Supporting Information:

Chemo- and Regioselective Ring-opening of Donor-Acceptor Oxiranes with *N*-Heteroaromatics

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Contents

1. General information S2

2. Synthesis of starting materials S3

3. General procedure for the ring-opening reaction S6

4. Optimization of reaction conditions for the asymmetric catalysis.....S8

5. Experimental procedure for the transformations of the product S10

6. The X-ray crystallographic data.....S13

7. Results for deuterium labeling experiment S20

8. Optimization of the reaction conditions.....S21

9. Hammett plot analysis.....S23

10. Kinetic experiments S27

11. Electronic conductivity experiments.....S34

12. Conversion of **4a** to **3a**.....S35

13. Unsuccessful substrates S36

14. Characterization data of new compounds S37

15. NMR spectra S85

16. Crude ^{1}H NMR data.....S145

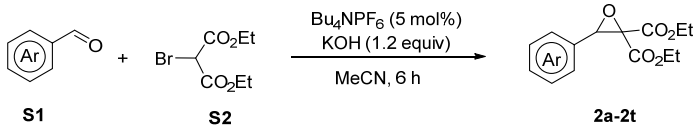
17. Reference S162

1. General information

^{1}H NMR spectra were recorded on Bruker Avance III HD 600 or Avance 400 MHz spectrometer. Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dq = doublet of quartets, dt = doublet of triplets, td = triplet of doublets, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected on Bruker Avance III HD 150 or Avance 100 MHz spectrometer. Enantiomer excesses were determined by chiral HPLC analysis on Chiralcel IF/IA in comparison with the authentic racemates. Chiral HPLC analysis recorded on Thermo scientific Dionex Ultimate 3000 and Agilent Technologies 1260 Infinity. HRMS were recorded on an ABI/Sciex QStar Mass Spectrometer (ESI). Single crystal X-ray crystallography data were obtained on Supernova Atlas S2 CCD detector. IR were detected by Bruker Tensor Ⅱ 400F. The electronic conductivity was determined by SevenCompact S230. Other solvents used for work-up and purification purposes were purchased in technical grade quality and distilled by rotary evaporator before use.

2. Synthesis of starting materials

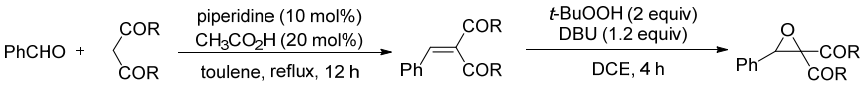
1) Synthesis of oxiranes:[1,2]



S1 **S2** **2a-2t**

The solution of aldehyde (1.0 mmol), diethyl 2-bromomalonate (239.1 mg, 1.0 mmol, 1.0 equiv), Bu_4NPF_6 (19.4 mg, 0.05 mmol, 5 mol%) in CH_3CN (3 mL) was stirred for 30 min. Then the powdered KOH (67.3 mg, 1.2 mmol, 1.2 equiv) was added. After the mixture was stirred at ambient temperature for 6 h, the solvent was removed under reduced pressure. Subsequently, water (5 mL) and Et_2O (10 mL) were added into the residue respectively. The organic layer was separated and the aqueous layer was extracted with Et_2O (3×5 mL). The combined organic layers were washed with water (3×5 mL) and dried over anhydrous Mg_2SO_4. After filtration and removal of the solvents, the resulted residue was purified by silica gel column chromatography using Pet/EtOAc system (Pet/EtOAc, 100/1 to 50/1, v/v) to afford oxiranes **2a-2t** (50-88% yields).

2) Synthesis of dimethyl 3-phenyloxirane-2,2-dicarboxylate and aryl oxiranyl diketones:[3]

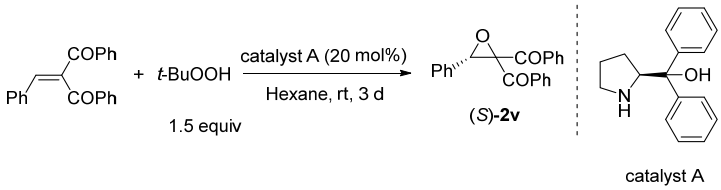


R = OMe, Ph

S3 **S4** **S5** **2u, 2v**

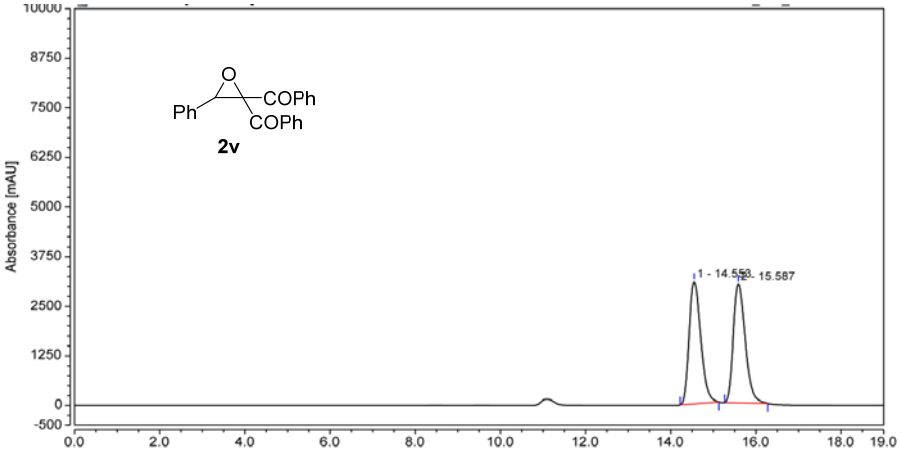
To a round bottom flask connected to a Dean-Stark apparatus, benzaldehyde (11.0 mmol), **S4** (10.0 mmol), acetic acid glacial (2.0 mmol), pyrrole (1.0 mmol) and toluene (20 mL) were added respectively. The mixture was heated at reflux until the starting materials were consumed as indicated by TLC analysis. After being cooled down to room temperature, the reaction mixture was concentrated under reduced pressure. The crude product was purified by silica gel chromatography to afford alkene **S5** in 85% and 86% yields, respectively. To a well-stirred solution of alkene (11 mmol) in DCE which was cooled in an ice bath were added *t*-BuOOH (2 equiv) and DBU (1.2 equiv). The reaction mixture was further stirred for 4 h. After removing the solvent DCE, the crude product was purified by silica gel column chromatography using Pet/EtOAc system (Pet/EtOAc, 100/1 to 10/1, v/v) and dried under vacuum, the pure products were obtained **2u** and **2v** (50 and 82% yields).

3) Synthesis of chiral oxirane 2v.[4]



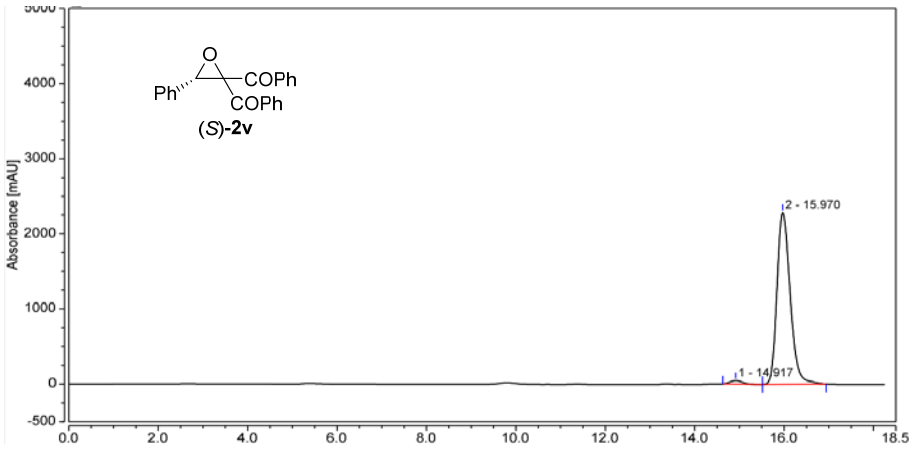
2v, 86% yield and 75% ee. By recrystallized from cyclohexane and ethyl acetate at 0 °C, its optical purity was enriched to 96% ee. The ee value was determined by HPLC, CHIRALCEL IF, n-hexane/2-propanol = 90/10, flow rate = 0.6 mL/min, λ = 256 nm, retention time: 14.92 min (minor), 15.97 min (major).

Figure S1. HPLC spectra of racemic **2v**



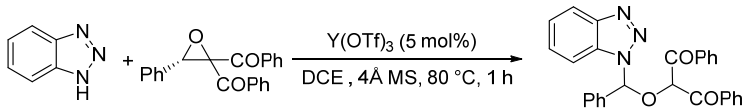
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	14.553	976.949	3081.642	50.04	50.67
2	15.587	975.533	2999.740	49.96	49.33
Total:		**1952.482**	**6081.383**	**100.00**	**100.00**

HPLC spectra of (*S*)-**2v**



Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	14.917	14.545	47.009	1.83	2.01
2	15.970	781.601	2288.585	98.17	97.99

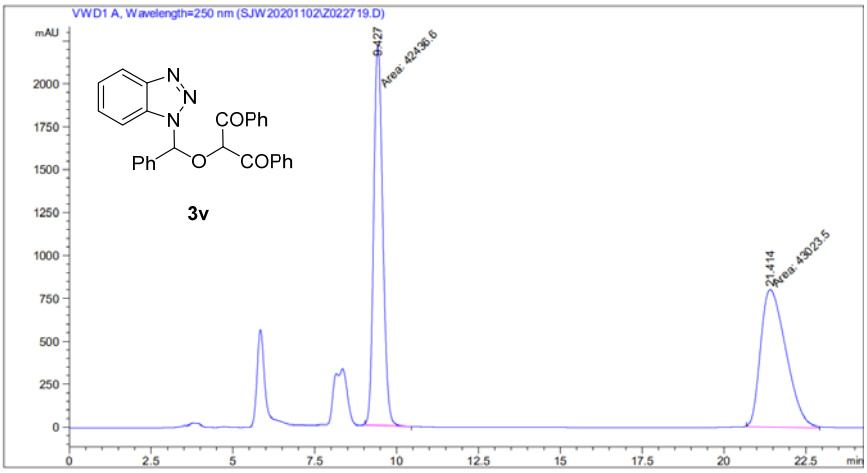
4) The asymmetric reaction of chiral oxirane 2v and 1a.



1a (*S*)-**2v** 96% ee **3v** 85% yield, racemic

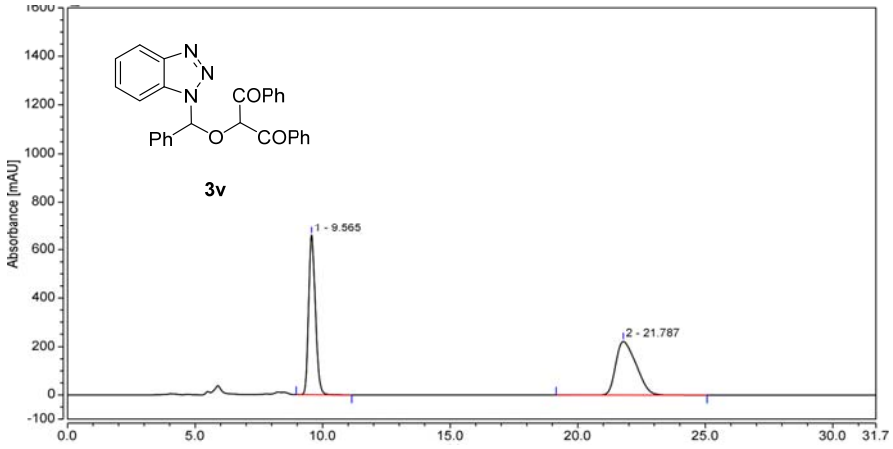
3v, 85% yield. The ee value was determined by HPLC, CHIRALCEL IA, n-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 256 nm, retention time: 9.57 min (minor), 21.79 min (major).

Figure S2. HPLC spectra of racemic **3v**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.427	MM	0.3196	4.24366e4	2212.86621	49.6566
2	21.414	MM	0.8973	4.30235e4	799.09314	50.3434

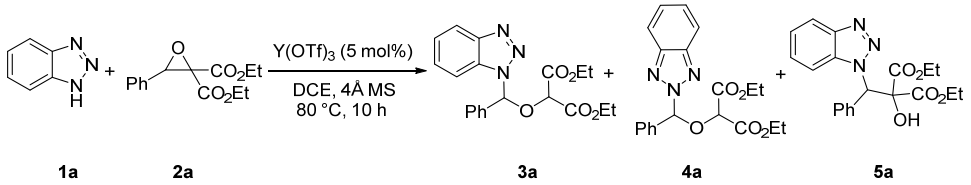
HPLC spectra of **3v** after asymmetric reaction



Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.565	203.540	659.581	49.79	74.80
2	21.787	205.250	222.268	50.21	25.20
Total:		**408.791**	**881.849**	**100.00**	**100.00**

3. General procedure for the ring-opening reaction

1) Procedure A:

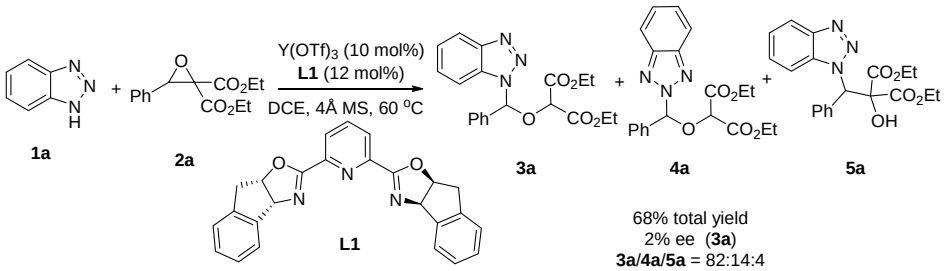


The reaction was performed in a 15 mL pressure tube, and phenyl oxiranyl dicarboxylate **2a** (26.4 mg, 0.1 mmol, 1.0 equiv) was dissolved in DCE (2 mL). Benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) were added respectively and the tube was sealed. The reaction mixture was stirred at 80 °C for 10 h (oil bath as the heat source). Upon completion, the reaction mixture was then purified by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 4/1, v/v) to give product **3a** as a colorless solid (36.1 mg, 94% yield). The ratio of isomers and chemoselectivity was determined by ^{1}H NMR analysis of the crude reaction mixture (**3a**:**4a**:**5a** = 96:4:0). Unless otherwise noted, **3b**-**3v** were synthesized in the same reaction conditions.

2) Gram-scale synthesis of 3a.

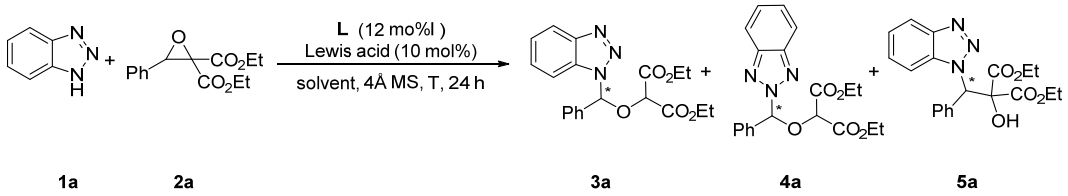
The reaction was performed in a 250 mL pressure tube, and phenyl oxiranyl dicarboxylate **2a** (1.32 g, 5.0 mmol, 1.0 equiv) was dissolved in DCE (100 mL). Benzotriazole **1a** (600 mg, 5.0 mmol), $Y(OTf)_3$ (135 mg, 0.25 mmol, 5 mol%), and activated 4Å molecular sieve (1.5 g) were added respectively and the tube was sealed. The reaction mixture was stirred at 80 °C for 10 h (oil bath as the heat source). Upon completion, the reaction mixture was then purified by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 4/1, v/v) to give product **3a** as a colorless solid (1.65 g, 86% yield). The ratio of isomers and chemoselectivity was determined by ^{1}H NMR analysis of the crude reaction mixture (**3a**:**4a**:**5a** = 96:4:0).

3) General procedure for the catalytic asymmetric reaction

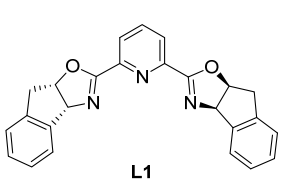


To a Schlenk tube equipped with a magnetic stir bar were added $Y(OTf)_3$ (5.4 mg, 0.01 mmol, 10 mol%), phenyl oxiranyl dicarboxylate **2a** (26.4 mg, 0.1 mmol, 1.0 equiv), **L** (8.4 mg, 0.012mmol, 12 mol%), 4Å MS (30 mg) and 1.0 mL of DCE. The mixture was stirred at 30 ^{o}C for 1 h. Benzotriazole **1a** (12 mg, 0.1 mmol) was then added into the tube. After being stirred at 60 ^{o}C for 24h. Upon completion, the reaction mixture was then purified by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 4/1, v/v) to give product **3a** (2% ee), **3a**/**4a**/**5a** = 82:14:4.

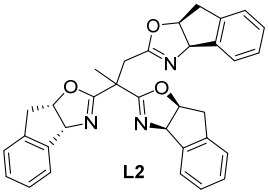
4. Optimization of reaction conditions for the asymmetric catalysis



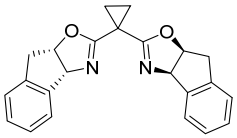
1a **2a** **3a** **4a** **5a**



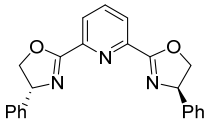
L1



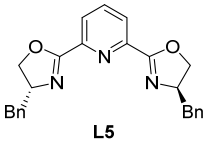
L2



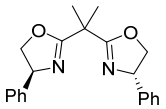
L3



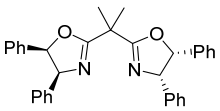
L4



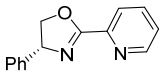
L5



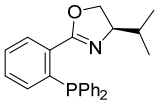
L6



L7



L8



L9

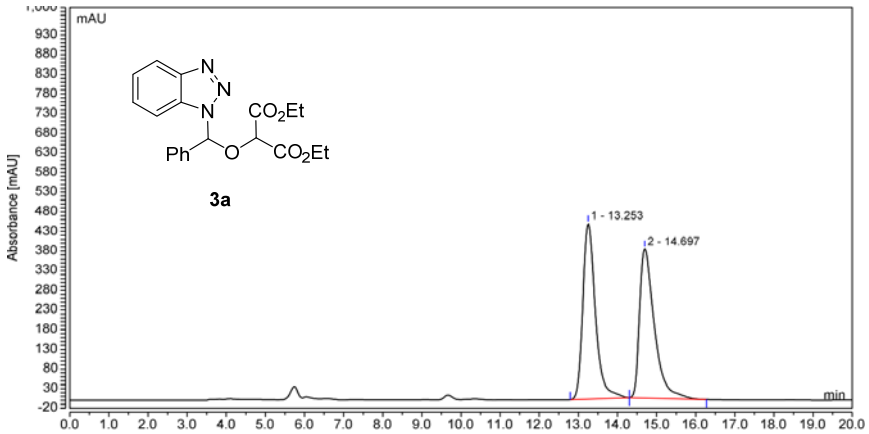
entry[a]	catalyst	solvent	**L**	T (^oC)	yield (%)[b]	ratio[c] **3a**/**4a**/**5a**	ee (%)[d] **3a**
1	$Ni(ClO_4)_2·6H_2O$	DCE	**L1**	30	NR	-	-
2	$Sc(OTf)_3$	DCE	**L1**	30	NR	-	-
3	$Yb(OTf)_3$	DCE	**L1**	30	NR	-	-
4	$Gd(OTf)_3$	DCE	**L1**	30	35	92/3/5	1
5	$Y(OTf)_3$	DCE	**L1**	30	49	86/4/10	2
6	$Y(OTf)_3$	DCE	**L2**	30	NR	-	-
7	$Y(OTf)_3$	DCE	**L3**	30	NR	-	-
8	$Y(OTf)_3$	DCE	**L4**	30	NR	-	-
9	$Y(OTf)_3$	DCE	**L5**	30	NR	-	-
10	$Y(OTf)_3$	DCE	**L6**	30	NR	-	-
11	$Y(OTf)_3$	DCE	**L7**	30	NR	-	-
12	$Y(OTf)_3$	DCE	**L8**	30	NR	-	-

13	$Y(OTf)_3$	DCE	**L9**	30	NR	-	-
14	$Y(OTf)_3$	DCE	**L1**	60	68	82/14/4	2
15	$Y(OTf)_3$	DCE	**L1**	80	91	89/11/0	1
16	$Y(OTf)_3$	DCM	**L1**	30	35	62/30/8	0
17	$Y(OTf)_3$	Toulene	**L1**	30	19	25/25/50	0

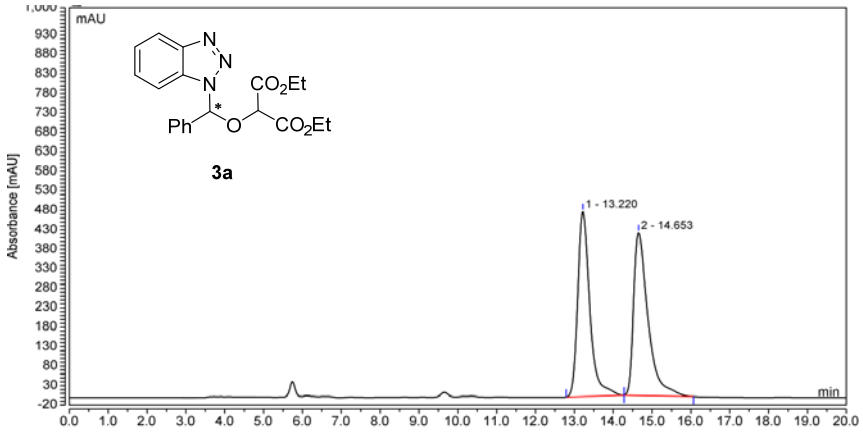
[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), Lewis acids (10 mol%), **L** (12 mol%), 4Å MS (30 mg) for 24 h. [b]The total yield was determined by ^{1}H NMR using CH_2Br_2 as an internal standard. [c]The ratio was determined by ^{1}H NMR analysis of the crude product. [d]Determined by chair HPLC ananlysis.

Figure S3. HPLC spectra of **3a**

The ee value was determined by HPLC, CHIRALCEL IA, n-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 13.22 min (minor), 14.65 min (major).

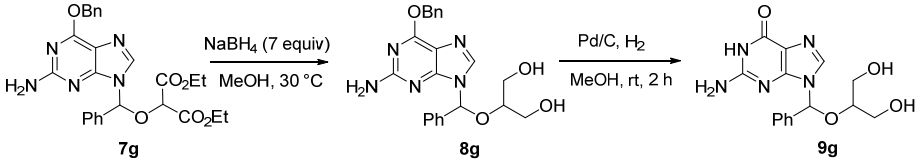


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	13.253	167.384	447.394	50.03	54.04
2	14.697	167.173	380.551	49.97	45.96
Total:		**334.557**	**827.945**	**100.00**	**100.00**



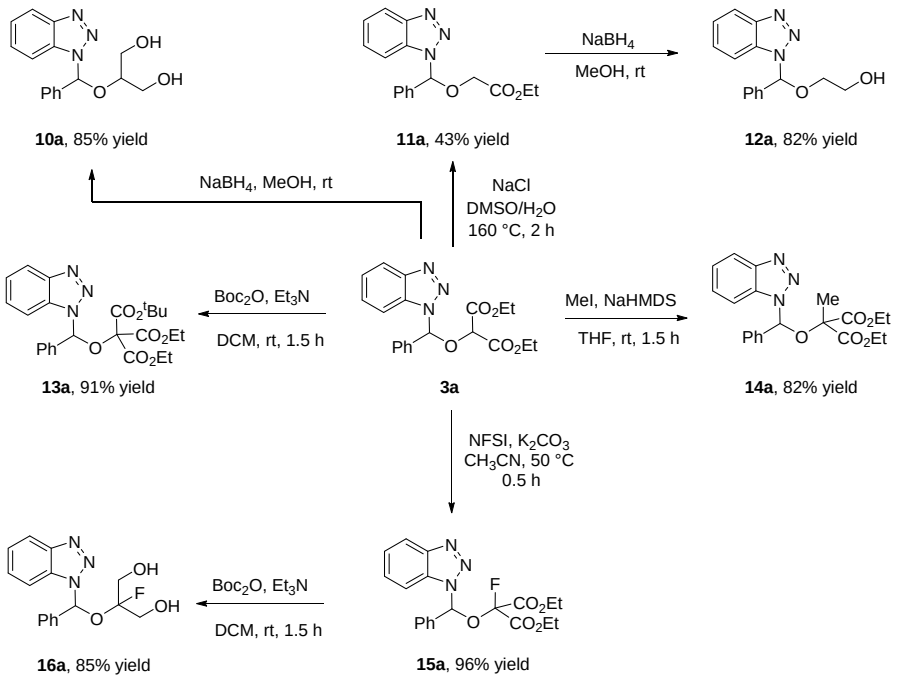
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	13.220	171.182	474.847	48.83	53.17
2	14.653	179.365	418.227	51.17	46.83
Total:		**350.547**	**893.074**	**100.00**	**100.00**

5. Experimental procedure for the transformations of the product



To a stirred solution of **7g** (50.5 mg, 0.1 mmol) in MeOH (2 mL), $NaBH_4$ (27 mg, 0.7 mmol, 7.0 equiv) was added. Then the reaction was performed at 30 °C for 0.5 h. The mixture was quenched with saturated NH_4Cl solution (1 mL), extracted with ethyl acetate (3×5 mL). The organic layers were combined and dried over anhydrous Mg_2SO_4. After filtration and removal of the solvents, the crude product was purified by silica gel column chromatography using DCM/MeOH system (DCM/MeOH, 10/1, v/v) to afford compound **8g** (38.3 mg, 91% yield).

A mixture of **8g** (42.1 mg, 0.1mmol) and 10% Pd/C (8.5 mg) in methanol (2 mL) was stirred at room temperature under H_2 for 2 h. The reaction mixture was filtered over celite, and the filtrate was concentrated in vacuo. the crude product was purified by silica gel column chromatography using DCM/MeOH system (DCM/MeOH, 2/1, v/v) to afford compound **9g** (30.8 mg, 93% yield).



To a stirred solution of **3a** (38.3 mg, 0.1 mmol) in MeOH (1 mL), $NaBH_4$ (18.9 mg, 0.5 mmol, 5.0 equiv) was added. Then the reaction was performed at room temperature for 0.5 h. The mixture was quenched with saturated NH_4Cl solution (1 mL), and extracted with ethyl acetate (3×5 mL). The organic layers were combined and dried over anhydrous Mg_2SO_4. After filtration

and removal of the solvents, the crude product was purified by silica gel column chromatography using Pet/EtOAc system (Pet/EtOAc, 1/1, v/v) to afford compound **10a** (25.4 mg, 85% yield).

To the solution of **3a** (191.5 mg, 0.5 mmol, 1.0 equiv) in DMSO (1 mL, 0.5 M) was added NaCl (44.5 mg, 1.05 mmol, 2.1 equiv) and H_2O (10 μL, 0.55 mmol, 1.1 equiv). The reaction was allowed to stir at 160 ^oC for 2 h (oil bath as the heat source) and then quenched with EtOAc/H_2O, extracted with EtOAc, dried with Na_2SO_4, filtered, and concentrated in vacuo. This crude mixture was then immediately purified by flash chromatography on silica gel (Pet/EtOAc, 4/1, v/v) to afford the product **11a** (65.9 mg, 43% yield).

To a stirred solution of **11a** (62.2 mg, 0.2 mmol) in MeOH (2 mL), $NaBH_4$ (37.8 mg, 1.0 mmol, 5.0 equiv) was added. Then the reaction was performed at room temperature for 0.5 h. The mixture was quenched with saturated NH_4Cl solution (2 mL), and extracted with ethyl acetate (3×10 mL). The organic layers were combined and dried over anhydrous Mg_2SO_4. After filtration and removal of the solvents, the crude product was purified by silica gel column chromatography (Pet/EtOAc, 2/1, v/v) to afford compound **12a** (44.1 mg, 82% yield).

To a solution of adduct **3a** (38.3 mg, 0.1 mmol, 1.0 equiv) in DCM (1.0 mL) was added 4-dimethylaminopyridine (1.8 mg, 0.015 mmol, 0.15 equiv), triethylamine (20.9 μL, 0.15 mmol, 1.5 equiv) and di-*tert*-butyl dicarbonate (34.4 μL, 0.015 mmol, 1.5 equiv) at room temperature. The mixture was allowed to stir at ambient temperature for 1.5 h. Purification by flash chromatography (Pet/EtOAc, 4/1, v/v) furnished the corresponding product **13a** in 44.0 mg (91% yield).

To a solution of adduct **3a** (38.3 mg, 0.1 mmol, 1.0 equiv) in THF (1.0 mL) was added sodium bis(trimethylsilyl)amide (0.6 M in toluene, 360 μL, 0.22 mmol, 1.1 equiv), methyl iodide (9.5 μL, 0.15 mmol, 1.5 equiv) was then added. After stirring at room temperature for 1.5 h, the crude compound was purified by column chromatography on silica gel (Pet/EtOAc, 4/1, v/v), affording the desired compound **14a** (32.6 mg, 82% yield).

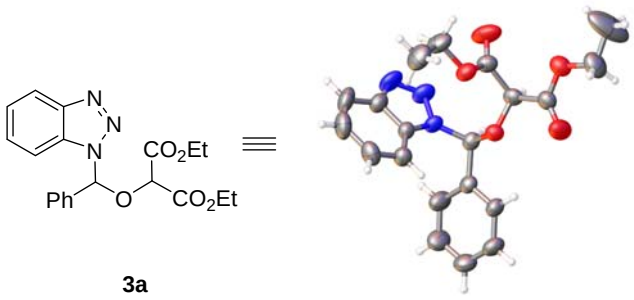
To a solution of adduct **3a** (38.3 mg, 0.1 mmol, 1.0 equiv) in MeCN (1.0 mL) was added K_2CO_3 (15.2 mg, 0.11 mmol, 1.1 equiv), NFSI (35 mg, 0.11mmol, 1.1 equiv) was then added. After stirring at 50 °C 0.5 h, the crude compound was purified by column chromatography on silica gel (Pet/EtOAc, 4/1, v/v), affording the desired compound **15a** (38.5 mg, 96% yield).

To a stirred solution of **15a** (40.1 mg, 0.1 mmol) in MeOH (1 mL), $NaBH_4$ (18.9 mg, 0.5 mmol, 5.0 equiv) was added. Then the reaction was performed at room temperature for 0.5 h. The

mixture was quenched with saturated NH_4Cl solution (1 mL), and extracted with ethyl acetate (3×5 mL). The organic layers were combined and dried over anhydrous Mg_2SO_4. After filtration and removal of the solvents, the crude product was purified by silica gel column chromatography using Pet/EtOAc system (Pet/EtOAc, 1/1, v/v) to afford compound **16a** (27.0 mg, 85% yield).

6. The X-ray crystallographic data

Figure S4. X-ray crystal structure of **3a** (The crystal was obtained by slow evaporation of **3a** in a mixture of Et_2O). (CCDC 2018326):



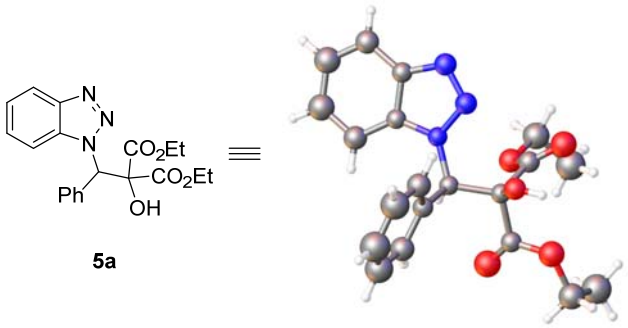
3a

Table S1 Crystal data and structure refinement for 3a.

Identification code	**3a**
Empirical formula	$C_{20}H_{21}N_3O_5$
Formula weight	383.40
Temperature/K	293.50(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.4068(5)
b/Å	21.5669(9)
c/Å	9.8567(6)
α/°	90
β/°	94.988(5)
γ/°	90
Volume/$Å^3$	1992.11(18)
Z	4
$\rho_{calc}g/cm^3$	1.278
μ/mm^{-1}	0.093
F(000)	808.0
Crystal size/mm^3	0.12 × 0.1 × 0.08
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/	6.874 to 58.084
Index ranges	$-12 \le h \le 11$, $-25 \le k \le 28$, $-11 \le l \le 13$
Reflections collected	12787
Independent reflections	4606 [R_{int} = 0.0275, R_{sigma} = 0.0367]
Data/restraints/parameters	4606/0/255
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0607, wR_2 = 0.1341
Final R indexes [all data]	R_1 = 0.0940, wR_2 = 0.1536

Largest diff. peak/hole / e $Å^{-3}$ 0.26/-0.30

Figure S5. X-ray crystal structure of **5a** (The crystal was obtained by slow evaporation of **5a** in a mixture of Et_2O). (CCDC 2018327):



5a

Table S2 Crystal data and structure refinement for 5a.

Identification code	**5a**
Empirical formula	$C_{20}H_{21}N_3O_5$
Formula weight	383.40
Temperature/K	292.8(4)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.3393(2)
b/Å	21.3081(6)
c/Å	11.1096(4)
α/°	90
β/°	100.128(3)
γ/°	90
Volume/$Å^3$	1943.35(10)
Z	4
$\rho_{calc}g/cm^3$	1.310
μ/mm^{-1}	0.793
F(000)	808.0
Crystal size/mm^3	0.13 × 0.11 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/	8.3 to 142.94
Index ranges	$-10 \le h \le 7$, $-25 \le k \le 26$, $-13 \le l \le 12$
Reflections collected	9682
Independent reflections	3721 [R_{int} = 0.0285, R_{sigma} = 0.0305]
Data/restraints/parameters	3721/0/259
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0557, wR_2 = 0.1330
Final R indexes [all data]	R_1 = 0.0661, wR_2 = 0.1388
Largest diff. peak/hole / e $Å^{-3}$	0.36/-0.20

Figure S6. X-ray crystal structure of **3j** (The crystal was obtained by slow evaporation of **3j** in a mixture of Et_2O). (CCDC 2027379):

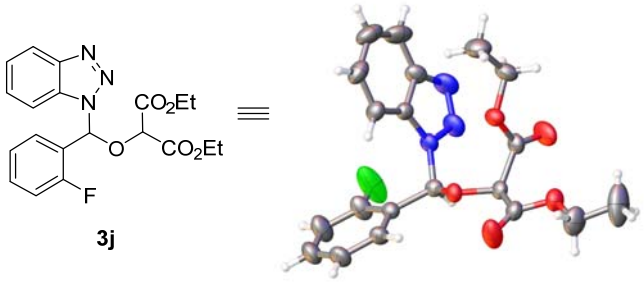


Table S3 Crystal data and structure refinement for 3j.

Identification code	**3j**
Empirical formula	$C_{20}H_{20}FN_3O_5$
Formula weight	401.39
Temperature/K	295.75(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.5126(2)
b/Å	21.7936(4)
c/Å	9.7318(3)
α/°	90
β/°	95.480(2)
γ/°	90
Volume/Å^3	2008.32(8)
Z	4
ρ_{calc}g/cm^3	1.328
μ/mm^{-1}	0.866
F(000)	840.0
Crystal size/mm^3	0.12 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/	8.114 to 142.848
Index ranges	-11 ≤ h ≤ 9, -26 ≤ k ≤ 16, -11 ≤ l ≤ 10
Reflections collected	8495
Independent reflections	3811 [R_{int} = 0.0243, R_{sigma} = 0.0321]
Data/restraints/parameters	3811/0/264
Goodness-of-fit on F^2	1.105
Final R indexes [I>=2σ (I)]	R_1 = 0.0570, wR_2 = 0.1406
Final R indexes [all data]	R_1 = 0.0662, wR_2 = 0.1492
Largest diff. peak/hole / e Å^{-3}	0.35/-0.43

Figure S7. X-ray crystal structure of **3t** (The crystal was obtained by slow evaporation of **3t** in a mixture of Et_2O). (CCDC 2018328):

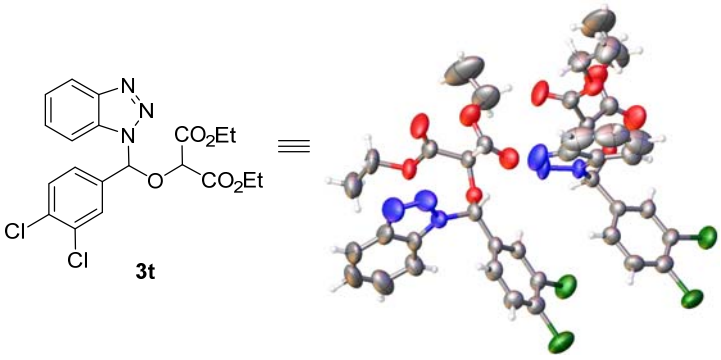
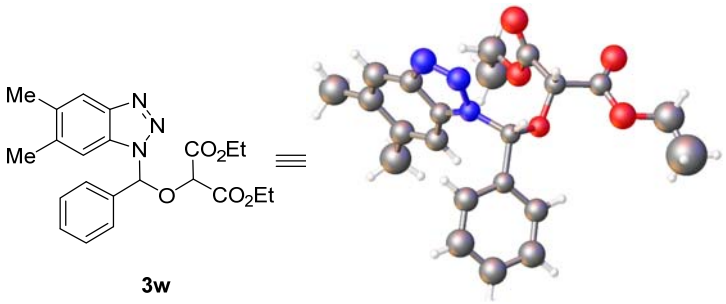


Table S4 Crystal data and structure refinement for 3t.

Identification code	**3t**
Empirical formula	$C_{20}H_{19}Cl_2N_3O_5$
Formula weight	452.28
Temperature/K	295.28(11)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	14.9392(5)
b/Å	15.2205(4)
c/Å	19.0810(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4338.7(2)
Z	8
ρ_{calc}g/cm^3	1.385
μ/mm^{-1}	3.011
F(000)	1872.0
Crystal size/mm^3	0.13 × 0.1 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/	7.43 to 143.072
Index ranges	-18 ≤ h ≤ 18, -12 ≤ k ≤ 18, -13 ≤ l ≤ 23
Reflections collected	13129
Independent reflections	7494 [R_{int} = 0.0404, R_{sigma} = 0.0550]
Data/restraints/parameters	7494/2/544
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0769, wR_2 = 0.2086
Final R indexes [all data]	R_1 = 0.0861, wR_2 = 0.2268
Largest diff. peak/hole / e Å^{-3}	0.42/-0.48
Flack parameter	0.44(2)

Figure S8. X-ray crystal structure of **3w** (The crystal was obtained by slow evaporation of **3w** in a mixture of Et_2O). (CCDC 2018329):

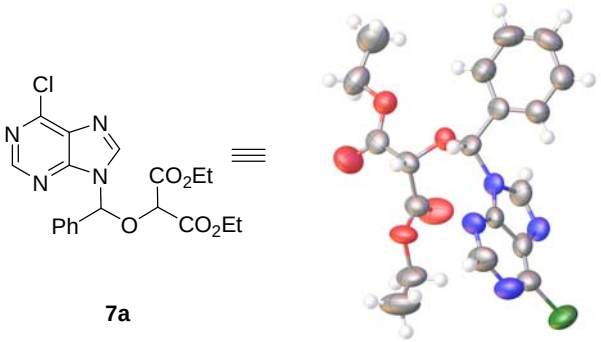


3w

Table S5 Crystal data and structure refinement for 3w.

Identification code	**3w**
Empirical formula	$C_{22}H_{25}N_3O_5$
Formula weight	411.45
Temperature/K	290(4)
Crystal system	triclinic
Space group	P-1
a/Å	9.5779(5)
b/Å	11.3128(7)
c/Å	11.8490(8)
α/°	61.499(7)
β/°	78.529(5)
γ/°	86.047(5)
Volume/Å^3	1105.24(13)
Z	2
ρ_{calc}g/cm^3	1.236
μ/mm^{-1}	0.730
F(000)	436.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/	8.648 to 142.958
Index ranges	-9 ≤ h ≤ 11, -11 ≤ k ≤ 13, -14 ≤ l ≤ 14
Reflections collected	8787
Independent reflections	4210 [R_{int} = 0.0193, R_{sigma} = 0.0229]
Data/restraints/parameters	4210/8/276
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0619, wR_2 = 0.1864
Final R indexes [all data]	R_1 = 0.0668, wR_2 = 0.1923
Largest diff. peak/hole / e Å^{-3}	0.44/-0.48

Figure S9. X-ray crystal structure of **7a** (The crystal was obtained by slow evaporation of **7a** in a mixture of MeOH). (CCDC 2040250):

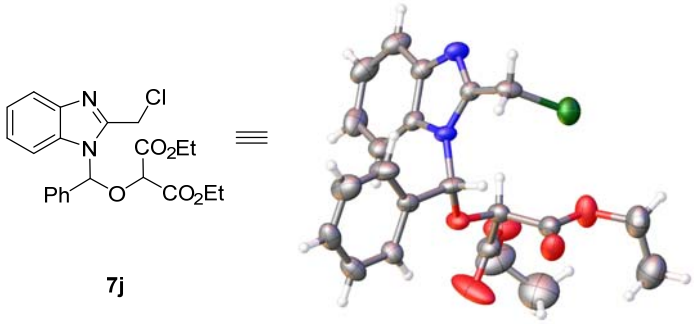


7a

Table S6 Crystal data and structure refinement for 7a.

Identification code	**7a**
Empirical formula	$C_{19}H_{19}ClN_4O_5$
Formula weight	418.83
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.8048(9)
b/Å	15.1785(10)
c/Å	16.7524(12)
α/°	89.985(6)
β/°	87.821(6)
γ/°	80.497(6)
Volume/Å^3	2958.3(4)
Z	6
ρ_{calc}g/cm^3	1.411
μ/mm^{-1}	0.233
F(000)	1308.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/	4.064 to 50
Index ranges	-13 ≤ h ≤ 14, -15 ≤ k ≤ 18, -17 ≤ l ≤ 19
Reflections collected	23126
Independent reflections	10386 [R_{int} = 0.0531, R_{sigma} = 0.0762]
Data/restraints/parameters	10386/26/821
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0752, wR_2 = 0.1823
Final R indexes [all data]	R_1 = 0.0985, wR_2 = 0.2015
Largest diff. peak/hole / e Å^{-3}	0.68/-0.51

Figure S10. X-ray crystal structure of **7j** (The crystal was obtained by slow evaporation of **7j** in a mixture of Et_2O). (CCDC 2038626):

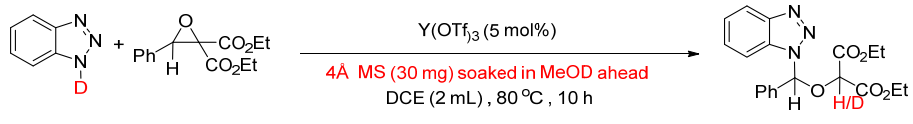


7j

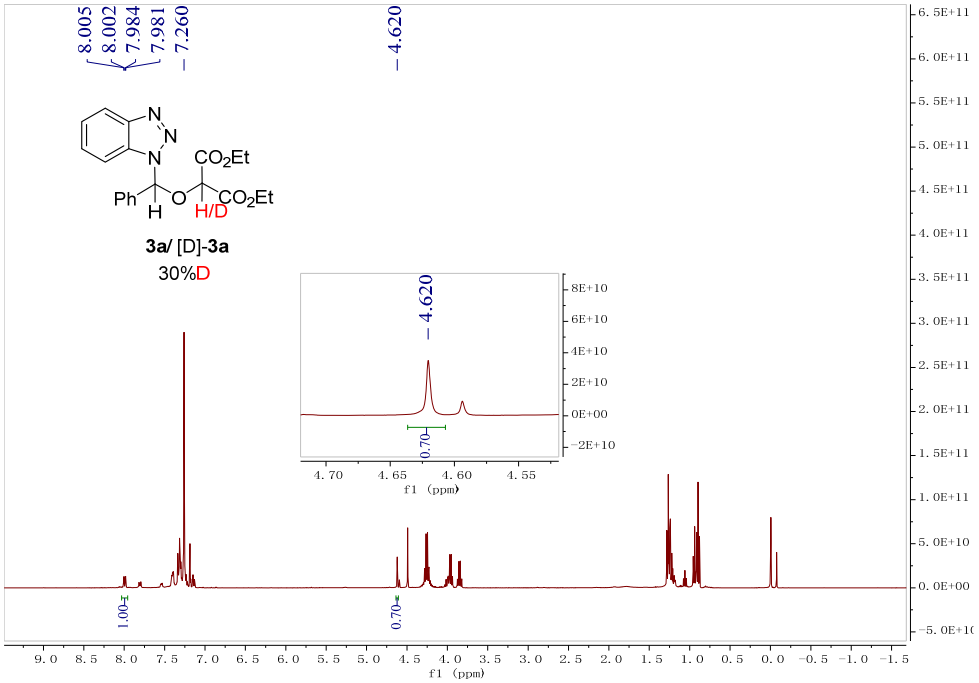
Table S7 Crystal data and structure refinement for 7j.

Identification code	**7j**
Empirical formula	$C_{22}H_{23}ClN_2O_5$
Formula weight	430.87
Temperature/K	149.98(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.756(4)
b/Å	14.590(3)
c/Å	9.628(2)
α/°	90
β/°	103.67(2)
γ/°	90
Volume/Å^3	2150.5(9)
Z	4
ρ_{calc}g/cm^3	1.331
μ/mm^{-1}	0.213
F(000)	904.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/	5.172 to 50
Index ranges	-18 ≤ h ≤ 16, -17 ≤ k ≤ 13, -11 ≤ l ≤ 11
Reflections collected	8937
Independent reflections	3783 [R_{int} = 0.0935, R_{sigma} = 0.1431]
Data/restraints/parameters	3783/0/273
Goodness-of-fit on F^2	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0789, wR_2 = 0.1861
Final R indexes [all data]	R_1 = 0.1496, wR_2 = 0.2389
Largest diff. peak/hole / e Å^{-3}	0.43/-0.36

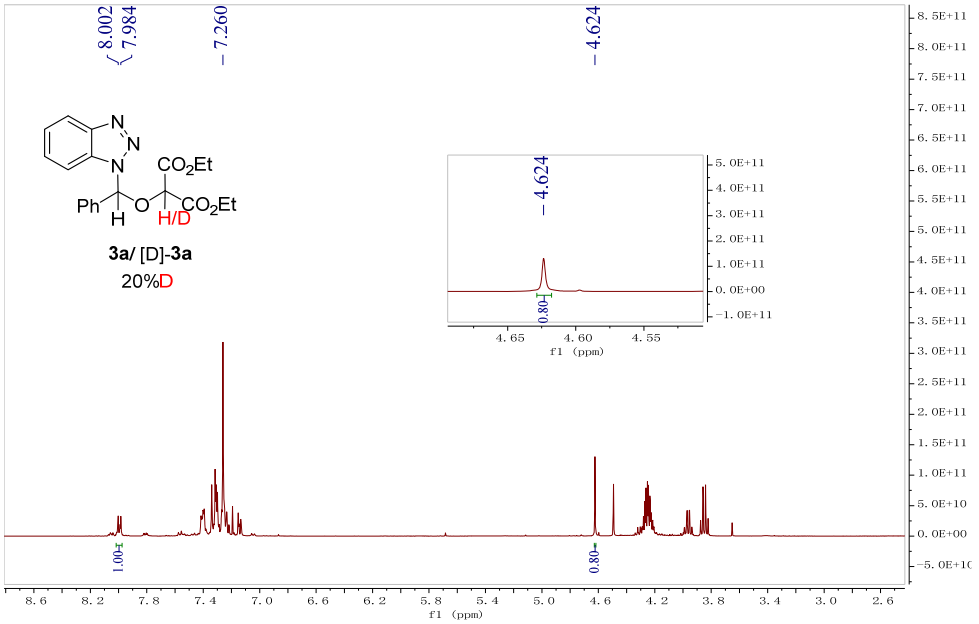
7. Results for deuterium labeling experiment[5]



^{1}H NMR spectrums of isotopic labeling experiments of the crude product 3a/ [D]-3a

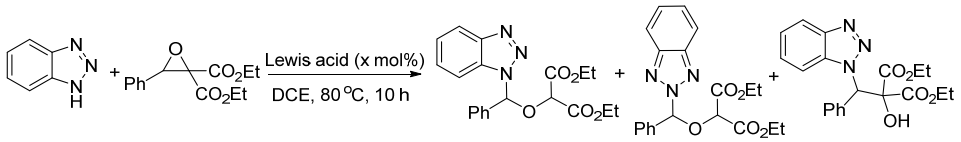


^{1}H NMR spectrums of isotopic labeling experiments under standard conditions of the crude product 3a/ [D]-3a



8. Optimization of the reaction conditions

Table S8: Optimization of Lewis acid[a]

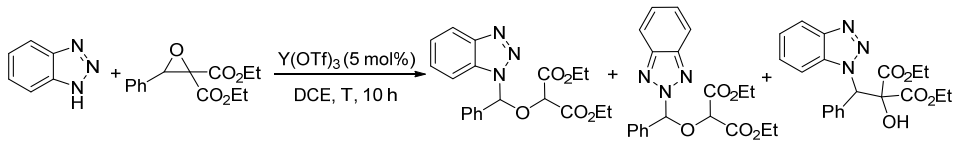


1a 2a 3a 4a 5a

entry	Lewis acid	x	yield (%)[b] (**3a**+**4a**+**5a**)	ratio[c] (**3a**/**4a**/**5a**)
1	-	-	NR	-
2	$Cu(OTf)_2$	5	trace	-
3[d]	$AlCl_3$	5	trace	-
4[d]	$BF_3{\cdot}Et_2O$	5	NR	-
5[d]	MgI_2	5	NR	-
6	$Ni(ClO_4)_2{\cdot}6H_2O$	5	trace	-
7	$Gd(OTf)_3$	5	60	67:23:10
8	$Sc(OTf)_3$	5	33	82:11:7
9	$Y(OTf)_3$	5	99	96: 4: 0
10	$Y(OTf)_3$	3	36	67:28:5
11	$Y(OTf)_3$	7	93	92:4:4
12	$Y(OTf)_3$	10	88	95:4:1

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), Lewis acid (x mol%), 4Å MS (30 mg) and DCE (2 mL) at 80 °C for 10 h in the pressure tube. [b]The yield was determined by ^{1}H NMR using CH_2Br_2 as an internal standard. [c]The ratio was determined by ^{1}H NMR analysis of the crude product.[d]Solvent was toluene.

Table S9: Optimization of temperatures[a]



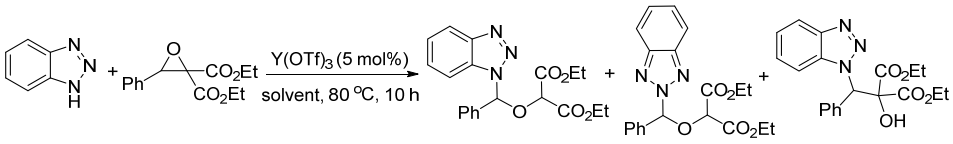
1a 2a 3a 4a 5a

entry	T (°C)	yield (%)[b] (**3a**+**4a**+**5a**)	ratio[c] (**3a**/**4a**/**5a**)
1	rt	trace	-
2	40	32	56:33:11
3	50	36	56:33:11
4	60	60	64:29:7

5	70	93	87:13:0
6	80	99	96:4:0

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), $Y(OTf)_3$ (5 mol%), 4Å MS (30 mg) and DCE (2 mL) for 10 h in the pressure tube. [b]The yield was determined by ^1H NMR using CH_2Br_2 as an internal standard. [c]The ratio was determined by ^1H NMR analysis of the crude product.

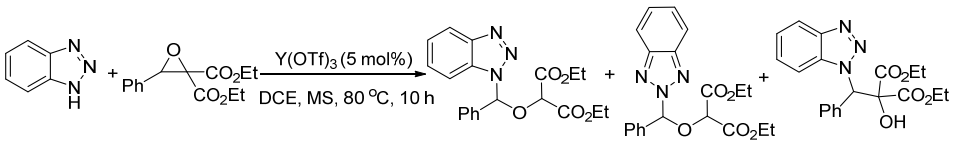
Table S10: Optimization of solvents[a]



entry	solvent	volume (mL)	yield (%)[b] (**3a**+**4a**+**5a**)	ratio[c] (**3a**/**4a**/**5a**)
1	Et_2O	2	NR	-
2	THF	2	trace	-
3	toluene	2	40	50:35:15
4	$CHCl_3$	2	24	40:40:20
5	DCM	2	84	75:24:2
6	DCE	2	99	96:4:0
7	DCE	1	68	70:22:8
8	DCE	0.5	66	65:25:10

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), $Y(OTf)_3$ (5 mol%), 4Å MS (30 mg) and solvent at 80 °C for 10 h in the pressure tube. [b]The yield was determined by ^1H NMR using CH_2Br_2 as an internal standard. [c]The ratio was determined by ^1H NMR analysis of the crude product.

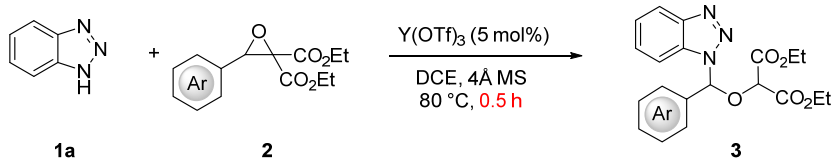
Table S11: Optimizations of molecular sieve[a]



entry	MS	H_2O	yield (%)[b] (**3a**+**4a**+**5a**)	ratio[c] (**3a**/**4a**/**5a**)
1	3Å	-	83	75:23:2
2	4Å	-	99	96:4:0
3	4Å	10 μL	11	65:16:19
4	5Å	-	43	50:36:14
5	-	-	NR	-

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), $Y(OTf)_3$ (5 mol%), MS (30 mg) and DCE (2 mL) at 80 °C for 10 h in the pressure tube. [b]The yield was determined by ^1H NMR using CH_2Br_2 as an internal standard. [c]The ratio was determined by ^1H NMR analysis of the crude product.

9. Hammett plot analysis

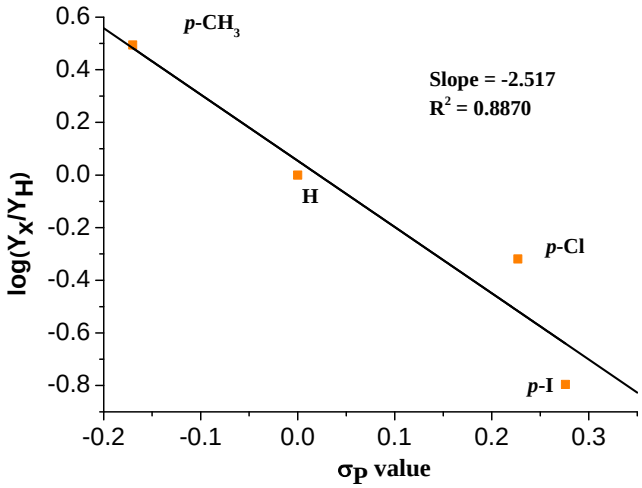


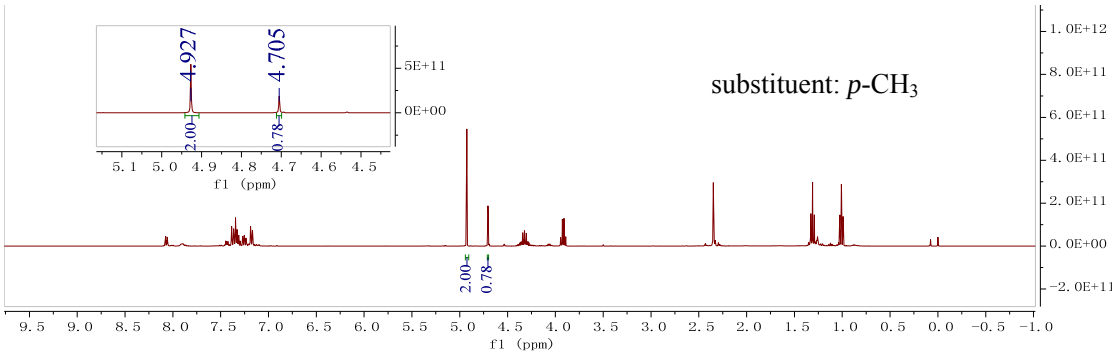
1a **2** **3**

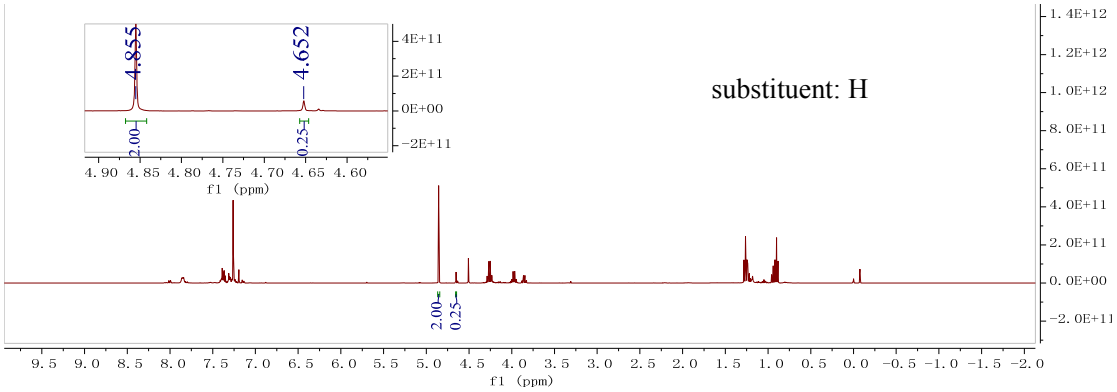
The reaction was performed in a 15 mL pressure tube, aryl oxiranyl dicarboxylates **2** (0.1 mmol, 1.0 equiv) were dissolved in DCE (2 mL), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) were added respectively and the tube was sealed. The reaction mixture was stirred at 80 °C for 0.5 h. The yields were determined by ^1H NMR using CH_2Br_2 as an internal standard.

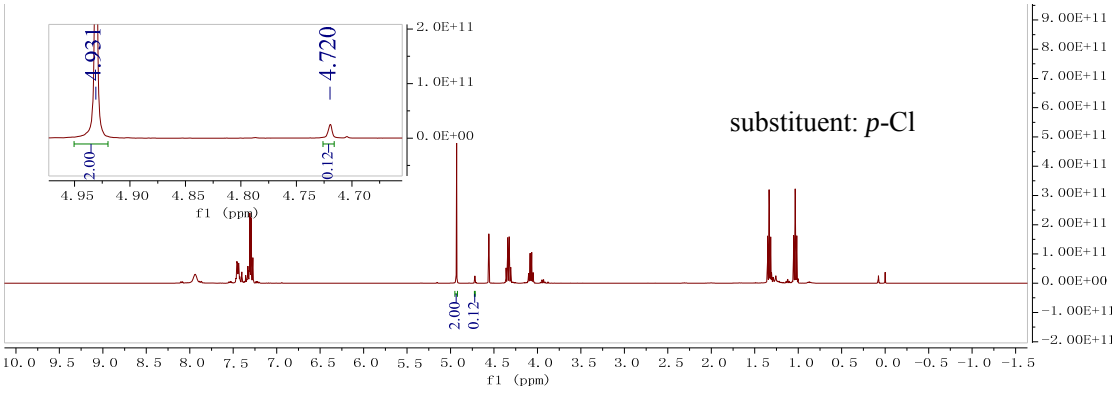
Table S12: Hammett study of relative initial rates of *para*-substituent

entry	substituent	yield (%)	σ	$\log(Y_x/Y_H)$
1	*p*-CH_3	78	-0.170	0.494
2	H	25	0	0
3	*p*-Cl	12	0.227	-0.319
4	*p*-I	4	0.276	-0.796




substituent: p-CH3
4.927
4.705
2.00
0.78
f1 (ppm)


substituent: H
4.855
4.652
2.00
0.25
f1 (ppm)


substituent: p-Cl
4.931
4.720
2.00
0.12
f1 (ppm)

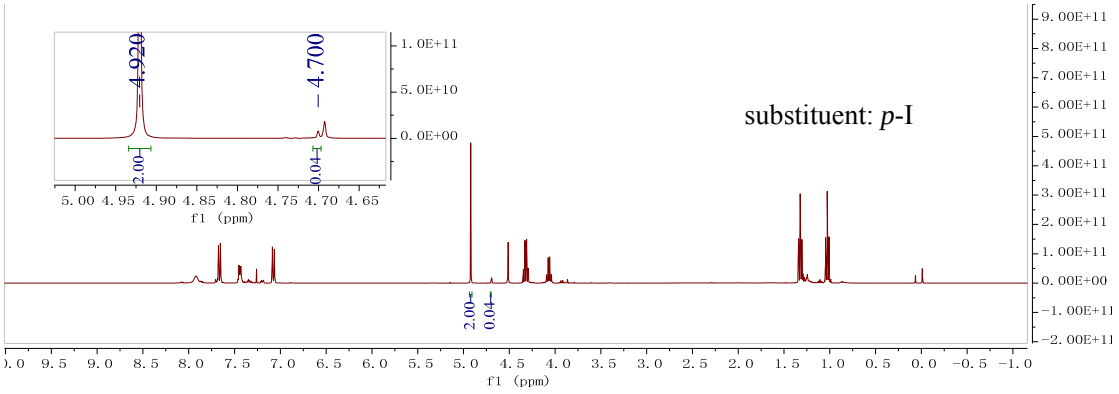
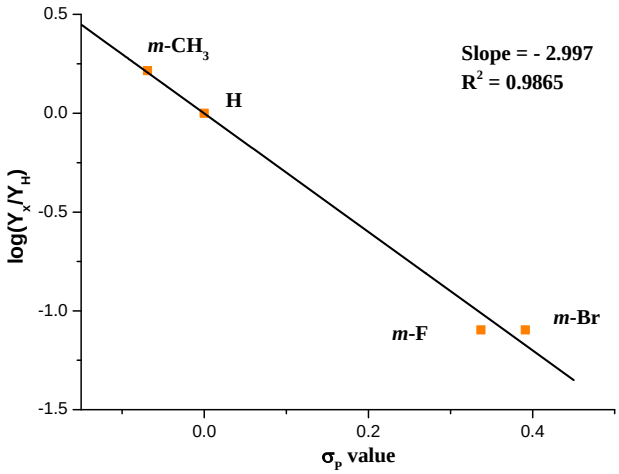
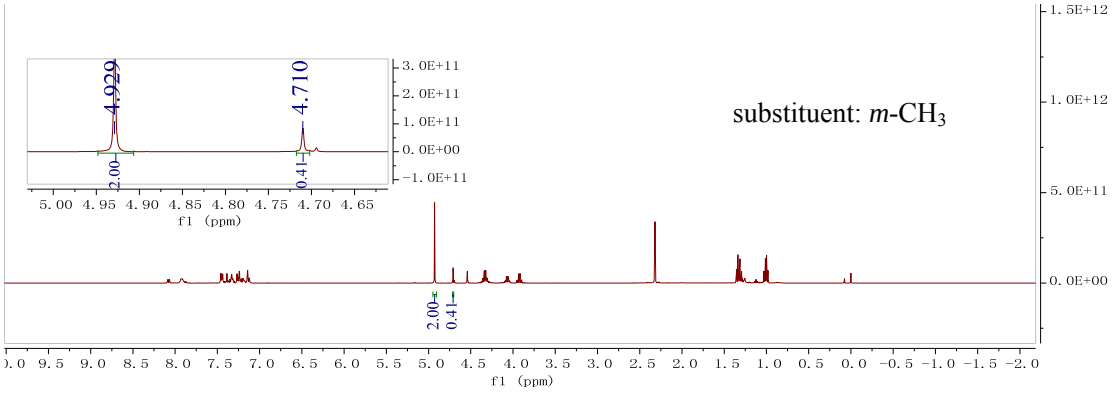
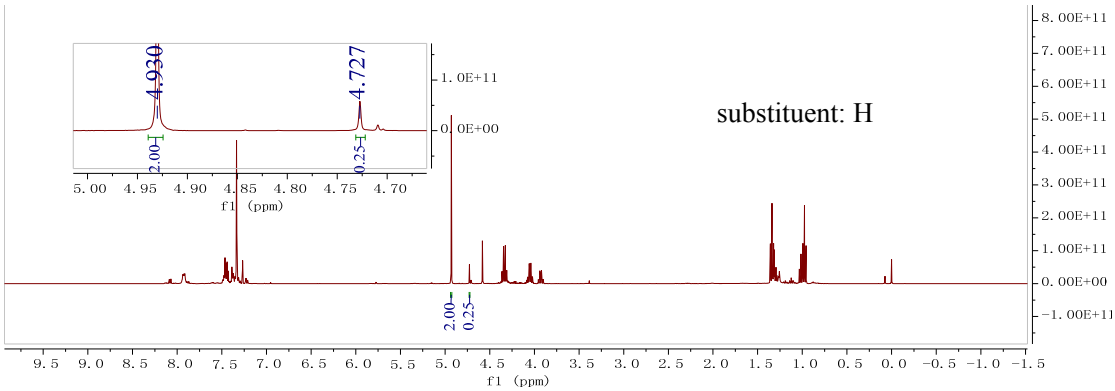

substituent: p-I
4.920
4.700
2.00
0.04
f1 (ppm)

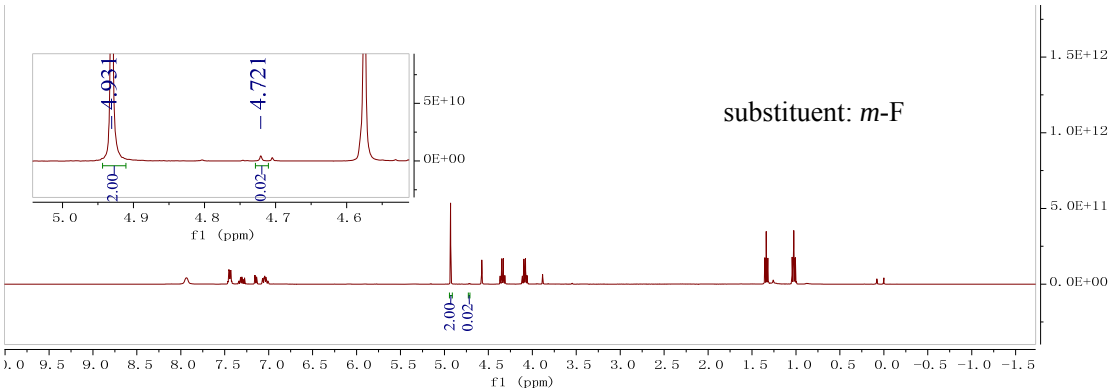
Table S13: The Hammett study of relative initial rates of *meta*-substituent

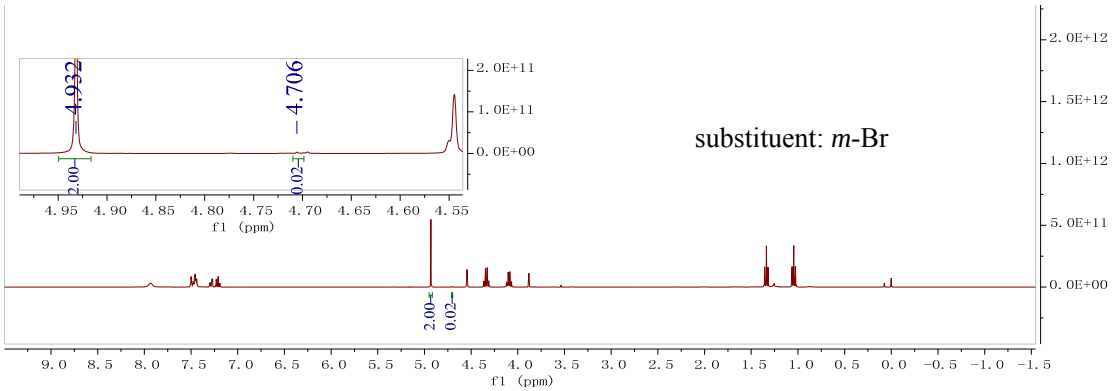
entry	substituent	yield (%)	σ	$\log(Y_x/Y_H)$
1	*m*-CH_3	41	-0.069	0.215
2	H	25	0	0
3	*m*-F	2	0.337	-1.097
4	*m*-Br	2	0.391	-1.097




substituent: *m*-CH_3
4.929
4.710
2.00
0.41
f1 (ppm)

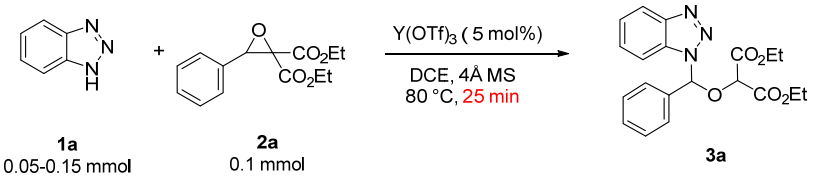

substituent: H
4.930
4.727
2.00
0.25
f1 (ppm)


substituent: *m*-F
4.931
4.721
2.00
0.02
f1 (ppm)


substituent: *m*-Br
4.932
4.706
2.00
0.02
f1 (ppm)

10. Kinetic experiments

1) Order in 1a



The reaction was performed in a 15 mL pressure tube, **2a** (0.1 mmol, 1.0 equiv) were dissolved in DCE (2 mL), benzotriazole **1a** (6-18 mg, 0.05-0.15 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) were added respectively and the tube was sealed. The reaction mixture was stirred at 80 °C for 25 min. The yields were determined by ^1H NMR using CH_2Br_2 as an internal standard.

entry	**1a** (mmol)	yield (%)
1	0	0
2	0.05	20
3	0.075	20
4	0.1	20
5	0.125	20
6	0.15	20

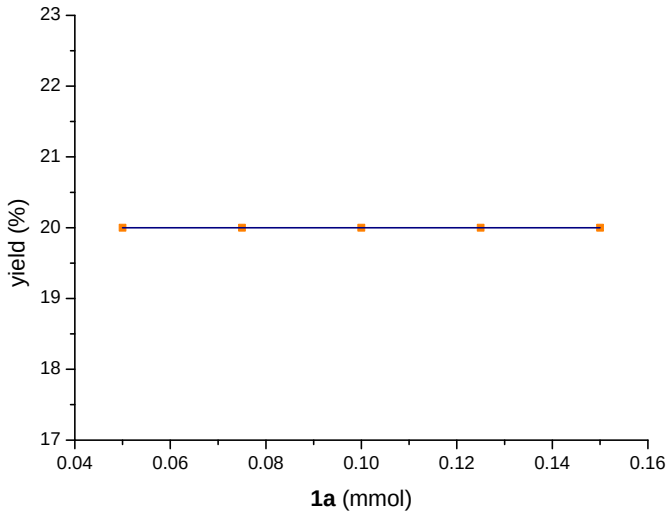
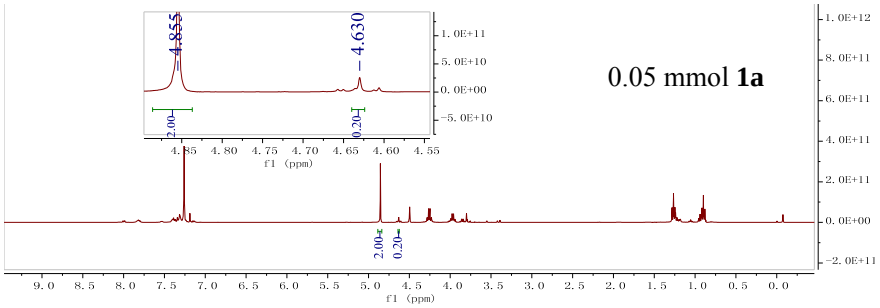
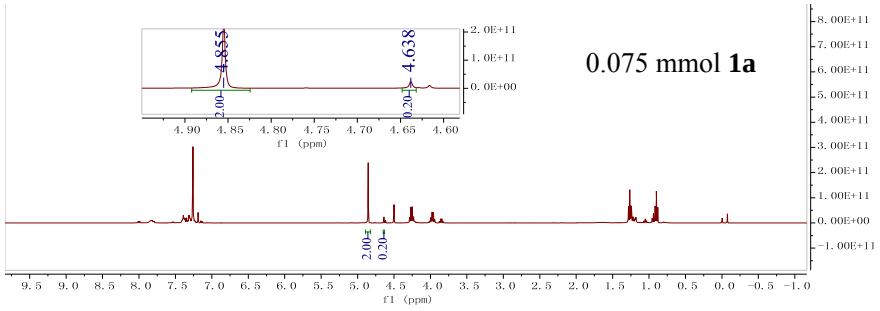


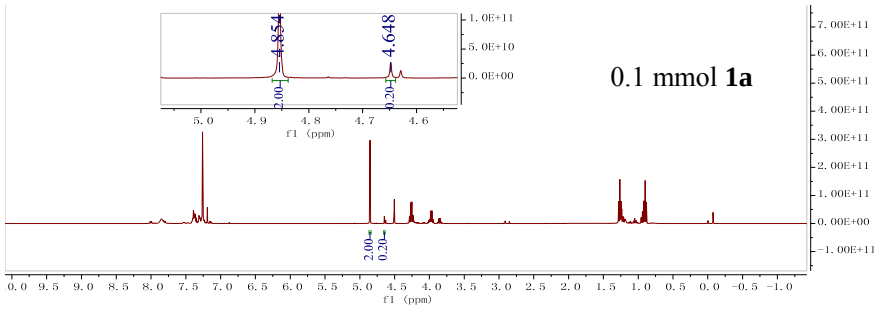
Figure S11. Plot of initial rates versus concentration of **1a**.



