Supporting Information

Cu-Catalyzed Convenient Synthesis of 2-Trifluoromethyl Benzimidazoles *via* Cyclization of *o*-Phenylenediamines with Hexafluoroacetylacetone

Xia Chen,[†,‡] Xiao-Yu Zhou,[*,‡] Hai-Long Liu,[‡] Sheng Zhang,[†] and Ming Bao[*,†]

[†]State Key Laboratory of Fine Chemicals, Frontier Science Center for Smart Materials, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China

[‡]School of Chemistry and Materials Engineering, Liupanshui Normal University, Liupanshui 553004, China

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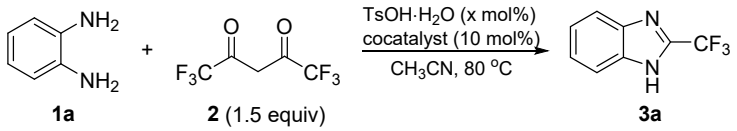
1. General Information.

Unless otherwise noted, all reactions were carried out in oven-dried 25-mL Schlenk tubes under a nitrogen atmosphere. IKA plate was used as the heat source. All reagents and solvents were of pure analytical grade. Thin layer chromatography (TLC) was performed on HSGF254 silica gel, pre-coated on glass-backed plates coated with 0.2 mm silica and revealed with either a UV lamp (λ_{max} = 254 nm). The products were purified by flash column chromatography on silica gel 200-300 mesh. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker Avance NEO 600M NMR Spectrometer (600 MHz for ^{1}H, 151 MHz for ^{13}C, 565 MHz for ^{19}F) using d_6-DMSO or $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard and cadmium acetylacetonate as the relaxation reagent at room temperature. The chemical shifts are reported in ppm downfield (δ) from TMS, the coupling constants J are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High resolution mass spectra were recorded on either a Q-TOF mass spectrometry or a LTQ Orbitrap XL mass spectrometry.

2. Screen of Catalysts for the Synthesis of 2-Trifluoromethyl Benzimidazoles.

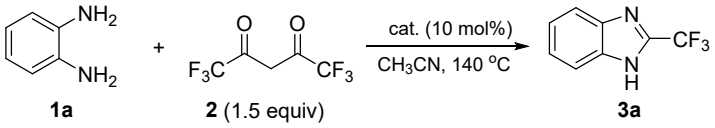
Table S1. Preliminary experiments using $TsOH{\cdot}H_2O$ as catalyst[a]



Entry	Cat. (x mol%)	Yield (%)
1	$TsOH{\cdot}H_2O$ (5)	< 5
2	$TsOH{\cdot}H_2O$ (20)	13 (19[b], 29[c])
3	$TsOH{\cdot}H_2O$ (40)	33[c]
4	CuCl (10.0)/$TsOH{\cdot}H_2O$ (40)	71[c]
5	CuI (10.0)/$TsOH{\cdot}H_2O$ (40)	98[c]
6	$CuCl_2$ (10.0)/$TsOH{\cdot}H_2O$ (40)	41[c]
7	Cu_2O (10.0)/$TsOH{\cdot}H_2O$ (40)	94[c]

[a]Reaction conditions: **1a** (0.50 mmol), **2** (1.5 equiv.) and catalyst (5.0-40 mol%) in CH_3CN (3 mL) at 80 °C under an air atmosphere for 24 h, isolated yield. [b]Conducted at 90 °C. [c]Conducted at 140 °C.

Table S2. Optimization study of catalysts[a]

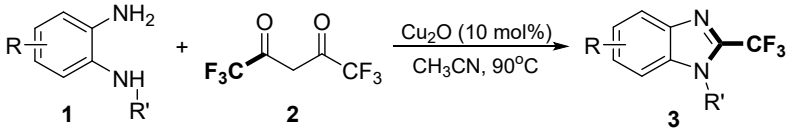


Entry	cat.	Yield (%)
1	CuCl	89
2	CuI	91

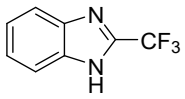
3	$CuCl_2$	37
4	Cu_2O	93
5	$CuBr_2$	56
6	CuBr	92
7	none	NR

[a]Reaction conditions: **1a** (0.50 mmol), **2** (1.5 equiv.) and catalyst (10 mol%) in solvent (3 mL) at 140 °C under an air atmosphere for 24 h, isolated yield.

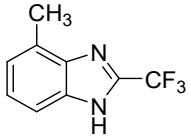
3. The Typical Procedure for the Synthesis of 2-Trifluoromethyl Benzimidazoles.



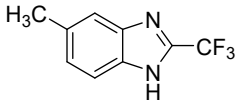
To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was added Cu_2O (7.2 mg, 10 mol%), *o*-phenylenediamines substrate **1** (0.50 mmol, 1.0 equiv.), hexafluoroacetylacetone **2** (0.75 mmol, 1.5 equiv.), and CH_3CN (3 mL) under an air atmosphere. The reaction mixture was stirred at 90 °C for 18 or 24 h, and then cooled to room temperature. The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography to afford the desired products **3**.



2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3a)[1]**:** Yield: >99%, 93.0 mg, white solid, mp 200-202 °C, R_f = 0.43 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 13.81 (s, 1H), 7.72 (s, 2H), 7.36 (dd, J = 5.8, 2.9 Hz, 2H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 141.6 (q, $J_{C\text{-}F}$ = 39.2 Hz), 139.1, 124.0, 119.9 (q, $J_{C\text{-}F}$ = 270.6 Hz), 117.1. ^{19}F NMR (565 MHz, d_6-DMSO) δ -62.7 (s, 3F). HRMS calcd for $C_8H_5F_3N_2$ 186.0405, found 186.0411.

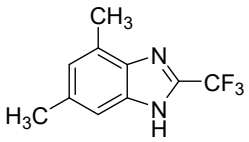


4-methyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3b)[1]**:** Yield: 85%, 85.0 mg, light yellow solid, mp 144-146 °C, R_f = 0.47 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 13.79 (d, J = 36.3 Hz, 1H), 7.50 (d, J = 101.6 Hz, 1H), 7.18 (dd, J = 63.8, 25.6 Hz, 2H), 2.55 (s, 3H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 140.2, 138.7, 137.6, 127.6, 124.4, 124.2, 119.8 (q, $J_{C\text{-}F}$ = 269.3 Hz), 113.9, 17.1. ^{19}F NMR (565 MHz, d_6-DMSO) δ -62.6 (s, 3F). HRMS calcd for $C_9H_7F_3N_2$ 200.0561, found 200.0565.

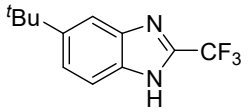


5-methyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3c) [1]**:** Yield: >99%, 99.9 mg, light yellow solid, mp 162-164 °C, R_f = 0.42 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 13.74 (s, 1H), 7.54 (dd, J = 90.1, 56.4 Hz, 2H), 7.16 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 141.5 (q,

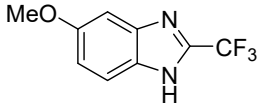
$J_{C\text{-}F}$ = 37.4 Hz), 139.2, 138.1, 133.2, 125.3, 120.1 (q, $J_{C\text{-}F}$ = 270.6 Hz), 117.2, 116.0, 21.7. ^{19}F NMR (565 MHz, d_6-DMSO) δ -62.4 (s, 3F). HRMS calcd for $C_9H_7F_3N_2$ 200.0561, found 200.0569.



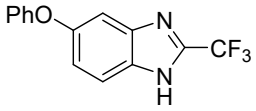
4,6-dimethyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3d): Yield: 77%, 82.0 mg, white solid, mp 125-127 °C, R_f = 0.37 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 13.65 (s, 1H), 7.21 (s, 1H), 6.94 (s, 1H), 2.51 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 141.9 (q, $J_{C\text{-}F}$ = 38.4 Hz), 139.2, 138.8, 132. 7, 127.2, 125.0, 120.5 (q, $J_{C\text{-}F}$ = 270.3 Hz), 113.2, 21.7, 17.2. ^{19}F NMR (565 MHz, d_6-DMSO) δ -62.0 (s, 3F). HRMS calcd for $C_{10}H_9F_3N_2$ 214.0718, found 214.0721.



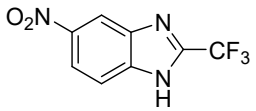
5-(*tert*-butyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3e)[1]**:** Yield: 91%, 110.0 mg, colorless oil, R_f = 0.47 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 13.78 (brs, 1H), 7.64 (s, 2H), 7.44 (s, 1H), 1.32 (s, 9H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 140.3(q, $J_{C\text{-}F}$ = 39.1 Hz), 134.4, 132.2, 119.6 (q, $J_{C\text{-}F}$ = 270.4 Hz), 112.5, 108.7, 35.1, 31.8. ^{19}F NMR (565 MHz, d_6-DMSO) δ -62.7 (s, 3F). HRMS calcd for $C_{12}H_{13}F_3N_2$ 242.1031, found 242.1029.



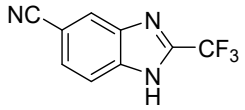
5-methoxy-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3f)[1]**:** Yield: 64%, 69.3 mg, white solid, mp 152-154 °C, R_f = 0.37 (H/E 5:1).^{1}H NMR (600 MHz, d_6-DMSO) δ 13.74 (s, 1H), 7.60 (d, J = 72.4 Hz, 1H), 7.37 – 6.80 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 158.1, 139.3 (q, $J_{C\text{-}F}$ = 42.2 Hz), 136.7, 135.1, 121.5, 119.5 (q, $J_{C\text{-}F}$ = 270.2 Hz), 114.2, 95.0, 56.0. ^{19}F NMR (565 MHz, d_6-DMSO) δ -62.5 (s, 3F). HRMS calcd for $C_9H_7F_3N_2O$ 216.0510, found 216.0514.



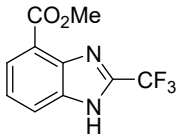
5-phenoxy-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3g): Yield: 76%, 106.1 mg, white solid, mp 158-160 °C, R_f = 0.41 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 13.97 (d, J = 93.5 Hz, 1H), 7.75 (d, J = 71.9 Hz, 1H), 7.57 – 6.86 (m, 7H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 157.7, 154.9, 141.0 (q, $J_{C\text{-}F}$ = 35.8 Hz), 138.7, 135.0, 130.5, 123.8, 122.2, 119.4 (q, $J_{C\text{-}F}$ = 270.8 Hz), 118.9, 118.2, 114.4, 110.6, 102.4. ^{19}F NMR (565 MHz, d_6-DMSO) δ -62.9 (s, 3F). HRMS calcd for $C_{14}H_9F_3N_2O$ 278.0667, found 278.0665.



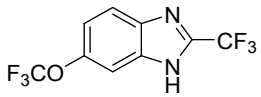
5-nitro-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3h): Yield: >99%, 115.2 mg, light yellow solid, mp 148-150 °C, R_f = 0.41 (H/E 3:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.64 (brs, 1H), 8.64 – 8.46 (m, 1H), 8.18 (dd, J = 9.0, 2.3 Hz, 1H), 7.83 (d, J = 9.0 Hz, 1H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 144.5 (q, $J_{C\text{-}F}$ = 40.1 Hz), 144.4, 140.9, 139.3, 120.0, 118.9 (q, $J_{C\text{-}F}$ = 271.2 Hz), 116.4, 115.1. ^{19}F NMR (565 MHz, d_6-DMSO) δ -63.6 (s, 3F). HRMS calcd for $C_8H_4F_3N_3O_2$ 231.0256, found 231.0257.



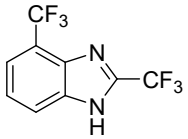
2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole-5-carbonitrile (3i)[1]**:** Yield: >99%, 105.1 mg, white solid, mp 176-178 °C, R_f = 0.39 (H/E 3:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.53 (brs, 1H), 8.32 (s, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 143.4 (q, $J_{C\text{-}F}$ = 39.8 Hz), 127.7, 119.7, 119.0 (q, $J_{C\text{-}F}$ = 271.2 Hz), 106.6. ^{19}F NMR (565 MHz, d_6-DMSO) δ -63.4 (s, 3F). HRMS calcd for $C_9H_4F_3N_3$ 211.0357, found 211.0357.



methyl 2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole-4-carboxylate (3j): Yield: 84%, 102.9 mg, white solid, mp 88-90 °C, R_f = 0.38 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 13.65 (s, 1H), 8.04 (dd, J = 59.7, 5.9 Hz, 2H), 7.45 (t, J = 7.6 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 170.1, 147.7, 147.1 (q, $J_{C\text{-}F}$ = 40.7 Hz), 138.1, 132.5, 131.4, 128.1, 124.0 (q, $J_{C\text{-}F}$ = 271.7 Hz), 120.6, 57.4. ^{19}F NMR (565 MHz, d_6-DMSO) δ -57.5 (s, 3F). HRMS calcd for $C_{10}H_7ClF_3N_2O_2$ 244.0460, found 244.0465.

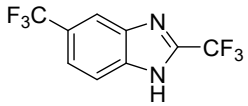


6-(trifluoromethoxy)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3k): Yield: >99%, 135.0 mg, white solid, mp 128-130 °C, R_f = 0.51 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.25 (s, 1H), 7.75 (d, J = 53.4 Hz, 2H), 7.33 (s, 1H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 145.1, 143.5 (q, $J_{C\text{-}F}$ = 39.2 Hz), 139.4, 137.5, 120.7 (q, $J_{C\text{-}F}$ = 255.7 Hz), 119.5 (q, $J_{C\text{-}F}$ = 271.0 Hz), 118.0, 110.2. ^{19}F NMR (565 MHz, d_6-DMSO) δ -57.4 (s, 3F), -63.2 (s, 3F). HRMS calcd for $C_9H_4F_6N_2O$ 270.0228, found 270.0231.

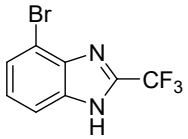


2,4-bis(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3l): Yield: >99%, 126.9 mg, light yellow solid, mp 121-123 °C, R_f = 0.44 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.51 (s, 1H), 7.95 (s, 1H), 7.68 (d, J = 6.1 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 142.9 (q, $J_{C\text{-}F}$ = 39.6 Hz), 137.4, 124.20 (q, $J_{C\text{-}F}$ = 272.3 Hz), 124.18, 120.99, 120.95, 119.56, 119.55, 119.4 (q,

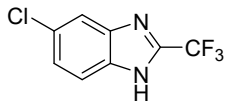
$J_{C\text{-}F}$ = 271.0 Hz). ^{19}F NMR (565 MHz, d_6-DMSO) δ -59.9 (s, 3F), -62.9 (s, 3F). HRMS calcd for $C_9H_4F_6N_2$ 254.0279, found 254.0285.



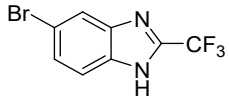
2,5-bis(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3m)[1]**:** Yield: 95%, 120.6 mg, white solid, mp 194-196 °C, R_f = 0.47 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.43 (s, 1H), 8.10 (s, 1H), 7.89 (s, 1H), 7.65 (d, J = 8.2 Hz, 1H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 144.6 (q, $J_{C\text{-}F}$ = 39.4 Hz), 140.9, 139.7, 125.2 (q, $J_{C\text{-}F}$ = 271.9 Hz), 124.2 (q, $J_{C\text{-}F}$ = 31.6 Hz), 120.3, 119.7 (q, $J_{C\text{-}F}$ = 271.0 Hz), 117.5, 115.7. ^{19}F NMR (565 MHz, d_6-DMSO) δ -59.5 (s, 3F), -63.2 (s, 3F). HRMS calcd for $C_9H_4F_6N_2$ 254.0279, found 254.0287.



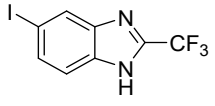
4-bromo-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3n): Yield: 87%, 114.8 mg, light yellow solid, mp 167-169 °C, R_f = 0.45 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.34 (brs, 1H), 7.78 – 7.52 (m, 2H), 7.32 (t, J = 7.6 Hz, 1H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 143.5 (q, $J_{C\text{-}F}$ = 38.7 Hz), 140.9, 138.9, 125.7, 124.9, 120.1 (q, $J_{C\text{-}F}$ = 270.9 Hz), 115.2, 111.6. ^{19}F NMR (565 MHz, d_6-DMSO) δ -62.5 (s, 3F). HRMS calcd for $C_8H_4BrF_3N_2$ 263.9510, found 263.9517.



5-chloro-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3o)[2]**:** Yield: 98%, 108.1 mg, light yellow solid, mp 194-196 °C, R_f = 0.41 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.14 (s, 1H), 7.74 (d, J = 34.7 Hz, 2H), 7.36 (d, J = 7.7 Hz, 1H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 145.9, 142.2, 140.0, 126.8, 122.8, 120.6 (q, $J_{C\text{-}F}$ = 269.4 Hz), 118.6, 116.9. ^{19}F NMR (565 MHz, d_6-DMSO) δ -63.0 (s, 3F). HRMS calcd for $C_8H_4ClF_3N_2$ 220.0015, found 220.0016.

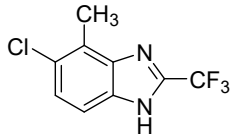


5-bromo-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3p)[2]**:** Yield: 90%, 119.4 mg, white solid, mp 176-1786 °C, R_f = 0.36 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.14 (s, 1H), 8.12 – 7.35 (m, 3H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 143.4 (q, $J_{C\text{-}F}$ = 38.6 Hz), 141.1, 138.5, 126.6, 119.9, 119.8 (q, $J_{C\text{-}F}$ = 270.9 Hz), 118.8, 115.9. ^{19}F NMR (565 MHz, d_6-DMSO) δ -62.8 (s, 3F). HRMS calcd for $C_8H_4BrF_3N_2$ 263.9510, found 263.9512.

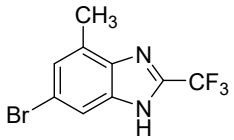


5-iodo-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3q): Yield: 23%, 36.4 mg, yellow solid, mp 200-202 °C, R_f = 0.47 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 13.93 (brs, 1H), 7.73 (s, 2H),

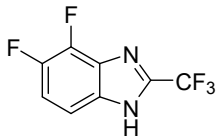
7.38 (dd, J = 5.7, 2.8 Hz, 2H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 143.6 (q, $J_{C\text{-}F}$ = 37.3 Hz), 140.8, 122.8, 120.7 (q, $J_{C\text{-}F}$ = 270.7 Hz), 117.3. ^{19}F NMR (565 MHz, d_6-DMSO) δ -58.0 (s, 3F). HRMS calcd for $C_8H_4F_3IN_2$ 311.9371, found 311.9375.



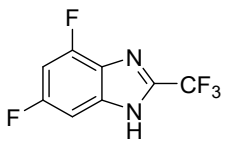
5-chloro-4-methyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3r): Yield: >99%, 116.4 mg, yellow solid, mp 144-146 °C, R_f = 0.47 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.02 (brs, 1H), 7.67 – 7.11 (m, 2H), 2.54 (s, 3H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 142.5 (q, $J_{C\text{-}F}$ = 38.9 Hz), 140.7, 136.9, 127.6, 125.4, 124.8, 119.8 (q, $J_{C\text{-}F}$ = 270.7 Hz), 114.8, 14.5. ^{19}F NMR (565 MHz, d_6-DMSO) δ -62.6 (s, 3F). HRMS calcd for $C_9H_6ClF_3N_2$ 234.0172, found 234.0175.



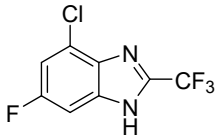
6-bromo-4-methyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3s): Yield: 90%, 124.8 mg, yellow solid, mp 158-160 °C, R_f = 0.42 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.02 (s, 1H), 7.61 (s, 1H), 7.28 (s, 1H), 2.52 (s, 3H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 142.3 (q, $J_{C\text{-}F}$ = 38.7 Hz), 139.7, 138.5, 129.7, 126.6, 119.7 (q, $J_{C\text{-}F}$ = 270.9 Hz), 116.7, 116.2, 16.9. ^{19}F NMR (565 MHz, d_6-DMSO) δ -62.6 (s, 3F). HRMS calcd for $C_9H_6BrF_3N_2$ 277.9666, found 277.9671.



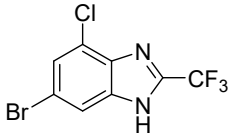
4,5-difluoro-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3t): Yield: 85%, 94.0 mg, white solid, mp 178-180 °C, R_f = 0.31 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.47 (s, 1H), 7.60 – 7.28 (m, 2H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 146.0 (dd, $J_{C\text{-}F}$ = 236.3, 9.4 Hz), 143.6 (q, $J_{C\text{-}F}$ = 38.7 Hz), 140.4 (dd, $J_{C\text{-}F}$ = 253.3, 15.1 Hz), 136.1, 130.8, 119.4 (q, $J_{C\text{-}F}$ = 270.9 Hz), 114.0 (d, $J_{C\text{-}F}$ = 22.2 Hz), 111.3. ^{19}F NMR (565 MHz, d_6-DMSO) δ -58.5 (s, 3F), -148.80 (s, 1F), -148.83 (s, 1F). HRMS calcd for $C_8H_3F_5N_2$ 222.0216, found 222.0217.



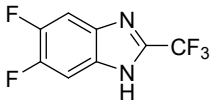
4,6-difluoro-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3u): Yield: 99%, 110.1 mg, light yellow solid, mp 196-198 °C, R_f = 0.46 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.43 (s, 1H), 7.28 (s, 1H), 7.14 (s, 1H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 159.3 (d, $J_{C\text{-}F}$ = 239.6 Hz), 152.9 (d, $J_{C\text{-}F}$ = 255.9 Hz), 143.1, 139.2, 127.2, 119.4 (q, $J_{C\text{-}F}$ = 270.2 Hz), 99.0 (t, $J_{C\text{-}F}$ = 25.0 Hz), 97.4. ^{19}F NMR (565 MHz, d_6-DMSO) δ -63.1 (s, 3F), -155.2 (s, 1F), -124.2 (s, 1F). HRMS calcd for $C_8H_3F_5N_2$ 222.0216, found 222.0219.



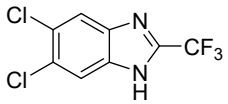
4-chloro-6-fluoro-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3v): Yield: 92%, 109.1 mg, light yellow solid, mp 193-195 °C, R_f = 0.45 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.48 (brs, 1H), 7.48 – 7.40 (m, 2H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 159.1 (d, $J_{C\text{-}F}$ = 236.5 Hz), 143.6 (q, $J_{C\text{-}F}$ = 39.0 Hz), 137.89, 135.77, 123.74, 119.5 (q, $J_{C\text{-}F}$ = 269.8 Hz), 112.4 (d, $J_{C\text{-}F}$ = 28.7 Hz), 100.85. ^{19}F NMR (565 MHz, d_6-DMSO) δ -62.9 (s, 3F), -116.3 (s, 1F). HRMS calcd for $C_8H_3ClF_4N_2$ 237.9921, found 237.9927.



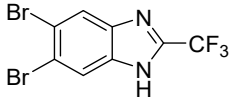
6-bromo-4-chloro-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3w): Yield: 92%, 137.3 mg, white solid, mp 186-188 °C, R_f = 0.38 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.54 (s, 1H), 7.83 (s, 1H), 7.59 (s, 1H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 143.7 (q, $J_{C\text{-}F}$ = 39.0 Hz), 139.5, 138.0, 125.5, 123.9, 119.5 (q, $J_{C\text{-}F}$ = 271.0 Hz), 117.3, 116.0. ^{19}F NMR (565 MHz, d_6-DMSO) δ -62.9 (s, 3F). HRMS calcd for $C_8H_3BrClF_3N_2$ 297.9120, found 297.9126.



5,6-difluoro-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3x)[1]**:** Yield: 88%, 97.2 mg, light yellow solid, mp 204-206 °C, R_f = 0.42 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.25 (s, 1H), 7.78 (s, 2H). ^{3}C NMR (151 MHz, d_6-DMSO) δ 148.5 (dd, $J_{C\text{-}F}$ = 243.2, 17.4 Hz), 142.6 (q, $J_{C\text{-}F}$ = 39.6 Hz), 134.1, 119.2 (q, $J_{C\text{-}F}$ = 207.8 Hz), 104.6 (d, $J_{C\text{-}F}$ = 21.7 Hz). ^{9}F NMR (565 MHz, d_6-DMSO) δ -63.0 (s, 3F), -141.2 (s, 2F). HRMS calcd for $C_8H_3F_5N_2$ 222.0216, found 222.0222.

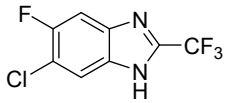


5,6-dichloro-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3y): Yield: 83%, 105.5 mg, white solid, mp 248-250 °C, R_f = 0.51 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.33 (s, 1H), 7.97 (s, 2H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 145.9 (q, $J_{C\text{-}F}$ = 40.6 Hz), 140.1, 125.5, 120.0 (q, $J_{C\text{-}F}$ = 271.2 Hz), 118. 6. ^{19}F NMR (565 MHz, d_6-DMSO) δ -62.8 (s, 3F). HRMS calcd for $C_8H_3Cl_2F_3N_2$ 253.9625, found 253.9633.

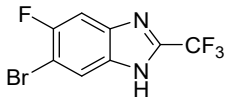


5,6-dibromo-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3z): Yield: 89%, 152.9 mg, white solid, mp 204-206 °C, R_f = 0.36 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.31 (s, 1H), 8.10 (s, 2H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 144.6 (q, $J_{C\text{-}F}$ = 38.7 Hz), 140.2, 121.7, 119.7 (q, $J_{C\text{-}F}$ = 271.1

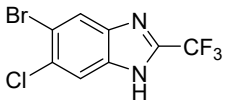
Hz), 117.8. ^{19}F NMR (565 MHz, d_6-DMSO) δ -62.9 (s, 3F). HRMS calcd for $C_8H_3Br_2F_3N_2$ 341.8615, found 341.8626.



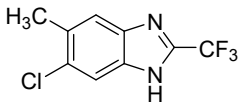
6-chloro-5-fluoro-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3aa): Yield: 88%, 104.5 mg, light yellow solid, mp 211-213 °C, R_f = 0.51 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.27 (s, 1H), 7.92 (s, 1H), 7.72 (s, 1H). ^{3}C NMR (151 MHz, d_6-DMSO) δ 154.6 (d, $J_{C\text{-}F}$ = 240.4 Hz), 143.7 (q, $J_{C\text{-}F}$ = 37.6 Hz), 137.7, 136.2, 119.4 (q, $J_{C\text{-}F}$ = 270.9 Hz), 118.42, 116.6 (d, $J_{C\text{-}F}$ = 20.9 Hz), 103.9 (d, $J_{C\text{-}F}$ = 25.5 Hz). ^{9}F NMR (565 MHz, d_6-DMSO) δ -63.0 (s, 3F), -120.6 (s, 1F). HRMS calcd for $C_8H_3ClF_4N_2$ 237.9921, found 237.9924.



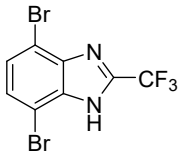
6-bromo-5-fluoro-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3bb): Yield: 87%, 122.4 mg, white solid, mp 202-204 °C, R_f = 0.40 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.27 (s, 1H), 8.04 (s, 1H), 7.69 (s, 1H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 155.3 (d, $J_{C\text{-}F}$ = 238.4 Hz), 143.8 (q, $J_{C\text{-}F}$ = 39.0 Hz), 138.4 (d, $J_{C\text{-}F}$ = 12.2 Hz), 137.1, 121.3, 119.5 (q, $J_{C\text{-}F}$ = 270.8 Hz), 104.4 (d, $J_{C\text{-}F}$ = 24.7 Hz), 103.7 (d, $J_{C\text{-}F}$ = 26.5 Hz). ^{19}F NMR (565 MHz, d_6-DMSO) δ -63.0 (s, 3F), -113.0 (s, 1F). HRMS calcd for $C_8H_3BrF_4N_2$ 281.9416, found 281.9423.



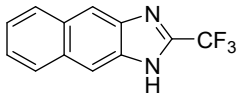
5-bromo-6-chloro-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3cc): Yield: 94%, 140.7 mg, white solid, mp 218-220 °C, R_f = 0.51 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.30 (s, 1H), 8.08 (s, 1H), 7.94 (s, 1H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 144.1 (q, $J_{C\text{-}F}$ = 39.2 Hz), 139.3, 139.2, 128.1, 121.7, 119.5 (q, $J_{C\text{-}F}$ = 271.1 Hz), 118.3, 116.2. ^{19}F NMR (565 MHz, d_6-DMSO) δ -63.0 (s, 3F). HRMS calcd for $C_8H_3BrClF_3N_2$ 297.9120, found 297.9120.



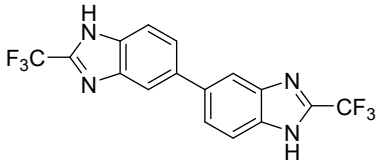
6-chloro-5-methyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3dd): Yield: 81%, 94.9 mg, white solid, mp 175-177 °C, R_f = 0.37 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 13.96 (s, 1H), 7.78 (s, 1H), 7.64 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 143.0 (q, $J_{C\text{-}F}$ = 38.6 Hz), 139.3, 138.1, 130.9, 128.9, 119.9 (q, $J_{C\text{-}F}$ = 270.7 Hz), 117.8, 117.3, 20.7. ^{19}F NMR (565 MHz, d_6-DMSO) δ -62.7 (s, 3F). HRMS calcd for $C_9H_6ClF_3N_2$ 234.0172, found 234.0179.



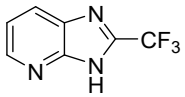
4,7-dibromo-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3ee): Yield: 84%, 144.7 mg, yellow solid, mp 244-246 °C, R_f = 0.38 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.69 (s, 1H), 7.49 (s, 2H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 142.5 (q, $J_{C\text{-}F}$ = 39.1 Hz), 138.3, 128.1, 119.1 (q, $J_{C\text{-}F}$ = 271.4 Hz), 109.0. ^{19}F NMR (565 MHz, d_6-DMSO) δ -62.6 (s, 3F). HRMS calcd for $C_8H_3Br_2F_3N_2$ 341.8615, found 341.8616.



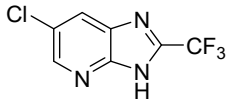
2-(trifluoromethyl)-1*H*-naphtho[2,3-*d*]imidazole (3ff) [1]**:** Yield: >99%, 117.9 mg, light yellow solid, mp 274-276 °C, R_f = 0.32 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 13.95 (s, 1H), 8.42-8.07 (m, 4H), 7.45 (s, 2H). ^{3}C NMR (151 MHz, d_6-DMSO) δ 150.0 (q, $J_{C\text{-}F}$ = 36.9 Hz), 142.9, 130.2, 128.3, 123.3, 121.0 (q, $J_{C\text{-}F}$ = 271.4 Hz), 113.4. ^{9}F NMR (565 MHz, d_6-DMSO) δ -62.7 (s, 3F). HRMS calcd for $C_{12}H_7F_3N_2$ 236.0561, found 236.0563.



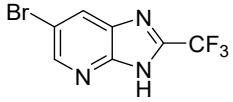
2,2'-bis(trifluoromethyl)-1*H*,1'*H*-5,5'-bibenzo[*d*]imidazole (3gg)[2]**:** Yield: 94%, 173.6 mg, light yellow solid, mp 295-297 °C, R_f = 0.31 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.02 (brs, 2H), 8.14 – 7.64 (m, 6H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 147.3 (q, $J_{C\text{-}F}$ = 39.1 Hz), 144.6, 143.7, 141.9, 128.5, 124.8 (q, $J_{C\text{-}F}$ = 269.5 Hz), 122.4, 119.8. ^{19}F NMR (565 MHz, d_6-DMSO) δ -57.9 (s, 6F). HRMS calcd for $C_{16}H_8F_6N_4$ 370.0653, found 370.0657.



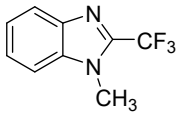
2-(trifluoromethyl)-3*H*-imidazo[4,5-*b*]pyridine (3hh)[2]**:** Yield: 60%, 56.5 mg, white solid, mp 253-255 °C, R_f = 0.30 (H/E 2:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.58 (s, 1H), 8.53 (s, 1H), 8.22 (d, J = 5.9 Hz, 1H), 7.41 (s, 1H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 153.0, 145.9 (q, $J_{C\text{-}F}$ = 37.8 Hz), 144. 7, 133.7, 126.6, 120.4 (q, $J_{C\text{-}F}$ = 270.9 Hz), 118.5. ^{19}F NMR (565 MHz, d_6-DMSO) δ -63.1 (s, 3F). HRMS calcd for $C_7H_4F_3N_3$ 187.0357, found 187.0363.



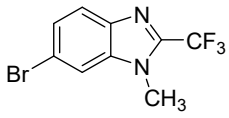
6-chloro-2-(trifluoromethyl)-3*H*-imidazo[4,5-*b*]pyridine (3ii): Yield: 50%, 54.9 mg, white solid, mp 286-288 °C, R_f = 0.35 (H/E 2:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.79 (s, 1H), 8.54 (s, 1H), 8.36 (s, 1H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 151.9, 147.1 (q, $J_{C\text{-}F}$ = 38.2 Hz), 143.7, 133.8, 125.5, 125.1, 120.1 (q, $J_{C\text{-}F}$ = 271.1 Hz). ^{19}F NMR (565 MHz, d_6-DMSO) δ -63.3 (s, 3F). HRMS calcd for $C_7H_3ClF_3N_3$ 220.9968, found 220.9970.



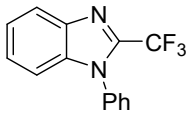
6-bromo-2-(trifluoromethyl)-3*H*-imidazo[4,5-*b*]pyridine (3jj): Yield: 40%, 52.7 mg, white solid, mp 292-294 °C, R_f = 0.35 (H/E 2:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 14.79 (s, 1H), 8.62 (s, 1H), 8.50 (s, 1H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 154.2, 149.5 (q, $J_{C\text{-}F}$ = 36.6 Hz), 144.2, 136.2, 127.8, 120.9 (q, $J_{C\text{-}F}$ = 271.1 Hz), 112.3. ^{19}F NMR (565 MHz, d_6-DMSO) δ -63.0 (s, 3F). HRMS calcd for $C_7H_3BrF_3N_3$ 264.9462, found 264.9467.



1-methyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3kk)[1]**:** Yield: 89%, 89.3 mg, white solid, mp 82-84 °C, R_f = 0.45 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 7.82 (d, J = 8.2 Hz, 1H), 7.77 (d, J = 8.3 Hz, 1H), 7.52 – 7.45 (m, 1H), 7.42 – 7.35 (m, 1H), 3.97 (s, 3H). ^{3}C NMR (151 MHz, d_6-DMSO) δ 145.6, 144.9 (q, $J_{C\text{-}F}$ = 38.0 Hz), 141.3, 130.4, 128.7, 125.9, 124.3 (q, $J_{C\text{-}F}$ = 271.1 Hz), 116.8, 36.1. ^{9}F NMR (565 MHz, d_6-DMSO) δ -56.8 (s, 3F). HRMS calcd for $C_9H_7F_3N_2$ 200.0561, found 200.0561.

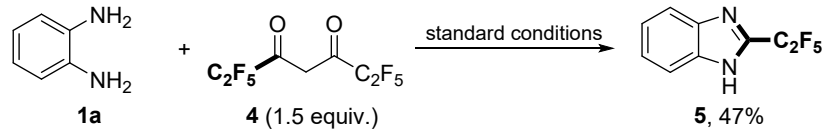


6-bromo-1-methyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3ll)[1]**:** Yield: 94%, 130.5 mg, white solid, mp 148-150 °C, R_f = 0.63 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 8.13 (s, 1H), 7.77 (d, J = 8.6 Hz, 1H), 7.55 – 7.47 (m, 1H), 3.96 (s, 3H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 140.9 (q, $J_{C\text{-}F}$ = 38.2 Hz), 139.8, 137.7, 127.1, 122.9, 119.3 (q, $J_{C\text{-}F}$ = 271.5 Hz), 118.3, 115.3, 31.6. ^{19}F NMR (565 MHz, d_6-DMSO) δ -61.8 (s, 3F). HRMS calcd for $C_9H_6BrF_3N_2$ 277.9666, found 277.9677.

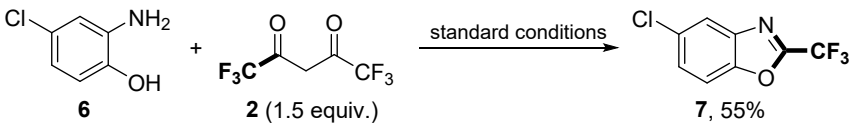


1-phenyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3mm)[1]**:**: Yield: 67%, 87.7 mg, yellow oil, R_f = 0.53 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 7.98 – 7.90 (m, 1H), 7.70 – 7.64 (m, 3H), 7.61 (dd, J = 6.7, 2.7 Hz, 2H), 7.45 (dd, J = 6.3, 3.1 Hz, 2H), 7.20 – 7.15 (m, 1H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 140.6, 140.4 (q, $J_{C\text{-}F}$ = 38.1 Hz), 137.5, 134.4, 130.6, 130.4, 128.0, 126.6, 124.5, 121.4, 119.3 (q, $J_{C\text{-}F}$ = 271.7 Hz), 111.9. ^{19}F NMR (565 MHz, d_6-DMSO) δ -59.6 (s, 3F). HRMS calcd for $C_{14}H_9F_3N_2$ 262.0718, found 262.0723.

4. Substrate Extension Studies.



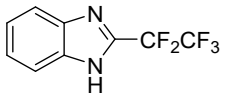
(1)



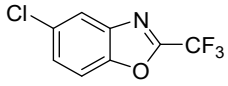
(2)

Method A: To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was added Cu_2O (7.2 mg, 10 mol%), *o*-phenylenediamines substrate **1** (0.50 mmol, 1.0 equiv.), with 1,1,1,2,2,6,6,7,7,7-decafluoroheptane-3,5-dione **4** (0.75 mmol, 1.5 equiv.), and CH_3CN (3 mL) under an air atmosphere. The reaction mixture was stirred at 90 °C for 24 h, and then cooled to room temperature. The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography to afford the desired products **5** as a white solid (55.3 mg, yield: 47%).

Method B: To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was added Cu_2O (7.2 mg, 10 mol%), *o*-aminophenols **6** (0.50 mmol, 1.0 equiv.), with hexafluoroacetylacetone **2** (0.75 mmol, 1.5 equiv.), and CH_3CN (3 mL) under an air atmosphere. The reaction mixture was stirred at 90 °C for 24 h, and then cooled to room temperature. The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography to afford the desired products **7** as a white solid (61.3 mg, yield: 55%).

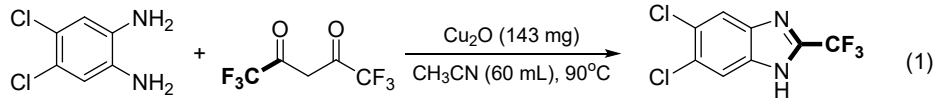


2-(perfluoroethyl)-1*H*-benzo[*d*]imidazole (5): Yield: 47%, 55.3 mg, white solid, mp 187-189 °C, R_f = 0.45 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 13.99 (s, 1H), 7.75 (d, J = 97.1 Hz, 2H), 7.39 (s, 2H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 143.9 (q, $J_{C\text{-}F}$ = 27.0 Hz), 142.1, 122.1, 119.2 (qt, $J_{C\text{-}F}$ = 286.0, 38.1 Hz), 117.4, 110.8 (tq, $J_{C\text{-}F}$ = 253.7, 38.2 Hz). ^{19}F NMR (565 MHz, d_6-DMSO) δ -82.4 (s, 3F), -111.1 (s, 2F). HRMS calcd for $C_9H_5F_5N_2$ 236.0373, found 236.0374.



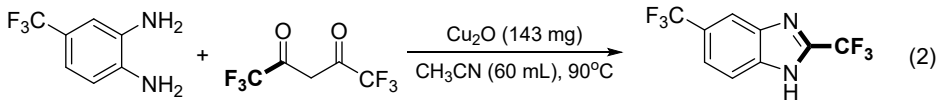
5-chloro-2-(trifluoromethyl)benzo[*d*]oxazole (7)[1]**:** Yield: 55%, 61.3 mg, light yellow solid, mp 222-224 °C, R_f = 0.46 (H/E 5:1). ^{1}H NMR (600 MHz, d_6-DMSO) δ 7.42 (s, 1H), 7.13 (d, J = 7.4 Hz, 1H), 6.91 (d, J = 8.4 Hz, 1H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 155.4 (q, $J_{C\text{-}F}$ = 36.2 Hz), 150.7, 127.4, 126.0, 125.8, 122.2, 117.8, 116.7 (q, $J_{C\text{-}F}$ = 288.4 Hz). ^{19}F NMR (565 MHz, d_6-DMSO) δ -73.7 (s, 3F). HRMS calcd for $C_8H_3ClF_3NO$ 220.9855, found 220.9860.

5. Large–scale Synthesis.



(1)

1y, 1.77 g **2**, 3.12 g **3y**, 2.34 g, 92% yield



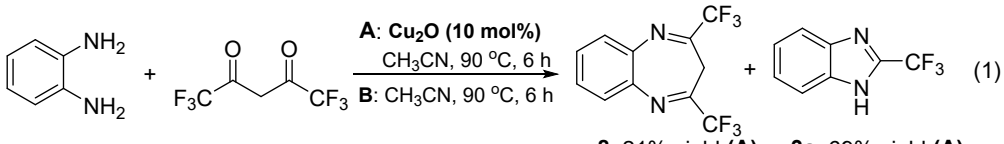
(2)

1m, 1.76 g **2**, 3.12 g **3m**, 2.48 g, 98% yield

To an oven-dried 120 mL Schlenk tube equipped with a magnetic stir bar was added Cu_2O (143 mg, 10 mol%), **1y** or **1m** (10 mmol), with hexafluoroacetylacetone **2** (15 mmol), and CH_3CN (60 mL) under an air atmosphere. The reaction mixture was stirred at 90 °C for 24 h, and then cooled to room temperature. The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography to afford the desired products **3y** or **3m**.

6. Control Experiments.

(1) The isolation of intermediate.

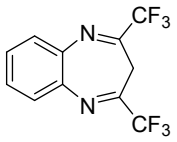


(1)

1a **2** (1.5 equiv) **8**, 21% yield **(A)** 67% yield **(B)** **3a**, 69% yield **(A)** <5% yield **(B)**

Method A: To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was added **1a** (54.1 mg, 0.50 mmol), **2** (0.75 mmol, 1.5 equiv.), Cu_2O (7.2 mg, 10 mol%) and CH_3CN (3 mL) under an air atmosphere. The reaction mixture was stirred at 90 °C for 6 h, and then cooled to room temperature. Then the corresponding reaction mixture was purified by silica gel column chromatography to give intermediate 2,4-bis(trifluoromethyl)-3*H*-benzo[*b*]azepine **8** in 21% yield and final product **3a** in 69% yield.

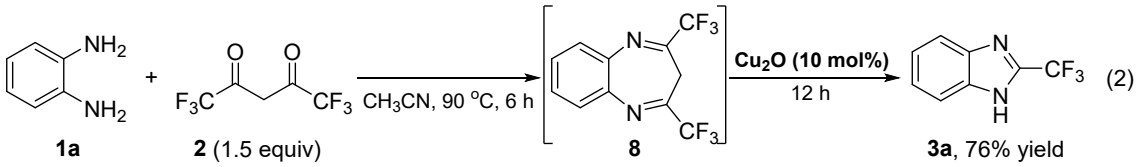
Method B: To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was added **1a** (54.1 mg, 0.50 mmol), **2** (0.75 mmol, 1.5 equiv.), and CH_3CN (3 mL) under an air atmosphere. The reaction mixture was stirred at 90 °C for 6 h, and then cooled to room temperature. Then the corresponding reaction mixture was purified by silica gel column chromatography to give intermediate 2,4-bis(trifluoromethyl)-3*H*-benzo[*b*]azepine **8** in 67% yield.



2,4-bis(trifluoromethyl)-3*H*-benzo[*b*][1,4]diazepine (8): white solid, mp 88-90 °C, R_f = 0.87 (H/E 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H), 7.54 – 7.50 (m, 2H), 3.25 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.3 (q, $J_{C\text{-}F}$ = 36.7 Hz), 137.4, 129.3, 128.5, 118.4 (q, $J_{C\text{-}F}$ = 277.4

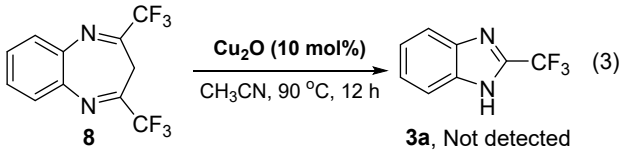
Hz), 29.9. ^{19}F NMR (565 MHz, $CDCl_3$) δ -71.2 (s, 6F). HRMS calcd for [M+H] $C_{11}H_7F_6N_2$ 281.0513, found 281.0515.

(2) One-pot two-step reaction for the synthesis of final product.

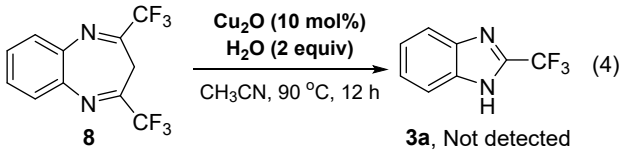


Method C: To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was added **1a** (54.1 mg, 0.50 mmol), **2** (0.75 mmol, 1.5 equiv.), and CH_3CN (3 mL) under an air atmosphere. The reaction mixture was stirred at 90 °C for 6 h followed by adding 10 mol% of Cu_2O to continue stirring for 12 h, and then cooled to room temperature. Then the corresponding reaction mixture was purified by silica gel column chromatography to give final product **3a** in 76% yield.

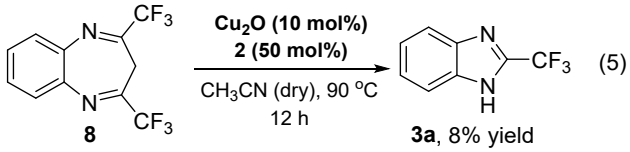
(3) Control experiments.



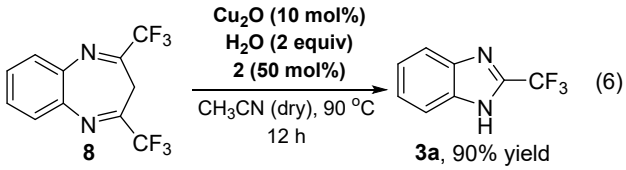
Method D: To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was added **8** (140.1 mg, 0.50 mmol), Cu_2O (7.2 mg, 10 mol%) and CH_3CN (3 mL) under an air atmosphere. The reaction mixture was stirred at 90 °C for 12 h, and then cooled to room temperature. Then the corresponding reaction mixture was detected by TLC.



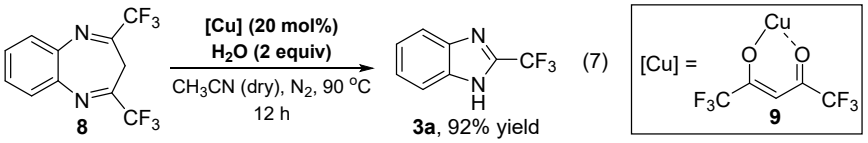
Method E: To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was added **8** (140.1 mg, 0.50 mmol), H_2O (18.0 mg, 2 equiv.), Cu_2O (7.2 mg, 10 mol%), and CH_3CN (3 mL) under an air atmosphere. The reaction mixture was stirred at 90 °C for 12 h, and then cooled to room temperature. Then the corresponding reaction mixture was detected by TLC.



Method F: To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was added **8** (140.1 mg, 0.50 mmol), **2** (52.0 mg, 0.25 mol), Cu_2O (7.2 mg, 10 mol%), and dry CH_3CN (3 mL) under an air atmosphere. The reaction mixture was stirred at 90 °C for 12 h, and then cooled to room temperature. Then the corresponding reaction mixture was purified by silica gel column chromatography to give final product **3a** in 8% yield.

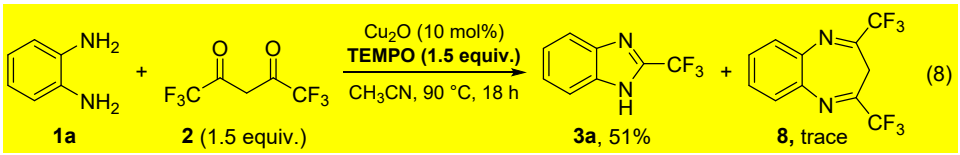


Method G: To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was added **8** (140.1 mg, 0.50 mmol), **2** (52.0 mg, 0.25 mol), H_2O (18.0 mg, 2 equiv.), Cu_2O (7.2 mg, 10 mol%), and dry CH_3CN (3 mL) under an air atmosphere. The reaction mixture was stirred at 90 °C for 12 h, and then cooled to room temperature. Then the corresponding reaction mixture was purified by silica gel column chromatography to give final product **3a** in 90% yield.



