Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Hypervalent Iodine(III) Promoted Tandem Reaction of *o*-Fluoroanilines with Formamides to Construct 2-Aminobenzoxazoles

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Supporting Information

List of Contents

A. General method

Melting points were investigated using a melting point instrument and are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained on a 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, chloroform is solvent with TMS as the internal standard unless otherwise noted. Mass spectra were recorded on a GC-MS spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). High resolution mass spectra (HRMS) (TOF) were measured using an electrospray ionization (ESI) mass spectrometry. Silica gel (300-400 mesh) was used for flash column chromatograph, eluting (unless otherwise stated) with ethyl acetate/petroleum ether (PE) (60-90 ºC) mixture.

B. ^{19}F NMR Experiments

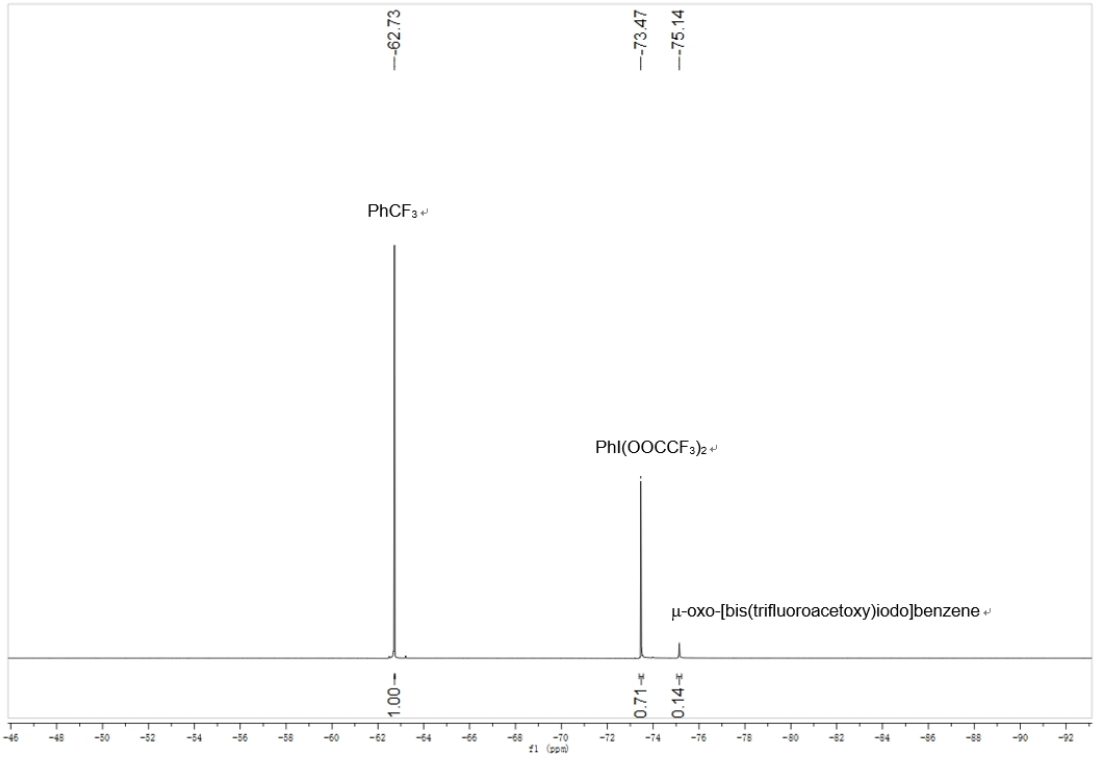


Figure S1 ^{19}F NMR (376.5 MHz) study on commercial PIFA using $C_6H_5CF_3$ as the internal standard (0.16 M in $CDCl_3$).

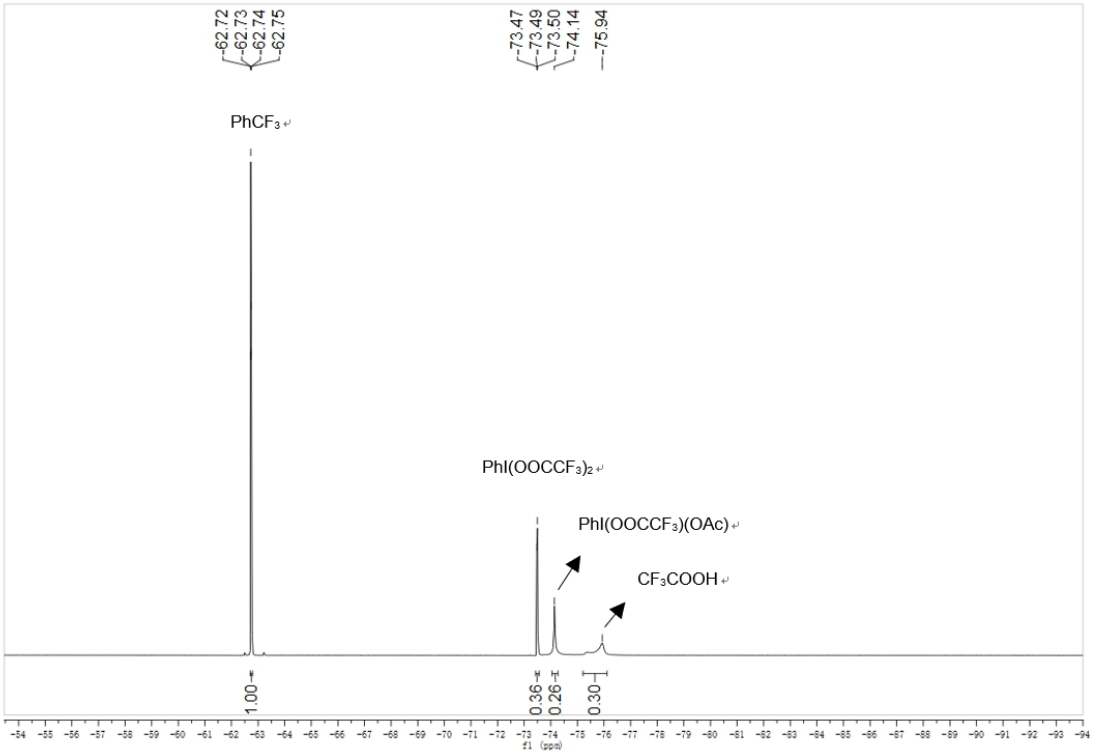


Figure S2 ^{19}F NMR (376.5 MHz) study on a mixture of commercial PIDA and 2 eqiv of CF_3COOH after 16 h using $C_6H_5CF_3$ as the internal standard (0.16 M in $CDCl_3$).

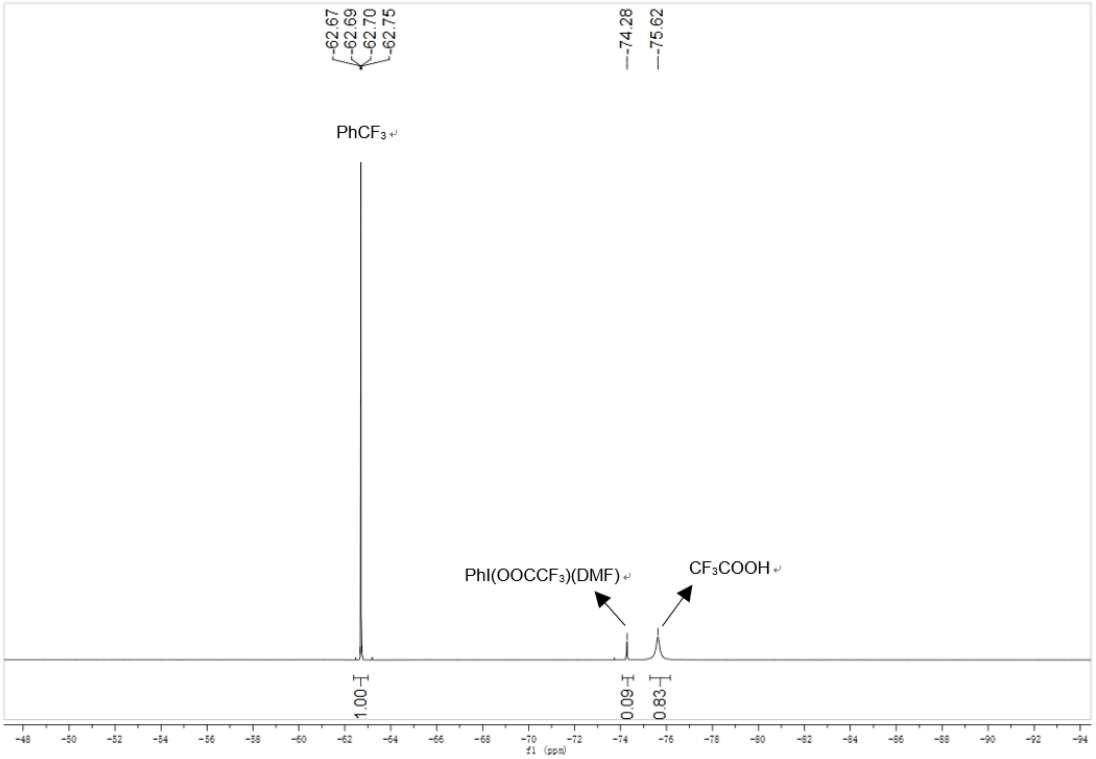


Figure S3 ^{19}F NMR (376.5 MHz) study on the experiment in Figure 2 added 40 eqiv DMF using $C_6H_5CF_3$ as the internal standard (0.16 M in $CDCl_3$).

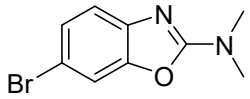
Note: *For the commercial PIFA shown in Figure S1, the major proton signals correspond to PIFA while the minor signals correspond to* μ-*oxo-[bis(trifluoroacetoxy)iodo]benzene, which could be formed via the decomposition of PIFA. As showed in Figure S2, upon the addition of* CF_3COOH *in the solution of* $PhI(OAc)_2$ *after 16 h, the signal of* CF_3COOH *(-75.94 ppm in* ^{19}F *NMR) diminished and the signal of PIFA (-73.49 ppm in* ^{19}F *NMR), the signal of* $PhI(OOCCF_3)(OAc)$ *(-74.14 ppm in* ^{19}F *NMR) emerged, which correspond to transesterification of PIDA with trifluoroacetic acid and intermediate A and B generated. When 40 eqiv DMF was added to the mixture of PIDA and* CF_3COOH*, as showed in Figure S3, the signal of PIFA was disappeared, and the content of hypervalent iodine with one* CF_3COO *ligand was reduced from 0.26 to 0.09 (with the ratio of external standard* $PhCF_3$*). However, the content of trifluoroacetic acid increased from 0.3 to 0.89. These* ^{19}F *NMR experiments indicate that DMF substituted trifluoroacetic acid and coordinated with hypervalent iodine.*

C. General procedure for the synthesis of *N,N*-dimethylbenzo[*d*]oxazol-2-amine

To a suspension of arylamine (0.2 mmol) and DMF (8.0 mmol) in DCM (1.0 mL) $PhI(OAc)_2$ (0.2 mmol) was added, followed by CF_3COOH (0.4 mmol). The mixture was stirred in the air at room temperature for 8 h. After the reaction was finished, ethyl acetate (5mL) was added. Washed with saturated $NaHCO_3$ solution (3 × 5 ml), then the aqueous layers were extracted with ethyl acetate (3 × 5 ml). The organic layer was dried by Na_2SO_4 and concentrated under reduced pressure. The residue was separated by column chromatography to obtain pure sample.

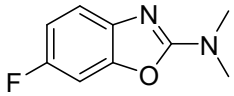
Note: Reaction quenching must be performed in a well-ventilated fume hood wearing appropriate protective equipment.

D. Analytical data



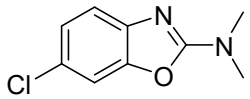
6-bromo-*N,N*-dimethylbenzo[*d*]oxazol-2-amine (3a)[1]

The title compound was achieved as a beige solid, 41.3 mg, 86% yield; m.p. 95-96 °C; R_f = 0.57 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 (d, J = 1.8 Hz, 1H), 7.21 (dd, J = 8.3, 1.8 Hz, 1H), 7.13 (d, J = 8.3 Hz, 1H), 3.12 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.2, 149.5, 143.0, 126.9, 116.8, 112.1, 112.0, 37.6.



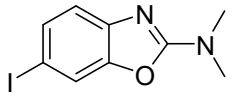
6-fluoro-*N,N*-dimethylbenzo[*d*]oxazol-2-amine (3b)

The title compound was achieved as a white solid, 23.0 mg, 64% yield; m.p. 84-85 °C; R_f = 0.50 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22 (dd, J = 8.6, 4.8 Hz, 1H), 7.00 (dd, J = 8.1, 2.5 Hz, 1H), 6.88 (ddd, J = 9.9, 8.6, 2.5 Hz, 1H), 3.17 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.4, 157.7 (d, J = 240.1 Hz), 148.7 (d, J = 14.4 Hz), 139.6, 115.5 (d, J = 9.5 Hz), 110.6 (d, J = 23.0 Hz), 97.5 (d, J = 29.0 Hz), 37.7. HRMS (ESI): m/z calcd. for $C_9H_{10}FN_2O$ $[M + H]^+$: 181.0772, found: 181.0777.



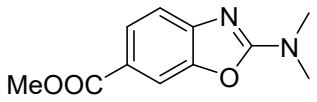
6-chloro-*N,N*-dimethylbenzo[*d*]oxazol-2-amine (3c)[1, 2]

The title compound was achieved as a yellow solid, 28.2 mg, 72% yield; m.p. 101-102 °C; R_f = 0.48 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 (d, J = 2.0 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.11 (dd, J = 8.4, 2.0 Hz, 1H), 3.17 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.3, 149.2, 142.4, 125.2, 124.1, 116.2, 109.4, 37.7. HRMS (ESI): m/z calcd. for $C_9H_{10}ClN_2O$ $[M + H]^+$: 197.0476, found: 197.0482.



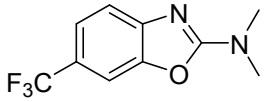
6-iodo-*N,N*-dimethylbenzo[*d*]oxazol-2-amine (3d)

The title compound was achieved as a fuchsia solid, 43.4 mg, 75% yield; m.p. 122-123 °C; R_f = 0.19 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 (d, J = 1.6 Hz, 1H), 7.43 (dd, J = 8.2, 1.6 Hz, 1H), 7.08 (d, J = 8.2 Hz, 1H), 3.17 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.9, 149.8, 143.7, 132.9, 117.6, 81.1, 37.7. HRMS (ESI): m/z calcd. for $C_9H_{10}IN_2O$ $[M + H]^+$: 288.9832, found: 288.9840.



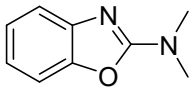
2-(dimethylamino)benzo[*d*]oxazol-6-yl acetate (3e)

The title compound was achieved as an orange solid, 18.5 mg, 42% yield; m.p. 115-116 °C; R_f = 0.32 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (dd, J = 7.9, 1.3 Hz, 2H), 7.32 (dd, J = 7.7, 1.1 Hz, 1H), 3.90 (s, 3H), 3.24 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.1, 164.5, 148.7, 148.1, 126.7, 122.2, 115.1, 110.0, 52.0, 37.7. HRMS (ESI): m/z calcd. for $C_{11}H_{13}N_2O_3$ $[M + H]^+$: 221.0921, found: 221.0928.



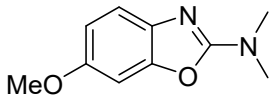
***N,N*-dimethyl-6-(trifluoromethyl)benzo[*d*]oxazol-2-amine (3f)**

The title compound was achieved as a yellow solid, 23.1 mg, 50% yield; m.p. 114-115 °C; R_f = 0.22 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 (s, 1H), 7.44 (dd, J = 8.2, 0.9 Hz, 1H), 7.37 (d, J = 8.2 Hz, 1H), 3.24 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.2, 148.5, 146.6, 124.6 (q, J_1 = 271.2 Hz), 122.4 (q, J_2 = 32.9 Hz), 115.61 (s, 4H), 106.1 (q, J_3 = 3.8 Hz), 37.7. HRMS (ESI): m/z calcd. for $C_{10}H_{10}F_3N_2O$ $[M + H]^+$: 231.0740, found: 231.0733.



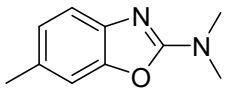
***N,N*-dimethylbenzo[*d*]oxazol-2-amine (3g)[1, 2]**

The title compound was achieved as a brown solid, 19.8 mg, 61% yield; m.p. 87-88 °C; R_f = 0.51 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 (dd, J = 7.8, 0.6 Hz, 1H), 7.23 (dd, J = 7.9, 0.4 Hz, 1H), 7.14 (td, J = 7.7, 1.1 Hz, 1H), 6.98 (td, J = 7.8, 1.2 Hz, 1H), 3.18 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.1, 149.1, 143.5, 123.9, 120.2, 116.0, 108.6, 37.7.



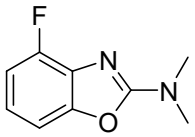
6-methoxy-*N,N*-dimethylbenzo[*d*]oxazol-2-amine (3h)

The title compound was achieved as a orange solid, 34.2 mg, 89% yield; m.p. 94-95 °C; R_f = 0.38 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22 (d, J = 8.6 Hz, 1H), 6.88 (d, J = 2.4 Hz, 1H), 6.76 – 6.73 (m, 1H), 3.80 (s, 3H), 3.17 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.8, 154.8, 149.5, 136.9, 115.6, 110.0, 96.0, 56.1, 37.8. HRMS (ESI): m/z calcd. for $C_{10}H_{13}N_2O_2$ $[M + H]^+$: 193.0972, found: 193.0966.



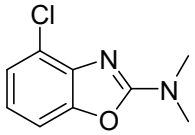
***N,N*,6-trimethylbenzo[*d*]oxazol-2-amine (3i)[2]**

The title compound was achieved as a orange solid, 30.6 mg, 87% yield; m.p. 57-58 °C; R_f = 0.49 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20 (d, J = 7.9 Hz, 1H), 7.05 – 7.02 (m, 1H), 6.93 (ddd, J = 7.9, 1.5, 0.6 Hz, 1H), 3.14 (s, 6H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.9, 149.3, 141.1, 130.1, 124.5, 115.4, 109.2, 37.7, 21.4. HRMS (ESI): m/z calcd. for $C_{10}H_{13}N_2O$ $[M + H]^+$: 177.1022, found: 177.1021.



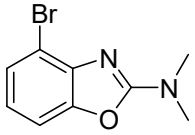
4-fluoro-*N,N*-dimethylbenzo[*d*]oxazol-2-amine (3j)

The title compound was achieved as a yellow solid, 18.1 mg, 50% yield; m.p. 107-108 °C; R_f = 0.72 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.07 – 7.03 (m, 1H), 6.93 – 6.88 (m, 2H), 3.20 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.9, 151.3 (d, J = 9.0 Hz), 151.2 (d, J = 248.0 Hz), 131.7 (d, J = 16.0 Hz), 120.1 (d, J = 7.0 Hz), 110.6 (d, J = 18.0 Hz), 104.9 (d, J = 4.0 Hz), 37.7. HRMS (ESI): m/z calcd. for $C_9H_{10}FN_2O$ $[M + H]^+$: 181.0772, found: 181.0777.



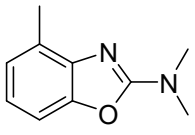
4-chloro-*N,N*-dimethylbenzo[*d*]oxazol-2-amine (3k)

The title compound was achieved as a brown solid, 21.6 mg, 55% yield; m.p. 77-78 °C; R_f = 0.53 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.14 (dd, J = 2.5, 0.9 Hz, 1H), 7.12 (d, J = 1.7 Hz, 1H), 6.90 (t, J = 8.0 Hz, 1H), 3.21 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.2, 149.5, 141.5, 124.1, 120.5, 120.0, 107.1, 37.8. HRMS (ESI): m/z calcd. for $C_9H_{10}ClN_2O$ $[M + H]^+$: 197.0476, found: 197.0483.



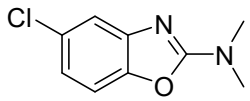
4-bromo-*N,N*-dimethylbenzo[*d*]oxazol-2-amine (3l)

The title compound was achieved as a reddish-brown solid, 34.6 mg, 72% yield; m.p. 84-85 °C; R_f = 0.67 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 (dd, J = 8.1, 0.8 Hz, 1H), 7.15 (dd, J = 7.9, 0.8 Hz, 1H), 6.84 (t, J = 8.0 Hz, 1H), 3.20 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.0, 148.9, 143.2, 127.0, 120.9, 108.0, 107.6, 37.8. HRMS (ESI): m/z calcd. for $C_9H_{10}BrN_2O$ $[M + H]^+$: 240.9971, found: 240.9979.



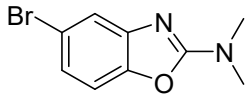
***N,N*,4-trimethylbenzo[*d*]oxazol-2-amine (3m)[2]**

The title compound was achieved as a brown solid, 18.3 mg, 52% yield; m.p. 53-54 °C; R_f = 0.71 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.08 (dd, J = 7.8, 0.6 Hz, 1H), 6.98 – 6.94 (m, 1H), 6.89 (t, J = 7.7 Hz, 1H), 3.20 (s, 6H), 2.49 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.7, 148.7, 142.5, 126.2, 124.7, 119.9, 106.0, 37.8, 16.5.



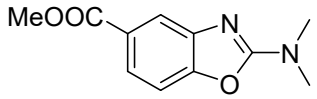
5-chloro-*N,N*-dimethylbenzo[*d*]oxazol-2-amine (3n)[2]

The title compound was achieved as a brown solid, 29.8 mg, 76% yield; m.p. 85-86 °C; R_f = 0.18 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 (d, J = 2.1 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 6.92 (dd, J = 8.4, 2.1 Hz, 1H), 3.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.8, 147.7, 145.0, 129.2, 120.0, 116.0, 109.1, 37.6.



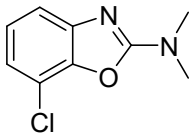
5-bromo-*N,N*-dimethylbenzo[*d*]oxazol-2-amine (3o)[2]

The title compound was achieved as a brown solid, 38.5 mg, 80% yield; m.p. 66-67 °C; R_f = 0.30 (petroleum ether / ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 (t, J = 1.2 Hz, 1H), 7.07 (d, J = 1.2 Hz, 2H), 3.17 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.6, 148.1, 145.5, 122.8, 119.0, 116.6, 109.6, 37.7.



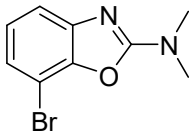
2-(dimethylamino)benzo[*d*]oxazol-5-yl acetate (3p)

The title compound was achieved as a orange solid, 19.4 mg, 44% yield; m.p. 113-114 °C; R_f = 0.35 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 – 7.98 (m, 1H), 7.77 (dd, J = 8.4, 1.7 Hz, 1H), 7.25 (d, J = 8.5 Hz, 1H), 3.90 (s, 3H), 3.20 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.2, 163.6, 152.2, 143.7, 126.3, 122.8, 117.4, 108.2, 52.1, 37.7. HRMS (ESI): m/z calcd. for $C_{11}H_{13}N_2O_3$ $[M + H]^+$: 221.0921, found: 221.0928.



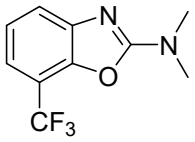
7-chloro-*N,N*-dimethylbenzo[*d*]oxazol-2-amine (3q)

The title compound was achieved as a reddish-brown solid, 21.2 mg, 54% yield; m.p. 88-89 °C; R_f = 0.58 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22 (dd, J = 7.8, 1.0 Hz, 1H), 7.06 (dd, J = 8.0, 2.7 Hz, 1H), 6.97 (dd, J = 8.1, 1.0 Hz, 1H), 3.22 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.9, 145.4, 144.9, 124.7, 120.8, 114.4, 113.9, 37.8. HRMS (ESI): m/z calcd. for $C_9H_{10}ClN_2O$ $[M + H]^+$: 197.0476, found: 197.0482.



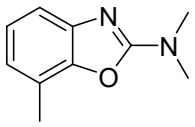
7-bromo-*N*,*N*-dimethylbenzo[*d*]oxazol-2-amine (3r)

The title compound was achieved as a reddish-brown solid, 39.4 mg, 82% yield; m.p. 96-97 °C; R_f = 0.49 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25 (dd, J = 7.8, 1.1 Hz, 1H), 7.11 (dd, J = 8.1, 1.1 Hz, 1H), 7.01 (dd, J = 10.5, 5.3 Hz, 1H), 3.22 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.6, 147.0, 144.4, 125.1, 123.4, 114.9, 100.6, 37.8. HRMS (ESI): m/z calcd. for $C_9H_{10}BrN_2O$ $[M + H]^+$: 240.9971, found: 240.9963.



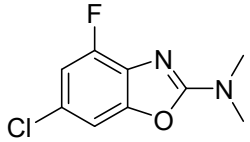
***N*,*N*-dimethyl-7-(trifluoromethyl)benzo[*d*]oxazol-2-amine (3s)**

The title compound was achieved as a yellow solid, 17.5 mg, 38% yield; m.p. 83-84 °C; R_f = 0.56 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 – 7.46 (m, 1H), 7.23 – 7.17 (m, 2H), 3.22 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.4, 145.0, 123.8, 123.1 (q, J_1 = 271.1 Hz), 119.3, 116.9 (q, J_3 = 4.3 Hz), 112.7 (q, J_2 = 34.6 Hz), 37.7. HRMS (ESI): m/z calcd. for $C_{10}H_{10}F_3N_2O$ $[M + H]^+$: 231.0740, found: 231.0747.



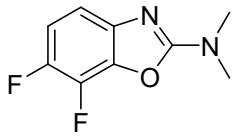
***N*,*N*,7-trimethylbenzo[*d*]oxazol-2-amine (3t)[2]**

The title compound was achieved as a reddish-brown oil, 23.9 mg, 68% yield; R_f = 0.6 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.18 (dd, J = 7.8, 0.5 Hz, 1H), 7.04 (t, J = 7.7 Hz, 1H), 6.80 (d, J = 7.5 Hz, 1H), 3.20 (s, 6H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.9, 148.1, 143.1, 123.7, 121.8, 119.0, 113.5, 37.7, 14.9.



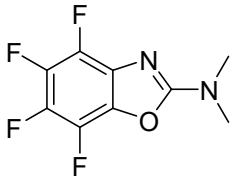
6-chloro-4-fluoro-*N*,*N*-dimethylbenzo[*d*]oxazol-2-amine (3u)

The title compound was achieved as a light brown solid, 24.8 mg, 58% yield; m.p. 99-100 °C; R_f = 0.24 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.02 (dd, J = 1.7, 0.7 Hz, 1H), 6.89 (dd, J = 9.8, 1.8 Hz, 1H), 3.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.1, 151.0 (d, J = 11.0 Hz), 150.2 (d, J = 252.1 Hz), 130.8 (d, J = 16.1 Hz), 124.7 (d, J = 9.4 Hz), 111.8 (d, J = 21.7 Hz), 106.0 (d, J = 5.0 Hz), 37.7. HRMS (ESI): m/z calcd. for $C_9H_9ClFN_2O$ $[M + H]^+$: 215.0382, found: 215.0389.



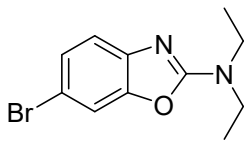
6,7-difluoro-*N*,*N*-dimethylbenzo[*d*]oxazol-2-amine (3v)

The title compound was achieved as a yellow solid, 17.0 mg, 43% yield; m.p. 86-87 °C; R_f = 0.50 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.00 – 6.93 (m, 2H), 3.21 (d, J = 0.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.43 (s), 145.9 (dd, J_1 = 239.1, J_2 = 10.1 Hz), 141.74 (s, 4H), 135.9 (dd, J = 6.1, J = 5.9 Hz), 135.5 (dd, J_1 = 251.1 J_2 = 18.3 Hz), 111.78 (d, J = 19.7 Hz), 109.93 (dd, J = 7.3, 3.8 Hz), 37.78 (s). HRMS (ESI): m/z calcd. for $C_9H_9F_2N_2O$ $[M + H]^+$: 199.0677, found: 199.0668.



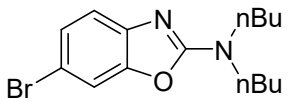
4,5,6,7-tetrafluoro-*N*,*N*-dimethylbenzo[*d*]oxazol-2-amine (3w)

The title compound was achieved as a yellow solid, 16.8 mg, 36% yield; m.p. 85-86 °C; R_f = 0.67 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.23 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.53 (s), 139.86 (m), 137.58 – 136.65 (m), 135.07 – 134.48 (m), 133.96 – 133.54 (m), 132.17 (m), 131.25 (m), 37.86 (s). HRMS (ESI): m/z calcd. for $C_9H_7F_4N_2O$ $[M + H]^+$: 235.0489, found: 235.0482.



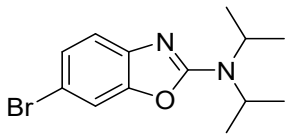
6-bromo-*N*,*N*-diethylbenzo[*d*]oxazol-2-amine (4a)[3]

The title compound was achieved as a white solid, 45.0 mg, 84% yield; m.p. 49-50 °C; R_f = 0.73 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 (d, J = 1.8 Hz, 1H), 7.23 (dd, J = 8.3, 1.8 Hz, 1H), 7.16 (d, J = 8.3 Hz, 1H), 3.54 (q, J = 7.1 Hz, 4H), 1.25 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.3, 149.2, 142.8, 126.8, 116.6, 112.0, 111.8, 43.1, 13.4.



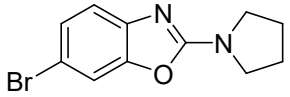
6-bromo-*N*,*N*-dibutylbenzo[*d*]oxazol-2-amine (4b)[4]

The title compound was achieved as a brown oil, 51.8 mg, 80% yield; R_f = 0.64 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, J = 1.6 Hz, 1H), 7.24 (dd, J = 8.3, 1.8 Hz, 1H), 7.17 (d, J = 8.3 Hz, 1H), 3.50 – 3.45 (m, 4H), 1.64 (dd, J = 9.0, 6.2 Hz, 4H), 1.37 (dd, J = 15.1, 7.5 Hz, 4H), 0.95 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.8, 149.2, 143.1, 126.8, 116.6, 112.0, 111.7, 48.4, 30.1, 20.0, 13.8.



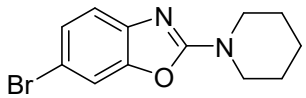
6-bromo-*N*,*N*-diisopropylbenzo[*d*]oxazol-2-amine (4c)

The title compound was achieved as a brown solid, 42.6 mg, 72% yield; m.p. 52-53 °C; R_f = 0.48 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 (d, J = 1.8 Hz, 1H), 7.24 (dd, J = 8.3, 1.8 Hz, 1H), 7.17 (d, J = 8.3 Hz, 1H), 4.19 (dt, J = 13.7, 6.8 Hz, 2H), 1.36 (s, 6H), 1.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.4, 149.0, 142.3, 126.7, 116.4, 111.9, 111.7, 47.9, 20.8. HRMS (ESI): m/z calcd. for $C_{13}H_{18}BrN_2O$ $[M + H]^+$: 297.0597, found: 297.0606.



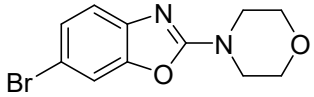
6-bromo-2-(pyrrolidin-1-yl)benzo[*d*]oxazole (4d)

The title compound was achieved as a white solid, 43.1 mg, 81% yield; m.p. 132-133 °C; R_f = 0.22 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 (d, J = 1.4 Hz, 1H), 7.24 (dt, J = 8.3, 1.6 Hz, 1H), 7.17 (dd, J = 8.3, 1.1 Hz, 1H), 3.63 – 3.59 (m, 4H), 2.02 (dd, J = 7.5, 5.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.1, 149.5, 143.0, 126.9, 116.8, 112.1, 111.9, 47.5, 25.6. HRMS (ESI): m/z calcd. for $C_{11}H_{12}BrN_2O$ $[M + H]^+$: 267.0128, found: 267.0116.



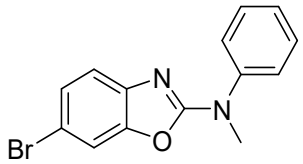
6-bromo-2-(piperidin-1-yl)benzo[*d*]oxazole (4e)

The title compound was achieved as a brown solid, 47.6 mg, 85% yield; m.p. 76-77 °C; R_f = 0.32 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 (d, J = 1.7 Hz, 1H), 7.22 (dd, J = 8.3, 1.7 Hz, 1H), 7.15 (d, J = 8.3 Hz, 1H), 3.61 (s, 4H), 1.65 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.5, 149.1, 142.6, 126.9, 116.8, 112.2, 112.1, 46.6, 25.2, 24.0. HRMS (ESI): m/z calcd. for $C_{12}H_{14}BrN_2O$ $[M + H]^+$: 281.0284, found: 281.0292.



