Supporting Information for

Selective *S*-Arylation of 2-Oxazolidinethiones and Selective *N*-Arylation of 2-Benzoxazolinones/2-Benzimidazolinones

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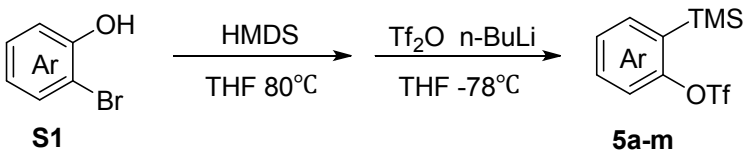
Contents

General Information and Materials

NMR spectra were recorded using Bruker AV-300 / AV-400 spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra were acquired on an agilent 6230 spectrometer and were obtained by peak matching. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator and/or by exposure to phosphormolybdic acid/cerium (IV) sulfate/ ninhydrine followed by brief heating with a heat gun. Liquid chromatography (flash chromatography) was performed on 200-300 Å mesh silica gel (SiO_2). All reactions were carried out under nitrogen or argon with anhydrous solvents in oven-dried glassware, unless otherwise noted. Commercially available reagents were used without further purification. Solvents were purified prior to use according to the standard methods.

Preparation of substrates 5a-m [1]

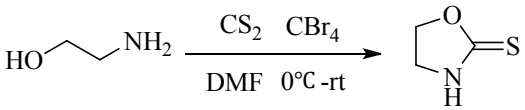


S1 **5a-m**

To a solution of **S1** (34.8mmol) in THF was added HMDS (69mmol) at rt. The resulting mixture was refluxed for 3h. After cooled to rt, the solvent and HMDS were removed under reduced pressure. The residue was subjected to next reaction without further purification. To a solution of the crude silyl-methr (34.8mmol) in THF (45ml) was dropwise n-BuLi (2.5M in hexanes, 69mmol) at -78℃. The reaction mixture was stirred for 30min. Then Tf_2O (69mmol) was added dropwise to the mixture, and the stirring was continued for 30min. The mixture was quenched with cold saturated aqueous $NaHCO_3$, and the resulting mixture was extracted with EtOAc three times. The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes) to afford the product.

Preparation of substrates 1

Method A (1a was prepared via this method).

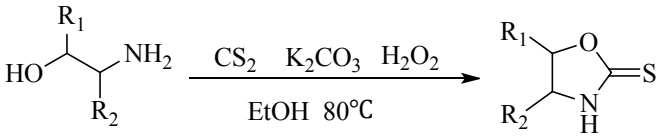


1a

1a was prepared according to previously reported synthetic procedure [2] and all data correspond to previously reported material. CS_2 (312mg, 4mmol, 0.5eq) was added to a solution of 2-aminoethanol (500mg, 8mmmol, 1eq) in 10ml dry DMF at 0℃, the

mixture was stirred 5min. CBr_4 (1.3g, 4mmol, 0.5eq) was added to the solution and stirred 30min at rt. The solution was poured into water and extracted with DCM (3×20ml). The collected organic layers were washed with saturated salt water and dried over Na_2SO_4. The residue were concentrated and purified by column chromatography (PE/EA=10:1～2:1).to give the desired product **1a.**

Method B (1b-1g were prepared via this method).

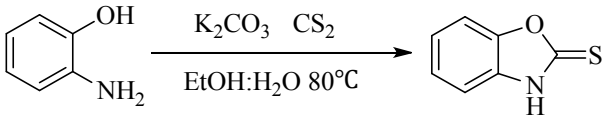


1b-1g

R1=H, Me
R2=H, Me, i-Pr, Bn, Ph.

Following the reported procedure[3] to obtain **1b-1g**. K_2CO_3 (0.5eq) was added to a solution of amino alcohol (1eq) in ethanol at rt, followed by CS_2 (2eq).A solution of H_2O_2 (30%, 1.5eq) was slowly added to the reaction mixture under ice-cold water. After the mixture were stirred for a further 30min at 80℃, cooled to rt, and then filtered through kieselguhr. An aqueous saturated solution of NH_4Cl was added to the filtrate and crude product was extracted with EA 3 times. The combined organic phases were dried with $MgSO_4$, filtered, then concentrated under vacuum, and the crude product purified by flash chromatography.

Method C (2h was prepared via this method) [4]

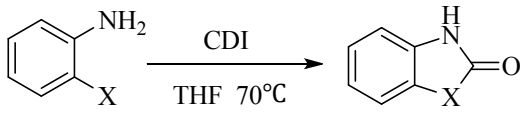


1i

To a well stirred o-Aminophenol (0.05mol) and K_2CO_3 (0.075mol) in an ethanol-

water mixture (1:0.5) was added CS_2 (0.075mol) dropwise. After complete addition CS_2, the reaction mixture was allowed to followed by heating at 80℃ for 8h..The reaction mixture was then cooled to rt, water was added. The mixture was acidified with 2N HCl and the solid was filtered.

Preparation of substrates 6

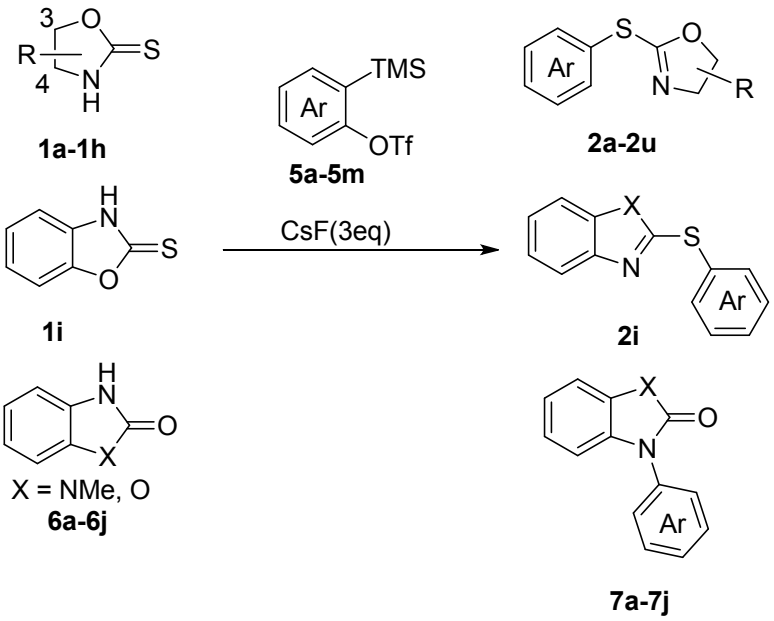


6 **6a-6j**

X= OH, $NHCH_3$

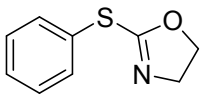
6a-6j was prepared according to previously reported synthetic procedure [5]. To a stirred solution of appropriate **6** (1 mmol) in dry THF (20 ml) was added 1,1′-carbonyldiimidazole (CDI) (1.2 mmol) at rt. The solution was stirred for about 4 h at 70℃ (monitored by TLC), and solvent evaporated under reduced pressure. The residue was further diluted with water (20 ml) and ethyl acetate (20 ml) and the layers separated. The organic layer was washed with 2 N HCl (15 ml), water (10 ml), dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using hexane: ethyl acetate as eluent to give the corresponding product (**4a-4j**) in good yield.

Preparation of 2a-2u and 7a-7j



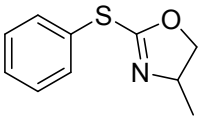
A flame dried 10 mL of Schlenk tube was charged with **1a-1i/6a-6j** (50mg, 1eq.), CsF (3eq.), **5a-5m** (1.2 eq.) and dry MeCN (2 mL). The tube was degassed and filled with N_2. Then the solution was stirred for 12h at 90 ℃. After the reaction was completed by TLC, the solvent was removed under vacuum. Then the crude product was purified by column chromatography to give the desired product.

Characterization of Substrates



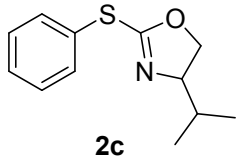
2a

2-(phenylthio)-4,5-dihydrooxazole (2a). (81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.61 (m, 2H), 7.40 – 7.38 (m, 3H), 4.34 (t, *J* = 9.2 Hz, 2H), 3.87 (t, *J* = 9.2 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 134.7, 129.6, 129.3, 127.9, 69.3, 55.2. HRMS (ESI) *m/z* Calculated for $C_9H_{10}NOS^+$ $[M+H]^+$ 180.0478, found 180.0481.



2b

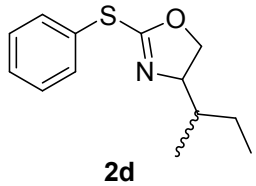
4-methyl-2-(phenylthio)-4, 5-dihydrooxazole (2b). (91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.58(m, 2H), 7.37 – 7.35 (m, 3H), 4.38 (t, *J* = 8.4 Hz, 1H), 4.25 – 4.16 (m, 1H), 3.84 (t, *J* = 7.6 Hz, 1H), 1.24 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 134.4, 129.3 , 128.1, 75.4, 62.5, 21.3. HRMS (ESI) *m/z* Calculated for $C_{10}H_{12}NOS^+$ $[M+H]^+$ 194.0634, found 194.0637.



2c

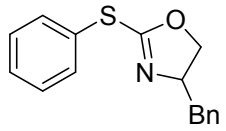
4-isopropyl-2-(phenylthio)-4, 5-dihydrooxazole (2c). (87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 2H), 7.39-7.36 (m, 3H), 4.3 (t, *J* = 8.0 Hz, 1H), 4.0 (t, *J* = 8.0, 1H), 3.98-3.90 (m, 1H), 1.82-1.70 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 134.3, 129.2, 128.2, 72.8 , 71.6, 32.7,

18.7, 18.0. HRMS (ESI) *m/z* Calculated for $C_{12}H_{16}NOS^+$ $[M+H]^+$ 222.0947, found 222.0958.



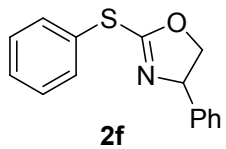
2d

2-(phenylthio)-4-propyl-4,5-dihydrooxazole (2d). (85%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 2H), 7.39 – 7.35 (m, 3H), 4.32 – 4.23 (m, 1H), 4.10 – 4.01 (m, 2H), 1.67 – 1.56 (m, 1H), 1.55 – 1.45 (m, 1H), 1.26 – 1.11 (m, 1H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 134.6, 134.0, 129.5, 128.8, 71.8, 71.2,70.9 70.5, 39.0, 38.9, 25.9, 14.4, 14.0 , 11.7, 11.4. HRMS (ESI) *m/z* Calculated for $C_{13}H_{18}NOS^+$ $[M+H]^+$ 236.1104, found 236.1117.



2e

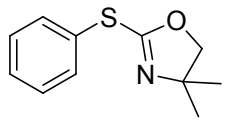
4- benzyl-2-(phenylthio)-4, 5-dihydrooxazole (2e). (83%)**.** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 2H), 7.32-7.31 (m, 3H), 7.23 – 7.16 (m, 3H), 7.12 – 7.09(m, 2H), 4.40-4.35 (m, 1H), 4.15 (t, *J* = 9.0 Hz, 1H), 4.00 (dd, *J* = 8.2, 6.9 Hz, 1H), 3.02 (dd, *J* = 13.7, 4.9 Hz, 1H), 2.61 (dd, *J* = 13.7, 8.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9, 137.5, 134.6, 129.5, 129.4, 129.3, 128.6, 127.9, 126.66, 73.2, 68.0, 41.4. HRMS (ESI) *m/z* Calculated for $C_{16}H_{16}NO2S^+$ $[M+H]^+$ 286.0896, found 286.0898.



2f

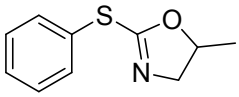
4-phenyl-2-(phenylthio)-4,5-dihydrooxazole (2f). (80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.64 (m, 2H), 7.39 – 7.37(m, 3H), 7.35 – 7.26 (m, 3H), 7.24 – 7.19 (m,

2H), 5.22 (dd, J = 9.8, 7.7 Hz, 1H), 4.67 (dd, J = 9.8, 8.2 Hz, 1H), 4.16 (t, J = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 142.0, 134.6, 129.5, 129.3, 128.7, 127.8, 127.7, 126.5, 76.3, 70.2. HRMS (ESI) *m/z* Calculated for $C_{15}H_{14}NOS^+$ $[M+H]^+$ 256.0718, found 256.0791.



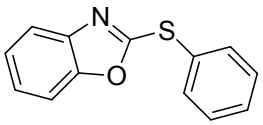
2g

4,4-dimethyl-2-(phenylthio)-4,5-dihydrooxazole (2g).(84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60-7.56 (m, 2H), 7.36 – 7.34 (m, 3H), 3.97 (s, 2H), 1.29 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.1, 134.1, 129.1, 128.2, 80.3, 68.5, 28.1. HRMS (ESI) *m/z* Calculated for $C_{11}H_{14}NOS^+$ $[M+H]^+$ 208.0791, found 207.0792.



2h

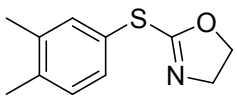
5-methyl-2-(phenylthio)-4,5-dihydrooxazole (2h). (37%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.60 (m, 2H), 7.40 – 7.38 (m, 3H), 4.81 – 4.76 (m, 1H), 3.96 (dd, J = 13.6, 9.1 Hz, 1H), 3.44 (dd, J = 13.6, 7.2 Hz, 1H), 1.36 (d, J = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 134.6, 129.4 ,129.3, 128.0, 78.4, 61.7, 20.8. HRMS (ESI) *m/z* Calculated for $C_{10}H_{12}NOS^+$ $[M+H]^+$ 194.0634, found 194.0637.



2i

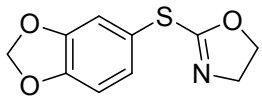
2-(phenylthio)benzo*[d]*oxazole (2i). (84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 – 7.69 (m, 2H), 7.61 – 7.58 (m, 1H), 7.48 – 7.38 (m, 4H), 7.27 – 7.23 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 151.9, 142.0, 134.5, 130.0, 129.7, 124.4,124.3, 119.1,

110.1. HRMS (ESI) *m/z* Calculated for $C_{13}H_{10}NOS^+$ $[M+H]^+$ 228.0478, found 228.0481.



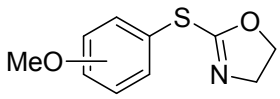
2j

2-((3,4-dimethylphenyl)thio)-4,5-dihydrooxazole (2j). (75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 10.8, 2.0 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 4.35 (t, *J* = 9.2 Hz, 2H), 3.86 (t, *J* = 9.2 Hz, 2H), 2.26 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 138.7, 137.8, 135.9, 132.5, 130.6, 124.2, 69.3, 55.2, 19.8,.19.7. HRMS (ESI) *m/z* Calculated for $C_{11}H_{14}NOS^+$ $[M+H]^+$ 208.0791, found 208.0793.



2k

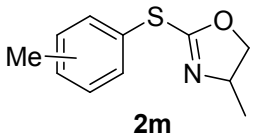
2-(benzo[d][1,3]dioxol-5-ylthio)-4,5-dihydrooxazole (2k). (46%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 – 7.06 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.00 (s, 2H), 4.36 (t, *J* = 9.2 Hz, 2H), 3.87 (t, *J* = 9.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 149.3, 148.1,129.5, 119.4, 115.3, 108.9, 101.7, 69.4, 55.1. HRMS (ESI) *m/z* Calculated for $C_{10}H_{10}NO_3S^+$ $[M+H]^+$ 224.0376, found 224.0379.



2l

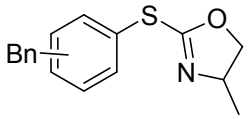
2-((methoxyphenyl)thio)-4,5-dihydrooxazole (2l). (79%, p / m =1.2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, J = 8.8 Hz, 2H), 7.34 – 7.24 (m, 1H), 7.17 (dd, J = 13.2, 7.8 Hz, 2H), 6.93 (dd, J = 2.6 Hz, 2H) 6.92 (dd, J = 8.7 Hz, 2H), 4.34 (td, J = 9.2, 2.3 Hz, 4H), 3.87 – 3.79 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 165.2, 160.8, 159.8, 136.7, 130.0, 128.7, 126.8, 119.7, 118.1, 115.5, 114.9, 69.4, 69.2, 55.4, 55.2,

55.1. HRMS (ESI) *m/z* Calculated for $C_{10}H_{12}NO_2S^+$ $[M+H]^+$ 210.0583, found 210.0586.



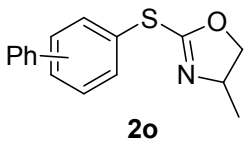
2m

Methyl -2-(p-tolylthio)-4,5-dihydrooxazole (2m). (91%**,** p / m = 1:1.2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.39 (m, 2H), 7.24 (t, J=5,1H), 7.17-7.15 (m, 3H), 4.40 – 4.35 (m, 2H), 4.20 (m, 2H), 3.85-3.81 (m, 2H), 2.33 (s, 6H), 1.22 (t, *J* = 5.6 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 139.7, 139.1, 135.0,134.6,131.6, 130.3, 130.1, 129.1, 127.5, 75.6, 62.5, 21.4, 21.3, 21.3, 21.2. HRMS (ESI) *m/z* Calculated for $C_{11}H_{14}NOS^+$ $[M+H]^+$ 208.0791, found 208.0793.



2n

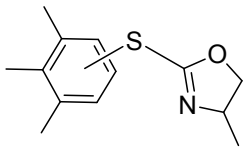
2-((benzylphenyl)thio)-4-methyl-4,5-dihydrooxazole (2n). (59%**,** p / m =~1:1**).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.29 (dd, *J* = 14.9, 7.5 Hz, 3H), 7.23 – 7.18 (m, 4H), 4.40 (td, *J* = 8.5, 4.3 Hz, 1H), 4.26 – 4.17 (m, 1H), 3.99 (s, 2H), 3.86 (td, *J* = 7.6, 4.9 Hz, 1H), 1.25 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0,142.3, 142.2, 140.3, 140.2, 134.7, 134.6, 132.0, 129.9,129.8, 129.2, 129.1, 129.0, 128.59 (d, *J* = 2.0 Hz), 128.1, 126.4, 126.3, 125.3, 75.5, 75.4, 62.5 , 41.7 , 21.3. HRMS (ESI) *m/z* Calculated for $C_{17}H_{18}NOS^+$ $[M+H]^+$ 284.1104, found 284.1107.



2o

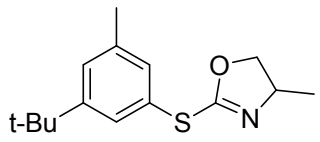
2-([1,1'-biphenyl]-ylthio)-4-methyl-4,5-dihydrooxazole (2o). (85%, p / m = ~1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.61 – 7.56 (m, 8H), 7.48 – 7.43 (m, 5H), 7.37 (t, *J* = 7.3 Hz, 2H), 4.46 – 4.41 (m, 2H), 4.25 (m, 2H), 3.92-3.87 (m, 2H), 1.29 (d, *J* = 1.7 Hz, 3H), 1.28 (d, *J* = 1.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 164,1, 142.3, 142.2, 140.1,140.0, 134.8, 133.2,133.1, 129.6, 128.9, 128.4,128.2 127.9, 127.8, 27.7, 127.2 127.2, 126.7, 75.6 ,75.5, 62.4, 21.3, 21.2. HRMS (ESI) *m/z* Calculated for $C_{16}H_{16}NOS^+$ $[M+H]^+$ 270.0749, found 270.0950.



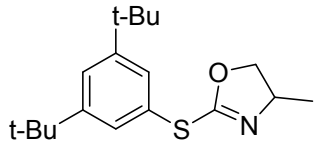
2p

4-methyl-2-((trimethylphenyl) thio)-4,5-dihydrooxazole (2p). (75%**,** o / m =1.1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 2H), 6.55 (d, *J* = 8.7 Hz, 1H), 3.93 (dd, *J* = 16.7, 7.9 Hz, 2H), 3.79 – 3.68(m, 2H), 3.47 – 3.36 (dd, J=16.2, 8.5, 2H), 1.99 (s, 3H), 1.82 (d, *J* = 4.5 Hz, 9H), 1.76 (s, 3H), 1.69 (s, 3H), 0.78 (dd, *J* = 7.9, 6.7 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8, 164.4, 140.7, 139.17, 137.6, 137.3, 136.7, 133.8, 133.4, 128.0, 124.5, 123.3, 75.5,75.5, 62.37 (d, *J* = 3.4 Hz), 21.5,21.3,21.1, 20.6, 18.1, 16.6, 15.5. HRMS (ESI) *m/z* Calculated for $C_{13}H_{18}NOS^+$ $[M+H]^+$ 236.1104, found 236.1107.



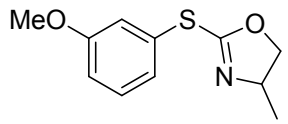
2q

2-((3-(tert-butyl)-5-methylphenyl)thio)-4-methyl-4,5-dihydrooxazole (2q). (70%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.24 (d, *J* = 0.5 Hz, 1H), 7.20 (s, 1H), 4.40 (dd, *J* = 9.0, 7.8 Hz, 1H), 4.26 – 4.18 (m, 1H), 3.86 (t, *J* = 7.6 Hz, 1H), 2.35 (s, 3H), 1.30 (s, 9H), 1.27 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 156.0, 138.5, 132.0, 128.6, 127.5 , 127.1 , 75.4 , 62.5 , 34.7 , 31.2, 21.6, 21.3. HRMS (ESI) *m/z* Calculated for $C_{15}H_{22}NOS^+$ $[M+H]^+$ 264.1417, found 264.1419.



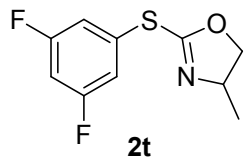
2r

2-((3, 5-di-tert-butylphenyl)thio)-4-methyl-4,5-dihydrooxazole (2r). (52%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 1.6 Hz, 2H), 7.41 (d, *J* = 1.5 Hz, 1H), 4.41 (dd, *J* = 9.0, 7.9 Hz, 1H), 4.29 – 4.17 (m, 1H), 3.87 (t, J=7.6, 1H), 1.32 (s, 18H), 1.28 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 151.5, 128.4, 127.0, 123.4, 75.3, 62.4, 35.0, 31.3, 21.3. HRMS (ESI) *m/z* Calculated for $C_{18}H_{28}NOS^+$ $[M+H]^+$ 306.1886, found 306,1891.



2s

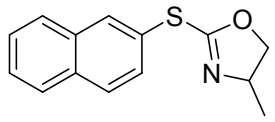
2-((3-methoxyphenyl)thio)-4-methyl-4,5-dihydrooxazole (2s). (71%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.0 Hz, 1H), 7.16 – 7.08 (m, 2H), 6.86 (m, 1H), 4.36 (dd, *J* = 9.0, 7.9 Hz, 1H), 4.23 – 4.10 (m, 1H), 3.82 (t, *J* = 7.6 Hz, 1H), 3.75 (s, 3H), 1.21 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 159.7, 130.0, 128.9, 126.5, 119.5, 115.4, 75.4, 62.5, 55.4, 21.3. HRMS (ESI) *m/z* Calculated for $C_{10}H_{14}NO_2S^+$ $[M+H]^+$ 210.0583, found 210.0586.



2t

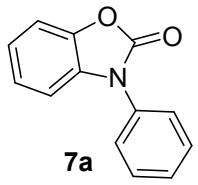
2-((3, 5-difluorophenyl)thio)-4-methyl-4,5-dihydrooxazole(2t). (78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.14 (m, 2H), 6.83-6.76 (m, 1H), 4.47 (dd, *J* = 9.0, 8.1 Hz, 1H), 4.31 – 4.22 (m, 1H), 3.92 (t, *J* = 7.7 Hz, 1H), 1.29 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 162.6 (d, *J* = 237), 116.7(d, *J* = 27), 105.1(d, *J* = 25), 75.7, 62.4, 21.1. HRMS (ESI) *m/z* Calculated for $C_{10}H_{10}F_2NOS^+$ $[M+H]^+$ 230.0446, found 230.0443.



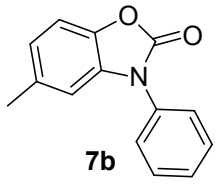
2u

4-methyl-2-(naphthalen-2-ylthio)-4,5-dihydrooxazole (2u). (82%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.85-7.80 (m, 3H), 7.64 (dd, *J* = 8.7, 1.6Hz, 1H), 7.51–7.49 (m, 2H), 4.41 (t, *J* = 8.5, 1H), 4.23 (m, 1H), 3.87 (t, *J* = 7.7Hz, 1H), 1.26 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 134.0, 133.5,133.3, 131.1, 128.9, 128.0, 127.8, 127.2, 126.8, 125.3,75.5, 62.5, 21.3. HRMS (ESI) *m/z* Calculated for $C_{14}H_{14}NOS^+$ $[M+H]^+$ 244.0791, found 244.0795.



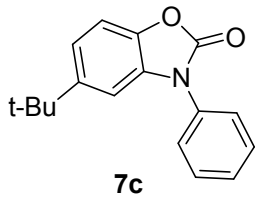
7a

3-phenylbenzo[d]oxazol-2(3H)-one(7a)[6a]**.** (93%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.57-7.56 (m,, 4H), 7.49 – 7.40 (m, 1H), 7.30 – 7.26 (m, 1H), 7.21 – 7.15 (m, 2H), 7.10 – 7.07 (m, 1H).



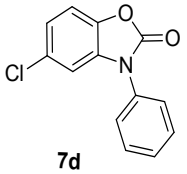
7b

5-methyl-3-phenylbenzo[d]oxazol-2(3H)-one (7b). (85%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.56 – 7.55 (m, 4H), 7.47 – 7.42 (m, 1H), 7.15 (d, J = 8.2 Hz, 1H), 6.99-6.95 (m, 1H), 6.89 – 6.88 (m, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 140.8, 134.0, 133.7, 131.1, 129.8, 128.3, 125.2, 123.6, 109.9,109.8 21.5. HRMS (ESI) *m/z* Calculated for $C_{14}H_{11}NNaO_2^+$ $[M+Na]^+$ 248.0682, found 248.0687.



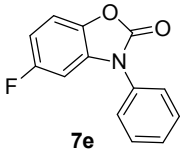
7c

5 -(tert-butyl)-3-phenylbenzo[d]oxazol-2(3H)-one (7c). (80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.26 (m, 4H), 7.16-7.15 (m, 1H), 6.90 (s, 2H), 6.77 (s, 1H), 1.00 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 147.7, 140.6, 135.1, 133.6 129.8, 128.2, 125.1 , 120.0, 109.5, 106.3, 34.9, 31.6. HRMS (ESI) *m/z* Calculated for $C_{17}H_{17}NNaO_2^+$ $[M+Na]^+$ 290.1151, found 290,1200.



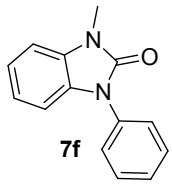
7d

5-chloro-3-phenylbenzo[d]oxazol-2(3H)-one (7d).(70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.52 (m, 4H), 7.49-7.45 (m, 1H), 7.21 (d, J = 8.5 Hz, 1H), 7.15 (d, J = 8.7 Hz, 1H), 7.06 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0 (s), 141.2, 133.2, 130.0, 129.6, 128.8, 126.5, 125.1, 123.1, 111.2, 109.8. HRMS (ESI) *m/z* Calculated for $C_{13}H_8ClKNO_2^+$ $[M+K]^+$ 283.9875, found 283.9803.



