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Electronic Supporting Information

Visible-Light-Induced Mn(0)-Catalyzed Direct C–3 Mono-, Di- and Perfluoroalkylations of 2*H*-Indazoles

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Contents

1. General information:

All reagents were purchased from commercial sources and used without further purification. ^{1}H NMR spectra were determined on 400 MHz spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (δ) and the signals were reported as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and coupling constants (J) were given in Hz. $^{13}C\{^{1}H\}$ NMR spectra were recorded at 100 MHz in $CDCl_3$ solution. Moreover, ^{19}F $\{^{1}H$ decoupled$\}$ and ^{31}P NMR spectra were recorded at 376.5 MHz, and 162 MHz in $CDCl_3$ solution. Chemical shifts are referenced to $CDCl_3$ (δ = 7.26 for ^{1}H and δ = 77.16 for $^{13}C\{^{1}H\}$ NMR) as internal standard. High-resolution mass spectra (HRMS) were collected using electrospray ionization (ESI) on a time-of-flight (TOF) mass spectrometer. TLC was done on silica gel coated glass slide. All solvents were dried and distilled before use. All reactions involving moisture sensitive reactants were executed using oven dried glassware. All the 2*H*-indazoles[1] and bromodifluoroacetamide derivatives[2] were prepared by reported method. Melting points (mp.) were determined after recrystallization of solid compounds from a solution of dichloromethane/petroleum ether (1:3).

2. Light information:

Kessil 34 W blue LED (Model No. H150-BLUE) was used as a light source for light promoted reactions.

Rating of LED: 24VDC 1.5A 34W

Model: H150-BLUE

Range of wavelength: 450-530 nm. Manufacturer: Kessil, 1689 Regatta blvd, Richmond, CA94804 (www.kessil.com).

3. Pictorial presentation of the reaction set-up:

The Borosilicate glass reaction tube was used to carry out light-promoted reaction. The reaction tube was kept 5-7 cm apart from the exposed of Kessil 34 W blue LED. Regular fan was used to keep up the temperature 28 to 30 °C during the reaction. We did not use any filter.

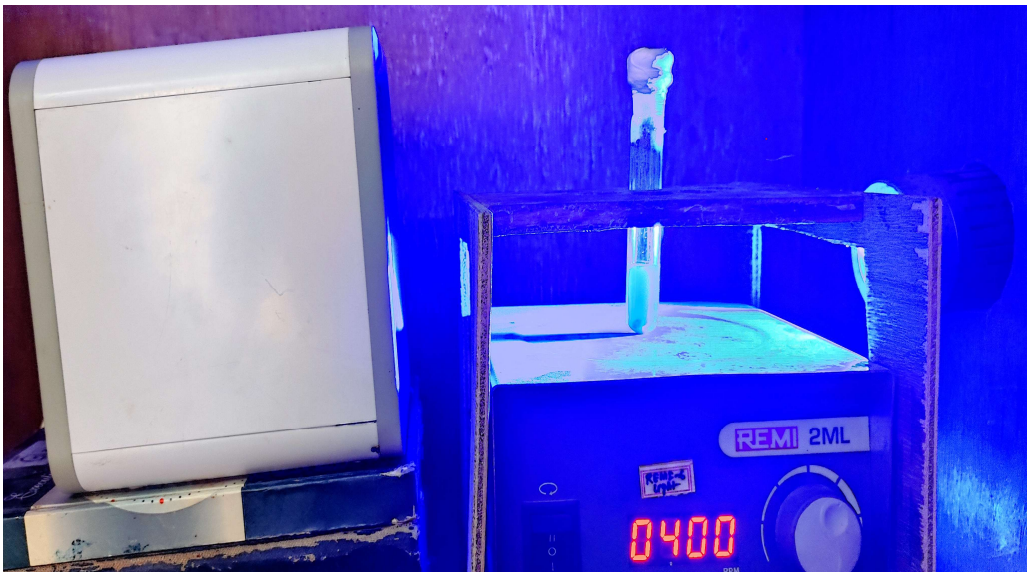
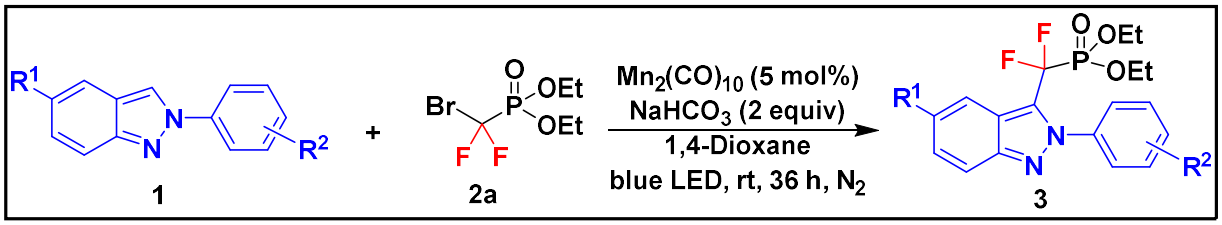


Fig: S1.1: LED reaction set-up

Fig: S1.2: LED reaction set-up

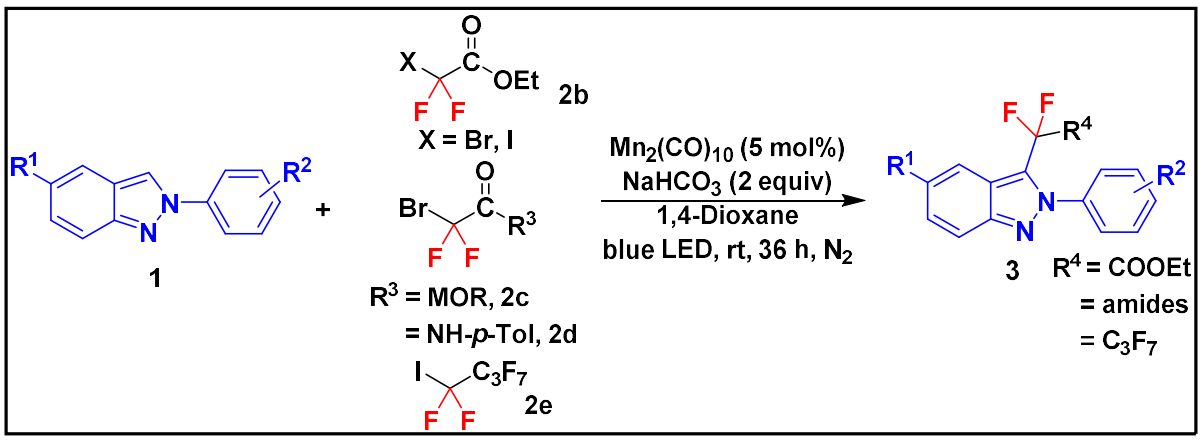
4. Experimental procedures:

4.1. Typical experimental procedure for the synthesized compounds 3aa-3pa:



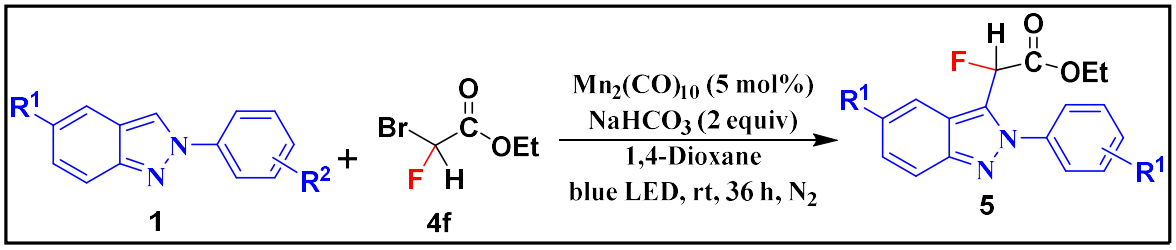
A mixture of 2-Arylindazoles (0.2 mmol) (**1**), $BrCF_2PO(OEt)_2$ (0.4 mmol, 106.8 mg) (**2a**), $Mn_2(CO)_{10}$ (5 mol %, 3.9 mg), $NaHCO_3$ (2.0 equiv, 33.6 mg), and 1,4-Dioxane (2 mL) was added to an oven-dried reaction vessel (tube) equipped with a magnetic stirrer, and the reaction vessel was irradiated with Kessil 34 W blue LED at room temperature under nitrogen atmosphere for 36 h. After completion of the reaction (TLC), the reaction mixture was extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4. The crude residue was obtained after evaporating the solvent in vacuum and was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as an eluting solvent to afford the pure products **3aa-3pa**.

4.2. Experimental procedure for the synthesized compounds 3ab-3ge:



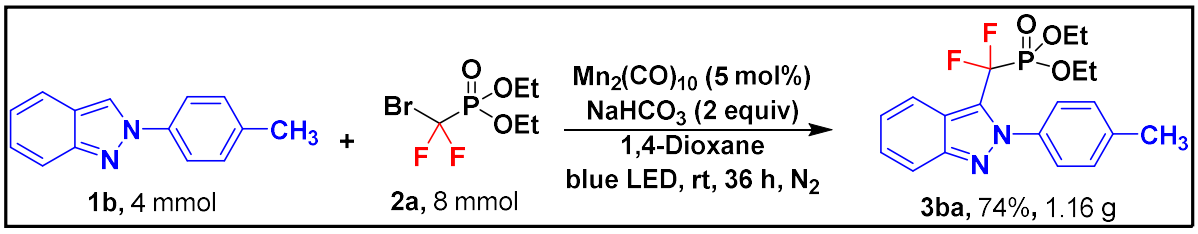
A mixture of 2-Arylindazoles (0.2 mmol) (**1**), XCF_2R^4 (X=Br, I, R^4= –COOEt, amides, $–C_3F_7$) (0.4 mmol) (**2**), $Mn_2(CO)_{10}$ (5 mol %, 3.9 mg), $NaHCO_3$ (2.0 equiv, 33.6 mg), and 1,4-Dioxane (2 mL) was added to an oven-dried reaction tube equipped with a magnetic stirrer, and the reaction vessel was irradiated with Kessil 34 W blue LED at room temperature under nitrogen atmosphere for 36 h. After completion of the reaction (TLC), the reaction mixture was extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4. The crude residue was obtained after evaporating the solvent in vacuum and was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as an eluting solvent to afford the pure products **3ab-3ge**.

4.3. Experimental procedure for the synthesized compounds 5af-5nf:



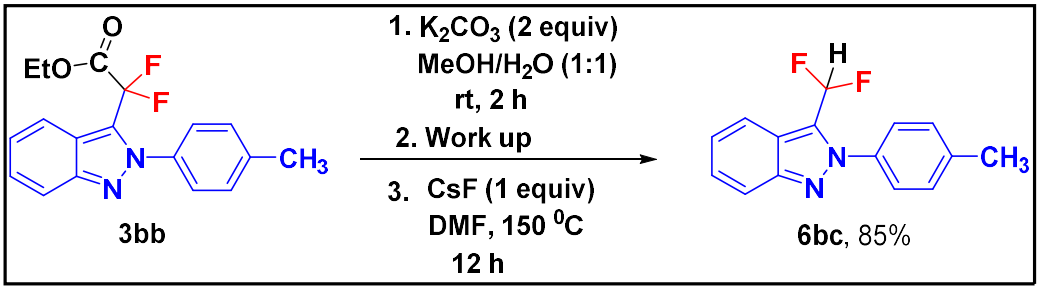
A mixture of 2-Arylindazoles (0.2 mmol) (**1**), $BrCFHCO(OEt)_2$ (0.4 mmol, 74 mg) (**4f**), $Mn_2(CO)_{10}$ (5 mol %, 3.9 mg), $NaHCO_3$ (2.0 equiv, 33.6 mg), and 1,4-Dioxane (2 mL) was added to an oven-dried reaction vessel (tube) equipped with a magnetic stirrer, and the reaction vessel was irradiated with Kessil 34 W blue LED at room temperature under nitrogen atmosphere for 36 h. After completion of the reaction (TLC), the reaction mixture was extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4. The crude residue was obtained after evaporating the solvent in vacuum and was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as an eluting solvent to afford the pure products **5af-5nf.**

5. Gram-scale preparation of 3ba:



A mixture of 2-(*p*-tolyl)-2*H*-indazole (4.0 mmol, 832.0 mg) (**1b**), $BrCF_2PO(OEt)_2$ (8.0 mmol, 2.14 g) (**2a**), $Mn_2(CO)_{10}$ (5 mol %, 78 mg), $NaHCO_3$ (2.0 equiv, 672 mg), and 1,4-Dioxane (30 mL) was added to an oven-dried reaction vessel (tube) equipped with a magnetic stirrer, and the reaction vessel was irradiated with Kessil 34 W blue LED at room temperature under nitrogen atmosphere for 36 h. After completion of the reaction (TLC), the reaction mixture was extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4. The crude residue was obtained after evaporating the solvent in vacuum and was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as an eluting solvent to afford the pure product **3ba** (1.16 g, 74%) as a yellow solid.

6. Synthetic utility of C–3 difluoroacetated products: Synthesis of 3-(difluoromethyl)-2-(*p*-tolyl)-2*H*-indazole (6bc):



A mixture of ethyl 2,2-difluoro-2-(2-(*p*-tolyl)-2*H*-indazol-3-yl)acetate (0.3 mmol, 99 mg) (**3bb**), K_2CO_3 (2.0 equiv, 82.9 mg) and 2 mL of MeOH: H_2O (1:1) as solvent in an oven-dried reaction tube equipped with magnetic bar was stirred for 2 h at room temperature. Thereafter, evaporation of the solvent mixture was done and then workup with crude ethyl

acetate and water. Finally, the crude mixture was taken in an oven-dried reaction tube and added 1.0 equiv of CsF in 2 mL of DMF and stirred at 150 ^{0}C temperature for 12 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was dried over anhydrous Na_2SO_4 and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with petroleum ether and ethyl acetate (9:1) to afford the product **6bc** (85%, 65 mg) as white solid.

7. Structure determination (X-ray crystallographic data for 3fa):

The colourless crystal of **3fa** was obtained by crystallization from a solution in dichloromethane/petroleum ether after purification by column chromatography. Chemical formula: $C_{19}H_{18}F_5N_2O_3P$.

For single crystal structure determination, a suitable single crystal was carefully selected under a polarizing microscope and glued carefully to a thin glass fiber. The single crystal data were collected on a Bruker D8 Quest diffractometer at 293 (2) K (Fig. S2). The X-ray generator was operated at 50 kV and 1 mA using Mo Kα radiation (λ = 0.71073 Å), controlled by the APEX3 software package[3]. Data were collected with ω scan width of 0.3º. A total of 408 frames were collected in three different setting of φ (0, 90, 180º) keeping sample-to-detector distance fixed at 6.03 cm and the detector position (2θ) fixed at -25º. The data were reduced using SAINTPLUS, and an empirical absorption correction was applied using the SADABS program. The structure was solved and refined using SHELXL97[4] present in the OLEX 2[5] suit of programs.

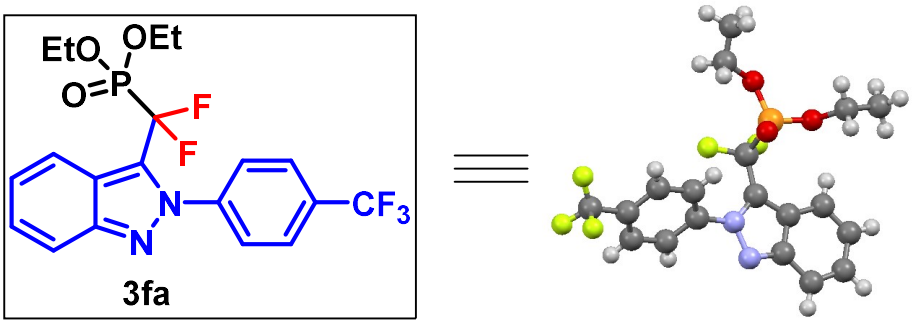


Fig: S2.1

Wavelength	0.71073 Å	
Formula	$C_{19}H_{18}F_5N_2O_3P$	
Crystal system	Monoclinic	
Space group	P 2_1/n	
Unit cell dimensions	a = 8.144(2) Å	α = 90 °
	b = 9.764(2) Å	β = 98.77(3) °
	c = 26.580(5) Å	γ = 90 °
Volume	2088.9(8) $Å^3$	
Z	4	
R-factor (%)	7.7	

The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication with a CCDC reference number CCDC 2191201.

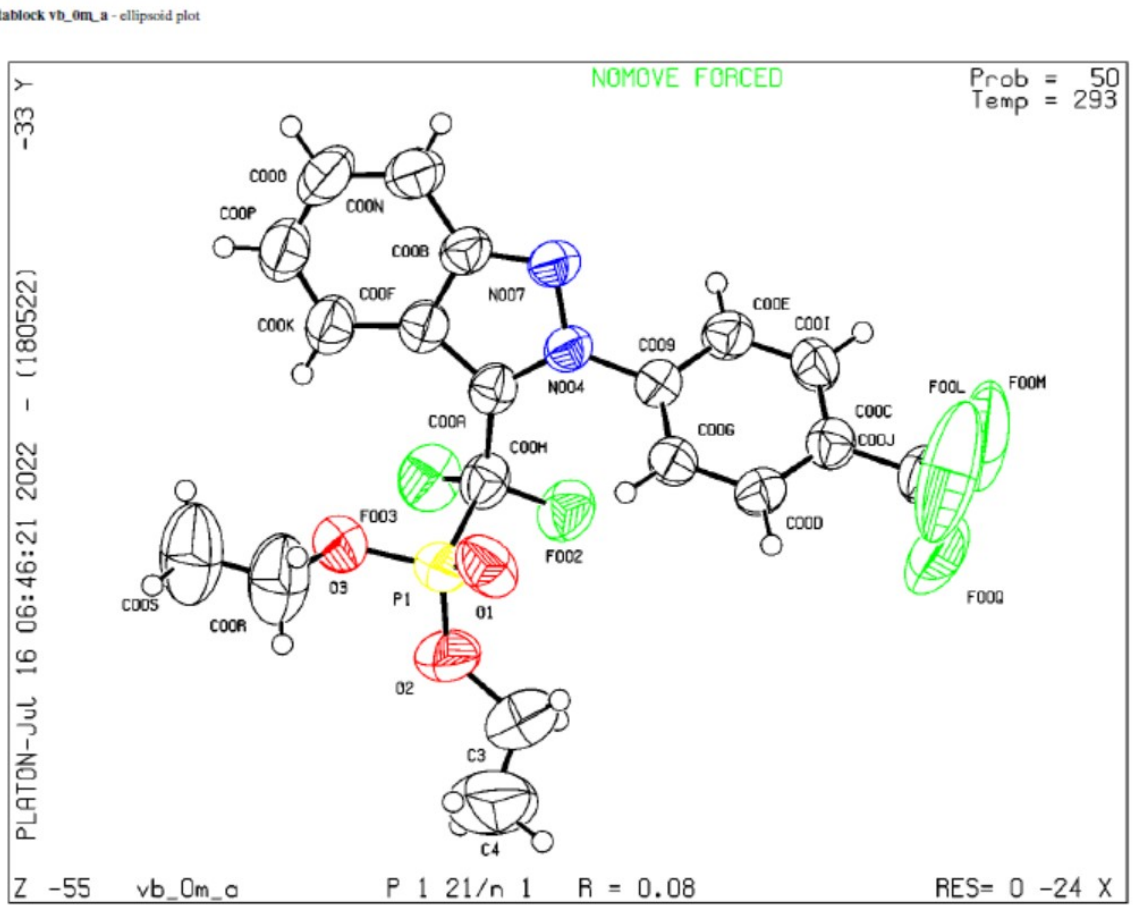


Fig: S2.2

View of ORTEP diagram for the crystal structure of the compound **Diethyl (difluoro(2-(4-(trifluoromethyl)phenyl)-2*H*-indazol-3-yl)methyl)phosphonate (3fa)** (Thermal ellipsoid contour at 50% probability level).

8. Mechanistic studies of the reaction:

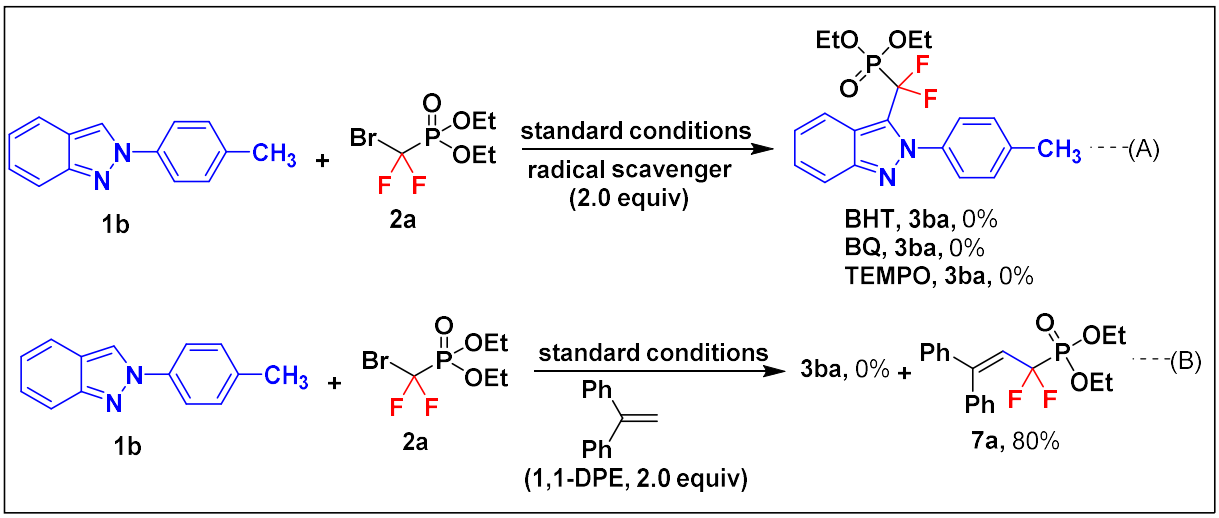
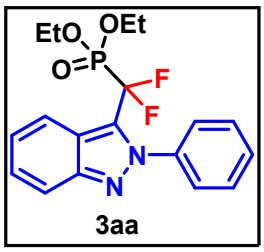


Fig: S3

Different radical inhibitors such as 2,6-di-*tert*-butyl-4-methyl phenol (BHT), benzoquinone (BQ), and 2,2,6,6-tetramethyl-1-oxylpiperidine (TEMPO) in the reaction which completely suppressed the desired product of the reaction (Fig S3, eq A). Furthermore, the radical adduct diethyl (1,1-difluoro-3,3-diphenylallyl)phosphonate (**7a**) was produced in 80% yield by the addition of 2.0 equiv of 1,1-diphenylethylene to the present reactions (Fig S3, eq B). The above experimental outputs suggest that a radical pathway might be involved in the reaction.

9. Physical data of the compounds:

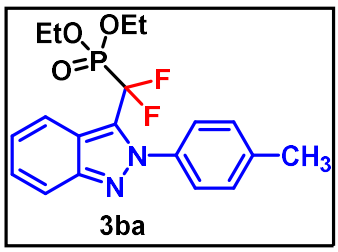
Diethyl (difluoro(2-phenyl-2H-indazol-3-yl)methyl)phosphonate (3aa):



3aa

Yellow liquid (60 mg, 80%); R_f 0.4 (PET:EtOAc = 7:3); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.85 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.68–7.66 (m, 2H), 7.52–7.48 (m, 3H), 7.39–7.35 (m, 1H), 7.25–7.21 (m, 1H), 4.19–4.01 (m, 4H), 1.25 (t, J = 7.2 Hz, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 148.5, 140.7, 129.6, 128.5, 127.2 (d, $J_{C\text{-}F}$ = 5.0 Hz) 125.9, 124.1, 122.3, 120.7, 118.2, 117.0, 114.8, 65.2 (d, $J_{C\text{-}F}$ = 7.0 Hz), 16.4 (d, $J_{C\text{-}F}$ = 6.0 Hz); **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -101.6 (d, $J_{F\text{-}P}$ = 116.71 Hz); **^{31}P NMR** ($CDCl_3$, 162 MHz): δ 4.94 (t, $J_{P\text{-}F}$ = 118.2 Hz); **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{18}H_{20}F_2N_2O_3P]^+$: 381.1174; Found 381.1159.

Diethyl (difluoro(2-(p-tolyl)-2H-indazol-3-yl)methyl)phosphonate (3ba):

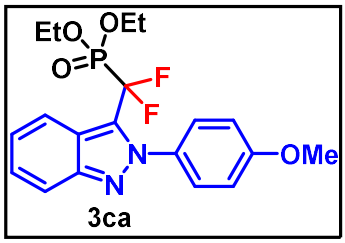


3ba

Yellow solid (64 mg, 82%); mp. 64−65 °C; R_f 0.4 (PET:EtOAc = 7:3); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.85 (d, J = 8.8 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.54 (d, J = 8.0 Hz, 2H), 7.38–7.34 (m, 1H), 7.29–7.25 (m, 2H), 7.23–7.20 (m, 1H), 4.20–3.99 (m, 4H), 2.44 (s, 3H), 1.25 (t, J = 7.2 Hz, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 148.5, 139.6, 138.3, 129.0,

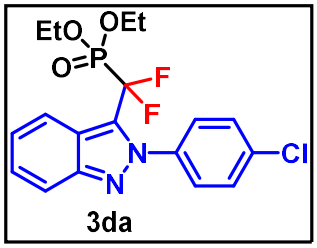
127.0 (d, $J_{C\text{-}F}$ = 8.0 Hz), 123.9 (d, $J_{C\text{-}F}$ = 9.0 Hz), 122.3, 120.7, 119.7, 118.1, 117.4, 114.5, 65.1 (d, $J_{C\text{-}F}$ = 7.0 Hz), 21.4, 16.4 (d, $J_{C\text{-}F}$ = 5.0 Hz); **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -101.5 (d, $J_{F\text{-}P}$ = 116.7 Hz); **^{31}P NMR** ($CDCl_3$, 162 MHz): δ 4.97 (t, $J_{P\text{-}F}$ = 116.6 Hz); **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{19}H_{22}F_2N_2O_3P]^+$: 395.1331; Found 395.1314

Diethyl (difluoro(2-(4-methoxyphenyl)-2H-indazol-3-yl)methyl)phosphonate (3ca):



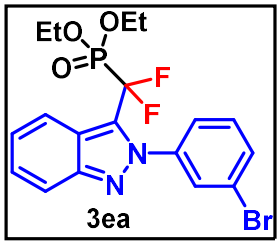
Yellow solid (66 mg, 81%); mp. 84−85 °C; R_f 0.4 (PET:EtOAc = 3:2); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.84 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.58 (d, J = 8.8 Hz, 2H), 7.36 (t, J = 8.0 Hz, 1H), 7.23–7.20 (m, 1H), 7.00–6.96 (m, 2H), 4.19–4.02 (m, 4H), 3.87 (s, 3H), 1.25 (t, J = 7.2 Hz, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 160.3, 148.4, 133.6, 128.4, 127.0, 126.0 (d, $J_{C\text{-}F}$ = 45.0 Hz) , 123.9, 122.3, 120.7, 118.1, 114.8, 113.5, 65.1 (d, $J_{C\text{-}F}$ = 6.0 Hz), 55.6, 16.4 (d, $J_{C\text{-}F}$ = 5.0 Hz); **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -101.8 (d, $J_{F\text{-}P}$ = 112.9 Hz); **^{31}P NMR** ($CDCl_3$, 162 MHz): δ 4.97 (t, $J_{P\text{-}F}$ = 116.6 Hz); Anal. Calcd for **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{19}H_{22}F_2N_2O_4P]^+$: 411.1280; Found 411.1285.

Diethyl ((2-(4-chlorophenyl)-2H-indazol-3-yl)difluoromethyl)phosphonate (3da):



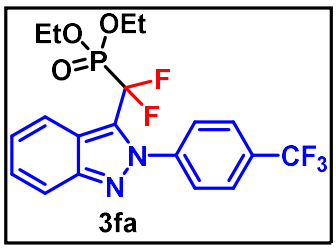
Yellow solid (70 mg, 85%); mp. 80−81 °C; R_f 0.5 (PET:EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.83 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.38 (t, J = 8.4 Hz, 1H), 7.26–7.21 (m, 1H), 4.23–4.03 (m, 4H), 1.27 (t, J = 7.2 Hz, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 148.7, 139.2, 135.6 128.6 (d, $J_{C\text{-}F}$ = 22.0 Hz), 127.4, 124.3, 122.4, 120.6, 119.4 (d, $J_{C\text{-}F}$ = 44.0 Hz), 118.2, 117.1 (d, $J_{C\text{-}F}$ = 38.0 Hz), 114.7, 65.3 (d, $J_{C\text{-}F}$ = 6.0 Hz), 16.4 (d, $J_{C\text{-}F}$ = 6.0 Hz); **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -101.9 (d, $J_{F\text{-}P}$ = 116.7 Hz); **^{31}P NMR** ($CDCl_3$, 162 MHz): δ 4.82 (t, $J_{P\text{-}F}$ = 115.0 Hz); **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{18}H_{19}ClF_2N_2O_3P]^+$: 415.0784; Found 415.0790.

Diethyl ((2-(3-bromophenyl)-2H-indazol-3-yl)difluoromethyl)phosphonate (3ea):



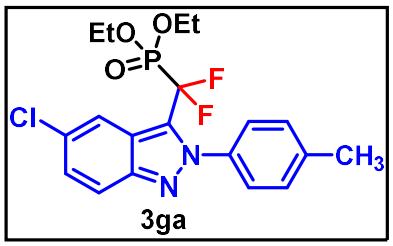
Yellow liquid (76 mg, 83%); R_f 0.5 (PET:EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.89 (s, 1H), 7.84 (d, J = 8.8 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.69–7.63 (m, 2H), 7.40–7.35 (m, 2H), 7.25–7.21 (m, 1H), 4.25–4.05 (m, 4H), 1.28 (t, J = 7.2 Hz, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 148.7, 141.7, 132.7, 130.4, 129.7, 127.4, 126.0, 124.3, 122.4 (d, $J_{C\text{-}F}$ = 3.0 Hz), 121.8, 120.7, 118.2, 117.1 (d, $J_{C\text{-}F}$ = 37.0 Hz), 114.5 (d, $J_{C\text{-}F}$ = 35.0 Hz), 65.3 (d, $J_{C\text{-}F}$ = 7.0 Hz), 16.4 (d, $J_{C\text{-}F}$ = 5.0 Hz); **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -101.7 (d, $J_{F\text{-}P}$ = 112.9 Hz); **^{31}P NMR** ($CDCl_3$, 162 MHz): δ 4.91 (t, $J_{P\text{-}F}$ = 113.4 Hz); **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{18}H_{19}BrF_2N_2O_3P]^+$: 459.0279; Found 459.0266.

Diethyl (difluoro(2-(4-(trifluoromethyl)phenyl)-2H-indazol-3-yl)methyl)phosphonate (3fa):



White solid (71 mg, 80%); mp. 79−80 °C; R_f 0.5 (PET:EtOAc = 7:3); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.89–7.83 (m, 3H), 7.77 (d, J = 8.8 Hz, 3H), 7.39 (t, J = 8.4 Hz, 1H), 7.27–7.23 (m, 1H), 4.24–4.04 (m, 4H), 1.27 (t, J = 7.2 Hz, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 148.9, 143.5, 131.3 (q, $J_{C\text{-}F}$ = 63.0 Hz), 127.6 (d, $J_{C\text{-}F}$ = 15.0 Hz), 125.7 (q, $J_{C\text{-}F}$ = 4.0 Hz), 125.1, 124.5, 122.5 (t, $J_{C\text{-}F}$ = 7.0 Hz), 120.7, 118.2, 116.9, 114.7 (d, $J_{C\text{-}F}$ = 3.0 Hz), 65.3 (d, $J_{C\text{-}F}$ = 7.0 Hz), 16.4 (d, $J_{C\text{-}F}$ = 5.0 Hz); **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -62.6, -101.6 (d, $J_{F\text{-}P}$ = 116.7 Hz); **^{31}P NMR** ($CDCl_3$, 162 MHz): δ 4.79 (t, $J_{P\text{-}F}$ = 113.4 Hz); **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{19}H_{19}F_5N_2O_3P]^+$: 449.1048; Found 449.1053.

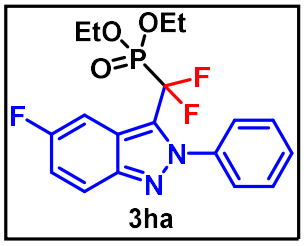
Diethyl ((5-chloro-2-(p-tolyl)-2H-indazol-3-yl)difluoromethyl)phosphonate (3ga):



Reddish yellow liquid (72 mg, 84%); R_f 0.4 (PET:EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.82 (s, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.53 (d, J = 8.0 Hz, 2H), 7.31–7.25 (m, 3H), 4.21–4.05 (m, 4H), 2.43 (s, 3H), 1.28 (t, J = 7.2 Hz, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 146.7, 142.0, 139.9, 137.9, 129.7, 129.1, 128.5, 126.7, 122.6, 119.6 (d, $J_{C\text{-}F}$ = 18.0 Hz), 116.8, 114.3 (d, $J_{C\text{-}F}$ = 37.0 Hz), 65.2 (d, J = 7.0 Hz), 21.4, 16.4 (d, J = 6.0 Hz); **^{19}F NMR**

(376.5 MHz, $CDCl_3$): δ -102.1 (d, $J_{F\text{-}P}$ = 112.9 Hz); **^{31}P NMR** ($CDCl_3$, 162 MHz): δ 4.65 (t, $J_{P\text{-}F}$ = 116.6 Hz); **HRMS** (ESI–TOF) m/z: [M + H]+ Calcd for $[C_{19}H_{21}ClF_2N_2O_3P]^+$: 429.0941; Found 429.0925.

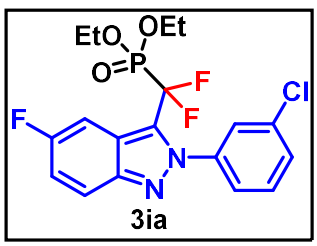
Diethyl (difluoro(5-fluoro-2-phenyl-2H-indazol-3-yl)methyl)phosphonate (3ha):



3ha

Yellow solid (65 mg, 82%); mp. 81−82 °C; R_f 0.4 (PET:EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.77–7.74 (m, 1H), 7.67–7.65 (m, 2H), 7.53–7.48 (m, 3H), 7.43 (d, J = 9.6 Hz, 1H), 7.20–7.15 (m, 1H), 4.22–4.03 (m, 4H), 1.27 (t, J = 7.2 Hz, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 159.5 (d, $J_{C\text{-}F}$ = 241.0 Hz), 145.9, 140.6, 129.7, 128.5, 127.1, 122.0 (d, $J_{C\text{-}F}$ = 11.0 Hz), 120.4 (d, $J_{C\text{-}F}$ = 10.0 Hz), 119.0 (d, $J_{C\text{-}F}$ = 29.0 Hz), 116.8, 114.6, 103.5 (d, $J_{C\text{-}F}$ = 26.0 Hz), 65.2 (d, $J_{C\text{-}F}$ = 7.0 Hz), 16.4 (d, $J_{C\text{-}F}$ = 5.0 Hz); **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -101.9 (d, $J_{F\text{-}P}$ = 112.9 Hz), -116.2; **^{31}P NMR** ($CDCl_3$, 162 MHz): δ 4.81 (t, $J_{P\text{-}F}$ = 116.6 Hz); **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{18}H_{19}F_3N_2O_3P]^+$: 399.1080; Found 399.1085.

Diethyl ((2-(3-chlorophenyl)-5-fluoro-2H-indazol-3-yl)difluoromethyl)phosphonate (3ia):

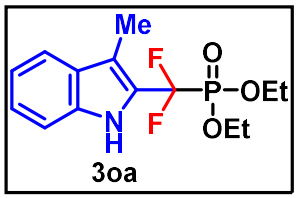


3ia

Yellow solid (67 mg, 78%); mp. 78−79 °C; R_f 0.4 (PET:EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.77–7.72 (m, 2H), 7.62 (d, J = 7.6 Hz, 1H), 7.51–7.49 (m, 1H), 7.46–7.42 (m, 2H),

7.22–7.16 (m, 1H), 4.27–4.08 (m, 4H), 1.30 (t, J = 7.2 Hz, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 161.9, 159.6 (d, $J_{C\text{-}F}$ = 244.0 Hz), 146.1, 141.4, 134.2, 129.7 (d, $J_{C\text{-}F}$ = 36.0 Hz), 127.5, 125.4, 123.3, 122.0 (t, $J_{C\text{-}F}$ = 5.0 Hz), 120.5 (d, $J_{C\text{-}F}$ = 9.0 Hz), 119.4 (d, $J_{C\text{-}F}$ = 29.0 Hz), 114.5, 103.5 (d, $J_{C\text{-}F}$ = 26.0 Hz) 65.3 (d, $J_{C\text{-}F}$ = 7.0 Hz), 16.4 (d, $J_{C\text{-}F}$ = 5.0 Hz); **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -102.1 (d, $J_{F\text{-}P}$ = 112.9 Hz), -115.6; **^{31}P NMR** ($CDCl_3$, 162 MHz): δ 4.78 (t, $J_{P\text{-}F}$ = 115.0 Hz); **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{18}H_{18}ClF_3N_2O_3P]^+$: 433.0690; Found 433.0696.

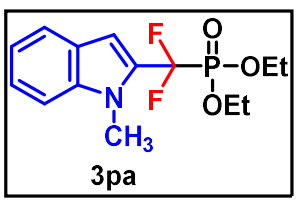
Diethyl (difluoro(3-methyl-1H-indol-2-yl)methyl)phosphonate (3oa):[6]



3oa

Brown gummy (47 mg, 75%); R_f 0.45 (PET:EtOAc = 7:3); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.91 (s, br, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.28–7.25 (m, 1H), 7.17–7.13 (m, 1H), 4.28–4.13 (m, 4H), 2.47 (q, J = 2.8 Hz, 2.4 Hz, 3H), 1.32 (t, J = 7.2 Hz, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 136.0, 128.4, 124.1, 123.2 (d, $J_{C\text{–}F}$ = 13.0 Hz), 119.8 (d, $J_{C\text{–}F}$ = 15.0 Hz), 117.6, 115.4, 114.1 (t, $J_{C\text{–}F}$ = 3.0 Hz), 111.7, 65.3 (d, $J_{C\text{–}F}$ = 6.0 Hz), 16.4 (d, $J_{C\text{–}F}$ = 5.0 Hz), 8.8; **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -105.1 (d, $J_{F\text{–}P}$ = 112.9 Hz); **^{31}P NMR** ($CDCl_3$, 162 MHz): δ 5.75 (t, $J_{P\text{–}F}$ = 115.0 Hz).

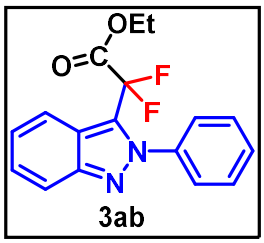
Diethyl (difluoro(1-methyl-1H-indol-2-yl)methyl)phosphonate (3pa):[6]



3pa

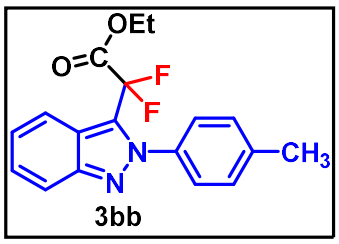
Brown gummy (38 mg, 61%); R_f 0.50 (PET:EtOAc = 3:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.65 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.34–7.30 (m, 1H), 7.17–7.13 (m, 1H), 6.93 (d, J = 0.8 Hz, 1H), 4.30–4.16 (m, 4H), 3.92 (s, 3H), 1.34 (t, J = 7.2 Hz, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 139.1, 127.7, 126.3, 123.9, 121.9, 120.3, 117.2, 109.9, 105.4 (t, J_{C-F} = 10.0 Hz), 65.2 (d, J_{C-F} = 7.0 Hz), 31.7, 16.4 (d, J_{C-F} = 6.0 Hz); **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -102.5 (d, J_{F-P} = 112.9 Hz); **^{31}P NMR** ($CDCl_3$, 162 MHz): δ 5.10 (t, J_{P-F} = 115.0 Hz).

Ethyl 2,2-difluoro-2-(2-phenyl-2H-indazol-3-yl)acetate (3ab):



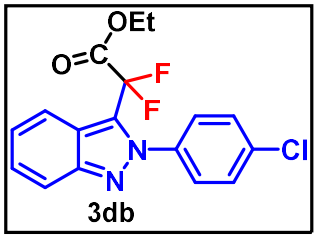
Light yellow solid (53 mg, 84%); mp. 140−141 °C; R_f 0.6 (PET:EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.88 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.56–7.51 (m, 4H), 7.42–7.38 (m, 1H), 7.28–7.24 (m, 1H), 4.04 (q, J = 8.8 Hz, 2H), 1.13 (t, J = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 162.1 (t, J_{C-F} = 35.0 Hz), 148.5, 139.6, 130.0, 129.0, 127.2, 126.7, 126.1 (d, J_{C-F} = 33.0 Hz), 124.5, 122.1, 120.2 (t, J_{C-F} = 3.0 Hz), 118.3, 110.9 (d, J_{C-F} = 249.0 Hz), 63.7, 13.7; **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -94.5; **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{17}H_{15}F_2N_2O_2]^+$: 317.1096; Found 317.1104.

Ethyl 2,2-difluoro-2-(2-(p-tolyl)-2H-indazol-3-yl)acetate (3bb):



Yellow solid (53 mg, 81%); mp. 132−133 °C; R_f 0.65 (PET:EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.87 (d, J = 8.8 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.42–7.37 (m, 3H), 7.30 (d, J = 8.0 Hz, 2H), 7.27–7.23 (m, 1H), 4.05 (q, J = 7.2 Hz, 2H), 2.45 (s, 3H), 1.14 (t, J = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 162.2 (t, $J_{C\text{-}F}$ = 50.0 Hz), 148.5, 140.2, 137.1, 130.2 (d, $J_{C\text{-}F}$ = 4.0 Hz), 129.6, 127.1, 126.5, 124.3, 122.1, 120.2 (t, $J_{C\text{-}F}$ = 5.0 Hz), 118.2, 111.0 (t, $J_{C\text{-}F}$ = 248.0 Hz), 63.7, 21.4, 13.7; **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -94.74; **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{18}H_{17}F_2N_2O_2]^+$: 331.1253; Found 331.1258.

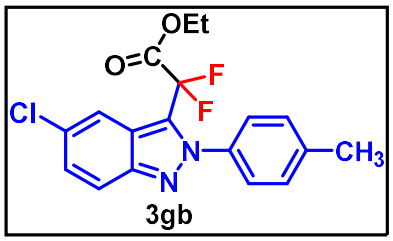
Ethyl 2-(2-(4-chlorophenyl)-2H-indazol-3-yl)-2,2-difluoroacetate (3db):



Yellow liquid (55 mg, 79%); R_f 0.65 (PET:EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.85 (d, J = 8.8 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.506–7.500 (m, 4H), 7.42–7.38 (m, 1H), 7.28–7.23 (m, 1H), 4.13 (q, J = 7.2 Hz, 2H), 1.18 (t, J = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 162.2 (t, $J_{C\text{-}F}$ = 34.0 Hz), 148.7, 138.2, 136.1, 129.9, 129.2, 128.0, 127.5, 124.7, 122.3 (d, $J_{C\text{-}F}$ = 13.0 Hz), 120.1 (t, $J_{C\text{-}F}$ = 4.0 Hz), 118.3, 110.8 (t, $J_{C\text{-}F}$ = 250.0 Hz), 63.9, 13.8;

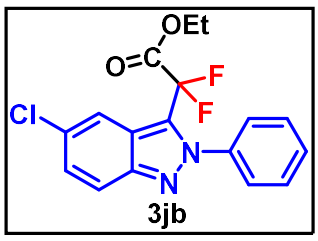
^{19}F NMR (376.5 MHz, CDCl3): δ -95.0; **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{17}H_{14}ClF_2N_2O_2]^+$: 351.0706; Found 351.0711.

Ethyl 2-(5-chloro-2-(p-tolyl)-2H-indazol-3-yl)-2,2-difluoroacetate (3gb):



Yellow liquid (54 mg, 75%); R_f 0.6 (PET:EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.87 (s, 1H), 7.73 (d, J = 9.2 Hz, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.34–7.29 (m, 3H), 4.05 (q, J = 7.2 Hz, 2H), 2.45 (s, 3H), 1.14 (t, J = 7.6 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 161.9 (t, $J_{C\text{-}F}$ = 34.0 Hz), 146.8, 140.5, 136.7, 130.3 (d, $J_{C\text{-}F}$ = 12.0 Hz), 129.7, 128.7, 126.3, 122.4, 120.9 (d, $J_{C\text{-}F}$ = 39.0 Hz), 119.8, 119.0 (t, $J_{C\text{-}F}$ = 3.0 Hz), 110.7 (t, $J_{C\text{-}F}$ = 249.0 Hz), 63.8, 21.4, 13.7; **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -94.9. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $[C_{18}H_{16}ClF_2N_2O_2]^+$: 365.0863; Found 365.0887.

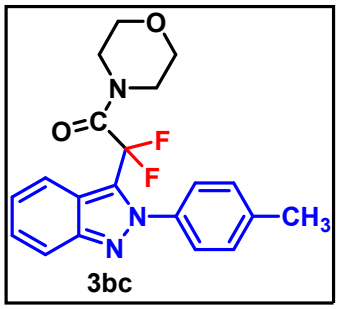
Ethyl 2-(5-chloro-2-phenyl-2H-indazol-3-yl)-2,2-difluoroacetate (3jb):



White solid (58 mg, 83%); mp. 165−166 °C; R_f 0.65 (PET:EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.88 (s, 1H), 7.76–7.73 (m, 1H), 7.55–7.51 (m, 5H), 7.35–7.32 (m, 1H), 4.04 (q, J = 7.2 Hz, 2H), 1.14 (t, J = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 161.9 (t, $J_{C\text{-}F}$ = 35.0 Hz), 146.9, 139.3, 130.3 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.7, 129.2, 128.8, 126.6, 122.5 (d,

$J_{C\text{-}F}$ = 7.0 Hz), 120.9, 119.8, 119.1 (t, $J_{C\text{-}F}$ = 3.0 Hz), 110.7 (t, $J_{C\text{-}F}$ = 248.0 Hz), 63.9, 13.7; **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -94.8; **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{17}H_{14}ClF_2N_2O_2]^+$: 351.0706; Found 351.0712.

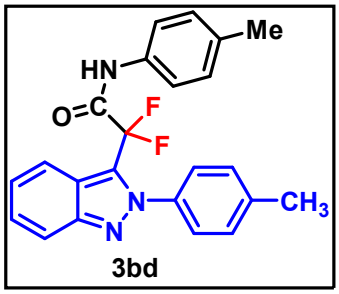
2,2-Difluoro-1-morpholino-2-(2-(p-tolyl)-2H-indazol-3-yl)ethan-1-one (3bc):



3bc

Light yellow liquid (63 mg, 85%); R_f 0.4 (PET:EtOAc = 7:3); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.79 (t, J = 10.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.41–7.37 (m, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.27–7.23 (m, 1H), 3.60–3.58 (m, 2H), 3.44–3.42 (m, 2H), 3.37–3.35 (m, 2H), 3.20–3.18 (m, 2H), 2.44 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 160.0 (t, $J_{C\text{-}F}$ = 31.0 Hz), 148.5, 140.2, 137.2, 129.6, 127.2, 126.7 (d, $J_{C\text{-}F}$ = 32.0 Hz), 126.2, 124.6, 121.4, 119.7, 118.5, 112.3 (t, $J_{C\text{-}F}$ = 247.0 Hz), 66.4, 66.1, 46.3, 43.3, 21.4; **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -88.4; **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{20}H_{20}F_2N_3O_2]^+$: 372.1518; Found 372.1524.

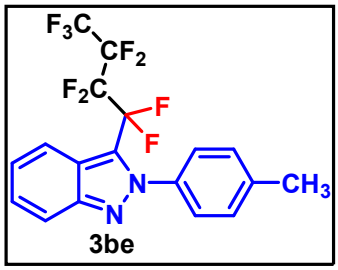
2,2-difluoro-N-(p-tolyl)-2-(2-(p-tolyl)-2H-indazol-3-yl)acetamide (3bd):



3bd

Colourless liquid (65 mg, 84%); R_f 0.5 (PET:EtOAc = 4:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.89 (d, J = 8.8 Hz, 1H), 7.81–7.73 (m, 2H), 7.41–7.32 (m, 3H), 7.26–7.23 (m, 1H), 7.18 (d, J = 8.8 Hz, 3H), 7.13–7.08 (m, 2H), 2.31, 2.30 (2s, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 159.7 (t, $J_{C\text{-}F}$ = 30.0 Hz), 148.4, 140.4, 136.9, 135.6, 133.0, 130.2 (d, $J_{C\text{-}F}$ = 11.0 Hz), 129.6 (t, $J_{C\text{-}F}$ = 14.0 Hz), 127.0 (d, $J_{C\text{-}F}$ = 17.0 Hz), 126.4 (d, $J_{C\text{-}F}$ = 33.0 Hz), 125.5, 124.5, 122.4, 121.1 (d, $J_{C\text{-}F}$ = 16.0 Hz), 120.2 (d, $J_{C\text{-}F}$ = 19.0 Hz), 118.2, 112.5 (t, $J_{C\text{-}F}$ = 252.0 Hz), 21.3, 21.0; **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -94.7; **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{23}H_{20}F_2N_3O]^+$: 392.1569; Found 392.1597.

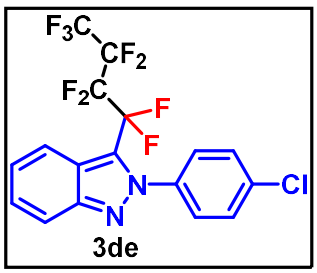
3-(Perfluorobutyl)-2-(p-tolyl)-2H-indazole (3be):



3be

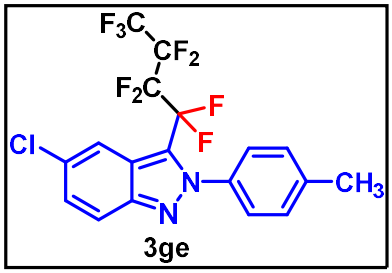
White solid (64 mg, 76%); mp. 62−63 °C; R_f 0.85 (PET:EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.83–7.76 (m, 2H), 7.43–7.40 (m, 1H), 7.36–7.34 (m, 2H), 7.32–7.28 (m, 3H), 2.46 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 148.3, 140.3, 137.6, 130.3, 129.3, 127.3, 126.8 (t, $J_{C\text{-}F}$ = 8.0 Hz), 125.4, 125.2, 123.2 (d, $J_{C\text{-}F}$ = 13.0 Hz), 122.4, 122.1 (d, $J_{C\text{-}F}$ = 8.0 Hz), 121.1 (d, $J_{C\text{-}F}$ = 7.0 Hz), 119.8, 118.5, 21.4; **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -80.8–-80.9 (m, 3F), -103.7–-103.8 (m, 2F), -121.4–-121.5 (m, 2F), -125.9–-126.0 (m, 2F); **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{18}H_{12}F_9N_2]^+$: 427.0851; Found 427.0857.

