Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


Supporting Information

# Base-induced synthesis of *N*-dialkylaminomethyl-*2H*-1,2,3-triazoles from *N*-sulfonyl-1,2,3-triazoles

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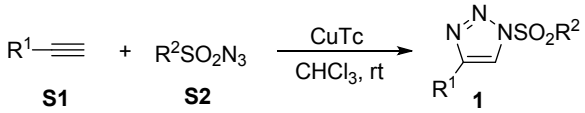
**CONTENTS**

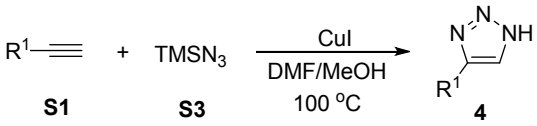
**General Remarks**: $^{1}H$ NMR spectra were recorded on a Bruker AM-400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; J-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. All of the compounds reported in this paper gave satisfactory HRMS analytic data. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in $cm^{-1}$. THF, toluene and $Et_2O$ were distilled from sodium (Na) under argon (Ar) atmosphere. $CH_3CN$, 1,2-dichloroethane, dichloromethane and chloroform were distilled from $CaH_2$ under argon (Ar) atmosphere. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

**General procedure for the synthesis of compounds 1**:



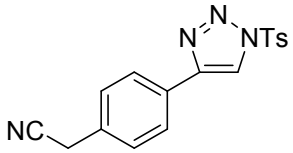

Under inert atmosphere, CuTC (0.1 mmol, 0.02 eq) and alkyne **S1** (5.0 mmol, 1.0 eq) were dissolved in $CHCl_3$ (15 mL) in a Schlenk tube. The reaction mixture was cooled in an ice-water bath. Subsequently, azide **S2** (5.0 mmol, 1.0 eq) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred until judged complete by TLC. Then, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography ($SiO_2$) to give the corresponding products **1** in moderate to good yields. The analytical data of compounds **1a-1d**, **1f-1m**, **1o**, and **1p** have been already reported.[1-9]

**General procedure for the synthesis of compounds 4**:

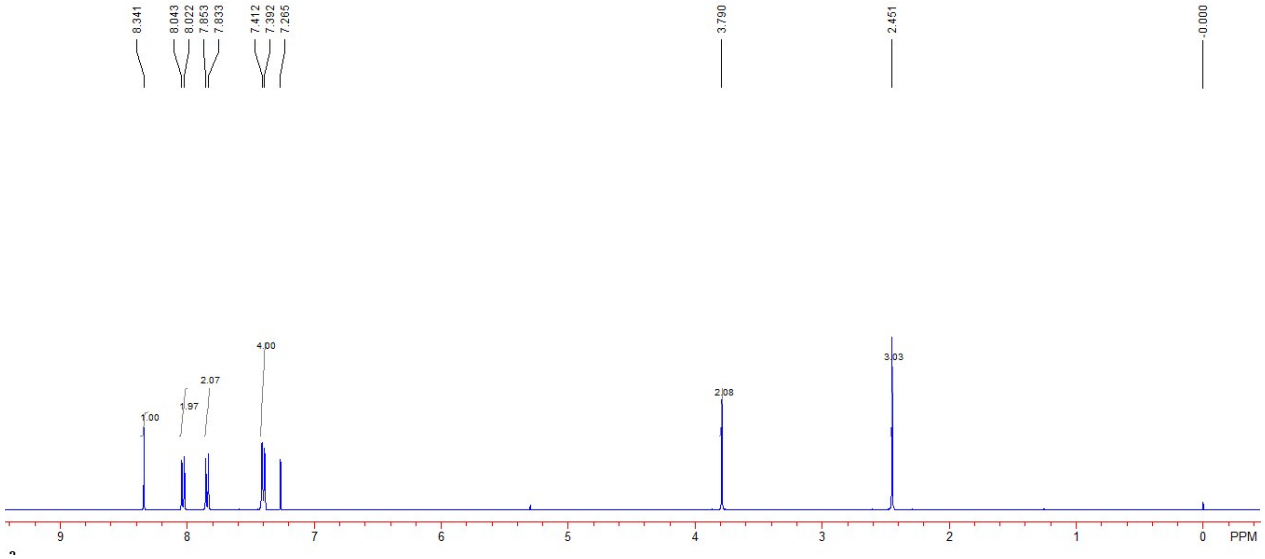


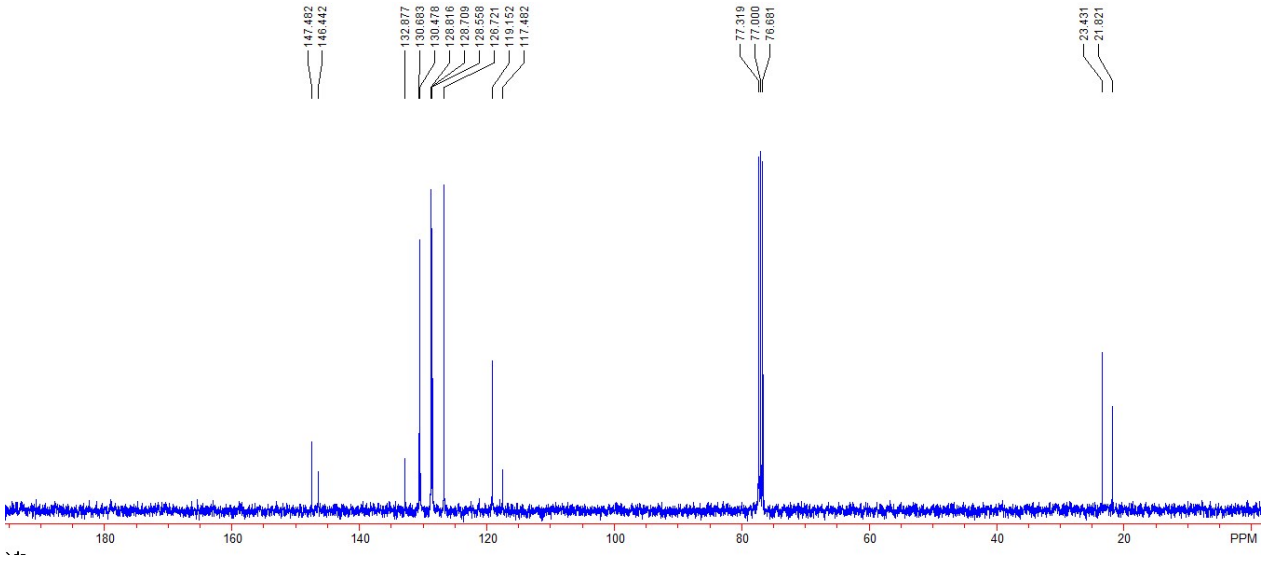

Under inert atmosphere, alkyne **S1** (5.0 mmol, 1.0 eq), $TMSN_3$ (5.0 mmol, 1.0 eq), CuI (0.1 mmol, 0.02 eq) were dissolved in DMF/MeOH (4/1, 20 mL) in a sealed tube. The reaction mixture was allowed to warm to 80 °C and was stirred until judged complete by TLC. Then, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography ($SiO_2$) to give the corresponding products **4** in moderate to good yields. The analytical data of compounds **4a-c**, **4g**, and **4m** have been already reported.[10, 11]

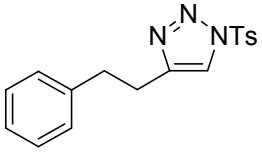
**Spectroscopic Data of Compounds 1 and 4**



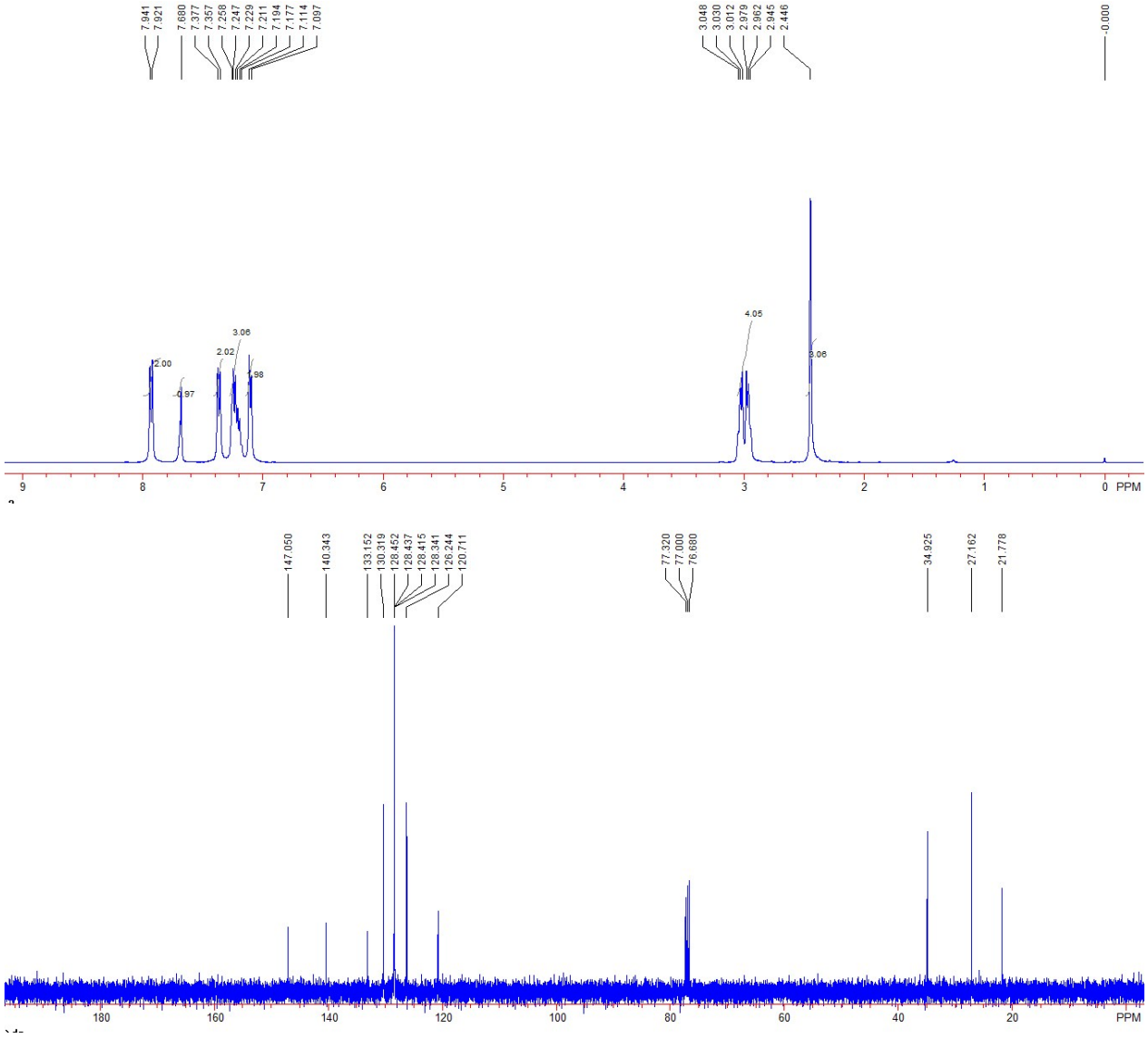

Compound **1e**: a white solid; Mp: 164-166 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (s, 3H), 3.79 (s, 2H), 7.40 (d, *J* = 8.0 Hz, 4H), 7.84 (d, *J* = 8.0 Hz, 2H), 8.03 (d, *J* = 8.0 Hz, 2H), 8.34 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 23.4, 117.5, 119.2, 126.7, 128.6, 128.7, 128.8, 130.5, 130.7, 132.9, 146.4, 147.5; IR ($CH_2Cl_2$) ν 3113, 3057, 2912, 1594, 1392, 1196, 1102, 996, 817, 704 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{17}H_{15}N_4O_2S$ $(M+H)^+$: 339.0910, found: 339.0910.

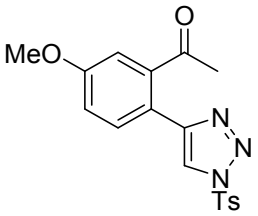


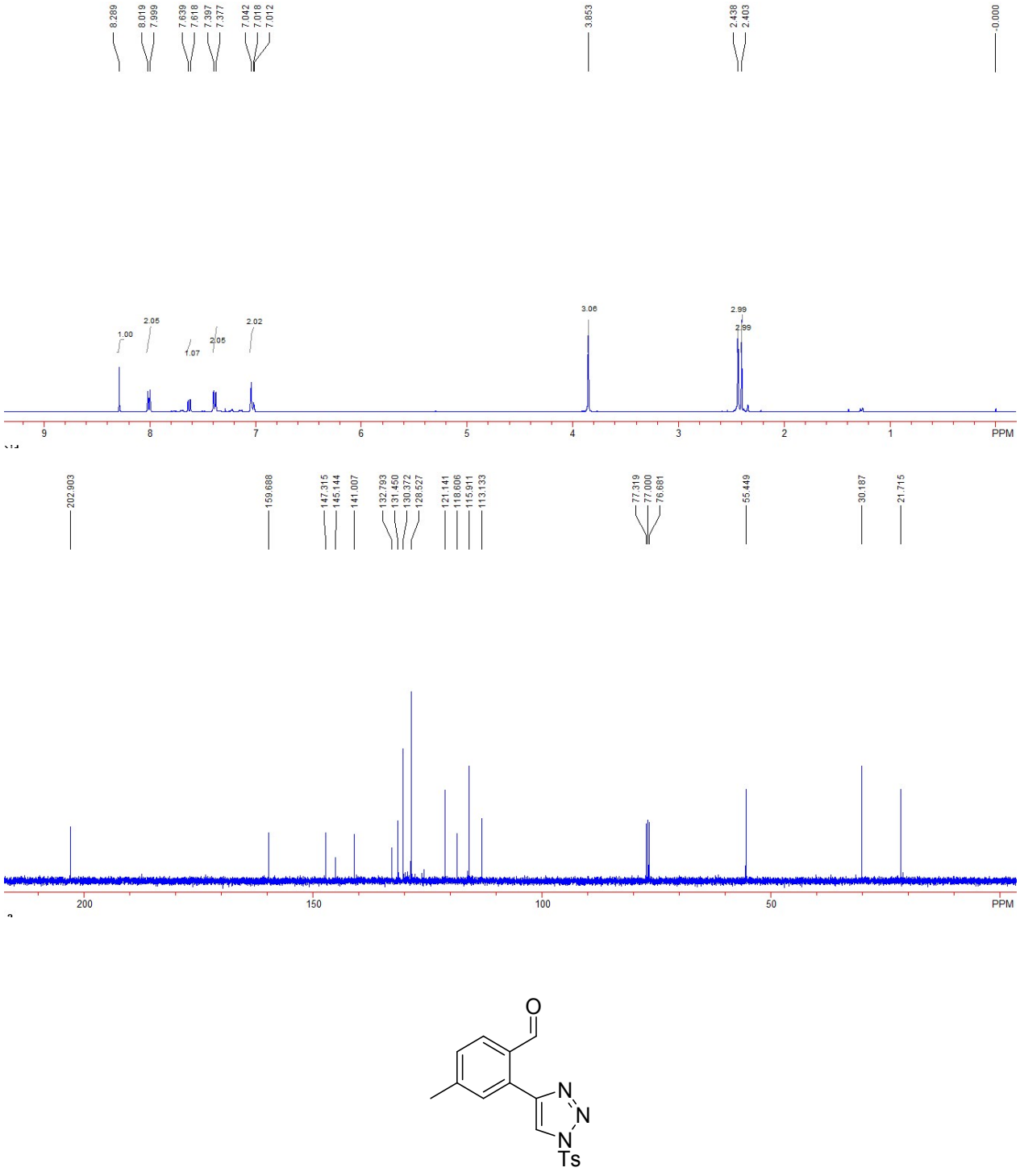
Compound **1n**: a white solid; Mp: 85-87 °C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (s, 3H), 2.44-3.05 (m, 4H), 7.09-7.12 (m, 2H), 7.17-7.26 (m, 3H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.68 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 27.2, 34.9, 120.7, 126.2, 128.3, 128.42, 128.44, 128.5, 130.3, 133.2, 140.3, 147.1; IR ($CH_2Cl_2$) ν 3141, 3023, 2922, 1594, 1384, 1171, 1010, 955, 808, 695 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{17}H_{18}N_3O_2S$ $(M+H)^+$: 328.1114, found: 328.1114.




Compound **1q**: a white solid; Mp: 98-100 °C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.40 (s, 3H),

2.44 (s, 3H), 3.85 (s, 3H), 7.01-7.05 (m, 2H), 7.39 (d, $J$ = 8.0 Hz, 2H), 7.63 (d, $J$ = 8.4 Hz, 1H), 8.01 (d, $J$ = 8.0 Hz, 2H), 8.29 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.7, 30.2, 55.4, 113.1, 115.9, 118.6, 121.1, 128.5, 130.4, 131.5, 132.8, 141.0, 145.1, 147.3, 159.7, 202.9; IR ($CH_2Cl_2$) ν 3143, 3006, 2926, 2839, 1704, 1478, 1298, 1193, 990, 809, 672 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{18}H_{18}N_3O_4S$ $(M+H)^+$: 372.1013, found: 372.1013.

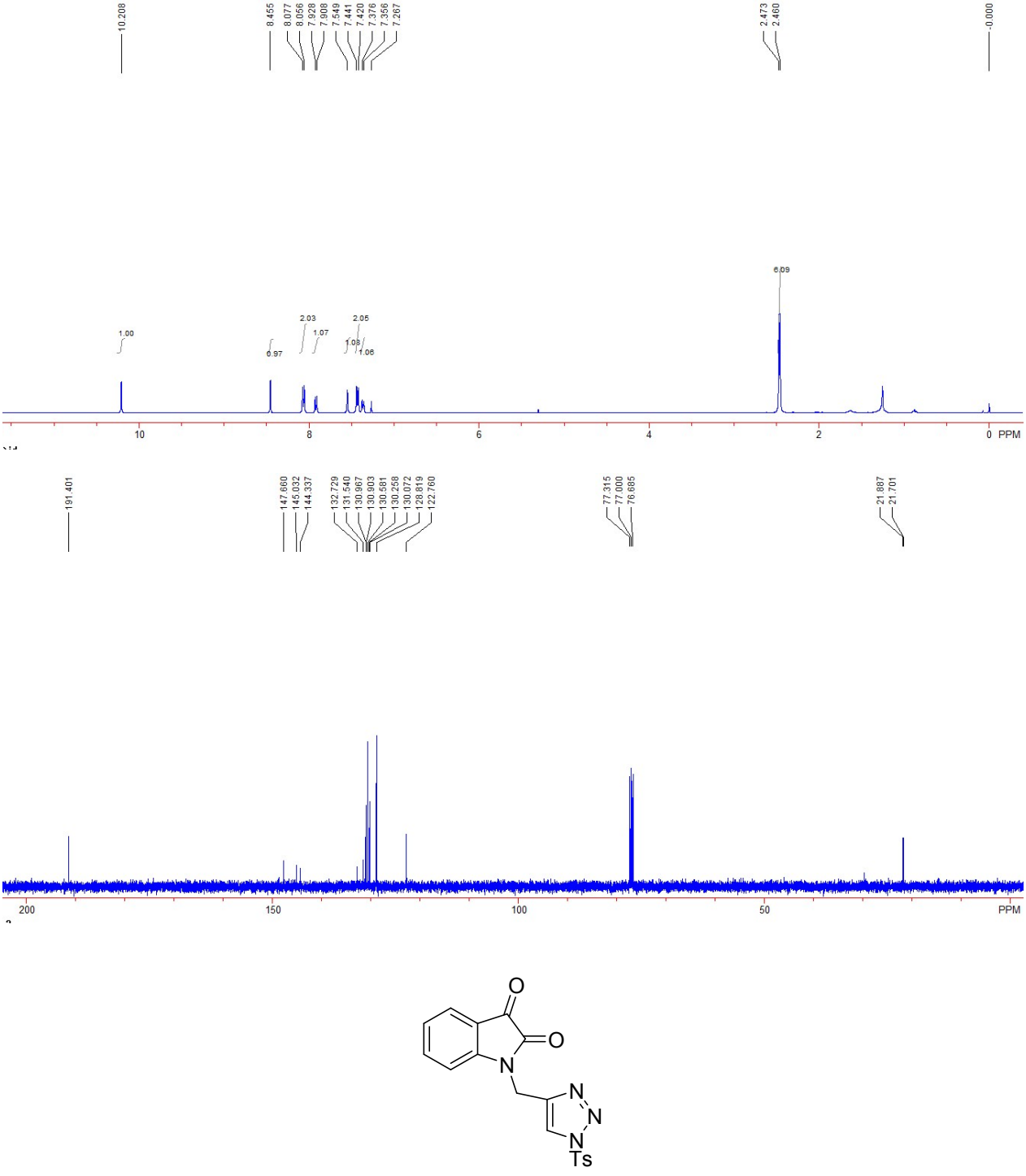






Compound **1r**: a white solid; Mp: 142-144 $^o$C; $^1$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.46 (s, 3H), 2.47 (s, 3H), 7.37 (d, $J$ = 8.0 Hz, 1H), 7.43 (d, $J$ = 8.4 Hz, 2H), 7.55 (s, 1H), 7.92 (d, $J$ = 8.0 Hz,

1H), 8.07 (d, $J$ = 8.4 Hz, 2H), 8.46 (s, 1H), 10.21 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.7, 21.9, 122.8, 128.8, 130.1, 130.3, 130.6, 130.9, 131.0, 131.5, 132.7, 144.3, 145.0, 147.7, 191.4; IR ($CH_2Cl_2$) ν 3128, 2922, 2853, 1678, 1389, 1193, 1008, 822, 668 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{17}H_{16}N_3O_3S$ $(M+H)^+$: 342.0907, found: 342.0909.