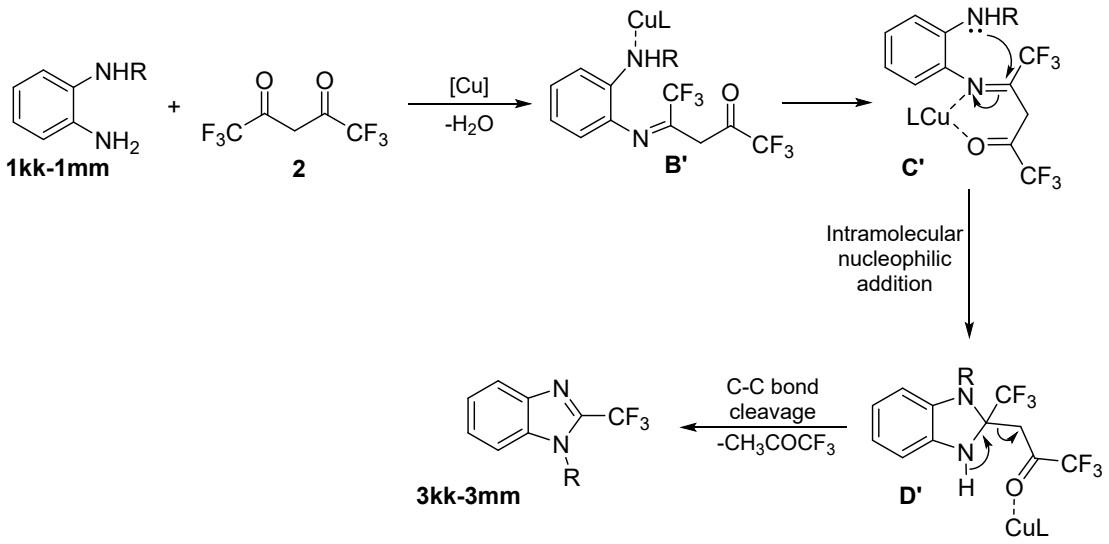
To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was added Cu_2O (71.5 mg, 0.50 mmol), **2** (228.9 mg, 1.0 mol) and CH_3CN (3 mL) under a N_2 atmosphere. The reaction mixture was stirred at 90 °C for 3 h, and then cooled to room temperature. The solvent was removed under reduced pressure. The remaining residue was dissolved in THF (10 mL), and the resulting suspension was filtered. Then, the solvent was removed again under reduced pressure to yield copper complex **9** as a green solid.

Method H: To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was added **8** (140.1 mg, 0.50 mmol), **9** (27.1 mg, 20 mol%), H_2O (18.0 mg, 2 equiv.), and CH_3CN (3 mL) under a N_2 atmosphere. The reaction mixture was stirred at 90 °C for 12 h, and then cooled to room temperature. Then the corresponding reaction mixture was purified by silica gel column chromatography to give final product **3a** in 92% yield.



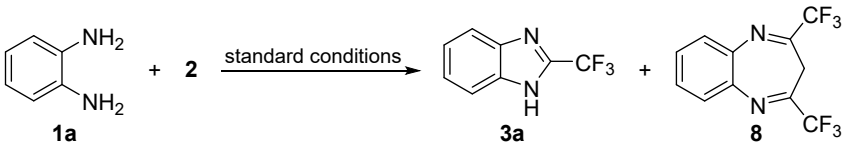
Method I: To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was added **1a** (54.1 mg, 0.50 mmol), **2** (0.75 mmol, 1.5 equiv.), Cu_2O (7.2 mg, 10 mol%), TEMPO (0.75 mmol, 1.5 equiv.) and CH_3CN (3 mL) under an air atmosphere. The reaction mixture was stirred at 90 °C for 18 h, and then cooled to room temperature. The yields of products were determined by ^{19}F NMR analysis using 1-fluoro-4-methylbenzene as the internal standard.

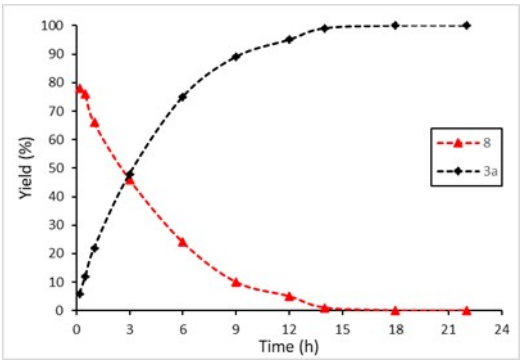
7. The Possible Mechanism for *N*-methyl or Phenyl Substrates.



The condensation of *N*-methyl or phenyl diamines **1kk-1mm** with **2** to lose monomolecular H_2O directly gives the intermediate **B'** in the presence of Cu species **9**. Cyclic intermediate **D'** would form via the intramolecular nucleophilic addition of intermediate **C'**. Finally, the C−C bond cleavage reaction of **D'** would occur to form target product **3kk-3mm** and regenerate Cu catalytic species.

8. Kinetic Study.





An oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with a mixture of **1a** (54.1 mg, 0.50 mmol), **2** (0.75 mmol, 1.5 equiv.), Cu_2O (7.2 mg, 10 mol%) and CH_3CN (3 mL) under an air atmosphere. The reaction mixture was stirred at 90 °C. The yields of products were determined by ^{19}F NMR analysis using 1-fluoro-4-methylbenzene as the internal standard during 10 min, 30 min, 1 h, 3h, 6 h, 9 h, 12 h, 14 h, 18 h and 22 h after initiation.

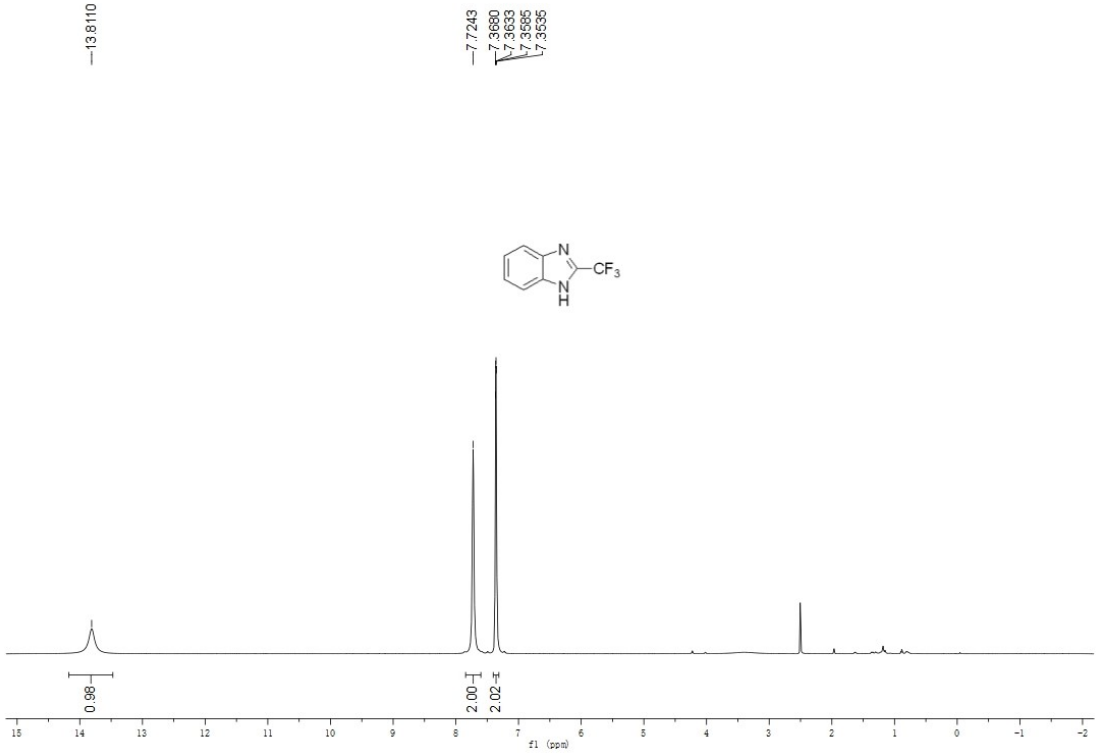
9. References.

[1] Lin, B.; Yao, Y.; Wu, M.; Qin, L.; Chen, S.; You, Y.; Weng, Z. *Org. Biomol. Chem.* **2023**, *21*, 4788–4793.

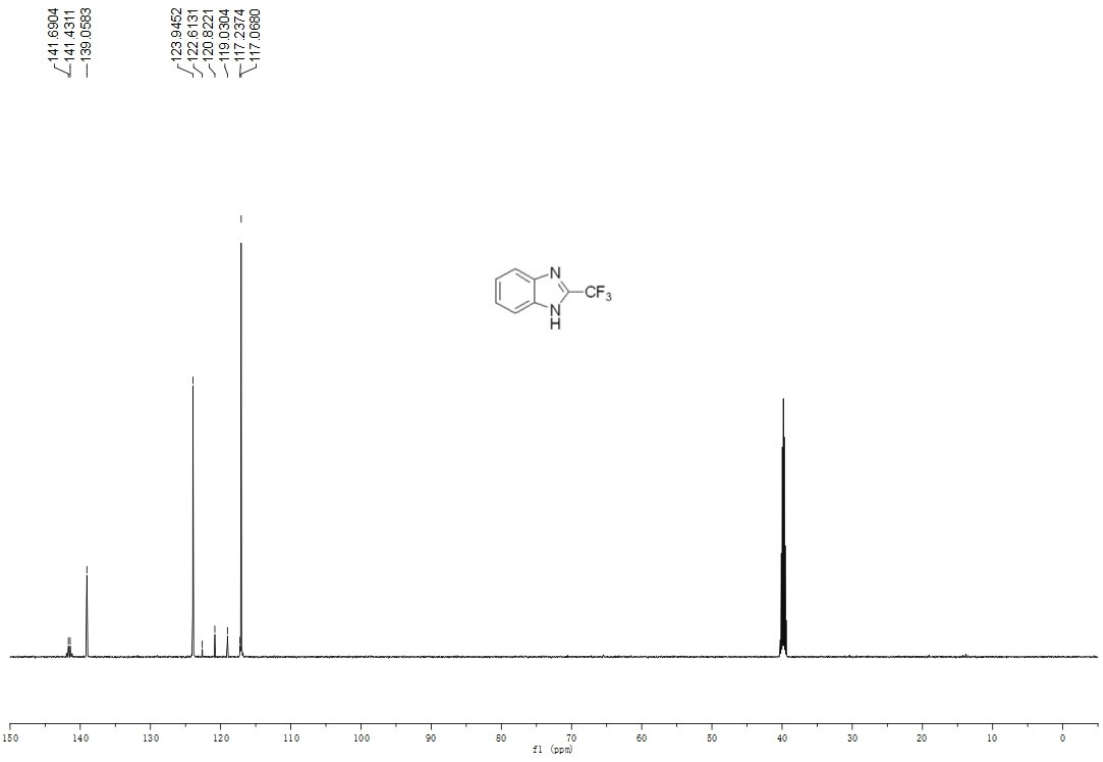
[2] Zhou, Y.; Shen, G.; Sui, Y.; Zhou, H. *Tetrahedron Lett.* **2016**, *57*, 3396–3399.

10. Copy of NMR Spectra.

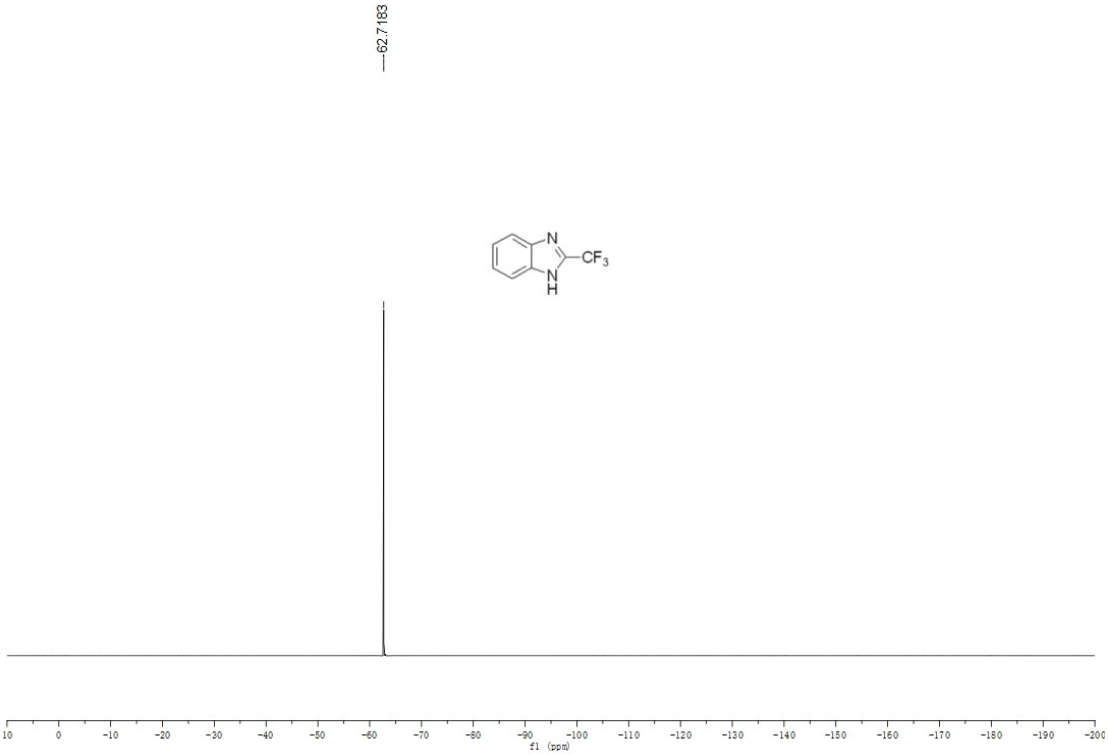
^{1}H NMR of 3a



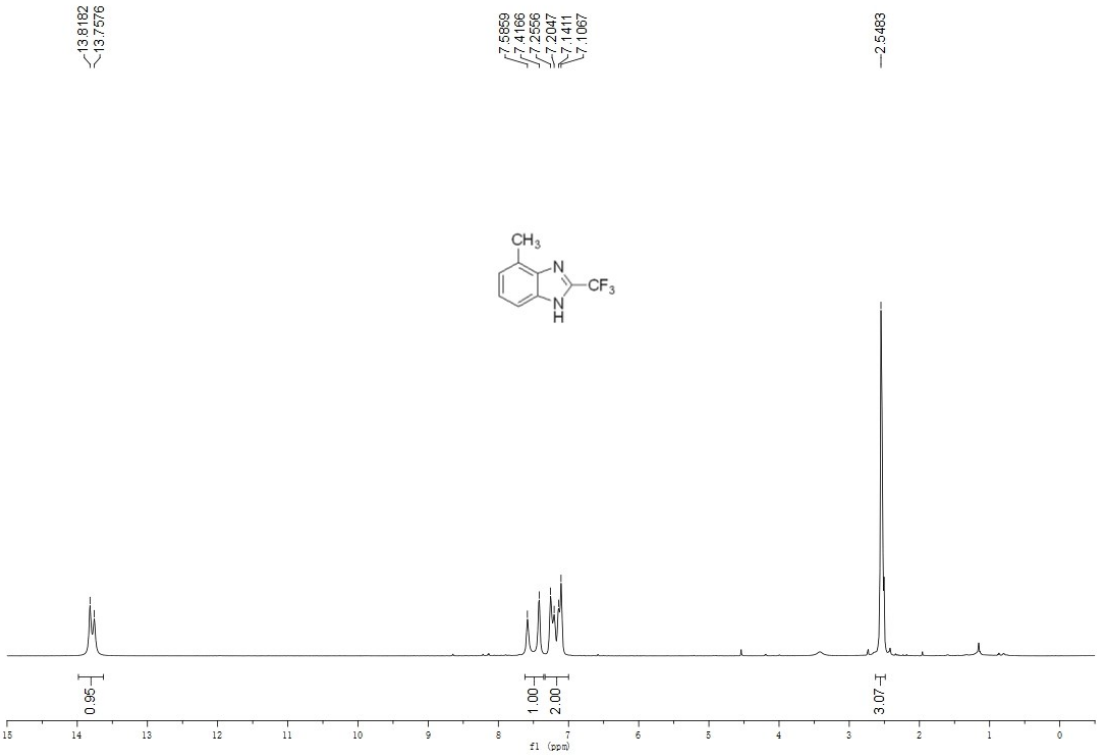
^{13}C NMR of 3a



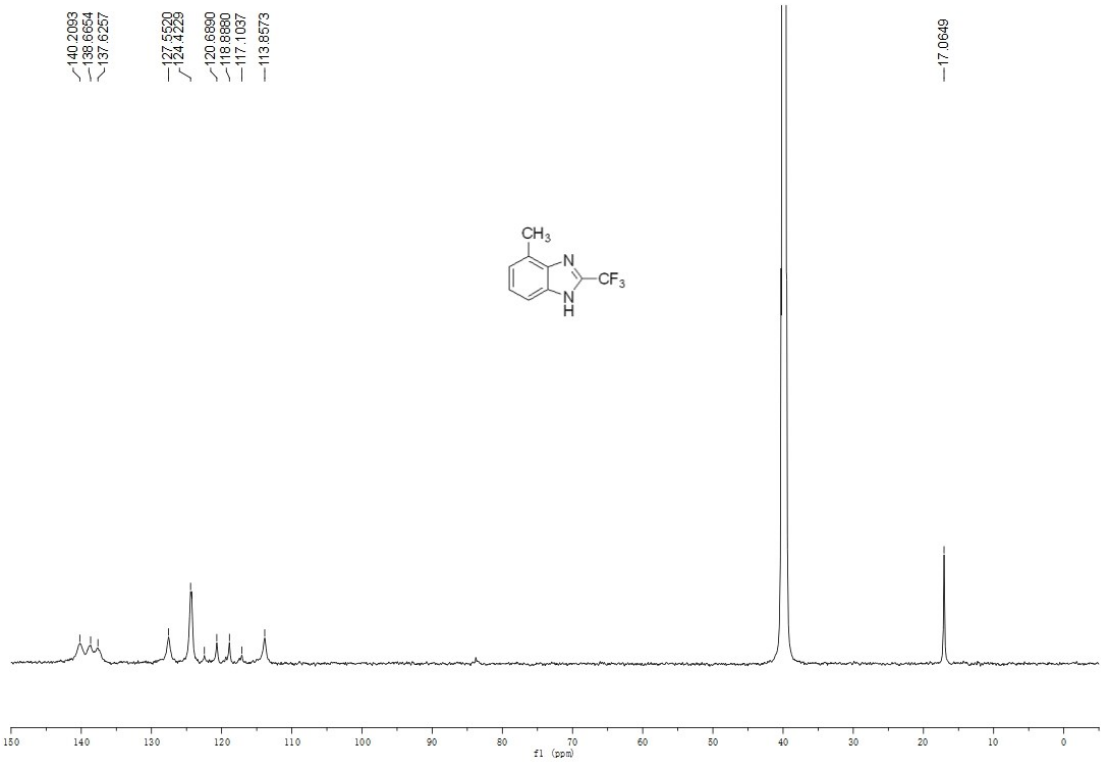
^{19}F NMR of 3a



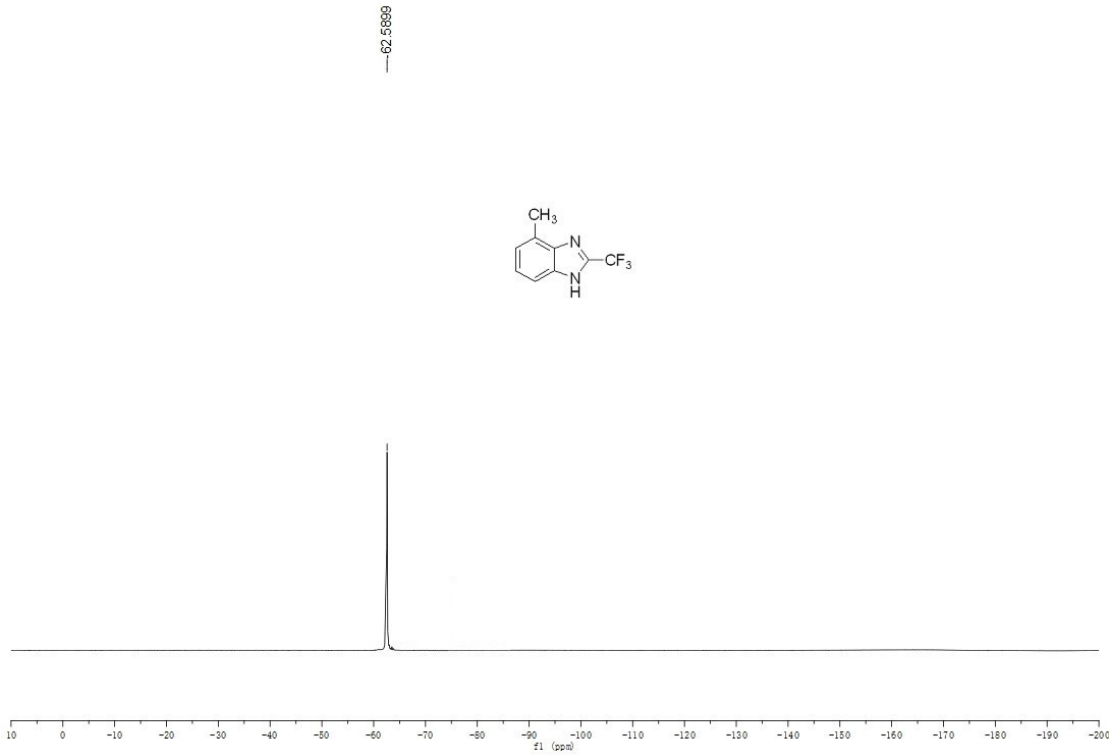
^{1}H NMR of 3b



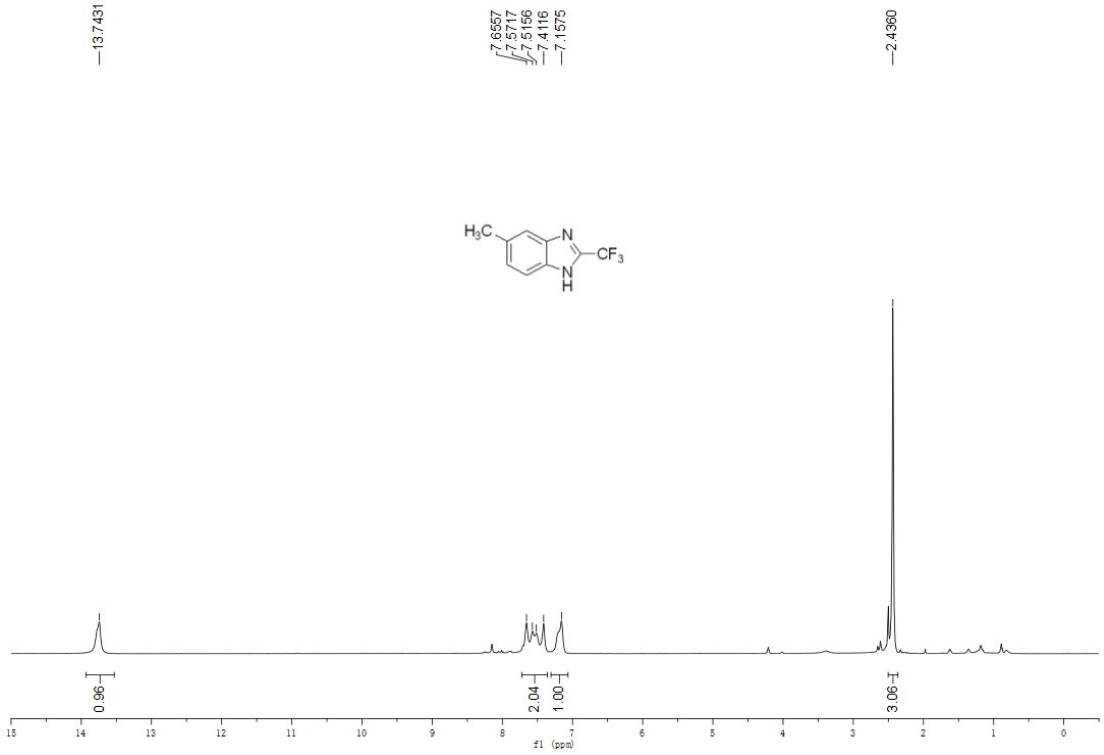
^{13}C NMR of 3b



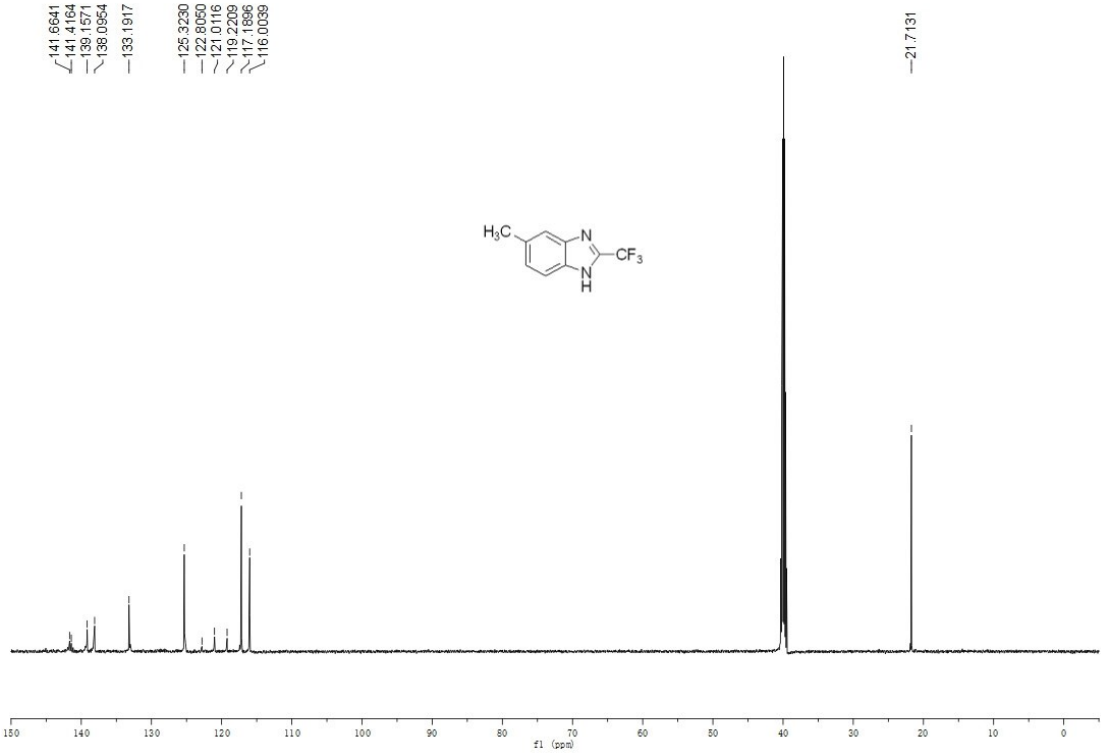
^{19}F NMR of 3b



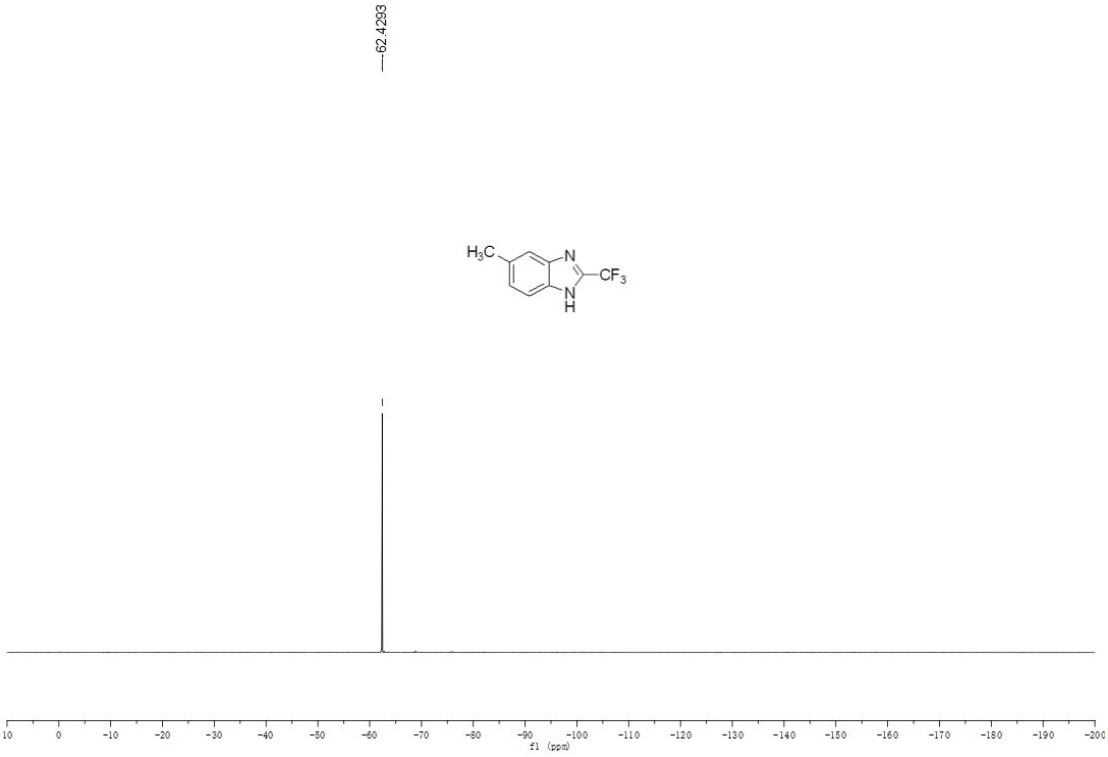
^{1}H NMR of 3c



^{13}C NMR of 3c



^{19}F NMR of 3c



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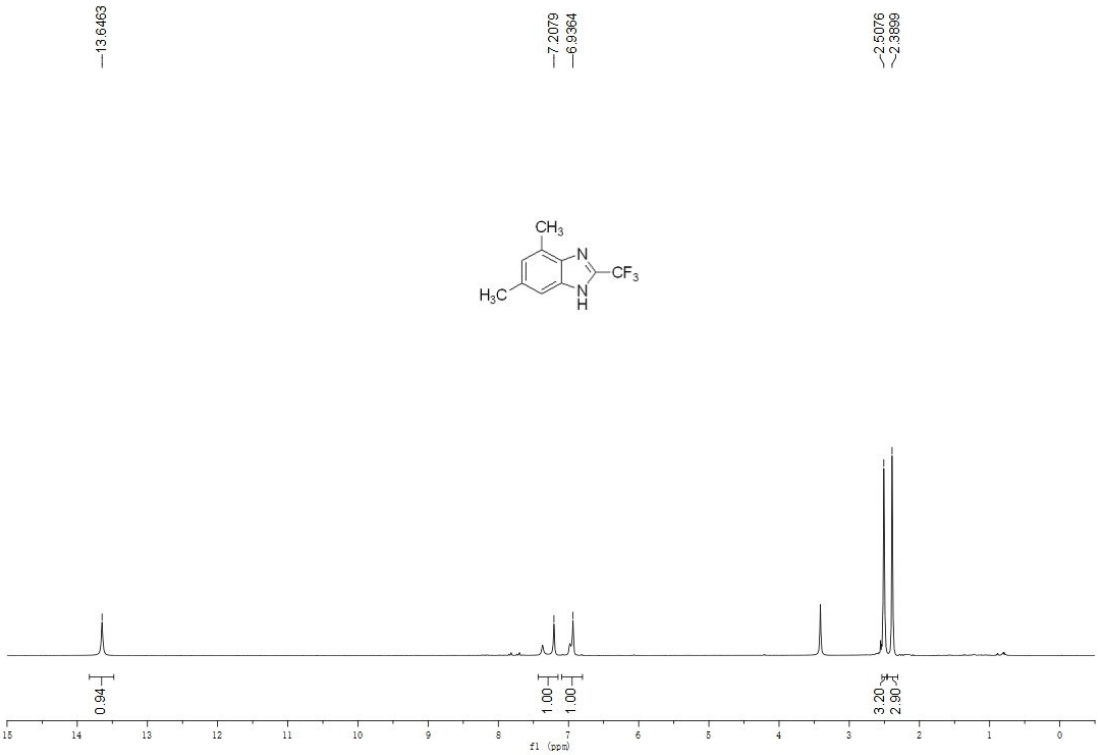

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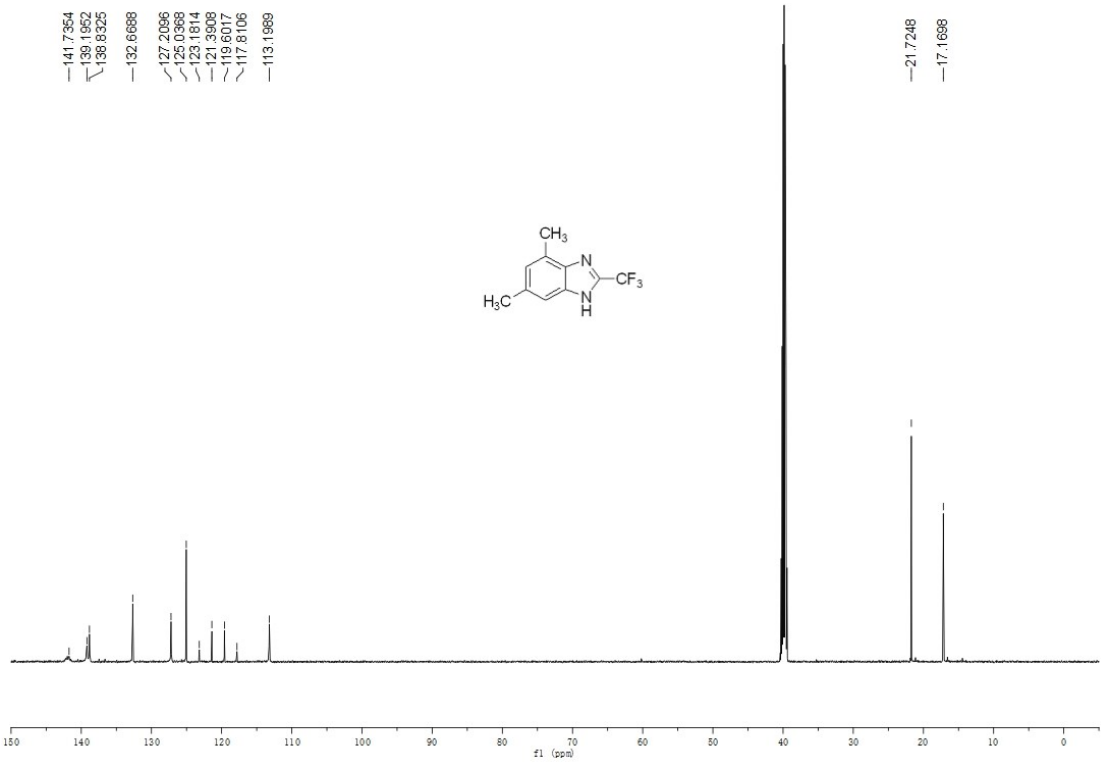

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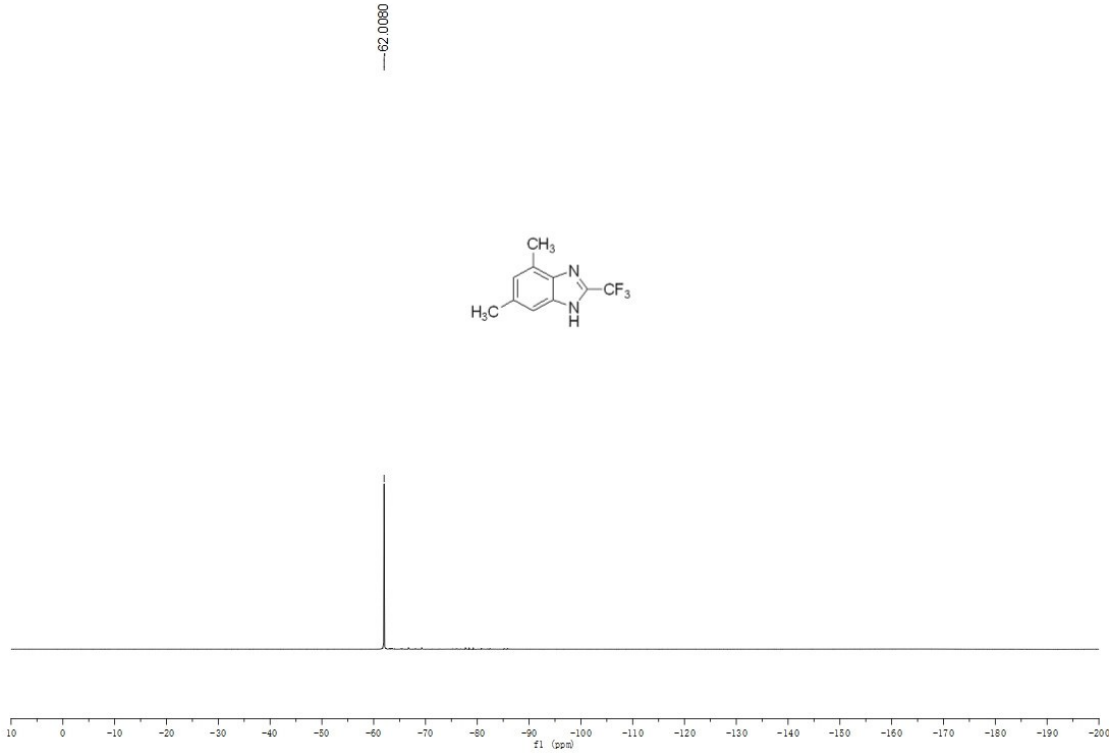

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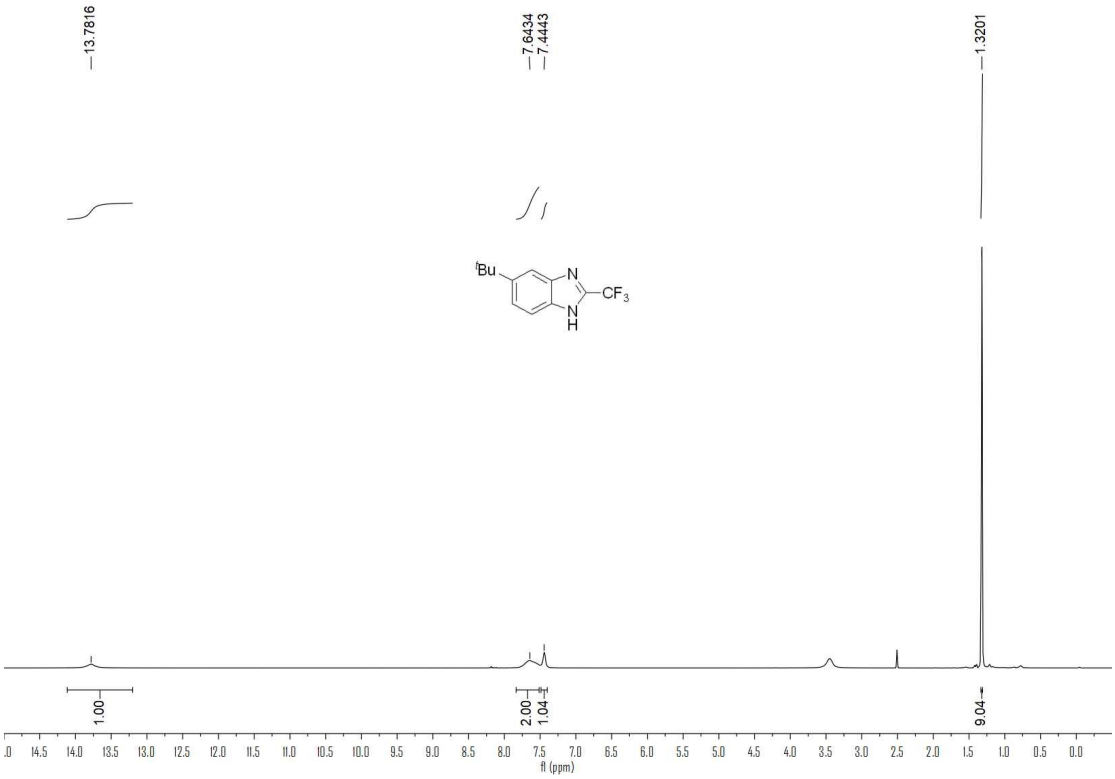
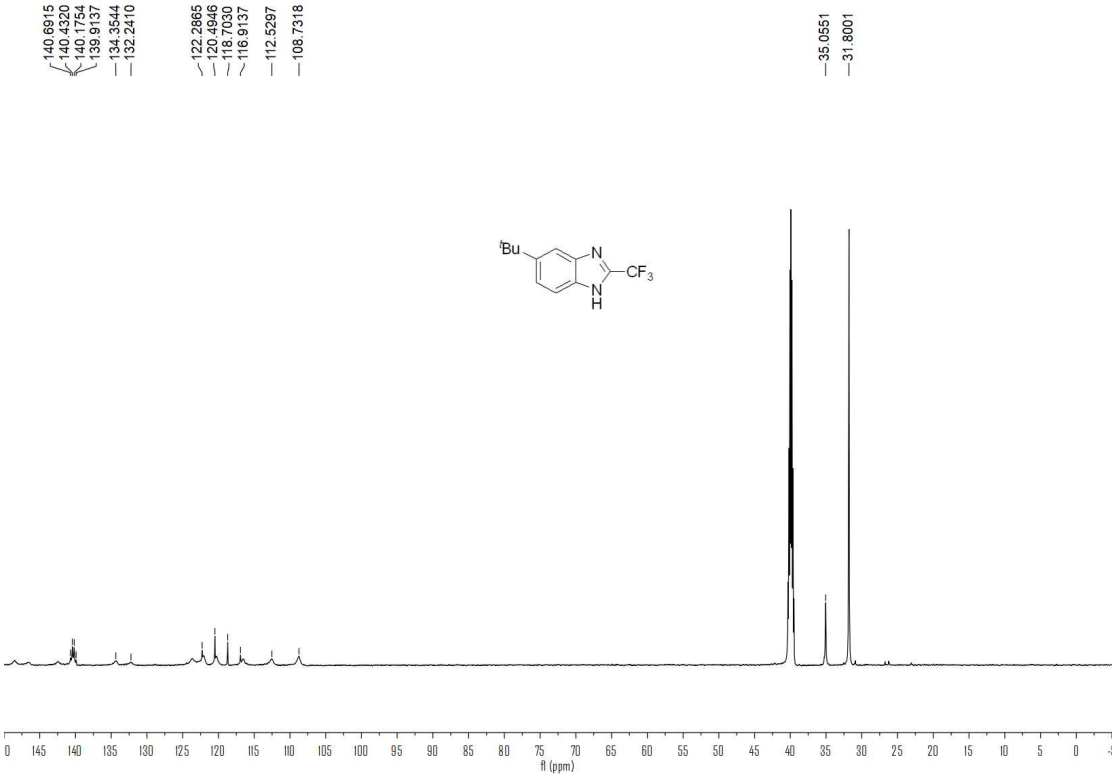


^{13}C NMR of 3e



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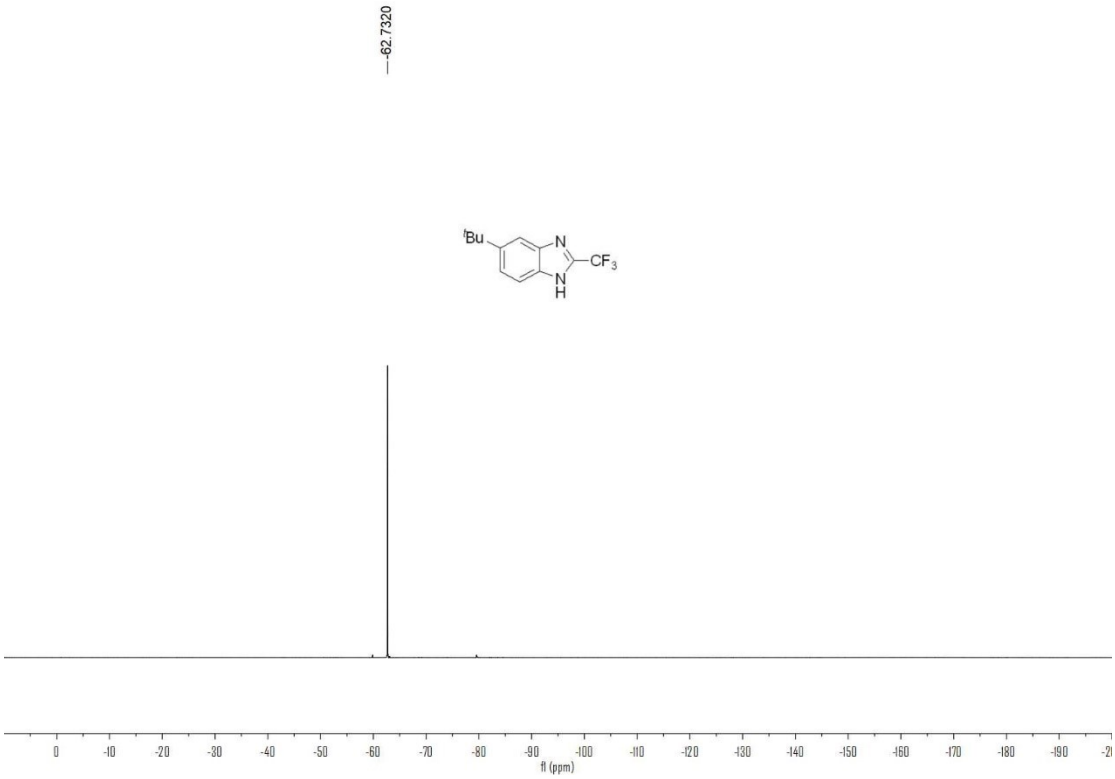
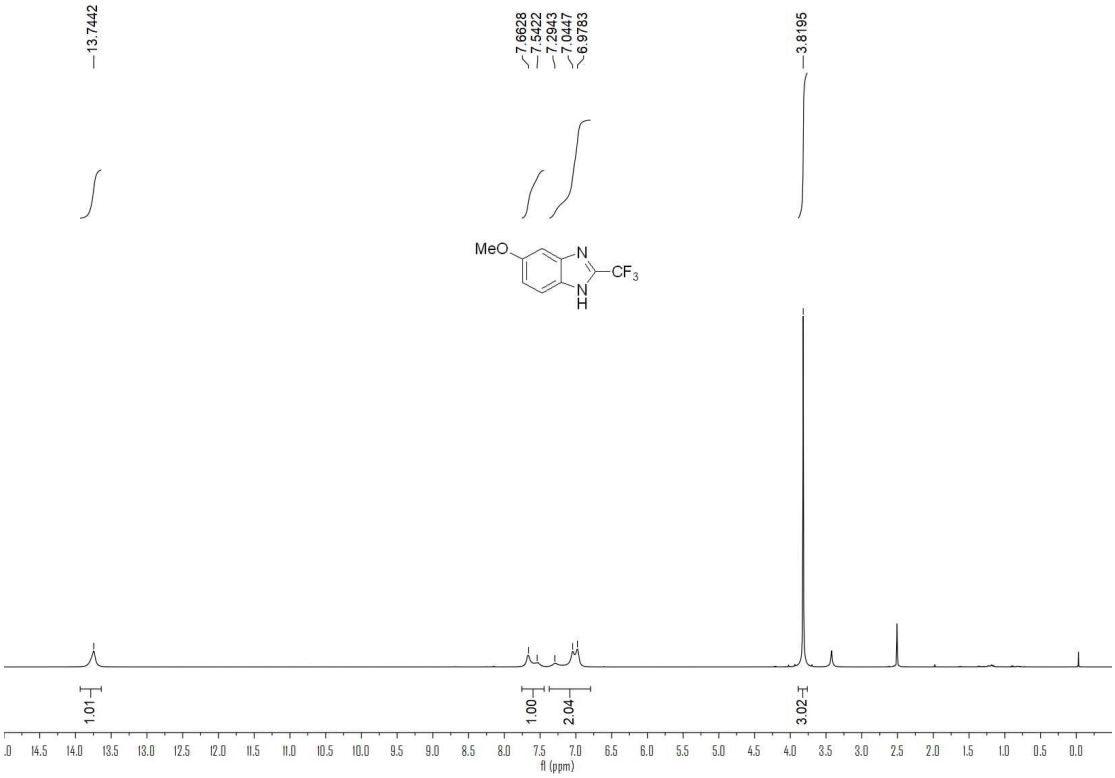
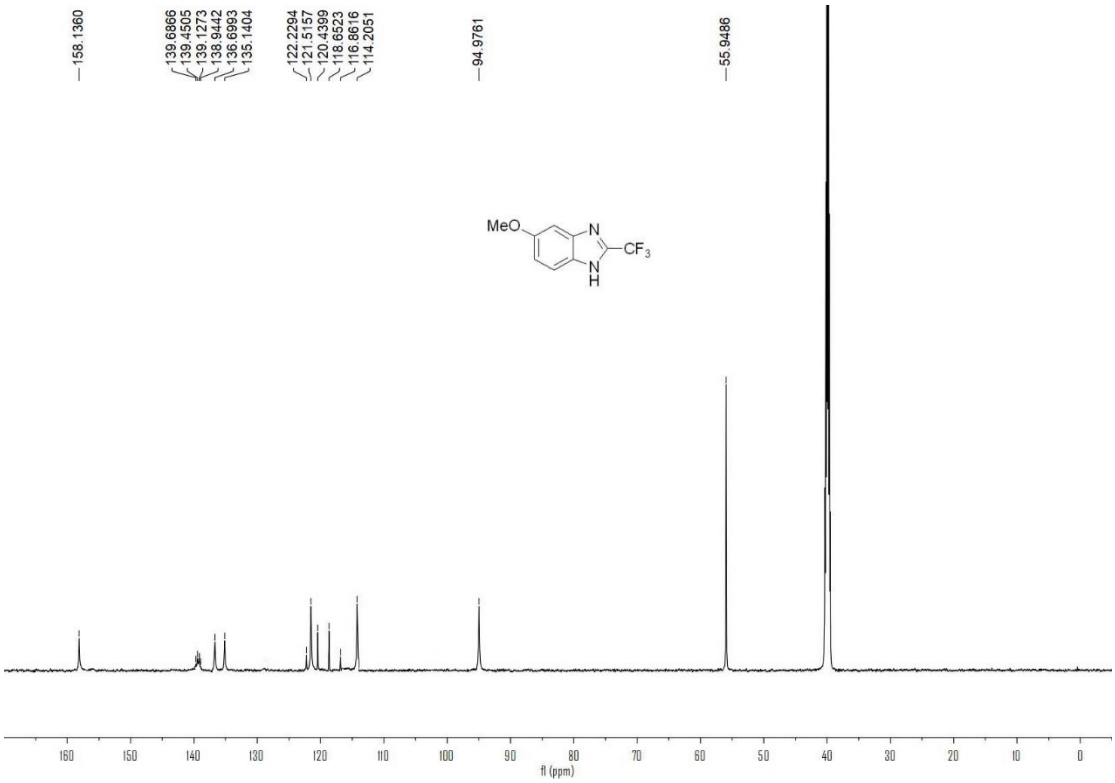


