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$B(C_6F_5)_3$-catalyzed site-selective N^1-alkylation of benzotriazoles with diazoalkanes

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Supporting Information

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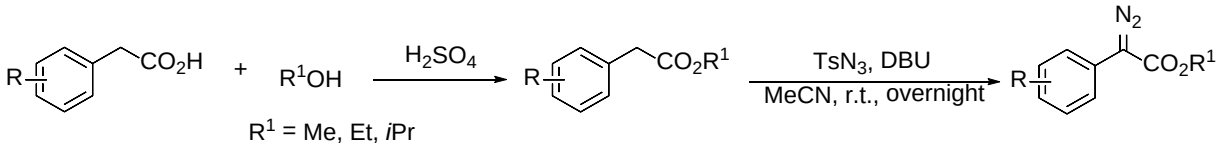
General information

All preparative procedures were performed in an inert atmosphere of dry, deoxygenated (O_2 < 0.5 ppm) argon, using glovebox techniques or standard Schlenk techniques unless otherwise specified. Solvents were stored over activated 3Å molecular sieves following drying procedures. Dichloromethane (DCM), tetrahydrofunan (THF) and hexane were purchased from Tedia Company, Inc. Toluene and ethyl ether (Et_2O) were purchased from Tedia Company, Inc. Deuterated solvents (C_6D_6, toluene-d_8, $CDCl_3$, CD_3CN) were purchased from Cambridge Isotope Laboratories, Inc. and used without further purification. Methyl phenylacetate was obtained from Energy Chemical. *p*-Tolyacetic acid, *p*-fluorophenylacetic acid, *p*-chlorophenylacetic acid, *p*-bromophenylacetic acid, *p*-*tert*-butylphenlacetic acid, *m*-methylphenylacetic acid, 2-(naphthalen-2-yl)acetic acid, *o*-tolylacetic acid, 2-bromophenylacetic acid and 3,4-dimethylphenylacetic acid were obtained from Aladdin. *p*-Iodophenylacetic acid, *p*-cyanophenylacetic acid, 3-bromophenylacetic acid, 4-methoxyphenylacetic acid, 3,4-(methylenedioxy)phenylacetic acid and *p*-toluenesulfonyl azide were obtained from Adamas-beta. *p*-(Trifluoromethyl)phenylacetic acid was obtained from Innochem. Thin-layer chromatography (TLC) was performed on EMD Silica Gel 60 F254 aluminum plates or EMD basic Aluminium Oxide 60 F254 plastic plates. Silicycle Silia-P Flash Silica Gel was used for all column chromatography.

All NMR spectra were collected at 298 K on Bruker 500 spectrometers in 5 mm diameter NMR tubes. ^{1}H chemical shifts are reported relative to proteo-solvent signals ($CDCl_3$, δ = 7.26 ppm; CD_2Cl_2, δ = 5.32 ppm). Data are reported as: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets), coupling constants (Hz), integration and assignment. ^{13}C{^{1}H} chemical shifts are reported relative to proteo-solvent signals ($CDCl_3$, δ = 77.00 ppm; CD_2Cl_2, δ = 53.84 ppm). ^{19}F NMR spectra were measured at 376 MHz and $CFCl_3$ (-63.2 ppm) was used as an external standard. Departmental facilities were used for mass spectrometry (FTMS ESI)

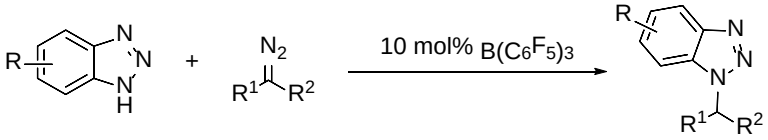
Preparation of α-diazo esters[1]



Phenylacetic acid derivatives (53.0 mmol) was dissolved in alcohols (80 mL) and concentrated sulfuric acid (0.5 mL) was added. The mixture was refluxed for 15 hours with stirring. Upon cooling the mixture and evaporating the excess alcohols, the mixture was subjected to column chromatography (1:50 ethyl acetate/petroleum ether), and ester was obtained as a colourless oil.

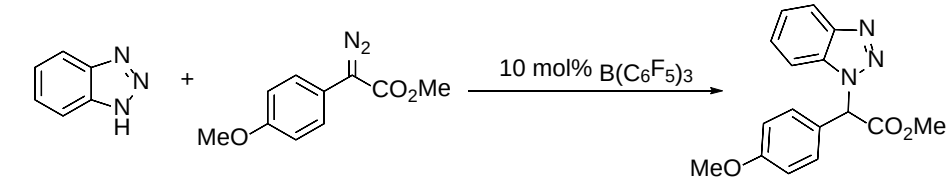
DBU (15.0 mmol) was added to ester (10.0 mmol) and *p*-toluenesulfonyl azide (2.960g, 15.0 mmol) in MeCN (15 mL). The reaction mixture was stirred overnight. TLC was used to confirm the consumption of the starting materials, and upon so doing, the reaction mixture was quenched with a saturated solution of NH_4Cl (5 mL). An extraction with DCM (3 x 30 mL), washing with brine (3 x 10 mL), drying over $MgSO_4$ was performed, before the mixture was concentrated under pressure to the crude product. Purification by column chromatography (1:100 ethyl acetate/petroleum ether) gave the α-diazoester as a dark orange oil.

General procedure for preparation of *N*[1]-alkylated benzotriazoles



In an inert atmosphere glovebox, to a solution of diazomethanes (0.10 mmol, 1 equiv.) and benzotriazoles (0.10 mmol, 1 equiv.) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was stirred for the specified time at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 8/1 to 4/1) on silica gel to afford the *N*-alkylated benzotriazole products.

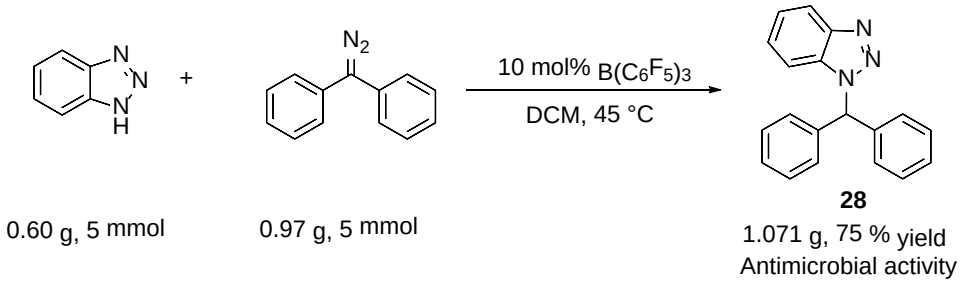
Typical procedure for gram-scale version of *N*-alkylation



In an inert atmosphere glovebox, a Schlenk flask (100 mL) was charged with methyl 4-methoxyphenyldiazoacetate (1.03 g, 5.0 mmol). Then, benzotriazole (0.60 g, 5.0 mmol) and DCM (30 mL) was added. Finally, a solution of $B(C_6F_5)_3$ (0.255 g, 0.5 mmol) in DCM (20 mL) was added

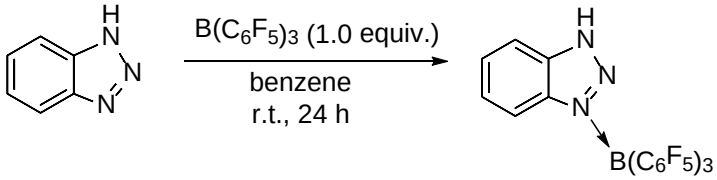
to the mixture under stirring. The reaction mixture was stirred at 45 °C for 24 hours. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **11** as a white solid (1.450 g, 98% yield).

Gram-scale synthesis of antimicrobial activity reagent



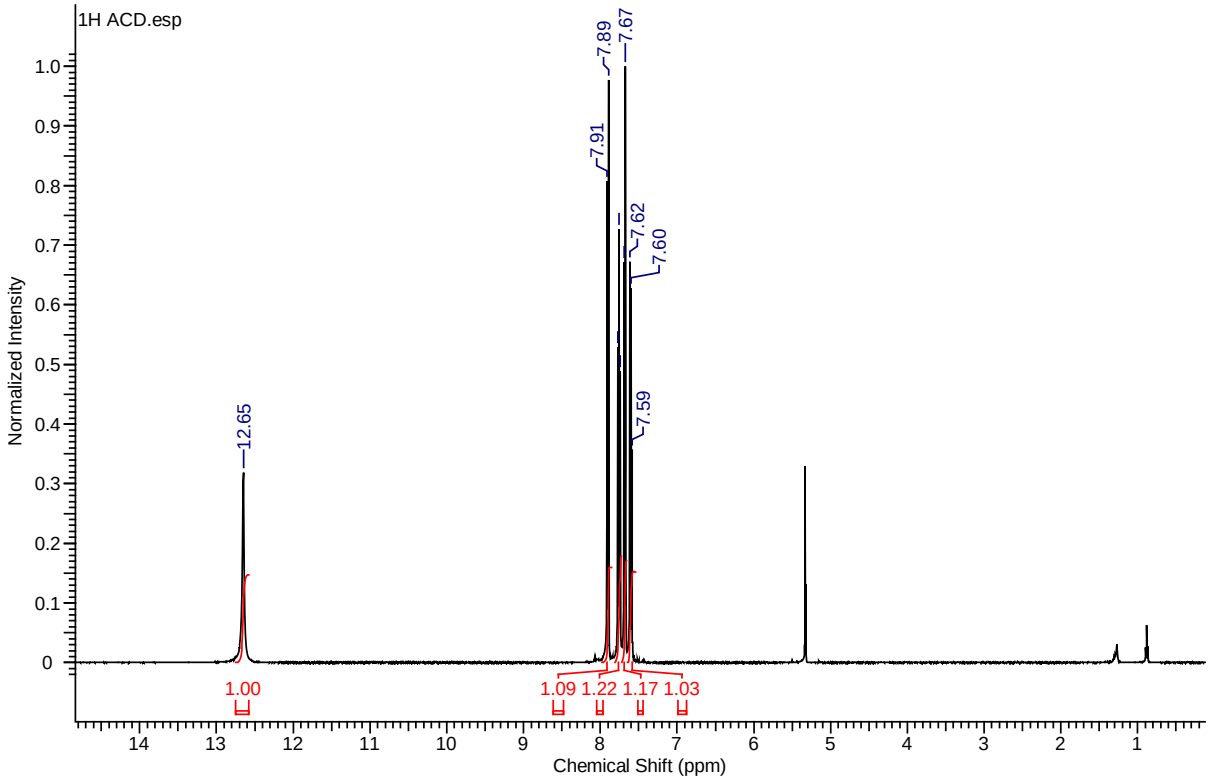
In an inert atmosphere glovebox, a Schlenk flask (100 mL) was charged with 1,1-diphenyldiazomethane (0.97 g, 5.0 mmol). Then, benzotriazole (0.60 g, 5.0 mmol) and DCM (30 mL) was added. Finally, a solution of $B(C_6F_5)_3$ (0.255 g, 0.5 mmol) in DCM (20 mL) was added to the mixture under stirring. The reaction mixture was stirred at 45 °C for 1 hour. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 8/1) on silica gel to afford the product **28** as a white solid (1.071 g, 75 yield).

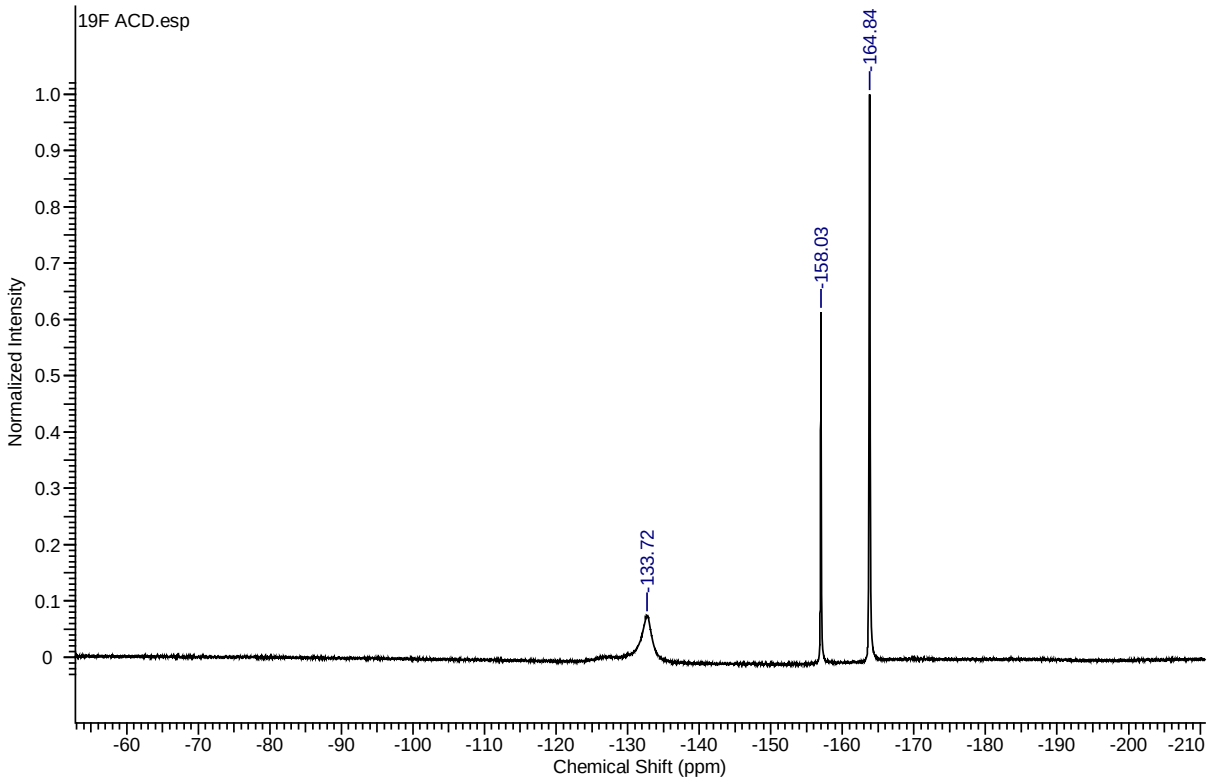
Stoichiometric reaction of benzotriazole and $B(C_6F_5)_3$



In an inert atmosphere glovebox, into a 3 mL vial equipped with a stir bar, $B(C_6F_5)_3$ (0.123 g, 0.24 mmol, 1.0 equiv.) and benzotriazole (0.029 g, 0.24 mmol, 1.0 equiv.) were taken in benzene (2.0 mL). [*Note: benzotriazole itself is not soluble in benzene but the mixture of two is soluble*]. The reaction mixture was stirred at room temperature for 24 h. All volatiles were removed in vacuo. The residue was washed with *n*-hexanes (3 x 3 mL) and dried in vacuo. The white residue was crystallized with a mixture of solvent of DCM: *n*-hexane (1:5) and stored at -30 °C for two days. Colourless block crystals were collected and dried in affording the compound $(C_6H_4NHN_2)B(C_6F_5)_3$ (0.082 g, 54%). This was unambiguously confirmed by X-ray crystallography and NMR spectroscopy. ^{1}H NMR (500 MHz, CD_2Cl_2), δ: 12.65 (br s, 1 H, -N_3H), 7.90 (d, *J* = 8.7 Hz, 1 H, Ar-

H), 7.75 (ddd, *J* = 8.2, 7.5, 0.84 Hz, 1 H, Ar-*H*), 7.68 (d, *J* = 8.7 Hz, 1 H, Ar-*H*), 7.59 (ddd, *J* = 8.7, 7.0, 0.65 Hz, 1 H, Ar-*H*); ^{19}F NMR (471 MHz, CD_2Cl_2), δ: -133.7 (br s, 6 F, *o*-C_6F_5), -158.0 (s, 3 F, *p*-C_6F_5), -164.8 (s, 6 F, *m*-C_6F_5); ^{11}B{^{1}H} NMR (161 MHz, CD_2Cl_2), δ: -6.1 (br s, 1 B, N_3-$B(C_6F_5)_3$); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2), δ: 150.1 – 149.3 (br, m), 148.1 – 147.5 (br, m), 142.0 – 141.5 (m), 139.9 – 139.4 (m), 138.9 – 138.4 (m), 138.7 (s), 136.9 – 136.4 (m), 133.8 (s), 131.2 (s), 129.9 (s), 116.4 (s), 112.8 (s).

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0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-60
-70
-80
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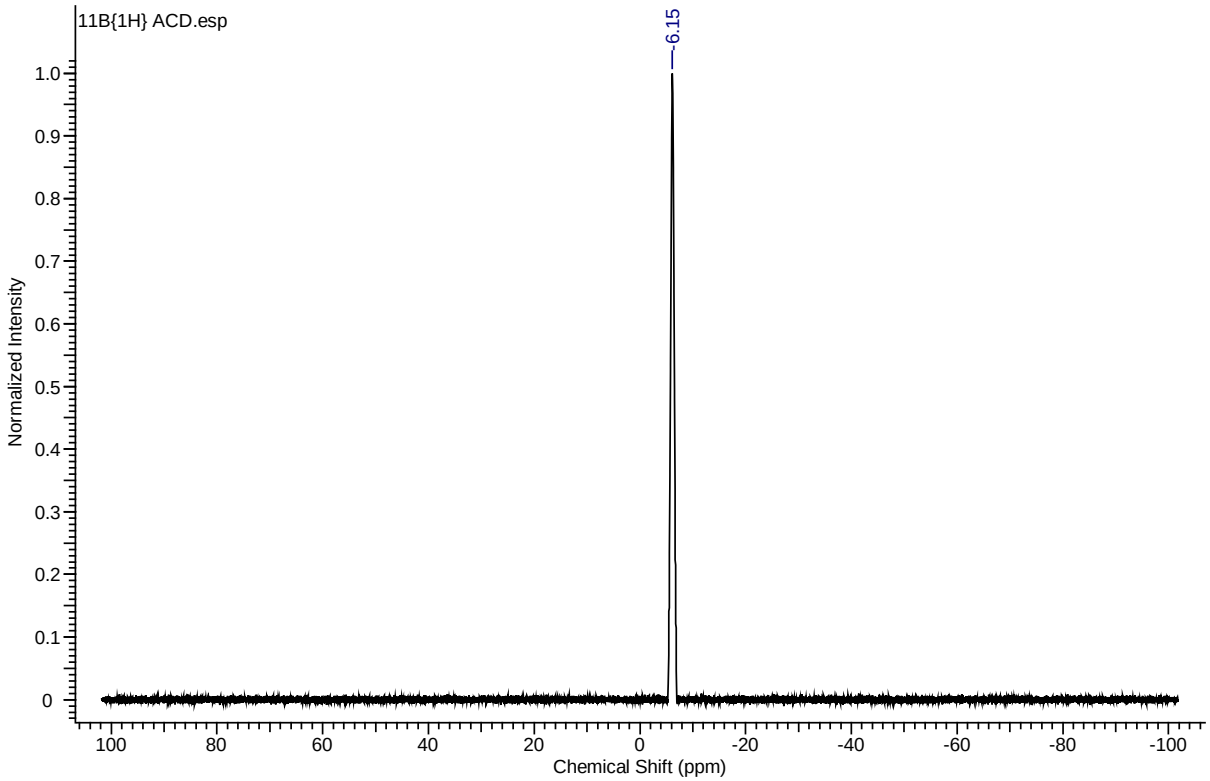
Chemical Shift (ppm)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60
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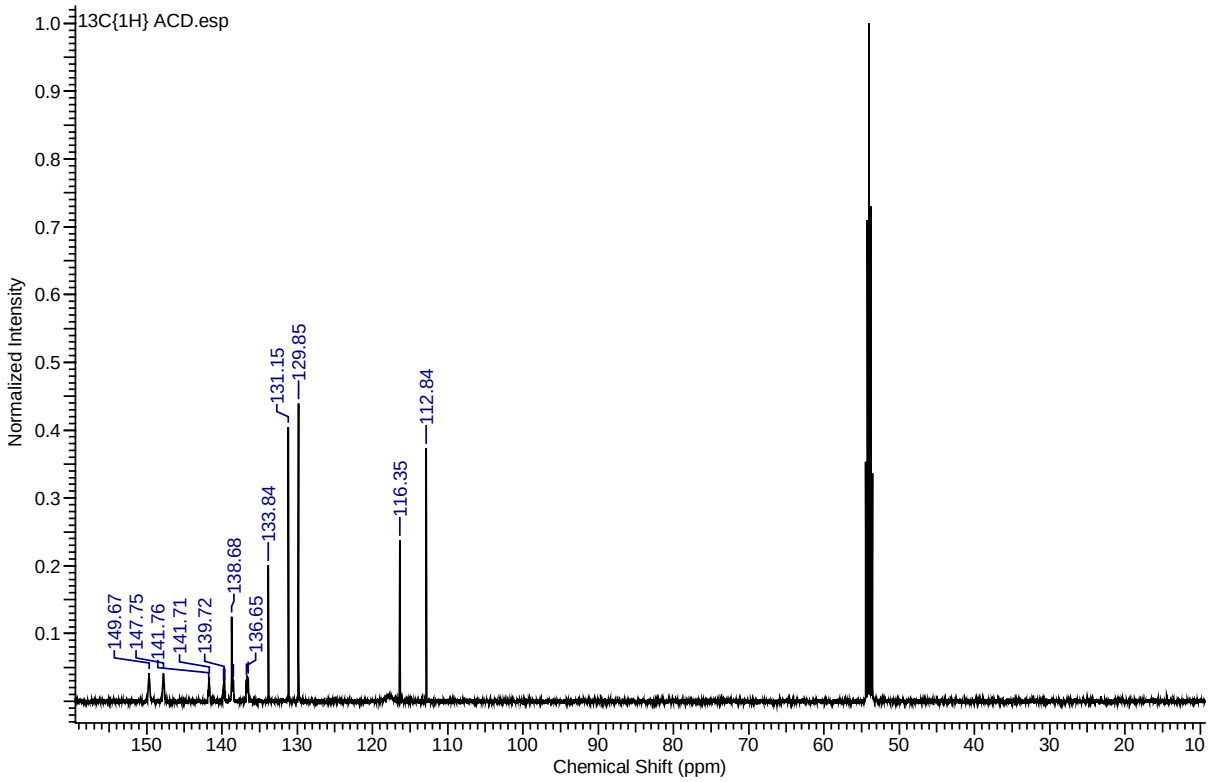
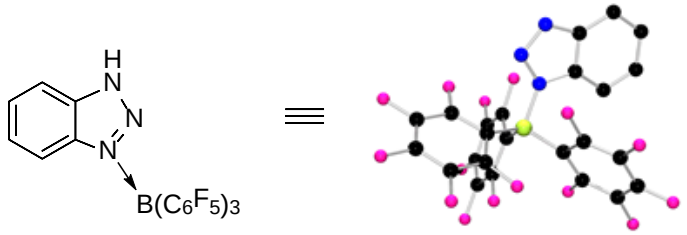
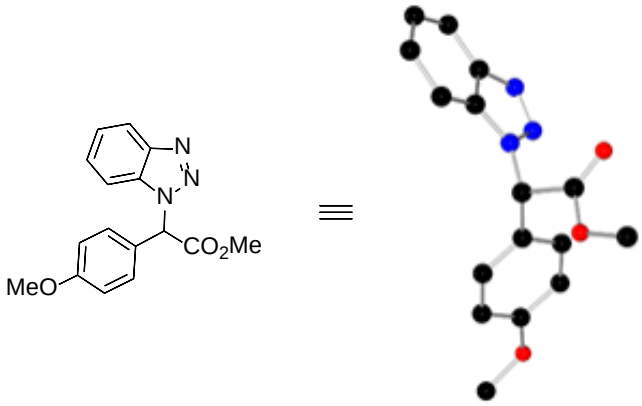
Chemical Shift (ppm)



Single crystal X-ray crystallography

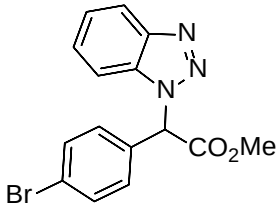
X-ray crystallographic data were collected on a Bruker D8 QUEST diffractometer using Cu (60W, Diamond, μKα = 12.894 mm^{-1}) micro-focus X-ray sources at 161 K. The structure was solved and refined using Full-matrix least-squares based on F^2 with program SHELXS and SHELXL[2] within OLEX2.[3]





Characterization data

Preparation of methyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-(4-bromophenyl)acetate (1a)



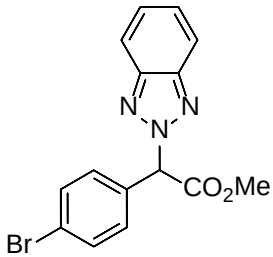
To a solution of methyl 4-bromophenyldiazoacetate (25.5 mg, 0.10 mmol) and benzotriazole (12.0 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **1a** as a light-yellow solid (31.0 mg, 90% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.06 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.51 (m, 2H), 7.41 – 7.32 (m, 2H), 7.28 – 7.22 (m, 3H), 6.83 (s, 1H), 3.86 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 167.67, 146.43, 132.41, 132.29, 131.45, 129.82, 127.81, 124.15, 123.75, 120.23, 110.68, 64.88, 53.32.

HRMS (ESI, m/z): Calcd. for $C_{15}H_{13}Br^{79.9183}N_3O_2^+$, ([M+H]$^+$): 346.0186; Found: 346.0182; $C_{15}H_{13}Br^{80.9163}N_3O_2^+$ ([M+H]$^+$): 348.0156; Found: 348.0161.

Preparation of methyl 2-(2*H*-benzo[*d*][1,2,3]triazol-2-yl)-2-(4-bromophenyl)acetate (1b)

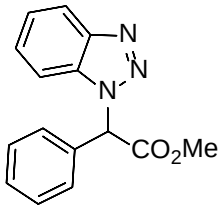


^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.87 (dd, *J* = 7.0 Hz, 3.5 Hz, 2H), 7.59 – 7.55 (m, 2H), 7.52 – 7.48 (m, 2H), 7.39 (dd, *J* = 7.0 Hz, 3.0 Hz, 2H), 6.68 (s, 1H), 3.82 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 167.32, 144.54, 132.13, 131.54, 131.10, 126.95, 124.13, 118.38, 71.19, 53.50.

HRMS (ESI, m/z): Calcd. for $C_{15}H_{12}Br^{79.9183}N_3O_2Na^+$, ([M+Na]$^+$): 368.0005 Found: 368.0005; $C_{15}H_{12}Br^{80.9163}N_3O_2Na^+$ ([M+Na]$^+$): 369.9985; Found: 369.9984.

Preparation of methyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-phenylacetate (2)



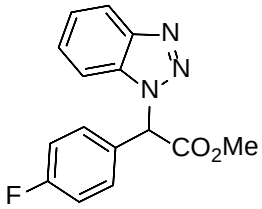
To a solution of methyl phenyldiazoacetate (17.6 mg, 0.10 mmol) and benzotriazole (12.0 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **2** as a white solid (24.5 mg, 92% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.07 – 8.04 (m, 1H), 7.43 – 7.37 (m, 5H), 7.37 – 7.30 (m, 2H), 7.20 – 7.17 (m, 1H), 6.94 (s, 1H), 3.87 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.18, 146.47, 132.54, 132.34, 129.43, 129.12, 128.18, 127.58, 123.98, 120.07, 111.10, 65.70, 53.14.

HRMS (ESI, *m/z*): Calcd. for $C_{15}H_{14}N_3O_2^+$, ([M+H]$^+$): 268.1081; Found: 268.1081.

Preparation of methyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-(4-fluorophenyl)acetate (3)



To a solution of methyl 4-fluorophenyldiazoacetate (19.4 mg, 0.10 mmol) and benzotriazole (12.0 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **3** as a white solid (26.5 mg, 93% yield).

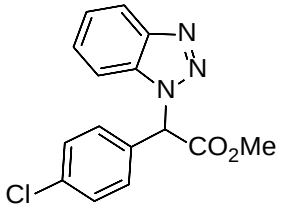
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.06 (dt, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.41 – 7.32 (m, 4H), 7.22 (dt, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.12 – 7.06 (m, 2H), 6.86 (s, 1H), 3.86 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 167.96, 163.08 (d, $J_{C\text{-}F}$ = 250.1 Hz), 146.44, 132.44, 130.22 (d, $J_{C\text{-}F}$ = 8.7 Hz), 128.30 (d, $J_{C\text{-}F}$ = 3.6 Hz), 127.74, 124.10, 120.20, 116.19 (d, $J_{C\text{-}F}$ = 21.9 Hz), 110.70, 64.83, 53.27.

^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$) δ: -111.29.

HRMS (ESI, *m/z*): Calcd. for $C_{15}H_{13}FN_3O_2^+$, ([M+H]$^+$): 286.0981; Found: 286.0984.

Preparation of methyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-(4-chlorophenyl)acetate (4)



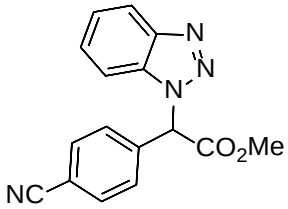
To a solution of methyl 4-chlorophenyldiazoacetate (21.0 mg, 0.10 mmol) and benzotriazole (12.0 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **4** as a light-yellow solid (26.6 mg, 88% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.07 (dt, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.41 – 7.31 (m, 6H), 7.25 – 7.22 (dt, *J* = 8.5 Hz, 1.0 Hz, 1H), 6.85 (s, 1H), 3.86 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 167.75, 146.43, 135.59, 132.42, 130.93, 129.58, 129.34, 127.82, 124.16, 120.24, 110.70, 64.85, 53.33.

HRMS (ESI, *m/z*): Calcd. for $C_{15}H_{13}Cl^{34.9689}N_3O_2^+$, ([M+H]$^+$): 302.0691; Found: 302.0691; $C_{15}H_{13}Cl^{35.4500}N_3O_2^+$, ([M+H]$^+$): 304.0661; Found: 304.0659.

Preparation of methyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-(4-cyanophenyl)acetate (5)



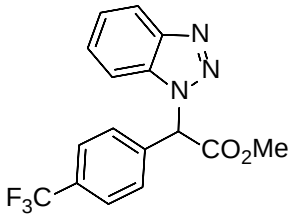
To a solution of methyl 4-cyanophenyldiazoacetate (20.1 mg, 0.10 mmol) and benzotriazole (12.0 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 3 days at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **5** as a colorless oil (20.0 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$), δ: 8.09 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.45 – 7.36 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 1H), 6.89 (s, 1H), 3.87 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), δ: 167.04, 146.34, 137.50, 132.77, 132.39, 128.95, 128.16, 124.41, 120.44, 117.86, 113.49, 110.20, 64.69, 53.60.

HRMS (ESI, *m/z*): Calcd. for $C_{16}H_{12}N_4O_2Na^+$, ([M+Na]$^+$): 315.0852; Found: 315.0854.

Preparation of methyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-(4-trifluoromethylphenyl)acetate (6)



To a solution of methyl 4-trifluoromethylphenyldiazoacetate (24.4 mg, 0.10 mmol) and benzotriazole (12.0 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 3 days at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **6** as a light-yellow solid (28.5 mg, 85% yield).

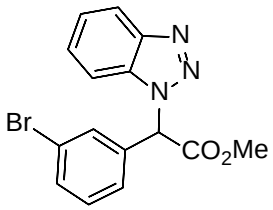
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.09 (dt, *J* = 8.5 Hz, 1.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.35 (m, 2H), 7.25 – 7.22 (dt, *J* = 8.0 Hz, 1.0 Hz, 1H), 6.92 (s, 1H), 3.88 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 167.43, 146.43, 136.38 (d, $J_{C\text{-}F}$ = 1.0 Hz), 132.44, 131.63 (d, $J_{C\text{-}F}$ = 33.0 Hz), 128.62, 128.02, 126.95 (q, $J_{C\text{-}F}$ = 3.8 Hz) 124.30, 123.59 (d, $J_{C\text{-}F}$ = 273.0 Hz), 120.38, 110.49, 64.89, 53.48.

^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$) δ: -62.91.

