

Visible-light-initiated Difluoromethylation of Arenediazonium Tetrafluoroborates

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1. General information

All chemical reagents are obtained from commercial suppliers and used without further purification. All unknown compounds are characterized by ^1H NMR, ^{13}C NMR, MS and elemental analyses. Analytical thin-layer chromatography are performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. Mass spectra are taken on a Thermo Scientific ISQ LT GC-MS instrument in the electron ionization (EI) mode. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra are recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz, 125 MHz and 470 MHz in CDCl_3 , respectively, and chemical shifts are reported in ppm. GC analyses are performed on an Agilent 7890A instrument (Column: Agilent 19091J-413:30 m \times 320 μm \times 0.25 μm , H, FID detection). GC-MS data was recorded on a 5975C Mass Selective Detector, coupled with a 7890A Gas Chromatograph (Agilent Technologies). High-resolution mass spectra data were obtained on Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight) and Waters Micromass GCT Premier spectrometer (electrospray ionization: EI).

2. General procedure

General procedure for the preparation of arene diazonium tetrafluoroborates:

Compounds **1** were prepared according to literature.¹ The appropriate aniline (5 mmol) was dissolved in a mixture of absolute ethanol (3 mL) and an aqueous solution of HBF_4 (50%, 1.25 mL, 10 mmol). After cooling the reaction mixture to 0 $^\circ\text{C}$, tert-butyl nitrile (1.40 mL, 10 mmol) was added dropwise. The resulting mixture was stirred at room temperature for 1 h. Diethyl ether (10 mL) was added to precipitate the aryl diazonium tetrafluoroborate. It was then filtered off and washed with diethyl ether (3 \times 10 mL). The aryl diazonium tetrafluoroborate **1** was dried in *vacuo* and directly used without further purification.

General procedure for the preparation of trimethylsilyl difluoroenol ethers:

Compounds **2** were prepared according to literature.² To a mixture of chlorotrimethylsilane (2.60 g, 24 mmol) and Mg (0.58 g, 24 mmol) in THF (24 mL) cooled down to 0 $^\circ\text{C}$ under an argon atmosphere, trifluoroacetophenone (1.04 g, 6.0 mmol) was added dropwise and then the reaction mixture was stirred for additional 30 min. After evaporation of solvent, hexane (50 mL) was added to the residue, and the resulting salt was filtered, and the filtrate was concentrated to give crude **2a** (1.1 g, the purity of this crude **2a** was detected by GC (> 95%). The crude difluoroenol silyl ether **2a** was used for later reactions without further purification. Other difluoroenol silyl ethers were prepared according to the standard conditions.

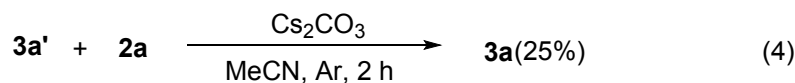
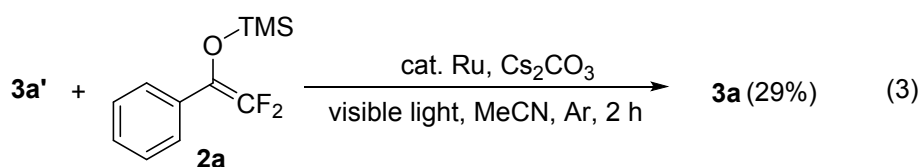
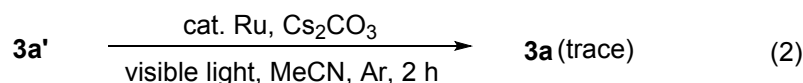
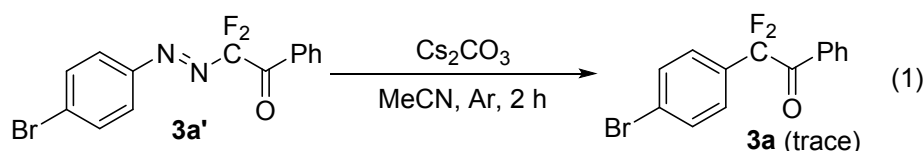
General procedure for visible-light-mediated difluoromethylation of diazonium salts:

A 25 mL oven-dried Schlenk tube with a magnetic stirring bar was equipped with diazonium salt (0.25 mmol) and Cs_2CO_3 (0.75 mmol), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfill (three times).

Ru(bpy)₃Cl₂·6H₂O (0.8 mg, 0.00125 mmol) was dissolved in 10 mL anhydrous MeCN, taking 1 mL to the Schlenk tube by syringe. Then, A solution of the α -aryl- β,β -difluoroenol silyl (0.375 mmol) in 1 mL anhydrous MeCN was added immediately via syringe. The mixture was irradiated with a LED (23 W) and stirred at room temperature for 2 h. Upon completion, the reaction mixture was diluted with H₂O (15 mL). The aqueous layer was washed with diethyl ether (5×3 mL). The combined organic layer were dried over MgSO₄, filtered and concentrated in vacuum. The residue was purified by flash chromatography using petrol ether/ethyl acetate as the eluent. The conditions for chromatography and data for characterization of the products are given below.

General procedure for the one-pot synthesis of difluoromethylarenes³: A 25 mL oven-dried Schlenk tube with a magnetic stirring bar was equipped with diazonium salt (0.25 mmol) and Cs₂CO₃ (0.75 mmol), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfill (three times). Ru(bpy)₃Cl₂·6H₂O (0.8 mg, 0.00125 mmol) was dissolved in 10 ml anhydrous MeCN, taking 1 mL to the Schlenk tube by syringe. Then, A solution of the α -aryl- β,β -difluoroenol silyl (0.375 mmol) in 1mL anhydrous MeCN was added via syringe. The mixture was irradiated with a LED (23 W) and stirred at room temperature for 2 h. To the mixture, was added KOH (2 mmol) and H₂O (0.1 mL), and the resulting suspension was stirred at 100 °C for 2 h. Upon completion, the reaction mixture was diluted with H₂O (15 mL). The aqueous layer was washed with diethyl ether (5 × 3 mL). The combined organic layer were dried over MgSO₄, filtered and concentrated in vacuum. The residue was purified by flash chromatography using petrol ether/ethyl acetate as the eluent. The conditions for chromatography and data for characterization of the products are given below.

The procedures of control experiments



Scheme S1 Control experiments

Equation 1: A 25 mL oven-dried Schlenk tube with a magnetic stirring bar was

equipped with diazonium salt **1a** (0.25 mmol), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfill (three times). **2a** (0.25 mmol) was dissolved in 1 mL anhydrous MeCN, taking to the Schlenk tube by syringe. The mixture was stirred at room temperature for 10 min. To the mixture, was added Cs₂CO₃ (0.75 mmol), and the resulting suspension was stirred at room temperature for 2 h. The aqueous layer was washed with diethyl ether (5×3 mL). The combined organic layer was monitored by GC-MS.

Equation 2; A 25 mL oven-dried Schlenk tube with a magnetic stirring bar was equipped with diazonium salt **1a** (0.25 mmol), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfill (three times). **2a** (0.25 mmol) was dissolved in 1 mL anhydrous MeCN, taking to the Schlenk tube by syringe. The mixture was stirred at room temperature for 10 min. To the mixture, was added Cs₂CO₃ (0.75 mmol). Ru(bpy)₃Cl₂·6H₂O (0.8 mg, 0.00125 mmol) was dissolved in 10 mL anhydrous MeCN, taking 1 mL to the Schlenk tube by syringe. The mixture was irradiated with a LED (23 W) and stirred at room temperature for 2 h. The aqueous layer was washed with diethyl ether (5×3 mL). The combined organic layer was monitored by GC-MS.

Equation 3: A 25 mL oven-dried Schlenk tube with a magnetic stirring bar was equipped with diazonium salt **1a** (0.25 mmol), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfill (three times). **2a** (0.25 mmol) was dissolved in 1 mL anhydrous MeCN, taking to the Schlenk tube by syringe. The mixture was stirred at room temperature for 10 min. To the mixture, was added Cs₂CO₃ (0.75 mmol). Ru(bpy)₃Cl₂·6H₂O (0.8 mg, 0.00125 mmol) was dissolved in 10 mL anhydrous MeCN, taking 1 mL to the Schlenk tube by syringe. Then, A solution of the **2a** (0.25 mmol) in 1 mL anhydrous MeCN was added via syringe. The mixture was irradiated with a LED (23 W) and stirred at room temperature for 2 h. The aqueous layer was washed with diethyl ether (5×3 mL). The combined organic layer were dried over MgSO₄, filtered and concentrated in vacuum. The residue was purified by flash chromatography using petrol ether/ethyl acetate (100:0-99:1) as the eluent.

Equation 4: A 25 mL oven-dried Schlenk tube with a magnetic stirring bar was equipped with diazonium salt **1a** (0.25 mmol), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfill (three times). **2a** (0.25 mmol) was dissolved in 1 mL anhydrous MeCN, taking to the Schlenk tube by syringe. The mixture was stirred at room temperature for 10 min. To the mixture, was added Cs₂CO₃ (0.75 mmol). Then, A solution of the **2a** (0.25 mmol) in 1 mL anhydrous MeCN was added via syringe. The mixture was stirred at room temperature for 2 h. The aqueous layer was washed with diethyl ether (5×3 mL). The combined organic layer were dried over MgSO₄, filtered and concentrated in vacuum. The residue was purified by flash chromatography using petrol ether/ethyl acetate (100:0-99:1) as the eluent.

The control experiment (Equation 4) was monitored by ¹⁹F NMR spectroscopy. During the 2 hour reaction process, five fluorine peaks, including **3a'** ($\delta = -92.62$ ppm), PhC(O)CF₂H ($\delta = -123.65$ ppm), **1a** ($\delta = -151.10$ ppm), TMSF ($\delta = -157.49$ ppm),

ppm), and product **3a** ($\delta = -97.72$ ppm) were observed (Figure S1). The **3a'** peak disappeared after 2 hours. The amount of **3a** increased during the reaction process.

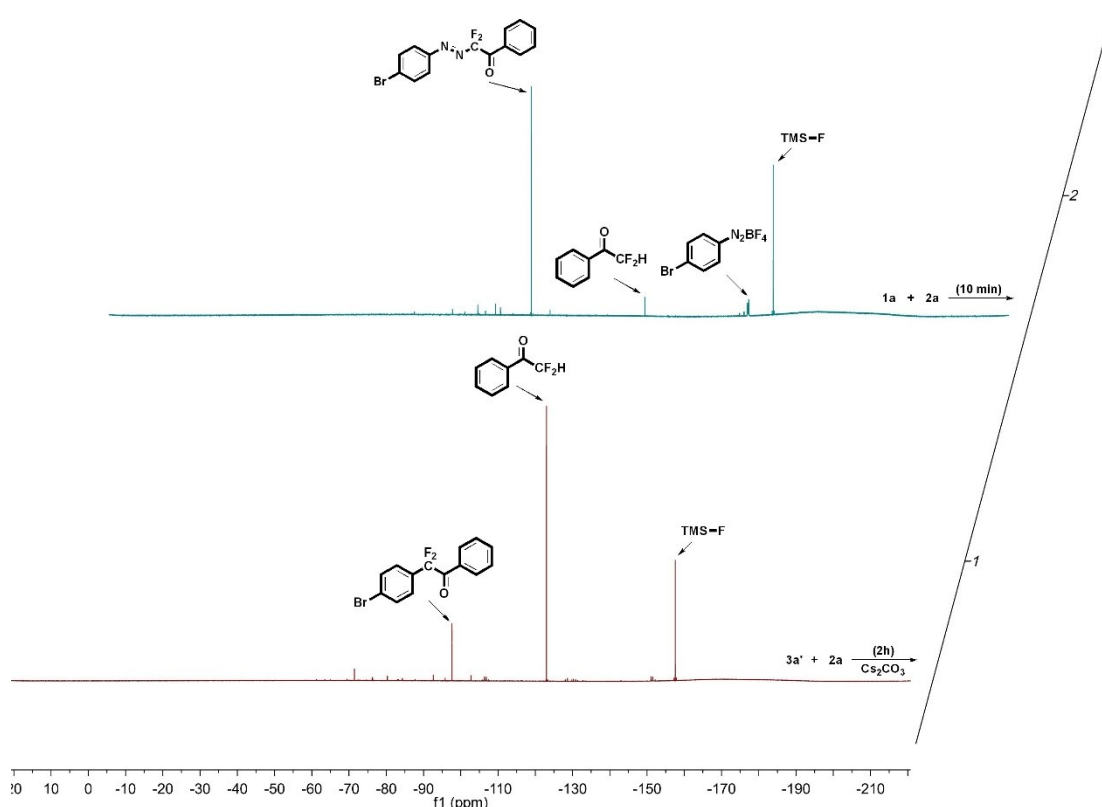


Figure S1 Progress of the control experiment (Equation 4) by ^{19}F NMR

3. Quantum Chemical Calculations

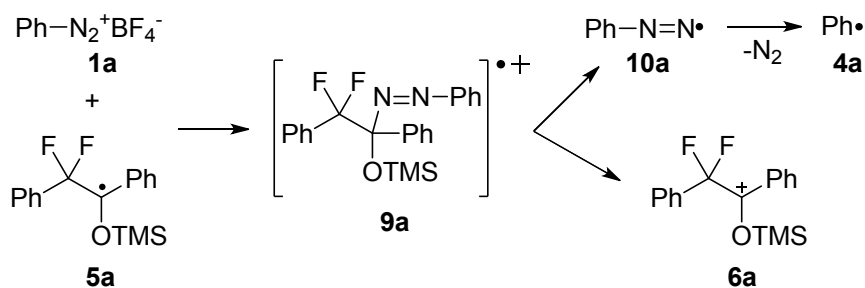


Figure S2 The proposed process from **1**, **5** to **4**, **6**

QM calculations were performed using the Gaussian09 program at the B3LYP/6-31G* level. To explore the possible reaction paths involved in the process of from **1a**, **5a** to **4a**, **6a** (Figure S2), we applied the AFIR method⁴⁻⁶ as implemented in the GRRM program to study the association of **1a** and **5a**.⁷⁻⁹ In the AFIR method, a distant dependent energy term was employed to overcome the reaction barrier so that the association reaction could occur. The dissociation of the intermediate complex **9a** was studied using the multi-coordinate driven (MCD) method.¹⁰ In MCD calculations, one first chooses by chemical intuition a set of active coordinates to drive a reaction

from the reactant to the product. The remaining coordinates only change adiabatically, i.e., they are energy minimized at each fixed value of the reaction coordinate.