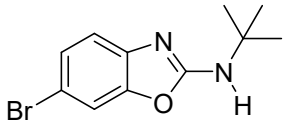
6-bromo-2-morpholinobenzo[*d*]oxazole (4f)

The title compound was achieved as a light brown solid, 49.6 mg, 88% yield; m.p. 111-112 °C; R_f = 0.21 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, J = 1.8 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.18 (d, J = 8.3 Hz, 1H), 3.79 – 3.76 (m, 4H), 3.65 – 3.62 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.2, 149.2, 142.2, 127.2, 117.3, 112.9, 112.4, 66.1, 45.7. HRMS (ESI): m/z calcd. for $C_{11}H_{12}BrN_2O_2$ $[M + H]^+$: 283.0077, found: 283.0084.



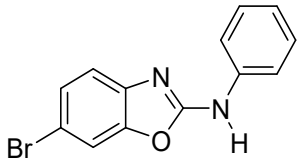
6-bromo-N-methyl-N-phenylbenzo[*d*]oxazol-2-amine (4g)

The title compound was achieved as a white solid, 49.5 mg, 82% yield; m.p. 104-105 °C; R_f = 0.48 (petroleum ether / ethyl acetate = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 – 7.42 (m, 2H), 7.42 – 7.37 (m, 3H), 7.32 – 7.26 (m, 3H), 3.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.6, 149.2, 142.6, 142.1, 129.4, 127.3, 126.5, 124.7, 117.6, 113.2, 112.6, 39.2. HRMS (ESI): m/z calcd. for $C_{14}H_{12}BrN_2O$ $[M + H]^+$: 303.0128, found: 303.0117.



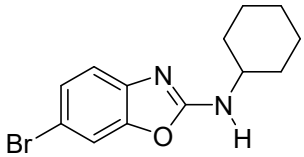
6-bromo-N-(tert-butyl)benzo[*d*]oxazol-2-amine (4h)

The title compound was achieved as a brown solid, 45.5 mg, 85% yield; m.p. 96-97 °C; R_f = 0.66 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (d, J = 1.8 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.18 (d, J = 8.3 Hz, 1H), 5.65 (s, 1H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.1, 148.6, 142.3, 126.8, 117.0, 112.6, 112.1, 52.3, 29.1. HRMS (ESI): m/z calcd. for $C_{11}H_{14}BrN_2O$ $[M + H]^+$: 269.0284, found: 269.0279.



6-bromo-N-phenylbenzo[*d*]oxazol-2-amine (4i)[5]

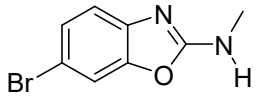
The title compound was achieved as a brown solid, 34.0 mg, 59% yield; m.p. 172-174 °C; R_f = 0.67 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.15 (s, 1H), 7.60 – 7.56 (m, 2H), 7.50 (d, J = 1.7 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.34 (dd, J = 11.7, 5.0 Hz, 2H), 7.15 – 7.11 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.6, 148.3, 141.5, 137.4, 129.4, 127.5, 123.7, 118.6, 117.9, 114.0, 112.7.



6-bromo-N-cyclohexylbenzo[*d*]oxazol-2-amine (4j)

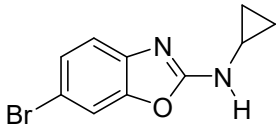
The title compound was achieved as a brown solid, 39.4 mg, 67% yield; m.p. 129-130 °C; R_f = 0.58 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, J = 1.4 Hz, 1H), 7.26 (dd, J = 5.3, 2.9 Hz, 1H), 7.19 (d, J = 8.3 Hz, 1H), 5.33 (s, 1H), 3.72 (s, 1H), 2.11 (dd, J = 11.8, 2.7 Hz, 2H), 1.80 – 1.74 (m, 2H), 1.68 – 1.62 (m, 1H), 1.42 (ddd, J = 13.2, 10.0, 4.0 Hz, 2H), 1.33 – 1.25 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.7, 148.8, 142.3, 127.0, 116.9, 112.6, 112.2, 52.2, 33.4, 25.4, 24.7.

HRMS (ESI): m/z calcd. for $C_{13}H_{16}BrN_2O$ $[M + H]^+$: 295.0441, found: 295.0428.



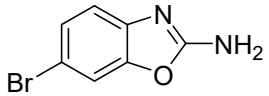
6-bromo-N-methylbenzo[*d*]oxazol-2-amine (4k)

The title compound was achieved as a brown solid, 34.3 mg, 76% yield; m.p. 155-156 °C; R_f = 0.30 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.95 (d, J = 4.5 Hz, 1H), 7.57 (d, J = 1.8 Hz, 1H), 7.24 (dd, J = 8.3, 1.9 Hz, 1H), 7.16 (d, J = 8.3 Hz, 1H), 2.90 (d, J = 4.7 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 163.8, 149.3, 143.4, 126.9, 117.0, 112.2, 111.6, 29.3. HRMS (ESI): m/z calcd. for $C_8H_8BrN_2O$ $[M + H]^+$: 226.9815, found: 226.9806.



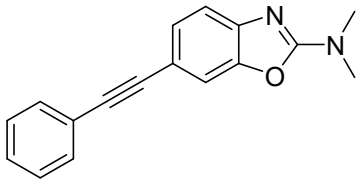
6-bromo-N-cyclopropylbenzo[*d*]oxazol-2-amine (4l)

The title compound was achieved as a white solid, 33.2 mg, 66% yield; m.p. 118-119 °C; R_f = 0.28 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 (s, 1H), 7.31 – 7.24 (m, 2H), 5.86 (s, 1H), 2.84 (tt, J = 6.9, 3.5 Hz, 1H), 0.89 (q, J = 6.7 Hz, 2H), 0.75 – 0.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.0, 149.1, 142.2, 127.1, 117.3, 113.0, 112.4, 24.4, 7.3. HRMS (ESI): m/z calcd. for $C_{10}H_{10}BrN_2O$ $[M + H]^+$: 252.9971, found: 252.9962.



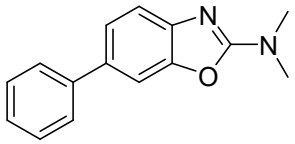
6-bromobenzo[*d*]oxazol-2-amine (4m)[6]

The title compound was achieved as a brown solid, 22.0 mg, 52% yield; m.p. 152-153 °C; R_f = 0.32 (petroleum ether / ethyl acetate = 1:1); ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.57 (d, J = 1.7 Hz, 1H), 7.55 (s, 2H), 7.24 (dd, J = 8.3, 1.9 Hz, 1H), 7.12 (d, J = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 163.6, 149.1, 143.7, 126.8, 116.9, 112.2, 111.5.



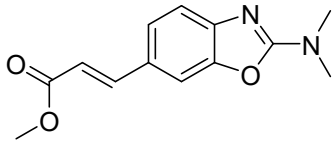
***N,N*-dimethyl-6-(phenylethynyl)benzo[*d*]oxazol-2-amine (5)**

The title compound was achieved as a yellow solid, 44.6 mg, 85% yield; m.p. 136-137 °C; R_f = 0.23 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 – 7.51 (m, 2H), 7.40 (d, J = 1.2 Hz, 1H), 7.38 – 7.35 (m, 1H), 7.34 (d, J = 5.6 Hz, 1H), 7.32 (dt, J = 3.8, 1.8 Hz, 2H), 7.27 (s, 1H), 3.20 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.7, 148.7, 144.3, 131.5, 128.4, 128.3, 128.0, 123.6, 115.7, 114.7, 111.7, 90.1, 88.0, 37.7. HRMS (ESI): m/z calcd. for $C_{17}H_{15}N_2O$ $[M + H]^+$: 263.1179, found: 263.1173.



***N,N*-dimethyl-6-phenylbenzo[*d*]oxazol-2-amine (6)**

The title compound was achieved as a yellow solid, 41.9 mg, 88% yield; m.p. 125-126 ^{o}C; R_f = 0.22 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 (dt, J = 8.2, 1.7 Hz, 2H), 7.49 (d, J = 0.9 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.41 – 7.40 (m, 2H), 7.34 – 7.29 (m, 1H), 3.22 (d, J = 0.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.4, 149.8, 143.1, 141.4, 134.1, 128.8, 127.1, 126.7, 123.2, 115.9, 107.4, 37.7. HRMS (ESI): m/z calcd. for $C_{15}H_{15}N_2O$ $[M + H]^+$: 239.1179, found: 239.1174.



methyl (E)-3-(2-(dimethylamino)benzo[*d*]oxazol-6-yl)acrylate (7)

The title compound was achieved as a yellow solid, 44.8 mg, 91% yield; m.p. 104-106 ^{o}C; R_f = 0.28 (petroleum ether / ethyl acetate = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (d, J = 15.9 Hz, 1H), 7.41 (d, J = 1.3 Hz, 1H), 7.33 (dd, J = 8.2, 1.5 Hz, 1H), 7.30 – 7.27 (m, 1H), 6.51 – 6.11 (m, 1H), 3.79 (s, 3H), 3.21 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.8, 164.0, 149.5, 146.3, 145.4, 127.1, 125.7, 115.8, 115.1, 107.4, 51.6, 37.7. HRMS (ESI): m/z calcd. for $C_{13}H_{15}N_2O_3$ $[M + H]^+$: 247.1077, found: 247.1073.

E. Reference

1. A. Lukin, N. Kalinchenkova, T. Vedekhina, N. Zhurilo and M. Krasavin, Diversity-oriented synthesis of N,N-dimethylamino-substituted azoles employing TBTU, *Tetrahedron Lett.*, 2018, **59**, 2732-2735.
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3. M. Pattarawarapan, D. Yamano, N. Wiriya and W. Phakhodee, Metal-Free Synthesis of 2-N,N-Dialkylaminobenzoxazoles Using Tertiary Amines as the Nitrogen Source, *J. Org. Chem.*, 2019, **84**, 6516-6523.
4. M. Pattarawarapan, N. Wiriya, S. Yimklan, S. Wangngae and W. Phakhodee, Zwitterionic Ring-Opened Oxyphosphonium Species from the $Ph_3P–I_2$ Mediated Reactions of Benzo[*d*]oxazol-2(3H)-ones with Secondary Amines, *J. Org. Chem.*, 2020, **85**, 6151-6158.
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6. M. Kasthuri, H. S. Babu, K. S. Kumar, C. Sudhakar and P. V. N. Kumar, A Facile Synthesis of 2-Aminobenzoxazoles and 2-Aminobenzimidazoles Using N-Cyano-N-phenyl-p-toluenesulfonamide (NCTS) as an Efficient Electrophilic Cyanating Agent, *Synlett*, 2015, **26**, 897-900.

F. Copies of ^{1}H and ^{13}C NMR spectra

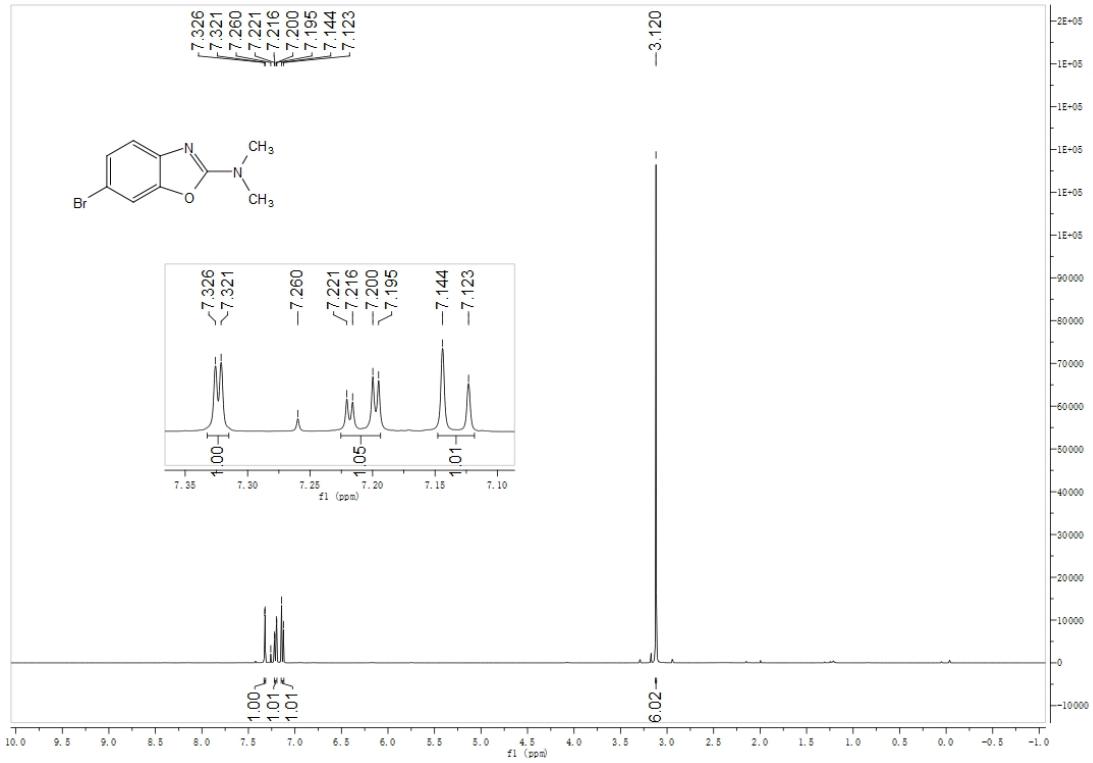

Figure S1. ^{1}H NMR Spectrum of 3a (400 MHz, $CDCl_3$)

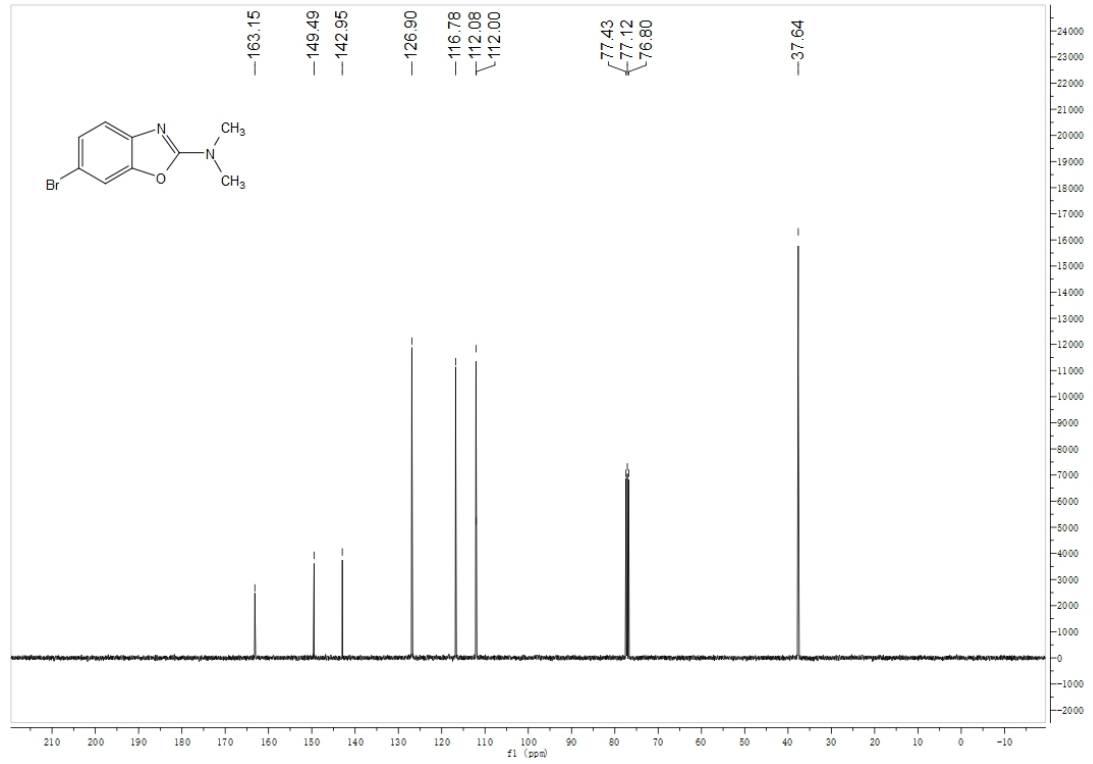

Figure S2. ^{13}C NMR Spectrum of 3a (100 MHz, $CDCl_3$)

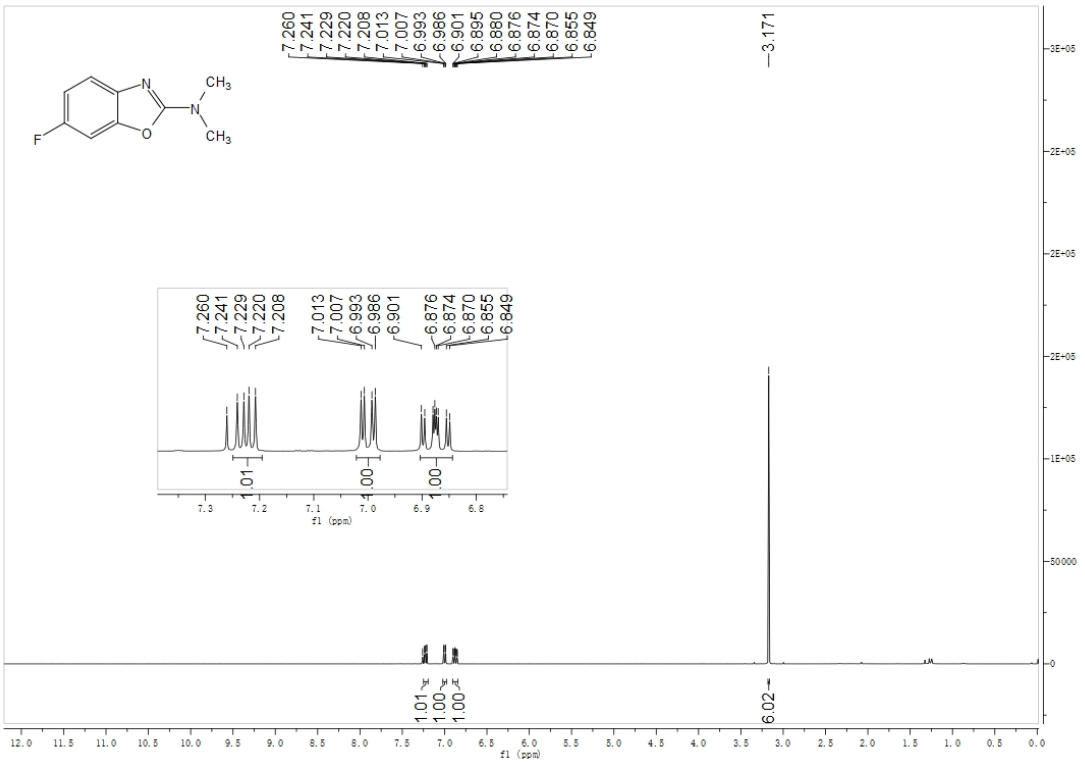

Figure S3. ^{1}H NMR Spectrum of 3b (400 MHz, $CDCl_3$)

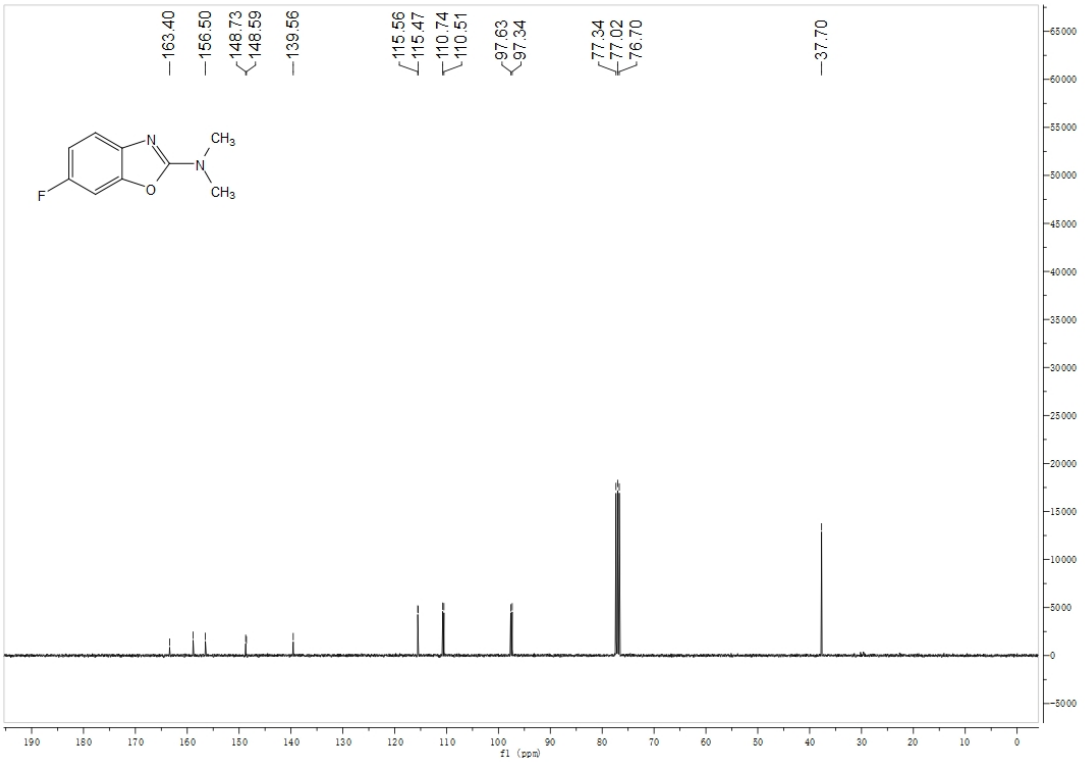

Figure S4. ^{13}C NMR Spectrum of 3b (100 MHz, $CDCl_3$)

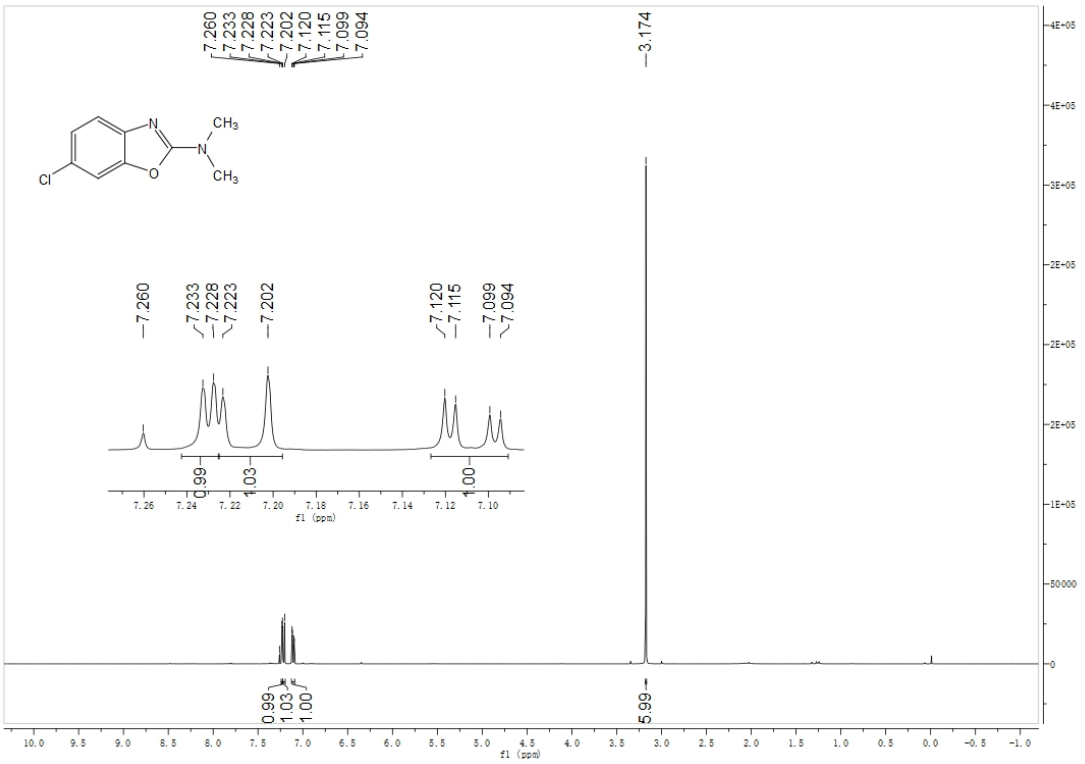

Figure S5. ^{1}H NMR Spectrum of 3c (400 MHz, $CDCl_3$)

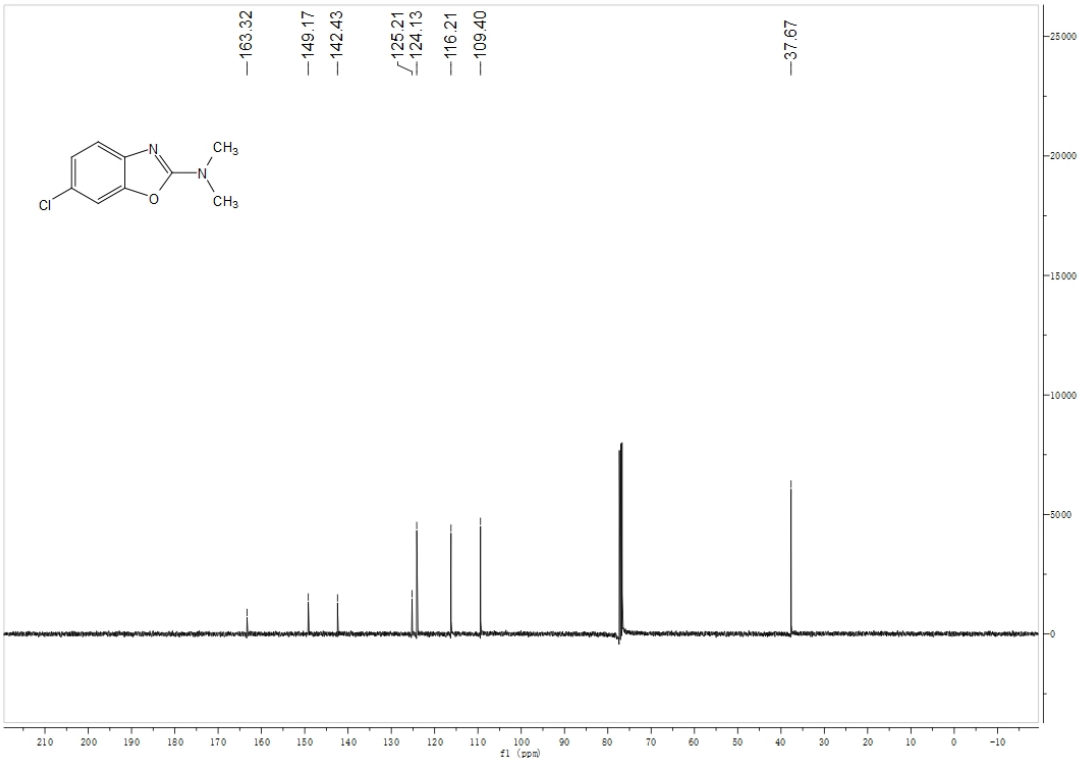

Figure S6. ^{13}C NMR Spectrum of 3c (100 MHz, $CDCl_3$)

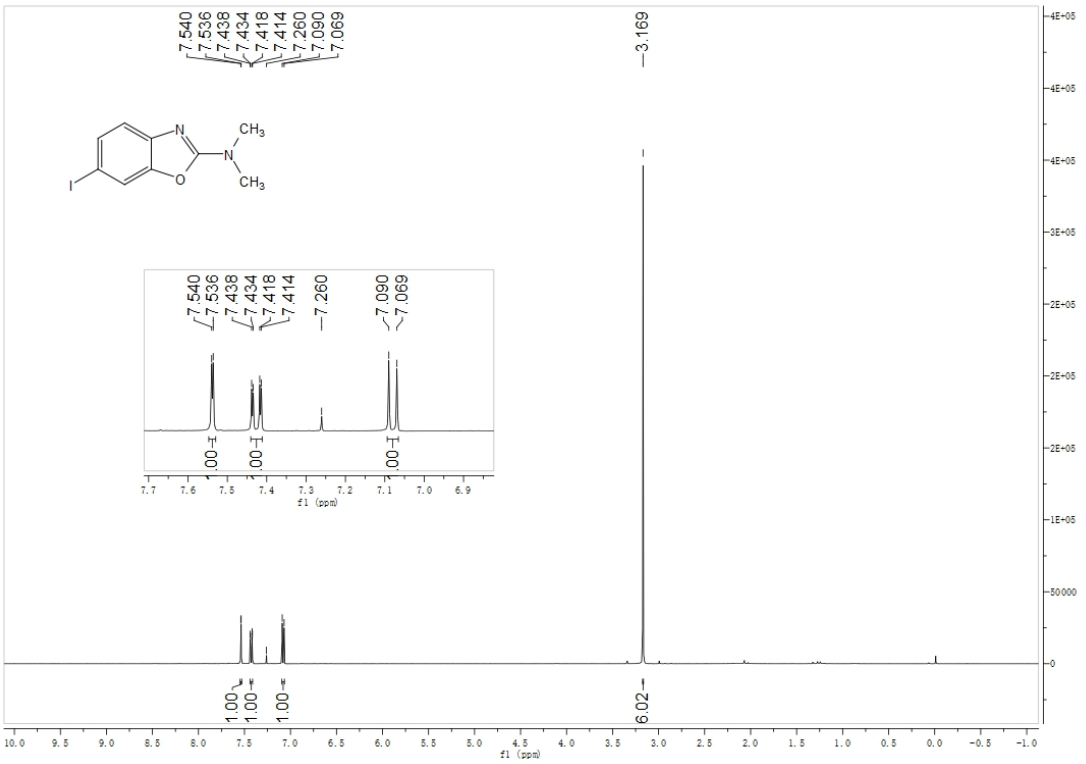

Figure S7. ^{1}H NMR Spectrum of 3d (400 MHz, $CDCl_3$)

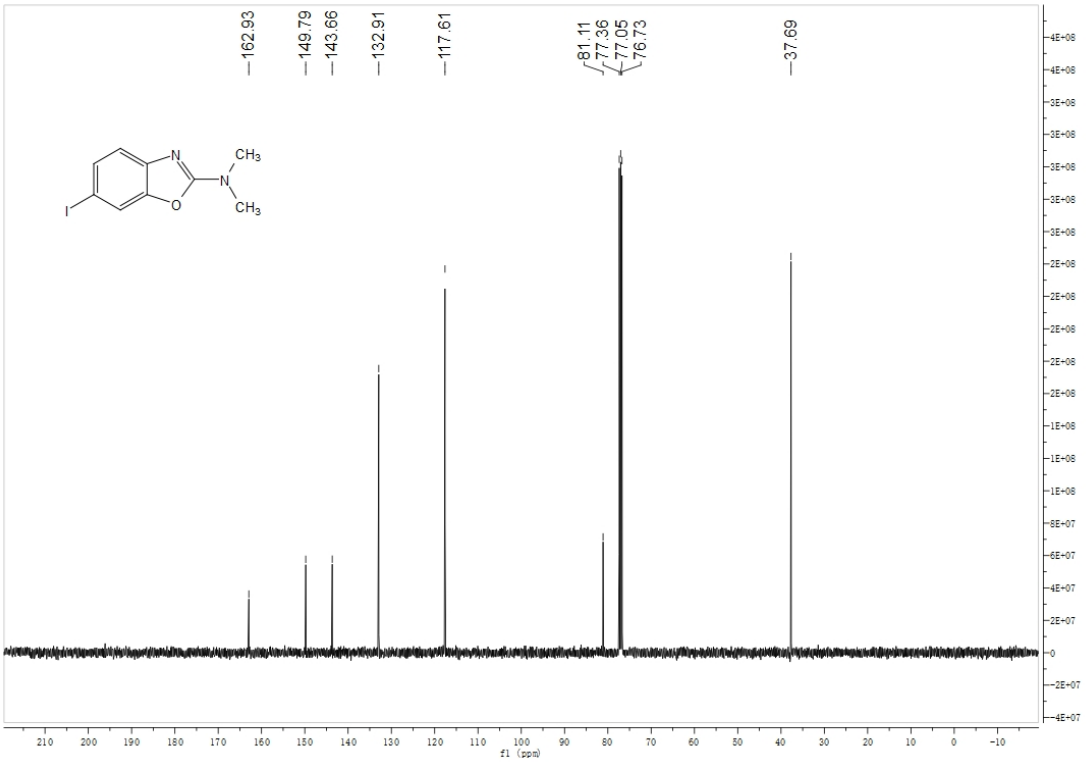

Figure S8. ^{13}C NMR Spectrum of 3d (100 MHz, $CDCl_3$)

