Electronic Supplementary Material (ESI) for Green Chemistry.
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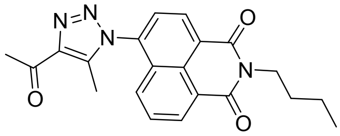
Supplementary Materials for

Integrated High-throughput Strategy Enables Discovery of Multifunctional Ionic Liquids for Sustainable Chemical Processes

General Information and Materials

Solvents were dried using traditional methods, and freshly distilled prior to use. Reactions were monitored by thin-layer chromatography (TLC) on silica gel GF254-precoated plates and RP-HPLC. Compounds were detected under UV light and/or visualized by phosphomolybdic acid in ethanol solution. Solvents were evaporated under reduced pressure and below 50 °C. Mass spectra were obtained on Bruker APEX. High-resolution MS were performed with Bruker BIFLEX III and Bruker Daltonics. Inc. APEX II. ^{1}H NMR spectra were recorded on 400 or 600 MHz using TMS as internal standard. Chemical shifts were reported in parts per million and coupling constants quoted in Hz. The LC-MS were calibrated by authentic standards. High-resolution mass spectra (HRMS) were acquired in the electron-impact mode (EI) using a TOF mass analyzer. Dicarbonyls (**2a-2l**) were from Alfa Aesar. Peptide **1n** was purchased from GL Biochem (Shanghai) Ltd. Azides (**1a** to **1m**) was prepared with the method used in our previous work.

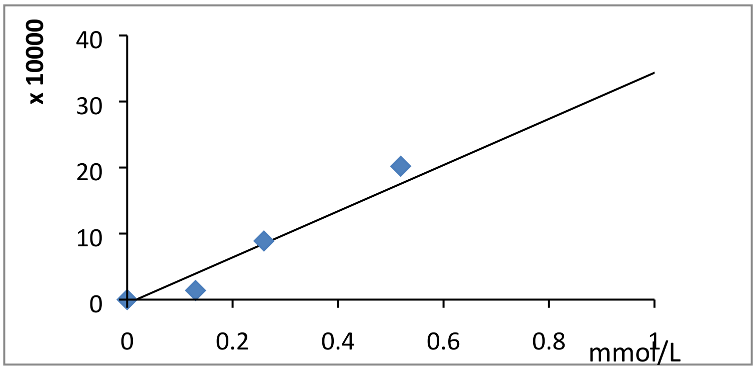
Preparation of fluorescent compound 3a



To an oven-dried round bottom flask, 6-azido-2-butyl-1H-benzo [de]isoquinoline-1,3(2H)-dione (58.8 mg, 0.2 mmol), ethyl acetoacetate (24.0 mg, 0.24 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.02 mmol) were added, and the mixture was left for reaction at 50 °C for 2h, followed by column chromatography to afford the product **3a** (35.7 mg 48%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77-8.71 (m, 2H), 7.85-7.66 (m, 2H), 7.65-7.62 (m, 1H), 4.24-4.20 (m, 2H), 2.84 (s, 3H), 2.48 (s, 3H), 1.77-1.75 (m, 2H), 1.50-1.45 (m, 2H) and 1.02-0.98 (m, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.2, 163.5, 163.0, 143.5, 139.4, 136.1, 132.3, 130.4, 129.0, 128.4, 127.9, 125.9, 125.1, 123.3, 58.5, 40.6, 30.2, 28.0, 20.4, 18.4, 13.8, and 9.8 ppm. HRMS-ESI (m/z) [M+Na$^+$] calcd for $C_{21}H_{20}N_4NaO_3^+$, 399.1427; found: 399.1426.

Figure S1. Fluorescence standard curve for the determination of compound 3a[a]

C_{3a}（mmol/l）	Fluorescence intensity (382 nm)
0	0
0.1297	13840
0.2594	88765
0.5188	201934
1.0377	345573



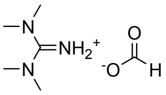
[a] The fluorescence intensity of compound **3a** was measured by a multifunctional enzyme analyzer (PerkinElmer) under fluorescence excitation (Ex=340nm).

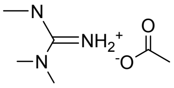
Typical experimental procedure of the screening model

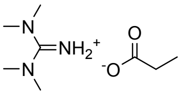
To each of 10 oven-dried round bottom flasks, 6-azido-2-butyl-1H-benzo [de]isoquinoline-1,3(2H)-dione (10 mg, 0.034 mmol) was added with ethyl acetoacetate (4 mg, 0.04 mmol)，then ionic liquids IL-1 to IL-10 (0.034 mmol) was added, respectively. The mixture was left for reaction at 50°C for 2h followed by column chromatography separation to obtain the product **3a**. The isolated yields of **3a** from the reactions with IL-1 to IL-10 were calculated, respectively, as shown in Table S1.

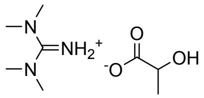
To each of 10 oven-dried round bottom flasks, 6-azido-2-butyl-1H-benzo [de]isoquinoline-1,3(2H)-dione (10 mg, 0.034 mmol) was added with ethyl acetoacetate (4 mg, 0.04mmol), then ionic liquids IL-1 to IL-10 (0.034 mmol) was added respectively. The mixture was left for reaction at 50°C. After 2h, ethyl acetoacetate was added, respectively, to the flask to dilute the mixture to 27 times that of the original volume. Once the systems were mixed evenly, 200 μL of the reaction mixture was taken as sample, and transferred to 96-well plates. Plate reader was used to read the fluorescence intensity at 382 nm for each sample. The fluorescence yields were calculated based on the standard curve, and the results were shown in Table S1 below.

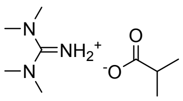
Table S1. Isolated yields, fluorescence intensity and fluorescence yields measured in the screening model with IL-1 to IL10

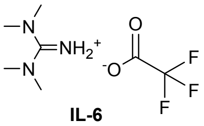

IL-1

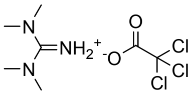

IL-2

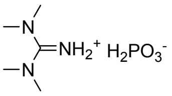

IL-3

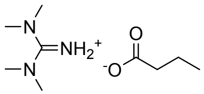

IL-4

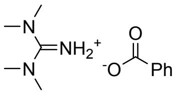

IL-5


IL-6


IL-7


IL-8


IL-9


IL-10

Number of IL	Isolated yield (%)				Fluorescence yield (%)			
	1	2	3	Average	1	2	3	Average
IL-1	61.1	63.5	64.7	63.1	69.7	65.1	71.3	68.7
IL-2	55.2	56	60.4	57.2	60.9	61.6	62.0	61.5
IL-3	70.5	72.5	55.5	61.5	55.4	55.6	57.0	56.0
IL-4	53.9	54.2	56.6	54.9	53.4	48.7	53.6	51.9
IL-5	71.0	71.5	59.4	67.3	61.2	54.4	62.1	59.2
IL-6	10.2	11.4	24	15.2	13.2	12.4	14.0	13.2
IL-7	40.3	42	59.9	47.4	46.4	35.4	46.9	42.9
IL-8	8.0	8.5	13.5	10	13.2	13.2	13.3	13.2
IL-9	53.1	53.5	66.2	57.6	62.9	61.8	63.1	62.6
IL-10	53.0	53	65	57	62.6	65.4	62.8	63.6

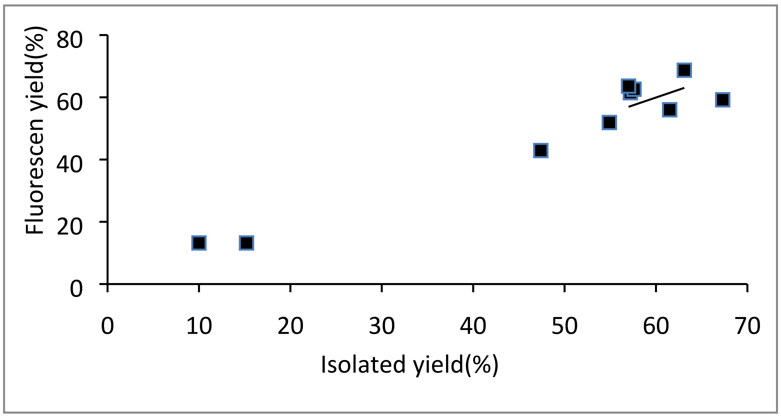


Figure S2 The correlation between fluorescence yields and isolated yields.

Experimental procedure for high-throughput preparation of ILs

Four hundreds of 1.5 ml centrifuge tubes were used to form a square of 400 tubes of 20 base×20 acid cross combinations. Then corresponding base (0.02 mmol) was added to each centrifuge tubes in the ice bath, and 100 μl of methanol solution was added. The acid corresponding to the same amount of substance (0.02 mmol) was also added. When the heat release was over, covered the lid and removed the tubes from the ice bath. Place each of the tubes in a shaker for 48 hours at room temperature. The solvents were evaporated under reduced press after reactions. Considering the possible volatilities of acids and bases that used for building of ILs pool, we dried the samples under reduced pressures with 50°C for 12 hours or 25°C for 24 hours respectively for different types of ILs (Table S2). The dried ILs were checked by ^{1}H NMR to confirm the 1:1 stoichiometry of cations to anions, and the water contents were measured by karl fisher experiments to less than 0.5% (Table S3).

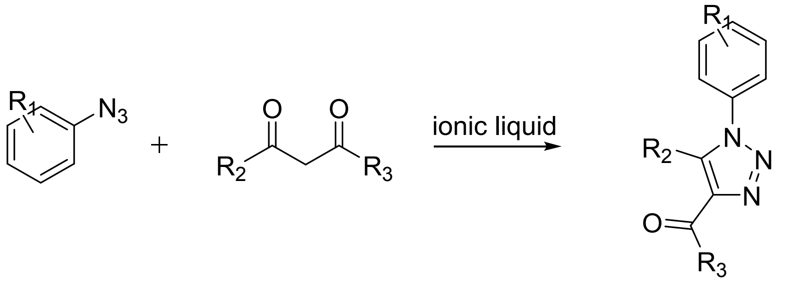
Table S2 Drying protocol for different ILs

Drying protocol	ILs
Drying under reduced pressure (0.1MP) for 24 hours at 25 °C	(1) A1-B1, …A1-B20, (ILs bearing tetramethylguanidinium); (2) A5-B1, … A5-B20, (ILs bearing $(CH_3)_2NH^+CH_2CH_3$) ; (3) A18-B1, … A18-B20, (ILs bearing N,N-Diisopropylethylamine salts);

	(4) A20-B1, … A20-B20, (ILs bearing triethylamine salts); (5) A2-B1, A3-B1, …. A19-B1, A20-B1, (ILs bearing formates).
Drying under reduced press (0.1MP) for 12 hours at 50 °C	Other ILs bearing cations of A2, A3, A4, A6, A7, A8, A9, A10, A11, A12, A13, A14, A15, A16, A17, A19, and anions of B2,…B20.

Experimental procedure for High-throughput screening of ILs

Adding 200 μl of stock solution (1.04 mmol/L at a concentration of **1a** soluble in acetylacetone) to each of the 400 centrifuge tubes that contained ionic liquids prepared by the above method. After the lid was tightly closed, each of the tubes were shocked on oscillator for 20 seconds, then incubated in a table concentrator shaker at 50°C for 2 hours. The samples containing reaction mixtures were transferred into 96-well paltes, and fluorescence intensities were determined at 382 nm with plater reader.



Reaction conditions: **1a**: **2a**: IL = 1: 1.2: 1. The reaction was stirred at 50 °C without solvents.

Scheme S1. Synthesis of 1,4,5-trisubstituted 1,2,3-triazoles.

General procedure for the synthesis of 1,4,5-tri-substituted triazoles from dicarbonyls and azides

To an oven-dried round bottom flask, azide (0.20 mmol), dicarbonyl compounds (0.24 mmol), and choline trichloroacetate (0.20 mmol) were added. The reaction mixture was stirred at 50 °C for the specified time. After the completion of reaction, as indicated by TLC, 1.5 mL ethyl acetate was added to the reaction mixture. The phase of IL was recovered, and organic phase containing products was obtained. The crude product was obtained after the evaporation of solvent, which could be further purified by using column chromatography with petroleum ether /ethyl acetate as the eluent.

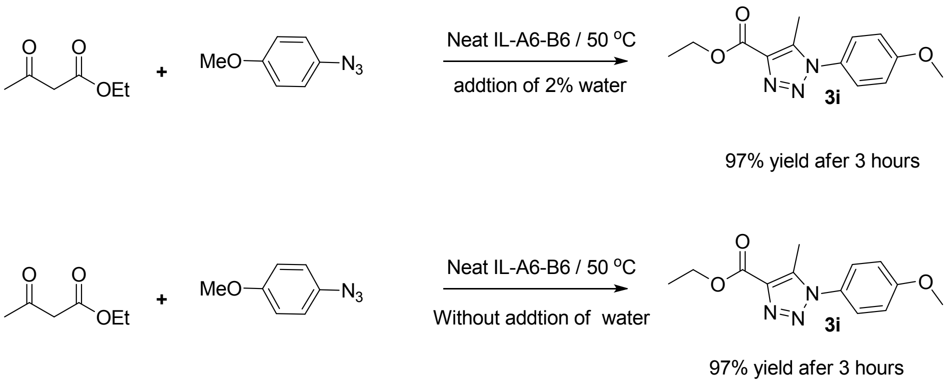
The post-modification of the peptides with the ILs-promoted reaction

The peptide **1n** containing the end group azide (5.0 mg, 0.007 mmol), acetyl methylamine (1.0 mg, 0.008 mmol) and IL A13-B12 (15 mg, 0.07 mmol) were added into a 5 mL flask, and the mixture was stirred at 50°C. The reaction was quenched in 10% acetonitrile/water solution after 8 hours. Purification of the reaction mixture was performed by semipreparative HPLC on a C18 reversed-phase column, eluted with a linear gradient of 0–65% CH_3CN containing 0.1% TFA to give the target molecule **3x** with a yield of 76% after lyophilization. ^1H NMR (600 MHz, DMSO): δ 12.52 (s, 2H), 8.68 (s, 1H), 8.55 (s, 1H), 8.23 (s, 1H), 8.11 (m, 3H), 8.01 (m, 2H), 7.78 (s, 2H), 7.20 (m, 5H), 6.86 (s, 2H), 4.52 (m, 2H), 4.32 (s, 2H), 3.77 (dm, 3H), 3.08 (s, 3H), 2.80 (s, 4H), 2.57 (s, 3H), 1.75 – 1.42 (m, 7H), 1.24 (s, 3H) and 0.87 (m, 6H) ppm. HRMS-ESI (m/z) [$M+H^+$] calcd for $C_{38}H_{53}N_{12}O_8^+$, 805.4103; found: 805.4119.

Table S3 Water content of ILs A1B2 to A1B20, A6B2 to A6B20 and A13B2 to A13B20

ILs	Water content (ppm)	ILs	Water content (ppm)	ILs	Water content (ppm)
A1-B1	--	A6-B1	--	A13-B1	--
A1-B2	665	A6-B2	3269	A13-B2	2703
A1-B4	944	A6-B4	583	A13-B4	2917
A1-B5	1273	A6-B5	2777	A13-B5	2430
A1-B6	836	A6-B6	825	A13-B6	585
A1-B7	1579	A6-B7	4796	A13-B7	3301
A1-B8	3217	A6-B8	2168	A13-B8	1475
A1-B9	1779	A6-B9	955	A13-B9	4037

A1-B10	3485	A6-B10	2409	A13-B10	3530
A1-B11	1454	A6-B11	1278	A13-B11	2906
A1-B12	918	A6-B12	4881	A13-B12	2654
A1-B13	844	A6-B13	3904	A13-B13	1033
A1-B14	1653	A6-B14	3488	A13-B14	1619
A1-B15	1183	A6-B15	3075	A13-B15	1556
A1-B16	2423	A6-B16	2275	A13-B16	2146
A1-B17	1515	A6-B17	3785	A13-B17	2031
A1-B218	943	A6-B218	2669	A13-B218	3982
A1-B19	3588	A6-B19	2634	A13-B19	2095
A1-B20	1093	A6-B20	4113	A13-B20	2521
A1-B21	1778	A6-B21	1505	A13-B21	1853



Scheme S2. The effect of water content on the ILs-promoted cycloaddition reactions.

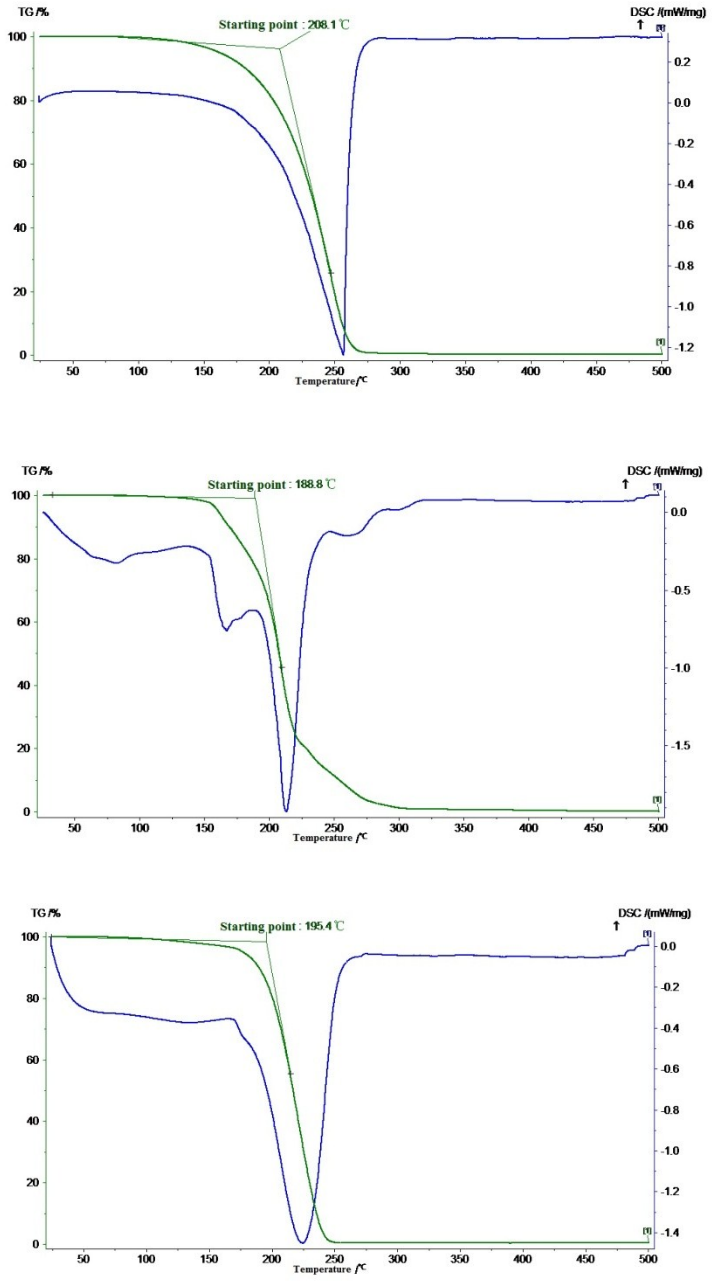


Figure S3 Thermogravimetric analysis (TGA) of IL A13-B2, A6-B6 and A6-B10

Characterization data of ILs A1B1 to A1B20, A6B1 to A6B20 and A13B1 to A13B20

A1-B1: ^{1}H NMR (600 MHz, DMSO) δ 8.53 (s, 1H), 2.88 (s, 12H). IR: ν 2939, 2664, 1559, 1409, 1373, 1339, 1238, 1098, 1064, 1035, 881, 753,715, 540 cm^{-1}.

A1-B2: ^{1}H NMR (600 MHz, D_2O) δ 2.96 (s, 12H), 1.92 (s, 3H). IR: ν 2939, 1551, 1387, 1329, 1239, 1099, 1065, 1035, 1008, 914, 881, 721, 641 cm^{-1}.

A1-B3: ^{1}H NMR (600 MHz, D_2O) δ 2.95 (s, 12H), 2.19 (q, 2H), 1.05(t, 3H). IR: ν 2937, 1670, 1596, 1551, 1461, 1407, 1289, 1215, 1098, 1065, 1035, 881, 811 cm^{-1}.

A1-B4: ^{1}H NMR (600 MHz, D_2O) δ 4.11 (q, 1H), 2.96 (s, 12H), 1.33 (d, 3H). IR: ν 2967, 1595, 1563, 1451, 1407, 1372, 1342, 1238, 1115, 1091, 1064, 1033, 880 cm^{-1}.

A1-B5: ^{1}H NMR (600 MHz, D_2O) δ 2.95 (s, 12H). IR: ν 3097, 1669, 1600, 1567, 1410, 1197, 1169, 1180, 1063, 1037, 879, 827,799, 717 cm^{-1}.

A1-B6: ^{1}H NMR (400 MHz, D_2O) δ 2.97 (s, 12H). IR: ν 2975, 2611, 1598, 1454, 1424, 1407, 1352, 1257, 1194, 1089, 1059,999, 880, 840 cm^{-1}.

A1-B7: ^{1}H NMR (400 MHz, D_2O) δ 3.98 (s, 2H), 2.88 (s, 12H). IR: ν 3278, 3101, 1744, 1644, 1605, 1558, 1412, 1317, 1155, 1077, 1062, 1037, 873, 727, 679 cm^{-1}.

A1-B8: ^{1}H NMR (400 MHz, D_2O) δ 2.95 (s, 12H), 2.16 (t, 2H), 1.60 – 1.50 (m, 2H), 0.89 (t, 3H). IR: ν 2957, 1596, 1548, 1454, 1389, 1305, 1255, 1084, 1094, 1064, 1036, 882, 688, 645, 541 cm^{-1}.

A1-B9: ^{1}H NMR (600 MHz, D_2O) δ 2.96 (s, 12H), 2.39 (dt, 1H), 1.06 (d, 6H). IR: ν 2958, 1595, 1546, 1469, 1399, 1358, 1279, 1087, 1084, 1036, 919, 882, 719, 527 cm^{-1}.

A1-B10: ^{1}H NMR (600 MHz, D_2O) δ 2.96 (s, 12H), 2.21 (t, 2H), 1.56 – 1.50 (m, 2H), 1.31 (dd, 2H), 0.89 (t, 3H). IR: ν 2954, 1547, 1454, 1389, 1237, 1096, 1065, 1035, 883, 727, 652, 542 cm^{-1}.

A1-B11: ^{1}H NMR (600 MHz, D_2O) δ 2.96 (s, 12H), 2.18 (t, 2H), 1.58 – 1.52 (m, 2H), 1.34 – 1.23 (m, 4H), 0.87 (t, 3H). IR: ν 2955, 2929, 2859, 1676, 1596, 1551, 1455, 1407, 1239, 1188,1096, 1065, 1036, 882 cm^{-1}.

A1-B12: ^{1}H NMR (600 MHz, D_2O) δ 2.95 (s, 12H). IR: ν 3056, 2326, 1670, 1593, 1569, 1460, 1419, 1402, 1233, 1119, 1052, 992, 939, 864 cm^{-1}.

A1-B13: ^{1}H NMR (600 MHz, D_2O) δ 2.96 (s, 12H), 2.21 (dd, 1H), 1.96 (dd, 2H), 1.23 (dd, 1H), 1.11 (dd, 1H), 0.96 – 0.88 (m, 12H). IR: ν 2590, 2359, 2342, 1593, 1551, 1466, 1389, 1244, 1102, 1065, 1035, 883, 754, 721, 649 cm^{-1}.

A1-B14: ^{1}H NMR (600 MHz, D_2O) δ 7.88 (d, 2H), 7.52 (dt, 3H), 2.95 (s, 12H). IR: ν 2590, 2359, 2342, 1593, 1551, 1466, 1389, 1244, 1102, 1065, 1035, 883, 754, 721, 649 cm^{-1}. IR: ν 3012, 2906, 2817, 1592, 1536, 1477, 1434, 1411, 1364, 1265, 1238, 1211, 1168, 1151 cm^{-1}.

A1-B15: ^{1}H NMR (400 MHz, D_2O) δ 2.88 (s, 12H), 2.75 (dd, 4H). IR: ν 3344, 3184, 2939, 2523, 1719, 1657, 1604, 1561, 1409, 1185, 1061, 1036, 875, 789 cm^{-1}.

A1-B16: ^{1}H NMR (600 MHz, D_2O) δ 2.95 (s, 12H), 2.32 (dd, 1H), 1.52 – 1.45 (m, 1H), 1.30 (t, 3H), 1.05 (dd, 3H), 0.87 (td, 3H). IR: ν 2956, 2929, 2871, 1545, 1455, 1396, 1359, 1304, 1238, 1203, 1153, 1096, 1035, 883 cm^{-1}.

A1-B17: ^{1}H NMR (600 MHz, D_2O) δ 6.65 (dq, 1H), 5.83 (d, 1H), 2.95 (s, 12H), 1.80 (d, 3H). IR: ν 3014, 2821, 1655, 1593, 1536, 1481, 1438, 1409, 1360, 1291, 1245, 1213, 1156, 1107 cm^{-1}.

A1-B18: ^{1}H NMR (600 MHz, D_2O) δ 2.95 (s, 12H), 2.06 (d, 2H), 1.95 (dt,1H), 0.91 (d, 6H). IR: ν 2951, 1547, 1453, 1386, 1322, 1257, 1168, 1098, 1064, 1035, 883, 726, 639, 543, 477 cm^{-1}.

A1-B19: ^{1}H NMR (600 MHz, D_2O) δ 3.94 (s, 2H), 2.96 (s, 12H). IR: ν 3219, 3006, 2929, 2879, 1684, 1600, 1561, 1482, 1454, 1428, 1410, 1390, 1311, 1235 cm^{-1}.

A1-B20: ^{1}H NMR (600 MHz, D_2O) δ 6.01 (s, 1H), 2.86 (s, 12H). IR: ν 3013, 1643, 1596, 1564, 1453, 1408, 1347, 1212, 1145, 1097, 1063, 1036, 909, 881 cm^{-1}.

A6-B1: ^{1}H NMR (600 MHz, D_2O) δ 8.43 (s, 1H), 4.06 (d, 2H), 3.55 – 3.49 (m, 2H), 3.20 (s, 9H). IR: ν 3202, 1588, 1479, 1375, 1336, 1087, 1007, 953, 866, 754, 550 cm^{-1}

A6-B2: ^{1}H NMR (600 MHz, D_2O) δ 4.06 (d, 2H), 3.54 – 3.50 (m, 2H), 3.20 (s, 9H), 1.92 (s, 3H). IR: ν 3144, 1568, 1481, 1384, 1330, 1139, 1089, 1008, 954, 915, 867, 640, 463 cm^{-1}.

A6-B3: ^{1}H NMR (600 MHz, D_2O) δ 4.06 (d, 2H), 3.57 – 3.49 (m, 2H), 3.20 (s, 9H), 2.18 (dd, 2H), 1.06 (t, 3H). IR: ν 3027, 1567, 1462, 1388, 1361, 1287, 1214, 1139, 1089, 1007, 954, 867, 814, 617 cm^{-1}.

A6-B4: ^{1}H NMR (600 MHz, D_2O) δ 4.11 (dd, 1H), 4.06 (d, 2H), 3.52 (d, 2H), 3.20 (s, 9H), 1.33 (d, 3H). IR: ν 3204, 1592, 1479, 1402, 1341, 1119, 1087, 1032, 954, 865, 772, 645, 531 cm^{-1}.

A6-B5: ^{1}H NMR (600 MHz, D_2O) δ 4.06 (d, 2H), 3.58 – 3.47 (m, 2H), 3.20 (s, 9H). IR: ν 3283, 1681, 1481, 1411, 1197, 1167, 1114, 1006, 954, 867, 824, 800, 717,518 cm^{-1}.

A6-B6: ^{1}H NMR (600 MHz, D_2O) δ 4.06 (d, 2H), 3.56 – 3.47 (m, 2H), 3.20 (s, 9H). IR: ν 3027, 1631, 1480, 1375, 1329, 1278, 1139, 1089, 954, 866, 838, 686, 552 cm^{-1}.

A6-B7: ^{1}H NMR (400 MHz, D_2O) δ 4.04 – 3.96 (m, 4H), 3.49 – 3.42 (m, 2H), 3.14 (s, 9H). IR: ν 3242, 1743, 1477, 1426, 1405, 1346, 1197, 1091, 947, 868, 619, 454 cm^{-1}.

A6-B8: ^{1}H NMR (600 MHz, D_2O) δ 4.12 – 4.01 (m, 2H), 3.57 – 3.44 (m, 2H), 3.20 (s, 9H), 2.15 (t, 2H), 1.60 – 1.51 (m, 2H), 0.89 (t, 3H). IR: ν 3174, 1563, 1481, 1387, 1305, 1090, 955, 868, 611 cm^{-1}.

A6-B9: ^{1}H NMR (600 MHz, D_2O) δ 4.04 (dd, 2H), 3.52 – 3.47 (m, 2H), 3.18 (s, 9H), 2.43 – 2.30 (m, 1H), 1.04 (d, 6H). IR: ν 3174, 2962, 2868, 1562, 1471, 1398, 1356, 1278, 1087, 954, 526 cm^{-1}.

A6-B10: ^{1}H NMR (600 MHz, D_2O) δ 4.05 (dd, 2H), 3.56 – 3.42 (m, 2H), 3.19 (s, 9H), 2.16 (td, 2H), 1.55 – 1.47 (m, 2H), 1.32 – 1.25 (m, 2H), 0.88 (td, 3H). IR: ν 3175, 2956, 2861, 1563, 1480, 1388, 1309, 1090, 954, 867, 646 cm^{-1}.

A6-B11: ^{1}H NMR (600 MHz, D_2O) δ 4.05 (d, 2H), 3.51 (d, 2H), 3.19 (s, 9H), 2.16 (t, 2H), 1.55 (dd, 2H), 1.34 – 1.22 (m, 4H), 0.87 (t, 3H). IR: ν 2928, 2858, 1567, 1481, 1384, 1304, 1091, 955, 867, 614, 555, 454 cm^{-1}.

A6-B12: ^{1}H NMR (600 MHz, D_2O) δ 4.06 (d, 2H), 3.60 – 3.47 (m, 2H), 3.20 (d, 9H). IR: ν 3037, 2852, 2338, 1596, 1480, 1239, 1077, 936, 865, 507 cm^{-1}.

A6-B13: ^{1}H NMR (400 MHz, D_2O) δ 3.99 (dd, 1H), 3.44 (dd, 1H), 2.18 – 2.09 (m, 1H), 1.93 – 1.79 (m, 1H), 1.16 (d, 1H), 1.07 – 1.01 (m, 1H), 0.92 – 0.80 (m, 6H). IR: ν 3021, 2949, 1566, 1464, 1379, 1363, 1107. 1075, 966, 954, 896, 631, 454 cm^{-1}.

A6-B14: ^{1}H NMR (400 MHz, D_2O) δ 7.80 (d, 2H), 7.44 (dt, 3H), 3.92 (dd, 2H), 3.44 – 3.31 (m, 2H), 3.07 (s, 9H). IR: ν 3024, 1597, 1558, 1479, 1359, 1137, 1089, 953, 826, 719, 669 cm^{-1}.

A6-B15: ^{1}H NMR (400 MHz, D_2O) δ 3.98 (s, 2H), 3.49 – 3.37 (m, 2H), 3.11 (s, 10H), 2.83 – 2.64 (m, 4H). IR: ν 3335, 2922, 1711, 1478, 1273, 1168, 1081, 1002, 601 cm^{-1}.

A6-B16: ^{1}H NMR (600 MHz, D_2O) δ 4.05 (d, 2H), 3.51 (dd, 2H), 3.19 (s, 9H), 2.28 (dd, 1H), 1.48 (dd, 1H), 1.27 (s, 3H), 1.04 (d, 3H), 0.87 (dd, 3H). IR: ν 3175, 2958, 2929, 2871, 1564, 1463, 1394, 1359, 1283, 1091, 1007, 955, 548 cm^{-1}.

A6-B17: ^{1}H NMR (600 MHz, D_2O) δ 6.71 – 6.58 (m, 1H), 5.83 (d, 1H), 4.05 (d, 2H), 3.53 – 3.47 (m, 2H), 3.19 (s, 9H), 1.80 (d, 3H). IR: ν 3024, 2854, 1656,1558, 1480, 1358, 1286, 1242, 1090, 954, 862, 716, 555 cm^{-1}.

A6-B18: ^{1}H NMR (600 MHz, D_2O) δ 4.05 (dt, 2H), 3.53 – 3.46 (m, 2H), 3.19 (s, 9H), 2.04 (d, 2H), 2.00 – 1.88 (m, 1H), 0.90 (d, 6H). IR: ν 2953, 2868, 1565, 1481, 1379, 1091, 955, 712, 641 cm^{-1}.

A6-B19: ^{1}H NMR (400 MHz, D_2O) δ 3.99 (d, 2H), 3.86 (s, 2H), 3.51 – 3.36 (m, 2H), 3.13 (s, 9H). IR: ν 3191, 2853, 1590, 1480, 1358, 1079, 1006, 954, 900, 685 cm^{-1}.

A6-B20: ^{1}H NMR (400 MHz, D_2O) δ 5.99 (s, 1H), 4.01 (t, 2H), 3.51 – 3.39 (m, 2H), 3.13 (s, 9H). IR: ν 3230, 1737, 1647, 1478, 1352, 1199, 1084, 952, 814, 677 cm^{-1}.

A13-B1: ^{1}H NMR (600 MHz, D_2O) δ 8.46 (s, 1H), 3.58 - 3.56 (m, 2H), 3.54 - 3.52 (m, 2H), 3.33 - 3.31 (m, 2H), 2.63 - 2.62 (m, 2H), 2.03 - 2.01 (m, 2H), 1.75 – 1.69 (m, 6H). IR: ν 2930, 2661, 1642, 1579, 1446, 1322, 1205, 1107, 985, 748, 690, 529 cm^{-1}.

A13-B2: ^{1}H NMR (600 MHz, D_2O) δ 3.57 – 3.55 (m, 2H), 3.53 - 3.51 (m, 2H), 3.32 - 3.30 (m, 2H), 2.62 – 2.61 (m, 2H), 2.02 – 2.00 (m, 2H), 1.91 (s, 3H), 1.74 – 1.68 (m, 6H). IR: ν 2928, 1642, 1561, 1385, 1321, 1204, 1158, 690, 613, 528 cm^{-1}.

A13-B3: ^{1}H NMR (600 MHz, D_2O) δ 3.57 – 3.55 (m, 2H), 3.53 - 3.51 (m, 2H), 3.32 - 3.31 (m, 2H), 2.63 – 2.61 (m, 2H), 2.19 - 2.17 (q, 2H), 2.03 – 2.00 (m, 2H), 1.75 - 1.68 (m, 6H), 1.06 -1.04 (t, 3H). IR: ν 2929, 2861, 1641, 1556, 1460, 1387, 1359, 1322, 1284, 1203, 863, 689, 528 cm^{-1}.

A13-B4: ^{1}H NMR (600 MHz, D_2O) δ 4.05 - 4.02 (q, 1H), 3.53 – 3.51 (m, 2H), 3.49 - 3.48 (m, 2H), 3.28 - 3.26 (m, 2H), 2.59 – 2.57 (m, 2H), 1.97 – 1.95 (m, 2H), 1.70 - 1.64 (m, 6H), 1.28 - 1.27 (d, 3H). IR: ν 2930, 2862, 1741, 1644, 1596, 1447, 1369, 1321, 1205, 1111, 1032, 842, 691,529 cm^{-1}.

A13-B5: ^{1}H NMR (600 MHz, D_2O) δ 3.56 (s, 2H), 3.53 (s, 2H), 3.32 (s, 2H), 2.62 (s, 2H), 2.02 (s, 2H), 1.73 – 1.69 (m, 6H). IR: ν 2934, 1687, 1641, 1448, 1324, 1195, 1162, 1108, 985, 821, 797, 717 cm^{-1}.

A13-B6: ^{1}H NMR (600 MHz, D_2O) δ 3.58 – 3.57 (d, 2H), 3.54 – 3.52 (t, 2H), 3.34 – 3.32 (t, 2H), 2.64 – 2.62 (d, 2H), 2.03 – 2.01 (m, 2H), 1.76 – 1.69 (m, 6H). IR: ν 2924, 2855, 1609, 1442, 1355, 1314, 1207, 1097, 992, 834, 746, 690, 507 cm^{-1}.

A13-B7: ^{1}H NMR (400 MHz, D_2O) δ 4.00 (s, 2H), 3.64 – 3.34 (m, 4H), 3.25 (t, 2H), 2.68 – 2.40 (m, 2H), 2.06 – 1.83 (m, 2H), 1.64 (dd, 6H). IR: ν 3193, 3086, 3032, 2859, 1745, 1640, 1586, 1419, 1386, 984, 733 cm^{-1}.

A13-B8: ^{1}H NMR (600 MHz, D_2O) δ 3.50 - 3.49 (m, 2H), 3.46 - 3.44 (m, 2H), 3.26 - 3.24 (m, 2H), 2.57 – 2.56 (m, 2H), 2.06 - 2.04 (t, 2H), 1.95 – 1.93 (m, 2H), 1.67 – 1.61 (m, 6H), 1.48 - 1.47 (m, 2H), 0.84 - 0.81 (t, 3H). IR: ν 2931, 2869, 1643, 1553, 1447, 1389, 1323, 1204, 1106, 984, 690 cm^{-1}.

A13-B9: ^{1}H NMR (600 MHz, D_2O) δ 3.54 – 3.53 (m, 2H), 3.50 - 3.49 (d, 2H), 3.30 - 3.29 (d, 2H), 2.60 – 2.59 (m, 2H), 2.35 – 2.33 (m, 1H), 1.99 – 1.97 (m, 2H), 1.72 - 1.65 (m, 6H), 1.03 - 1.02 (dd, 3.0 Hz, 6H). IR: ν 2930, 2864, 1643, 1551, 1470, 1398, 1355, 1323, 1276, 1205, 1187, 690, 528 cm^{-1}.

A13-B10: ^{1}H NMR (600 MHz, D_2O) δ 3.56 – 3.55 (m, 2H), 3.52 – 3.50 (m, 2H), 3.32 – 3.30 (m, 2H), 2.62 – 2.60 (m, 2H), 2.17 – 2.15 (t, 2H), 2.01 – 1.99 (m, 2H), 1.74 – 1.68 (m, 6H), 1.67 – 1.51 (m, 2H), 1.30 – 1.26 (m, 2H), 0.89 – 0.87 (t, 3H). IR: ν 2929, 2859, 1642, 1554, 1446, 1384, 1322, 1202, 1158, 1107, 689 cm^{-1}.

A13-B11: ^{1}H NMR (600 MHz, D_2O) δ 3.56 – 3.52 (m, 2H), 3.51 – 3.50 (m, 2H), 3.31 – 3.30 (m, 2H), 2.6 – 2.60 (m, 2H), 2.16 – 2.13 (t, 2H), 2.01 – 1.99 (m, 2H), 1.74 –

1.70 (m, 6H), 1.30 – 1.28 (m, 2H), 1.27 – 1.25 (m, 4H), 0.87 – 0.85 (t, 3H). IR: ν 3242, 2928, 2858, 1644, 1558, 1447, 1386, 1322, 1205, 1158, 1099, 1052, 884, 882 cm^{-1}.

A13-B12: ^{1}H NMR (600 MHz, D_2O) δ 3.57 – 3.56 (m, 2H), 3.53 – 3.51 (m, 2H), 3.33 – 3.31 (m, 2H), 2.63 – 2.61 (m, 2H), 2.03 – 1.99 (m, 2H), 1.75 – 1.69 (m, 6H). IR: ν 2925, 2856, 2326, 1644, 1604, 1348, 1252, 1203, 1063, 939, 865, 688,516 cm^{-1}.

A13-B13: ^{1}H NMR (600 MHz, D_2O) δ 3.54 – 3.52 (m, 2H), 3.49 – 3.48 (m, 2H), 3.29 – 3.28 (m, 2H), 2.61 – 2.60 (m, 2H), 1.98 – 1.97 (m, 1H), 1.71 – 1.70 (m, 4H), 1.68 – 1.64 (m, 6H), 1.21 – 1.18 (m, 1H), 1.07 – 1.03 (m, 1H), 0.91 – 0.88 (m, 12H). IR: ν 2936, 2864, 1644, 1553, 1447, 1323, 1246, 753, 504 cm^{-1}.

A13-B14: ^{1}H NMR (600 MHz, D_2O) δ 7.87 – 7.85 (m, 2H), 7.48 – 7.47 (m, 1H), 7.44 – 7.41 (m, 2H), 3.33 – 3.32 (m, 2H), 3.28 – 3.27 (m, 2H), 3.13 – 3.12 (m, 2H), 2.41 – 2.39 (m, 2H), 1.82 – 1.80 (m, 2H), 1.58 – 1.49 (m, 6H). IR: ν 2938, 2855, 1647, 1596, 1553, 1354, 1325, 1207, 1159, 1060, 820, 717, 691, 669, 528 cm^{-1}.

A13-B15: ^{1}H NMR (600 MHz, D_2O) δ 3.57 – 3.55 (m, 2H), 3.53 – 3.51 (m, 2H), 3.32 – 3.31 (t, 2H), 2.90 – 2.87 (d, 2H), 2.78 – 2.75 (d, 2H), 2.62 – 2.61 (m, 2H), 2.02 – 2.00 (m, 2H), 1.74 – 1.68 (m, 6H). IR: ν 3252, 2931, 1719, 1645, 1581, 1445, 1322, 1203, 1047, 983, 879, 791, 689, 604 cm^{-1}.

A13-B16: ^{1}H NMR (600 MHz, D_2O) δ 3.56 – 3.55 (m, 2H), 3.52 – 3.50 (m, 2H), 3.32 – 3.30 (m, 2H), 2.62 – 2.60 (m, 2H), 2.31 – 2.28 (m, 1H), 2.01 – 1.99 (m, 2H), 1.74 – 1.67 (m, 6H), 1.31 – 1.28 (m, 1H), 1.27 – 1.25 (m, 3H), 1.04 – 1.03 (d, 3H), 0.88 – 0.85 (t, 3H). IR: ν 2954, 2929, 2868, 1643, 1552, 1457, 1392, 1366, 1322, 1204, 1108, 690, 528 cm^{-1}.

A13-B17: ^{1}H NMR (600 MHz, D_2O) δ 6.60 – 6.54 (m, 1H), 5.79 – 5.76 (d, J = 15.6 Hz, 1H), 3.50 – 3.48 (m, 2H), 3.46 – 3.44 (t, J = 5.8 Hz, 2H), 3.26 – 3.24 (t, J = 5.6 Hz, 2H), 2.56 – 2.55 (m, 2H), 1.976 – 1.92 (m, 2H), 1.76 – 1.74 (d, J = 6.8 Hz, 3H), 1.68 – 1.61 (m, 6H). IR: ν 2925, 2861, 2466, 1894, 1637, 1545, 1378, 1350, 1319, 1279, 1157, 974, 897, 715, 685, 635, 529 cm^{-1}.

A13-B18: ^{1}H NMR (600 MHz, D_2O) δ 3.54 – 3.53 (m, 2H), 3.50 – 3.48 (t, 2H), 3.30 – 3.28 (m, 2H), 2.60 – 2.59 (m, 2H), 2.01 – 2.00 (m, 2H), 1.99 – 1.97 (m, 2H), 1.93 – 1.92 (m, 1H), 1.732 – 1.65 (m, 6H), 0.88 (s, 3H), 0.87 (s, 3H). IR: ν 2930, 2866, 1643, 1552, 1447, 1381, 1322, 1204, 1159, 1107, 839, 690, 527 cm^{-1}.

A13-B19: ^{1}H NMR (600 MHz, D_2O) δ 3.92 (s, 2H), 3.55 – 3.54 (m, 2H), 3.51 – 3.50 (m, 2H), 3.31 – 3.29 (m, 2H), 2.61 – 2.59 (m, 2H), 2.01 – 1.97 (m, 2H), 1.72 – 1.66 (m, 6H). IR: ν 2927, 1643, 1604, 1355, 1321, 1205, 1107, 1057, 985, 895, 689, 589, 505 cm^{-1}.

A13-B20: ^{1}H NMR (600 MHz, D_2O) δ 6.04 (s, 1H), 3.58 – 3.56 (m, 2H), 3.54 – 3.52 (m, 2H), 3.34 – 3.32 (m, 2H), 2.64 – 2.62 (m, 2H), 2.03 – 2.01 (m, 2H), 1.75 – 1.69 (m, 6H). IR: ν 2931, 1639, 1446, 1350, 1322, 1205, 1106, 984,821, 764, 690 cm^{-1}.

Data of high throughput screening obtained from plate reader (Figure S4 to Figure S23).