To investigate further the process of from **1a**, **5a** to **4a**, **6a** (Figure S2), we employed quantum mechanical (QM) density functional theory (DFT) calculations to explore the mechanism at the atomic level. We started from preparing an initial structure of the two reactants in which the cation **1a** was placed in the proximity of molecule **5** and the N atom of the former approaches the C atom bonded to OTMS in the former. Then we used the AFIR method to explore the potential product resulting from the association of the two reactants. This leads to the production of a novel intermediate (Figure S3), a complex formed from the C-N covalent bond. By nature, this complex **9a** is both a cation and a radical. Its stability is similar to that of the two separated reactants and the reaction barrier in gas phase is around 8.77 kcal/mol (36.7 kJ/mol) as suggested by the AFIR potential energy surface (PES). We further carried out MCD calculations to study the dissociation of **9a**. The resulting reaction path was illustrated in Figure S4. We can see that the dissociation is a consecutive two-step process. In the first step, the complex is broken into **6a** and **10a**. The key characteristic of this step is the charge transfer from **6a** to **10a**: the former becomes a cation while the latter switches to a radical. The reaction barrier is around 2.73 kcal/mol (11.4 kJ/mol), suggesting that this is a fast process. Afterwards, the radical **10a** further dissociates into a nitrogen molecule and a benzene radical **4a** with the barrier around 10.06 kcal/mol (42.1 kJ/mol). The relatively high barrier is mainly due to the formation of the unstable benzene radical.

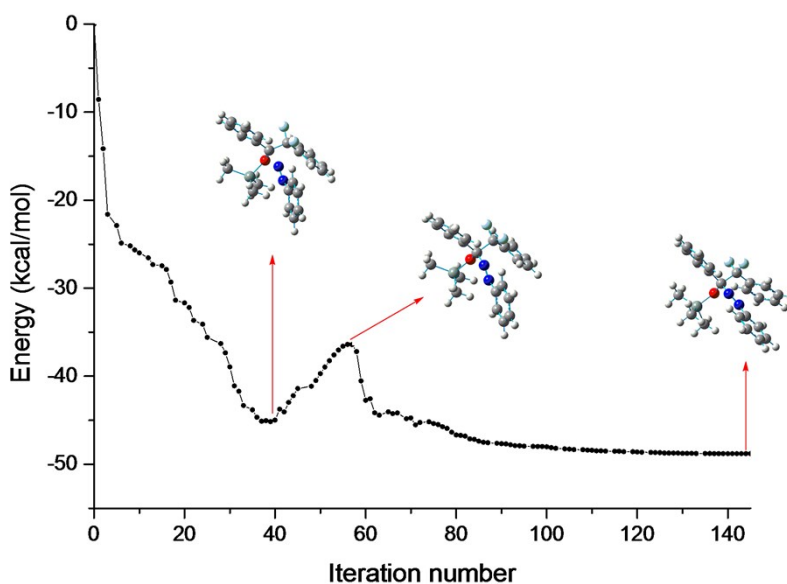


Figure S3 AFIR path: association of **1a** and **5a** to form **9a**

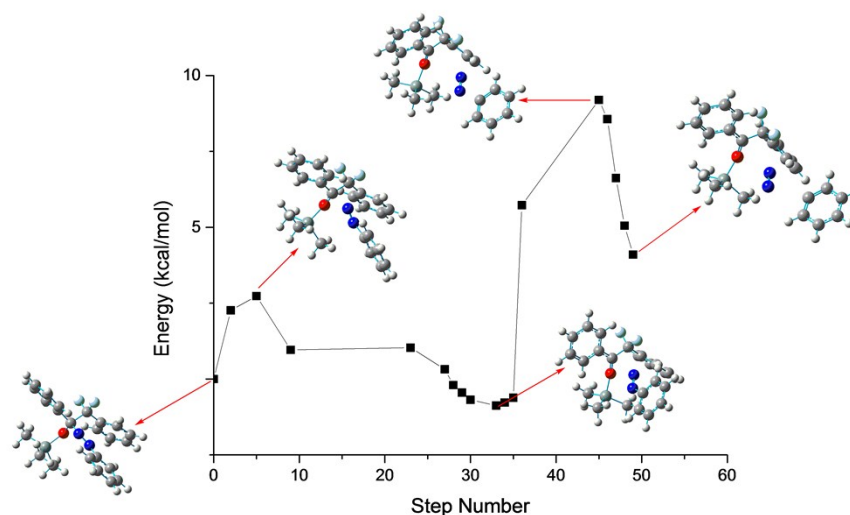
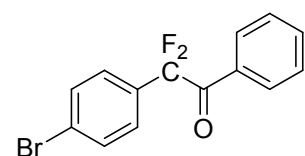


Figure S4 MCD path: dissociation of **9a** to form **4a** and **6a**

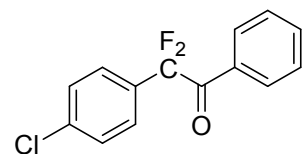
4. Characterization data

2-(4-bromophenyl)-2,2-difluoro-1-phenylethan-1-one (**3a**)¹²



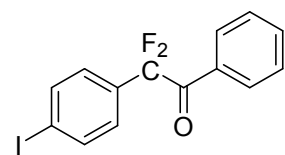
The title compound was isolated as a yellow liquid after chromatography on silica with a Combiflash system (100:0-99:1 petrol ether/ethyl acetate). Yield: 80%. ¹H NMR (500 MHz, CDCl₃) δ 8.04 (d, *J* = 7.8 Hz, 2H), 7.64 – 7.61 (m, 3H), 7.50 – 7.27 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ 188.66 (t, *J* = 31.4 Hz), 135.03 (s), 134.56 (s), 132.23 (s), 130.05 (s), 130.39 (s), 129.78 (s), 128.88 (s), 127.56 (s), 116.80 (t, *J* = 252.5 Hz). ¹⁹F NMR (470 MHz, CDCl₃) δ -97.56 (s).

2-(4-chlorophenyl)-2,2-difluoro-1-phenylethan-1-one (**3b**)³



The title compound was isolated as a yellow liquid after chromatography on silica with a Combiflash system (100:0-99:1 petrol ether/ethyl acetate). Yield: 76%. ¹H NMR (500 MHz, CDCl₃) δ 8.04 (d, *J* = 7.8 Hz, 2H), 7.64 – 7.61 (m, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.45 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ 188.66 (t, *J* = 31.5 Hz), 134.73 (s), 134.54 (s), 132.90 (s), 132.22 (s), 132.06 (s), 130.38 (s), 128.87 (s), 127.56 (s), 116.80 (t, *J* = 254.5 Hz). ¹⁹F NMR (470 MHz, CDCl₃) δ -97.36 (s).

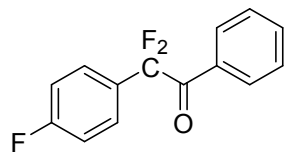
2,2-difluoro-2-(4-iodophenyl)-1-phenylethan-1-one (**3c**)



The title compound was isolated as a slightly yellow solid after chromatography on silica with a Combiflash system (100:0-98:2 petrol ether/ethyl acetate), m.p. 50-53 °C. Yield: 70%. ¹H NMR (500 MHz, CDCl₃) δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ

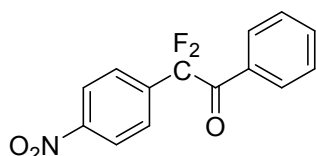
188.64 (t, 30.5 Hz), 138.16 (s), 134.54 (s), 134.32 (s), 133.08 (s), 132.88 (s), 132.68 (s), 132.05 (s), 130.38 (s), 128.87 (s), 127.54 (s), 166.87 (t, $J = 254.5$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ -97.88 (s). HRMS (EI) Calcd. For 357.9666, $\text{C}_{14}\text{H}_9\text{F}_2\text{IO}$, found 357.9660.

2,2-difluoro-2-(4-fluorophenyl)-1-phenylethan-1-one (3d)³



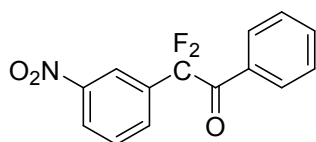
The title compound was isolated as a slightly yellow liquid after chromatography on silica with a Combiflash system (100:0-99:1 petrol ether/ethyl acetate). Yield: 82%. ^1H NMR (500 MHz, CDCl_3) δ 8.03 (d, $J = 7.8$ Hz, 2H), 7.62 – 7.59 (m, 3H), 7.46 (t, $J = 7.8$ Hz, 2H), 7.15 (t, $J = 8.5$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 188.88 (t, $J = 31.5$ Hz), 165.27 (s), 163.27 (s), 134.47 (s), 132.13 (s), 130.38 (s), 128.84 (s), 128.14 (s), 116.78 (t, $J = 253.9$ Hz), 116.22 (d, $J = 22.7$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ -96.54 (d, $J = 3.1$ Hz), -109.00 (t, $J = 3.7$ Hz).

2,2-difluoro-2-(4-nitrophenyl)-1-phenylethan-1-one (3e)³



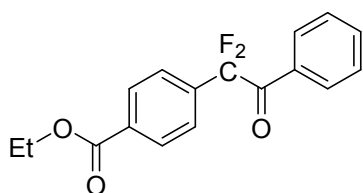
The title compound was isolated as a slightly yellow solid after chromatography on silica with a Combiflash system (100:0-90:10 petrol ether/ethyl acetate), m.p. 84-86 °C. Yield: 90%. ^1H NMR (500 MHz, CDCl_3) δ 8.34 (d, $J = 8.6$ Hz, 2H), 8.08 (d, $J = 7.8$ Hz, 2H), 7.81 (d, $J = 8.7$ Hz, 2H), 7.66 (t, $J = 7.4$ Hz, 1H), 7.51 (t, $J = 7.8$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 188.05 (t, $J = 31.5$ Hz), 149.56 (s), 139.31 (t, $J = 25.2$ Hz), 134.95 (s), 131.67 (s), 130.41 (s), 129.05 (s), 127.44 (s), 124.02 (s), 116.42 (t, $J = 257.04$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ -97.81 (s).

2,2-difluoro-2-(3-nitrophenyl)-1-phenylethan-1-one (3f)



The title compound was isolated as a slightly yellow solid after chromatography on silica with a Combiflash system (100:0-90:10 petrol ether/ethyl acetate), m.p. 72-74 °C. Yield: 87%. ^1H NMR (500 MHz, CDCl_3) δ 8.50 (s, 1H), 8.39 (d, $J = 8.2$ Hz, 1H), 8.11 (d, $J = 7.5$ Hz, 2H), 7.92 (d, $J = 7.8$ Hz, 1H), 7.72 – 7.65 (m, 2H), 7.52 (t, $J = 7.9$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 188.07 (t, $J = 31.6$ Hz), 148.45 (s), 135.20 (t, $J = 25.2$ Hz), 134.95 (s), 132.14 (s), 131.65 (s), 130.45 (s), 130.11 (s), 129.06 (s), 125.85 (s), 121.45 (s), 116.30 (t, $J = 257.0$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ -97.24 (s). HRMS (ESI) Calcd. For 300.0448, $\text{C}_{14}\text{H}_9\text{F}_2\text{NO}_3$ [M-Na]⁺, found 300.0468.

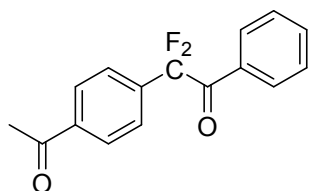
ethyl 4-(1,1-difluoro-2-oxo-2-phenylethyl)benzoate (3g)³



The title compound was isolated as a slightly yellow liquid after chromatography on silica with a Combiflash system (100:0-95:5 petrol ether/ethyl acetate). Yield: 87%. ^1H NMR (500 MHz, CDCl_3) δ 8.14 (d, $J = 8.4$ Hz, 2H), 8.04 (d, $J = 7.6$ Hz, 2H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.47 (t, J

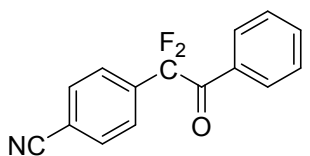
= 7.9 Hz, 2H), 4.40 (q, $J = 7.2$ Hz, 2H), 1.40 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 188.57 (t, $J = 32.0$ Hz), 165.74 (s), 137.35 (t, $J = 25.2$ Hz), 134.57 (s), 133.00 (s), 132.03 (s), 130.38 (s), 130.08 (s), 128.88 (s), 125.97 (s), 116.73 (t, $J = 255.2$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ -98.07 (s).

2-(4-acetylphenyl)-2,2-difluoro-1-phenylethan-1-one (3h)²



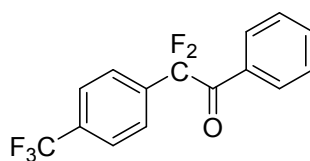
The title compound was isolated as a slightly yellow solid after chromatography on silica with a Combiflash system (100:0-95:5 petrol ether/ethyl acetate), m.p. 60-63 °C. Yield: 85%. ^1H NMR (500 MHz, CDCl_3) δ 8.05 (d, $J = 8.1$ Hz, 4H), 7.72 (d, $J = 8.4$ Hz, 2H), 7.62 (t, $J = 7.5$ Hz, 1H), 7.48 (t, $J = 7.8$ Hz, 2H), 2.63 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 197.32 (s), 188.53 (t, $J = 30.9$ Hz), 139.06 (s), 137.50 (t, $J = 25.8$ Hz), 134.63 (s), 131.99 (s), 130.39 (s), 128.91 (s), 128.76 (s), 126.30 (s), 116.72 (t, $J = 254.5$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ -98.07 (s).

4-(1,1-difluoro-2-oxo-2-phenylethyl)benzonitrile (3i)²



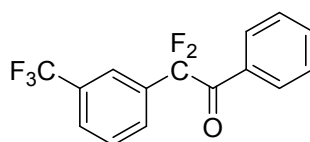
The title compound was isolated as a slightly yellow solid after chromatography on silica with a Combiflash system (100:0-95:5 petrol ether/ethyl acetate), m.p. 78-80 °C. Yield: 83%. ^1H NMR (500 MHz, CDCl_3) δ 8.07 (d, $J = 7.6$ Hz, 2H), 7.79 (d, $J = 8.5$ Hz, 2H), 7.73 (d, $J = 8.4$ Hz, 2H), 7.66 (t, $J = 7.5$ Hz, 1H), 7.51 (t, $J = 7.9$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 188.14 (t, $J = 31.5$ Hz), 137.67 (t, $J = 25.4$ Hz), 134.88 (s), 132.63 (s), 131.74 (s), 130.39 (s), 129.02 (s), 126.92 (s), 117.91 (s), 116.40 (t, $J = 256.4$ Hz), 115.14 (s). ^{19}F NMR (470 MHz, CDCl_3) δ -98.22 (s).