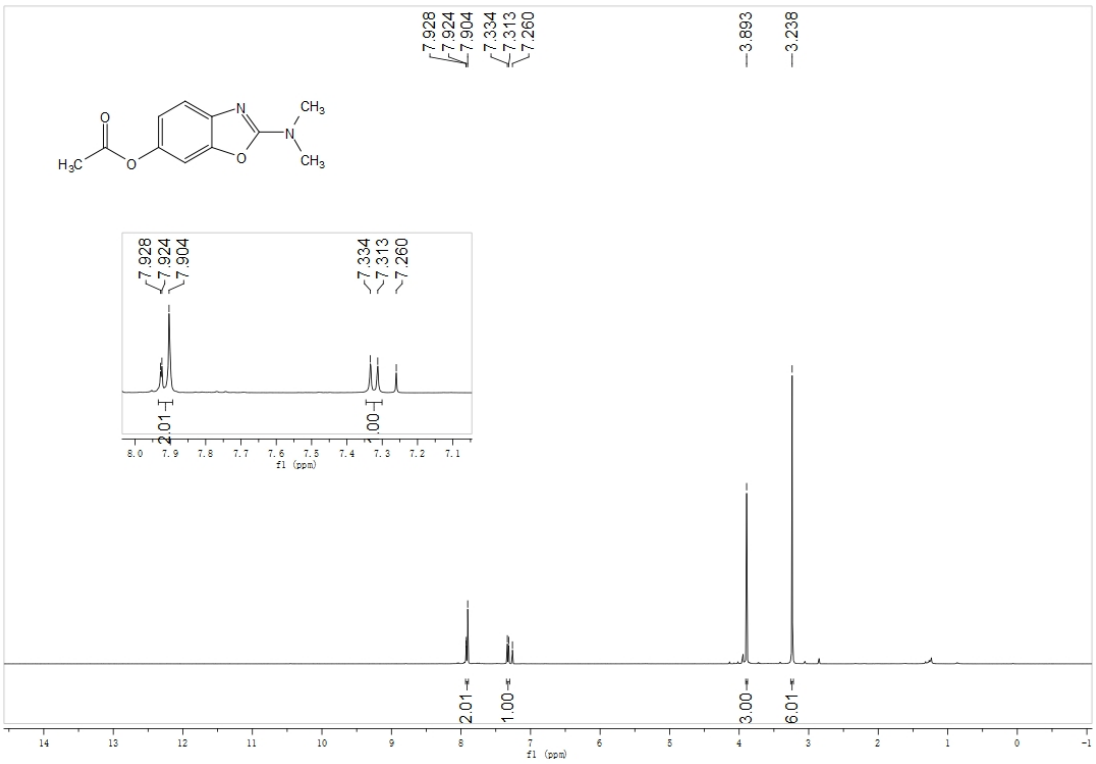

Figure S9. ^{1}H NMR Spectrum of 3e (400 MHz, $CDCl_3$)

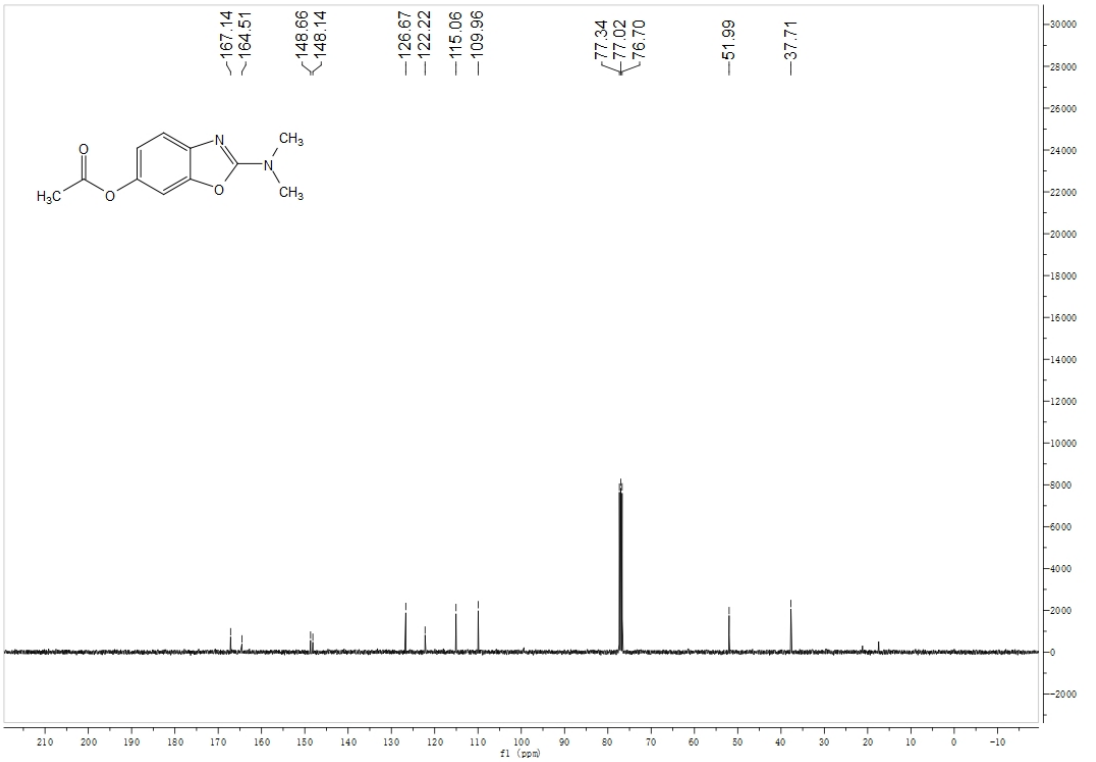

Figure S10. ^{13}C NMR Spectrum of 3e (100 MHz, $CDCl_3$)

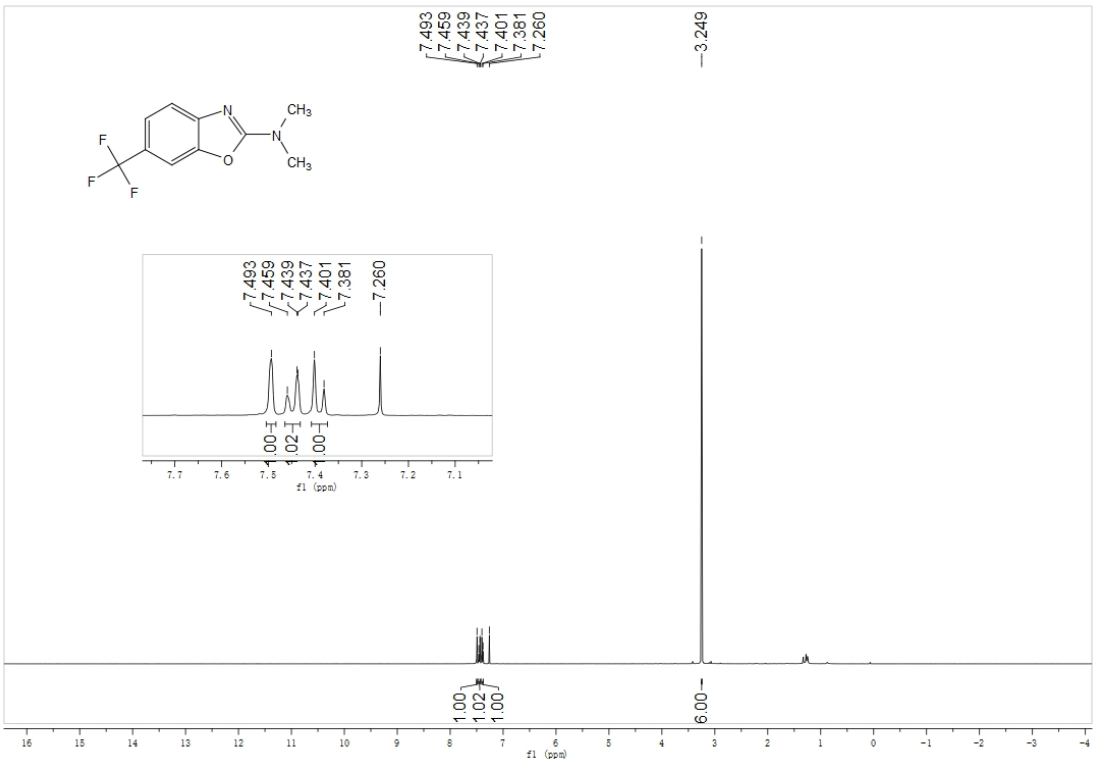

Figure S11. ^{1}H NMR Spectrum of 3f (400 MHz, $CDCl_3$)

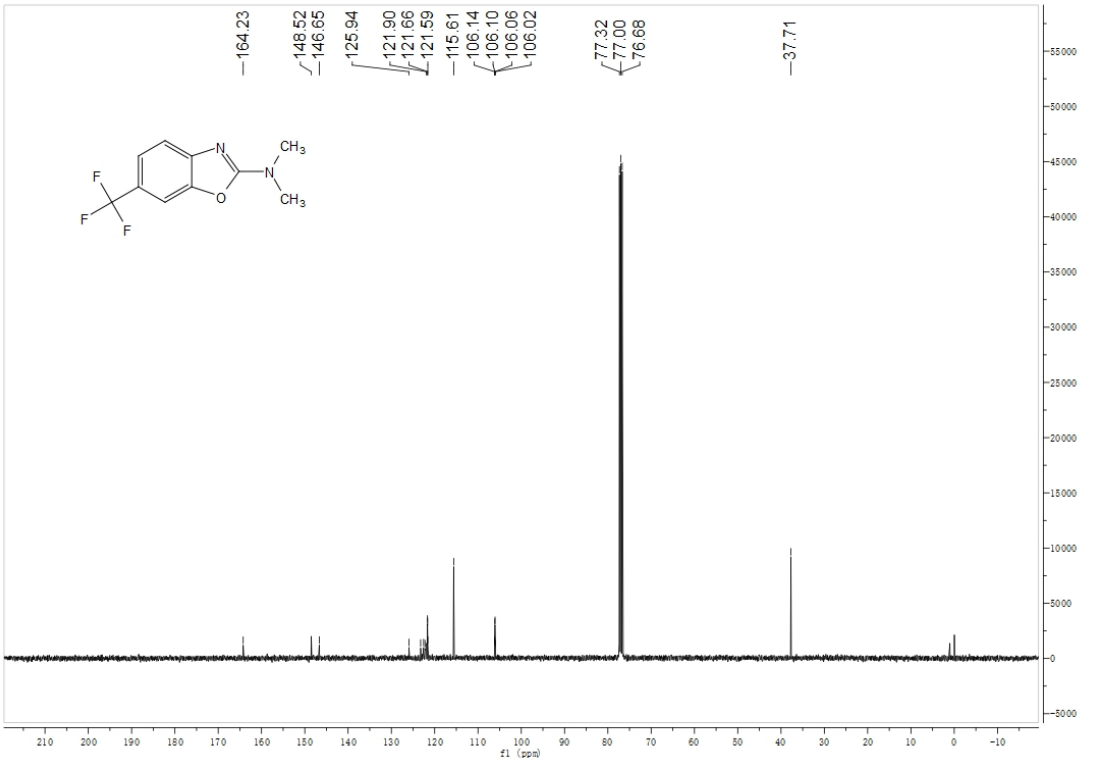

Figure S12. ^{13}C NMR Spectrum of 3f (100 MHz, $CDCl_3$)

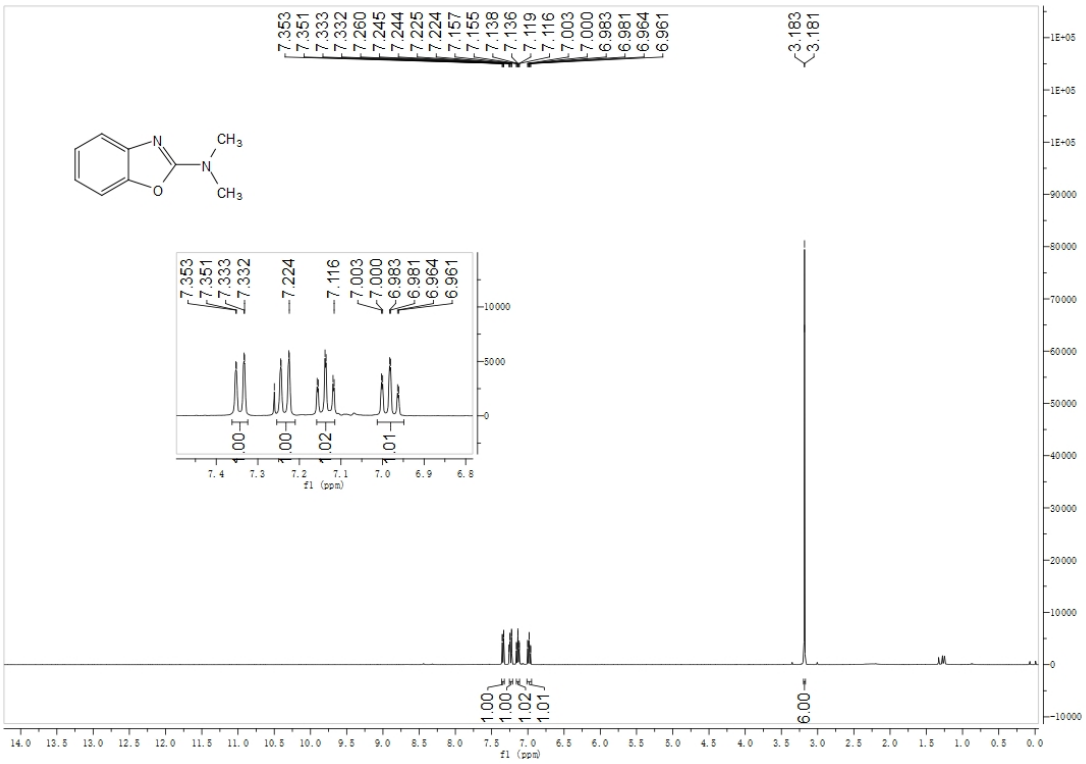

Figure S13. ^{1}H NMR Spectrum of 3g (400 MHz, $CDCl_3$)

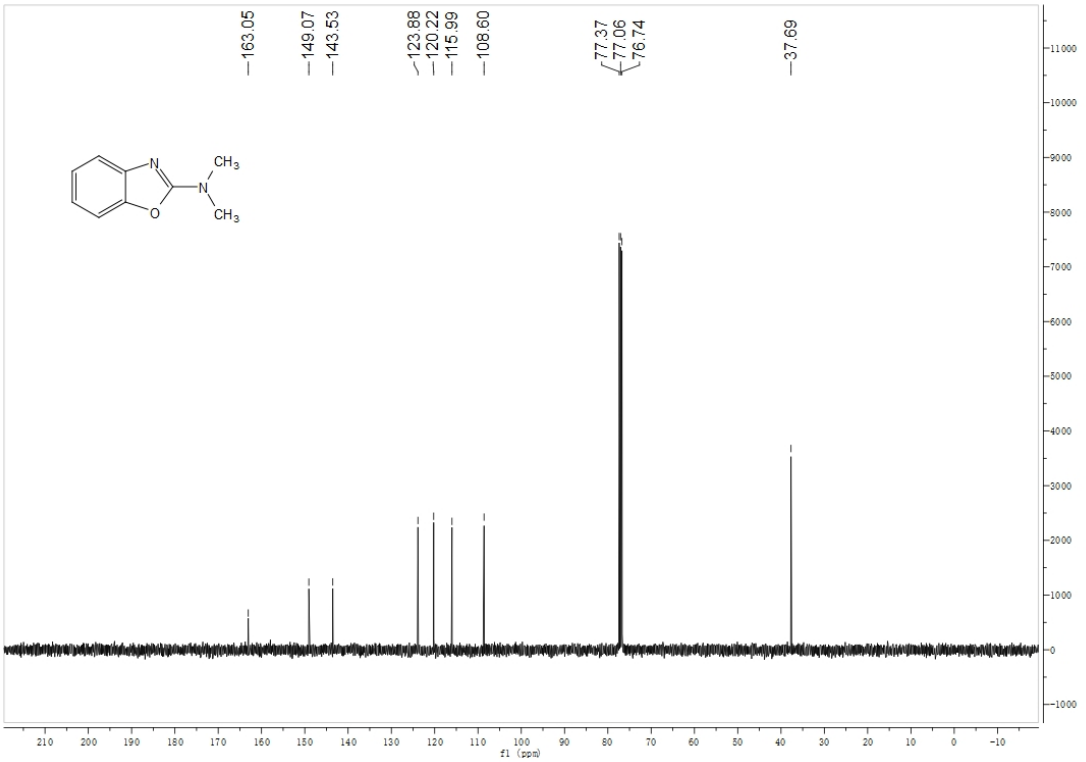

Figure S14. ^{13}C NMR Spectrum of 3g (100 MHz, $CDCl_3$)

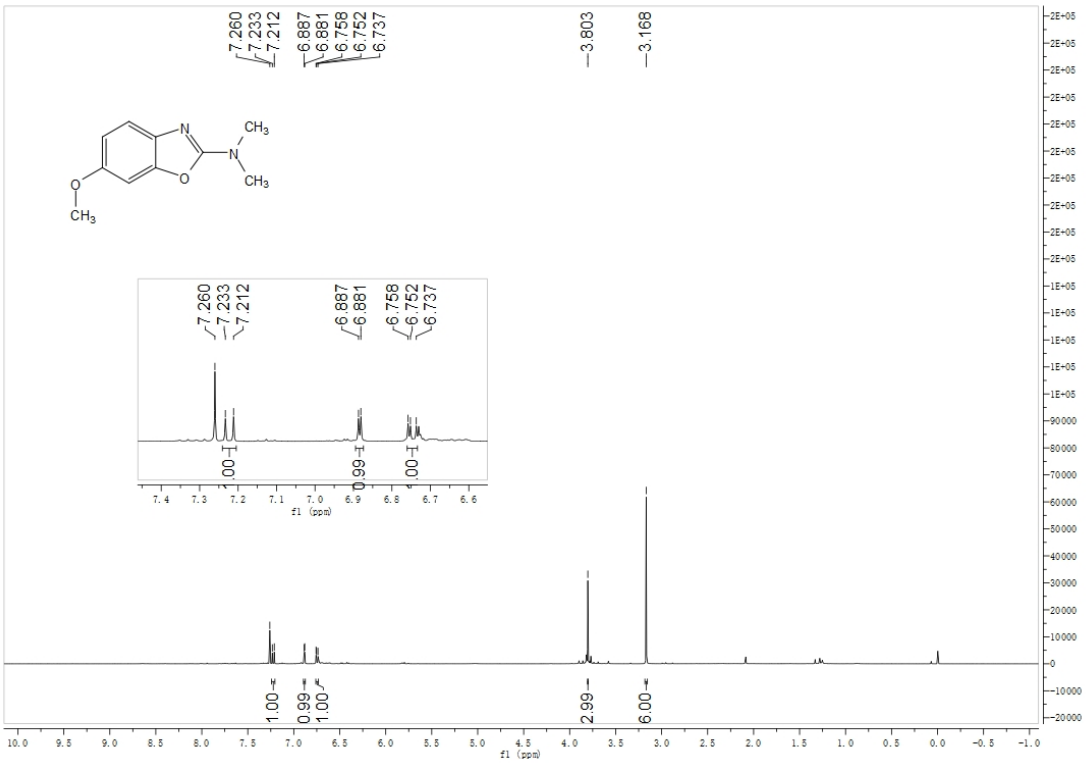

Figure S15. ^{1}H NMR Spectrum of 3h (400 MHz, $CDCl_3$)

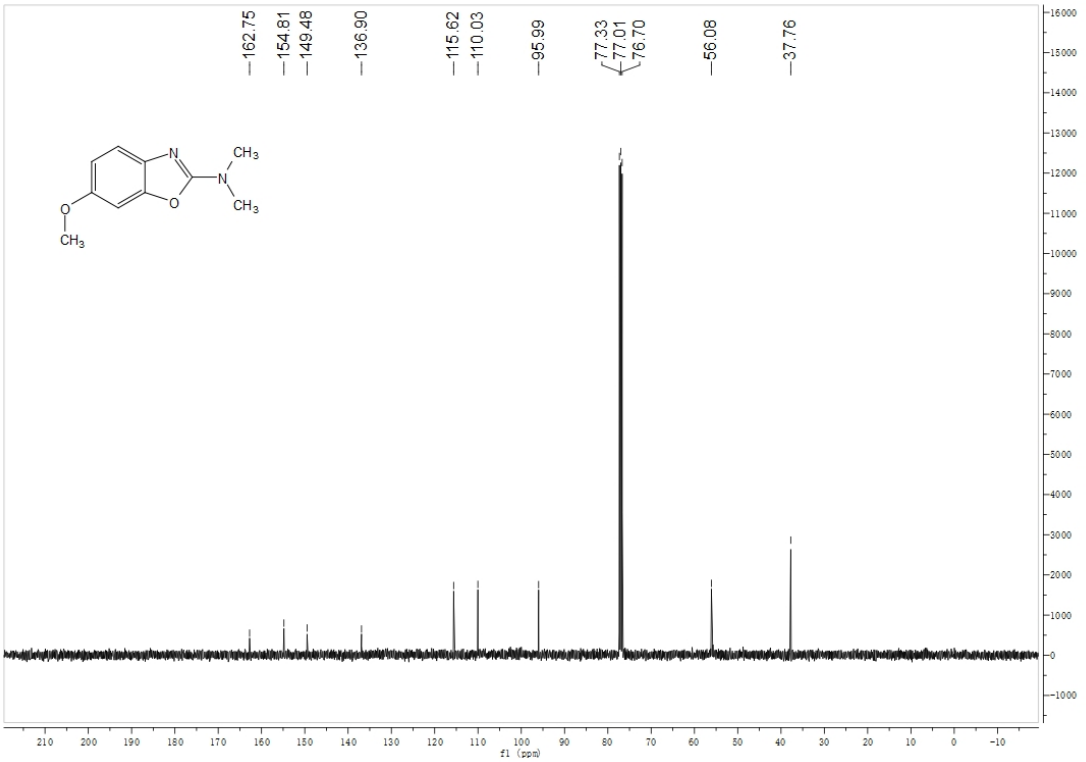

Figure S16. ^{13}C NMR Spectrum of 3h (100 MHz, $CDCl_3$)

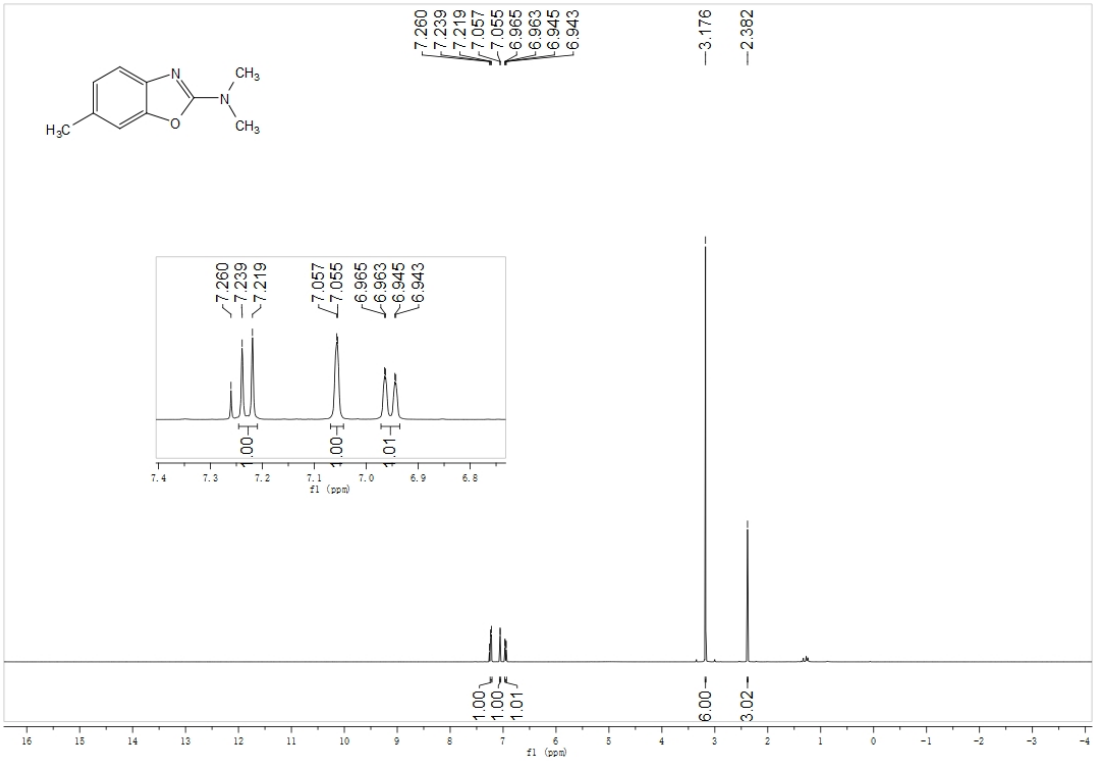

Figure S17. ^{1}H NMR Spectrum of 3i (400 MHz, $CDCl_3$)

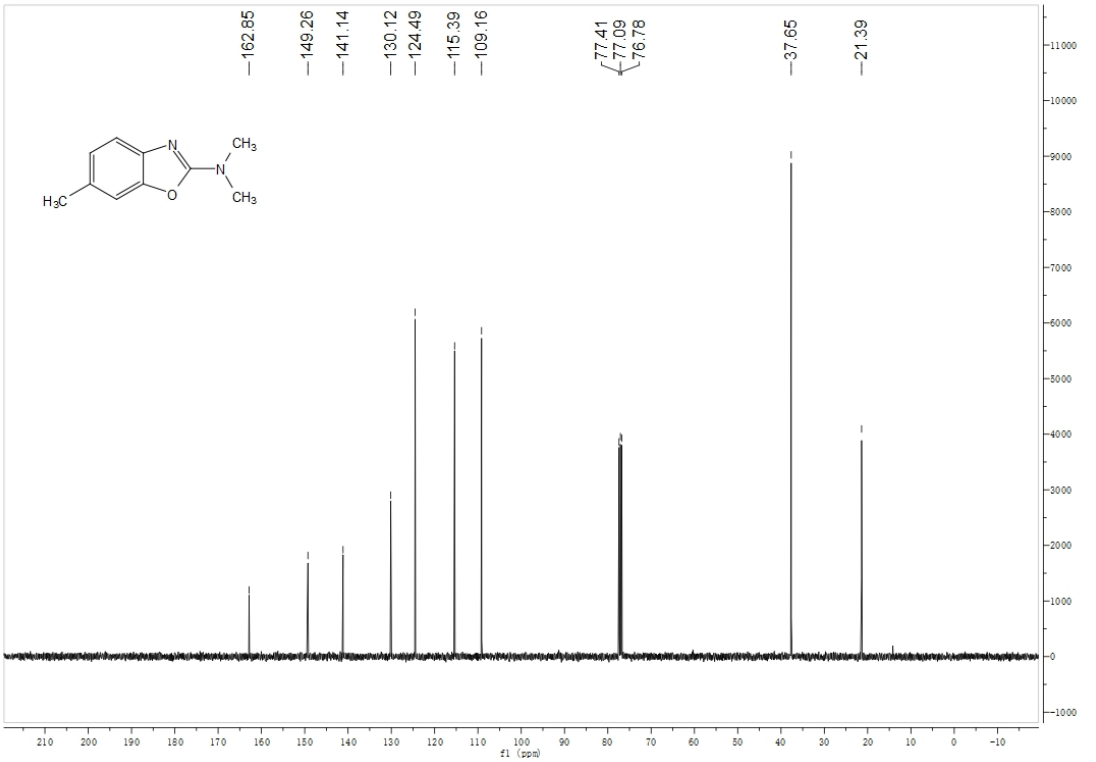

Figure S18. ^{13}C NMR Spectrum of 3i (100 MHz, $CDCl_3$)

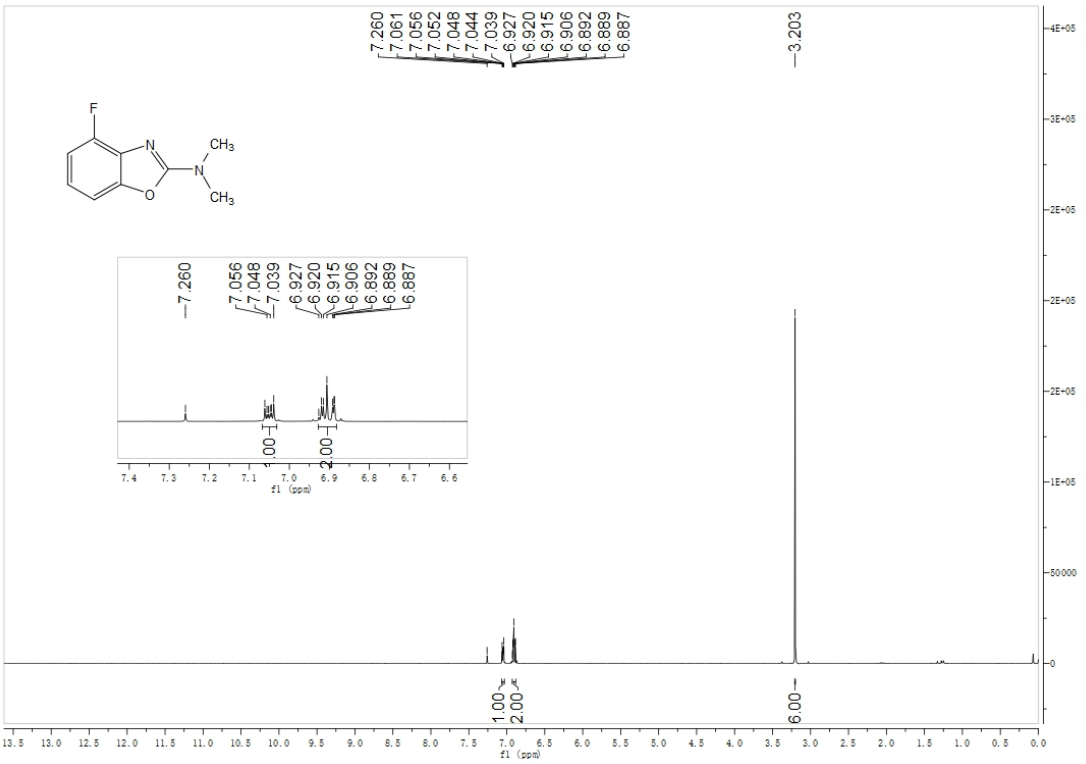

Figure S19. ^{1}H NMR Spectrum of 3j (400 MHz, $CDCl_3$)

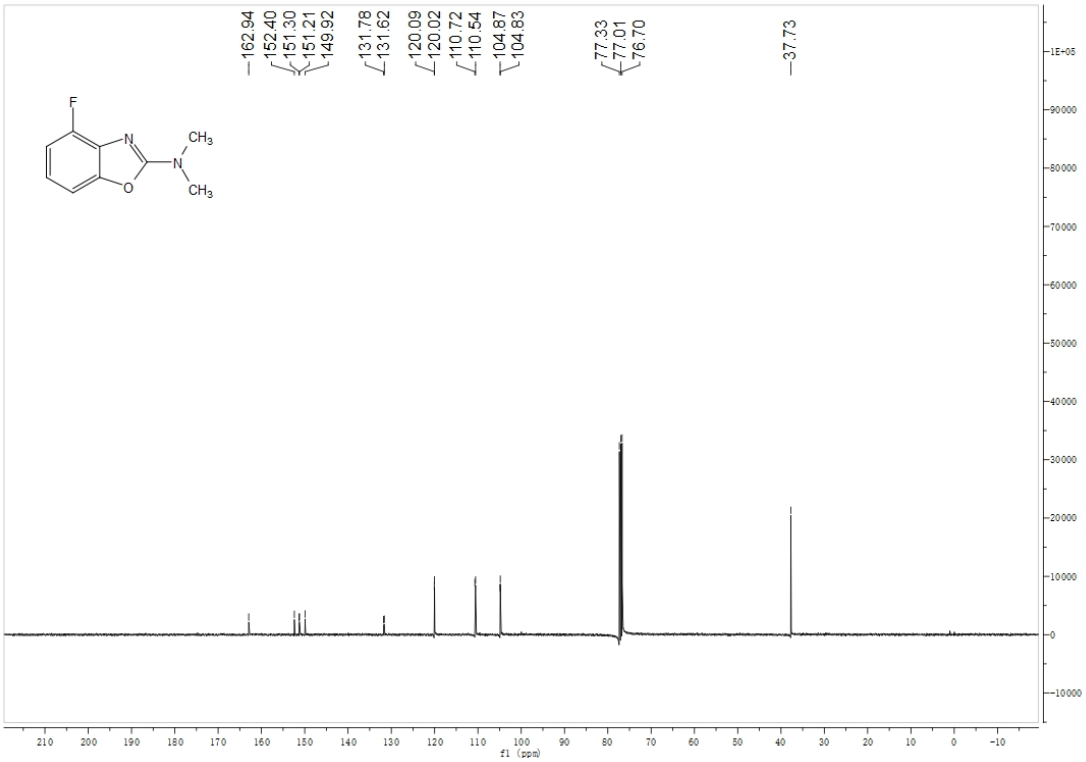

Figure S20. ^{13}C NMR Spectrum of 3j (100 MHz, $CDCl_3$)