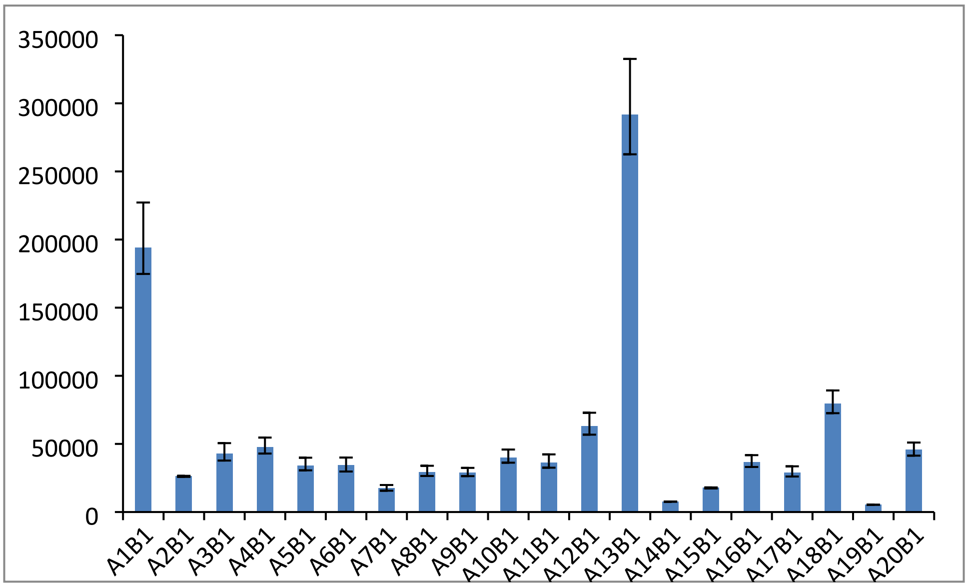


Figure S4

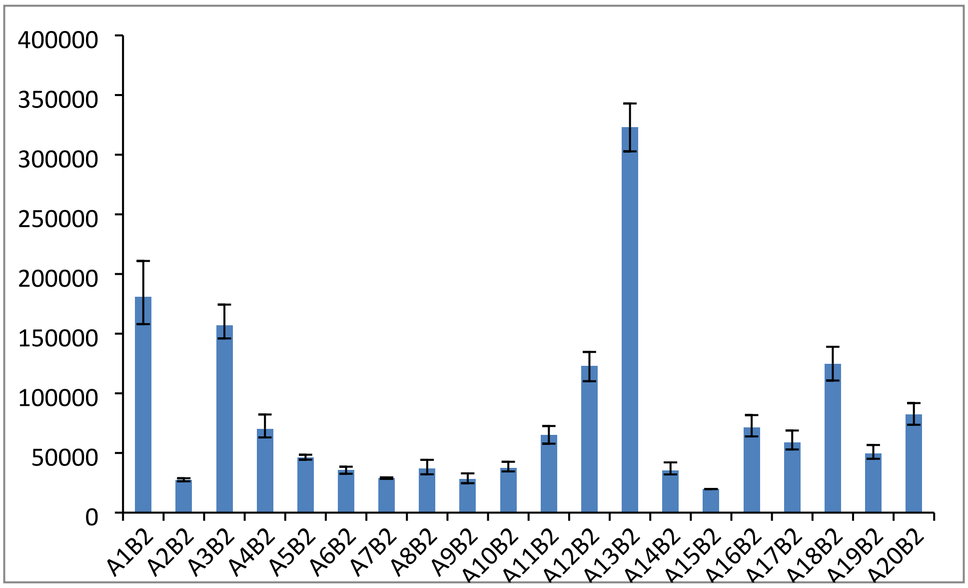


Figure S5

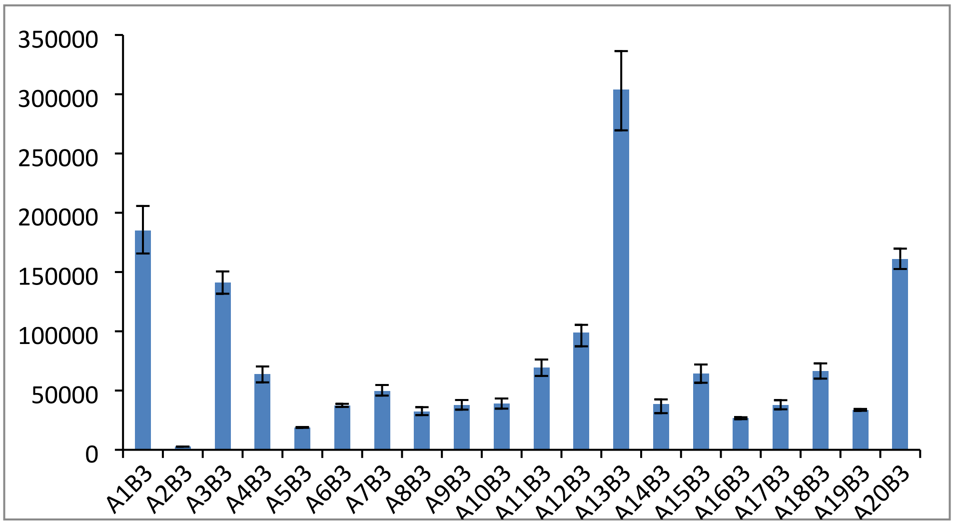


Figure S6

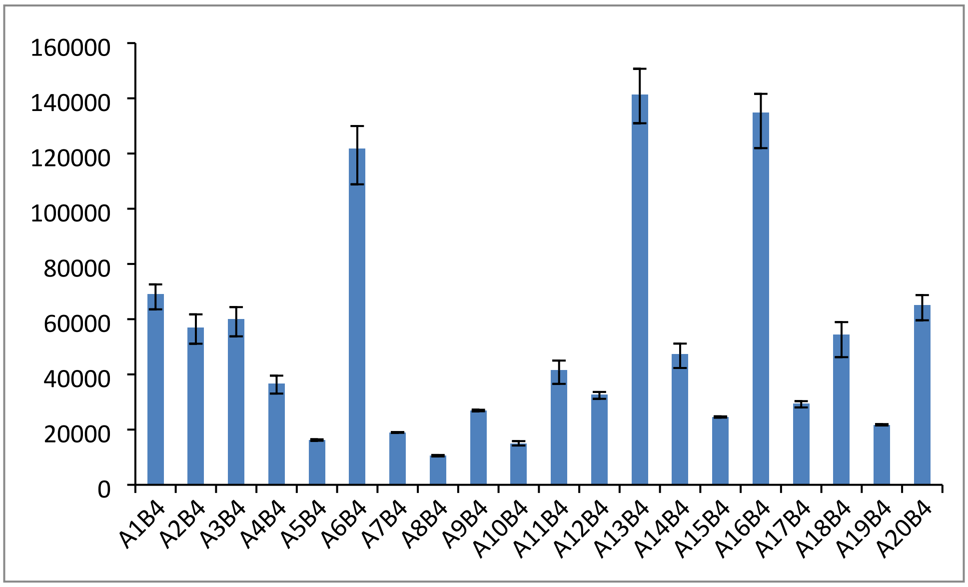


Figure S7

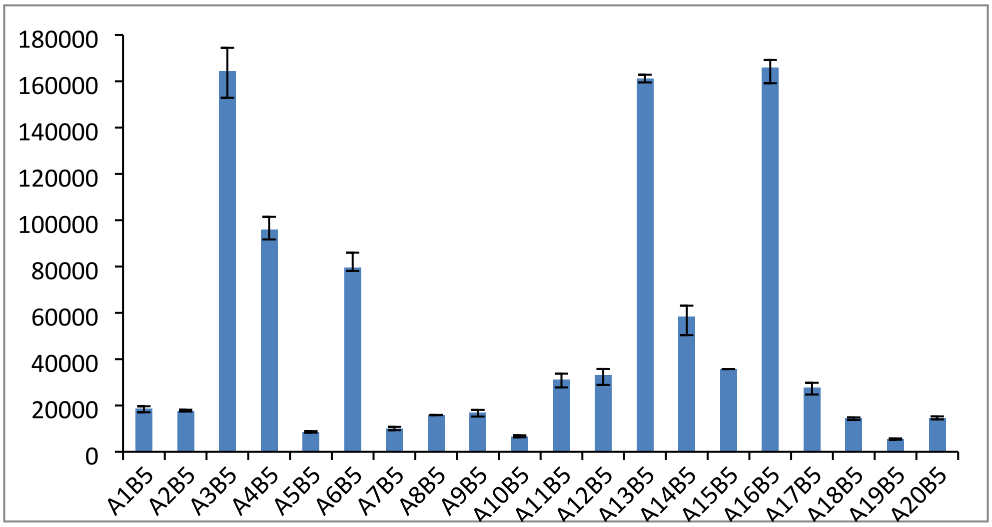


Figure S8

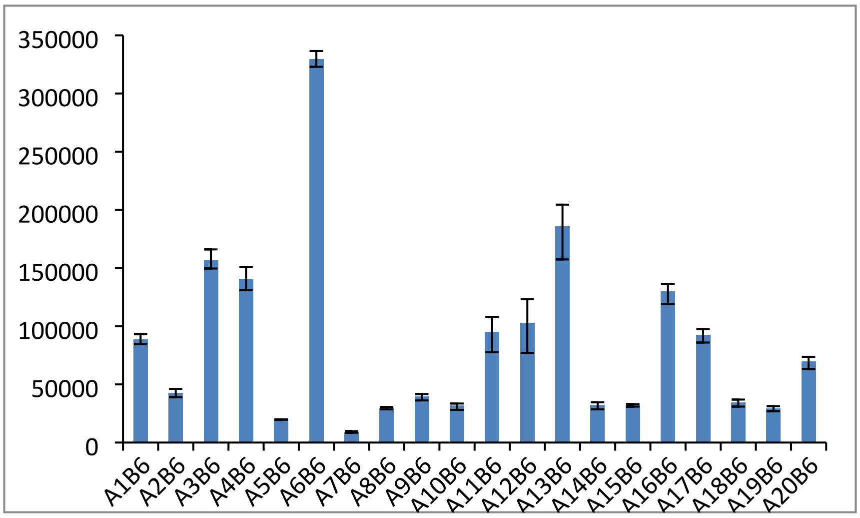


Figure S9

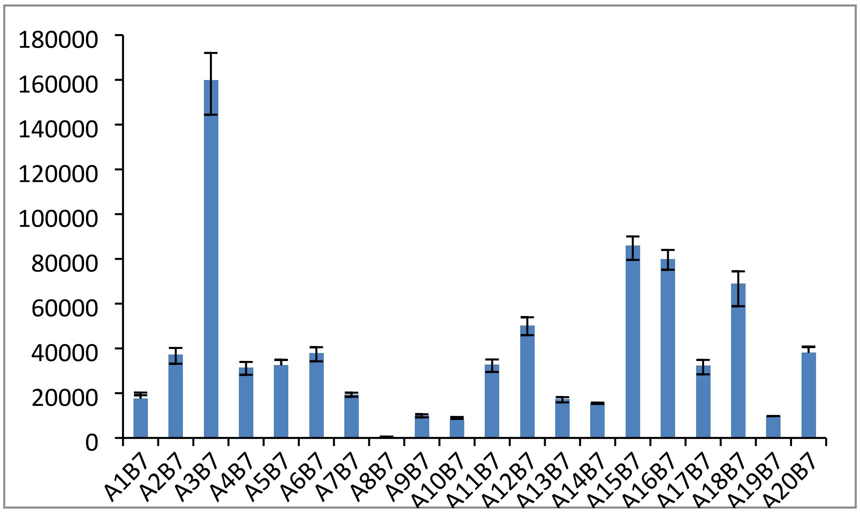


Figure S10

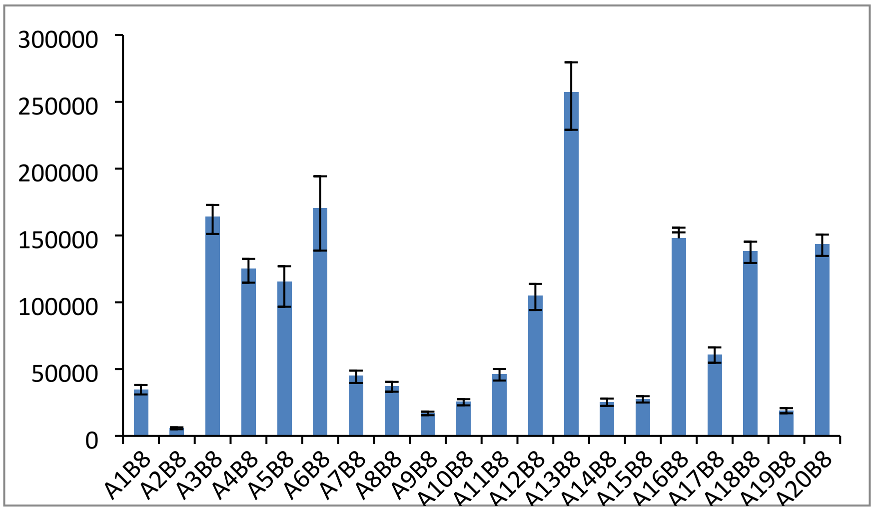


Figure S11

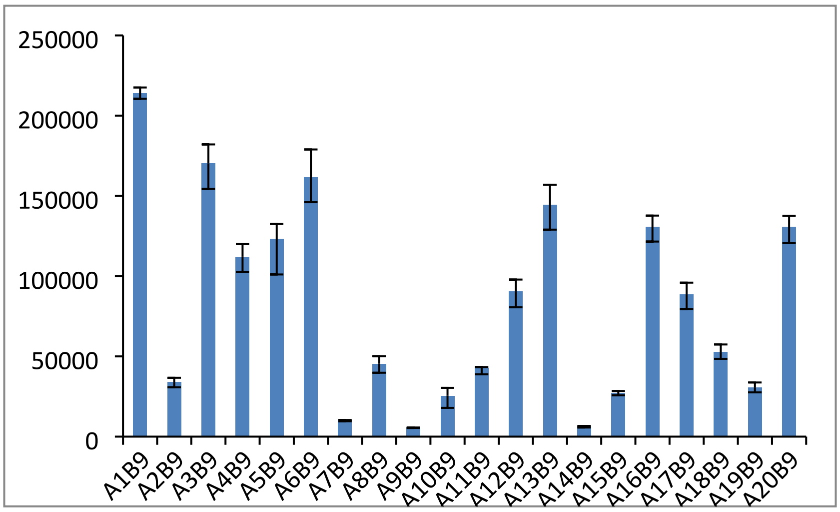


Figure S12

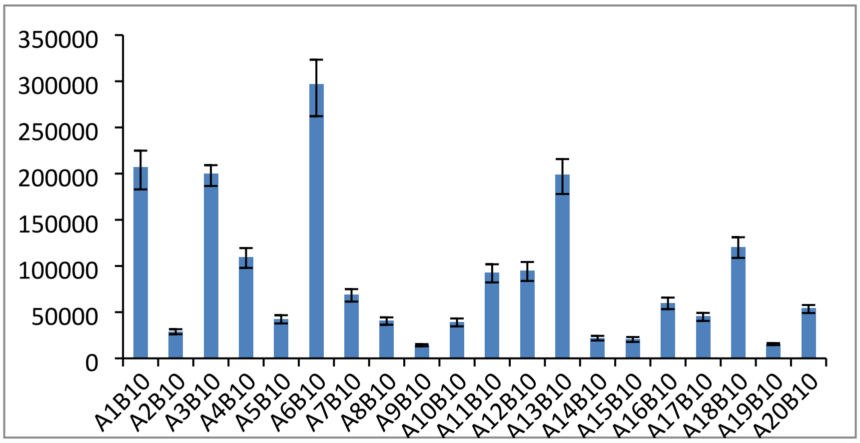


Figure S13

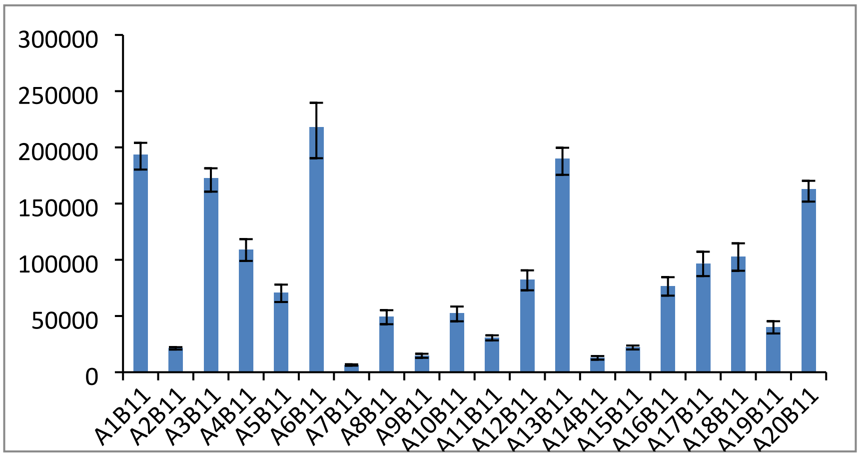


Figure S14

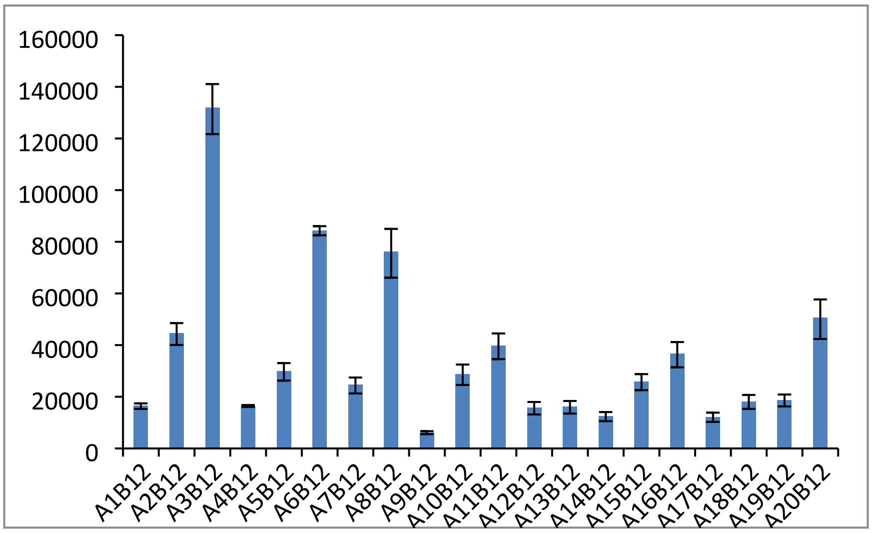


Figure S15

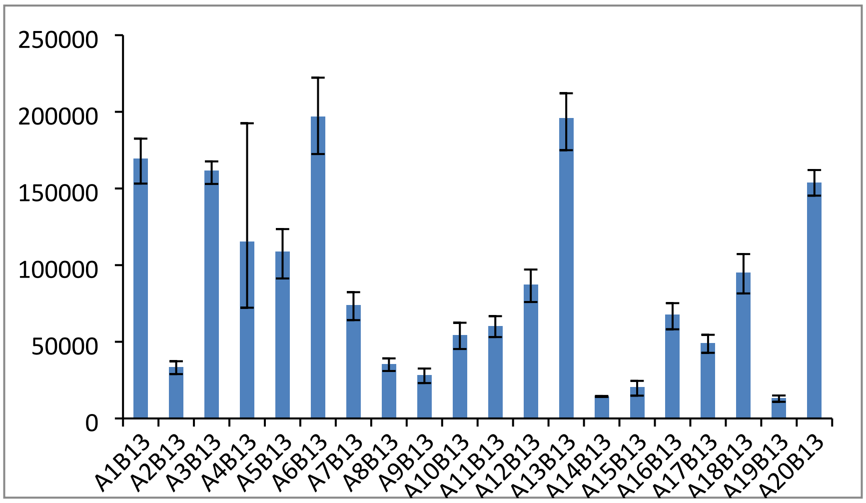


Figure S16

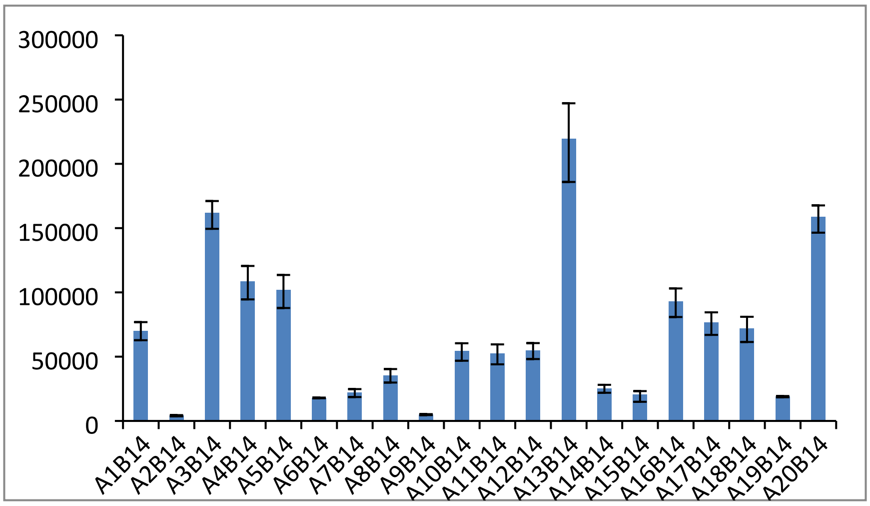


Figure S17

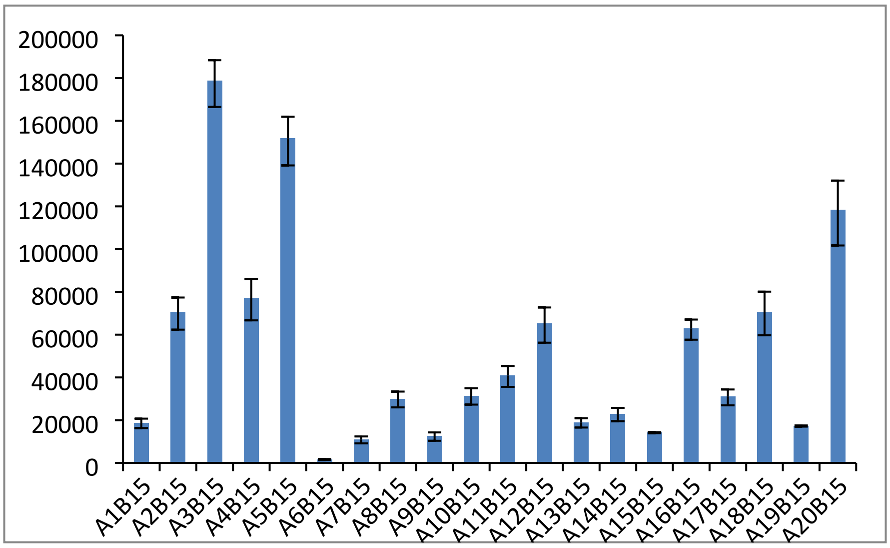


Figure S18

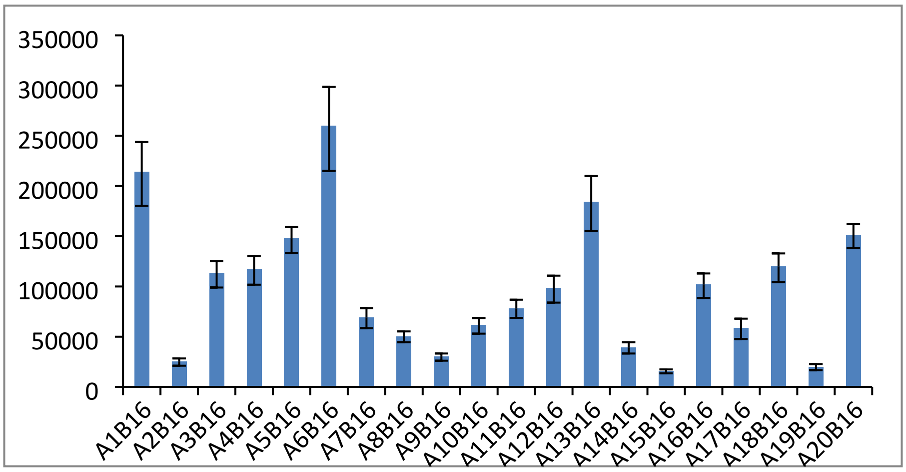


Figure S19

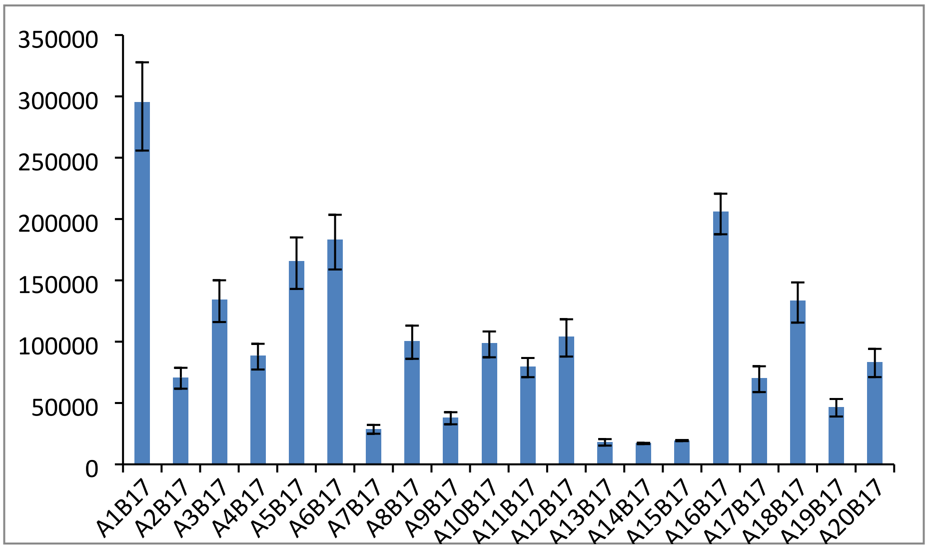


Figure S20

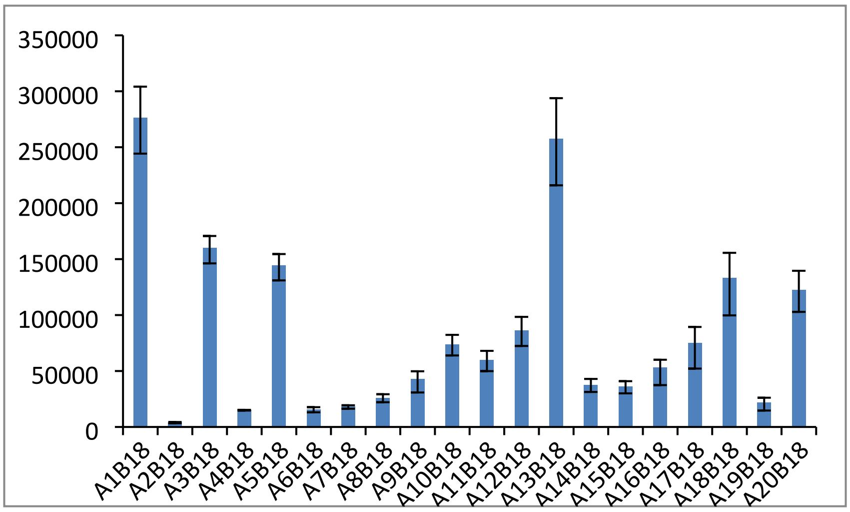


Figure S21

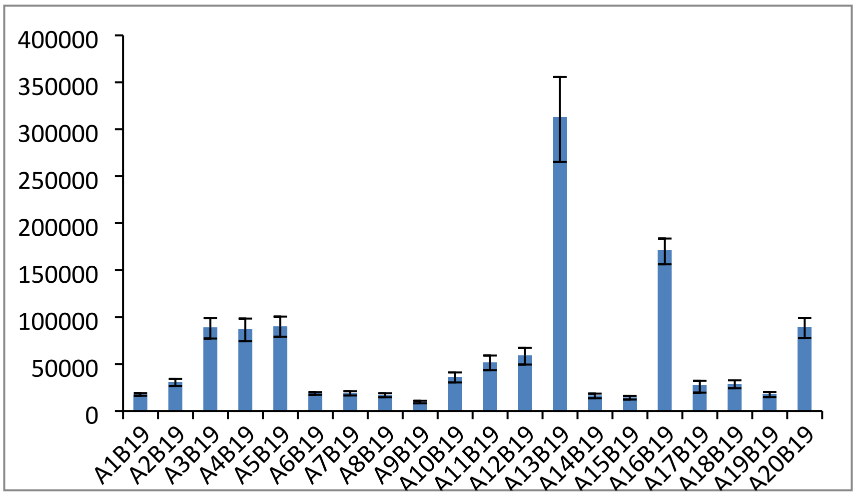


Figure S22

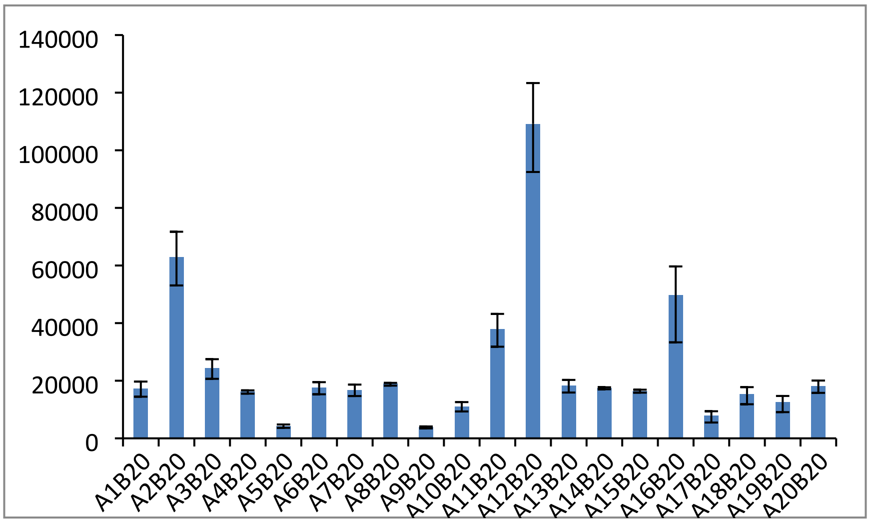
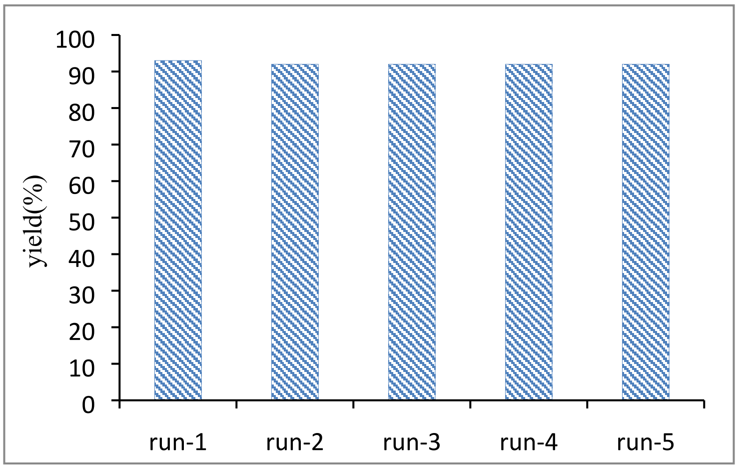
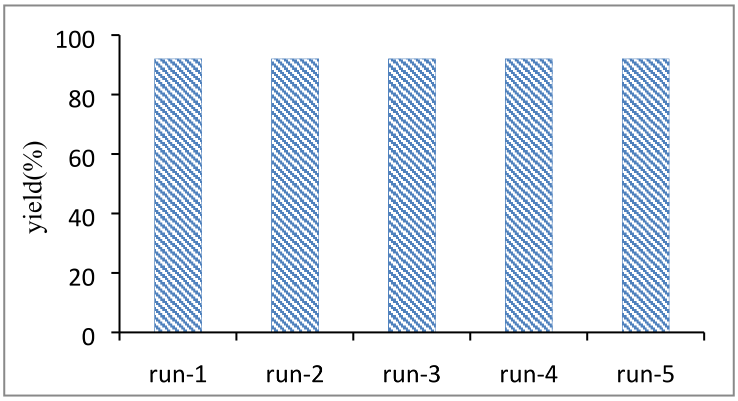


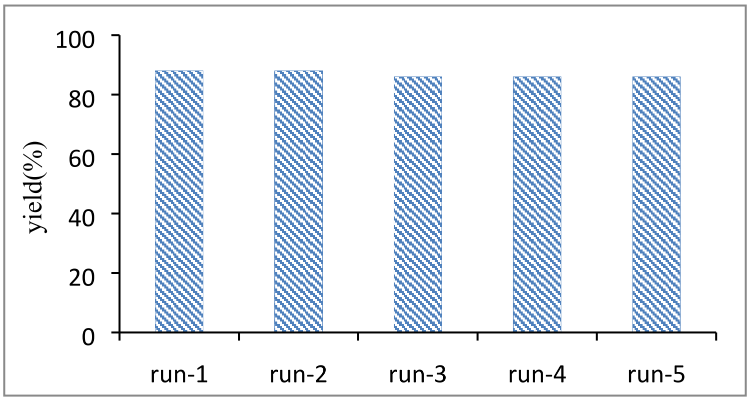
Figure S23



(A)

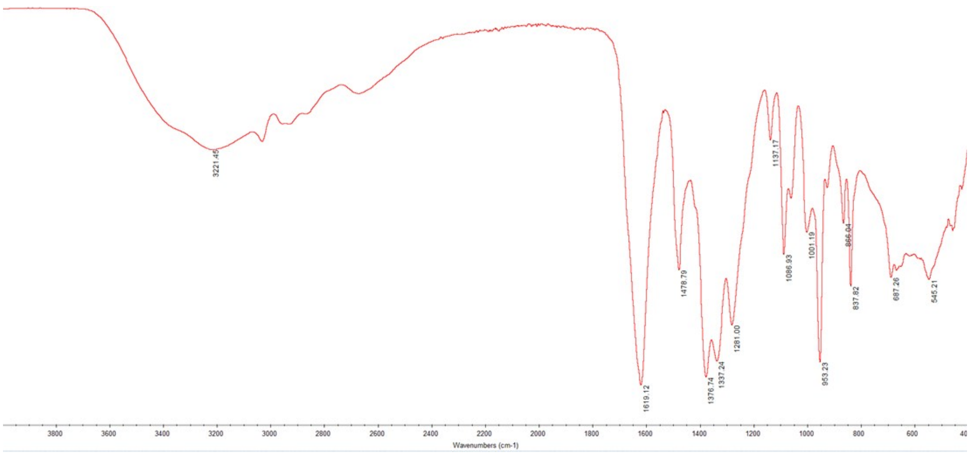


(B)

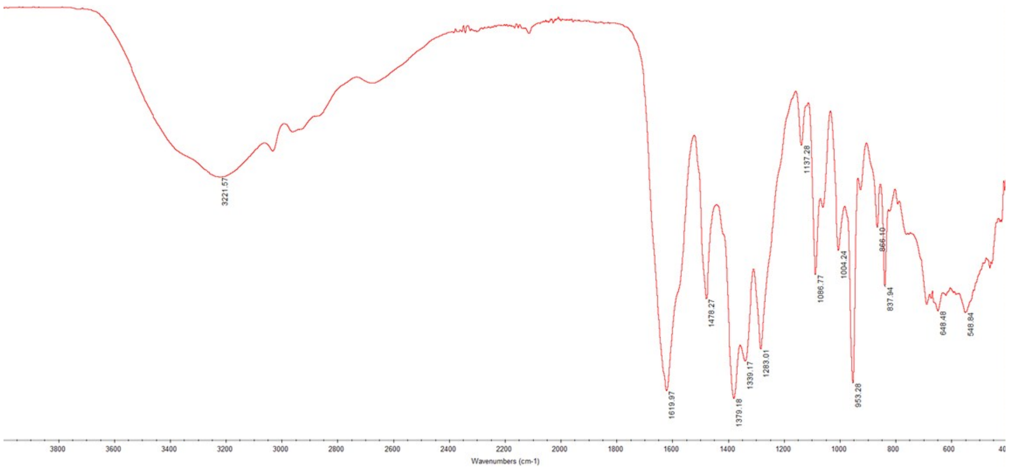


(C)

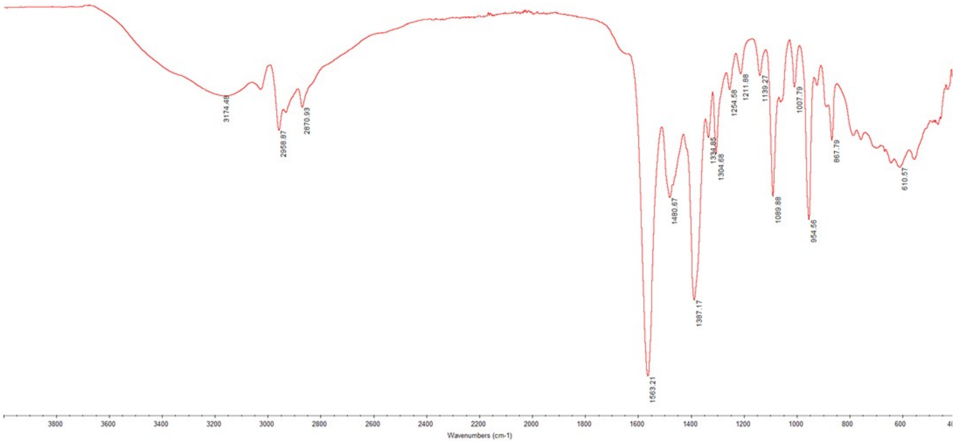
Figure S24 Reuses of ILs after recoveries. The reaction of **1d** and **2a** was taken as the model reaction for the recycle experiments. The reaction conditions are based on the typical procedure shown in Scheme 1. (A) The reuses of IL A6-B6 for five runs. (B) The reuses of IL A6-B10 for five runs. (C) The reuses of IL A13-B12 for five runs.



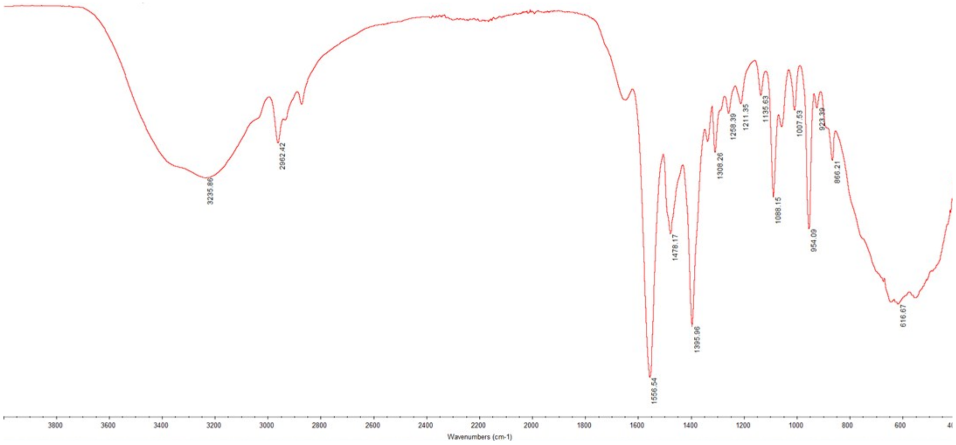
IL: A6-B6 (fresh)



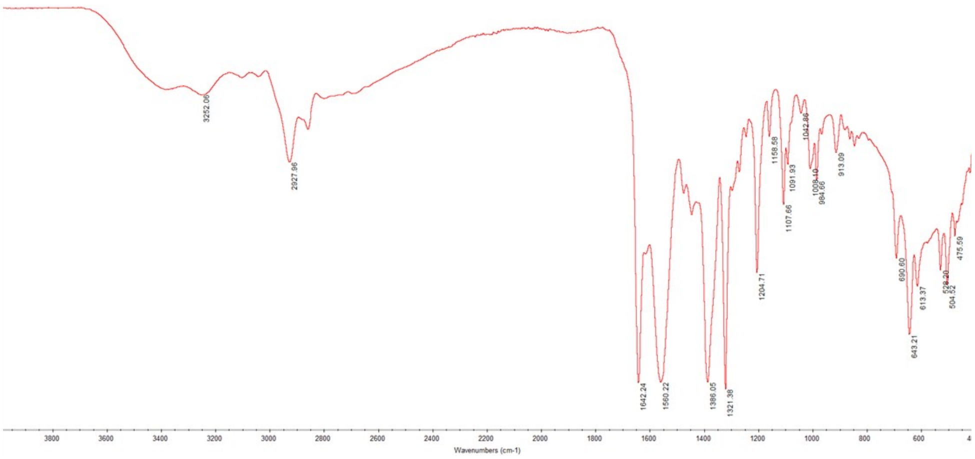
IL: A6-B6 after recycles



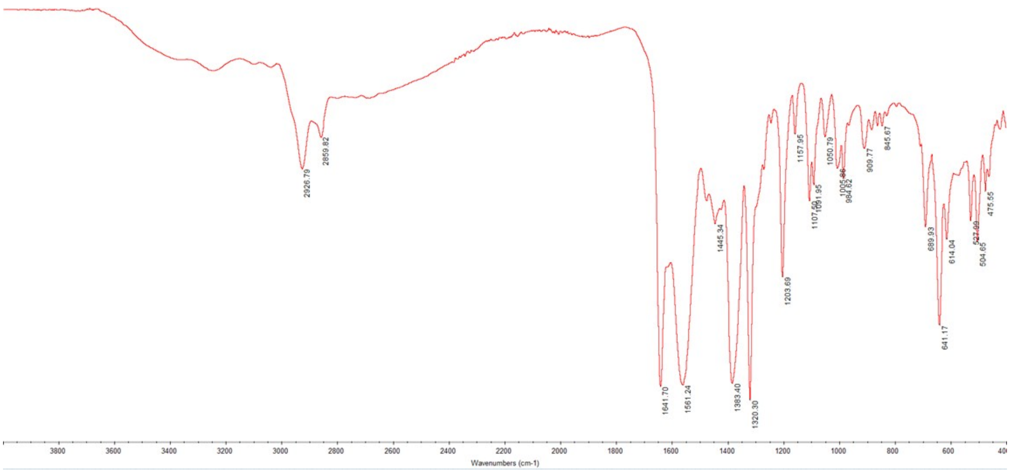
IL: A6-B10 (fresh)



IL: A6-B10 after five recycles



IL: A13-B2 (fresh)



IL: A13-B2 after five recycles

Figure S25 Comparisons of IR spectra of recovered ILs and fresh ILs

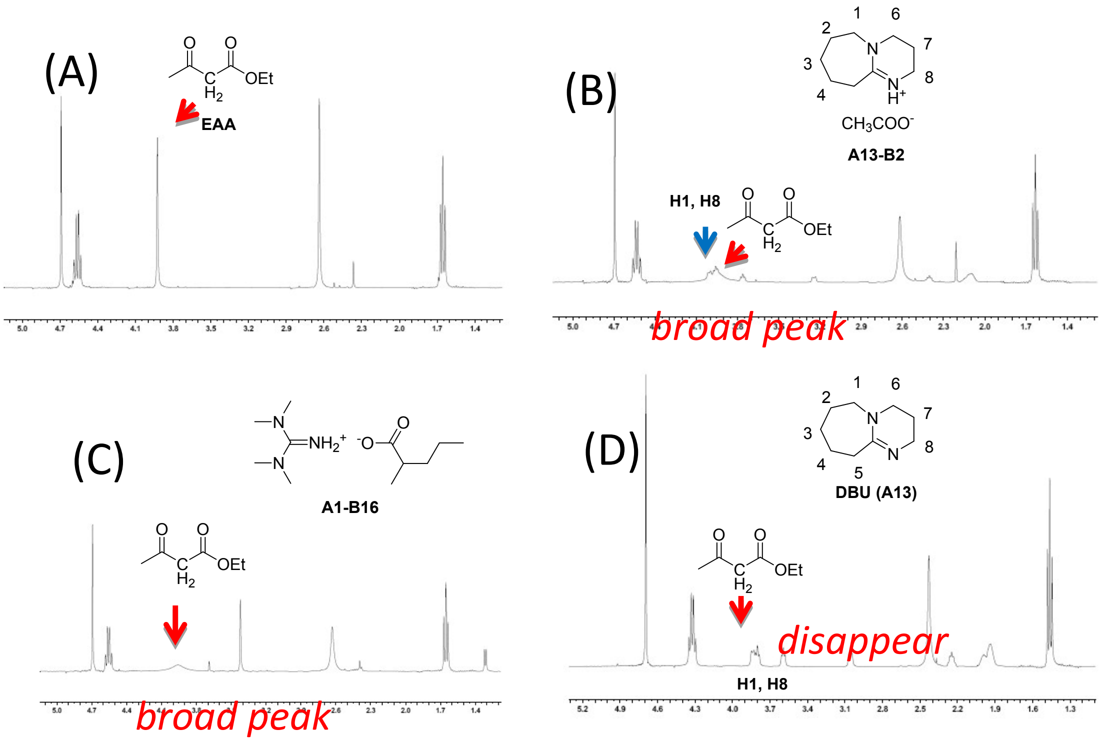
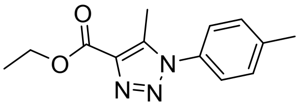


Figure S26 Investigations of H-bond formation of ILs and acetacetic ester by 1H NMR.

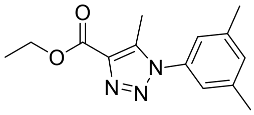
Characterization data of 3b-3w

Compound 3b:



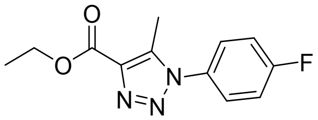
To an oven-dried round bottom flask, methylazide (26.6 mg, 0.20 mmol) was added with ethyl acetoacetate (31.2 mg, 0.24 mmol) and ionic liquid (0.2 mmol). The mixture was left for reaction at 50 °C for 2h followed by column chromatography separation to afford the product **3b** (45.2 mg, 91%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.28 (m, 4H), 4.46-4.40 (m, 2H), 2.54 (s, 3H), 2.43 (s, 3H) and 1.43-1.40 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8, 140.3, 138.8, 136.6, 132.9, 130.2, 125.1, 61.0, 21.2, 14.4 and 10.0 ppm. HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{13}H_{15}N_3NaO_2^+$: 268.1056; found: 268.1061.

Compound 3c



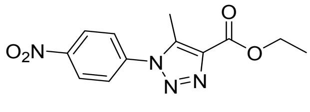
To an oven-dried round bottom flask, 1-azido-3,5-dimethylbenzene (29.4 mg, 0.2 mmol) was added with ethyl acetoacetate (31.2 mg, 0.24 mmol) and ionic liquid (0.2 mmol). The mixture was left for reaction at 50 °C for 2h followed by column chromatography separation to give the product **3c** (46.1 mg, 92%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (s, 1H), 7.03 (s, 2H), 4.47 – 4.44 (m, 2H), 2.58 (s, 3H), 2.40-2.39 (m, 6H) and 1.45-1.44 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8, 139.6, 138.8, 136.5, 135.2, 131.7, 123.0, 61.0, 21.2, 14.4 and 10.0 ppm. HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{14}H_{17}N_3NaO_2^+$: 282.1213; found: 282.1220.

Compound 3d



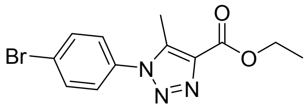
To an oven-dried round bottom flask 1-azido-4-fluorobenzene (27.4 mg，0.2 mmol) was added with ethyl acetoacetate (31.2 mg, 0.24 mmol) and ionic liquid (0.2 mmol). The mixture was left for reaction at 50 °C for 2h followed by column chromatography separation to afford the product **3d** (47.3mg, 95%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.43 (m 2H), 7.29-7.25 (m, 2H), 4.49-4.43 (m, 2H), 2.58 (s, 3H) and and 1.46-1.43 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 161.9, 161.6, 138.9, 136.7, 131.5, 127.5, 127.4, 116.9, 116.7, 61.1 14.4 and 9.9 ppm. HRMS-ESI (m/z) $[M+Na^+]$ calcd for $C_{12}H_{12}FN_3NaO_2^+$: 272.0806; found: 282.0815.

Compound 3e



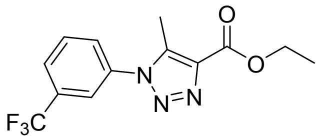
To an oven-dried round bottom flask, 1-azido-4-nitrobenzene (32.8 mg, 0.2 mmol) was added with ethyl acetoacetate (31.2 mg, 0.24 mmol) and ionic liquid (0.2 mmol). The mixture was left for reaction at 50°C for 2h followed by column chromatography separation to give the product **3e** (51.2 mg, 93%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49-8.46 (m, 2H), 7.75 (d, J = 9.0 Hz, 2H), 4.51-4.45 (m, 2H), 2.70 (s, 3H) and 1.48-1.44 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3, 148.2, 140.2, 138.8, 137.5, 125.9, 125.2, 61.4, 14.4 and 10.2 ppm. HRMS-ESI (m/z) [M+Na$^+$] calcd for $C_{21}H_{20}N_4NaO_3^+$: 299.0751; found: 299.0752.

Compound 3f



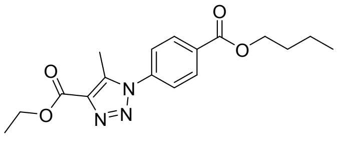
To an oven-dried round bottom flask, 1-azido-4-bromobenzene (39.6 mg, 0.2 mmol) was added with ethyl acetoacetate (31.2 mg, 0.24 mmol) and ionic liquid (0.2 mmol). The mixture was left for reaction at 50 °C for 2h followed by column chromatography separation to give the product **3f** (59.2 mg, 96%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 14.2 Hz, 2H), 7.38-7.35 (m, 2H), 4.50-4.45 (m, 2H), 2.60 (s, 3H) and 1.47-1.44 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 138.8, 136.9, 134.4, 133.0, 126.8, 124.3 61.2, 14.4 and 10.0 ppm. HRMS-ESI (m/z) [M+Na]$^+$ calcd for $C_{12}H_{12}BrN_3NaO_2^+$: 332.0005; found: 332.0008.

Compound 3g



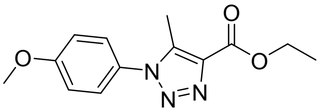
To an oven-dried round bottom flask, 1-azido-3-(trifluoromethyl) benzene (37.4 mg, 0.2 mmol) was added with ethyl acetoacetate (31.2 mg, 0.24 mmol) and ionic liquid (0.2 mmol). The mixture was left for reaction at 50 °C for 2h followed by column chromatography separation to afford the product **3g** (56.2 mg, 94%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86-7.84 (m, 1H), 7.78-7.74 (m, 2H), 7.70-7.68 (m, 1H), 4.51-4.45 (m, 2H), 2.64 (s, 3H) and 1.48-1.44 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 135.9, 132.6, 132.3, 130.5, 128.6, 126.9, 126.9, 124.5, 122.5, 122.4, 122.4, 122.4, 121.8, 61.3, 14.4 and 10.0 ppm. HRMS-ESI (m/z) [M+Na]$^+$ calcd for $C_{13}H_{12}F_3N_3NaO_2^+$: 322.0773; found: 322.0765.

Compound 3h



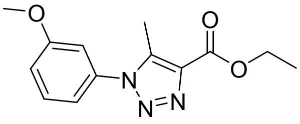
To an oven-dried round bottom flask, butyl 4-azidobenzoate (43.8 mg,0.2 mmol) was added with ethyl acetoacetate (31.2 mg, 0.24 mmol) and ionic liquid (0.2 mmol). The mixture was left for reaction at 50 °C for 2h followed by column chromatography separation to have the product **3h** (60.8 mg, 92%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25-8.23 (m, 2H), 7.58-7.56 (m, 2H), 4.48-4.43 (m, 2H), 4.38-4.35 (m, 2H), 2.63 (s, 3H), 1.79-1.75 (m, 2H), 1.51-1.45 (m, 2H), 1.44-1.42 (m, 3H) and 1.00-0.96(m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 161.6, 138.8, 137.1, 131.9, 131.0, 125.1, 65.5, 61.2, 30.7, 19.2, 14.4, 13.7 and 10.1 ppm. HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{17}H_{21}N_3NaO_4^+$: 354.1424; found: 354.1424.

Compound 3i



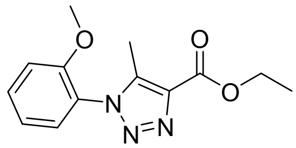
To an oven-dried round bottom flask, 1-azido-4-methoxybenzene (31.8 mg, 0.2 mmol) was added with ethyl acetoacetate (31.2 mg, 0.24 mmol) and ionic liquid (0.2 mmol). The mixture was left for reaction at 50 °C for 2h followed by column chromatography separation to have the product **3i** (50.4 mg, 97%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, $J = 9.0$ Hz, 2H), 7.04 (d, $J = 9.0$ Hz, 2H), 4.47-4.41 (m, 2H), 3.87 (s, 3H), 2.54 (s, 3H) and 1.45-1.41 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8, 160.7, 139.0, 136.5, 128.2, 126.8, 114.8, 61.0, 55.7, 14.4 and 9.9 ppm. HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{13}H_{15}N_3NaO_3^+$: 284.1006; found: 284.1010.