2-(4-Chlorophenyl)-3-(perfluorobutyl)-2H-indazole (3de):



White solid (65 mg, 73%); mp. 59−60 °C; R_f 0.85 (PET:EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.81 (d, J = 9.2 Hz, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.54–7.48 (m, 2H), 7.45–7.42 (m, 3H), 7.33–7.30 (m, 1H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 148.6, 138.6 (d, $J_{C\text{-}F}$ = 12.0 Hz), 136.4, 130.0, 129.9, 129.0, 128.5, 127.7, 125.7 (d, $J_{C\text{-}F}$ = 27.0 Hz), 123.3, 122.6, 122.4 (q, $J_{C\text{-}F}$ = 8.0 Hz), 122.0 (t, $J_{C\text{-}F}$ = 8.0 Hz), 119.7, 118.5; **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -80.8–-80.9 (m, 3F), -103.6–-103.7 (m, 2F), -121.4–-121.5 (m, 2F), -125.9–-126.0 (m, 2F); **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{17}H_9ClF_9N_2]^+$: 447.0305; Found 447.0311.

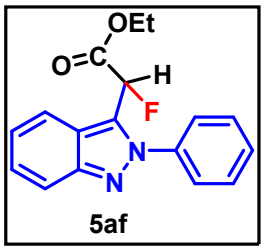
5-Chloro-3-(perfluorobutyl)-2-(p-tolyl)-2H-indazole (3ge):



White liquid (66 mg, 72%); R_f 0.85 (PET:EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.78–7.75 (m, 2H), 7.37–7.33 (m, 3H), 7.31–7.29 (m, 2H), 2.46 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 146.7, 140.6, 138.1, 137.4, 136.8, 131.3, 130.3 (d, $J_{C\text{-}F}$ = 6.0 Hz), 129.4, 128.9, 126.6 (q, $J_{C\text{-}F}$ = 15.0 Hz), 123.5 (d, $J_{C\text{-}F}$ = 12.0 Hz), 123.2 (d, $J_{C\text{-}F}$ = 6.0 Hz), 121.2 (t, $J_{C\text{-}F}$ = 17.0 Hz), 120.1, 118.4 (d, $J_{C\text{-}F}$ = 12.0 Hz), 21.4; **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -80.8–-80.9 (m, 3F), -103.8–-103.9 (m, 2F), -121.3–-121.4 (m, 2F), -125.8–-125.9

(m, 2F); **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{18}H_{11}ClF_9N_2]^+$: 461.0462; Found 461.0467.

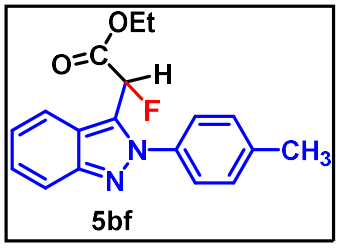
Ethyl 2-fluoro-2-(2-phenyl-2H-indazol-3-yl)acetate (5af):



5af

Yellow liquid (45 mg, 77%); R_f 0.65 (PET:EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.82 (d, J = 8.8 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.70–7.67 (m, 2H), 7.61–7.53 (m, 3H), 7.40–7.37 (m, 1H), 7.22 (t, J = 8.0 Hz, 1H), 6.12 (d, J = 47.6 Hz, 1H), 4.30–4.15 (m, 2H), 1.20 (t, J = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 166.7 (d, $J_{C\text{-}F}$ = 30.0 Hz), 148.8, 139.0, 129.8, 129.6, 127.3 (d, $J_{C\text{-}F}$ = 25.0 Hz), 126.4, 124.0, 121.8, 121.2 (d, $J_{C\text{-}F}$ = 6.0 Hz), 119.3, 118.3, 80.4 (d, $J_{C\text{-}F}$ = 184.0 Hz), 62.7, 14.1; **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -168.7 (d, J = 48.9 Hz); **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{17}H_{16}FN_2O_2]^+$: 299.1190; Found 299.1196.

Ethyl 2-fluoro-2-(2-(p-tolyl)-2H-indazol-3-yl)acetate (5bf):

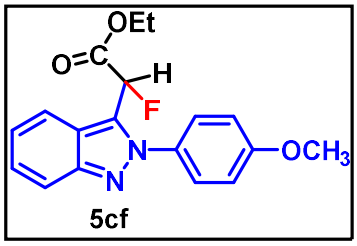


5bf

Light yellow solid (51 mg, 82%); mp. 109−110 °C; R_f 0.65 (PET:EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.81 (d, J = 8.8 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 8.4 Hz, 2H), 7.39–7.36 (m, 3H), 7.23–7.19 (m, 1H), 6.11 (d, J = 47.6 Hz, 1H), 4.30–4.15 (m, 2H),

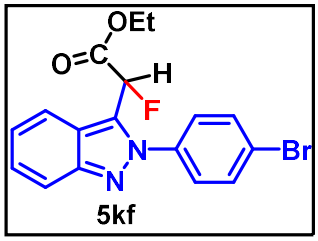
2.47 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 166.7 (d, $J_{C\text{-}F}$ = 30.0 Hz), 148.7, 140.1, 136.4, 130.1, 127.4, 127.1 (d, $J_{C\text{-}F}$ = 7.0 Hz), 126.1, 123.8, 121.3 (d, $J_{C\text{-}F}$ = 60.0 Hz), 119.3, 118.3, 80.4 (d, $J_{C\text{-}F}$ = 184.0 Hz), 62.6, 21.4, 14.1; **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -168.7 (d, J = 48.9 Hz); **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{18}H_{18}FN_2O_2]^+$: 313.1347; Found 313.1352.

Ethyl 2-fluoro-2-(2-(4-methoxyphenyl)-2H-indazol-3-yl)acetate (5cf):



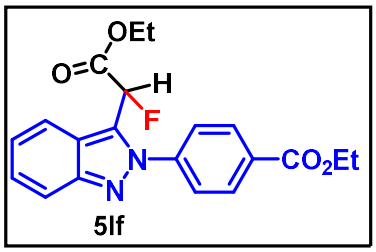
Yellow liquid (49 mg, 75%); R_f 0.5 (PET:EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.80 (d, J = 8.8 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.61–7.57 (m, 2H), 7.38 (t, J = 8.0 Hz, 1H), 7.21 (t, J = 8.0 Hz, 1H), 7.08–7.04 (m, 2H), 6.09 (d, J = 47.6 Hz, 1H), 4.29–4.17 (m, 2H), 3.89 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 166.7 (d, $J_{C\text{-}F}$ = 30.0 Hz), 160.6, 148.6, 134.3, 131.8, 127.6 (d, $J_{C\text{-}F}$ = 16.0 Hz), 127.1 (d, $J_{C\text{-}F}$ = 21.0 Hz), 126.2, 123.8, 121.6, 119.2 (d, $J_{C\text{-}F}$ = 100.0 Hz), 114.6, 80.4 (d, $J_{C\text{-}F}$ = 184.0 Hz), 62.6, 55.8, 14.1; **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -168.7 (d, J = 52.7 Hz); **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{18}H_{18}FN_2O_3]^+$: 329.1296; Found 329.1301.

Ethyl 2-(2-(4-bromophenyl)-2H-indazol-3-yl)-2-fluoroacetate (5kf):



Yellow solid (58 mg, 78%); mp. 110−111 °C; R_f 0.7 (PET:EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.80 (d, J = 8.8 Hz, 1H), 7.73–7.70 (m, 3H), 7.60–7.56 (m, 2H), 7.39 (t, J = 8.0 Hz, 1H), 7.25–7.21 (m, 1H), 6.10 (d, J = 47.6 Hz, 1H), 4.29–4.18 (m, 2H), 1.20 (t, J = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 166.4 (d, $J_{C\text{-}F}$ = 29.0 Hz), 148.9 (d, $J_{C\text{-}F}$ = 5.0 Hz), 141.4, 137.9, 132.8, 127.8, 127.4 (d, $J_{C\text{-}F}$ = 5.0 Hz), 127.2, 124.1 (d, $J_{C\text{-}F}$ = 21.0 Hz), 122.0, 119.3, 118.3, 80.2 (d, $J_{C\text{-}F}$ = 185.0 Hz), 62.8, 14.1; **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -168.2 (d, J = 48.9 Hz); **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{17}H_{15}BrFN_2O_2]^+$: 377.0295; Found 377.0295.

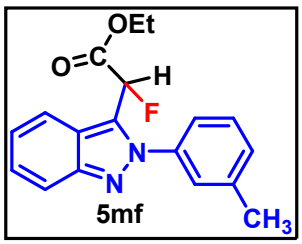
Ethyl 4-(3-(2-ethoxy-1-fluoro-2-oxoethyl)-2H-indazol-2-yl)benzoate (5lf):



5lf

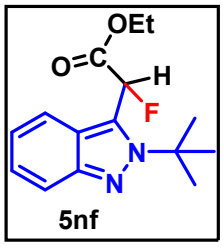
Yellow liquid (51 mg, 70%); R_f 0.65 (PET:EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.27 (d, J = 8.4 Hz, 2H), 7.81 (t, J = 8.4 Hz, 3H), 7.74 (d, J = 8.8 Hz, 1H), 7.40 (t, J = 8.4 Hz, 1H), 7.26–7.22 (m, 1H), 6.13 (d, J = 47.6 Hz, 1H), 4.43 (q, J = 7.2 Hz, 2H), 4.28–4.17 (m, 2H), 1.43 (t, J = 7.2 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 166.4 (d, $J_{C\text{-}F}$ = 29.0 Hz), 165.5, 149.0 (d, $J_{C\text{-}F}$ = 4.0 Hz), 142.3, 131.6, 130.9, 127.6, 127.3 (d, $J_{C\text{-}F}$ = 24.0 Hz), 126.1, 124.3, 122.1, 119.3, 118.4, 80.1 (d, $J_{C\text{-}F}$ = 185.0 Hz), 62.8, 61.7, 14.4, 14.1; **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -168.2 (d, J = 45.1 Hz); **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{20}H_{20}FN_2O_4]^+$: 371.1402; Found 371.1407.

Ethyl 2-fluoro-2-(2-(m-tolyl)-2H-indazol-3-yl)acetate (5mf):



Yellow liquid (46 mg, 74%); R_f 0.65 (PET:EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.81 (d, J = 8.8 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.51 (s, 1H), 7.48–7.43 (m, 2H), 7.40–7.35 (m, 2H), 7.21 (t, J = 7.6 Hz, 1H), 6.13 (d, J = 47.2 Hz, 1H), 4.31–4.16 (m, 2H), 2.47 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 166.7 (d, $J_{C\text{-}F}$ = 29.0 Hz), 148.7 (d, $J_{C\text{-}F}$ = 3.0 Hz), 139.9, 138.8, 130.6, 129.3, 127.3, 127.1 (d, $J_{C\text{-}F}$ = 4.0 Hz), 126.9, 123.9, 123.3, 121.7, 119.3, 118.3, 80.4 (d, $J_{C\text{-}F}$ = 184.0 Hz), 62.6, 21.4, 14.1; **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -168.7 (d, J = 45.1 Hz).

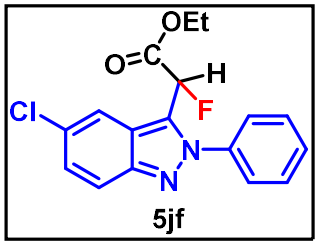
Ethyl 2-(2-(tert-butyl)-2H-indazol-3-yl)-2-fluoroacetate (5nf):



Colourless liquid (26 mg, 47%); R_f 0.65 (PET:EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.73 (d, J = 8.8 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.29-7.26 (m, 1H), 7.11 (t, J = 7.6 Hz, 1H), 6.64 (d, J = 47.2 Hz, 1H), 4.35-4.22 (m, 2H), 1.88 (s, 9H), 1.21 (t, J = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 167.0 (d, $J_{C\text{-}F}$ = 30.0 Hz), 146.2 (d, $J_{C\text{-}F}$ = 5.0 Hz), 125.9 (d, $J_{C\text{-}F}$ = 8.0 Hz), 125.6, 123.0 (d, $J_{C\text{-}F}$ = 35.0 Hz), 120.3, 119.5 (d, $J_{C\text{-}F}$ = 27.0 Hz), 118.1, 81.0 (d, $J_{C\text{-}F}$ = 184.0 Hz), 63.0, 62.5, 31.5, 14.1; **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -169.5 (d, J = 48.9

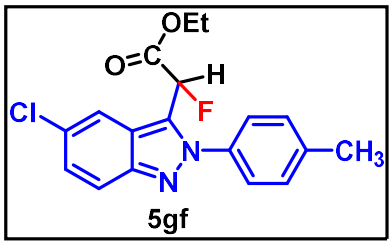
Hz); Anal. Calcd for $C_{15}H_{19}FN_2O_2$: C, 64.73; H, 6.88; N, 10.07%; Found C, 64.54; H, 6.93; N, 10.18%.

Ethyl 2-(5-chloro-2-phenyl-2H-indazol-3-yl)-2-fluoroacetate (5jf):



Yellow solid (55 mg, 83%); mp. 83−84 °C; R_f 0.6 (PET:EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.76–7.74 (m, 2H), 7.68–7.65 (m, 2H), 7.61–7.56 (m, 3H), 7.33–7.30 (m, 1H), 6.08 (d, J = 47.2 Hz, 1H), 4.32–4.18 (m, 2H), 1.23 (t, J = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 166.3 (d, $J_{C\text{-}F}$ = 29.0 Hz) , 147.1 (d, $J_{C\text{-}F}$ = 3.0 Hz), 138.7, 130.1, 129.8 (d, $J_{C\text{-}F}$ = 3.0 Hz), 129.7, 128.7, 127.1 (d, $J_{C\text{-}F}$ = 26.0 Hz) , 126.3, 122.1, 119.9, 118.2, 80.3 (d, $J_{C\text{-}F}$ = 186.0 Hz), 62.8, 14.1; **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -169.4 (d, J = 41.4 Hz); **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{17}H_{15}ClFN_2O_2]^+$: 333.0801; Found 333.0806.

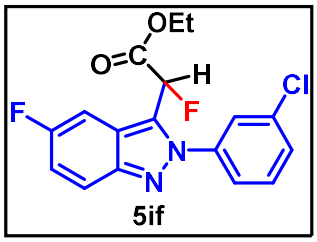
Ethyl 2-(5-chloro-2-(p-tolyl)-2H-indazol-3-yl)-2-fluoroacetate (5gf):



Yellow solid (55 mg, 80%); mp. 109−110 °C; R_f 0.65 (PET:EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.74 (d, J = 9.2 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.32–7.29 (m, 1H), 6.06 (d, J = 47.2 Hz, 1H), 4.31–4.19 (m, 2H), 2.47 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 166.4 (d, $J_{C\text{-}F}$ = 29.0 Hz), 147.0, 140.4,

136.1, 130.2, 129.6, 128.6, 127.1 (d, $J_{C\text{-}F}$ = 25.0 Hz), 126.0, 122.0, 119.8, 118.2, 80.3 (d, $J_{C\text{-}F}$ = 185.0 Hz), 62.8, 21.4, 14.1; **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -169.4 (d, J = 48.9 Hz); **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{18}H_{17}ClFN_2O_2]^+$: 347.0957; Found 347.0957.

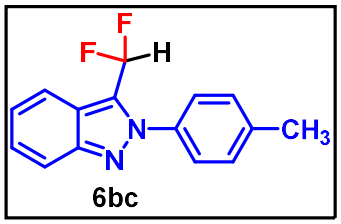
Ethyl 2-(2-(3-chlorophenyl)-5-fluoro-2H-indazol-3-yl)-2-fluoroacetate (5if):



5if

Yellow solid (51 mg, 73%); mp. 81−82 °C; R_f 0.7 (PET:EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.80–7.77 (m, 1H), 7.73–7.72 (m, 1H), 7.60–7.52 (m, 3H), 7.33–7.31 (m, 1H), 7.22–7.18 (m, 1H), 6.08 (d, J = 47.2 Hz, 1H), 4.32–4.21 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 166.2 (d, $J_{C\text{-}F}$ = 29.0 Hz), 160.8, 158.4, 146.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 139.7, 135.5, 130.6, 130.2, 127.7 (d, $J_{C\text{-}F}$ = 9.0 Hz), 125.4 (d, $J_{C\text{-}F}$ = 228.0 Hz), 120.7 (d, $J_{C\text{-}F}$ = 10.0 Hz) , 119.4 (d, $J_{C\text{-}F}$ = 19.0 Hz), 114.4, 102.1 (d, $J_{C\text{-}F}$ = 25.0 Hz), 80.1 (d, $J_{C\text{-}F}$ = 186.0 Hz), 62.9, 14.1; **^{19}F NMR** (376.5 MHz, CDCl3): δ -115.5, -168.9 (d, J = 45.1 Hz); **HRMS** (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $[C_{17}H_{13}ClF_2N_2NaO_2]^+$: 373.0526; Found 373.0526.

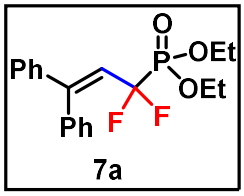
3-(Difluoromethyl)-2-(p-tolyl)-2H-indazole (6bc):



6bc

White solid (43 mg, 85%); mp. 89−90 °C; R_f 0.75 (PET:EtOAc = 9:1); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.92–7.90 (m, 1H), 7.82–7.79 (m, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.41–7.35 (m, 3H), 7.26–7.23 (m, 1H), 6.89 (t, J = 50.0 Hz, 1H), 2.47 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 148.6 (d, $J_{C\text{-}F}$ = 2.0 Hz), 140.2, 136.6, 130.2, 127.8, 127.3 (d, $J_{C\text{-}F}$ = 31.0 Hz), 125.6, 124.1, 121.1, 119.9, 118.2, 110.0 (t, $J_{C\text{-}F}$ = 233.0 Hz), 21.3; **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -109.1 (d, J = 52.7 Hz); **HRMS** (ESI–TOF) m/z: $[M + H]^+$ Calcd for $[C_{15}H_{13}F_2N_2]^+$: 259.1041; Found 259.1047.

Diethyl (1,1-difluoro-3,3-diphenylallyl)phosphonate (7a):



7a

Light yellow liquid (58 mg, 80%); R_f 0.4 (PET:EtOAc = 7:3); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.35–7.33 (m, 3H), 7.32–7.27 (m, 5H), 7.26–7.23 (m, 2H), 6.19–6.10 (m, 1H), 4.27–4.17 (m, 4H), 1.34 (t, J = 7.2 Hz, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 151.1 (q, $J_{C\text{-}F}$ = 8.0 Hz), 141.5, 138.2, 129.6, 129.0, 128.4, 128.0 (d, $J_{C\text{-}F}$ = 7.0 Hz), 127.6, 118.6, 117.1 (q, $J_{C\text{-}F}$ = 20.0 Hz), 116.4, 64.7 (d, $J_{C\text{-}F}$ = 7.0 Hz), 16.5 (d, $J_{C\text{-}F}$ = 6.0 Hz); **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ -102.0 (d, $J_{F\text{-}P}$ = 15.0 Hz), -102.3 (d, $J_{F\text{-}P}$ = 15.0 Hz); **^{31}P NMR** ($CDCl_3$, 162 MHz): δ 6.70 (t, $J_{P\text{-}F}$ = 113.4 Hz); **HRMS** (ESI–TOF) m/z: $[M + Na]^+$ Calcd for $[C_{19}H_{21}F_2NaO_3P]^+$: 389.1089; Found 389.1094.

10. References:

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2. (a) H. Morimoto, R. Fujiwara, Y. Shimizu, K. Morisaki and T. Ohshima, *Org. Lett.,* 2014, **16**, 2018; (b) L. Wang, X.-J. Wei, W.-L. Jia, J.-J. Zhong, L.-Z. Wu and Q. Liu, *Org. Lett*., 2014, **16**, 5842.

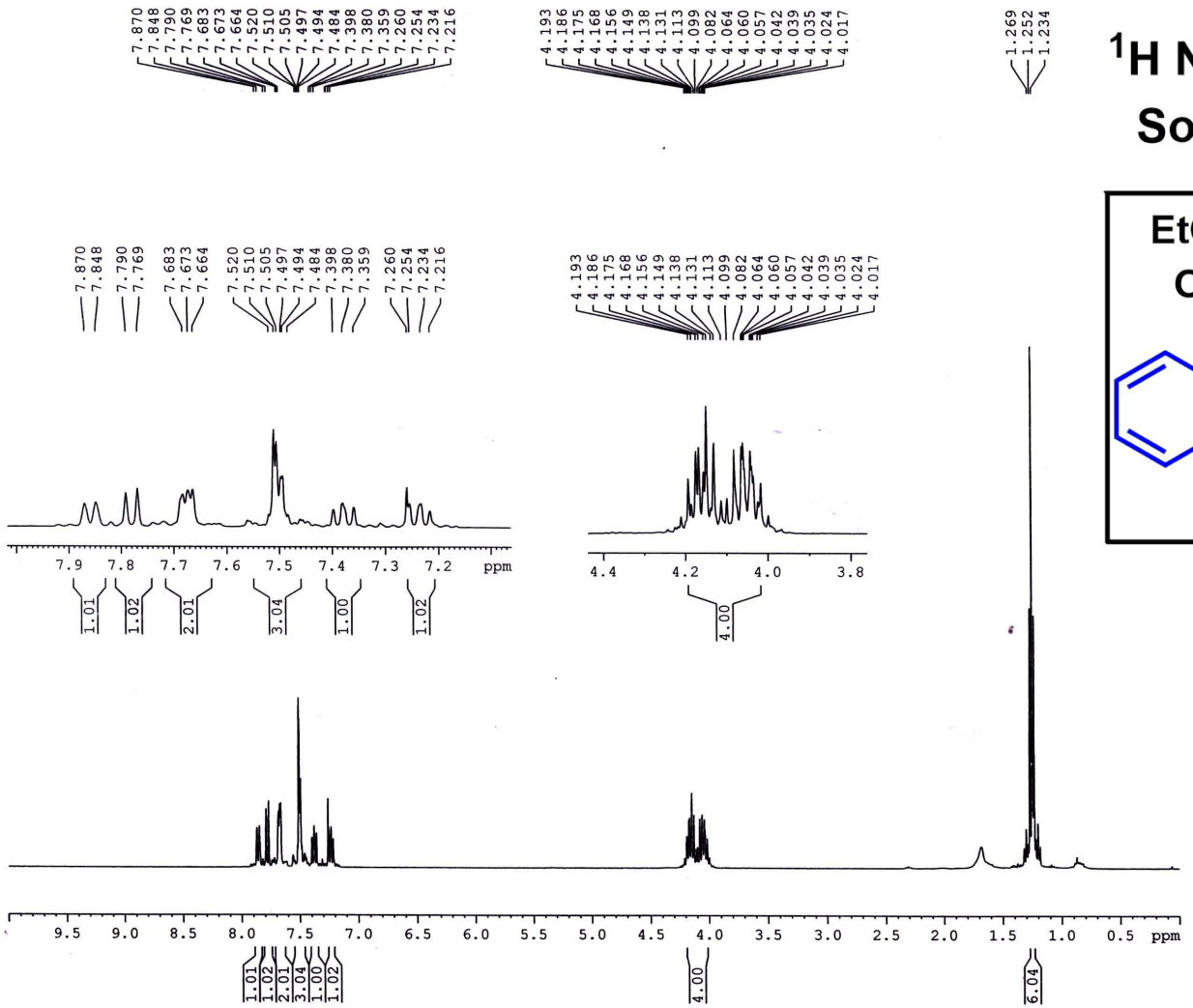
3. 2009 Ed. APEX II, Bruker Analytical X-ray Systems Inc. Madison, WI, 2009.

4. G. M. Sheldrick, "SHELXL97. University of Gottingen, Germany, 1997.

5. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: *J. Appl. Crystallogr*. 2009, **42**, 339.

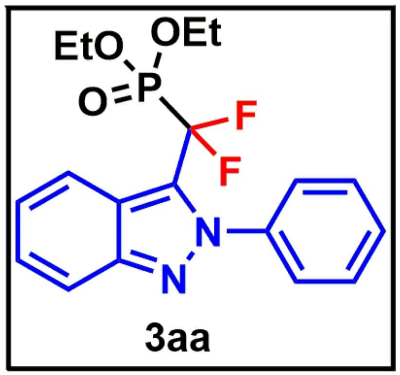
6. M. Singsardar, S. Mondal, S. Laru and A. Hajra, *Org. Lett*., 2019, **21**, 5606.

11. NMR spectra [^{1}H, ^{13}C{^{1}H}, ^{19}F, and ^{31}P] of synthesized products

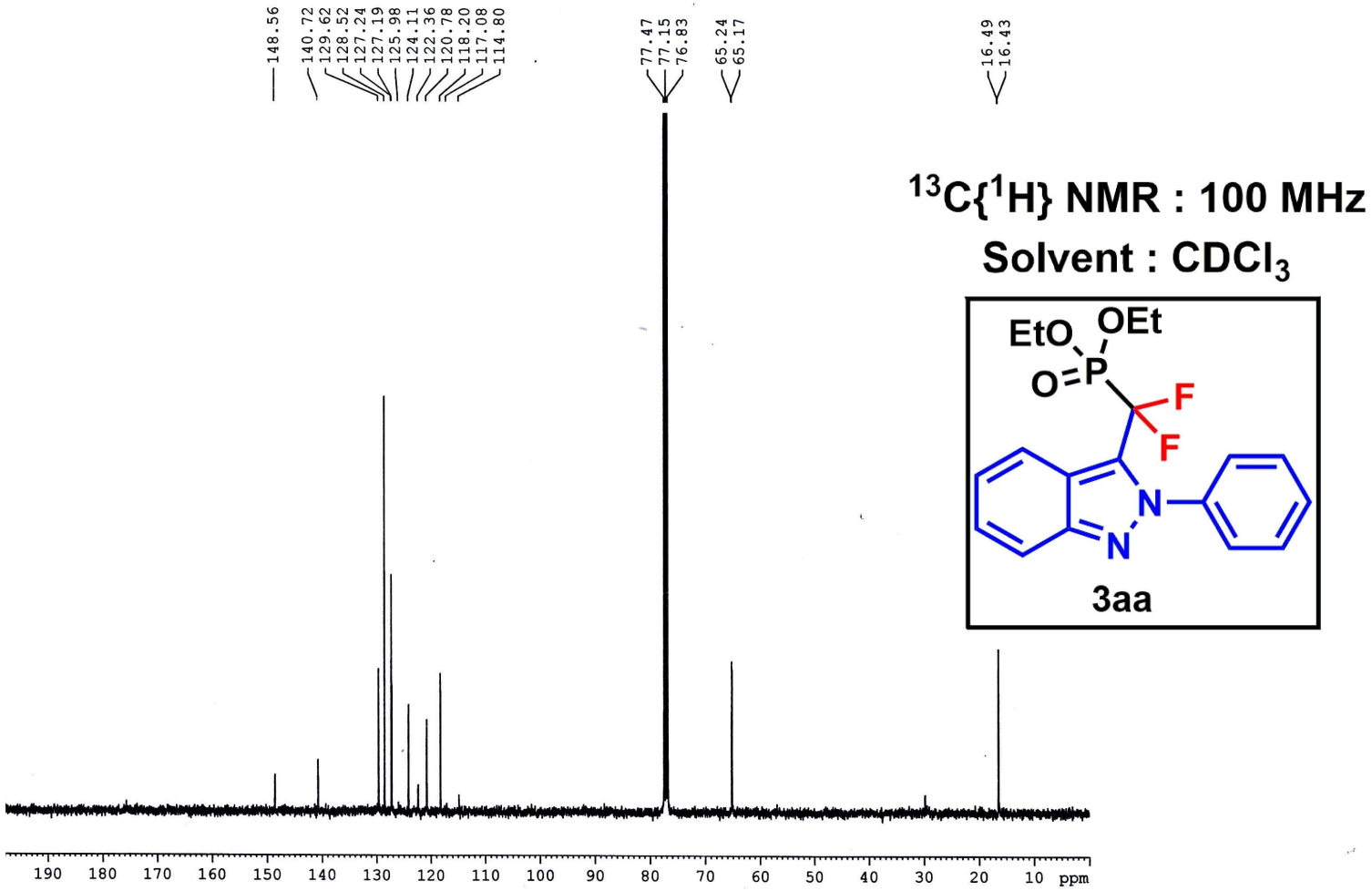


^{1}H NMR : 400 MHz

Solvent : $CDCl_3$



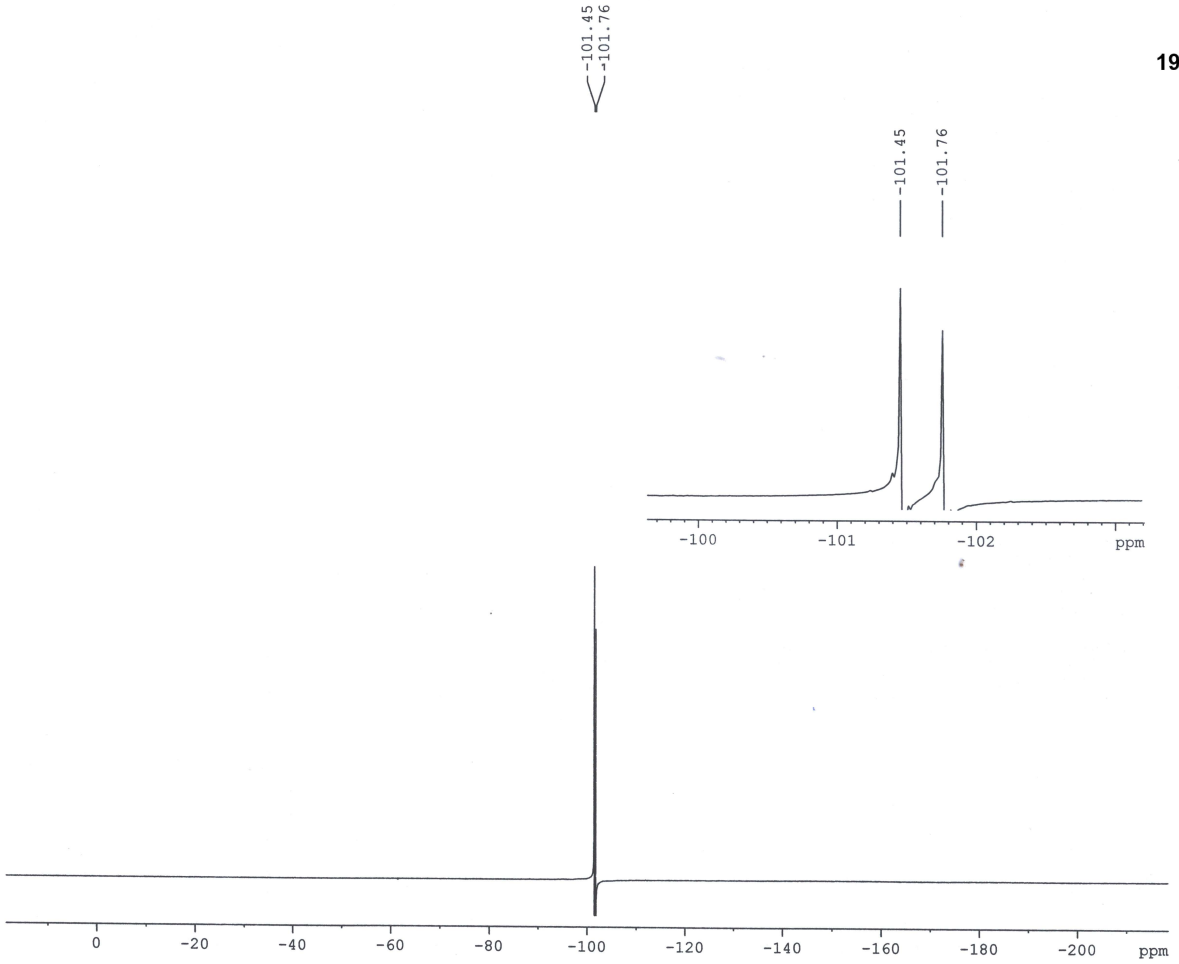
3aa



$^{13}C\{^{1}H\}$ NMR : 100 MHz

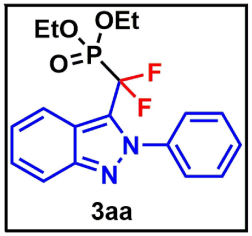
Solvent : $CDCl_3$

3aa



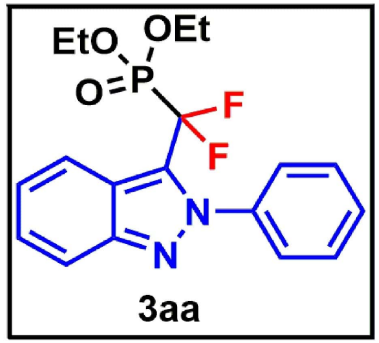
^{19}F NMR : 376.5 MHz

Solvent : $CDCl_3$



^{31}P NMR : 162 MHz

Solvent : $CDCl_3$



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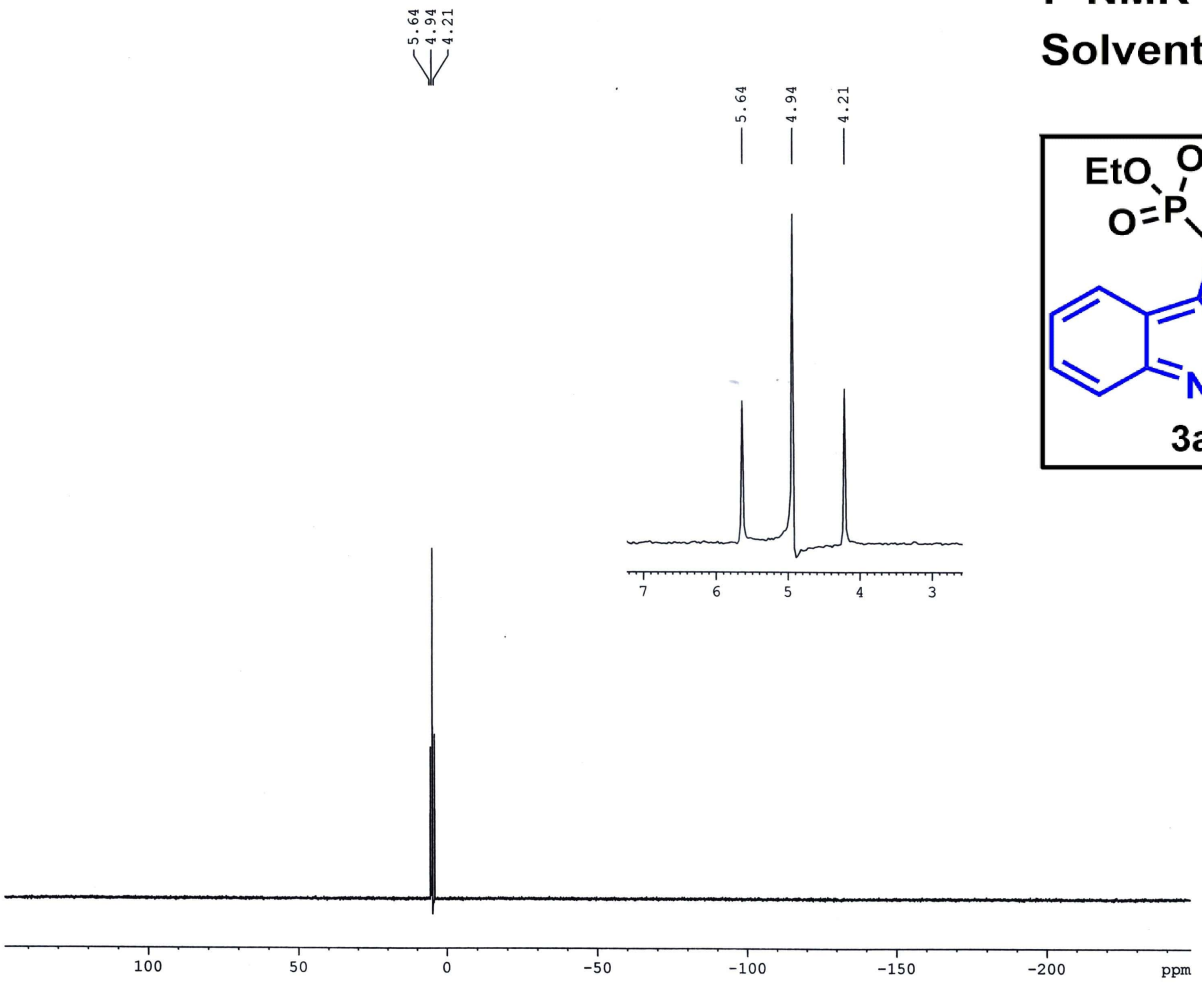
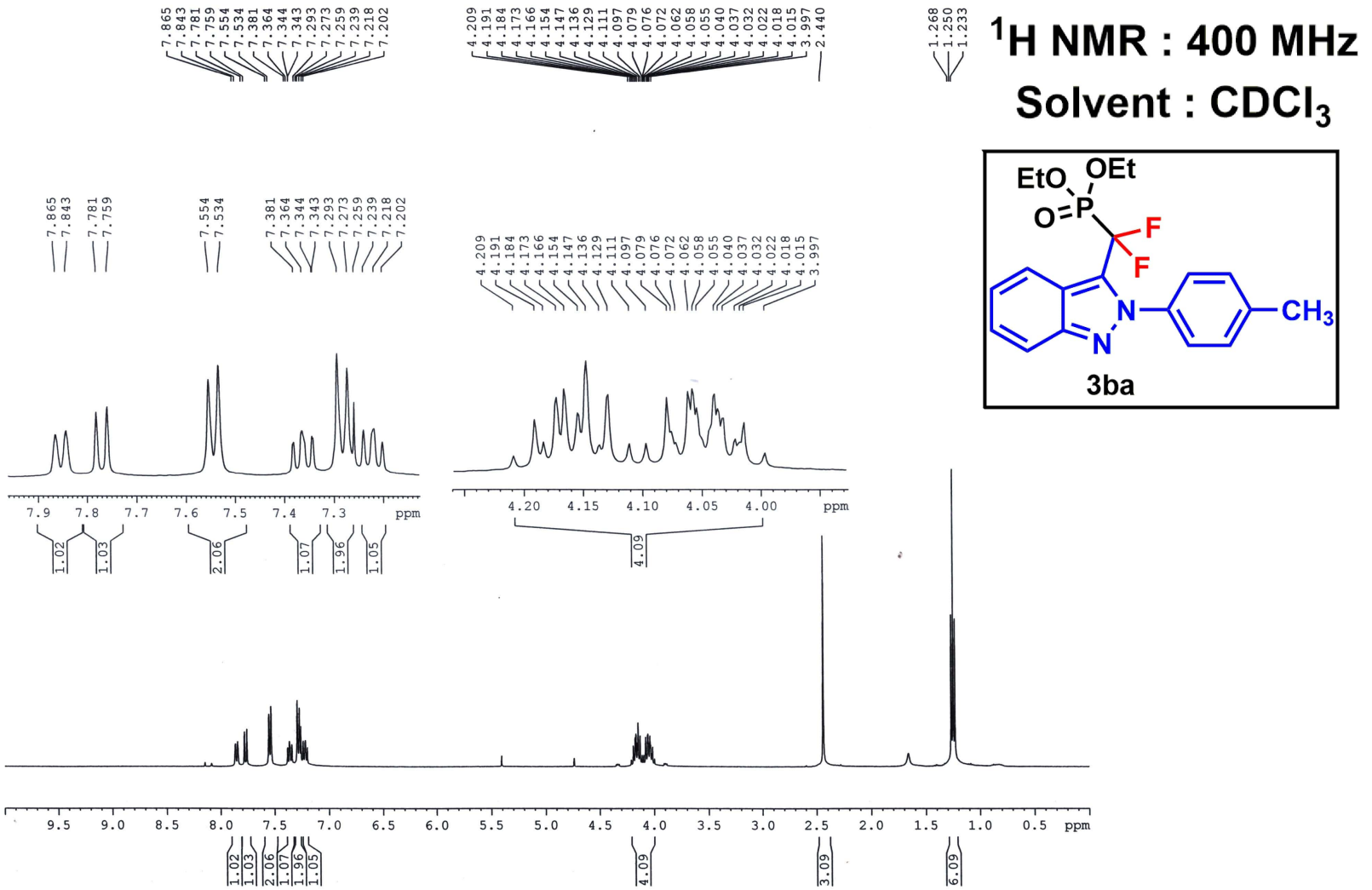




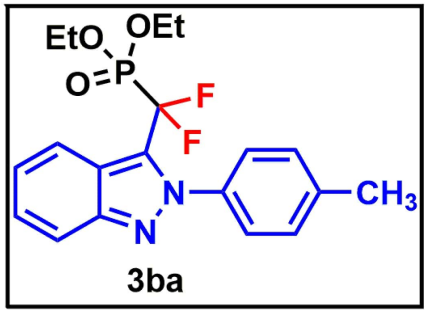
^{1}H NMR : 400 MHz

Solvent : $CDCl_3$

3ba

$^{13}C\{^{1}H\}$ NMR : 100 MHz

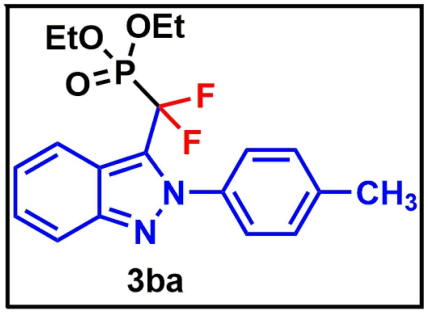
Solvent : $CDCl_3$



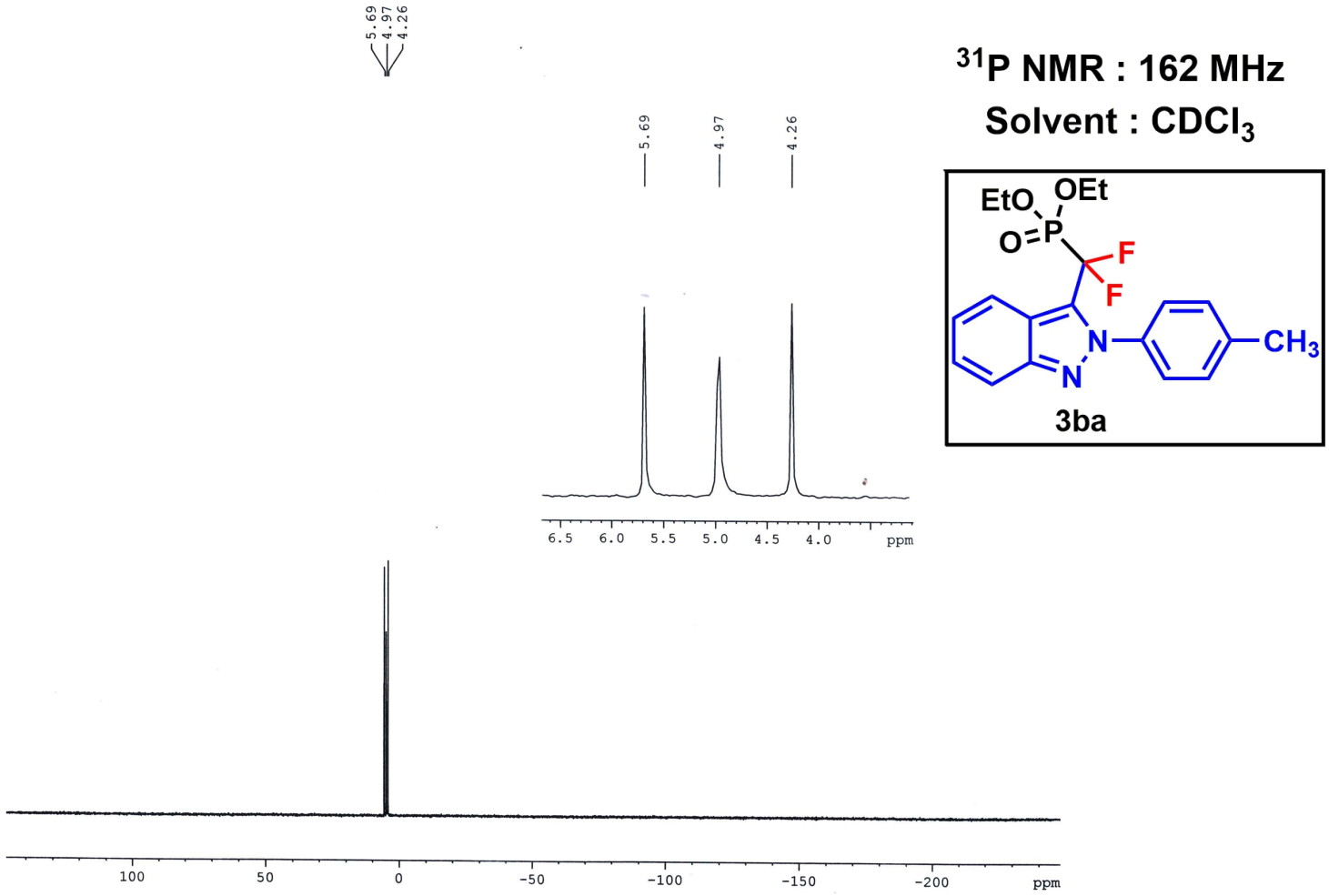
3ba

^{19}F NMR : 376.5 MHz

Solvent : $CDCl_3$



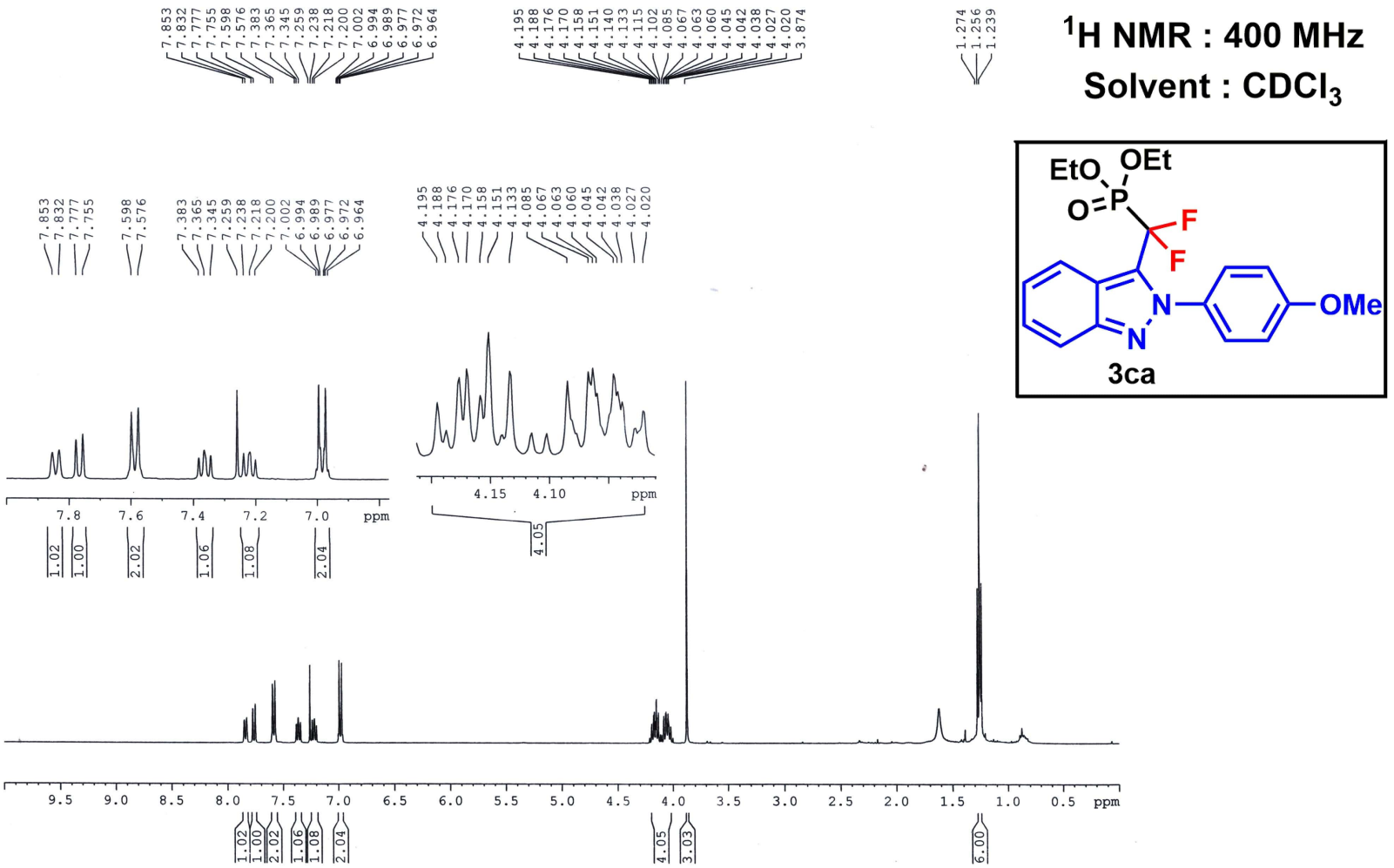
3ba



^{31}P NMR : 162 MHz

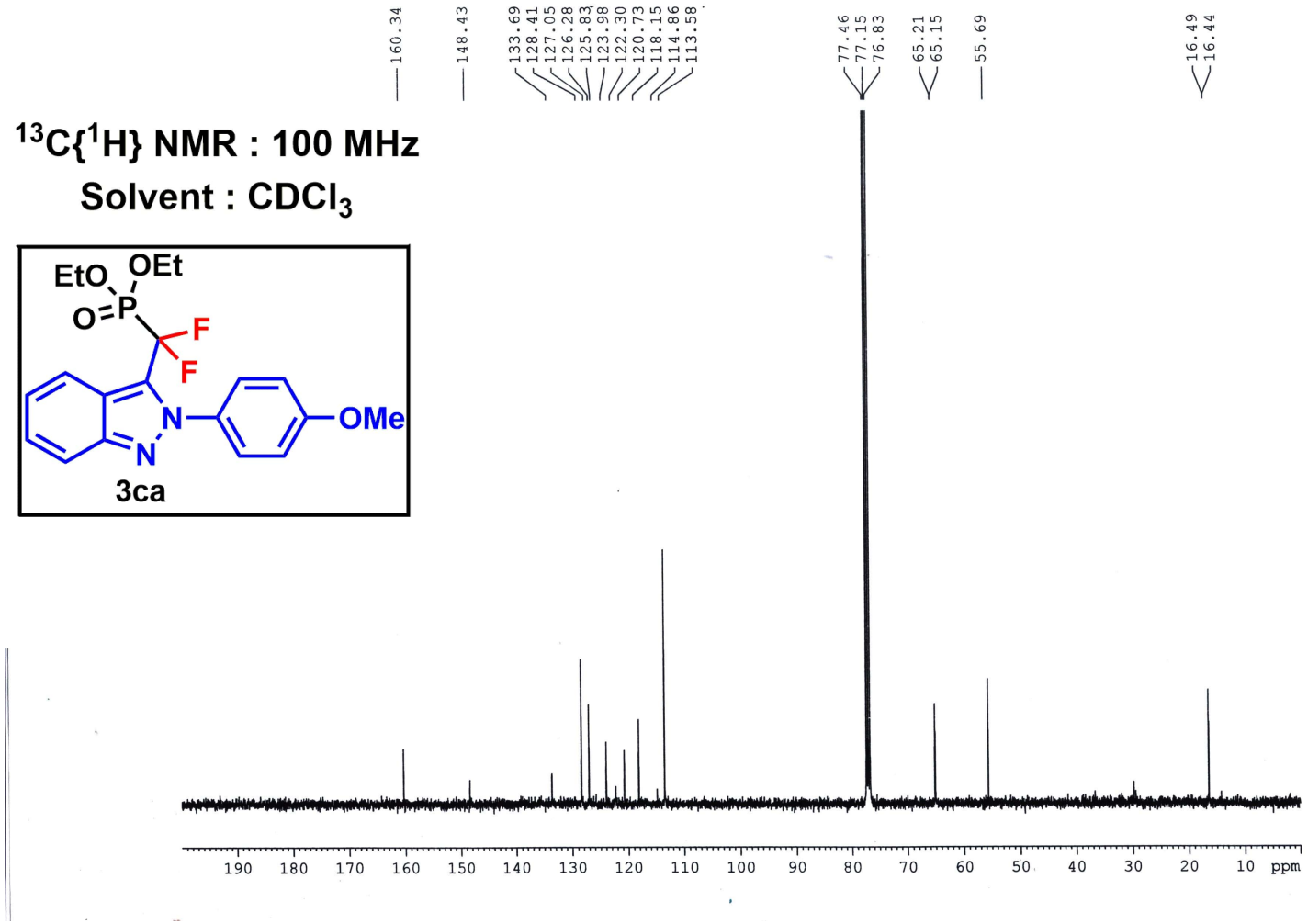
Solvent : $CDCl_3$

3ba



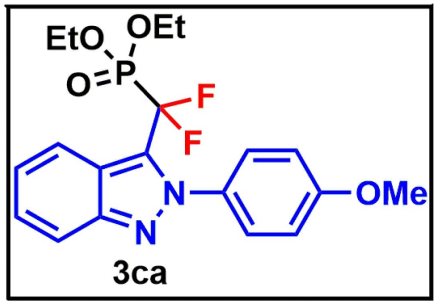
^{1}H NMR : 400 MHz

Solvent : $CDCl_3$


160.34
148.43
133.69
128.41
127.05
126.28
125.83
123.98
122.30
120.73
118.15
114.86
113.58
77.46
77.15
76.83
65.21
65.15
55.69
16.49
16.44
13C{1H} NMR : 100 MHz
Solvent : CDCl3
EtO
OEt
O=P
F
F
N
N
OMe
3ca
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{19}F NMR : 376.5 MHz