2,2-difluoro-1-phenyl-2-(4-(trifluoromethyl)phenyl)ethan-1-one (3j)²



The title compound was isolated as a slightly yellow solid after chromatography on silica with a Combiflash system (100:0-99:1 petrol ether/ethyl acetate), m.p. 30-32 °C. Yield: 89%. ^1H NMR (500 MHz, CDCl_3) δ 8.07 (d, $J = 7.7$ Hz, 2H), 7.75 (s, 4H), 7.64 (t, $J = 7.5$ Hz, 1H), 7.50 (t, $J = 7.8$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 188.45 (t, $J = 30.9$ Hz), 136.83 (t, $J = 26.5$ Hz), 134.71 (s), 133.13 (q, $J = 31.5$ Hz), 131.91 (s), 130.40 (s), 128.95 (s), 126.56 (s), 123.67 (q, $J = 272.5$ Hz), 116.58 (t, $J = 255.2$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ -63.01 (s), -97.87 (s).

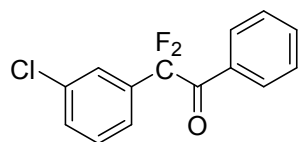
2,2-difluoro-1-phenyl-2-(3-(trifluoromethyl)phenyl)ethan-1-one (3k)



The title compound was isolated as a slighted yellow liquid after chromatography on silica with a Combiflash system (100:0-99:1 petrol ether/ethyl acetate). Yield: 86%. ^1H NMR (500 MHz, CDCl_3) δ 8.08 (d, $J = 7.6$ Hz, 2H), 7.90 (s, 1H), 7.79 (t, $J = 6.6$ Hz, 2H),

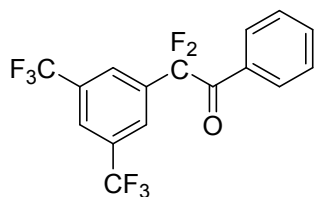
7.64 (dd, $J = 18.1, 7.7$ Hz, 2H), 7.50 (t, $J = 7.9$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 188.47 (t, $J = 31.5$ Hz), 134.72 (s), 134.27 (t, $J = 25.8$ Hz), 131.91 (s), 131.53 (q, $J = 32.8$ Hz), 130.41 (s), 129.51 (s), 128.95 (s), 127.87 (s), 123.66 (q, $J = 270.0$ Hz), 122.96 (s), 116.59 (t, $J = 256.4$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ -62.78 (s), -97.43 (s). HRMS (EI) Calcd. For 300.0574, $\text{C}_{15}\text{H}_9\text{F}_5\text{O}$, found 300.0581.

2-(3-chlorophenyl)-2,2-difluoro-1-phenylethan-1-one (3l)



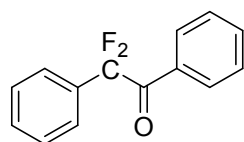
The title compound was isolated as a yellow liquid after chromatography on silica with a Combiflash system (100:0-99:1 petrol ether/ethyl acetate). Yield: 65%. ^1H NMR (500 MHz, CDCl_3) δ 8.05 (d, $J = 7.7$ Hz, 2H), 7.64 – 7.61 (m, 2H), 7.50 – 7.47 (m, 4H), 7.42 (d, $J = 7.9$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 188.54 (t, $J = 31.5$ Hz), 135.11 (s), 134.58 (s), 132.02 (s), 131.28 (s), 130.40 (s), 128.89 (s), 126.15 (s), 124.14 (s), 116.38 (t, $J = 255.2$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ -97.54 (s). HRMS (EI) Calcd. For 266.0310, $\text{C}_{14}\text{H}_9\text{ClF}_2\text{O}$, found 266.0313.

2-(3,5-bis(trifluoromethyl)phenyl)-2,2-difluoro-1-phenylethan-1-one (3m)



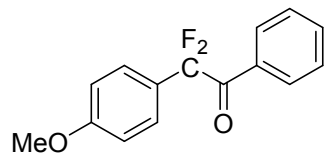
The title compound was isolated as a slightly yellow liquid after chromatography on silica with a Combiflash system (100:0-99:1 petrol ether/ethyl acetate). Yield: 90%. ^1H NMR (500 MHz, CDCl_3) δ 8.13 (d, $J = 7.5$ Hz, 2H), 8.05 (s, 3H), 7.70 (t, $J = 7.5$ Hz, 1H), 7.55 (t, $J = 7.9$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 187.82 (t, $J = 32.8$ Hz), 135.69 (t, $J = 26.3$ Hz), 135.11 (s), 132.46 (q, $J = 33.8$ Hz), 131.47 (s), 130.47 (s), 129.10 (s), 126.71 (s), 124.98 (s), 122.92 (q, $J = 271.3$ Hz), 116.25 (t, $J = 258.3$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ -62.95 (s), -97.21 (s). HRMS (ESI) Calcd. For 407.0084, $\text{C}_{16}\text{H}_8\text{F}_8\text{O}$ [M-K] $^+$, found 407.0063.

2,2-difluoro-1,2-diphenylethan-1-one (3n)²



The title compound was isolated as a yellow liquid after chromatography on silica with a Combiflash system (100:0-99:1 petrol ether/ethyl acetate). Yield: 67%. ^1H NMR (500 MHz, CDCl_3) δ 8.04 (d, $J = 7.8$ Hz, 2H), 7.63 – 7.58 (m, 3H), 7.49–7.44 (m, 5H). ^{13}C NMR (125 MHz, CDCl_3) δ 189.12 (t, $J = 30.2$ Hz), 134.33 (s), 133.28 (t, $J = 25.2$ Hz), 132.31 (s), 131.05 (s), 130.42 (s), 128.96 (s), 128.78 (s), 125.77 (s), 117.04 (t, $J = 253.3$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ -97.51 (s).

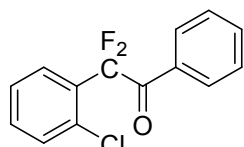
2,2-difluoro-2-(4-methoxyphenyl)-1-phenylethan-1-one (3o)³



The title compound was isolated as a yellow liquid after chromatography on silica with a Combiflash system (100:0-95:5 petrol ether/ethyl acetate). Yield: 50%. ^1H NMR (500 MHz, CDCl_3) δ 8.02 (d, $J = 7.7$ Hz, 2H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.54 (d, $J = 8.8$

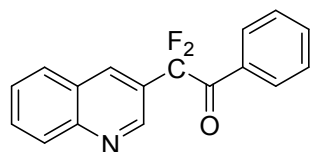
Hz, 2H), 7.45 (t, $J = 7.8$ Hz, 2H), 6.97 (d, $J = 8.8$ Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 189.34 (t, $J = 32.1$ Hz), 161.63 (s), 134.23 (s), 134.42 (s), 130.41 (s), 128.74 (s), 127.39 (s), 125.33 (t, $J = 25.8$ Hz), 117.19 (t, $J = 253.3$ Hz), 11.15 (s), 4.37 (s). ^{19}F NMR (470 MHz, CDCl_3) δ -96.19 (s).

2-(2-chlorophenyl)-2,2-difluoro-1-phenylethan-1-one (3p)



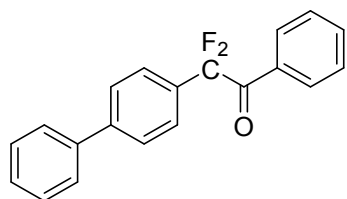
The title compound was isolated as a slightly yellow liquid after chromatography on silica with a Combiflash system (100:0-98:2 petrol ether/ethyl acetate). Yield: 40%. ^1H NMR (500 MHz, CDCl_3) δ 8.10 (d, $J = 7.8$ Hz, 2H), 7.86 – 7.82 (m, 1H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.49 (t, $J = 7.8$ Hz, 2H), 7.44 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 187.97 (t, $J = 31.2$ Hz), 134.26 (s), 132.54 (s), 132.17 (s), 130.95 (s), 130.18 (s), 128.77 (s), 127.61 (s), 127.05 (s), 116.03 (t, $J = 255.8$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ -97.42 (s). HRMS (ESI) Calcd. For 289.0208, $\text{C}_{14}\text{H}_9\text{ClF}_2\text{O}$, $[\text{M}-\text{Na}]^+$, found 289.0223.

2,2-difluoro-1-phenyl-2-(quinolin-3-yl)ethan-1-one (3r)¹³



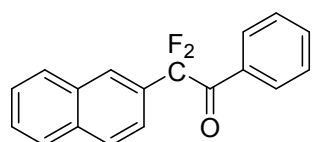
The title compound was isolated as a slightly yellow oil after chromatography on silica with a Combiflash system (100:0-97:3 petrol ether/ethyl acetate). Yield: 45%. ^1H NMR (500 MHz, CDCl_3) δ 9.10 (s, 1H), 8.41 (s, 1H), 8.18 (d, $J = 8.5$ Hz, 1H), 8.13 (d, $J = 7.6$ Hz, 2H), 7.91 (d, $J = 8.1$ Hz, 1H), 7.83 (t, $J = 7.7$ Hz, 1H), 7.65 (t, $J = 7.5$ Hz, 3H), 7.51 (t, $J = 7.9$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 188.49 (t, $J = 31.5$ Hz), 149.01 (s), 147.06 (s), 134.79 (s), 134.53 (s), 131.90 (s), 131.48 (s), 130.48 (s), 129.62 (s), 129.00 (s), 128.66 (s), 127.83 (s), 126.77 (s), 116.80 (t, $J = 255.8$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ -97.06 (s).

2-([1,1'-biphenyl]-4-yl)-2,2-difluoro-1-phenylethan-1-one (3s)¹⁴



The title compound was isolated as a slightly yellow solid after chromatography on silica with a Combiflash system (100:0-99:1 petrol ether/ethyl acetate), m.p. 84-86 °C. Yield: 55%. ^1H NMR (500 MHz, CDCl_3) δ 8.09 (d, $J = 7.7$ Hz, 2H), 7.70 (s, 4H), 7.60 (d, $J = 7.3$ Hz, 3H), 7.47 (dd, $J = 11.8, 7.9$ Hz, 4H), 7.41 (d, $J = 7.3$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 189.13 (t, $J = 31.5$ Hz), 144.01 (s), 140.02 (s), 134.39 (s), 132.33 (s), 130.46 (s), 129.07 (s), 128.82 (s), 127.69 (s), 127.37 (s), 126.84 (s), 126.30 (s), 117.18 (t, $J = 253.3$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ -97.21 (d, $J = 1.6$ Hz).

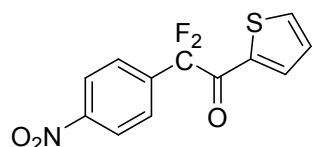
2,2-difluoro-2-(naphthalen-2-yl)-1-phenylethan-1-one (3t)³



The title compound was isolated as a slightly yellow solid after chromatography on silica with a Combiflash system (100:0-99:1

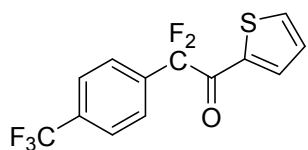
petrol ether/ethyl acetate), m.p. 67-69 °C. Yield: 50%. ¹H NMR (500 MHz, CDCl₃) δ 8.15 (s, 1H), 8.08 (d, *J* = 7.8 Hz, 2H), 7.96 – 7.88 (m, 3H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.58 (dd, *J* = 13.5, 7.1 Hz, 3H), 7.45 (t, *J* = 7.8 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 189.16 (t, *J* = 30.87 Hz), 134.37 (s), 132.68 (s), 132.34 (s), 130.46 (s), 129.16 (s), 128.81 (s), 127.94 (d, *J* = 1.34 Hz), 127.11 (s), 126.10 (s), 122.17 (s), 117.24 (t, *J* = 125.3 Hz). ¹⁹F NMR (470 MHz, CDCl₃) δ -96.99 (s).

2,2-difluoro-2-(4-nitrophenyl)-1-(thiophen-2-yl)ethan-1-one (3u)



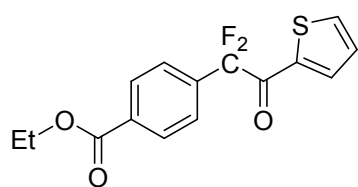
The title compound was isolated as a slightly yellow solid after chromatography on silica with a Combiflash system (100:0-90:10 petrol ether/ethyl acetate), m.p. 82-84 °C. Yield: 89%. ¹H NMR (500 MHz, CDCl₃) δ 8.33 (d, *J* = 8.6 Hz, 2H), 8.06 (d, *J* = 2.6 Hz, 1H), 7.85 (t, *J* = 6.3 Hz, 3H), 7.23 (t, *J* = 4.4 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 181.27 (t, *J* = 32.8 Hz), 149.61 (s), 138.97 (t, *J* = 25.2 Hz), 137.61 (s), 137.44 (s), 136.38 (s), 129.13 (s), 127.45 (s), 124.02 (s), 115.90 (t, *J* = 256.4 Hz). ¹⁹F NMR (470 MHz, CDCl₃) δ -99.54 (s). HRMS (EI) Calcd. For 283.0115, C₁₂H₇F₂NO₃S, found 283.0113.

2,2-difluoro-1-(thiophen-2-yl)-2-(4-(trifluoromethyl)phenyl)ethan-1-one (3v)



The title compound was isolated as a yellow liquid after chromatography on silica with a Combiflash system (100:0-95:5 petrol ether/ethyl acetate). Yield: 85%. ¹H NMR (500 MHz, CDCl₃) δ 8.02 (d, *J* = 2.6 Hz, 1H), 7.82 (d, *J* = 4.9 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.21 (t, *J* = 4.4 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 181.72 (t, *J* = 33.4 Hz), 137.86 (s), 137.10 (s), 136.51 (s), 136.24 (s), 133.20 (q, *J* = 32.8 Hz), 129.01 (s), 126.58 (s), 125.93 (s), 123.65 (q, *J* = 271.3 Hz), 116.12 (t, *J* = 255.2 Hz). ¹⁹F NMR (470 MHz, CDCl₃) δ -63.03 (s), -99.69 (s). HRMS (ESI) Calcd. For 329.0035, C₁₃H₇F₅OS [M-Na]⁺, found 329.0049.