Compound 3j



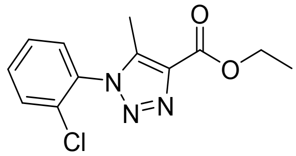
To an oven-dried round bottom flask, 1-azido-3-methoxybenzene (31.8 mg, 0.20 mmol) was added with ethyl acetoacetate (31.2 mg, 0.24 mmol) and ionic liquid (0.2 mmol). The mixture was left for reaction at 50 °C for 2h followed by column chromatography separation to afford the product **3j** (48.3 mg, 93%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.44(m, 1H), 7.08-7.06 (m, 1H), 6.99 (d, $J = 10.8$ Hz, 2H), 4.48-4.43 (m, 2H), 3.86 (s, 3H), 2.59 (s, 3H) and 1.46-1.42(m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8, 160.4, 139.1, 136.7, 136.3, 130.4, 117.4, 116.0, 111.4, 61.1, 55.6, 14.3 and 10.2 ppm. HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{13}H_{15}N_3NaO_3^+$: 284.1006; found: 284.1012.

Compound 3k



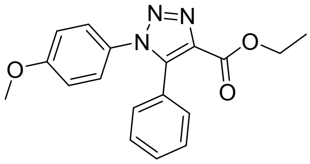
To an oven-dried round bottom flask, 1-azido-2-methoxybenzene (31.8 mg, 0.2 mmol) was added with ethyl acetoacetate (31.2 mg, 0.24 mmol) and ionic liquid (0.2 mmol). The mixture was left for reaction at 50 °C for 2h followed by column chromatography separation to give the product **3k** (48.5 mg, 94%) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (t, *J* = 8.0 Hz, 1H), 7.37-7.35 (m, 1H), 7.14-7.09 (m, 2H), 4.49-4.44 (m, 2H), 3.80 (s, 3H), 2.43 (s, 3H) and 1.47-1.43 (m, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.9, 154.0, 140.9, 136.0, 132.1, 128.5, 124.1, 121.1, 112.2, 60.9, 55.8, 14.4 and 9.4 ppm. HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{13}H_{15}N_3NaO_3^+$: 284.1006; found: 284.1015.

Compound 3l



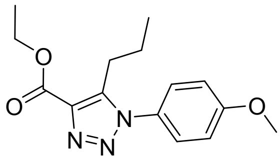
To an oven-dried round bottom flask, 1-azido-2-chlorobenzene (30.7 mg, 0.2 mmol) was added with ethyl acetoacetate (31.2 mg, 0.24 mmol) and ionic liquid (0.2 mmol). The mixture was left for reaction at 50 °C for 2h followed by column chromatography separation to give the product **3l** (48.4 mg, 91%) as a yellow liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.63-7.43 (m, 1H), 4.49-4.44 (m, 2H), 2.46 (s, 3H) and 1.47-1.43 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 140.6, 136.2, 133.0, 132.1, 131.7, 130.7, 129.2, 128.1, 77.4, 77.1, 76.8, 61.1, 14.4 and 9.4 ppm. HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{12}H_{12}ClN_3NaO_2^+$: 288.0510; found: 288.0518.

Compound 3m



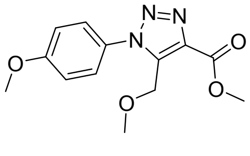
To an oven-dried round bottom flask, 1-azido-4-methoxybenzene (29.8 mg, 0.2 mmol) was added with ethyl 3-oxo-3-phenylpropanoate (46.1 mg, 0.24 mmol) and ionic liquid (0.2 mmol). The mixture was left for reaction at 50 °C for 2h followed by column chromatography separation to afford the product **3m** (58.2 mg, 90%) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3): δ 7.43 – 7.31 (m, 3H), 7.29-7.28 (m, 2H), 7.20 (d, J = 9.0 Hz, 2H), 6.87 (d, J = 9.0 Hz, 2H), 4.41-4.35(m, 2H), 3.82 (s, 3H) and 1.35-1.32 (m, 3H) ppm. ^{13}C NMR (100 MHz, CDCl3) δ 161.1, 160.1, 140.9, 136.8, 130.3, 129.8, 128.7, 128.3, 126.6, 125.9, 125.9, 114.4, 61.2, 55.5 and 14.2 ppm. HRMS-ESI (m/z) [M+Na]$^+$ calcd for $C_{18}H_{17}N_3NaO_3^+$: 346.1162; found: 346.1170.

Compound 3n



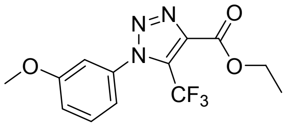
To an oven-dried round bottom flask, 1-azido-4-methoxybenzene (29.8 mg, 0.2 mmol) was added with ethyl 3-oxohexanoate (37.9 mg, 0.24 mmol) and ionic liquid (0.2 mmol). The mixture was left for reaction at 50 for 2h followed by column chromatography separation to afford the product **3n** (51.0 mg, 88%) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3): δ 7.33-7.31 (m, 2H), 7.06-7.04 (m, 2H), 4.49-4.43 (m, 2H), 3.89 (s, 3H), 2.93-2.89 (m, 2H), 1.59 – 1.50 (m, 2H), 1.47-1.43 (m, 3H) and 0.88-0.84 (m, 3H) ppm. ^{13}C NMR (100 MHz, CDCl3): δ 161.7, 160.8, 143.5, 136.2, 128.3, 127.2, 114.7, 61.0, 55.7, 25.2, 22.2, 14.4 and 13.8 ppm. HRMS-ESI (m/z) [M+H]$^+$ calcd for $C_{15}H_{20}N_3O_3^+$: 290.1499; found: 290.1497.

Compound 3o



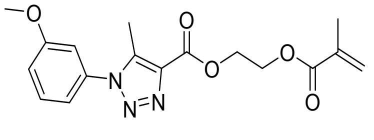
To an oven-dried round bottom flask, 1-azido-4-methoxybenzene (29.8 mg, 0.2 mmol) was added with methyl 4-methoxy-3-oxobutanoate (35.1 mg, 0.24 mmol) and ionic liquid (0.2 mmol). The mixture was left for reaction at 50 °C for 2h followed by column chromatography separation to give afforded the product **3o** (50.4 mg, 91%) as a white solid. ^{1}H NMR (400 MHz, CDCl3): δ 7.60-7.57 (m, 2H), 7.07-7.04 (m, 2H), 4.73 (s, 2H), 4.02 (s, 3H), 3.89 (s, 3H) and 3.42 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8, 160.8, 137.9, 137.5, 128.4, 126.4, 114.6, 60.6, 58.5, 55.7 and 52. 3 ppm. HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{13}H_{15}N_3NaO_4^+$: 300.0954; found: 3600.0950.

Compound 3p



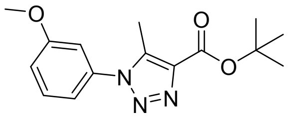
To an oven-dried round bottom flask, 1-azido-3-methoxybenzene (29.8 mg,0.2 mmol) was added with ethyl 4,4,4-trifluoro-3-oxobutanoate (44.1 mg, 0.24 mmol) and ionic liquid (0.2 mmol). The mixture was left for reaction at 50 °C for 2h followed by column chromatography separation to have the product **3p** (58.9mg, 94%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.45 (m, 1H), 7.15 (d, *J* = 6.0 Hz, 1H), 7.06-7.04 (m, 1H), 7.00 (d, *J* = 4.4 Hz, 1H), 4.53-4.48 (m, 2H), 3.87 (s, 3H), 1.47-1.43 (m, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 160.2, 159.1, 139.4, 136.4, 130.4, 119.6, 118.0, 117.2, 111.5, 62.4, 55.7, 14.1 ppm. HRMS for $C_{13}H_{12}F_3N_3NaO_3^+$ $[M+Na]^+$: 338.0722, found: 338.0719.

Compound 3q



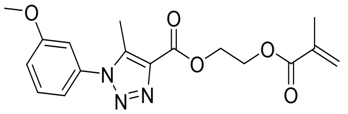
To an oven-dried round bottom flask, 1-azido-3-methoxybenzene (29.8 mg, 0.2 mmol) was added with 2-(methacryloyloxy)ethyl 3-oxobutanoate (51.4 mg, 0.24 mmol) and ionic liquid (0.2 mmol). The mixture was left for reaction at 50 °C for 2h followed by column chromatography separation to give the product **3q** (60.3mg, 87%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.45 (m, 1H), 7.09 (d, *J* = 9.4 Hz, 1H), 7.01-7.00 (m, 2H), 6.15 (s, 1H),5.59 (m, 1H), 4.68-4.65 (m, 2H), 4.54-4.51 (m, 2H), 3.87 (s, 3H), 2.59 (s, 3H) and 1.95 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.1, 161.4, 160.5, 139.1, 136.3, 135.9, 130.5, 126.3, 117.4, 116.0, 111.4, 62.4, 55.6, 18.3 and 10.2 ppm. HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{17}H_{19}N_3NaO_5^+$: 368.1216; found: 368.1214.

Compound 3r



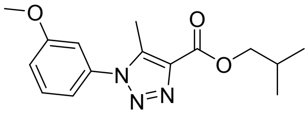
To an oven-dried round bottom flask, 1-azido-3-methoxybenzene (29.8 mg,0.2 mmol) was added with tert-butyl 3-oxobutanoate (37.9 mg, 0.24 mmol) and ionic liquid (0.2 mmol). The mixture was left for reaction at 50 °C for 2h followed by column chromatography separation to afford the product **3r** (52.6 mg, 91%) as a white solid. ^{1}H NMR (400 MHz, CDCl3): δ 7.47-7.43 (m, 1H), 7.08-7.06 (m, 1H), 6.99-6.97 (m, 2H), 3.86 (s, 3H), 2.56 (s, 3H) and 1.64 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 160.4, 138.2, 137.8, 136.5, 130.4, 117.4, 1115.7, 111.3, 82.1, 55.6, 28.3 and 10.2 ppm. HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{15}H_{19}N_3NaO_3^+$: 312.1318; found: 312.1307.

Compound 3s



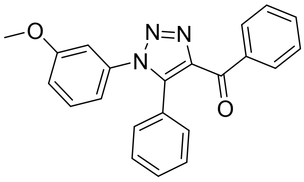
To an oven-dried round bottom flask, 1-azido-3-methoxybenzene (29.8 mg, 0.2 mmol) was added with 2-(methacryloyloxy)ethyl 3-oxobutanoate (51.4 mg, 0.24 mmol) and ionic liquid (0.2 mmol). The mixture was left for reaction at 50 °C for 2h followed by column chromatography separation to have the product **3s** (60.5 mg, 87%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (t, $J = 8.2$ Hz, 1H), 7.09 (d, $J = 9.4$ Hz, 1H), 7.02-7.00 (m, 2H), 6.11-6.03 (m, 1H), 5.47-5.43 (m, 1H), 5.33-5.30 (m, 1H), 4.91-4.90 (m, 2H), 3.87 (s, 3H) and 2.60 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.4, 160.4, 139.1, 136.5, 136.3, 131.9, 130.4, 119.0, 117.3, 115.9, 111.2, 65.6, 55.8 and 10.1 ppm. HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{17}H_{19}N_3NaO_5^+$: 368.1216; found: 368.1214.

Compound 3t



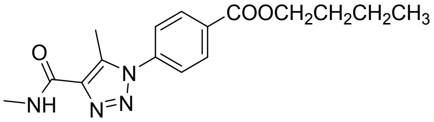
To an oven-dried round bottom flask, 1-azido-3-methoxybenzene (29.8 mg, 0.2 mmol) was added with isobutyl 3-oxobutanoate (37.9 mg, 0.24 mmol) and ionic liquid (0.2 mmol). The mixture was left for reaction at 50 °C for 2h followed by column chromatography separation to have the product **3t** (51.5 mg, 89%) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3): δ 7.48-7.44 (m, 1H), 7.08-7.06 (m, 1H), 7.01-6.99 (m, 2H), 4.18 (d, J = 6.8 Hz, 2H), 3.86 (s, 3H), 2.59 (s, 3H), 2.19-2.09 (m, 1H) and 1.04-1.02 (m, 6H) ppm. ^{13}C NMR (100 MHz, CDCl3) δ 161.8, 160.4, 138.7, 136.8, 136.4, 130.4, 117.4, 115.8, 111.2, 71.1, 55.7, 27.8, 19.2 and 10.1 ppm. HRMS-ESI (m/z) [M+H$^+$] calcd for $C_{15}H_{19}N_3NaO_3^+$ [M+Na]$^+$: 312.1318; found: 312.1310.

Compound 3u



To an oven-dried round bottom flask, 1-azido-3-methoxybenzene (29.8 mg, 0.2 mmol) was added with 1,3-diphenylpropane-1,3-dione (53.8 mg, 0.24 mmol) and ionic liquid (0.2 mmol). The mixture was left for reaction at 50 °C for 2h followed by column chromatography separation to give the product **3u** (67.1 mg, 95%) as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.31-8.29 (m, 2H), 7.63-7.59 (m, 1H), 7.59-7.43 (m, 2H), 7.43-7.38 (m, 5H), 7.29-7.27 (m, 1H), 6.97-6.95(m, 1H), 6.90-6.88 (m, 2H) and 3.71 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 186.7, 160.1, 143.6, 141.2, 137.2, 136.8, 133.2, 130.7, 130.2, 130.1, 129.9, 128.6, 128.3, 126.2, 117.4, 115.6, 110.7 and 55.5 ppm. HRMS-ESI (m/z) [M+H$^+$] calcd for $C_{22}H_{17}N_3NaO_2^+$ [M+Na]$^+$: 378.1213; found: 378.1219.

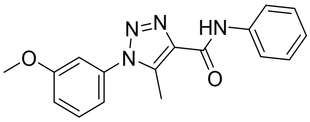
Compound 3v



To an oven-dried round bottom flask, butyl 4-azidobenzoate (37.4 mg, 0.2 mmol) was added with 3-oxo-3-phenylpropanenitrile (34.8 mg, 0.24 mmol) and ionic liquid (0.2

mmol). The mixture was left for reaction at 50 °C for 2h followed by column chromatography separation to have the product **3v** (56.9 mg, 90%) as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.26-8.24 (m, 2H), 7.59-7.56 (m, 2H), 4.40-4.37 (m, 2H), 3.04 (d, *J* = 5.0 Hz, 3H), 2.68 (s, 3H), 1.81-1.77 (m, 2H), 1.53-1.47 (m, 2H) and 1.02-1.98(m, 3H) ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ 165.3, 161.8, 139.0, 139.0, 136.4, 131.9, 131.0, 124.9, 65.5, 30.7, 25.7, 19.3, 13.8 and 9.9 ppm. HRMS-ESI (m/z) [M+Na]$^+$ calcd for $C_{16}H_{20}N_4NaO_3^+$: 339.1427; found: 339.1425.

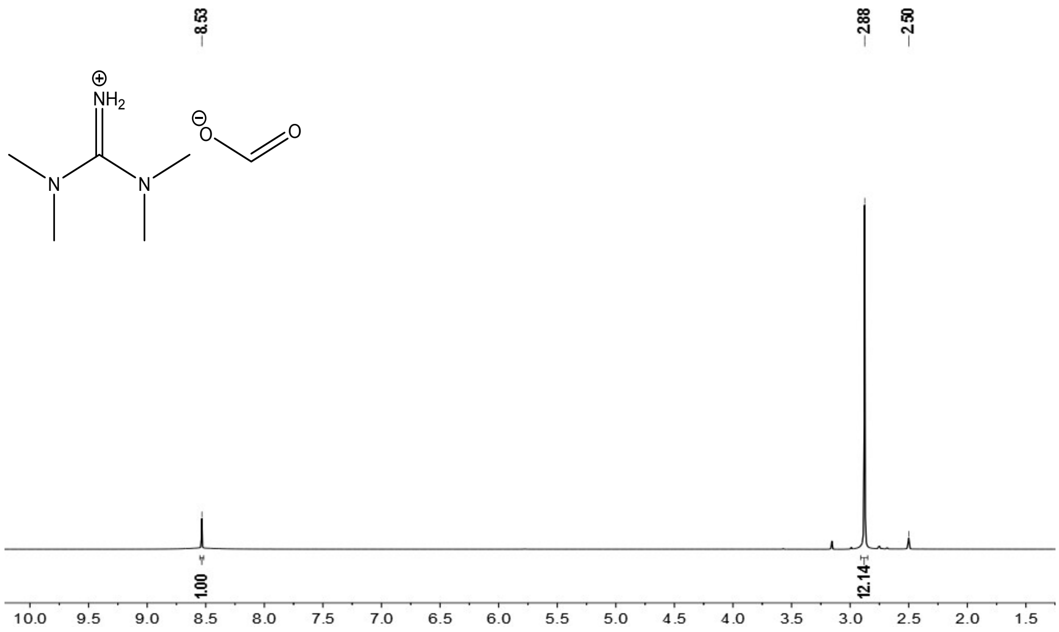
Compound 3w



To an oven-dried round bottom flask, 1-azido-3-methoxybenzene (29.8 mg,0.2 mmol) was added with 3-oxo-N-phenylbutanamide (35.4 mg, 0.24 mmol) and ionic liquid (0.2mmol). The mixture was left for reaction at 50 °C for 2h followed by column chromatography separation to afford the product **3w** (55.6mg, 90%) as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.11 (s, 1H), 7.73 (d, *J* = 7.7 Hz, 2H), 7.49 (t, *J* = 8.1 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 2H), 3.88 (s, 3H) and 2.70 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$): δ 160.4, 159.2, 138.6, 137.7, 137.5, 136.4, 130.5, 129.1, 124.4, 119.8, 117.4, 115.9, 111.2, 55.8 and 9.9 ppm. HRMS-ESI (m/z) [M+Na]$^+$ calcd for $C_{17}H_{16}N_4NaO_2^+$: 331.1165; found: 331.1173.

Copies of ^{1}H NMR of ILs A1B1-A1B20, A6B1-A6B20 and A13B1-A13B20

A1-B1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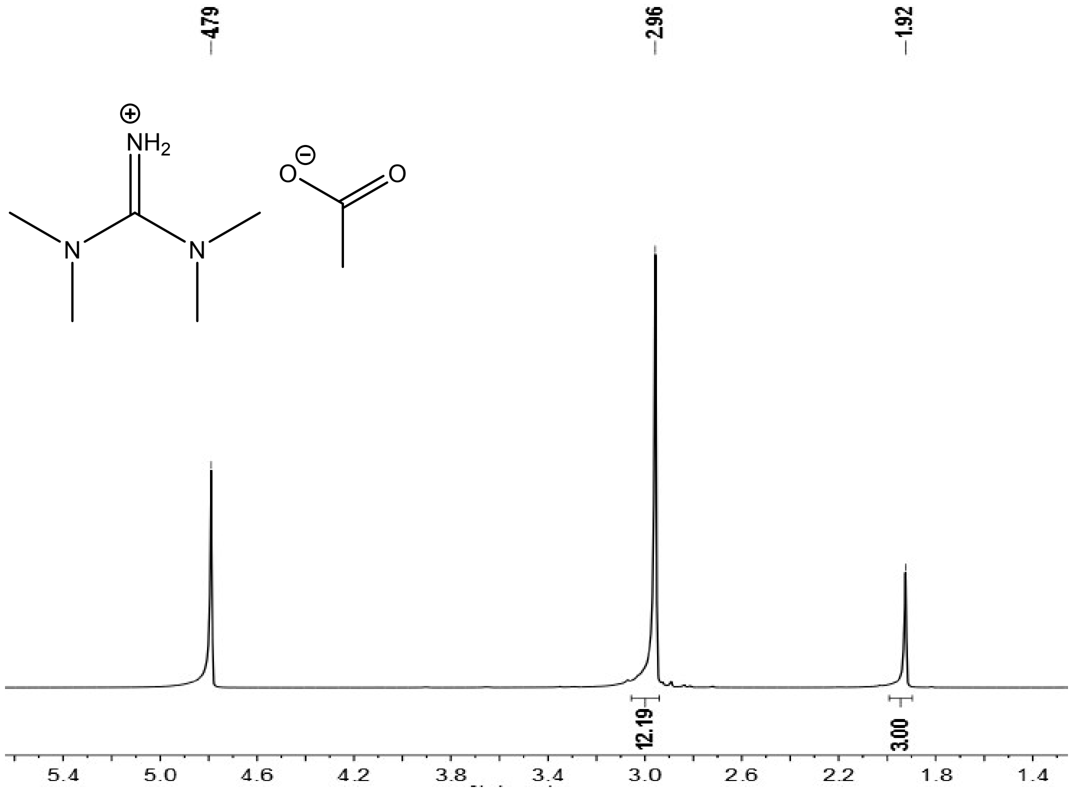
1.5

A1-B2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3.4
3.0
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2.2
1.8
1.4

A1-B3

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2.17
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1.05
1.04
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3.01
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6.5
6.0
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1.5
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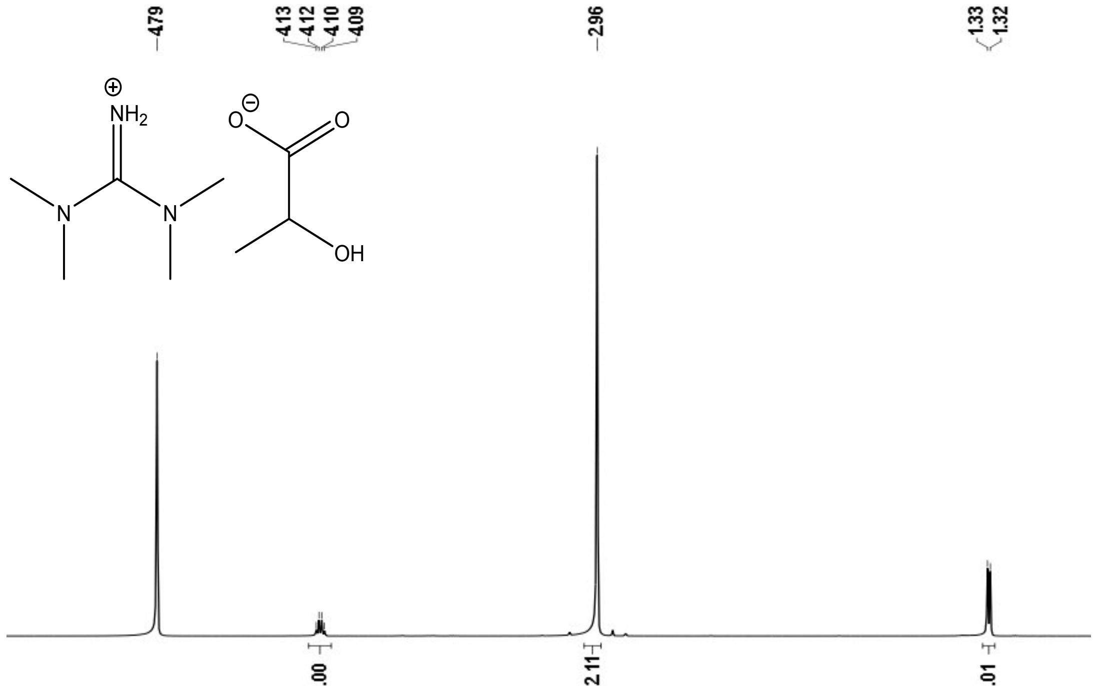
0.5

A1-B4



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3.01
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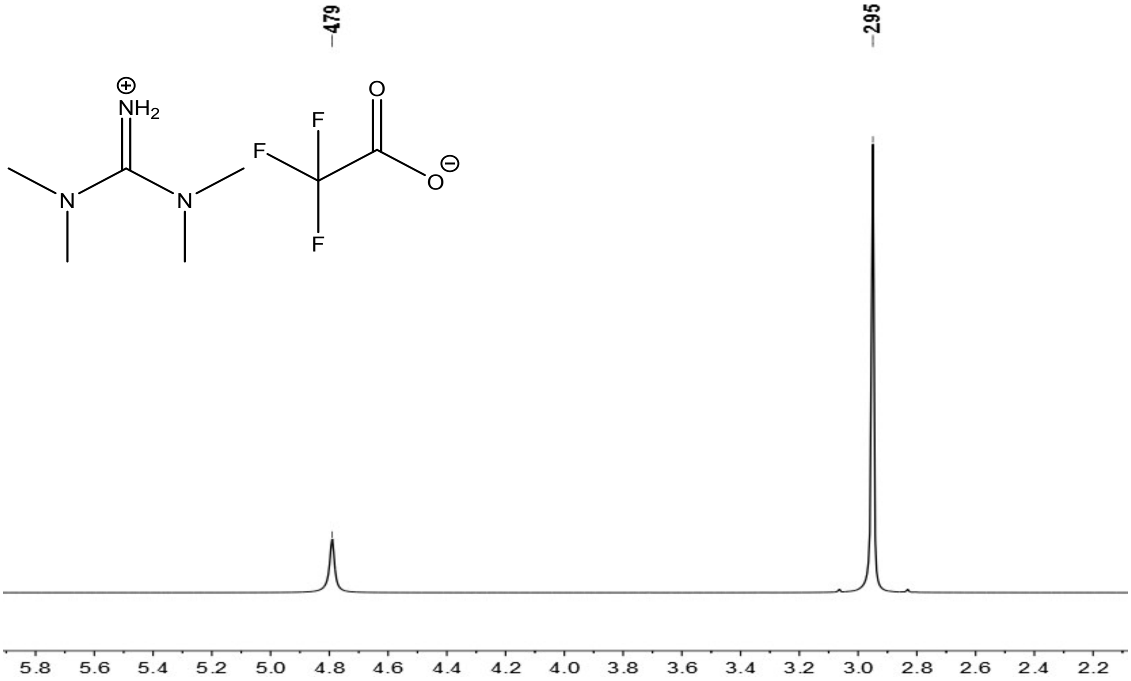
2.4
2.0
1.6
1.2

A1-B5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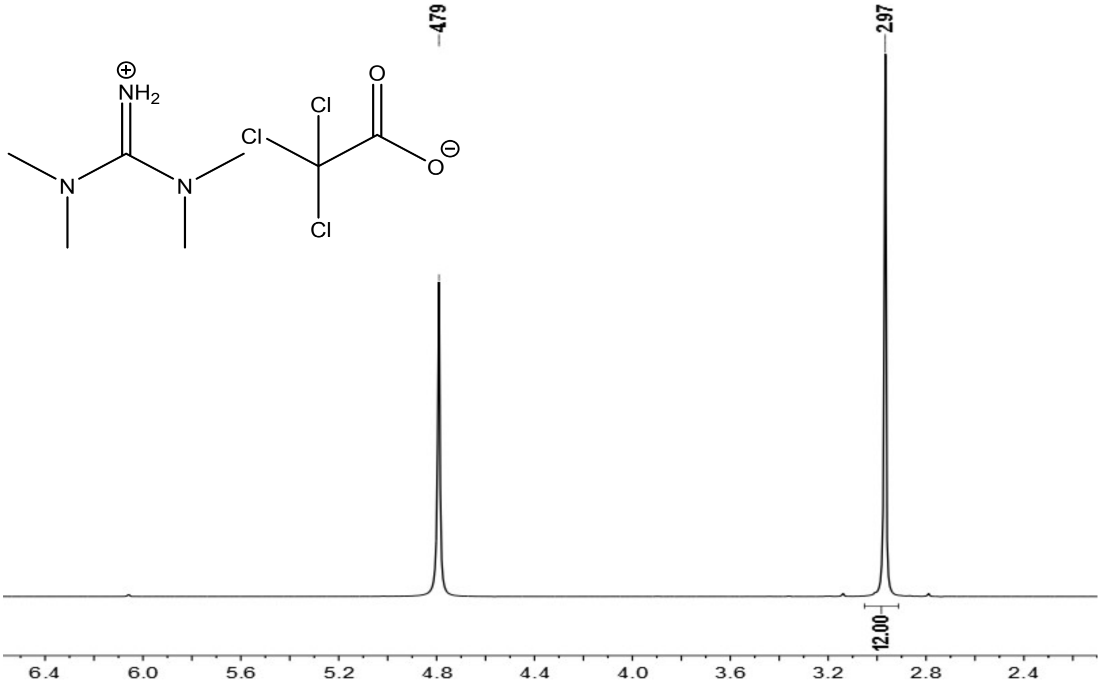
2.6
2.4
2.2

A1-B6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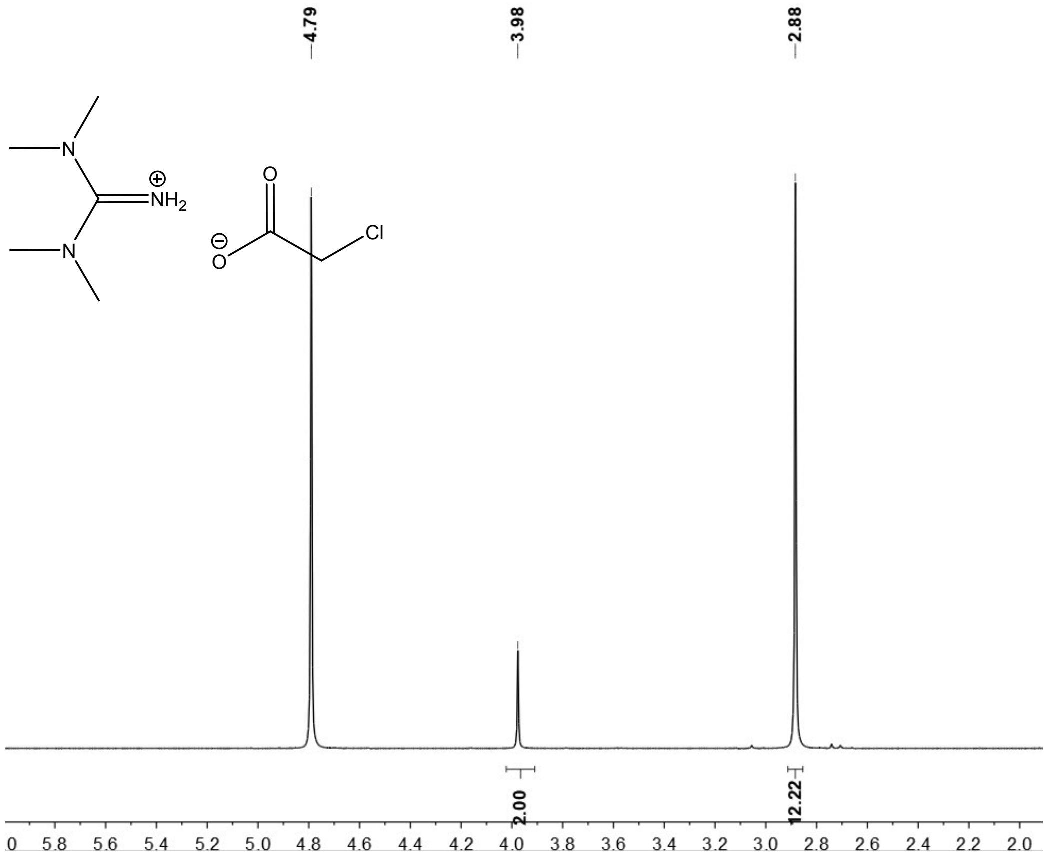
2.8
2.4

A1-B7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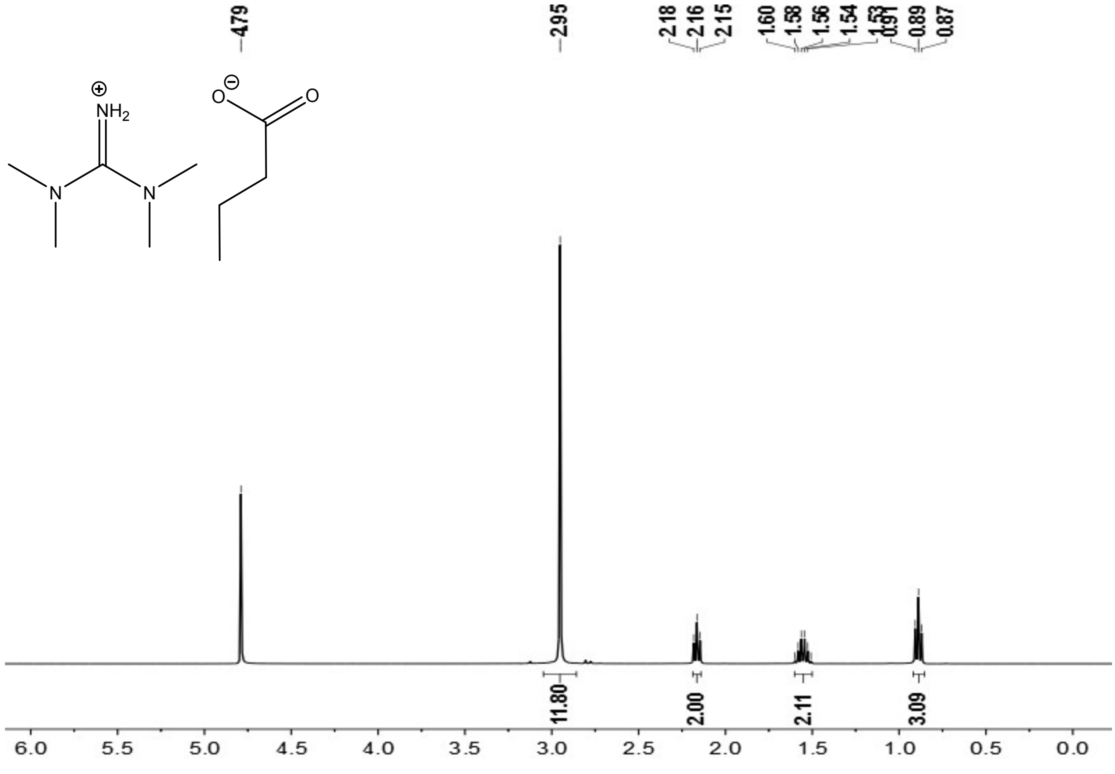
A1-B8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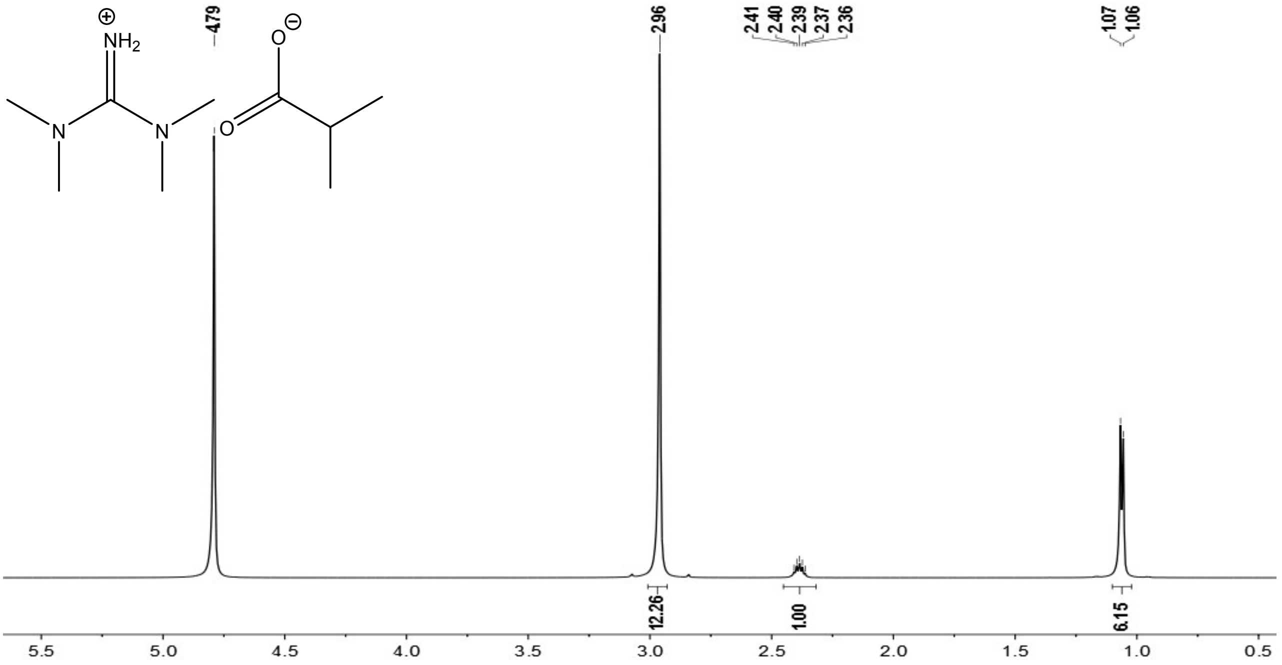
A1-B9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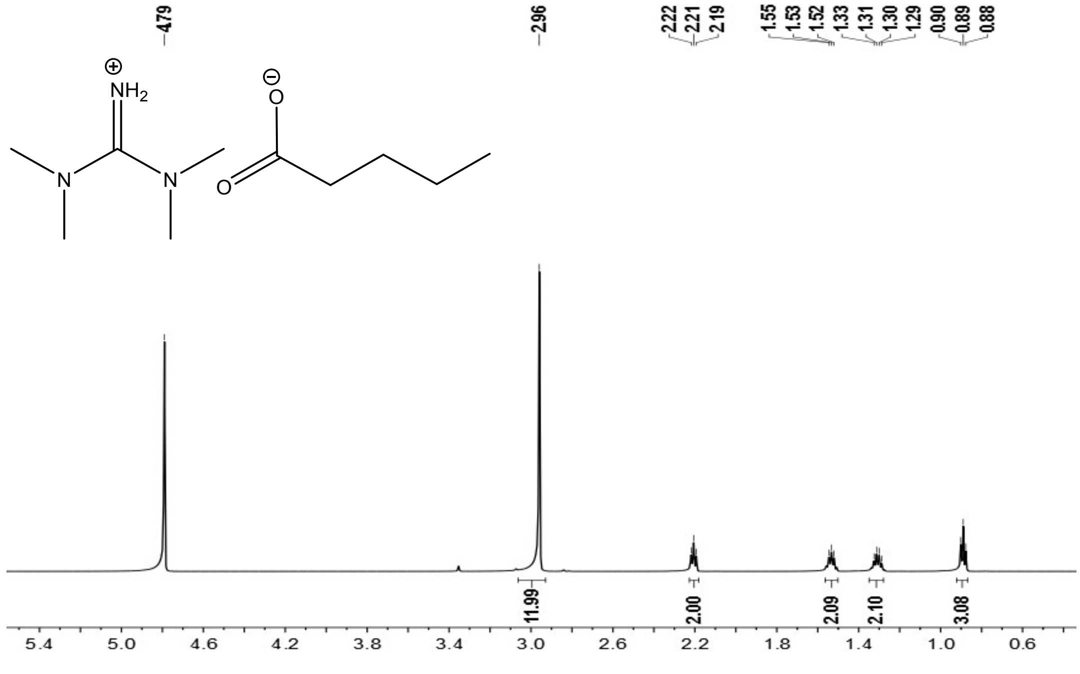
A1-B10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2.09
2.10
3.08
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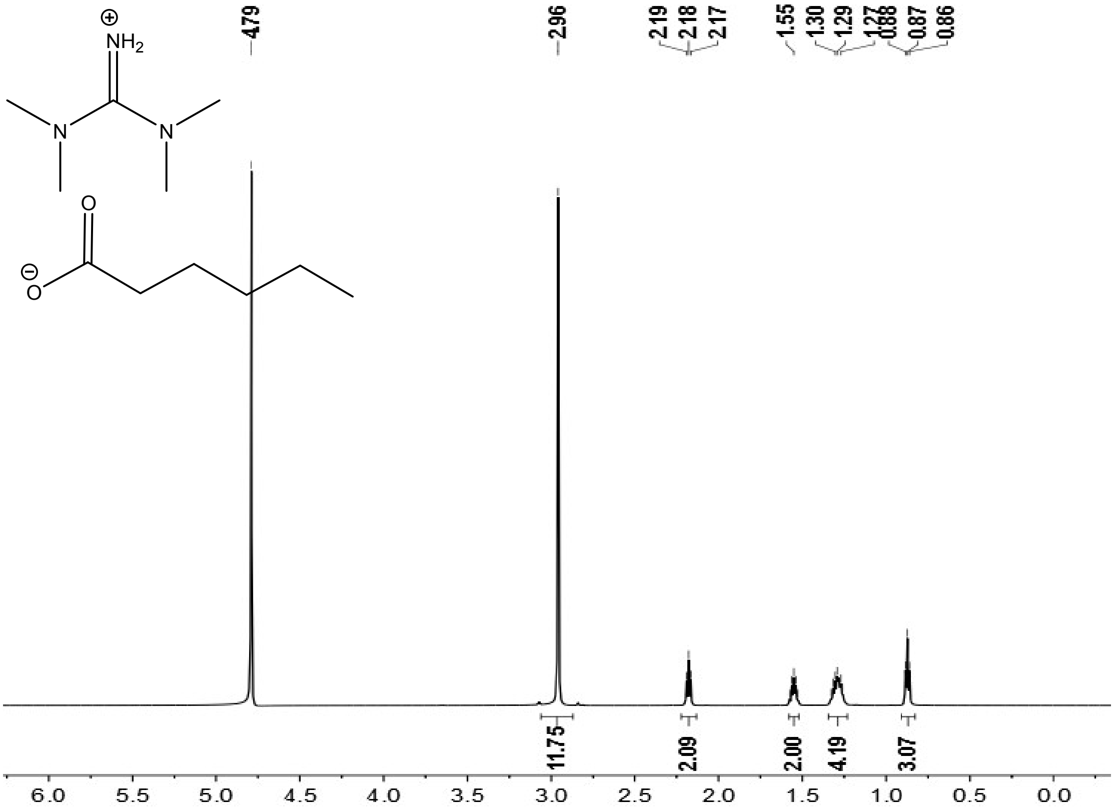
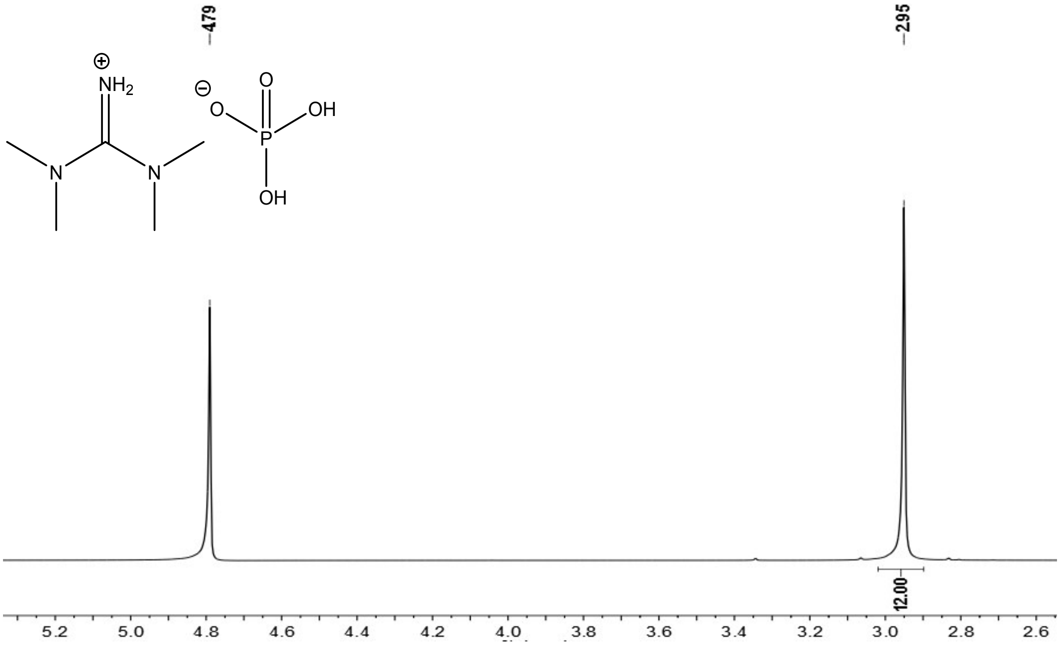
O

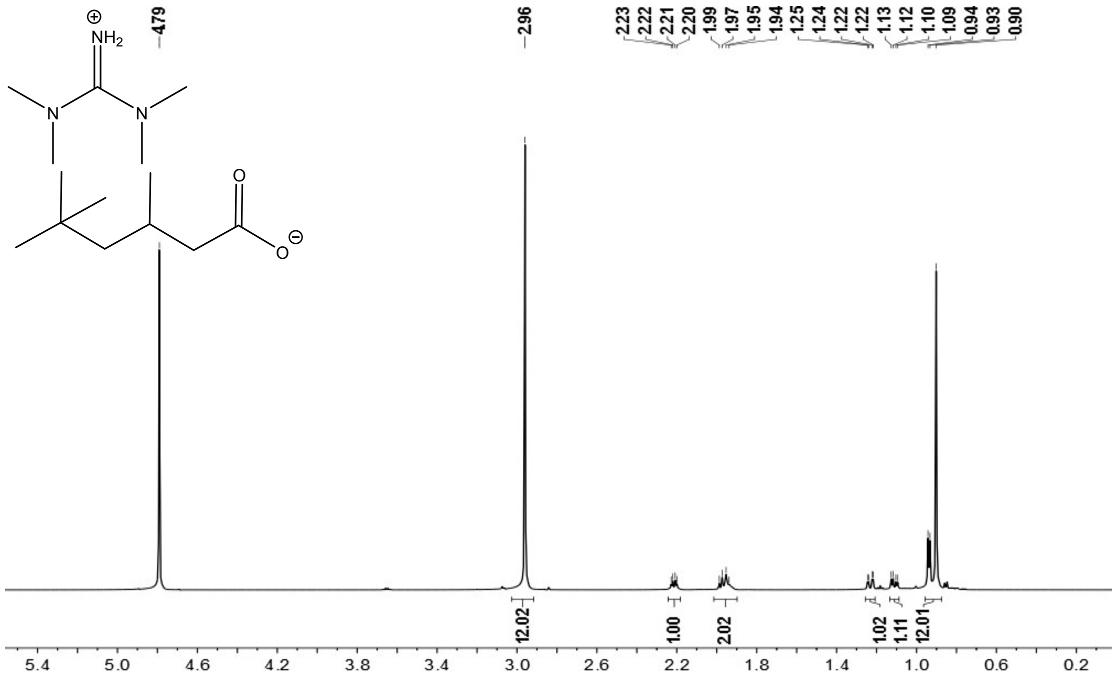
A1-B11



A1-B12



A1-B13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1.22
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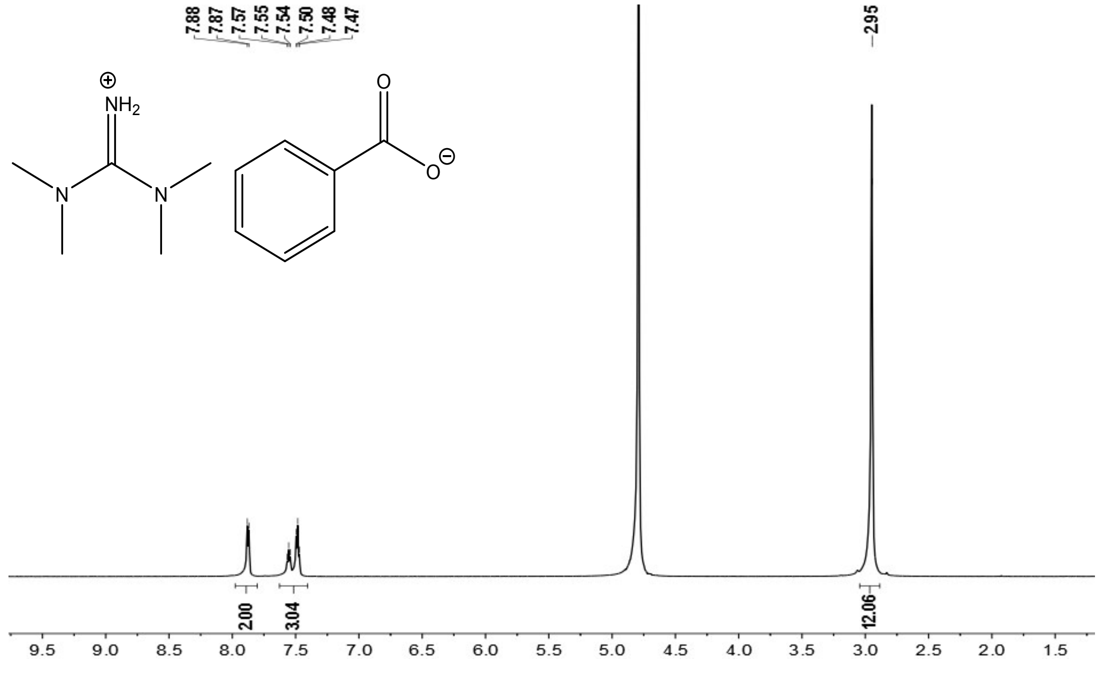
A1-B14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A1-B15


