Supporting Information

Pd(II)-catalyzed aerobic 1,2-difunctionalization of conjugated dienes: efficient synthesis of morpholines and 2-morpholones

Ke Wen,[a] Zhengxing Wu,[a] Buyun Chen,[a] Jianzhong Chen,[a] and Wanbin Zhang*[a]

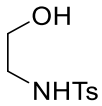
[a] Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China

CONTENTS

1. Preparation of *β*-aminoalcohol and *α*-aminoacid substrates

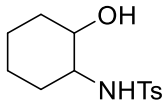
All of the reagents for the synthesis were commercially available and used without further purification.

***N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide (1a)**[1a]



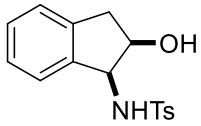
Under air, 2-aminoethanol (0.61 mL, 10.0 mmol, 1.0 equiv) and 4-toluene sulfonyl chloride (1.91 g, 10.0 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (30 mL) and the mixture was stirred at 0 ^oC for 10 min, then Et_3N (1.38 mL, 10.0 mmol, 1.0 equiv) was added to the mixture dropwise in 10 min at 0 ^oC. The resulting mixture was stirred at room tempetature for 18 h. Then the reaction mixture was washed with H_2O (30 mL, 3 times) and saturated NaCl solution (30 mL, once). The organic phase was collected and dried over over Na_2SO_4. Removal of the solvent under reduced pressure gave the crude product as a gummy oil. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) gave **1a** as a white solid (1.7868 g, 83% yield). **Known compound**. **^{1}H NMR** (400 MHz, CDCl3) δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.83 (t, *J* = 6.0 Hz, 1H), 3.65 (t, *J* = 5.0 Hz, 2H), 3.11 (br, 1H), 3.04 (dd, *J* = 10.6, 5.4 Hz, 2H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 136.5, 129.8, 127.1, 61.2, 45.2, 21.5.

***N*-(2-hydroxycyclohexyl)-4-methylbenzenesulfonamide (1b)**[1b]



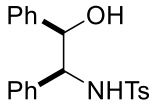
Using the same method and molar quantity as **1a**, the product **1b** was obtained as a white solid (2.0471 g, 76% yield). **Known compound**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 4.93 (d, *J* = 7.6 Hz, 1H), 3.78 (dt, *J* = 4.8, 2.4 Hz, 1H), 3.23 (ddd, *J* = 10.4, 7.6, 4.0 Hz, 1H), 2.43 (s, 3H), 1.70 – 1.34 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.4, 138.0, 129.7, 127.0, 68.8, 55.1, 31.5, 28.0, 23.3, 21.5, 19.8.

***N*-(2-hydroxy-2,3-dihydro-1*H*-inden-1-yl)-4-methylbenzenesulfonamide (1c)**[1c]



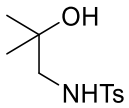
Using the same method and molar quantity as **1a**, the product **1c** was obtained as a yellow solid (2.6697 g, 88% yield). **Known compound**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.17 – 7.04 (m, 3H), 6.98 (d, *J* = 7.4 Hz, 1H), 5.36 (d, *J* = 9.2 Hz, 1H), 4.59 (dd, *J* = 9.0, 4.8 Hz, 1H), 4.22 (td, *J* = 5.0, 1.6 Hz, 1H), 2.95 (dd, *J* = 16.8, 5.0 Hz, 1H), 2.79 (d, *J* = 16.8 Hz, 1H), 2.38 (s, 3H), 1.96 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.8, 139.5, 139.4, 137.6, 129.9, 128.5, 127.3, 127.2, 125.4, 124.6, 72.8, 61.3, 39.3, 21.6.

***N*-(2-hydroxy-1,2-diphenylethyl)-4-methylbenzenesulfonamide (1d)**[1d]



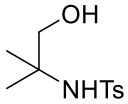
Using the same method and molar quantity as **1a**, the product **1d** was obtained as a white solid (1.8373 g, 50% yield). **Known compound**. **^{1}H NMR** (400 MHz, DMSO) δ 8.11 (d, *J* = 9.6 Hz, 1H), 7.29 (d, *J* = 7.4 Hz, 2H), 7.19 (d, *J* = 6.2 Hz, 2H), 7.15 – 7.09 (m, 2H), 7.09 – 6.97 (m, 8H), 5.37 (d, *J* = 5.8 Hz, 1H), 4.62 (t, *J* = 5.8 Hz, 1H), 4.28 (dd, *J* = 9.2, 7.0 Hz, 1H), 2.26 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 143.2, 142.1, 139.4, 139.1, 129.4, 128.7, 128.0, 127.5, 127.4, 127.2, 126.9, 126.6, 75.8, 63.8, 21.3.

***N*-(2-hydroxy-2-methylpropyl)-4-methylbenzenesulfonamide (1e)**[1e]



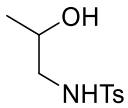
Using the same method and molar quantity as **1a**, the product **1e** was obtained as a white solid (1.3626 g, 56% yield). **Known compound**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 5.19 (t, *J* = 6.2 Hz, 1H), 2.78 (d, *J* = 6.6 Hz, 2H), 2.35 (s, 3H), 2.06 (br, 1H), 1.15 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 136.8, 129.8, 127.1, 70.2, 53.4, 27.1, 21.5.

***N*-(1-hydroxy-2-methylpropan-2-yl)-4-methylbenzenesulfonamide (1f)**[1f]



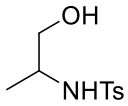
Using the same method and molar quantity as **1a**, the product **1f** was obtained as a white solid (1.9708 g, 81% yield). **Known compound**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 5.16 (s, 1H), 3.46 (s, 2H), 2.43 (s, 3H), 2.35 (br, 1H), 1.12 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.3, 139.8, 129.6, 127.0, 70.1, 57.9, 24.5, 21.5.

***N*-(2-hydroxy-2-methylpropyl)-4-methylbenzenesulfonamide (1g)**[1e]



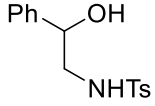
Using the same method and molar quantity as **1a**, the product **1g** was obtained as a white solid (1.4446 g, 63% yield). **Known compound**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 5.24 (br, 1H), 3.91 (dqd, *J* = 12.6, 6.4, 3.2 Hz, 1H), 3.04 (dd, *J* = 13.0, 3.0 Hz, 1H), 2.77 (dd, *J* = 13.0, 8.2 Hz, 1H), 2.43 (s, 3H), 2.21 (br, 1H), 1.15 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.6, 136.6, 129.8, 127.1, 66.6, 50.0, 21.5, 20.6.

***N*-(1-hydroxypropan-2-yl)-4-methylbenzenesulfonamide (1h)**[1g]



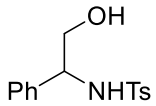
Using the same method and molar quantity as **1a**, the product **1h** was obtained as a white solid (1.9261 g, 84% yield). **Known compound**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.98 (br, 1H), 3.50 (dd, *J* = 11.0, 3.8 Hz, 1H), 3.33 (ddd, *J* = 20.4, 10.6, 6.2 Hz, 2H), 2.36 (s, 3H), 1.97 (br, 1H), 0.96 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.8, 137.7, 130.0, 127.3, 66.5, 51.7, 21.7, 17.9.

***N*-(2-hydroxy-2-phenylethyl)-4-methylbenzenesulfonamide (1i)**[1h]



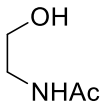
Using the same method and molar quantity as **1a**, the product **1i** was obtained as a white solid (2.2727 g, 78% yield). **Known compound**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.19 (m, 7H), 5.10 (dd, *J* = 8.0, 4.6 Hz, 1H), 4.72 (dd, *J* = 8.8, 3.6 Hz, 1H), 3.16 (ddd, *J* = 13.2, 8.2, 3.6 Hz, 1H), 2.94 (ddd, *J* = 13.4, 8.8, 4.6 Hz, 1H), 2.67 (br, 1H), 2.34 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.6, 140.8, 136.7, 129.8, 128.7, 128.2, 127.1, 125.9, 72.8, 50.2, 21.5.

***N*-(2-hydroxy-1-phenylethyl)-4-methylbenzenesulfonamide (1j)**[1i]



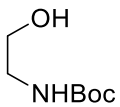
Using the same method and molar quantity as **1a**, the product **1j** was obtained as a white solid (1.8356 g, 63% yield). **Known compound**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.12 – 6.98 (m, 7H), 5.78 (t, *J* = 6.4 Hz, 1H), 4.35 (dd, *J* = 11.8, 6.6 Hz, 1H), 3.68 – 3.60 (m, 2H), 2.28 (s, 3H), 2.23 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.3, 137.6, 137.1, 129.4, 128.5, 127.8, 127.2, 126.9, 66.2, 59.7, 21.5.

***N*-(2-hydroxyethyl)acetamide (1k)**



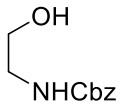
Commercially available. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (br, 1H), 4.53 (br, 1H), 3.67 (t, *J* = 4.8 Hz, 2H), 3.35 (t, *J* = 4.8 Hz, 2H), 1.99 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 61.5, 42.6, 23.2.

***tert*-butyl (2-hydroxyethyl)carbamate (1l)**



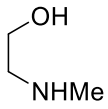
Commercially available. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.10 (br, 1H), 3.69 (t, *J* = 4.6 Hz, 2H), 3.28 (d, *J* = 4.8 Hz, 2H), 1.45 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.9, 79.7, 62.4, 43.1, 28.4.

benzyl (2-hydroxyethyl)carbamate (1m)



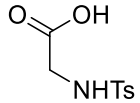
Commercially available. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H), 5.17 (br, 1H), 5.11 (s, 2H), 3.80 – 3.62 (m, 2H), 3.36 (dd, *J* = 10.4, 5.2 Hz, 2H), 2.19 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.4, 128.6, 128.2, 128.1, 66.9, 62.4, 43.5.

2-(methylamino)ethan-1-ol (1n)



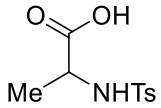
Commercially available. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.74 – 3.61 (m, 2H), 3.49 (br, 2H), 2.76 – 2.65 (m, 2H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 60.2, 53.5, 35.9.

tosylglycine (4a)[2a]



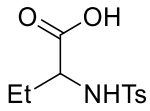
Under air, glycine (750.6 mg, 10.0 mmol, 1.0 equiv) and 4-toluene sulfonyl chloride (1.91 g, 10.0 mmol, 1.0 equiv) was dissolved in H_2O (30 mL) at room temperature, followed by the slow addition of NaOH (1.20 g, 30.0 mmol, 3.0 equiv). The mixture was heated to 40 °C and then stirred for 12 h. After the completion of reaction, the mixture was cooled to room temperature and diluted HCl solution was added until the mixture's pH = 1. Then the mixture was extracted with EtOAc (30 mL, 3 times) and washed with H_2O (10 mL, 3 times). The organic phase was collected and dried over over Na_2SO_4. Removal of the solvent under reduced pressure gave the product as a white solid (2.1320 g, 93% yield), which was pure enough and used without further purification. **Known compound**. **^{1}H NMR** (400 MHz, DMSO) δ 12.60 (br, 1H), 7.93 (t, *J* = 6.0 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 3.55 (d, *J* = 5.8 Hz, 2H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 170.7, 143.1, 138.3, 130.0, 127.0, 44.2, 21.4.

tosylalanine (4b)[2b]



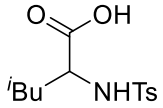
Using the same method and molar quantity as **4a**, the product **4b** was obtained as a white solid (2.1865 g, 90% yield). **Known compound**. **^{1}H NMR** (400 MHz, DMSO) δ 8.00 (d, *J* = 7.4 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 3.71 (p, *J* = 7.2 Hz, 1H), 2.35 (s, 3H), 1.11 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 178.4, 147.7, 143.7, 134.7, 131.7, 56.3, 26.2, 23.6.

2-((4-methylphenyl)sulfonamido)butanoic acid (4c)[2c]



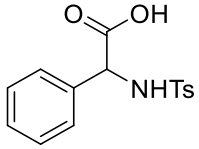
Using the same method and molar quantity as **4a**, the product **4c** was obtained as a white solid (2.2642 g, 88% yield). **Known compound**. **^{1}H NMR** (400 MHz, DMSO) δ 12.61 (br, 1H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 3.55 (td, *J* = 8.4, 5.6 Hz, 1H), 2.34 (s, 3H), 1.69 – 1.33 (m, 2H), 0.73 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 173.1, 142.9, 138. 9, 129.8, 126.9, 57.4, 25.9, 21.4, 10.4.

tosylleucine (4d)[2d]



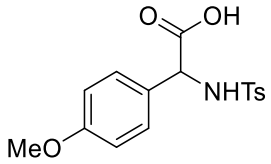
Using the same method and molar quantity as **4a**, the product **4d** was obtained as a white solid (2.4255 g, 85% yield). **Known compound**. **^{1}H NMR** (400 MHz, DMSO) δ 12.52 (br, 1H), 8.02 (d, *J* = 9.0 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 3.63 (td, *J* = 8.8, 6.4 Hz, 1H), 1.56 (tt, *J* = 13.4, 6.6 Hz, 1H), 1.37 (ddd, *J* = 9.0, 5.8, 3.4 Hz, 2H), 0.80 (d, *J* = 6.6 Hz, 3H), 0.68 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 173.7, 142.9, 138.8, 129.8, 127.0, 54.4, 41.4, 24.3, 23.0, 21.5, 21.4.

2-((4-methylphenyl)sulfonamido)-2-phenylacetic acid (4e)[2e]



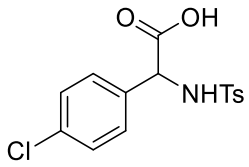
Using the same method and molar quantity as **4a**, the product **4e** was obtained as a white solid (2.6565 g, 87% yield). **Known compound**. **^{1}H NMR** (400 MHz, DMSO) δ 12.93 (br, 1H), 8.64 (d, *J* = 9.2 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.25 (m, 6H), 4.86 (d, *J* = 9.4 Hz, 1H), 2.33 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 171.4, 142.9, 138.7, 137.1, 129.7, 128.8, 128.3, 127.7, 127.0, 60.0, 21.4.

2-(4-methoxyphenyl)-2-((4-methylphenyl)sulfonamido)acetic acid (4f)[2f]



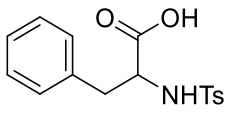
Using the same method and molar quantity as **4a**, the product **4f** was obtained as a yellow solid (2.4148 g, 72% yield). **Known compound**. **^{1}H NMR** (400 MHz, DMSO) δ 8.45 (br, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 4.75 (s, 1H), 3.70 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 176.4, 164.1, 147.6, 143.4, 134.4, 133.7, 131.7, 118.9, 64.2, 60.3, 26.1.

2-(4-chlorophenyl)-2-((4-methylphenyl)sulfonamido)acetic acid (4g)



Using the same method and molar quantity as **4a**, the product **4g** was obtained as a white solid (2.8541 g, 84% yield). Mp = 277~278 °C. **^{1}H NMR** (400 MHz, DMSO) δ 8.42 (br, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.22 (m, 6H), 4.80 (s, 1H), 2.33 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 175.7, 147.7, 143.2, 141.6, 137.5, 134.5, 134.4, 133.3, 131.8, 64.4, 26.1. HRMS (ESI) calcd for $C_{15}H_{14}ClNO_4S$ $[M+H]^+$ 340.0410, found 340.0411.

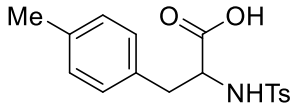
tosylphenylalanine (4h)[2d]



Using the same method and molar quantity as **4a**, the product **4h** was obtained as a white solid (2.8742 g, 90% yield). **Known compound**. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.54 (d, *J* = 7.8 Hz, 2H),

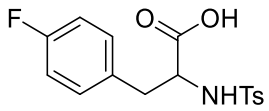
7.25 – 7.01 (m, 7H), 4.04 – 3.89 (t, *J* = 6.8 Hz, 1H), 3.02 (dd, *J* = 13.6, 5.6 Hz, 1H), 2.83 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, CD_3OD) δ 173.0, 143.0, 137.7, 136.4, 129.0, 129.0, 127.9, 126.6, 126.3, 57.4, 38.5, 20.0.

2-((4-methylphenyl)sulfonamido)-3-(p-tolyl)propanoic acid (4i)



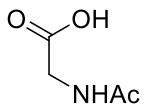
Using the same method and molar quantity as **4a**, the product **4i** was obtained as a white solid (2.7339 g, 82% yield). Mp = 225~226 °C. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.03 – 6.98 (m, 4H), 3.99 (dd, *J* = 8.4, 5.6 Hz, 1H), 3.01 (dd, *J* = 13.8, 5.6 Hz, 1H), 2.79 (dd, *J* = 13.8, 8.6 Hz, 1H), 2.42 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (100 MHz, CD_3OD) δ 173.1, 142.9, 137.7, 136.0, 133.3, 129.0, 128.9, 128.6, 126.6, 57.5, 38.0, 20.1, 19.8. HRMS (ESI) calcd for $C_{17}H_{19}NO_4S$ $[M+H]^+$ 334.1113, found 334.1109.

3-(4-fluorophenyl)-2-((4-methylphenyl)sulfonamido)propanoic acid (4j)



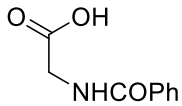
Using the same method and molar quantity as **4a**, the product **4j** was obtained as a yellow solid (2.2941 g, 68% yield). Mp = 180~181 °C. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.16 – 7.03 (m, 2H), 6.86 (t, *J* = 8.8 Hz, 2H), 3.98 (dd, *J* = 8.6, 5.4 Hz, 1H), 3.02 (dd, *J* = 13.8, 5.2 Hz, 1H), 2.79 (dd, *J* = 13.8, 8.8 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, CD_3OD) δ 172.9, 161.9 (d, *J* = 241.0 Hz), 143.1, 137.7, 132.4 (d, *J* = 3.0 Hz), 130.8 (d, *J* = 8.0 Hz), 129.1, 126.6, 114.6 (d, *J* = 21.0 Hz), 57.4, 37.6, 20.1. HRMS (ESI) calcd for $C_{16}H_{16}FNO_4S$ $[M+H]^+$338.0862, found 338.0862.

acetylglycine (4k)



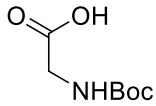
Commercially available. **^{1}H NMR** (400 MHz, DMSO) δ 12.44 (br, 1H), 8.14 (br, 1H), 3.70 (d, *J* = 5.8 Hz, 2H), 1.82 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 171.9, 170.0, 41.1, 22.8.

benzoylglycine (4l)



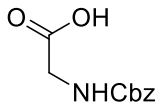
Commercially available. **^{1}H NMR** (400 MHz, DMSO) δ 12.57 (br, 1H), 8.81 (t, *J* = 5.2 Hz, 1H), 7.94 – 7.74 (m, 2H), 7.61 – 7.38 (m, 3H), 3.90 (d, *J* = 5.8 Hz, 2H). **^{13}C NMR** (100 MHz, DMSO) δ 171.8, 166.9, 134.3, 131.9, 128.8, 127.7, 41.7.

(*tert*-butoxycarbonyl)glycine (4m)



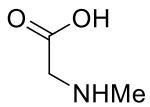
Commercially available. **^{1}H NMR** (400 MHz, DMSO) δ 12.39 (br, 1H), 7.02 (t, *J* = 6.2 Hz, 1H), 3.55 (d, *J* = 6.2 Hz, 2H), 1.36 (s, 9H). **^{13}C NMR** (100 MHz, DMSO) δ 172.2, 156.3, 78.5, 42.3, 28.6.

((benzyloxy)carbonyl)glycine (4n)



Commercially available. **^{1}H NMR** (400 MHz, DMSO) δ 12.53 (br, 1H), 7.57 – 7.23 (m, 5H), 5.03 (s, 2H), 3.66 (dd, *J* = 6.2, 2.4 Hz, 2H). **^{13}C NMR** (100 MHz, DMSO) δ 172.2, 157.2, 137.7, 129.0, 128.5, 128.4, 66.2, 42.8.

methylglycine (4o)

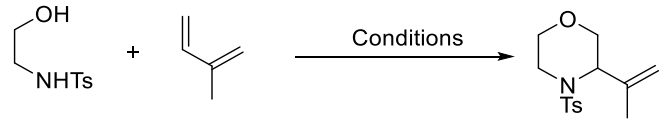


Commercially available. **^{1}H NMR** (400 MHz, D_2O) δ 3.62 (d, *J* = 1.0 Hz, 2H), 2.75 (s, 3H). **^{13}C NMR** (100 MHz, D_2O) δ 171.4, 50.8, 32.6.

2. Pd(II)-catalyzed aerobic intermolecular 1,2-difunctionalization for the synthesis of functionalized morpholines

General procedure A: To a sealed tube (15 mL) were added substrate **1** (0.2 mmol, 1 equiv), $Pd(OAc)_2$ (4.4 mg, 0.1 equiv), $Cu(OAc)_2$ (7.3 mg, 0.2 equiv) and DMSO (1 mL) at room temperature. The resulting mixture was kept stirring for 15 min. Afterwards, the system was degassed and recharged with O_2 for three times. Finally, the conjugated diene **2** (detailed equivalents are mentioned in the manuscript) was added and the tube was sealed and heated to 80 °C. After stirring for 24 h, the mixture was cooled to room temperature and firstly filtered through a thin silica gel pad (100-200 mesh) using EtOAc to remove DMSO and metal species. The solvent was then removed by rotary evaporation. The residue was purified by preparative TLC on silica gel (PE:EA = 5:1) to give the product **3**.

Table S1. Optimization of the Reaction Conditions for Morpholine Synthesis[a]



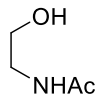
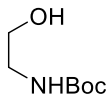
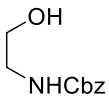
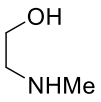
1a **2a** **3aa**

Entry	Pd(II) (equiv)	Oxidant (equiv)	Solvent	Temp	Yield (%)[b]
1	$Pd(OAc)_2$ (0.1)	O_2 (1 atm)	MeCN	80 °C	ND
2	$Pd(OAc)_2$ (0.1)	O_2 (1 atm)	DMA	80 °C	ND
3	$Pd(OAc)_2$ (0.1)	O_2 (1 atm)	DMF	80 °C	ND
4	$Pd(OAc)_2$ (0.1)	O_2 (1 atm)	DCE	80 °C	ND
5	$Pd(OAc)_2$ (0.1)	O_2 (1 atm)	Toluene	80 °C	ND
6	$Pd(OAc)_2$ (0.1)	O_2 (1 atm)	THF	80 °C	ND
7	$Pd(OAc)_2$ (0.1)	O_2 (1 atm)	1,4-Dioxane	80 °C	ND
8	$Pd(OAc)_2$ (0.1)	O_2 (1 atm)	MeOH	80 °C	ND
9	$Pd(OAc)_2$ (0.1)	O_2 (1 atm)	EtOH	80 °C	ND
10	$Pd(TFA)_2$ (0.1)	O_2 (1 atm)	DMSO	80 °C	Trace
11	$PdBr_2$ (0.1)	O_2 (1 atm)	DMSO	80 °C	ND
12	$PdCl_2$ (0.1)	O_2 (1 atm)	DMSO	80 °C	ND
13	$Pd(MeCN)_2Cl_2$ (0.1)	O_2 (1 atm)	DMSO	80 °C	ND
14	$Pd(OAc)_2$ (0.1)	$PhI(OAc)_2$ (1.2)	DMSO	80 °C	Trace
15	$Pd(OAc)_2$ (0.1)	Ag_2O (1.2)	DMSO	80 °C	ND
16	$Pd(OAc)_2$ (0.1)	$Cu(OAc)_2$ (0.2) + O_2 (1 atm)	DMSO	70 °C	64
17	$Pd(OAc)_2$ (0.1)	$Cu(OAc)_2$ (0.2) + O_2 (1 atm)	DMSO	90 °C	86

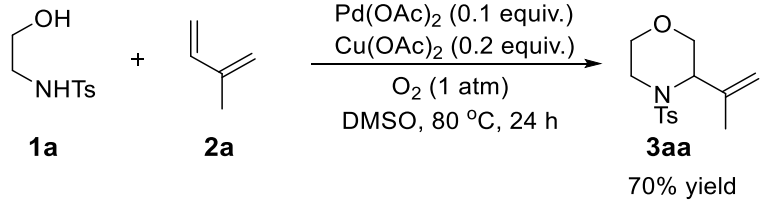
18	-	-	DMSO	80 °C	ND
19	-	$Cu(OAc)_2$ (0.2) + O_2 (1 atm)	DMSO	80 °C	ND

[a]The reaction was carried out with **1a** (0.2 mmol, 1 equiv), **2a** (2.0 mmol, 10 equiv) according to General Procedure A unless otherwise noted. [b]Isolated yields.

Other attempted substrates

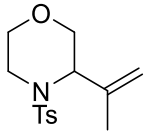
			
1k	**1l**	**1m**	**1n**
ND	ND	ND	ND

Scale-up of the reaction



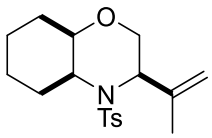
To a sealed tube (100 mL) were added substrate **1a** (0.86 g, 4.0 mmol, 1 equiv), $Pd(OAc)_2$ (90.0 mg, 0.1 equiv), $Cu(OAc)_2$ (146.1 mg, 0.2 equiv) and DMSO (25 mL) at room temperature. The resulting mixture was kept stirring for 15 min. Afterwards, the system was degassed and recharged with O_2 for three times. Finally, the isoprene **2a** (3.5 mL, 40.0 mmol, 10 equiv) was added and the tube was sealed and heated to 80 °C. After stirring for 24 h, the mixture was cooled to room temperature and firstly filtered through a silica gel pad (100-200 mesh) using EtOAc to remove DMSO and metal species. The solvent was then removed by rotary evaporation. The residue was purified by silica gel chromatography (PE:EA = 5:1) to give the product **3aa** (0.78 g, 70% yield).

3-(prop-1-en-2-yl)-4-tosylmorpholine (3aa)



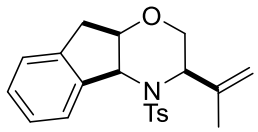
Colorless gummy oil (48.9 mg, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 5.09 – 5.00 (m, 2H), 4.13 – 4.07 (m, 1H), 3.98 (dd, *J* = 12.0, 2.4 Hz, 1H), 3.69 – 3.63 (m, 1H), 3.50 – 3.35 (m, 4H), 2.44 (s, 3H), 1.75 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 140.9, 137.2, 129.8, 127.3, 115.2, 67.8, 65.9, 57.7, 42.2, 21.6, 20.8. HRMS (ESI) calcd for $C_{14}H_{19}NO_3S$ $[M+H]^+$ 282.1164, found 282.1174.

3-(prop-1-en-2-yl)-4-tosyloctahydro-2*H*-benzo[*b*][1,4]oxazine (3ba)



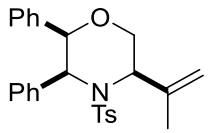
White solid (dr > 10:1, 57.1 mg, 85% overall yield; 49.9 mg isolated for **3ba** as major isomer). Mp = 188~189 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.21 – 5.17 (m, 1H), 5.06 (dt, *J* = 2.8, 1.4 Hz, 1H), 4.29 (d, *J* = 12.4 Hz, 1H), 4.19 – 4.10 (m, 1H), 3.62 (ddd, *J* = 12.8, 4.6, 3.2 Hz, 1H), 3.28 (dd, *J* = 12.4, 4.2 Hz, 1H), 3.17 – 3.03 (m, 1H), 2.44 (s, 3H), 2.16 (qd, *J* = 11.8, 3.2 Hz, 1H), 1.92 (s, 3H), 1.83 – 1.74 (m, 1H), 1.71 – 1.61 (m, 2H), 1.36 – 1.14 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.7, 143.3, 138.6, 129.9, 126.9, 113.5, 74.0, 66.6, 55.3, 54.2, 31.6, 27.3, 25.4, 21.6, 21.5, 19.6. HRMS (ESI) calcd for $C_{18}H_{25}NO_3S$ $[M+H]^+$336.1633, found 336.1652.

3-(prop-1-en-2-yl)-4-tosyl-2,3,4,4a,9,9a-hexahydroindeno[2,1-*b*][1,4]oxazine (3ca)



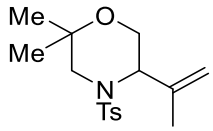
White solid (dr > 10:1, 60.7 mg, 82% overall yield; 52.2 mg isolated for **3ca** as major isomer). Mp = 180~182 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.45 (dd, *J* = 6.0, 2.6 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.12 (m, 3H), 5.07 (d, *J* = 4.8 Hz, 1H), 4.85 – 4.83 (m, 1H), 4.58 (d, *J* = 1.0 Hz, 1H), 4.17 – 4.14 (m, 1H), 3.96 (t, *J* = 4.8 Hz, 1H), 3.87 (dd, *J* = 12.2, 1.8 Hz, 1H), 3.26 (dd, *J* = 12.2, 4.0 Hz, 1H), 2.98 (dd, *J* = 16.8, 4.8 Hz, 1H), 2.88 (d, *J* = 16.8 Hz, 1H), 2.47 (s, 3H), 1.74 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.7, 141.9, 140.0, 138.7, 137.7, 130.0, 127.7, 127.2, 126.5, 124.9, 124.5, 115.0, 75.8, 65.1, 59.2, 55.0, 38.3, 21.6, 21.4. HRMS (ESI) calcd for $C_{21}H_{23}NO_3S$ $[M+H]^+$370.1477, found 370.1478.

2,3-diphenyl-5-(prop-1-en-2-yl)-4-tosylmorpholine (3da)



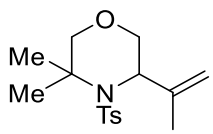
White solid (dr > 10:1, 63.4 mg, 73% overall yield; 52.5 mg isolated for **3da** as major isomer). Mp = 162~163 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 6.0 Hz, 1H), 7.22 – 6.95 (m, 7H), 5.40 (d, *J* = 3.6 Hz, 1H), 5.00 (s, 1H), 4.72 (s, 1H), 4.58 (d, *J* = 12.4 Hz, 1H), 4.52 (d, *J* = 3.6 Hz, 1H), 4.35 – 4.29 (m, 1H), 3.56 (dd, *J* = 12.4, 4.2 Hz, 1H), 2.44 (s, 3H), 1.31 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.8, 142.5, 138.6, 138.5, 135.3, 131.6, 130.3, 128.1, 127.1, 127.0, 126.9, 126.9, 124.8, 114.1, 78.6, 67.0, 57.9, 55.0, 21.6, 20.6. HRMS (ESI) calcd for $C_{26}H_{27}NO_3S$ $[M+H]^+$434.1790, found 434.1798.

2,2-dimethyl-5-(prop-1-en-2-yl)-4-tosylmorpholine (3ea)



White gummy oil (51.9 mg, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.95 (s, 1H), 4.90 (s, 1H), 4.04 – 3.96 (m, 1H), 3.85 (d, *J* = 3.6 Hz, 2H), 3.15 (q, *J* = 13.0 Hz, 2H), 2.42 (s, 3H), 1.65 (s, 3H), 1.18 (s, 3H), 1.12 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.3, 140.9, 136.8, 129.5, 127.4, 115.2, 70.8, 62.5, 57.5, 50.7, 26.3, 22.3, 21.6, 20.7. HRMS (ESI) calcd for $C_{16}H_{23}NO_3S$ $[M+H]^+$310.1477, found 310.1462.

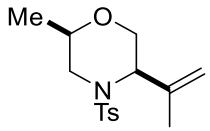
3,3-dimethyl-5-(prop-1-en-2-yl)-4-tosylmorpholine (3fa)



White gummy oil (45.9 mg, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 7.0 Hz, 2H), 5.24 – 5.01 (m, 2H), 4.47 (s, 1H), 4.27 (dd, *J* = 11.8, 2.6 Hz, 1H), 3.75 (dd, *J* = 11.8, 4.0 Hz, 1H), 3.54 (d, *J* = 11.6 Hz, 1H), 3.18 (d, *J* = 11.5 Hz, 1H), 2.42 (s, 3H), 1.89 (s, 3H), 1.52

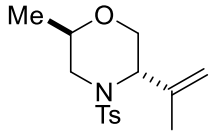
(s, 3H), 1.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.3, 142.8, 141.4, 129.4, 126.9, 114.9, 76.8, 67.7, 58.4, 58.3, 26.4, 24.9, 21.6, 21.5. HRMS (ESI) calcd for $C_{16}H_{23}NO_3S$ $[M+H]^+$310.1477, found 310.1472.

2-methyl-5-(prop-1-en-2-yl)-4-tosylmorpholine (3ga)



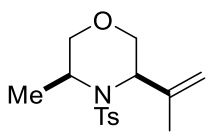
White gummy oil (dr = 1.2:1, 52.0 mg isolated as a mixture with **3ga'**, 88% overall yield; 25.7 mg isolated for **3ga**). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.07 – 5.00 (m, 2H), 4.24 – 4.19 (m, 1H), 4.07 (d, *J* = 12.0 Hz, 1H), 3.57 (dd, *J* = 13.8, 2.8 Hz, 1H), 3.52 (dd, *J* = 12.2, 3.8 Hz, 1H), 3.33 (dtt, *J* = 12.4, 6.2, 3.2 Hz, 1H), 2.89 (dd, *J* = 13.8, 11.0 Hz, 1H), 2.43 (s, 3H), 1.71 (s, 3H), 1.06 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.3, 140.6, 138.1, 129.8, 127.1, 115.1, 71.0, 67.5, 56.0, 47.1, 21.5, 21.3, 18.5. HRMS (ESI) calcd for $C_{15}H_{21}NO_3S$ $[M+H]^+$296.1320, found 296.1320.

2-methyl-5-(prop-1-en-2-yl)-4-tosylmorpholine (3ga')



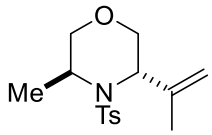
White solid (dr = 1.2:1, 52.0 mg isolated as a mixture with **3ga**, 88% overall yield; 21.2 mg isolated for **3ga'**). Mp = 117~118 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 5.00 – 4.96 (m, 1H), 4.90 (d, *J* = 0.6 Hz, 1H), 3.73 – 3.55 (m, 4H), 3.10 (dd, *J* = 9.0, 4.8 Hz, 1H), 2.45 (s, 3H), 2.17 (dd, *J* = 11.8, 10.2 Hz, 1H), 1.90 (s, 3H), 1.14 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.0, 142.9, 131.5, 129.5, 128.6, 115.1, 71.3, 69.8, 62.9, 52.3, 21.6, 18.6, 18.3. HRMS (ESI) calcd for $C_{15}H_{21}NO_3S$ $[M+H]^+$296.1320, found 296.1322.

3-methyl-5-(prop-1-en-2-yl)-4-tosylmorpholine (3ha)



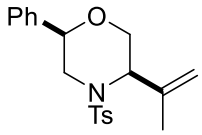
White gummy oil (dr = 1.7:1, 51.9 mg isolated as a mixture with **3ha'**, 88% overall yield; 27.0 mg isolated for **3ha**). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 3H), 7.26 (d, *J* = 8.2 Hz, 3H), 5.13 – 5.10 (m, 1H), 5.06 – 5.02 (m, 1H), 4.37 (t, *J* = 4.4 Hz, 1H), 3.95 – 3.82 (m, 2H), 3.72 (dd, *J* = 12.0, 3.8 Hz, 1H), 3.62 (dd, *J* = 11.4, 3.0 Hz, 1H), 3.45 (dd, *J* = 11.4, 7.0 Hz, 1H), 2.42 (s, 3H), 1.67 (s, 3H), 1.25 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.1, 140.6, 140.2, 129.3, 127.6, 117.0, 72.3, 68.9, 59.0, 50.8, 21.5, 20.7, 15.2. HRMS (ESI) calcd for $C_{15}H_{21}NO_3S$ $[M+H]^+$296.1320, found 296.1333.

3-methyl-5-(prop-1-en-2-yl)-4-tosylmorpholine (3ha')



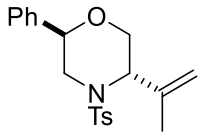
White gummy oil (dr = 1.7:1, 51.9 mg isolated as a mixture with **3ha**, 88% overall yield; 19.9 mg isolated isolated for **3ha'**). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.22 – 5.17 (m, 1H), 5.10 – 5.05 (m, 1H), 4.22 (d, *J* = 12.4 Hz, 2H), 3.90 – 3.80 (m, 1H), 3.47 (d, *J* = 11.6 Hz, 1H), 3.17 (ddd, *J* = 18.6, 12.0, 3.6 Hz, 2H), 2.44 (s, 3H), 1.93 (s, 3H), 1.39 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.3, 143.4, 138.3, 129.9, 127.0, 113.7, 70.2, 66.3, 54.7, 49.4, 21.6, 21.5, 19.1. HRMS (ESI) calcd for $C_{15}H_{21}NO_3S$ $[M+H]^+$296.1320, found 296.1329.

2-phenyl-5-(prop-1-en-2-yl)-4-tosylmorpholine (3ia)



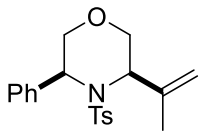
White solid (dr = 2:1, 60.7 mg isolated as a mixture with **3ia'**, 85% overall yield; 37.4 mg isolated for **3ia**). Mp = 128~129 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 3.79 – 3.68 (m, 7H), 5.19 – 5.16 (m, 1H), 5.12 – 5.07 (m, 1H), 4.35 – 4.30 (m, 1H), 4.25 (d, *J* = 12.4 Hz, 2H), 3.79 – 3.68 (m, 2H), 3.13 (dd, *J* = 14.0, 11.2 Hz, 1H), 2.44 (s, 3H), 1.75 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.6, 140.8, 138.8, 138.0, 129.9, 128.5, 128.3, 127.2, 126.0, 115.5, 67.7, 56.0, 47.3, 21.6, 21.4. HRMS (ESI) calcd for $C_{20}H_{23}NO_3S$ $[M+H]^+$358.1477, found 358.1477.

2-phenyl-5-(prop-1-en-2-yl)-4-tosylmorpholine (3ia')



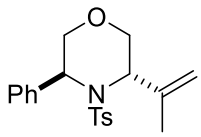
White solid (dr = 2:1, 60.7 mg isolated as a mixture with **3ia**, 85% overall yield; 17.6 mg isolated for **3ia'**). Mp = 145~146 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.27 (m, 7H), 5.04 (dd, *J* = 3.0, 1.4 Hz, 1H), 4.97 – 4.94 (m, 1H), 4.64 (dd, *J* = 10.2, 2.6 Hz, 1H), 3.93 (dd, *J* = 11.8, 2.6 Hz, 1H), 3.86 – 3.69 (m, 2H), 3.19 (dd, *J* = 9.8, 4.4 Hz, 1H), 2.44 (s, 3H), 2.36 (dd, *J* = 11.6, 10.4 Hz, 1H), 1.97 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.1, 142.9, 138.5, 131.2, 129.6, 128.7, 128.6, 128.3, 126.0, 115.5, 77.4, 70.4, 63.3, 53.0, 21.6, 18.2. HRMS (ESI) calcd for $C_{20}H_{23}NO_3S$ $[M+H]^+$358.1477, found 358.1478.

3-phenyl-5-(prop-1-en-2-yl)-4-tosylmorpholine (3ja)



White solid (dr = 2:1, 63.1 mg isolated as a mixture with **3ja'**, 88% overall yield; 40.0 mg isolated for **3ja**). Mp = 208~209 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.61 – 7.55 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.20 (m, 3H), 4.90 – 4.86 (m, 2H), 4.62 (d, *J* = 1.2 Hz, 1H), 4.29 (dd, *J* = 12.2, 1.6 Hz, 1H), 4.19 – 4.08 (m, 2H), 3.41 (dd, *J* = 12.2, 4.2 Hz, 1H), 3.32 (dd, *J* = 11.8, 3.8 Hz, 1H), 2.47 (s, 3H), 1.46 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.7, 142.1, 138.8, 138.0, 130.1, 129.0, 127.6, 127.3, 127.2, 114.5, 66.8, 66.2, 55.9, 54.2, 21.6, 20.7. HRMS (ESI) calcd for $C_{20}H_{23}NO_3S$ $[M+H]^+$358.1477, found 358.1476.

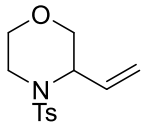
3-phenyl-5-(prop-1-en-2-yl)-4-tosylmorpholine (3ja')



White solid (dr = 2:1, 63.1 mg isolated as a mixture with **3ja**, 88% overall yield; 18.7 mg isolated for **3ja'**). Mp = 210~211 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 1H), 7.23 – 7.04 (m, 6H), 6.98 (d, *J* = 8.0 Hz, 2H), 5.25 – 5.21 (m, 1H), 5.17 (d, *J* = 1.0 Hz, 1H), 4.88 (dd, *J* = 7.6, 3.6 Hz, 1H),

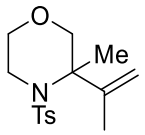
4.45 (t, *J* = 4.0 Hz, 1H), 4.14 – 4.06 (m, 2H), 3.93 (dd, *J* = 11.8, 3.8 Hz, 2H), 2.33 (s, 3H), 1.87 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.4, 142.1, 138.8, 135.8, 129.7, 128.7, 127.9, 127.8, 127.4, 115.9, 70.4, 69.0, 59.4, 57.8, 21.4, 21.2. HRMS (ESI) calcd for $C_{20}H_{23}NO_3S$ $[M+H]^+$358.1477, found 358.1480.

4-tosyl-3-vinylmorpholineoline (3ab)[3]



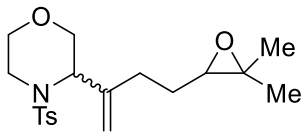
Colorless gummy oil (37.4 mg, 70% yield). **Known compound**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.85 (ddd, *J* = 17.4, 10.6, 7.2 Hz, 1H), 5.21 (ddt, *J* = 20.8, 10.6, 1.2 Hz, 2H), 4.14 – 4.06 (m, 1H), 3.85 – 3.72 (m, 2H), 3.69 – 3.52 (m, 2H), 3.38 – 3.24 (m, 2H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 136.0, 133.1, 129.6, 127.7, 118.6, 70.9, 66.5, 56.5, 42.2, 21.6.

3-methyl-3-(prop-1-en-2-yl)-4-tosylmorpholine (3ac)



Yellow gummy oil (33.7 mg, 57% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 5.12 – 5.09 (m, 1H), 5.09 – 5.06 (m, 1H), 3.76 (d, *J* = 11.8 Hz, 1H), 3.70 – 3.64 (m, 2H), 3.60 (ddd, *J* = 13.4, 5.0, 3.6 Hz, 1H), 3.34 (ddd, *J* = 13.4, 6.8, 4.6 Hz, 1H), 3.25 (d, *J* = 12.0 Hz, 1H), 2.43 (s, 3H), 1.86 (s, 3H), 1.42 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.4, 143.2, 139.3, 129.6, 127.3, 114.1, 74.9, 66.8, 64.2, 43.8, 21.5, 20.3, 19.8. HRMS (ESI) calcd for $C_{15}H_{21}NO_3S$ $[M+H]^+$296.1320, found 296.1340.

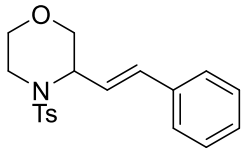
3-(4-(3,3-dimethyloxiran-2-yl)but-1-en-2-yl)-4-tosylmorpholine (3ad)



A mixture of two isomers (dr = 1:1). Yellow gummy oil (58.3 mg, 80% overall yield). **^{1}H NMR** (400 MHz, $CDCl_3$) 1H NMR (400 MHz, CDCl3) δ 7.72 (d, *J* = 8.4, 2H), 7.70 (d, *J* = 8.4, 2H), 7.32 (d, *J*

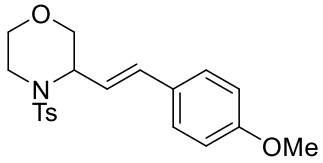
= 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.23 (d, *J* = 4.6 Hz, 1H), 5.23 (d, *J* = 4.6 Hz, 1H), 5.15 – 5.10 (m, 1H), 5.15 – 5.10 (m, 1H), 4.18 (d, *J* = 15.2 Hz, 1H), 4.18 (d, *J* = 15.2 Hz, 1H), 4.00 (ddd, *J* = 12.0, 5.0, 1.6 Hz, 1H), 4.00 (ddd, *J* = 12.0, 5.0, 1.6 Hz, 1H), 3.69 – 3.59 (m, 1H), 3.69 – 3.59 (m, 1H), 3.51 – 3.30 (m, 4H), 3.51 – 3.30 (m, 4H), 2.75 – 2.67 (m, 1H), 2.75 – 2.67 (m, 1H), 2.44 (s, 3H), 2.44 (s, 3H), 2.22 (t, *J* = 8.0 Hz, 2H), 2.18 – 2.07 (m, 2H), 1.75 – 1.63 (m, 2H), 1.75 – 1.63 (m, 2H), 1.31 (s, 3H), 1.31 (s, 3H), 1.29 (s, 3H), 1.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.0, 143.9, 143.6, 143.6, 137.6, 137.5, 129.9, 129.9, 127.3, 127.3, 114.8, 114.8, 67.3, 67.3, 65.8, 65.7, 64.0, 63.8, 58.5, 58.4, 56.4, 56.4, 42.1, 41.9, 30.4, 30.2, 27.3, 27.3, 24.9, 24.9, 21.6, 21.6, 18.8, 18.8. HRMS (ESI) calcd for $C_{19}H_{27}NO_4S$ $[M+H]^+$366.1739, found 366.1749.

(*E*)-3-styryl-4-tosylmorpholine (3ae)



Yellow gummy oil (57.1 mg, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.15 (m, 7H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.09 (dd, *J* = 16.0, 8.2 Hz, 1H), 4.28 (d, *J* = 8.2 Hz, 1H), 3.88 (dt, *J* = 11.6, 2.8 Hz, 1H), 3.80 (ddd, *J* = 26.0, 11.6, 3.0 Hz, 2H), 3.66 (td, *J* = 11.2, 3.0 Hz, 1H), 3.49 – 3.40 (m, 1H), 3.34 – 3.24 (m, 1H), 2.32 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 136.2, 135.8, 133.7, 129.5, 128.5, 127.9, 127.8, 126.5, 123.5, 71.4, 66.7, 56.5, 42.4, 21.4. HRMS (ESI) calcd for $C_{19}H_{22}NO_3S$ $[M+H]^+$344.1320, found 344.1321.

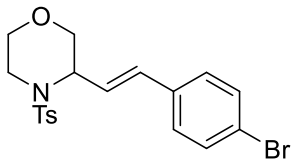
(*E*)-3-(4-methoxystyryl)-4-tosylmorpholine (3af)



Yellow gummy oil (59.7 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 5.95 (dd, *J* = 16.0, 8.2 Hz, 1H), 4.30 – 4.20 (m, 1H), 3.89 – 3.73 (m, 6H), 3.69 – 3.61 (m, 1H), 3.43 (dt, *J* = 12.4, 2.6 Hz, 1H), 3.33 – 3.24 (m, 1H), 2.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.4, 143.4,

135.9, 133.2, 129.4, 129.0, 127.9, 127.7, 121.2, 113.9, 71.5, 66.6, 56.6, 55.3, 42.4, 21.4. HRMS (ESI) calcd for $C_{20}H_{23}NO_4S$ $[M+H]^+$374.1426, found 374.1422.

(*E*)-3-(4-bromostyryl)-4-tosylmorpholine (3ag)

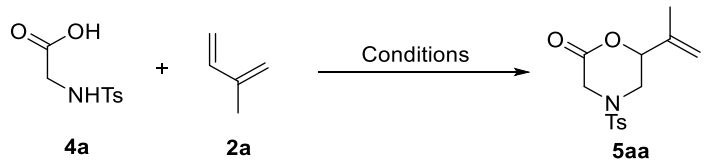


Brown gummy oil (75.9 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.10 (dd, *J* = 16.0, 8.0 Hz, 1H), 4.31 – 4.24 (m, 1H), 3.87 (dt, *J* = 11.6, 3.0 Hz, 1H), 3.78 (ddd, *J* = 28.2, 11.6, 3.0 Hz, 2H), 3.64 (ddd, *J* = 11.4, 10.6, 3.0 Hz, 1H), 3.45 (dt, *J* = 12.0, 2.4 Hz, 1H), 3.28 (ddd, *J* = 12.8, 10.6, 3.4 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.6, 135.8, 135.1, 132.4, 131.6, 129.5, 128.0, 127.8, 124.5, 121.8, 71.2, 66.6, 56.3, 42.3, 21.5. HRMS (ESI) calcd for $C_{19}H_{20}BrNO_3S$ $[M+H]^+$422.0426, found 422.0421.

3. Pd(II)-catalyzed aerobic intermolecular 1,2-difunctionalization for the synthesis of functionalized 2-morpholones

General procedure B: To a glass tube (15 mL) were added substrate **4** (0.2 mmol, 1 equiv), $Pd(OAc)_2$ (4.4 mg, 0.1 equiv) and DMSO (1 mL) at room temperature. The resulting mixture was kept stirring for 15 min with the tube in an autoclave. Afterwards, the conjugated diene **2** (detailed equivalents are mentioned in the manuscript) was added and the tube was immediately capped with a plastic cap with a tiny hole on it (for the ingression of O_2). The autoclave was sealed, charged with O_2 (5 atm) and heated to 70 °C. After stirring for 24 h, the mixture was cooled to room temperature and firstly filtered through a thin silica gel pad (100-200 mesh) using EtOAc to remove DMSO and metal species. The solvent was then removed by rotary evaporation. The residue was purified by preparative TLC on silica gel (PE:EA = 5:1) to give the product **5**.

Table S2. Optimization of the reaction conditions for 2-morpholone synthesis[a]



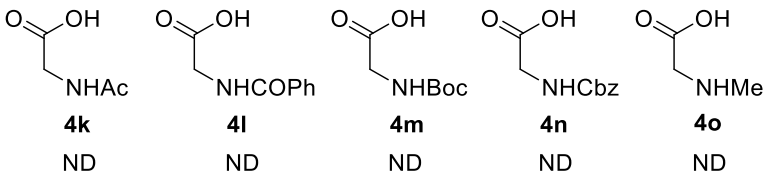
4a **2a** **5aa**

Entry	Pd(II) (equiv)	Oxidant (equiv)	Solvent	Temp	Yield (%)[b]
1	$Pd(OAc)_2$ (0.1)	O_2 (1 atm)	MeCN	80 °C	ND
2	$Pd(OAc)_2$ (0.1)	O_2 (1 atm)	DMA	80 °C	ND
3	$Pd(OAc)_2$ (0.1)	O_2 (1 atm)	DMF	80 °C	ND
4	$Pd(OAc)_2$ (0.1)	O_2 (1 atm)	DCE	80 °C	ND
5	$Pd(OAc)_2$ (0.1)	O_2 (1 atm)	Toluene	80 °C	ND
6	$Pd(OAc)_2$ (0.1)	O_2 (1 atm)	THF	80 °C	ND
7	$Pd(OAc)_2$ (0.1)	O_2 (1 atm)	1,4-Dioxane	80 °C	ND
8	$Pd(OAc)_2$ (0.1)	O_2 (1 atm)	MeOH	80 °C	ND
9	$Pd(OAc)_2$ (0.1)	O_2 (1 atm.)	EtOH	80 °C	ND
10	$Pd(TFA)_2$ (0.1)	O_2 (1 atm.)	DMSO	80 °C	ND
11	$PdBr_2$ (0.1)	O_2 (1 atm)	DMSO	80 °C	ND
12	$PdCl_2$ (0.1)	O_2 (1 atm)	DMSO	80 °C	ND
13	$Pd(MeCN)_2Cl_2$ (0.1)	O_2 (1 atm)	DMSO	80 °C	ND
14	$Pd(OAc)_2$ (0.1)	NBS (1.2)	DMSO	80 °C	ND
15	$Pd(OAc)_2$ (0.1)	Ag_2O (1.2)	DMSO	80 °C	ND

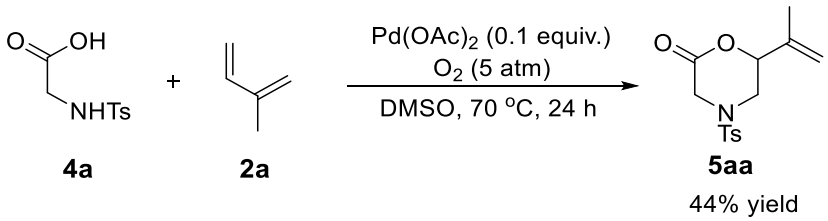
16	$Pd(OAc)_2$ (0.1)	H_2O_2 (3.0)	DMSO	80 °C	Trace
17	$Pd(OAc)_2$ (0.1)	O_2 (5 atm)	DMSO	80 °C	65
18	$Pd(OAc)_2$ (0.1)	O_2 (5 atm)	DMSO	90 °C	59
19	$Pd(OAc)_2$ (0.1)	O_2 (5 atm)	DMSO	60 °C	50
20	-	O_2 (5 atm)	DMSO	70 °C	ND

[a]The reaction was carried out with **4a** (0.2 mmol, 1 equiv), **2a** (2.0 mmol, 10 equiv) according to General Procedure B unless otherwise noted. [b]Isolated yields.

Other attempted substrates

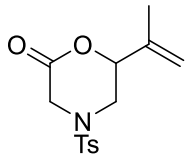


Scale-up of the reaction



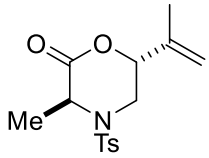
To a glassware (100 mL) were added substrate **4a** (0.92 g, 4.0 mmol, 1 equiv), $Pd(OAc)_2$ (90.0 mg, 0.1 equiv) and DMSO (25 mL) at room temperature. The resulting mixture was kept stirring for 15 min with the tube in an autoclave. Afterwards, the isoprene **2a** (3.5 mL, 10.0 mmol, 10 equiv) was added and the tube was immediately capped with a plastic cap with a tiny hole on it (for the ingression of O_2). The autoclave was sealed, charged with O_2 (5 atm) and heated to 70 °C. After stirring for 24 h, the mixture was cooled to room temperature and firstly filtered through a silica gel pad (100-200 mesh) using EtOAc to remove DMSO and metal species. The solvent was then removed by rotary evaporation. The residue was purified by silica gel chromatography (PE:EA = 5:1) to give the product **5aa** (0.52 g, 44% yield).

6-(prop-1-en-2-yl)-4-tosylmorpholin-2-one (5aa)



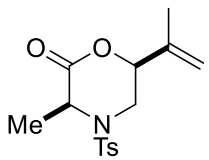
White gummy oil (39.1 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 5.12 – 5.10 (m, 1H), 5.10 – 5.07 (m, 1H), 4.92 (dd, *J* = 9.0, 3.0 Hz, 1H), 4.15 (dd, *J* = 17.6, 1.2 Hz, 1H), 3.73 (ddd, *J* = 12.8, 3.2, 1.2 Hz, 1H), 3.60 (d, *J* = 17.6 Hz, 1H), 2.84 (dd, *J* = 12.8, 9.0 Hz, 1H), 2.46 (s, 3H), 1.78 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 145.0, 138.9, 131.6, 130.3, 127.8, 115.4, 81.0, 46.6, 45.9, 21.6, 18.3. HRMS (ESI) calcd for $C_{14}H_{17}NO_4S$ $[M+H]^+$296.0957, found 296.0958.

3-methyl-6-(prop-1-en-2-yl)-4-tosylmorpholin-2-one (5ba)



White gummy oil (dr = 7:1, 25.7 mg, 42% overall yield; 21.0 mg isolated for **5ba** as major isomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 5.12 – 5.10 (m, 1H), 5.10 – 5.07 (m, 1H), 4.91 (d, *J* = 9.0 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 1H), 3.83 (dd, *J* = 12.2, 2.6 Hz, 1H), 2.94 (dd, *J* = 12.2, 9.0 Hz, 1H), 2.45 (s, 3H), 1.75 (s, 3H), 1.69 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.8, 144.7, 138.6, 133.4, 130.2, 127.5, 115.4, 78.8, 53.3, 45.9, 21.7, 21.6, 18.5. HRMS (ESI) calcd for $C_{15}H_{19}NO_4S$ $[M+H]^+$310.1113, found 310.1113.

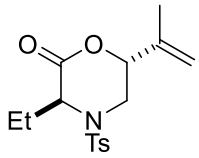
3-methyl-6-(prop-1-en-2-yl)-4-tosylmorpholin-2-one (5ba')



White gummy oil (dr = 7:1, 25.7 mg, 42% overall yield; 2.8 mg isolated for **5ba'** as minor isomer). **^{1}H NMR** (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.07 – 4.99 (m, 2H), 4.63 (q, *J* = 7.0 Hz, 1H), 4.59 – 4.51 (m, 1H), 3.89 (ddd, *J* = 14.8, 3.4, 1.2 Hz, 1H), 3.22 (dd, *J* = 14.8, 10.8 Hz, 1H), 2.45 (s, 3H), 1.74 (s, 3H), 1.52 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100

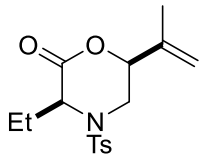
MHz, $CDCl_3$) δ 168.2, 144.6, 138.9, 136.5, 130.3, 127.1, 115.0, 81.3, 52.2, 42.5, 21.6, 18.6, 17.9. HRMS (ESI) calcd for $C_{15}H_{19}NO_4S$ $[M+H]^+$310.1113, found 310.1116.

3-ethyl-6-(prop-1-en-2-yl)-4-tosylmorpholin-2-one (5ca)



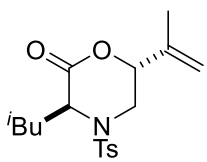
White solid (dr = 8:1, 48.6 mg, 75% overall yield; 40.9 mg isolated for **5ca** as major isomer). Mp = 96~97 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 5.08 (d, *J* = 18.8 Hz, 2H), 4.90 (dd, *J* = 10.2, 1.8 Hz, 1H), 4.16 (dd, *J* = 7.6, 5.8 Hz, 1H), 3.83 (dd, *J* = 12.0, 2.6 Hz, 1H), 2.84 (dd, *J* = 12.0, 10.4 Hz, 1H), 2.45 (s, 3H), 2.17 – 2.04 (m, 2H), 1.74 (s, 3H), 1.09 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 144.7, 138.6, 133.0, 130.2, 127.6, 115.4, 78.0, 59.0, 46.6, 28.9, 21.6, 18.3, 9.9. HRMS (ESI) calcd for $C_{16}H_{21}NO_4S$ $[M+H]^+$324.1270, found 324.1274.

3-ethyl-6-(prop-1-en-2-yl)-4-tosylmorpholin-2-one (5ca')



White gummy oil (dr = 8:1, 48.6 mg, 75% overall yield; 7.0 mg isolated for **5ca'** as minor isomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 4.99 (d, *J* = 8.4 Hz, 2H), 4.43 (ddd, *J* = 14.6, 9.6, 4.4 Hz, 2H), 3.95 (dd, *J* = 15.2, 3.4 Hz, 1H), 3.19 (dd, *J* = 15.4, 11.4 Hz, 1H), 2.45 (s, 3H), 2.15 – 2.02 (m, 2H), 1.70 (s, 3H), 0.99 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 144.7, 138.9, 130.3, 127.1, 114.8, 99.9, 80.6, 57.3, 43.1, 26.4, 21.6, 17.7, 10.3. HRMS (ESI) calcd for $C_{16}H_{21}NO_4S$ $[M+H]^+$324.1270, found 324.1281.

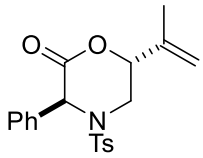
3-isobutyl-6-(prop-1-en-2-yl)-4-tosylmorpholin-2-one (5da)



White solid (dr > 10:1, 50.6 mg, 72% overall yield; 44.5 mg isolated for **5da** as major isomer). Mp = 100~101 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 5.07 (d,

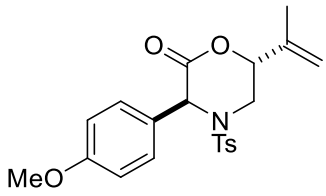
J = 19.2 Hz, 2H), 4.92 (d, *J* = 10.2 Hz, 1H), 4.32 (d, *J* = 6.2 Hz, 1H), 3.80 (d, *J* = 12.2 Hz, 1H), 2.92 (t, *J* = 11.2 Hz, 1H), 2.44 (s, 3H), 1.88 (s, 2H), 1.77 (dd, *J* = 16.8, 8.2 Hz, 1H), 1.72 (s, 3H), 1.07 (d, *J* = 4.4 Hz, 3H), 0.99 (d, *J* = 4.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 144.6, 138.5, 133.2, 130.2, 127.5, 115.5, 55.8, 46.3, 44.5, 24.5, 22.9, 21.7, 21.6, 18.3. HRMS (ESI) calcd for $C_{18}H_{25}NO_4S$ $[M+H]^+$352.1583, found 352.1589.

3-phenyl-6-(prop-1-en-2-yl)-4-tosylmorpholin-2-one (5ea)



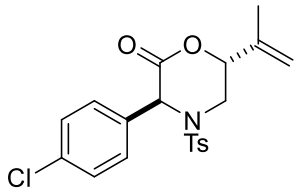
White solid (dr > 10:1, 45.3 mg, 61% overall yield; 40.1 mg isolated for **5ea** as major isomer). Mp = 104~105 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.32 (m, 5H), 5.69 (s, 1H), 4.98 (d, *J* = 7.0 Hz, 2H), 4.61 (dd, *J* = 11.2, 3.0 Hz, 1H), 3.89 (dd, *J* = 11.8, 3.2 Hz, 1H), 3.16 (t, *J* = 11.6 Hz, 1H), 2.45 (s, 3H), 1.66 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 144.8, 138.1, 134.5, 133.7, 130.2, 129.3, 128.8, 127.5, 125.8, 115.6, 60.2, 46.4, 21.6, 18.1. HRMS (ESI) calcd for $C_{20}H_{21}NO_4S$ $[M+H]^+$372.1270, found 372.1271.

3-(4-methoxyphenyl)-6-(prop-1-en-2-yl)-4-tosylmorpholin-2-one (5fa)



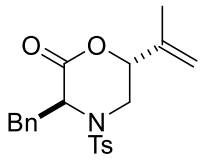
Yellow solid (dr > 10:1, 62.6 mg, 78% overall yield; 55.8 mg isolated for **5fa** as major isomer). Mp = 110~111 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 9.0 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.62 (s, 1H), 5.02 – 4.97 (m, 2H), 4.63 (dd, *J* = 11.4, 3.2 Hz, 1H), 3.92 – 3.73 (m, 4H), 3.13 (t, *J* = 11.6 Hz, 1H), 2.45 (s, 3H), 1.66 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 159.9, 144.7, 138.1, 133.7, 130.2, 127.4, 127.1, 126.3, 115.5, 114.7, 59.8, 55.4, 46.4, 21.6, 18.2. HRMS (ESI) calcd for $C_{21}H_{23}NO_5S$ $[M+H]^+$402.1375, found 402.1375.

3-(4-chlorophenyl)-6-(prop-1-en-2-yl)-4-tosylmorpholin-2-one (5ga)



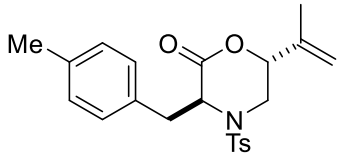
White solid (dr > 10:1, 48.7 mg, 60% overall yield; 43.3 mg isolated for **5ga** as major isomer). Mp = 105~106 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.33 (m, 4H), 5.60 (s, 1H), 5.04 – 4.97 (m, 2H), 4.59 (dd, *J* = 11.0, 2.6 Hz, 1H), 3.89 (dd, *J* = 11.8, 3.0 Hz, 1H), 3.22 – 3.05 (m, 1H), 2.46 (s, 3H), 1.68 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 145.0, 137.8, 134.9, 133.3, 133.2, 130.3, 129.5, 127.5, 127.4, 115.8, 59.8, 46.5, 21.7, 18.2. HRMS (ESI) calcd for $C_{20}H_{20}ClNO_4S$ $[M+H]^+$406.0880, found 406.0888.

3-benzyl-6-(prop-1-en-2-yl)-4-tosylmorpholin-2-one (5ha)



White gummy oil (dr > 10:1, 61.8 mg, 80% overall yield; 54.9 mg isolated for **5ha** as major isomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.29 (m, 5H), 4.89 – 4.85 (m, 1H), 4.73 (d, *J* = 1.0 Hz, 1H), 4.44 (dd, *J* = 5.8, 3.0 Hz, 1H), 3.65 (dd, *J* = 13.6, 5.8 Hz, 1H), 3.58 (dd, *J* = 11.8, 2.2 Hz, 1H), 3.34 (dd, *J* = 13.6, 3.0 Hz, 1H), 3.31 – 3.25 (m, 1H), 2.57 (dd, *J* = 11.8, 10.2 Hz, 1H), 2.46 (s, 3H), 1.51 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.2, 144.9, 138.2, 135.3, 132.2, 130.6, 130.3, 128.7, 127.8, 127.6, 115.3, 77.6, 59.1, 46.4, 41.4, 21.6, 18.2. HRMS (ESI) calcd for $C_{21}H_{23}NO_4S$ $[M+H]^+$386.1426, found 386.1430.

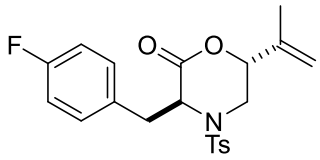
3-(4-methylbenzyl)-6-(prop-1-en-2-yl)-4-tosylmorpholin-2-one (5ia)



White gummy oil (dr > 10:1, 64.9 mg, 81% overall yield; 58.6 mg isolated for **5ia** as major isomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 4.91 – 4.84 (m, 1H), 4.73 (d, *J* = 0.8 Hz, 1H), 4.42 (dd, *J* = 6.0, 3.2 Hz,

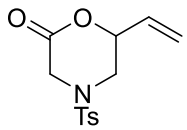
1H), 3.61 – 3.54 (m, 2H), 3.37 – 3.27 (m, 2H), 2.58 (dd, *J* = 11.8, 10.2 Hz, 1H), 2.45 (s, 3H), 2.34 (s, 3H), 1.52 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 144.8, 138.4, 137.3, 132.3, 132.1, 130.4, 130.2, 129.4, 127.7, 115.2, 59.2, 46.4, 41.1, 21.6, 21.1, 18.2. HRMS (ESI) calcd for $C_{22}H_{25}NO_4S$ $[M+H]^+$400.1583, found 400.1570.

3-(4-fluorobenzyl)-6-(prop-1-en-2-yl)-4-tosylmorpholin-2-one (5ja)



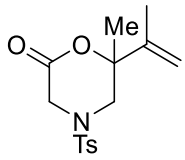
Yellow gummy oil (dr > 10:1, 58.1 mg, 72% overall yield; 51.5 mg isolated for **5ja** as major isomer). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.04 (t, *J* = 8.6 Hz, 2H), 4.93 – 4.89 (m, 1H), 4.82 – 4.78 (m, 1H), 4.38 (dd, *J* = 5.6, 3.0 Hz, 1H), 3.72 – 3.57 (m, 2H), 3.46 (ddd, *J* = 10.2, 1.4, 0.6 Hz, 1H), 3.32 (dd, *J* = 14.0, 2.8 Hz, 1H), 2.61 – 2.53 (m, 1H), 2.46 (s, 3H), 1.55 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 162.4 (d, *J* = 245.0 Hz), 145.0, 138.2, 132.1 (d, *J* = 7.8 Hz), 131.9, 131.0 (d, *J* = 3.4 Hz), 130.3, 127.8, 115.6 (d, *J* = 21.0 Hz), 115.4, 77.9, 59.1, 46.5, 40.5, 21.6, 18.3. HRMS (ESI) calcd for $C_{21}H_{23}FNO_4S$ $[M+H]^+$404.1332, found 404.1323.

4-tosyl-6-vinylmorpholin-2-one (5ab)



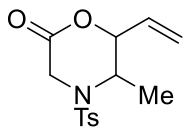
Yellow solid (32.4 mg, 58% yield). Mp = 89~90 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 5.93 – 5.75 (m, 1H), 5.50 – 5.37 (m, 2H), 5.04 – 4.94 (m, 1H), 4.13 (dd, *J* = 17.6, 1.2 Hz, 1H), 3.71 (ddd, *J* = 12.8, 3.2, 1.2 Hz, 1H), 3.62 (d, *J* = 17.6 Hz, 1H), 2.81 (dd, *J* = 12.7, 8.7 Hz, 1H), 2.46 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.2, 145.0, 134.2, 131.8, 130.3, 127.8, 120.2, 78.8, 46.7, 21.6. HRMS (ESI) calcd for $C_{13}H_{15}NO_4S$ $[M+H]^+$282.0800, found 282.0802.

6-methyl-6-(prop-1-en-2-yl)-4-tosylmorpholin-2-one (5ac)



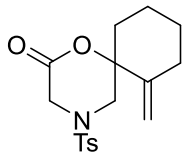
Yellow solid (55.6 mg, 90% yield). Mp = 88~89 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 5.07 (d, *J* = 0.6 Hz, 1H), 5.05 – 5.00 (m, 1H), 3.91 (d, *J* = 17.8 Hz, 1H), 3.66 – 3.62 (m, 2H), 2.89 (d, *J* = 12.6 Hz, 1H), 2.46 (s, 3H), 1.85 (s, 3H), 1.52 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.9, 144.8, 144.4, 131.7, 130.2, 127.7, 113.6, 84.9, 49.6, 46.0, 24.1, 21.6, 18.9. HRMS (ESI) calcd for $C_{15}H_{19}NO_4S$ $[M+H]^+$310.1113, found 310.1110.