HRMS (ESI, *m/z*): Calcd. for $C_{16}H_{13}F_3N_3O_2^+$, ([M+H]$^+$): 336.0954; Found: 336.0956.

Preparation of methyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-(3-bromophenyl)acetate (7)



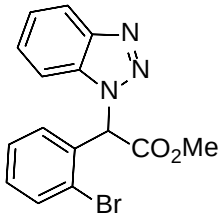
To a solution of methyl 3-bromophenyldiazoacetate (25.5 mg, 0.10 mmol) and benzotriazole (12.0 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **7** as a colorless oil (26.0 mg, 75% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.08 (dt, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.44 – 7.34 (m, 2H), 7.34 – 7.26 (m, 3H), 6.85 (s, 1H), 3.88 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 167.52, 146.42, 134.55, 132.62, 132.43, 131.24, 130.58, 127.89, 126.81, 124.19, 123.07, 120.26, 110.65, 64.80, 53.39.

HRMS (ESI, m/z): Calcd. for $C_{15}H_{13}Br^{79.9183}N_3O_2^+$, ([M+H]$^+$): 346.0186; Found: 346.0184; $C_{15}H_{13}Br^{80.9163}N_3O_2^+$ ([M+H]$^+$): 348.0156; Found: 348.0163.

Preparation of methyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-(2-bromophenyl)acetate (8)



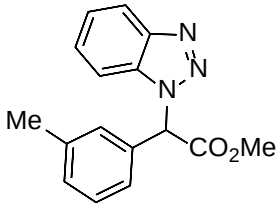
To a solution of methyl 2-bromophenyldiazoacetate (25.5 mg, 0.10 mmol) and benzotriazole (12.0 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **8** as a colorless oil (31.4 mg, 91% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.09 (d, *J* = 8.5 Hz, 1H), 7.63 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.40 – 7.33 (m, 3H), 7.30 – 7.26 (m, 1H), 7.13 (s, 1H), 3.85 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 167.50, 145.87, 133.38, 132.99, 132.49, 131.01, 130.12, 127.98, 127.90, 124.74, 124.14, 120.27, 109.64, 64.39, 53.46.

HRMS (ESI, m/z): Calcd. for $C_{15}H_{13}Br^{79.9183}N_3O_2^+$, ([M+H]$^+$): 346.0186; Found: 346.0184; $C_{15}H_{13}Br^{80.9163}N_3O_2^+$ ([M+H]$^+$): 348.0156; Found: 348.0162.

Preparation of methyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-(3-methylphenyl)acetate (9)



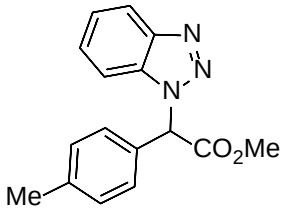
To a solution of methyl 3-methylphenyldiazoacetate (19.0 mg, 0.10 mmol) and benzotriazole (12.0 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **9** as a light-yellow solid (20.8 mg, 74% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.07 – 8.04 (m, 1H), 7.37 – 7.27 (m, 3H), 7.22 – 7.17 (m, 4H), 6.89 (s, 1H), 3.87 (s, 3H), 2.33 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 168.29, 146.46, 139.06, 132.58, 132.19, 130.24, 128.95, 128.93, 127.54, 125.19, 123.95, 120.04, 111.16, 65.73, 53.11, 21.40.

HRMS (ESI, *m/z*): Calcd. for $C_{16}H_{15}N_3O_2Na^+$, ($[M+Na]^+$): 304.1056; Found: 304.1058.

Preparation of methyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-(4-methylphenyl)acetate (10)



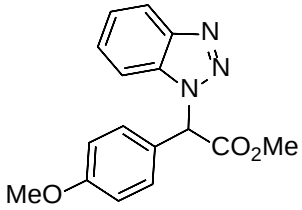
To a solution of methyl 4-methylphenyldiazoacetate (19.0 mg, 0.10 mmol) and benzotriazole (12.0 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **10** as a light-yellow solid (27.1 mg, 96% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.06 – 8.03 (m, 1H), 7.36 – 7.29 (m, 2H), 7.29 – 7.26 (m, 2H), 7.22 – 7.18 (m, 3H), 6.90 (s, 1H), 3.86 (s, 3H), 2.36 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 168.35, 146.42, 139.52, 132.55, 129.80, 129.28, 128.14, 127.51, 123.95, 120.01, 111.19, 65.56, 53.09, 21.16.

HRMS (ESI, *m/z*): Calcd. for $C_{16}H_{16}N_3O_2^+$, ($[M+H]^+$): 282.1237; Found: 282.1237.

Preparation of methyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-(4-methoxyphenyl)acetate (11)



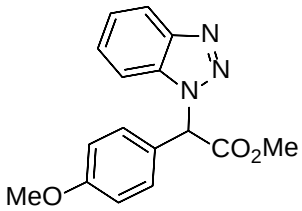
To a solution of methyl 4-methoxyphenyldiazoacetate (20.6 mg, 0.10 mmol) and benzotriazole (12.0 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **11** as a white solid (29.6 mg, 99% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.06 – 8.03 (m, 1H), 7.37 – 7.29 (m, 4H), 7.22 – 7.20 (m, 1H), 6.94 – 6.88 (m, 2H), 6.88 (s, 1H), 3.85 (s, 3H), 3.80 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 168.44, 160.27, 146.44, 132.52, 129.68, 127.50, 124.18, 123.92, 120.01, 114.45, 111.09, 65.25, 55.30, 53.08.

HRMS (ESI, *m/z*): Calcd. for $C_{16}H_{16}N_3O_3^+$, ($[M+H]^+$): 298.1186; Found: 298.1184.

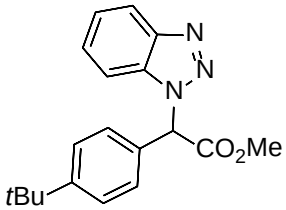
Gram-scale of methyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-(4-methoxyphenyl)acetate (11)



^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.06 – 8.03 (m, 1H), 7.36 – 7.29 (m, 4H), 7.20 – 7.17 (m, 1H), 6.93 – 6.89 (m, 2H), 6.86 (s, 1H), 3.85 (s, 3H), 3.80 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.36, 160.19, 146.36, 132.46, 129.63, 127.42, 124.13, 123.84, 119.90, 114.36, 111.01, 65.14, 55.21, 52.99.

Preparation of methyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2(4-(*tert*-butyl)phenyl)acetate (12)



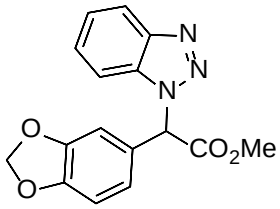
To a solution of methyl 4-*tert*-butylphenyldiazoacetate (23.2 mg, 0.10 mmol) and benzotriazole (12.0 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **12** as a white solid (32.0 mg, 99% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.06 – 8.03 (m, 1H), 7.43 – 7.39 (m, 2H), 7.37 – 7.29 (m, 4H), 7.26 – 7.23 (m, 1H), 6.91 (s, 1H), 3.85 (s, 3H), 1.30 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.36, 152.58, 146.44, 132.56, 129.28, 127.94, 127.48, 126.04, 123.91, 120.00, 111.22, 65.45, 53.06, 34.65, 31.14.

HRMS (ESI, *m/z*): Calcd. for $C_{19}H_{22}N_3O_2^+$, ($[M+H]^+$): 324.1707; Found: 324.1707.

Preparation of methyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-(benzo[*d*][1,3]dioxol-5-yl)acetate (13)



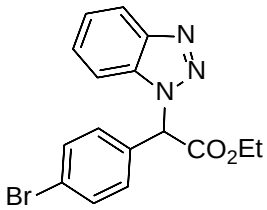
To a solution of methyl 2-(benzo[*d*][1,3]dioxol-5-yl)-2-diazoacetate (22.0 mg, 0.10 mmol) and benzotriazole (12.0 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **13** as a light-yellow solid (29.2 mg, 94% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.07 – 8.04 (m, 1H), 7.40 – 7.31 (m, 2H), 7.28 – 7.25 (m, 1H), 6.90 – 6.86 (m, 2H), 6.81 (d, *J* = 8 Hz, 1H), 6.79 (s, 1H), 5.98 (dd, *J* = 6.0 Hz, 1.5 Hz, 2H), 3.86 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.18, 148.58, 148.38, 146.45, 132.49, 127.63, 125.86, 124.03, 122.17, 120.11, 111.02, 108.76, 108.52, 101.62, 65.43, 53.20.

HRMS (ESI, *m/z*): Calcd. for $C_{16}H_{14}N_3O_4^+$, ([M+H]$^+$): 312.0979; Found: 312.0977.

Preparation of ethyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-(4-bromophenyl)acetate (14)



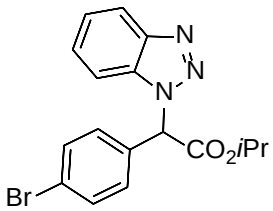
To a solution of ethyl 4-bromophenyldiazoacetate (26.9 mg, 0.10 mmol) and benzotriazole (12.0 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 3days at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **14** as a light-yellow solid (32.5 mg, 90% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.06 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.41 – 7.32 (m, 2H), 7.28 – 7.23 (m, 3H), 6.82 (s, 1H), 4.39 – 4.28 (m, 2H), 1.28 (t, *J* = 7.0 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDC_{l3}) δ: 167.18, 146.46, 132.43, 132.28, 131.60, 129.81, 127.74, 124.12, 123.69, 120.21, 110.85, 65.06, 62.76, 14.01.

HRMS (ESI, m/z): Calcd. for $C_{16}H_{15}Br^{79.9183}N_3O_2^+$, ([M+H]$^+$): 360.0342; Found: 360.0341; $C_{16}H_{15}Br^{80.9163}N_3O_2^+$ ([M+H]$^+$): 362.0322; Found: 362.0320.

Preparation of isopropyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-(4-bromophenyl)acetate (15)



To a solution of isopropyl 4-bromophenyldiazoacetate (28.2 mg, 0.10 mmol) and benzotriazole (12.0 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10

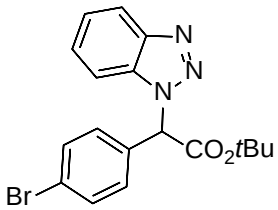
mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **15** as a light-yellow solid (33.6 mg, 90% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.08 (d, *J* = 8.5 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.42 – 7.34 (m, 2H), 7.30 – 7.27 (m, 3H), 6.81 (s, 1H), 5.25 – 5.17 (m, 1H), 1.28 (d, *J* = 6.5 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 166.67, 146.44, 132.44, 132.25, 131.69, 129.79, 127.67, 124.09, 123.61, 120.16, 110.94, 70.99, 65.20, 21.60, 21.54.

HRMS (ESI, m/z): Calcd. for $C_{17}H_{17}Br^{79.9183}N_3O_2^+$, ([M+H]$^+$): 374.0499; Found: 374.0498; $C_{17}H_{17}Br^{80.9163}N_3O_2^+$ ([M+H]$^+$): 376.0478; Found: 376.0477.

Preparation of *tert*-butyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-(4-bromophenyl)acetate (16)



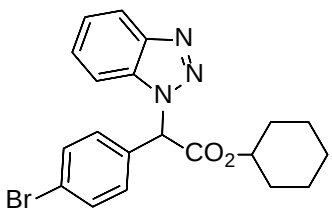
To a solution of *tert*-butyl 4-bromophenyldiazoacetate (29.7 mg, 0.10 mmol) and benzotriazole (12.0 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 10/1) on silica gel to afford the product **16** as a white solid (32.6 mg, 84% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.05 (dt, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.54 – 7.51 (m, 2H), 7.39 – 7.31 (m, 2H), 7.29 – 7.23 (m, 3H), 6.73 (s, 1H), 1.47 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 166.16, 146.42, 132.44, 132.21, 131.97, 129.81, 127.58, 124.03, 123.48, 120.12, 111.04, 84.36, 65.69, 27.85.

HRMS (ESI, m/z): Calcd. for $C_{18}H_{18}Br^{79.9183}N_3O_2Na^+$, ([M+Na]$^+$): 410.0475; Found: 410.0473; $C_{18}H_{18}Br^{80.9163}N_3O_2Na^+$, ([M+Na]$^+$): 412.0454; Found: 412.0452.

Preparation of cyclohexyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-(4-bromophenyl)acetate (17)



To a solution of cyclohexyl 4-bromophenldiazoacetate (32.3 mg, 0.10 mmol) and benzotriazole (12.0 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was

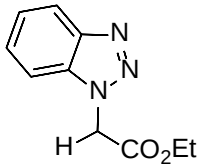
purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **17** as a colorless oil (36.8 mg, 89% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.05 (dt, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.39 – 7.31 (m, 2H), 7.29 – 7.22 (m, 3H), 6.82 (s, 1H), 4.99 – 4.93 (m, 1H), 1.96 – 1.80 (m, 2H), 1.62 – 1.53 (m, 2H), 1.47 – 1.38 (m, 2H), 1.38 – 1.16 (m, 4H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 166.57, 146.45, 132.46, 132.22, 131.73, 129.80, 127.63, 124.06, 123.57, 120.15, 110.97, 75.57, 65.23, 31.20, 31.17, 25.01, 23.26.

HRMS (ESI, m/z): Calcd. for $C_{20}H_{20}Br^{79.9183}N_3O_2Na^+$, ([M+Na]$^+$): 436.0631; Found: 436.0633; $C_{20}H_{20}Br^{80.9163}N_3O_2Na^+$, ([M+Na]$^+$): 438.0611; Found: 438.0611.

Preparation of methyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)acetate (18)



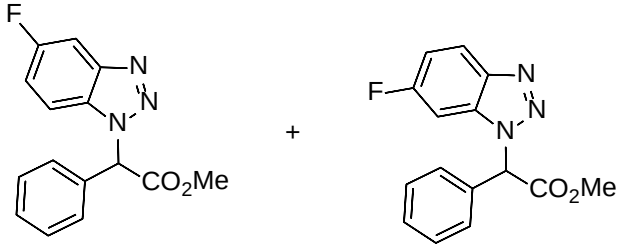
To a solution of ethyl diazoacetate, 95 wt.% dichloromethane (21.0 mg, 0.20 mmol) and benzotriazole (12.0 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **18** as a colourless oil (19.1 mg, 93% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.08 (dt, *J* = 8.5 Hz, 1.0 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.42 – 7.38 (m, 1H), 5.42 (s, 2H), 4.25 (q, *J* = 7.0 Hz, 2H), 1.26 (t, *J* = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 166.32, 146.00, 133.36, 127.90, 124.11, 120.21, 109.19, 62.32, 49.09, 14.04.

HRMS (ESI, m/z): Calcd. for $C_{10}H_{11}N_3O_2Na^+$, ([M+Na]$^+$): 228.0743; Found: 228.0745.

Preparation of methyl 2-(5-fluoro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-phenylacetate (19) and methyl 2-(6-fluoro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-phenylacetate (19')



To a solution of methyl phenyldiazoacetate (17.6 mg, 0.10 mmol) and 5-fluoro-1*H*-benzo[*d*][1,2,3]triazole (13.7 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45

°C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **19** and **19'** as a colorless oil (25.9 mg, 91% yield, 1:1).

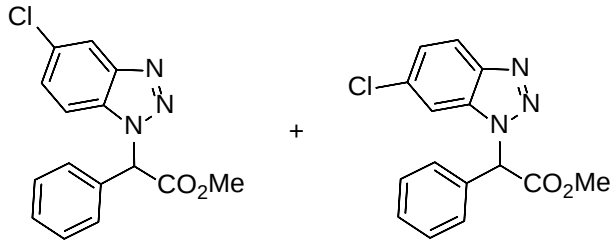
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.00 (dd, *J* = 4.5 Hz, 1H), 7.66 (dt, *J* = 8.0 Hz, 1.5Hz, 1H), 7.44 – 7.40 (m, 6H), 7.37 – 7.34 (m, 4H), 7.13 – 7.06 (m, 3H), 6.94 (s, 1H), 6.92 (s, 1H), 3.88 (s, 3H), 3.88 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.09, 168.07, 162.03 (d, $J_{C\text{-}F}$ = 248.6 Hz), 159.58 (d, $J_{C\text{-}F}$ = 244.2 Hz), 146.82 (d, $J_{C\text{-}F}$ = 12.1 Hz), 143.40, 132.95 (d, $J_{C\text{-}F}$ = 14.5 Hz), 131.96 (d, $J_{C\text{-}F}$ = 22.2 Hz), 129.64 (d, $J_{C\text{-}F}$ = 4.0 Hz), 129.51, 129.27 (d, $J_{C\text{-}F}$ = 5.1 Hz), 128.11, 128.07, 121.43 (d, *J* = 10.84 Hz), 117.58 (d, $J_{C\text{-}F}$ = 27.85 Hz), 114.17, 113.96, 112.31 (d, $J_{C\text{-}F}$ = 9.95 Hz), 104.62, 104.43, 97.33, 97.10, 65.95, 65.78, 53.22.

^{19}F NMR (471 MHz, $CDCl_3$) δ: -111.23, -117.74.

HRMS (ESI, *m/z*): Calcd. for $C_{15}H_{12}FN_3O_2Na^+$, ([M+Na]$^+$): 308.0806; Found: 308.0807.

Preparation of methyl 2-(5-chloro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-phenylacetate (20) and methyl 2-(6-chloro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-phenylacetate (20')



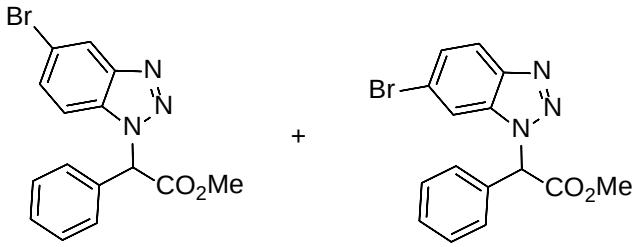
To a solution of methyl phenyldiazoacetate (17.6 mg, 0.10 mmol) and 5-chloro-1*H*-benzo[*d*][1,2,3]triazole (15.4 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **20** and **20'** as a white solid (27.7 mg, 92% yield, 1.4:1).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.02 (d, *J* = 2.0 Hz, 0.41H), 7.96 (d, *J* = 8.5 Hz, 0.59H), 7.43 – 7.27 (m, 5.1H), 7.30 – 7.27 (m, 0.9H), 7.17 (d, *J* = 2.0 Hz, 0.59H), 7.09 (d, *J* = 9.0 Hz, 0.41H), 6.94 (s, 0.41H), 6.91 (s, 0.59H), 3.89 (s, 1.77H), 3.88 (s, 1.23H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.00, 147.20, 145.12, 134.03, 133.09, 131.97, 131.89, 131.22, 129.91, 129.68, 129.64, 129.30, 129.25, 128.52, 128.11, 128.05, 125.28, 120.93, 119.37, 112.25, 111.04, 65.91, 65.78, 53.26, 53.23.

HRMS (ESI, *m/z*): Calcd. for $C_{15}H_{13}Cl^{34.9689}N_3O_2^+$, ([M+H]$^+$): 302.0691; Found: 302.0693; $C_{15}H_{13}Cl^{35.4500}N_3O_2^+$, ([M+H]$^+$): 304.0661; Found: 304.0661.

Preparation of methyl 2-(5-bromo-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-phenylacetate (21) and methyl 2-(6-bromo-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-phenylacetate (21')



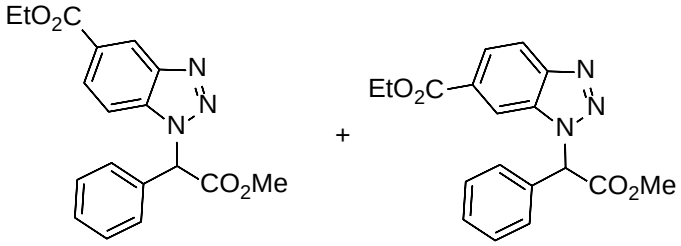
To a solution of methyl phenyldiazoacetate (17.6 mg, 0.10 mmol) and 5-bromo-1*H*-benzo[*d*][1,2,3]triazole (19.8 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **21** and **21'** as a white solid (31.5 mg, 91% yield, 1.5:1).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.20 (d, *J* = 1.5 Hz, 0.4H), 7.90 (d, *J* = 8.5 Hz, 0.6H), 7.44 – 7.40 (m, 4H), 7.38 – 7.33 (m, 2.6H), 7.04 (d, *J* = 8.5 Hz, 0.4H), 6.94 (s, 0.4H), 6.90 (s, 0.6H), 3.89 (s, 1.8H), 3.88 (s, 1.2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 167.98, 147.72, 145.38, 133.54, 131.95, 131.88, 131.50, 130.95, 129.69, 129.65, 129.30, 129.26, 128.12, 128.05, 127.80, 122.63, 122.06, 121.17, 117.29, 114.12, 112.57, 65.91, 65.78, 53.27, 53.24.

HRMS (ESI, m/z): Calcd. for $C_{15}H_{12}Br^{79.9183}N_3O_2Na^+$, ([M+Na]$^+$): 368.0005, Found: 368.0009; $C_{15}H_{12}Br^{80.9163}N_3O_2Na^+$ ([M+Na]$^+$): 369.9985; Found: 369.9987.

Preparation of ethyl 1-(2-methoxy-2-oxo-1-phenylethyl)-1*H*-benzo[*d*][1,2,3]triazole-5-carboxylate (22) and ethyl 1-(2-methoxy-2-oxo-1-phenylethyl)-1*H*-benzo[*d*][1,2,3]triazole-6-carboxylate (22')



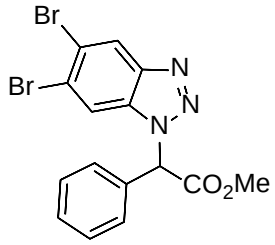
To a solution of methyl phenyldiazoacetate (17.6 mg, 0.10 mmol) and ethyl 1*H*-benzo[*d*][1,2,3]triazole-5-carboxylate (19.1 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **22** and **22'** as a colorless oil (29.2 mg, 86% yield, 1.7:1).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.78 (t, *J* = 1.5 Hz, 0.37H), 8.09 – 8.06 (m, 0.63H), 8.04 – 7.98 (m, 1H), 7.92 (t, *J* = 1.5 Hz, 0.63H), 7.45 – 7.35 (m, 5H), 7.19 – 7.16 (m, 0.37H), 6.96 (s, 0.37H), 6.93 (s, 0.63H), 4.42 – 4.33 (m, 2H), 3.88 (s, 3H), 1.42 – 1.36 (m, 3H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 167.98, 167.93, 165.89, 165.82, 148.36, 146.33, 134.81, 132.41, 131.98, 131.95, 129.74, 129.72, 129.64, 129.25, 128.42, 128.35, 128.15, 126.76, 124.68, 122.80, 119.87, 113.51, 111.03, 65.88, 65.84, 61.45, 61.29, 53.31, 53.25, 14.27, 14.21.

HRMS (ESI, m/z): Calcd. for $C_{18}H_{18}N_3O_4^+$, ($[M+H]^+$): 340.1292, Found: 340.1284.

Preparation of methyl 2-(5-fl-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-phenylacetate (23)



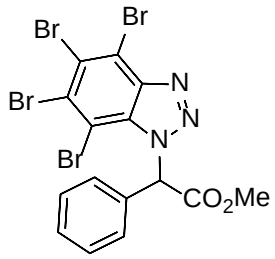
To a solution of methyl phenyldiazoacetate (17.6 mg, 0.10 mmol) and 5,6-dibromo-1*H*-benzo[*d*][1,2,3]triazole (27.7 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **23** as a white solid (34.1 mg, 80% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.35 (s, 1H), 7.50 (s, 1H), 7.46 – 7.42 (m, 3H), 7.37 – 7.33 (m, 2H), 6.91 (s, 1H), 3.90 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 167.86, 146.51, 132.37, 131.61, 129.88, 129.42, 128.06, 124.61, 124.19, 120.17, 115.80, 65.97, 53.36.

HRMS (ESI, m/z): Calcd. for $C_{15}H_{12}Br_2{}^{79.9183}N_3O_2Na^+$, ($[M+H]^+$): 423.9291, Found: 423.9291; $C_{15}H_{12}Br_2{}^{80.9163}N_3O_2^+$ ($[M+H]^+$): 425.9270; Found: 425.9271.

Preparation of methyl 2-(perbromo-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-phenylacetate (24)



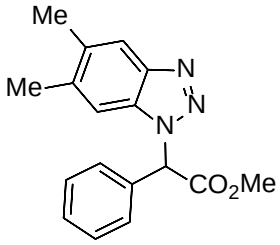
To a solution of methyl phenyldiazoacetate (17.6 mg, 0.10 mmol) and 4,5,6,7-tetrabromo-1*H*-benzo[*d*][1,2,3]triazole (43.4 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 2 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **24** as a white solid (46.6 mg, 80% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.50 – 7.47 (m, 2H), 7.44 – 7.40 (m, 3H), 7.35 (s, 1H), 3.82 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 167.79, 145.47, 132.52, 131.85, 130.00, 129.57, 129.37, 128.96, 124.74, 117.20, 105.49, 65.66, 53.64.

HRMS (ESI, m/z): Calcd. for $C_{15}H_9Br_4^{79.9183}N_3O_2Na^+$, ([M+Na]$^+$): 603.7300; Found: 603.7304; $C_{15}H_9Br_4^{80.9163}N_3O_2Na^+$ ([M+Na]$^+$): 605.7280; Found: 605.7285.

Preparation of methyl 2-(5-fl-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-phenylacetate (25)



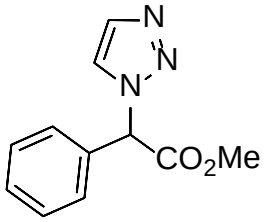
To a solution of methyl phenyldiazoacetate (17.6 mg, 0.10 mmol) and 5,6-dimethyl-1*H*-benzo[*d*][1,2,3]triazole (13.3 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **25** as a white solid (24.9 mg, 84% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.78 (s, 1H), 7.41 – 7.35 (m, 5H), 6.95 (s, 1H), 6.87 (s, 1H), 3.86 (s, 3H), 2.35 (s, 3H), 2.29 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.29, 145.61, 137.97, 133.89, 132.56, 131.58, 129.29, 129.03, 128.12, 119.05, 110.39, 65.50, 53.09, 20.96, 20.29.

HRMS (ESI, *m/z*): Calcd. for $C_{17}H_{17}N_3O_2Na^+$, ([M+Na]$^+$): 318.1213; Found: 318.1212.

Preparation of methyl 2-(5-fl-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-phenylacetate (26)



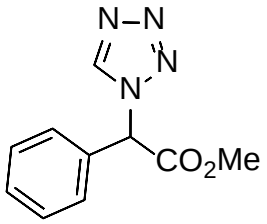
To a solution of methyl phenyldiazoacetate (17.6 mg, 0.10 mmol) and triazole (6.9 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 48 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **26** as a colorless oil (16.1 mg, 74% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.69 (s, 2H), 7.44 – 7.41 (m, 3H), 7.40 – 7.37 (m, 2H), 6.63 (s, 1H), 3.84 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 168.16, 133.82, 132.93, 129.81, 129.47, 127.97, 123.50, 65.80, 53.25.

HRMS (ESI, *m/z*): Calcd. for $C_{11}H_{11}N_3O_2Na^+$, ([M+Na]$^+$): 240.0743; Found: 240.0744.

Preparation of methyl 2-(5-fl-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-phenylacetate (27)



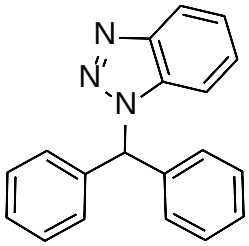
To a solution of methyl phenyldiazoacetate (17.6 mg, 0.10 mmol) and tetrazole (7.0 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 1 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **27** as a colorless oil (14.0 mg, 64% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.55 (s, 1H), 7.59 – 7.56 (m, 2H), 7.47 – 7.43 (m, 3H), 6.72 (s, 1H), 3.82 (s, 3H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$), δ: 166.82, 153.02, 131.19, 130.08, 129.34, 129.14, 68.80, 53.58.

HRMS (ESI, *m/z*): Calcd. for $C_{10}H_{10}N_4O_2Na^+$, ($[M+Na]^+$): 241.0696; Found: 241.0695.

Preparation of antimicrobial activity reagent 1-benzhydryl-1*H*-benzo[*d*][1,2,3]triazole (28)



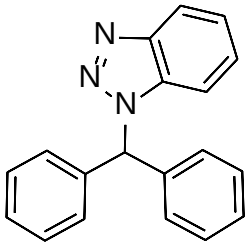
To a solution of 1,1-diphenyldiazomethane (19.4 mg, 0.10 mmol) and benzotriazole (12.0 mg, 0.10 mmol) in DCM (0.6 mL) was added a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in DCM (0.4 mL). The reaction was complete after 4 hours at 45 °C. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 8/1) on silica gel to afford the product **28** as a white solid (23.8 mg, 84% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.11 – 8.06 (m, 1H), 7.39 (s, 1H), 7.38 – 7.31 (m, 8H), 7.24 – 7.20 (m, 4H), 7.12 – 7.08 (m, 1H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$), δ: 146.29, 137.66, 133.02, 128.78, 128.43, 128.29, 127.32, 123.85, 120.15, 110.55, 67.14.

HRMS (ESI, *m/z*): Calcd. for $C_{19}H_{15}N_3Na^+$, ($[M+Na]^+$): 308.1158; Found: 308.1155.

Gram-scale of antimicrobial activity reagent 1-benzhydryl-1*H*-benzo[*d*][1,2,3]triazole (28)



^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.11 – 8.06 (m, 1H), 7.39 (s, 1H), 7.37 – 7.31 (m, 8H), 7.25 – 7.20 (m, 4H), 7.11 – 7.07 (m, 1H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 146.31, 137.67, 133.03, 128.80, 128.44, 128.31, 127.34, 123.87, 120.18, 110.56, 67.16.

References

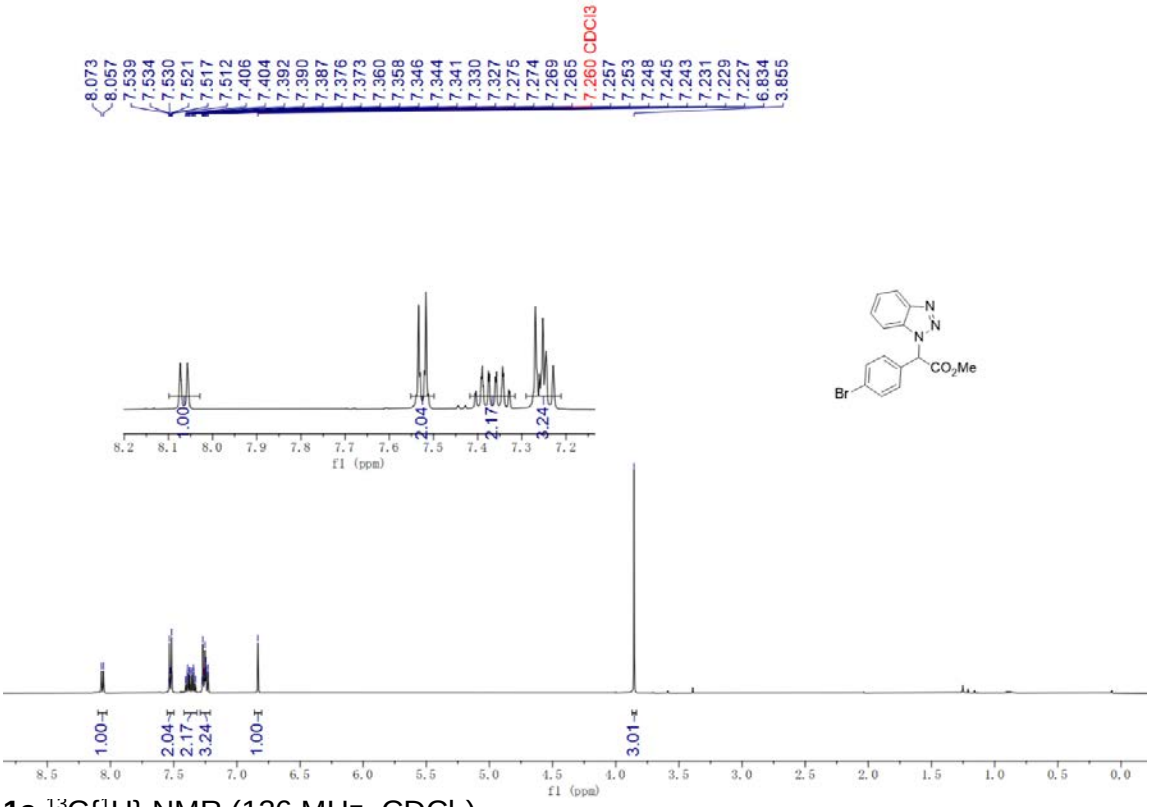
1 S. Lee, G.-S. Hwang and D. H. Ryu, *J. Am. Chem. Soc.*, **2013**, *135*, 7126.

