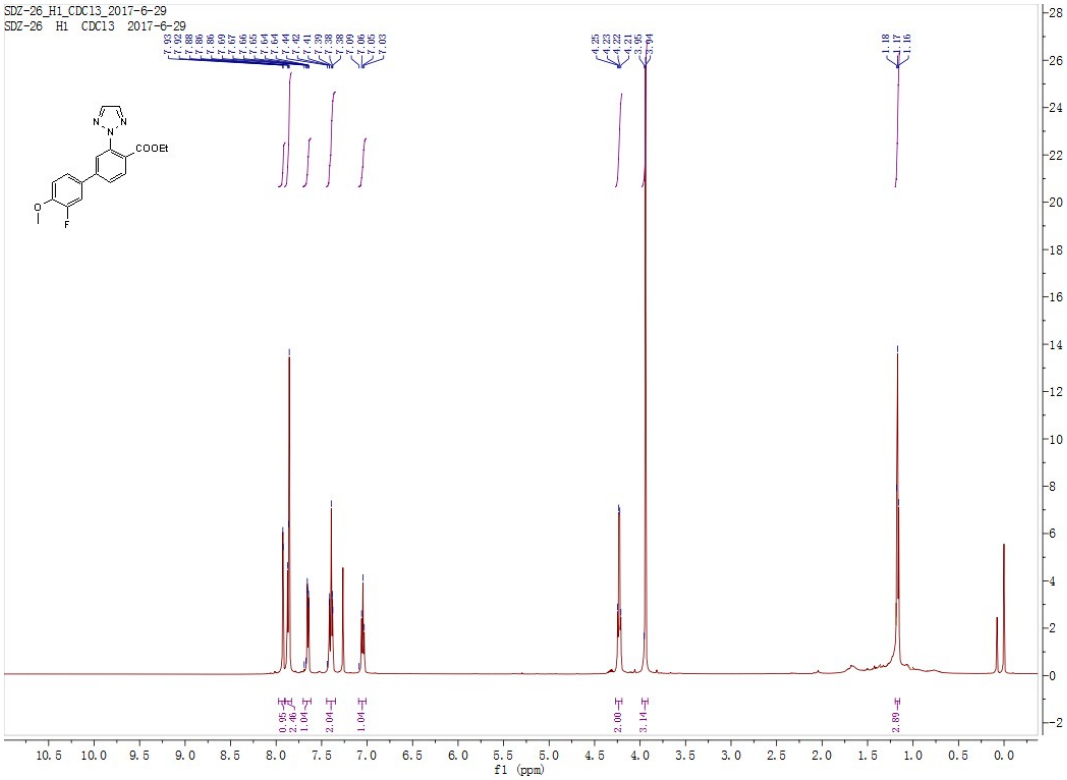

SR-02-CDCL3-C13-2017-6-24
SR-02-CDCL3-C13-2017-6-24
COOEt
f1 (ppm)

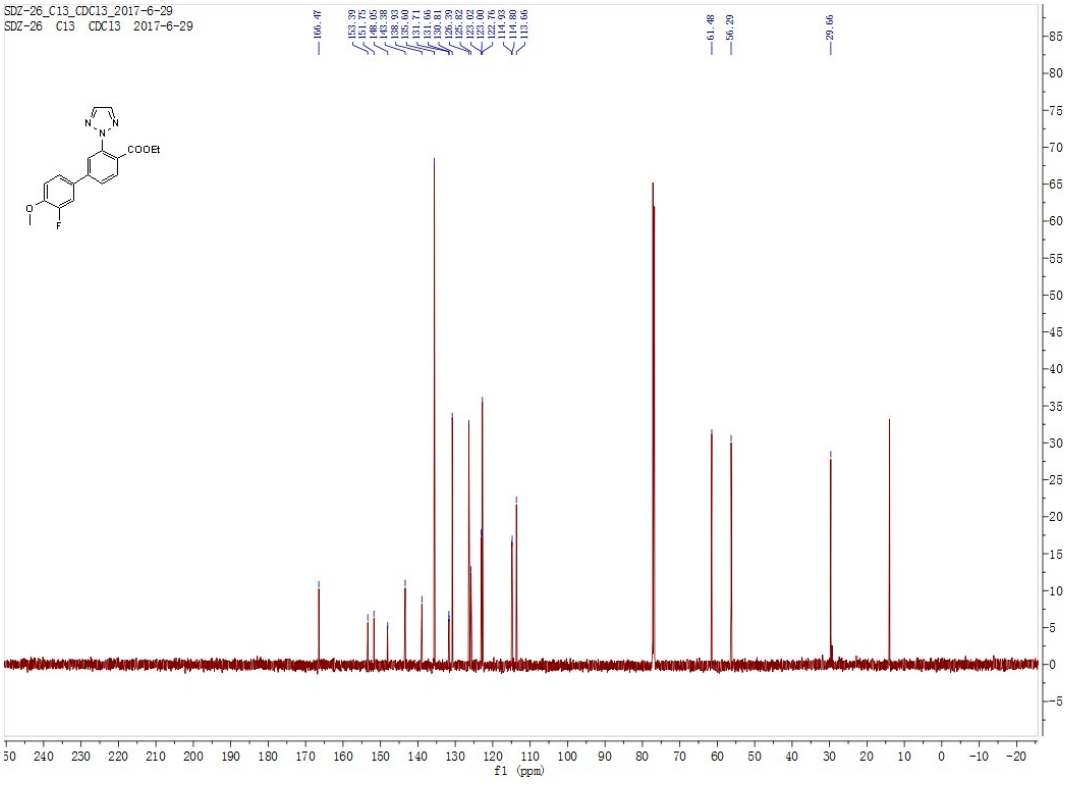

SDZ-07_H1_CDCl3_2017-6-5
SDZ-07 H1 CDCl3 2017-6-5
COOEt
Br
f1 (ppm)

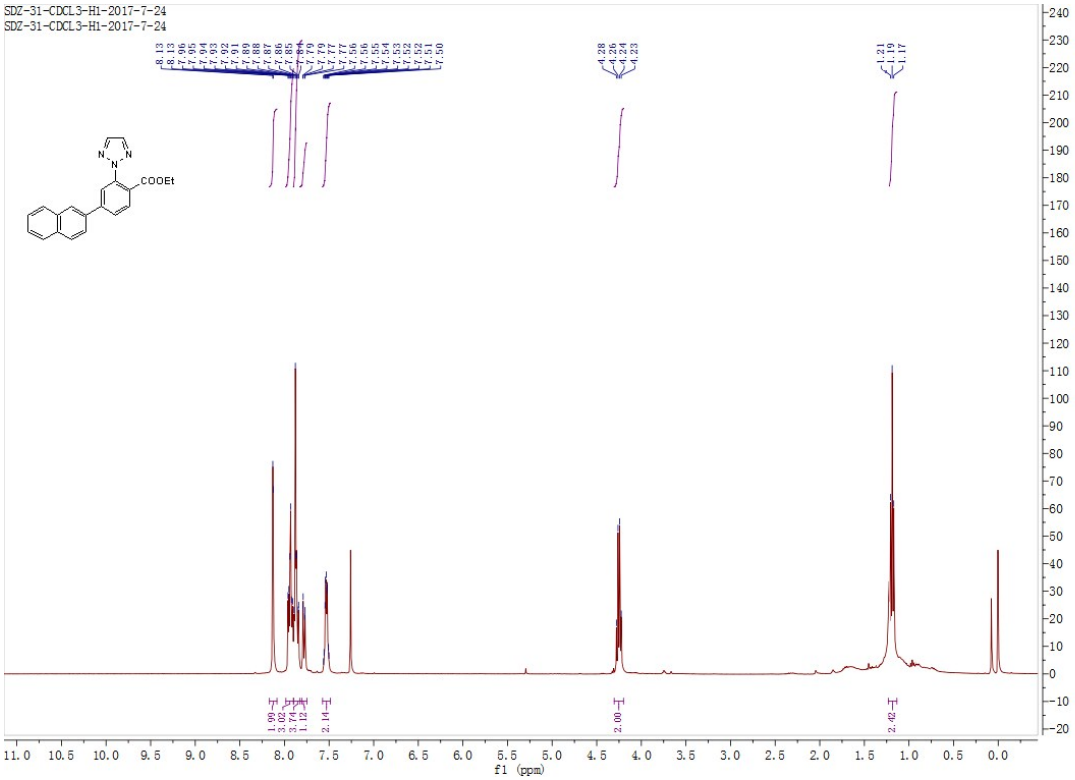

ZHL170626-2-CDCL3-C13-2017-6-29
ZHL170626-2-CDCL3-C13-2017-6-29
COOEt
Br
f1 (ppm)

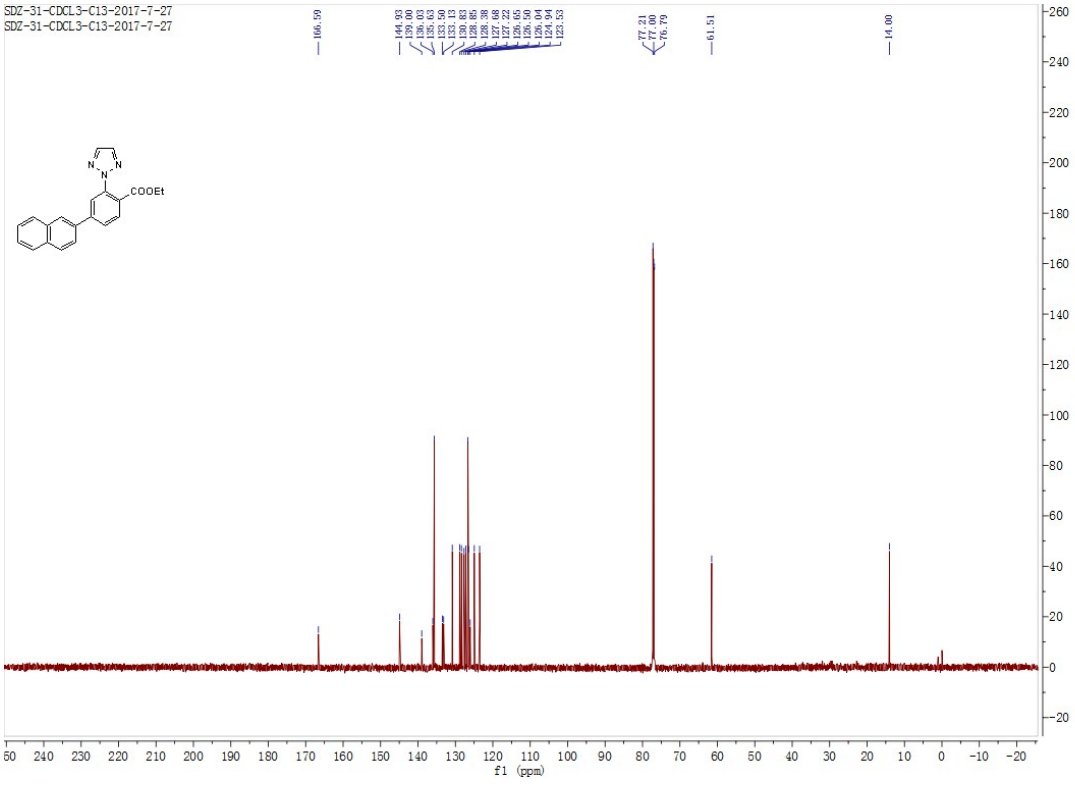

SDZ-08_H1_CDCl3_2017-4-28
SDZ-08 H1 CDCl3 2017-4-28
8.80
8.79
8.31
8.30
8.29
7.89
7.88
7.86
4.36
4.34
4.32
4.30
1.26
1.24
1.22
Br
O
0.51
0.83
1.07
0.93
2.09
3.25
f1 (ppm)


ZHL170626-1-CDCL3-C13-2017-6-28
ZHL170626-1-CDCL3-C13-2017-6-28
165.71
149.09
138.10
136.61
131.89
130.72
122.37
118.46
62.30
13.82
COOEt
O2N
f1 (ppm)


SDZ-26_H1_CDCl3_2017-6-29
SDZ-26 H1 CDCl3 2017-6-29
COOEt
f1 (ppm)


SDZ-26_C13_CDCl3_2017-6-29
SDZ-26 C13 CDCl3 2017-6-29
COOEt
f1 (ppm)


SDZ-31-CDCL3-H1-2017-7-24
SDZ-31-CDCL3-H1-2017-7-24
COOEt
f1 (ppm)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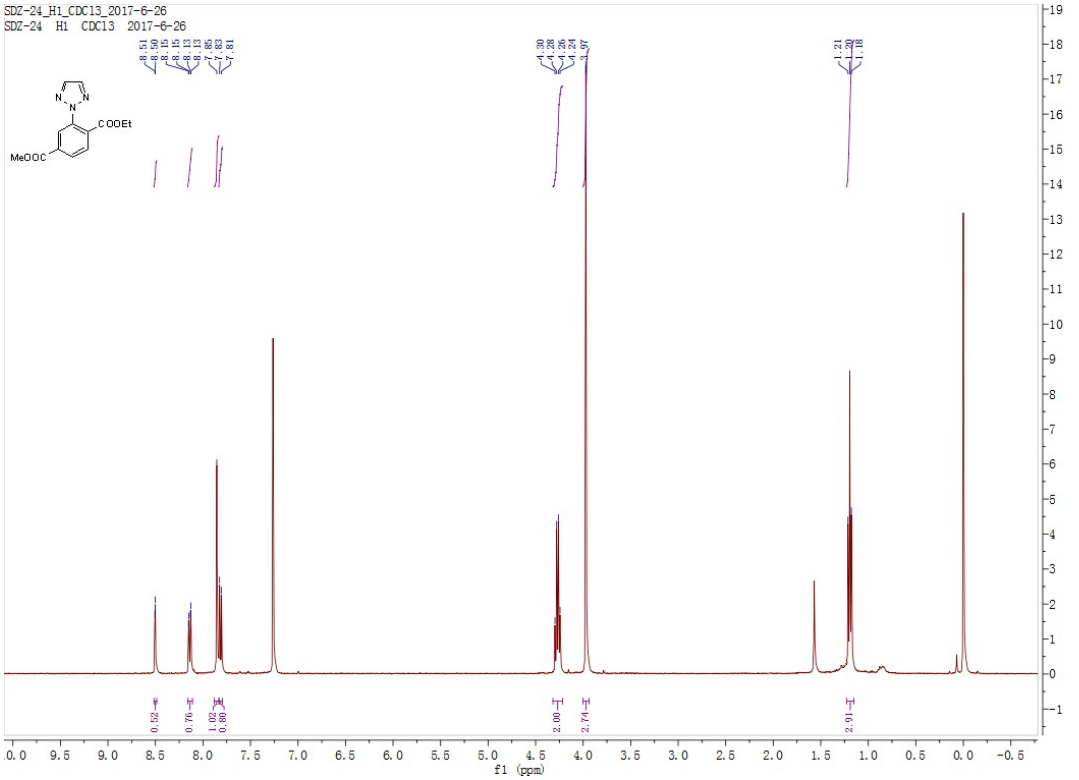
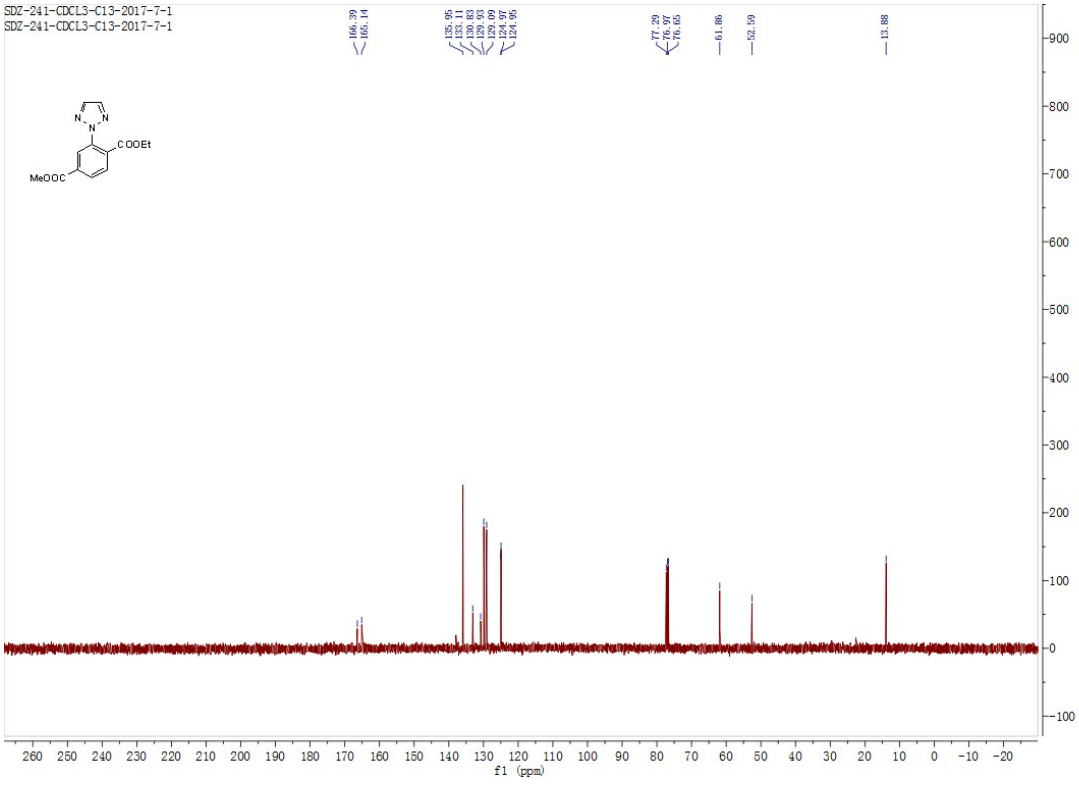
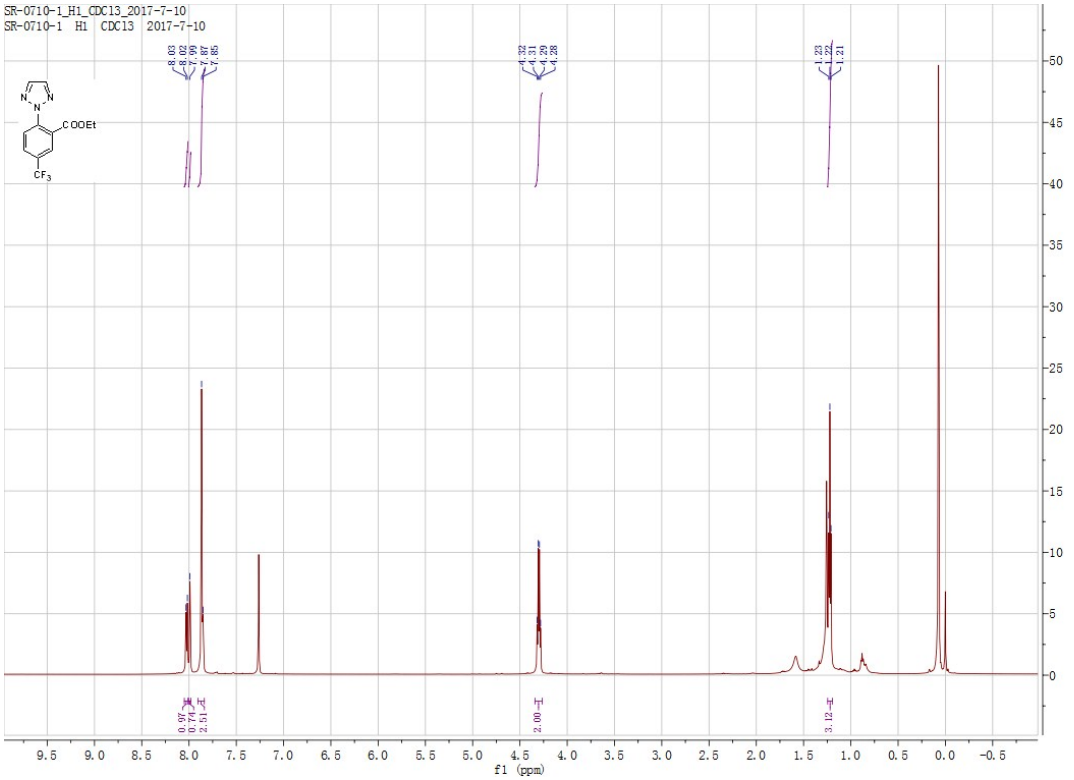
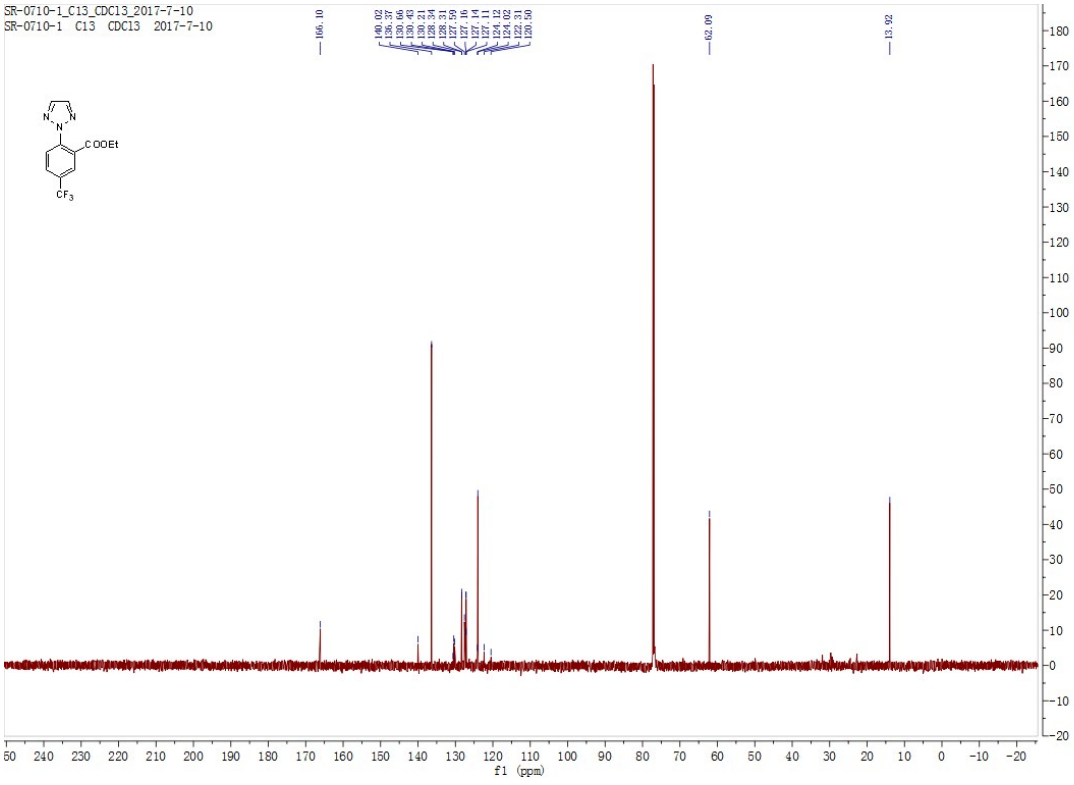
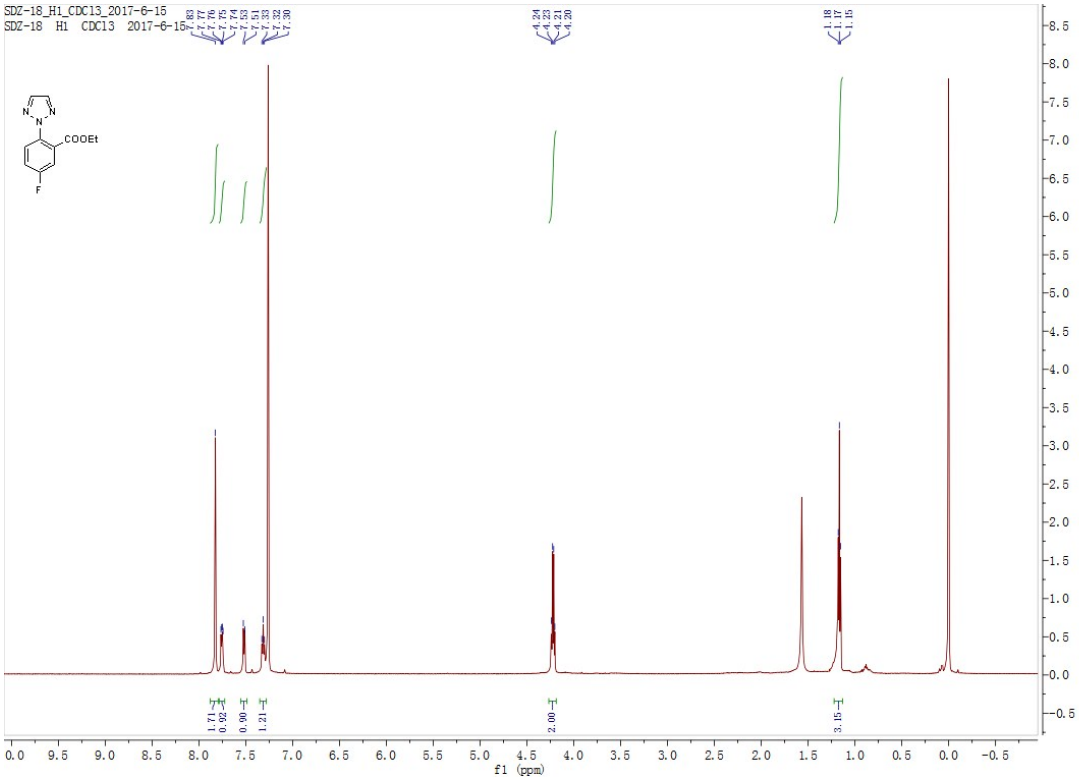
SDZ-31-CDCL3-C13-2017-7-27
COOEt
f1 (ppm)