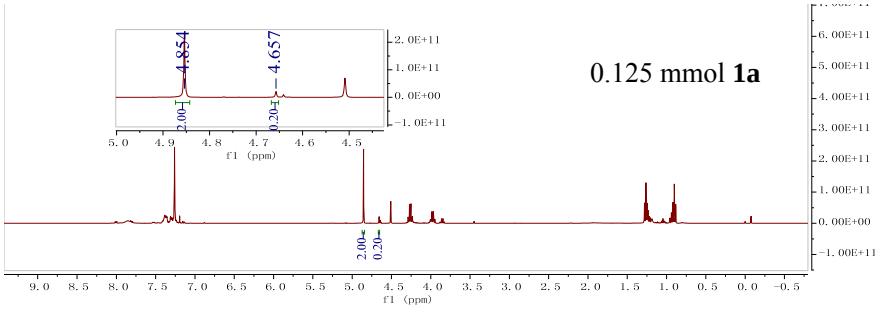
0.05 mmol **1a**



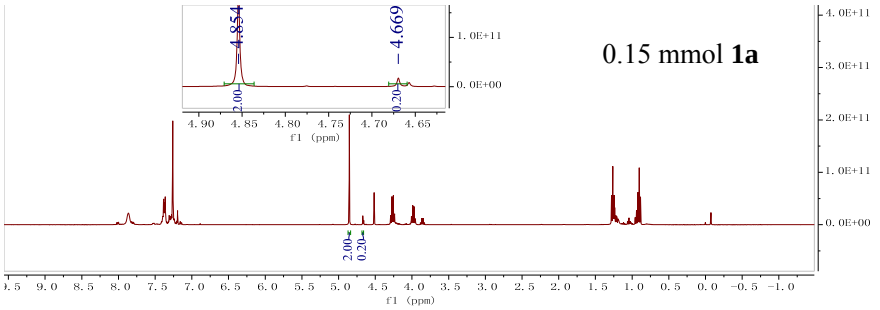
0.075 mmol **1a**



0.1 mmol **1a**

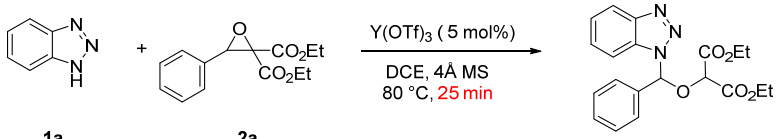


0.125 mmol **1a**



0.15 mmol **1a**

2) Order in 2a



1a 0.1 mmol + **2a** 0.05-0.15 mmol → **3a**

The reaction was performed in a 15 mL pressure tube, **2a** (13.2-39.6mg, 0.05-0.15 mmol) were dissolved in DCE (2 mL), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) were added respectively and the tube was sealed. The reaction mixture was stirred at 80 °C for 25 min. The yields were determined by ^1H NMR using CH_2Br_2 as an internal standard.

entry	**2a** (mmol)	yield (%)
1	0	0
2	0.05	12
3	0.075	15
4	0.1	20
5	0.125	25
6	0.15	26

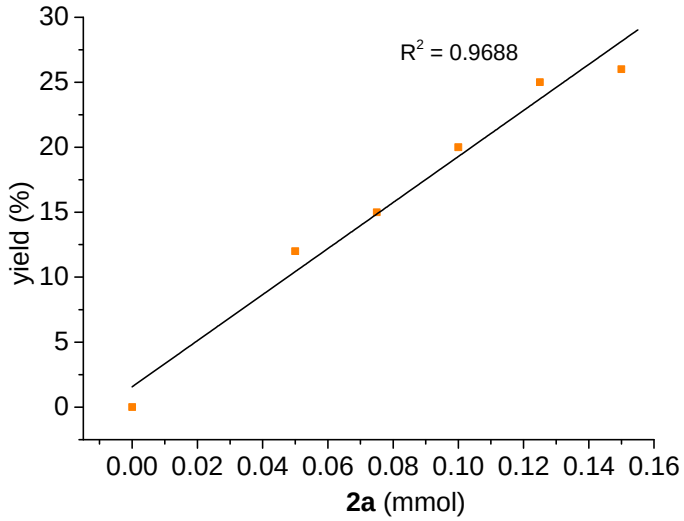
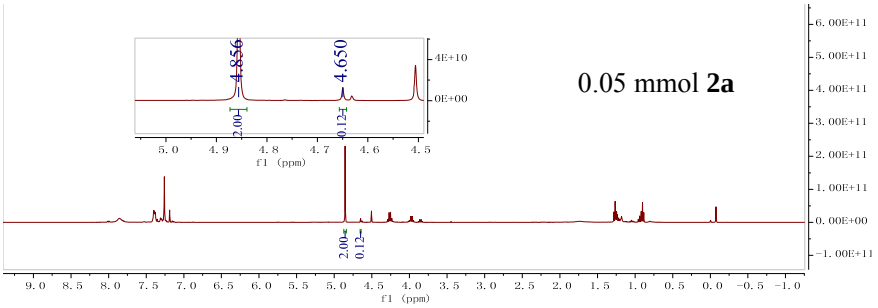
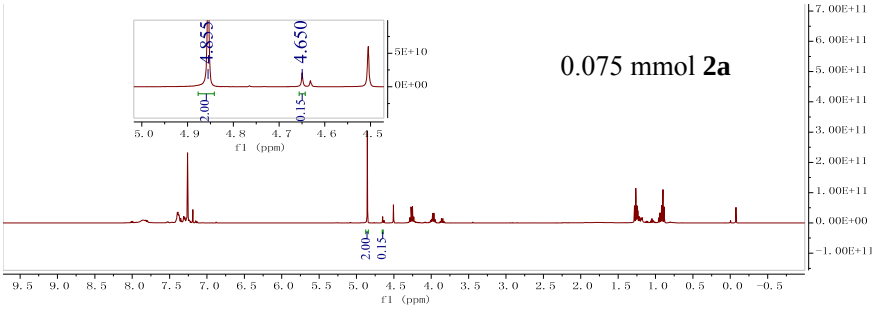


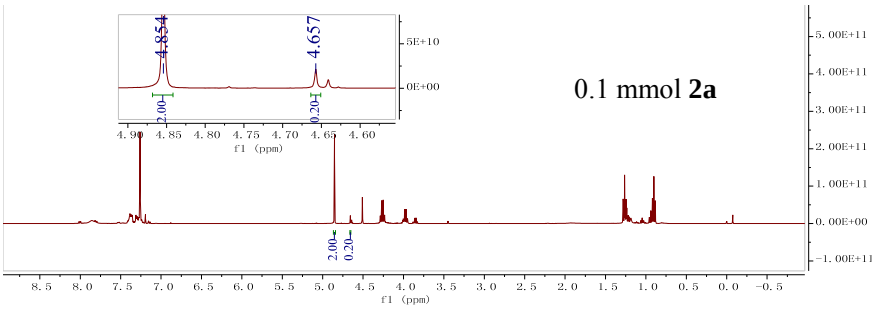
Figure S12. Plot of initial rates versus concentration of **2a**.



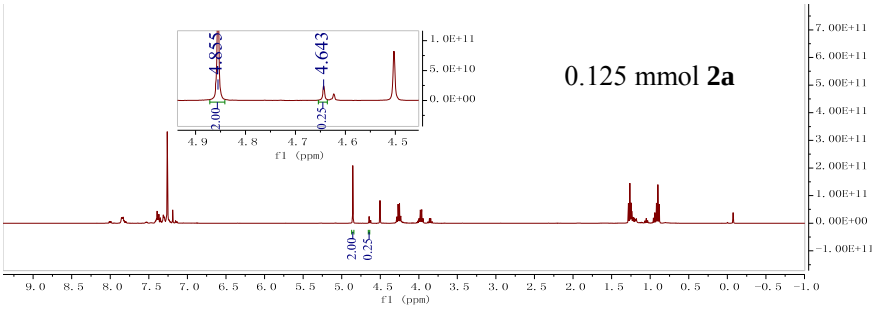
0.05 mmol **2a**



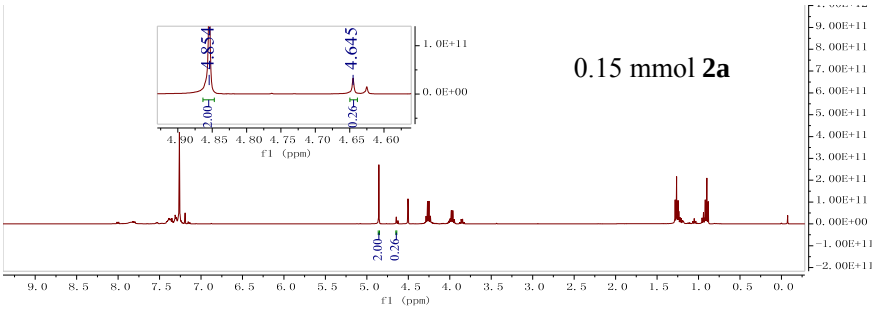
0.075 mmol **2a**



0.1 mmol **2a**

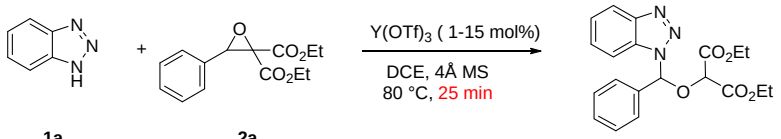


0.125 mmol **2a**



0.15 mmol **2a**

3) Order in $Y(OTf)_3$



1a 0.1 mmol + **2a** 0.1 mmol → **3a**

The reaction was performed in a 15 mL pressure tube, **2a** (0.1 mmol) were dissolved in DCE (2 mL), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (0.54-8.1 mg, 1-15 mol%), and activated 4Å molecular sieve (30 mg) were added respectively and the tube was sealed. The reaction mixture was stirred at 80 °C for 25 min. The yields were determined by ^1H NMR using CH_2Br_2 as an internal standard.

entry	$Y(OTf)_3$ (mol%)	yield (%)
1	0	0
2	1	4
3	2.5	10
4	3	13
5	4	18
6	5	20
7	7.5	32
8	10	39
9	12.5	46
10	15	53

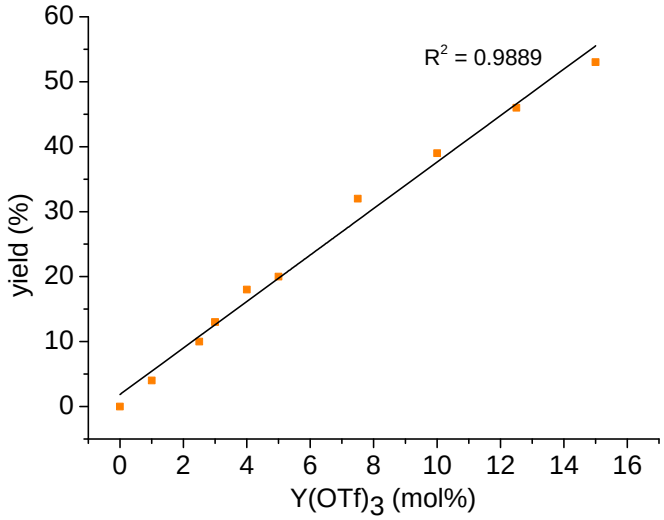
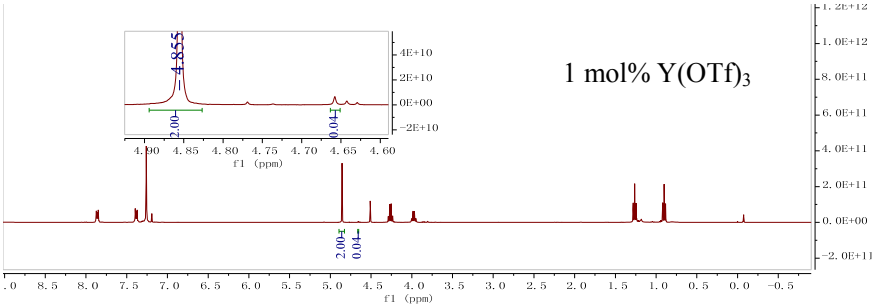
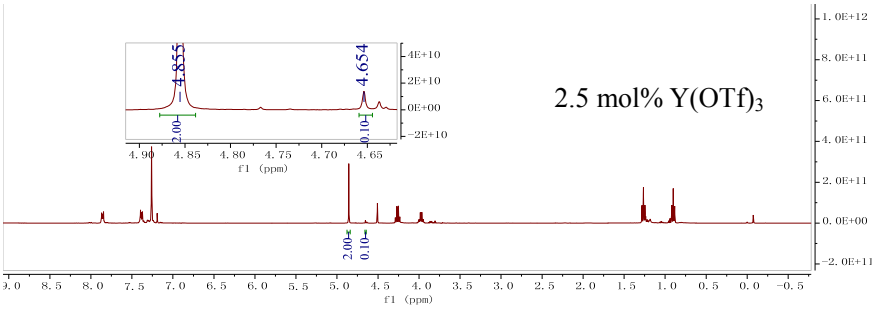
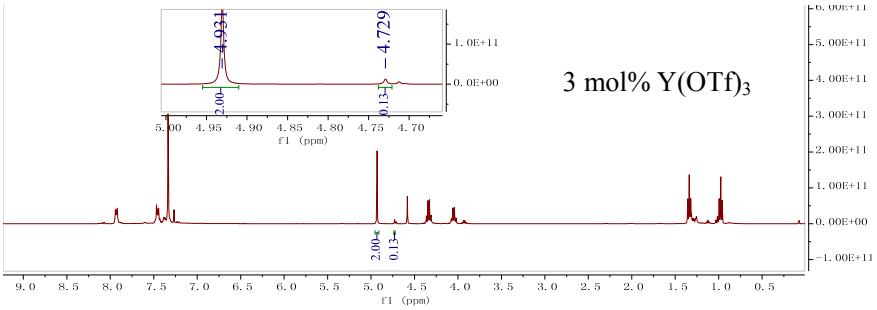
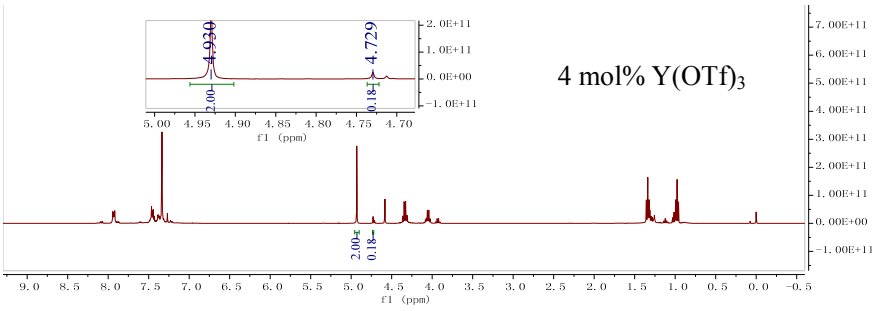


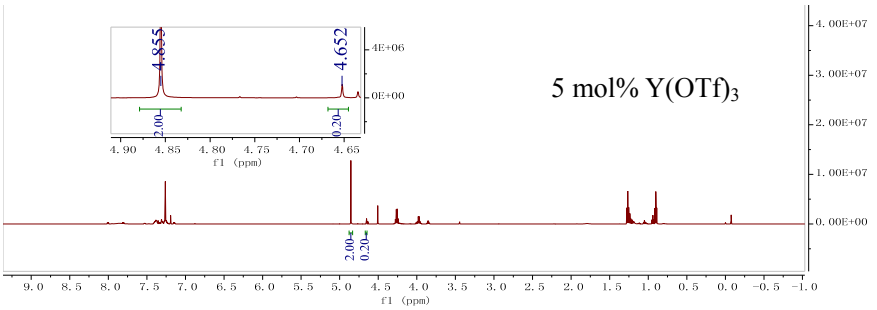
Figure S13. Plot of initial rates versus concentration of $Y(OTf)_3$.

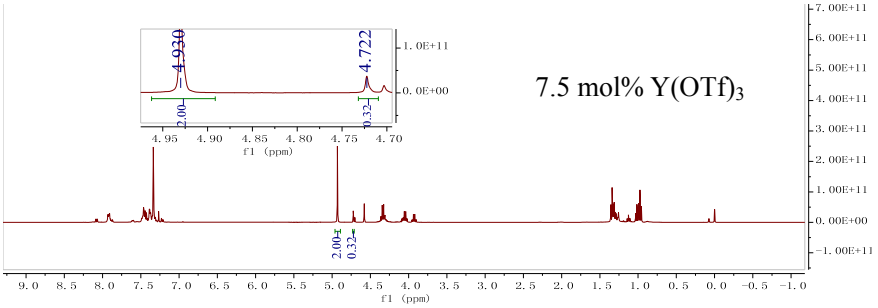

1 mol% Y(OTf)3
4.855
2.00
0.04
f1 (ppm)

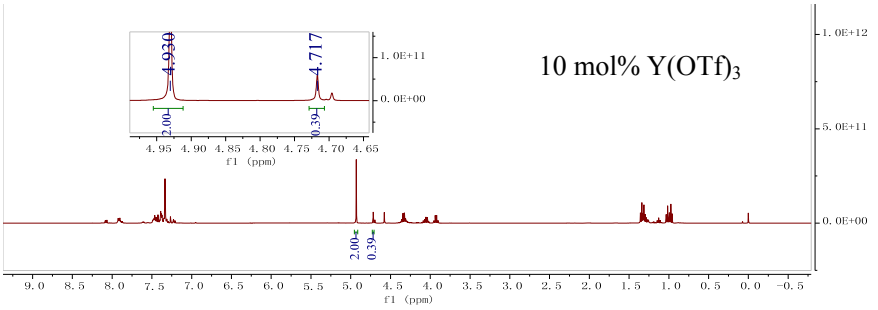

2.5 mol% Y(OTf)3
4.855
4.654
2.00
0.10
f1 (ppm)

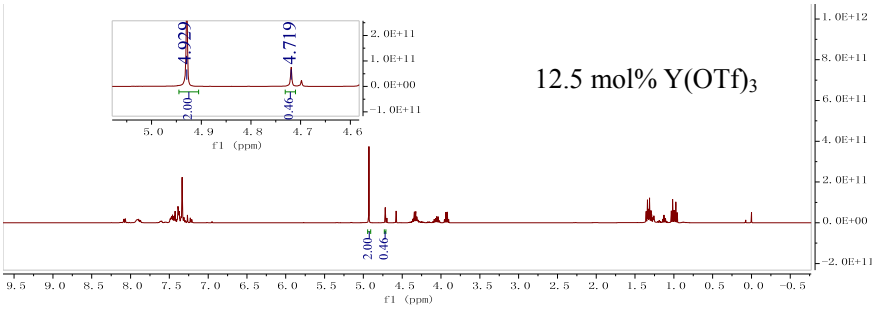

3 mol% Y(OTf)3
4.931
4.729
2.00
0.13
f1 (ppm)

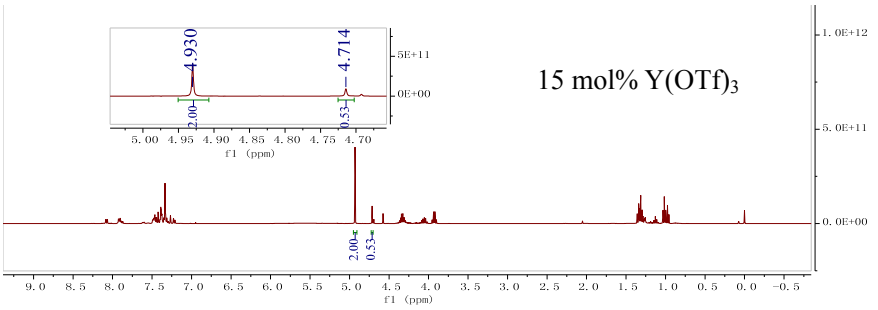

4 mol% Y(OTf)3
4.930
4.729
2.00
0.18
f1 (ppm)


5 mol% Y(OTf)3
4.855
4.652
2.00
0.20
f1 (ppm)


4.930
4.722
2.00
0.32
7.5 mol% Y(OTf)3
f1 (ppm)


4.930
4.717
2.00
0.39
10 mol% Y(OTf)3
f1 (ppm)


4.929
4.719
2.00
0.46
12.5 mol% Y(OTf)3
f1 (ppm)


4.930
4.714
2.00
0.53
15 mol% Y(OTf)3
f1 (ppm)

11. Electronic conductivity experiments

The electronic conductivity of the mixture of D-A oxirane **2a** with $Y(OTf)_3$ (Figure S14) and $Sc(OTf)_3$ (Figure S15) were tracked in the reaction. The test temperature is 40 ℃, the solvent is DCE. Plot the measured data and find the linear intersection point is the conductivity.

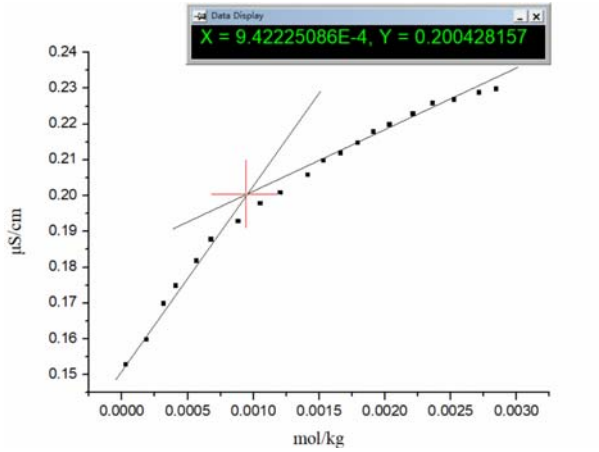


Figure S14

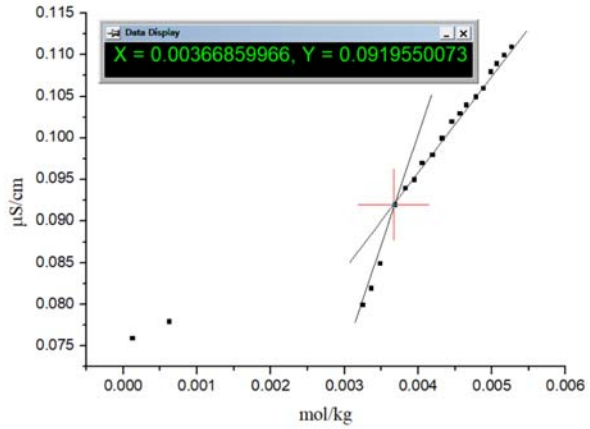
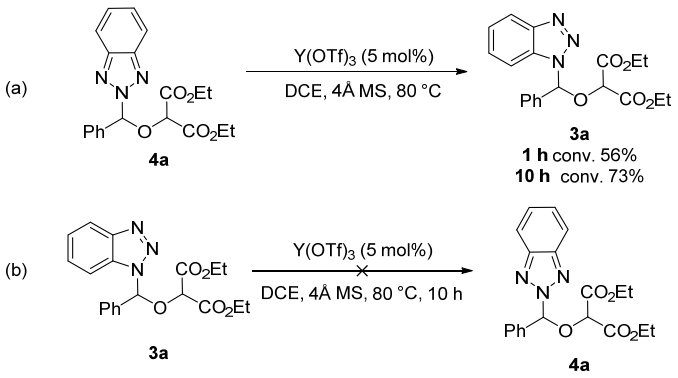


Figure S15

entry	catalyst	T (℃)	solvent	concentration ($mol \cdot kg^{-1}$)	conductivity ($\mu S \cdot cm^{-1}$)
1	$Y(OTf)_3$	40	DCE	0.077	0.200
2	$Sc(OTf)_3$	40	DCE	0.00368	0.092

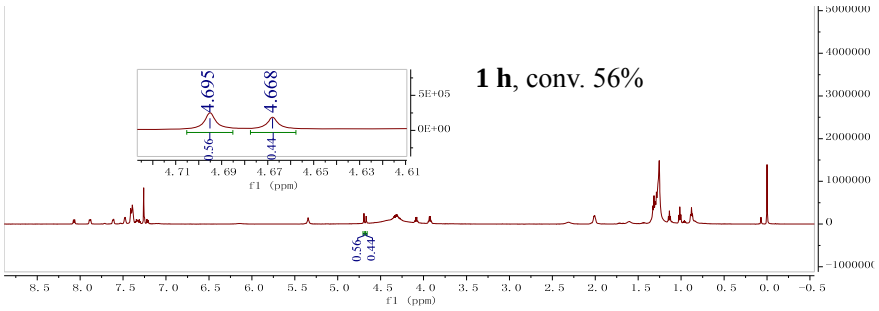
12. Conversion of 4a to 3a

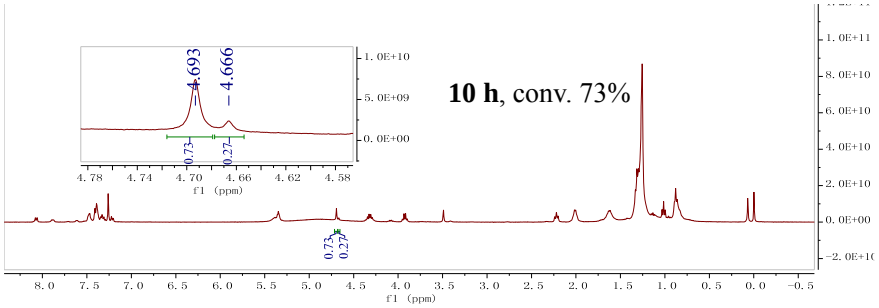


The reaction was performed in a 15 mL pressure tube, **3a** or **4a** (0.05mmol) were dissolved in DCE (1 mL), $Y(OTf)_3$ (1.4 mg, 5 mol%), and activated 4Å molecular sieve (15 mg) were added respectively and the tube was sealed. The reaction mixture was stirred at 80 °C. The conversion rates were determined by ^1H NMR using CH_2Br_2 as an internal standard.

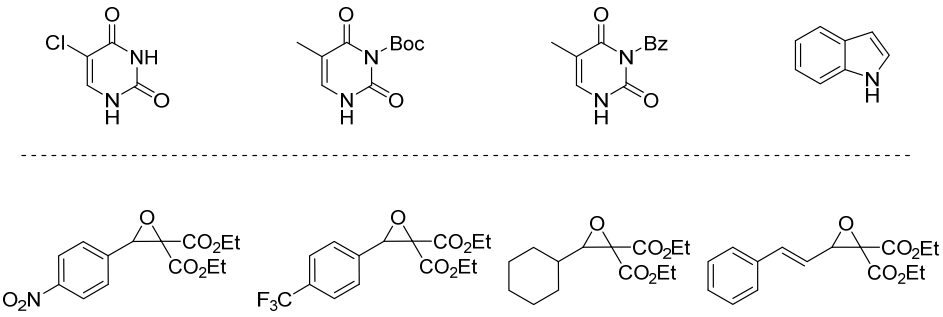
(a) When N^2 alkylated product **4a** was treated with $Y(OTf)_3$ in DCE with 4Å MS at 80 ^oC for 1 h, the N^1 alkylated product **3a** was detected in 56% conversion. When the reaction was prolonged to 10 h, N^1 alkylated product **3a** was observed with 73% conversion.

(b) By contrast, when N^1 alkylated product **3a** was treated with $Y(OTf)_3$ in DCE with 4Å MS at 80 ^oC for 10 h, the N^2 alkylated product **4a** could not be detected.



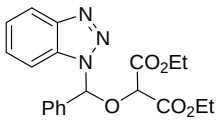


13. Unsuccessful substrates



14. Characterization data of new compounds

Diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenyl)methoxy)malonate (3a)



3a

Prepared according to general procedure A using phenyl oxiranyl dicarboxylate **2a** (26.4 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 4/1, v/v) to give product **3a** as a colorless solid (36.1 mg, 94% yield).

m.p. : 74.5 - 79.6 ^{o}C.

R_f = 0.56 (Pet/EtOAc, 4/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 - 8.05 (m, 1H), 7.49 - 7.46 (m, 2H), 7.41 (s, 1H), 7.40 - 7.36 (m, 3H), 7.34 - 7.29 (m, 2H), 7.22 - 7.20 (m, 1H), 4.70 (s, 1H), 4.37 - 4.28 (m, 2H), 3.92 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H).

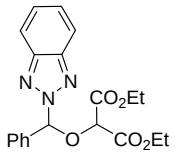
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 164.9, 147.2, 134.8, 131.4, 129.6, 128.8, 128.0, 126.3, 124.6, 120.1, 112.1, 89.3, 76.4, 62.6, 62.2, 14.2, 13.7.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{20}H_{21}N_3NaO_5$ 406.1373; Found 406.1373.

IR(neat): 2988, 1740, 1613, 1500, 1450, 1250, 1017, 734.

Crude ^{1}H NMR Ratio of N^1/N^2 = 96:4

Diethyl 2-((2*H*-benzo[*d*][1,2,3]triazol-2-yl)(phenyl)methoxy)malonate (4a)



4a

Prepared according to general procedure A using phenyl oxiranyl dicarboxylate **2a** (132 mg, 0.5 mmol, 1.0 equiv), benzotriazole **1a** (60 mg, 1 mmol), $Y(OTf)_3$ (13.5 mg, 0.05 mmol, 5 mol%), and activated 4Å molecular sieve (150 mg) in DCM (10 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 4/1, v/v) to give product **4a** as a thick colorless oil (38.3 mg, 20% yield).

R_f = 0.59 (Pet/EtOAc, 4/1, v/v).

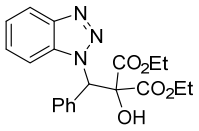
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 - 7.79 (m, 2H), 7.55 - 7.53 (m, 2H), 7.34 - 7.30 (m, 5H), 7.18 (s, 1H), 4.60 (s, 1H), 4.26 - 4.16 (m, 2H), 4.00 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 164.8, 144.7, 135.1, 129.8, 128.6, 127.3, 126.9, 118.8, 93.8, 76.7, 62.6, 62.3, 14.1, 13.9.

HRMS (ESI) m/*z*: $[M + Na]^+$ Calcd for $C_{20}H_{21}N_3NaO_5$ 406.1373; Found 406.1373.

IR(neat): 2985, 1740, 1498, 1450, 1240, 1110, 852.

Diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenyl)methyl)-2-hydroxymalonate (5a)



5a

Prepared according to general procedure A using phenyl oxiranyl dicarboxylate **2a** (264 mg, 1 mmol, 1.0 equiv), benzotriazole **1a** (120 mg, 1 mmol), $Y(OTf)_3$ (27 mg, 0.05 mmol, 5 mol%), and activated 4Å molecular sieve (300 mg) in DCM (20 mL) at room temperature for 24 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **5a** as a colorless solid (42.1 mg, 11% yield).

m.p. : 76.8 - 82.1 ^{o}C.

R_f = 0.42 (Pet/EtOAc, 4/1, v/v).

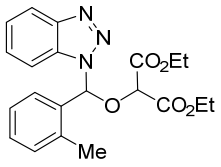
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 - 7.99 (m, 1H), 7.55 - 7.53 (m, 2H), 7.34 - 7.29 (m, 6H), 6.93 (s, 1H), 4.80 (s, 1H), 4.18 (dq, *J* = 7.2, 29.6 Hz, 4H), 1.17 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 167.2, 145.9, 133.3, 133.2, 129.3, 129.2, 128.7, 127.8, 124.3, 120.0, 111.2, 82.6, 65.9, 63.8, 63.3, 13.9, 13.8.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{20}H_{21}N_3NaO_5$ 406.1373; Found 406.1375.

IR(neat): 3360, 2920, 1740, 1629, 1494, 1453, 1260, 1030, 744.

Diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(*o*-tolyl)methoxy)malonate (3b)



3b

Prepared according to general procedure A using aryl oxiranyl dicarboxylate **2b** (27.8 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3b** as a colorless solid (33.4 mg, 84% yield).

m.p. : 65.6 - 70.3 ^{o}C.

R_f = 0.50 (Pet/EtOAc, 4/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.44 (s, 1H), 7.42 - 7.25 (m, 4H), 7.12 - 7.09 (m, 2H), 4.81 (s, 1H), 4.35 - 4.27 (m, 2H), 3.92 (q, *J* = 7.2 Hz, 2H), 1.93 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H).

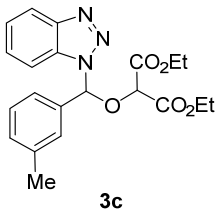
^{13}C NMR (150 MHz, $CDCl_3$) δ 165.8, 165.1, 147.0, 136.2, 132.4, 131.5, 131.3, 129.8, 128.0, 126.7, 126.3, 124.5, 120.1, 111.7, 87.2, 76.4, 62.6, 62.2, 19.0, 14.2, 13.8.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{21}H_{23}N_3NaO_5$ 420.1530; Found 420.1524.

IR(neat): 2988, 1765, 1730, 1606, 1447, 1205, 1078, 810, 750.

Crude ^{1}H NMR Ratio of N^1/N^2 = 94:6

Diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(*m*-tolyl)methoxy)malonate (3c)



3c

Prepared according to general procedure A using aryl oxiranyl dicarboxylate **2c** (27.8 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3c** as a thick colorless oil (31.8 mg, 80% yield).

R_f = 0.55 (Pet/EtOAc, 4/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 - 8.06 (m, 1H), 7.37 (s, 1H), 7.35 - 7.30 (m, 3H), 7.27 - 7.23 (m, 3H), 7.20 - 7.17 (m, 1H), 4.68 (s, 1H), 4.37 - 4.28 (m, 2H), 3.92 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H).

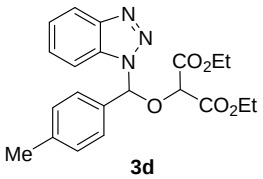
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 164.9, 147.2, 138.6, 134.7, 131.4, 130.3, 128.7, 127.9, 126.9, 124.6, 123.3 120.0, 112.2, 89.4, 76.4, 62.6, 62.2, 21.6, 14.1, 13.7.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{21}H_{23}N_3NaO_5$ 420.1530; Found 420.1530.

IR(neat): 2983, 1743, 1591, 1492, 1450, 1235, 1076, 820, 747.

Crude ^{1}H NMR Ratio of N^1/N^2 = 92:8

Diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(*p*-tolyl)methoxy)malonate (3d)



3d

Prepared according to general procedure A using aryl oxiranyl dicarboxylate **2d** (27.8 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3d** as a thick colorless oil (34.6 mg, 87% yield).

R_f = 0.50 (Pet/EtOAc, 4/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 - 8.05 (m, 1H), 7.37 - 7.29 (m, 5H), 7.25 - 7.22 (m, 1H), 7.18 (d, *J* = 8 Hz, 2H), 4.68 (s, 1H), 4.36 - 4.27 (m, 2H), 3.92 (q, *J* = 7.2 Hz, 2H), 2.35 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.00 (t, *J* = 7.2 Hz, 3H).

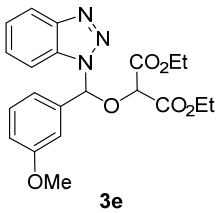
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.0, 147.2, 139.5, 131.8, 131.4, 129.5, 127.9, 126.2, 124.6, 120.0, 112.2, 89.5, 76.5, 62.6, 62.2, 21.4, 14.2, 13.7.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{21}H_{23}N_3NaO_5$ 420.1530; Found 420.1530.

IR(neat): 2983, 1743, 1614, 1492, 1450, 1236, 1077, 830, 747.

Crude ^{1}H NMR Ratio of N^1/N^2 > 95:5

diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(3-methoxyphenyl)methoxy)malonate (3e)



3e

Prepared according to general procedure A using aryl oxiranyl dicarboxylate **2e** (29.4 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3e** as a thick colorless oil (31.4 mg, 76% yield).

R_f = 0.40 (Pet/EtOAc, 3/1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 - 8.05 (m, 1H), 7.37 (s, 1H), 7.35 - 7.31 (m, 2H), 7.29 - 7.26 (m, 2H), 7.09 (s, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.91 (dd, *J* = 3.0, 8.4 Hz, 1H), 4.68 (s, 1H), 4.36 - 4.27 (m, 2H), 3.92 (q, *J* = 7.2 Hz, 1H), 3.77 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H).

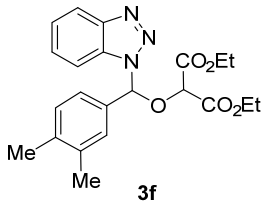
^{13}C NMR (150 MHz, $CDCl_3$) δ 165.8, 164.8, 160.0, 147.1, 136.3, 131.4, 129.9, 127.9, 124.6, 120.0, 118.5, 115.1, 112.1, 112.0, 89.1, 76.5, 62.5, 62.1, 55.4, 14.1, 13.7.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{21}H_{23}N_3NaO_6$ 436.1479; Found 436.1479.

IR(neat): 2983, 1743, 1603, 1236, 1492, 1451, 1076, 814, 748.

Crude ^{1}H NMR Ratio of N^1/N^2 = 93:7

Diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(3,4-dimethylphenyl)methoxy)malonate (3f)



3f

Prepared according to general procedure A using aryl oxiranyl dicarboxylate **2f** (29.2 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3f** as a colorless solid (39.9 mg, 97% yield).

m.p. : 64.7 - 68.3 ^{o}C.

R_f = 0.50 (Pet/EtOAc, 4/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 - 8.04 (m, 1H), 7.35 - 7.26 (m, 5H), 7.17 - 7.10 (m, 2H), 4.67 (s, 1H), 4.36 - 4.27 (m, 2H), 3.91 (q, *J* = 7.2 Hz, 2H), 2.23 (d, *J* = 9.6 Hz, 6H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.00 (t, *J* = 7.2 Hz, 3H).

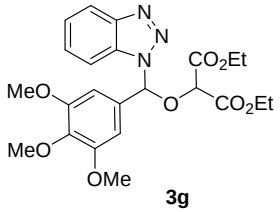
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.0, 147.2, 138.1, 137.2, 132.1, 131.5, 130.0, 127.8, 127.4, 124.6, 123.6, 120.0, 112.3, 89.5, 76.4, 62.6, 62.2, 20.0, 19.7, 14.2, 13.7.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{22}H_{25}N_3NaO_5$ 434.1686; Found 434.1683.

IR(neat): 2990, 1736, 1615, 1494, 1450, 1237, 1085, 803, 742.

Crude ^{1}H NMR Ratio of N^1/N^2 > 95:5

diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(3,4,5-trimethoxyphenyl)methoxy)malonate (3g)



3g

Prepared according to general procedure A using aryl oxiranyl dicarboxylate **2g** (36.0 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3g** as a colorless solid (41.0 mg, 86% yield).

m.p. : 67.2 - 74.3 ^{o}C.

$\mathbf{R_f}$ = 0.33 (Pet/EtOAc, 2/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 - 8.05 (m, 1H), 7.37 - 7.31 (m, 4H), 6.71 (s, 2H), 4.68 (s, 1H), 4.36 - 4.27 (m, 2H), 3.94 - 3.91 (m, 2H), 3.84 (s, 3H), 3.76 (s, 6H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H).

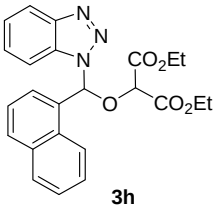
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 164.9, 153.6, 147.2, 138.9, 131.5, 130.2, 128.0, 124.7, 120.0, 112.1, 103.7, 89.3, 89.2, 76.5, 62.6, 62.2, 60.9, 56.3, 14.1, 13.7.

HRMS (ESI) m/*z*: $[M + Na]^+$ Calcd for $C_{23}H_{27}N_3NaO_8$ 496.1690; Found 496.1690.

IR(neat): 2985, 1746, 1593, 1491, 1452, 1229, 1082, 800, 761.

Crude ^{1}H NMR Ratio of N^1/N^2 >95:5

Diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(naphthalen-1-yl)methoxy)malonate (3h)



3h

Prepared according to general procedure A using aryl oxiranyl dicarboxylate **2h** (31.4 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3h** as a thick colorless oil (39.0 mg, 90% yield).

R_f = 0.53 (Pet/EtOAc, 4/1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 (d, *J* = 7.2 Hz, 1H), 8.01 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.83 - 7.81 (m, 2H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 8.4 Hz, 1H), 7.21 (dt, *J* = 7.2, 24.0 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 1H), 4.88 (s, 1H), 4.36 - 4.29 (m, 2H), 3.95 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H).

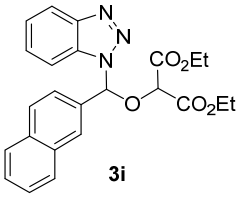
^{13}C NMR (150 MHz, $CDCl_3$) δ 165.8, 165.1, 147.1, 133.8, 131.6, 130.8, 130.1, 129.2, 129.0, 128.0, 127.3, 126.1, 125.2, 125.0, 124.5, 122.3, 120.0, 111.7, 87.1, 76.5, 62.6, 62.2, 14.1, 13.8.

HRMS (ESI) m/*z*: $[M + Na]^+$ Calcd for $C_{24}H_{23}N_3NaO_5$ 456.1530; Found 456.1530.

IR(neat): 2982, 1742, 1611, 1492, 1449, 1234, 1111, 818, 796.

Crude ^{1}H NMR Ratio of N^1/N^2 = 93:7

Diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(naphthalen-2-yl)methoxy)malonate (3i)



3i

Prepared according to general procedure A using aryl oxiranyl dicarboxylate **2i** (31.4 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3i** as a colorless solid (39.0 mg, 90% yield).

m.p. : 94.2 - 98.4 ^{o}C.

R_f = 0.53 (Pet/EtOAc, 4/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.88 - 7.80 (m, 3H), 7.57 (s, 1H), 7.53 - 7.51 (m, 2H), 7.41 - 7.39 (m, 1H), 7.35 - 7.30 (m, 1H), 7.27 - 7.20 (m, 2H), 4.77 (s, 1H), 4.39 - 4.30 (m, 2H), 3.94 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H).

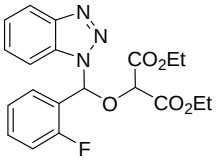
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.0, 147.3, 133.7, 133.0, 132.0, 131.5, 128.9, 128.7, 128.0, 127.8, 127.1, 126.8, 126.0, 124.7, 123.4, 120.1, 112.1, 89.4, 76.5, 62.7, 62.3 14.2, 13.7.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{24}H_{23}N_3NaO_5$ 456.1530; Found 456.1530.

IR(neat): 2995, 1749, 1605, 1495, 1473, 1234, 1071, 795, 749

Crude ^{1}H NMR Ratio of N^1/N^2 = 95:5

Diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(2-fluorophenyl)methoxy)malonate (3j)



3j

Prepared according to general procedure A using aryl oxiranyl dicarboxylate **2j** (28.2 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 100 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3j** as a colorless solid (28.1 mg, 70% yield).

m.p. : 54.5 - 60.6 ^{o}C.

R_f = 0.55 (Pet/EtOAc, 4/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 - 8.14 (m, 1H), 8.07 - 8.04 (m, 1H), 7.58 (s, 1H), 7.43 - 7.39 (m, 1H), 7.36 - 7.32 (m, 3H), 7.28 - 7.24 (m, 1H), 7.02 - 6.97 (m, 1H), 4.77 (s, 1H), 4.36 - 4.27 (m, 2H), 3.99 - 3.94 (m, 2H), 1.30 (t, J = 7.2 Hz, 3H), 1.05 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 164.9, 160.0 (d, $^{1}J_{C\text{-}F}$ = 249.2 Hz), 146.9, 131.8 (d, $^{3}J_{C\text{-}F}$ = 8.3 Hz), 131.5, 128.3 (d, $^{4}J_{C\text{-}F}$ = 2.3 Hz), 128.0, 124.5, 124.5, 122.2 (d, $^{3}J_{C\text{-}F}$ = 11.3 Hz), 120.2, 116.0 (d, $^{2}J_{C\text{-}F}$ = 20.2 Hz), 111.1, 84.4 (d, $^{4}J_{C\text{-}F}$ = 2.8 Hz), 76.2, 62.6, 62.3, 14.1, 13.7.

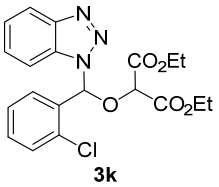
^{19}F NMR (376 MHz, $CDCl_3$): -116.1.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{20}H_{20}FN_3NaO_5$ 424.1279; Found 424.1279.

IR(neat): 2924, 1743, 1617, 1491, 1451, 1380, 1234, 1077, 815, 747.

Crude ^{1}H NMR Ratio of N^1/N^2 = 83:17

Diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(2-chlorophenyl)methoxy)malonate (3k)



3k

Prepared according to general procedure A using aryl oxiranyl dicarboxylate **2k** (29.8 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 100 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3k** as a thick colorless oil (25.9 mg, 62% yield).

R_f = 0.50 (Pet/EtOAc, 4/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 - 8.32 (m, 1H), 8.05 - 8.03 (m, 1H), 7.55 (s, 1H), 7.52 - 7.48 (m, 1H), 7.41 - 7.37 (m, 1H), 7.34 - 7.29 (m, 3H), 7.12 - 7.10 (m, 1H), 4.83 (s, 1H), 4.32 - 4.26 (m, 2H), 3.95 (q, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H).

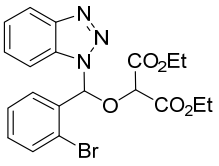
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 165.0, 146.8, 133.1, 132.0, 131.7, 131.2, 130.3, 128.9, 128.0, 127.2, 124.5, 120.2, 111.0, 85.9, 76.3, 62.7, 62.3, 14.1, 13.8.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{20}H_{20}ClN_3NaO_5$ 440.0984; Found 440.0983.

IR(neat): 2984, 1743, 1614, 1492, 1448, 1238, 1070, 811, 746.

Crude ^{1}H NMR Ratio of N^1/N^2 > 95:5

Diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(2-bromophenyl)methoxy)malonate (3l)



3l

Prepared according to general procedure A using aryl oxiranyl dicarboxylate **2l** (34.2 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 100 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3l** as a colorless solid (32.7 mg, 71% yield).

m.p. : 69.3 - 74.7 ^{o}C.

R_f = 0.48 (Pet/EtOAc, 4/1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.8 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.57 - 7.52 (m, 2H), 7.50 (s, 1H), 7.33 - 7.29 (m, 3H), 7.09 (d, *J* = 7.8 Hz, 1H), 4.86 (s, 1H), 4.35 - 4.26 (m, 2H), 3.96 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 7.2 Hz, 3H).

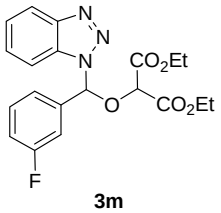
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 165.0, 146.8, 133.7, 133.5, 131.8, 131.4, 129.4, 128.1, 127.8, 124.5, 122.7, 120.3, 111.0, 87.6, 76.3, 62.7, 62.3, 14.1, 13.8.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{20}H_{20}BrN_3NaO_5$ 484.0479; Found 484.0476.

IR(neat): 2985, 1761, 1600, 1490, 1448, 1238, 1068, 854, 747.

Crude ^{1}H NMR Ratio of N^1/N^2 > 95:5

Diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(3-fluorophenyl)methoxy)malonate (3m)



3m

Prepared according to general procedure A using aryl oxiranyl dicarboxylate **2m** (28.2 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 100 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3m** as a thick colorless oil (30.1 mg, 75% yield).

R_f = 0.53 (Pet/EtOAc, 4/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 - 8.06 (m, 1H), 7.38 (s, 1H), 7.36 - 7.29 (m, 4H), 7.23 - 7.21 (m, 1H), 7.15 - 7.12 (m, 1H), 7.10 - 7.05 (m, 1H), 4.66 (s, 1H), 4.34 - 4.27 (m, 2H), 3.93 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 164.7, 163.0 (d, $^1J_{C\text{-}F}$ = 245.6 Hz), 147.2, 137.3 (d, $^3J_{C\text{-}F}$ = 7.8 Hz), 131.3, 130.5 (d, $^3J_{C\text{-}F}$ = 7.9 Hz), 128.2, 124.8, 122.0 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 120.2, 116.6 (d, $^2J_{C\text{-}F}$ = 21.0 Hz), 113.8 (d, $^2J_{C\text{-}F}$ = 23.6 Hz), 111.9, 88.4 (d, $^4J_{C\text{-}F}$ = 2.5 Hz), 76.3, 62.7, 62.3, 14.1, 13.7.

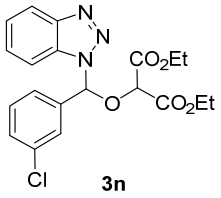
^{19}F NMR (376 MHz, $CDCl_3$): -111.5.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{20}H_{20}FN_3NaO_5$ 424.1279; Found 424.1280.

IR(neat): 2984, 1743, 1615, 1490, 1447, 1236, 1074, 859, 747.

Crude ^{1}H NMR Ratio of N^1/N^2 > 95:5

Diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(3-chlorophenyl)methoxy)malonate (3n)



3n

Prepared according to general procedure A using aryl oxiranyl dicarboxylate **2n** (29.8 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 100 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3n** as a thick colorless oil (30.9 mg, 74% yield).

R_f = 0.50 (Pet/EtOAc, 4/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 - 8.02 (m, 1H), 7.55 (s, 1H), 7.33 - 7.29 (m, 4H), 7.24 - 7.17 (m, 3H), 4.61 (s, 1H), 4.32 - 4.23 (m, 2H), 3.92 - 3.86 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H).

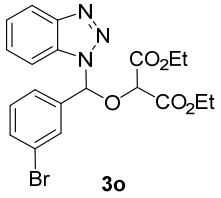
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 164.7, 147.2, 136.8, 135.0, 131.2, 130.2, 129.8, 128.2, 126.7, 124.8, 124.5, 120.2, 111.9, 88.4, 76.3, 62.7, 62.3, 14.1, 13.7.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{20}H_{20}ClN_3NaO_5$ 440.0984; Found 440.0985.

IR(neat): 2983, 1743, 1616, 1492, 1450, 1236, 1076, 859, 748.

Crude ^{1}H NMR Ratio of N^1/N^2 > 95:5

Diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(3-bromophenyl)methoxy)malonate (3o)



3o

Prepared according to general procedure A using aryl oxiranyl dicarboxylate **2o** (34.2 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 100 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3o** as a thick colorless oil (35.0 mg, 76% yield).

R_f = 0.55 (Pet/EtOAc, 3/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 - 8.07 (m, 1H), 7.76 (s, 1H), 7.53 - 7.50 (m, 1H), 7.37 - 7.34 (m, 3H), 7.29 - 7.20 (m, 3H), 4.65 (s, 1H), 4.37 - 4.28 (m, 2H), 3.97 - 3.91 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H).

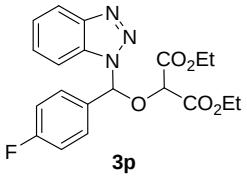
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 164.7, 147.3, 137.0, 132.8, 131.2, 130.4, 129.5, 128.2, 125.0, 124.8, 123.1, 120.3, 111.9, 88.3, 76.3, 62.8, 62.3, 14.2, 13.8.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{20}H_{20}BrN_3NaO_5$ 484.0479; Found 484.0479.

IR(neat): 2984, 1743, 1613, 1492, 1450, 1236, 1076, 859, 748.

Crude ^{1}H NMR Ratio of N^1/N^2 > 95:5

Diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(4-fluorophenyl)methoxy)malonate (3p)



3p

Prepared according to general procedure A using aryl oxiranyl dicarboxylate **2p** (28.2 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3p** as a thick colorless oil (34.5 mg, 86% yield).

R_f = 0.51 (Pet/EtOAc, 4/1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.2 Hz, 1H), 7.47 - 7.45 (m, 2H), 7.38 (s, 1H), 7.36 - 7.32 (m, 2H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 8.4 Hz, 2H), 4.67 (s, 1H), 4.37 - 4.27 (m, 2H), 3.95 - 3.91 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 165.8, 163.4, (d, $^1J_{C\text{-}F}$ = 247.2 Hz), 162.6, 147.3, 131.3, 130.7, (d, $^3J_{C\text{-}F}$ = 3.5 Hz), 128.4, (d, $^2J_{C\text{-}F}$ = 8.0 Hz), 128.1, 124.8, 120.2, 116.0, 115.8, 112.0, 88.8, 76.3, 62.7, 62.3, 14.2, 13.8.

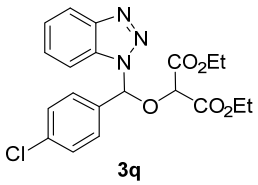
^{19}F NMR (376 MHz, $CDCl_3$): -111.8.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{20}H_{20}FN_3NaO_5$ 424.1279; Found 424.1279.

IR(neat): 2983, 1743, 1614, 1492, 1450, 1236, 1073, 859, 748.

Crude ^{1}H NMR Ratio of N^1/N^2 = 94:6

Diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(4-chlorophenyl)methoxy)malonate (3q)



3q

Prepared according to general procedure A using aryl oxiranyl dicarboxylate **2q** (29.8 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3q** as a thick colorless oil (33.8 mg, 81% yield).

R_f = 0.56 (Pet/EtOAc, 3/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 - 8.07 (m, 1H), 7.42 - 7.33 (m, 7H), 7.21 - 7.19 (m, 1H), 4.67 (s, 1H), 4.37 - 4.27 (m, 2H), 3.96 - 3.91 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H).

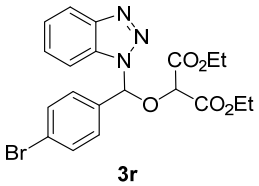
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 164.7, 147.3, 135.7, 133.4, 131.3, 129.1, 128.2, 127.8, 124.8, 120.2, 111.9, 88.7, 76.3, 62.7, 62.3, 14.2, 13.8.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{20}H_{20}ClN_3NaO_5$ 440.0984; Found 440.0987.

IR(neat): 2985, 1743, 1616, 1493, 1450, 1236, 1090 859, 747.

Crude ^{1}H NMR Ratio of N^1/N^2 = 93:7

Diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(4-bromophenyl)methoxy)malonate (3r)



3r

Prepared according to general procedure A using aryl oxiranyl dicarboxylate **2r** (34.2 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3r** as a thick colorless oil (36.9 mg, 80% yield).

R_f = 0.52 (Pet/EtOAc, 3/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 - 8.06 (m, 1H), 7.53 - 7.50 (m, 2H), 7.37 - 7.32 (m, 5H), 7.21 - 7.19 (m, 1H), 4.66 (s, 1H), 4.35 - 4.28 (m, 2H), 3.96 - 3.90 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H).

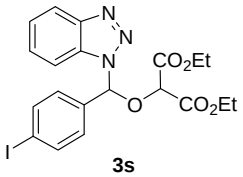
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 164.7, 147.3, 133.9, 132.1, 131.3, 128.2, 128.1, 124.8, 123.9, 120.3, 111.9, 88.7, 76.3, 62.8, 62.3, 14.2, 13.8.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{20}H_{20}BrN_3NaO_5$ 484.0479; Found 484.0474.

IR(neat): 2984, 1743, 1616, 1493, 1450, 1236, 1090, 859, 747.

Crude ^{1}H NMR Ratio of N^1/N^2 > 95:5

Diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(4-iodophenyl)methoxy)malonate (3s)



3s

Prepared according to general procedure A using aryl oxiranyl dicarboxylate **2s** (39.0 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3s** as a thick colorless oil (40.7 mg, 80% yield).

R_f = 0.49 (Pet/EtOAc, 3/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 - 8.06 (m, 1H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.38 - 7.32 (m, 3H), 7.20 (d, *J* = 8.4 Hz, 3H), 4.66 (s, 1H), 4.36 - 4.27 (m, 2H), 3.96 - 3.90 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H).

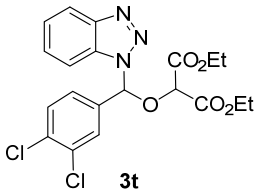
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 164.7, 147.3, 138.0, 134.6, 131.3, 128.2, 128.2, 124.8, 120.2, 111.9, 95.8, 88.8, 76.3, 62.7, 62.3, 14.2, 13.8.

HRMS (ESI) m/*z*: $[M + Na]^+$ Calcd for $C_{20}H_{20}IN_3NaO_5$ 532.0340; Found 532.0340.

IR(neat): 2983, 1743, 1614, 1490, 1450, 1235, 1108, 860, 747.

Crude ^{1}H NMR Ratio of N^1/N^2 > 95:5

Diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(3,4-dichlorophenyl)methoxy)malonate (3t)



3t

Prepared according to general procedure A using aryl oxiranyl dicarboxylate **2t** (33.2 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3t** as a colorless solid (34.3 mg, 76% yield).

m.p. : 63.1 - 69.4 ^{o}C.

R_f = 0.51 (Pet/EtOAc, 4/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 - 8.07 (m, 1H), 7.69 - 7.68 (m, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.38 - 7.34 (m, 3H), 7.24 - 7.17 (m, 2H), 4.64 (s, 1H), 4.37 - 4.27 (m, 2H), 3.97 - 3.92 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H).

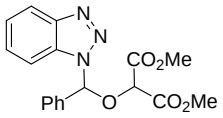
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 164.5, 147.3, 135.0, 134.0, 133.4, 131.1, 130.9, 128.6, 128.4, 125.7, 124.9, 120.3, 111.7, 87.9, 76.2, 62.8, 62.4, 14.1, 13.7.

HRMS (ESI) m/*z*: $[M + Na]^+$ Calcd for $C_{20}H_{19}Cl_2N_3NaO_5$ 474.0594; Found 474.0596.

IR(neat): 2987, 1743, 1616, 1485, 1450, 1236, 1109, 829, 748.

Crude ^{1}H NMR Ratio of N^1/N^2 >95:5

Dimethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenyl)methoxy)malonate (3u)



3u

Prepared according to general procedure A using phenyl oxiranyl dicarboxylate **2u** (23.6 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3u** as a thick colorless oil (24.9 mg, 70% yield).

R_f = 0.50 (Pet/EtOAc, 4/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 - 8.06 (m, 1H), 7.49 - 7.47 (m, 2H), 7.41 - 7.36 (m, 4H), 7.35 - 7.30 (m, 2H), 7.20 - 7.17 (m, 1H), 4.74 (s, 1H), 3.87 (s, 3H), 4.46 (s, 3H).

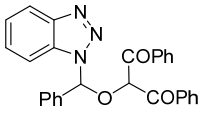
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.3, 147.2, 134.6, 131.4, 129.7, 128.9, 128.0, 126.3, 124.7, 120.1, 112.1, 89.2, 76.2, 53.4, 53.0.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{18}H_{17}N_3NaO_5$ 378.1060; Found 378.1060.

IR(neat): 2953, 1745, 1622, 1465, 1450, 1235, 1110, 859, 746.

Crude ^{1}H NMR Ratio of N^1/N^2 > 95:5

2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenyl)methoxy)-1,3-diphenylpropane-1,3-dione (3v)



3v

Prepared according to general procedure A using phenyl oxiranyl diketone **2v** (33.0 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1a** (12 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by recrystallization at 0 °C using Pet/Et_2O system to give product **3v** as a yellow solid (38.9 mg, 87% yield).

m.p. : 138.7 - 147.9 ^{o}C.

R_f = 0.47 (Pet/EtOAc, 10/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 - 8.00 (m, 3H), 7.64 (d, *J* = 7.2 Hz, 2H), 7.59 - 7.55 (m, 1H), 7.53 - 7.48 (m, 2H), 7.46 - 7.35 (m, 7H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.21 - 7.14 (m, 3H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.01 (s, 1H).

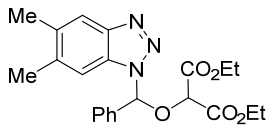
^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 191.7, 134.8, 134.6, 134.4, 134.1, 134.0, 131.5, 129.6, 129.4, 129.0, 128.9, 128.6, 128.0, 126.4, 124.6, 120.2, 111.9, 89.0, 84.8.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{28}H_{21}N_3NaO_3$ 470.1475; Found 470.1475.

IR(neat): 2955, 1746, 1614, 1495, 1451, 1237, 1110, 858, 731.

Crude ^{1}H NMR Ratio of N^1/N^2 > 95:5

Diethyl 2-((5,6-dimethyl-1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenyl)methoxy)malonate (3w)



3w

Prepared according to general procedure A using phenyl oxiranyl dicarboxylate **2a** (26.4 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1b** (14.7 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3w** as a colorless solid (37.4 mg, 91% yield).

m.p. : 67.9 - 76.0 ^{o}C.

R_f = 0.50 (Pet/EtOAc, 3/1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.46 - 7.44 (m, 2H), 7.36 (t, *J* = 3.6 Hz, 3H), 7.34 (s, 1H), 6.95 (s, 1H), 4.67 (s, 1H), 4.33 - 4.29 (m, 2H), 3.94 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 2.23 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H).

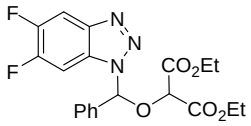
^{13}C NMR (150 MHz, $CDCl_3$) δ 165.9, 164.9, 146.4, 138.3, 134.9, 134.4, 130.4, 129.4, 128.7, 126.3, 119.1, 111.3, 89.1, 76.3, 62.5, 62.2, 20.9, 20.5, 14.1, 13.7.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{22}H_{25}N_3NaO_5$ 434.1686; Found 434.1678.

IR(neat): 2954, 1749, 1629, 1499, 1453, 1237, 1090, 871, 725.

Crude ^{1}H NMR Ratio of N^1/N^2 =95:5

Diethyl 2-((5,6-difluoro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenyl)methoxy)malonate (3x)



3x

Prepared according to general procedure A using phenyl oxiranyl dicarboxylate **2a** (26.4 mg, 0.1 mmol, 1.0 equiv), benzotriazole **1c** (15.5 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **3x** as a white solid (35.6 mg, 85% yield).

m.p. : 60.1 - 71.3 ^{o}C.

R_f = 0.55 (Pet/EtOAc, 4/1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 - 7.80 (m, 1H), 7.45 - 7.39 (m, 5H), 7.36 (s, 1H), 7.01 - 6.98 (m, 1H), 4.70 (s, 1H), 4.36 - 4.29 (m, 2H), 4.03 - 3.99 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 165.6, 164.8, 151.4 (dd, $J_{C\text{-}F}$ = 16.5, 312.9 Hz), 149.7 (dd, $J_{C\text{-}F}$ = 17.0, 309.3 Hz), 142.3 (d, $J_{C\text{-}F}$ = 9.6 Hz), 134.1, 130.0, 129.1, 127.3 (d, $J_{C\text{-}F}$ = 11.9 Hz), 126.2, 106.5 (d, $J_{C\text{-}F}$ = 20.0 Hz), 99.6 (d, $J_{C\text{-}F}$ = 23.9 Hz), 89.5, 76.6, 62.8, 62.4, 14.1, 13.8.

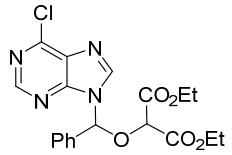
^{19}F NMR (565 MHz, $CDCl_3$): -130.8, -130.9, -137.0, -137.0.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{20}H_{19}F_2N_3NaO_5$ 442.1185; Found 442.1186.

IR(neat): 2985, 1765, 1603, 1497, 1455, 1240, 1097, 853, 721.

Crude ^{1}H NMR Ratio of N^1/N^2 > 95:5

Diethyl 2-((6-chloro-9*H*-purin-9-yl)(phenyl)methoxy)malonate (7a)



7a

Prepared according to general procedure A using phenyl oxiranyl dicarboxylate **2a** (26.4 mg, 0.1 mmol, 1.0 equiv), purine **6a** (15.4 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **7a** as a colorless solid (27.2 mg, 65% yield).

m.p. : 77.3 - 86.7 ^{o}C.

$\mathbf{R_f}$ = 0.55 (Pet/EtOAc, 2/1, v/v).

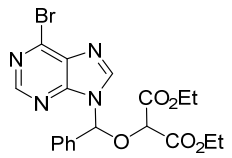
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.12 (s, 1H), 7.52 - 7.50 (m, 2H), 7.42 (t, *J* = 3.2Hz, 3H), 7.18 (s, 1H), 4.81 (s, 1H), 4.34 - 4.25(m, 2H), 4.10 - 4.01 (m, 2H), 1.29 (t, *J* = 7.2Hz, 3H), 1.13 (t, *J* = 7.2Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 165.0, 152.6, 152.3, 151.6, 144.0, 135.2, 131.4, 130.1, 129.2, 126.3, 84.1, 77.5, 62.7, 62.6, 14.1, 13.9.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{19}H_{19}ClN_4NaO_5$ 441.0936; Found 441.0927.

IR(neat): 2985, 1744, 1601, 1585, 1491, 1453, 1231, 1100, 856, 735.

Diethyl 2-((6-bromo-9*H*-purin-9-yl)(phenyl)methoxy)malonate (7b)



7b

Prepared according to general procedure A using phenyl oxiranyl dicarboxylate **2a** (26.4 mg, 0.1 mmol, 1.0 equiv), purine **6b** (19.7 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **7b** as a thick colorless oil (31.0 mg, 67% yield).

R_f = 0.53 (Pet/EtOAc, 2/1, v/v).

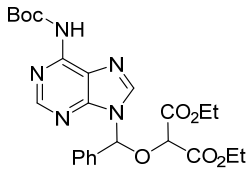
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.13 (s, 1H), 7.51 - 7.49 (m, 2H), 7.43 (t, *J* = 3.2 Hz, 3H), 7.17 (s, 1H), 4.80 (s, 1H), 4.32 - 4.28 (m, 2H), 4.10 - 4.02 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 165.0, 152.6, 151.0, 143.9, 143.6, 135.2, 134.0, 130.1, 129.2, 126.3, 84.1, 77.5, 62.7, 62.6, 14.1, 13.9.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{19}H_{19}BrN_4NaO_5$ 485.0431; Found 485.0429.

IR(neat): 2983, 1742, 1585, 1557, 1453, 1432, 1231, 1107, 857, 735.

Diethyl 2-((6-((*tert*-butoxycarbonyl)amino)-9*H*-purin-9-yl)(phenyl)methoxy)malonate (7c)



7c

Prepared according to general procedure A using phenyl oxiranyl dicarboxylate **2a** (26.4 mg, 0.1 mmol, 1.0 equiv), *N*,*N*-Ditert-butoxycarbonyl-9*H*-purin-6-amine **6c** (33.5 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 2/1, v/v) to give product **7c** as a thick colorless oil (22.5 mg, 45% yield).

R_f = 0.25 (Pet/EtOAc, 1/1, v/v).

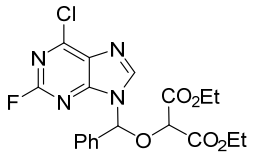
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.20 (s, 1H), 7.92 (s, 1H), 7.51 - 7.50 (m, 2H), 7.42 - 7.41 (m, 3H), 7.15 (s, 1H), 4.84 (s, 1H), 4.31 - 4.28(m, 2H), 4.08 - 4.00 (m, 2H), 1.55 (s, 9H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 165.6, 165.2, 153.6, 151.8, 150.2, 149.8, 141.3, 135.6, 129.9, 129.1, 126.4, 121.2, 83.5, 82.5, 77.5, 62.6, 62.5, 28.3, 14.1, 13.9.

HRMS (ESI) m/*z*: $[M + H]^+$ Calcd for $C_{24}H_{30}N_5O_7$ 500.2140; Found 500.2140.

IR(neat): 3357, 2923, 1744, 1658, 1609, 1453, 1227, 1104, 862, 737.