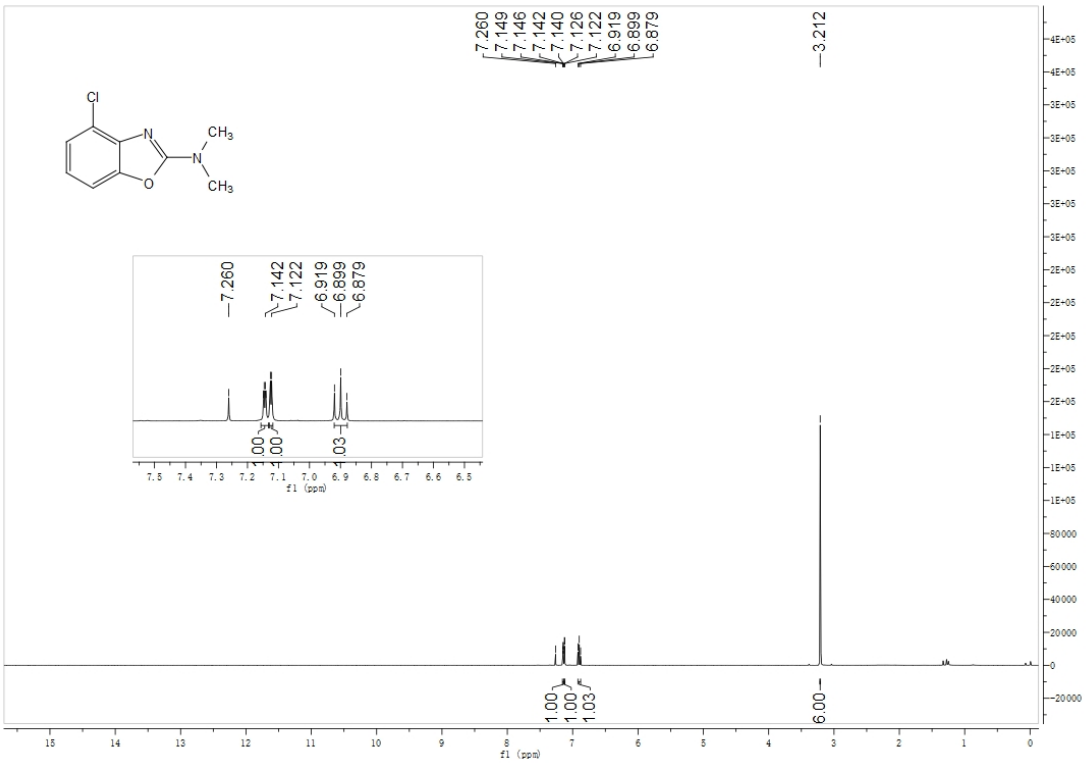

Figure S21. ^{1}H NMR Spectrum of 3k (400 MHz, $CDCl_3$)

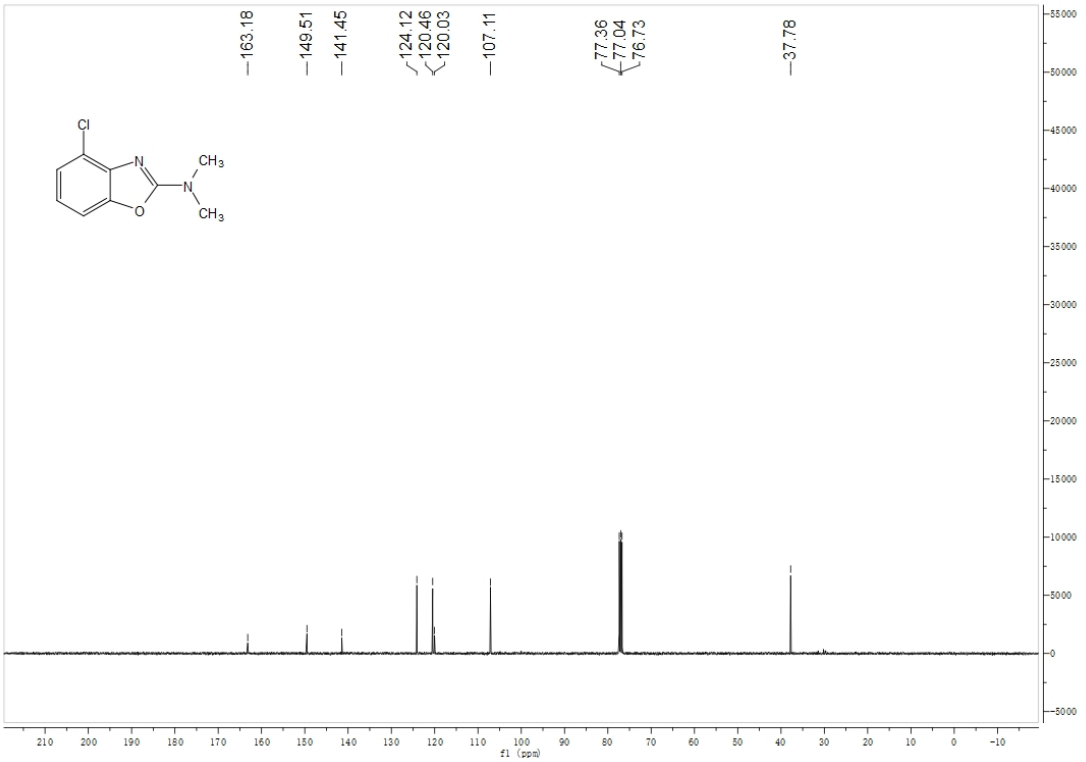

Figure S22. ^{13}C NMR Spectrum of 3k (100 MHz, $CDCl_3$)

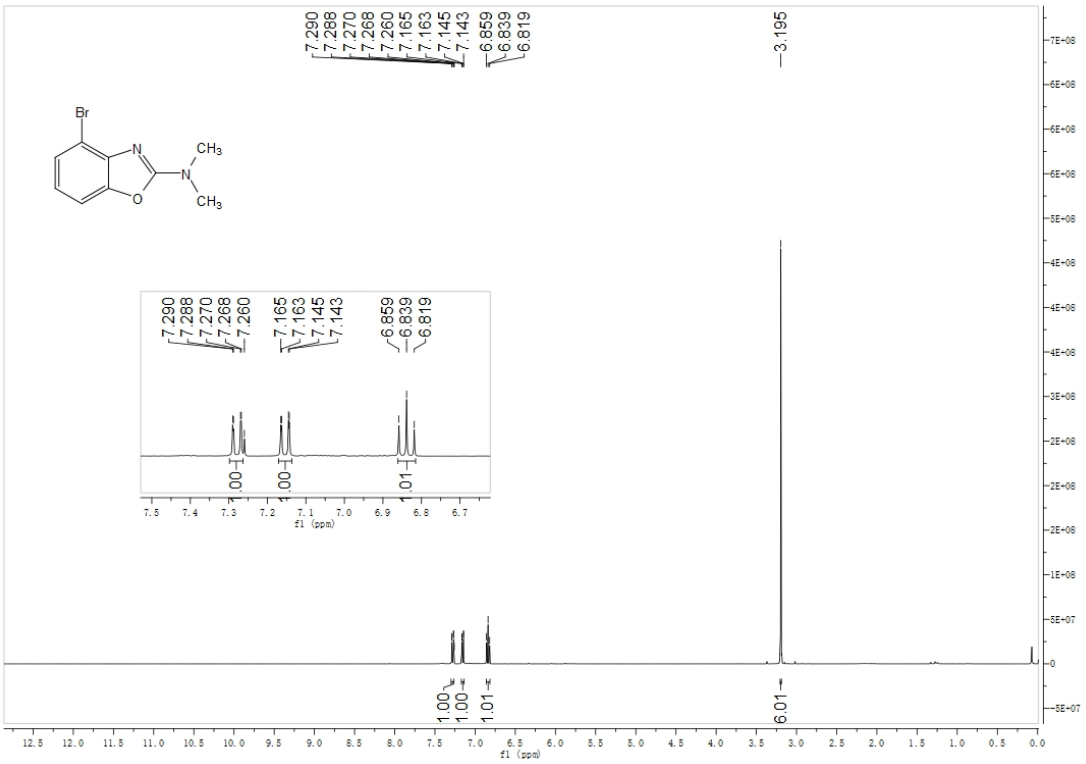

Figure S23. ^{1}H NMR Spectrum of 3l (400 MHz, $CDCl_3$)

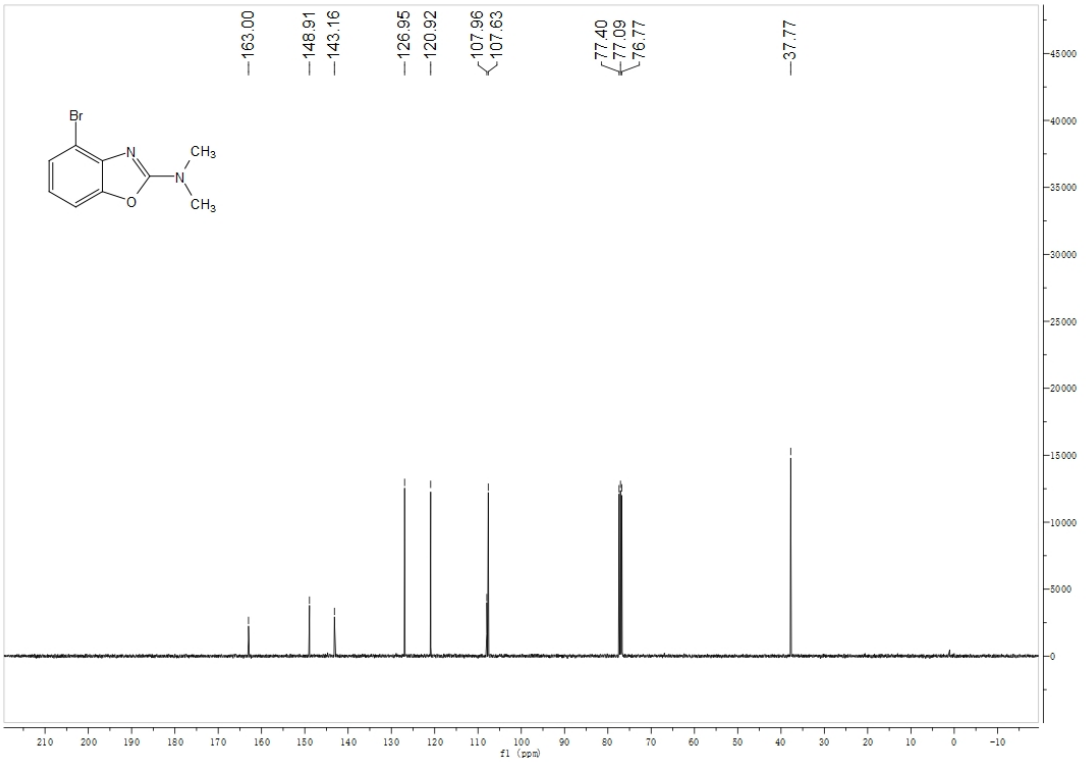

Figure S24. ^{13}C NMR Spectrum of 3l (100 MHz, $CDCl_3$)

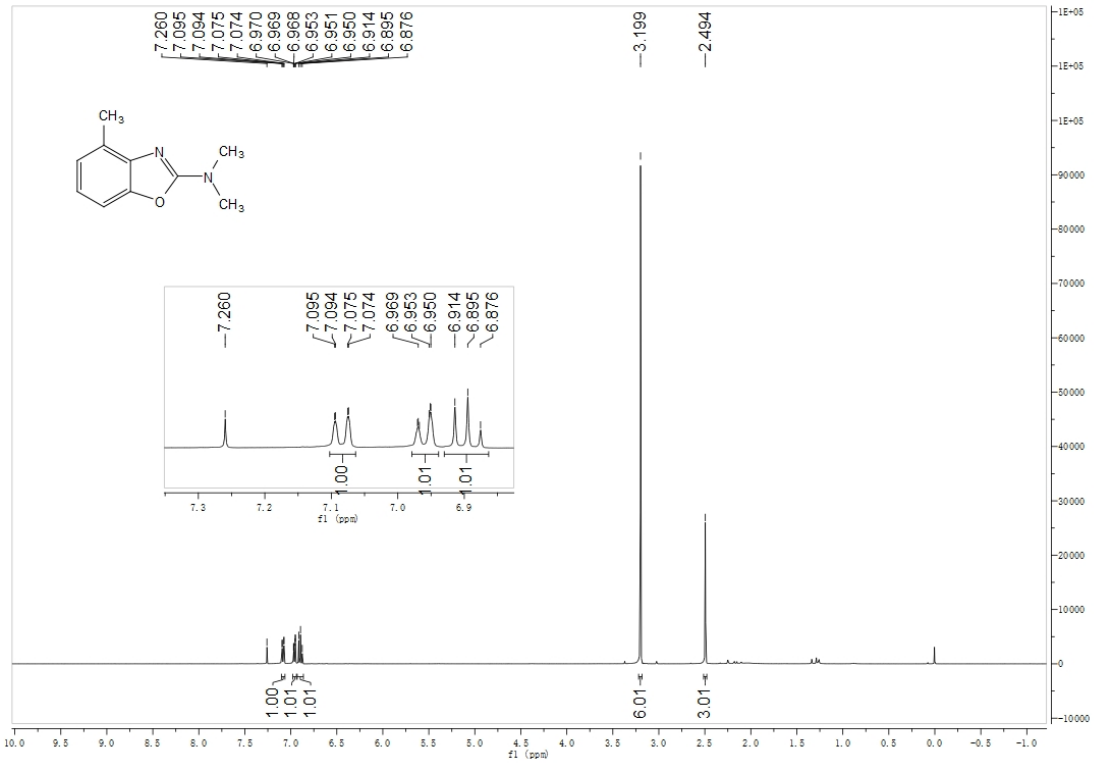

Figure S25. ^{1}H NMR Spectrum of 3m (400 MHz, $CDCl_3$)

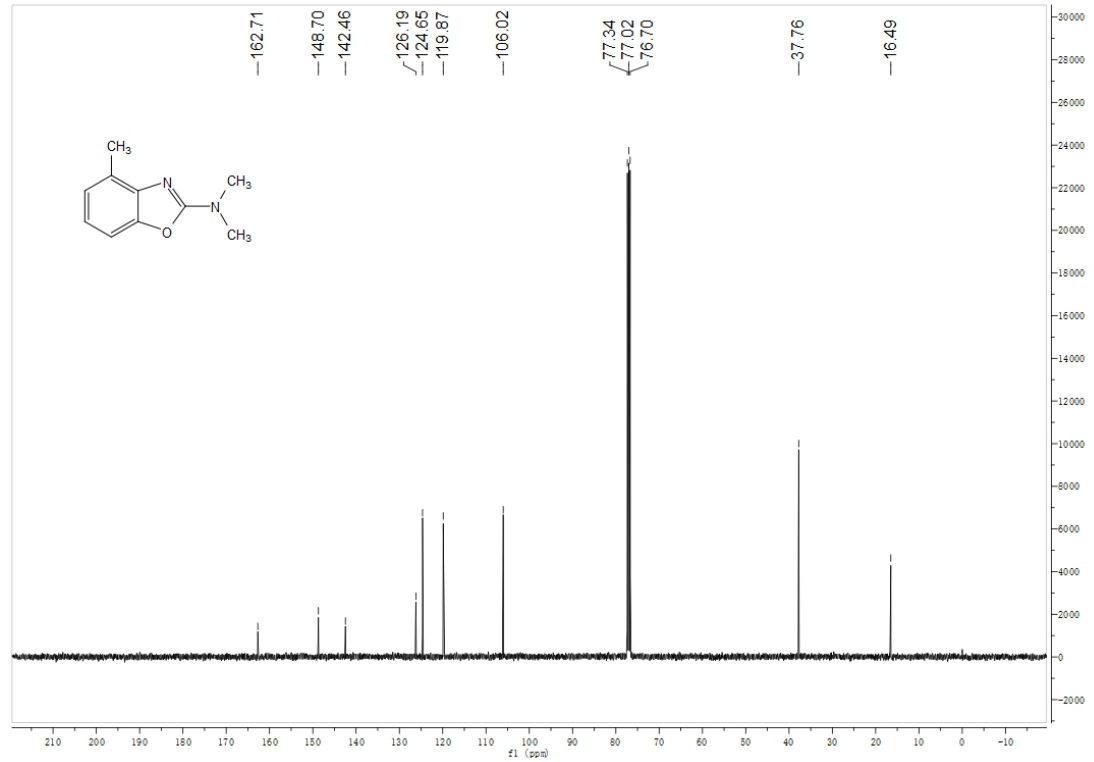

Figure S26. ^{13}C NMR Spectrum of 3m (100 MHz, $CDCl_3$)

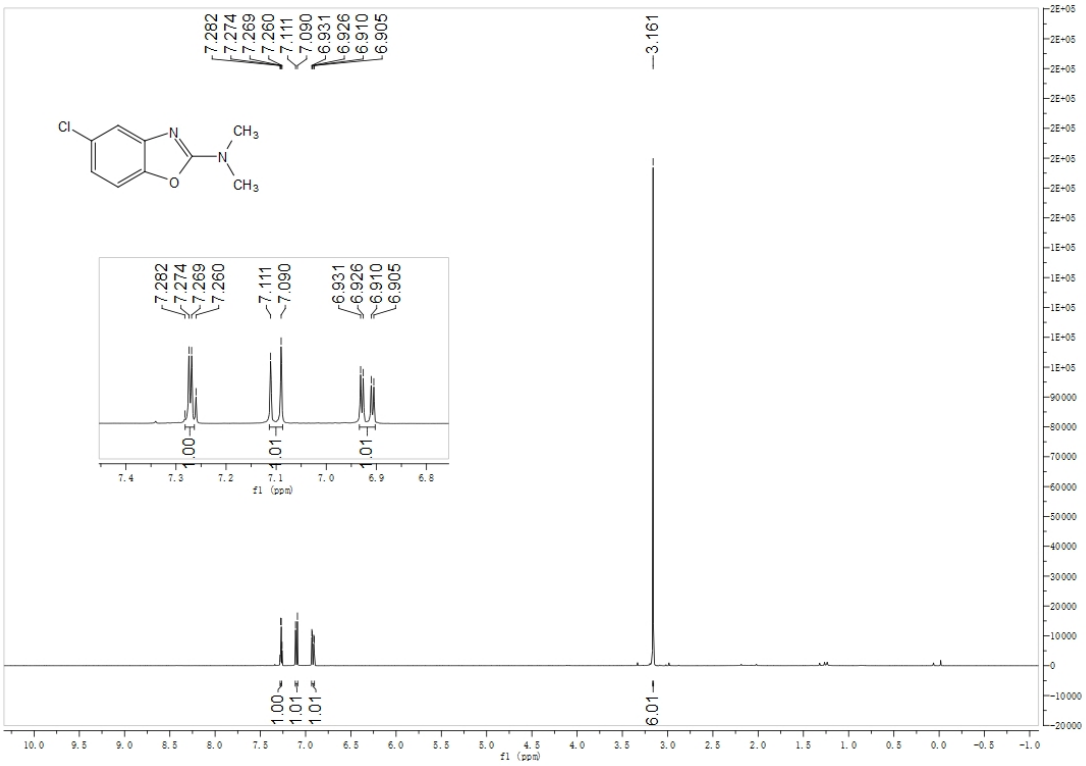

Figure S27. ^{1}H NMR Spectrum of 3n (400 MHz, $CDCl_3$)

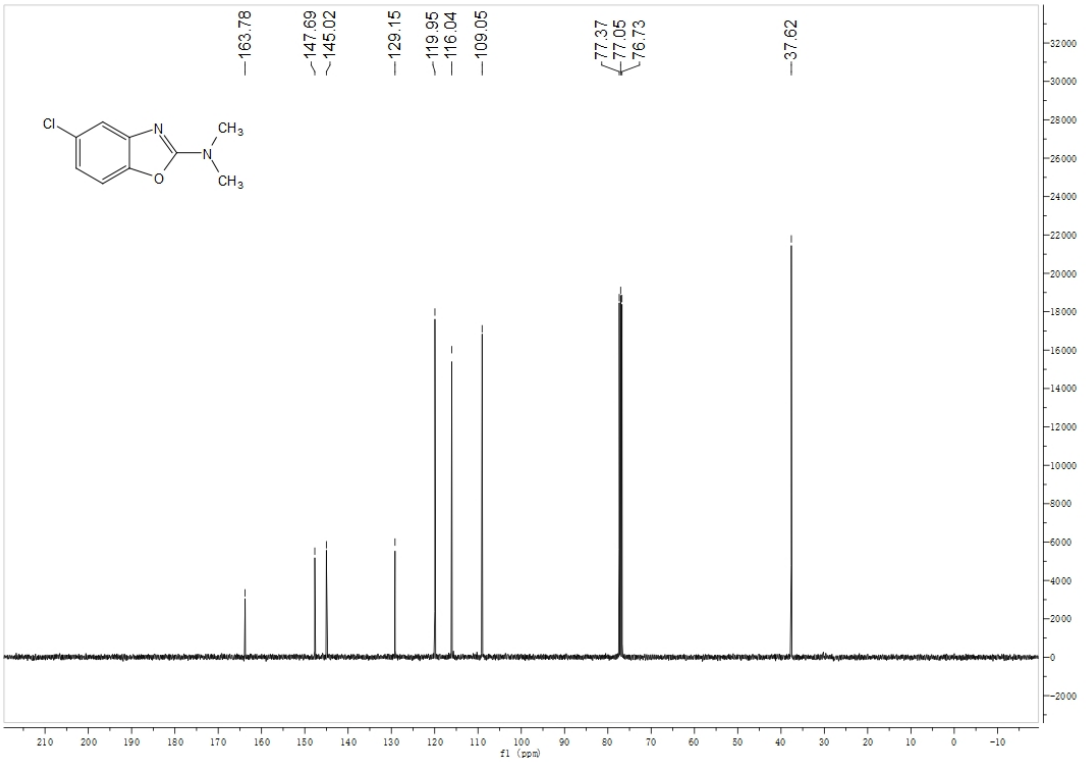

Figure S28. ^{13}C NMR Spectrum of 3n (100 MHz, $CDCl_3$)

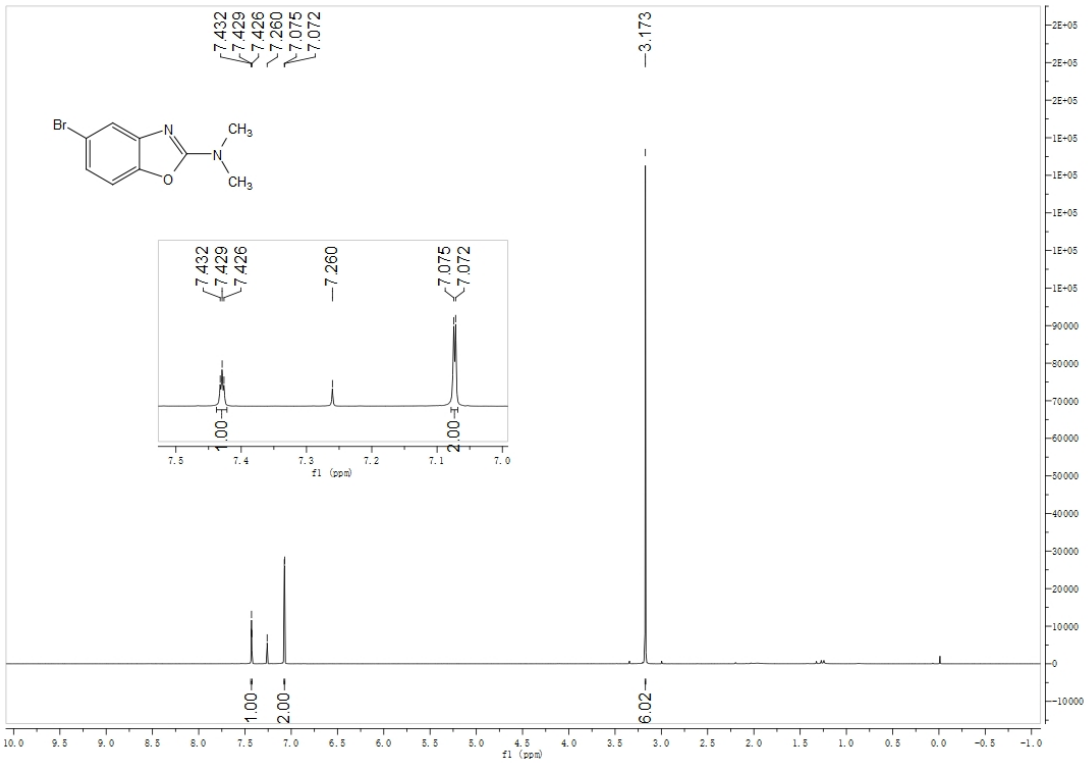

Figure S29. ^{1}H NMR Spectrum of 3o (400 MHz, $CDCl_3$)

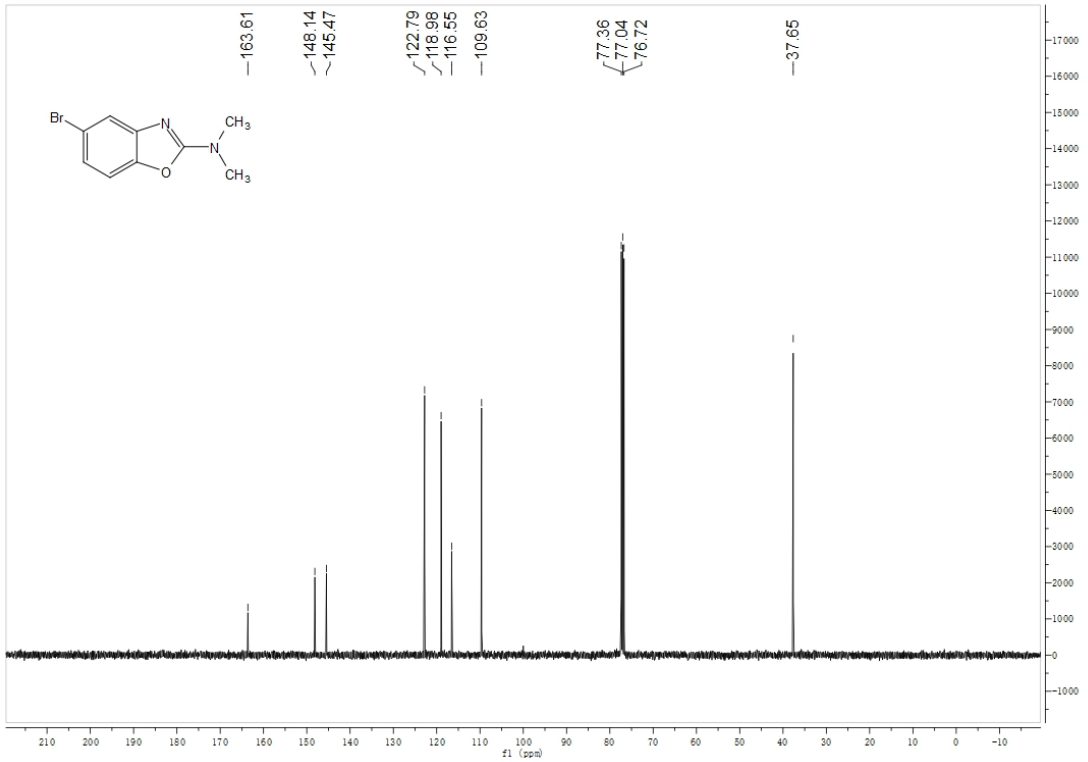

Figure S30. ^{13}C NMR Spectrum of 3o (100 MHz, $CDCl_3$)

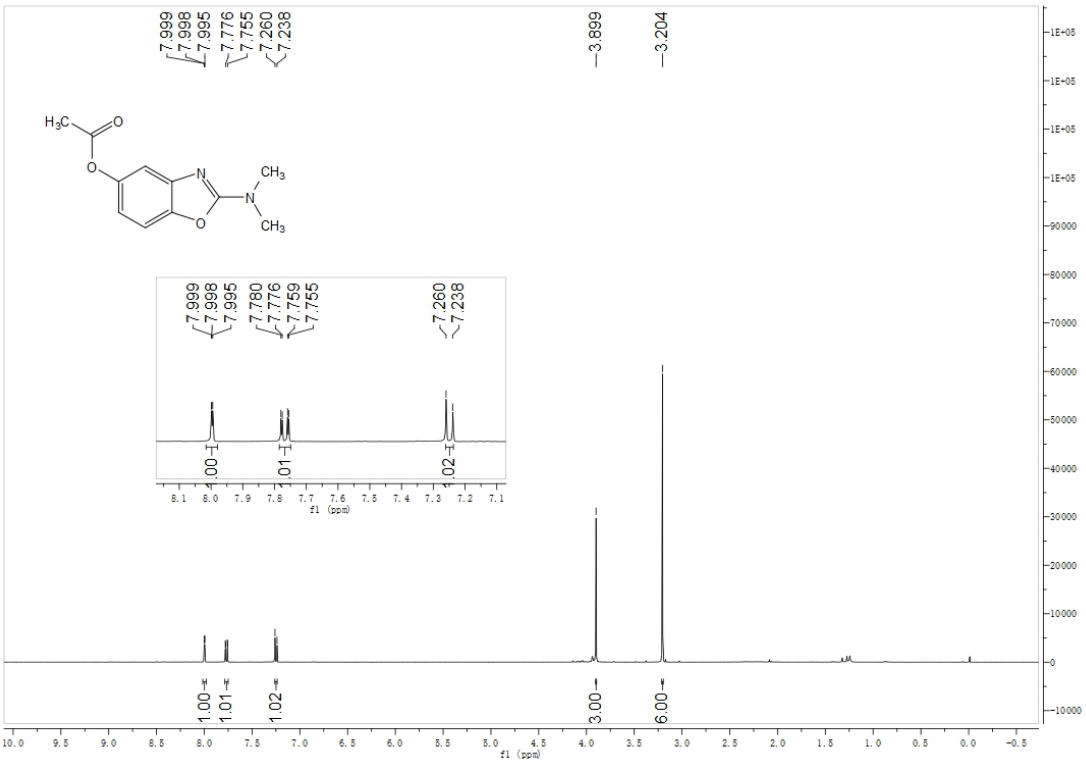

Figure S31. ^{1}H NMR Spectrum of 3p (400 MHz, $CDCl_3$)

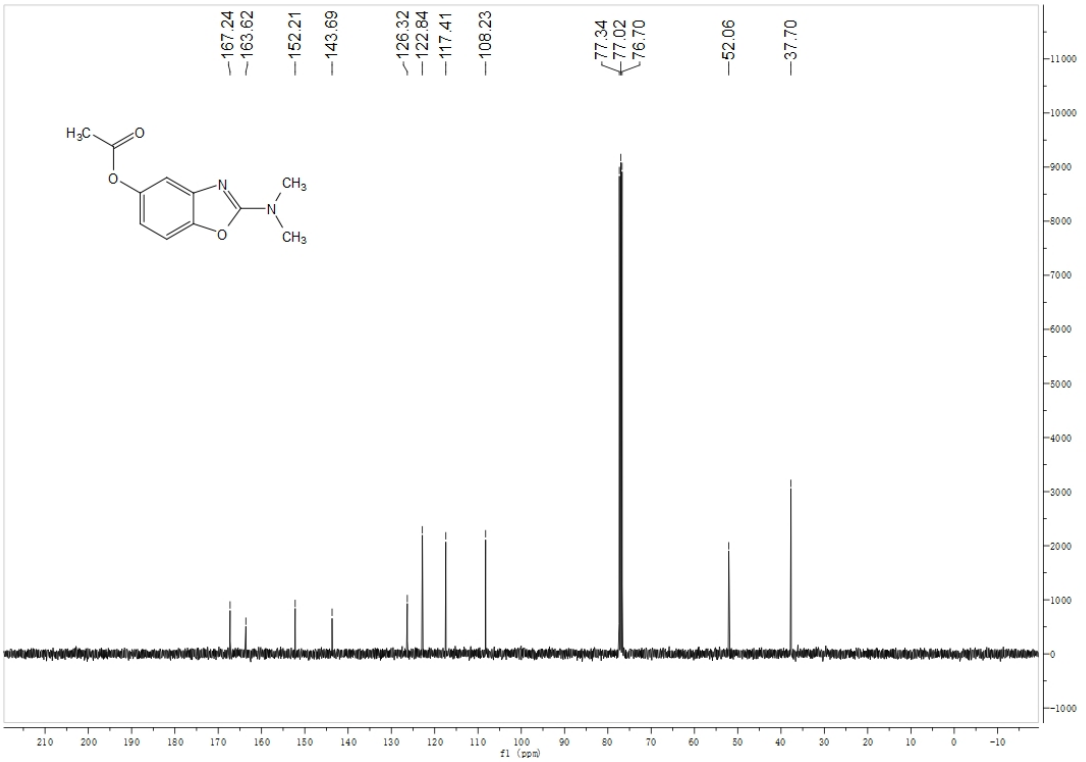

Figure S32. ^{13}C NMR Spectrum of 3p (100 MHz, $CDCl_3$)