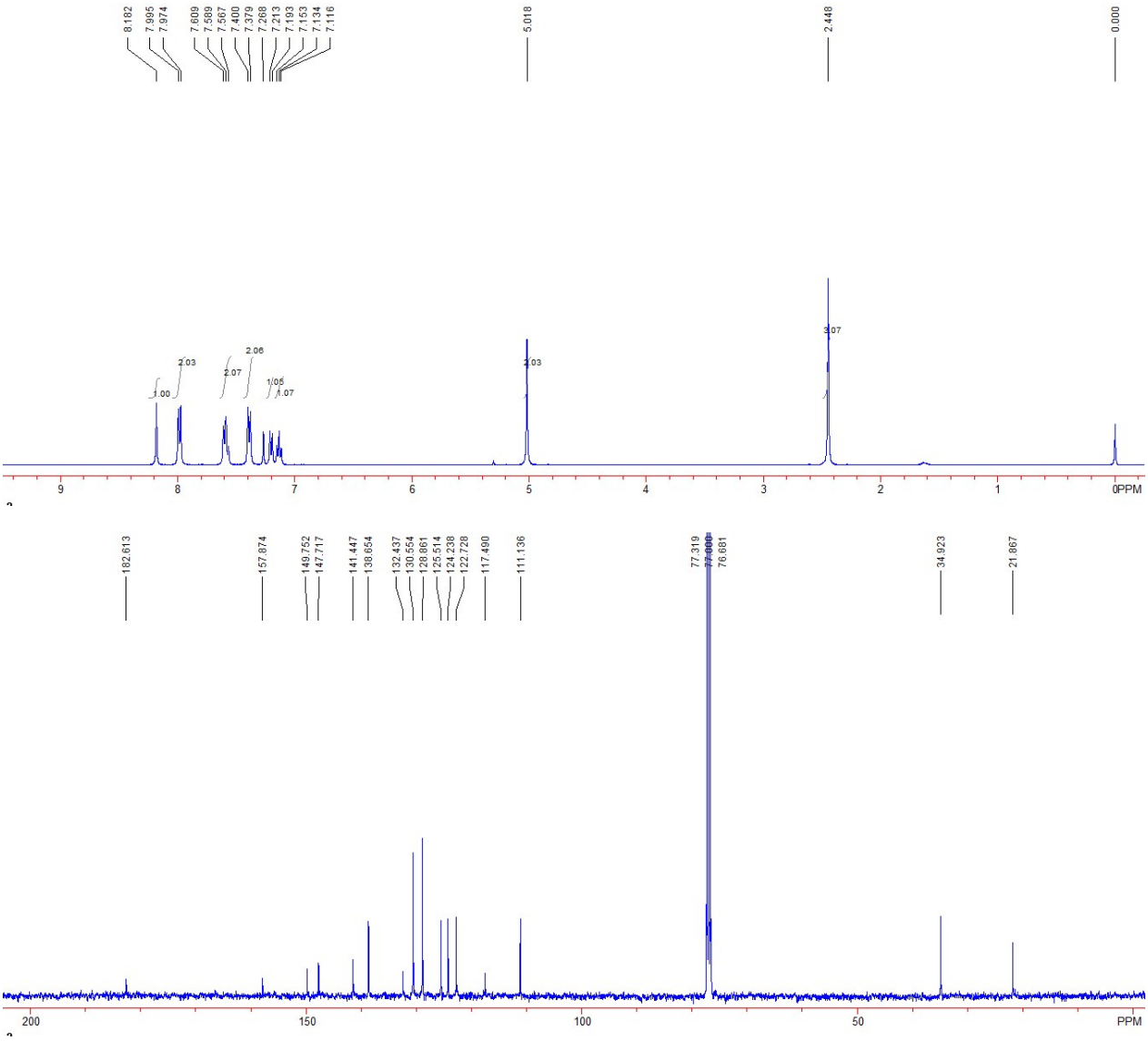


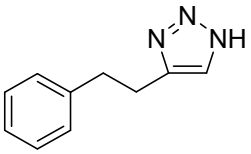




Compound **1s**: a white solid; Mp: 209-211 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (s, 3H), 5.02 (s, 2H), 7.13 (dd, $J$ = 8.0 Hz, $J$ = 8.0 Hz, 1H), 7.20 (d, $J$ = 8.0 Hz, 1H), 7.39 (d, $J$ = 8.4 Hz, 2H), 7.59 (dd, $J$ = 8.0 Hz, $J$ = 8.0 Hz, 2H), 7.98 (d, $J$ = 8.4 Hz, 2H), 8.18 (s, 1H); $^{13}$C NMR

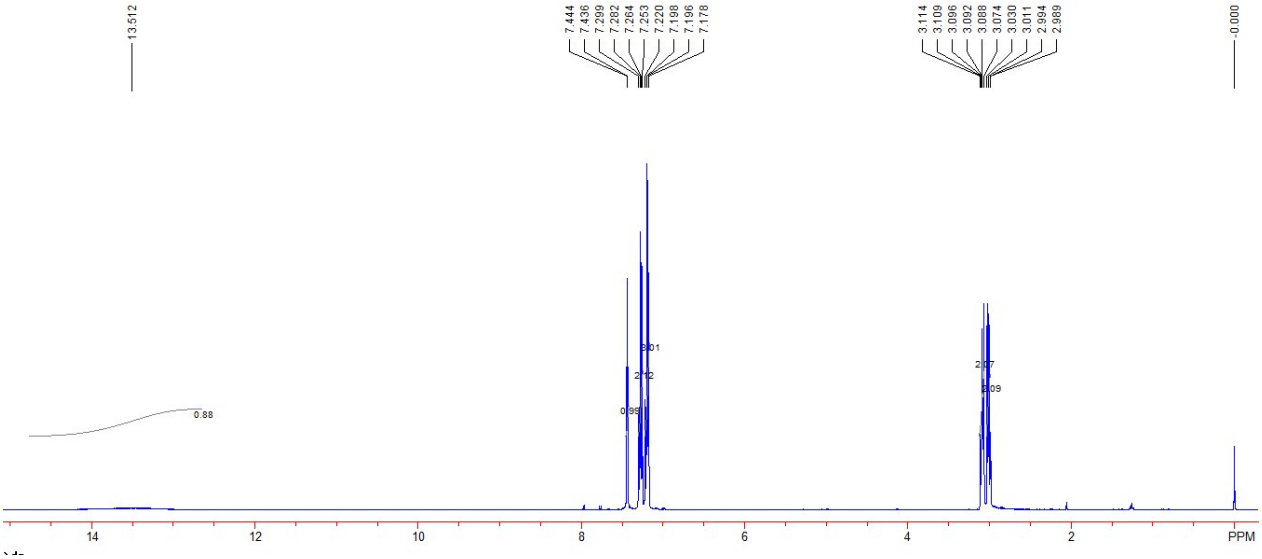
($CDCl_3$, 100 MHz, TMS) δ 21.9, 34.9, 111.1, 117.5, 122.7, 124.2, 125.5, 128.9, 130.6, 132.4, 138.7, 141.4, 147.7, 149.8, 157.9, 182.6; IR ($CH_2Cl_2$) ν 3138, 3052, 2935, 1732, 1612, 1371, 1193, 974, 757, 673 $cm^{-1}$; HRMS (ESI) Calcd. for $C_{18}H_{15}N_4O_4S$ $(M+H)^+$: 383.0809, found: 383.0808.

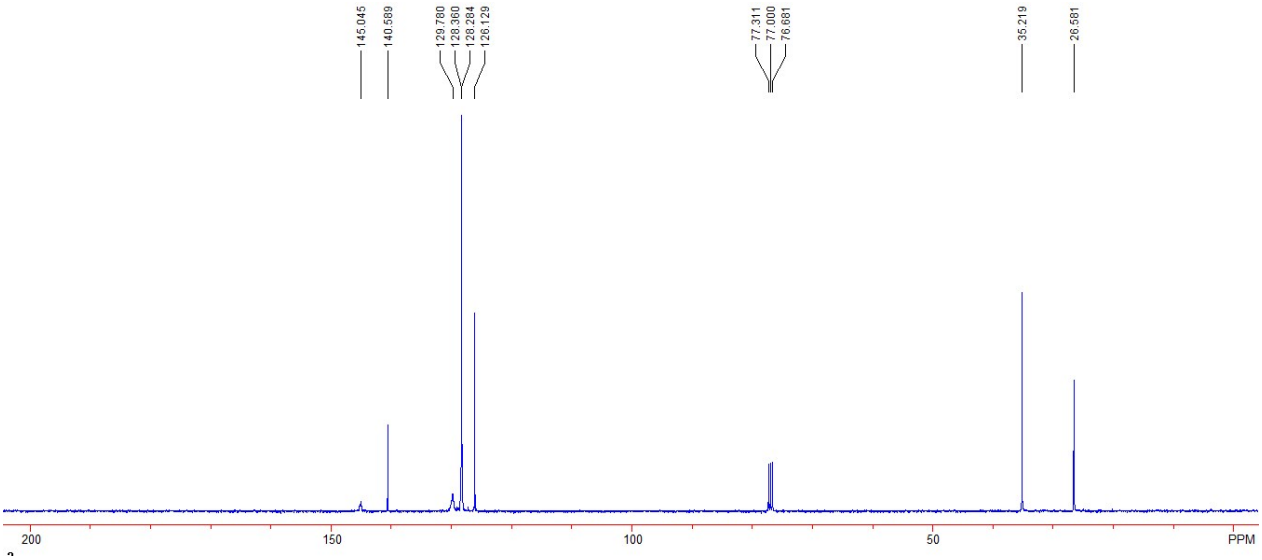


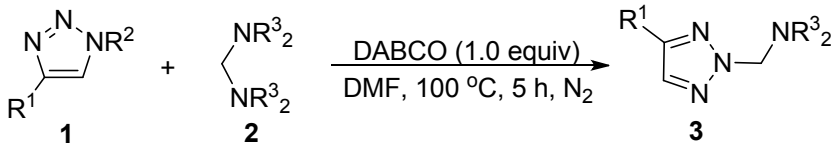

Compound **4n**: a white solid; Mp: 39-41 $^oC$; $^1H$ NMR ($CDCl_3$, 400 MHz, TMS) δ 2.98-3.03 (m, 2H), 3.07-3.12 (m, 2H), 7.17-7.22 (m, 3H), 7.25-7.32 (m, 2H), 7.43-7.45 (m, 1H), 13.51 (br, 1H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, TMS) δ 26.6, 35.2, 126.1, 128.3, 128.4, 129.8, 140.6, 145.0; IR ($CH_2Cl_2$) ν 3064, 3026, 2924, 2859, 1556, 1452, 1151, 969, 813, 696 $cm^{-1}$; HRMS (ESI) Calcd.

for $C_{10}H_{12}N_3$ $(M+H)^+$: 174.1026, found: 174.1027.



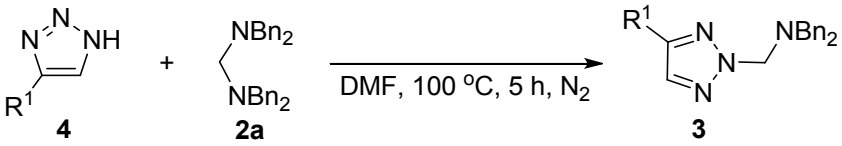



**General procedure for the synthesis of compounds 3**




**1** **2** **3**

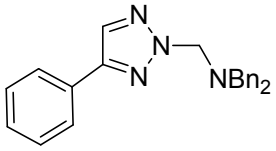
A solution of compound **1** (0.2 mmol), compound **2** (0.2 mmol), and DABCO (0.2 mmol) in DMF (2 mL) was stirred at 100 °C in a well-sealed tube under $N_2$ for an appropriate time. After completion of the reaction as indicated by TLC, the reaction was cooled to room temperature, and the mixture was purified by silica gel column flash chromatography (eluent: petroleum ether / ethyl acetate = 40 / 1) to afford the products **3** in moderate to good yields.



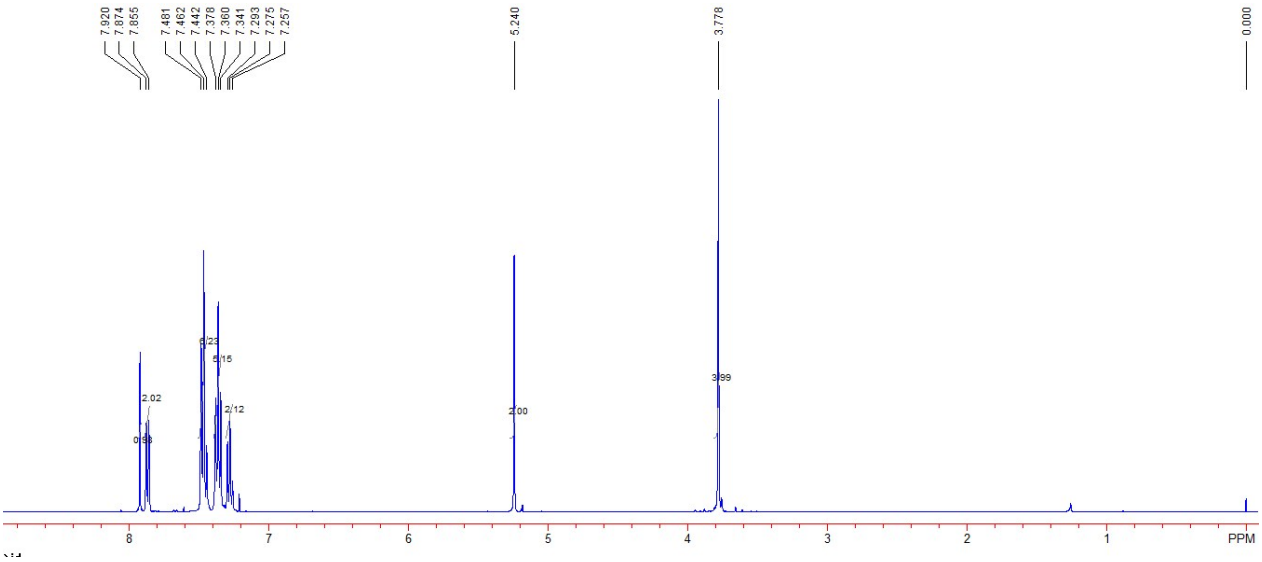

**4** **2a** **3**

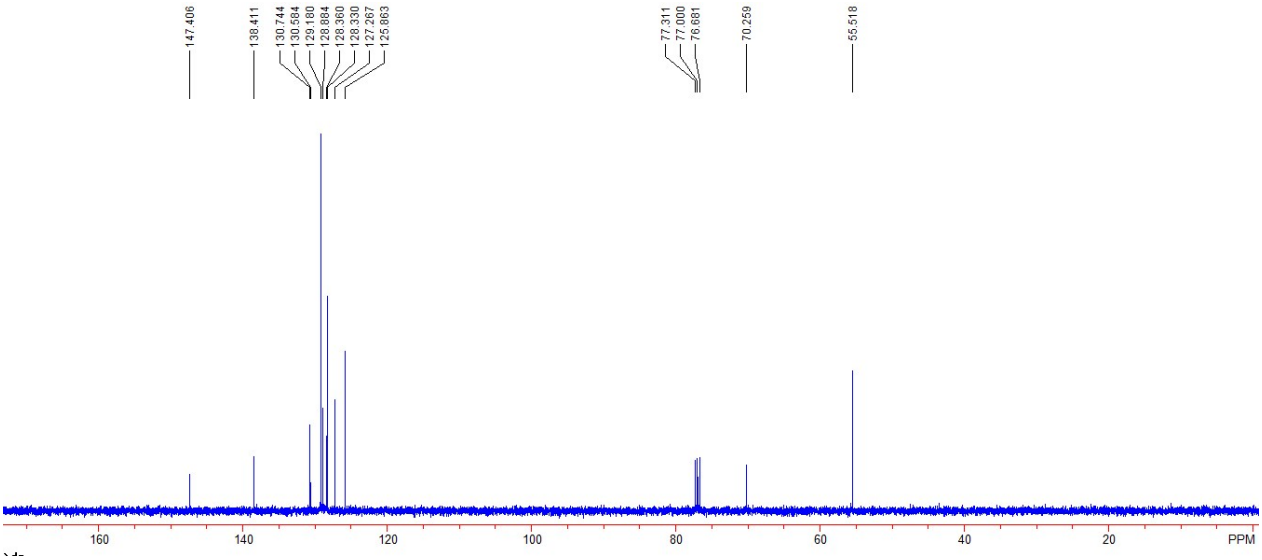
A solution of compound **4** (0.2 mmol) and compound **2a** (0.2 mmol) in DMF (2.0 mL) was stirred at 100 °C in a well-sealed tube under $N_2$ for an appropriate time. After completion of the reaction as indicated by TLC, the reaction was cooled to room temperature, and the mixture was purified by silica gel column flash chromatography (eluent: petroleum ether / ethyl acetate = 40 / 1) to afford the products **3** in moderate to good yields.