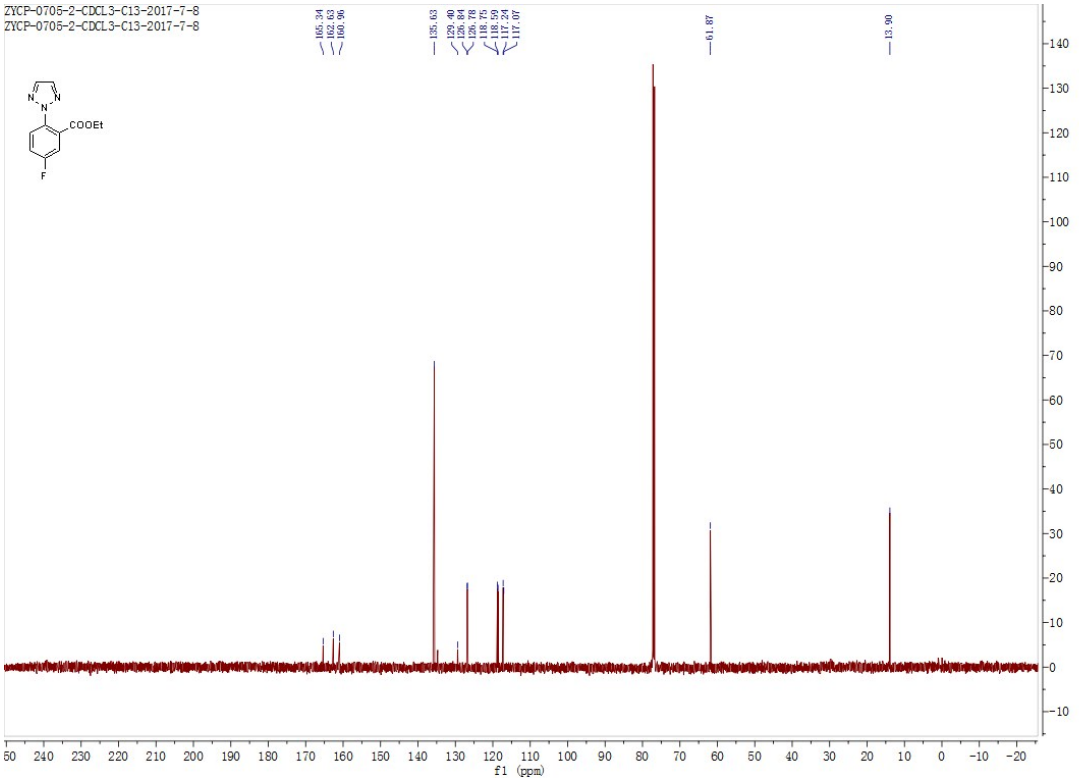

SDZ-24_H1_CDCl3_2017-6-26
SDZ-24 H1 CDCl3 2017-6-26
COOEt
MeOOC
f1 (ppm)

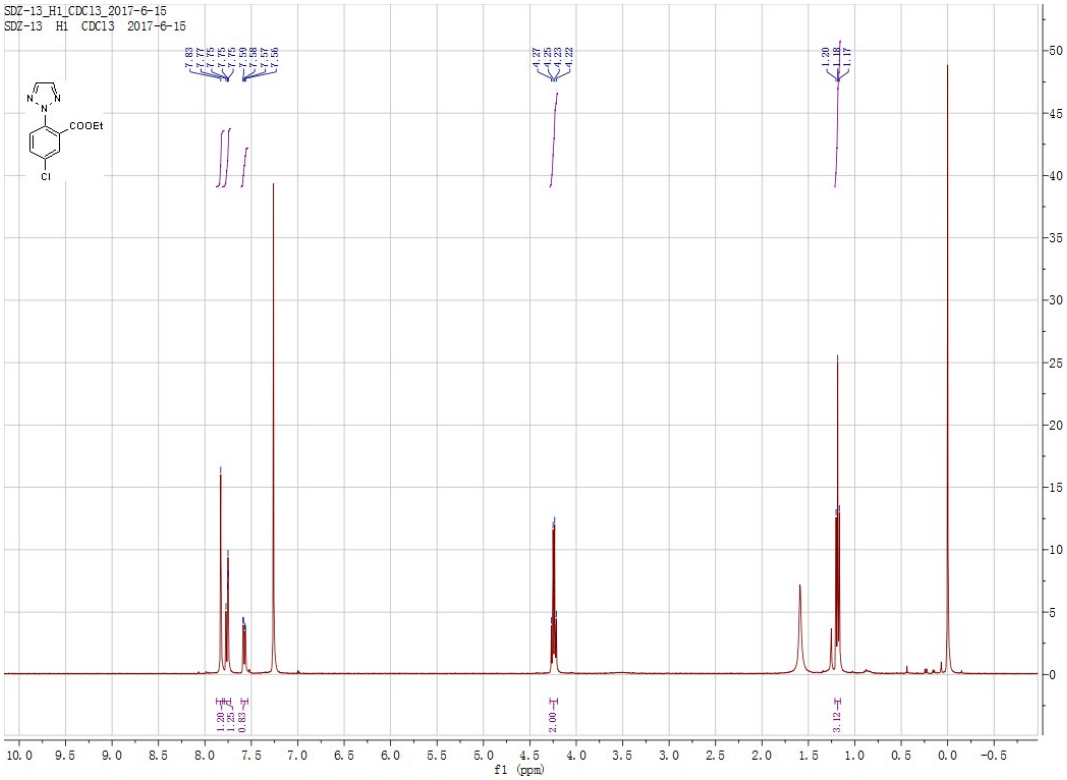

SDZ-241-CDCL3-C13-2017-7-1
SDZ-241-CDCL3-C13-2017-7-1
COOEt
MeOOC
f1 (ppm)

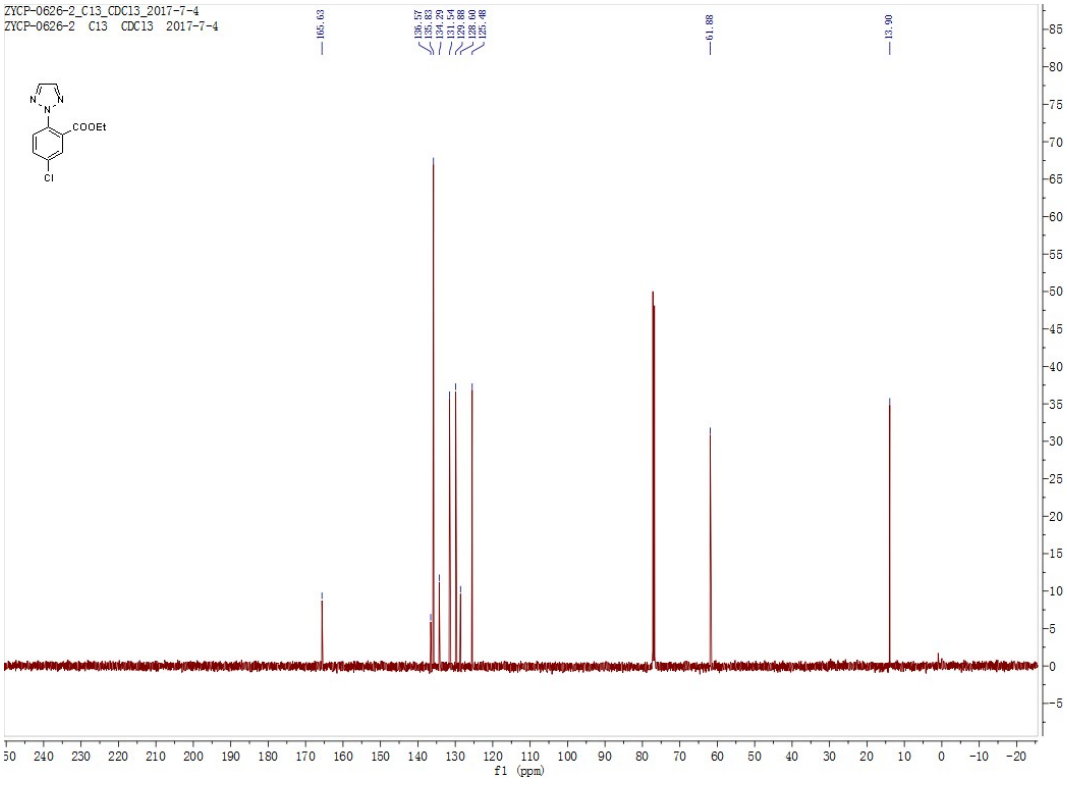

SR-0710-1_H1_CDCl3_2017-7-10
SR-0710-1 H1 CDCl3 2017-7-10
8.03
8.02
7.99
7.97
7.85
4.32
4.31
4.29
4.28
1.23
1.22
1.21
COOEt
CF3
0.97
0.79
2.51
2.00
3.12
f1 (ppm)

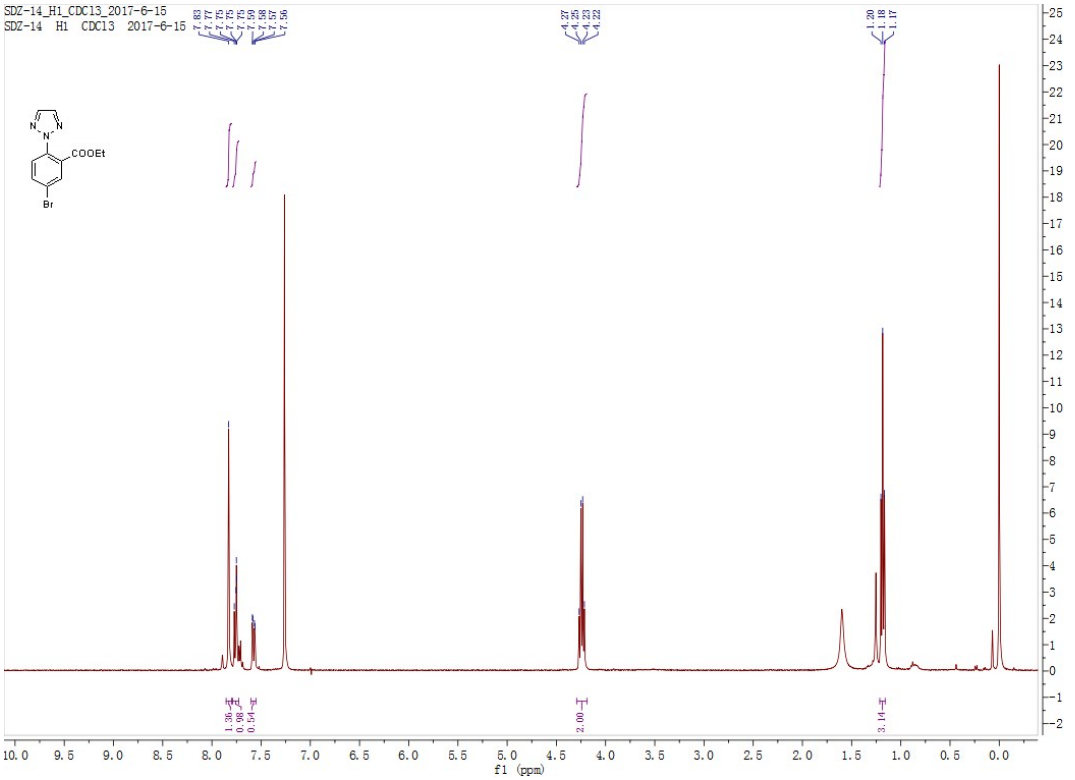

SR-0710-1_C13_CDCl3_2017-7-10
SR-0710-1 C13 CDCl3 2017-7-10
166.10
140.02
136.37
130.66
130.43
130.21
128.94
128.31
127.59
127.16
127.14
127.11
124.12
124.02
122.31
120.50
62.09
13.92
COOEt
CF3
f1 (ppm)

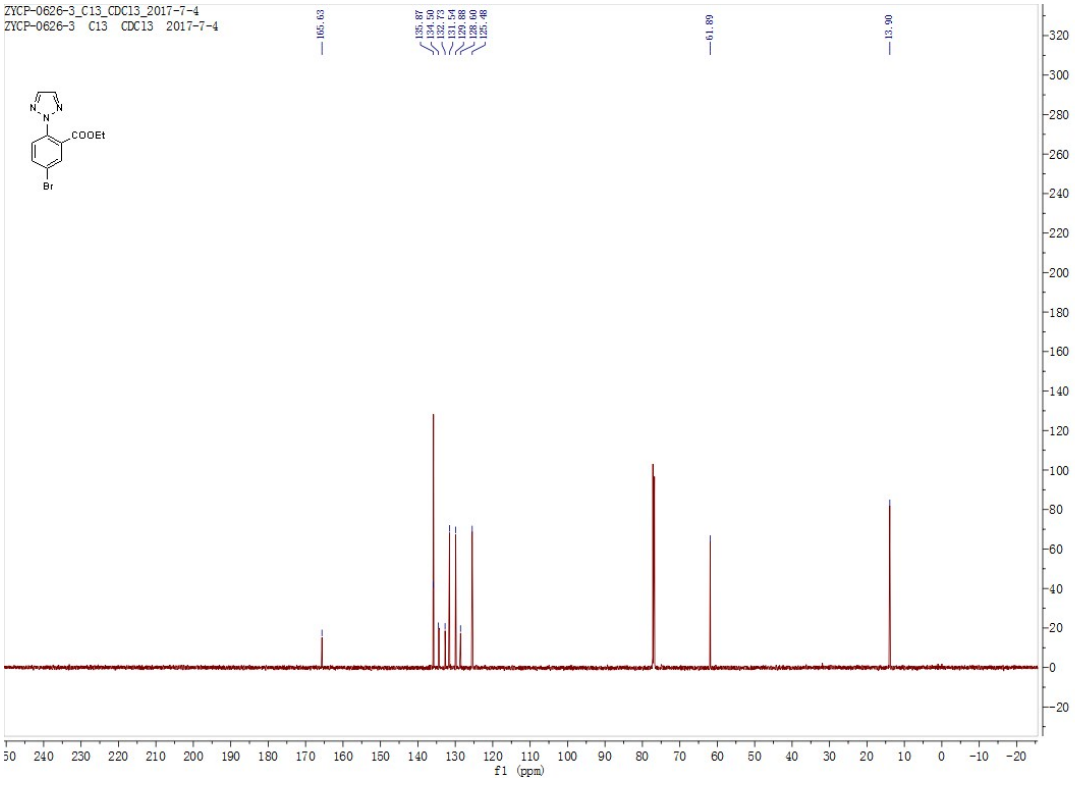

SDZ-18_H1_CDCl3_2017-6-15
SDZ-18 H1 CDCl3 2017-6-15
COOEt
F
f1 (ppm)

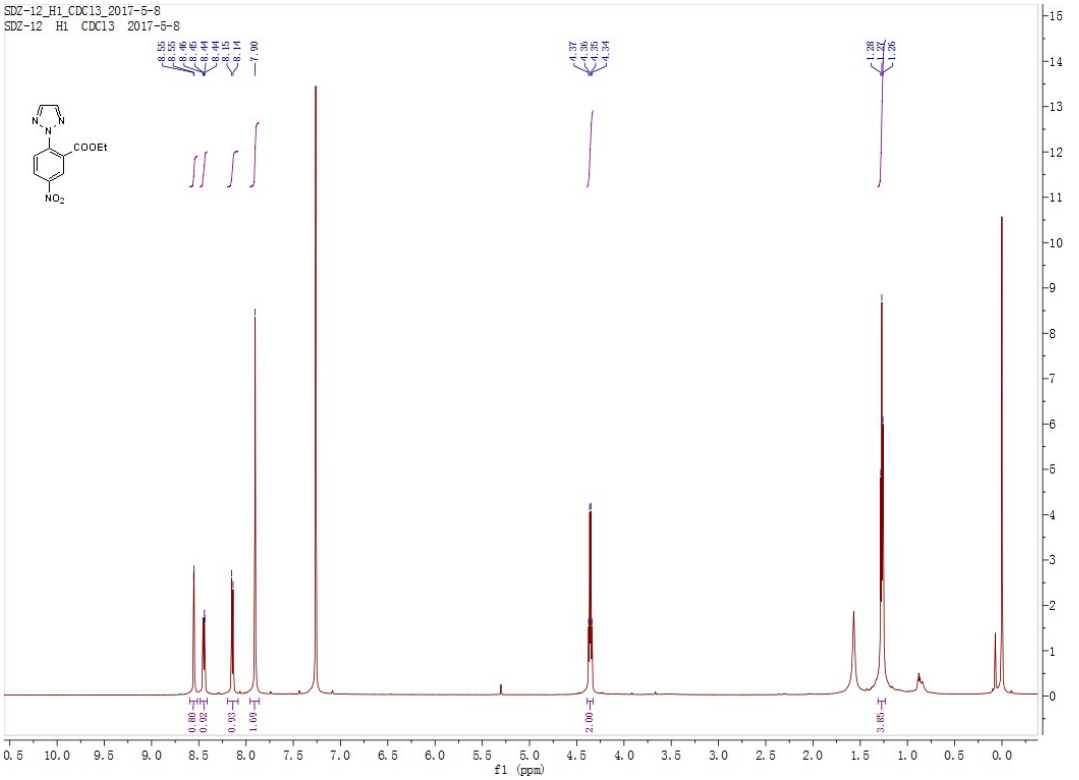

ZYCP-0705-2-CDCL3-C13-2017-7-8
ZYCP-0705-2-CDCL3-C13-2017-7-8
COOEt
F
f1 (ppm)