2 G. M. Sheldrick, *Acta Crystallographica Section A* **2008**, *64*, 112.

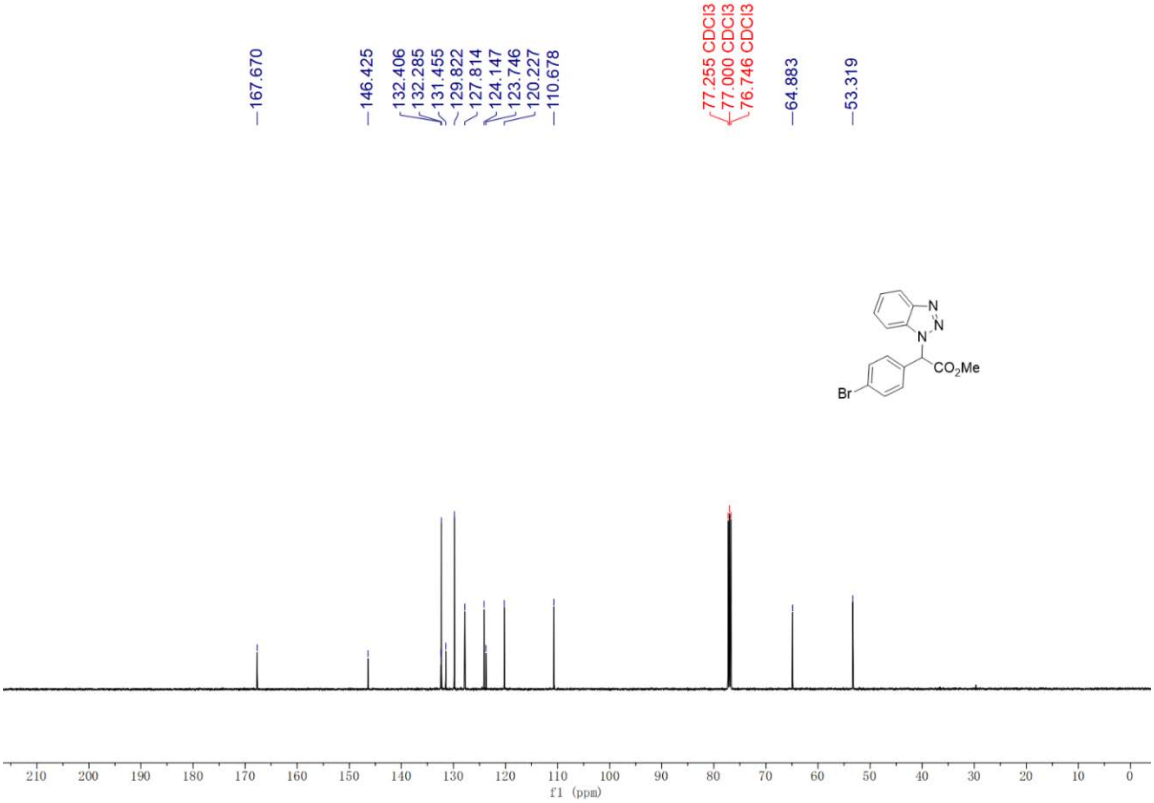
3 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.

NMR spectra of isolated compounds

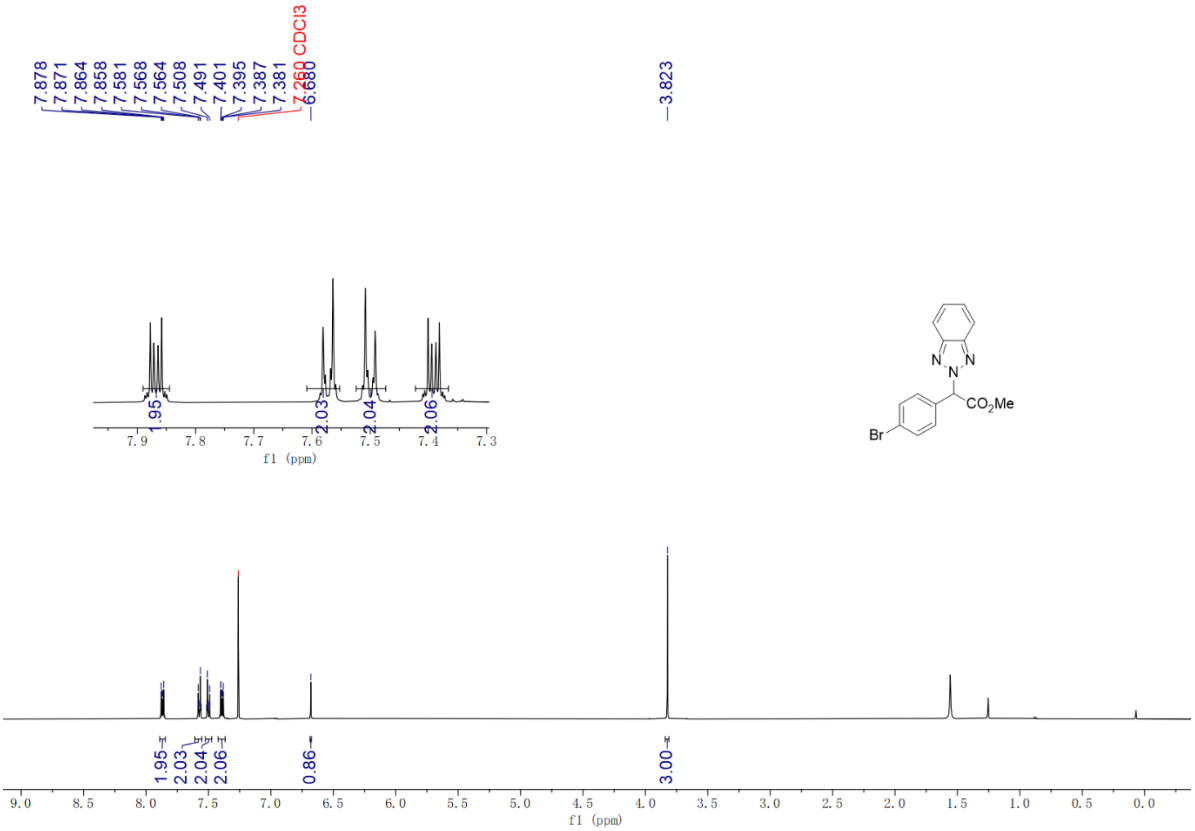
1a ^{1}H NMR (500 MHz, $CDCl_3$)



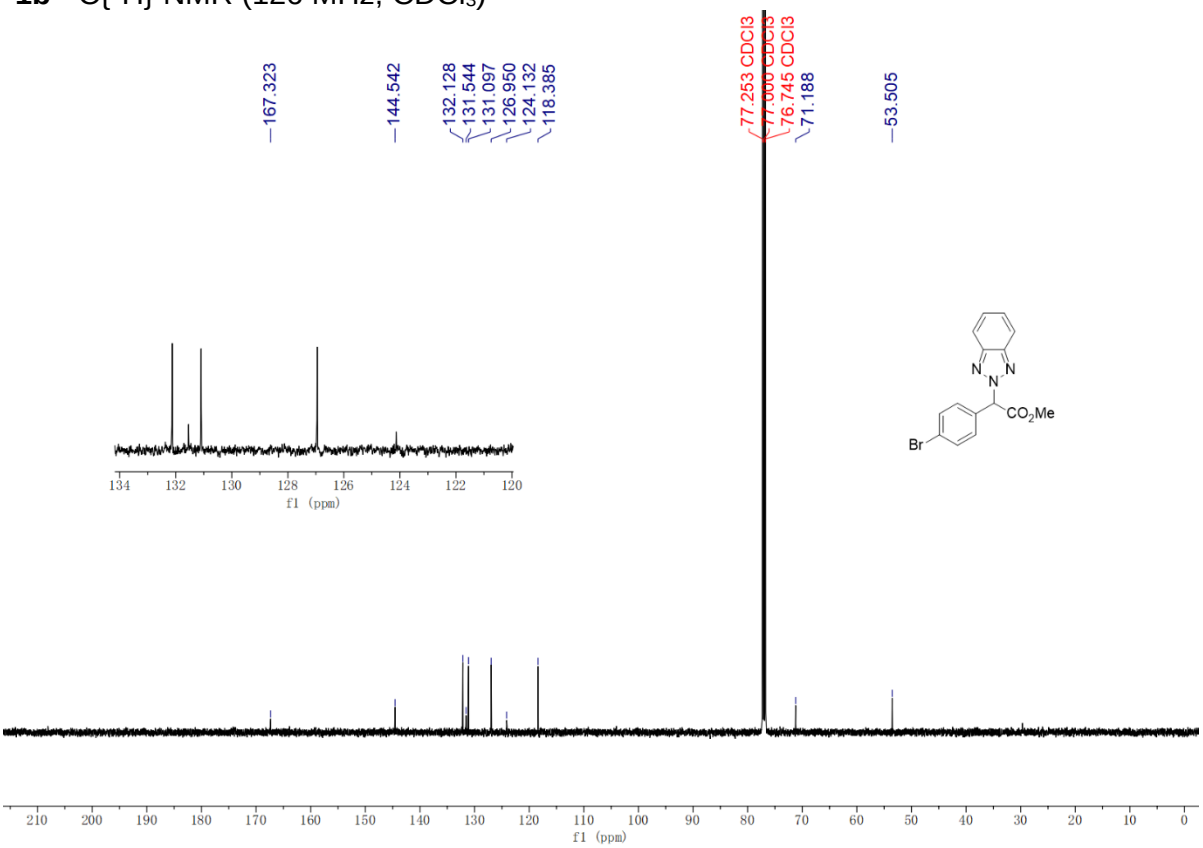
1a ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



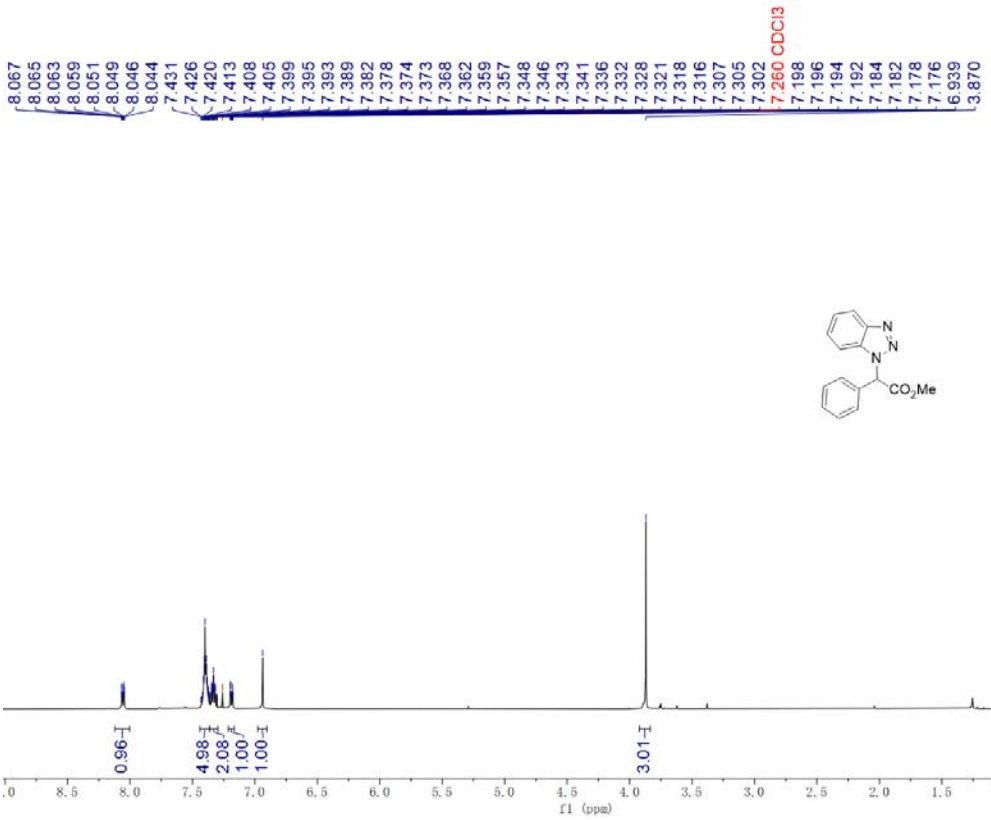
1b ^{1}H NMR (500 MHz, $CDCl_3$)



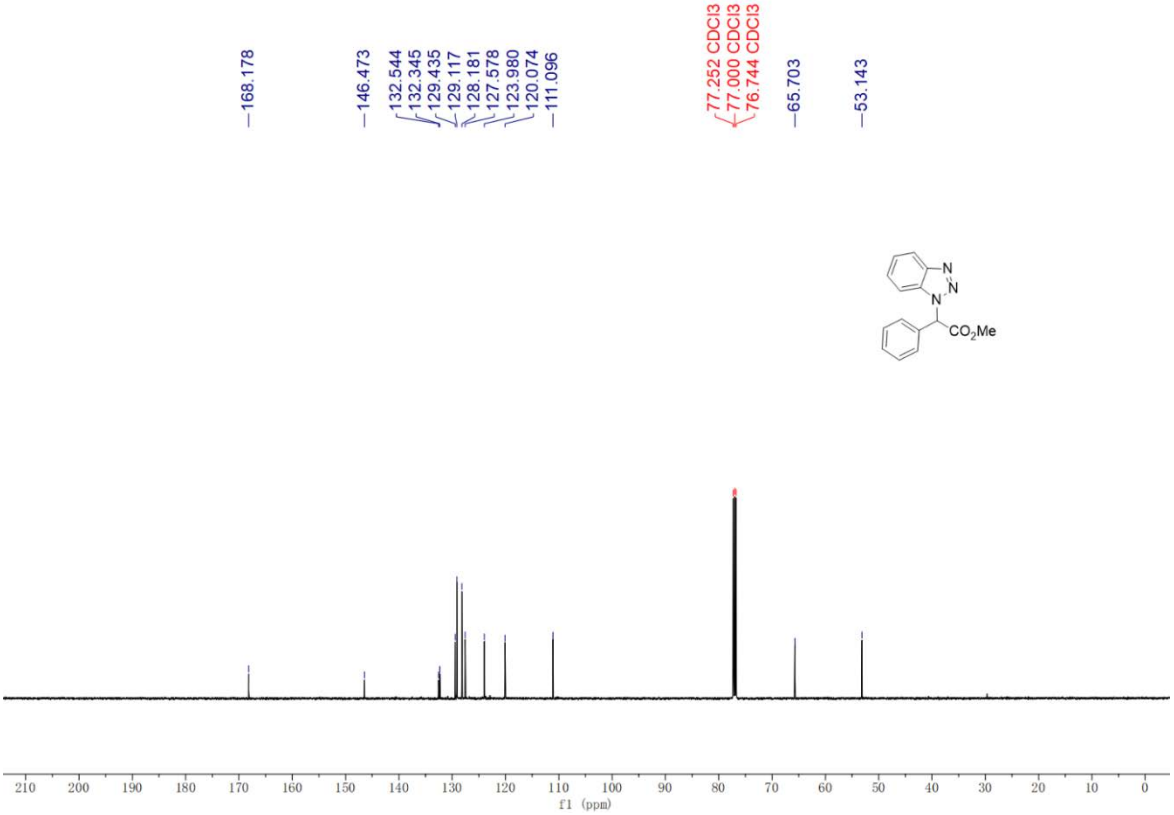
1b ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



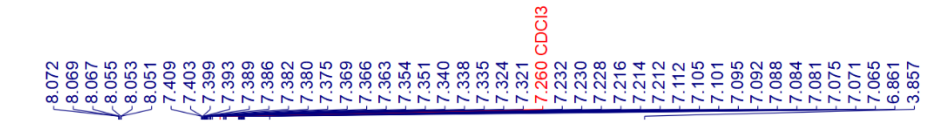
2 ^{1}H NMR (500 MHz, $CDCl_3$)

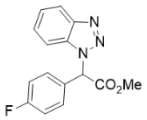


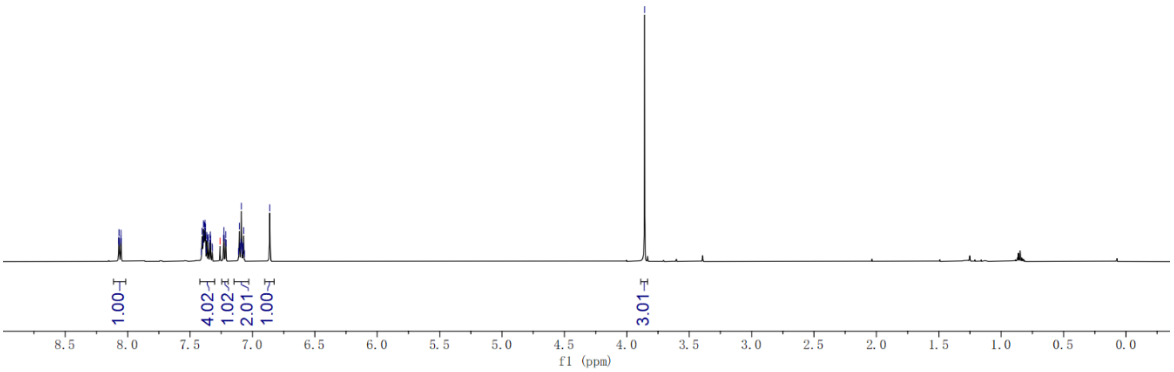
2 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



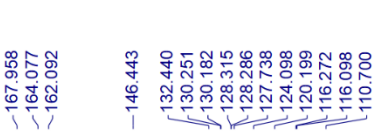
3 ^{1}H NMR (500 MHz, $CDCl_3$)

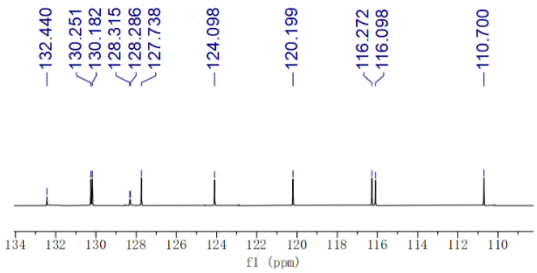


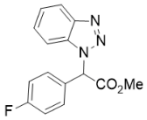


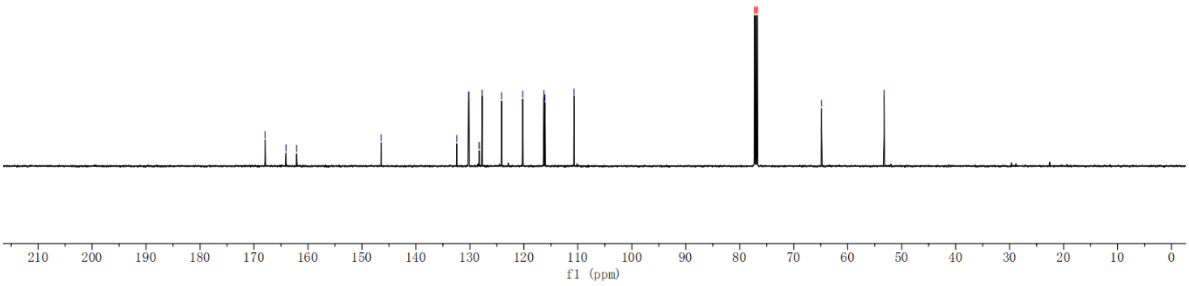


3 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

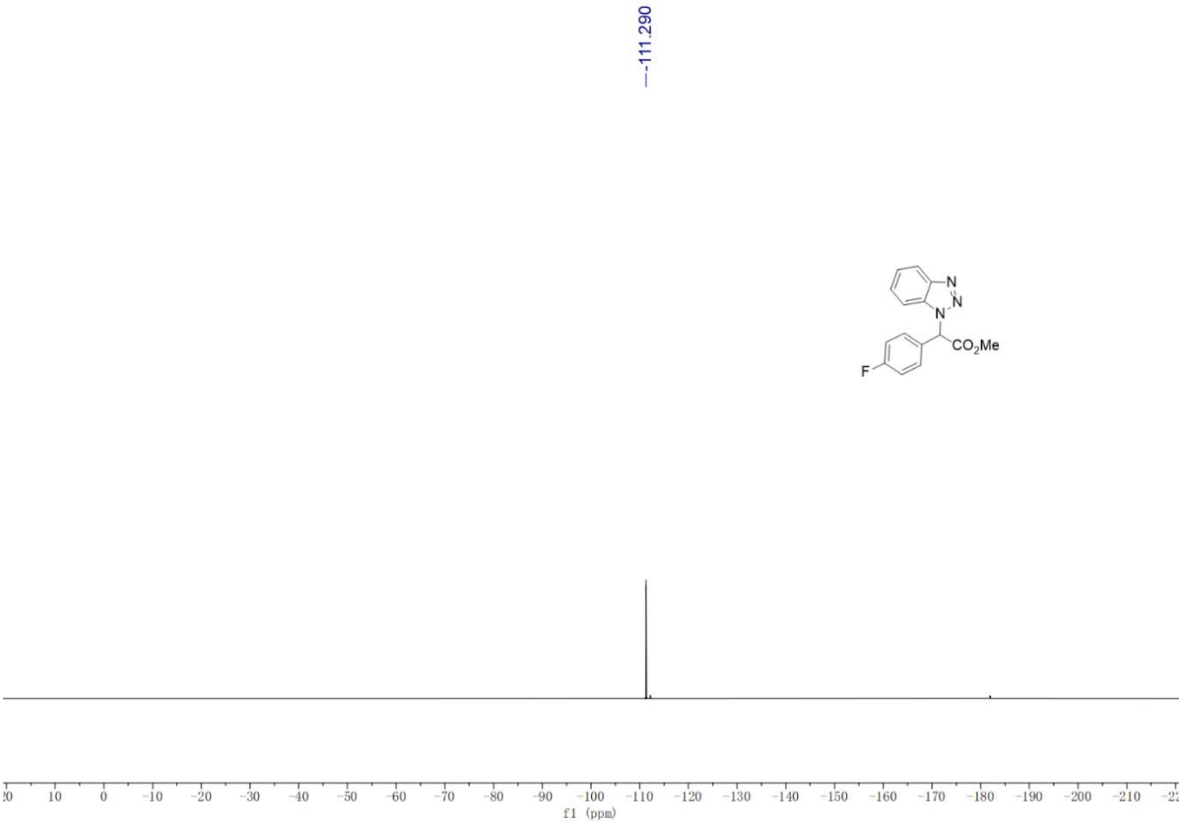




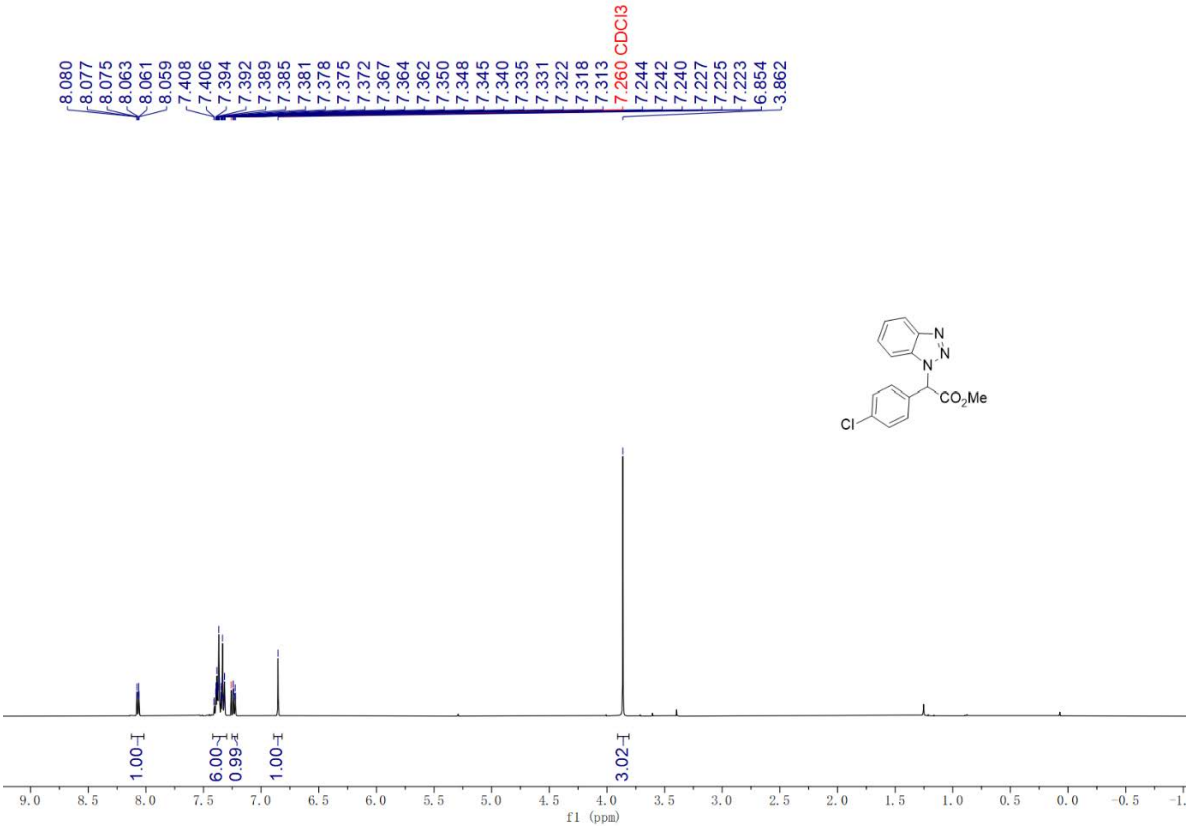




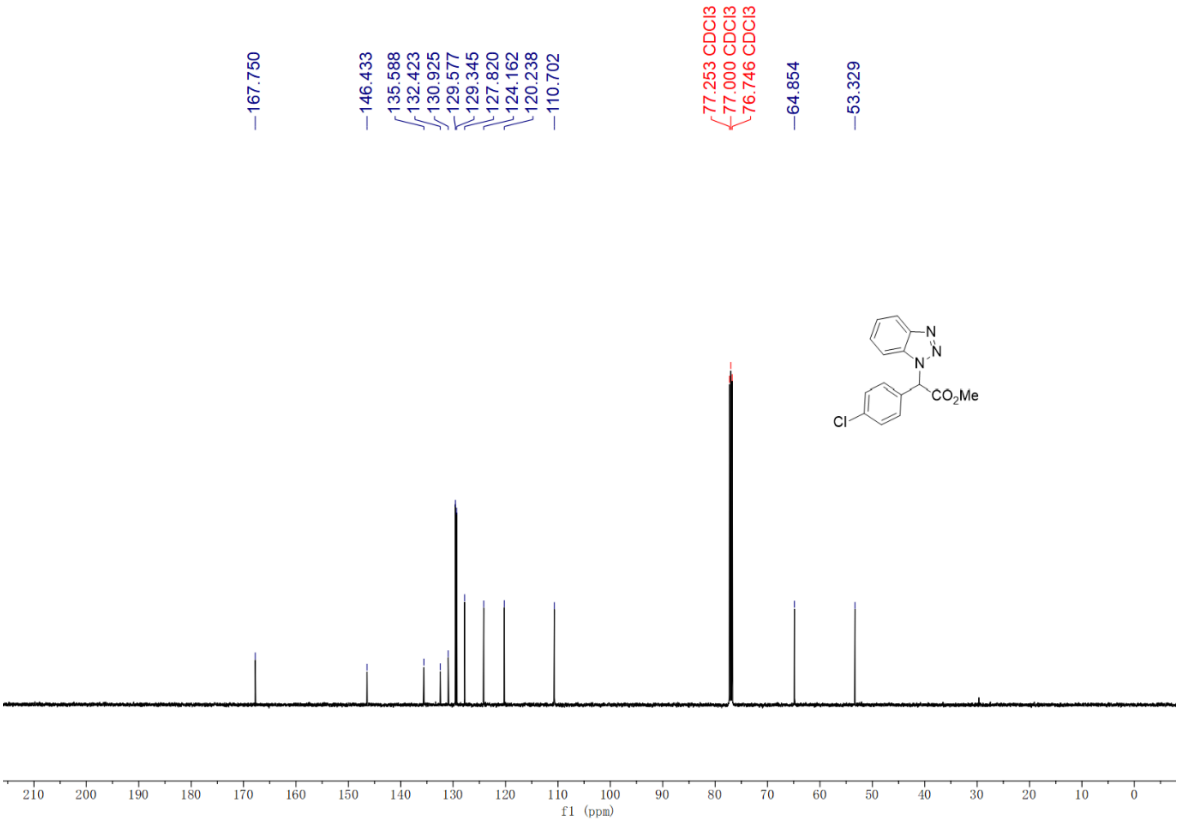
3 $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



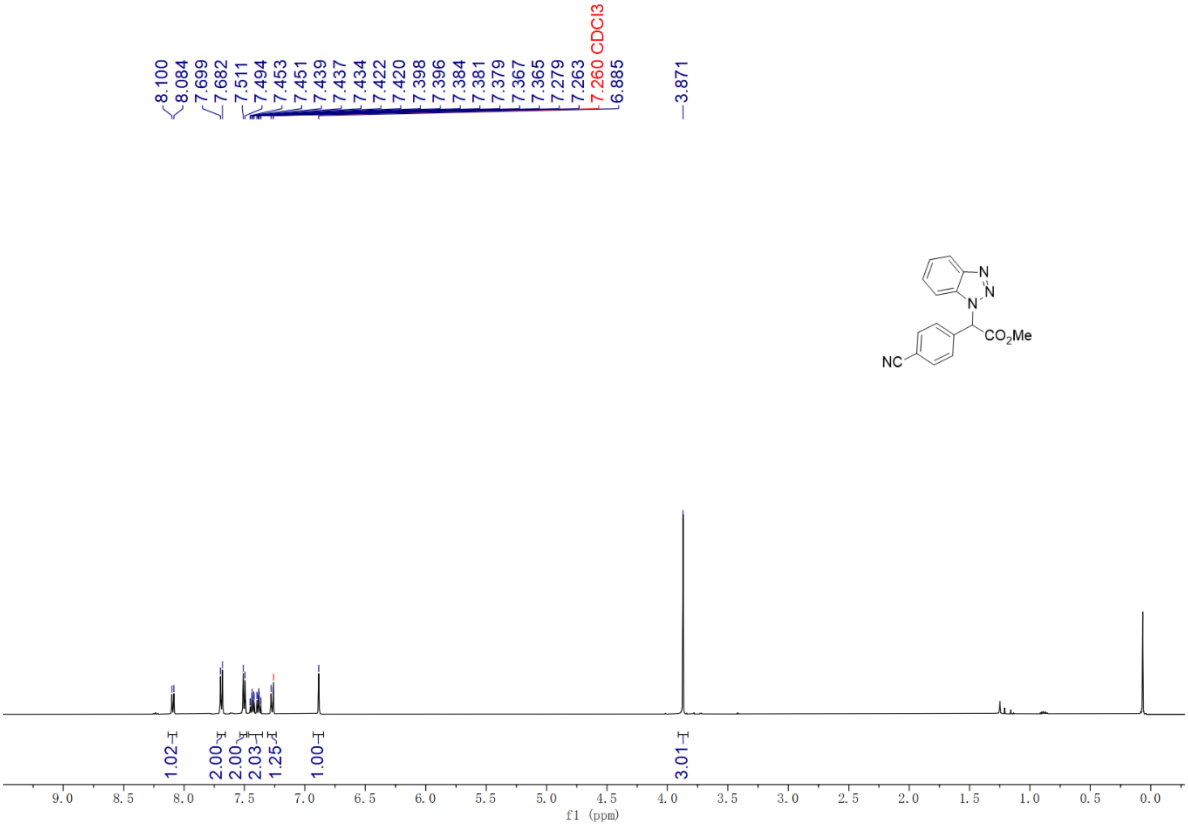
4 ^{1}H NMR (500 MHz, $CDCl_3$)