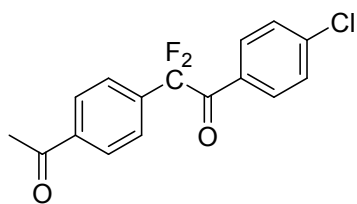
ethyl 4-(1,1-difluoro-2-oxo-2-(thiophen-2-yl)ethyl)benzoate (3w)



The title compound was isolated as a slightly yellow solid after chromatography on silica with a Combiflash system (100:0-90:10 petrol ether/ethyl acetate), m.p. 45-48 °C. Yield: 88%. ¹H NMR (500 MHz, CDCl₃) δ 8.13 (d, *J* = 8.3 Hz, 2H), 7.99 (d, *J* = 2.7 Hz, 1H), 7.80 (d, *J* = 4.9 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.18 (t, *J* = 5 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 181.71 (t, *J* = 32.8 Hz), 165.73 (s), 137.98 (s), 136.90 (s), 136.16 (s), 133.04 (s), 130.04 (s), 128.94 (s), 126.01 (s), 116.33 (t, *J* = 255.2 Hz), 61.54 (s), 14.40 (s). ¹⁹F NMR (470 MHz, CDCl₃) δ -99.85 (s). HRMS (EI) Calcd. For 310.0475, C₁₅H₁₂F₂O₃S, found 310.0473.

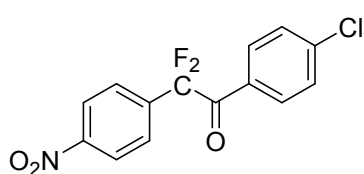
2-(4-acetylphenyl)-1-(4-chlorophenyl)-2,2-difluoroethan-1-one (3x)

The title compound was isolated as a white solid after chromatography on silica with a



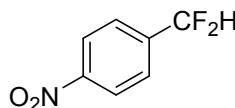
Combiflash system (100:0-95:5 petrol ether/ethyl acetate), m.p. 69-71 °C. Yield: 86%. ¹H NMR (500 MHz, CDCl₃) δ 8.05 (d, *J* = 8.2 Hz, 2H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 2.64 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 197.26 (s), 187.43 (t, *J* = 30.8 Hz), 141.45 (s), 139.16 (s), 137.11 (t, *J* = 24.6 Hz), 131.77 (s), 130.22 (s), 129.35 (s), 128.80 (s), 126.29 (s), 116.68 (t, *J* = 255.2 Hz). ¹⁹F NMR (470 MHz, CDCl₃) δ -98.15 (s). HRMS (EI) Calcd. For 308.0416, C₁₆H₁₁ClF₂O₂, found 308.0419.

1-(4-chlorophenyl)-2,2-difluoro-2-(4-nitrophenyl)ethan-1-one (3y)



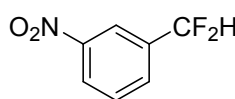
The title compound was isolated as a white solid after chromatography on silica with a Combiflash system (100:0-85:15 petrol ether/ethyl acetate), m.p. 48-50 °C.. Yield: 90%. ¹H NMR (500 MHz, CDCl₃) δ 8.35 (d, *J* = 8.6 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 186.96 (t, *J* = 32.1 Hz), 149.64 (s), 141.83 (s), 138.91 (t, *J* = 25.2 Hz), 131.79 (s), 129.92 (s), 129.50 (s), 127.45 (s), 124.04 (s), 116.41 (t, *J* = 257.0 Hz). ¹⁹F NMR (470 MHz, CDCl₃) δ -97.82 (s). HRMS (EI) Calcd. For 311.0161, C₁₄H₈ClF₂NO₃, found 311.0169.

1-(difluoromethyl)-4-nitrobenzene (4a)¹¹



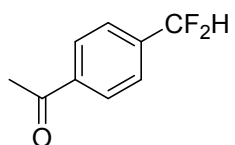
The title compound was isolated as a slightly yellow liquid after chromatography on silica with a Combiflash system (100:0-90:10 petrol ether/ethyl acetate). Yield: 84%. ¹H NMR (500 MHz, CDCl₃) δ 8.34 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 6.75 (t, *J* = 55.8 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 149.54 (s), 140.33 (t, *J* = 23.3 Hz), 126.98 (s), 124.14 (s), 113.29 (t, *J* = 241.9 Hz). ¹⁹F NMR (470 MHz, CDCl₃) δ -112.93 (s).

1-(difluoromethyl)-3-nitrobenzene (4b)¹⁵



The title compound was isolated as a slightly yellow liquid after chromatography on silica with a Combiflash system (100:0-90:10 petrol ether/ethyl acetate). Yield: 80%. ¹H NMR (500 MHz, CDCl₃) δ 8.41 (s, 1H), 8.37 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.70 (t, *J* = 7.9 Hz, 1H), 6.76 (t, *J* = 55.9 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 148.50 (s), 136.28 (t, *J* = 23.3 Hz), 131.61 (s), 130.22 (s), 125.71 (s), 121.18 (s), 113.19 (t, *J* = 240.7 Hz). ¹⁹F NMR (470 MHz, CDCl₃) δ -112.09 (s).

1-(4-(difluoromethyl)phenyl)ethan-1-one (4c)¹⁶



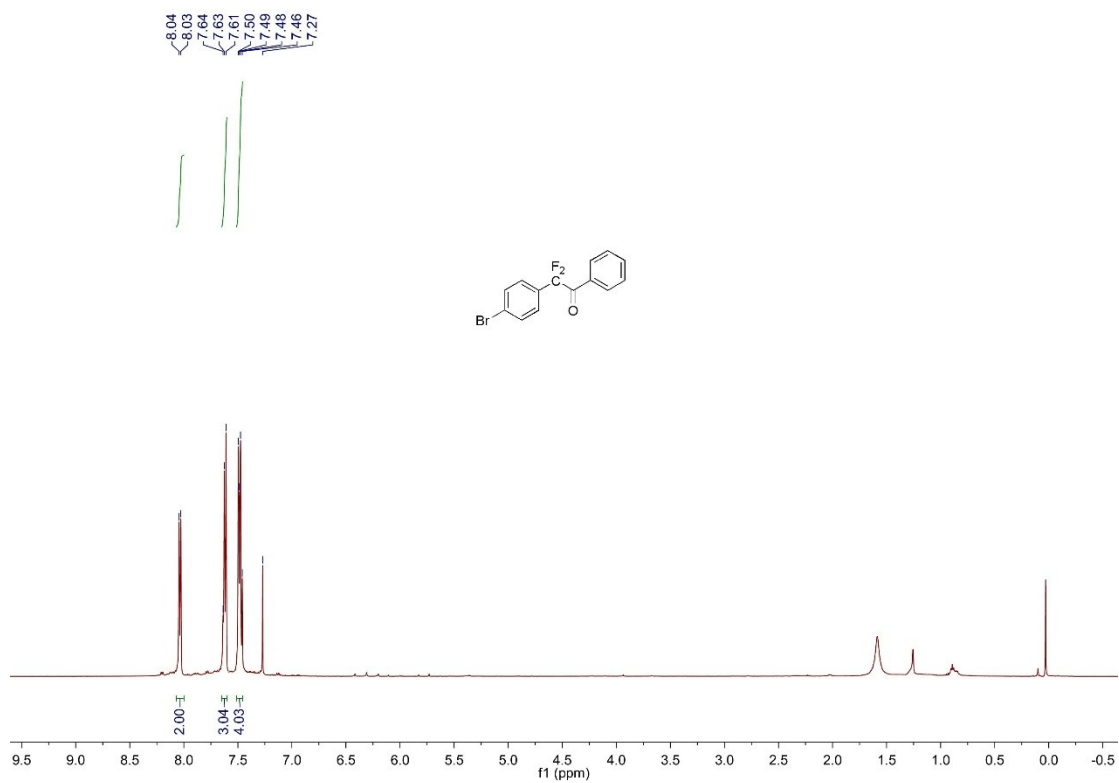
The title compound was isolated as a slightly yellow liquid after chromatography on silica with a Combiflash system (100:0-95:5 petrol ether/ethyl acetate). Yield: 75%. ¹H NMR (500 MHz, CDCl₃) δ 8.05 (d, *J* =

8.1 Hz, 2H), 7.63 (d, $J = 8.1$ Hz, 2H), 6.71 (t, $J = 56.1$ Hz, 1H), 2.65 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 197.46 (s), 139.01 (s), 138.64 (t, $J = 22.7$ Hz), 128.77 (s), 126.03 (s), 114.08 (t, $J = 245.7$ Hz). ^{19}F NMR (470 MHz, CDCl_3) δ -112.27 (s).

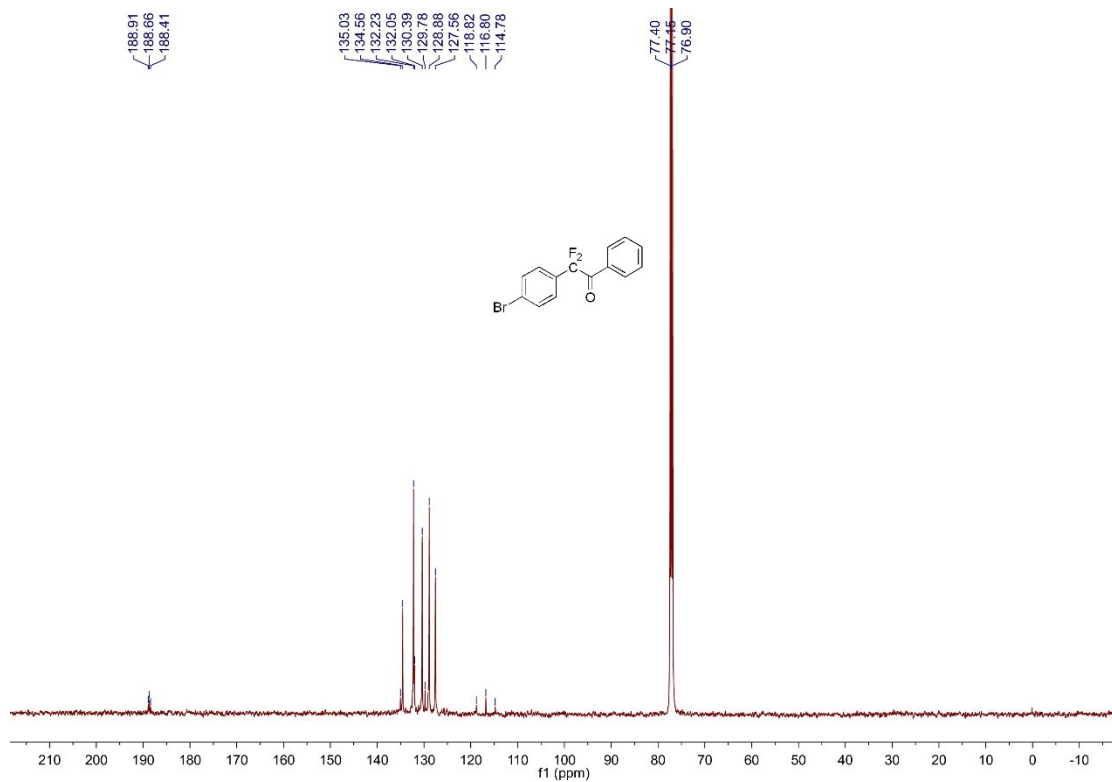
Reference

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- (12) CAS: 1409976-21-1.
- (13) CAS: 1630791-99-9.
- (14) CAS: 1409976-17-5.
- (15) Commercial chemical, CAS: 403-25-8.
- (16) Commercial chemical, CAS: 179990-93-3.