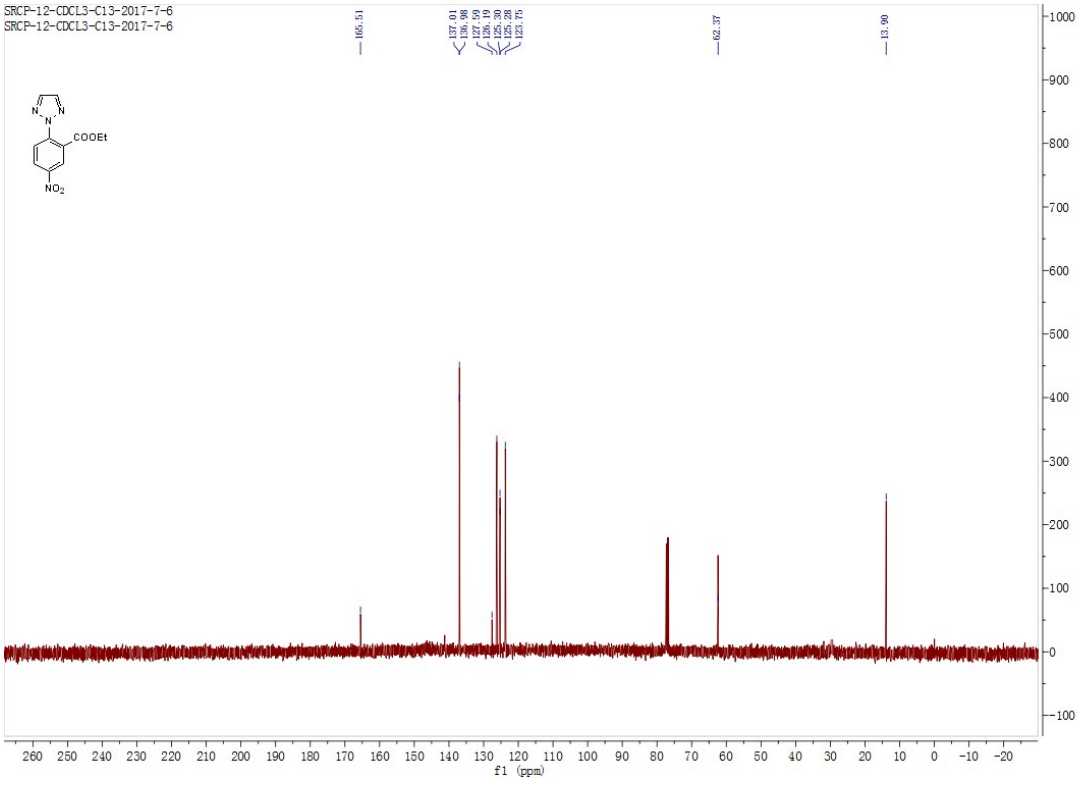

SDZ-13_H1_CDCl3_2017-6-15
SDZ-13 H1 CDCl3 2017-6-15
COOEt
Cl
f1 (ppm)

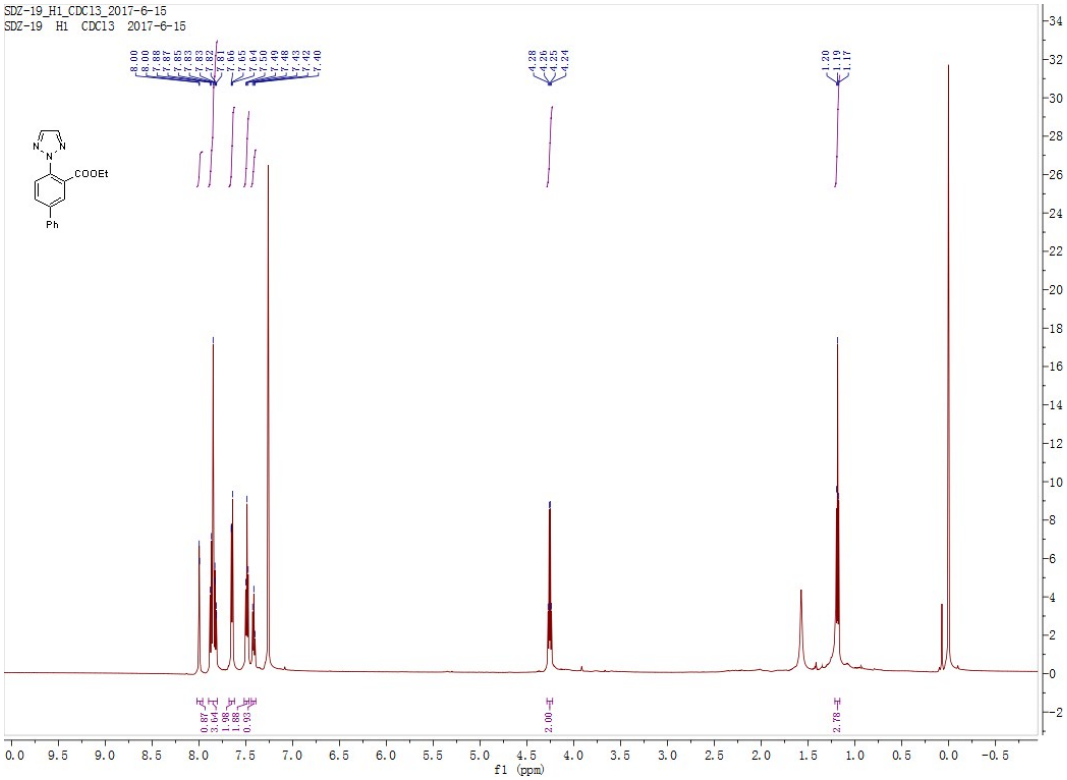

ZYCP-0626-2_C13_CDCl3_2017-7-4
ZYCP-0626-2 C13 CDCl3 2017-7-4
COOEt
Cl
f1 (ppm)

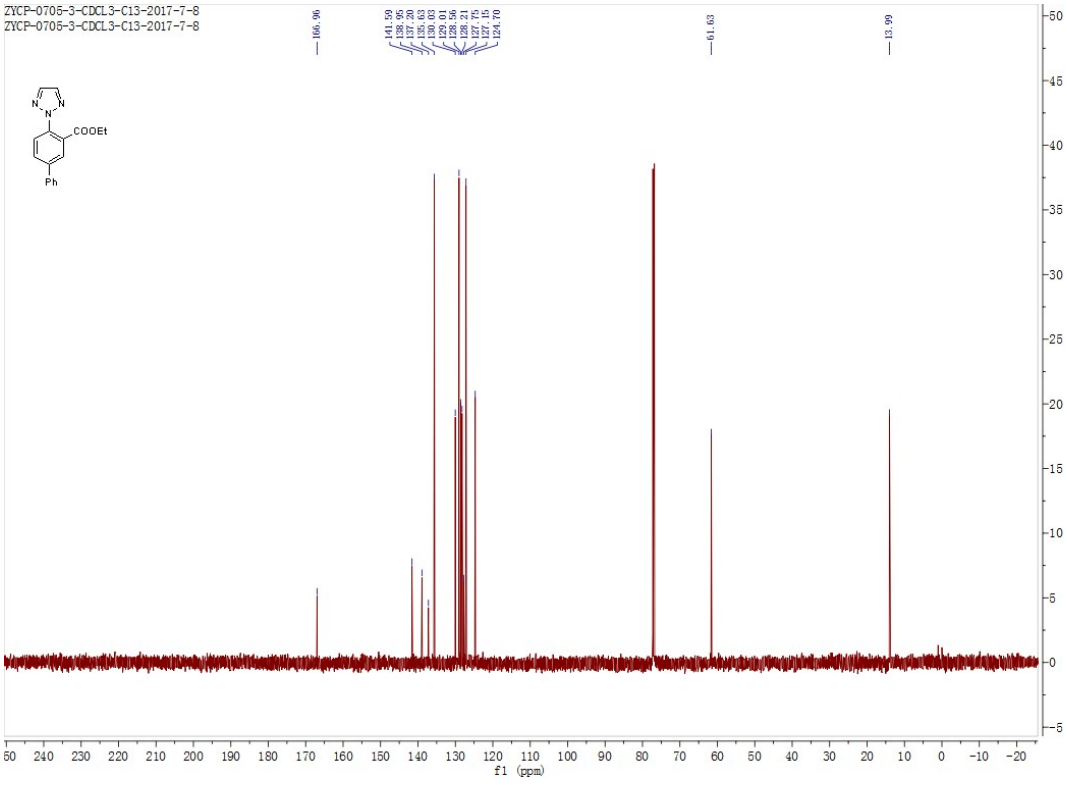

SDZ-14_H1_CDCl3_2017-6-15
SDZ-14 H1 CDCl3 2017-6-15
7.83
7.77
7.75
7.75
7.75
7.59
7.58
7.57
7.56
4.27
4.25
4.23
4.22
1.20
1.18
1.17
COOEt
Br
1.36
0.98
0.54
2.00
3.14
f1 (ppm)

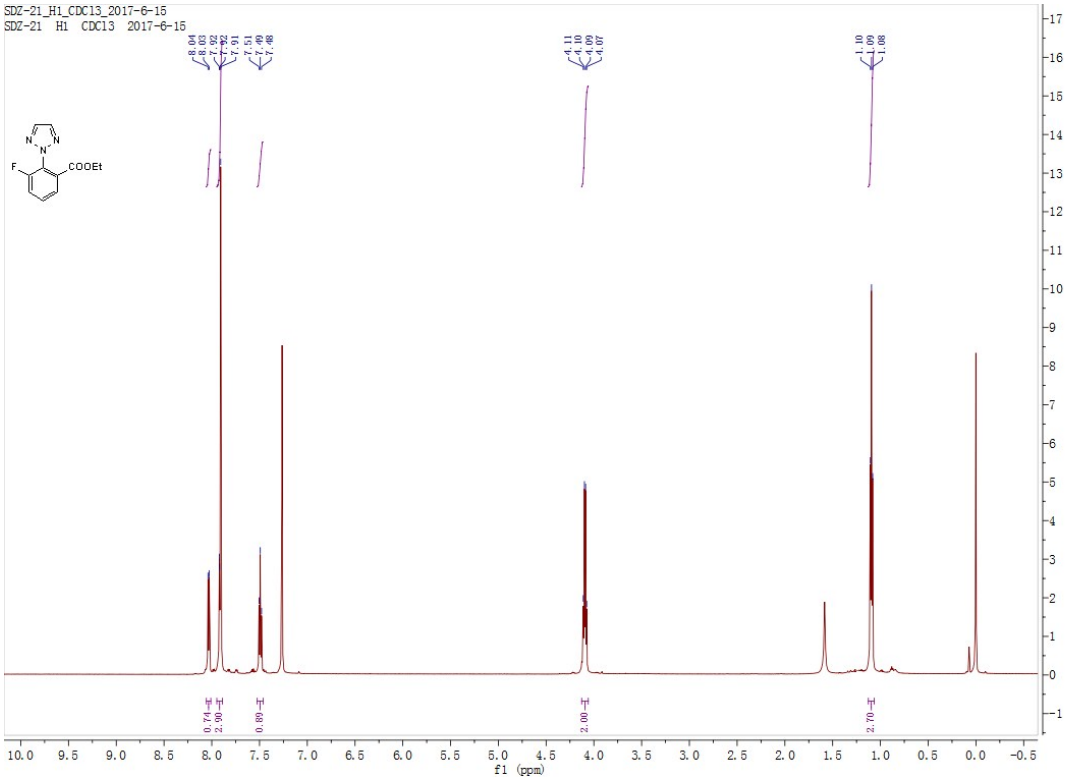

ZYCP-0626-3_C13_CDCl3_2017-7-4
ZYCP-0626-3 C13 CDCl3 2017-7-4
165.63
135.87
134.59
132.73
131.54
129.88
128.60
125.48
61.89
13.90
COOEt
Br
f1 (ppm)

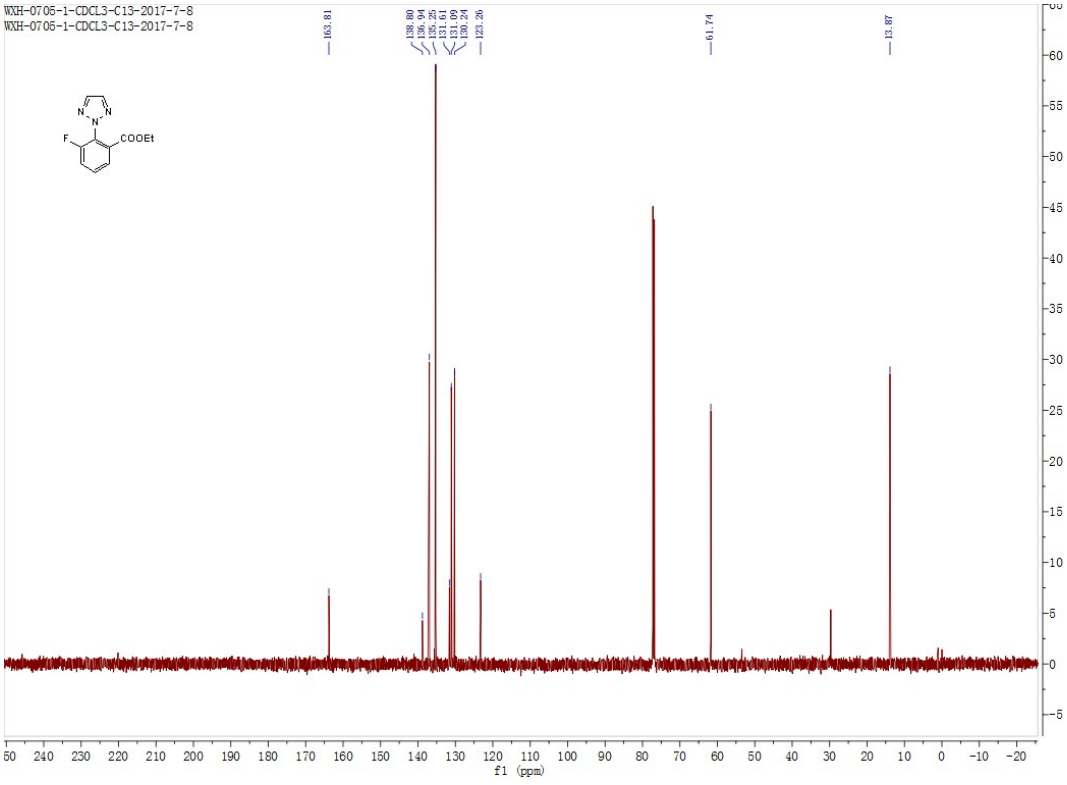

SDZ-12_H1_CDCl3_2017-6-8
SDZ-12 H1 CDCl3 2017-6-8
8.55
8.55
8.46
8.45
8.44
8.44
8.15
8.14
7.90
4.37
4.36
4.35
4.34
1.28
1.27
1.26
COOEt
NO2
0.80
0.92
0.93
1.09
2.00
3.85
f1 (ppm)


SRCP-12-CDCL3-C13-2017-7-6
SRCP-12-CDCL3-C13-2017-7-6
165.51
137.01
136.98
127.59
126.19
125.39
125.28
123.75
62.37
13.90
COOEt
NO2
f1 (ppm)


SDZ-19_H1_CDCl3_2017-6-15
SDZ-19 H1 CDCl3 2017-6-15
COOEt
Ph
f1 (ppm)


ZYCP-0705-3-CDCL3-C13-2017-7-8
ZYCP-0705-3-CDCL3-C13-2017-7-8
166.96
141.59
138.95
137.20
135.63
130.03
129.01
128.56
128.21
127.75
127.15
124.70
61.63
13.99
COOEt
Ph
f1 (ppm)


SDZ-21_H1_CDCl3_2017-6-15
SDZ-21 H1 CDCl3 2017-6-15
8.04
8.03
7.92
7.91
7.51
7.50
7.48
4.11
4.10
4.09
4.07
1.10
1.09
1.08
COOEt
F
0.74
2.00
0.89
2.00
2.70
f1 (ppm)


WXH-0706-1-CDCL3-C13-2017-7-8
WXH-0706-1-CDCL3-C13-2017-7-8
163.81
138.80
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133.41
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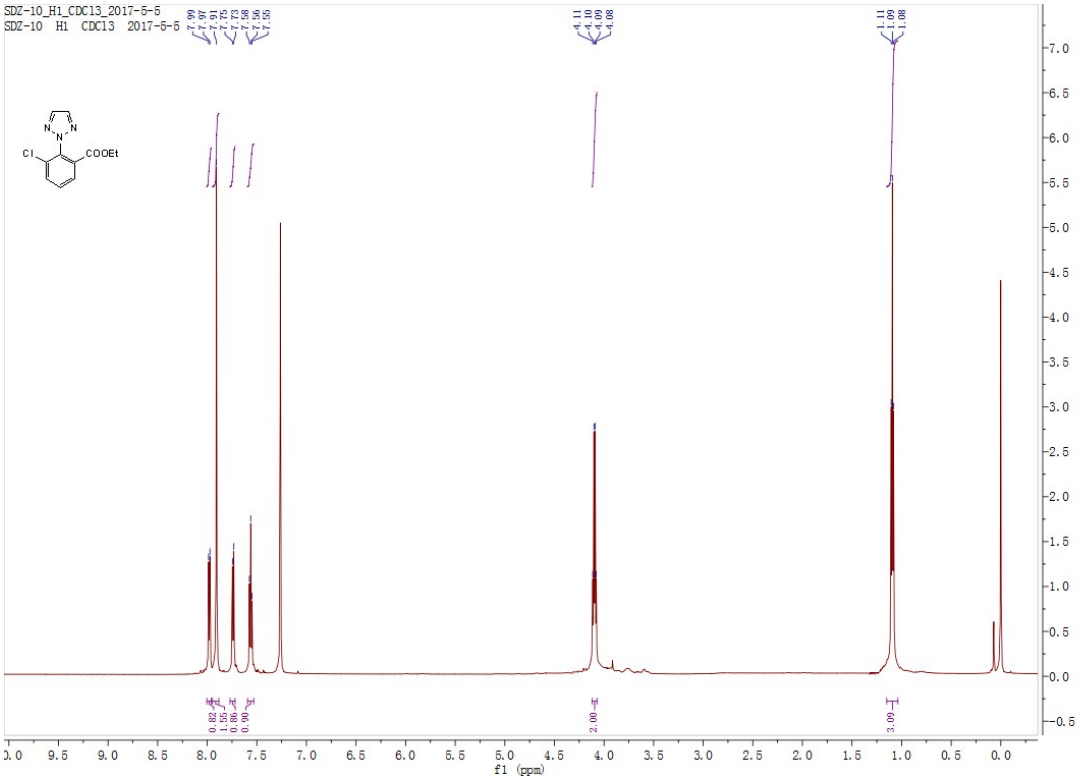
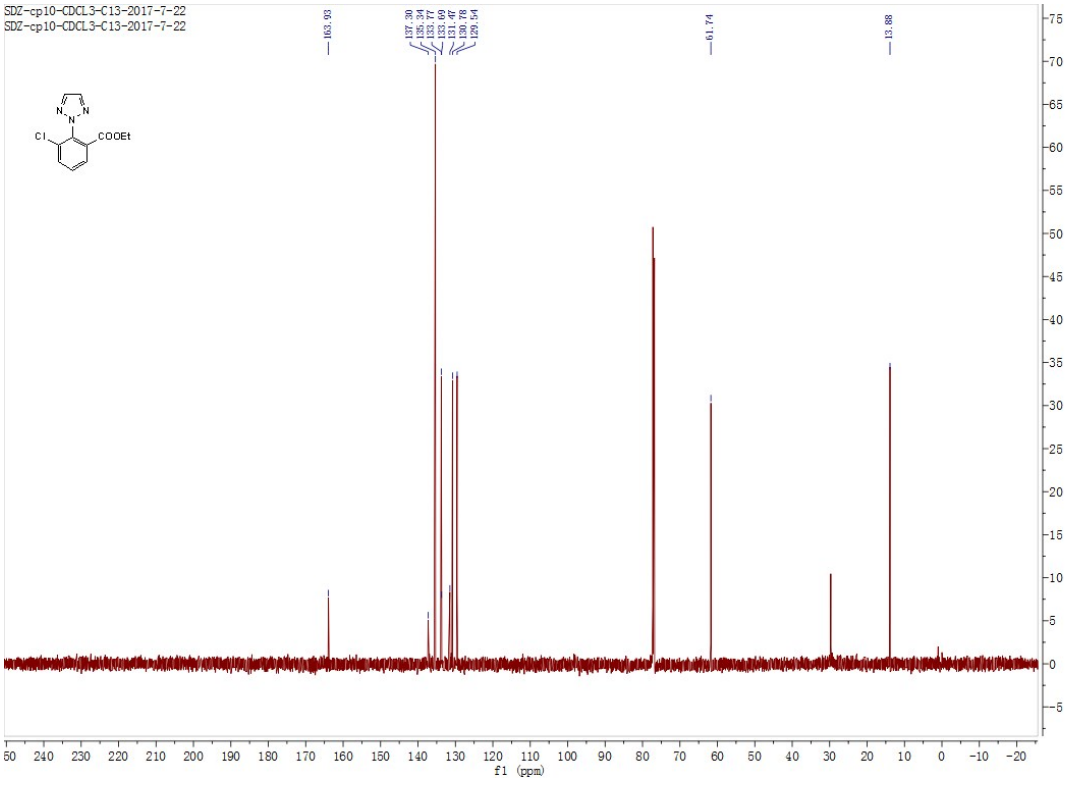
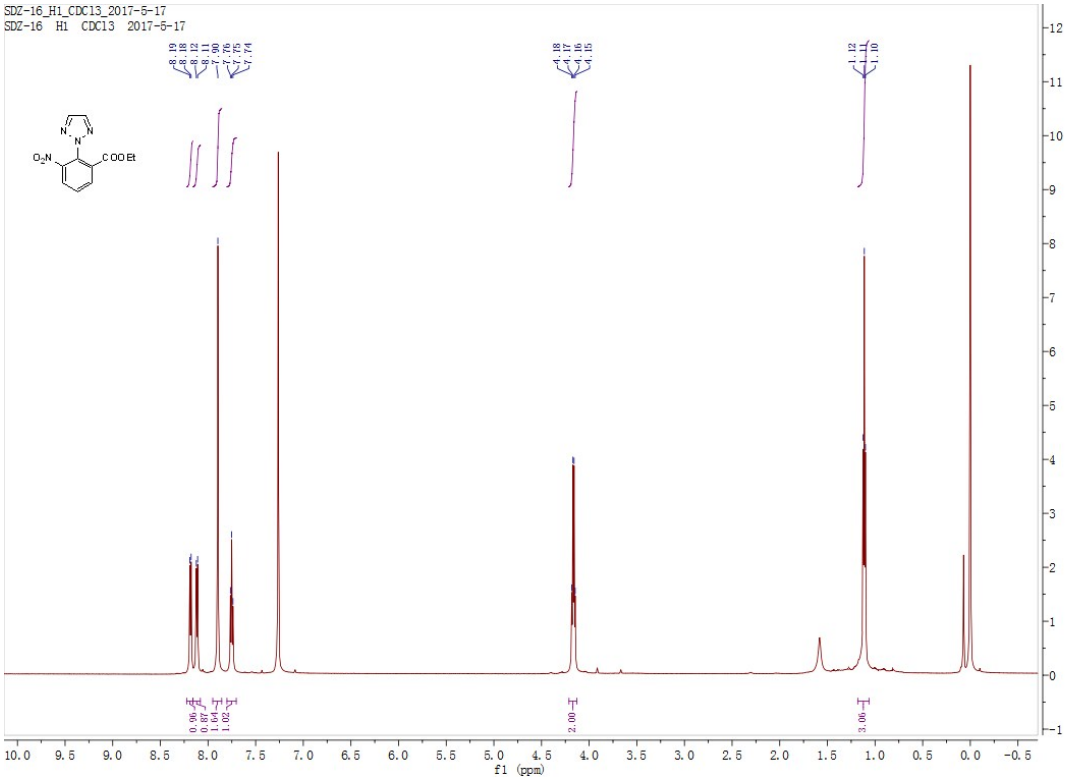
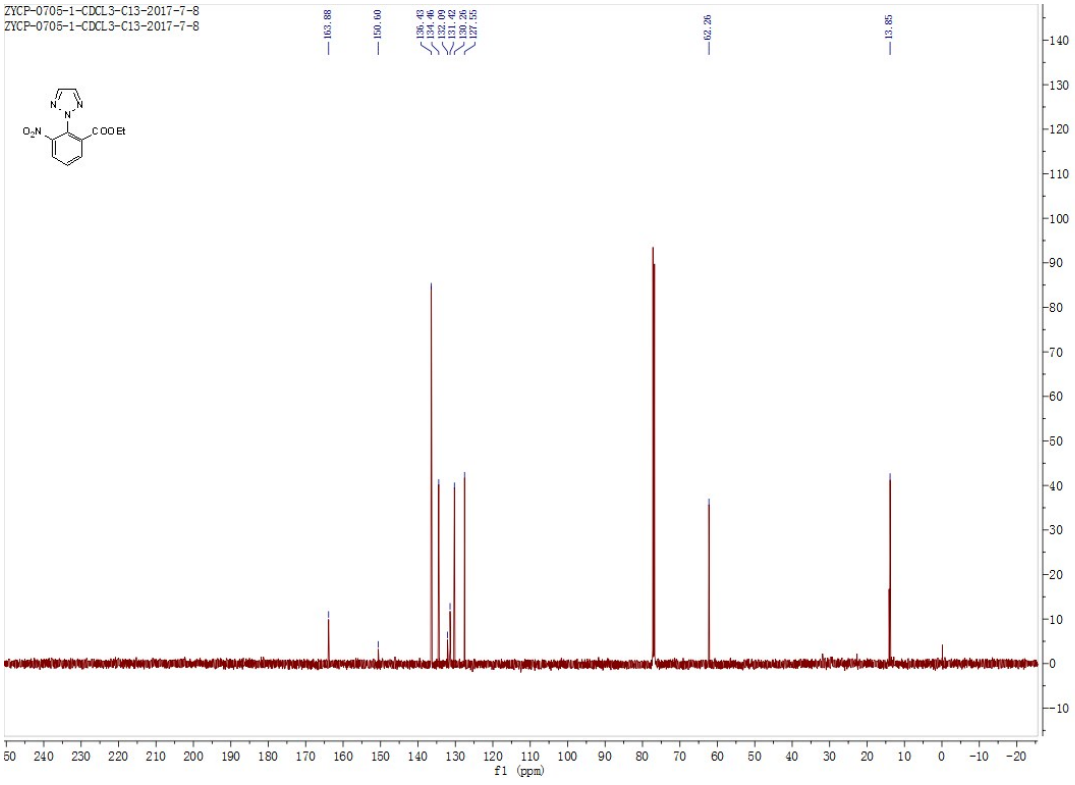
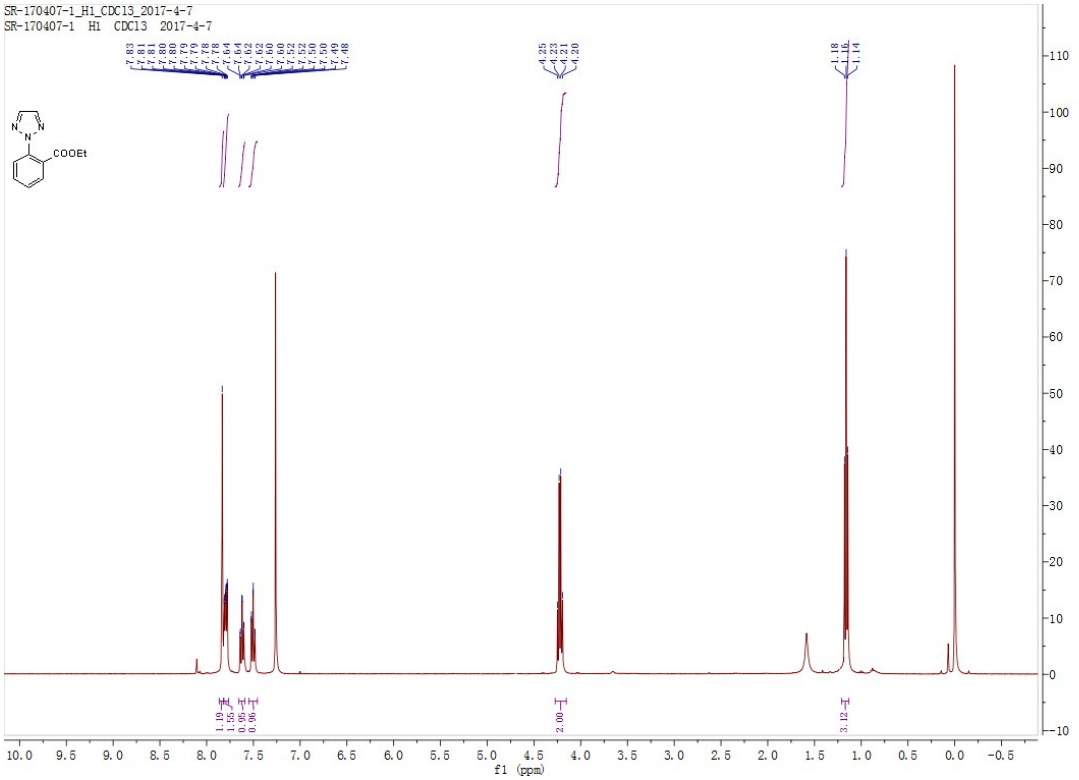
130.24
123.26
61.74
13.87
COOEt
F
f1 (ppm)