5-methyl-4-tosyl-6-vinylmorpholin-2-one (5ad)



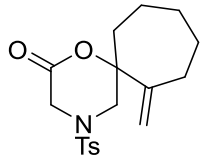
Yellow gummy oil (49.0 mg, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.73 (ddd, *J* = 17.0, 10.6, 5.6 Hz, 1H), 5.43 – 5.18 (m, 2H), 4.58 (ddt, *J* = 5.8, 4.6, 1.4 Hz, 1H), 4.22 (d, *J* = 18.0 Hz, 1H), 3.99 (qd, *J* = 6.8, 4.6 Hz, 1H), 3.88 (d, *J* = 18.0 Hz, 1H), 2.44 (s, 3H), 1.28 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 144.5, 134.9, 133.2, 130.0, 127.4, 120.1, 82.4, 51.2, 43.3, 21.6, 16.4. HRMS (ESI) calcd for $C_{14}H_{17}NO_4S$ $[M+H]^+$296.0957, found 296.0954.

7-methylene-4-tosyl-1-oxa-4-azaspiro[5.5]undecan-2-one (5ae)



White gummy oil (38.4 mg, 58% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.99 – 4.95 (m, 2H), 3.83 (dd, *J* = 47.0, 17.6 Hz, 2H), 3.36 (q, *J* = 12.8 Hz, 2H), 2.51 – 2.40 (m, 4H), 2.22 – 2.11 (m, 1H), 2.06 – 1.98 (m, 1H), 1.88 – 1.73 (m, 3H), 1.48 – 1.43 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5, 145.9, 144.8, 132.1, 130.2, 127.7, 110.5, 85.0, 48.0, 46.4, 36.5, 33.2, 27.1, 22.7, 21.6. HRMS (ESI) calcd for $C_{17}H_{21}NO_4S$ $[M+H]^+$336.1270, found 336.1287.

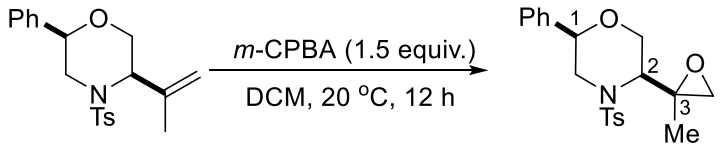
7-methylene-4-tosyl-1-oxa-4-azaspiro[5.6]dodecan-2-one (5af)



White gummy oil (52.4 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 5.15 – 5.10 (m, 1H), 5.08 – 5.04 (m, 1H), 3.90 (d, *J* = 17.6 Hz, 1H), 3.74 (d, *J* = 17.8 Hz, 1H), 3.26 (d, *J* = 12.8 Hz, 1H), 3.14 (d, *J* = 12.8 Hz, 1H), 2.46 (s, 3H), 2.44 – 2.39 (m, 1H), 2.13 (dd, *J* = 14.6, 7.8 Hz, 1H), 2.06 – 1.96 (m, 1H), 1.95 – 1.86 (m, 1H), 1.85 – 1.75 (m, 2H), 1.59 – 1.55 (m, 2H), 1.52 – 1.44 (m, 1H), 1.39 – 1.32 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 148.6, 144.7, 132.1, 130.2, 127.7, 115.8, 87.9, 51.2, 46.3, 38.5, 32.9, 31.2, 29.7, 22.6, 21.6. HRMS (ESI) calcd for $C_{18}H_{23}NO_4S$ $[M+H]^+$350.1426, found 350.1429.

4. Transformations

Procedure for synthesis of 6 and characterization data.

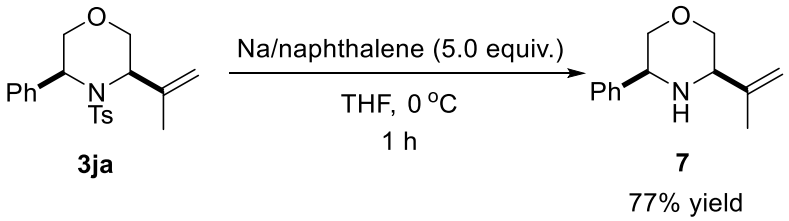


3ia **6**

87% overall yield
4:1 diastereoselectivity

Under air, **3ia** (71.5 mg, 0.2 mmol, 1 equiv) and *m*-CPBA (70%-75%, 51.7 mg, 0.3 mmol, 1.5 equiv) was added to 5 mL dry DCM and the mixture was stirred at 20 °C for 12 h. After the completion of reaction, the mixure was washed with saturated $NaHCO_3$ solution (5 mL, 2 times) and H_2O (5 mL, once). The organic layer was collected and dried over Na_2SO_4. The solvent was then evaporated and purification by chromatography (PE:EA = 3:1) gave pure product **6** as white gummy oil (dr = 4:1 (**C2** and **C3**), 65.0 mg, 87% overall yield; 46.8 mg isolated for major isomer, 10.5 mg isolated for minor isomer). For major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.29 (m, 5H), 7.20 (d, *J* = 6.8 Hz, 2H), 4.08 – 3.93 (m, 3H), 3.83 (d, *J* = 14.6 Hz, 1H), 3.41 (dd, *J* = 12.4, 3.8 Hz, 1H), 3.29 (d, *J* = 4.8 Hz, 1H), 3.20 (dd, *J* = 14.6, 11.4 Hz, 1H), 2.69 (d, *J* = 4.8 Hz, 1H), 2.46 (s, 3H), 1.42 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.0, 138.4, 138.1, 130.1, 128.6, 128.4, 127.1, 125.7, 76.0, 63.7, 55.6, 53.9, 52.7, 48.2, 21.6, 20.3. For minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.27 (m, 7H), 4.30 (d, *J* = 12.4 Hz, 1H), 4.22 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.84 (dd, *J* = 13.8, 3.2 Hz, 1H), 3.67 (dd, *J* = 12.4, 4.4 Hz, 1H), 3.47 (d, *J* = 4.2 Hz, 1H), 3.23 (dd, *J* = 13.8, 11.2 Hz, 1H), 2.97 (d, *J* = 4.8 Hz, 1H), 2.57 (d, *J* = 4.8 Hz, 1H), 2.45 (s, 3H), 1.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.9, 138.5, 137.4, 129.9, 128.6, 128.4, 127.0, 125.9, 77.2, 67.3, 57.5, 55.5, 55.2, 48.1, 21.6, 20.6. HRMS (ESI) calcd for $C_{20}H_{23}NO_4S$ $[M+H]^+$ 374.1426, found 374.1440.

Procedure for synthesis of 7 and characterization data.

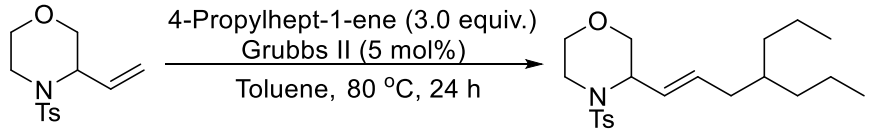


3ja **7**

77% yield

Under N_2 atmosphere, naphthalene (1.0 g, 7.8 mmol) and Na (170.0 mg, 7.4 mmol) were dissolved in 15 mL dry THF and the resulting mixture wad vigrously stirred for 3 h at room temperature. Under N_2 atmosphere, **3ja** (71.5 mg, 0.2 mmol, 1 equiv) was dissolved in 2 mL dry THF and the resulting solution was cooled to 0 °C. To the solution was added the above Na/naphthalene mixture (1.9 mL, 5.0 equiv) at 0 °C and the mixture was further stirred for 1 h with temperature maintaining. After the completion of reaction, the mixure was quenched with saturated NH_4Cl solution (2 mL) and extraced with EA (5 mL, 3 times). The organic layer was collected and dried over Na_2SO_4. The solvent was then evaporated and purification by chromatography (PE:EA = 8:1) gave pure product **7** as white gummy oil (31.1 mg, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.28 (m, 5H), 5.18 – 5.13 (m, 1H), 4.92 – 4.88 (s, 1H), 4.03 (dd, *J* = 10.2, 3.0 Hz, 1H), 3.85 (ddd, *J* = 32.6, 10.8, 2.8 Hz, 2H), 3.59 – 3.47 (m, 1H), 3.30 (td, *J* = 10.6, 4.2 Hz, 2H), 1.83 – 1.77 (m, 4H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.2, 140.6, 128.5, 127.8, 127.3, 111.8, 73.4, 71.3, 61.4, 60.5, 20.1. HRMS (ESI) calcd for $C_{13}H_{17}NO$ $[M+H]^+$ 204.1388, found 204.1377.

Procedure for synthesis of 8 and characterization data.

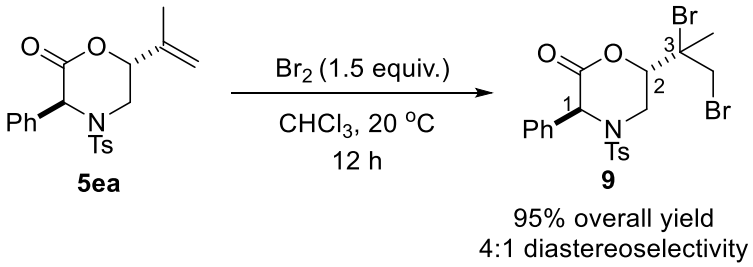


3ab **8**

63% yield

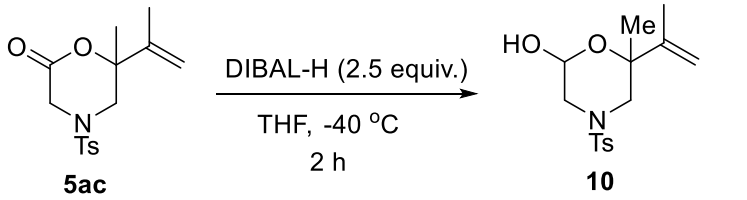
Under N_2 atmosphere, **3ab** (53.5 mg, 0.2 mmol, 1 equiv) and Grubbs II Catalyst (8.4 mg, 0.01 mmol, 0.05 equiv) were added to 3 mL of dry toluene and the resulting mixture was stirred for 15 min at room temperature. Afterwards, the mixure was heated to 80 °C followed by the dropwise addition of 4-propylhept-1-ene (84.8 mg, 0.6 mmol, 3 equiv). The resulting mixture was stirred at 80 °C for 24 h. After the completion of the reaction, the solvent was evaporated and purification by flash column chromatography (PE:EA = 5:1) provided the product **8** as white gummy oil (47.6 mg, 63% yield). **^{1}H NMR** (400 MHz, CDCl3) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.65 – 5.54 (m, 1H), 5.46 (dd, *J* = 15.6, 7.6 Hz, 1H), 4.18 – 4.06 (m, 1H), 3.81 (dt, *J* = 11.4, 3.0 Hz, 1H), 3.69 (qd, *J* = 11.4, 3.0 Hz, 2H), 3.63 – 3.54 (m, 1H), 3.36 (dt, *J* = 12.4, 2.6 Hz, 1H), 3.30 – 3.17 (m, 1H), 2.42 (s, 3H), 1.95 – 1.87 (m, 1H), 1.81 (dt, *J* = 14.2, 7.2 Hz, 1H), 1.38 – 1.27 (m, 3H), 1.23 – 1.08 (m, 6H), 0.86 (td, *J* = 7.2, 2.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.3, 136.2, 133.8, 129.5, 127.7, 125.3, 71.5, 66.6, 56.1, 42.2, 36.9, 36.4, 35.9, 35.7, 21.5, 19.8, 19.7, 14.5, 14.5. HRMS (ESI) calcd for $C_{21}H_{33}NO_3S$ $[M+H]^+$380.2295, found 380.2298.

Procedure for synthesis of 9 and characterization data.



Under air, **5ea** (74.3 mg, 0.2 mmol, 1 equiv) was added to 2 mL $CHCl_3$ and the resulting mixure was stirred at 0 °C. Br_2 (0.02 mL, 0.3 mmol, 1.5 equiv) was dissolved in 2 mL $CHCl_3$. The resulting Br_2 solution was added to the above mixuture dropwise at 0 °C with vigrous stirring. After the addition, the system was heated up to 20 °C and stirred for 12 h. After the completion of the reaction, saturated Na_2SO_3 solution (0.5 mL) was added to the reaction and the resulting mixture was extracted with DCM (5 mL, 2 times) and washed with H_2O (5 mL, 2 times). The organic layer was collected and dried over Na_2SO_4. The solvent was evaporated to give the product **9** as white gummy oil (dr = 4:1 (**C2** and **C3**), 100.9 mg, 95% overall yield; 76.3 mg isolated for major isomer, 16.8 mg isolated for minor isomer), which was pure enough. For major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 6.2 Hz, 2H), 7.46 – 7.35 (m, 5H), 5.74 (s, 1H), 4.32 (dd, *J* = 11.2, 3.6 Hz, 1H), 4.04 (dd, *J* = 11.8, 3.6 Hz, 1H), 3.72 (d, *J* = 11.2 Hz, 1H), 3.66 (d, *J* = 11.2 Hz, 1H), 3.50 (t, *J* = 11.4 Hz, 1H), 2.45 (s, 3H), 1.75 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.8, 144.9, 133.7, 133.2, 130.2, 129.5, 129.0, 127.5, 125.5, 76.3, 61.9, 60.1, 44.3, 38.9, 26.3, 21.7. For minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.47 – 7.35 (m, 5H), 5.73 (s, 1H), 4.25 (dd, *J* = 11.2, 3.8 Hz, 1H), 4.07 (d, *J* = 10.2 Hz, 1H), 3.84 (dd, *J* = 11.8, 3.8 Hz, 1H), 3.63 (dd, J = 23.8, 10.8 Hz, 2H), 2.45 (s, 3H), 1.68 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 145.0, 133.5, 133.1, 130.3, 129.5, 129.1, 127.6, 125.7, 74.6, 62.8, 60.3, 45.2, 38.8, 26.6, 21.7. HRMS (ESI) calcd for $C_{20}H_{21}Br_2NO_4S$ $[M+H]^+$529.9636, found 529.9644.

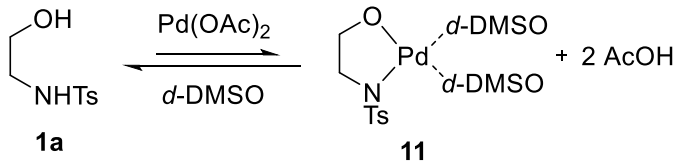
Procedure for synthesis of 10 and characterization data.[4]



Under N_2 atmosphere, **5ac** (61.9 mg, 0.2 mmol, 1 equiv) was added to 10 mL dry THF. The solution was then cooled to -40 °C. With vigrous stirring, DIBAL-H (1.0 mol/L in toluene, 0.5 mL, 0.5 mmol, 2.5 equiv) was added to the mixture dropwise. The resulting mixture was then stirred under at -40 °C for 2 h. After the completion of the reaction, H_2O was added to the mixture carefully to quench the reaction and the mixture was extracted with EA (10 mL, 3 times). Then the combined organic layer were collected and dried over Na_2SO_4. The solvent was evaporated and purification by preparative TLC (PE:EA = 5:1) afforded the product **10** as white solid (dr = 2.5:1, 57.9 mg, 93% overall yield). Mp = 171~172 °C. For major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 5.21 – 5.16 (m, 1H), 5.11 – 5.07 (m, 1H), 4.99 (br, 1H), 3.91 (d, *J* = 12.0 Hz, 1H), 3.70 (d, *J* = 10.4 Hz, 1H), 2.87 (d, *J* = 5.6 Hz, 1H), 2.45 (s, 3H), 2.11 (d, *J* = 11.6 Hz, 1H), 2.06 – 1.95 (m, 1H), 1.79 (s, 3H), 1.25 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ144.1, 143.8, 132.0, 129.9, 127.8, 114.4, 88.9, 76.1, 51.0, 50.3, 26.4, 21.6, 18.7. For minor isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 5.18 (br, 1H), 5.14 – 5.11 (m, 1H), 4.93 – 4.89 (m, 1H), 3.39 (d, *J* = 12.4 Hz, 1H), 3.15 – 3.07 (m, 2H), 2.83 (d, *J* = 11.6 Hz, 1H), 2.45 (s, 3H), 2.06 – 1.95 (m, 1H), 1.82 (s, 3H), 1.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.6, 144.2, 132.2, 129.9, 127.7, 111.3, 89.4, 76.1, 52.1, 51.0, 22.3, 18.8. HRMS (ESI) calcd for $C_{15}H_{21}NO_4S$ $[M+H]^+$ 312.1270, found 312.1278.

5. Preliminary mechanism study

In situ ^{1}H NMR Spectroscopy of Substrate 1a



Scheme S1. The speculative equilibrium for substrate **1a**

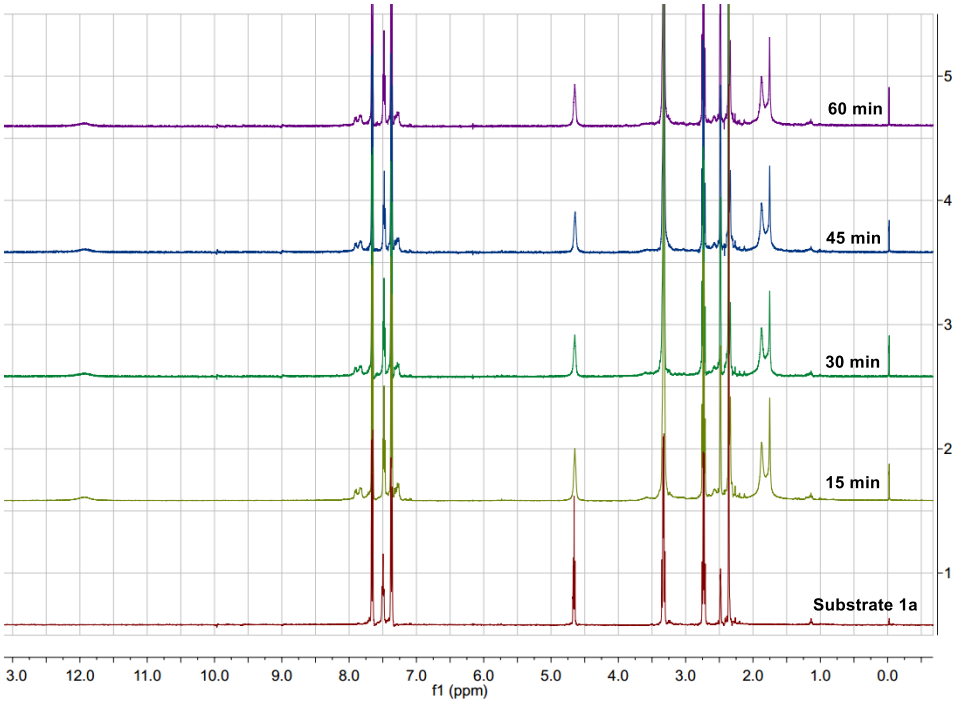


Figure S1. The *in situ* ^{1}H NMR in *d*-DMSO with time

The speculative equilibrium in *d*-DMSO was shown in Scheme S1. Reaction of $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.5 equiv.) and substrate **1a** (8.6 mg, 0.04 mmol, 1 equiv.) in *d*-DMSO with time was monitored by ^{1}H NMR spectroscopy (Figure S1). $Pd(OAc)_2$ was reacted with substrate **1a** in *d*-DMSO (0.5 mL) at 20 °C. The NMR spectra were recorded at 20 °C. The *in situ* ^{1}H NMR shows that the amount of a new complex was increased with time, and the equilibrium was stable until 30 min. These results show that a new Pd(II)-complex was formed in the equilibrium.

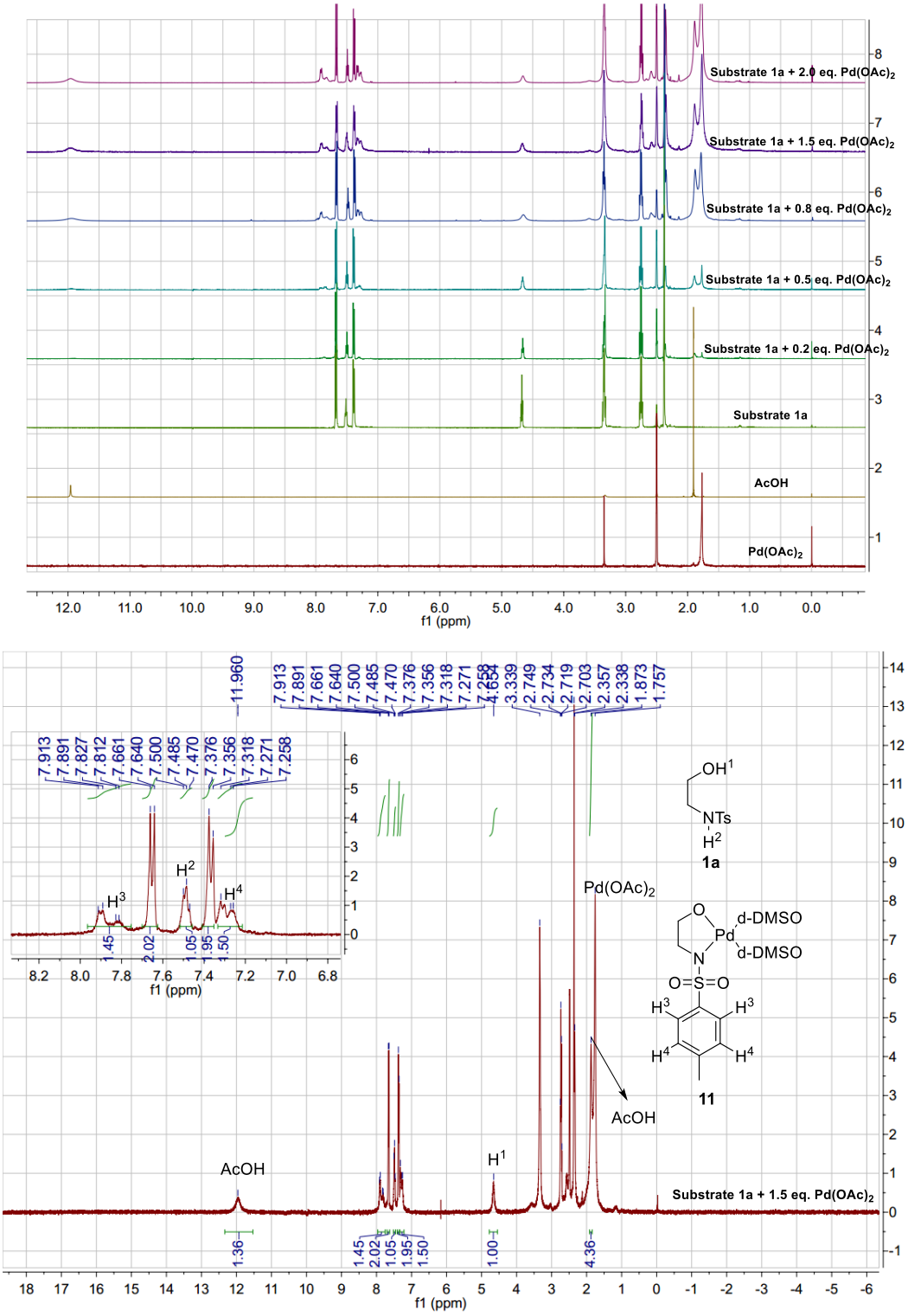


Figure S2. The *in situ* ^{1}H NMR with different amount of $Pd(OAc)_2$ for substrate **1a**

Reactions of different amounts of $Pd(OAc)_2$ and substrate **1a** (8.6 mg, 0.04 mmol, 1 equiv.) were monitored by ^{1}H NMR spectroscopy (Figure S2). $Pd(OAc)_2$ was reacted with substrate **1a** in *d*-DMSO (0.5 mL) at 20 °C for 60 min. The NMR specta were recorded at 20 °C. These results show the amount

of substrate **1a** reduced and the amount of new complex increased with the amount of $Pd(OAc)_2$. We found that the peak areas of active hydrogens (H^1 and H^2) in substrate **1a** are always almost the same and the peak area of AcOH is double of those of the new complex (entry 7). This suggests that bidentate complex **11** is likely to be formed.

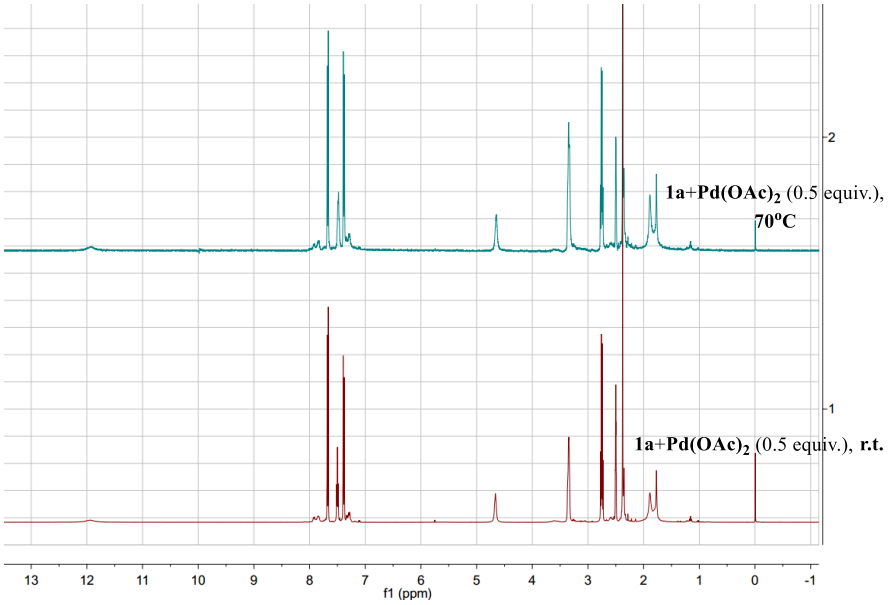


Figure S3. The *in situ* ^{1}H NMR at different tempratures for substrate **1a**

Reactions of of $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.5 equiv.) and substrate **1a** (8.6 mg, 0.04 mmol, 1 equiv.) were monitored by ^{1}H NMR spectroscopy in different tempratures (Figure S3). $Pd(OAc)_2$ was reacted with substrate **1a** in *d*-DMSO (0.5 mL) at different tempratures for 60 min. The peaks are almost unchanged at 70 °C (compared with 20 °C).

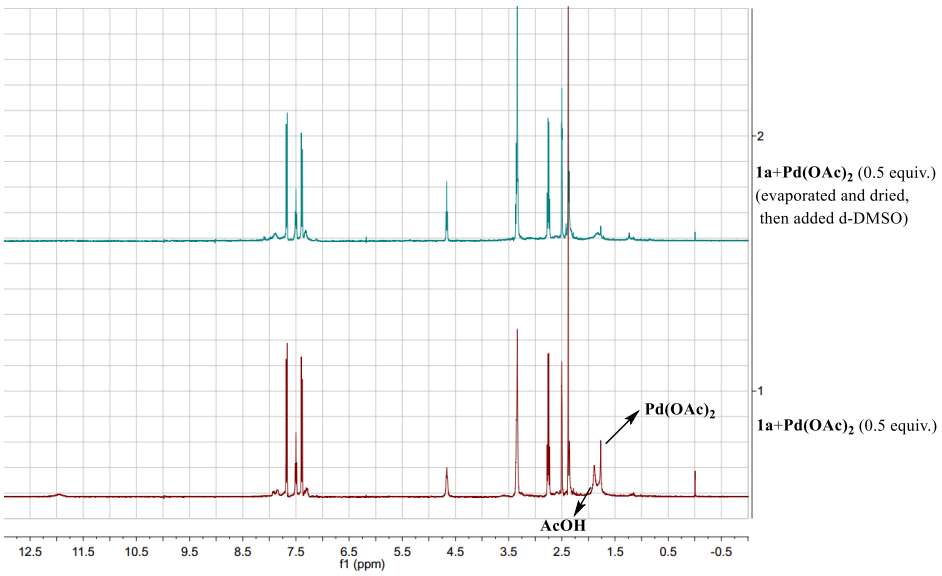
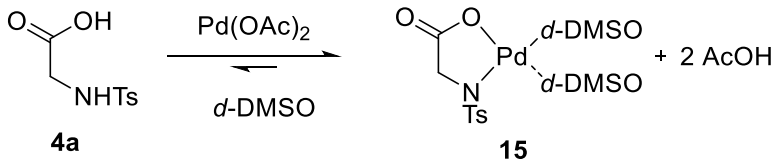


Figure S4. The *in situ* ^{1}H NMR for substrate **1a**

$Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.5 equiv.) was reacted with substrate **1a** (8.6 mg, 0.04 mmol, 1 equiv.) in *d*-DMSO (0.5 mL) in a NMR tube at 20 ^{o}C for 60 min. The NMR specta were recorded at 20 ^{o}C (Figure S4, entry 1). Then the mixture was evaporated and vacuum drying, and *d*-DMSO was added again (Figure S4, entry 2). The peaks of AcOH disappeared (the peaks of $Pd(OAc)_2$ also reduced a lot along with the removal of AcOH due to the chemical equilibrium shift), and the rest peaks of are almost unchanged. These results further exclude the the possibility of forming monodentate complex.

***In situ* ^{1}H NMR Spectroscopy of substrate 4a**



Scheme S2. The speculative equilibrium in *d*-DMSO for substrate **4a**

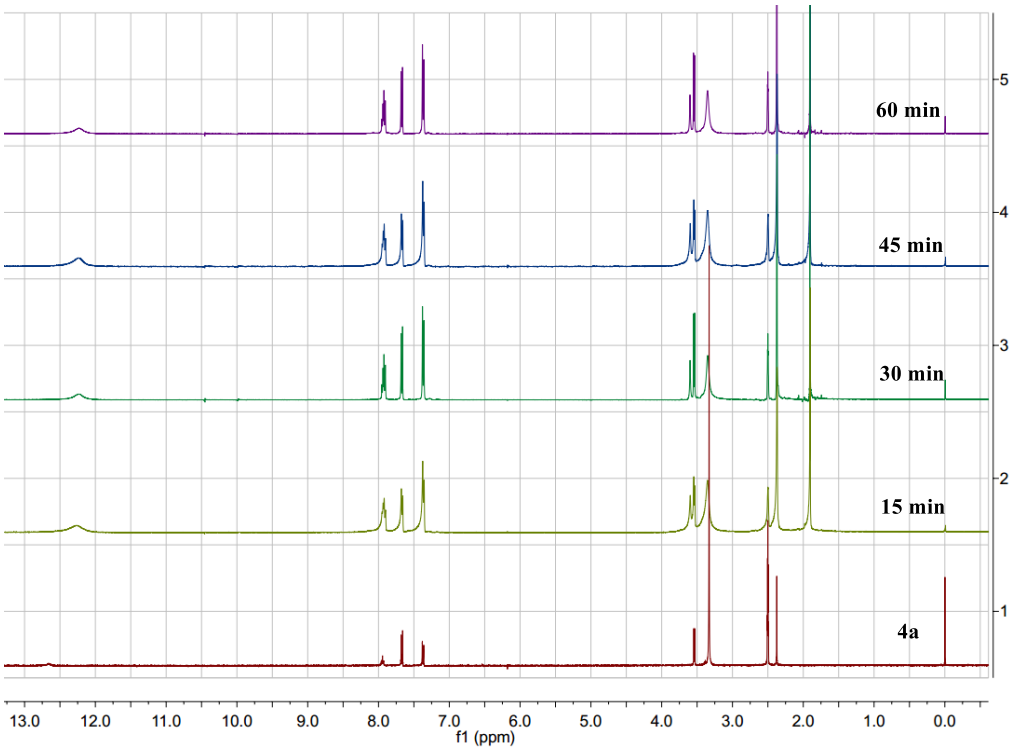


Figure S5. The *in situ* ^{1}H NMR with time for substrate **4a**

The speculative equilibrium in *d*-DMSO was shown in Scheme S2. Reaction of $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.5 equiv.) and substrate **4a** (9.2 mg, 0.04 mmol, 1 equiv.) in *d*-DMSO with time was monitored by ^{1}H NMR spectroscopy (Figure S5). $Pd(OAc)_2$ was reacted with substrate **4a** in *d*-DMSO (0.5 mL) in a NMR tube at 20 °C. The NMR spectra were recorded at 20 °C. The *in situ* ^{1}H NMR shows that the reaction reached the equilibrium quickly.

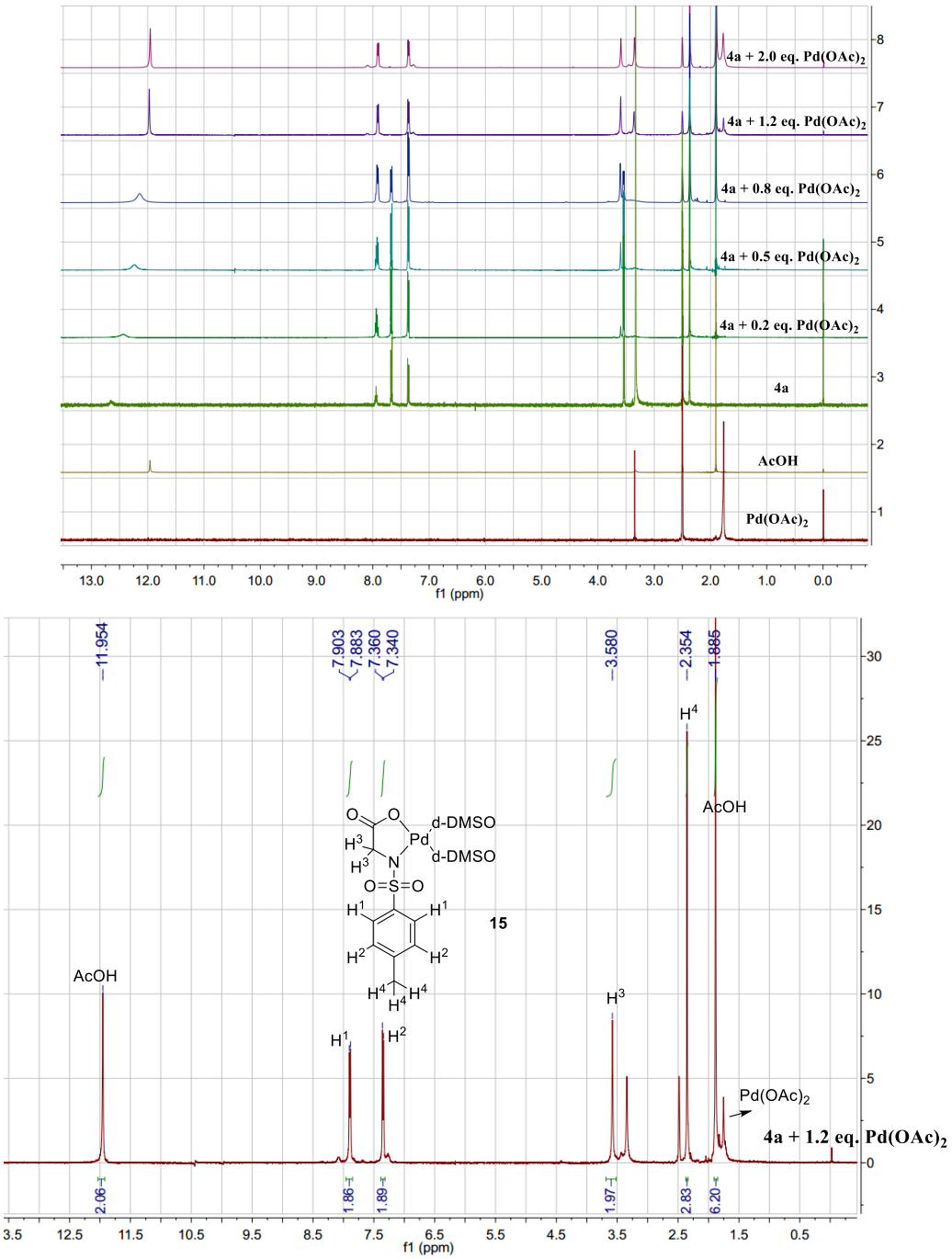


Figure S6. The *in situ* ^{1}H NMR with different amount of $Pd(OAc)_2$ for substrate **4a**

Reactions of different amounts of $Pd(OAc)_2$ and substrate **1a** (9.2 mg, 0.04 mmol, 1 equiv.) were monitored by ^{1}H NMR spectroscopy (Figure S6). $Pd(OAc)_2$ was reacted with substrate **4a** in *d*-DMSO (0.5 mL) in a NMR tube at 20 °C for 30 min. The NMR specta were recorded at 20 °C. The new complex was increased along with the amount of $Pd(OAc)_2$. We found that the substrate **4a** almost disppeared and the peak area of AcOH is double of those of the new complex (entry 7). This suggests that bidentate complex **15** is likely to be formed.

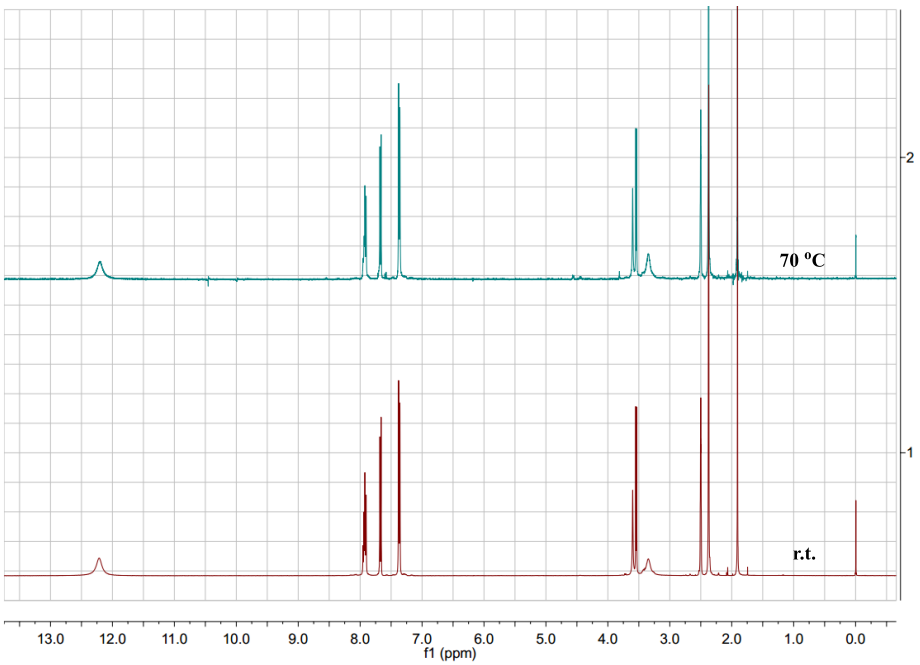


Figure S7. The *in situ* ^{1}H NMR at different tempratures for substrate **4a**

Reactions of of $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.5 equiv.) and substrate **4a** (9.2 mg, 0.04 mmol, 1 equiv.) were monitored by ^{1}H NMR spectroscopy at different tempratures (Figure S7). $Pd(OAc)_2$ was reacted with substrate **4a** in *d*-DMSO (0.5 mL) at different tempratures for 60 min. The peaks are almost unchanged at 70 °C.

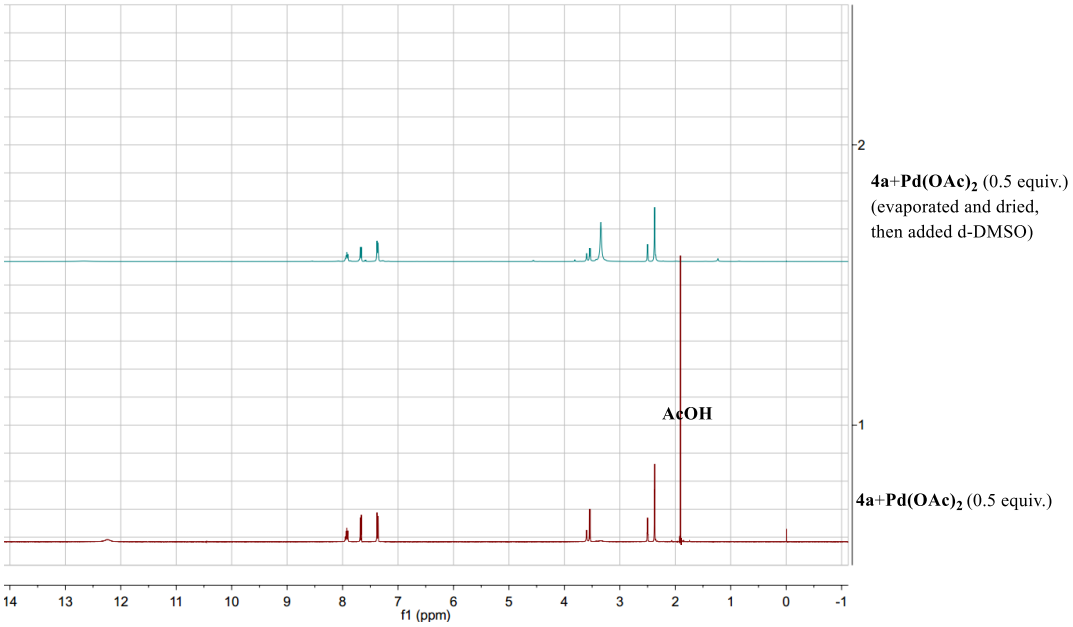
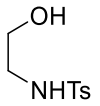


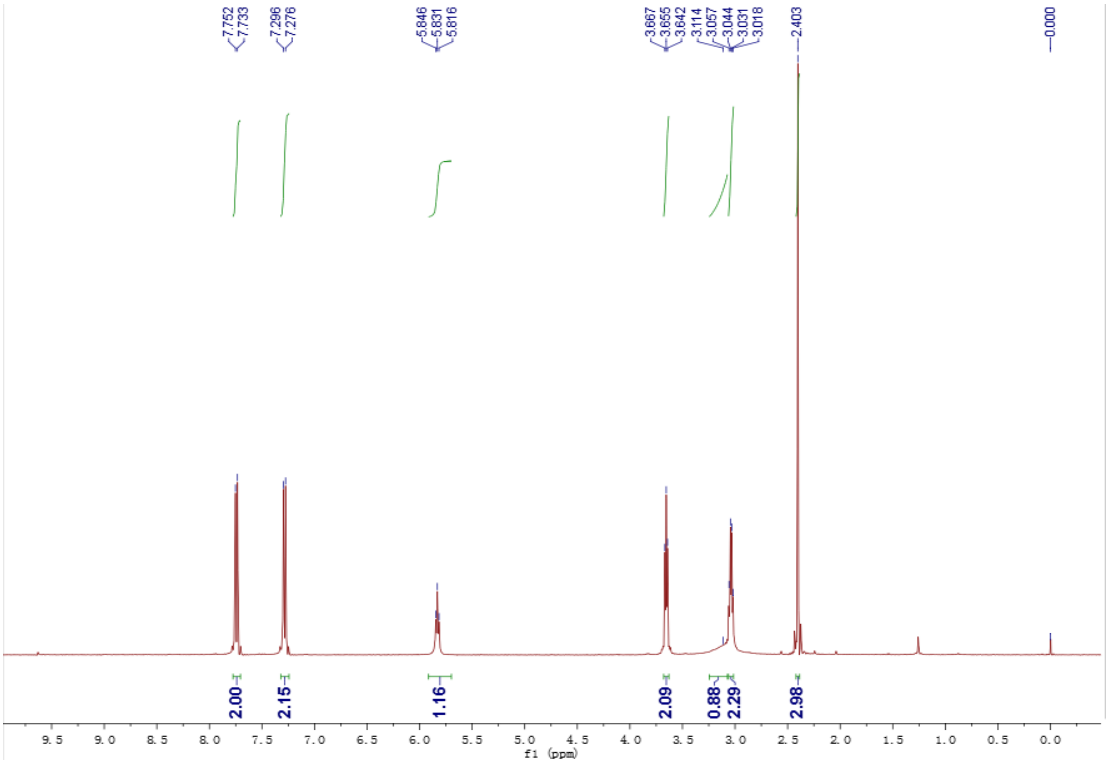
Figure S8. The *in situ* ^{1}H NMR in *d*-DMSO

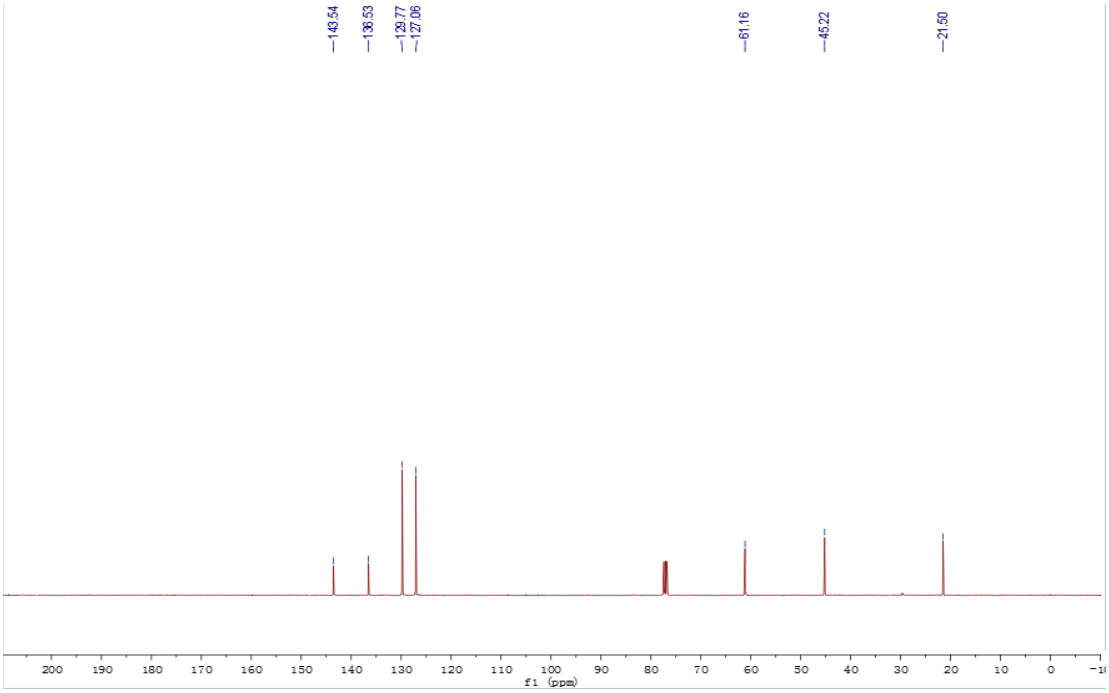
$Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.5 equiv.) was reacted with substrate **4a** (9.2 mg, 0.04 mmol, 1 equiv.) in *d*-DMSO (0.5 mL) in a NMR tube at 20 ^{o}C for 60 min. The NMR specta were recorded at 20 ^{o}C (Figure S8, entry 1). Then the mixture was evaporated and vacuum drying, and *d*-DMSO was added again (Figure S8, entry 2). The peaks of AcOH almost disappeared and the peaks of **15** are almost unchanged. These results further exclude the the possibility of forming monodentate complex.

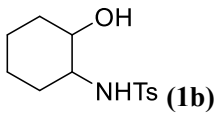
6. NMR spectra



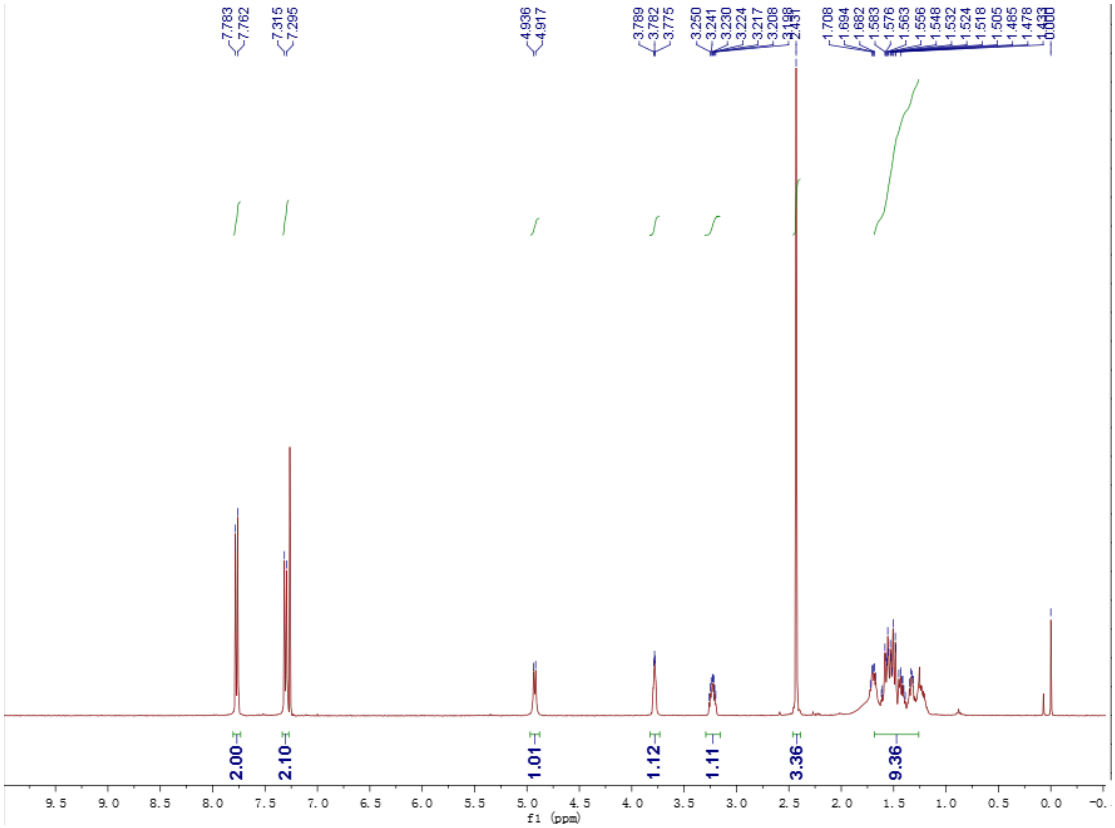
(1a)






OH
NHTs

(1b)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3.224
3.217
3.208
1.708
1.694
1.682
1.583
1.576
1.563
1.556
1.548
1.532
1.524
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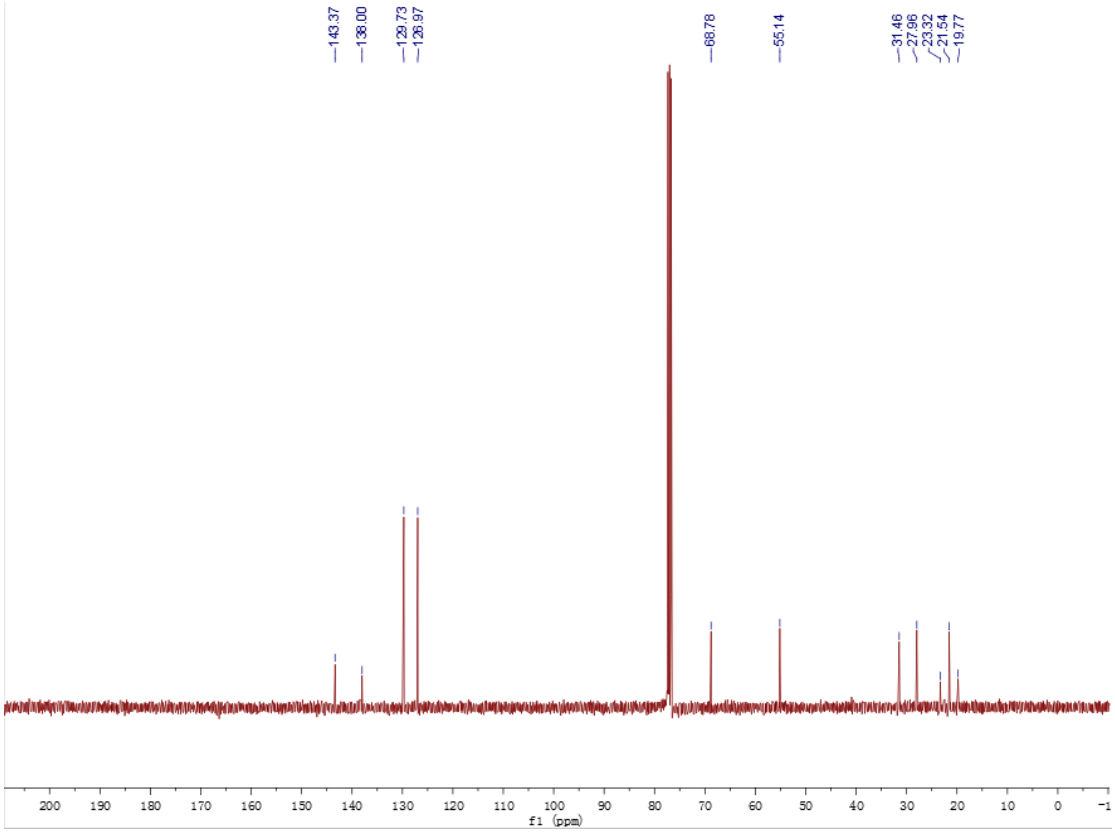
9.36
f1 (ppm)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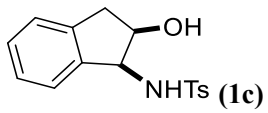
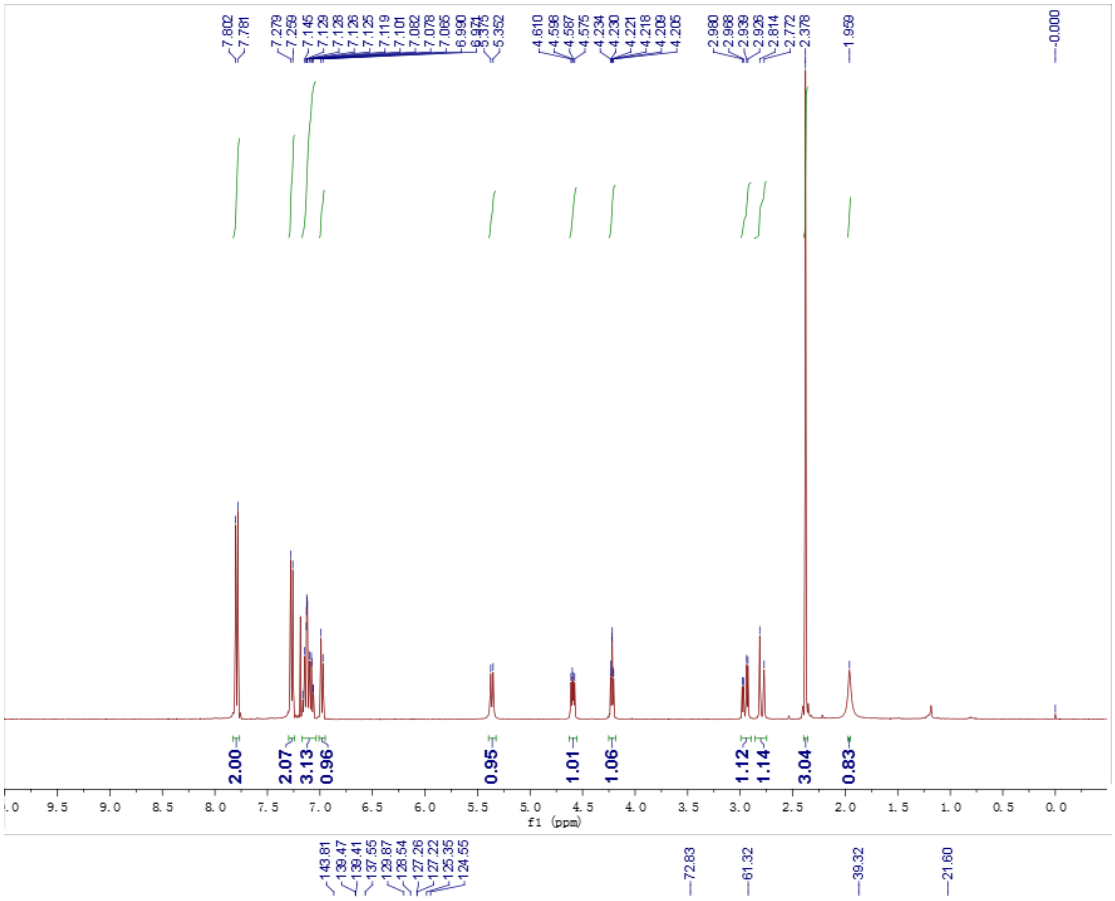

OH
NHTs

(1c)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7.066
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6.971
5.375
5.352
4.610
4.598
4.587
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4.209
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2.926
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2.772
2.378
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2.00
2.07
3.13
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0.95
1.01
1.06
1.12
1.14
3.04
0.83
f1 (ppm)

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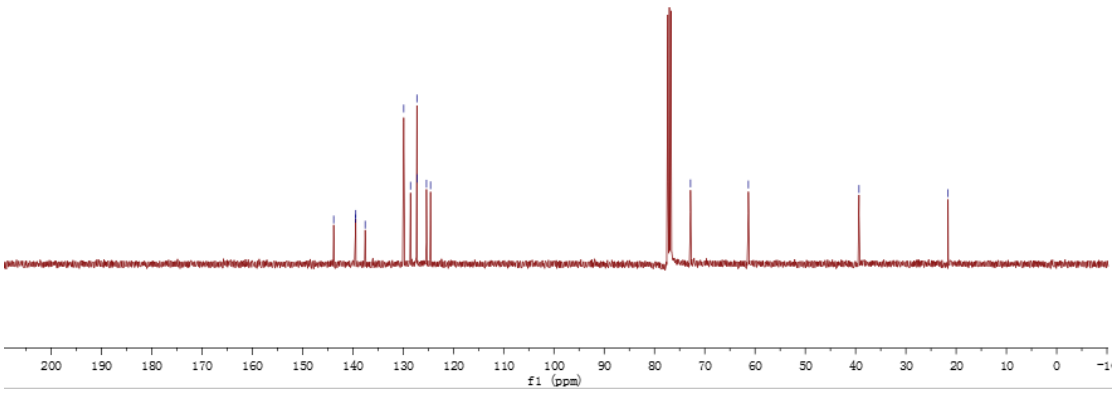
39.32
21.60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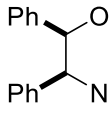
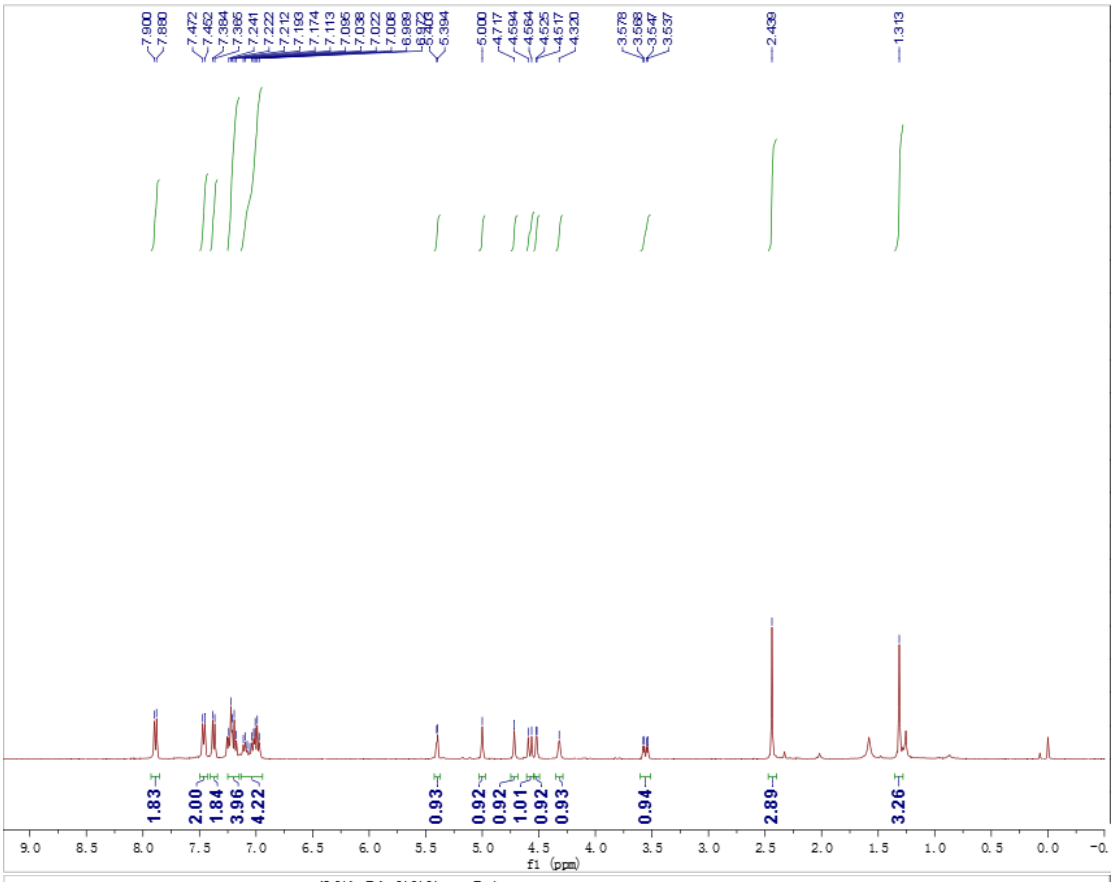

Ph
OH
Ph
NHTs

(1d)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5.000
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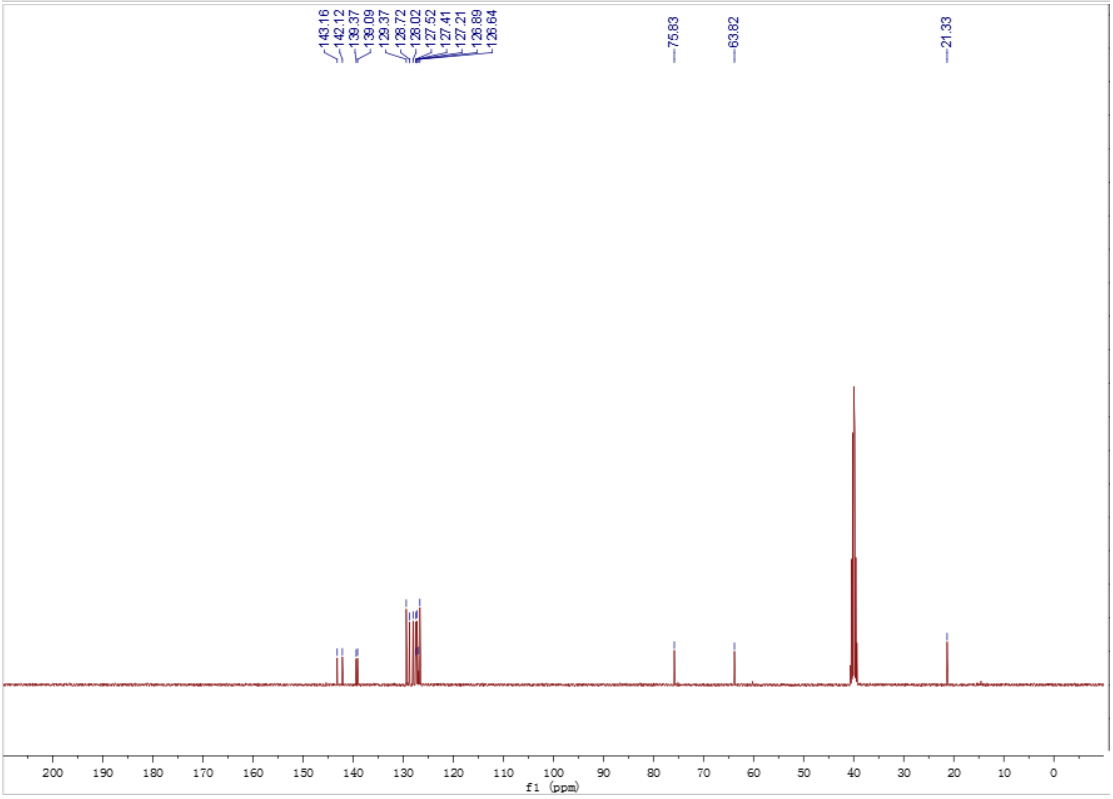
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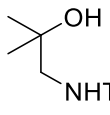
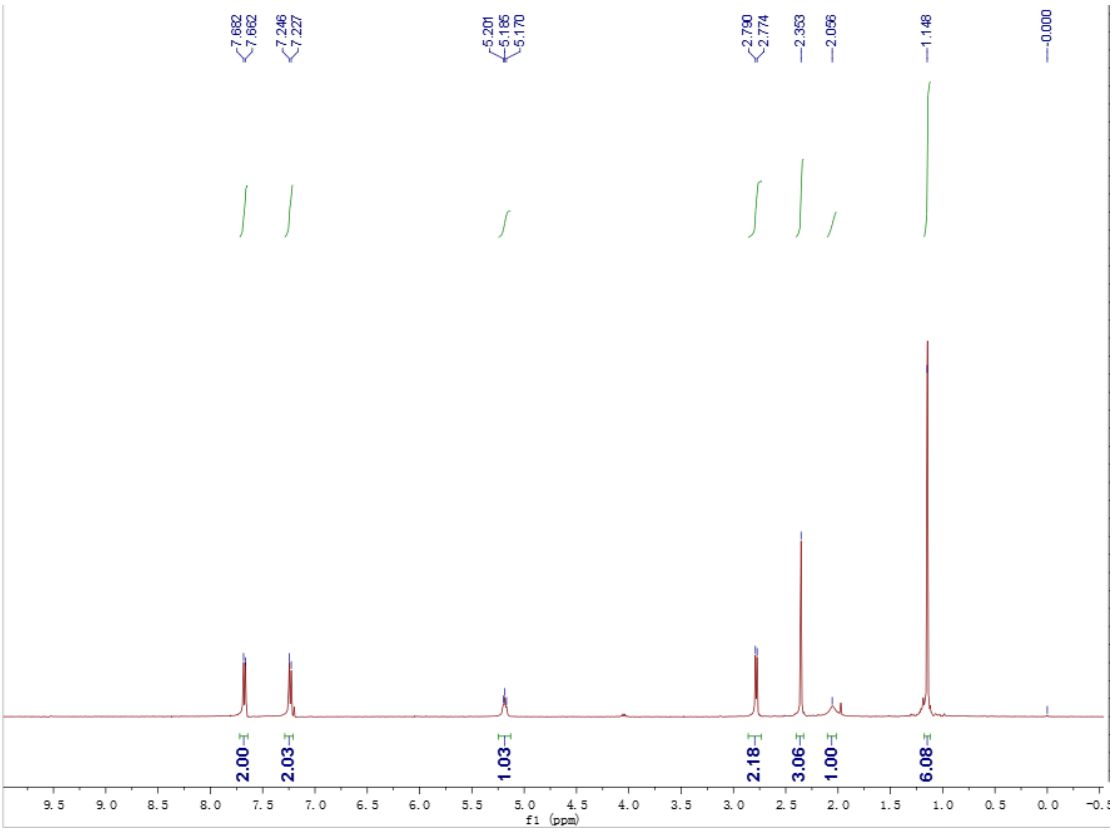
f1 (ppm)


OH
NHTs

(1e)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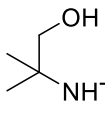
f1 (ppm)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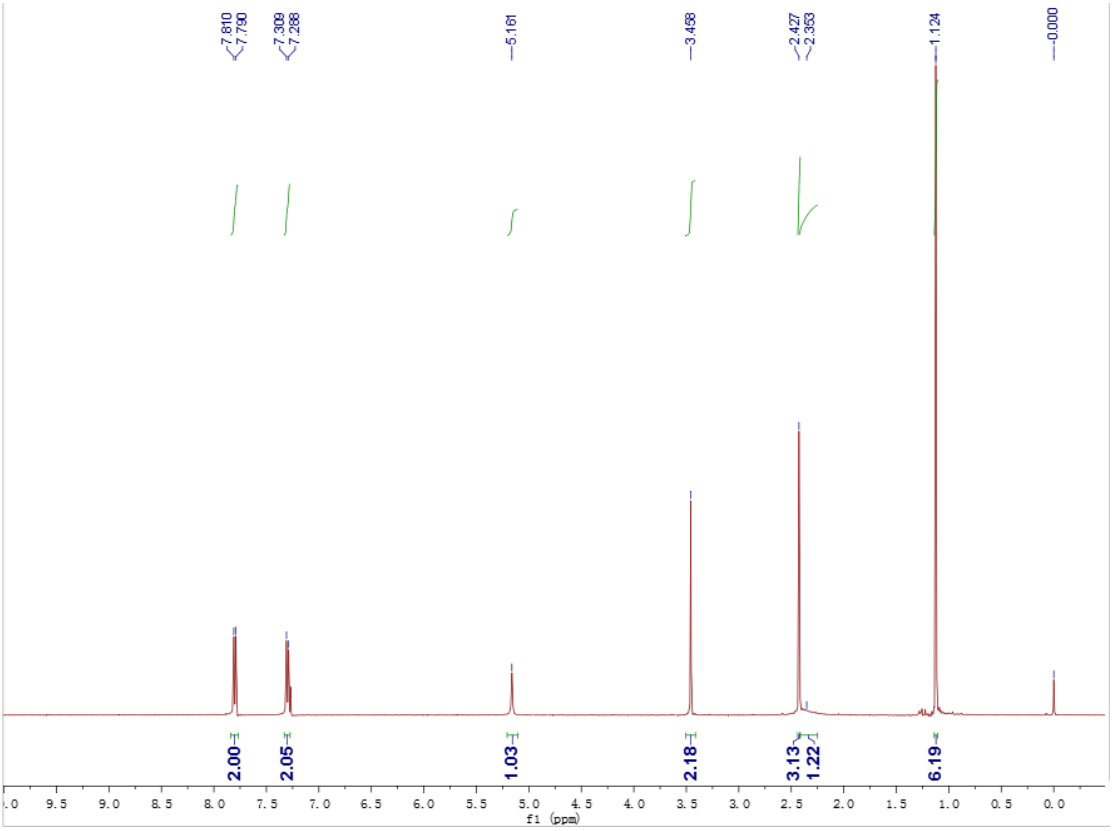
(1f)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1.22
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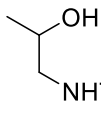
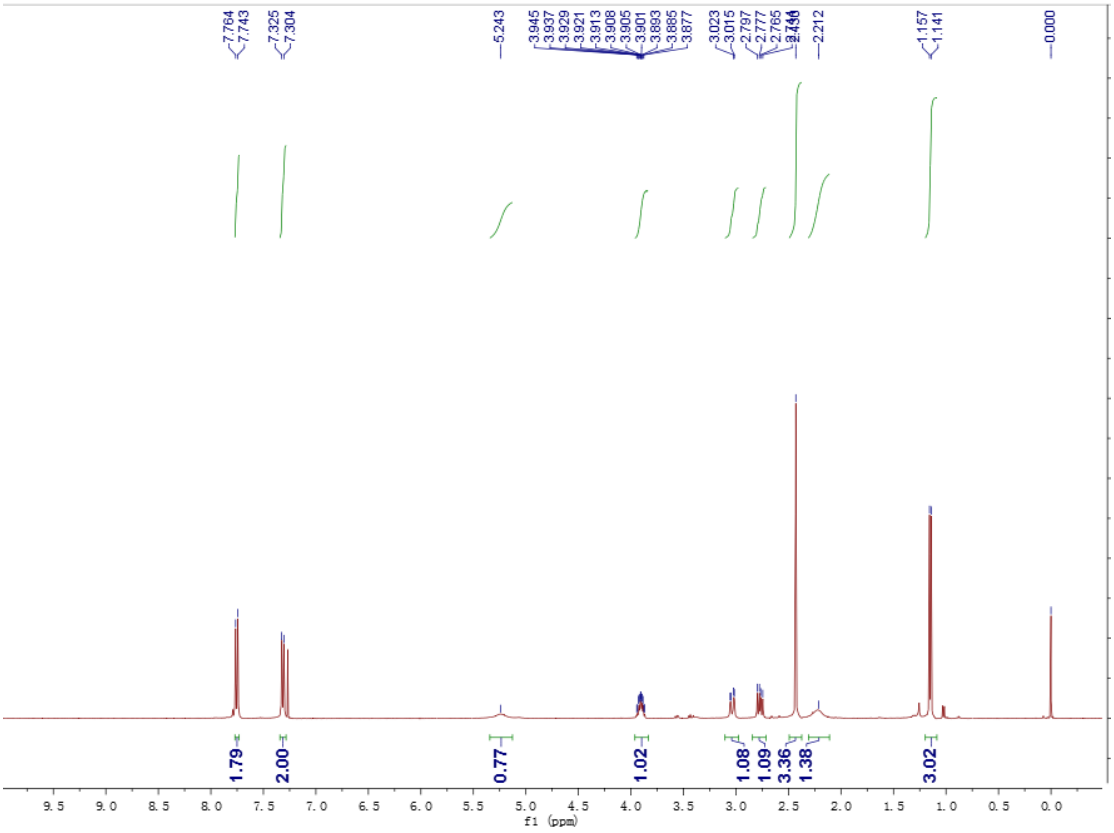
f1 (ppm)