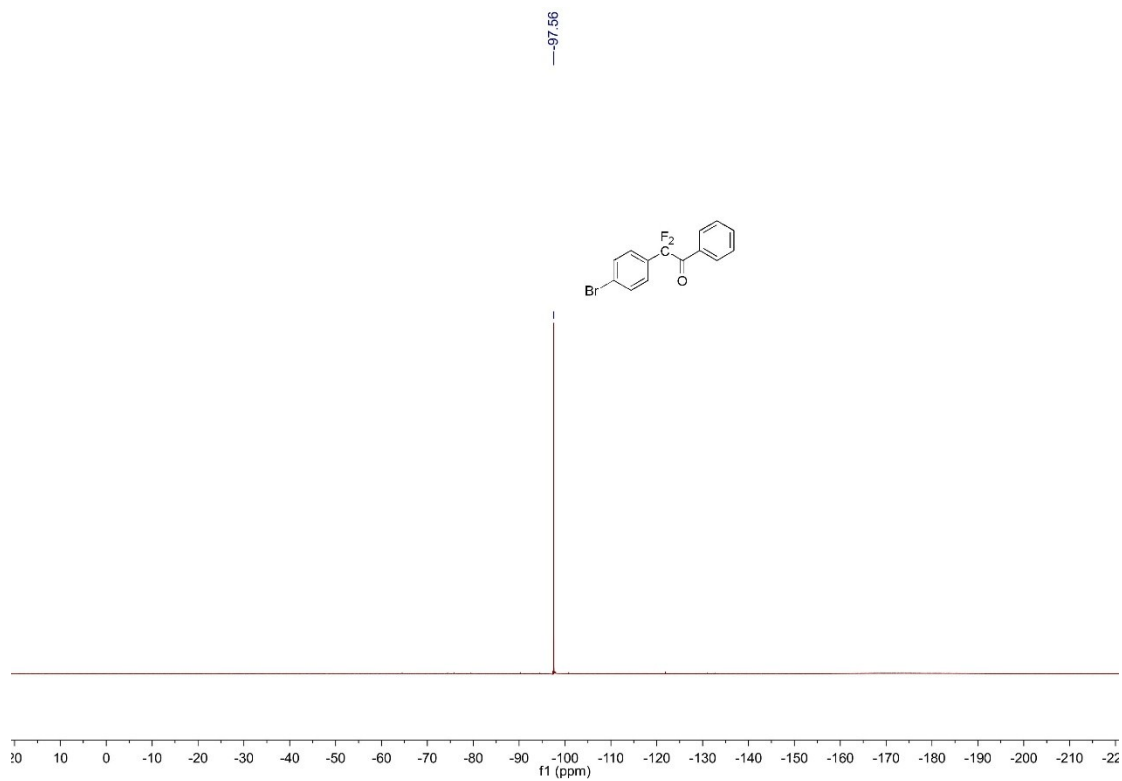
5. NMR Spectra of all products



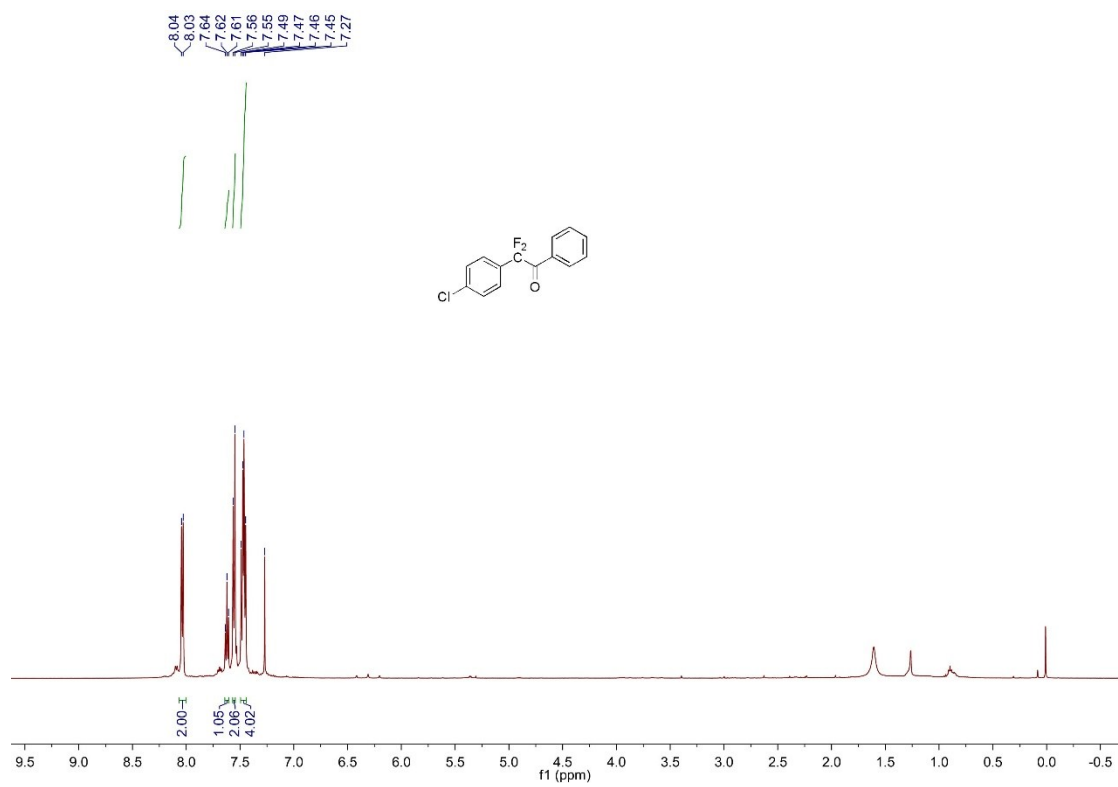
$^1\text{H NMR}$ 3a



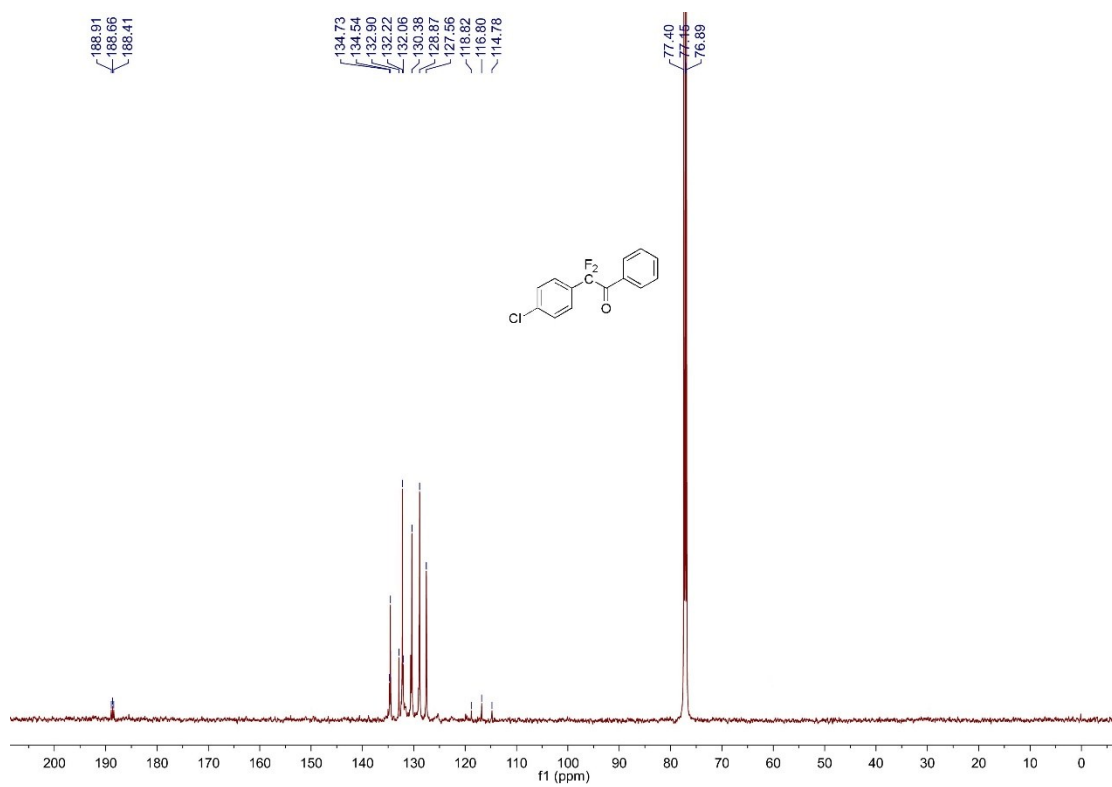
$^{13}\text{C NMR}$ 3a



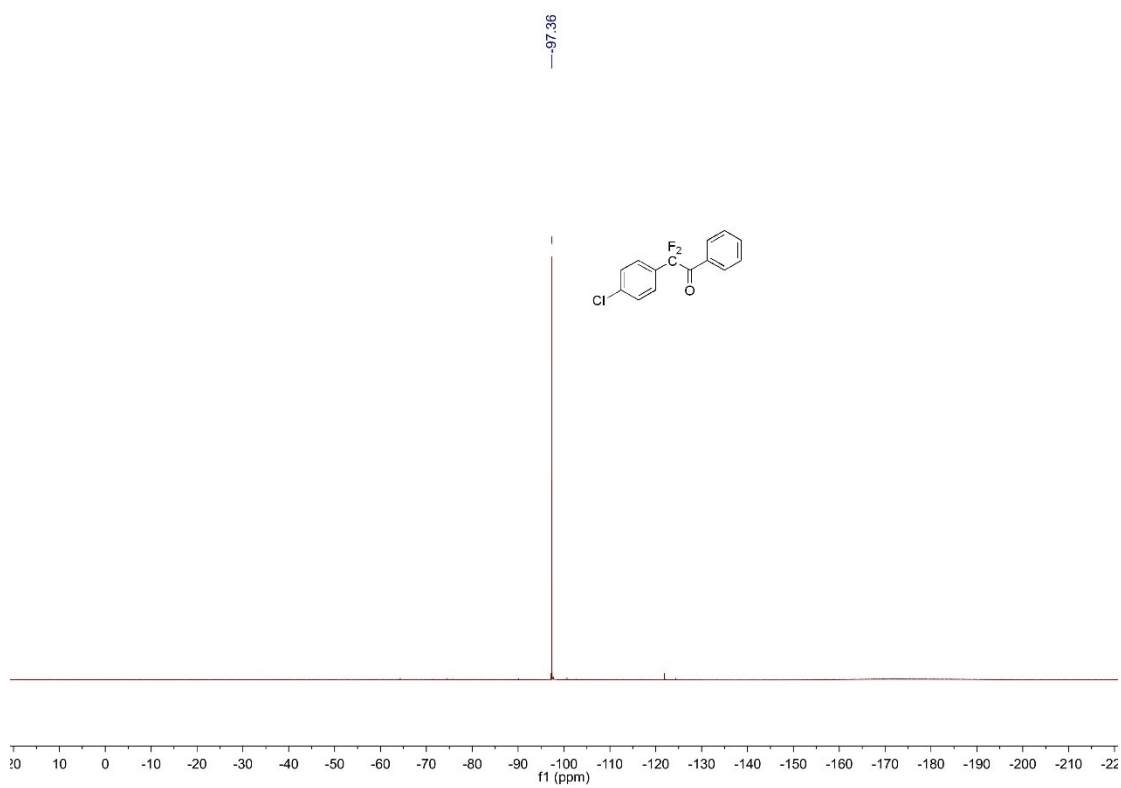
^{19}F NMR **3a**



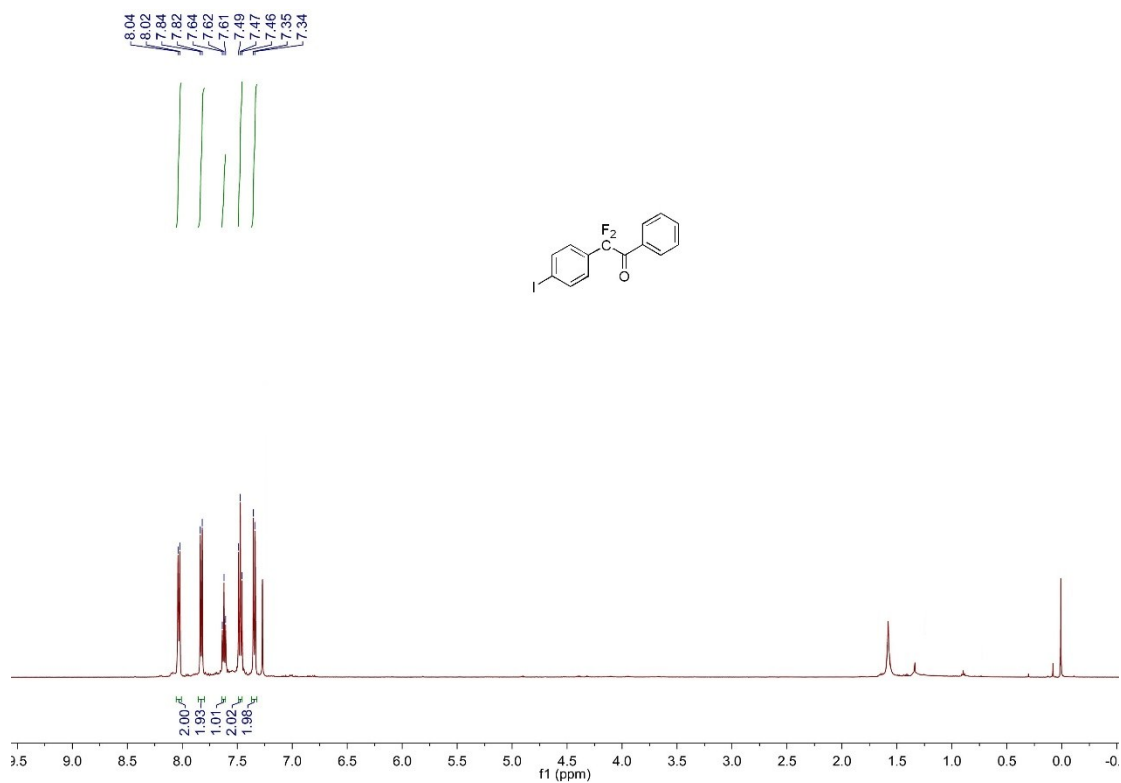