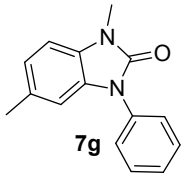
7e

5-fluoro-3-phenylbenzo[d]oxazol-2(3H)-one (7e).(75%)**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59– 7.45 (m, 4H), 7.46 (t, J = 7.1 Hz, 1H), 7.22 (dd, J = 8.6, 4.1 Hz, 1H), 6.90 – 6.81 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3(d, J = 237 Hz), 153.8, 134.7, 130.9 (d, J = 12.1 Hz), 129.6, 127.7, 125.8, 125.4, 109.0 (d, J = 9.3 Hz), 107.8 (d, J = 23.9 Hz), 96.2 (d, J = 28.4 Hz), 27.5. HRMS (ESI) *m/z* Calculated for C13H9FNO2$^+$ $[M+H]^+$ 230.0612, found 230.0614.



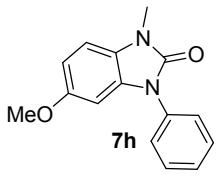
7f

1-methyl-3-phenyl-1H-benzo[d]imidazol-2(3H)-one (7f)[6b]**.** (73%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 4H), 7.40 (m, 1H), 7.19-7.14 (m, 1H), 7.10 – 7.04 (m, 3H), 3.50 (s, 3H).



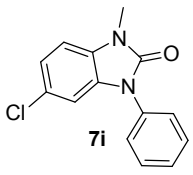
7g

1,5-dimethyl-3-phenyl-1H-benzo[d]imidazol-2(3H)-one (7g)[6c]**.**(50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.52 (m, 4H), 7.42-7.39 (m, 1H), 6.97 – 6.89 (m, 3H), 3.47 (s, 3H), 2.36 (s, 3H).



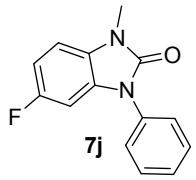
7h

5-methoxy-1-methyl-3-phenyl-1H-benzo[d]imidazol-2(3H)-one (7h)[6d]**.** (56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 4H), 7.42-7.37 (m, 1H), 6.92 (d, J = 8.4 Hz, 1H), 6.75 – 6.65 (m, 2H), 3.77 (s, 3H), 3.46 (s, 3H).



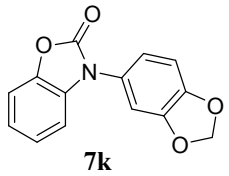
7i

5-chloro-1-methyl-3-phenyl-1H-benzo[d]imidazol-2(3H)-one (7i) [6b]**.**(56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 4H), 7.44-7.40 (m, 1H), 7.12 (d, J = 8.3 Hz, 1H), 7.06 (s, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 3.48 (s, 3H).



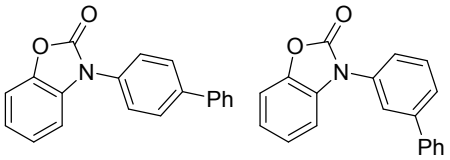
7j

5-fluoro-1-methyl-3-phenyl-1H-benzo[d]imidazol-2(3H)-one (7j)[6b]**.** (55%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 4H), 7.42 – 7.36 (m, 1H), 7.00-6.96 (m, 1H), 6.81 – 6.76(m, 2H), 3.47 (s, 3H).



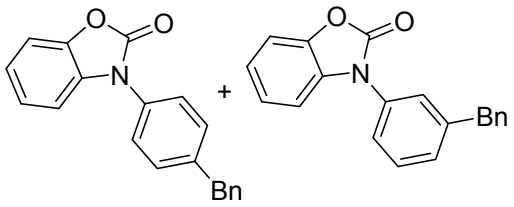
7k

3-(benzo[d][1,3]dioxol-5-yl)benzo[d]oxazol-2(3H)-one(7k). (53%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (t, *J* = 1.5 Hz, 1H), 7.14 (dd, *J* = 5.0, 4.8 Hz, 2H), 7.00-6.90 (m, 4H), 6.04 (s, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 148.6, 147.7, 142.6, 131.6, 126.9, 110.6, 109.9,109.5,109.1,108.6, 107.1, 106.6, 102.0. HRMS (ESI) *m/z* Calculated for $C_{14}H_9NNaO_4^+$[M+Na]$^+$ 278.2148, found 278.2143.



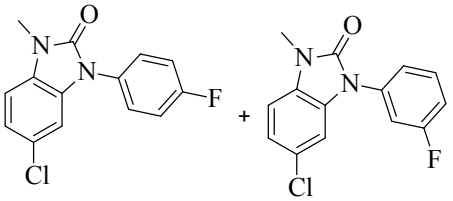
7I p:m=1:1

3-([1,1'-biphenyl]-4-yl)benzo[d]oxazol-2(3H)-one/3-([1,1'-biphenyl]-3-yl)benzo[d]oxazol-2(3H)-one (p:m=~1:1).(53%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.76 (m, 3H), 7.67 – 7.61(m, 9H), 7.56 (t, *J* = 1.9 Hz, 1H), 7.54 – 7.47 (m, 5H), 7.45– 7.40 (m, 2H), 7.31-7.29(m, 2H), 7.22 – 7.16 (m, 4H), 7.15-7.12 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 143.2, 142.9, 141.4, 140.0,138.8, 134.0, 132.6, 131.2,130.6, 129.9, 129.4, 128.8,128.7, 128.4,128.2,127.6,127.4, 126.9,126.8, 125.6, 124.9, 124.4,124.1,123.8,123.6,123.5, 122..9, 110.7, 110.1, 109.8, 109.2. HRMS (ESI) *m/z* Calculated for $C_{19}H_{13}NNaO_2^+$[M+Na] $^+$310.0838, found 310.0834.



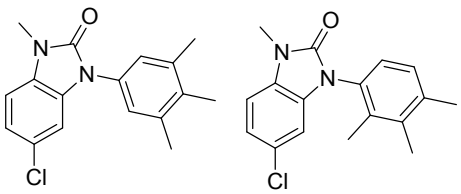
7m p:m=~1:1

3-(4-benzylphenyl)benzo[d]oxazol-2(3H)-one/3-(3-benzylphenyl)benzo[d]oxazol-2(3H)-one. (p:m=~1:1).(43%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.30 (s, 1H), 7.27 – 7.03 (m, 6H), 7.11 – 7.03 (m, 2H), 7.00 – 6.90 (m, 1H), 3.98 (d, *J* = 3.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3,153.2, 143.3, 142.7, 141.6, 140.3,140.2, 133.7, 132.1, 131.5, 131.5,131.3, 130.2, 129.8, 129.1,129.0, 128.9,128.7,128.6, 126.5,126.4, 125.4, 125.1, 123.94,123.92, 123.11 (d, *J* = 2.5 Hz), 122.7, 116.0, 110.3, 109.38,109.36, 41.7,41.6. HRMS (ESI) *m/z* Calculated for $C_{20}H_{15}NNaO_2^+$[M+Na] $^+$324.0995, found 324.0991.



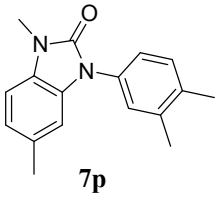
7n p:m=1:1.6

5-chloro-3-(4-fluorophenyl)-1-methyl-1H-benzo[d]imidazol-2(3H)-one/5-chloro-3-(3-fluorophenyl)-1-methyl-1H-benzo[d]imidazol-2(3H)-one (7n p:m=1:1.6). (46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.38 (m, 4H), 7.14 (d, *J* = 8.2 Hz, 1H), 7.05 (d, *J* = 12.5 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 3.47 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 139.8, 138.1, 134.06 (s), 131.5, 130.5,130.4,1 30.3, 129.5, 128.84 (d, *J* = 12.9 Hz), 127.0, 126.7, 125.9, 123.0, 121.74 (d, *J* =4.9 Hz), 109.05 (d, *J* = 5.6 Hz), 108.24 (d, *J* = 1.7 Hz), 27.4. HRMS (ESI) *m/z* Calculated for $C_{14}H_{10}ClFKN_2O$+ [M+H]+ 318.2403,found 318.2401



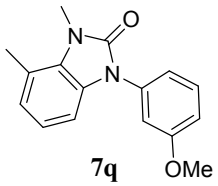
7o p:m/3:1

5-chloro-1-methyl-3-(3,4,5-trimethylphenyl)-1H-benzo[d]imidazol-2(3H)-one/5-chloro-1-methyl-3-(2,3,4-trimethylphenyl)-1H-benzo[d]imidazol-2(3H)-one(7o p:m/3:1). (60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.0 Hz, 3H), 7.10 - 7.08(m, 3H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.98 (s, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.66 (s, 1H), 3.49 (s, 3H), 3.47 (s, 3H), 2.35 (d, *J* = 1.3 Hz, 3H), 2.34 (s, 6H), 2.26 (s, 3H), 2.22 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 138.1, 135.6, 130.8, 128.7, 126.9, 125.2, 121.5,125.4, 109.0, 108.1, 27.4, 20.8, 15.3, 14.9. HRMS (ESI) *m/z* Calculated for $C_{17}H_{18}ClN_2O^+$[M+H]$^+$ 301.1102, found 301.1099.



7p

3-(3,4-dimethylphenyl)-1,5-dimethyl-1H-benzo[d]imidazol-2(3H)-one(7p) (55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.4 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 1H), 6.95 (dd, *J* = 15.0, 7.9Hz, 2H), 6.85 (s, 1H), 3.49 (s, 3H), 2.37 (s, 3H), 2.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 138.0, 136.4, 132.3, 131.2), 130.5, 129.9, 128.0, 127.4, 123.6, 122.2, 109.2, 107.2, 27.3, 21.5, 19.9, 19.6. HRMS (ESI) *m/z* Calculated for $C_{17}H_{19}N_2O^+$[M+H]$^+$267,1492, found 267.1492.



7q

1-(3-methoxyphenyl)-3,4-dimethyl-1H-benzo[d]imidazol-2(3H)-one(7p).(54%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (s, 1H), 7.13 (d, *J* = 7.1 Hz, 1H), 7.09 (s, 1H), 7.02 (dd, *J* = 7.9, 5.5 Hz, 2H), 6.98 – 6.95 (m, 1H), 6.77-6.74 (m, *J* = 8.3, 2.4, 0.7 Hz, 1H), 3.82 (s, 3H), 3.68 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 155.4, 138.8, 133.5, 130.1, 128.8, 122.7, 121.6, 110.9, 110.6, 106.0, 104.9, 55.5, 28.7, 16.6. HRMS (ESI) *m/z* Calculated for $C_{16}H_{17}N_2O_2^+$[M+H]$^+$ 269.1285, found 269.1284.

References

[1] Hirofumi Ueda, Kei Yoshida, and Hidetoshi Tokuyama. *Org.Let*t. 2016, 16(16),4194-4197.

[2] Fushun Liang, Jing Tan, Chengri Piao, Qun Liu. *Synthesis*. 2008, 22, 3579-3584.

[3] Gaël Jalce, Xavier Franck, Bruno Figadère. *Eur.J.Org.Chem*. 2009, 378-386.

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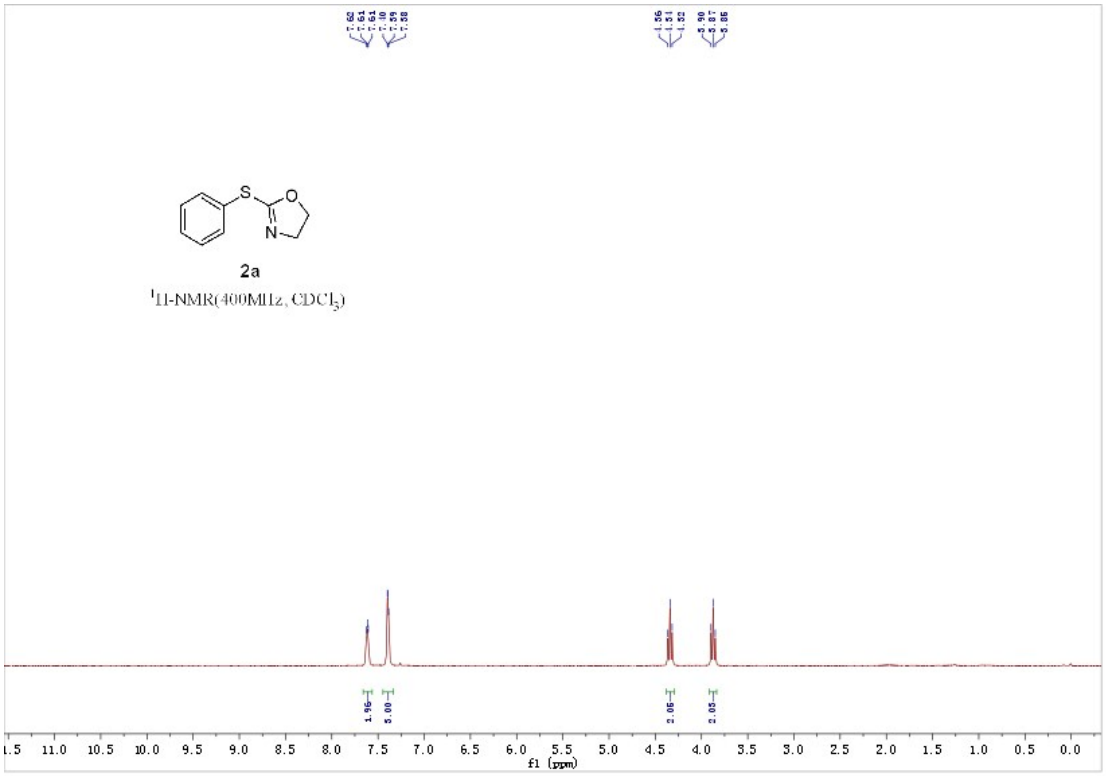
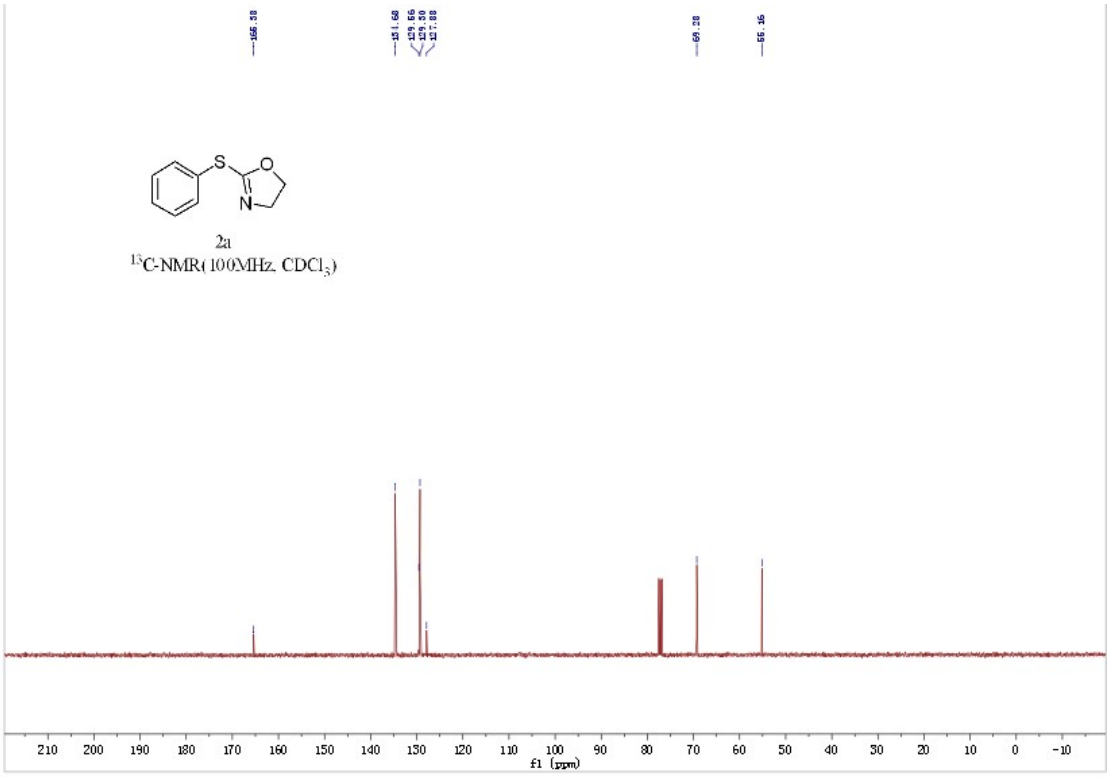
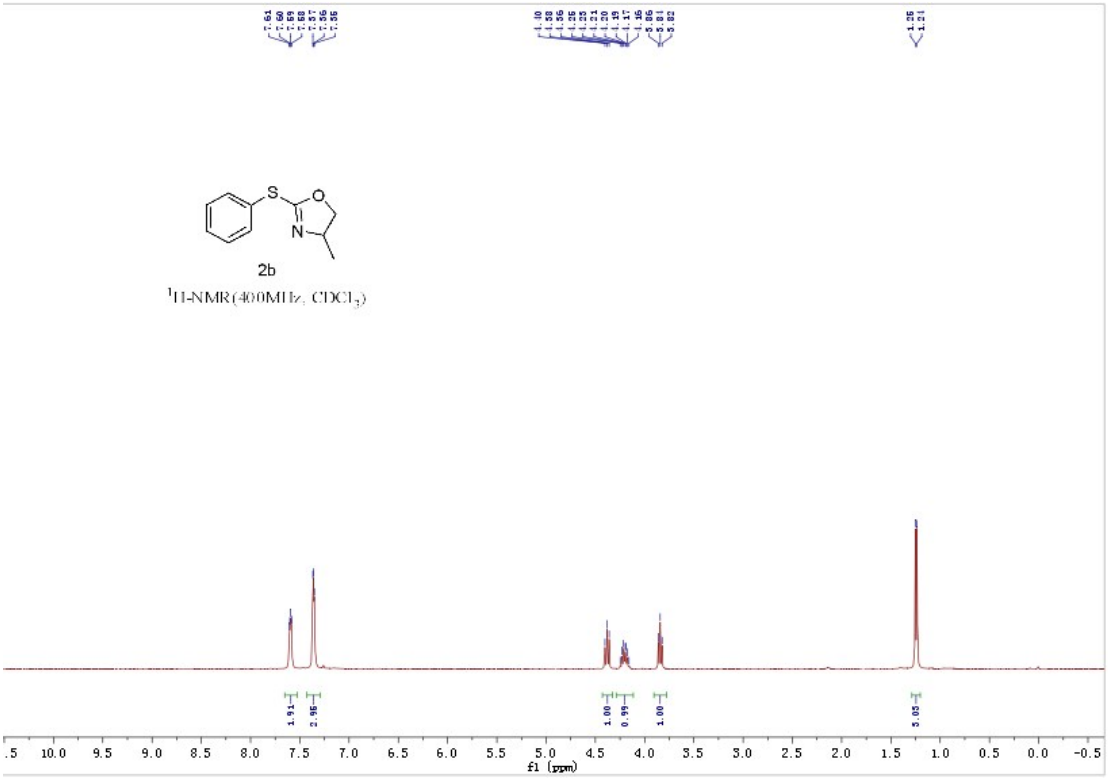
[6] (a) William Mahy, Pawel K. Plucinski, and Christopher G. Frost. *Org.Let*t. **2014,** 16, 5020-5023.(b) Astrid Beyer, Christine M. M. Reucher, and Carsten Bolm. *Org.Lett*. **2011**,13(11), 2876-2879. (c) Hua Fu et al. *Eur. J. Org. Chem*. **2015**, 5869–5875. [d] Bianchi, Mario et al. *European Journal of Medicinal Chemistry*. **1981**, 16(4), 321-326.

NMR Spectra of compounds


2a
^{1}H-NMR(400MHz, $CDCl_3$)
f1 (ppm)


2a
^{13}C-NMR(100MHz, $CDCl_3$)
f1 (ppm)


2b
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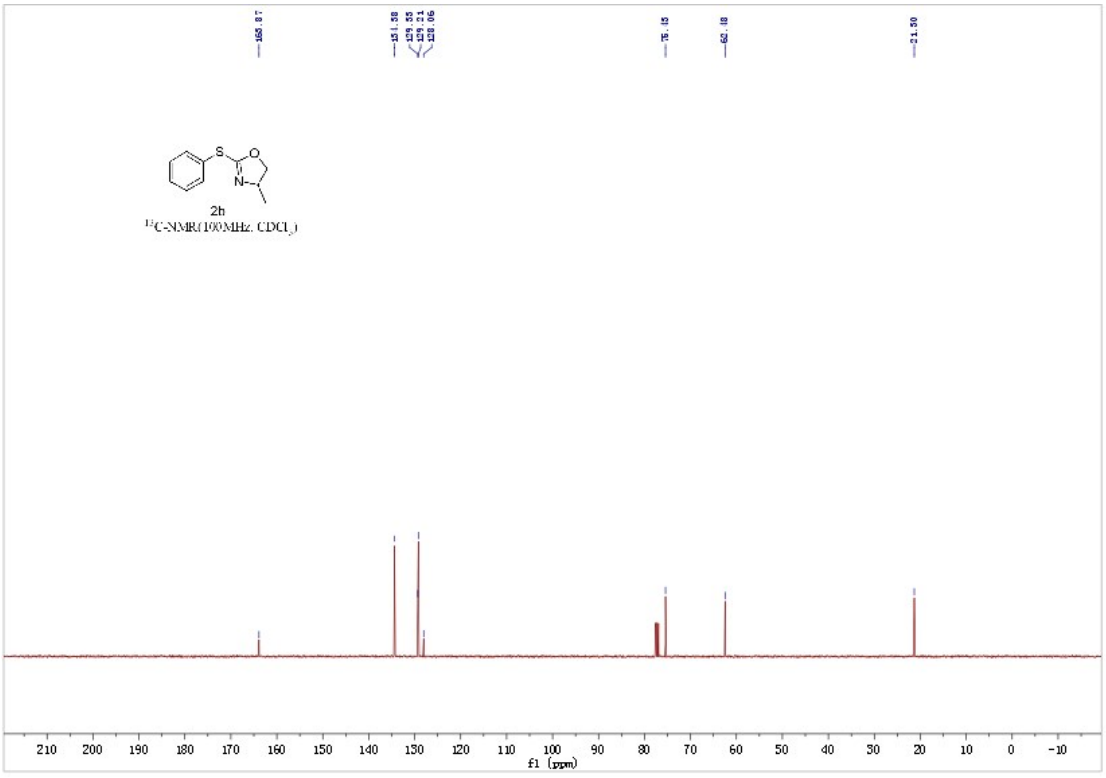
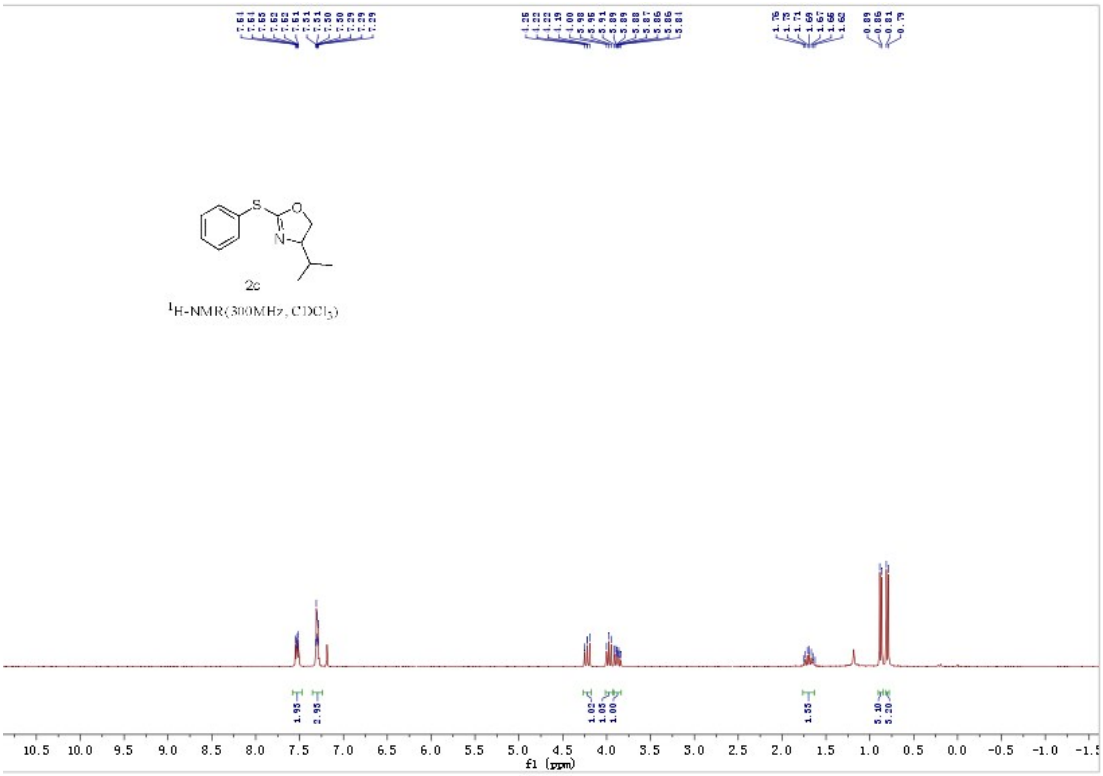
f1 (ppm)