Diethyl 2-((6-chloro-2-fluoro-9*H*-purin-9-yl)(phenyl)methoxy)malonate (7d)



7d

Prepared according to general procedure A using phenyl oxiranyl dicarboxylate **2a** (26.4 mg, 0.1 mmol, 1.0 equiv), purine **6d** (17.2 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **7d** as a thick colorless oil (33.6 mg, 77% yield).

R_f = 0.53 (Pet/EtOAc, 2/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.51 - 7.49 (m, 2H), 7.45 - 7.42 (m, 3H), 7.04 (s, 1H), 4.76 (s, 1H), 4.31 - 4.28 (m, 2H), 4.12 - 4.09 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.17 (t, *J* = 7.2 Hz, 3H).

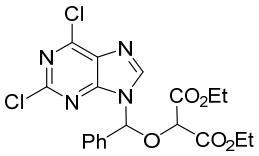
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 165.0, 157.6 (d, $^1J_{C\text{-}F}$ = 220.3 Hz), 154.0 (d, $^2J_{C\text{-}F}$ = 16.7 Hz), 153.3 (d, $^2J_{C\text{-}F}$ = 17.3 Hz), 144.5 (d, $^3J_{C\text{-}F}$ = 3.0 Hz), 134.8, 130.3, 130.1 (d, $^3J_{C\text{-}F}$ = 5.0 Hz), 129.3, 126.3, 84.3, 77.5, 62.8, 62.7, 14.1, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$): -48.7.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{19}H_{18}ClFN_4NaO_5$ 459.0842; Found 459.0831.

IR(neat): 2985, 1742, 1594, 1497, 1452, 1216, 1104, 924, 731.

Diethyl 2-((2,6-dichloro-9*H*-purin-9-yl)(phenyl)methoxy)malonate (7e)



7e

Prepared according to general procedure A using phenyl oxiranyl dicarboxylate **2a** (26.4 mg, 0.1 mmol, 1.0 equiv), purine **6e** (18.8 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **7e** as a thick colorless oil (35.7 mg, 79% yield).

R_f = 0.55 (Pet/EtOAc, 2/1, v/v).

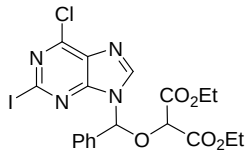
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.49 - 7.48 (m, 2H), 7.43 - 7.41 (m, 3H), 7.08 (s, 1H), 4.76 (s, 1H), 4.34 - 4.26 (m, 2H), 4.13 - 4.05 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 165.0, 153.6, 153.5, 152.2, 144.6, 134.8, 130.6, 130.2, 129.2, 126.3, 84.3, 77.6, 62.8, 62.7, 14.1, 13.9.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{19}H_{18}Cl_2N_4NaO_5$ 475.0546; Found 475.0540.

IR(neat): 2292, 1766, 1588, 1558, 1497, 1450, 1208, 1153, 881, 765.

Diethyl 2-((6-chloro-2-iodo-9*H*-purin-9-yl)(phenyl)methoxy)malonate (7f)



7f

Prepared according to general procedure A using phenyl oxiranyl dicarboxylate **2a** (26.4 mg, 0.1 mmol, 1.0 equiv), purine **6f** (28.0 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **7f** as a thick colorless oil (43.5 mg, 80% yield).

$\mathbf{R_f}$ = 0.48 (Pet/EtOAc, 2/1, v/v).

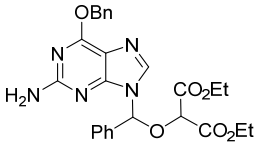
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.49 - 7.46(m, 2H), 7.42 - 7.40 (m, 3H), 7.05 (s, 1H), 4.77(s, 1H), 4.31 - 4.28 (m, 2H), 4.10 - 4.06 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 165.0, 153.2, 149.5, 143.9, 137.8, 134.8, 130.2, 129.2, 126.2, 122.8, 84.2, 62.8, 62.7, 14.1, 13.9.

HRMS (ESI) m/*z*: $[M + Na]^+$ Calcd for $C_{19}H_{18}ClIN_4NaO_5$ 556.9903; Found 556.9903.

IR(neat): 2290, 1749, 1589, 1498, 1450, 1220, 1105, 918, 743.

Diethyl 2-((2-amino-6-(benzyloxy)-9*H*-purin-9-yl)(phenyl)methoxy)malonate (7g)



7g

Prepared according to general procedure A using phenyl oxiranyl dicarboxylate **2a** (26.4 mg, 0.1 mmol, 1.0 equiv), purine **6g** (24.1 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 2/1, v/v) to give product **7g** as a thick colorless oil (20.2 mg, 40% yield).

R_f = 0.33 (Pet/EtOAc, 1/1, v/v).

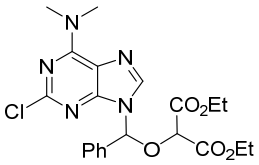
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.52 - 7.46 (m, 4H), 7.40 - 7.30 (m, 6H), 6.93 (s, 1H), 5.57 (s, 2H), 4.95 (s, 2H), 4.81 (s, 1H), 4.35 - 4.26 (m, 2H), 4.06 (q, *J* = 7.2 Hz, 2H). 1.29 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.4, 161.2, 159.7, 154.8, 138.0, 136.4, 136.1, 129.5, 128.8, 128.5, 128.4, 128.2, 126.4, 115.0, 83.0, 77.1, 68.3, 62.5, 62.4, 14.2, 13.9.

HRMS (ESI) m/*z*: $[M + H]^+$ Calcd for $C_{26}H_{28}N_5O_6$ 506.2034; Found 506.2050.

IR(neat): 3452, 3344, 3224, 2980, 1741, 1579, 1470, 1458, 1206, 1142, 996, 790.

Diethyl 2-((2-chloro-6-(dimethylamino)-9*H*-purin-9-yl)(phenyl)methoxy)malonate (7h)



7h

Prepared according to general procedure A using phenyl oxiranyl dicarboxylate **2a** (26.4 mg, 0.1 mmol, 1.0 equiv), purine **6h** (19.7 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **7h** as a thick colorless oil (29.0 mg, 63% yield).

R_f = 0.50 (Pet/EtOAc, 2/1, v/v).

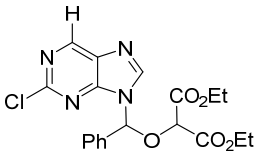
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.49 - 7.47 (m, 2H), 7.40 - 7.38 (m, 3H), 7.03 (s, 1H), 4.78 (s, 1H), 4.36 - 4.28(m, 2H), 4.14 - 4.06 (m, 2H), 3.69 (s, 3H), 3.34 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.4, 155.3, 154.5, 152.5, 137.4, 136.0, 129.6, 128.9, 126.4, 118.5, 83.2, 77.3, 62.6, 62.4, 14.2, 14.0.

HRMS (ESI) m/*z*: $[M + Na]^+$ Calcd for $C_{21}H_{24}ClN_5NaO_5$ 484.1358; Found 484.1357.

IR(neat): 2984, 1765, 1598, 1554, 1498, 1476, 1214, 1280, 1116, 970, 723.

Diethyl 2-((2-chloro-9*H*-purin-9-yl)(phenyl)methoxy)malonate (7i)



7i

Prepared according to general procedure A using phenyl oxiranyl dicarboxylate **2a** (26.4 mg, 0.1 mmol, 1.0 equiv), purine **6i** (15.4 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 3/1, v/v) to give product **7i** as a white solid (21.3 mg, 51% yield).

m.p. : 79.6 - 89.7 ^{o}C.

R_f = 0.55 (Pet/EtOAc, 2/1, v/v).

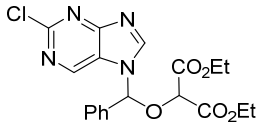
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.07 (s, 1H), 7.51 - 7.50 (m, 2H), 7.43 (t, *J* = 3.6 Hz, 3H), 7.13 (s, 1H), 4.79 (s, 1H), 4.33 - 4.28 (m, 2H), 4.10 - 4.03 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 165.3, 165.1, 155.1, 153.6, 150.7, 144.8, 135.1, 132.9, 130.1, 129.2, 126.3, 83.7, 77.7, 62.8, 62.6, 14.1, 13.9.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{19}H_{19}ClN_4NaO_5$ 441.0936; Found 441.0935.

IR(neat): 2981, 1769, 1593, 1573, 1492, 1449, 1229, 1120, 924, 747.

Diethyl 2-((2-chloro-7*H*-purin-7-yl)(phenyl)methoxy)malonate (7i')



7i'

Prepared according to general procedure A using phenyl oxiranyl dicarboxylate **2a** (26.4 mg, 0.1 mmol, 1.0 equiv), purine **6i** (15.4 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 2/1, v/v) to give product **7i'** as a thick colorless oil (5.85 mg, 14% yield).

R_f = 0.41 (Pet/EtOAc, 1/1, v/v).

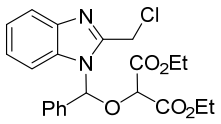
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.29 (s, 1H), 7.49 - 7.44 (m, 5H), 6.86 (s, 1H), 4.63 (s, 1H), 4.31 - 4.15 (m, 4H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 165.1, 163.6, 155.6, 148.4, 144.5, 133.6, 131.0, 129.7, 126.8, 123.6, 87.2, 76.1, 62.9, 14.1, 14.0.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{19}H_{19}ClN_4NaO_5$ 441.0936; Found 441.0932.

IR(neat): 2981, 1770, 1589, 1555, 1498, 1450, 1229, 1119, 925, 747.

Diethyl 2-((2-(chloromethyl)-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methoxy)malonate (7j)



7j

Prepared according to general procedure A using phenyl oxiranyl dicarboxylate **2a** (26.4 mg, 0.1 mmol, 1.0 equiv), imidazole **6j** (16.6 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 5/1, v/v) to give product **7j** as a colorless solid (34.4 mg, 80% yield).

m.p. : 85.7 - 96.0 ^{o}C.

R_f = 0.55 (Pet/EtOAc, 4/1, v/v).

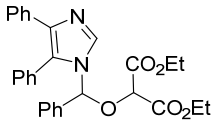
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 - 7.77 (m, 1H), 7.34 - 7.31 (m, 6H), 7.29 - 7.25 (m, 1H), 7.19 - 7.15 (m, 1H), 7.07 (s, 1H), 4.91 (d, *J* = 13.2 Hz, 1H), 4.76 (d, *J* = 12.8 Hz, 1H), 4.68 (s, 1H), 4.35 - 4.25 (m, 2H), 4.05 - 3.99 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 165.0, 149.4, 142.6, 135.8, 134.0, 129.4, 128.9, 126.3, 124.4, 123.5, 120.5, 113.3, 85.1, 75.9, 62.7, 62.4, 37.1, 14.2, 13.9.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{22}H_{23}N_2NaO_5$ 453.1188; Found 453.1188.

IR(neat): 2924, 1760, 1518, 1495, 1450, 1234, 1098, 959, 740.

Diethyl 2-((4,5-diphenyl-1*H*-imidazol-1-yl)(phenyl)methoxy)malonate (7k)



7k

Prepared according to general procedure A using phenyl oxiranyl dicarboxylate **2a** (26.4 mg, 0.1 mmol, 1.0 equiv), imidazole **6k** (22.0 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 5/1, v/v) to give product **7k** as a thick colorless oil (39.2 mg, 81% yield).

R_f = 0.53 (Pet/EtOAc, 4/1, v/v).

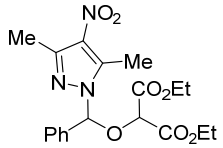
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (m, 1H), 7.52 - 7.49 (m, 2H), 7.43 - 7.41 (m, 3H), 7.37 (s, 5H), 7.33 - 7.30 (m, 2H), 7.24 - 7.16 (m, 3H), 6.22 (s, 1H), 4.51 (s, 1H), 4.23 - 4.08 (m, 4H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.1, 138.1, 137.1, 136.1, 134.1, 131.2, 129.9, 129.4, 129.4, 129.3, 128.8, 128.7, 128.3, 126.8, 126.8, 126.4, 84.6, 76.1, 62.6, 62.4, 14.1.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{29}H_{28}N_2NaO_5$ 507.1890; Found 507.1891.

IR(neat): 2923, 1742, 1603, 1503, 1444, 1231, 1108, 951, 696.

diethyl 2-((3,5-dimethyl-4-nitro-1*H*-pyrazol-1-yl)(phenyl)methoxy)malonate (7l)



7l

Prepared according to general procedure A using phenyl oxiranyl dicarboxylate **2a** (26.4 mg, 0.1 mmol, 1.0 equiv), pyrazole **6l** (16.0 mg, 0.1 mmol), $Y(OTf)_3$ (2.7 mg, 0.005 mmol, 5 mol%), and activated 4Å molecular sieve (30 mg) in DCE (2 mL) at 80 °C for 10 h. Purification by preparative thin layer chromatography using Pet/EtOAc system (Pet/EtOAc, 5/1, v/v) to give product **7l** as a thick colorless oil (37.3 mg, 92% yield).

R_f = 0.50 (Pet/EtOAc, 4/1, v/v).

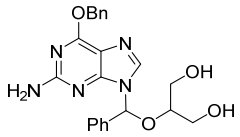
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 - 7.34 (m, 5H), 6.70 (s, 1H), 4.71 (s, 1H), 4.36 - 4.26 (m, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 165.1, 146.0, 142.3, 135.4, 133.2, 129.5, 128.9, 125.8, 92.5, 76.8, 62.7, 62.5, 14.3, 14.2, 14.0, 11.9.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{19}H_{23}N_3NaO_7$ 428.1428; Found 428.1425.

IR(neat): 2983, 1760, 1620, 1550, 1496, 1444, 1371, 1250, 950, 796.

2-((2-amino-6-(benzyloxy)-9*H*-purin-9-yl)(phenyl)methoxy)propane-1,3-diol (8g)



8g

R_f = 0.40 (DCM/MeOH, 10/1, v/v).

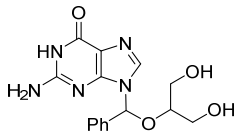
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 - 7.54 (m, 2H), 7.48 - 7.45 (m, 5H), 7.35 - 7.32 (m, 2H), 7.31 - 7.28 (m, 1H), 7.10 (s, 1H), 6.83 (s, 1H), 5.55 (s, 2H), 5.08 (s, 2H), 3.88 (dd, *J* = 3.0, 12.6 Hz, 2H), 3.80 - 3.73 (m, 2H), 3.69 (dd, *J* = 1.8, 4.2 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.6, 159.3, 153.9, 137.8, 136.3, 135.1, 130.3, 129.4, 128.6, 128.4, 128.2, 127.4, 116.1, 83.9, 79.0, 68.4, 62.9, 62.5.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{22}H_{23}N_5NaO_4$ 444.1642; Found 444.1641.

IR(neat): 3450, 3365, 3344, 3325, 3270, 2963, 1580, 1470, 1458, 1210, 1140, 970, 790.

2-amino-9-(((1,3-dihydroxypropan-2-yl)oxy)(phenyl)methyl)-1,9-dihydro-6*H*-purin-6-one (9g)



9g

R_f = 0.35 (DCM/MeOH, 10/1, v/v).

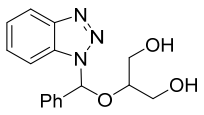
^{1}H NMR (600 MHz, DMSO) δ 10.85 (s, 1H), 7.74 (s, 1H), 7.40 - 7.34 (m, 5H), 6.84 (s, 1H), 6.84 (s, 2H), 4.86 (s, 1H), 4.66 (s, 1H), 3.68 - 3.65 (m, 1H), 3.58 - 3.51 (m, 2H), 3.38 - 3.36 (m, 2H).

^{13}C NMR (150 MHz, DMSO) δ 156.9, 154.1, 151.3, 138.8, 135.1, 128.7, 128.5, 126.0, 116.3, 82.8, 79.9, 61.0, 60.8.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{15}H_{17}N_5NaO_4$ 354.1173; Found 354.1173.

IR(neat): 3449, 3360, 3341, 3330, 3279, 1711, 1631, 1231, 1159, 1470, 1458, 958, 786.

2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenyl)methoxy)propane-1,3-diol (10a)



10a

m.p. : 69.1 - 80.3 ^{o}C.

R_f = 0.32 (Pet/EtOAc, 1/1, v/v).

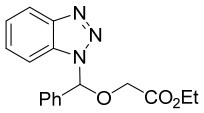
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 - 7.95 (m, 1H), 7.52 (s, 1H), 7.42 - 7.40 (m, 2H), 7.31 (t, *J* = 3.6 Hz, 3H), 7.29 - 7.26 (m, 3H), 4.00 (dd, *J* = 4.8, 12.0 Hz, 1H), 3.93 (dd, *J* = 4.8, 12.0 Hz, 1H), 3.83 - 3.79 (m, 1H), 3.66 (s, 1H), 3.45 (d, *J* = 4.8 Hz, 2H), 2.99 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 146.8, 136.0, 131.4, 129.4, 128.8, 128.0, 126.2, 124.7, 120.1, 111.5, 88.8, 79.1, 62.6, 62.3.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{16}H_{17}N_3NaO_3$ 322.1162; Found 322.1165.

IR(neat): 3364, 3270, 2906, 1611, 1493, 1450, 1281, 1083, 952, 695.

Ethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenyl)methoxy)acetate (11a)



11a

R_f = 0.56 (Pet/EtOAc, 5/1, v/v).

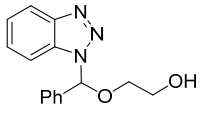
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 - 8.06 (m, 1H), 7.48 - 7.45 (m, 2H), 7.38 - 7.35 (m, 4H), 7.34 - 7.29 (m, 2H), 7.22 - 7.19 (m, 1H), 4.21 - 4.15 (m, 4H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 147.2, 135.4, 131.4, 129.4, 128.8, 127.9, 126.3, 124.5, 120.2, 111.9, 89.4, 65.5, 61.4, 14.2.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{17}H_{17}N_3NaO_3$ 334.1162; Found 334.1160.

IR(neat): 2988, 1740, 1629, 1494, 1450, 1245, 1100, 852, 744.

2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenyl)methoxy)ethan-1-ol (12a)



12a

R_f = 0.48 (Pet/EtOAc, 2/1, v/v).

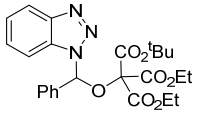
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.8 Hz, 1H), 7.45 - 7.44 (m, 2H), 7.38 - 7.35 (m, 3H), 7.34 - 7.30 (m, 2H), 7.28 (s, 1H), 7.26 (d, *J* = 7.8 Hz, 1H). 3.91 - 3.87 (m, 1H), 3.85 - 3.75 (m, 2H), 3.53 - 3.49 (m, 1H), 2.04 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 135.9, 131.2, 129.4, 128.8, 127.8, 126.1, 124.5, 120.2, 111.5, 89.9, 70.8, 61.6.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{15}H_{15}N_3NaO_2$ 292.1056; Found 292.1056.

IR(neat): 3360, 2981, 1630, 1495, 1450, 1240, 1017, 734.

1-*tert*-butyl 1,1-diethyl ((1*H*-benzo[*d*][1,2,3]triazol-1-yl) (phenyl)methoxy) methanetricarboxylate (13a)



13a

R_f = 0.59 (Pet/EtOAc, 4/1, v/v).

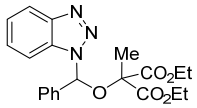
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 - 8.00 (m, 2H), 7.53 - 7.47 (m, 3H), 7.35 - 7.28 (m, 5H), 4.20 - 4.12 (m, 2H), 4.07 - 3.95 (m, 2H), 1.39 (s, 9H), 1.11 (td, *J* = 2.4, 7.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 164.1, 162.6, 146.9, 136.9, 131.6, 129.1, 128.6, 127.6, 126.1, 124.3, 119.7, 112.5, 86.9, 85.8, 85.2, 63.2, 63.1, 27.7, 13.7.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{25}H_{29}N_3NaO_7$ 506.1898; Found 506.1894.

IR(neat): 2982, 1741, 1615, 1495, 1451, 1249, 1114, 934, 734.

diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenyl)methoxy)-2-methylmalonate (14a)



14a

R_f = 0.59 (Pet/EtOAc, 4/1, v/v).

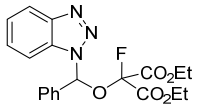
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 - 8.02 (m, 1H), 7.75 (s, 1H), 7.43 - 7.40 (m, 3H), 7.34 - 7.31 (m, 5H), 4.11 - 3.94 (m, 4H), 1.71 (s, 3H), 1.13 (td, *J* = 2.8, 7.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 168.0, 146.9, 136.8, 131.6, 129.2, 128.6, 127.7, 126.2, 124.4, 119.9, 112.3, 86.2, 82.3, 62.6, 62.3, 20.9, 13.9, 13.8.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{21}H_{23}N_3NaO_5$ 420.1530; Found 420.1530.

IR(neat): 2982, 1740, 1617, 1495, 1454, 1232, 1118, 934, 734.

diethyl 2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenyl)methoxy)-2-fluoromalonate (15a)



15a

R_f = 0.59 (Pet/EtOAc, 4/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 - 8.04 (m, 1H), 7.86 (s, 1H), 7.43 - 7.30 (m, 8H), 4.25 (q, *J* = 7.2 Hz, 2H), 4.15 - 4.07 (m, 1H), 3.93 - 3.83 (m, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H).

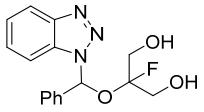
^{13}C NMR (150 MHz, $CDCl_3$) δ 162.2 (d, $^2J_{C\text{-}F}$ = 38.0 Hz), 162.2 (d, $^3J_{C\text{-}F}$ = 6.0 Hz), 146.9, 134.6, 131.5, 129.7, 128.9, 128.1, 126.2, 124.6, 120.1, 111.9, 103.0 (d, $^1J_{C\text{-}F}$ = 164.0 Hz), 84.8 (d, $^3J_{C\text{-}F}$ = 2.0 Hz),63.7, 63.6, 13.9, 13.6.

^{19}F NMR (376 MHz, $CDCl_3$): -121.1.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{20}H_{20}FN_3NaO_5$ 424.1279; Found 424.1277.

IR(neat): 2980, 1765, 1745, 1617, 1495, 1450, 1240, 1111, 934, 734.

2-((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenyl)methoxy)-2-fluoropropane-1,3-diol (16a)



16a

R_f = 0.30 (Pet/EtOAc, 1/1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 - 8.00 (m, 1H), 7.91 (s, 1H), 7.39 - 7.36 (m, 5H), 7.33 - 7.29 (m, 2H), 7.19 - 7.17 (m, 1H), 4.09 - 4.01 (m, 2H), 3.85 (d, *J* = 10.2 Hz, 2H), 3.00 (s, 1H), 2.75 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 146.7, 135.6, 131.6, 129.6, 128.9, 128.1, 126.2, 124.7, 120.1, 114.3 (d, $^1J_{C\text{-}F}$ = 226.5 Hz), 111.7, 83.0 (d, $^3J_{C\text{-}F}$ = 3.0 Hz), 62.4 (d, $^2J_{C\text{-}F}$ = 31.5 Hz)., 62.0 (d, $^2J_{C\text{-}F}$ = 34.5 Hz).

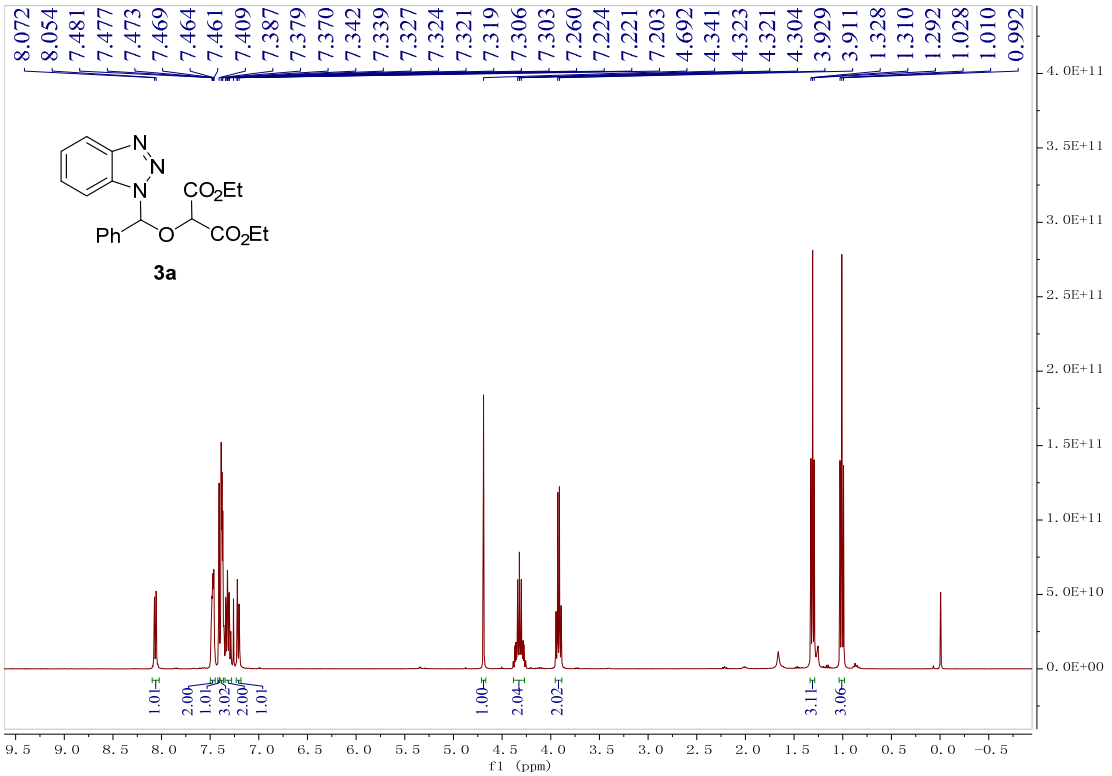
^{19}F NMR (565 MHz, $CDCl_3$): -129.6.

HRMS (ESI) m/z*:* $[M + Na]^+$ Calcd for $C_{16}H_{16}FN_3NaO_3$ 340.1068; Found 340.1068.

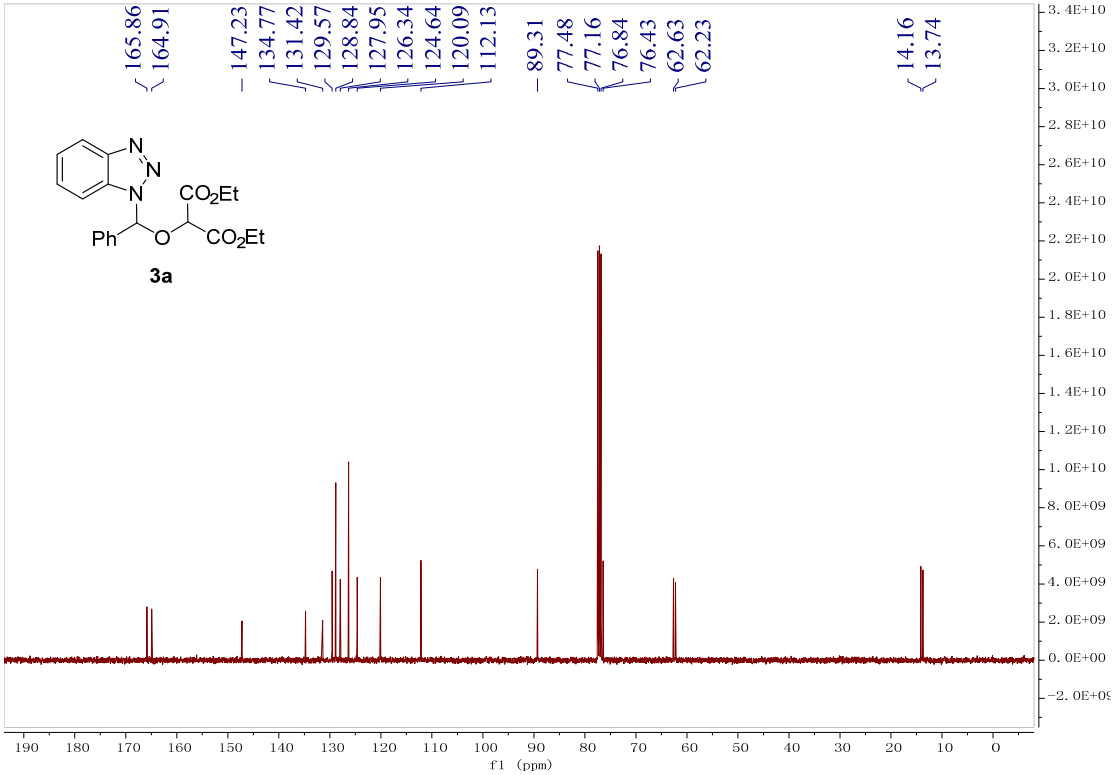
IR(neat): 3393, 2927, 1615, 1496, 1451, 1240, 1058, 937, 731.

15. NMR spectra

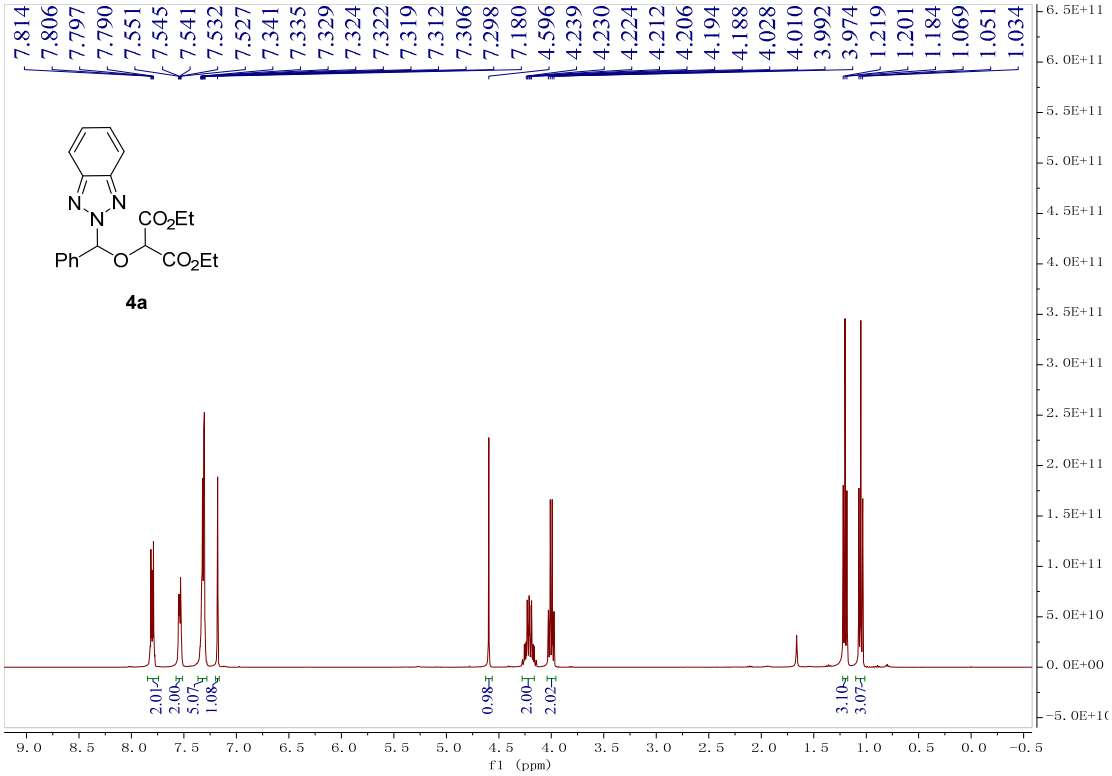
^{1}H NMR (400 MHz, $CDCl_3$) for 3a



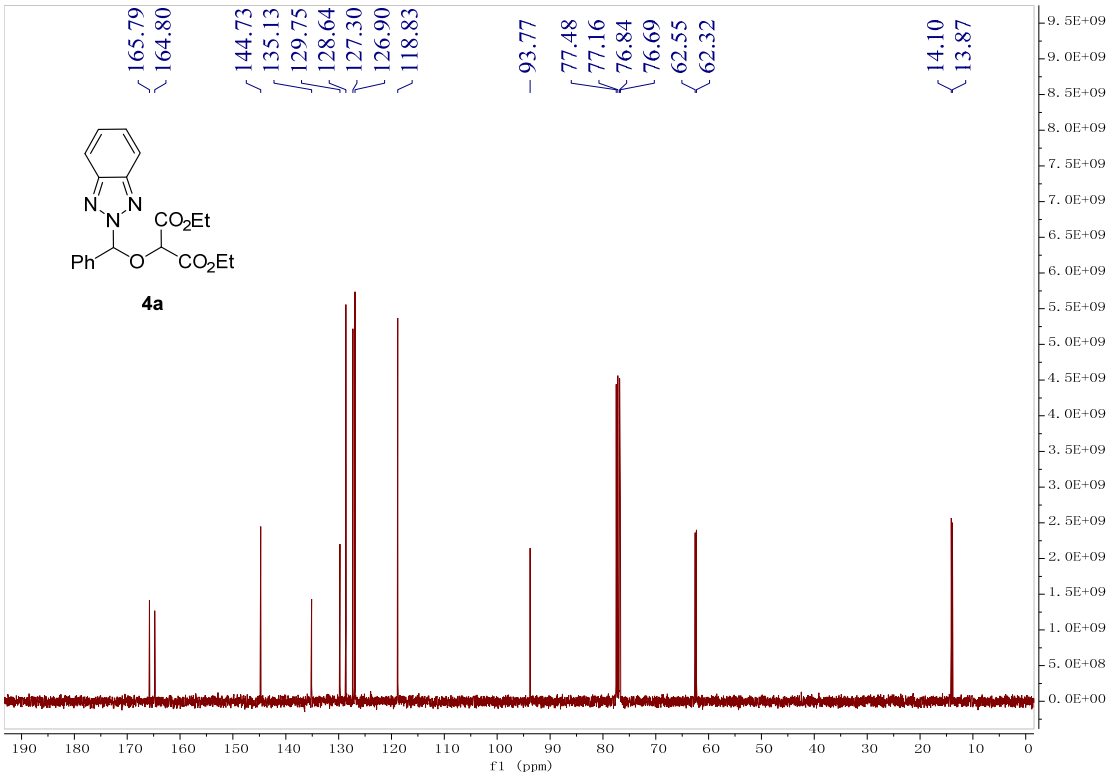
^{13}C NMR (100 MHz, $CDCl_3$) for 3a



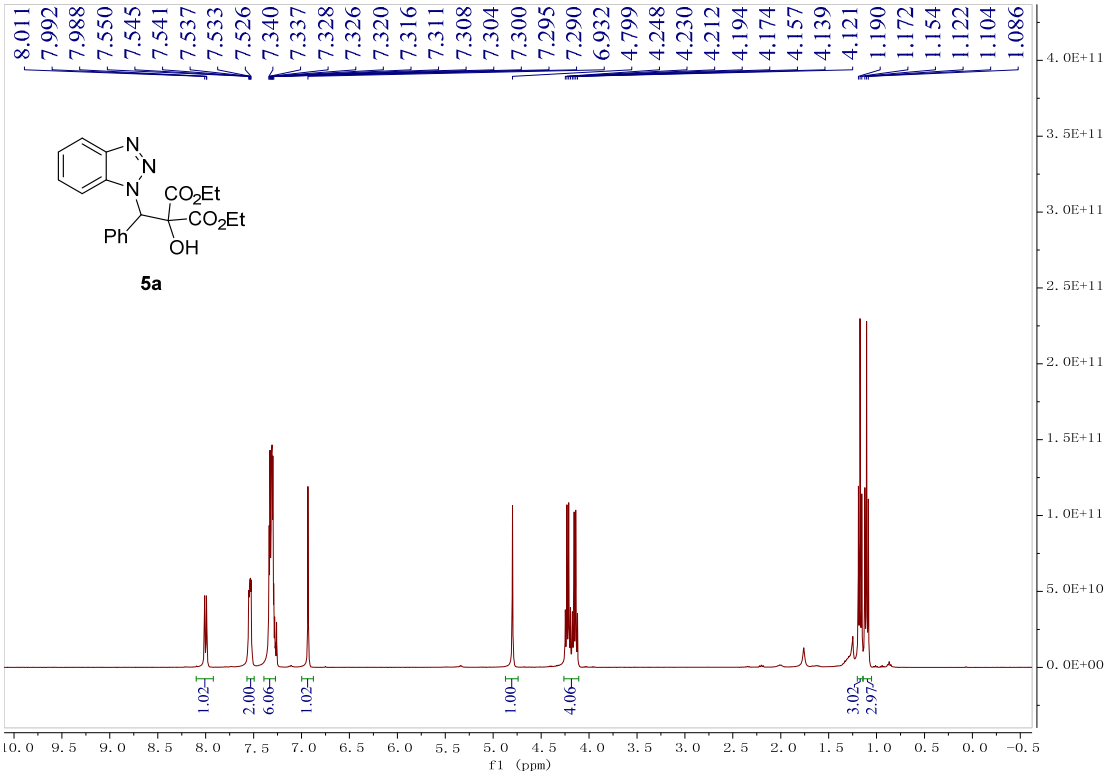
^{1}H NMR (400 MHz, $CDCl_3$) for 4a



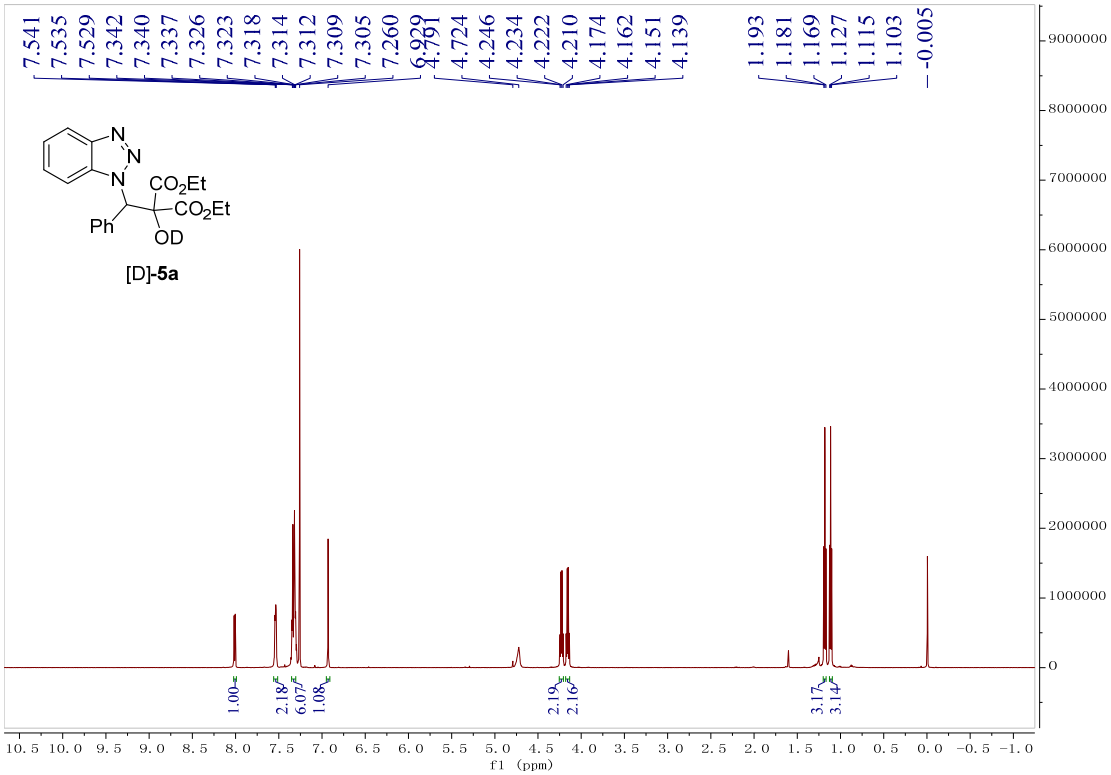
^{13}C NMR (100 MHz, $CDCl_3$) for 4a



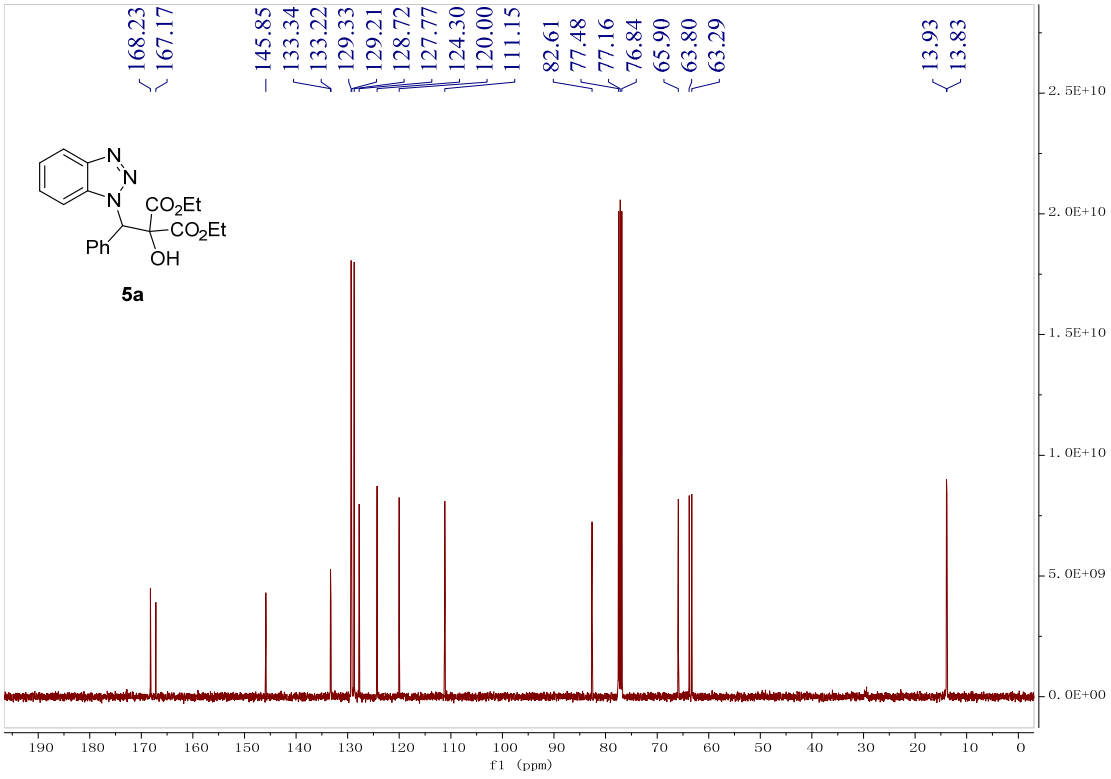
^{1}H NMR (100 MHz, $CDCl_3$) for 5a



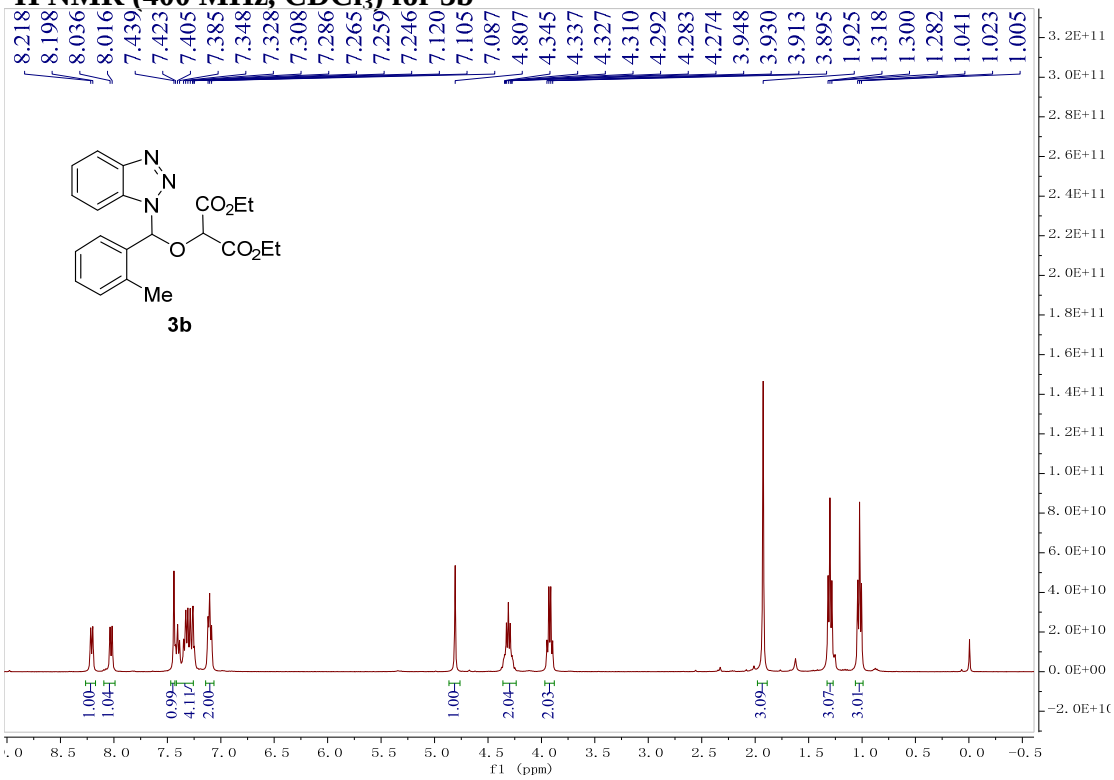
^{1}H NMR (400 MHz, $CDCl_3$) for 5a by D_2O exchange