^{1}H NMR of 3f



^{13}C NMR of 3f



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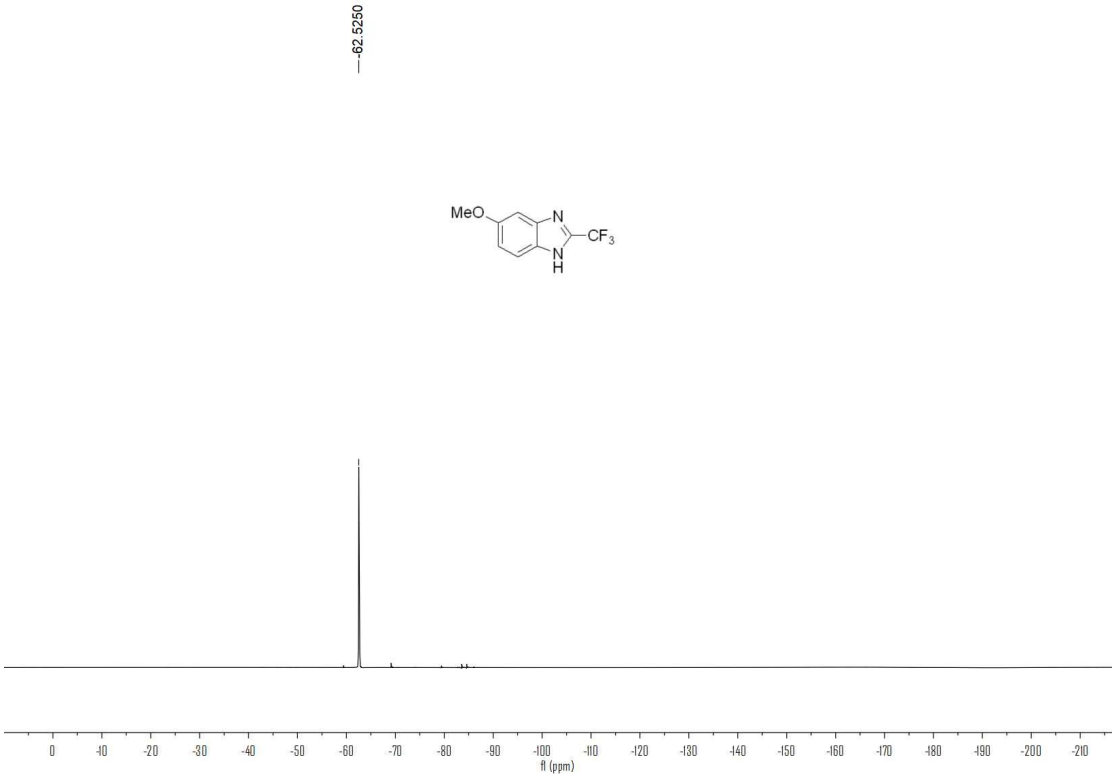
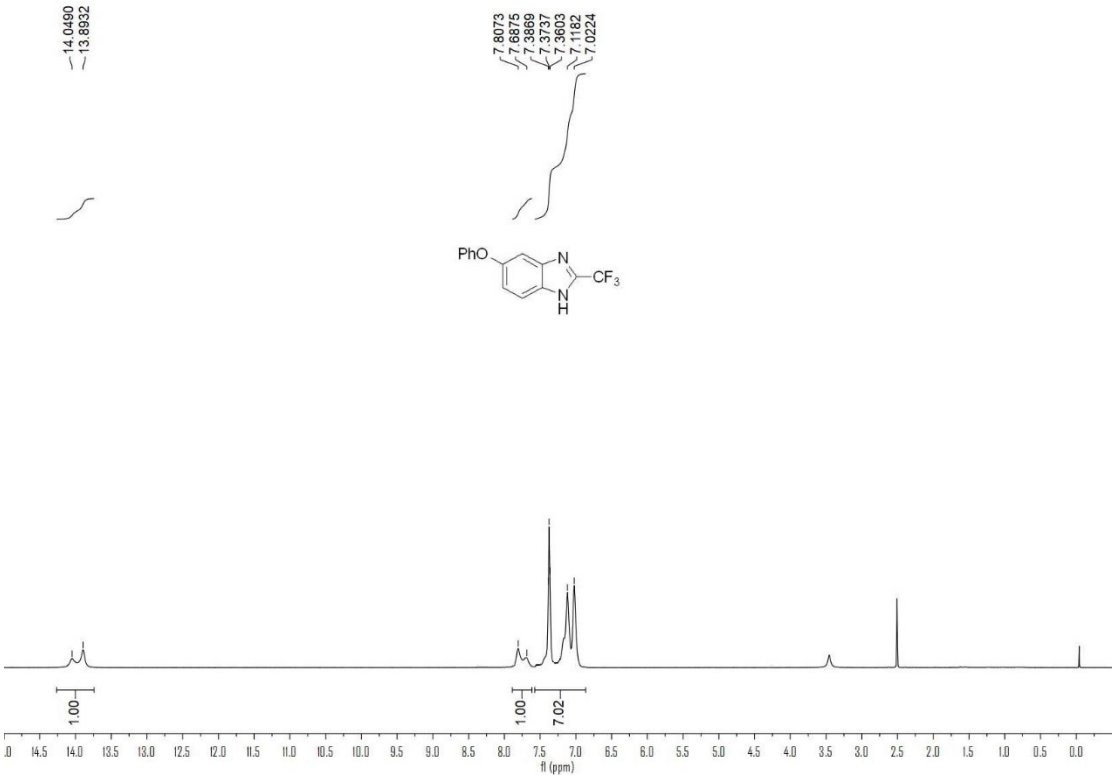


^{1}H NMR of 3g



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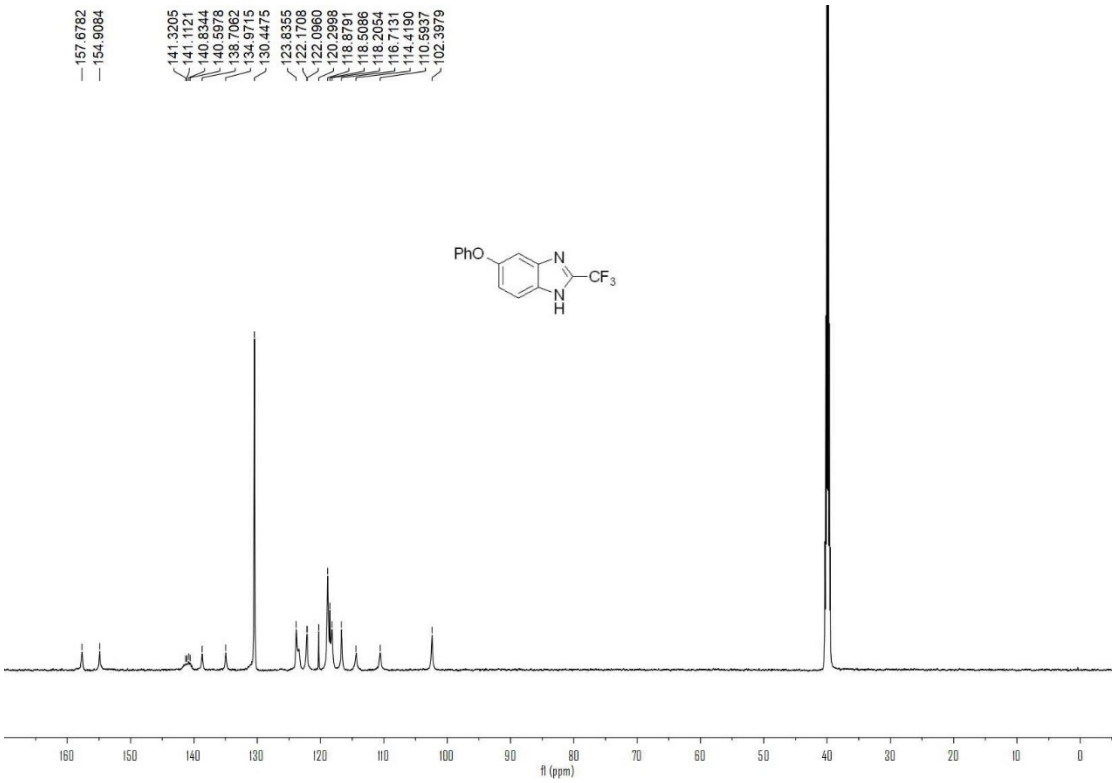

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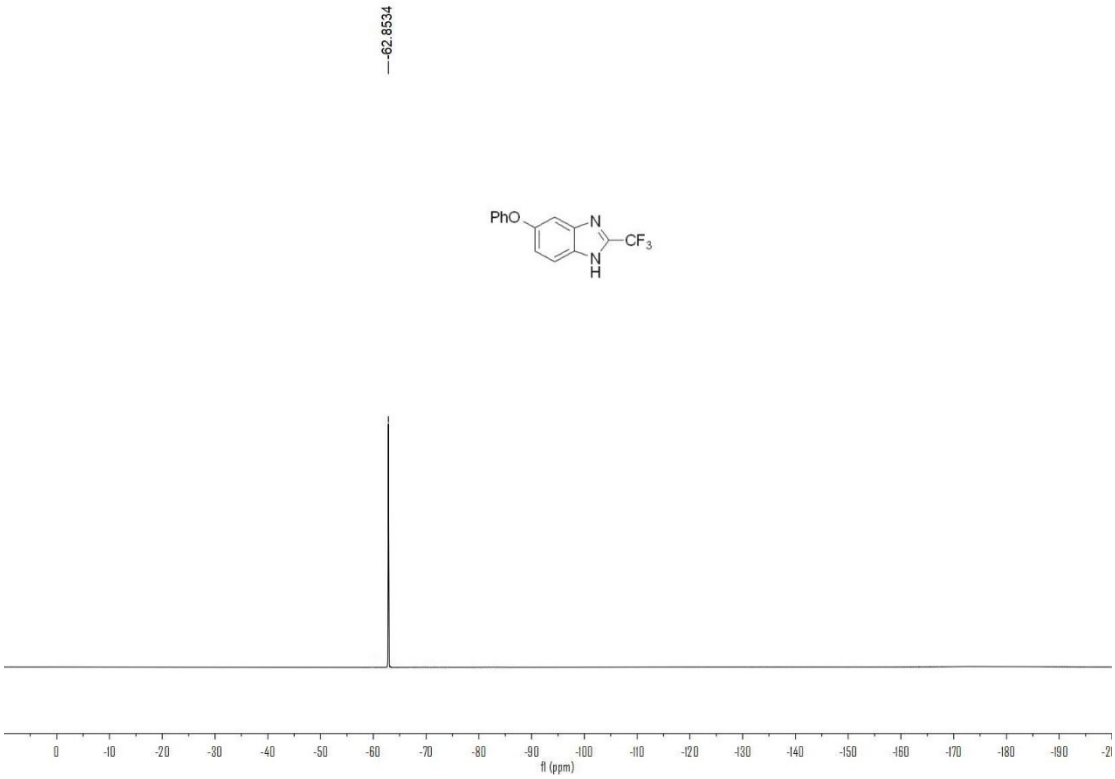
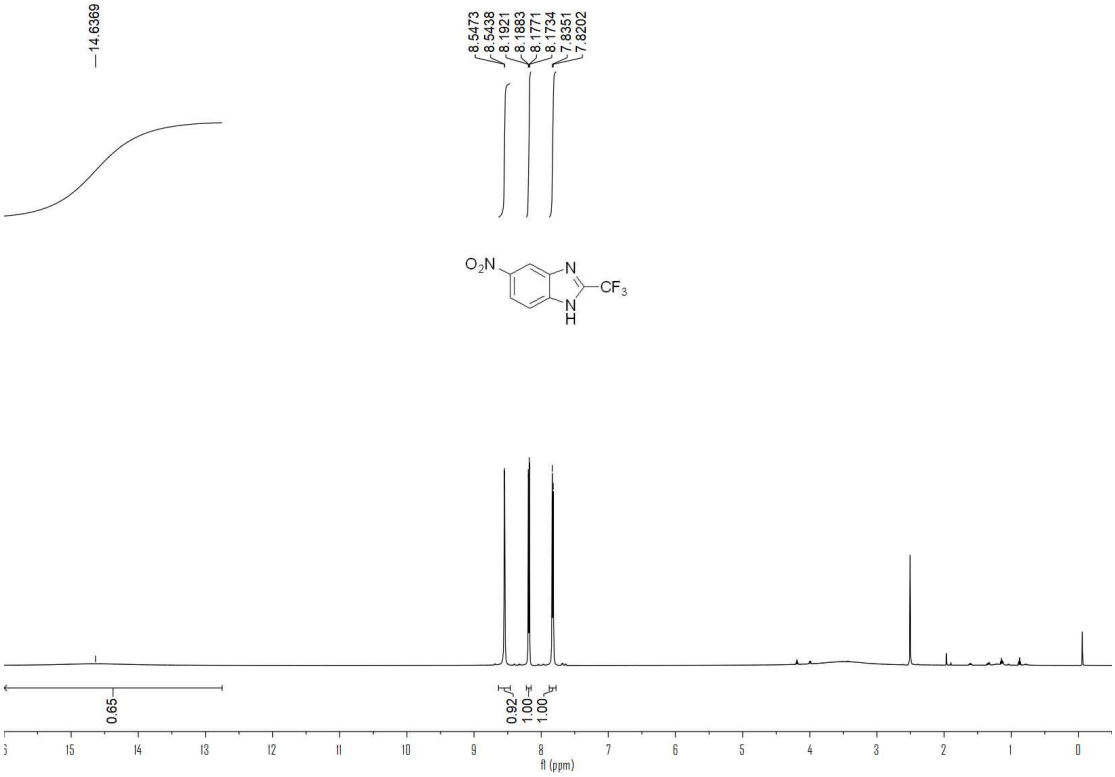
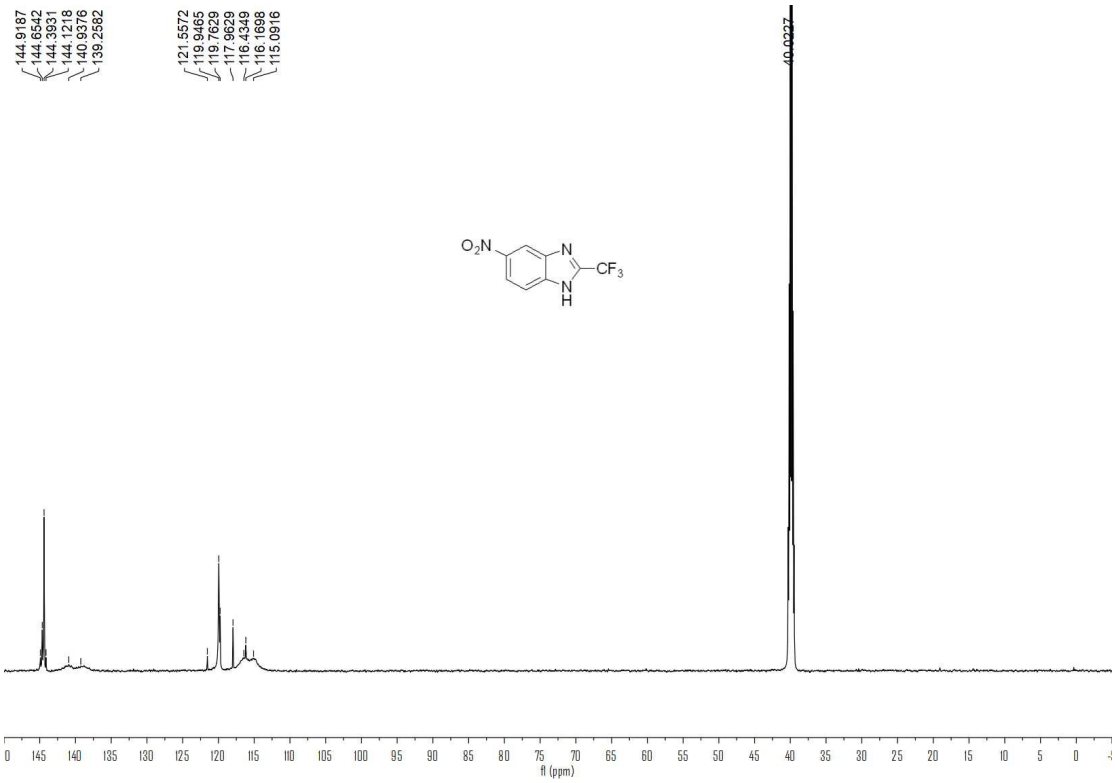


^{1}H NMR of 3h



^{13}C NMR of 3h



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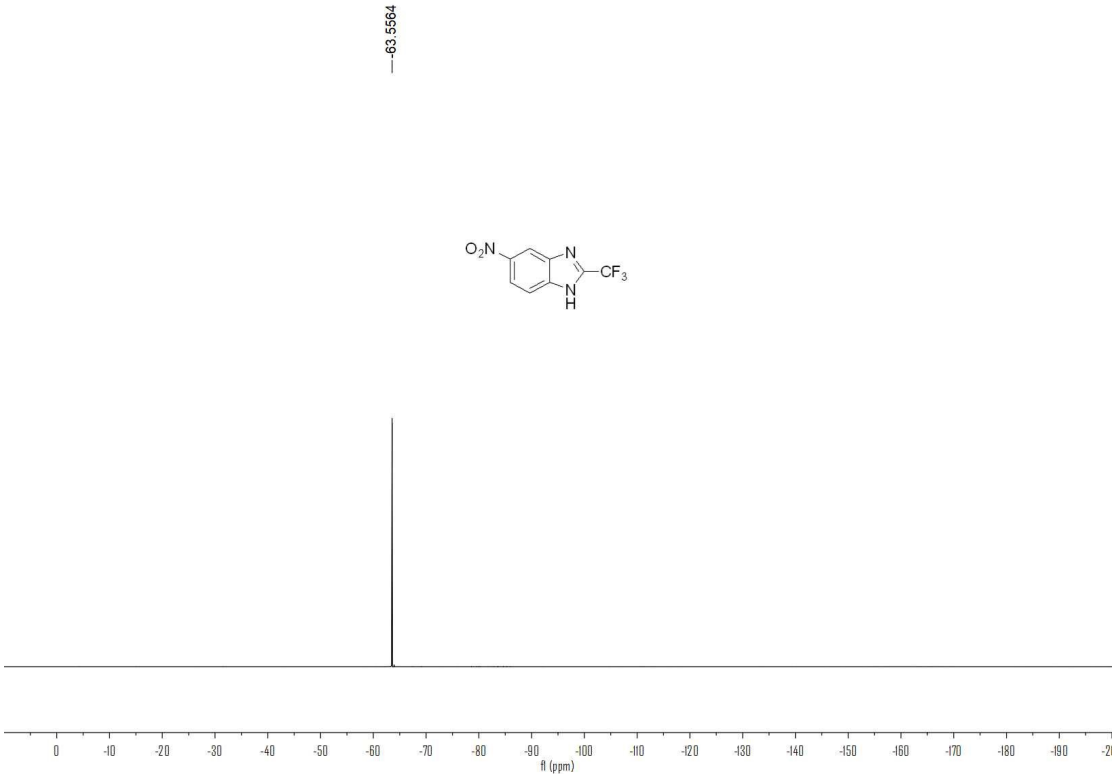
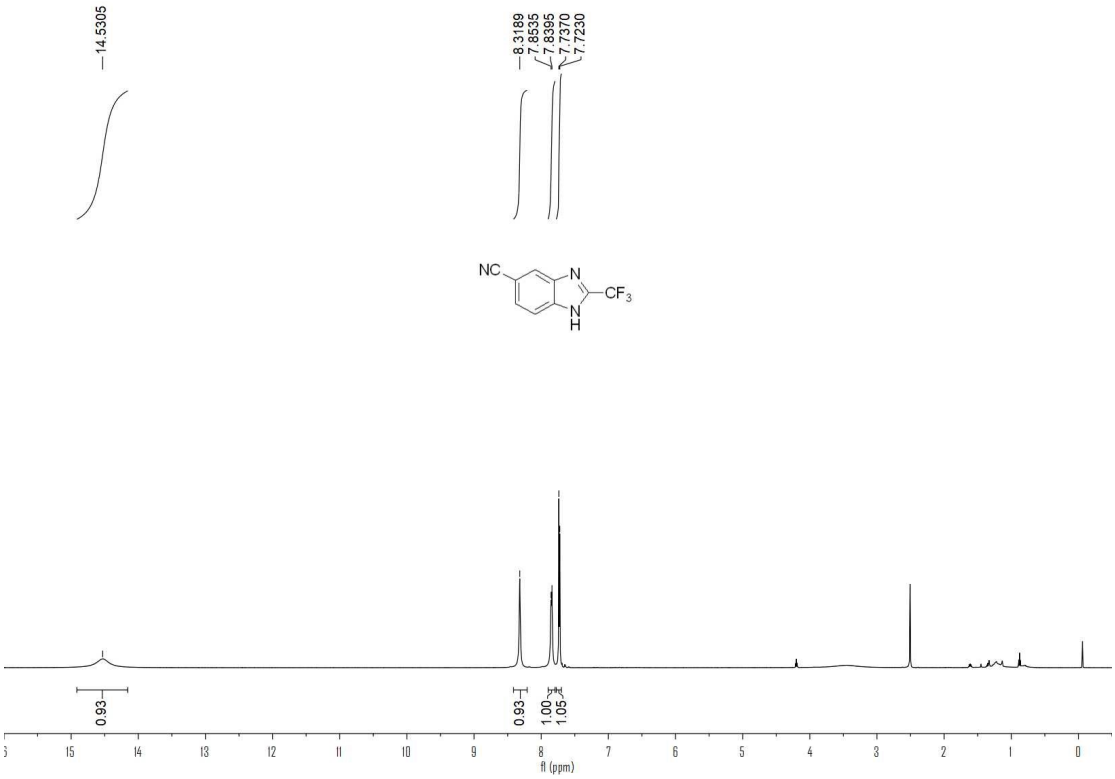
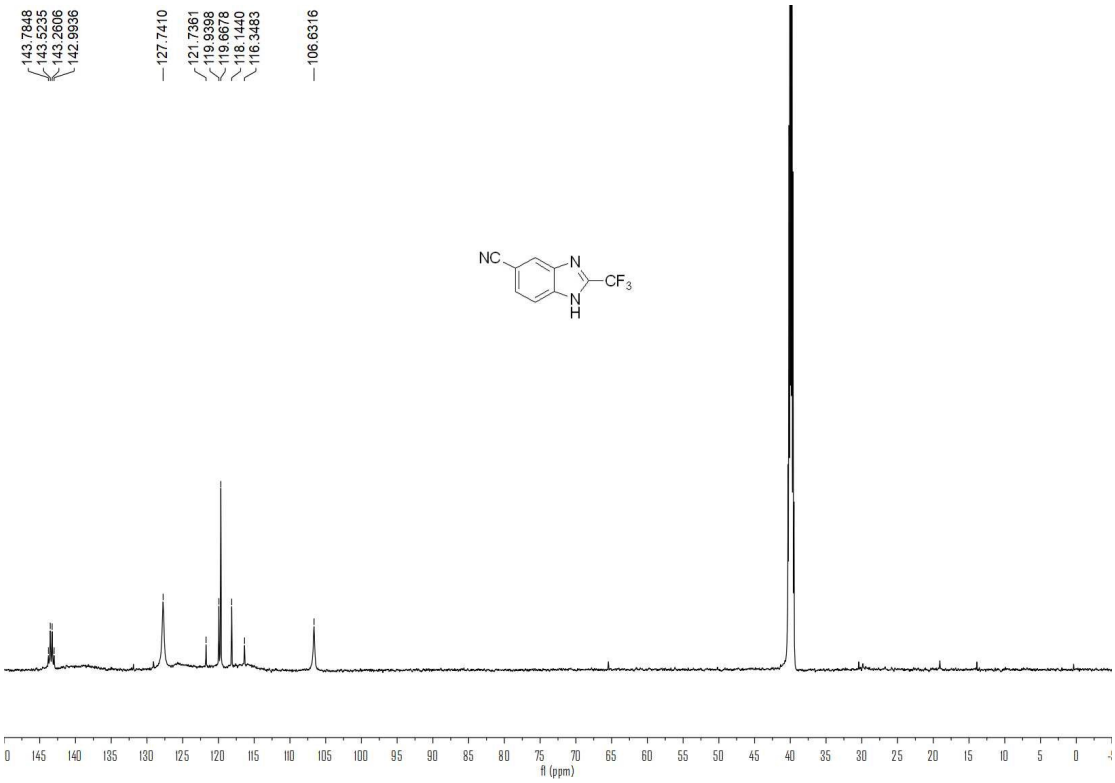


^{1}H NMR of 3i



^{13}C NMR of 3i



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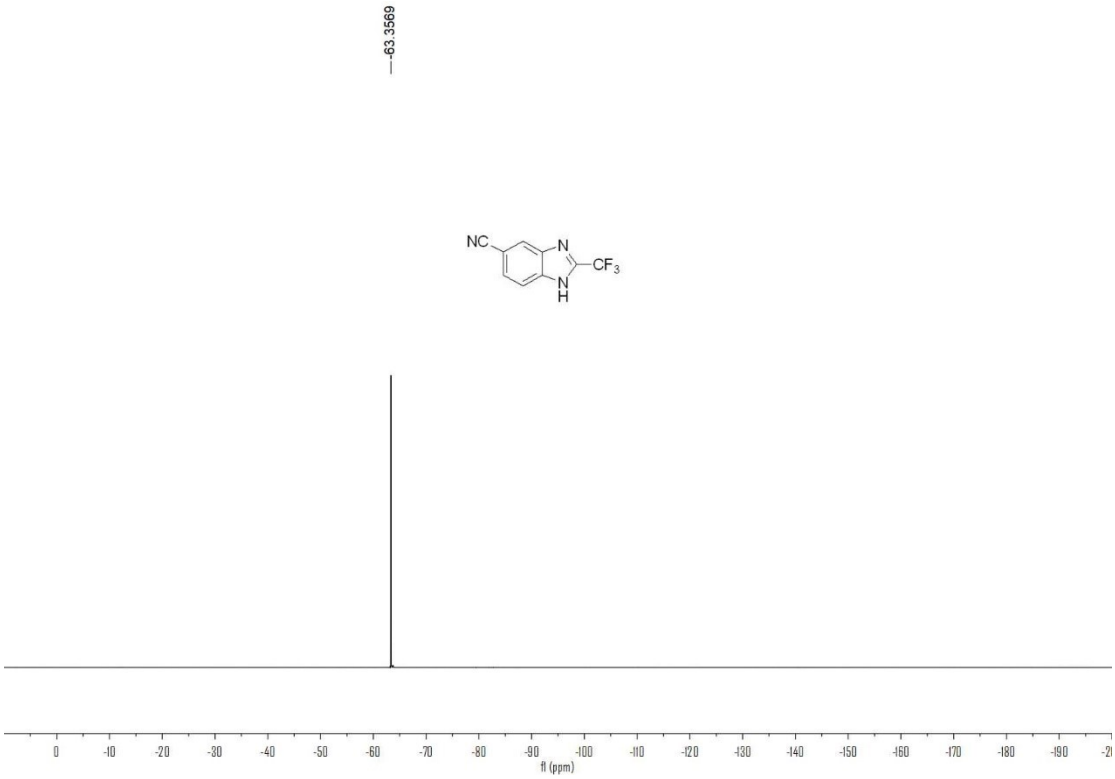

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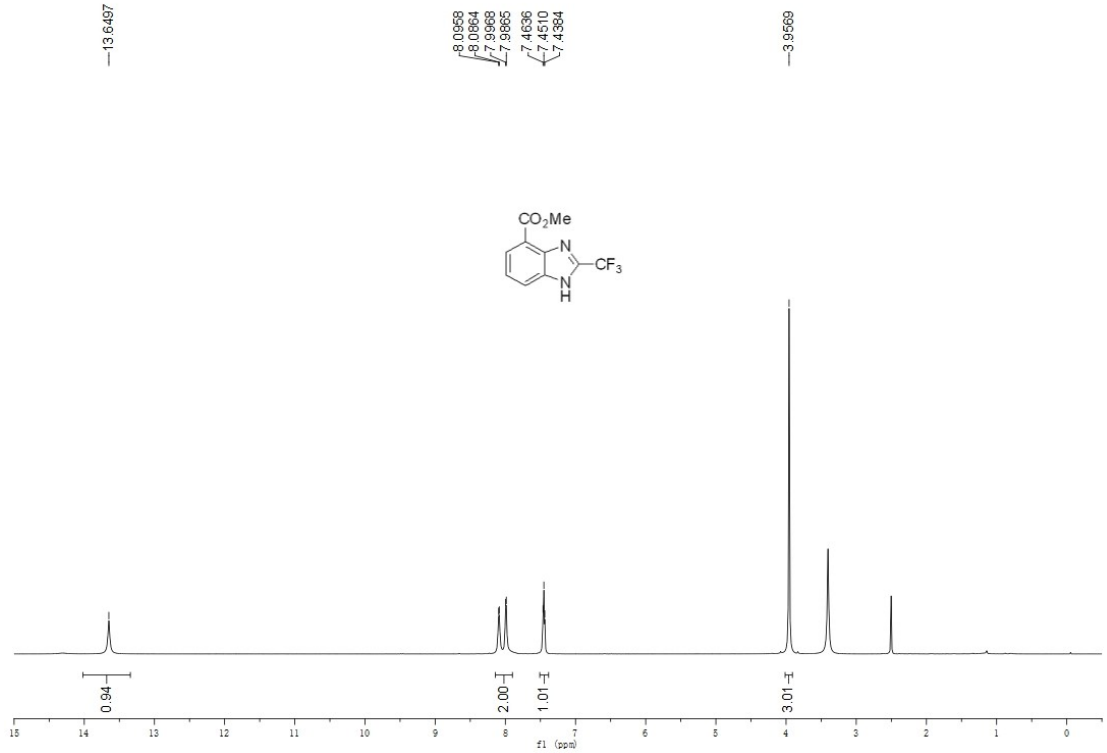

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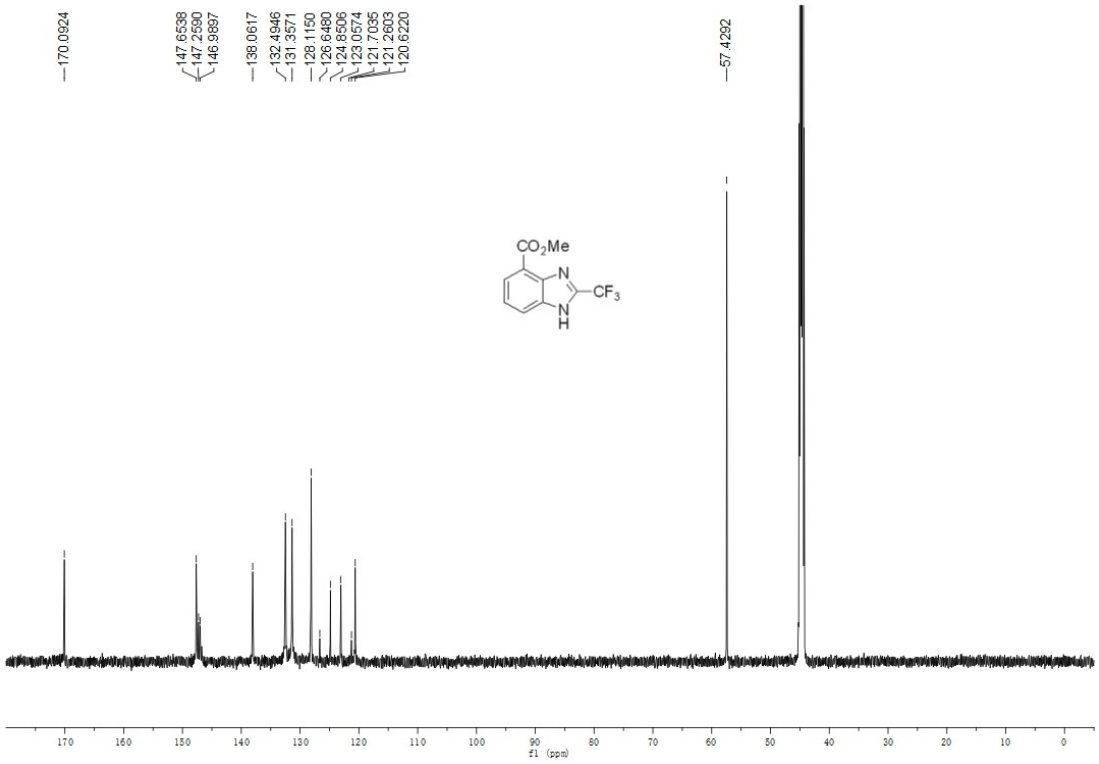

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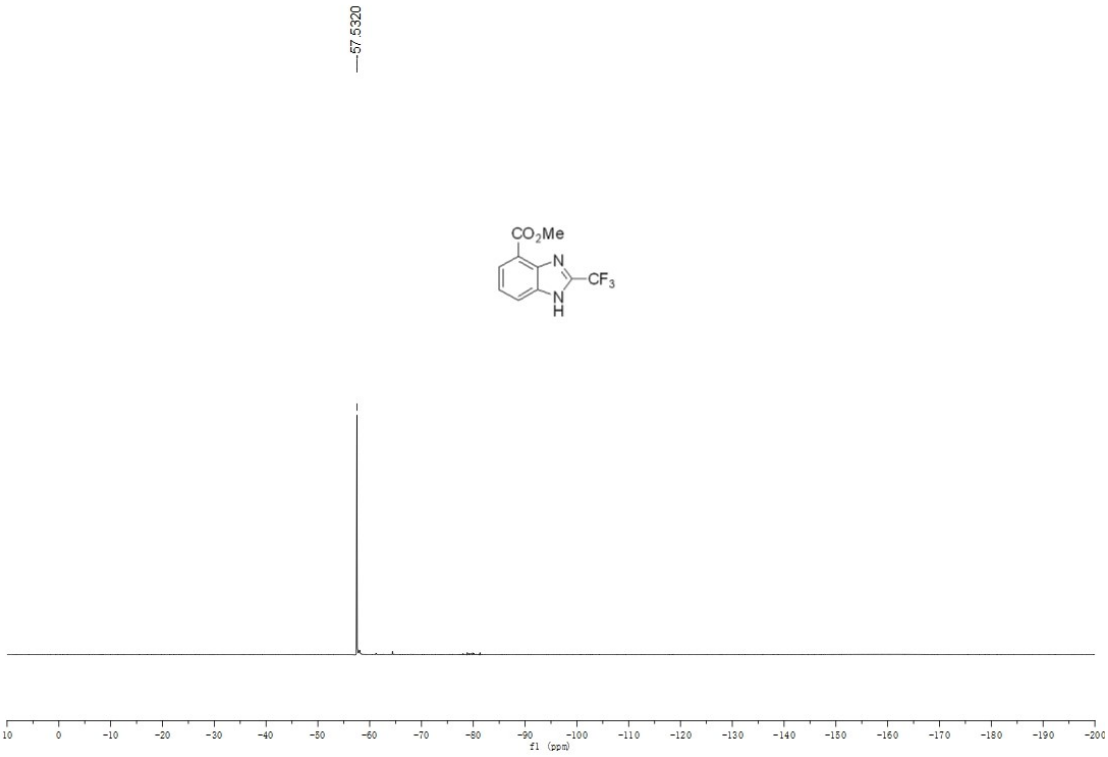

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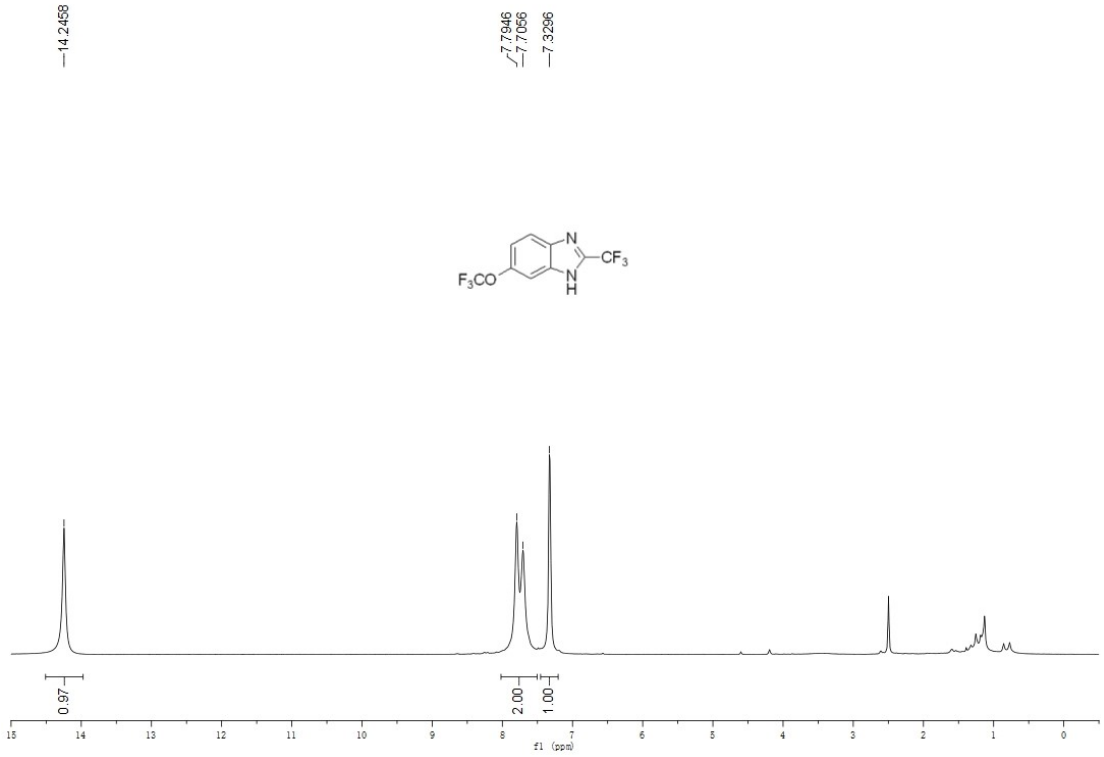

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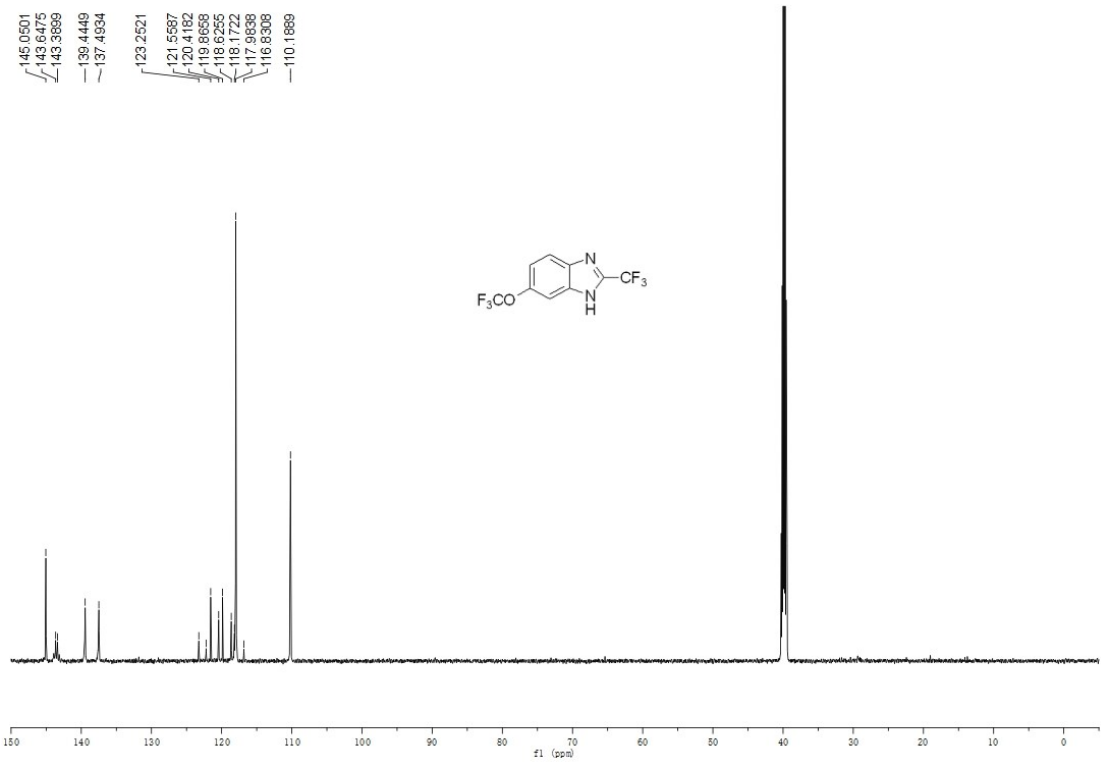

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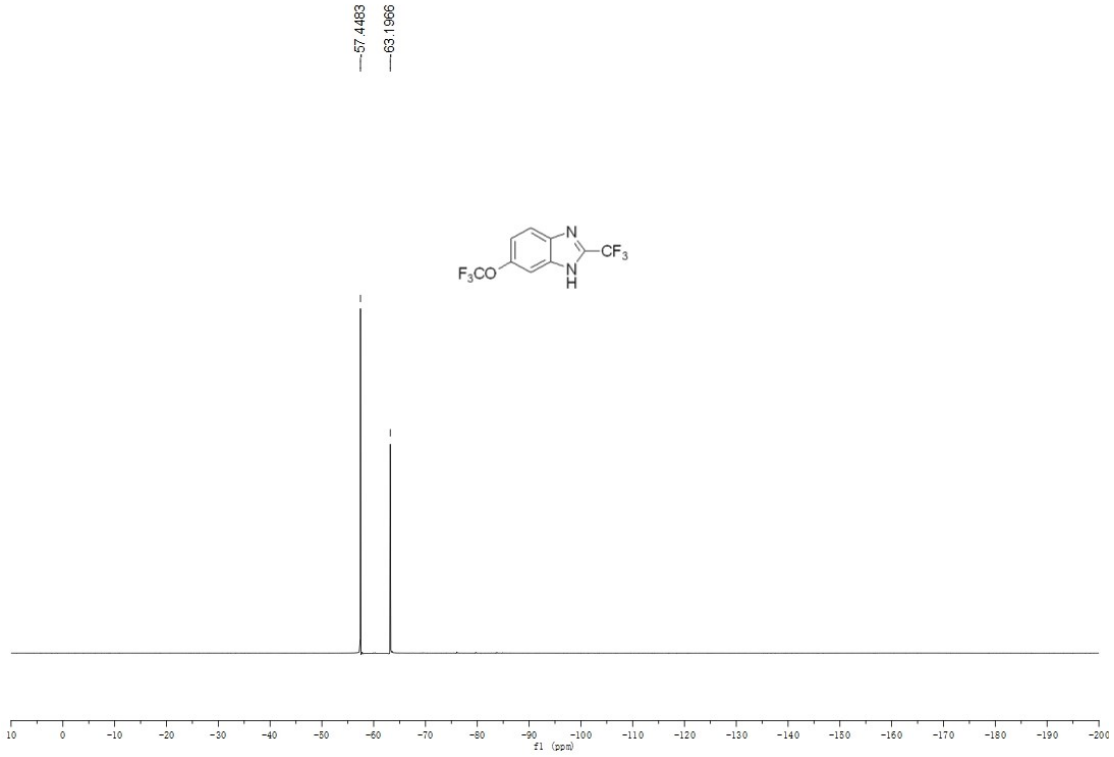
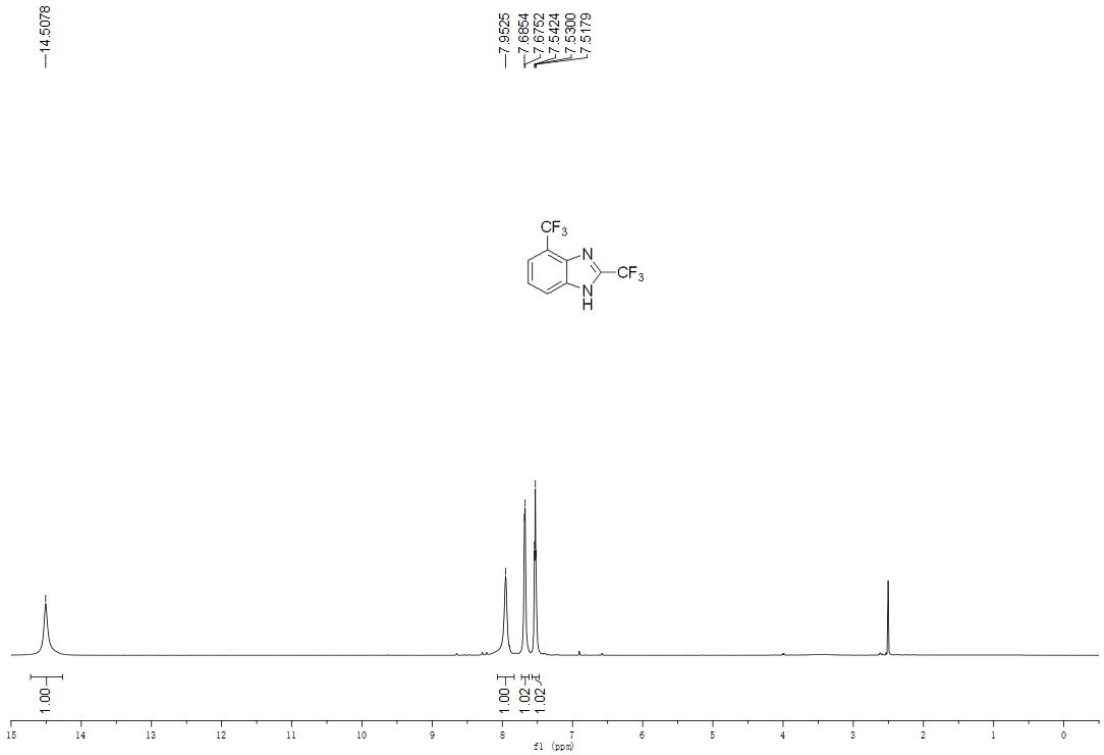