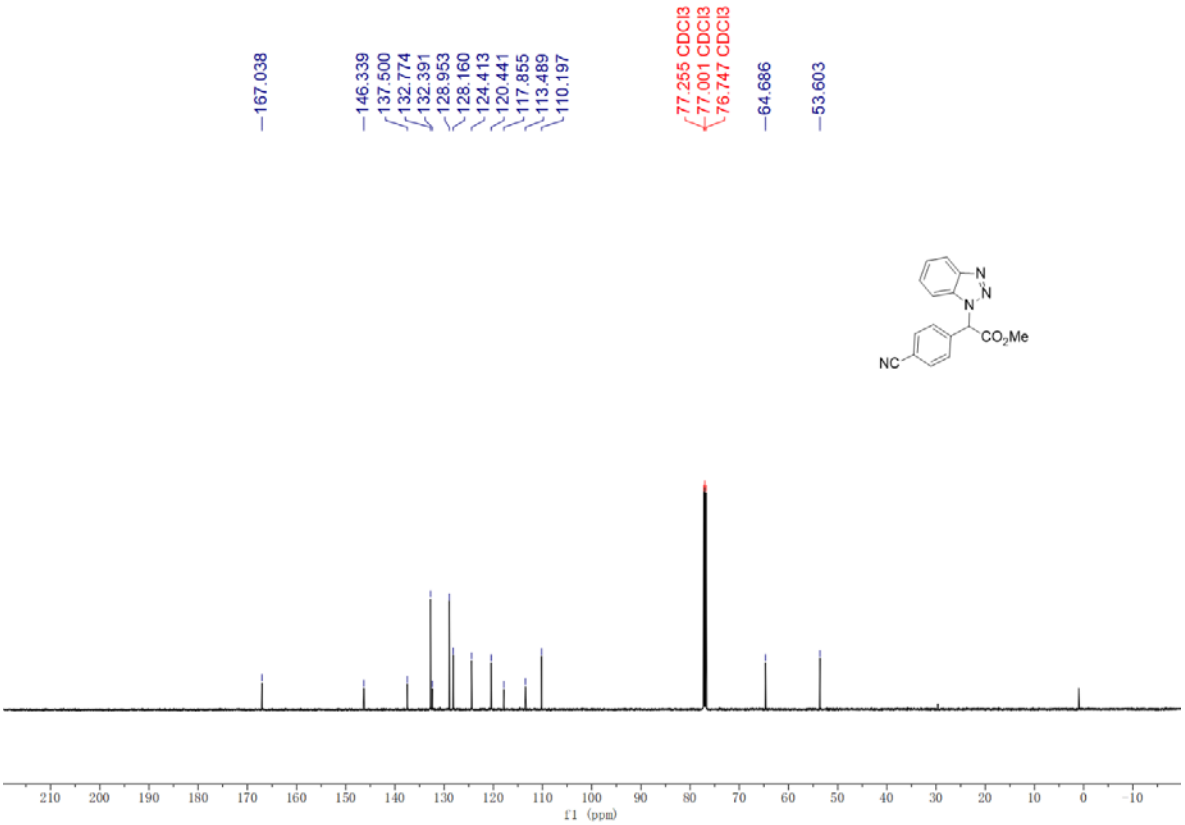
4 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



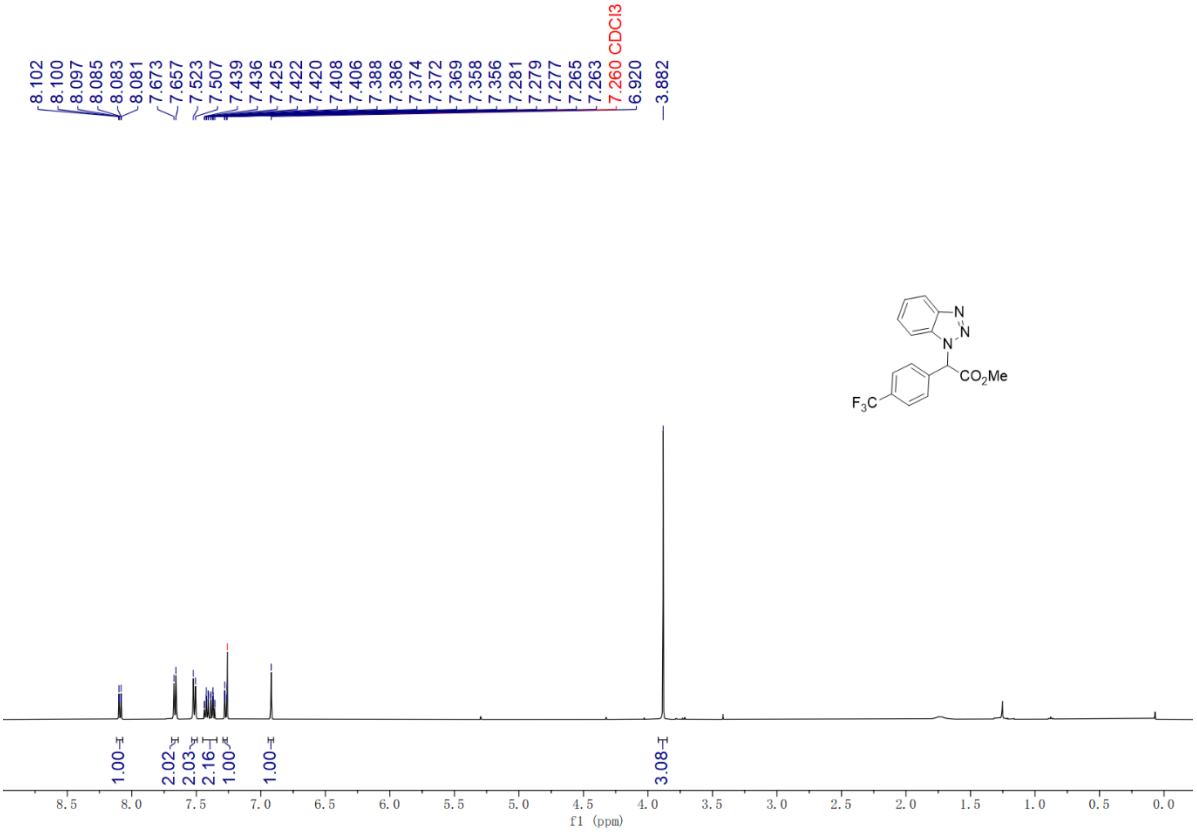
5 ^{1}H NMR (500 MHz, $CDCl_3$)



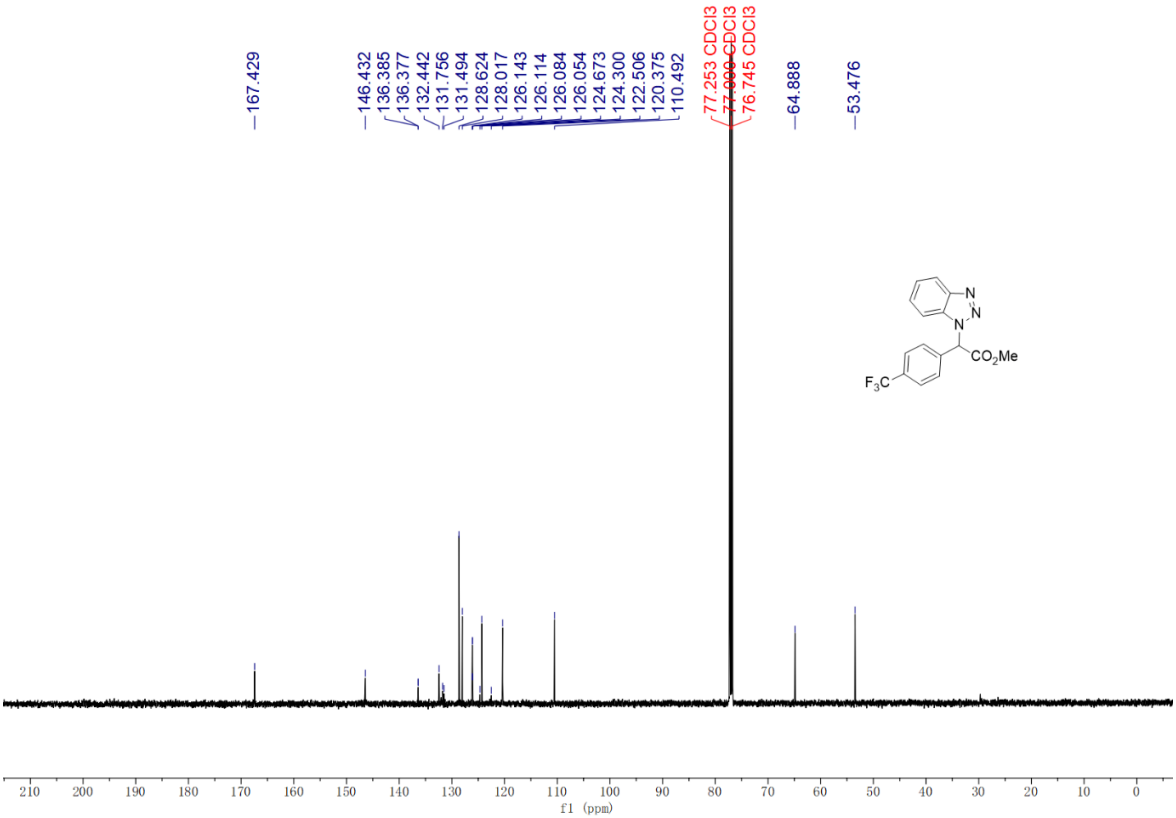
5 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



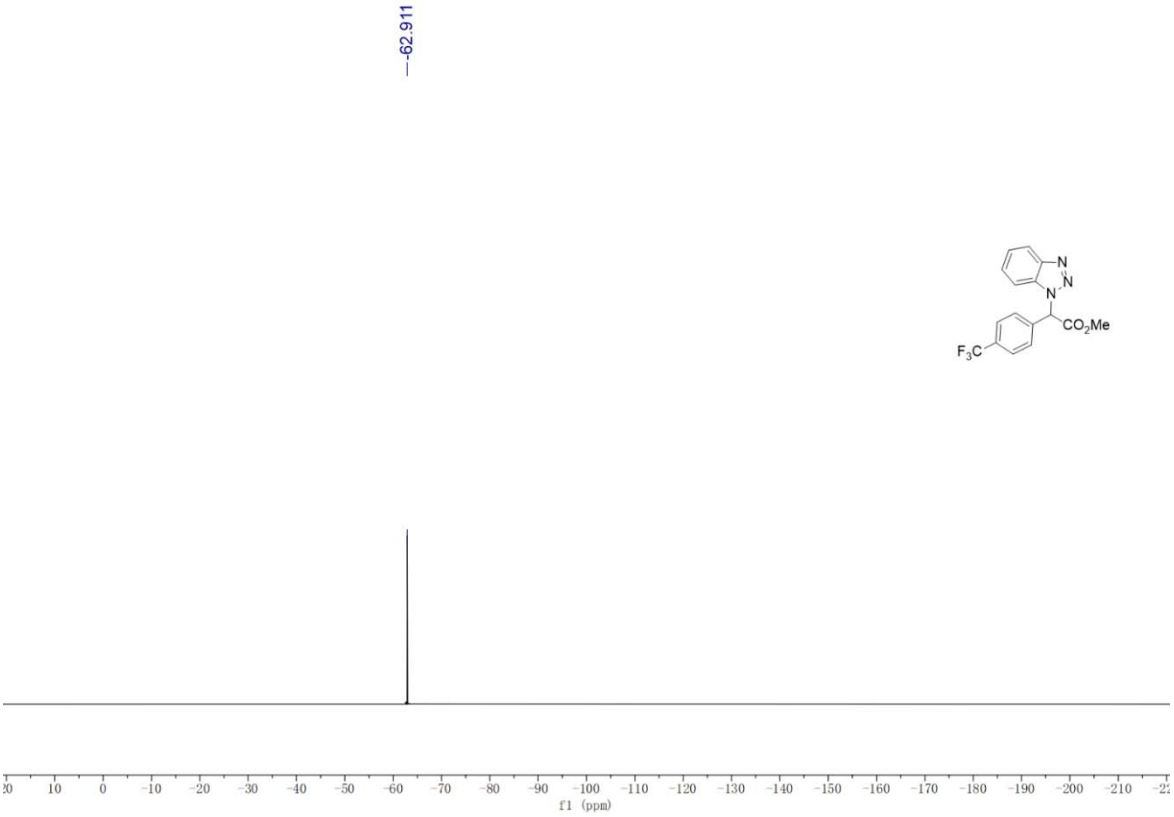
6 ^{1}H NMR (500 MHz, $CDCl_3$)



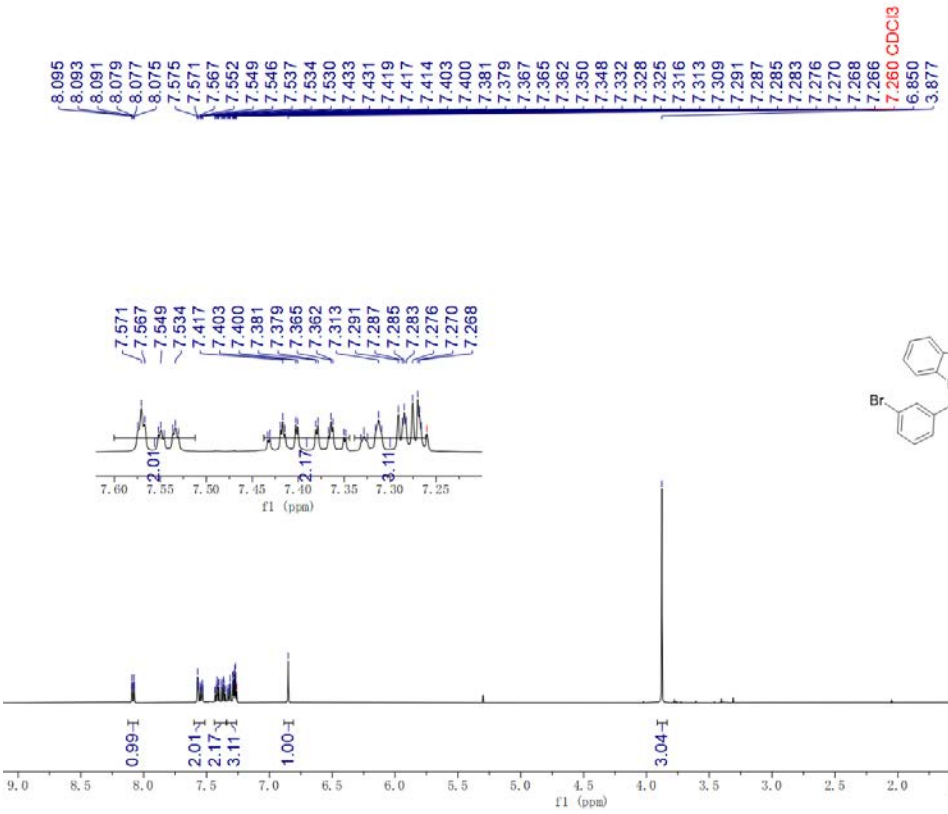
6 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



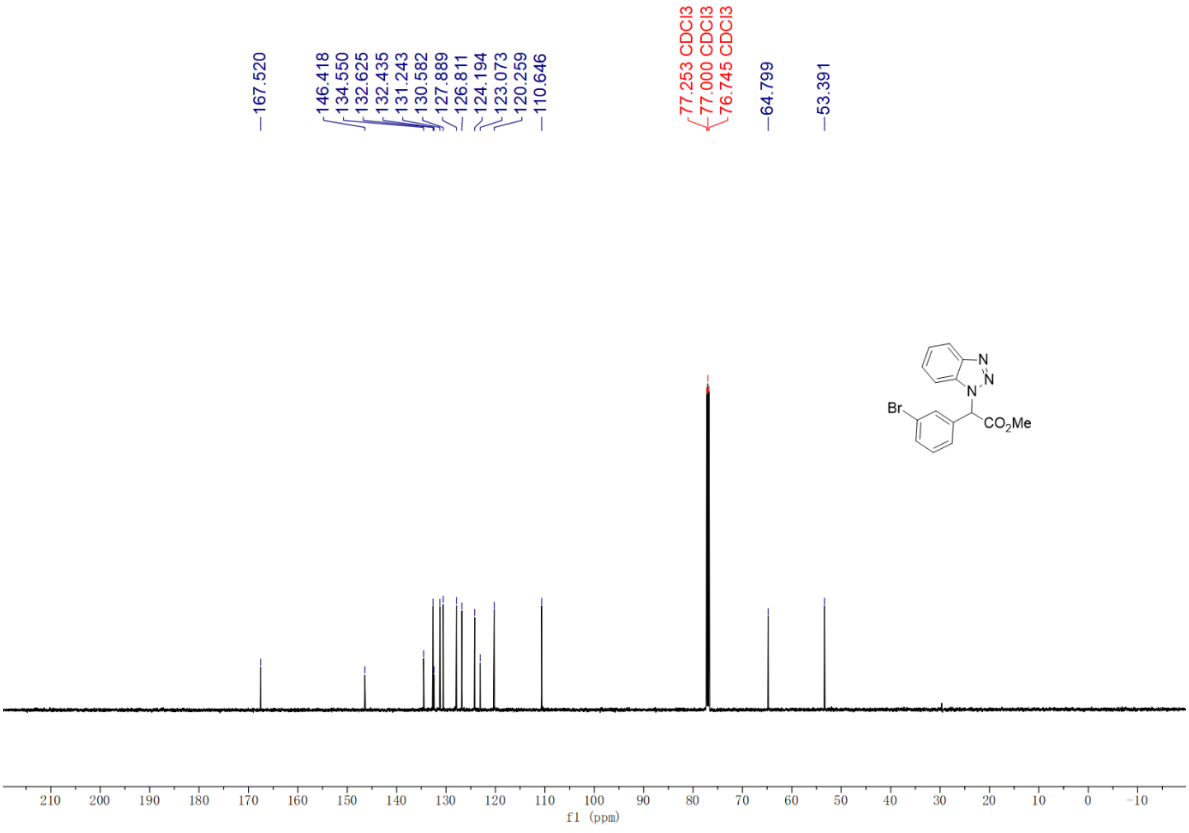
6 $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



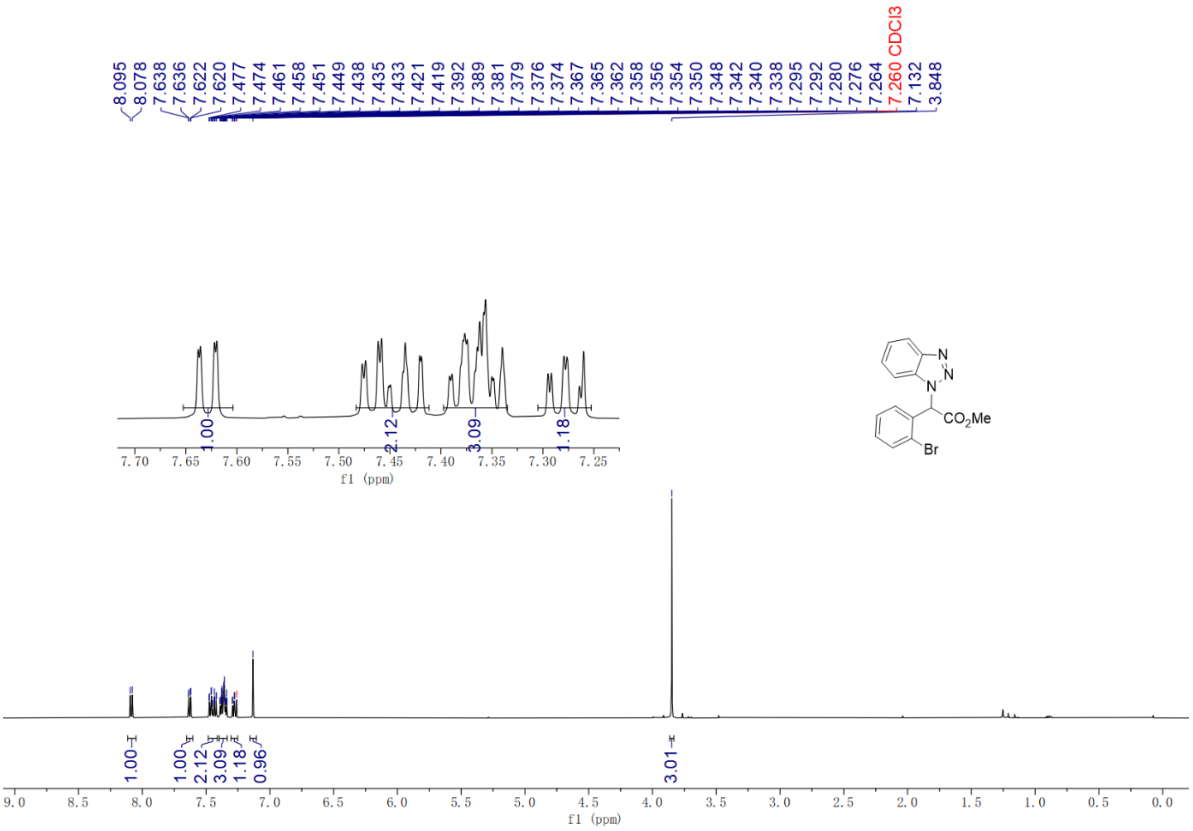
7 ^{1}H NMR (500 MHz, $CDCl_3$)



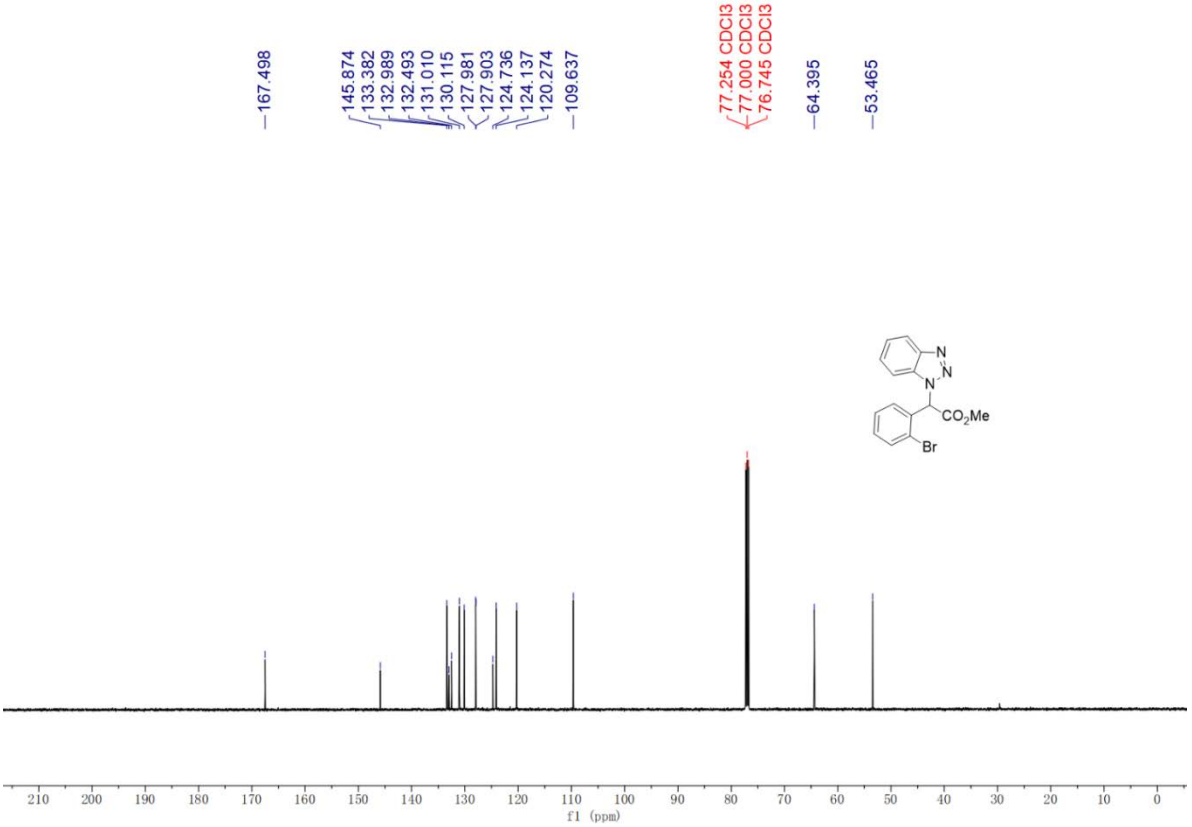
7 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



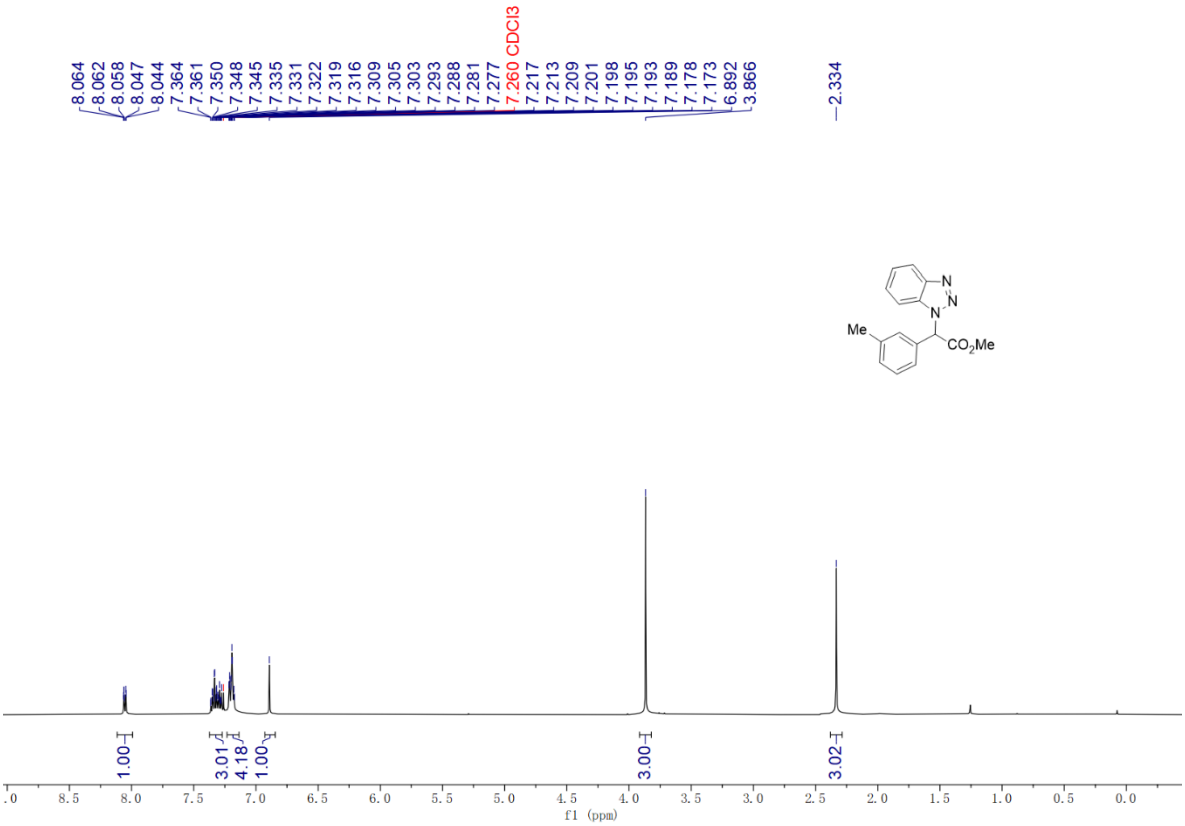
8 ^{1}H NMR (500 MHz, $CDCl_3$)



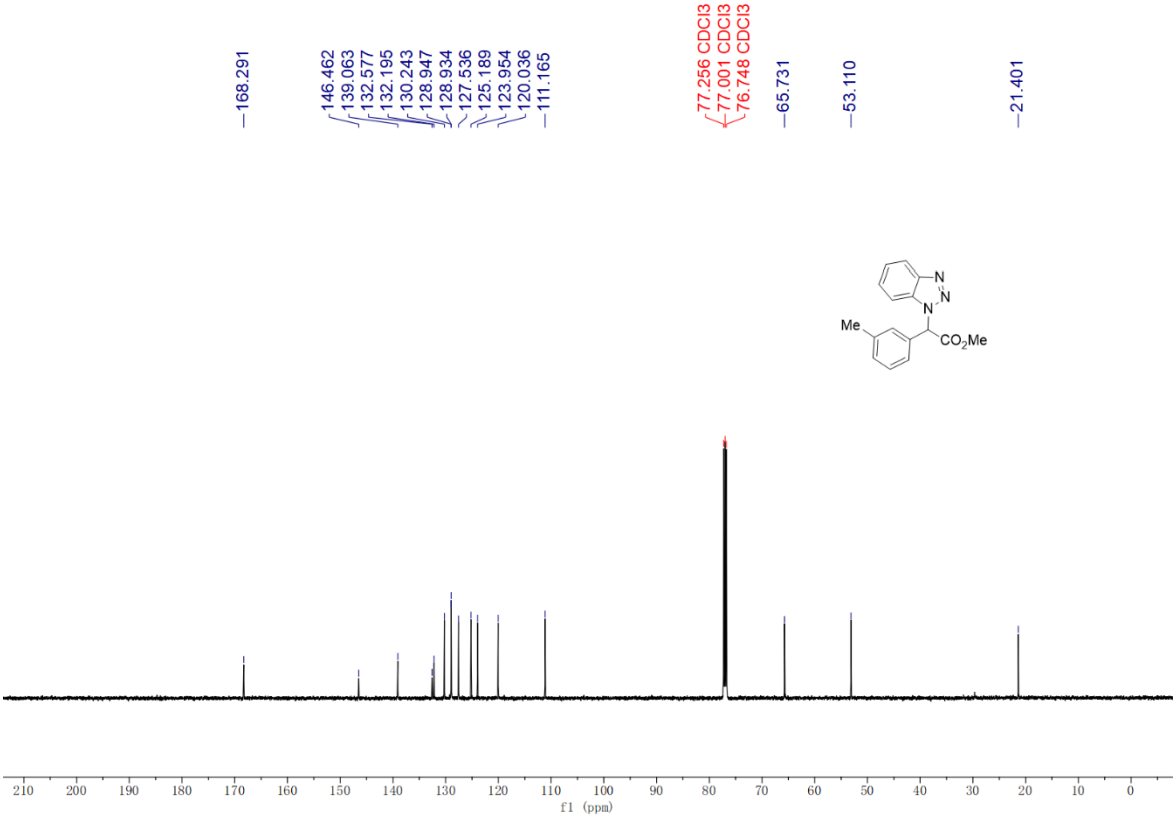
8 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