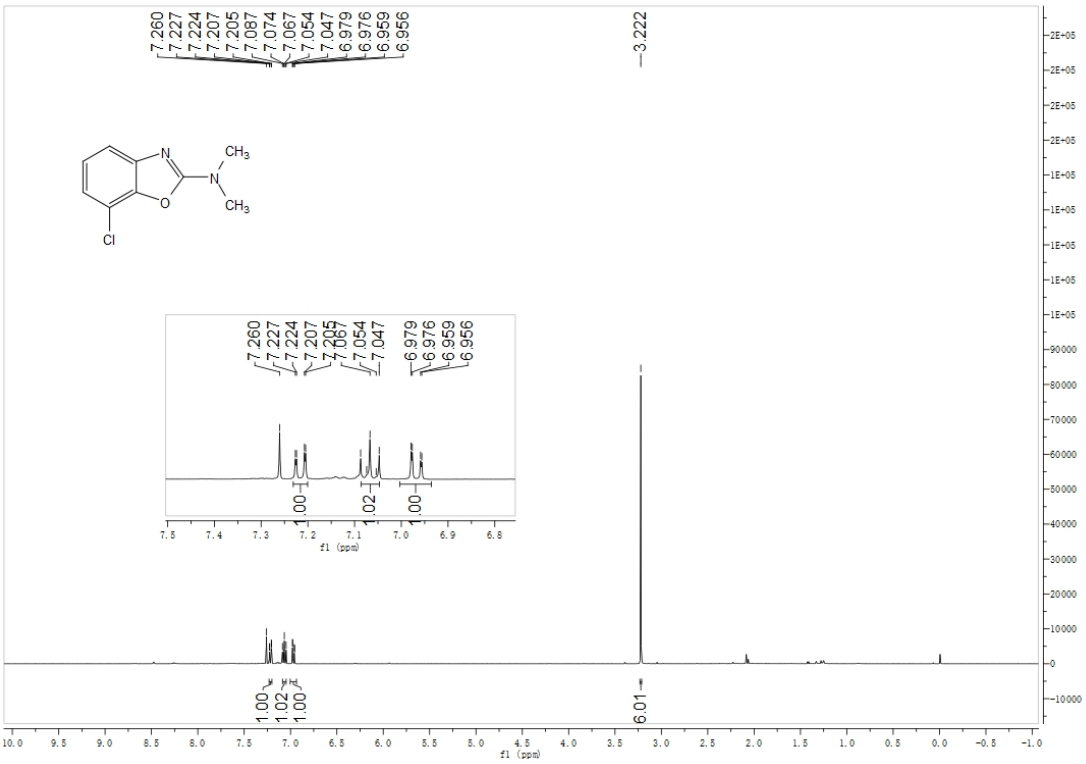

Figure S33. ^{1}H NMR Spectrum of 3q (400 MHz, $CDCl_3$)

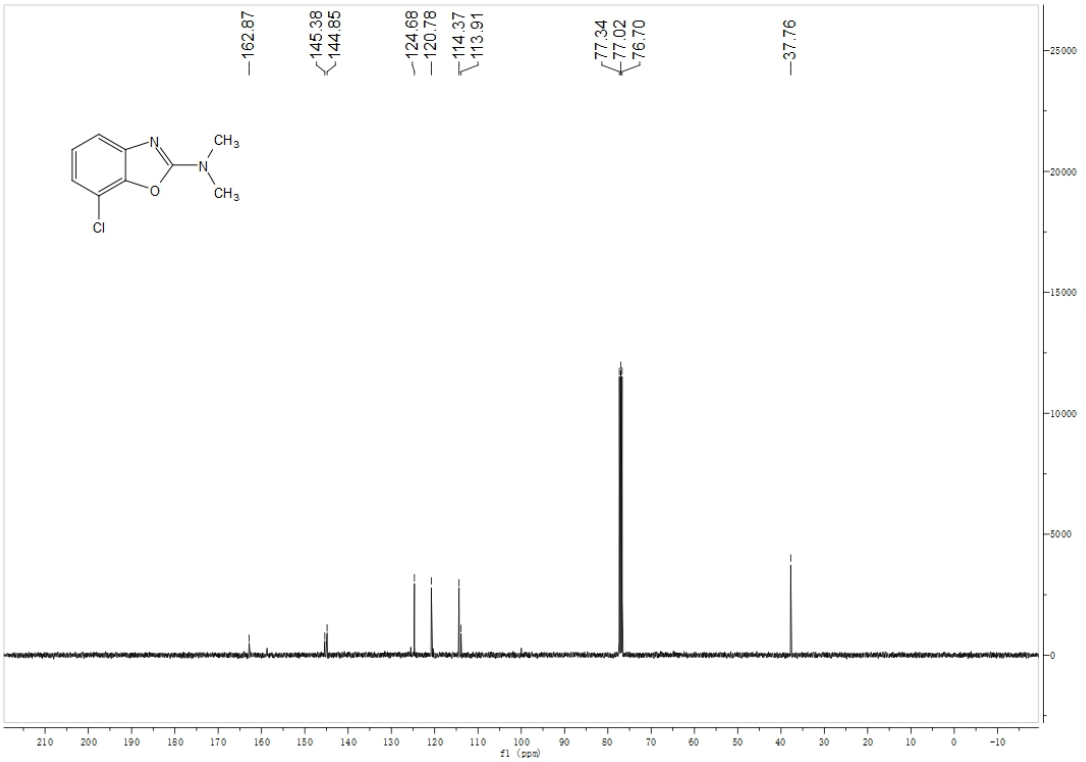

Figure S34. ^{13}C NMR Spectrum of 3q (100 MHz, $CDCl_3$)

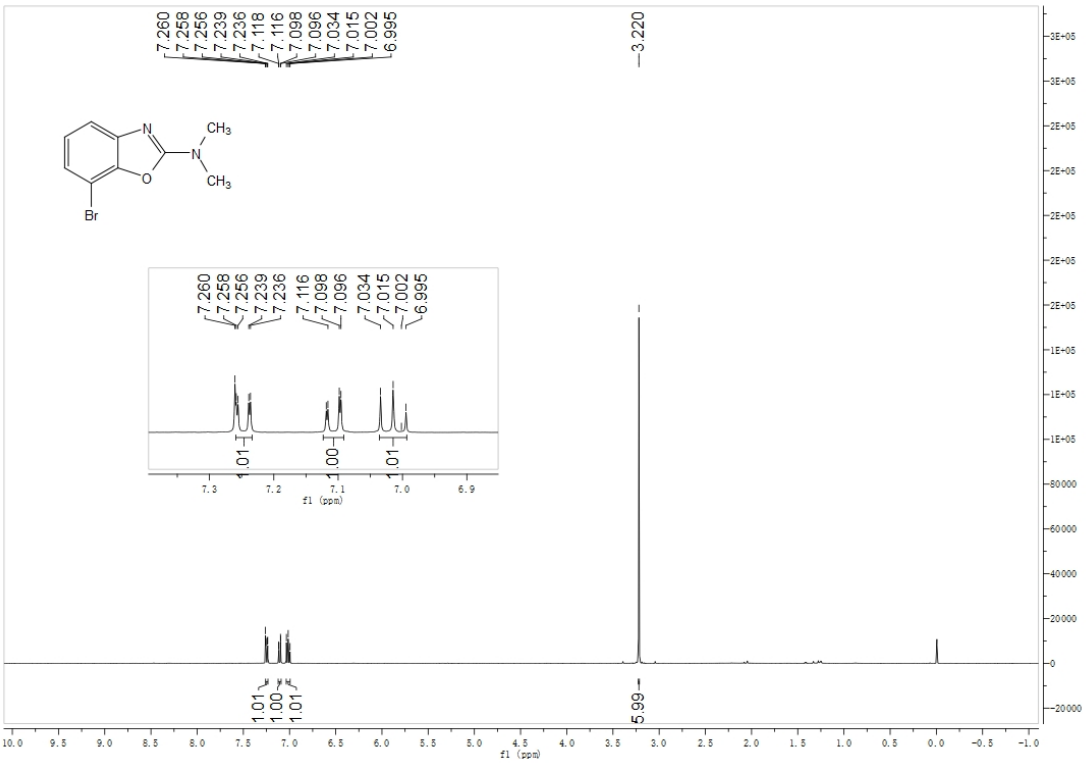

Figure S35. ^{1}H NMR Spectrum of 3r (400 MHz, $CDCl_3$)

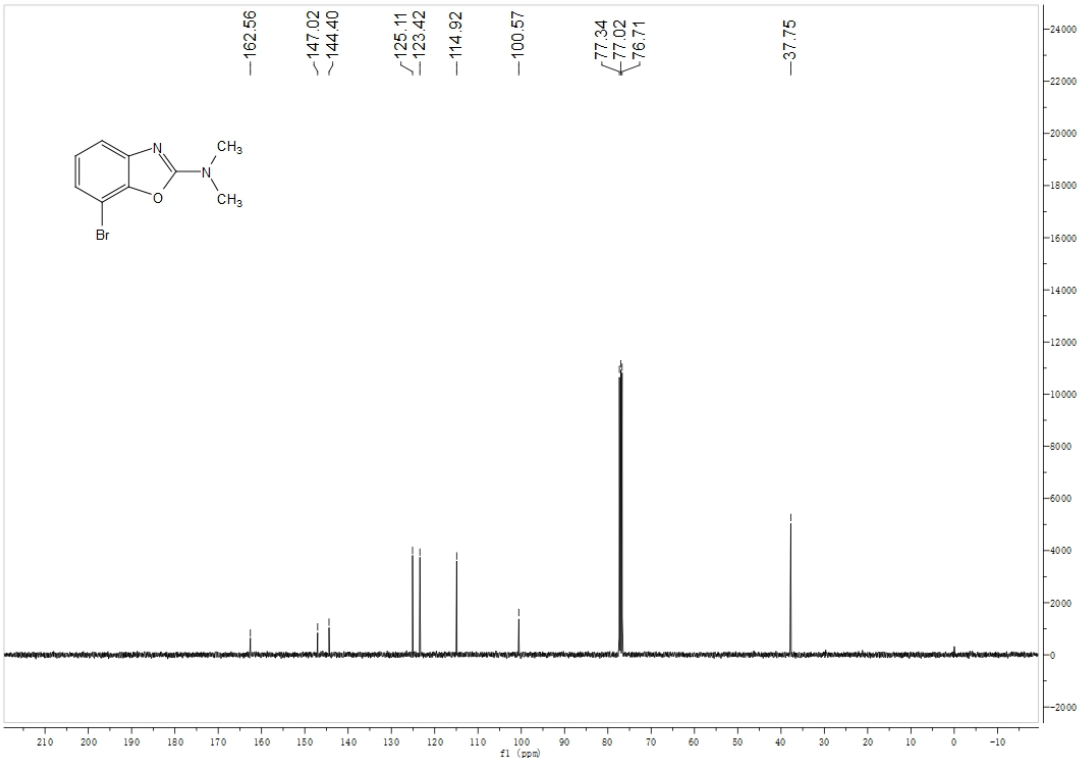

Figure S36. ^{13}C NMR Spectrum of 3r (100 MHz, $CDCl_3$)

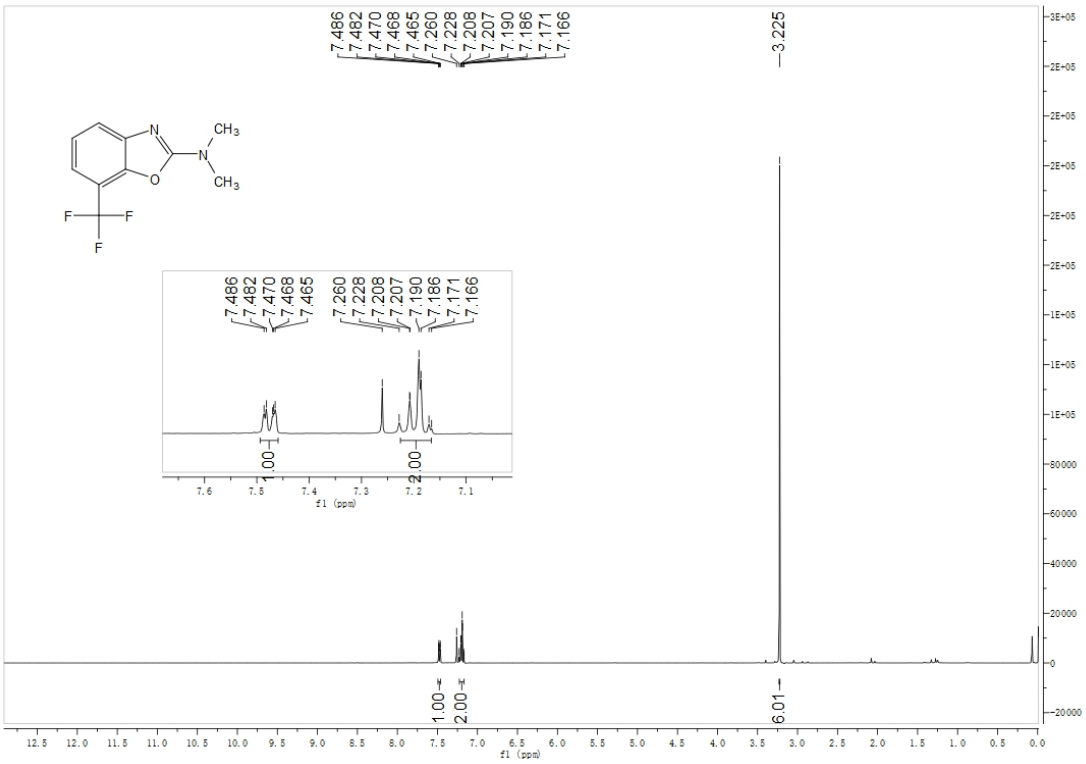

Figure S37. ^{1}H NMR Spectrum of 3s (400 MHz, $CDCl_3$)

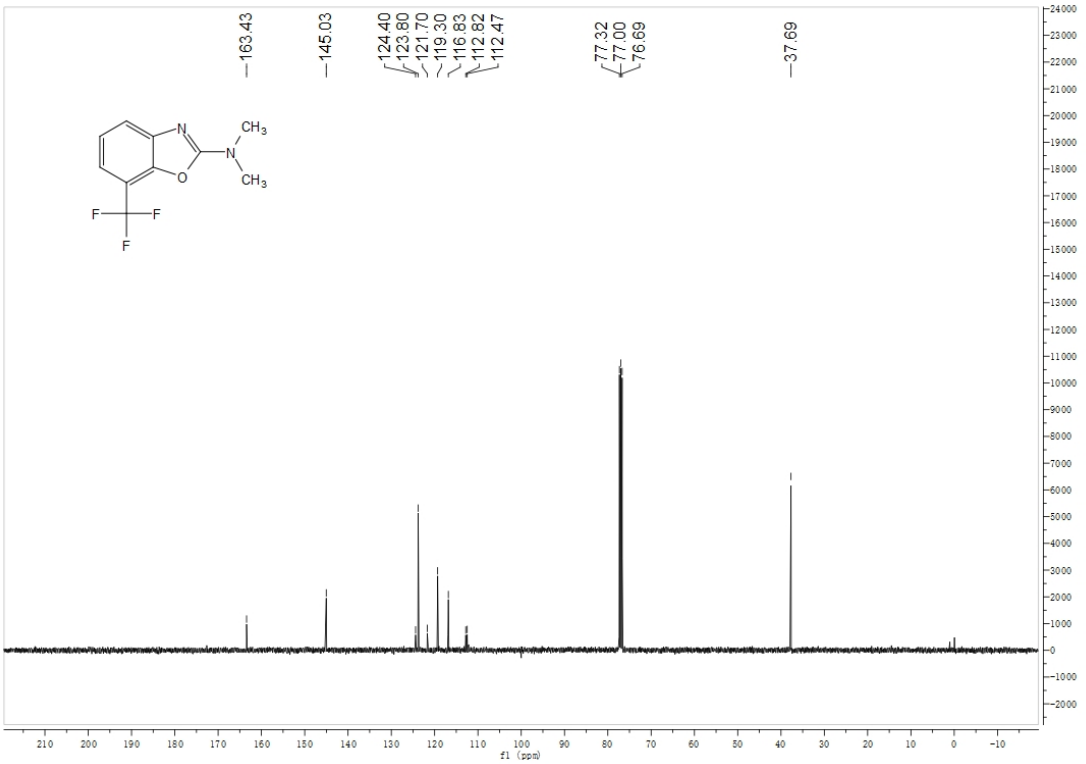

Figure S38. ^{13}C NMR Spectrum of 3s (100 MHz, $CDCl_3$)

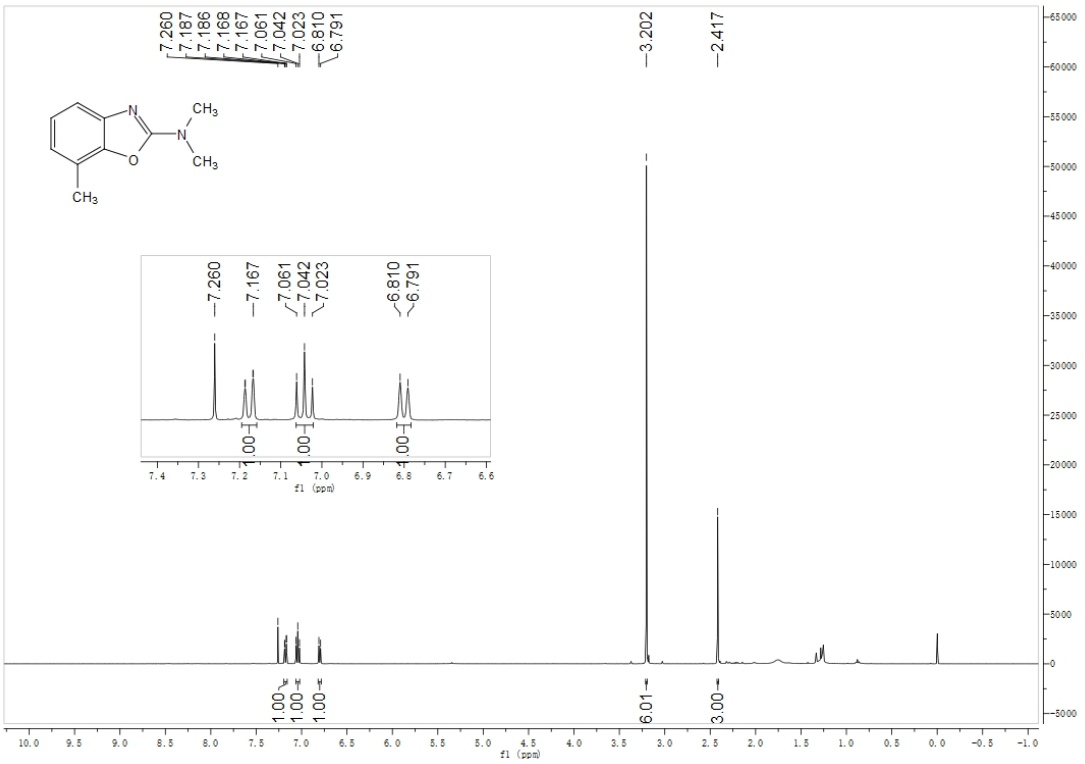

Figure S39. ^{1}H NMR Spectrum of 3t (400 MHz, $CDCl_3$)

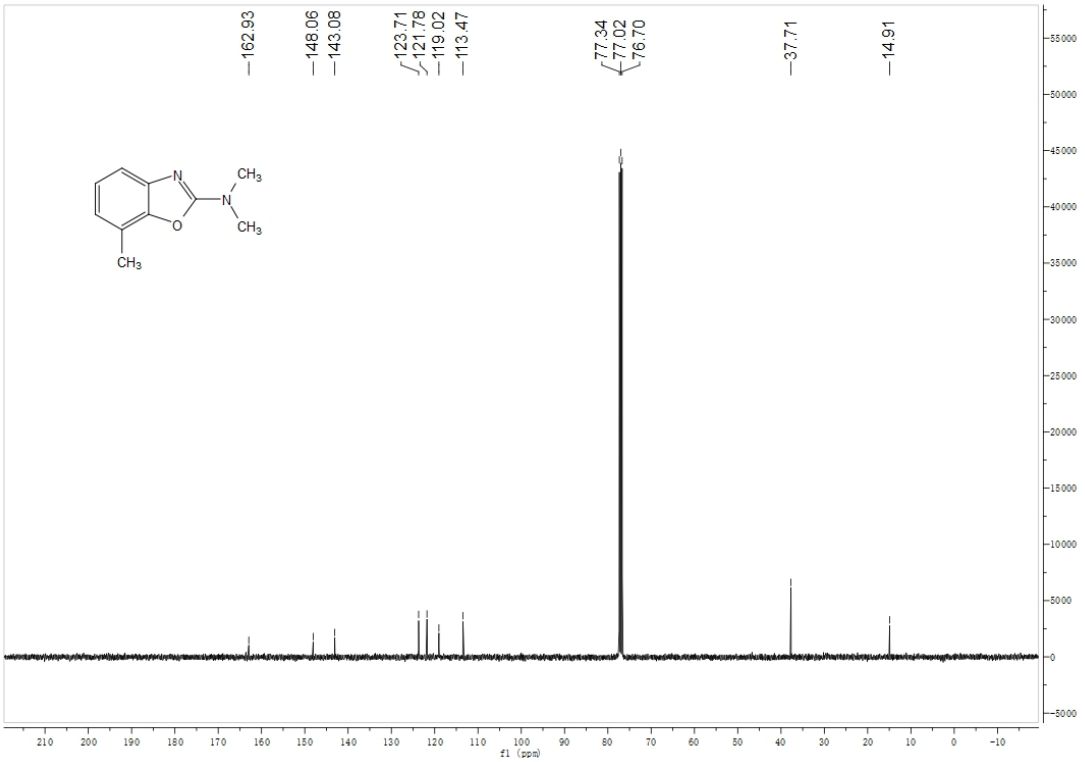

Figure S40. ^{13}C NMR Spectrum of 3t (100 MHz, $CDCl_3$)

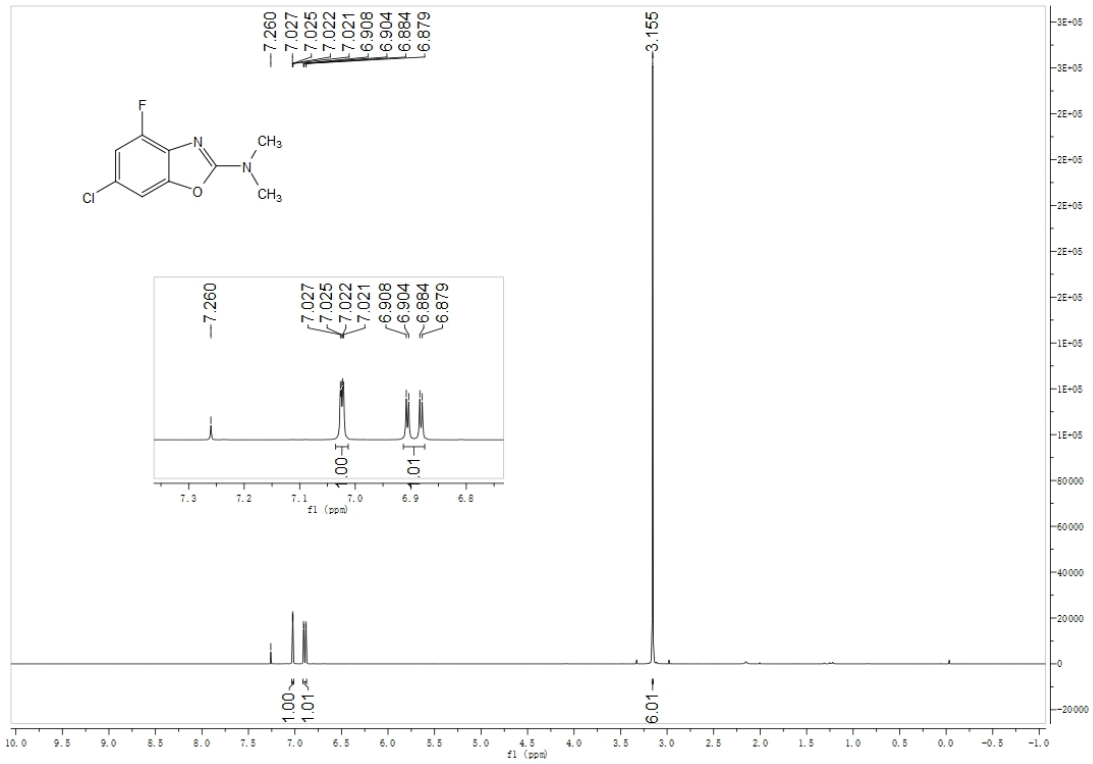

Figure S41. ^{1}H NMR Spectrum of 3u (400 MHz, $CDCl_3$)

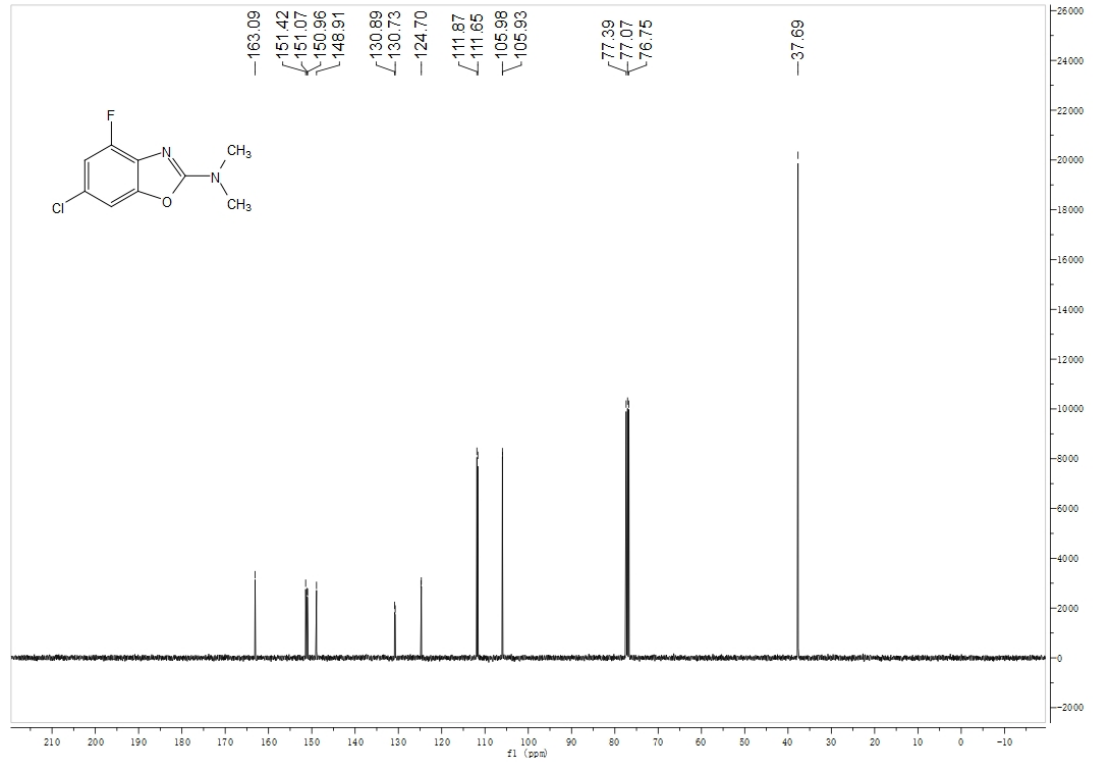

Figure S42. ^{13}C NMR Spectrum of 3u (100 MHz, $CDCl_3$)

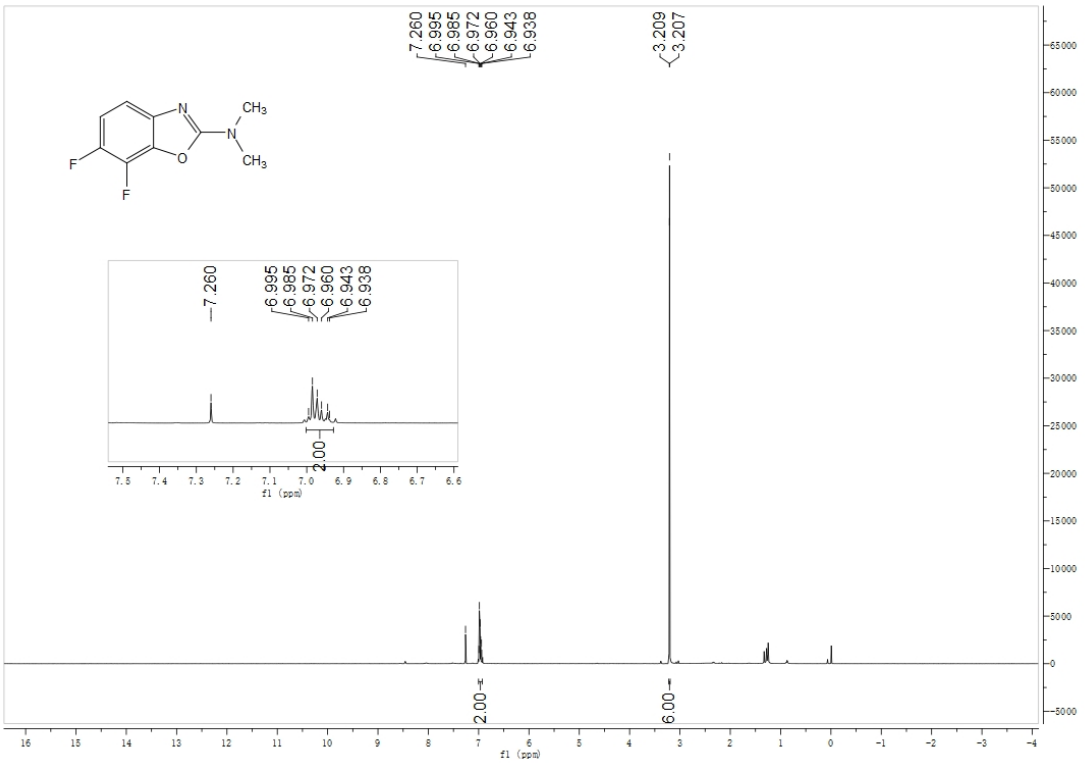

Figure S43. ^{1}H NMR Spectrum of 3v (400 MHz, $CDCl_3$)

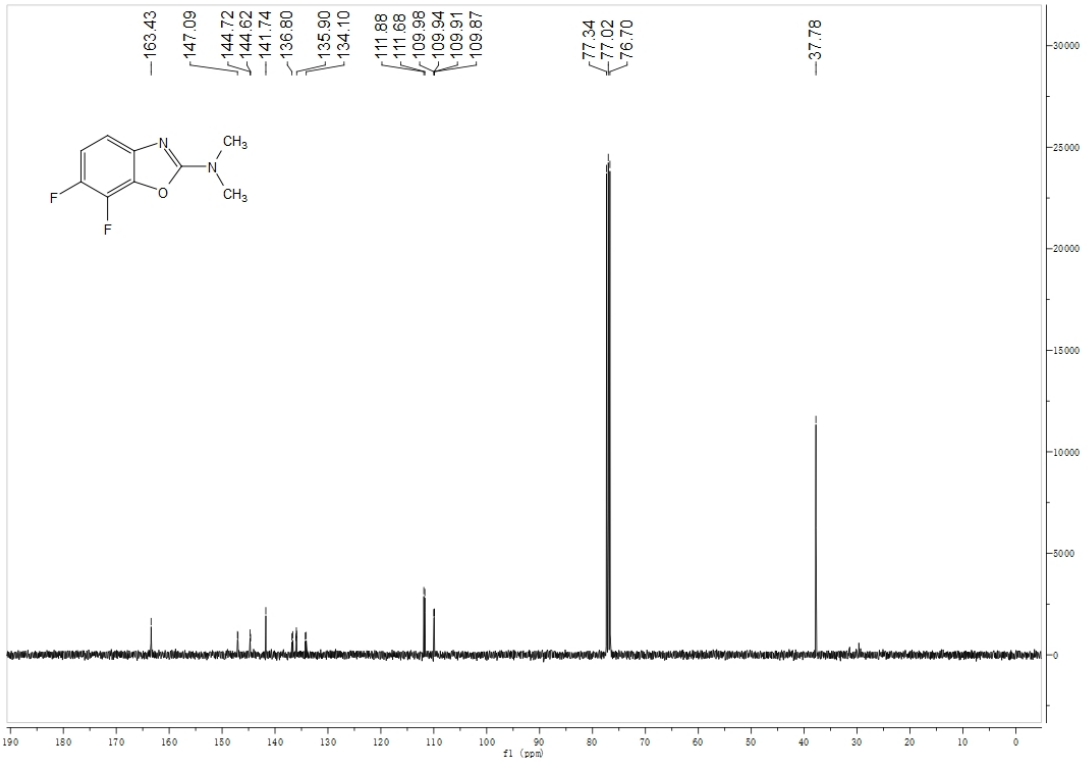

Figure S44. ^{13}C NMR Spectrum of 3v (100 MHz, $CDCl_3$)