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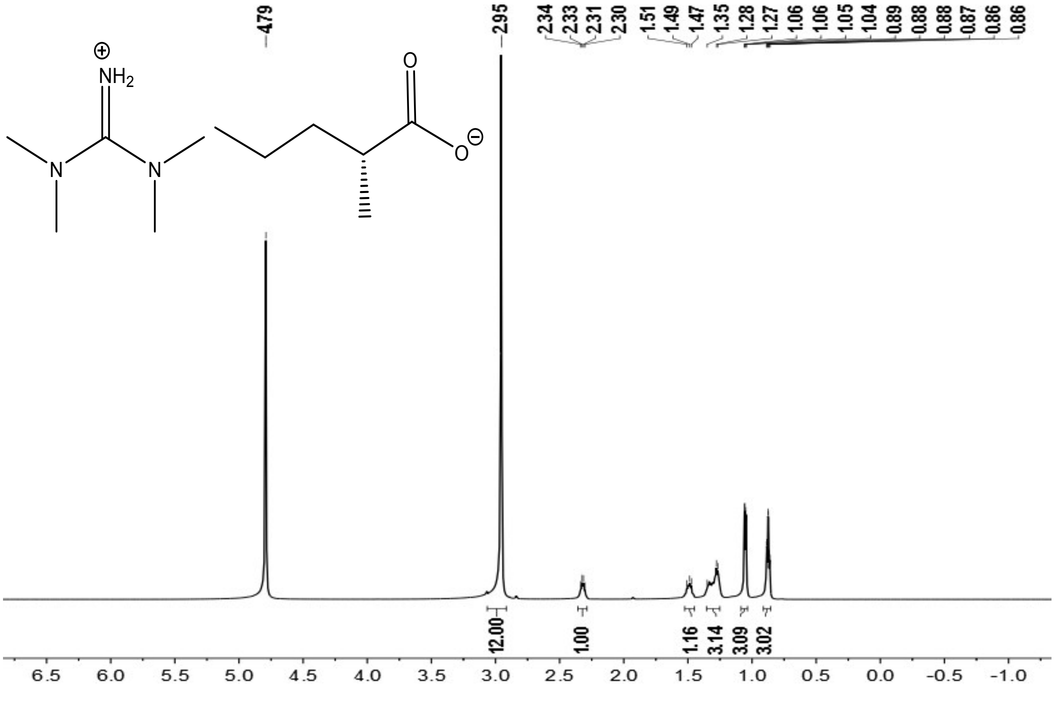
A1-B16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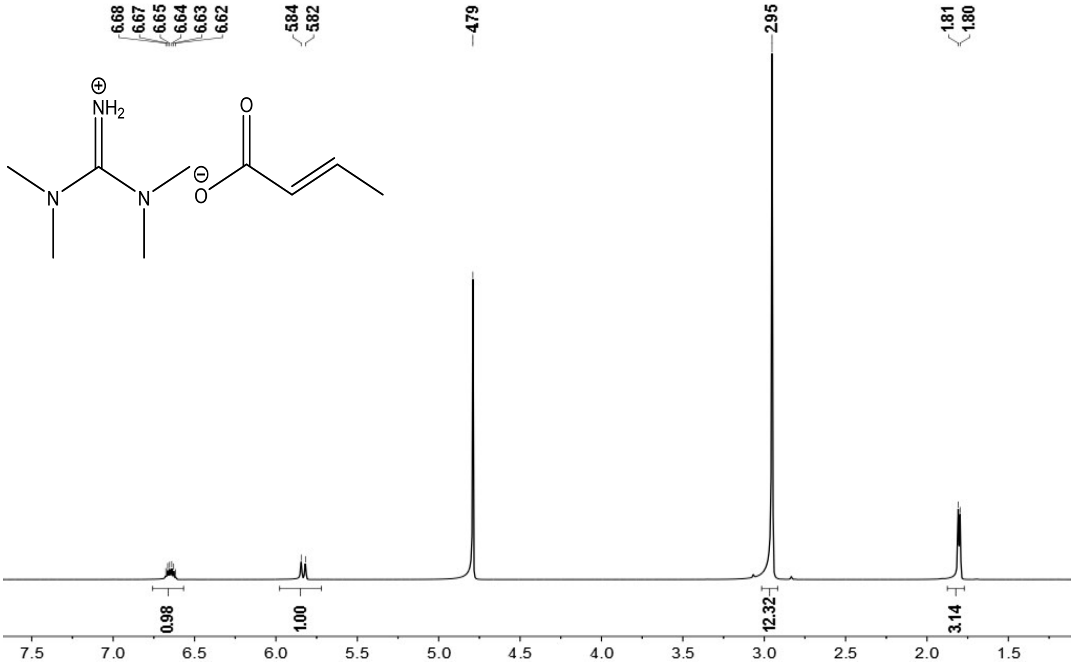
A1-B17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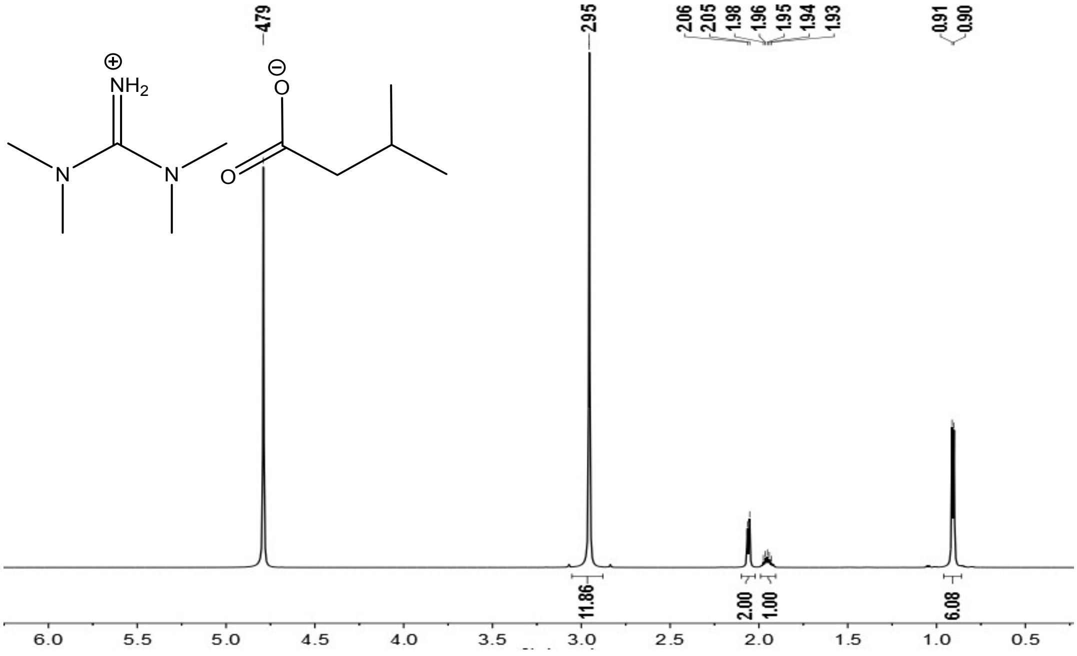
A1-B18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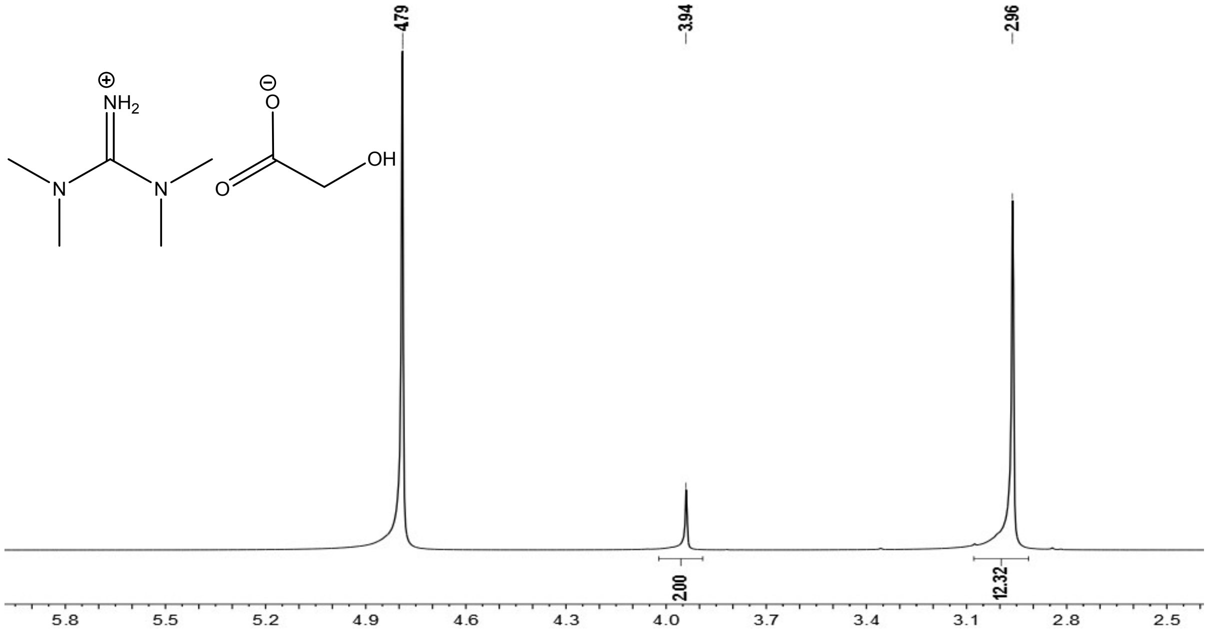
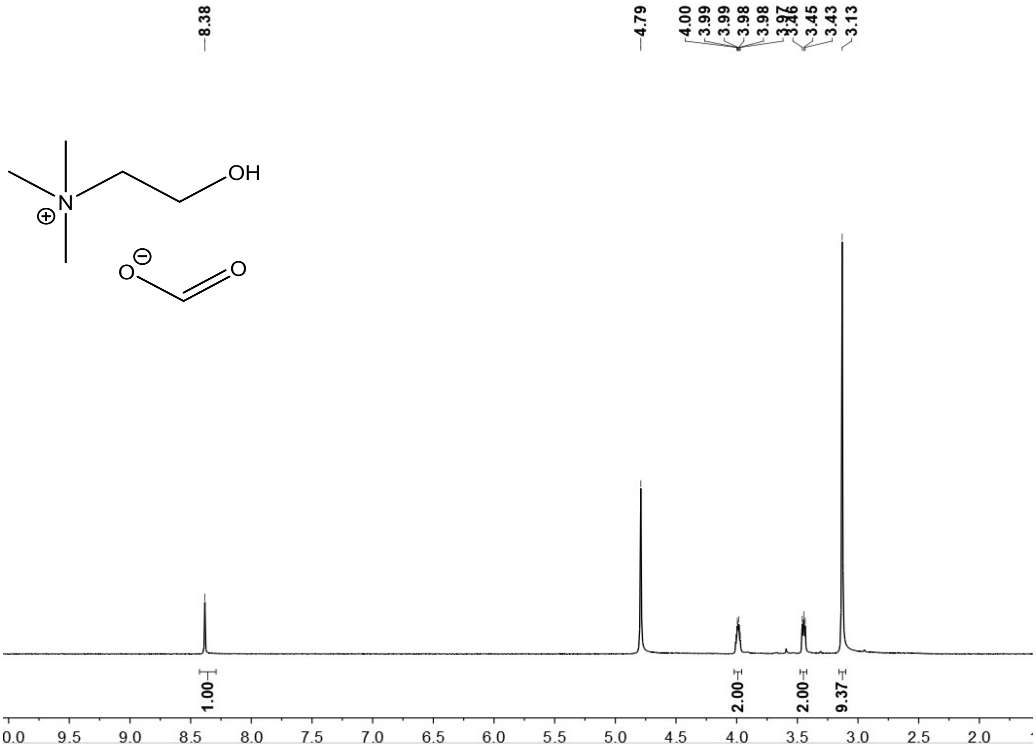
A1-B19



A1-B20

A6-B1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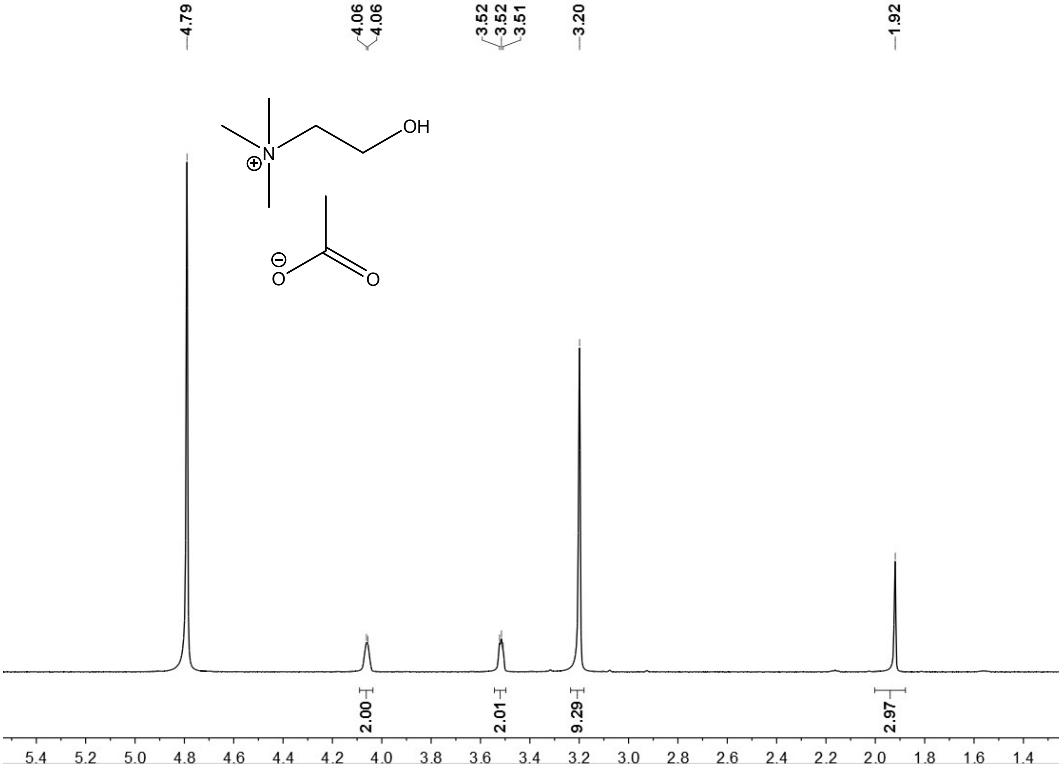
A6-B2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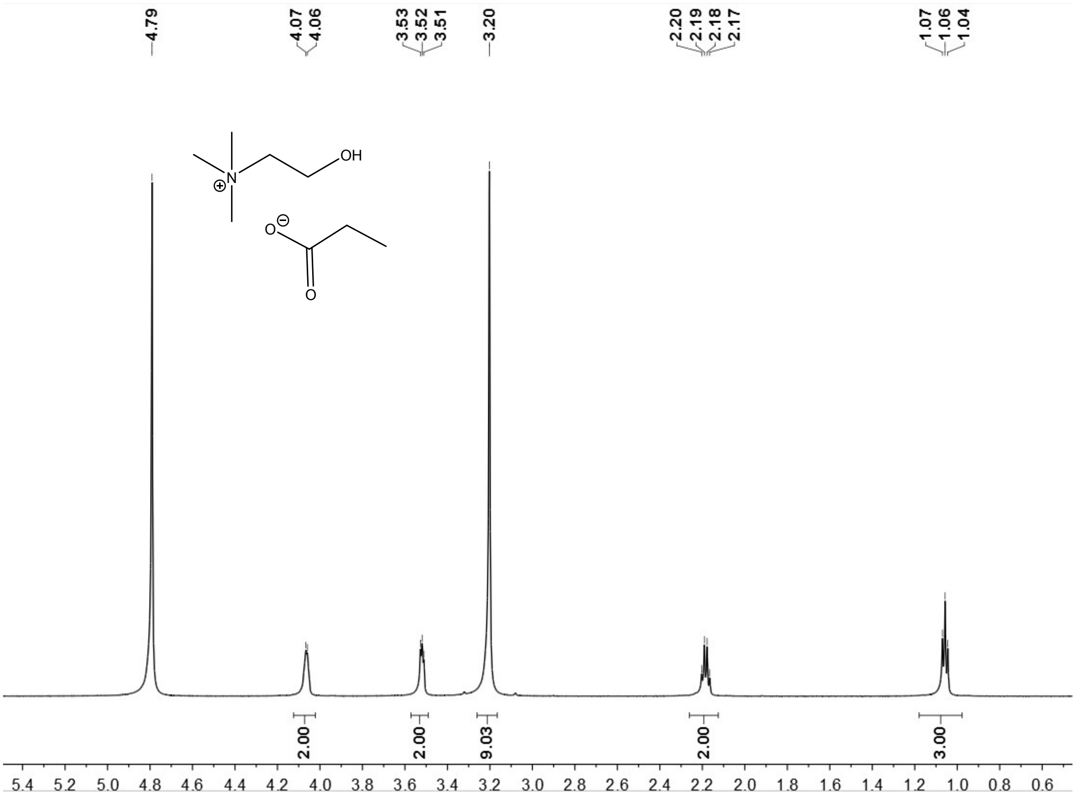
A6-B3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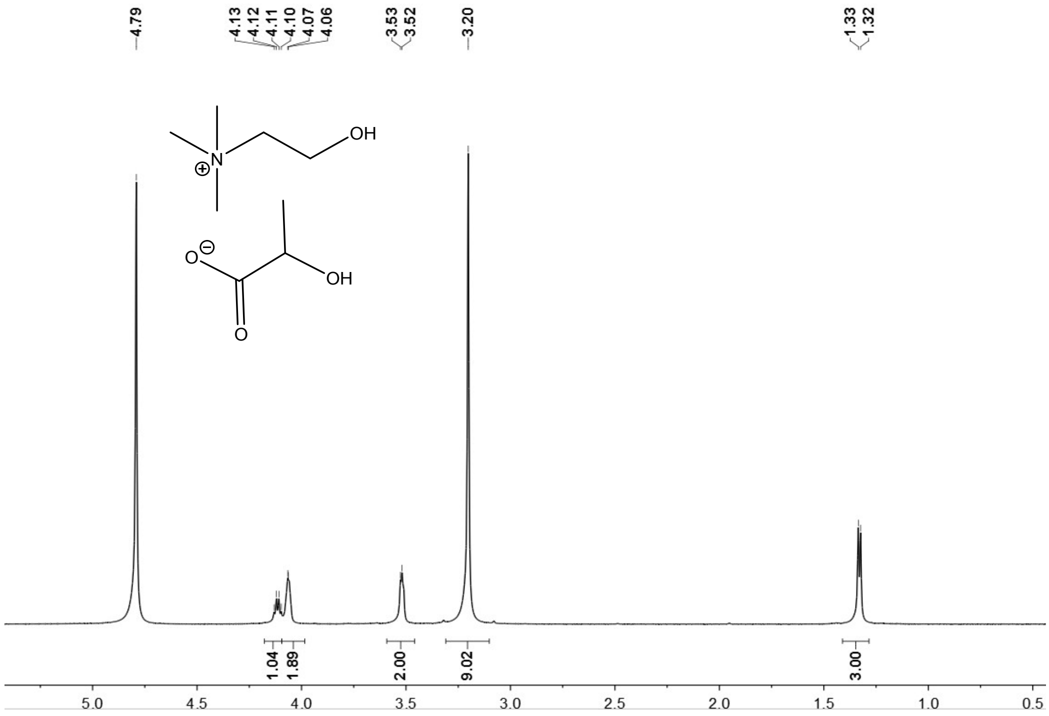
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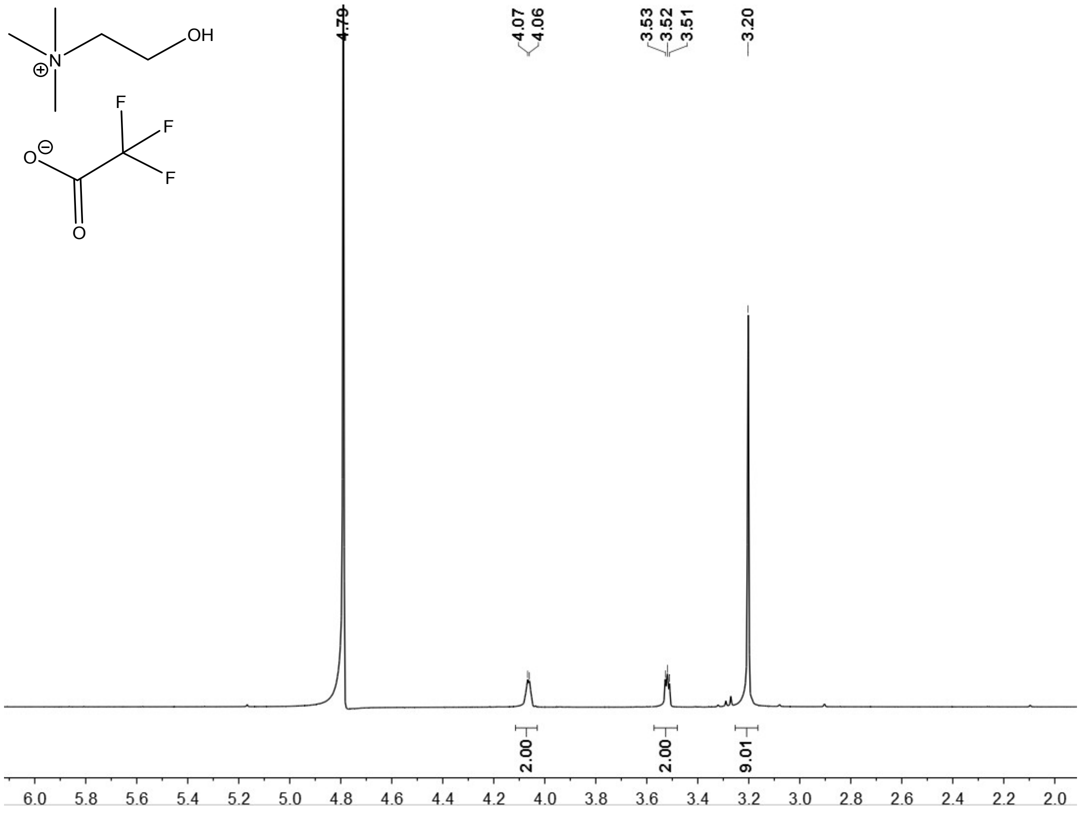
A6-B5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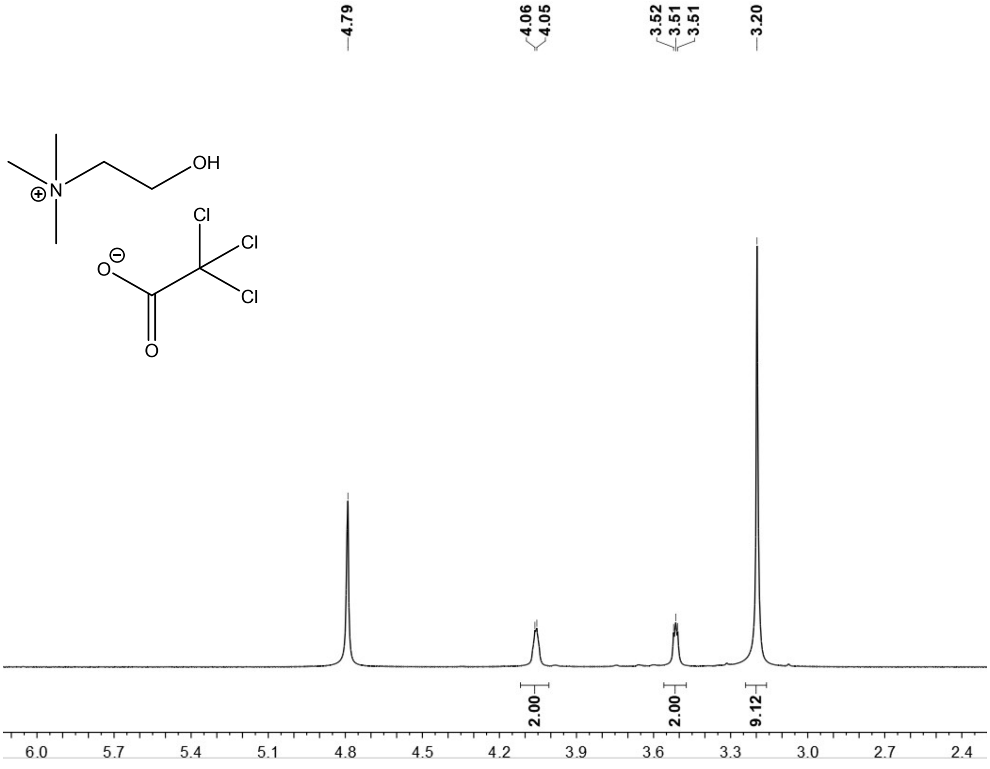
A6--B6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4.06
4.05
3.52
3.51
3.51
3.20
OH
N
Cl
Cl
Cl
O
O
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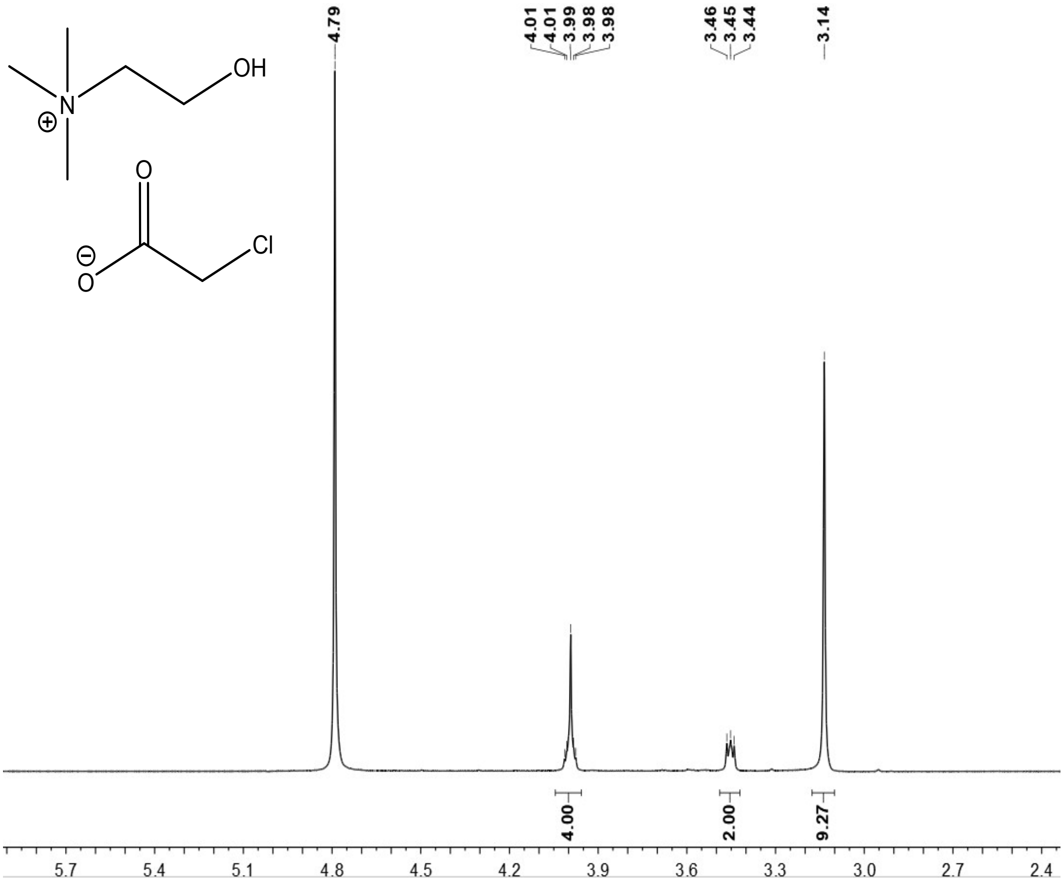
2.00
9.12
6.0 5.7 5.4 5.1 4.8 4.5 4.2 3.9 3.6 3.3 3.0 2.7 2.4

A6-B7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4.01
4.01
3.99
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3.98
3.46
3.45
3.44
3.14
OH
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O
O
Cl
4.00
2.00
9.27
5.7
5.4
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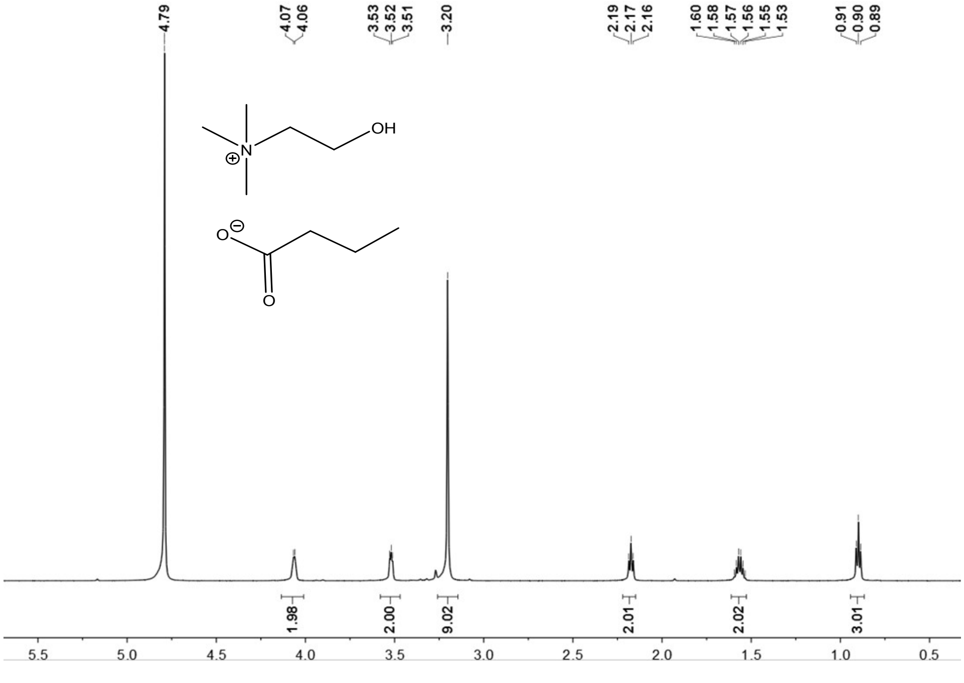
4.5
4.2
3.9
3.6
3.3
3.0
2.7
2.4

A6-B8


4.79
4.07
4.06
3.53
3.52
3.51
3.20
2.19
2.17
2.16
1.60
1.58
1.57
1.56
1.55
1.53
0.91
0.90
0.89
N
OH
O
O
1.98
2.00
9.02
2.01
2.02
3.01
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4.0
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3.0
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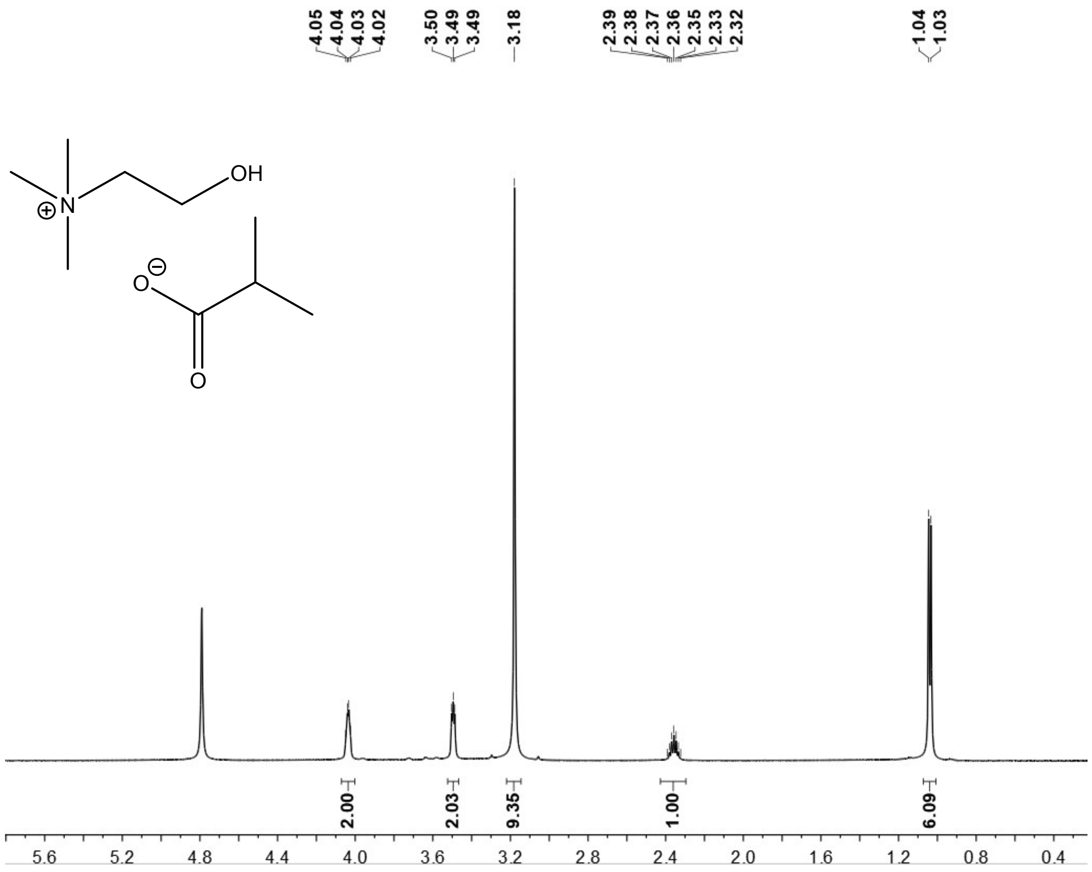
1.5
1.0
0.5

A6-B9



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4.03
4.02
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3.49
3.49
3.18
2.39
2.38
2.37
2.36
2.35
2.33
2.32
1.04
1.03
N
OH
O
O
2.00
2.03
9.35
1.00
6.09
5.6
5.2
4.8
4.4
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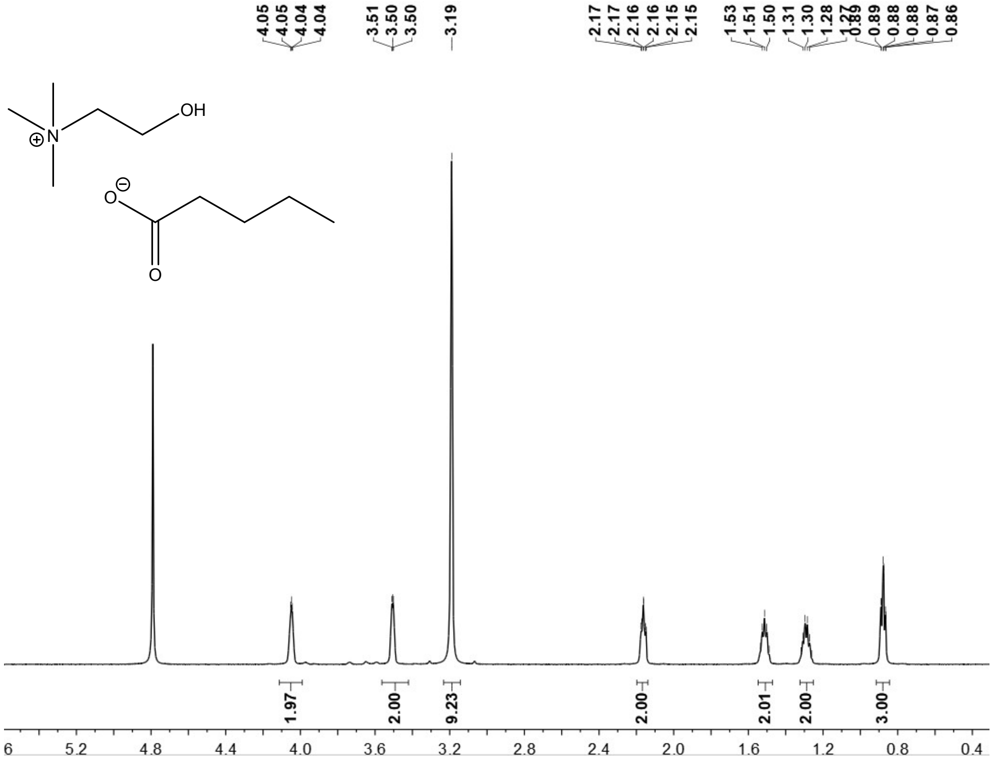
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4

A6-B10



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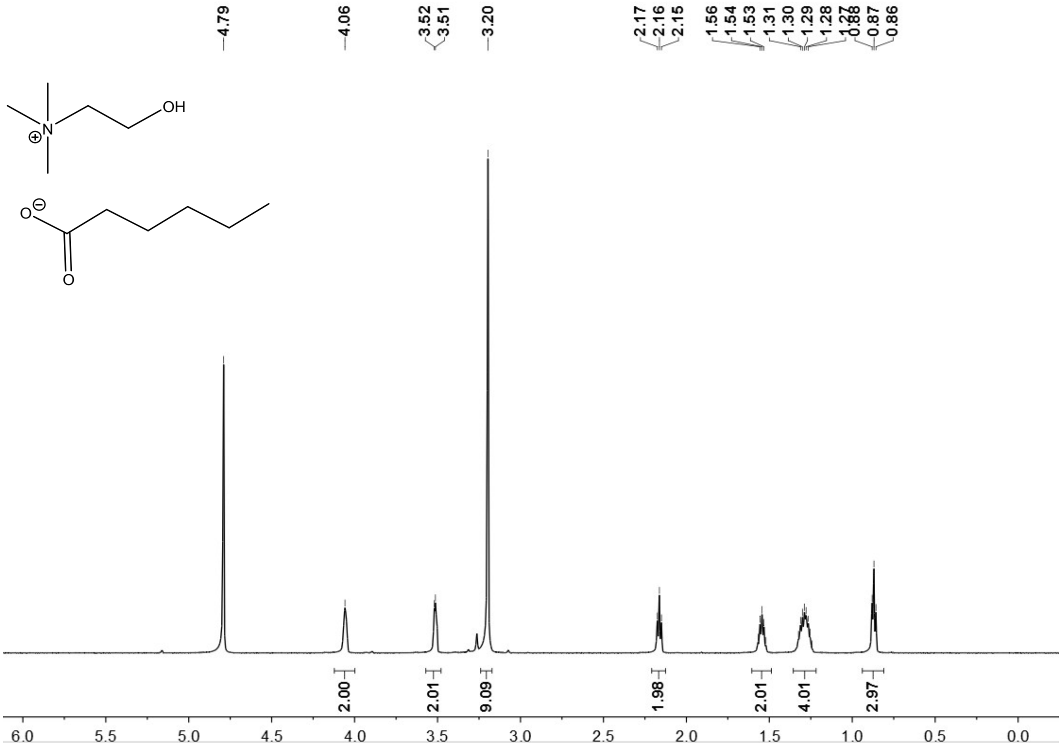
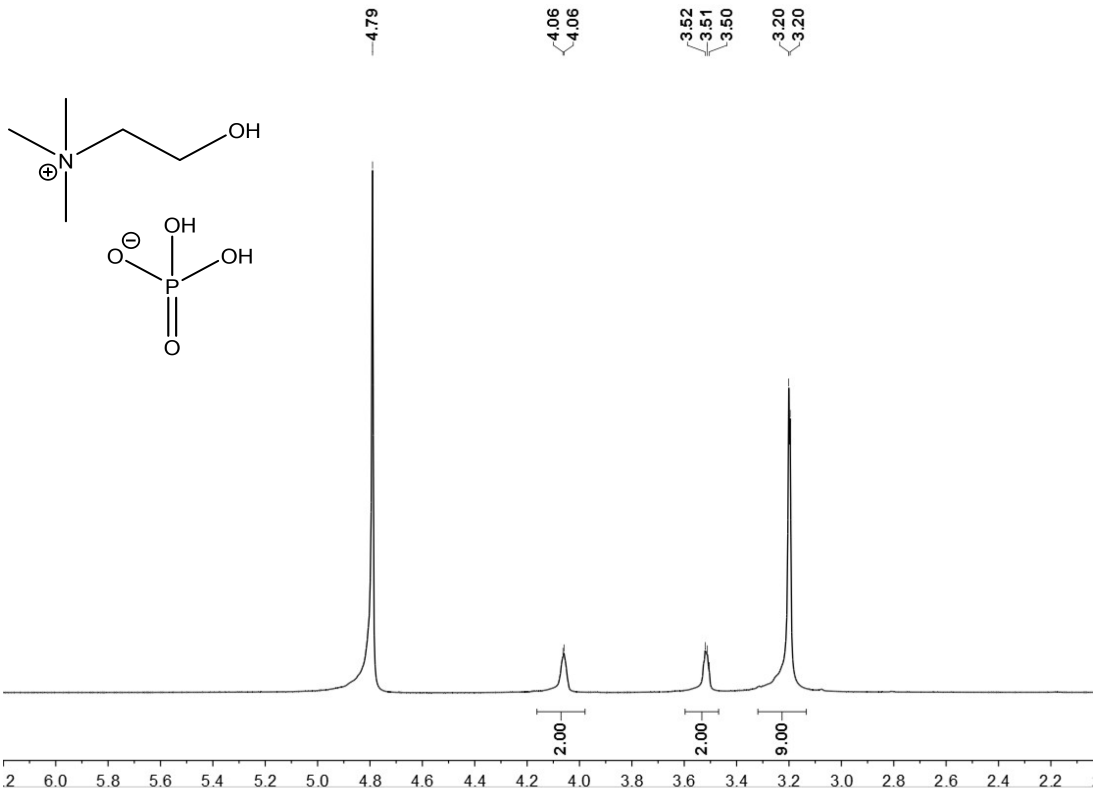
4.05
4.04
4.04
3.51
3.50
3.50
3.19
2.17
2.17
2.16
2.16
2.15
2.15
1.53
1.51
1.50
1.31
1.30
1.28
1.27
0.89
0.89
0.88
0.88
0.87
0.86
N
OH
O
O
1.97
2.00
9.23
2.00
2.01
2.00
3.00
6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4

A6-B11



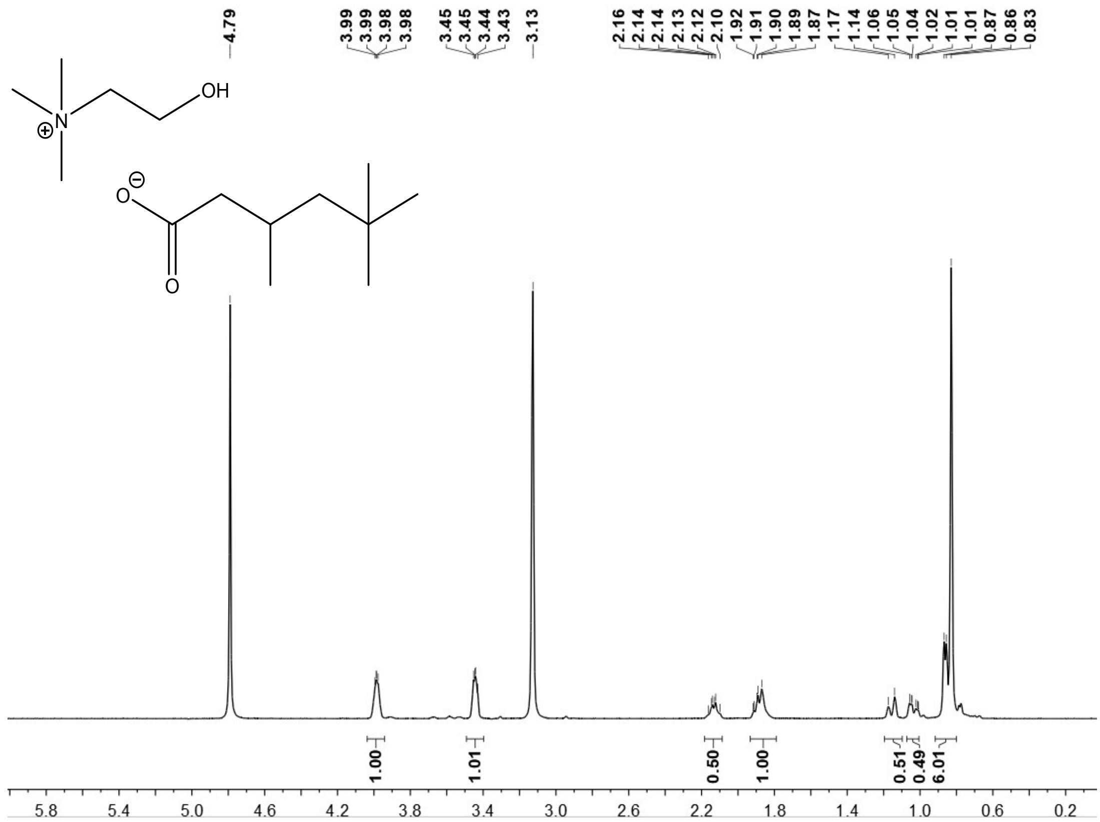
4.79
4.06
3.52
3.51
3.20
2.17
2.16
2.15
1.56
1.54
1.53
1.31
1.30
1.29
1.28
1.27
0.88
0.87
0.86
N
OH
O
O
2.00
2.01
9.09
1.98
2.01
4.01
2.97
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

A6-B12



4.79
4.06
4.06
3.52
3.51
3.50
3.20
3.20
N
OH
OH
O
OH
P
O
2.00
2.00
9.00
2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2

A6-B13


4.79
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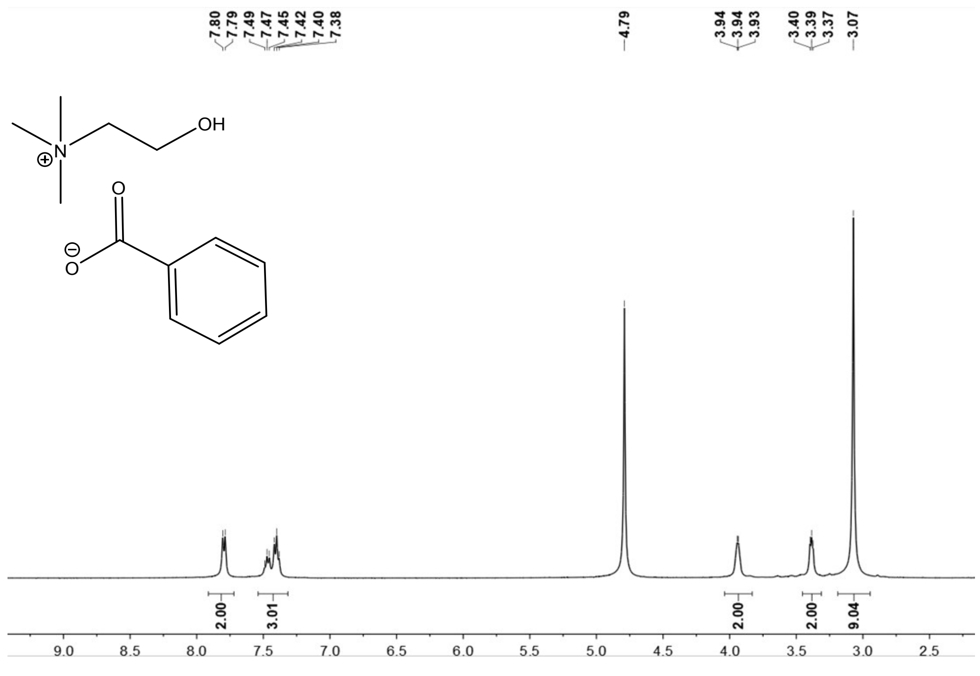
3.99
3.98
3.98
3.45
3.45
3.44
3.43
3.13
2.16
2.14
2.14
2.13
2.12
2.10
1.92
1.91
1.90
1.89
1.87
1.17
1.14
1.06
1.05
1.04
1.02
1.01
1.01
0.87
0.86
0.83
N
OH
O
O
1.00
1.01
0.50
1.00
0.51
0.49
6.01
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
0.6
0.2

A6-B14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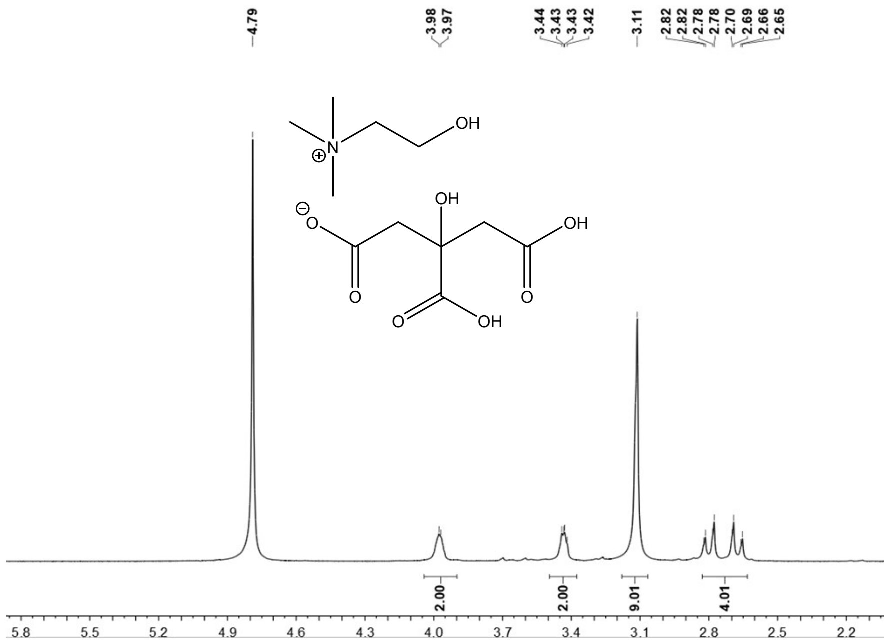
7.45
7.42
7.40
7.38
4.79
3.94
3.94
3.93
3.40
3.39
3.37
3.07
N
OH
O
O
2.00
3.01
2.00
2.00
9.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5