^1H NMR **3b**



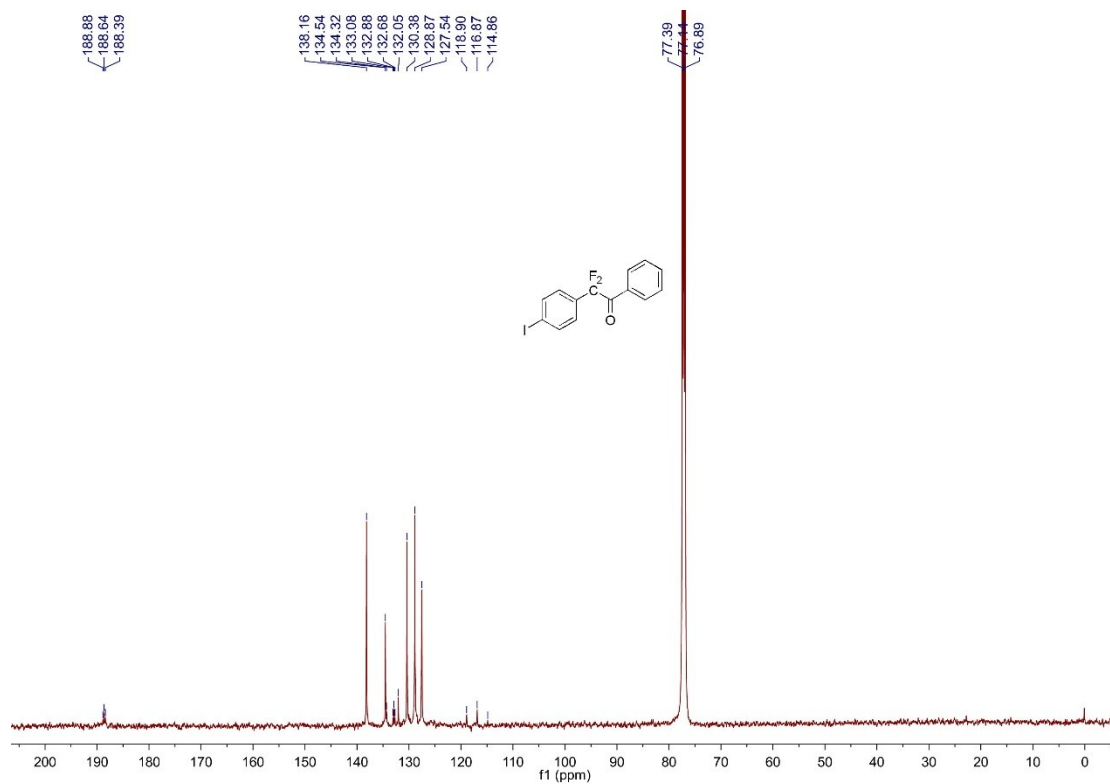
^{13}C NMR **3b**



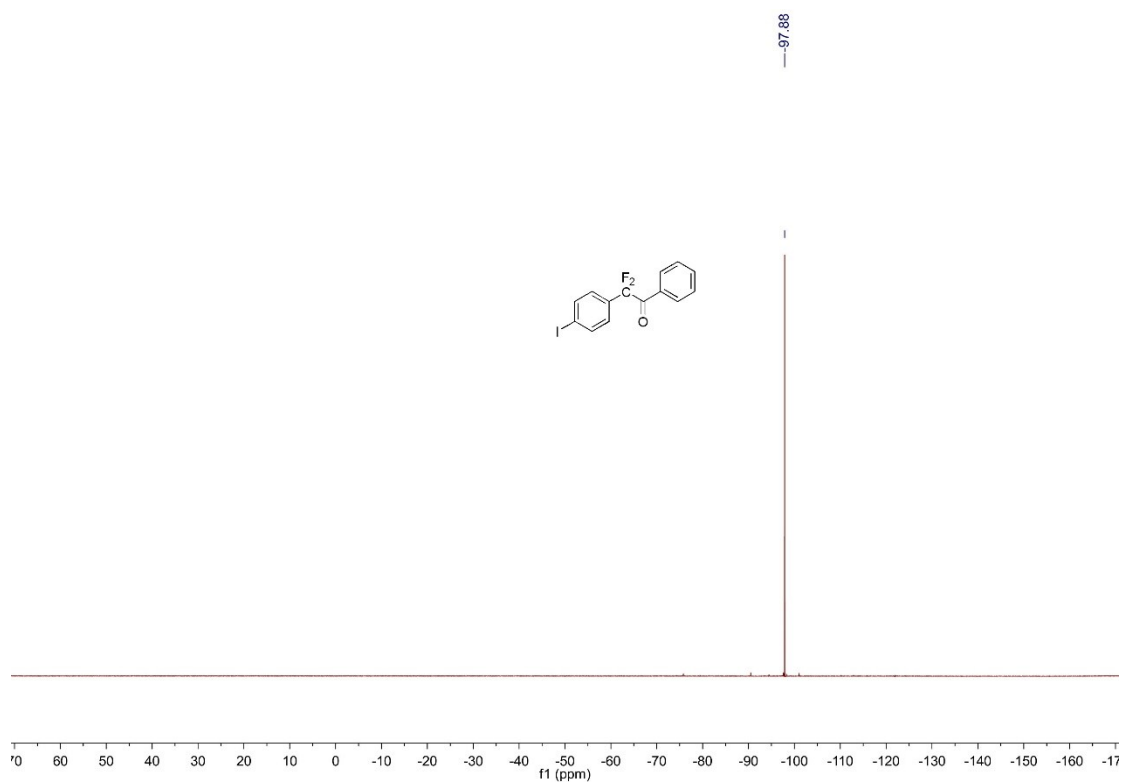
^{19}F NMR **3b**



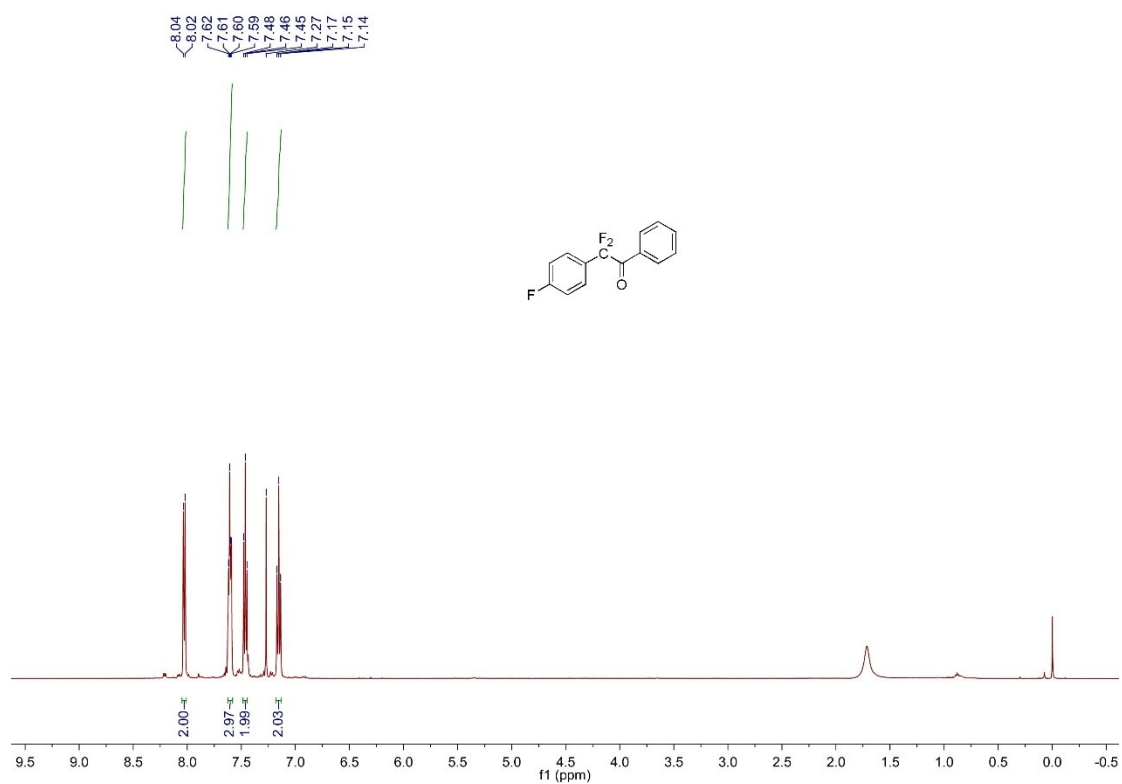
¹H NMR 3c



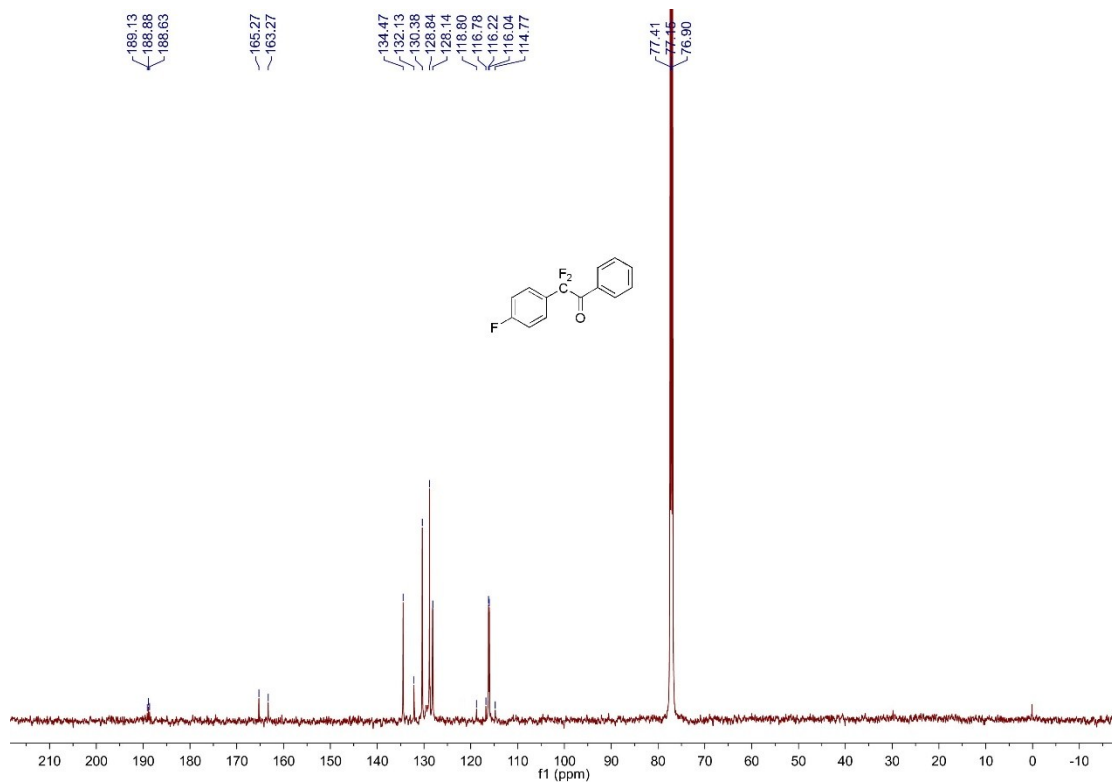
¹³C NMR 3c



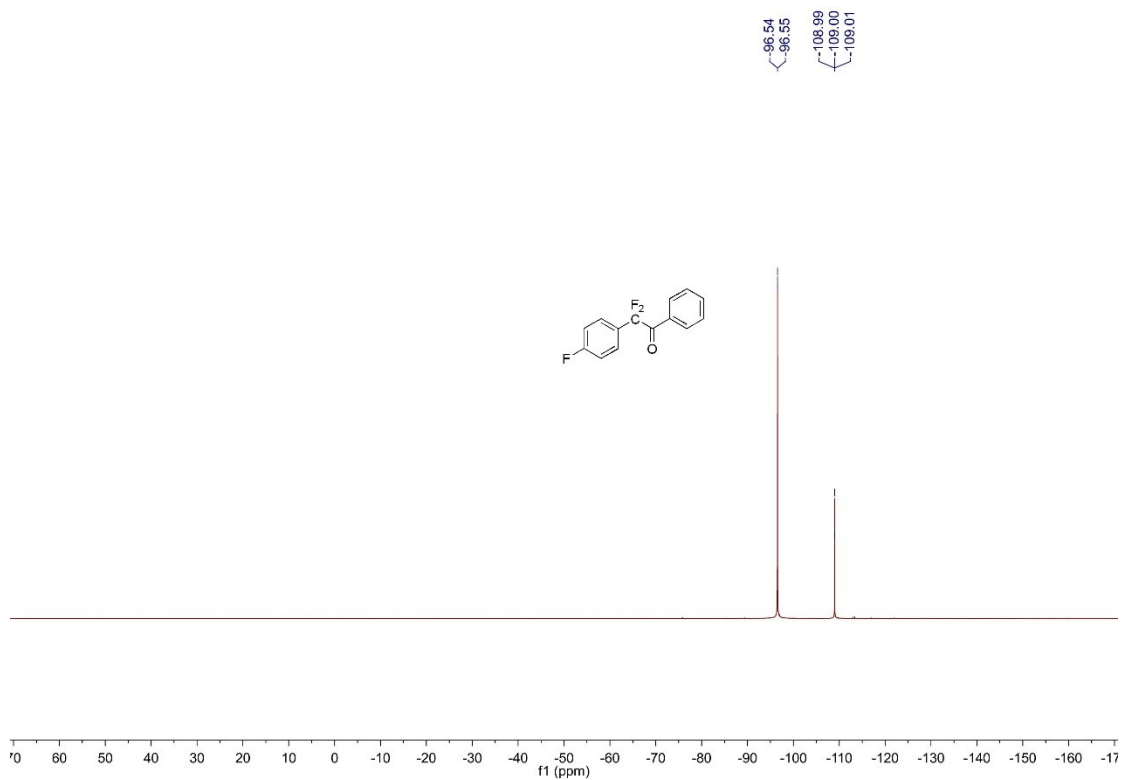