2b
^{13}C-NMR(100MHz, $CDCl_3$)
f1 (ppm)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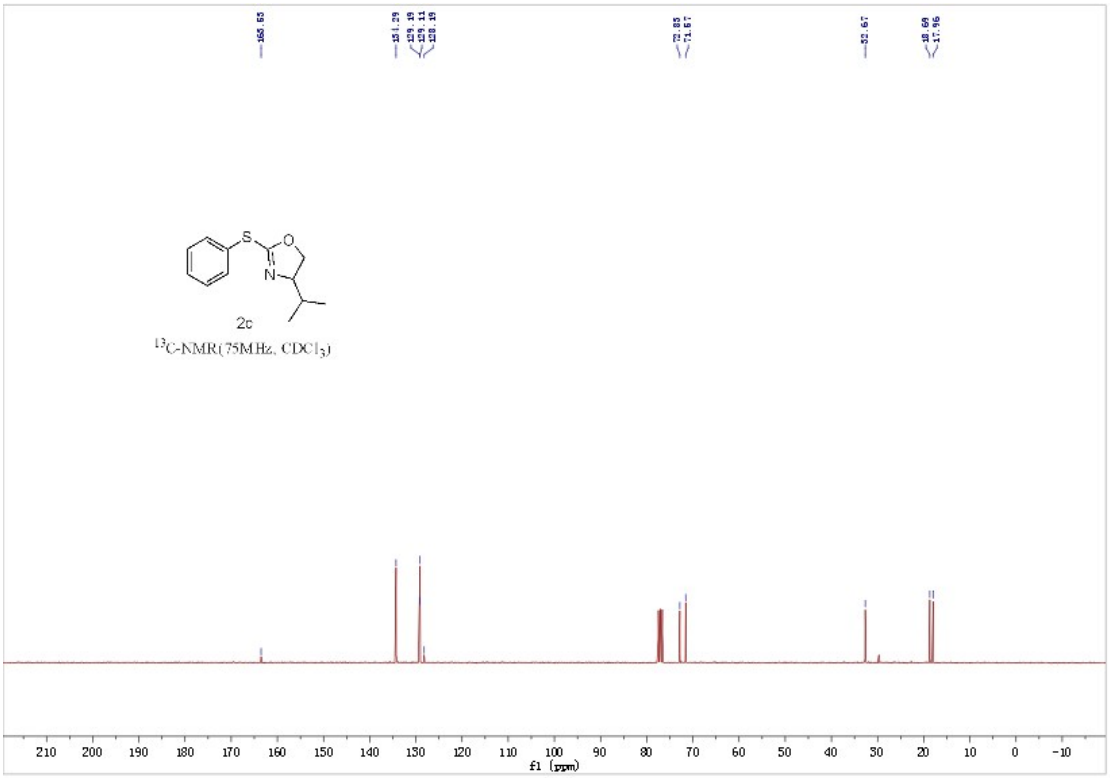
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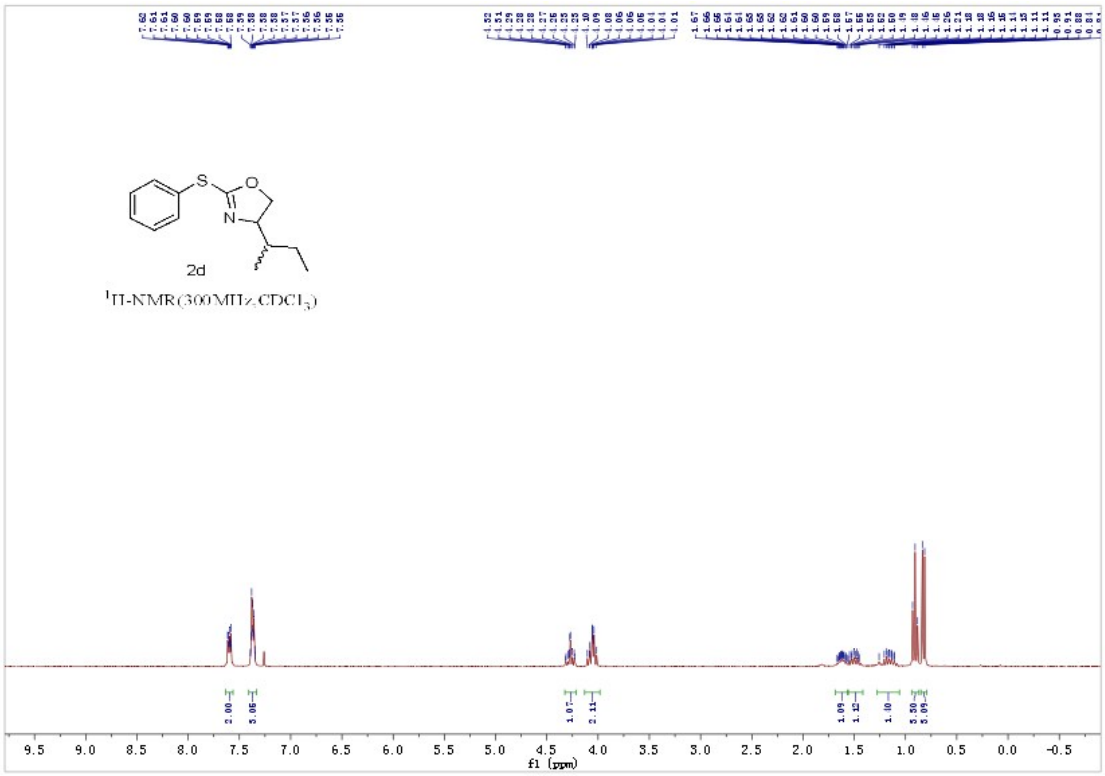
f1 (ppm)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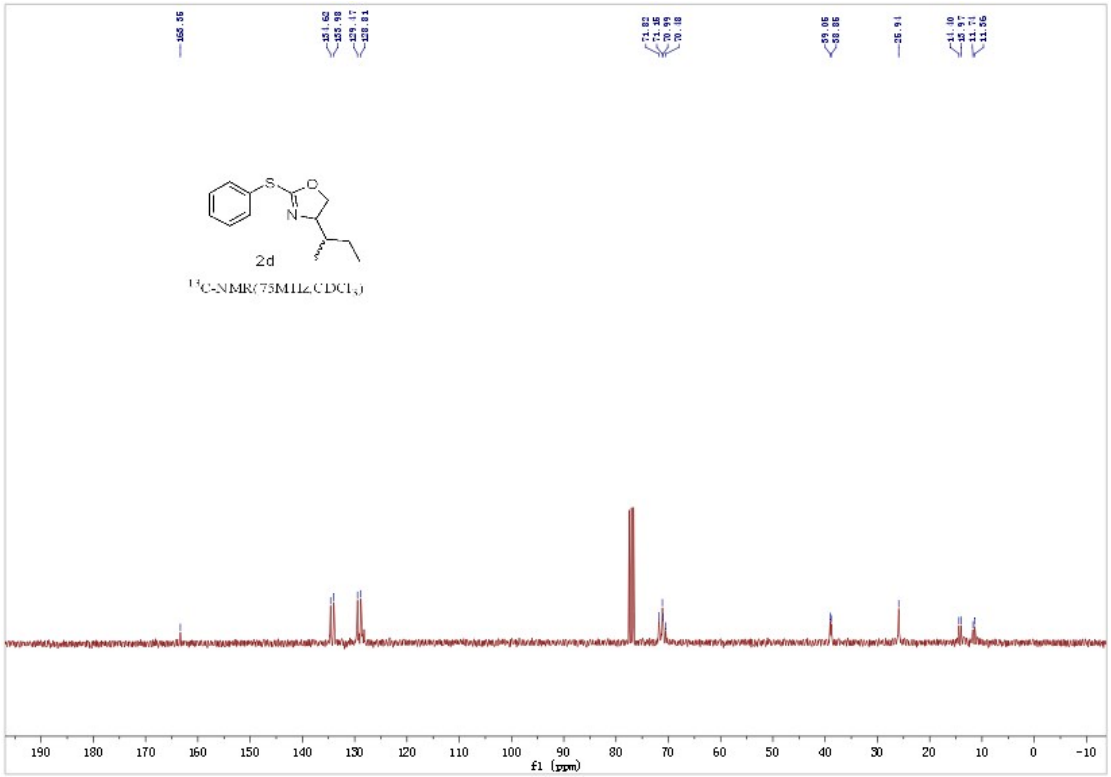
f1 (ppm)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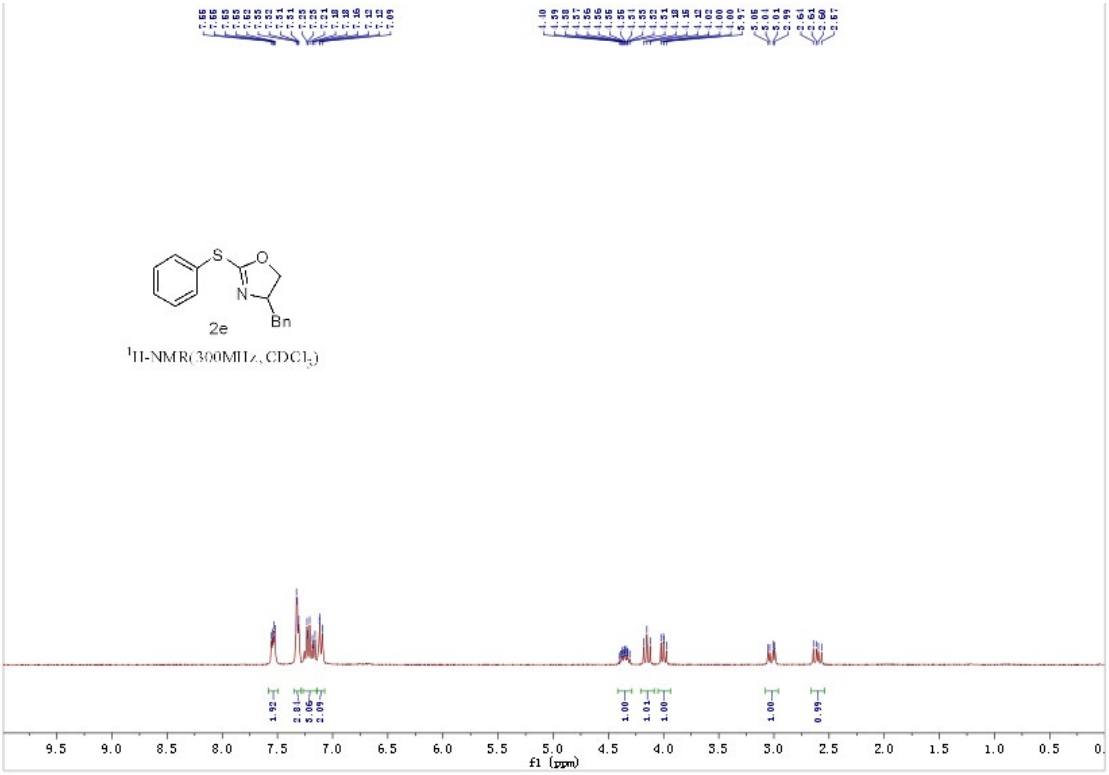
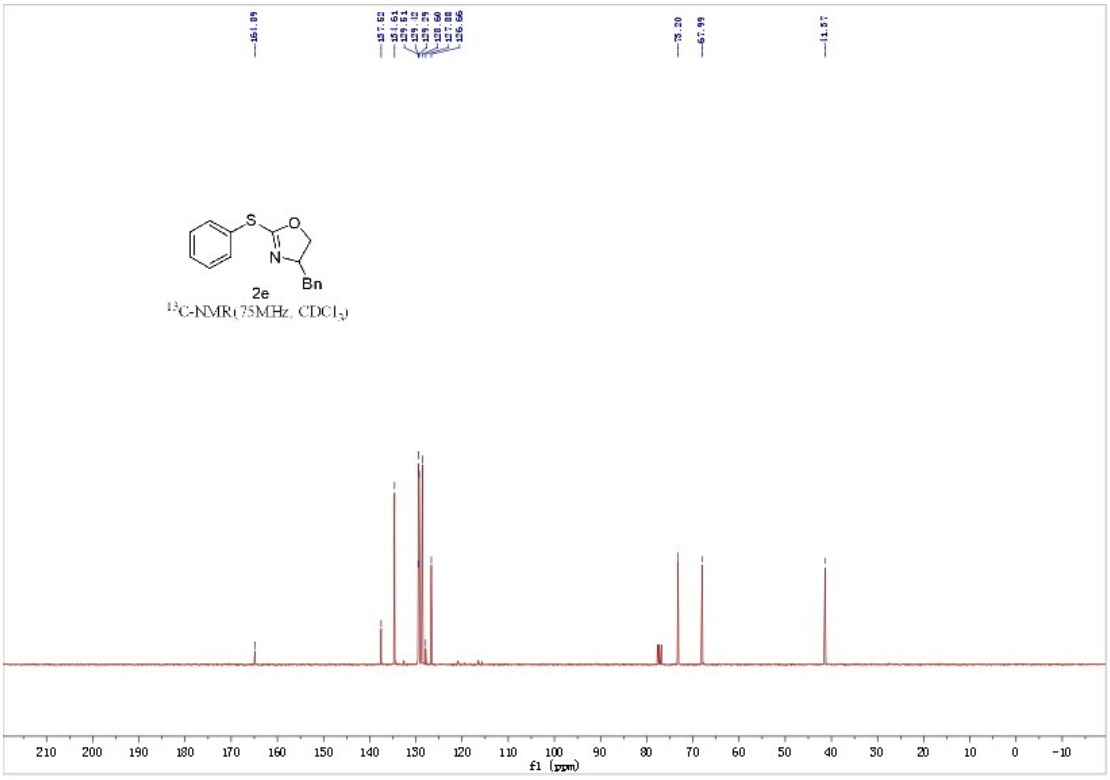
f1 (ppm)


S
O
N
Bn
2e
^{1}H-NMR(300MHz, $CDCl_3$)
f1 (ppm)


S
O
N
Bn
2e
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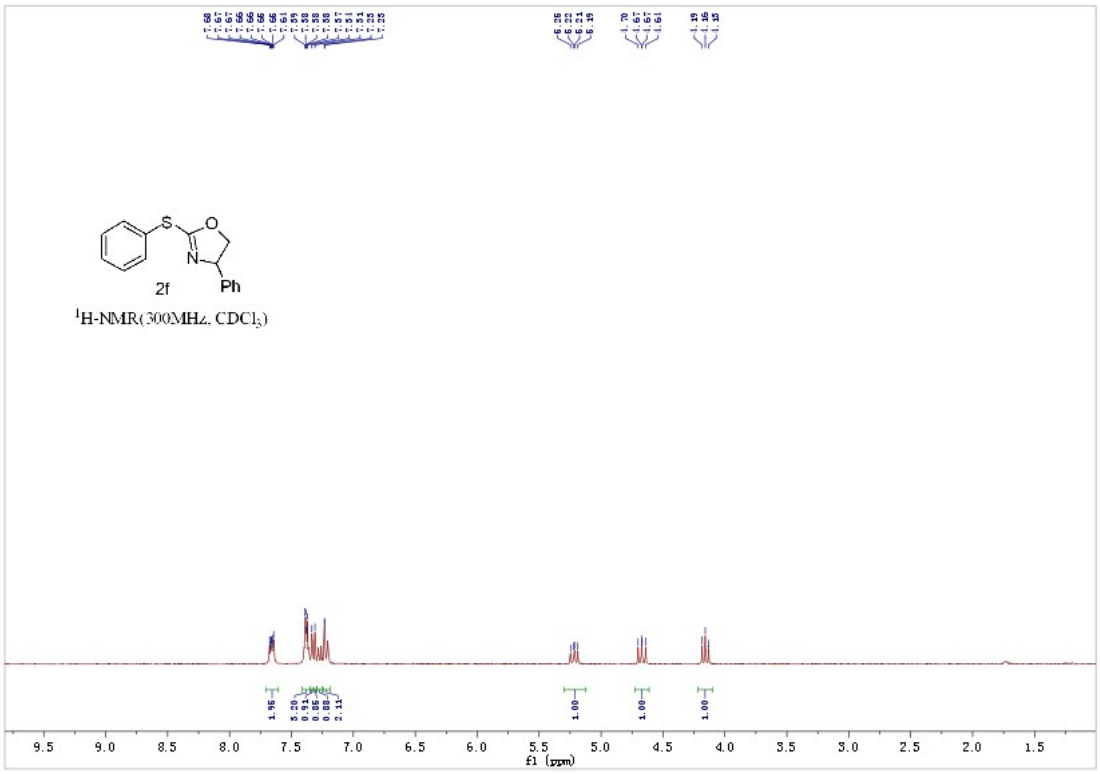
f1 (ppm)



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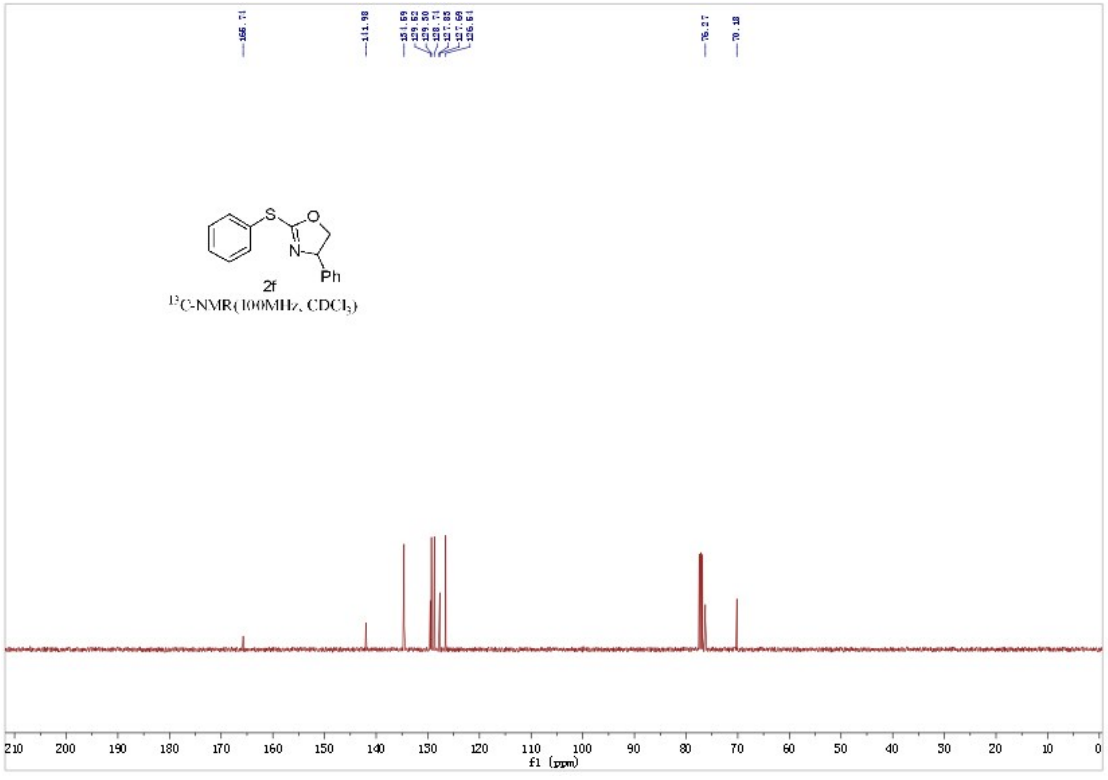

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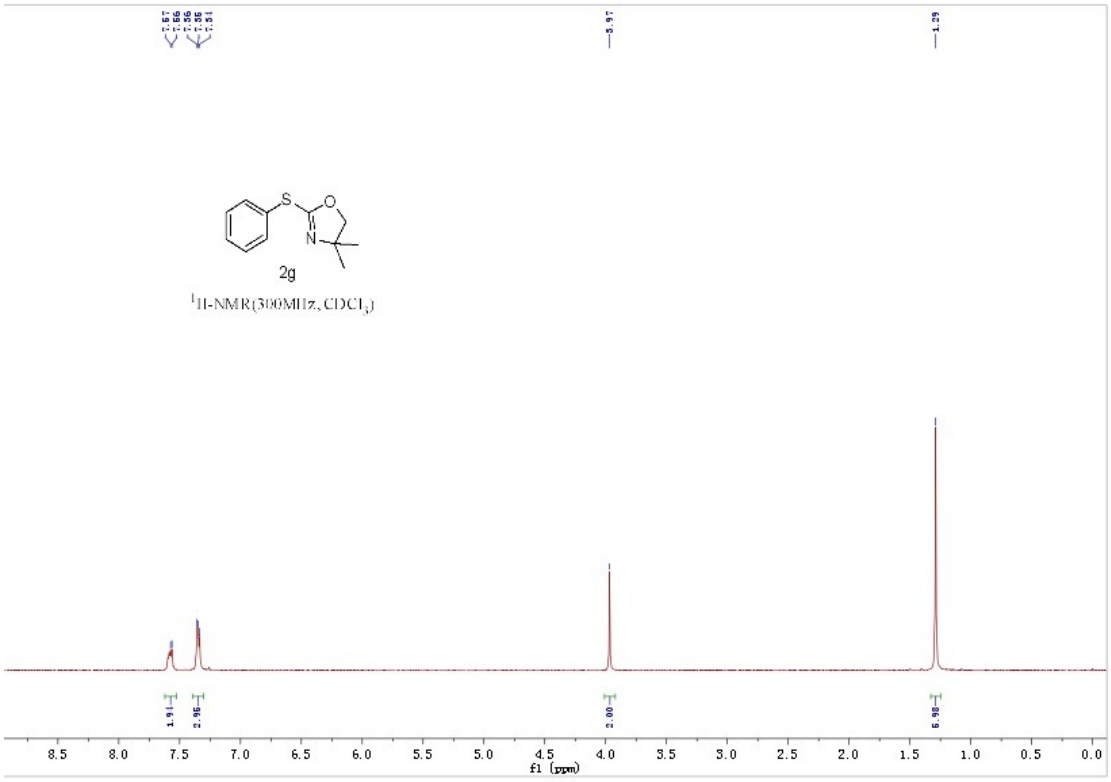

2g

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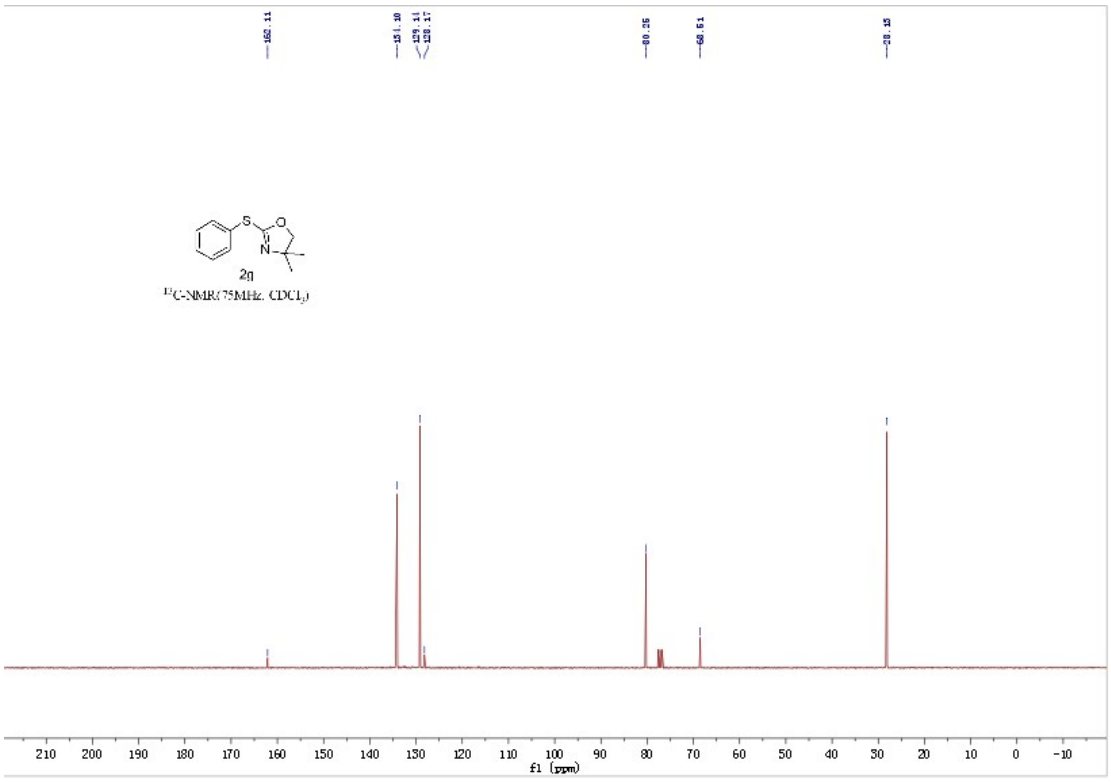