A6-B15


4.79
3.98
3.97
3.44
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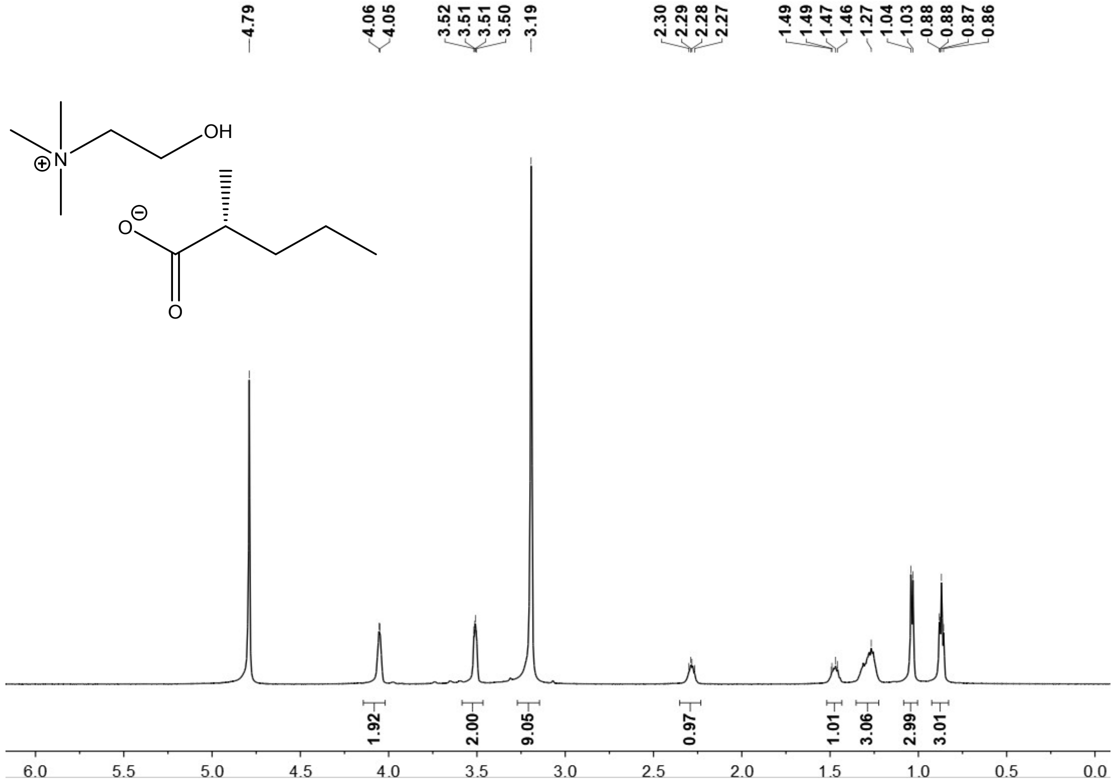
3.43
3.42
3.11
2.82
2.82
2.78
2.78
2.70
2.69
2.66
2.65
⊕
N
OH
⊖
O
OH
OH
O
O
O
OH
2.00
2.00
9.01
4.01
5.8
5.5
5.2
4.9
4.6
4.3
4.0
3.7
3.4
3.1
2.8
2.5
2.2

A6-B16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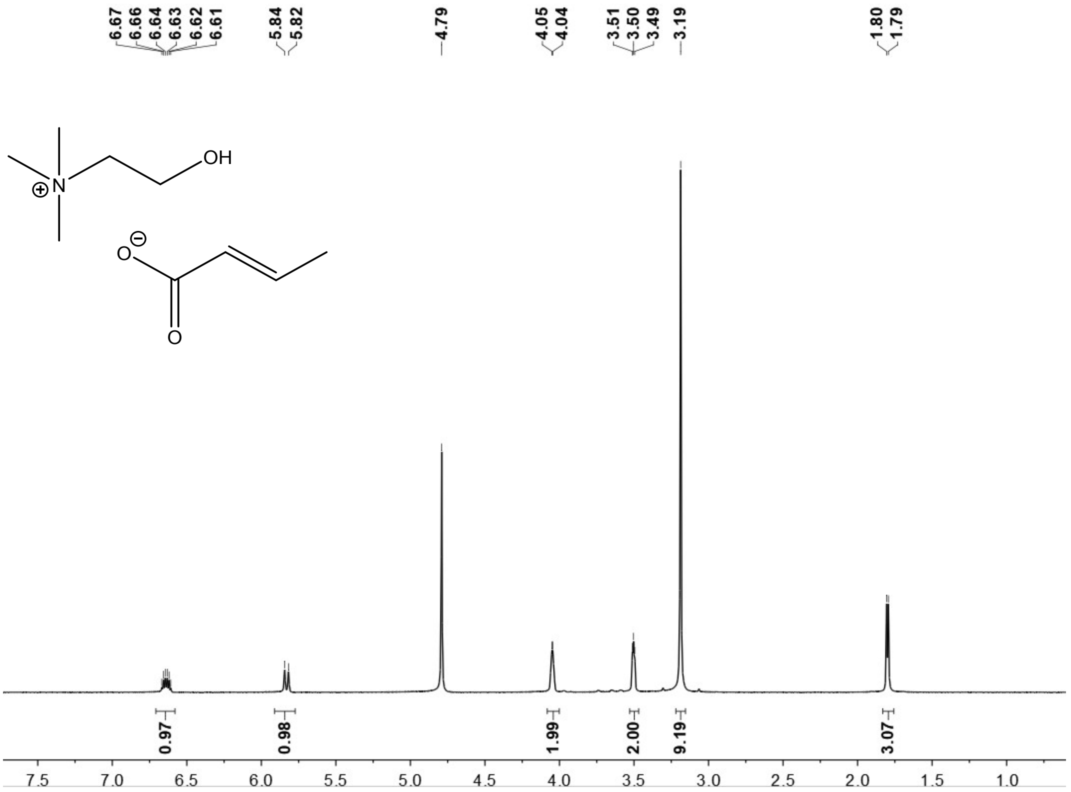
4.06
4.05
3.52
3.51
3.51
3.50
3.19
2.30
2.29
2.28
2.27
1.49
1.49
1.47
1.46
1.27
1.04
1.03
0.88
0.88
0.87
0.86
⊕
N
OH
⊖
O
O
1.92
2.00
9.05
0.97
1.01
3.06
2.99
3.01
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

A6-B17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4.05
4.04
3.51
3.50
3.49
3.19
1.80
1.79
OH
N
O
O
0.97
0.98
1.99
2.00
9.19
3.07
7.5
7.0
6.5
6.0
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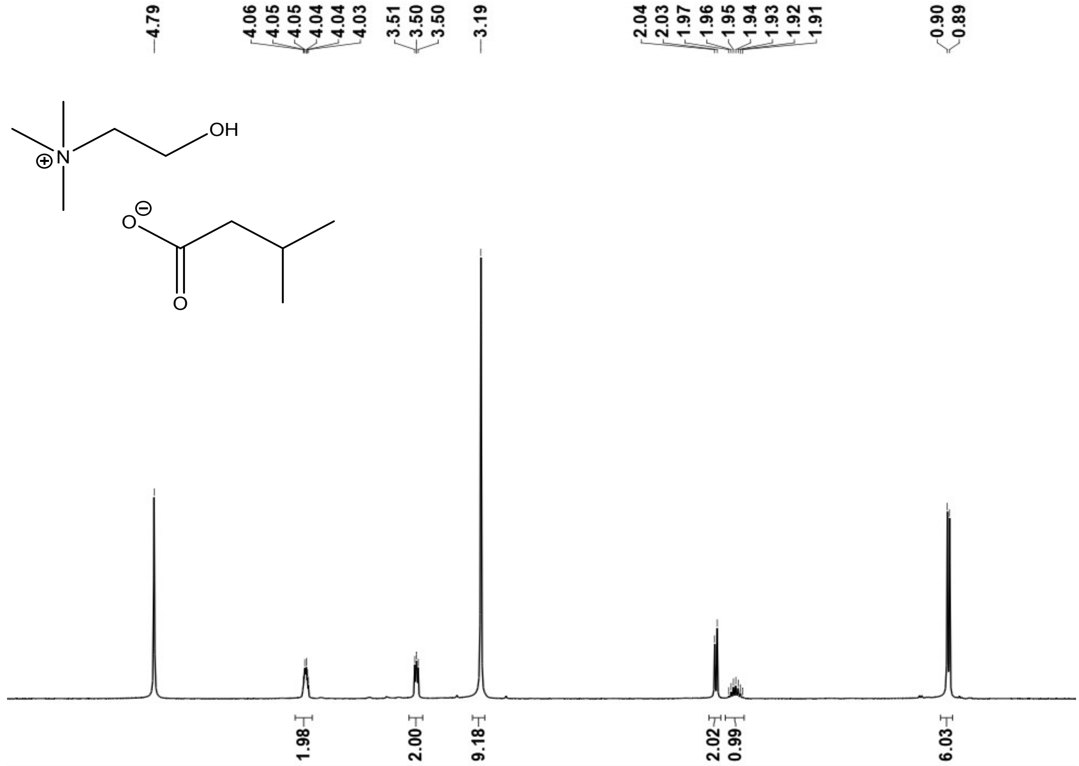
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

A6-B18


4.79
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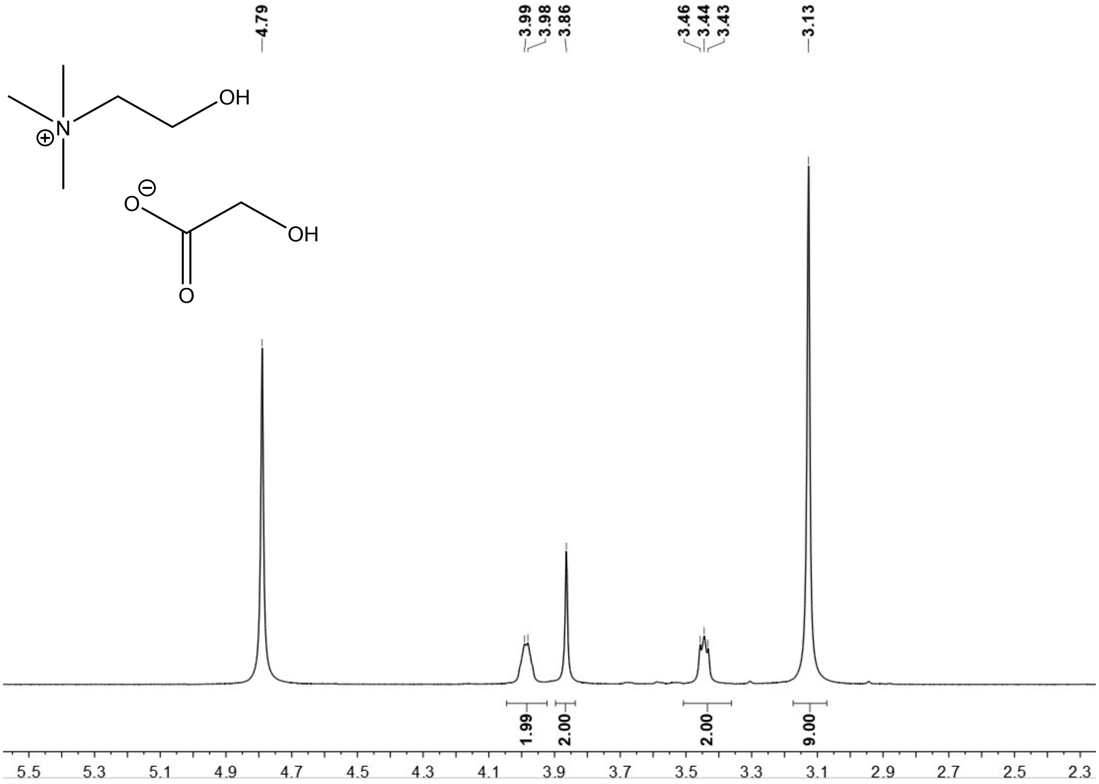
4.05
4.05
4.04
4.04
4.03
3.51
3.50
3.50
3.19
2.04
2.03
1.97
1.96
1.95
1.94
1.93
1.92
1.91
0.90
0.89
OH
N
O
O
1.98
2.00
9.18
2.02
0.99
6.03
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4

A6-B19


4.79
3.99
3.98
3.86
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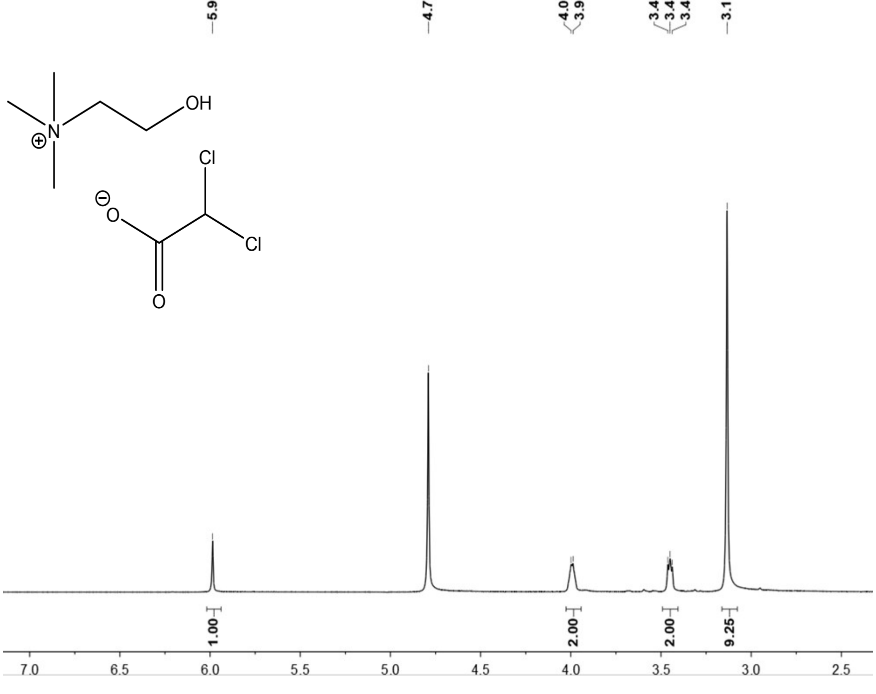
3.44
3.43
3.13
N
OH
O
OH
O
1.99
2.00
2.00
9.00
5.5
5.3
5.1
4.9
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3

A6-B20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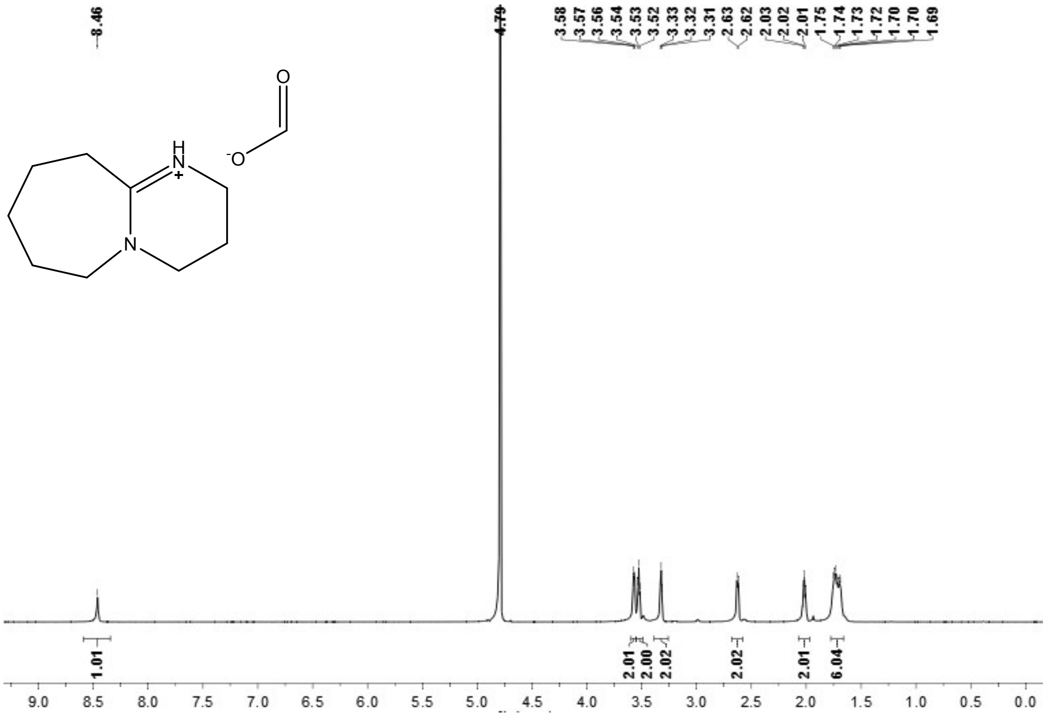
4.79
4.00
3.99
3.46
3.45
3.44
3.13
N
OH
Cl
O
Cl
O
1.00
2.00
2.00
9.25
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5

A13-B1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3.33
3.32
3.31
2.63
2.62
2.03
2.02
2.01
1.75
1.74
1.73
1.72
1.70
1.70
1.69
O
-O
H
N+
N
1.01
2.01
2.00
2.02
2.02
2.01
6.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
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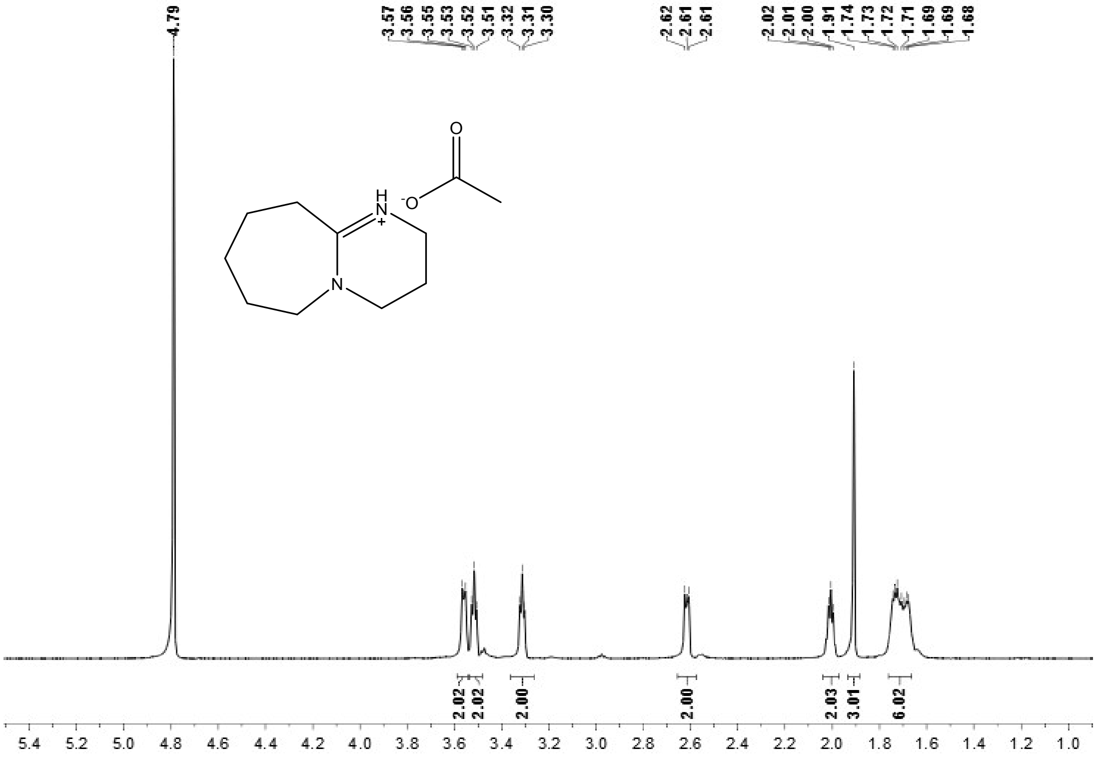
1.0
0.5
0.0

A13-B2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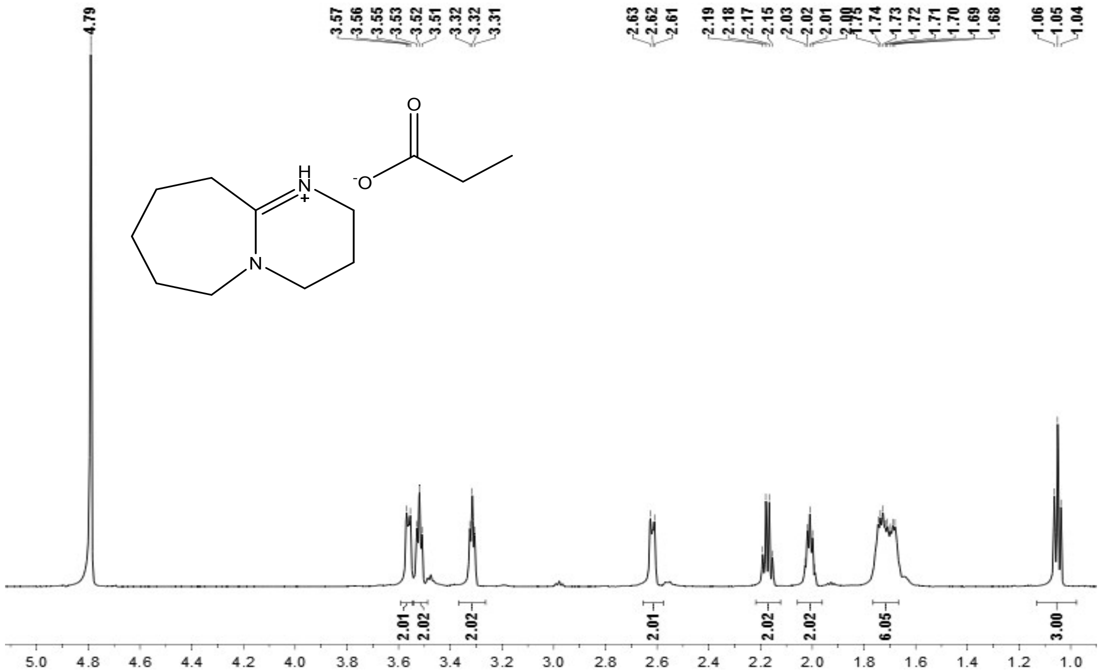
3.52
3.51
3.32
3.31
3.30
2.62
2.61
2.61
2.02
2.01
2.00
1.91
1.74
1.73
1.72
1.71
1.69
1.69
1.68
O
-O
H
N+
N
2.02
2.02
2.00
2.00
2.03
3.01
6.02
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0

A13-B3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3.57
3.56
3.55
3.53
3.52
3.51
3.32
3.32
3.31
2.63
2.62
2.61
2.19
2.18
2.17
2.15
2.03
2.02
2.01
2.00
1.75
1.74
1.73
1.72
1.71
1.70
1.69
1.68
1.06
1.05
1.04
O
H
N
+
-O
N
2.01
2.02
2.02
2.01
2.02
2.02
6.05
3.00
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
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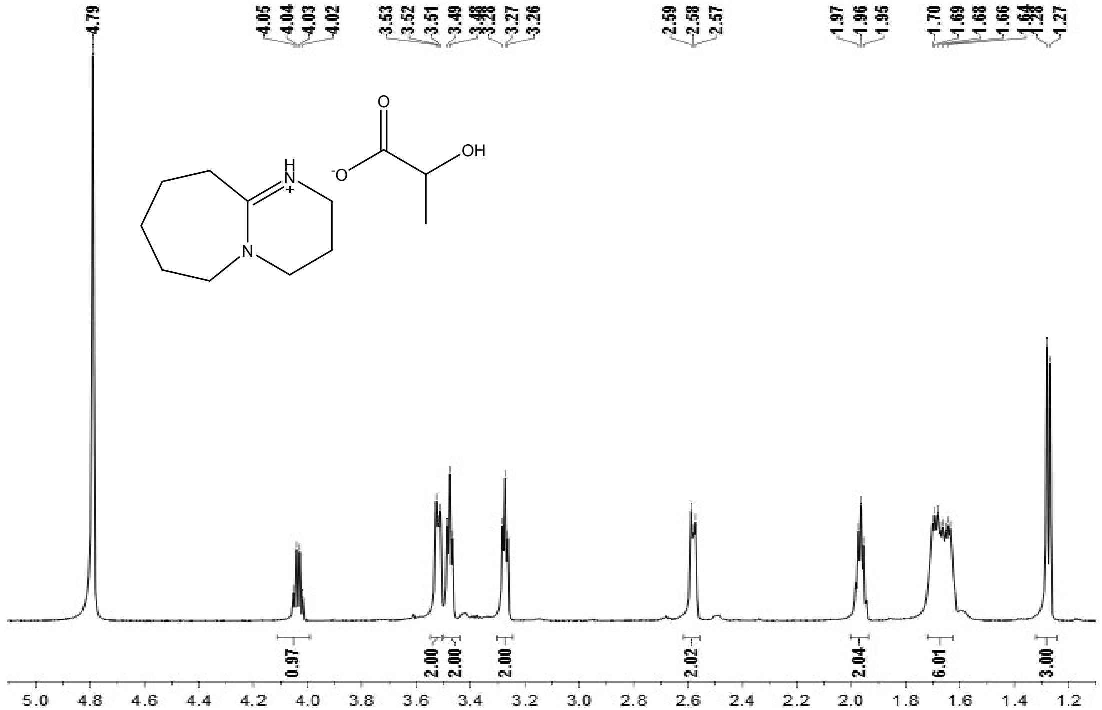
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0

A13-B4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4.03
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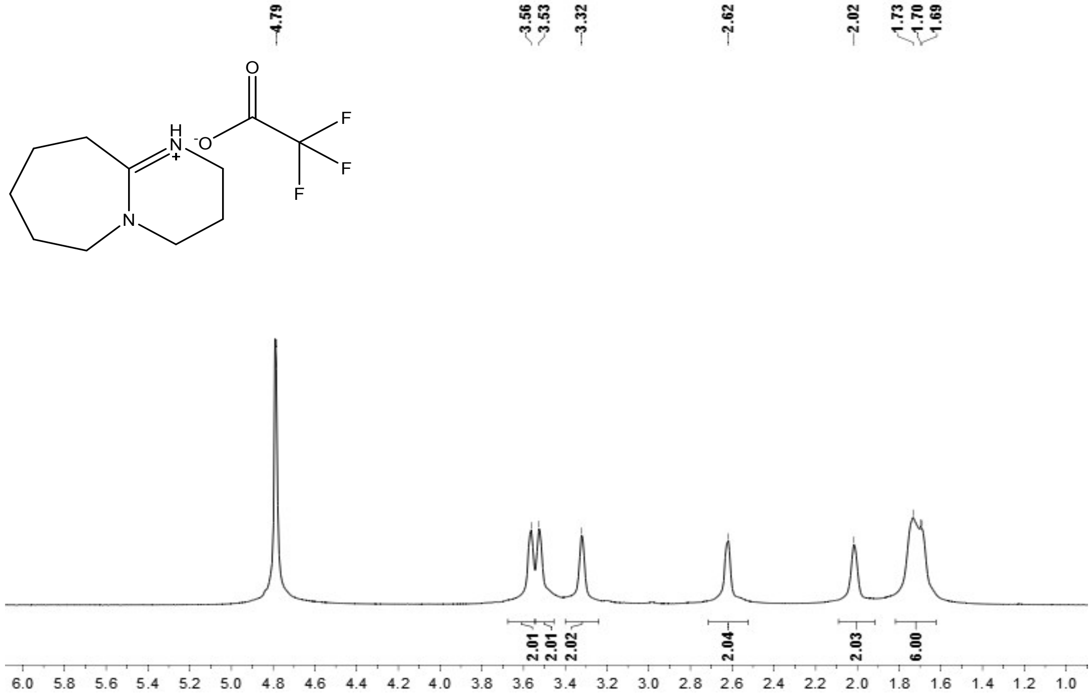
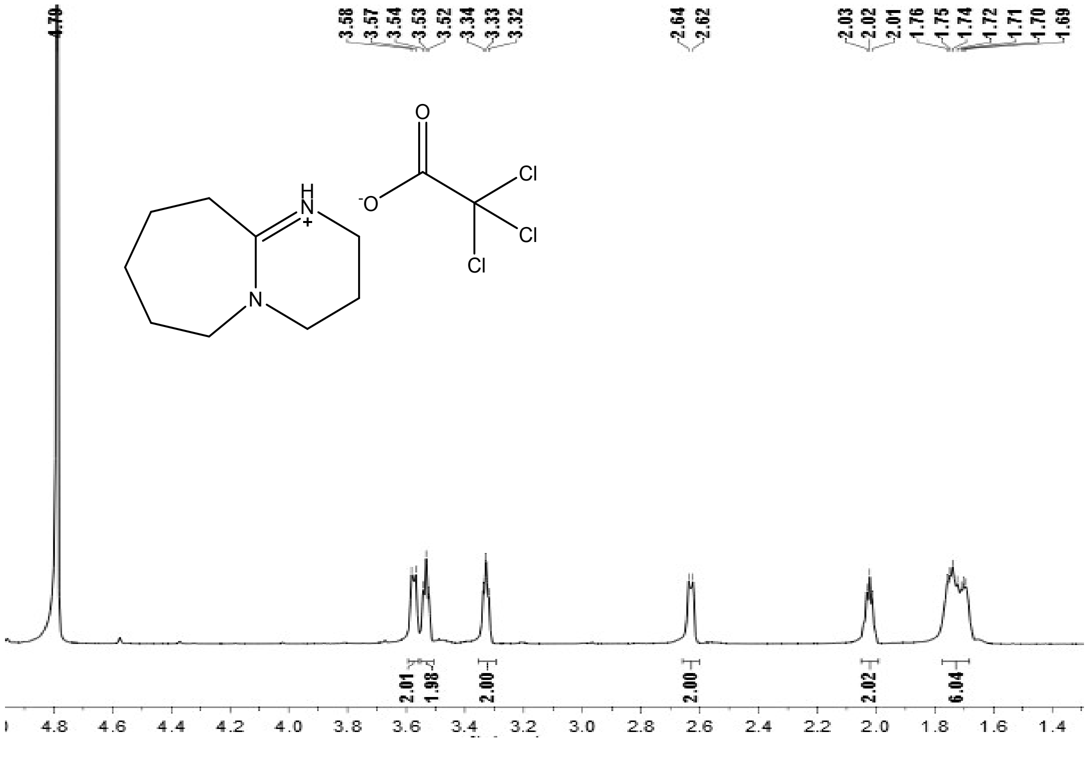
3.53
3.52
3.51
3.49
3.48
3.28
3.27
3.26
2.59
2.58
2.57
1.97
1.96
1.95
1.70
1.69
1.68
1.66
1.64
1.28
1.27
O
OH
H
N
+
-O
N
0.97
2.00
2.00
2.00
2.02
2.04
6.01
3.00
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2

A13-B5


4.79
3.56
3.53
3.32
2.62
2.02
1.73
1.70
1.69
O
H
N+
-O
F
F
F
N
2.01
2.01
2.02
2.04
2.03
6.00
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0

A13-B6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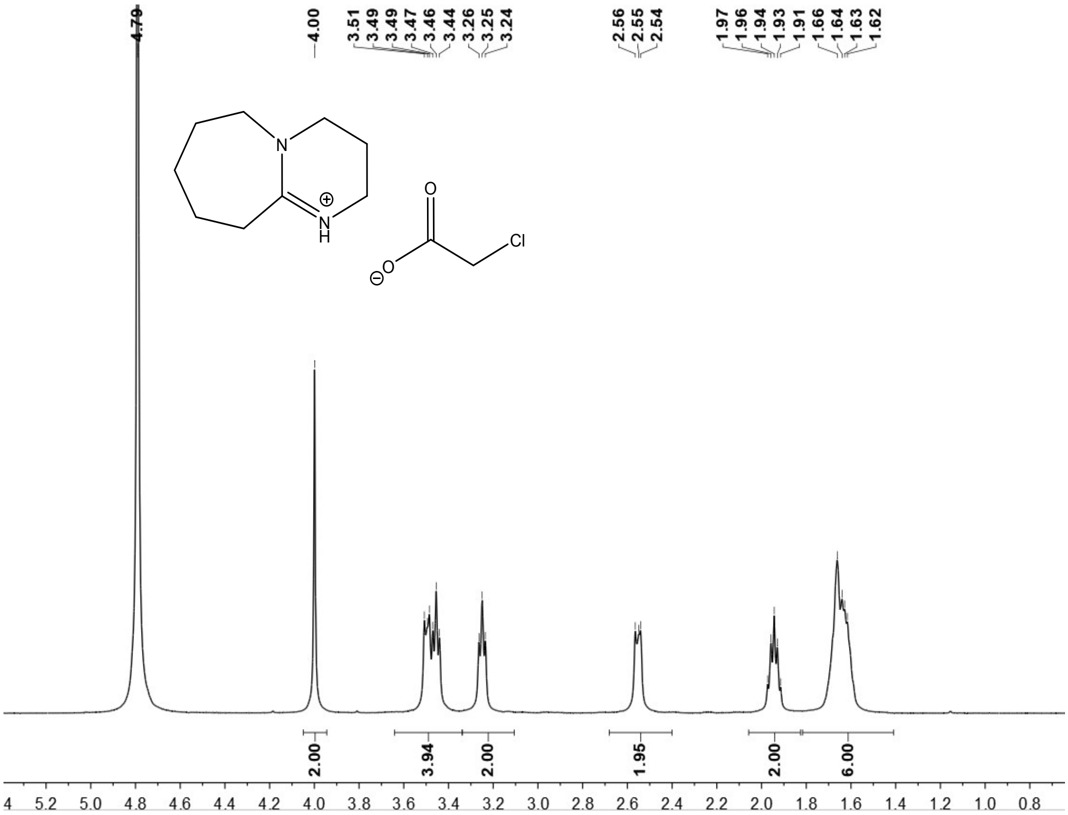
3.57
3.54
3.53
3.52
3.34
3.33
3.32
2.64
2.62
2.03
2.02
2.01
1.76
1.75
1.74
1.72
1.71
1.70
1.69
O
Cl
H
N+
-O
Cl
Cl
N
2.01
1.98
2.00
2.00
2.02
6.04
4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4

A13-B7



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3.49
3.47
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3.44
3.26
3.25
3.24
2.56
2.55
2.54
1.97
1.96
1.94
1.93
1.91
1.66
1.64
1.63
1.62
N
⊕
N
H
O
⊖O
Cl
2.00
3.94
2.00
1.95
2.00
6.00
4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
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2.6
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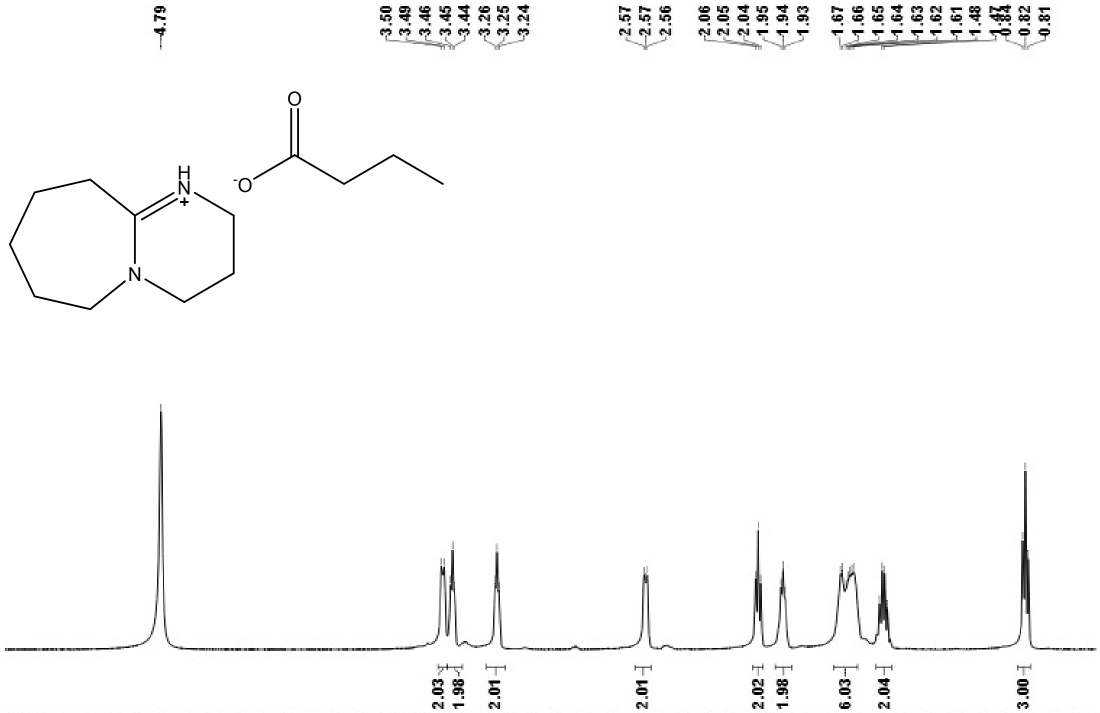
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8

A13-B8



4.79
3.50
3.49
3.46
3.45
3.44
3.26
3.25
3.24
2.57
2.57
2.56
2.06
2.05
2.04
1.95
1.94
1.93
1.67
1.66
1.65
1.64
1.63
1.62
1.61
1.48
1.47
0.84
0.82
0.81
O
H
N+
-O
N
2.03
1.98
2.01
2.01
2.02
1.98
6.03
2.04
3.00
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
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1.6
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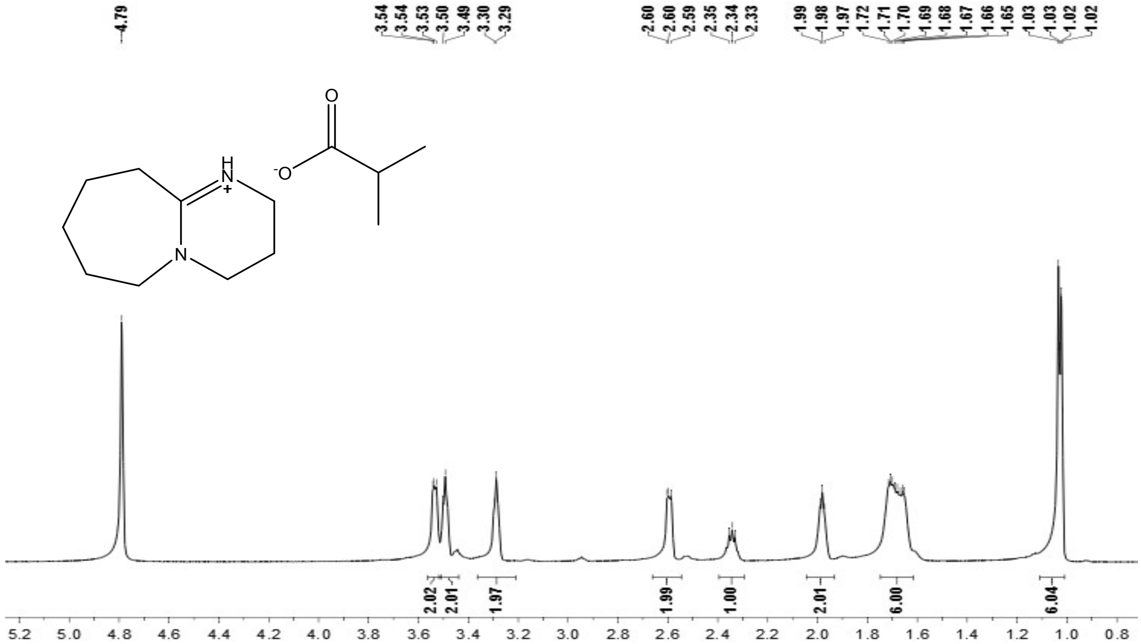
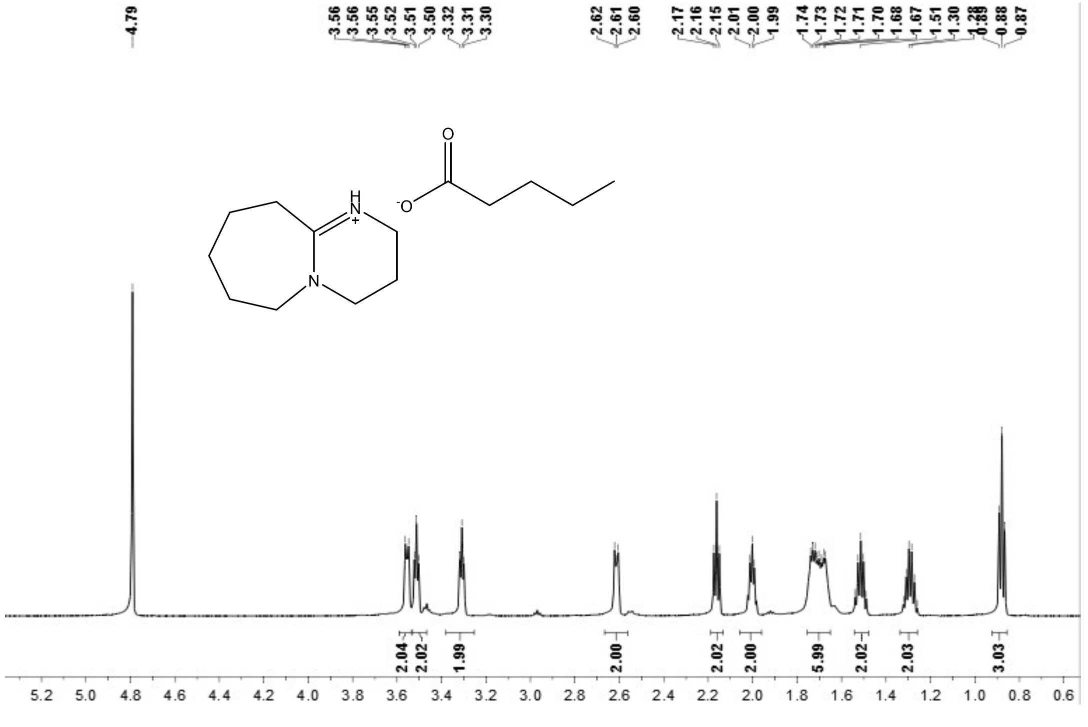
0.6

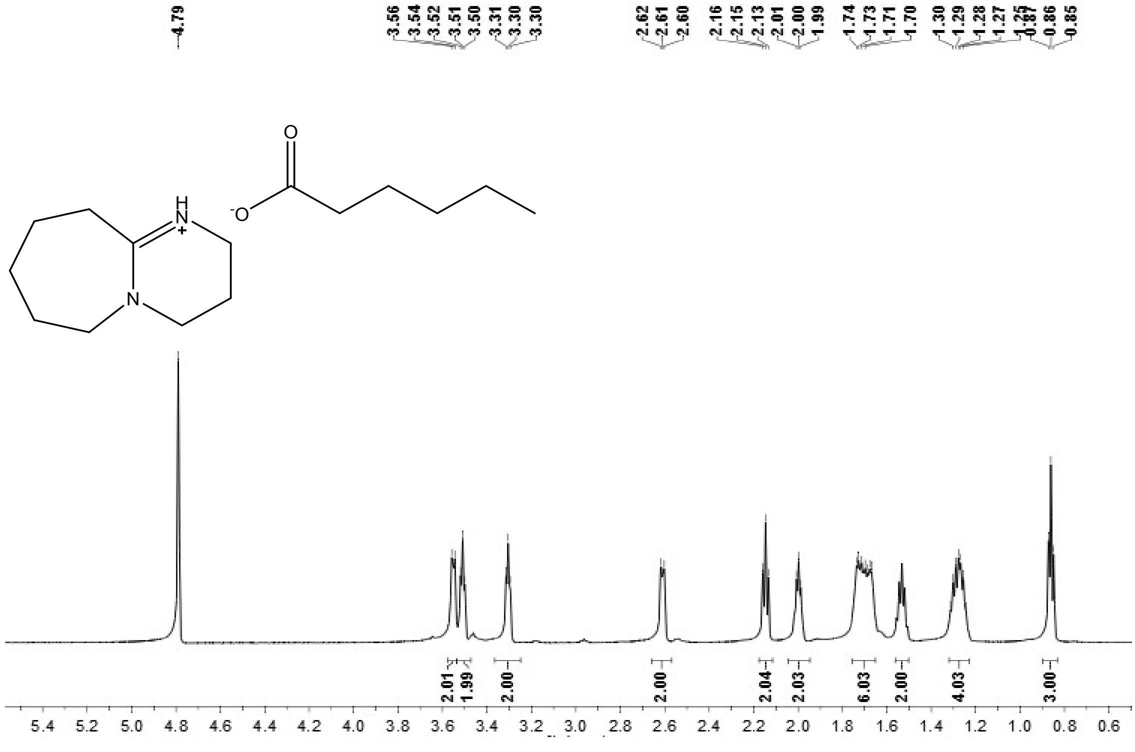
A13-B9



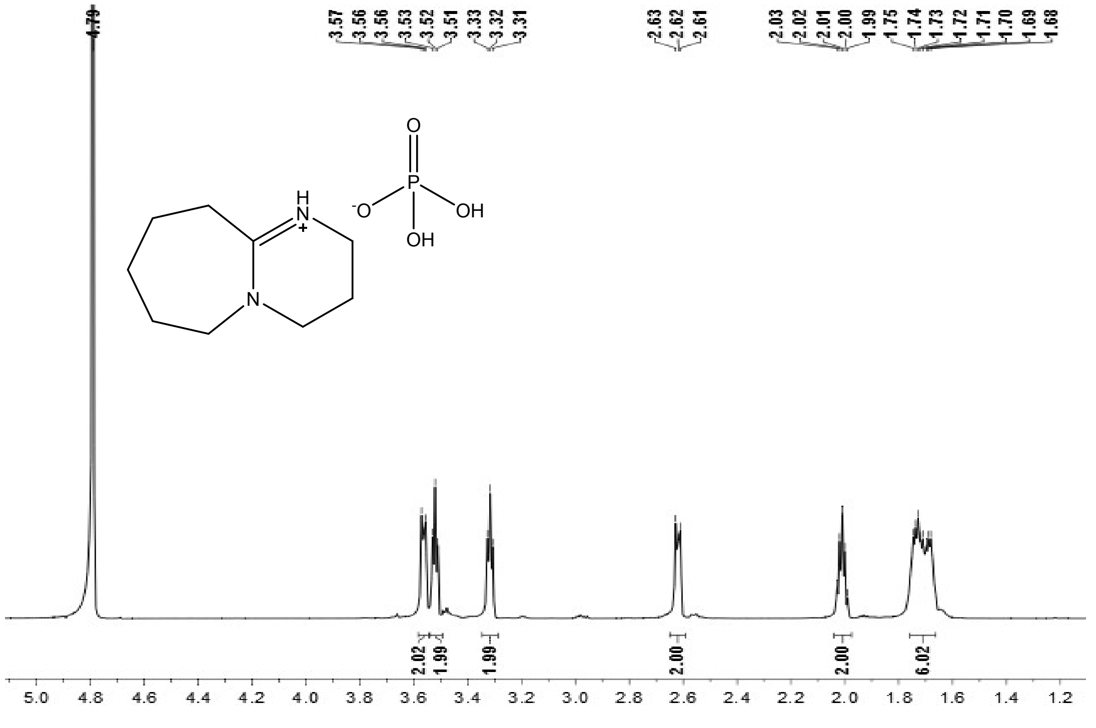
A13-B10



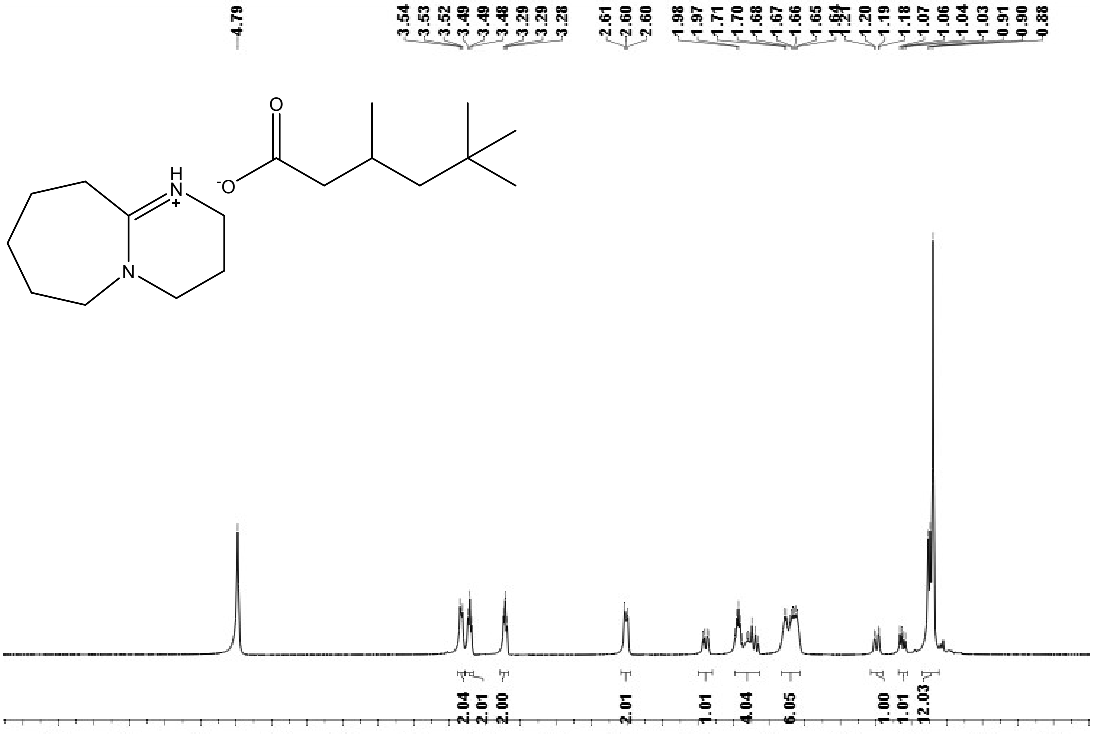
A13-B11



A13-B12



A13-B13



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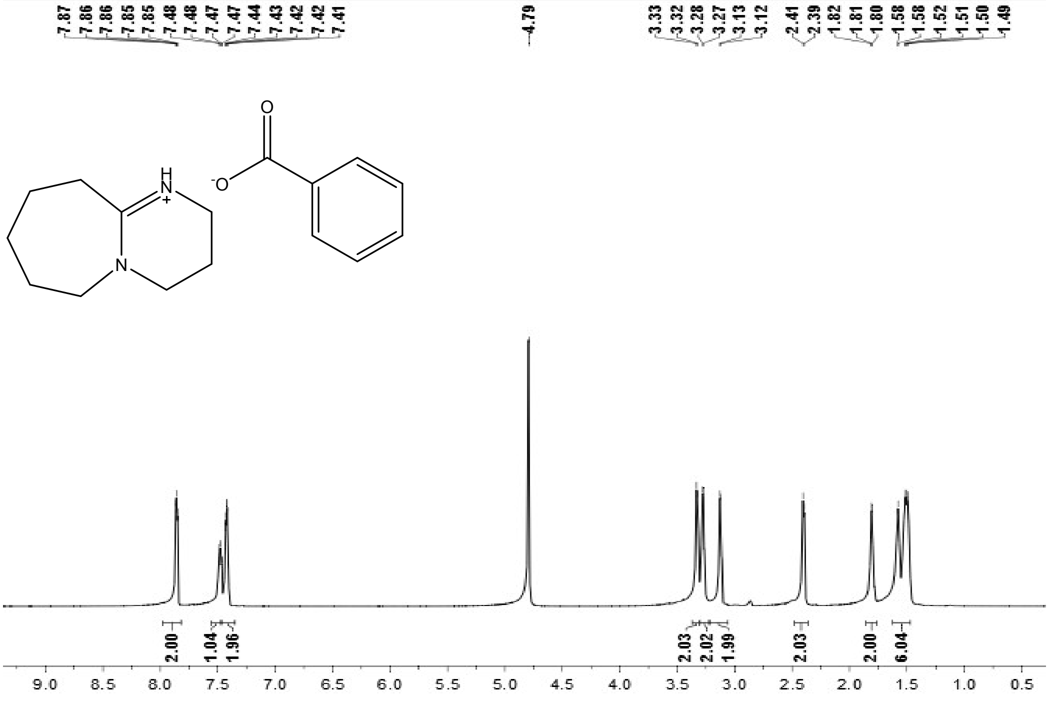