^{1}H NMR of 3l



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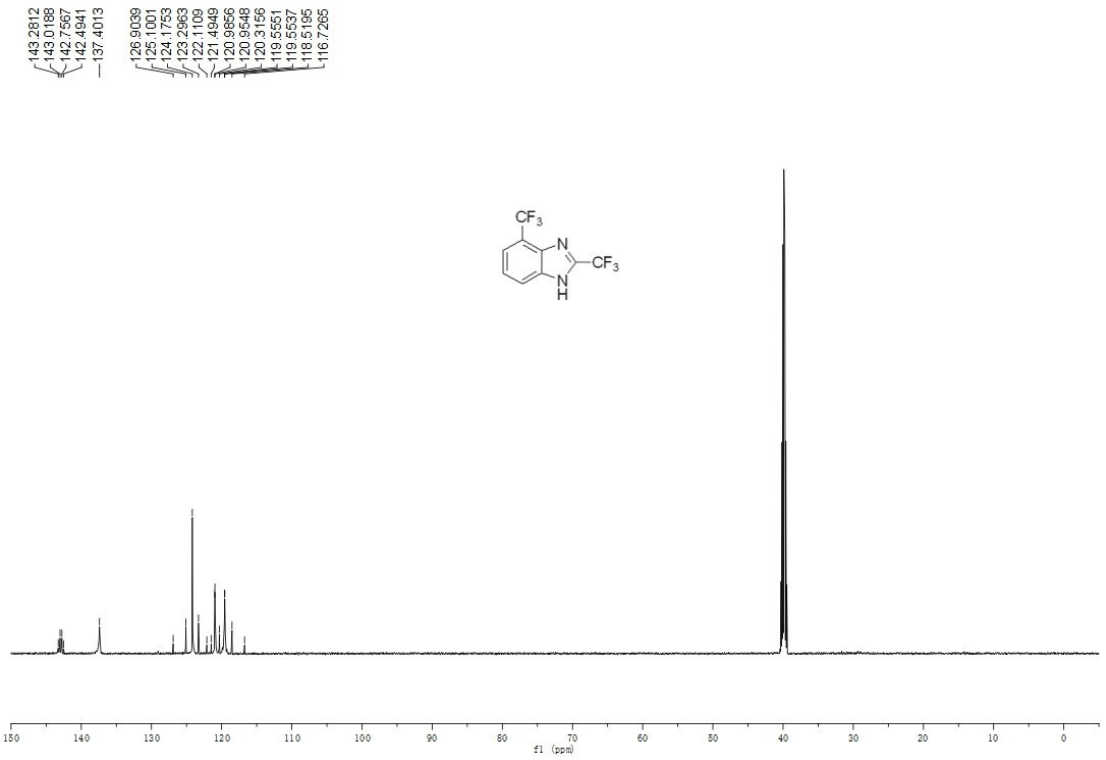

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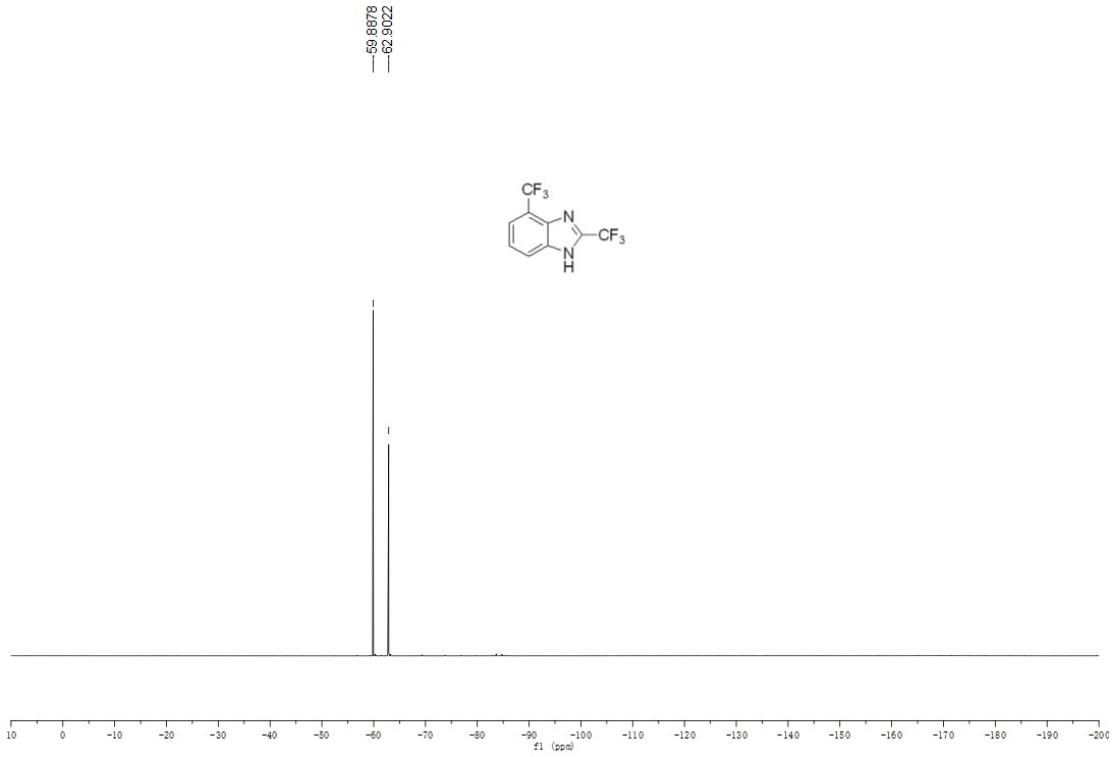
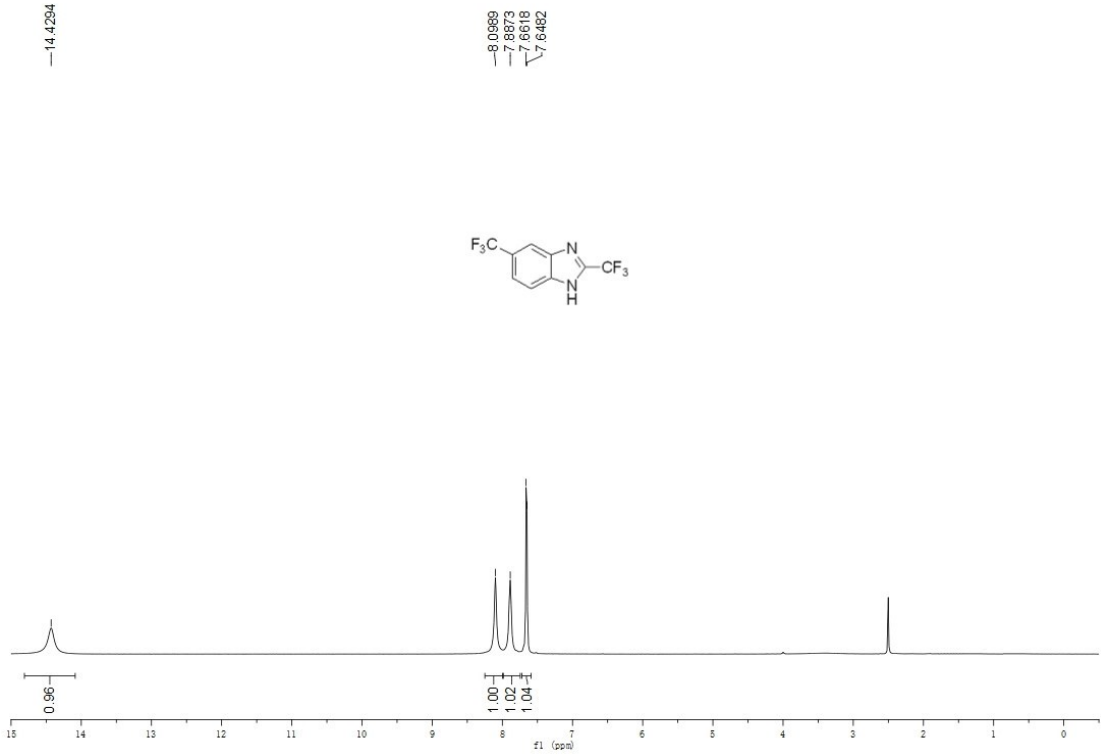
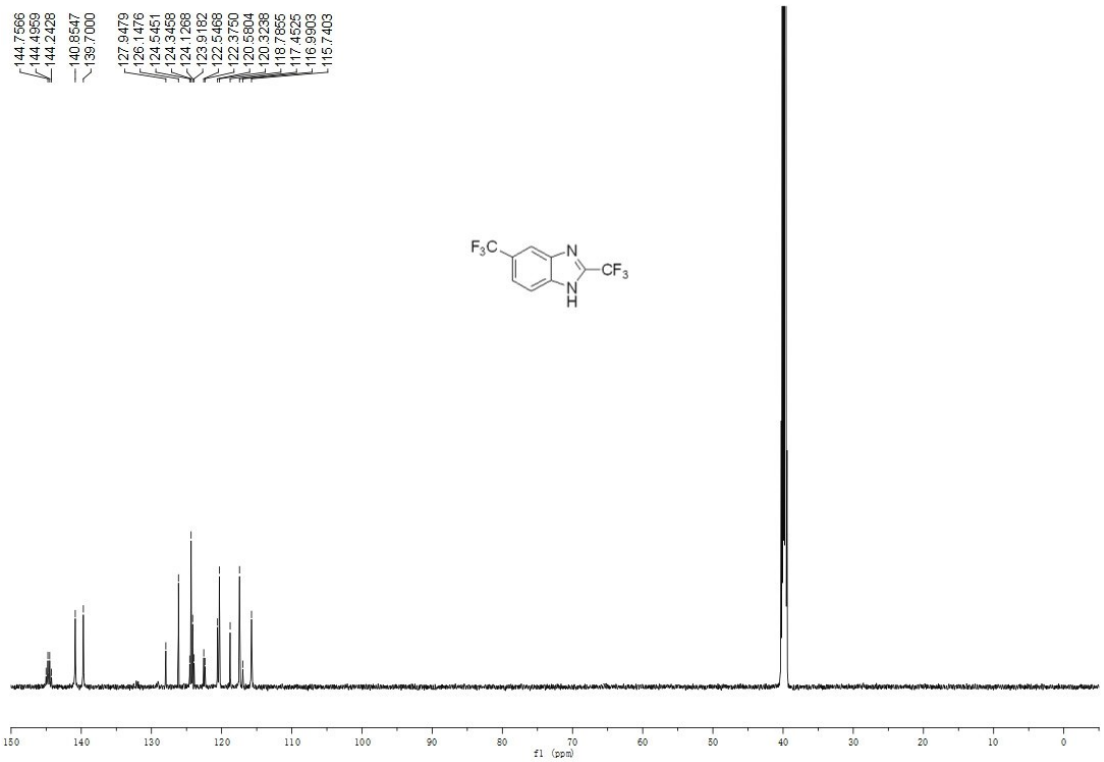


^{1}H NMR of 3m



^{13}C NMR of 3m



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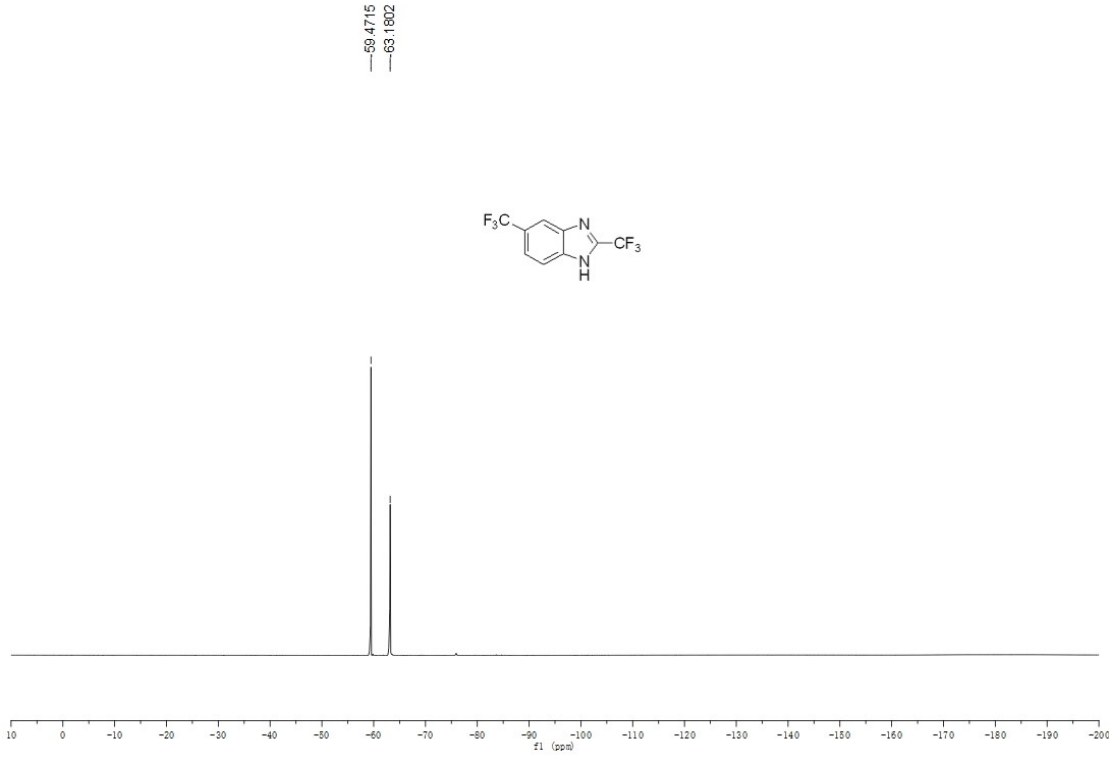

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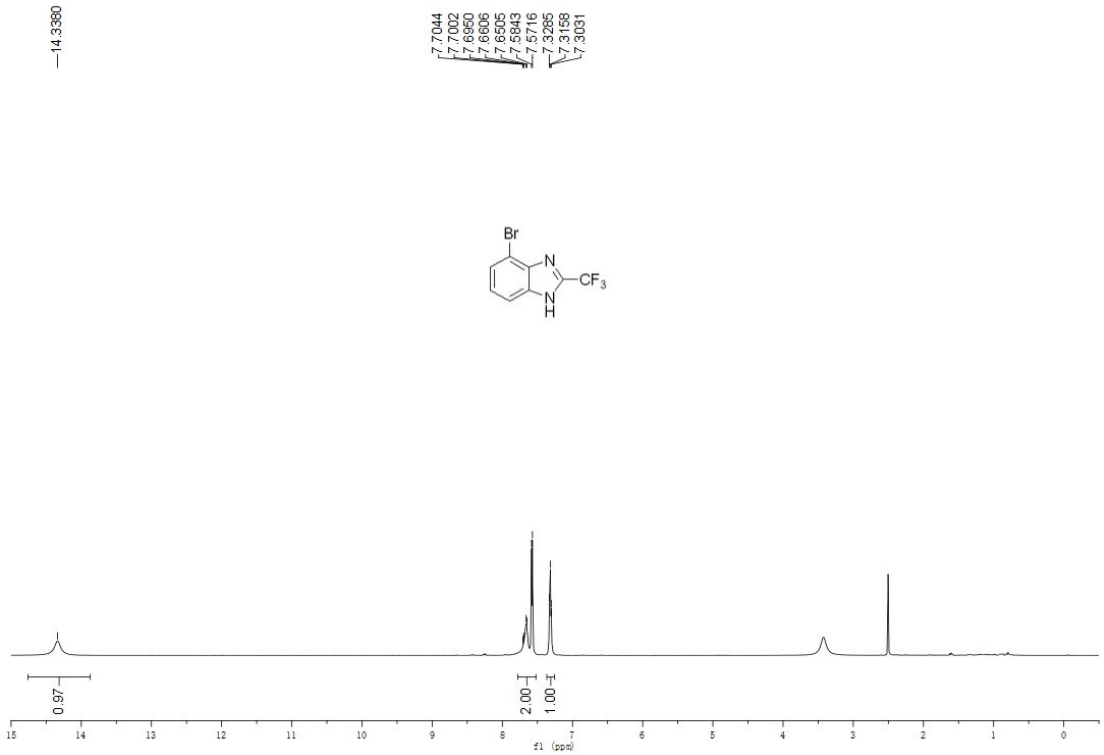
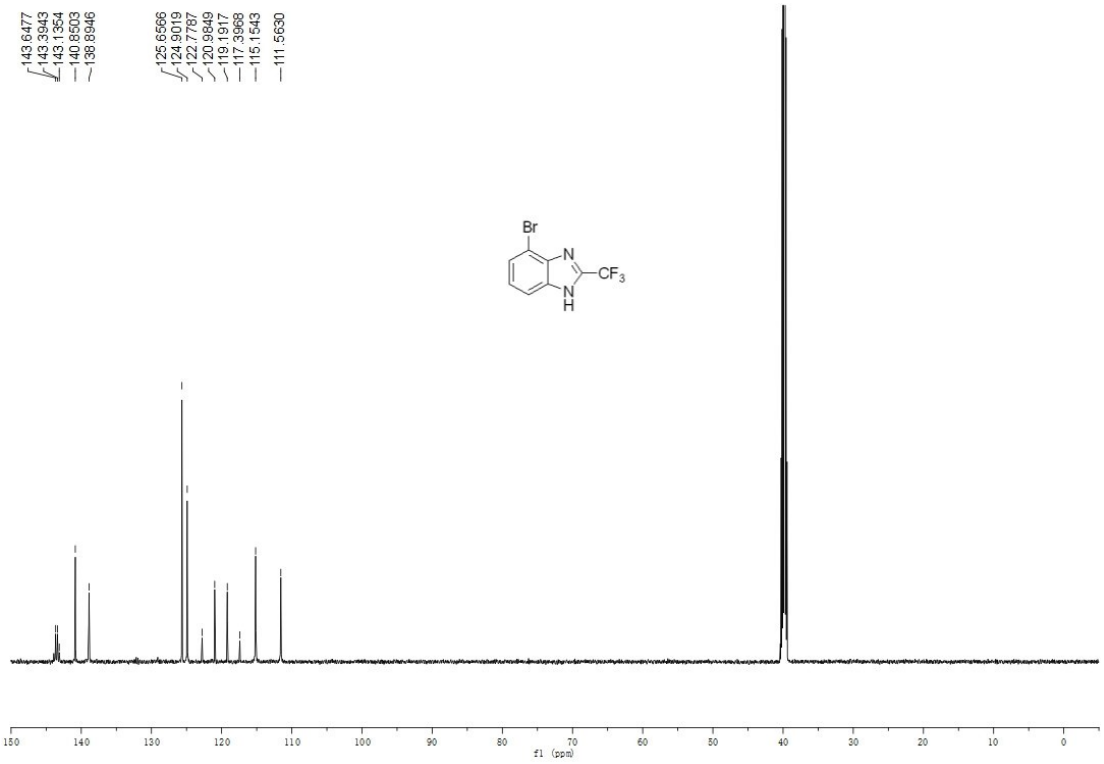
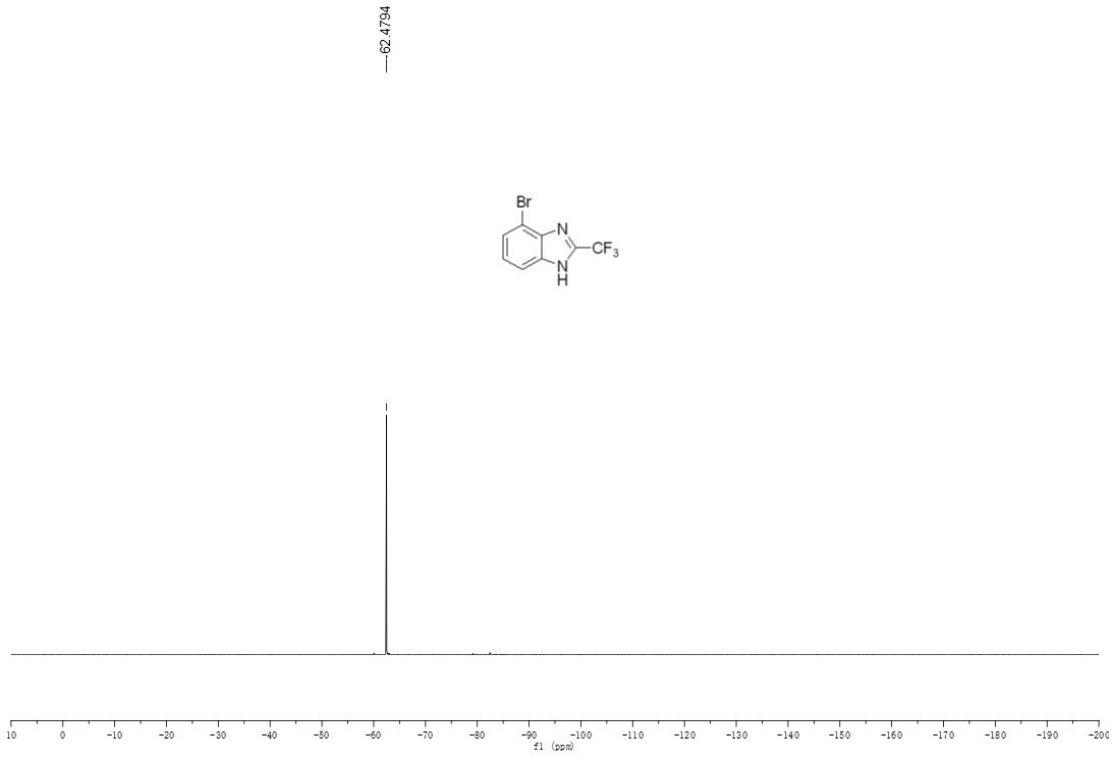


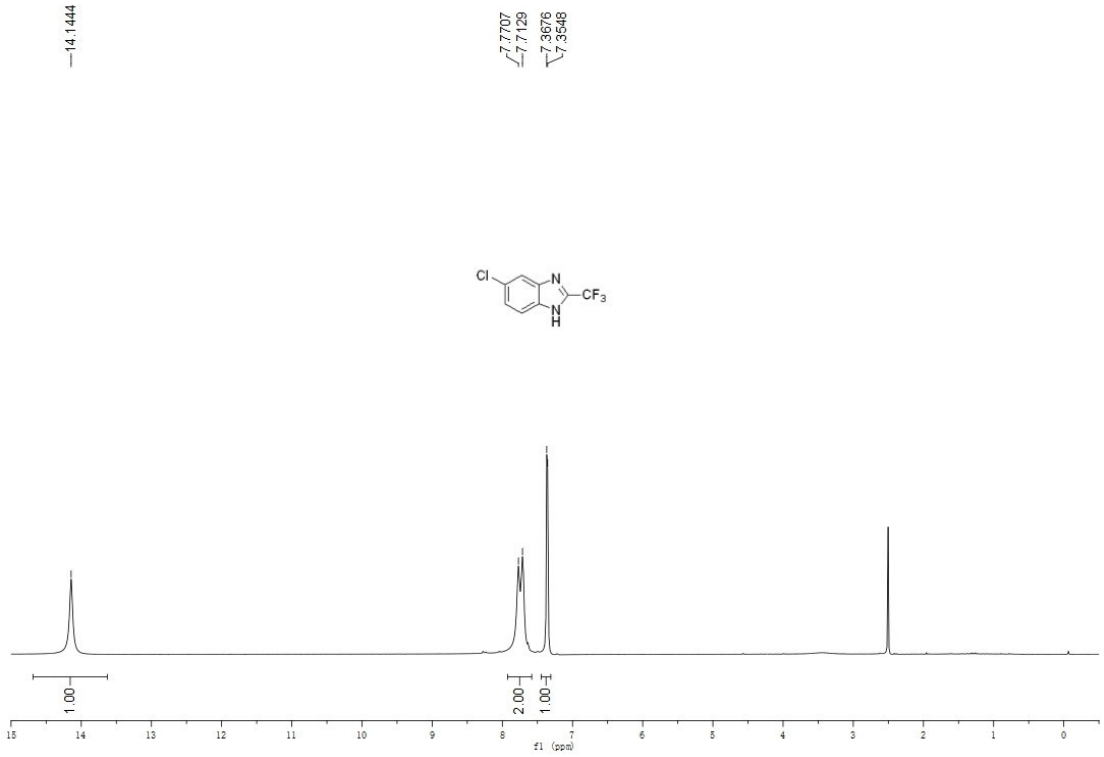
^{13}C NMR of 3n



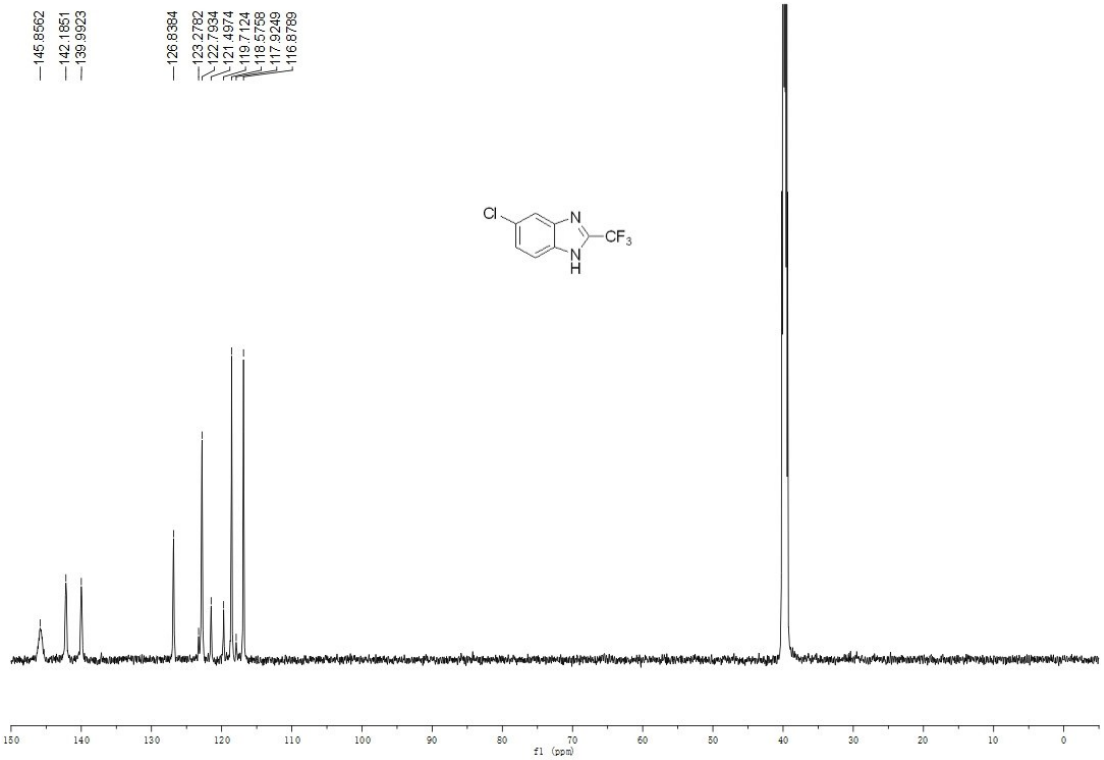
^{19}F NMR of 3n



^{1}H NMR of 3o



^{13}C NMR of 3o



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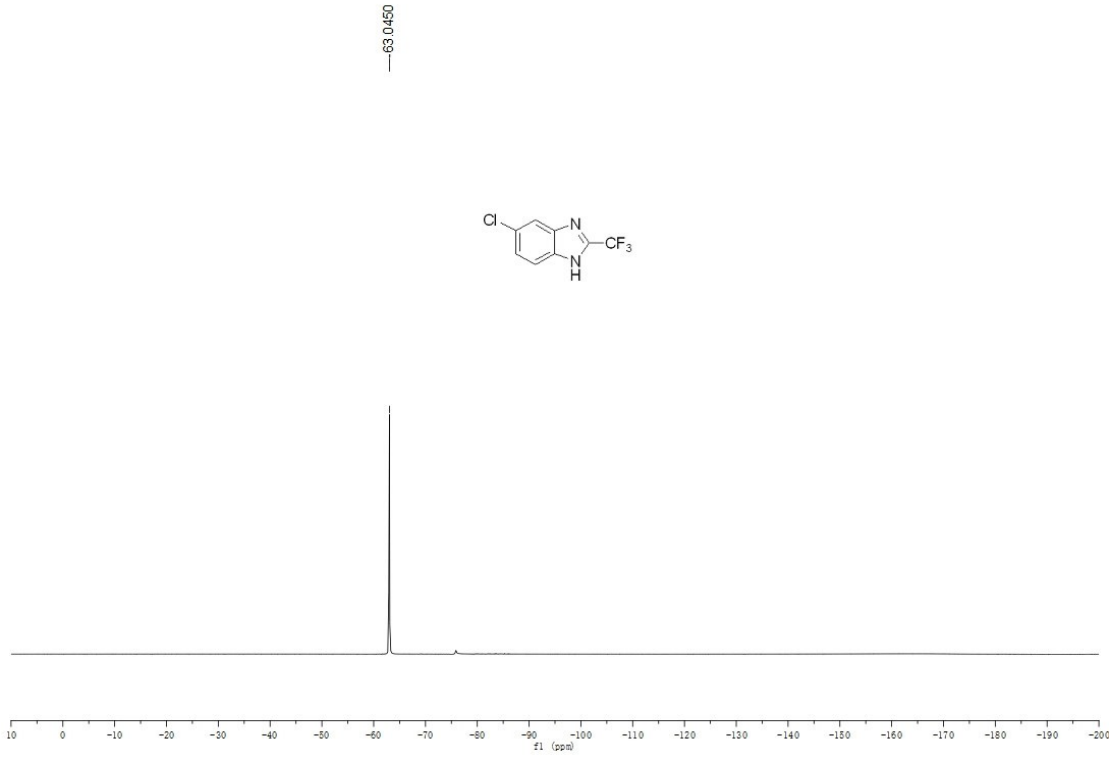
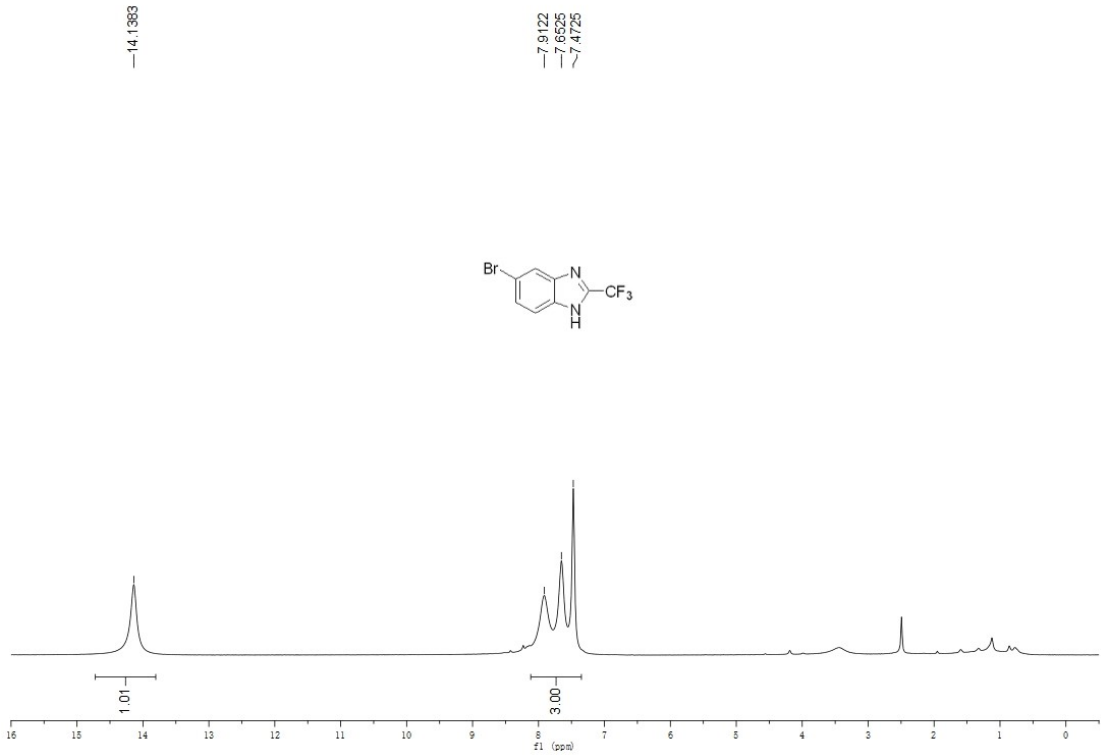
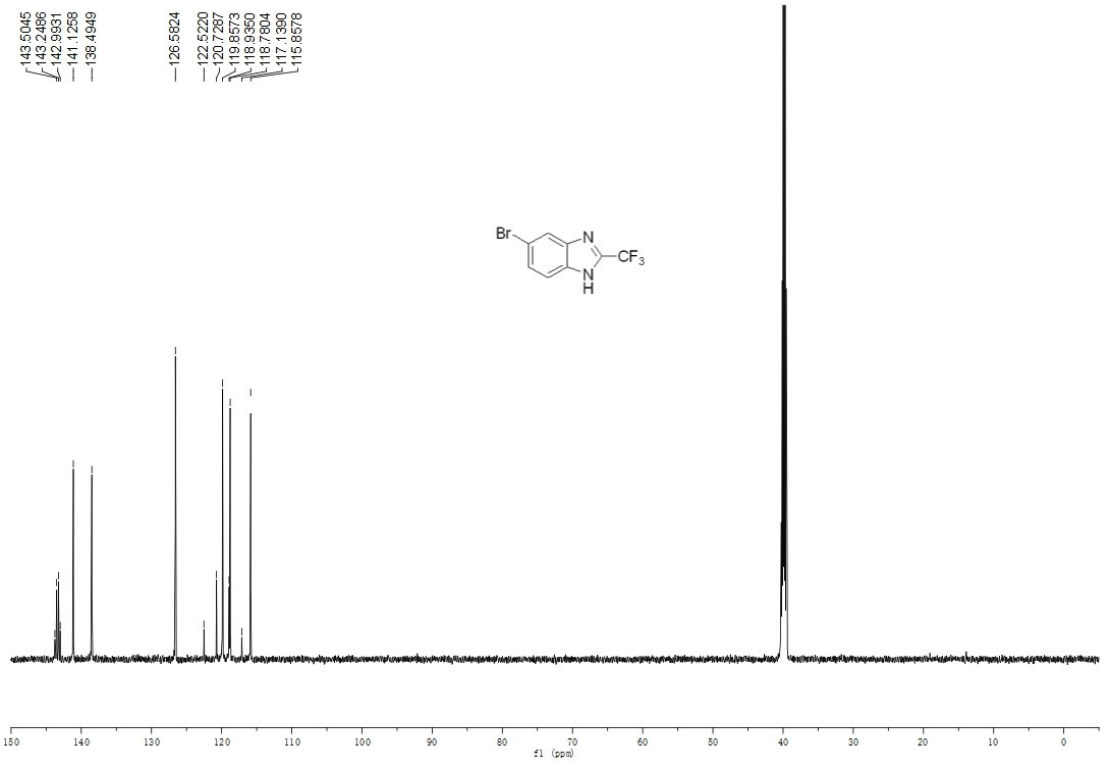


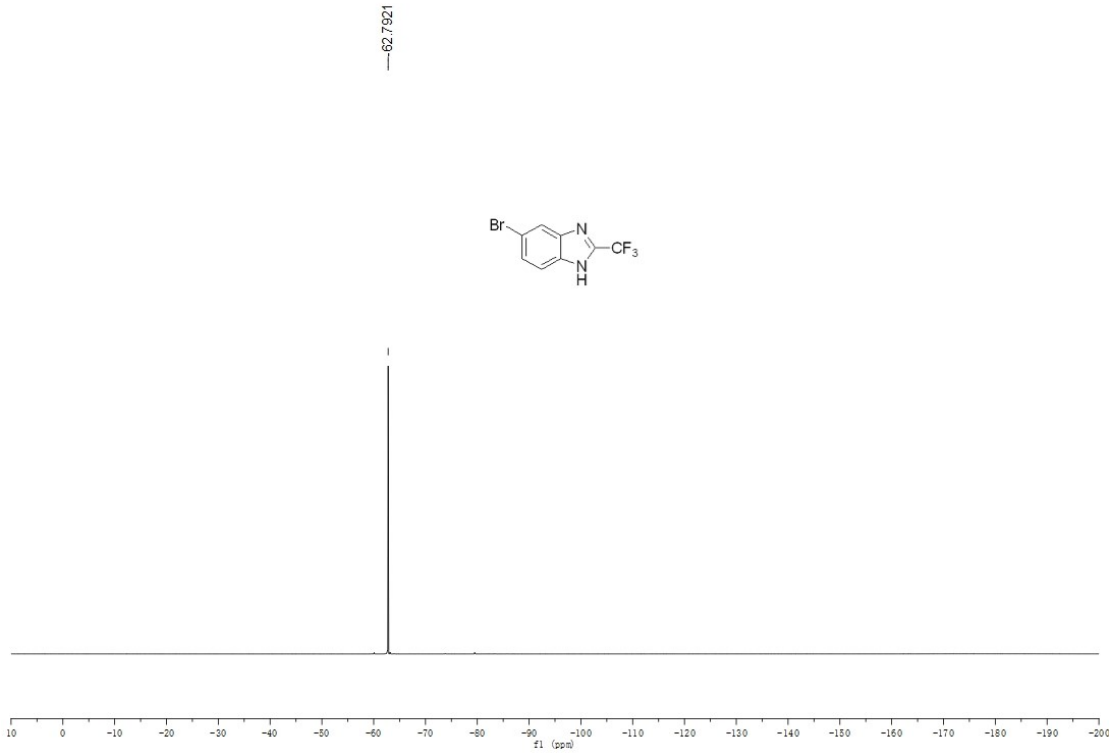
^{1}H NMR of 3p



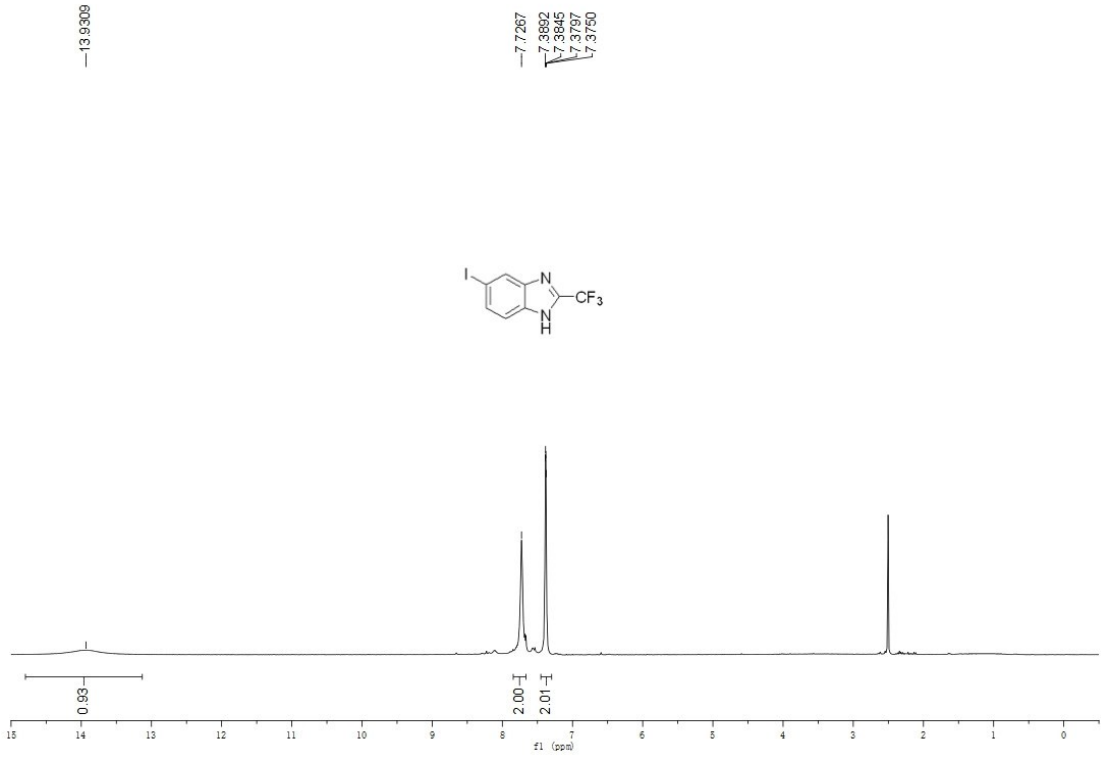
^{13}C NMR of 3p



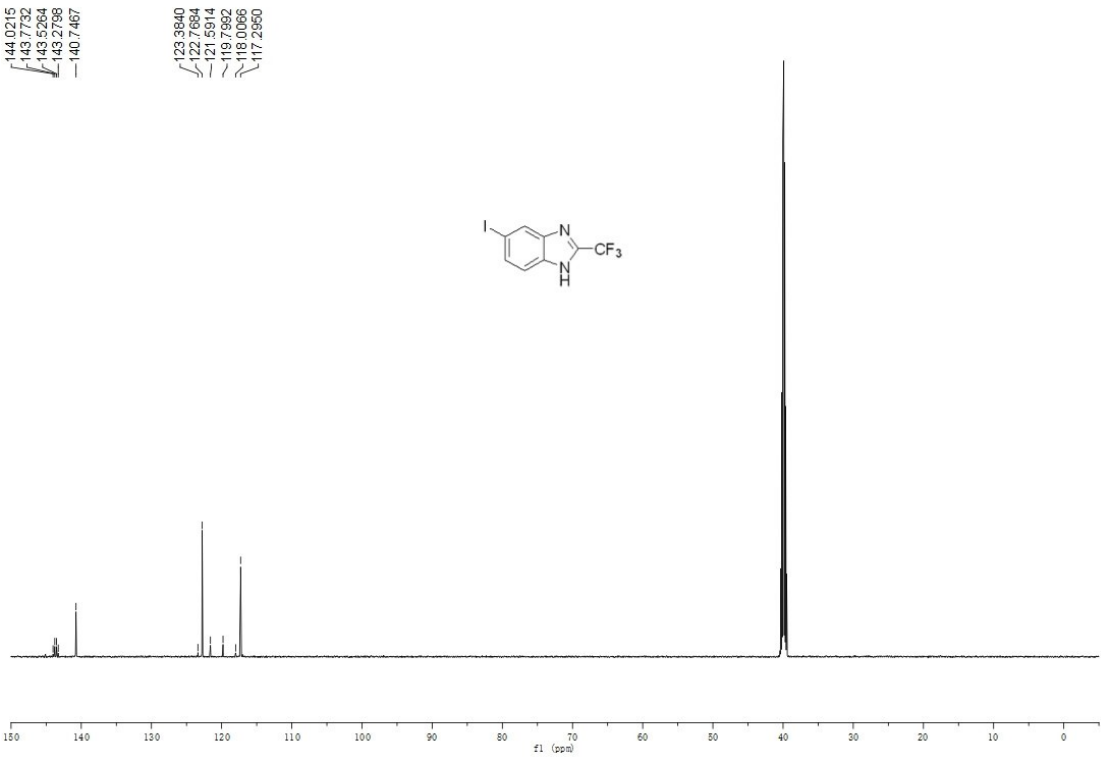
^{19}F NMR of 3p



^{1}H NMR of 3q

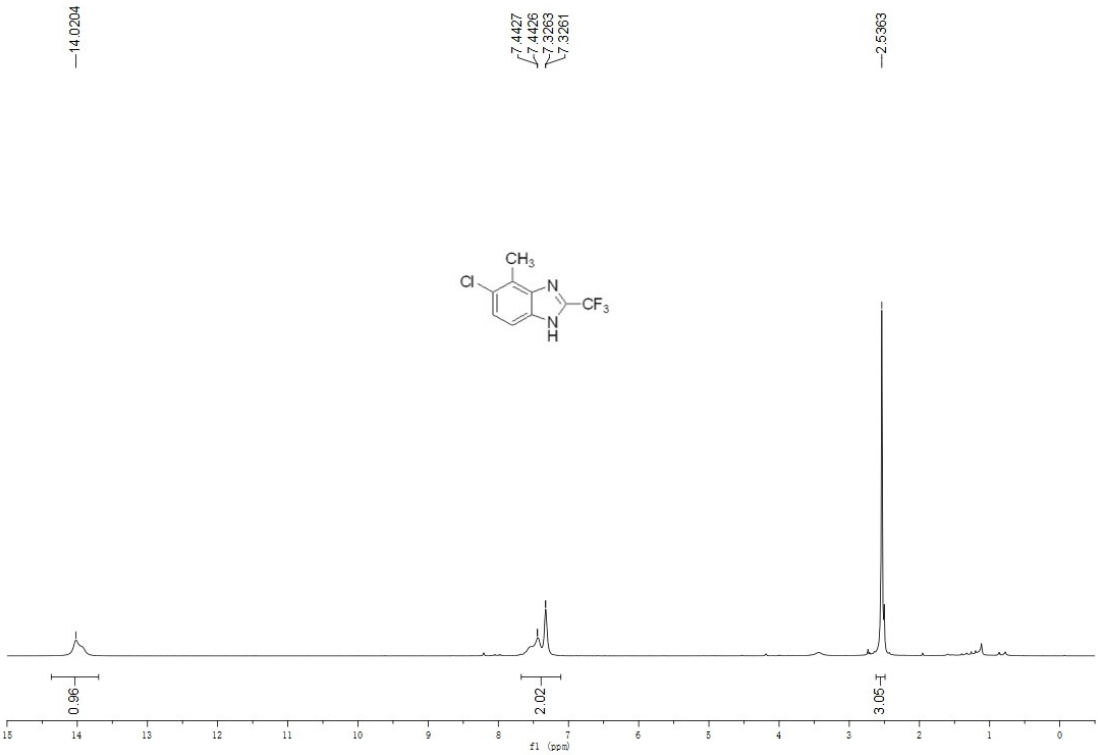


^{13}C NMR of 3q



^{19}F NMR of 3q

^{1}H NMR of 3r



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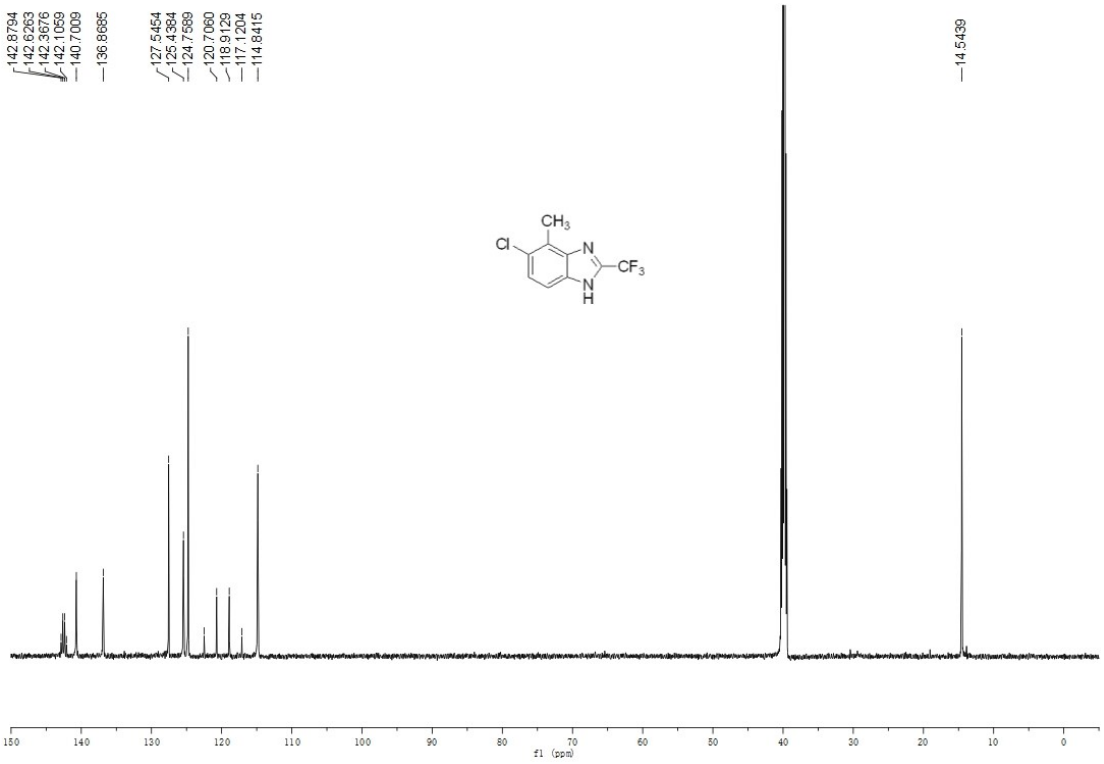