¹⁹F NMR 3c



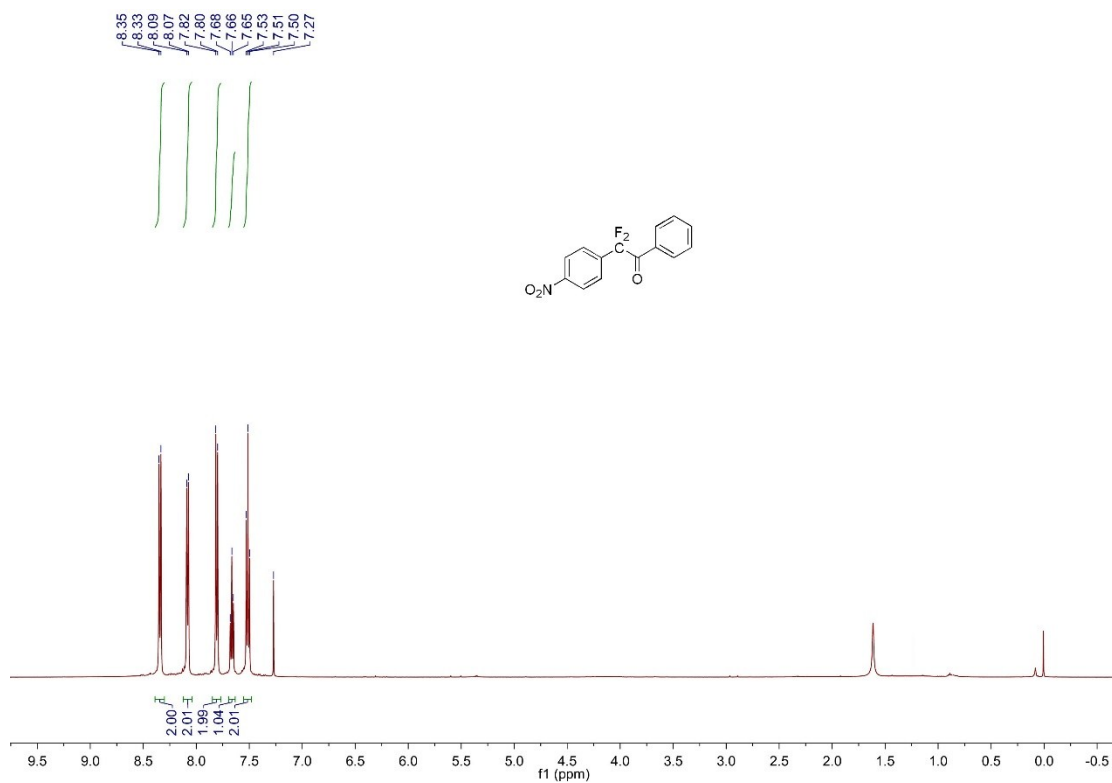
¹H NMR 3d



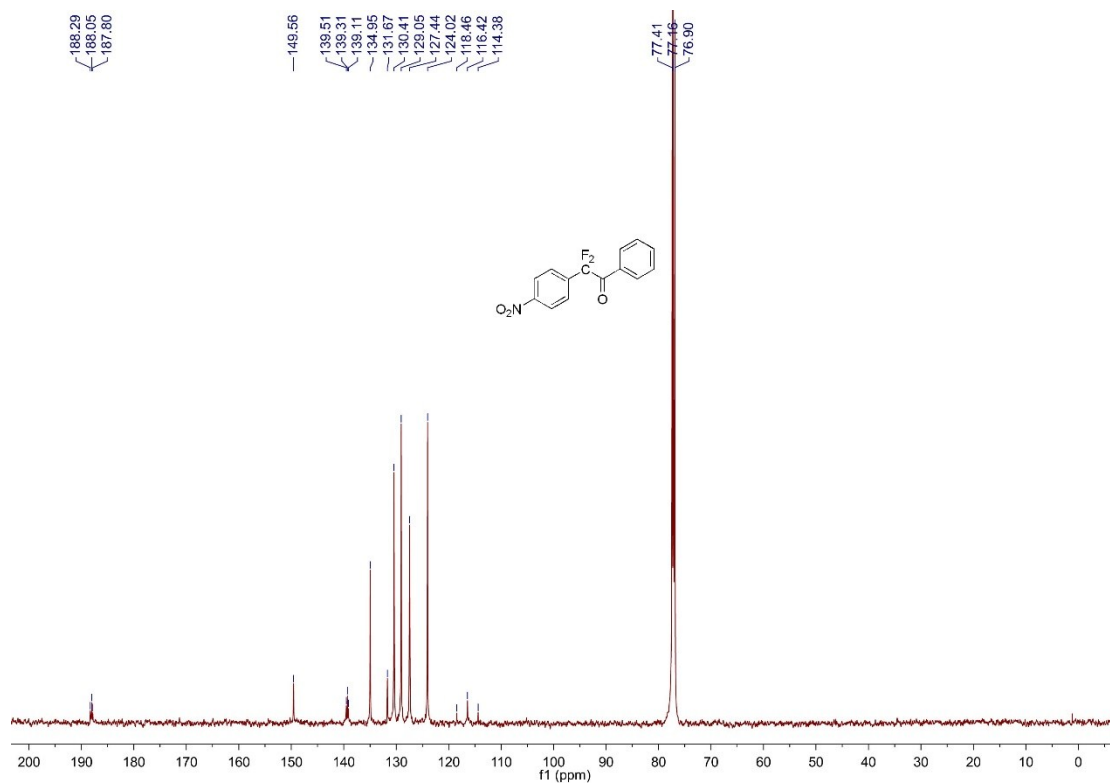
¹³C NMR 3d



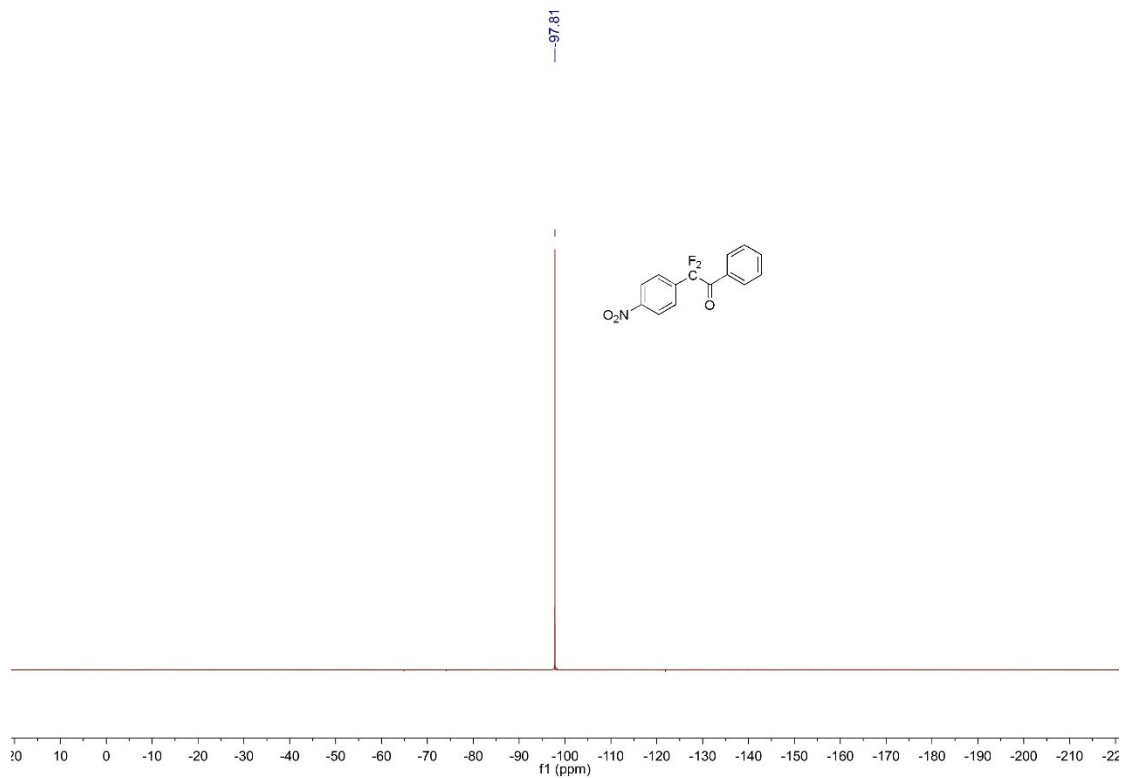
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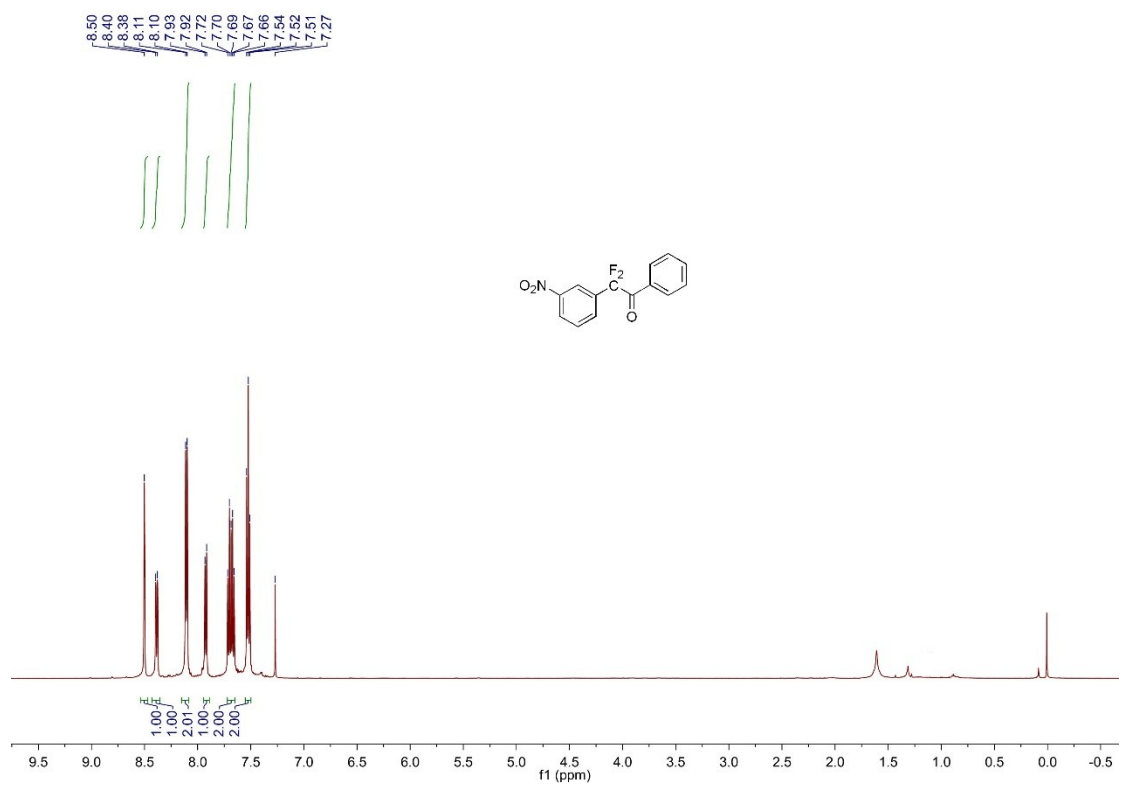
¹H NMR **3e**