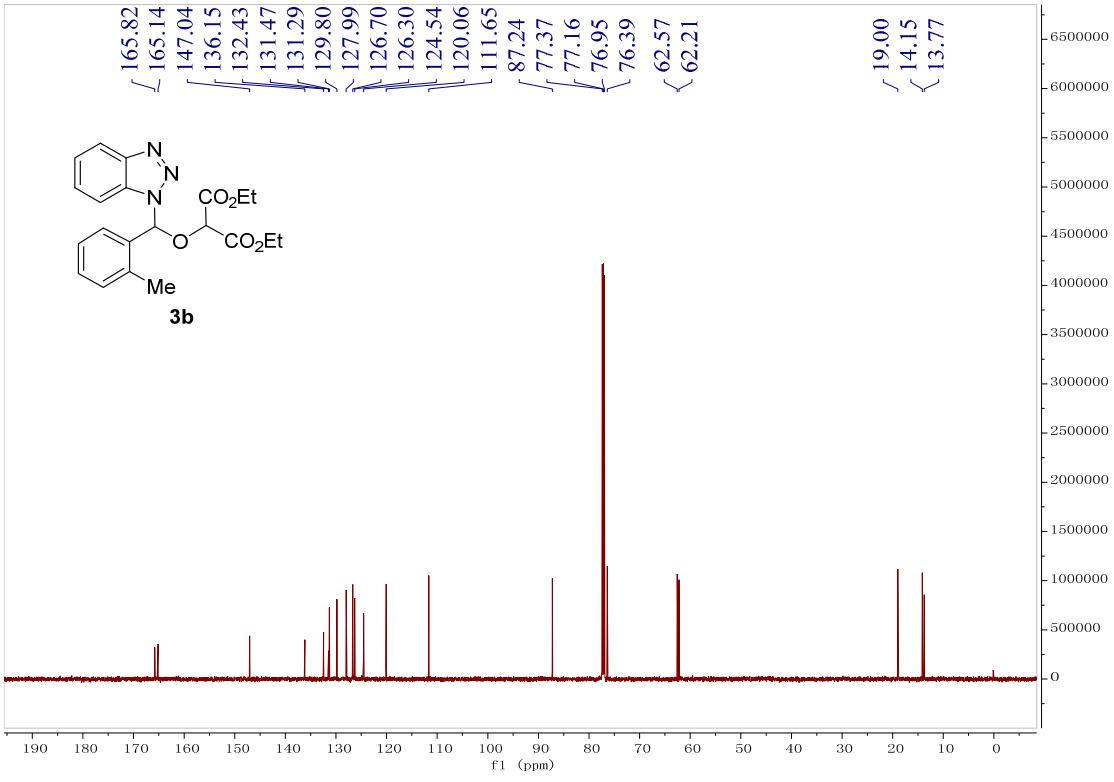
^{13}C NMR (100 MHz, $CDCl_3$) for 5a



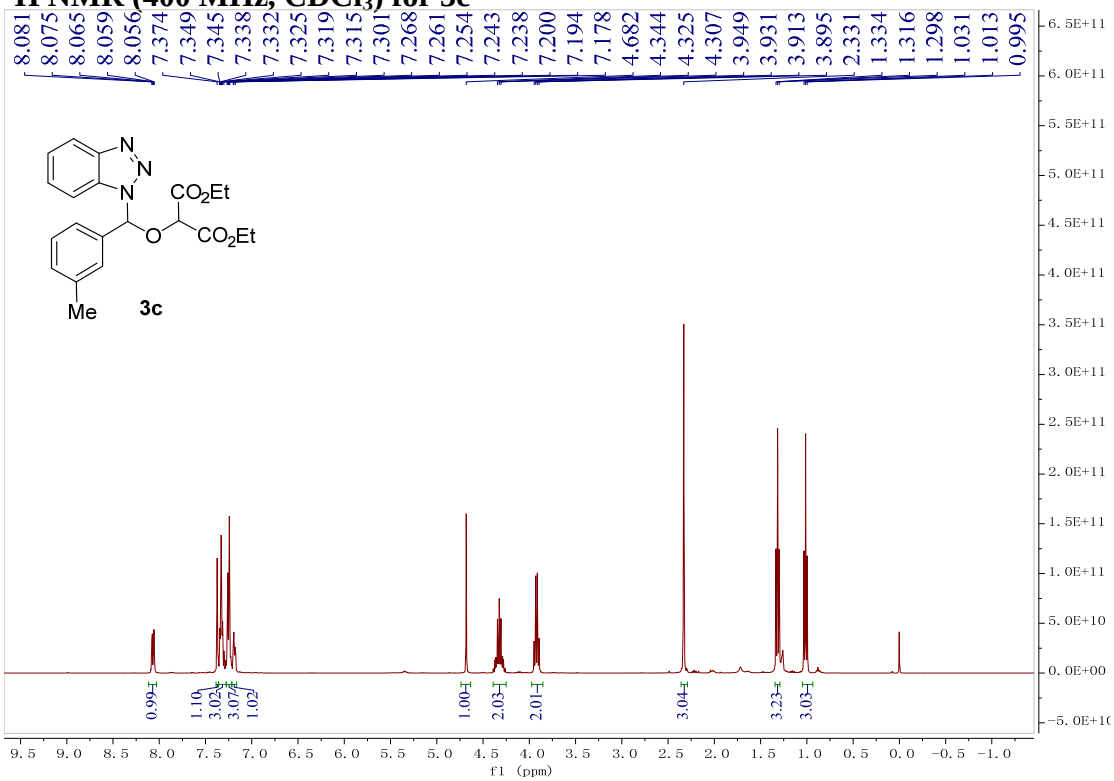
^{1}H NMR (400 MHz, $CDCl_3$) for 3b



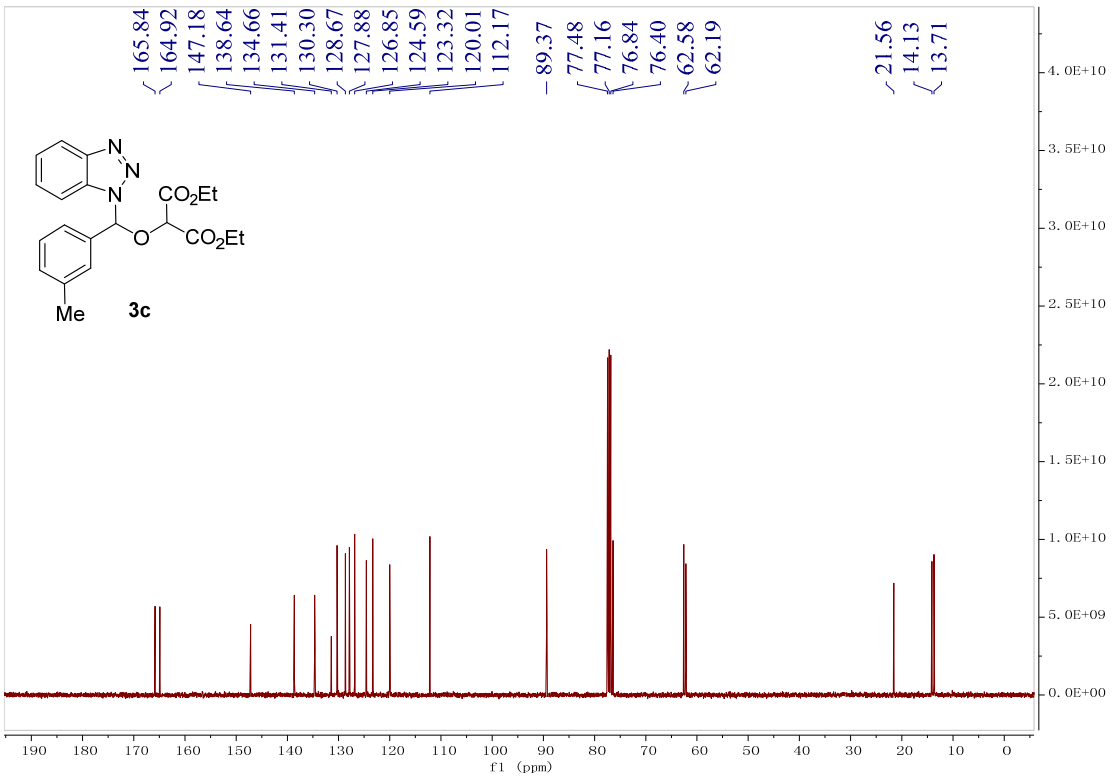
^{13}C NMR (150 MHz, $CDCl_3$) for 3b



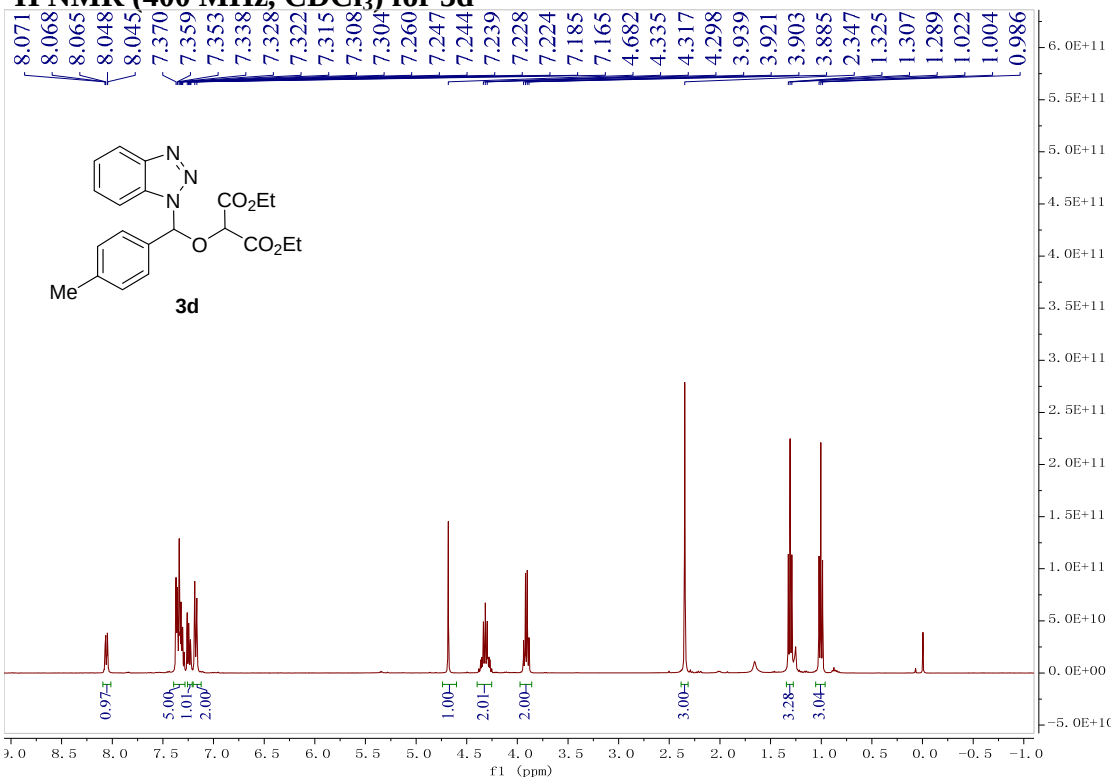
^{1}H NMR (400 MHz, $CDCl_3$) for 3c



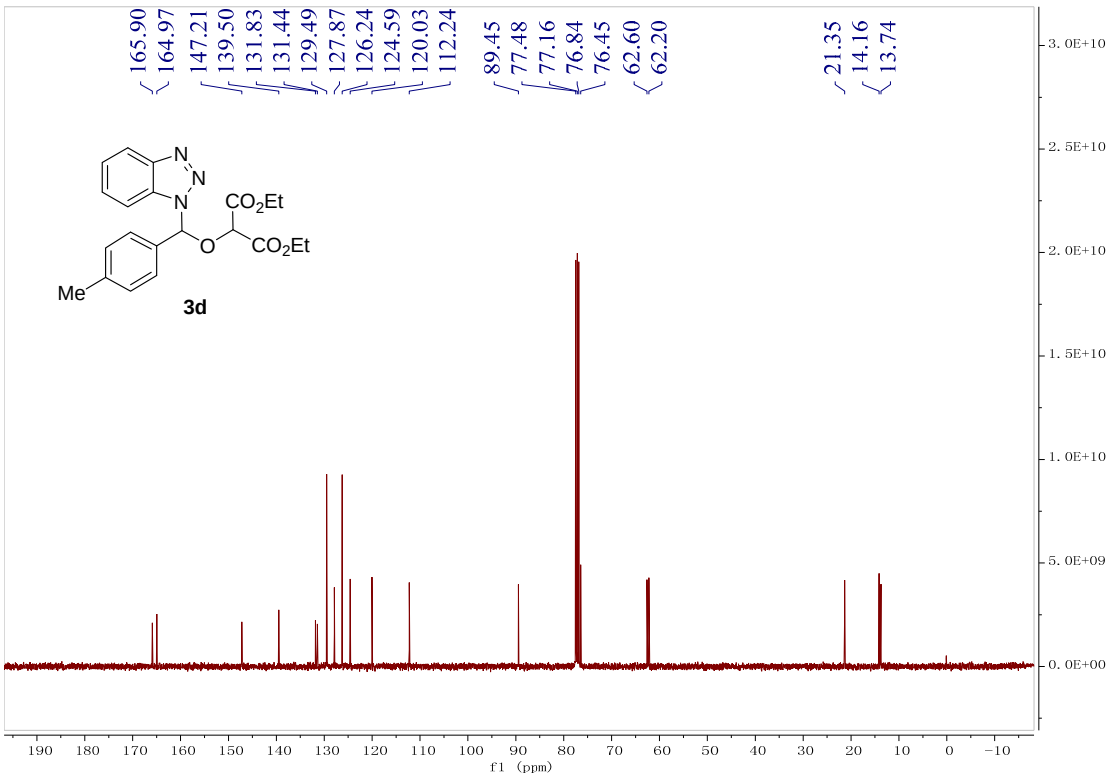
^{13}C NMR (100 MHz, $CDCl_3$) for 3c



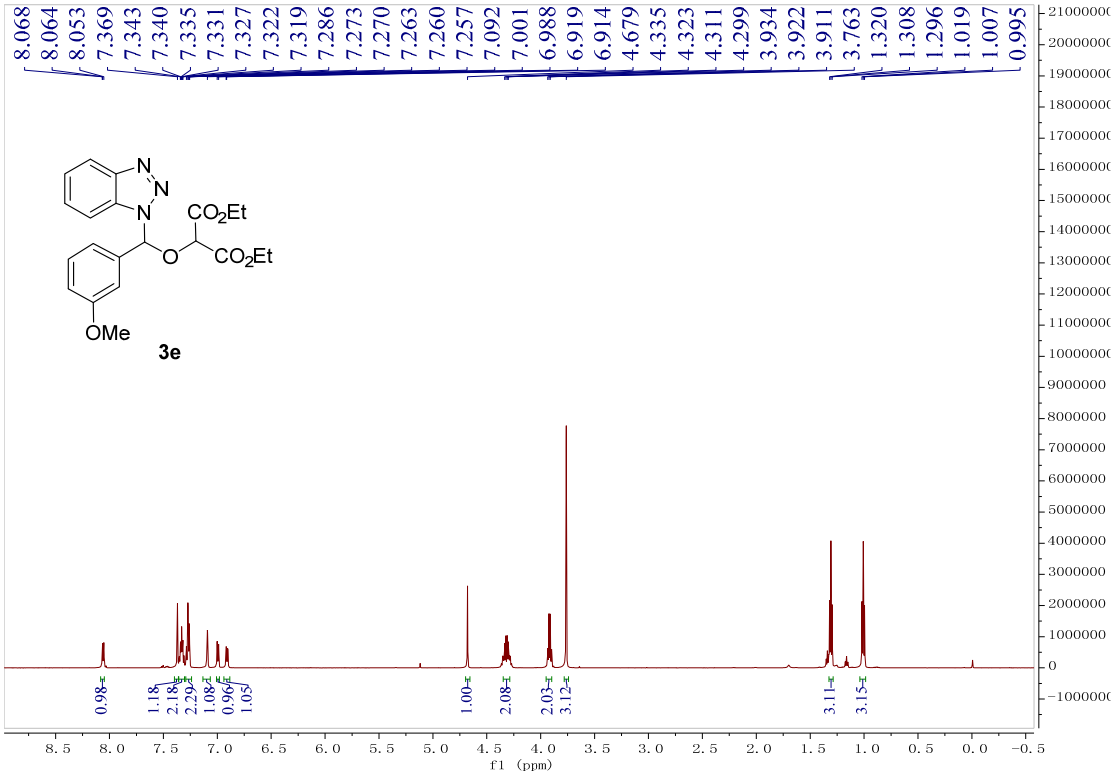
^{1}H NMR (400 MHz, $CDCl_3$) for 3d



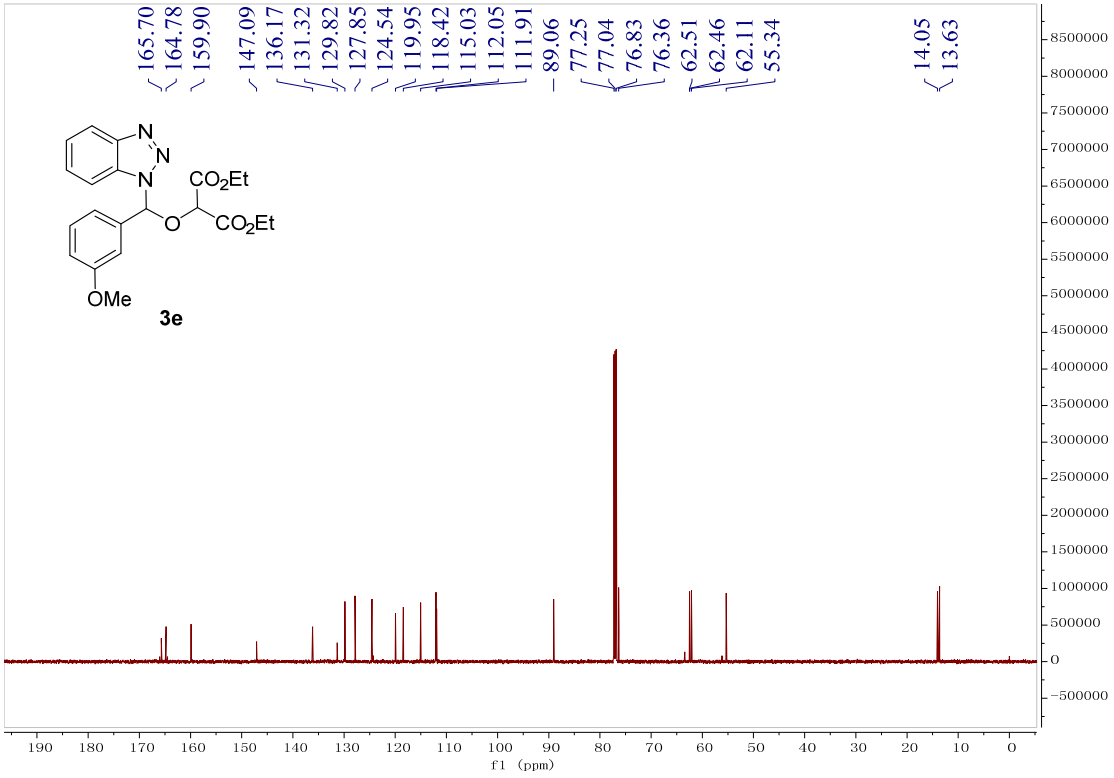
^{13}C NMR (100 MHz, $CDCl_3$) for 3d



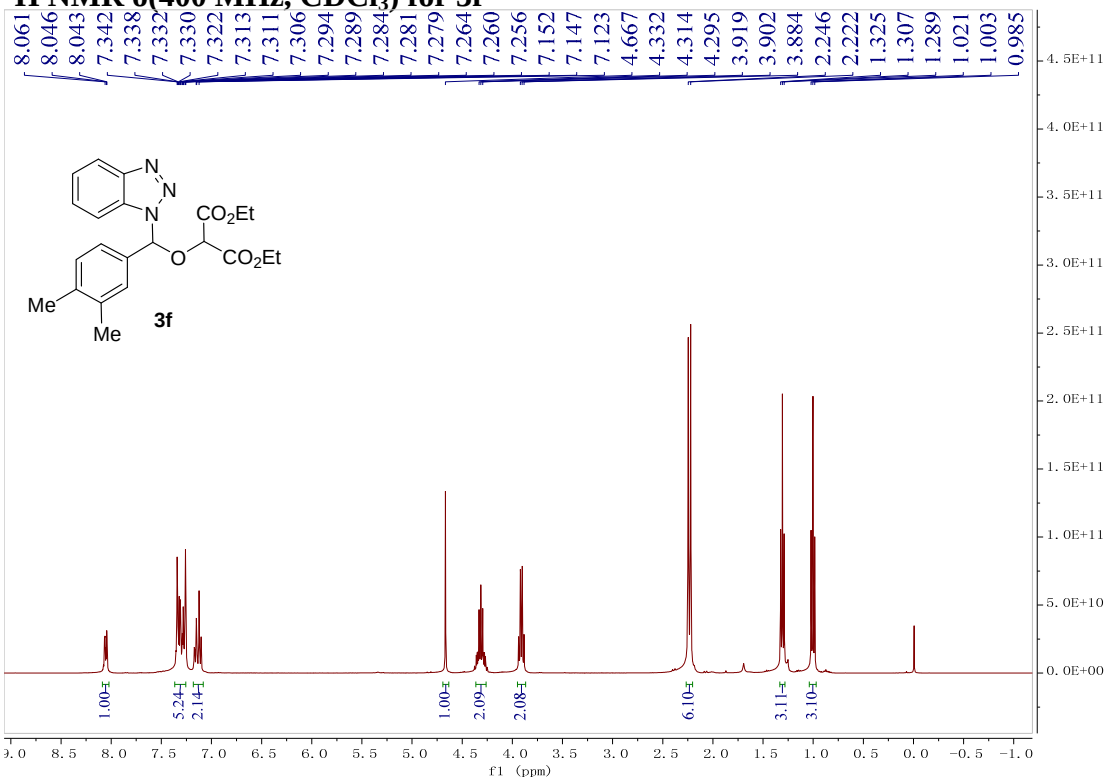
^{1}H NMR (600 MHz, $CDCl_3$) for 3e



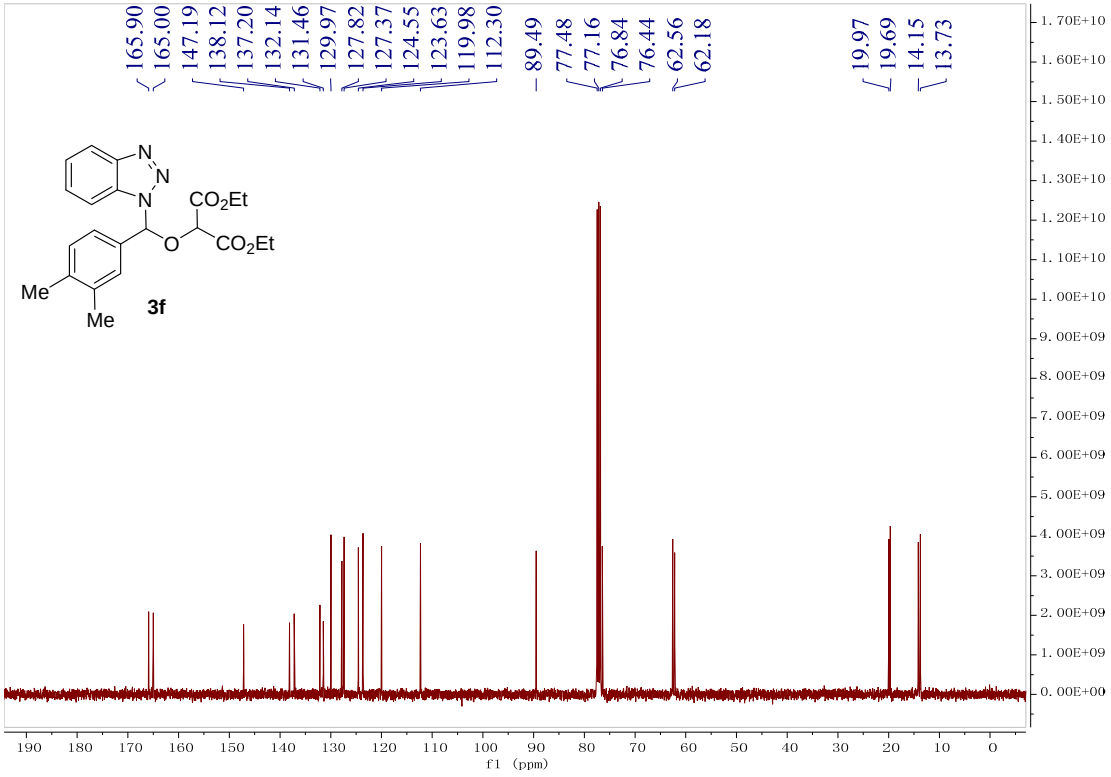
^{13}C NMR (150 MHz, $CDCl_3$) for 3e



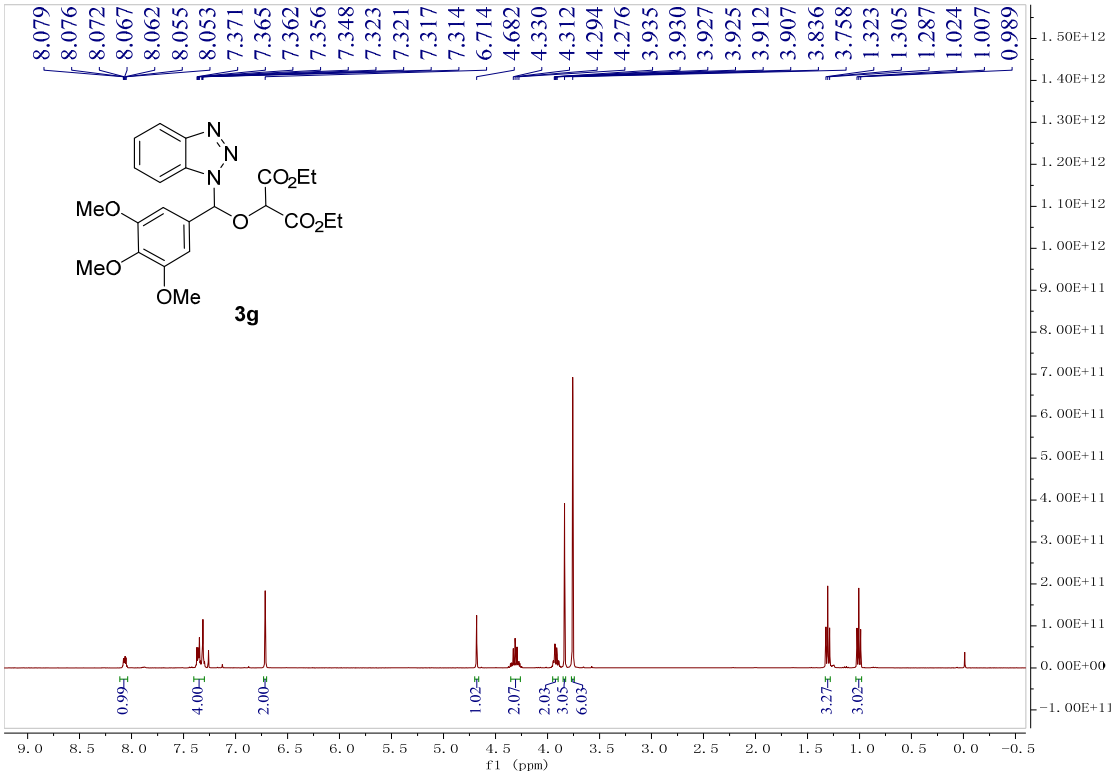
^{1}H NMR o(400 MHz, $CDCl_3$) for 3f



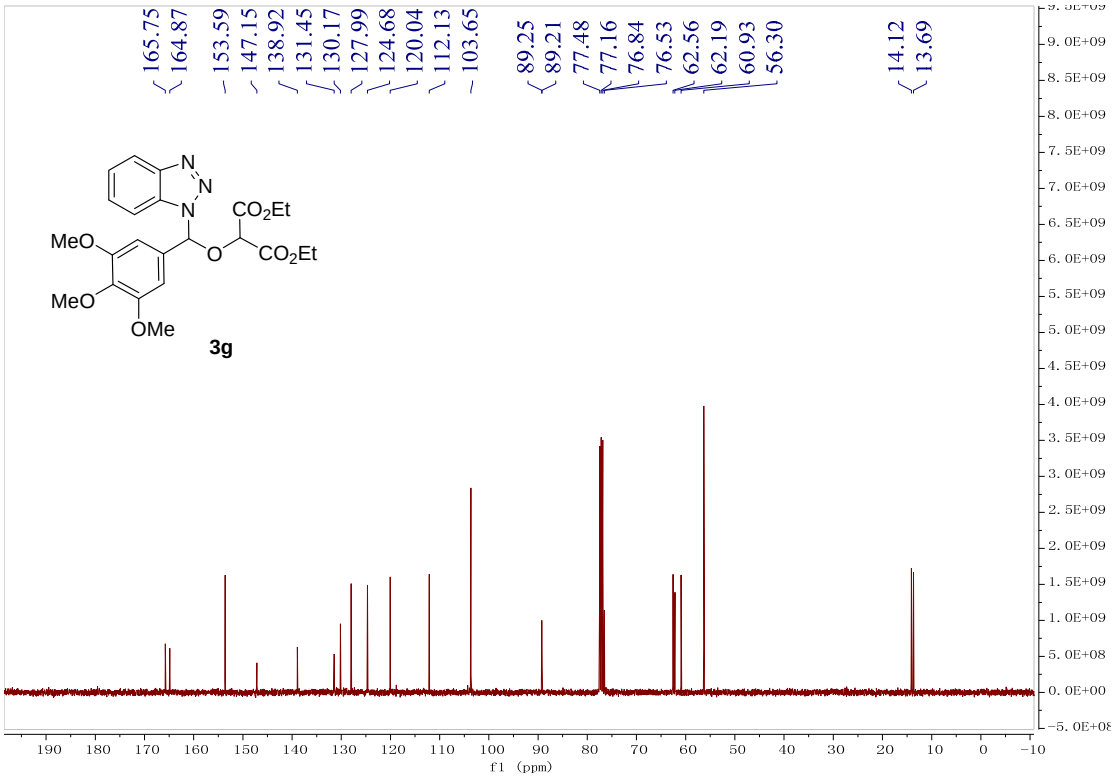
^{13}C NMR (100 MHz, $CDCl_3$) for 3f



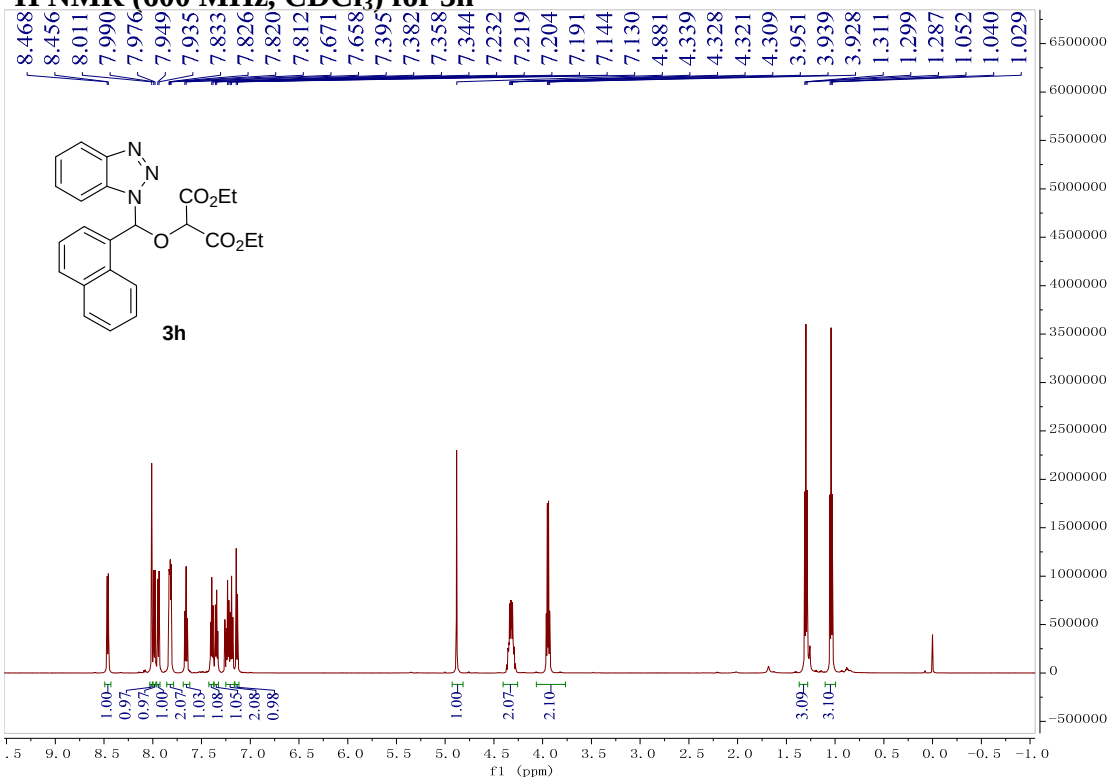
^{1}H NMR (400 MHz, $CDCl_3$) for 3g



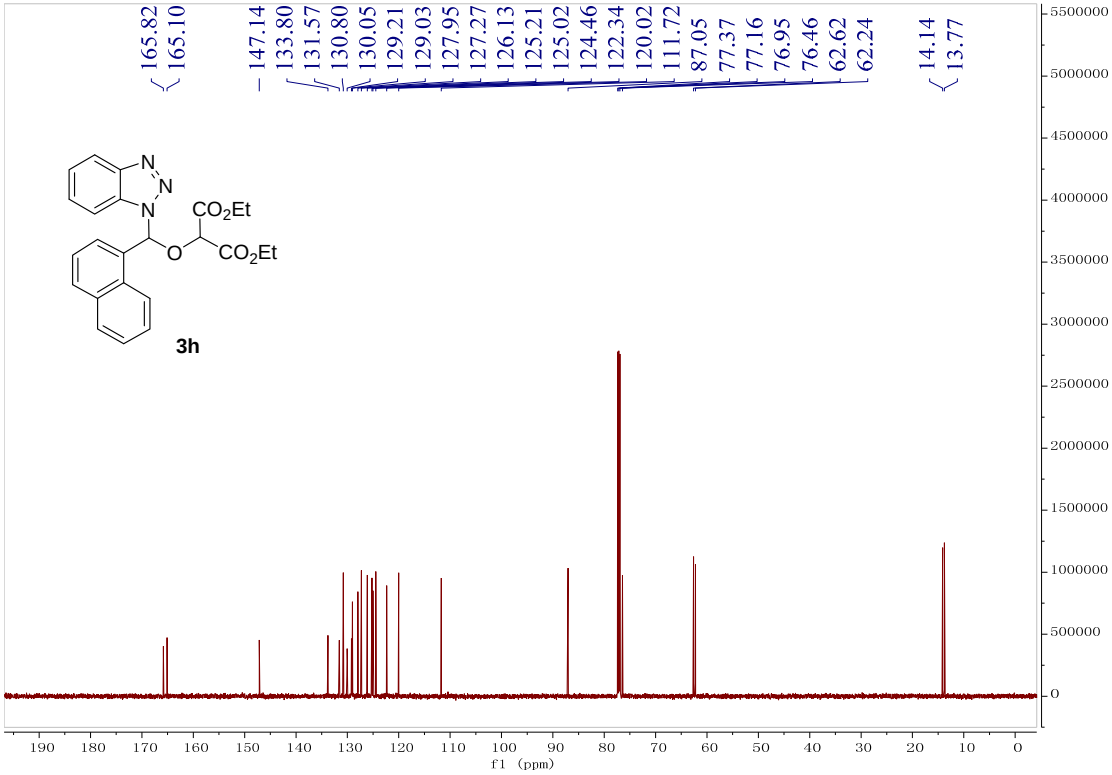
^{13}C NMR (100 MHz, $CDCl_3$) for 3g



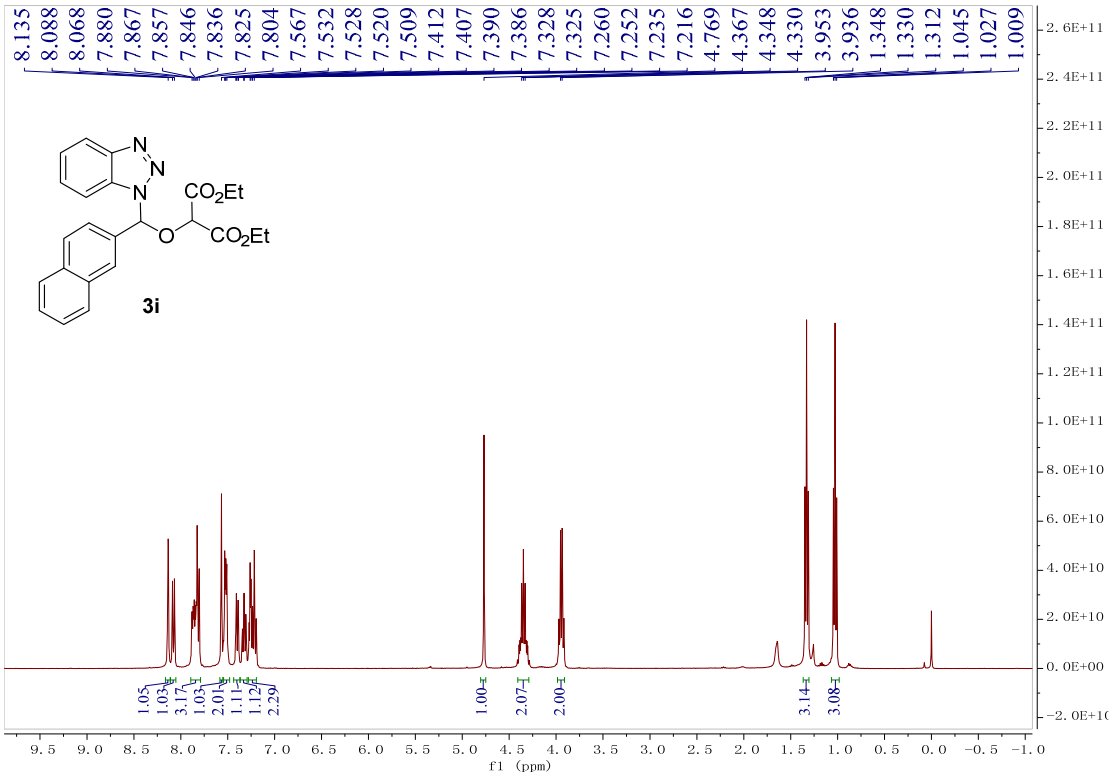
^{1}H NMR (600 MHz, $CDCl_3$) for 3h



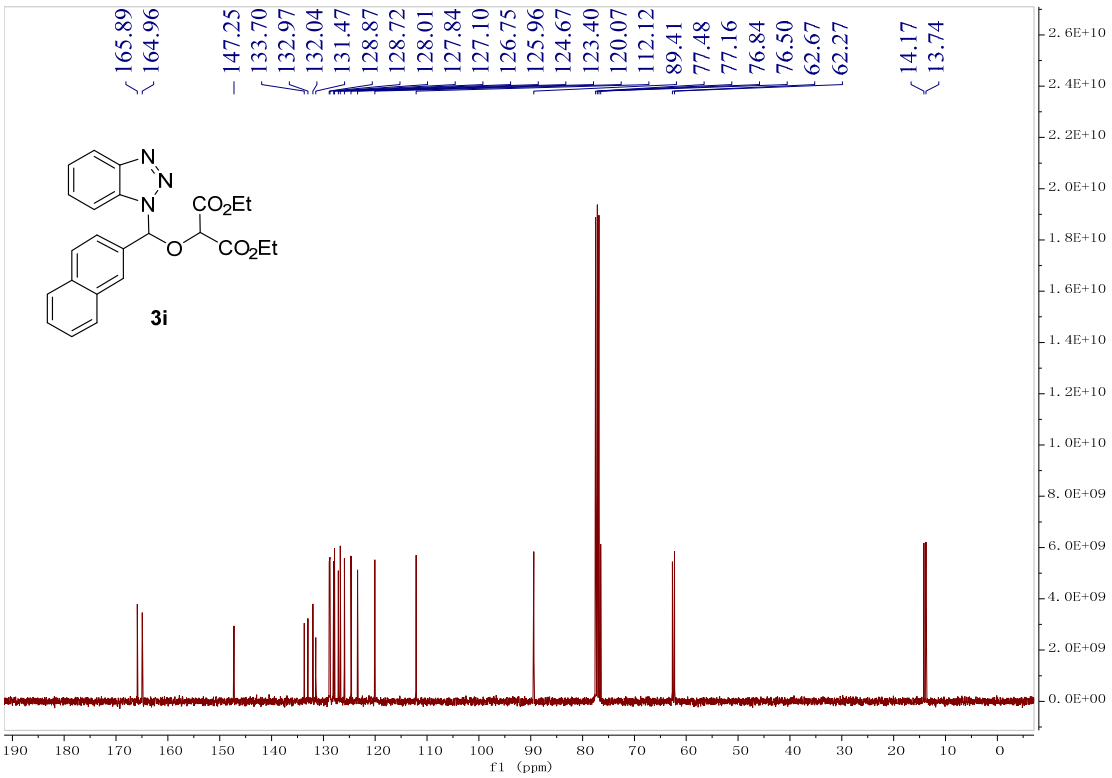
^{13}C NMR (150 MHz, $CDCl_3$) for 3h



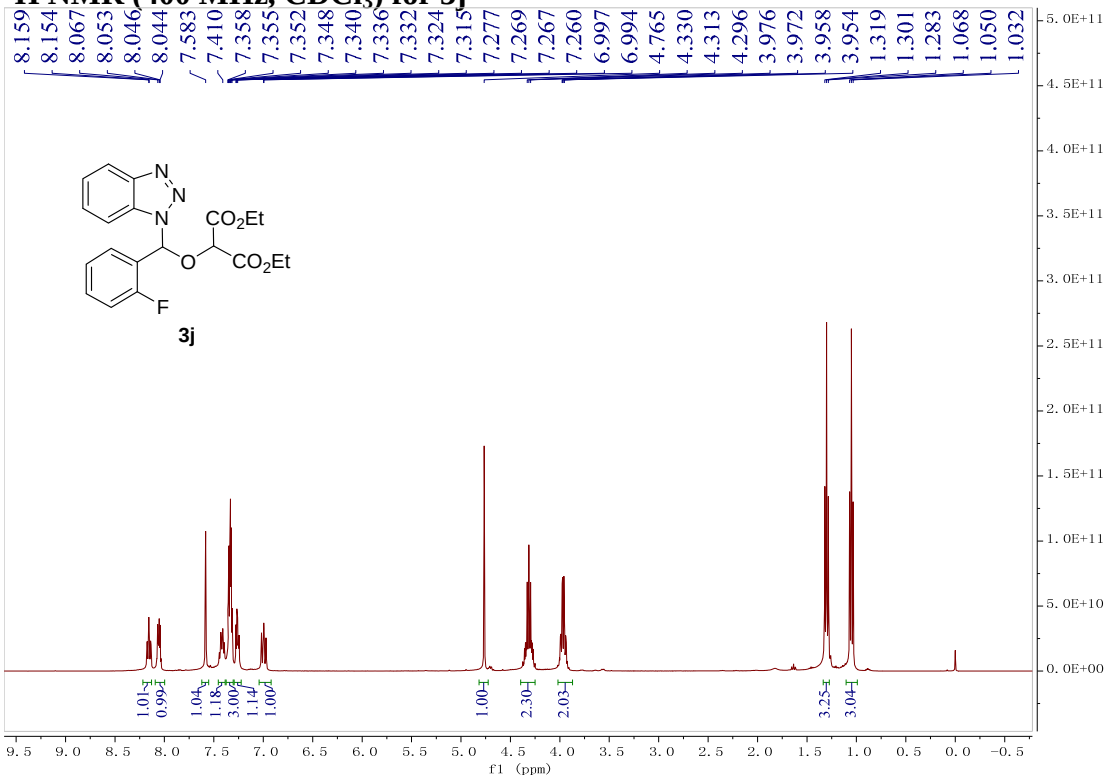
^{1}H NMR (400 MHz, $CDCl_3$) for 3i



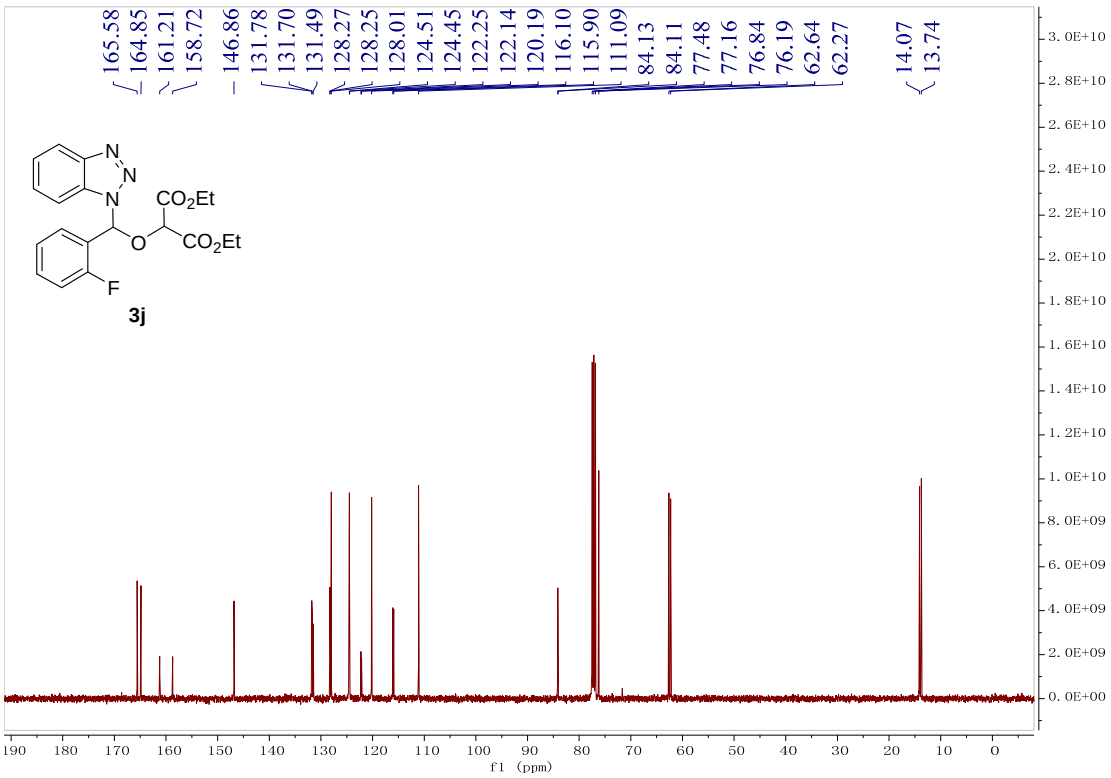
^{13}C NMR (100 MHz, $CDCl_3$) for 3i



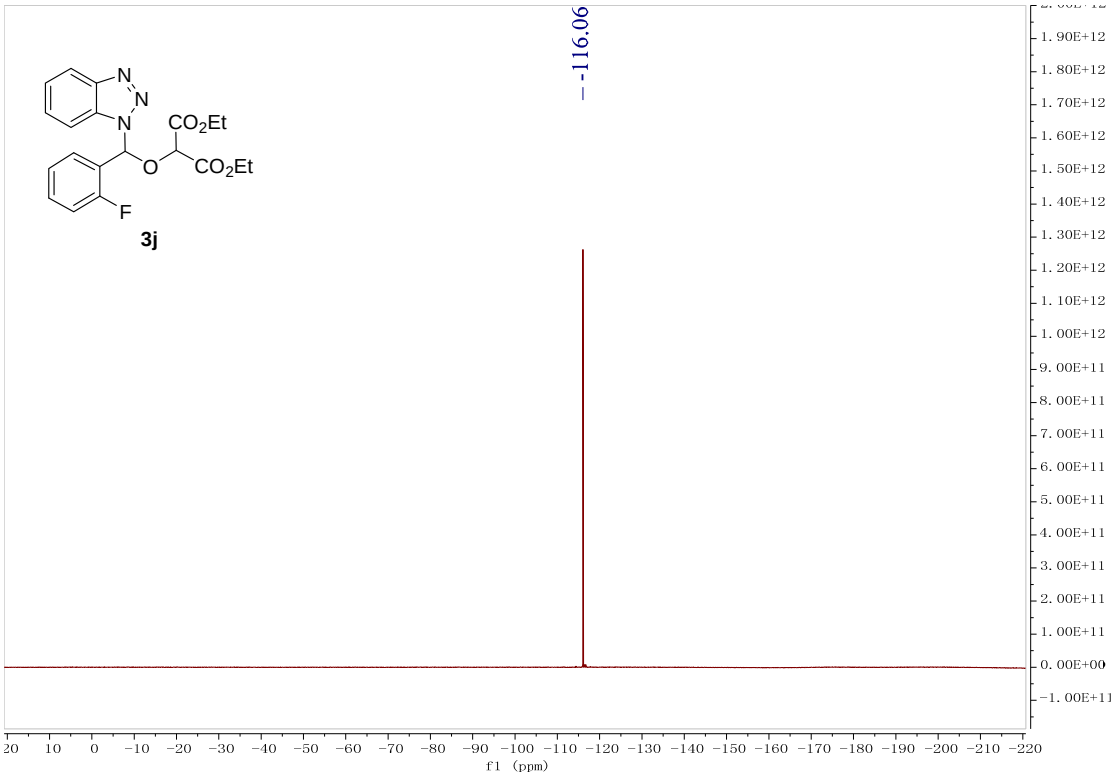
^{1}H NMR (400 MHz, $CDCl_3$) for 3j



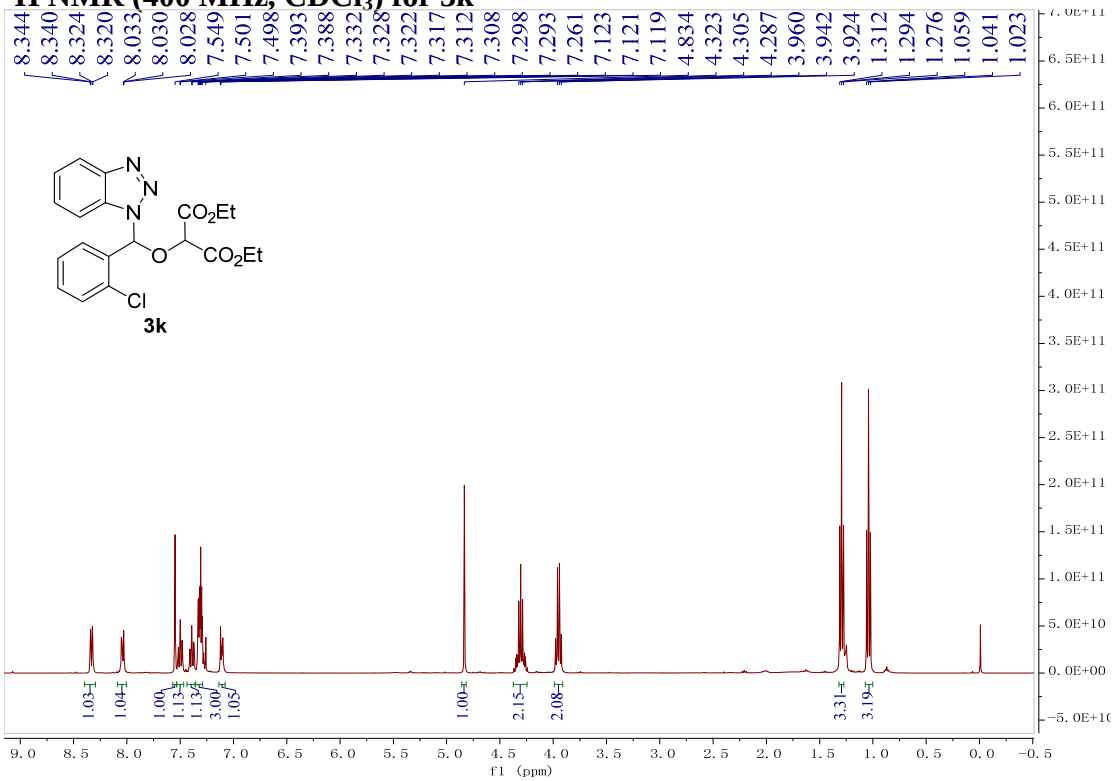
^{13}C NMR (100 MHz, $CDCl_3$) for 3j



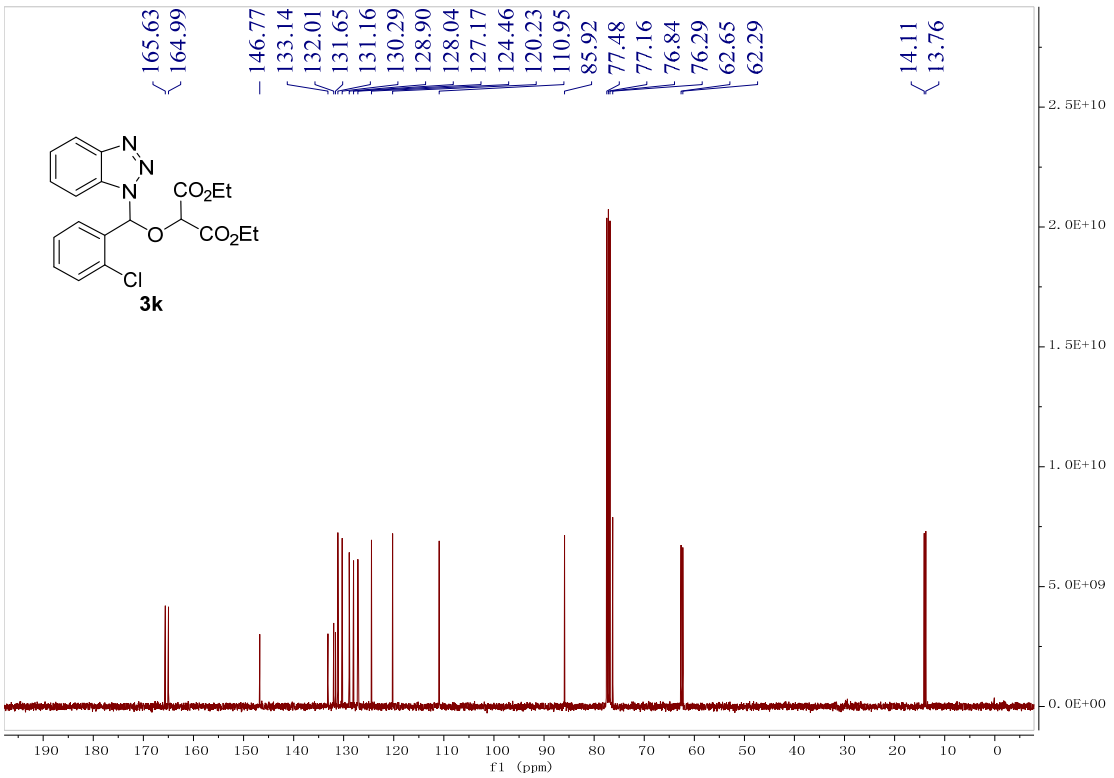
^{19}F NMR (376 MHz, $CDCl_3$) for 3j



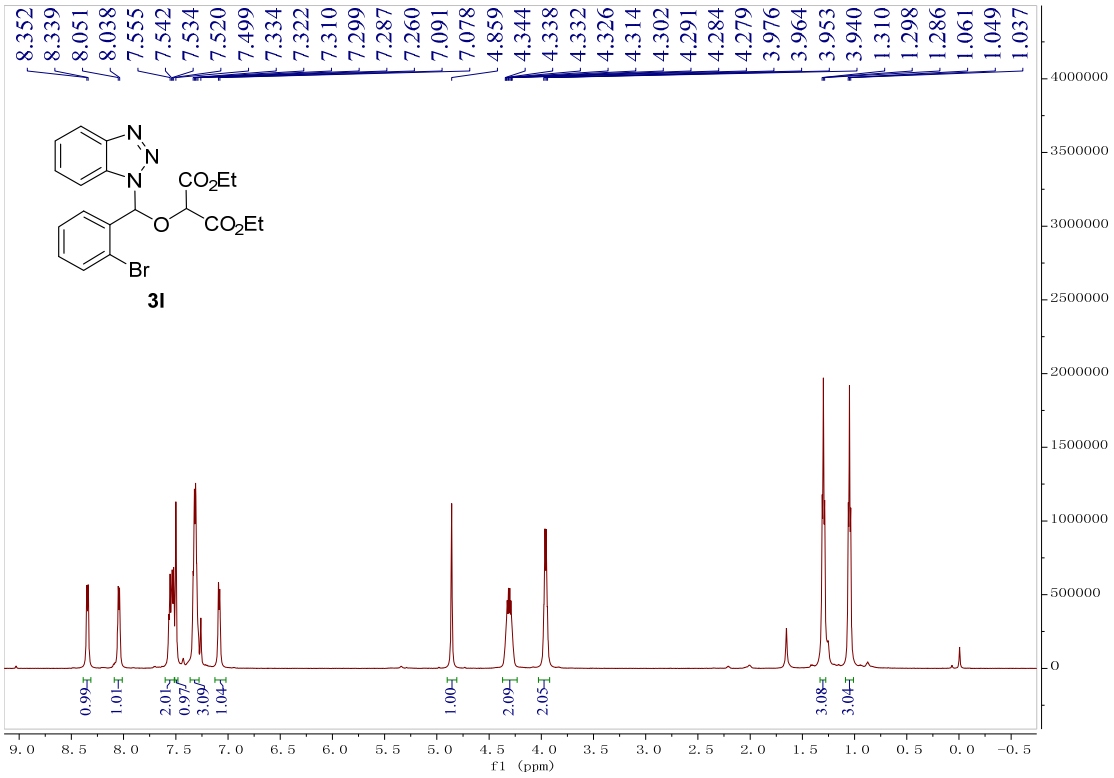
^{1}H NMR (400 MHz, $CDCl_3$) for 3k



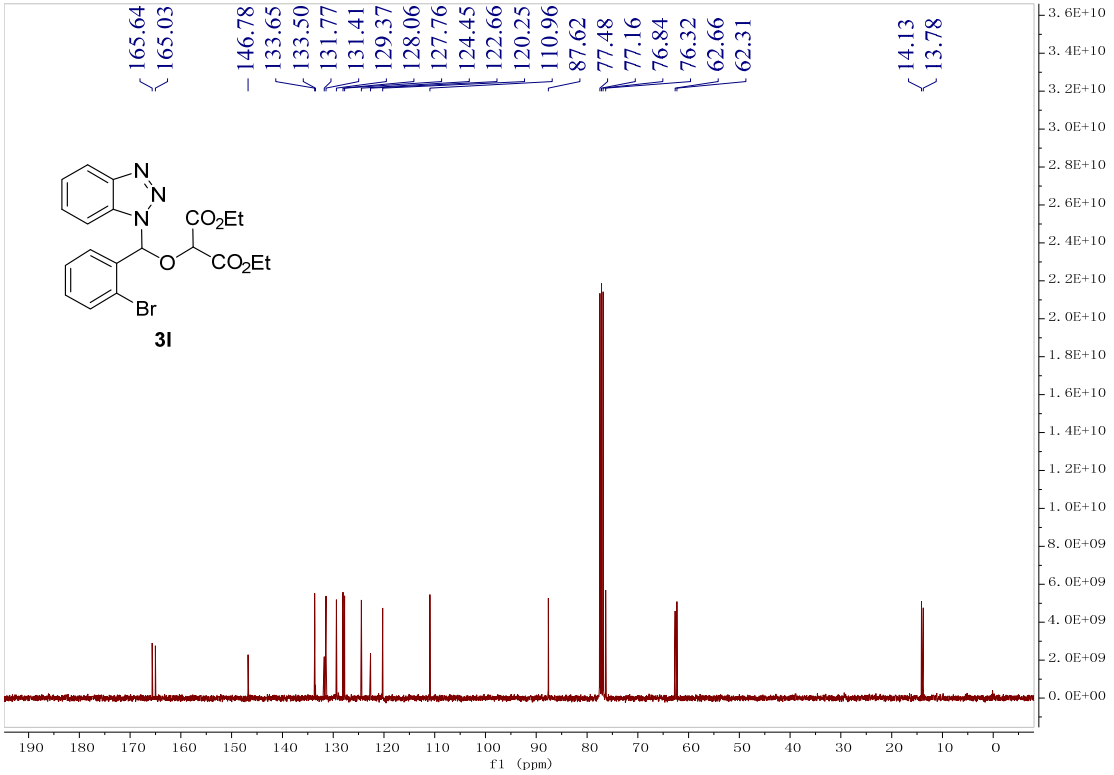
^{13}C NMR (100 MHz, $CDCl_3$) for 3k



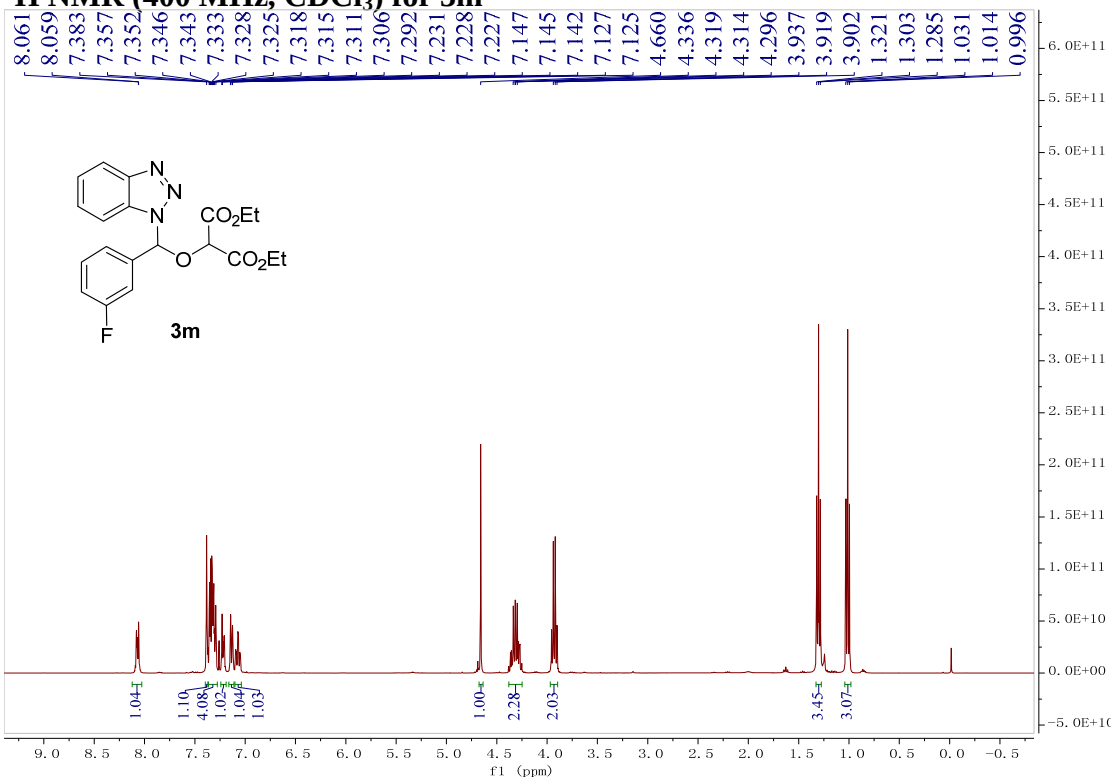
^{1}H NMR (400 MHz, $CDCl_3$) for 3l



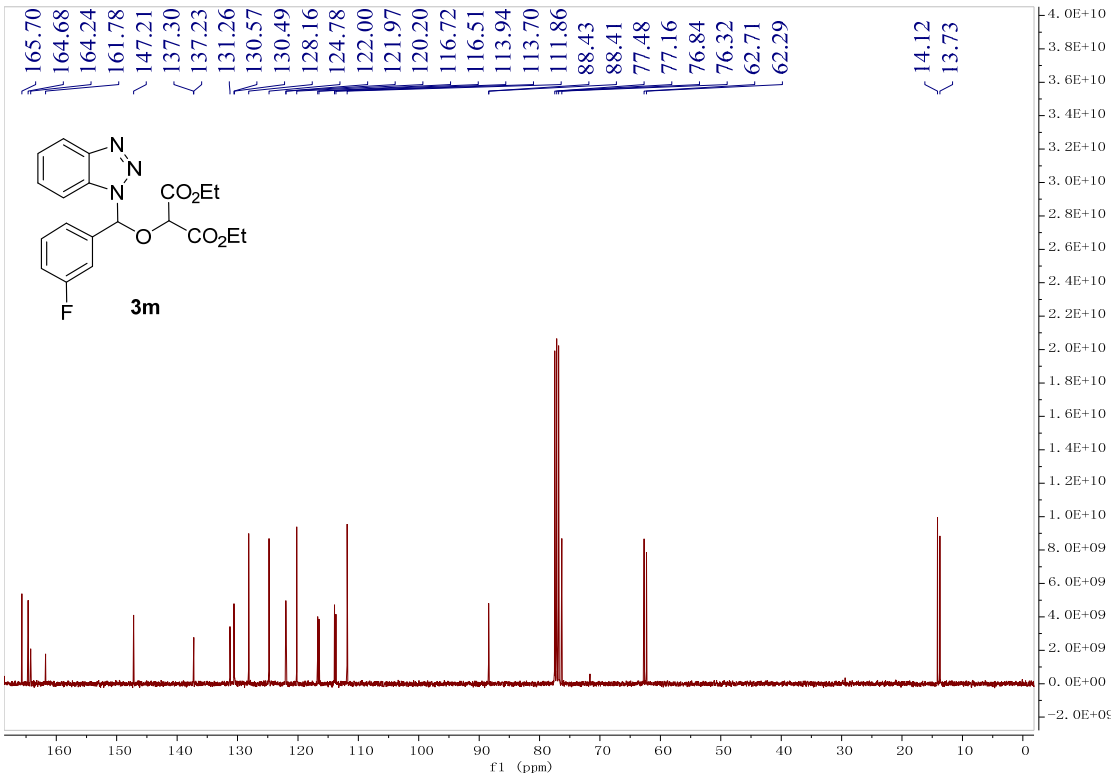
^{13}C NMR (100 MHz, $CDCl_3$) for 3l



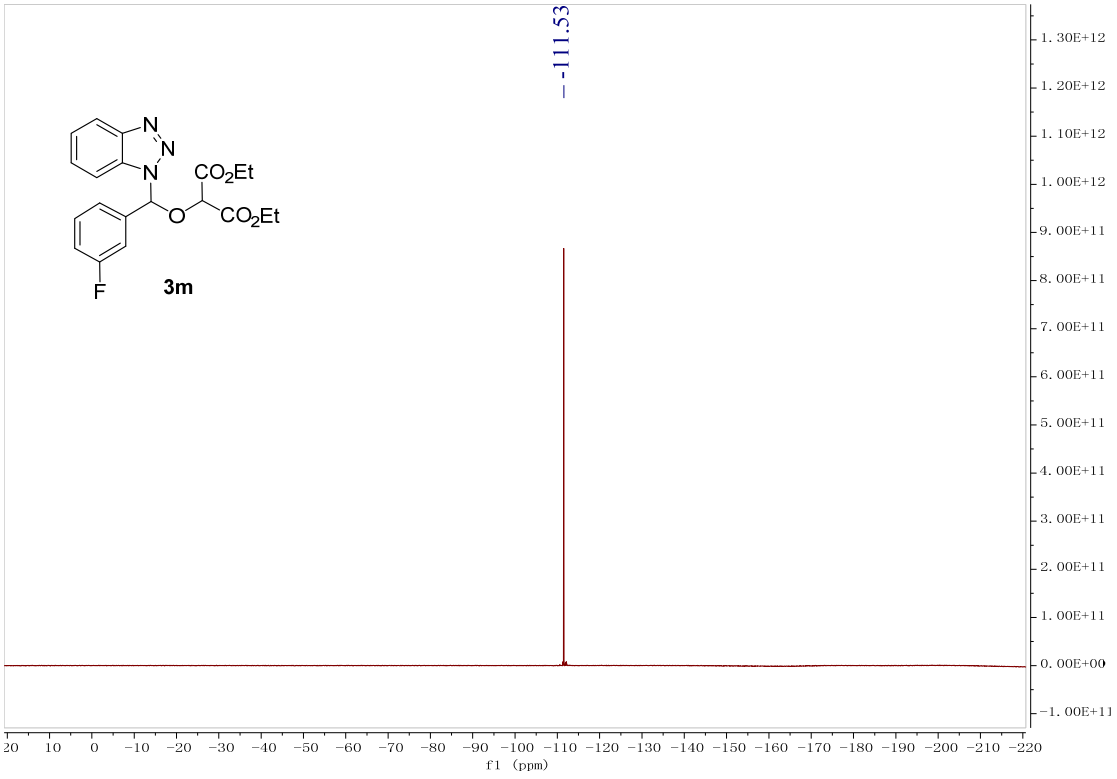
^{1}H NMR (400 MHz, $CDCl_3$) for 3m



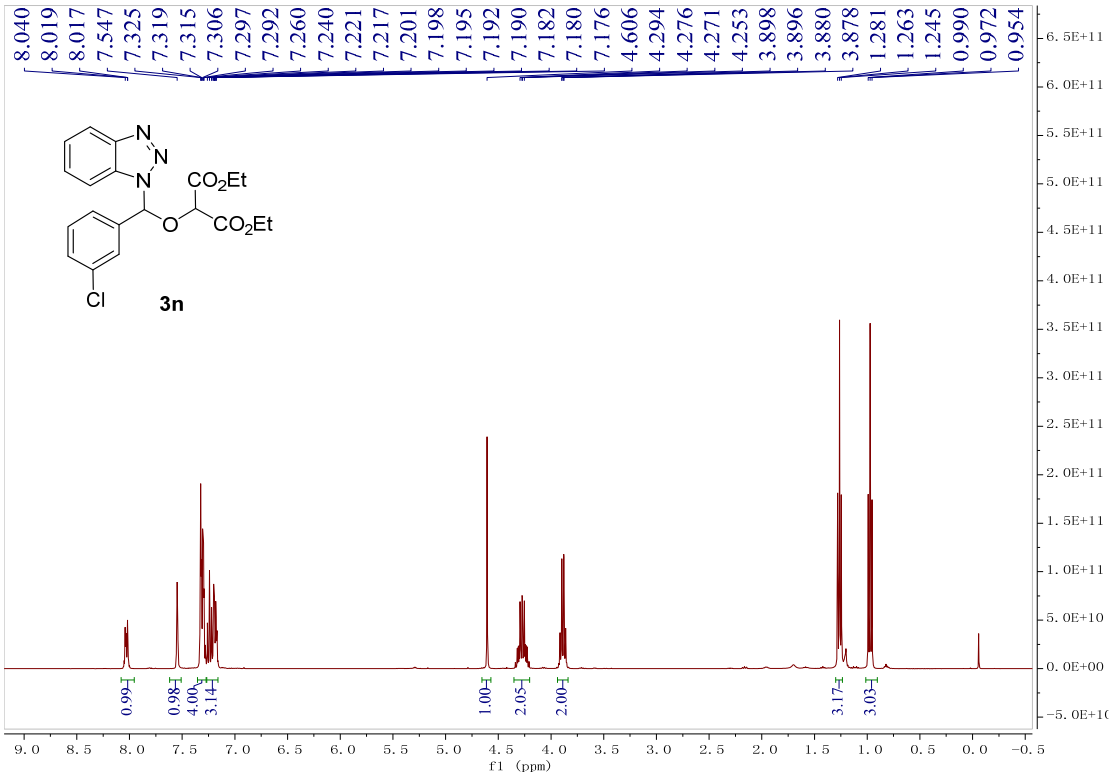