2g

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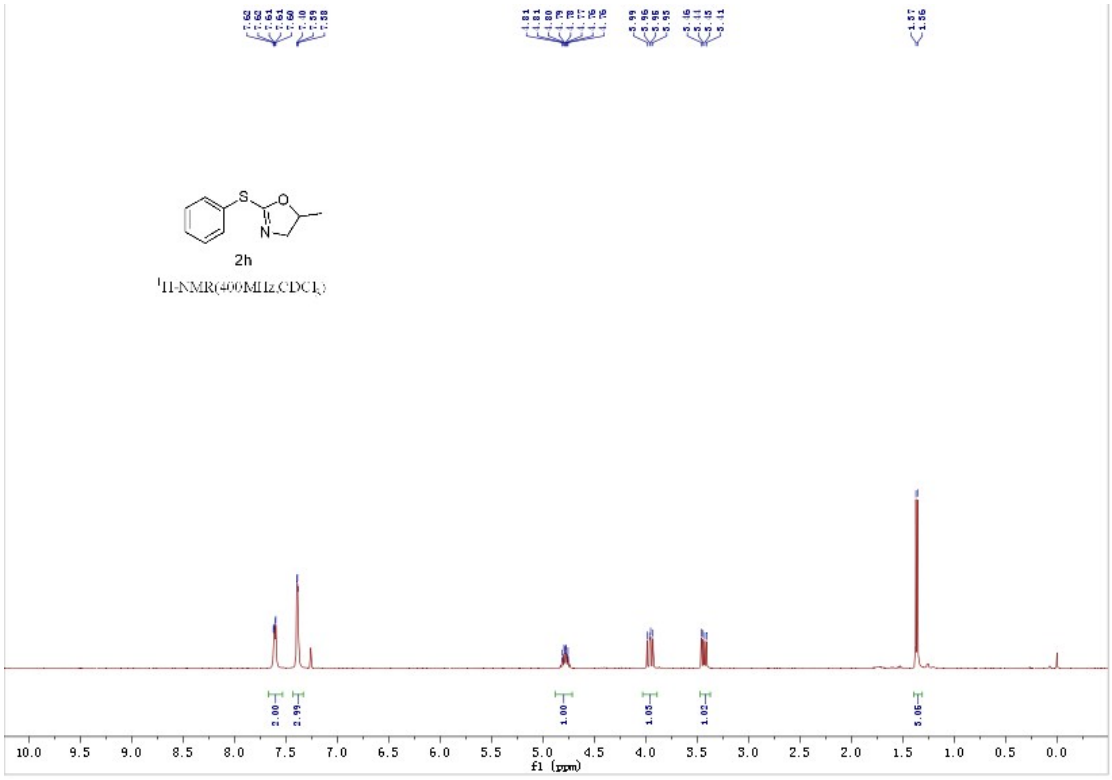
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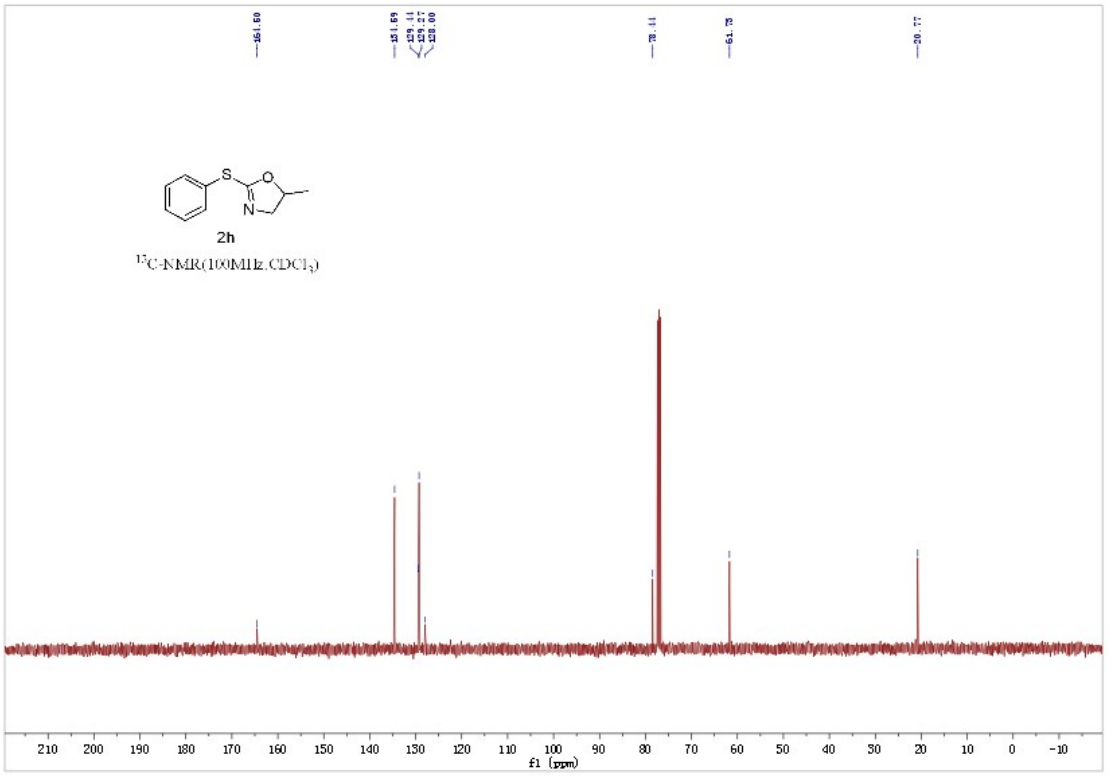
f1 (ppm)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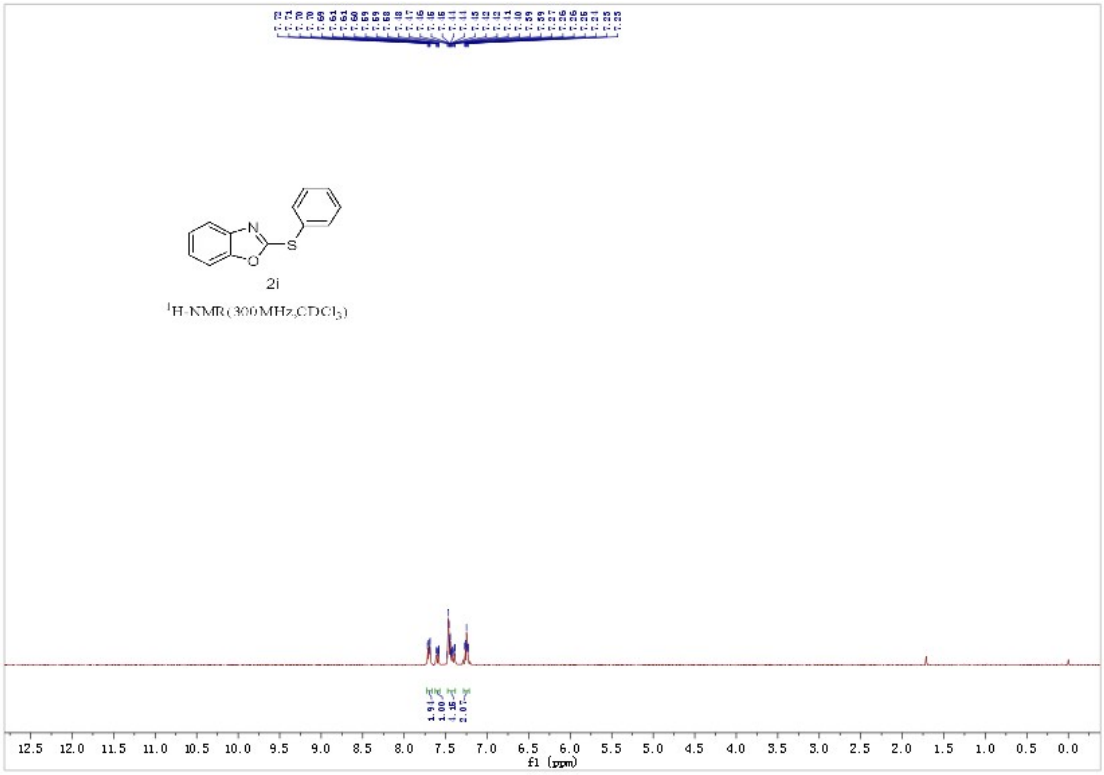
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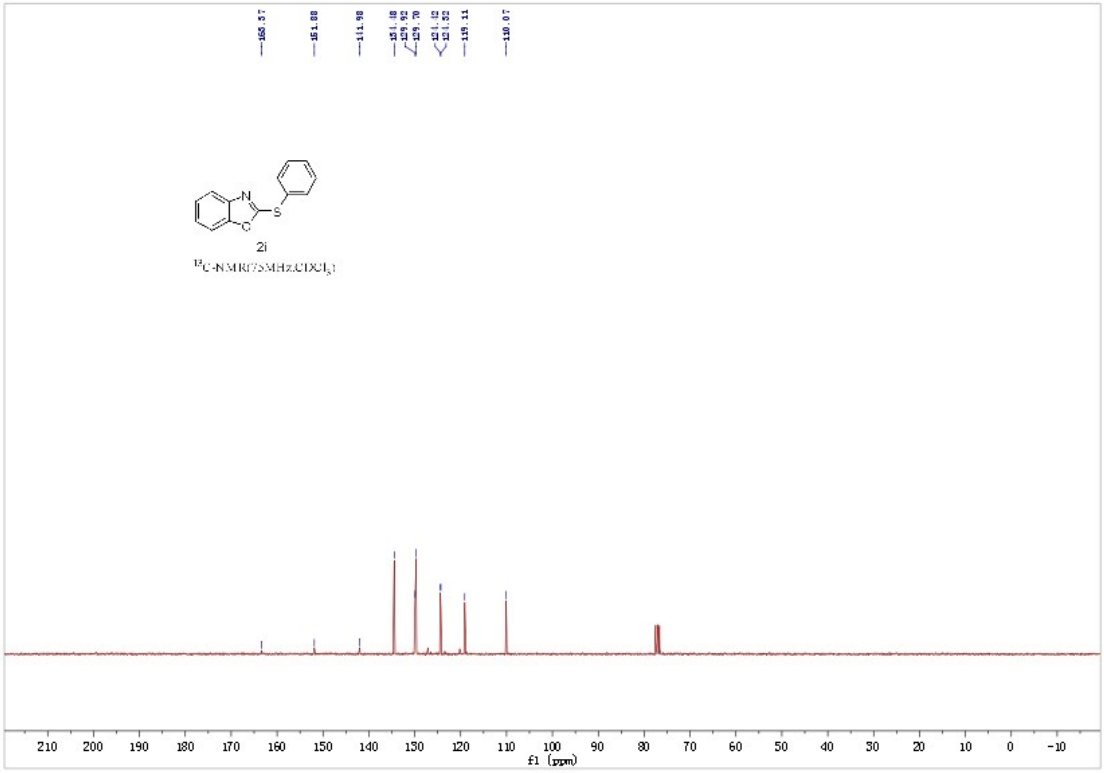
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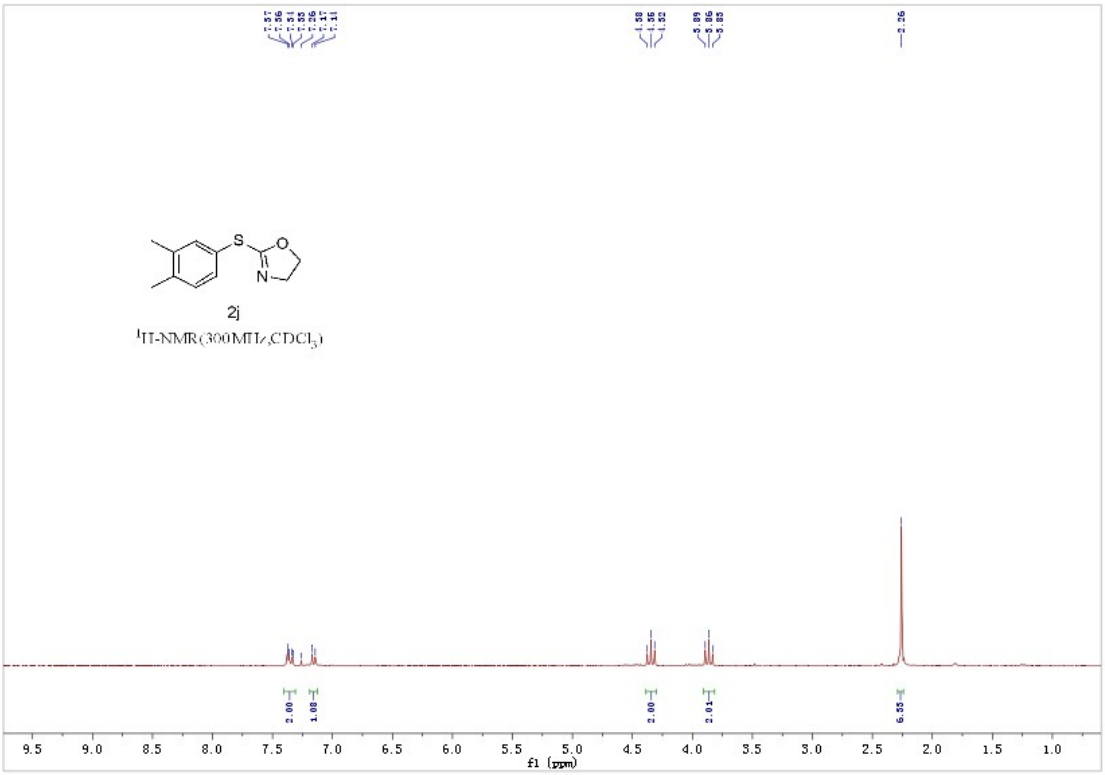
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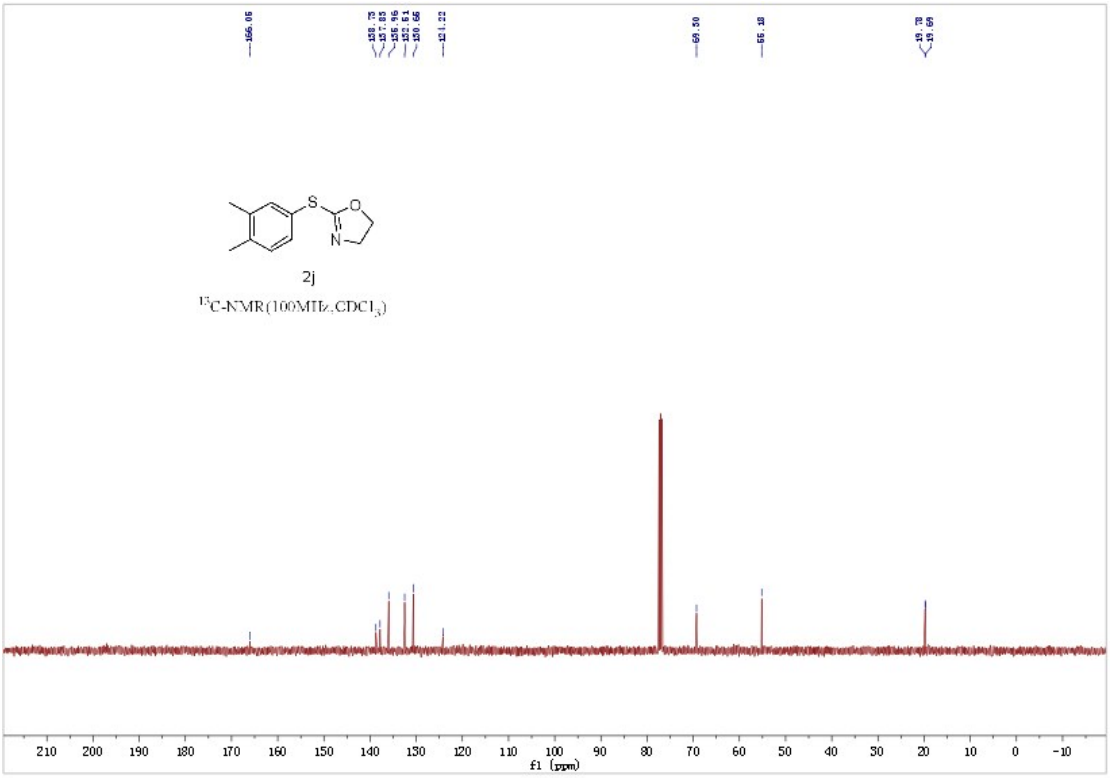
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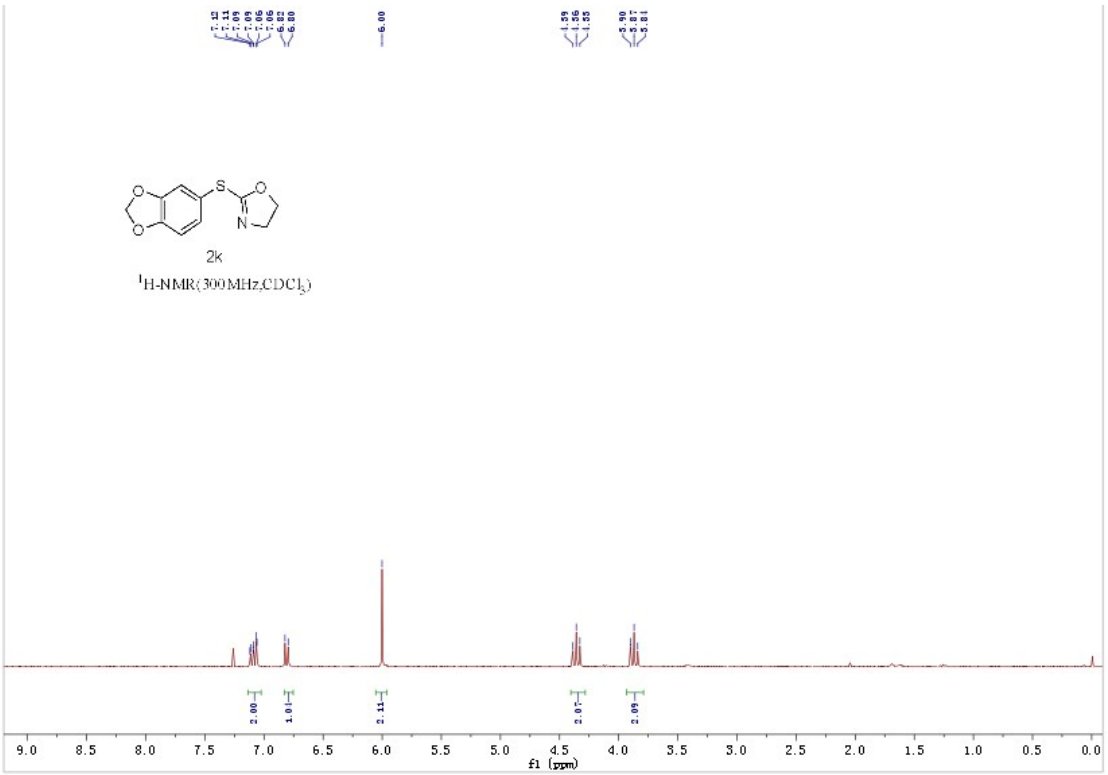
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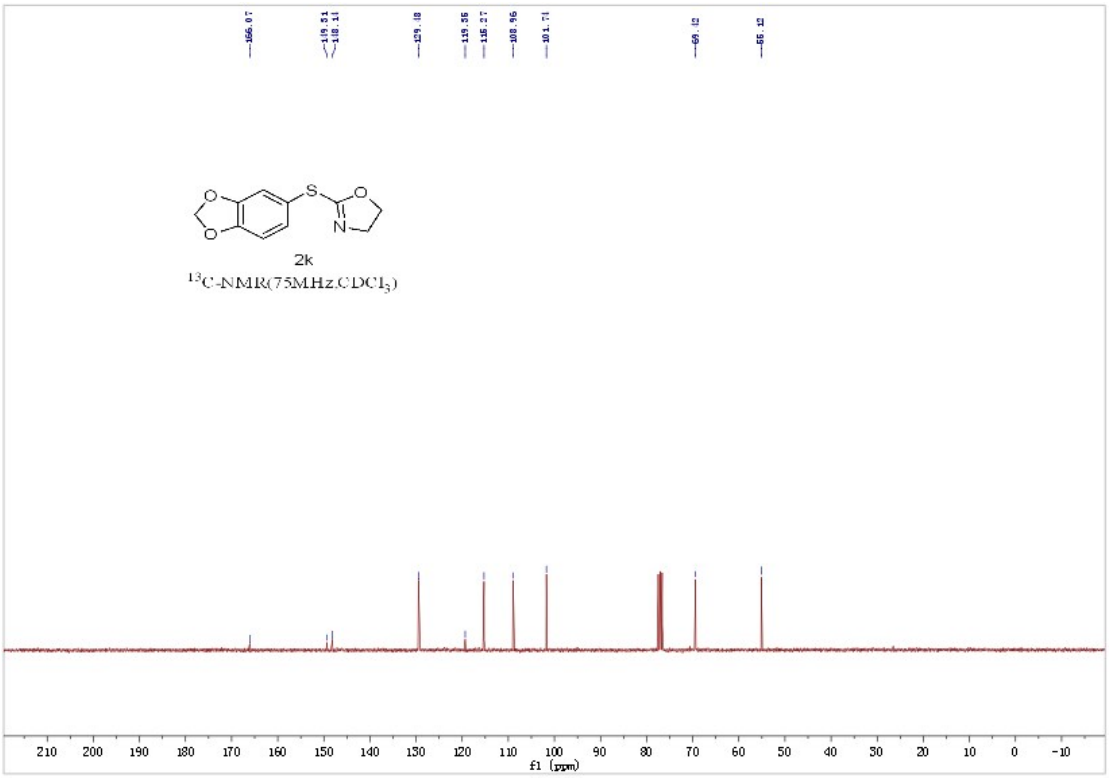
f1 (ppm)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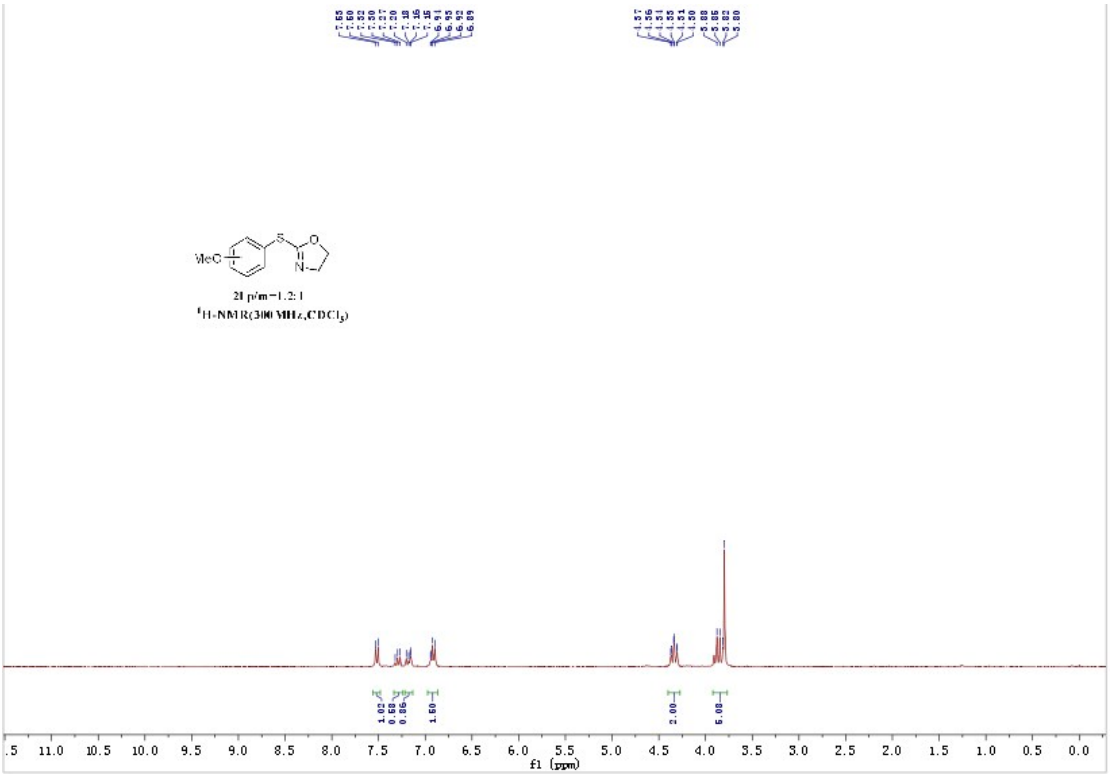
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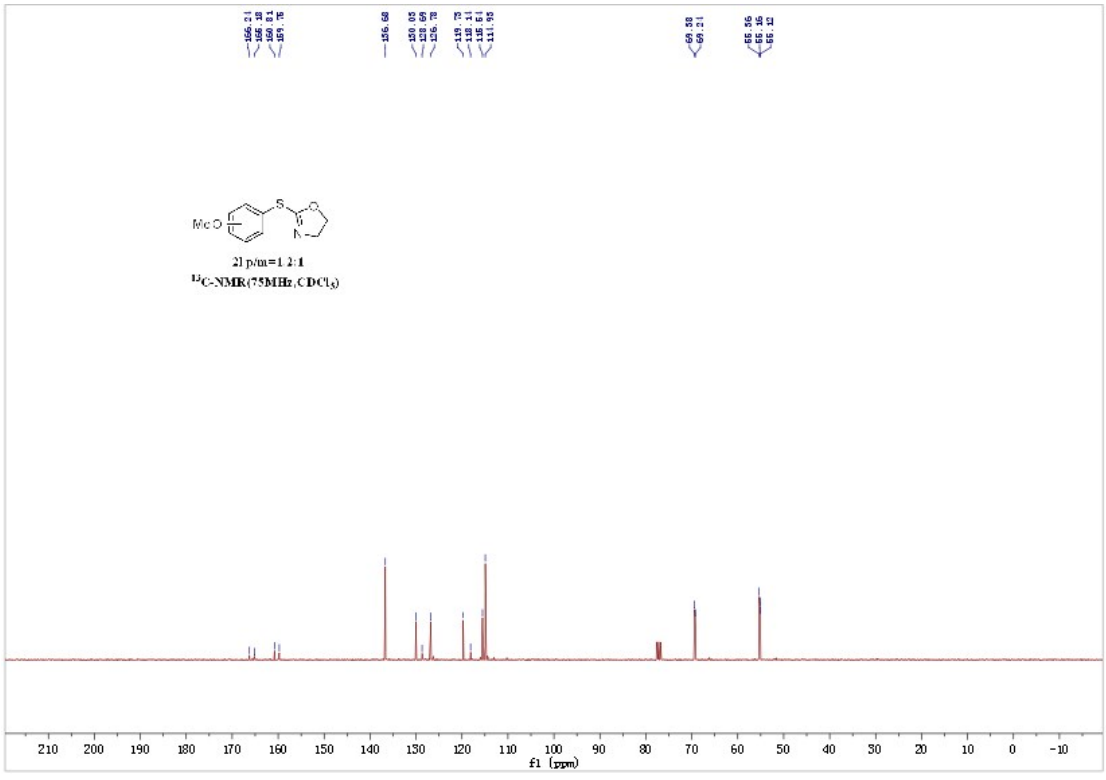
f1 (ppm)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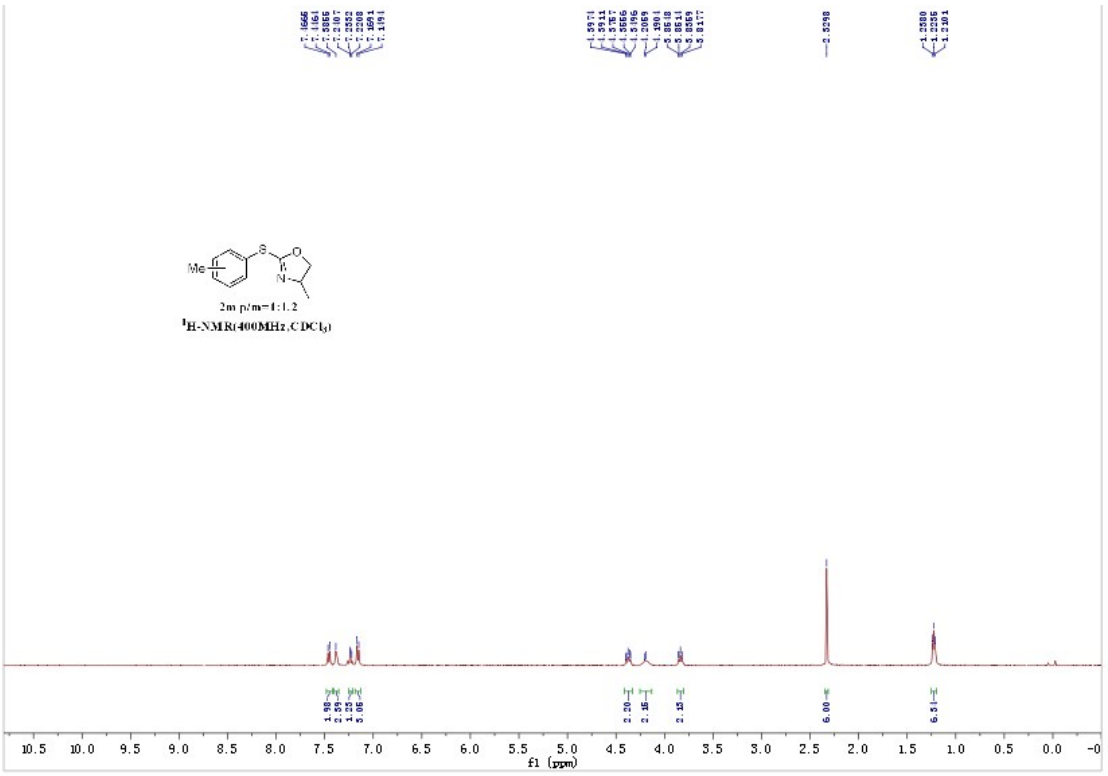
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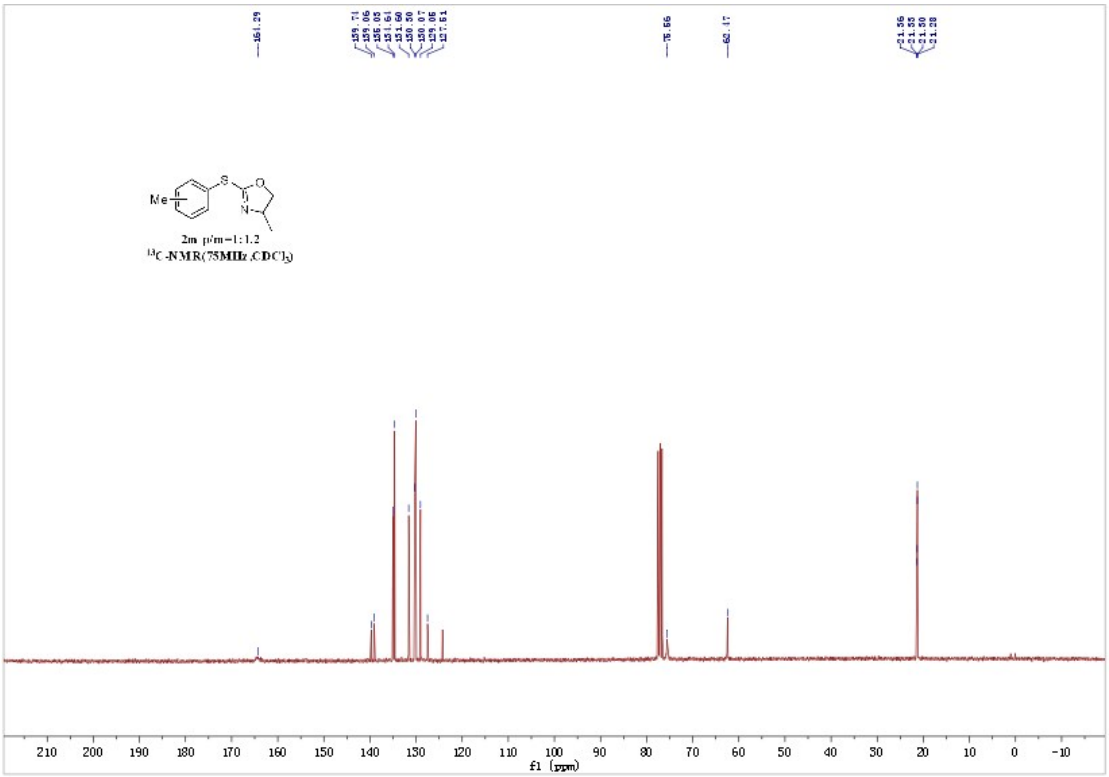
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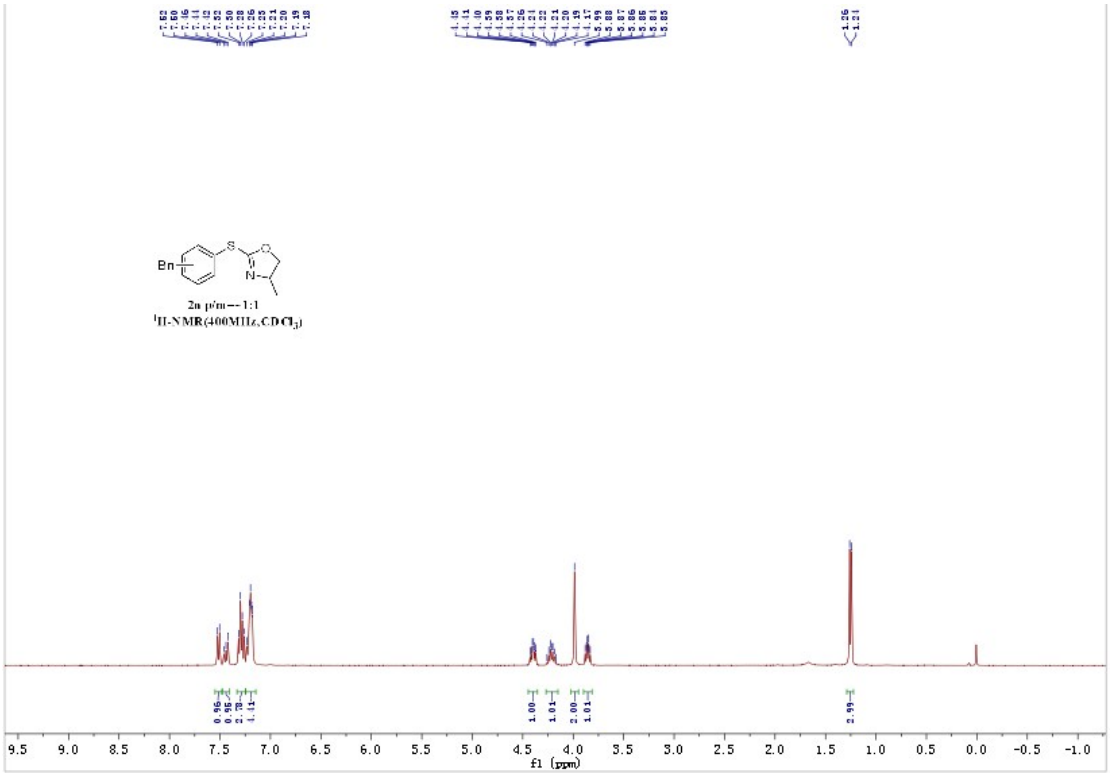
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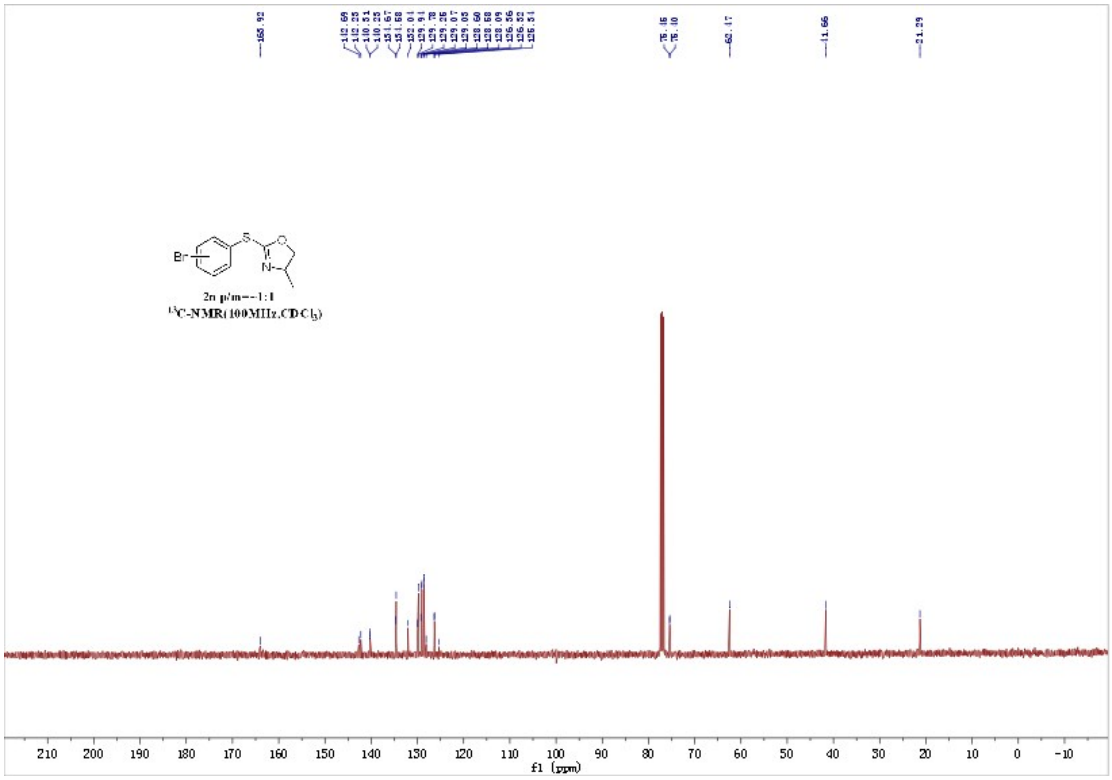
f1 (ppm)