OH
NHTs

(1g)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1.09
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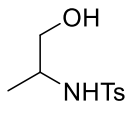
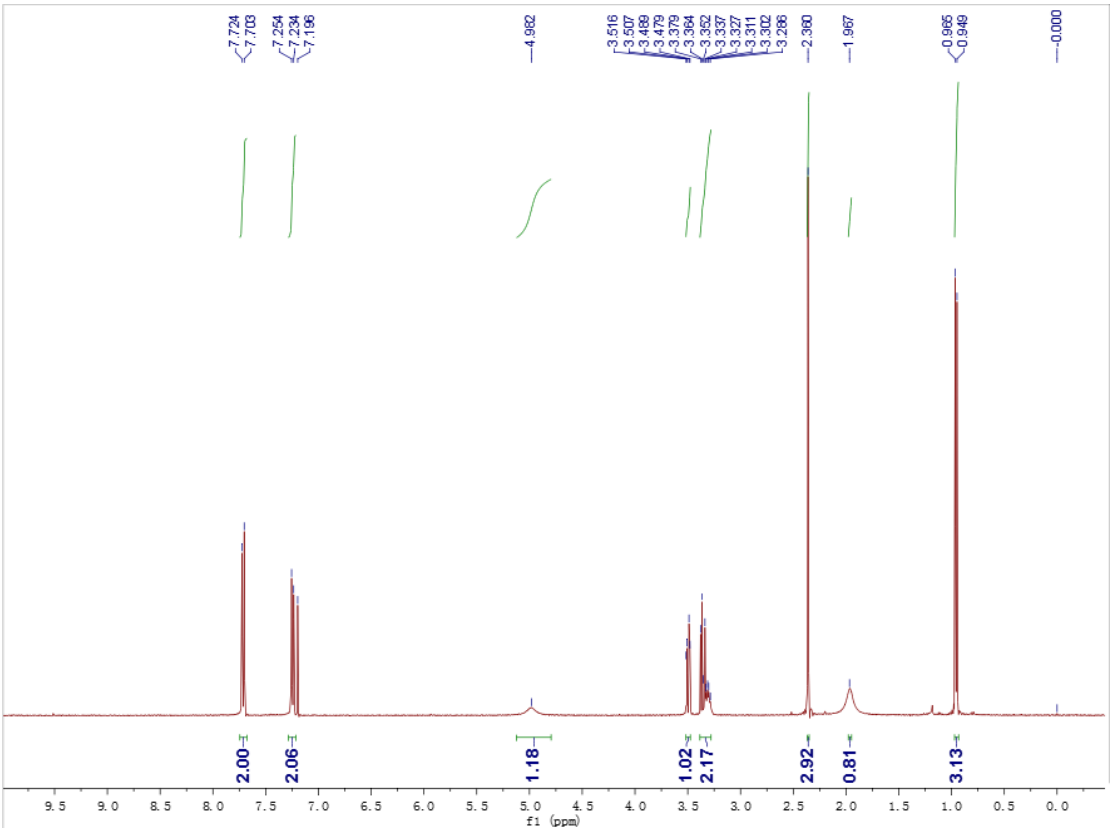
f1 (ppm)


OH
NHTs

(1h)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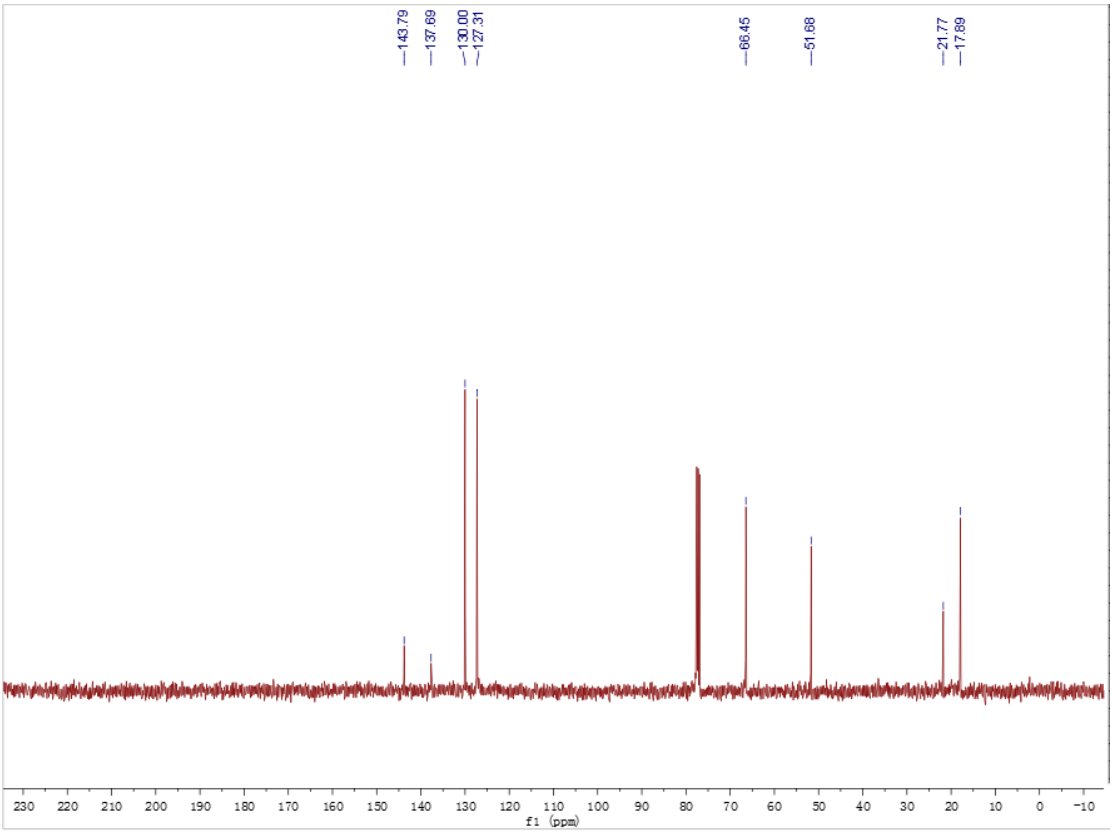
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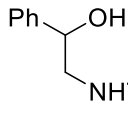
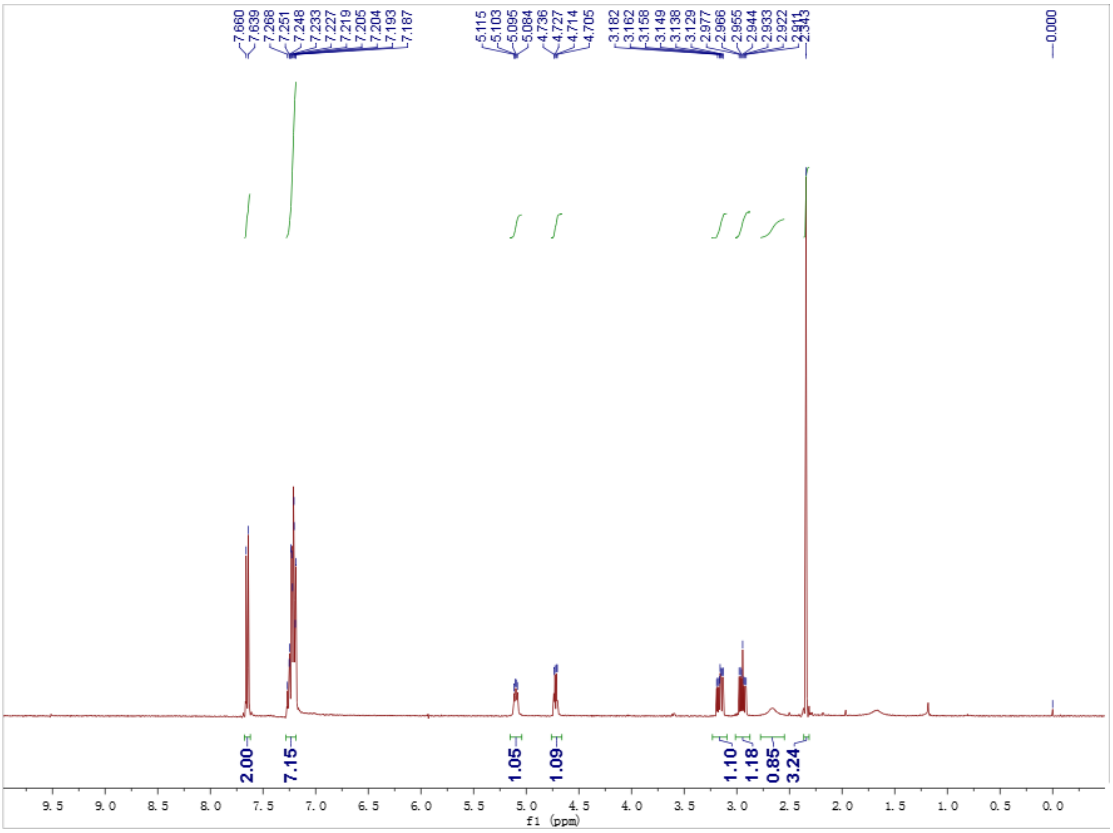

Ph
OH
NHTs

(1i)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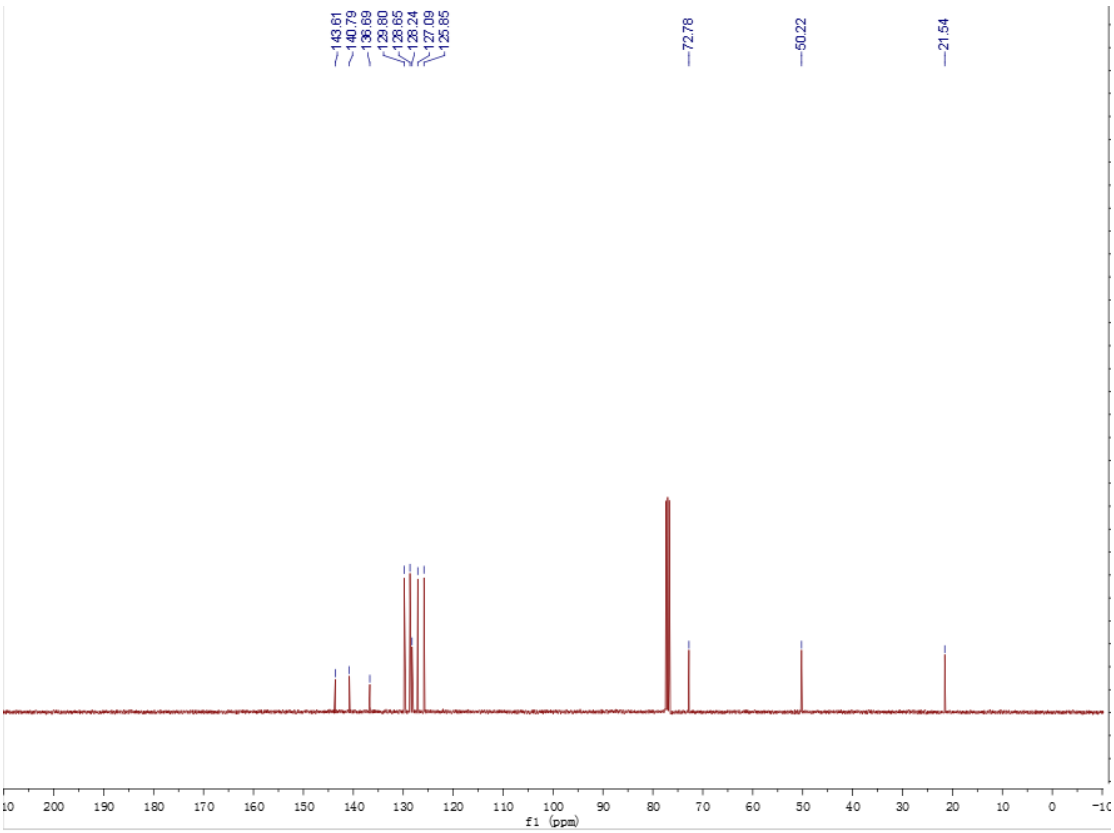
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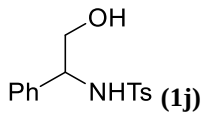
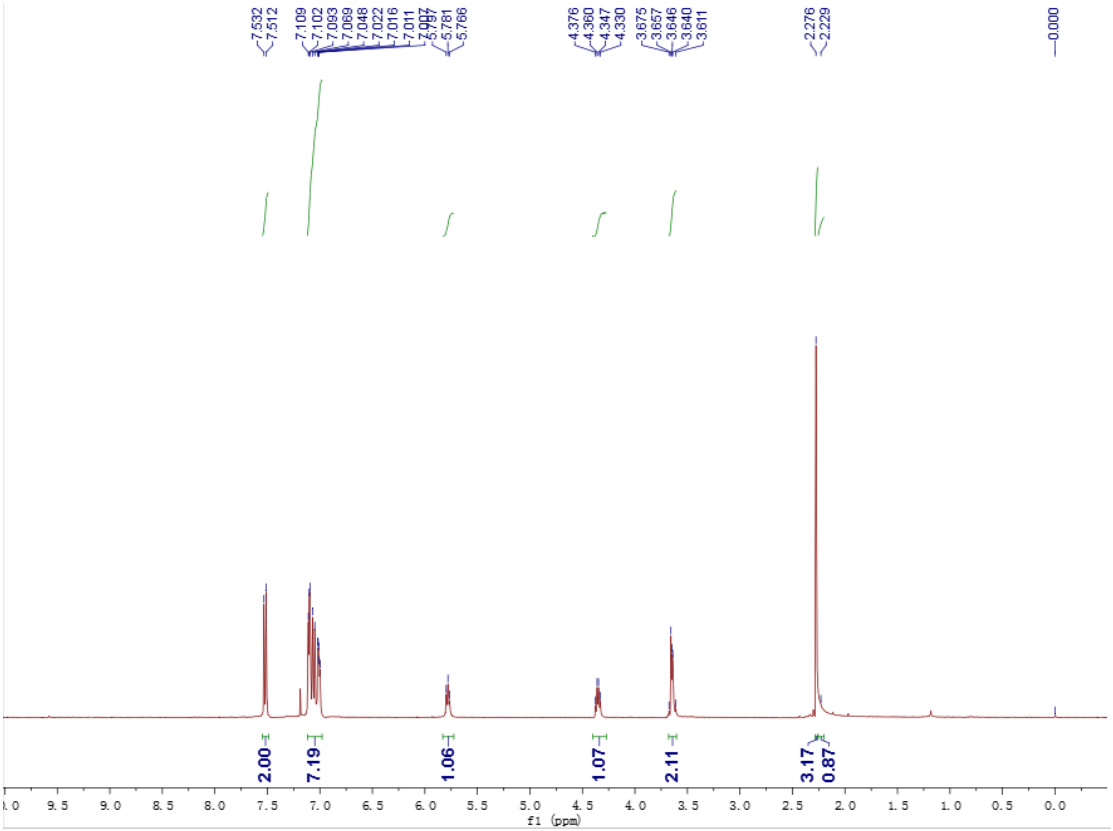

OH
Ph
NHTs

(1j)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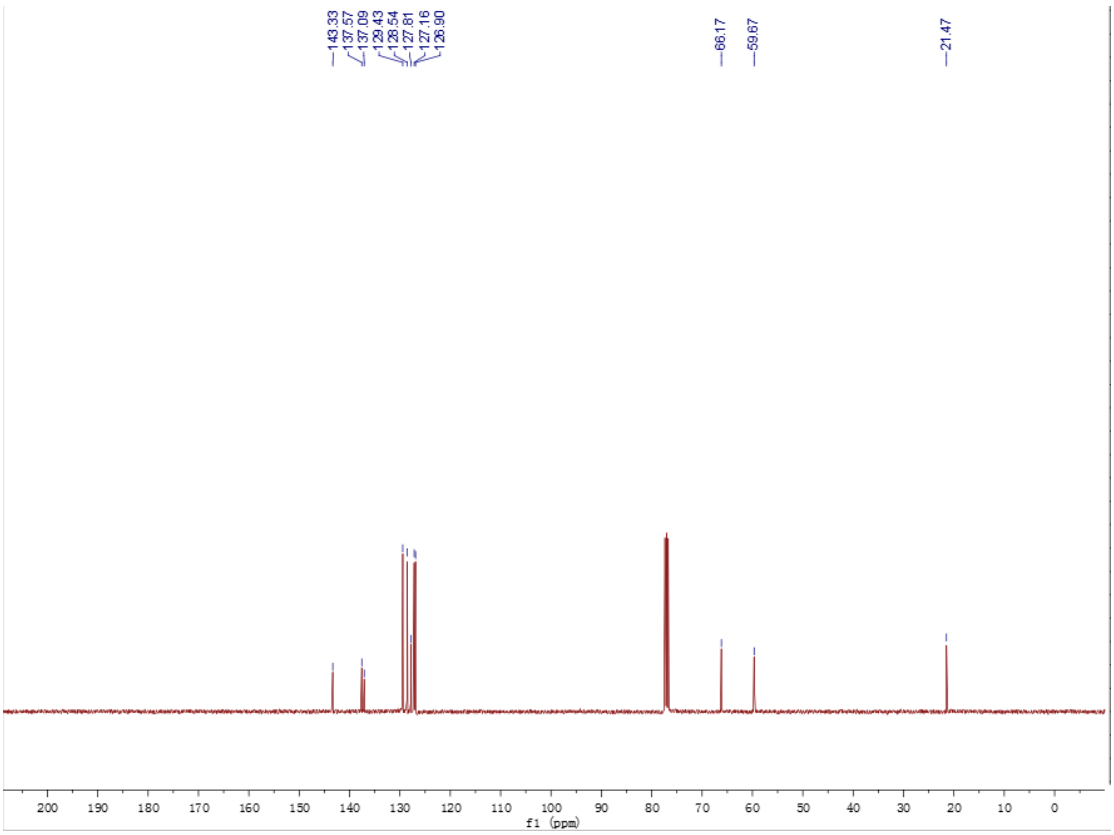
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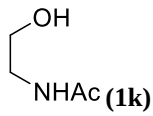
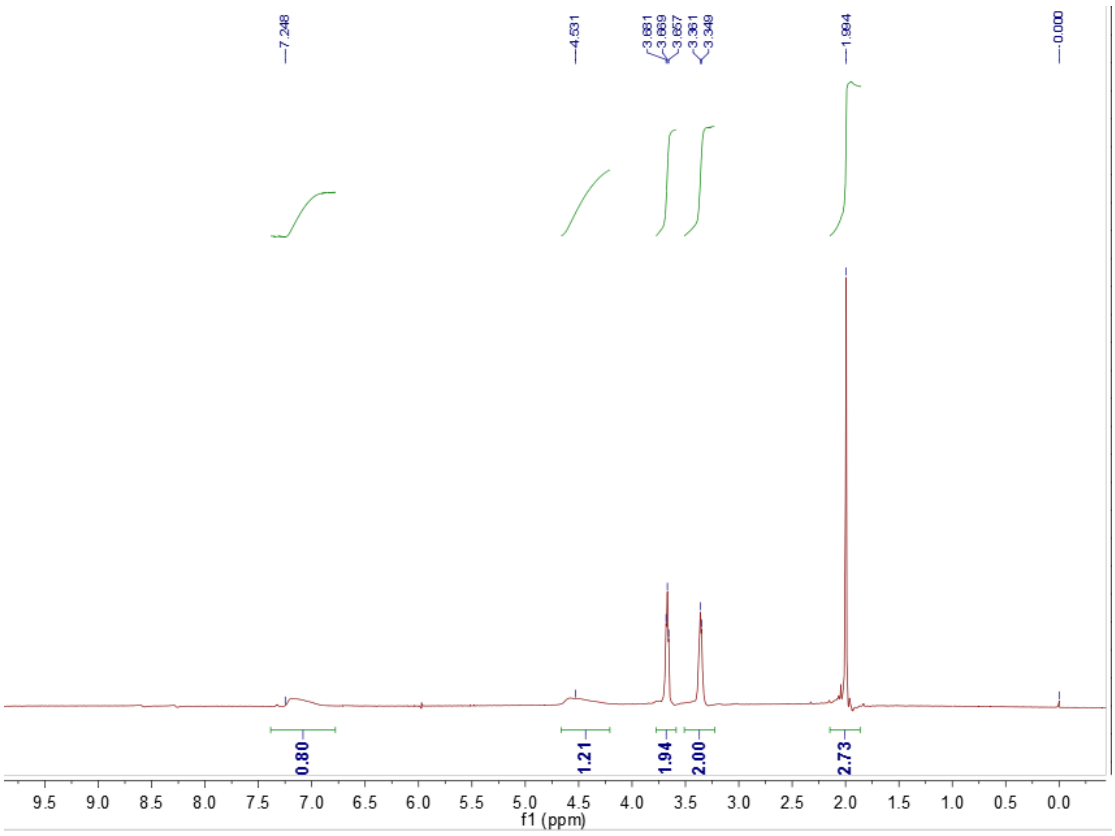
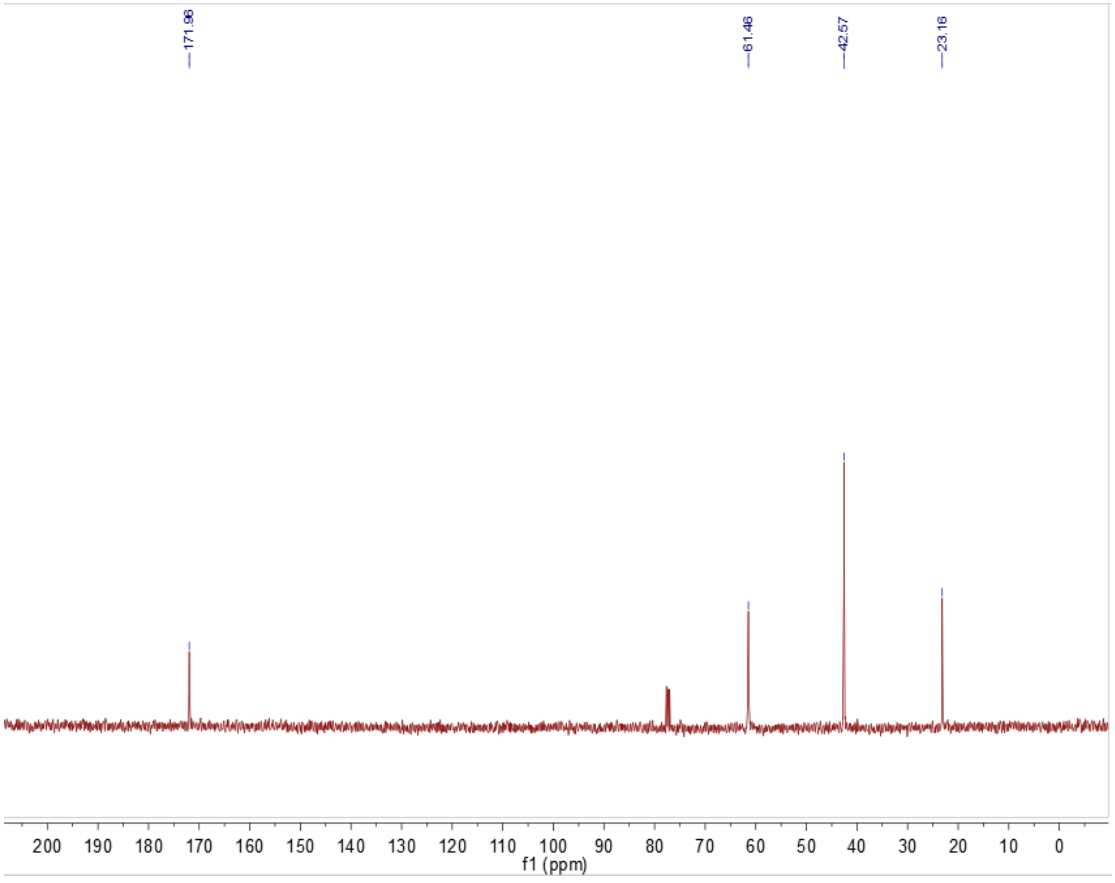
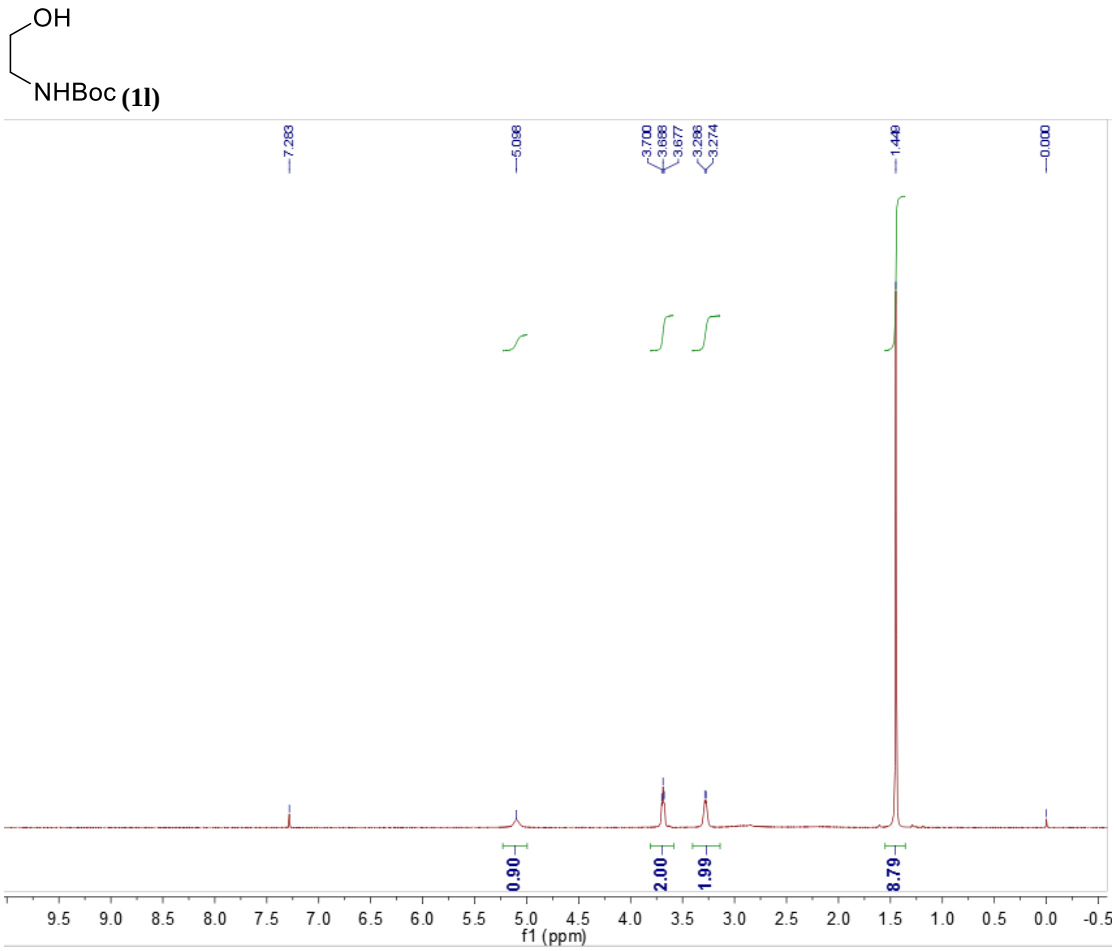
21.47
f1 (ppm)

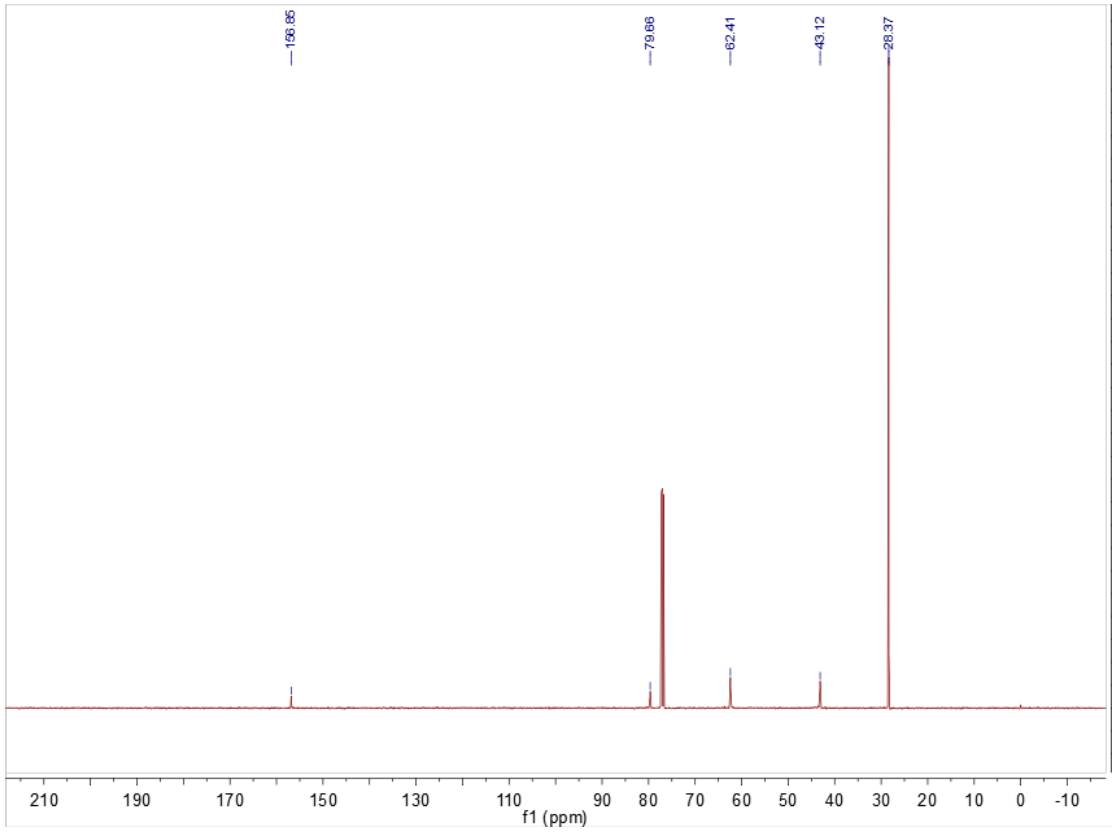

OH
NHAc

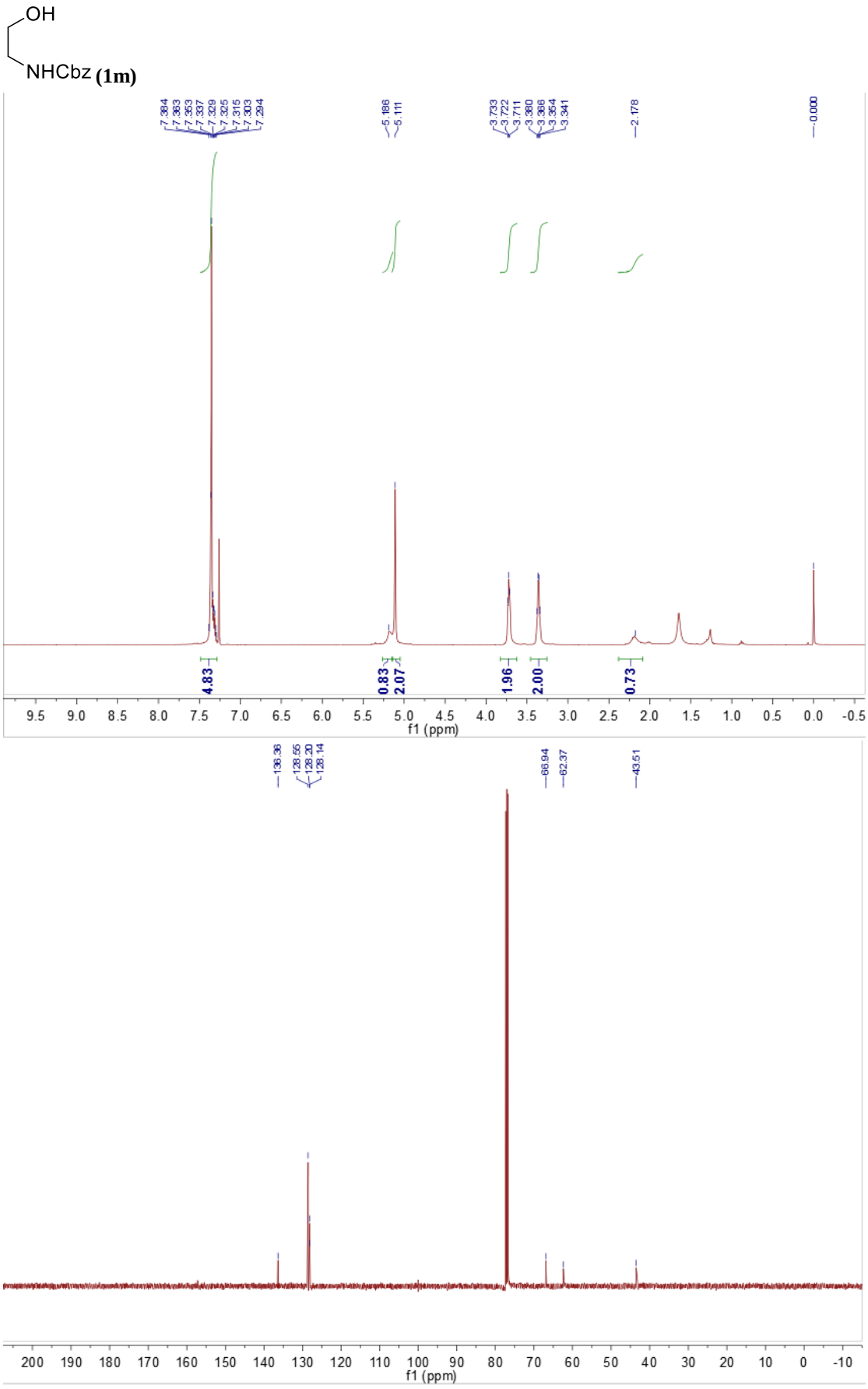
(1k)

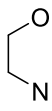

7.248
4.631
3.881
3.869
3.857
3.361
3.349
1.994
0.000
0.80
1.21
1.94
2.00
2.73
f1 (ppm)


171.96
61.46
42.57
23.16
f1 (ppm)

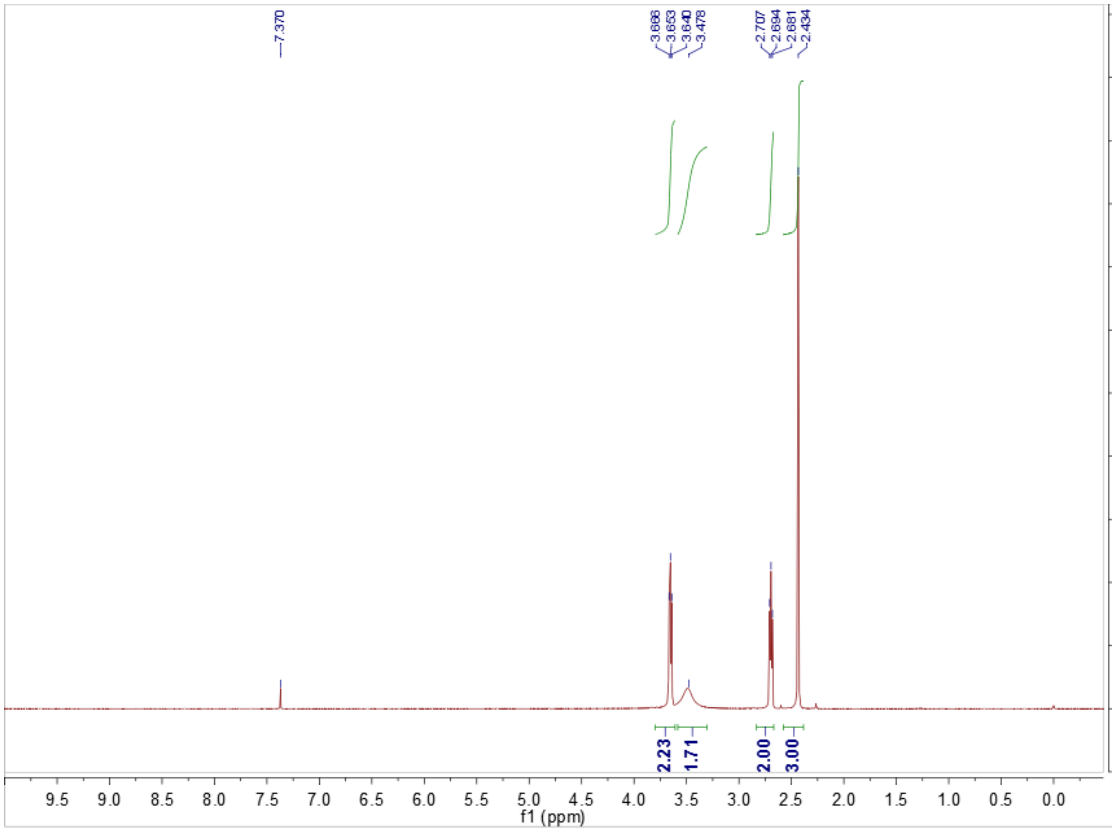

OH
NHBoc
(1l)
7.283
5.088
3.700
3.688
3.677
3.286
3.274
1.449
0.000
0.90
2.00
1.99
8.79
f1 (ppm)

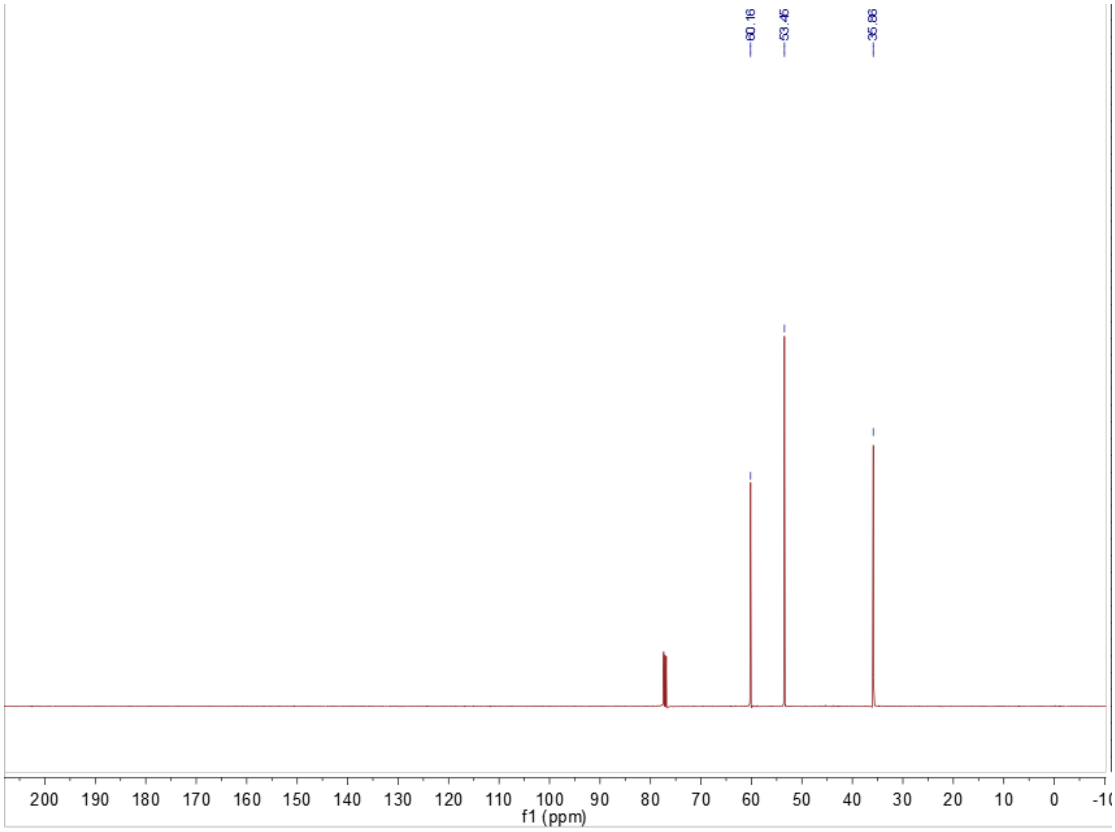

156.85
79.66
62.41
43.12
28.37
f1 (ppm)

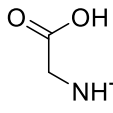

OH
NHCbz (1m)
7.364
7.363
7.353
7.337
7.329
7.325
7.315
7.303
7.294
5.186
5.111
3.733
3.722
3.711
3.380
3.366
3.354
3.341
2.178
0.000
4.83
0.83
2.07
1.96
2.00
0.73
f1 (ppm)
136.38
128.55
128.20
128.14
66.94
62.37
43.51
f1 (ppm)


OH
NHMe

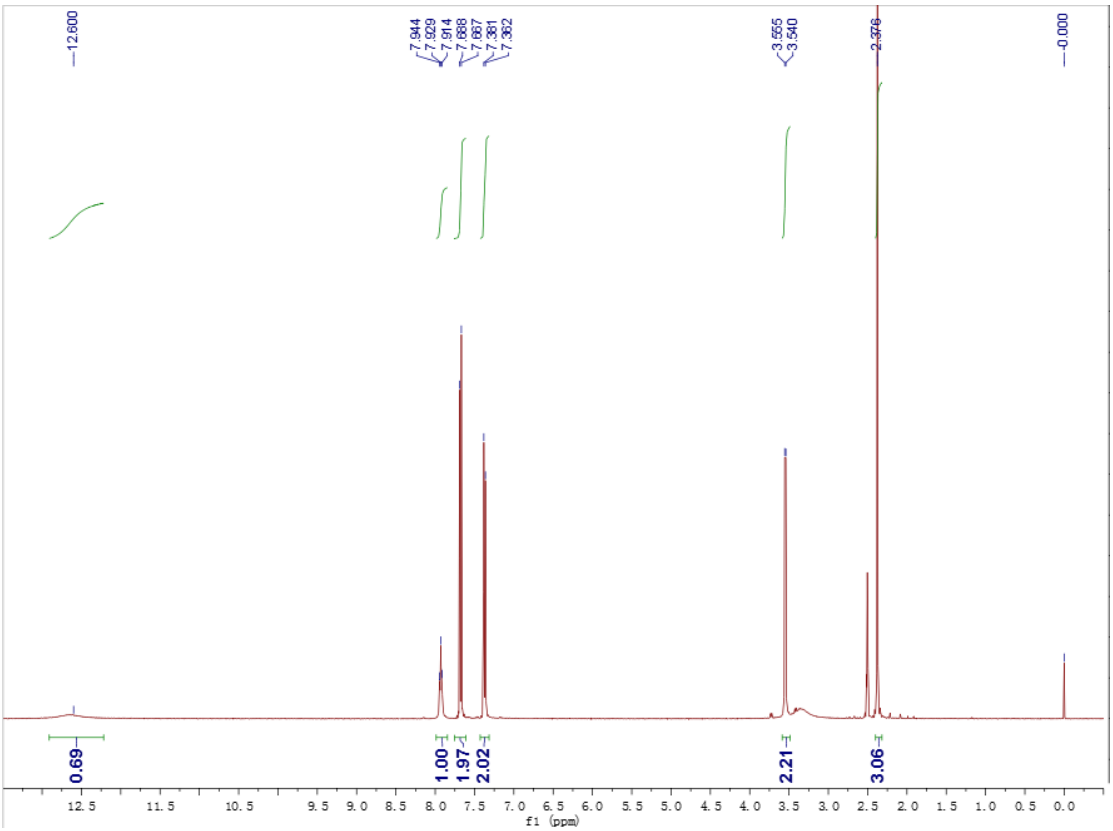
(1n)

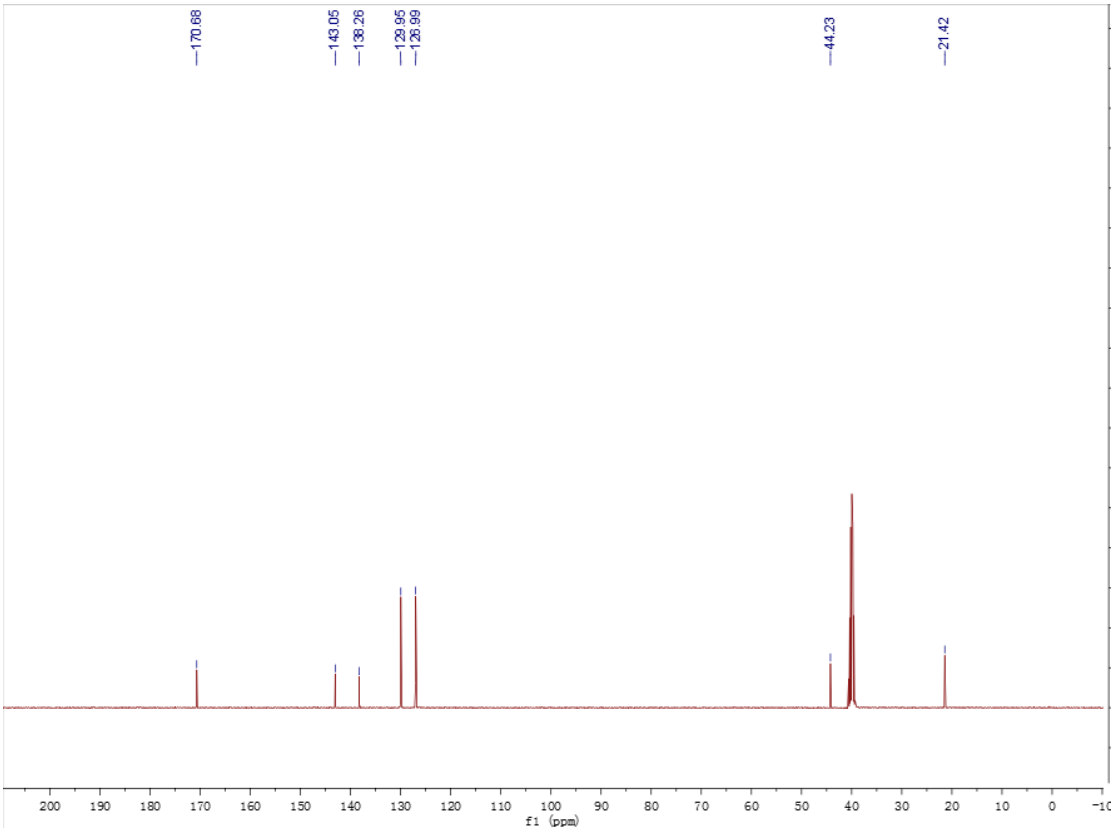

7.370
3.666
3.653
3.640
3.478
2.707
2.694
2.681
2.434
2.23
1.71
2.00
3.00
f1 (ppm)

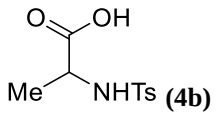

60.16
53.45
35.86
f1 (ppm)


O
OH
NHTs

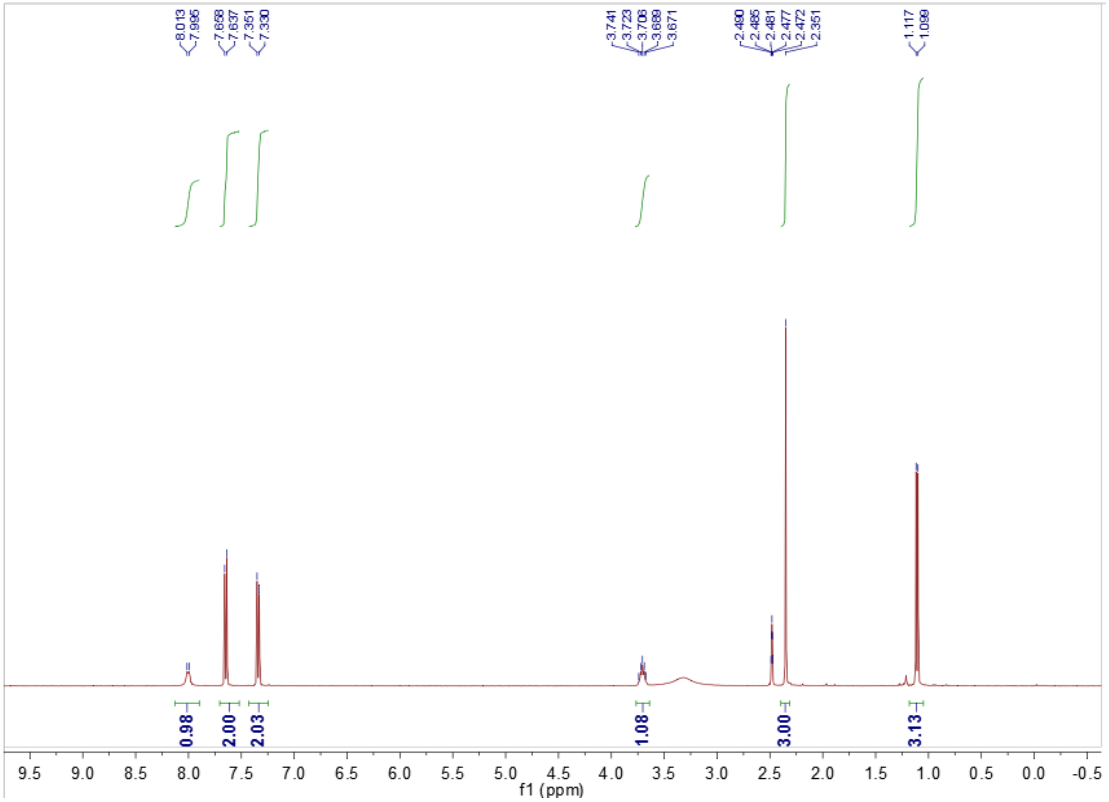
(4a)

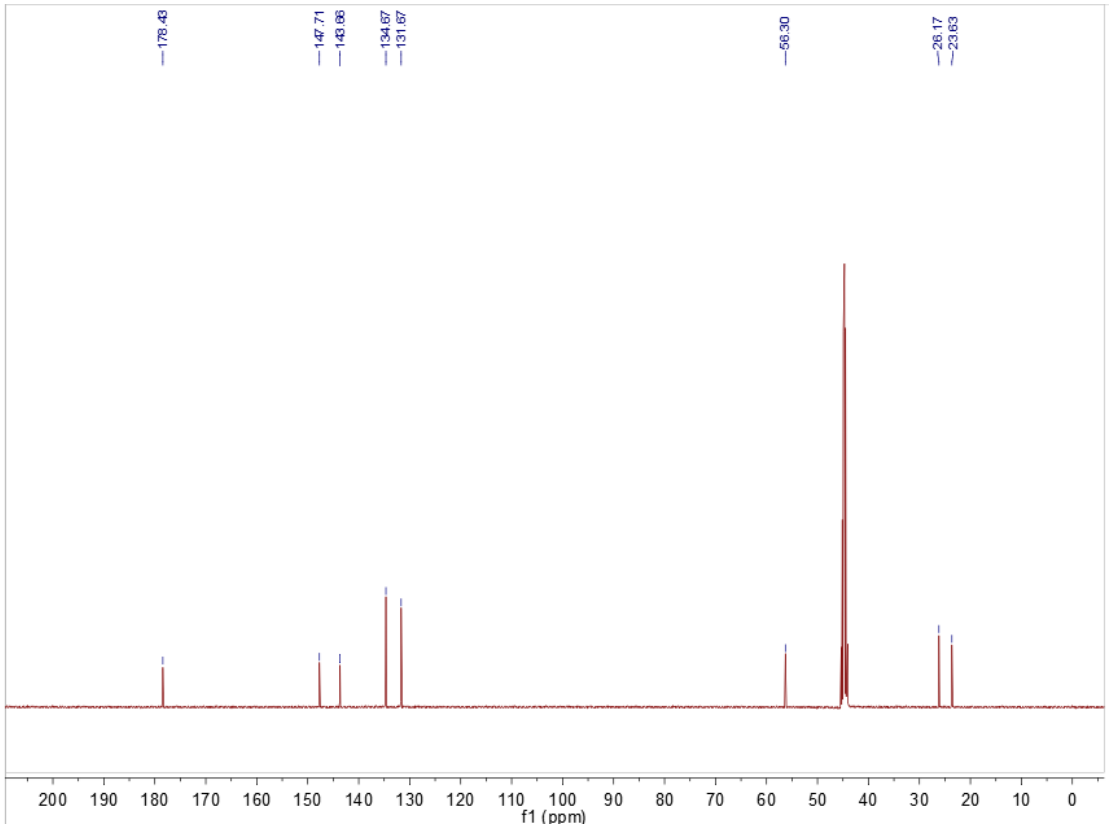

12.600
7.944
7.929
7.914
7.888
7.867
7.381
7.362
3.555
3.540
2.378
0.000
0.69
1.00
1.97
2.02
2.21
3.06
f1 (ppm)

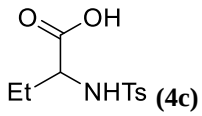

170.68
143.05
138.26
129.95
126.99
44.23
21.42
f1 (ppm)


O
OH
Me
NHTs

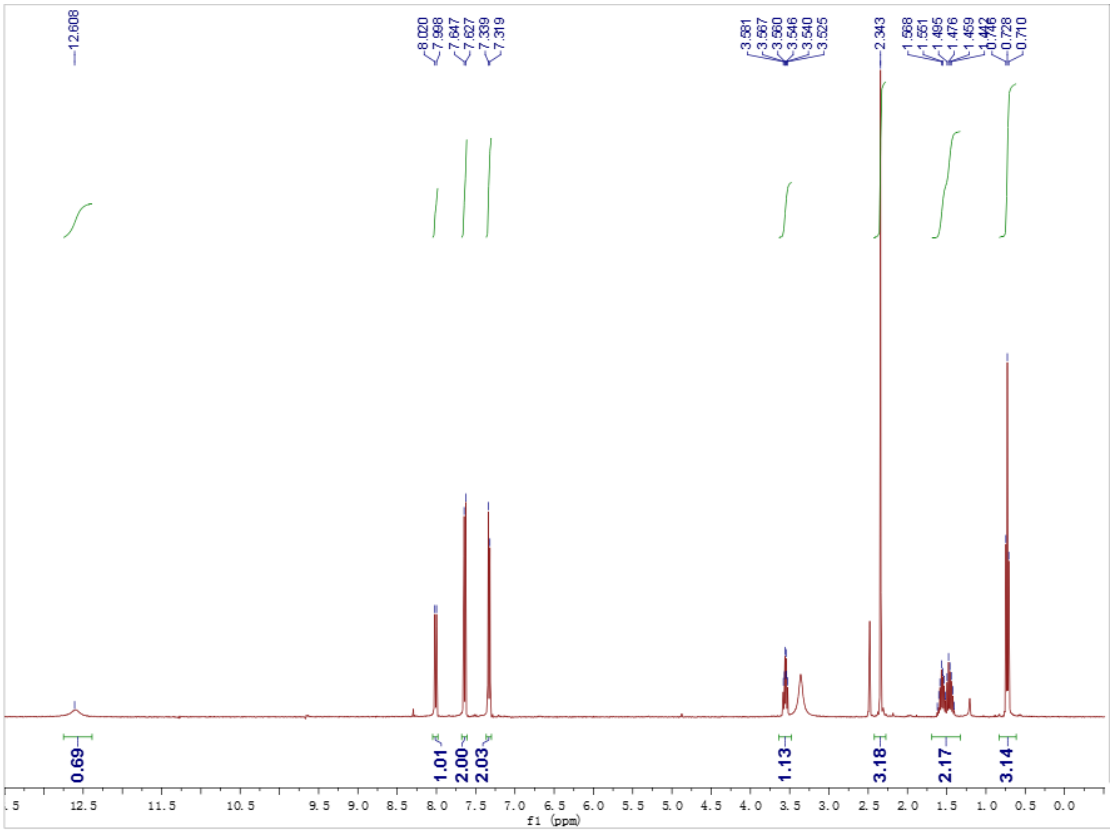
(4b)

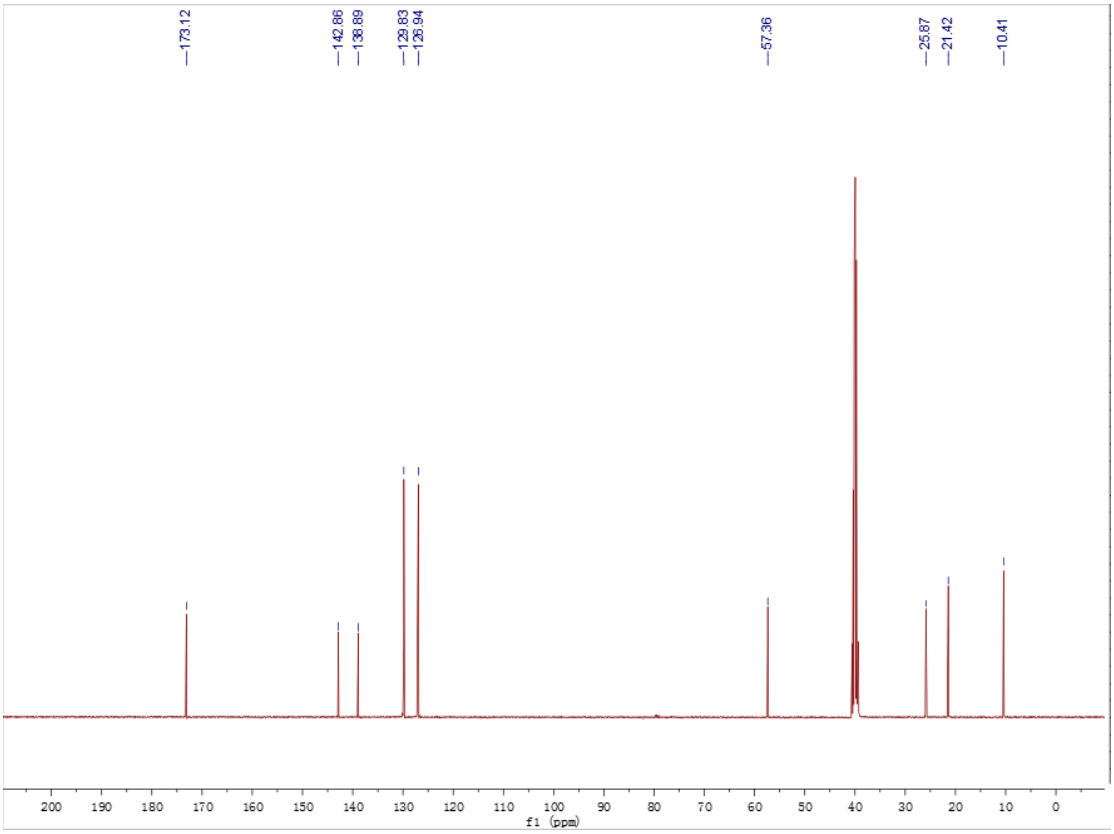

8.013
7.995
7.658
7.637
7.351
7.330
3.741
3.723
3.706
3.689
3.671
2.490
2.485
2.481
2.477
2.472
2.351
1.117
1.099
0.98
2.00
2.03
1.08
3.00
3.13
f1 (ppm)

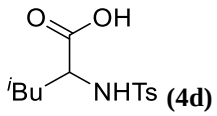

178.43
147.71
143.86
134.67
131.67
56.30
26.17
23.63
f1 (ppm)


O
OH
Et
NHTs

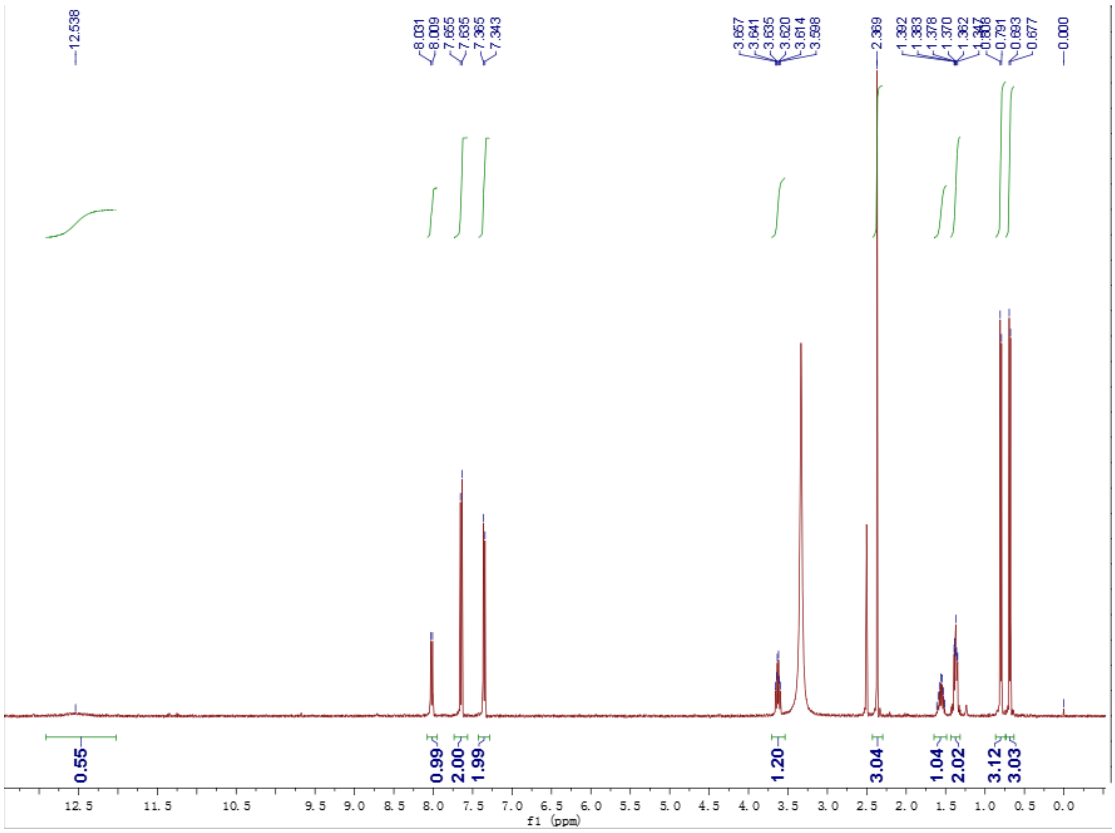
(4c)

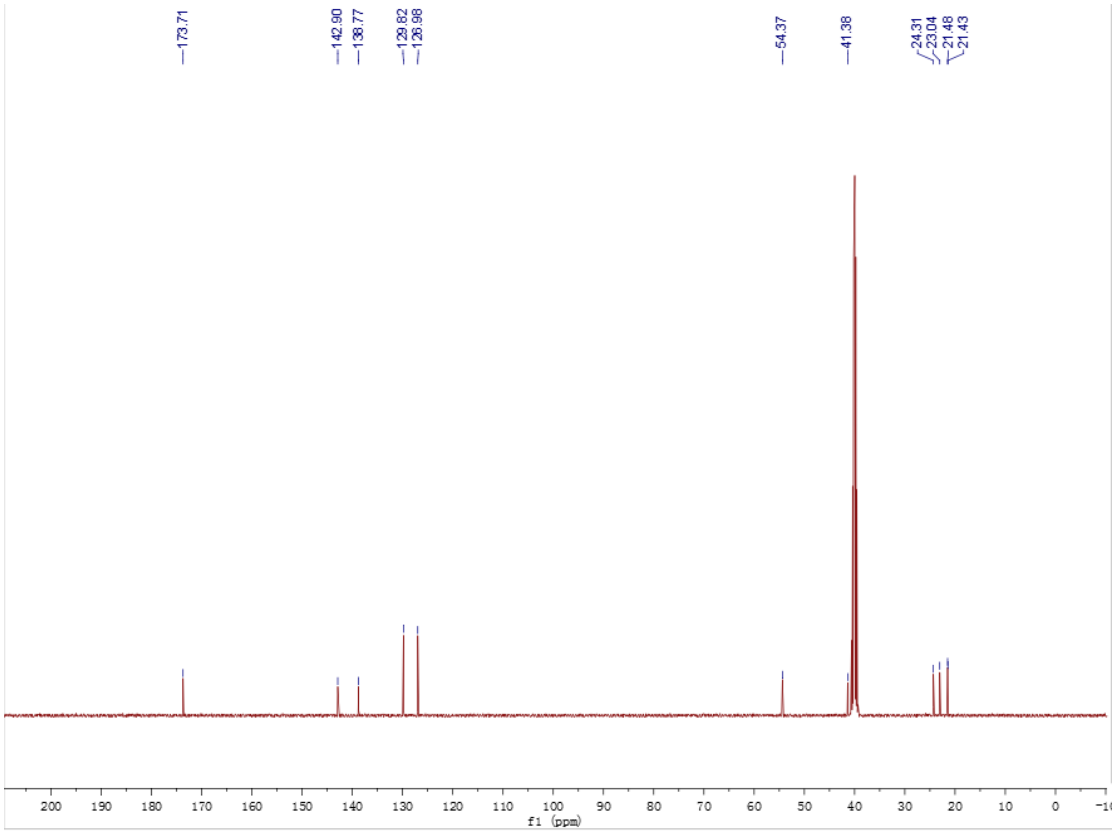

12.608
8.020
7.998
7.647
7.627
7.339
7.319
3.581
3.567
3.560
3.546
3.540
3.525
2.343
1.568
1.551
1.495
1.476
1.459
0.728
0.710
0.69
1.01
2.00
2.03
1.13
3.18
2.17
3.14
f1 (ppm)

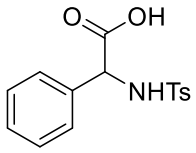

173.12
142.86
138.89
129.83
126.94
57.36
25.87
21.42
10.41
f1 (ppm)