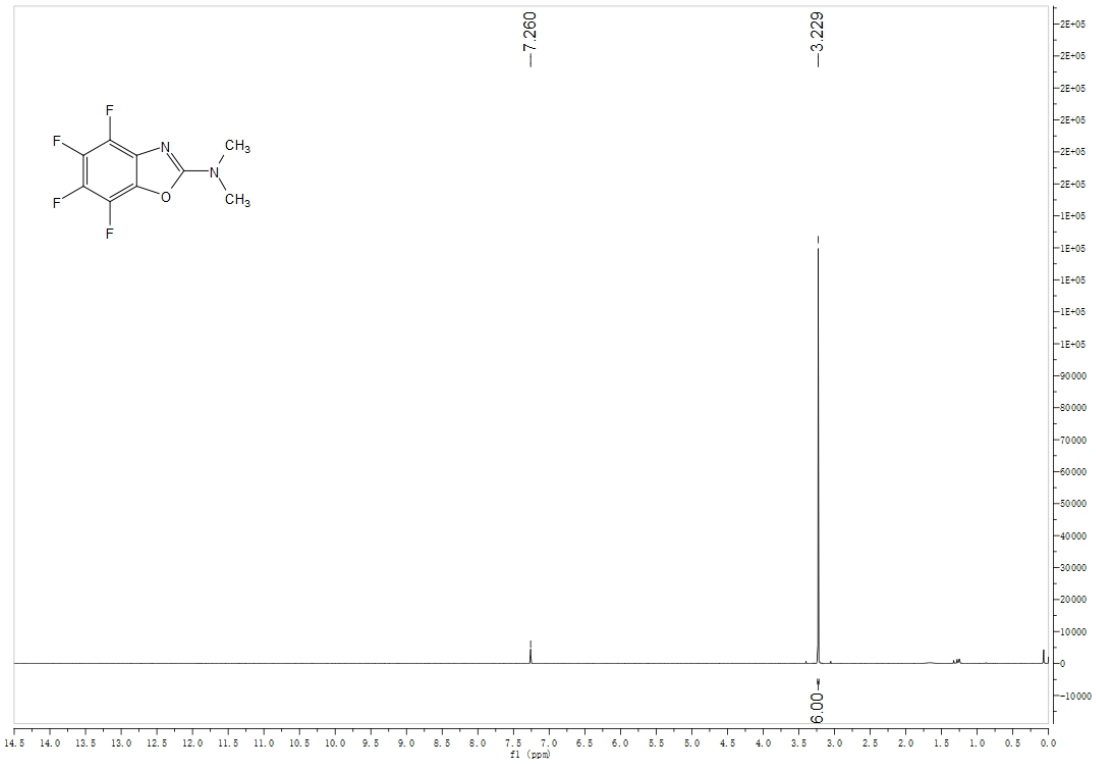

Figure S45. ^{1}H NMR Spectrum of 3w (400 MHz, $CDCl_3$)

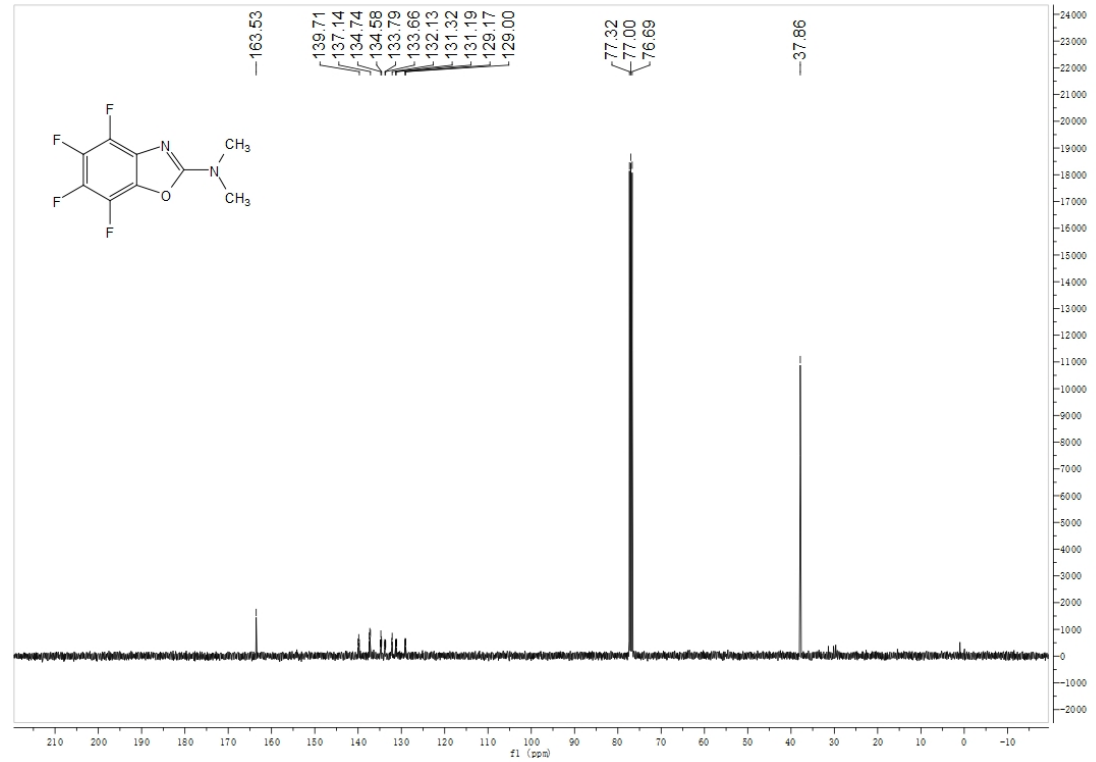

Figure S46. ^{13}C NMR Spectrum of 3w (100 MHz, $CDCl_3$)

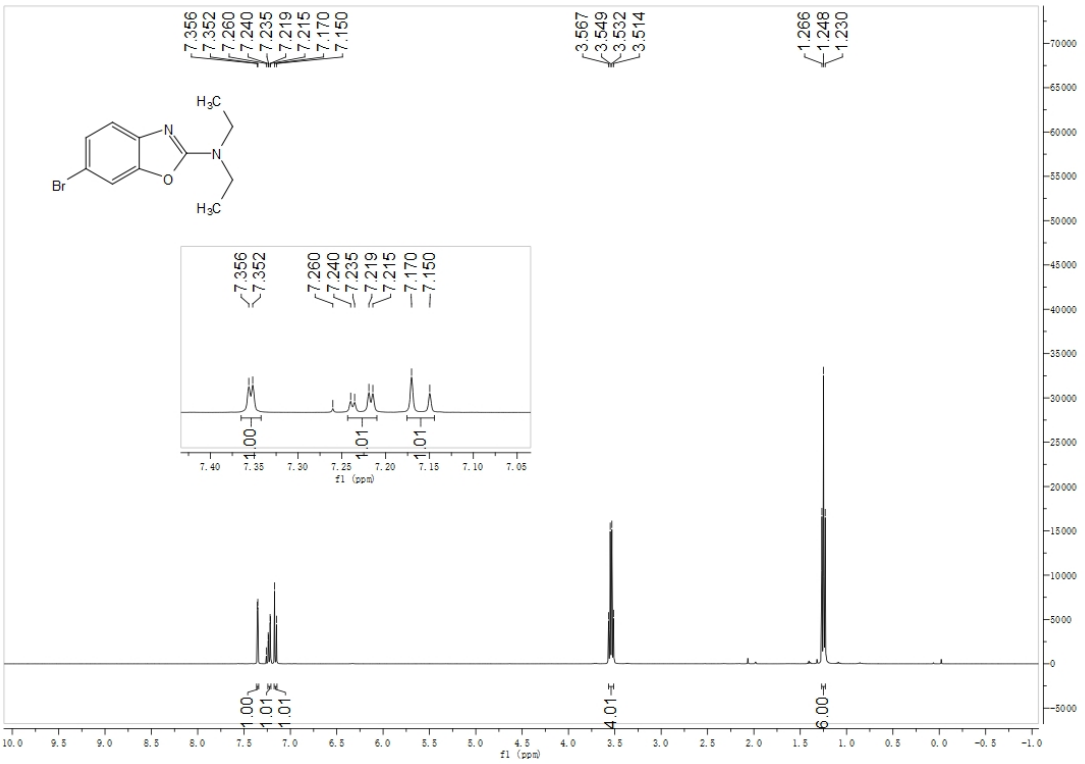

Figure S47. ^{1}H NMR Spectrum of 4a (400 MHz, $CDCl_3$)

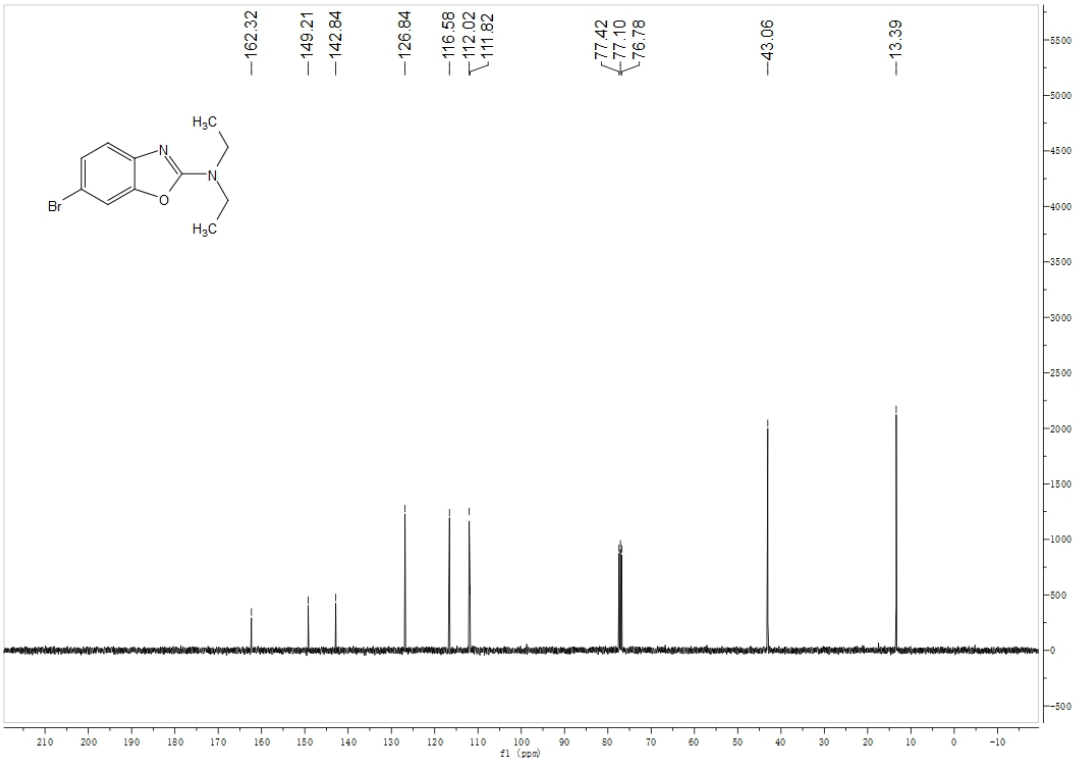

Figure S48. ^{13}C NMR Spectrum of 4a (100 MHz, $CDCl_3$)

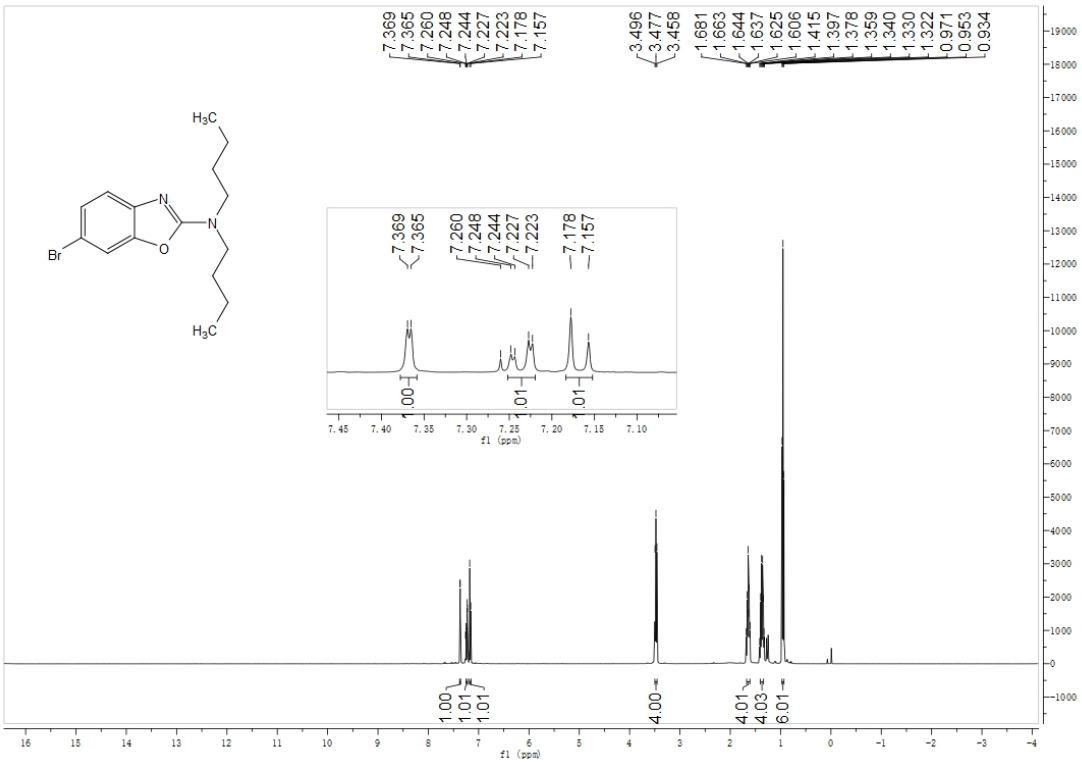

Figure S49. ^{1}H NMR Spectrum of 4b (400 MHz, $CDCl_3$)

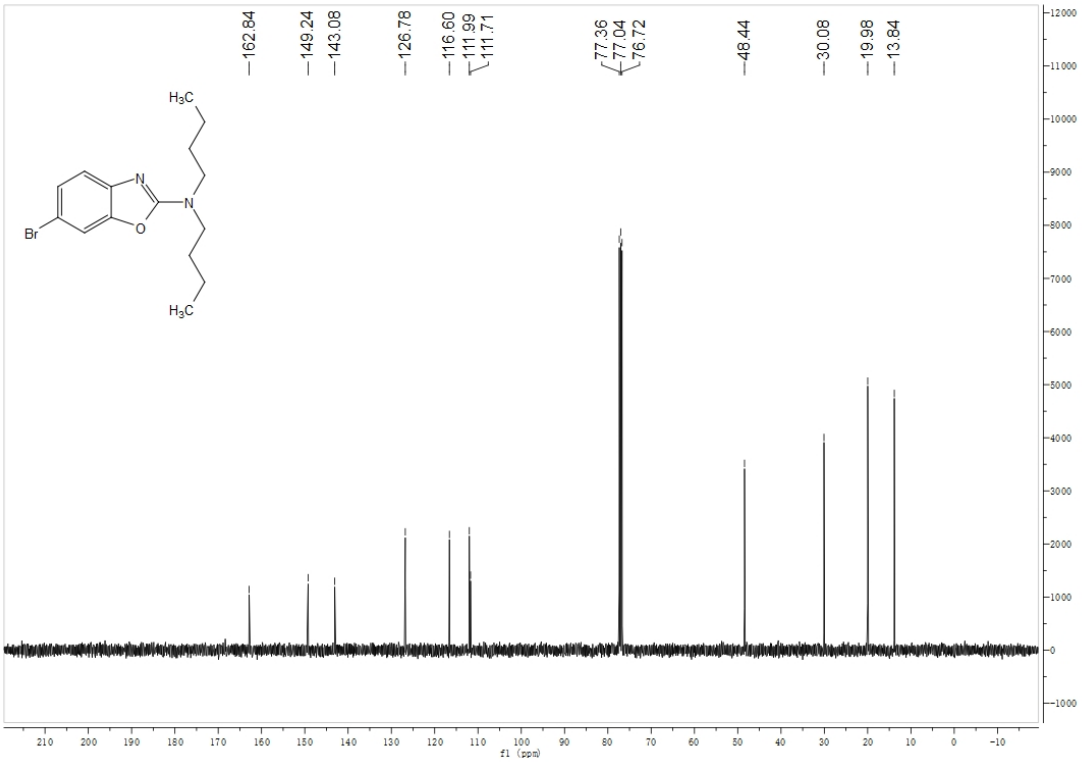

Figure S50. ^{13}C NMR Spectrum of 4b (100 MHz, $CDCl_3$)

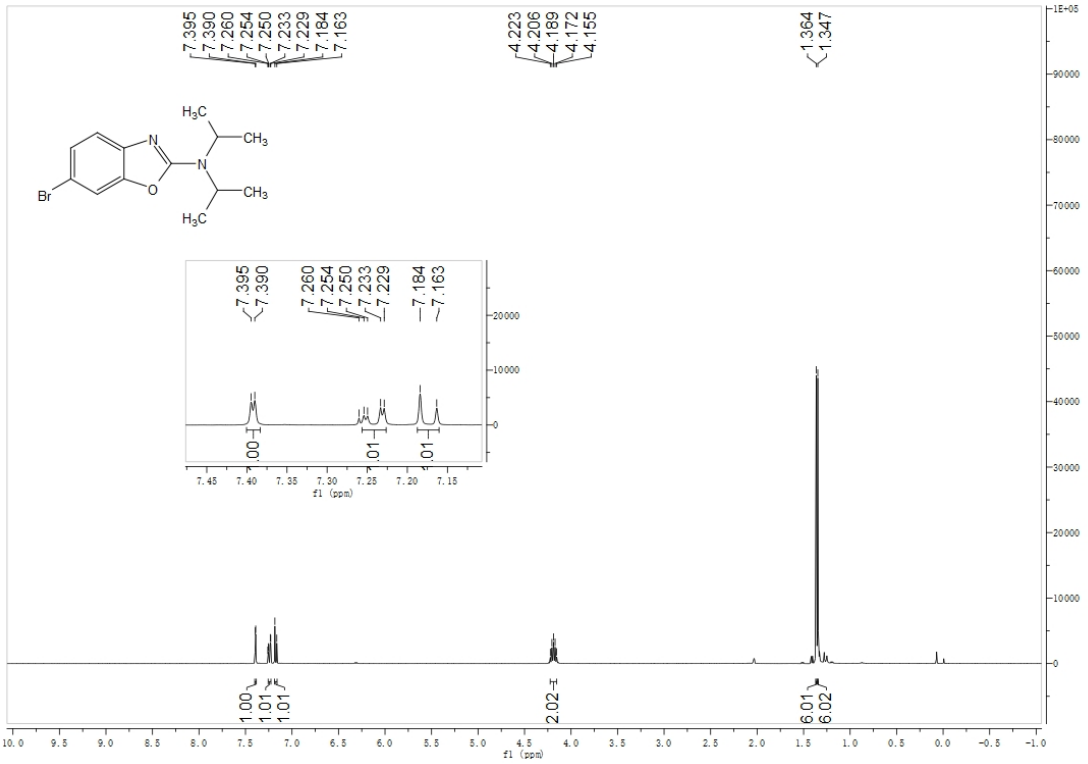

Figure S51. ^{1}H NMR Spectrum of 4c (400 MHz, $CDCl_3$)

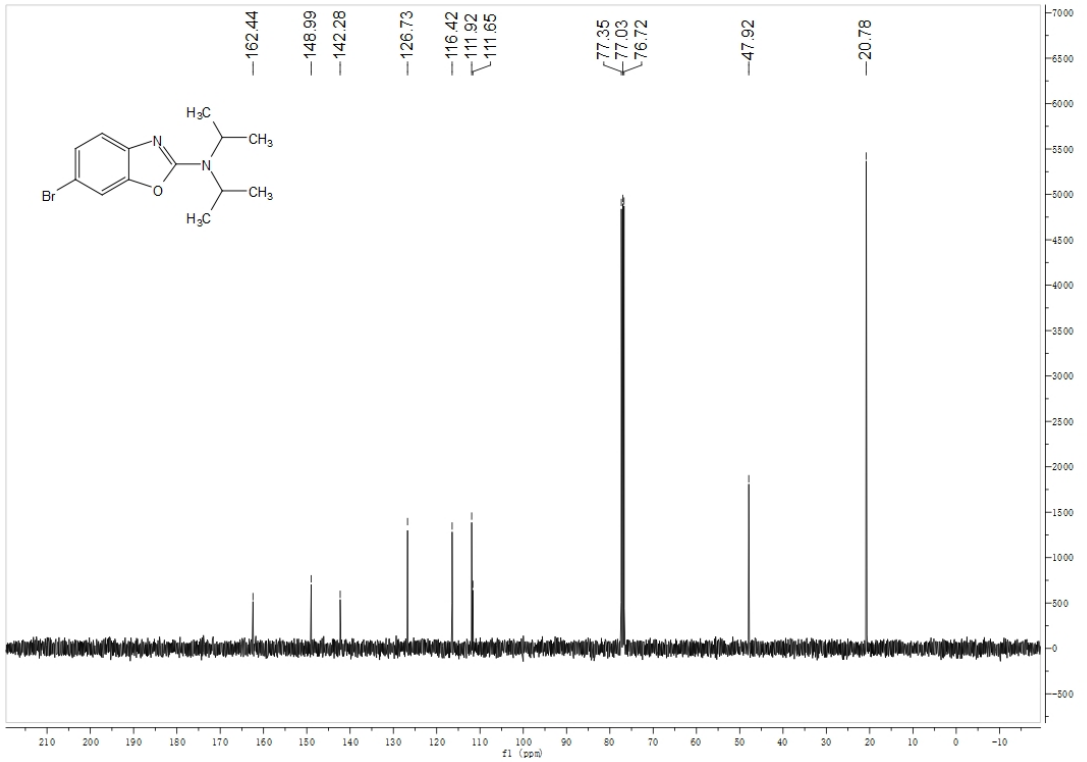

Figure S52. ^{13}C NMR Spectrum of 4c (100 MHz, $CDCl_3$)

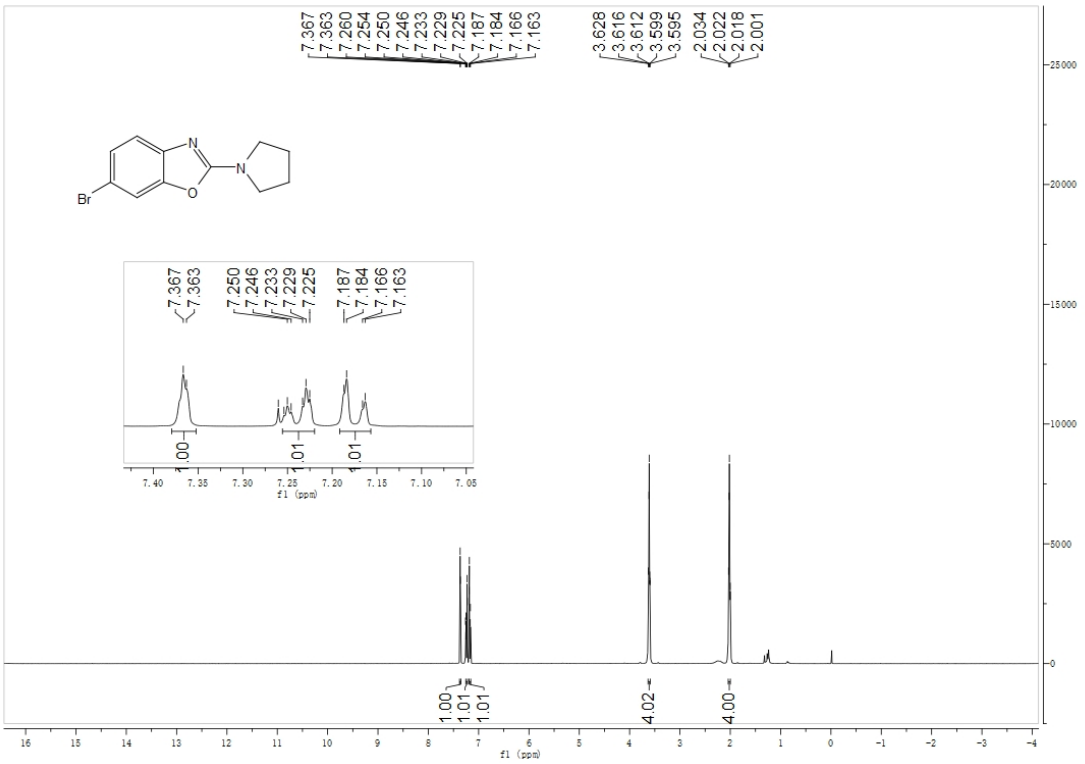

Figure S53. ^{1}H NMR Spectrum of 4d (400 MHz, $CDCl_3$)

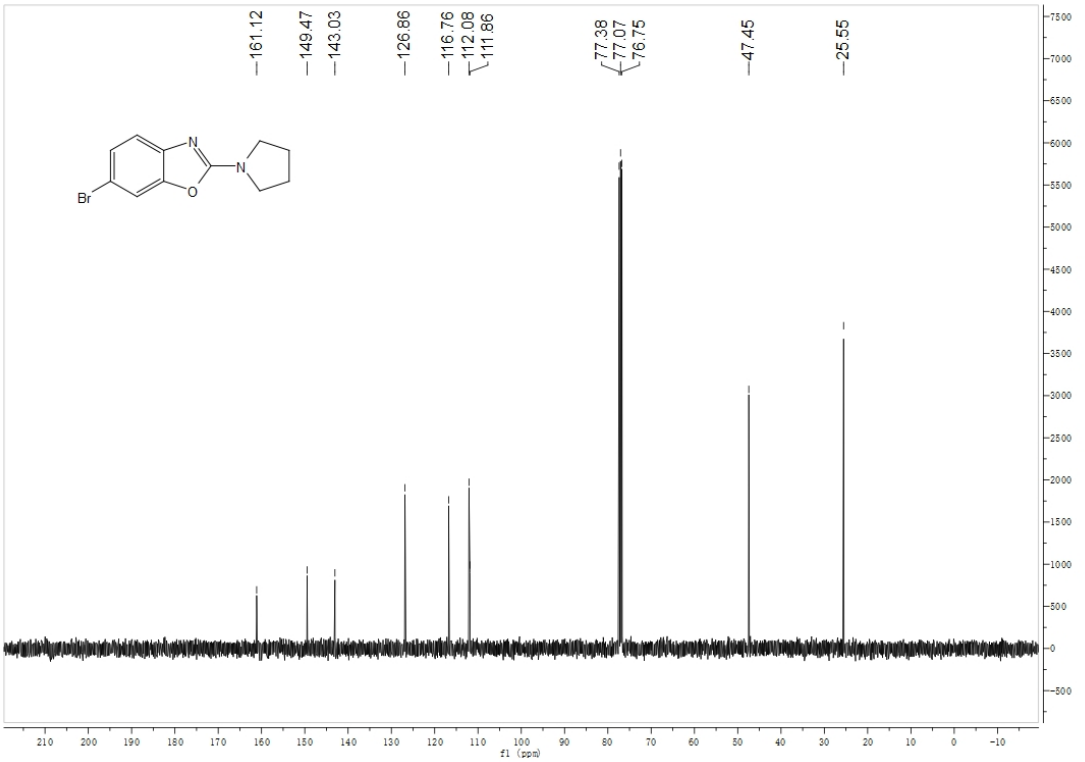

Figure S54. ^{13}C NMR Spectrum of 4d (100 MHz, $CDCl_3$)

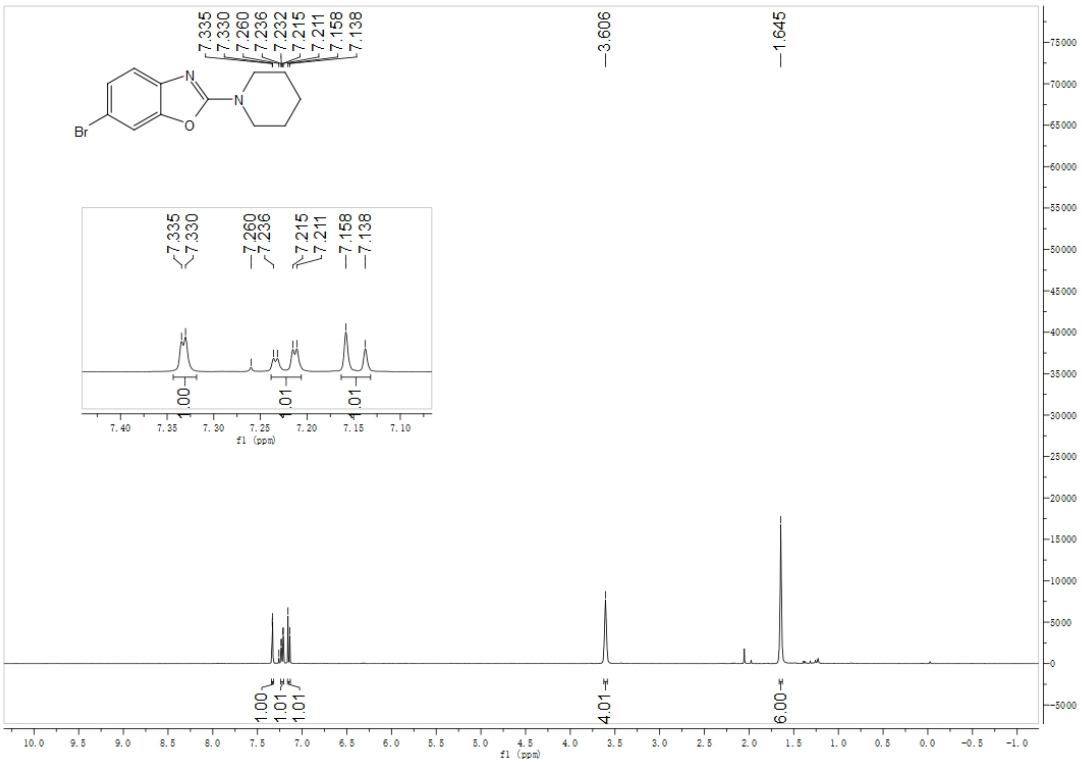

Figure S55. ^{1}H NMR Spectrum of 4e (400 MHz, $CDCl_3$)

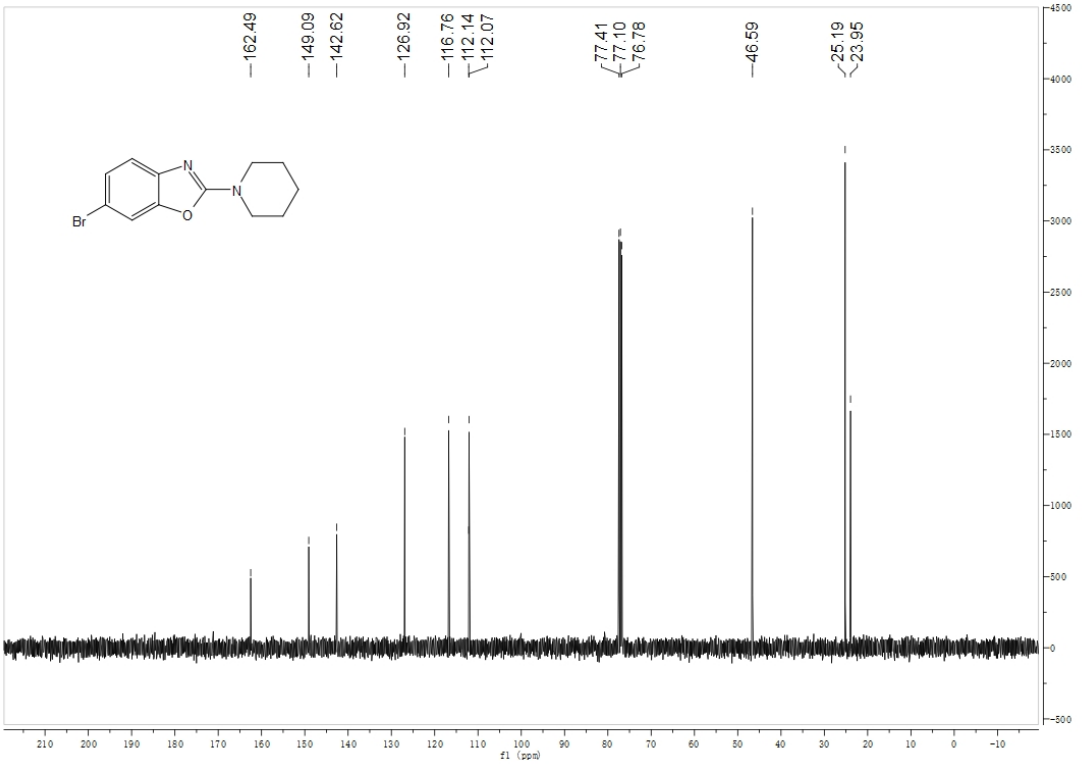

Figure S56. ^{13}C NMR Spectrum of 4e (100 MHz, $CDCl_3$)