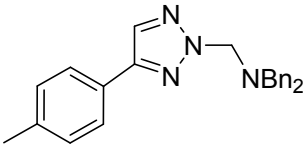
**Spectroscopic Data of Substrates 3:**



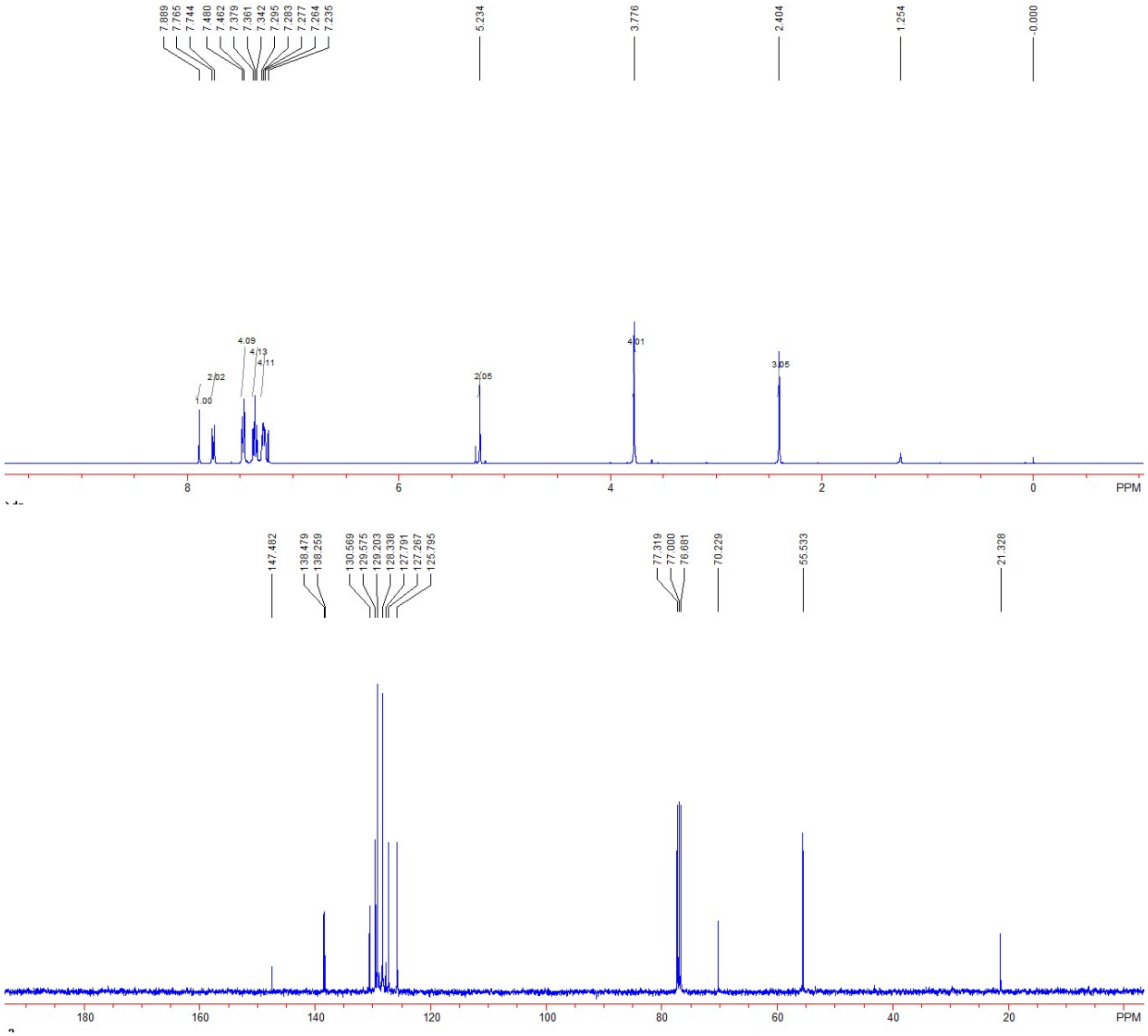

Compound **3aa**: for substrate **1a**: 64 mg, 90% yield; for substrate **4a**: 65 mg, 92% yield; a white solid; Mp: 63-65 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.78 (s, 4H), 5.24 (s, 2H), 7.28 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 2H), 7.34-7.38 (m, 5H), 7.44-7.49 (m, 6H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.92 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 55.5, 70.3, 125.9, 127.3, 128.3, 128.4, 128.9, 129.2, 130.6, 130.7, 138.4, 147.4; IR ($CH_2Cl_2$) ν 3030, 2957, 2838, 1601, 1495, 1150, 1086, 169, 693 cm$^{-1}$; HRMS (DART) Calcd. for $C_{23}H_{23}N_4$ $(M+H)^+$: 355.1917, found: 355.1917.

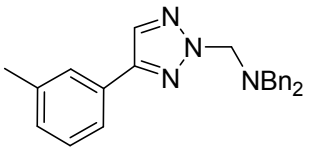


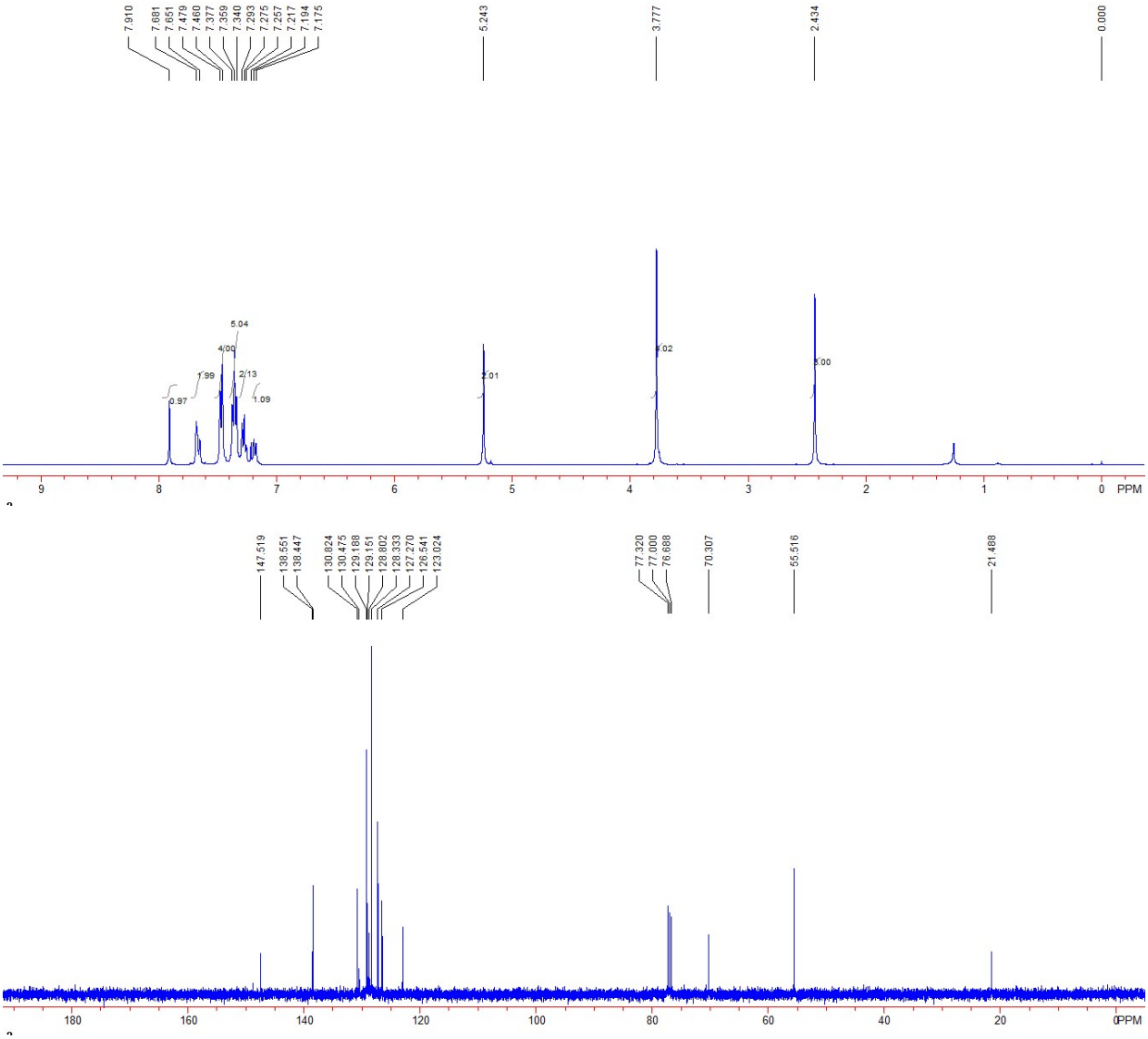


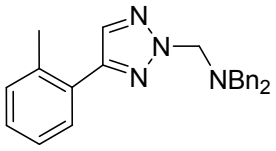

Compound **3ba**: 53 mg, 72% yield; a white solid; Mp: 99-101 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.40 (s, 3H), 3.78 (s, 4H), 5.23 (s, 2H), 7.23-7.30 (m, 4H), 7.36 (dd, $J$ = 7.2 Hz, $J$ = 7.2 Hz, 4H), 7.47 (d, $J$ = 7.2 Hz, 4H), 7.75 (d, $J$ = 8.4 Hz, 2H), 7.89 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 55.5, 70.2, 125.8, 127.3, 127.8, 128.3, 129.2, 129.6, 130.6, 138.3, 138.5, 147.5; IR ($CH_2Cl_2$) ν 3027, 2924, 2853, 1494, 1133, 1091, 997, 821, 734, 697 cm$^{-1}$; HRMS (DART) Calcd. for $C_{24}H_{25}N_4$ $(M+H)^+$: 369.2074, found: 369.2073.



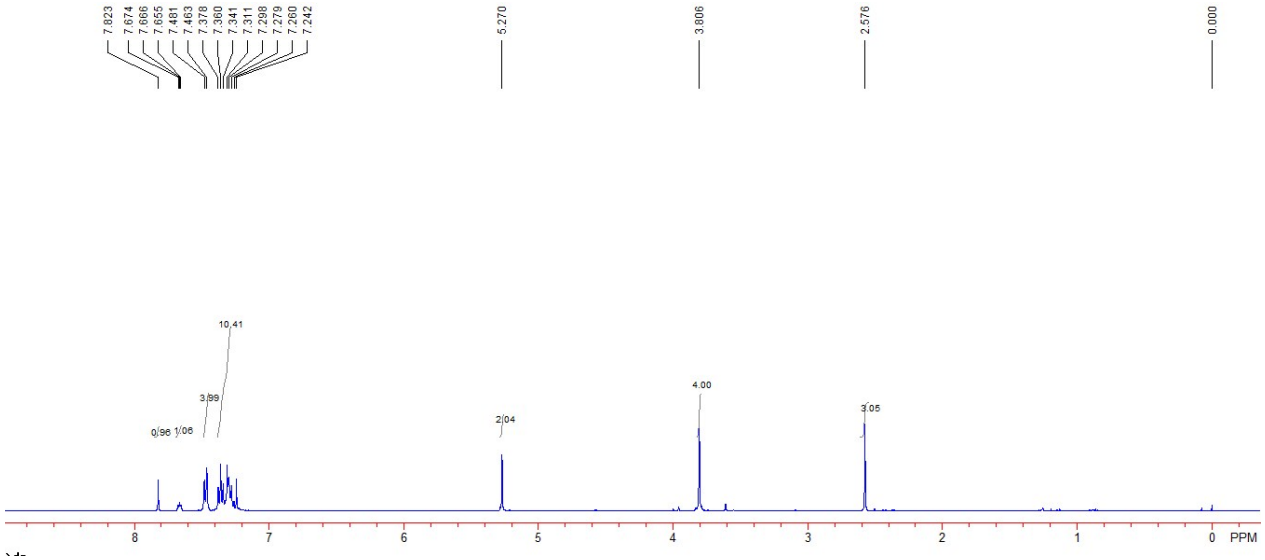


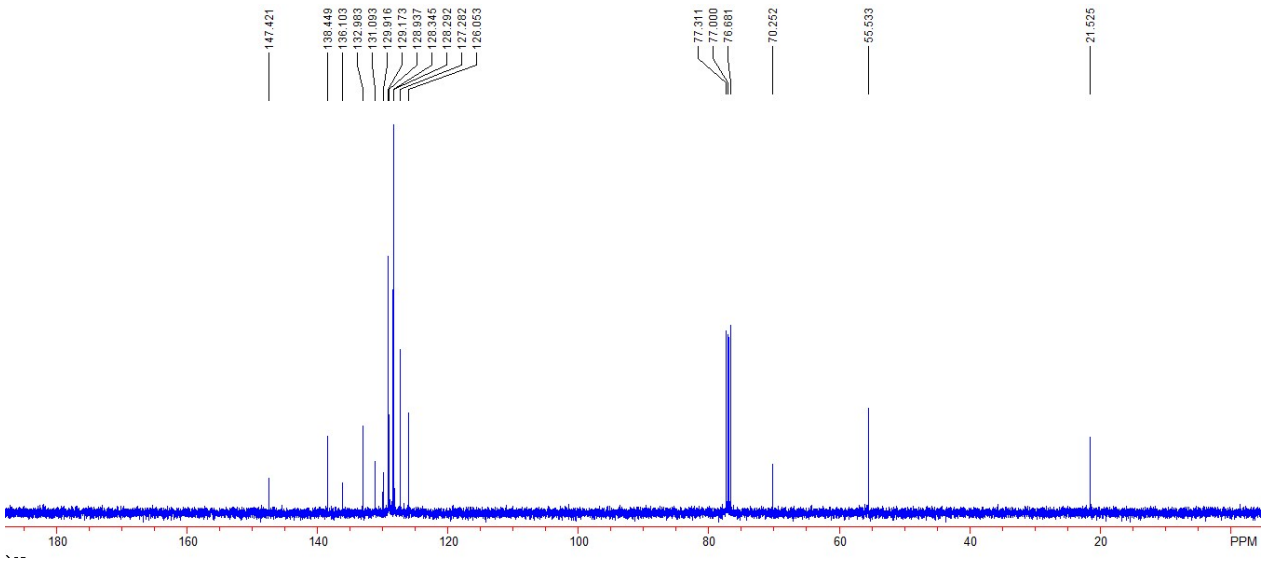

Compound **3ca**: 49 mg, 67% yield; a white solid; Mp: 79-80 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.43 (s, 3H), 3.78 (s, 4H), 5.24 (s, 2H), 7.17-7.22 (m, 1H), 7.28 (d, $J$ = 7.2 Hz, 2H), 7.34-7.38 (m, 5H), 7.47 (d, $J$ = 7.6 Hz, 4H), 7.65-7.69 (m, 2H), 7.91 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 55.5, 70.3, 123.0, 126.5, 127.3, 128.3, 128.8, 129.15, 129.19, 130.5, 130.8, 138.4, 138.6, 147.5; IR ($CH_2Cl_2$) ν 3026, 2919, 1494, 1370, 1139, 1090, 745, 693 cm$^{-1}$; HRMS (DART) Calcd. for $C_{24}H_{25}N_4$ $(M+H)^+$: 369.2074, found: 369.2074.

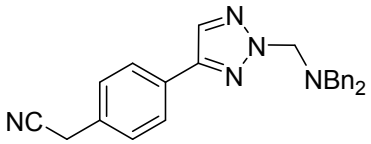




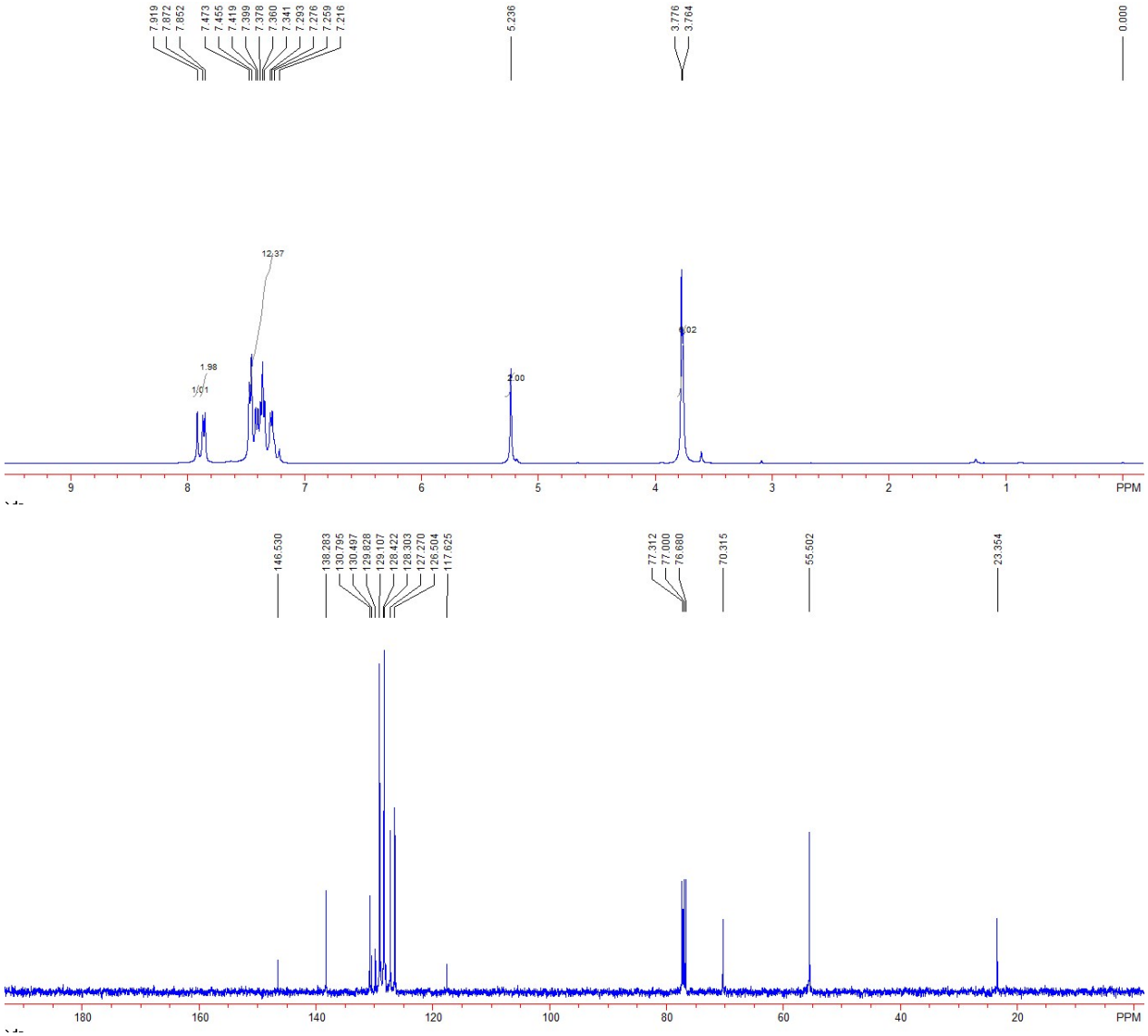

Compound **3da**: 52 mg, 71% yield; a colorless oil; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.58 (s, 3H), 3.81 (s, 4H), 5.27 (s, 2H), 7.17-7.22 (m, 1H), 7.24-7.38 (m, 9H), 7.47 (d, *J* = 7.2 Hz, 4H), 7.67 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H), 7.82 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 55.5, 70.3, 126.1, 127.3, 128.29, 128.34, 128.9, 129.2, 129.9, 131.1, 133.0, 136.1, 138.4, 147.4; IR ($CH_2Cl_2$) ν 3060, 2956, 2848, 1602, 1455, 1277, 1070, 979, 765, 696 cm$^{-1}$; HRMS (DART) Calcd. for $C_{24}H_{25}N_4$ $(M+H)^+$: 369.2074, found: 369.2070.