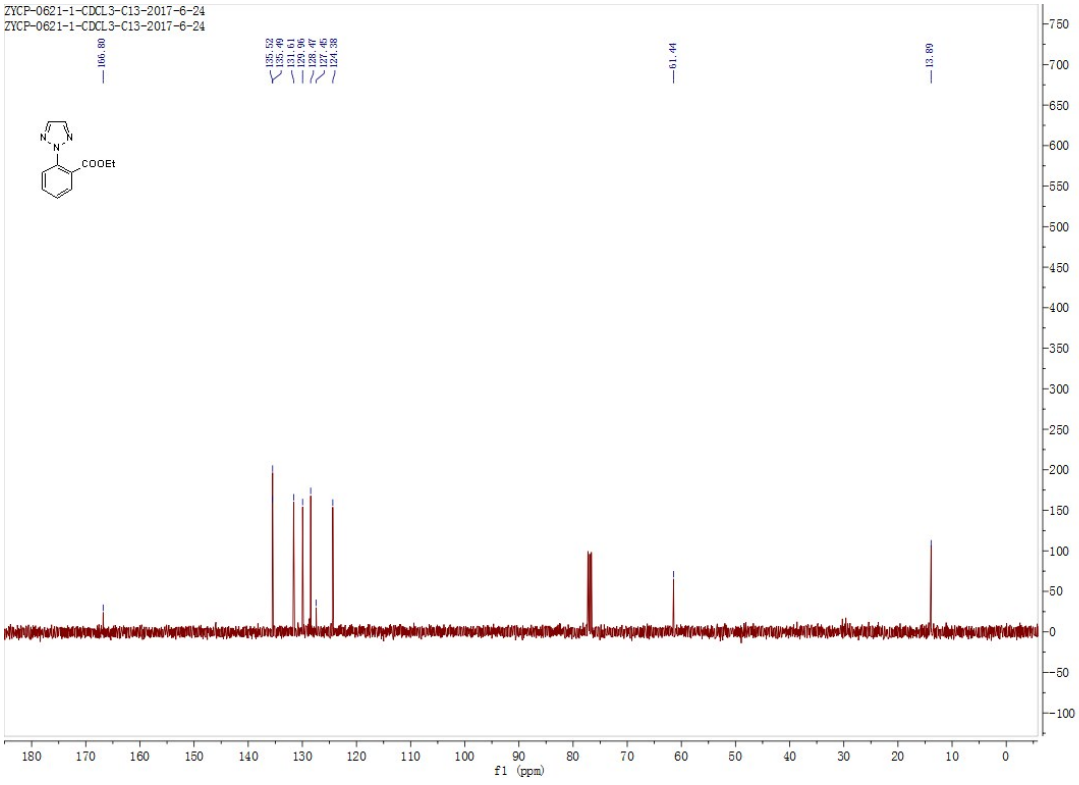

SDZ-10_H1_CDCl3_2017-6-6
SDZ-10 H1 CDCl3 2017-6-6
7.99
7.97
7.91
7.75
7.73
7.58
7.56
7.55
4.11
4.10
4.09
4.08
1.11
1.10
1.08
Cl
COOEt
0.82
1.55
0.96
0.90
2.00
3.09
f1 (ppm)

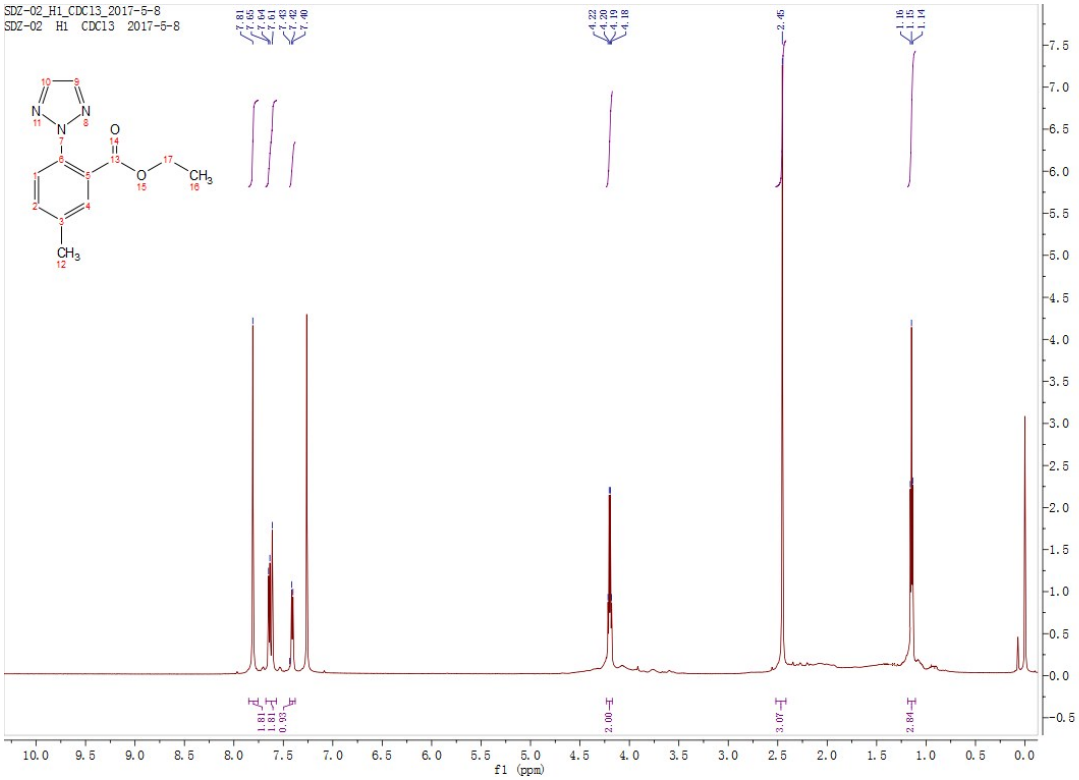

SDZ-cp10-CDCL3-C13-2017-7-22
SDZ-cp10-CDCL3-C13-2017-7-22
163.93
137.30
135.34
133.77
133.69
131.47
130.78
129.54
61.74
13.88
Cl
COOEt
f1 (ppm)

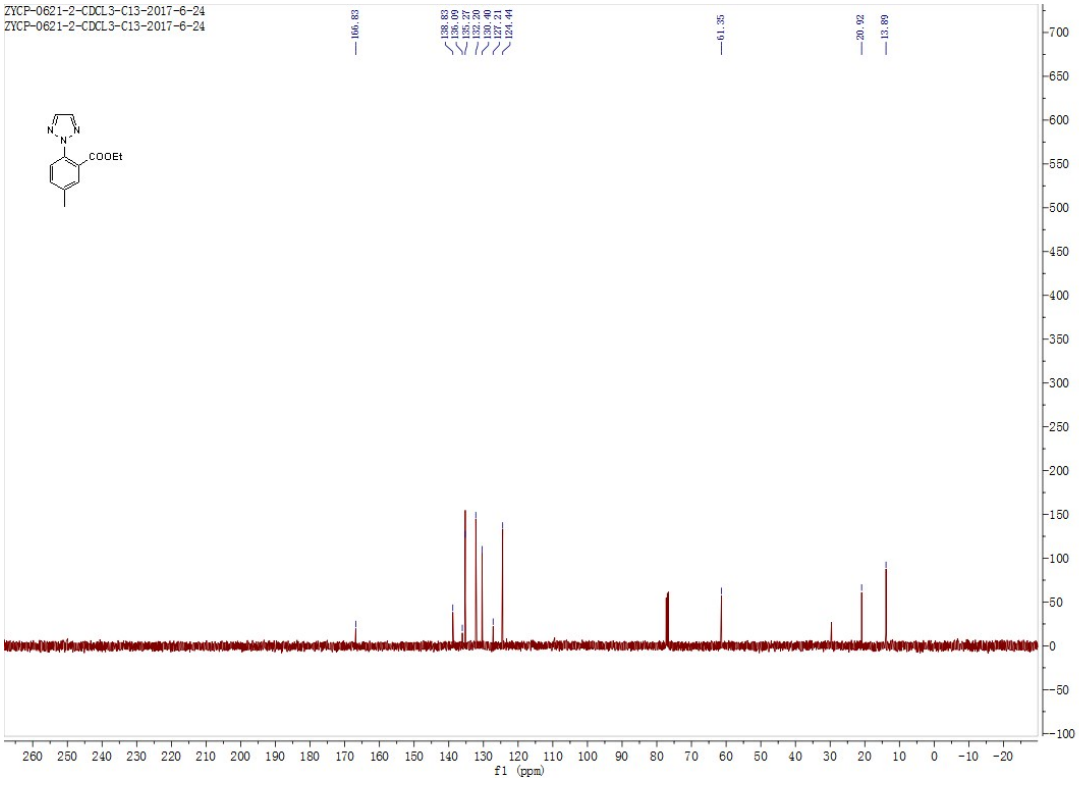

SDZ-16_H1_CDCl3_2017-5-17
SDZ-16 H1 CDCl3 2017-5-17
8.19
8.18
8.12
8.11
7.90
7.76
7.75
7.74
4.18
4.17
4.16
4.15
1.12
1.11
1.10
0.96
0.97
1.64
1.02
2.00
3.06
f1 (ppm)


ZYCP-0705-1-CDCL3-C13-2017-7-8
ZYCP-0705-1-CDCL3-C13-2017-7-8
163.88
150.60
136.43
134.46
132.09
131.42
130.26
127.35
62.26
13.85
f1 (ppm)

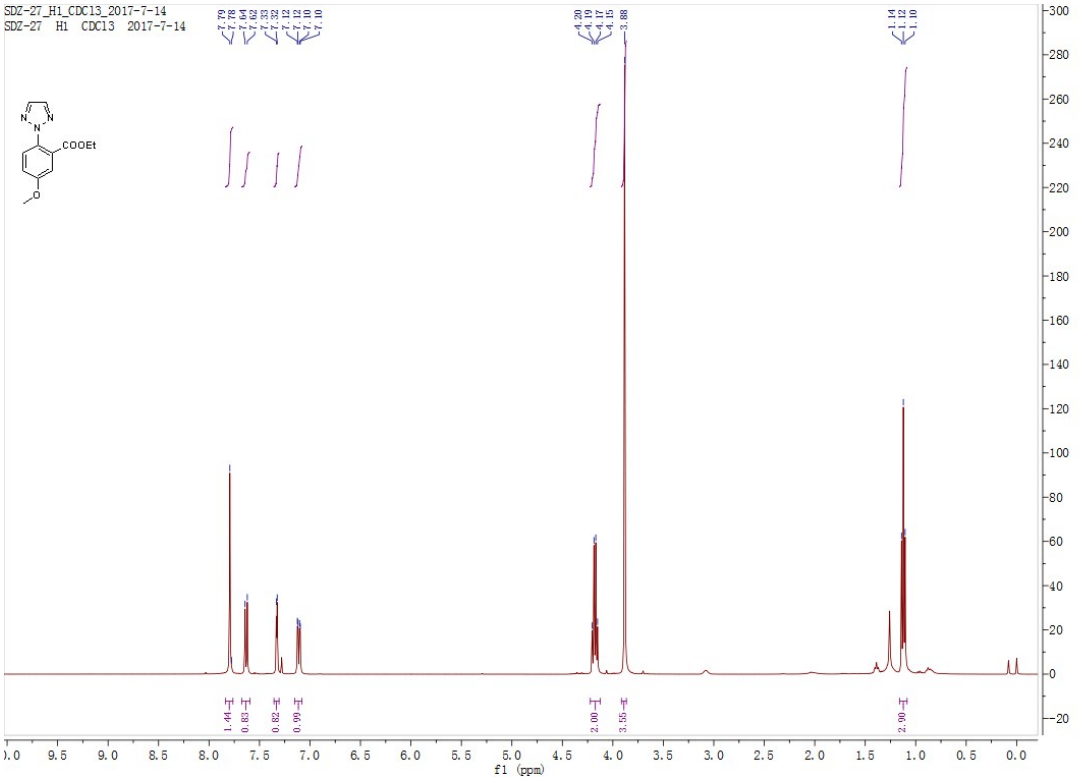

SR-170407-1_H1_CDCl3_2017-4-7
SR-170407-1 H1 CDCl3 2017-4-7
COOEt
f1 (ppm)

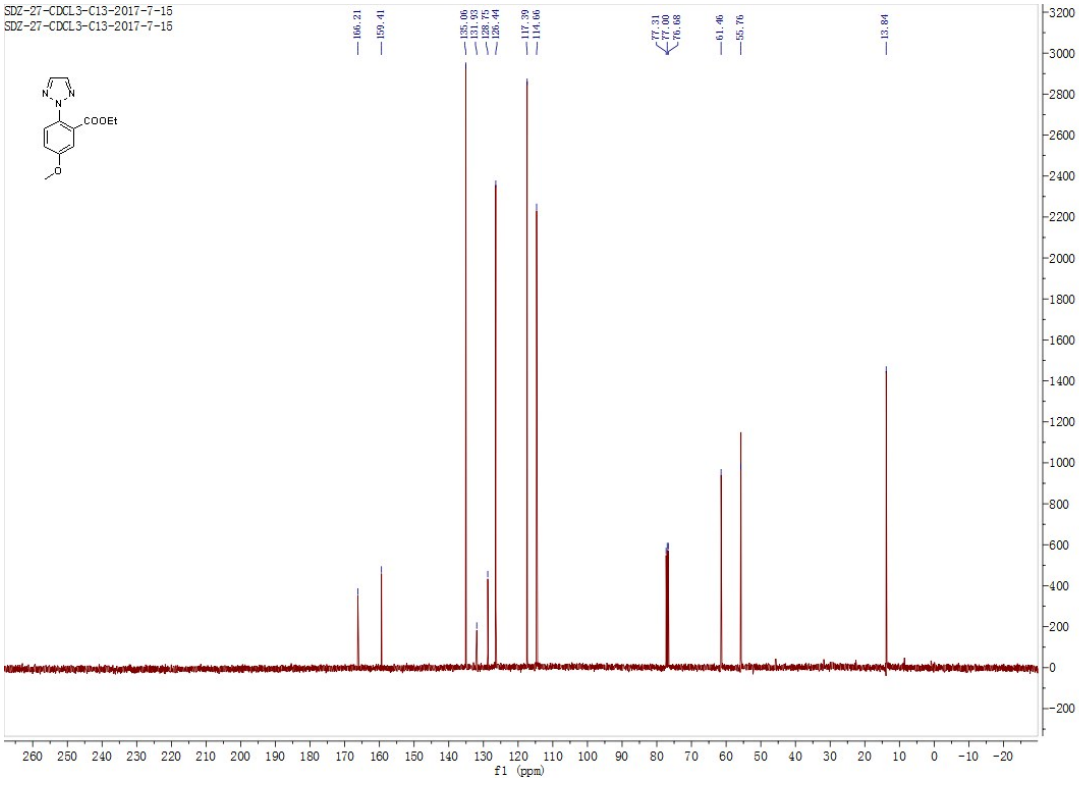

ZYCP-0621-1-CDCL3-C13-2017-6-24
ZYCP-0621-1-CDCL3-C13-2017-6-24
COOEt
f1 (ppm)