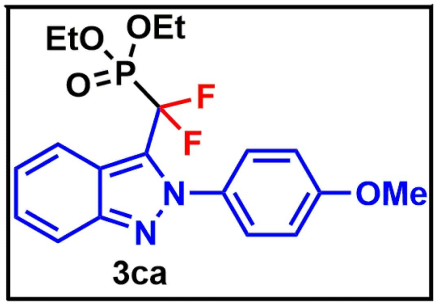
Solvent : $CDCl_3$



3ca

^{31}P NMR : 162 MHz

Solvent : $CDCl_3$



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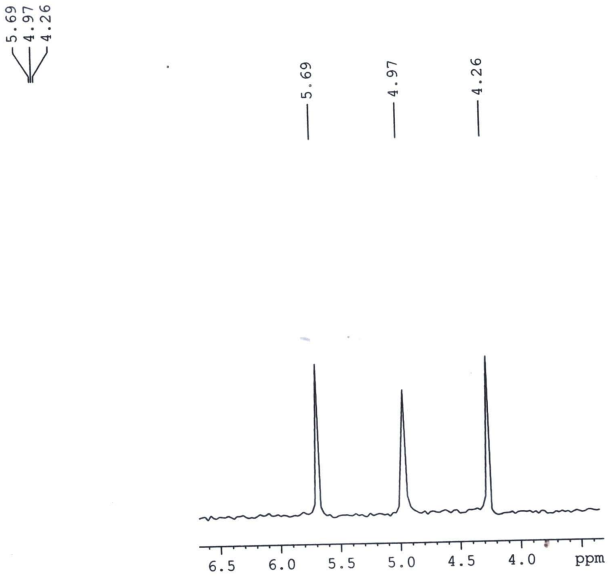
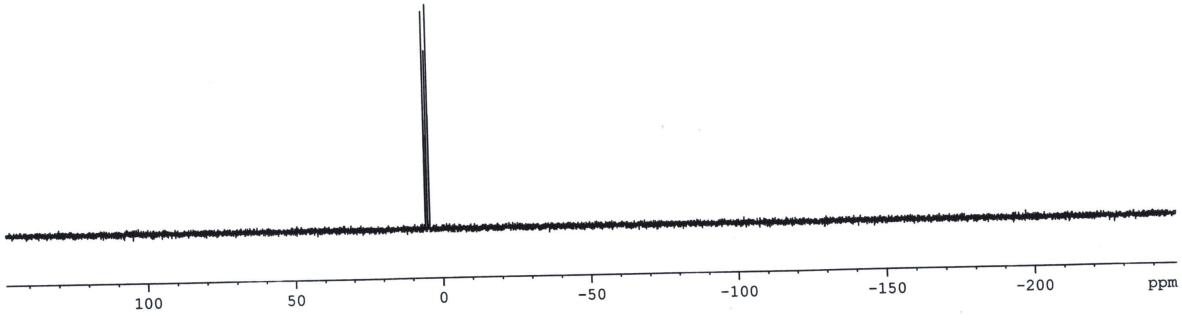
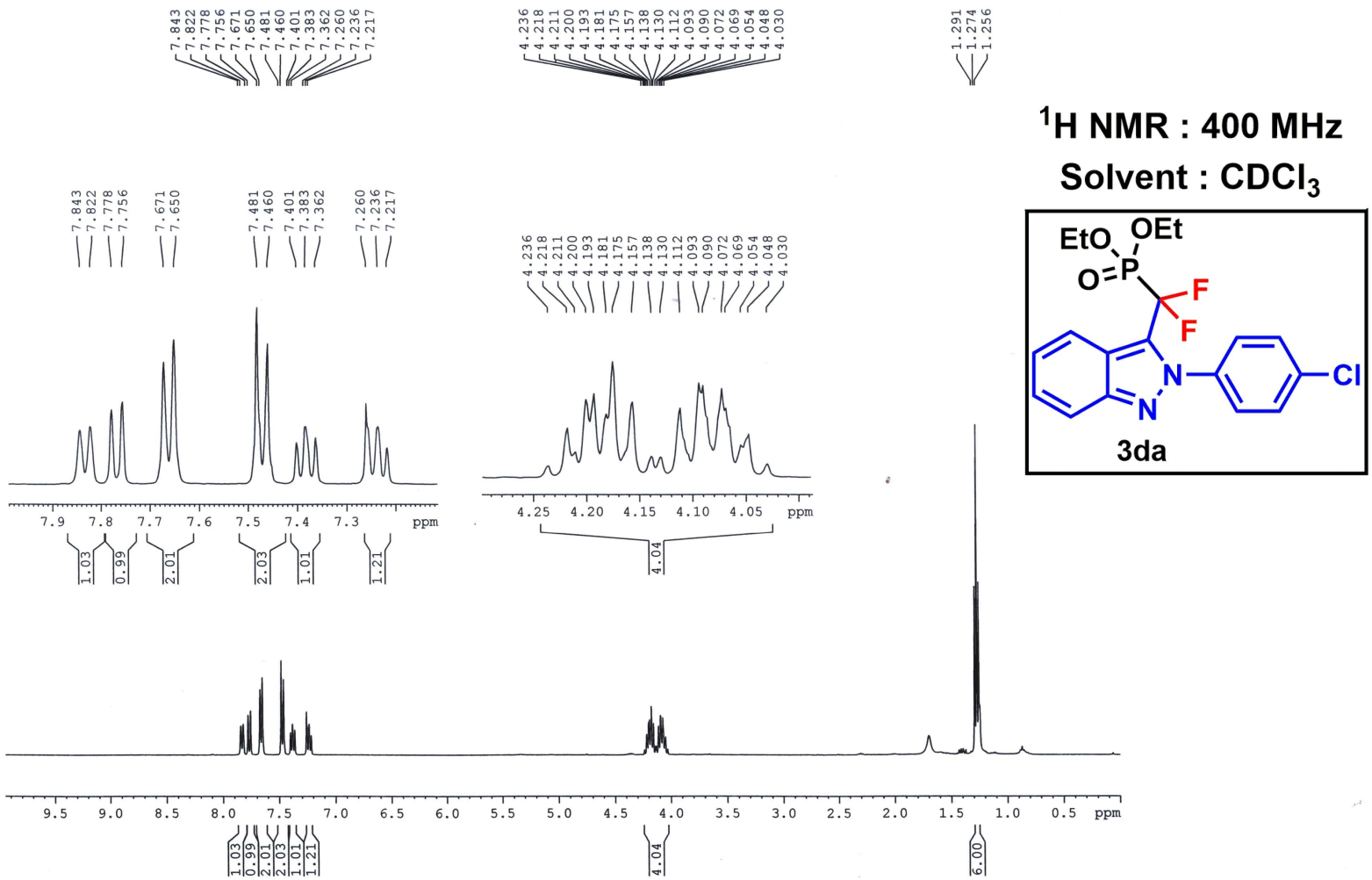






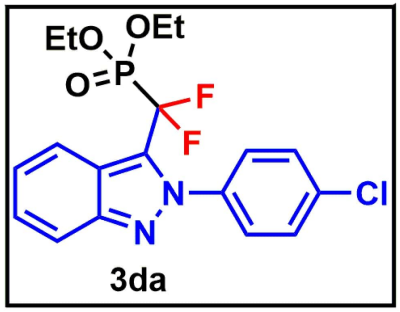
^{1}H NMR : 400 MHz

Solvent : $CDCl_3$

3da

$^{13}C\{^{1}H\}$ NMR : 100 MHz

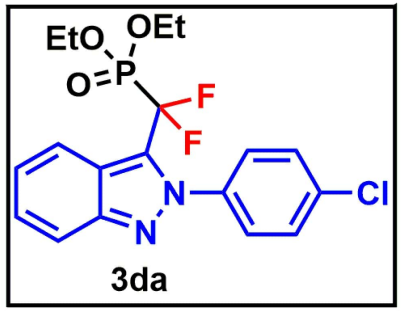
Solvent : $CDCl_3$



3da

^{19}F NMR : 376.5 MHz

Solvent : $CDCl_3$



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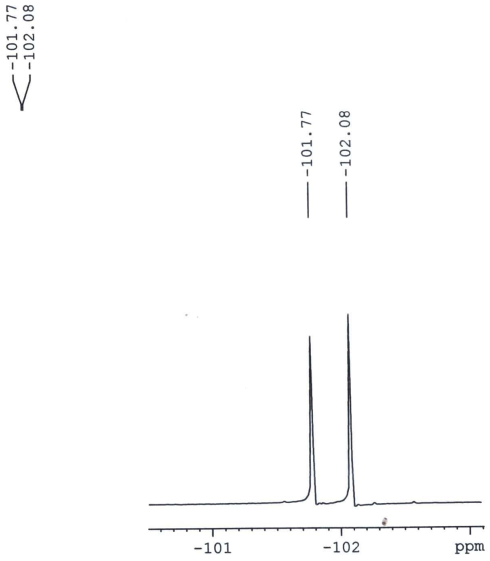
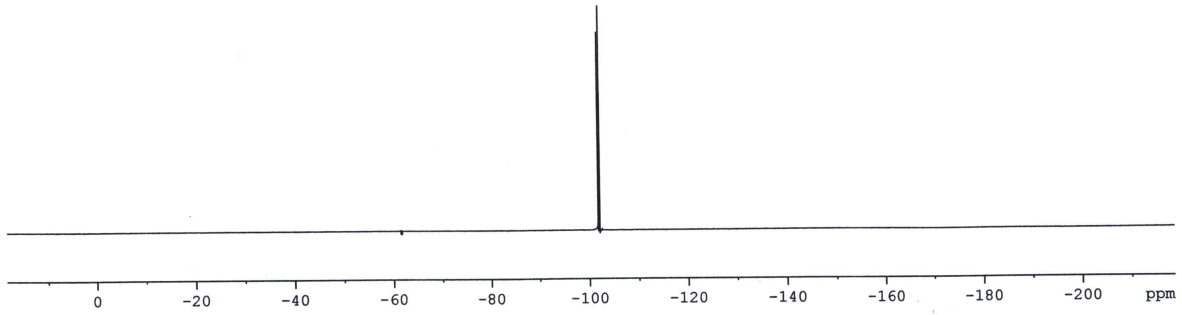
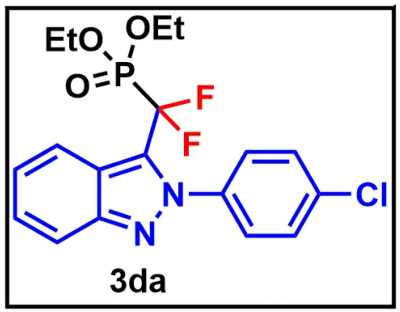


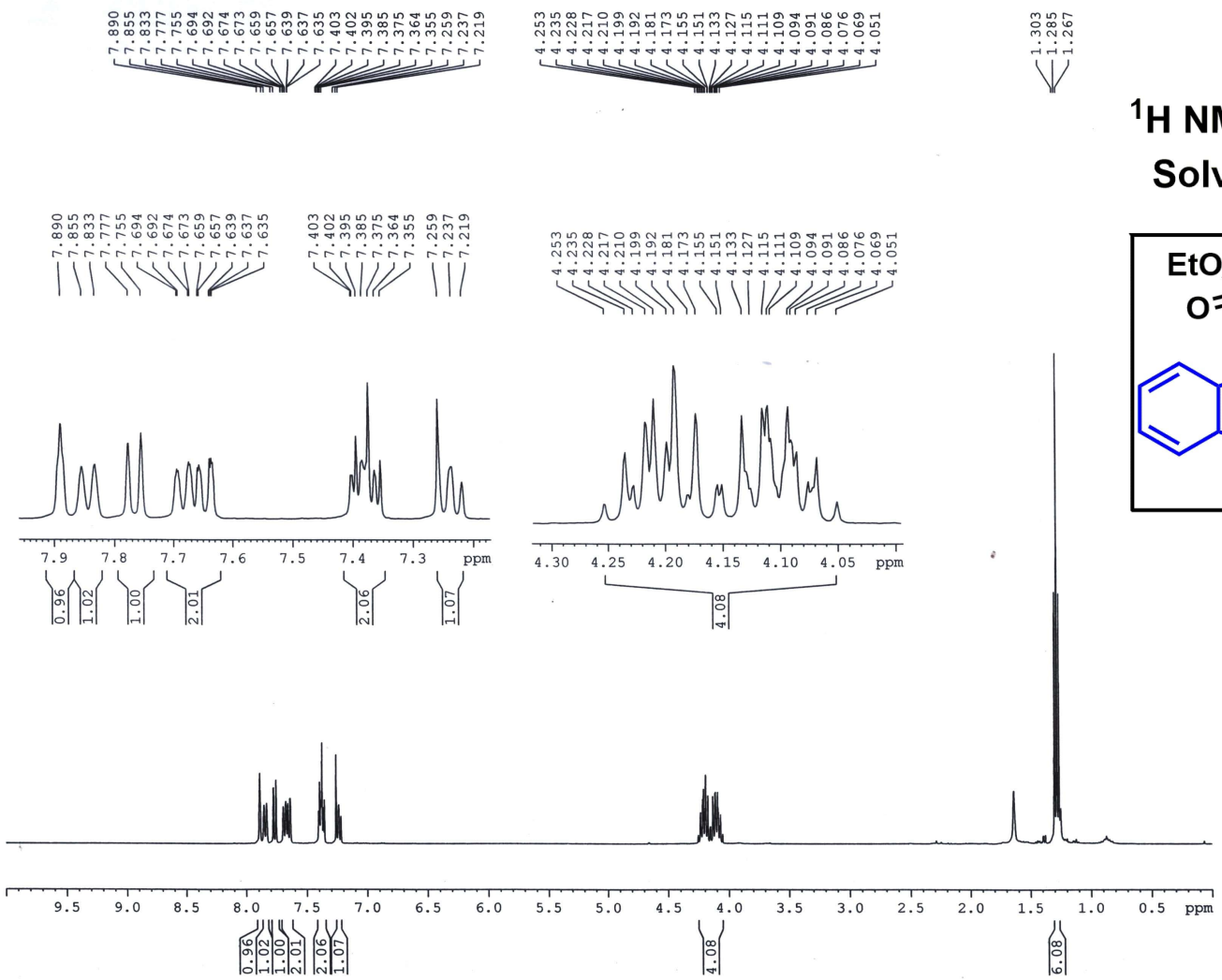


^{31}P NMR : 162 MHz

Solvent : $CDCl_3$

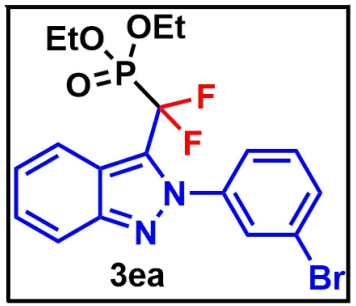


3da



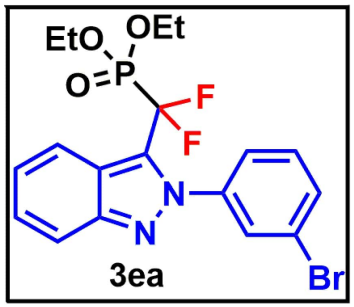
^{1}H NMR : 400 MHz

Solvent : $CDCl_3$



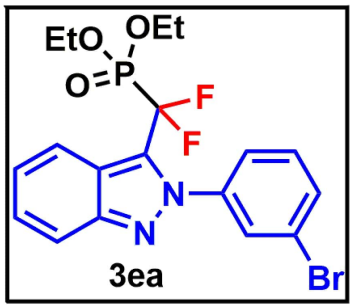
$^{13}C\{^{1}H\}$ NMR : 100 MHz

Solvent : $CDCl_3$



^{19}F NMR : 376.5 MHz

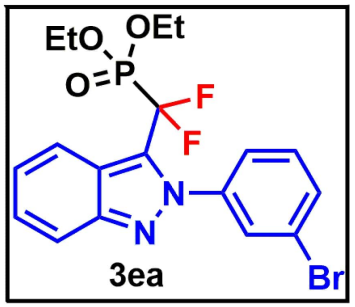
Solvent : $CDCl_3$



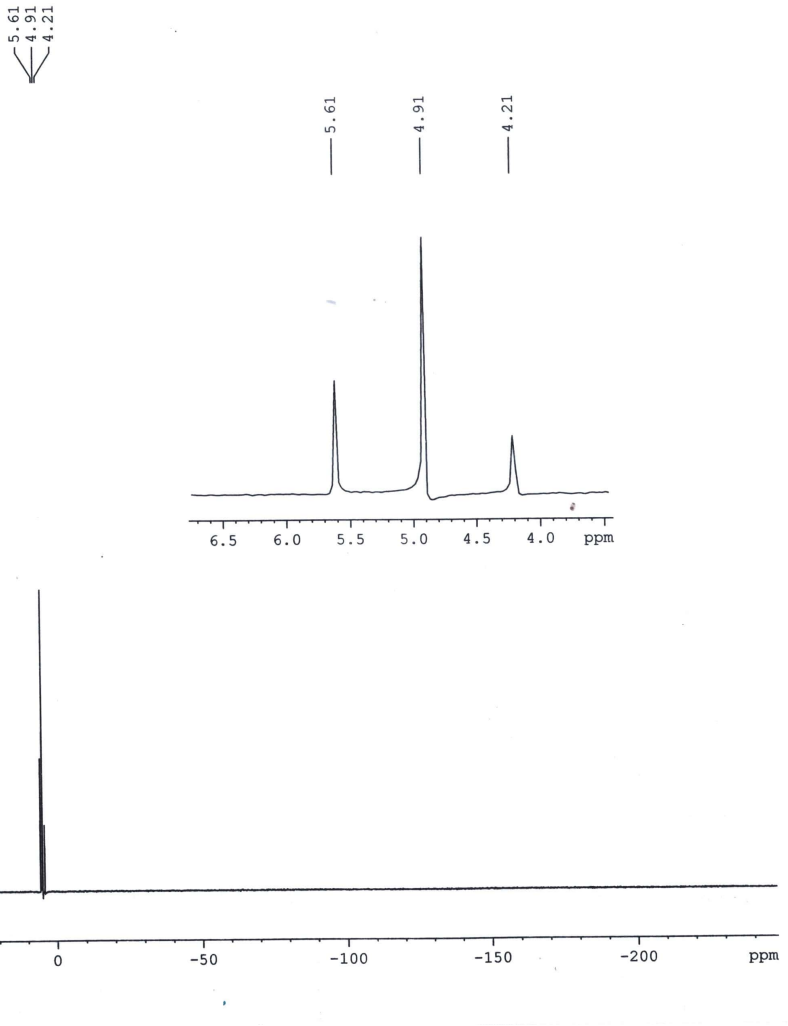
3ea

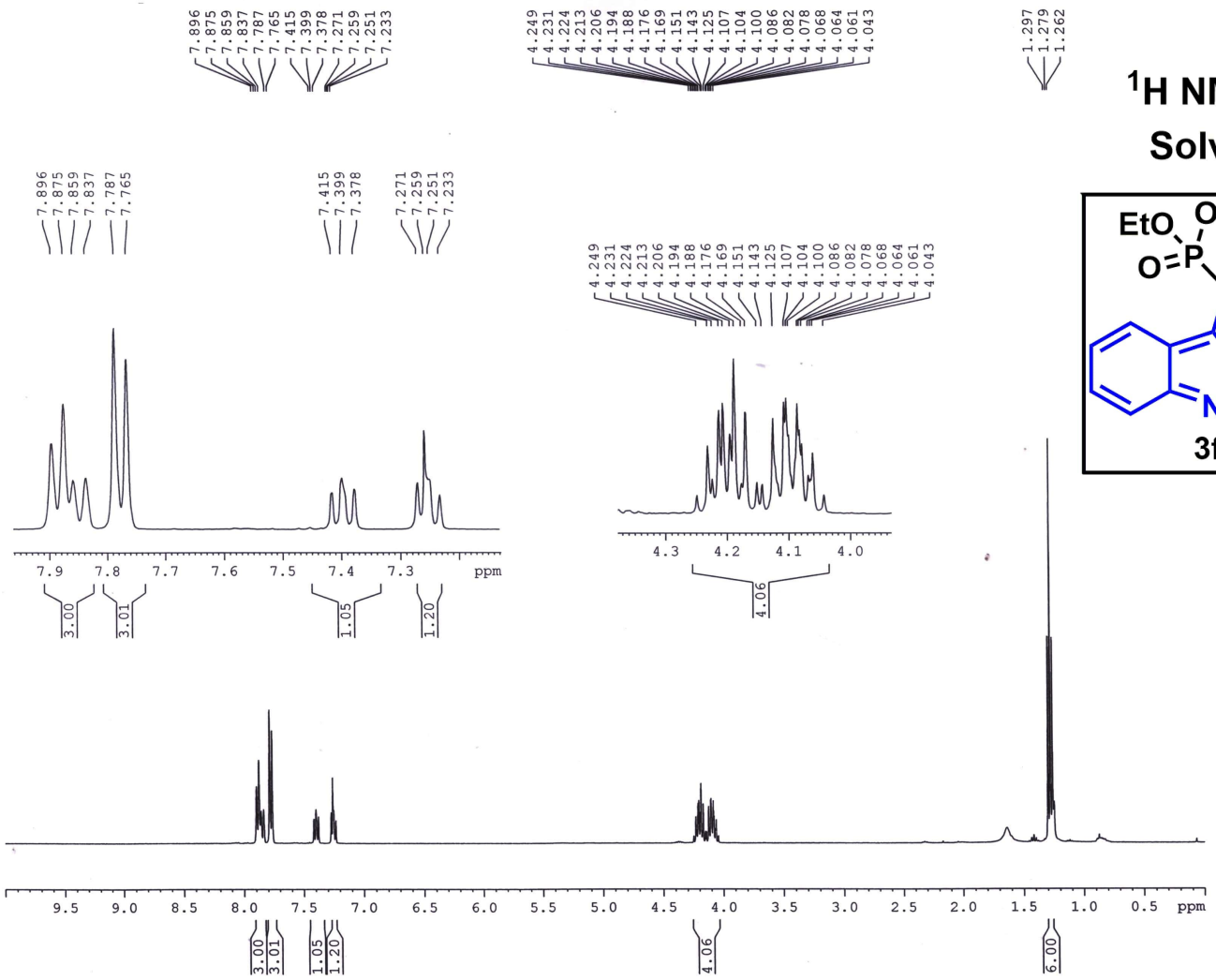
^{31}P NMR : 162 MHz

Solvent : $CDCl_3$



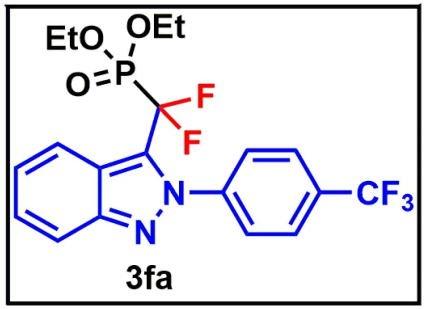
3ea



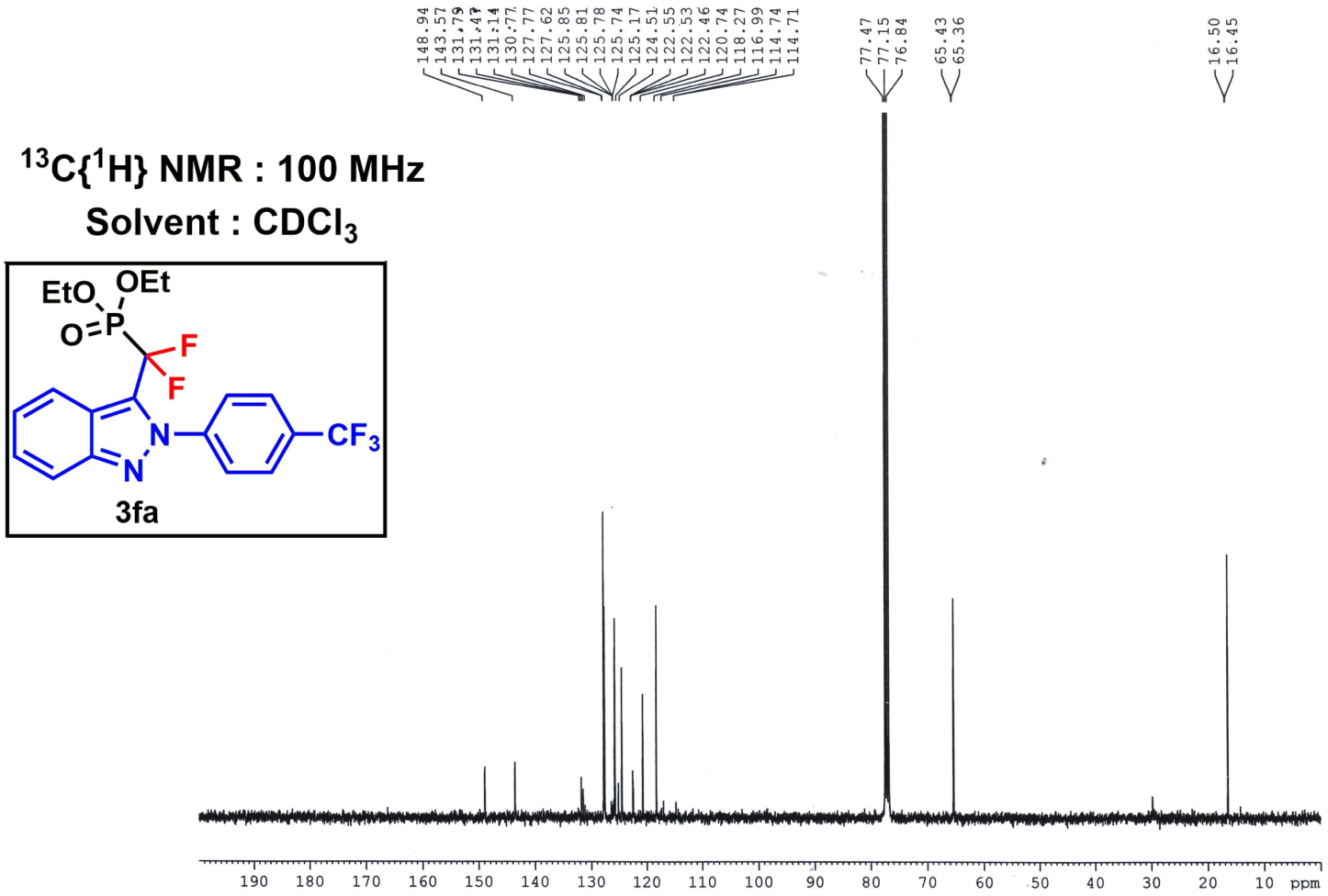


^{1}H NMR : 400 MHz

Solvent : $CDCl_3$



3fa



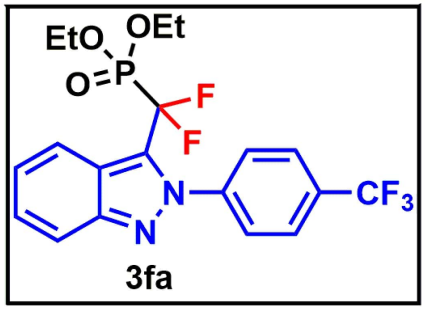
$^{13}C\{^{1}H\}$ NMR : 100 MHz

Solvent : $CDCl_3$

3fa

^{19}F NMR : 376.5 MHz

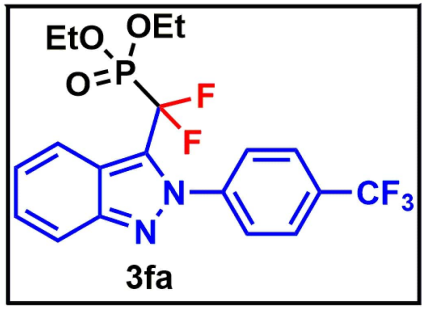
Solvent : $CDCl_3$



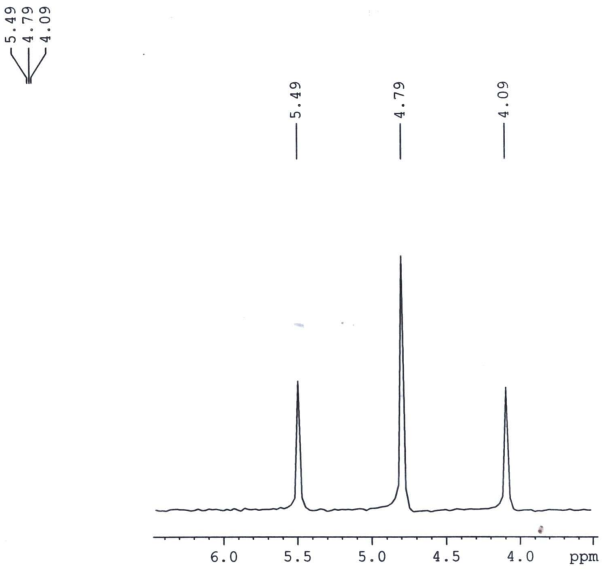
3fa

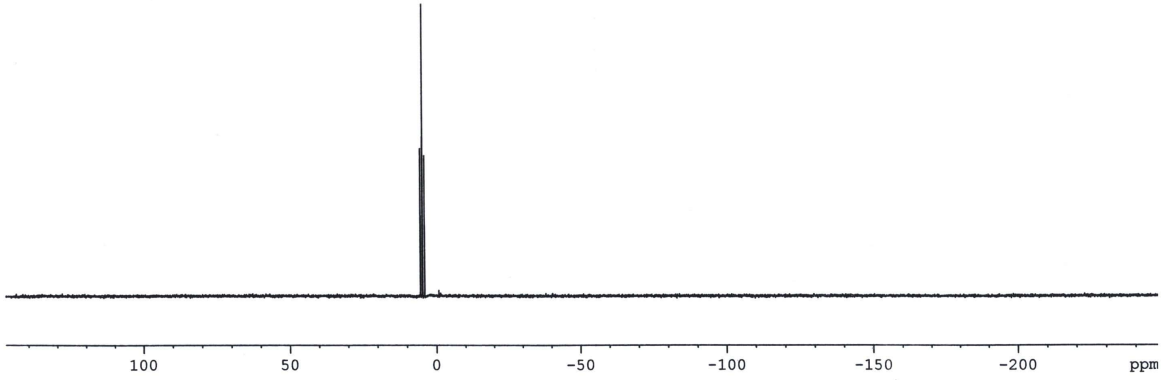
^{31}P NMR : 162 MHz

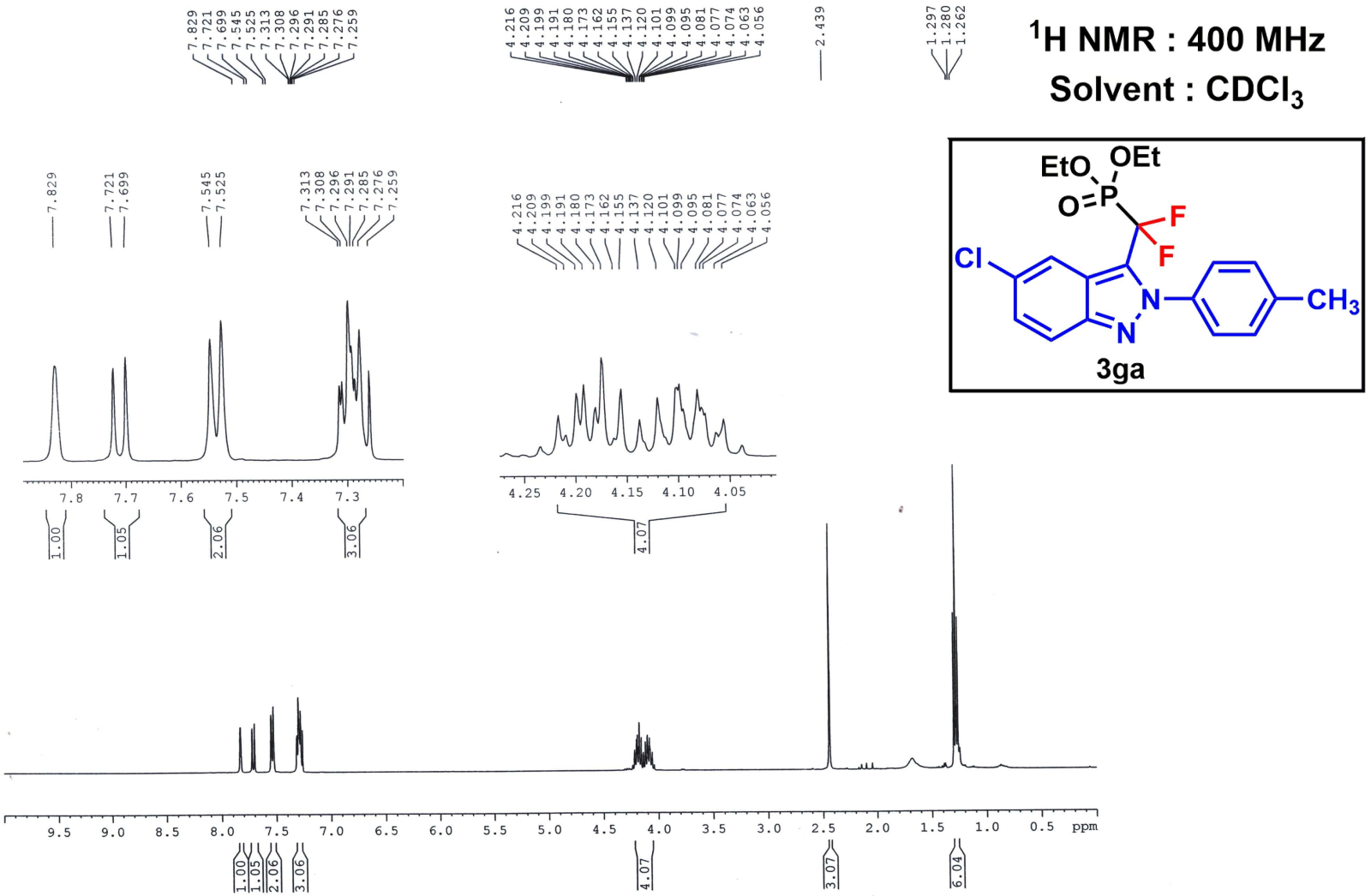
Solvent : $CDCl_3$



3fa



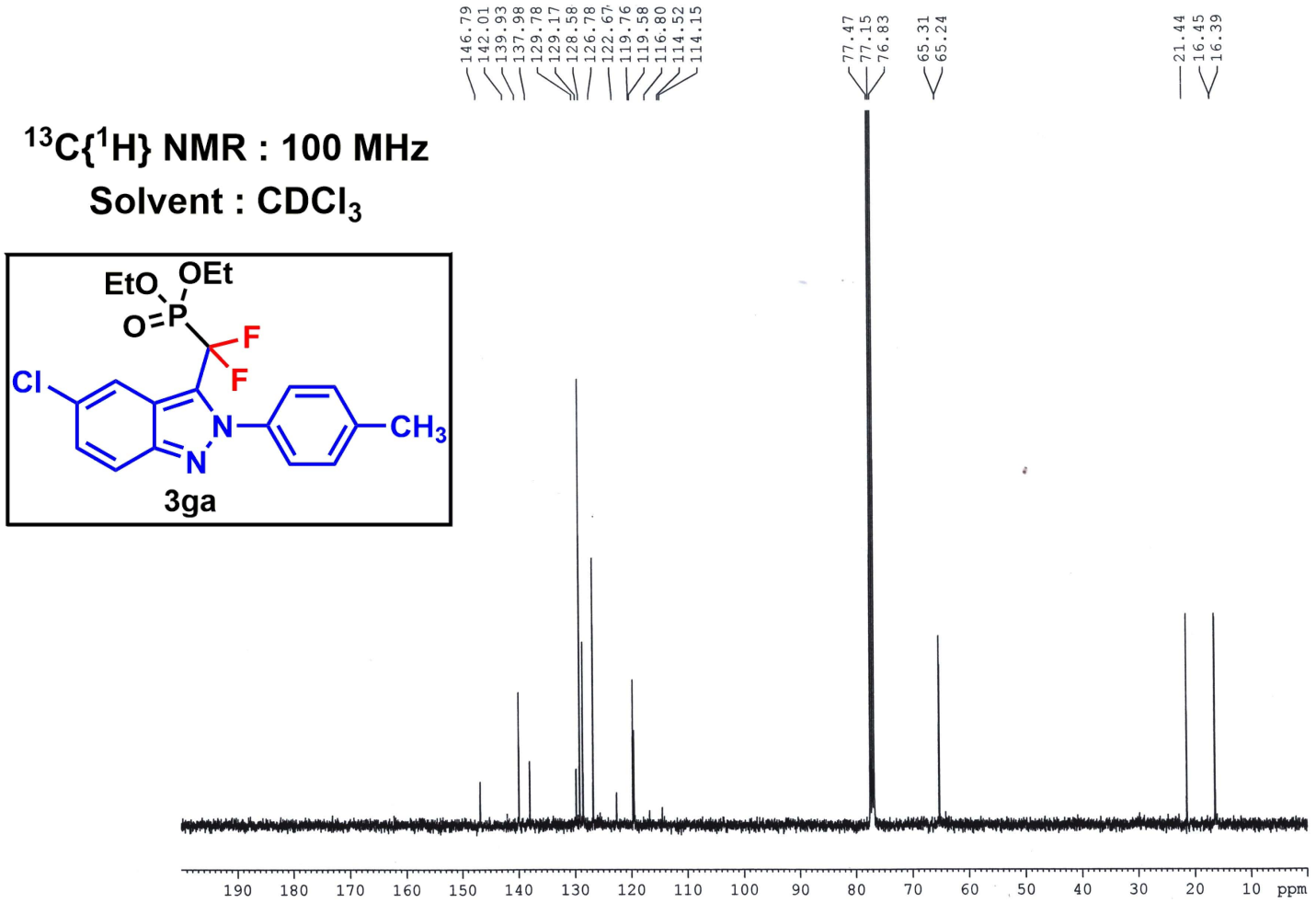




^{1}H NMR : 400 MHz

Solvent : $CDCl_3$

3ga



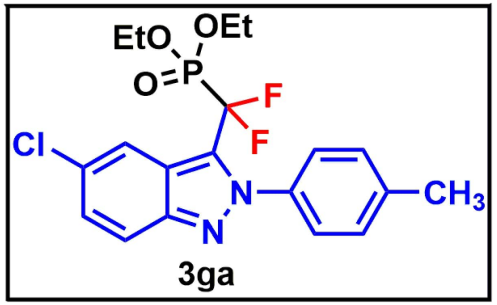
$^{13}C\{^{1}H\}$ NMR : 100 MHz

Solvent : $CDCl_3$

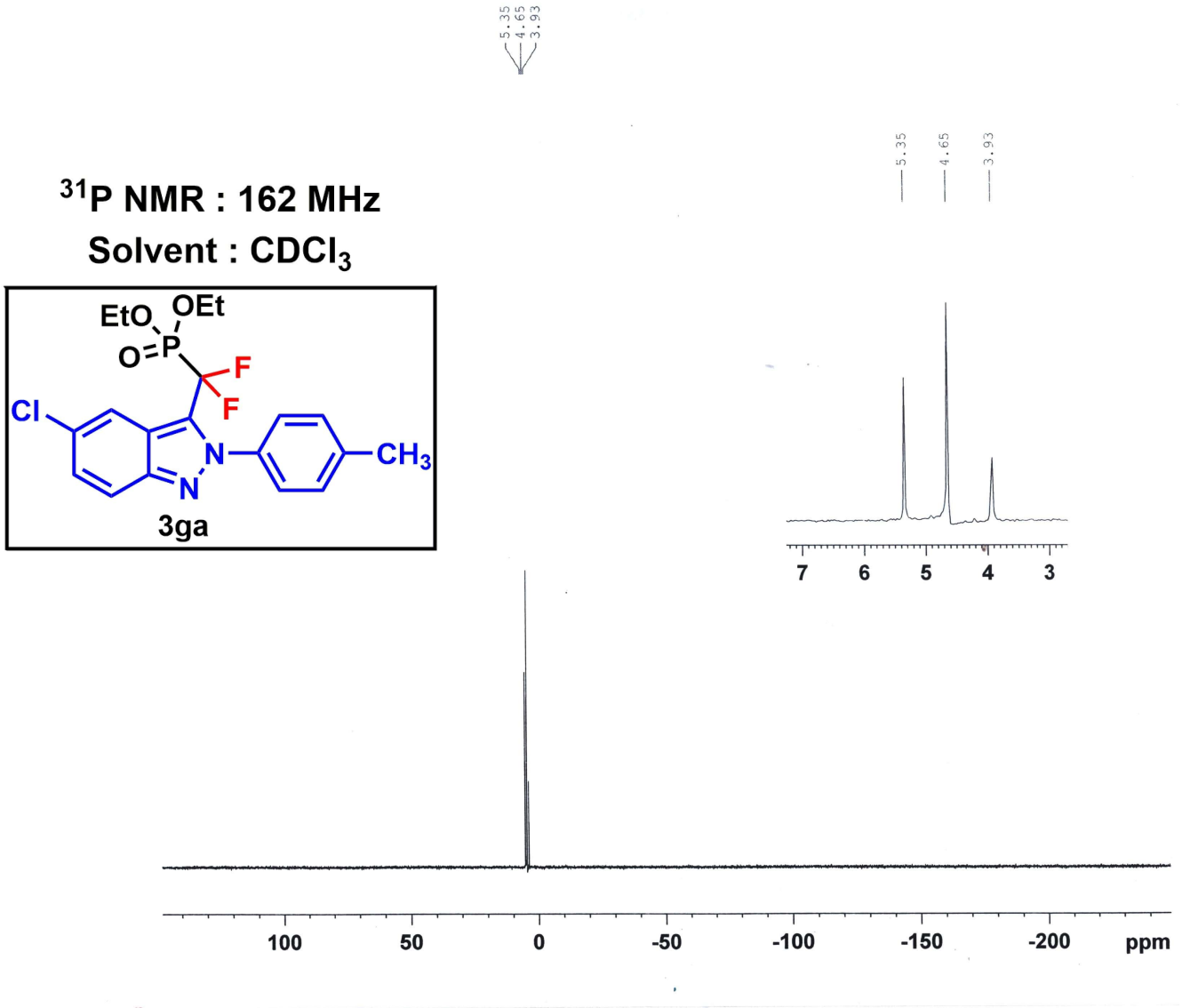
3ga

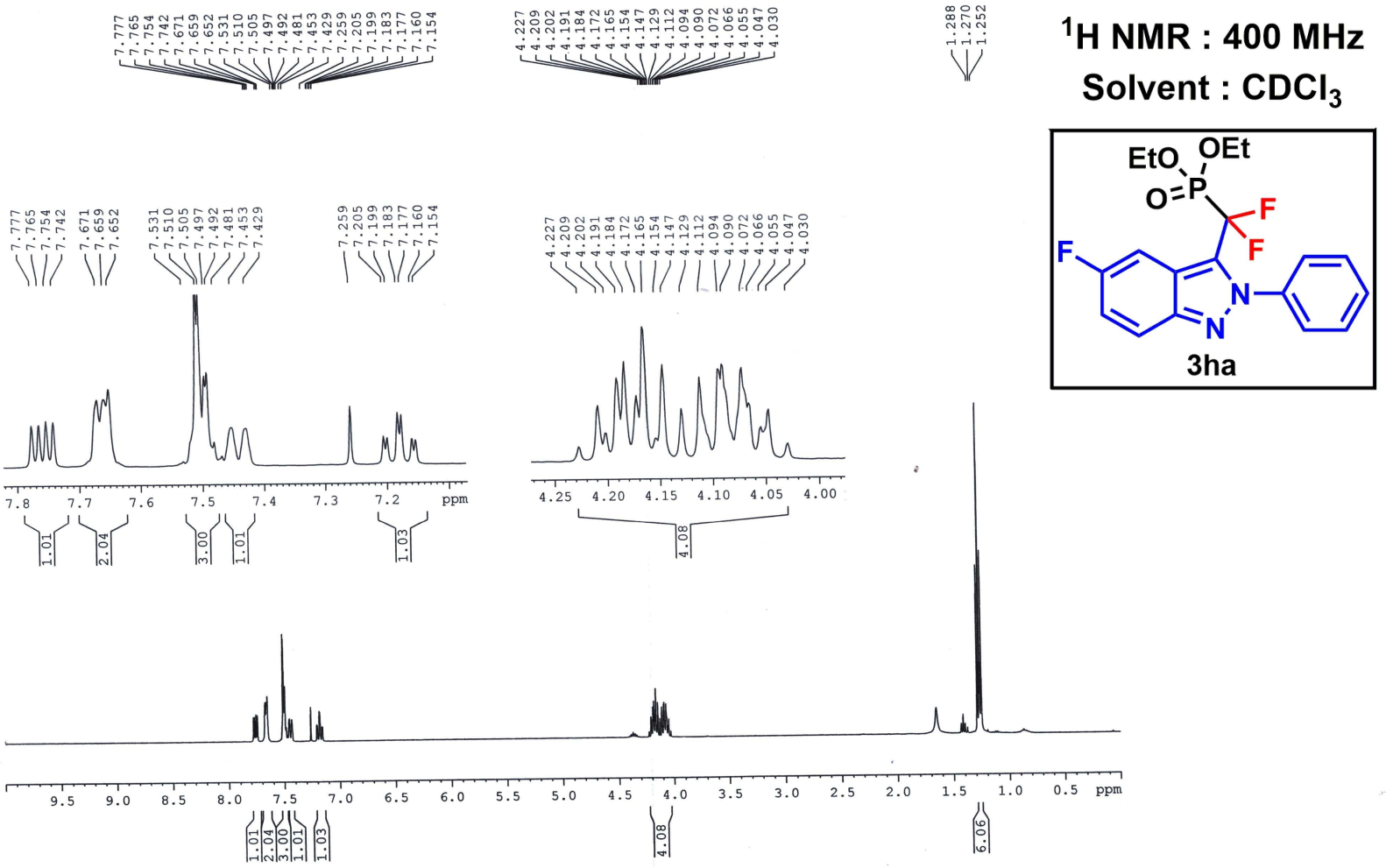
^{19}F NMR : 376.5 MHz

Solvent : $CDCl_3$



3ga


5.35
4.65
3.93
31P NMR : 162 MHz
Solvent : CDCl3
EtO
OEt
O=P
F
F
Cl
N
N
CH3
3ga
5.35
4.65
3.93
7
6
5
4
3
100
50
0
-50
-100
-150
-200
ppm