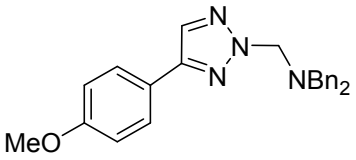


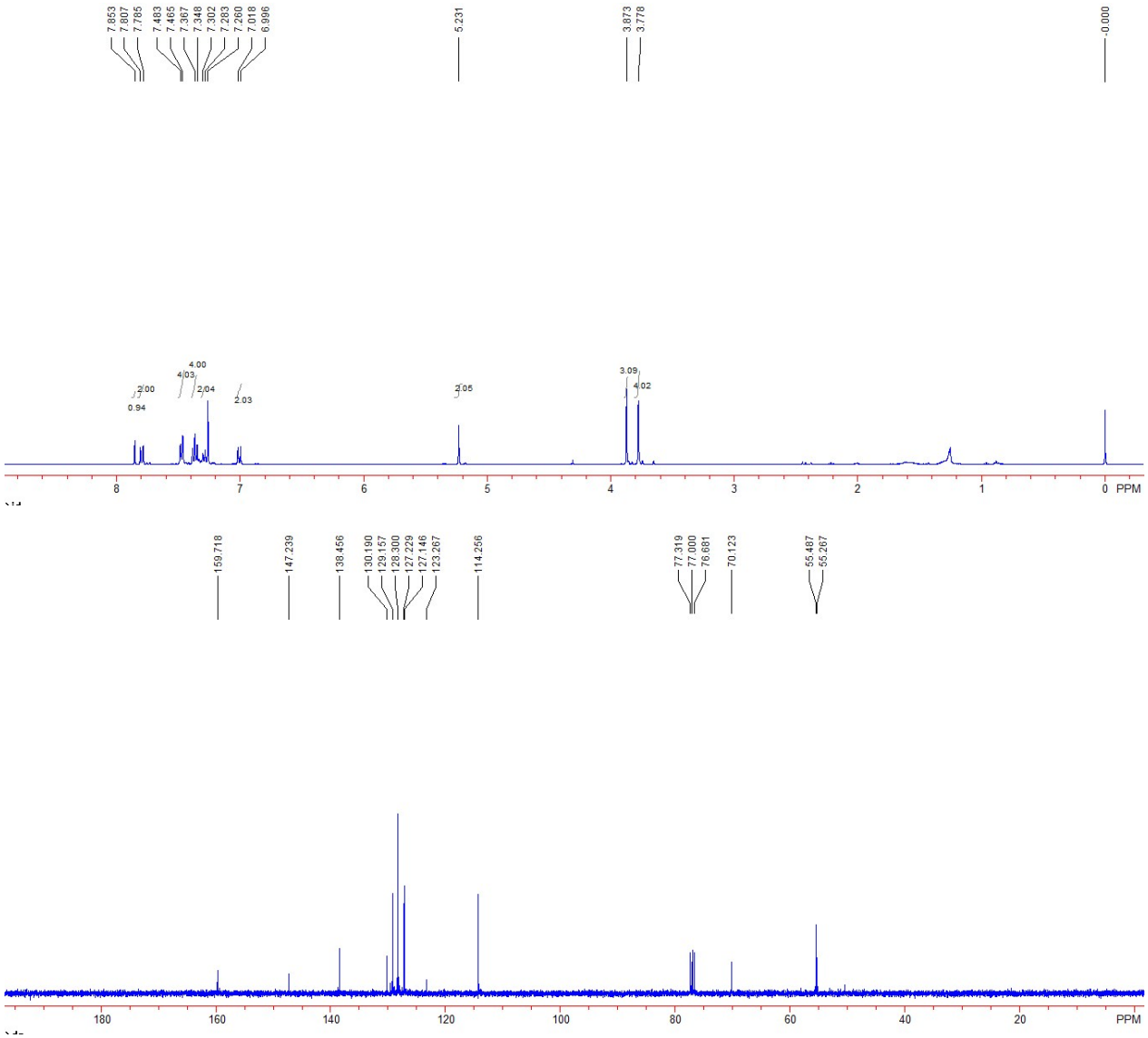


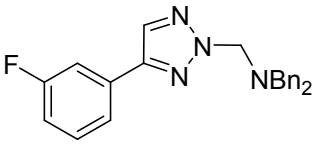

Compound **3ea**: 57 mg, 72% yield; a white solid; Mp: 145-147 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.76 (s, 2H), 3.78 (s, 4H), 5.24 (s, 2H), 7.21-7.48 (m, 12H), 7.86 (d, $J$ = 8.0 Hz, 2H), 7.92 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 23.4, 55.5, 70.3, 117.6, 126.5, 127.3, 128.3, 128.4, 129.1, 129.8, 130.5, 130.8, 138.3, 146.5; IR ($CH_2Cl_2$) ν 3025, 2960, 2859, 1601, 1494, 1139, 1000, 981, 815, 742, 698 cm$^{-1}$; HRMS (DART) Calcd. for $C_{25}H_{24}N_5$ $(M+H)^+$: 394.2026, found: 394.2025.



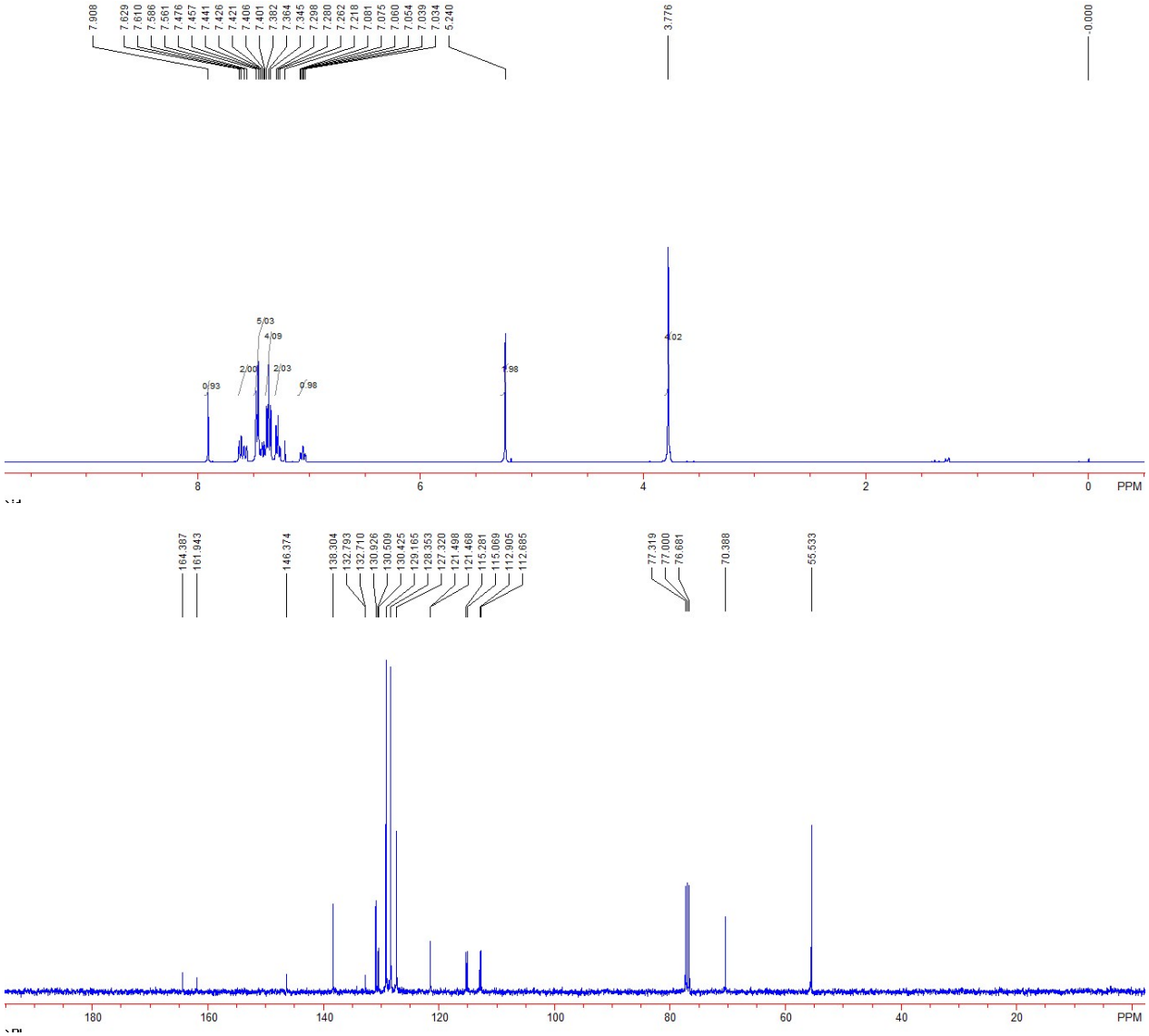


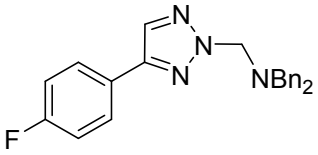

Compound **3fa**: for substrate **1f**: 54 mg, 70% yield; for substrate **4f**: 50 mg, 65% yield; a white solid; Mp: 84-86 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.78 (s, 4H), 3.87 (s, 3H), 5.23 (s, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 7.28 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 2H), 7.37 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 4H), 7.47 (d, *J* = 7.6 Hz, 4H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.85 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 55.3, 55.5, 70.1, 114.3, 123.3, 127.1, 127.2, 128.3, 129.2, 130.2, 138.5, 147.2, 159.7; IR ($CH_2Cl_2$) ν 3030, 2956, 2924, 2851, 1713, 1485, 1250, 1176, 1030, 832, 749, 699 cm$^{-1}$; HRMS (DART) Calcd. for $C_{24}H_{25}ON_4$ $(M+H)^+$: 385.2023, found: 385.2021.



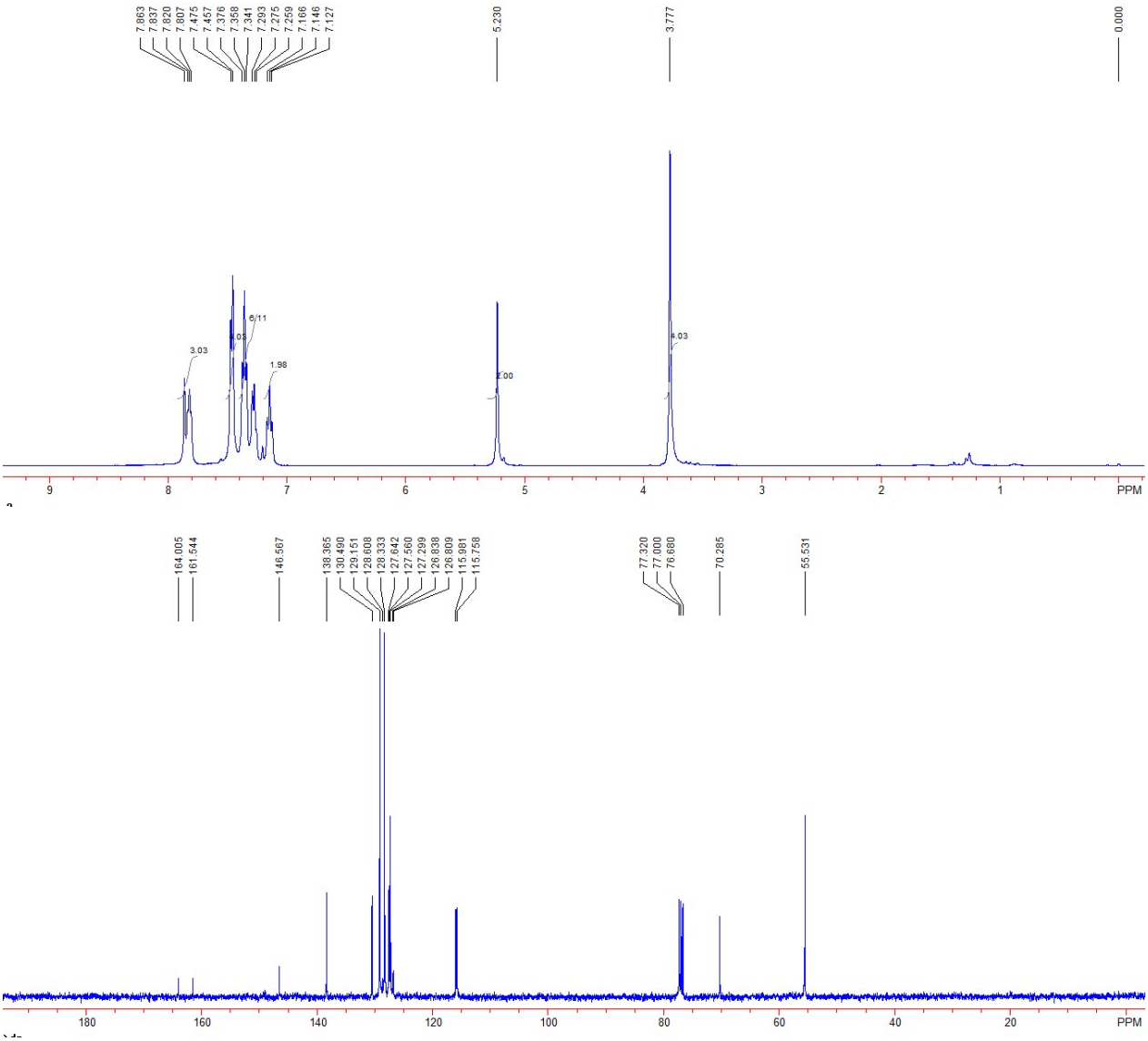


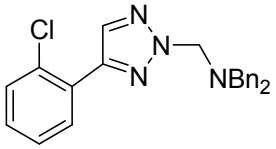

Compound **3ga**: for substrate **1g**: 60 mg, 81% yield; for substrate **4g**: 56 mg, 75% yield; a white solid; Mp: 62-64 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.78 (s, 4H), 5.24 (s, 2H), 7.06 (ddd, *J* = 8.4 Hz, *J* = 8.4 Hz, *J* = 2.4 Hz, 1H), 7.21-7.30 (m, 2H), 7.36 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 4H), 7.40-7.48 (m, 5H), 7.56-7.63 (m, 2H), 7.91 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 55.5, 70.4, 112.8 (d, *J* = 22.0 Hz), 115.2 (d, *J* = 21.2 Hz), 121.5 (d, *J* = 3.0 Hz), 127.3, 128.4, 129.2, 130.5 (d, *J* = 8.4 Hz), 130.9, 132.8 (d, *J* = 8.2 Hz), 138.3, 146.4, 163.2 (d, *J* = 244.4 Hz); IR ($CH_2Cl_2$) ν 3030, 2959, 2901, 2849, 1588, 1455, 1284, 1073, 862, 743, 697 cm$^{-1}$; HRMS (DART) Calcd. for $C_{23}H_{22}N_4F$ $(M+H)^+$: 373.1823, found: 373.1821.



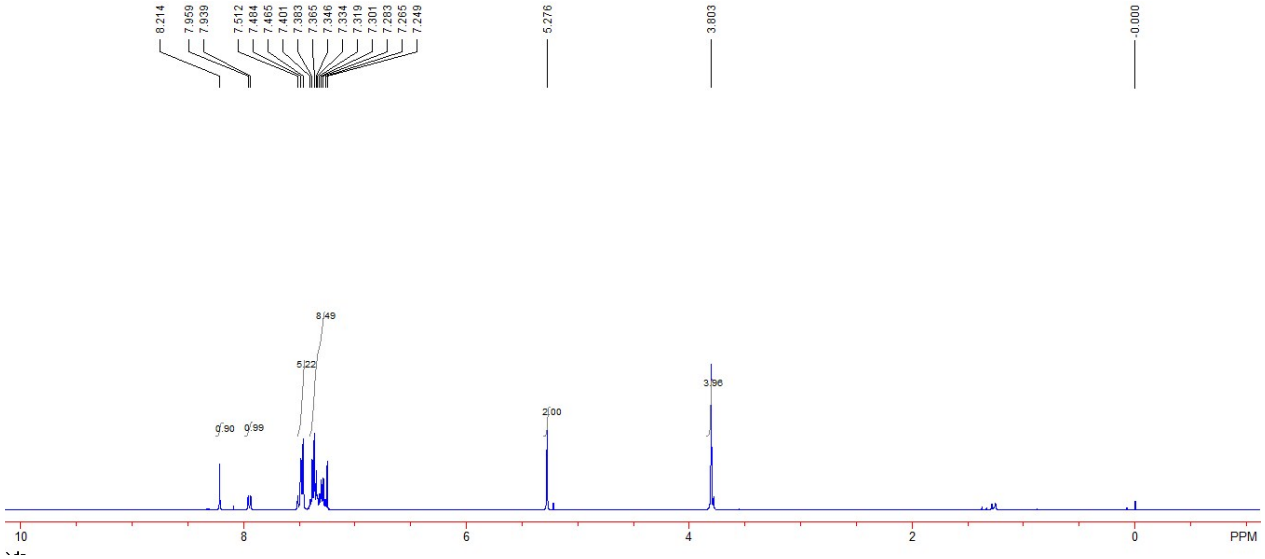


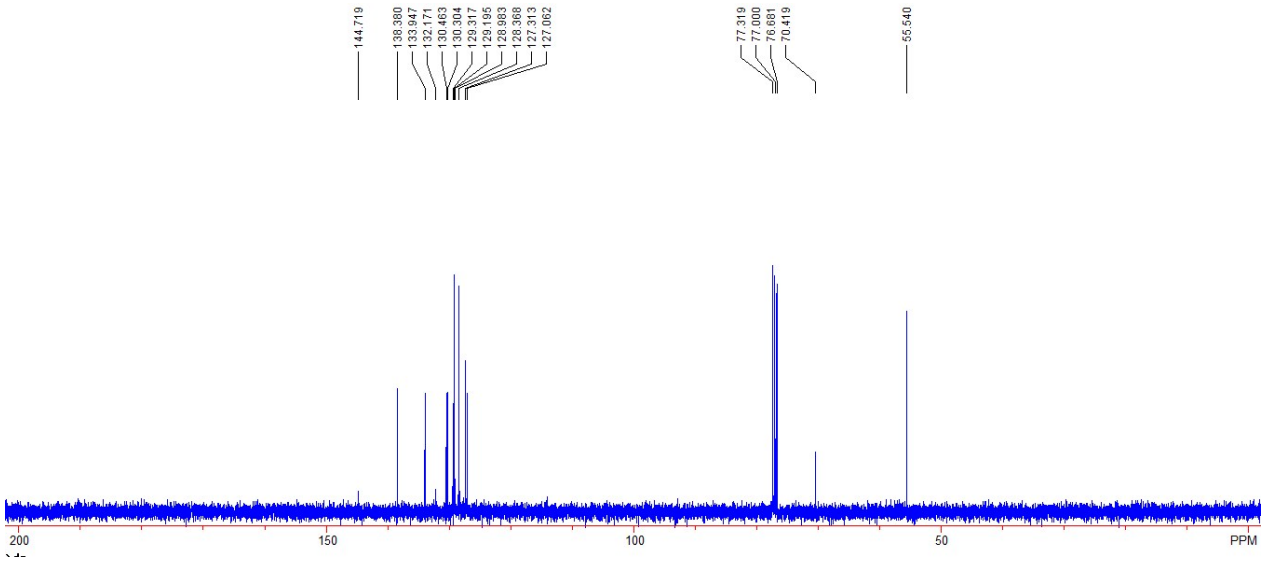

Compound **3ha**: 54 mg, 73% yield; a white solid; Mp: 104-106 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.78 (s, 4H), 5.23 (s, 2H), 7.15 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 2H), 7.25-7.38 (m, 6H), 7.45-7.48 (m, 4H), 7.80-7.84 (m, 2H), 7.86 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 55.5, 70.3, 115.9 (d, *J* = 22.3 Hz), 126.8 (d, *J* = 2.9 Hz), 127.3, 127.6 (d, *J* = 8.2 Hz), 128.3, 129.2, 130.5, 138.4, 146.6, 162.8 (d, *J* = 246.1 Hz); IR ($CH_2Cl_2$) ν 3119, 2971, 2922, 2857, 1545, 1486, 1137, 1094, 833, 745, 695 cm$^{-1}$; HRMS (DART) Calcd. for $C_{23}H_{22}N_4F$ $(M+H)^+$: 373.1823, found: 373.1823.