O
OH
iBu
NHTs

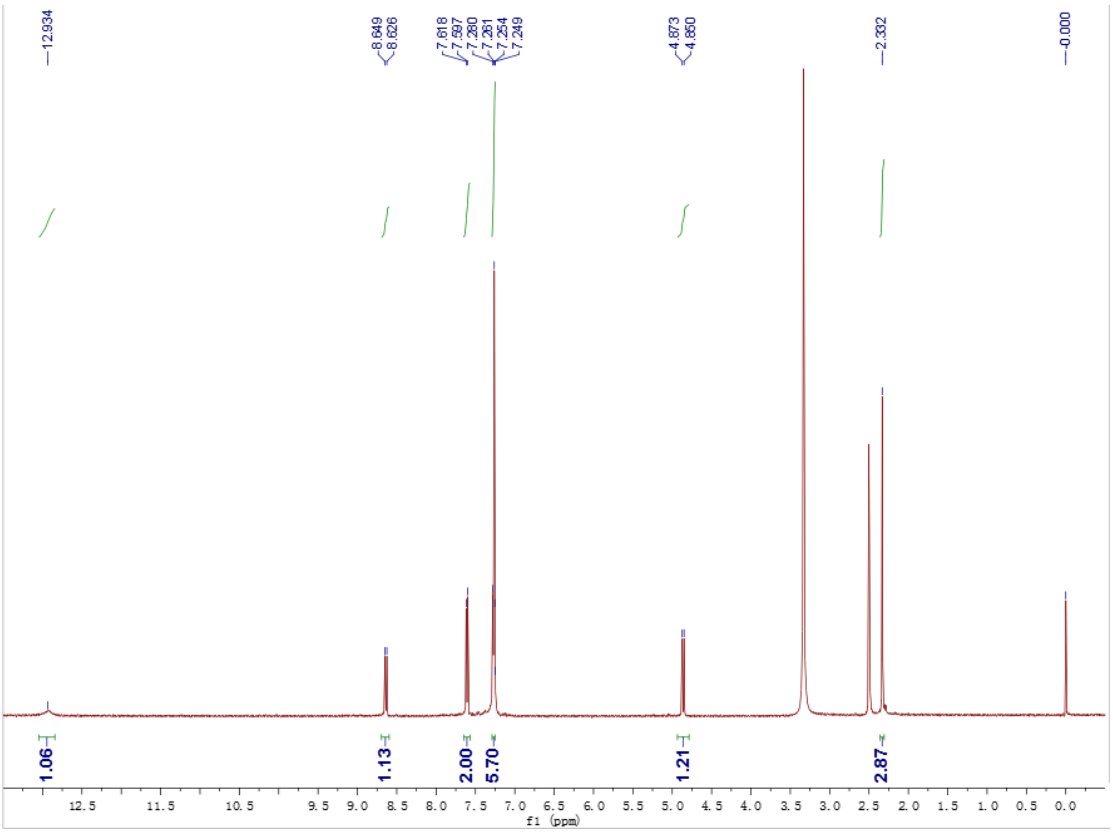
(4d)

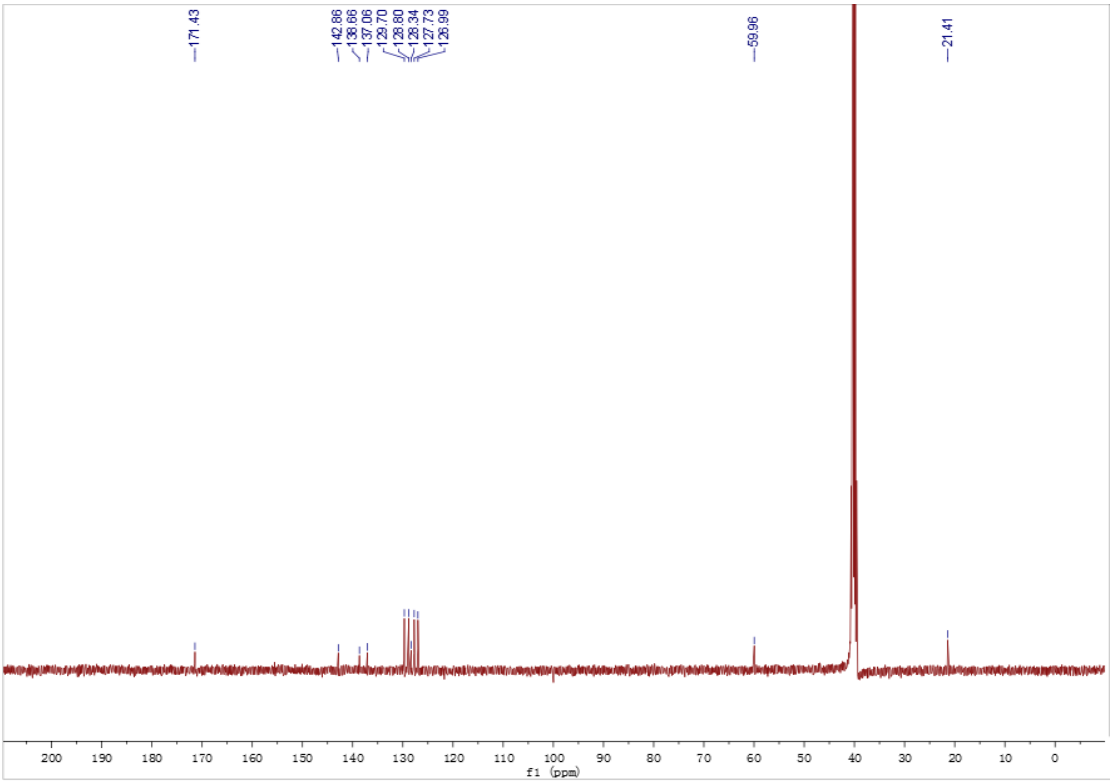

12.538
8.031
8.009
7.655
7.635
7.365
7.343
3.657
3.641
3.635
3.620
3.614
3.598
2.369
1.392
1.383
1.378
1.370
1.362
0.791
0.693
0.677
0.000
0.55
0.99
2.00
1.99
1.20
3.04
1.04
2.02
3.12
3.03
f1 (ppm)

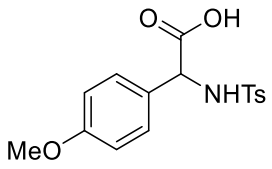

173.71
142.90
138.77
129.82
126.98
54.37
41.38
24.31
23.04
21.48
21.43
f1 (ppm)


O
OH
NHTs

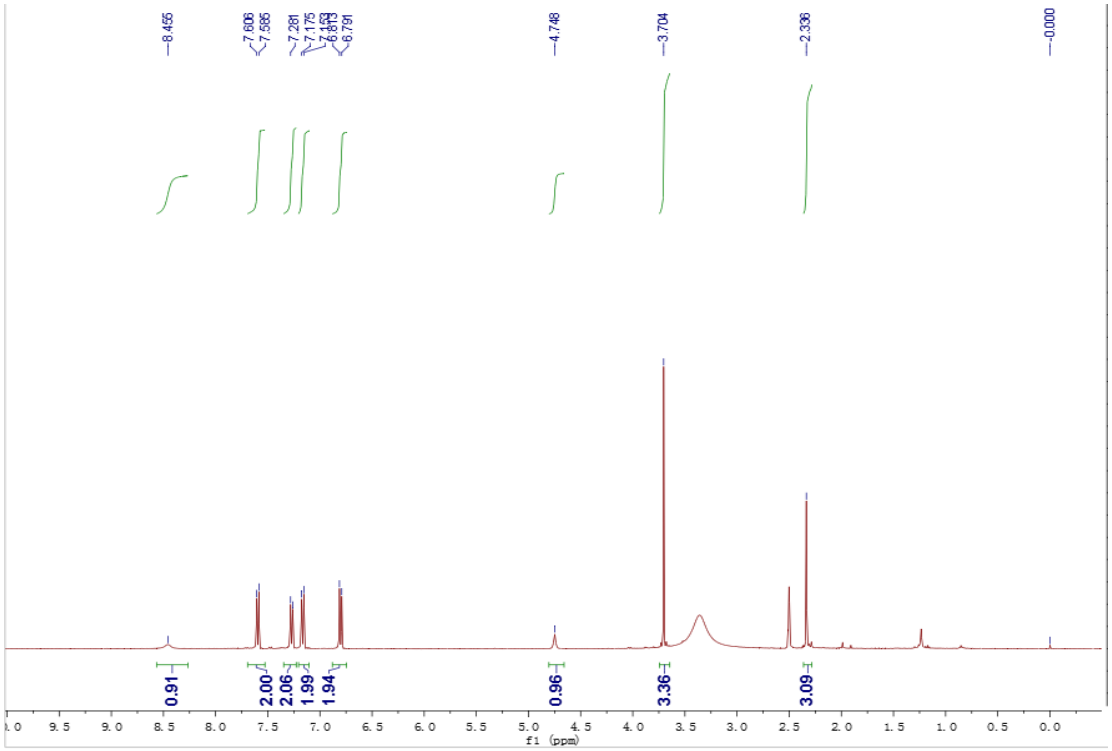
(4e)

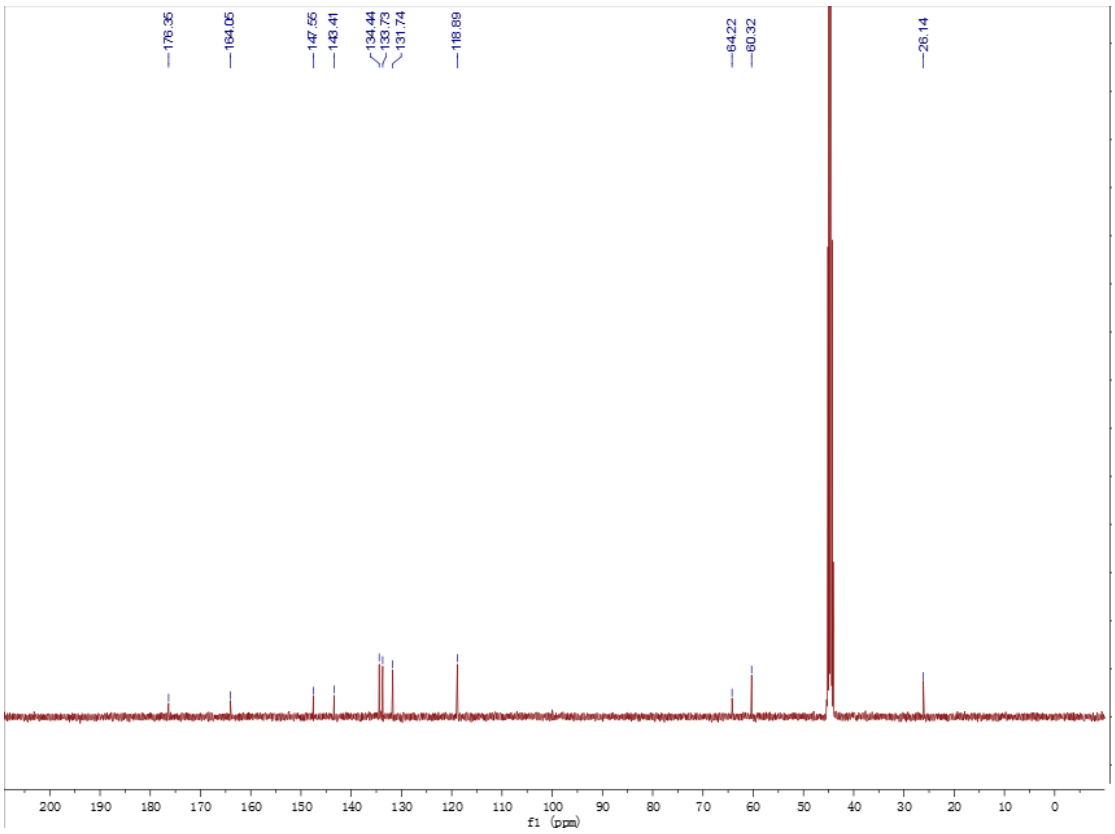

12.934
8.649
8.626
7.618
7.597
7.280
7.261
7.254
7.249
4.873
4.850
2.332
0.000
1.06
1.13
2.00
5.70
1.21
2.87
f1 (ppm)

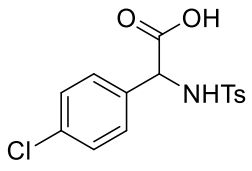

171.43
142.86
138.66
137.06
129.70
128.80
128.34
127.73
126.99
59.96
21.41
f1 (ppm)


O
OH
NHTs
MeO

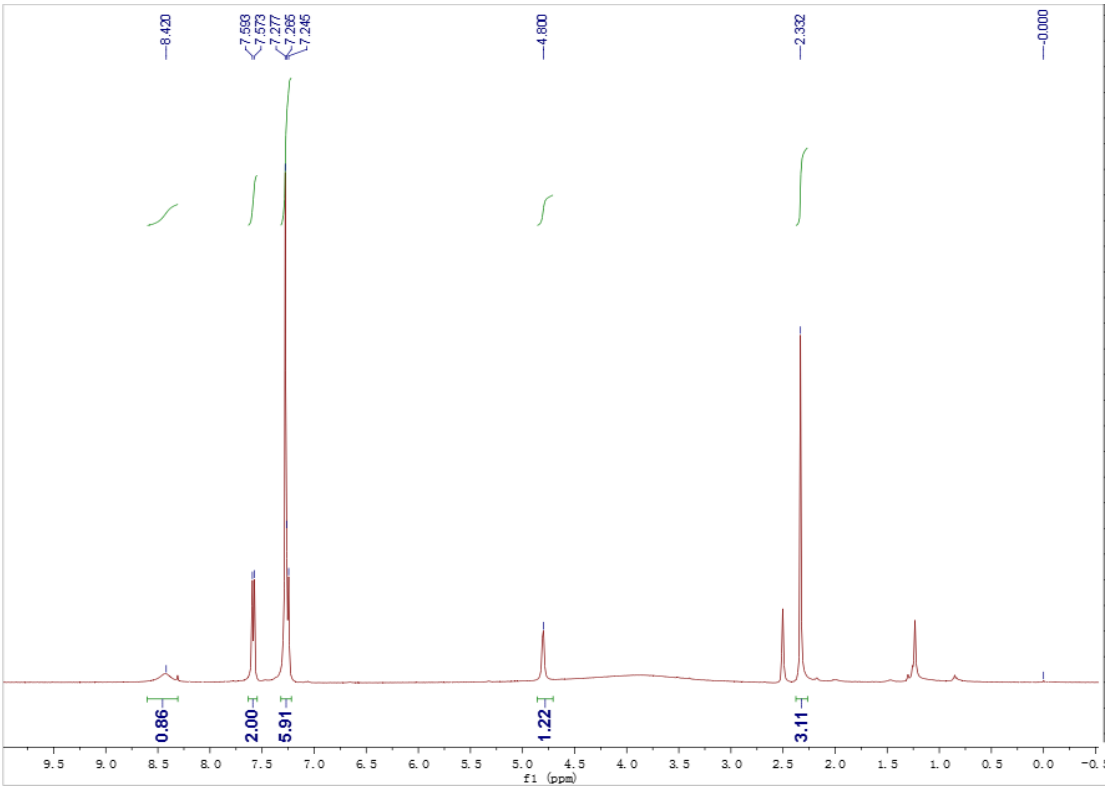
(4f)

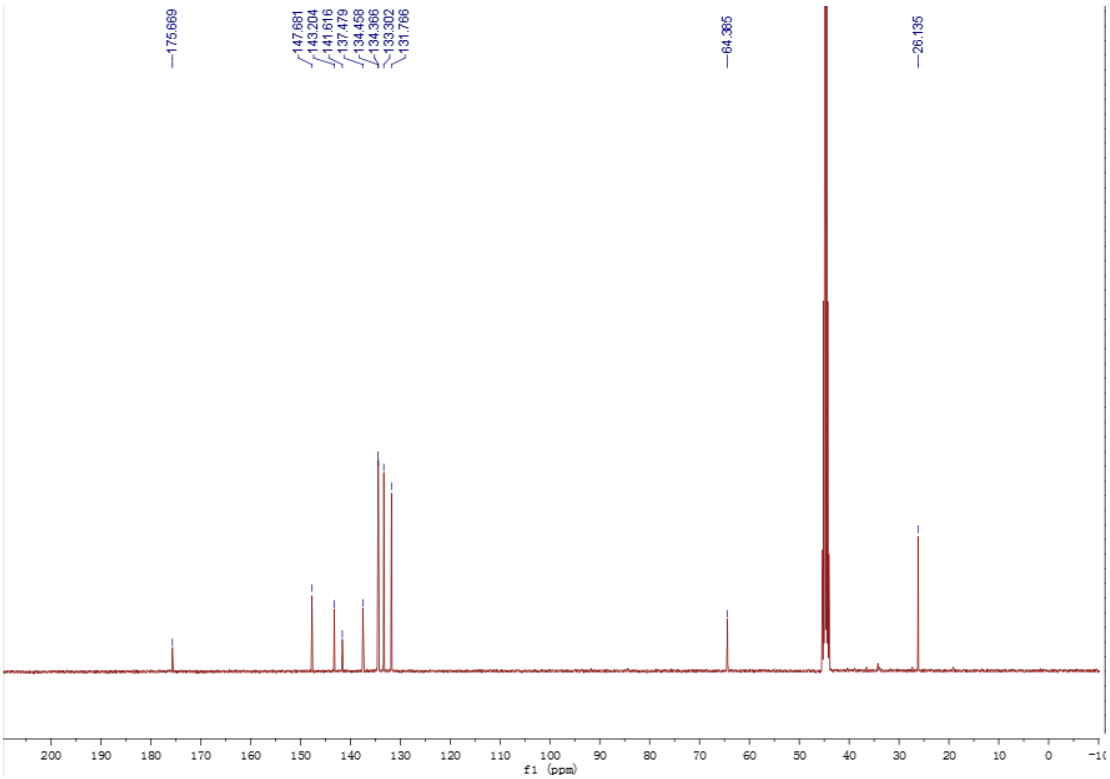

8.455
7.606
7.585
7.281
7.175
6.813
6.791
4.748
3.704
2.336
0.000
0.91
2.00
2.06
1.99
1.94
0.96
3.36
3.09
f1 (ppm)

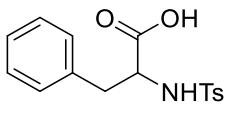

176.36
164.05
147.55
143.41
134.44
133.73
131.74
118.89
64.22
60.32
26.14
f1 (ppm)


O
OH
NHTs
Cl

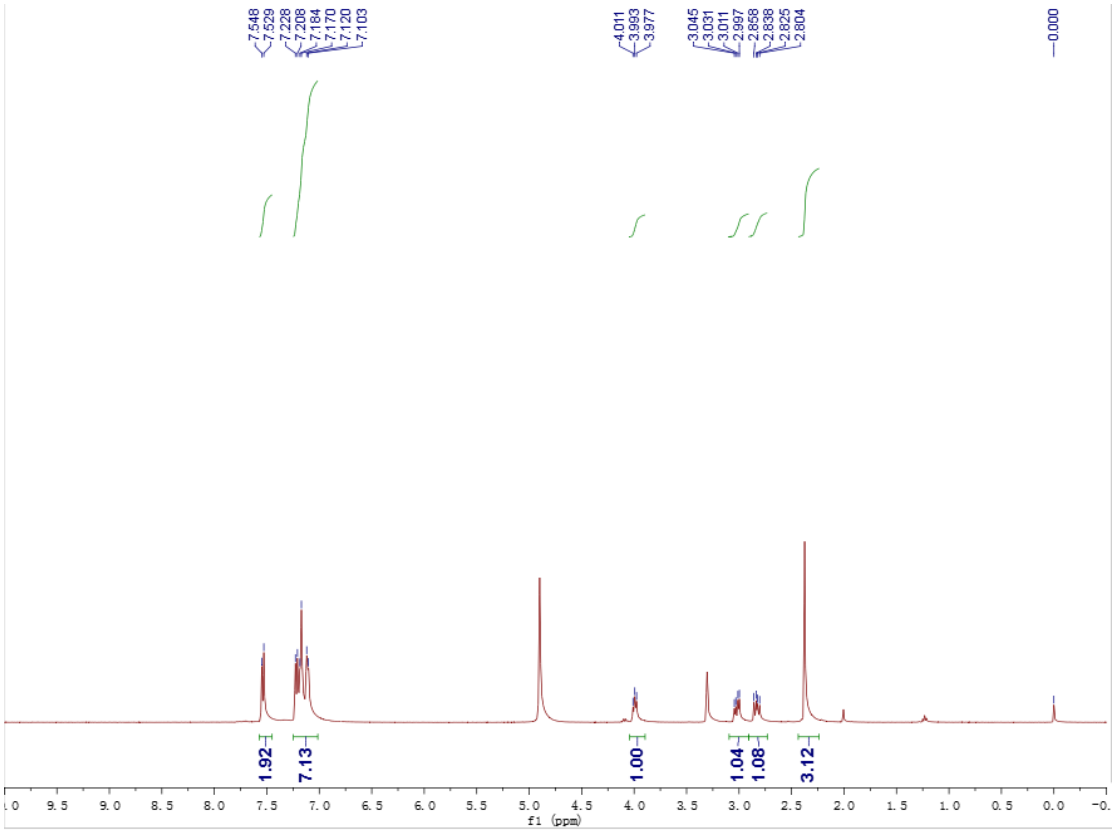
(4g)

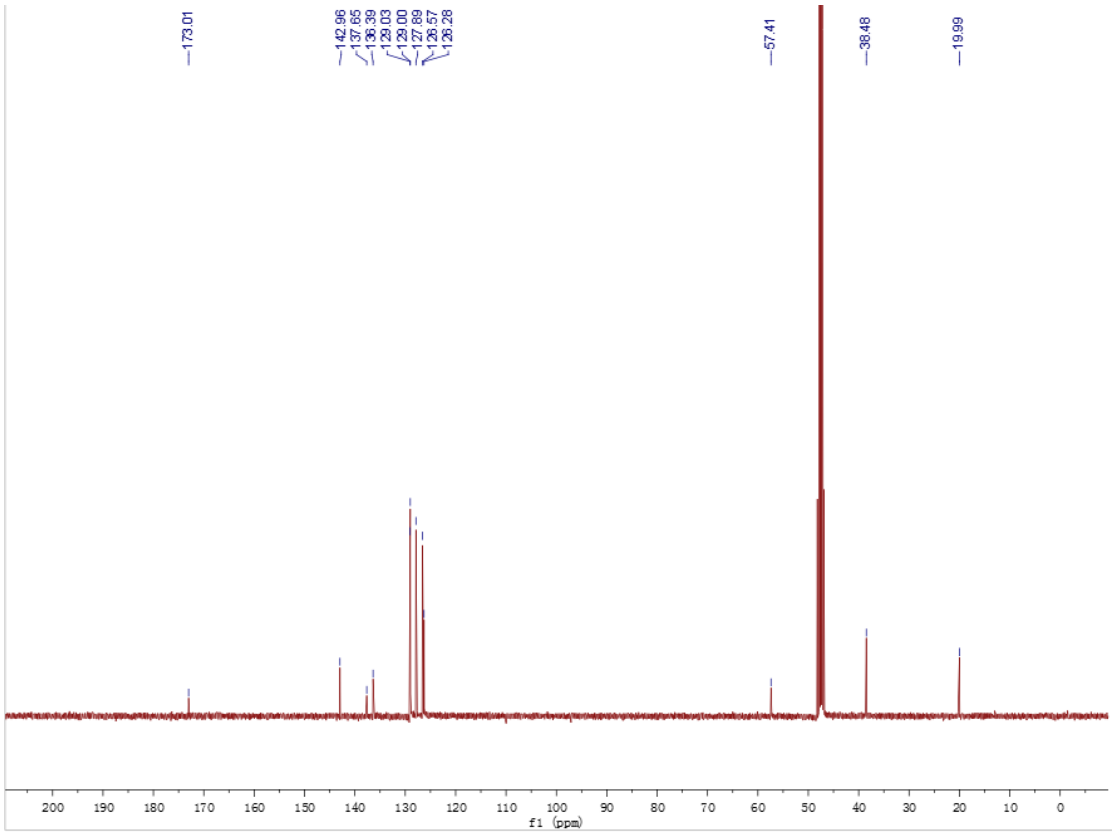

8.420
7.593
7.573
7.277
7.265
7.245
4.800
2.332
0.000
0.86
2.00
5.91
1.22
3.11
f1 (ppm)

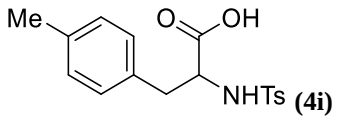

175.669
147.681
143.204
141.616
137.479
134.458
134.366
133.302
131.766
64.385
26.135
f1 (ppm)


O
OH
NHTs

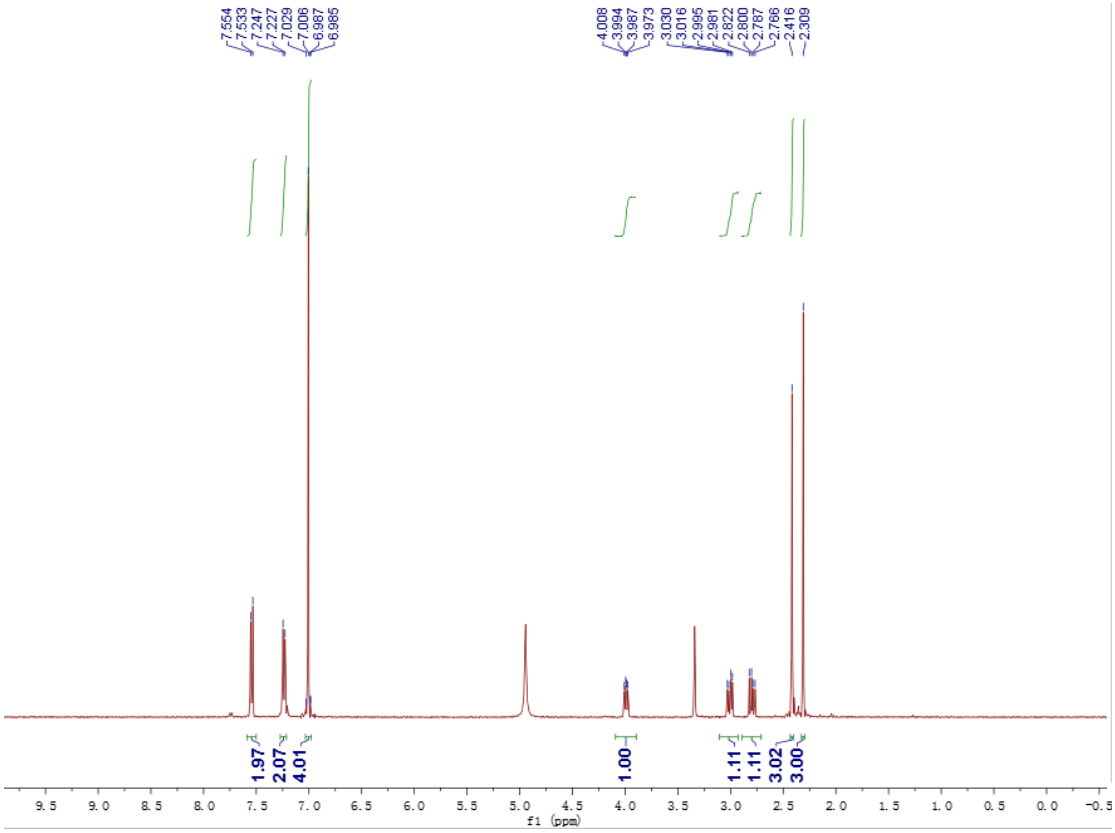
(4h)

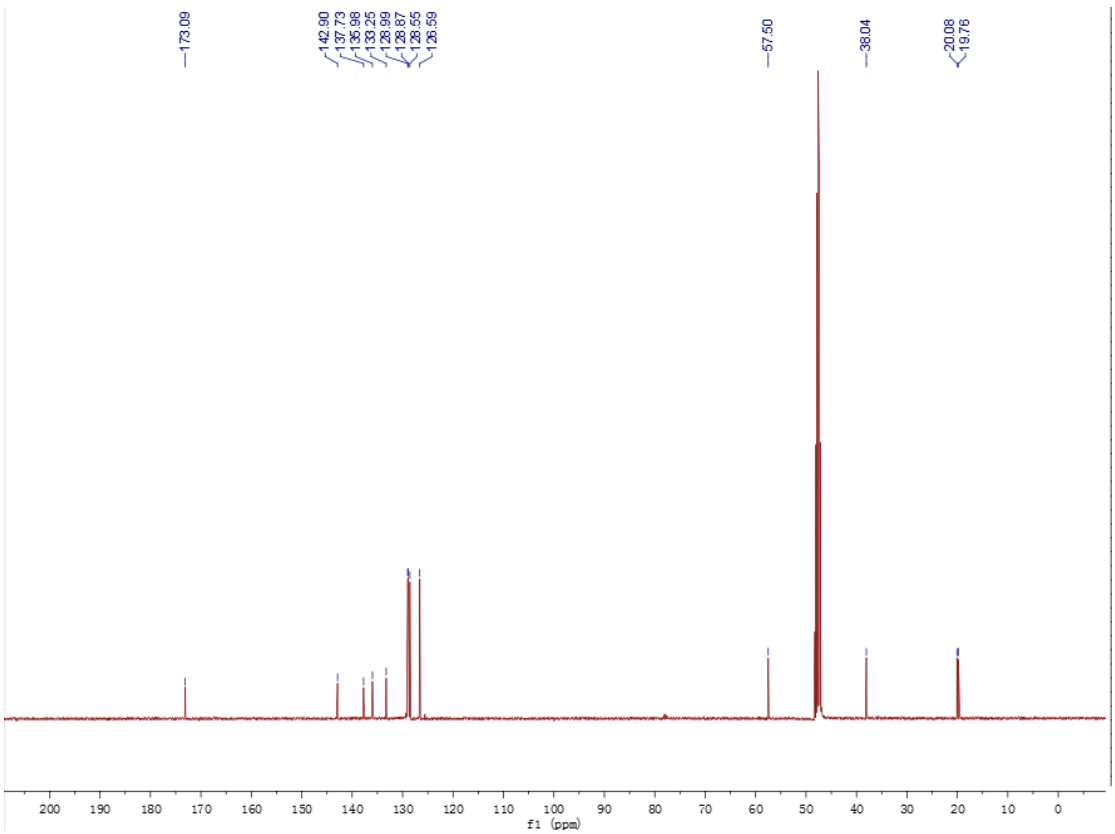

7.548
7.529
7.228
7.208
7.184
7.170
7.120
7.103
4.011
3.993
3.977
3.045
3.031
3.011
2.997
2.858
2.838
2.825
2.804
0.000
1.92
7.13
1.00
1.04
1.08
3.12
f1 (ppm)

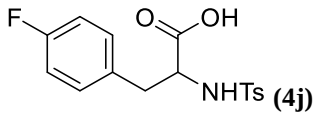

173.01
142.96
137.65
136.39
129.03
129.00
127.89
126.57
126.28
57.41
38.48
19.99
f1 (ppm)


Me
O
OH
NHTs

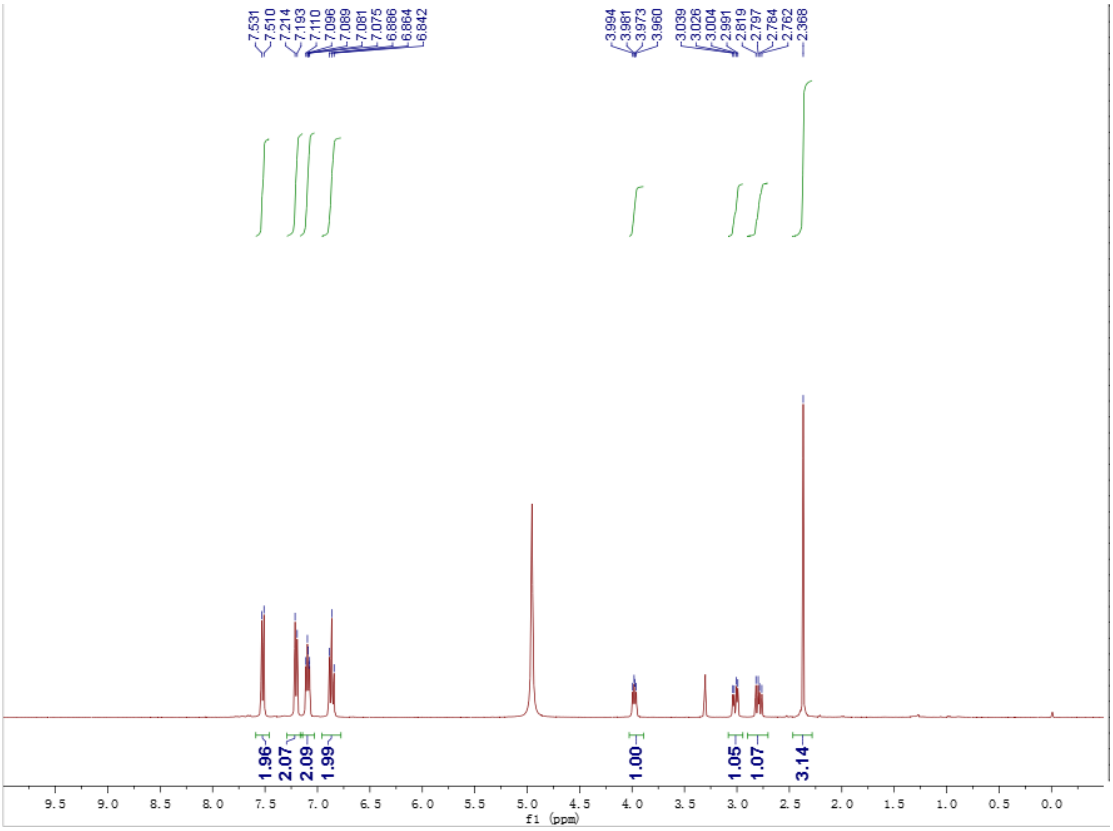
(4i)

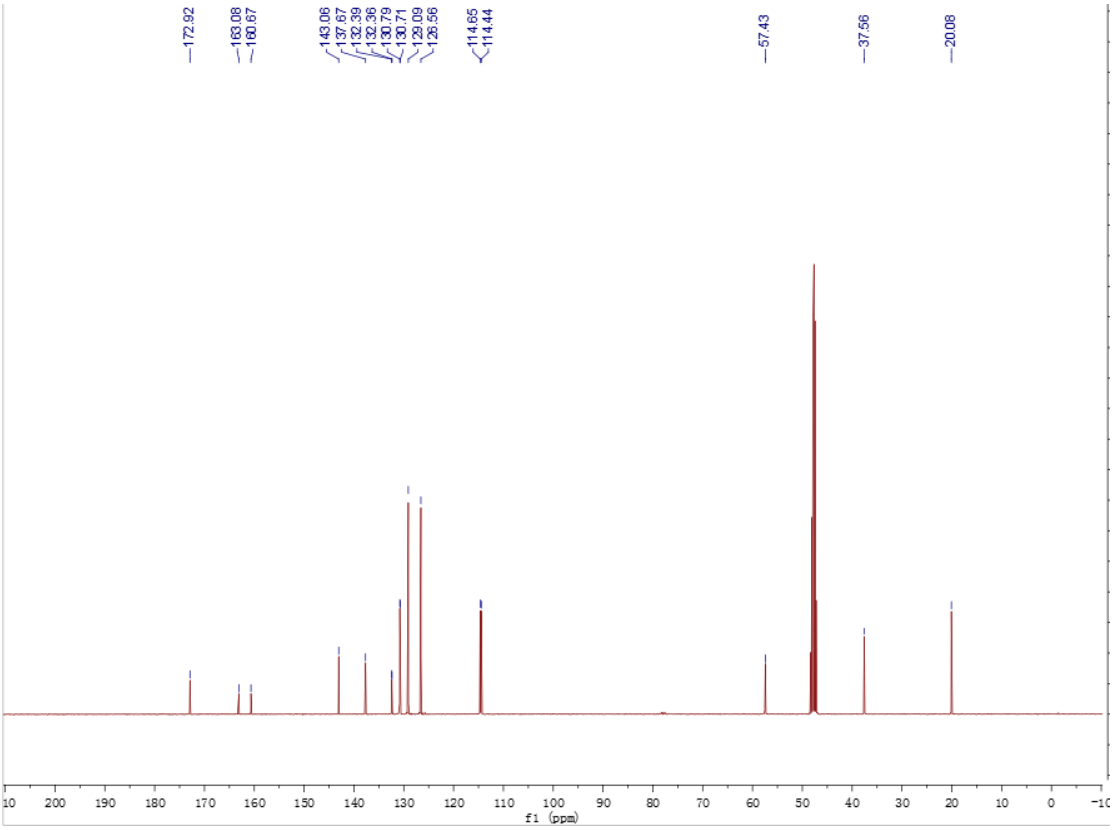

7.554
7.533
7.247
7.227
7.029
7.006
6.987
6.985
4.008
3.994
3.987
3.973
3.030
3.016
2.995
2.981
2.822
2.800
2.787
2.766
2.416
2.309
1.97
2.07
4.01
1.00
1.11
1.11
3.02
3.00
f1 (ppm)

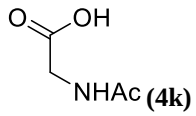

173.09
142.90
137.73
135.98
133.25
128.99
128.87
128.55
126.59
57.50
38.04
20.08
19.76
f1 (ppm)


F
O
OH
NHTs

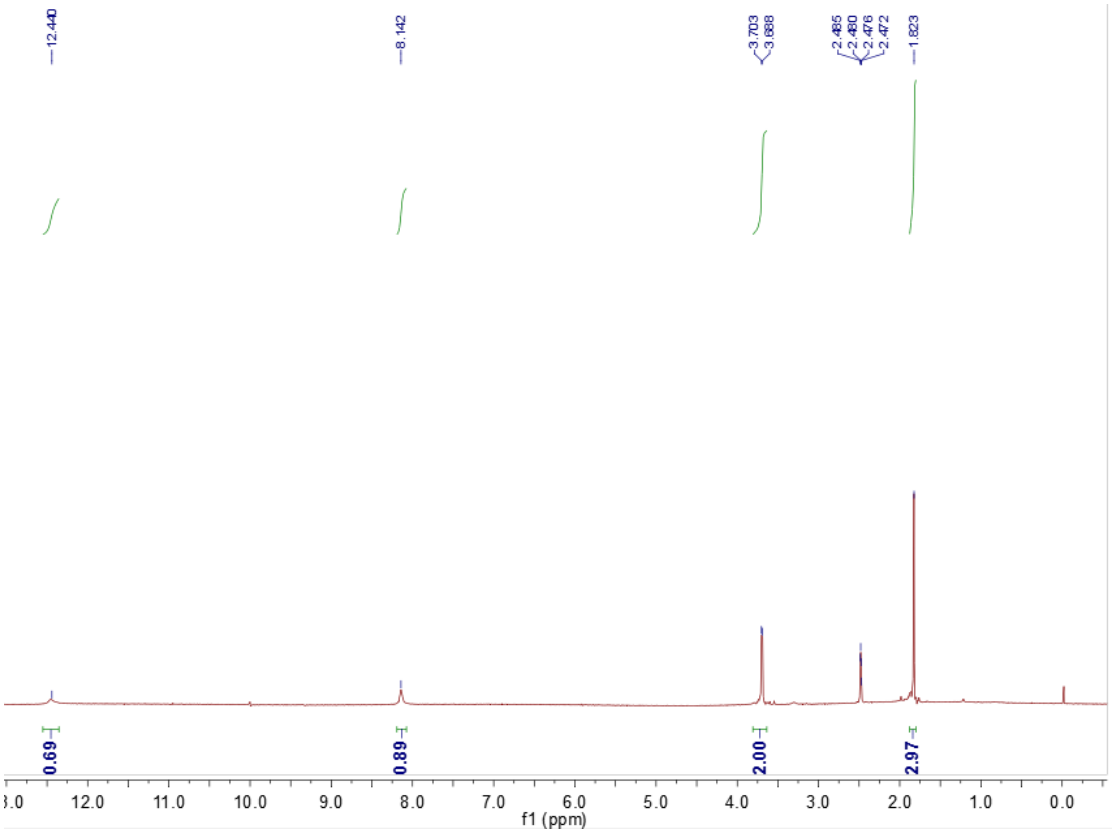
(4j)

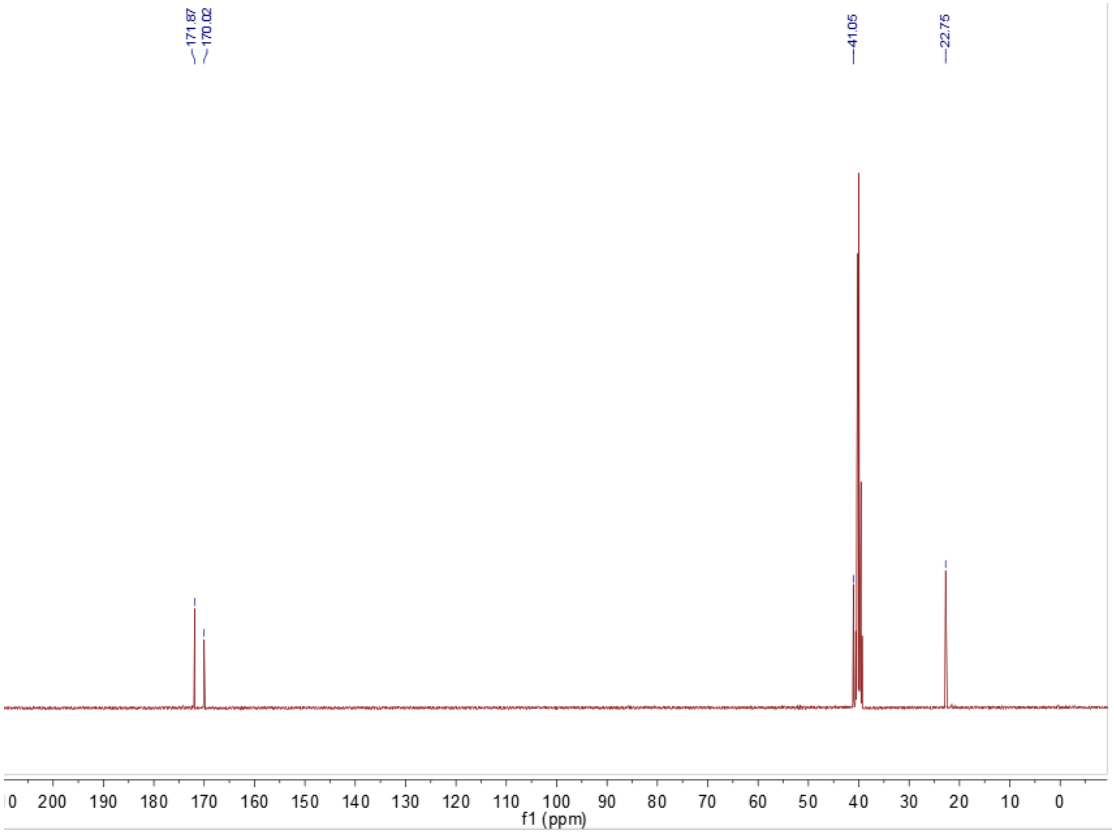

7.531
7.510
7.214
7.193
7.110
7.096
7.089
7.081
7.075
6.886
6.864
6.842
3.994
3.981
3.973
3.960
3.039
3.026
3.004
2.991
2.819
2.797
2.784
2.762
2.368
1.96
2.07
2.09
1.99
1.00
1.05
1.07
3.14
f1 (ppm)

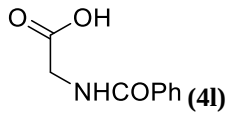

172.92
163.08
160.67
143.06
137.67
132.39
132.36
130.79
130.71
129.09
126.56
114.65
114.44
57.43
37.56
20.08
f1 (ppm)


O
OH
NHAc

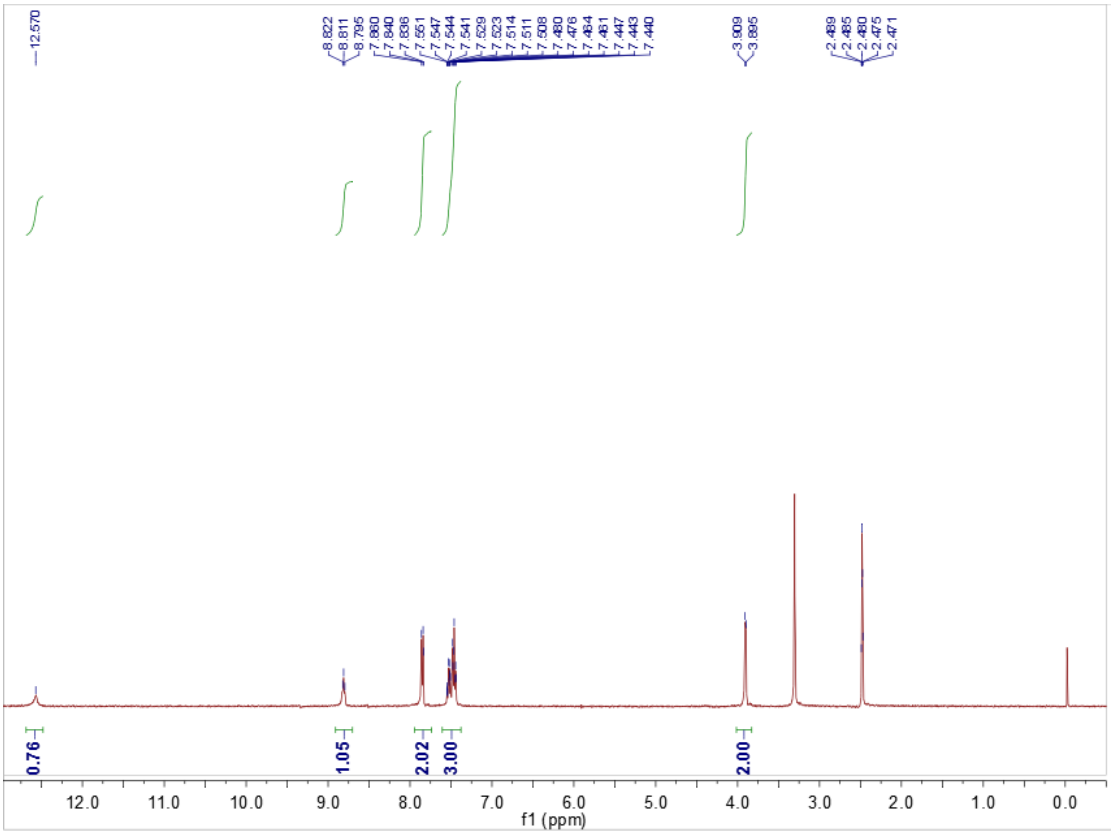
(4k)

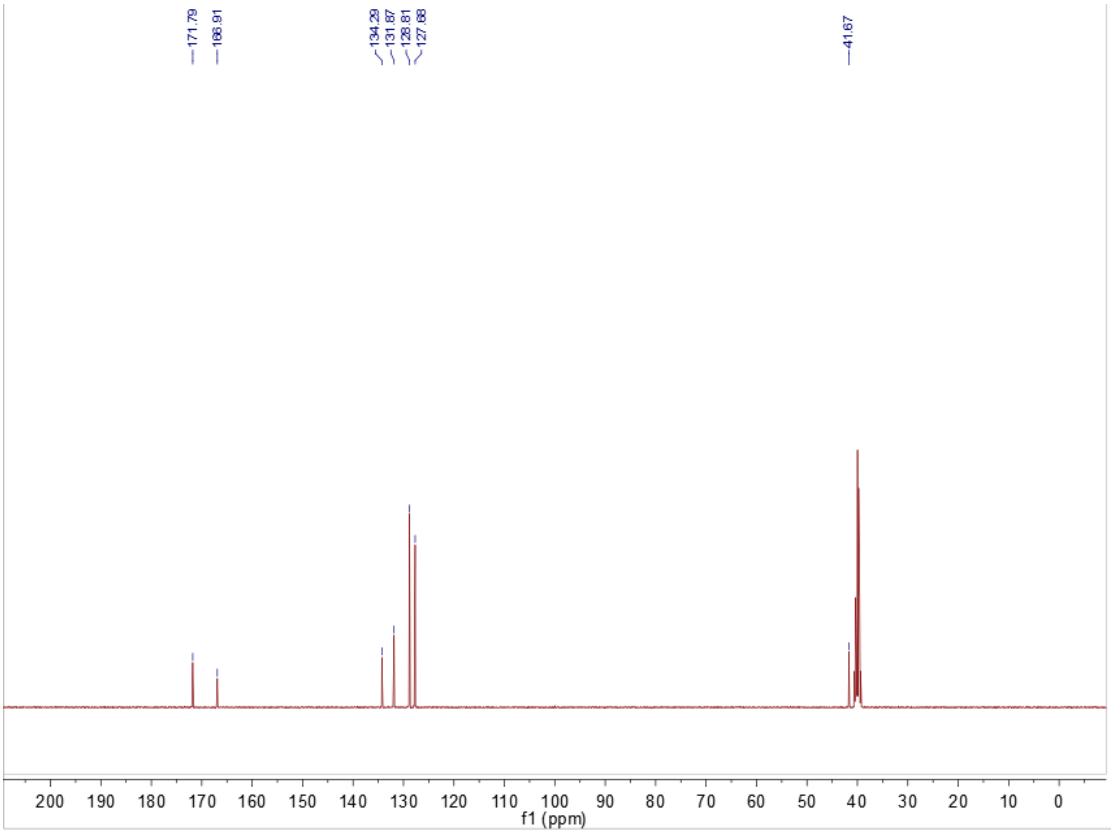

12.440
8.142
3.703
3.688
2.485
2.480
2.476
2.472
1.823
0.69
0.89
2.00
2.97
f1 (ppm)

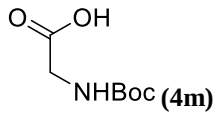

171.87
170.02
41.05
22.75
f1 (ppm)


O
OH
NHCOPh

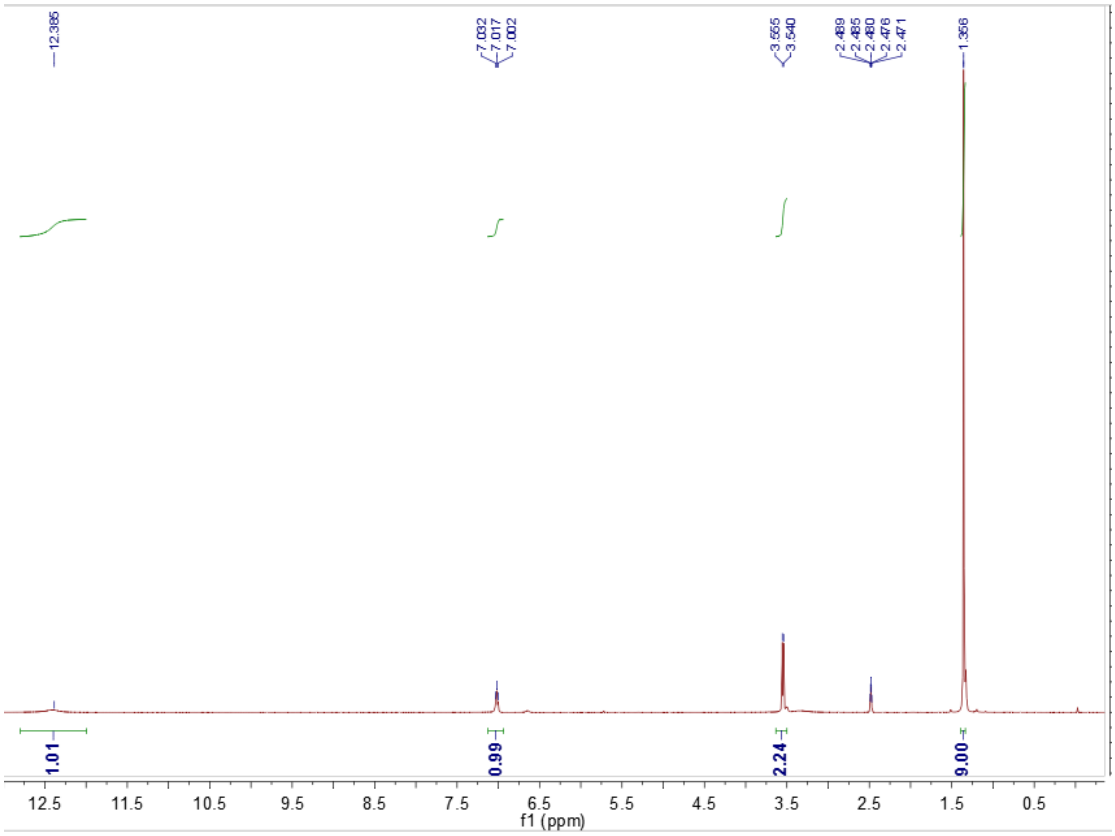
(4l)

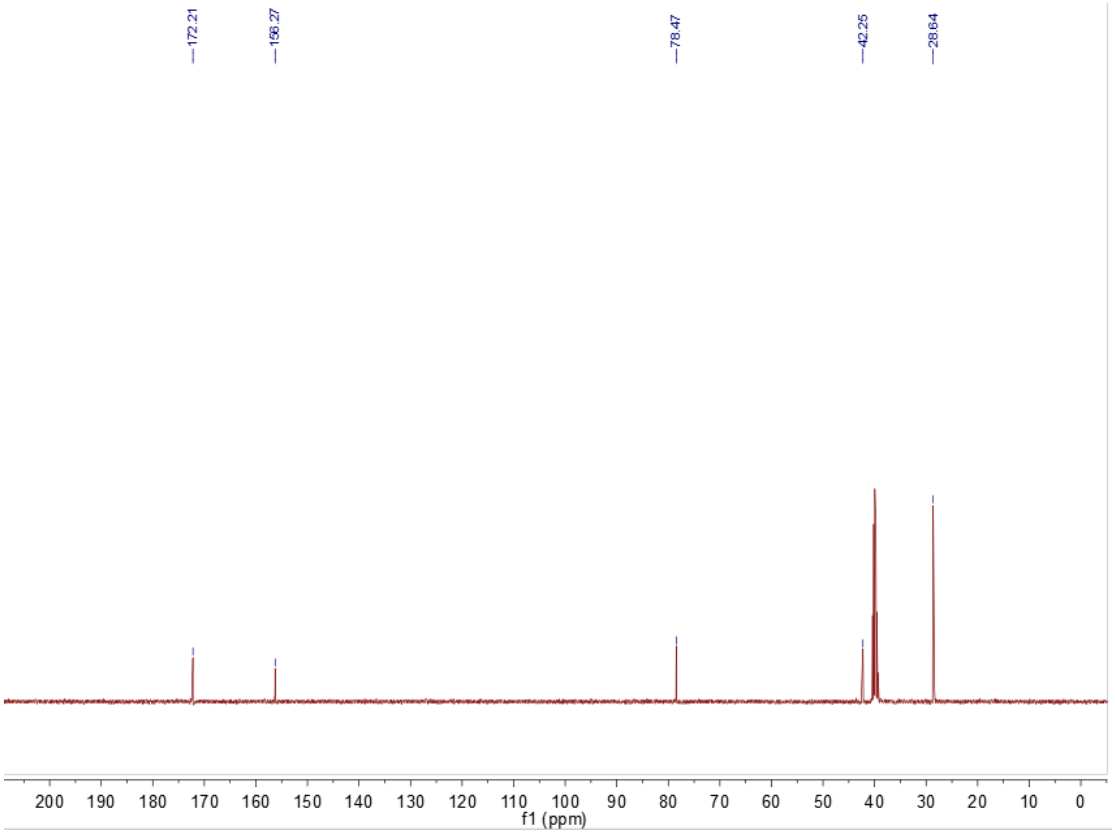

12.570
8.822
8.811
8.795
7.860
7.840
7.836
7.551
7.547
7.544
7.541
7.529
7.523
7.514
7.511
7.508
7.480
7.476
7.464
7.461
7.447
7.443
7.440
3.909
3.895
2.489
2.485
2.480
2.475
2.471
0.76
1.05
2.02
3.00
2.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

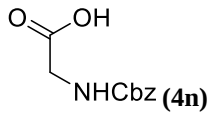

171.79
166.91
134.29
131.87
128.81
127.88
41.67
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
OH
NHBoc

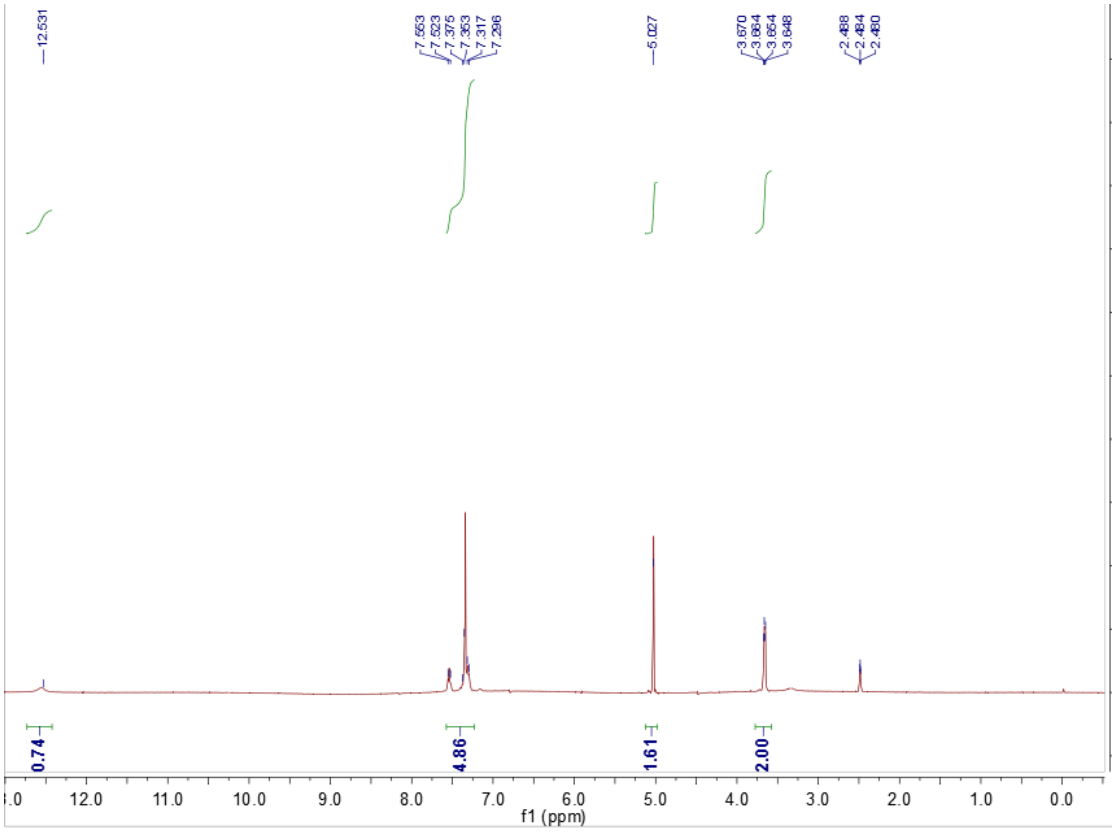
(4m)

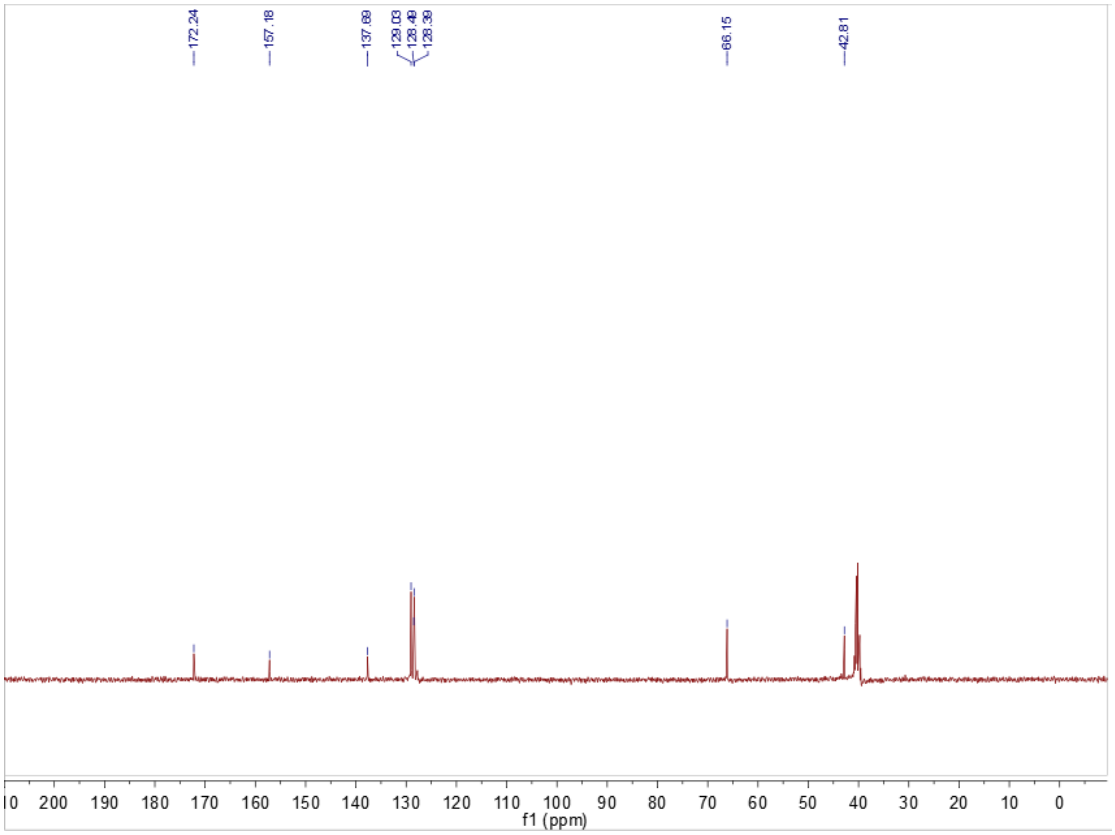

12.385
7.032
7.017
7.002
3.555
3.540
2.489
2.485
2.480
2.476
2.471
1.356
1.01
0.99
2.24
9.00
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

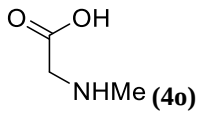

172.21
156.27
78.47
42.25
28.64
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
OH
NHCbz

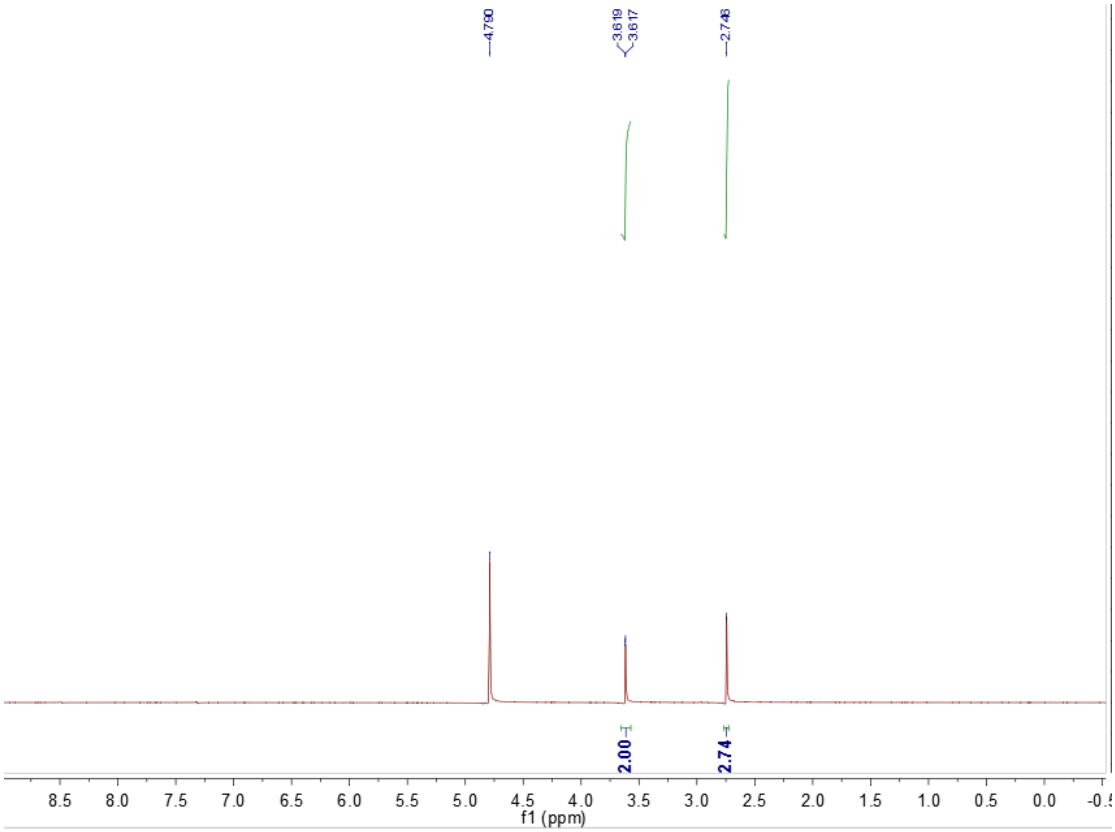
(4n)

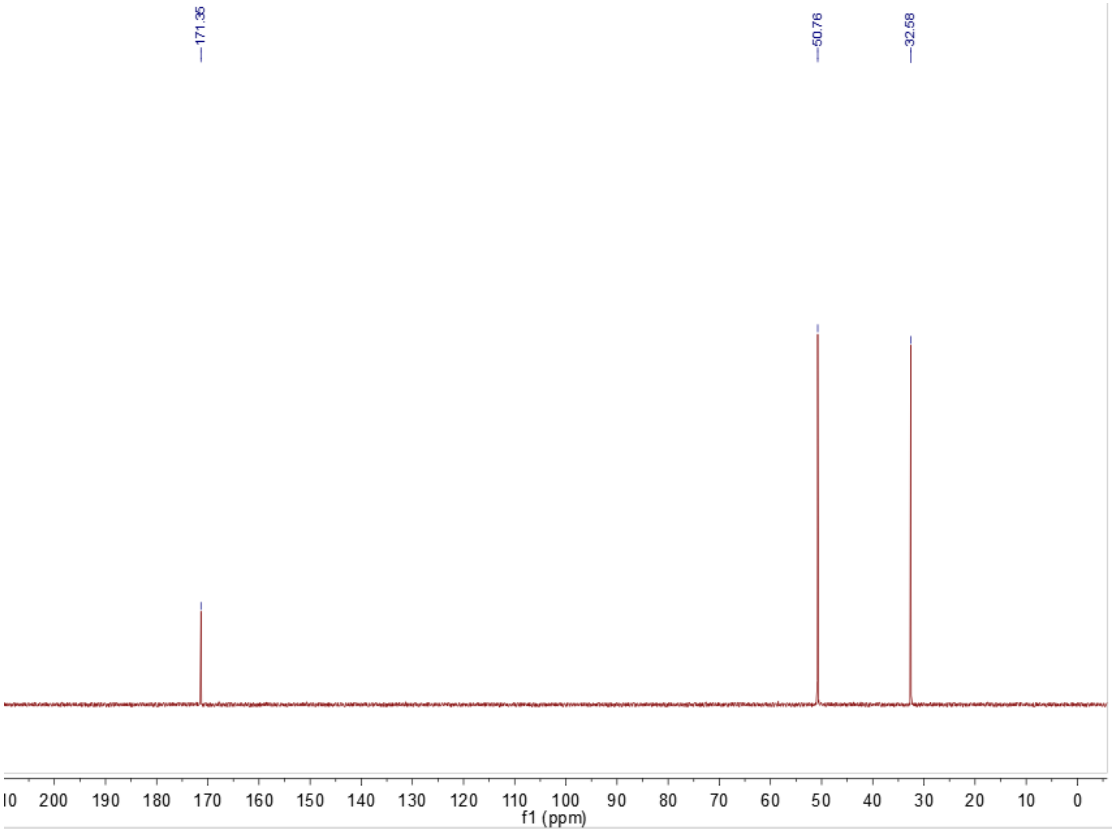

12.531
7.563
7.523
7.375
7.353
7.317
7.296
5.027
3.670
3.664
3.654
3.648
2.488
2.484
2.480
0.74
4.86
1.61
2.00
f1 (ppm)

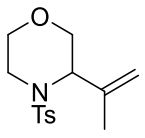

172.24
157.18
137.69
129.03
128.49
128.39
66.15
42.81
f1 (ppm)


O
OH
NHMe

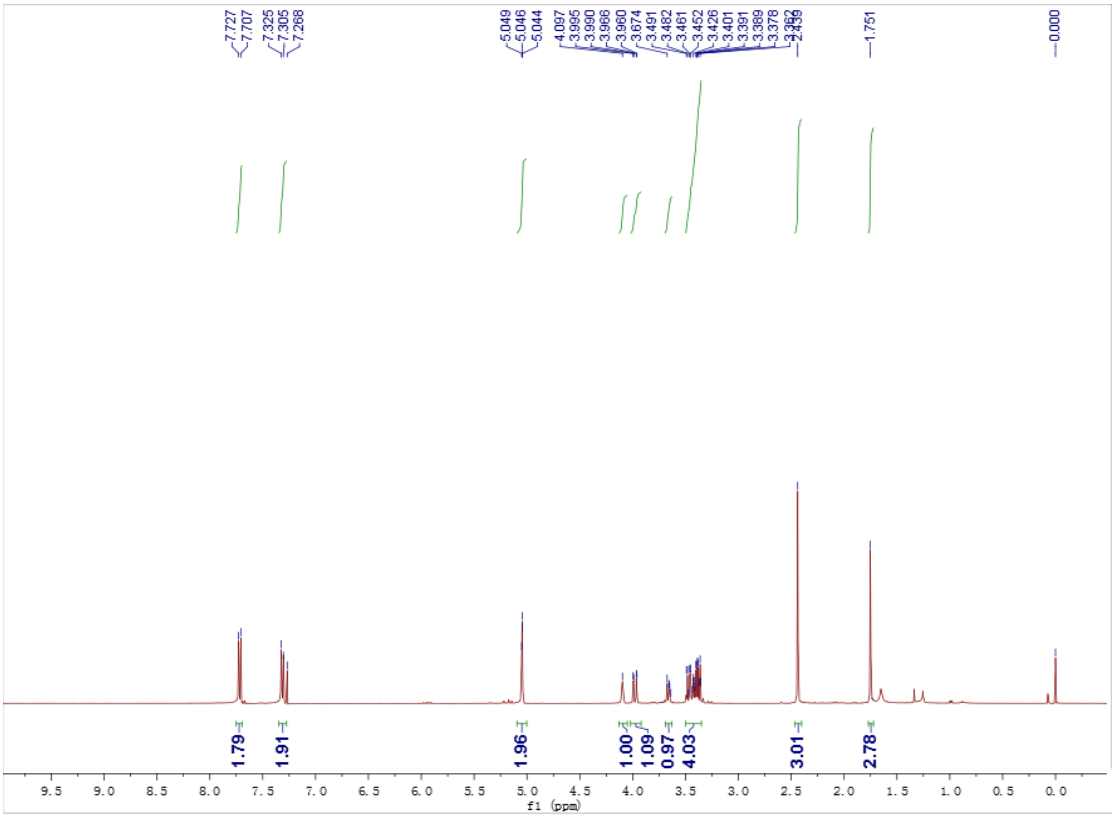
(4o)