^{13}C NMR (100 MHz, $CDCl_3$) for 3m



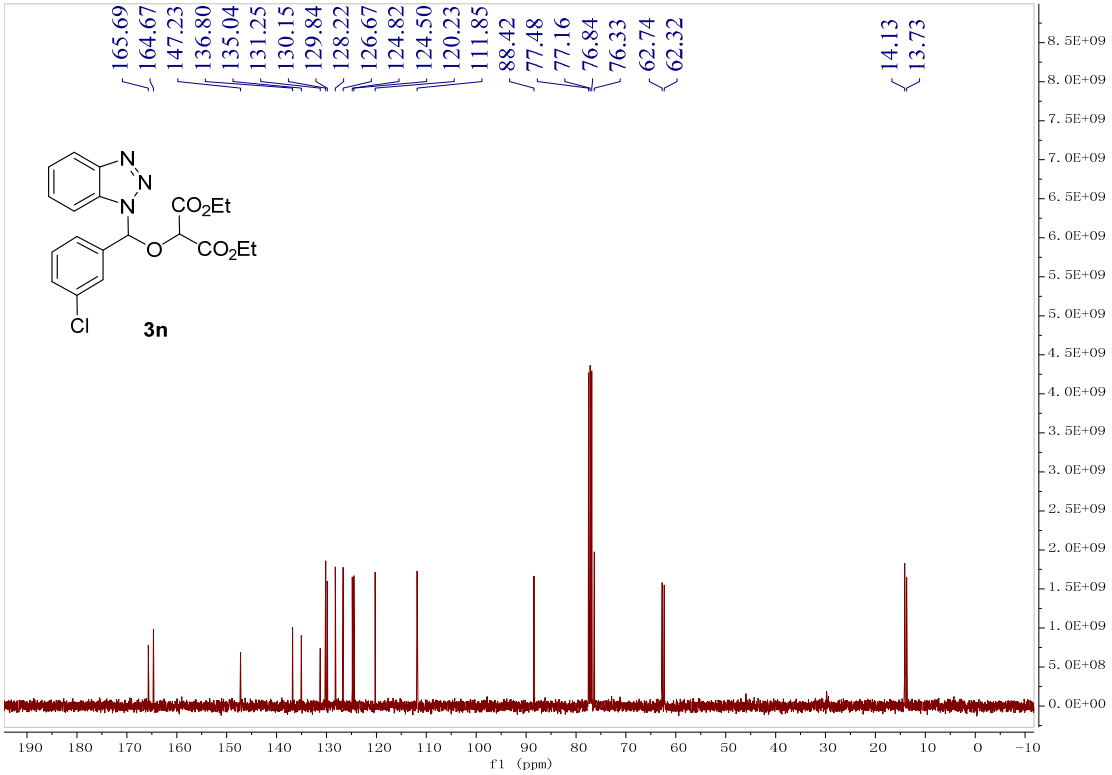
^{19}F NMR (376 MHz, $CDCl_3$) for 3m



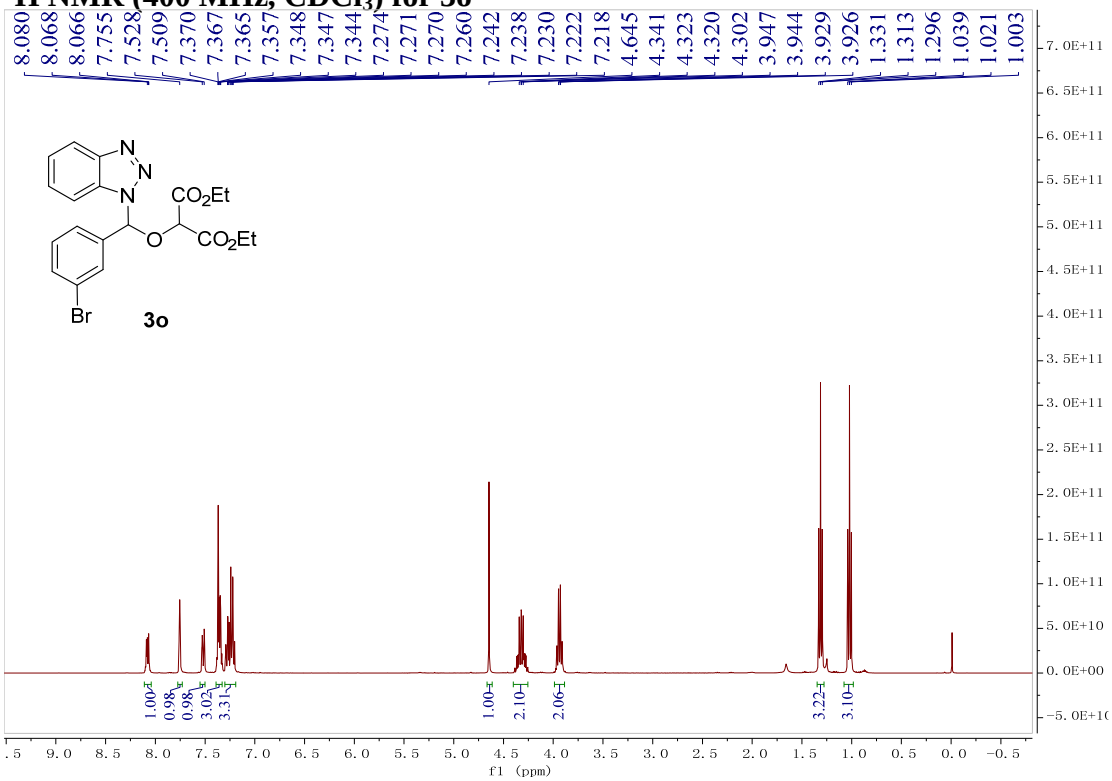
^{1}H NMR (400 MHz, $CDCl_3$) for 3n



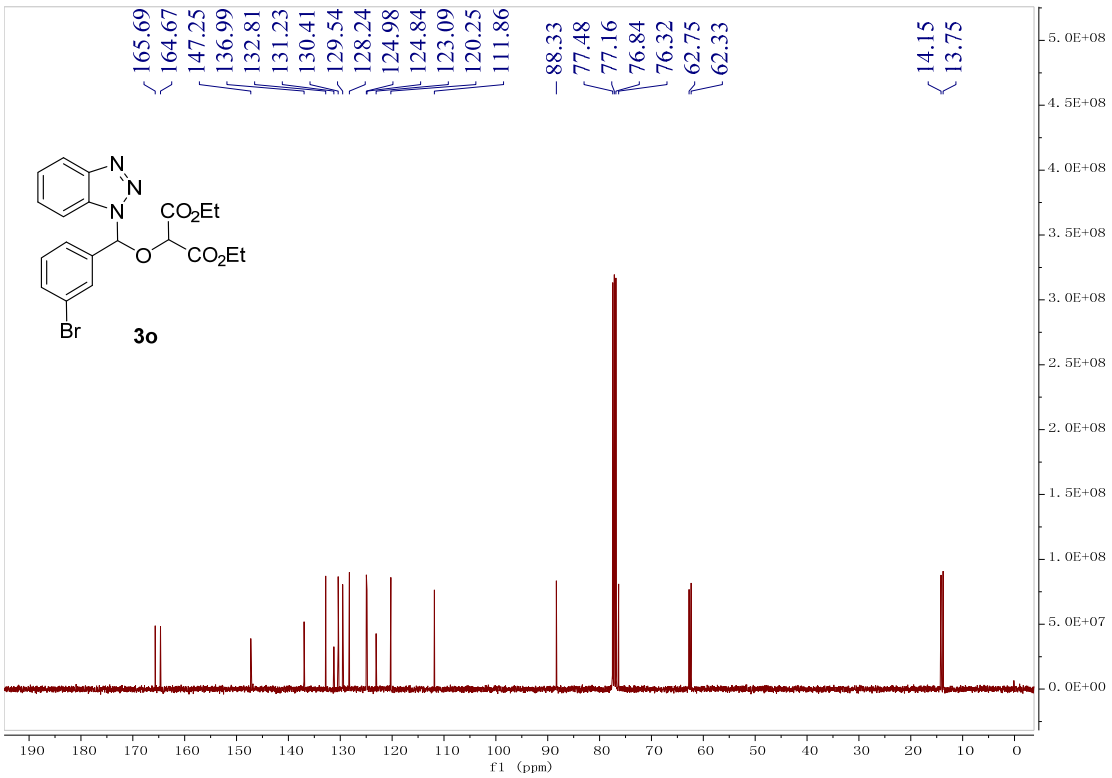
^{13}C NMR (100 MHz, $CDCl_3$) for 3n



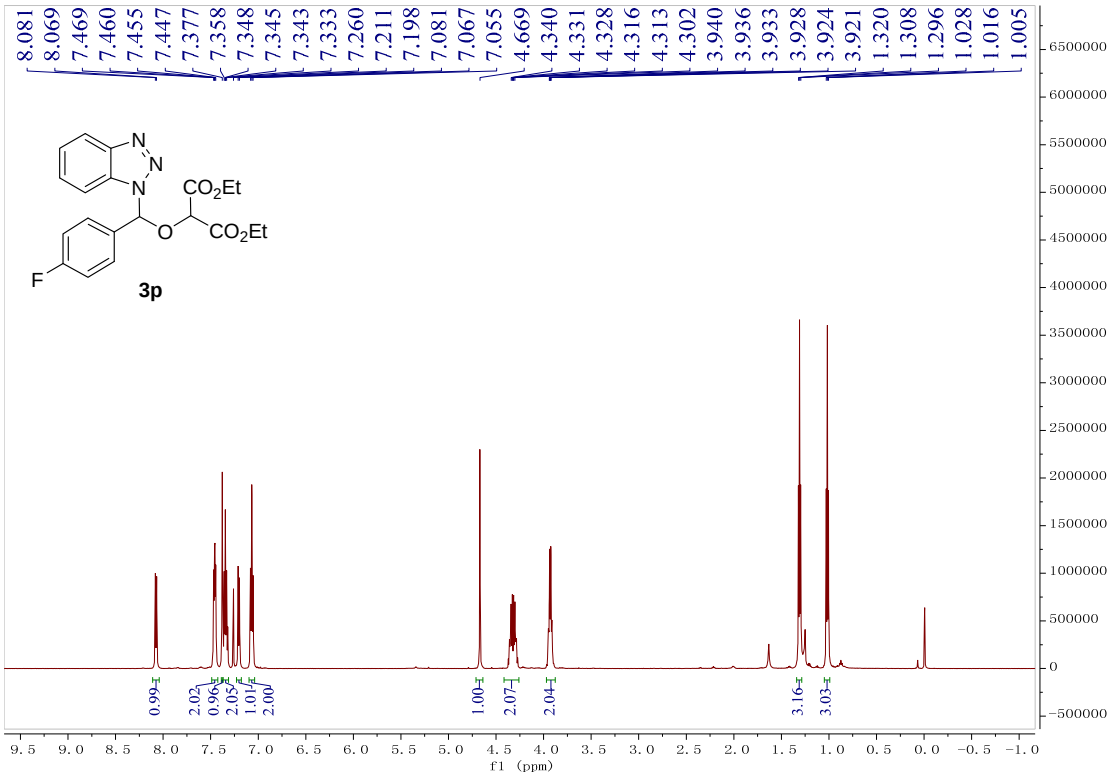
^{1}H NMR (400 MHz, $CDCl_3$) for 3o



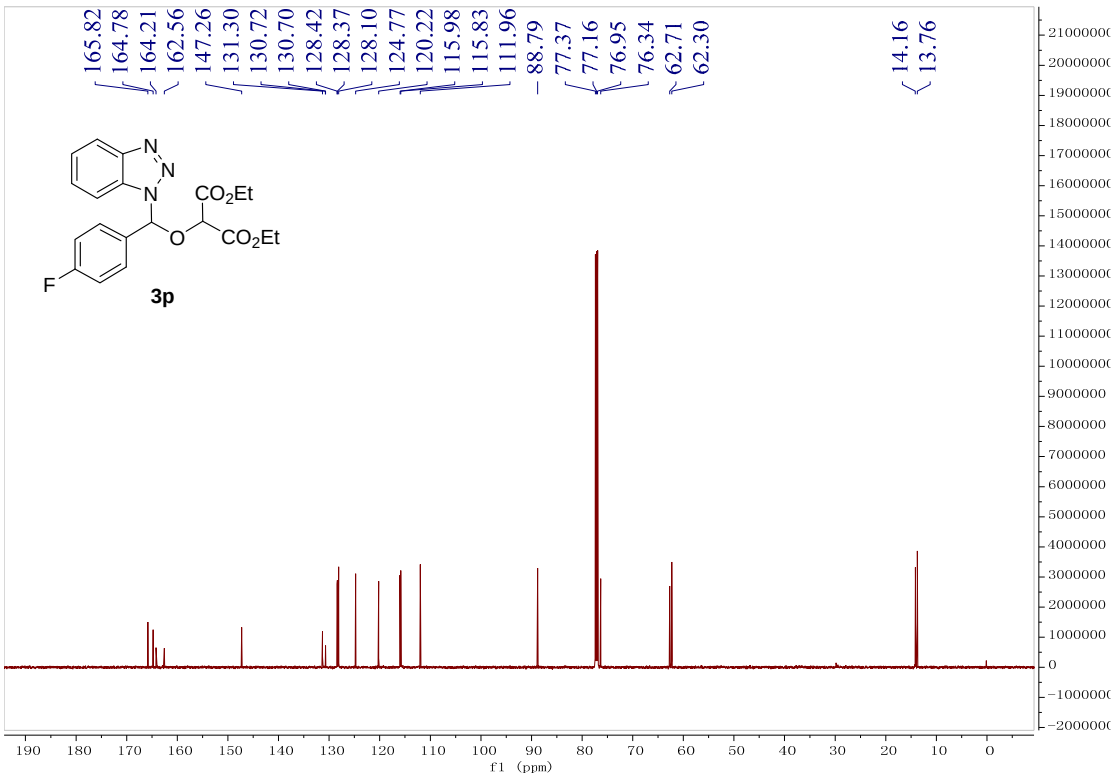
^{13}C NMR (100 MHz, $CDCl_3$) for 3o



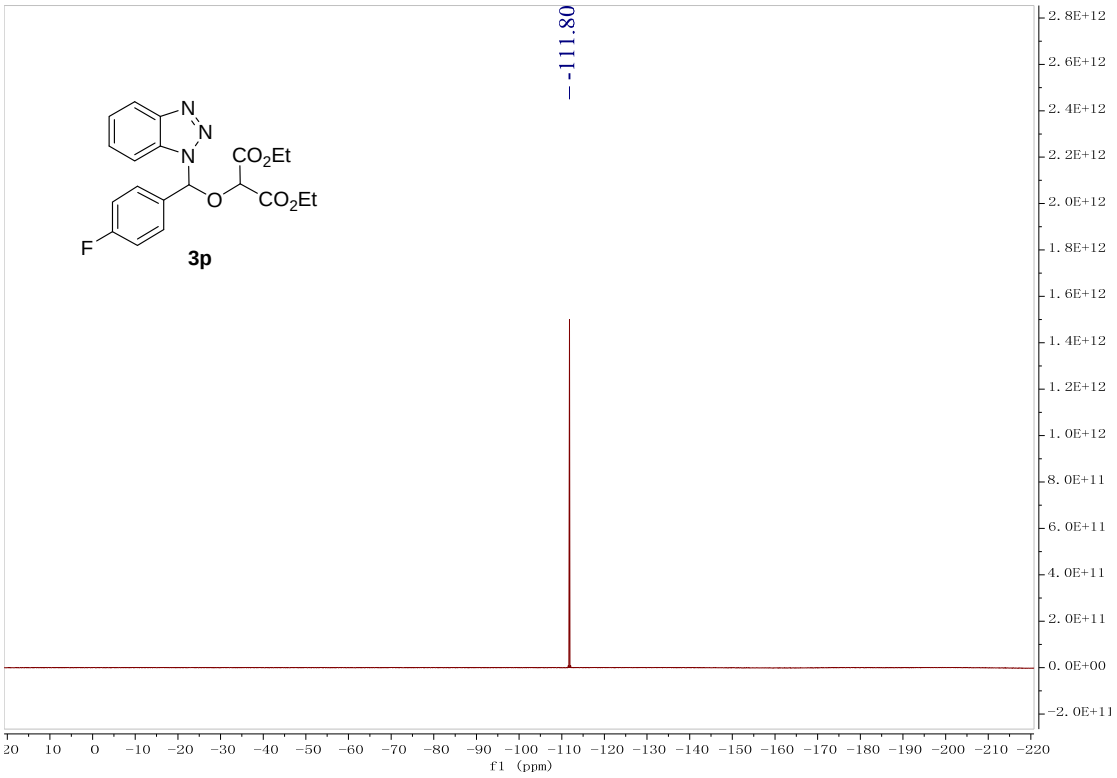
^{1}H NMR (600 MHz, $CDCl_3$) for 3p



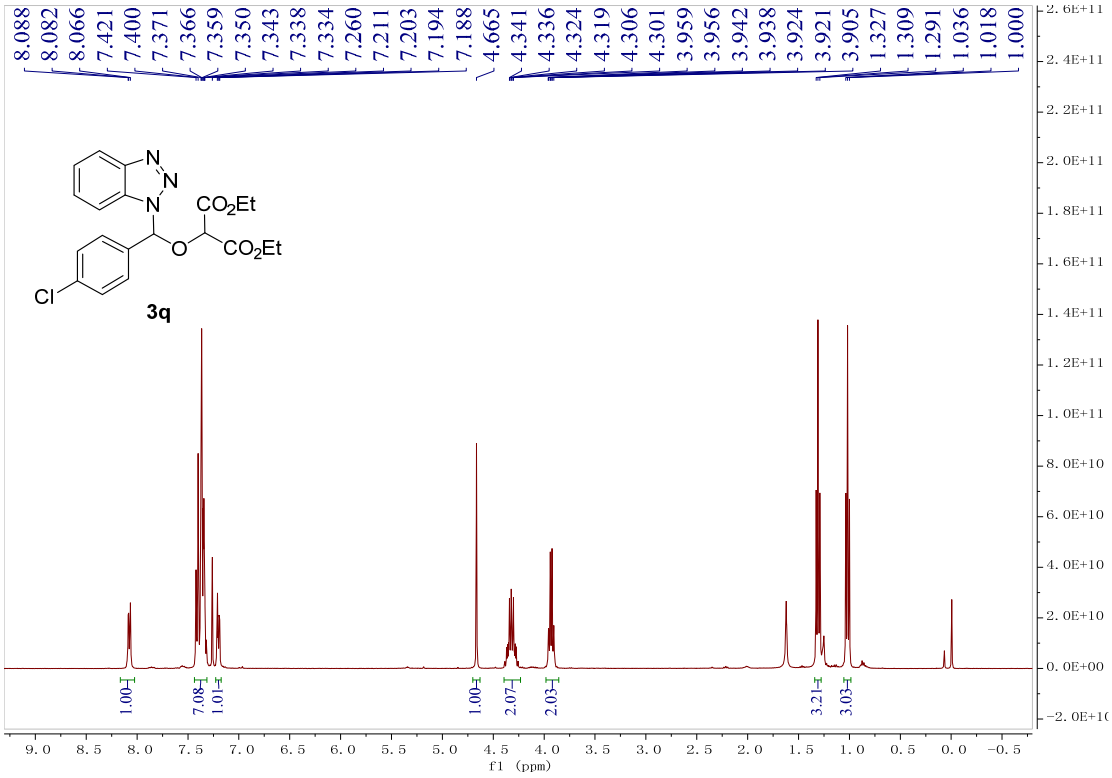
^{13}C NMR (150 MHz, $CDCl_3$) for 3p



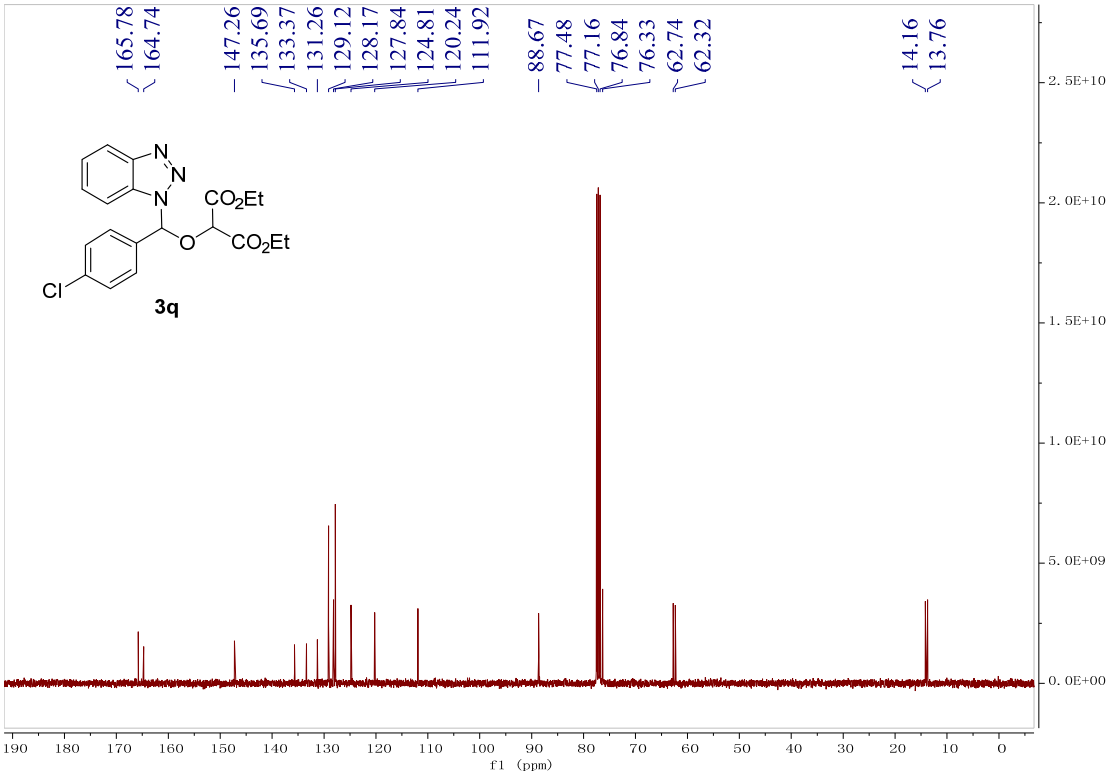
^{19}F NMR (376 MHz, $CDCl_3$) for 3p



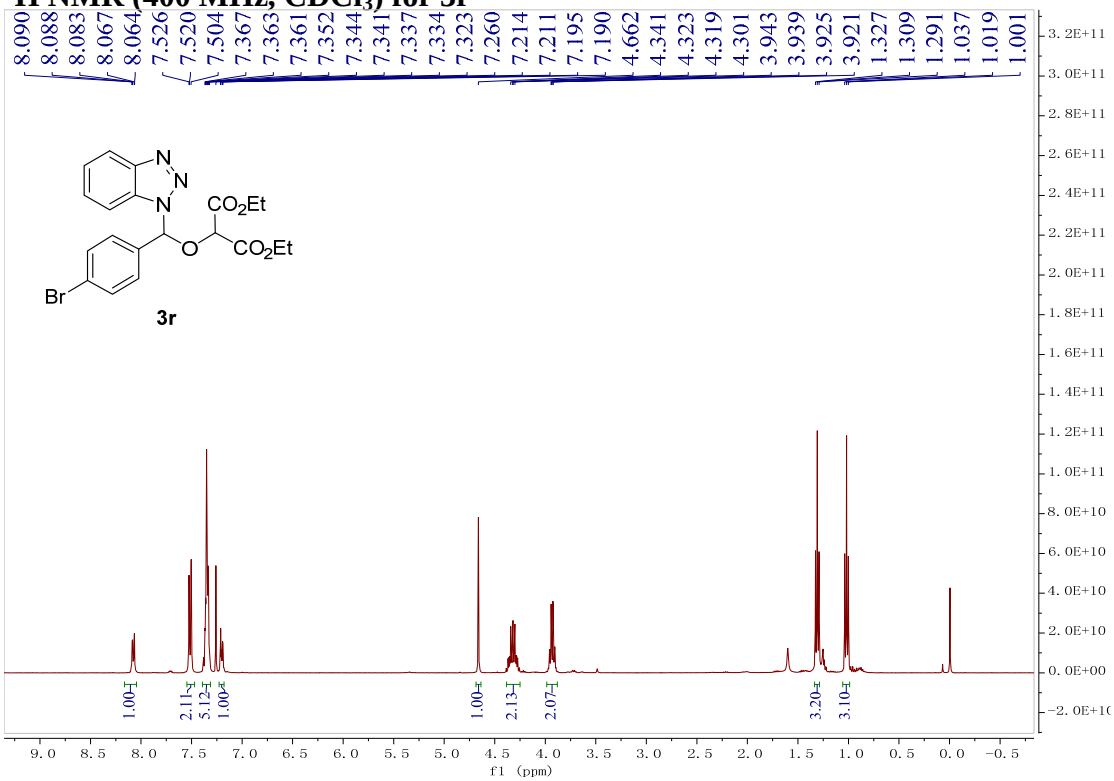
^{1}H NMR (400 MHz, $CDCl_3$) for 3q



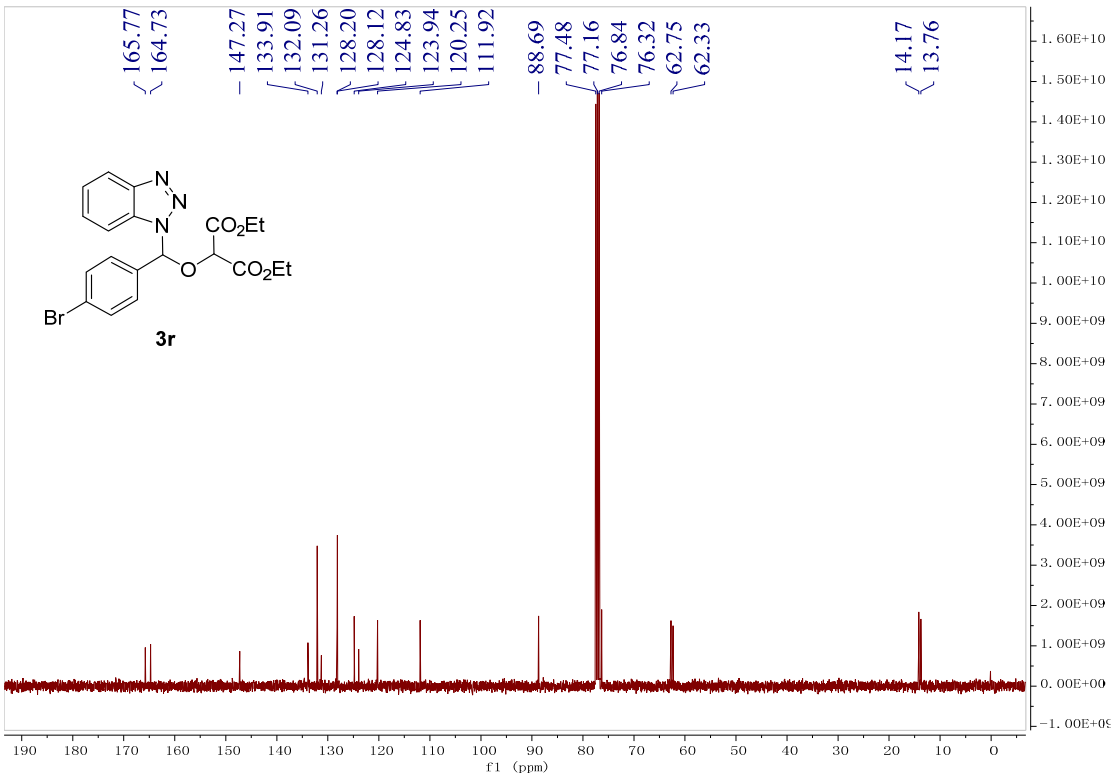
^{13}C NMR (100 MHz, $CDCl_3$) for 3q



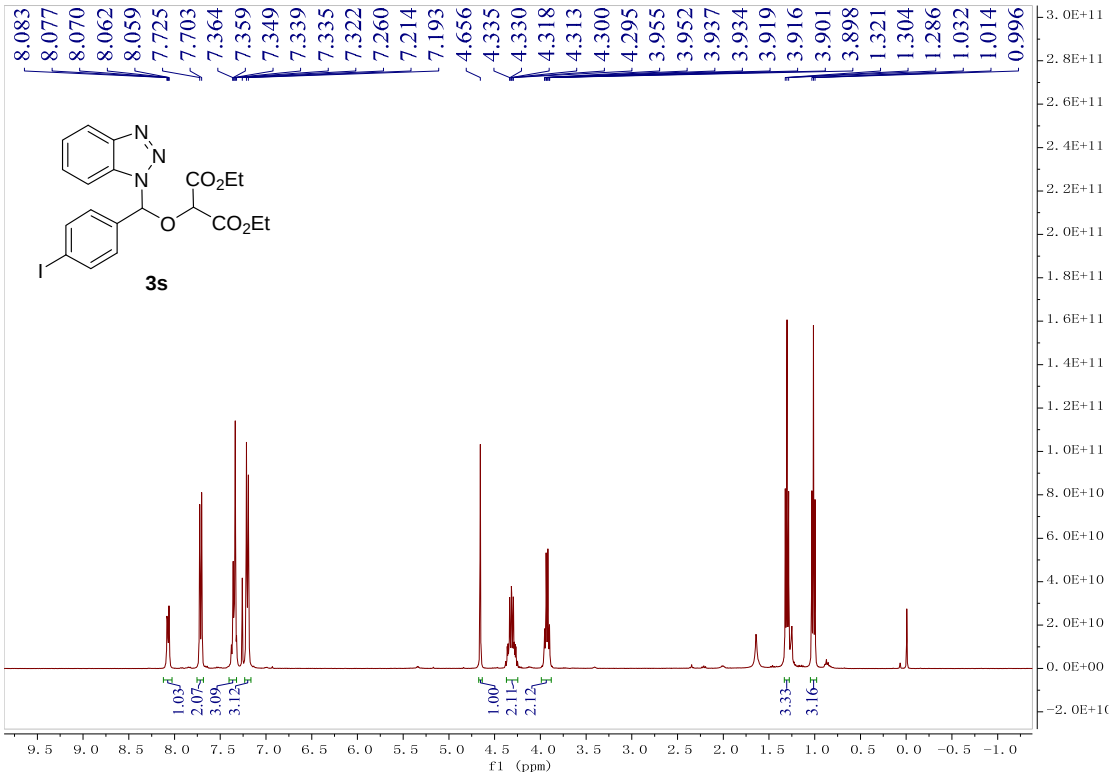
^{1}H NMR (400 MHz, $CDCl_3$) for 3r



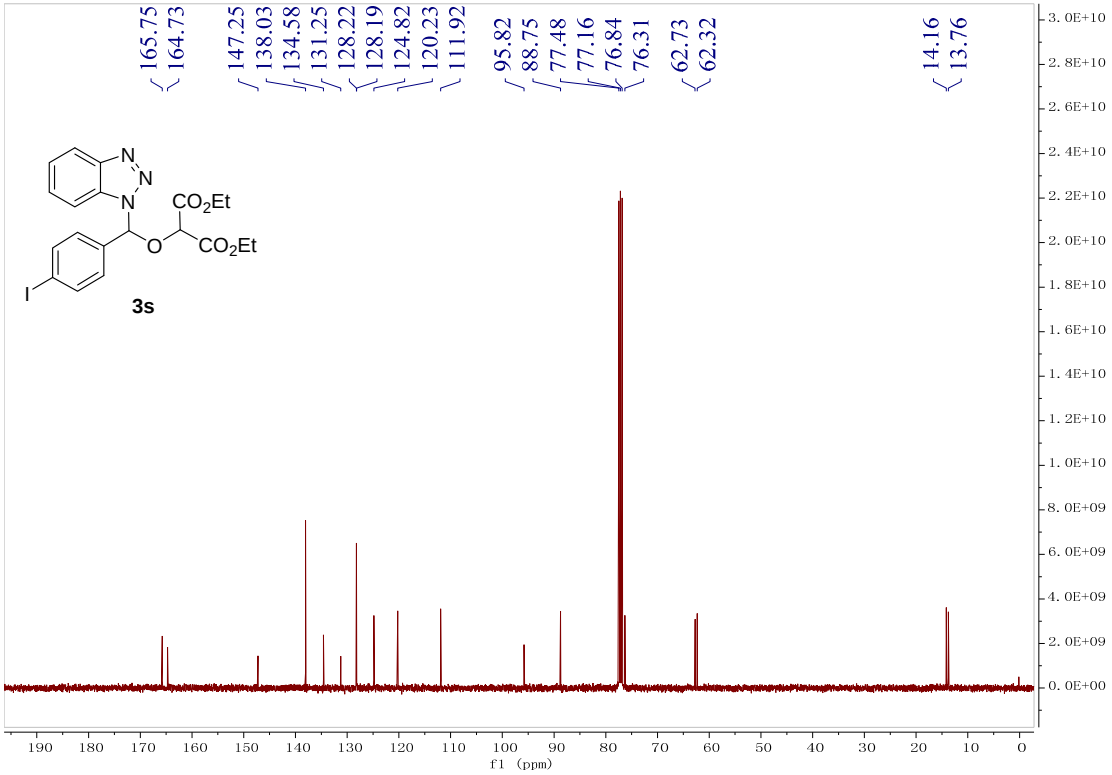
^{13}C NMR (100 MHz, $CDCl_3$) for 3r



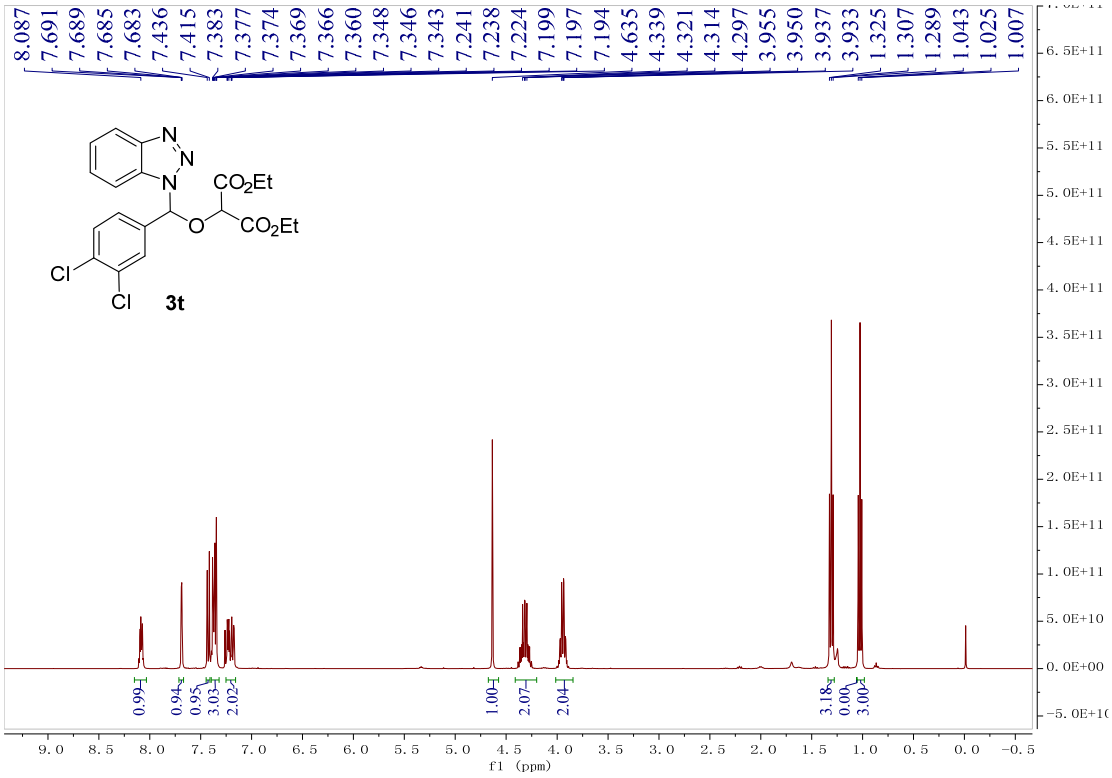
^{1}H NMR (400 MHz, $CDCl_3$) for 3s



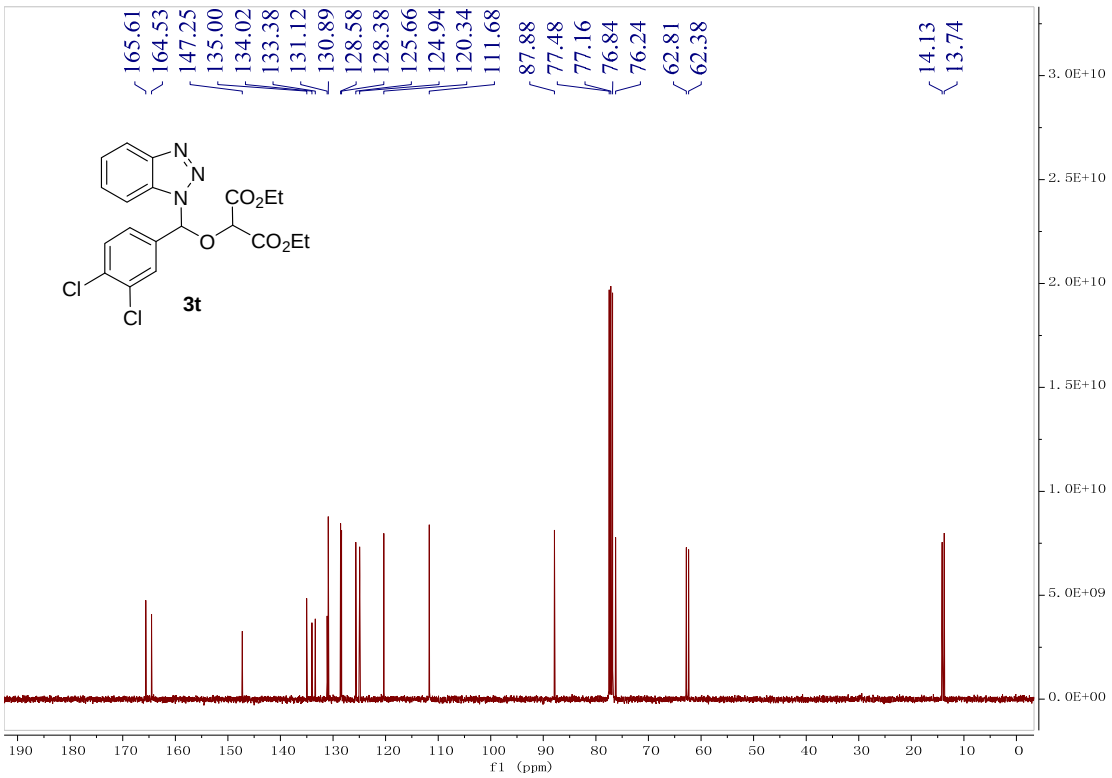
^{13}C NMR (100 MHz, $CDCl_3$) for 3s



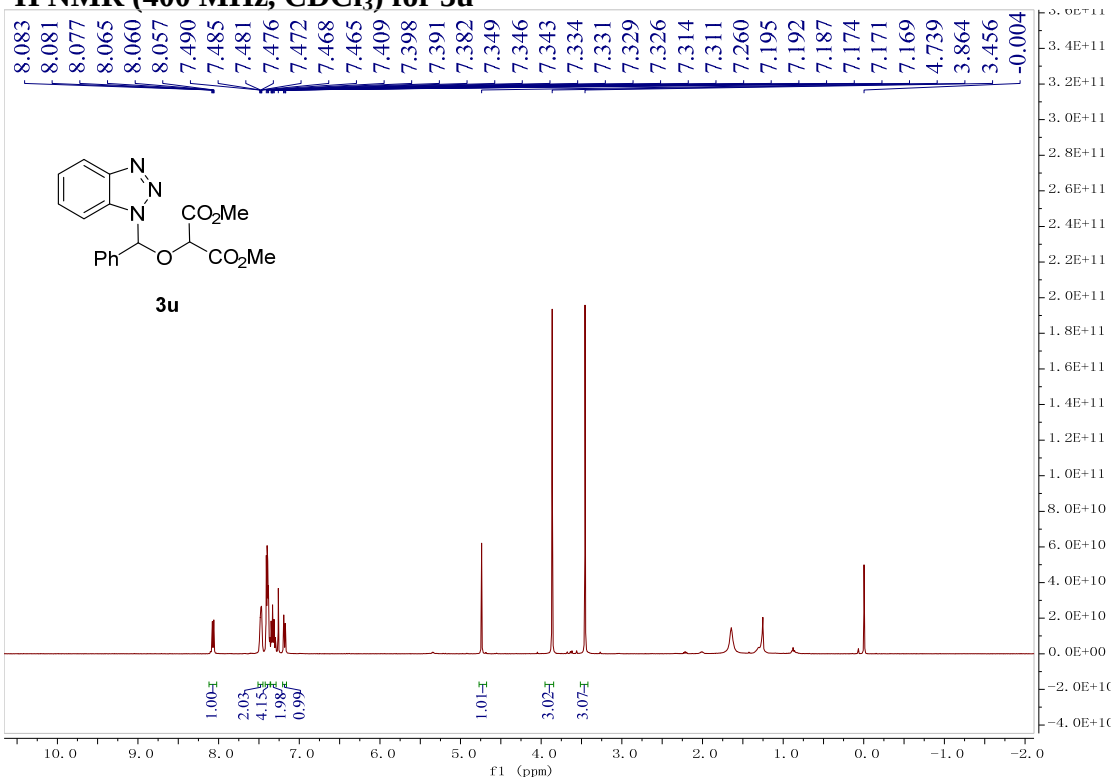
^{1}H NMR (400 MHz, $CDCl_3$) for 3t



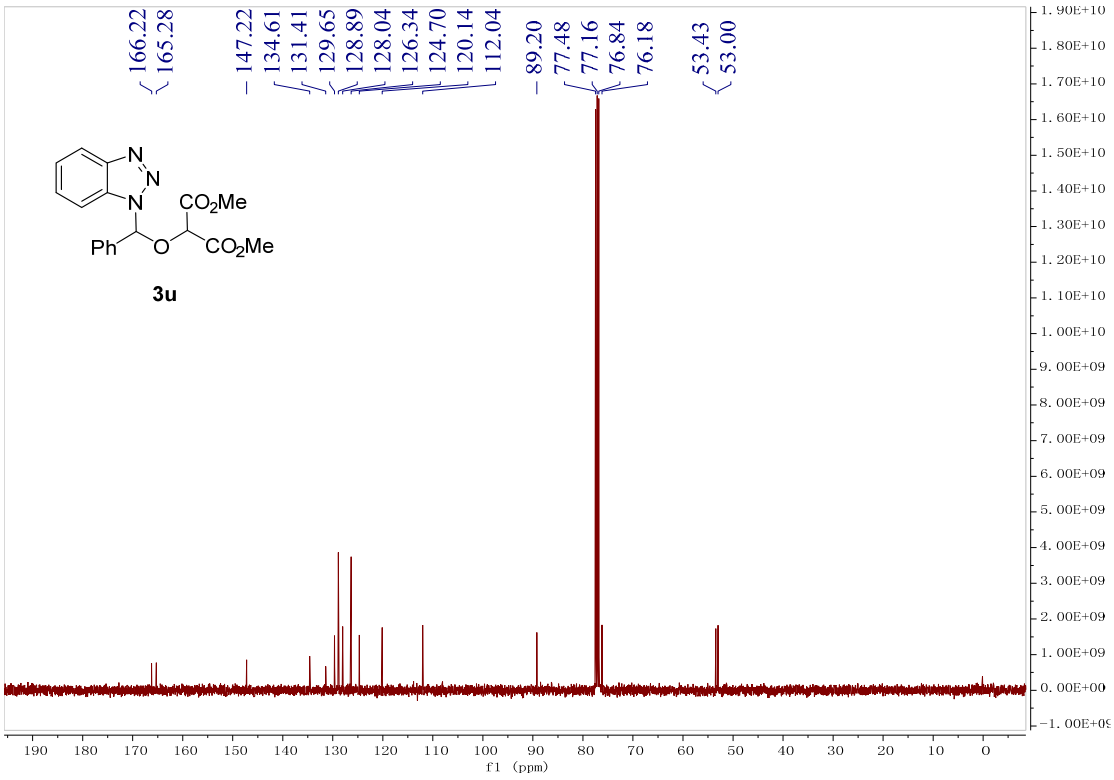
^{13}C NMR (100 MHz, $CDCl_3$) for 3t



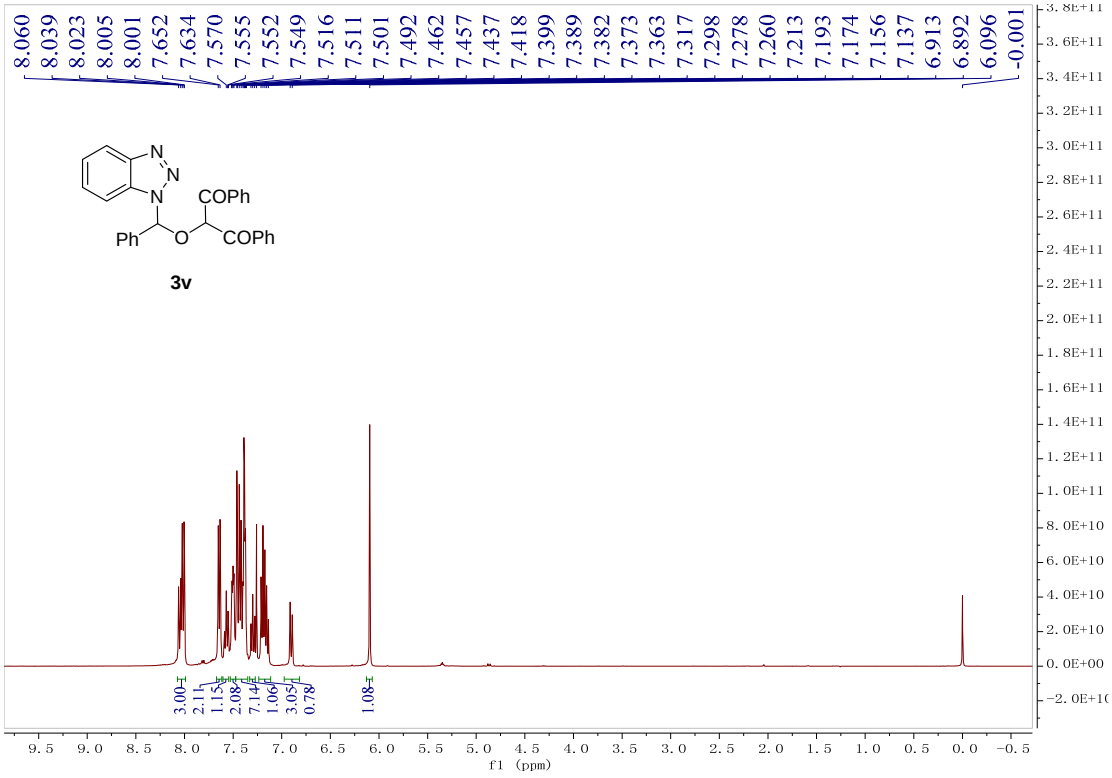
^{1}H NMR (400 MHz, $CDCl_3$) for 3u



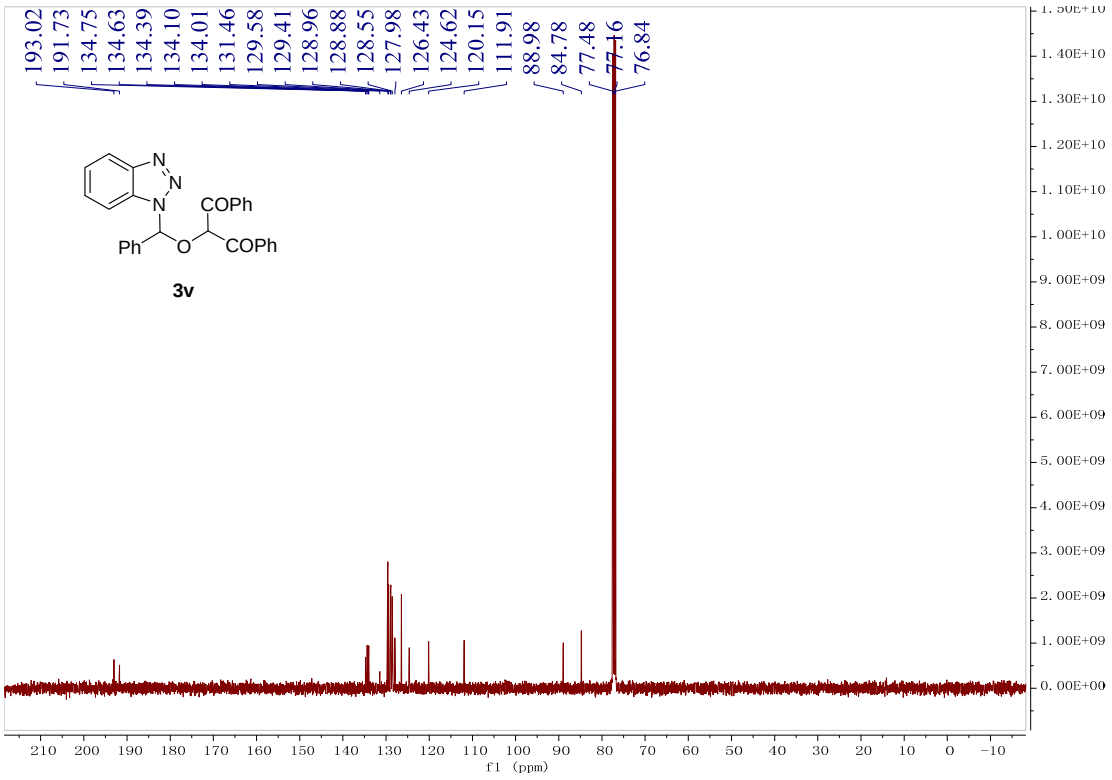
^{13}C NMR (100 MHz, $CDCl_3$) for 3u



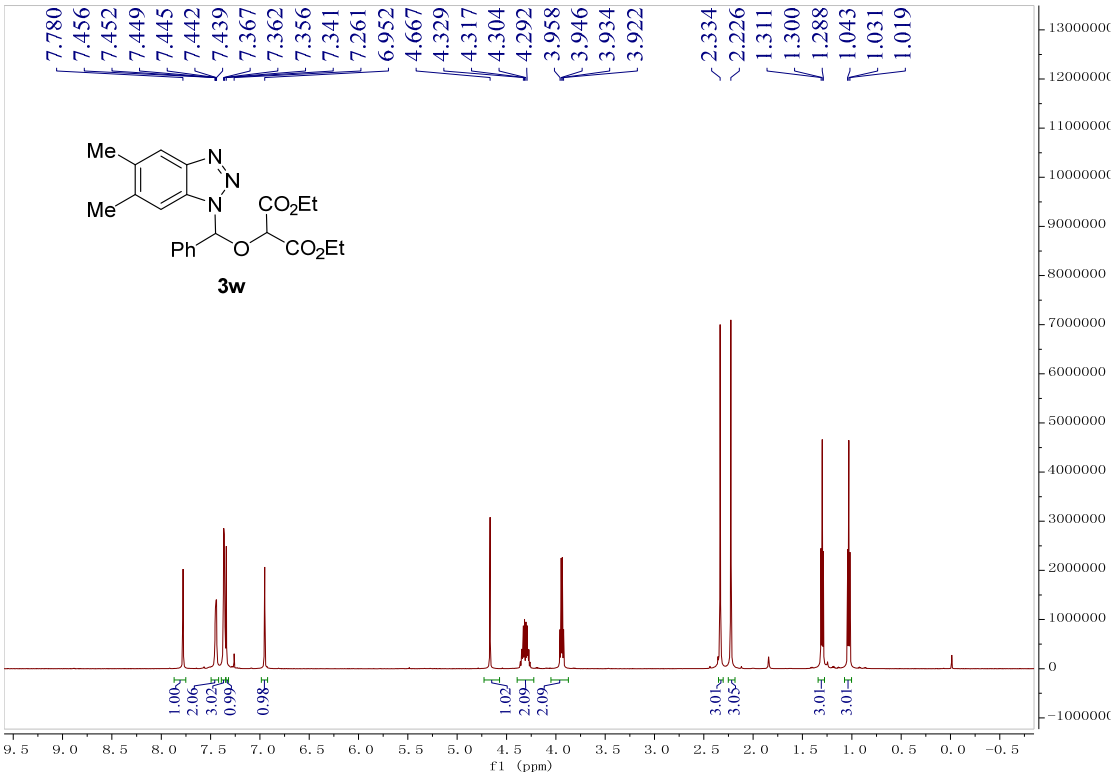
^{1}H NMR (400 MHz, $CDCl_3$) for 3v



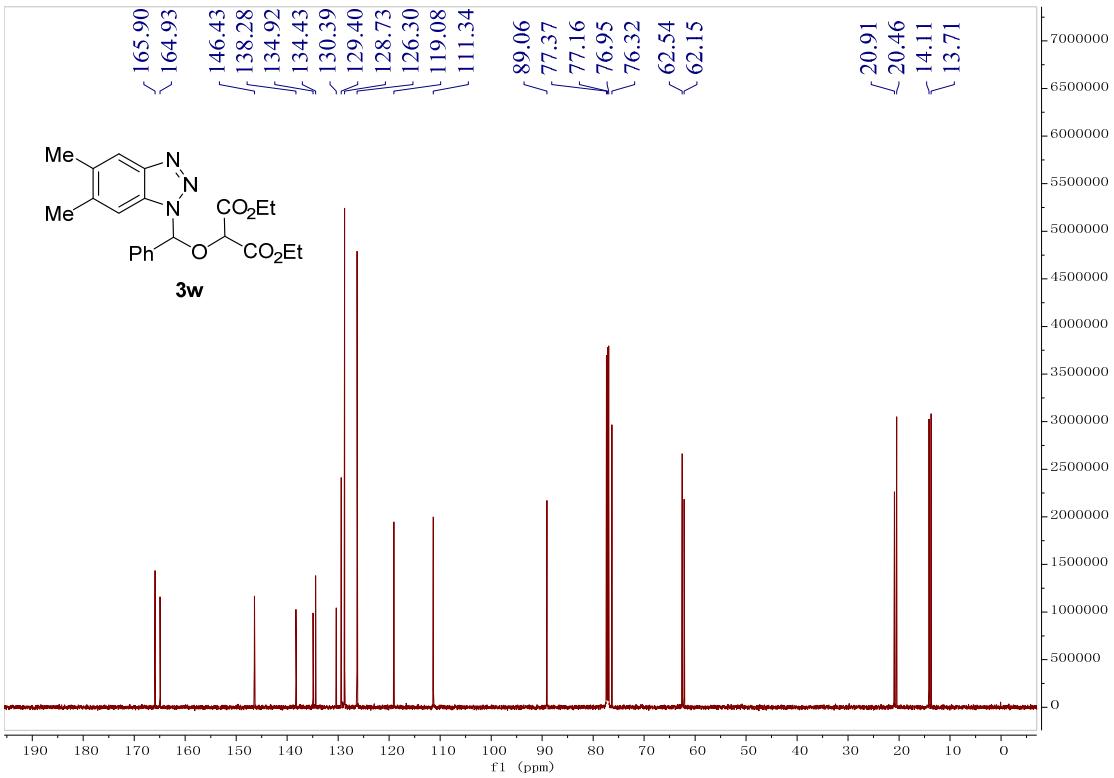
^{13}C NMR (100 MHz, $CDCl_3$) for 3v



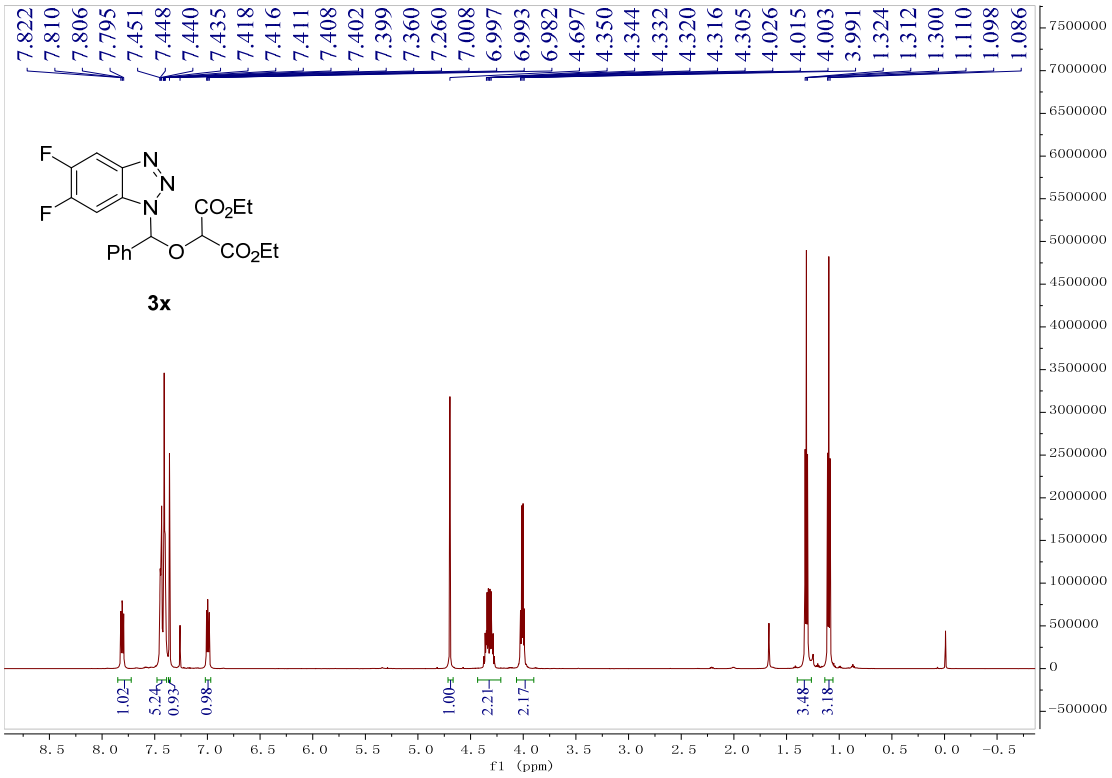
^{1}H NMR (600 MHz, $CDCl_3$) for 3w



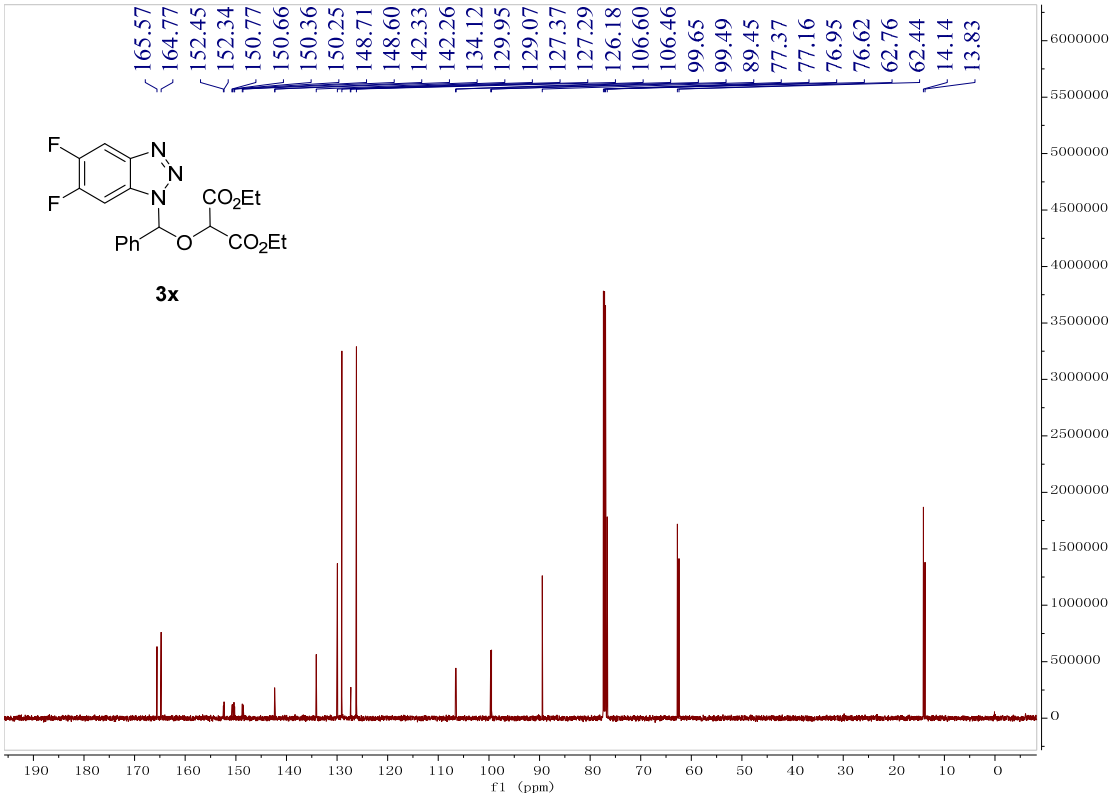
^{13}C NMR (150 MHz, $CDCl_3$) for 3w



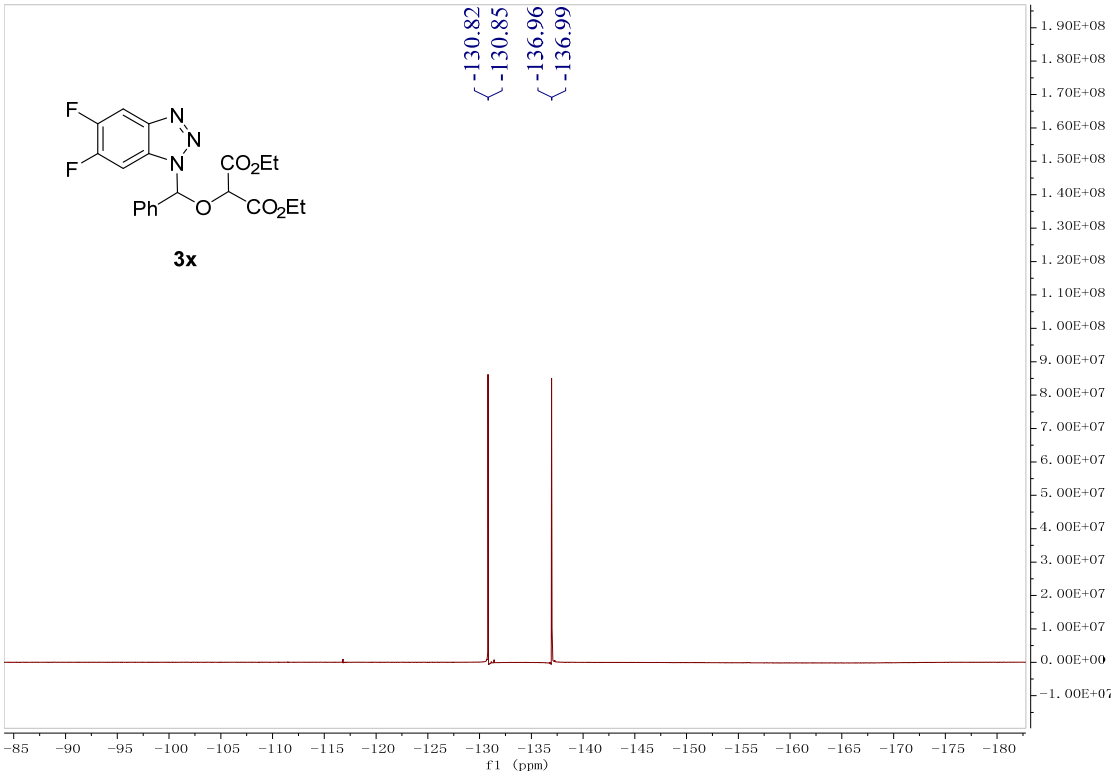
^{1}H NMR (600 MHz, $CDCl_3$) for 3x



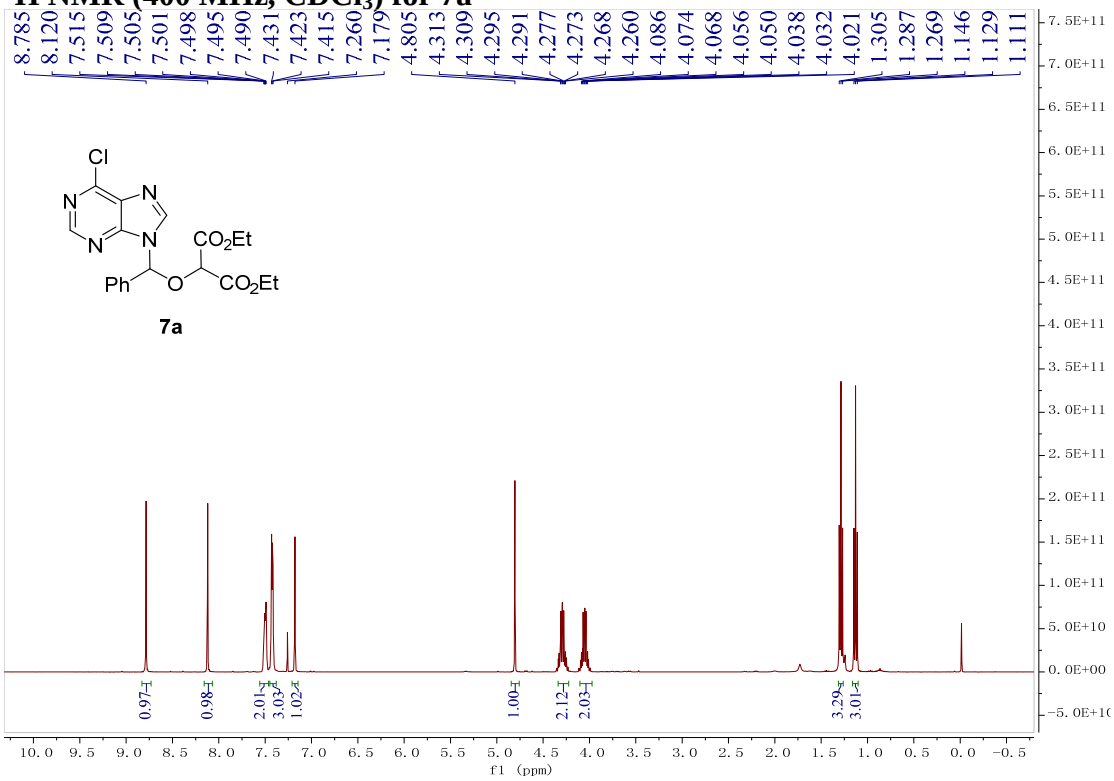
^{13}C NMR (150 MHz, $CDCl_3$) for 3x



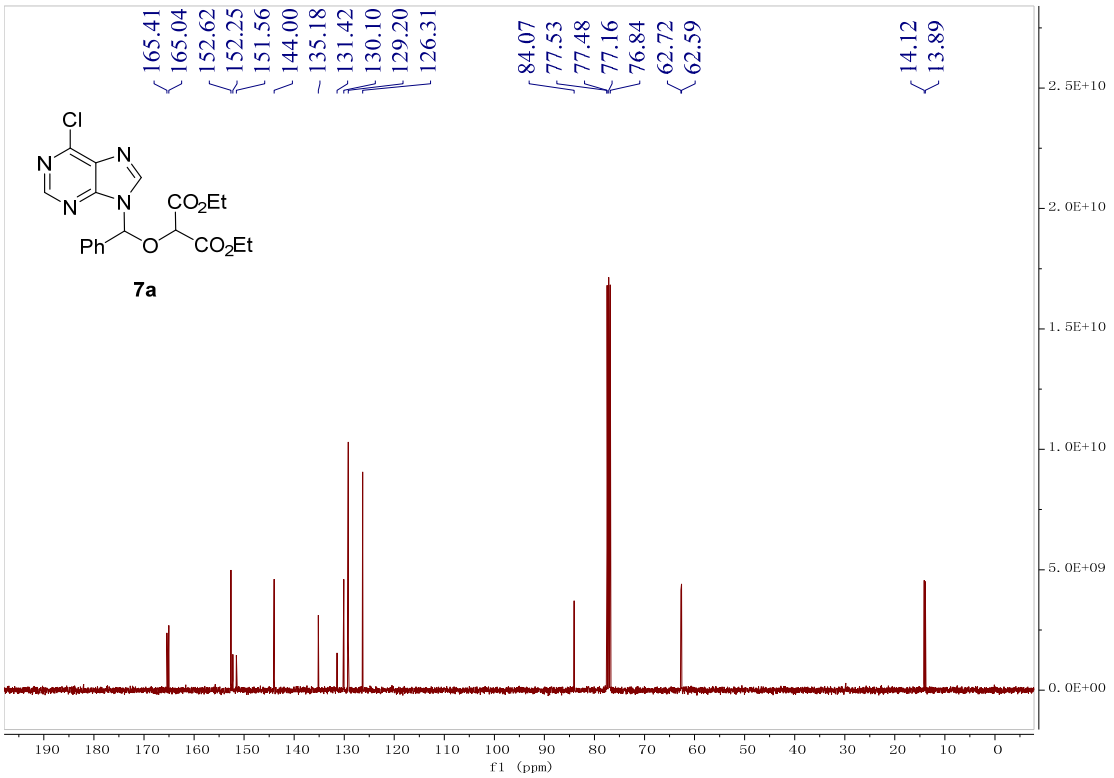