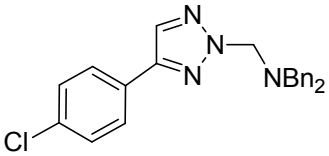




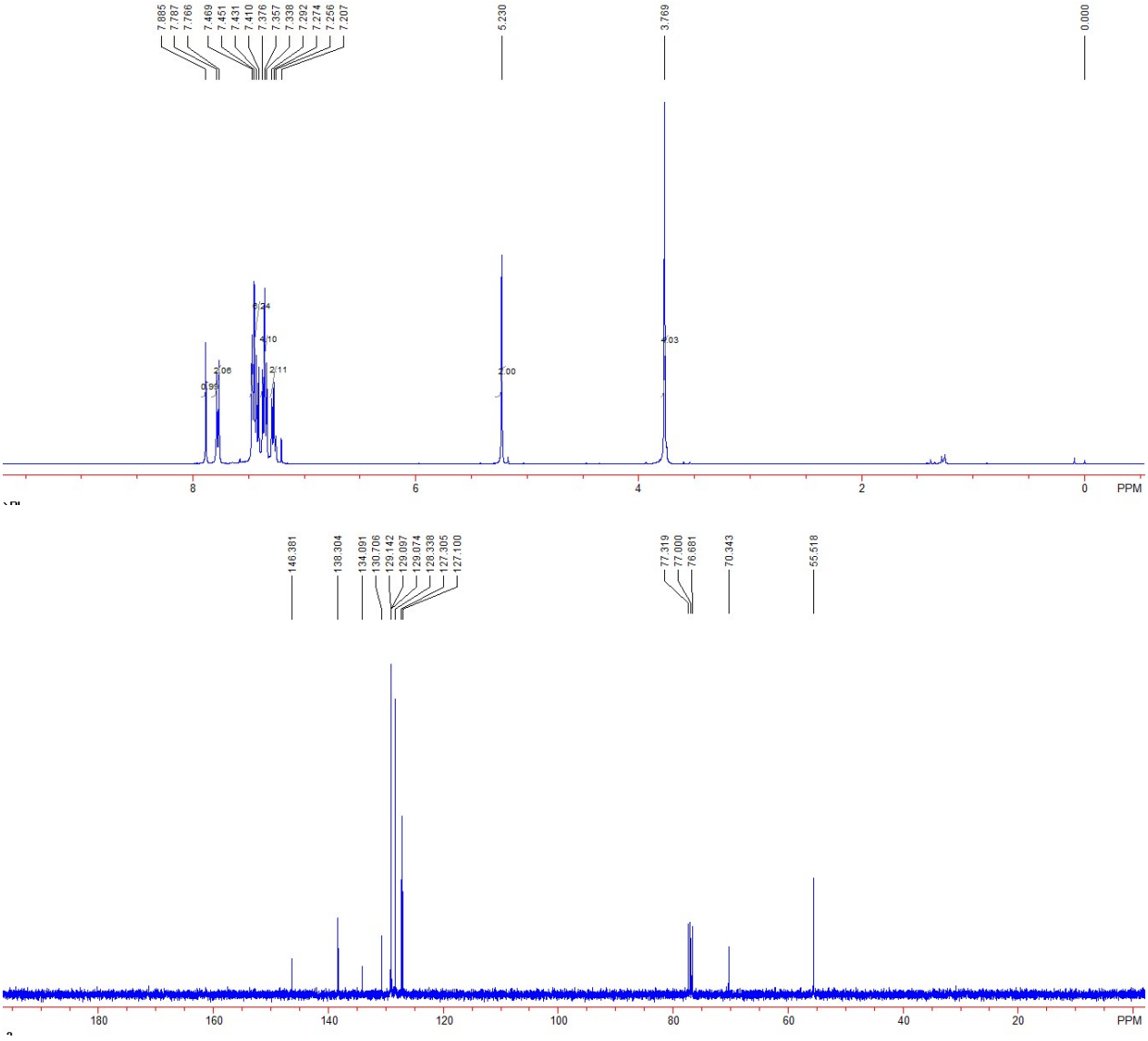

Compound **3ia**: 63 mg, 81% yield; a colorless oil; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.80 (s, 4H), 5.28 (s, 2H), 7.24-7.41 (m, 8H), 7.46-7.52 (m, 5H), 7.95 (d, *J* = 8.0 Hz, 1H), 8.21 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 55.5, 70.4, 127.1, 127.3, 128.4, 129.0, 129.2, 129.3, 130.3, 130.5, 132.2, 133.9, 138.4, 144.7; IR ($CH_2Cl_2$) ν 3062, 2958, 2849, 1601, 1455, 1144, 1074, 980, 748, 696 cm$^{-1}$; HRMS (DART) Calcd. for $C_{23}H_{22}N_4Cl$ $(M+H)^+$: 389.1528, found: 389.1526.

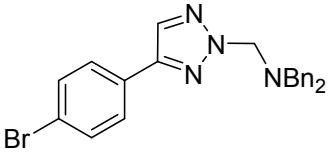


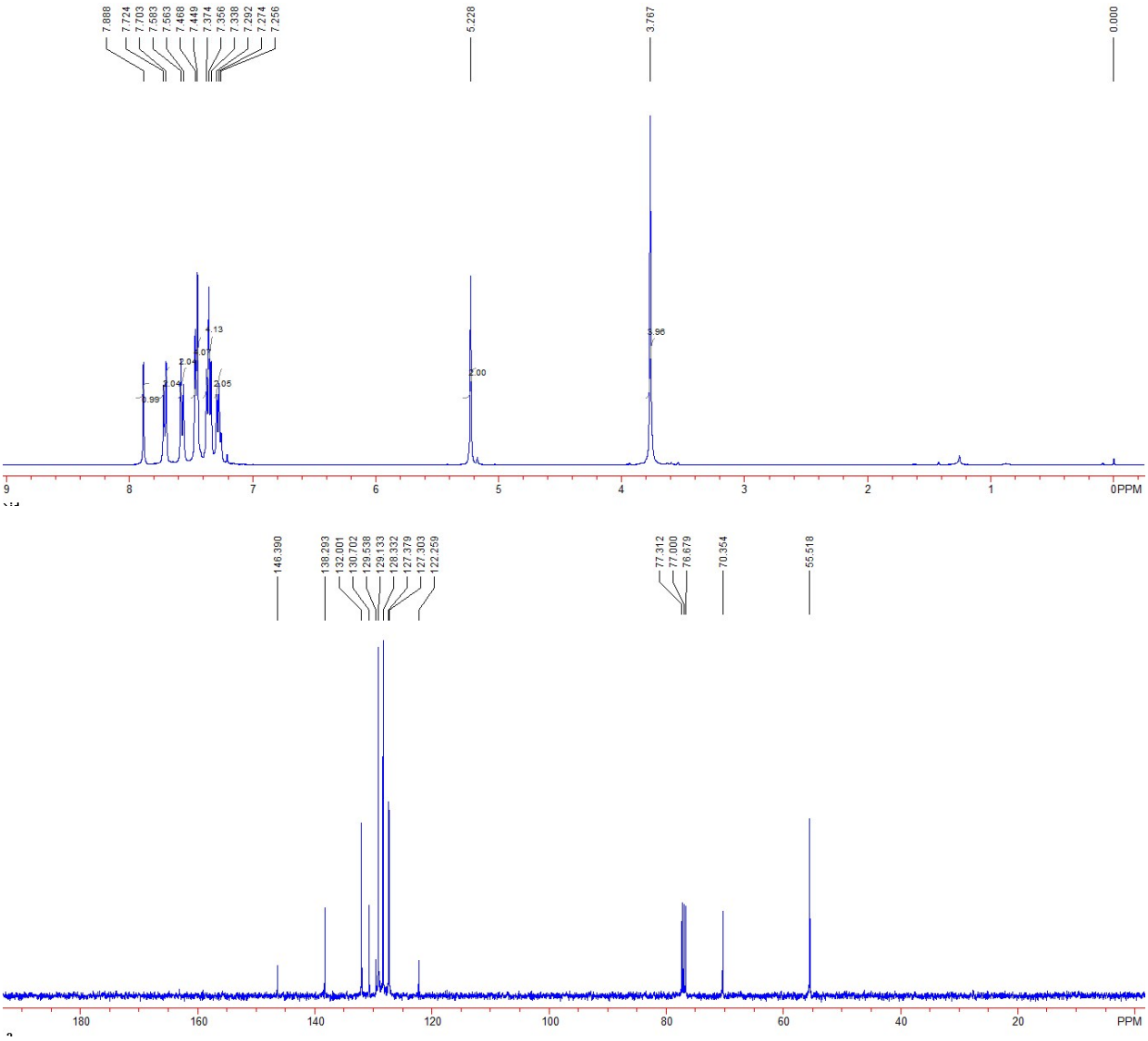
Compound **3ja**: for substrate **1j**: 61 mg, 79% yield; for substrate **4j**: 62 mg, 80% yield; a white solid; Mp: 95-96 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.77 (s, 4H), 5.23 (s, 2H), 7.20-7.30 (m, 2H), 7.36 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 4H), 7.41-7.47 (m, 6H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.89 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 55.5, 70.3, 127.1, 127.3, 128.3, 129.07, 129.10, 129.14, 130.7, 134.1, 138.3, 146.4; IR ($CH_2Cl_2$) ν 3116, 3027, 2851, 1495, 1136, 1096, 979, 755, 696 cm$^{-1}$; HRMS (DART) Calcd. for $C_{23}H_{22}N_4Cl$ $(M+H)^+$: 389.1528, found: 389.1529.

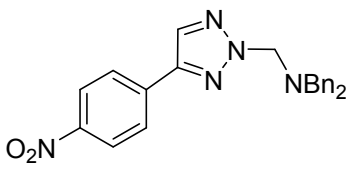



Compound **3ka**: 58 mg, 67% yield; a white solid; Mp: 98-99 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.77 (s, 4H), 5.23 (s, 2H), 7.28 (d, *J* = 7.2 Hz, 2H), 7.36 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 4H),

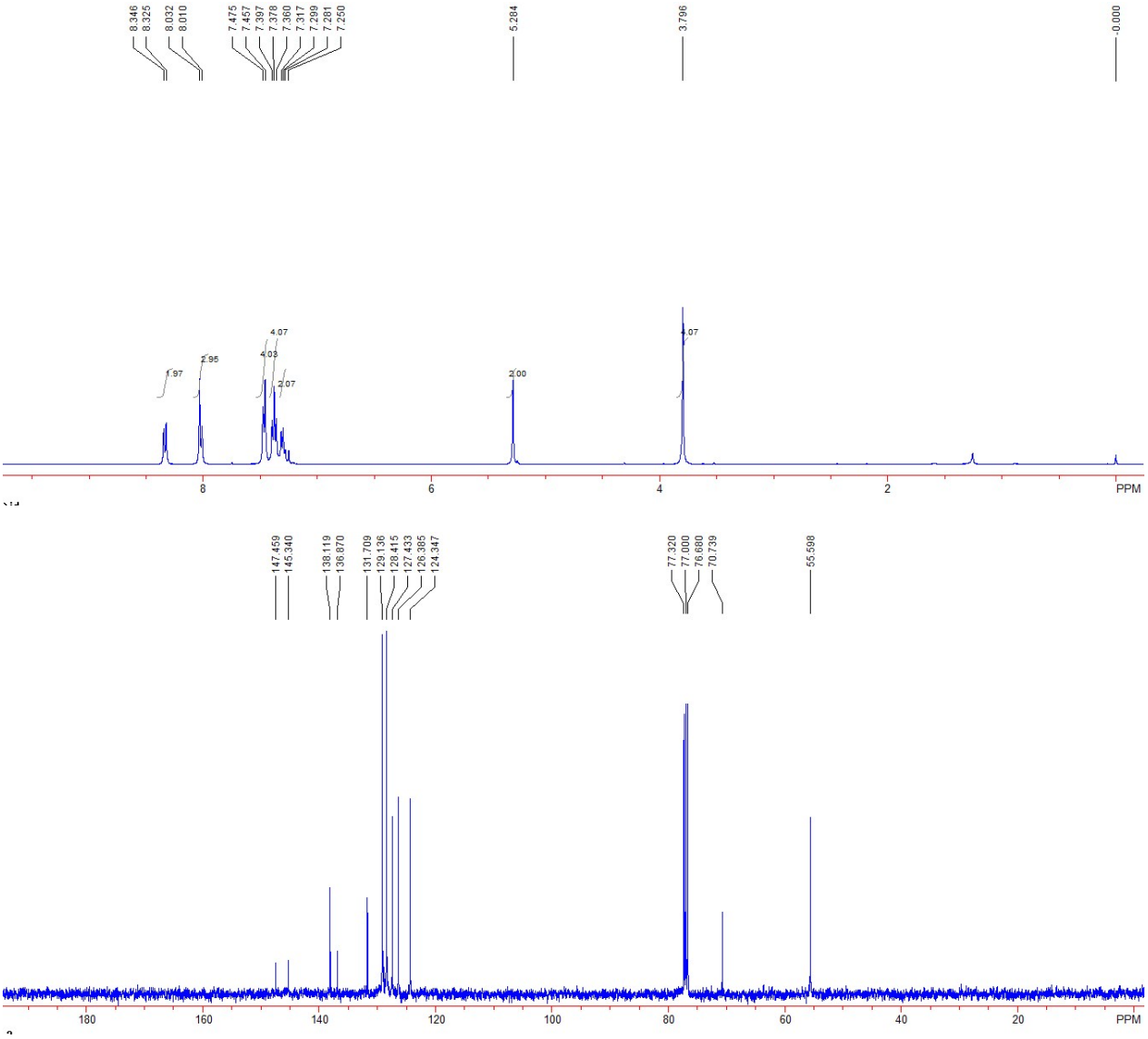
7.46 (d, $J$ = 7.2 Hz, 4H), 7.57 (d, $J$ = 8.4 Hz, 2H), 7.71 (d, $J$ = 8.4 Hz, 2H), 7.89 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 55.5, 70.4, 122.3, 127.3, 127.4, 128.3, 129.1, 129.5, 130.7, 132.0, 138.3, 146.4; IR ($CH_2Cl_2$) ν 3062, 2956, 2848, 1601, 1472, 1281, 1069, 979, 716, 696 cm$^{-1}$; HRMS (DART) Calcd. for $C_{23}H_{22}N_4Br$ $(M+H)^+$: 433.1022, found: 433.1024.

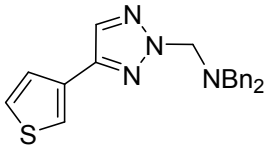



Compound **3la**: 58 mg, 73% yield; a white solid; Mp: 138-139 $^o$C; $^1$H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.80 (s, 4H), 5.28 (s, 2H), 7.30 (dd, $J$ = 7.2 Hz, $J$ = 7.2 Hz, 2H), 7.38 (dd, $J$ = 7.2 Hz, $J$ = 7.2 Hz, 4H), 7.47 (d, $J$ = 7.2 Hz, 4H), 8.02 (d, $J$ = 8.4 Hz, 2H), 8.03 (s, 1H), 8.34 (d, $J$ = 8.4 Hz,

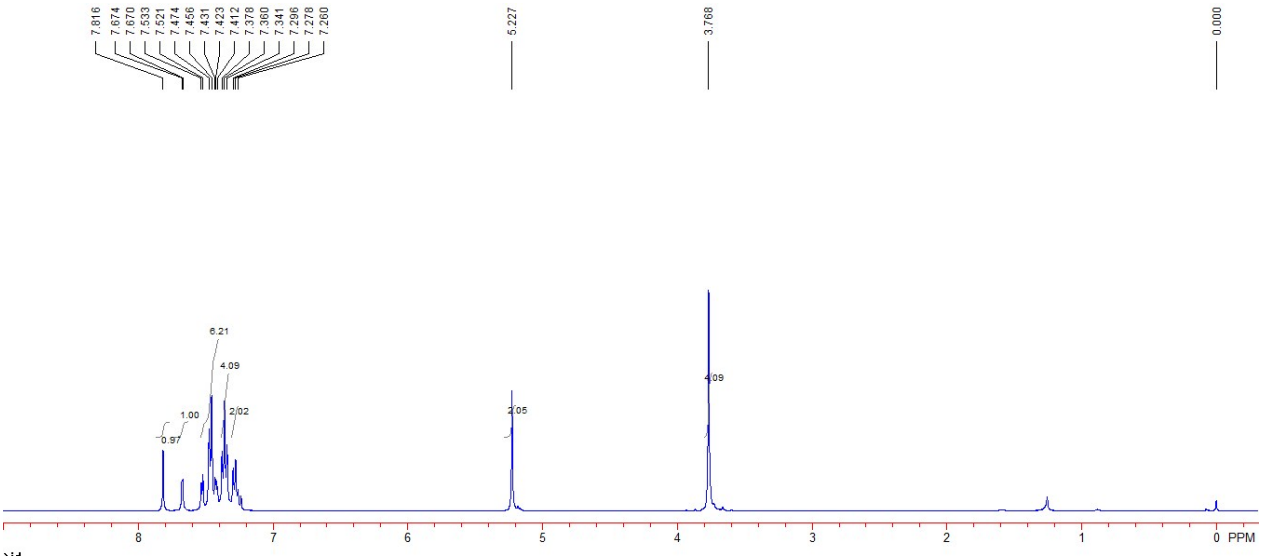
2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 55.6, 70.7, 124.3, 126.4, 127.4, 128.4, 129.1, 131.7, 136.9, 138.1, 145.3, 147.5; IR ($CH_2Cl_2$) ν 3026, 2922, 2851, 1605, 1519, 1346, 1141, 1002, 852, 738, 670 cm$^{-1}$; HRMS (DART) Calcd. for $C_{23}H_{22}O_2N_5$ $(M+H)^+$: 400.1768, found: 400.1768.

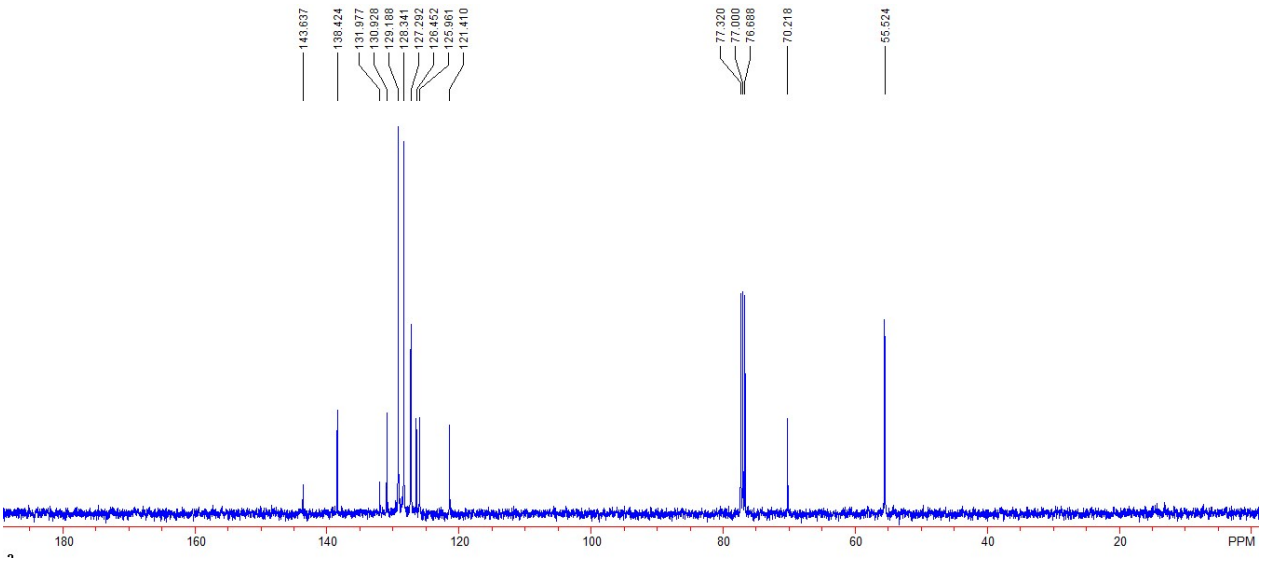


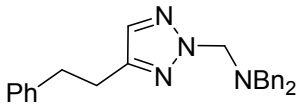




Compound **3ma**: for substrate **1m**: 60 mg, 83% yield; for substrate **4m**: 54 mg, 75% yield; a white solid; Mp: 96-97 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.77 (s, 4H), 5.23 (s, 2H), 7.28 (dd, $J$ = 7.2 Hz, $J$ = 7.2 Hz, 2H), 7.36 (dd, $J$ = 7.2 Hz, $J$ = 7.2 Hz, 4H), 7.41-7.53 (m, 6H), 7.67 (d, $J$ = 1.6 Hz, 1H), 7.82 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 55.5, 70.2, 121.4, 126.0, 126.5, 127.3, 128.3, 129.2, 130.9, 132.0, 138.4, 143.6; IR ($CH_2Cl_2$) ν 3026, 2660, 2920, 2849,

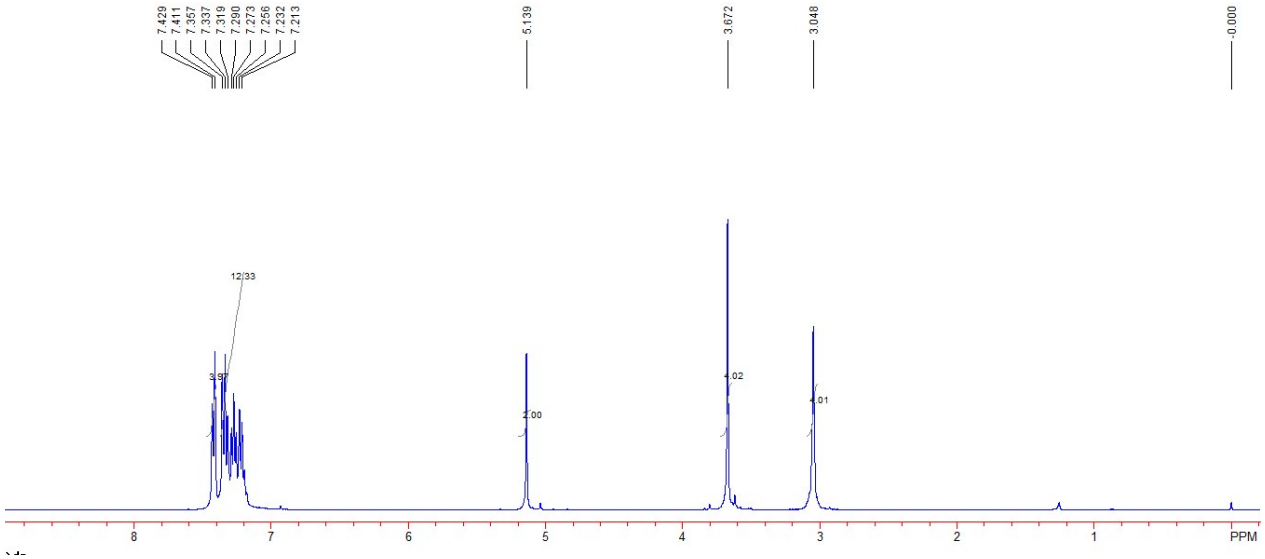
1579, 1494, 1371, 1132, 1094, 852, 745, 695 $cm^{-1}$; HRMS (DART) Calcd. for $C_{21}H_{21}N_4S$ $(M+H)^+$: 361.1481, found: 361.1480.