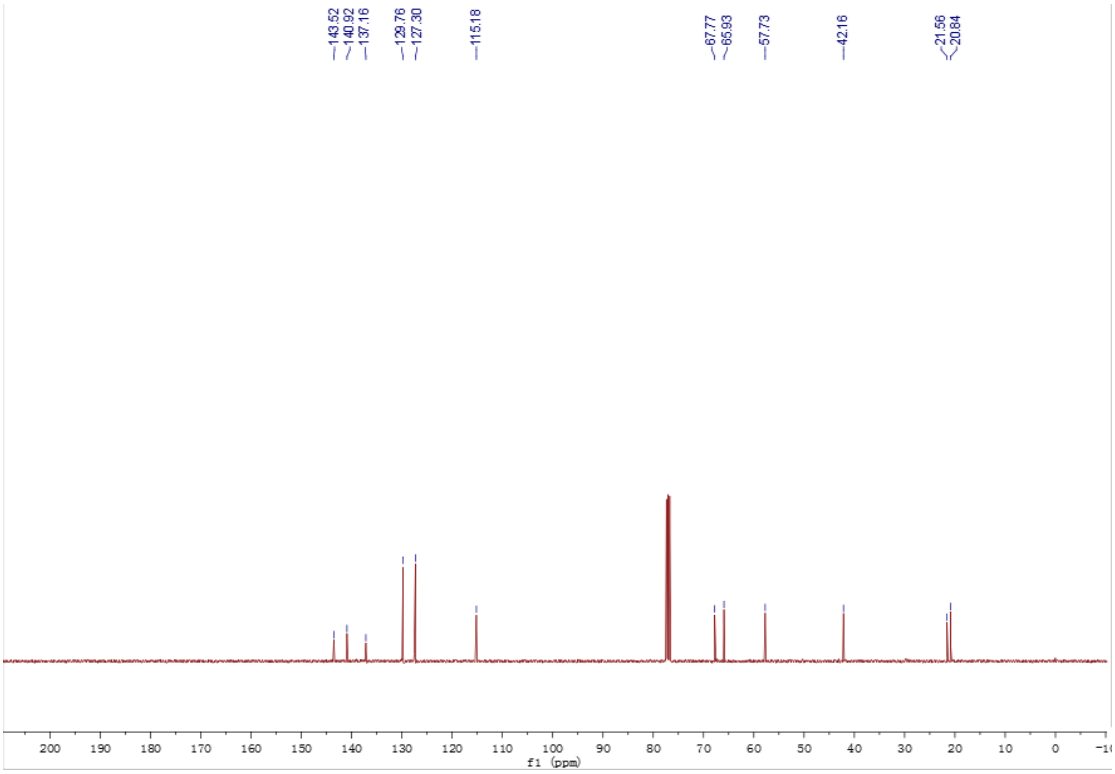

4.790
3.619
3.617
2.748
2.00
2.74
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

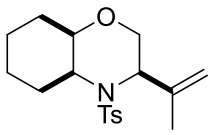

171.35
50.76
32.58
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
N
Ts

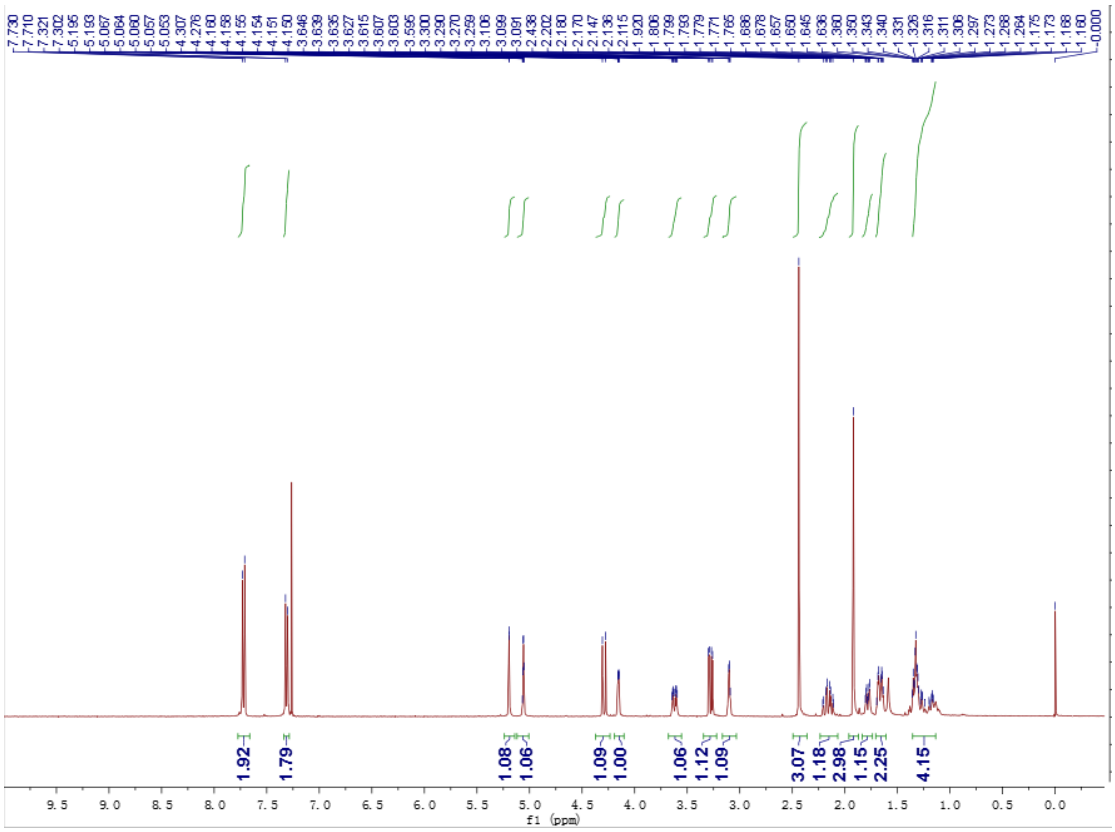
(3aa)

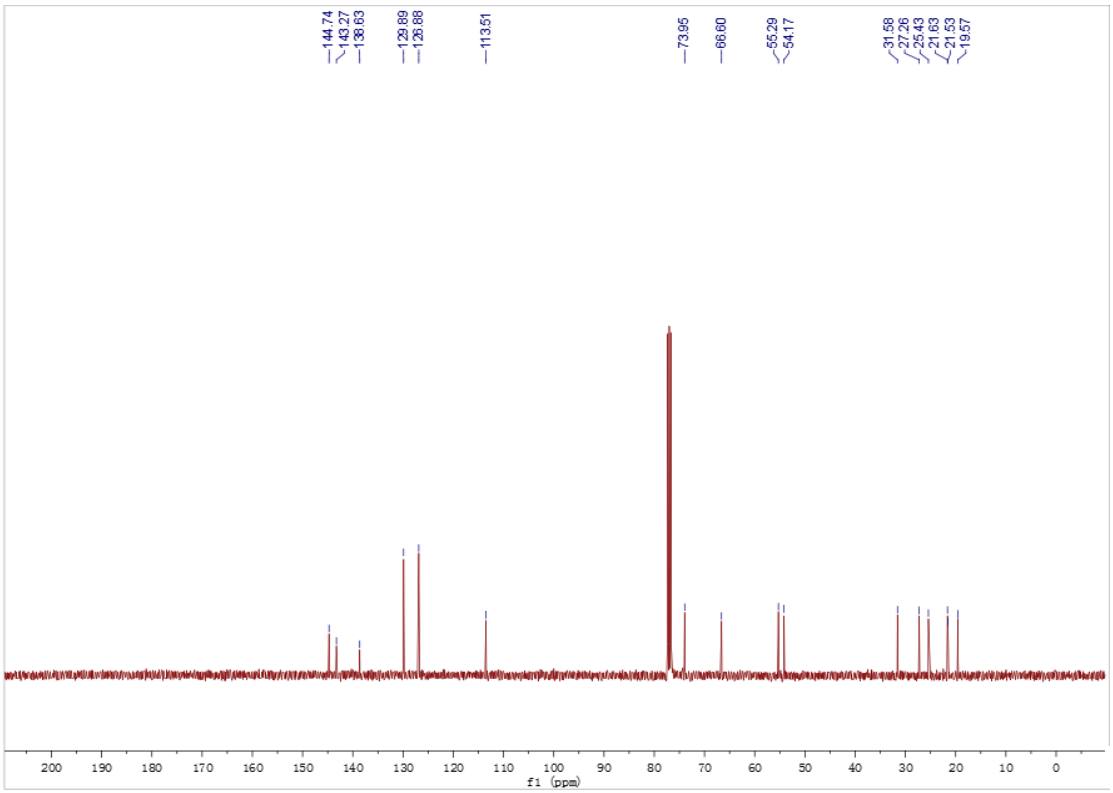

7.727
7.707
7.325
7.305
7.268
5.049
5.046
5.044
4.097
3.995
3.990
3.966
3.960
3.674
3.491
3.482
3.461
3.452
3.426
3.401
3.391
3.389
3.378
2.439
1.751
0.000
1.79
1.91
1.96
1.00
1.09
0.97
4.03
3.01
2.78
f1 (ppm)

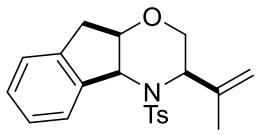

143.52
140.92
137.16
129.76
127.30
115.18
67.77
65.93
57.73
42.16
21.56
20.84
f1 (ppm)


O
N
Ts

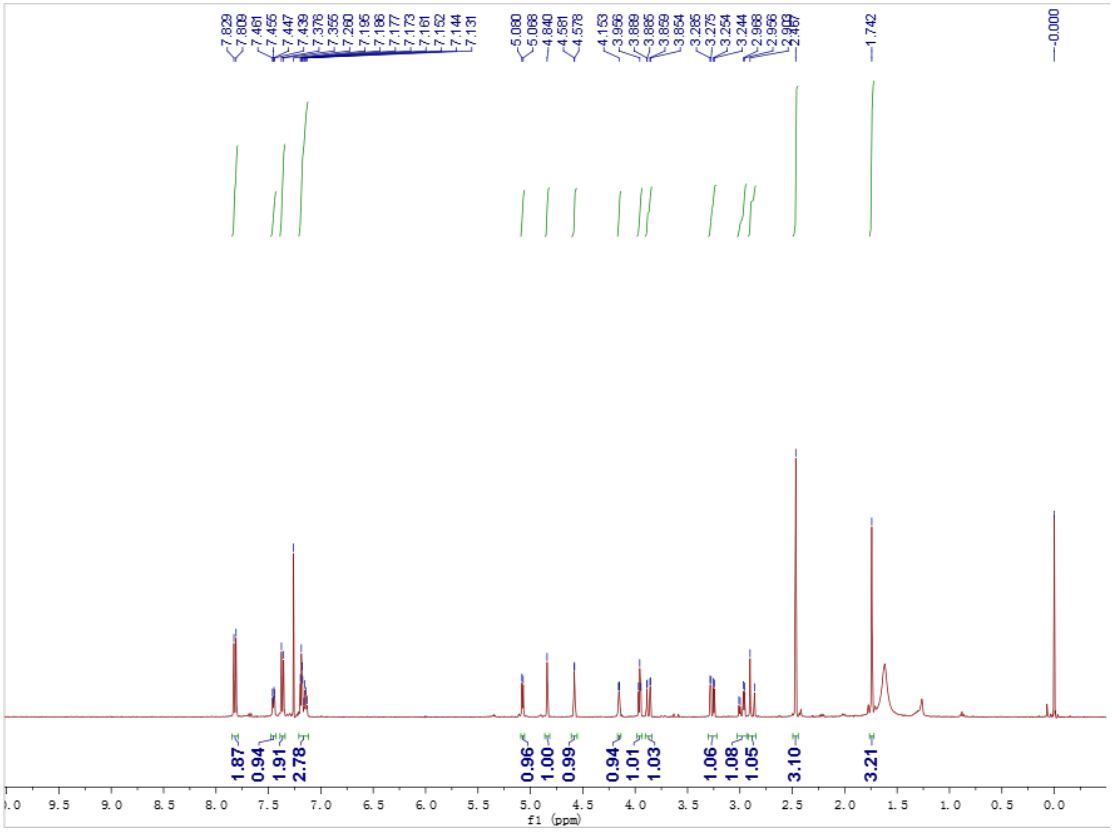
(3ba)

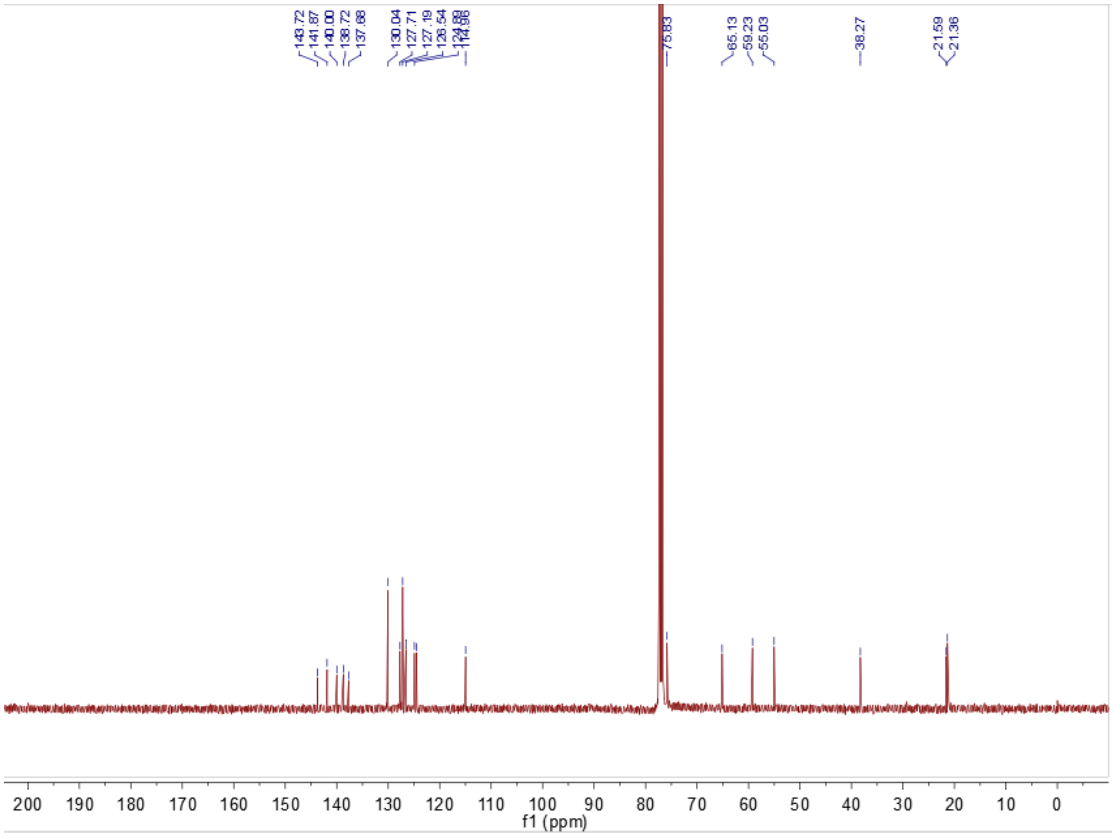

1.92
1.79
1.08
1.06
1.09
1.00
1.06
1.12
1.09
3.07
1.18
2.98
1.15
2.25
4.15
f1 (ppm)

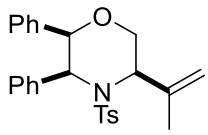

144.74
143.27
138.63
129.89
126.88
113.51
73.95
66.60
55.29
54.17
31.58
27.26
25.43
21.63
21.53
19.57
f1 (ppm)


O
N
Ts

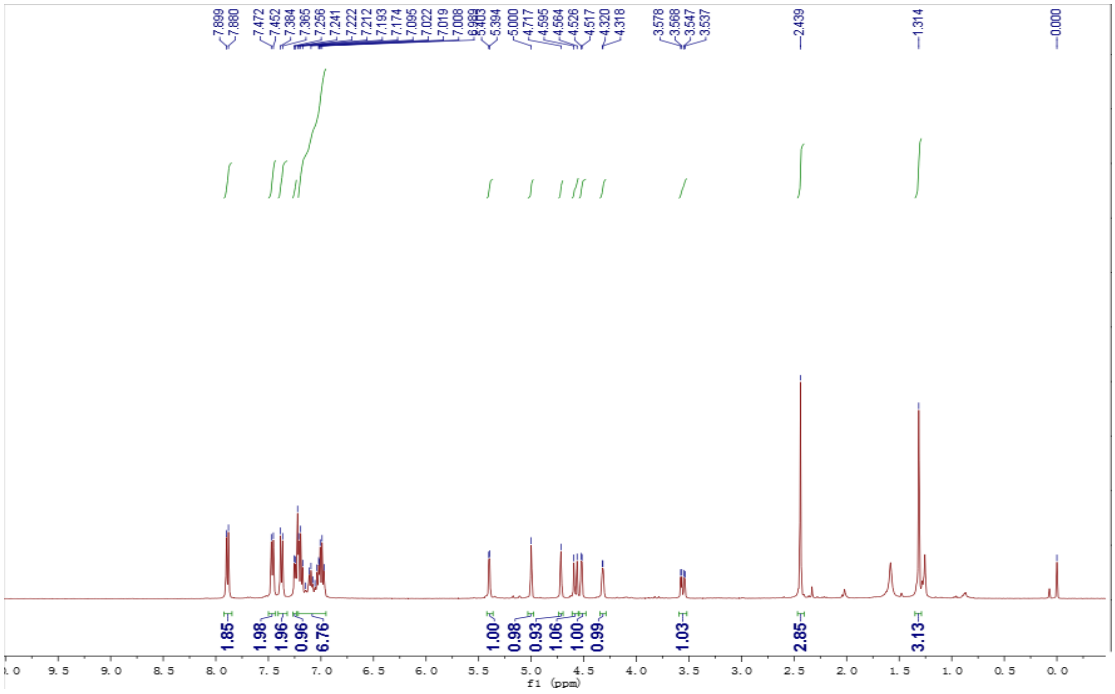
(3ca)

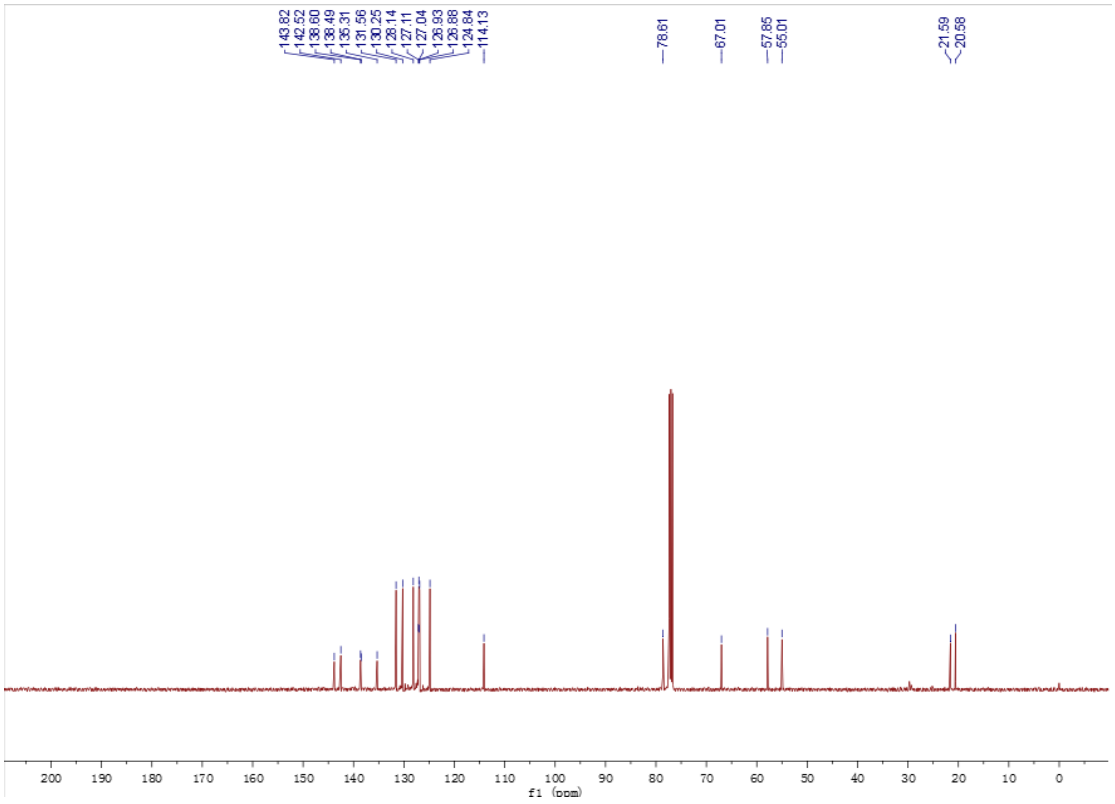

7.829
7.809
7.461
7.455
7.447
7.439
7.376
7.355
7.280
7.195
7.186
7.177
7.173
7.161
7.152
7.144
7.131
5.080
5.068
4.840
4.581
4.578
4.153
3.966
3.889
3.885
3.869
3.854
3.285
3.275
3.254
3.244
2.968
2.956
2.947
1.742
0.000
1.87
0.94
1.91
2.78
0.96
1.00
0.99
0.94
1.01
1.03
1.06
1.08
1.05
3.10
3.21
f1 (ppm)

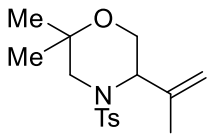

143.72
141.87
140.00
138.72
137.88
130.04
127.71
127.19
126.54
124.89
114.96
75.83
65.13
59.23
55.03
38.27
21.59
21.36
f1 (ppm)


Ph
O
Ph
N
Ts

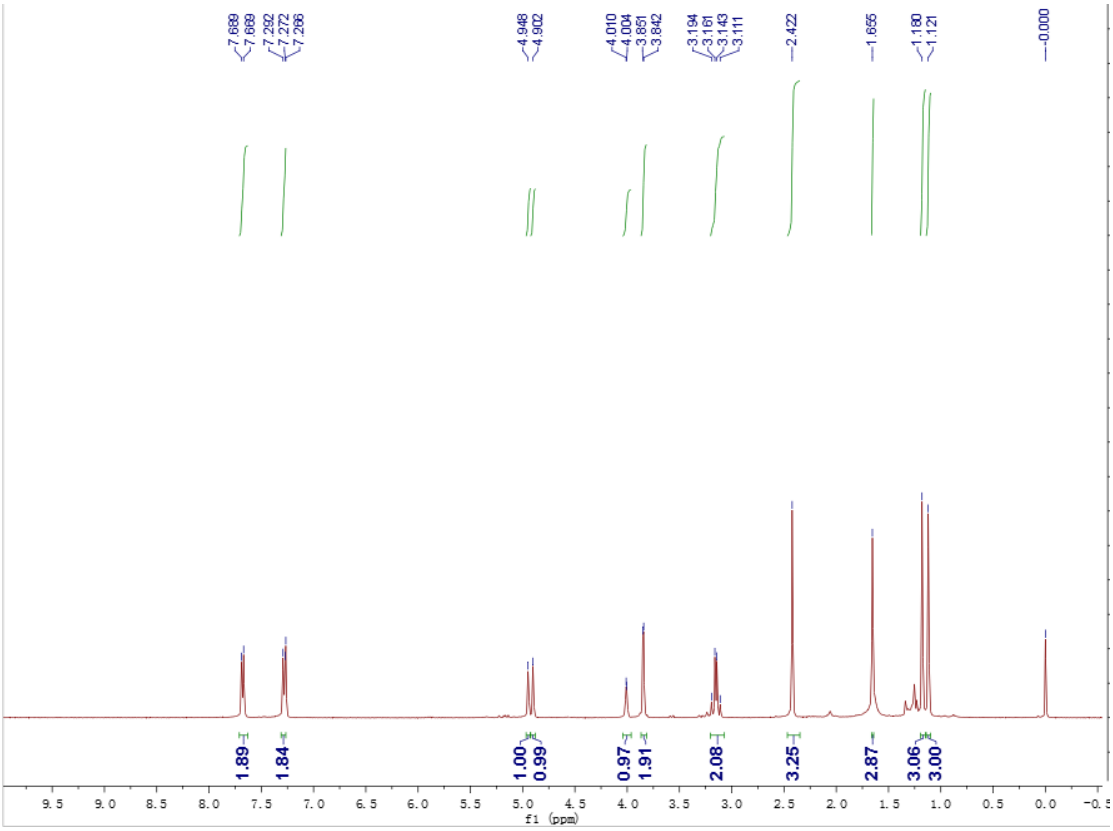
(3da)

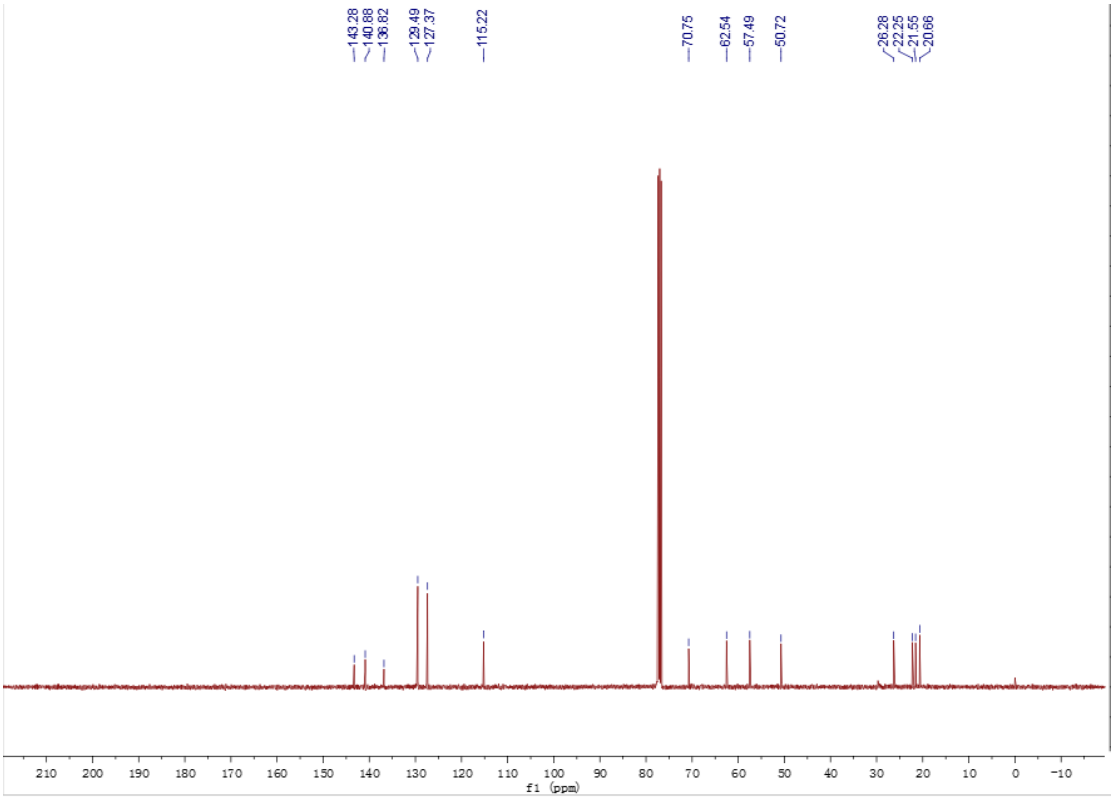

7.899
7.880
7.472
7.452
7.384
7.365
7.256
7.241
7.222
7.212
7.193
7.174
7.095
7.022
7.019
7.008
5.394
5.000
4.717
4.595
4.564
4.526
4.517
4.320
4.318
3.578
3.568
3.547
3.537
2.439
1.314
0.000
1.85
1.98
1.96
0.96
6.76
1.00
0.98
0.93
1.06
1.00
0.99
1.03
2.85
3.13
f1 (ppm)

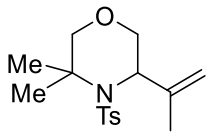

143.82
142.52
138.60
138.49
135.31
131.56
130.25
128.14
127.11
127.04
126.93
126.88
124.84
114.13
78.61
67.01
57.85
55.01
21.59
20.58
f1 (ppm)


Me
Me
O
N
Ts

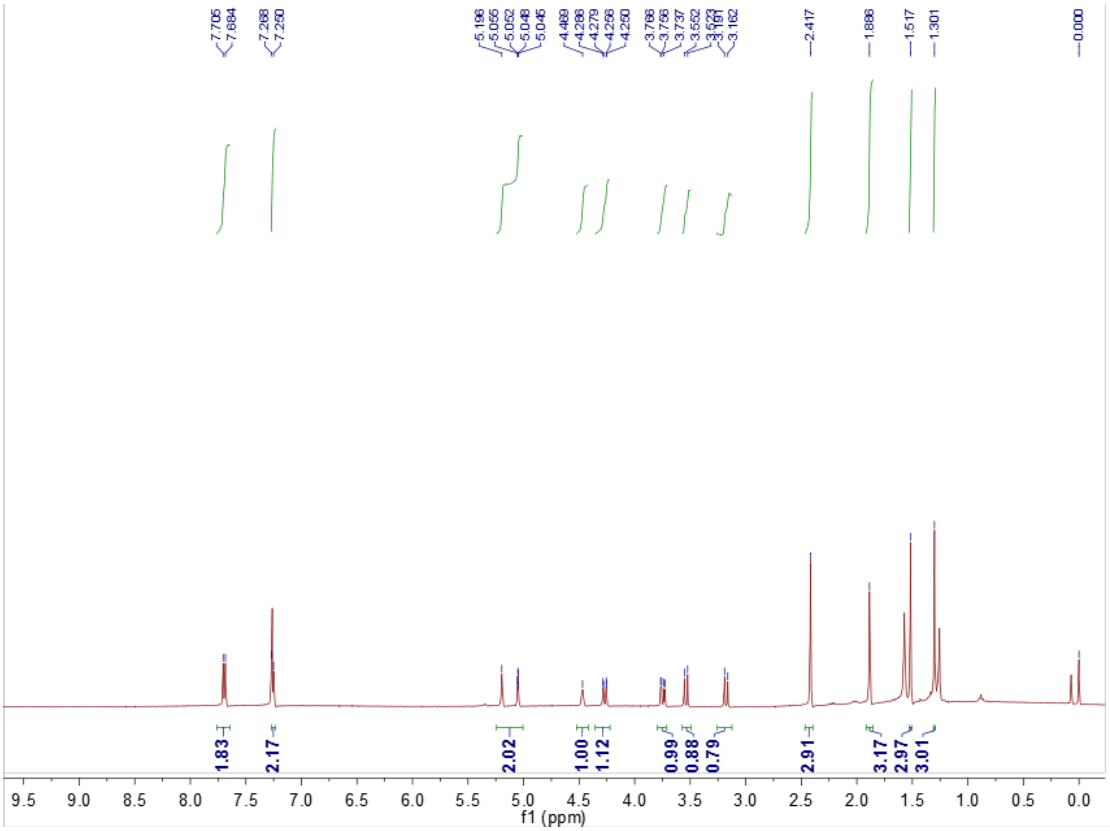
(3ea)


7.689
7.669
7.292
7.272
7.266
4.948
4.902
4.010
4.004
3.851
3.842
3.194
3.161
3.143
3.111
2.422
1.655
1.180
1.121
0.000
1.89
1.84
1.00
0.99
0.97
1.91
2.08
3.25
2.87
3.06
3.00
f1 (ppm)

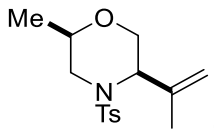

143.28
140.88
136.82
129.49
127.37
115.22
70.75
62.54
57.49
50.72
26.28
22.25
21.55
20.66
f1 (ppm)


O
Me
Me
N
Ts

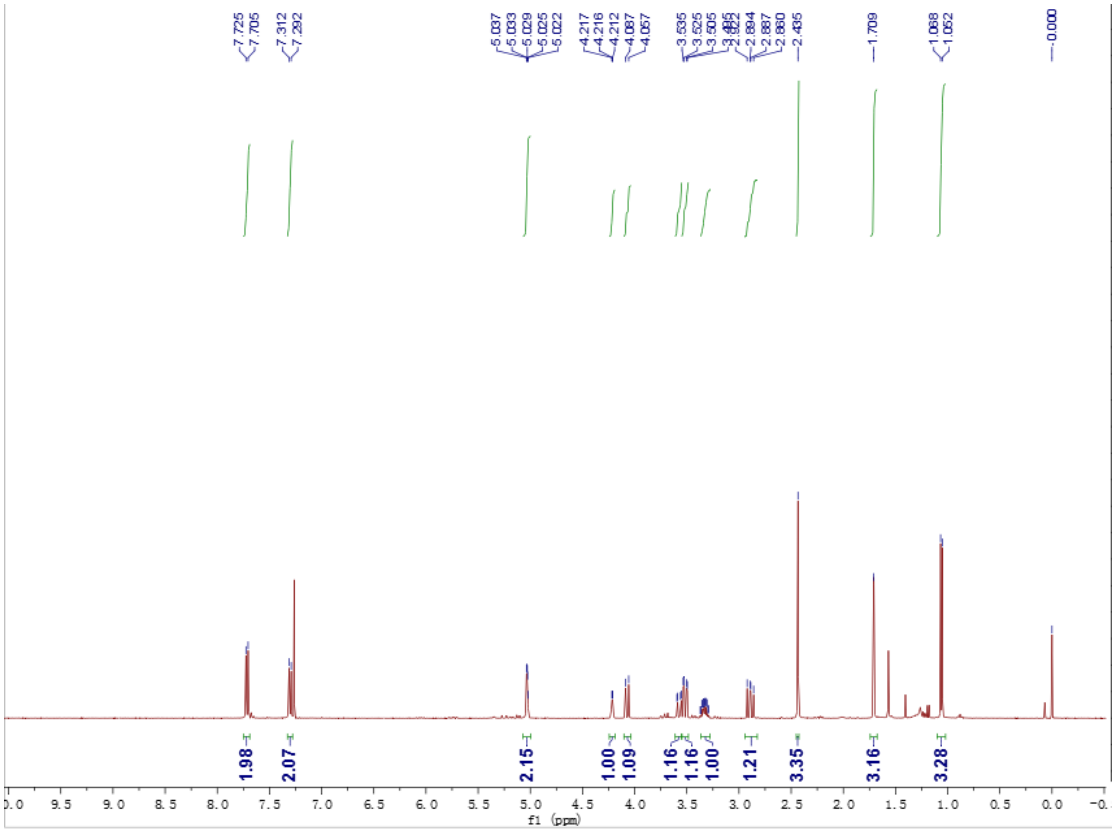
(3fa)

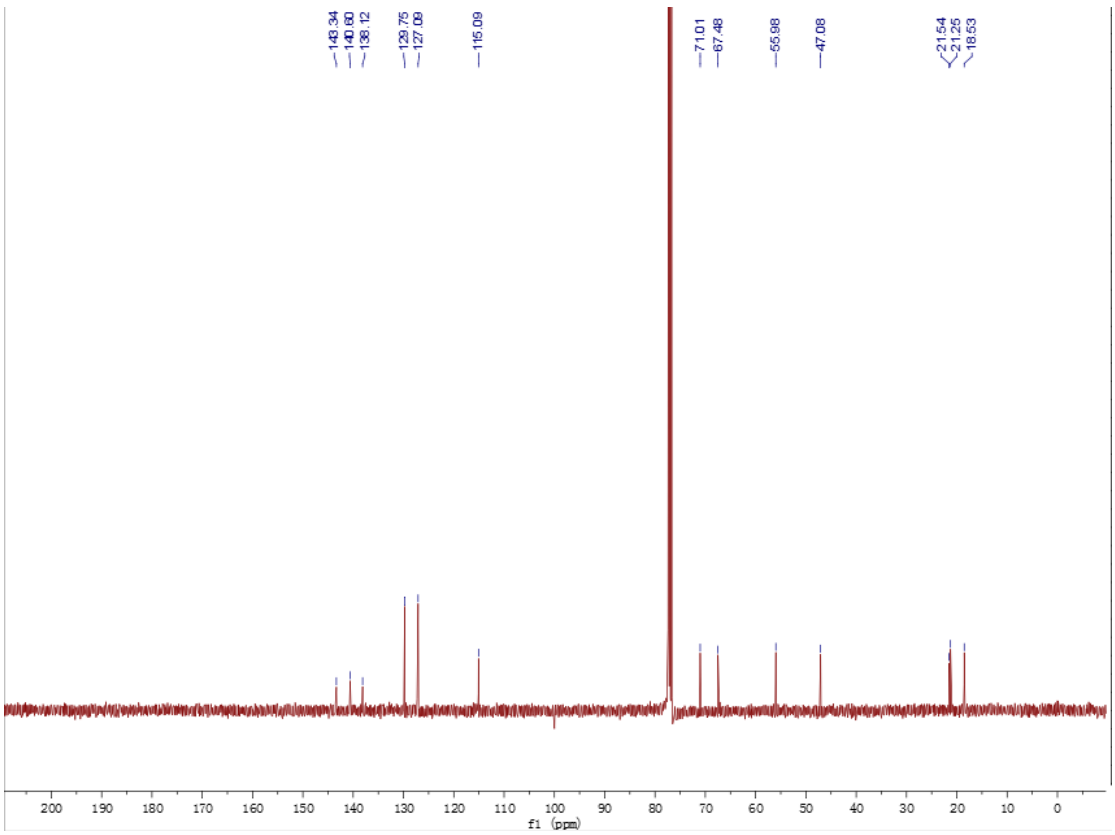

7.705
7.684
7.268
7.250
5.196
5.056
5.052
5.048
5.045
4.469
4.286
4.279
4.256
4.250
3.766
3.756
3.737
3.552
3.523
3.181
3.162
2.417
1.886
1.517
1.301
0.000
1.83
2.17
2.02
1.00
1.12
0.99
0.88
0.79
2.91
3.17
2.97
3.01
f1 (ppm)

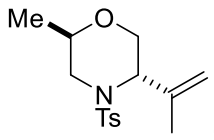

144.25
142.75
141.41
129.42
126.94
114.94
76.80
67.71
58.37
58.34
26.39
24.90
21.55
21.48
f1 (ppm)


Me
O
N
Ts

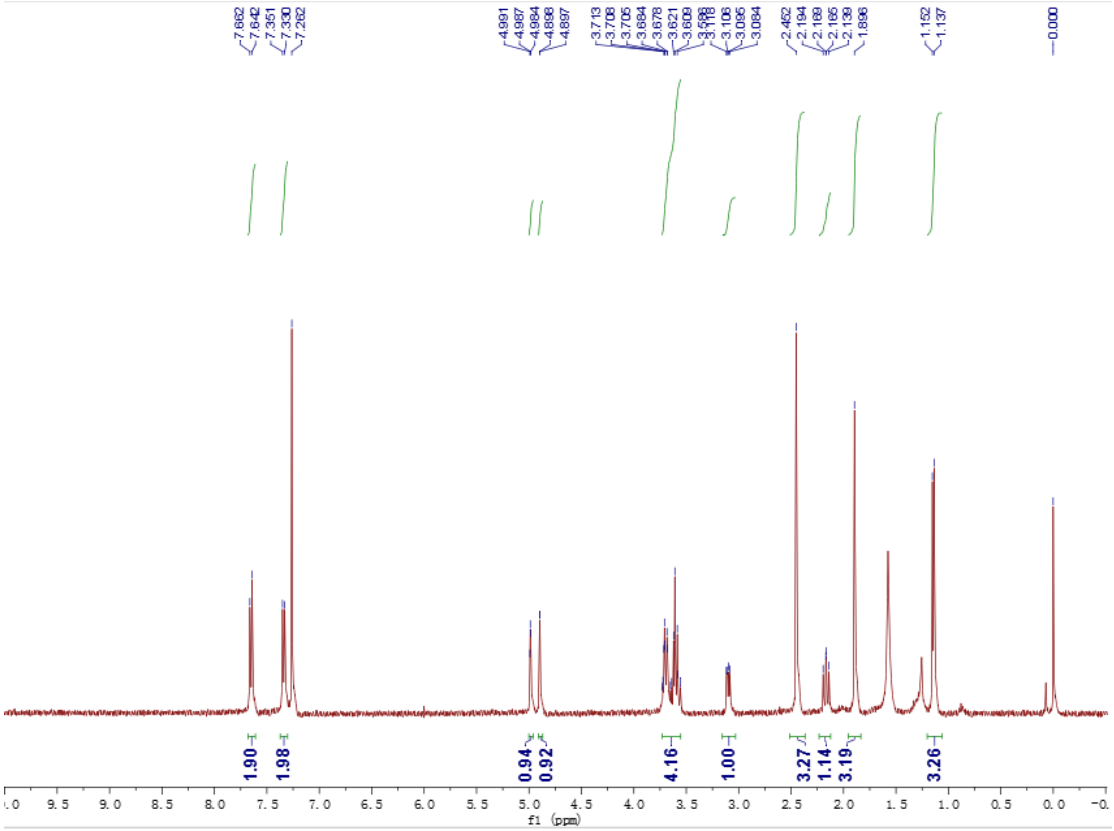
(3ga)

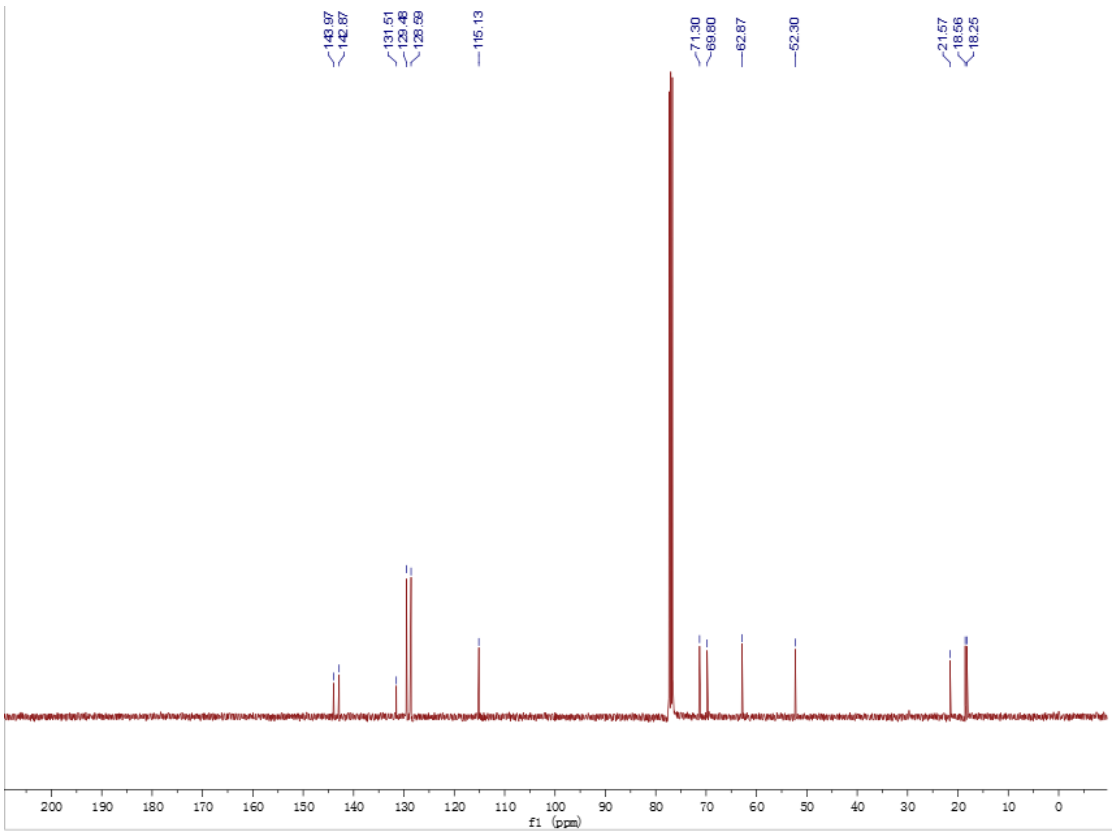

7.725
7.705
7.312
7.292
5.037
5.033
5.029
5.025
5.022
4.217
4.216
4.212
4.067
4.057
3.535
3.525
3.505
2.894
2.887
2.880
2.435
1.709
1.068
1.052
0.000
1.98
2.07
2.15
1.00
1.09
1.16
1.16
1.00
1.21
3.35
3.16
3.28
f1 (ppm)

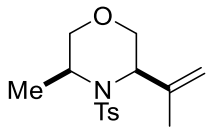

143.34
140.60
136.12
129.75
127.09
115.09
71.01
67.48
55.98
47.08
21.54
21.25
18.53
f1 (ppm)


Me
O
N
Ts

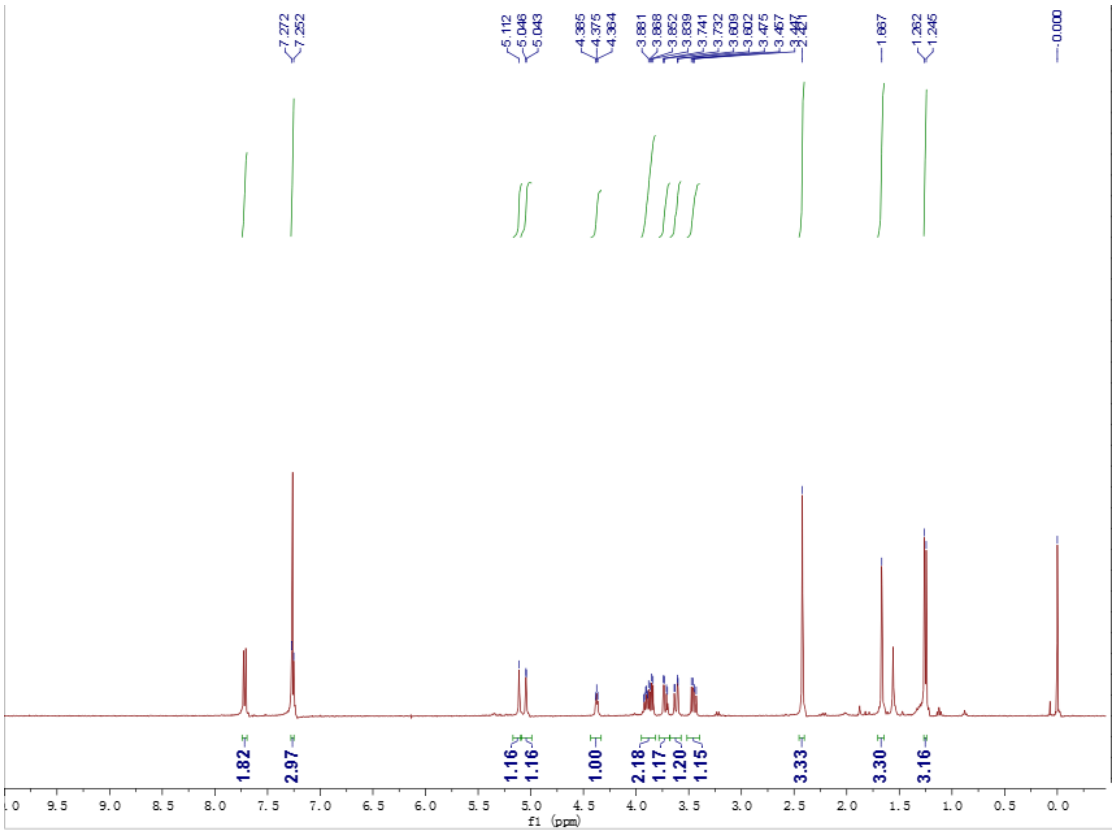
(3ga')

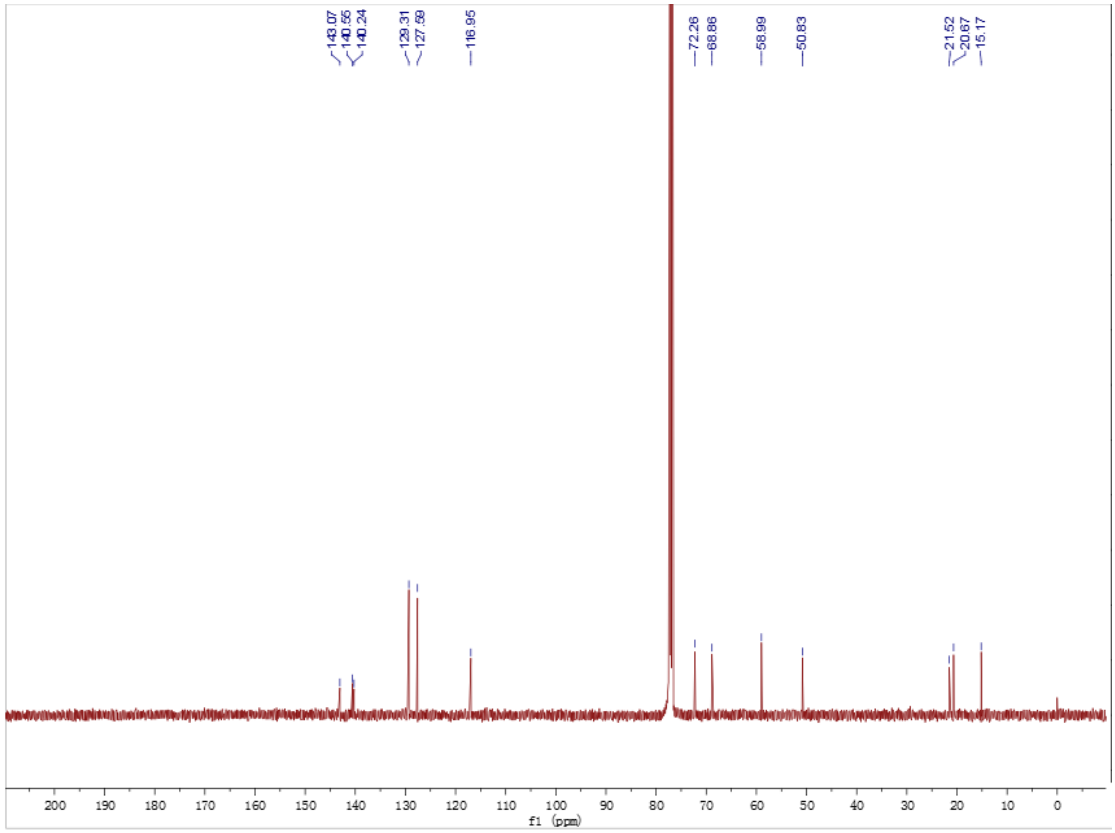

7.682
7.642
7.351
7.330
7.262
4.991
4.987
4.984
4.886
4.897
3.713
3.708
3.705
3.684
3.678
3.621
3.609
3.106
3.095
3.084
2.452
2.194
2.169
2.165
2.139
1.896
1.152
1.137
0.000
1.90
1.98
0.94
0.92
4.16
1.00
3.27
1.14
3.19
3.26
f1 (ppm)

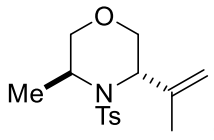

143.97
142.87
131.51
129.48
128.59
115.13
71.30
69.80
62.87
52.30
21.57
18.56
18.25
f1 (ppm)


O
Me
N
Ts

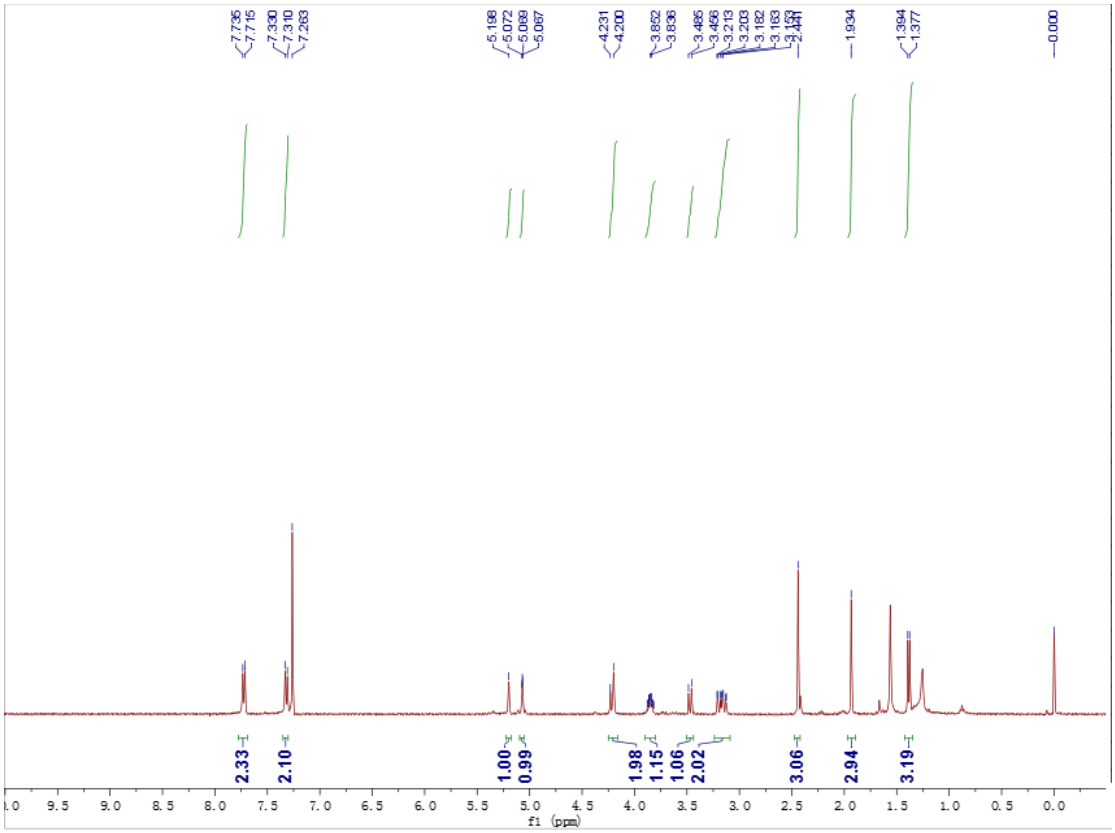
(3ha)

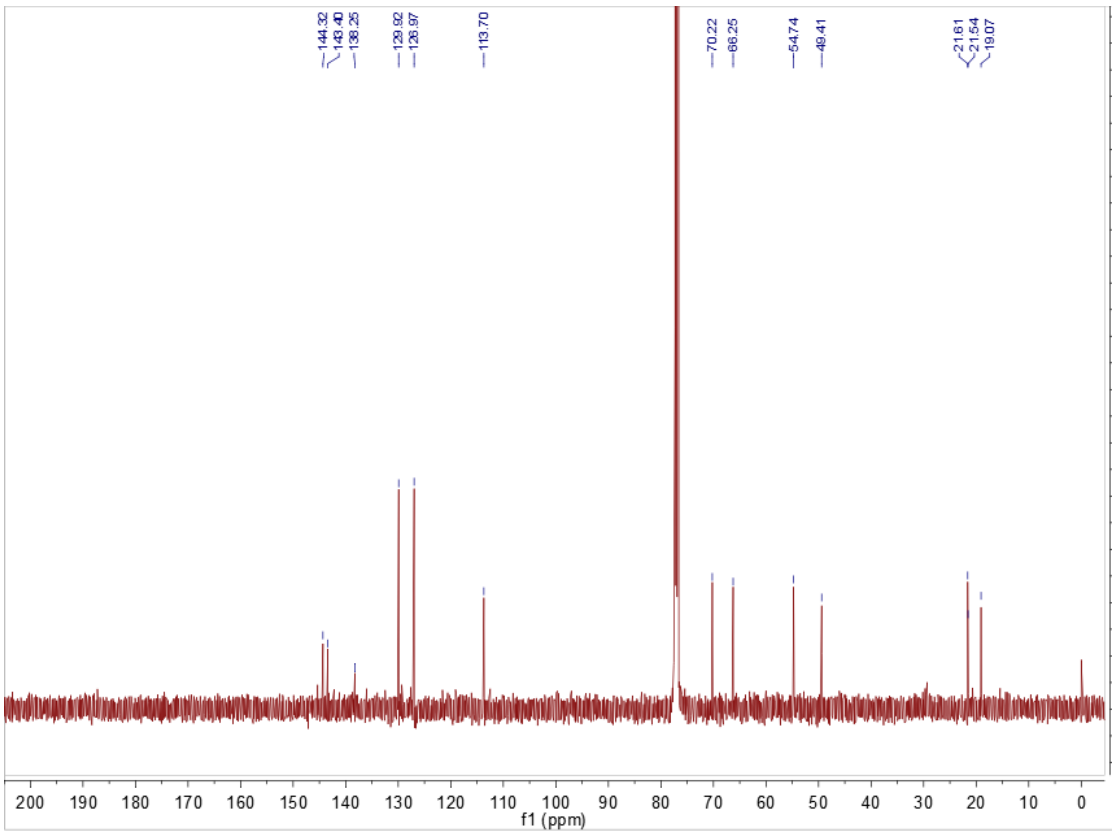

7.272
7.252
5.112
5.046
5.043
4.385
4.375
4.364
3.881
3.868
3.852
3.839
3.741
3.732
3.609
3.602
3.475
3.457
2.421
1.867
1.262
1.245
0.000
1.82
2.97
1.16
1.16
1.00
2.18
1.17
1.20
1.15
3.33
3.30
3.16
f1 (ppm)

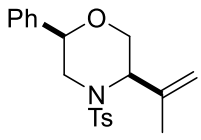

143.07
140.55
140.24
129.31
127.59
116.95
72.26
68.86
58.99
50.83
21.52
20.67
15.17
f1 (ppm)


O
Me
N
Ts

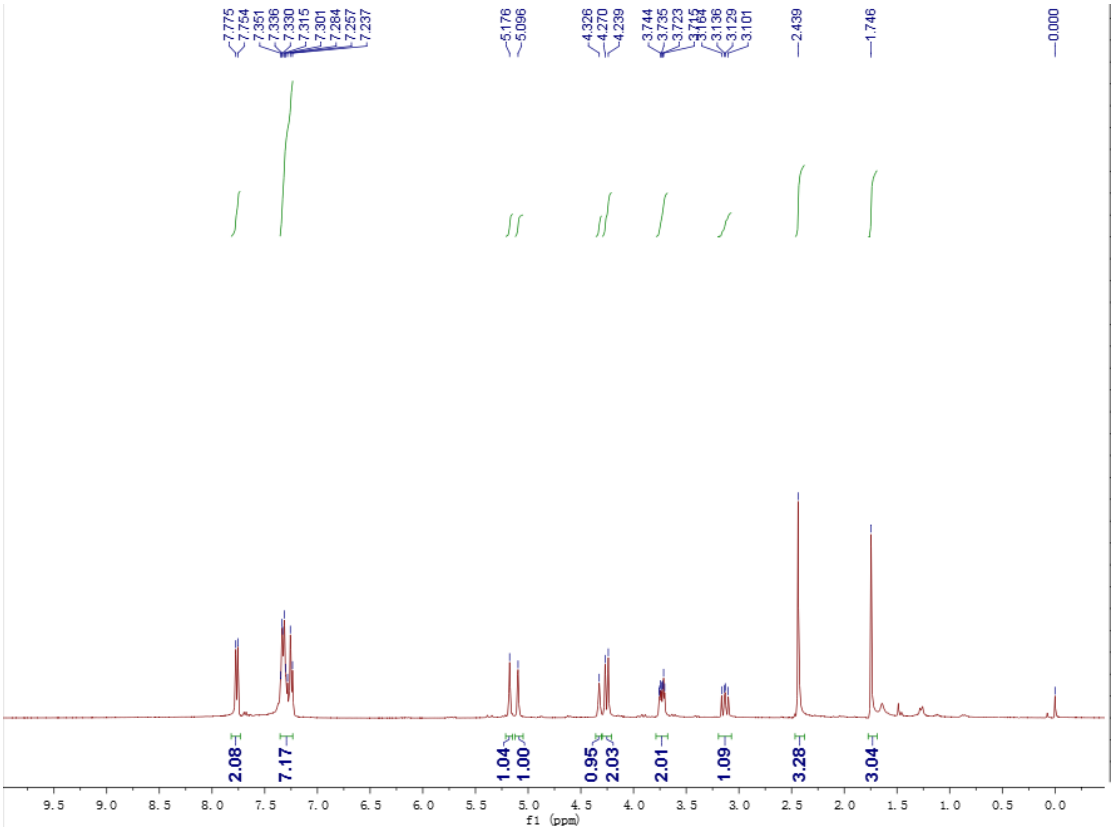
(3ha')


7.736
7.715
7.330
7.310
7.263
5.198
5.072
5.069
5.067
4.231
4.200
3.852
3.836
3.485
3.466
3.213
3.203
3.162
3.163
2.441
1.934
1.394
1.377
0.000
2.33
2.10
1.00
0.99
1.98
1.15
1.06
2.02
3.06
2.94
3.19
f1 (ppm)

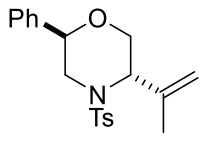

144.32
143.40
138.25
129.92
126.97
113.70
70.22
66.25
54.74
49.41
21.61
21.54
19.07
f1 (ppm)


Ph
O
N
Ts

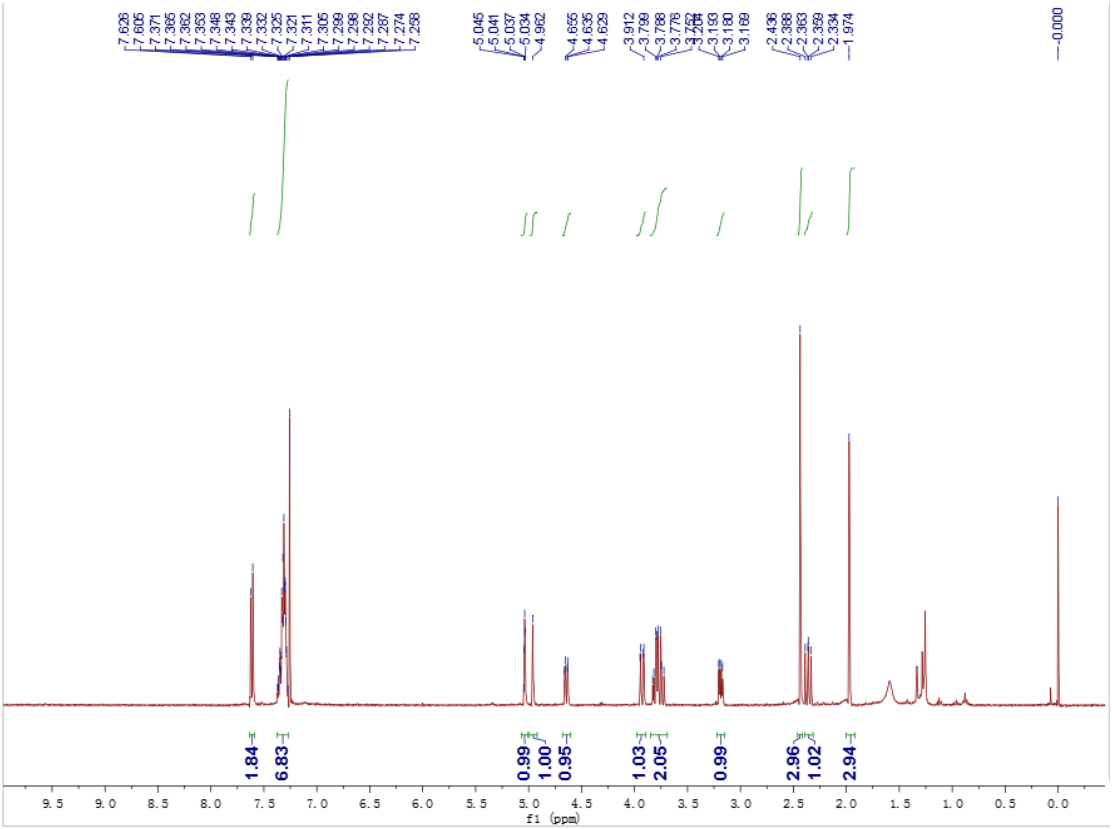
(3ia)

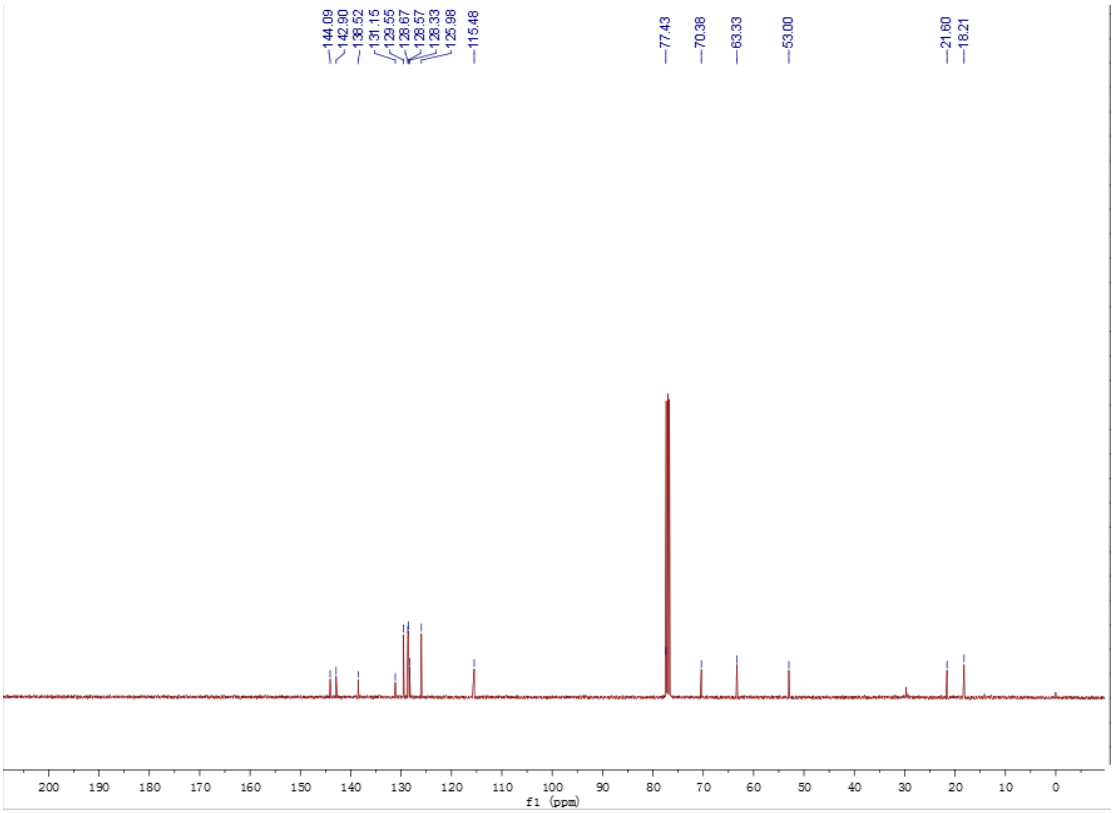

7.775
7.754
7.351
7.336
7.330
7.315
7.301
7.284
7.257
7.237
5.176
5.096
4.326
4.270
4.239
3.744
3.735
3.723
3.715
3.164
3.136
3.129
3.101
2.439
1.746
0.000
2.08
7.17
1.04
1.00
0.95
2.03
2.01
1.09
3.28
3.04
f1 (ppm)

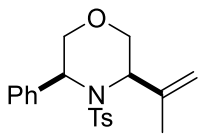

143.57
140.77
138.79
138.04
129.86
128.53
128.30
127.17
126.01
115.50
67.69
55.96
47.30
21.57
21.37
f1 (ppm)


Ph
O
N
Ts

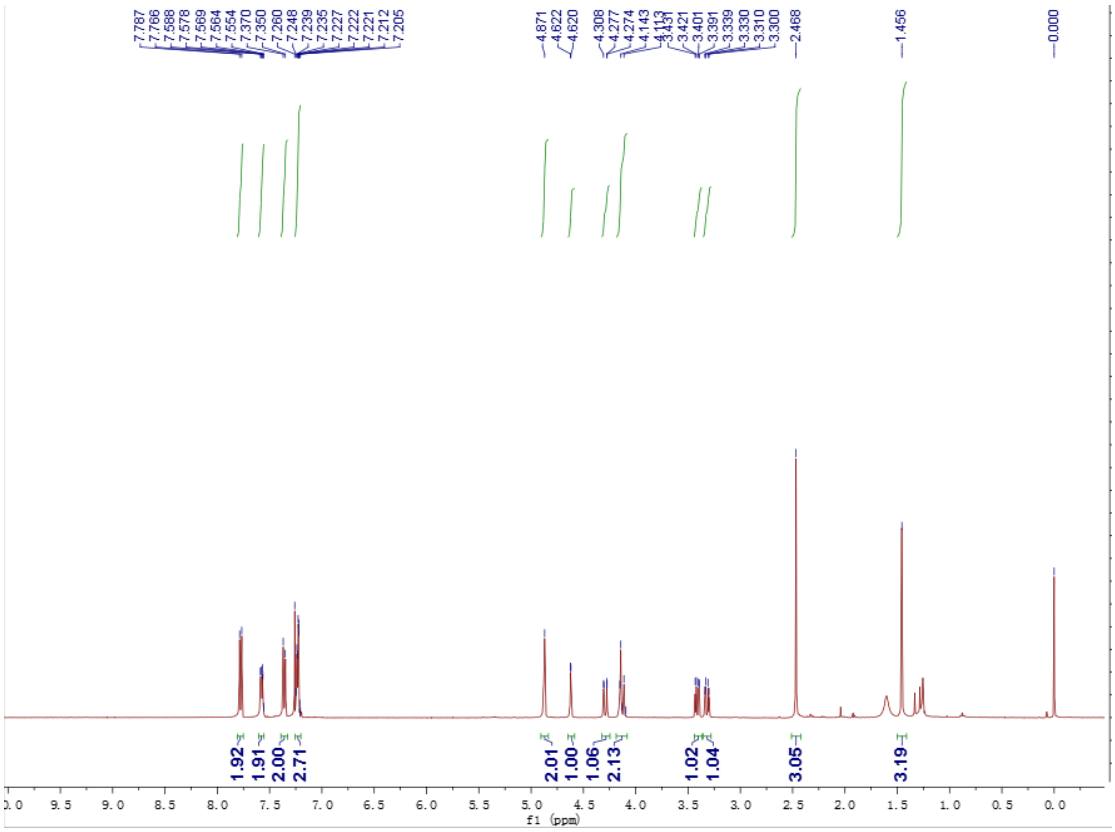
(3ia')