Br
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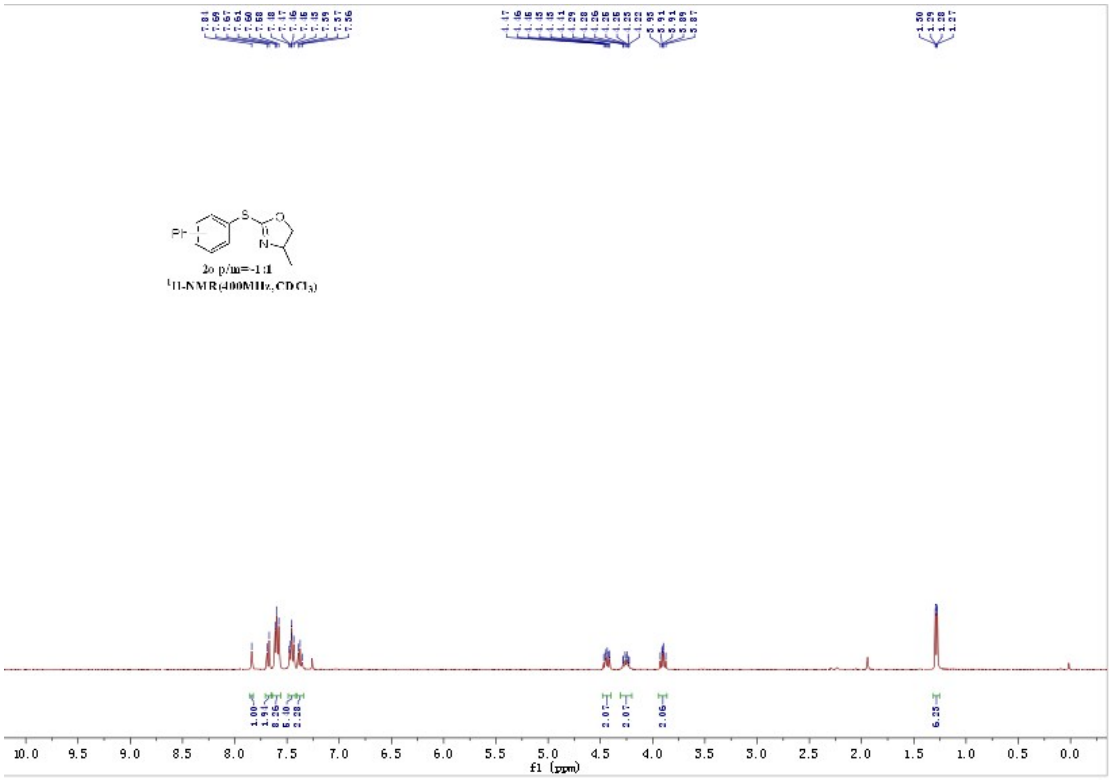
f1 (ppm)



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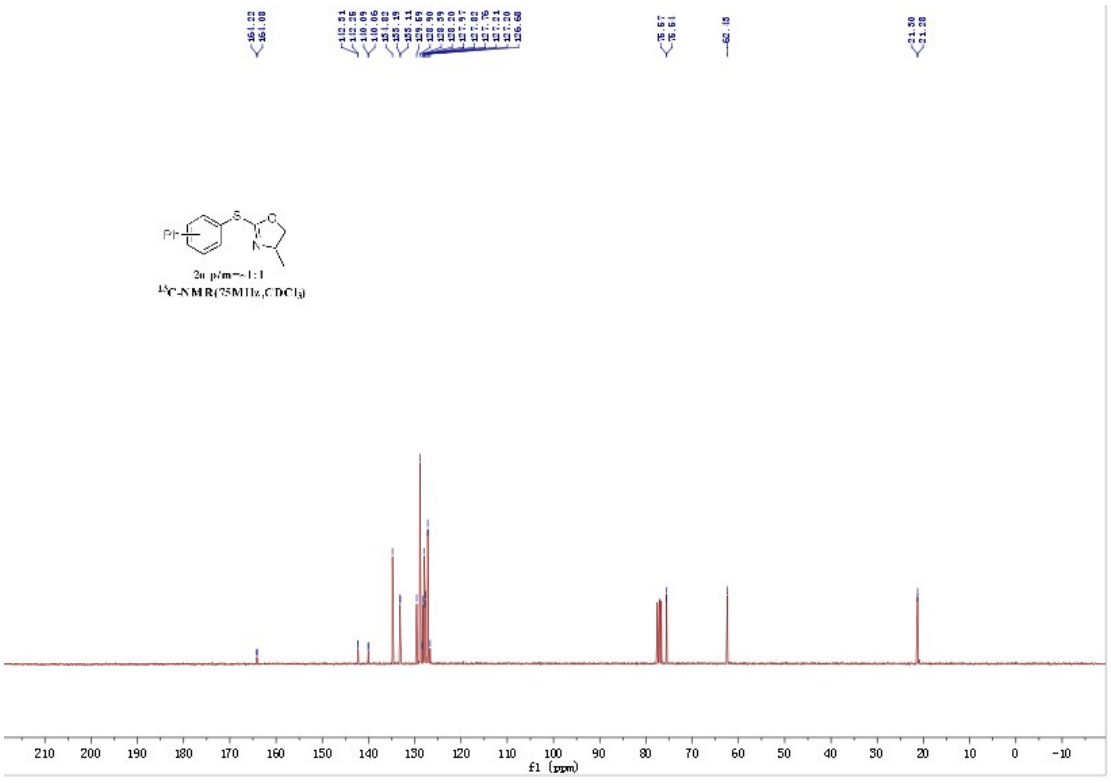

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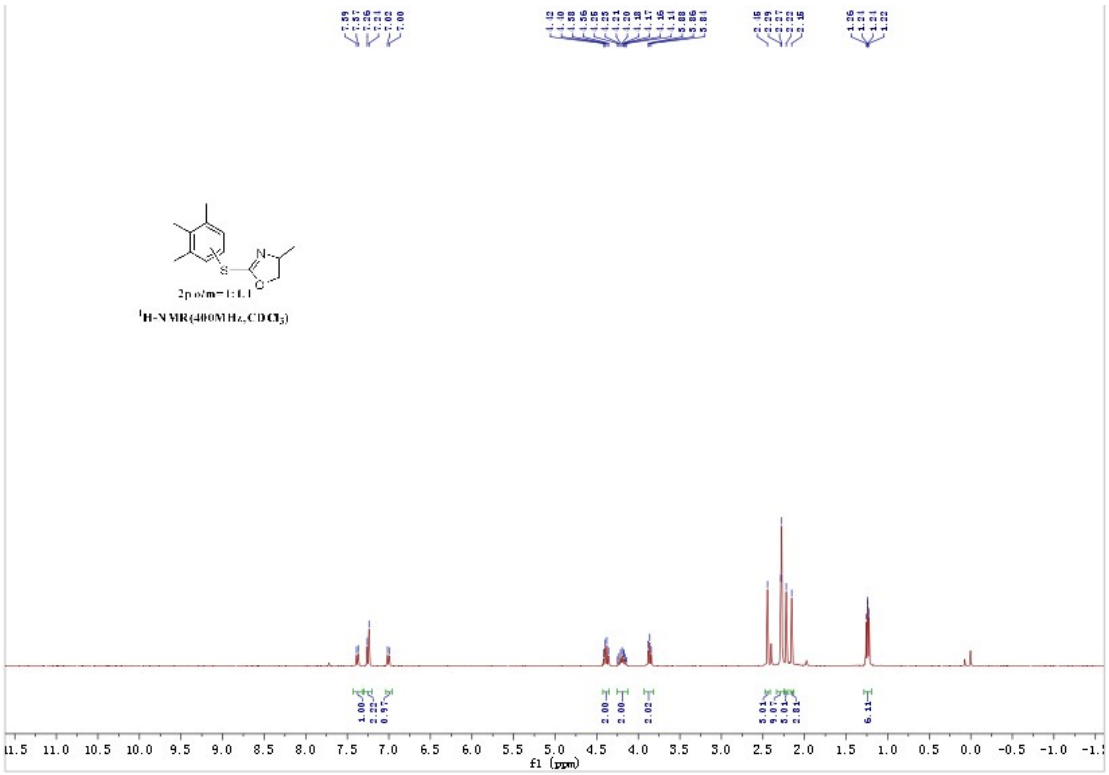
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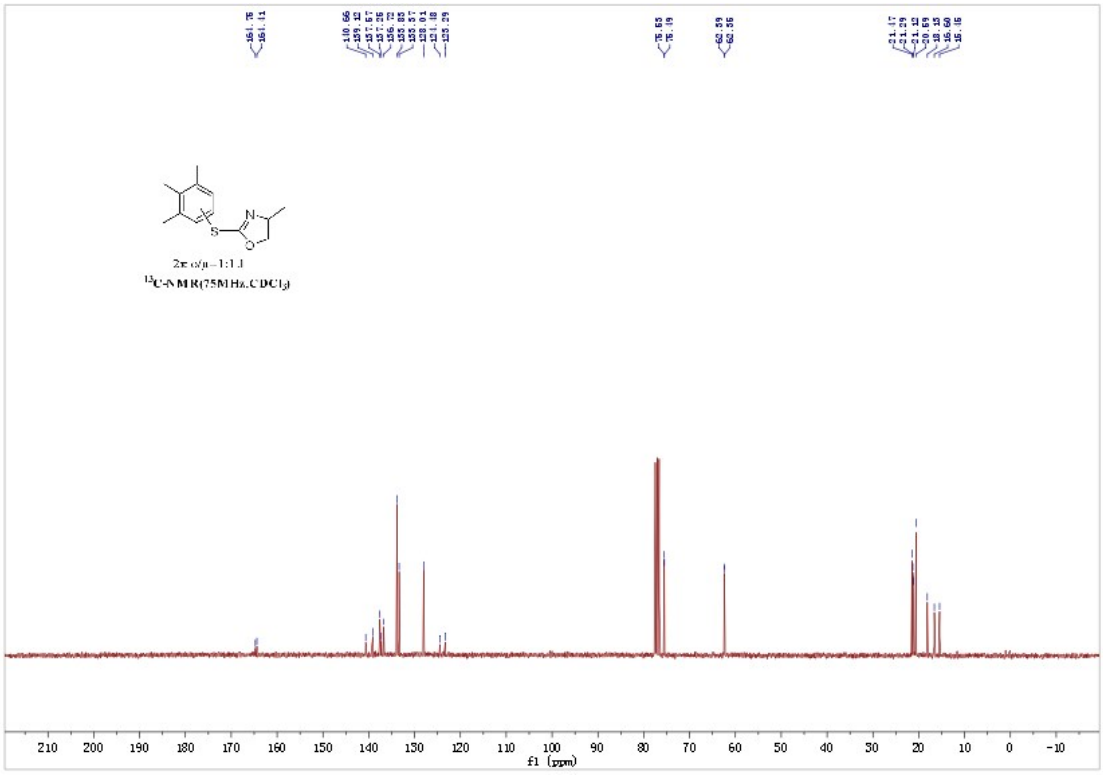
f1 (ppm)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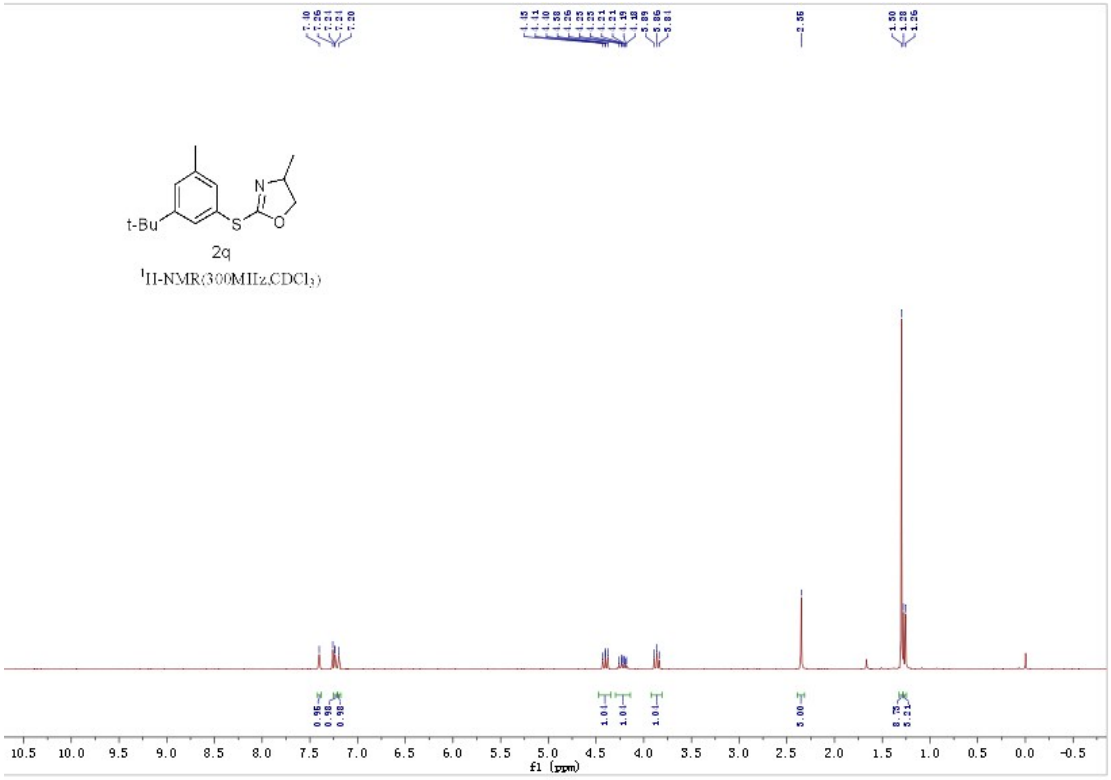
f1 (ppm)


t-Bu
N
S
O
2q
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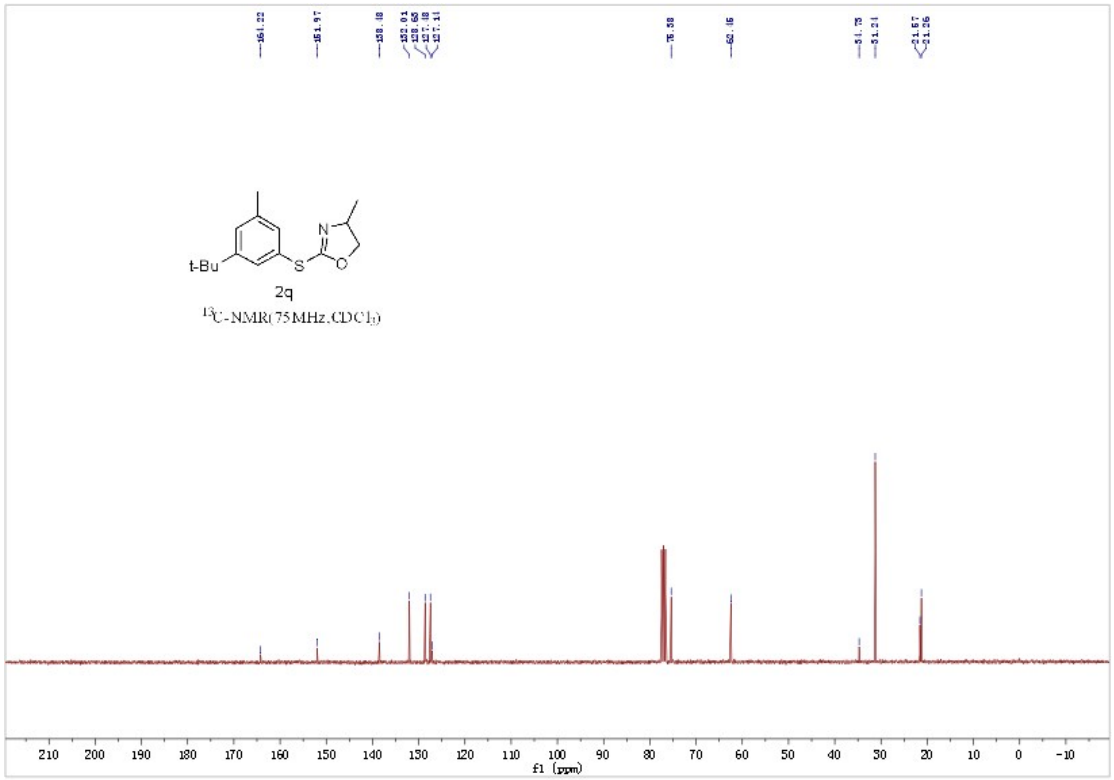
f1 (ppm)


t-Bu
N
S
O
2q
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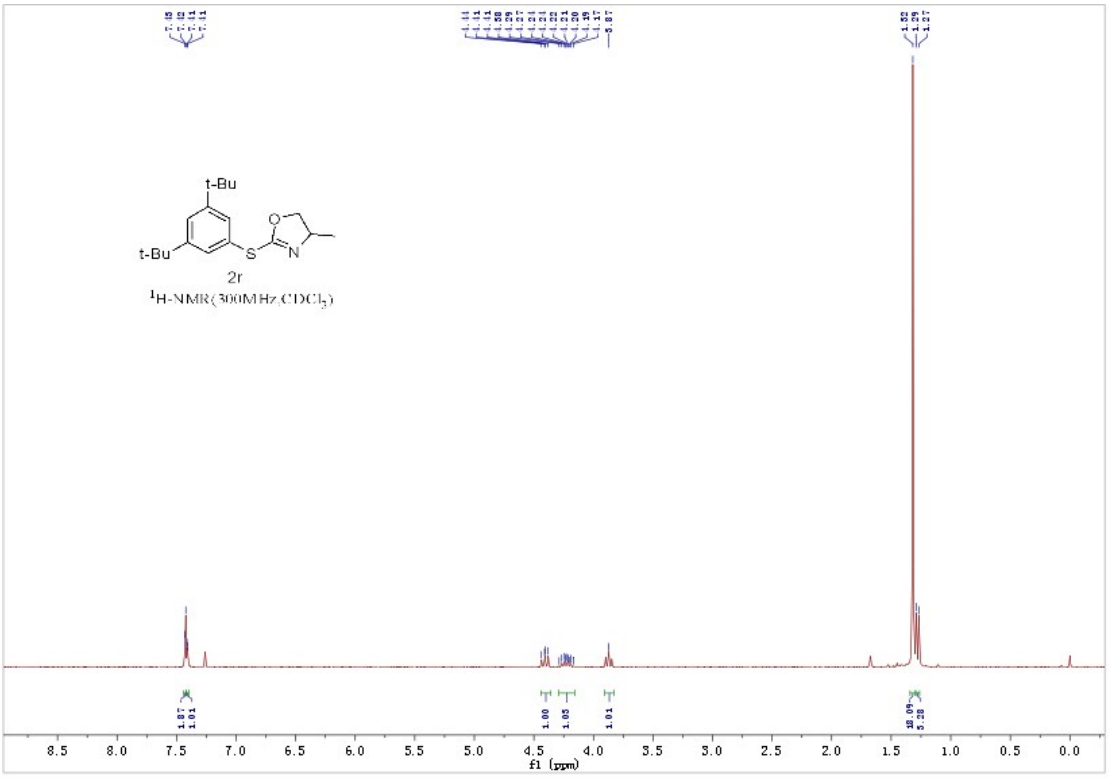
f1 (ppm)


t-Bu
t-Bu
S
O
N
2r
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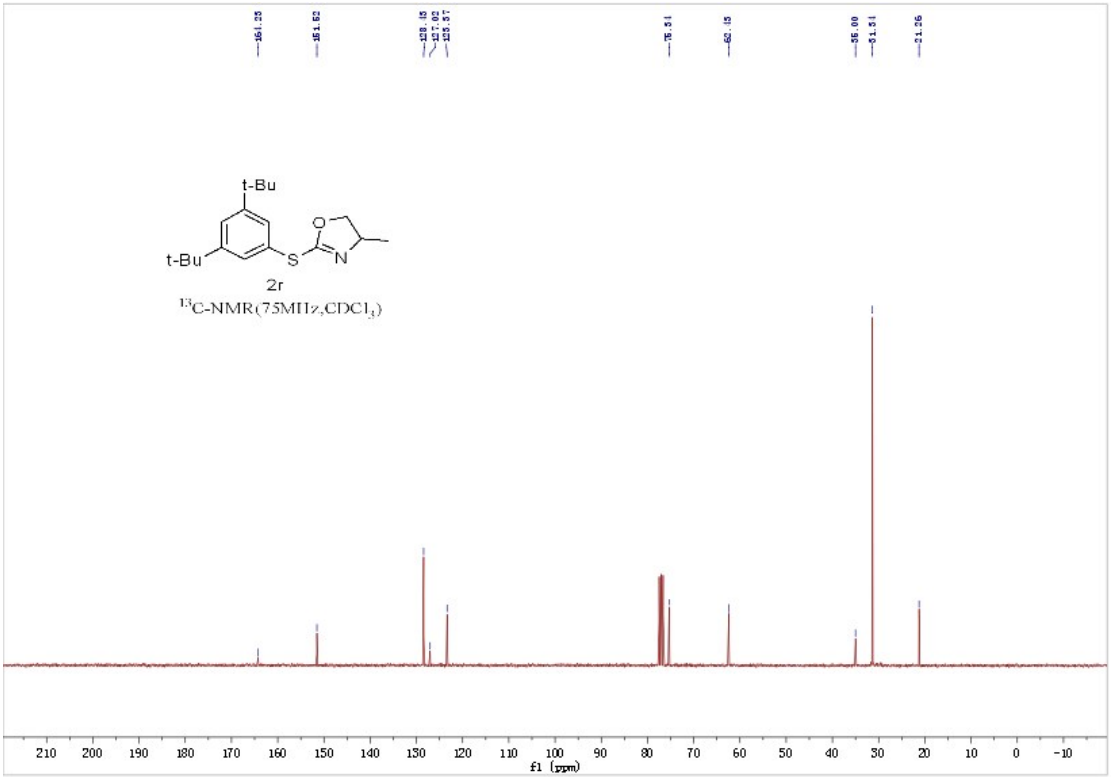
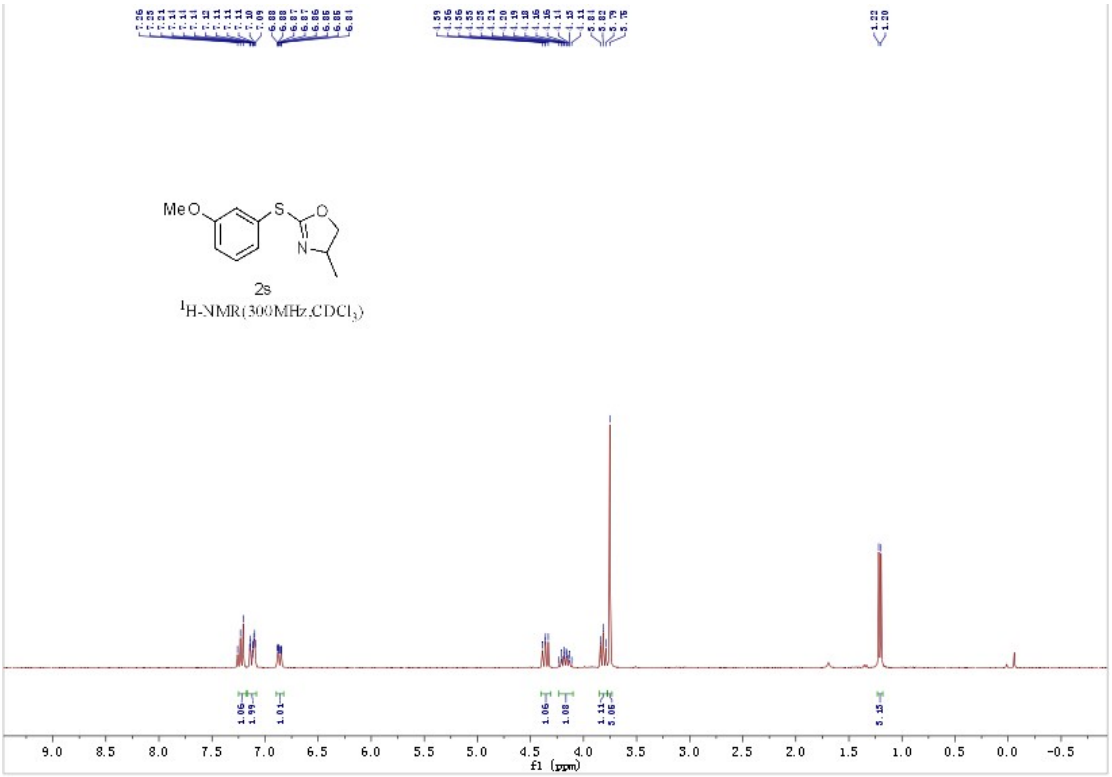
f1 (ppm)