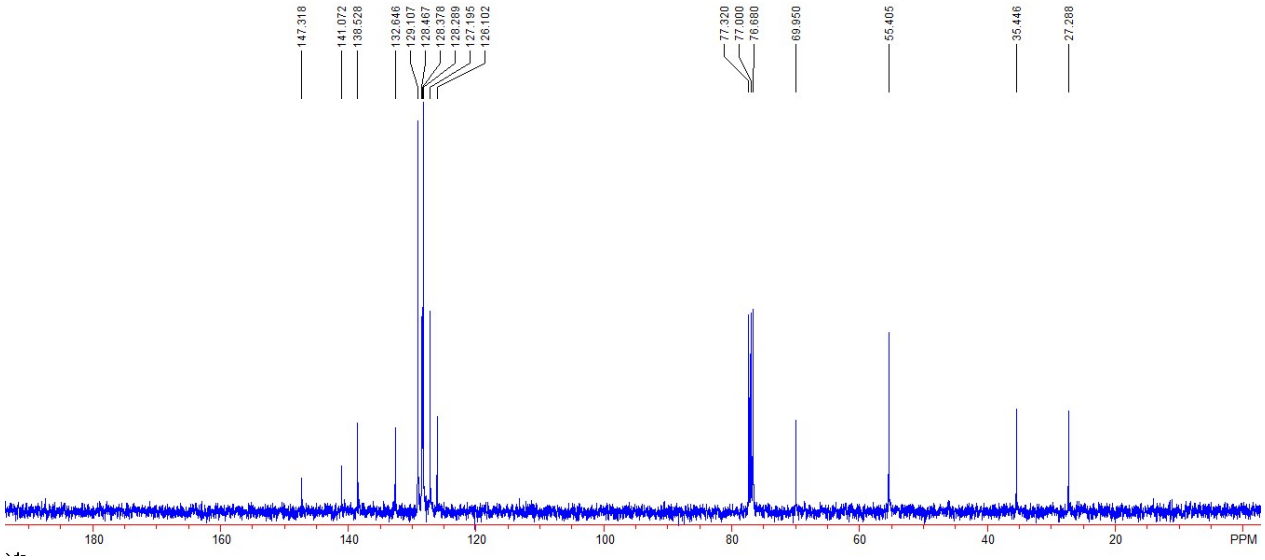


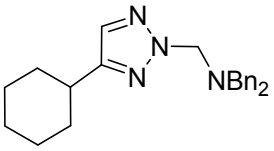



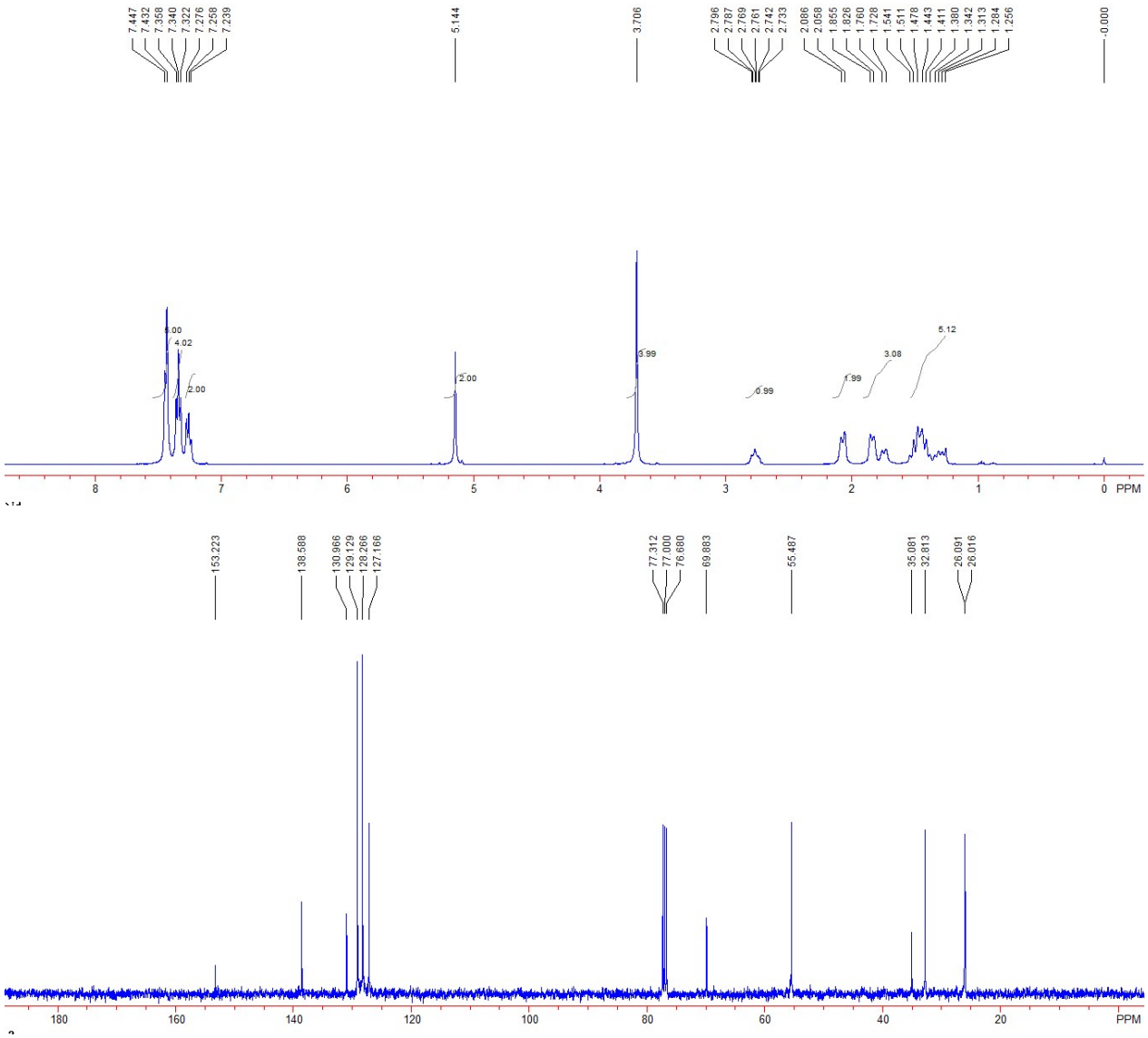

Compound **3na**: for substrate **1n**: 50 mg, 65% yield; for substrate **4n**: 50 mg, 65% yield; a white solid; Mp: 54-56 $^oC$; $^1H$ NMR ($CDCl_3$, 400 MHz, TMS) δ 3.05 (s, 4H), 3.67 (s, 4H), 5.14 (s, 2H), 7.21-7.36 (m, 12H), 7.41-7.43 (m, 4H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, TMS) δ 27.3, 35.4, 55.4, 70.0, 126.1, 127.2, 128.3, 128.4, 128.5, 129.1, 132.6, 138.5, 141.1, 147.3; IR ($CH_2Cl_2$) ν 3028, 2923, 2850, 1603, 1516, 1453, 1141, 1042, 744, 695 $cm^{-1}$; HRMS (DART) Calcd. for $C_{25}H_{27}N_4$ $(M+H)^+$: 383.2230, found: 383.2229.

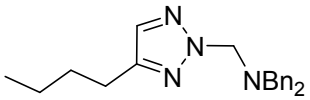


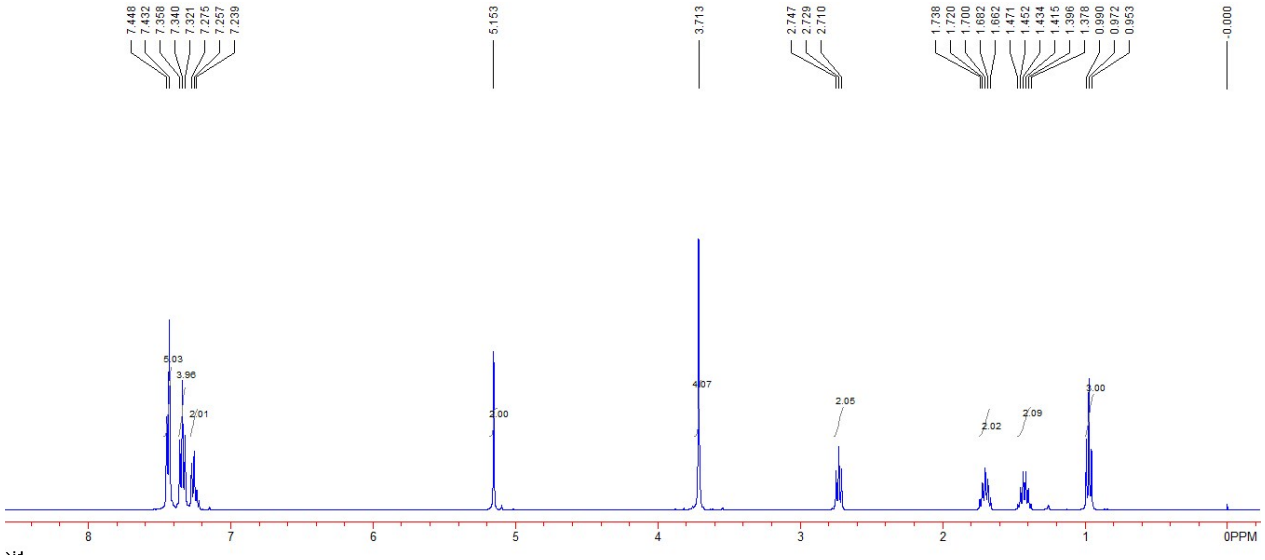



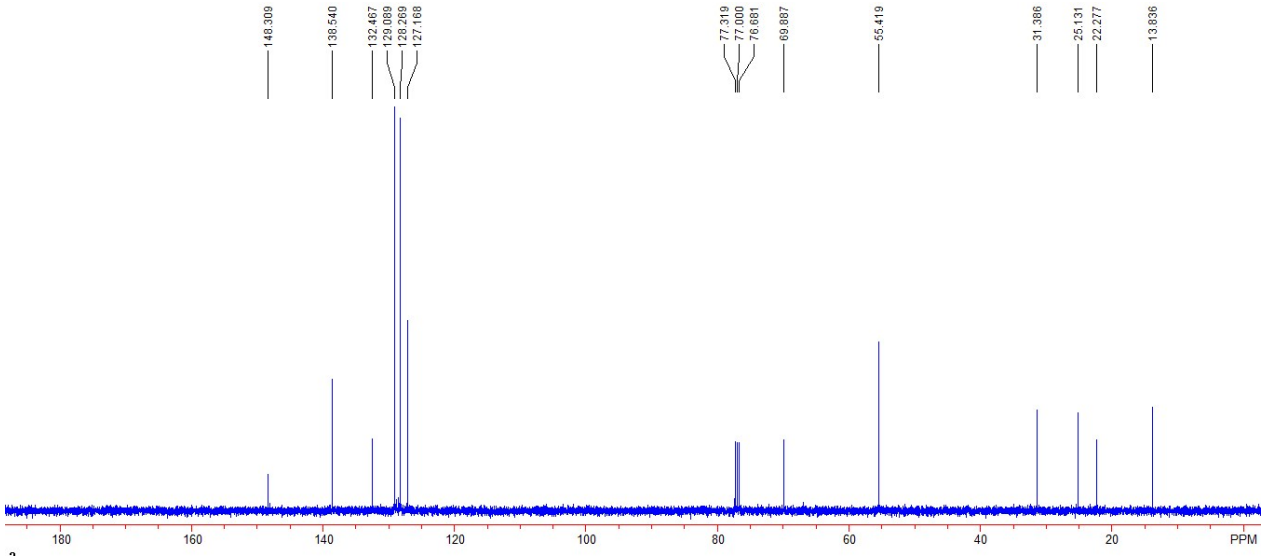

Compound **3oa**: 41 mg, 57% yield; a white solid; Mp: 92-94 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.25-1.55 (m, 5H), 1.72-1.86 (m, 3H), 2.05-2.09 (m, 2H), 2.73-2.80 (m, 1H), 3.71 (s, 4H), 5.14 (s, 2H), 7.26 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 2H), 7.34 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 4H), 7.43-7.45 (m, 5H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 26.0, 26.1, 32.8, 35.1, 55.5, 69.9, 127.2, 128.3, 129.1, 131.0, 138.6, 153.2; IR ($CH_2Cl_2$) ν 3033, 2923, 2851, 1495, 1289, 1141, 1106, 986, 744, 694 cm$^{-1}$; HRMS (DART) Calcd. for $C_{23}H_{29}N_4$ $(M+H)^+$: 361.2387, found: 361.2385.

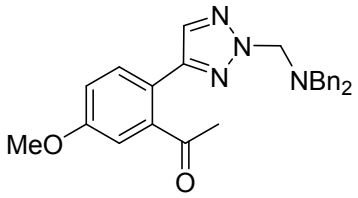


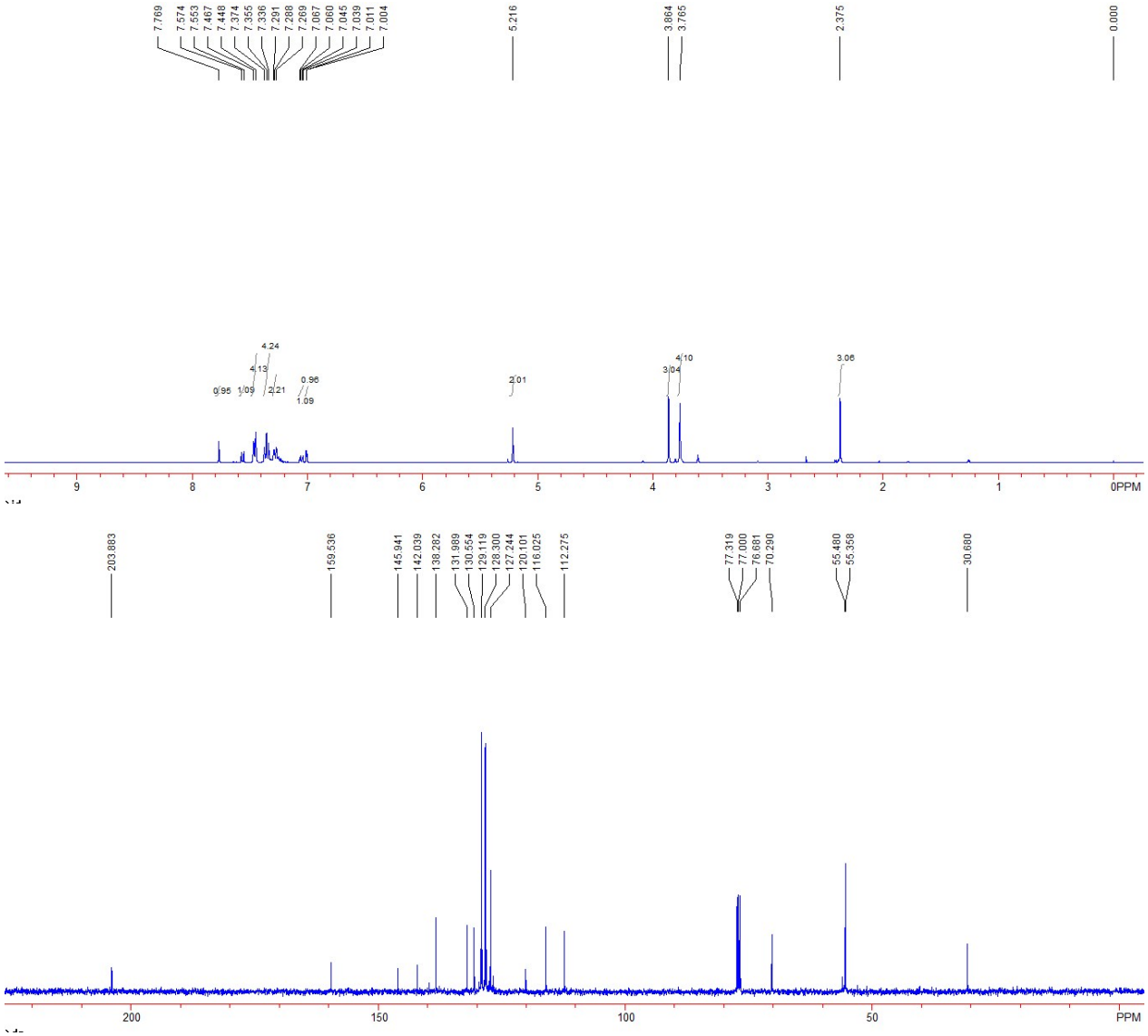

Compound **3pa**: 45 mg, 67% yield; a colorless oil; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.97 (t, *J* = 7.2 Hz, 3H), 1.37-1.48 (m, 2H), 1.66-1.74 (m, 2H), 2.73 (t, *J* = 7.2 Hz, 2H), 3.71 (s, 4H), 5.15 (s, 2H), 7.26 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 2H), 7.34 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 4H), 7.43-7.45 (m, 5H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.8, 22.3, 25.1, 31.4, 55.4, 69.9, 127.2, 128.3, 129.1, 132.5, 138.5, 148.3; IR ($CH_2Cl_2$) ν 3030, 2956, 2929, 2858, 1516, 1454, 1142, 1029, 745, 696 cm$^{-1}$; HRMS (DART) Calcd. for $C_{21}H_{27}N_4$ $(M+H)^+$: 335.2230, found: 335.2230.