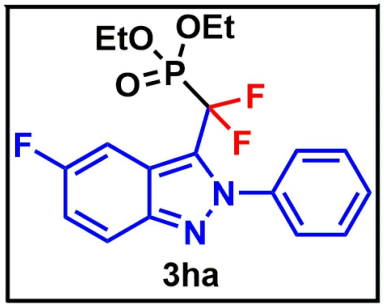
^{1}H NMR : 400 MHz

Solvent : $CDCl_3$

3ha

$^{13}C\{^{1}H\}$ NMR : 100 MHz

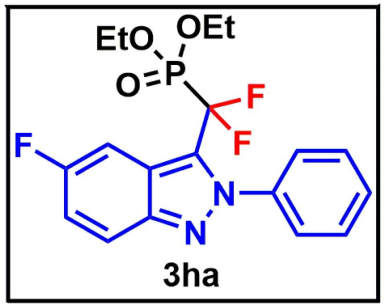
Solvent : $CDCl_3$



3ha

^{19}F NMR : 376.5 MHz

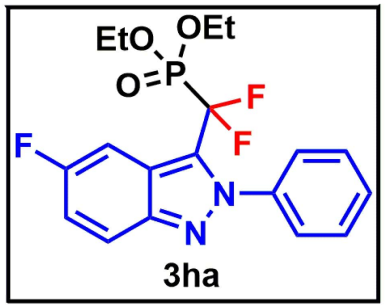
Solvent : $CDCl_3$



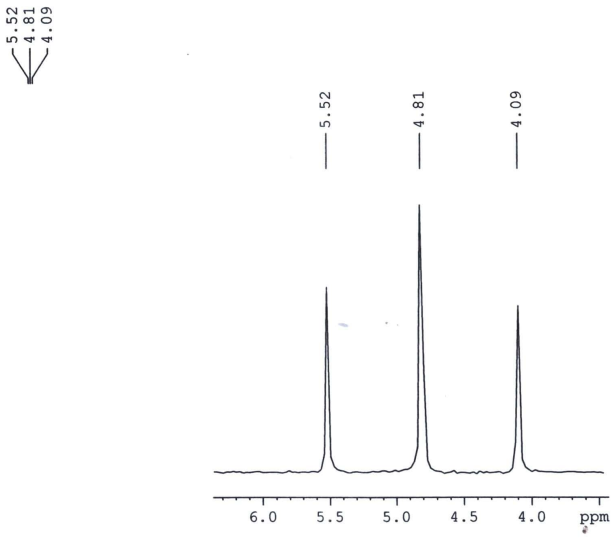
3ha

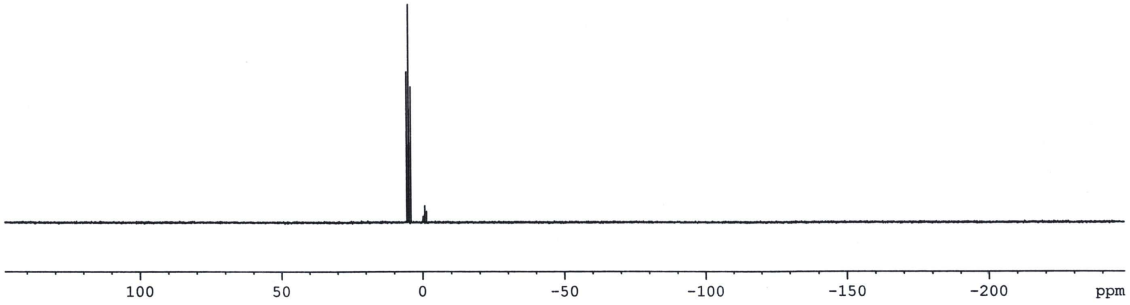
^{31}P NMR : 162 MHz

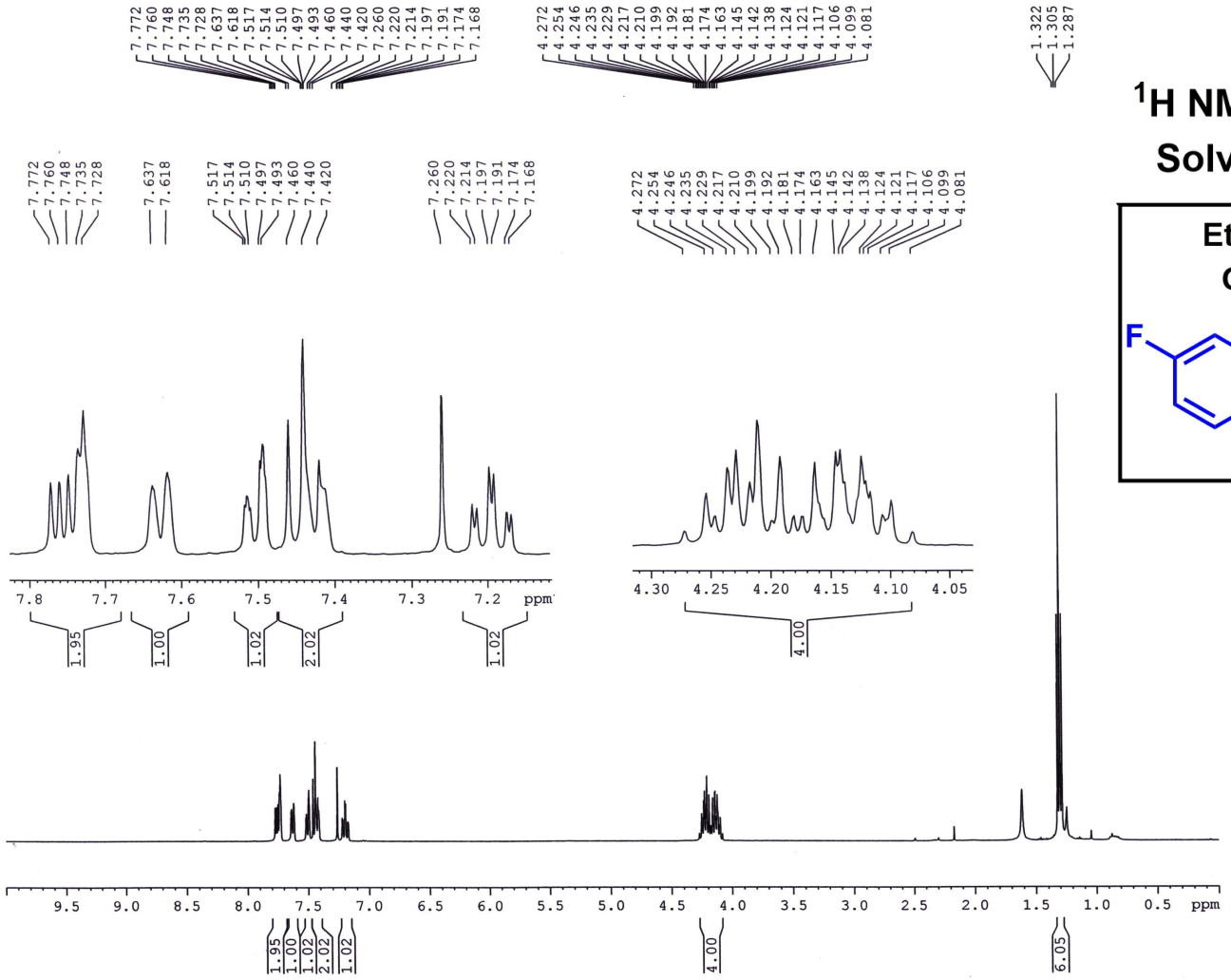
Solvent : $CDCl_3$



3ha

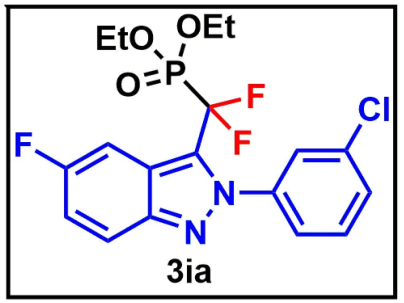


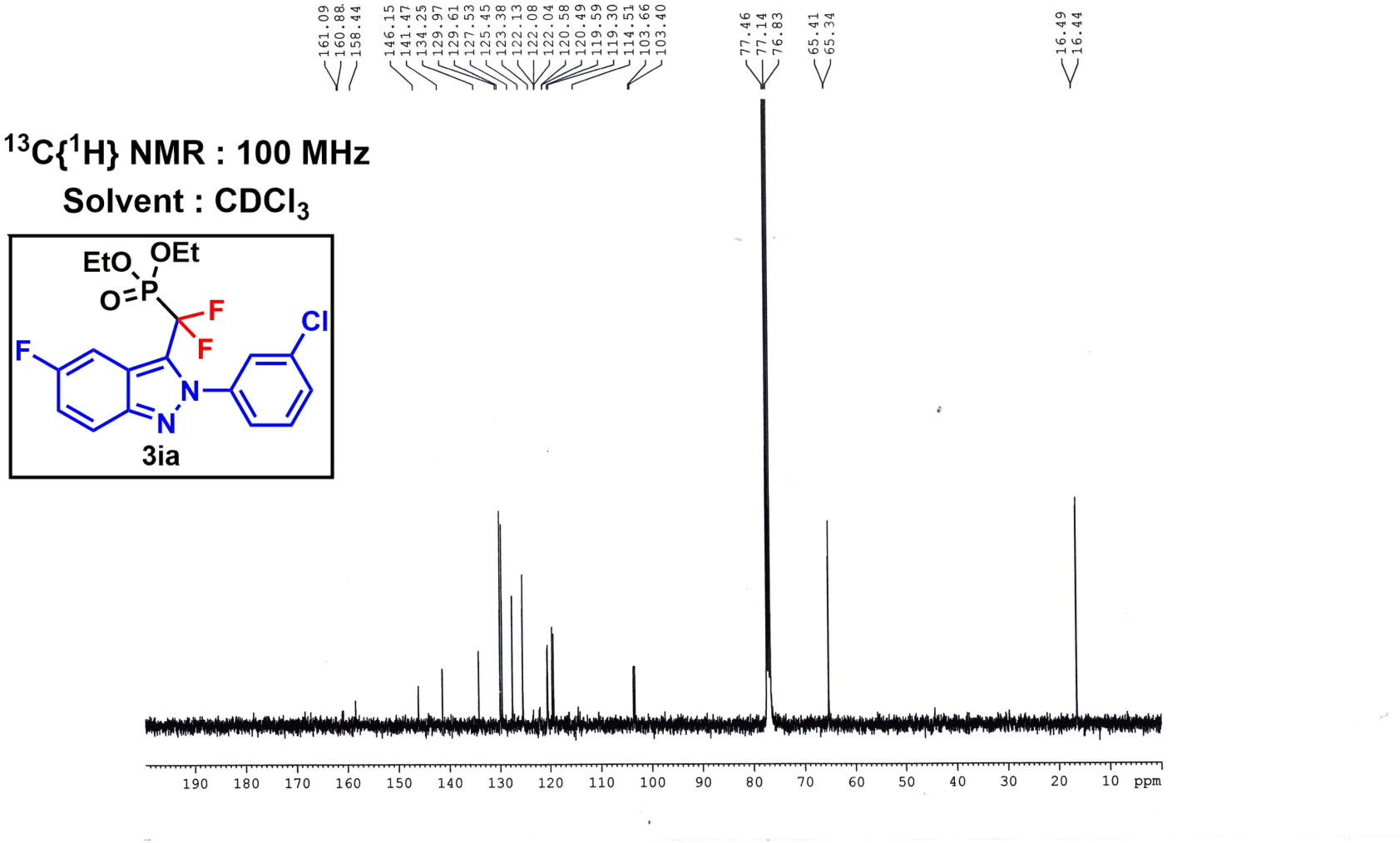




^{1}H NMR : 400 MHz

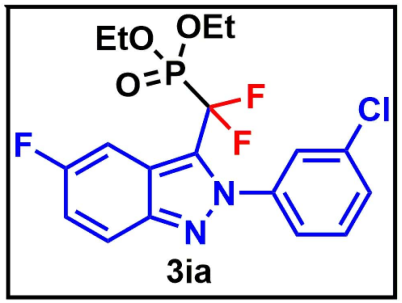
Solvent : $CDCl_3$




161.09
160.88
158.44
146.15
141.47
134.25
129.97
129.61
127.53
125.45
123.38
122.13
122.08
122.04
120.58
120.49
119.59
119.30
114.51
103.66
103.40
77.46
77.14
76.83
65.41
65.34
16.49
16.44
13C{1H} NMR : 100 MHz
Solvent : CDCl3
EtO
OEt
O=P
F
F
F
Cl
N
N
3ia
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{19}F NMR : 376.5 MHz

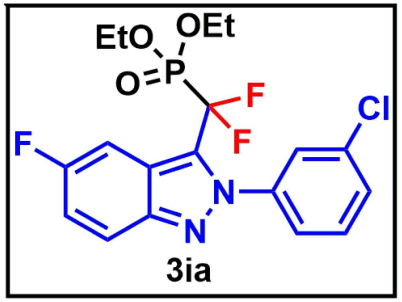
Solvent : $CDCl_3$



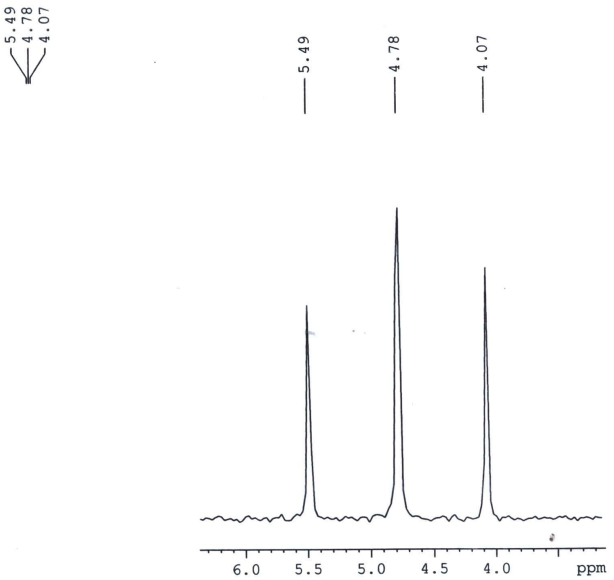
3ia

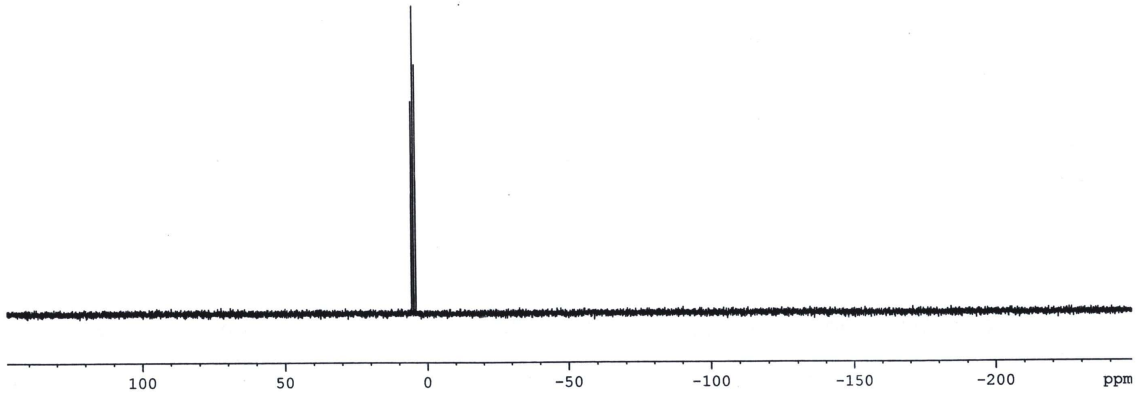
^{31}P NMR : 162 MHz

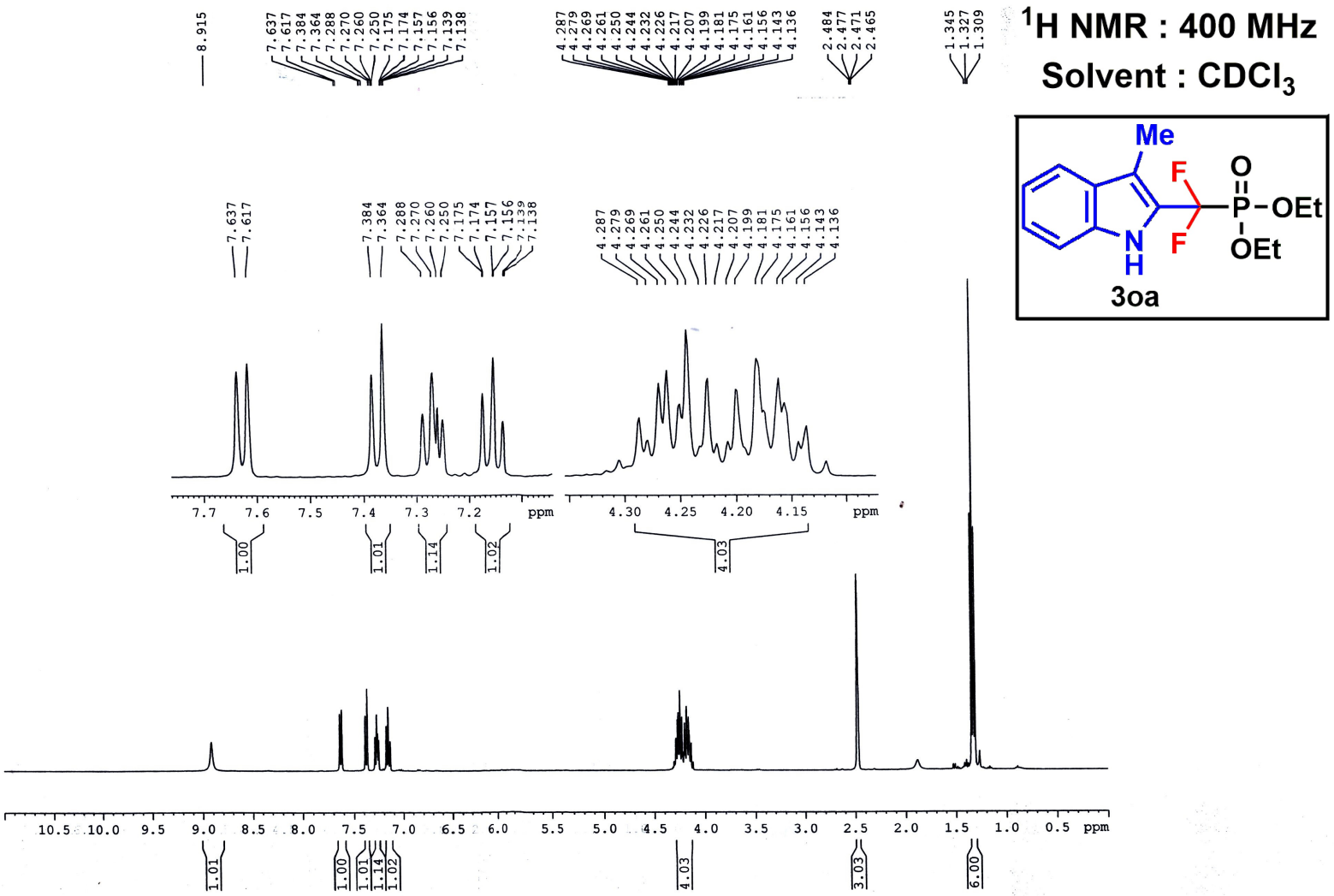
Solvent : $CDCl_3$



3ia







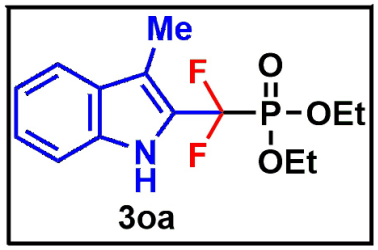
^{1}H NMR : 400 MHz

Solvent : $CDCl_3$

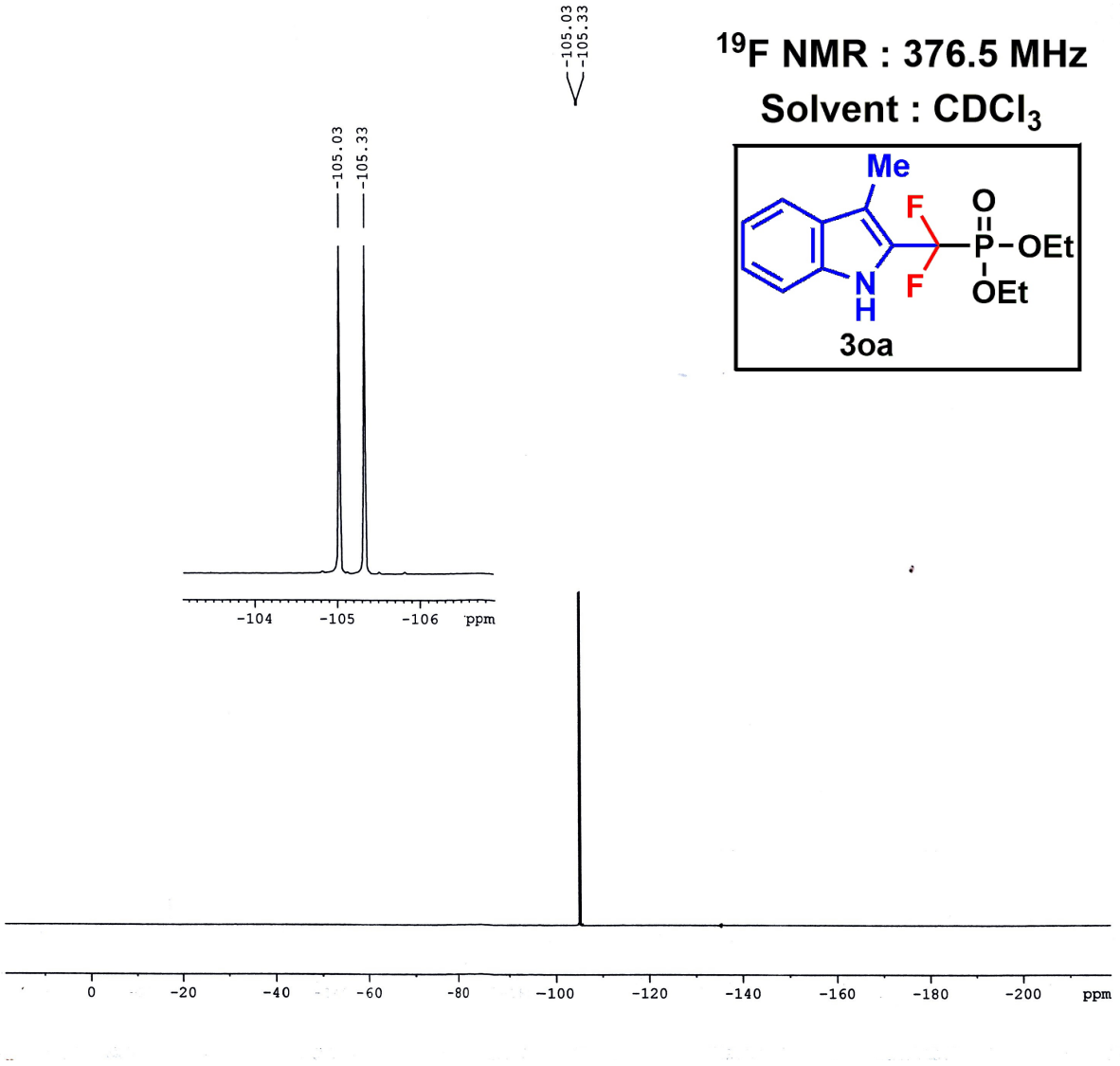
3oa

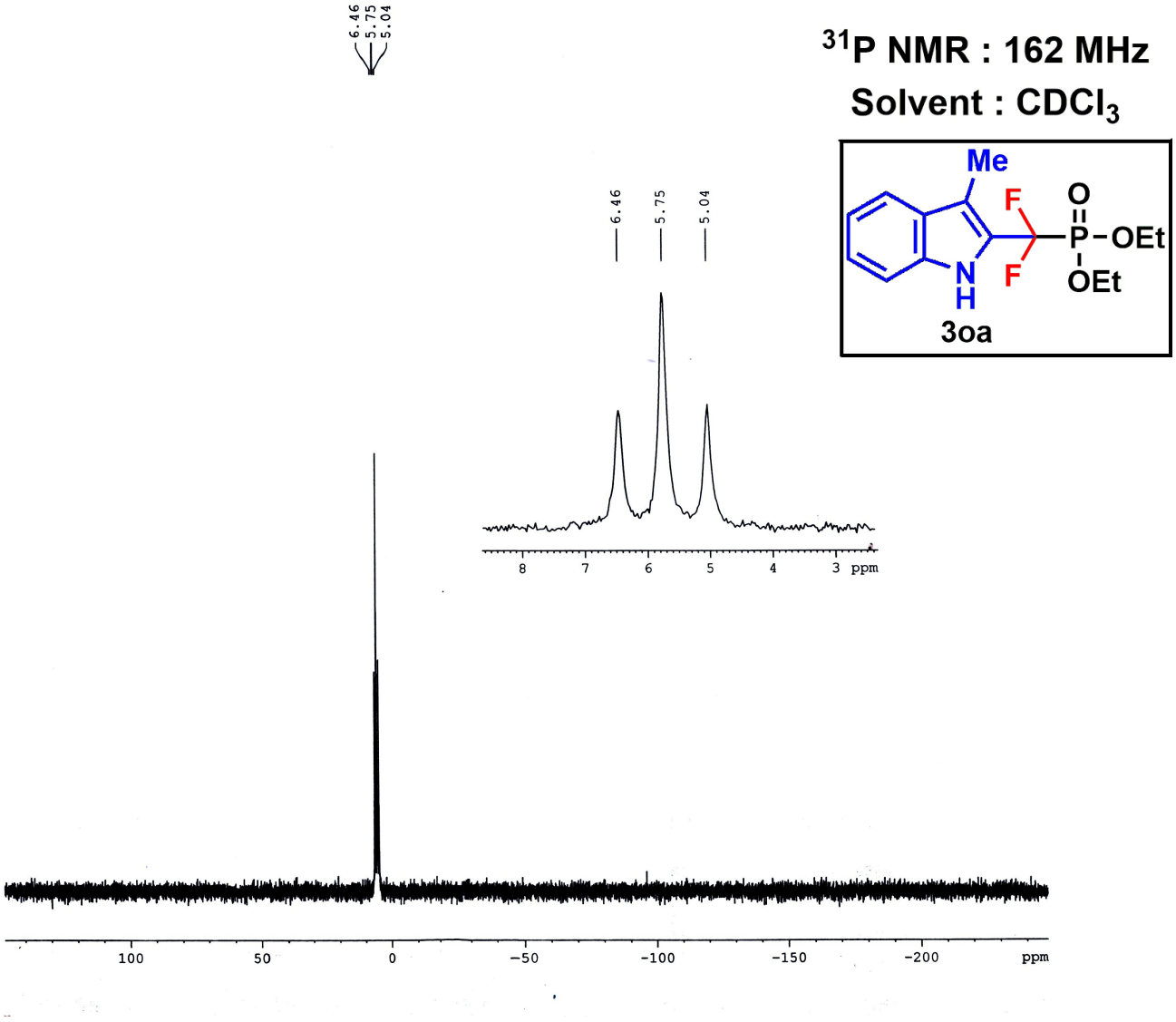
$^{13}C\{^{1}H\}$ NMR : 100 MHz

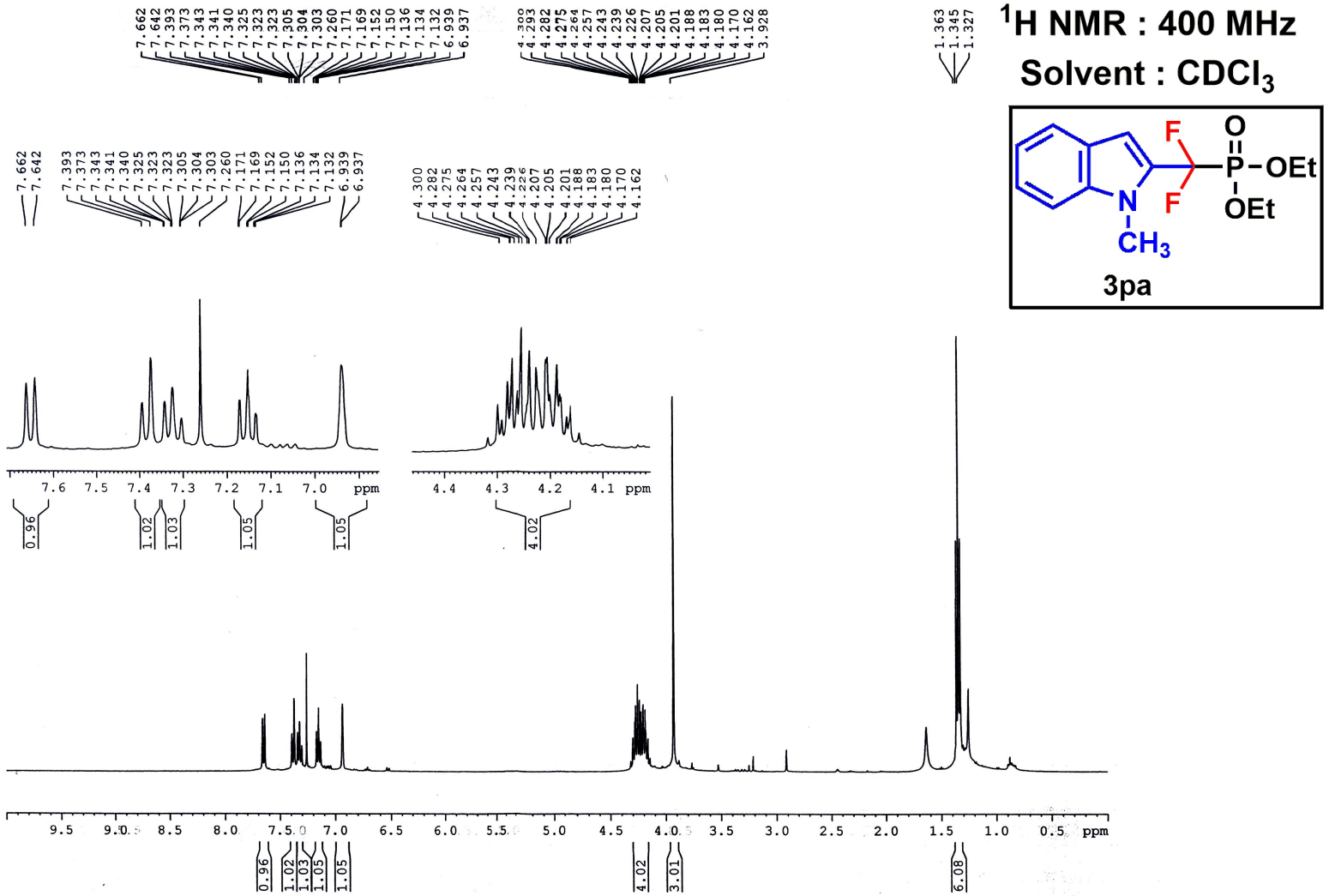
Solvent : $CDCl_3$



3oa


-105.03
-105.33
19F NMR : 376.5 MHz
Solvent : CDCl3
Me
F
F
O
P-OEt
OEt
N
H
3oa
-105.03
-105.33
-104
-105
-106
ppm
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

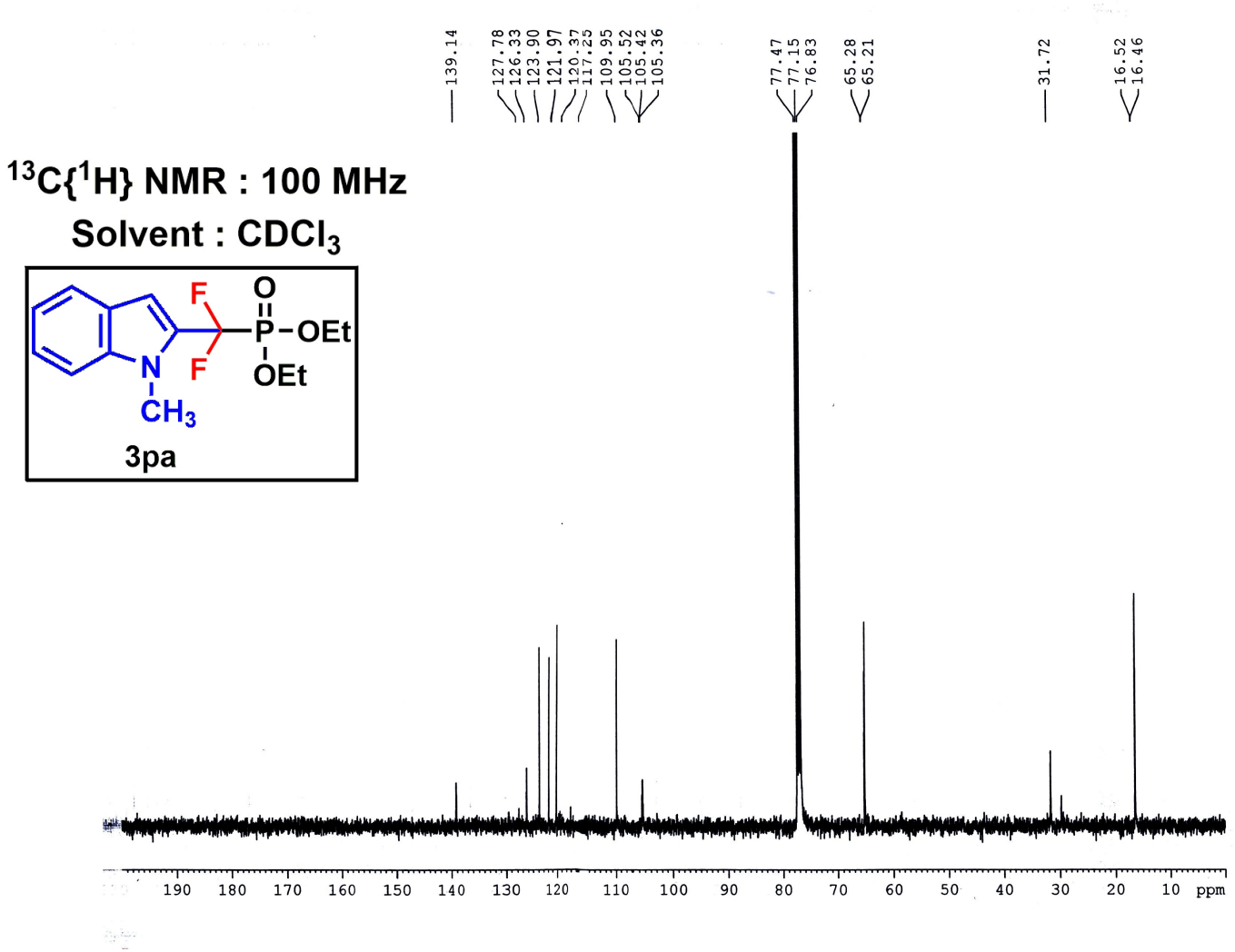

6.46
5.75
5.04
31P NMR : 162 MHz
Solvent : CDCl3
Me
F
O
P-OEt
F
OEt
N
H
3oa
6.46
5.75
5.04
8
7
6
5
4
3 ppm
100
50
0
−50
−100
−150
−200
ppm



^{1}H NMR : 400 MHz

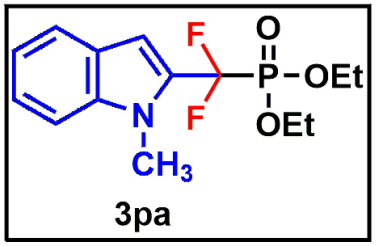
Solvent : $CDCl_3$

3pa

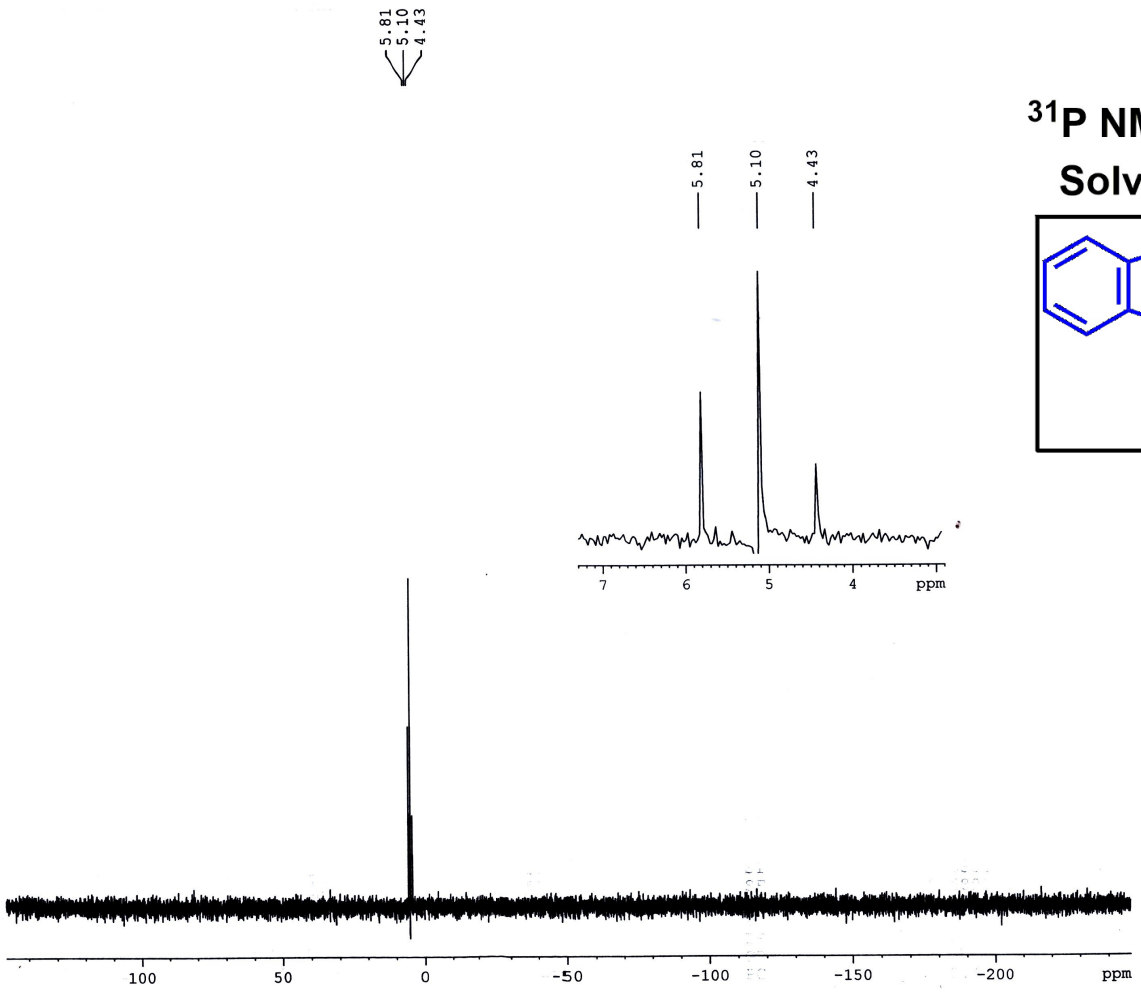

$^{13}C\{^{1}H\}$ NMR : 100 MHz
Solvent : $CDCl_3$
F
O
P
OEt
F
OEt
N
CH_3
3pa
139.14
127.78
126.33
123.90
121.97
120.37
117.25
109.95
105.52
105.42
105.36
77.47
77.15
76.83
65.28
65.21
31.72
16.52
16.46
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{19}F NMR : 376.5 MHz

Solvent : $CDCl_3$

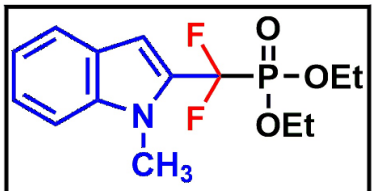


3pa

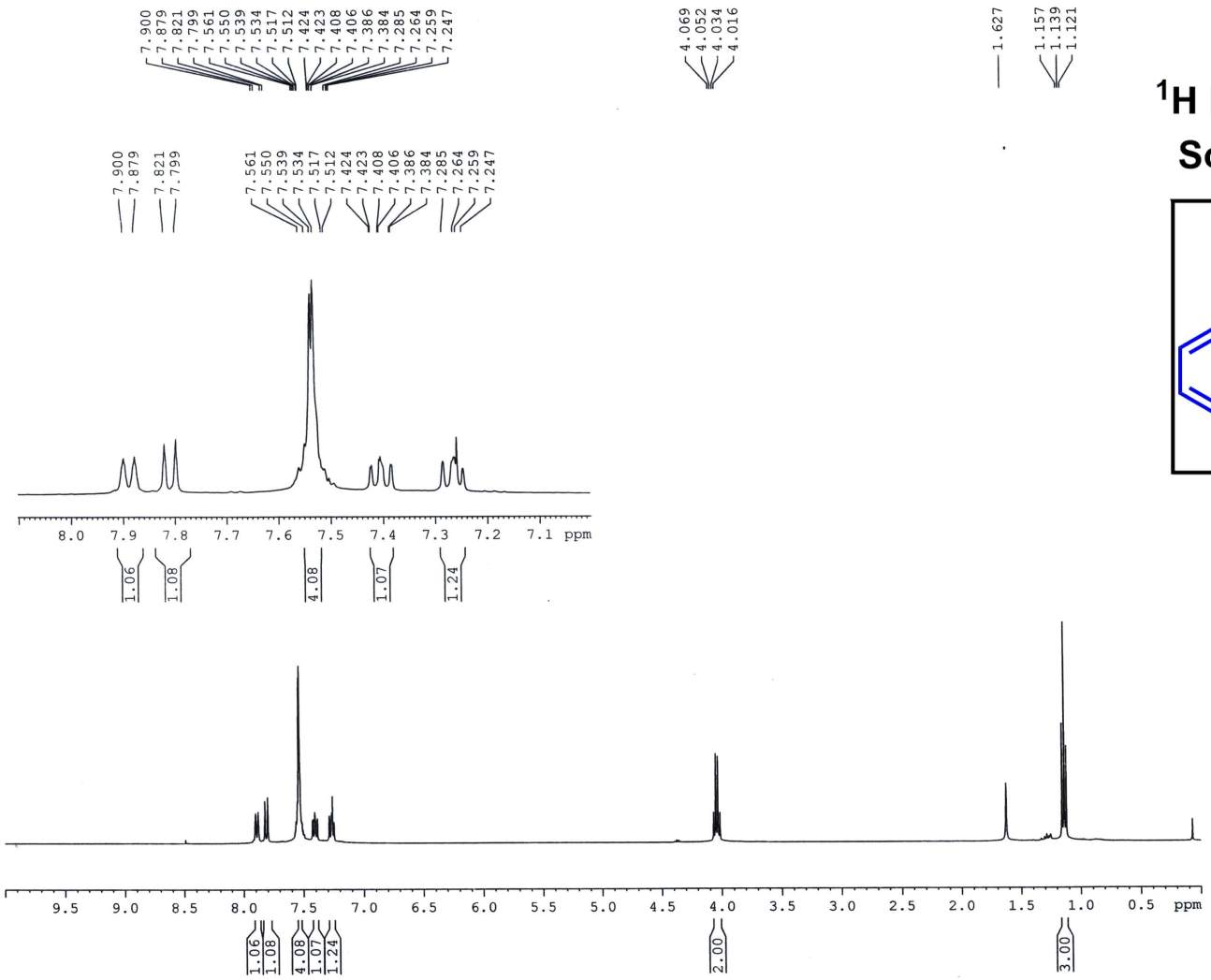


^{31}P NMR : 162 MHz

Solvent : $CDCl_3$

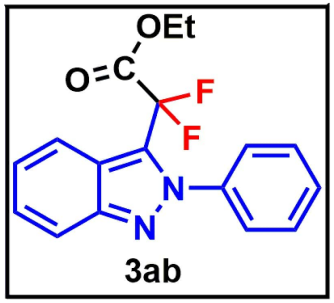


3pa



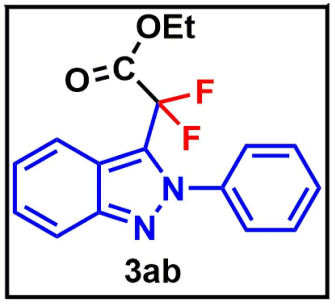
^{1}H NMR : 400 MHz

Solvent : $CDCl_3$

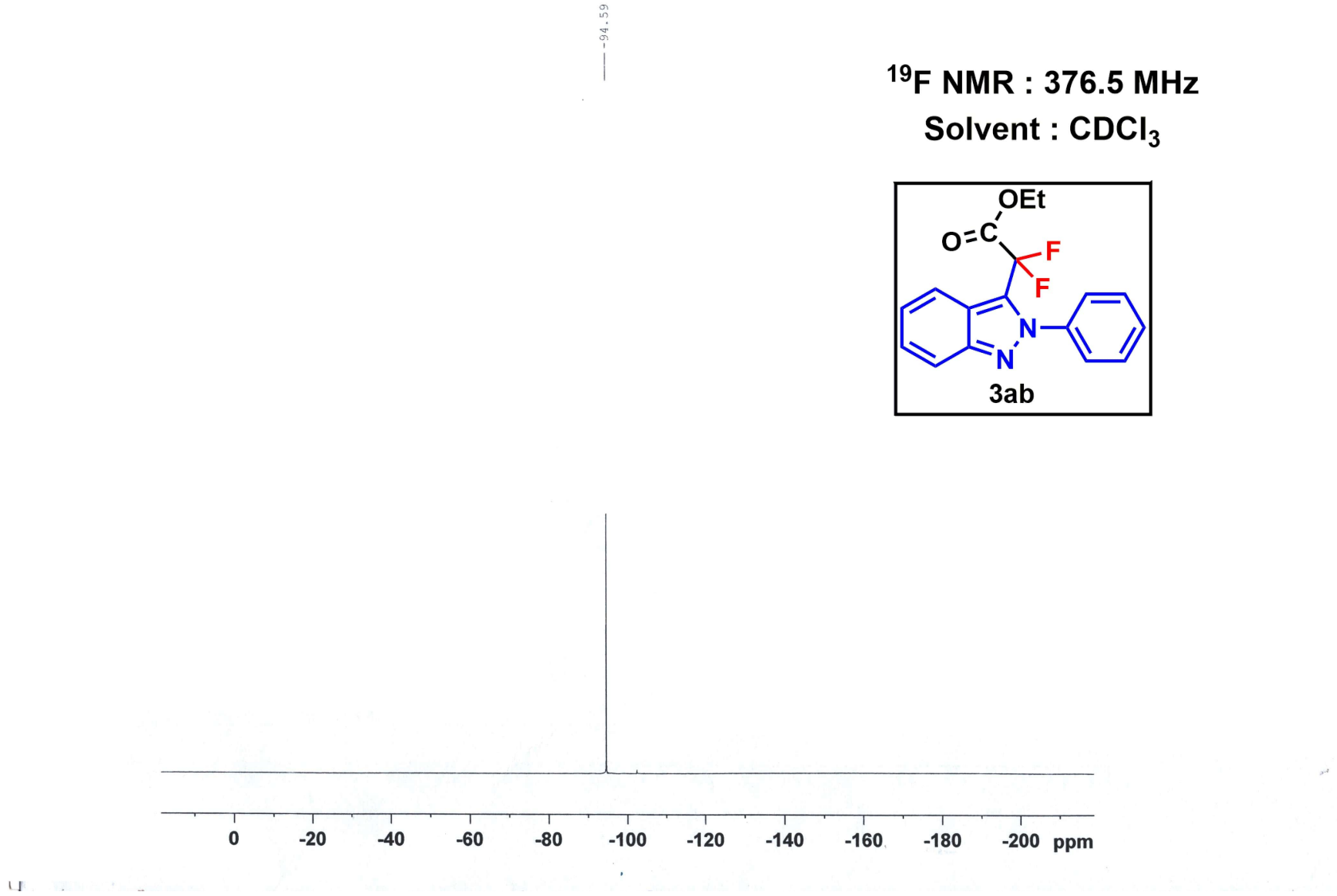


$^{13}C\{^{1}H\}$ NMR : 100 MHz

Solvent : $CDCl_3$

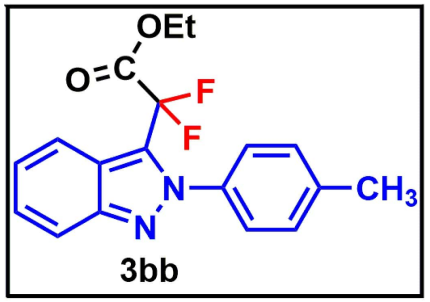


3ab

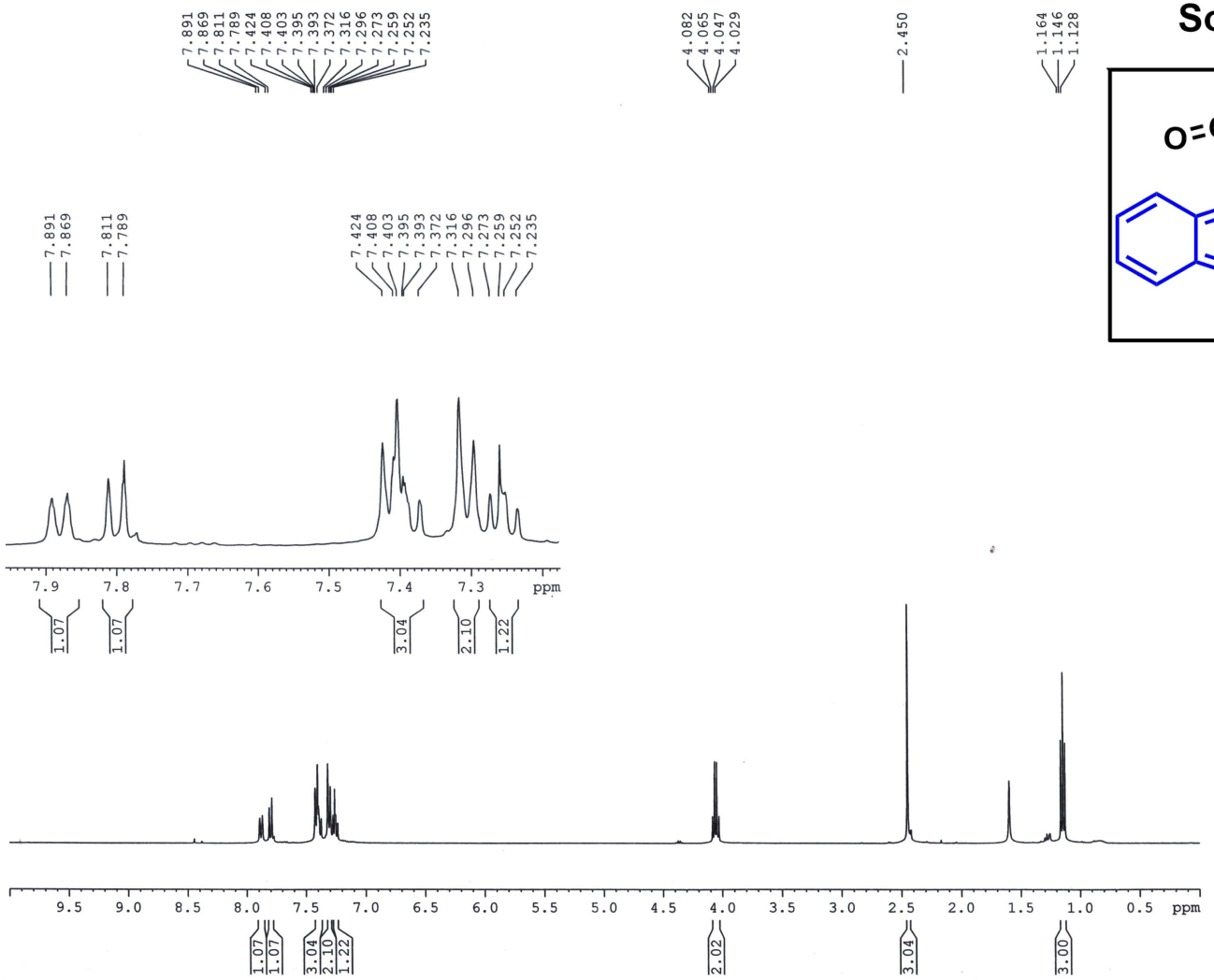

-94.59
19F NMR : 376.5 MHz
Solvent : CDCl3
OEt
O=C
F
F
N
N
3ab
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