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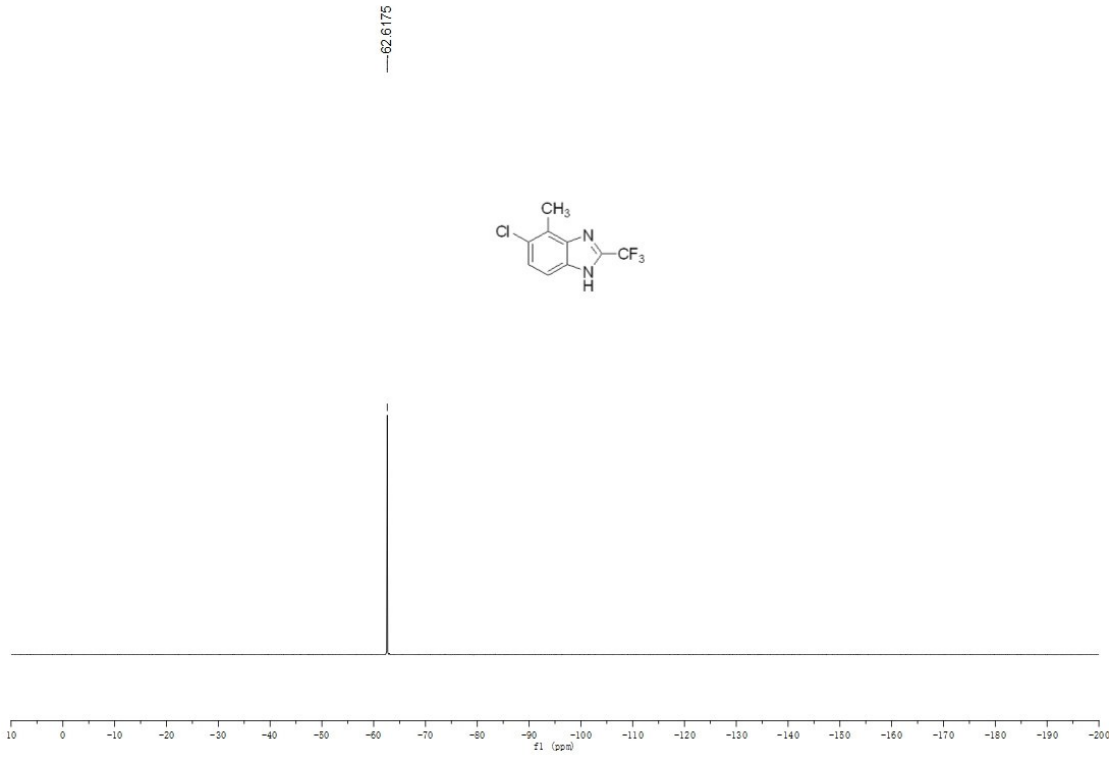
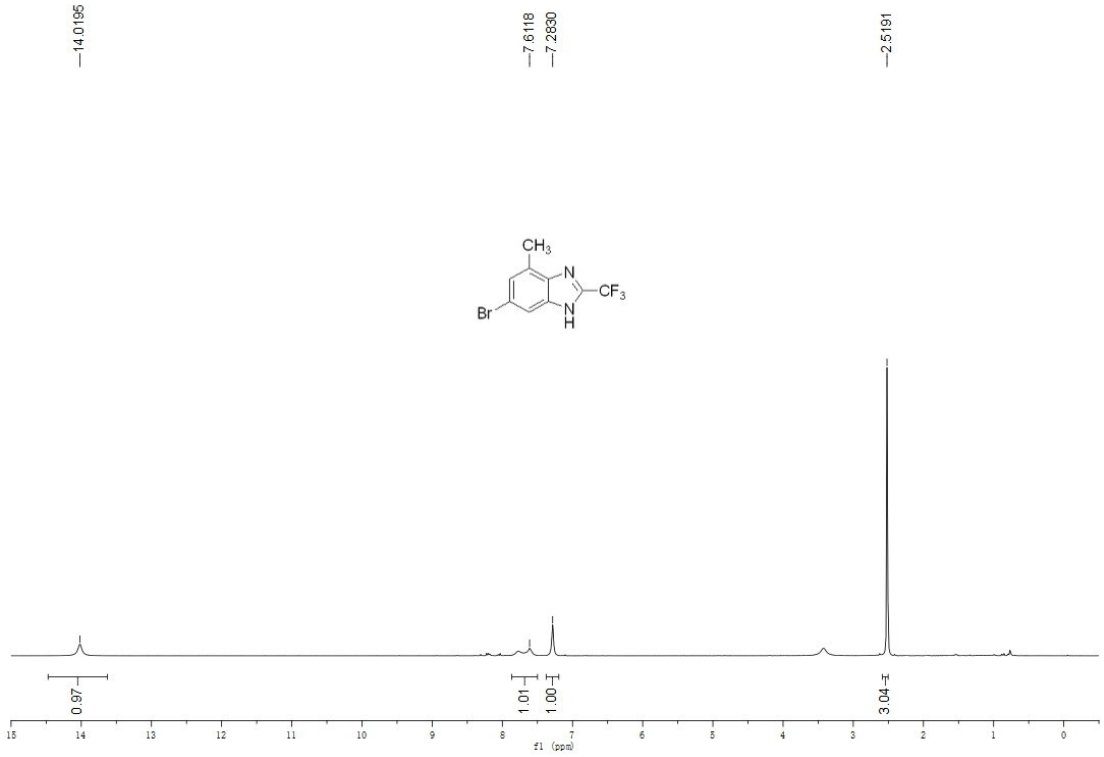


^{1}H NMR of 3s



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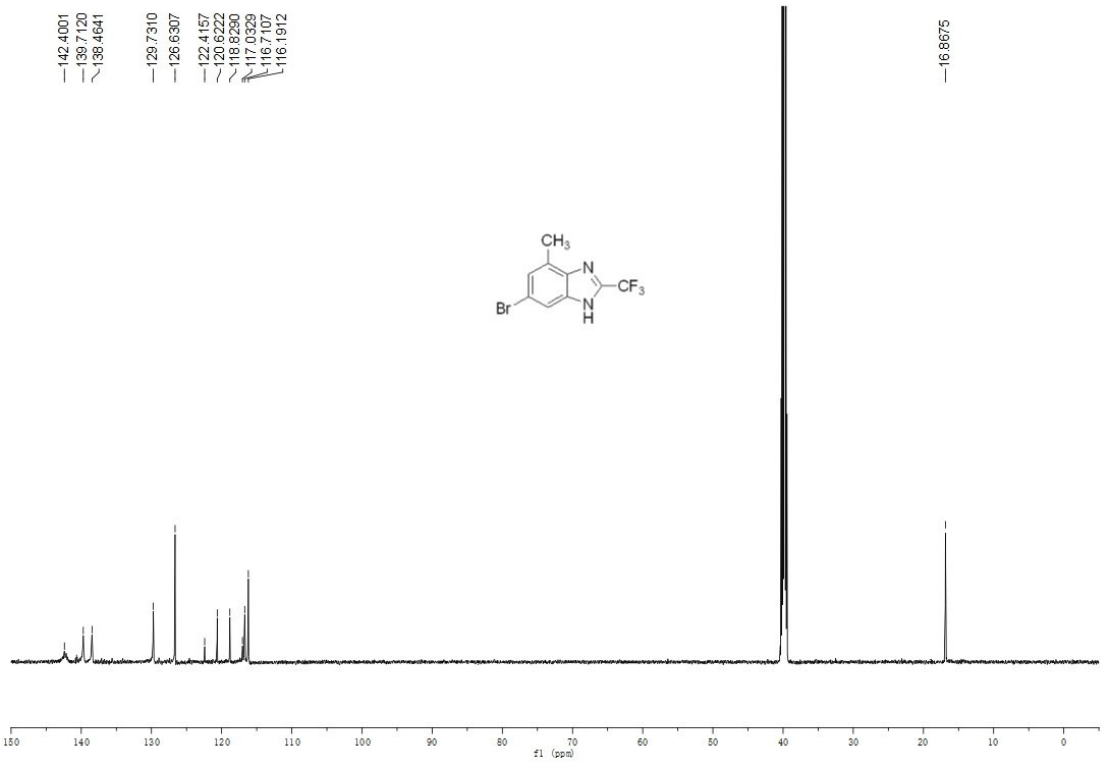

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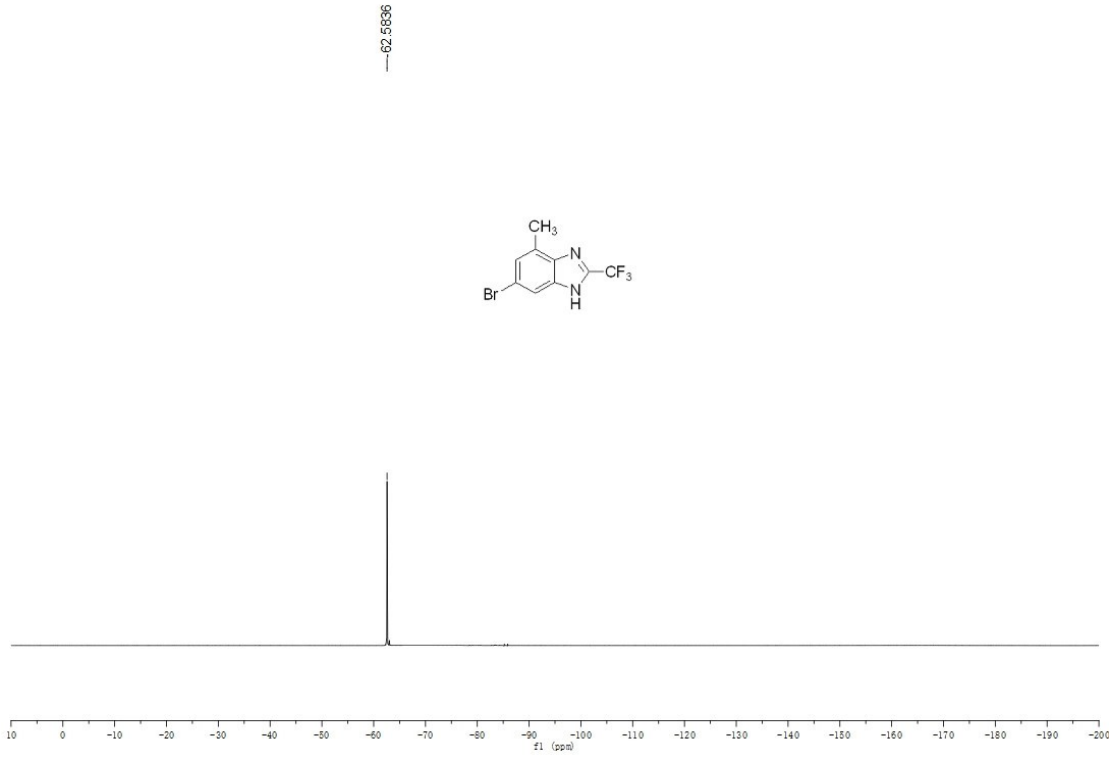

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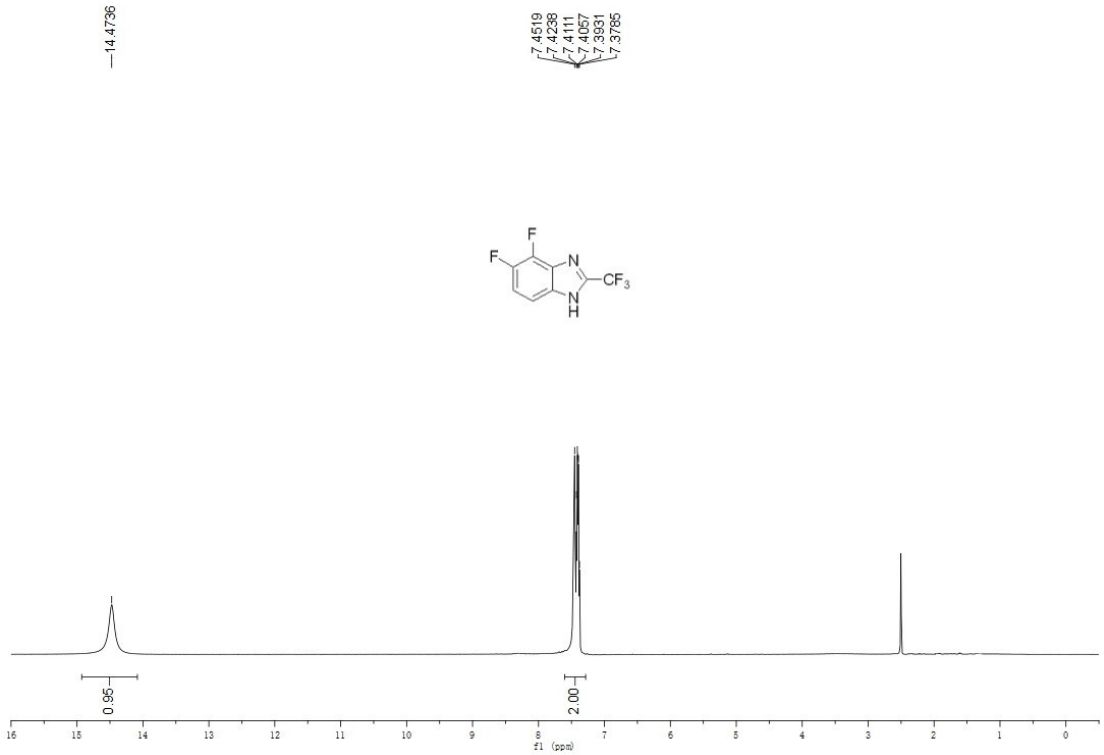

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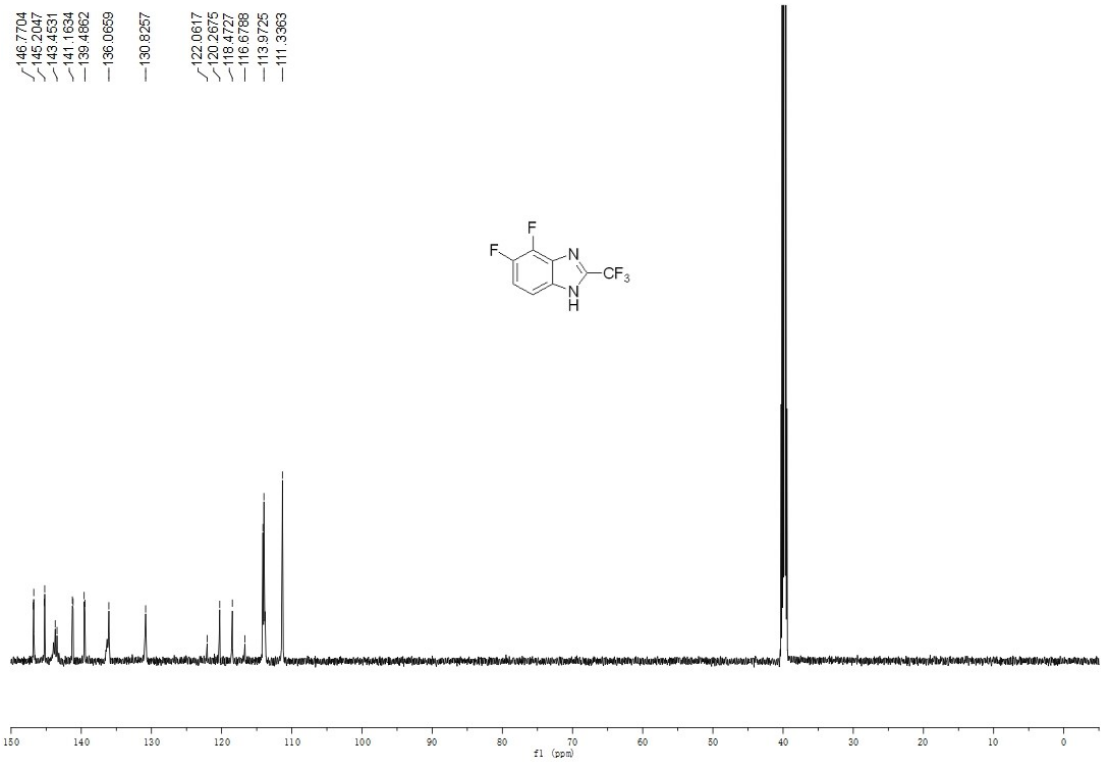

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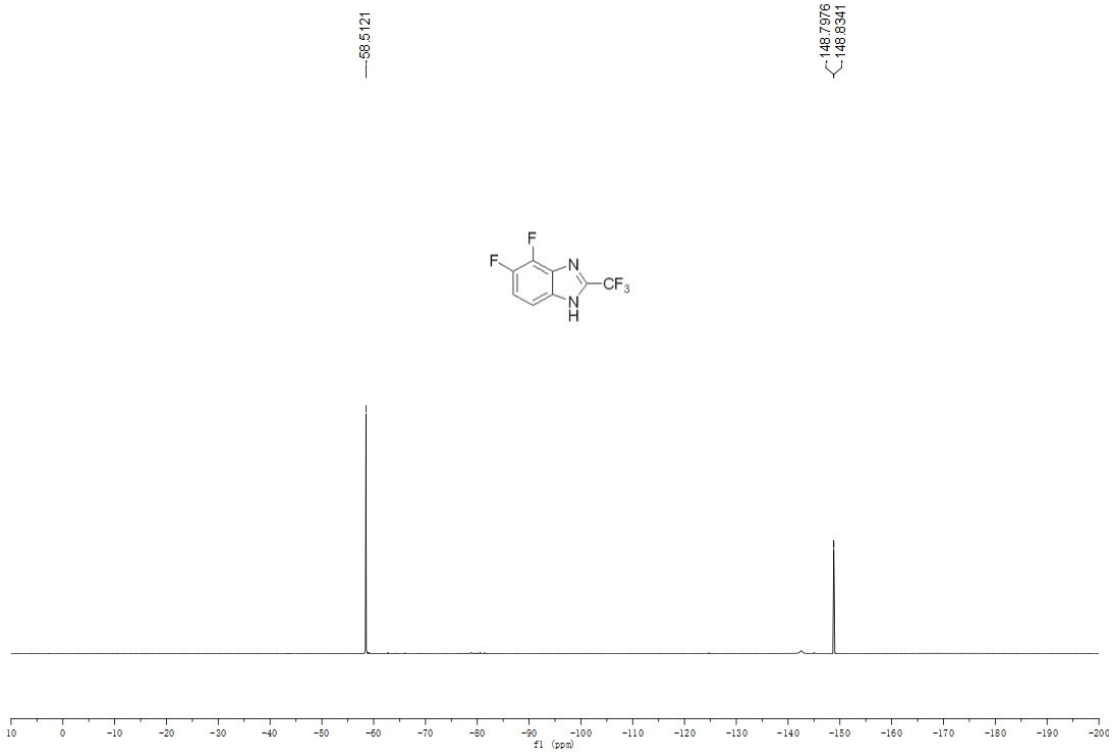

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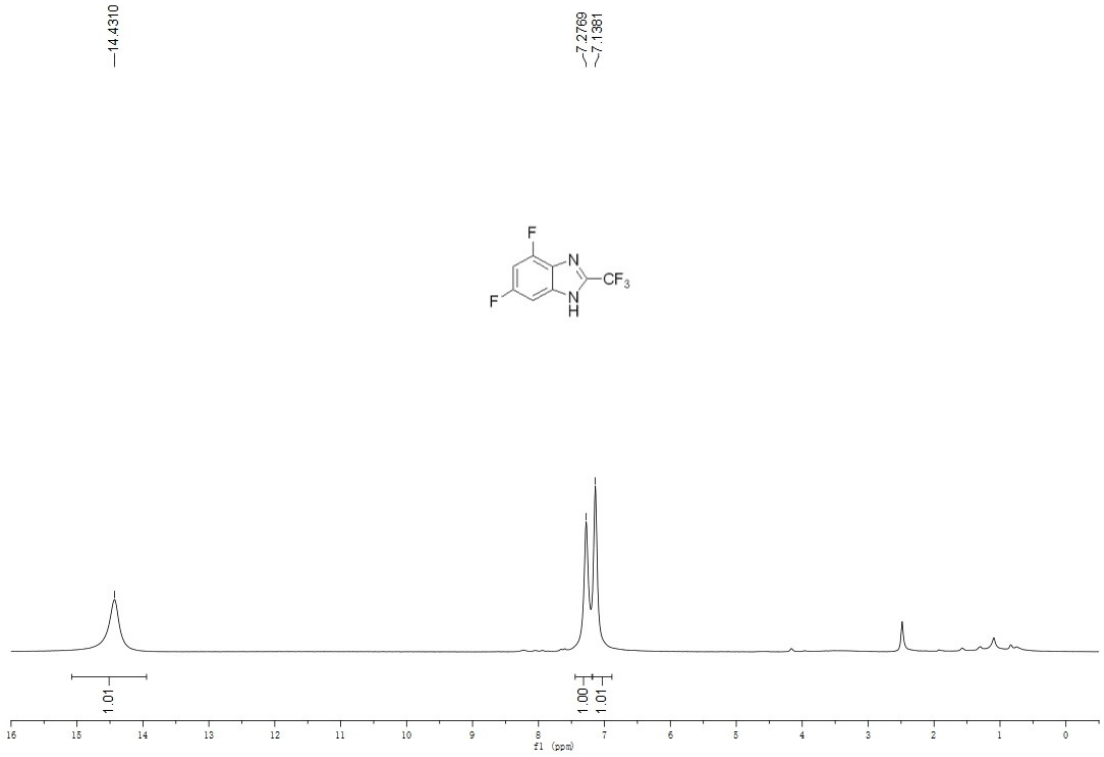

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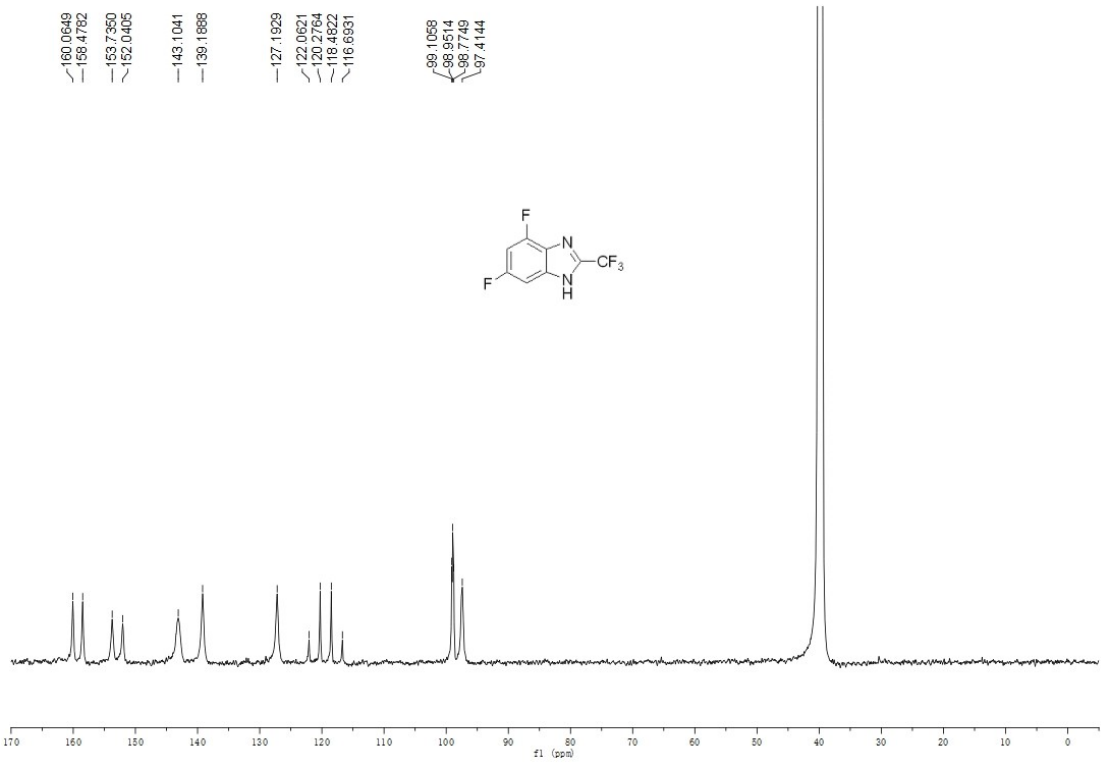

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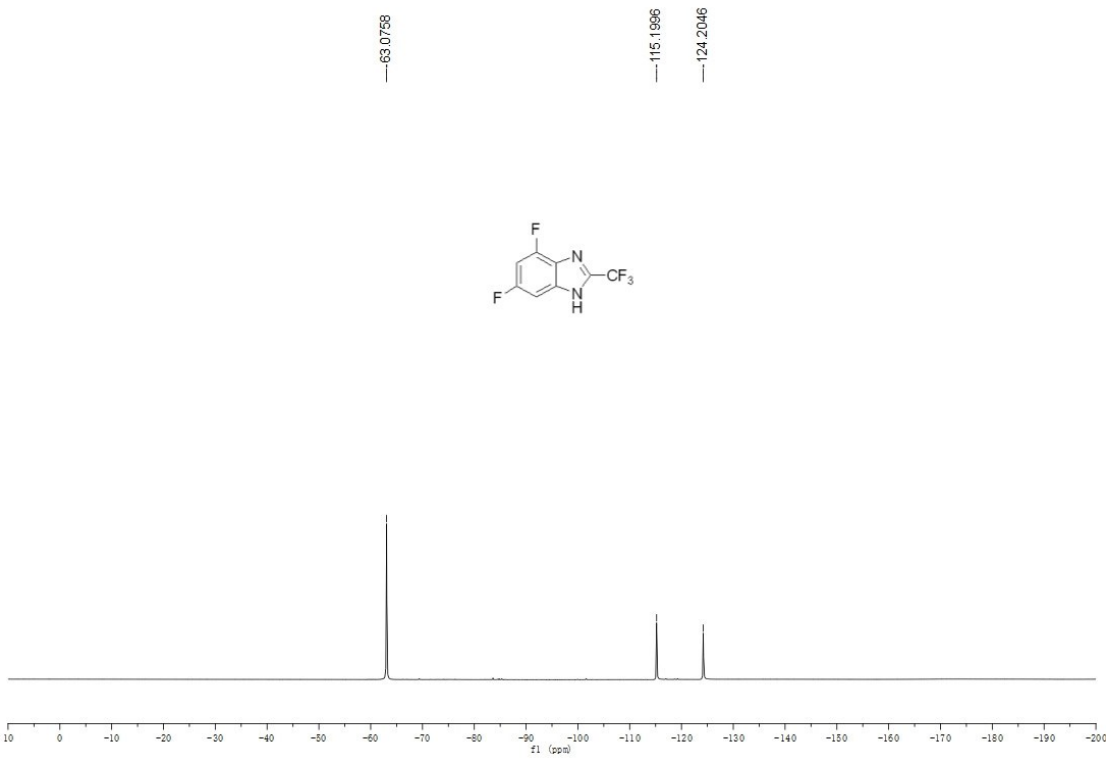

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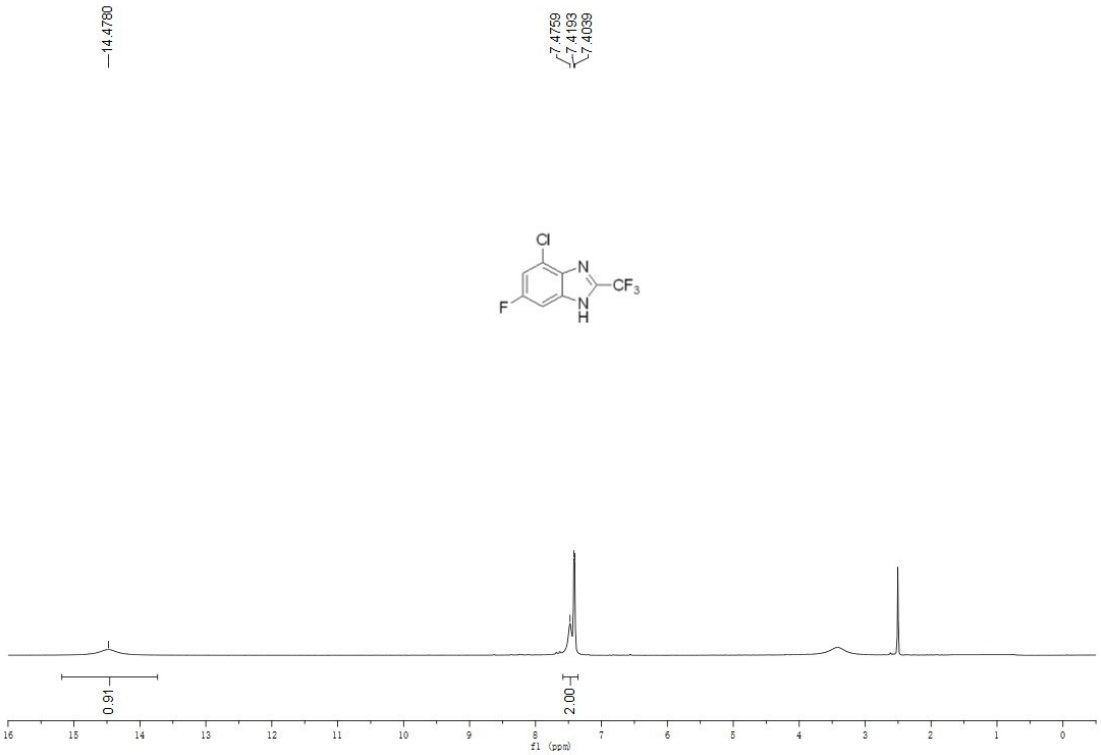
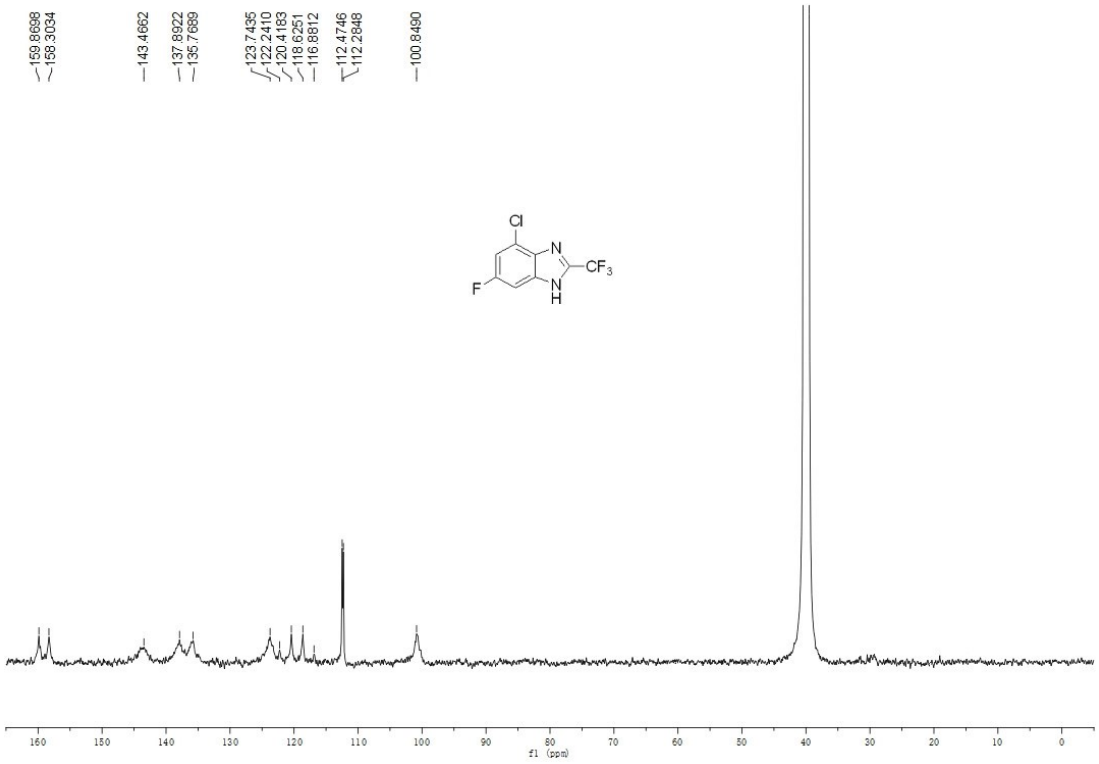
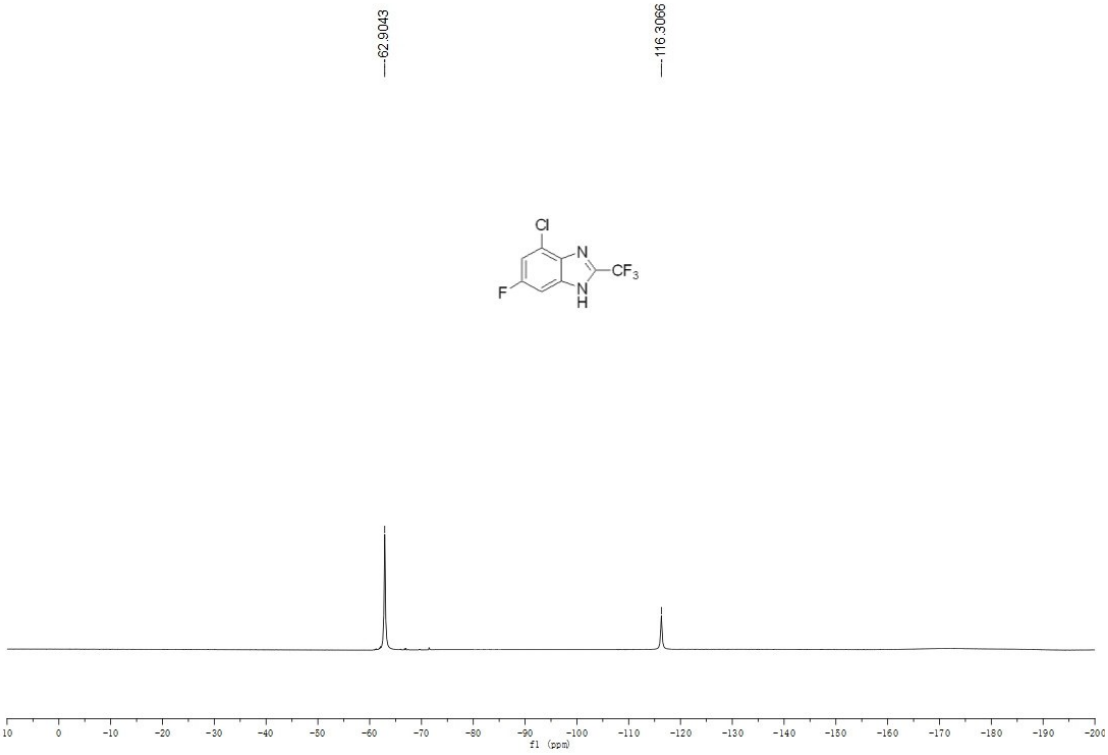


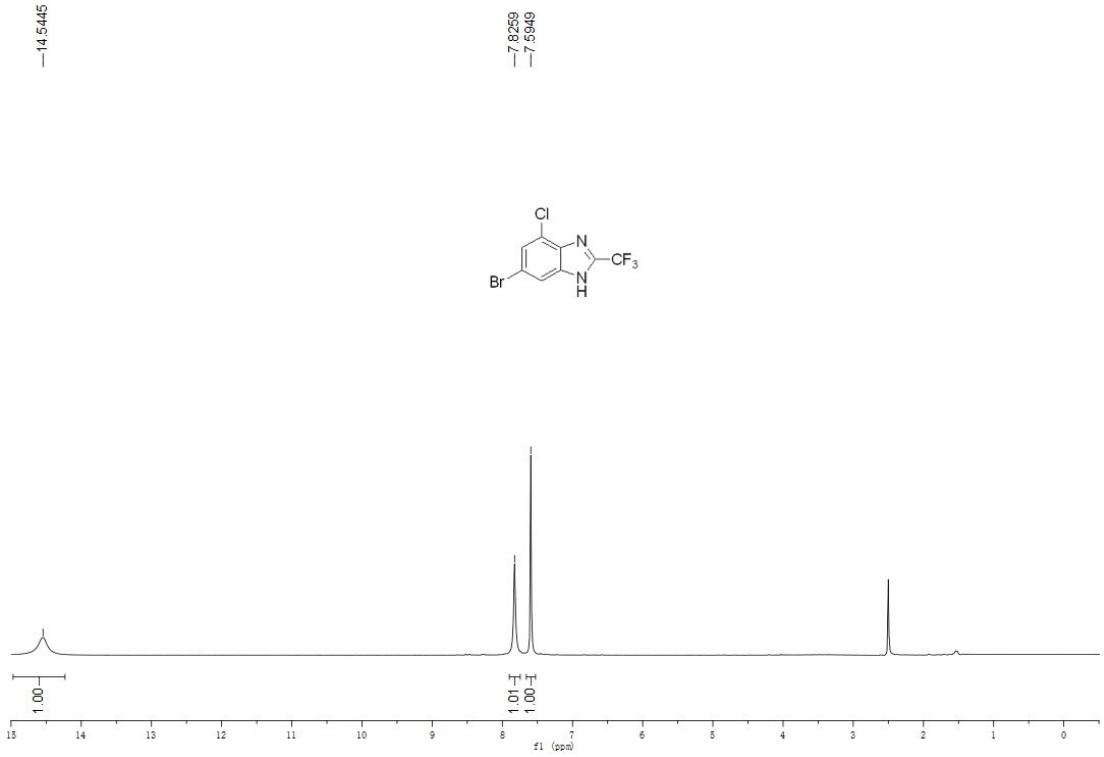
^{13}C NMR of 3v



^{19}F NMR of 3v



^{1}H NMR of 3w



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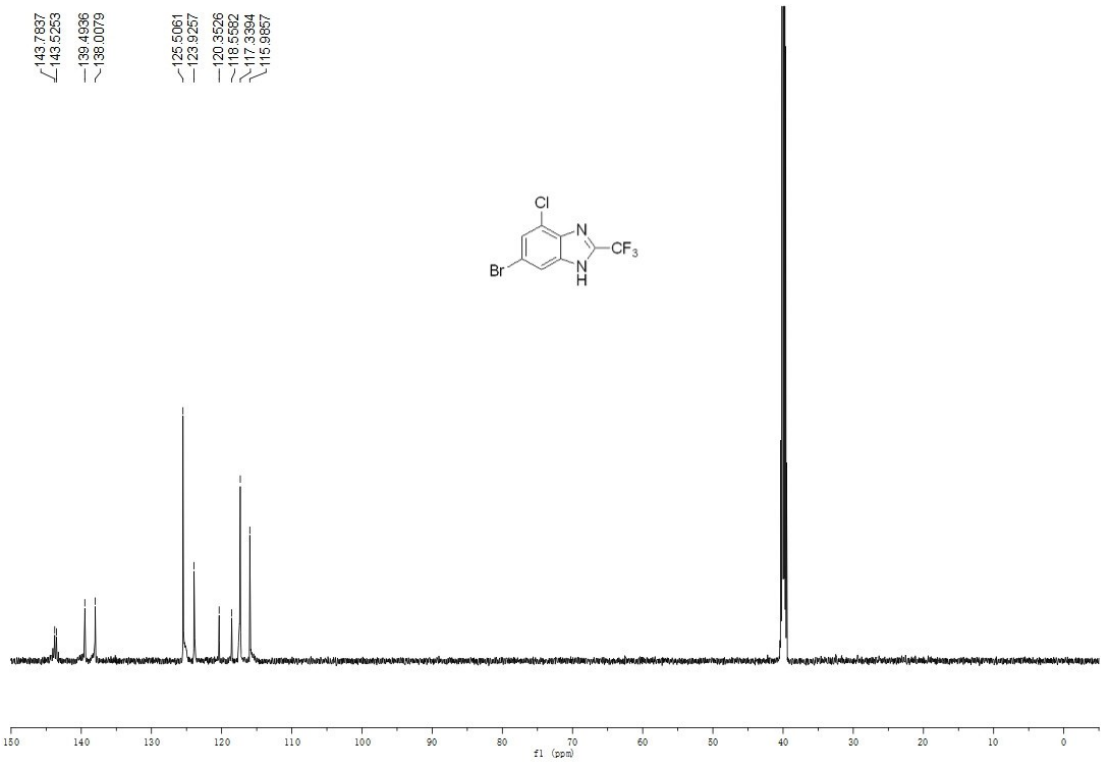

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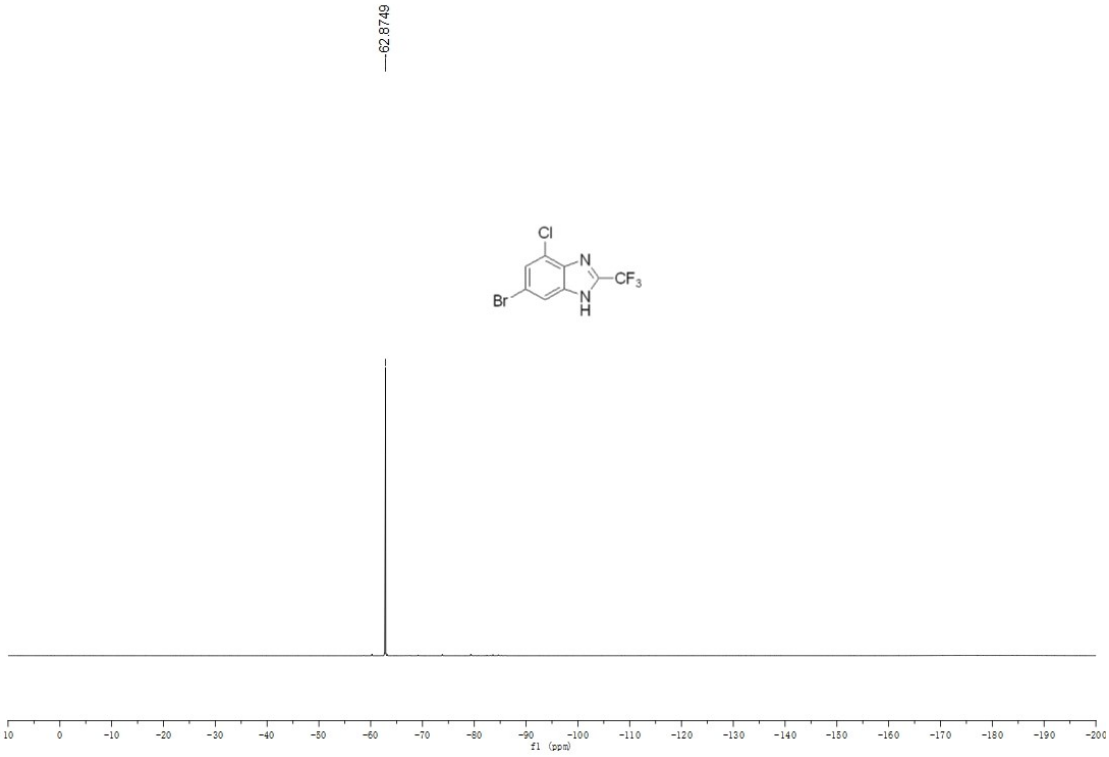
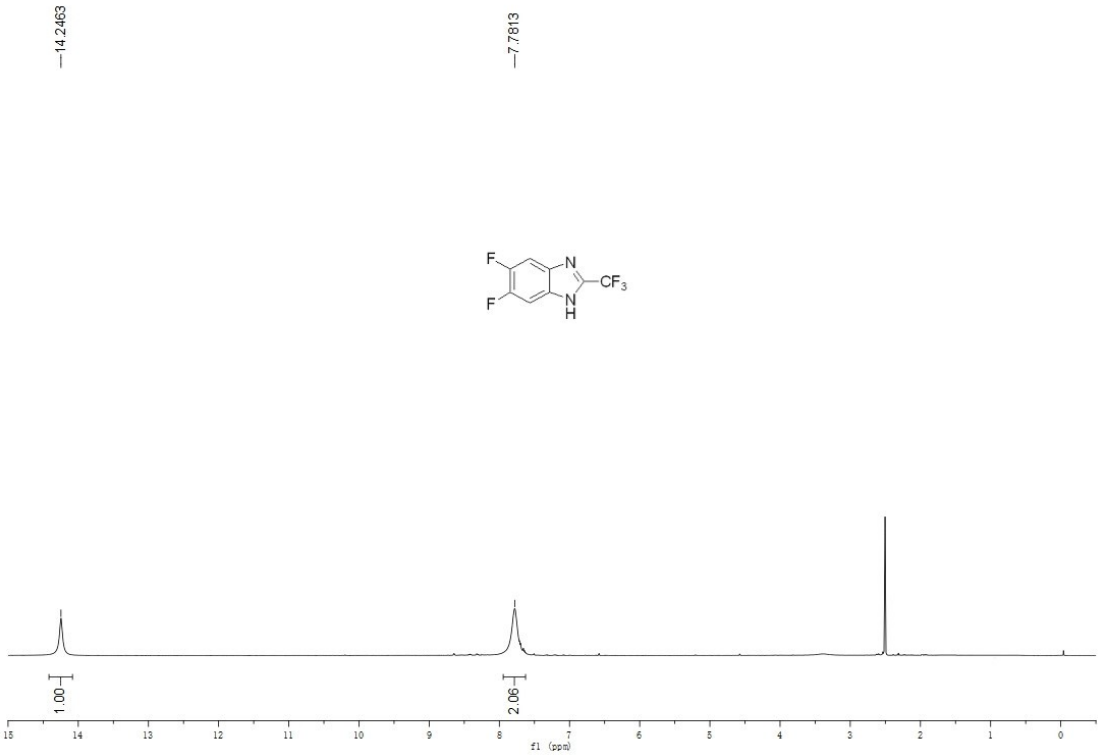


^{1}H NMR of 3x



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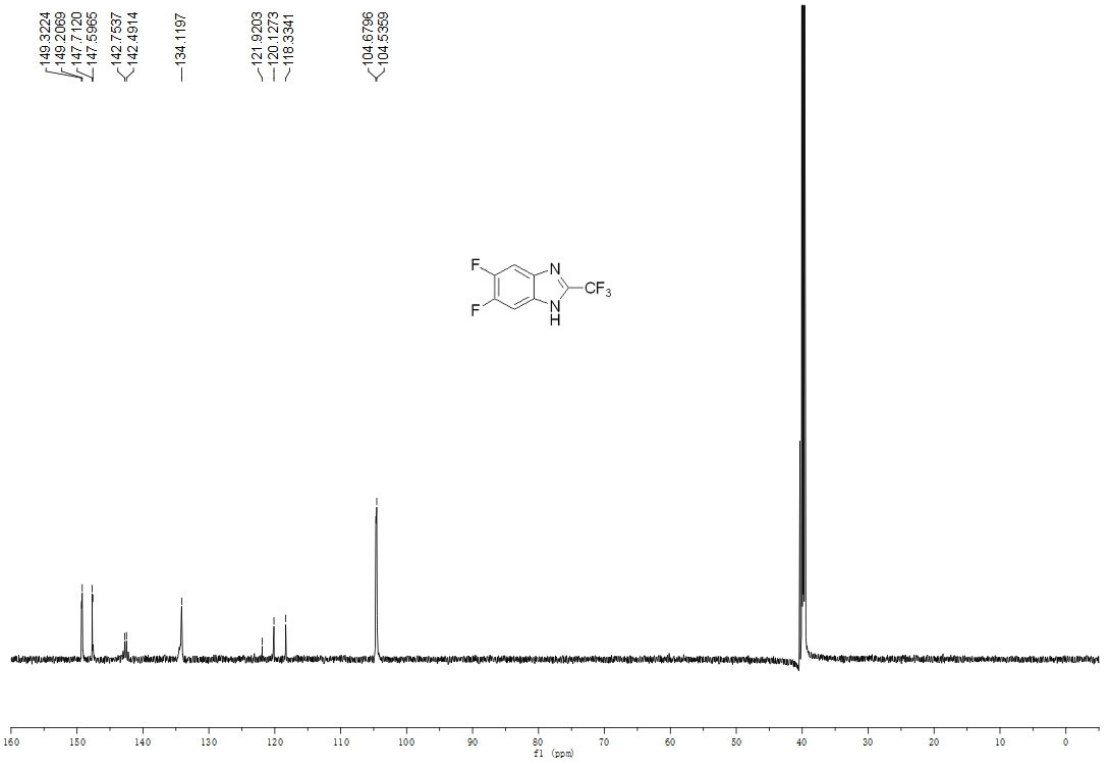