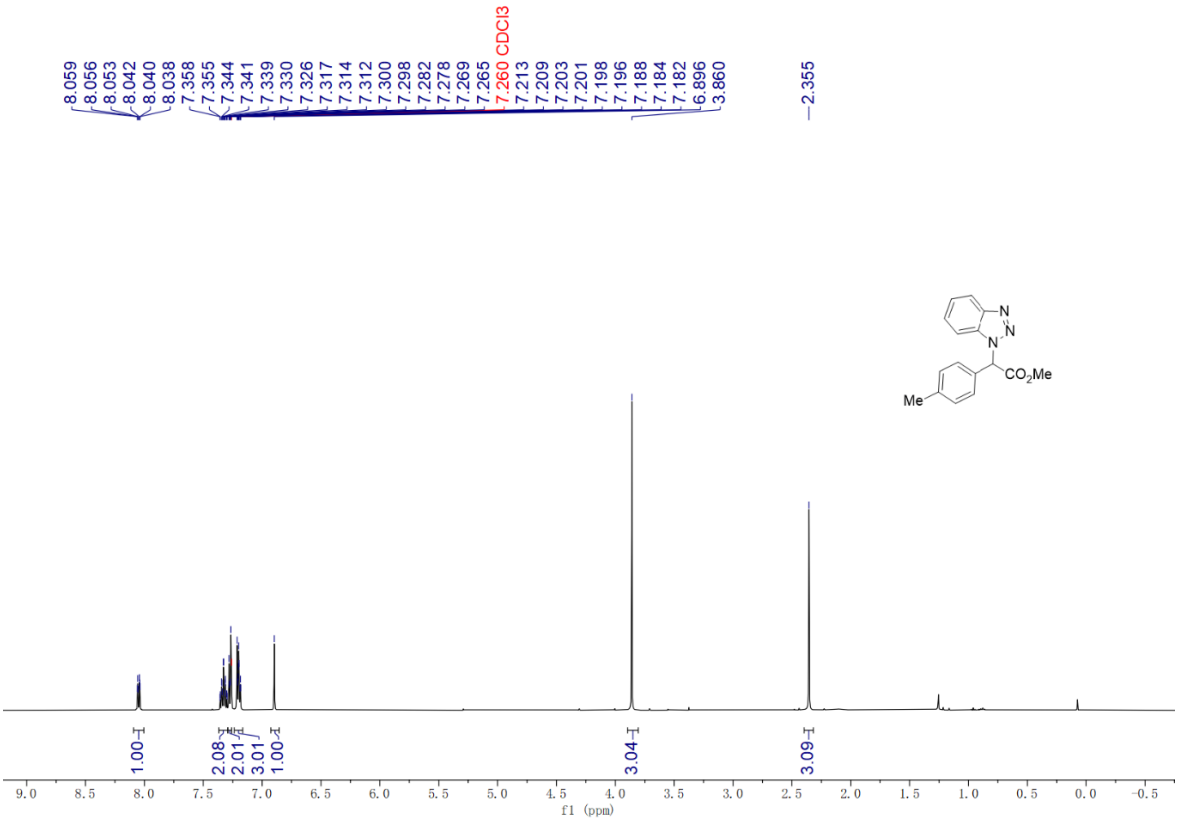
9 ^{1}H NMR (500 MHz, $CDCl_3$)



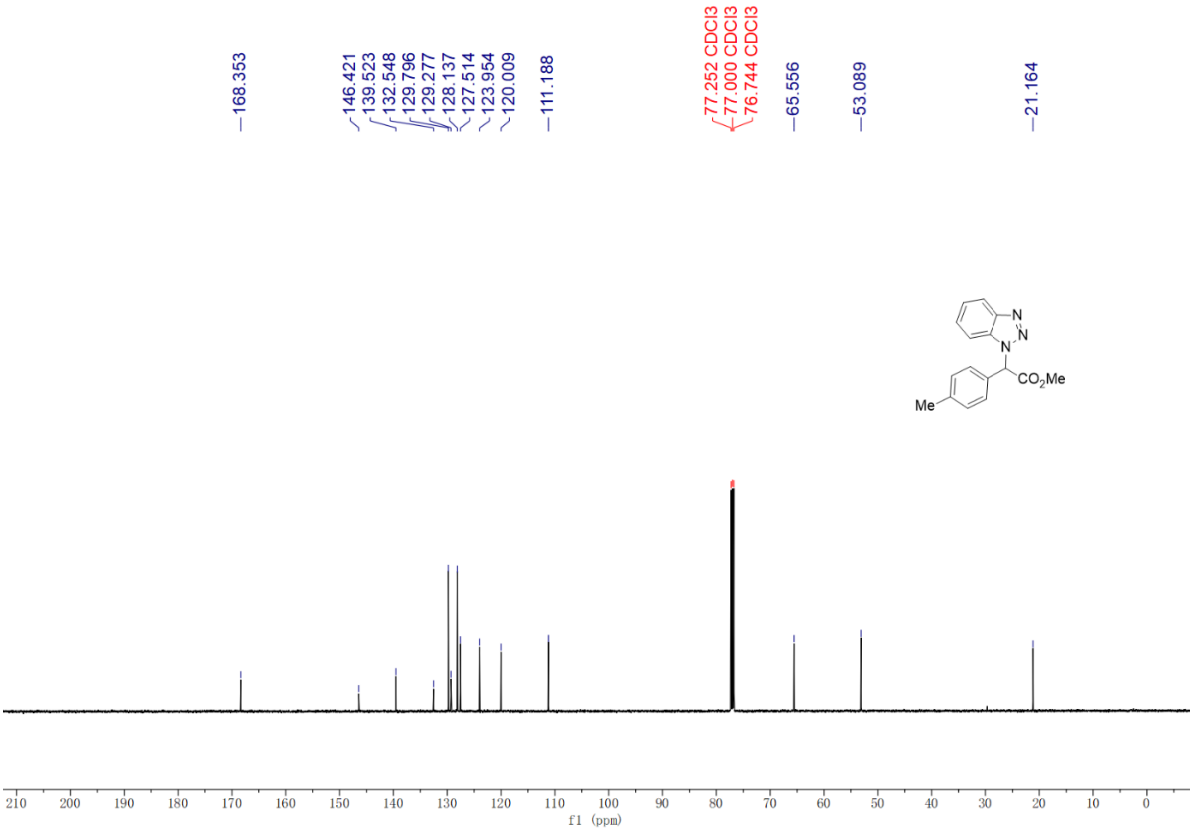
9 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



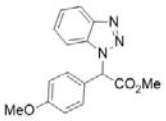
10 ^{1}H NMR (500 MHz, $CDCl_3$)

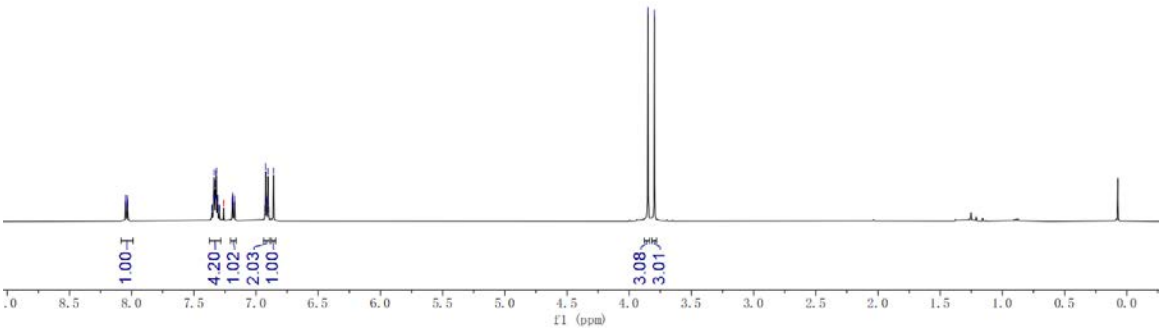


10 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

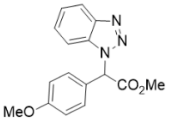


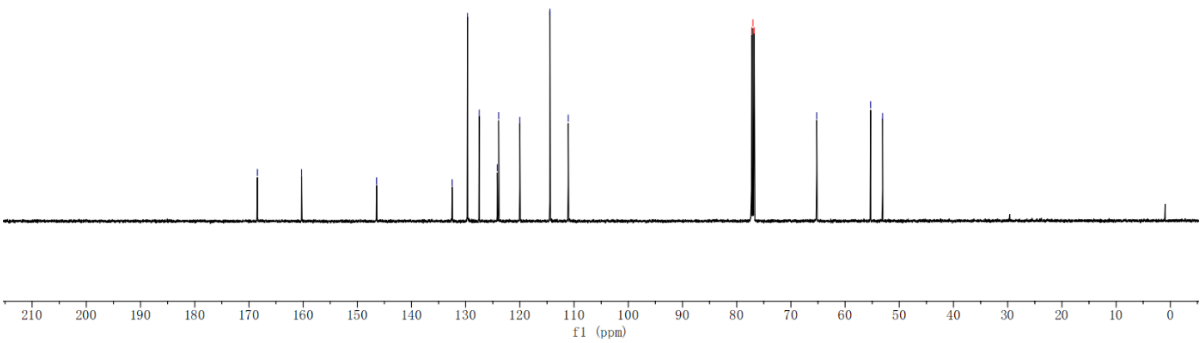
11 ^{1}H NMR (500 MHz, $CDCl_3$)



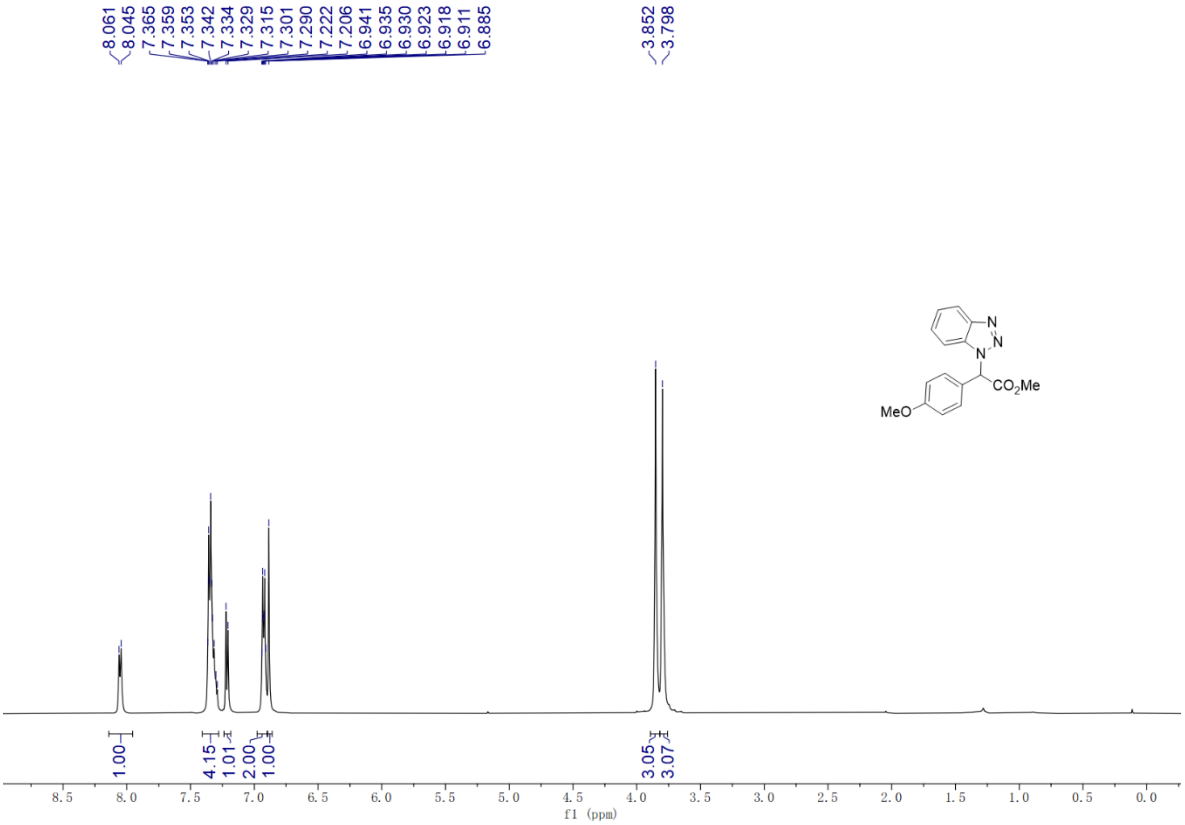


11 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

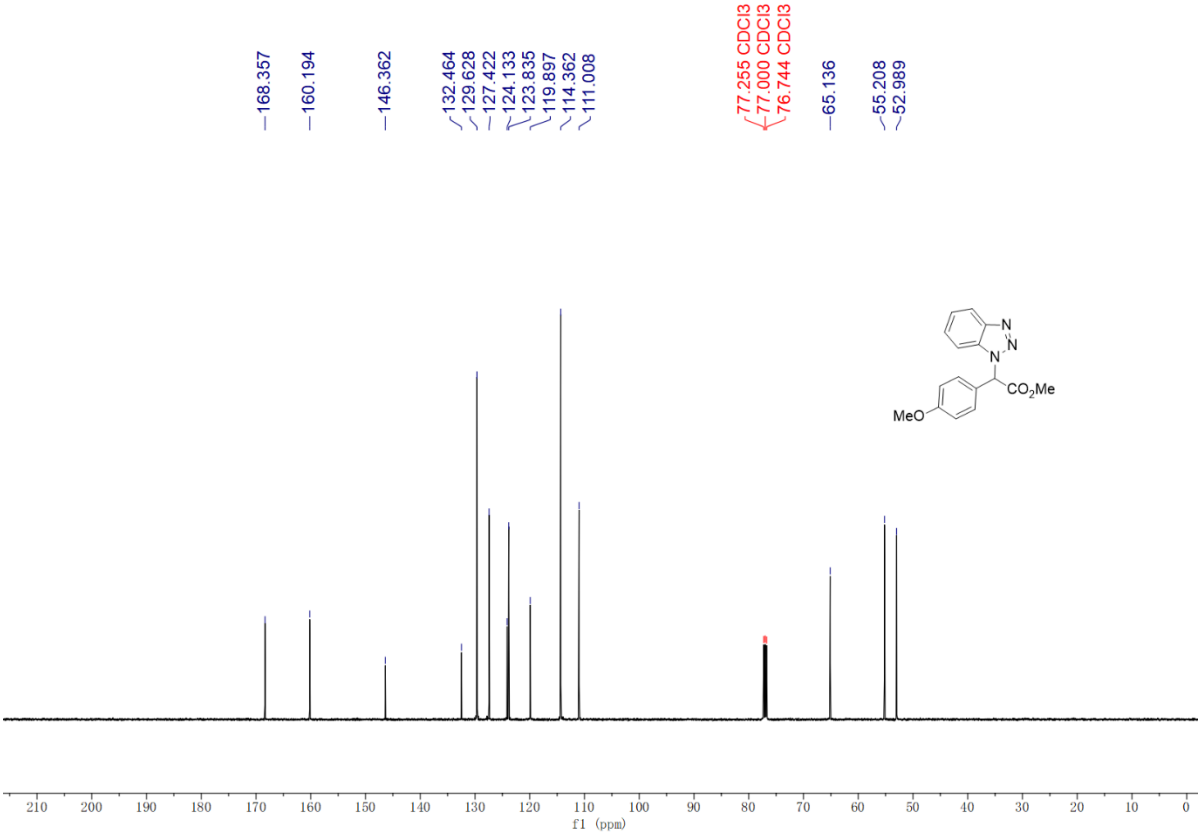




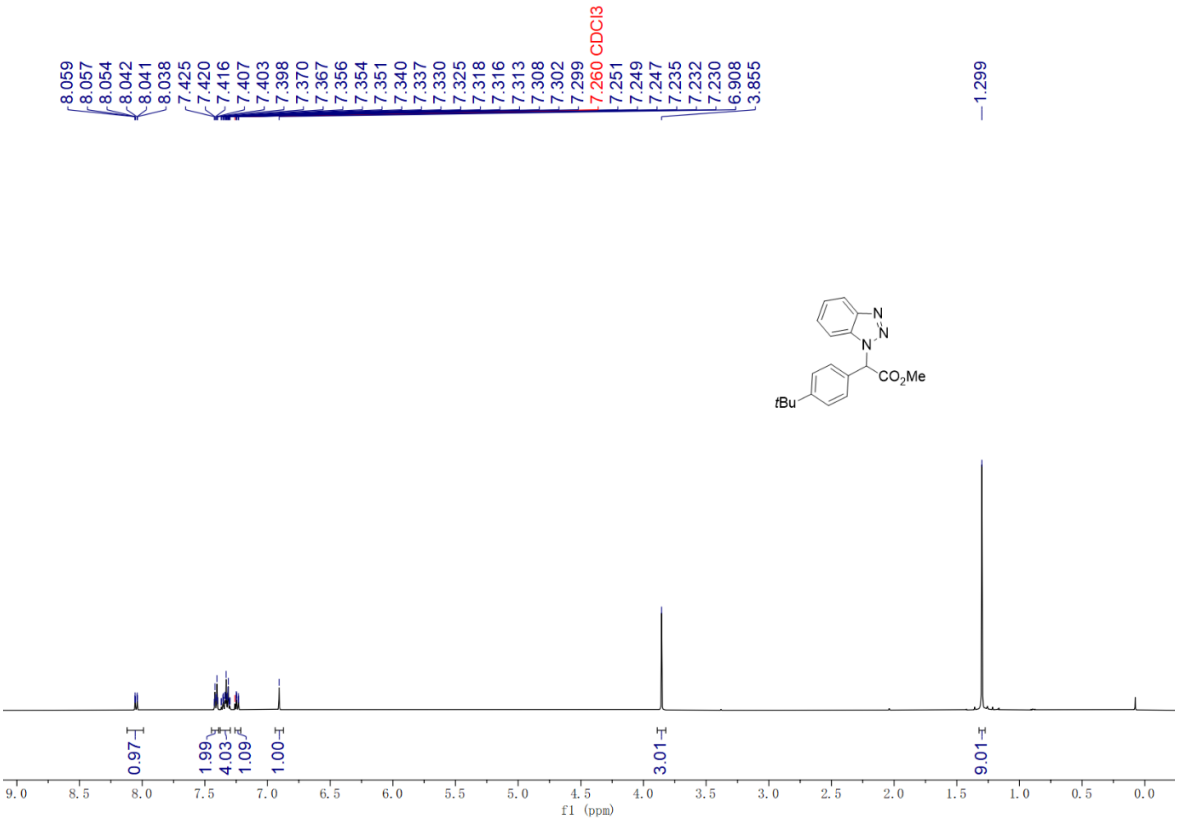
11 (Gram-scale) ^{1}H NMR (500 MHz, $CDCl_3$)



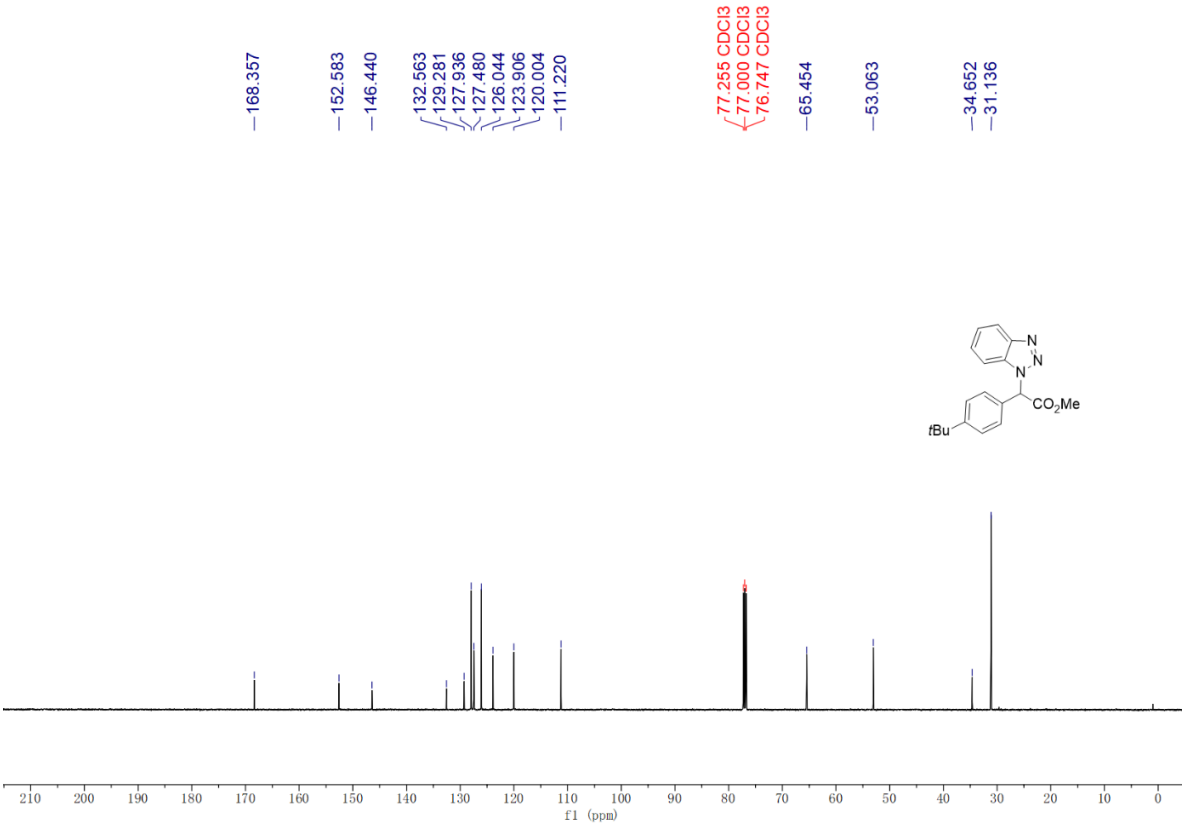
11 (Gram-scale) $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



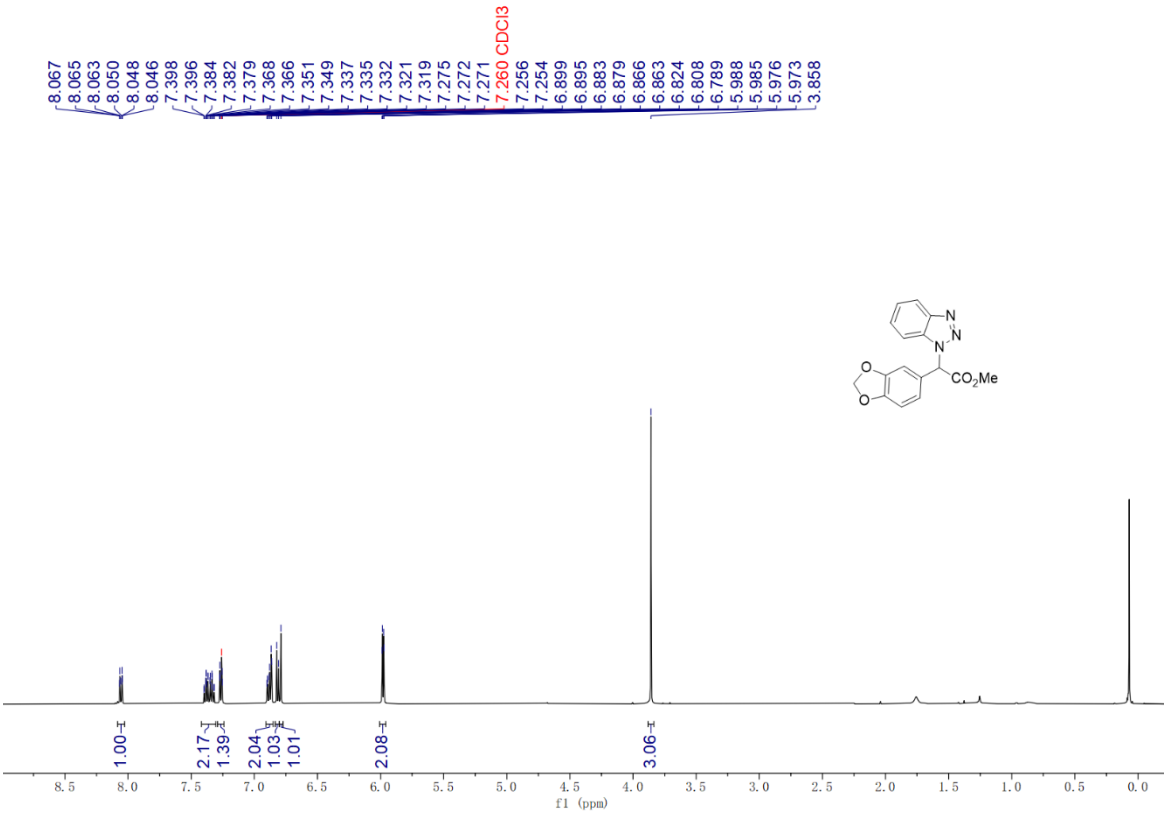
12 ^{1}H NMR (500 MHz, $CDCl_3$)



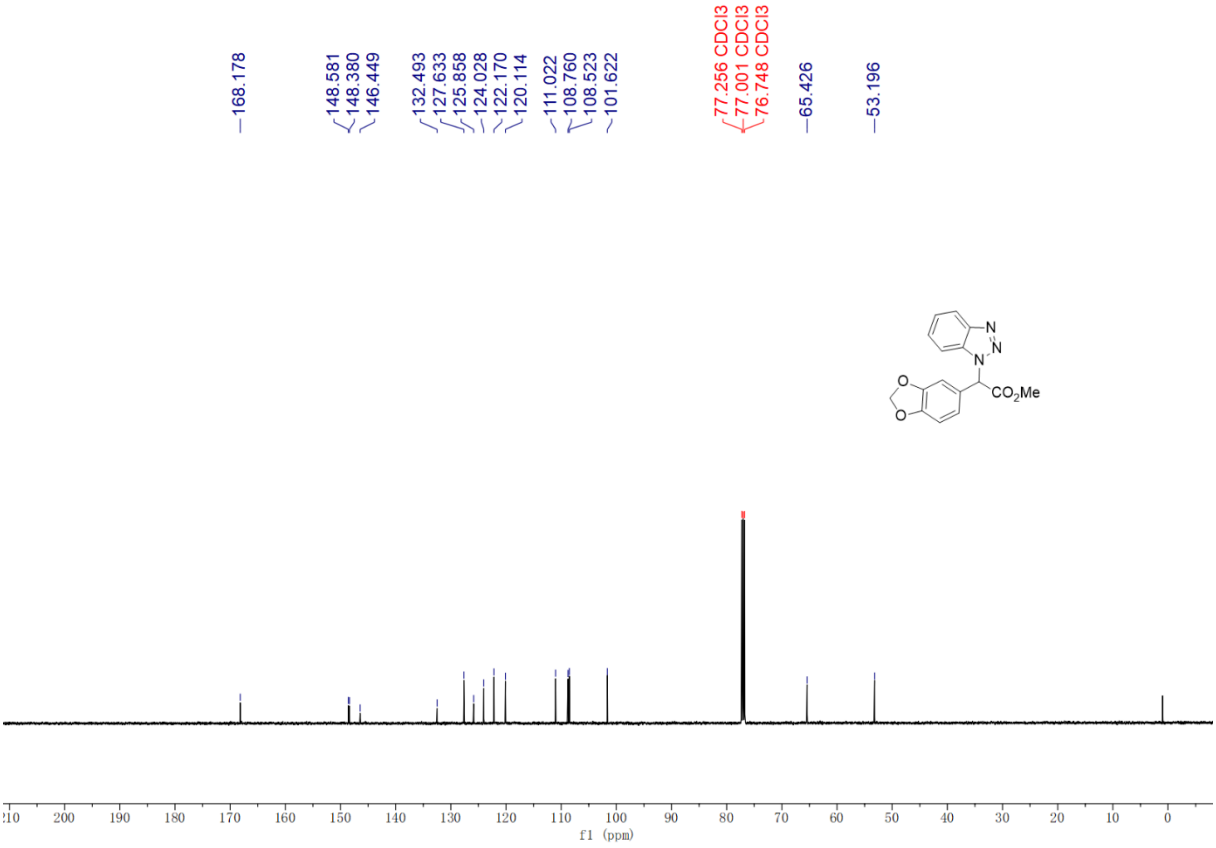
12 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



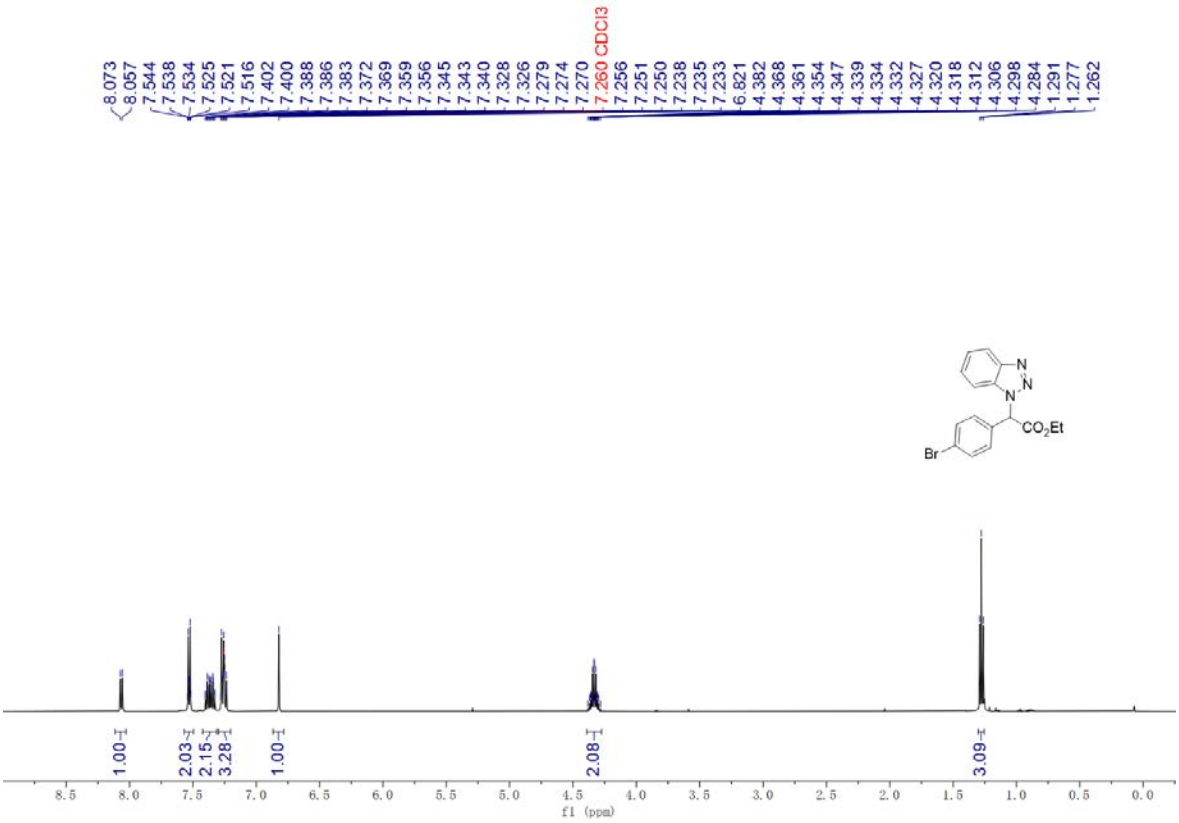
13 ^{1}H NMR (500 MHz, $CDCl_3$)