7.626
7.605
7.371
7.365
7.362
7.353
7.348
7.343
7.339
7.332
7.325
7.321
7.311
7.305
7.299
7.298
7.292
7.287
7.274
7.258
5.045
5.041
5.037
5.034
4.962
4.655
4.635
4.629
3.912
3.799
3.788
3.776
3.193
3.180
3.169
2.436
2.388
2.363
2.359
2.334
1.974
0.000
1.84
6.83
0.99
1.00
0.95
1.03
2.05
0.99
2.96
1.02
2.94
f1 (ppm)

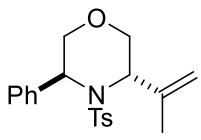

144.09
142.90
138.52
131.15
129.55
128.67
128.57
128.33
125.98
115.48
77.43
70.38
63.33
53.00
21.60
18.21
f1 (ppm)


O
Ph
N
Ts

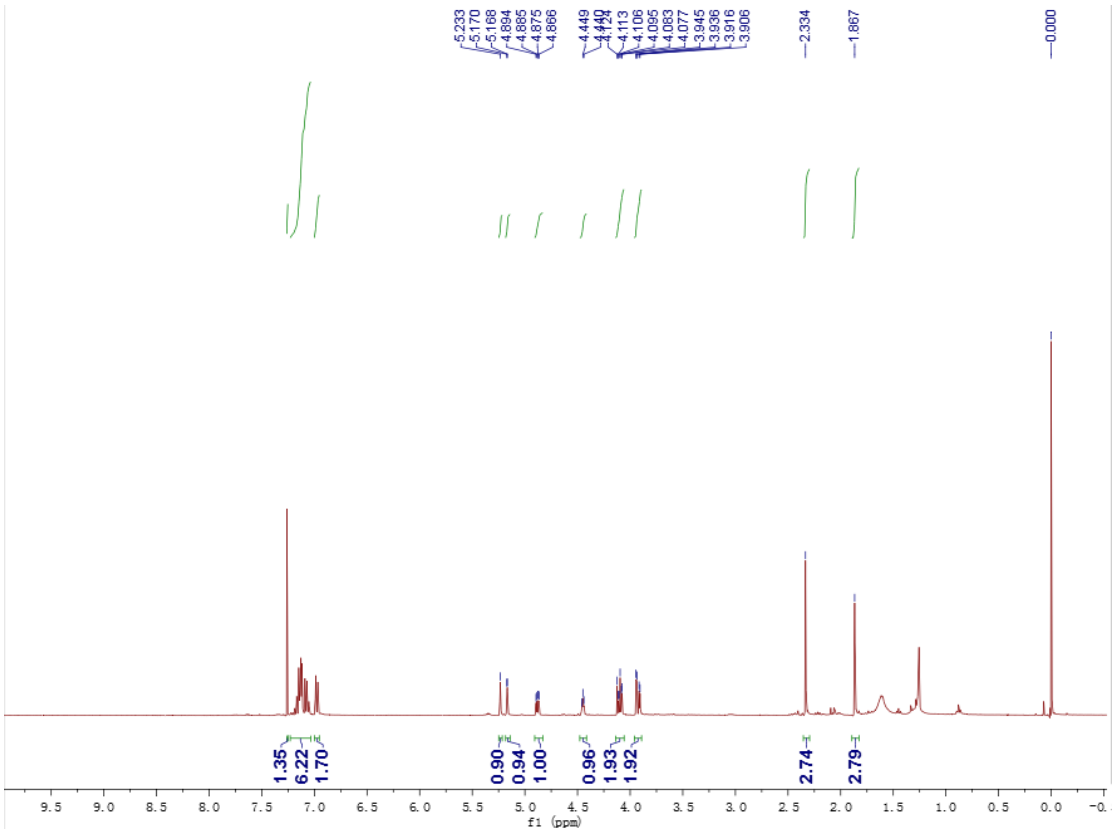
(3ja)

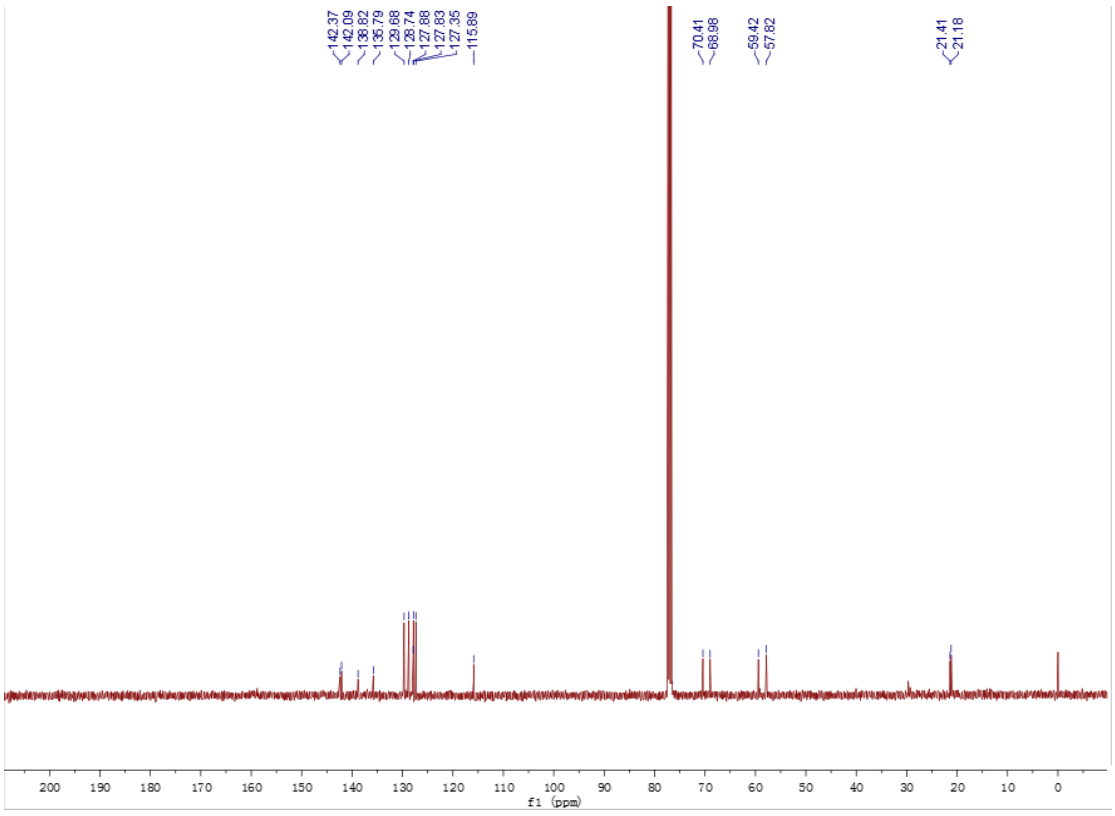

7.787
7.766
7.588
7.578
7.569
7.564
7.554
7.370
7.350
7.260
7.248
7.239
7.235
7.227
7.222
7.221
7.212
7.205
4.871
4.622
4.620
4.308
4.277
4.274
4.143
4.113
3.421
3.401
3.391
3.339
3.330
3.310
3.300
2.468
1.456
0.000
1.92
1.91
2.00
2.71
2.01
1.00
1.06
2.13
1.02
1.04
3.05
3.19
f1 (ppm)

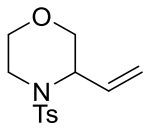

143.72
142.05
138.75
137.98
130.07
128.95
127.62
127.33
127.24
114.51
66.75
66.16
55.86
54.16
21.59
20.73
f1 (ppm)


O
Ph
N
Ts

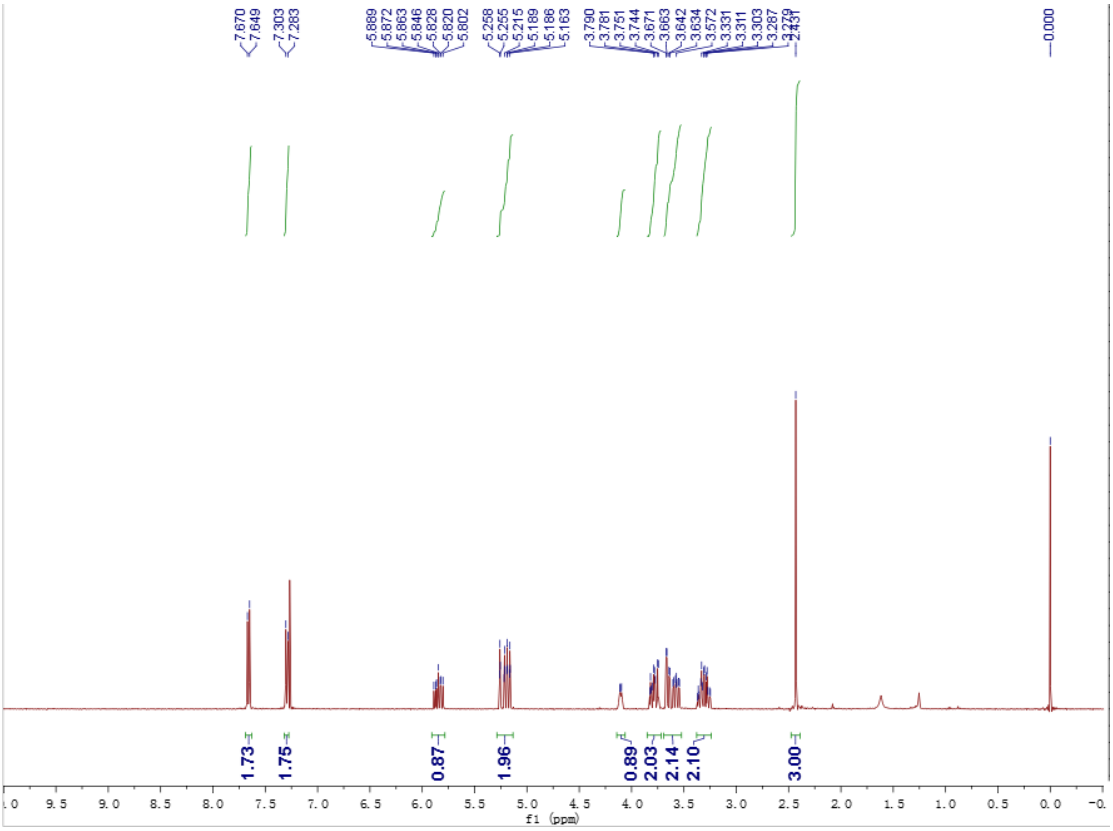
(3ja')

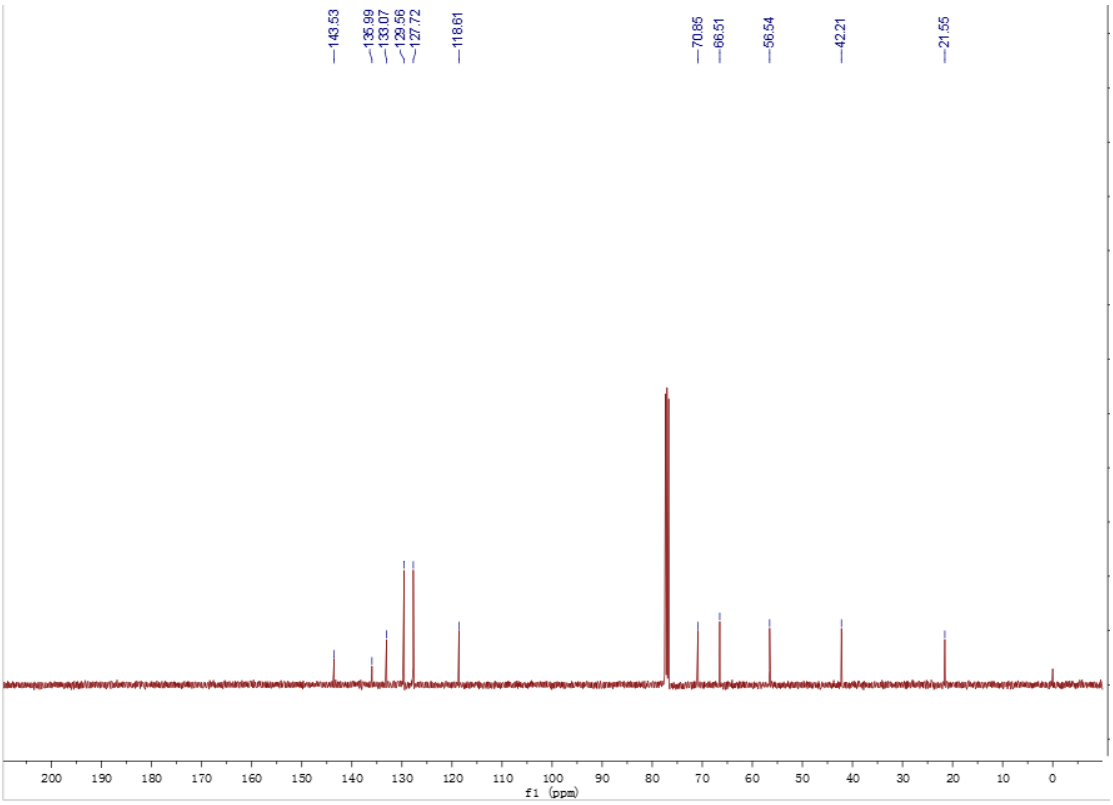

5.233
5.170
5.168
4.884
4.885
4.875
4.866
4.449
4.440
4.424
4.113
4.106
4.095
4.083
4.077
3.945
3.936
3.916
3.906
2.334
1.867
0.000
1.35
6.22
1.70
0.90
0.94
1.00
0.96
1.93
1.92
2.74
2.79
f1 (ppm)

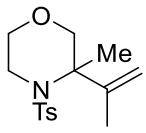

142.37
142.09
136.82
135.79
128.68
128.74
127.88
127.83
127.35
115.89
70.41
68.98
59.42
57.82
21.41
21.18
f1 (ppm)


O
N
Ts

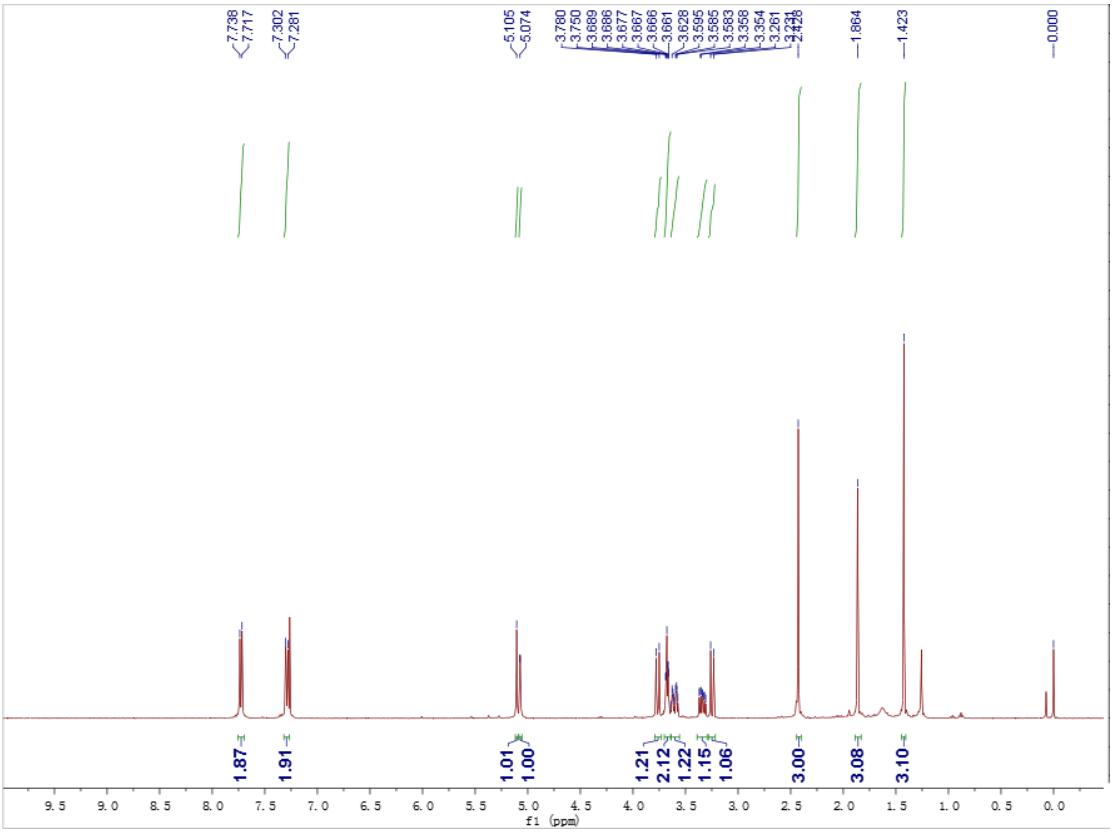
(3ab)

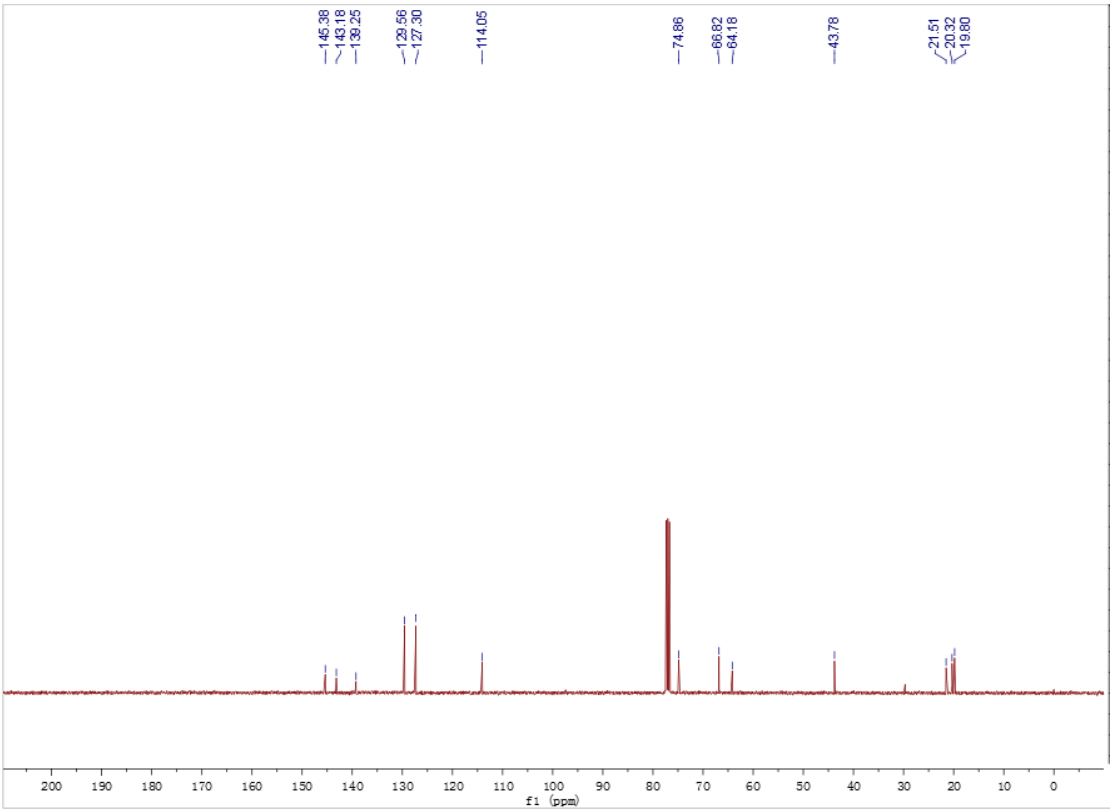

7.670
7.649
7.303
7.263
5.889
5.872
5.863
5.846
5.828
5.820
5.802
5.258
5.255
5.215
5.189
5.186
5.163
3.790
3.781
3.751
3.744
3.671
3.663
3.642
3.634
3.572
3.331
3.311
3.303
3.287
2.431
0.000
1.73
1.75
0.87
1.96
0.89
2.03
2.14
2.10
3.00
f1 (ppm)

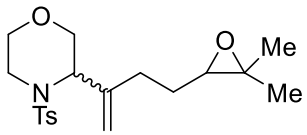

143.53
135.99
133.07
129.56
127.72
118.61
70.85
66.51
56.54
42.21
21.55
f1 (ppm)


O
Me
N
Ts

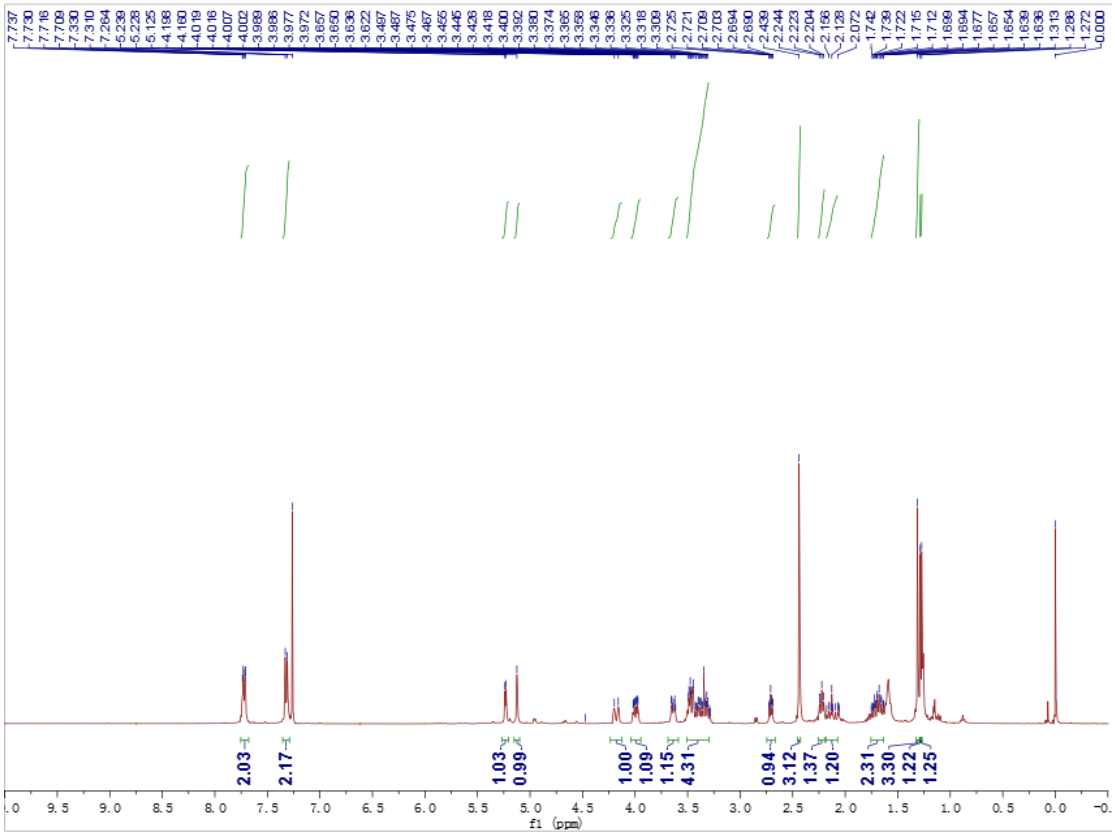
(3ac)

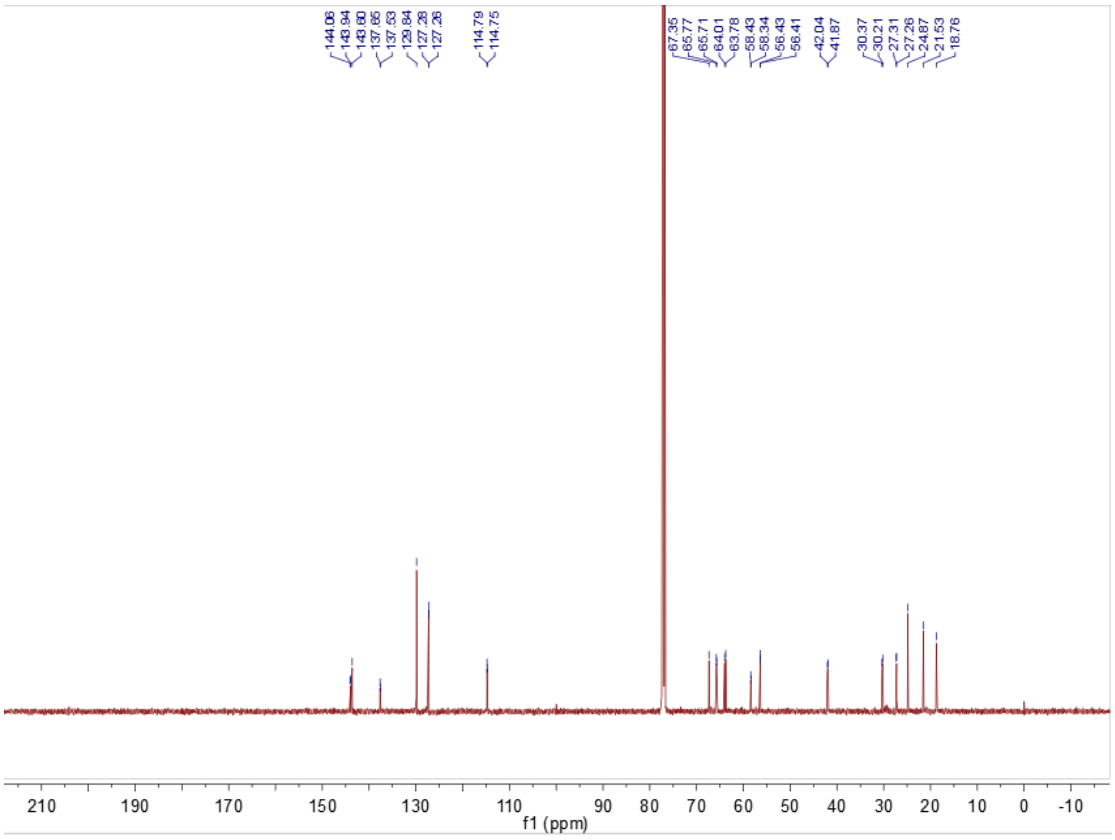

7.738
7.717
7.302
7.281
5.105
5.074
3.780
3.750
3.689
3.686
3.677
3.667
3.666
3.661
3.628
3.595
3.585
3.563
3.558
3.354
3.261
2.428
1.864
1.423
0.000
1.87
1.91
1.01
1.00
1.21
2.12
1.22
1.15
1.06
3.00
3.08
3.10
f1 (ppm)

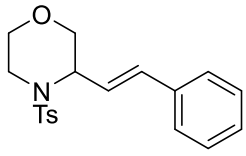

145.38
143.18
139.25
129.56
127.30
114.05
74.86
66.82
64.18
43.78
21.51
20.32
19.80
f1 (ppm)



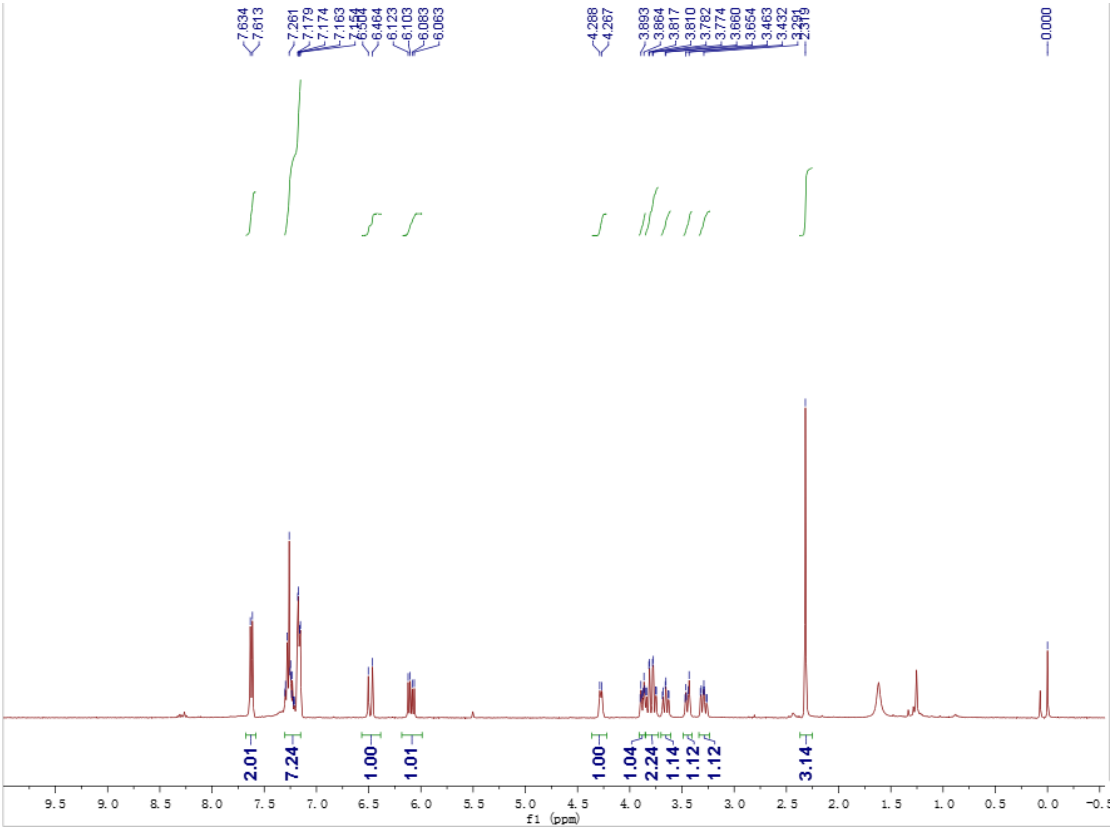
(3ad, 1:1 mixture of diastereoisomers)

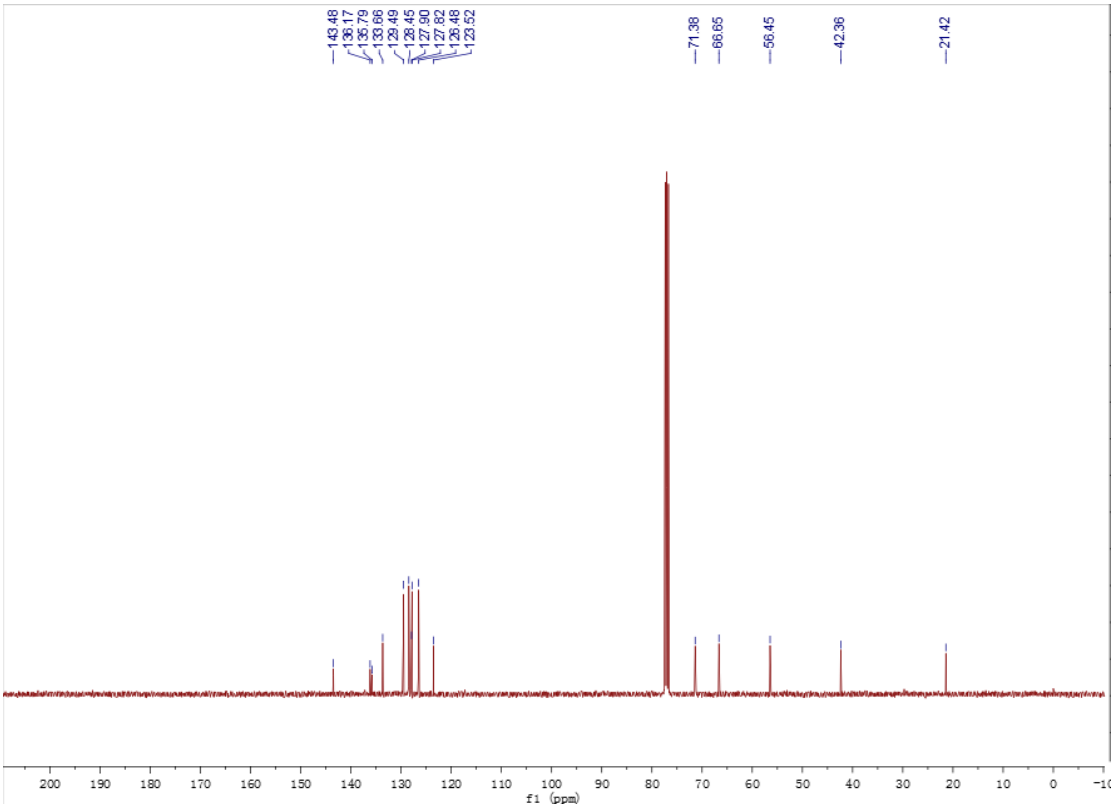


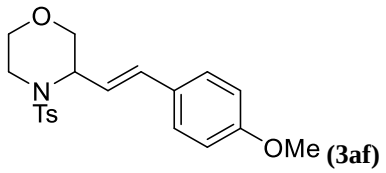



O
N
Ts

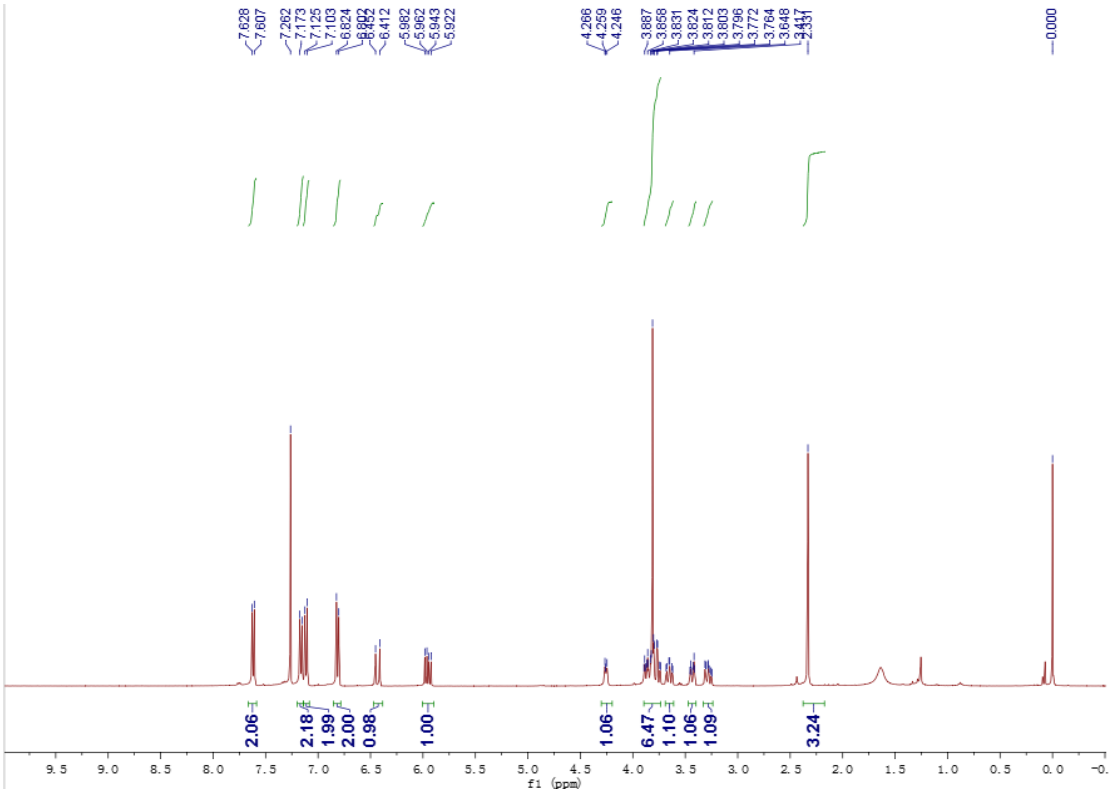
(3ae)

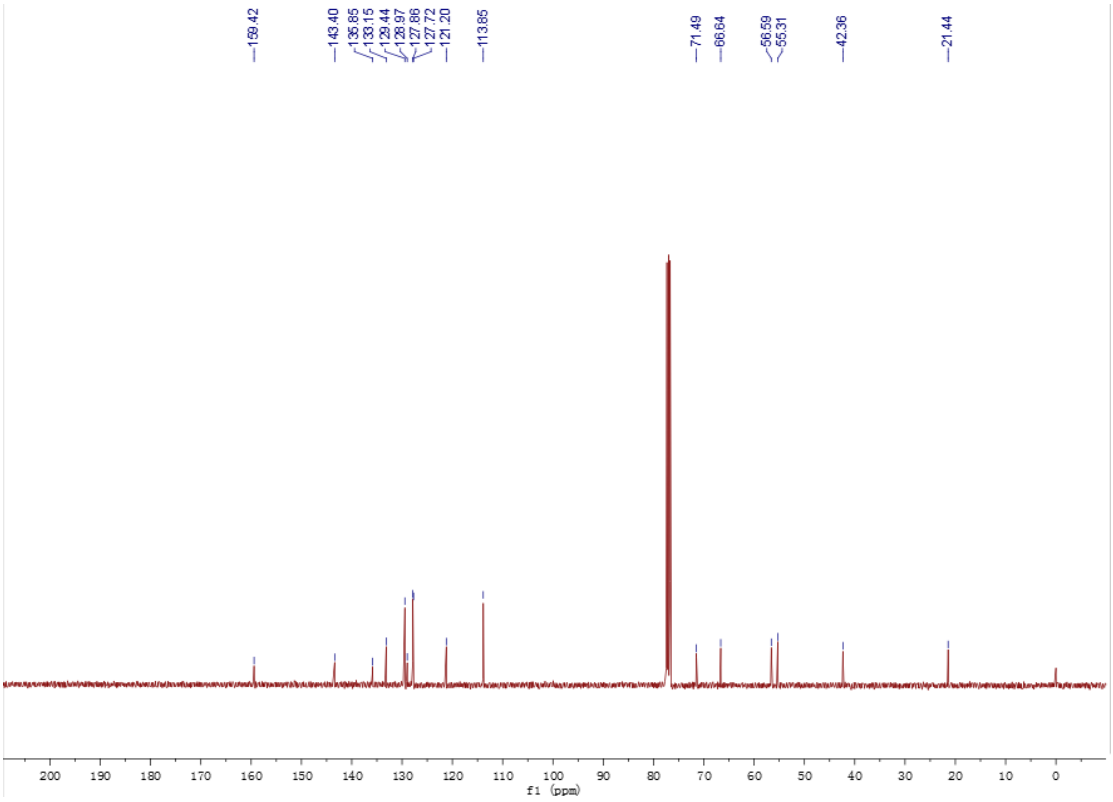

7.634
7.613
7.261
7.179
7.174
7.163
6.464
6.123
6.103
6.083
6.063
4.288
4.267
3.893
3.864
3.817
3.810
3.782
3.774
3.660
3.654
3.463
3.432
2.319
0.000
2.01
7.24
1.00
1.01
1.00
1.04
2.24
1.14
1.12
1.12
3.14
f1 (ppm)

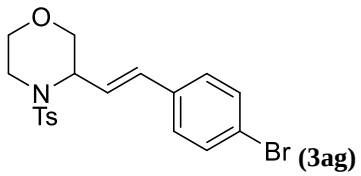

143.48
136.17
135.79
133.66
129.49
128.45
127.90
127.82
126.48
123.52
71.38
66.65
56.45
42.36
21.42
f1 (ppm)


O
N
Ts
OMe

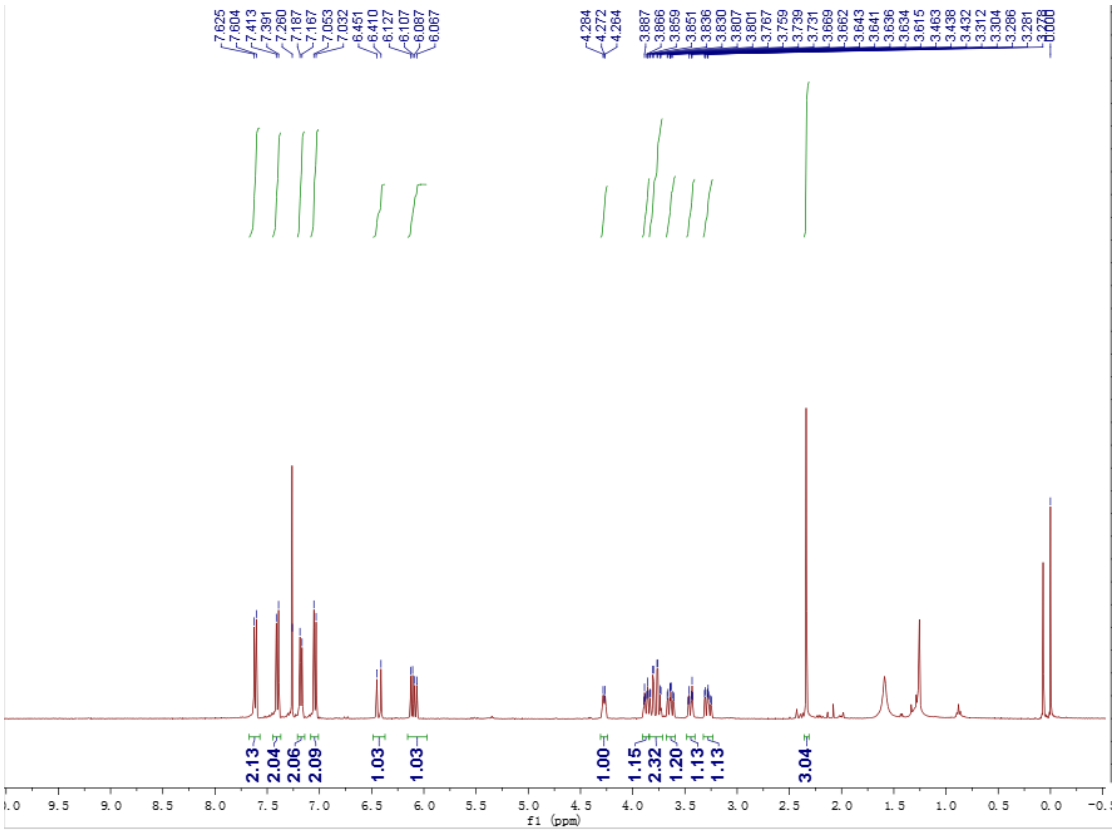
(3af)

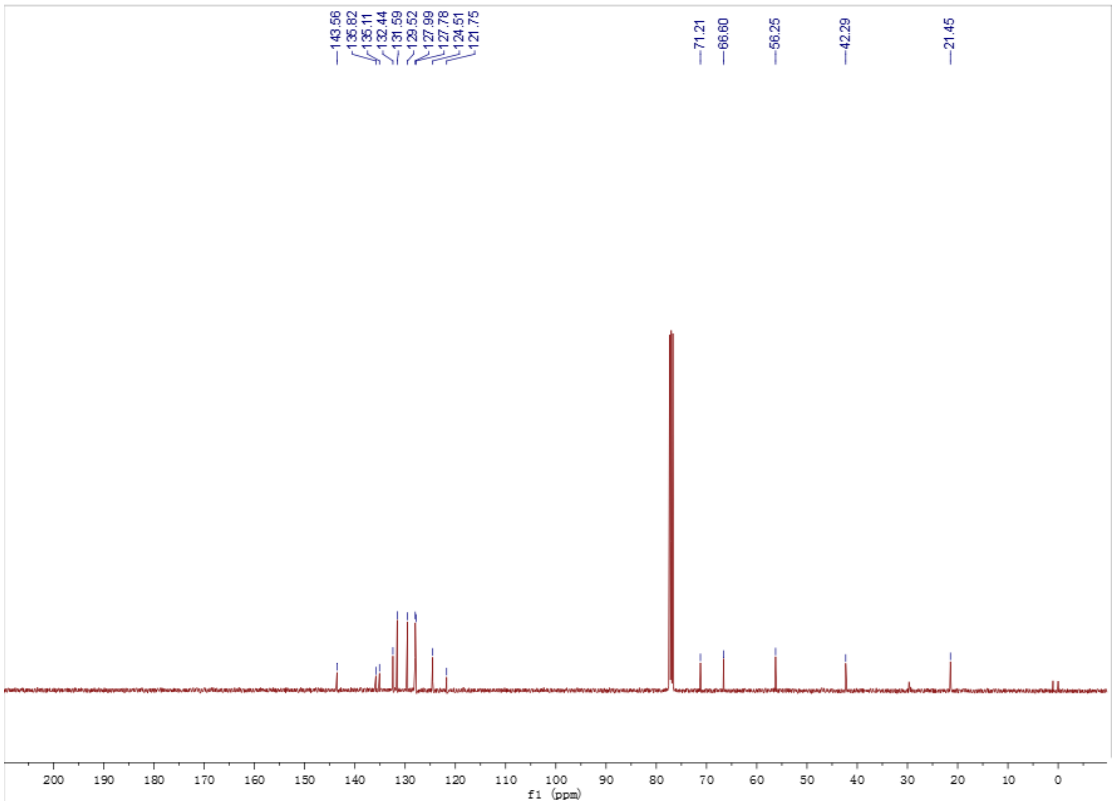

7.628
7.607
7.262
7.173
7.125
7.103
6.824
6.802
6.452
6.412
5.982
5.962
5.943
5.922
4.266
4.259
4.246
3.887
3.858
3.831
3.824
3.812
3.803
3.796
3.772
3.764
3.648
3.447
2.431
0.000
2.06
2.18
1.99
2.00
0.98
1.00
1.06
6.47
1.10
1.06
1.09
3.24
f1 (ppm)

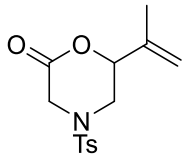

169.42
143.40
136.85
133.15
129.44
128.97
127.86
127.72
121.20
113.85
71.49
66.64
56.59
55.31
42.36
21.44
f1 (ppm)


O
N
Ts
Br

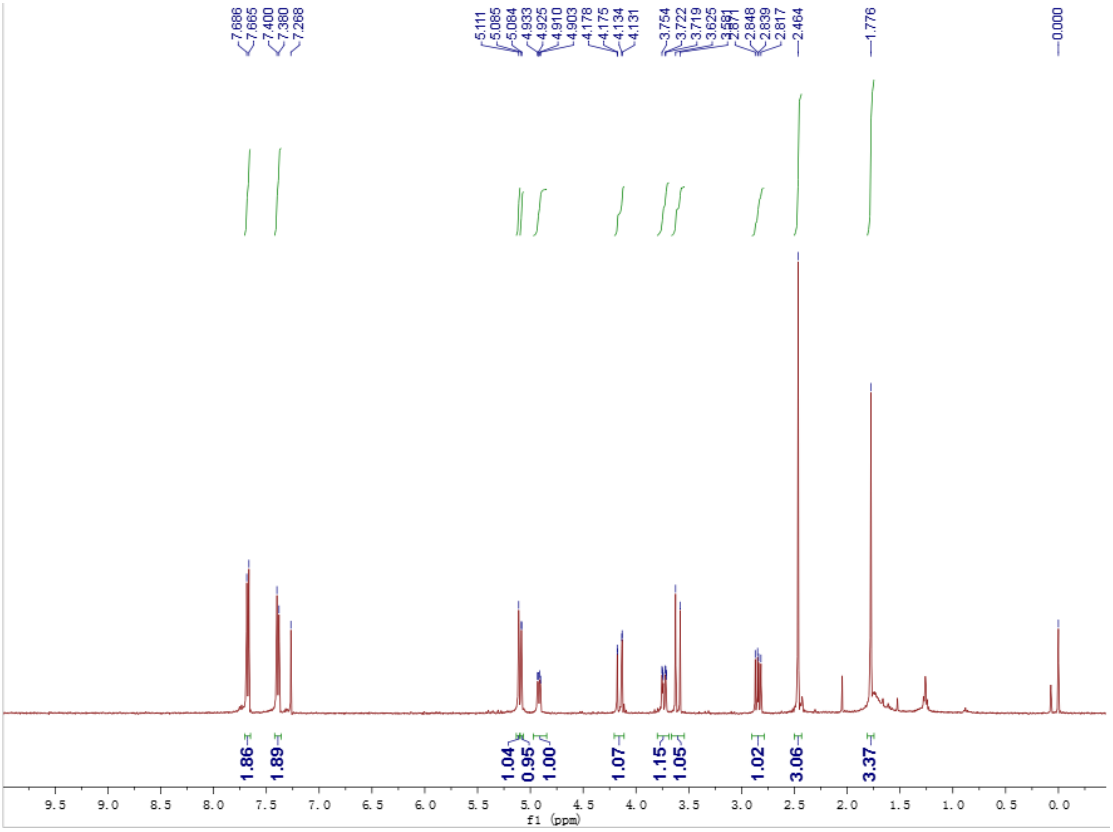
(3ag)


7.625
7.604
7.413
7.391
7.260
7.187
7.167
7.053
7.032
6.451
6.410
6.127
6.107
6.087
6.067
4.284
4.272
4.264
3.887
3.866
3.859
3.851
3.836
3.830
3.807
3.801
3.767
3.759
3.739
3.731
3.669
3.662
3.643
3.641
3.636
3.634
3.615
3.463
3.438
3.432
3.312
3.304
3.286
3.281
2.13
2.04
2.06
2.09
1.03
1.03
1.00
1.15
2.32
1.20
1.13
1.13
3.04
f1 (ppm)


143.56
136.82
135.11
132.44
131.59
129.52
127.99
127.78
124.51
121.75
71.21
66.60
56.25
42.29
21.45
f1 (ppm)


O
O
N
Ts

(5aa)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7.380
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5.111
5.085
5.084
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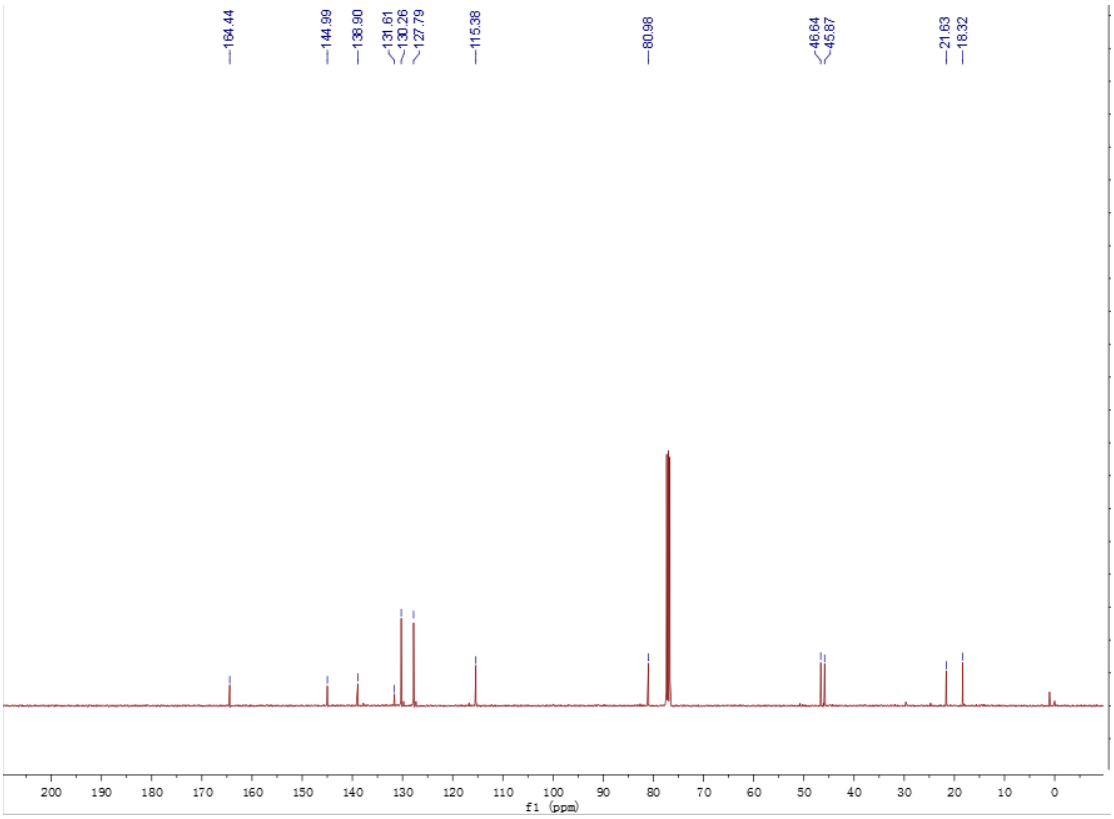
4.925
4.910
4.903
4.178
4.175
4.134
4.131
3.754
3.722
3.719
3.625
2.848
2.839
2.817
2.464
1.776
0.000
1.86
1.89
1.04
0.95
1.00
1.07
1.15
1.05
1.02
3.06
3.37
f1 (ppm)


164.44
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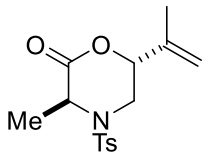
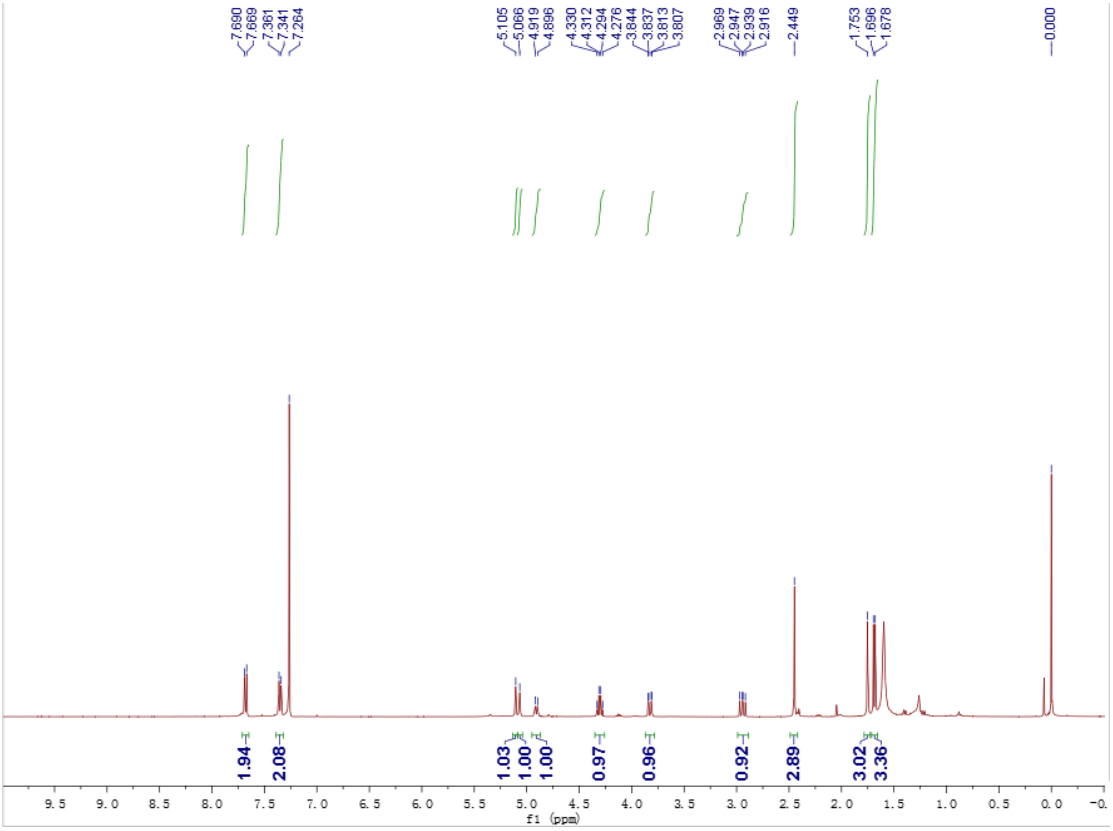
130.26
127.79
115.38
80.98
46.64
45.87
21.63
18.32
f1 (ppm)


O
O
Me
N
Ts

(5ba)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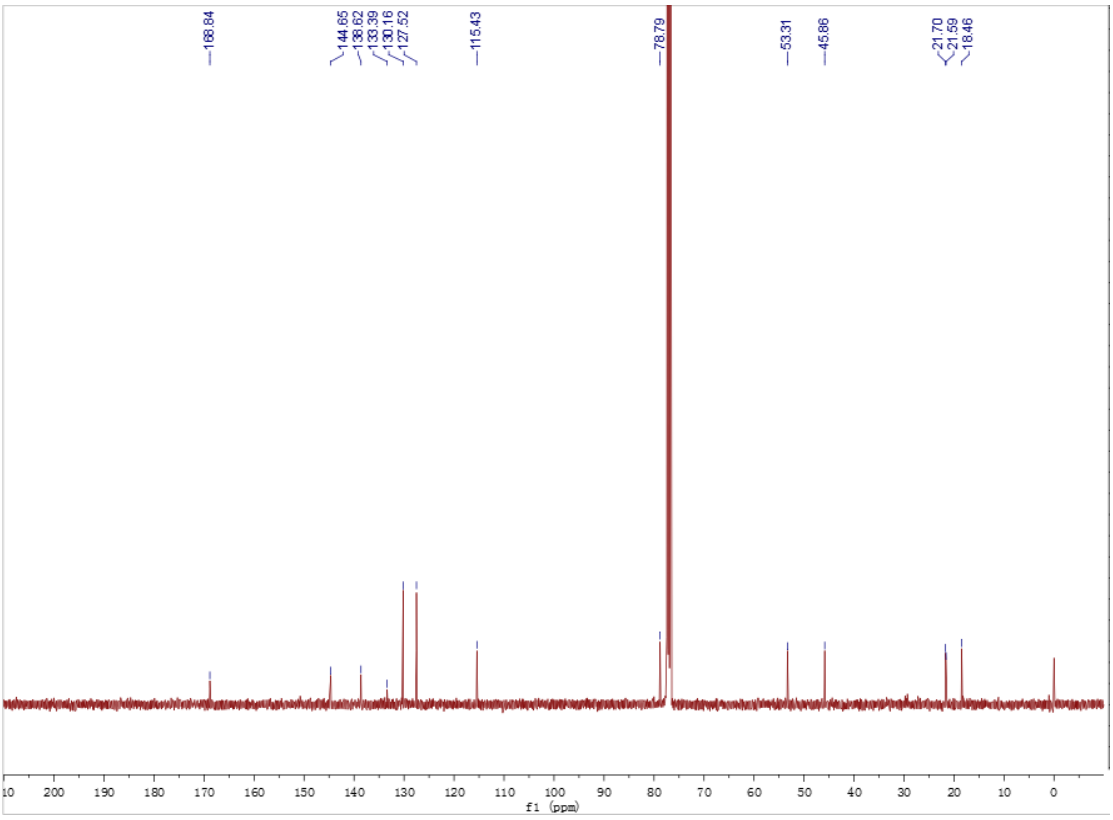
7.341
7.264
5.105
5.066
4.919
4.896
4.330
4.312
4.294
4.276
3.844
3.837
3.813
3.807
2.969
2.947
2.939
2.916
2.449
1.753
1.696
1.678
0.000
1.94
2.08
1.03
1.00
1.00
0.97
0.96
0.92
2.89
3.02
3.36
f1 (ppm)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144.65
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133.39
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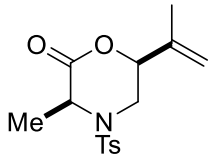
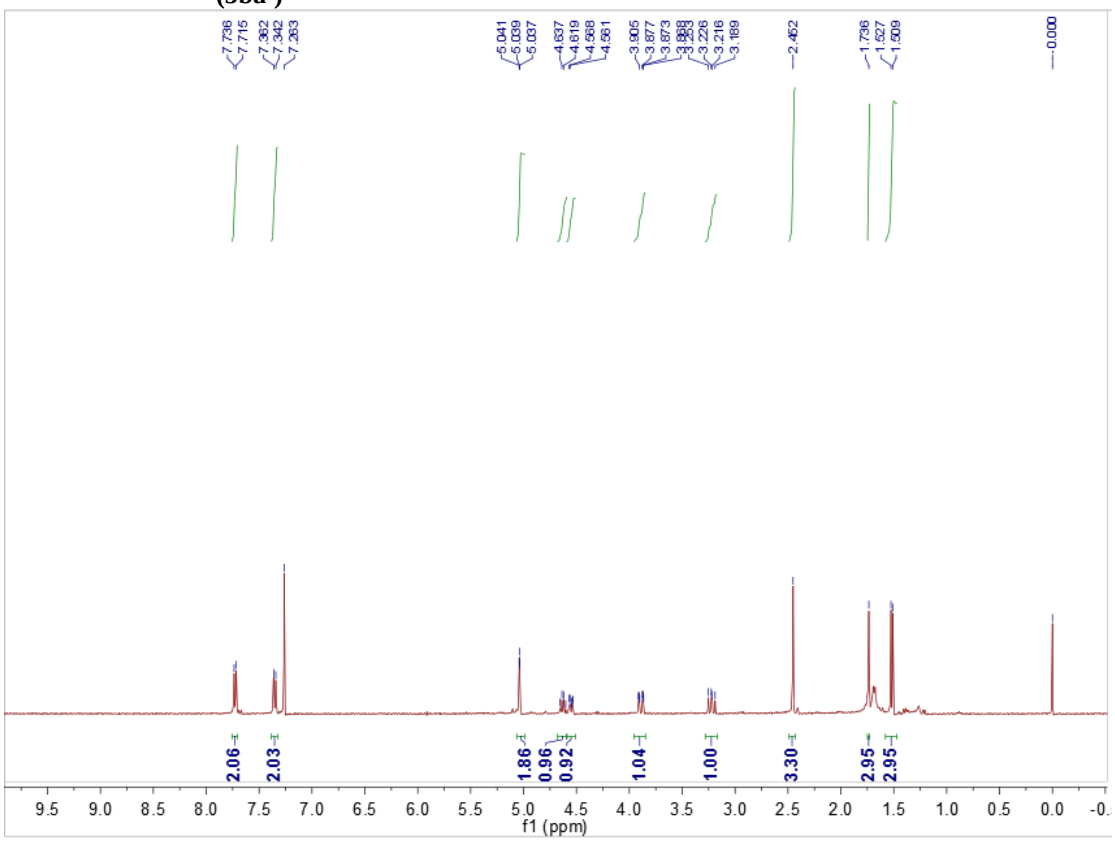
127.52
115.43
78.79
53.31
45.86
21.70
21.59
18.46
f1 (ppm)


O
O
Me
N
Ts

(5ba')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7.263
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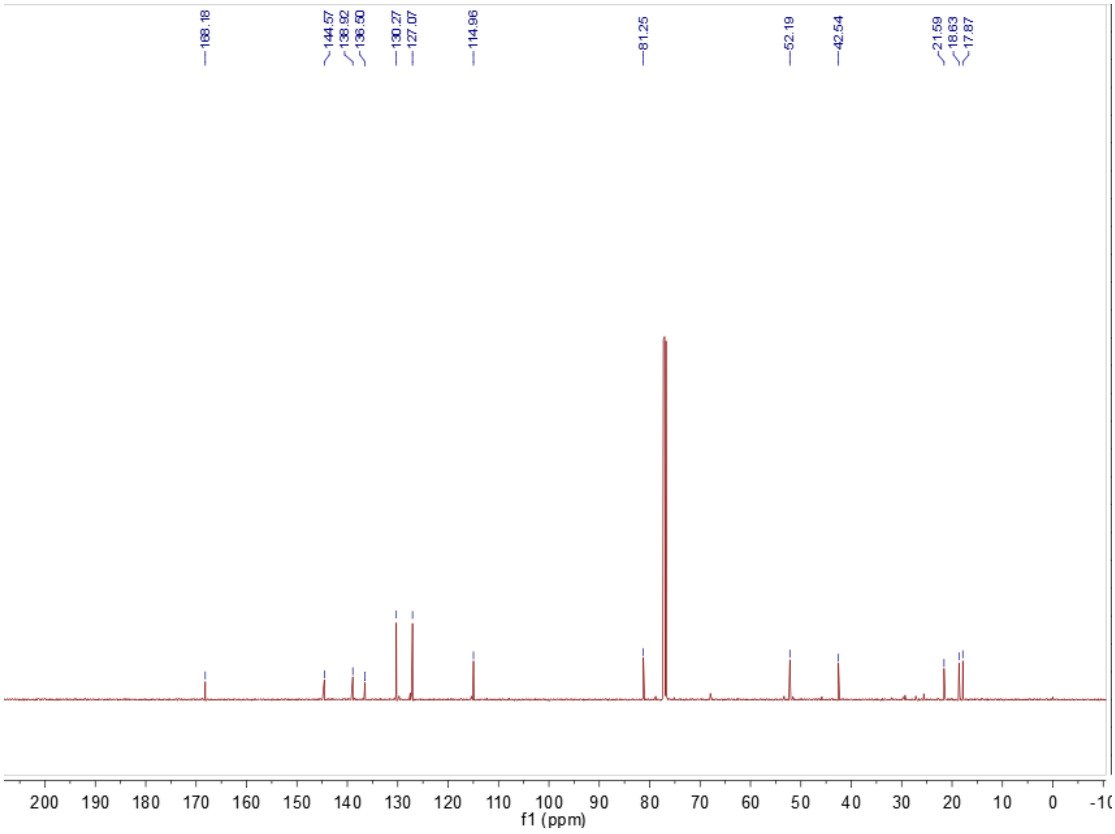
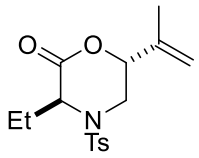
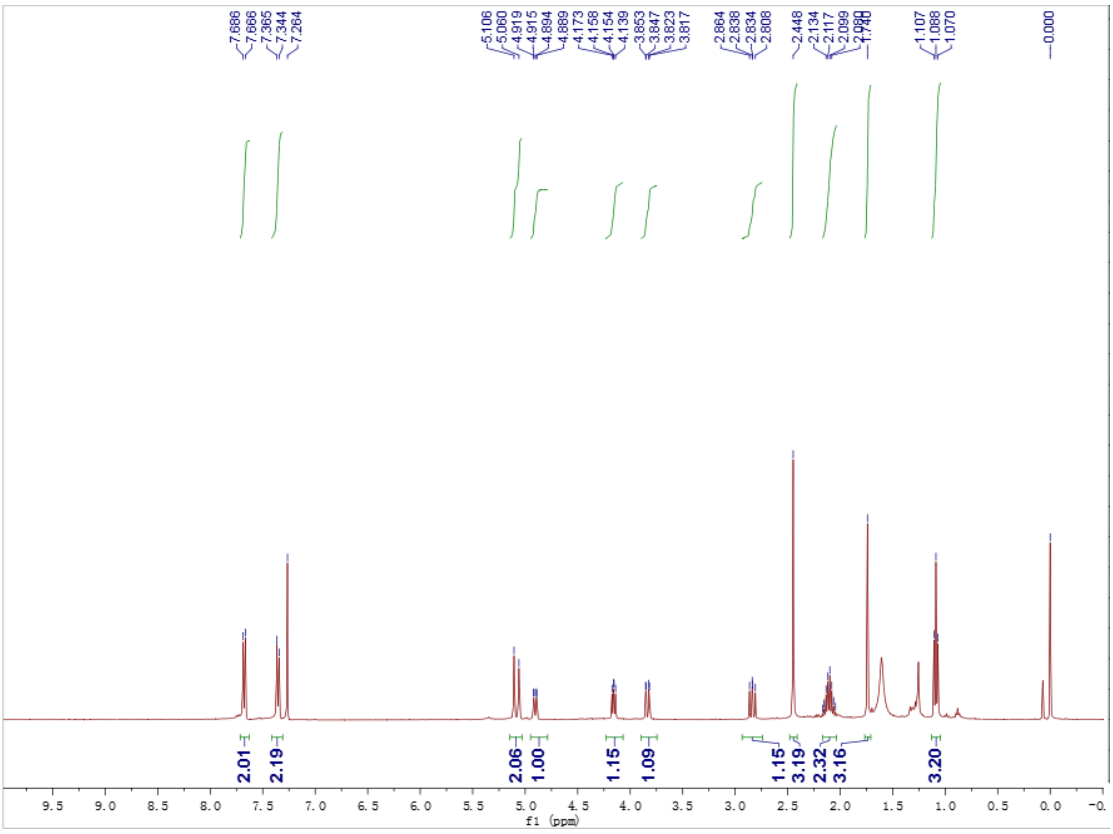
5.039
5.037
4.637
4.619
4.608
4.591
3.905
3.877
3.873
3.226
3.216
3.189
2.452
1.736
1.527
1.509
0.000
2.06
2.03
1.86
0.96
0.92
1.04
1.00
3.30
2.95
2.95
f1 (ppm)


188.18
144.57
138.92
136.50
130.27
127.07
114.96
81.25
52.19
42.54
21.59
18.63
17.87
f1 (ppm)