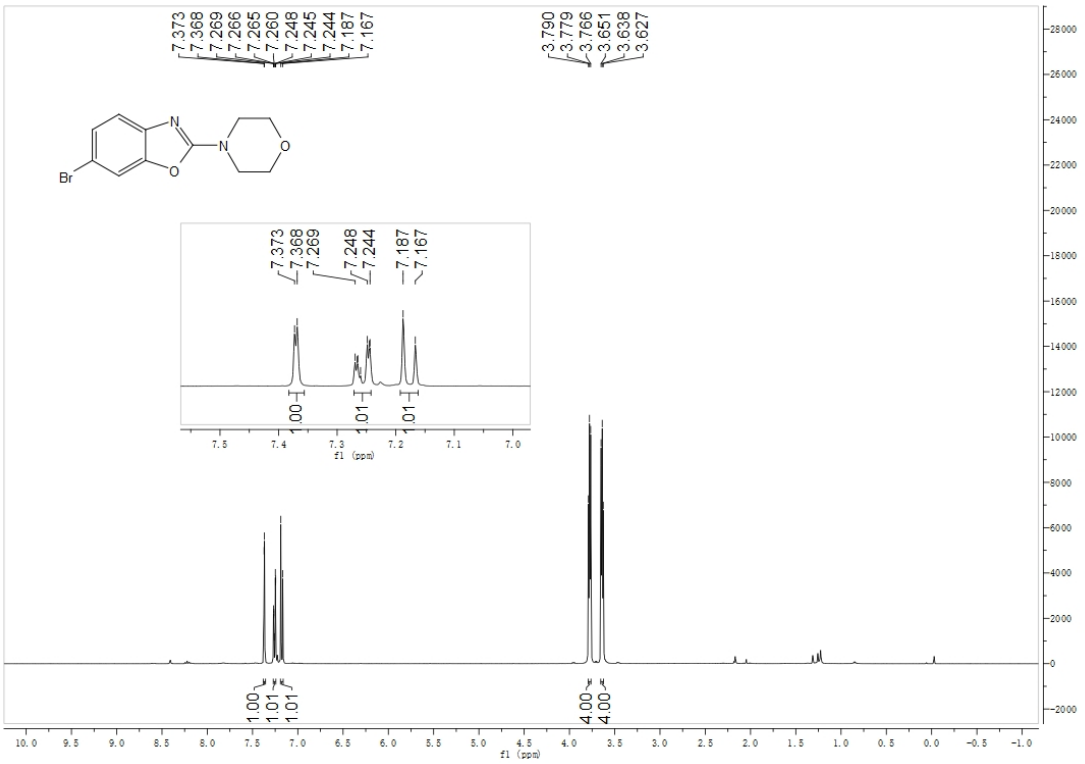

Figure S57. ^{1}H NMR Spectrum of 4f (400 MHz, $CDCl_3$)

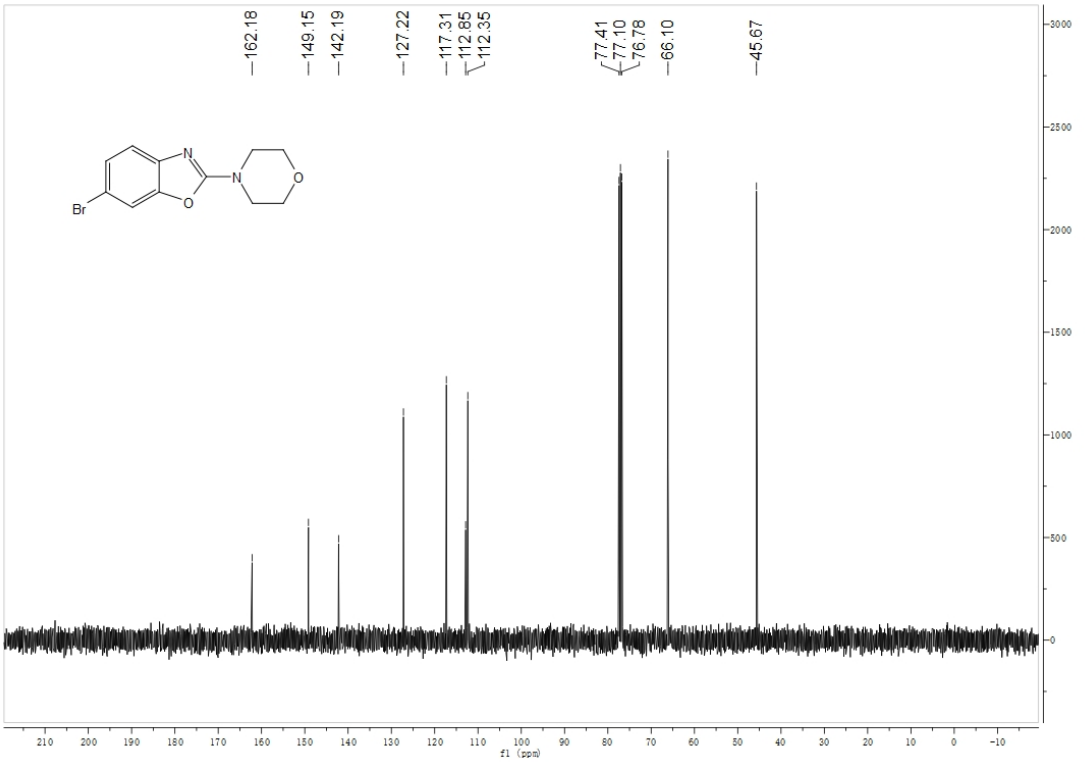

Figure S58. ^{13}C NMR Spectrum of 4f (100 MHz, $CDCl_3$)

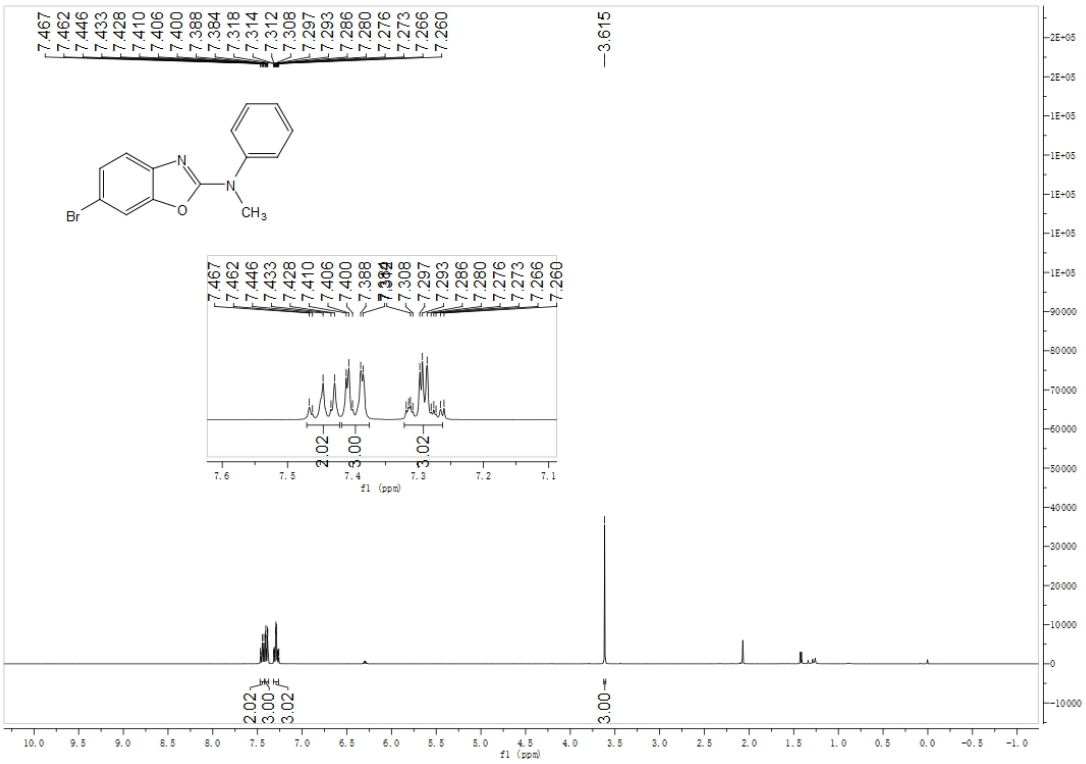

Figure S59. ^{1}H NMR Spectrum of 4g (400 MHz, $CDCl_3$)

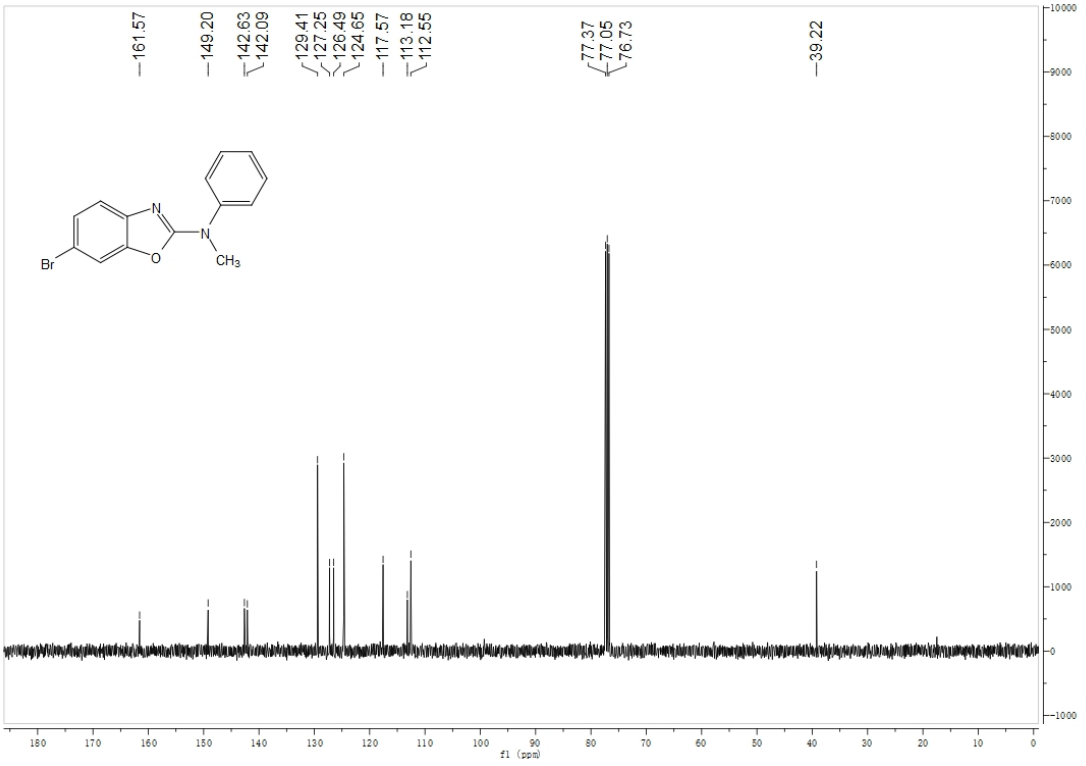

Figure S60. ^{13}C NMR Spectrum of 4g (100 MHz, $CDCl_3$)

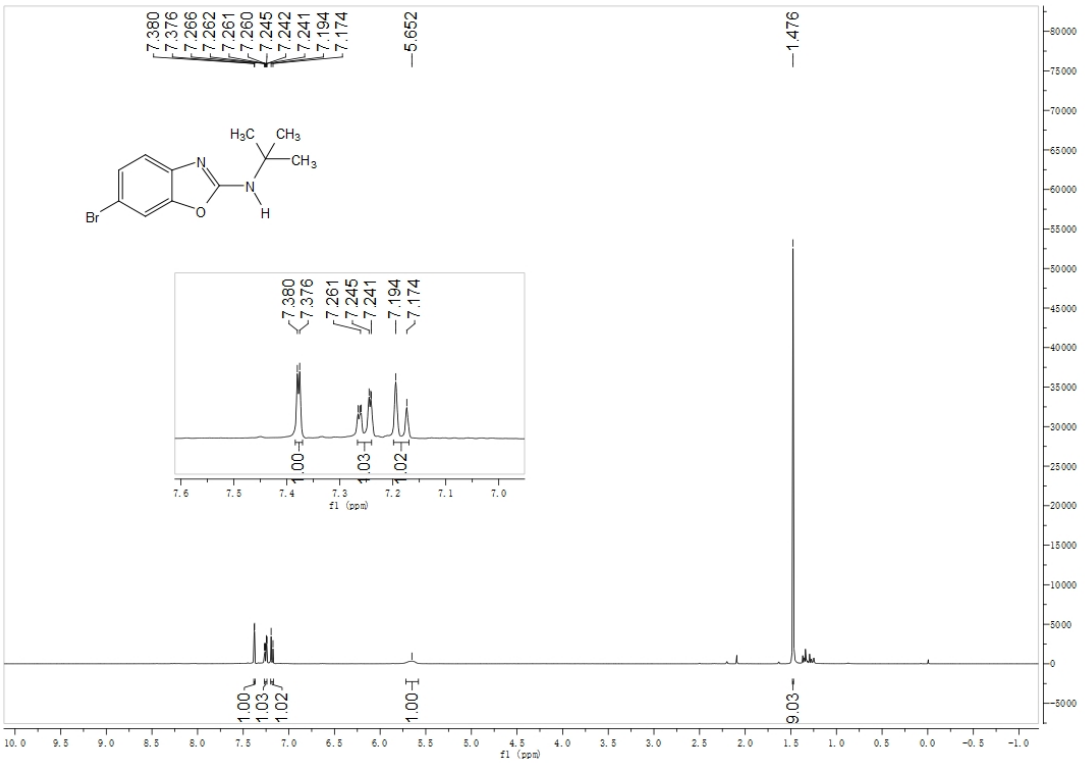

Figure S61. ^{1}H NMR Spectrum of 4h (400 MHz, $CDCl_3$)

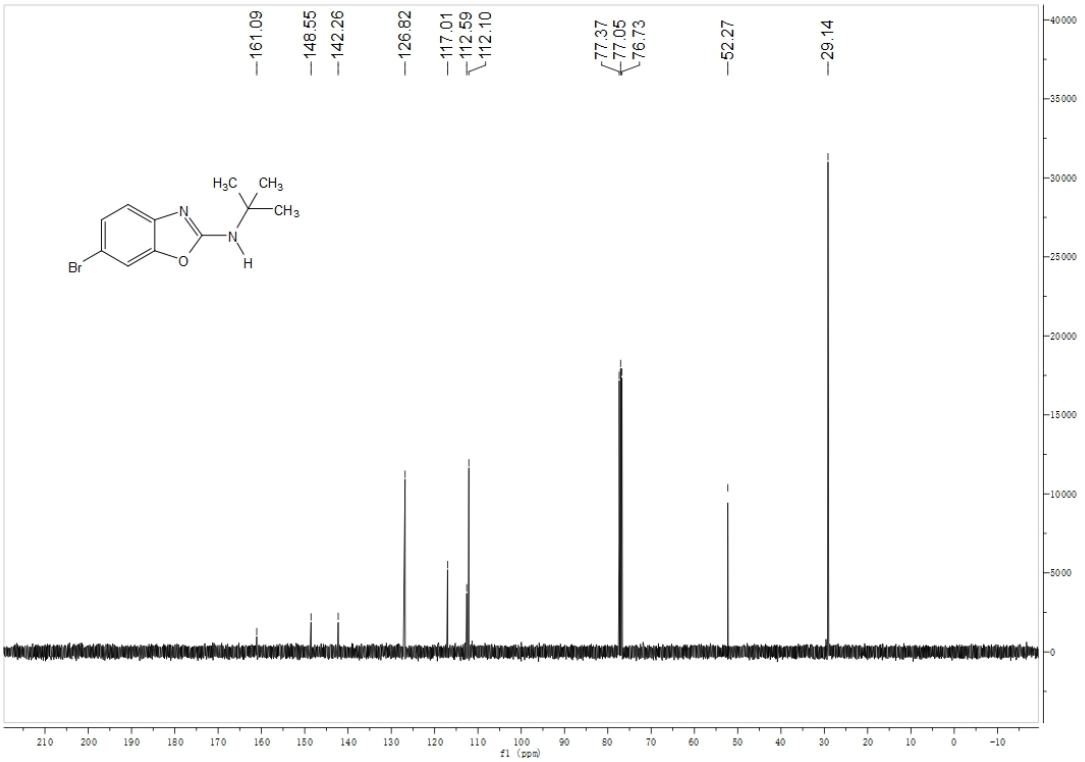

Figure S62. ^{13}C NMR Spectrum of 4h (100 MHz, $CDCl_3$)

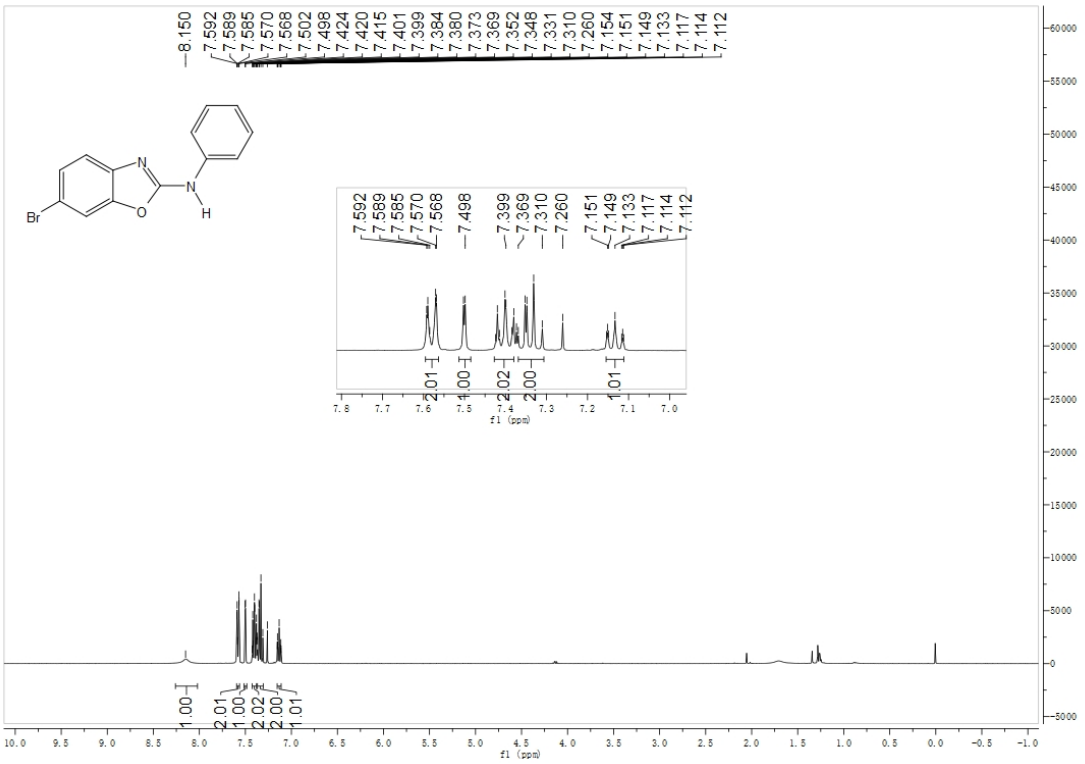

Figure S63. ^{1}H NMR Spectrum of 4i (400 MHz, $CDCl_3$)

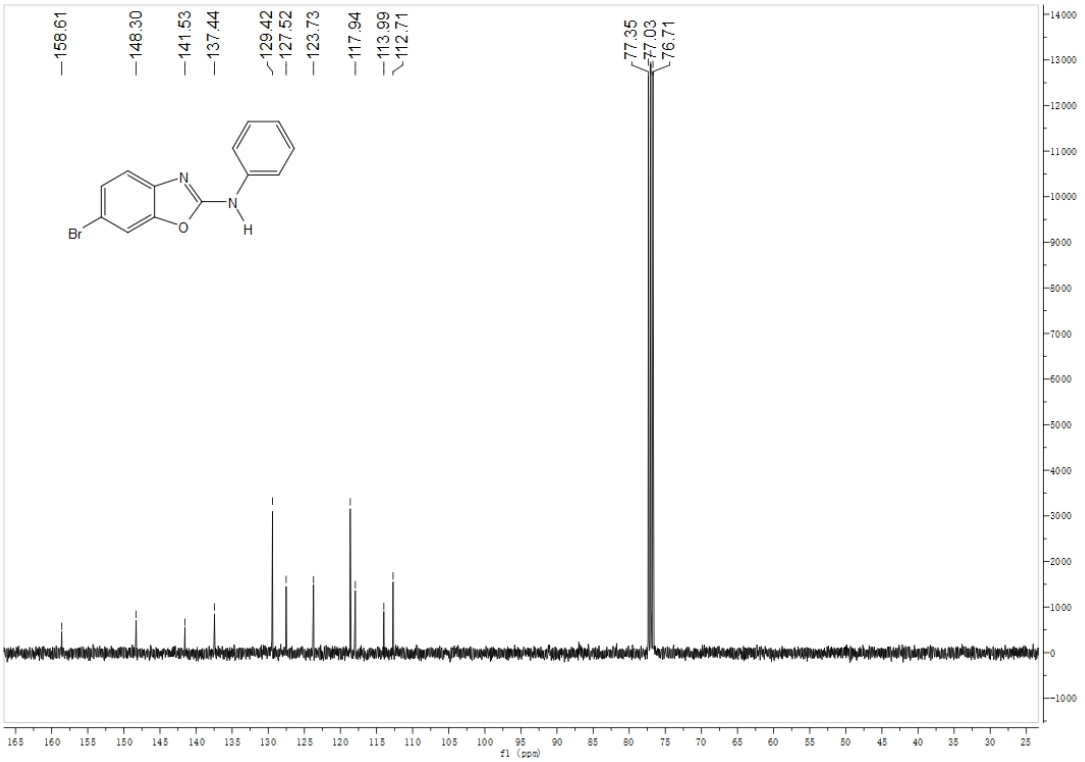

Figure S64. ^{13}C NMR Spectrum of 4i (100 MHz, $CDCl_3$)

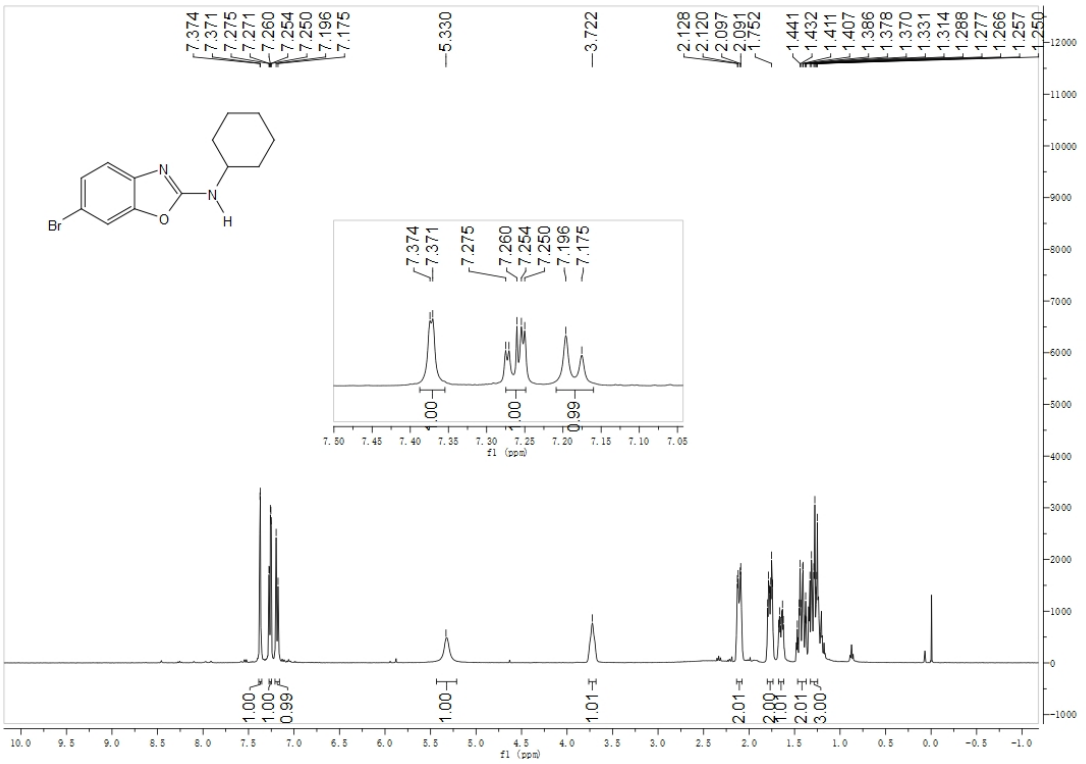

Figure S65. ^{1}H NMR Spectrum of 4j (400 MHz, $CDCl_3$)

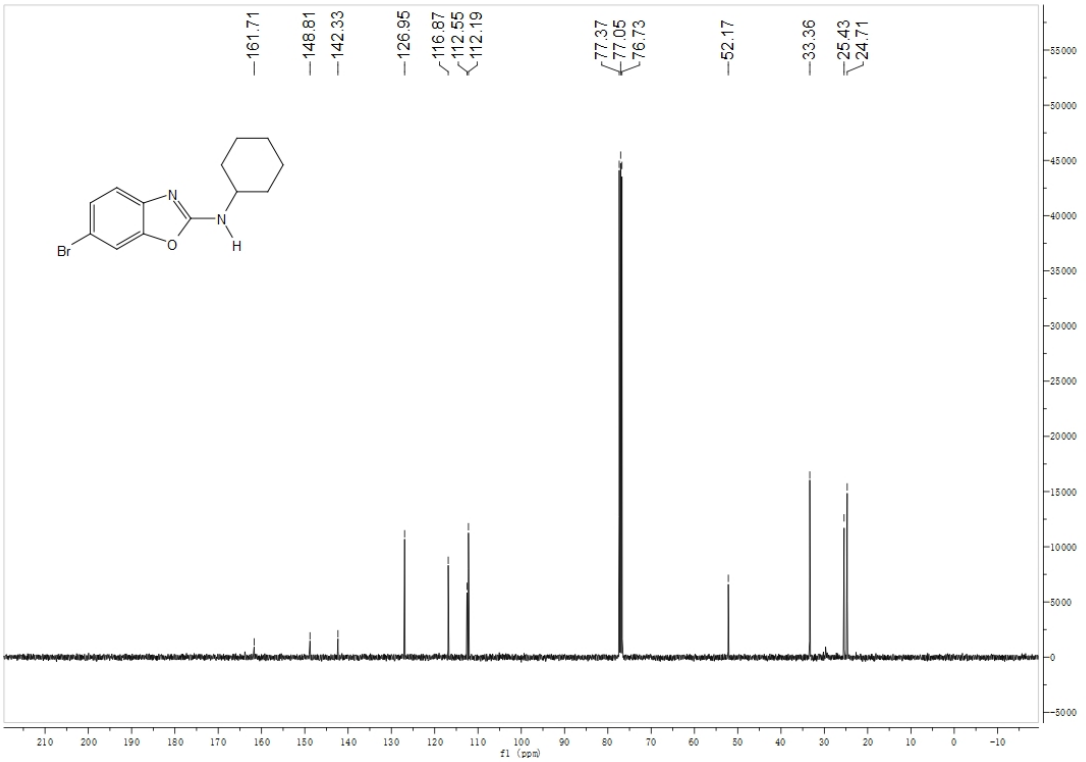

Figure S66. ^{13}C NMR Spectrum of 4j (100 MHz, $CDCl_3$)

Figure S67. ^{1}H NMR Spectrum of 4k (400 MHz, DMSO-d_6)

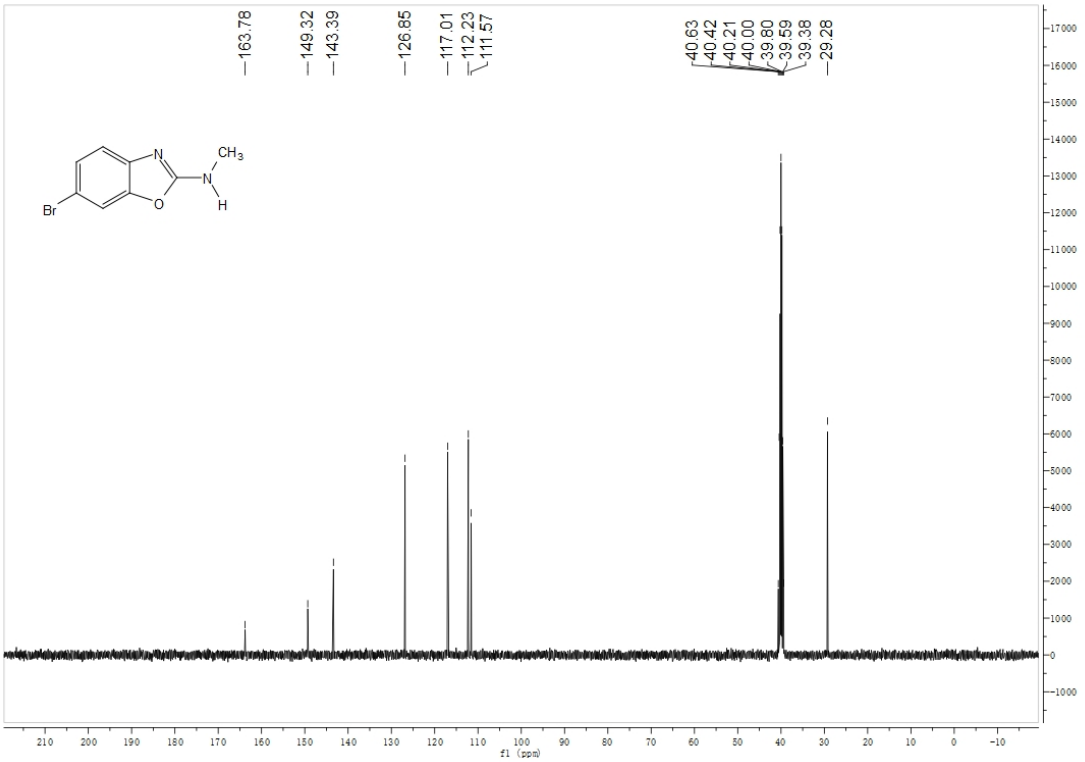

Figure S68. ^{13}C NMR Spectrum of 4k (100 MHz, DMSO-d_6)

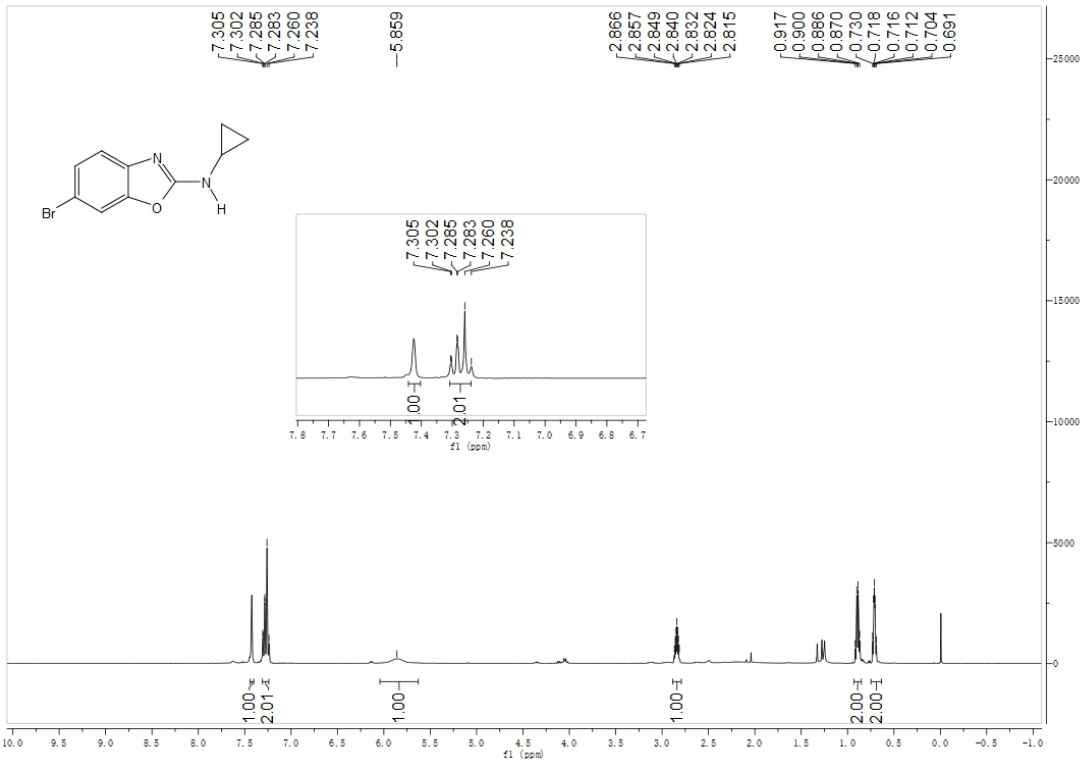

Figure S69. ^{1}H NMR Spectrum of 4l (400 MHz, $CDCl_3$)