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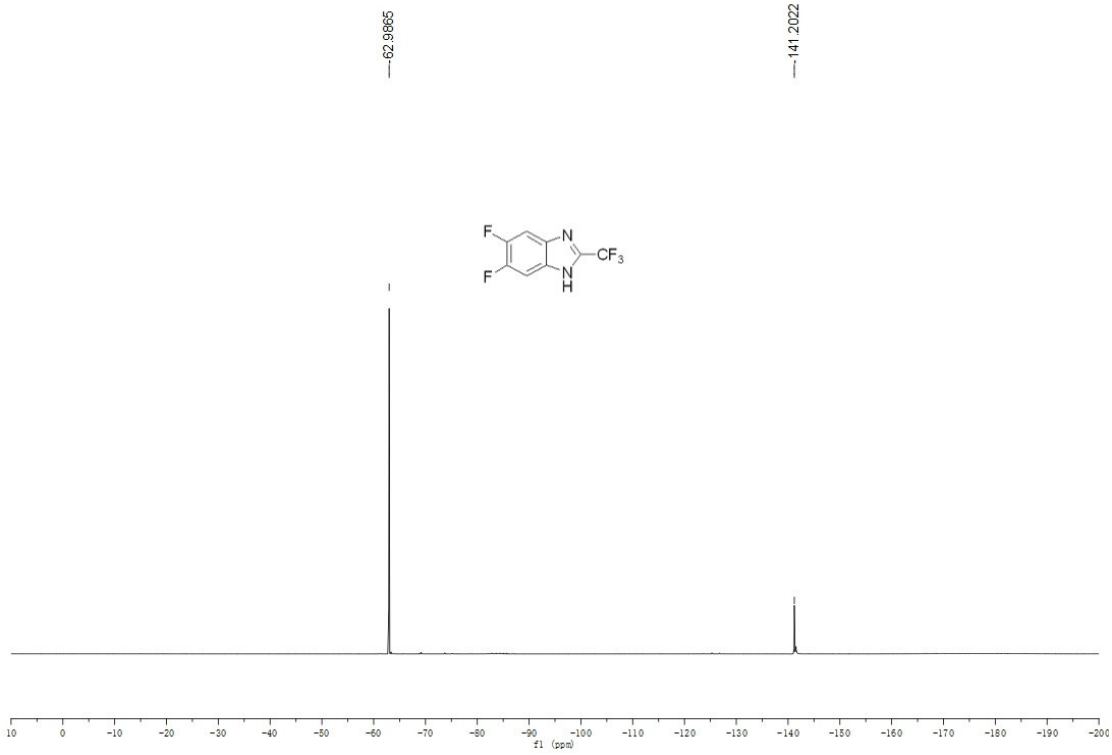
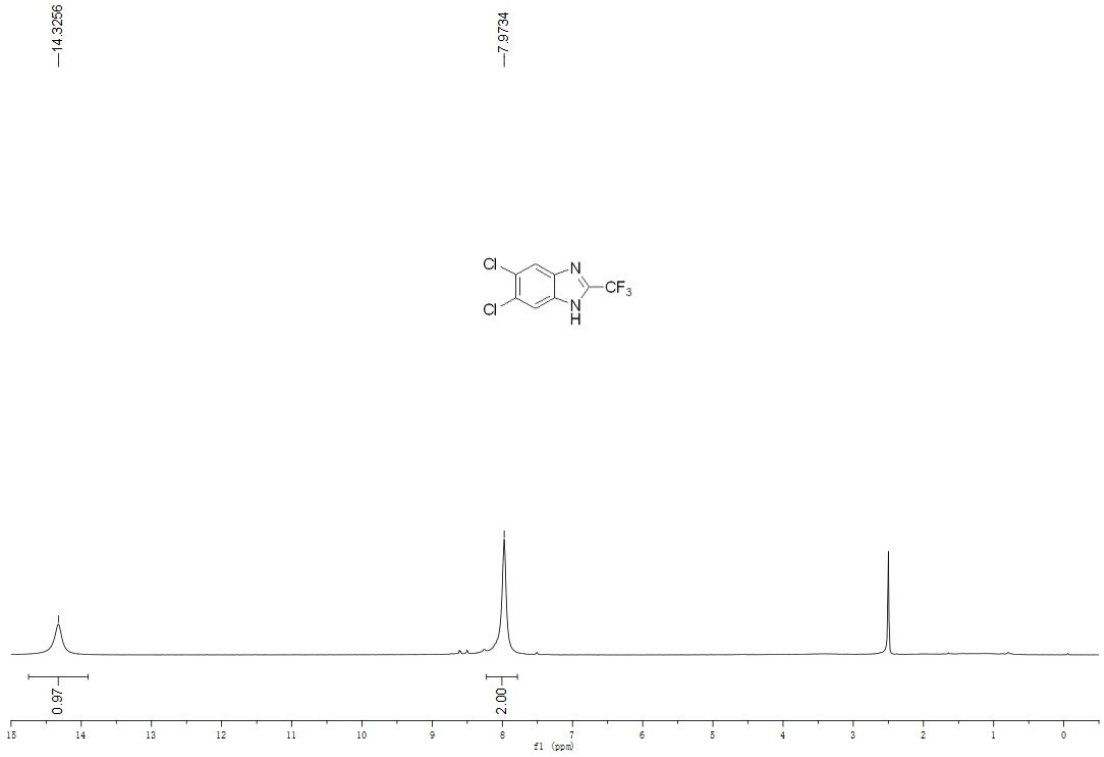
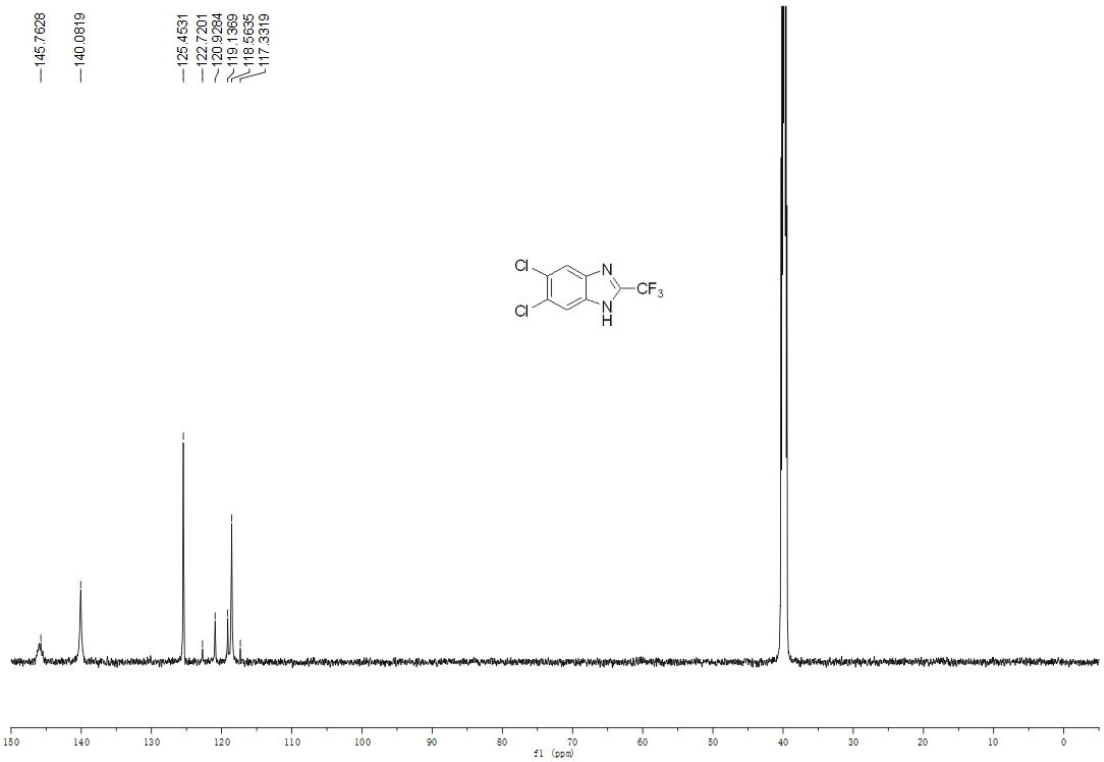


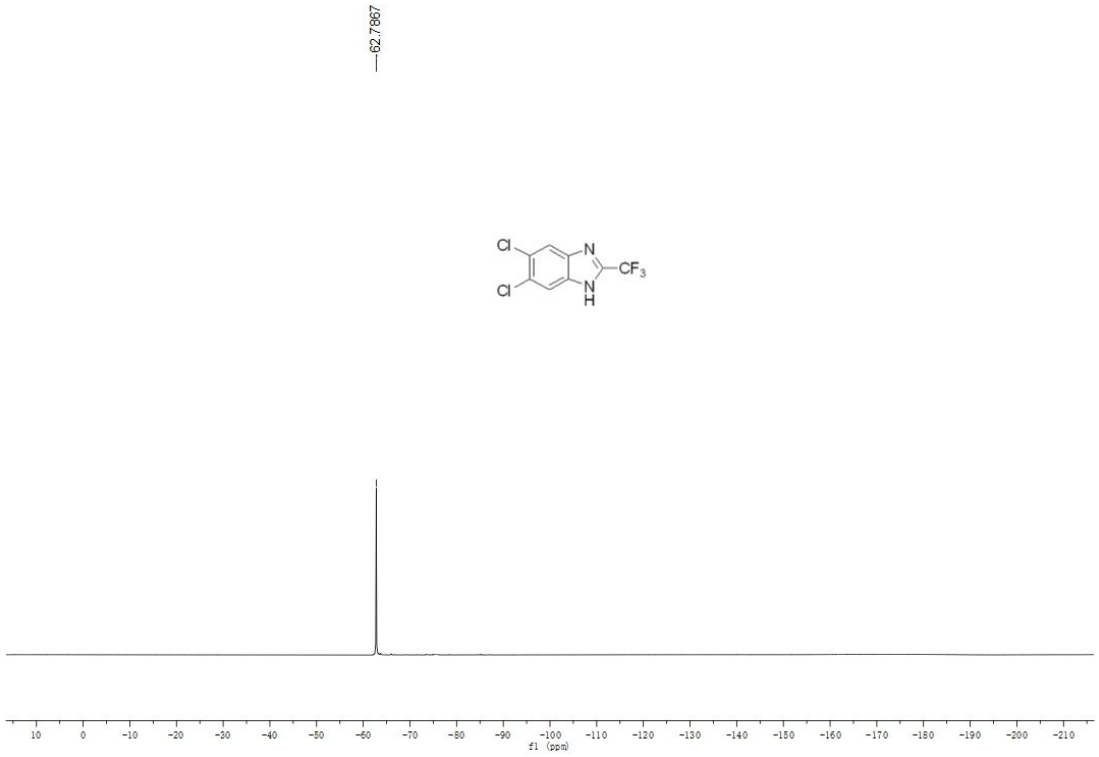
^{1}H NMR of 3y



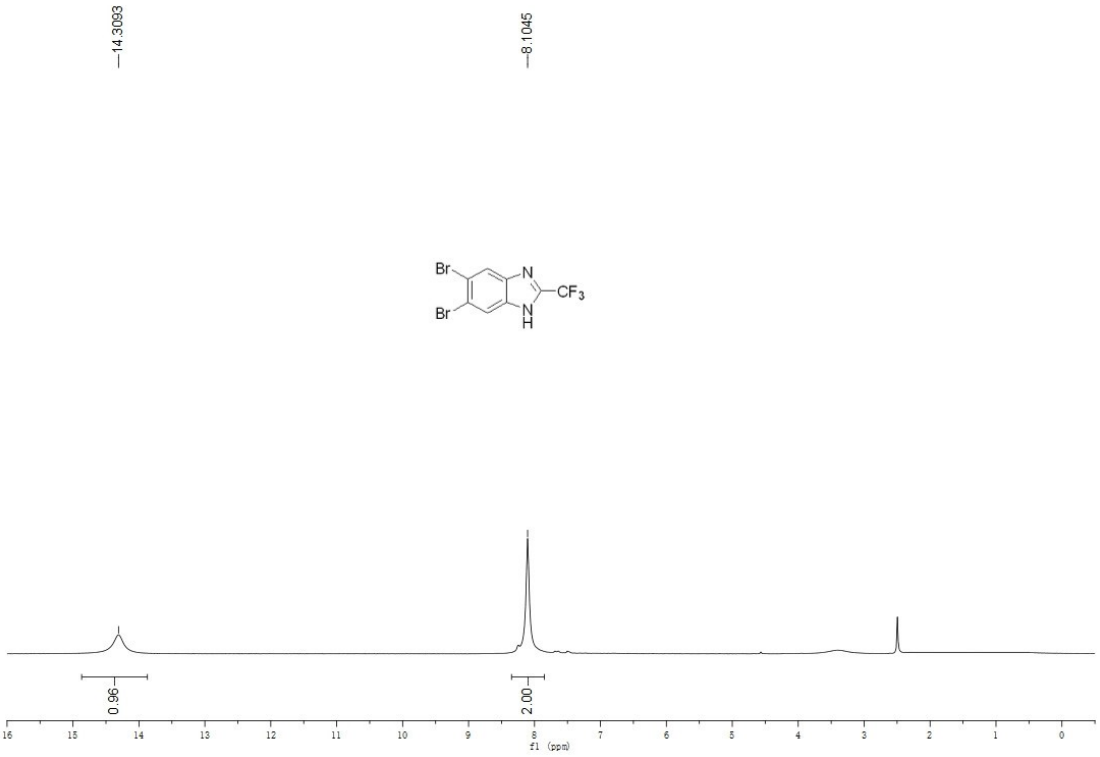
^{13}C NMR of 3y



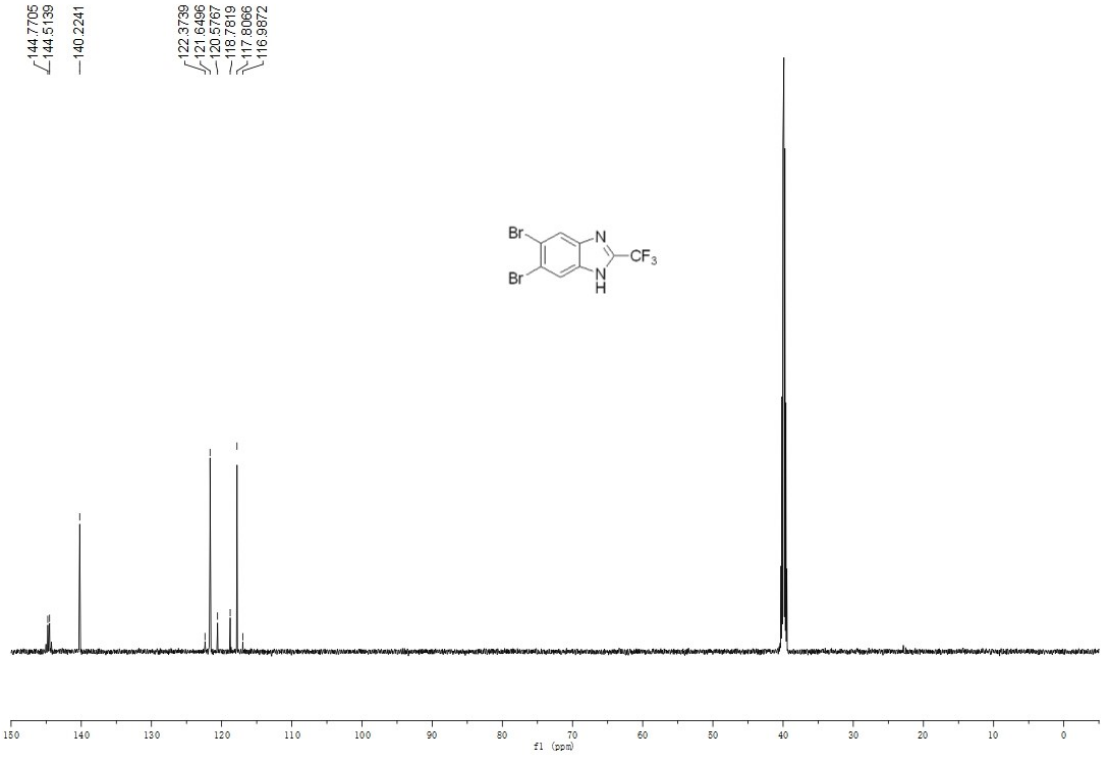
^{19}F NMR of 3y



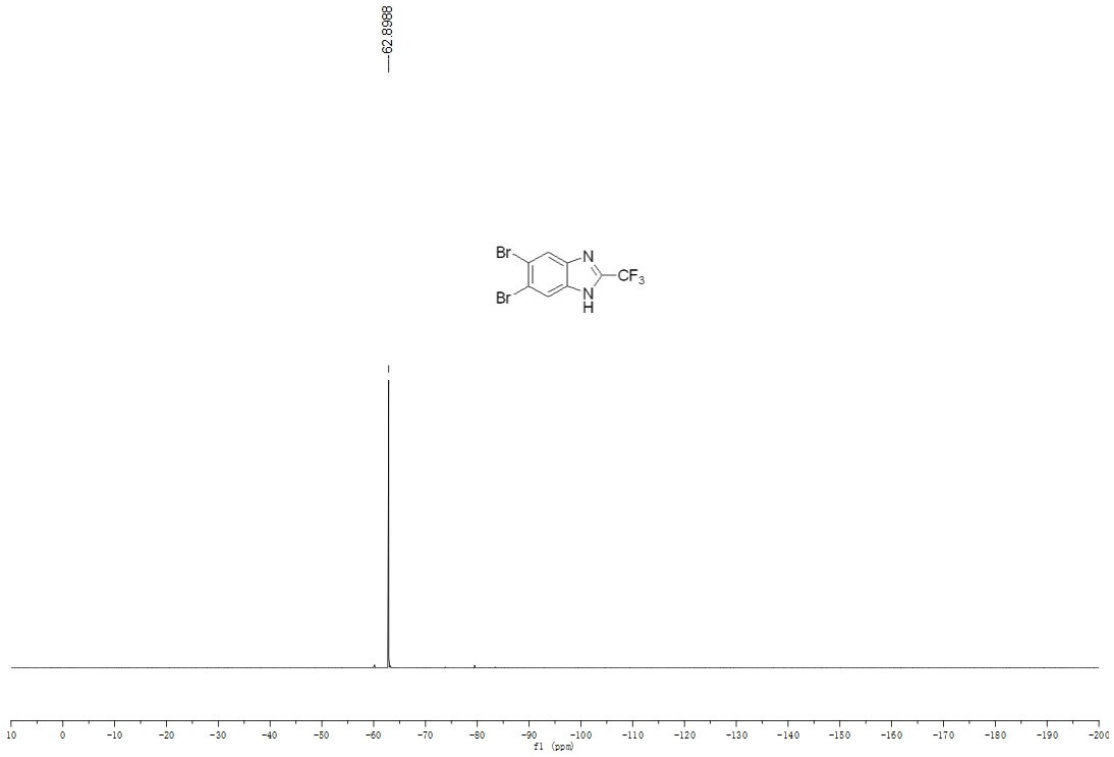
^{1}H NMR of 3z



^{13}C NMR of 3z



^{19}F NMR of 3z



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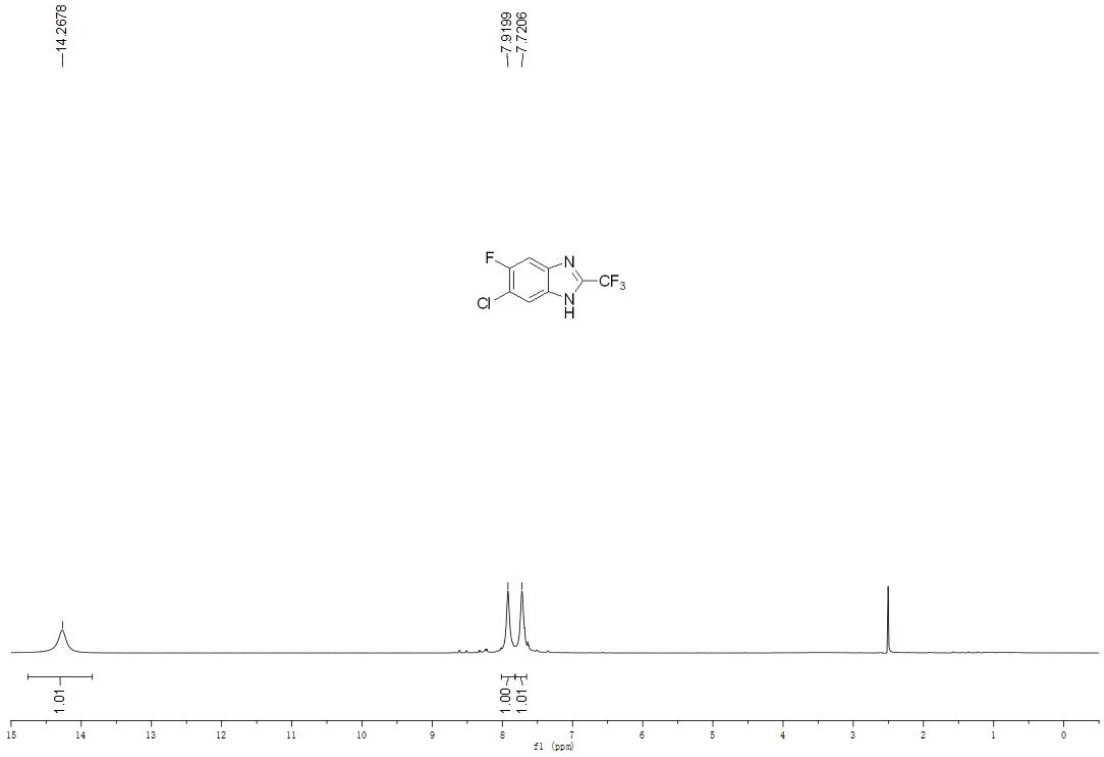

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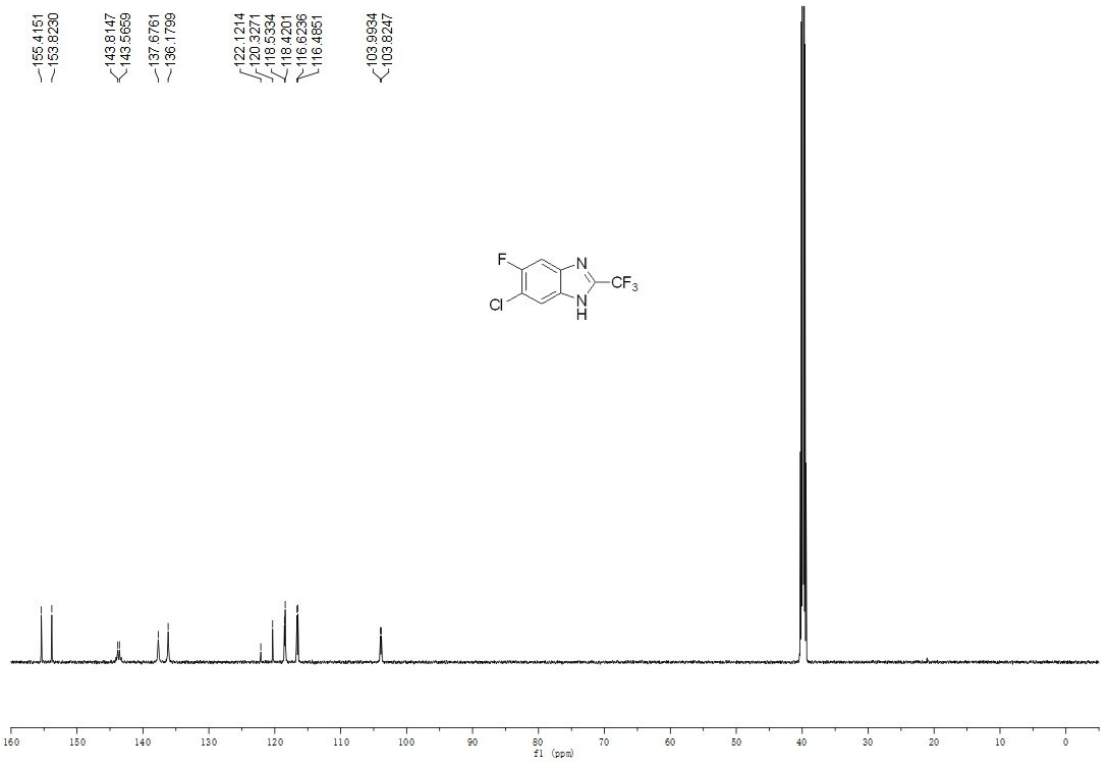
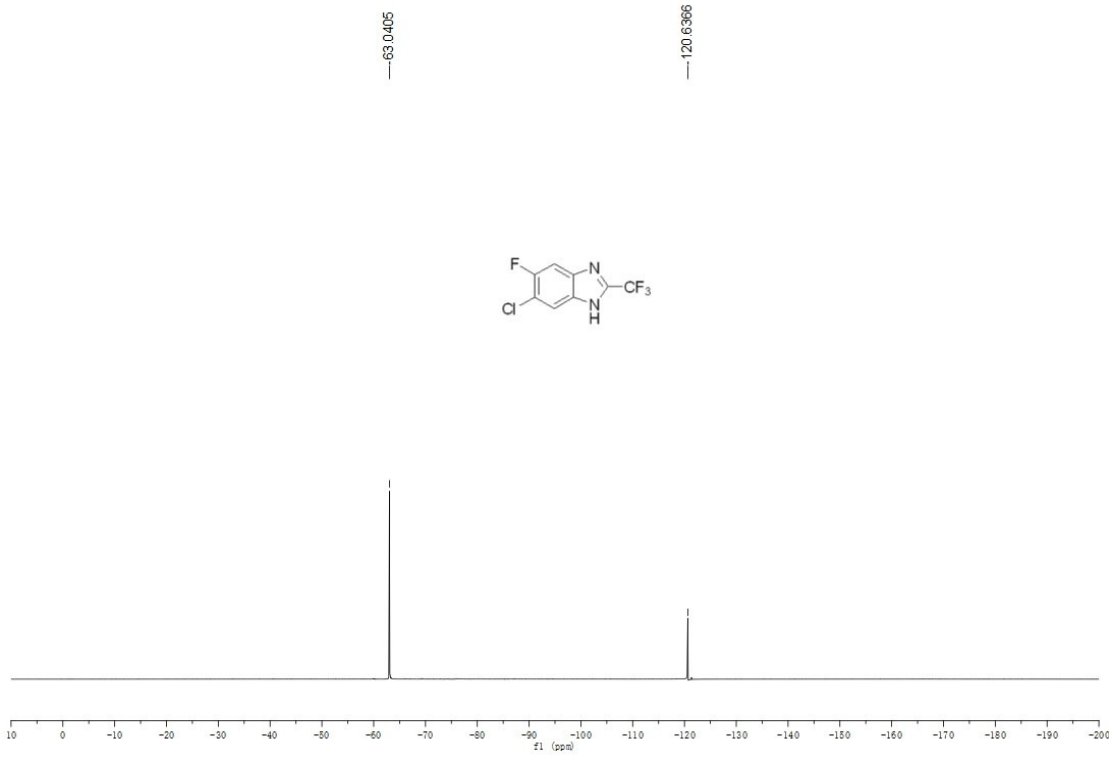
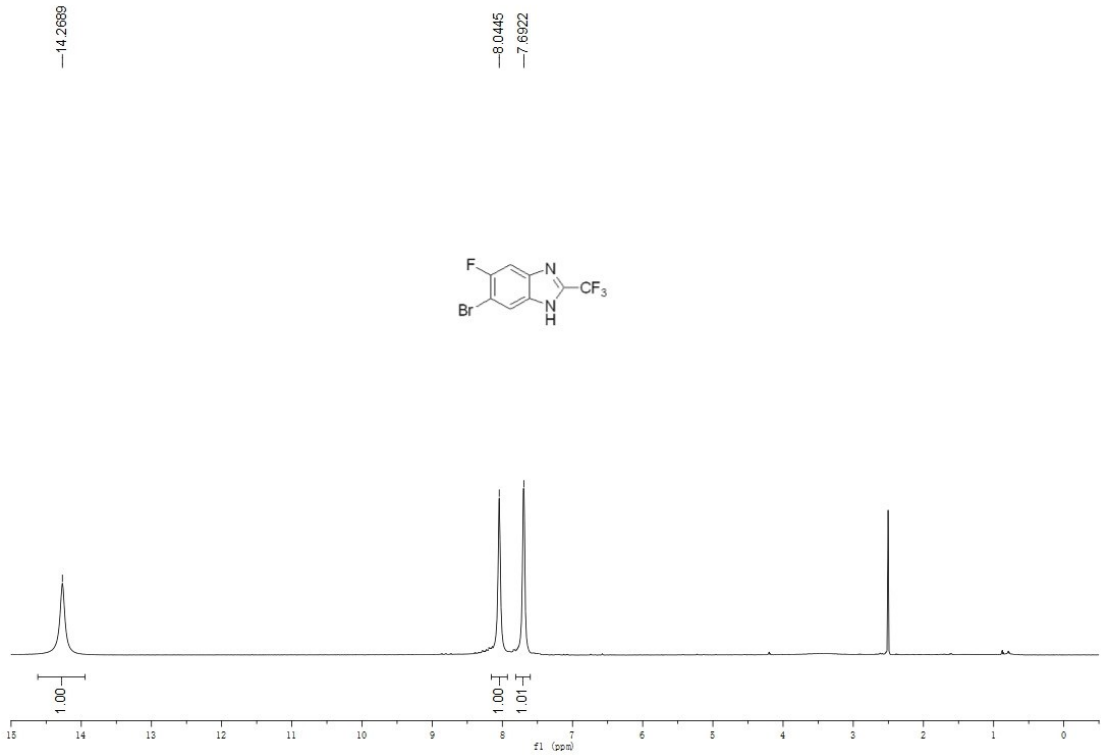


^{19}F NMR of 3aa



^{1}H NMR of 3bb



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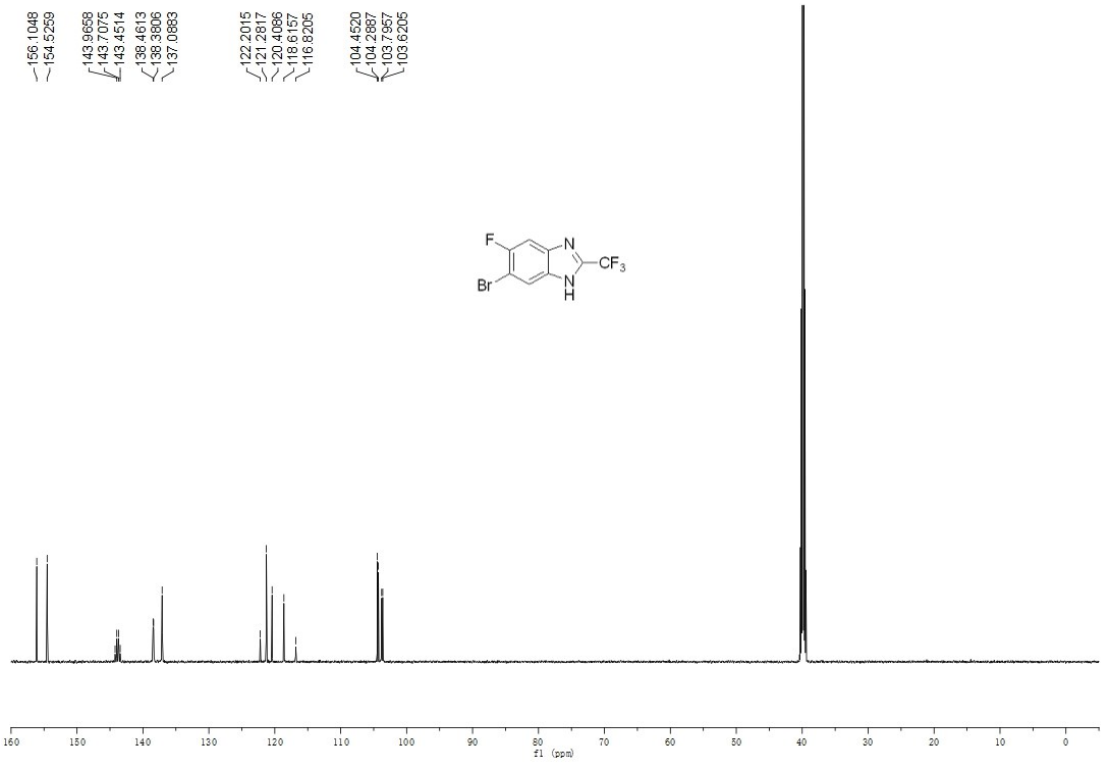
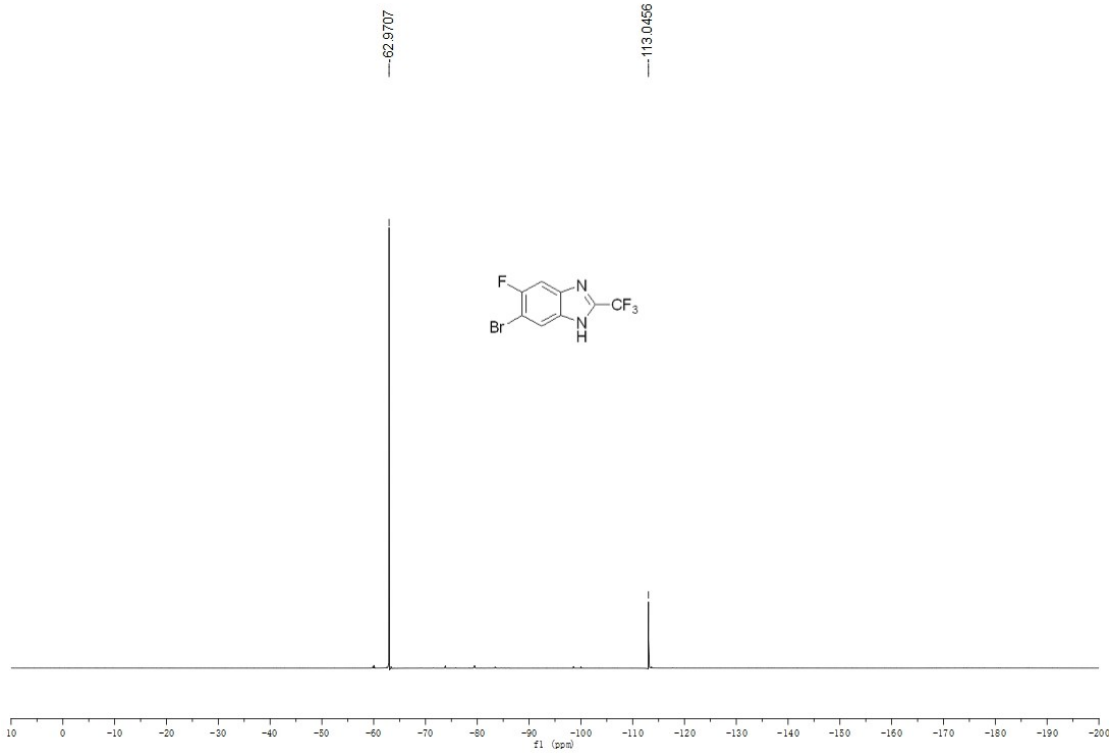


^{19}F NMR of 3bb



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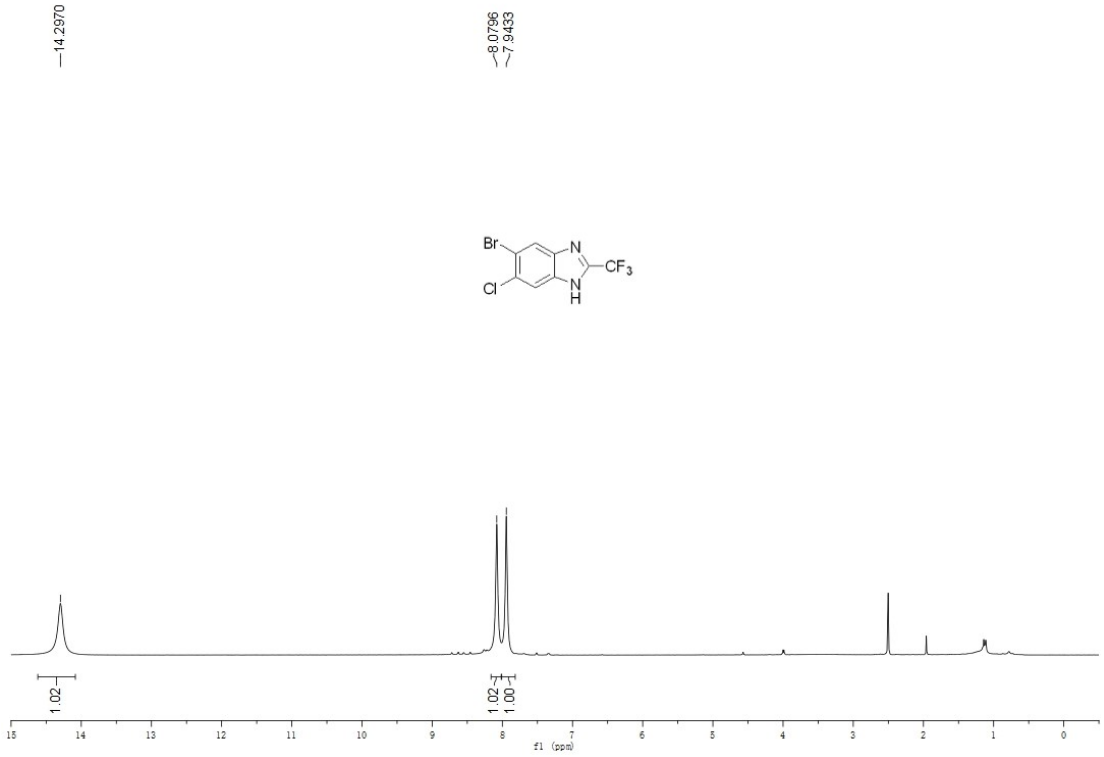

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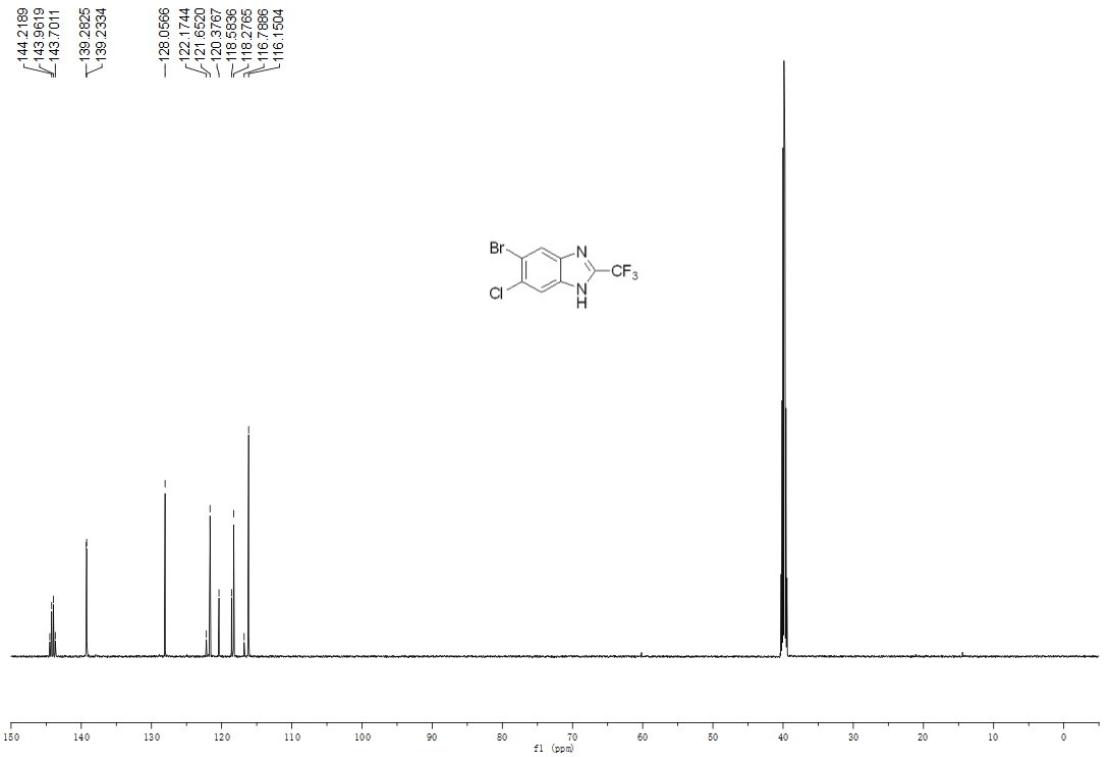

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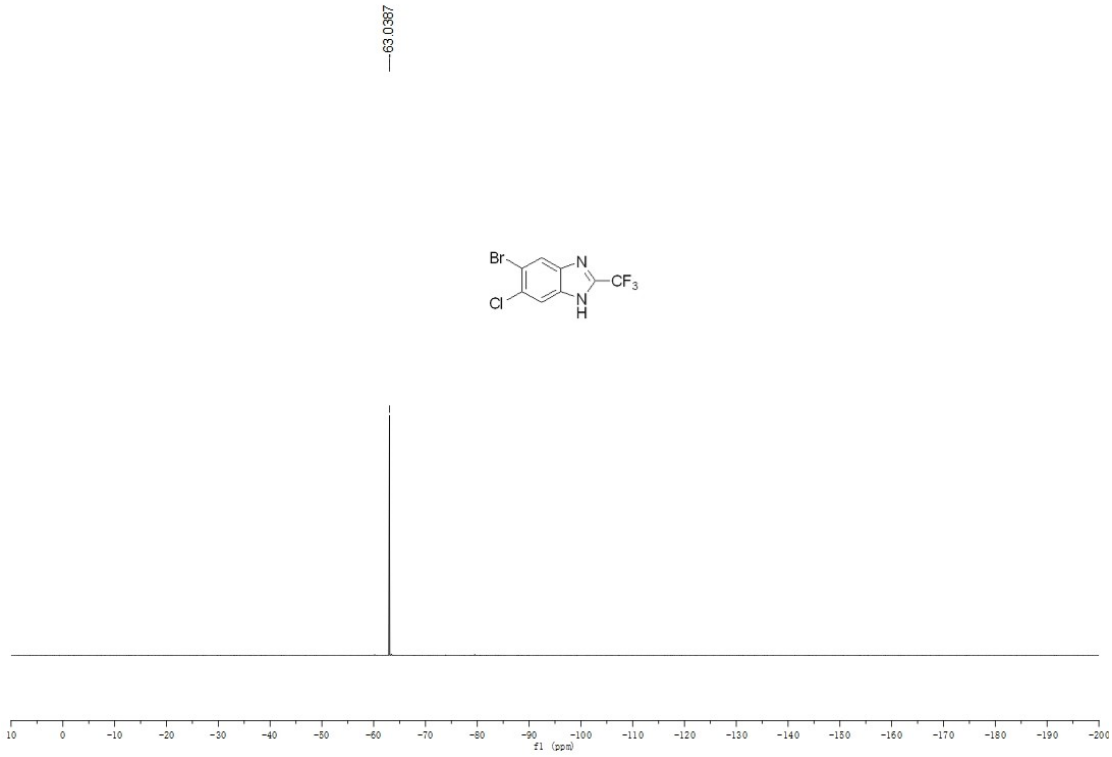

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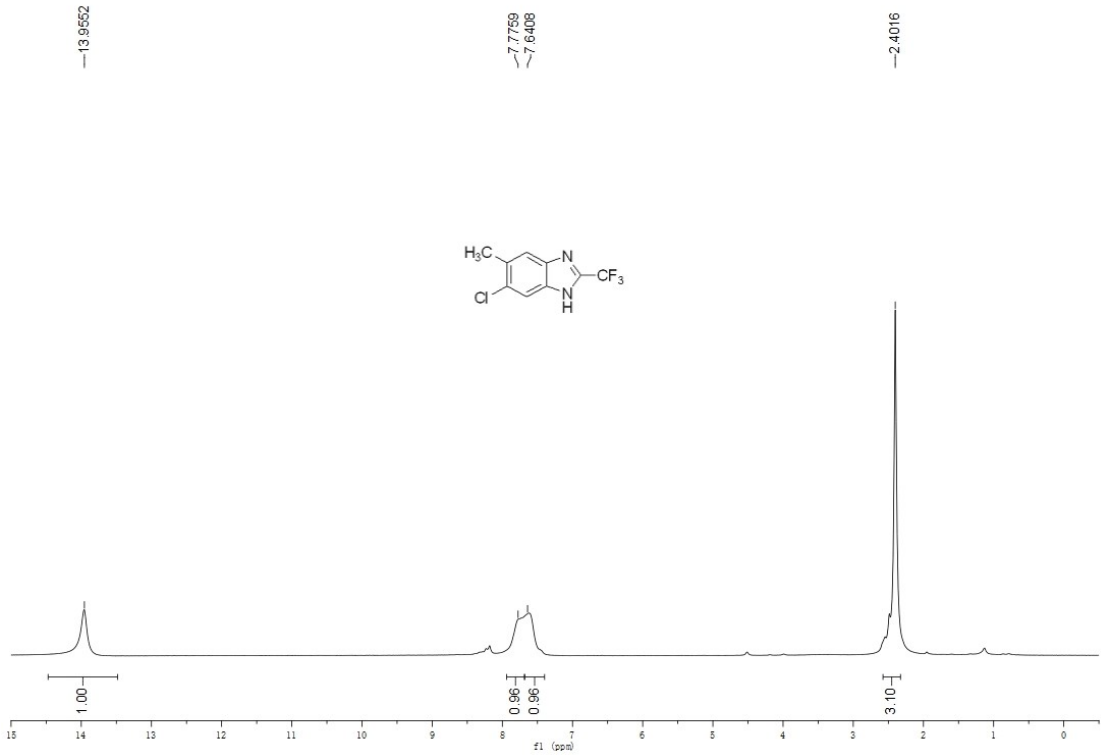

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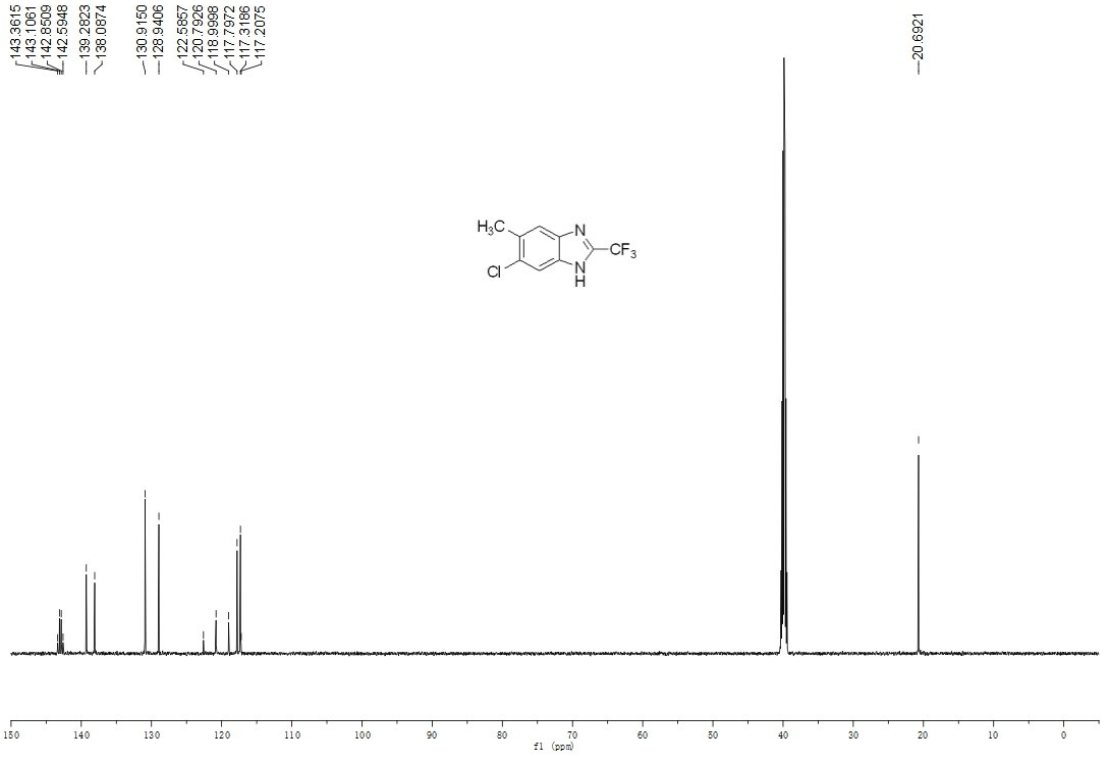