O
O
Et
N
Ts

(5ca)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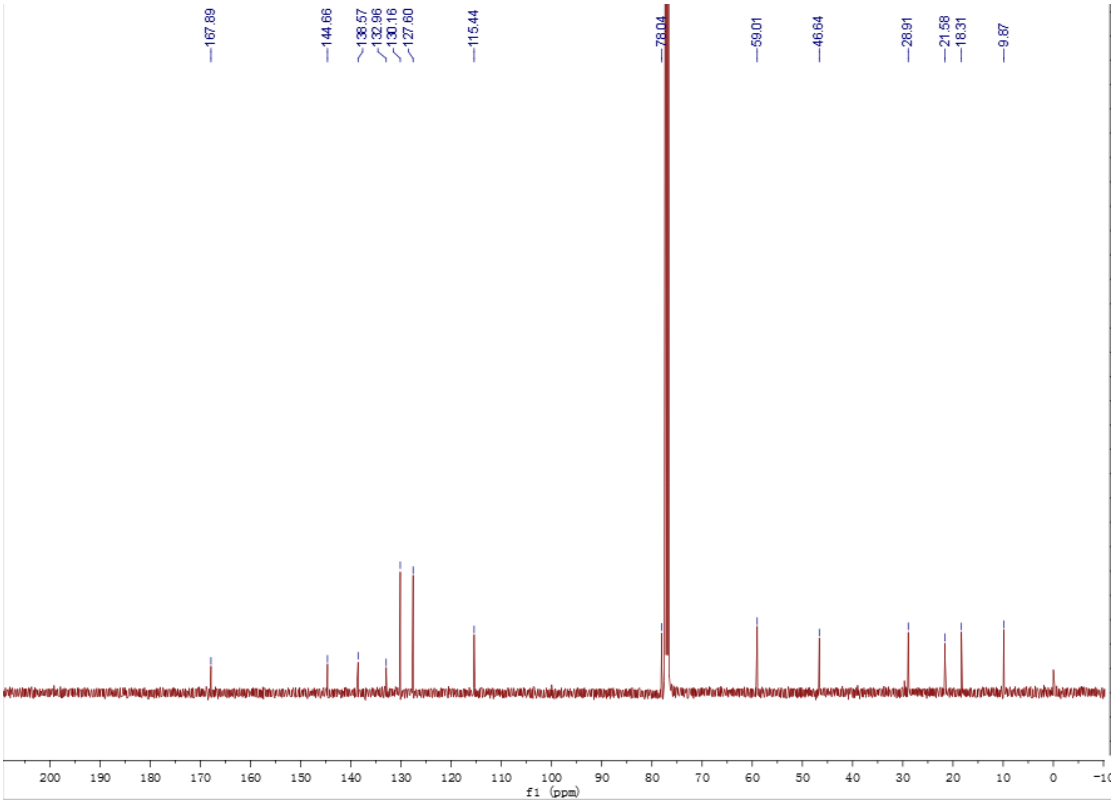
5.060
4.919
4.915
4.894
4.889
4.173
4.158
4.154
4.139
3.853
3.847
3.823
3.817
2.864
2.838
2.834
2.808
2.448
2.134
2.117
2.099
1.107
1.088
1.070
0.000
2.01
2.19
2.06
1.00
1.15
1.09
1.15
3.19
2.32
3.16
3.20
f1 (ppm)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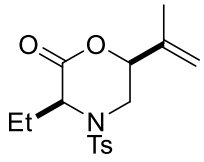
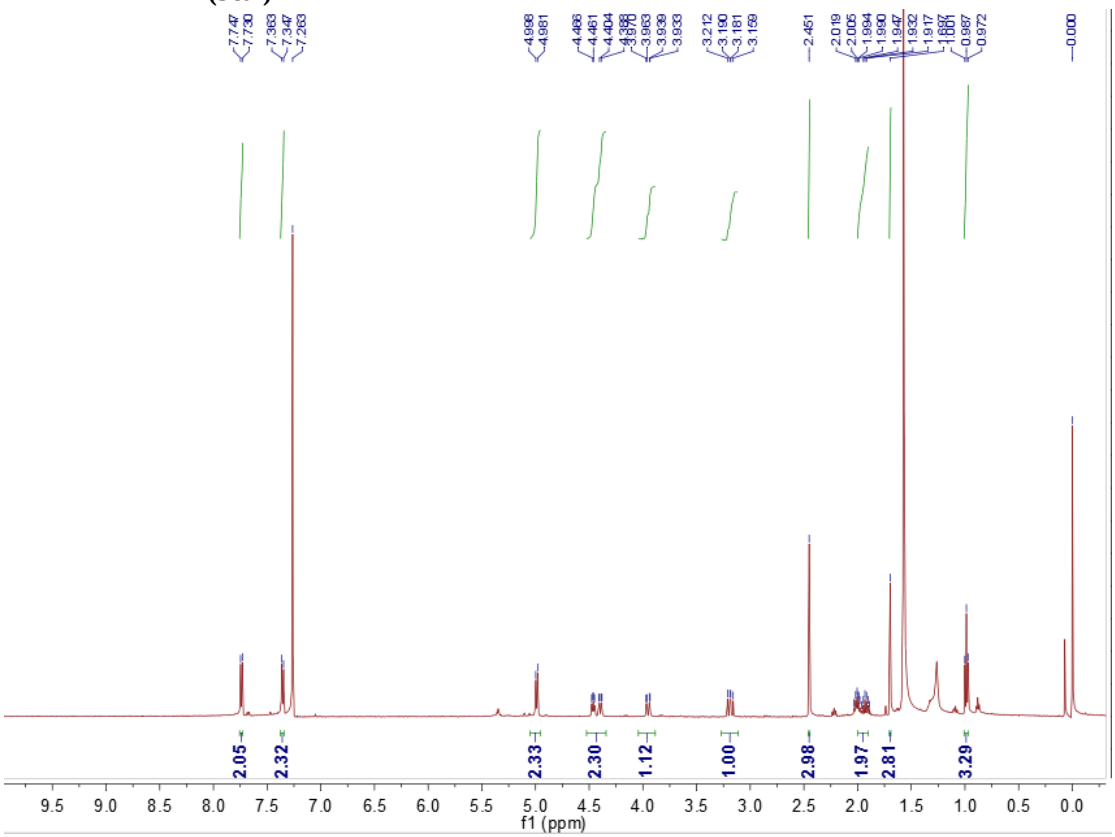
144.66
136.57
132.96
130.16
127.60
115.44
78.04
59.01
46.64
28.91
21.58
18.31
9.87
f1 (ppm)


O
O
Et
N
Ts

(5ca')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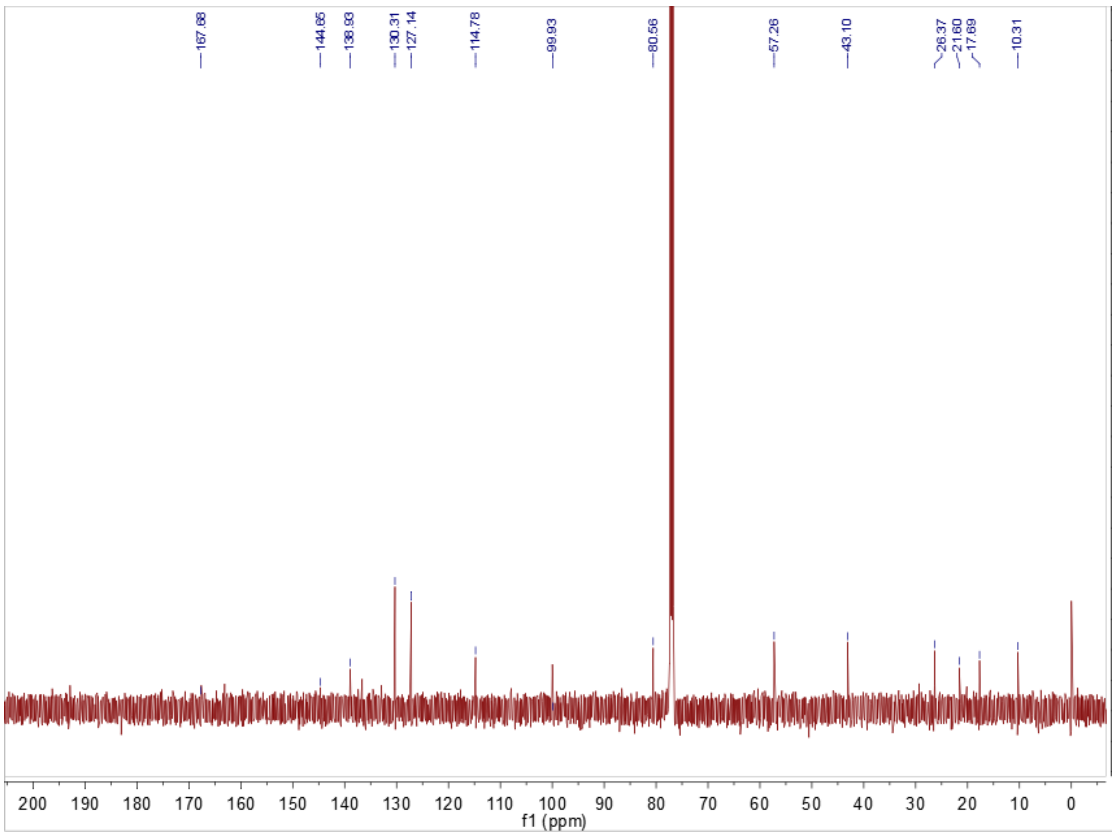
7.263
4.986
4.981
4.466
4.461
4.404
3.970
3.963
3.939
3.933
3.212
3.190
3.181
3.159
2.451
2.019
2.005
1.994
1.990
1.947
1.932
1.917
0.967
0.972
0.000
2.05
2.32
2.33
2.30
1.12
1.00
2.98
1.97
2.81
3.29
f1 (ppm)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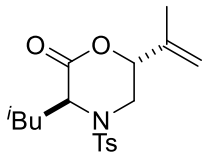
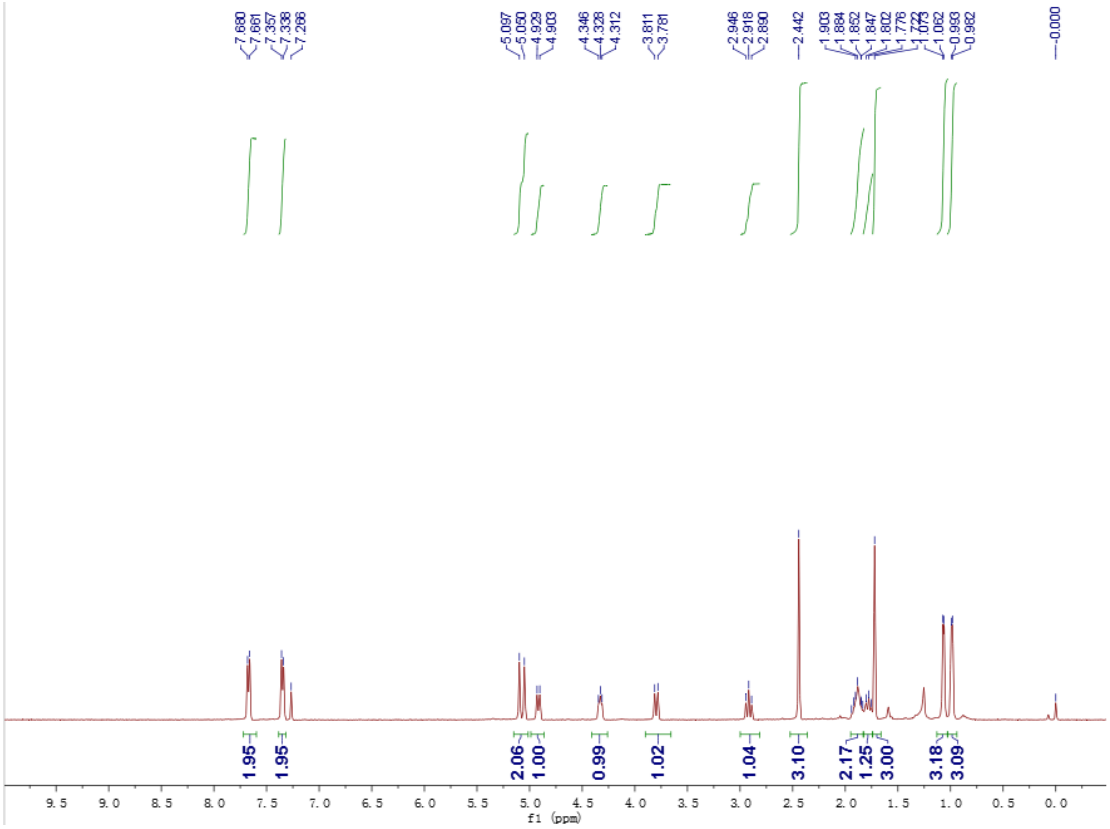
136.93
130.31
127.14
114.78
99.93
80.56
57.26
43.10
26.37
21.60
17.69
10.31
f1 (ppm)


O
O
iBu
N
Ts

(5da)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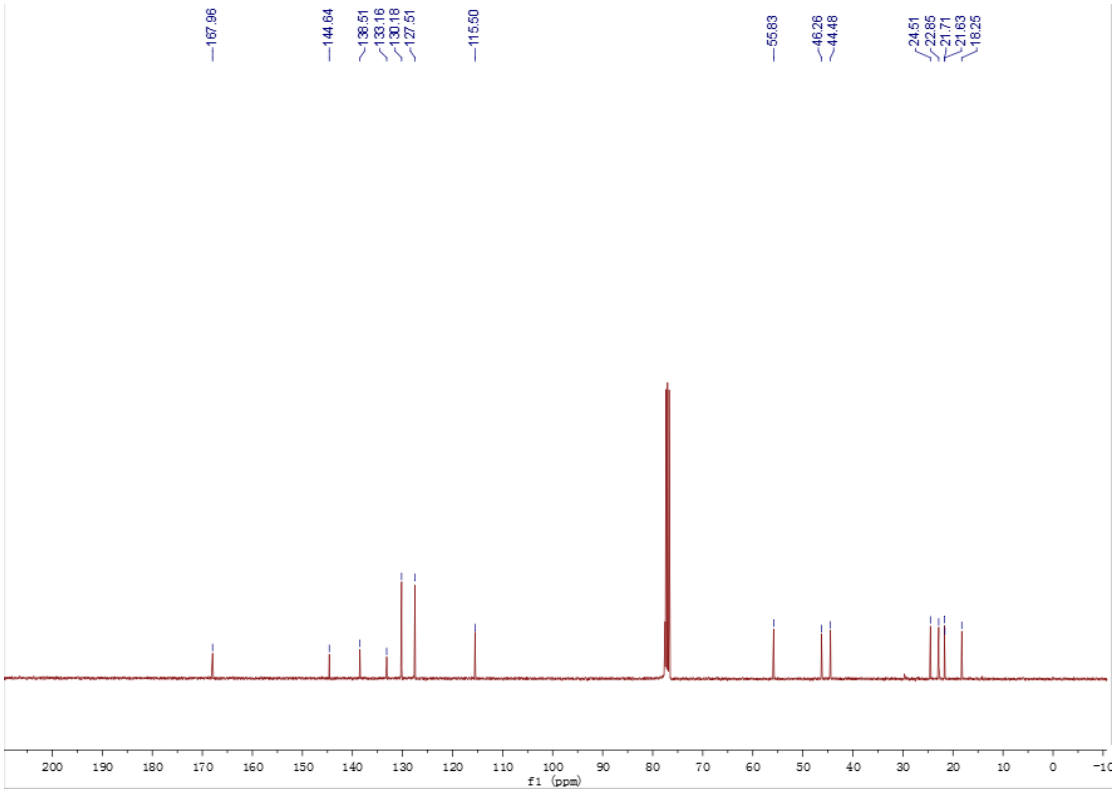
5.050
4.929
4.903
4.346
4.328
4.312
3.811
3.781
2.946
2.918
2.880
2.442
1.903
1.884
1.852
1.847
1.802
1.776
1.773
1.772
1.073
1.062
0.993
0.982
0.000
1.95
1.95
2.06
1.00
0.99
1.02
1.04
3.10
2.17
1.25
3.00
3.18
3.09
f1 (ppm)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136.51
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130.18
127.51
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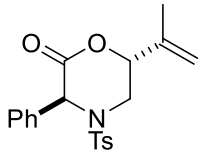
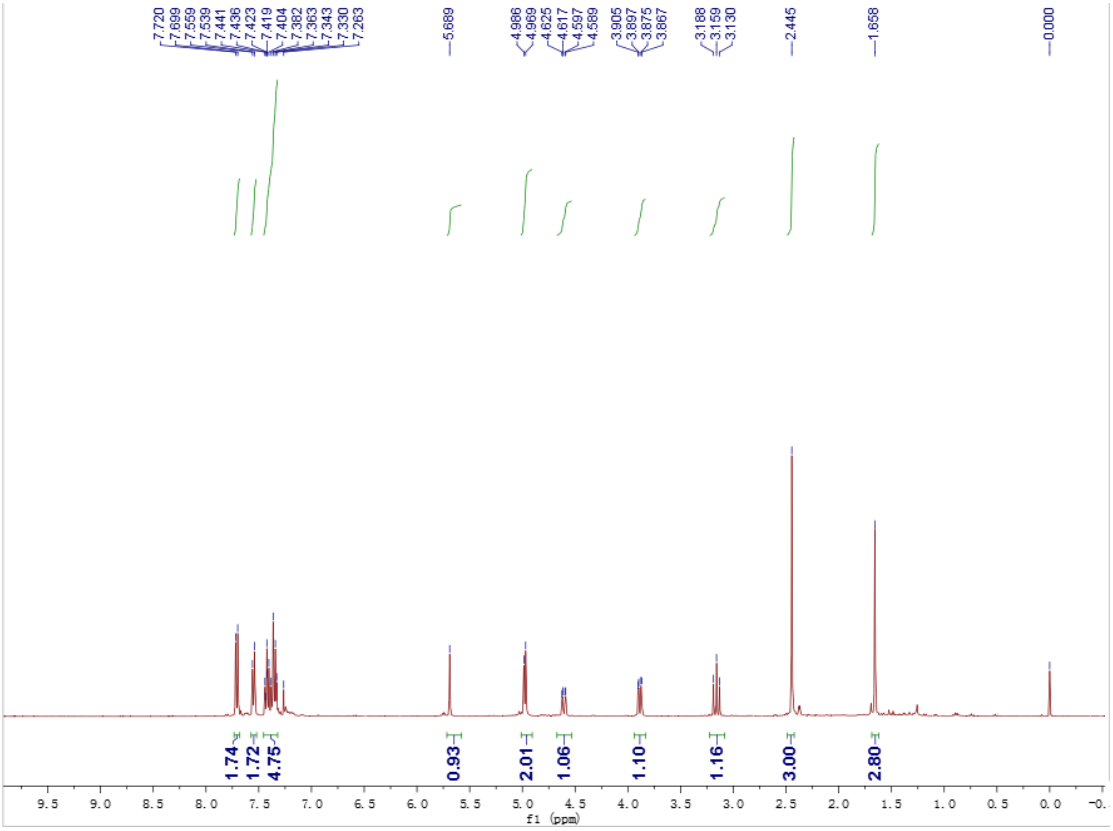
55.83
46.26
44.48
24.51
22.85
21.71
21.63
18.25
f1 (ppm)


O
O
Ph
N
Ts

(5ea)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7.436
7.423
7.419
7.404
7.382
7.363
7.343
7.330
7.263
5.689
4.986
4.969
4.625
4.617
4.597
4.589
3.905
3.897
3.875
3.867
3.188
3.159
3.130
2.445
1.658
0.000
1.74
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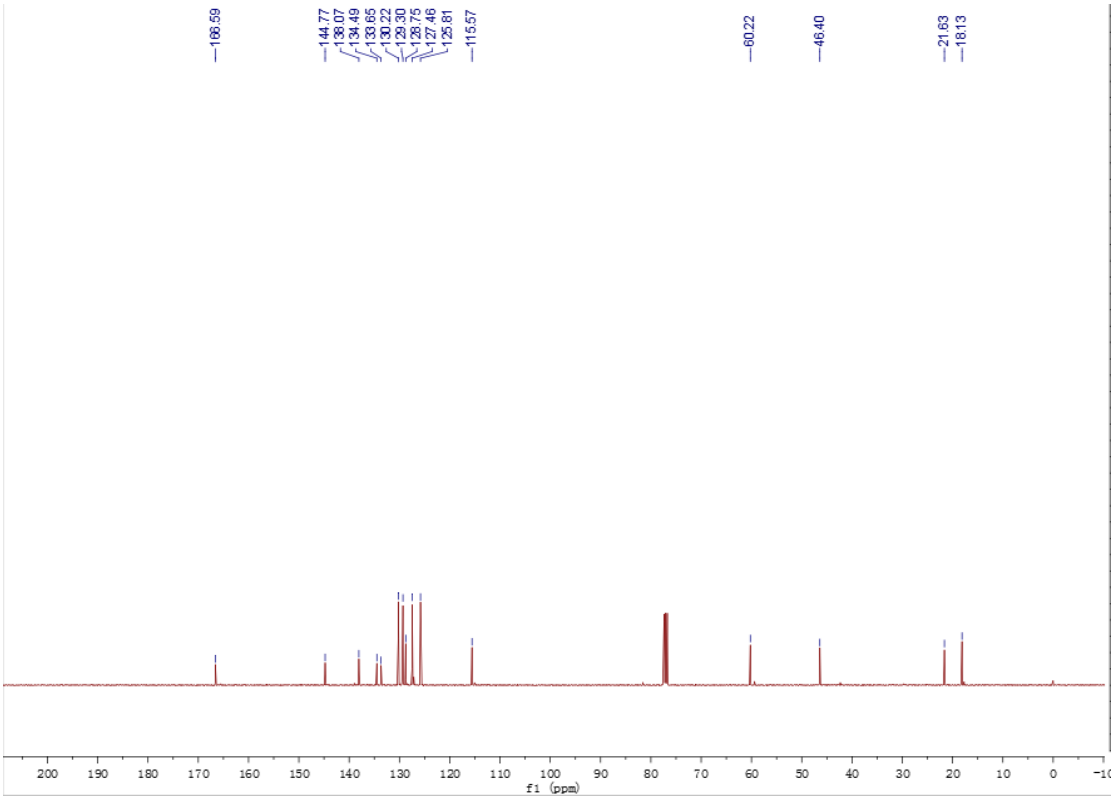
4.75
0.93
2.01
1.06
1.10
1.16
3.00
2.80
f1 (ppm)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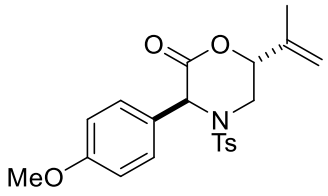
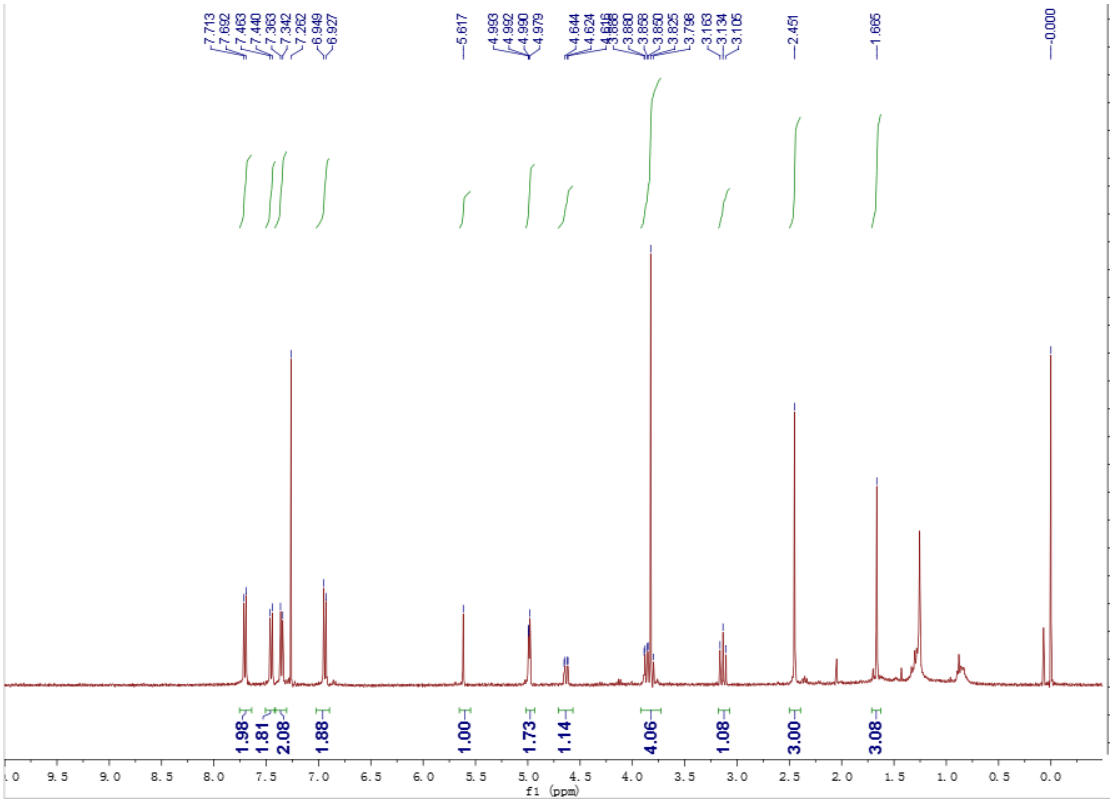
138.07
134.49
133.65
130.22
129.30
128.75
127.46
125.81
115.57
60.22
46.40
21.63
18.13
f1 (ppm)


O
O
N
Ts
MeO

(5fa)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6.927
5.617
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4.992
4.990
4.979
4.644
4.624
3.880
3.858
3.850
3.825
3.798
3.163
3.134
3.105
2.451
1.665
0.000
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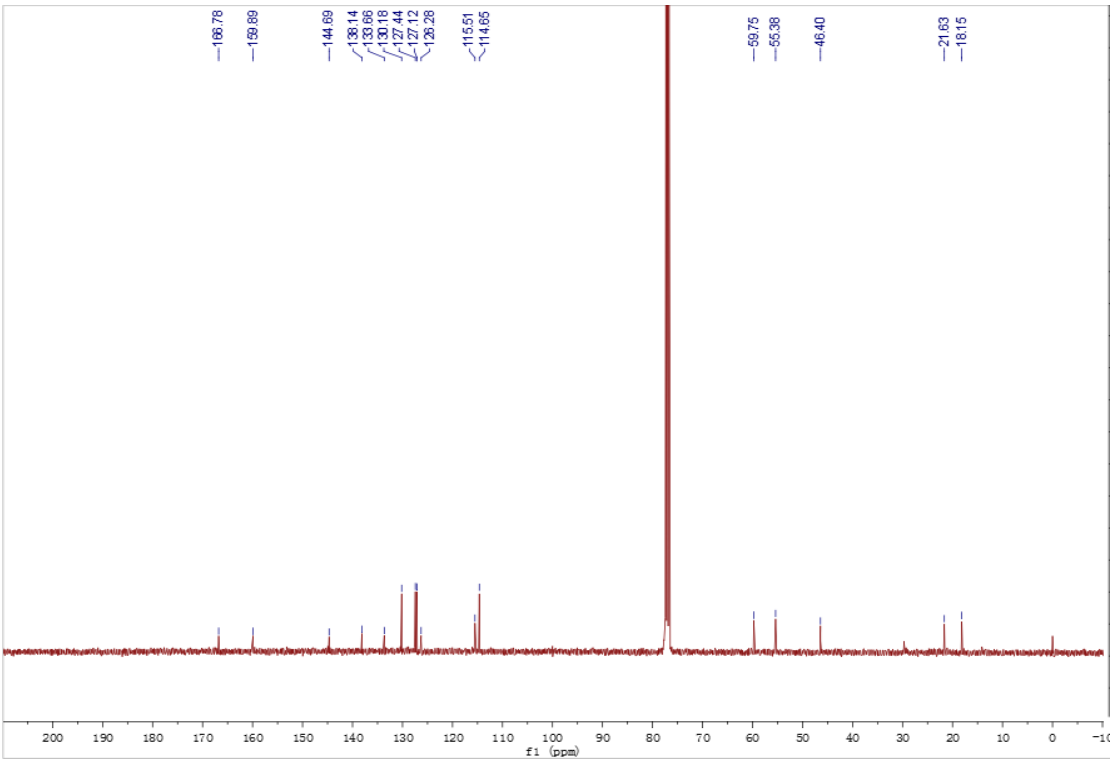
1.81
2.08
1.88
1.00
1.73
1.14
4.06
1.08
3.00
3.08
f1 (ppm)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138.14
133.66
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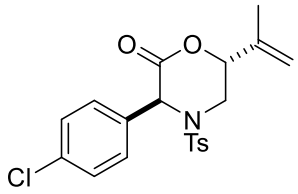
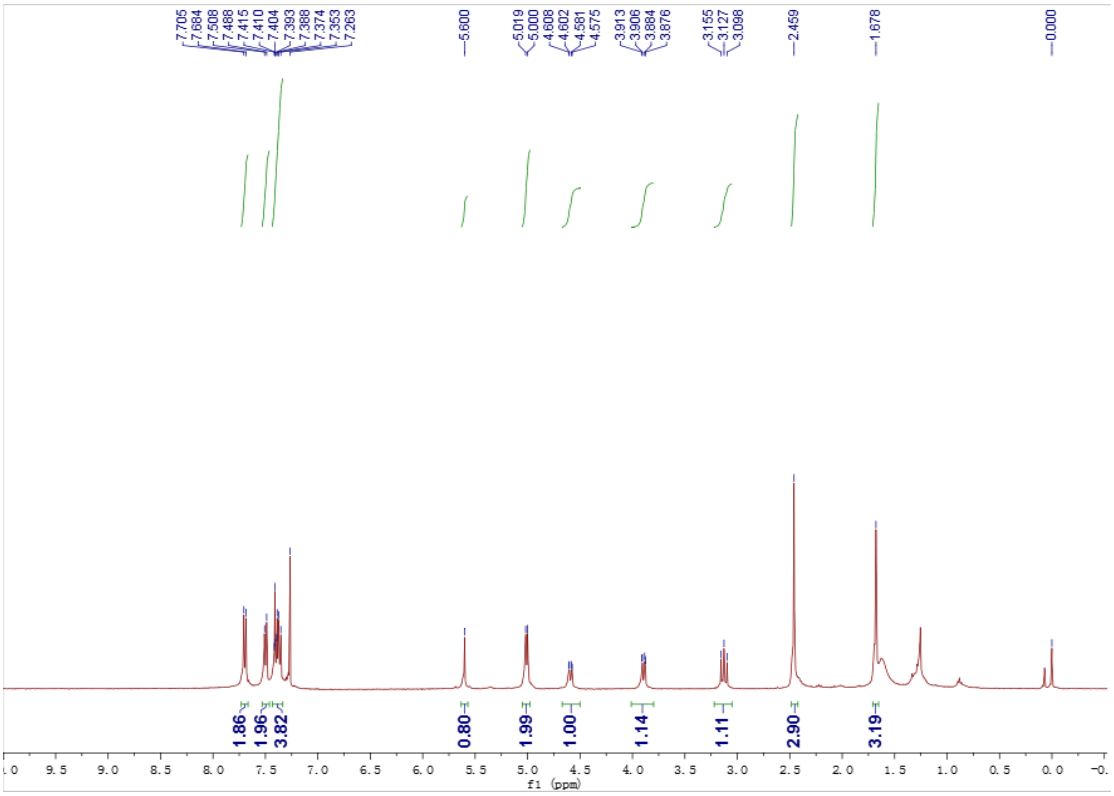
127.44
127.12
126.28
115.51
114.65
59.75
55.38
46.40
21.63
18.15
f1 (ppm)


O
O
N
Ts
Cl

(5ga)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7.353
7.263
5.600
5.019
5.000
4.608
4.602
4.581
4.575
3.913
3.906
3.884
3.876
3.155
3.127
3.098
2.459
1.678
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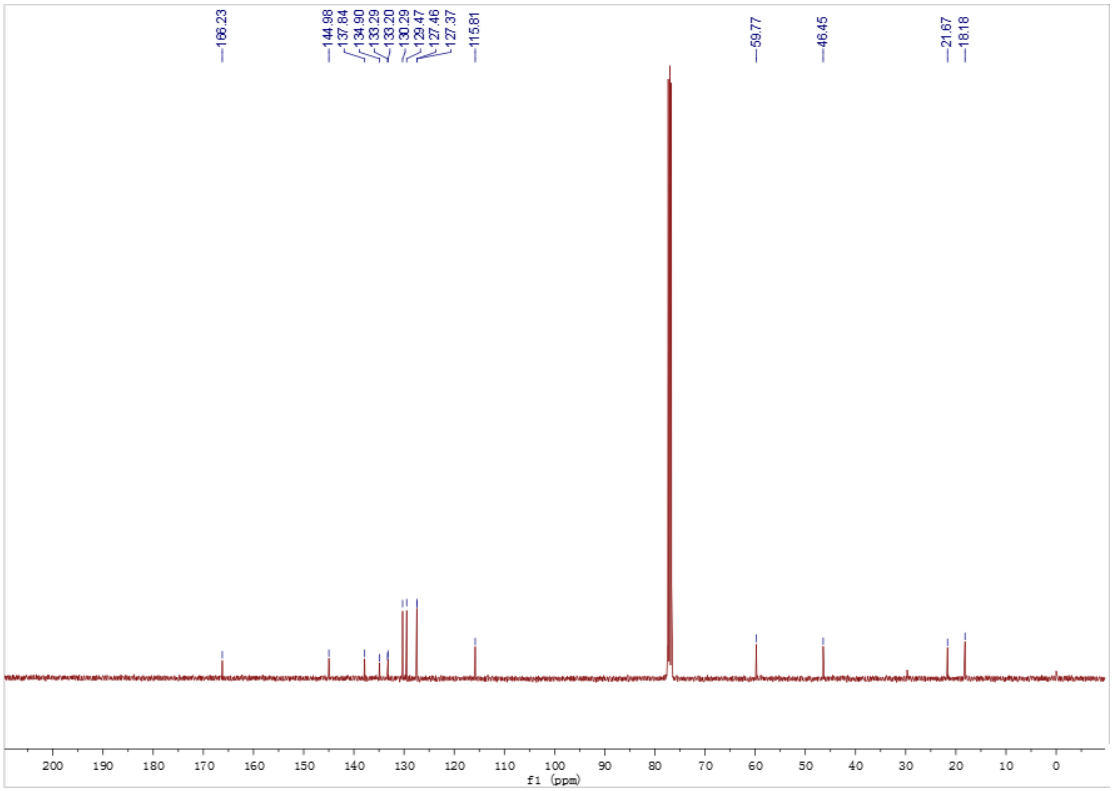
1.96
3.82
0.80
1.99
1.00
1.14
1.11
2.90
3.19
f1 (ppm)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137.84
134.90
133.29
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129.47
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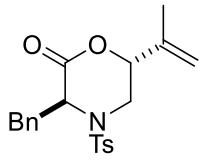
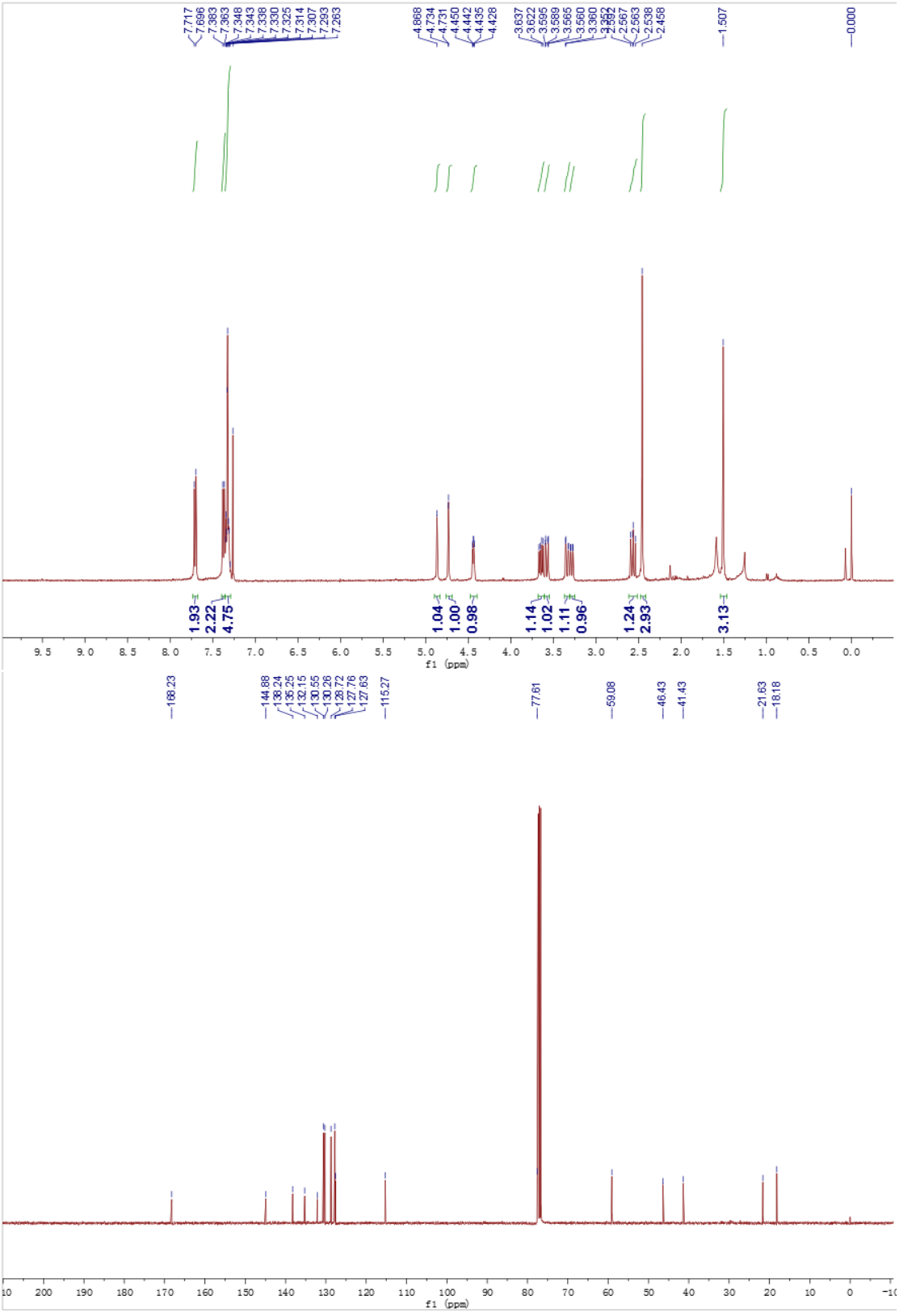
127.37
115.81
59.77
46.45
21.67
18.18
f1 (ppm)


O
O
Bn
N
Ts

(5ha)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7.314
7.307
7.293
7.263
4.868
4.734
4.731
4.450
4.442
4.435
4.428
3.637
3.622
3.595
3.589
3.565
3.560
3.360
2.567
2.563
2.538
2.458
1.507
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2.22
4.75
1.04
1.00
0.98
1.14
1.02
1.11
0.96
1.24
2.93
3.13
f1 (ppm)
168.23
144.88
138.24
135.25
132.15
130.55
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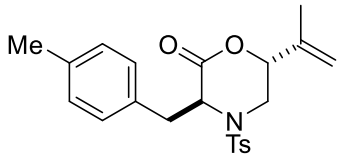
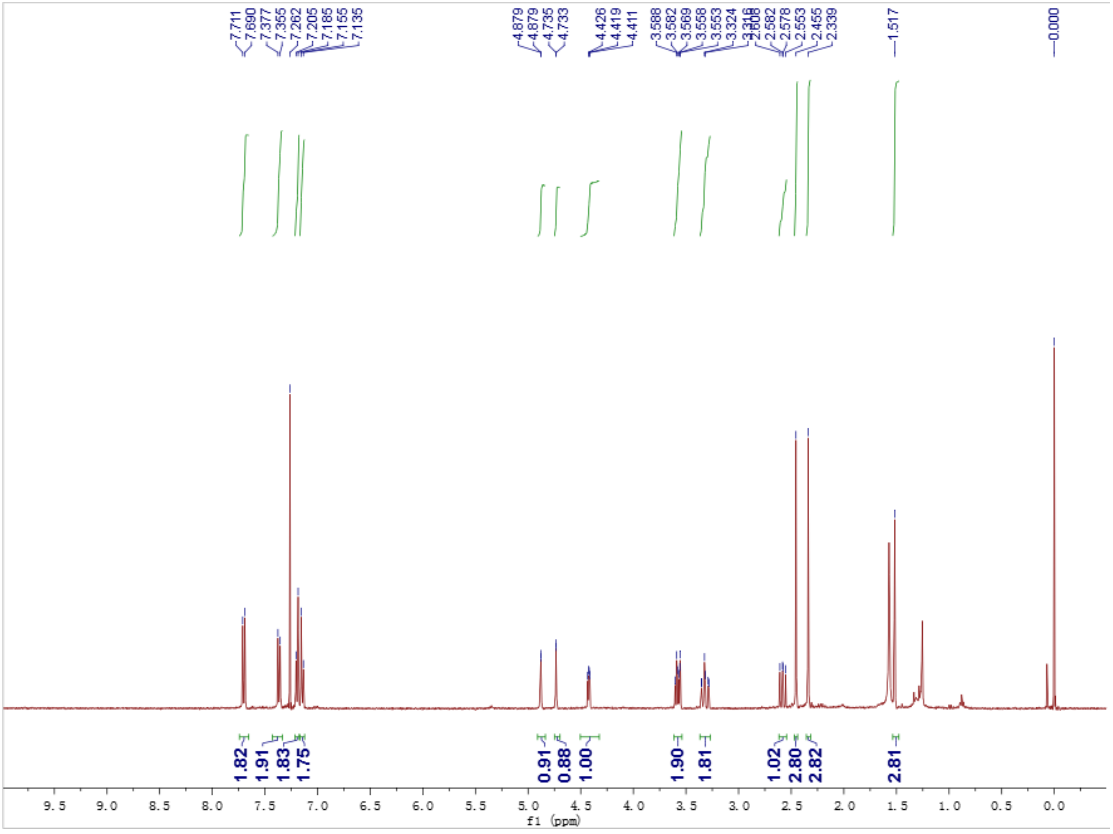
115.27
77.61
59.08
46.43
41.43
21.63
18.18
f1 (ppm)


Me
O
O
N
Ts

(5ia)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7.205
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7.155
7.135
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4.879
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4.733
4.426
4.419
4.411
3.588
3.582
3.569
3.558
3.553
3.324
2.592
2.578
2.562
2.553
2.455
2.339
1.517
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1.82
1.91
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0.88
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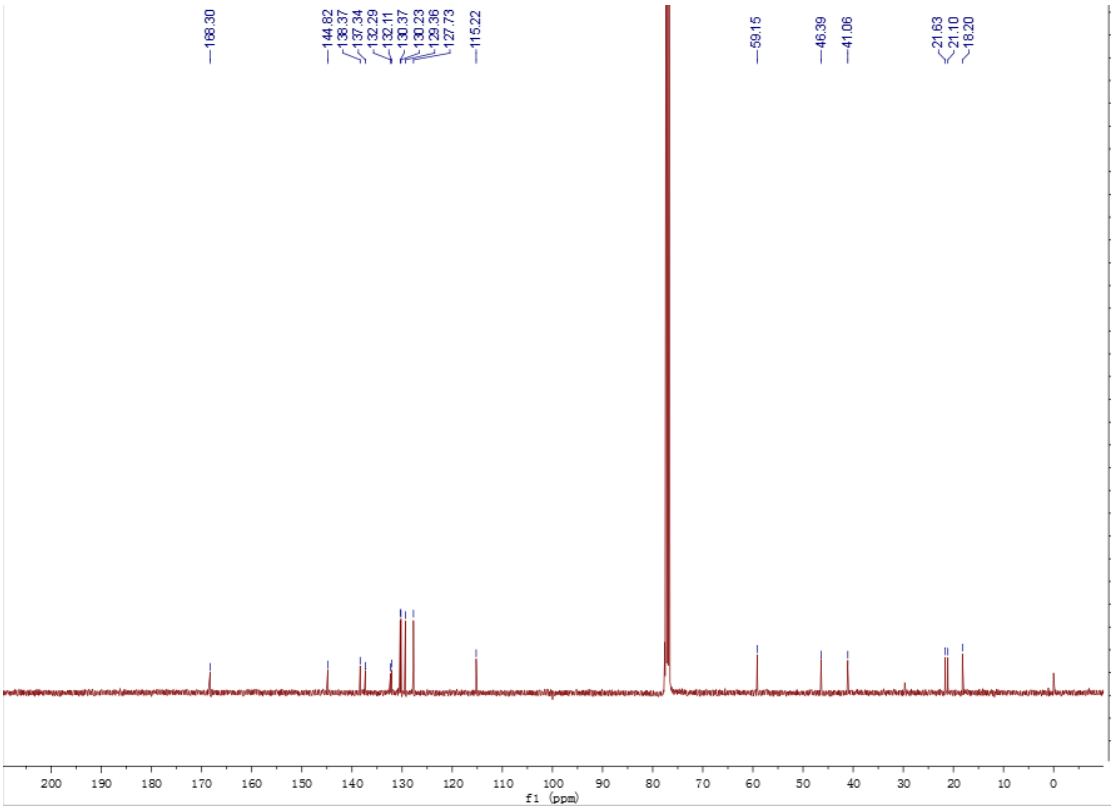
1.81
1.02
2.80
2.82
2.81
f1 (ppm)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137.34
132.29
132.11
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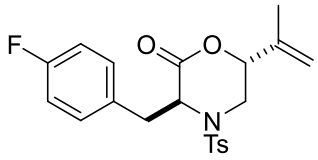
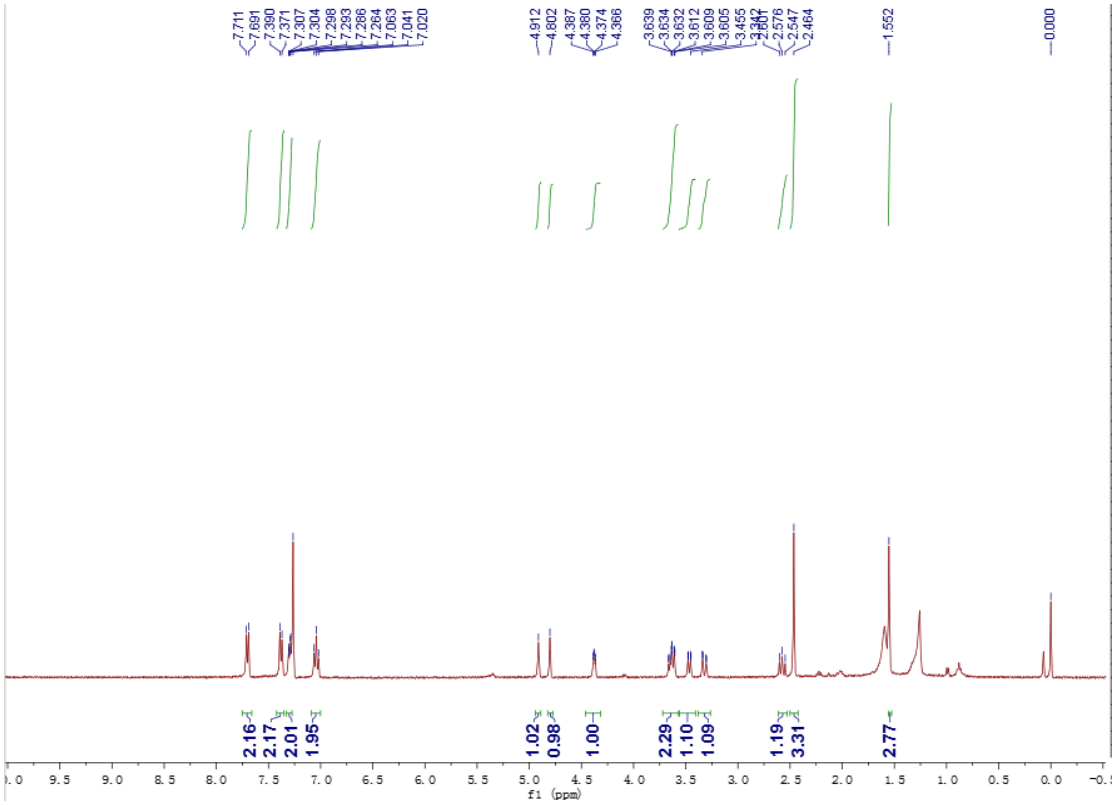
130.23
129.36
127.73
115.22
59.15
46.39
41.06
21.63
21.10
18.20
f1 (ppm)


F
O
O
N
Ts

(5ja)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7.293
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7.264
7.063
7.041
7.020
4.912
4.802
4.387
4.380
4.374
4.366
3.639
3.634
3.632
3.612
3.609
3.605
3.455
2.576
2.547
2.464
1.552
0.000
2.16
2.17
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1.95
1.02
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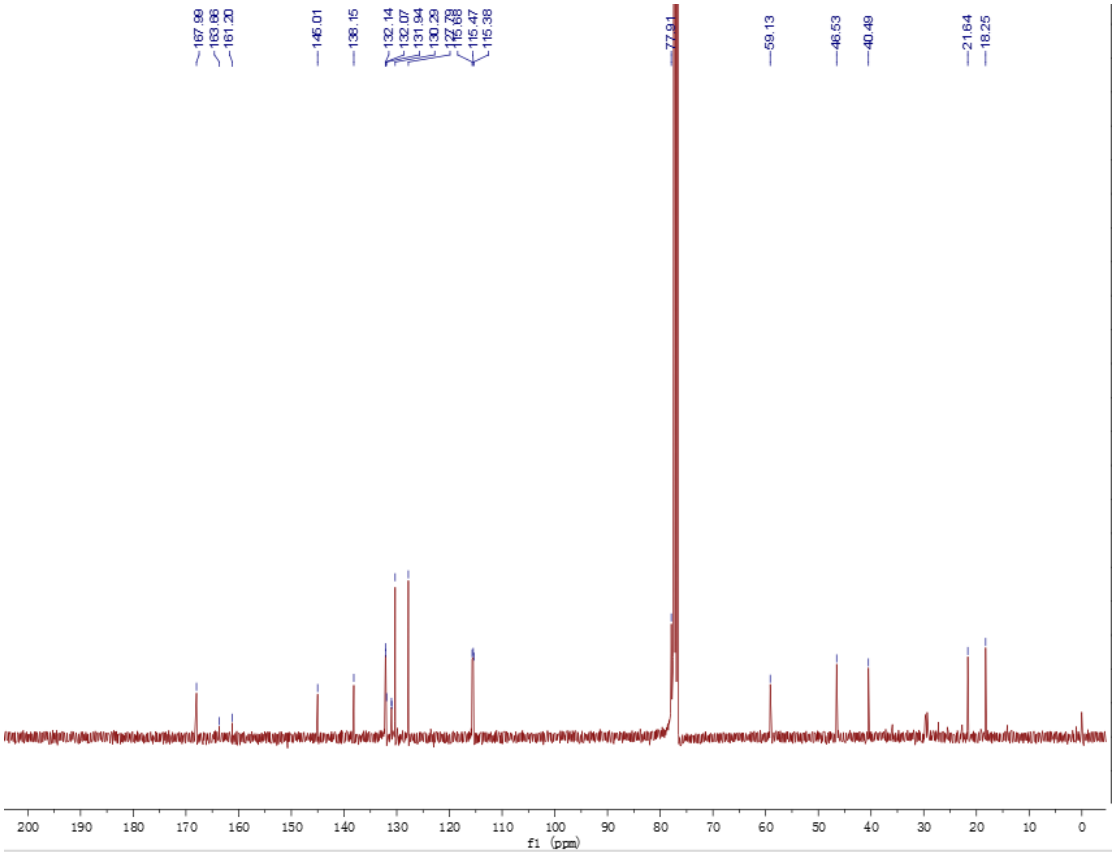
1.00
2.29
1.10
1.09
1.19
3.31
2.77
f1 (ppm)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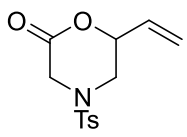
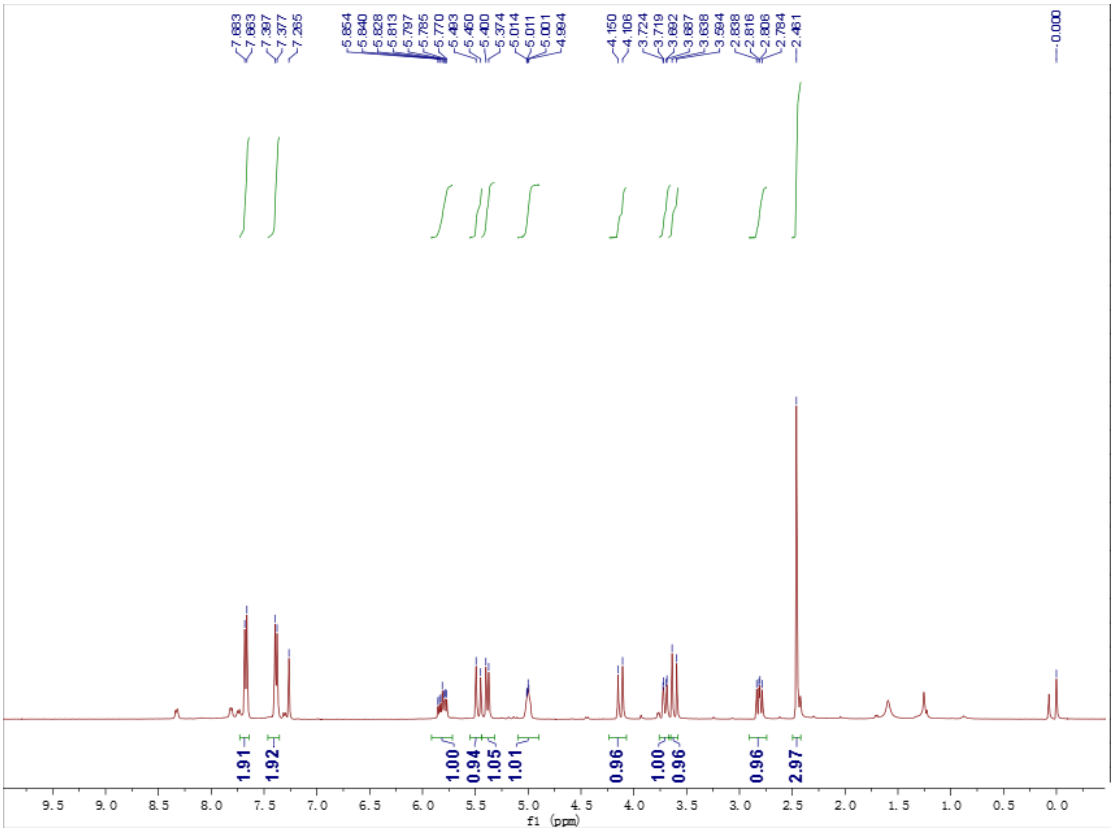
132.14
132.07
131.94
130.29
127.79
127.68
115.47
115.38
77.91
59.13
46.53
40.49
21.64
18.25
f1 (ppm)


O
O
N
Ts

(5ab)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7.285
5.854
5.840
5.828
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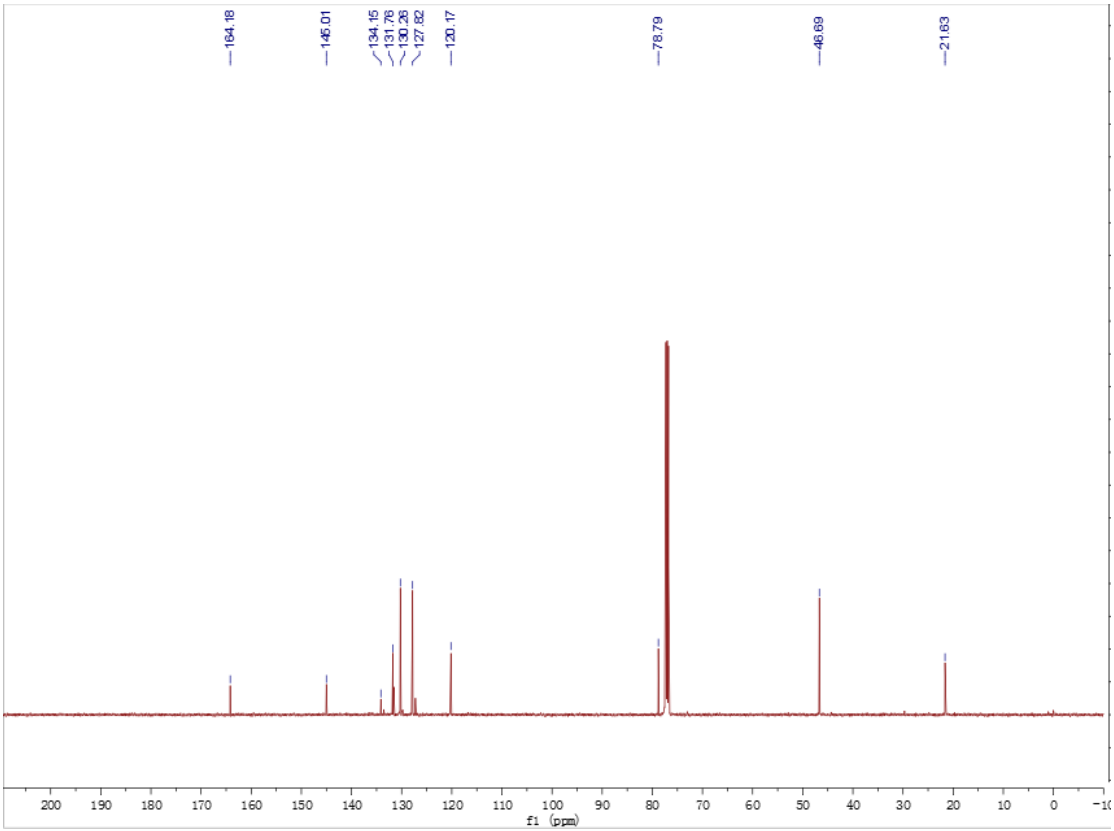
5.797
5.785
5.770
5.483
5.460
5.400
5.374
5.014
5.011
5.001
4.994
4.150
4.106
3.724
3.719
3.692
3.687
3.638
3.594
2.838
2.816
2.806
2.784
2.461
0.000
1.91
1.92
1.00
0.94
1.05
1.01
0.96
1.00
0.96
0.96
2.97
f1 (ppm)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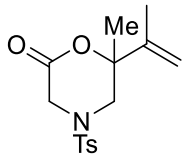
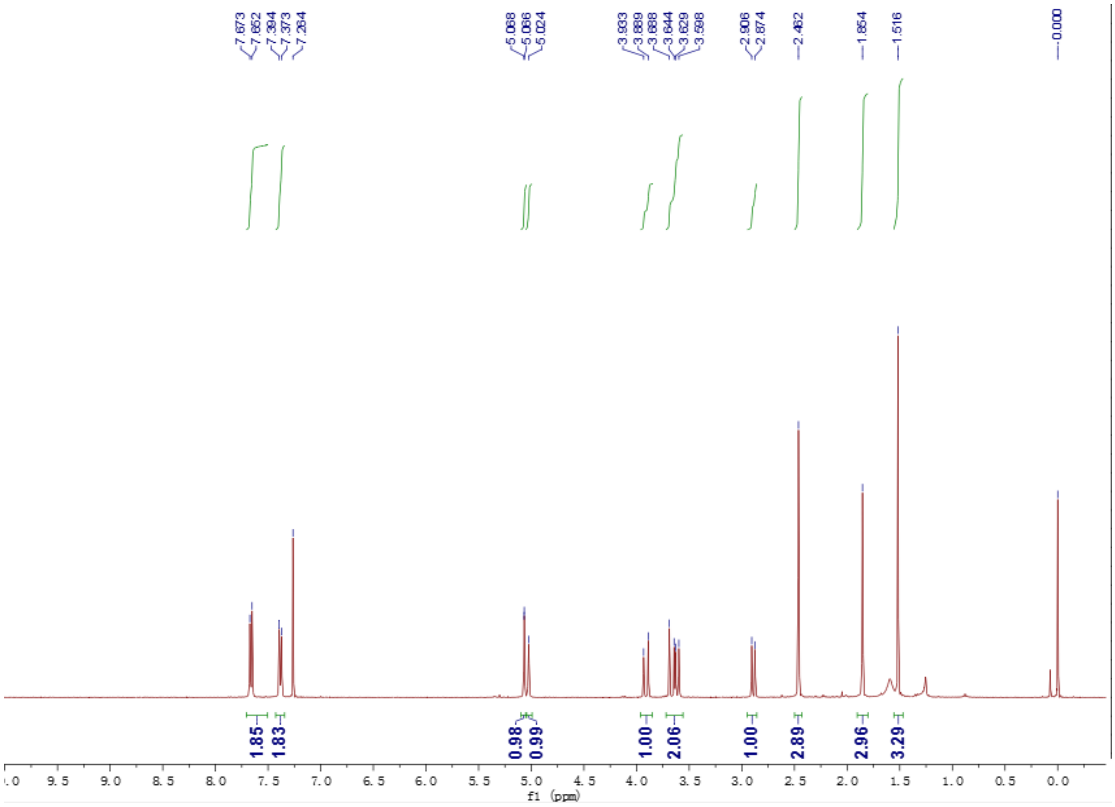
145.01
134.15
131.76
130.26
127.82
120.17
78.79
46.69
21.63
f1 (ppm)


Me
O
O
N
Ts

(5ac)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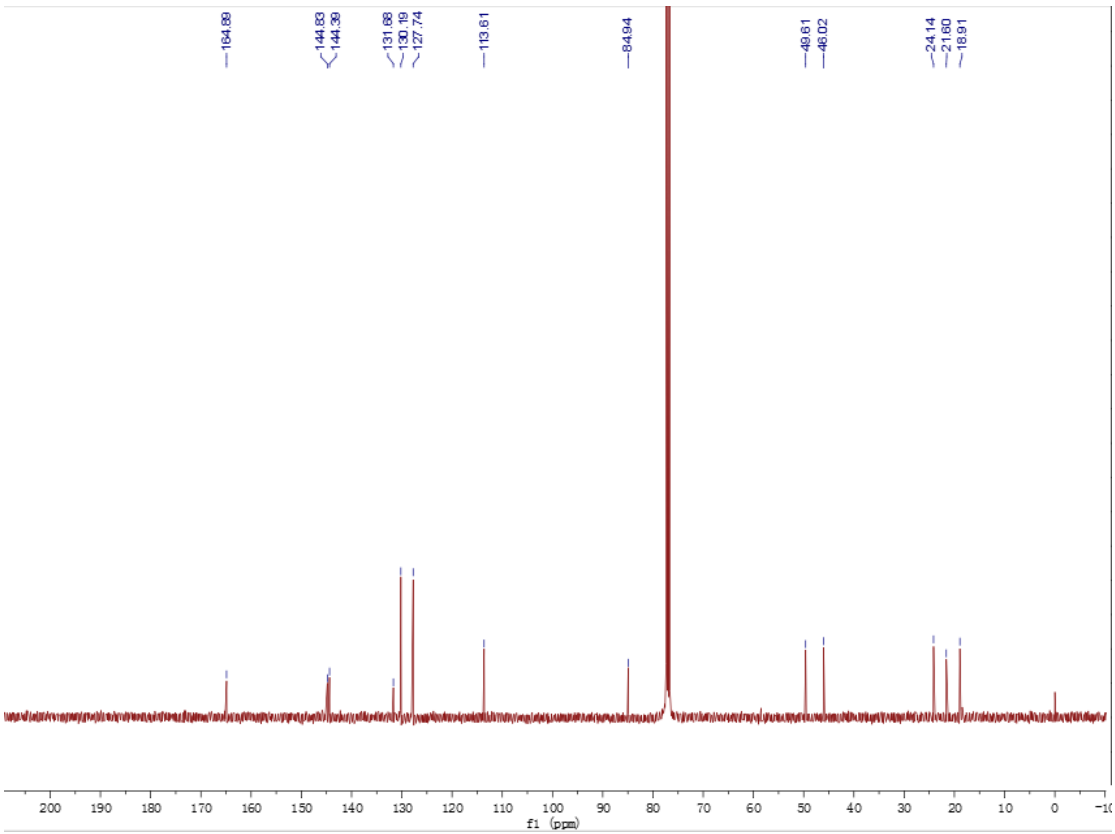
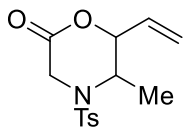
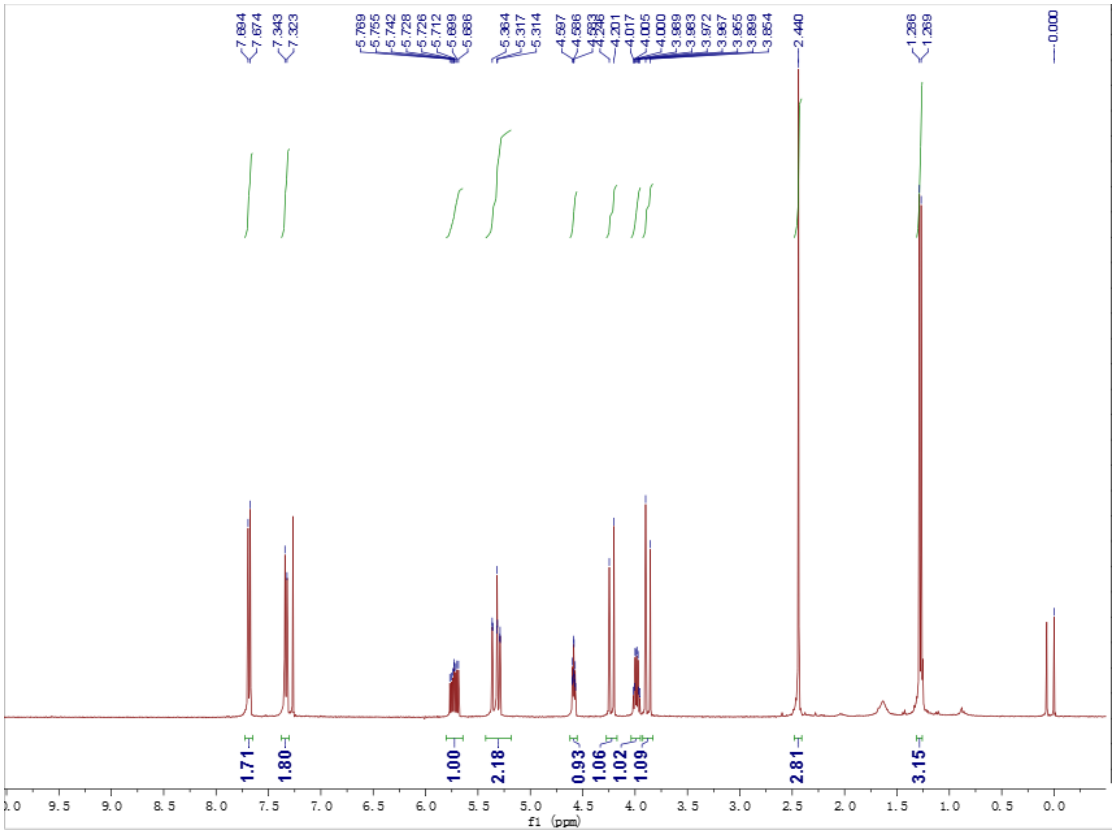
7.394
7.373
7.264
5.008
5.006
5.024
3.933
3.889
3.888
3.644
3.629
3.598
2.906
2.874
2.462
1.864
1.516
0.000
1.85
1.83
0.98
0.99
1.00
2.06
1.00
2.89
2.96
3.29
f1 (ppm)


164.89
144.83
144.39
131.68
130.19
127.74
113.61
84.94
49.61
46.02
24.14
21.60
18.91
f1 (ppm)