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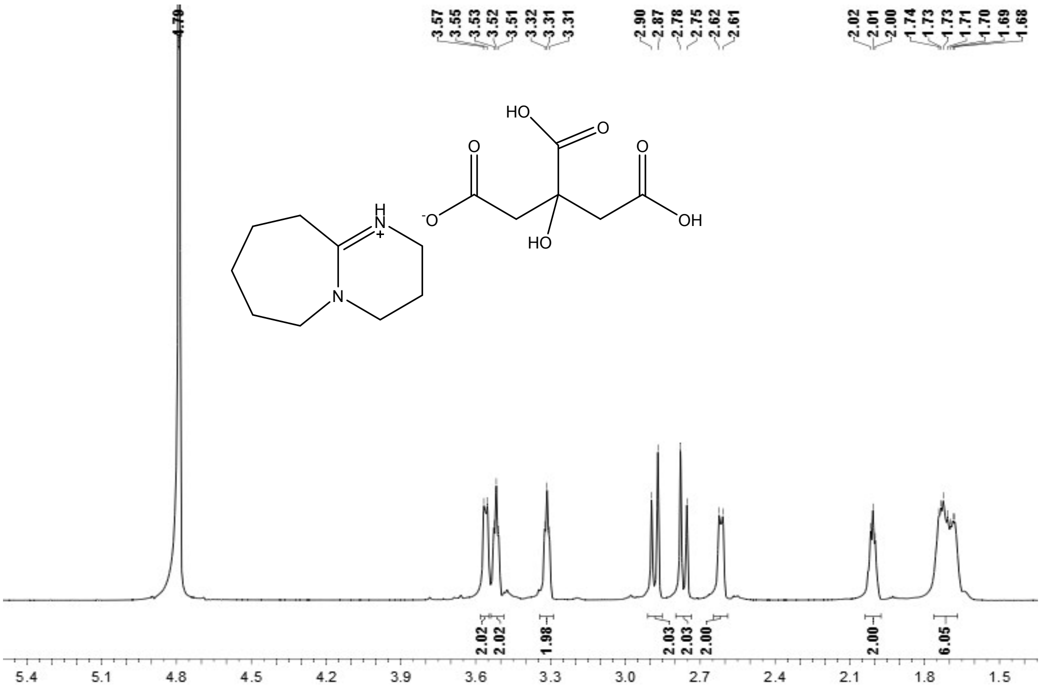

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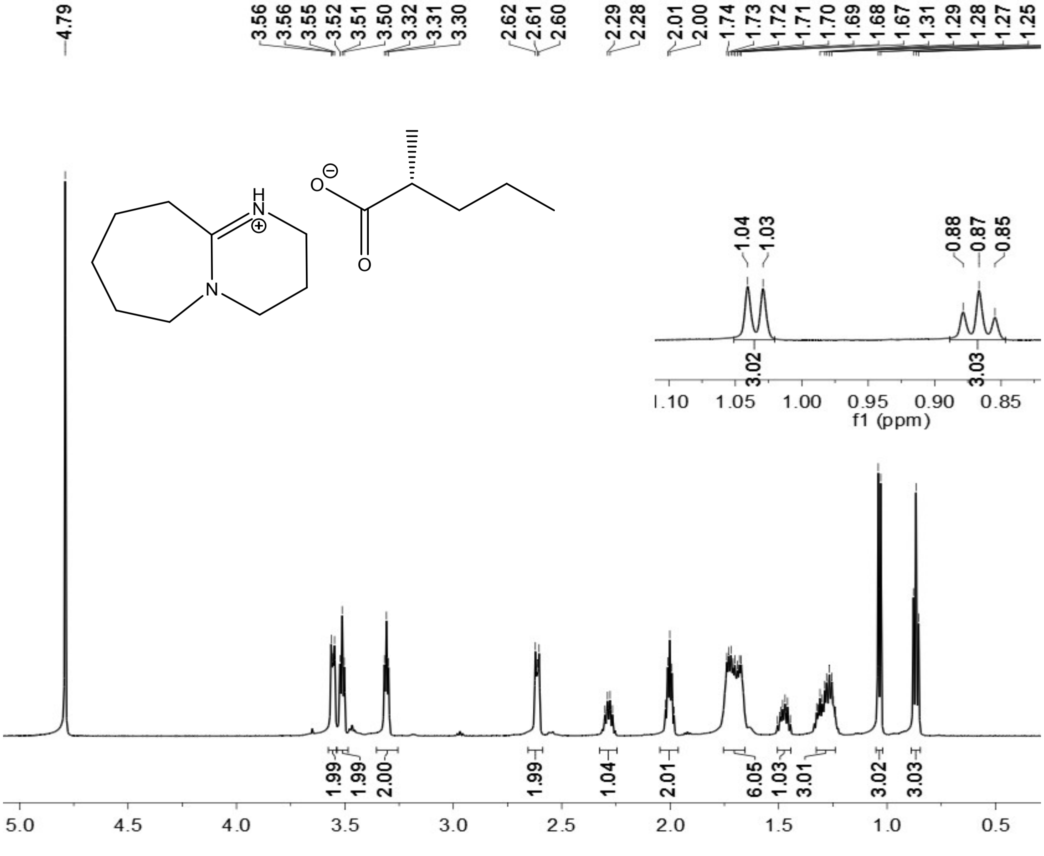

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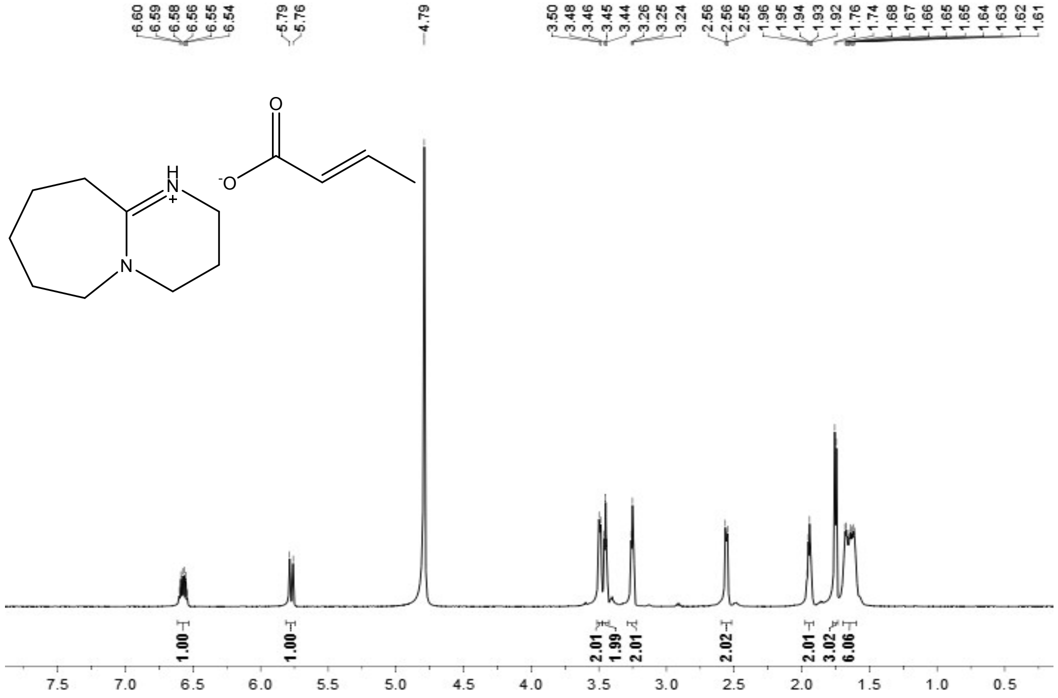

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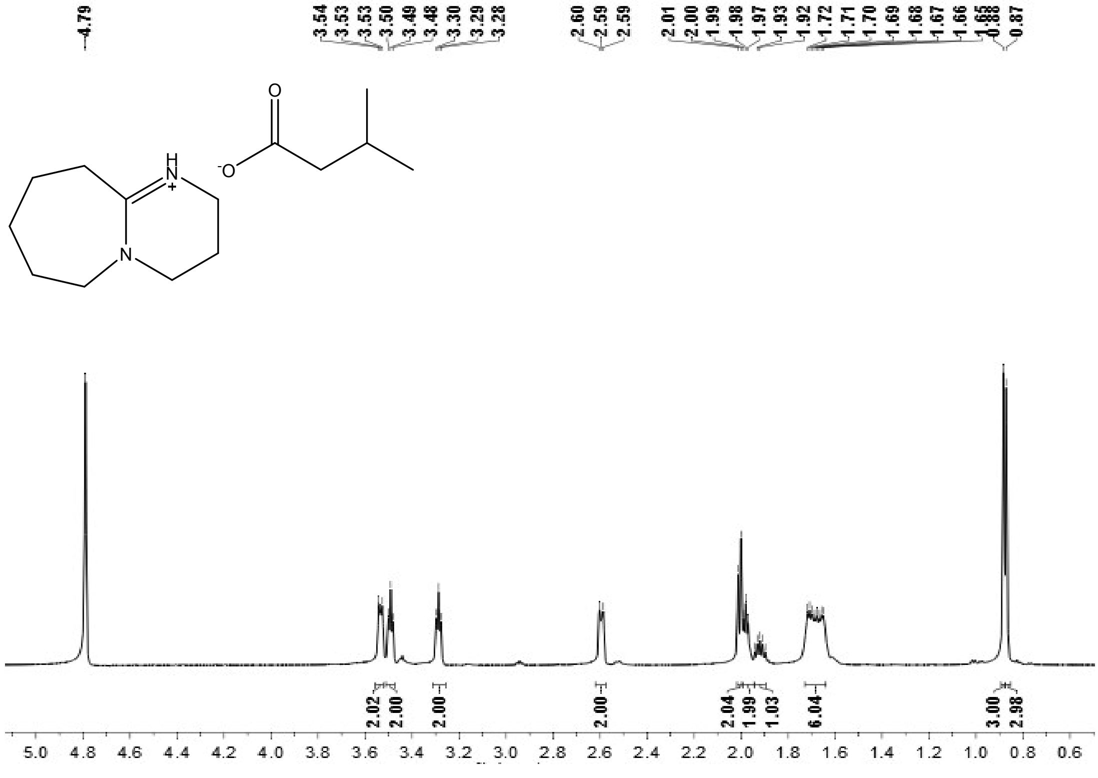

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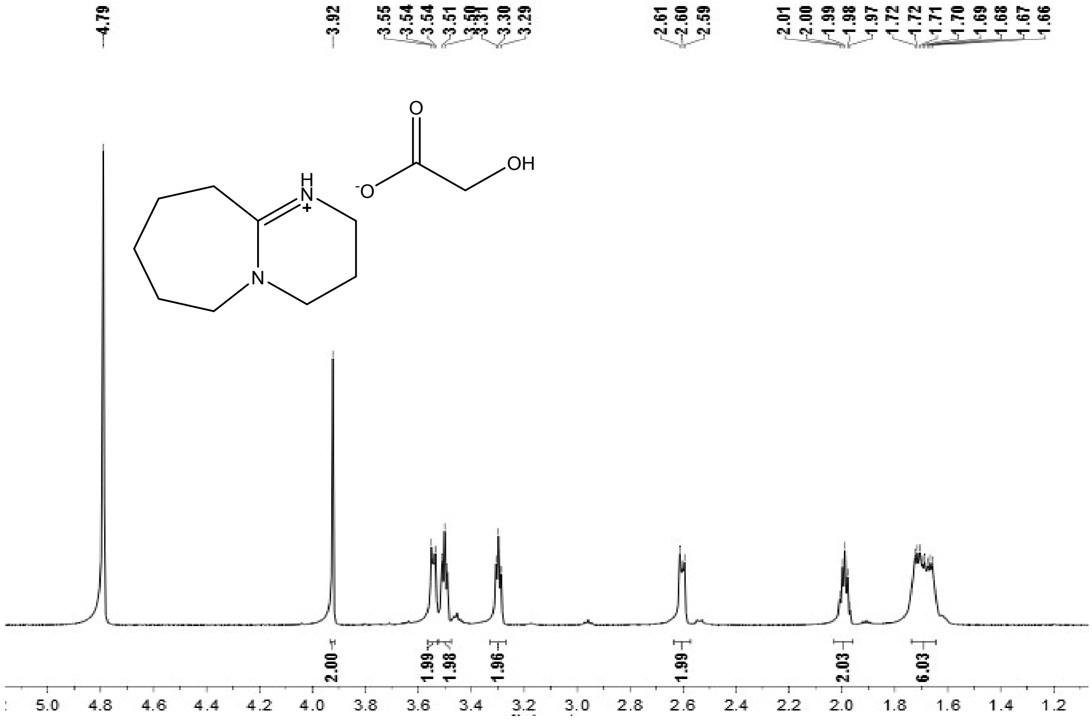
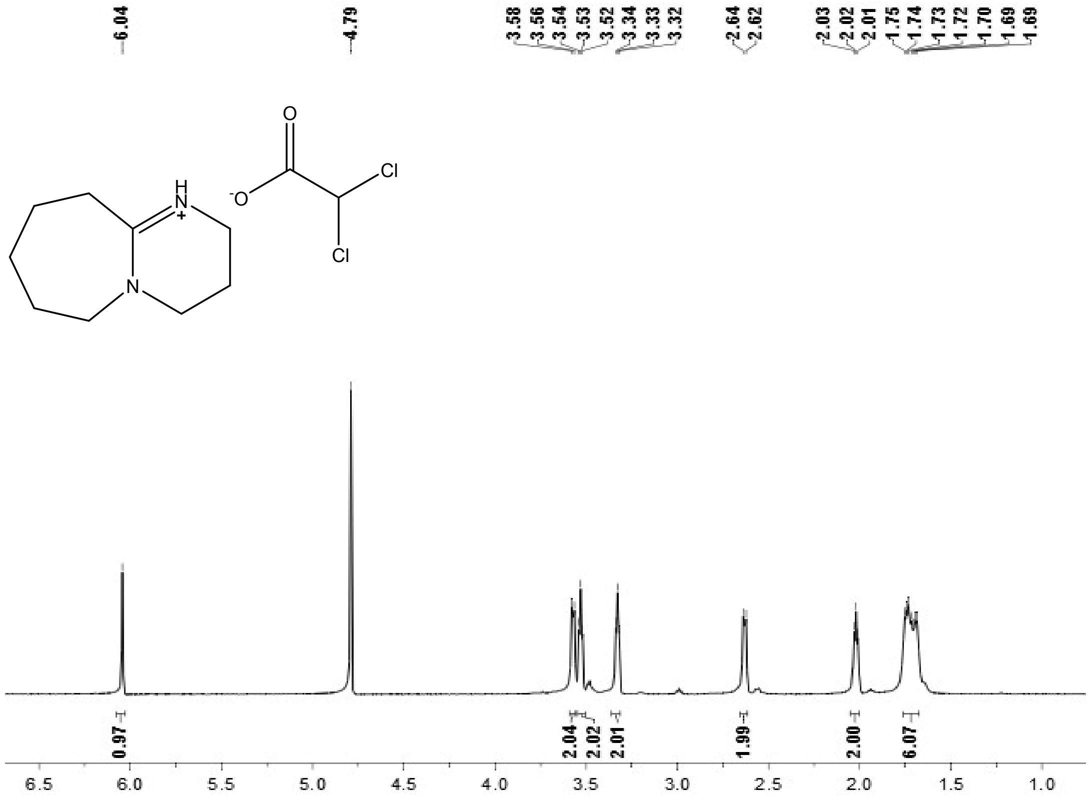
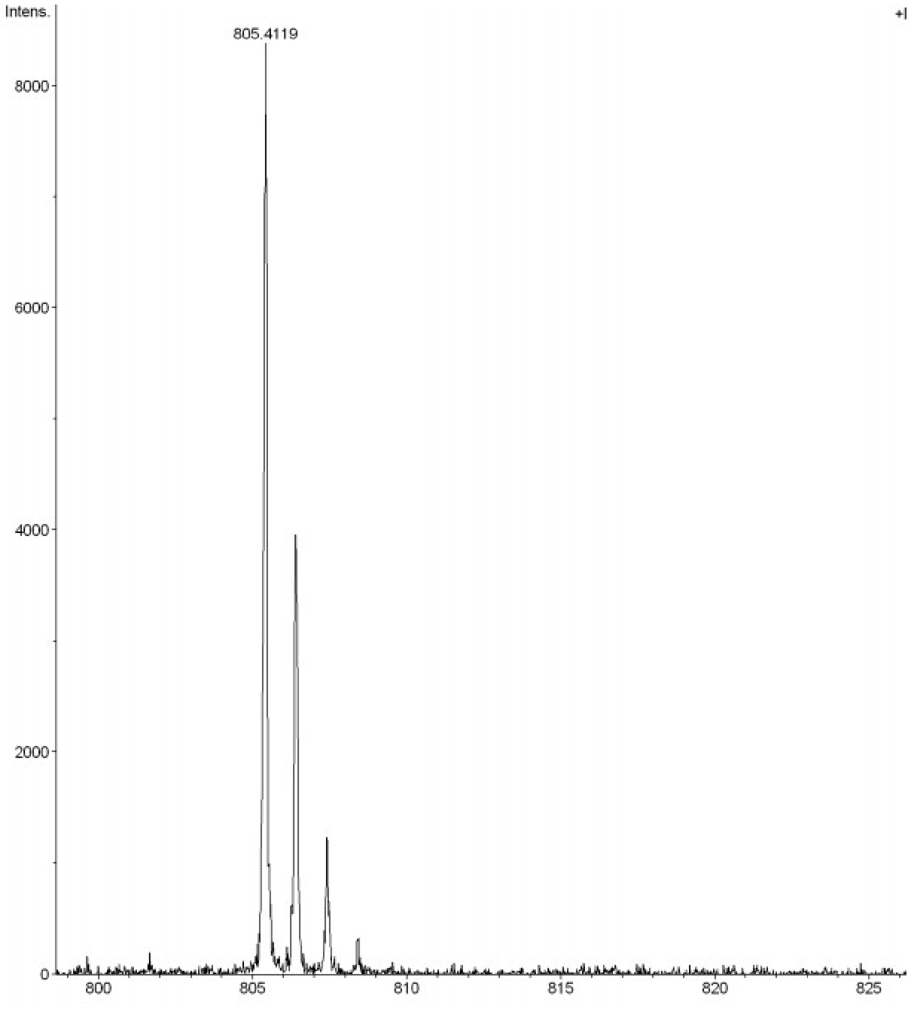


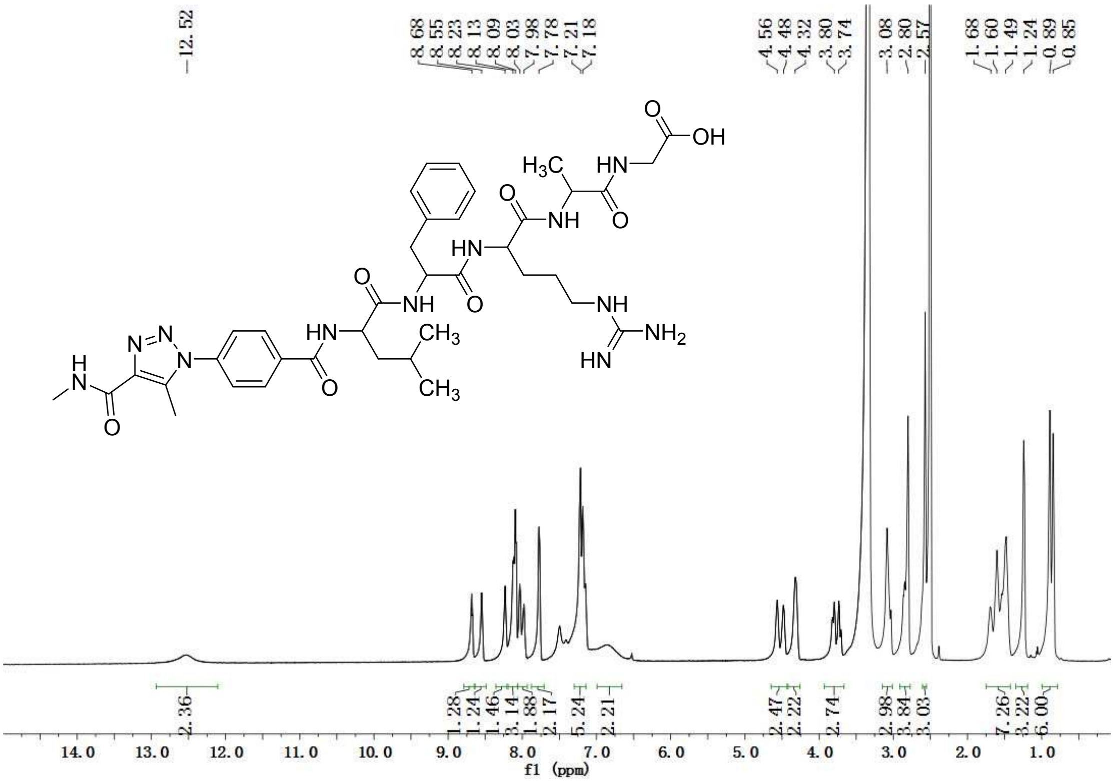
A13-B20



ESI-HRMS analysis of the peptide 3x

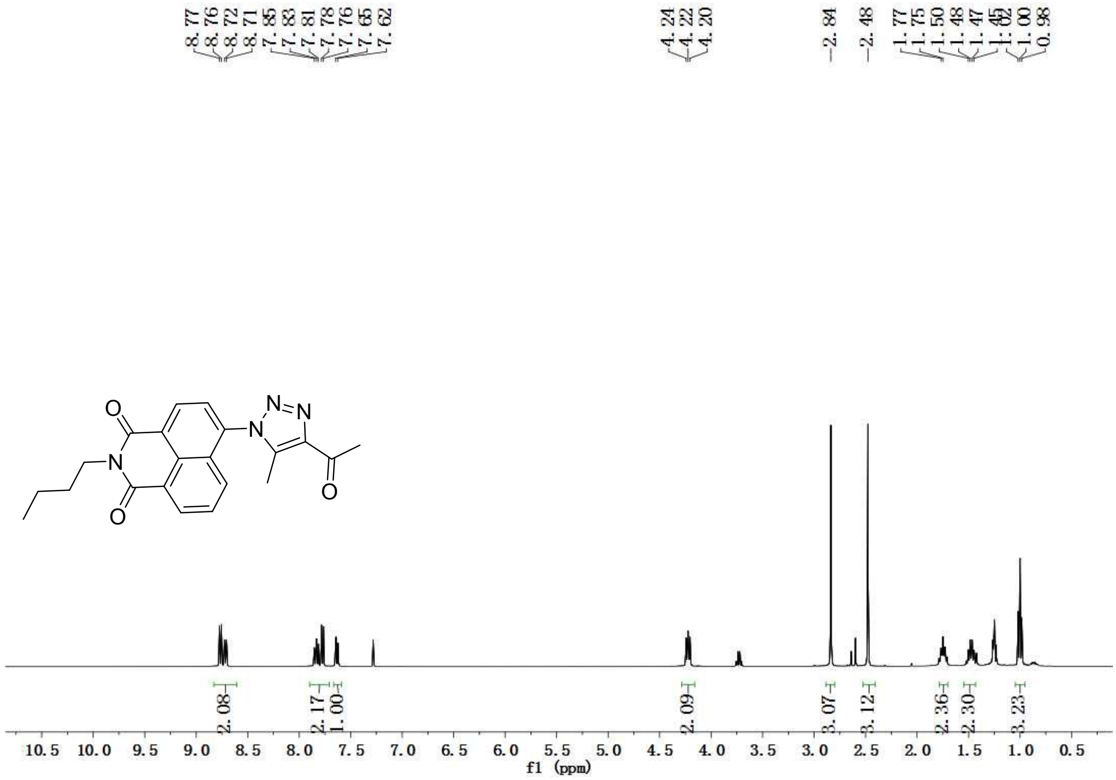


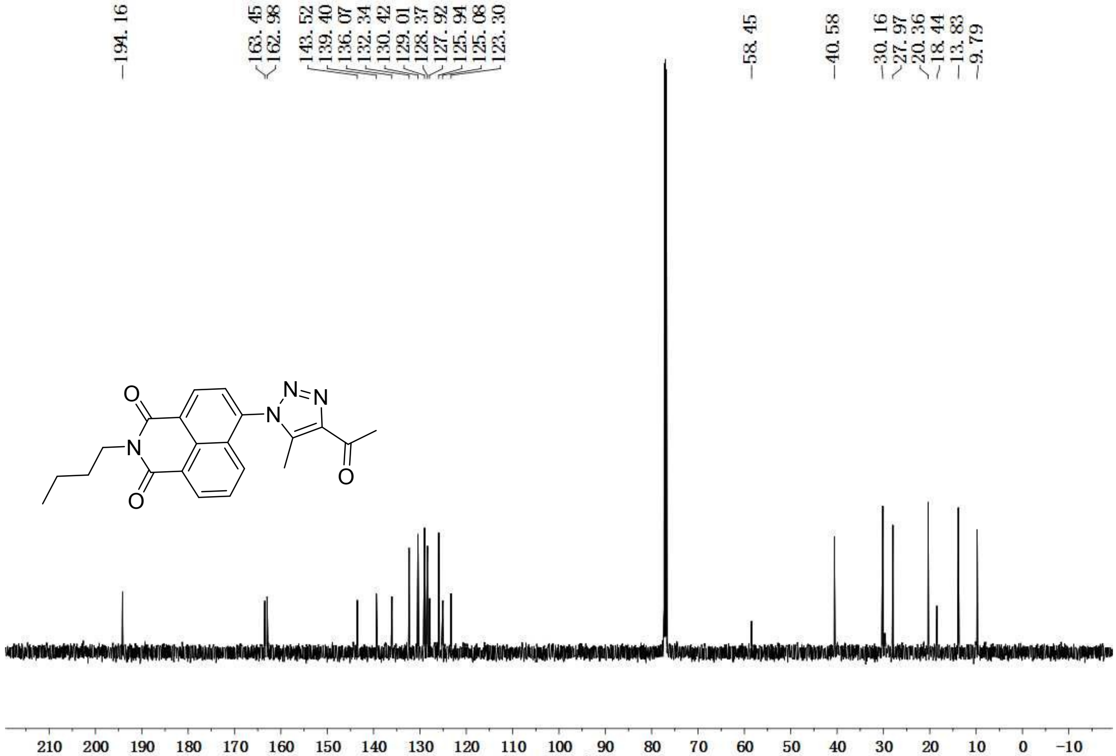
Copies of ^{1}H NMR spectrums for compounds 3x



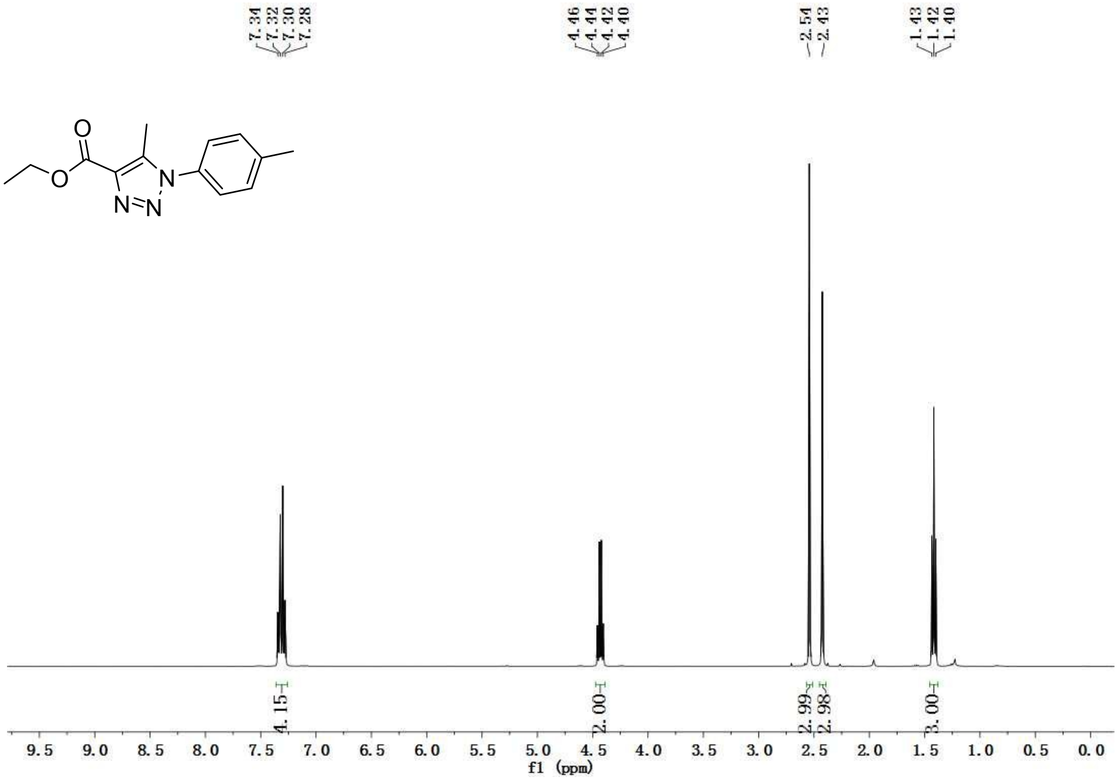
Copies of ^{1}H NMR and ^{13}C NMR spectrums for compounds 3a-3w