t-Bu
t-Bu
S
O
N
2r
^{13}C-NMR(75MHz,CDCl$_3$)
f1 (ppm)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S
O
N
2s
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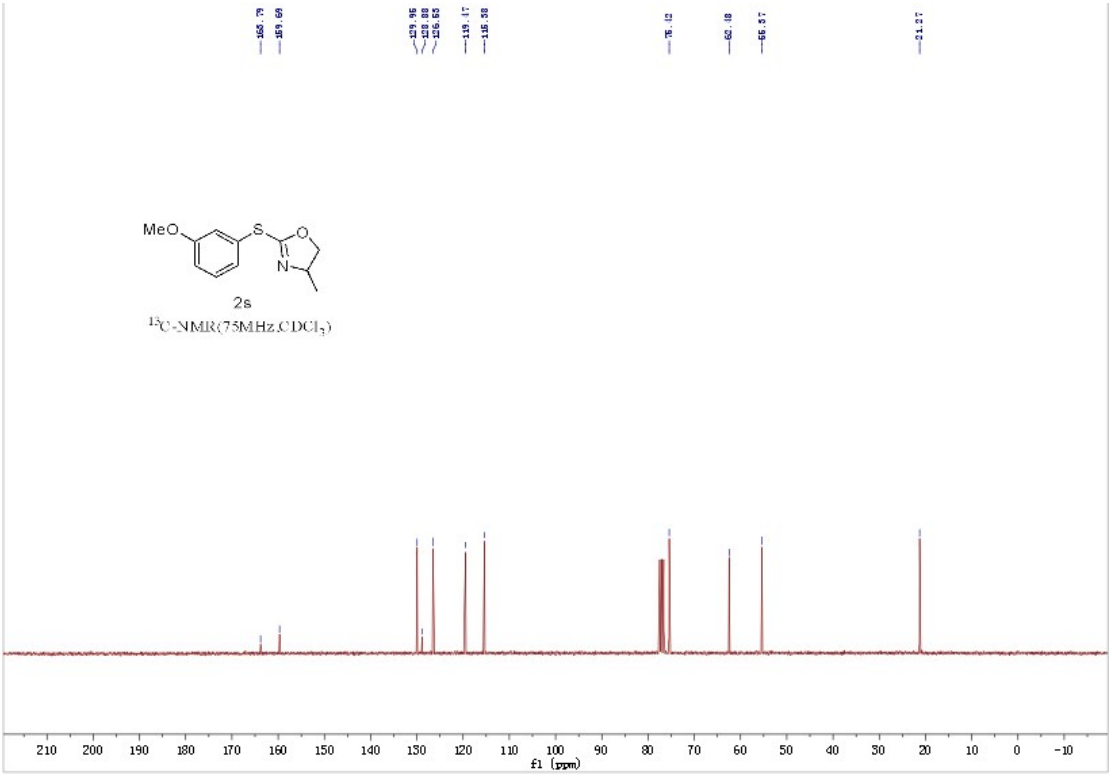
f1 (ppm)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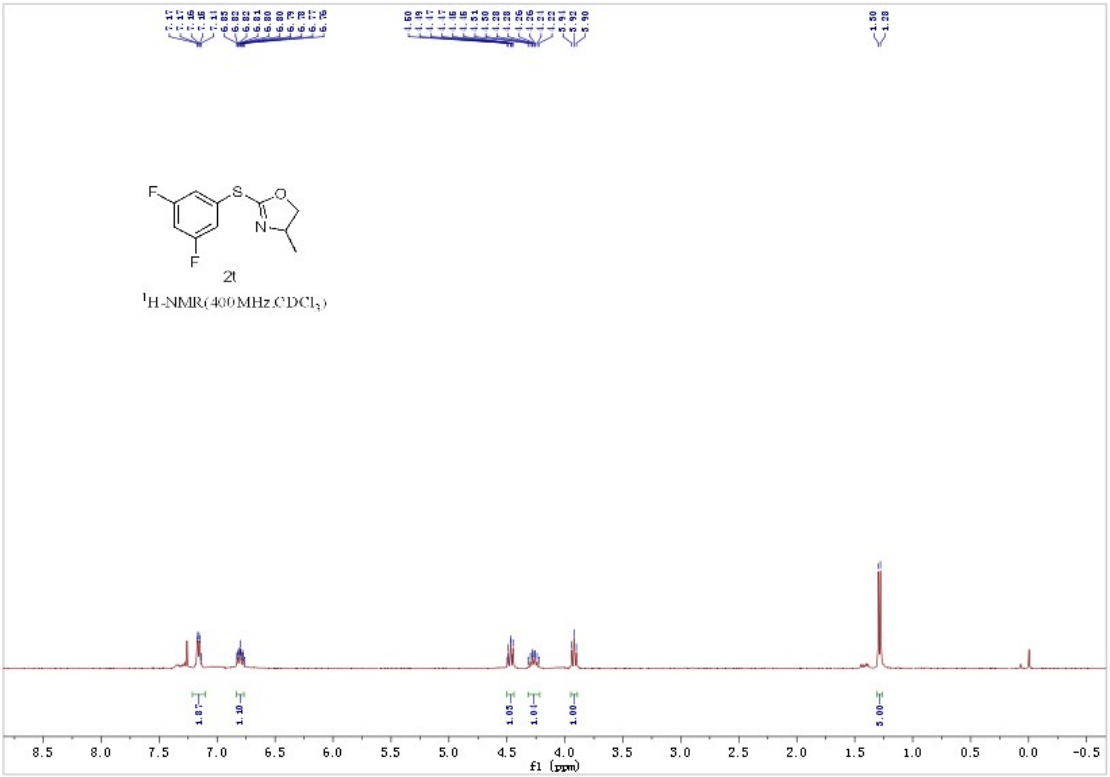
f1 (ppm)


F
S
O
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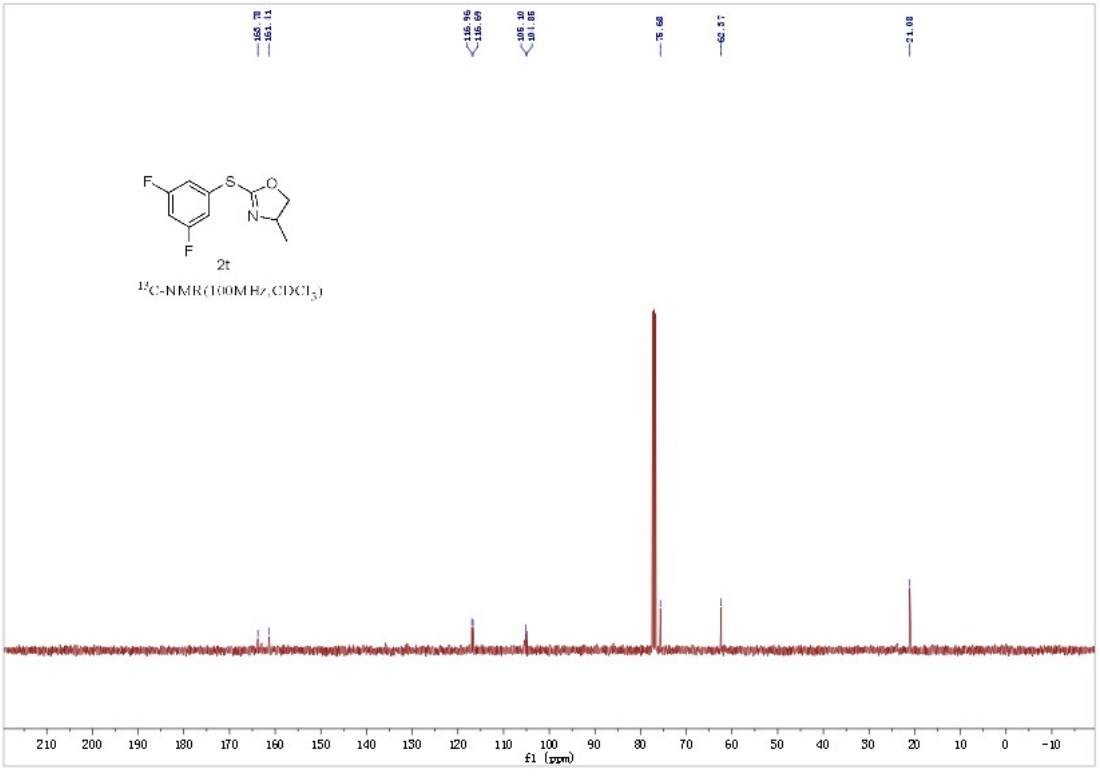
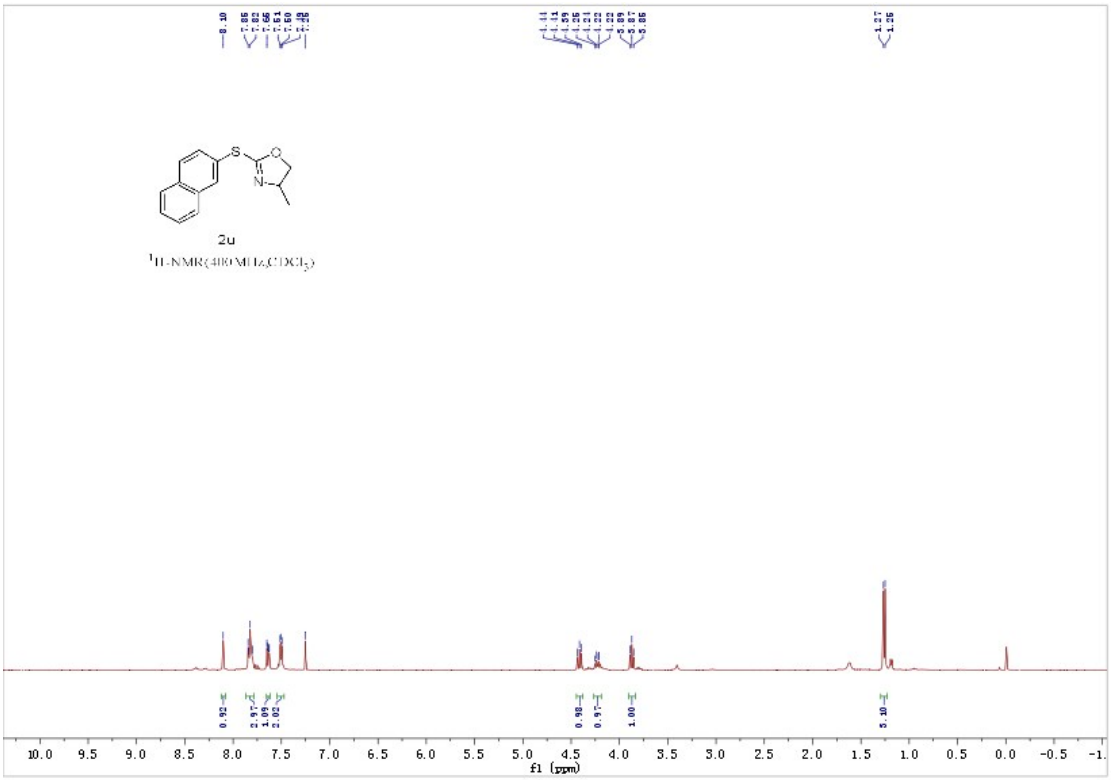
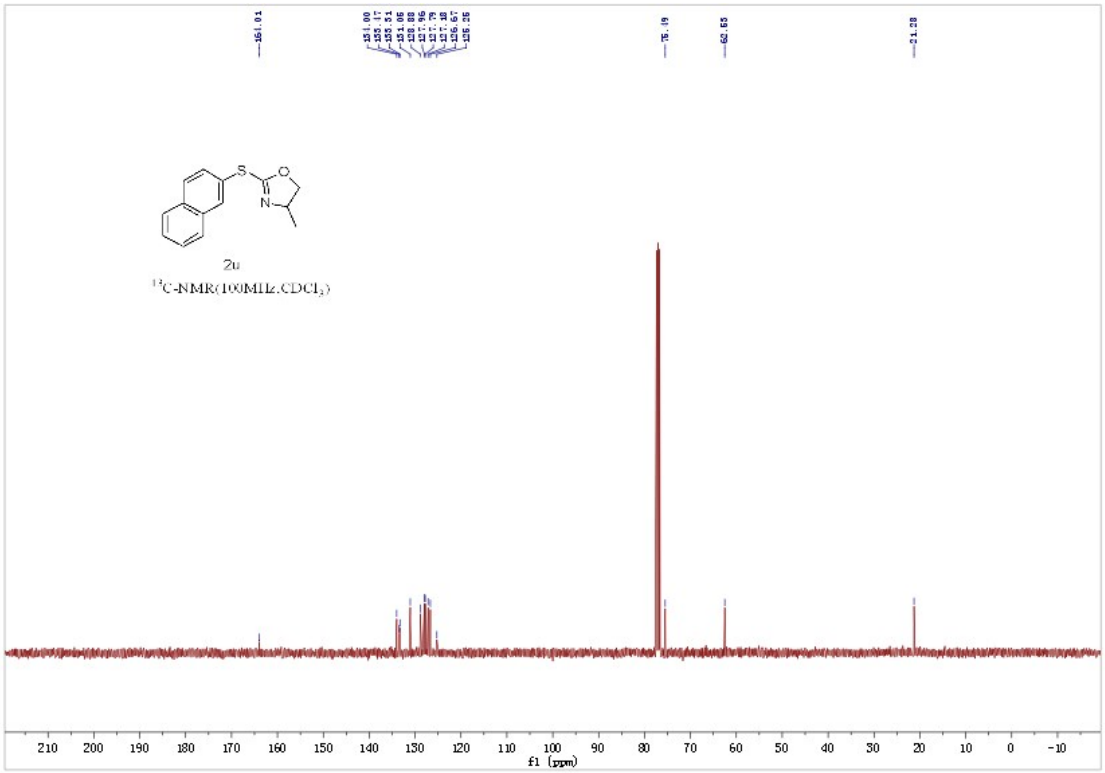
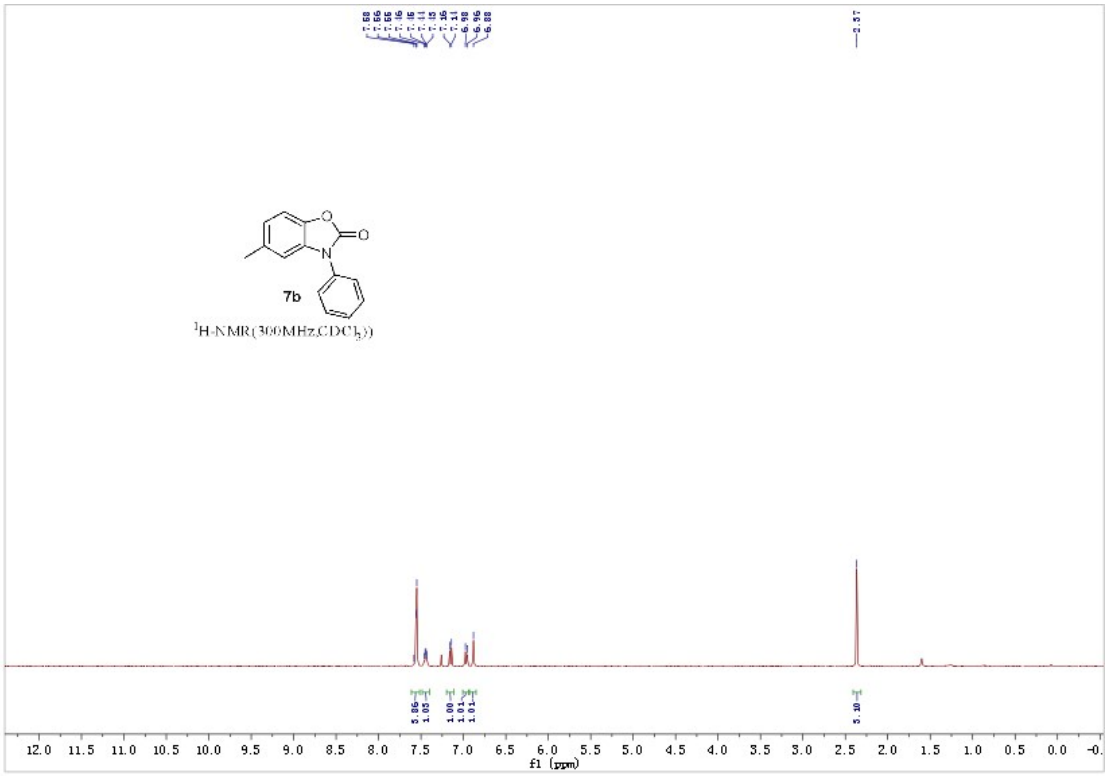
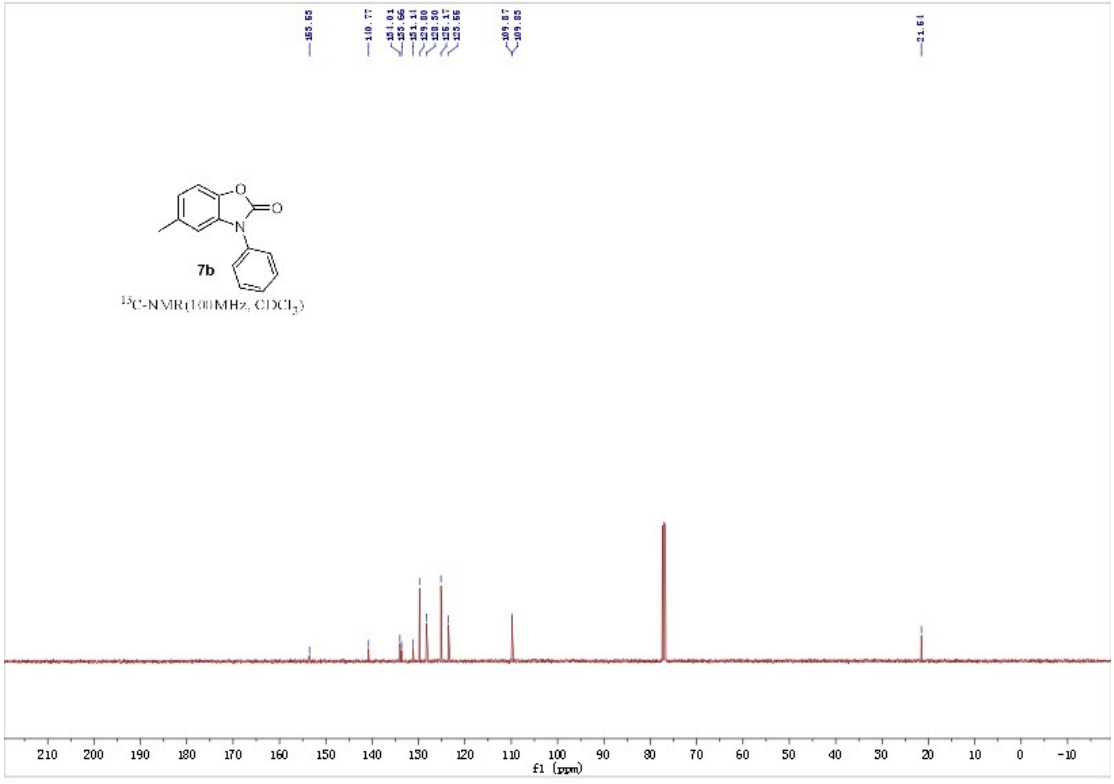
F
2t
^{1}H-NMR(400MHz,CDCl$_3$)
f1 (ppm)

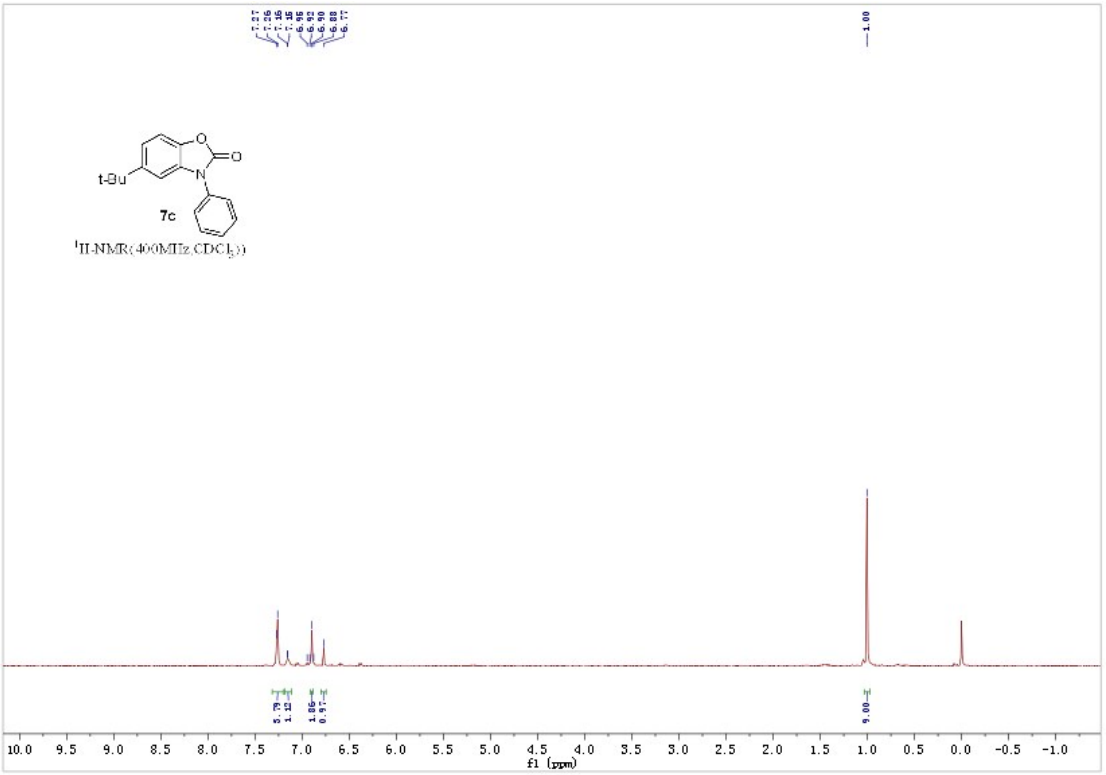

F
S
O
N
F
2t
^{13}C-NMR(100MHz,CDCl$_3$)
f1 (ppm)

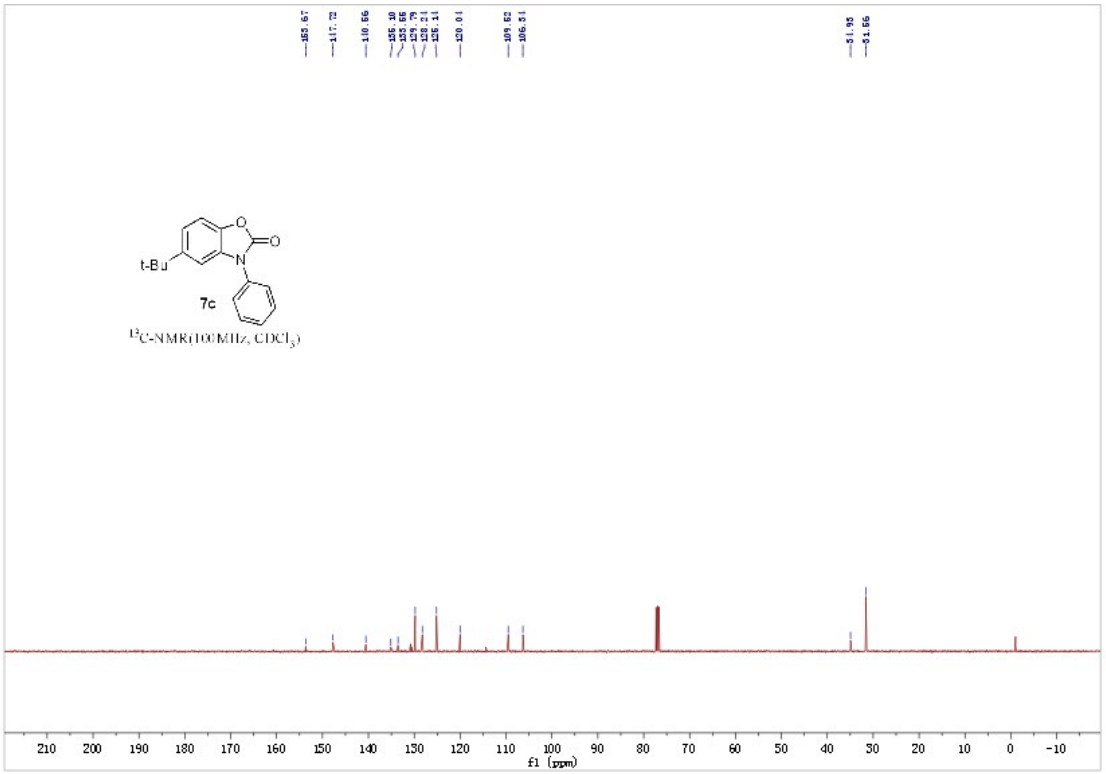

2u
^{1}H-NMR(400MHz,CDCl$_3$)
f1 (ppm)