^{1}H NMR : 400 MHz

Solvent : $CDCl_3$

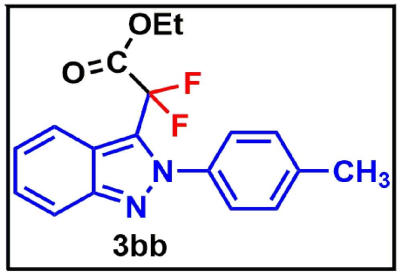


3bb

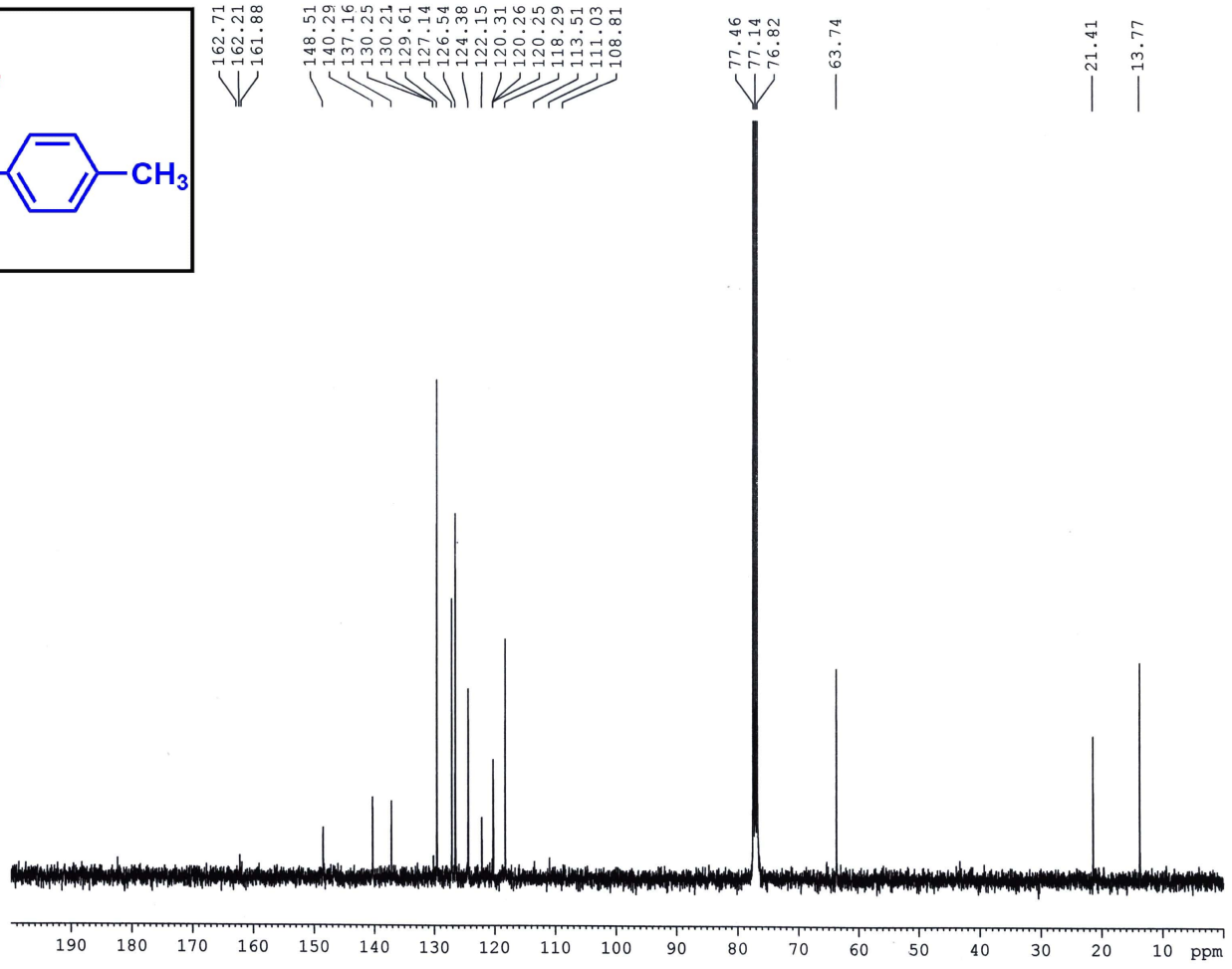


$^{13}C\{^{1}H\}$ NMR : 100 MHz

Solvent : $CDCl_3$

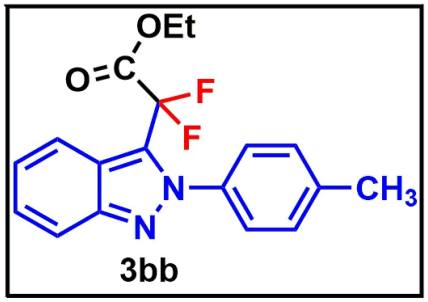


3bb

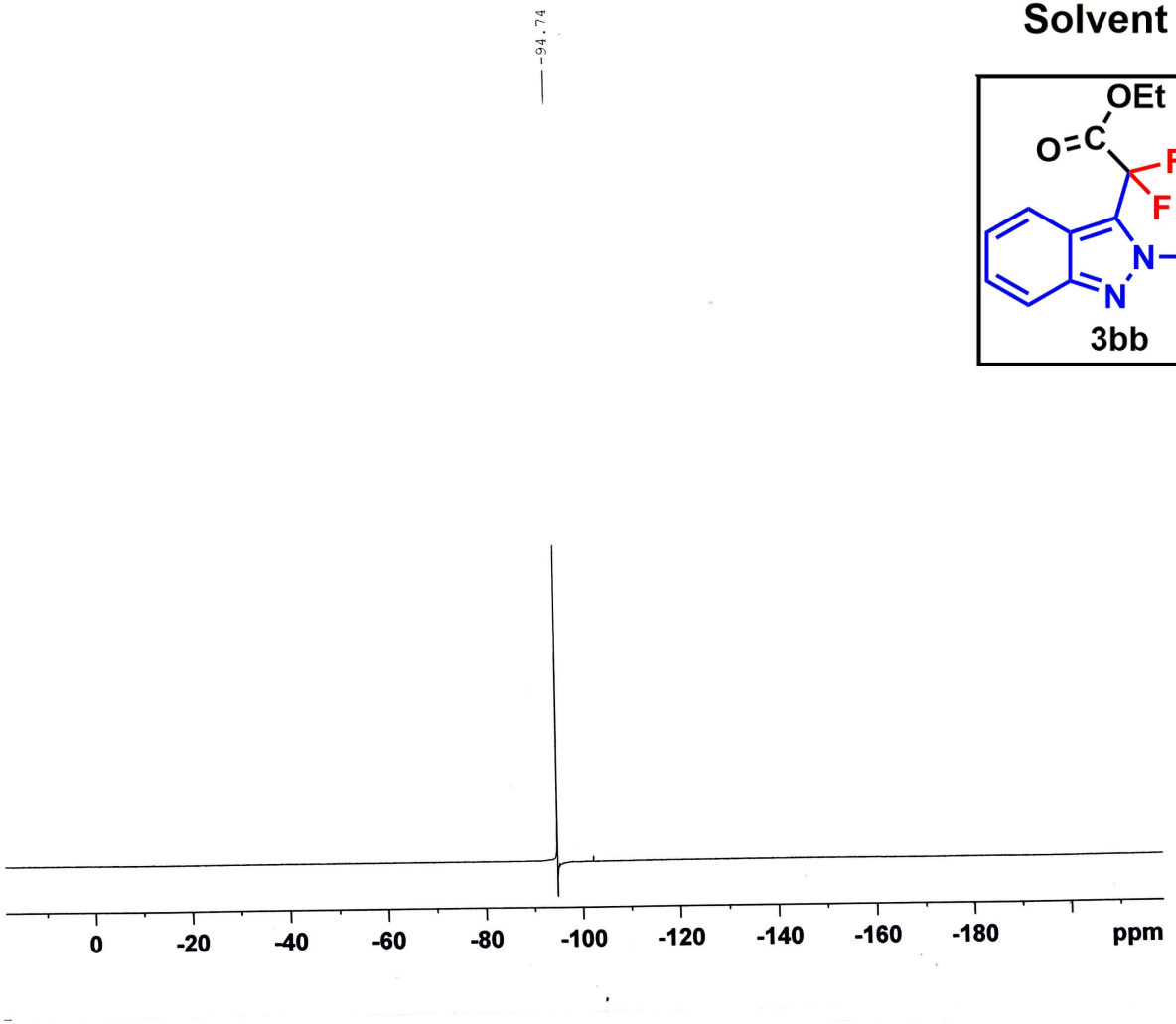


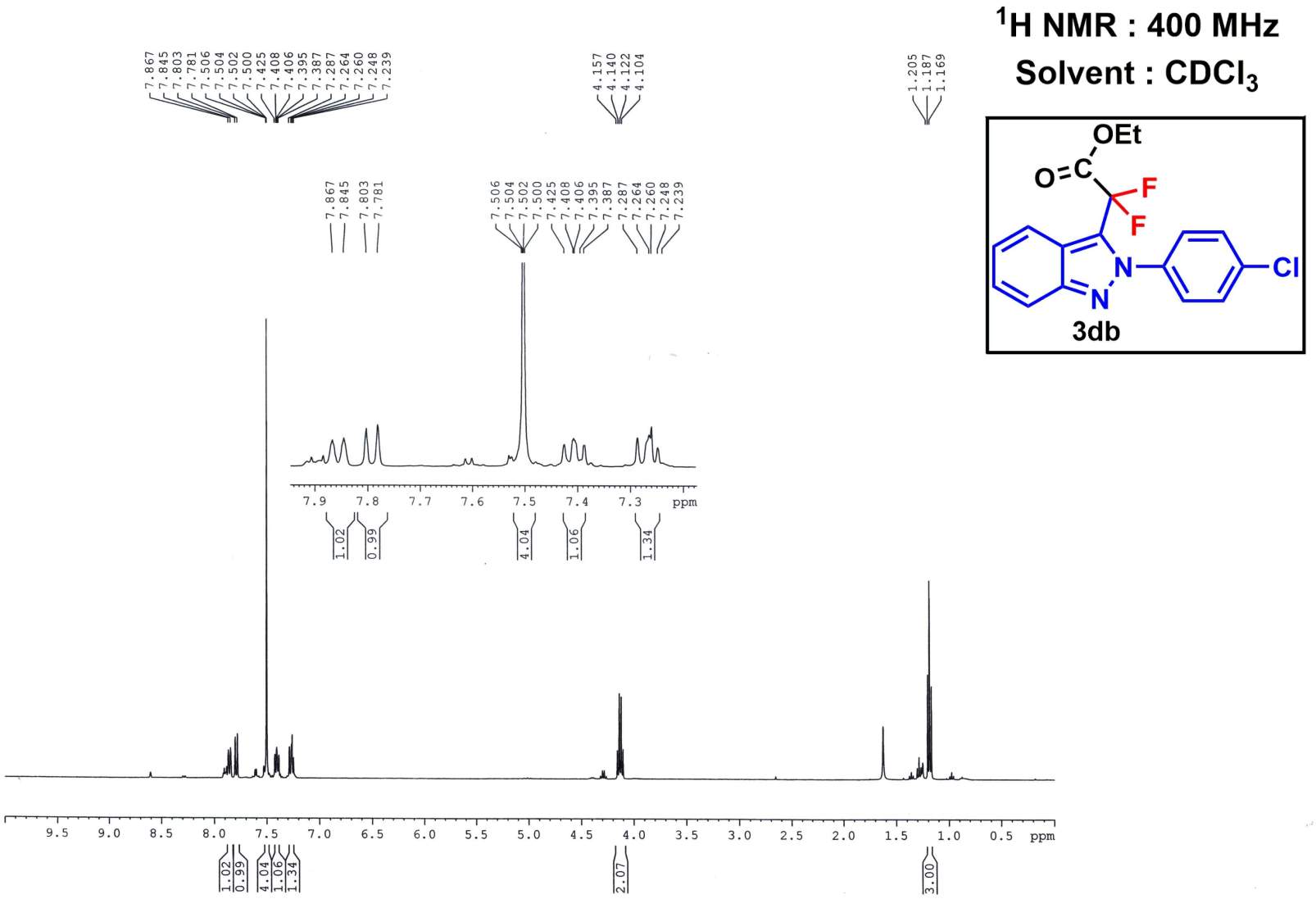
^{19}F NMR : 376.5 MHz

Solvent : $CDCl_3$



3bb





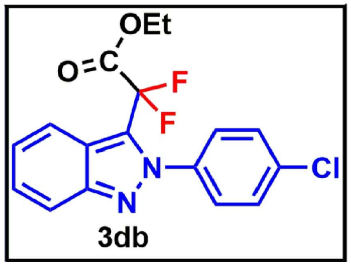
^{1}H NMR : 400 MHz

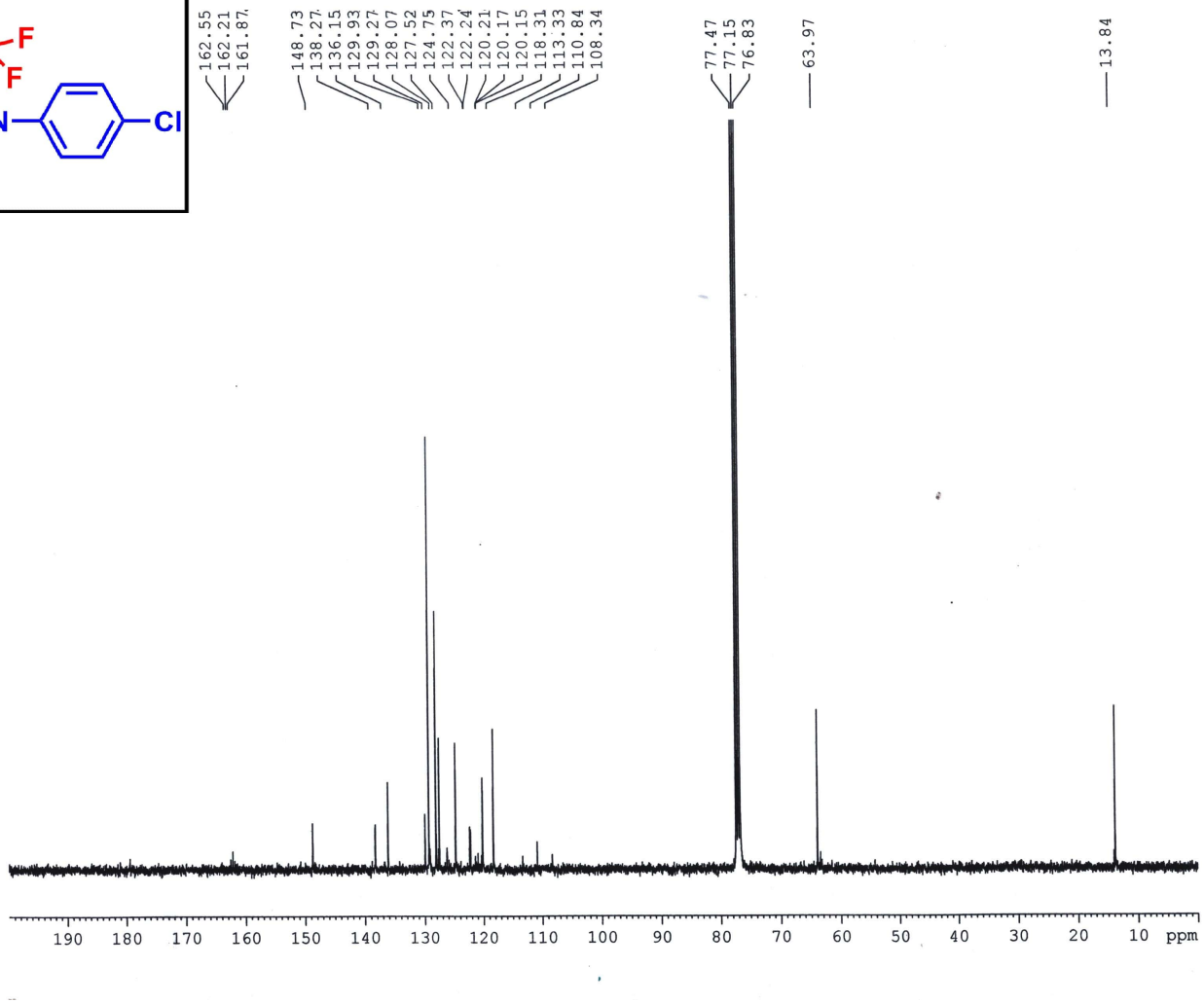
Solvent : $CDCl_3$

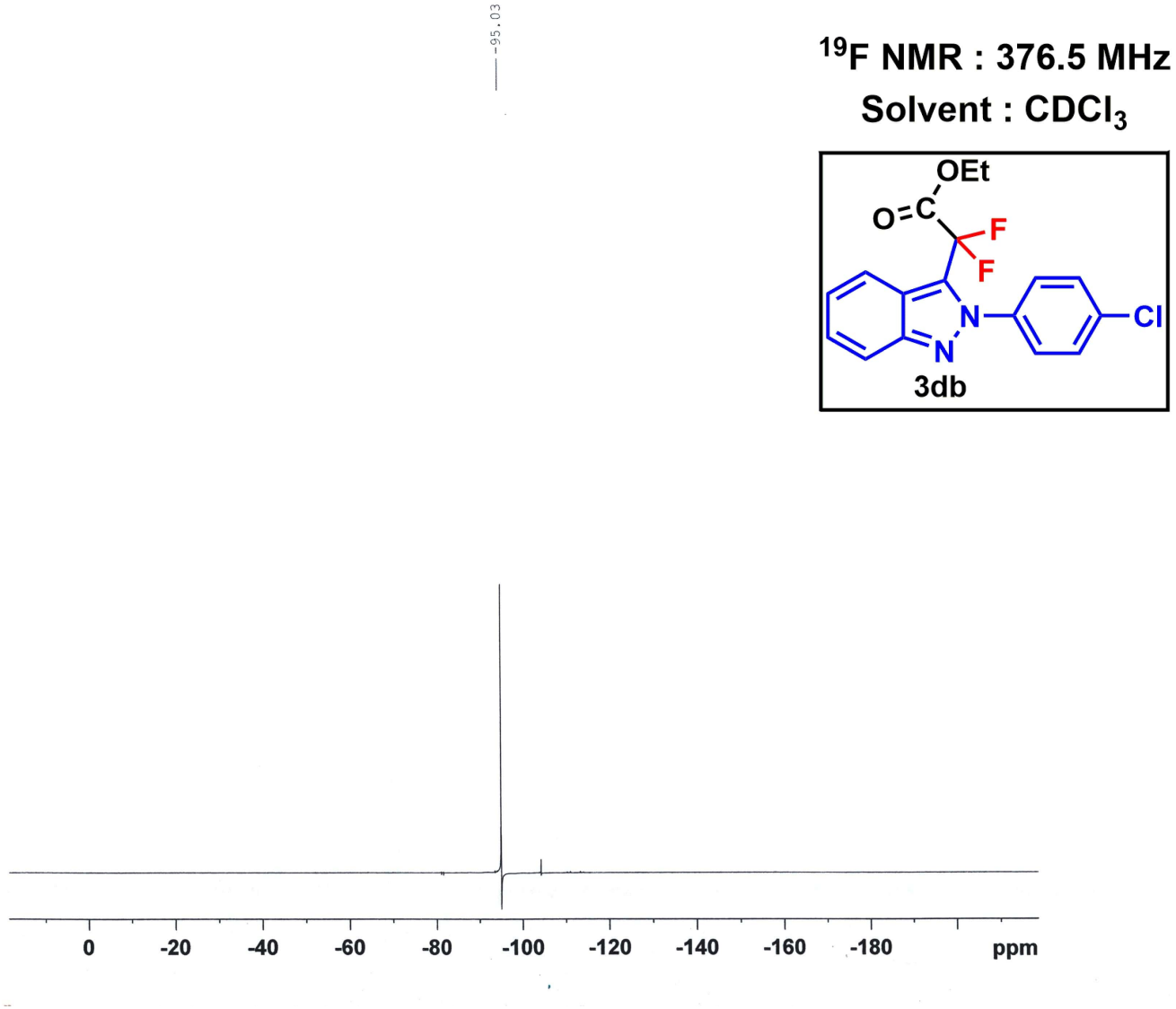
3db

$^{13}C\{^{1}H\}$ NMR : 100 MHz

Solvent : $CDCl_3$

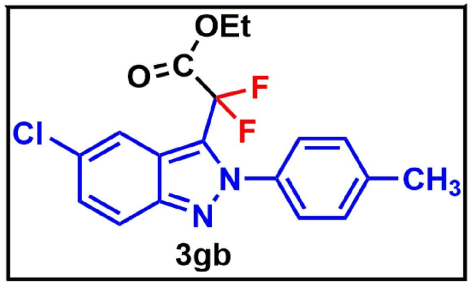


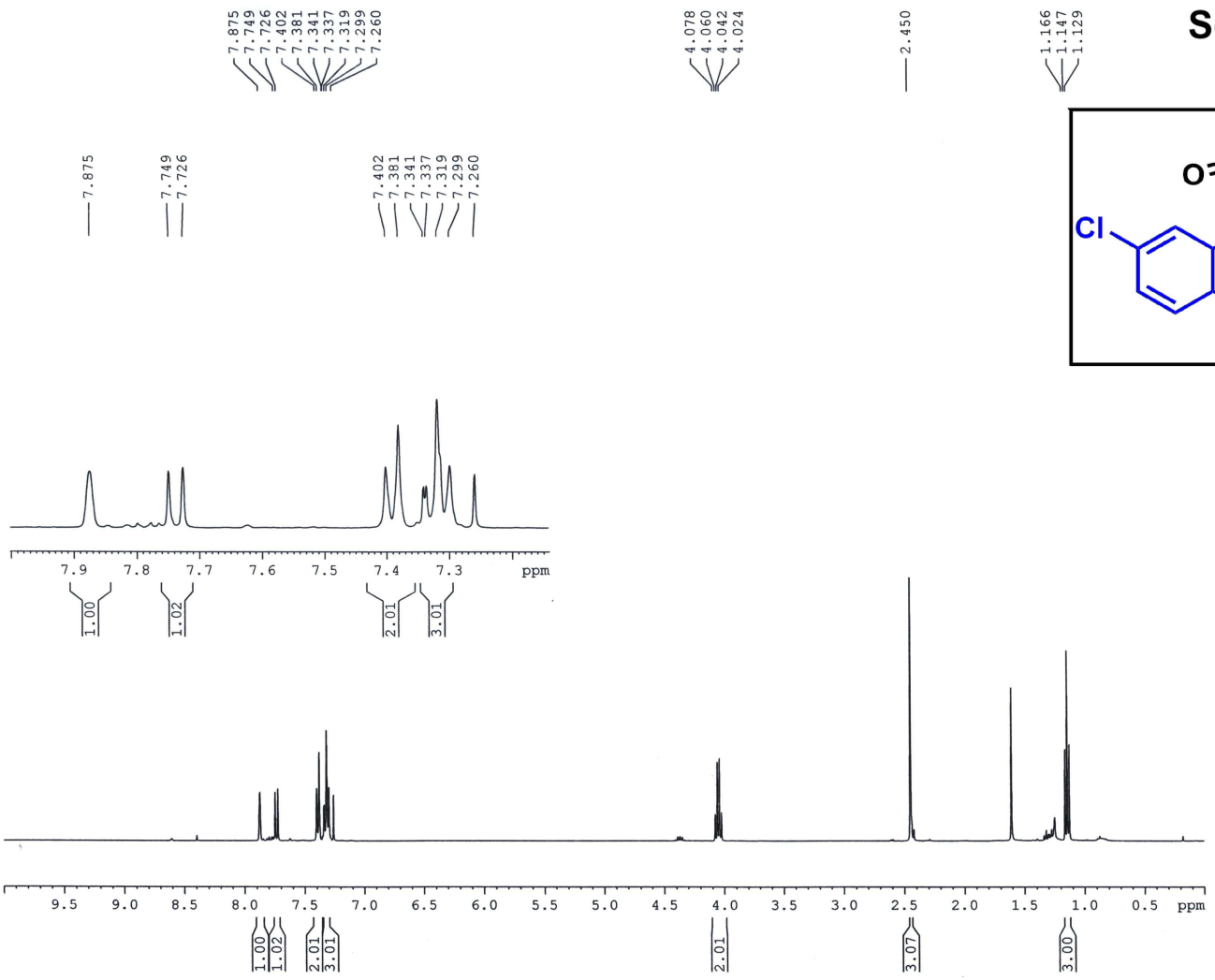



-95.03
^{19}F NMR : 376.5 MHz
Solvent : $CDCl_3$
OEt
O=C
F
F
N
N
Cl
3db
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