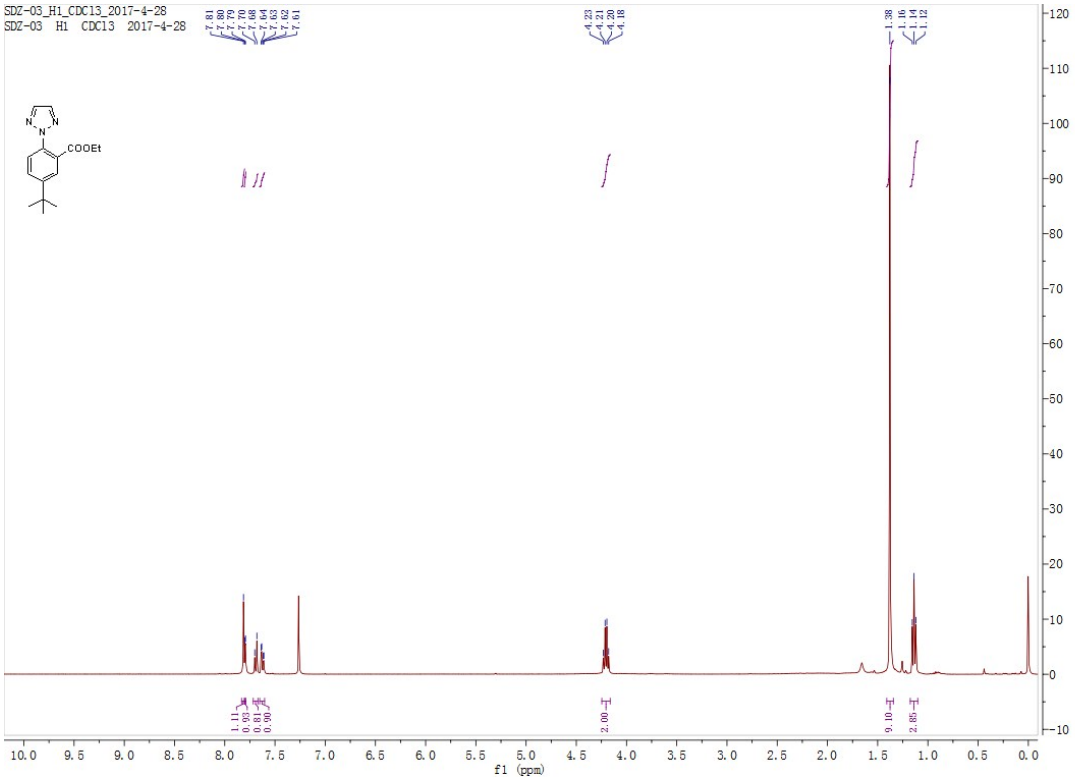

SDZ-02_H1_CDCl3_2017-6-8
SDZ-02 H1 CDCl3 2017-6-8
7.81
7.65
7.64
7.61
7.43
7.42
7.40
4.22
4.20
4.19
4.18
2.45
1.16
1.15
1.14
1.81
1.81
0.93
2.00
3.07
2.84
f1 (ppm)

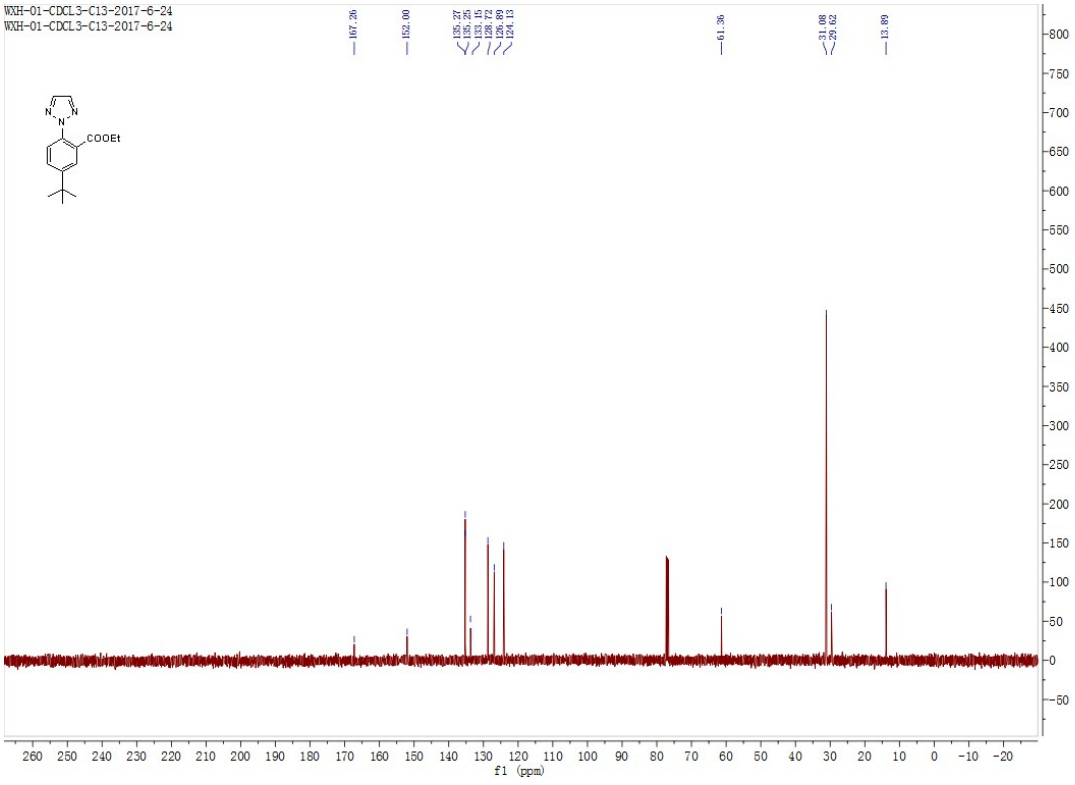

ZYCP-0621-2-CDCL3-C13-2017-6-24
ZYCP-0621-2-CDCL3-C13-2017-6-24
166.83
138.83
136.09
135.27
132.20
130.40
127.21
124.44
61.35
20.92
13.89
COOEt
f1 (ppm)

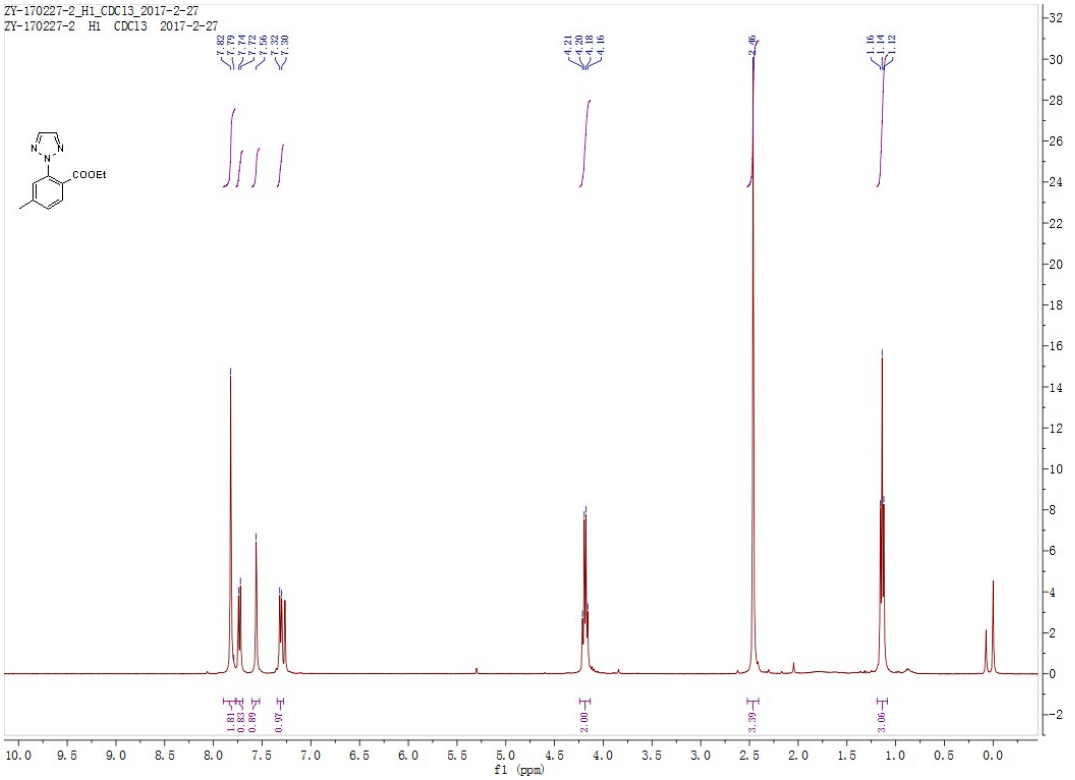
6

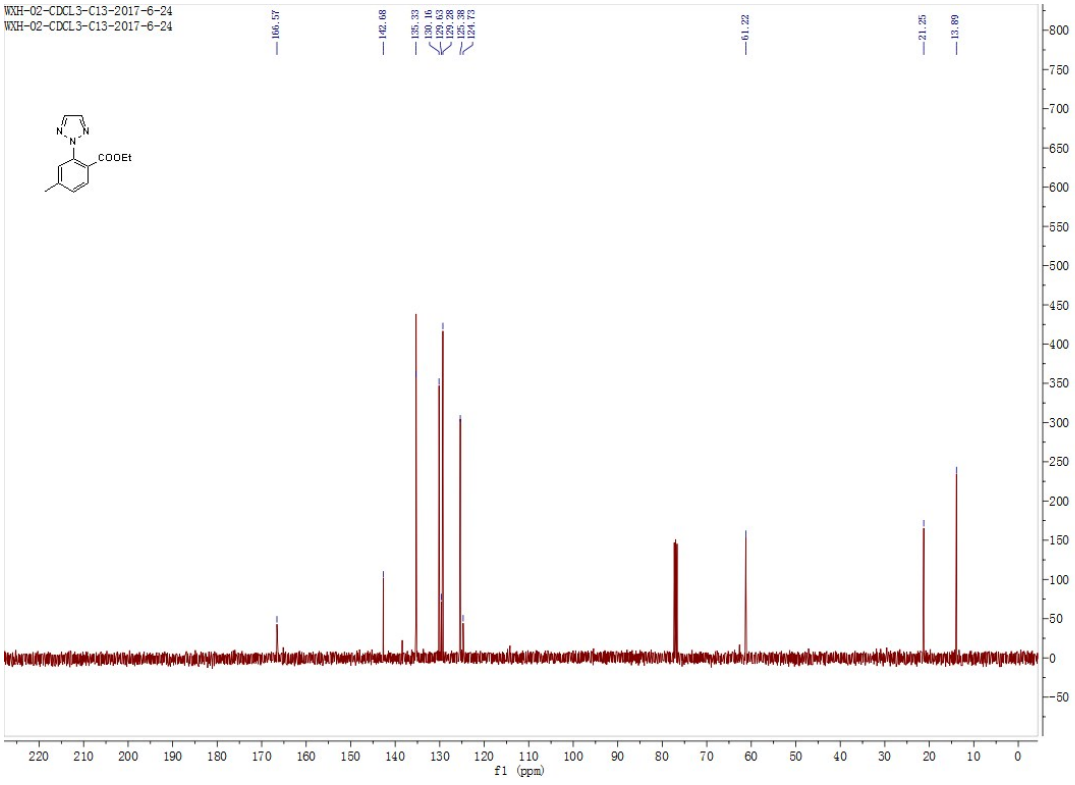

SDZ-27_H1_CDCl3_2017-7-14
SDZ-27 H1 CDCl3 2017-7-14
COOEt
f1 (ppm)

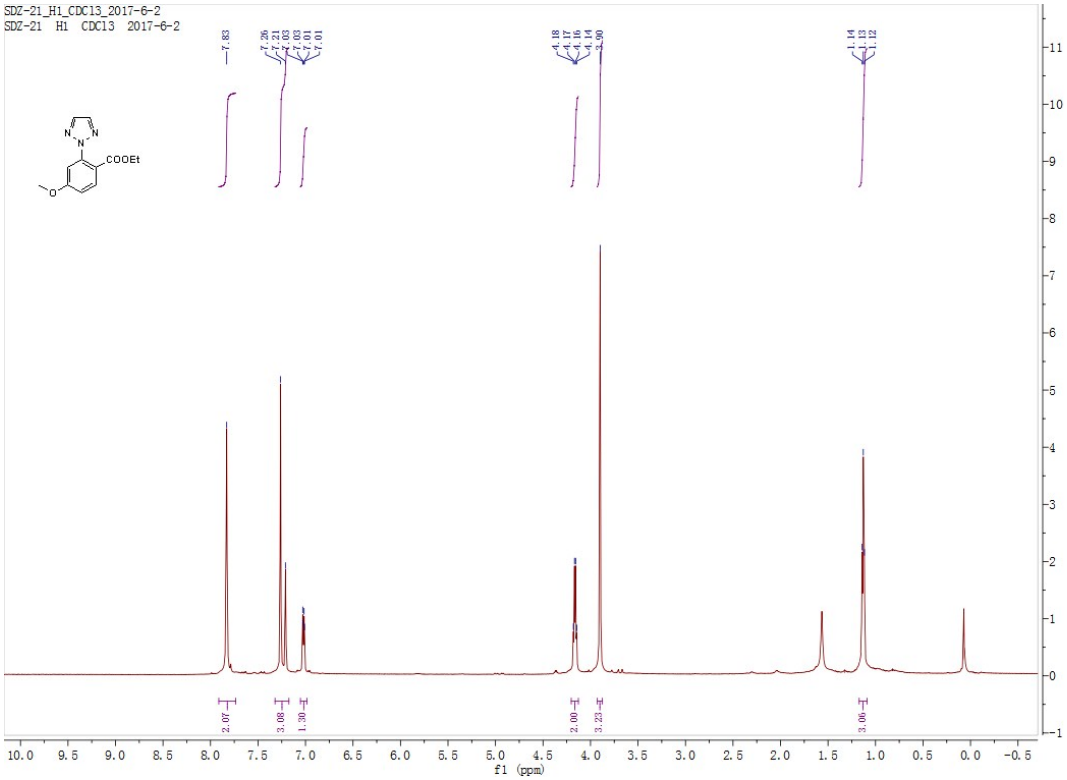

SDZ-27-CDCL3-C13-2017-7-15
SDZ-27-CDCL3-C13-2017-7-15
COOEt
f1 (ppm)

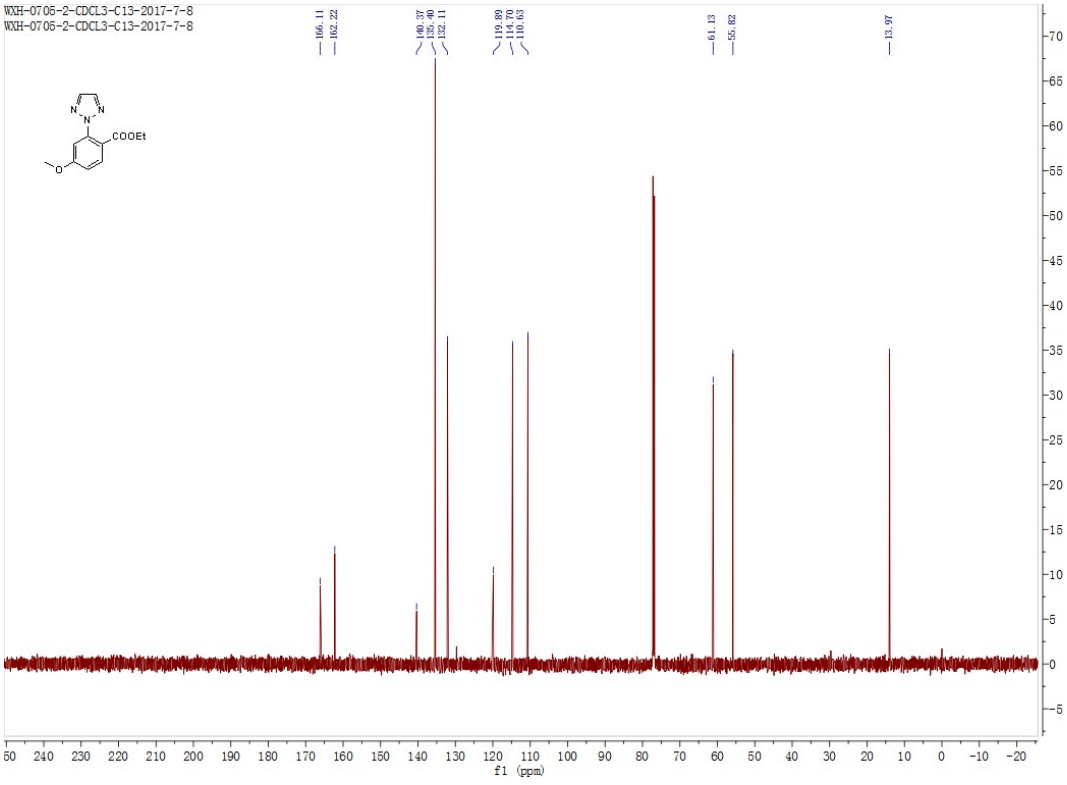

SDZ-03_H1_CDCl3_2017-4-28
SDZ-03 H1 CDCl3 2017-4-28
7.81
7.80
7.79
7.70
7.68
7.64
7.63
7.62
7.61
4.23
4.21
4.20
4.18
1.38
1.16
1.14
1.12
COOEt
1.11
0.93
0.81
0.90
2.00
9.10
2.85
f1 (ppm)

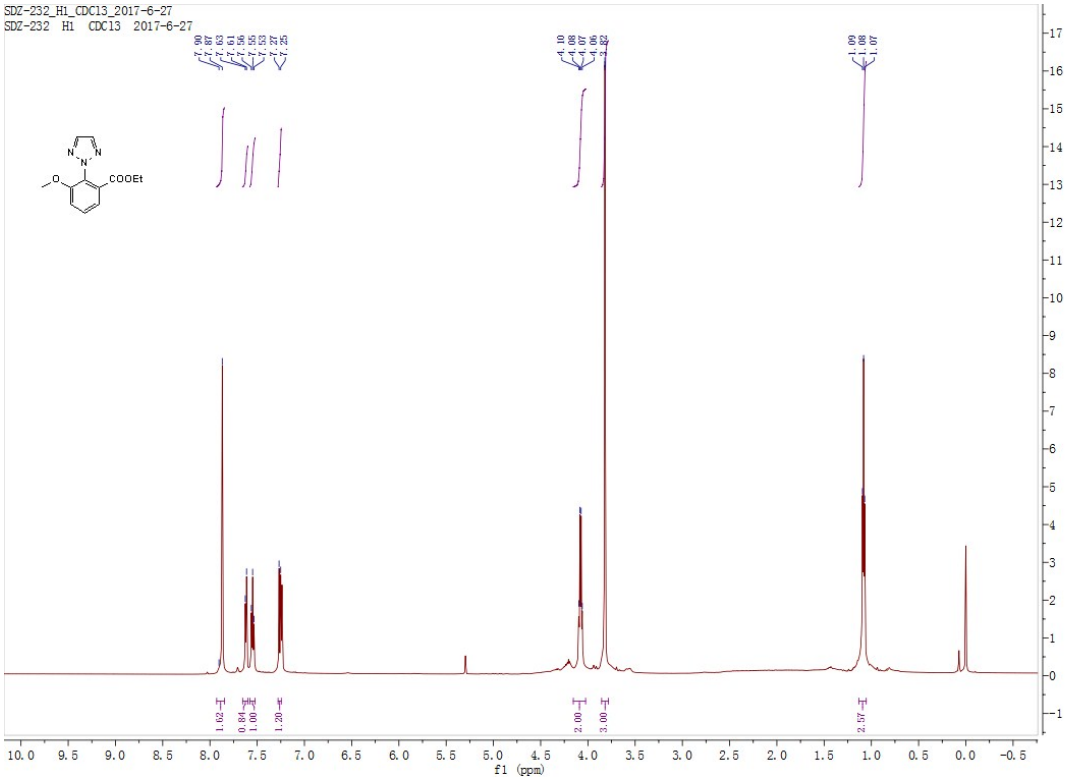

WXH-01-CDCL3-C13-2017-6-24
WXH-01-CDCL3-C13-2017-6-24
167.26
152.00
135.27
135.25
133.15
128.72
126.89
124.13
61.36
31.08
29.02
13.89
COOEt
f1 (ppm)

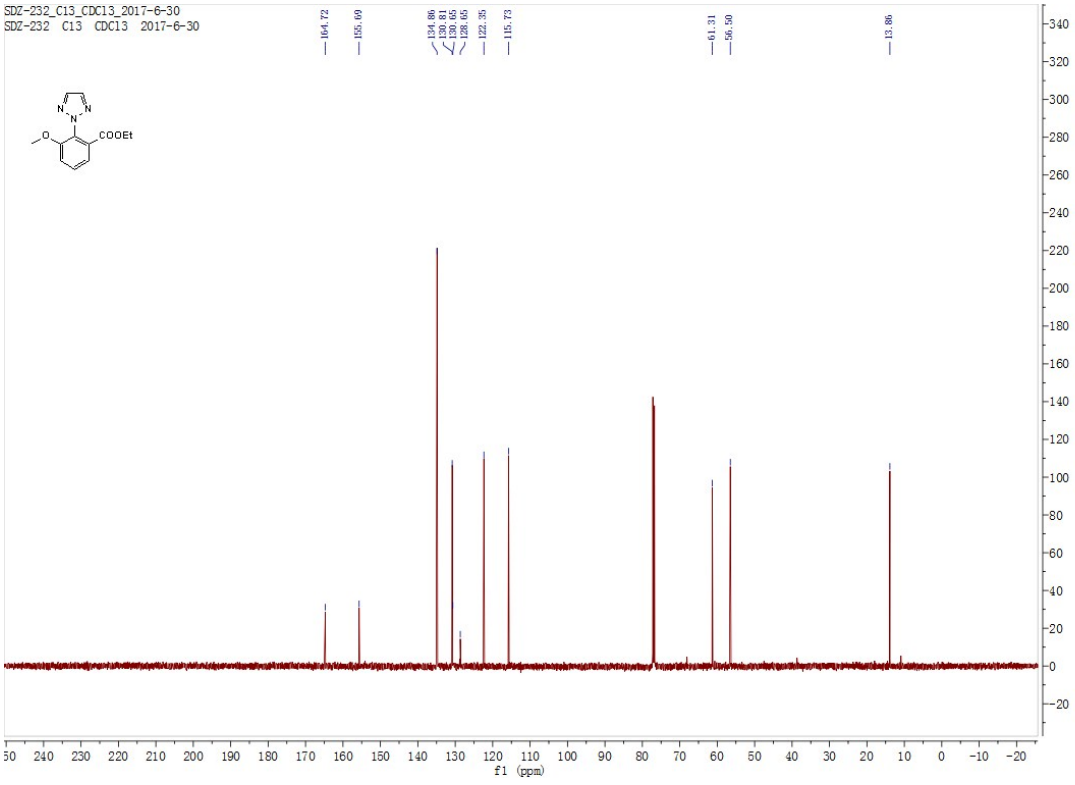

ZY-170227-2_H1_CDCl3_2017-2-27
ZY-170227-2 H1 CDCl3 2017-2-27
7.82
7.79
7.74
7.72
7.56
7.33
7.30
4.21
4.20
4.18
4.16
2.46
1.16
1.14
1.12
COOEt
1.81
0.83
0.89
0.97
2.00
3.39
3.06
f1 (ppm)