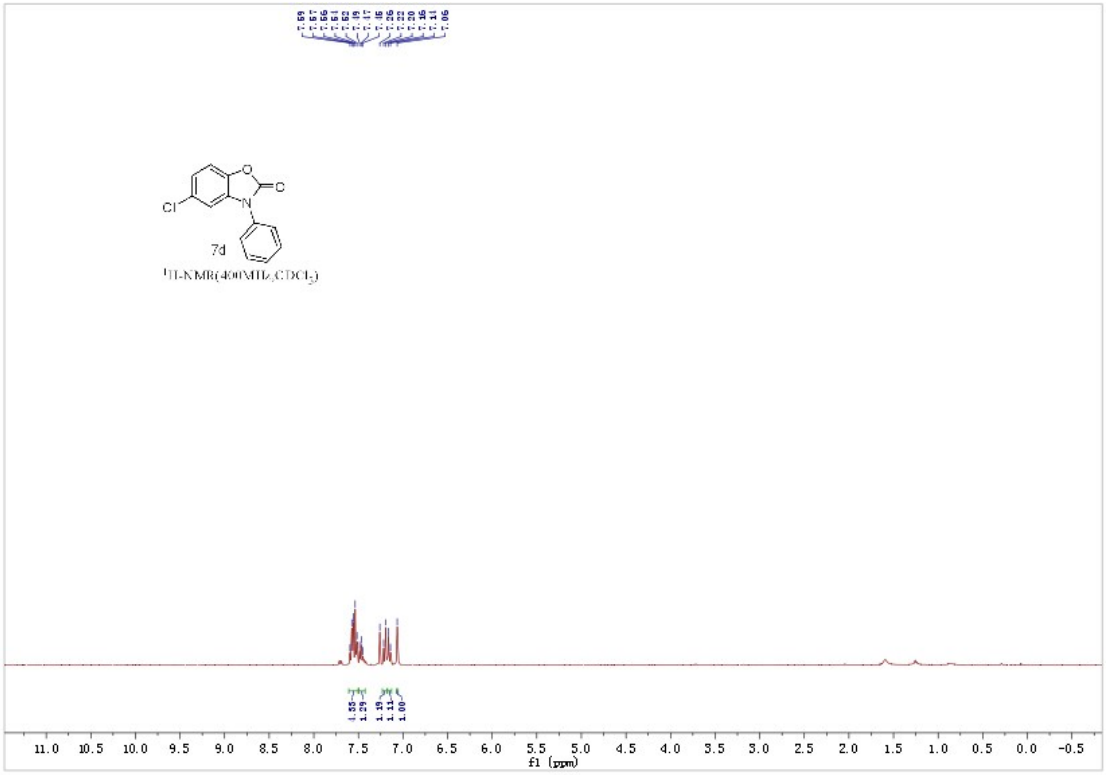

2u
^{13}C-NMR(100MHz,CDCl$_3$)
f1 (ppm)

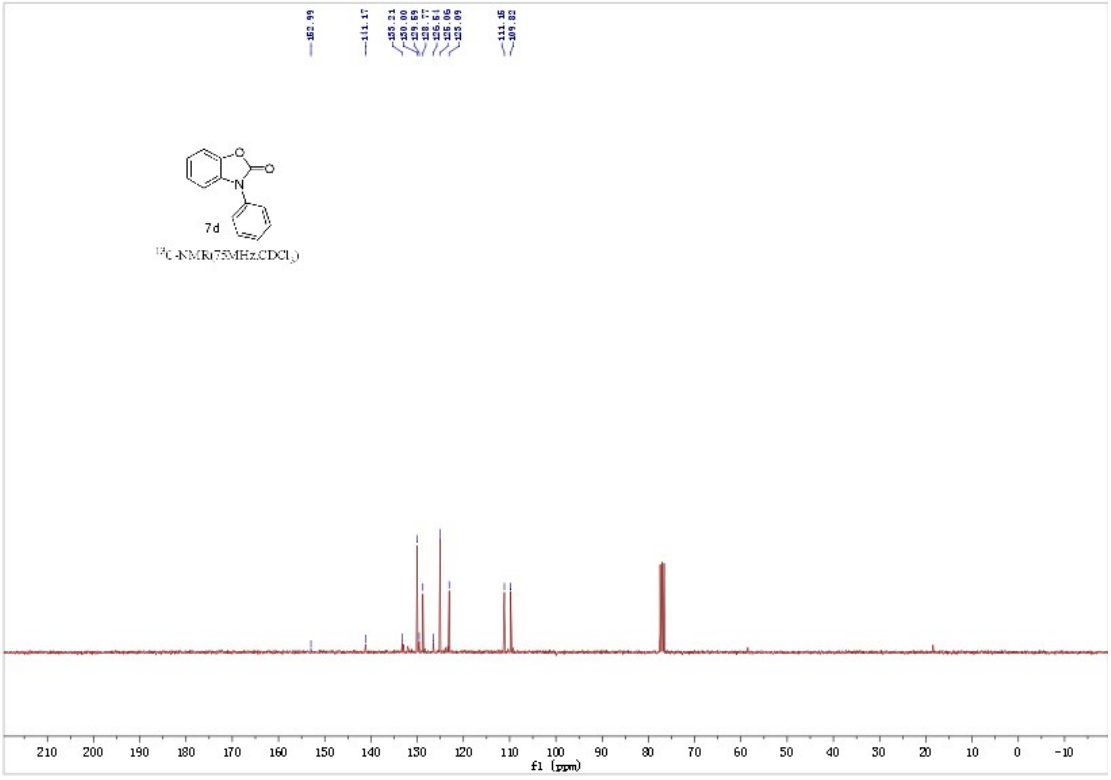

7b
^{1}H-NMR(300MHz,CDCl$_3$))
f1 (ppm)

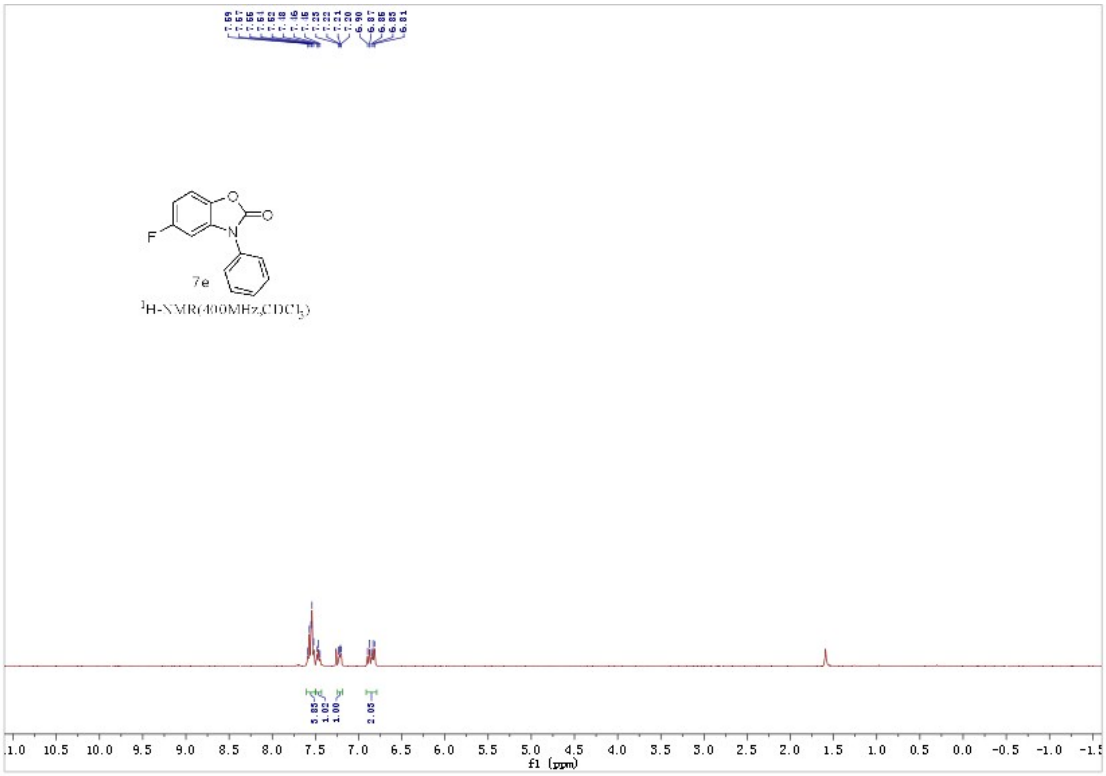

7b
^{13}C-NMR(100MHz, CDCl$_3$)
f1 (ppm)

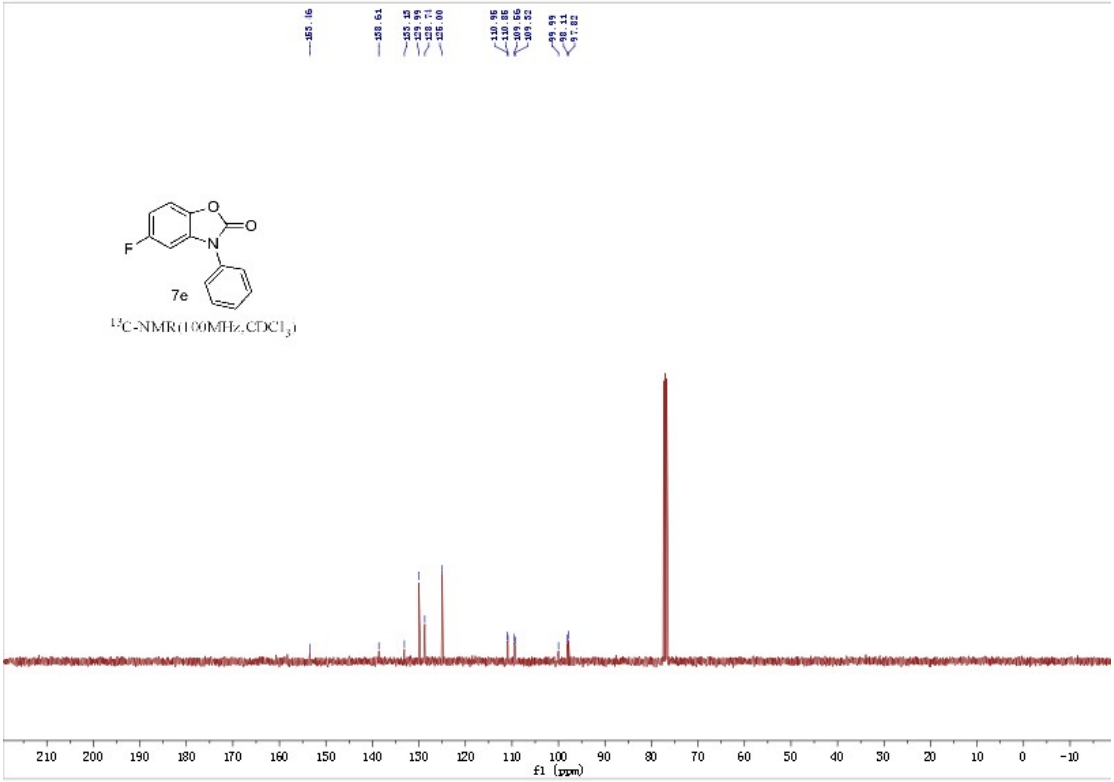

t-Bu
7c
^{1}H-NMR(400MHz,CDCl$_3$))
f1 (ppm)

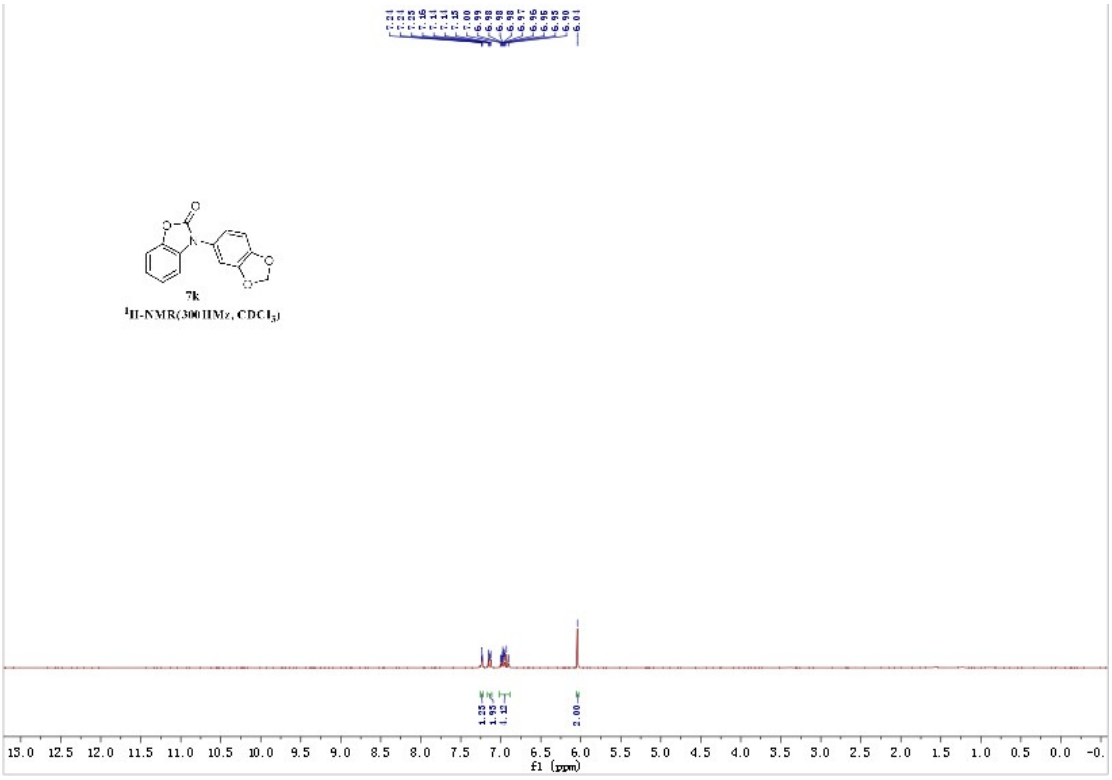

t-Bu
7c
^{13}C-NMR(100MHz, CDCl$_3$)
f1 (ppm)

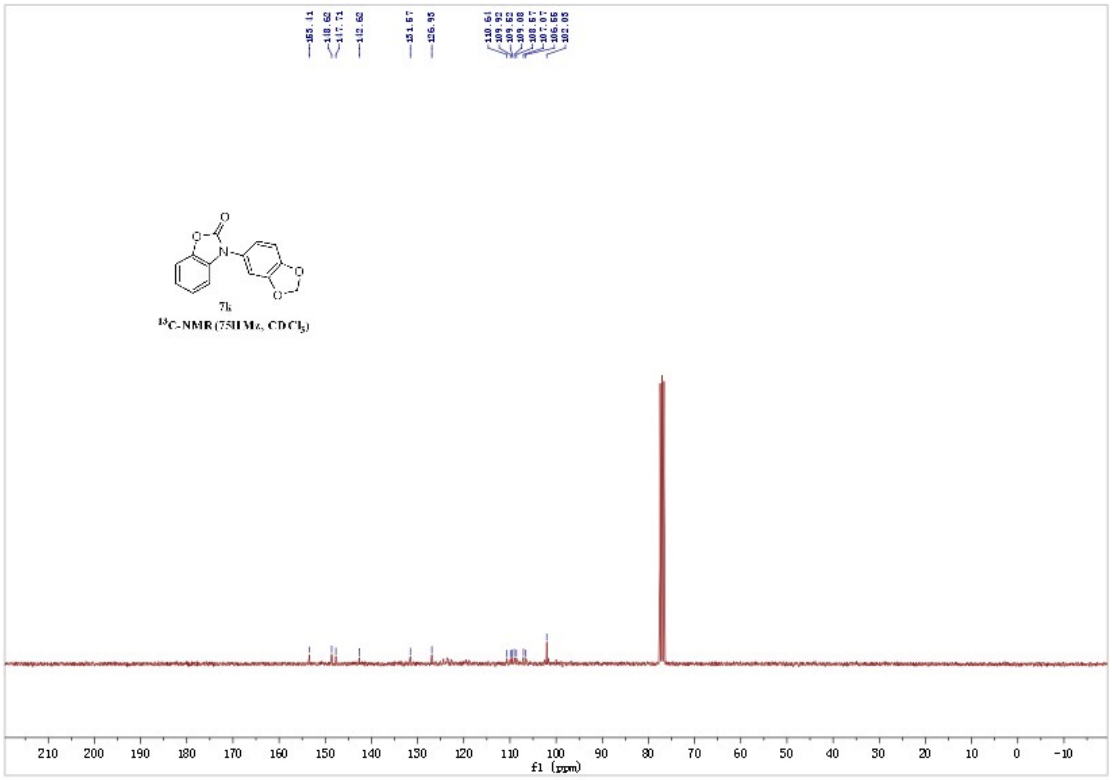

7d
^{1}H-NMR(400MHz,CDCl$_3$)
f1 (ppm)

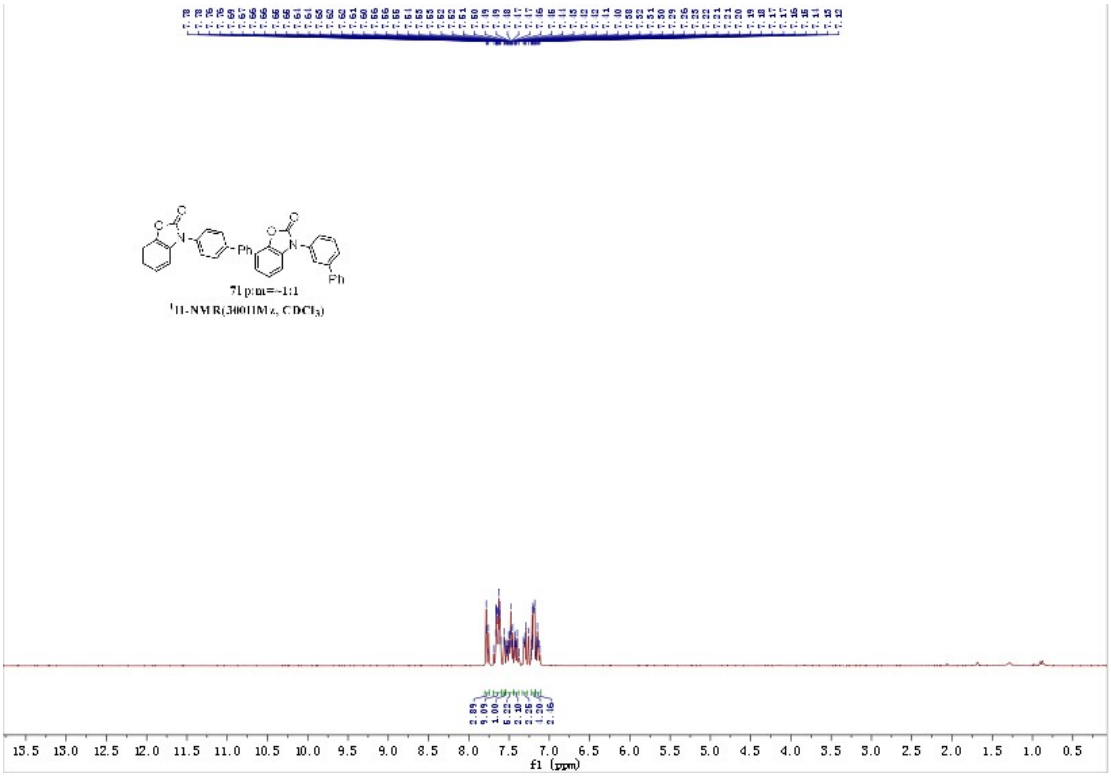

7d
^{13}C-NMR(75MHz,CDCl$_3$)
f1 (ppm)

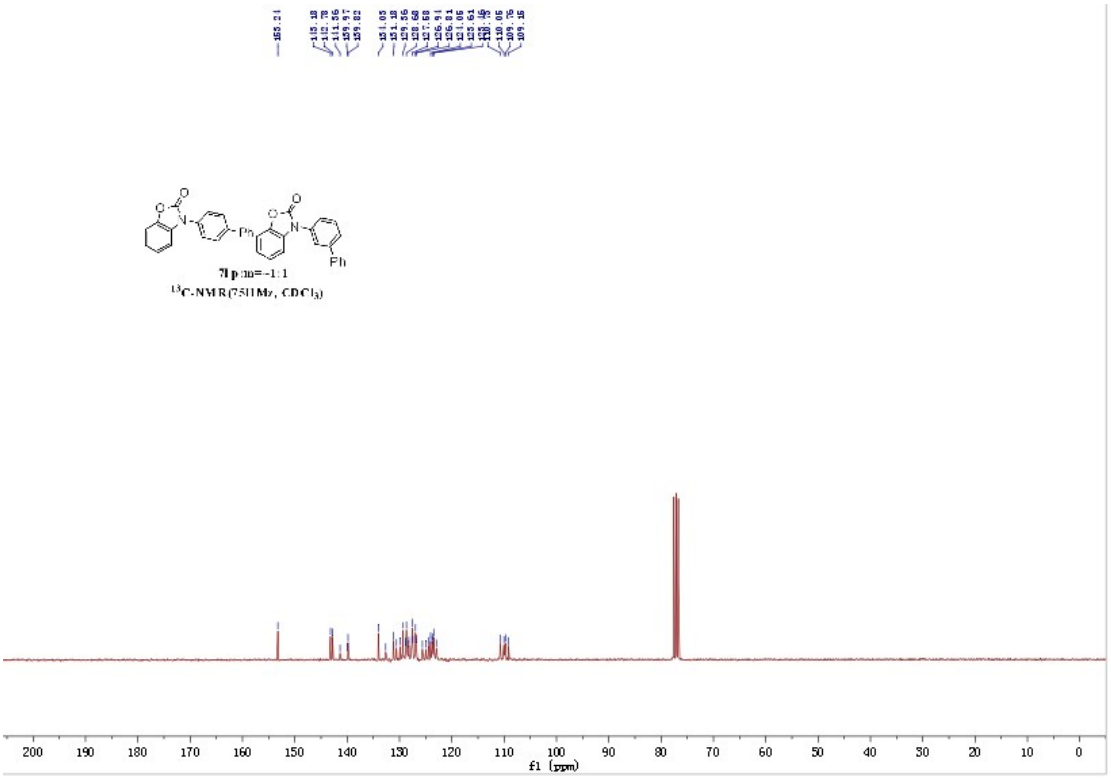

F
O
O
N
7e
^{1}H-NMR(400MHz,CDCl$_3$)
f1 (ppm)

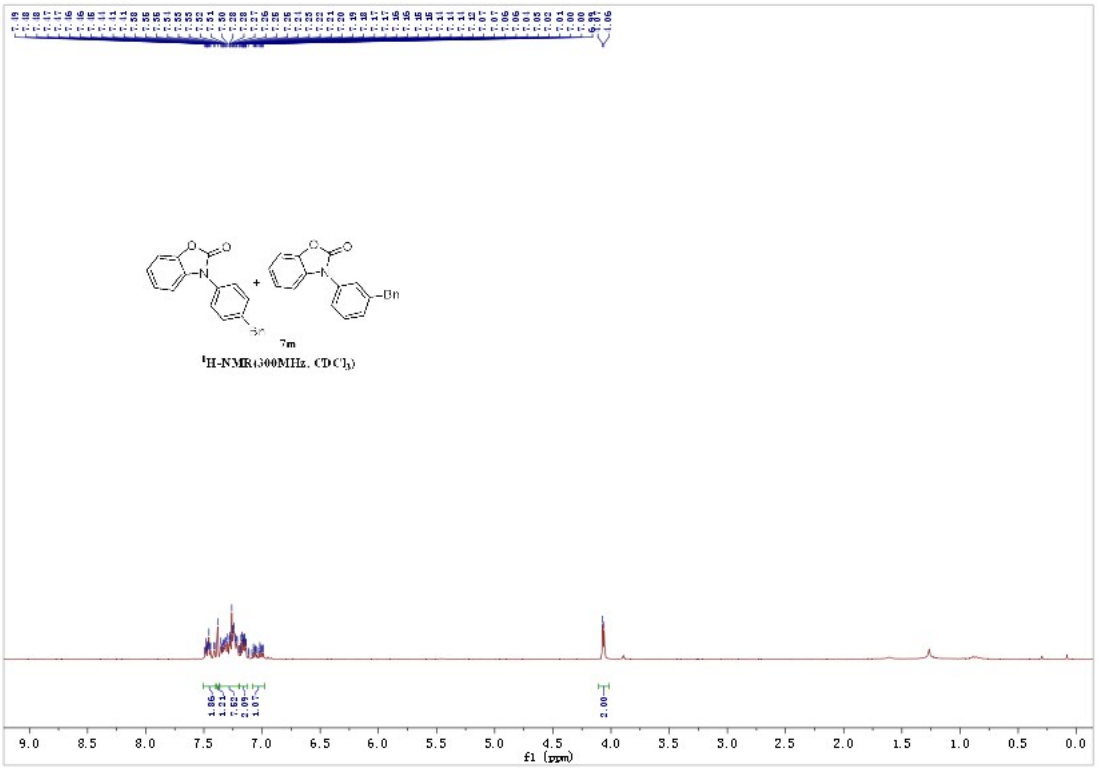

F
O
O
N
7e
^{13}C-NMR(100MHz,CDCl$_3$)
f1 (ppm)


7k
^{1}H-NMR(300HMz, CDCl$_3$)
f1 (ppm)

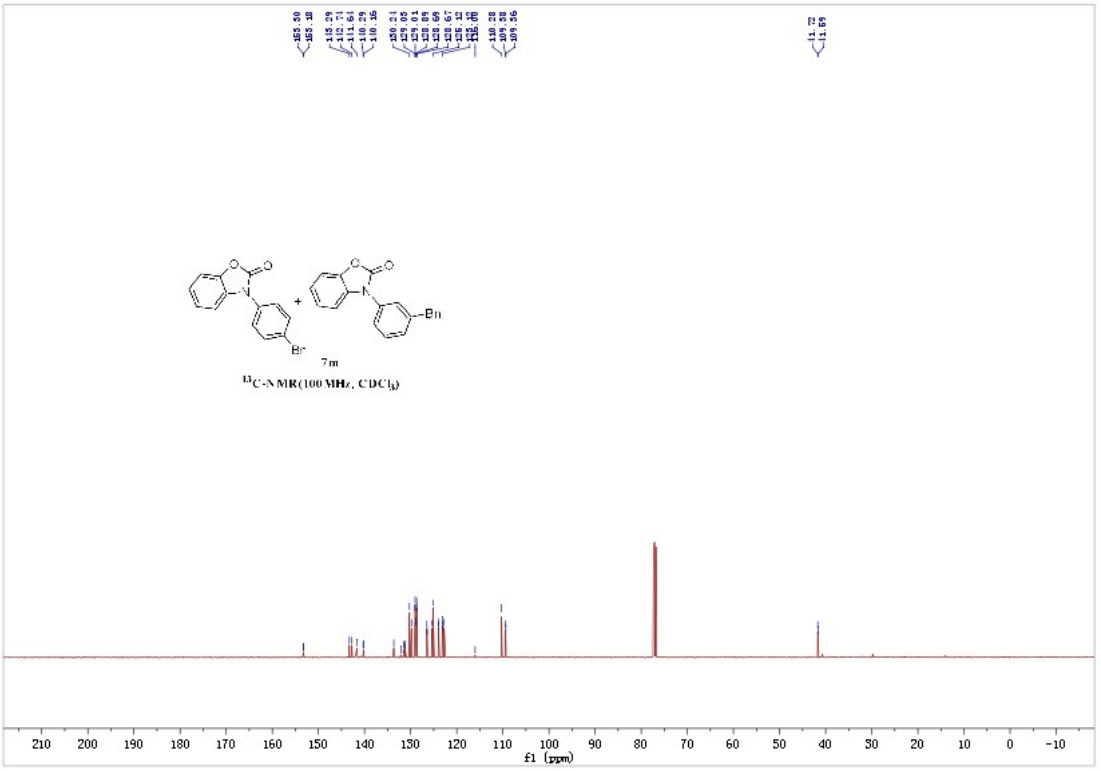

7k
^{13}C-NMR(75HMz, CDCl$_3$)
f1 (ppm)


7l p:m=~1:1
^{1}H-NMR(300HMz, CDCl$_3$)
f1 (ppm)