^{1}H NMR : 400 MHz

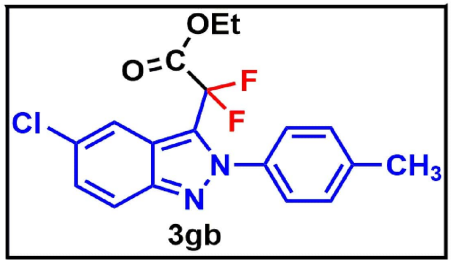
Solvent : $CDCl_3$





$^{13}C\{^{1}H\}$ NMR : 100 MHz

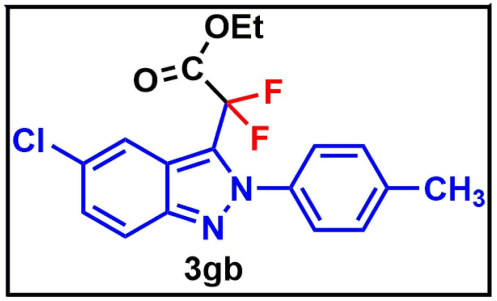
Solvent : $CDCl_3$



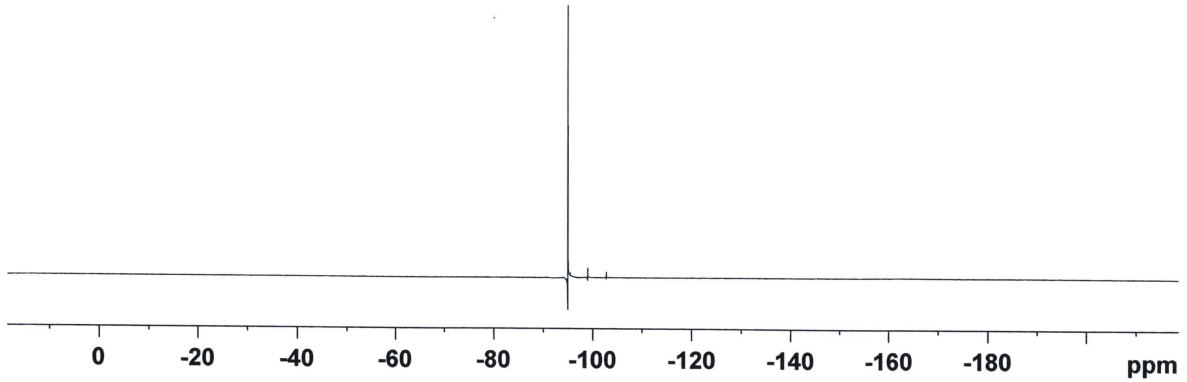
3gb

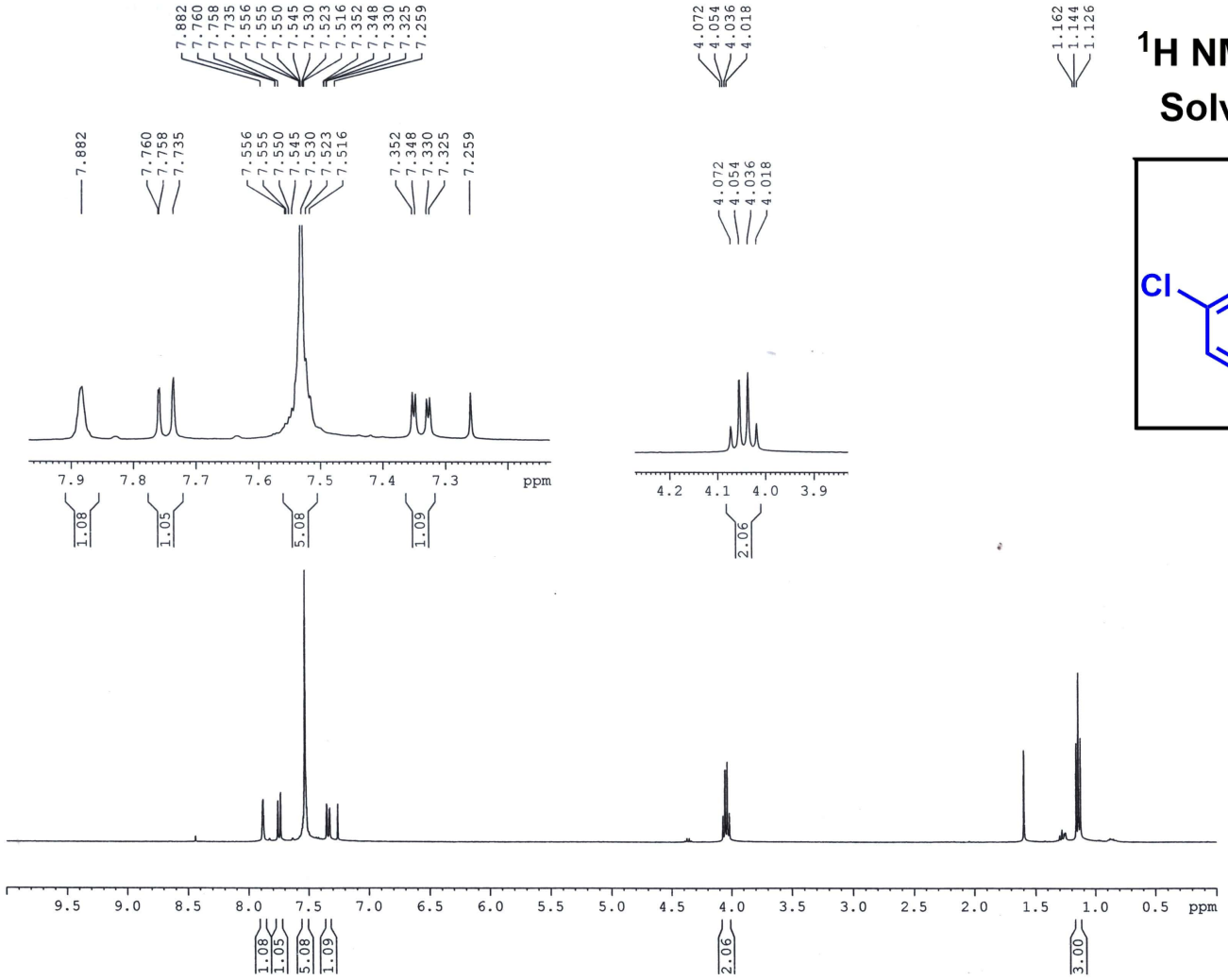
^{19}F NMR : 376.5 MHz

Solvent : $CDCl_3$



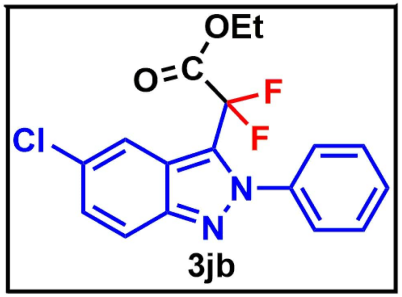
3gb





^{1}H NMR : 400 MHz

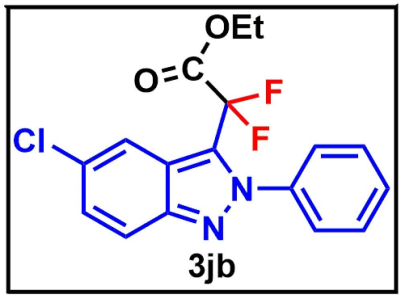
Solvent : $CDCl_3$



3jb

$^{13}C\{^{1}H\}$ NMR : 100 MHz

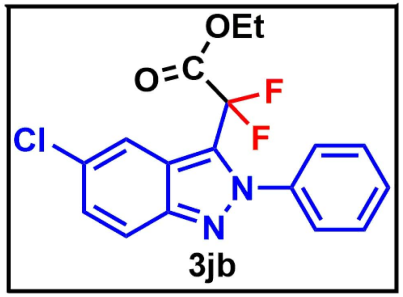
Solvent : $CDCl_3$



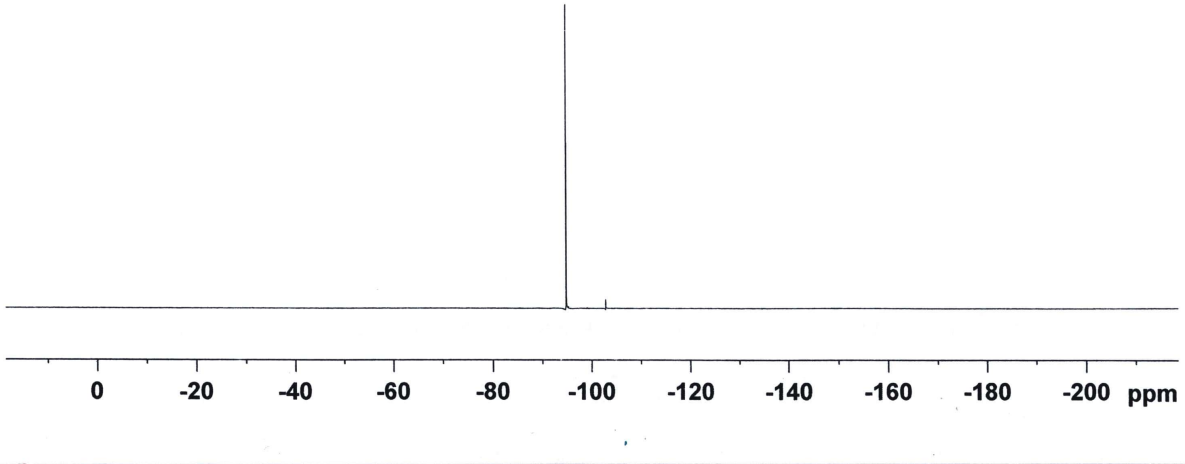
3jb

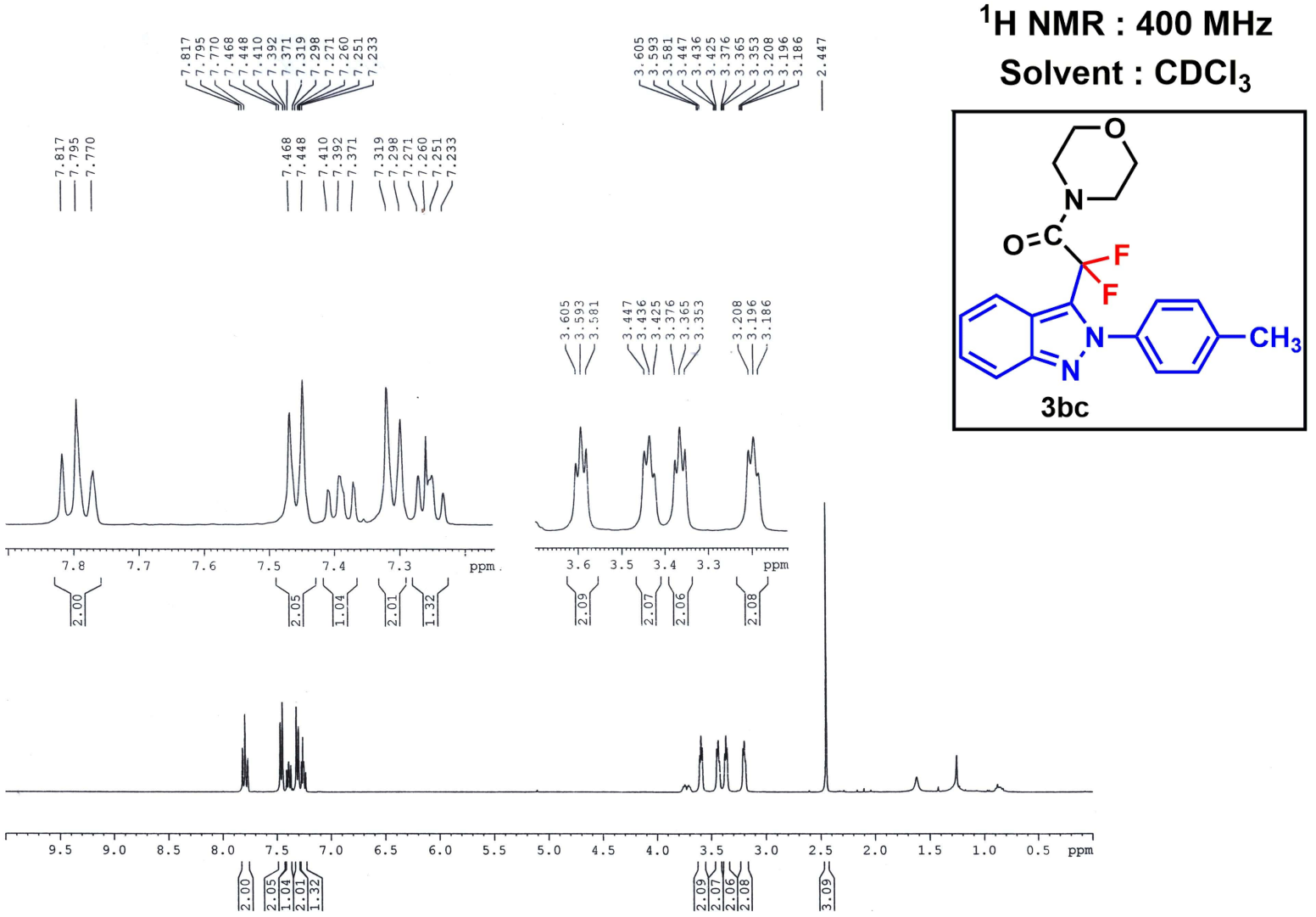
^{19}F NMR : 376.5 MHz

Solvent : $CDCl_3$



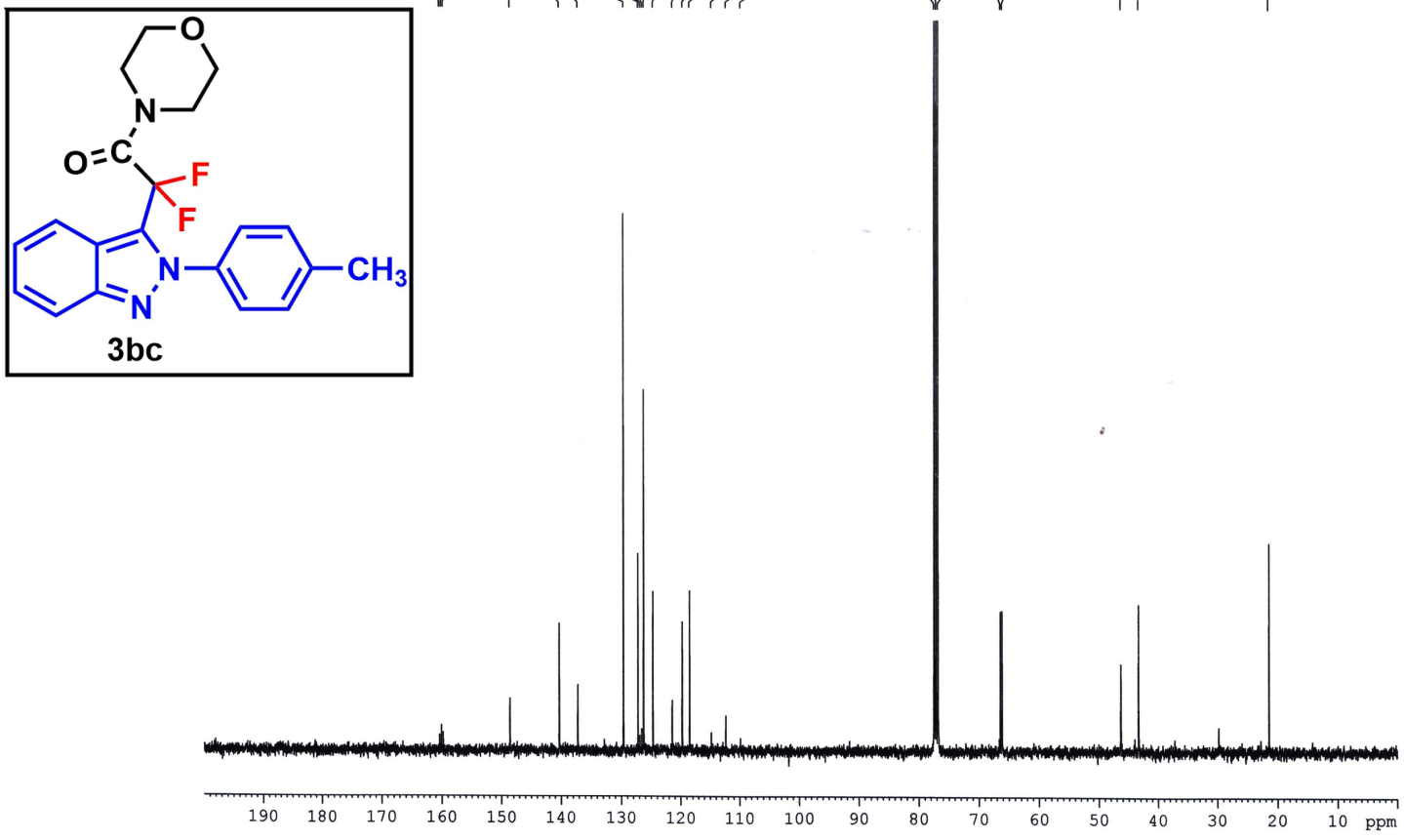
3jb




^{1}H NMR : 400 MHz
Solvent : $CDCl_3$
3bc

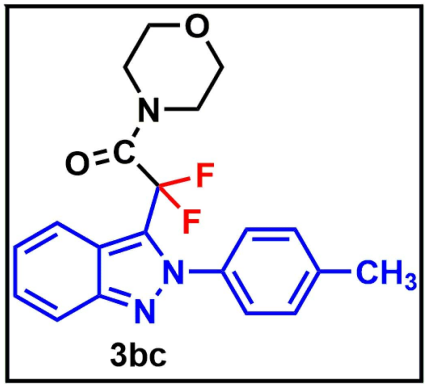
$^{13}C\{^{1}H\}$ NMR : 100 MHz

Solvent : $CDCl_3$

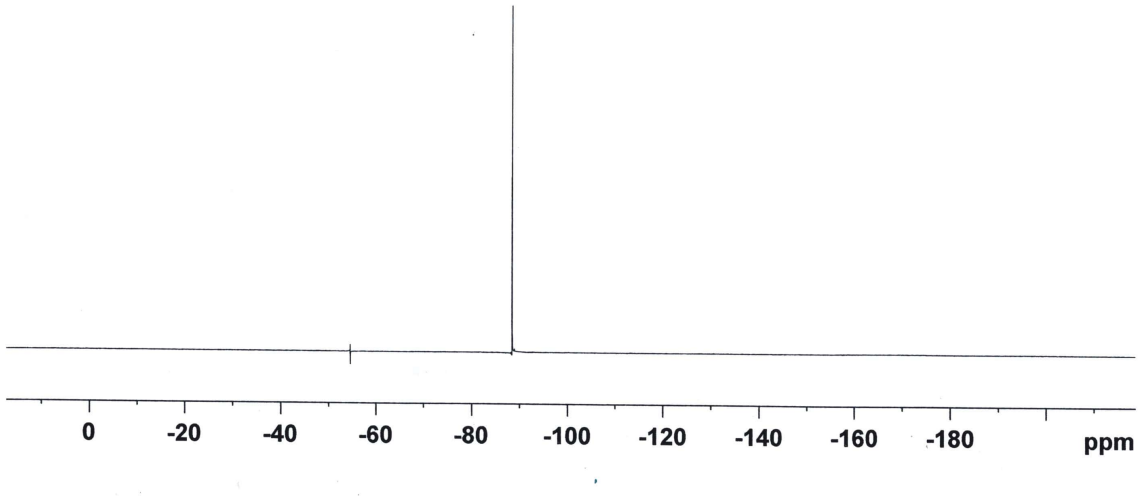


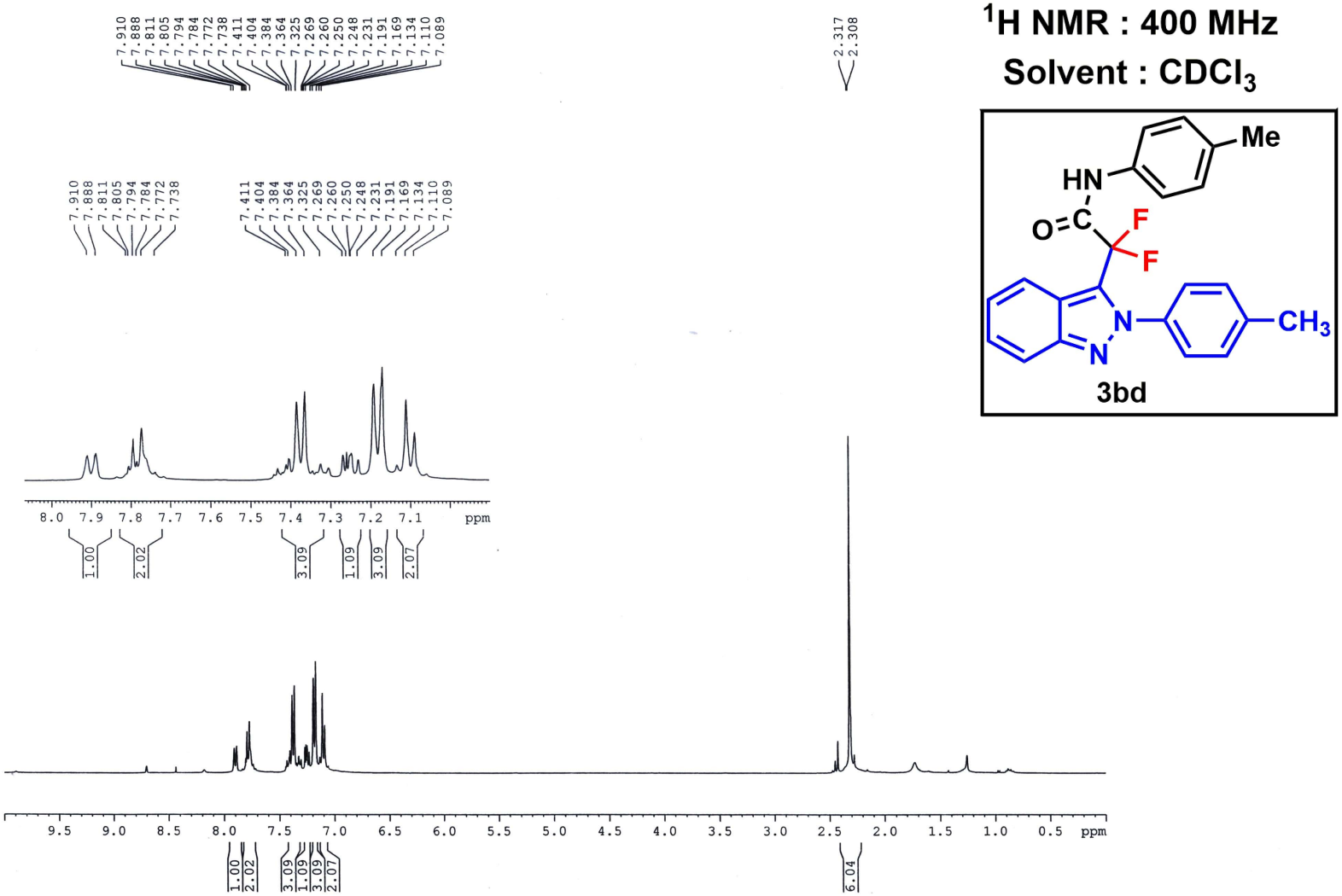
^{19}F NMR : 376.5 MHz

Solvent : $CDCl_3$



3bc





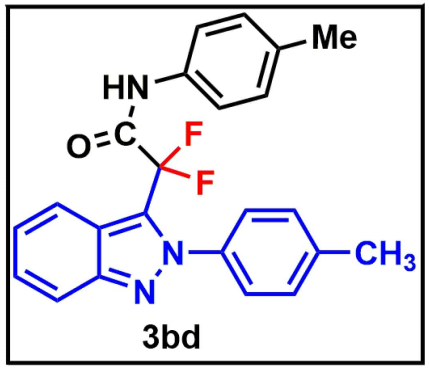
^{1}H NMR : 400 MHz

Solvent : $CDCl_3$

3bd

$^{13}C\{^{1}H\}$ NMR : 100 MHz

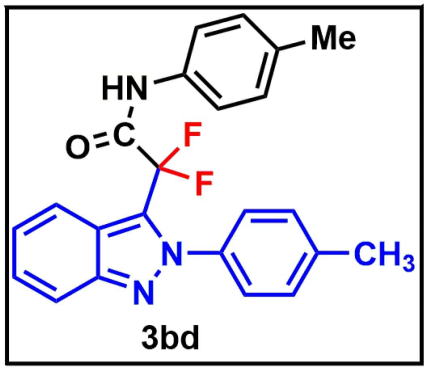
Solvent : $CDCl_3$



3bd

^{19}F NMR : 376.5 MHz

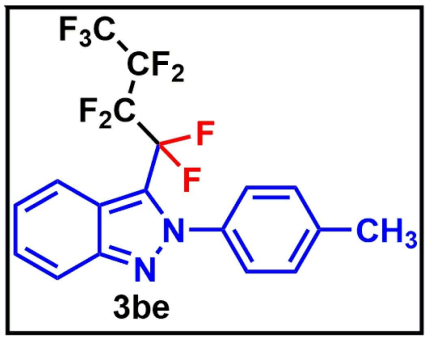
Solvent : $CDCl_3$



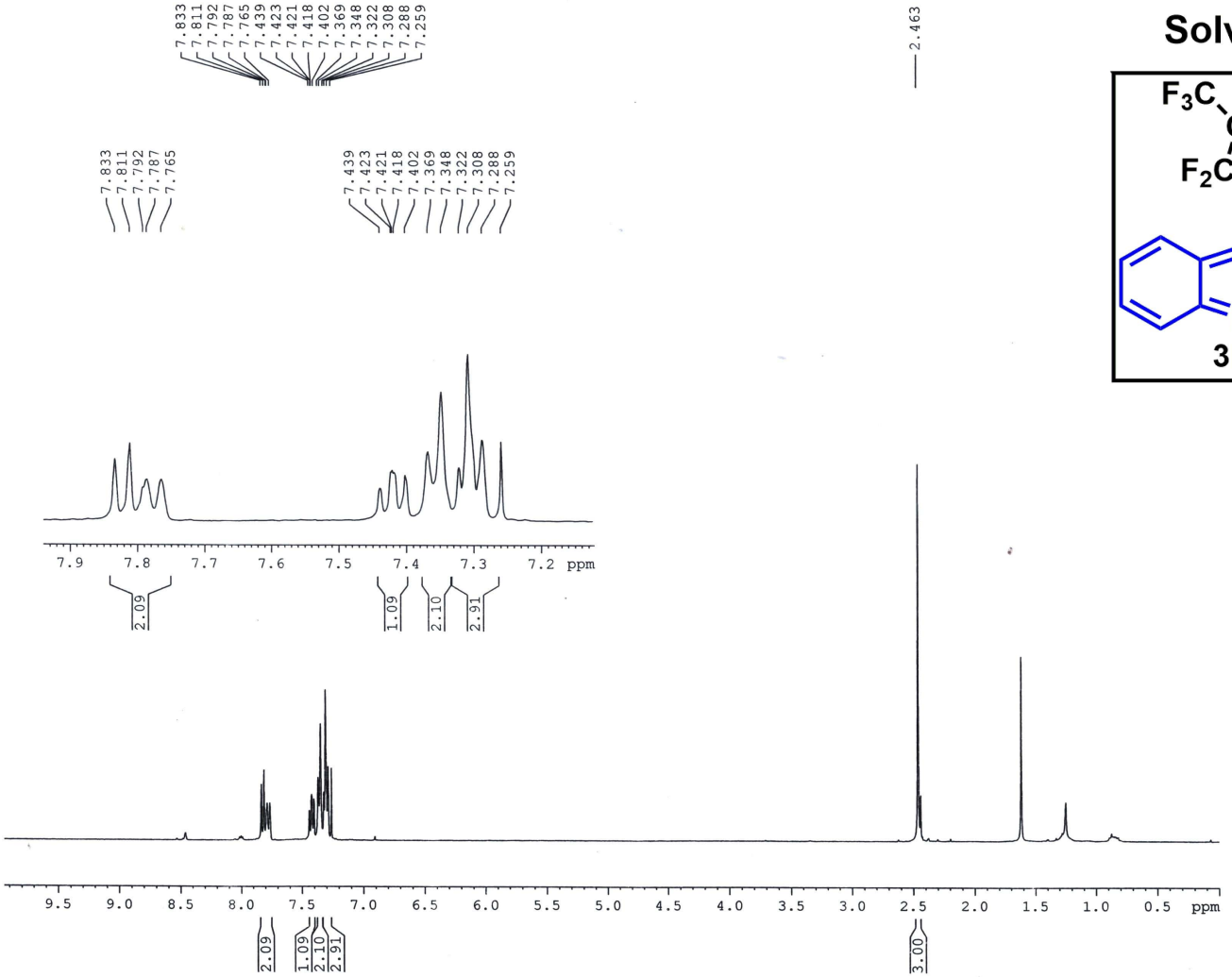
3bd

^{1}H NMR : 400 MHz

Solvent : $CDCl_3$

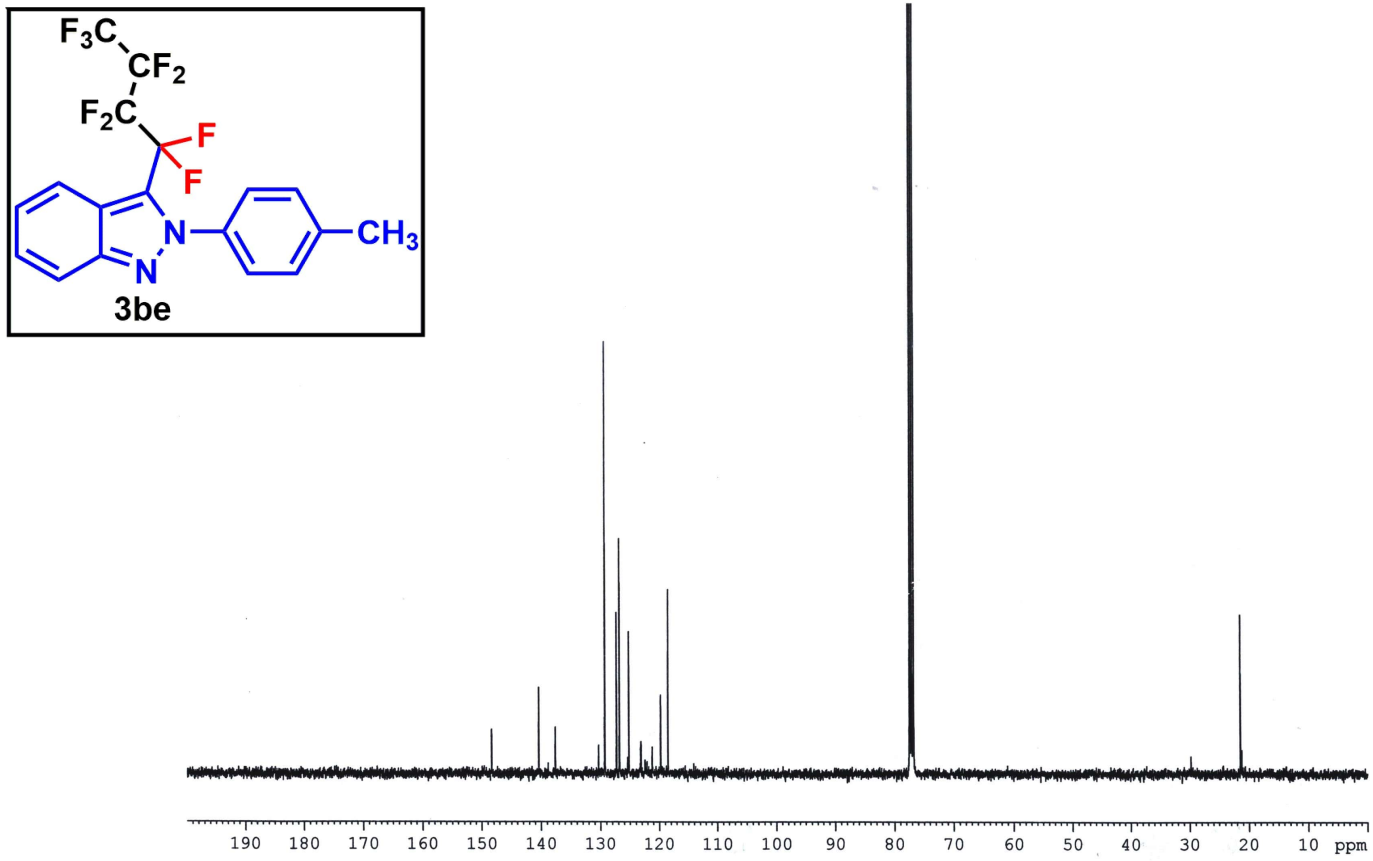


3be



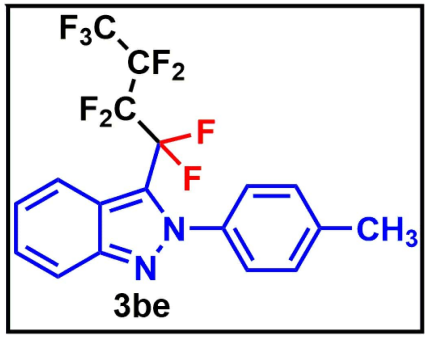
$^{13}C\{^{1}H\}$ NMR : 100 MHz

Solvent : $CDCl_3$

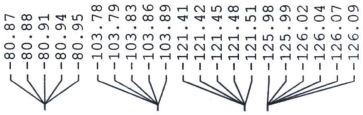


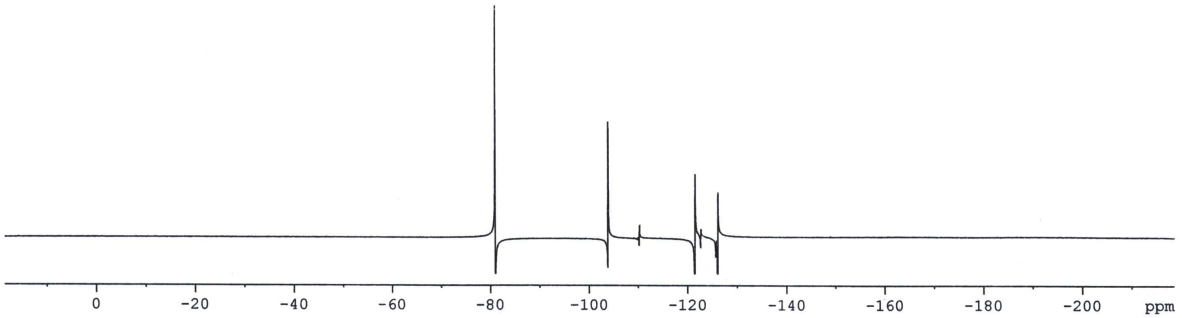
^{19}F NMR : 376.5 MHz

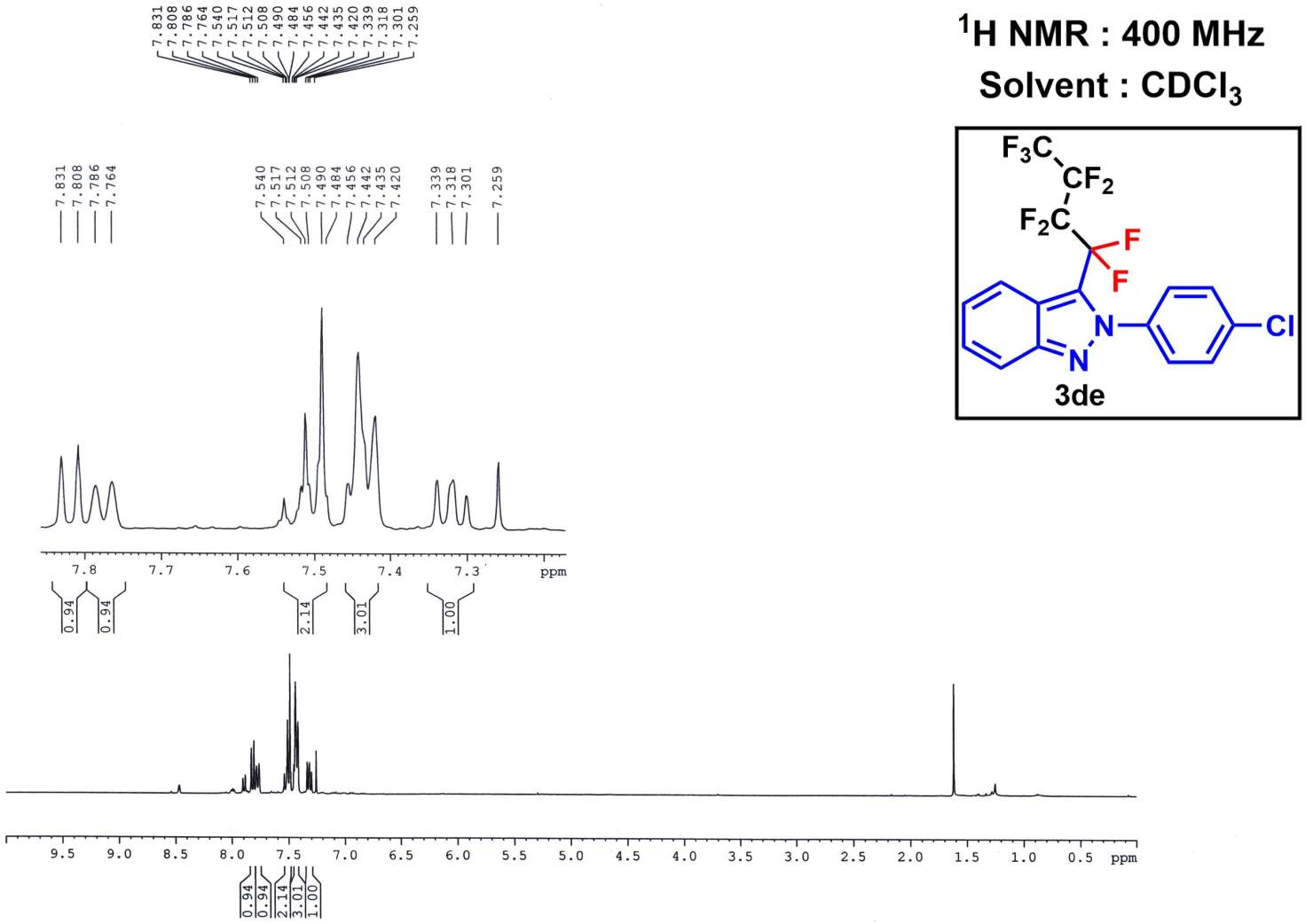
Solvent : $CDCl_3$



3be



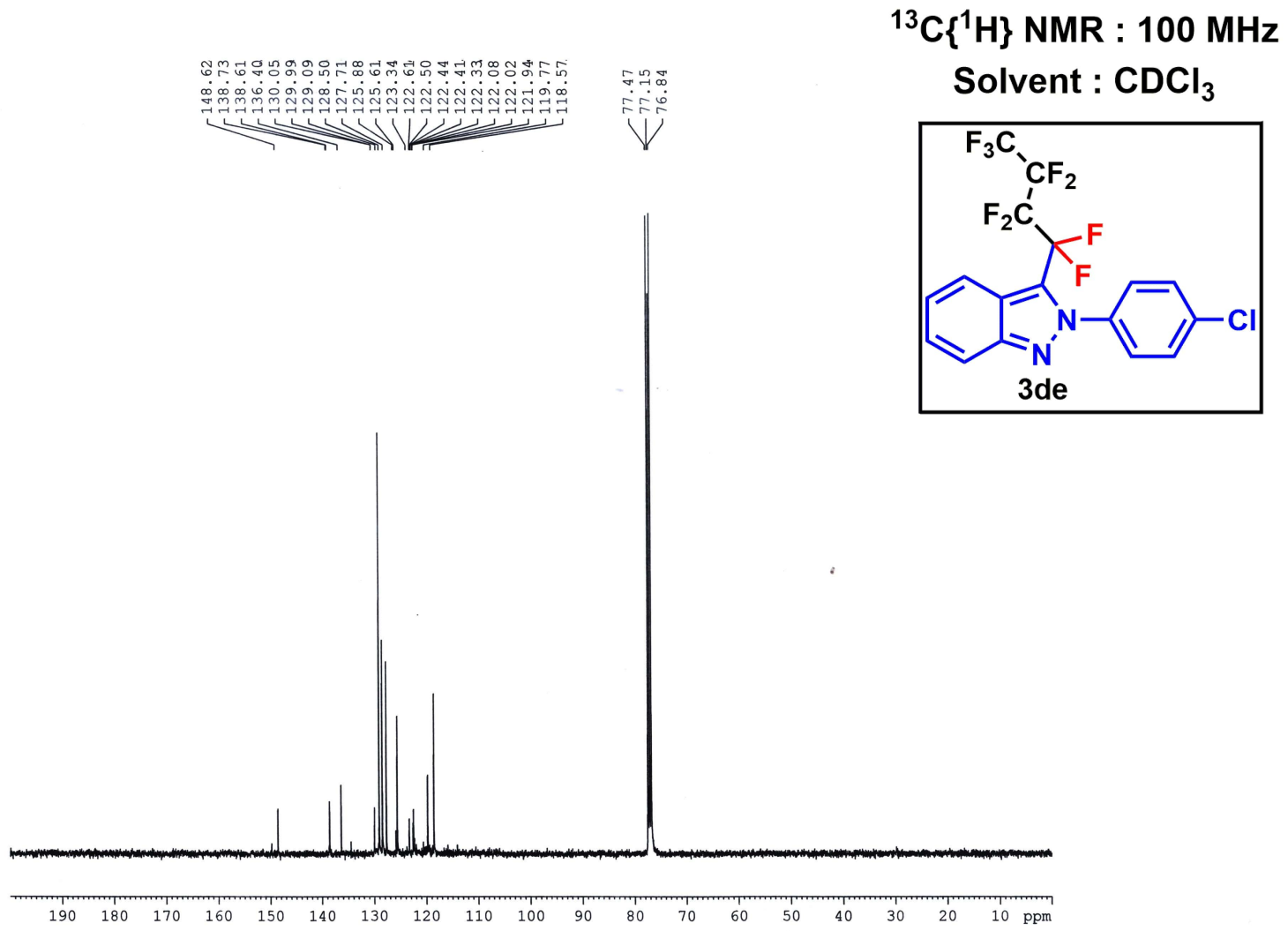




^{1}H NMR : 400 MHz

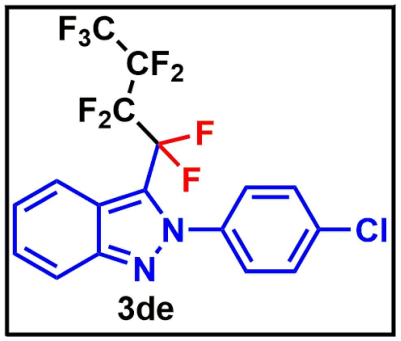
Solvent : $CDCl_3$

3de

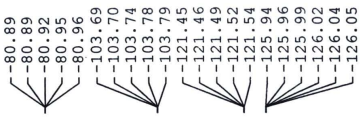

$^{13}C\{^{1}H\}$ NMR : 100 MHz
Solvent : $CDCl_3$
148.62
138.73
138.61
136.40
130.05
129.99
129.09
128.50
127.71
125.88
125.61
123.34
122.61
122.50
122.44
122.41
122.33
122.08
122.02
121.94
119.77
118.57
77.47
77.15
76.84
F_3C
CF_2
F_2C
F
F
N
N
Cl
3de
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

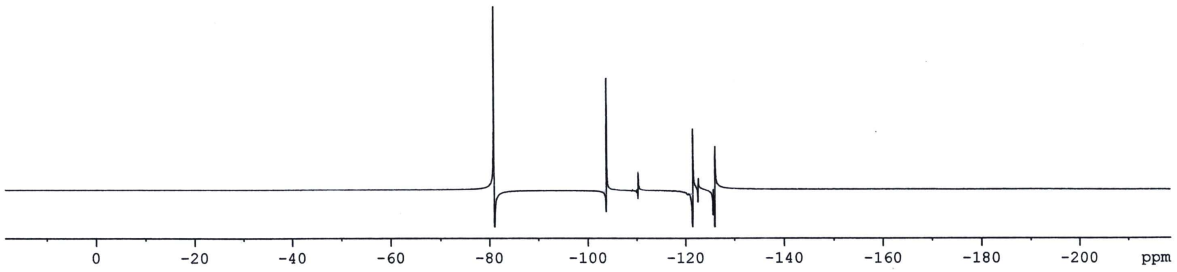
^{19}F NMR : 376.5 MHz

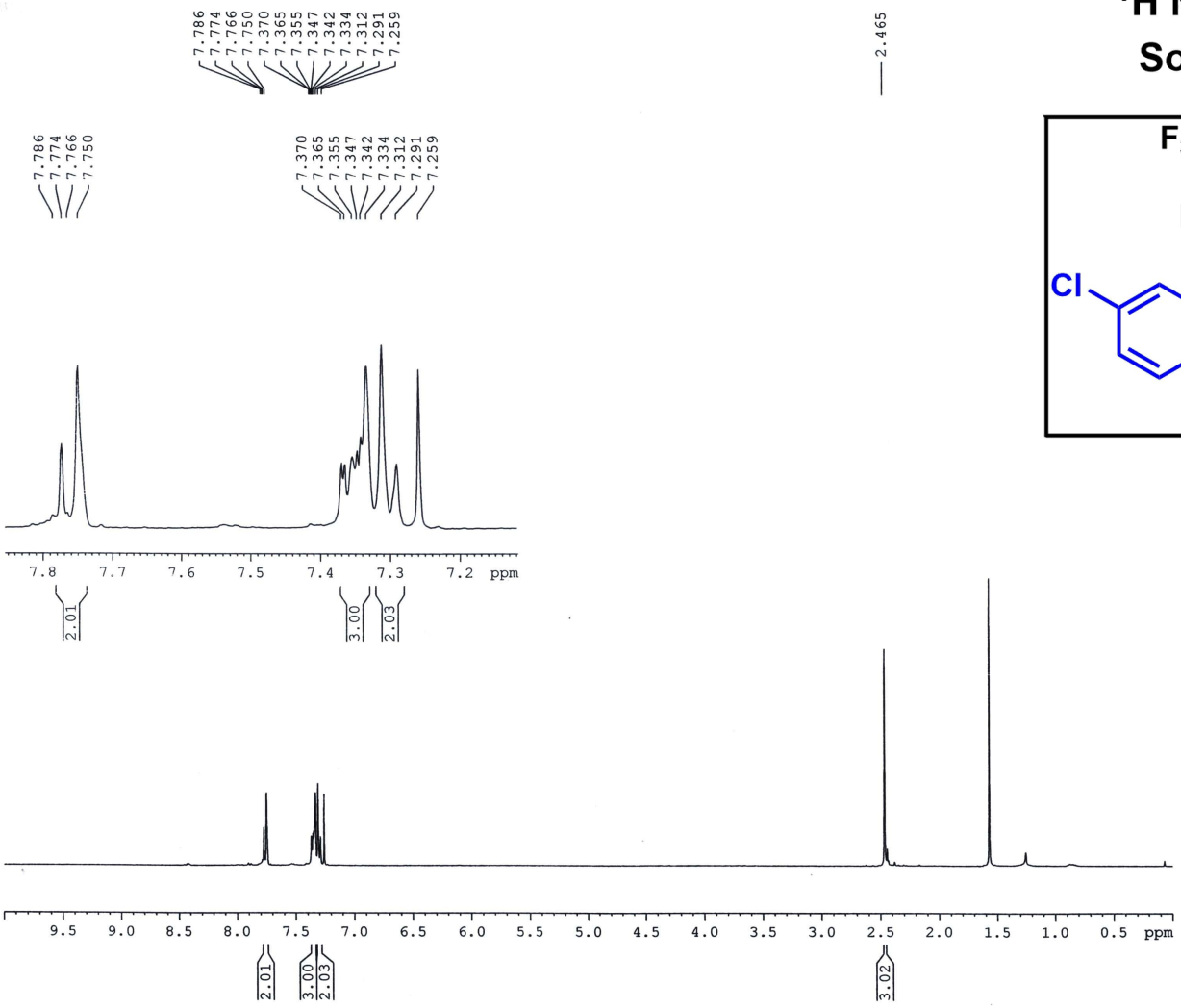
Solvent : $CDCl_3$



3de

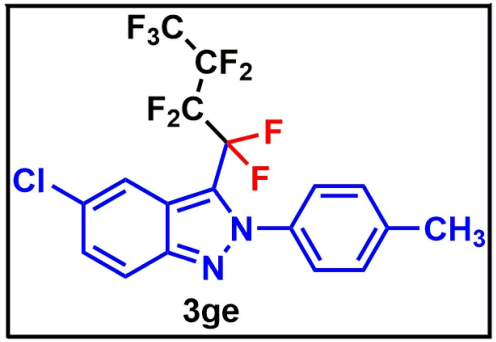




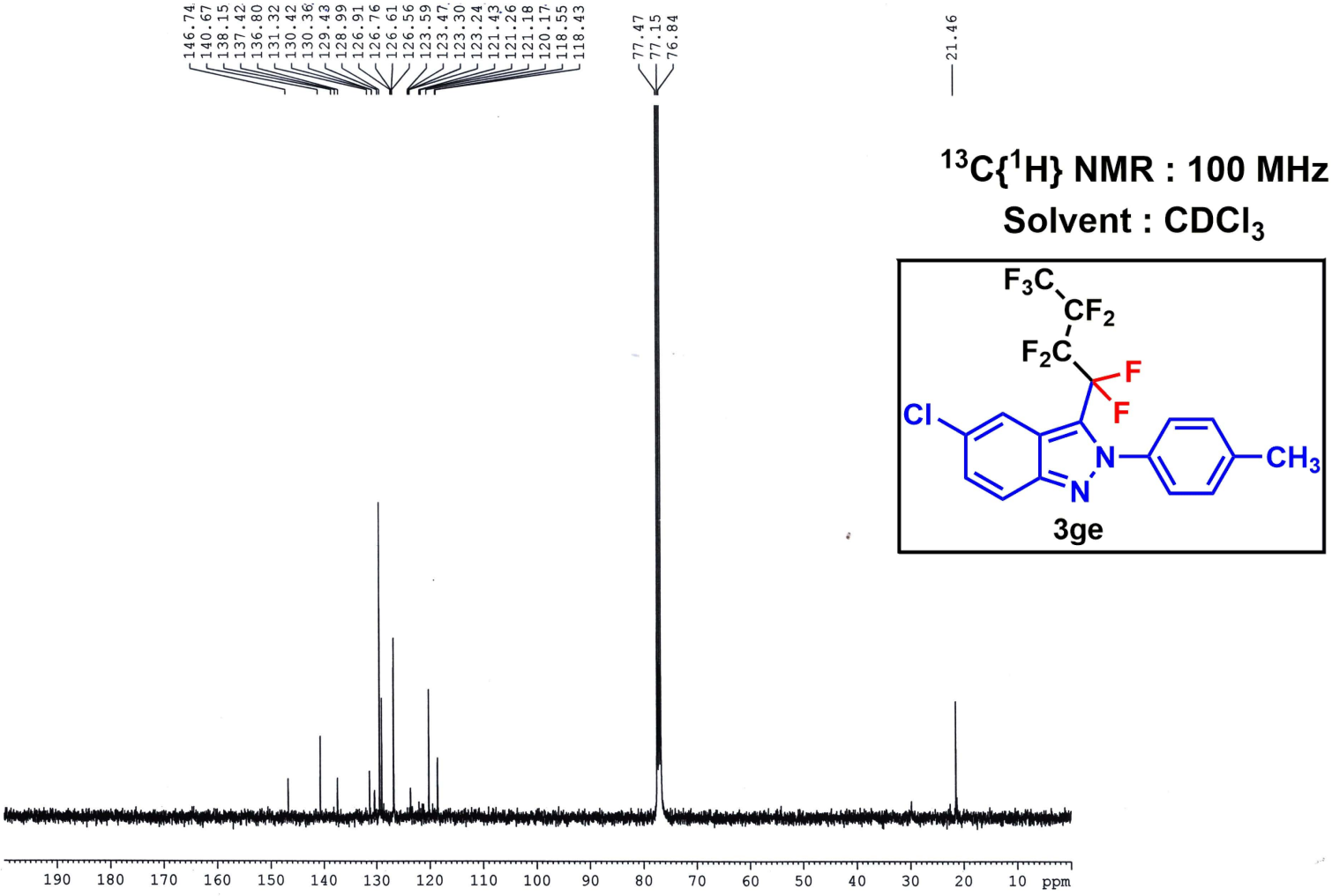


^{1}H NMR : 400 MHz

Solvent : $CDCl_3$



3ge



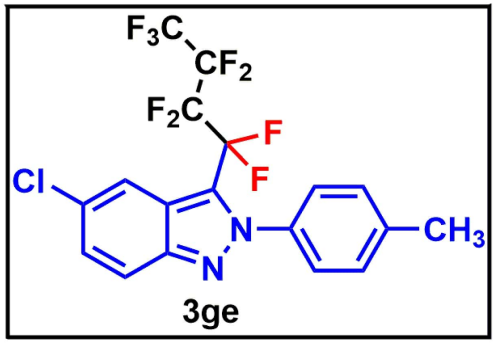
$^{13}C\{^{1}H\}$ NMR : 100 MHz

Solvent : $CDCl_3$

3ge

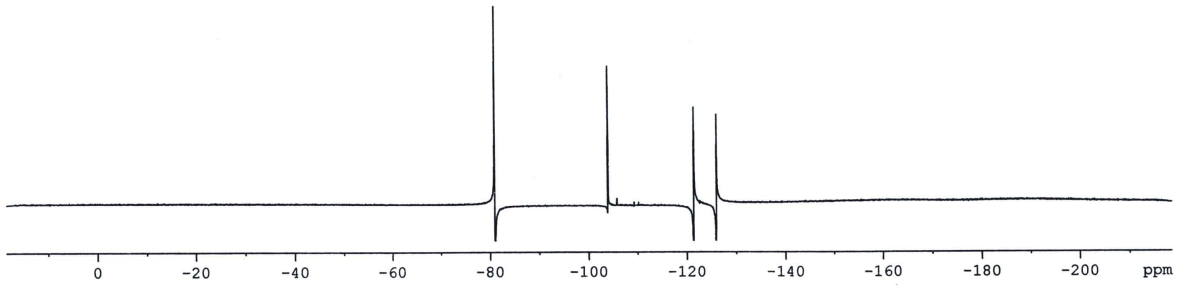
^{19}F NMR : 376.5 MHz

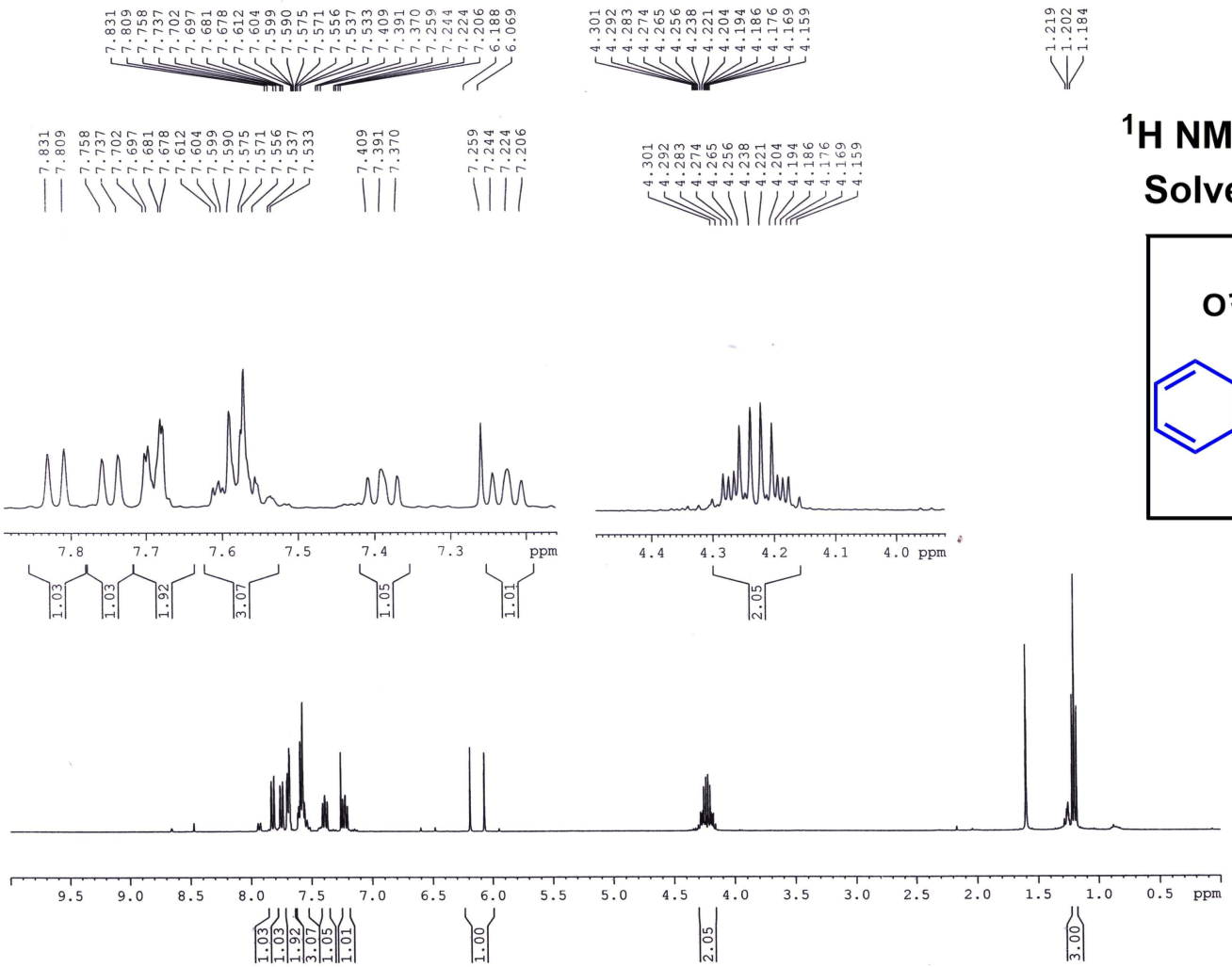
Solvent : $CDCl_3$



3ge

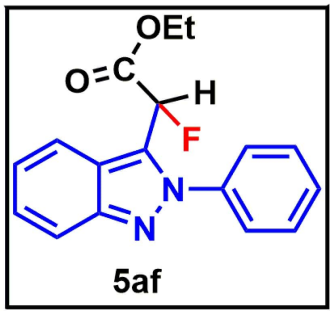
-80.87
-80.88
-80.91
-80.94
-80.95
-103.82
-103.84
-103.88
-103.91
-103.92
-121.31
-121.33
-121.36
-121.39
-121.41
-125.87
-125.89
-125.92
-125.94
-125.97
-125.98





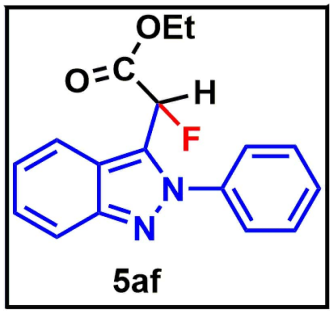
^{1}H NMR : 400 MHz

Solvent : $CDCl_3$

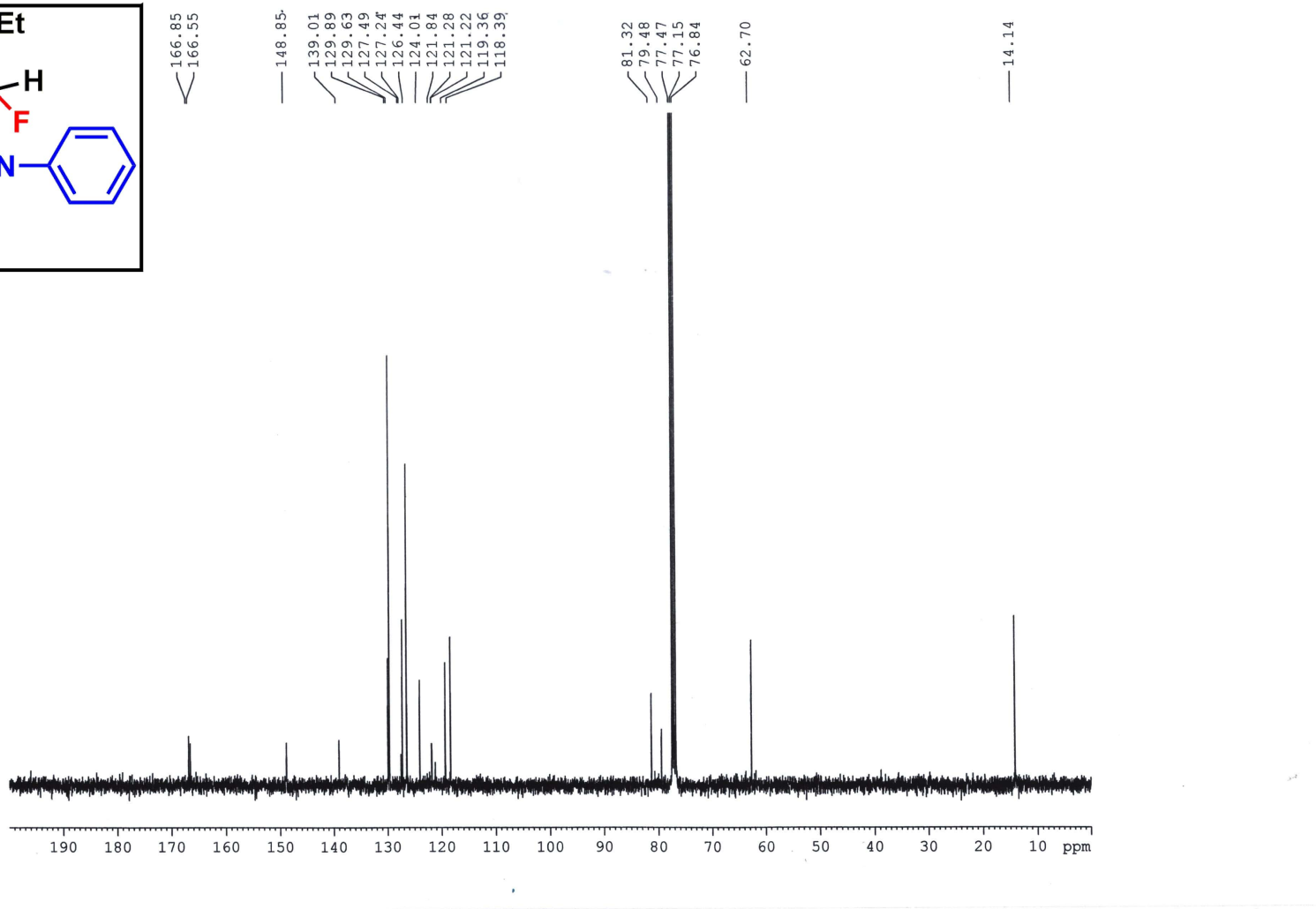


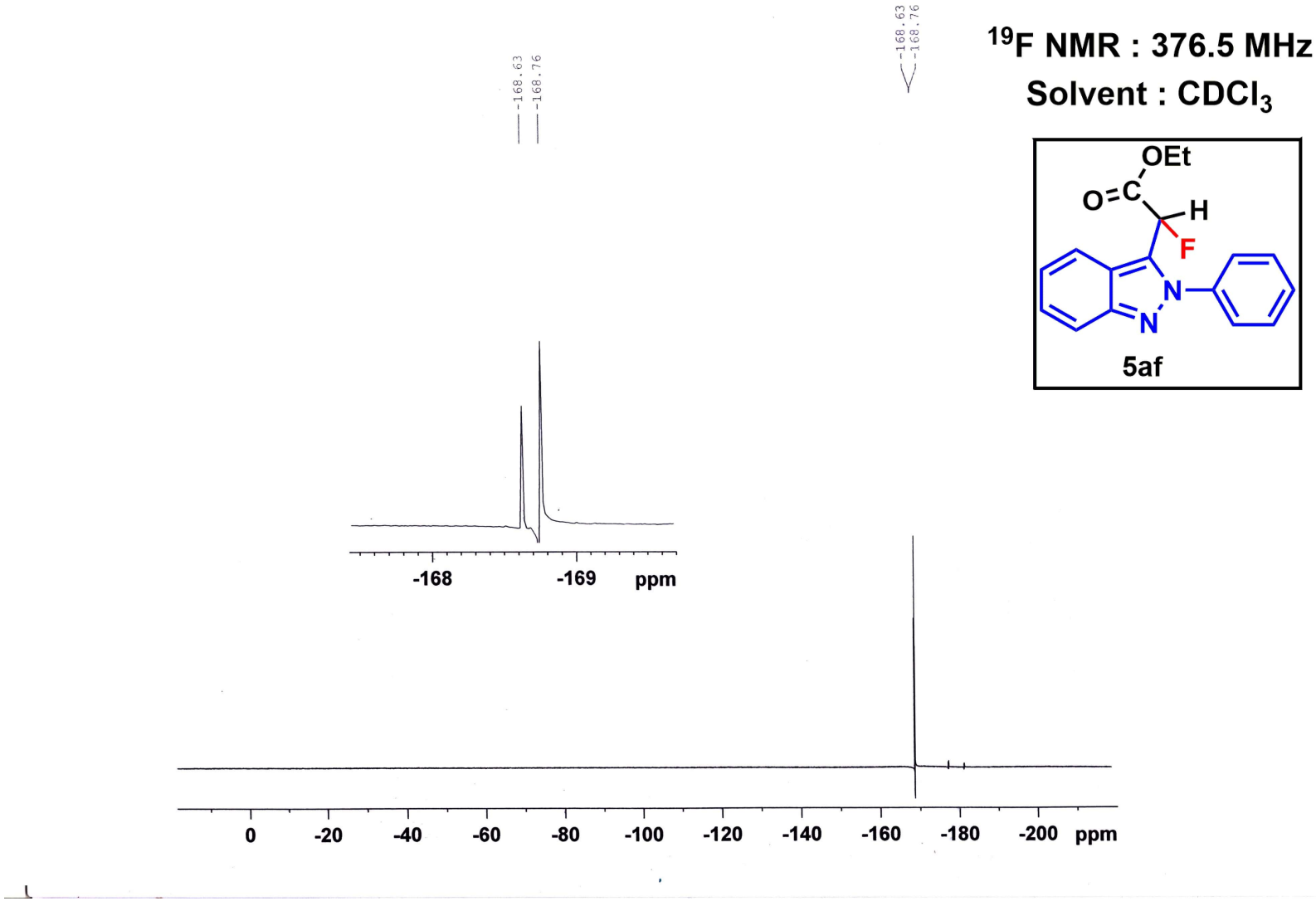
$^{13}C\{^{1}H\}$ NMR : 100 MHz

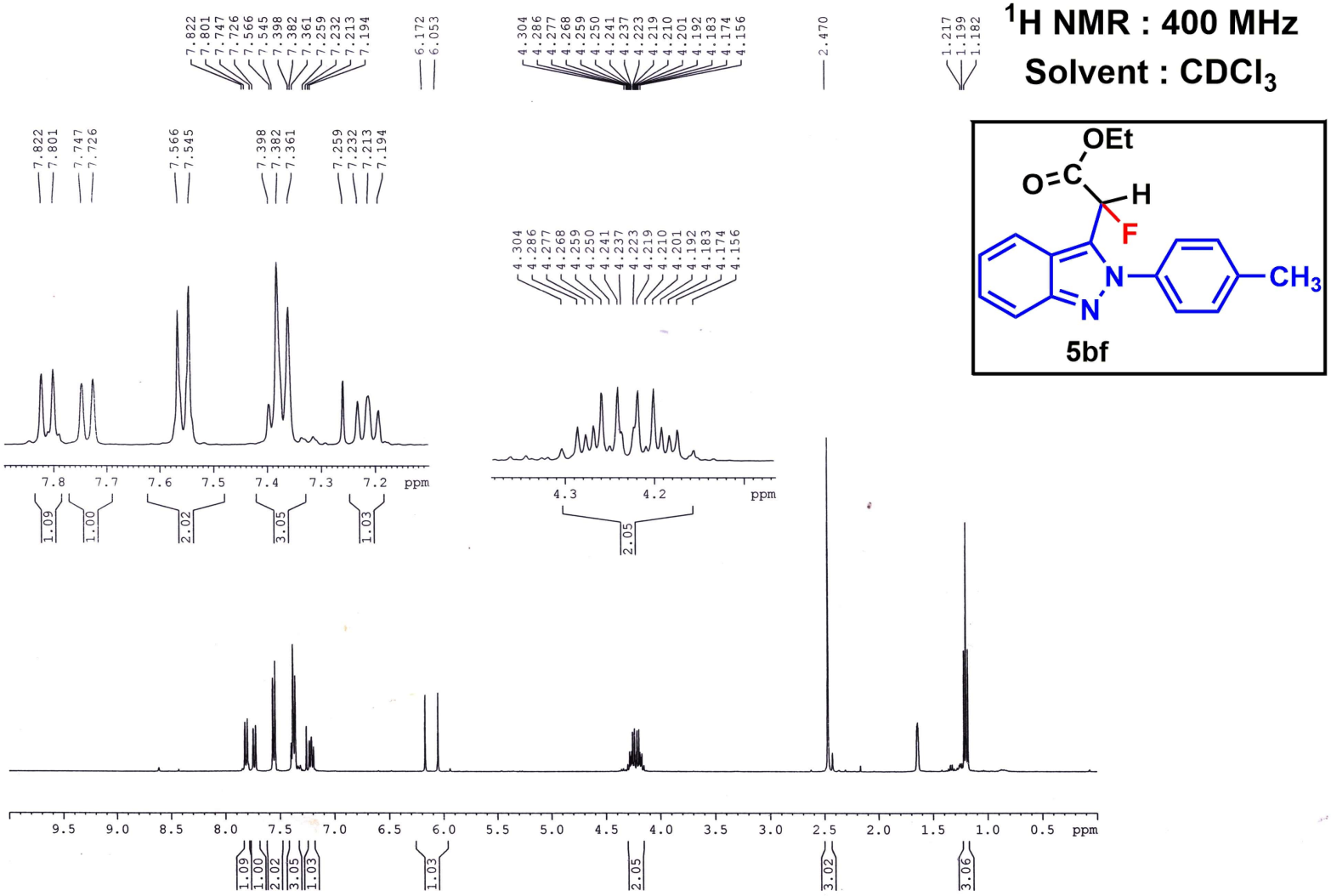
Solvent : $CDCl_3$



5af

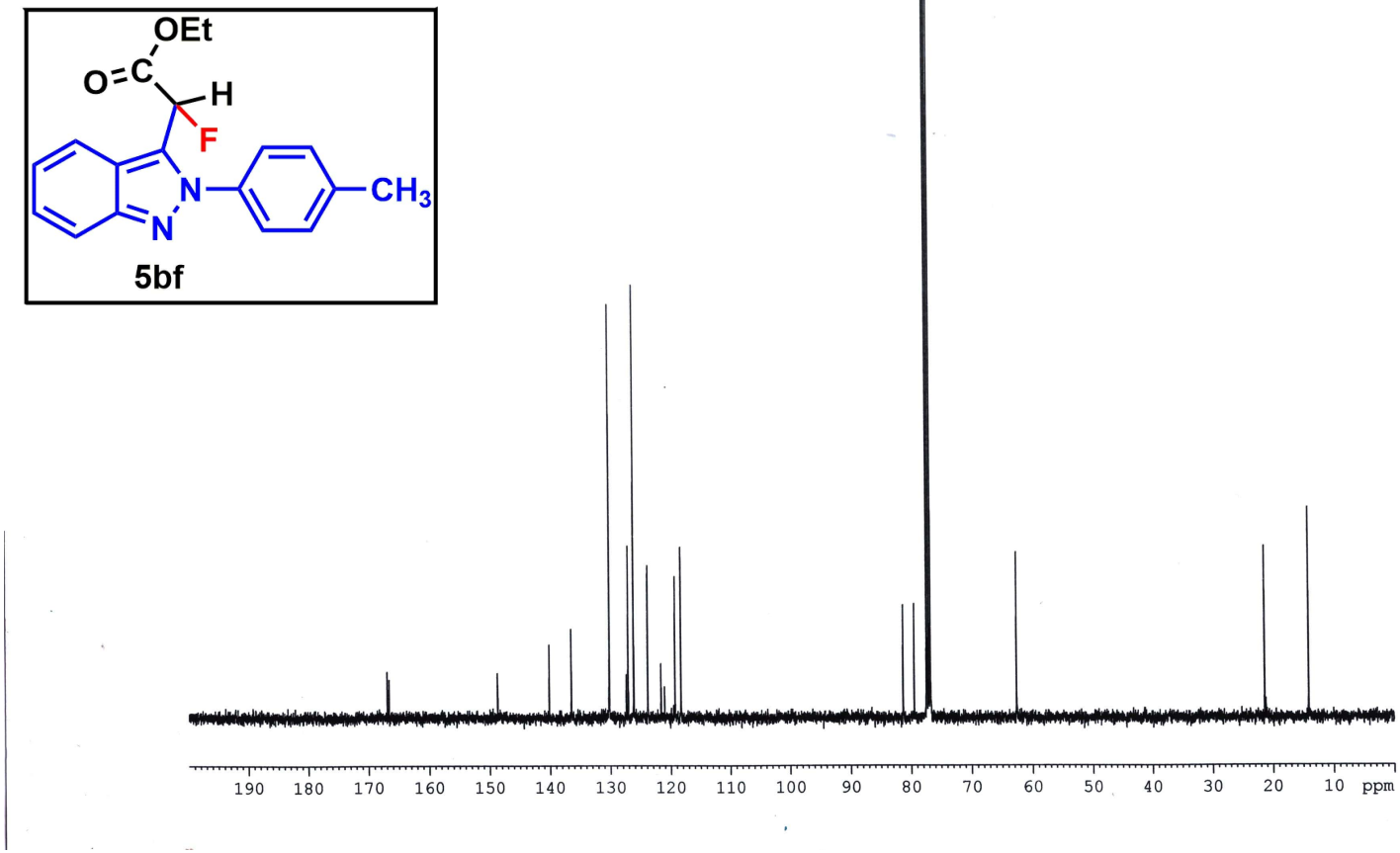


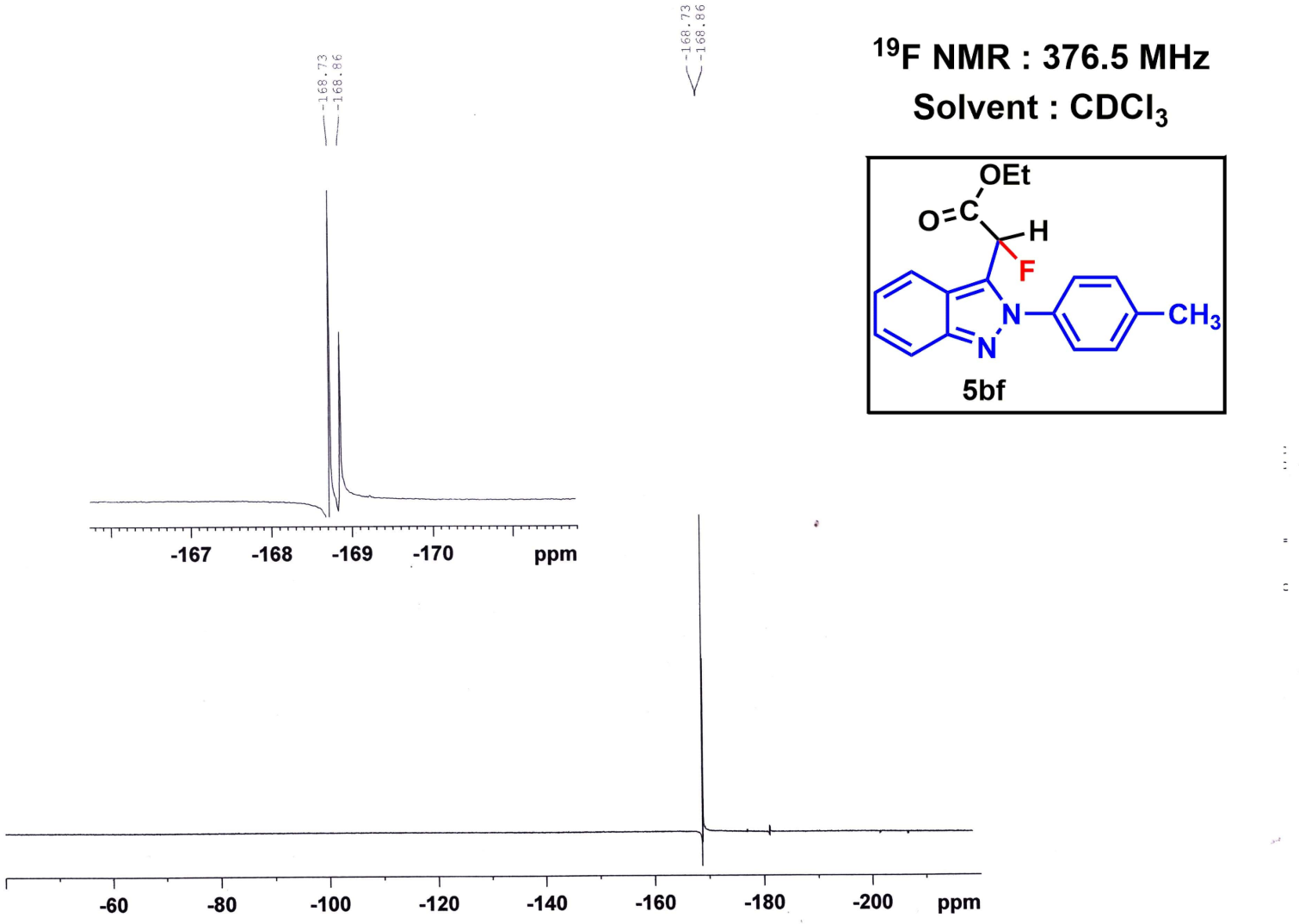

-168.63
-168.76
-168.63
-168.76
^{19}F NMR : 376.5 MHz
Solvent : $CDCl_3$
OEt
O=C
H
F
N
N
5af
-168
-169
ppm
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