O
O
N
Ts
Me

(5ad)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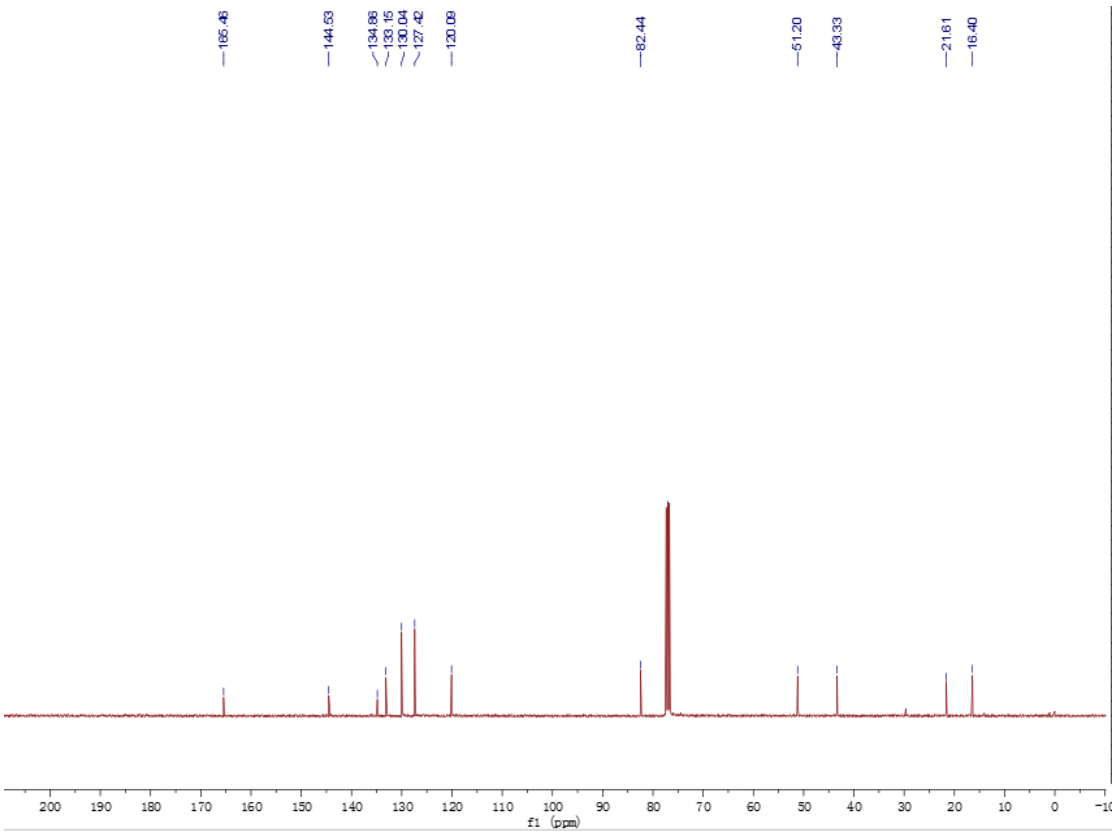
7.674
7.343
7.323
5.769
5.755
5.742
5.728
5.726
5.712
5.689
5.686
5.364
5.317
5.314
4.697
4.686
4.201
4.017
4.005
4.000
3.969
3.963
3.972
3.967
3.955
3.899
3.854
2.440
1.286
1.269
0.000
1.71
1.80
1.00
2.18
0.93
1.06
1.02
1.09
2.81
3.15
f1 (ppm)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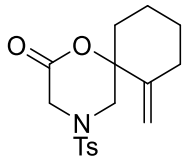
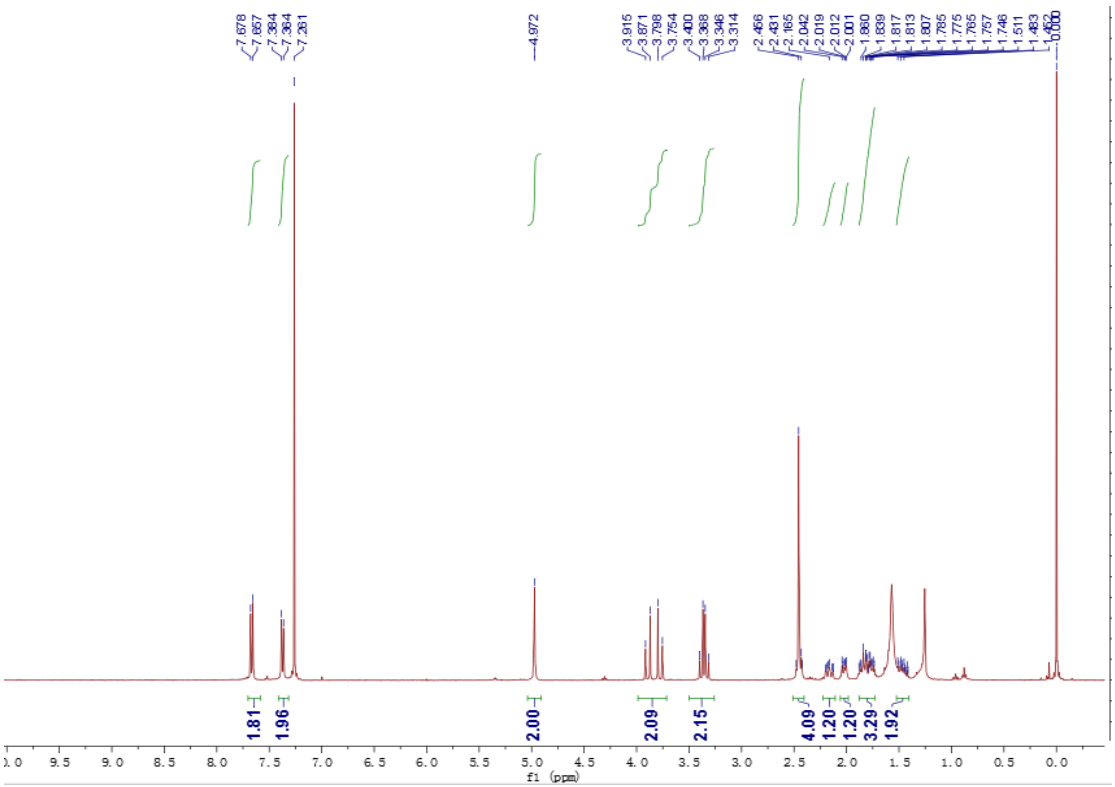
144.53
134.86
133.15
130.04
127.42
120.09
82.44
51.20
43.33
21.61
16.40
f1 (ppm)


O
O
N
Ts

(5ae)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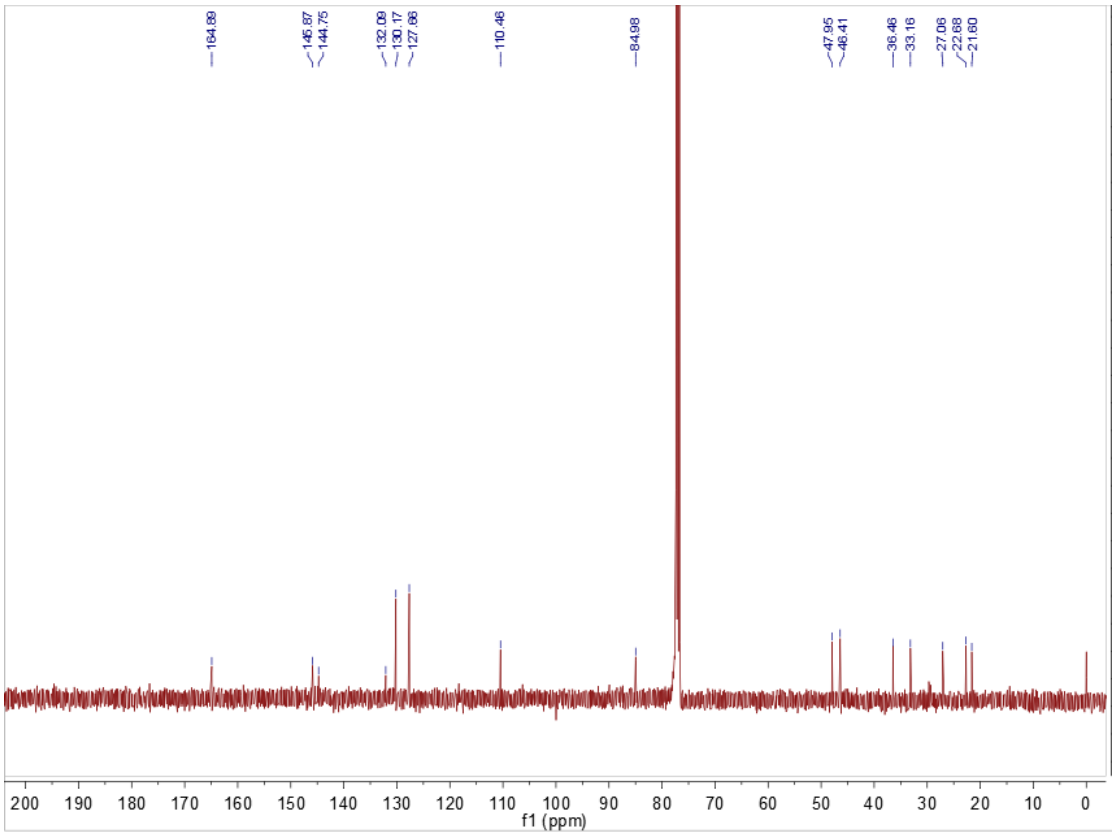
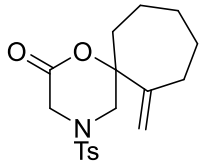
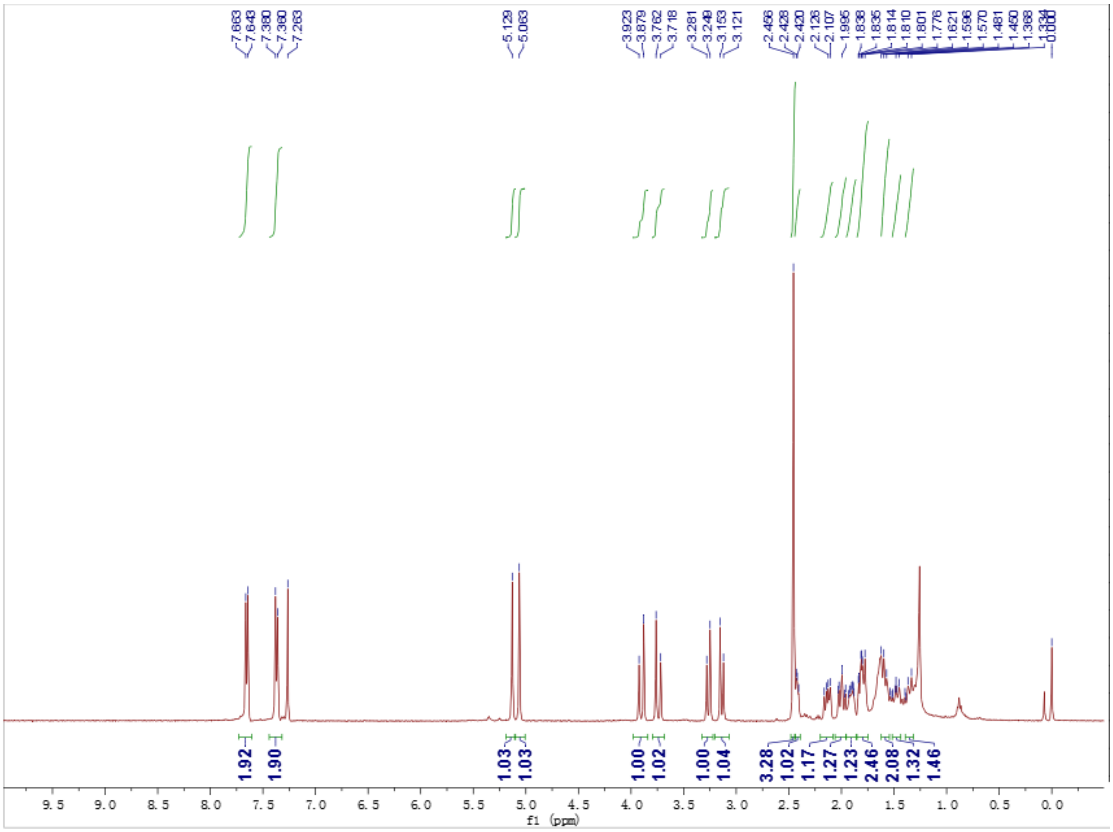
7.364
7.281
4.972
3.915
3.871
3.798
3.754
3.400
3.368
3.346
3.314
2.456
2.431
2.165
2.042
2.019
2.012
2.001
1.880
1.839
1.817
1.813
1.807
1.785
1.775
1.765
1.757
1.746
1.511
1.483
0.000
1.81
1.96
2.00
2.09
2.15
4.09
1.20
1.20
3.29
1.92
f1 (ppm)


164.89
145.87
144.75
132.09
130.17
127.86
110.46
84.98
47.95
46.41
36.46
33.16
27.06
22.68
21.60
f1 (ppm)



(5af)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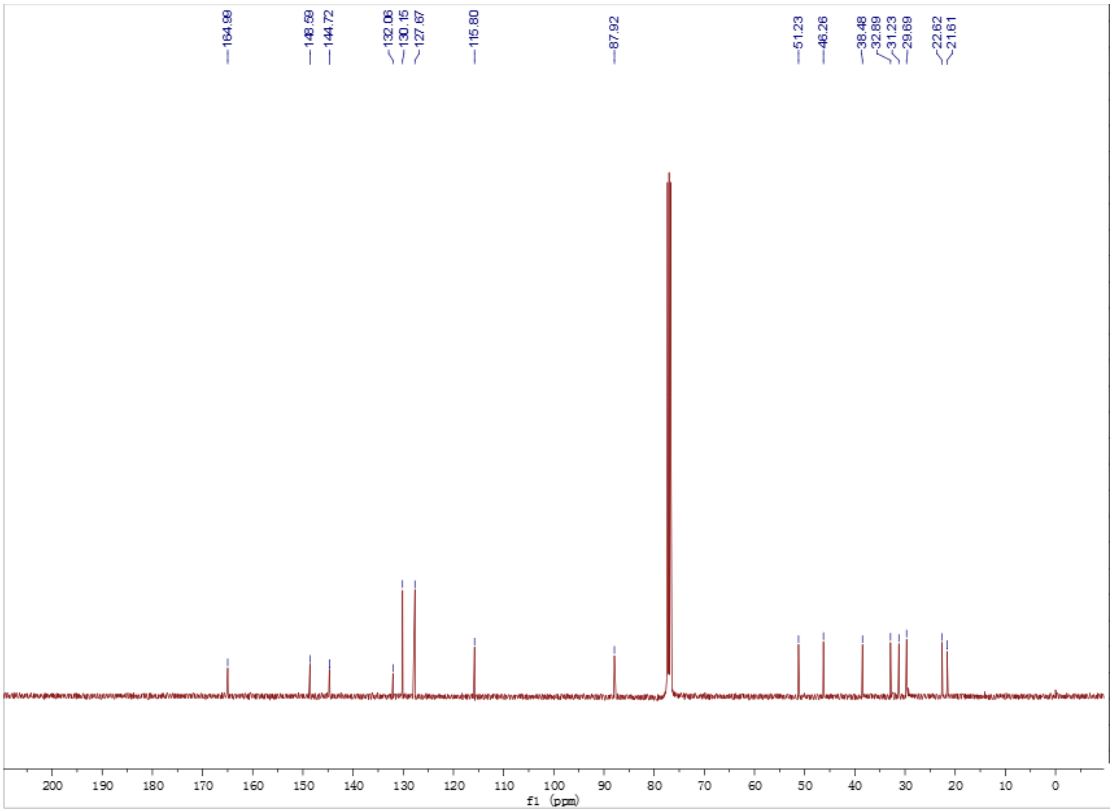
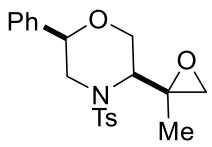
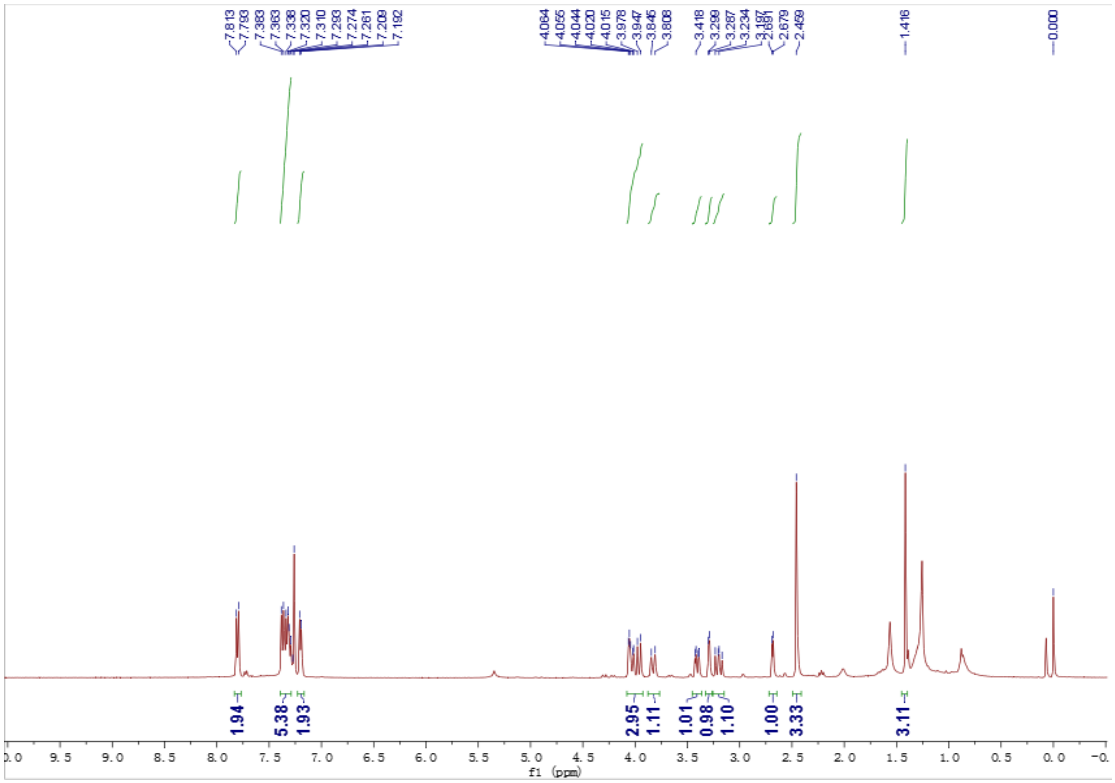
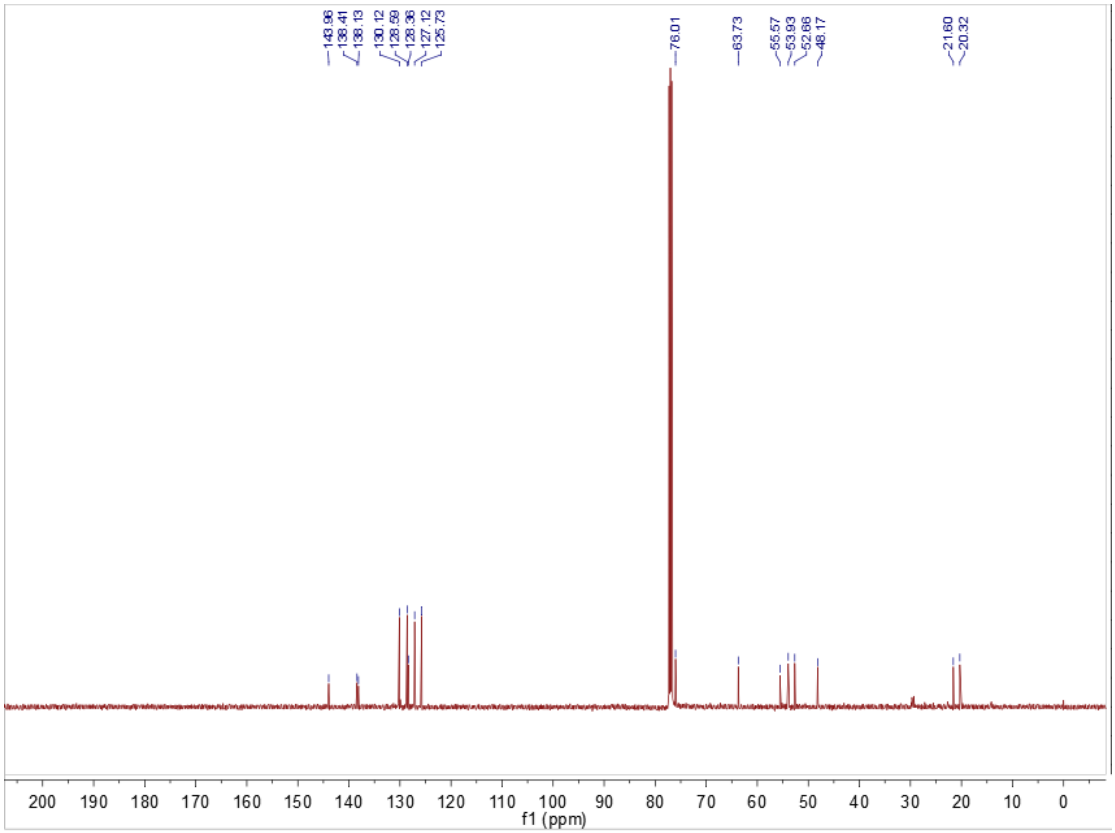
7.360
7.360
7.263
5.129
5.063
3.923
3.879
3.762
3.718
3.281
3.249
3.153
3.121
2.466
2.428
2.420
2.126
2.107
1.995
1.838
1.835
1.814
1.810
1.801
1.776
1.621
1.596
1.570
1.481
1.450
1.368
1.334
0.000
1.92
1.90
1.03
1.03
1.00
1.02
1.00
1.04
3.28
1.02
1.17
1.27
1.23
2.46
2.08
1.32
1.46
f1 (ppm)

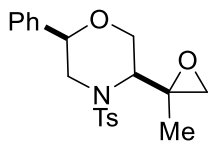

164.99
148.69
144.72
132.06
130.15
127.67
115.80
87.92
51.23
46.26
38.48
32.89
31.23
29.69
22.62
21.61
f1 (ppm)



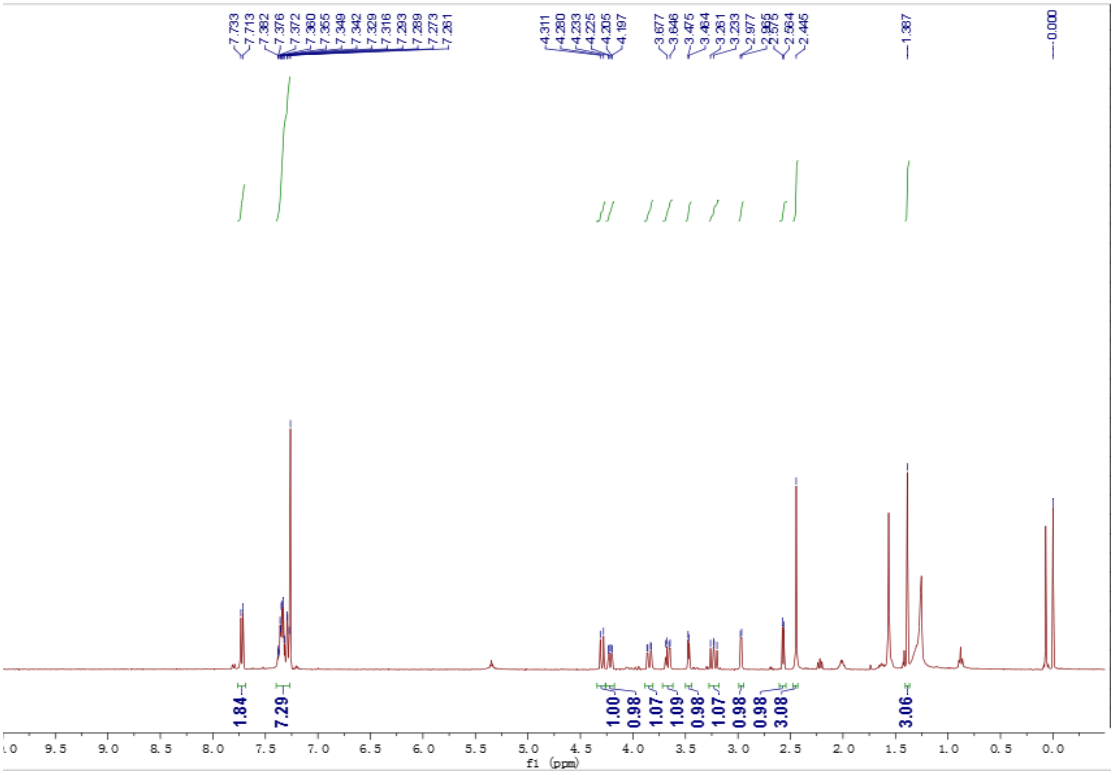
(6, major isomer)

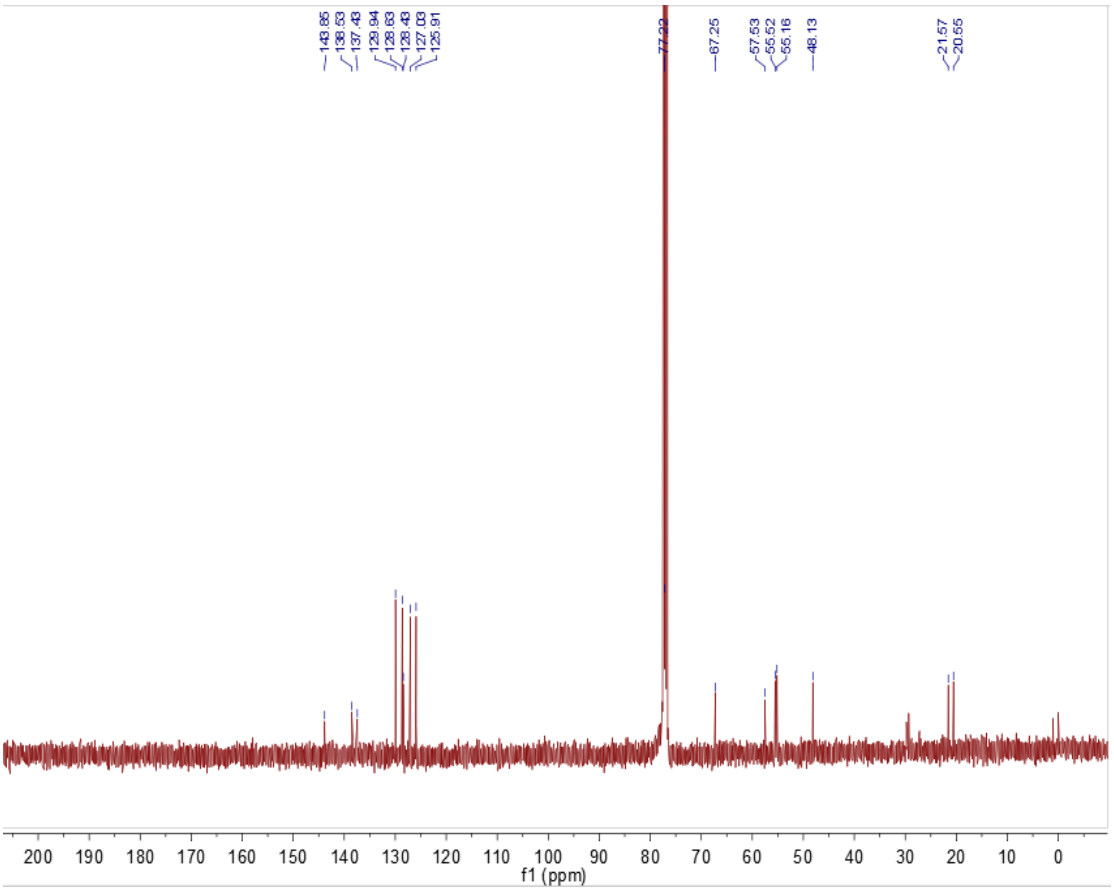


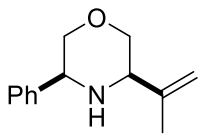




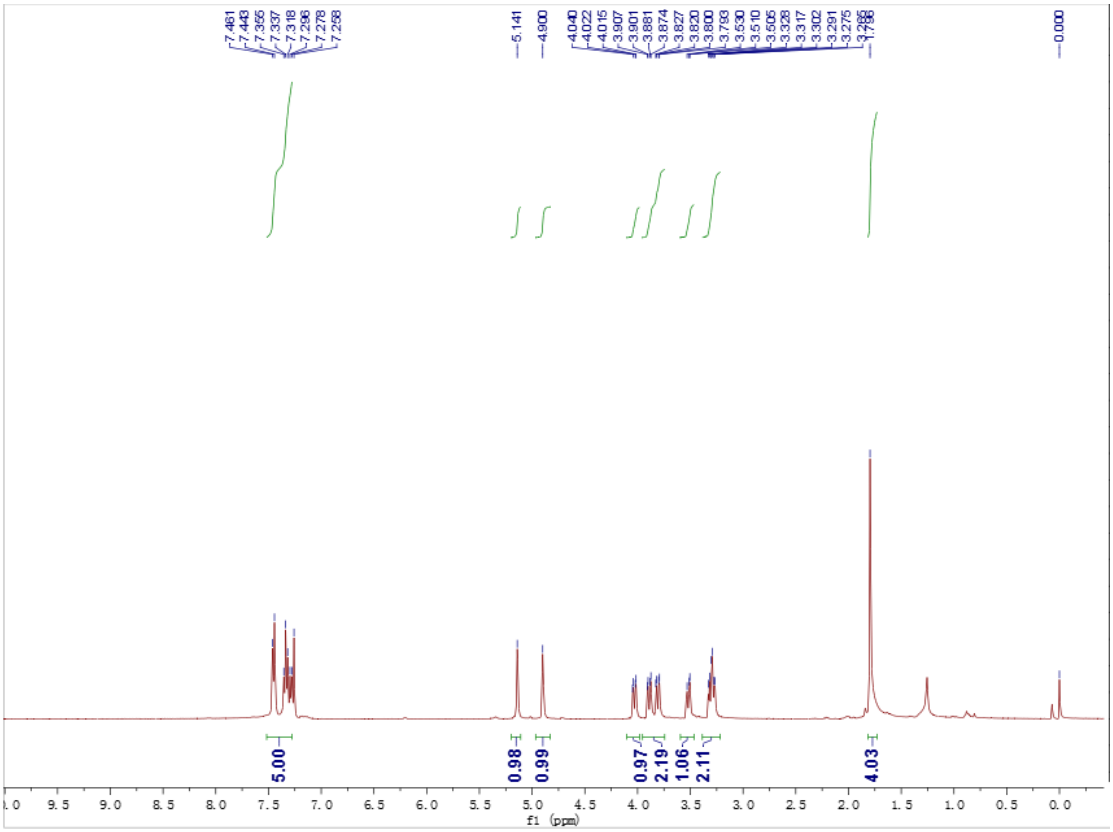
(6, minor isomer)






O
Ph
N
H

(7)


7.461
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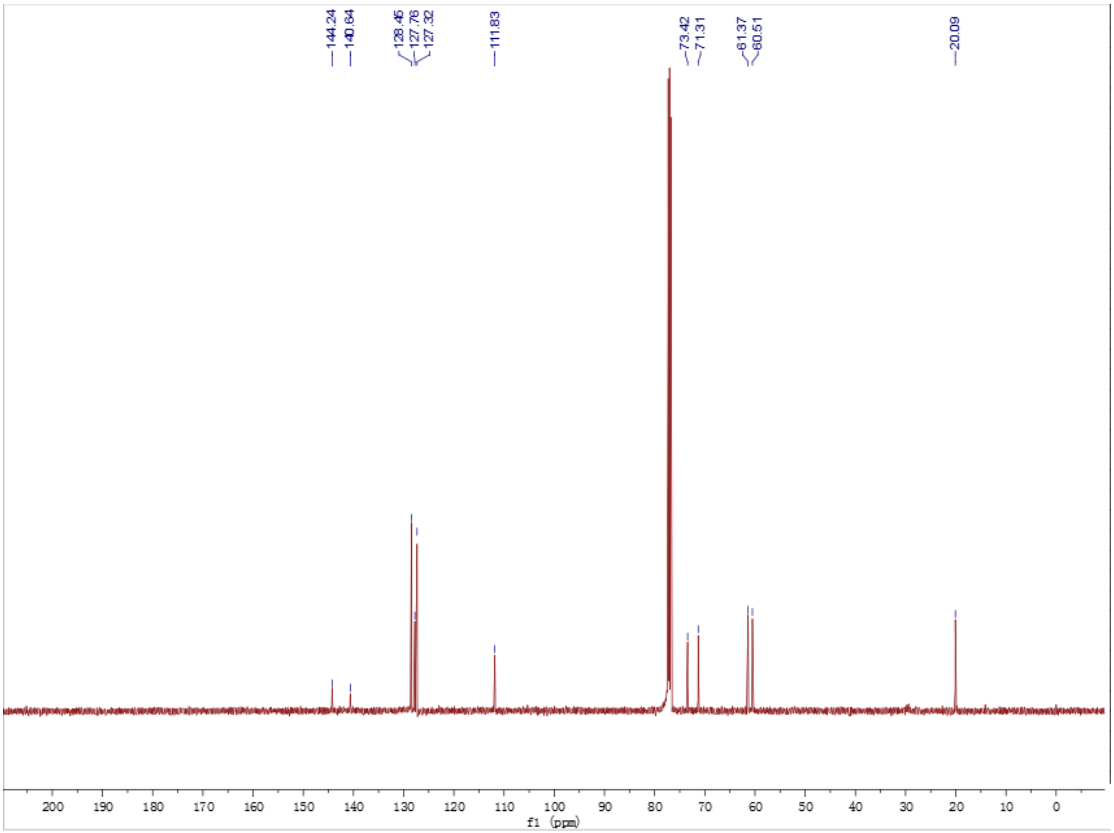
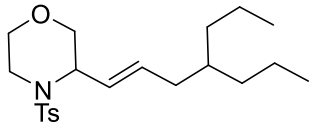
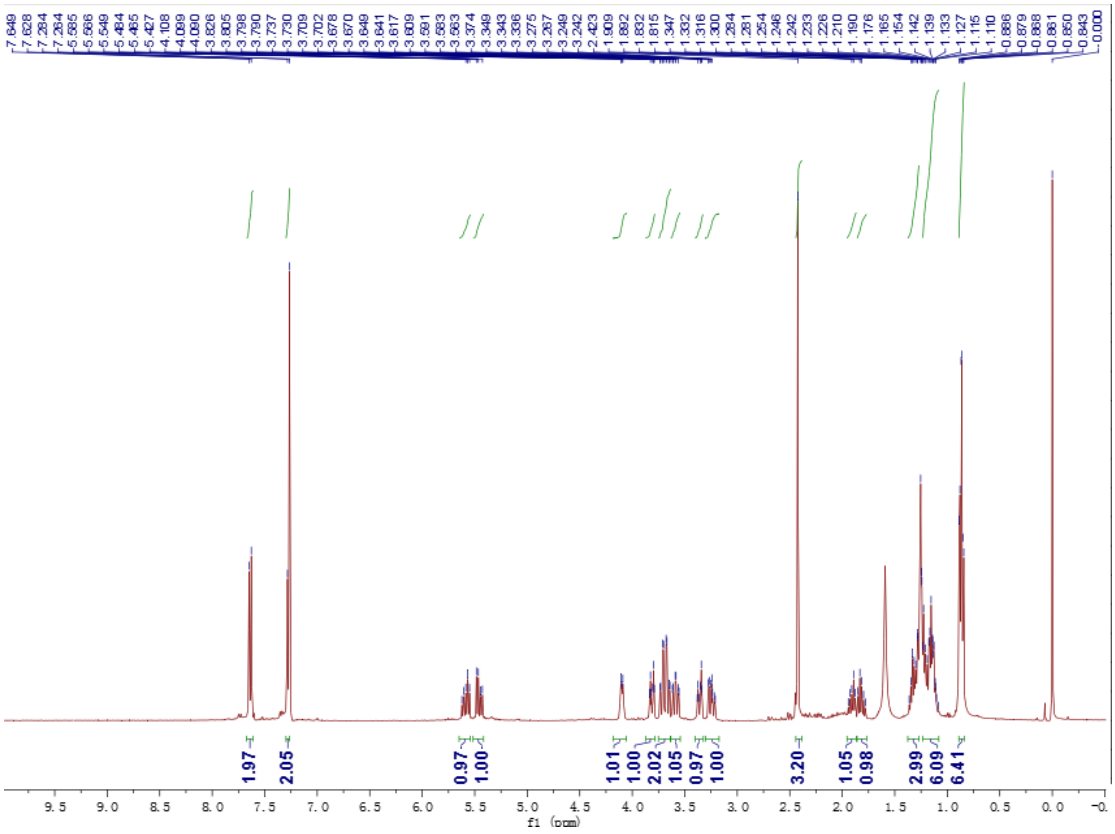
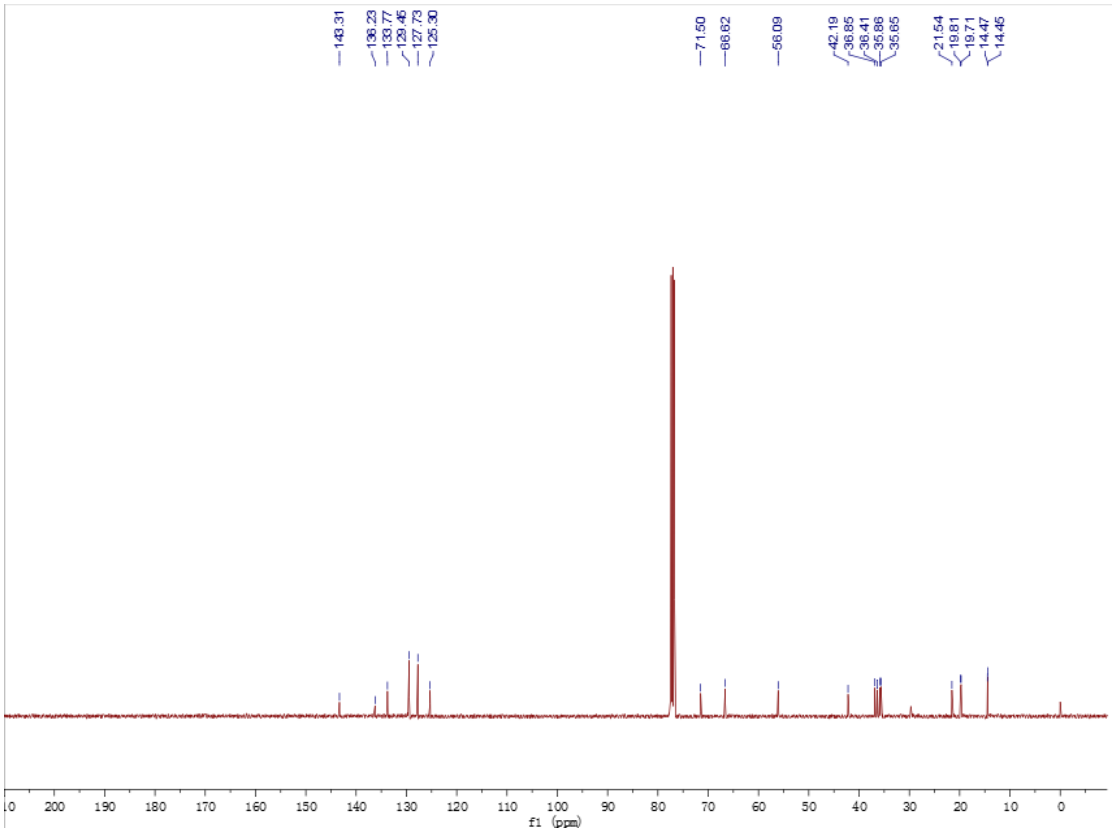
7.355
7.337
7.318
7.296
7.278
7.258
5.141
4.900
4.040
4.022
4.015
3.907
3.901
3.881
3.874
3.827
3.820
3.800
3.793
3.530
3.510
3.505
3.328
3.317
3.302
3.291
3.275
1.798
0.000
5.00
0.98
0.99
0.97
2.19
1.06
2.11
4.03
f1 (ppm)


144.24
140.64
128.45
127.76
127.32
111.83
73.42
71.31
61.37
60.51
20.09
f1 (ppm)


O
N
Ts

(8)


1.97
2.05
0.97
1.00
1.01
1.00
2.02
1.05
0.97
1.00
3.20
1.05
0.98
2.99
6.09
6.41
f1 (ppm)


143.31
136.23
133.77
129.45
127.73
125.30
71.50
66.62
56.09
42.19
36.85
36.41
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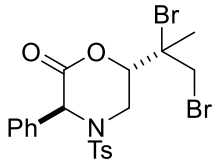
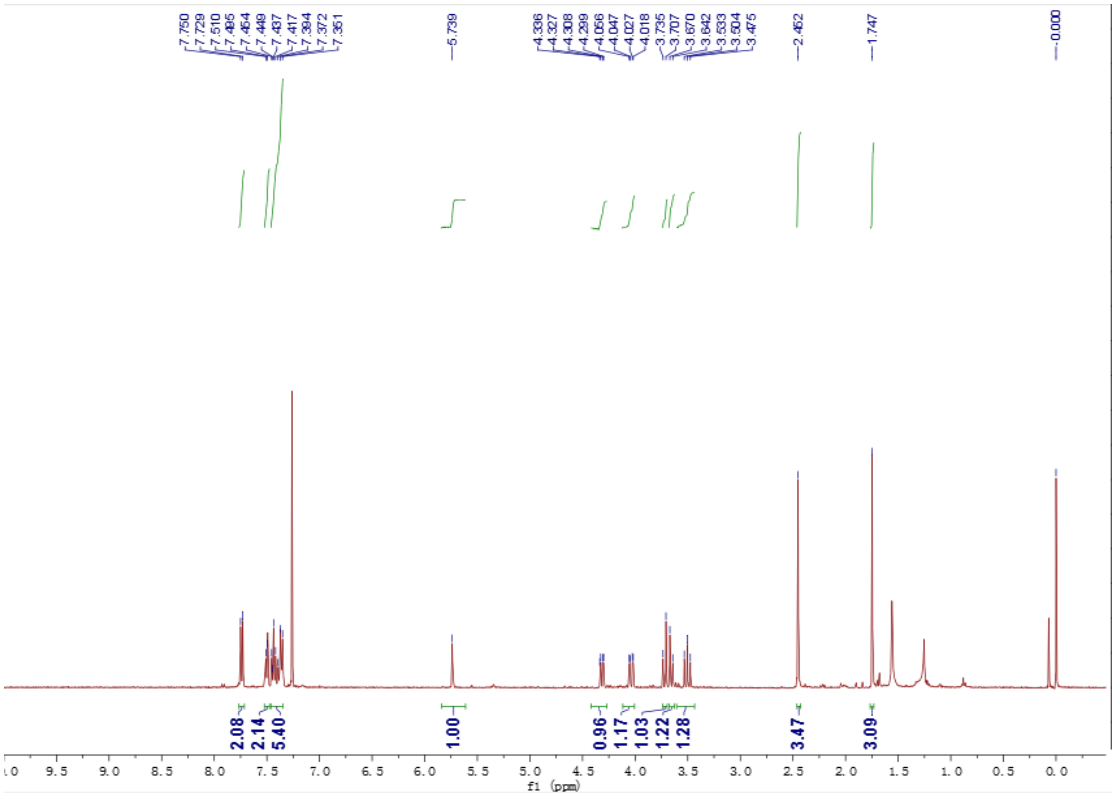
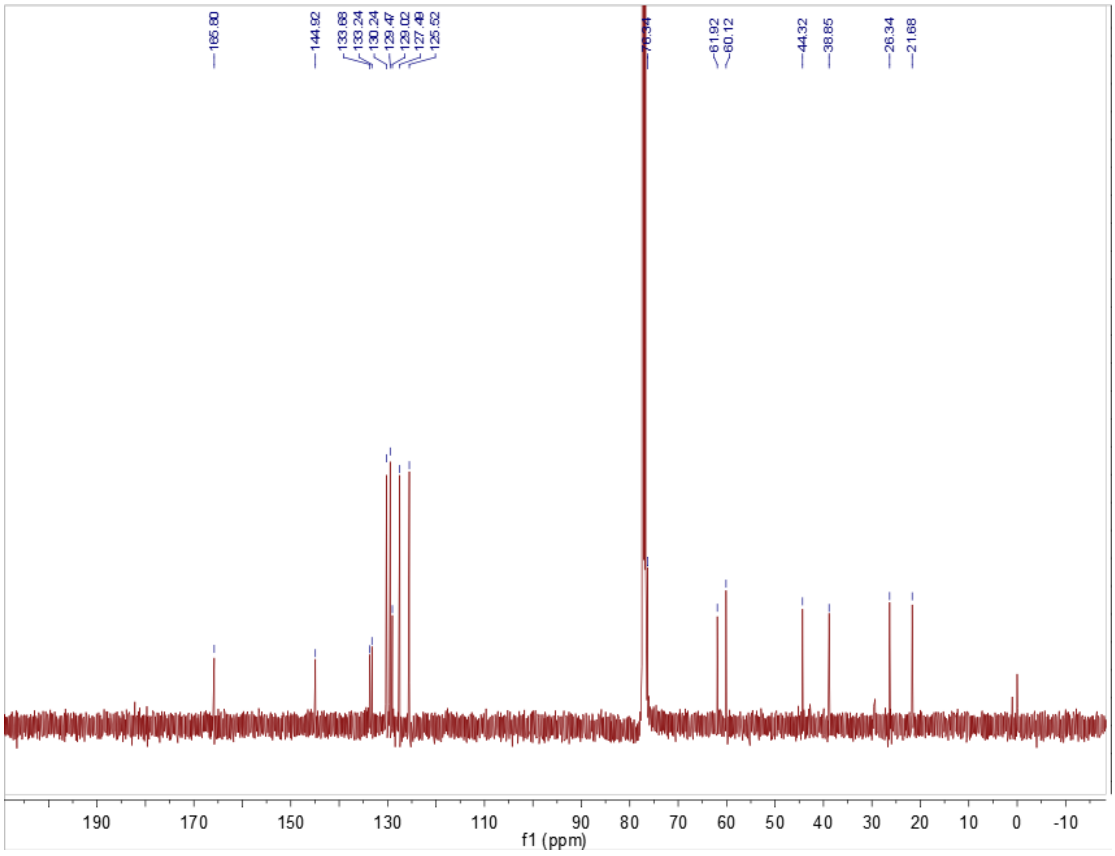
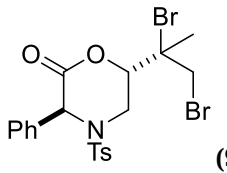
35.65
21.54
19.81
19.71
14.47
14.45
f1 (ppm)



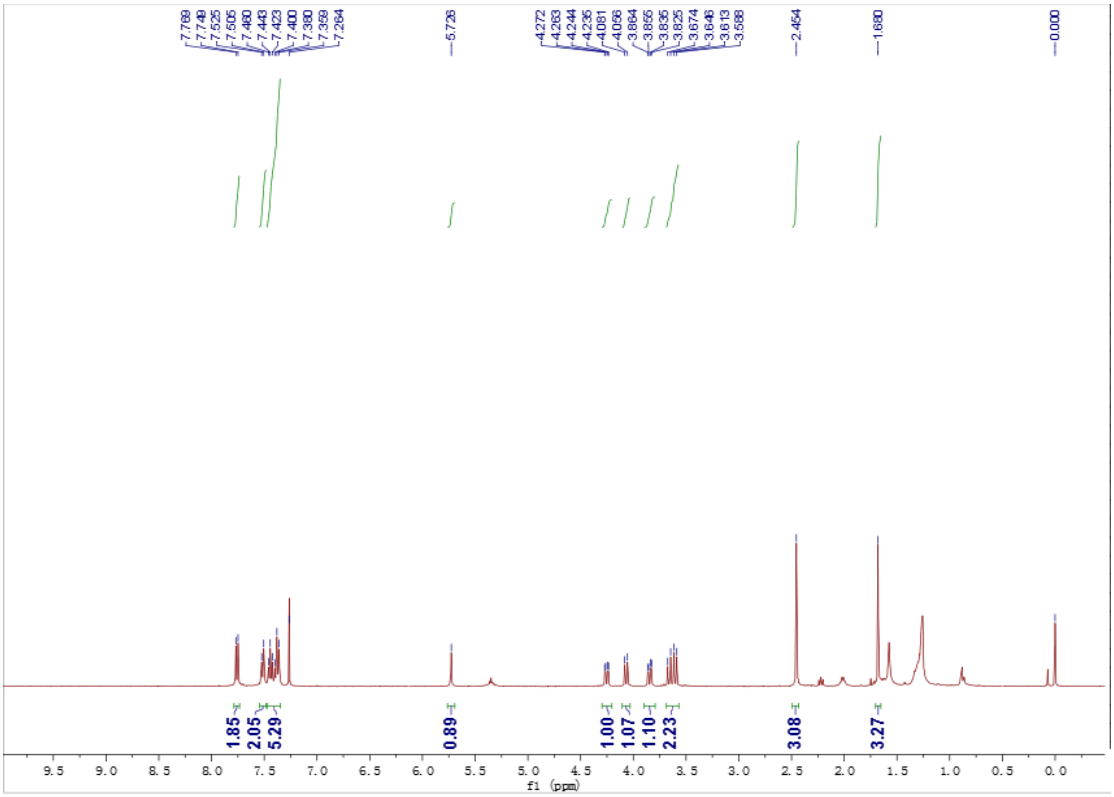
(9, major isomer)

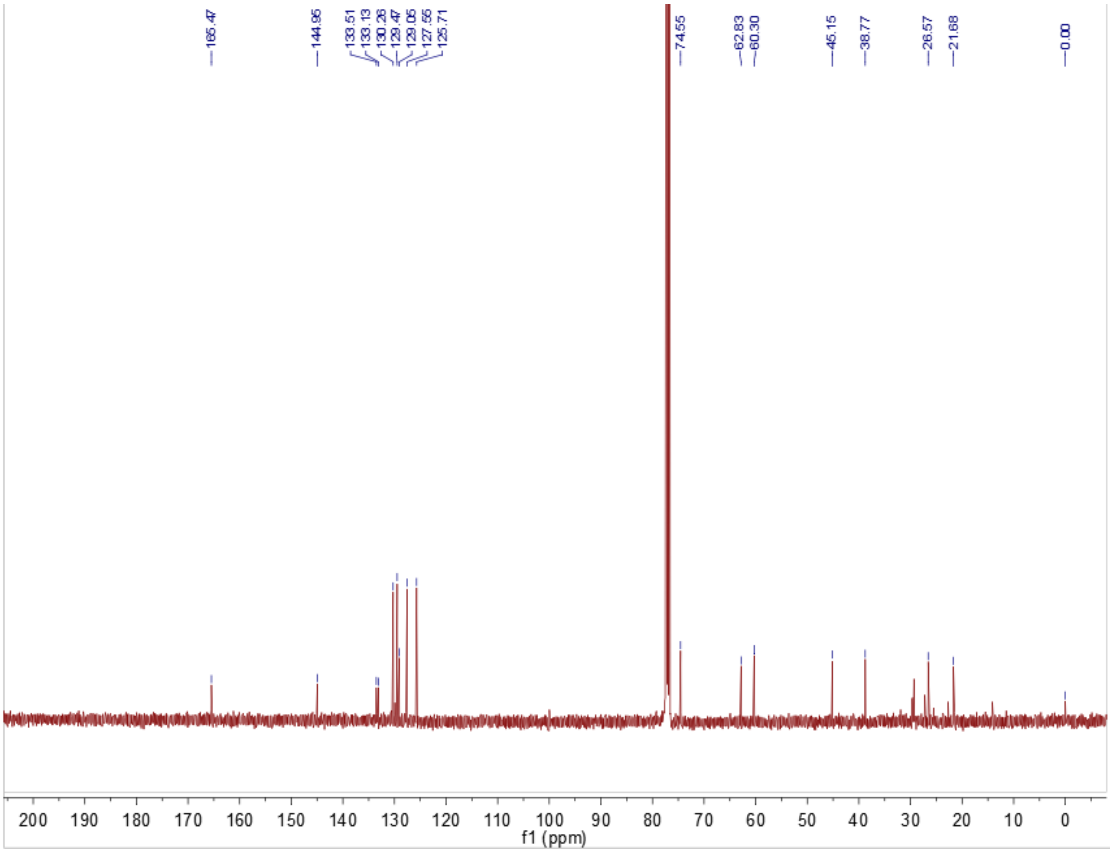


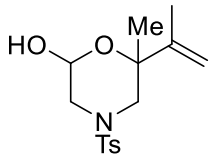




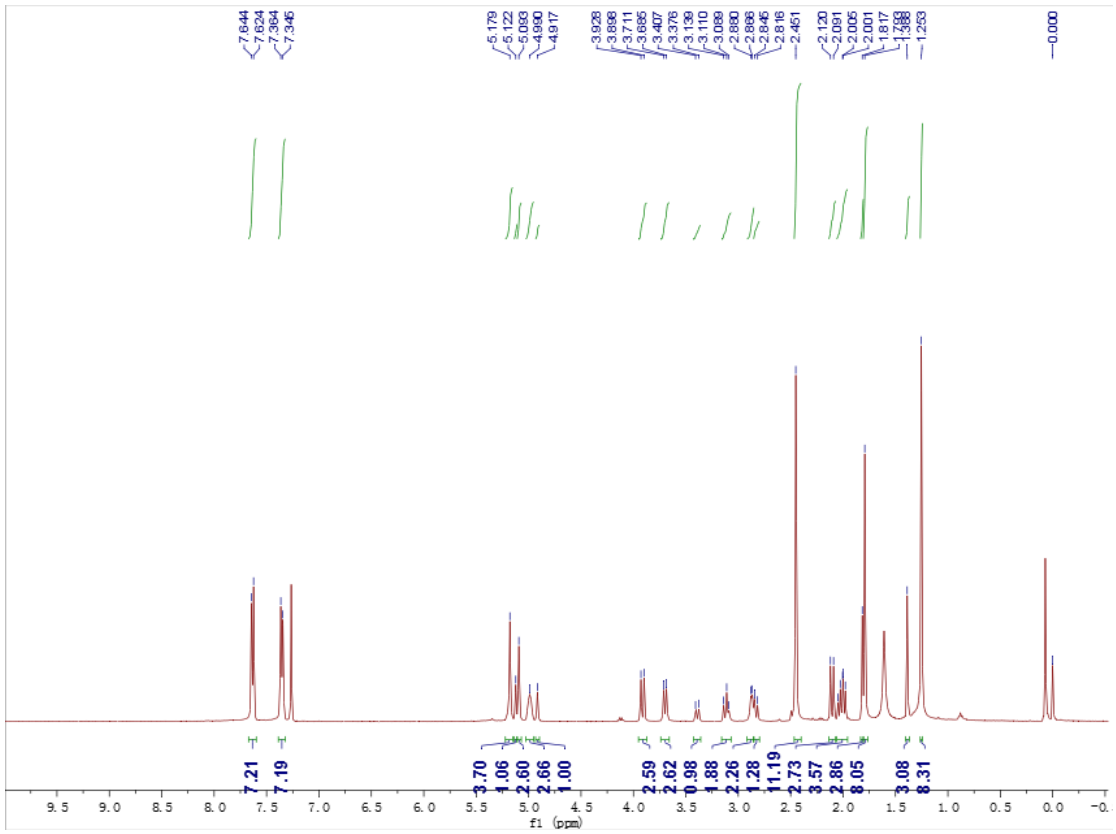
(9, minor isomer)

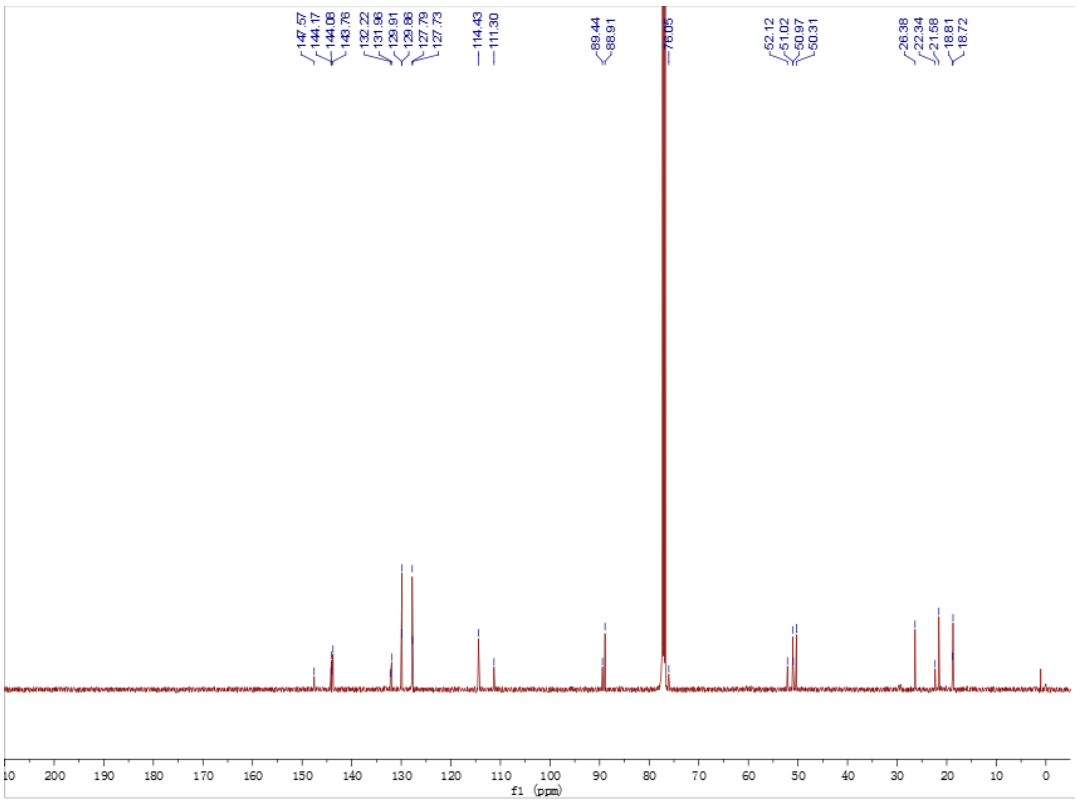






(10, mixture of diastereoisomers)



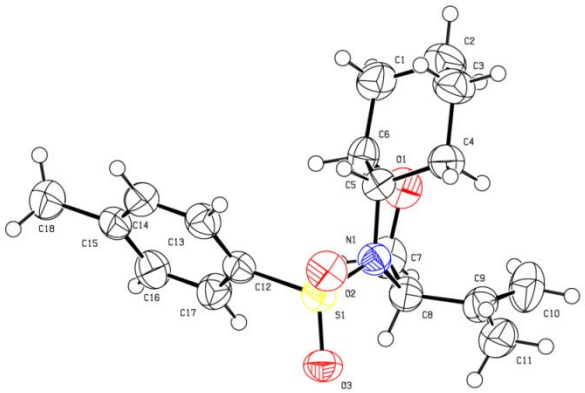


7. X-ray crystal structure analysis

The structure of **3ba**, **3ga'**, **3ia**, **5da**, **5ea** and **5ab** were determined by X-ray single crystal diffraction analysis. CCDC 1832181 (**3ba**), CCDC 1833770 (**3ga'**), CCDC 1832183 (**3ia**), CCDC 1832184 (**5da**), CCDC 1832182 (**5ea**) and CCDC 1836399 (**5ab**) contain the supplementary crystallographicdata for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre viawww.ccdc.cam.ac.uk/data_request/cif.

A suitable crystal was selected and mounted on a Xcalibur, Atlas, Gemini ultra diffractometer. Using Olex2[5], the structure was solved with the ShelXS[6] structure solution program using Direct Methods and refined with the ShelXL[6] refinement package using Least Squares minimisation.

X-Ray Crystallography Data for **3ba** (CCDC 1832181): A colorless crystal suitable for X-ray crystallography was obtained from a *n*-hexane/dichloromethane solution at room temperature under air.



Bond precision:	C-C = 0.0031 A	Wavelength=0.71073	
Cell:	a=11.6879(8)	b=18.2014(11)	c=8.4879(4)
	alpha=90	beta=102.767(5)	gamma=90
Temperature:	293 K		

	Calculated	Reported
Volume	1761.04(18)	1761.03(17)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C18 H25 N O3 S	C18 H25 N O3 S
Sum formula	C18 H25 N O3 S	C18 H25 N O3 S
Mr	335.45	335.45
Dx,g cm-3	1.265	1.265
Z	4	4
Mu (mm-1)	0.198	0.198
F000	720.0	720.0
F000'	720.80	
h,k,lmax	14,21,10	14,21,10
Nref	3218	3211
Tmin,Tmax	0.931,0.955	0.927,1.000
Tmin'	0.920	

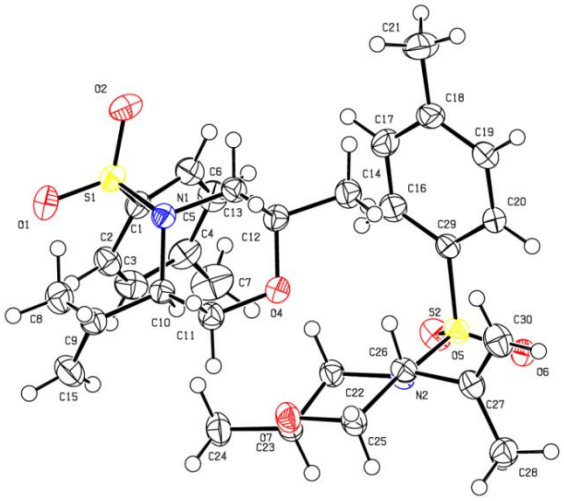
Correction method= # Reported T Limits: Tmin=0.927 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 25.350

R(reflections)= 0.0432(2382) wR2(reflections)= 0.1221(3211)

S = 1.037 Npar= 210

X-Ray Crystallography Data for **3ga**' (CCDC 1833770): A colorless crystal suitable for X-ray crystallography was obtained from a *n*-hexane/dichloromethane solution at room temperature under air.



Bond precision: C-C = 0.0025 A Wavelength=1.54178

Cell: a=9.1241(2) b=13.2825(2) c=25.2487(5)
alpha=90 beta=94.118(1) gamma=90
Temperature: 173 K

	Calculated	Reported
Volume	3052.01(10)	3052.01(10)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C15 H21 N O3 S	C15 H21 N O3 S
Sum formula	C15 H21 N O3 S	C15 H21 N O3 S
Mr	295.39	295.39
Dx,g cm-3	1.286	1.286
Z	8	8
Mu (mm-1)	1.944	1.944
F000	1264.0	1264.0
F000'	1270.12	
h,k,lmax	10,15,30	10,15,30
Nref	5389	5383
Tmin,Tmax	0.911,0.943	
Tmin'	0.907	

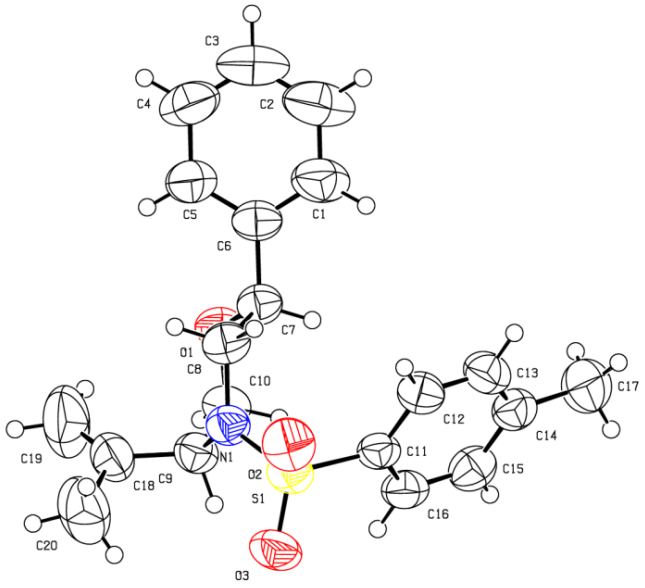
Correction method= Not given

Data completeness= 0.999 Theta(max)= 66.587

R(reflections)= 0.0344(4672) wR2(reflections)= 0.0910(5383)

S = 1.059 Npar= 367

X-Ray Crystallography Data for **3ia** (CCDC 1832183): A colorless crystal suitable for X-ray crystallography was obtained from a *n*-hexane/dichloromethane solution at room temperature under air.



Bond precision: C-C = 0.0051 A Wavelength=0.71073

Cell: a=27.193(3) b=8.6013(7) c=16.5250(17)
alpha=90 beta=101.302(11) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	3790.2(7)	3790.2(7)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	C20 H23 N O3 S	C20 H23 N O3 S
Sum formula	C20 H23 N O3 S	C20 H23 N O3 S
Mr	357.45	357.45
Dx,g cm-3	1.253	1.253
Z	8	8
Mu (mm-1)	0.189	0.189
F000	1520.0	1520.0
F000'	1521.63	
h,k,lmax	32,10,19	32,10,19
Nref	3478	3471
Tmin,Tmax	0.941,0.985	0.679,1.000
Tmin'	0.941	

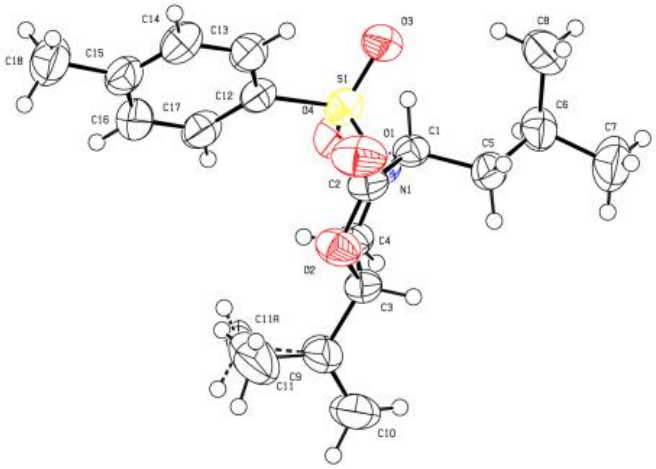
Correction method= # Reported T Limits: Tmin=0.679 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 25.350

R(reflections)= 0.0554(2089) wR2(reflections)= 0.1687(3471)

S = 1.048 Npar= 228

X-Ray Crystallography Data for **5da** (CCDC 1832184): A colorless crystal suitable for X-ray crystallography was obtained from a *n*-hexane/dichloromethane solution at room temperature under air.



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Bond precision:  C-C = 0.0039 A          Wavelength=0.71073

Cell:          a=8.2097(6)       b=11.3718(10)     c=11.4320(9)
               alpha=63.440(8)   beta=84.691(6)    gamma=84.975(7)
Temperature:   293 K

                Calculated                Reported
Volume          949.27(15)                949.27(15)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C18 H25 N O4 S            C18 H25 N O4 S
Sum formula     C18 H25 N O4 S            C18 H25 N O4 S
Mr              351.45                    351.45
Dx,g cm-3       1.230                     1.230
Z               2                         2
Mu (mm-1)       0.191                     0.191
F000            376.0                     376.0
F000'           376.42
h,k,lmax        9,13,13                   9,13,13
Nref            3475                      3462
Tmin,Tmax       0.929,0.948               0.837,1.000
Tmin'           0.926

Correction method= # Reported T Limits: Tmin=0.837 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.996          Theta(max)= 25.349

R(reflections)= 0.0524( 2133)     wR2(reflections)= 0.1075( 3462)

S = 0.952                 Npar= 232
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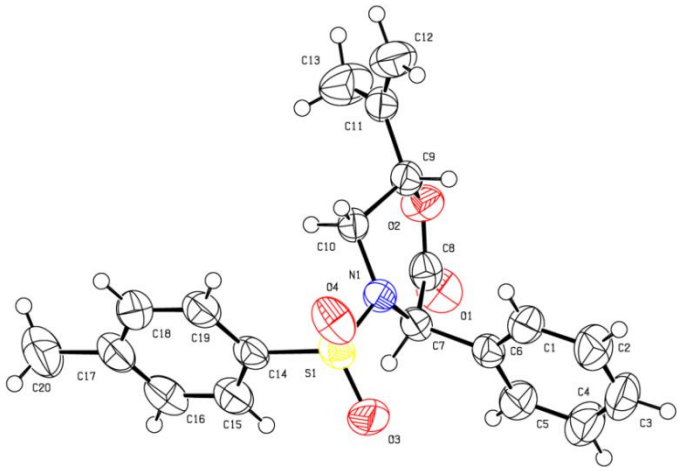
X-Ray Crystallography Data for **5ea** (CCDC 1832182): A colorless crystal suitable for X-ray crystallography was obtained from a *n*-hexane/dichloromethane solution at room temperature under air.



Bond precision: C-C = 0.0036 A Wavelength=0.71073

Cell: a=17.4085(10) b=6.2355(3) c=17.4828(11)
alpha=90 beta=99.565(6) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	1871.39(19)	1871.38(19)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C20 H21 N O4 S	C20 H21 N O4 S
Sum formula	C20 H21 N O4 S	C20 H21 N O4 S
Mr	371.44	371.44
Dx,g cm-3	1.318	1.318
Z	4	4
Mu (mm-1)	0.198	0.198
F000	784.0	784.0
F000'	784.86	
h,k,lmax	20,7,21	20,7,21
Nref	3426	3415
Tmin,Tmax	0.915,0.961	0.949,1.000
Tmin'	0.915	

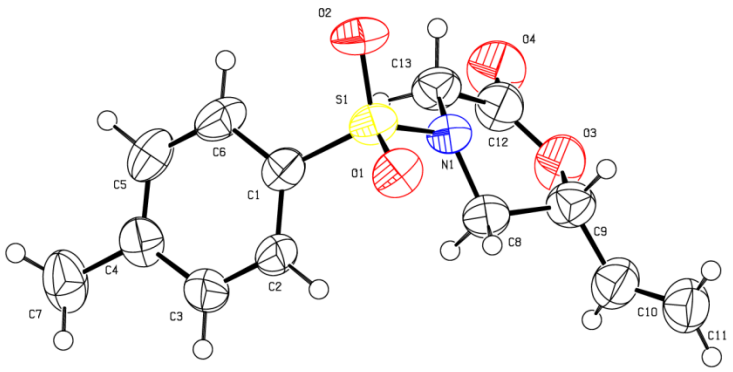
Correction method= # Reported T Limits: Tmin=0.949 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 25.350

R(reflections)= 0.0462(2519) wR2(reflections)= 0.1228(3415)

S = 1.023 Npar= 237

X-Ray Crystallography Data for **5ab** (CCDC 1836399): A colorless crystal suitable for X-ray crystallography was obtained from a *n*-hexane/dichloromethane solution at room temperature under air.



Bond precision: C-C = 0.0099 A Wavelength=1.54178

Cell: a=10.8106(10) b=5.4540(5) c=11.7245(10)
alpha=90 beta=104.012(5) gamma=90
Temperature: 223 K

	Calculated	Reported
Volume	670.72(11)	670.72(11)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C13 H15 N O4 S	C13 H15 N O4 S
Sum formula	C13 H15 N O4 S	C13 H15 N O4 S
Mr	281.32	281.32
Dx,g cm-3	1.393	1.393
Z	2	2
Mu (mm-1)	2.248	2.248
F000	296.0	296.0
F000'	297.56	
h,k,lmax	13,6,14	13,6,14
Nref	2471[1376]	2305
Tmin,Tmax	0.701,0.764	0.615,0.753
Tmin'	0.635	

Correction method= # Reported T Limits: Tmin=0.615 Tmax=0.753
AbsCorr = ?

Data completeness= 1.68/0.93 Theta(max)= 68.403

R(reflections)= 0.0544(1882) wR2(reflections)= 0.1550(2305)

S = 1.100 Npar= 174

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8. References

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