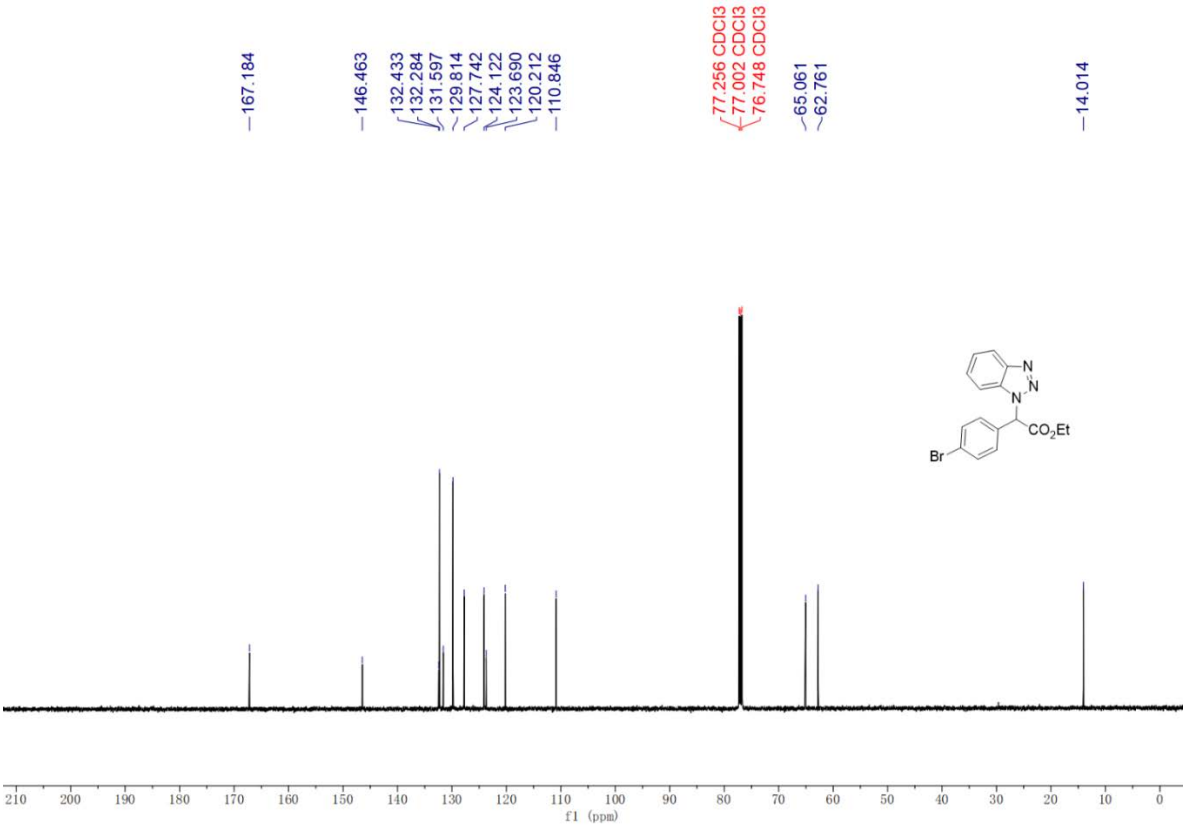
13 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



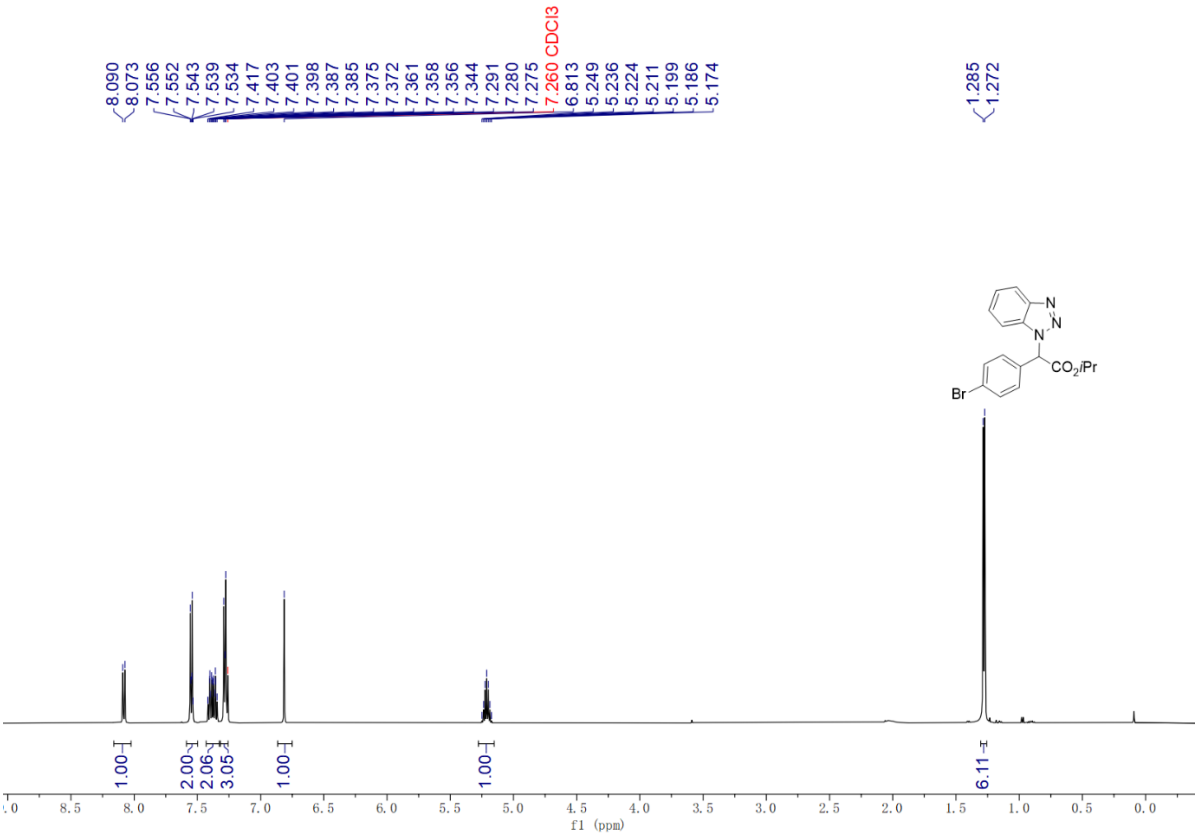
14 ^{1}H NMR (500 MHz, $CDCl_3$)



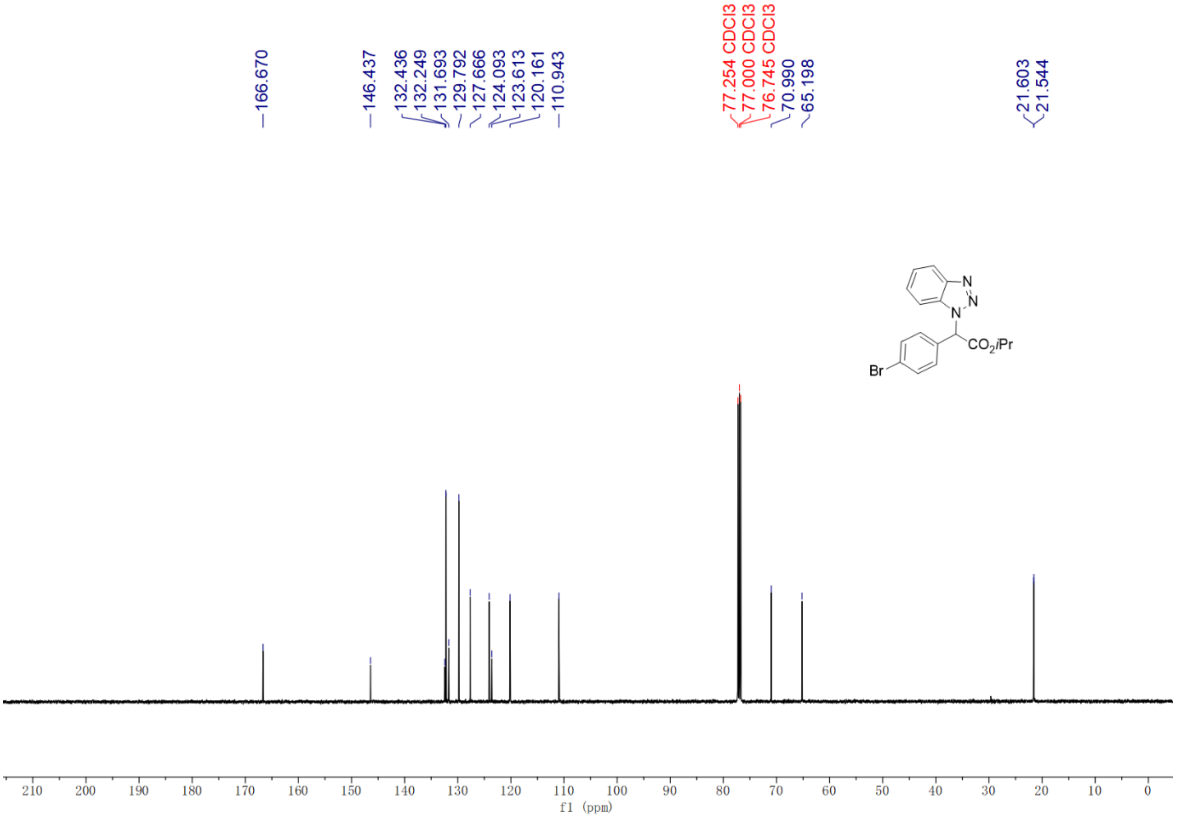
14 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



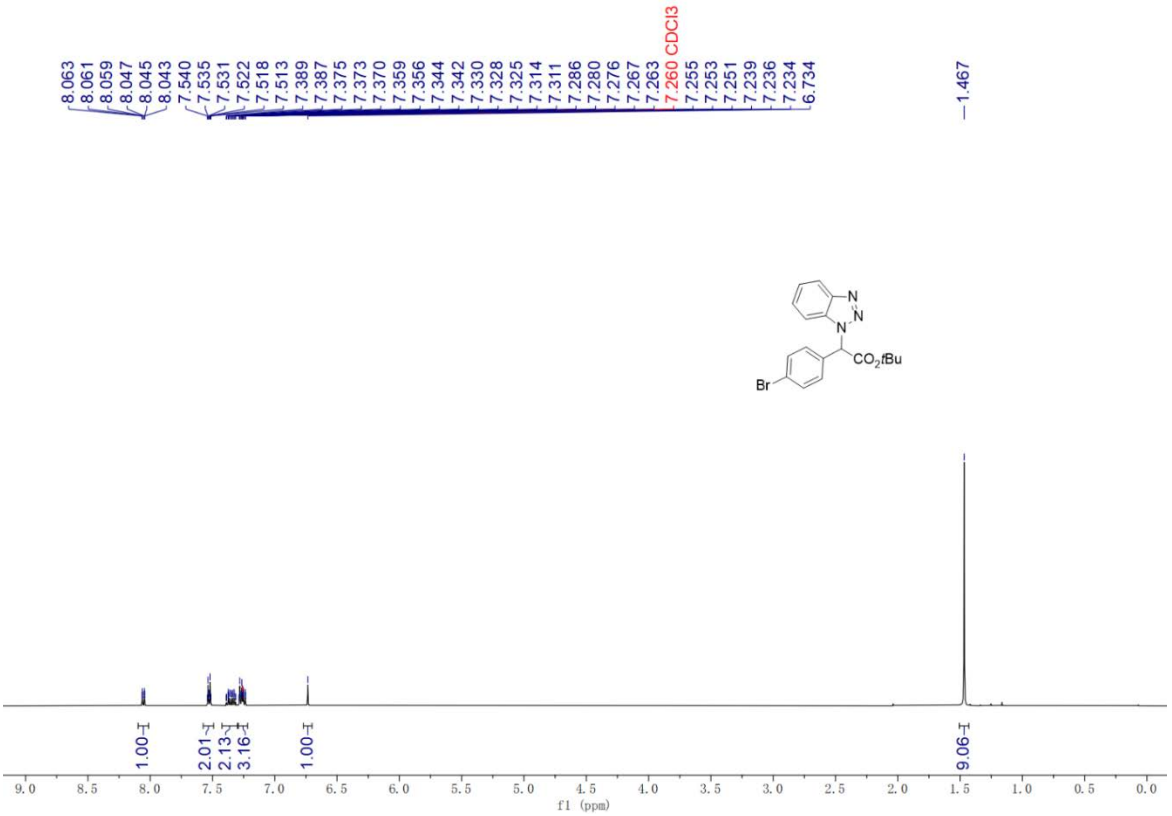
15 ^{1}H NMR (500 MHz, $CDCl_3$)



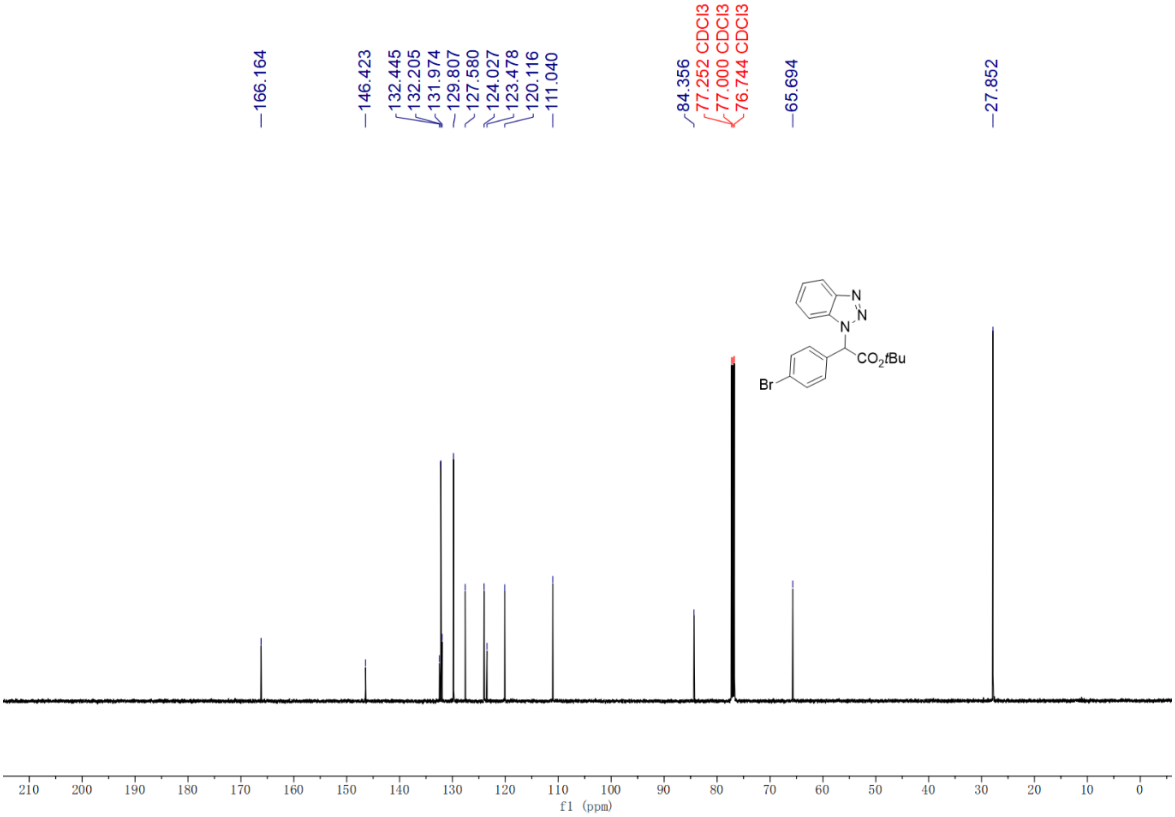
15 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



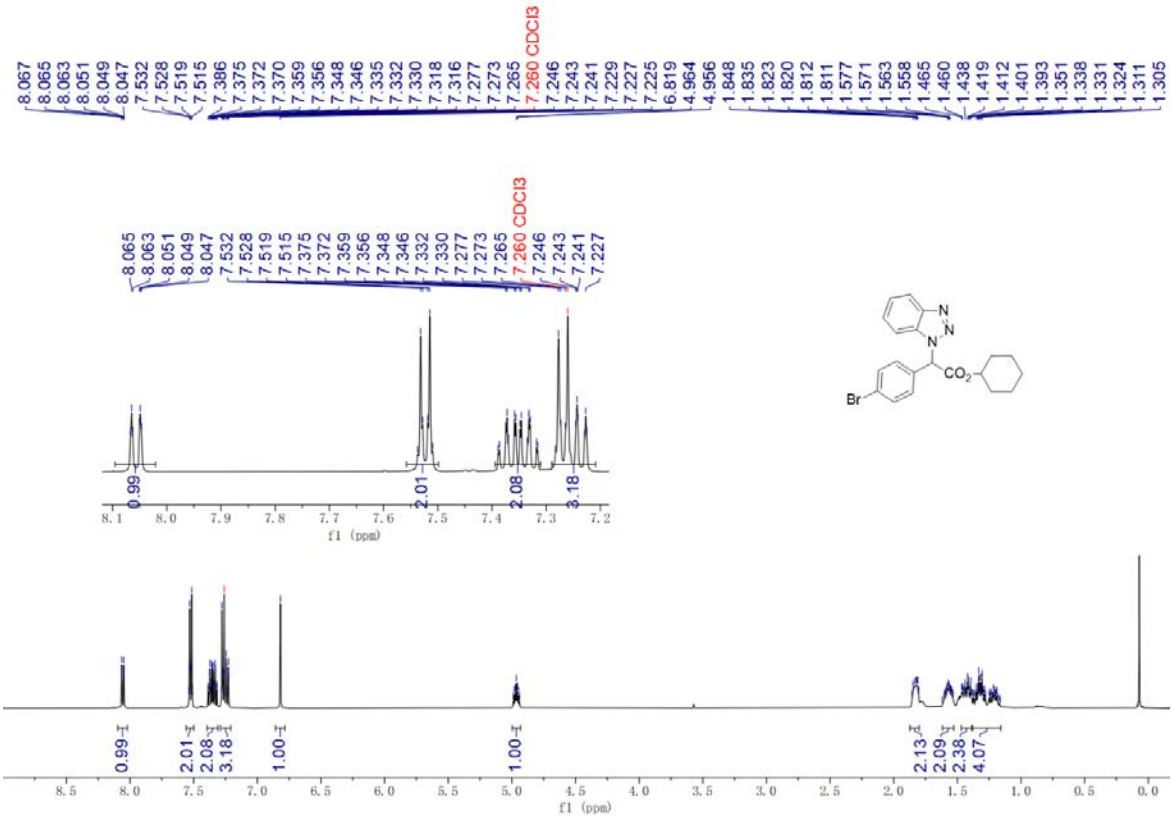
16 ^{1}H NMR (500 MHz, $CDCl_3$)



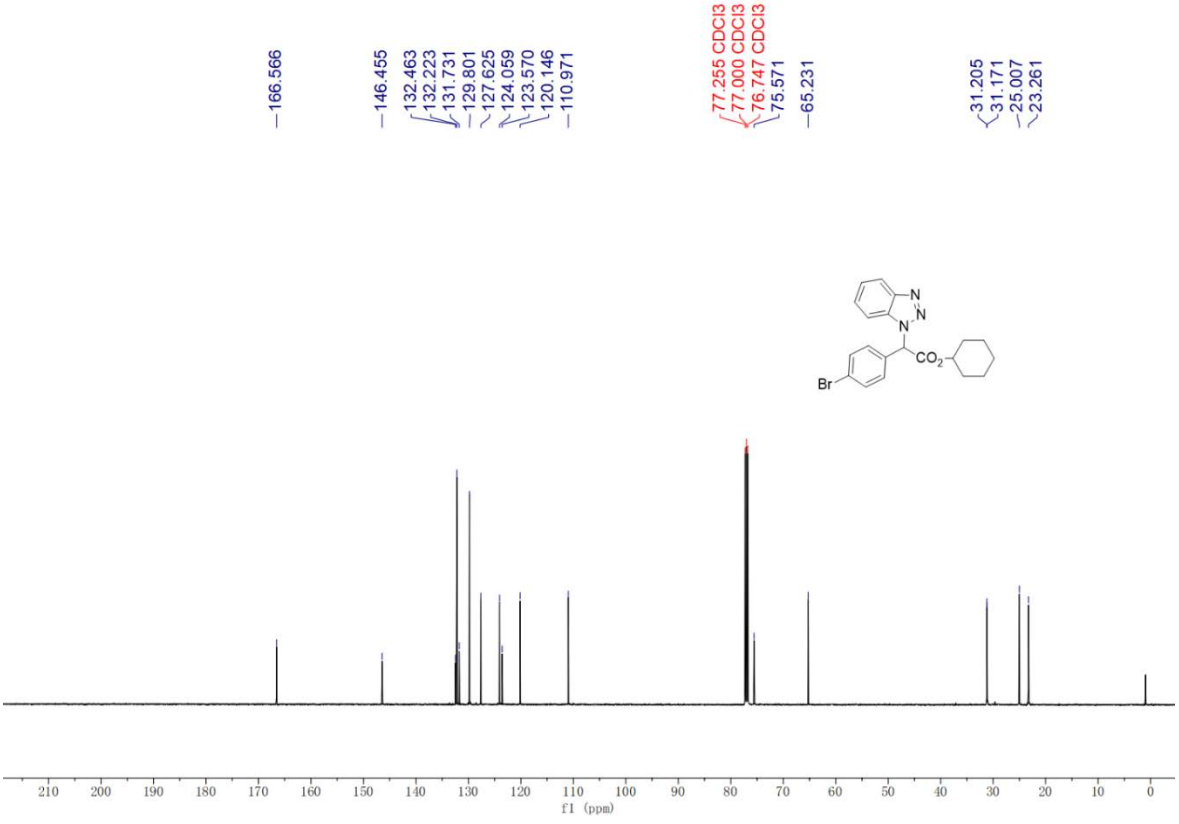
16 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



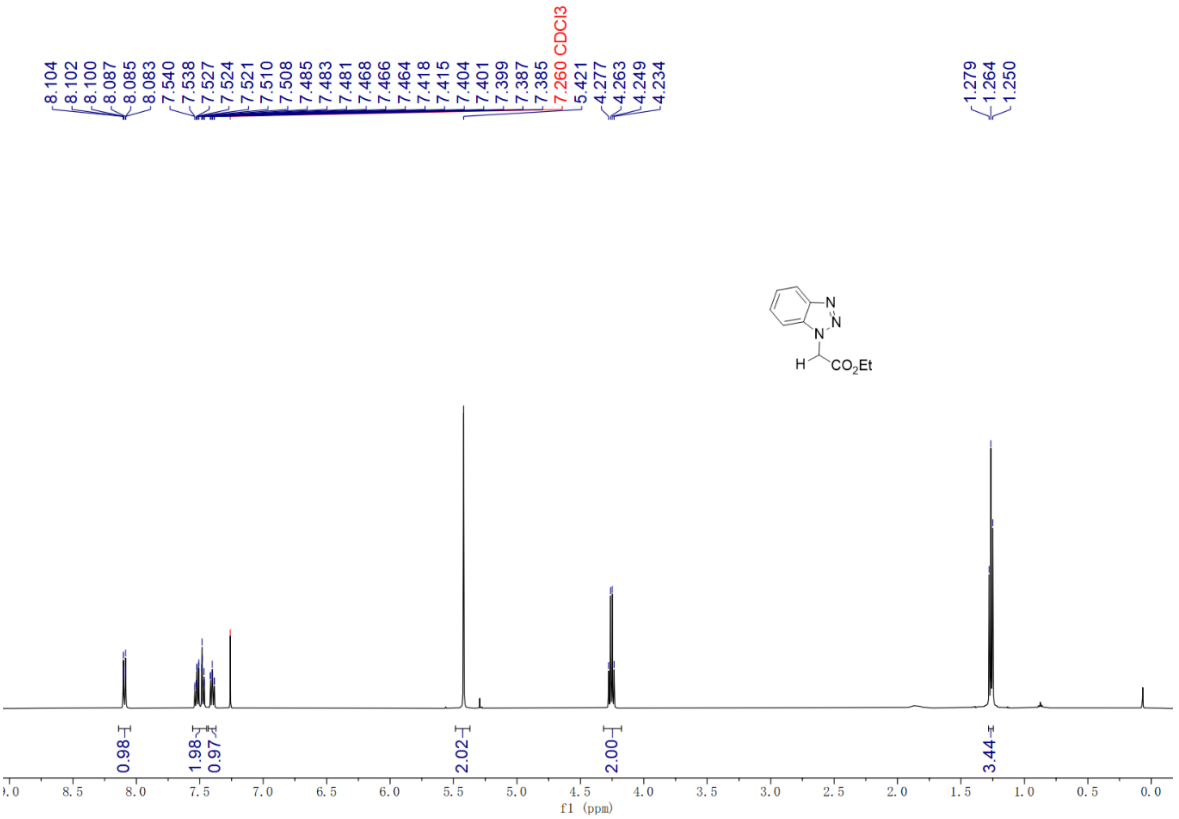
17 ^{1}H NMR (500 MHz, $CDCl_3$)



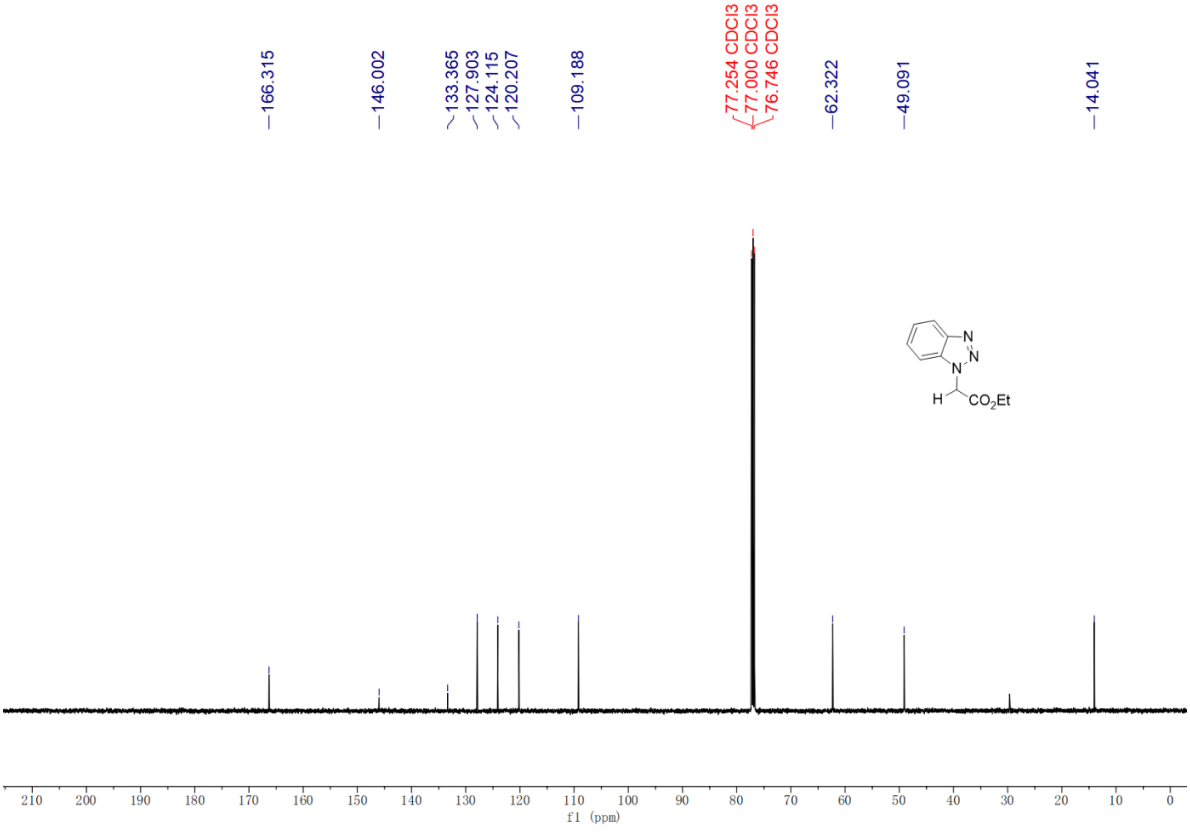
17 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



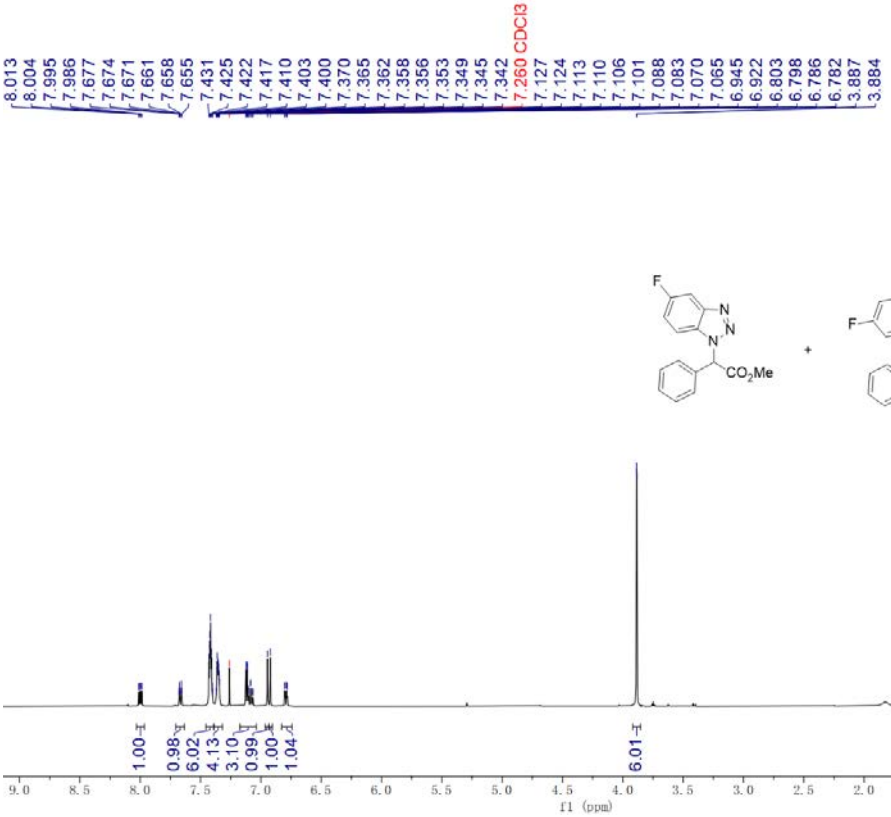
18 ^{1}H NMR (500 MHz, $CDCl_3$)



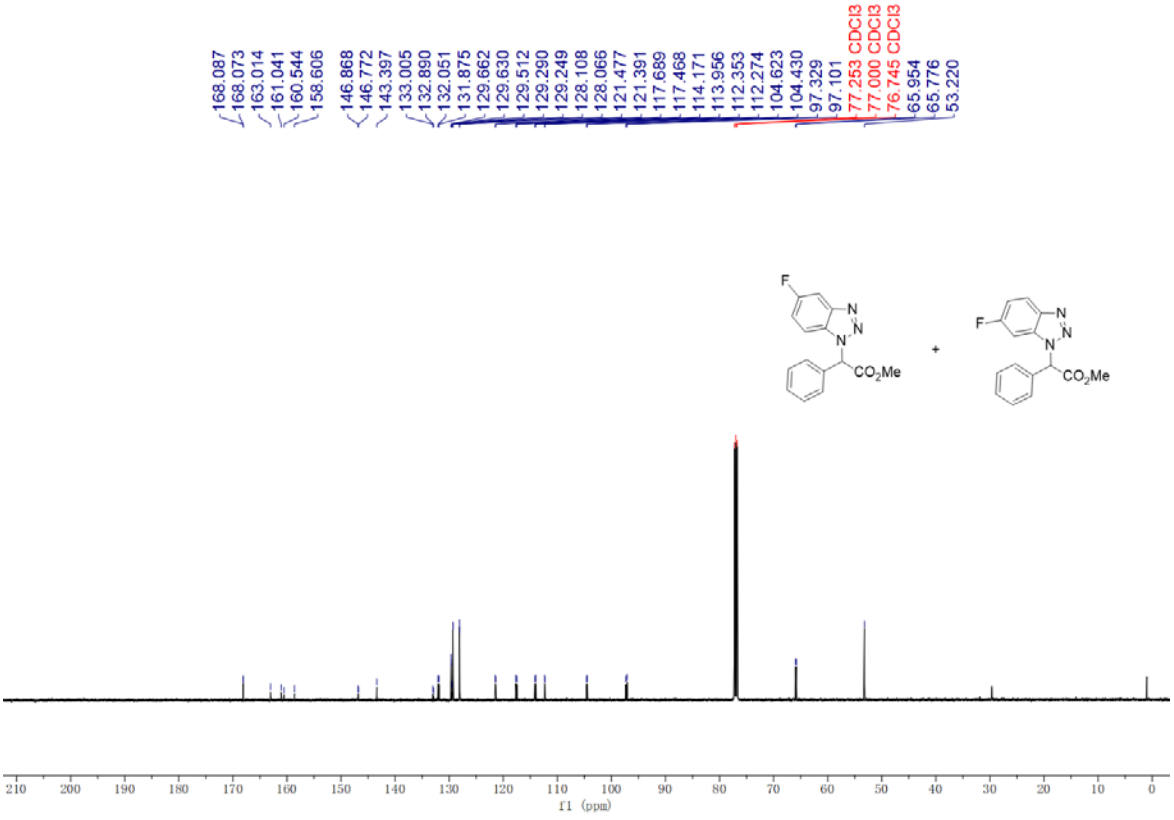
18 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