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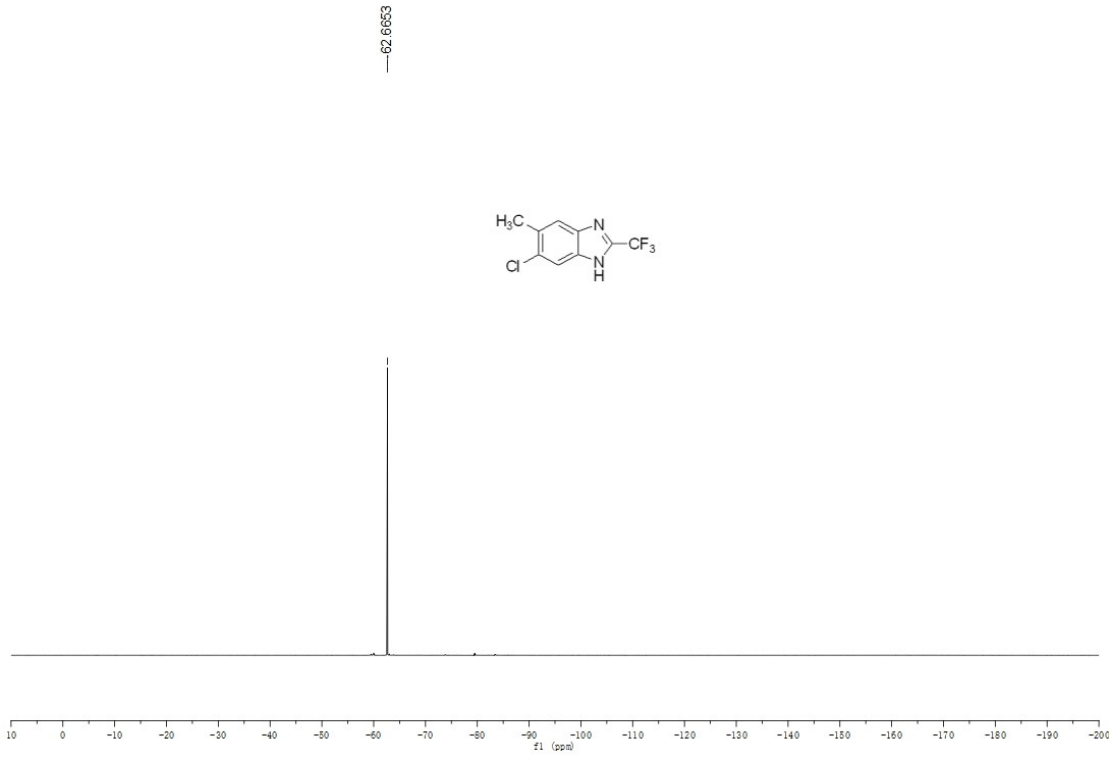
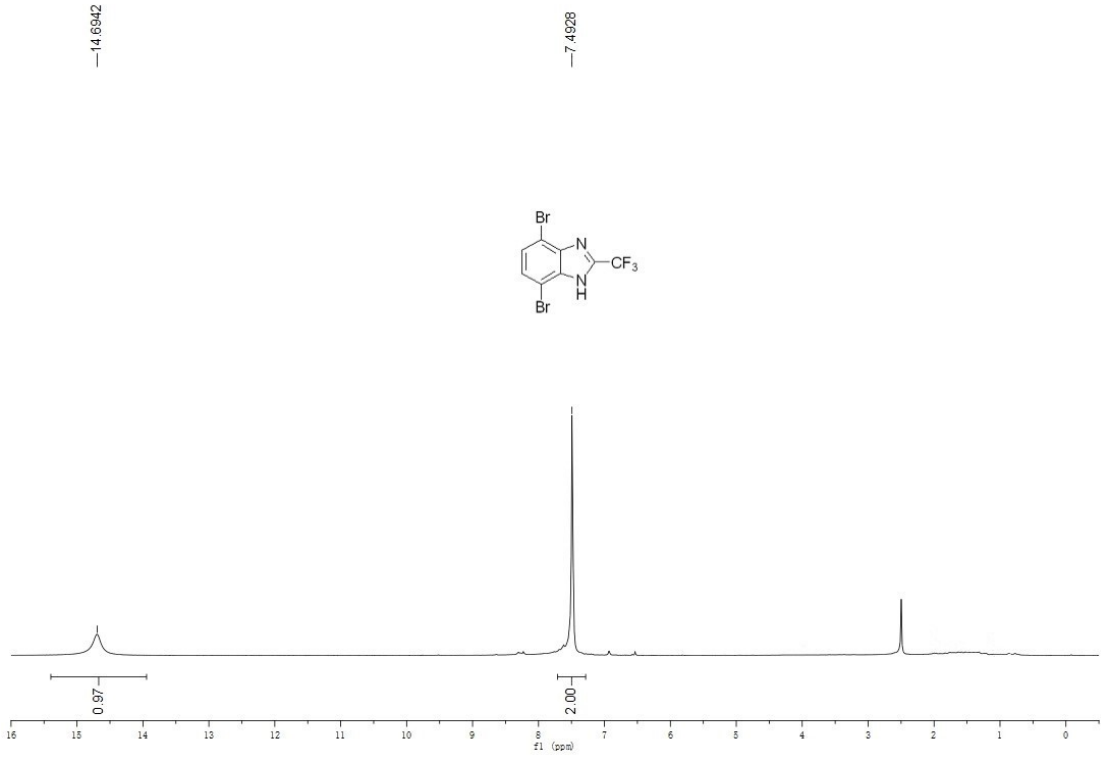


^{1}H NMR of 3ee



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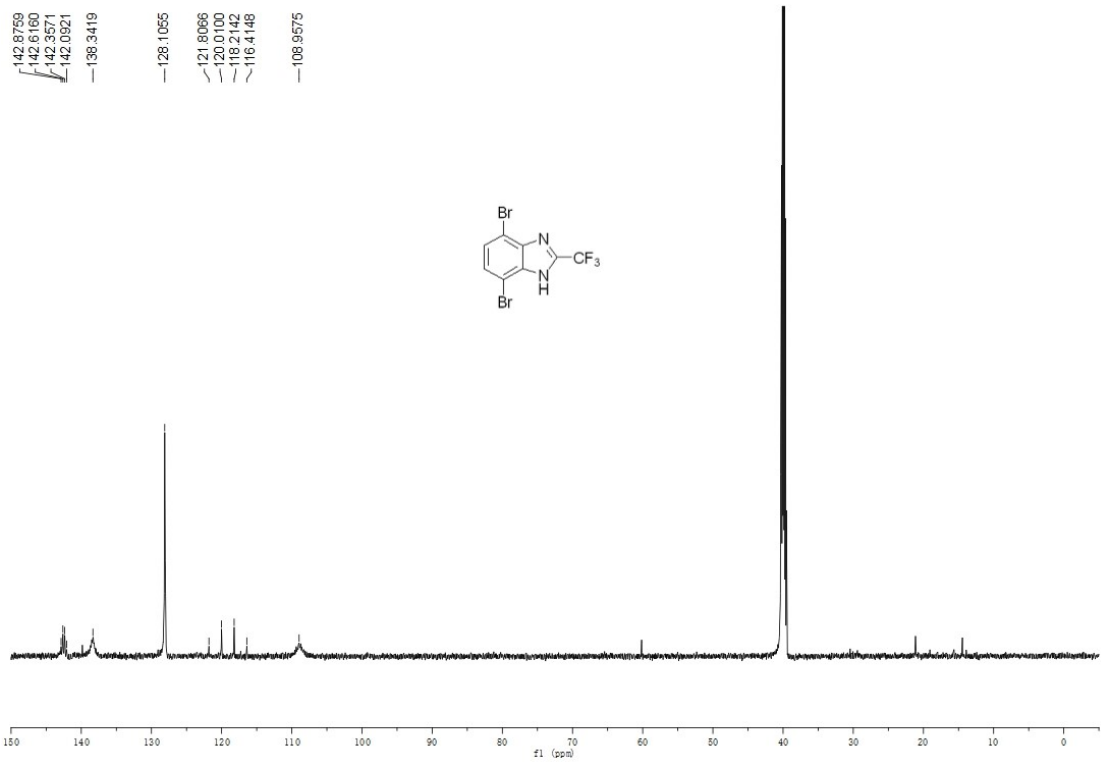

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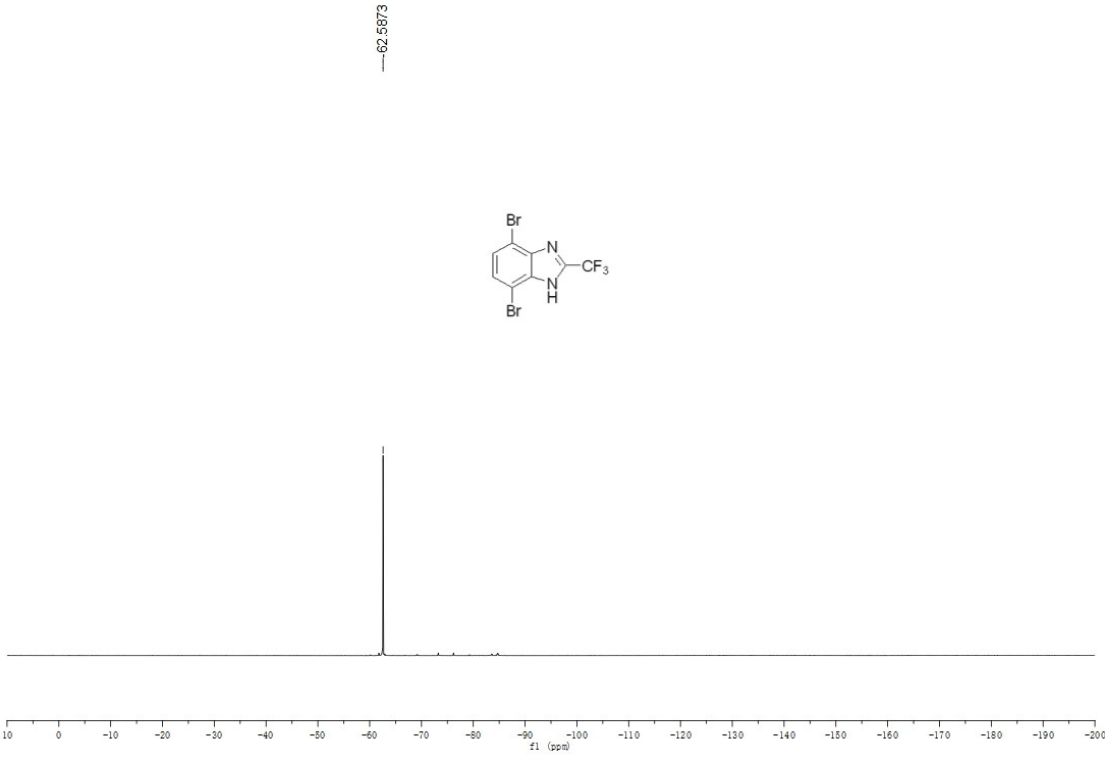

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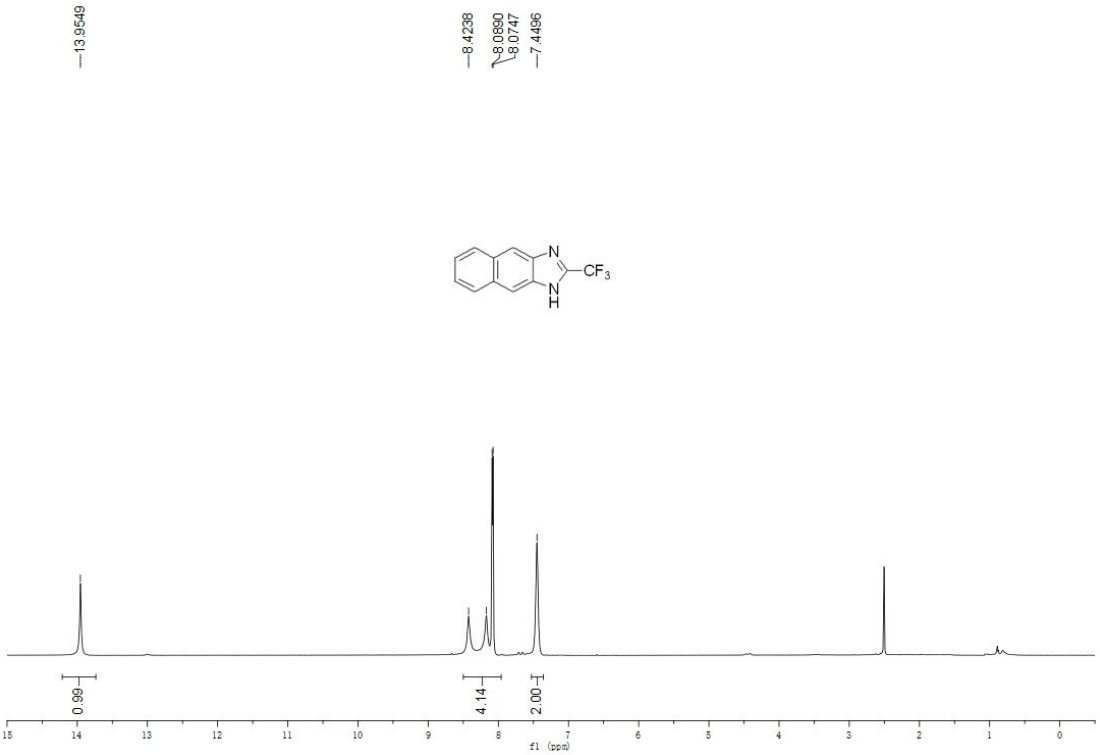

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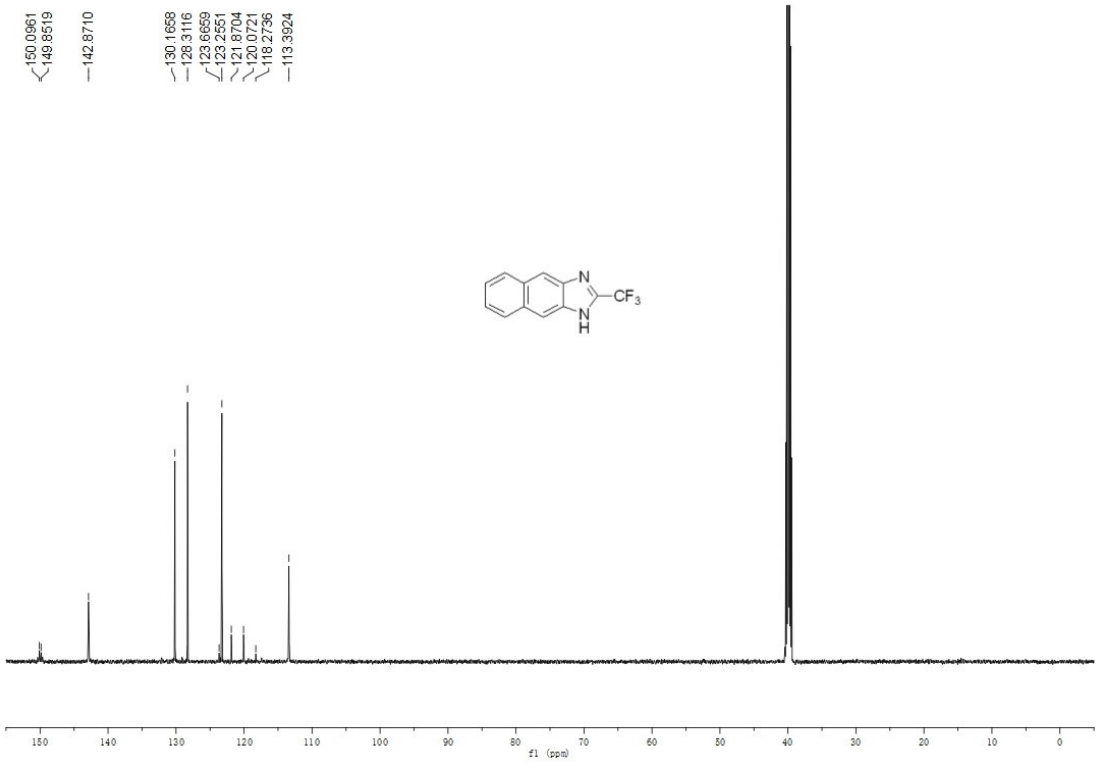

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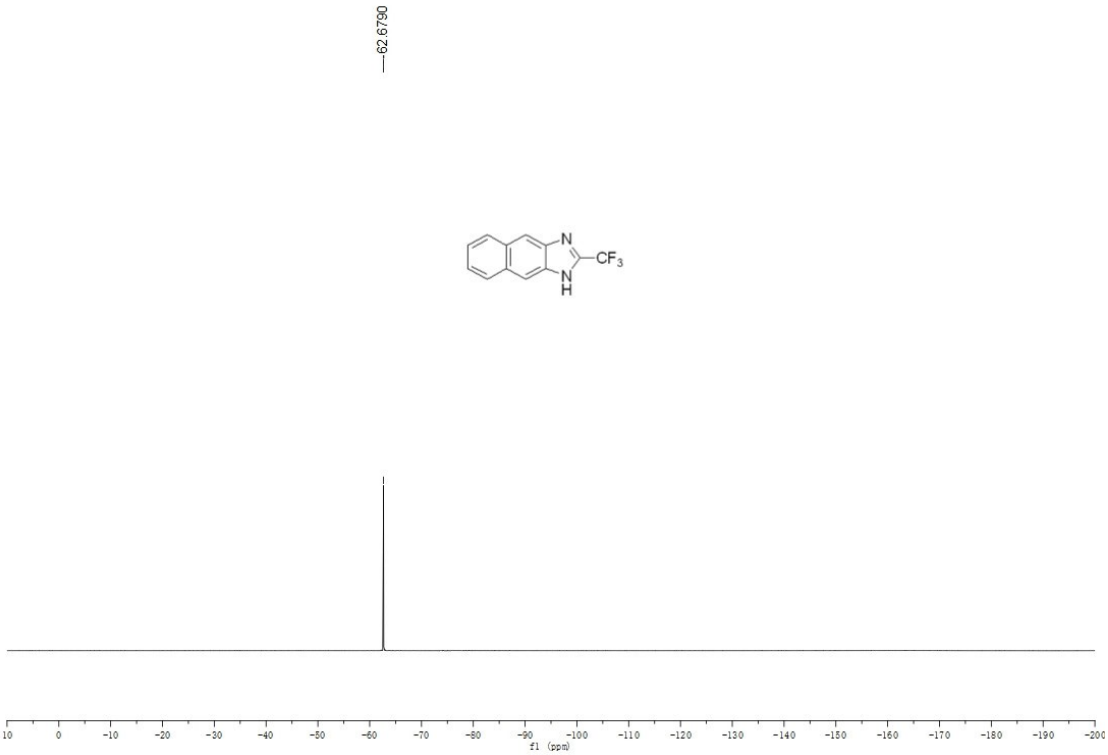

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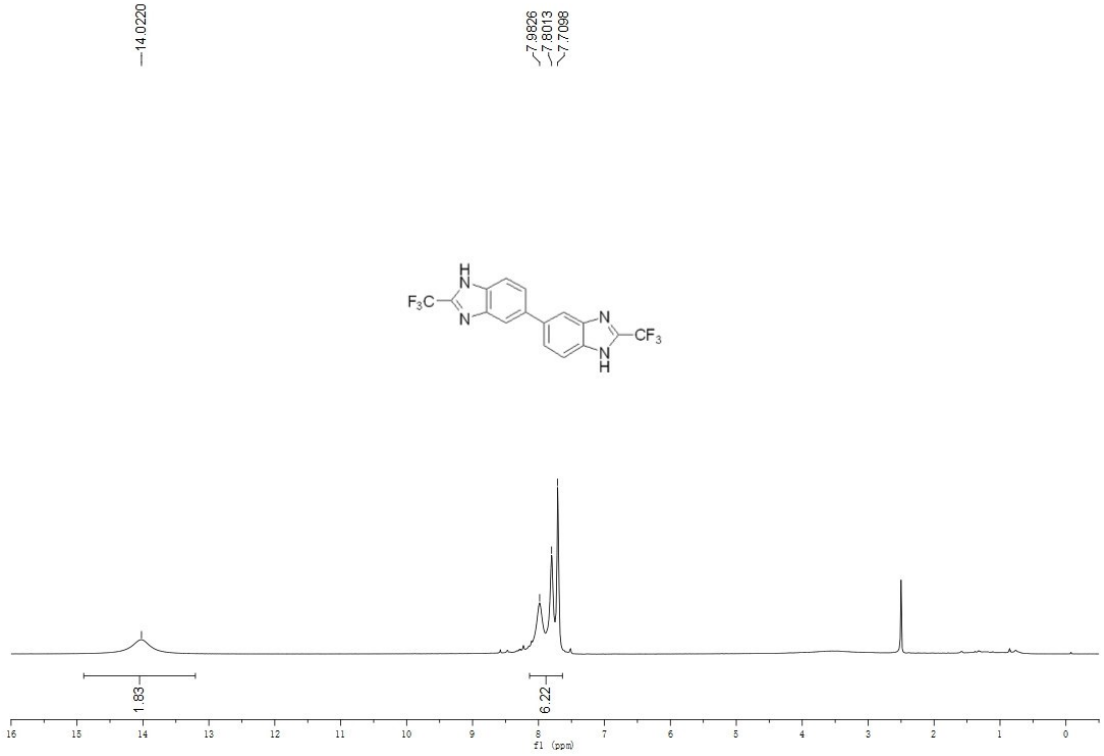

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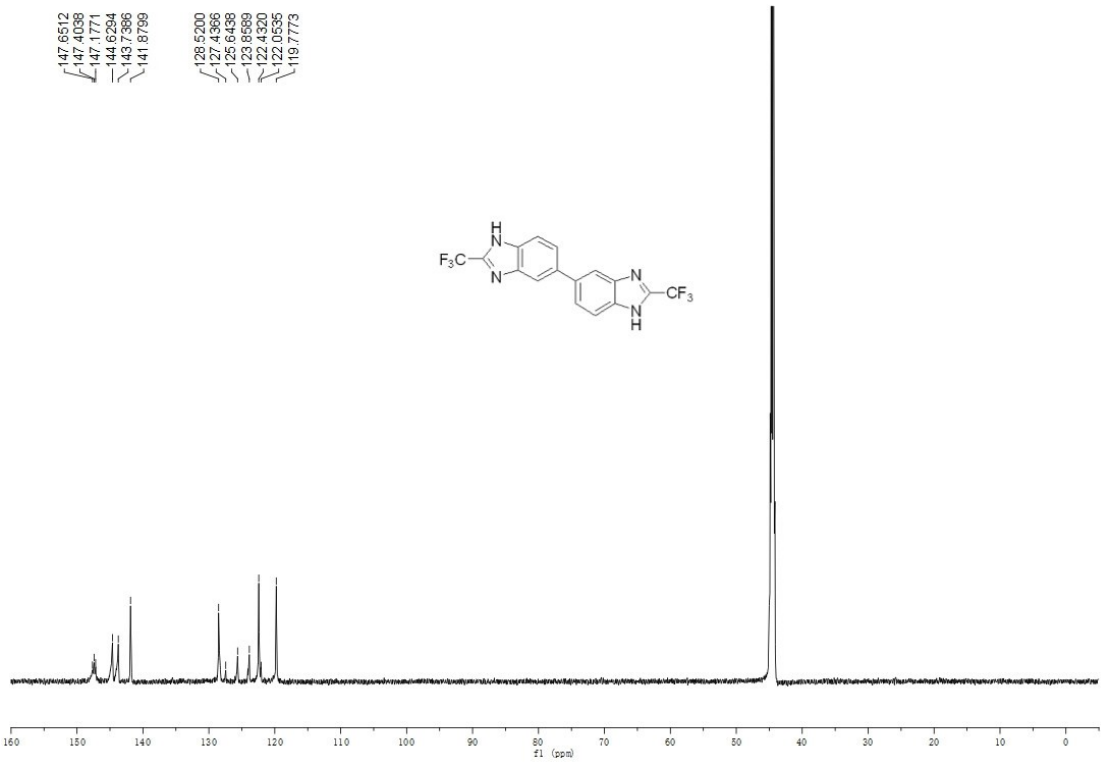

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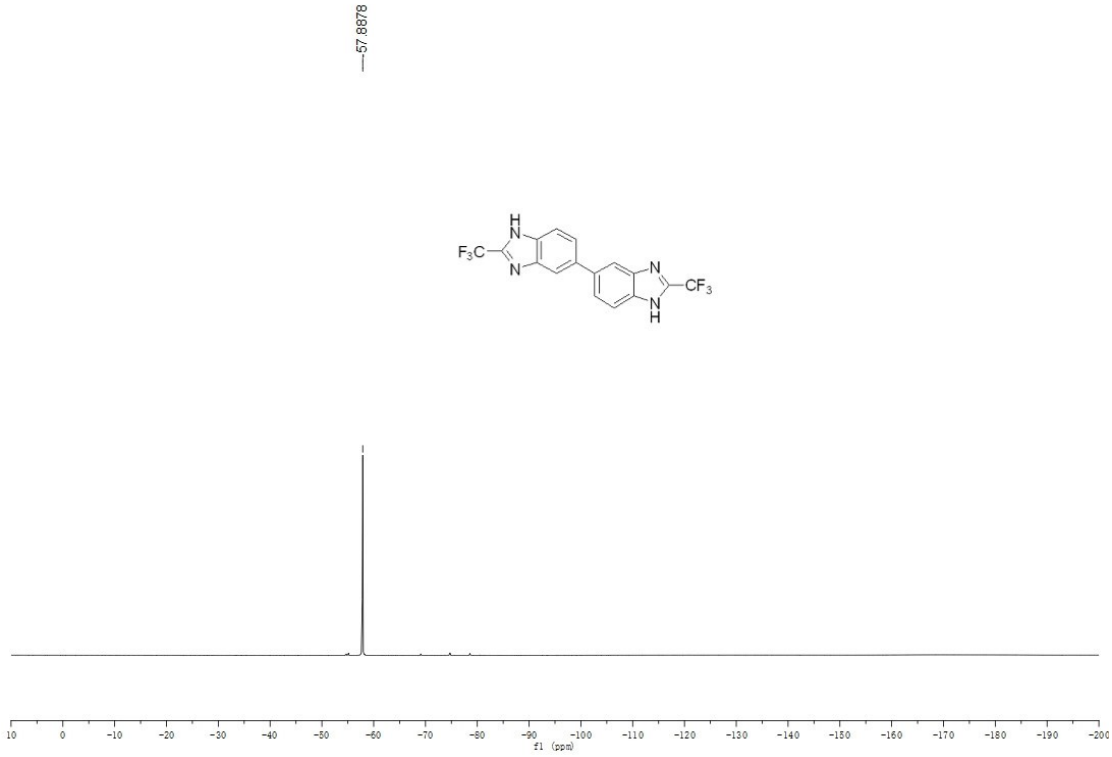

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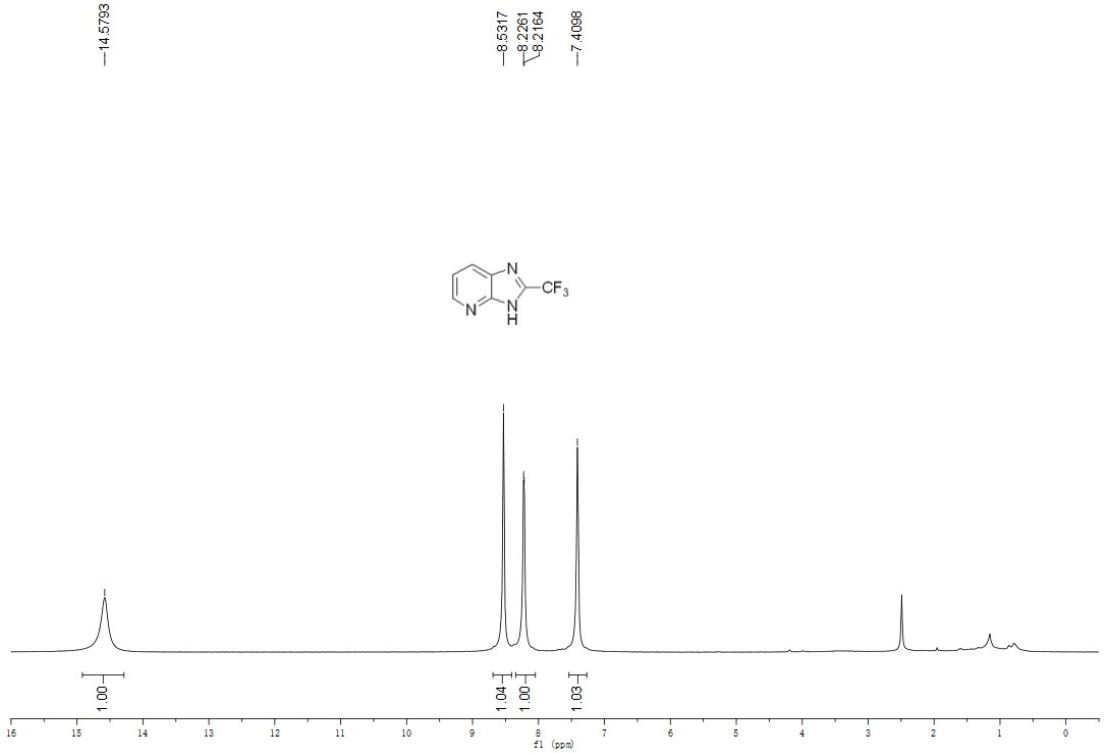

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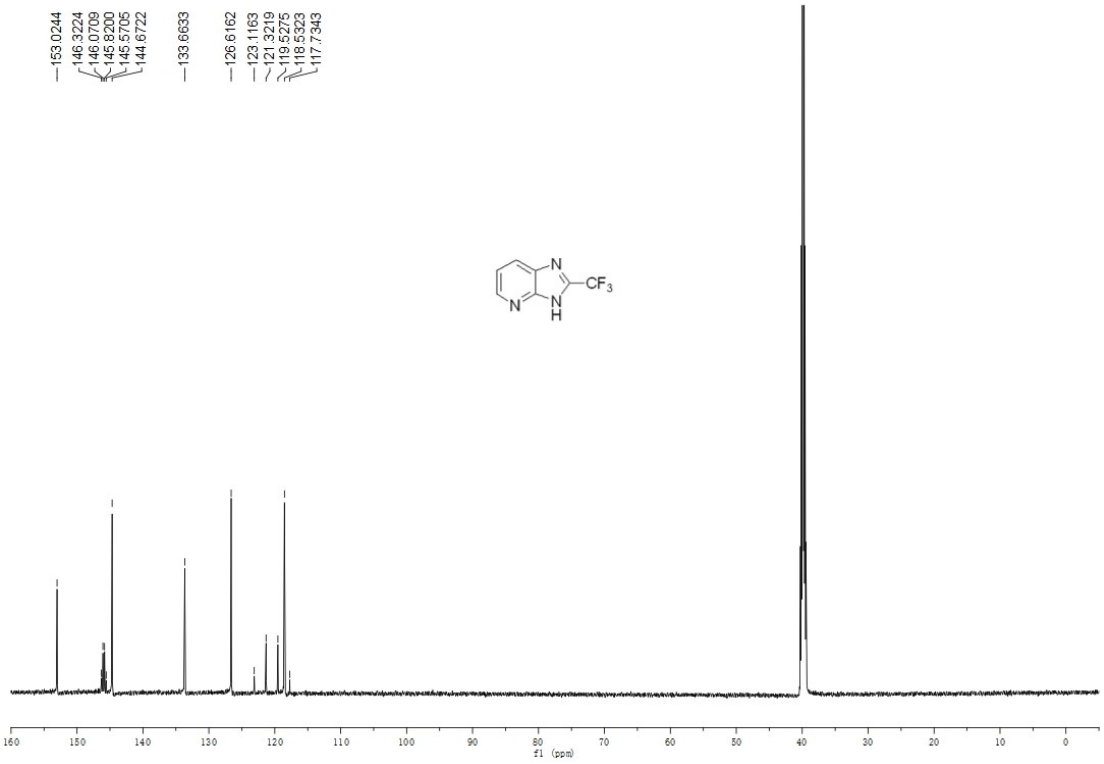

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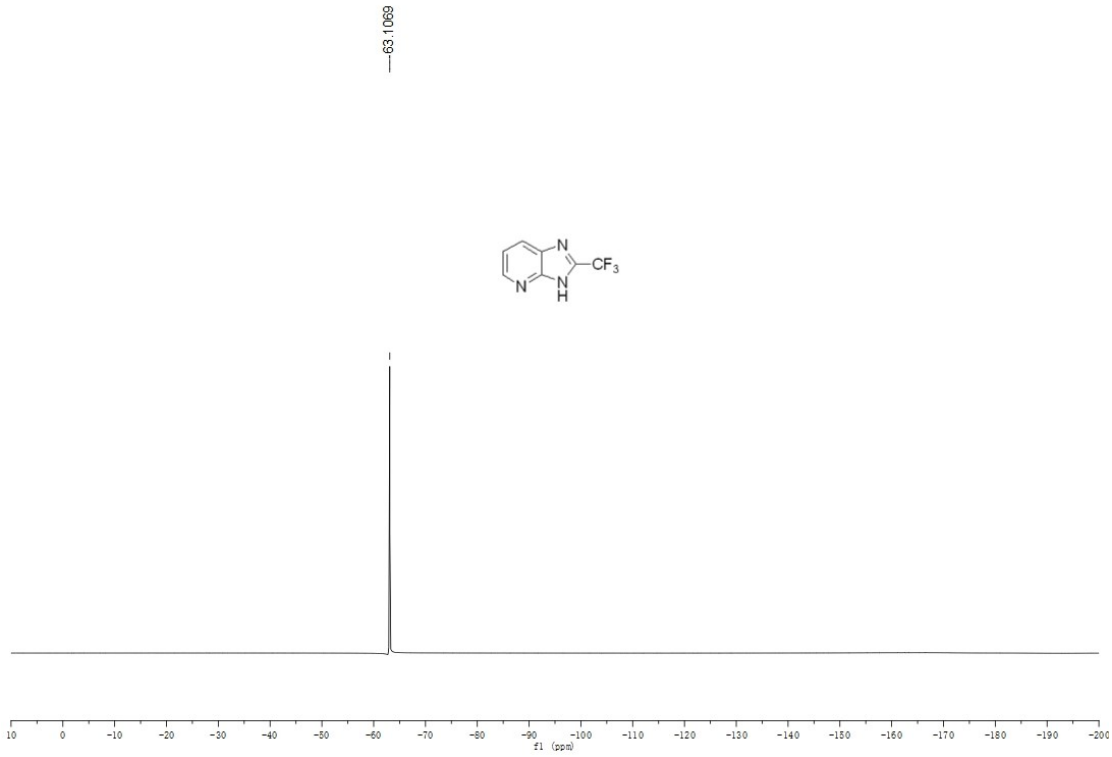

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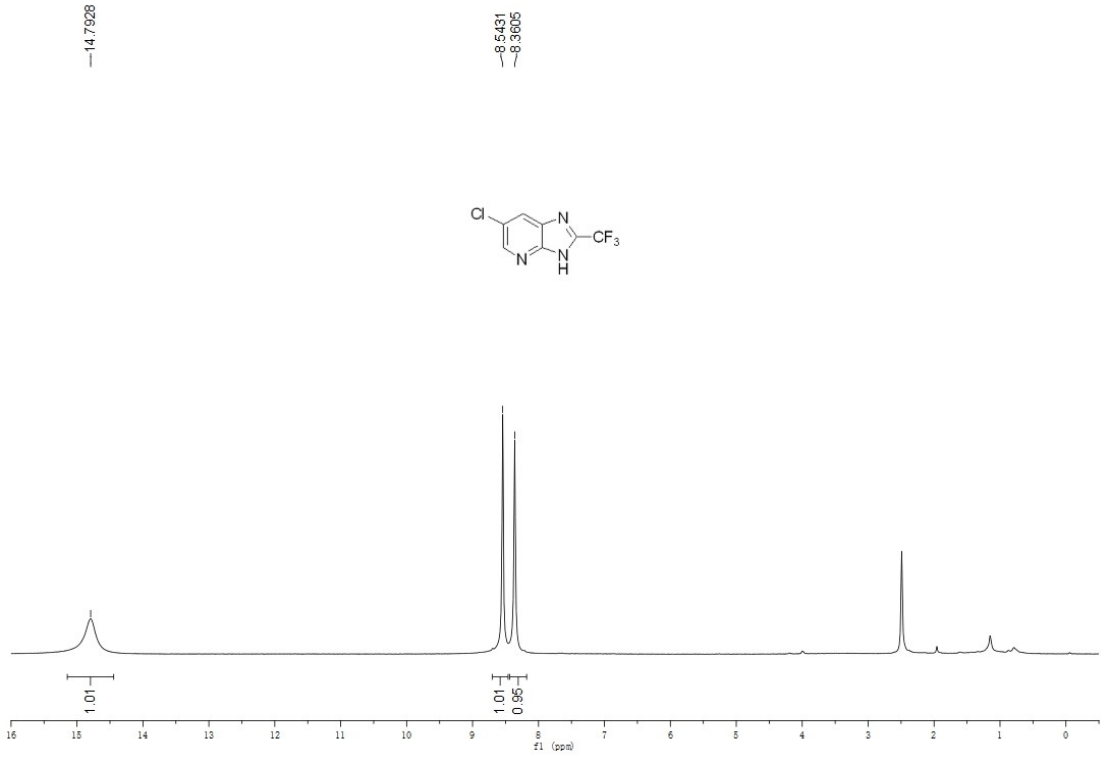

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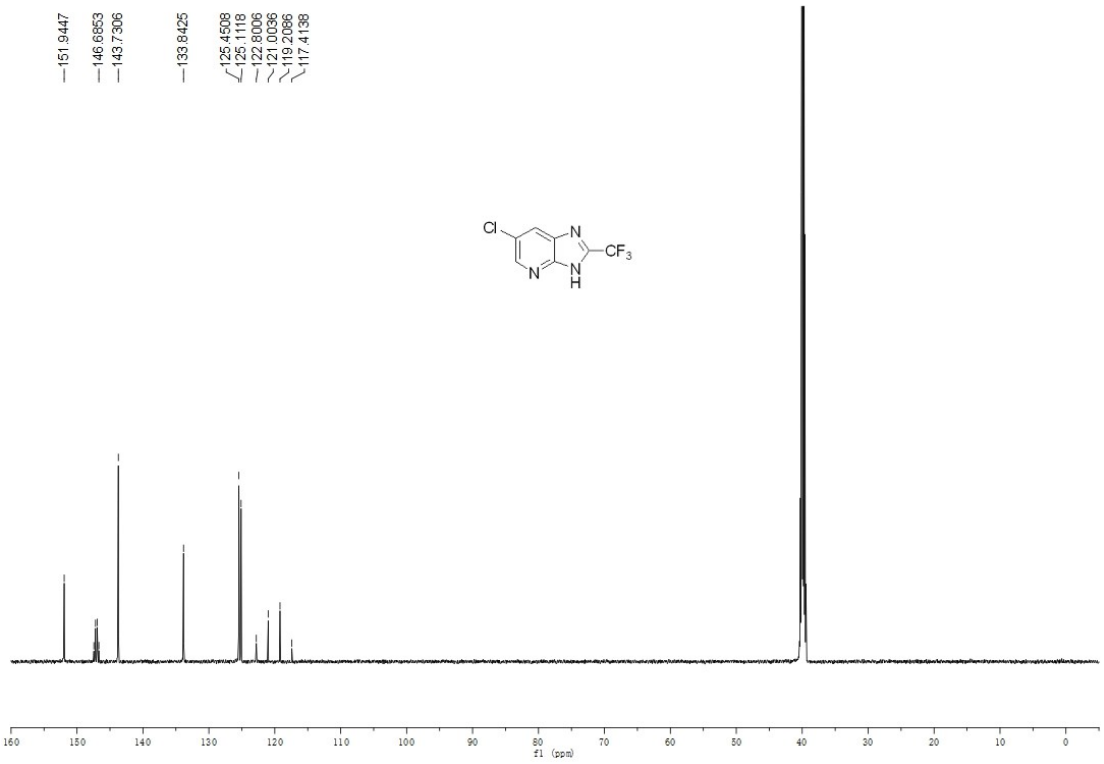

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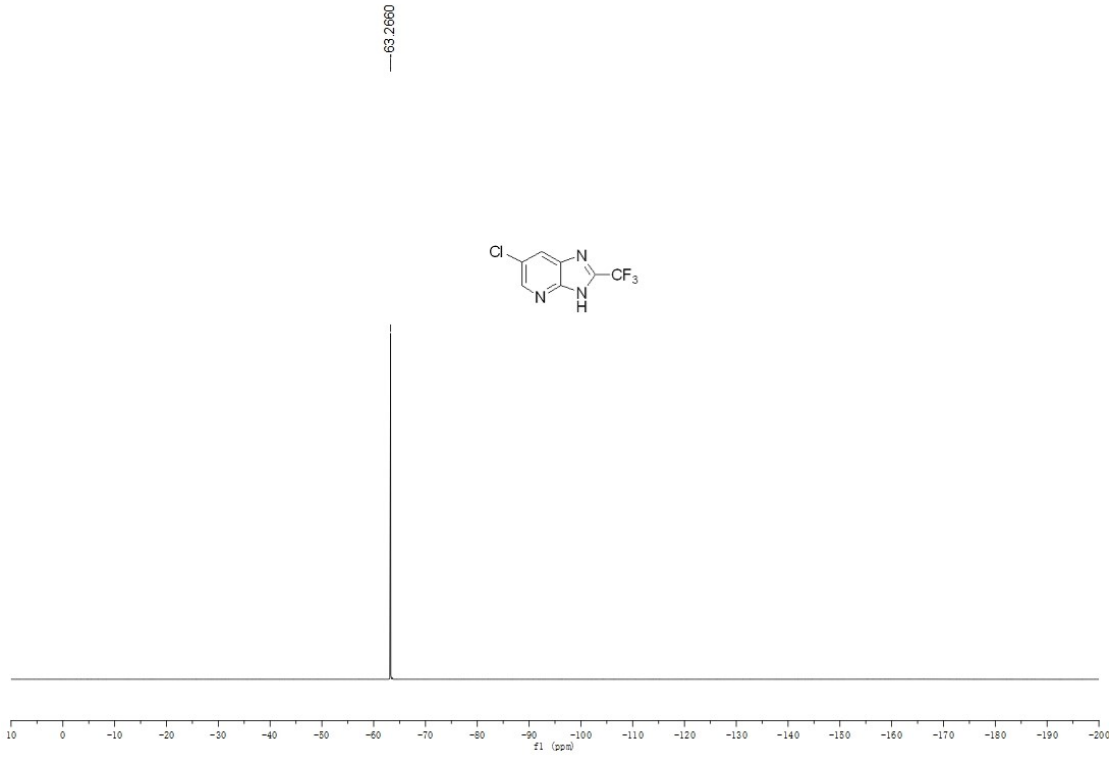
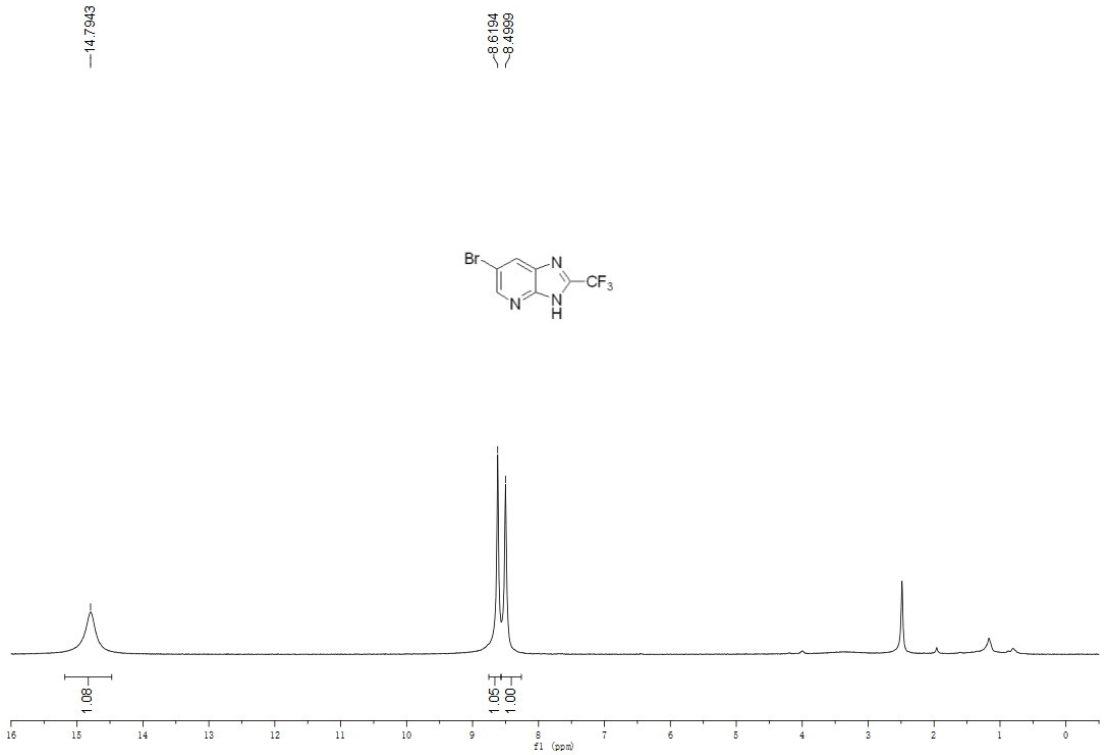


^{1}H NMR of 3jj



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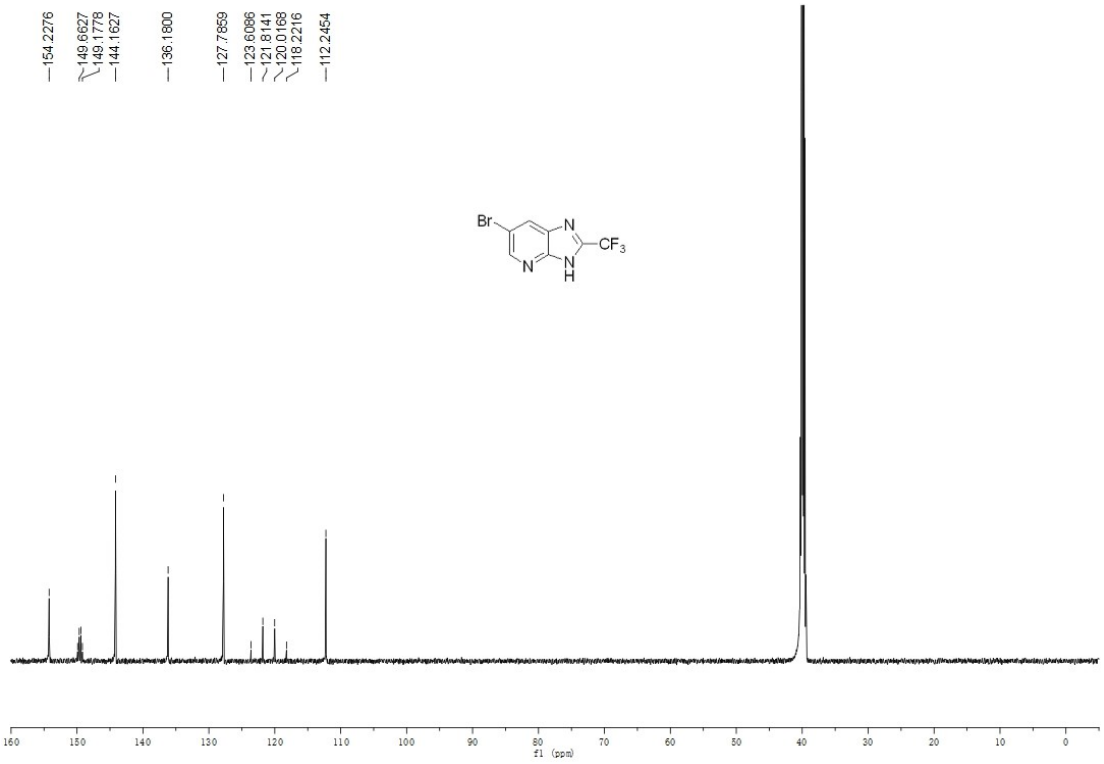