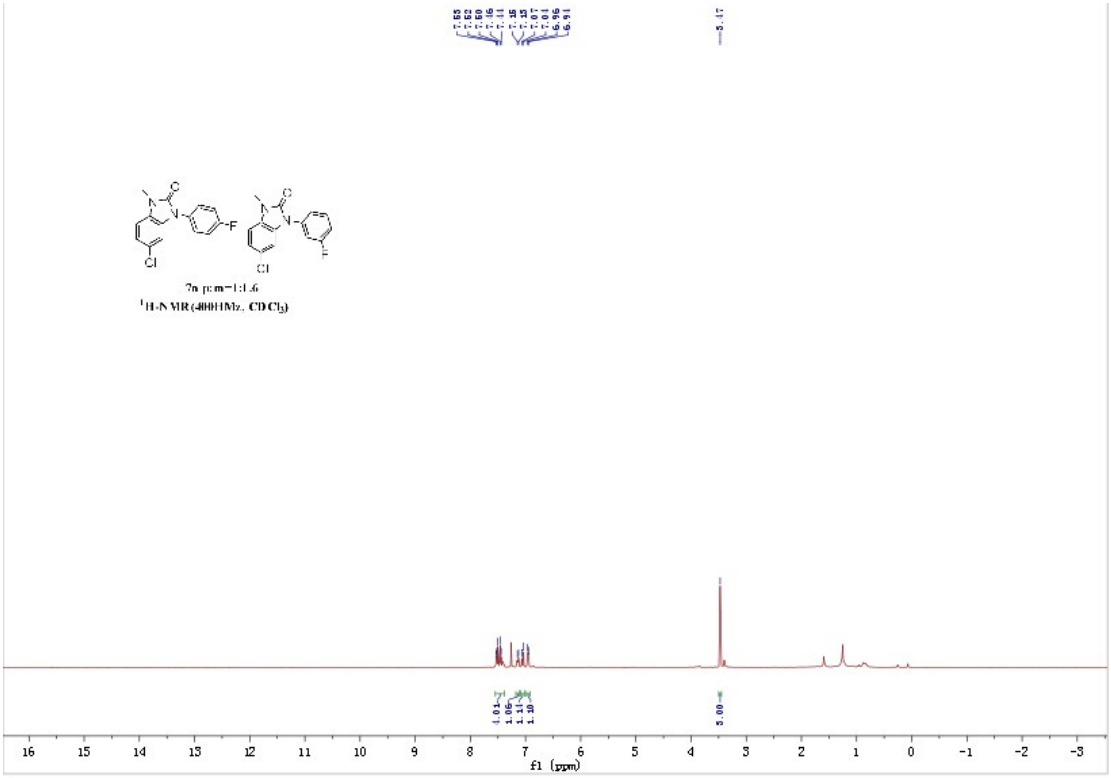

7l p:m=~1:1
^{13}C-NMR(75HMz, CDCl$_3$)
f1 (ppm)

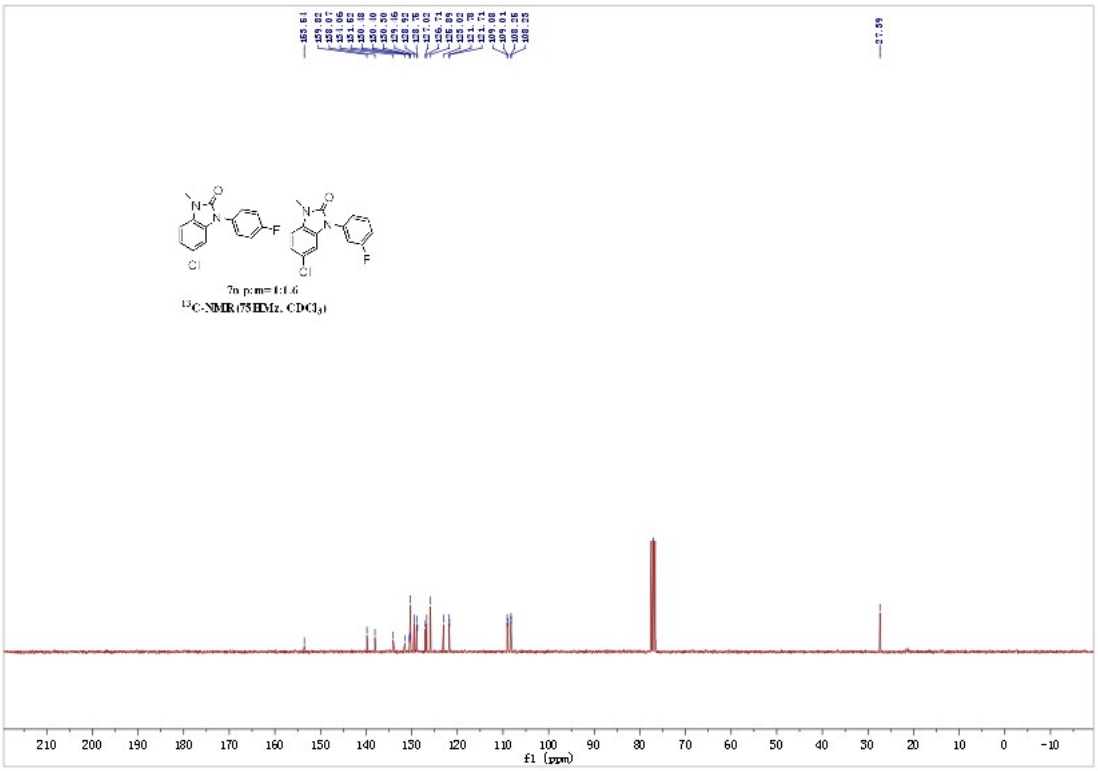


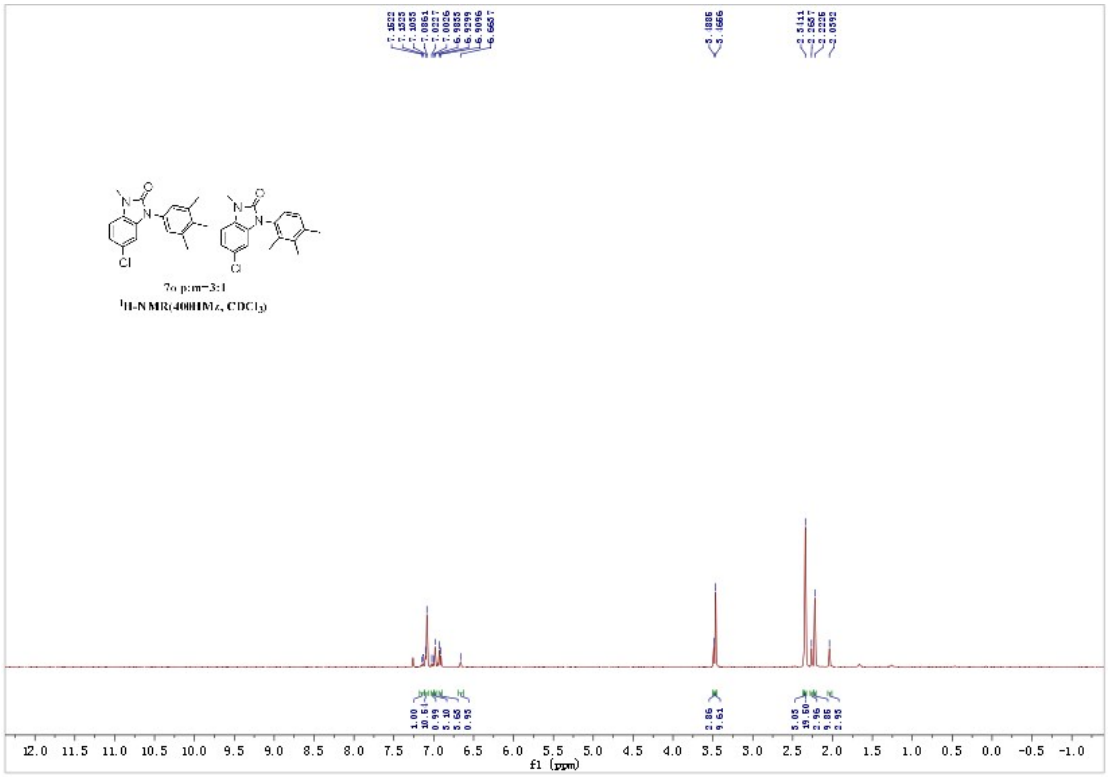
^{1}H-NMR(300MHz, $CDCl_3$)



^{13}C-NMR(100 MHz, $CDCl_3$)

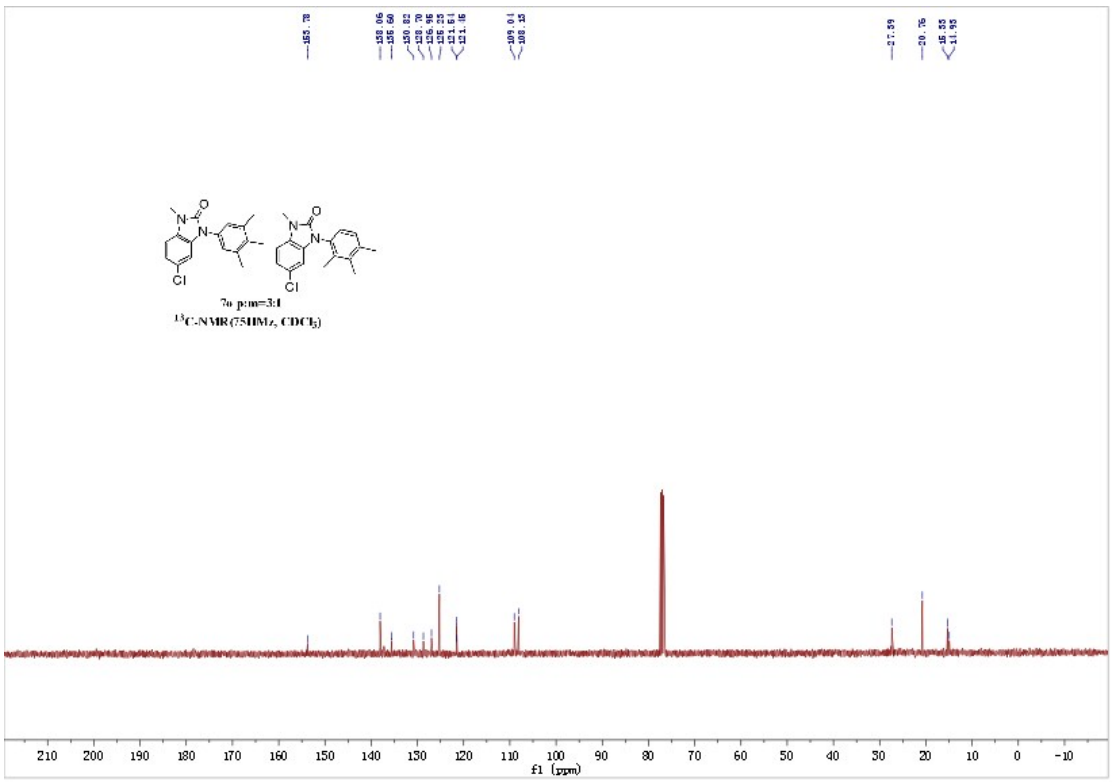

7n p:m=1:1.6
f1 (ppm)


7n p:m=1:1.6
f1 (ppm)



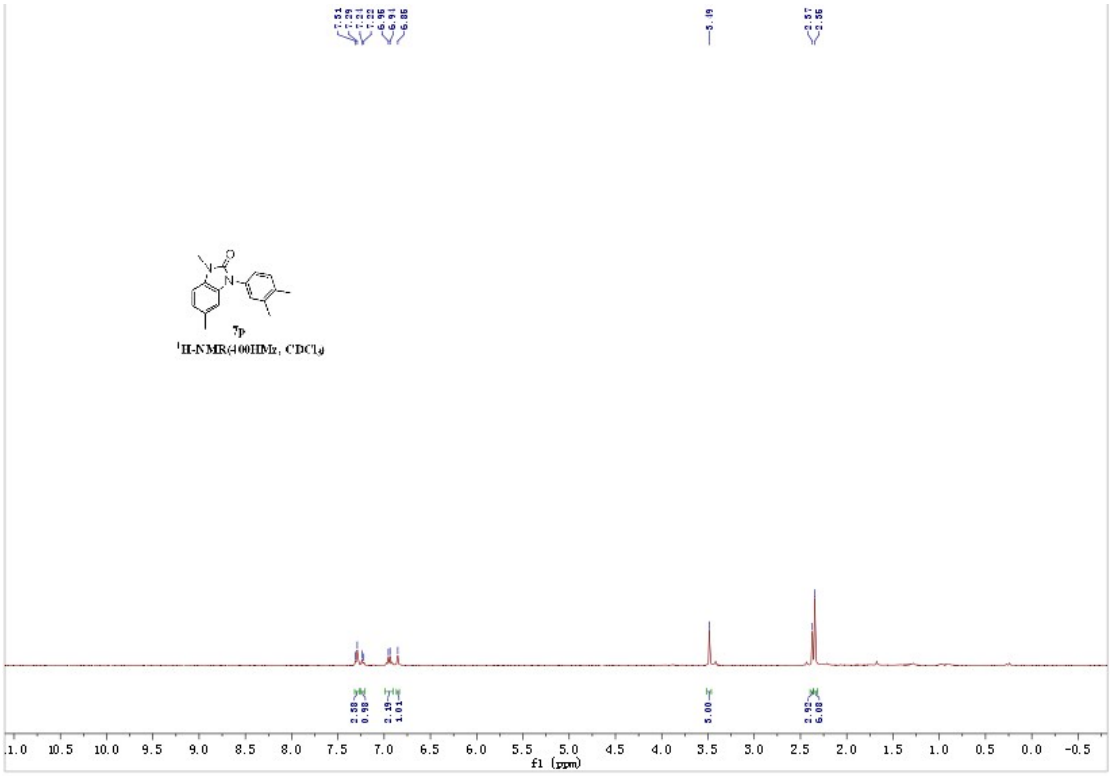
7o p:m=3:1

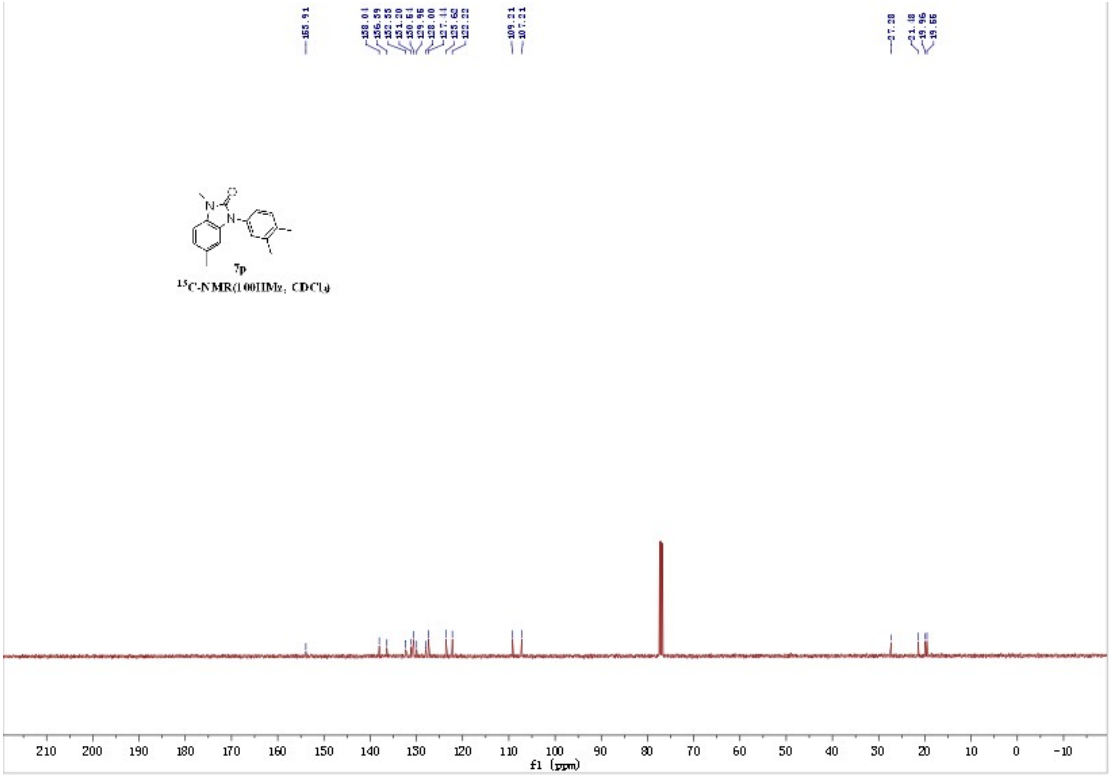
^{1}H-NMR(400HMz, $CDCl_3$)

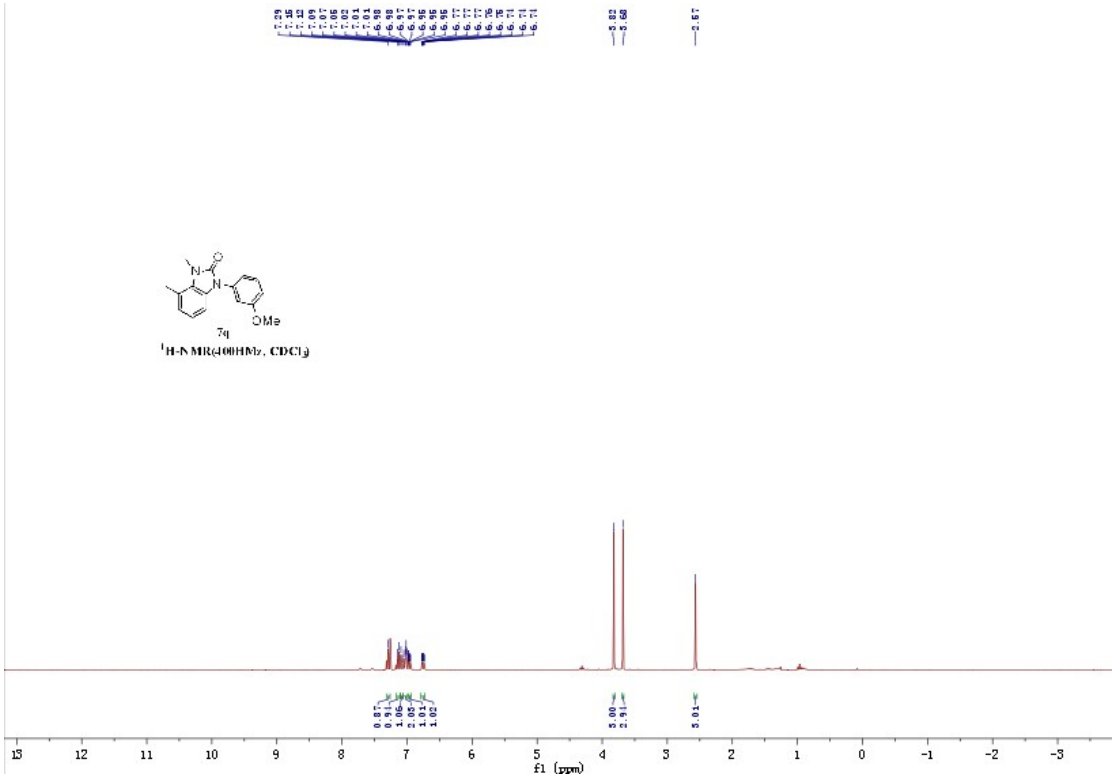


7o p:m=3:1

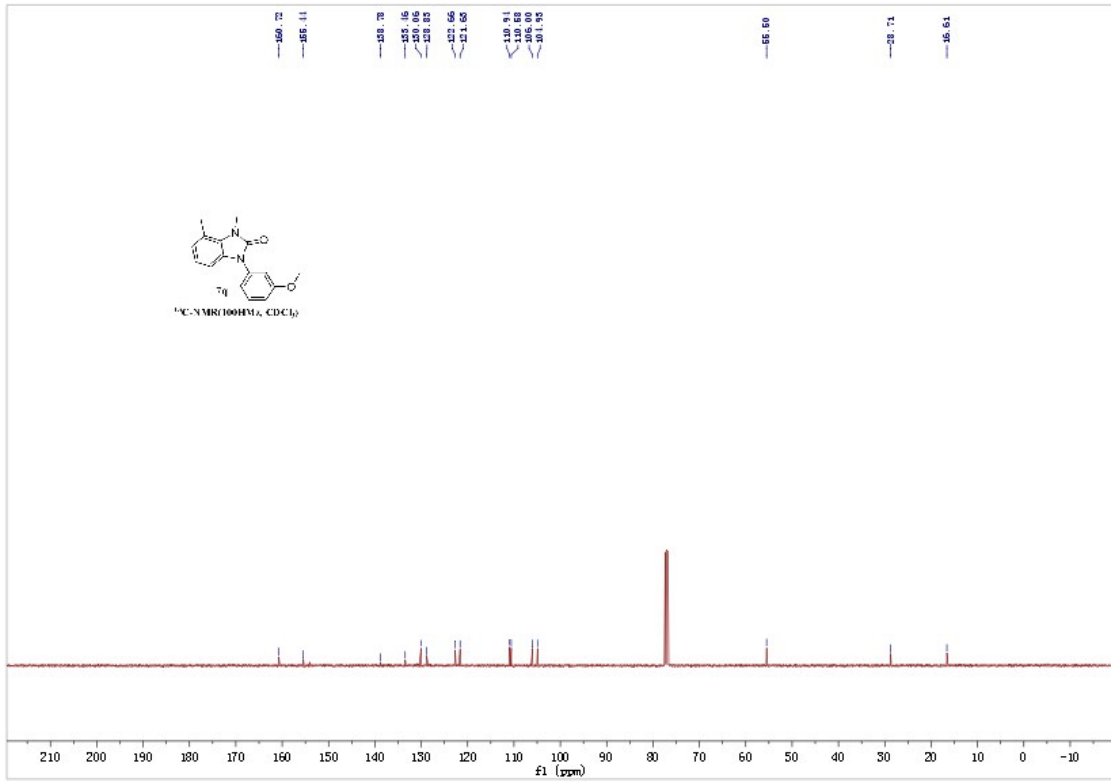
^{13}C-NMR(75HMz, $CDCl_3$)


7.54
7.53
7.21
7.22
6.96
6.91
6.85
3.49
2.57
2.56
7p
¹H-NMR(400HMz, CDCl₃)
2.58
0.98
2.19
1.01
3.00
2.92
6.00
f1 (ppm)


163.91
158.04
156.59
152.55
151.20
150.61
139.55
128.00
127.44
125.62
122.22
109.21
107.21
27.28
24.48
19.96
15.66
7p
¹⁵C-NMR(100HMz, CDCl₃)
f1 (ppm)

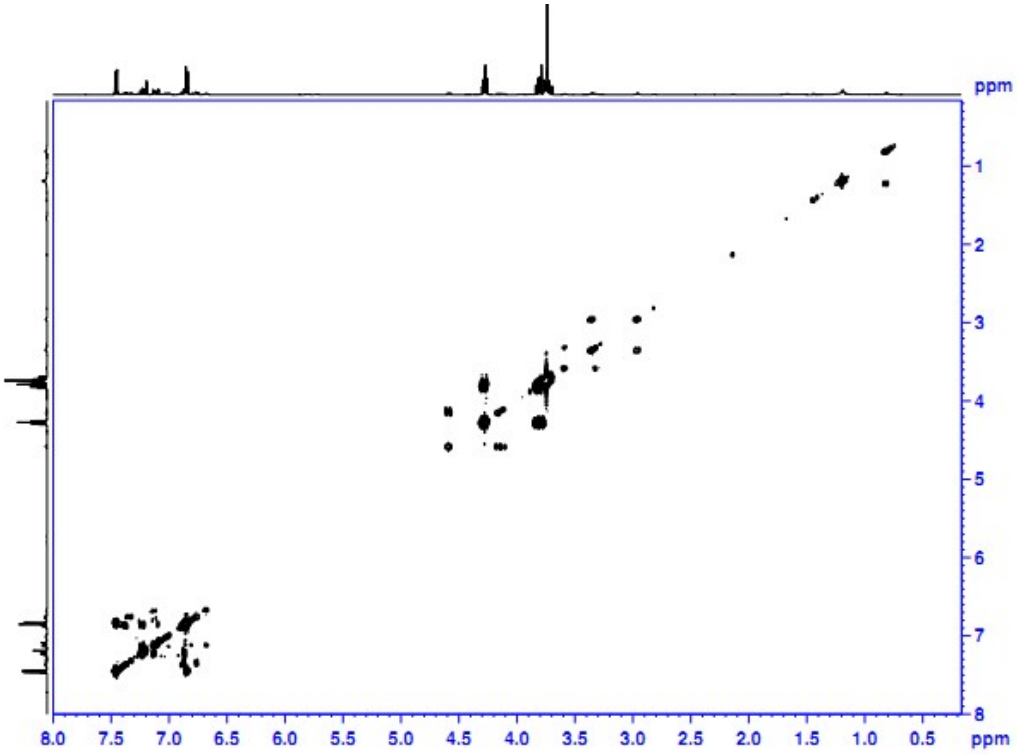


^{1}H-NMR(400HMz, CDCl$_3$)

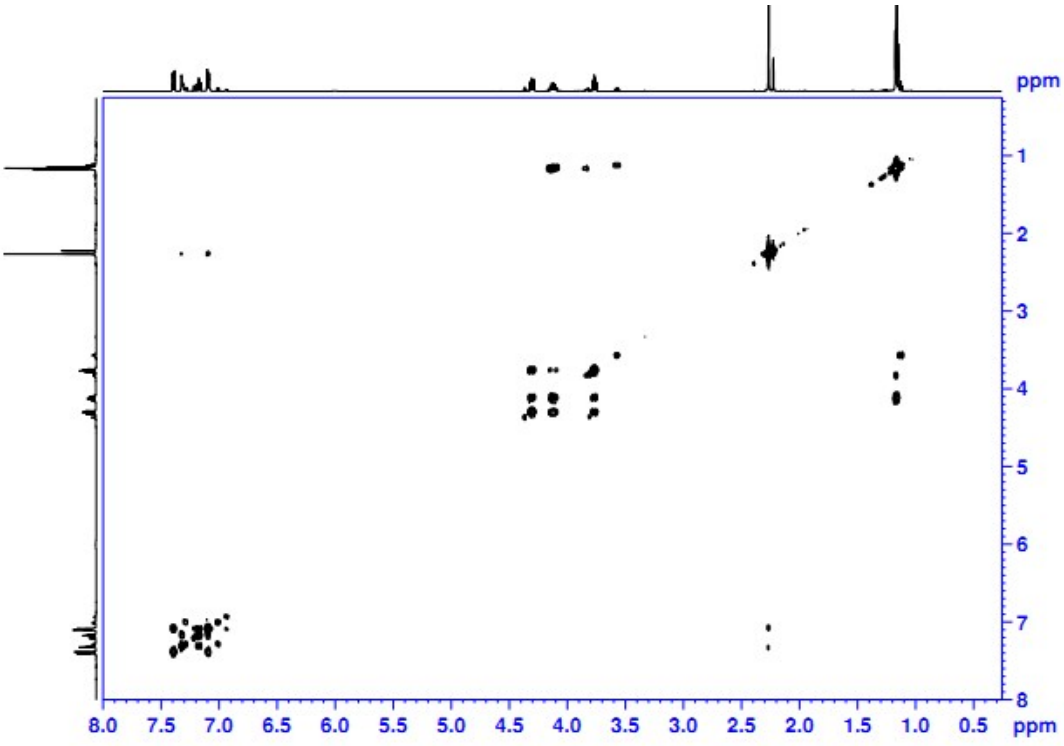


^{13}C-NMR(100HMz, CDCl$_3$)

^{1}H-^{1}H-COSY spectrum of 2l



^{1}H-^{1}H-COSY spectrum of 2m



^{1}H-^{1}H-COSY spectrum of 7n.