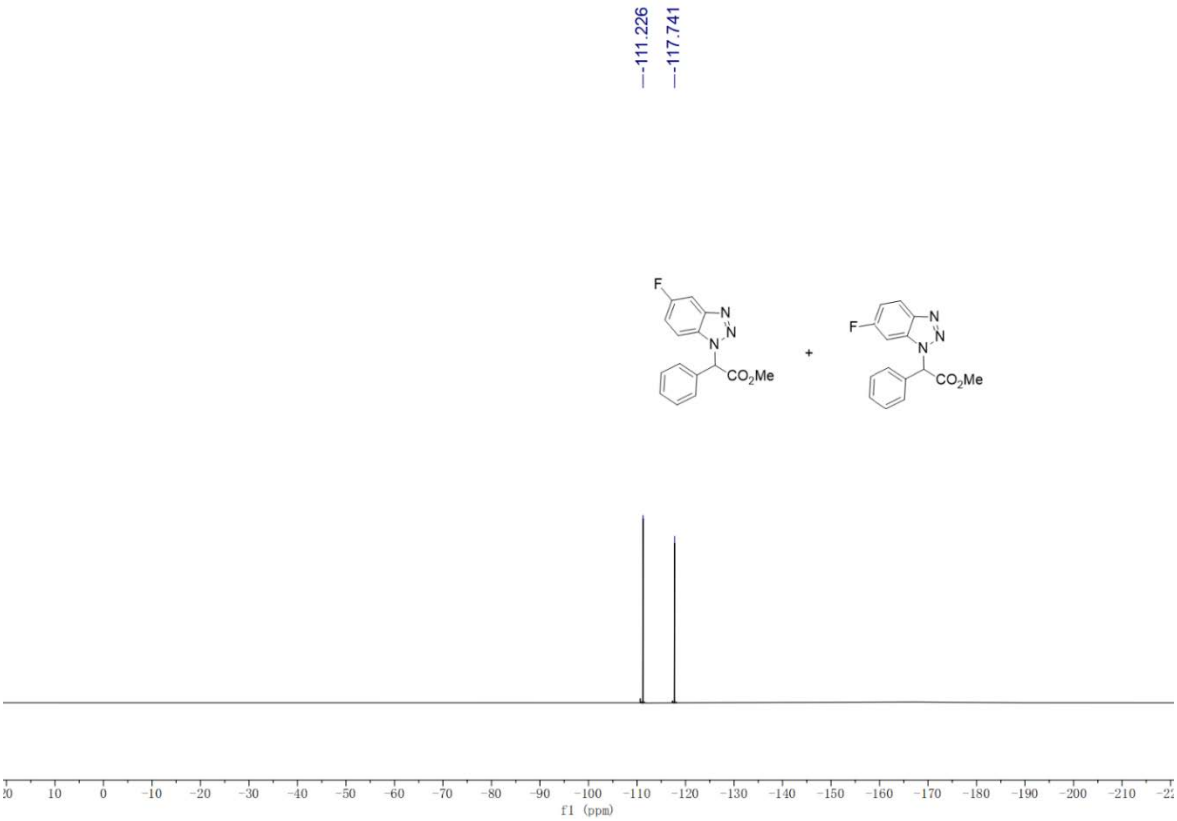
19 and **19'** ^{1}H NMR (500 MHz, $CDCl_3$)



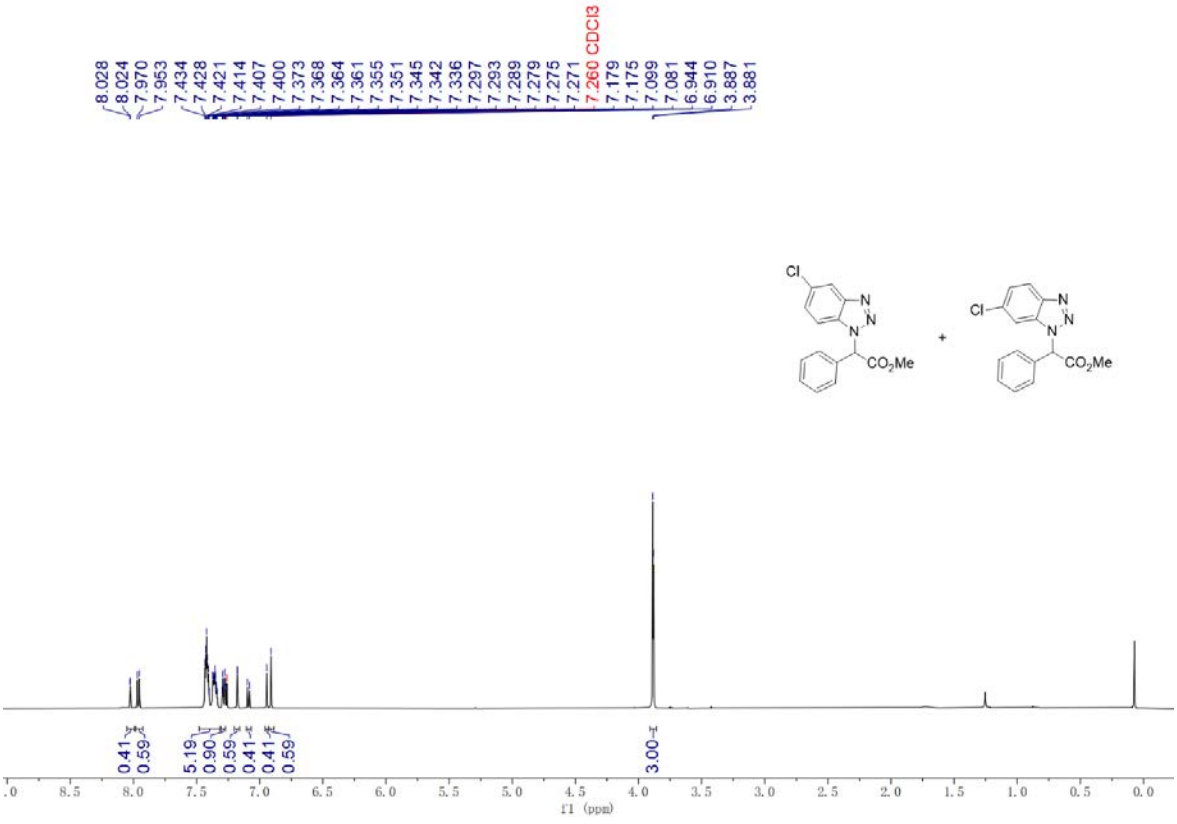
19 and **19'** $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



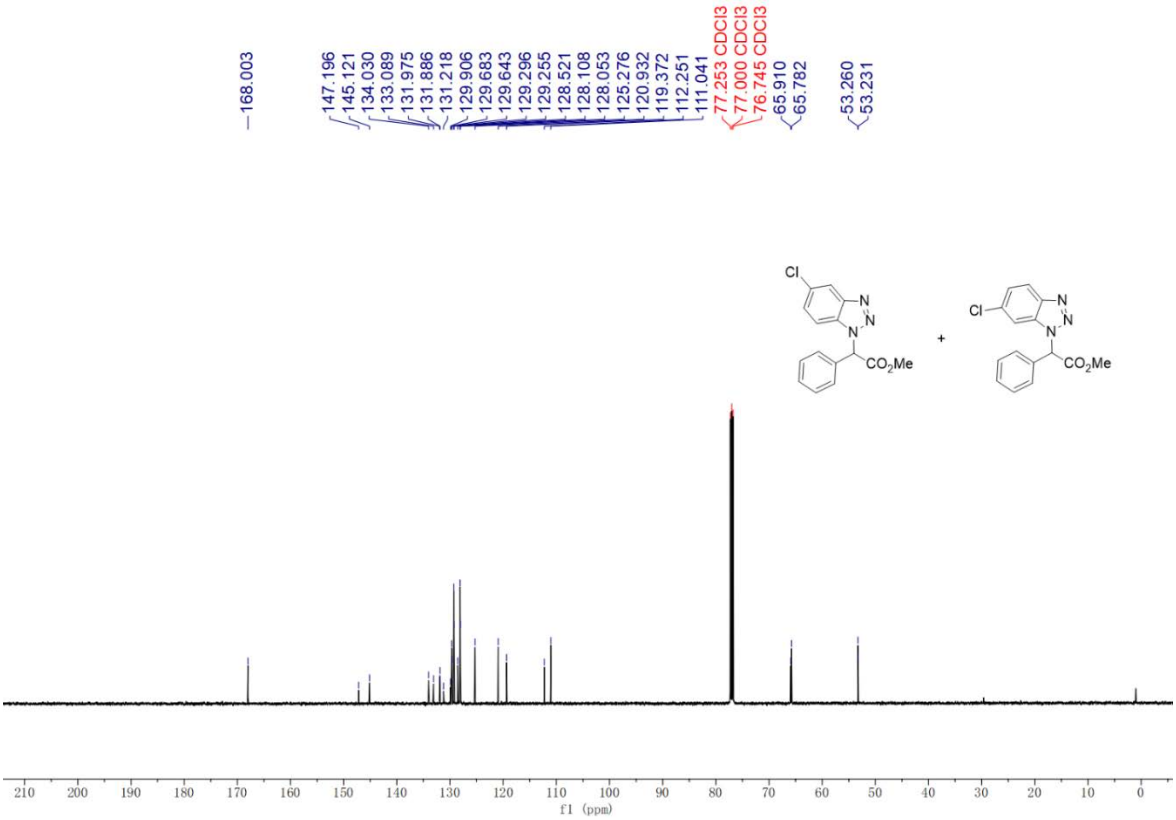
19 and **19'** $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



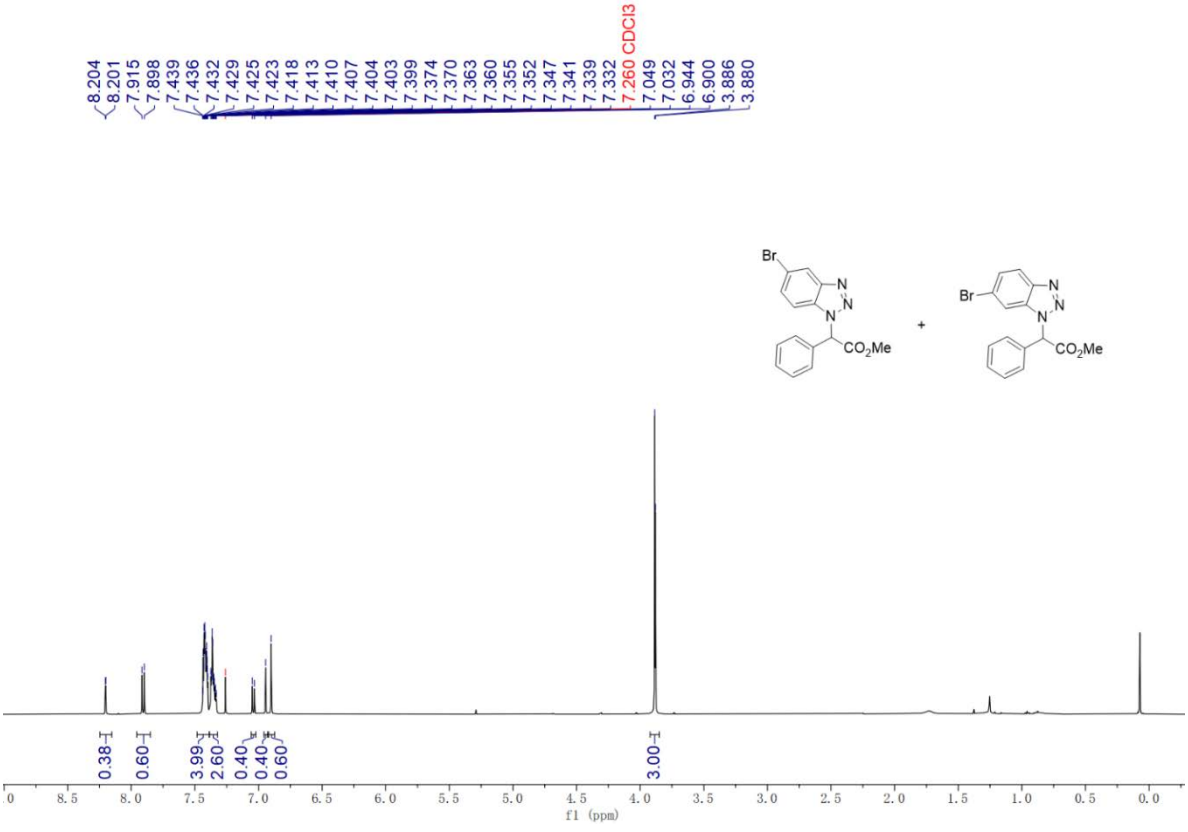
20 and **20'** ^{1}H NMR (500 MHz, $CDCl_3$)



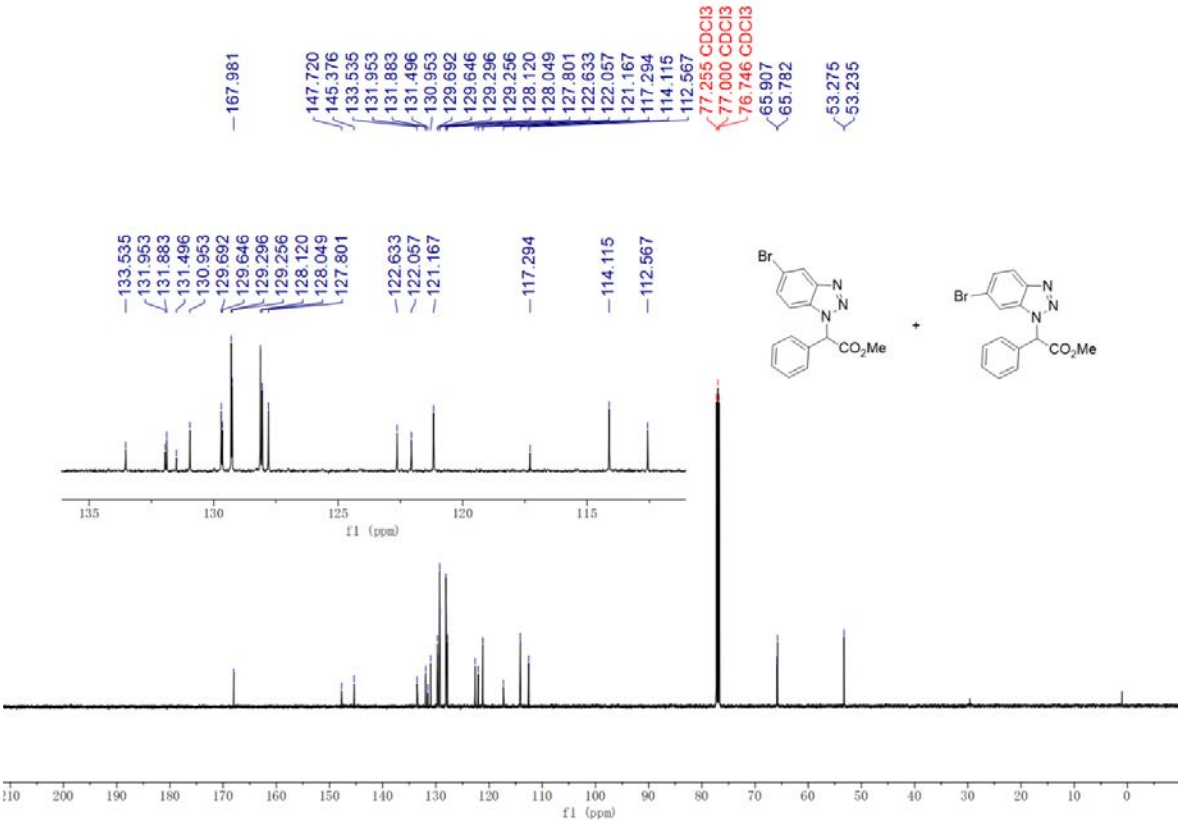
20 and **20'** $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



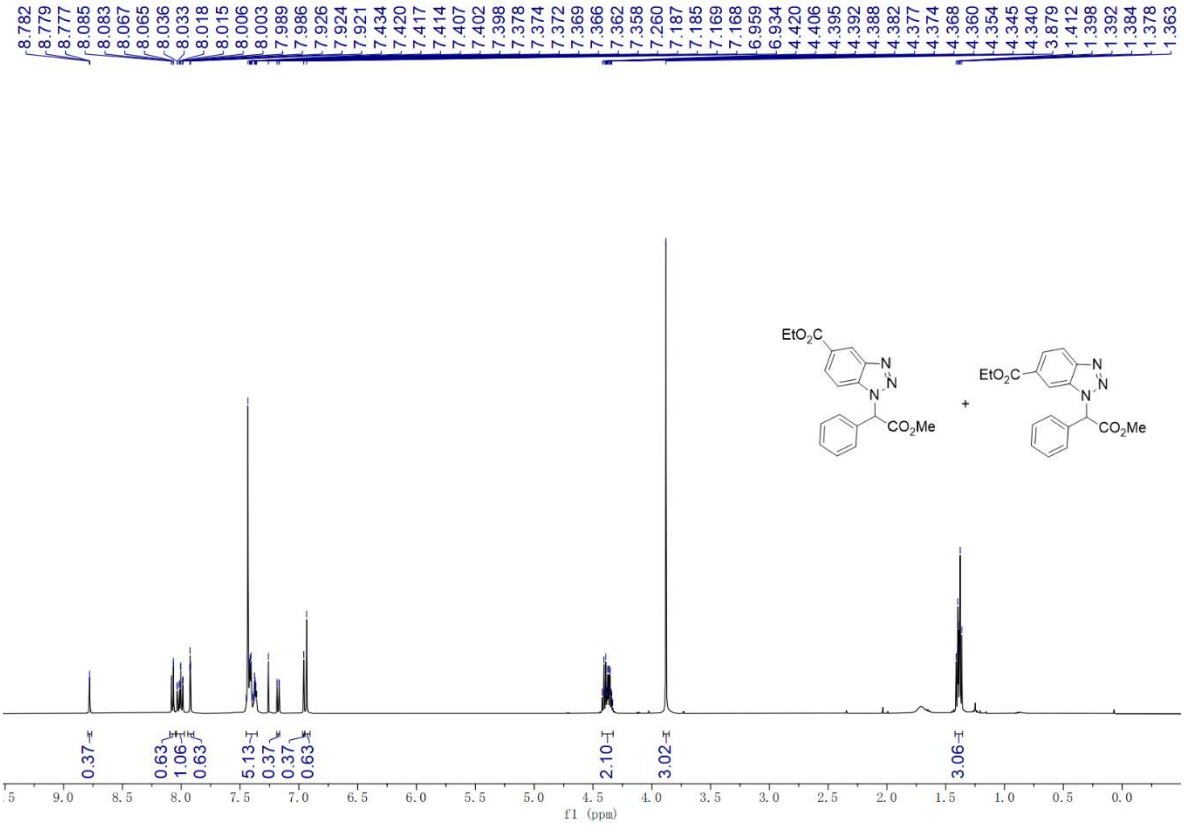
21 and **21'** ^{1}H NMR (500 MHz, $CDCl_3$)



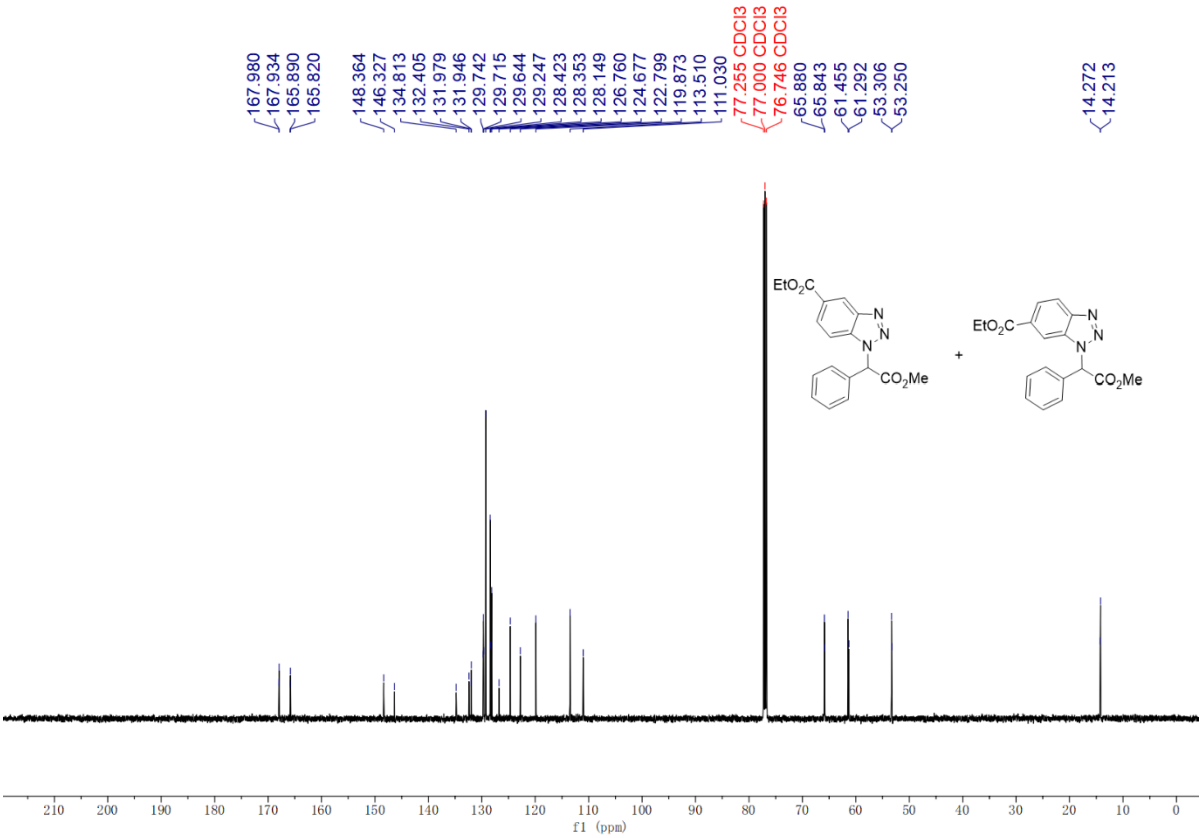
21 and **21'** $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



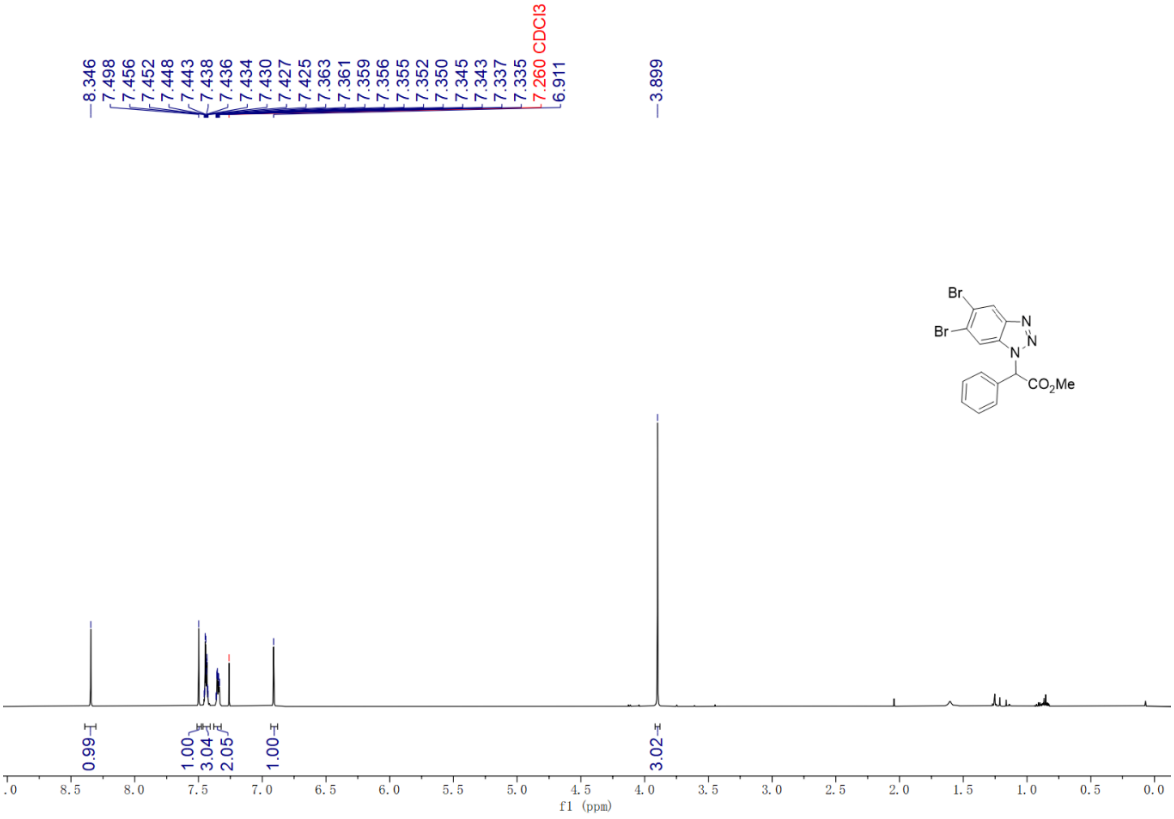
22 and **22'** ^{1}H NMR (500 MHz, $CDCl_3$)



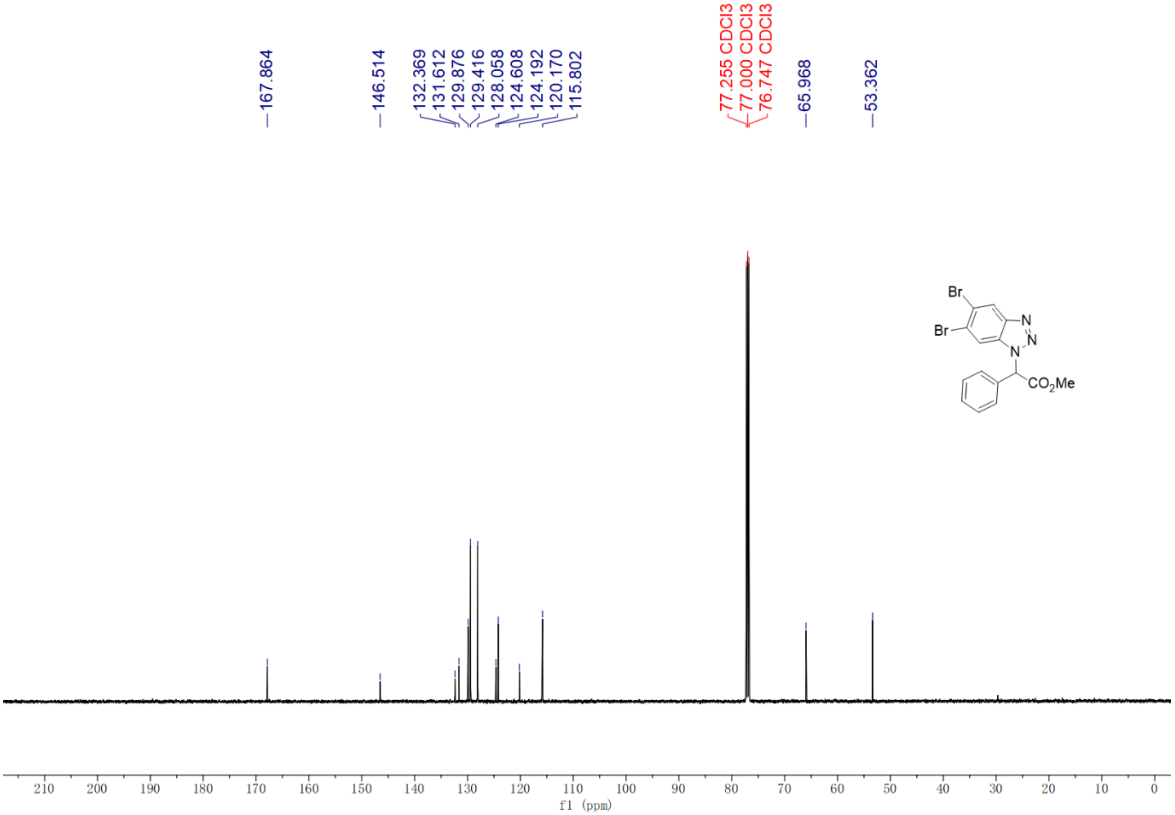
22 and **22'** $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



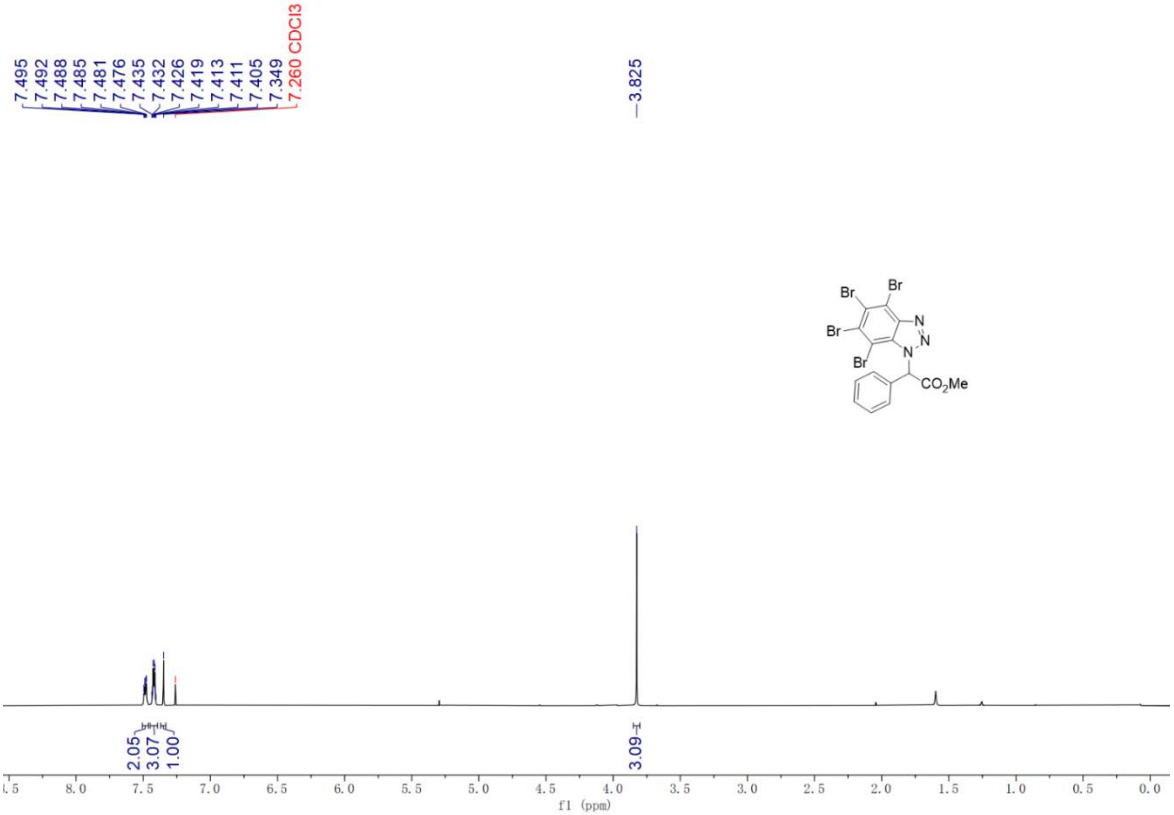
23 ^{1}H NMR (500 MHz, $CDCl_3$)