^{19}F NMR (565 MHz, $CDCl_3$) for 3x



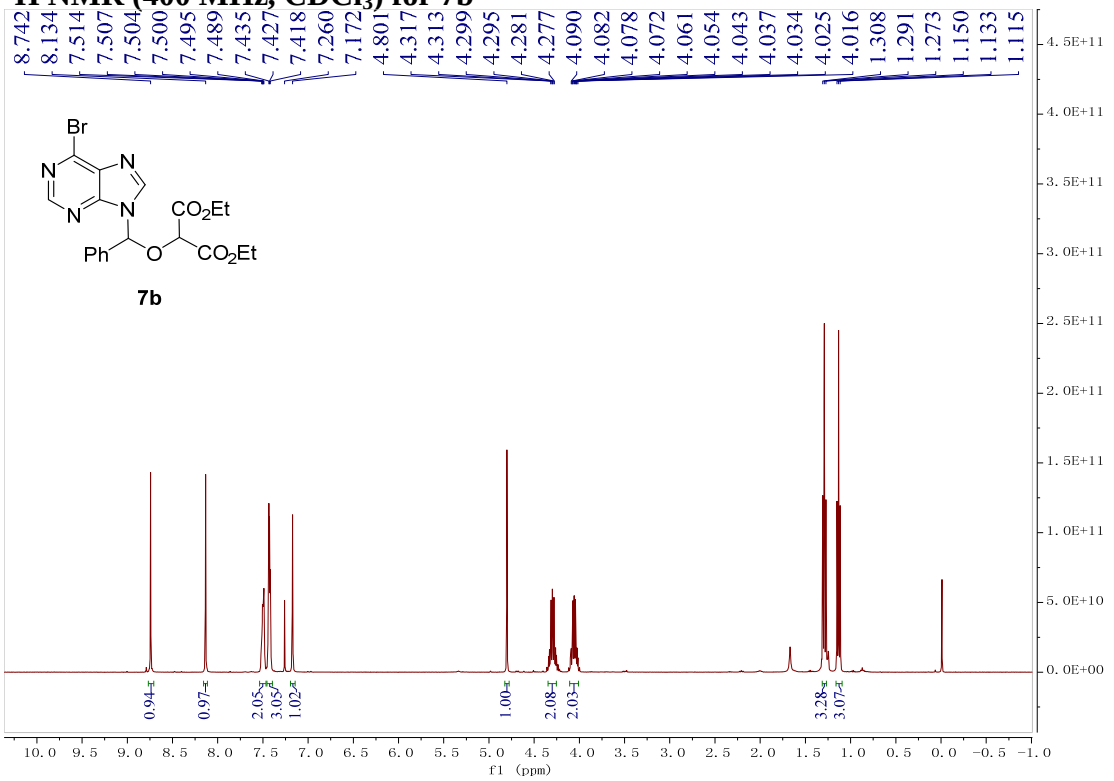
^{1}H NMR (400 MHz, $CDCl_3$) for 7a



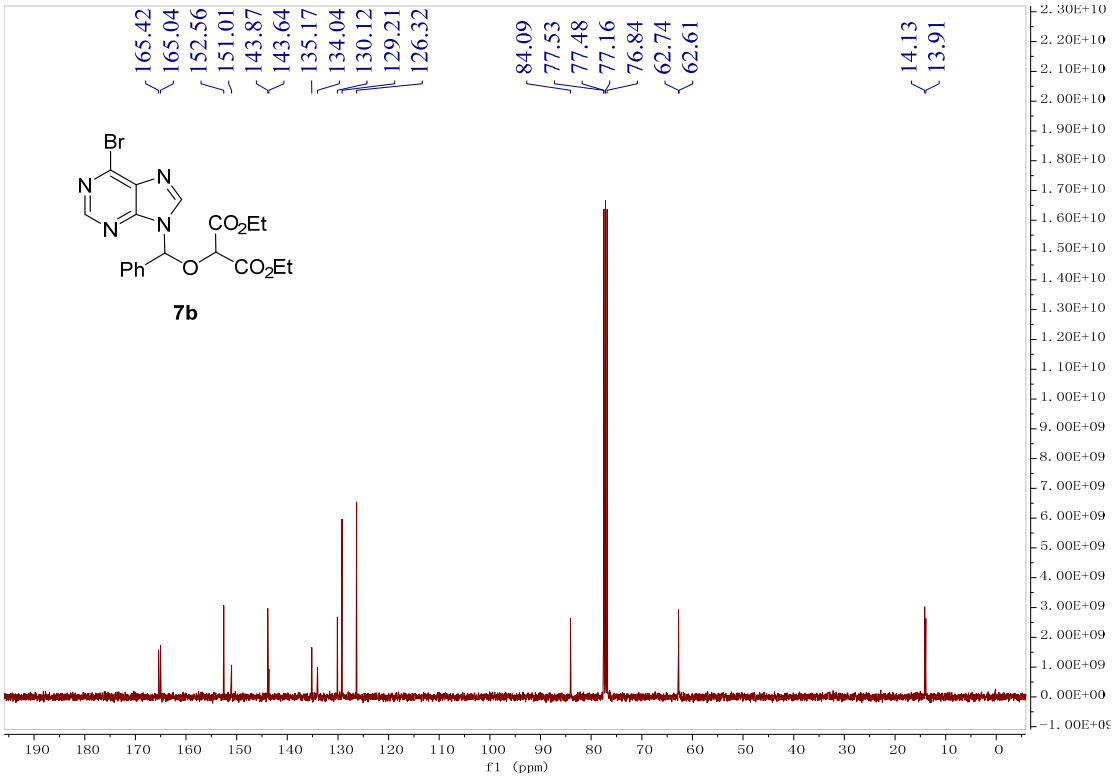
^{13}C NMR (100 MHz, $CDCl_3$) for 7a



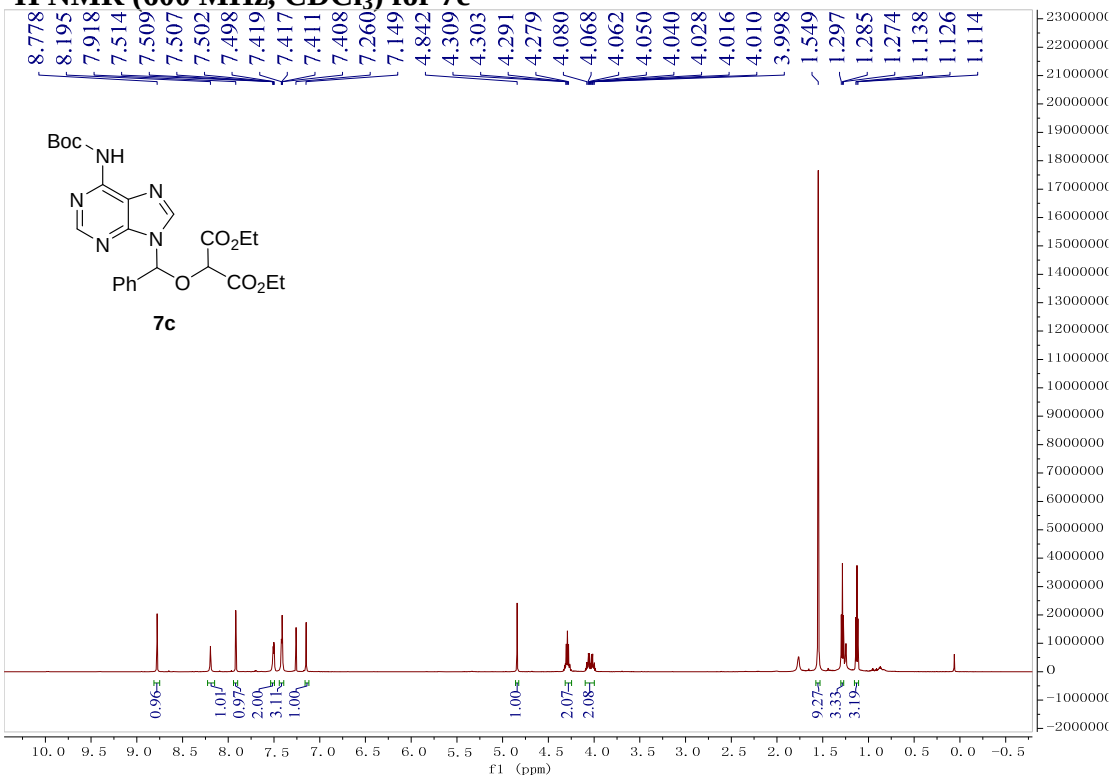
^{1}H NMR (400 MHz, $CDCl_3$) for 7b



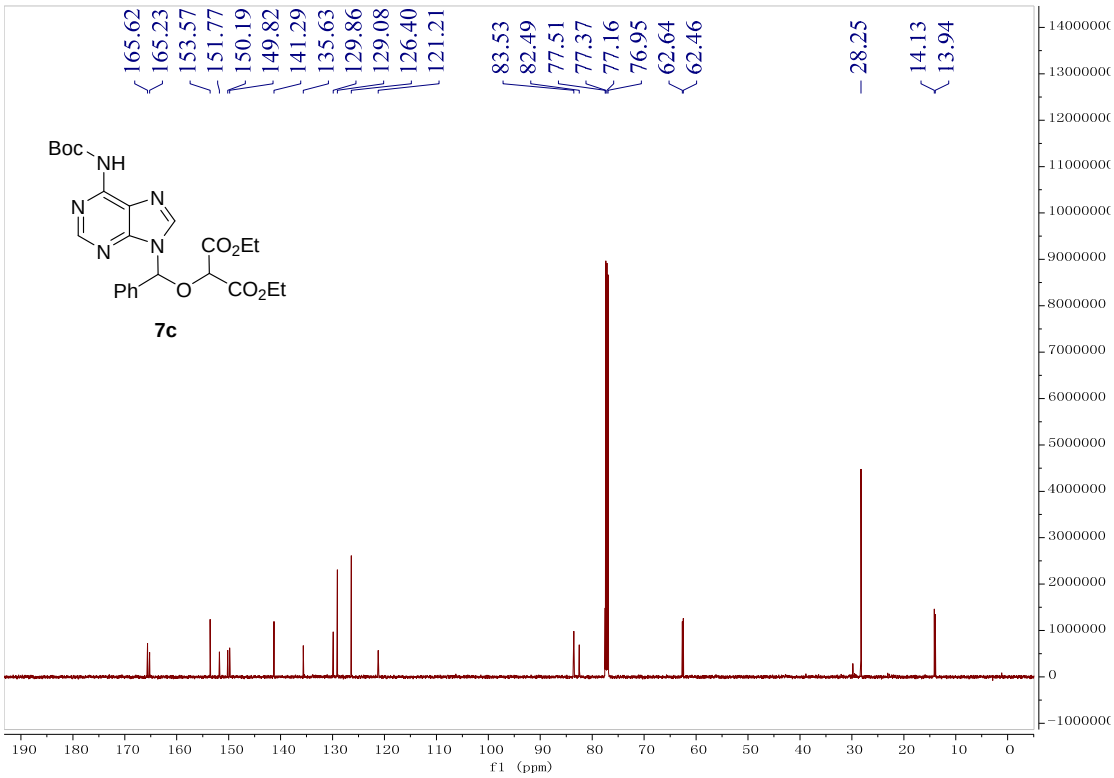
^{13}C NMR (100 MHz, $CDCl_3$) for 7b



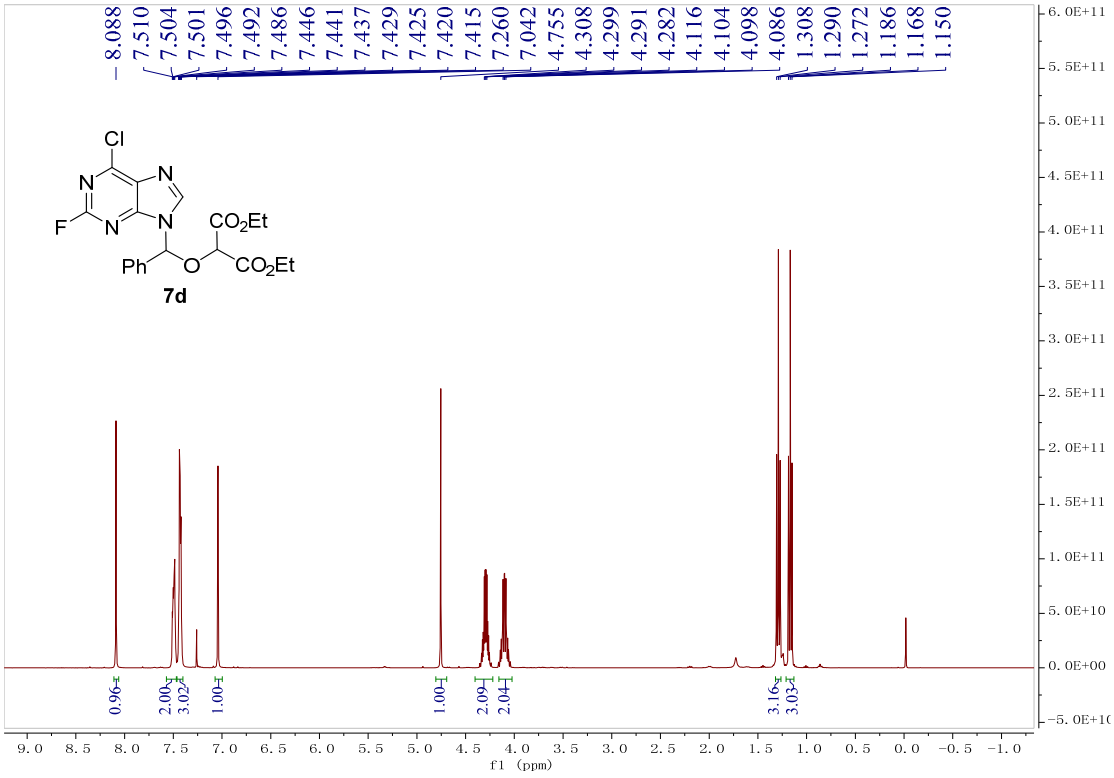
^{1}H NMR (600 MHz, $CDCl_3$) for 7c



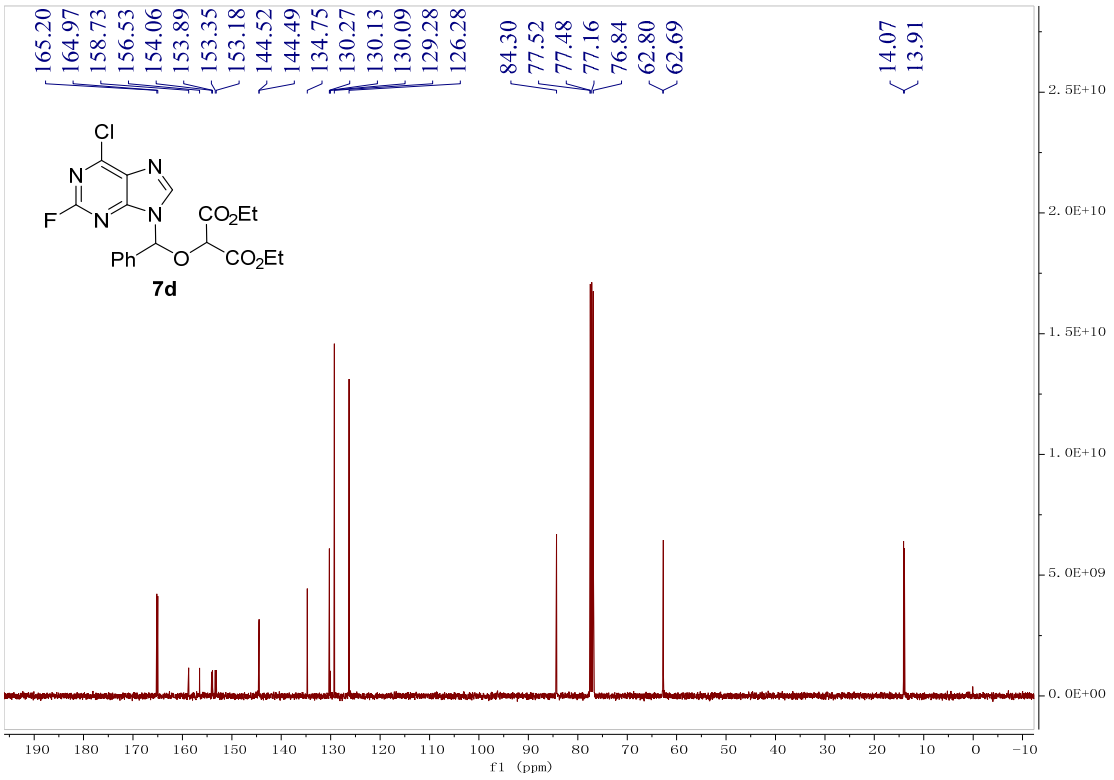
^{13}C NMR (150 MHz, $CDCl_3$) for 7c



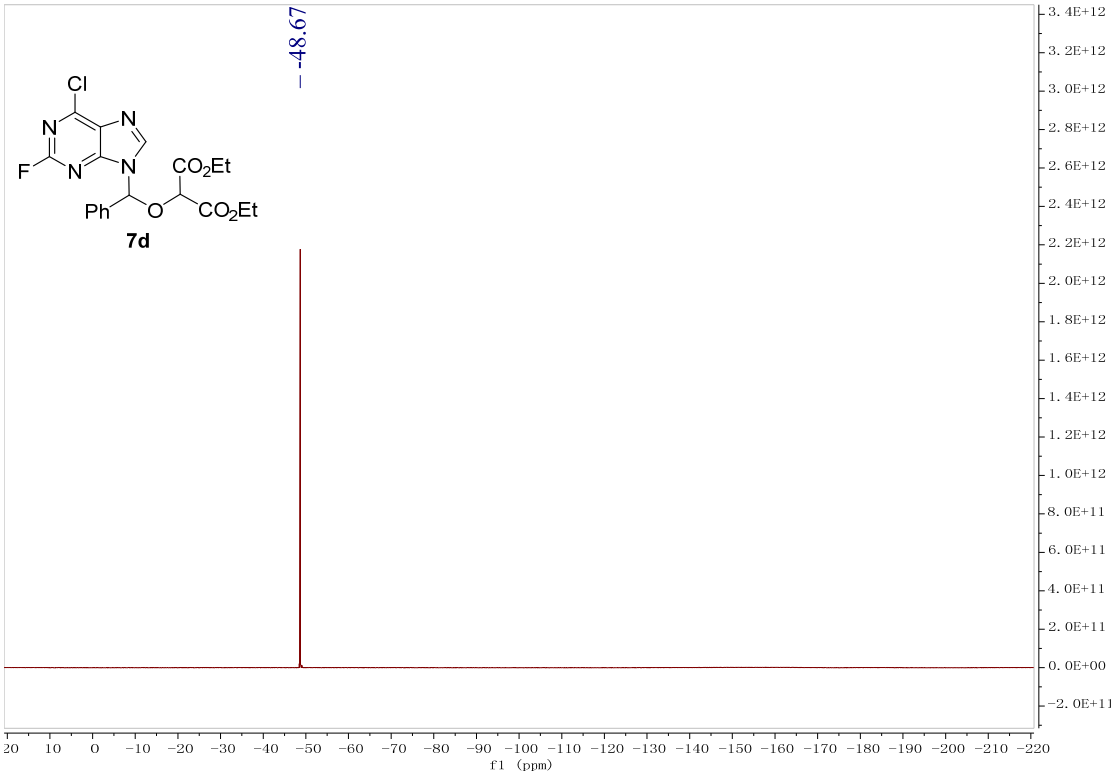
^{1}H NMR (400 MHz, $CDCl_3$) for 7d



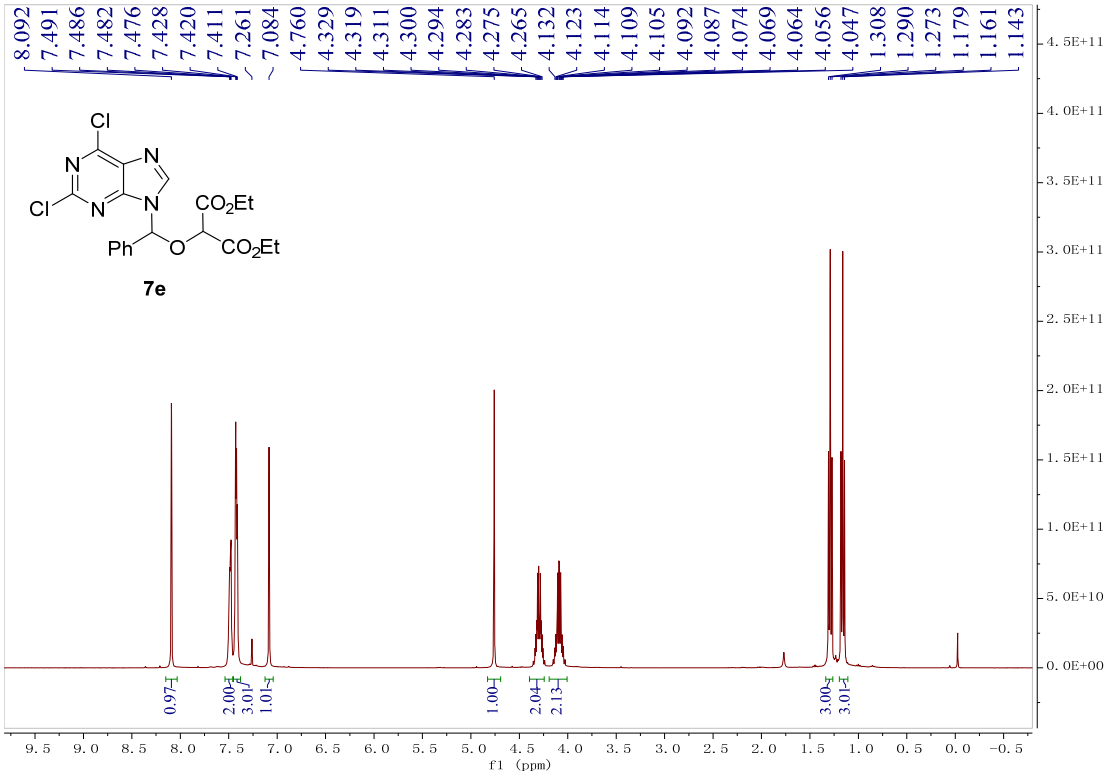
^{13}C NMR (100 MHz, $CDCl_3$) for 7d



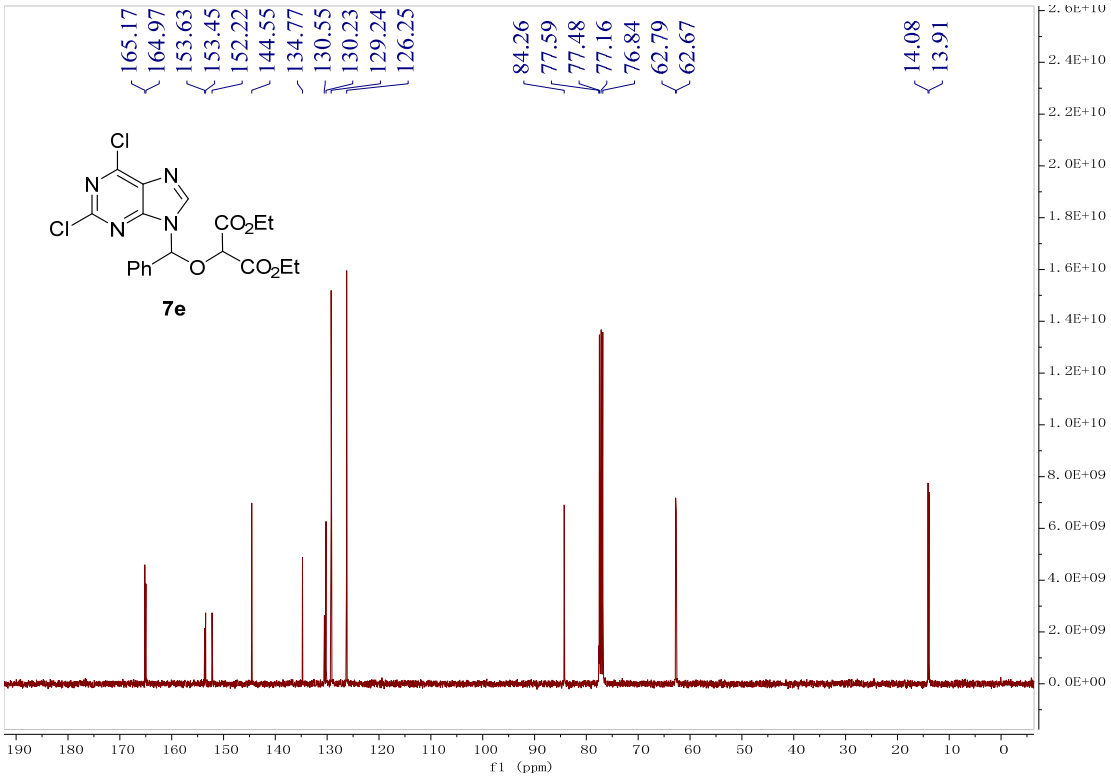
^{19}F NMR (376 MHz, $CDCl_3$) for 7d



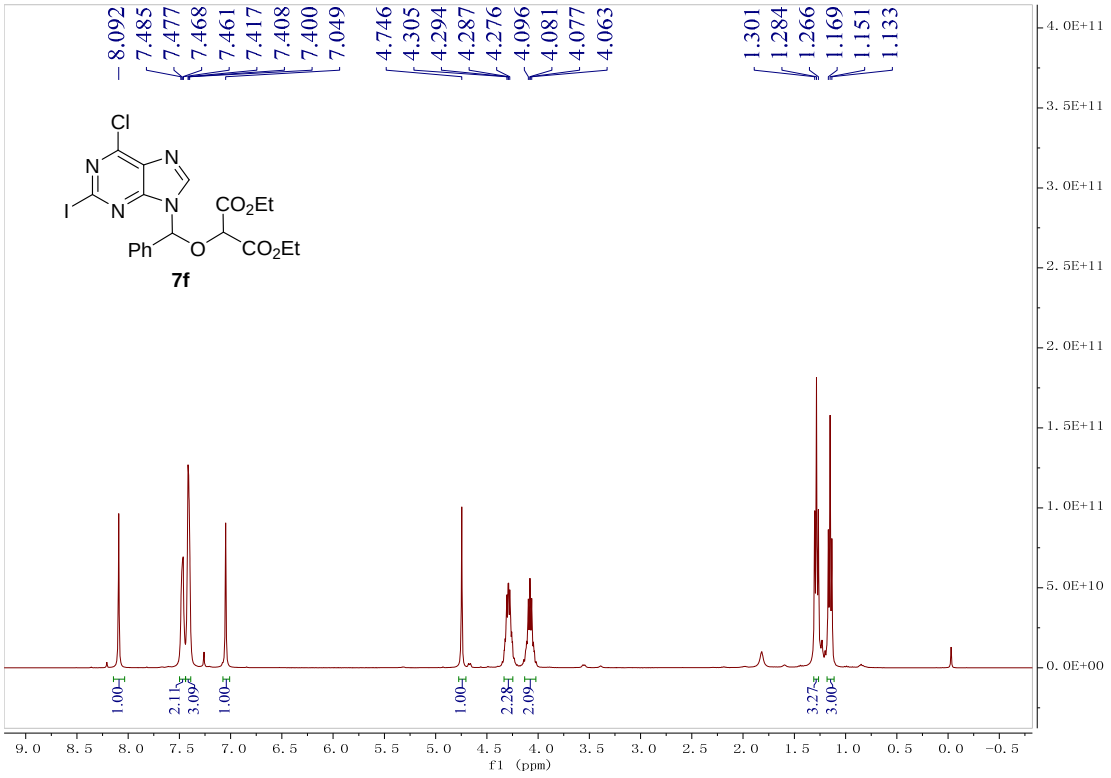
^{1}H NMR (400 MHz, $CDCl_3$) for 7e



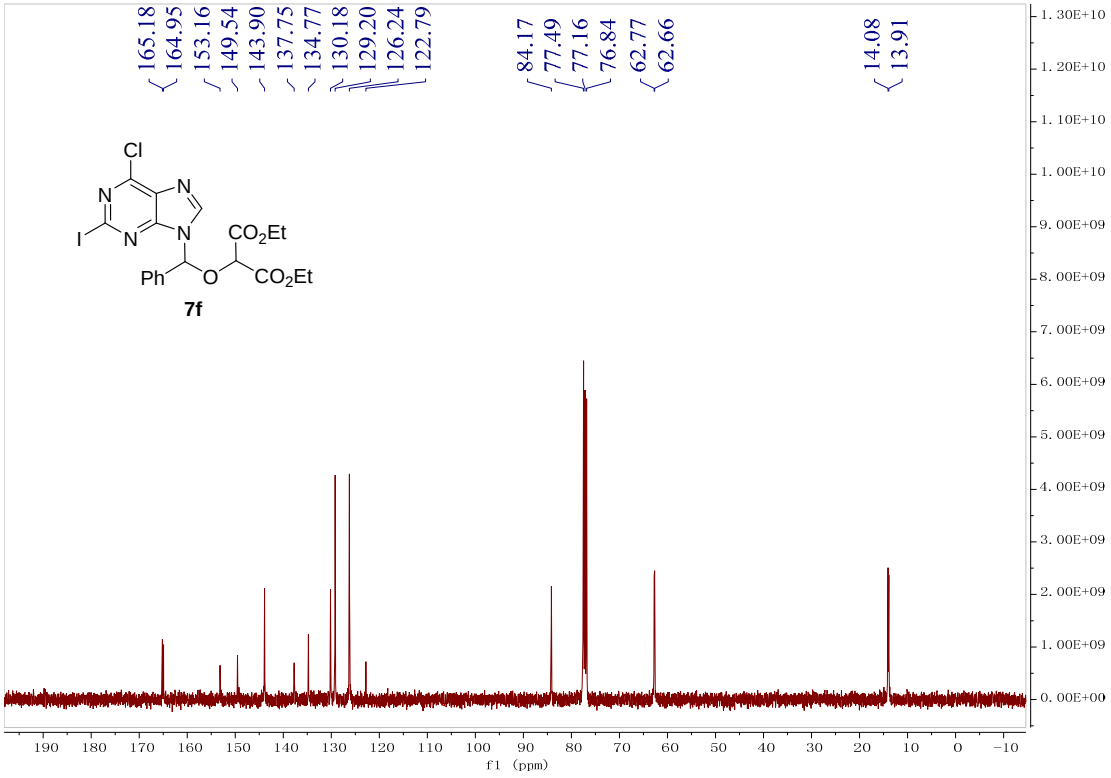
^{13}C NMR (100 MHz, $CDCl_3$) for 7e



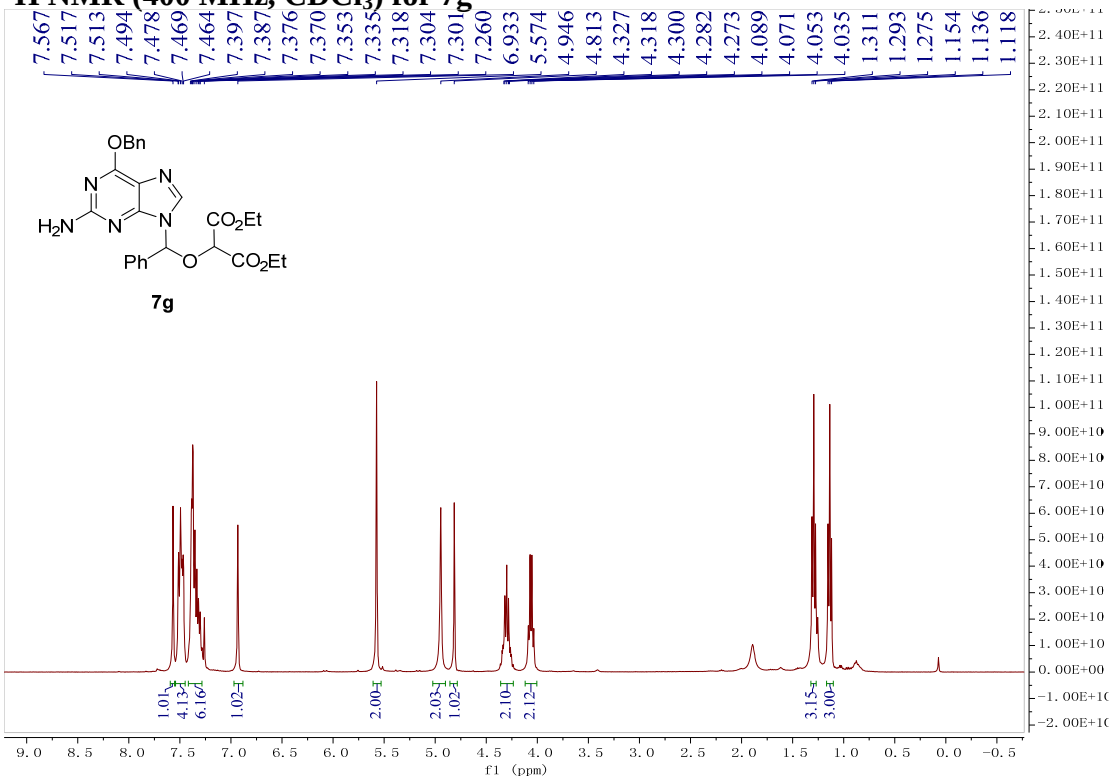
^{1}H NMR (400 MHz, $CDCl_3$) for 7f



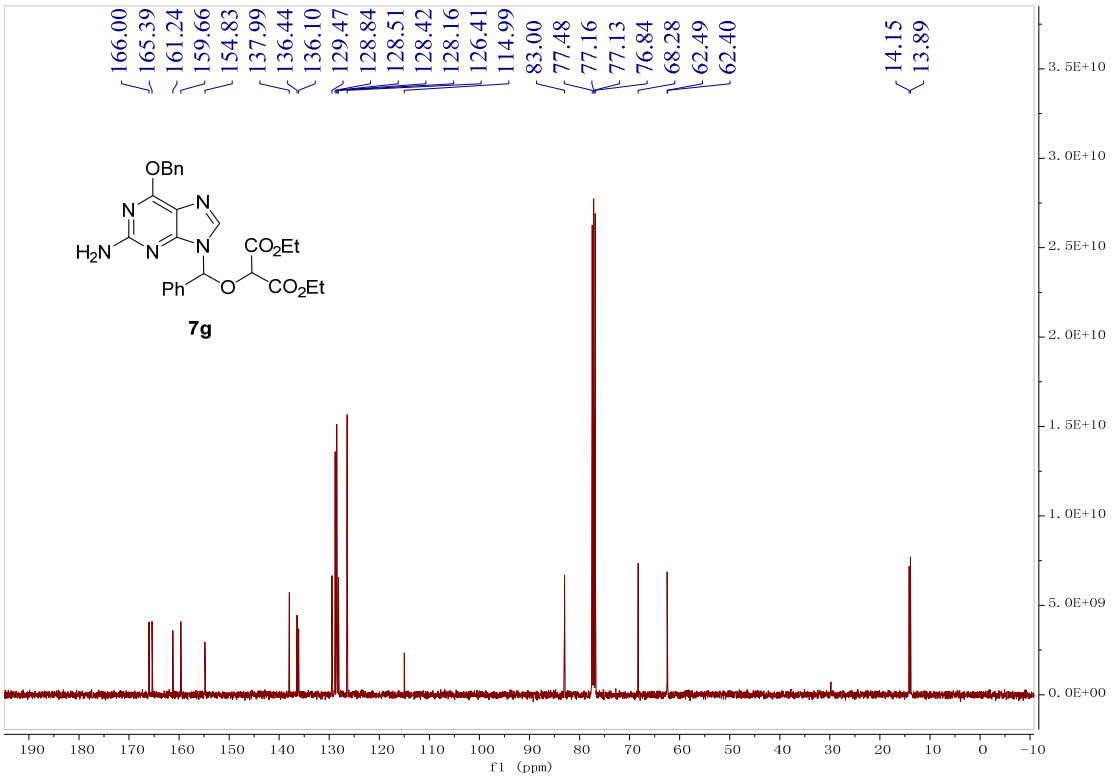
^{13}C NMR (100 MHz, $CDCl_3$) for 7f



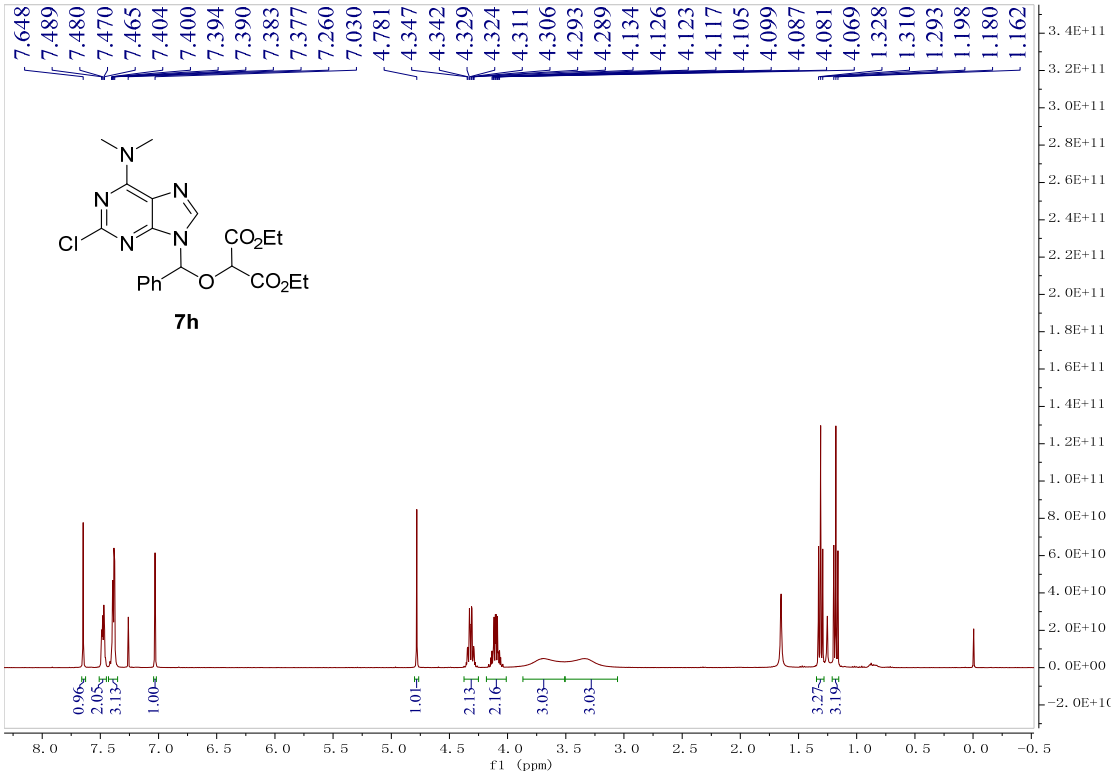
^{1}H NMR (400 MHz, $CDCl_3$) for 7g



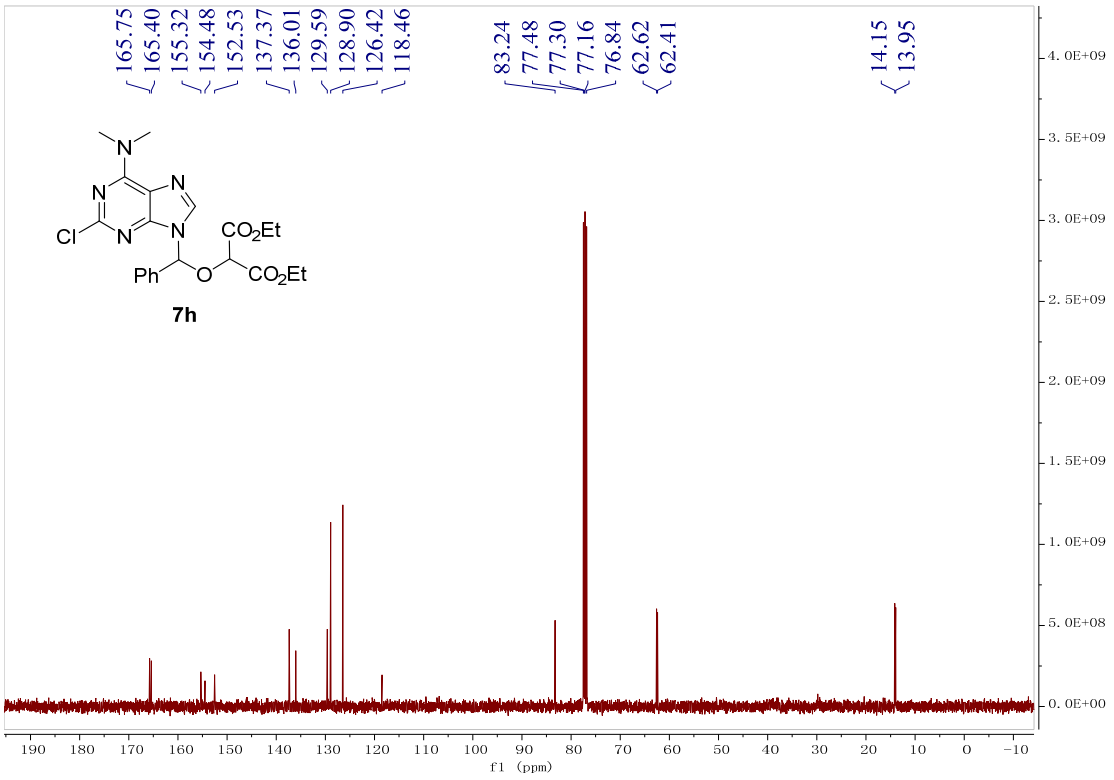
^{13}C NMR (100 MHz, $CDCl_3$) for 7g



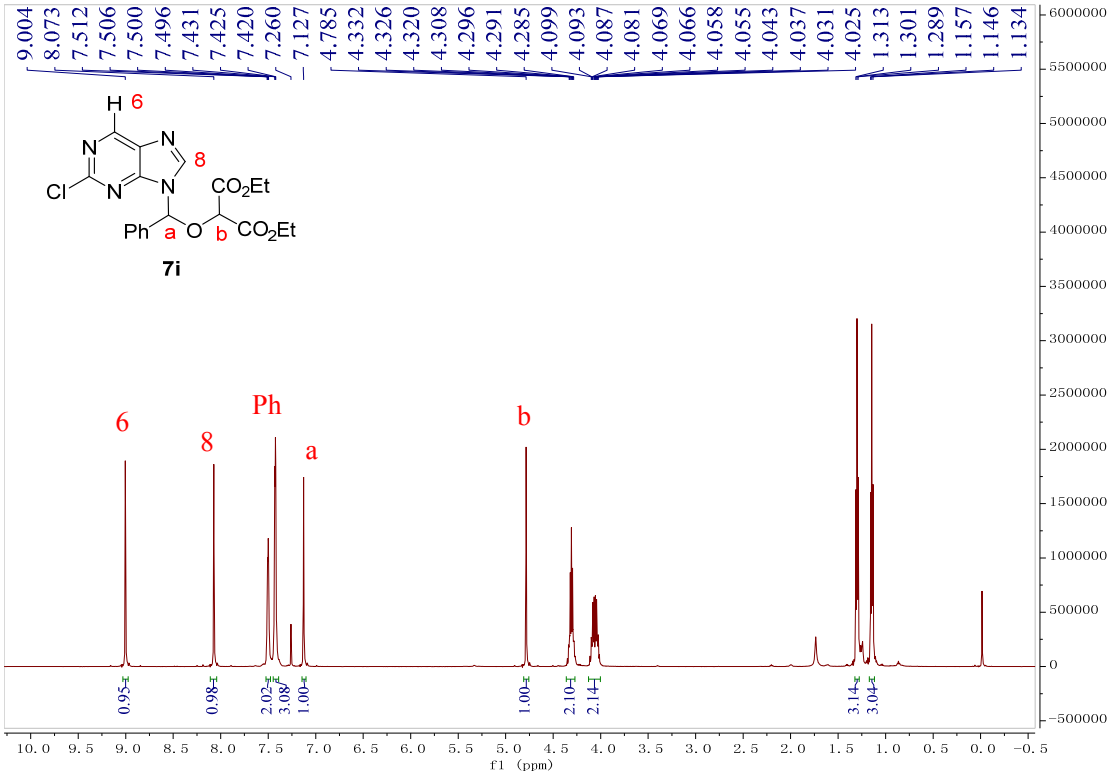
^{1}H NMR (400 MHz, $CDCl_3$) for 7h



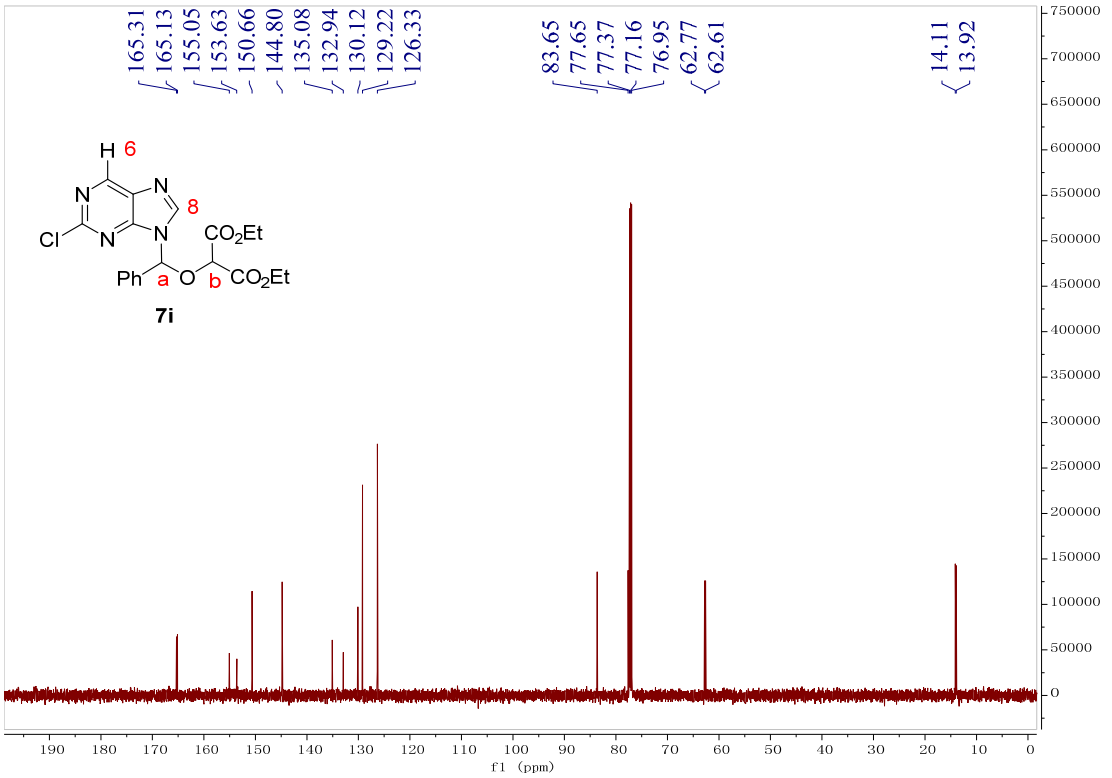
^{13}C NMR (100 MHz, $CDCl_3$) for 7h



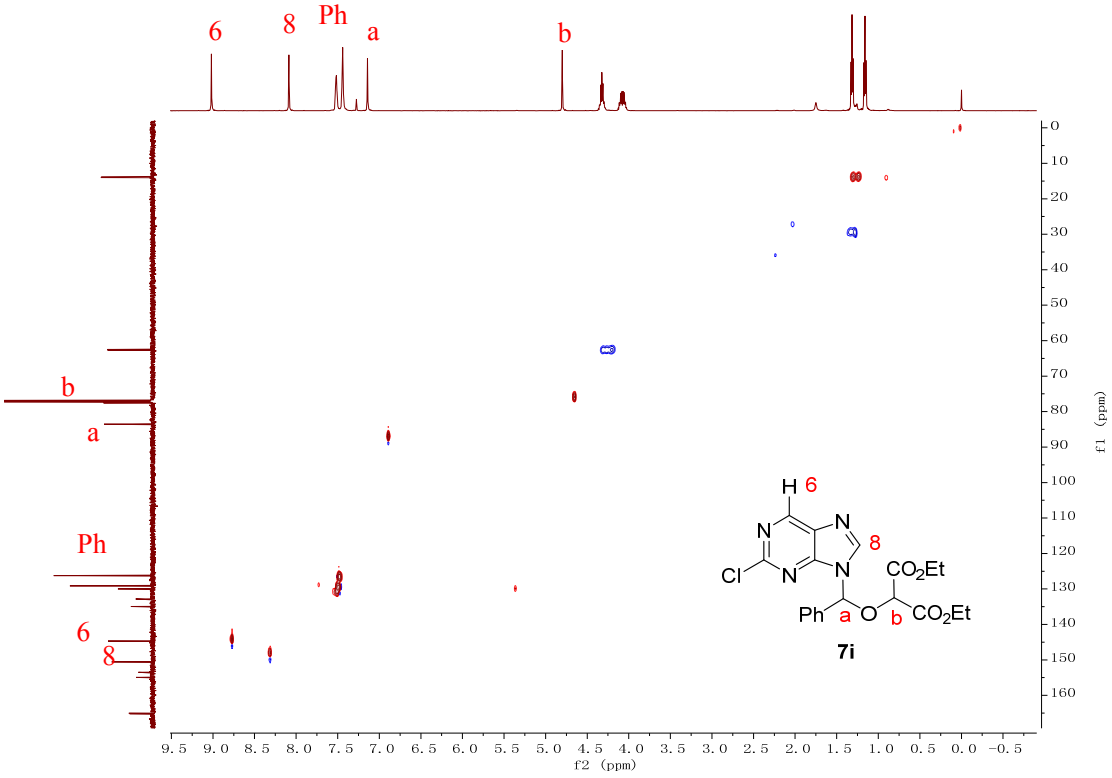
^{1}H NMR (600 MHz, $CDCl_3$) for 7i



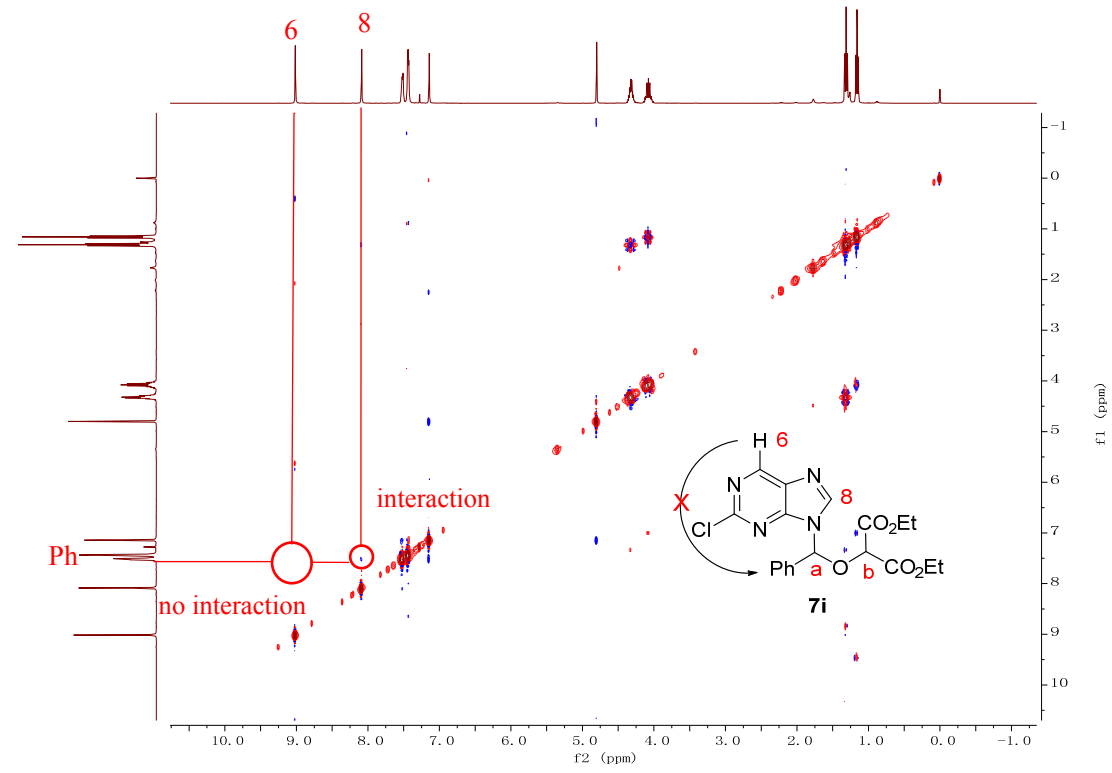
^{13}C NMR (150 MHz, $CDCl_3$) for 7i



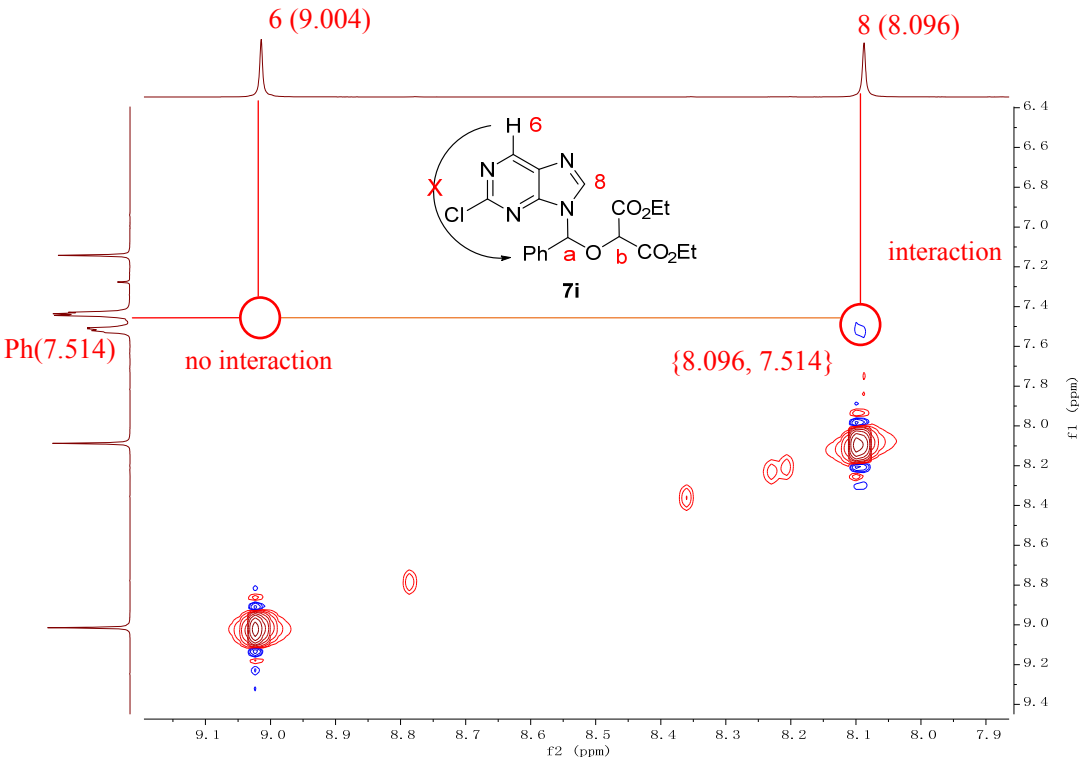
HSQC of 7i



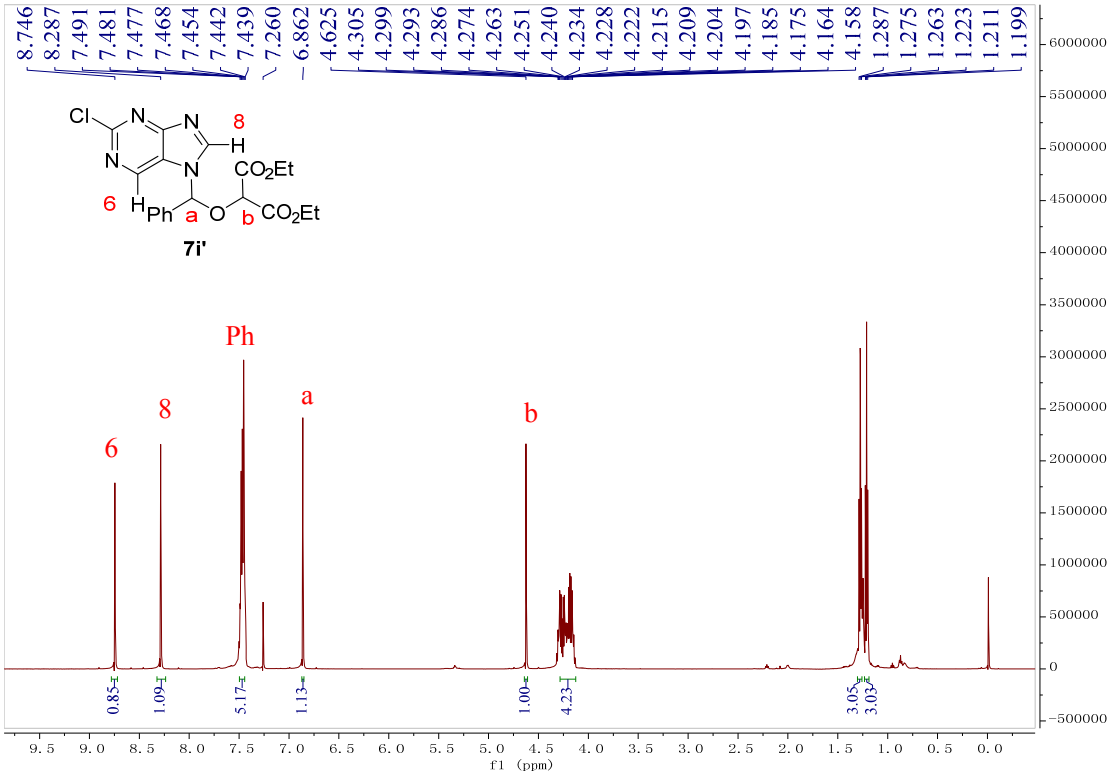
NOESY of 7i



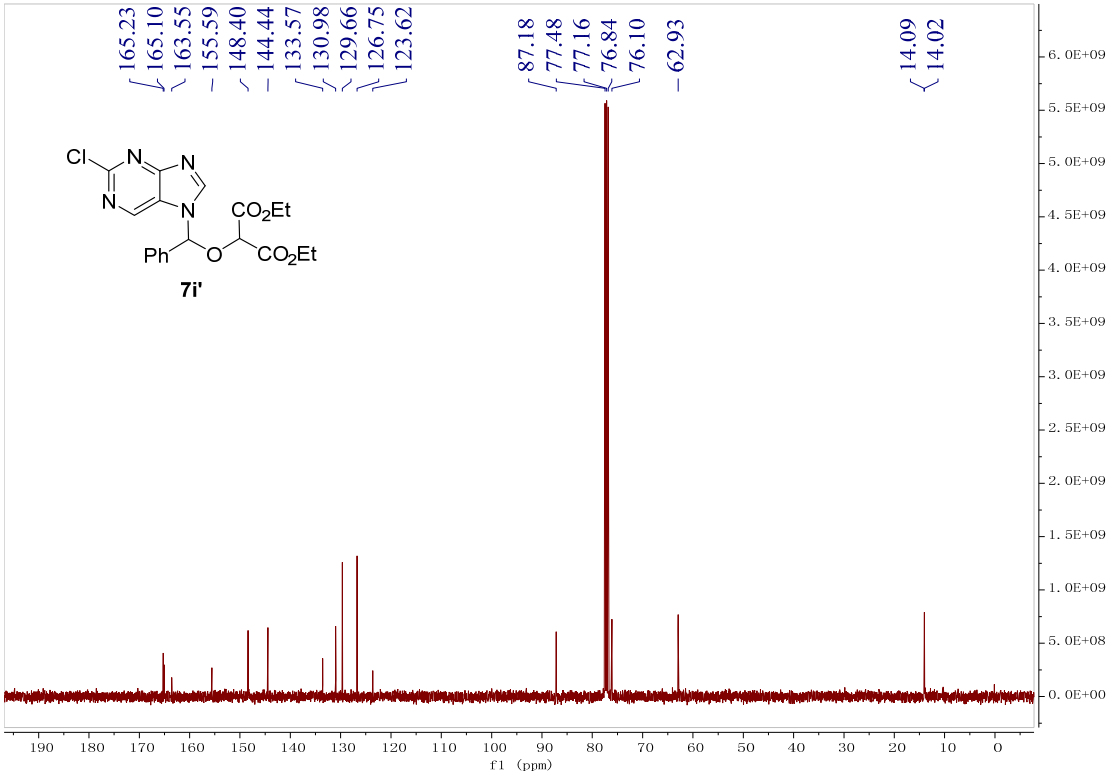
The enlarge NOE single is as follows



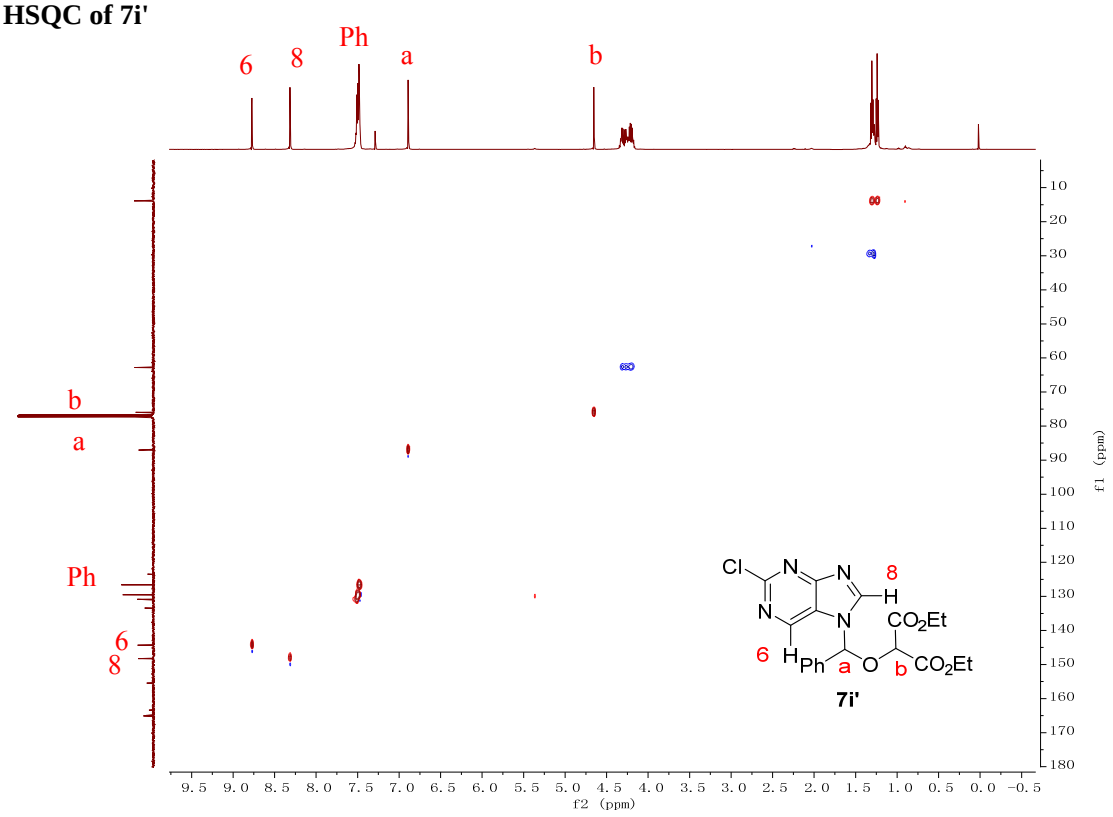
^{1}H NMR (600 MHz, $CDCl_3$) for 7i'



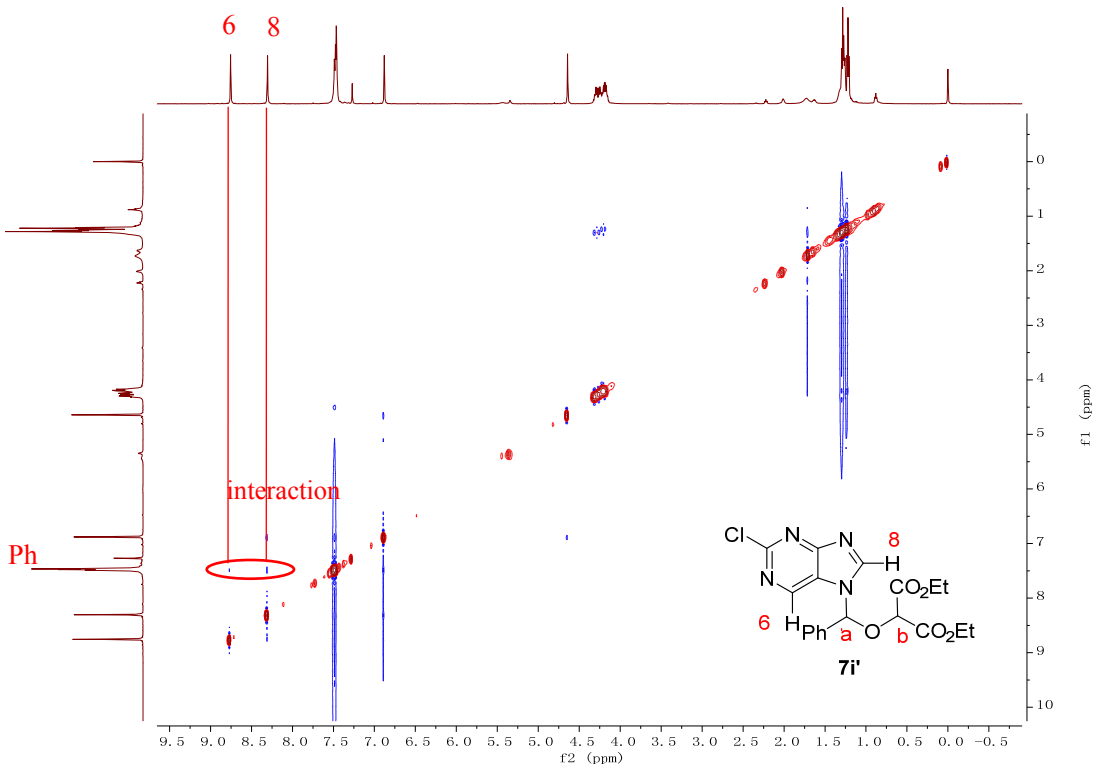
^{13}C NMR (100 MHz, $CDCl_3$) for 7i'



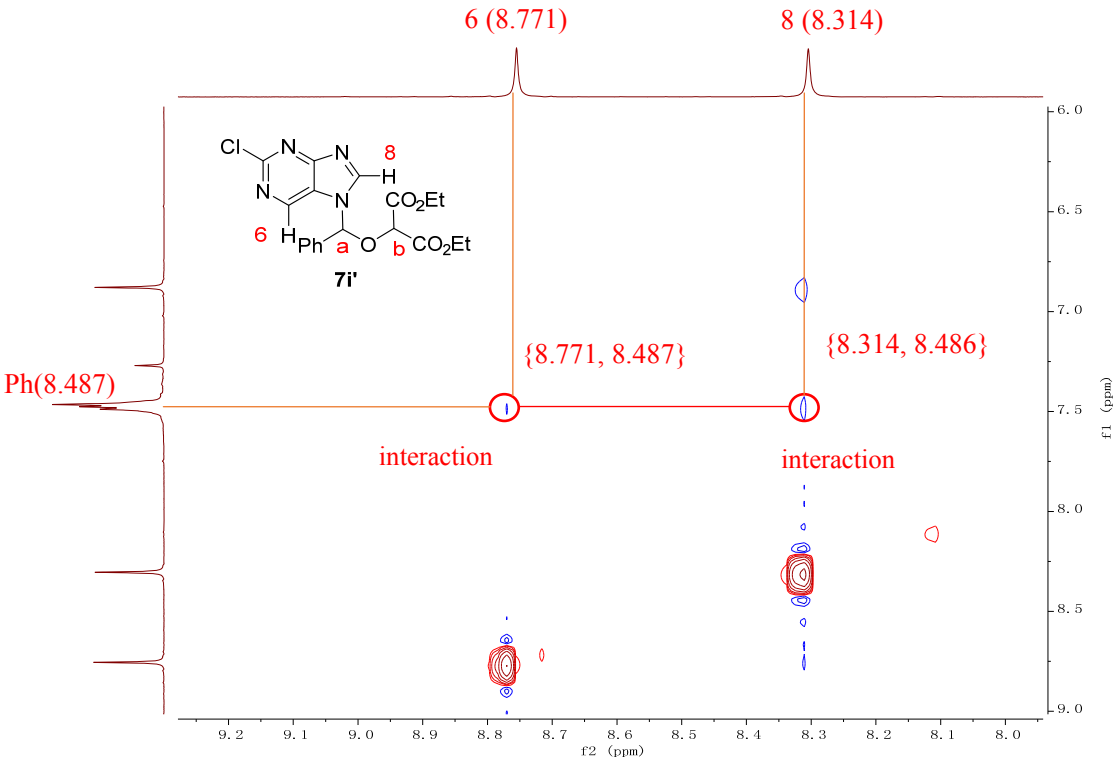
HSQC of 7i'



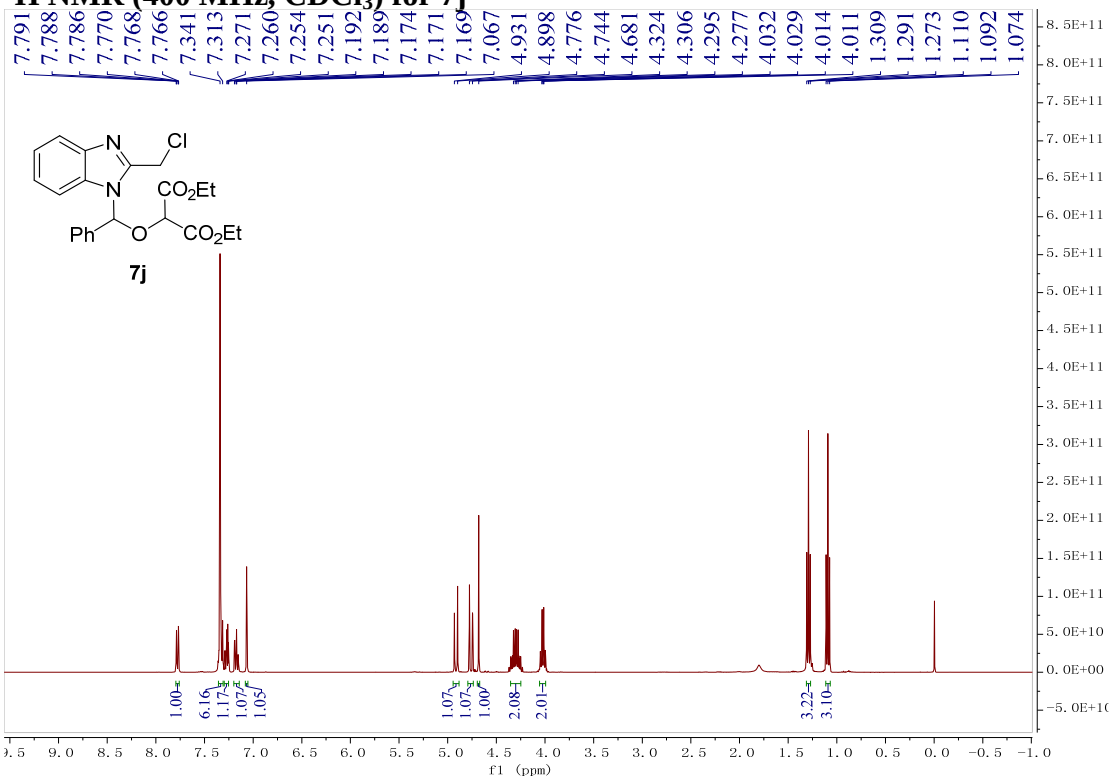
NOESY of 7i'