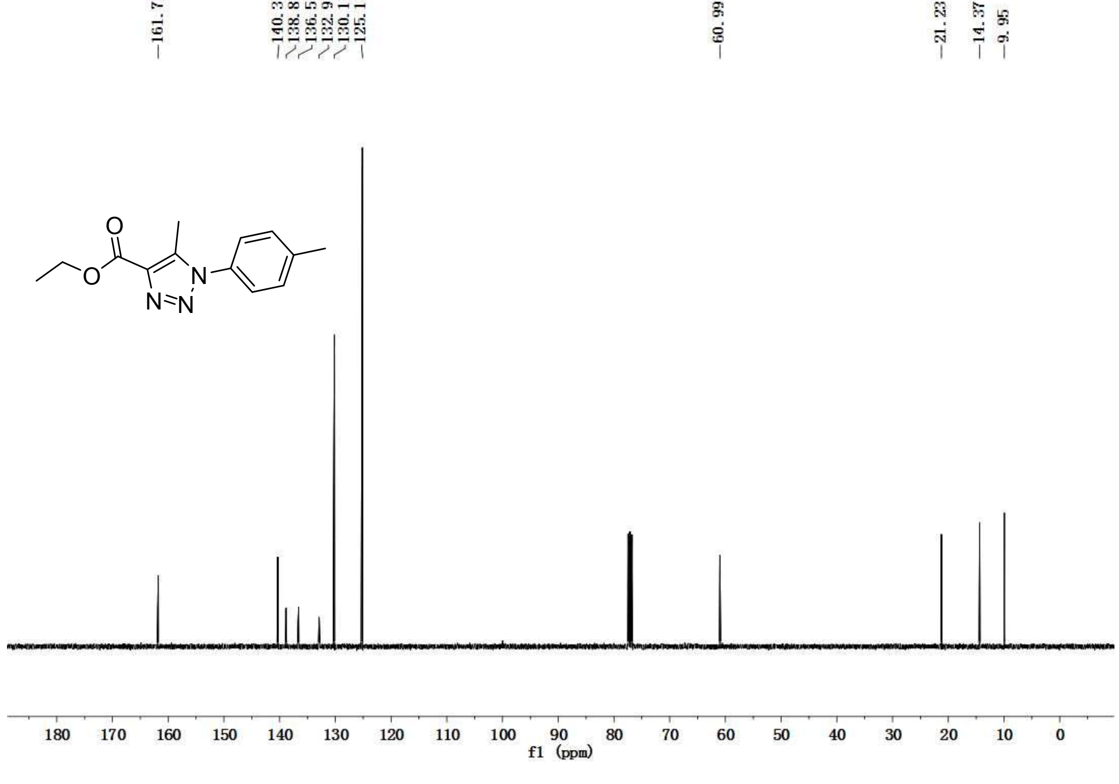
Compounds 3a ^{1}H NMR, ^{13}C NMR



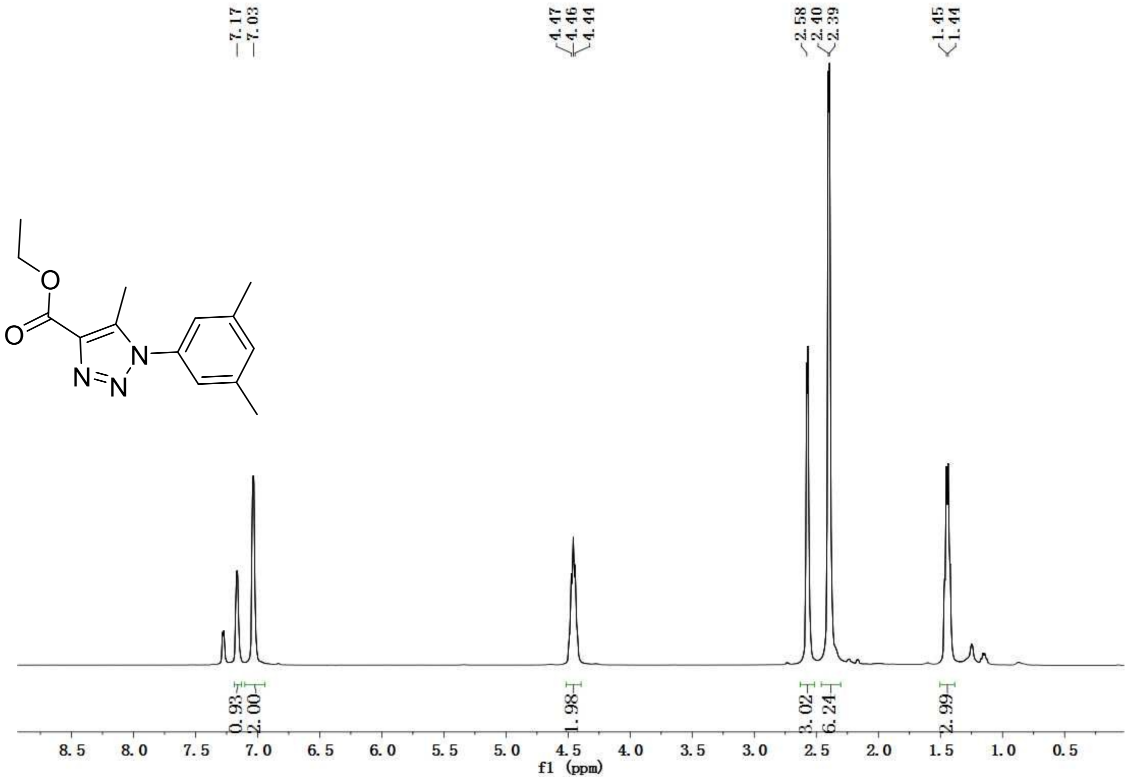


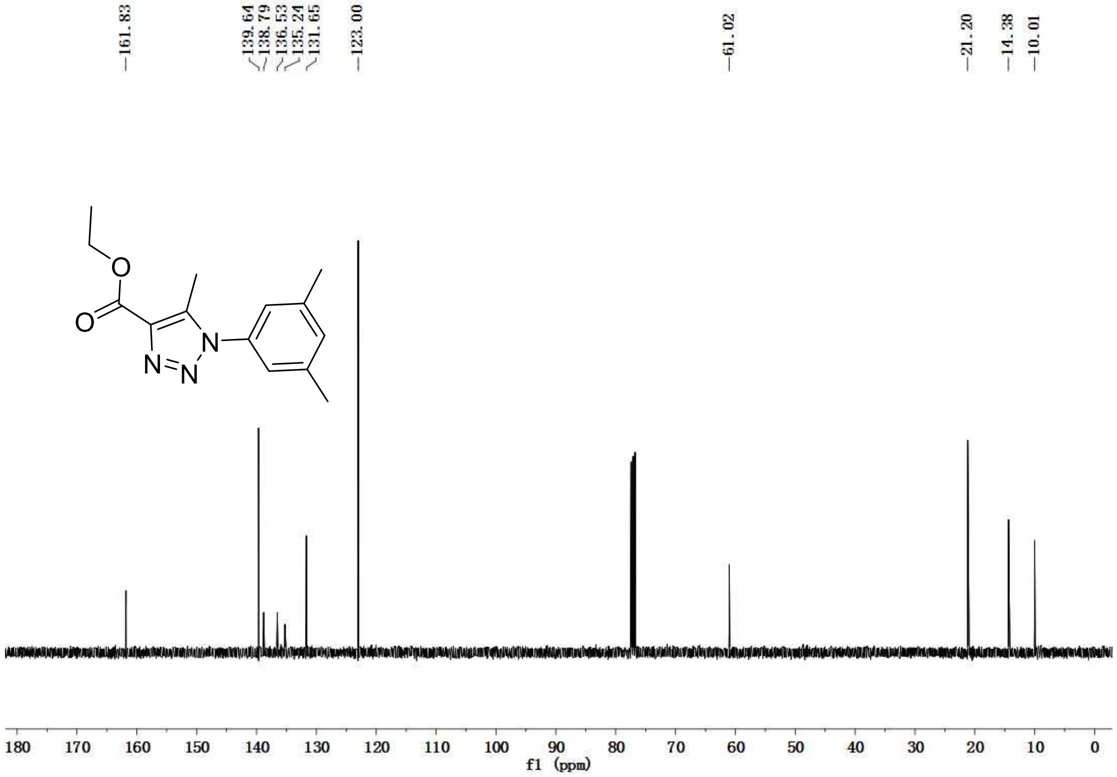
Compounds 3b ^{1}H NMR, ^{13}C NMR



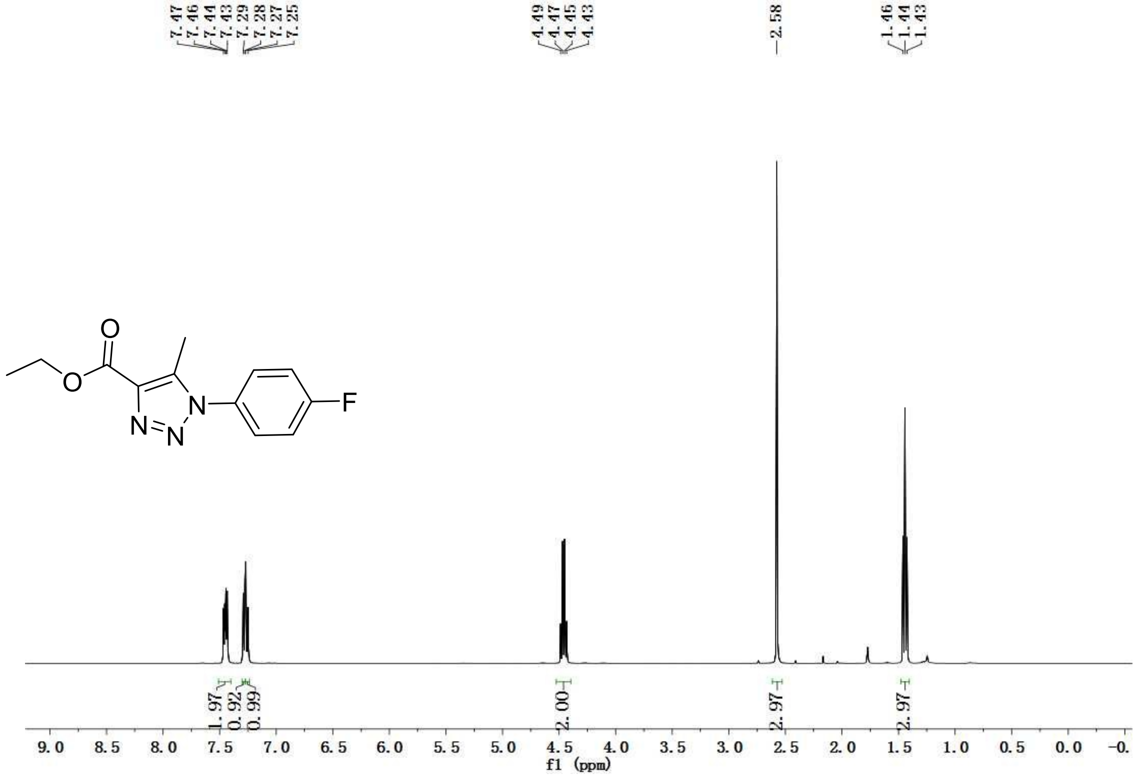


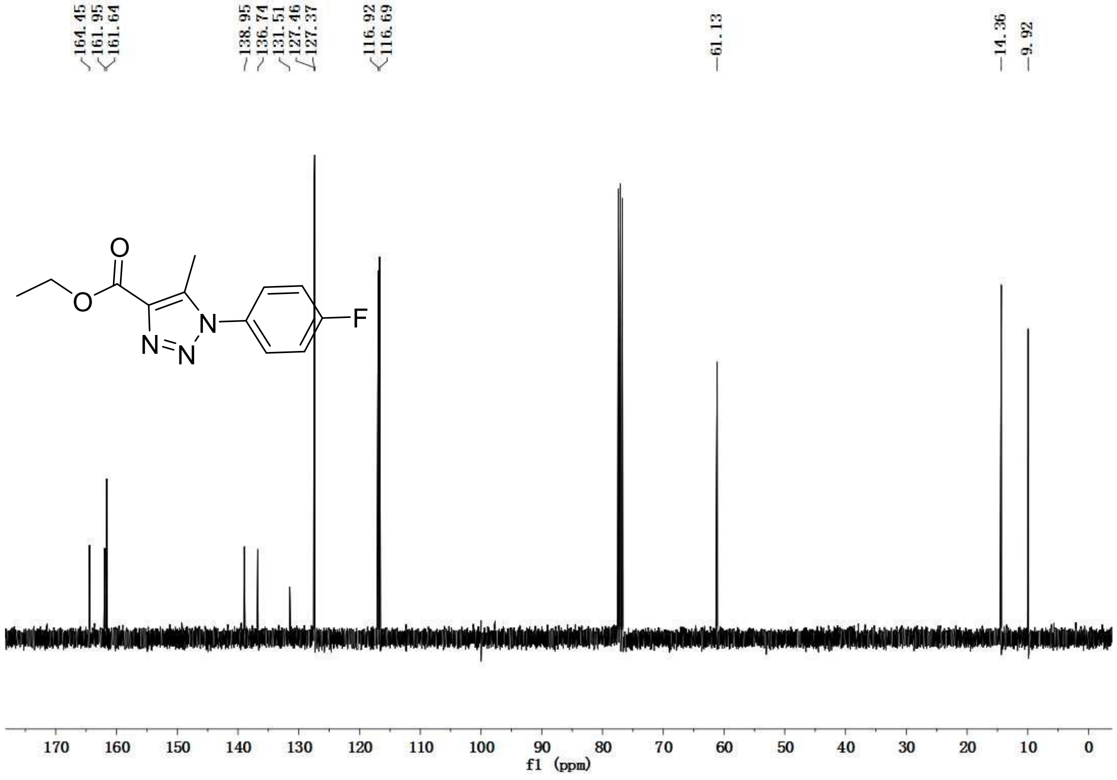
Compounds 3c ^{1}H NMR, ^{13}C NMR



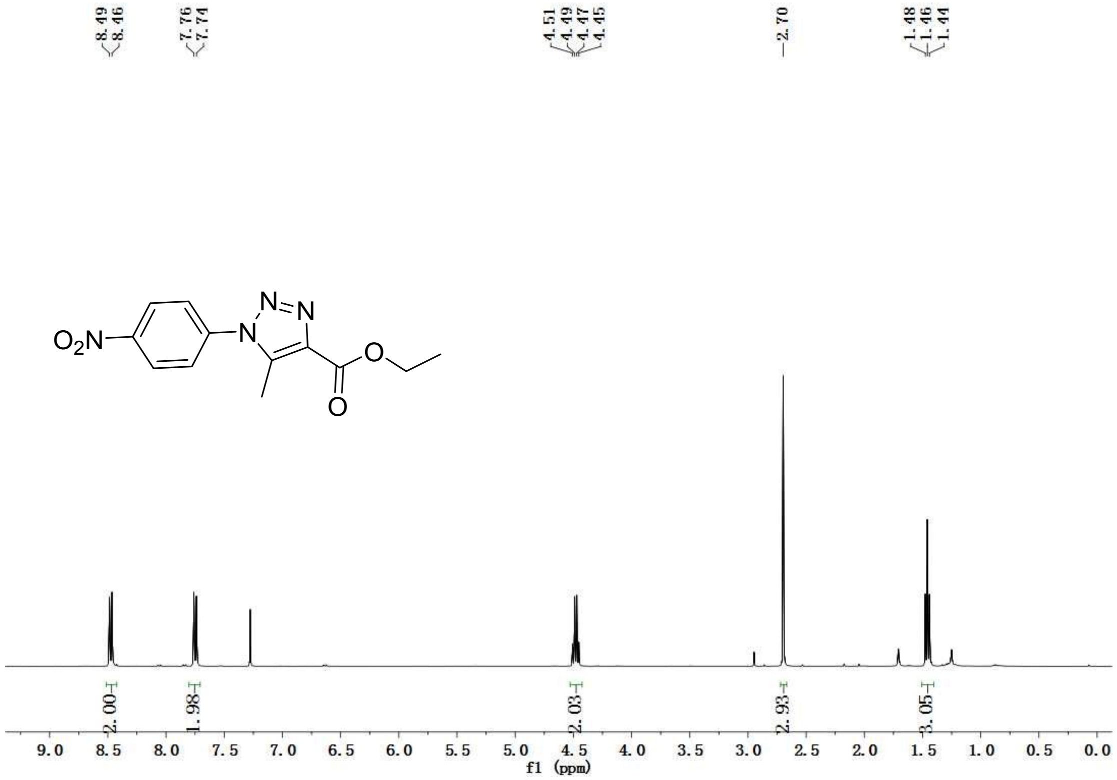


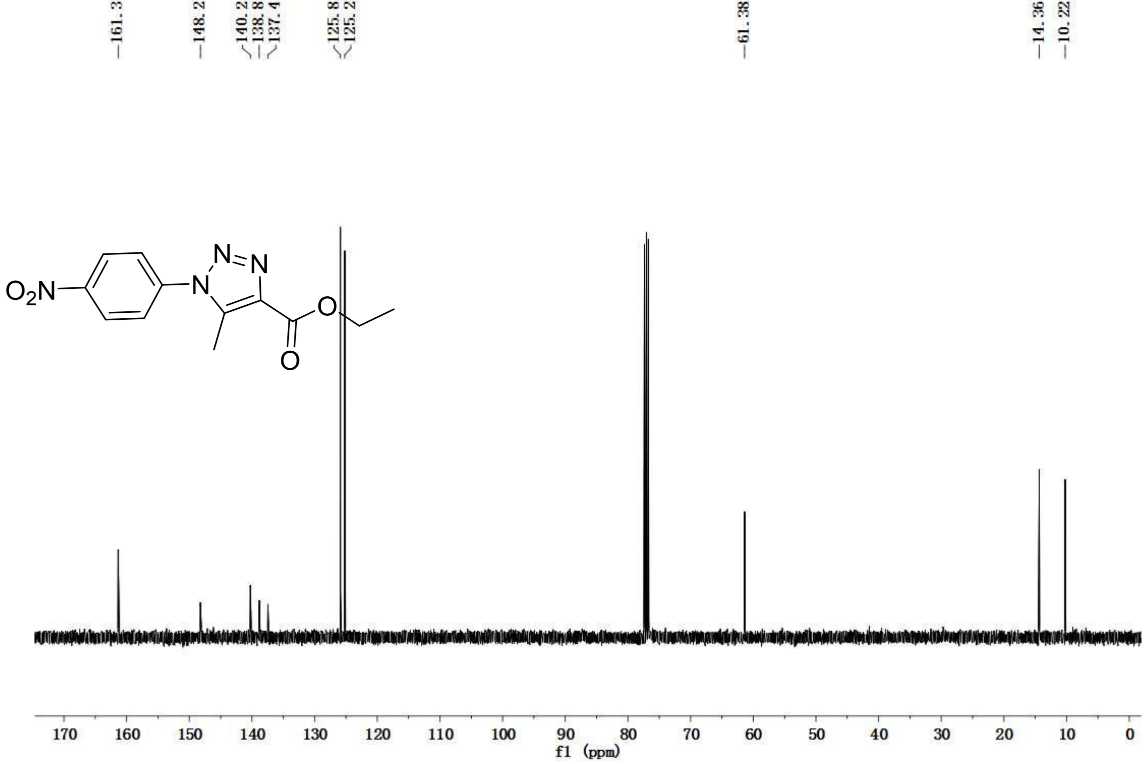
Compounds 3d ^1H NMR, ^{13}C NMR



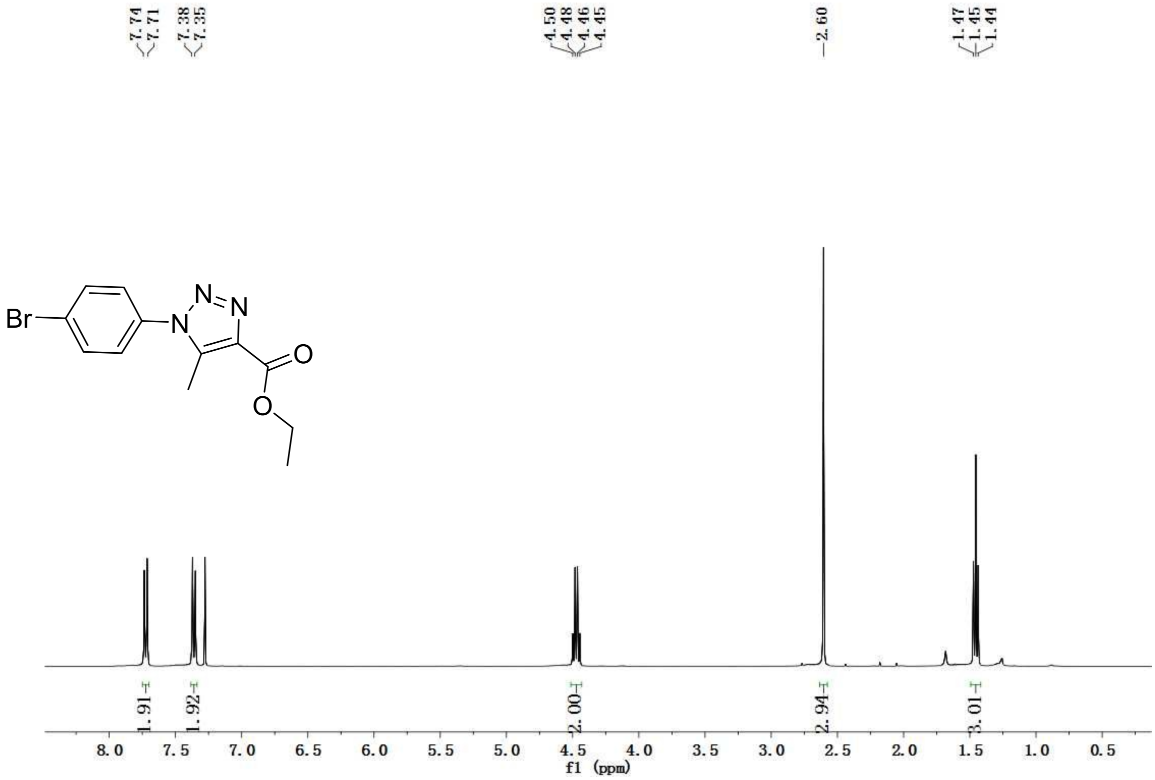


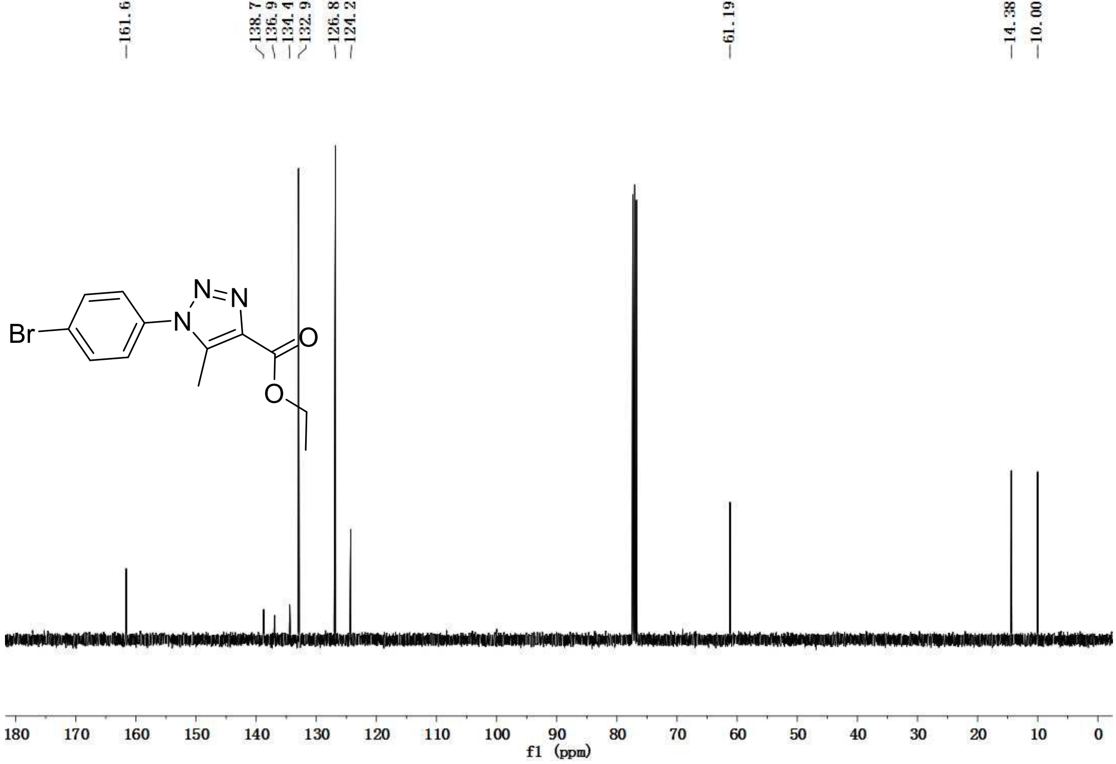
Compounds 3e ^{1}H NMR, ^{13}C NMR



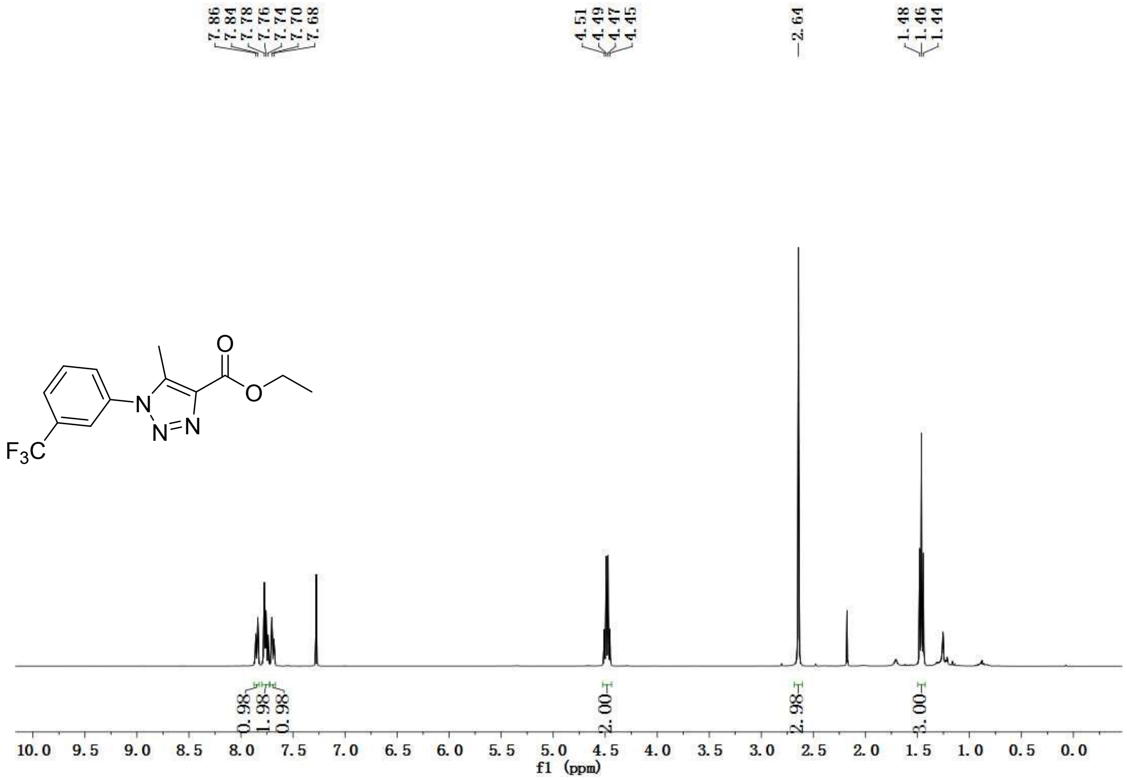


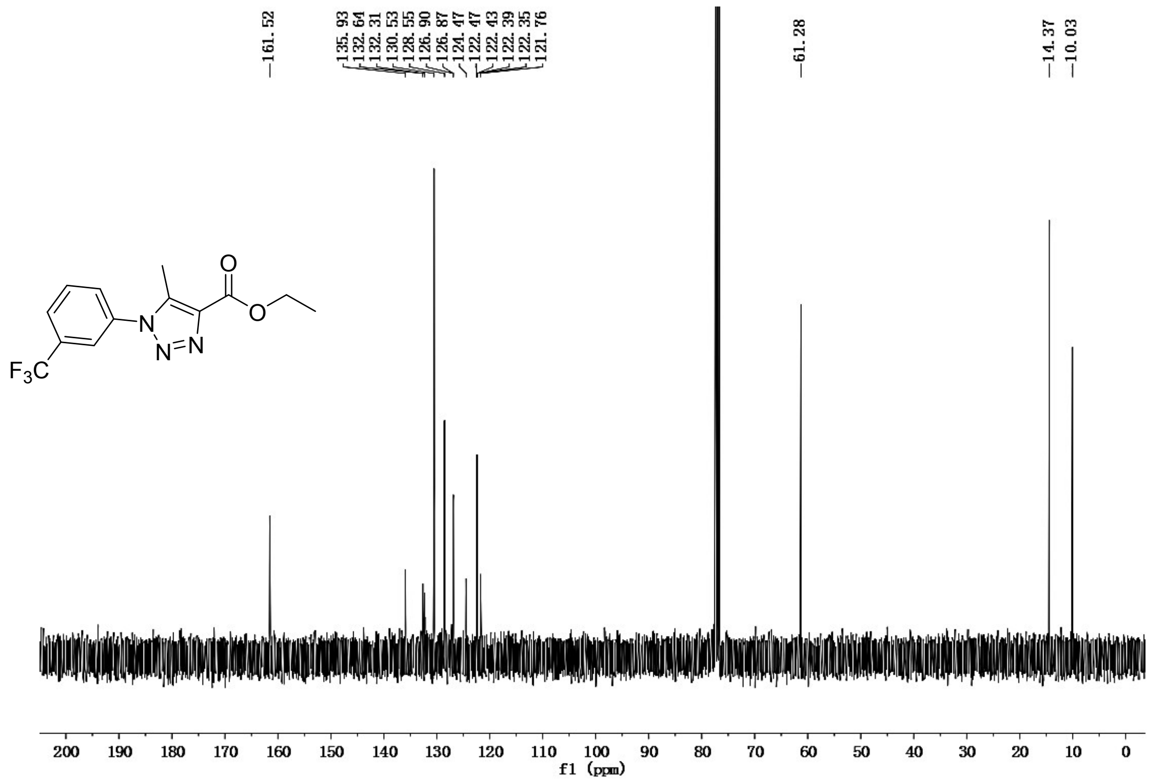
Compounds 3f ^{1}H NMR, ^{13}C NMR



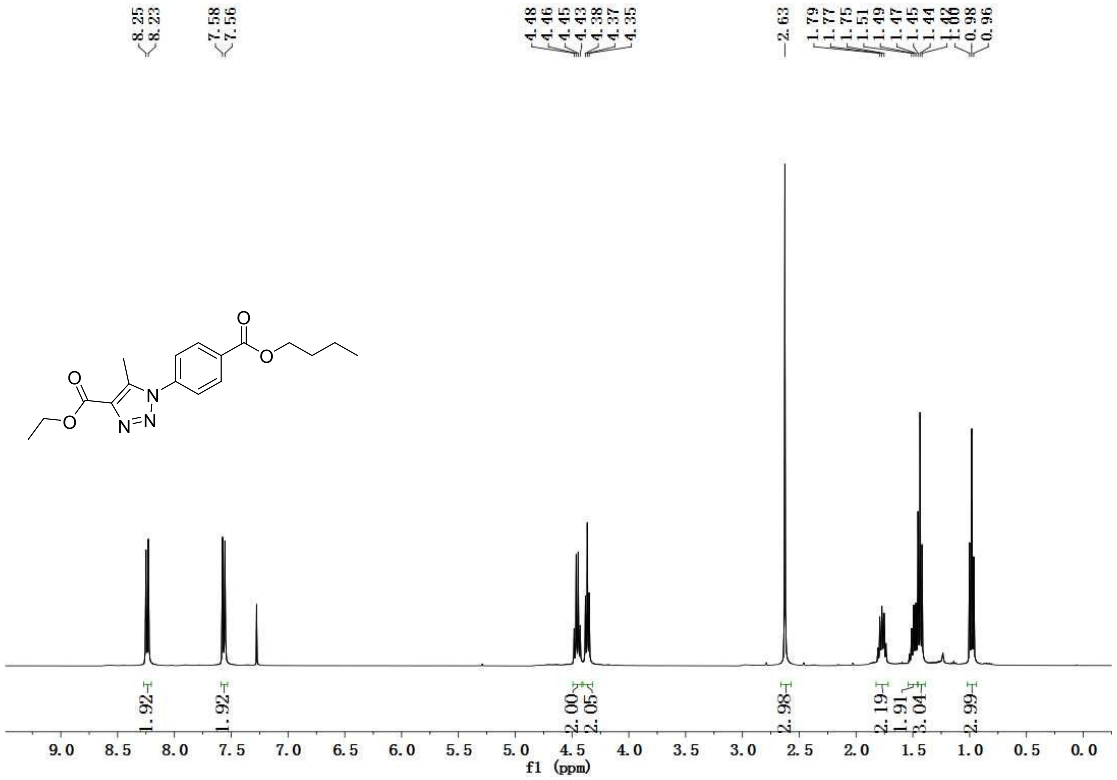


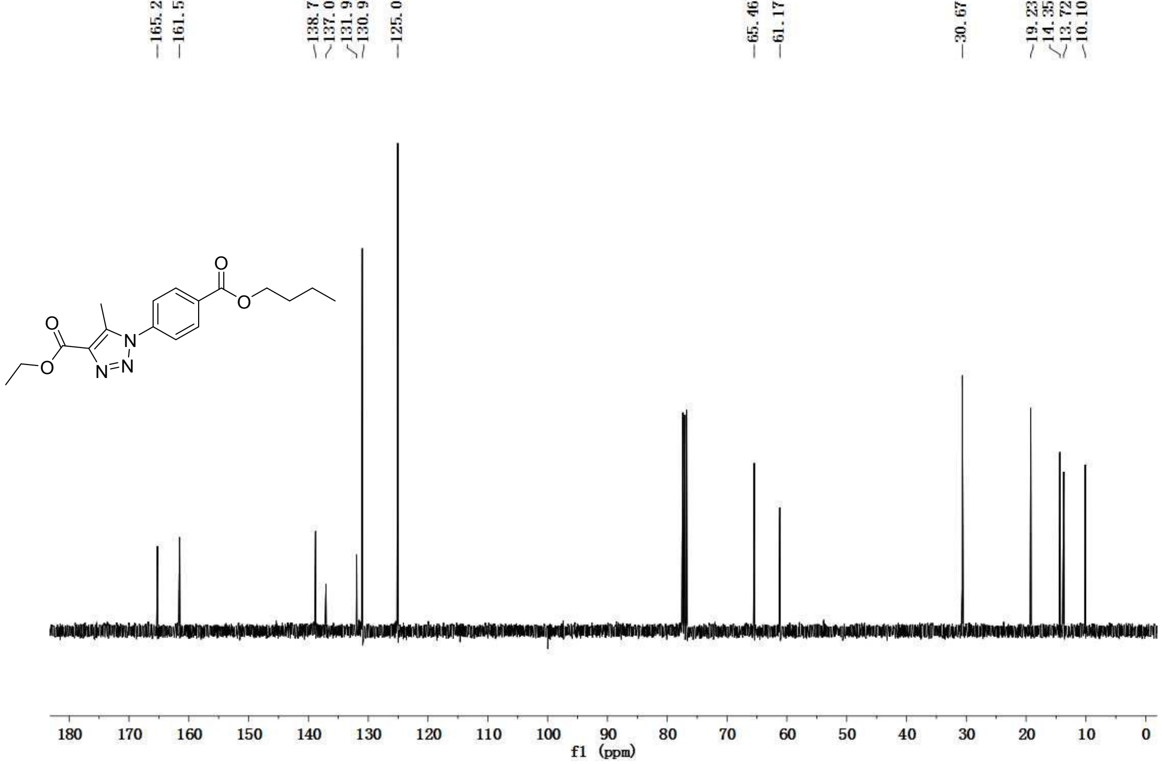
Compounds 3g ^{1}H NMR, ^{13}C NMR



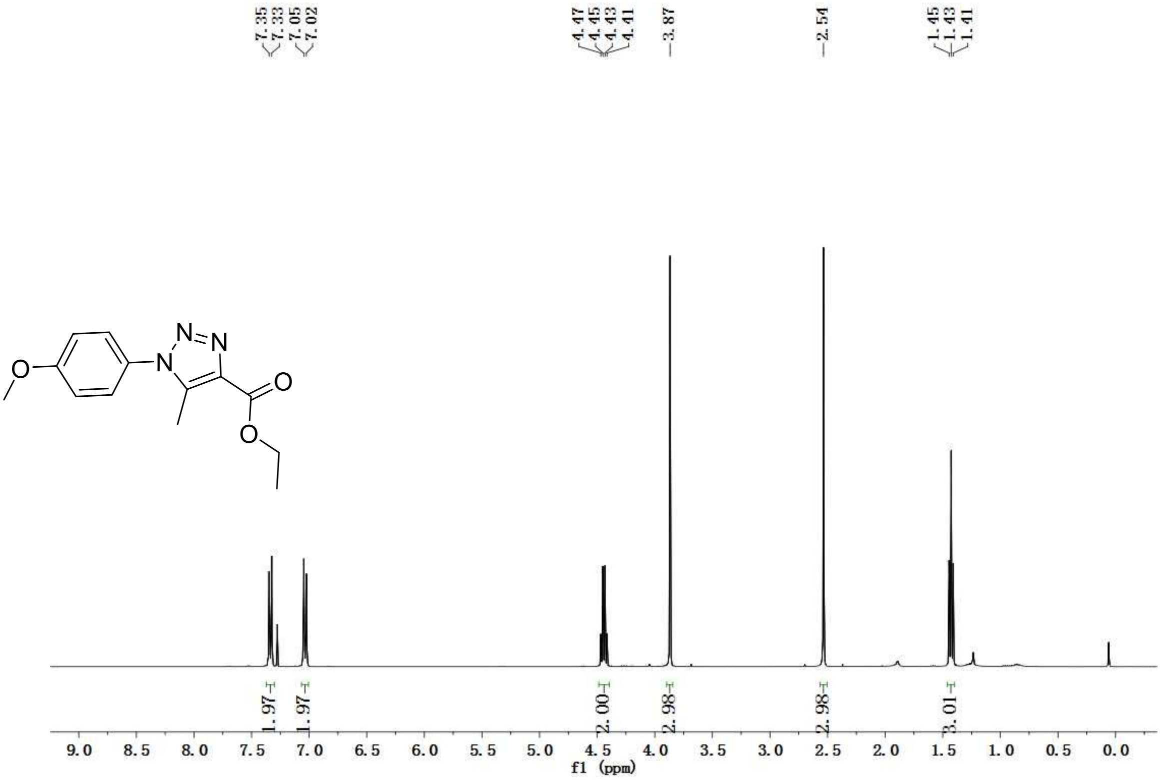


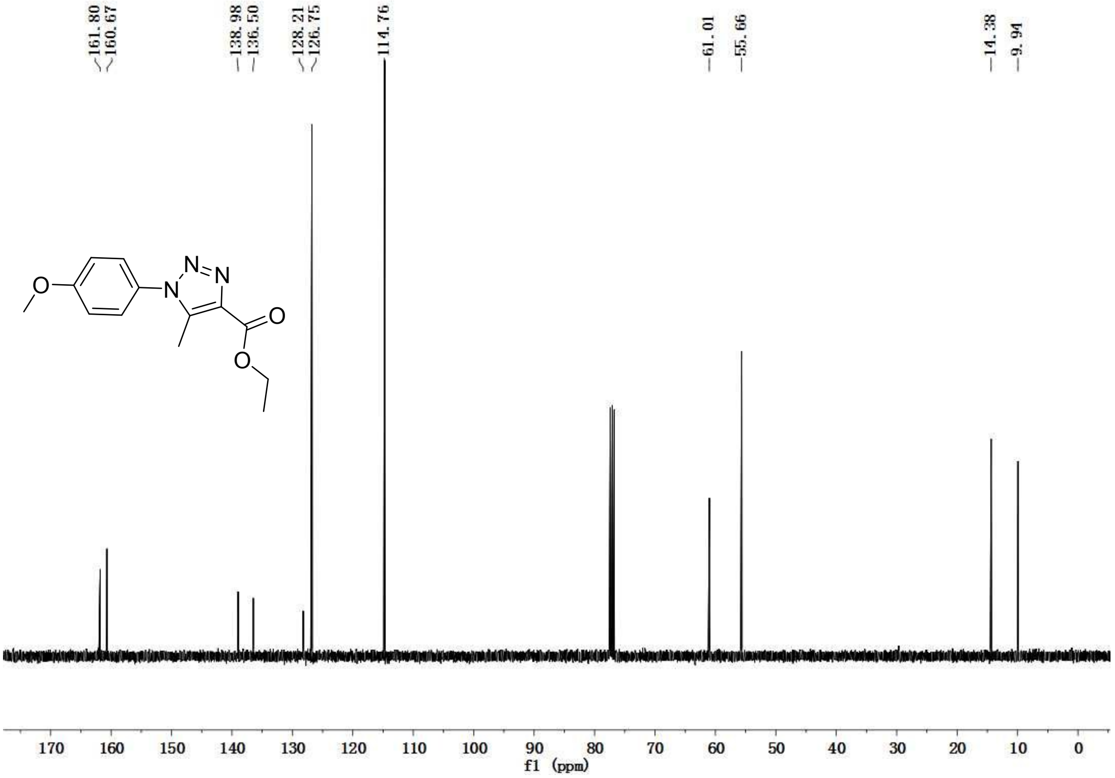
Compounds 3h ^{1}H NMR, ^{13}C NMR



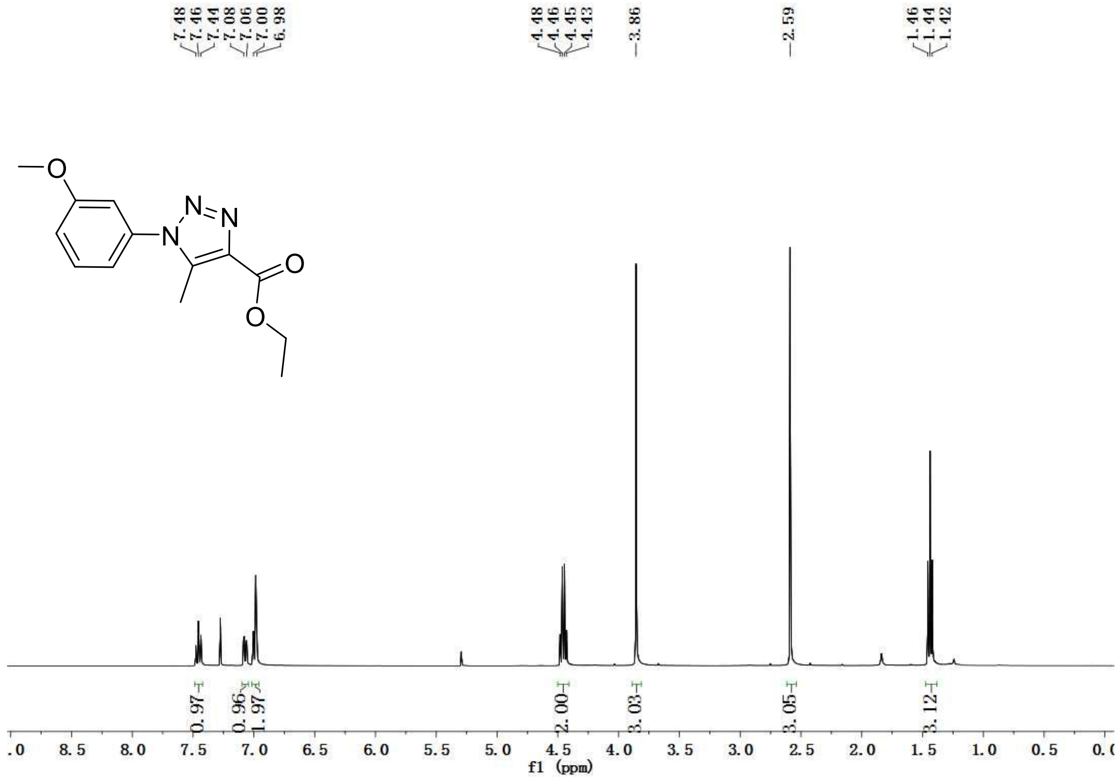


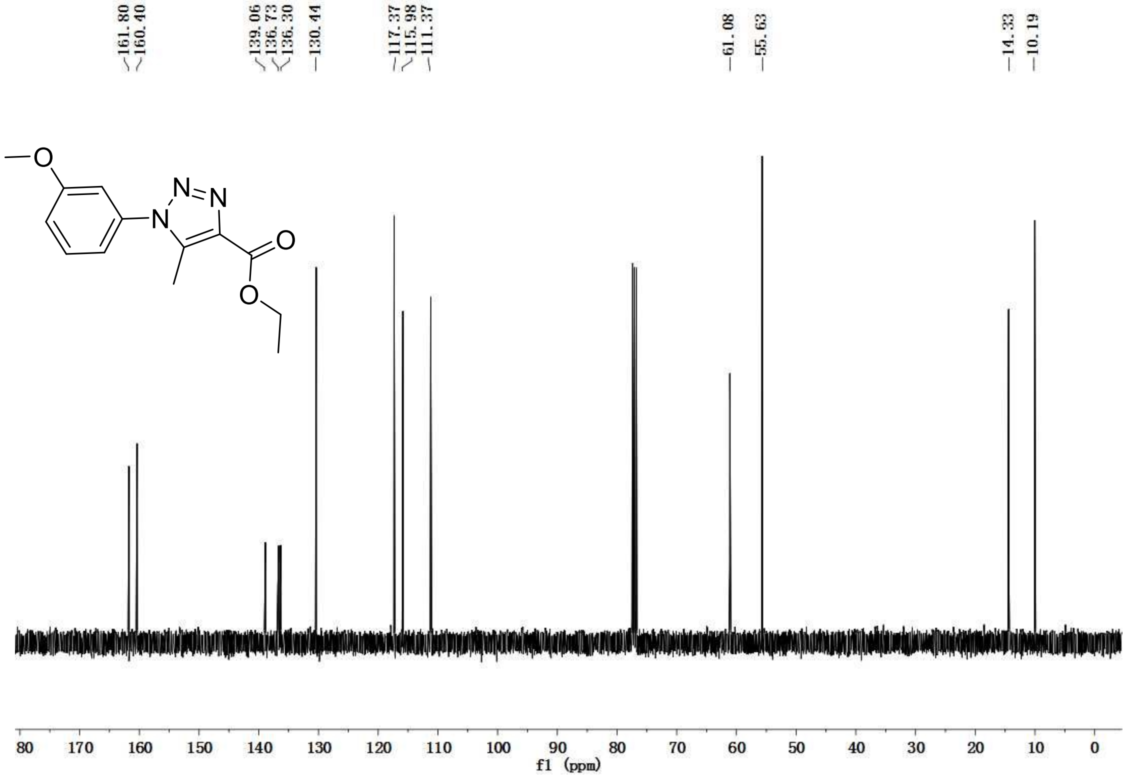
Compounds 3i ^{1}H NMR, ^{13}C NMR



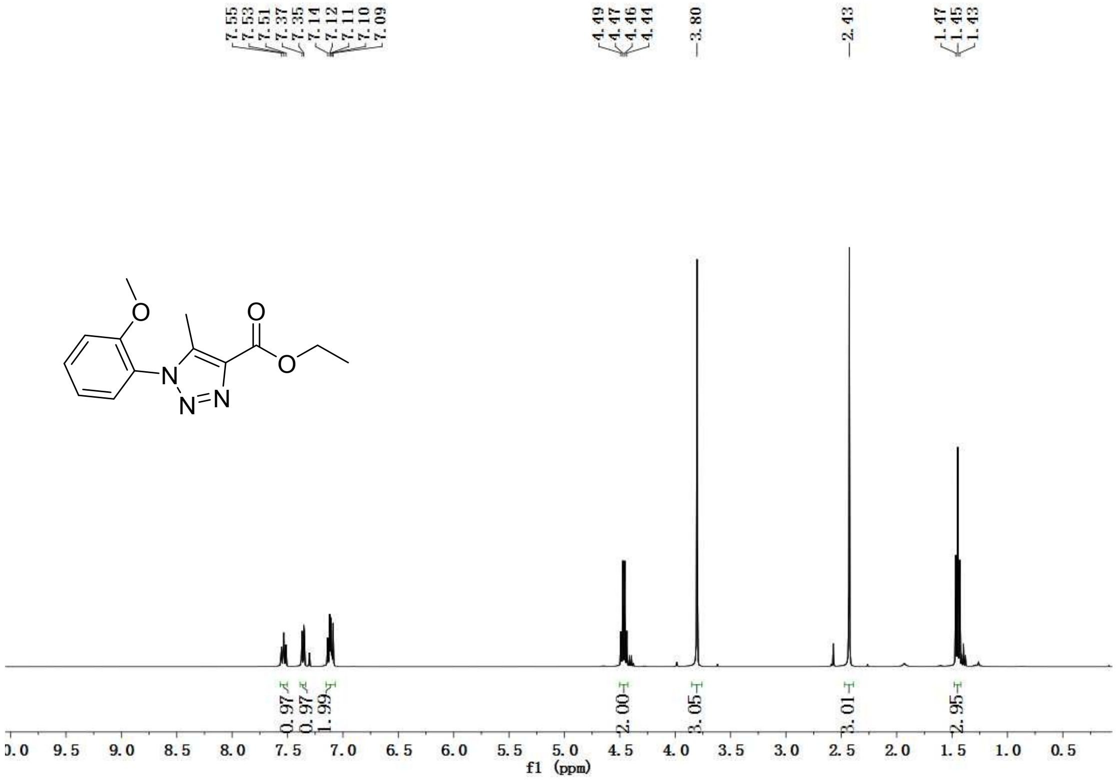


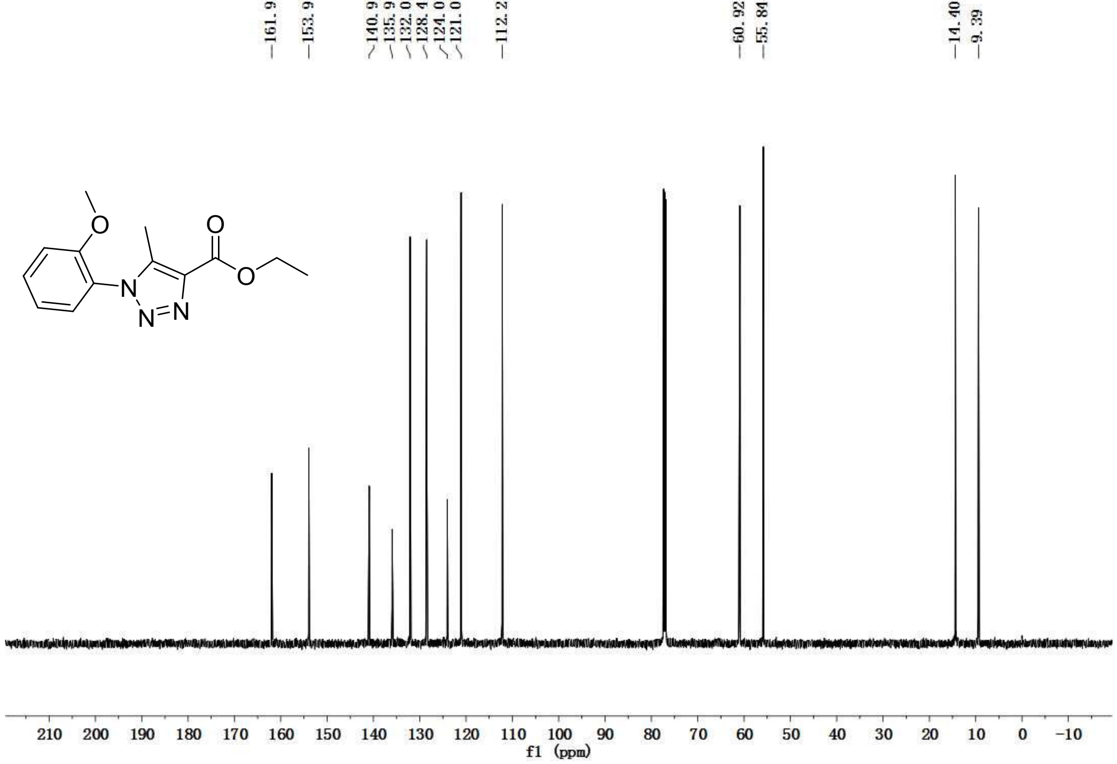
Compounds 3j ^{1}H NMR, ^{13}C NMR



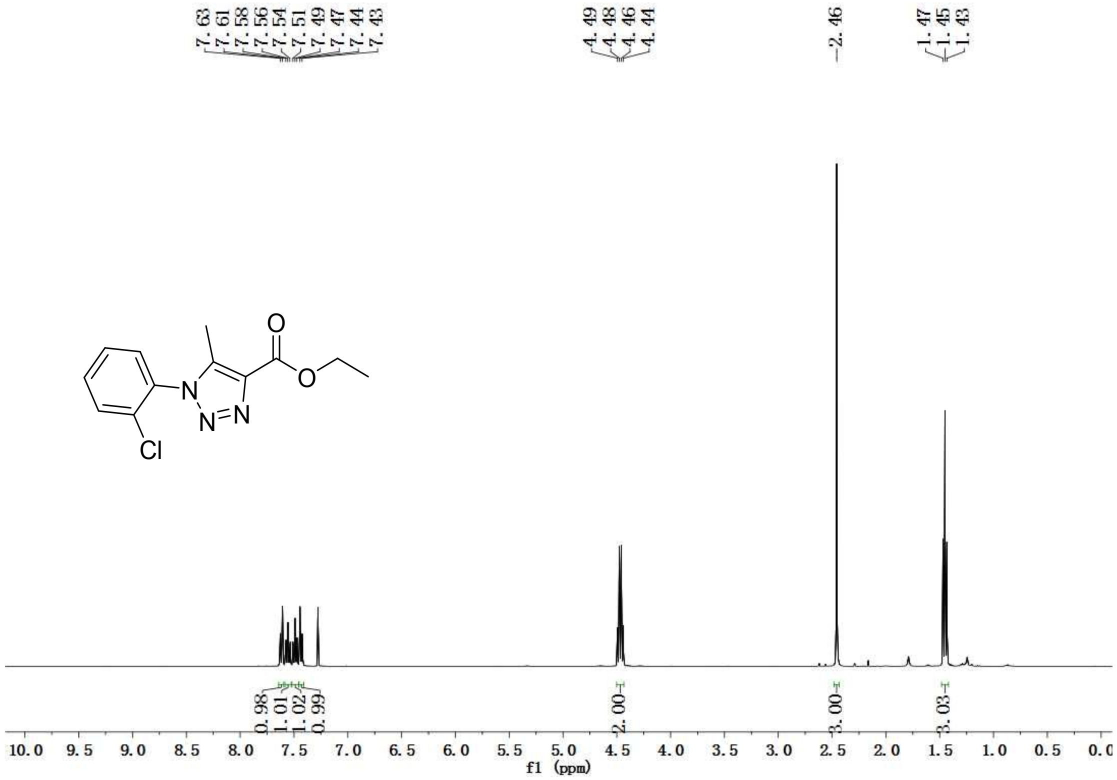


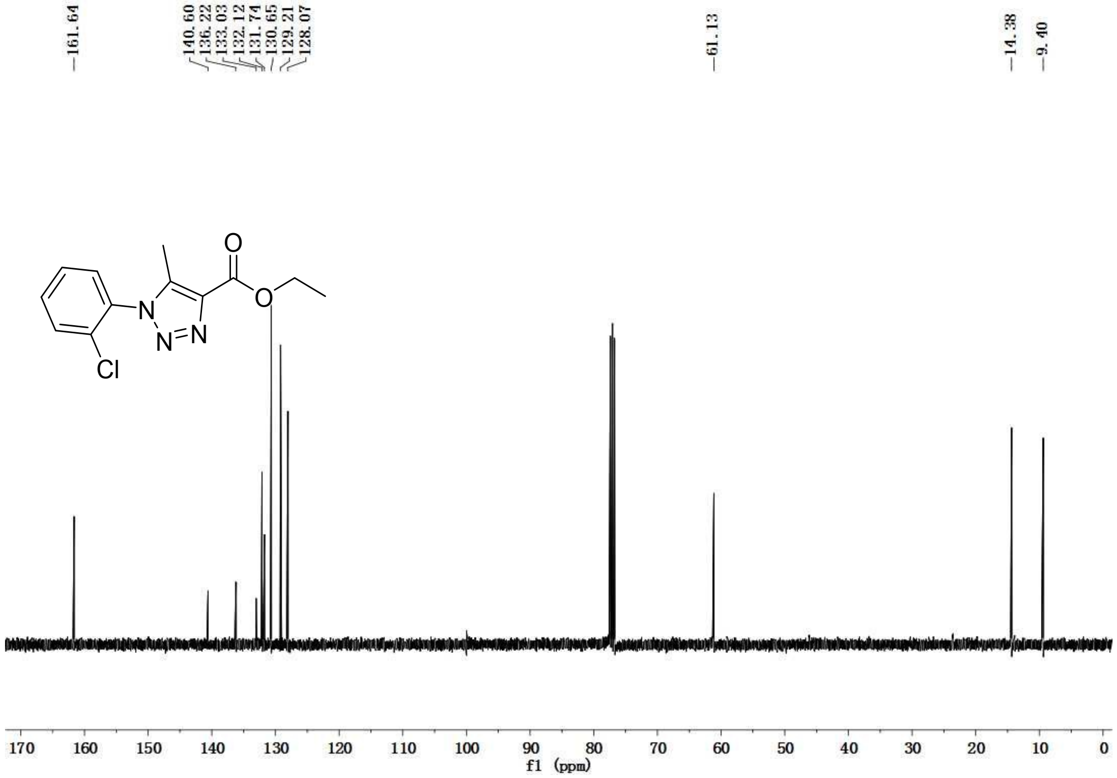
Compounds 3k ^{1}H NMR, ^{13}C NMR



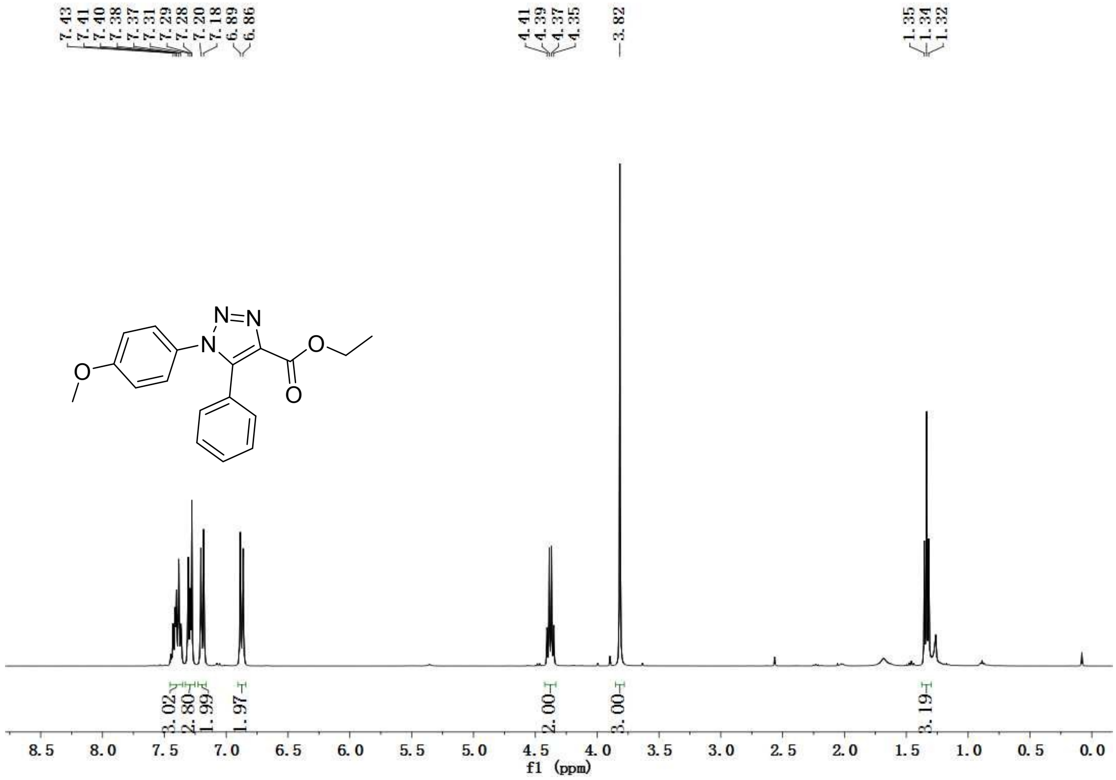