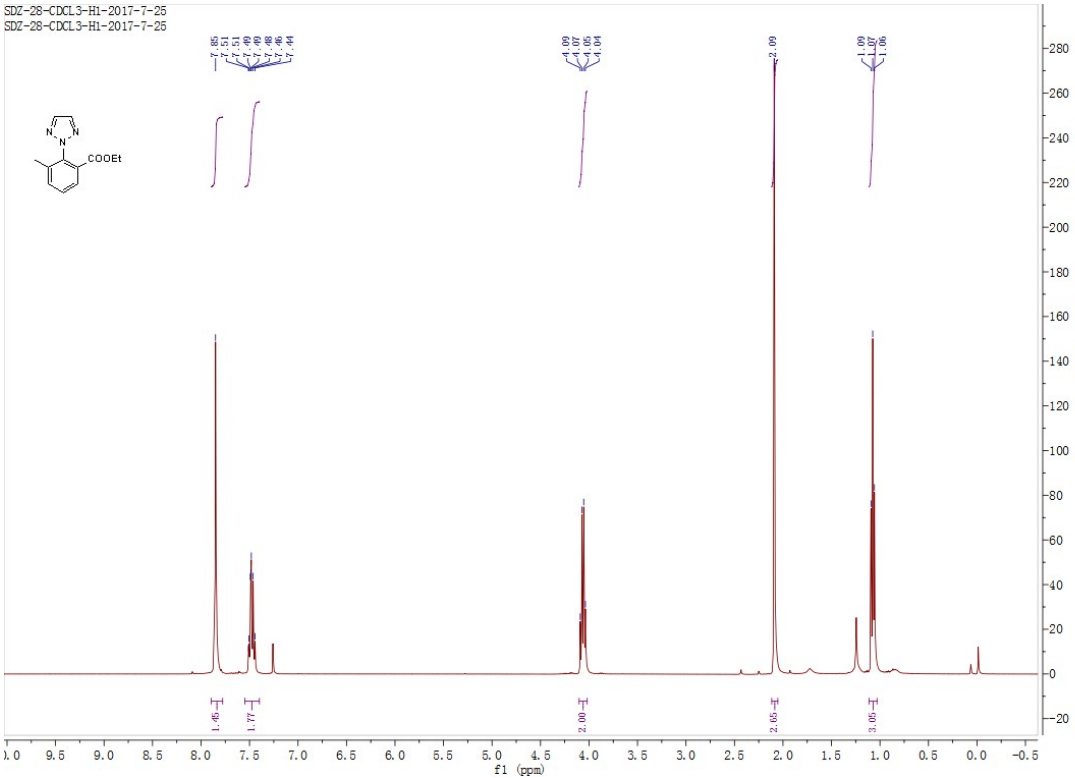

WXH-02-CDCL3-C13-2017-6-24
WXH-02-CDCL3-C13-2017-6-24
166.57
142.68
135.33
130.16
129.63
129.28
125.38
124.73
61.22
21.25
13.89
COOEt
f1 (ppm)

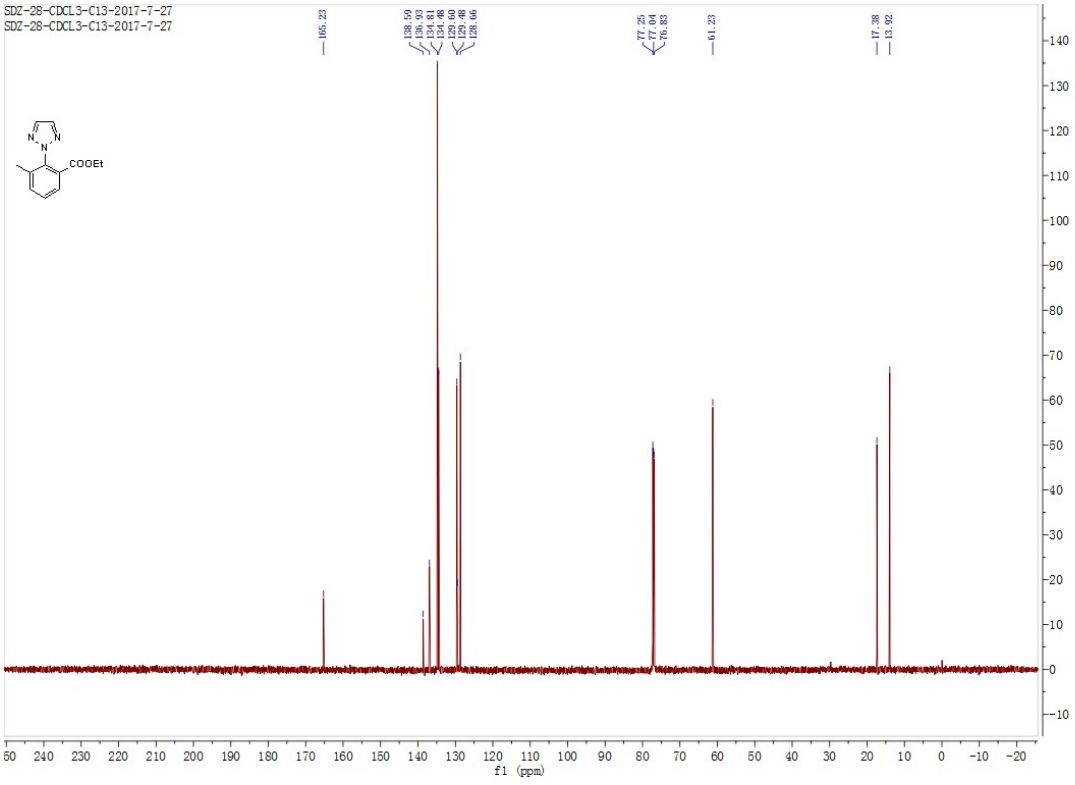

SDZ-21_H1_CDCl3_2017-6-2
SDZ-21 H1 CDCl3 2017-6-2
COOEt
f1 (ppm)

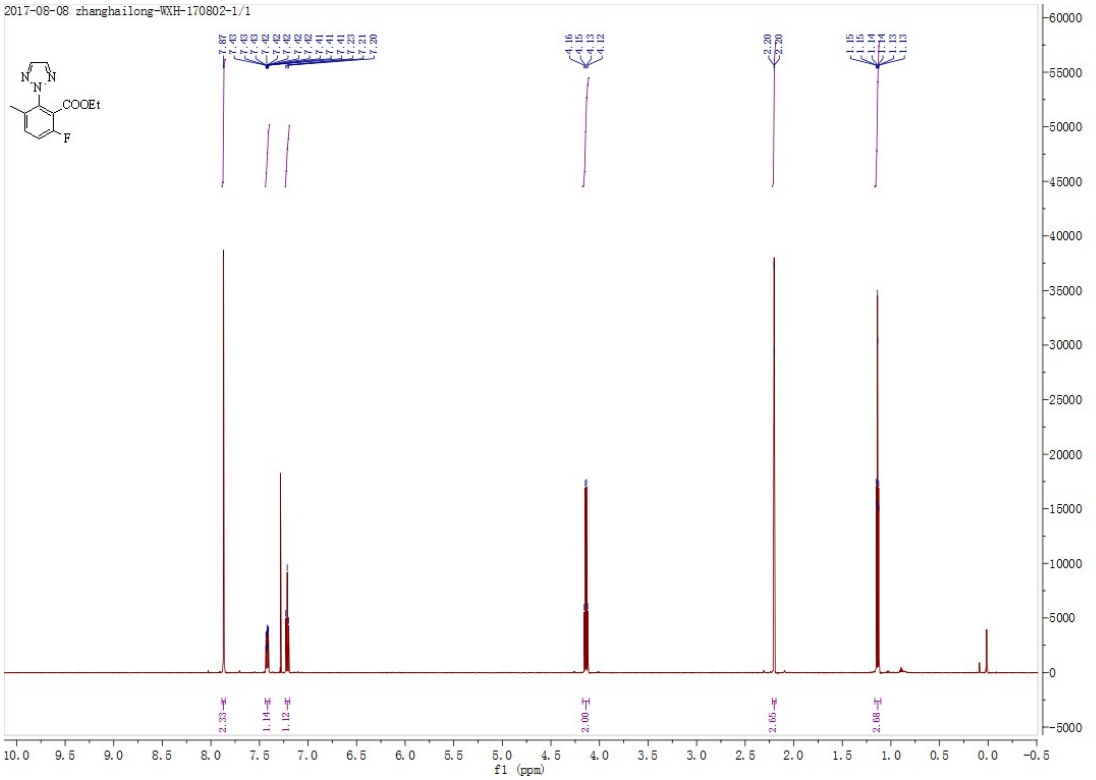

WXH-0706-2-CDCL3-C13-2017-7-8
WXH-0706-2-CDCL3-C13-2017-7-8
COOEt
f1 (ppm)

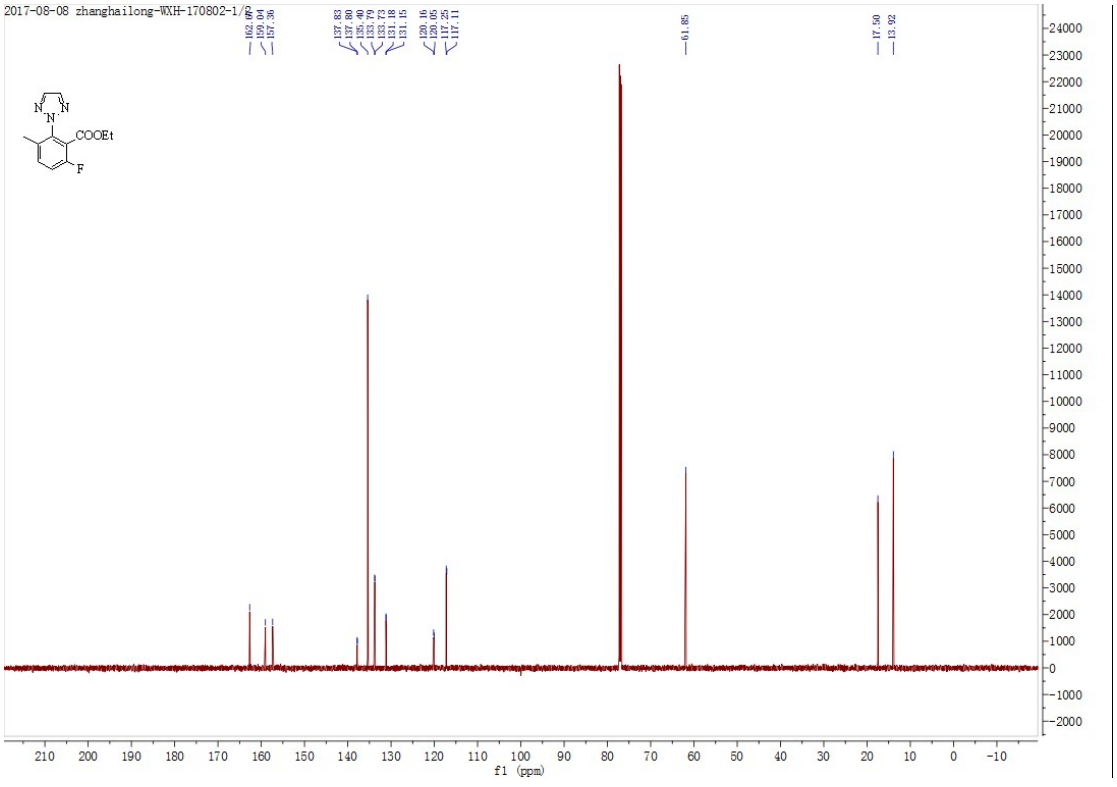

SDZ-232_H1_CDC13_2017-6-27
SDZ-232 H1 CDC13 2017-6-27
COOEt
f1 (ppm)

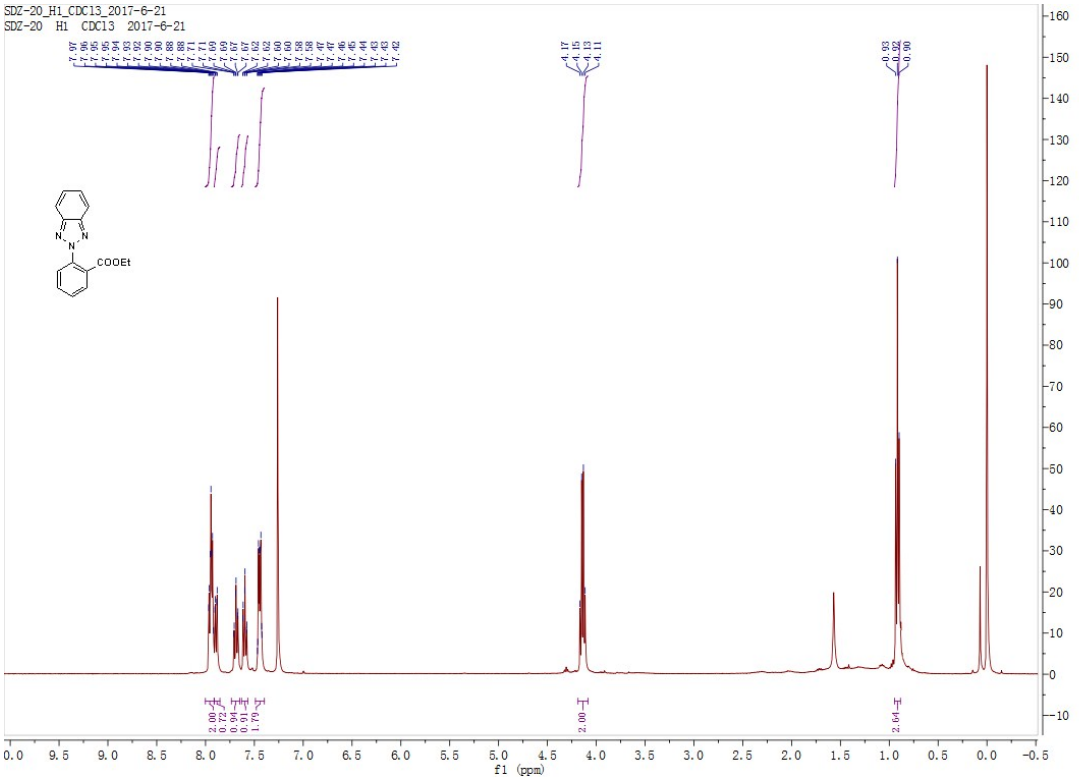

SDZ-232_C13_CDC13_2017-6-30
SDZ-232 C13 CDC13 2017-6-30
COOEt
f1 (ppm)

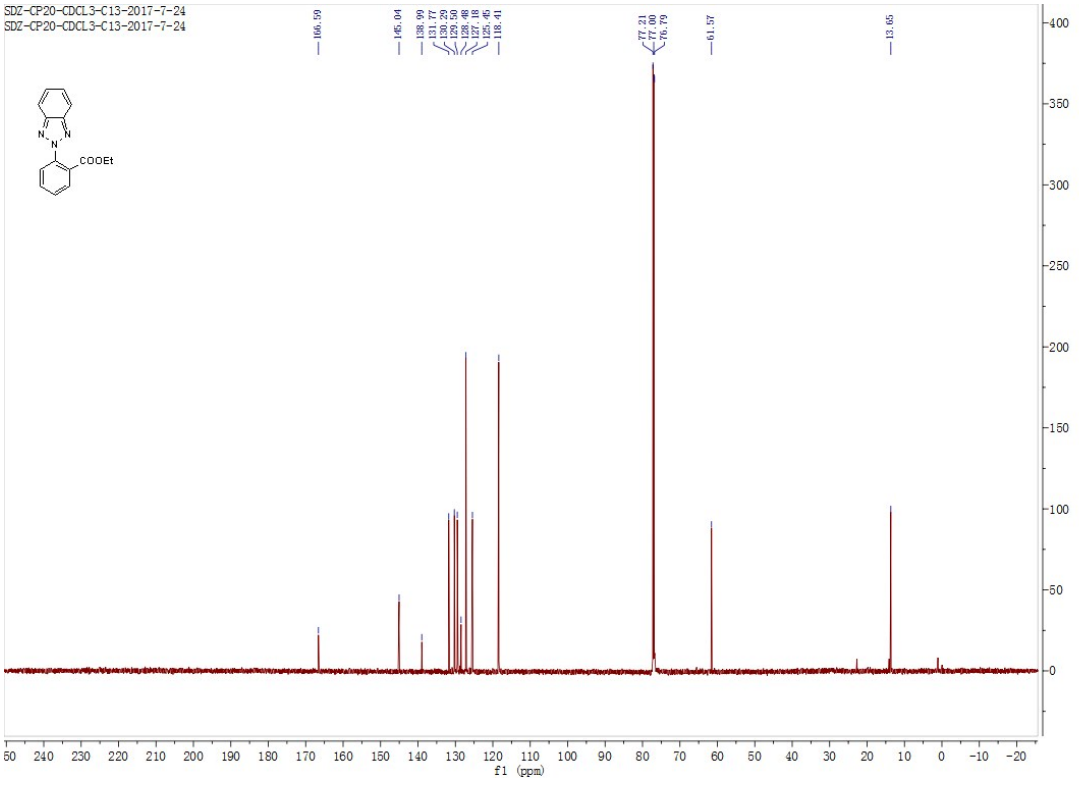

SDZ-28-CDCL3-H1-2017-7-25
SDZ-28-CDCL3-H1-2017-7-25
COOEt
f1 (ppm)

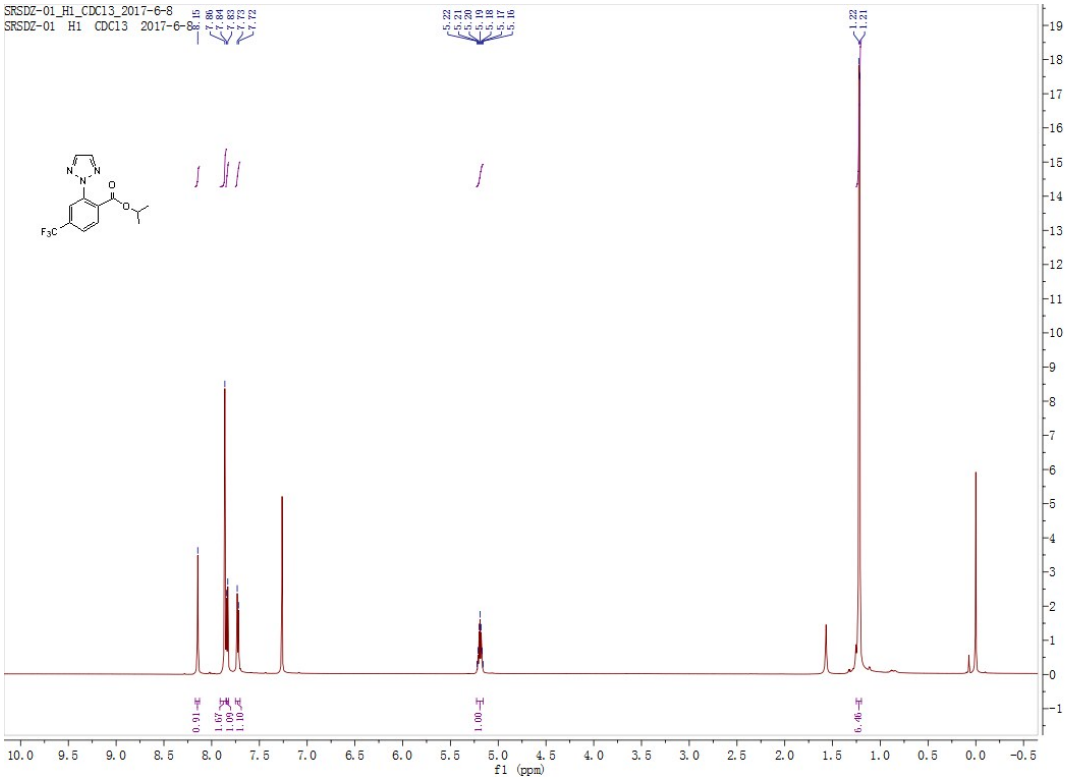

SDZ-28-CDCL3-C13-2017-7-27
SDZ-28-CDCL3-C13-2017-7-27
COOEt
f1 (ppm)

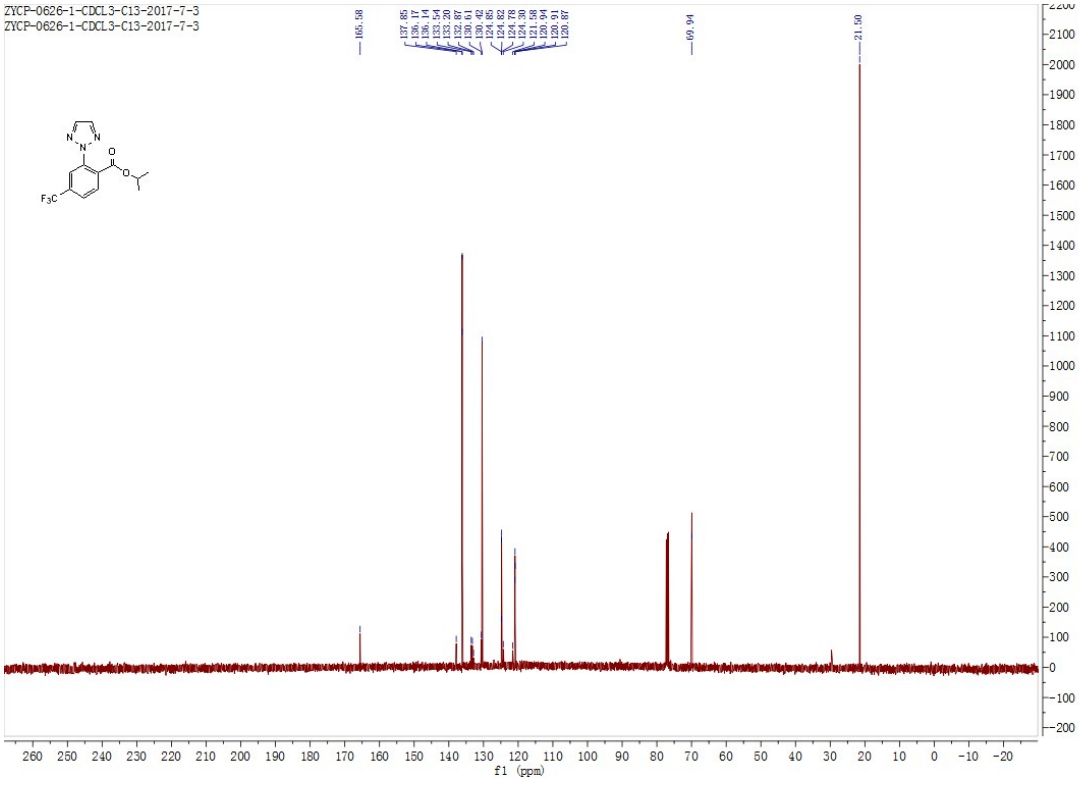

2017-08-08 zhanghailong-WXH-170802-1/1
COOEt
F
f1 (ppm)