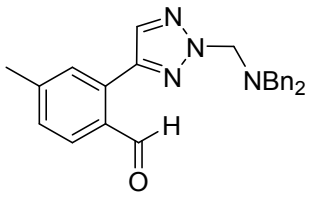


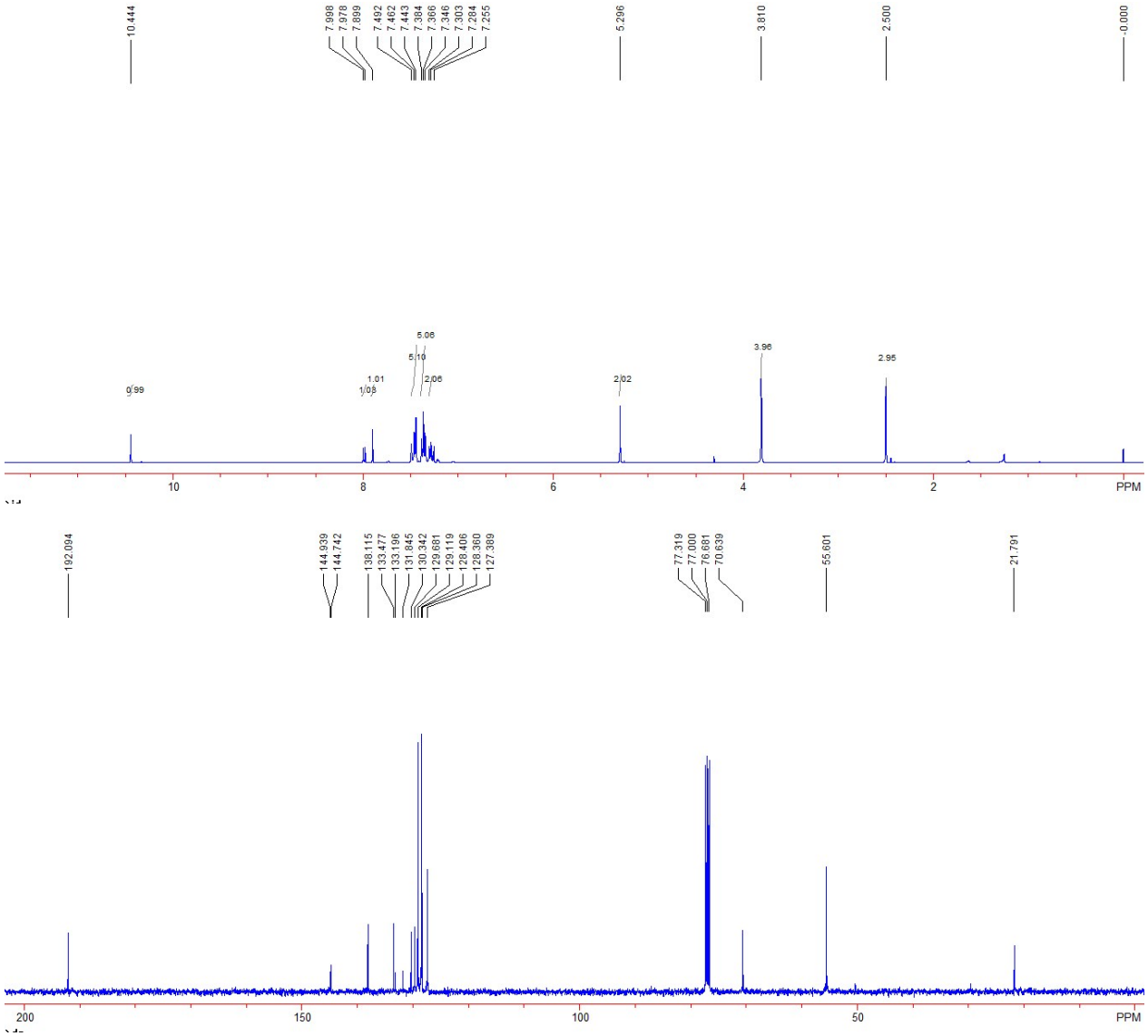



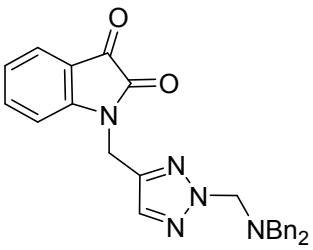

Compound **3qa**: 69 mg, 81% yield; a colorless oil; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.38 (s, 3H), 3.77 (s, 4H), 3.86 (s, 3H), 5.22 (s, 2H), 7.01 (d, *J* = 2.8 Hz, 1H), 7.05 (dd, *J* = 8.4 Hz, *J* = 2.8 Hz, 1H), 7.29 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 2H), 7.36 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 4H), 7.46 (d, *J* = 7.6 Hz, 4H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.77 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 30.7, 55.4, 55.5, 70.3, 112.3, 116.0, 120.1, 127.2, 128.3, 129.1, 130.6, 132.0, 138.3, 142.0, 145.9, 159.5, 203.9; IR ($CH_2Cl_2$) ν 3029, 2935, 2838, 1697, 1495, 1285, 1143, 1057, 978, 736, 670 cm$^{-1}$; HRMS (DART) Calcd. for $C_{26}H_{27}N_4O_2$ $(M+H)^+$: 427.2129, found: 427.2130.



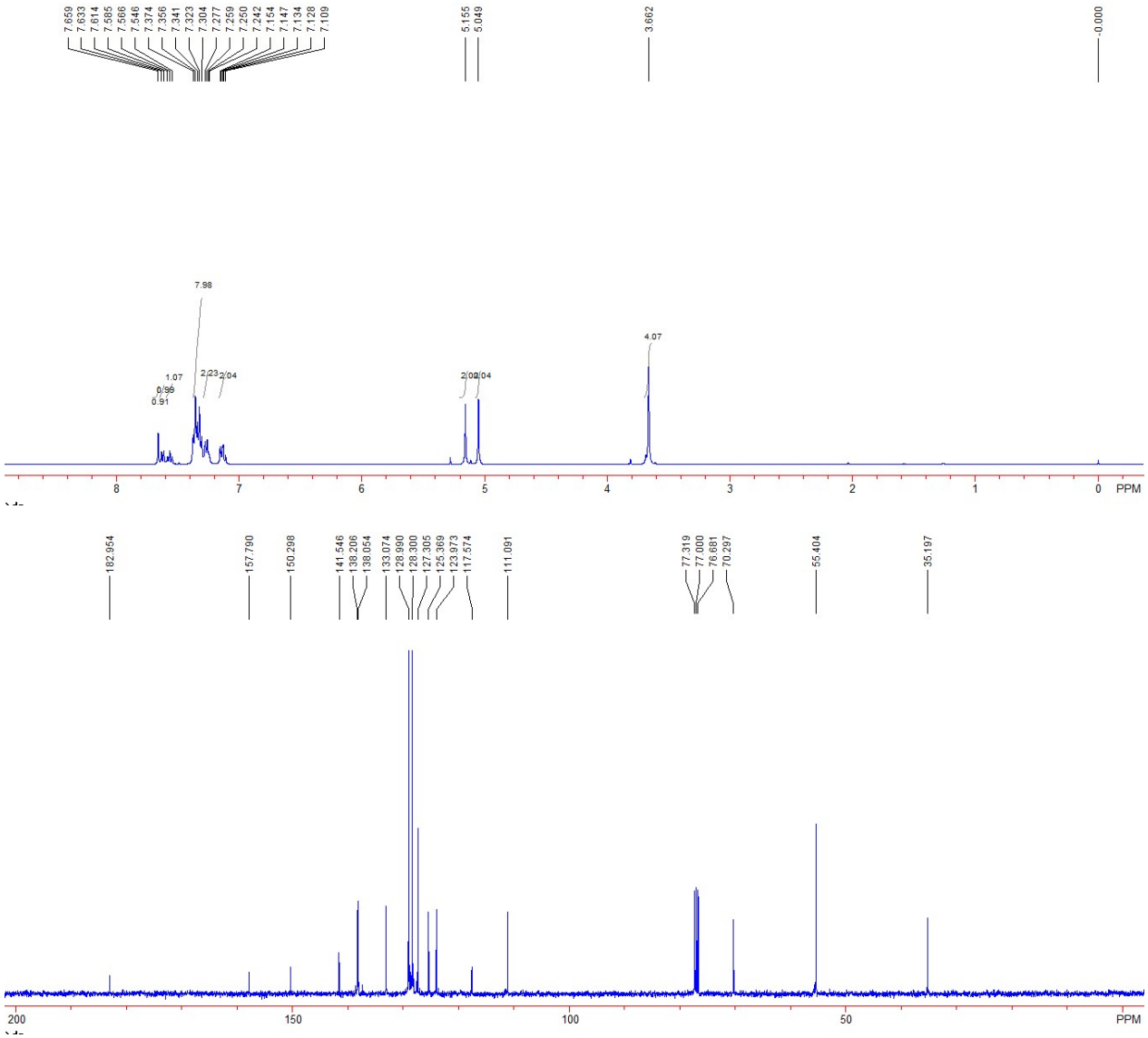

Compound **3ra**: 63 mg, 80% yield; a colorless oil; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.50 (s, 3H), 3.81 (s, 4H), 5.30 (s, 2H), 7.28 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 2H), 7.34-7.39 (m, 5H), 7.44-7.50 (m, 5H), 7.90 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 10.44 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 55.6, 70.6, 127.4, 128.36, 128.41, 129.1, 129.7, 130.3, 131.8, 133.2, 133.5, 138.1, 144.7, 144.9, 192.1; IR ($CH_2Cl_2$) ν 3030, 2923, 2852, 1688, 1606, 1495, 1220, 1069, 993, 746, 698 cm$^{-1}$; HRMS (DART) Calcd. for $C_{25}H_{25}N_4O$ $(M+H)^+$: 397.2023, found: 397.2025.

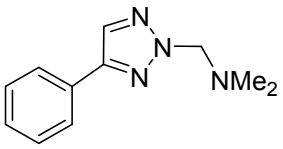


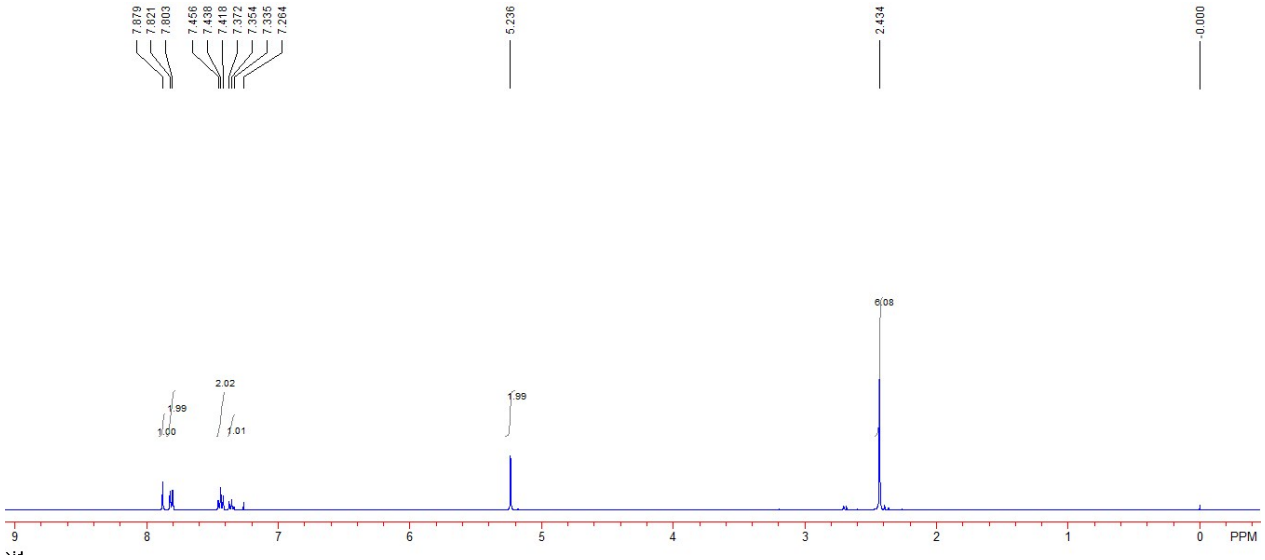

Compound **3sa**: 78 mg, 89% yield; a yellow solid; Mp: 116-118 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.67 (s, 4H), 5.05 (s, 2H), 5.16 (s, 2H), 7.10-7.16 (m, 2H), 7.24-7.26 (m, 2H), 7.27-7.38 (m, 8H), 7.57 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.66 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 35.2, 55.4, 70.3, 111.1, 117.6, 124.0, 125.4, 127.3, 128.3, 129.0, 133.1, 138.1, 138.2, 141.5, 150.3, 157.8, 183.0; IR ($CH_2Cl_2$) ν 3030, 2922, 2837, 1739, 1613, 1471, 1152, 1028, 741, 670 cm$^{-1}$; HRMS (DART) Calcd. for $C_{26}H_{24}N_5O_2$ $(M+H)^+$: 438.1925,

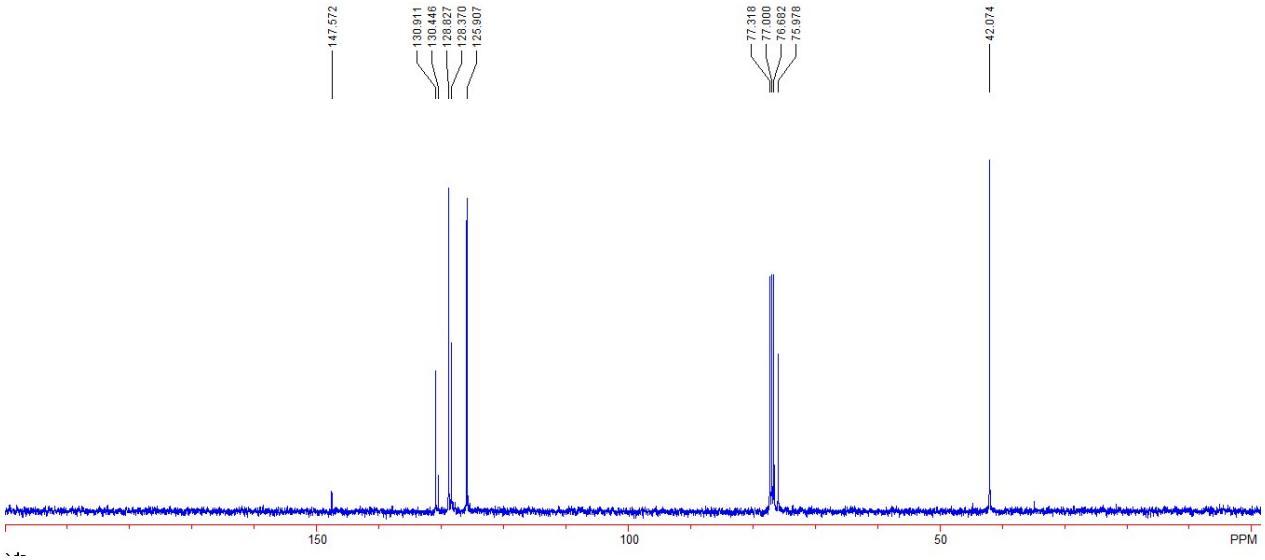
found: 438.1925.

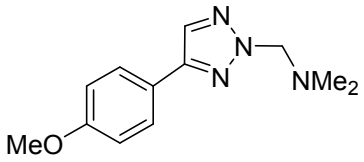


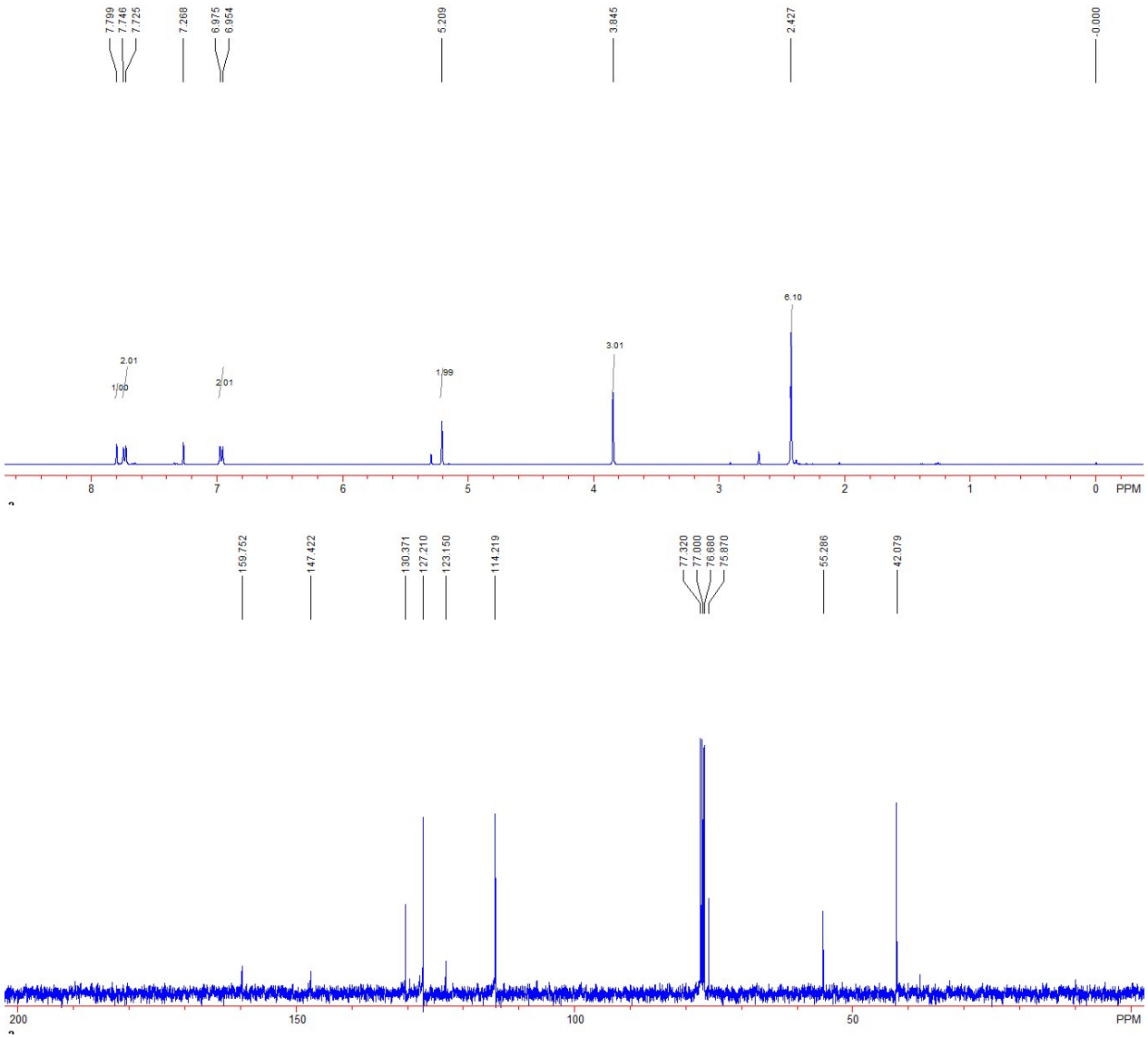

Compound **3ab**: 33 mg, 82% yield; a white solid; Mp: 66-68 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.43 (s, 6H), 5.24 (s, 2H), 7.35 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H), 7.44 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 2H), 7.81 (d, *J* = 7.2 Hz, 2H), 7.88 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 42.1, 76.0, 125.9, 128.4, 128.8, 130.4, 130.9, 147.6; IR ($CH_2Cl_2$) ν 2973, 2927, 2883, 1456, 1379, 1046, 898, 769, 695 cm$^{-1}$; HRMS (DART) Calcd. for $C_{11}H_{15}N_4$ $(M+H)^+$: 203.1291, found: 203.1290.