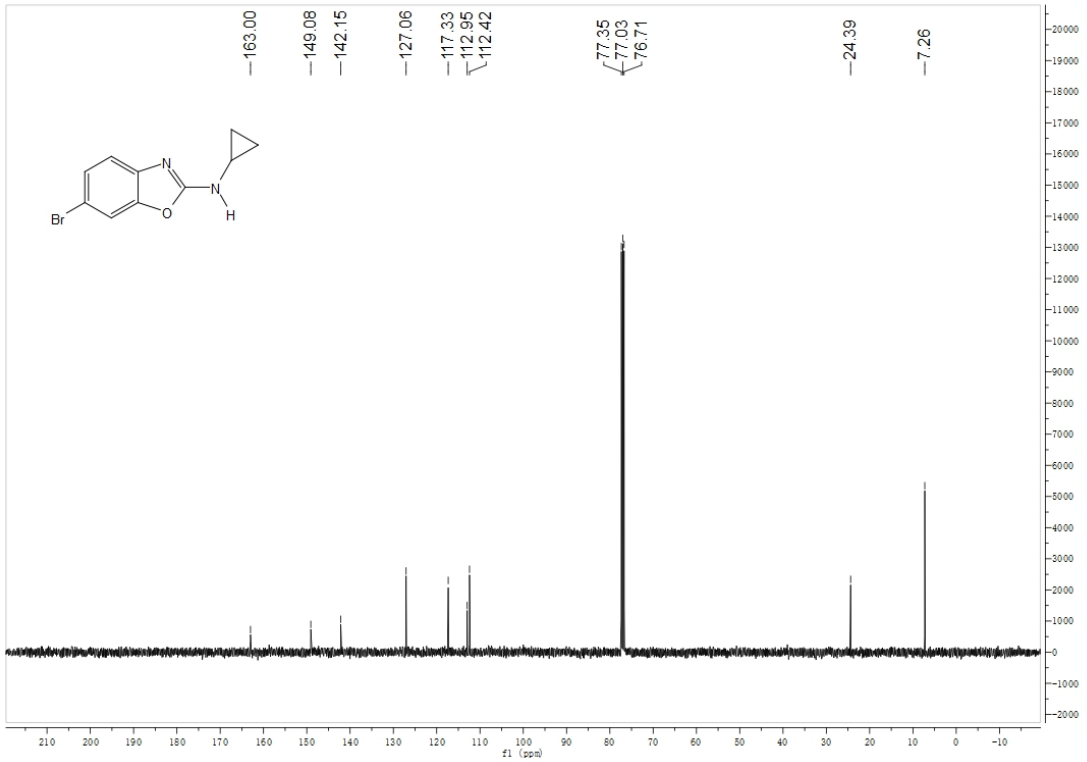

Figure S70. ^{13}C NMR Spectrum of 4l (100 MHz, $CDCl_3$)

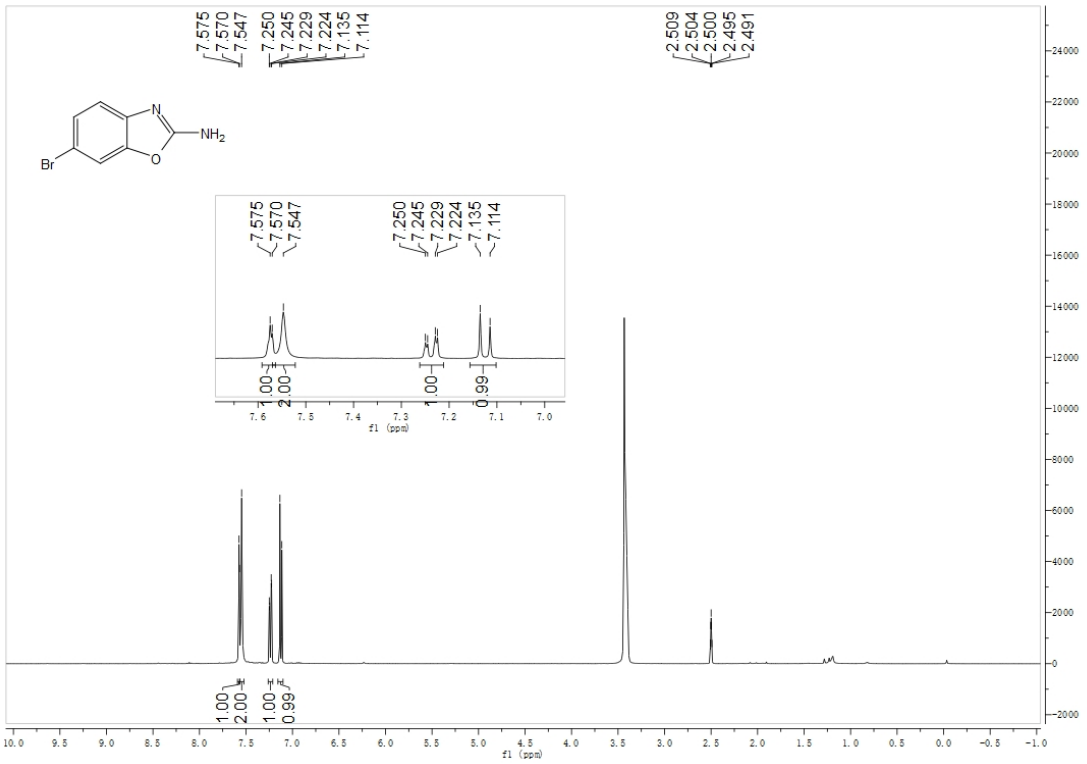

Figure S71. ^{1}H NMR Spectrum of 4m (400 MHz, DMSO-d_6)

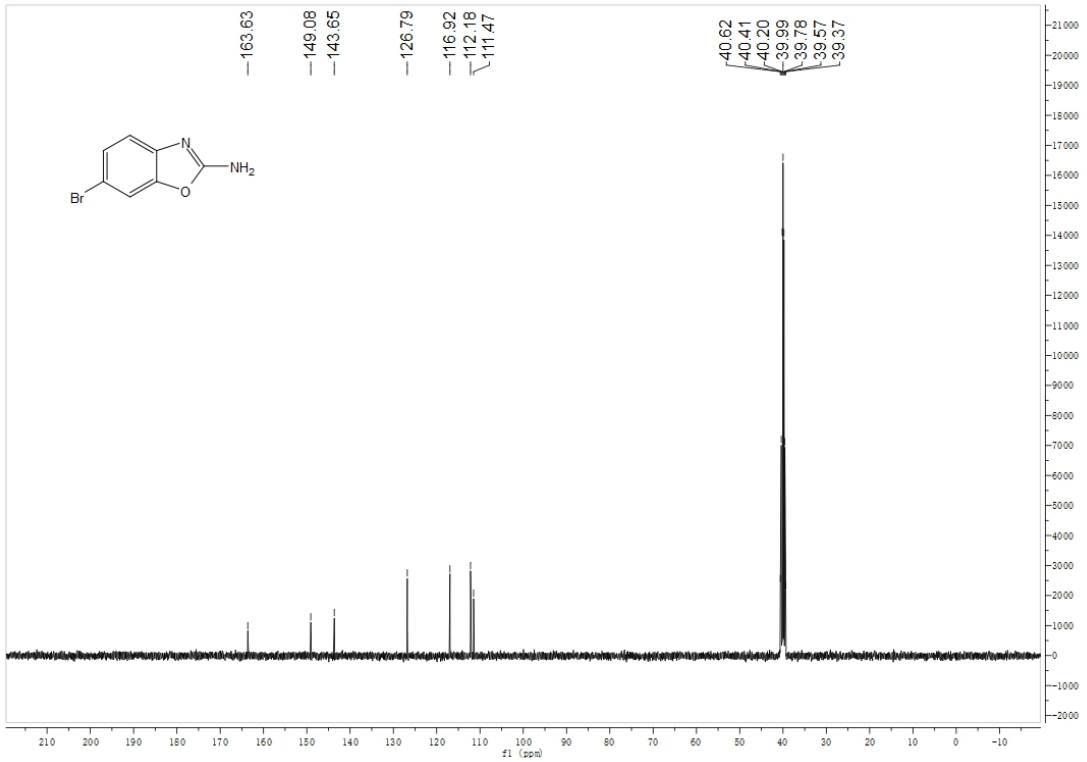

Figure S72. ^{13}C NMR Spectrum of 4m (100 MHz, DMSO-d_6)

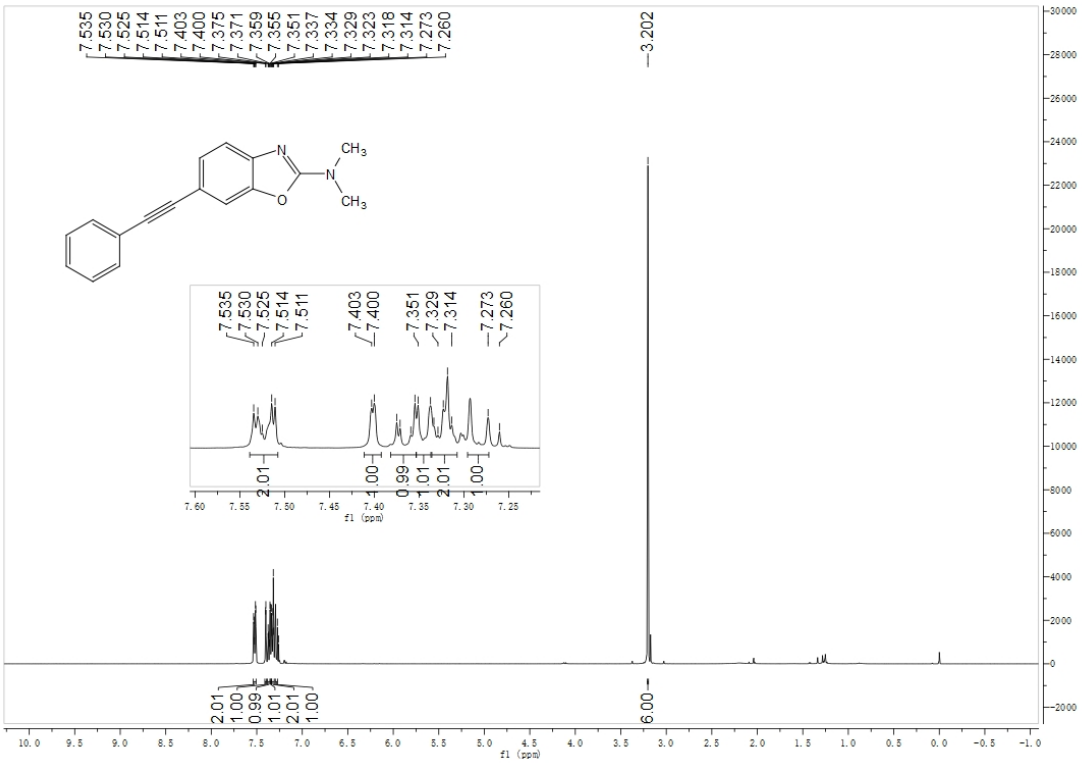

Figure S73. ^{1}H NMR Spectrum of 5 (400 MHz, $CDCl_3$)

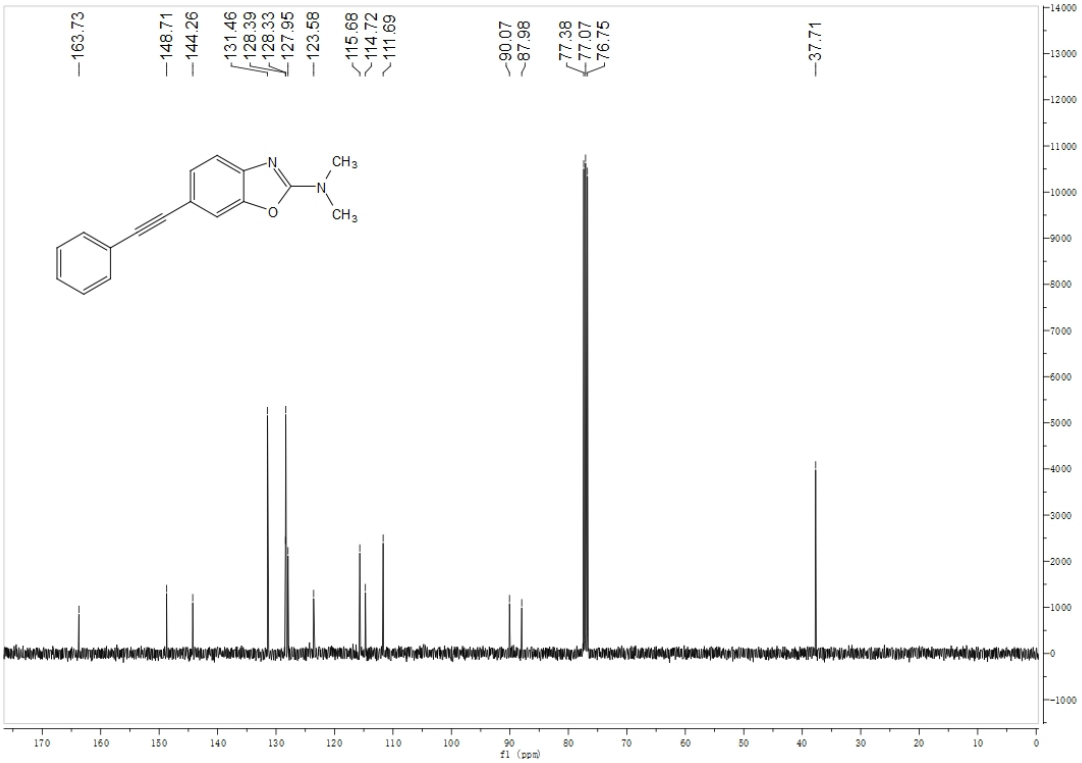

Figure S74. ^{13}C NMR Spectrum of 5 (100 MHz, $CDCl_3$)

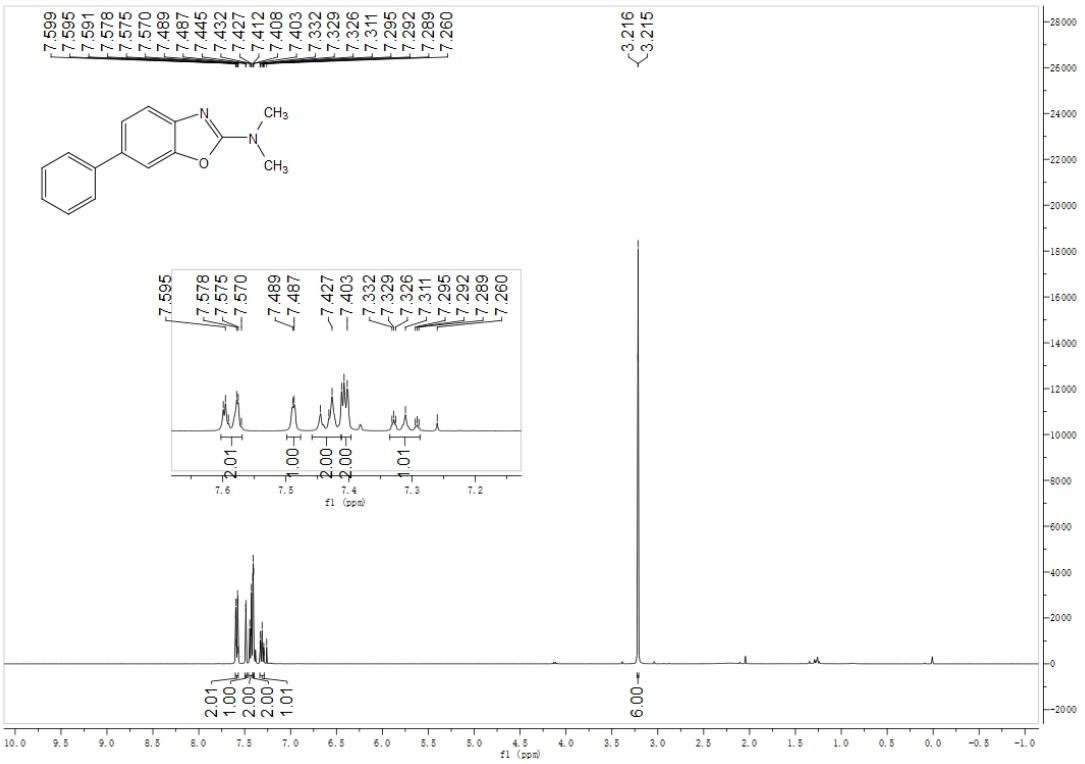

Figure S75. ^{1}H NMR Spectrum of 6 (400 MHz, $CDCl_3$)

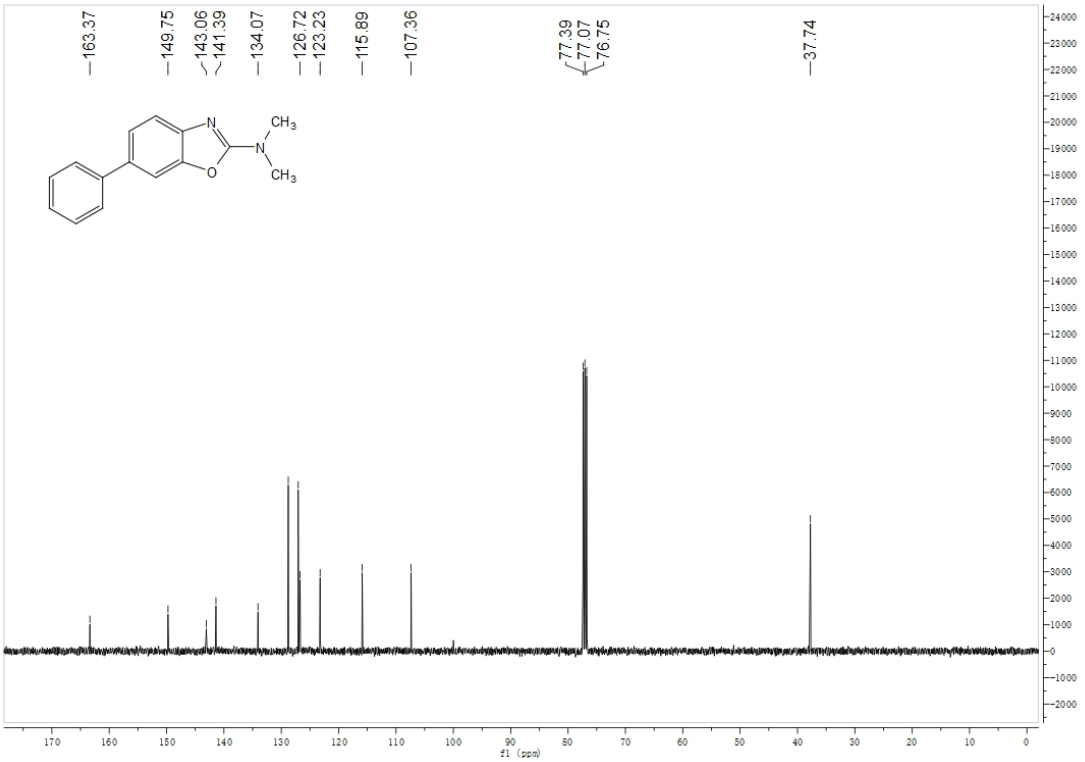

Figure S76. ^{13}C NMR Spectrum of 6 (100 MHz, $CDCl_3$)

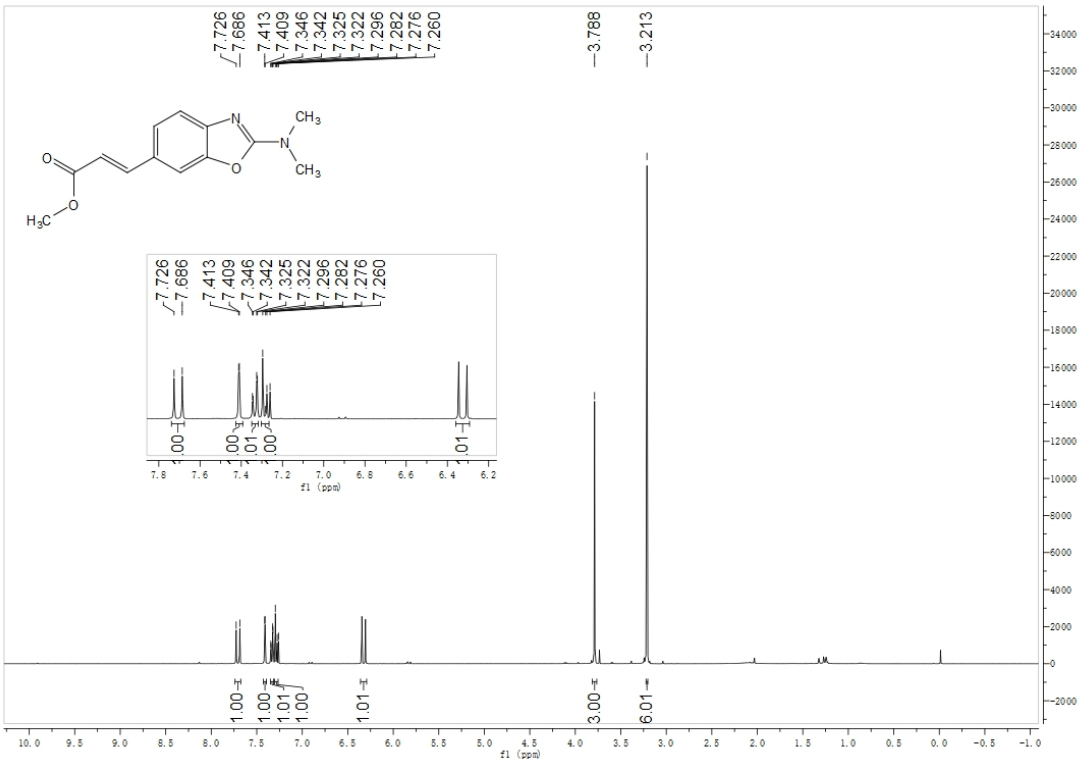

Figure S77. ^{1}H NMR Spectrum of 7 (400 MHz, $CDCl_3$)

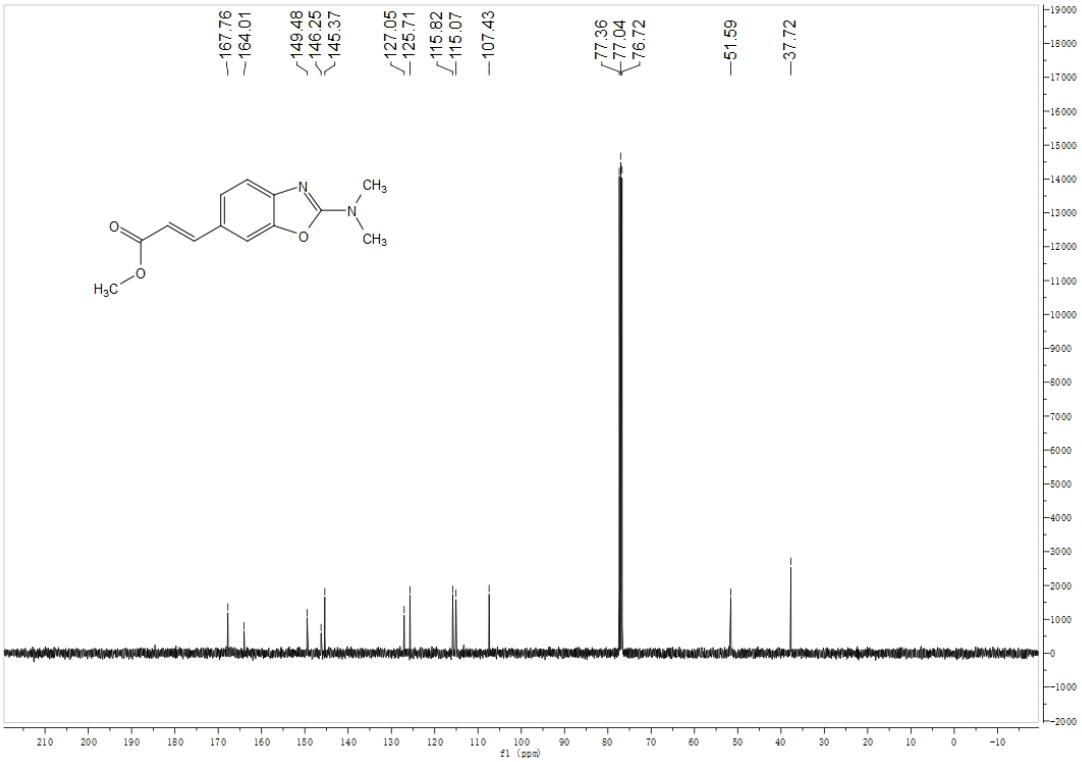

Figure S78. ^{13}C NMR Spectrum of 7 (100 MHz, $CDCl_3$)

G. X-ray crystallographic data

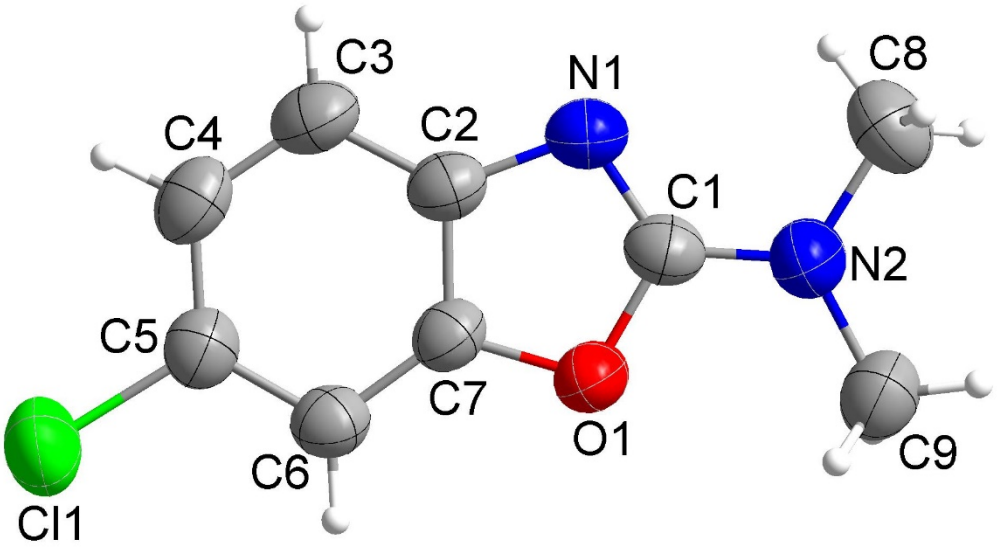

Figure S79. The Diamond diagram of 3c (thermal ellipsoids are shown at 50% probability)

Sample Preparation: A crystalline solid was obtained via slow evaporation of compound **3c** in EA: hexane= 1: 5 at room temperature.

Crystal data and structure refinement for compound **3c** (CCDC: 2132707)

Table S1 Crystal data and structure refinement for 3c.

Identification code	**3c**
Empirical formula	$C_9H_{10}ClN_2O$
Formula weight	197.64
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P21/c
a/Å	10.2788(8)
b/Å	7.8203(7)
c/Å	12.2421(10)
α/°	90
β/°	100.159(8)
γ/°	90
Volume/Å3	968.63(14)
Z	4
ρcalcg/cm3	1.355
μ/mm-1	0.355
F(000)	412.0
Crystal size/mm3	0.15 × 0.15 × 0.15
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.026 to 60
Index ranges	-13 ≤ h ≤ 14, -10 ≤ k ≤ 10, -17 ≤ l ≤ 16
Reflections collected	8357
Independent reflections	2667 [Rint = 0.0702, Rsigma = 0.0650]
Data/restraints/parameters	2667/0/120
Goodness-of-fit on F2	1.015
Final R indexes [I>=2σ (I)]	R1 = 0.0622, wR2 = 0.1612
Final R indexes [all data]	R1 = 0.1121, wR2 = 0.1956
Largest diff. peak/hole / e Å-3	0.25/-0.42

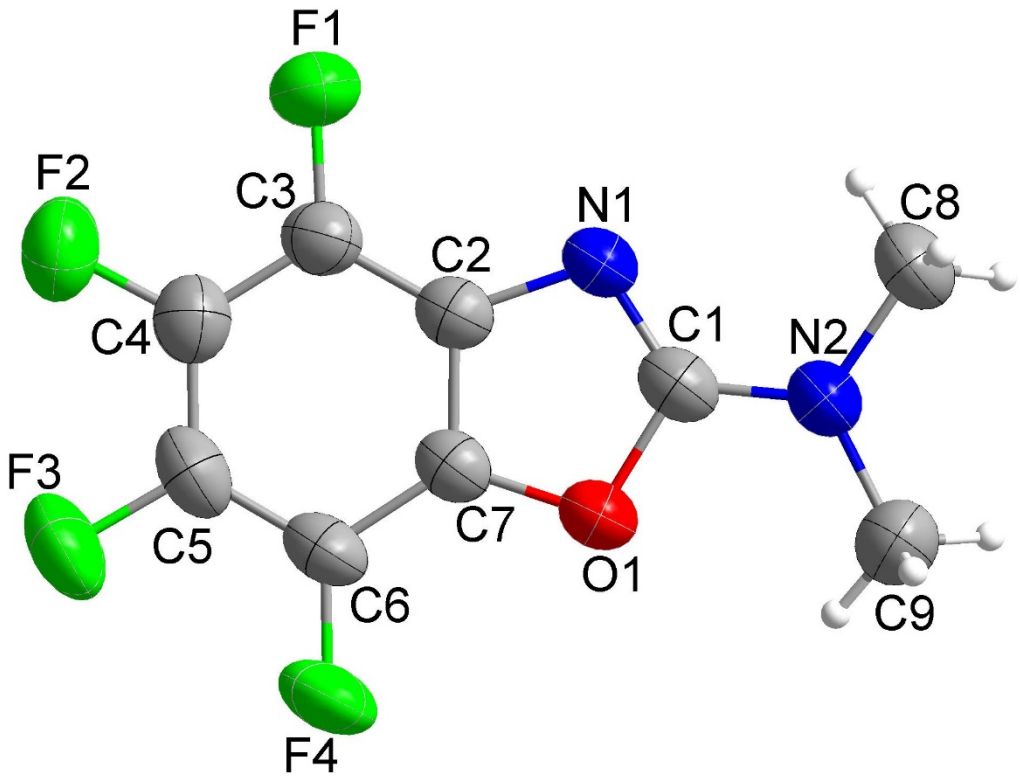

Figure S80. The Diamond diagram of 3x (thermal ellipsoids are shown at 50% probability)

Sample Preparation: A crystalline solid was obtained via slow evaporation of compound **3c** in EA: hexane= 1: 5 at room temperature.

Crystal data and structure refinement for compound **3w** (CCDC: 2131243)

Table S1 Crystal data and structure refinement for 3w.

Identification code	**3w**
Empirical formula	$C_9H_6F_4N_2O$
Formula weight	234.16
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	6.2144(4)
b/Å	8.2329(4)
c/Å	10.3279(6)
α/°	70.410(5)
β/°	72.569(6)
γ/°	86.651(5)
Volume/Å3	474.44(5)
Z	2
ρcalcg/cm3	1.639
μ/mm-1	0.162
F(000)	236.0
Crystal size/mm3	0.15 × 0.14 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.384 to 52.986
Index ranges	$-7 \leq h \leq 7$, $-10 \leq k \leq 10$, $-12 \leq l \leq 12$
Reflections collected	6312
Independent reflections	1934 [Rint = 0.0236, Rsigma = 0.0315]
Data/restraints/parameters	1934/0/147
Goodness-of-fit on F2	1.055
Final R indexes [I>=2σ (I)]	R1 = 0.0488, wR2 = 0.1287
Final R indexes [all data]	R1 = 0.0851, wR2 = 0.1503
Largest diff. peak/hole / e Å-3	0.16/-0.24