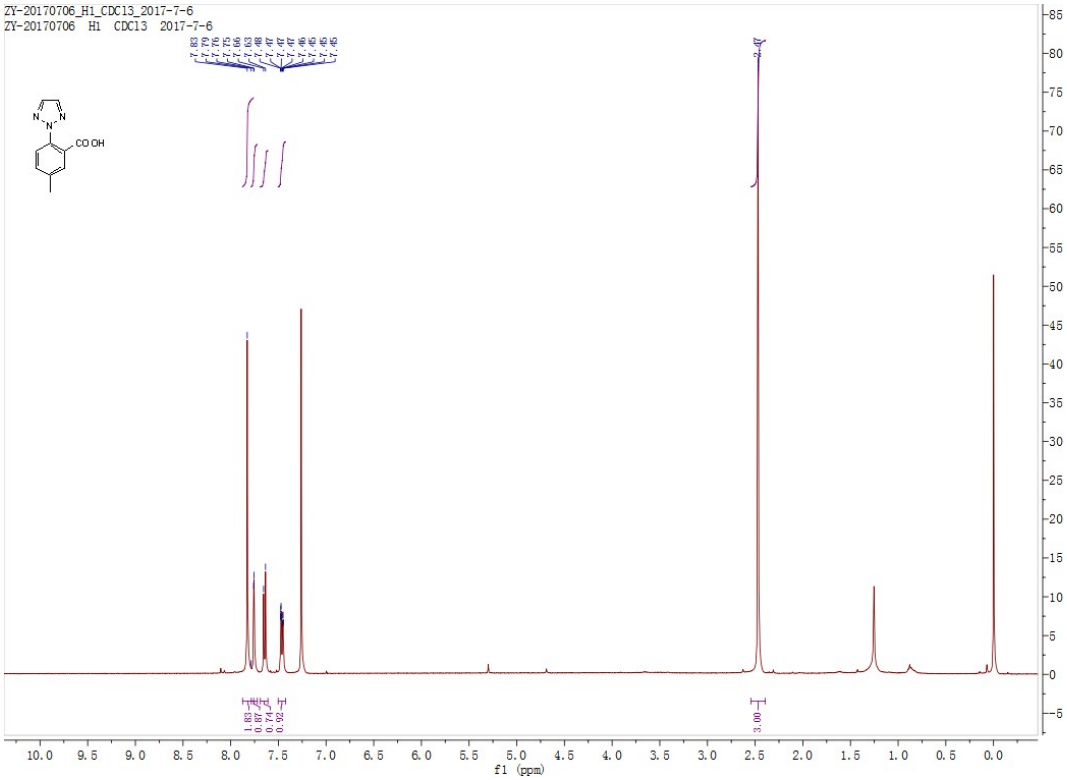

2017-08-08 zhanghailong-WXH-170802-1/P2
COOEt
F
f1 (ppm)

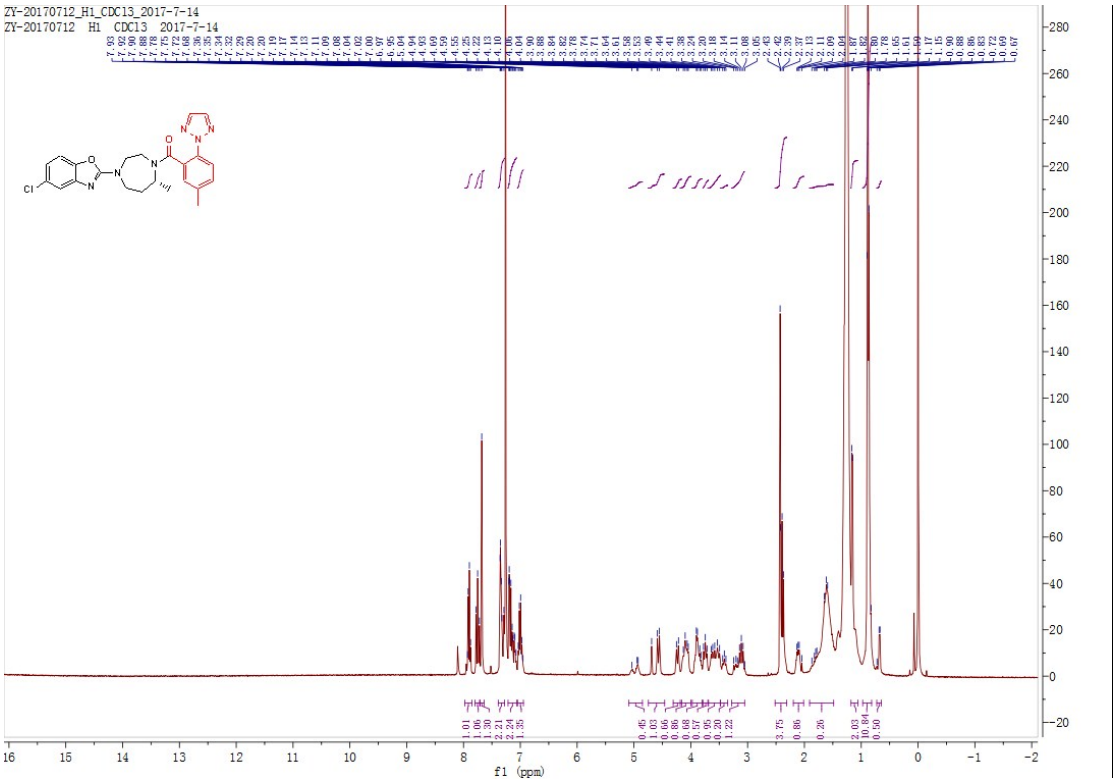

SDZ-20_H1_CDCl3_2017-6-21
SDZ-20 H1 CDCl3 2017-6-21
COOEt
f1 (ppm)

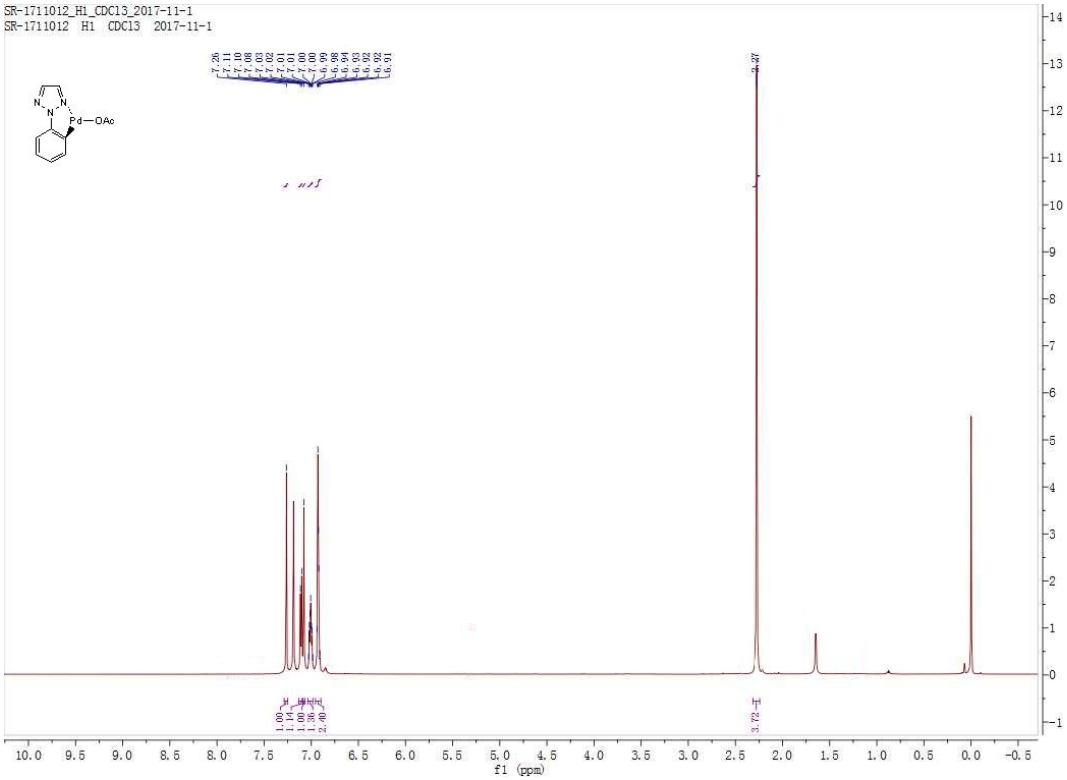

SDZ-CP20-CDCL3-C13-2017-7-24
SDZ-CP20-CDCL3-C13-2017-7-24
COOEt
f1 (ppm)

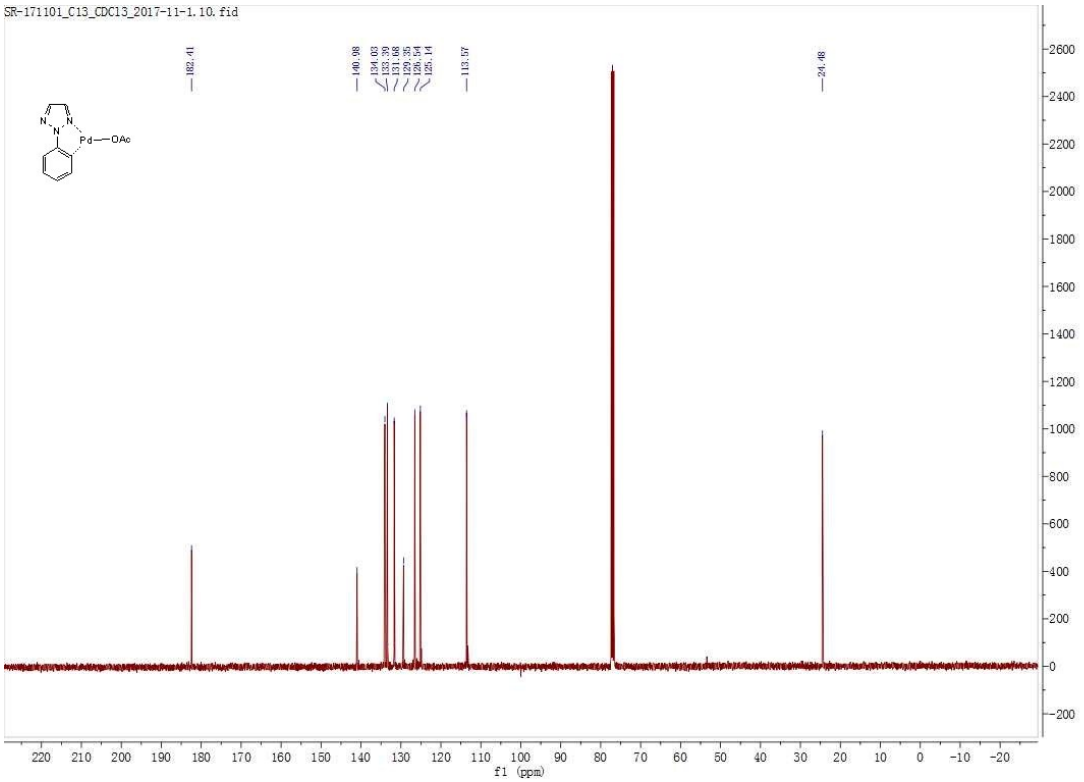

SRSDZ-01_H1_CDCl3_2017-6-8
SRSDZ-01 H1 CDCl3 2017-6-8
8.15
7.86
7.84
7.83
7.73
7.72
5.22
5.21
5.20
5.19
5.18
5.17
5.16
1.22
1.21
0.91
1.67
1.09
1.10
1.00
6.46
F3C
f1 (ppm)


ZYCP-0626-1-CDCL3-C13-2017-7-3
ZYCP-0626-1-CDCL3-C13-2017-7-3
165.58
137.85
136.17
136.14
133.54
133.20
132.87
130.61
130.42
124.85
124.82
124.78
124.30
121.58
120.94
120.91
120.87
69.94
21.50
F3C
f1 (ppm)

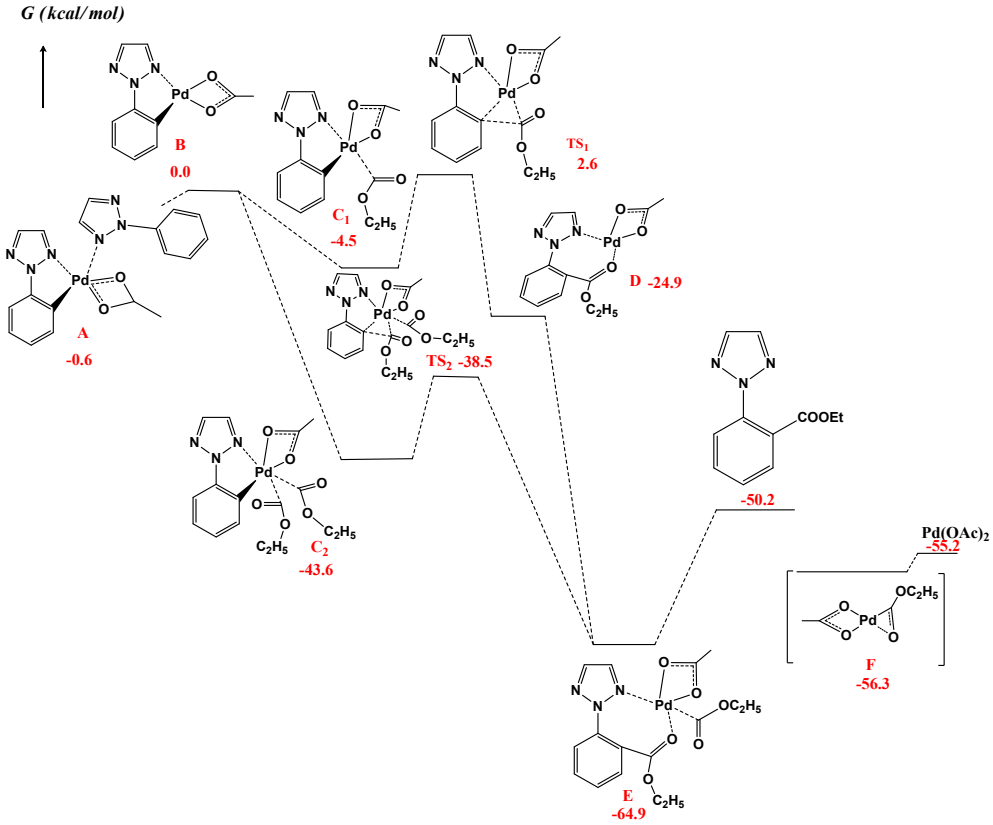

ZY-20170706_H1_CDC13_2017-7-6
ZY-20170706 H1 CDC13 2017-7-6
COOH
f1 (ppm)


ZY-20170712_H1_CDC13_2017-7-14
ZY-20170712 H1 CDC13 2017-7-14
Cl
f1 (ppm)

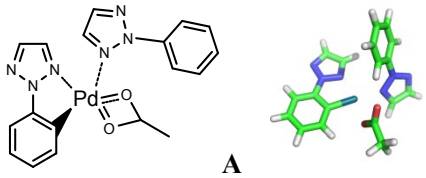

SR-1711012_H1_CDCl3_2017-11-1
SR-1711012 H1 CDCl3 2017-11-1
Pd—OAc
f1 (ppm)


SR-171101_C13_CDCl3_2017-11-1.10.fid
Pd—OAc
f1 (ppm)

7. DFT Calculations



DFT calculations: Relative energies (ZPVE included) are given in kcal/mol. All structures were optimized at the B3LYP/6-31G*/LANL2DZ ECP level of theory, followed by the frequency calculation at the same level. The final energy were further corrected using M06/6-311G+(d,p)/SRSC 1997 ECP with COSMO model. All calculations were done in NWChem6.6. Similar methods have been effectively used in reaction energy calculations of similar systems.



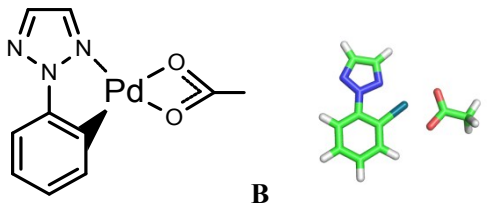
A

PhTriazole 2 with Pd, B3LYP/6-31G*/LANL2DZ ECP, Charge=0, Mult=1

Pd	-0.52265821	-0.51006556	0.34955350
N	2.10533848	-1.68830193	0.43028601
N	1.53229485	-0.50684281	0.71281237
N	3.40984444	-1.71786985	0.62681816
C	1.26850602	-2.73475785	-0.03982307
C	1.77060211	-3.99880237	-0.34005066
C	0.86983486	-4.96507967	-0.78633211
C	-0.48701828	-4.65368358	-0.91546000
C	-0.96274383	-3.37369644	-0.60610665
C	-0.08415468	-2.38491044	-0.16488822

C	2.53655848	0.28054367	1.11620914
C	3.70678958	-0.48377108	1.06126095
H	2.82850257	-4.20985245	-0.22415705
H	1.22892915	-5.96077700	-1.02981284
H	-1.18303668	-5.41452121	-1.25983005
H	-2.01756962	-3.13808357	-0.69943285
H	2.36785862	1.30894549	1.39339668
H	4.72236605	-0.21154460	1.30620776
N	-0.57155377	2.75242894	0.89348495
N	-1.06370918	1.52528093	1.12210606
N	-1.08492969	3.69782945	1.67599705
C	0.39098706	3.04323879	-0.12305256
C	0.30994205	2.39013628	-1.35492062
C	1.27035709	2.68807528	-2.32340879
C	2.27204574	3.62754488	-2.07131309
C	2.31917952	4.28537930	-0.83924015
C	1.37828931	3.99475760	0.14726591
C	-1.95614528	1.69359710	2.10181832
C	-1.96089820	3.04986300	2.44871292
H	-0.50055789	1.69160400	-1.55488270
H	1.21841125	2.18993533	-3.28710082
H	3.00968944	3.85491540	-2.83582597
H	3.09058892	5.02427194	-0.64191286
H	1.39256710	4.49796890	1.10804219
H	-2.52153766	0.85502735	2.47811178
H	-2.54088169	3.57590611	3.19232667
C	-2.98830207	-0.16298303	-1.03568069
C	-4.46391280	-0.45345389	-1.29141688
O	-2.35319930	0.60086257	-1.76378273
O	-2.50964084	-0.81917298	-0.00960185
H	-4.87838387	0.29169342	-1.97326883
H	-5.02814147	-0.46668003	-0.35430454
H	-4.56437622	-1.44529923	-1.74799318

M06 gas phase (au)	-1301.922429	TC to enthalpy (au)	0.349231
M06 sol phase (au)	-1301.946971	Entropy (cal/mol*K)	172.743
B3LYP gas phase(au)	-1301.252183	Cv (cal/mol*K)	89.029
ZPC to energy (au)	0.324271	H (kcal/mol)	-519986.5554
TC to energy (au)	0.348287	G (kcal/mol)	-520023.4685

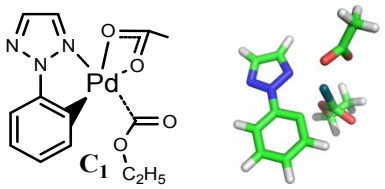


B

PhTriazole 1 with Pd, B3LYP/6-31G*/LANL2DZ ECP, Charge=0, Mult=1

Pd	-0.18555116	-0.80417158	-0.00504464
N	-0.93368996	1.97258039	0.00039278
N	-1.52181161	0.76492286	0.00147730
N	-1.77982354	2.98443950	0.00443876
C	0.48475460	2.00027224	-0.00464179
C	1.21620567	3.18419522	-0.00602599
C	2.60813523	3.08336566	-0.01107982
C	3.22599447	1.82914929	-0.01453669
C	2.46402309	0.65313431	-0.01299848
C	1.07359177	0.72822722	-0.00802166
C	-2.83631156	1.01184686	0.00654369
C	-2.98961734	2.40346208	0.00836236
H	0.70974110	4.14375897	-0.00319236
H	3.20950512	3.98761093	-0.01226350
H	4.31093648	1.76375800	-0.01845771
H	2.95028445	-0.31821324	-0.01561959
H	-3.55708464	0.20897578	0.00850118
H	-3.89020906	2.99870006	0.01223310
C	0.12799071	-3.29006769	-0.01320525
C	0.46007599	-4.75896210	-0.03454714
O	-1.06532102	-2.87561724	-0.00479842
O	1.09590121	-2.43802466	-0.01231009
H	-0.45120826	-5.35530019	0.03638470
H	1.13186940	-4.99951554	0.79560754
H	0.98756863	-5.00123867	-0.96351772

M06 gas phase (au)	-828.8323316	TC to enthalpy (au)	0.197646
M06 sol phase (au)	-828.848934	Entropy (cal/mol*K)	123.807
B3LYP gas phase(au)	-827.9546955	Cv (cal/mol*K)	52.522
ZPC to energy (au)	0.182431	H (kcal/mol)	-519986.5554
TC to energy (au)	0.196702	G (kcal/mol)	-520023.4685