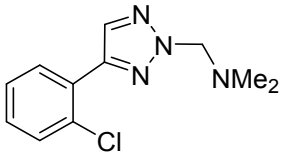


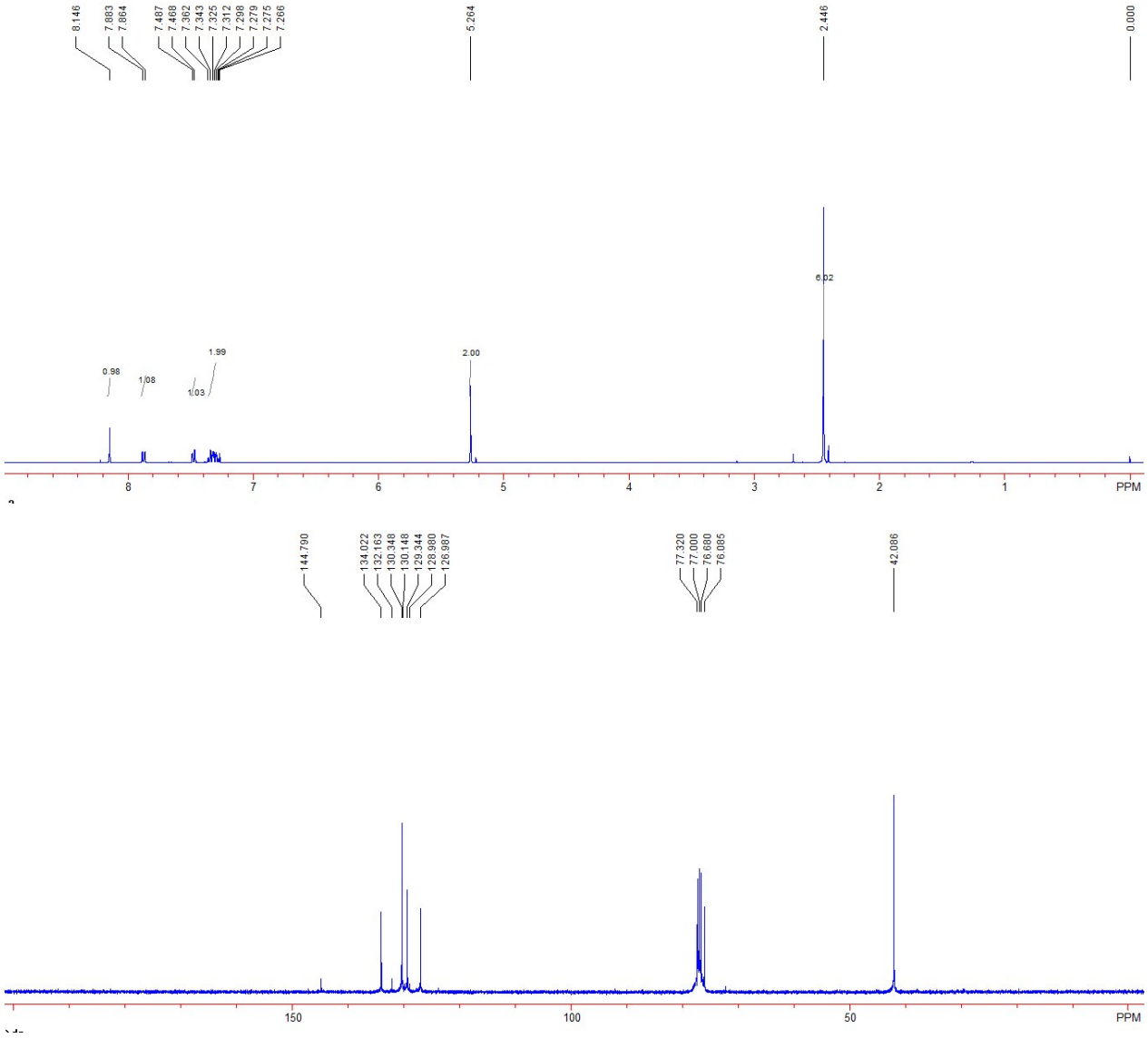



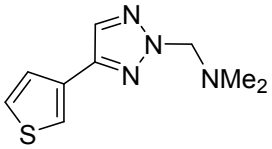

Compound **3fb**: 31 mg, 67% yield; a white solid; Mp: 80-82 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.43 (s, 6H), 3.85 (s,3H), 5.21 (s, 2H), 6.96 (d, $J$ = 8.4 Hz, 2H), 7.74 (d, $J$ = 8.4 Hz, 2H), 7.80 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 42.1, 55.3, 75.9, 114.2, 123.2, 127.2, 130.4, 147.4, 159.8; IR ($CH_2Cl_2$) ν 2944, 2836, 2790, 1615, 1486, 1177, 1029, 825, 736, 661 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{12}H_{17}N_4O$ $(M+H)^+$: 233.1397, found: 233.1397.



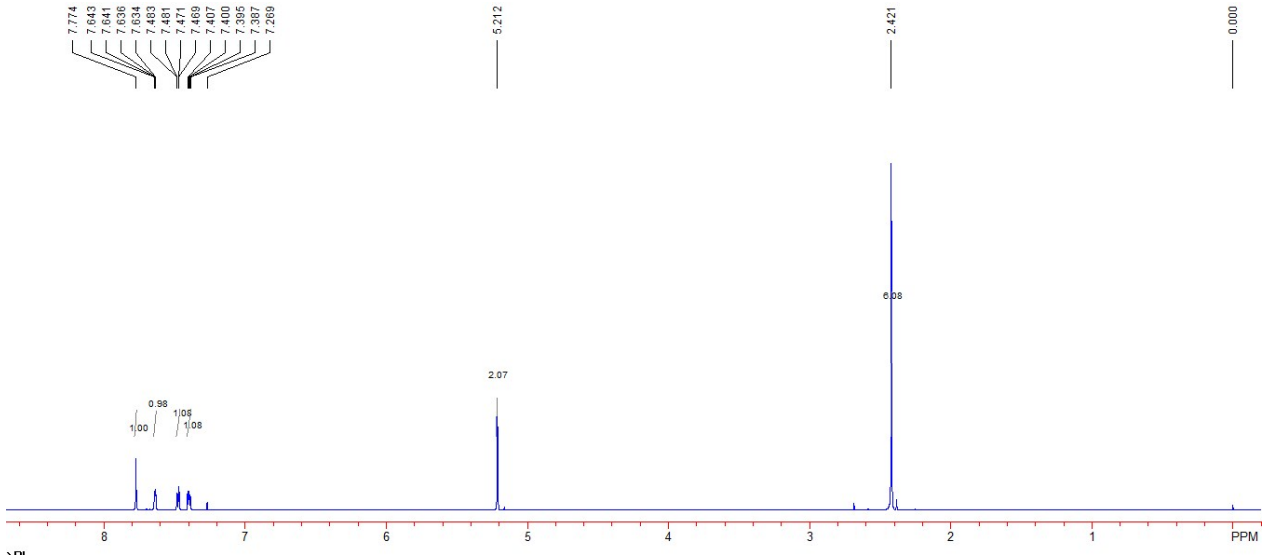



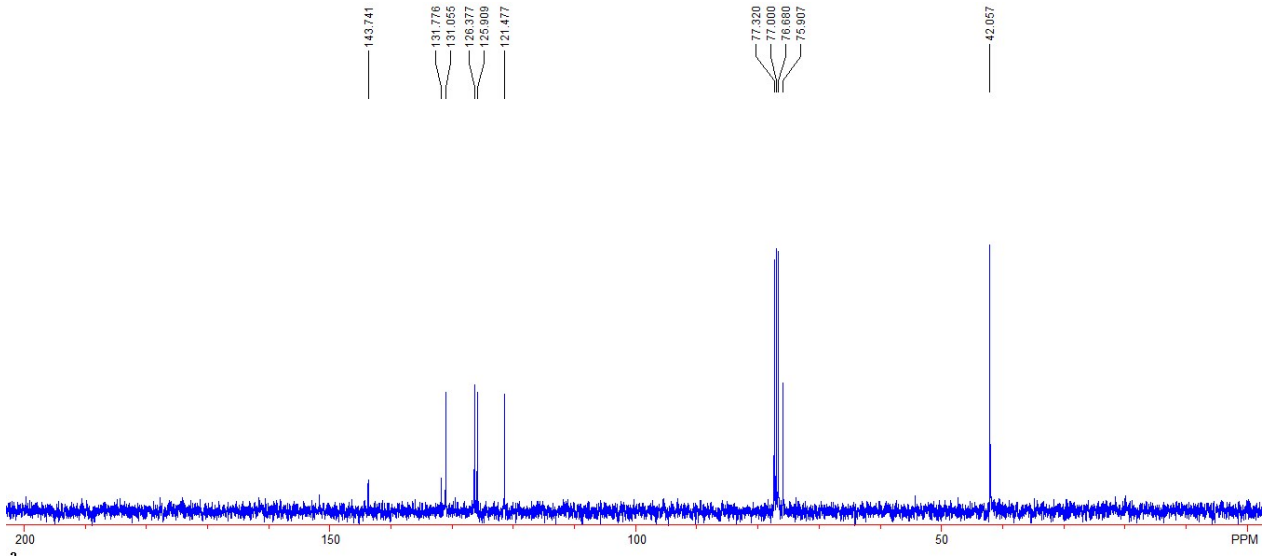

Compound **3ib**: 33 mg, 70% yield; a white solid; Mp: 82-83 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (s, 6H), 5.26 (s, 2H), 7.27-7.37 (m, 2H), 7.48 (d, $J$ = 7.6 Hz, 1H), 7.87 (d, $J$ = 7.6 Hz, 1H), 8.15 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 42.1, 76.1, 127.0, 129.0, 129.3, 130.1, 130.3, 132.2, 134.0, 144.8; IR ($CH_2Cl_2$) ν 2971, 2886, 2810, 1341, 1084, 1045, 879, 762, 666 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{11}H_{14}N_4Cl$ $(M+H)^+$: 237.0902, found: 237.0901.



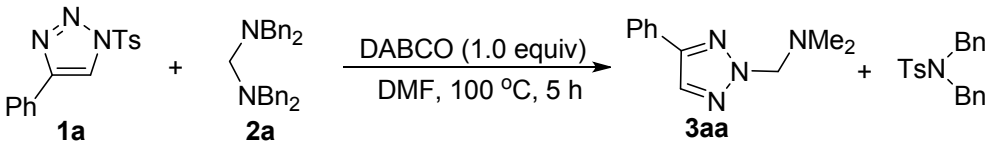




Compound **3mb**: 31 mg, 74% yield; a white solid; Mp: 56-58 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.42 (s, 6H), 5.21 (s, 2H), 7.40 (dd, $J$ = 4.8 Hz, $J$ = 2.8 Hz, 1H), 7.48 (dd, $J$ = 4.8 Hz, $J$ = 0.8 Hz, 2H), 7.64 (dd, $J$ = 2.8 Hz, $J$ = 0.8 Hz, 1H), 7.77 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 42.1, 75.9, 121.5, 125.9, 126.4, 131.1, 131.8, 143.7; IR ($CH_2Cl_2$) ν 3109, 2977, 2942, 2793, 1472, 1327, 1057, 1004, 862, 737, 657 cm$^{-1}$; HRMS (ESI) Calcd. for $C_9H_{13}N_4S$ $(M+H)^+$: 209.0855, found: 209.0855.

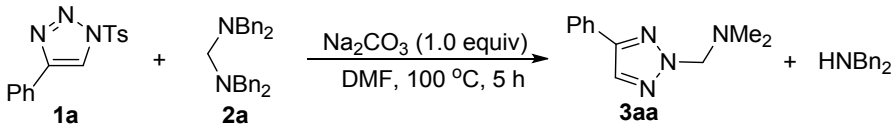

7.774
7.643
7.641
7.636
7.634
7.483
7.481
7.471
7.469
7.407
7.400
7.395
7.387
7.269
5.212
2.421
0.000
6.08
2.07
0.98
1.00
1.05
1.08
8
7
6
5
4
3
2
1
PPM


143.741
131.776
131.055
126.377
125.909
121.477
77.320
77.000
76.680
75.907
42.057
200
150
100
50
PPM

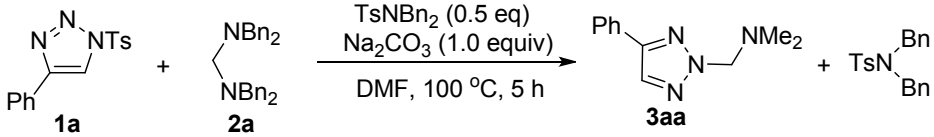
**Control experiments:**




A solution of compound **1a** (0.2 mmol), compound **2a** (0.2 mmol), and DABCO (0.2 mmol) in DMF (2 mL) was stirred at 100 °C in a well-sealed tube under $N_2$ for 5 h. After completion of the reaction, the reaction was cooled to room temperature, and the mixture was purified by silica gel column flash chromatography (eluent: petroleum ether / ethyl acetate = 20 / 1) to afford the desired $TsNBn_2$ in 91% yield.



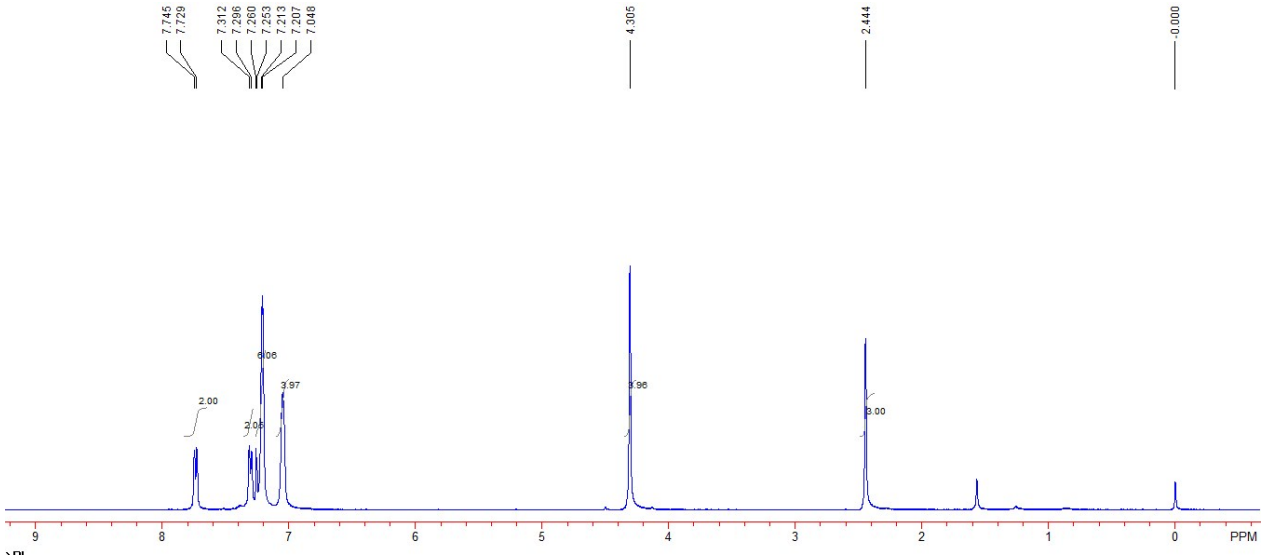

A solution of compound **1a** (0.2 mmol), compound **2a** (0.2 mmol), and $Na_2CO_3$ (0.2 mmol) in DMF (2 mL) was stirred at 100 °C in a well-sealed tube under $N_2$ for 5 h. After completion of the reaction, the reaction was cooled to room temperature, and the mixture was purified by silica gel column flash chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the desired $HNBn_2$ in 85% yield.




A solution of compound **1a** (0.2 mmol), compound **2a** (0.2 mmol), $TsNBn_2$ (0.1 mmol) and $Na_2CO_3$ (0.2 mmol) in DMF (2 mL) was stirred at 100 °C in a well-sealed tube under $N_2$ for 5 h. After completion of the reaction, the reaction was cooled to room temperature, and the mixture was purified by silica gel column flash chromatography (eluent: petroleum ether / ethyl acetate = 20 / 1) to afford the desired $TsNBn_2$ in 94% yield.

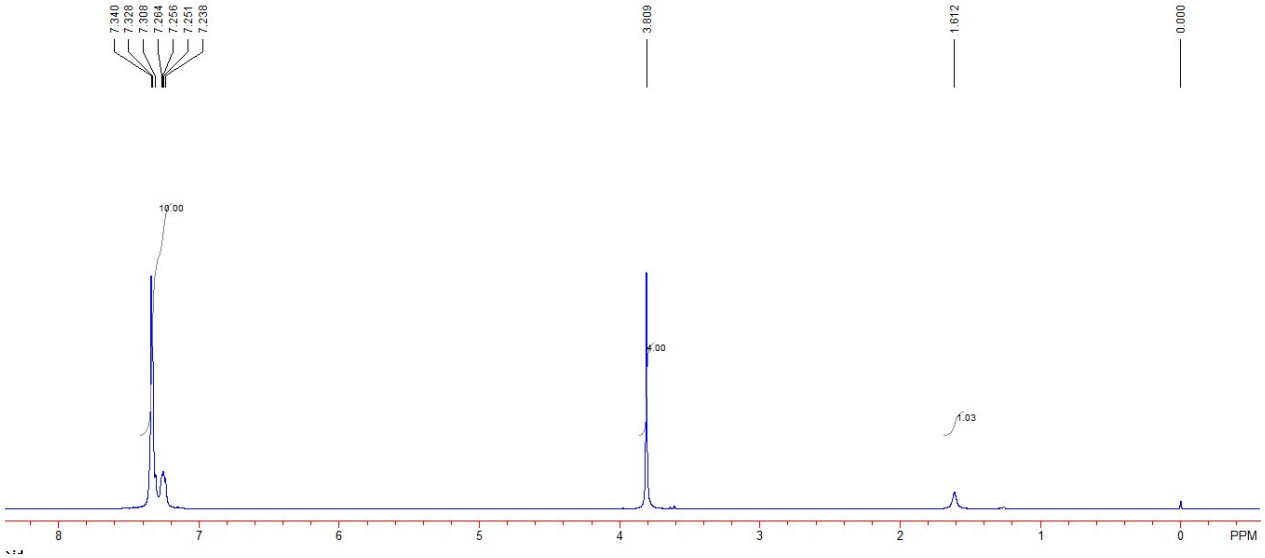
$TsNBn_2$

$^1H$ NMR ($CDCl_3$, 400 MHz, TMS) δ 2.44 (s, 3H), 4.31 (s, 4H), 7.04-7.05 (m, 4H), 7.20-7.26 (m, 6H), 7.30 (d, $J$ = 6.4 Hz, 2H), 7.74 (d, $J$ = 6.4 Hz, 2H).

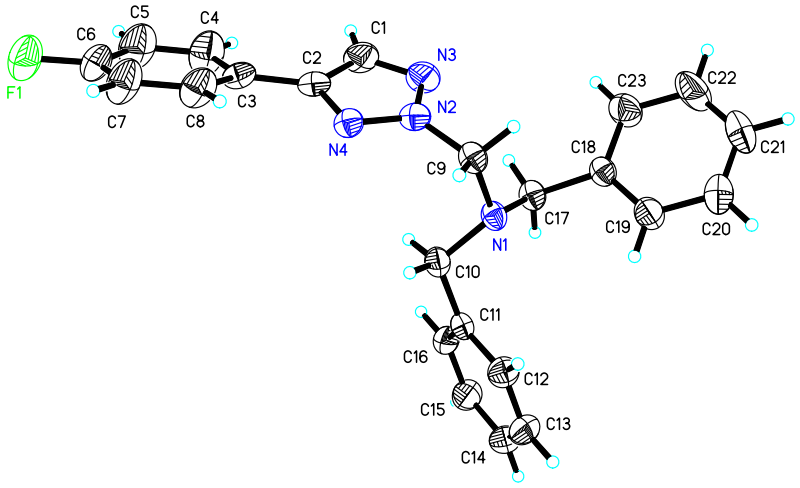



$HNBn_2$

$^1H$ NMR ($CDCl_3$, 400 MHz, TMS) δ 1.03 (br, 1H), 3.81 (s, 4H), 7.23-7.34 (m, 10H).



## X-ray Crystal Data




The crystal data of **3ha** have been deposited in CCDC with number 1465122. Empirical Formula: $C_{23}H_{21}FN_4$; Formula Weight: 372.44; Crystal Color, Habit: colorless, Crystal Dimensions: 0.210 x 0.170 x 0.120 $mm^3$; Crystal System: Triclinic; Lattice Parameters: a = 10.5273(12)Å, b = 11.4221(14)Å, c = 34.217(4)Å, α = 90.072(3)°, β = 98.137(3)°, γ = 105.697(3)°, V = 3917.7(8)$Å^3$; Space group: P -1; Z = 8; $D_{calc}$ = 1.263 $g/cm^3$; $F_{000}$ = 1568; Final R indices [I>2sigma(I)] R1 = 0.0679, wR2 = 0.1742.

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