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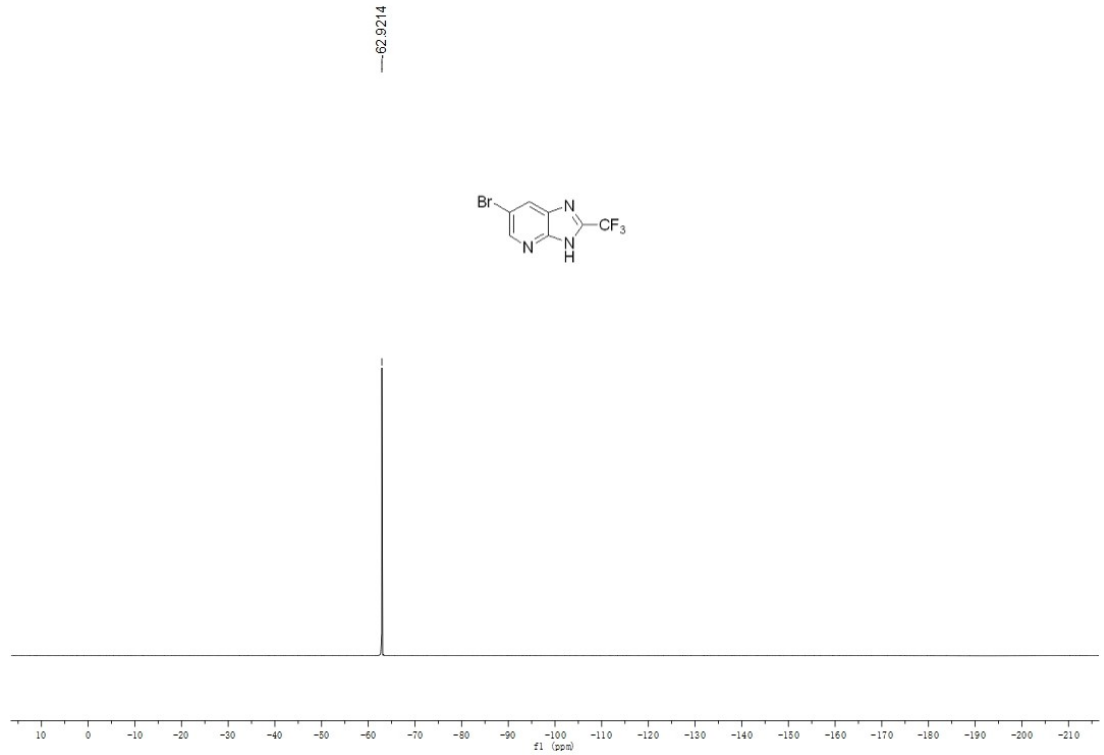

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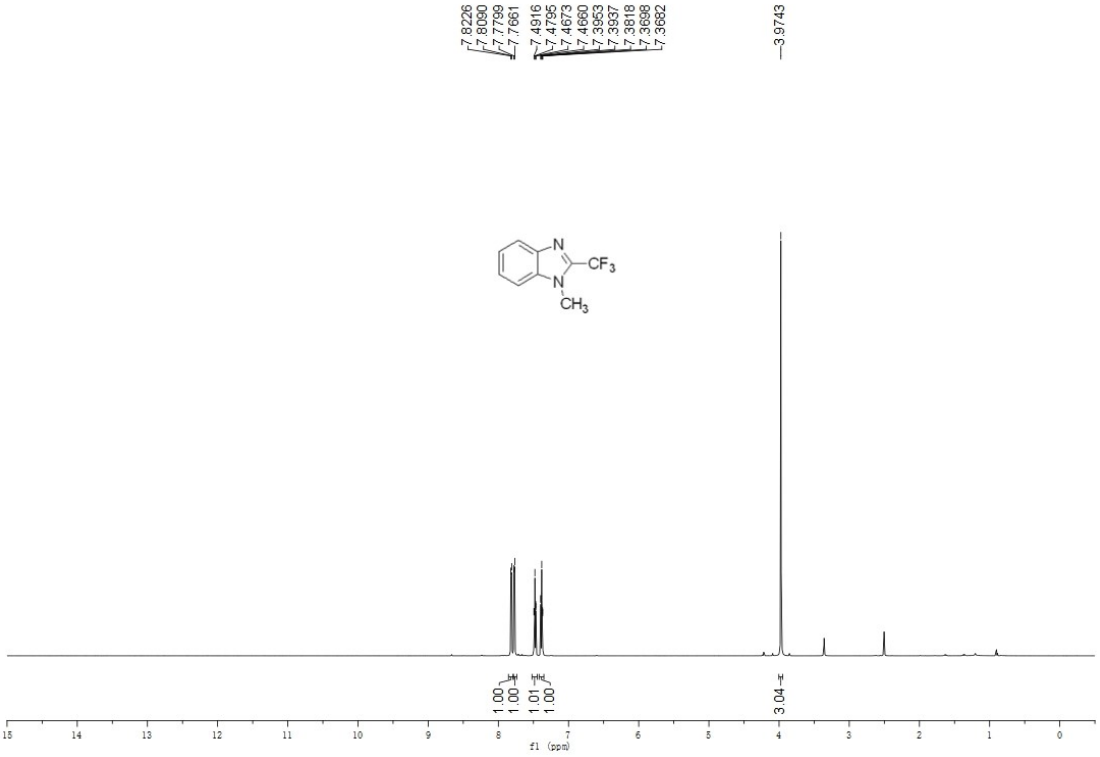

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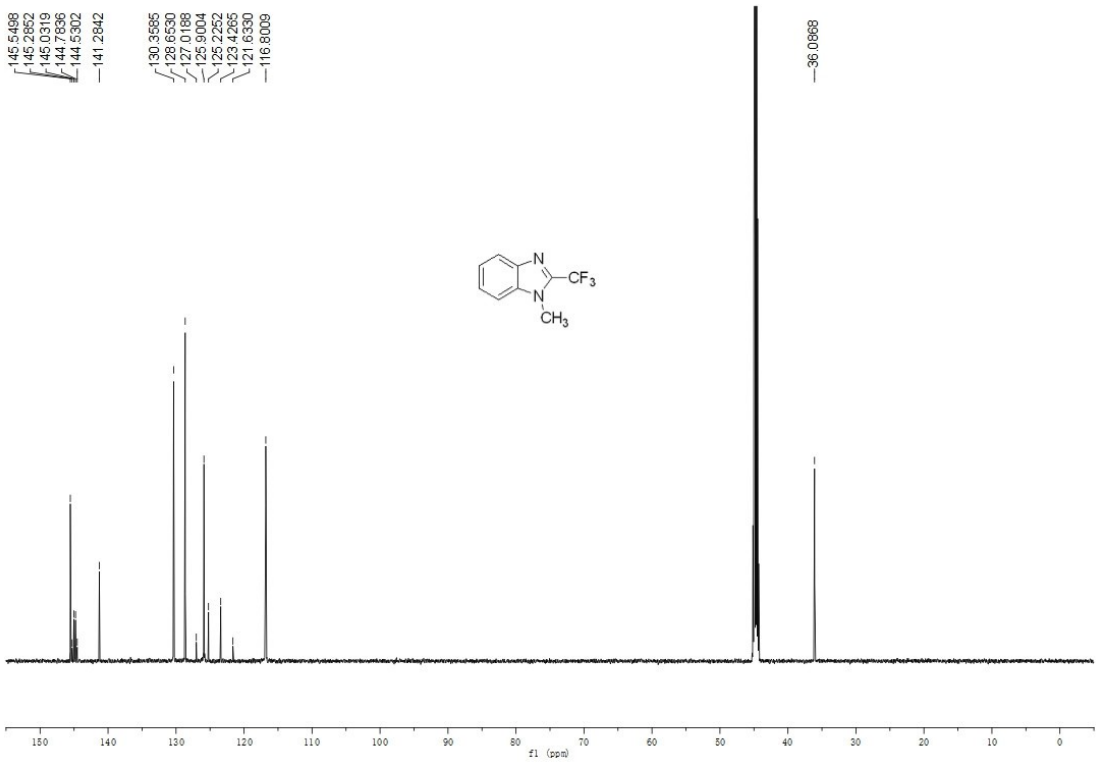

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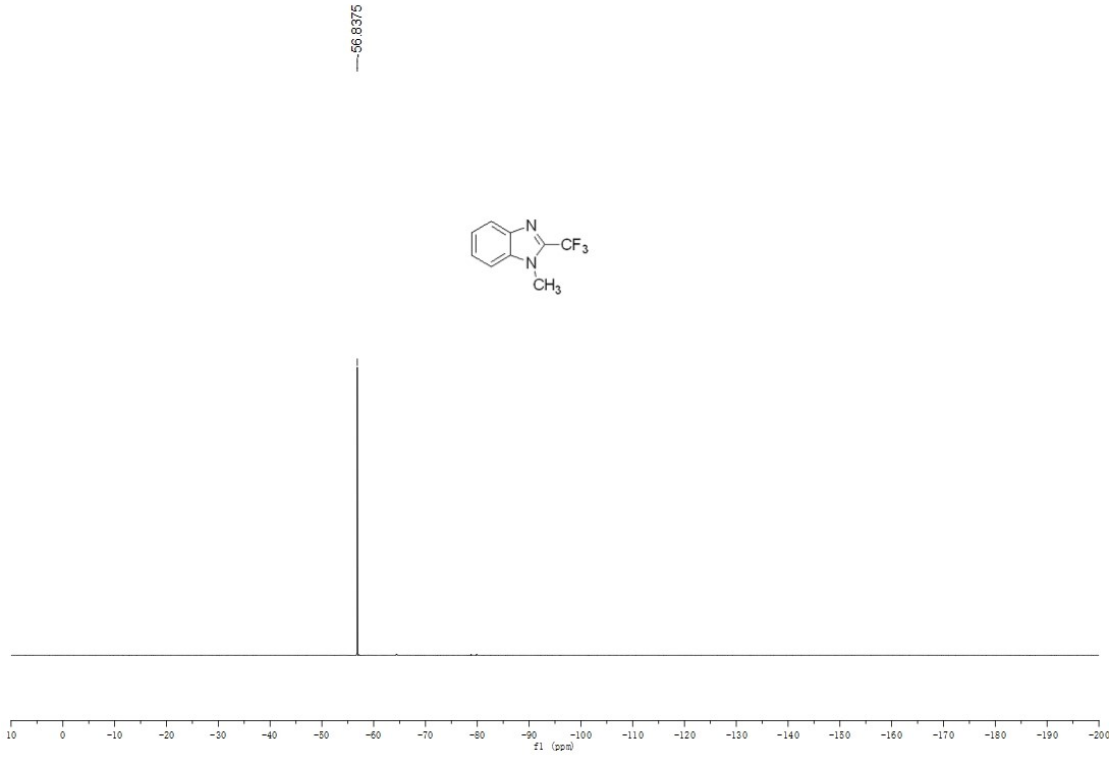

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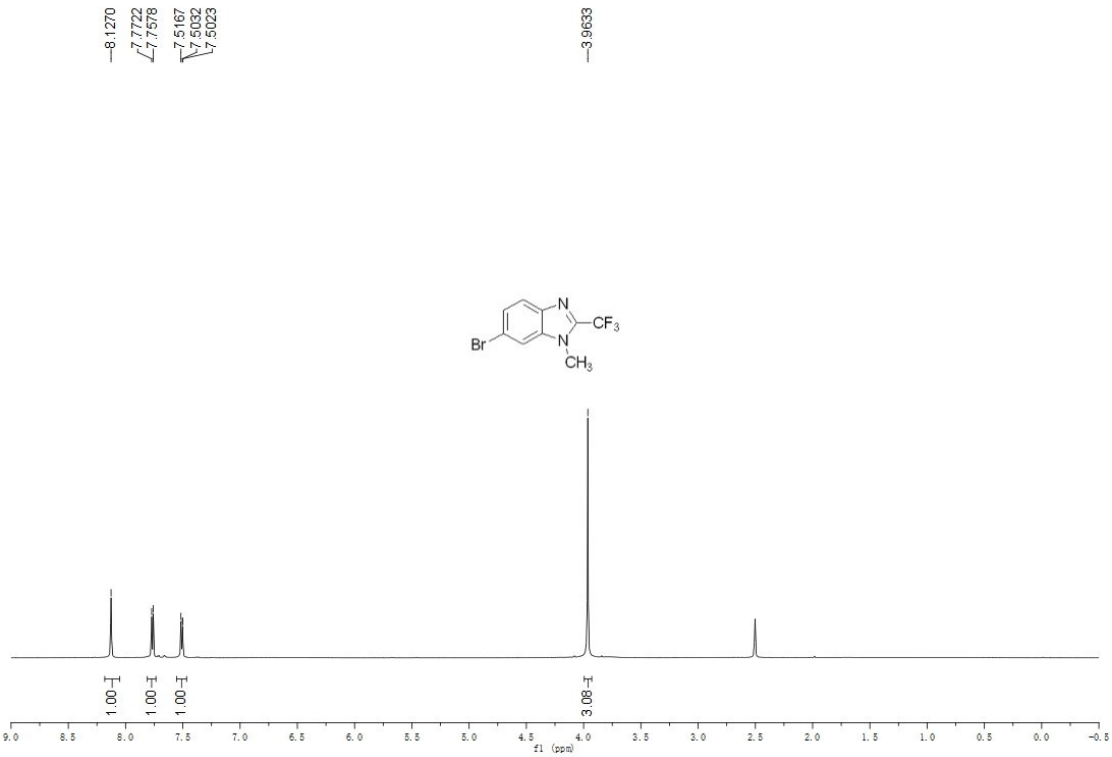

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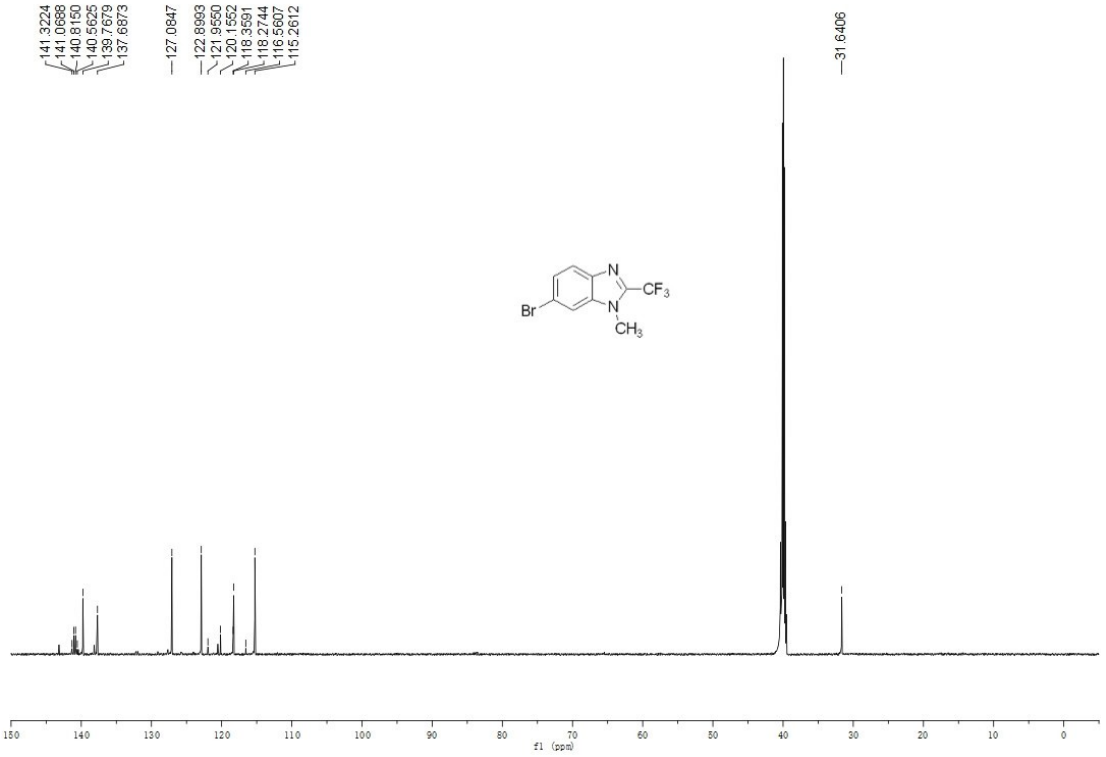

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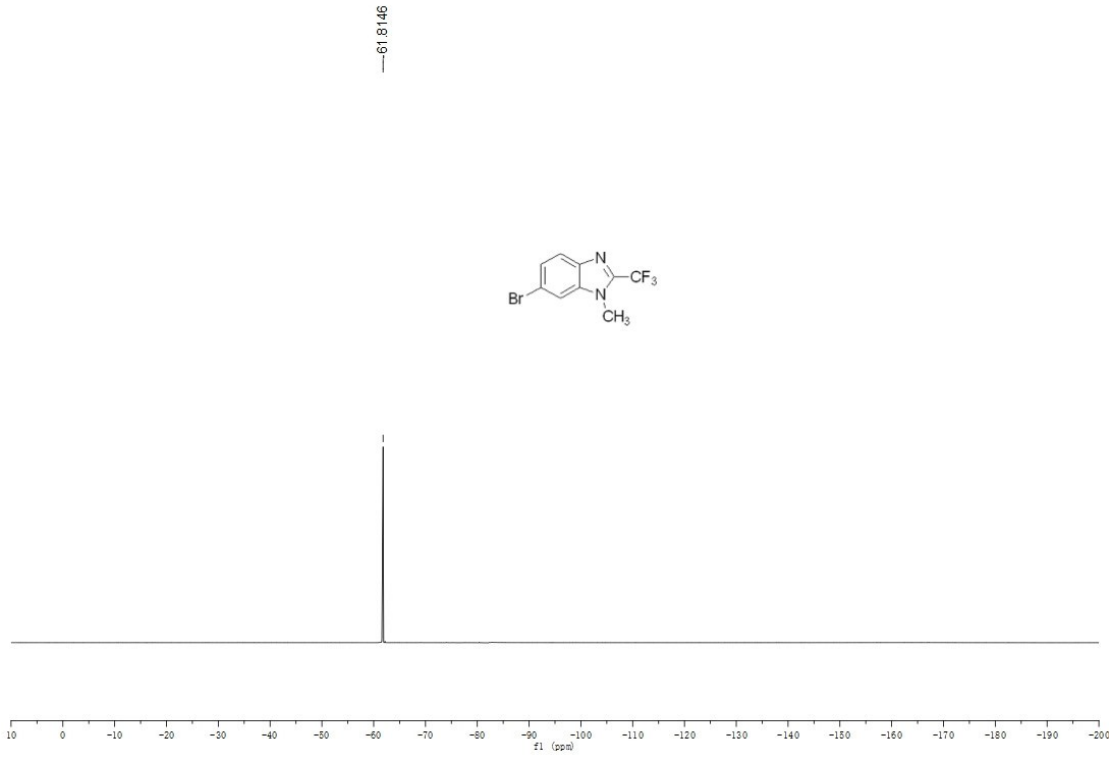

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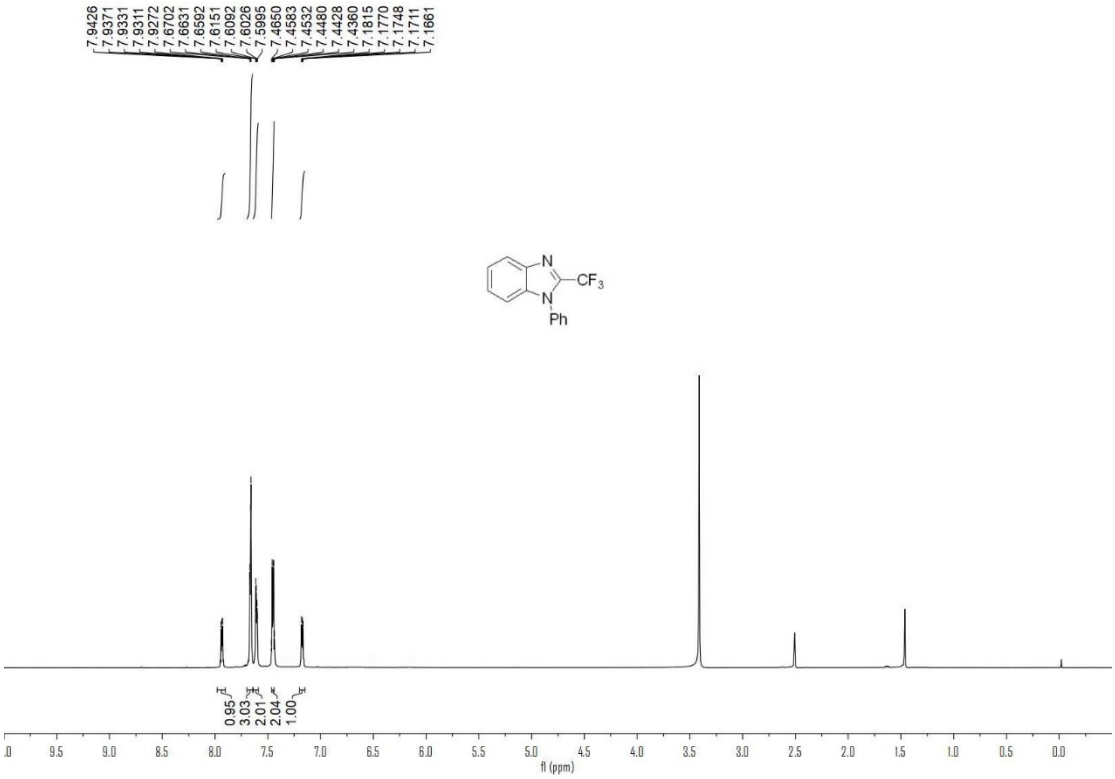

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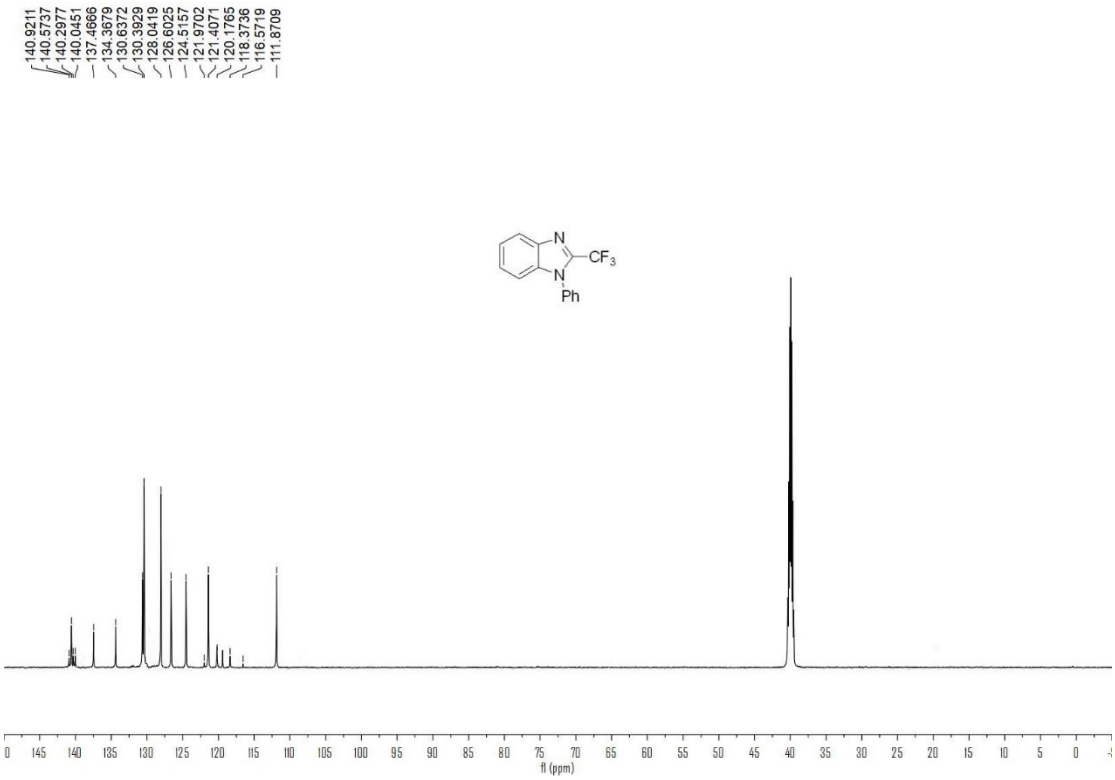

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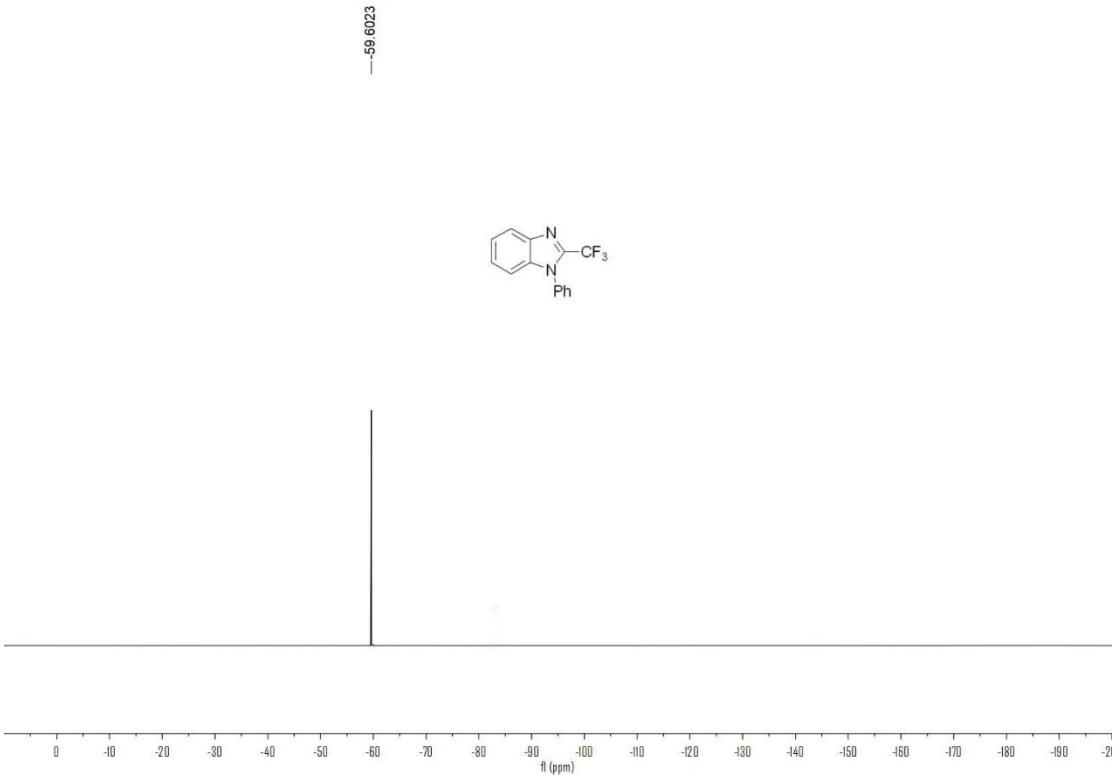

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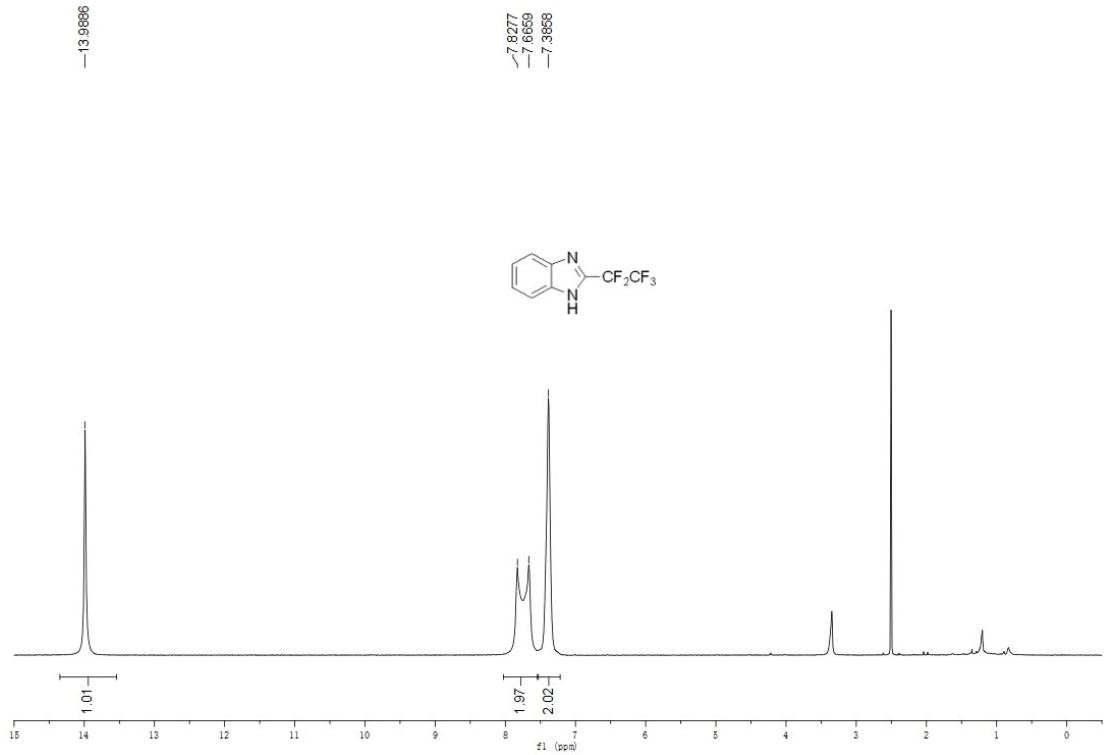

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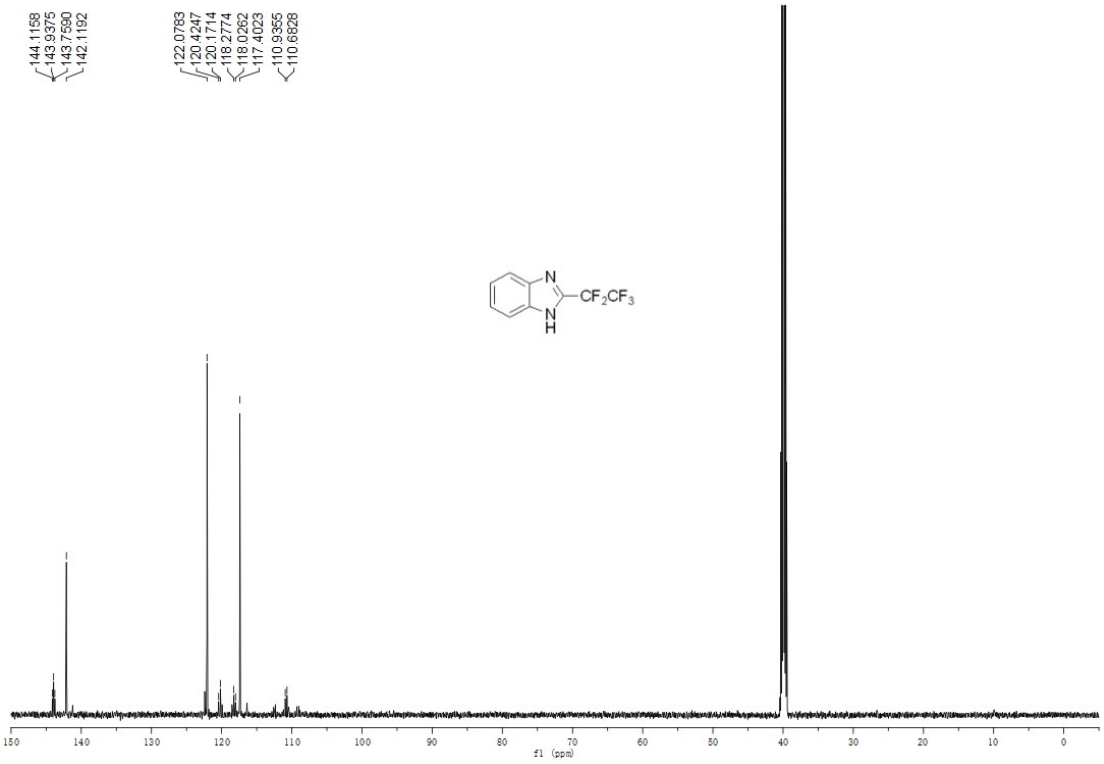

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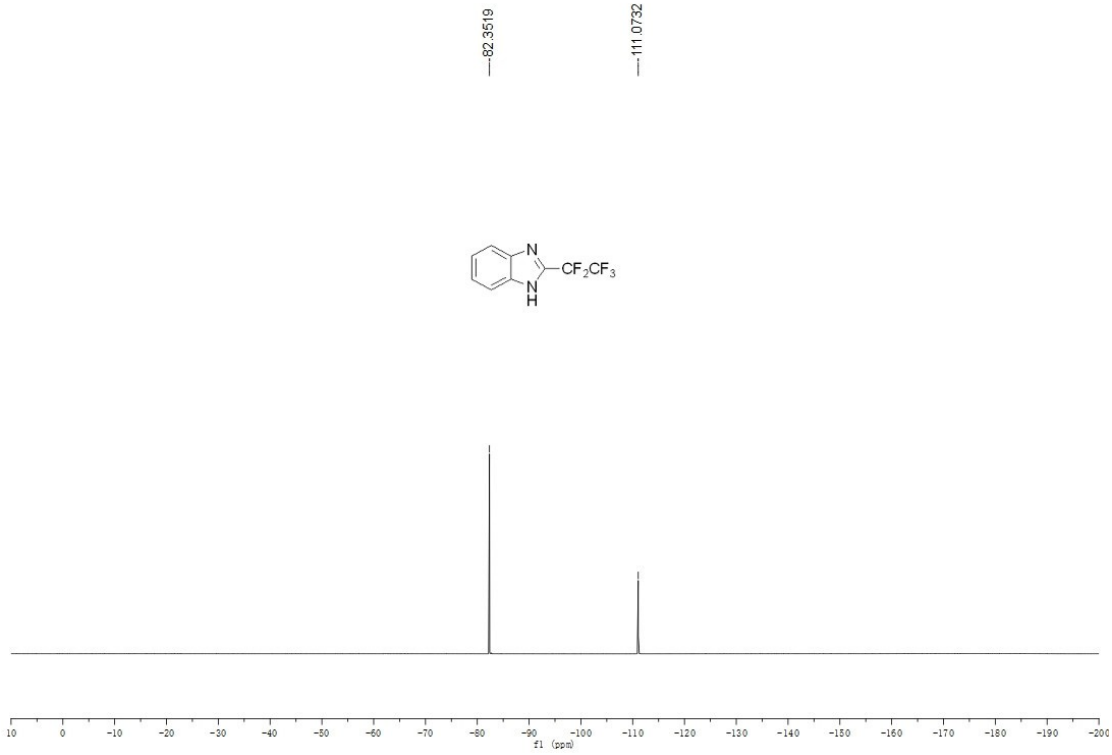

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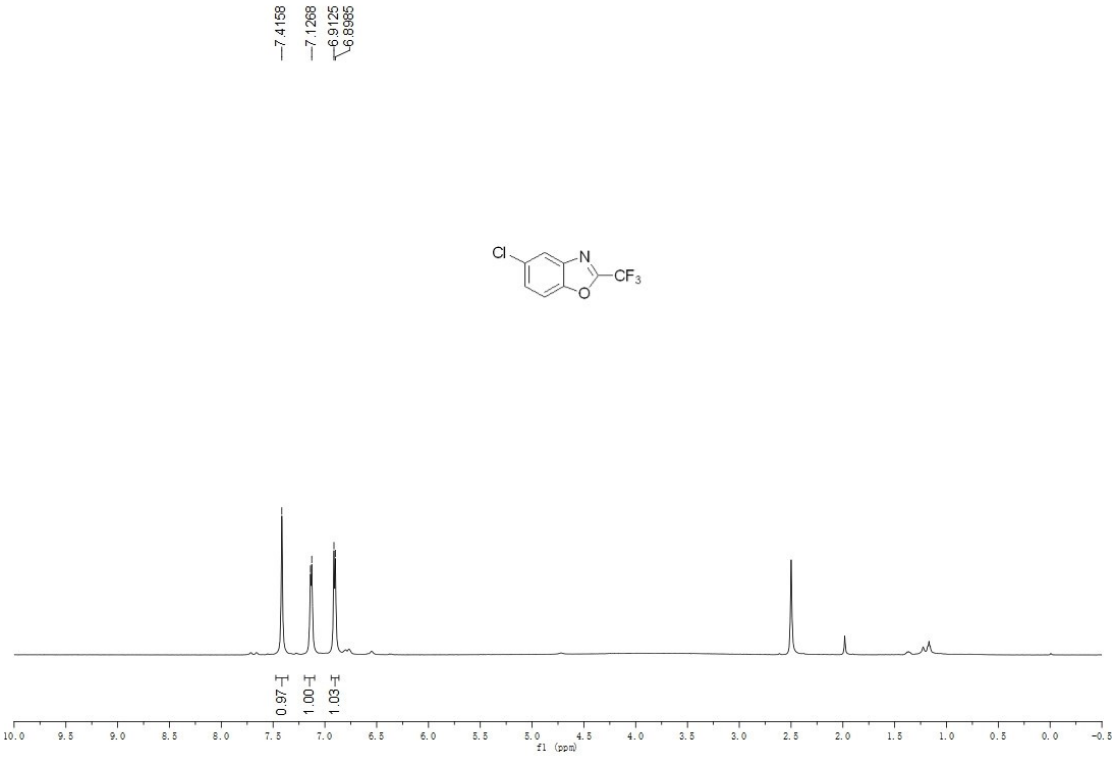

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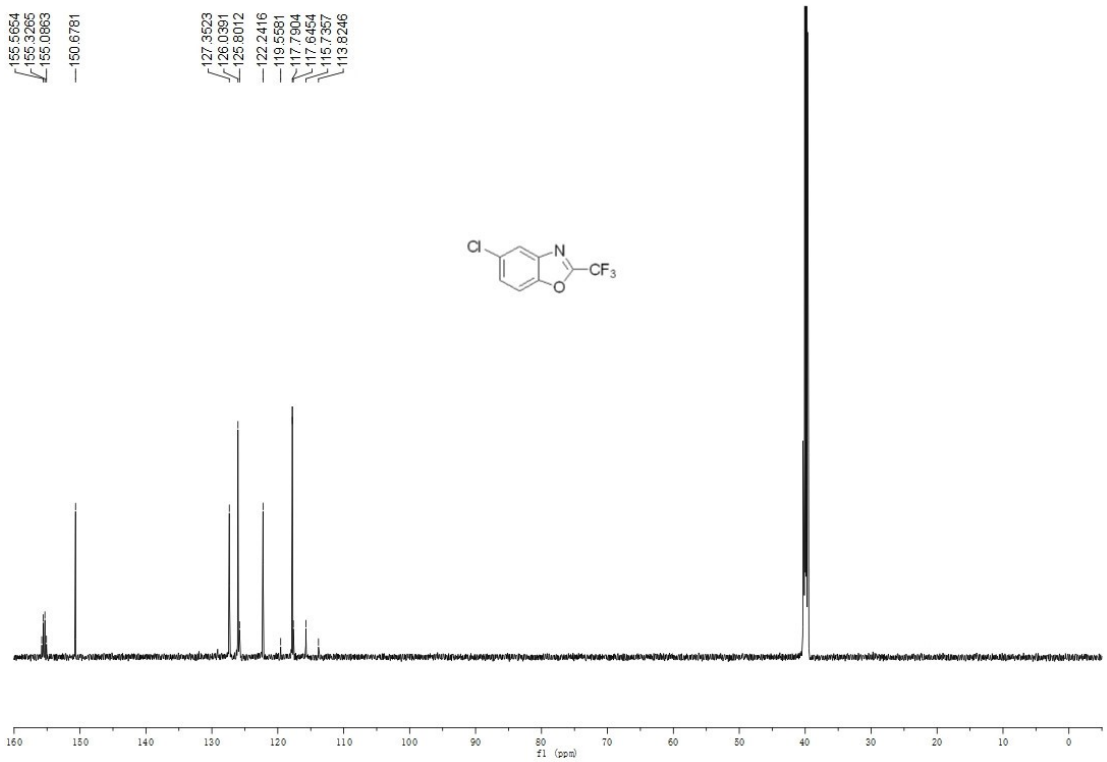
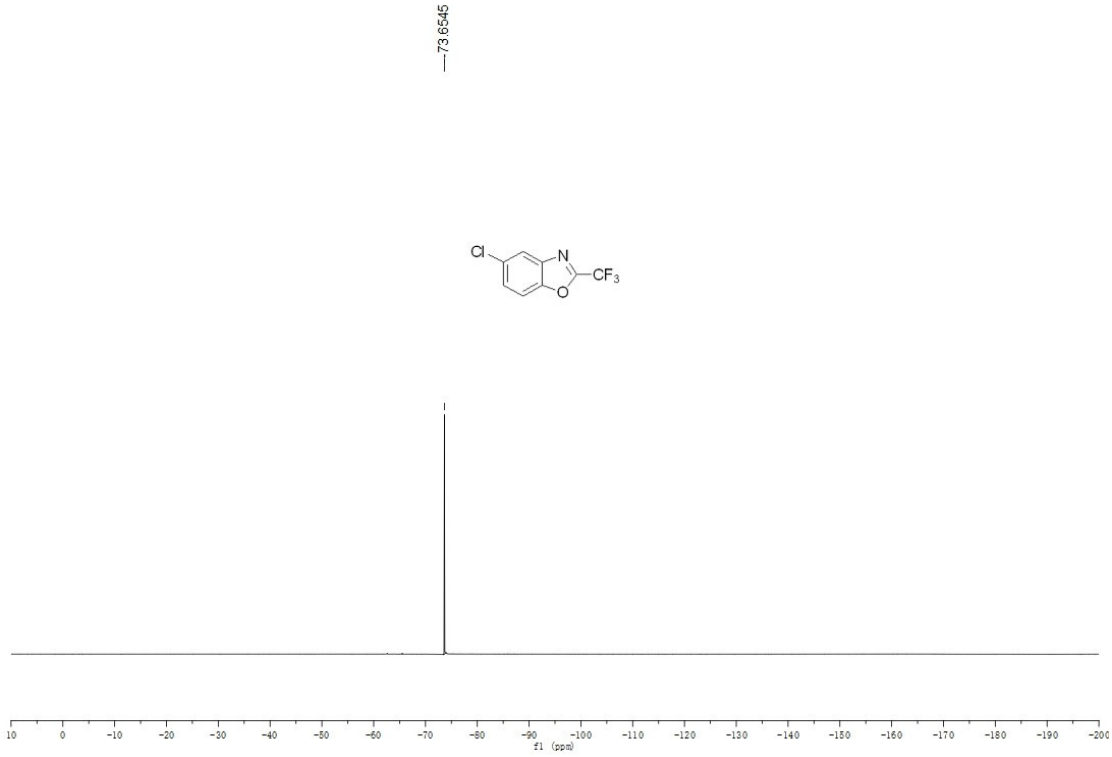
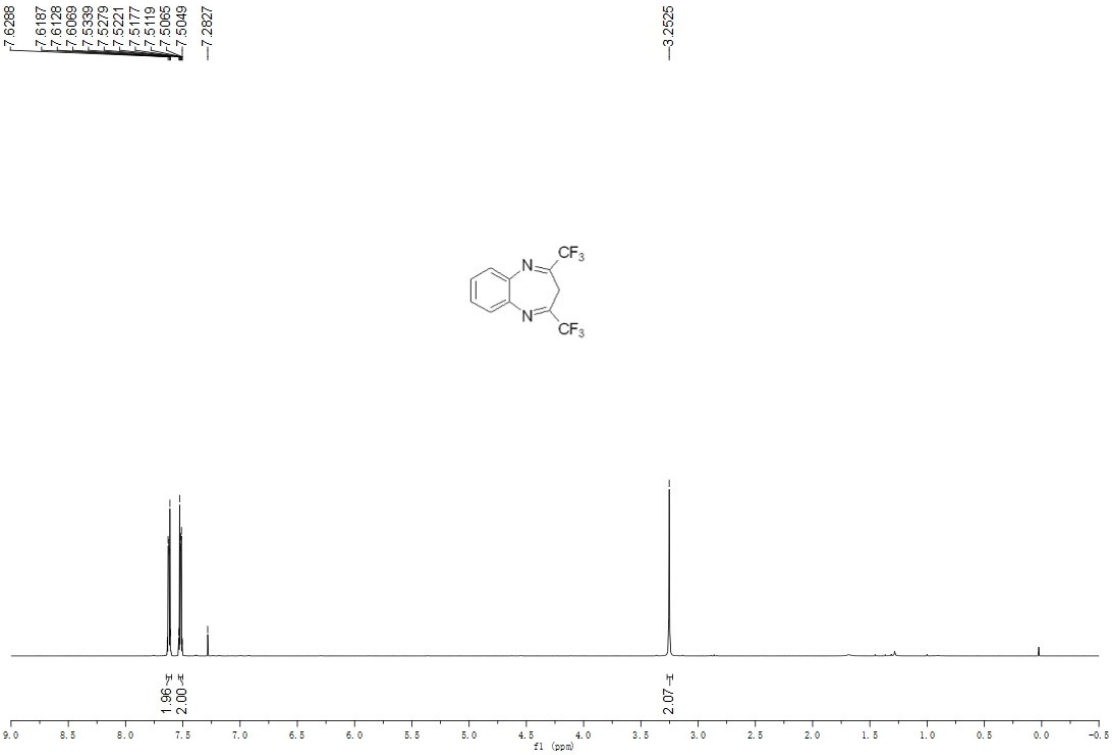


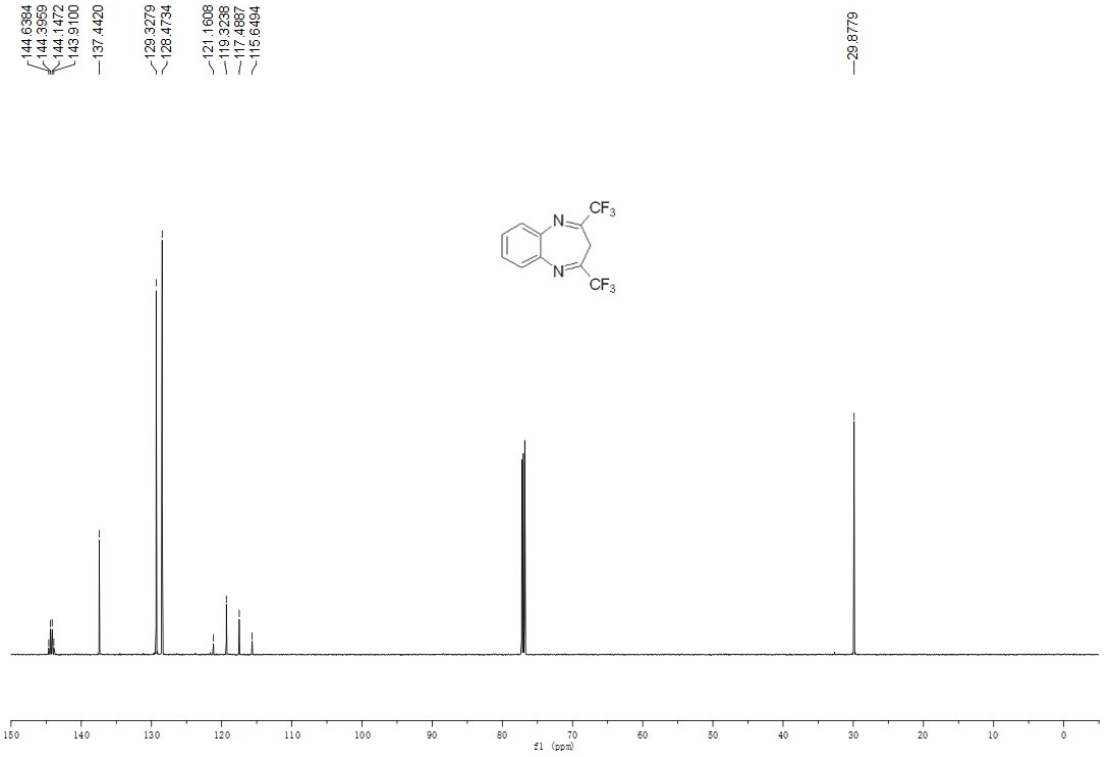
^{19}F NMR of 7



^{1}H NMR of 8



^{13}C NMR of 8



^{19}F NMR of 8