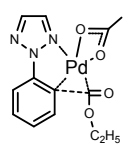


PhTriazole 3 with Pd, B3LYP/6-31G*/LANL2DZ ECP, Charge=0, Mult=2

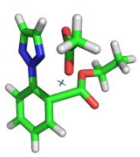
Pd	0.09412234	0.75382702	-0.48283814
N	1.08573754	-1.44050741	1.30408513
N	0.81686808	-0.14553271	1.49906910
N	1.53070046	-2.07103037	2.38138523
C	0.88899737	-2.02347295	0.02003589

C	1.22806881	-3.35648503	-0.21187264
C	1.02335007	-3.88013470	-1.48747504
C	0.48867718	-3.08059916	-2.50029637
C	0.15225128	-1.74586066	-2.24422110
C	0.36080934	-1.19812205	-0.98054868
C	1.10362291	0.08453003	2.78088240
C	1.55073844	-1.12542499	3.32938691
H	1.64298043	-3.95621532	0.59086655
H	1.28189383	-4.91579055	-1.68747486
H	0.32716013	-3.49497126	-3.49181492
H	-0.27898442	-1.13626862	-3.03372889
H	0.97802420	1.06522129	3.21353646
H	1.87754420	-1.35387218	4.33295830
C	1.37589341	2.99144893	-0.41769265
C	2.04762293	4.34529150	-0.40093883
O	0.14954941	2.90464853	-0.05682858
O	2.00832877	1.96620613	-0.80833102
H	1.69568081	4.93548730	0.44930159
H	1.78103657	4.88687287	-1.31628993
H	3.13343714	4.23322631	-0.36788106
C	-1.82526114	0.24260261	-0.43475518
C	-3.70690004	-0.52703029	0.79722573
C	-4.46266633	0.73184228	1.18485311
O	-2.26655153	-0.27405131	0.71098614
O	-2.48250056	0.49595612	-1.41722731
H	-3.78615923	-1.30293009	1.56119953
H	-4.04188776	-0.92389845	-0.16407283
H	-4.08598427	1.13719027	2.12929672
H	-5.52646244	0.49826071	1.30950651
H	-4.36818208	1.49649268	0.40880391

M06 gas phase (au)	-1096.520164	TC to enthalpy (au)	0.284802
M06 sol phase (au)	-1095.695896	Entropy (cal/mol*K)	160.436
B3LYP gas phase(au)	-1095.695896	Cv (cal/mol*K)	75.694
ZPC to energy (au)	0.262433	H (kcal/mol)	-687898.1042
TC to energy (au)	0.283859	G (kcal/mol)	-687945.9382



TS_1
2.6

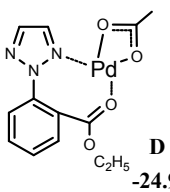


PhTriazole TS5 with Pd, B3LYP/6-31G*/LANL2DZ ECP, Charge=0, Mult=2

Pd	-0.29115817	-0.62711755	0.78668488
N	1.70047794	1.16435230	-0.56091181

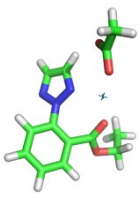
N	1.53383548	-0.16144882	-0.47210365
N	2.66657785	1.53848004	-1.39261862
C	0.88886443	2.02802127	0.21505383
C	1.29363321	3.33774794	0.46500843
C	0.51751998	4.13167520	1.30978134
C	-0.63720686	3.61557245	1.90186663
C	-1.04083279	2.30683985	1.62482450
C	-0.28479380	1.49224365	0.77904330
C	2.43075450	-0.68913448	-1.30126368
C	3.14117179	0.38272049	-1.87066823
H	2.20942163	3.70865011	0.01784022
H	0.82394314	5.15411593	1.51015509
H	-1.23564995	4.23600179	2.56276202
H	-1.97390071	1.92319780	2.02660782
H	2.48843050	-1.76122631	-1.41082183
H	3.95157219	0.37300299	-2.58461111
C	0.47401285	-3.48523411	0.63706757
C	0.41610610	-4.88126120	1.24452318
O	1.08030622	-3.25945618	-0.40891290
O	-0.17923804	-2.59266284	1.34118544
H	0.95820057	-5.58954144	0.61505941
H	-0.62627072	-5.20031024	1.35014607
H	0.85245473	-4.86887493	2.24923062
C	-1.63722336	0.43620520	-0.32993272
C	-2.27372490	0.69558129	-2.60621551
C	-2.78257160	-0.67065798	-3.03159129
O	-1.22466114	0.57984974	-1.59265579
O	-2.77606242	0.44348181	0.07177753
H	-1.77797068	1.21939783	-3.42582326
H	-3.07248172	1.32124731	-2.20059227
H	-1.96025445	-1.29832421	-3.38854985
H	-3.50753288	-0.55335204	-3.84544868
H	-3.27992624	-1.17782526	-2.20018320

M06 gas phase (au)	-1096.489975	TC to enthalpy (au)	0.283588
M06 sol phase (au)	-1096.510262	Entropy (cal/mol*K)	155.153
B3LYP gas phase(au)	-1095.680014	Cv (cal/mol*K)	74.14
ZPC to energy (au)	0.261835	H (kcal/mol)	-687892.6521
TC to energy (au)	0.282645	G (kcal/mol)	-687938.911



D

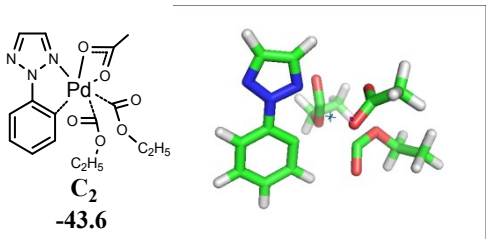
-24.9



PhTriazole 5 with Pd, B3LYP/6-31G*/LANL2DZ ECP, Charge=0, Mult=2

Pd	0.69698785	1.27614334	0.55690667
N	-1.48559001	-0.69947276	-0.93145245
N	-0.99059152	0.54623907	-0.78268588
N	-2.29211336	-0.84015469	-1.99292026
C	-1.43113424	-1.71374153	0.07303025
C	-2.65761725	-2.20302082	0.52990170
C	-2.70492244	-3.22978038	1.46868291
C	-1.52093871	-3.78722619	1.95087552
C	-0.29839368	-3.32194531	1.47717411
C	-0.22811226	-2.27660313	0.54275160
C	-1.46697948	1.23207125	-1.81888522
C	-2.27709413	0.36026987	-2.56952526
H	-3.56710925	-1.76915329	0.13095060
H	-3.66667850	-3.59000979	1.82118175
H	-1.54716606	-4.58756885	2.68394434
H	0.62570894	-3.76819794	1.82749624
H	-1.20074345	2.27789664	-1.91570141
H	-2.83175775	0.54270719	-3.47841903
C	1.13277177	-1.85686511	0.09321565
C	3.28379625	-2.65946697	-0.57445402
C	3.39980149	-2.34871605	-2.05732476
O	1.89716294	-2.91166319	-0.19534919
O	1.55735021	-0.70769898	0.02729451
H	3.79177547	-3.59030112	-0.31456631
H	3.67067377	-1.84565296	0.04247692
H	2.96723667	-3.15402468	-2.65921533
H	4.45751390	-2.24894123	-2.32529711
H	2.89592169	-1.40962333	-2.30151563
C	-0.09162943	4.07617774	0.32993172
C	-0.26761984	5.46962715	0.93022034
O	-0.31120606	3.87365995	-0.86999074
O	0.28493022	3.18673687	1.19997376
H	-0.50972510	6.19195122	0.14788265
H	0.64616920	5.77584432	1.45022584
H	-1.07189785	5.45318149	1.67450958

M06 gas phase (au)	-1096.528056	TC to enthalpy (au)	0.286487
M06 sol phase (au)	-1096.554211	Entropy (cal/mol*K)	160.766
B3LYP gas phase(au)	-1095.723003	Cv (cal/mol*K)	74.574
ZPC to energy (au)	0.264229	H (kcal/mol)	-687918.4114
TC to energy (au)	0.285543	G (kcal/mol)	-687966.3437

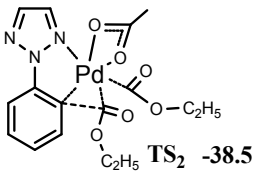


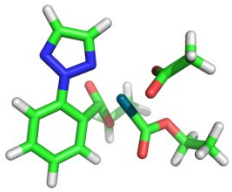
C_2
-43.6

Pd	0.44084676	0.12811056	0.01222026
N	0.65520136	-2.82514841	0.24827320
N	1.31393864	-1.79033981	0.77382208
N	1.08341272	-4.01012262	0.65867646
C	-0.41111313	-2.58325945	-0.66056329
C	-1.06002962	-3.65654190	-1.27288108
C	-2.09396238	-3.38843143	-2.16571147
C	-2.45752154	-2.06797511	-2.43609492
C	-1.79666299	-1.00375801	-1.81263416
C	-0.76055568	-1.24745202	-0.91655956
C	2.22860266	-2.32649804	1.58045717
C	2.08167174	-3.71880457	1.50287738
H	-0.74698810	-4.66989491	-1.04664836
H	-2.60994562	-4.21152681	-2.65131577
H	-3.25967506	-1.85807331	-3.13864169
H	-2.07543617	0.01643626	-2.04431985
H	2.90305575	-1.70353530	2.14734299
H	2.63076744	-4.50302477	2.00226506
C	2.82420192	1.10510161	-0.29665171
C	4.21369746	1.68775918	-0.42752816
O	2.15696228	1.31383788	0.77186856
O	2.32136196	0.44041625	-1.25174614
H	4.67867403	1.79828618	0.55496593
H	4.14099741	2.68172224	-0.88476351
H	4.82948586	1.06086971	-1.07668199
C	-0.37202824	1.78581838	-0.81251193
C	-0.70508163	4.10447021	-0.39604342
C	0.42644793	4.80083413	-1.13269502
O	-0.29344062	2.78515136	0.07439103
O	-0.79204793	1.87826587	-1.93651459
H	-0.97536509	4.63220924	0.52108347
H	-1.58935391	3.98738998	-1.02725692
H	1.31615131	4.86588355	-0.49849003
H	0.12009088	5.81746562	-1.40573265
H	0.68142500	4.26162404	-2.04940253
C	-0.94977349	0.15936662	1.48532137
C	-3.16350775	0.67070993	2.18272479
C	-3.04018980	1.99222801	2.92177676

O	-2.16884705	0.56285813	1.11609310
O	-0.60950900	-0.14796088	2.59776448
H	-3.04222418	-0.18234247	2.85429323
H	-4.11516645	0.58656427	1.65403731
H	-2.08007948	2.05834039	3.44073603
H	-3.84099427	2.07392517	3.66594311
H	-3.12702925	2.83481694	2.22845779

M06 gas phase (au)	-1364.22339	TC to enthalpy (au)	0.373153
M06 sol phase (au)	-1364.251206	Entropy (cal/mol*K)	189.873
B3LYP gas phase(au)	-1363.491913	Cv (cal/mol*K)	97.682
ZPC to energy (au)	0.344582	H (kcal/mol)	-855846.4354
TC to energy (au)	0.372209	G (kcal/mol)	-855903.046



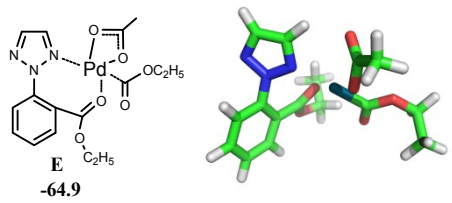


TS_2 -38.5

Pd	0.42554794	-0.21831757	0.03669272
N	0.75274811	2.73791743	-0.18652062
N	1.42969740	1.67360522	-0.62934221
N	1.23607301	3.90637764	-0.59599380
C	-0.36465002	2.55685040	0.66187156
C	-0.81675313	3.61524491	1.44494297
C	-1.87450902	3.39507038	2.32579301
C	-2.45412868	2.12802585	2.42941206
C	-2.00022787	1.07961362	1.63069364
C	-0.95655194	1.27355692	0.71533885
C	2.40838039	2.17069055	-1.37811278
C	2.28488057	3.57104112	-1.35191821
H	-0.32909981	4.58060135	1.36972311
H	-2.23437948	4.21374370	2.94201194
H	-3.26427891	1.95545430	3.13188420
H	-2.45485822	0.10028311	1.70394169
H	3.11269334	1.51982868	-1.87298394
H	2.88629239	4.32844852	-1.83227903
C	2.71222500	-1.56811923	0.13966769
C	3.99021089	-2.37499228	-0.01187230
O	1.96386428	-1.44984856	-0.89630875
O	2.39997298	-1.06706118	1.24553946
H	4.43236723	-2.21790266	-0.99916536
H	3.74920039	-3.44078662	0.07835117
H	4.70282600	-2.11287807	0.77270025

C	-0.48629935	-1.83149333	0.77910195
C	-0.98096626	-4.12323035	0.40489768
C	0.03919817	-4.88443234	1.23447076
O	-0.43206958	-2.85876996	-0.07497496
O	-0.98865374	-1.85333930	1.87566001
H	-1.23726494	-4.65936944	-0.51157835
H	-1.88999814	-3.91399327	0.97427034
H	0.95337478	-5.05872444	0.65816308
H	-0.37411947	-5.85628566	1.52929502
H	0.29301284	-4.32857232	2.14127286
C	-1.29812575	0.49334179	-0.99836135
C	-3.24855427	-0.48430624	-1.95229862
C	-2.71995142	-1.42269453	-3.02494291
O	-2.31787916	-0.37279947	-0.83625062
O	-1.12641132	1.19915976	-1.96320941
H	-3.43755545	0.51714512	-2.34665055
H	-4.15920663	-0.87088018	-1.48902195
H	-1.82296269	-1.01013100	-3.49413761
H	-3.48302916	-1.56340432	-3.79937488
H	-2.47323188	-2.39876998	-2.59627251

M06 gas phase (au)	-1364.213408	TC to enthalpy (au)	0.371559
M06 sol phase (au)	-1364.24354	Entropy (cal/mol*K)	185.779
B3LYP gas phase(au)	-1363.474303	Cv (cal/mol*K)	96.402
ZPC to energy (au)	0.343424	H (kcal/mol)	-855842.6249
TC to energy (au)	0.370615	G (kcal/mol)	-855898.015



E

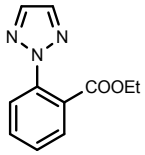
-64.9

PhTriazole 9 with Pd, B3LYP/6-31G*/LANL2DZ ECP, Charge=0, Mult=1

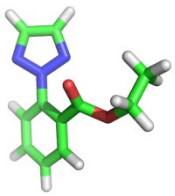
Pd	-0.25836511	0.82863474	-0.08911570
N	-1.62315030	-2.05619875	-0.38366626
N	-1.81456049	-0.73205095	-0.54509188
N	-2.52013994	-2.81434618	-1.02395468
C	-0.75227487	-2.63269889	0.59502425
C	-1.36479158	-3.43635312	1.55866358
C	-0.60637203	-4.06971490	2.53987141
C	0.77828007	-3.90758958	2.56033001
C	1.39505964	-3.12947938	1.58633241
C	0.65146286	-2.47809201	0.58845459
C	-2.85899105	-0.63158541	-1.36335546

C	-3.29467695	-1.93557102	-1.65851878
H	-2.44137935	-3.55631107	1.52287923
H	-1.10114425	-4.68155400	3.28813942
H	1.37808743	-4.38937341	3.32626845
H	2.47218914	-3.01381645	1.58343423
H	-3.20039958	0.35117226	-1.65877926
H	-4.10776059	-2.26798664	-2.28705366
C	1.40085576	-1.69533633	-0.43587823
C	3.51020354	-1.40248378	-1.51032127
C	3.29717447	-1.71042005	-2.98220252
O	2.60881353	-2.19344147	-0.66701389
O	0.99067791	-0.69616057	-1.02786193
H	4.50067395	-1.71335418	-1.17192414
H	3.35203624	-0.34906377	-1.27297150
H	3.40582183	-2.78185258	-3.17945515
H	4.04843111	-1.17519071	-3.57382626
H	2.30737389	-1.38414068	-3.31205913
C	-2.38843249	2.70182974	0.07500123
C	-3.20109665	3.77944855	0.78832922
O	-2.63568681	2.37846557	-1.09056923
O	-1.44197262	2.21184804	0.82491303
H	-4.09408356	4.02054073	0.20797092
H	-2.58756663	4.68102363	0.89658855
H	-3.48015824	3.45193576	1.79442946
C	1.31667929	1.97548484	0.17662338
C	2.24791775	4.16311831	0.30256393
C	2.53362615	4.39782016	1.77765147
O	1.09457372	3.29775941	0.11969822
O	2.41617341	1.47512521	0.34064792
H	1.96625833	5.08978023	-0.20326012
H	3.10746008	3.71801407	-0.20544688
H	1.65003454	4.80057717	2.28299534
H	3.35486839	5.11601235	1.88991240
H	2.82364656	3.46360804	2.26669132

M06 gas phase (au)	-1364.257476	TC to enthalpy (au)	0.374583
M06 sol phase (au)	-1364.286888	Entropy (cal/mol*K)	189.277
B3LYP gas phase(au)	-1363.526894	Cv (cal/mol*K)	96.467
ZPC to energy (au)	0.346281	H (kcal/mol)	-855867.9288
TC to energy (au)	0.373639	G (kcal/mol)	-855924.3617



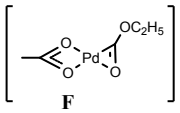
-50.2



phTriazole Et, B3LYP/6-31G*/LANL2DZ ECP, Charge=0, Mult=1

N	0.51551410	1.56090884	0.07504320
N	0.86340431	2.68432213	0.71606167
N	1.47059652	1.01001343	-0.68245449
C	-0.80740790	1.04340980	0.13139857
C	-1.86707319	1.95219817	0.11561561
C	-3.18050478	1.48864238	0.10371938
C	-3.43811154	0.11754114	0.07530018
C	-2.37692561	-0.78504271	0.09122415
C	-1.04912530	-0.34114056	0.14871189
C	2.13555276	2.86028141	0.36242244
C	2.51307413	1.81899920	-0.50523913
H	-1.64383484	3.01279793	0.10336896
H	-3.99971249	2.20178946	0.09519870
H	-4.46013484	-0.24861694	0.04665337
H	-2.56589267	-1.85297003	0.08596329
H	2.70457561	3.69861309	0.73752090
H	3.45460494	1.62747277	-0.99923847
C	0.04441405	-1.34455145	0.36507550
C	0.81138572	-3.51768671	-0.22453026
C	2.02130470	-3.29393588	-1.11872425
O	-0.15706073	-2.45129508	-0.38469183
O	0.94969994	-1.21138139	1.15912896
H	0.26477090	-4.42190575	-0.50384872
H	1.09961962	-3.57619082	0.82778928
H	1.71950214	-3.21204964	-2.16784056
H	2.71524798	-4.13709232	-1.02257291
H	2.54498520	-2.37837736	-0.83092166

M06 gas phase (au)	-746.2105259	TC to enthalpy (au)	0.256907
M06 sol phase (au)	-746.2266936	Entropy (cal/mol*K)	123.052
B3LYP gas phase(au)	-746.5326685	Cv (cal/mol*K)	55.489
ZPC to energy (au)	0.241409	H (kcal/mol)	-468103.1278
TC to energy (au)	0.255963	G (kcal/mol)	-468139.8158



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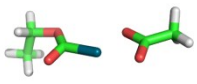
-56.3



PhTriazole 11 with Pd, B3LYP/6-31G*/LANL2DZ ECP, Charge=0, Mult=1

Pd	-1.18463131	0.25620678	-0.05367470
C	-0.73240685	-1.57063455	-0.30411376
C	0.41388879	-3.61363961	-0.67405091
C	0.47513855	-4.28432259	0.68565652
O	0.41975040	-2.14883325	-0.53763469
O	-1.84371312	-2.07814046	-0.19419769
H	1.30273116	-3.81534618	-1.27372399
H	-0.48053122	-3.89662889	-1.23430276
H	1.35457478	-3.95111816	1.24514190
H	0.54164166	-5.37025665	0.55297244
H	-0.42340472	-4.06688383	1.27040408
C	-0.30752228	2.61059166	0.06041574
C	0.36744256	3.95708886	0.10011376
O	-1.54810454	2.47387241	0.22400628
O	0.42919164	1.56970073	-0.15041127
H	-0.36874542	4.74078786	0.28637819
H	0.87730809	4.14244937	-0.85090004
H	1.12873619	3.96538596	0.88693360

M06 gas phase (au)	-624.0384591	TC to enthalpy (au)	0.145717
M06 sol phase (au)	-624.0533923	Entropy (cal/mol*K)	115.49
B3LYP gas phase(au)	-623.0238397	Cv (cal/mol*K)	40.31
ZPC to energy (au)	0.132403	H (kcal/mol)	-391507.9934
TC to energy (au)	0.144773	G (kcal/mol)	-391542.4267

$Pd(OAc)_2$

PhTriazole 12 with Pd, B3LYP/6-31G*/LANL2DZ ECP, Charge=0, Mult=1

Pd	-0.00220118	0.00000086	0.00031909
C	-0.00198438	-2.44687931	-0.00166625
C	0.00485645	-3.94331841	0.00051797
O	-1.09072032	-1.77658031	-0.00126850
O	1.08688401	-1.77450570	-0.00151966
H	-1.01801426	-4.32675784	-0.02965275
H	0.51283481	-4.30430973	0.90308781
H	0.56957743	-4.30802232	-0.86575492
C	-0.00195700	2.44687921	0.00199101
C	0.00484356	3.94331042	-0.00296937
O	-1.09070419	1.77658658	0.00187278
O	1.08689994	1.77450112	0.00223459
H	-1.01719258	4.32682042	0.04823807
H	0.49211117	4.30219908	-0.91788057

H	0.58903860	4.31002683	0.84931002

M06 gas phase (au)	-584.773636	TC to enthalpy (au)	0.115128
M06 sol phase (au)	-584.7875971	Entropy (cal/mol*K)	103.102
B3LYP gas phase(au)	-583.7412918	Cv (cal/mol*K)	34.925
ZPC to energy (au)	0.10367	H (kcal/mol)	-366887.5287
TC to energy (au)	0.114185	G (kcal/mol)	-366918.2686

8. References

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