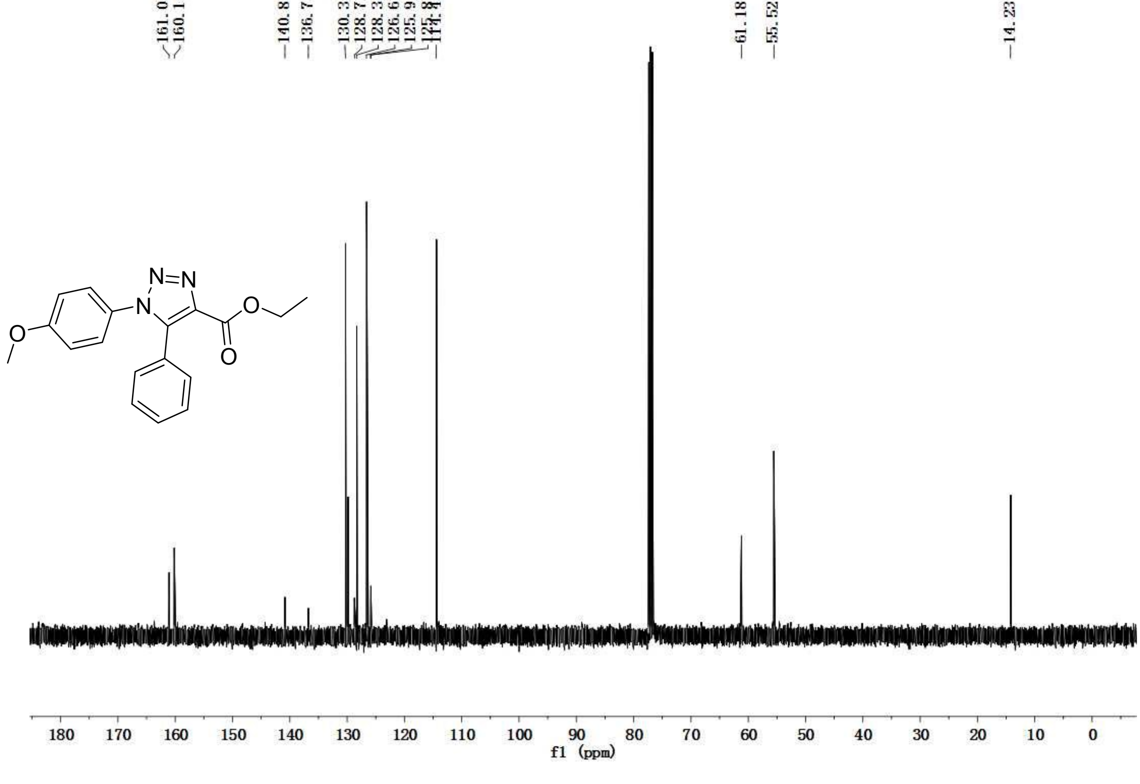
Compounds 3l ^{1}H NMR, ^{13}C NMR



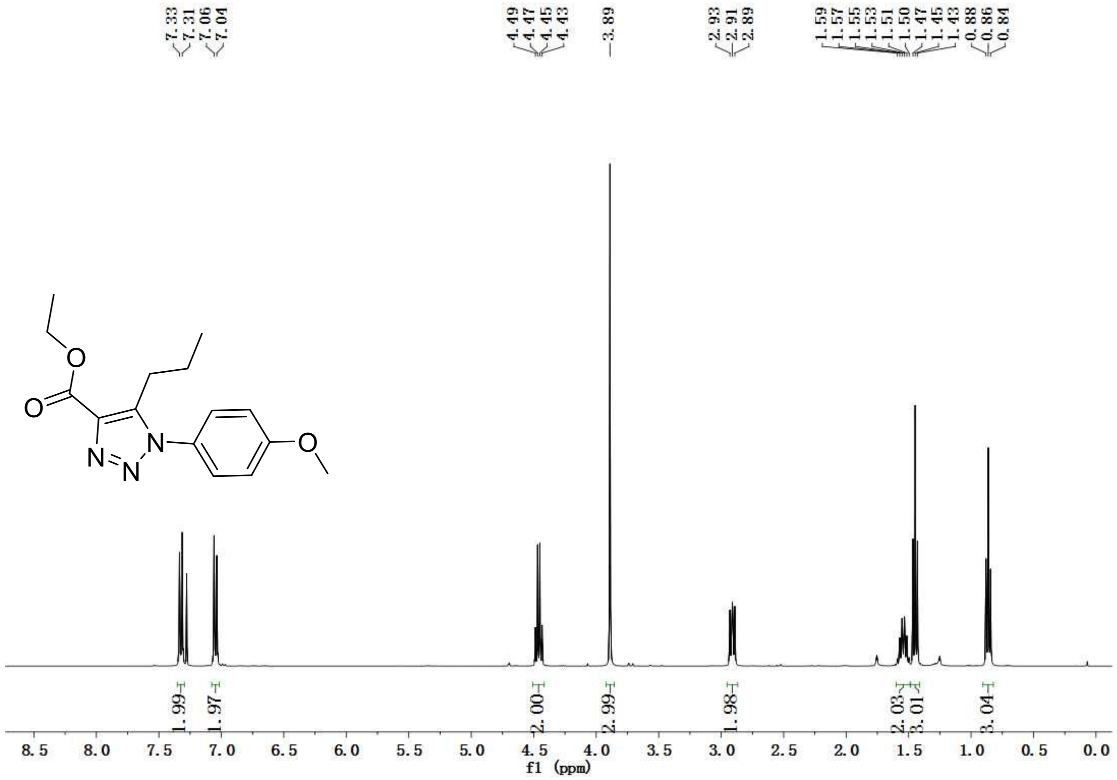


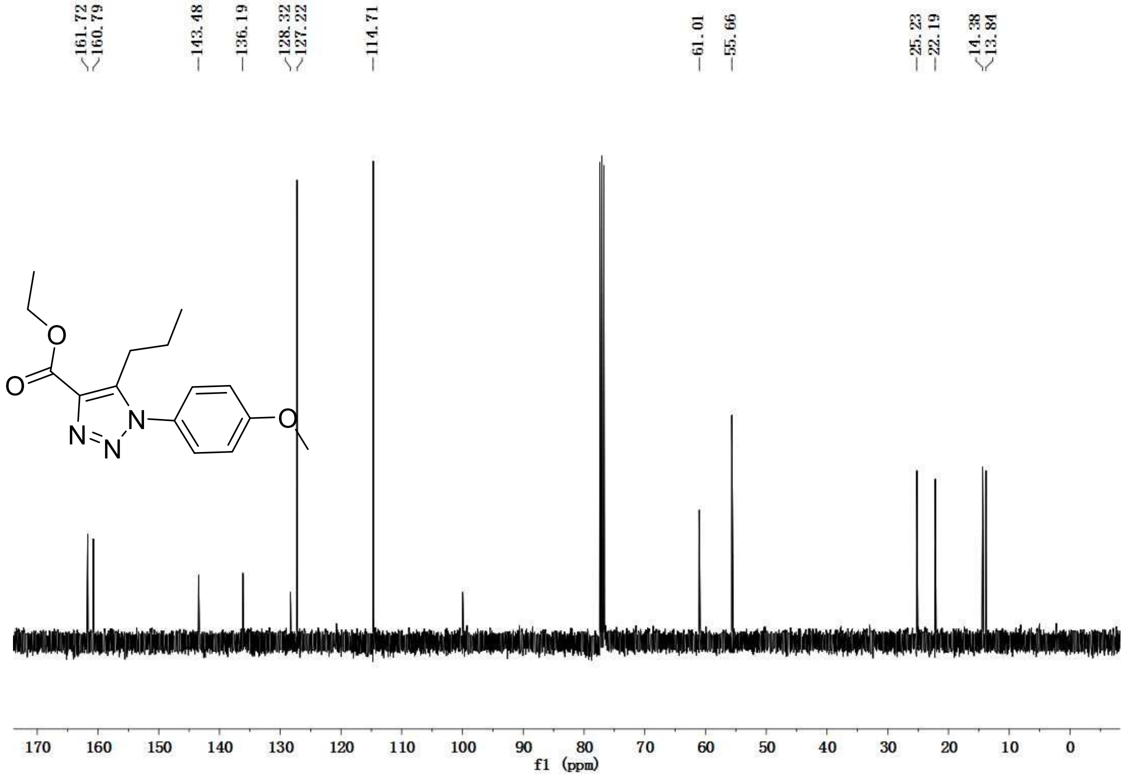
Compounds 3m ^{1}H NMR, ^{13}C NMR



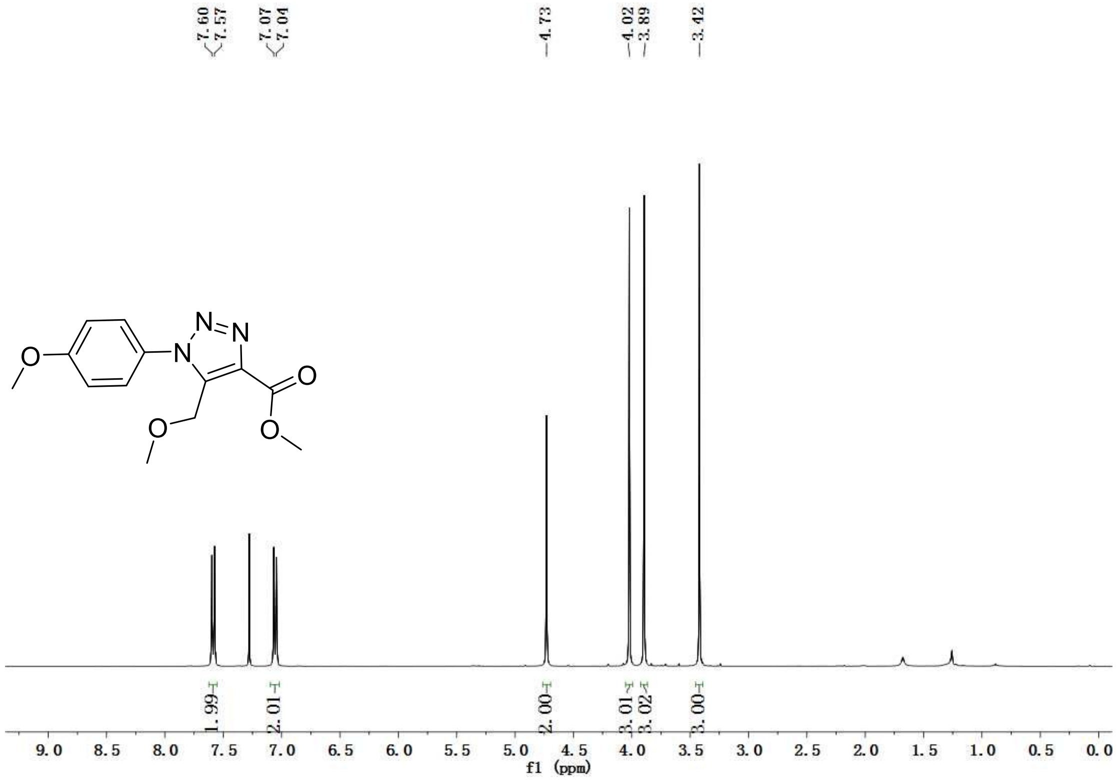


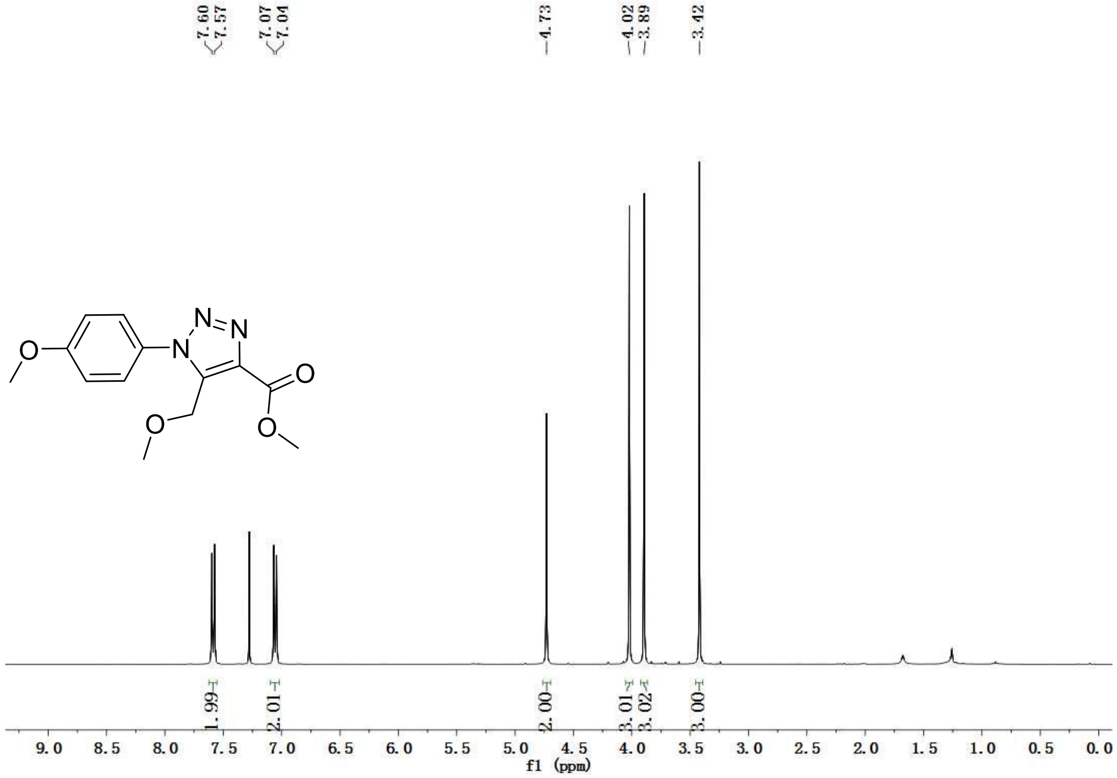
Compounds 3n ^{1}H NMR, ^{13}C NMR



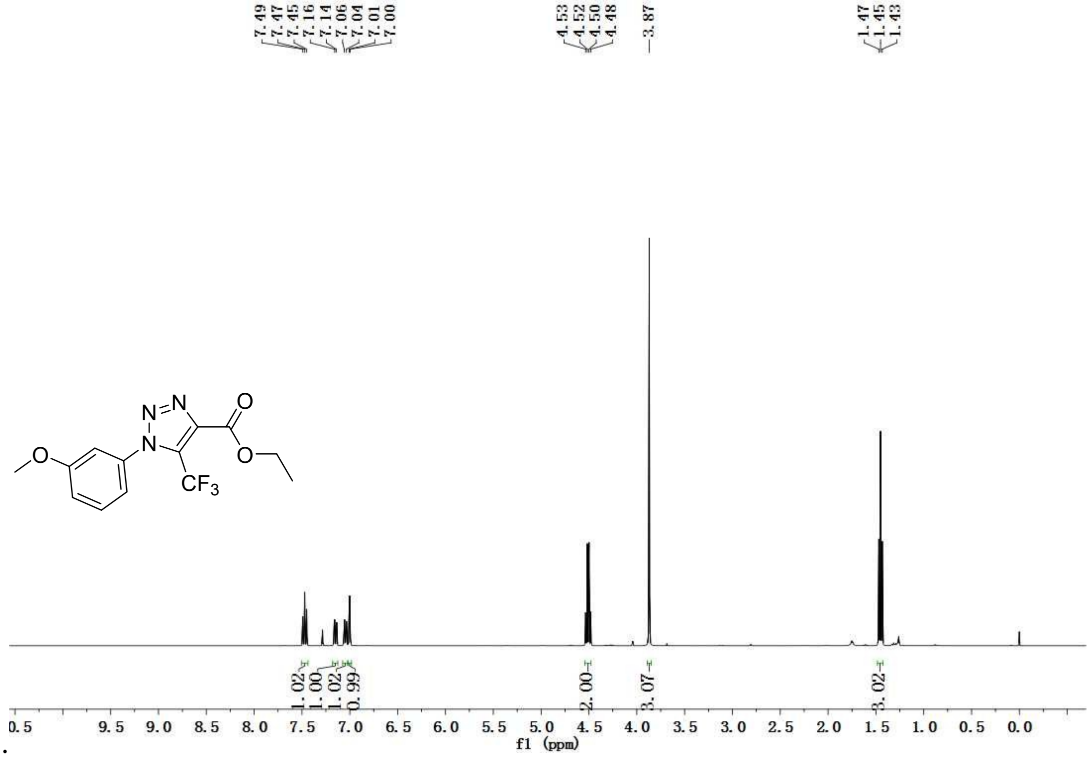


Compounds 3o ^{1}H NMR, ^{13}C NMR





Compounds 3p ^{1}H NMR, ^{13}C NMR



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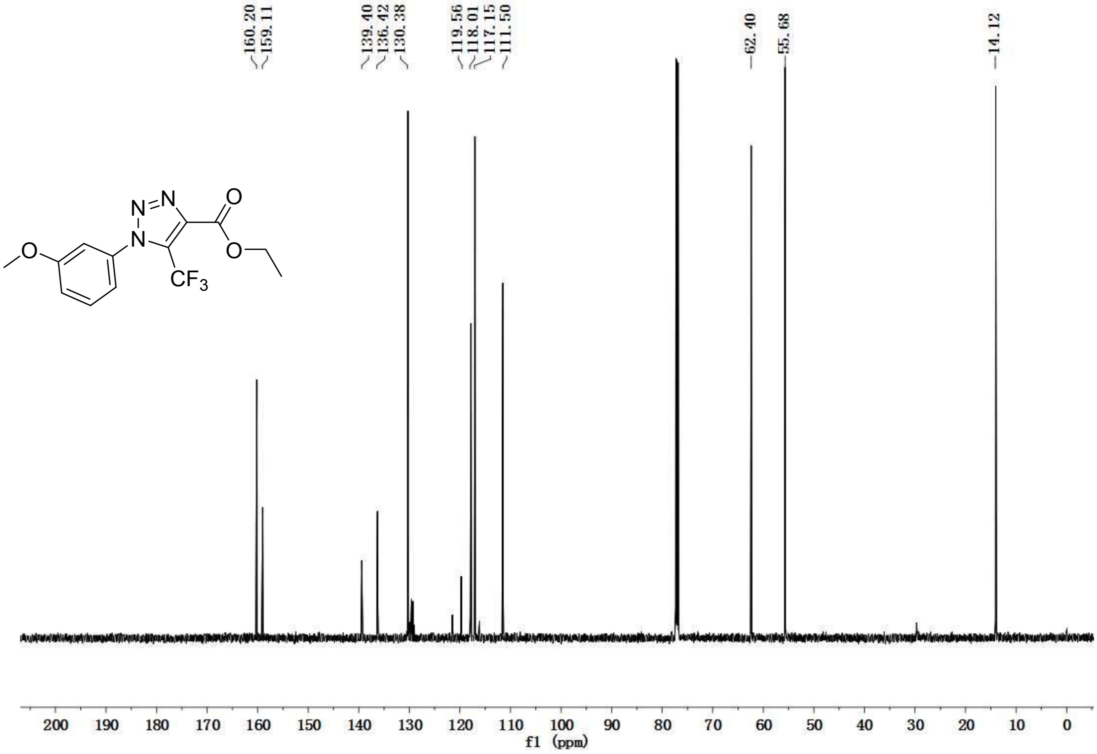
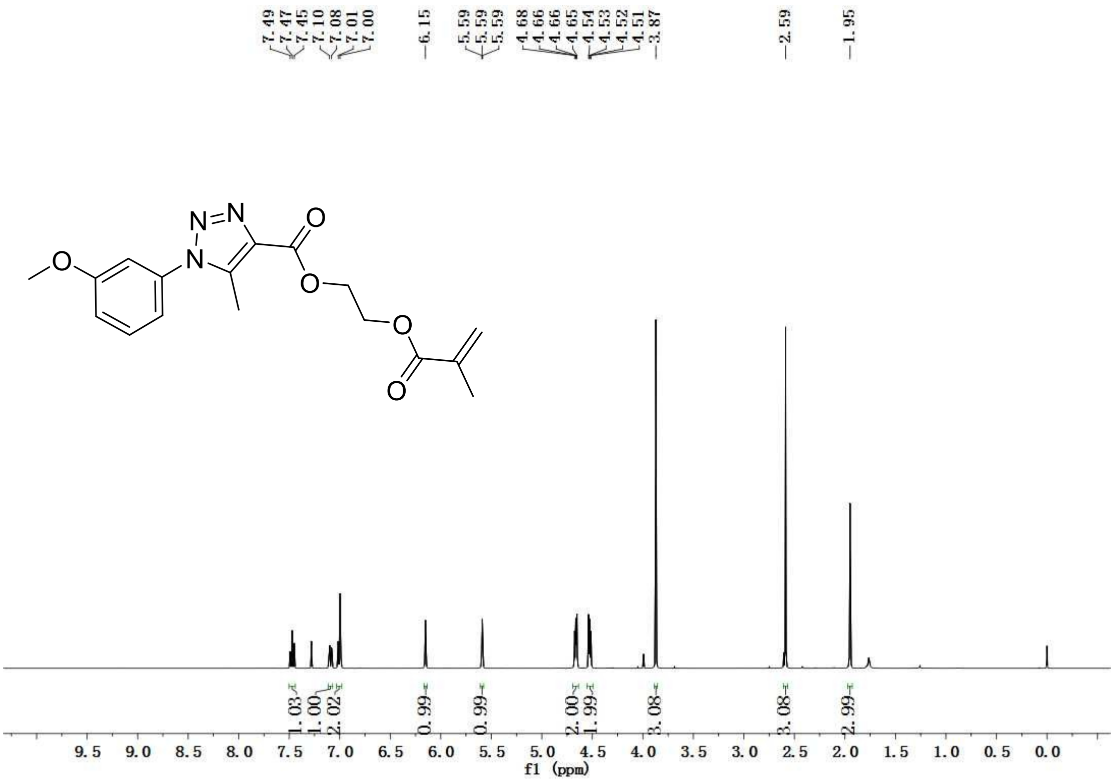
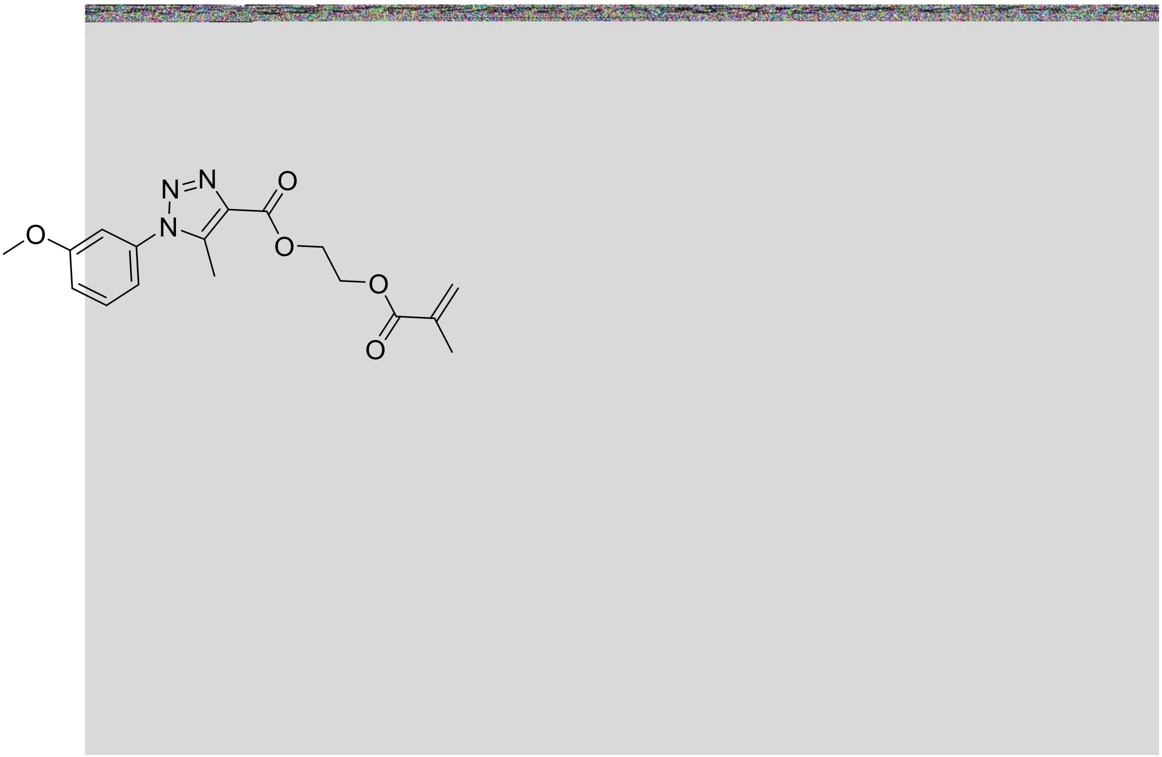
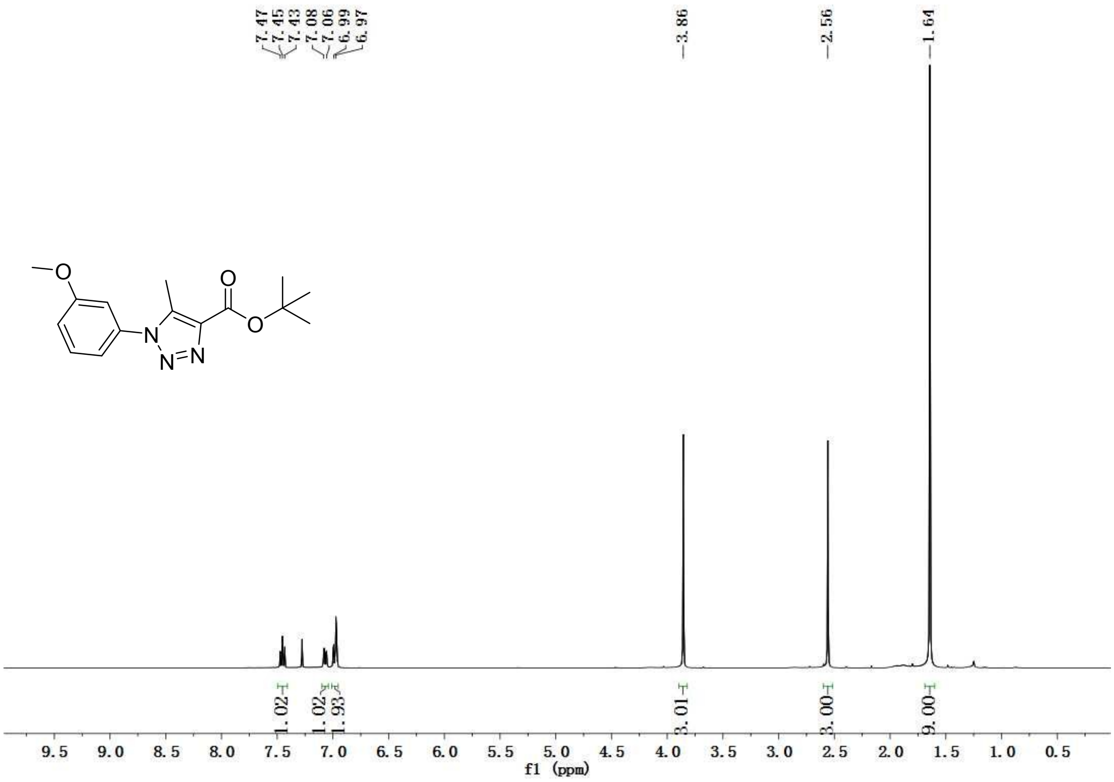


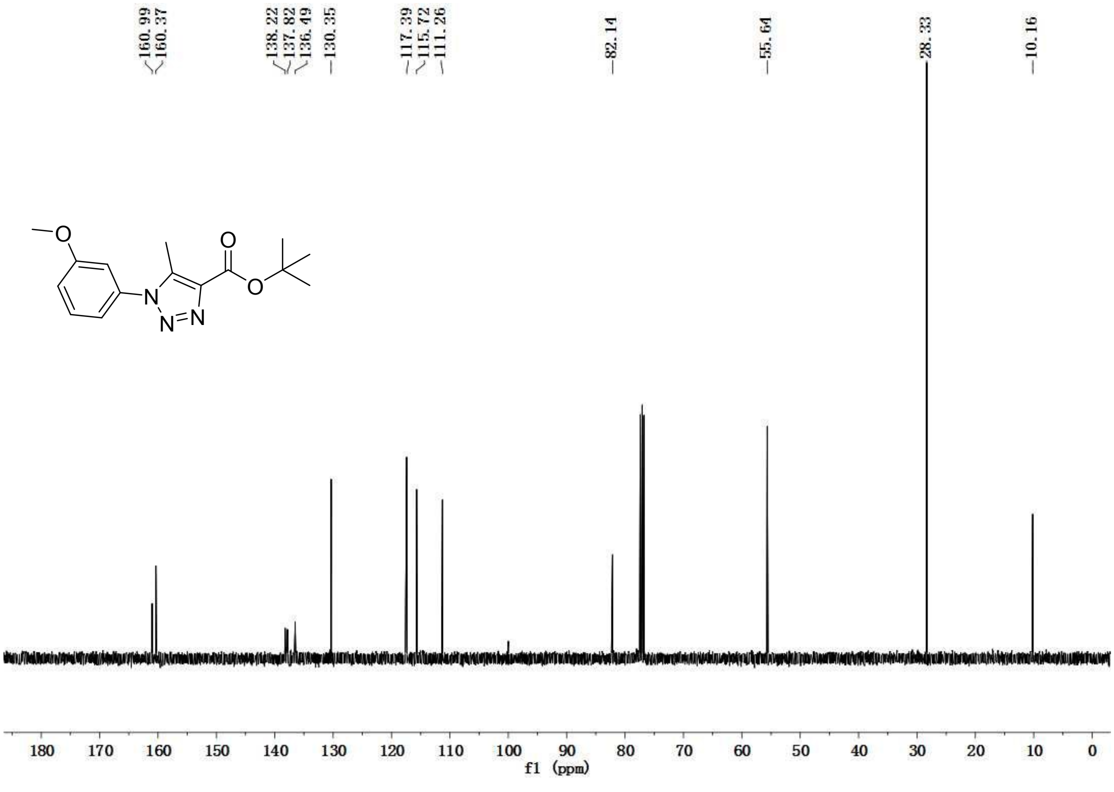
Compounds 3q ^{1}H NMR, ^{13}C NMR



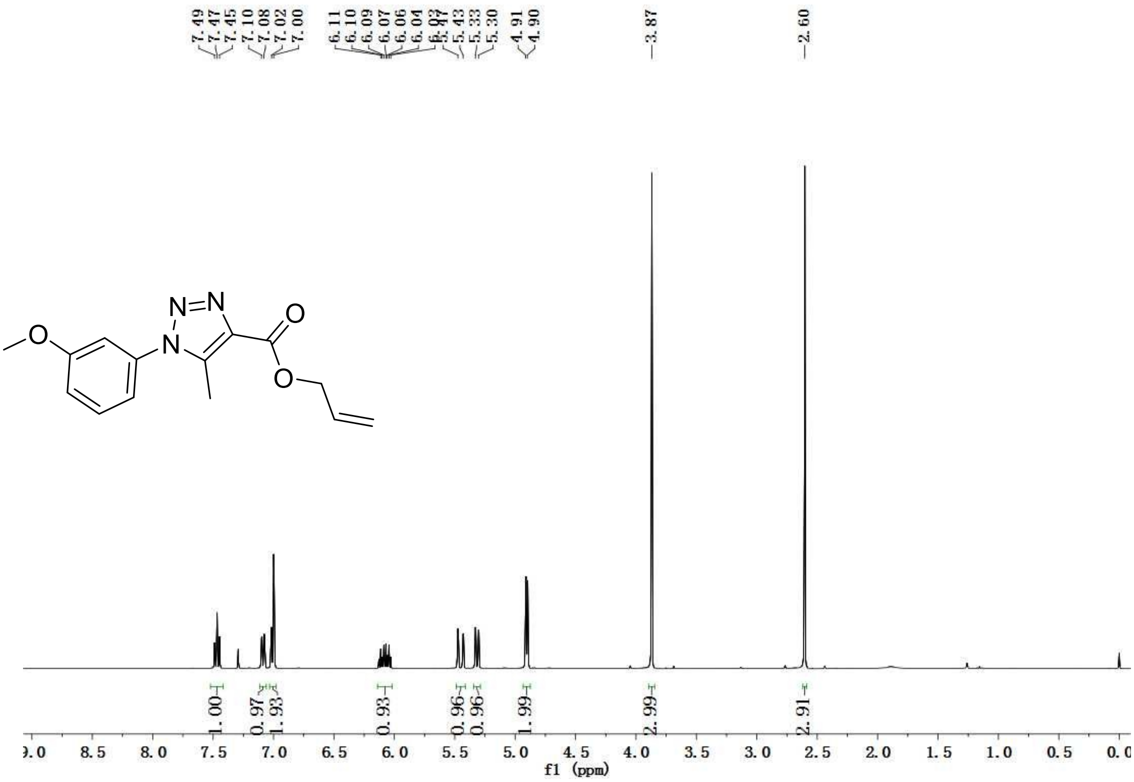


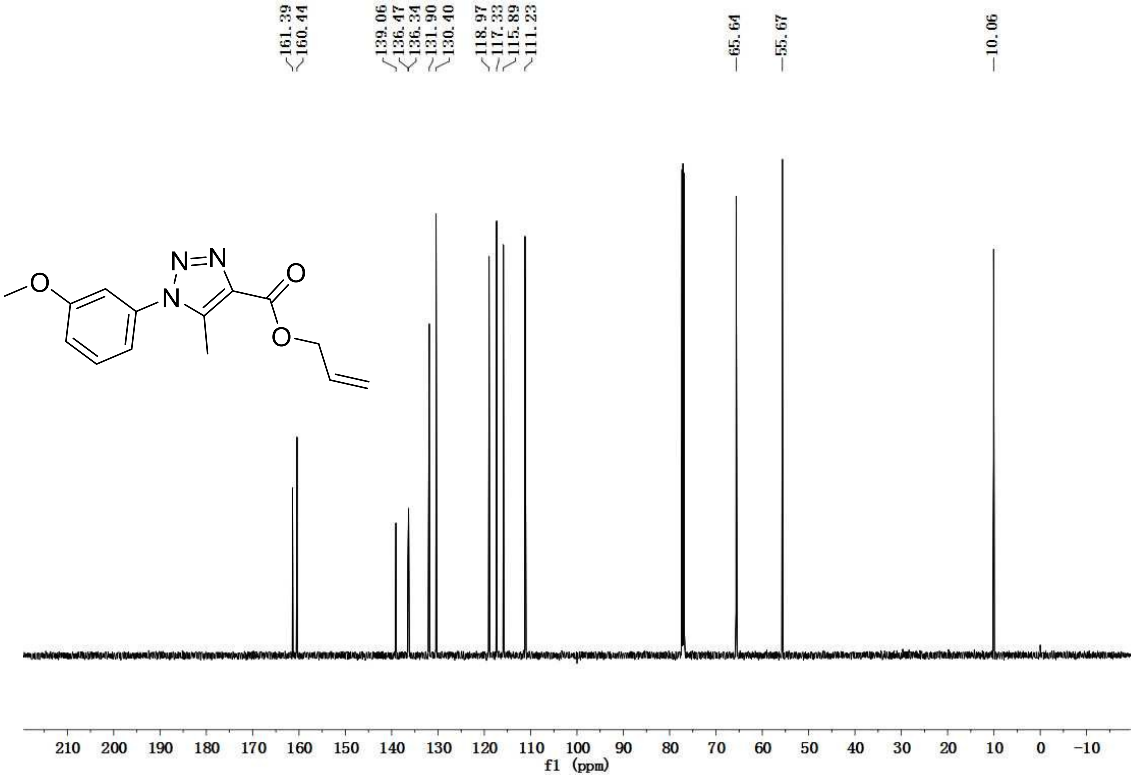
Compounds 3r ^{1}H NMR, ^{13}C NMR



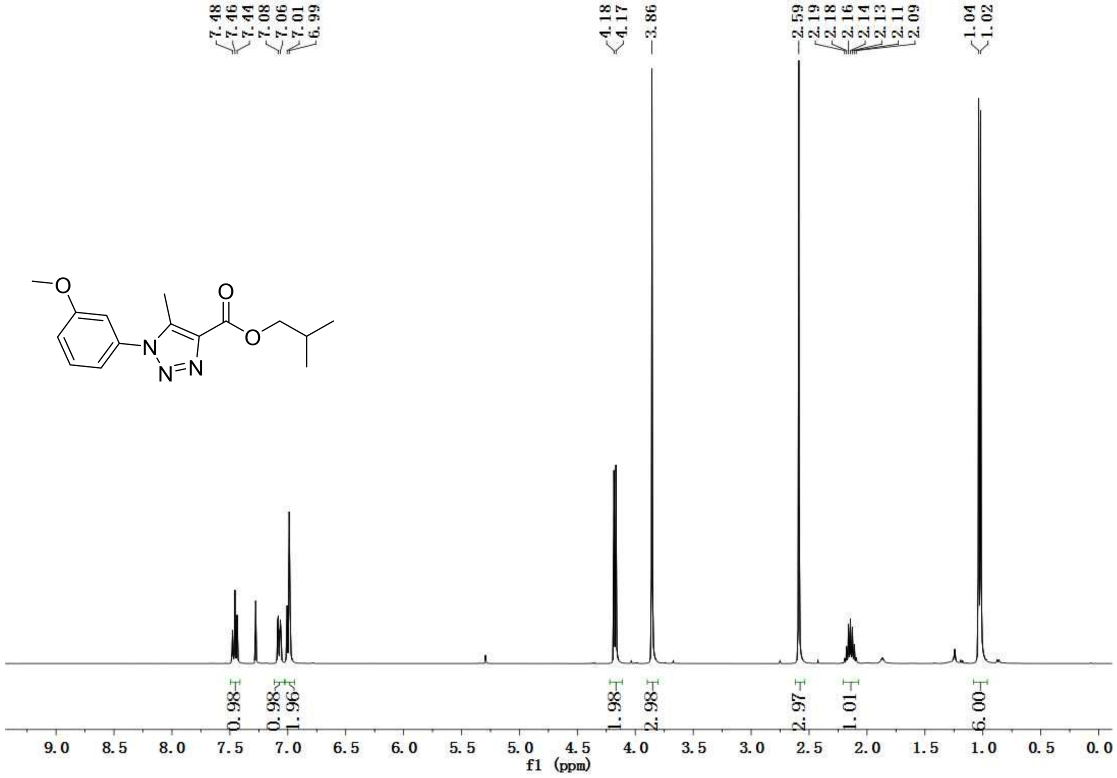


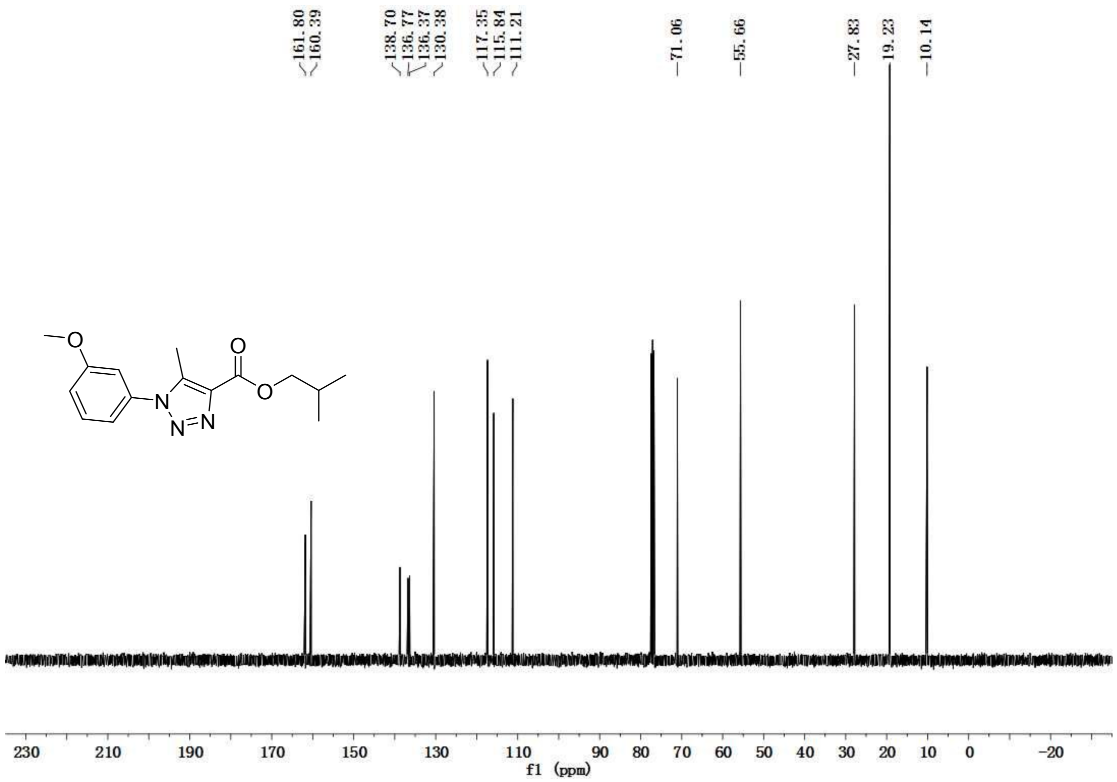
Compounds 3s ^{1}H NMR, ^{13}C NMR



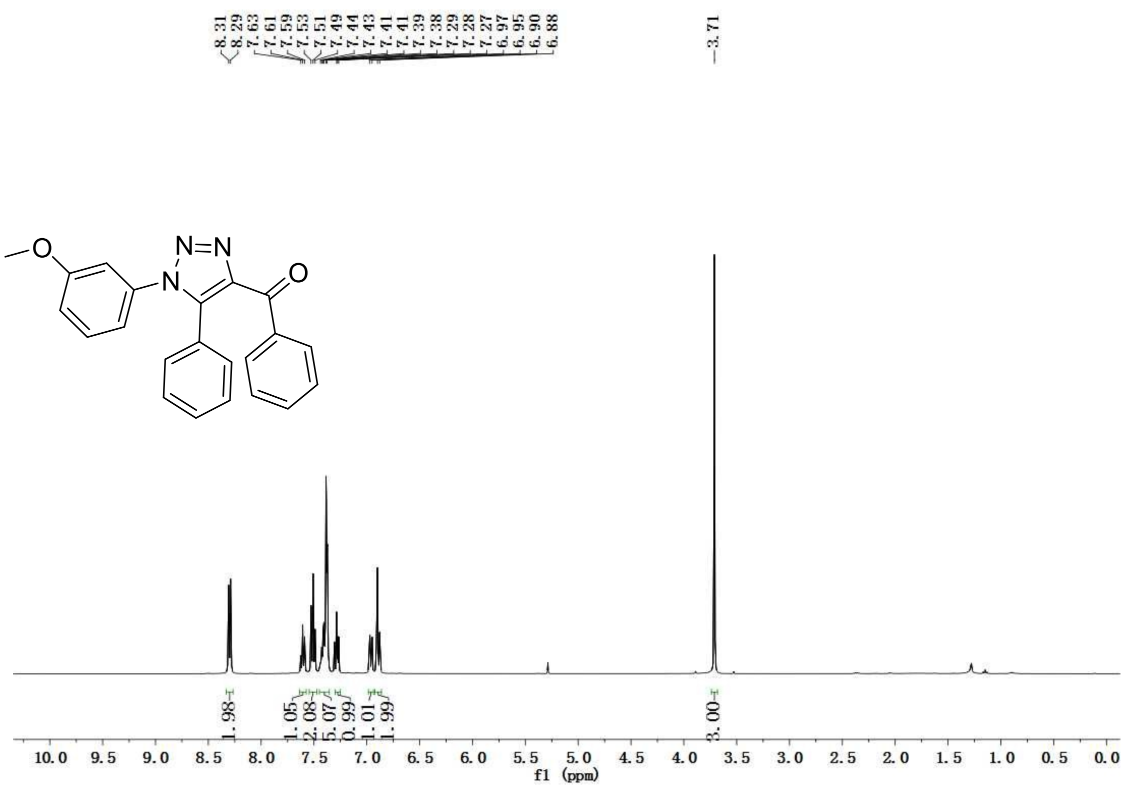


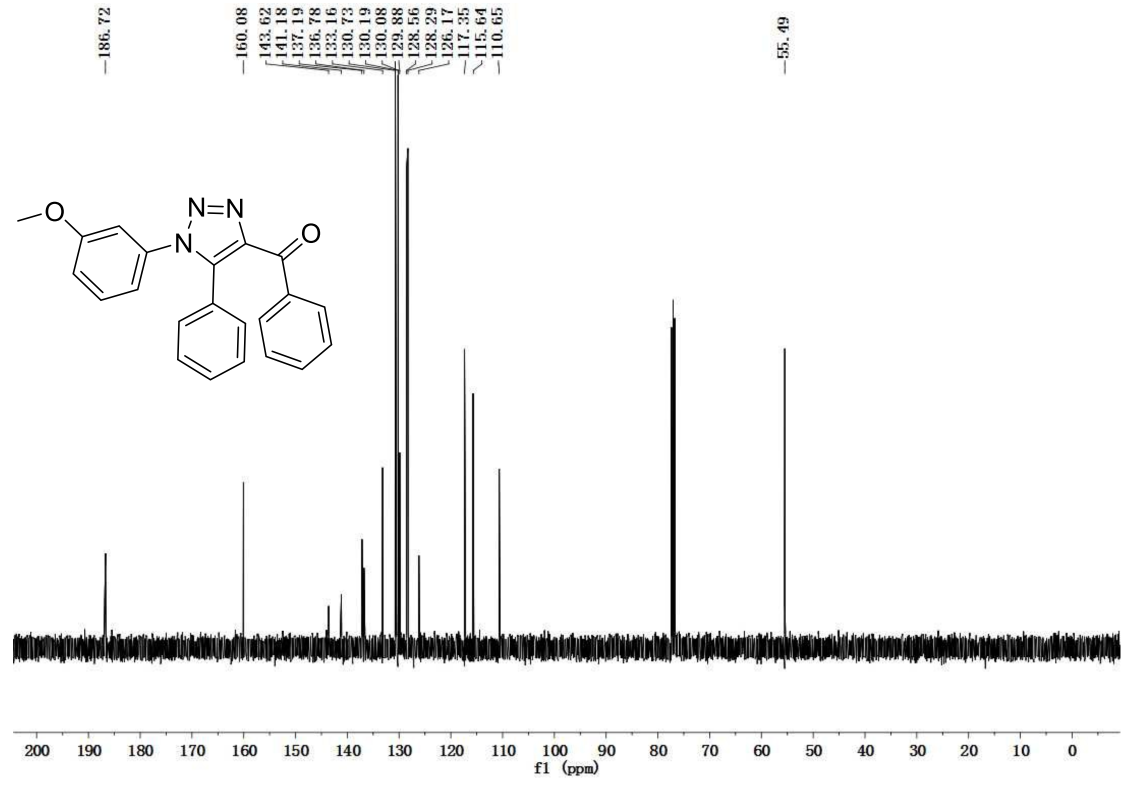
Compounds 3t ^{1}H NMR, ^{13}C NMR



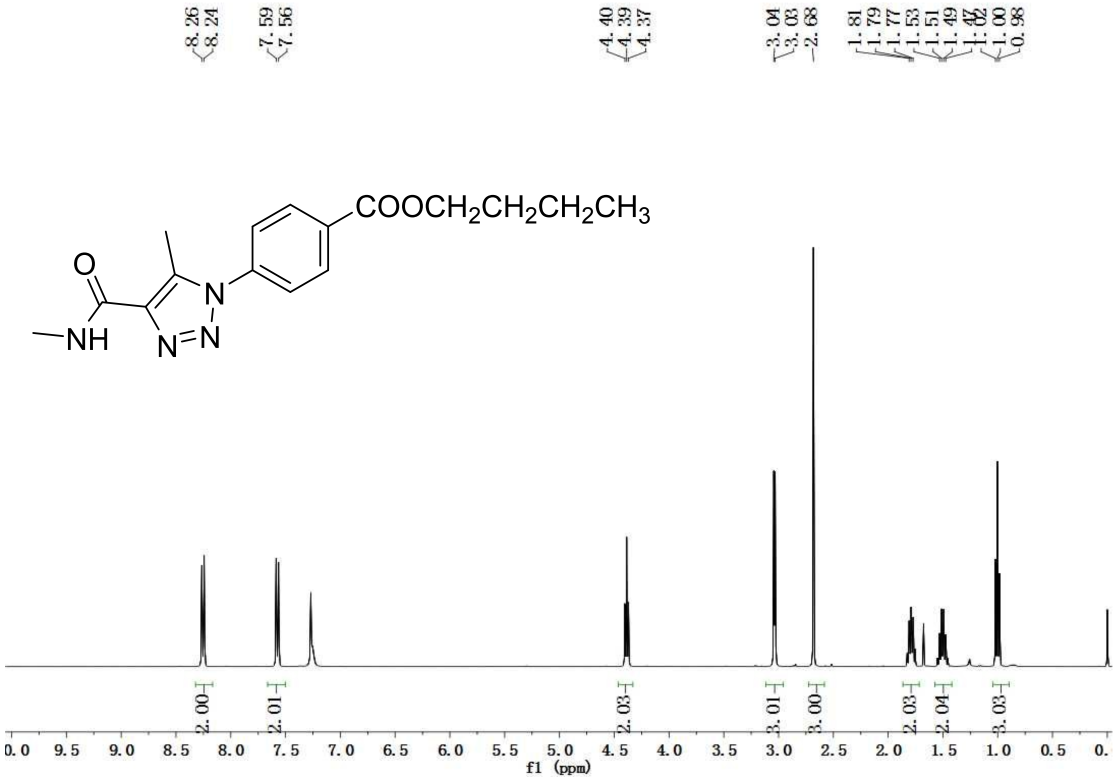


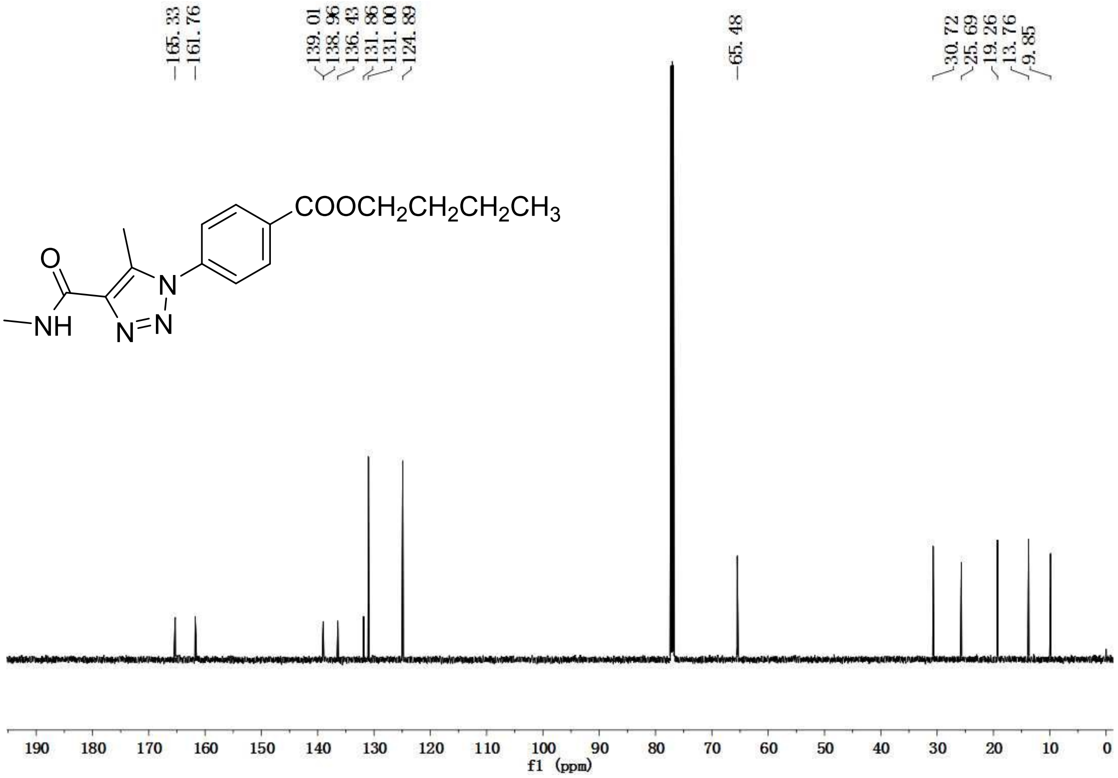
Compounds 3u ^{1}H NMR, ^{13}C NMR





Compounds 3v ^{1}H NMR, ^{13}C NMR





Compounds 3w ^{1}H NMR, ^{13}C NMR