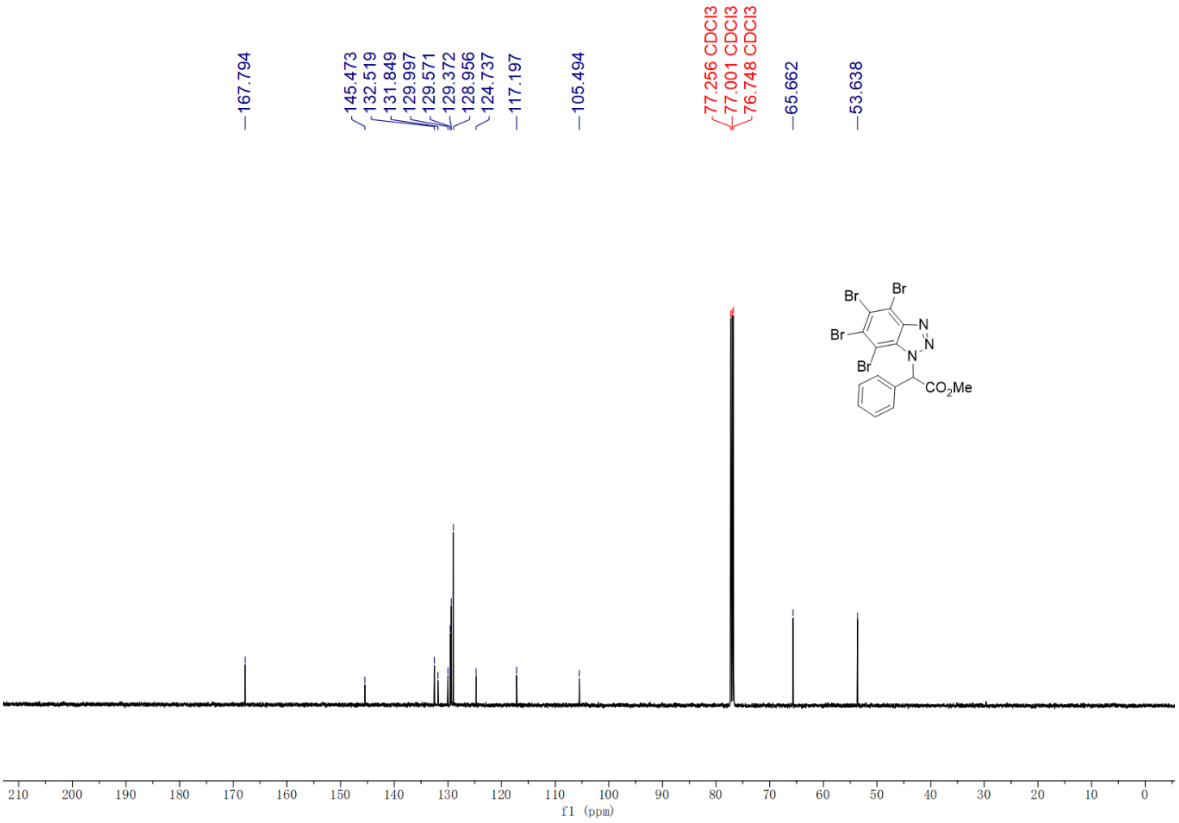
23 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



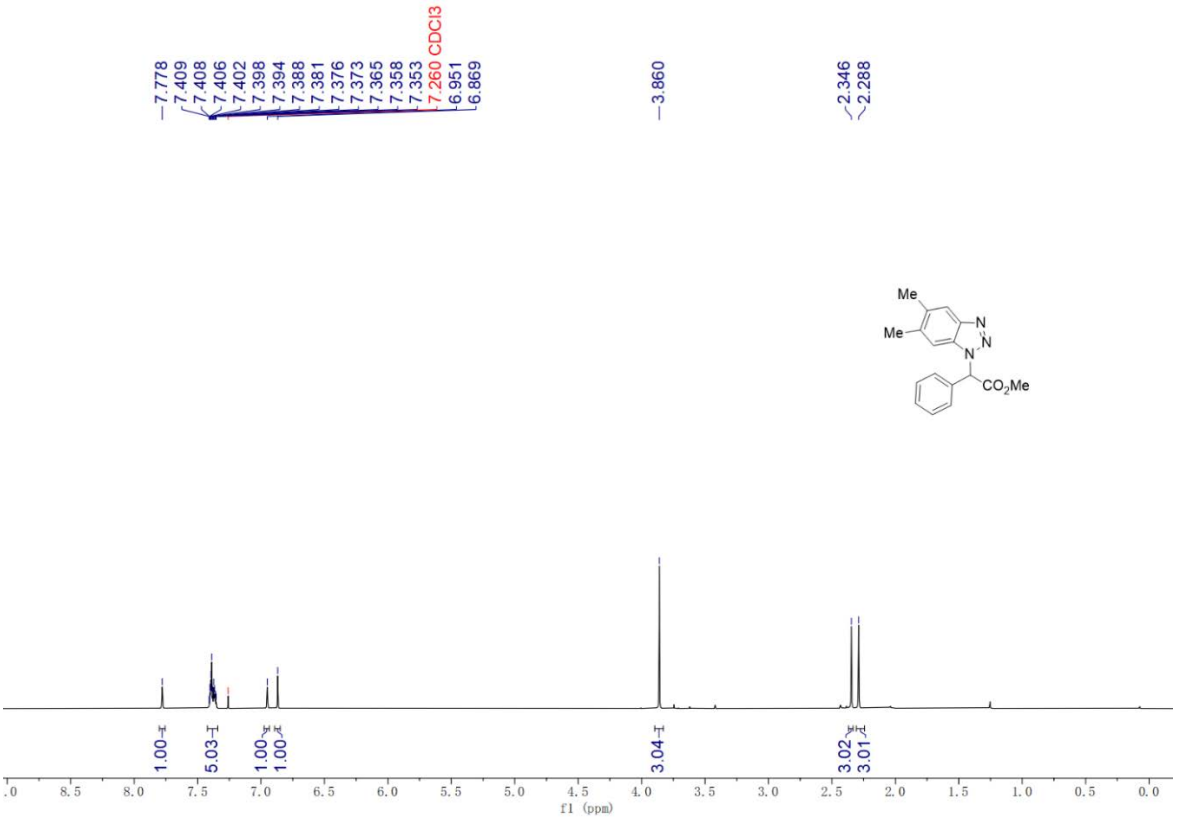
24 ^{1}H NMR (500 MHz, $CDCl_3$)



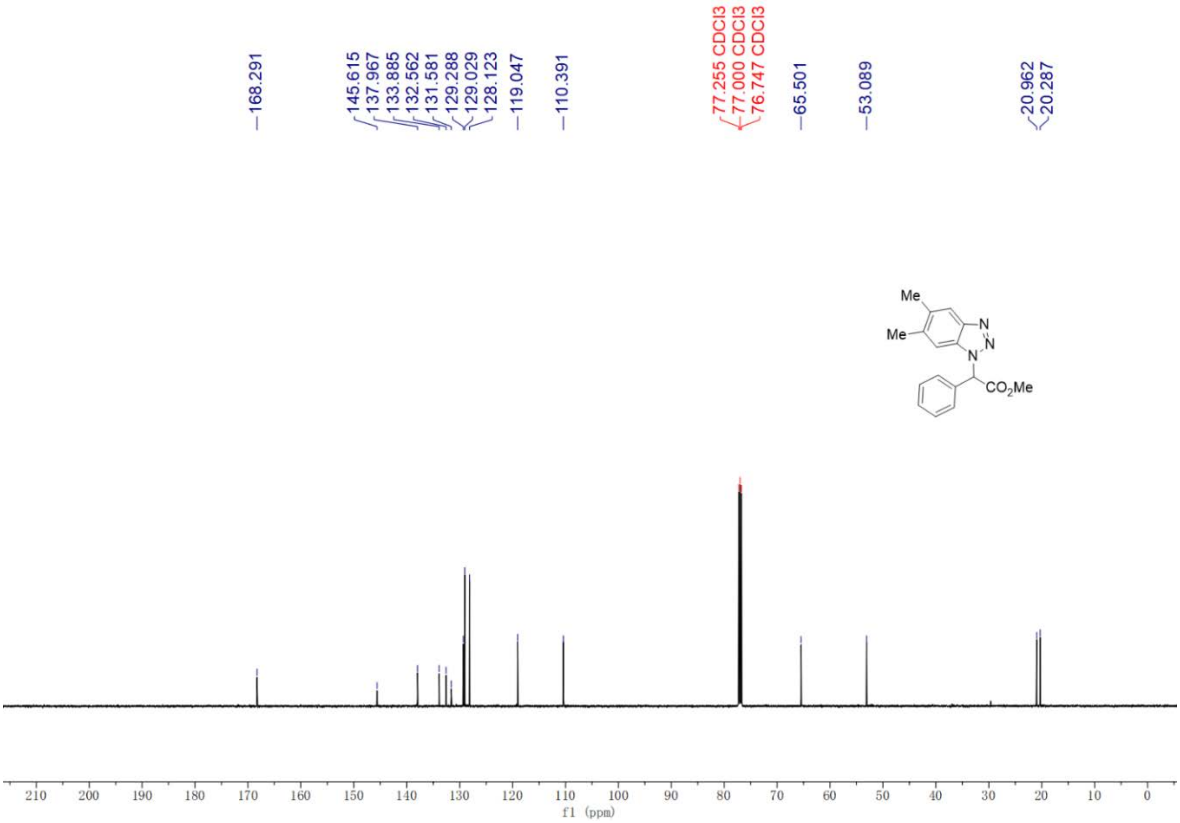
24 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



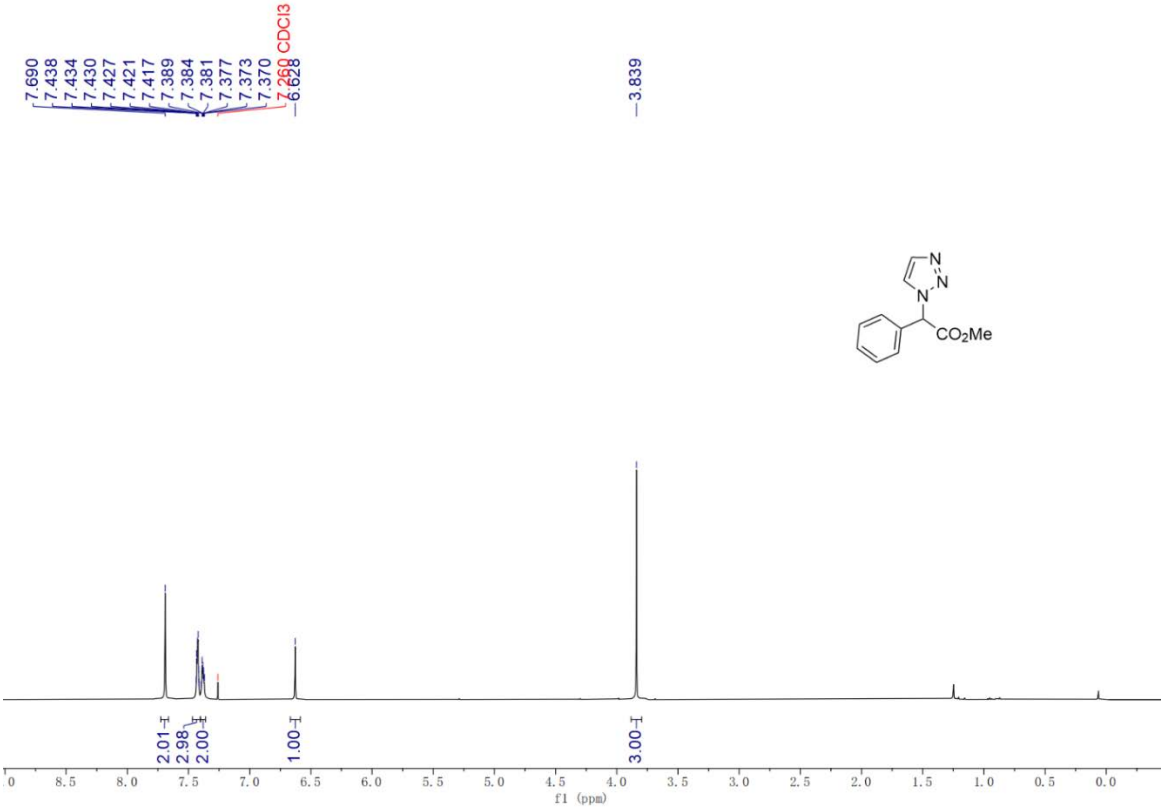
25 ^{1}H NMR (500 MHz, $CDCl_3$)



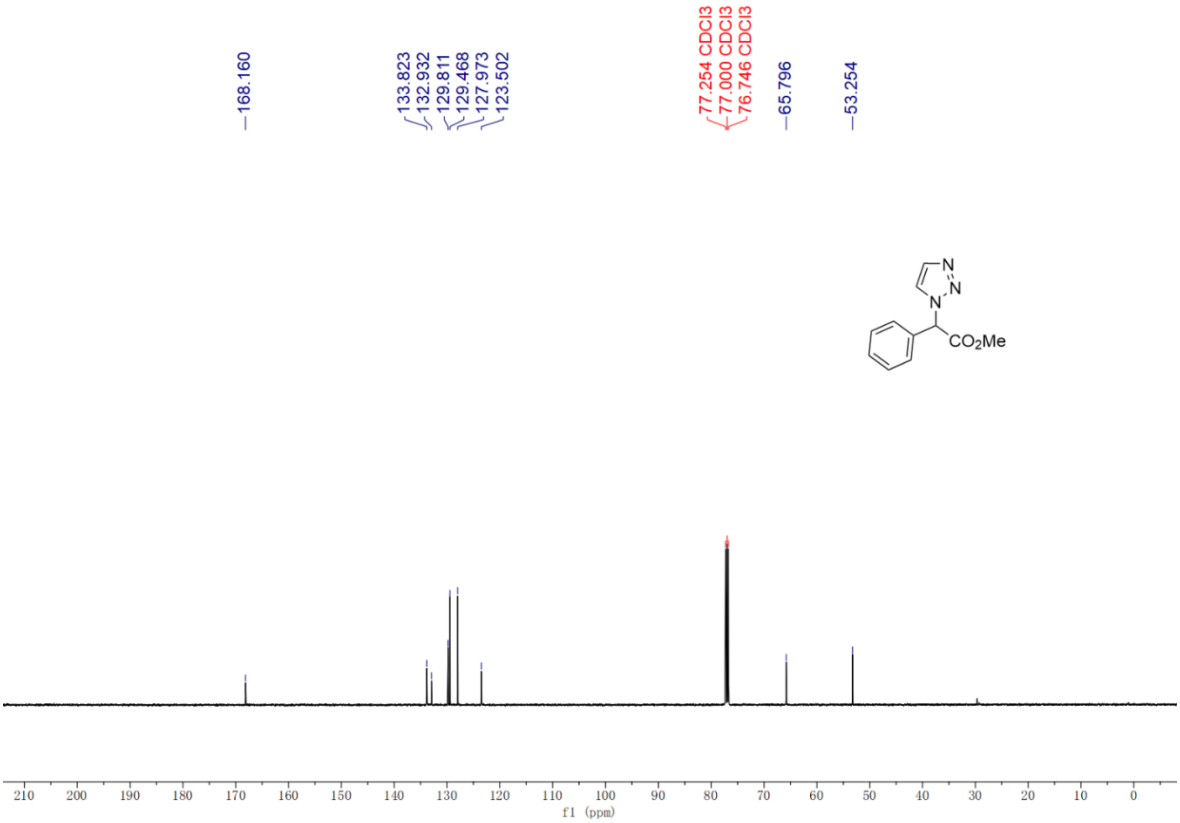
25 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



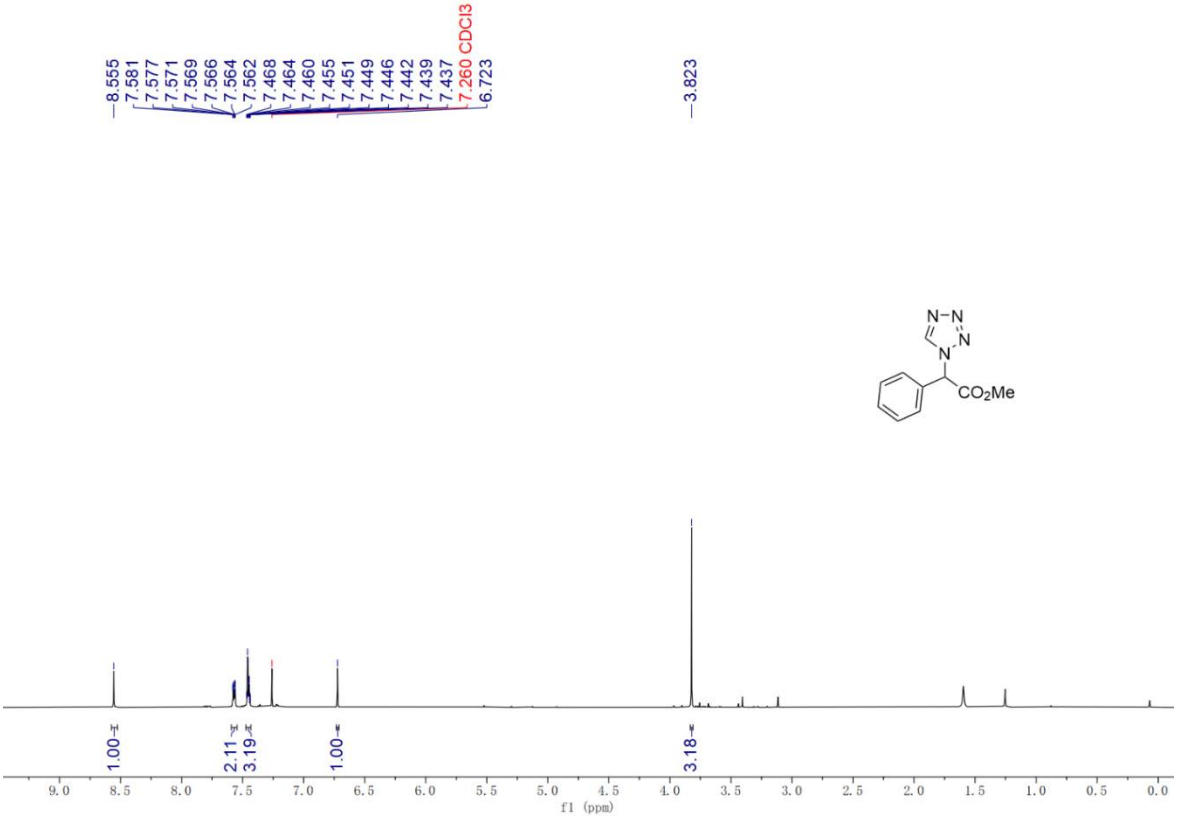
26 ^{1}H NMR (500 MHz, $CDCl_3$)



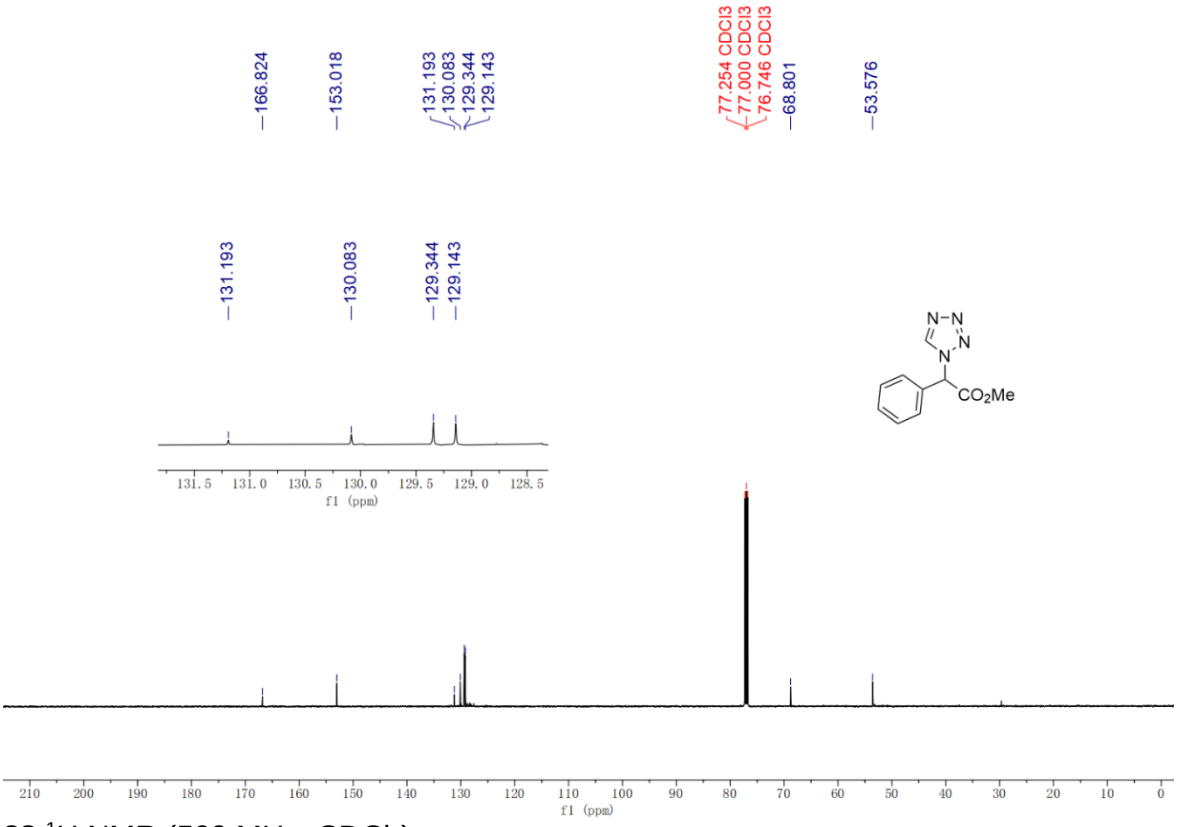
26 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



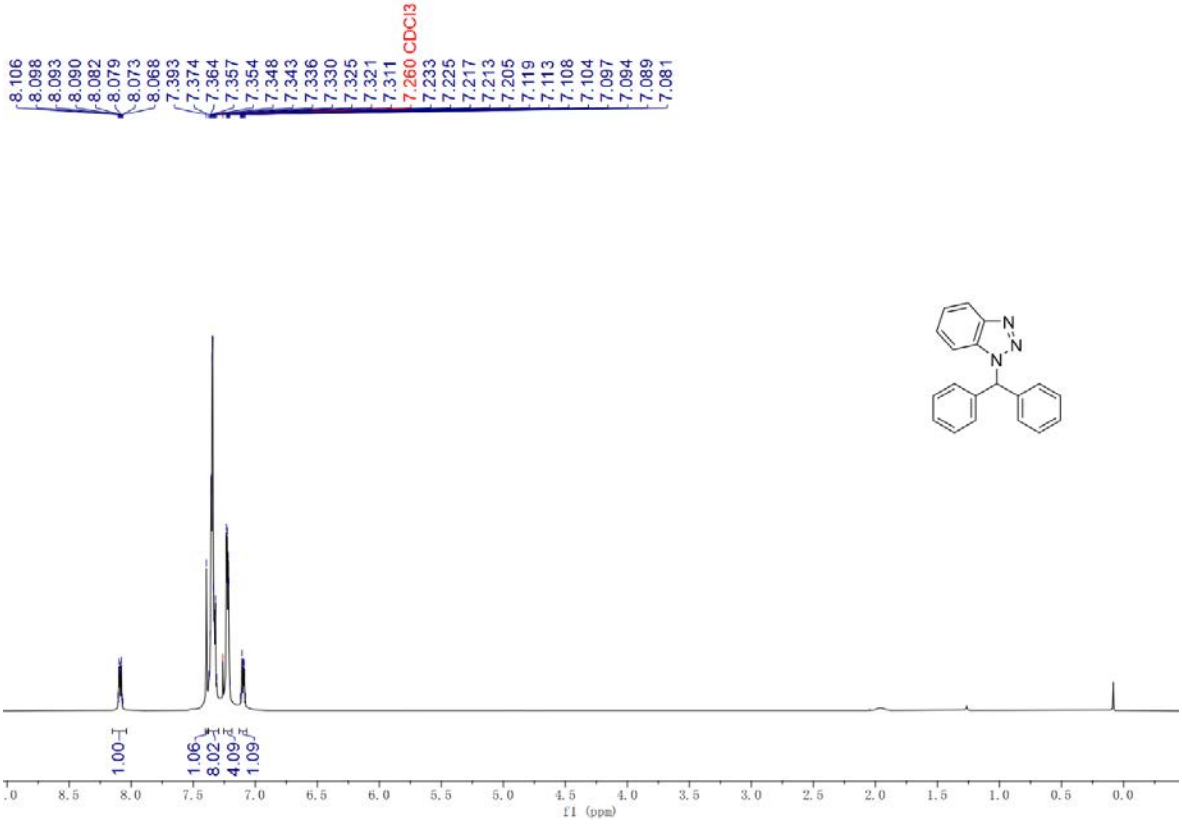
27 ^{1}H NMR (500 MHz, $CDCl_3$)



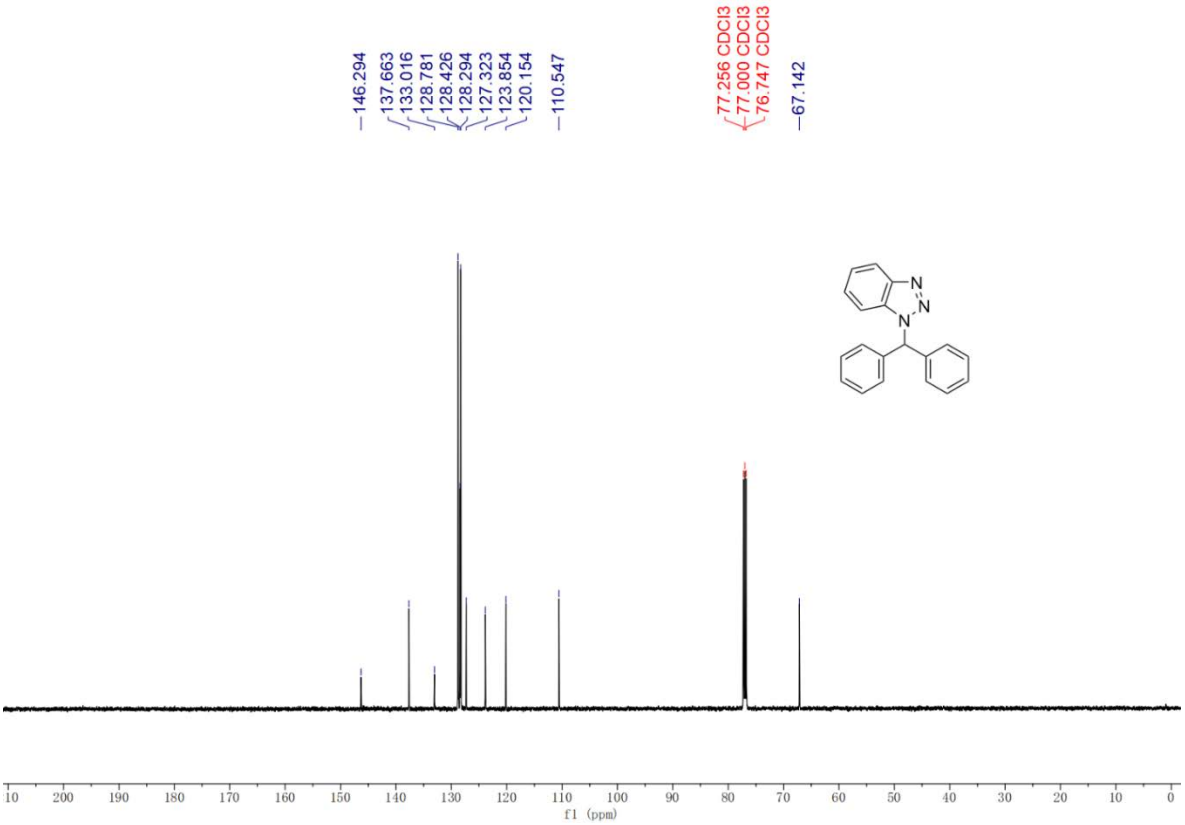
27 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



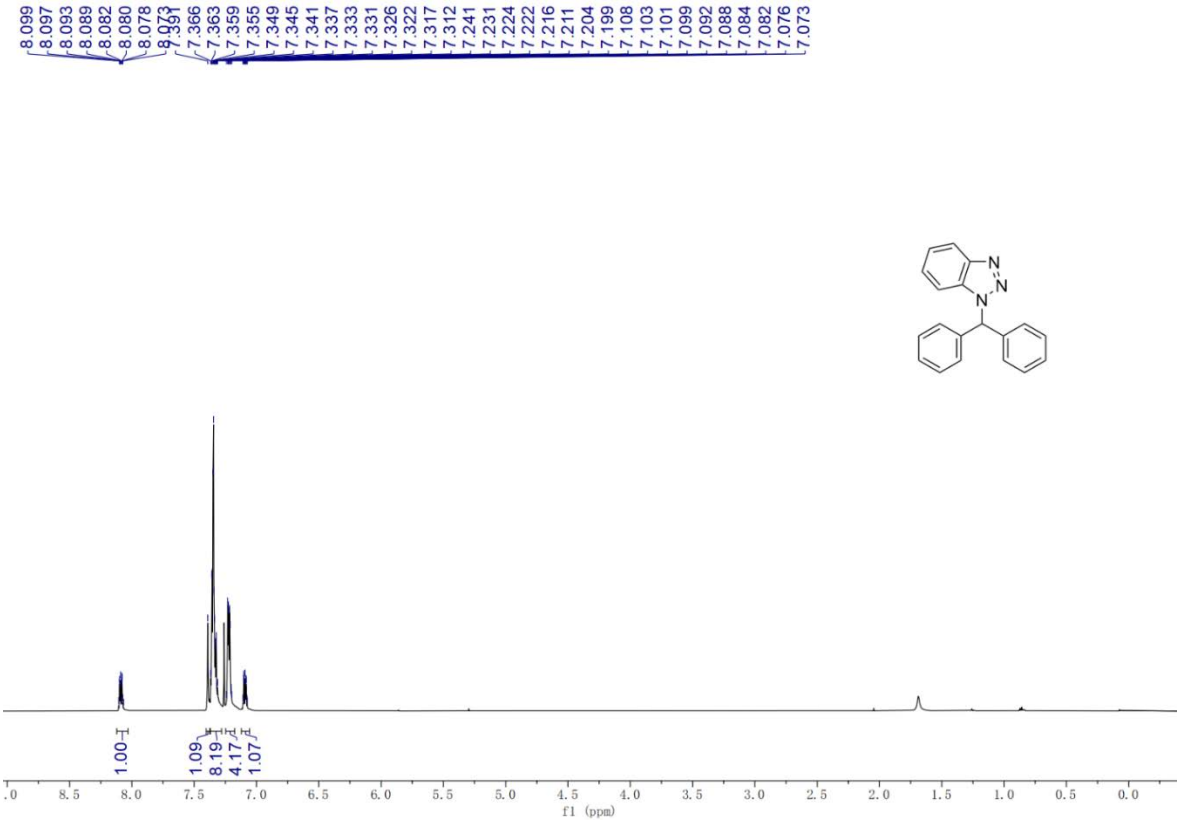
28 ^{1}H NMR (500 MHz, $CDCl_3$)



28 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



28 (Gram-scale) ^{1}H NMR (500 MHz, $CDCl_3$)



28 (Gram-scale) $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)