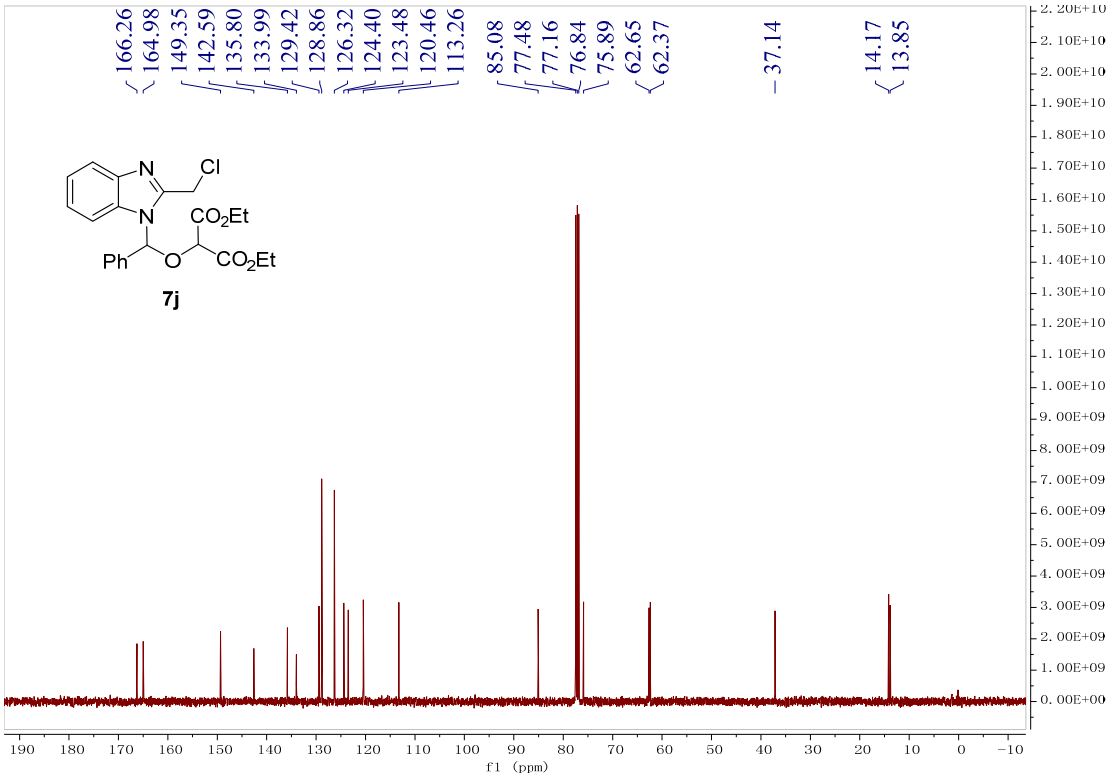
The enlarge NOE single is as follows



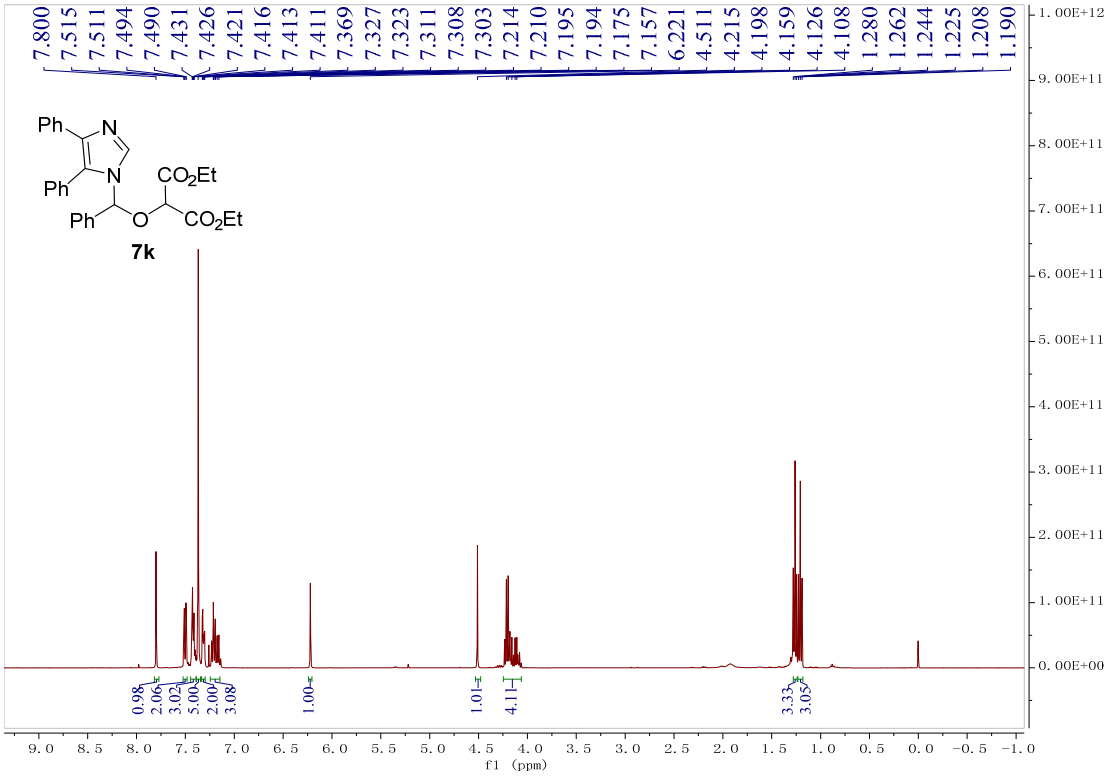
^{1}H NMR (400 MHz, $CDCl_3$) for 7j



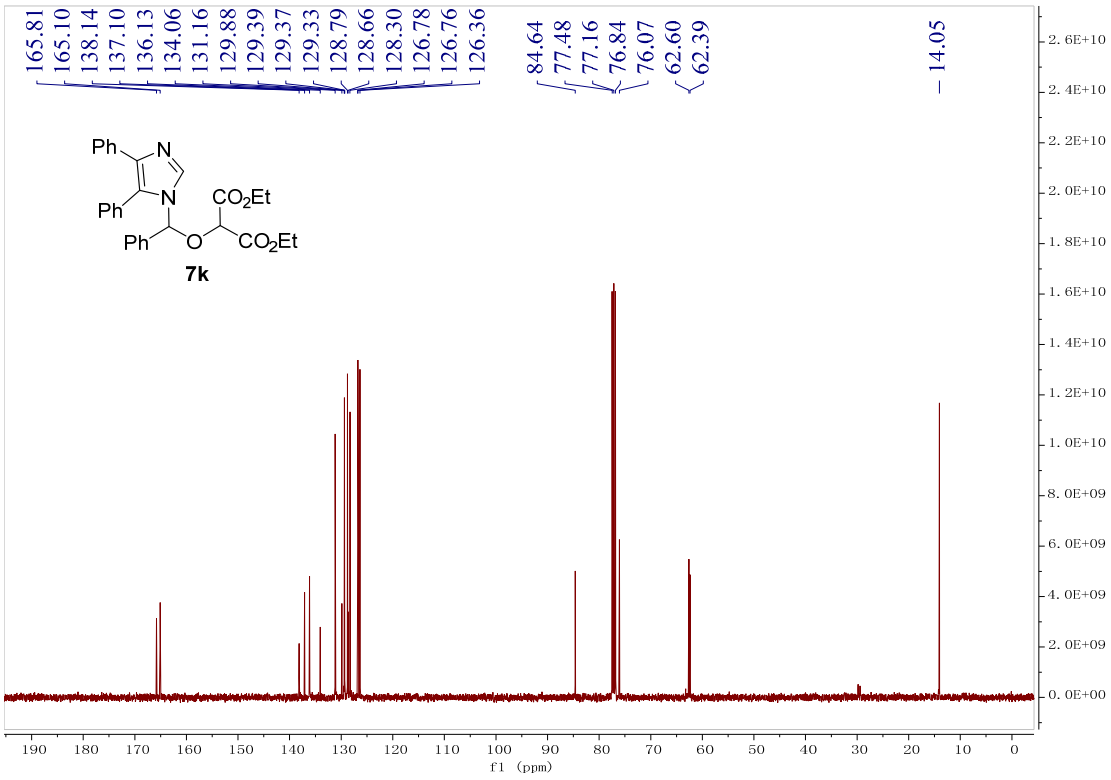
^{13}C NMR (100 MHz, $CDCl_3$) for 7j



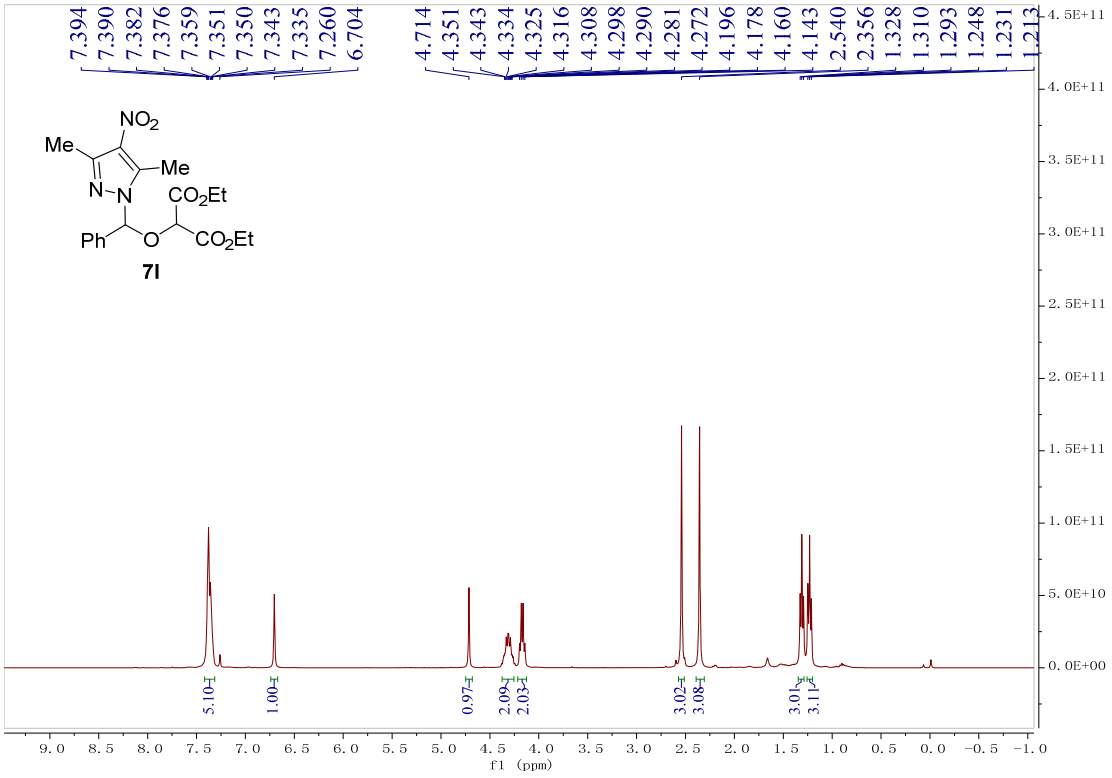
^{1}H NMR (400 MHz, $CDCl_3$) for 7k



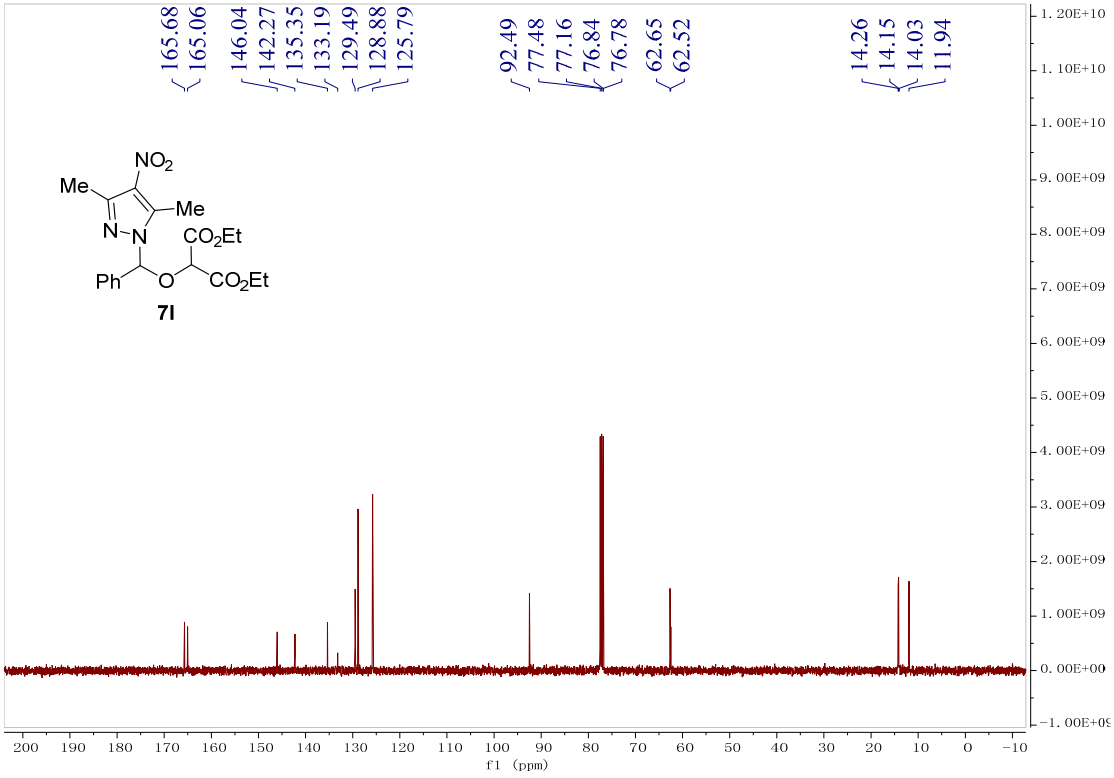
^{13}C NMR (100 MHz, $CDCl_3$) for 7k



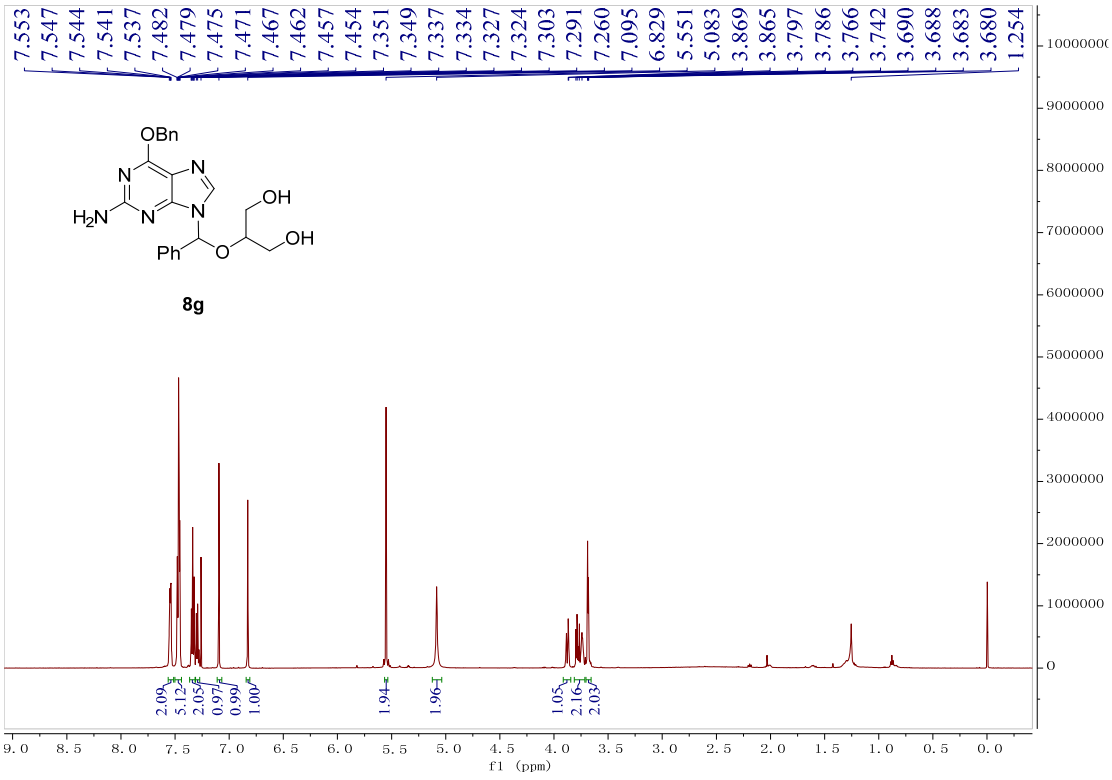
^{1}H NMR (400 MHz, $CDCl_3$) for 7l



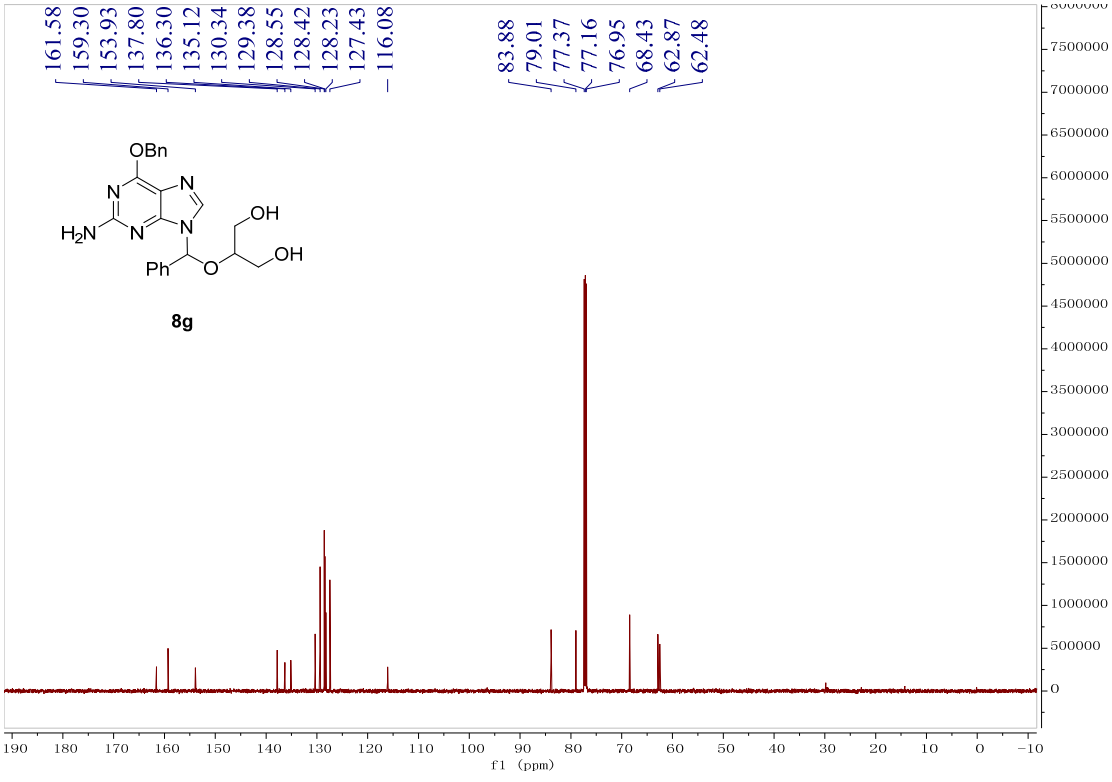
^{13}C NMR (100 MHz, $CDCl_3$) for 7l



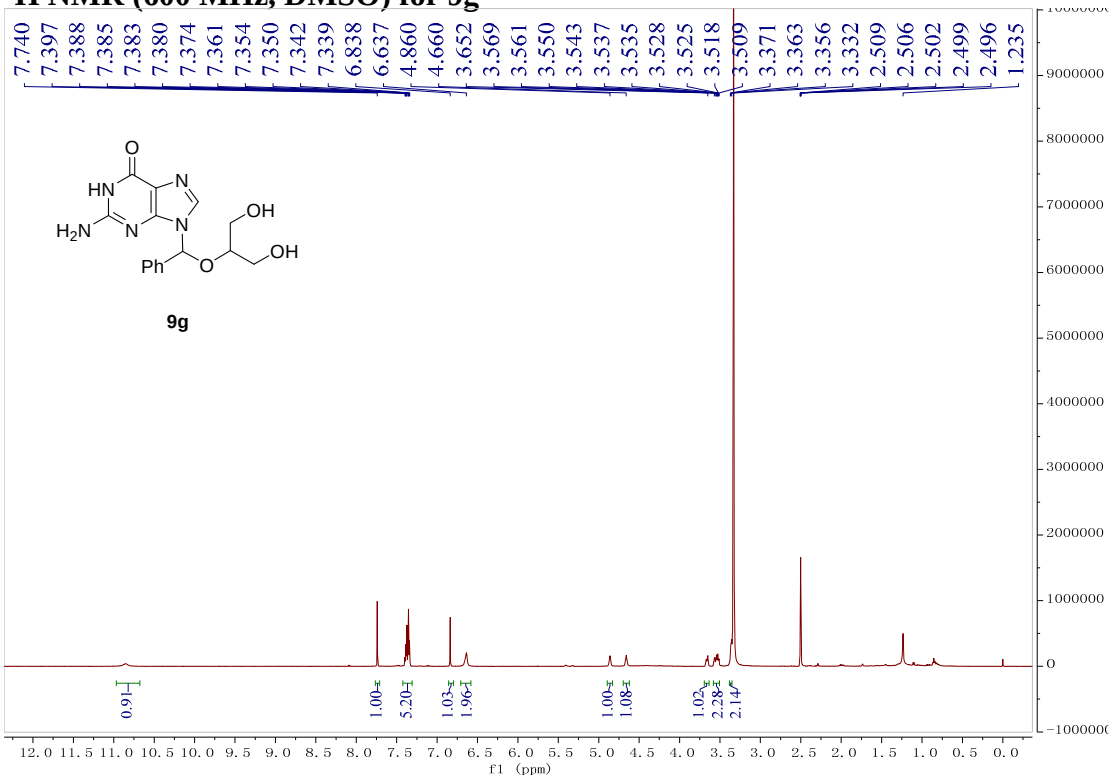
^{1}H NMR (600 MHz, $CDCl_3$) for 8g



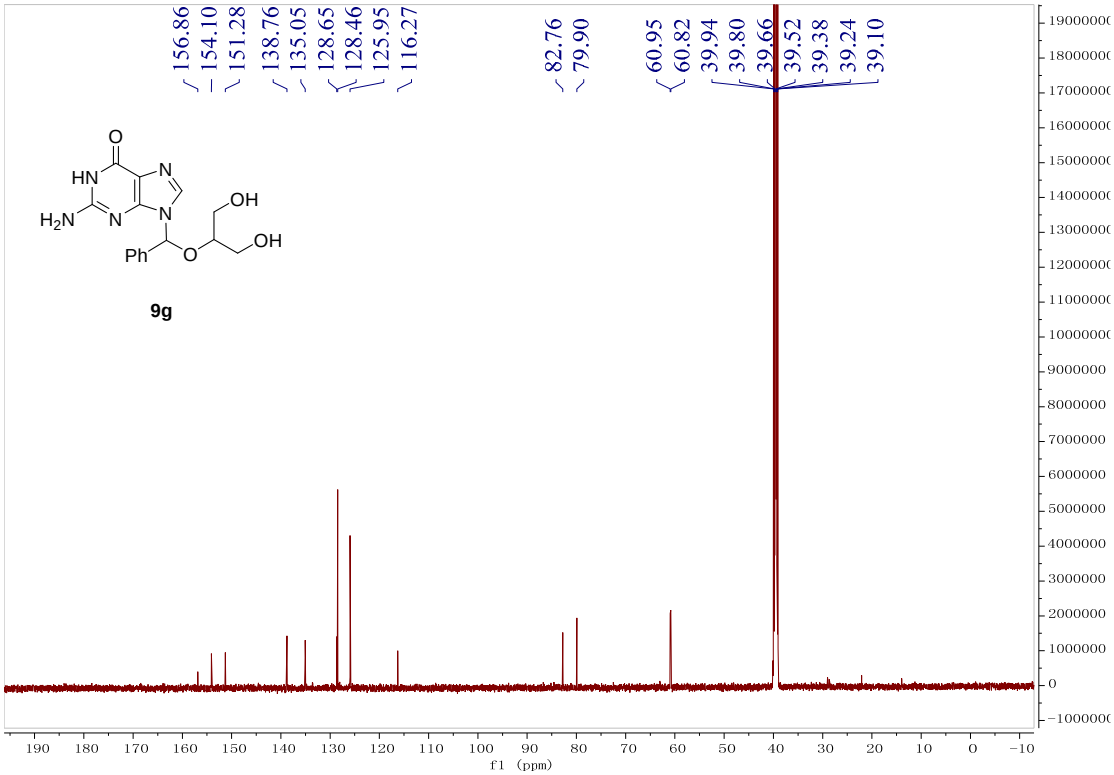
^{13}C NMR (150 MHz, $CDCl_3$) for 8g



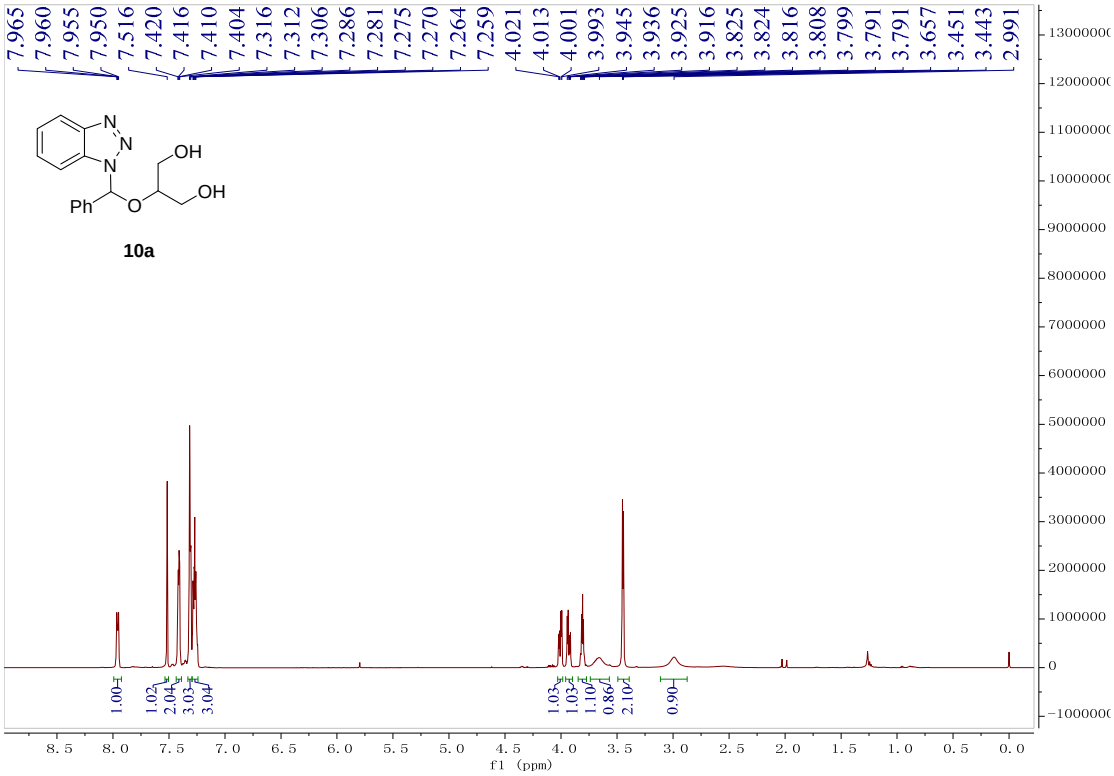
^{1}H NMR (600 MHz, DMSO) for 9g



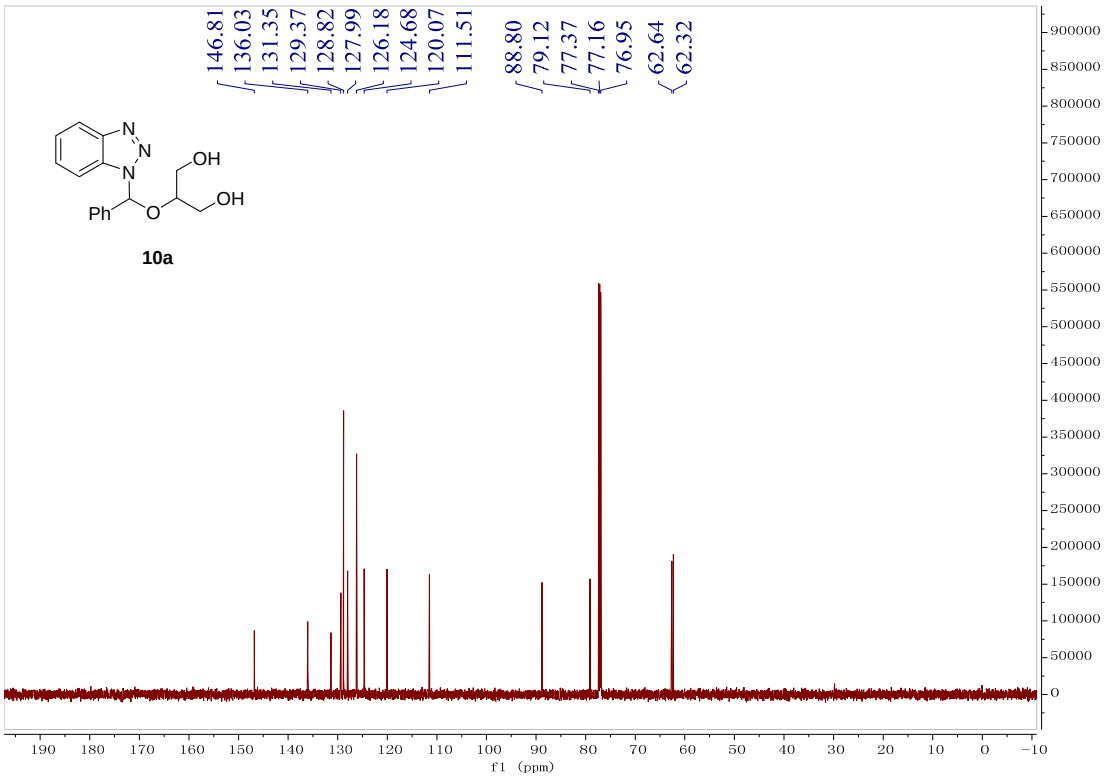
^{13}C NMR (150 MHz, DMSO) for 9g



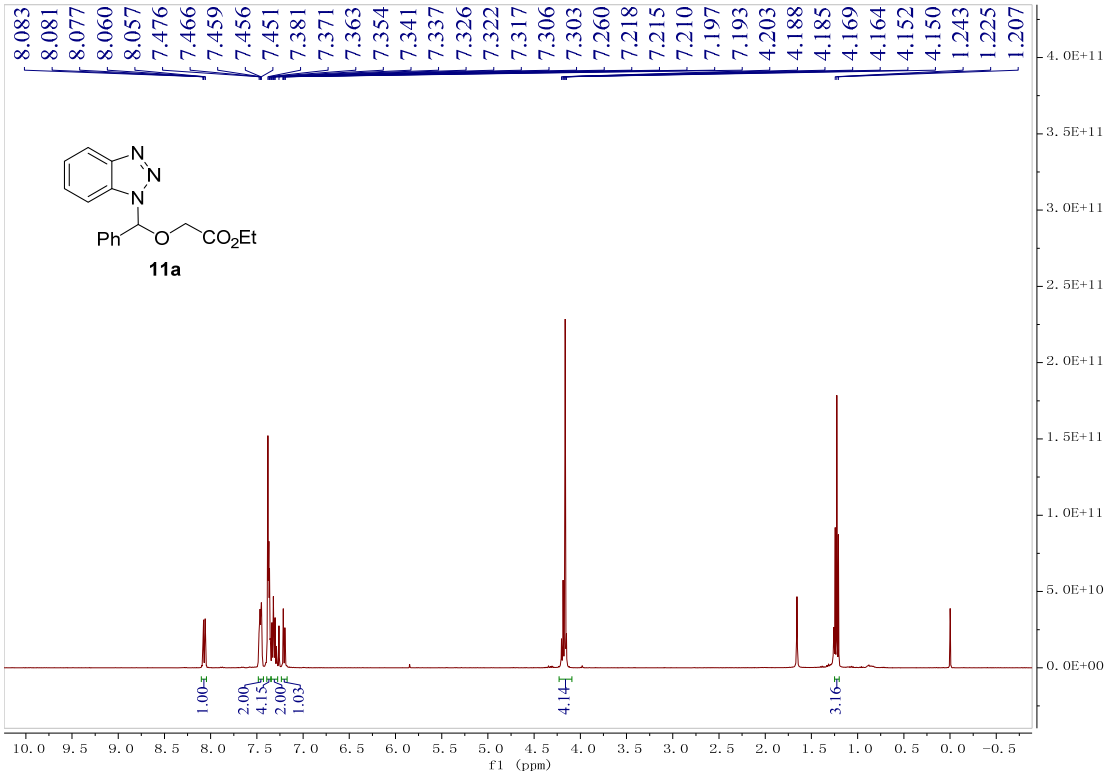
^{1}H NMR (600 MHz, $CDCl_3$) for 10a



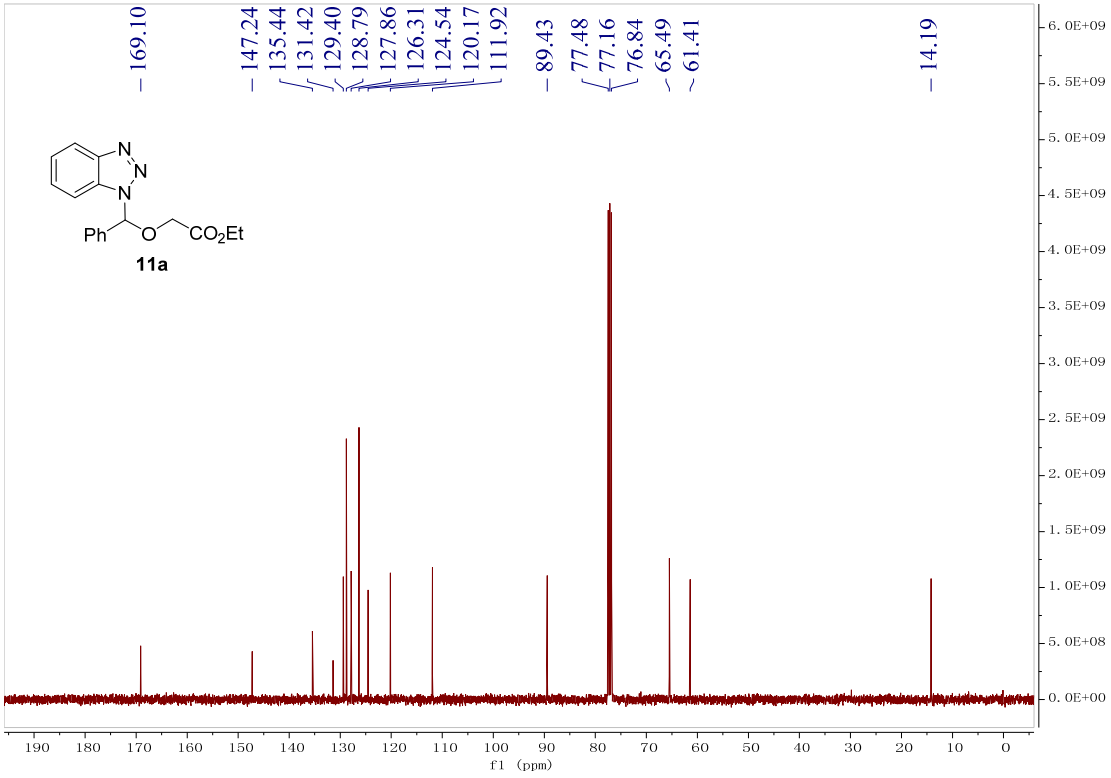
^{13}C NMR (150 MHz, $CDCl_3$) for 10a



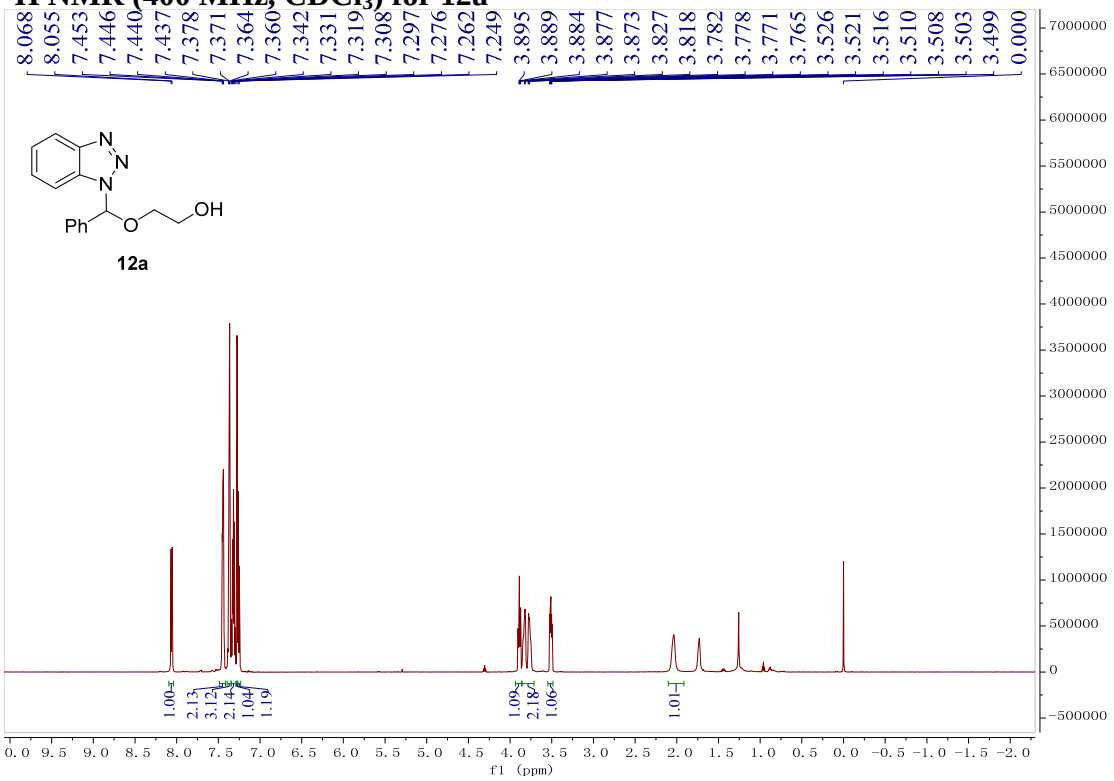
^{1}H NMR (400 MHz, $CDCl_3$) for 11a



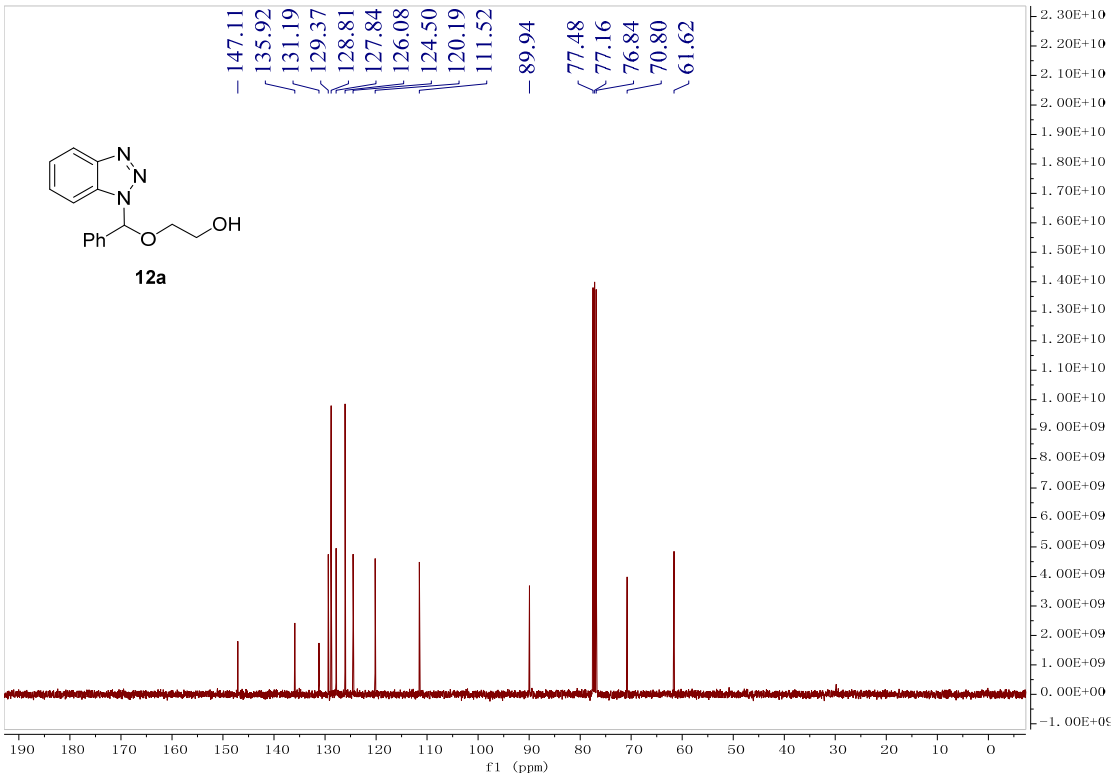
^{13}C NMR (100 MHz, $CDCl_3$) for 11a



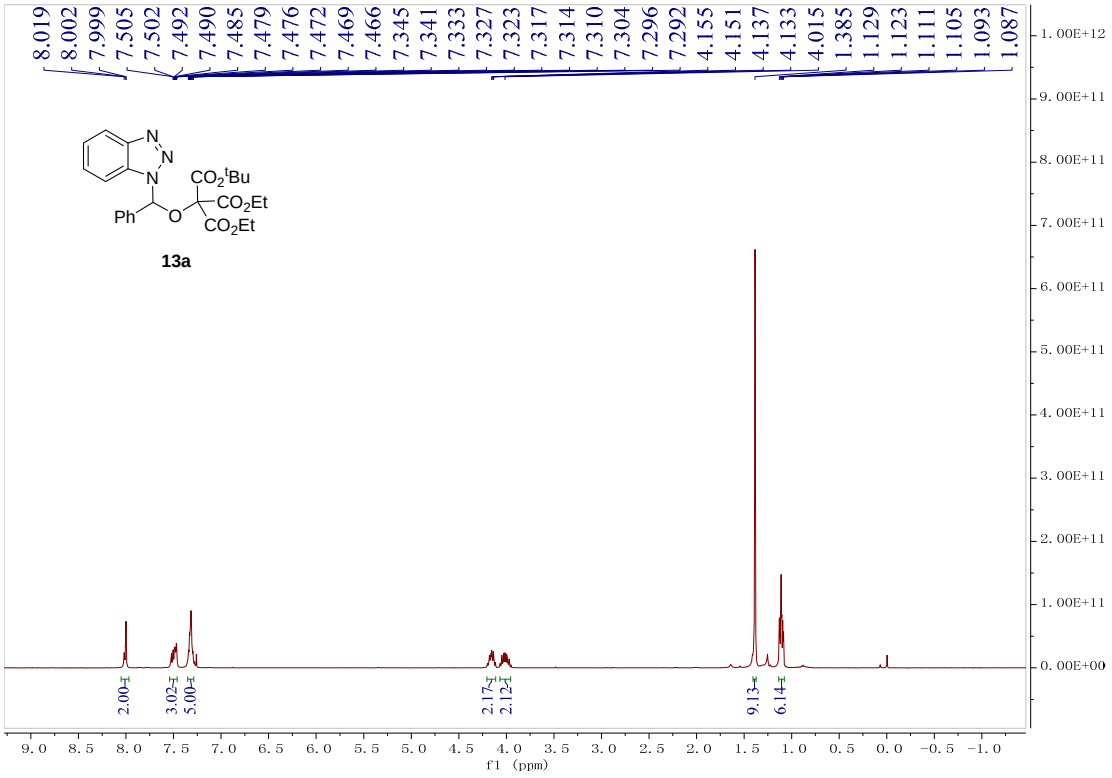
^{1}H NMR (400 MHz, $CDCl_3$) for 12a



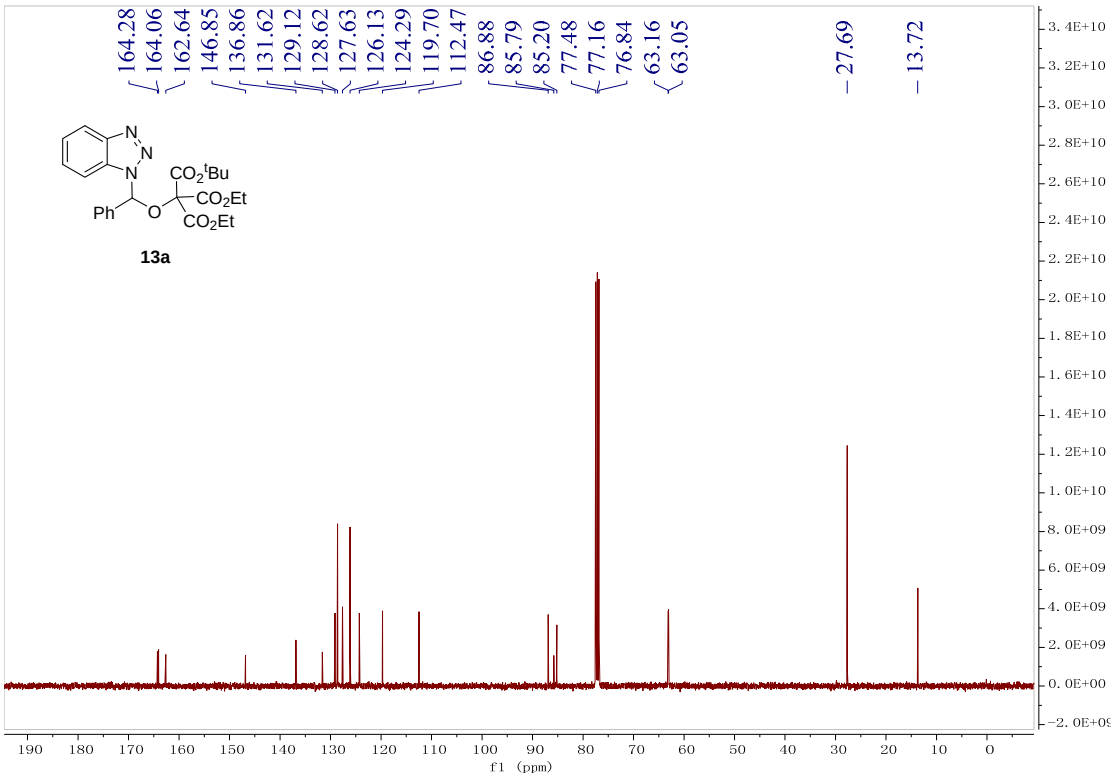
^{13}C NMR (100 MHz, $CDCl_3$) for 12a



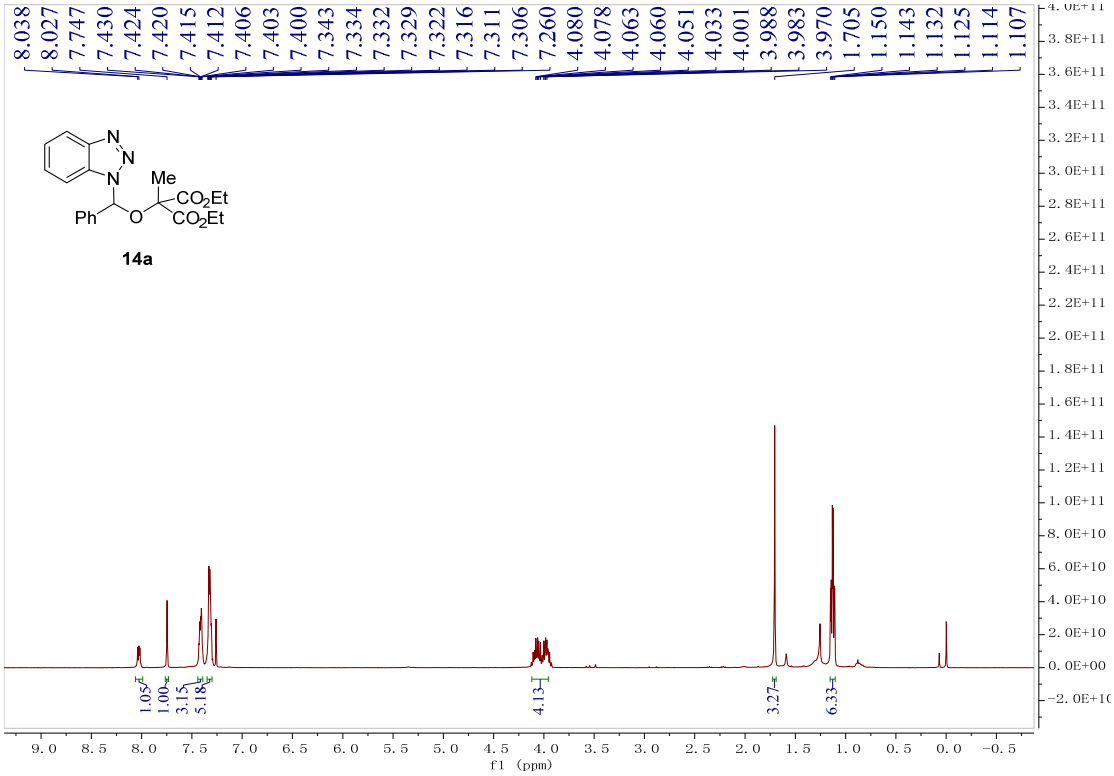
^{1}H NMR (400 MHz, $CDCl_3$) for 13a



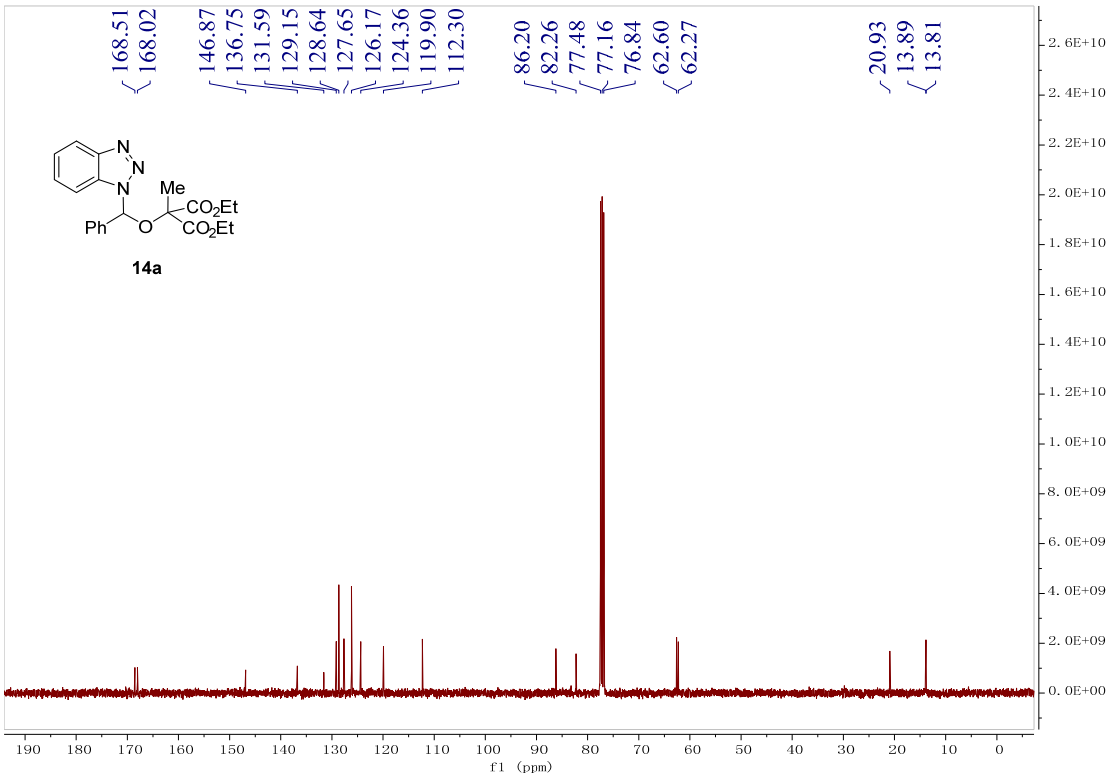
^{13}C NMR (100 MHz, $CDCl_3$) for 13a



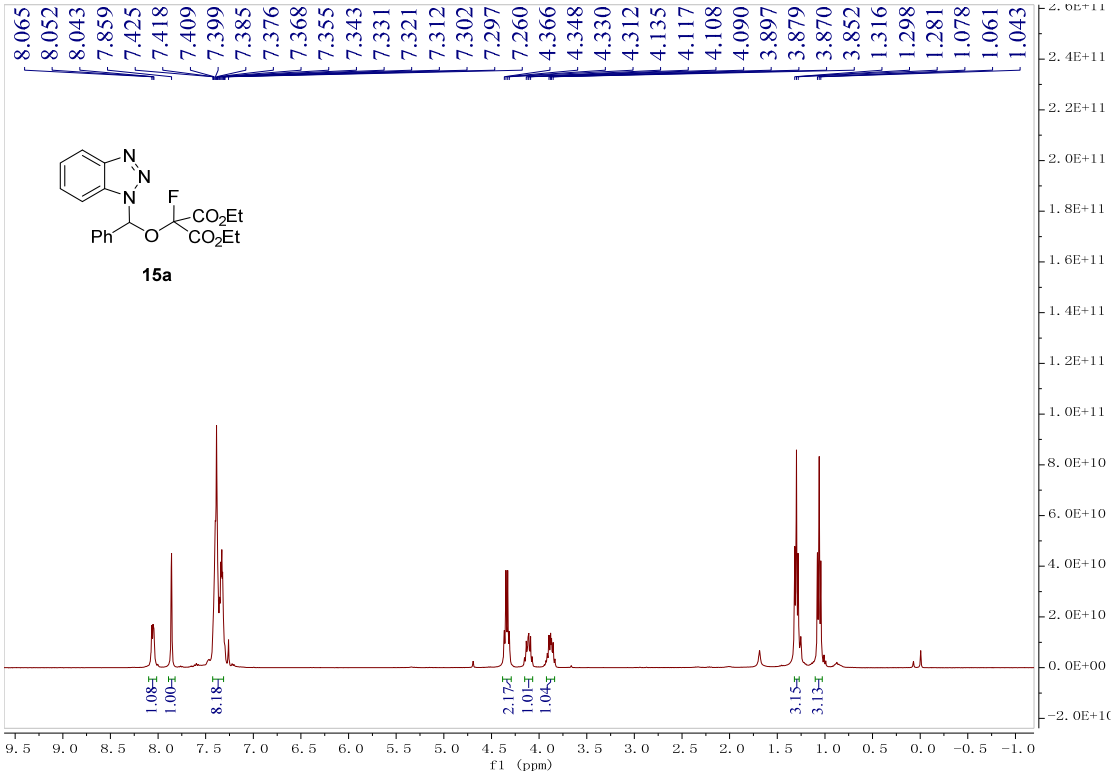
^{1}H NMR (400 MHz, $CDCl_3$) for 14a



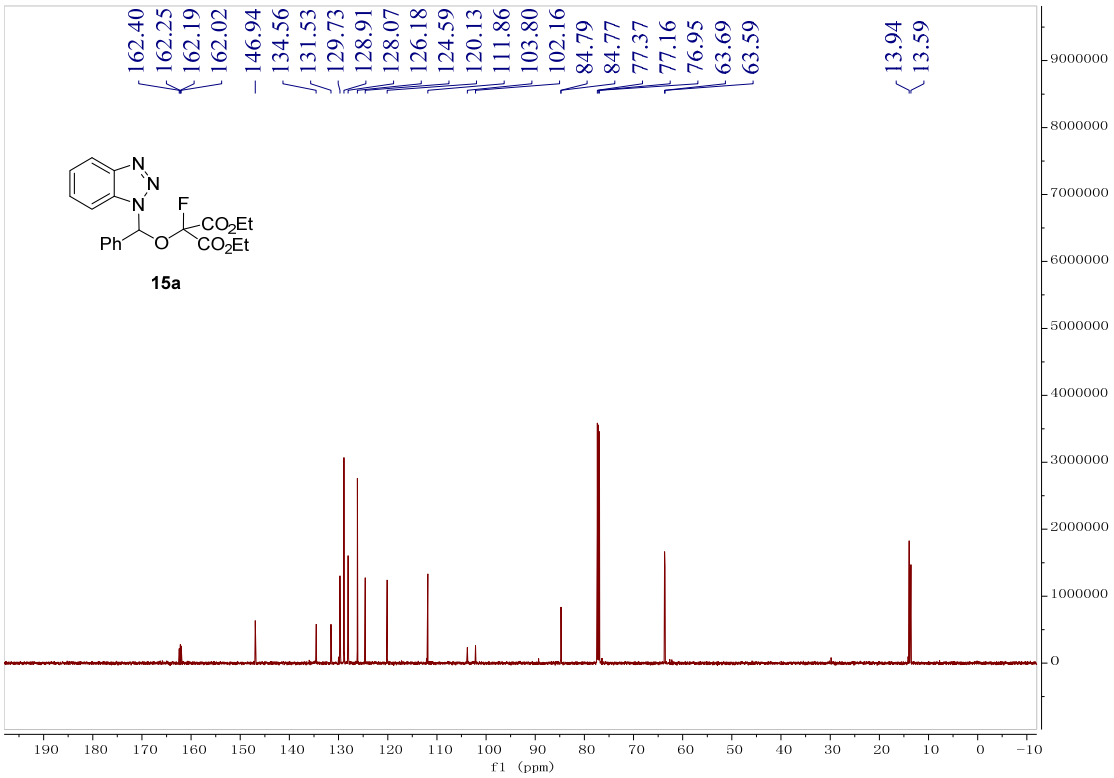
^{13}C NMR (100 MHz, $CDCl_3$) for 14a



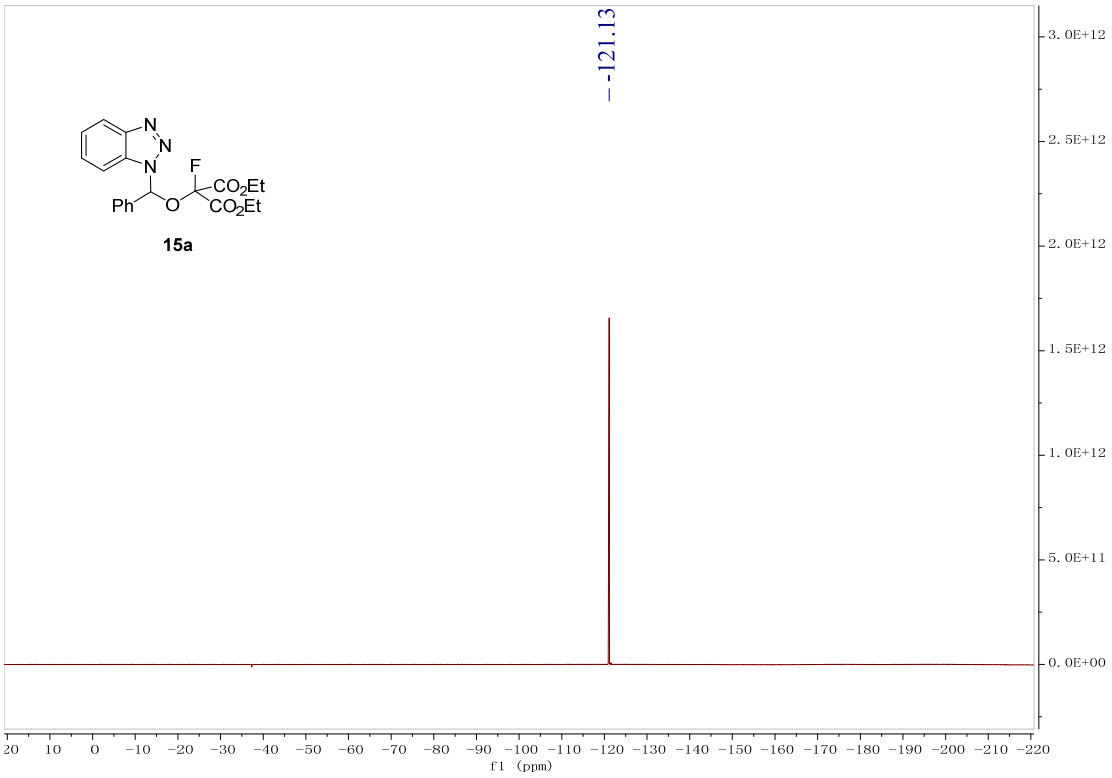
^{1}H NMR (400 MHz, $CDCl_3$) for 15a



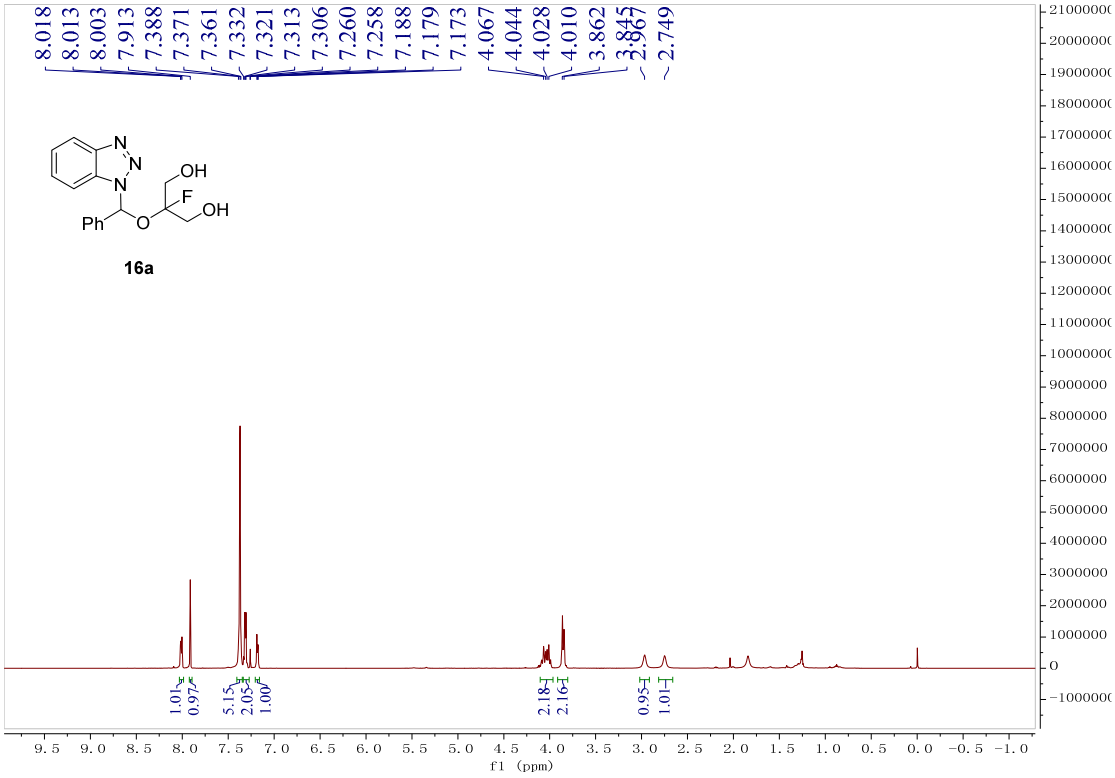
^{13}C NMR (150 MHz, $CDCl_3$) for 15a



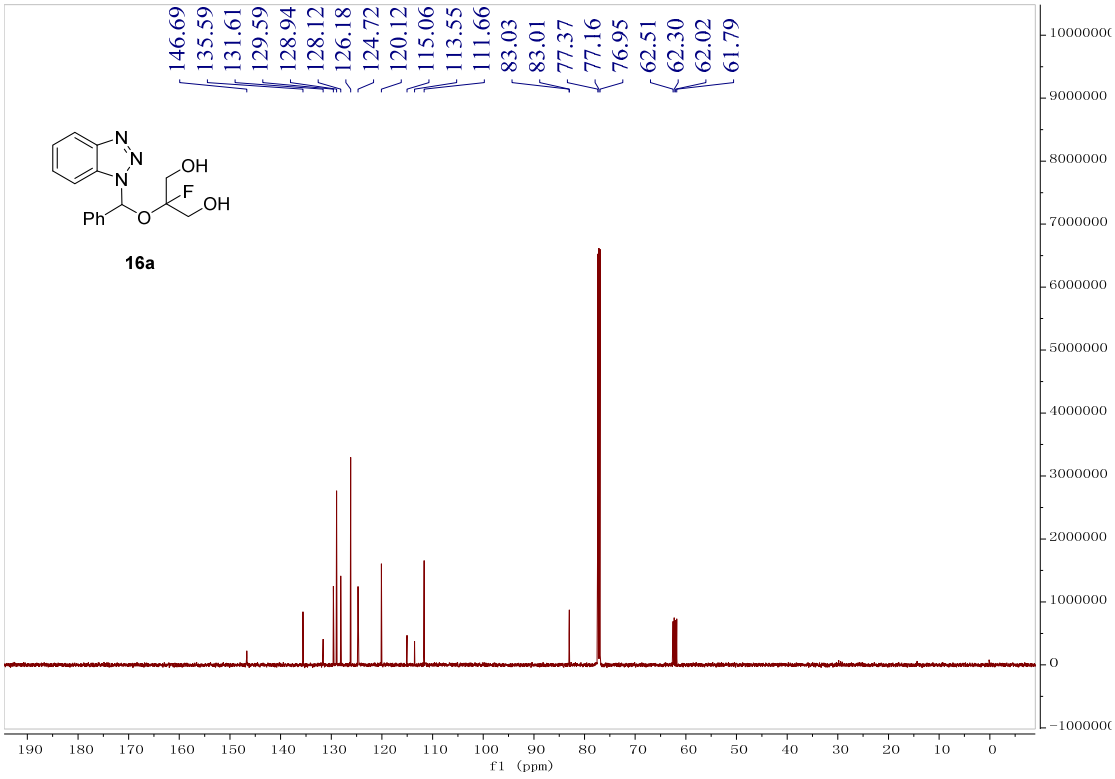
^{19}F NMR (376 MHz, $CDCl_3$) for 15a



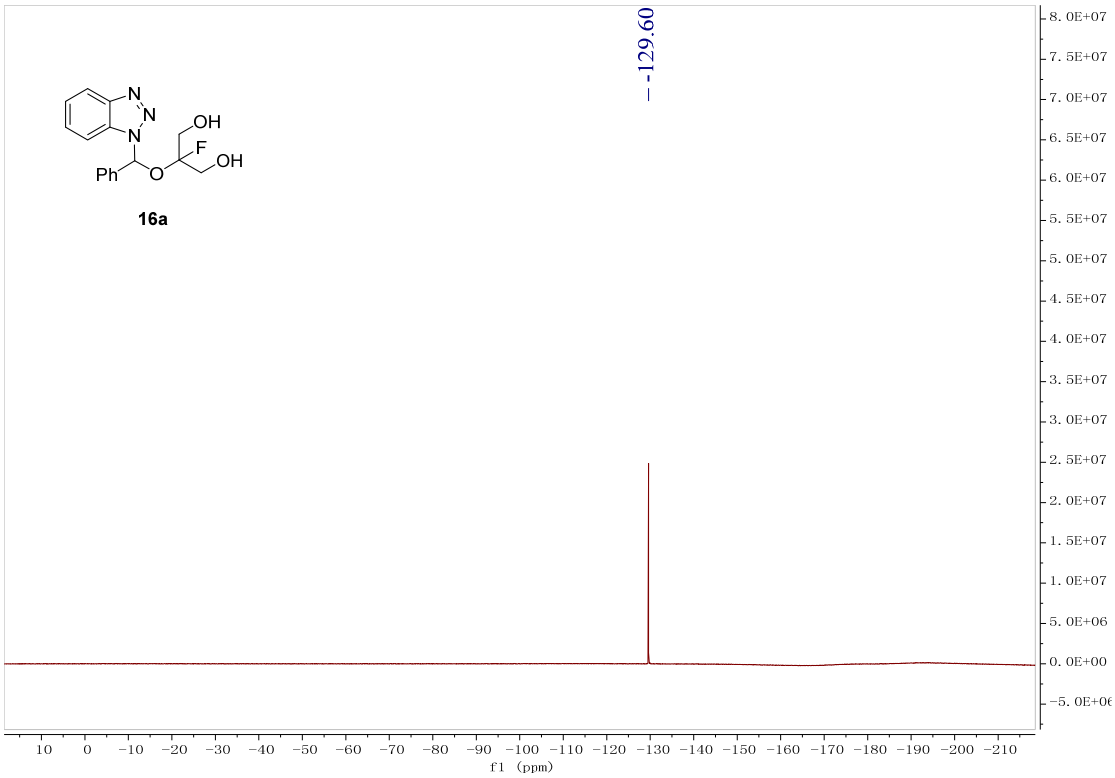
^{1}H NMR (600 MHz, $CDCl_3$) for 16a



^{13}C NMR (150 MHz, $CDCl_3$) for 16a



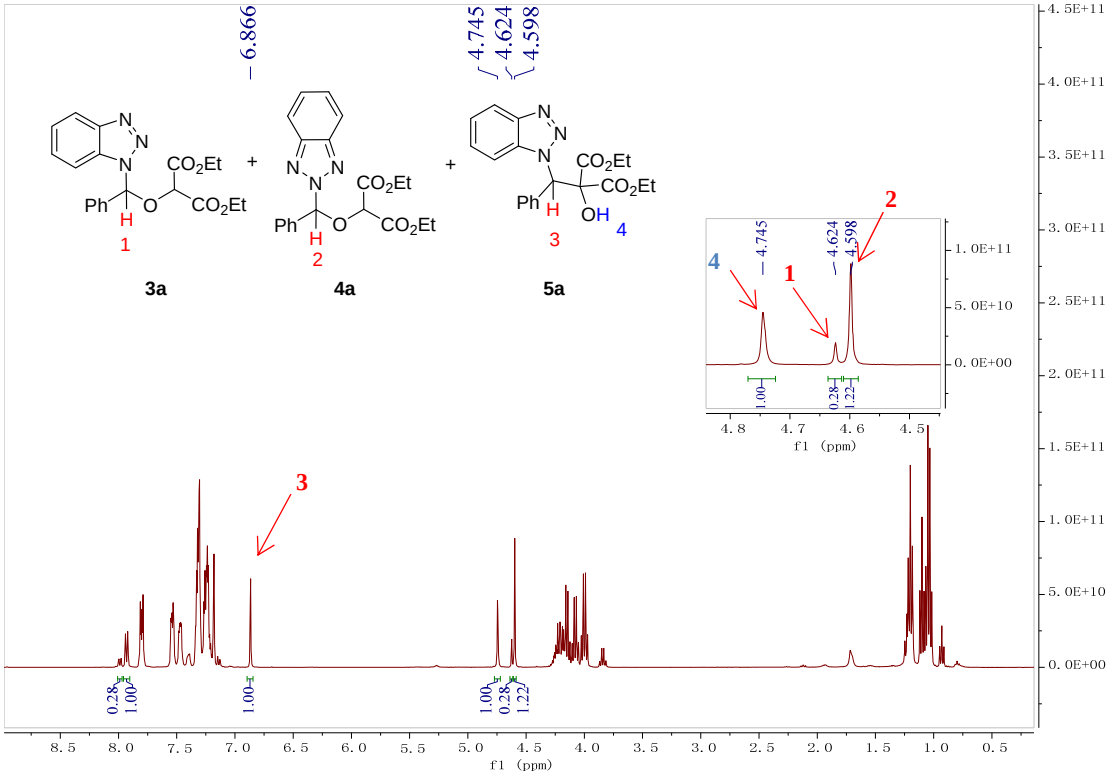
^{19}F NMR (565 MHz, $CDCl_3$) for 16a



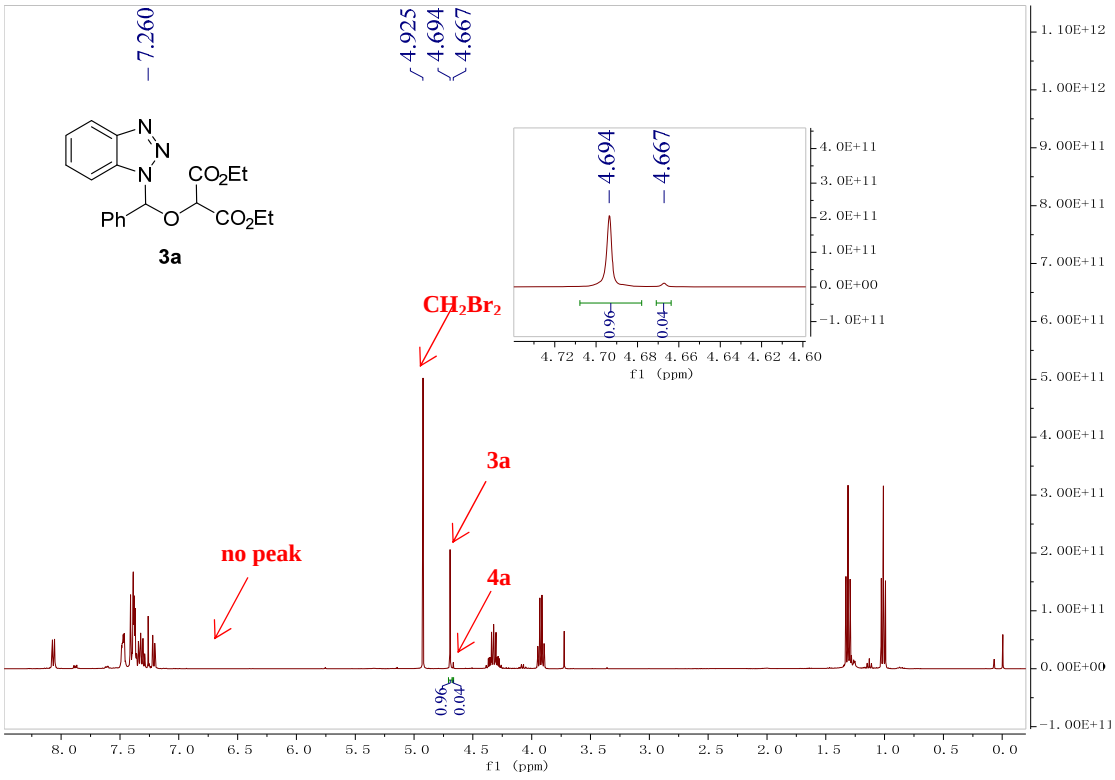
16. Crude ^{1}H NMR data

^{1}H NMR of mixed 3a, 4a and 5a

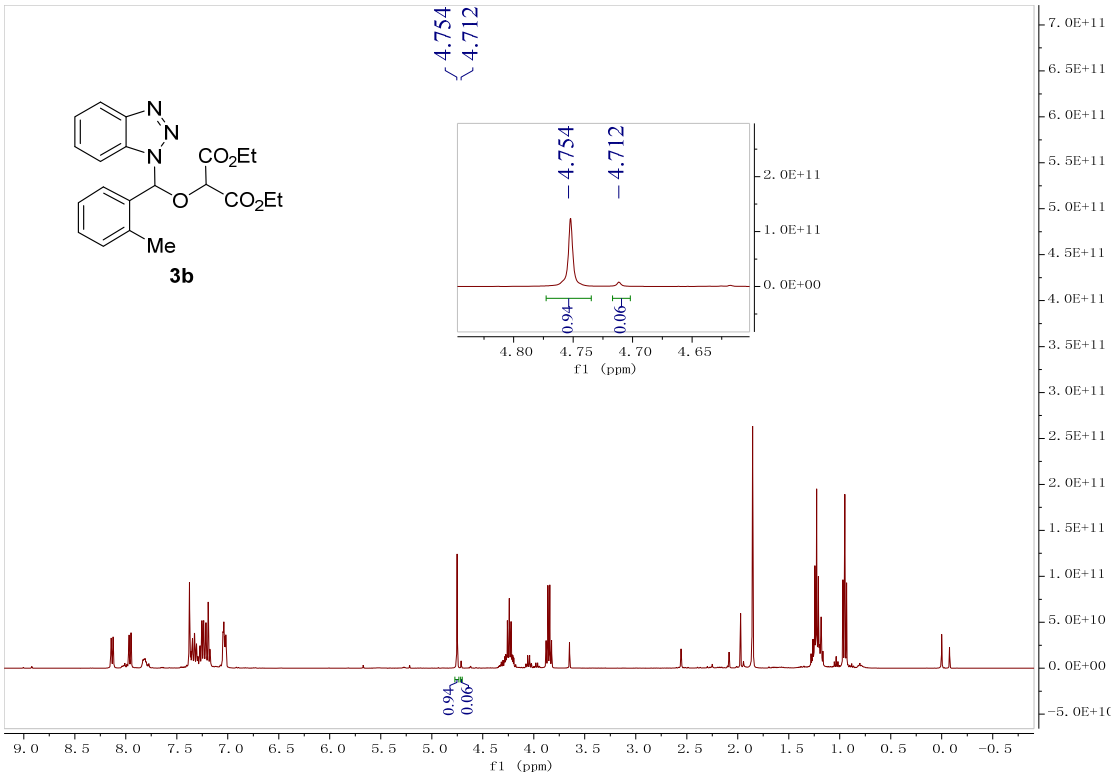
the characteristic peak in the mixture: **3a** (s, δ 4.62), **4a** (s, δ 4.60), **5a** (s, δ 6.87).



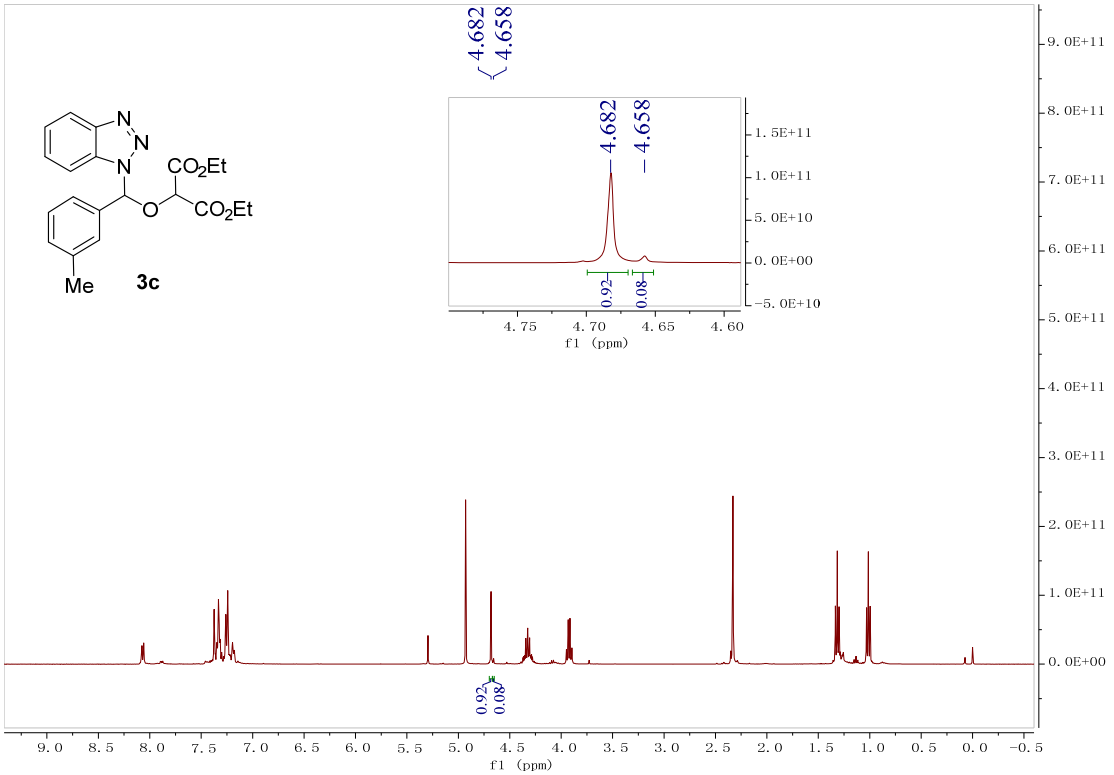
Crude ^{1}H NMR of the standard reaction, ratio of N^1/N^2 = 96:4