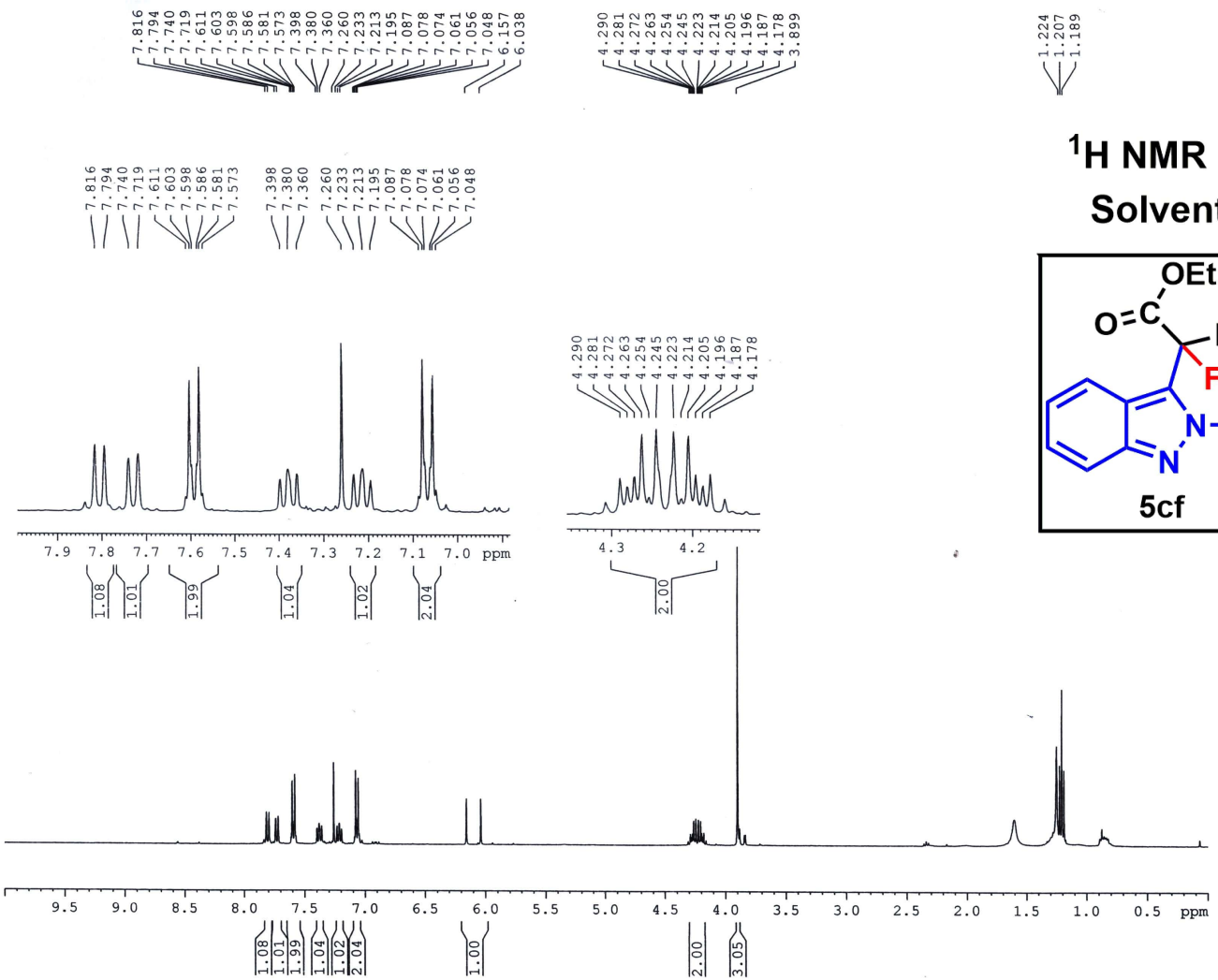

^{1}H NMR : 400 MHz
Solvent : $CDCl_3$
OEt
O=C
H
F
N
N
CH_3
5bf
7.822
7.801
7.747
7.726
7.566
7.545
7.398
7.382
7.361
7.259
7.232
7.213
7.194
6.172
6.053
4.304
4.286
4.277
4.268
4.259
4.250
4.241
4.237
4.223
4.219
4.210
4.201
4.192
4.183
4.174
4.156
2.470
1.217
1.199
1.182
ppm
1.09
1.00
2.02
3.05
1.03
2.05
3.02
3.06

$^{13}C\{^{1}H\}$ NMR : 100 MHz

Solvent : $CDCl_3$

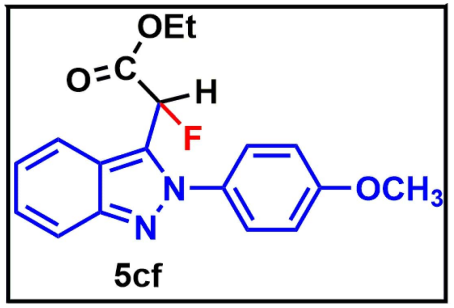



-168.73
-168.86
-168.73
-168.86
19F NMR : 376.5 MHz
Solvent : CDCl3
OEt
O=C
H
F
N
N
CH3
5bf
-167
-168
-169
-170
ppm
-60
-80
-100
-120
-140
-160
-180
-200
ppm



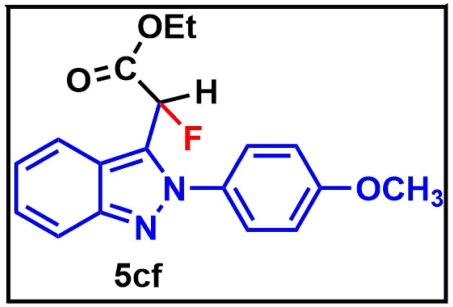
^{1}H NMR : 400 MHz

Solvent : $CDCl_3$

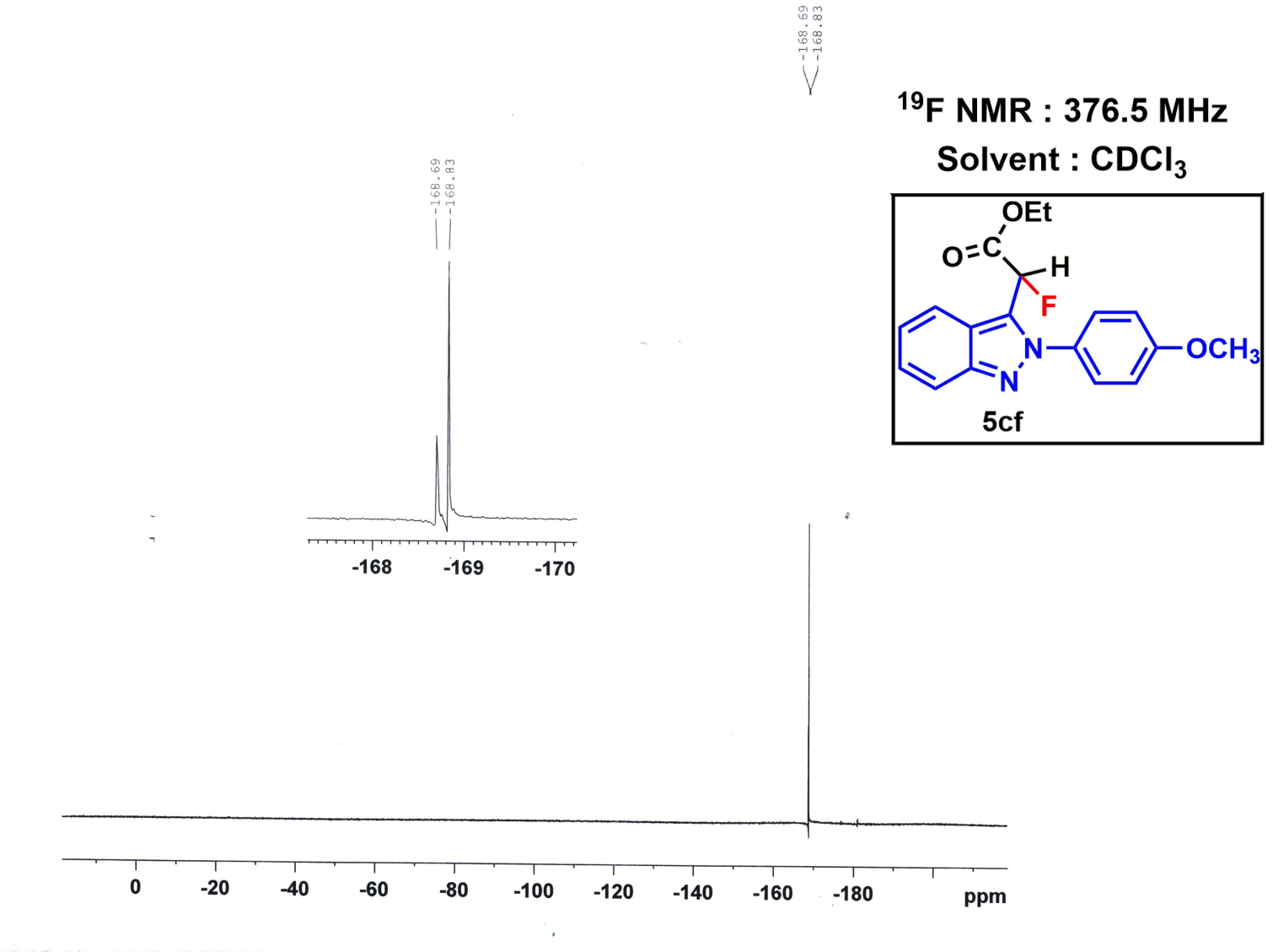


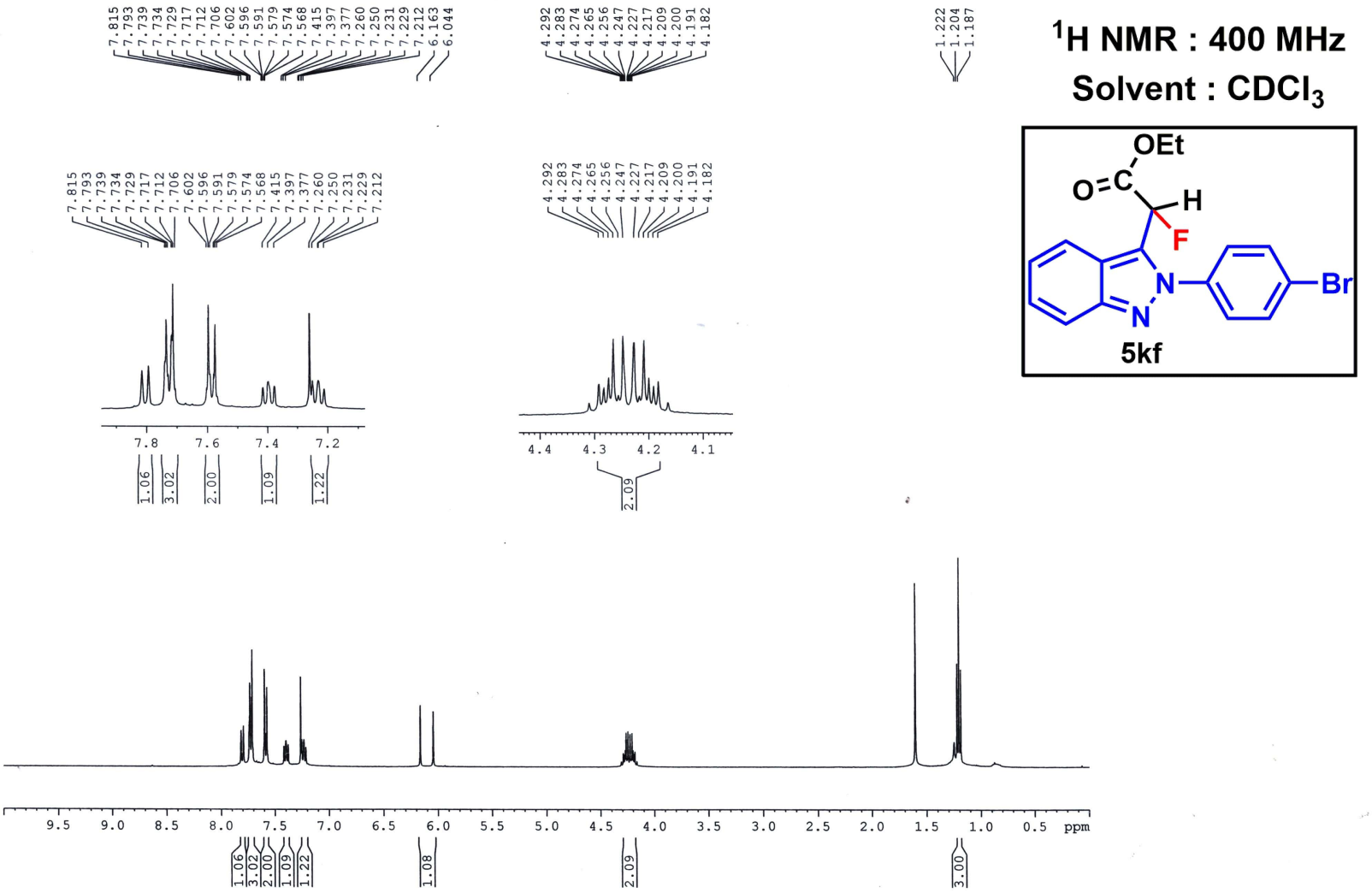
5cf

$^{13}C\{^{1}H\}$ NMR : 100 MHz
Solvent : $CDCl_3$



5cf


-168.69
-168.83
^{19}F NMR : 376.5 MHz
Solvent : $CDCl_3$
OEt
O=C
H
F
N
N
OCH_3
5cf
-168
-169
-170
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

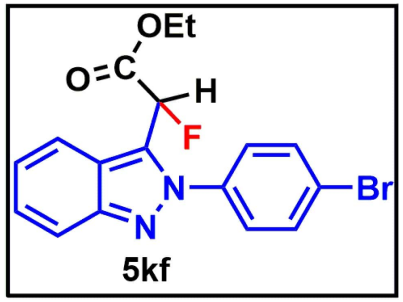


^{1}H NMR : 400 MHz

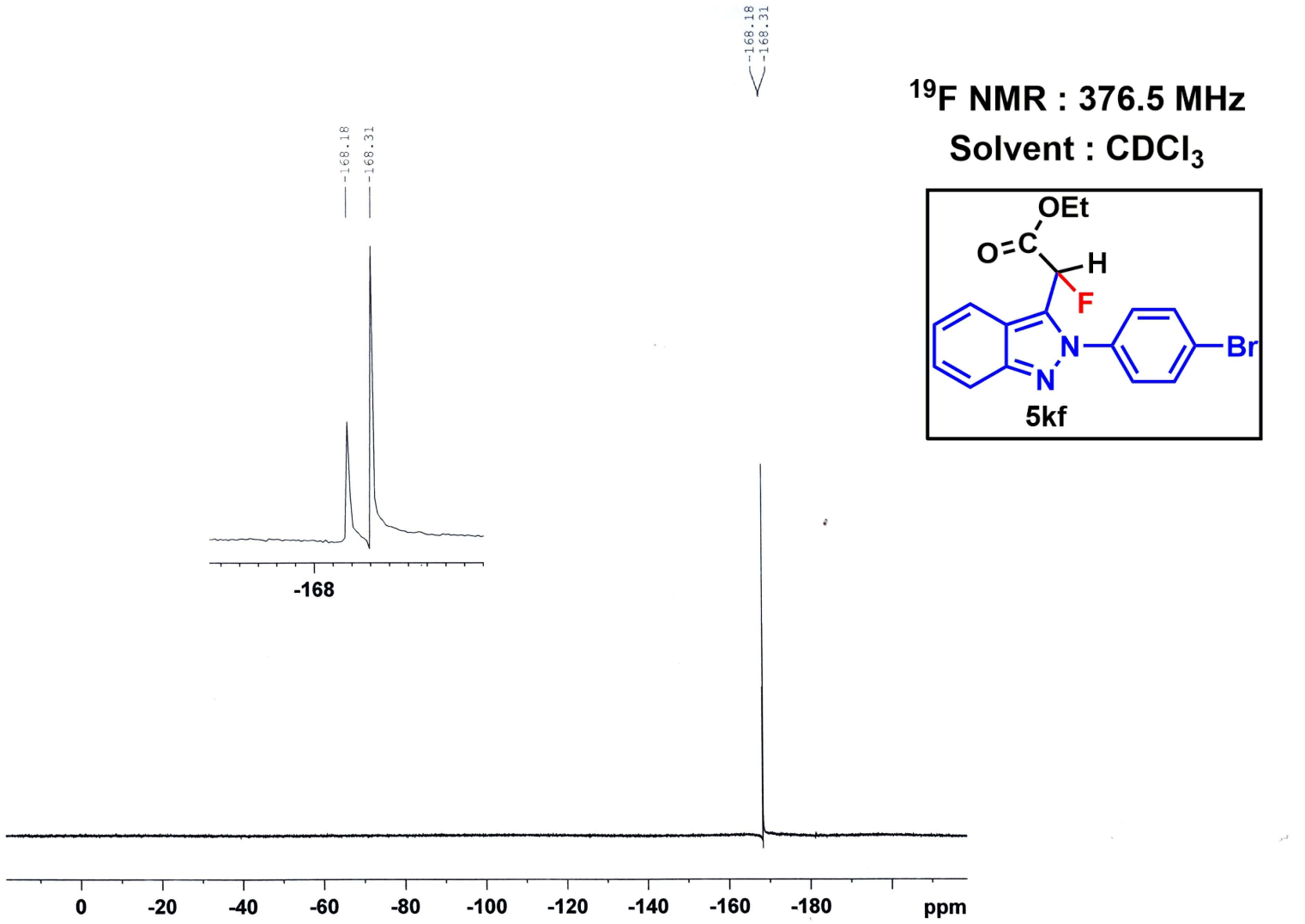
Solvent : $CDCl_3$

$^{13}C\{^{1}H\}$ NMR : 100 MHz

Solvent : $CDCl_3$



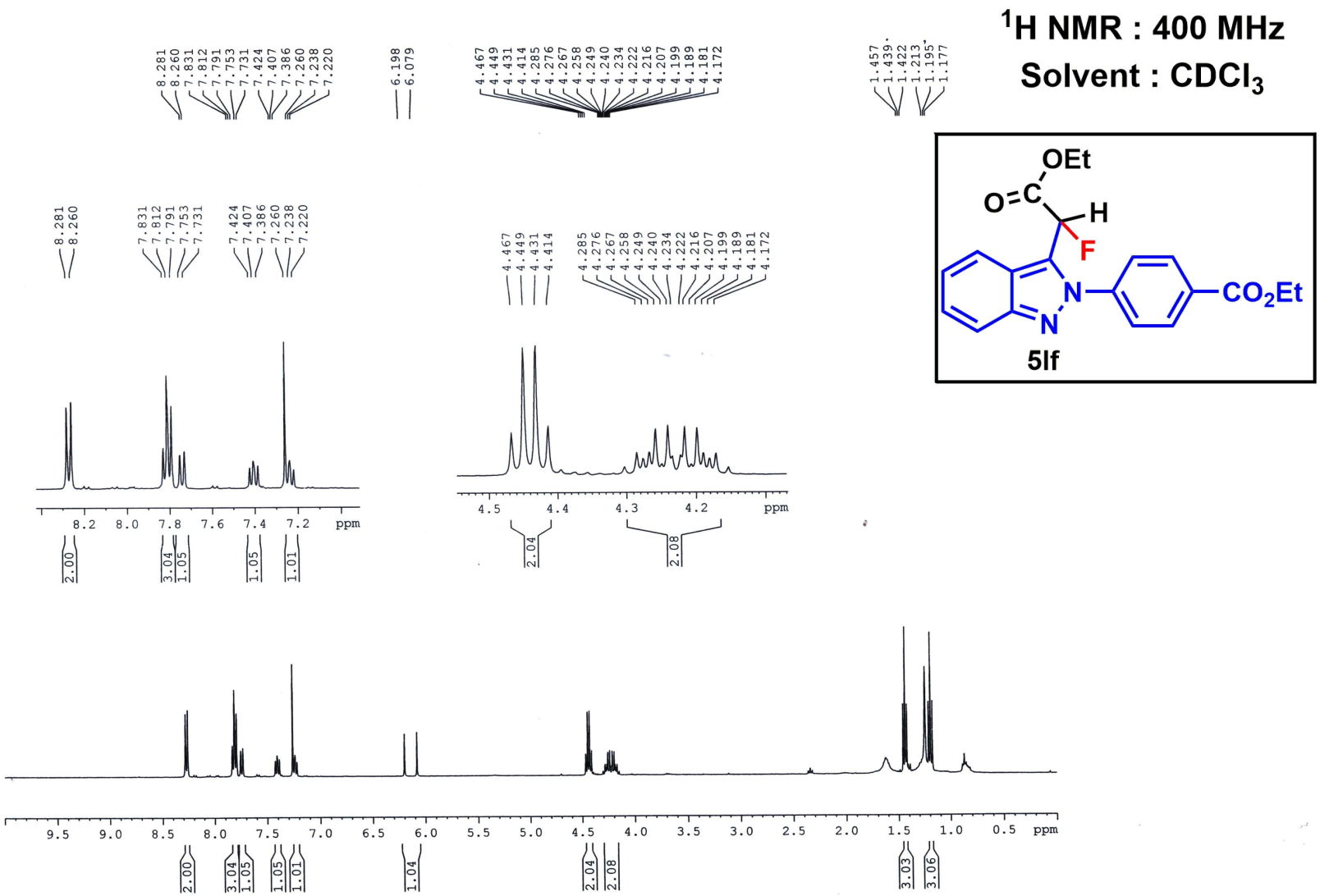
5kf



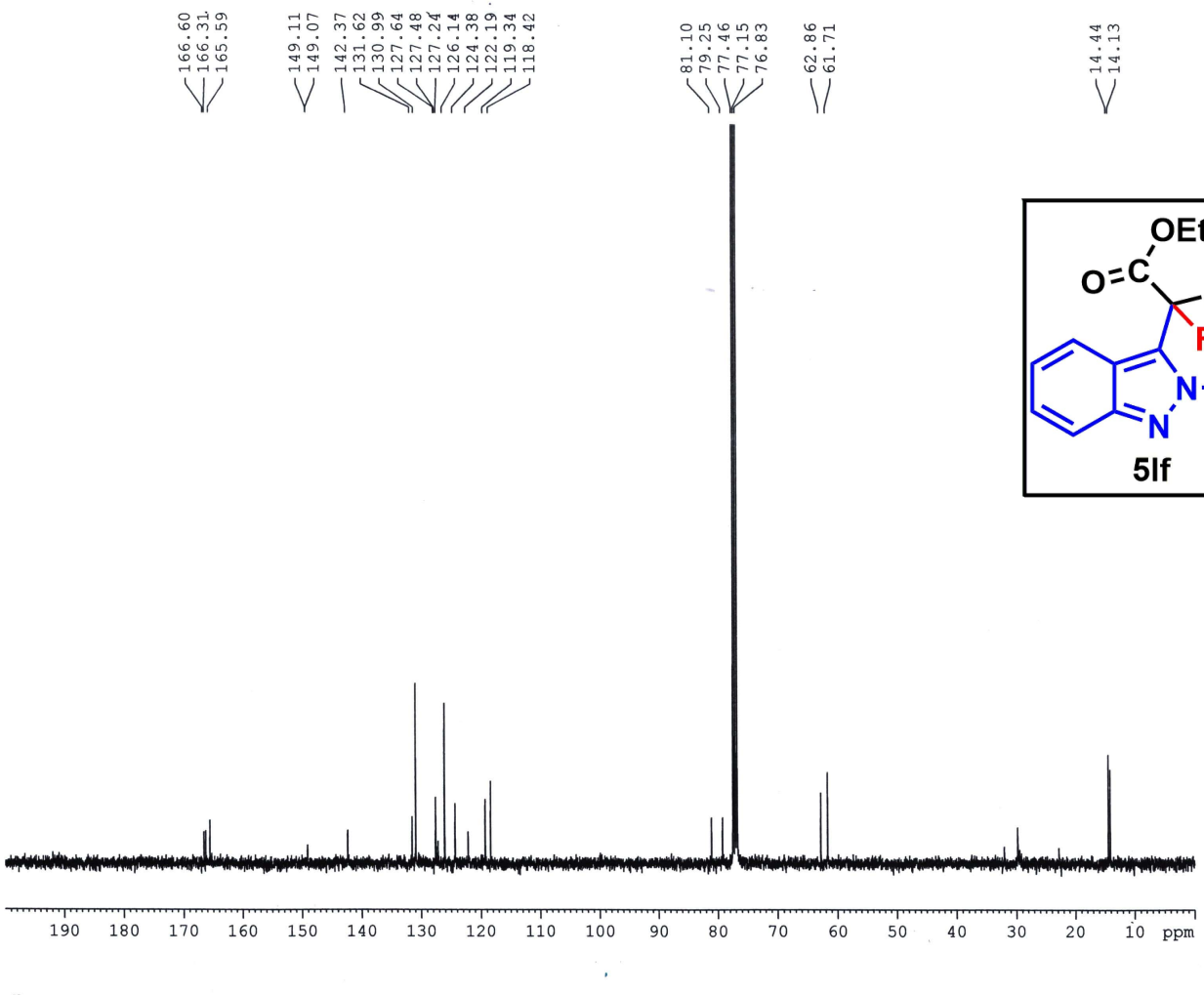
^{19}F NMR : 376.5 MHz

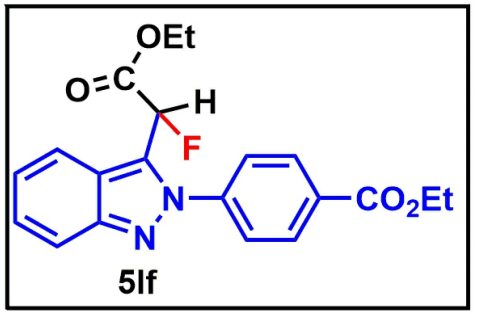
Solvent : $CDCl_3$

5kf

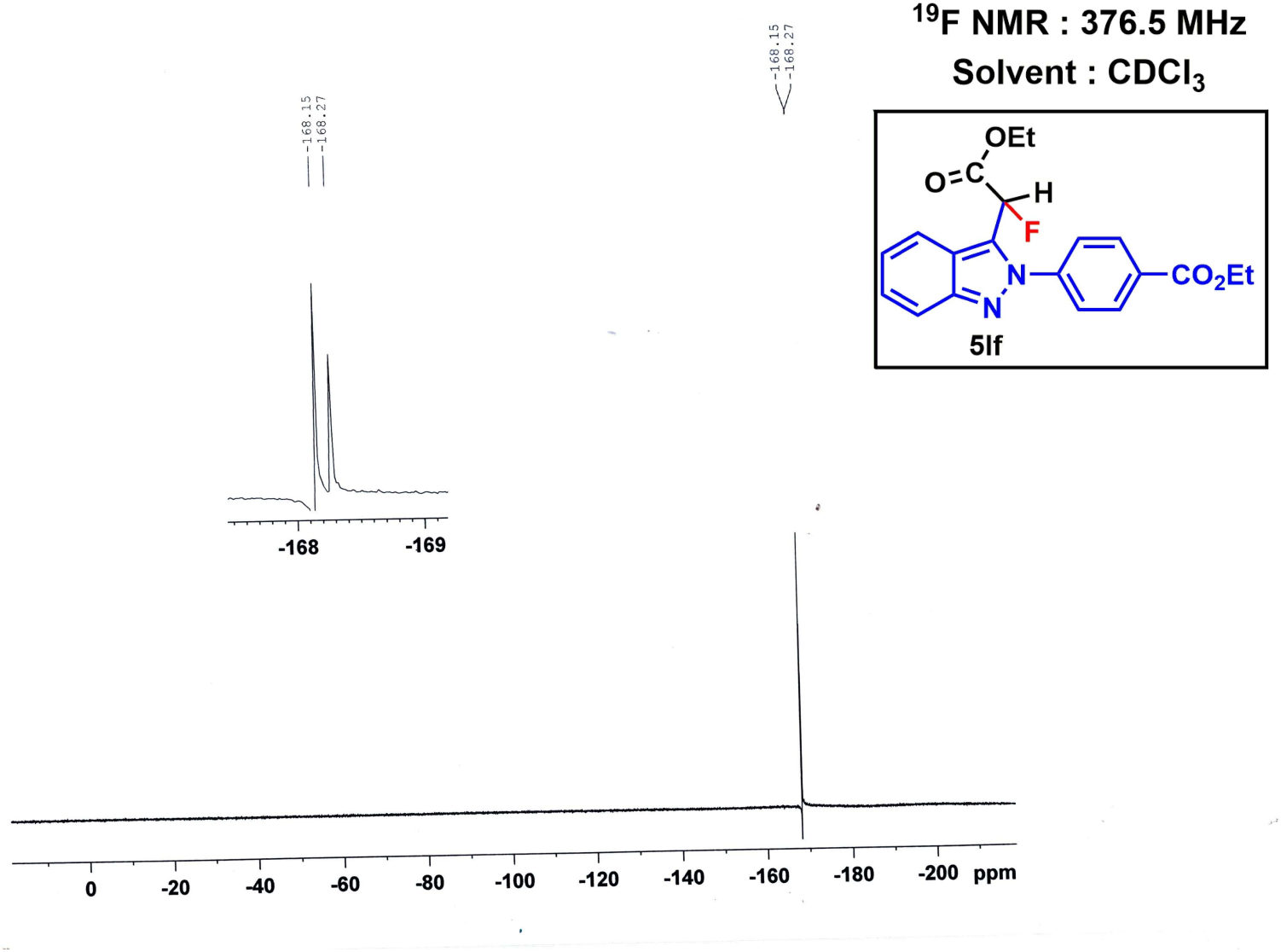

1H NMR : 400 MHz
Solvent : CDCl3
OEt
O=C
H
F
N
N
CO2Et
5lf

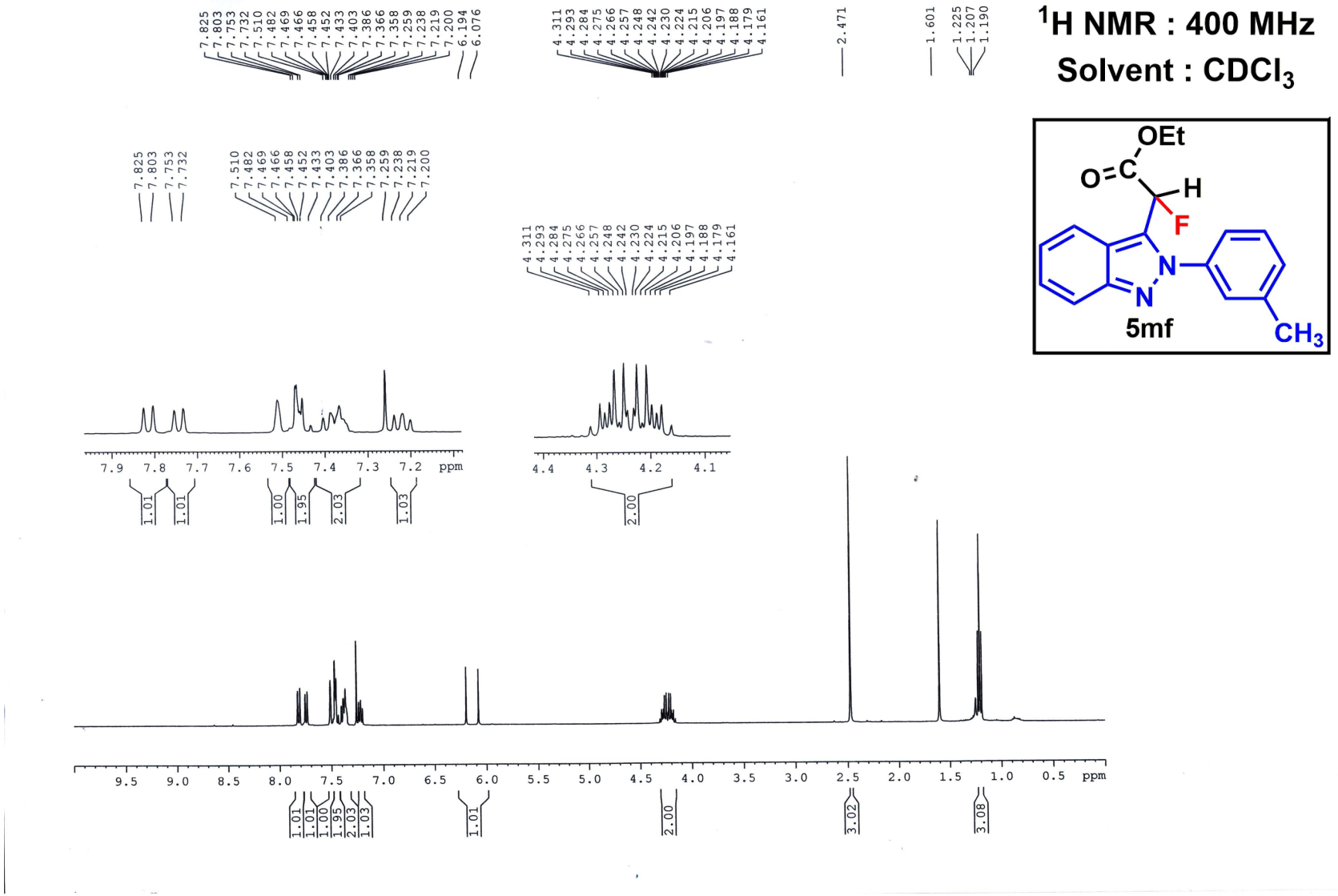
$^{13}C\{^{1}H\}$ NMR : 100 MHz
Solvent : $CDCl_3$





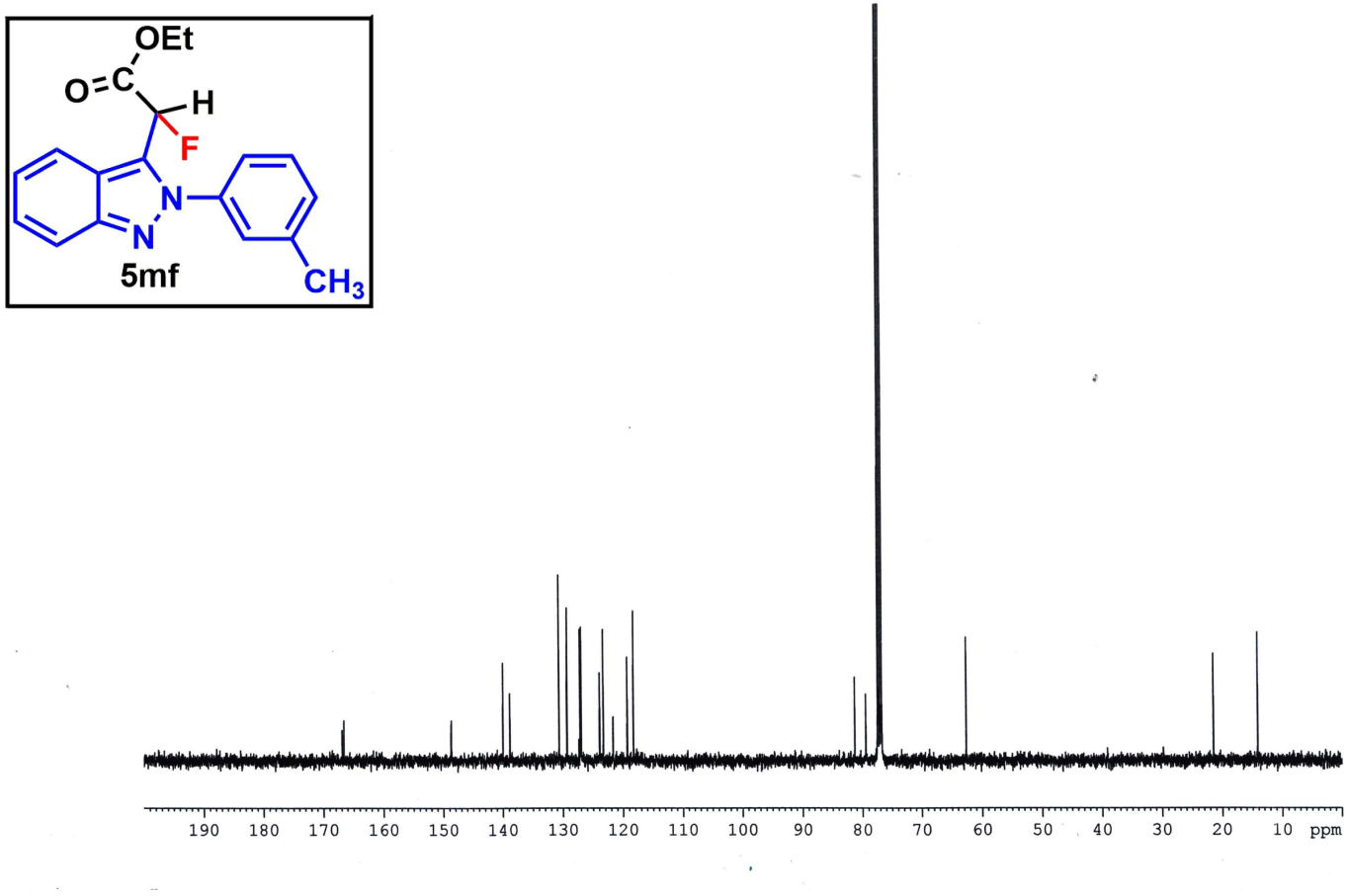
5lf

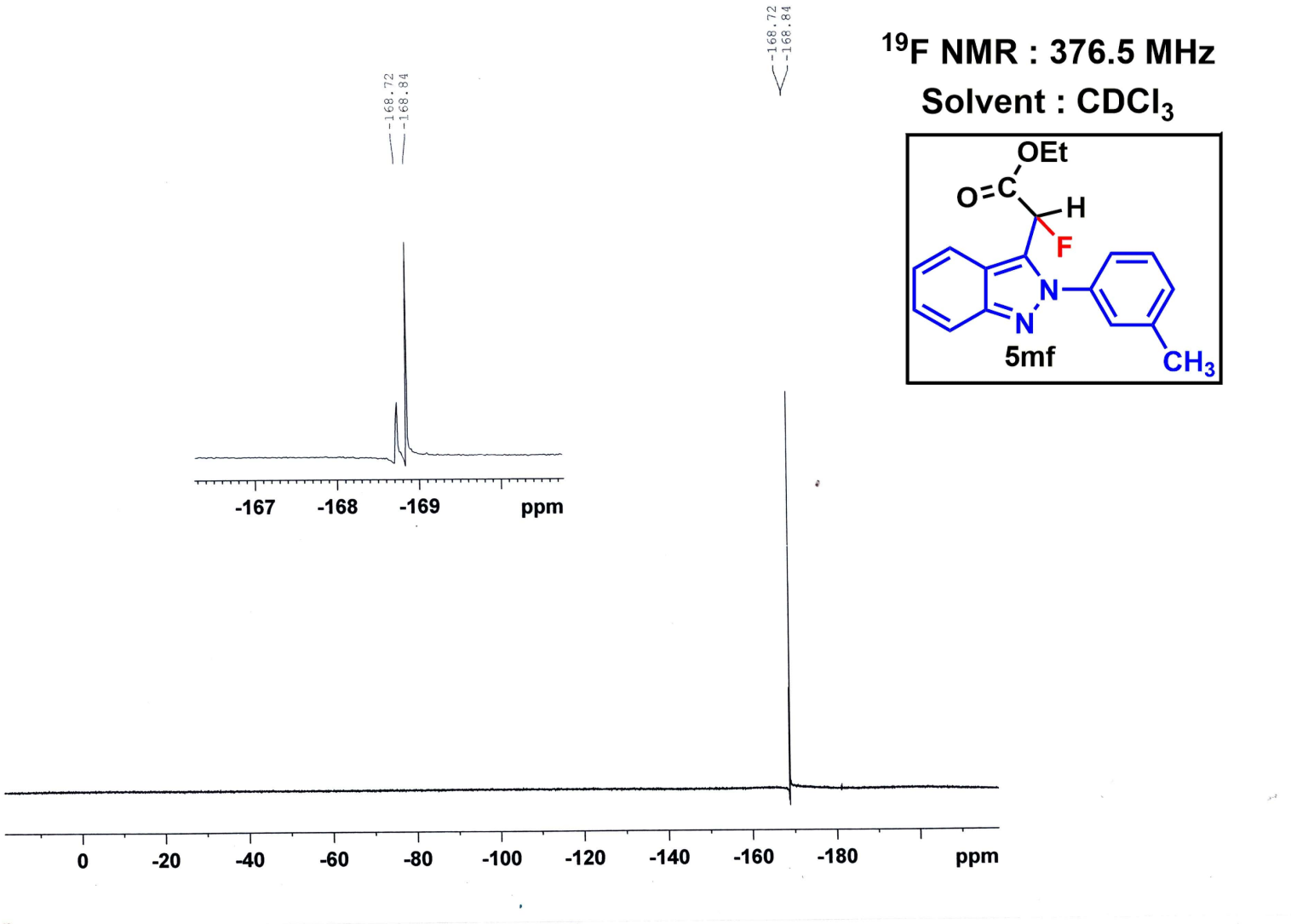

^{19}F NMR : 376.5 MHz
Solvent : $CDCl_3$
-168.15
-168.27
OEt
O=C
H
F
N
N
CO_2Et
5lf
-168
-169
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

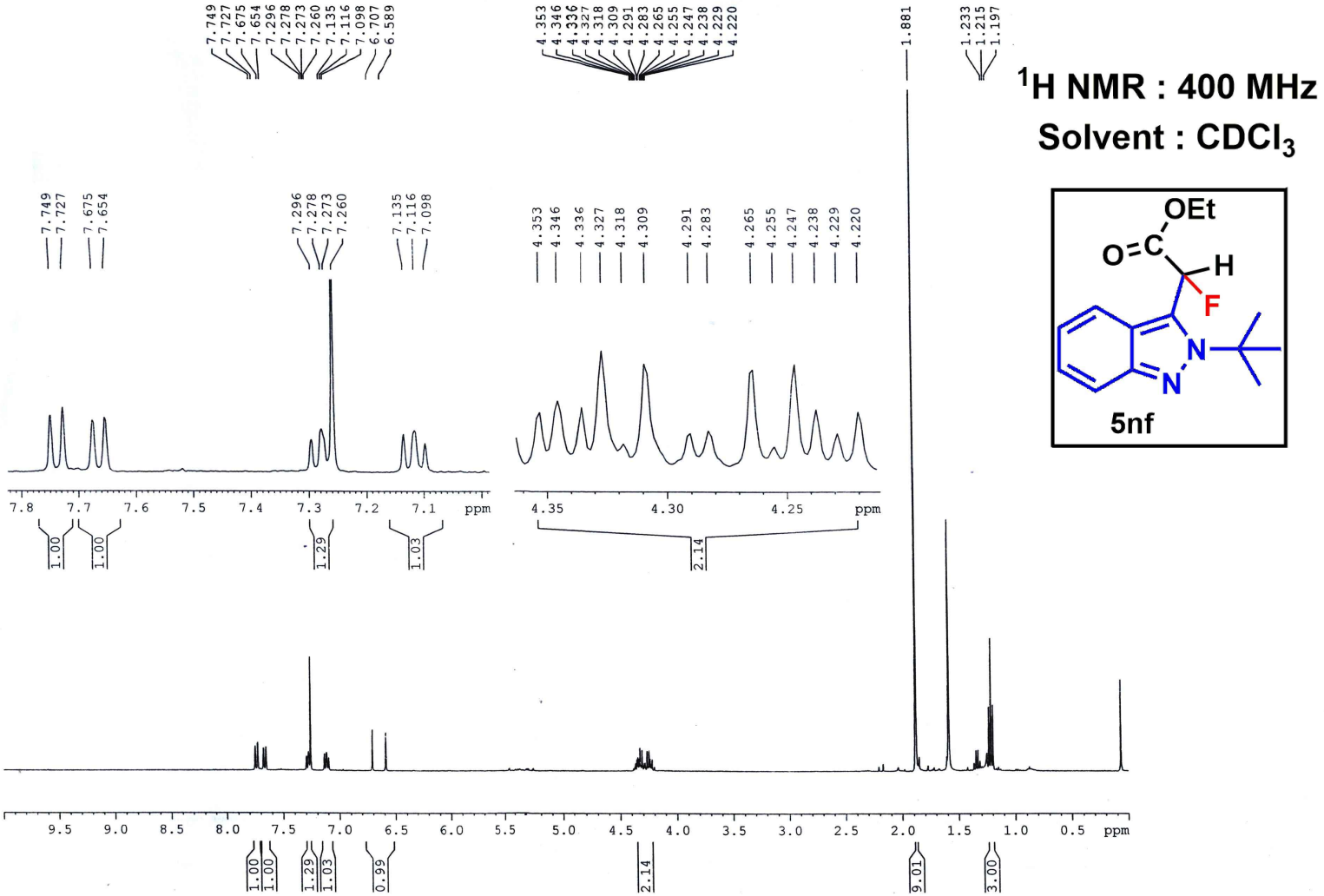

7.825
7.803
7.753
7.732
7.510
7.482
7.469
7.466
7.458
7.452
7.433
7.403
7.386
7.366
7.358
7.259
7.238
7.219
7.200
6.194
6.076
4.311
4.293
4.284
4.275
4.266
4.257
4.248
4.242
4.230
4.224
4.215
4.206
4.197
4.188
4.179
4.161
2.471
1.601
1.225
1.207
1.190
1H NMR : 400 MHz
Solvent : CDCl3
OEt
O=C
H
F
N
N
5mf
CH3
ppm
1.01
1.01
1.00
1.95
2.03
1.03
2.00
3.02
3.08

$^{13}C\{^{1}H\}$ NMR : 100 MHz

Solvent : $CDCl_3$

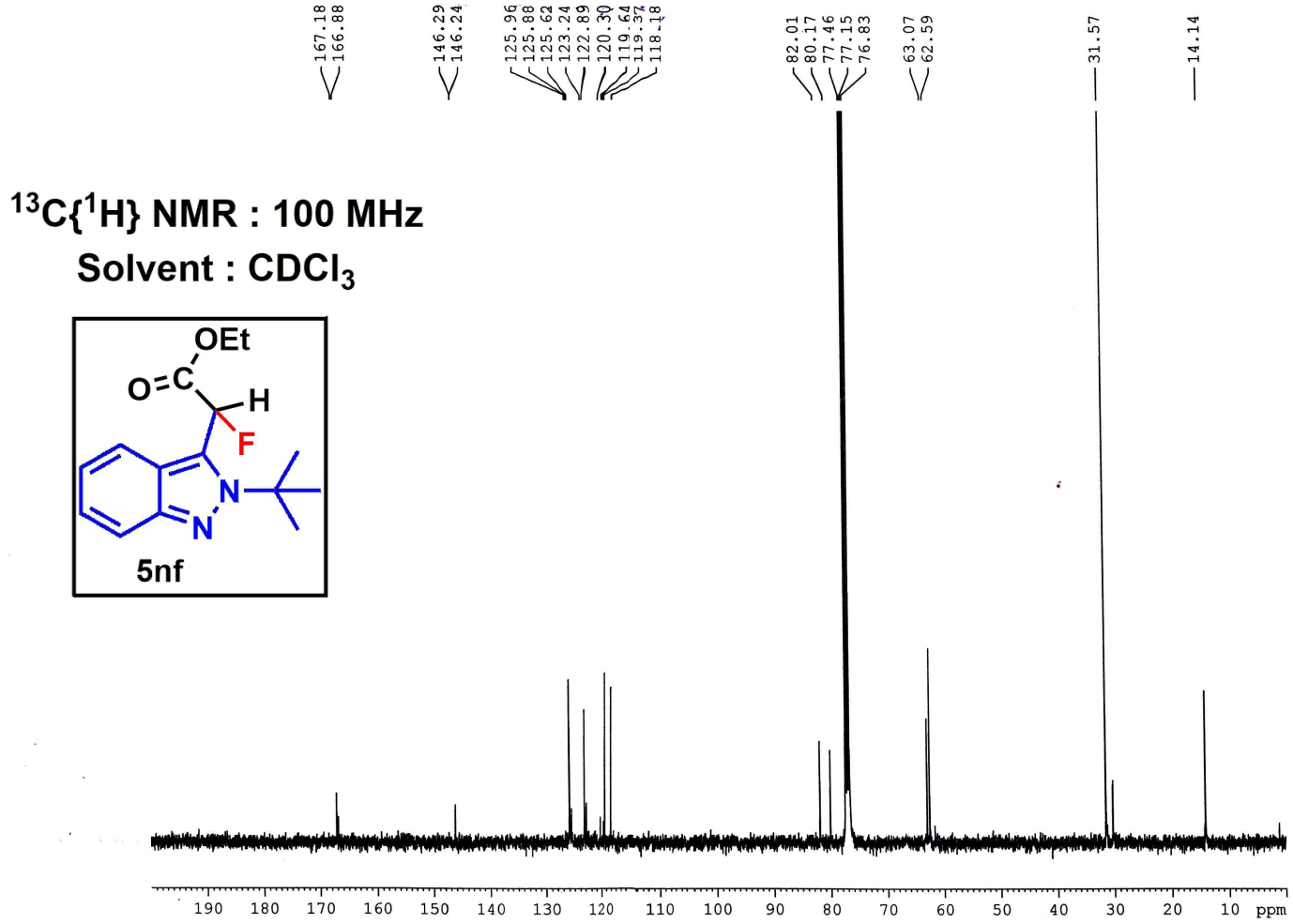


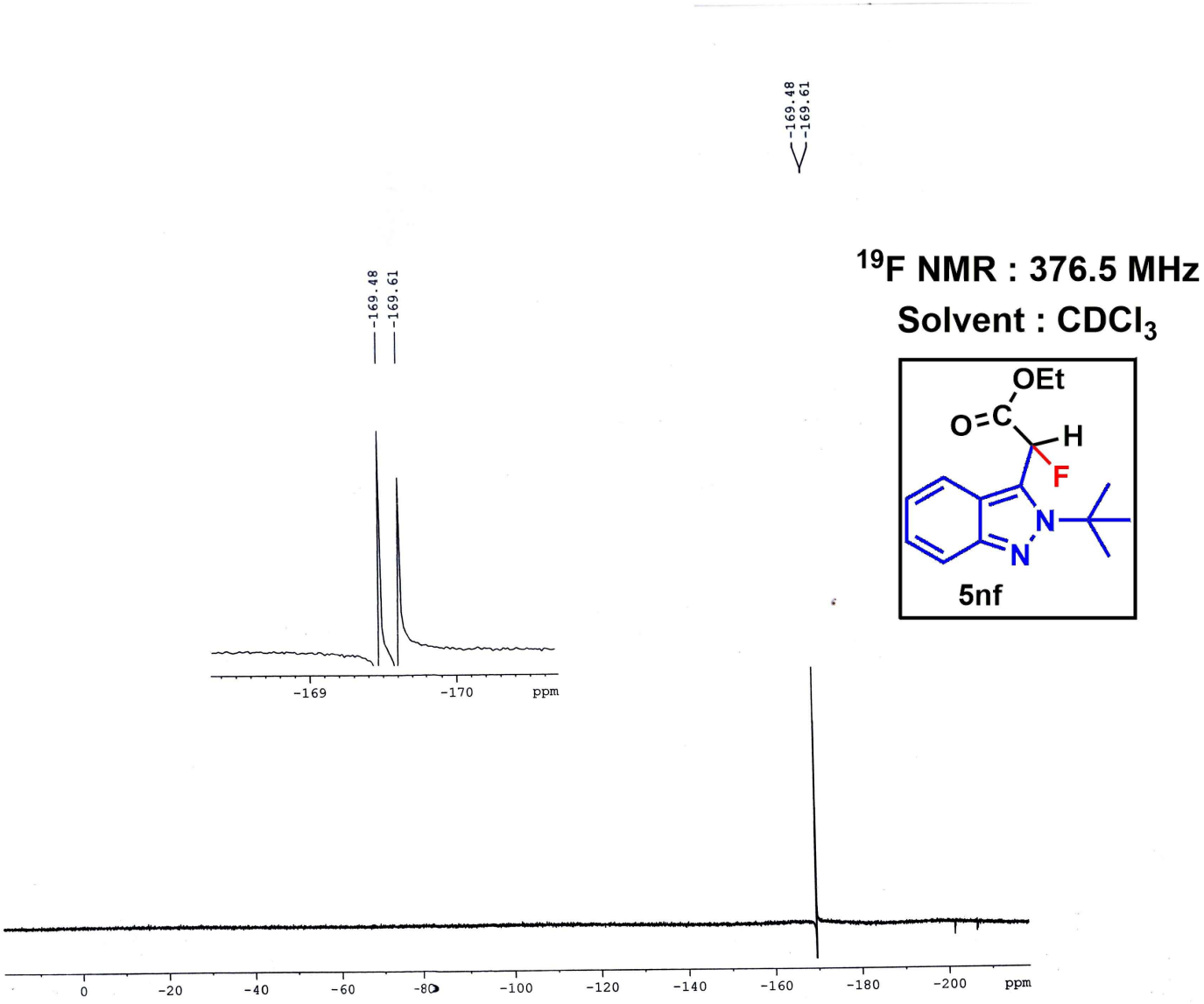

-168.72
-168.84
-168.72
-168.84
19F NMR : 376.5 MHz
Solvent : CDCl3
OEt
O=C
H
F
N
N
5mf
CH3
-167
-168
-169
ppm
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