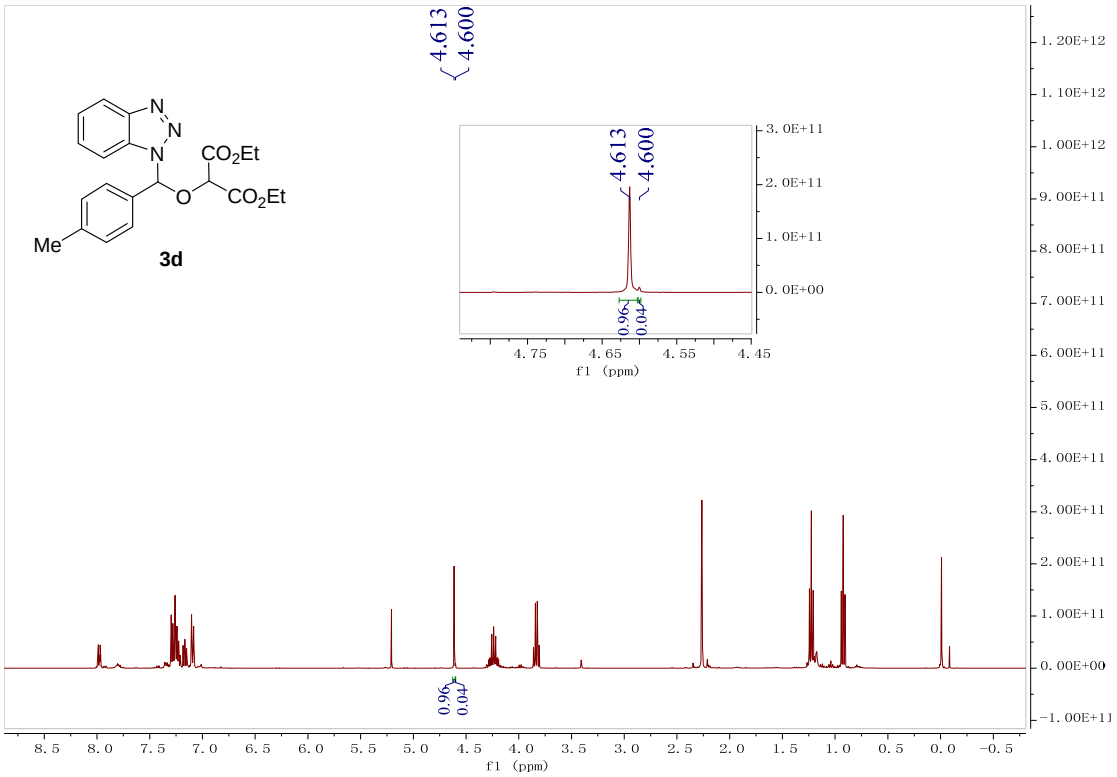
Crude ^{1}H NMR of 3b



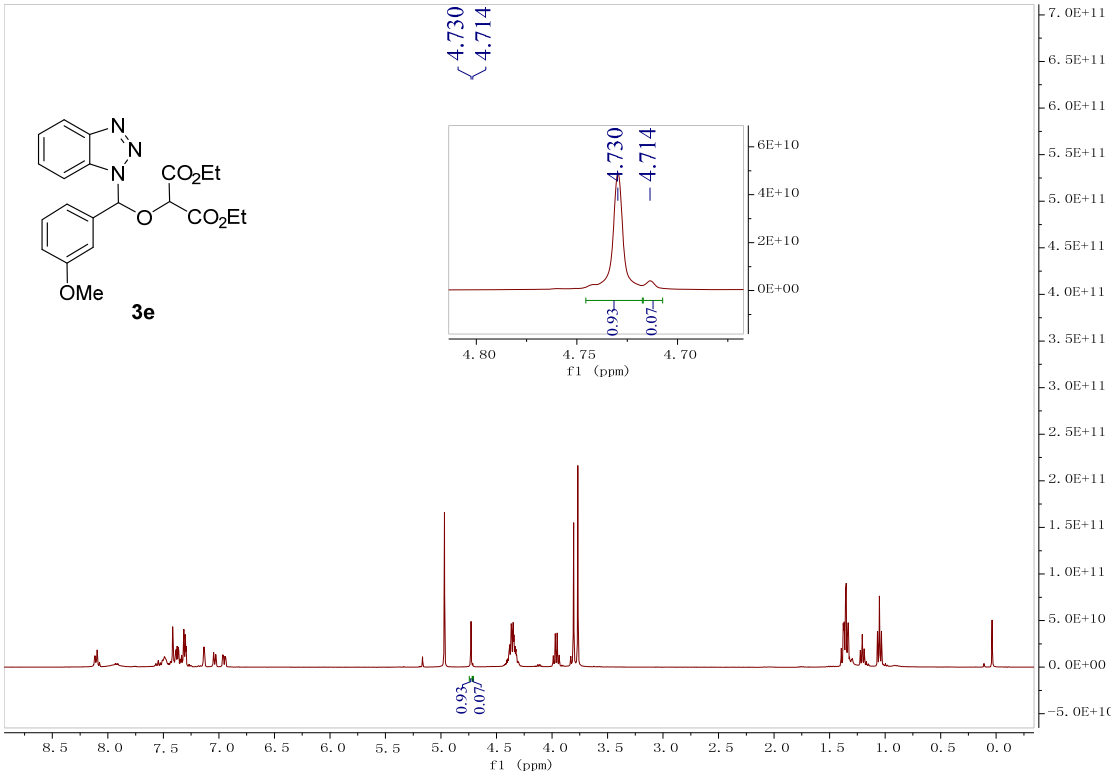
Crude ^{1}H NMR of 3c



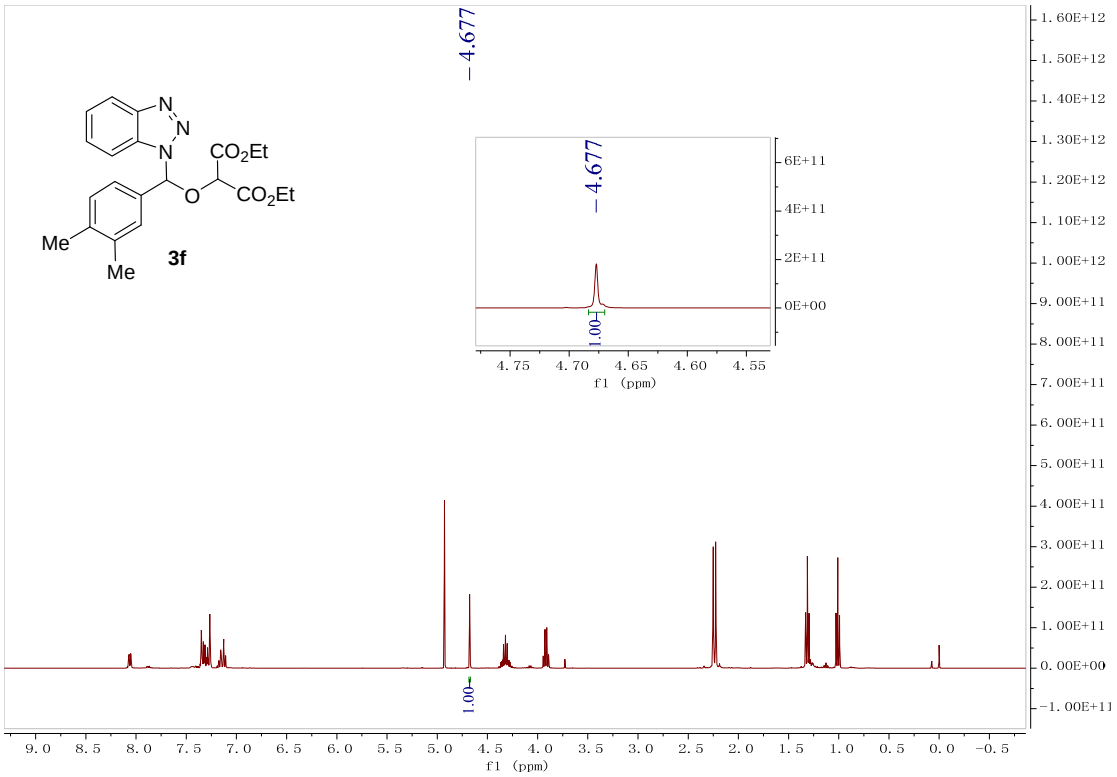
Crude ^{1}H NMR of 3d



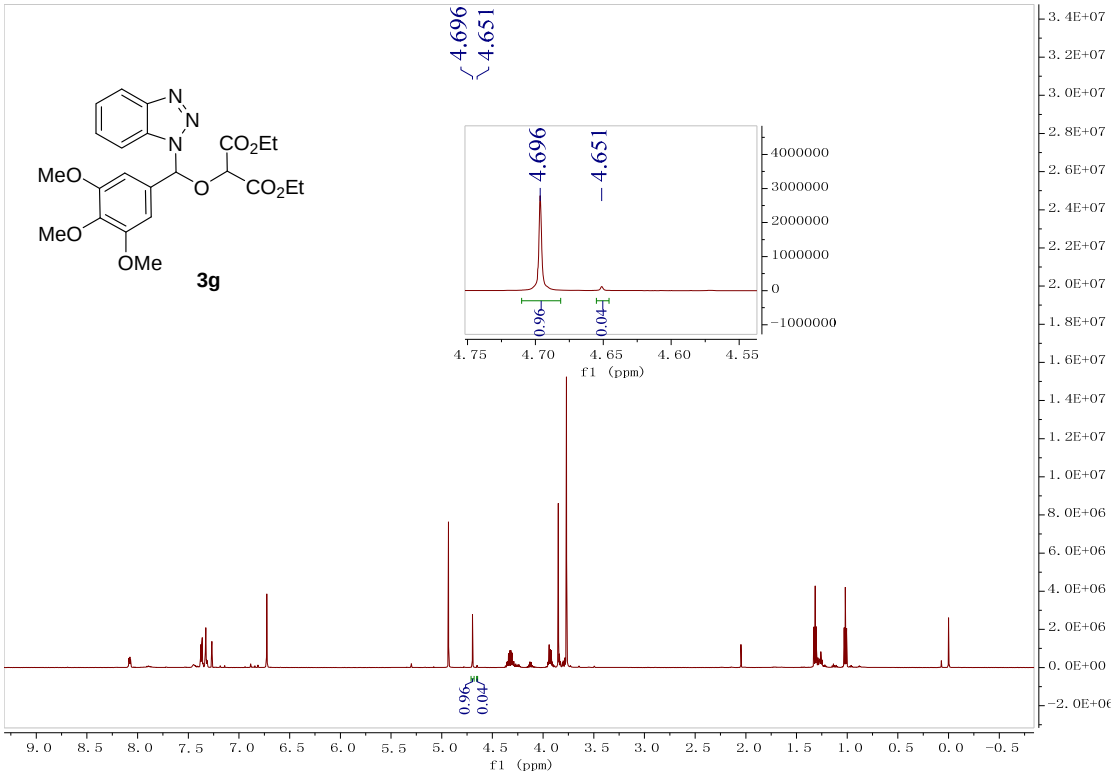
Crude ^{1}H NMR of 3e



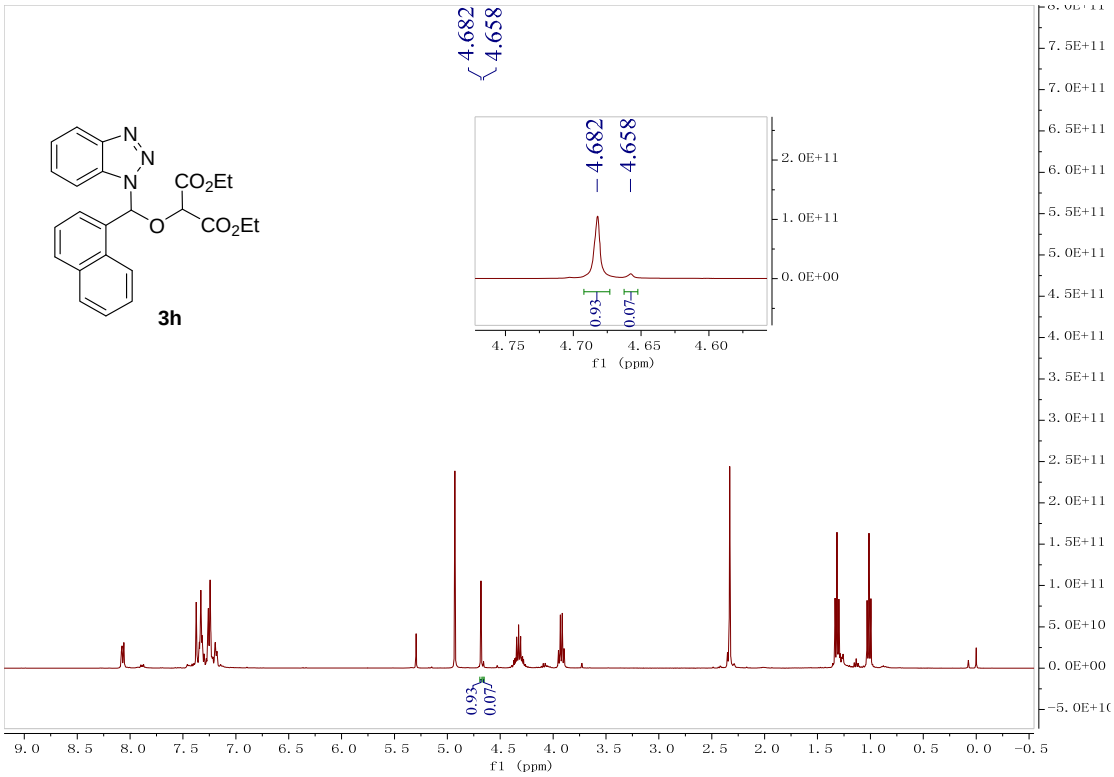
Crude ^{1}H NMR of 3f



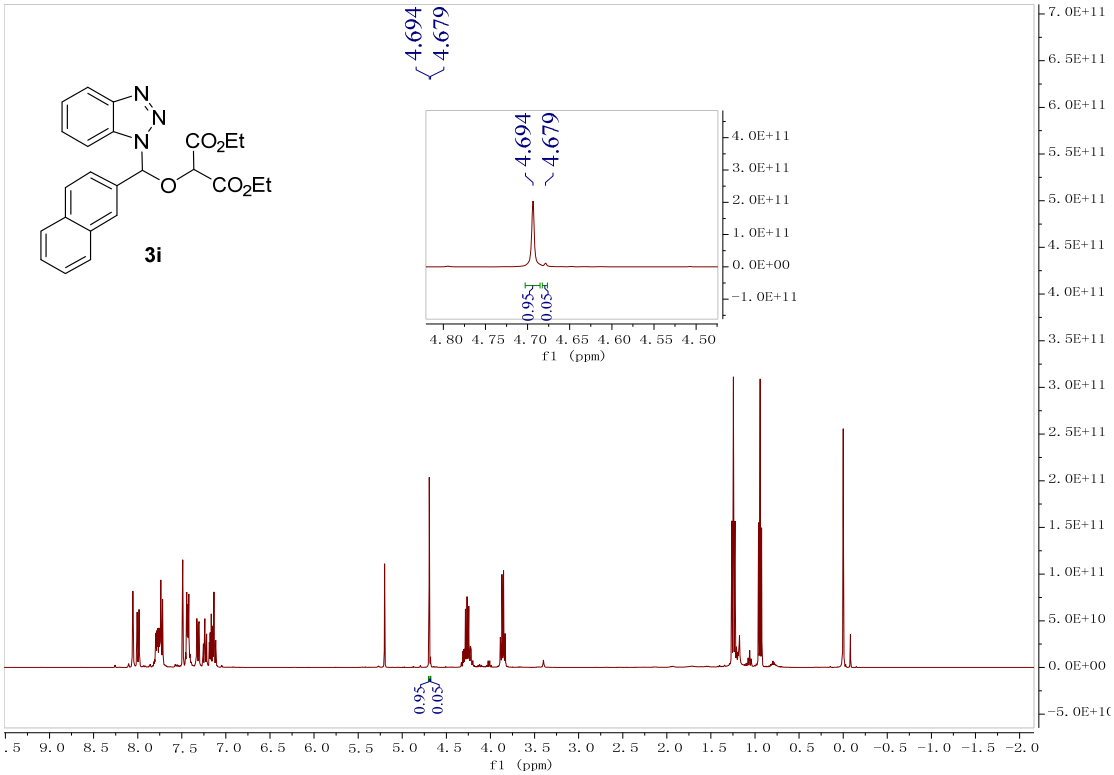
Crude ^{1}H NMR of 3g



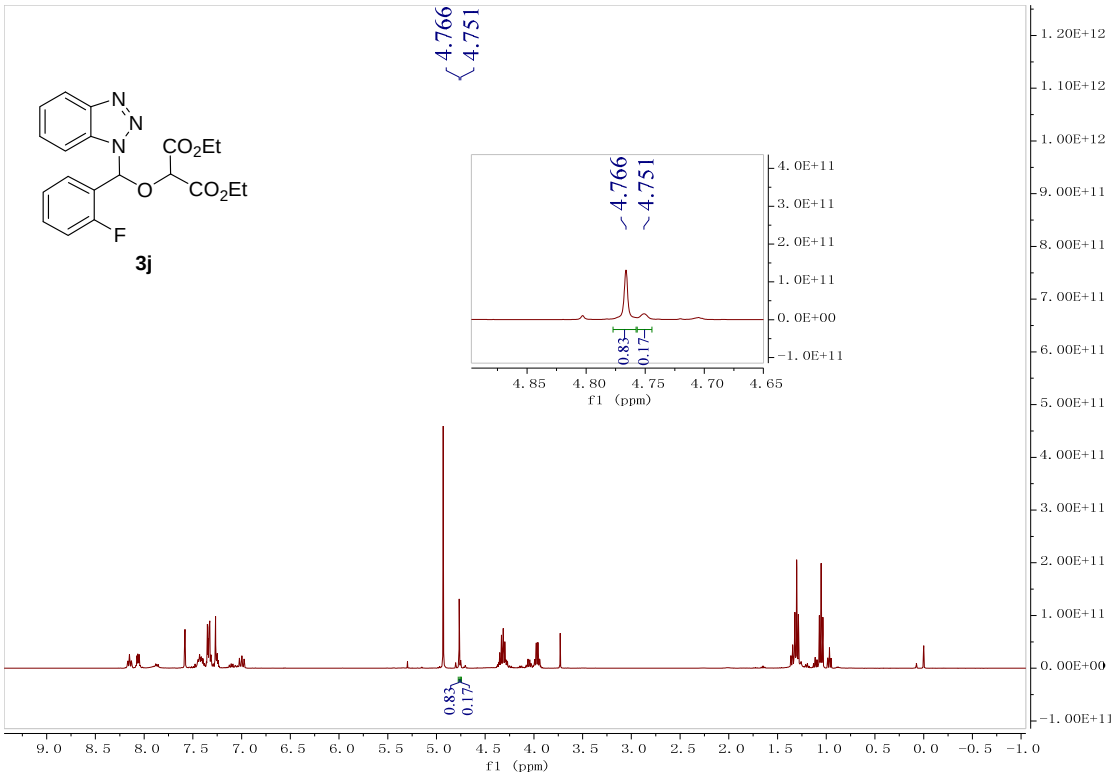
Crude ^{1}H NMR of 3h



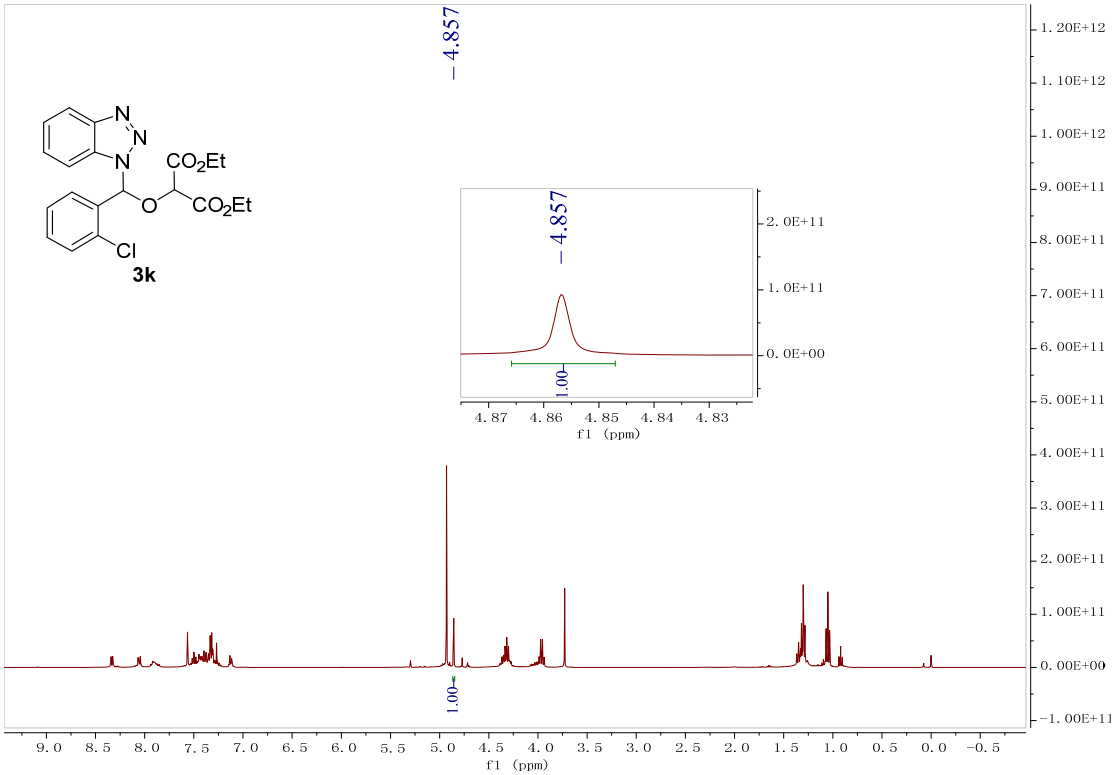
Crude ^{1}H NMR of 3i



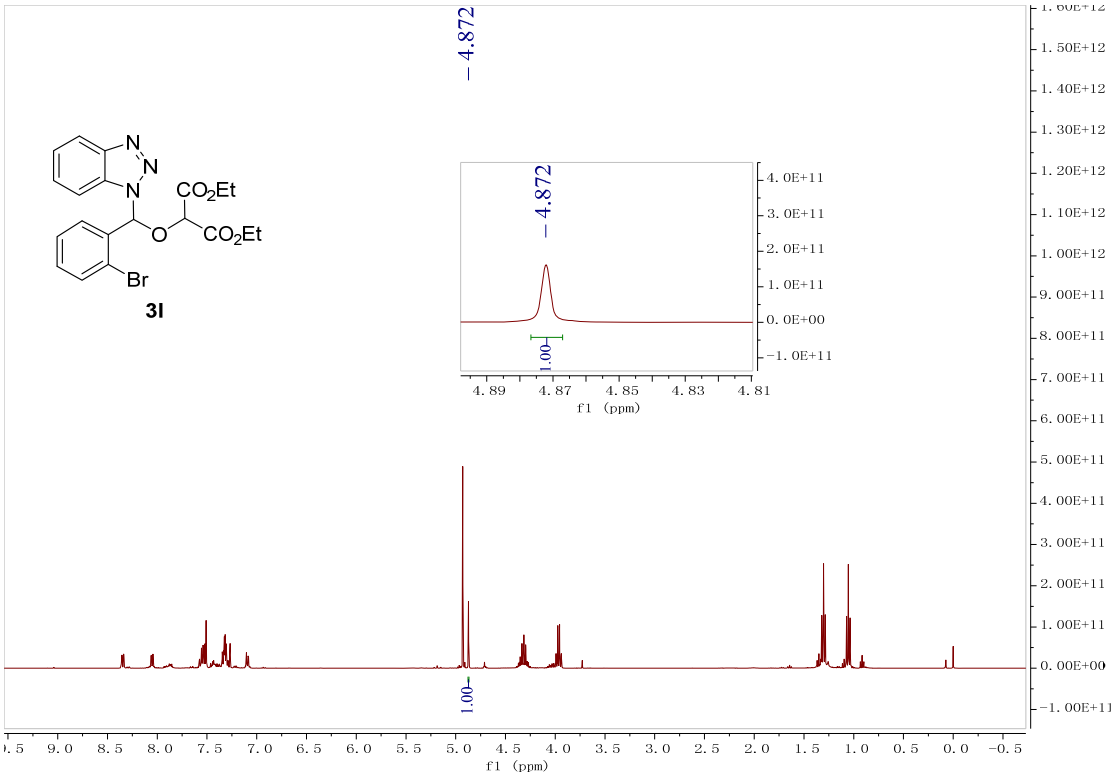
Crude ^{1}H NMR of 3j



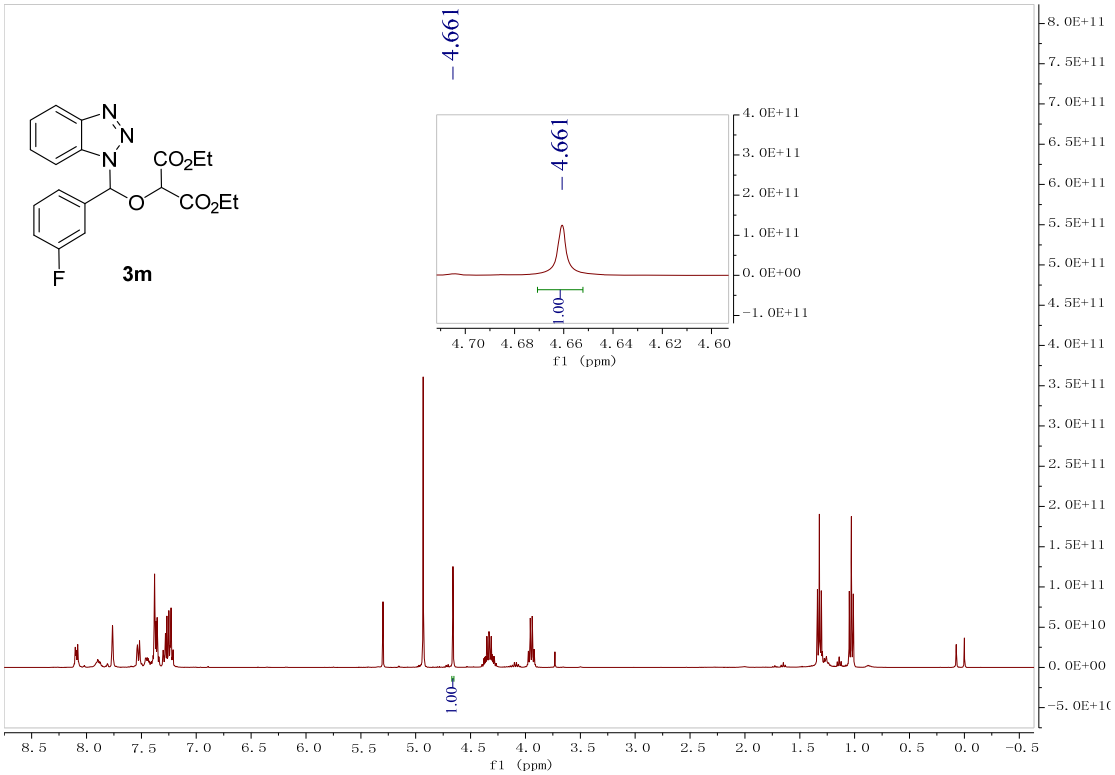
Crude ^{1}H NMR of 3k



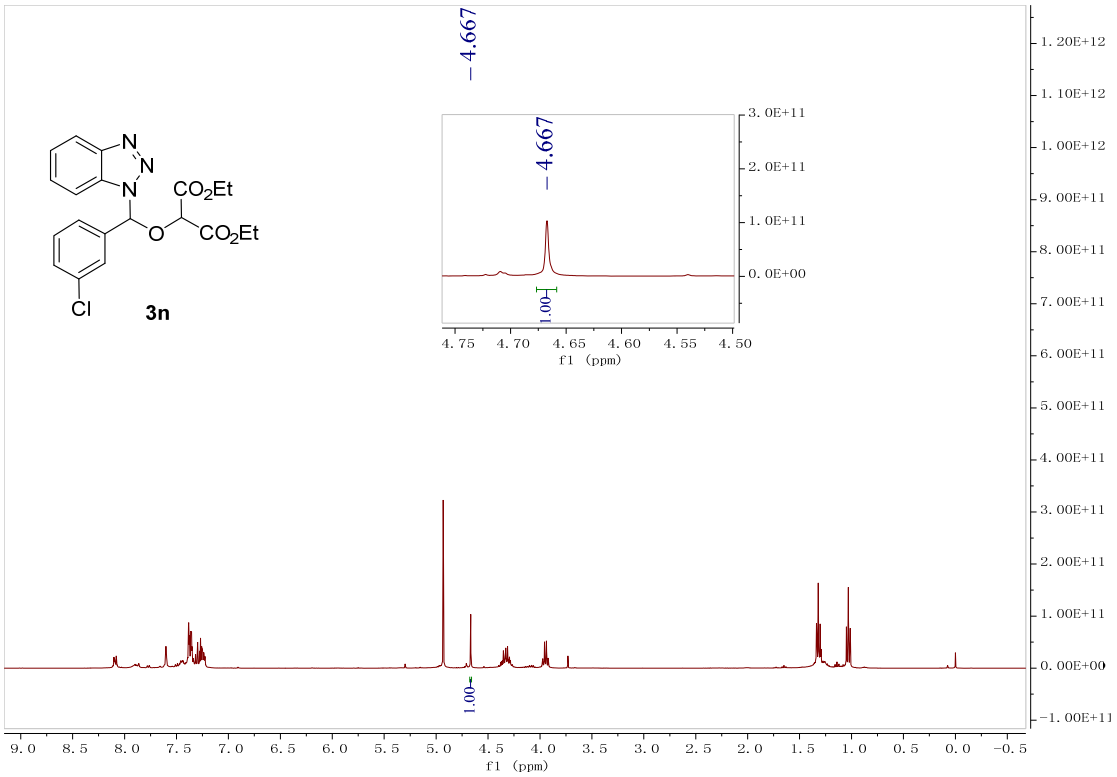
Crude ^{1}H NMR of 3l



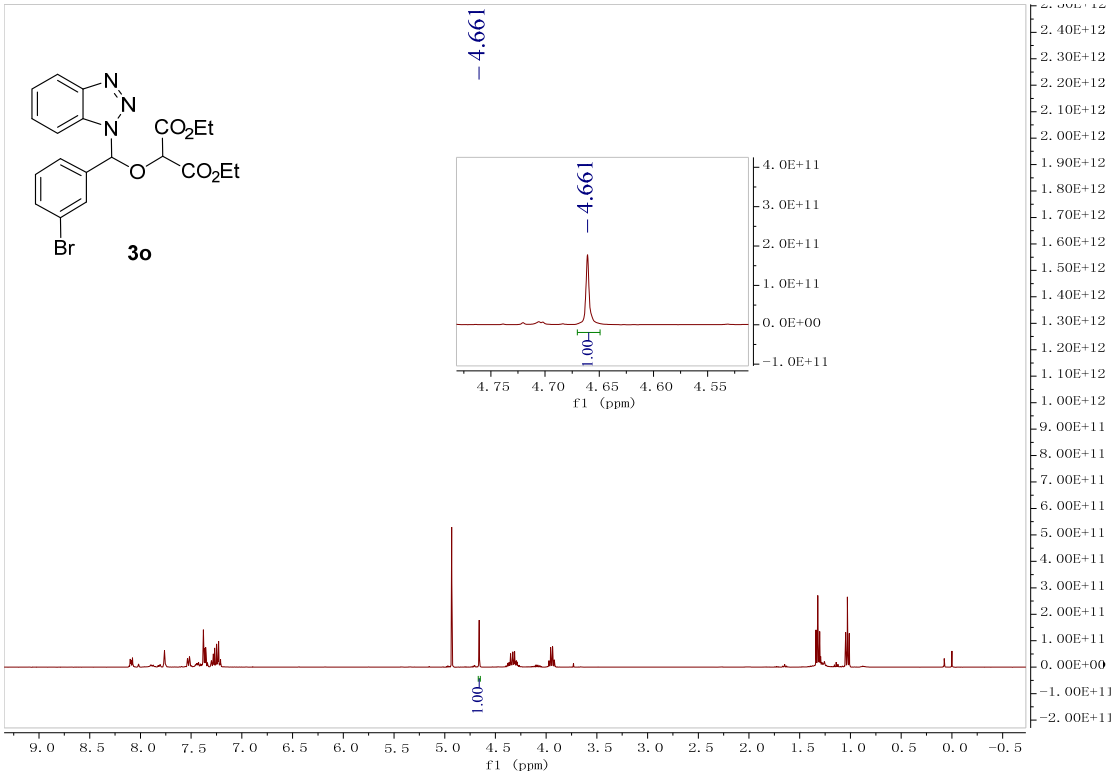
Crude ^{1}H NMR of 3m



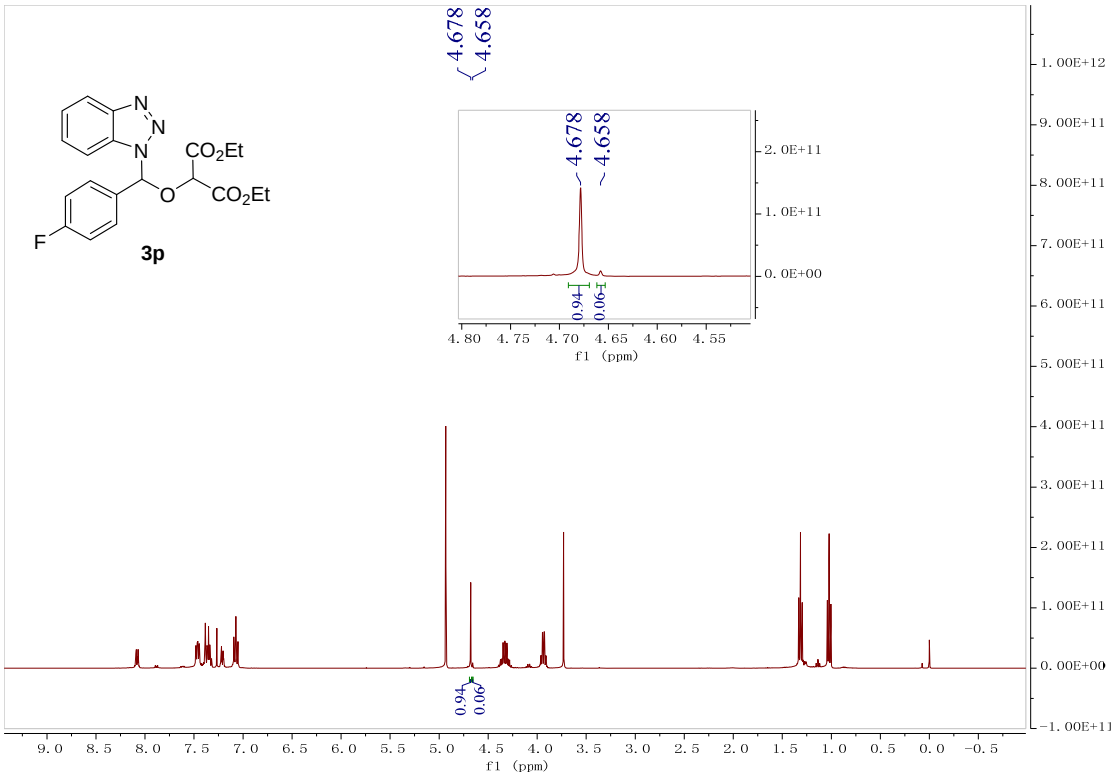
Crude ^{1}H NMR of 3n



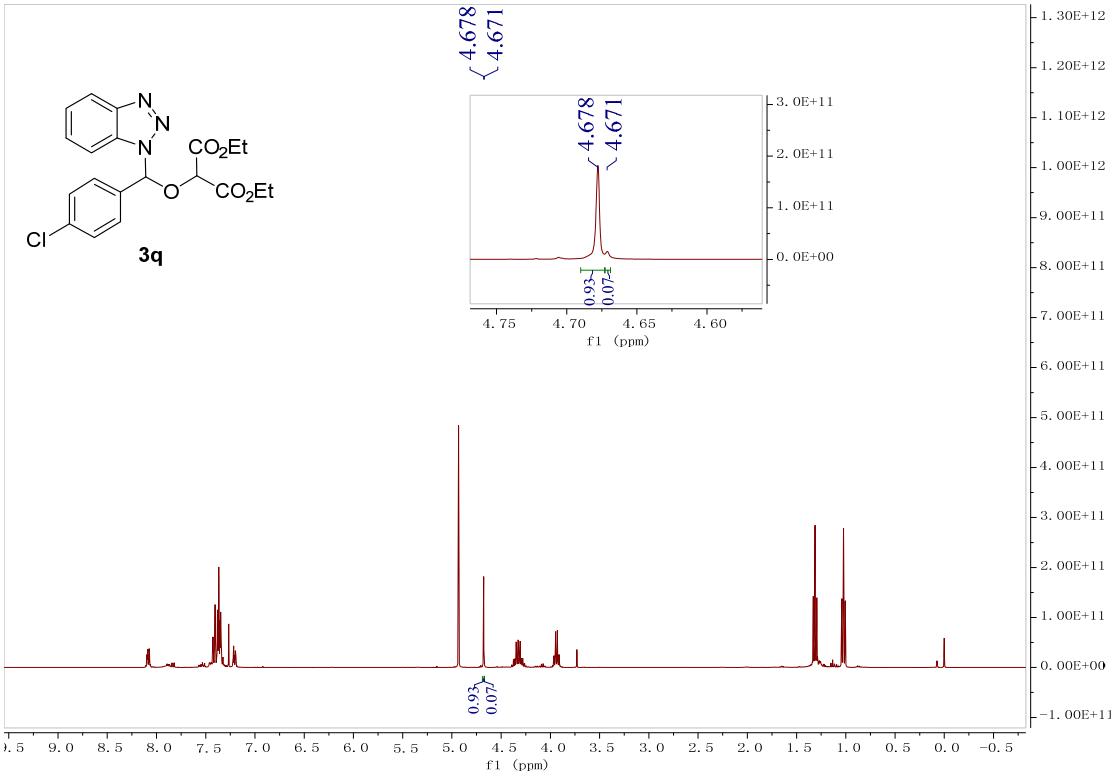
Crude ^{1}H NMR of 3o



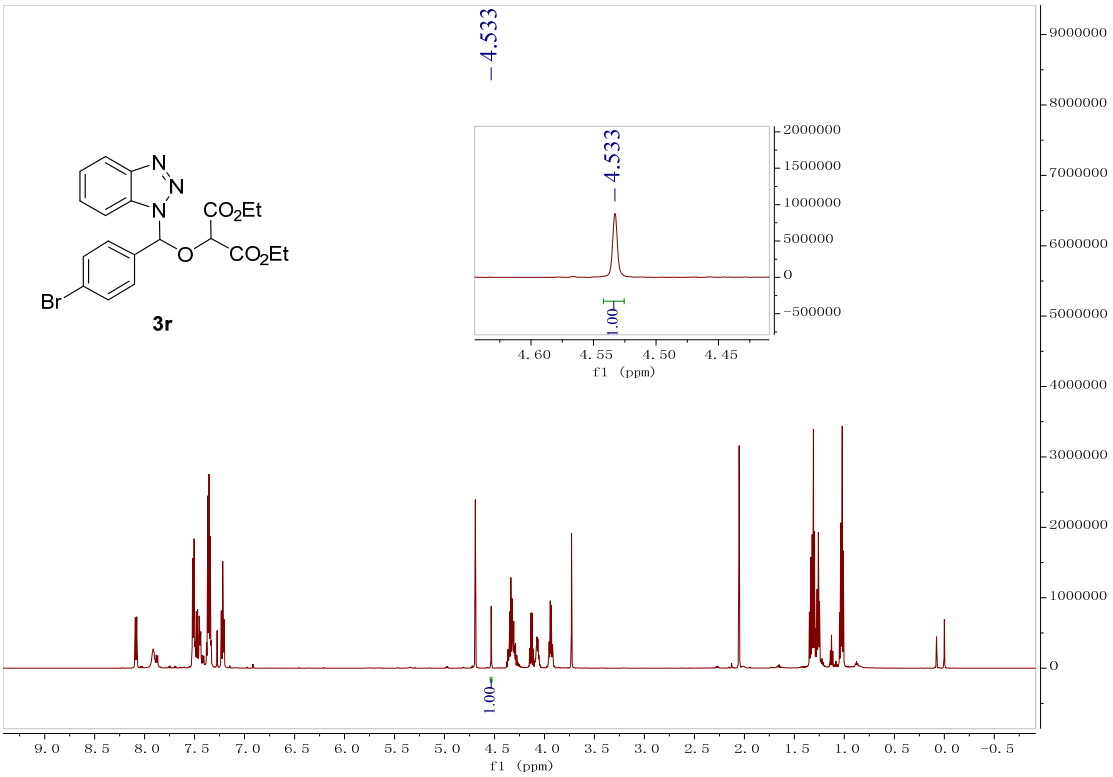
Crude ^{1}H NMR of 3p



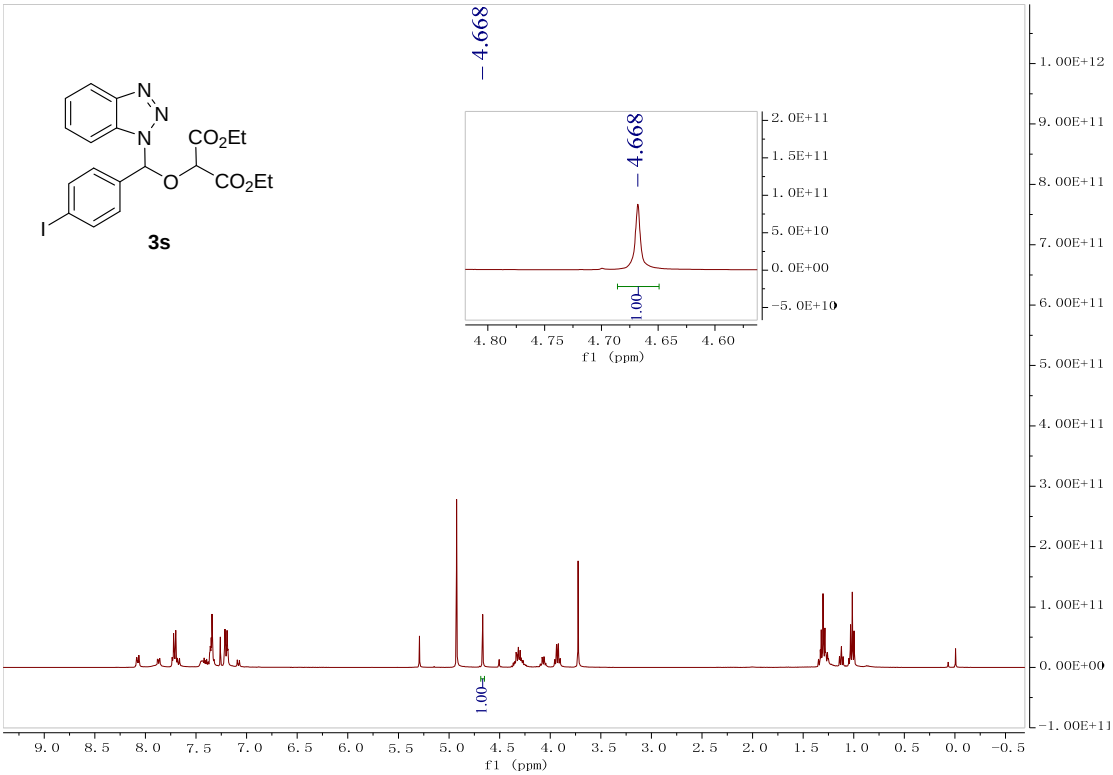
Crude ^{1}H NMR of 3q



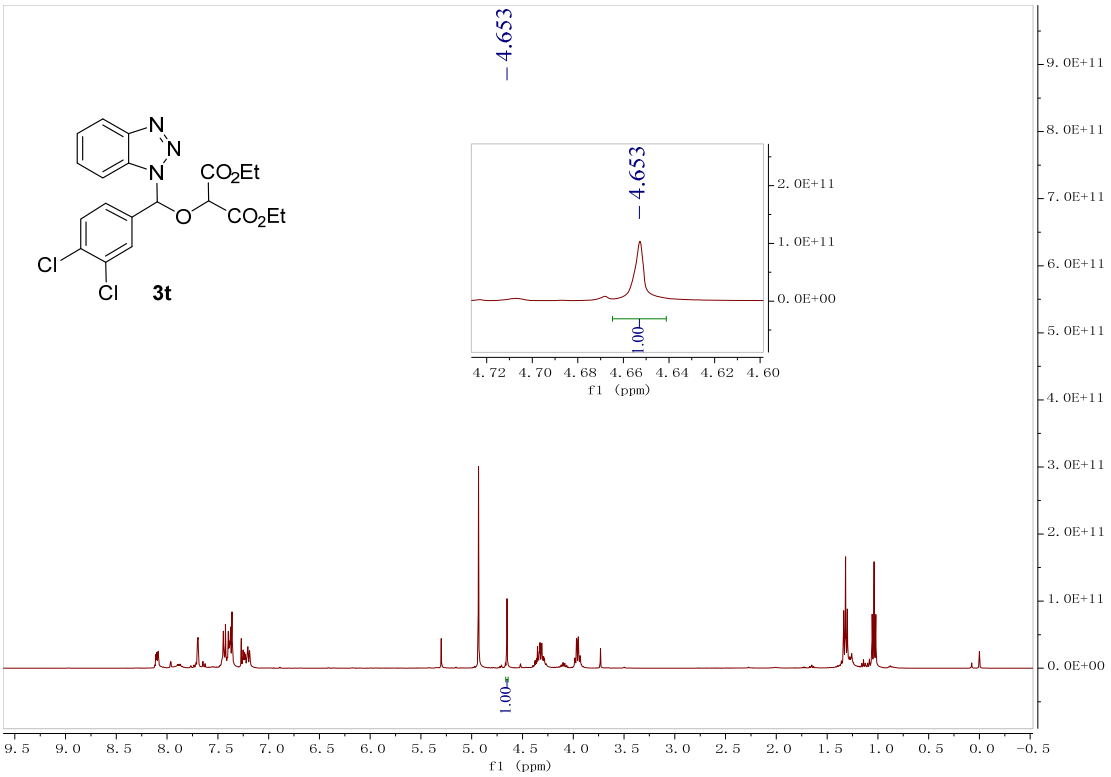
Crude ^{1}H NMR of 3r



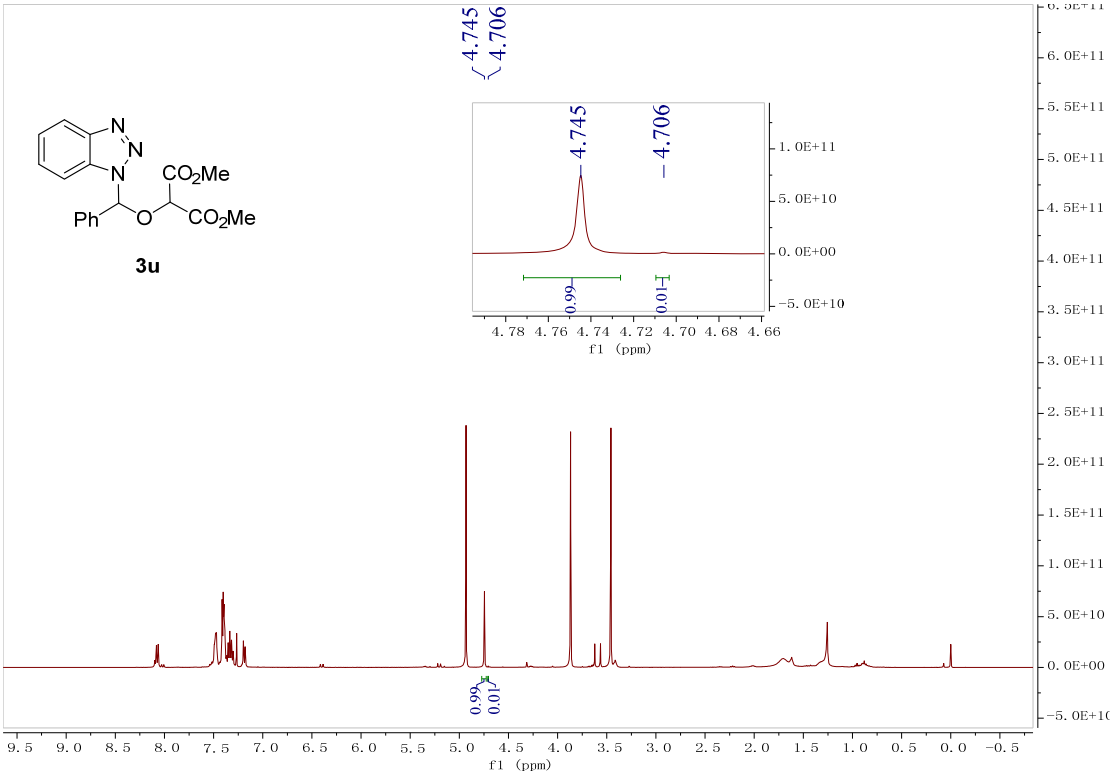
Crude ^{1}H NMR of 3s



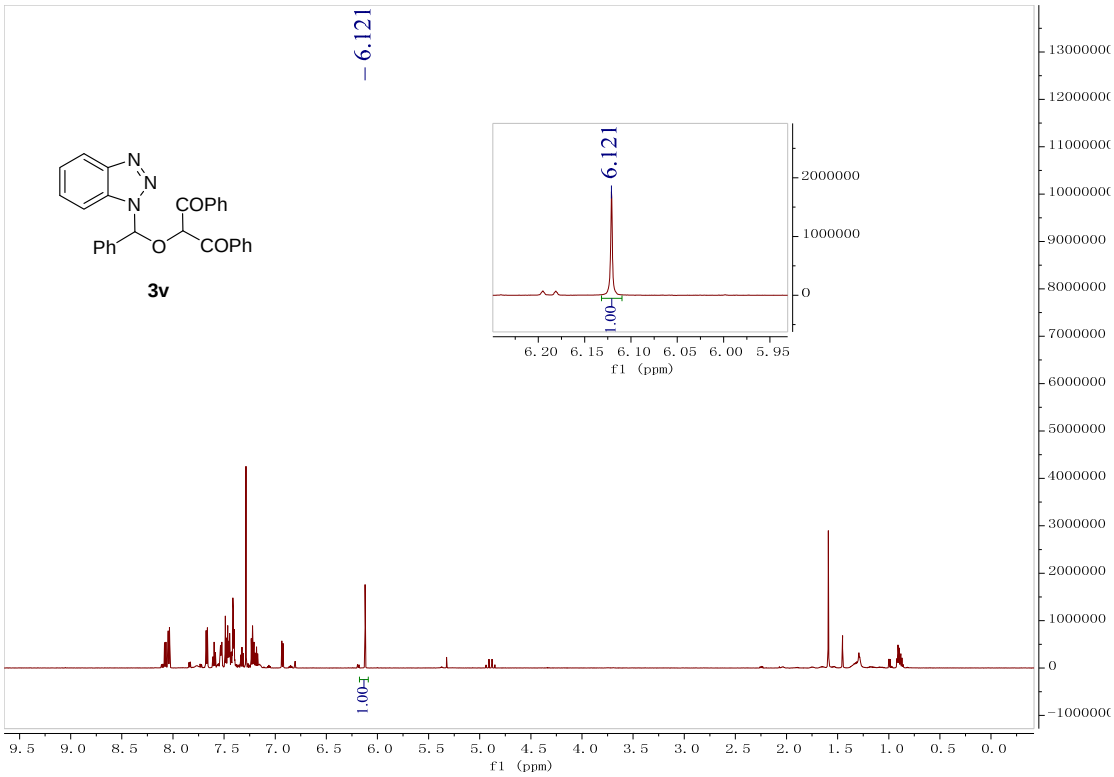
Crude ^{1}H NMR of 3t



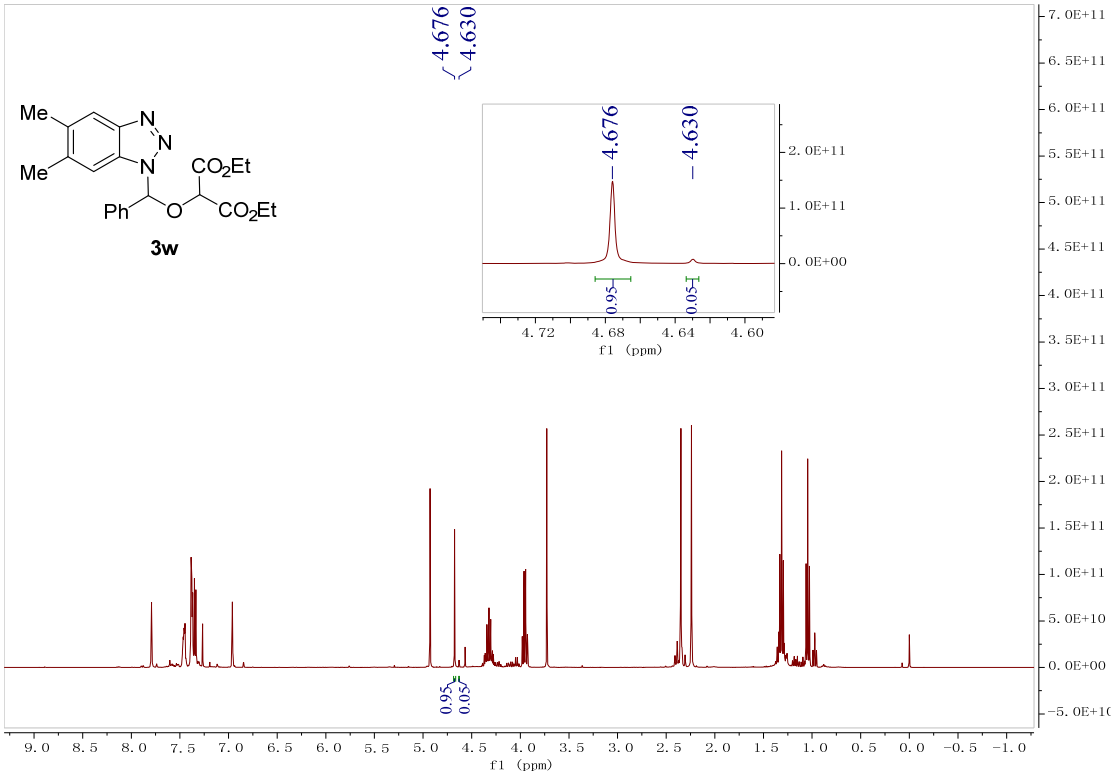
Crude ^{1}H NMR of 3u



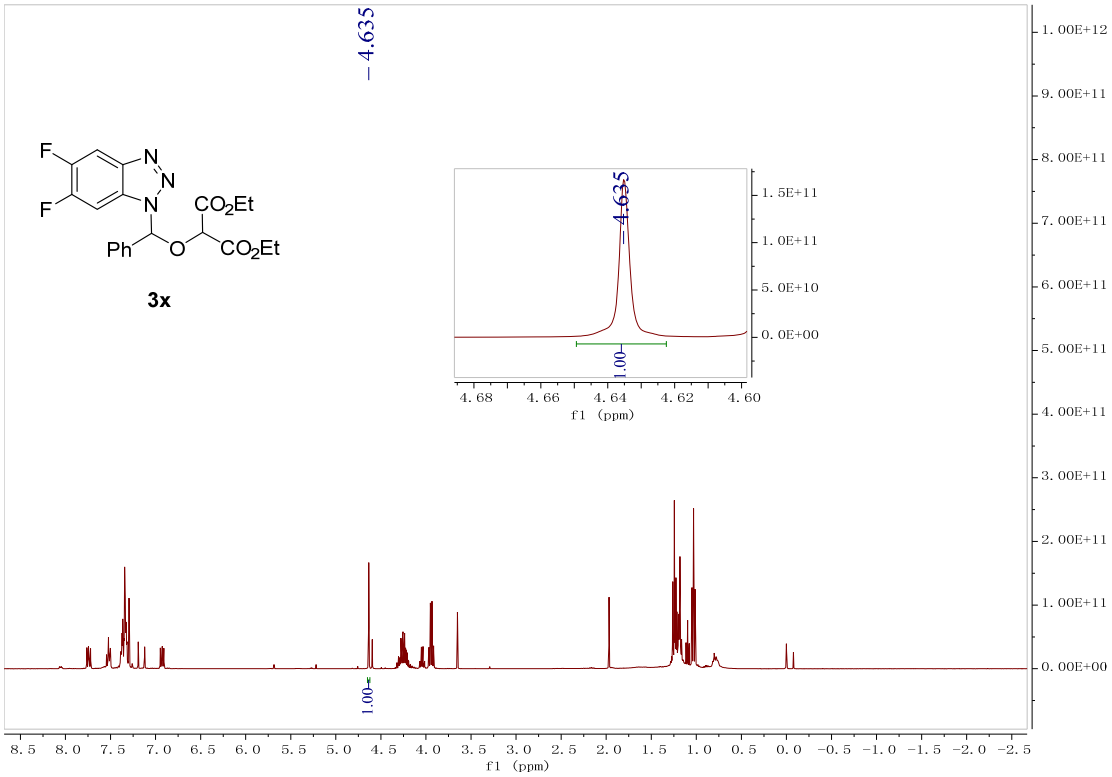
Crude ^{1}H NMR of 3v



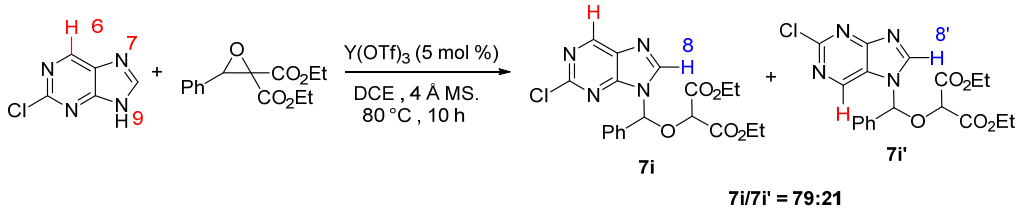
Crude ^{1}H NMR of 3w



Crude ^{1}H NMR of 3x

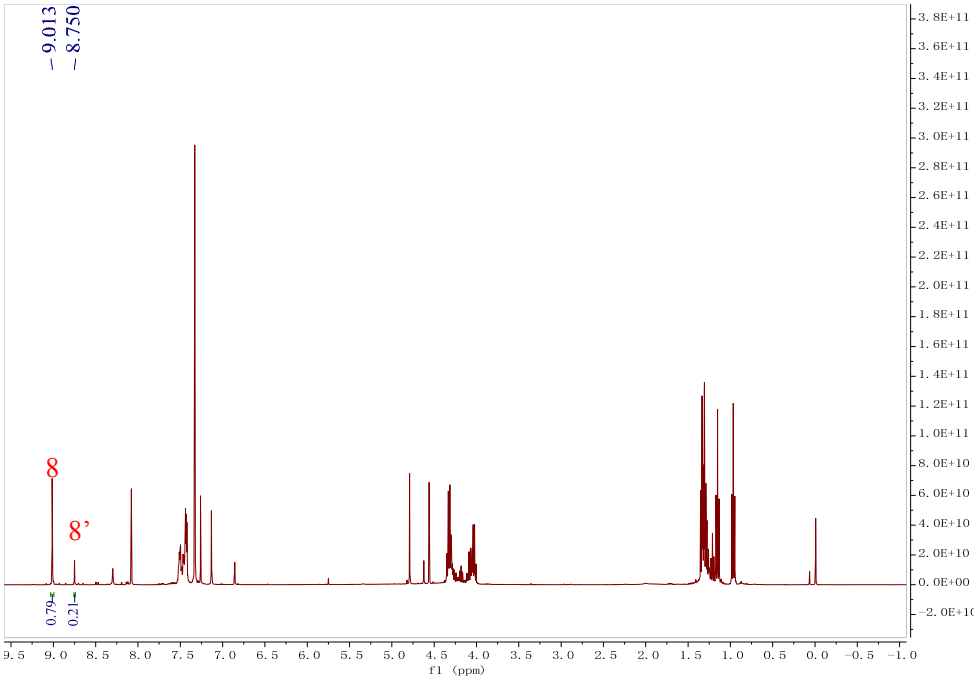


Crude ^{1}H NMR of 7i and 7i'

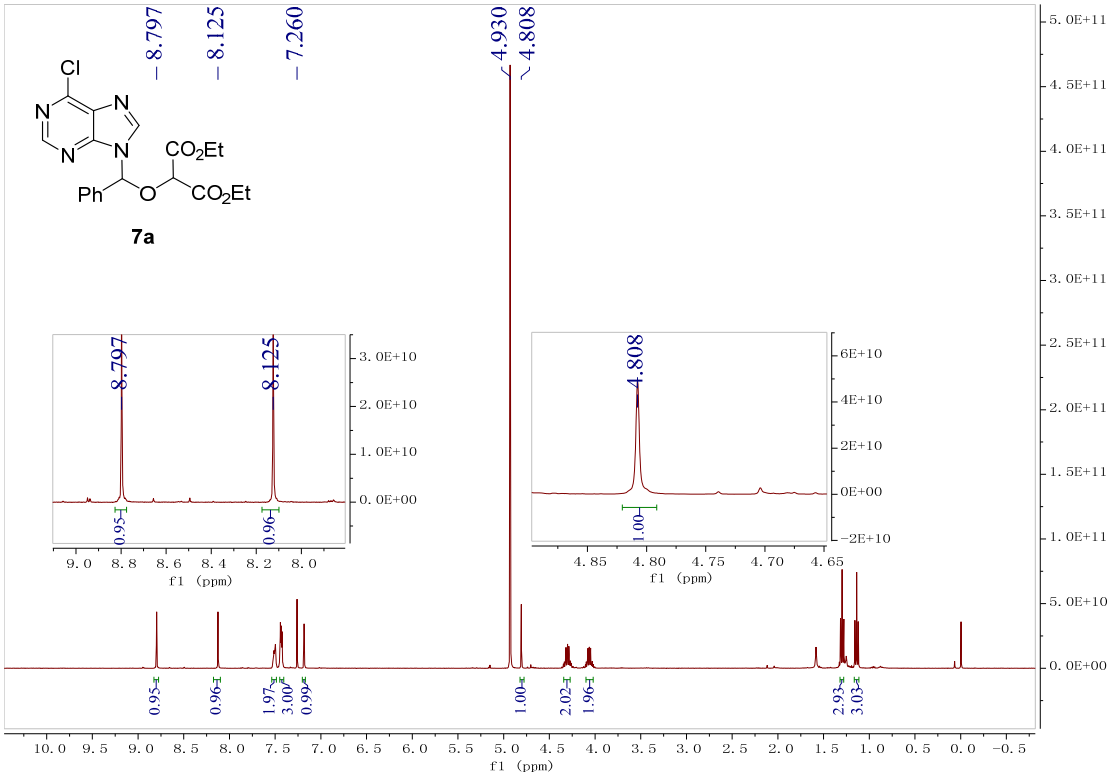


7i/7i' = 79:21

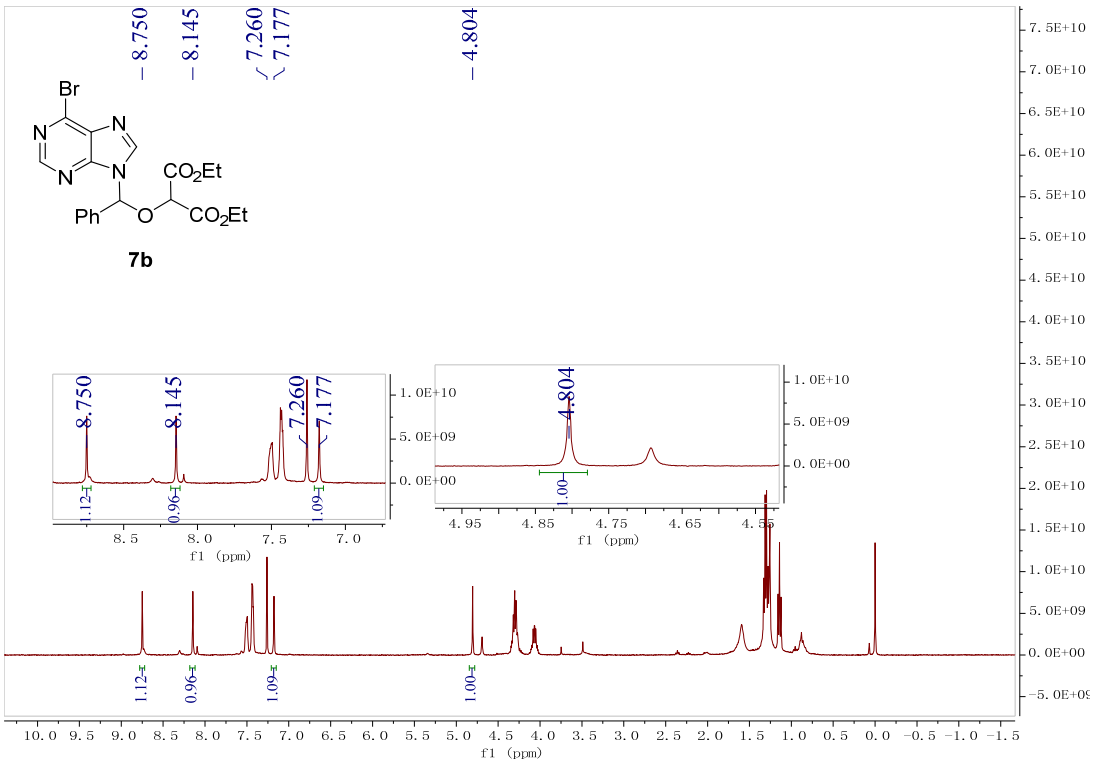
H8 (s, 0.79H), H8'(s, 0.21H)



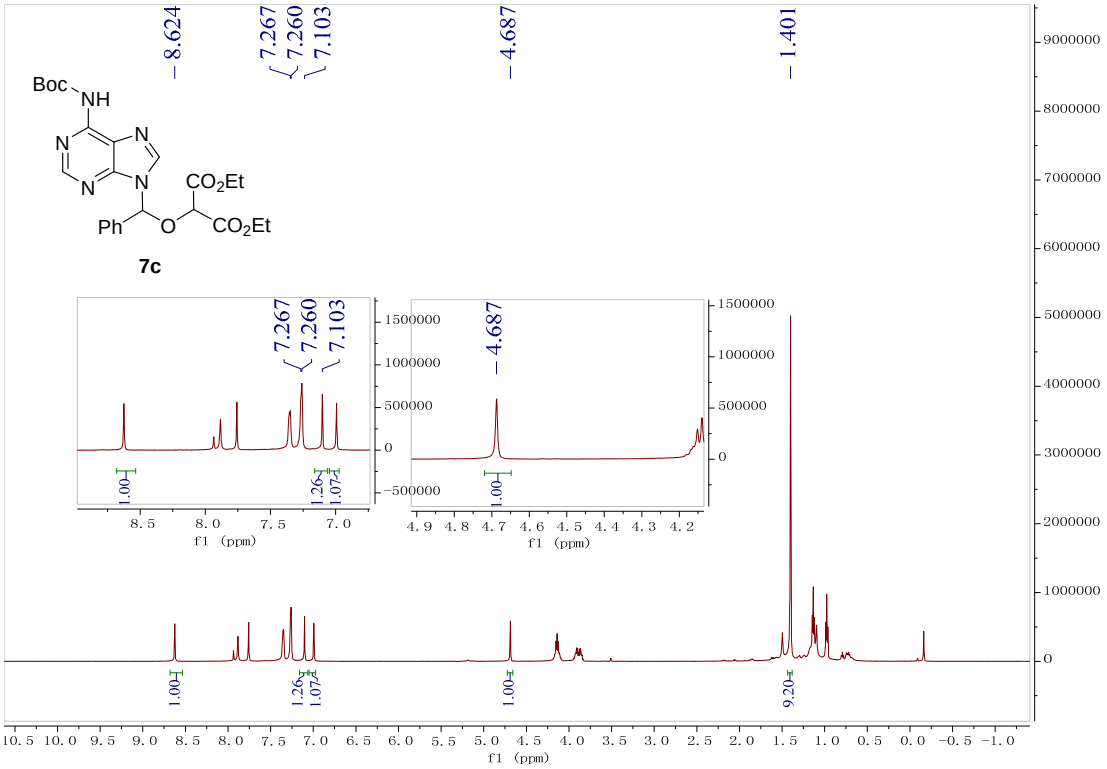
Crude ^{1}H NMR of 7a, N^9/N^7 > 95:5



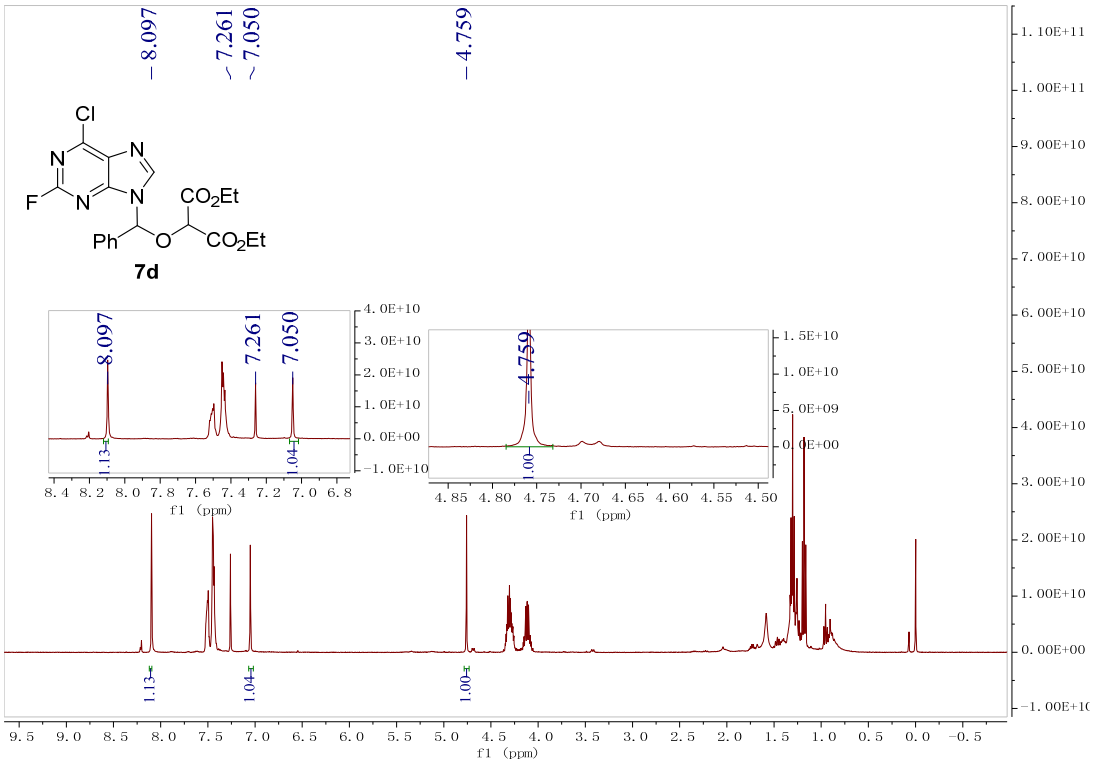
Crude ^{1}H NMR of 7b, N^9/N^7 > 95:5



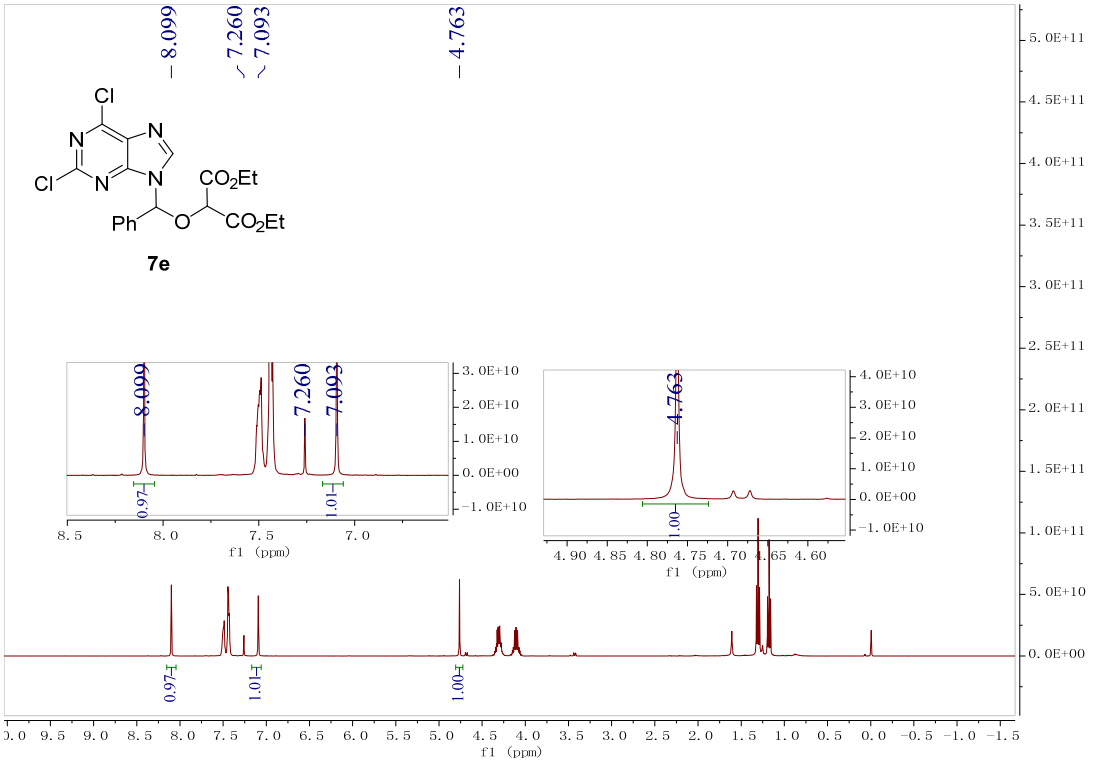
Crude ^{1}H NMR of 7c, N^9/N^7 > 95:5



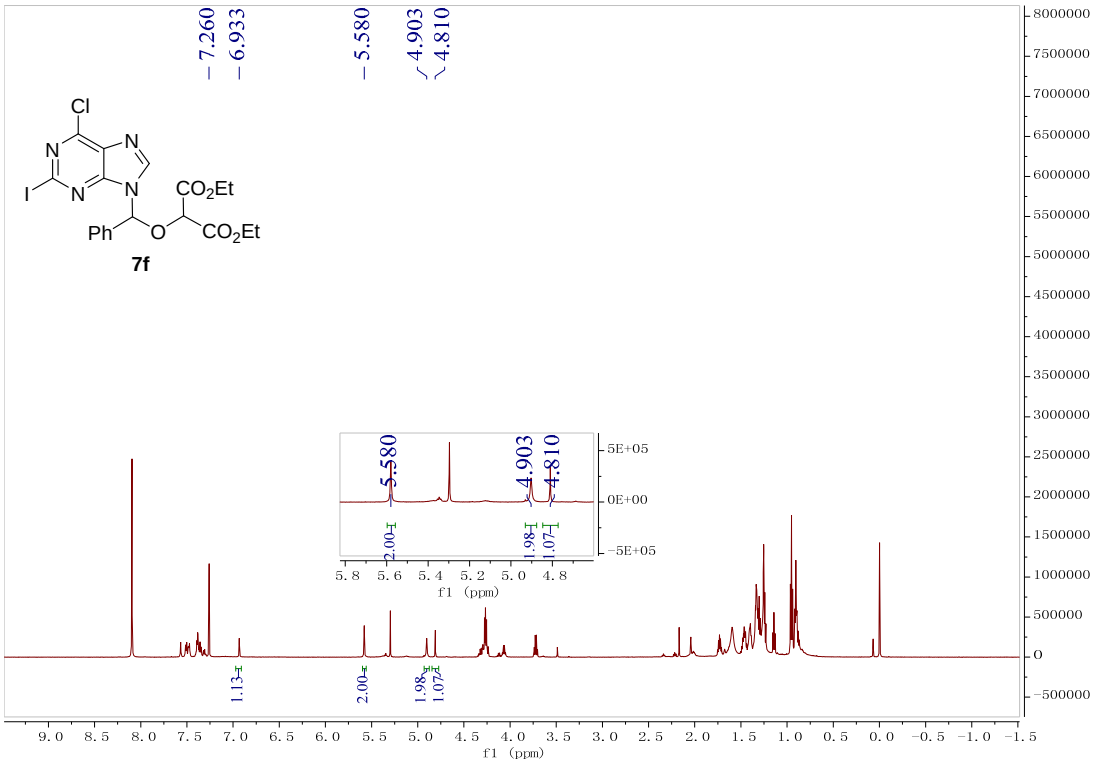
Crude ^{1}H NMR of 7d, N^9/N^7 > 95:5



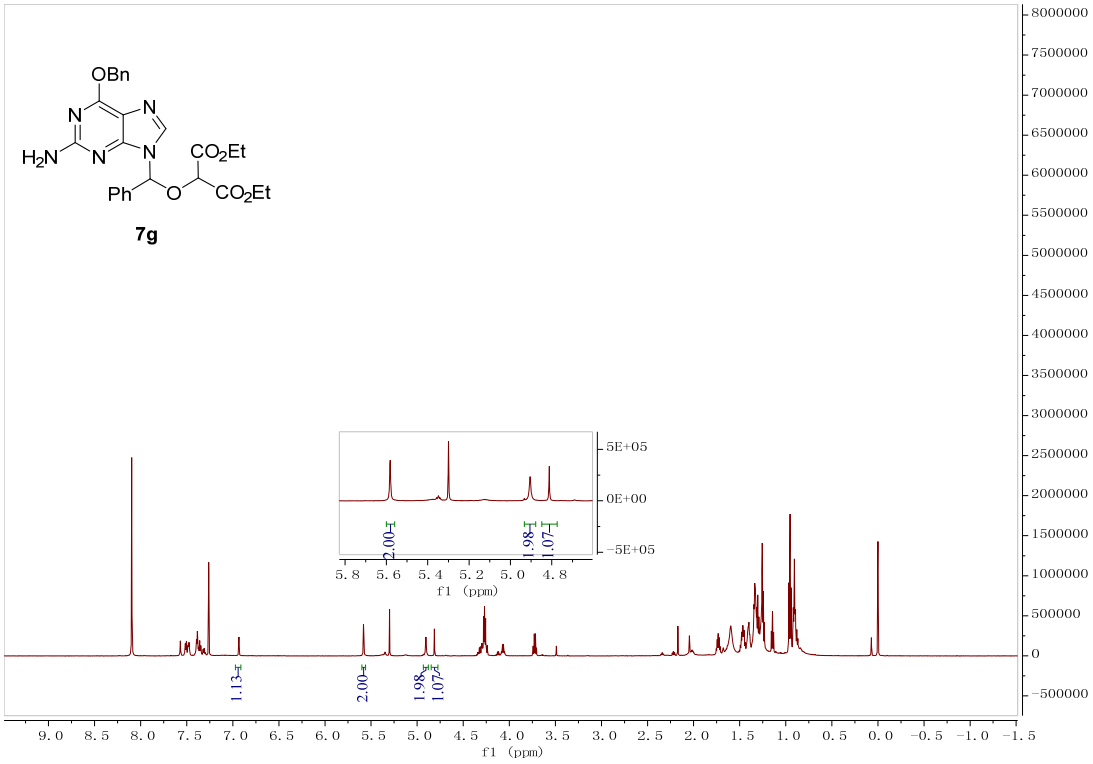
Crude ^{1}H NMR of 7e, N^9/N^7 > 95:5



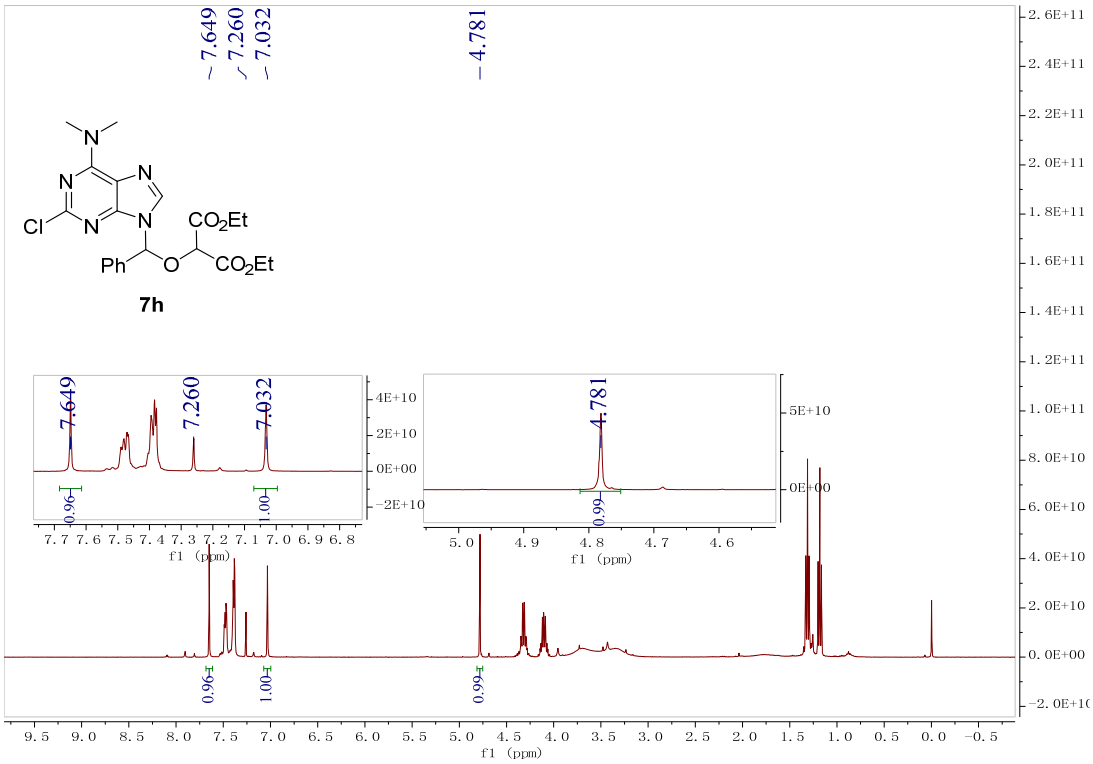
Crude ^{1}H NMR of 7f, N^9/N^7 > 95:5



Crude ^{1}H NMR of 7g, N^9/N^7 > 95:5



Crude ^{1}H NMR of 7h, N^9/N^7 > 95:5



17. Reference

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(2) G. V. Kryshtal, G. M. Zhdankina and S. G. Zlotin, *Mendeleev Commun.*, 2013, **23**, 24.

(3) X. Yuan, L. L. Lin, W. L Chen, W. B. Wu, X. H. Liu and X. M. Feng, *J. Org. Chem.* **2016**, **81**, 1237.

(4) A. Russo and A. Lattanzi, *Org. Biomol. Chem.*, 2010, **8**, 2633.

(5) K. Xu, N. Thieme and B. Breit, *Angew.Chem., Int. Ed.*, 2014, **126**, 7896.