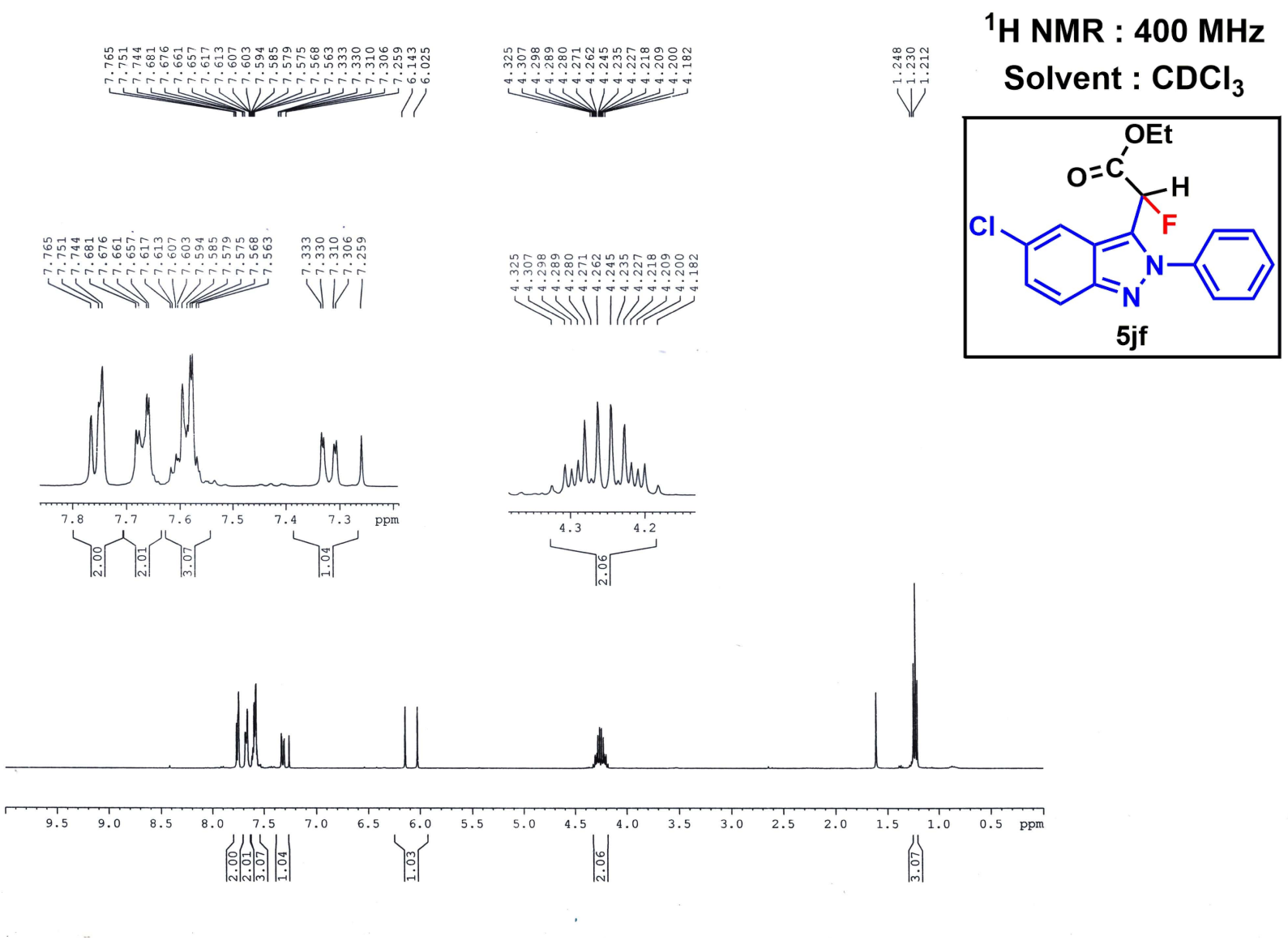


^{1}H NMR : 400 MHz

Solvent : $CDCl_3$


167.18
166.88
146.29
146.24
125.96
125.88
125.62
123.24
122.89
120.30
119.64
119.37
118.18
82.01
80.17
77.46
77.15
76.83
63.07
62.59
31.57
14.14
$^{13}C\{^{1}H\}$ NMR : 100 MHz
Solvent : $CDCl_3$
OEt
O=C
H
F
N
N
5nf
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


-169.48
-169.61
^{19}F NMR : 376.5 MHz
Solvent : $CDCl_3$
OEt
O=C
H
F
N
N
5nf
-169.48
-169.61
-169
-170
ppm
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm



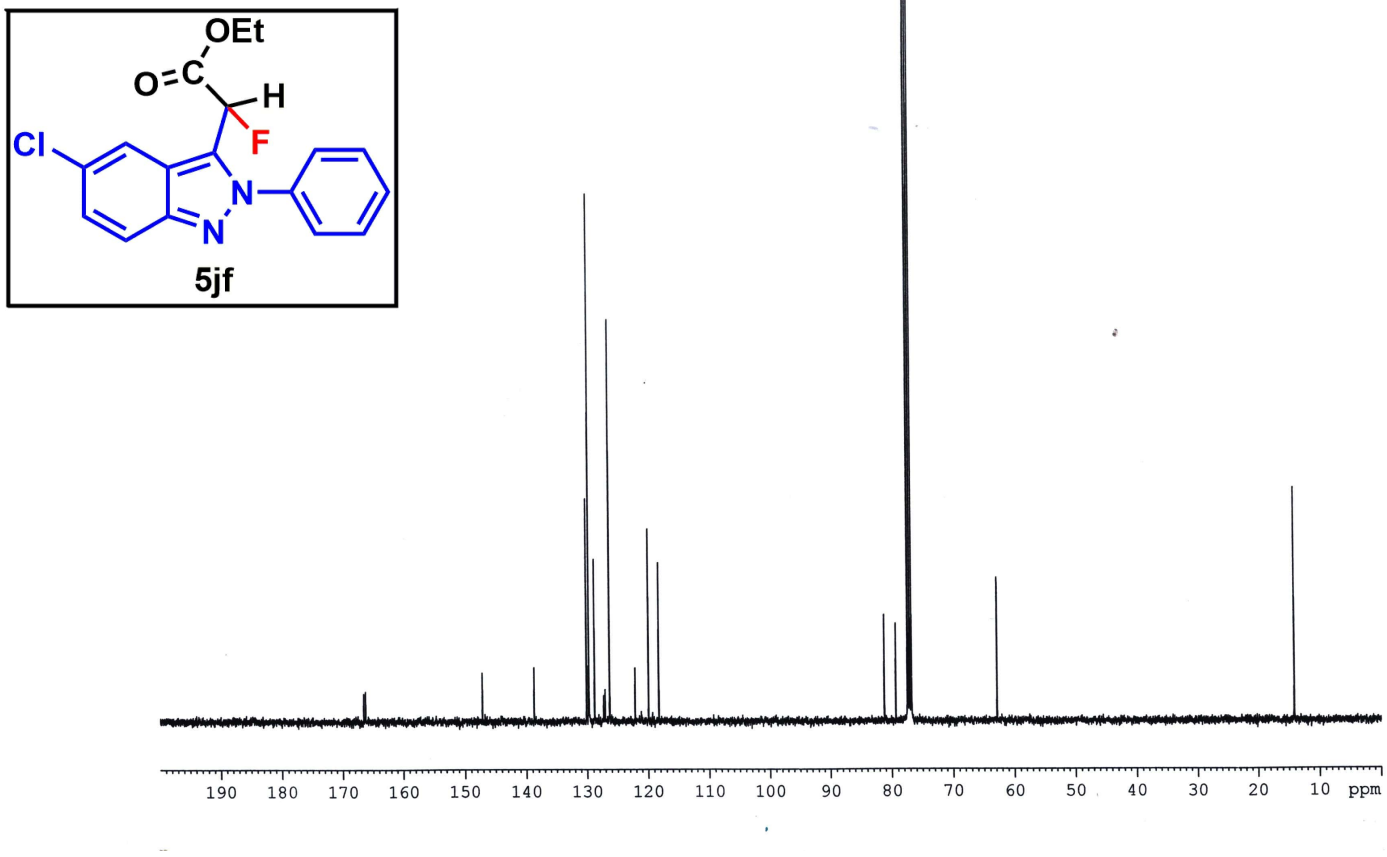
^{1}H NMR : 400 MHz

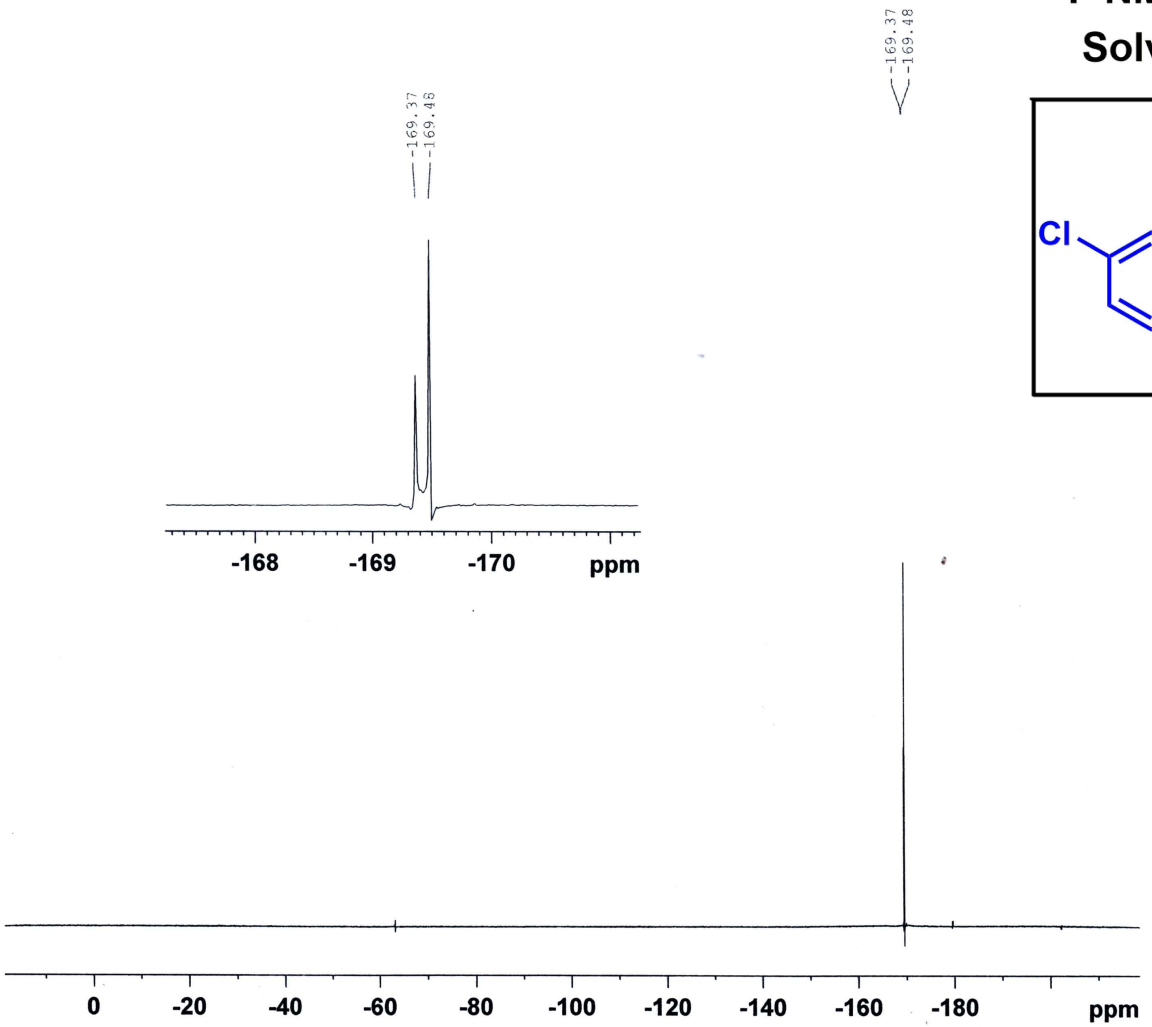
Solvent : $CDCl_3$

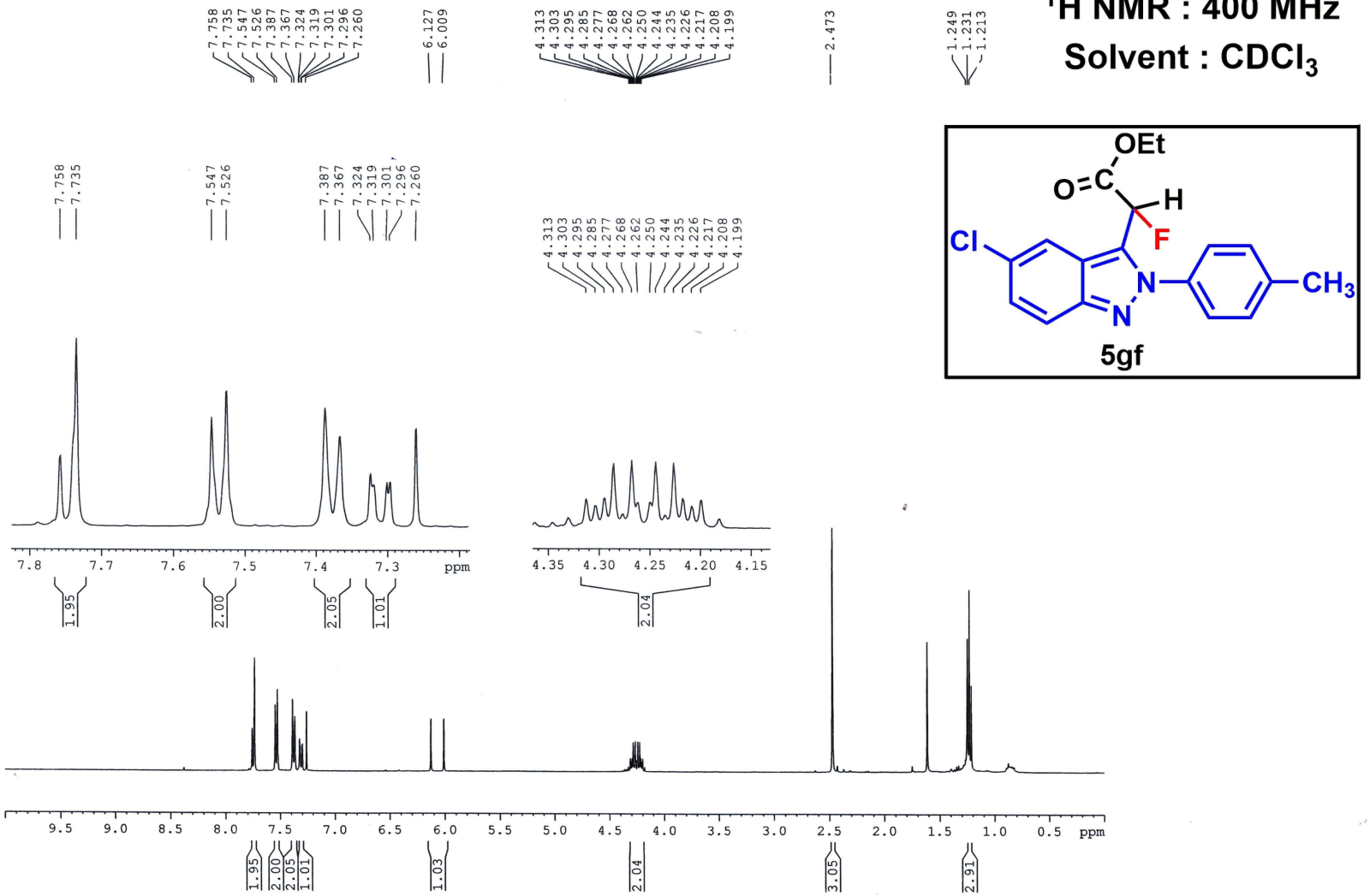
5jf

$^{13}C\{^{1}H\}$ NMR : 100 MHz

Solvent : $CDCl_3$

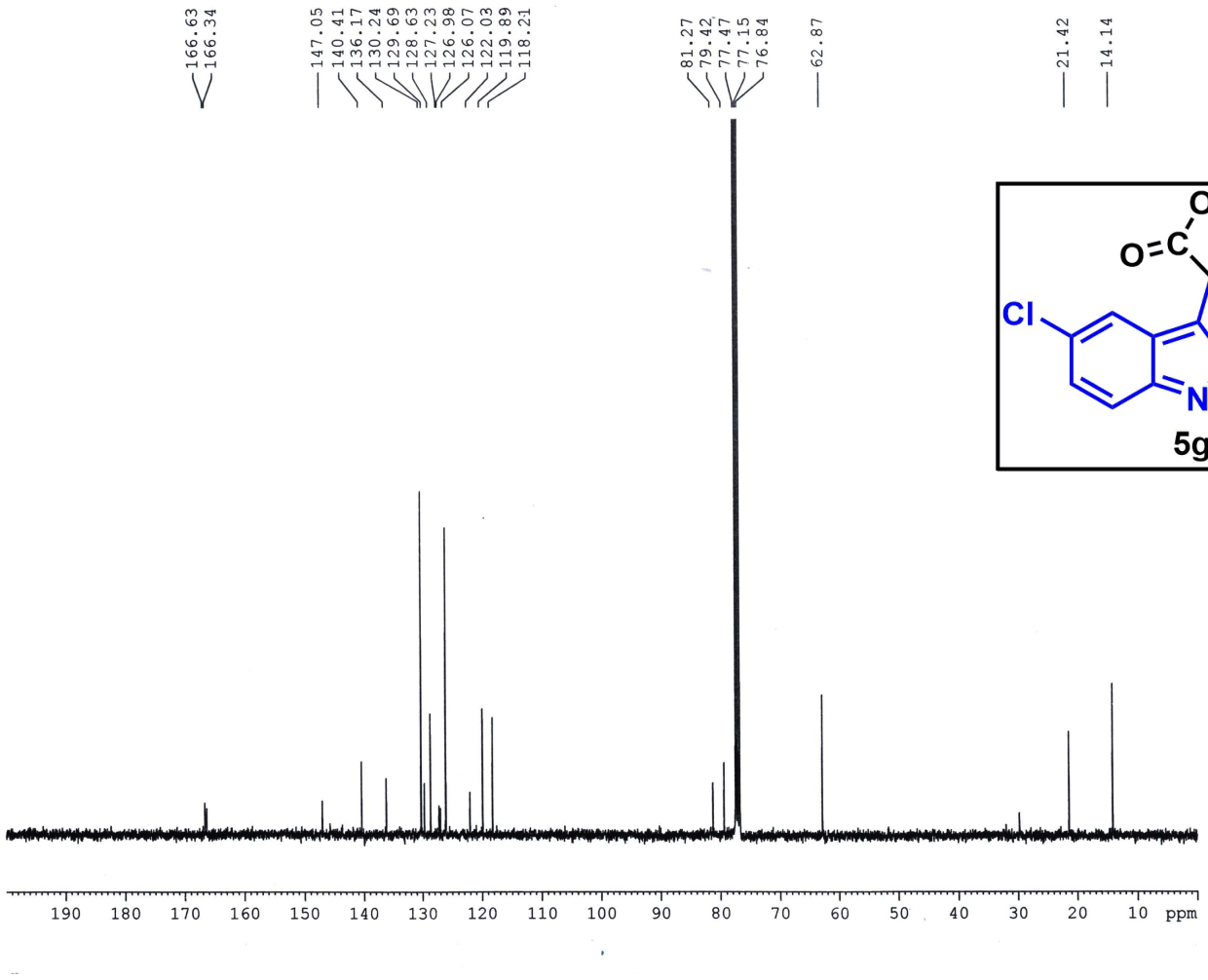


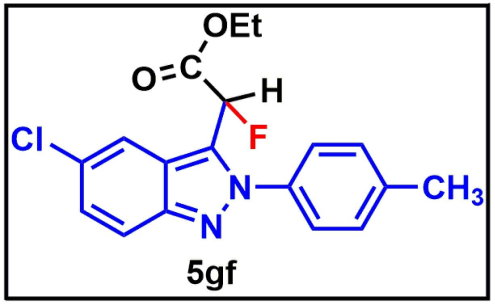

^{19}F NMR : 376.5 MHz
Solvent : $CDCl_3$
-169.37
-169.48
OEt
O=C
H
F
Cl
N
N
5jf
-168
-169
-170
ppm
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


7.758
7.735
7.547
7.526
7.387
7.367
7.324
7.319
7.301
7.296
7.260
6.127
6.009
4.313
4.303
4.295
4.285
4.277
4.268
4.262
4.250
4.244
4.235
4.226
4.217
4.208
4.199
2.473
1.249
1.231
1.213
1H NMR : 400 MHz
Solvent : CDCl3
OEt
O=C
H
F
Cl
N
N
CH3
5gf
ppm
1.95
2.00
2.05
1.01
2.04
1.03
3.05
2.91

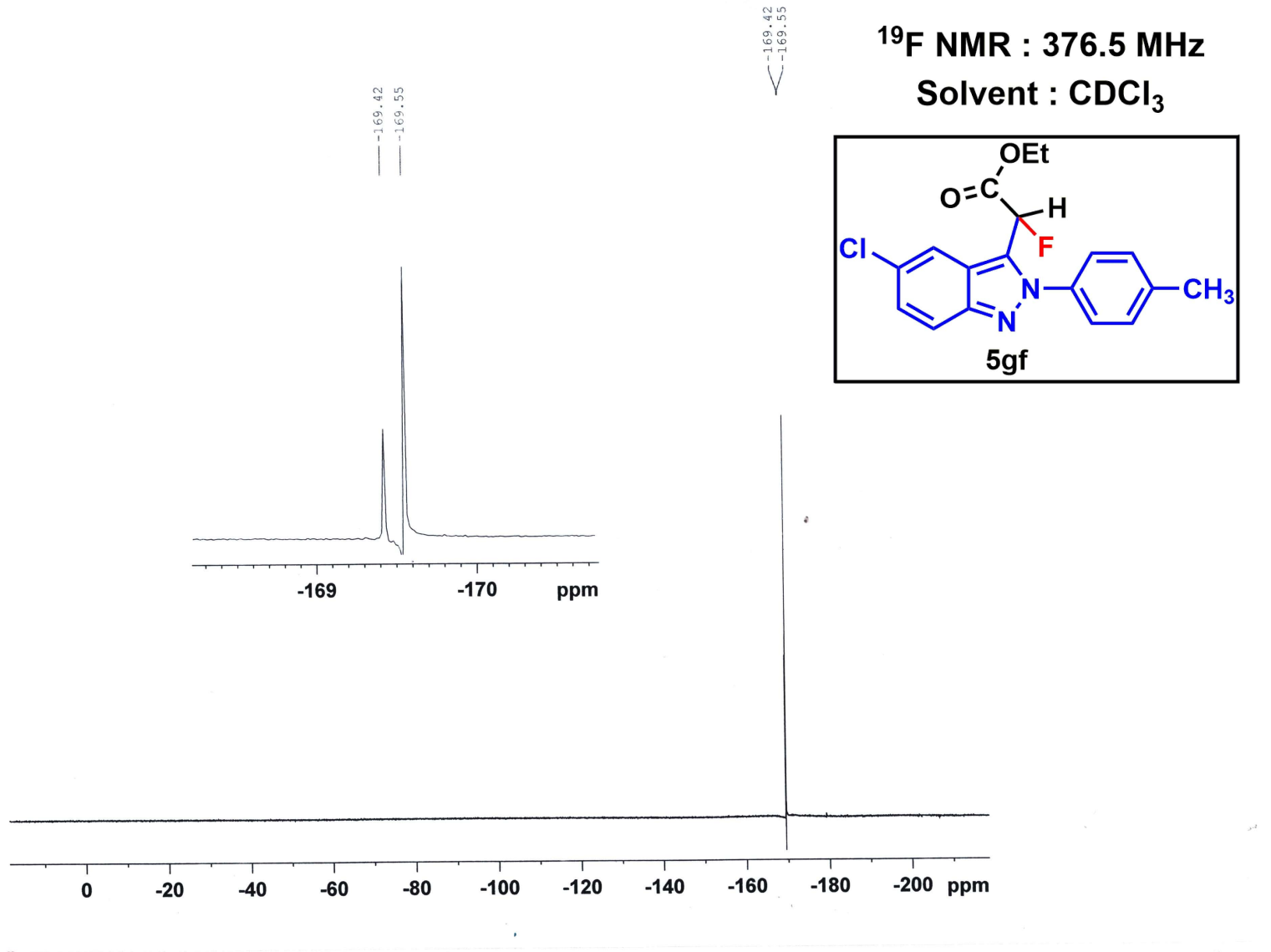
$^{13}C\{^{1}H\}$ NMR : 100 MHz

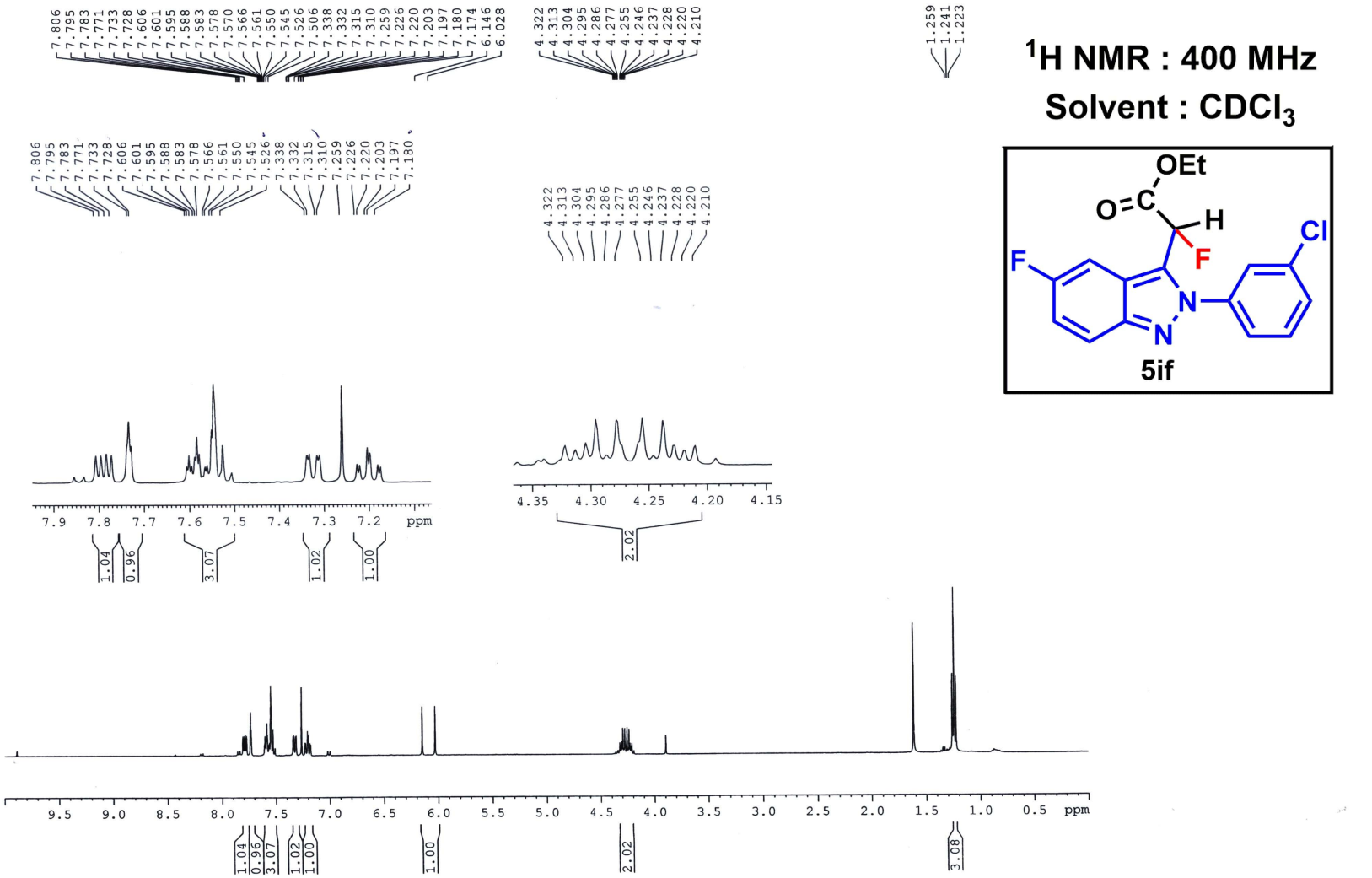
Solvent : $CDCl_3$





5gf


-169.42
-169.55
-169.42
-169.55
^{19}F NMR : 376.5 MHz
Solvent : $CDCl_3$
OEt
O=C
H
F
Cl
N
N
CH_3
5gf
-169
-170
ppm
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm



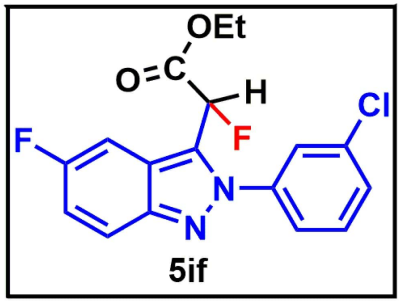
^{1}H NMR : 400 MHz

Solvent : $CDCl_3$

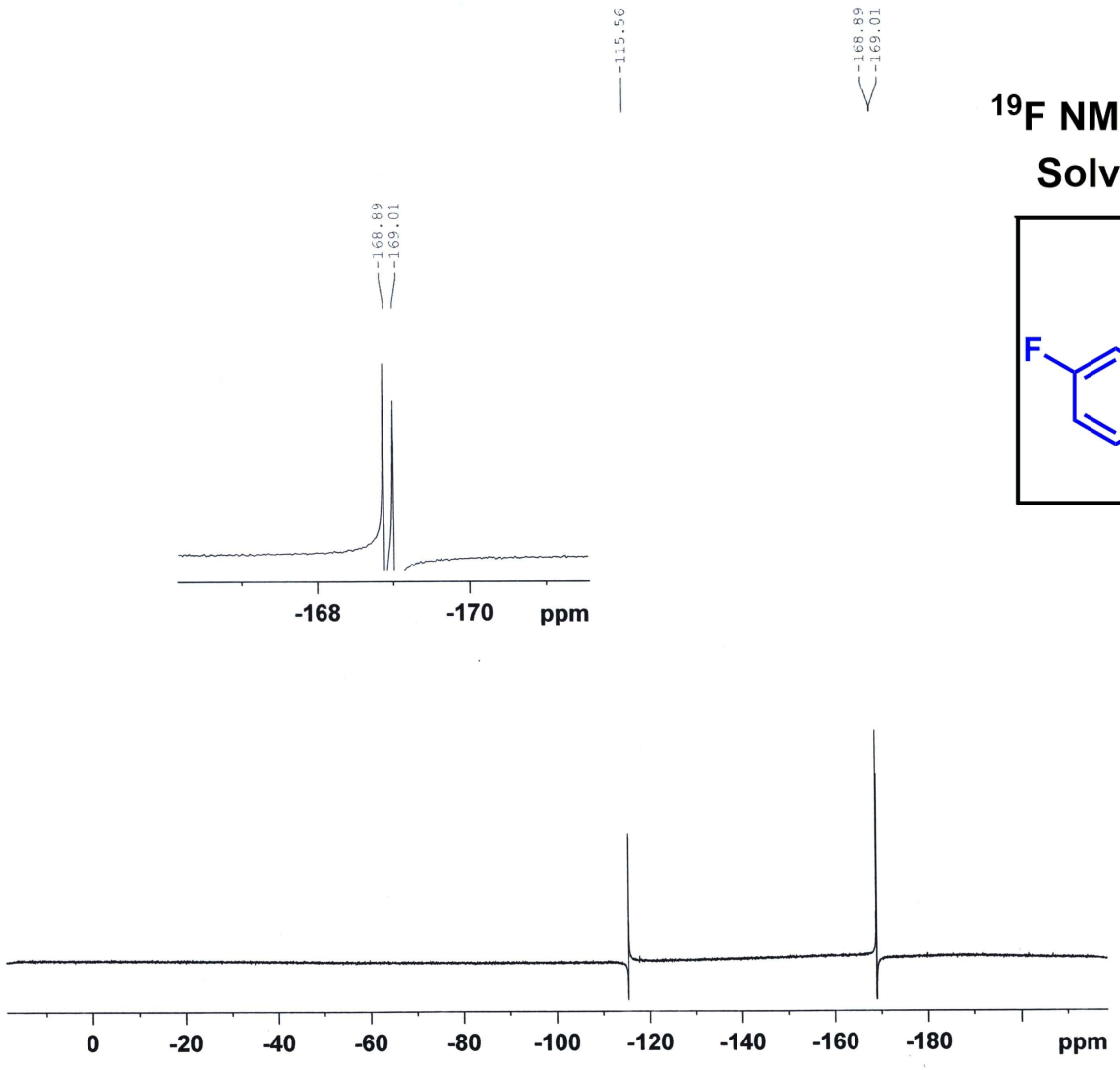
5if

$^{13}C\{^{1}H\}$ NMR : 100 MHz

Solvent : $CDCl_3$

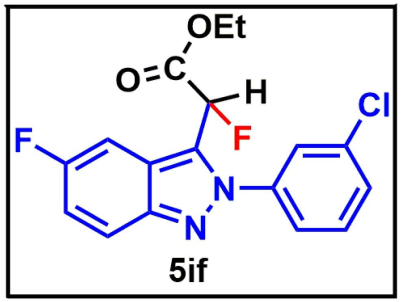


5if

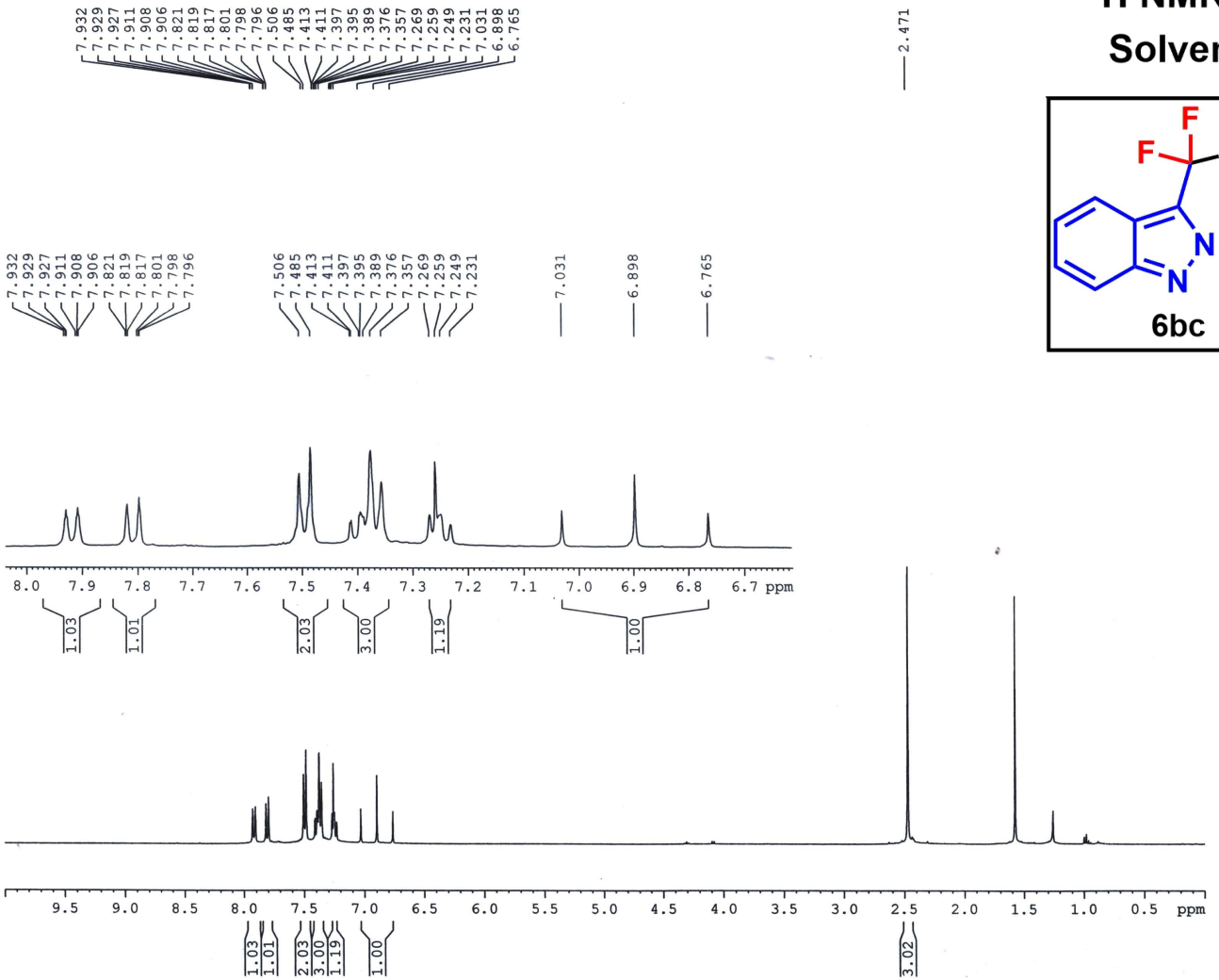


^{19}F NMR : 376.5 MHz

Solvent : $CDCl_3$

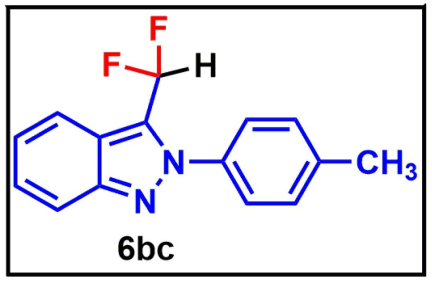


5if



^{1}H NMR : 400 MHz

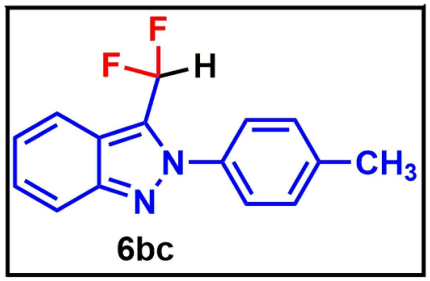
Solvent : $CDCl_3$



6bc

$^{13}C\{^{1}H\}$ NMR : 100 MHz

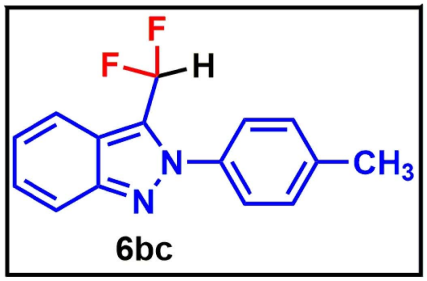
Solvent : $CDCl_3$



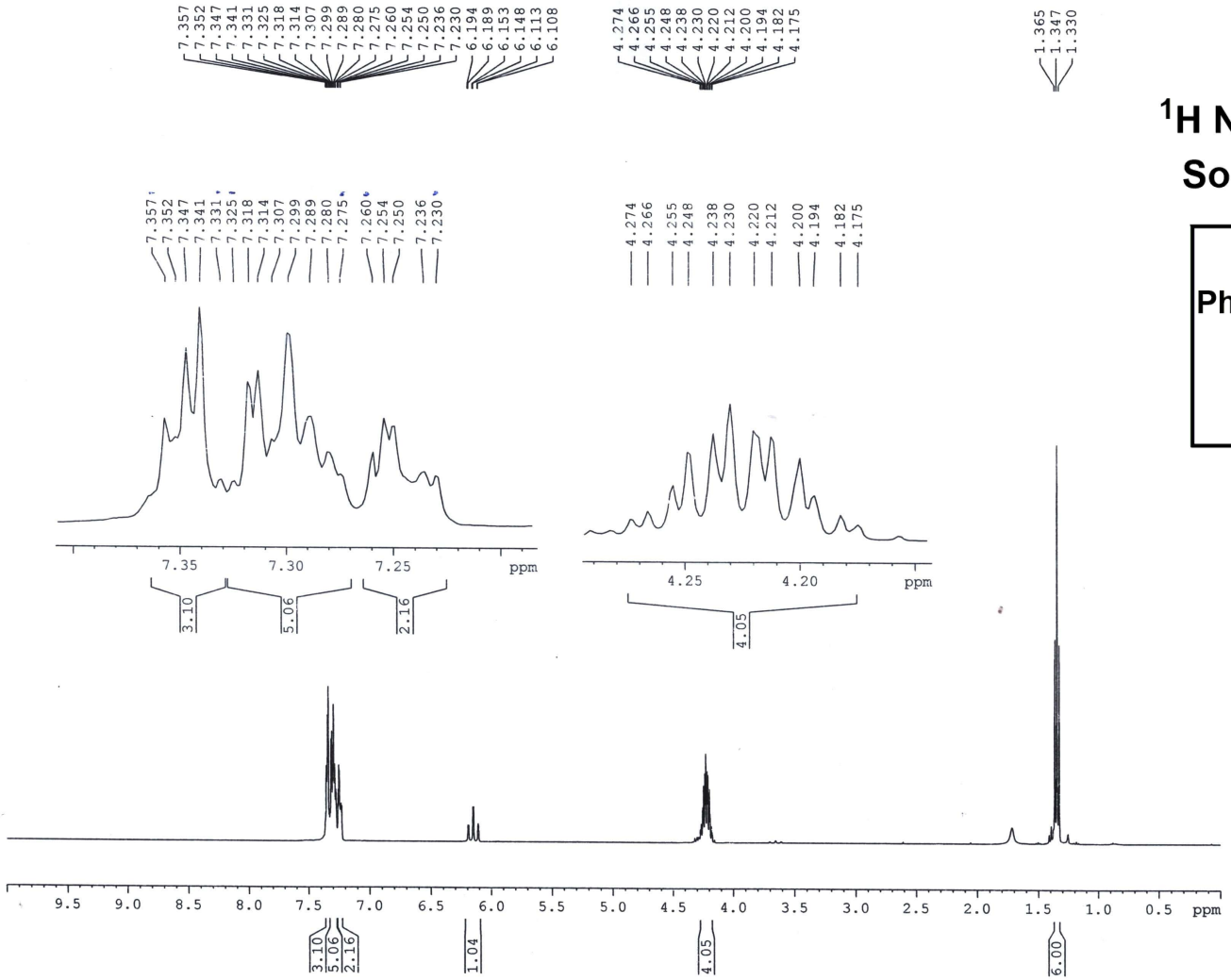
6bc

^{19}F NMR : 376.5 MHz

Solvent : $CDCl_3$

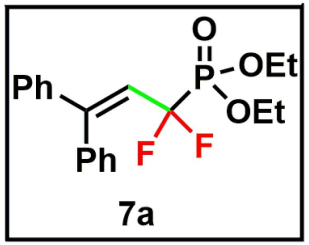


6bc



^{1}H NMR : 400 MHz

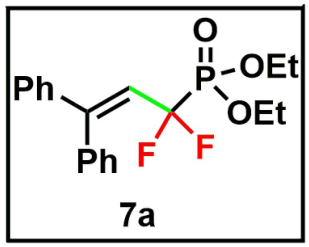
Solvent : $CDCl_3$



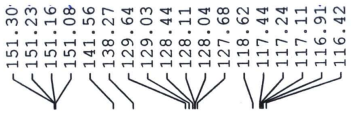
7a

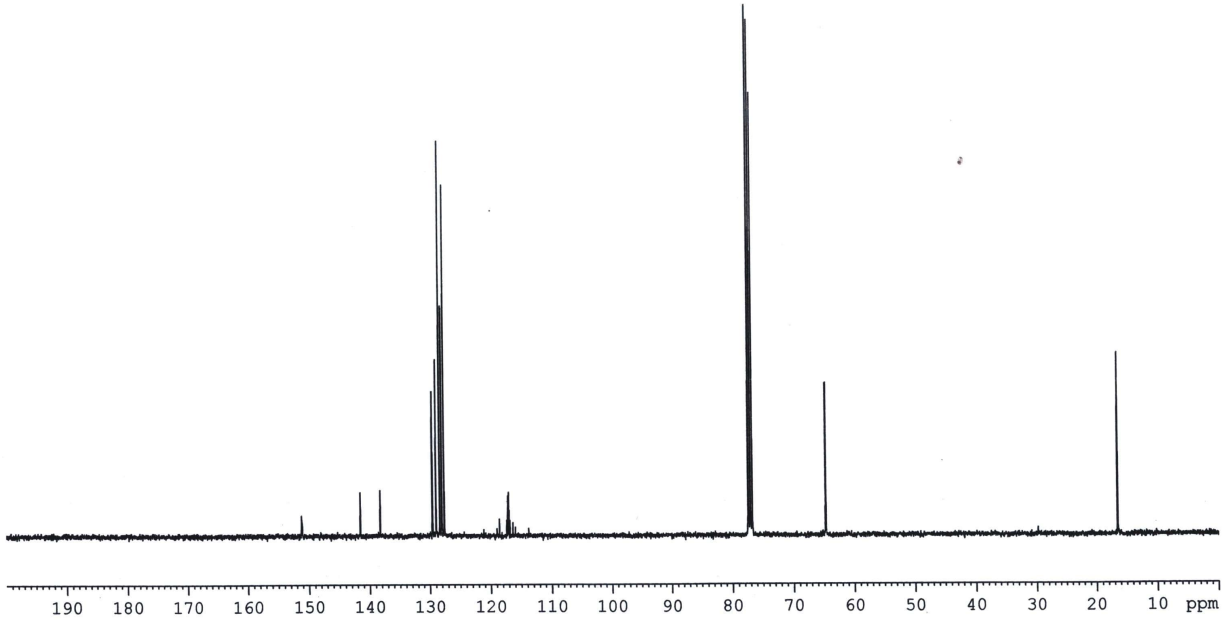
$^{13}C\{^{1}H\}$ NMR : 100 MHz

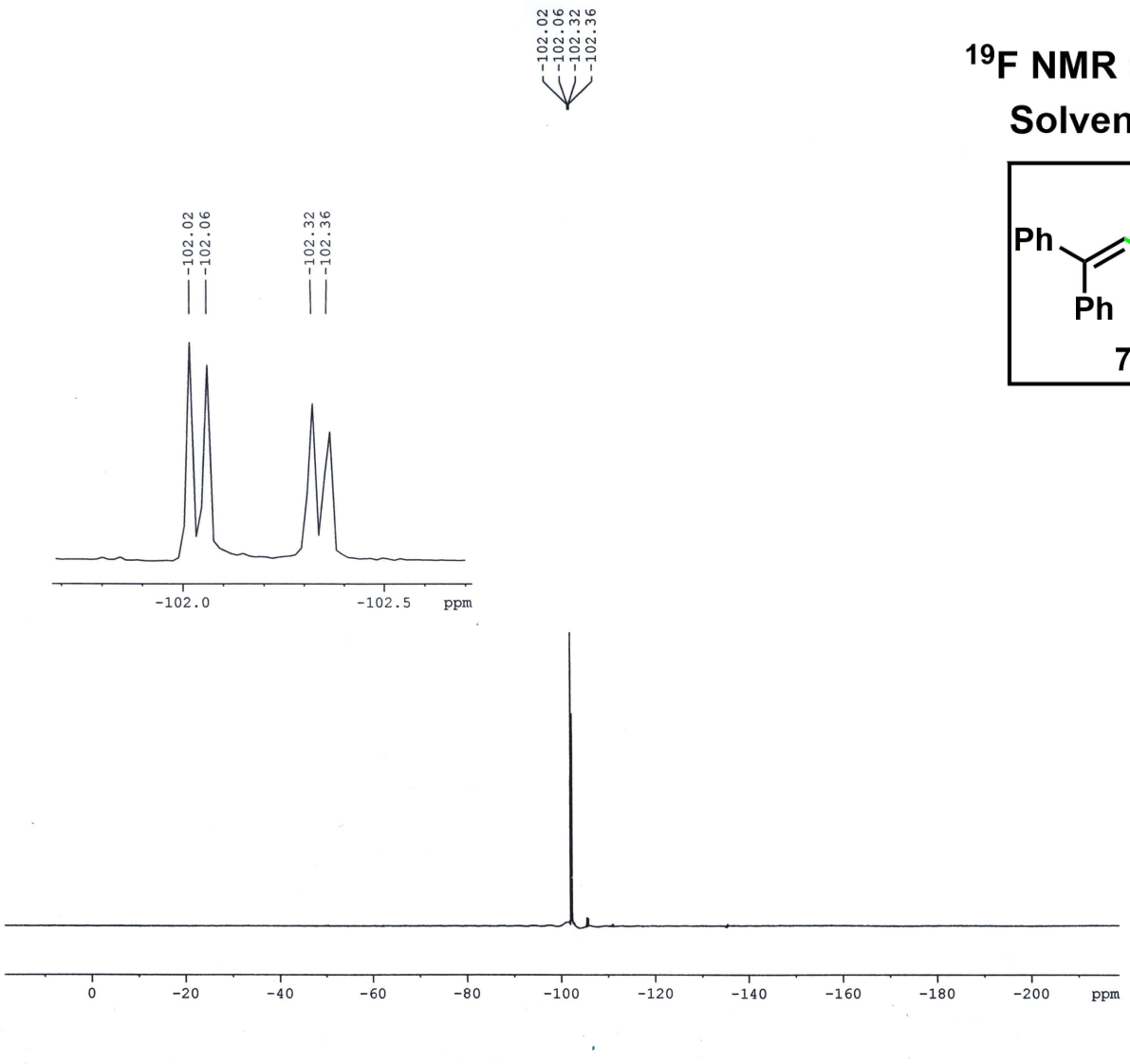
Solvent : $CDCl_3$



7a

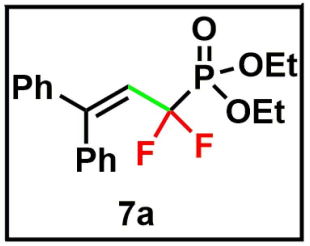






^{19}F NMR : 376.5 MHz

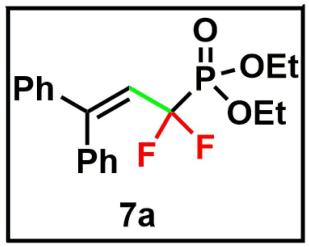
Solvent : $CDCl_3$



7a

^{31}P NMR : 162 MHz

Solvent : $CDCl_3$



7a