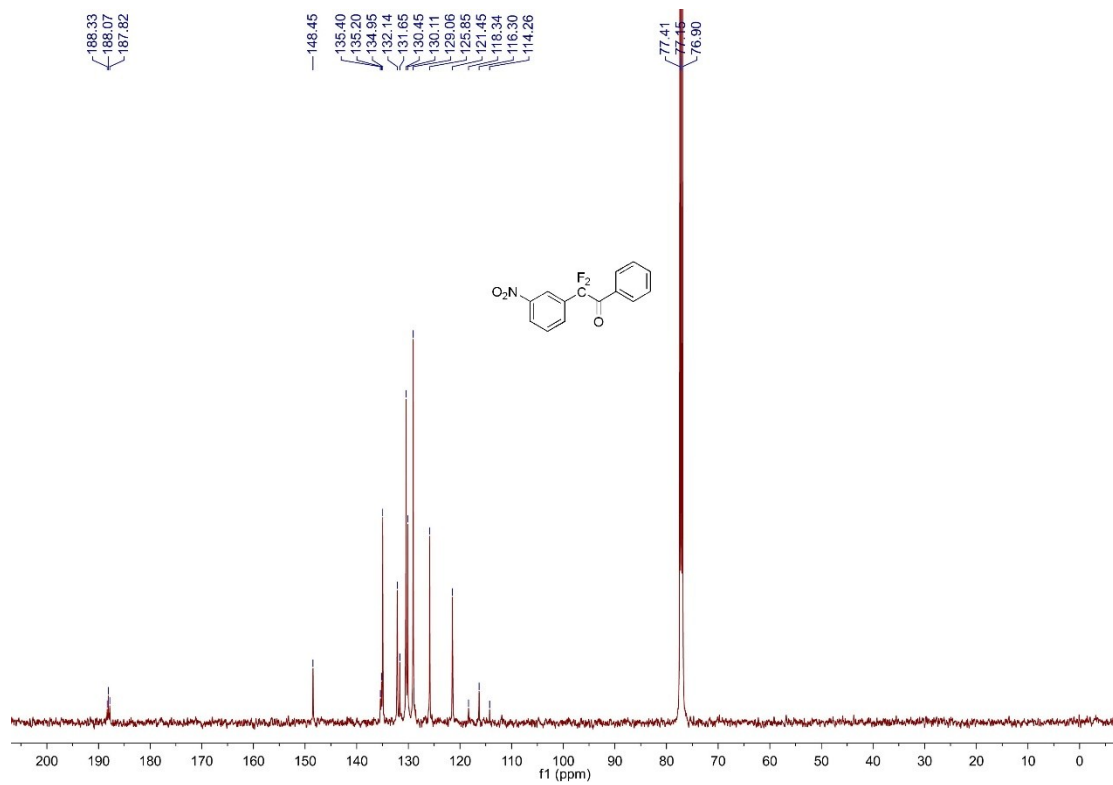
¹³C NMR **3e**



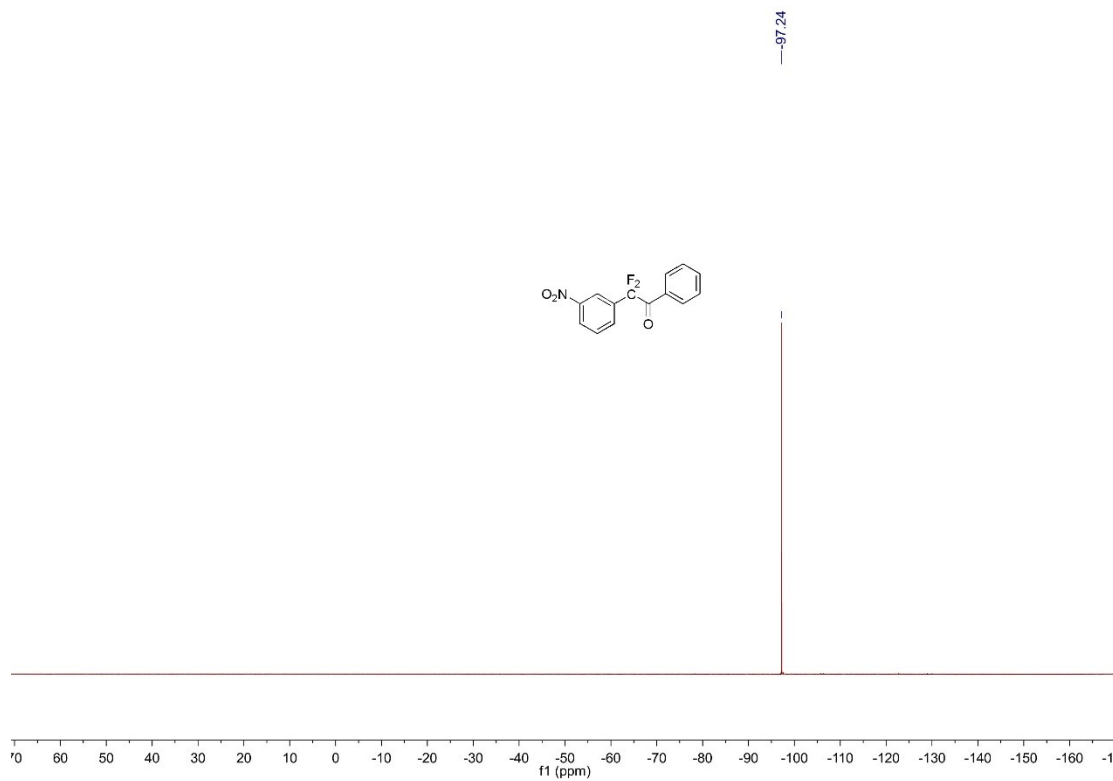
¹⁹F NMR 3e



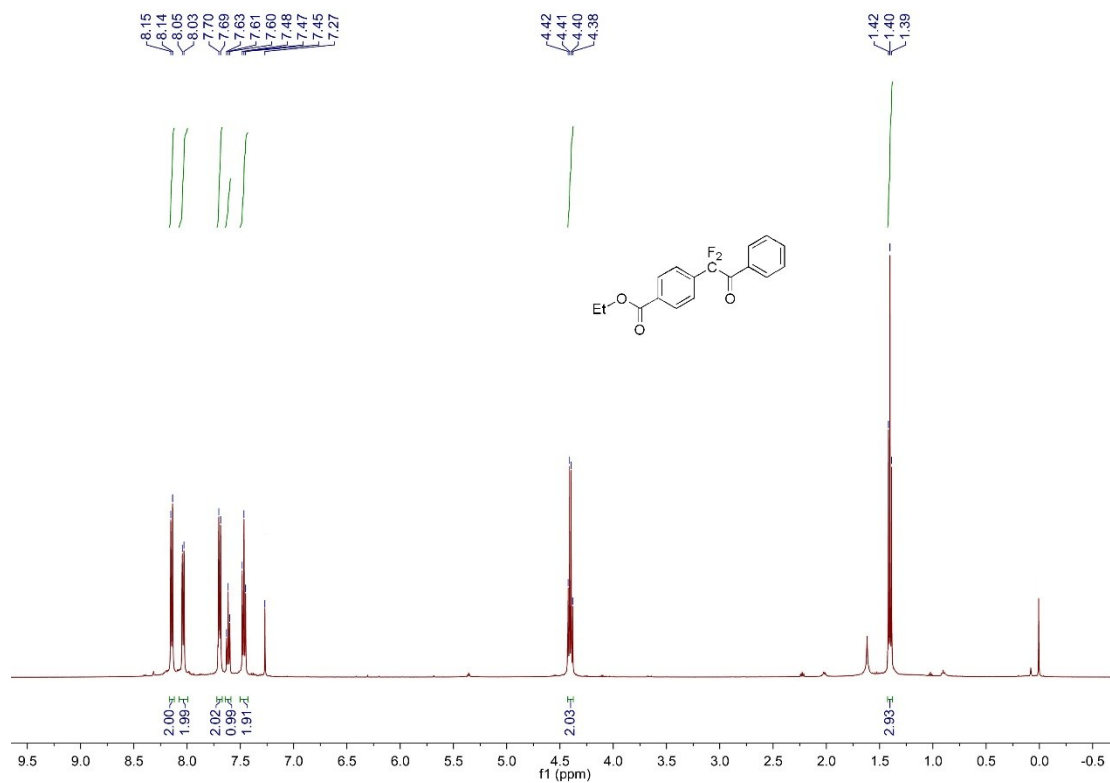
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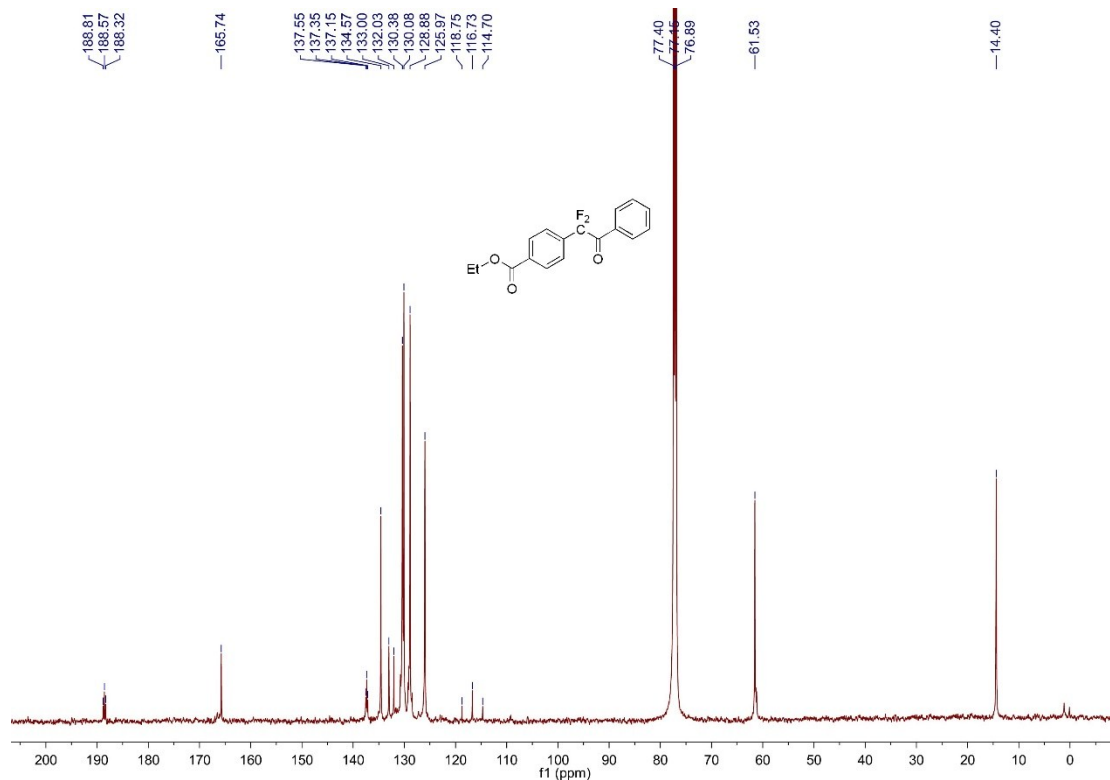
^{13}C NMR **3f**



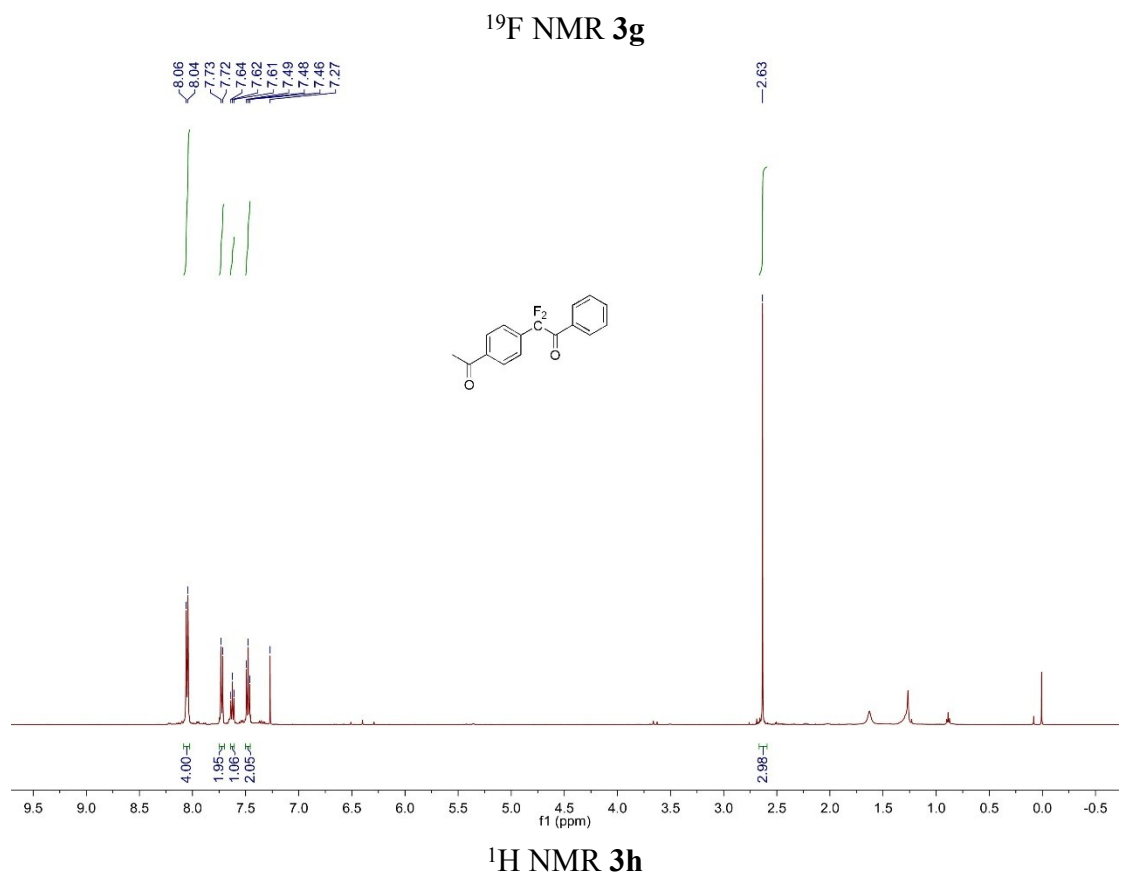
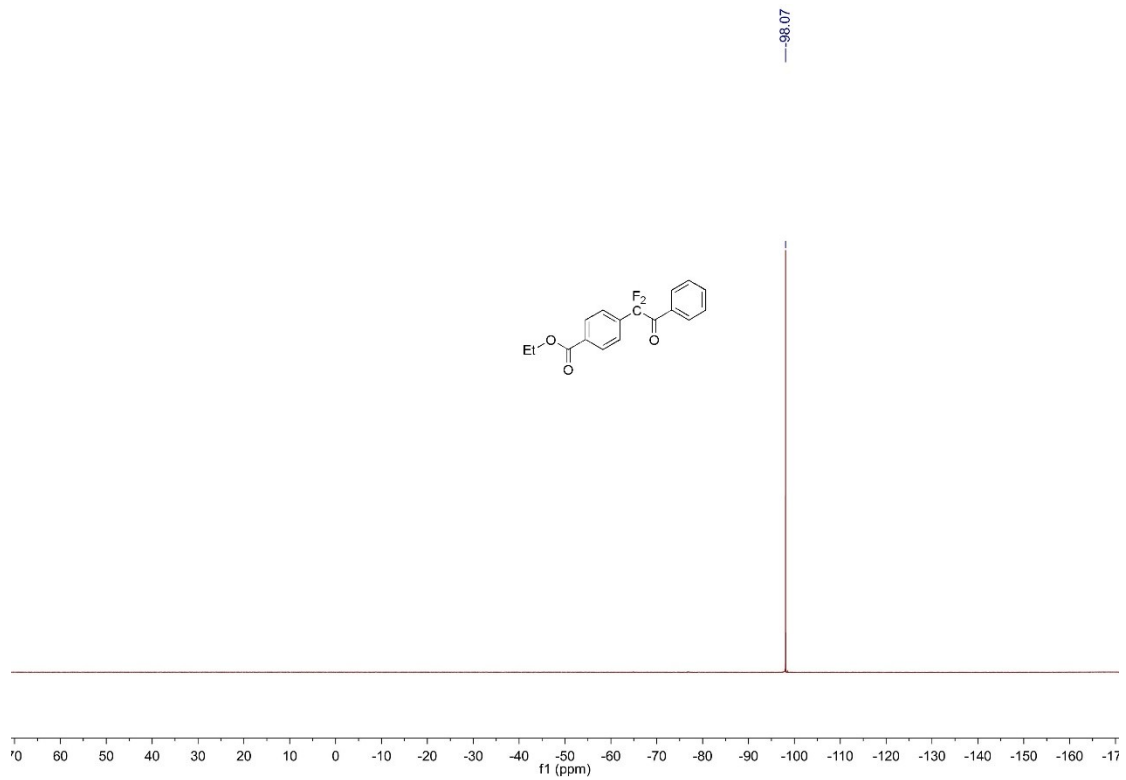
^{19}F NMR **3f**

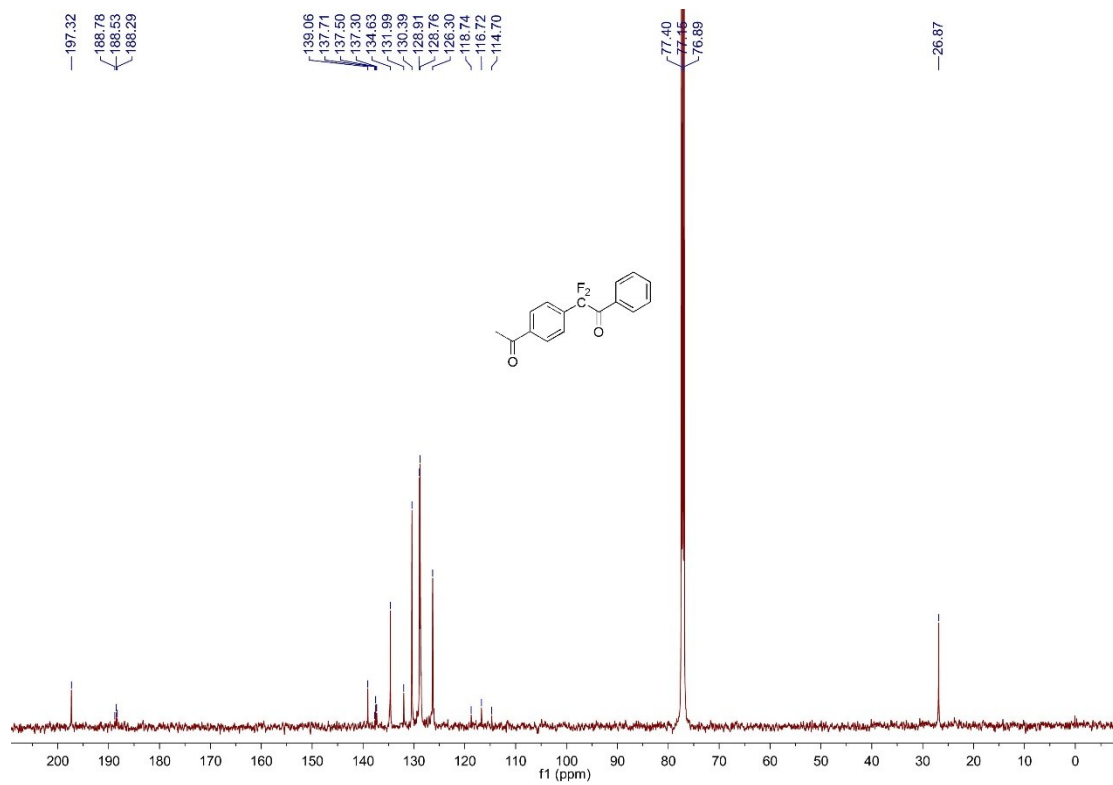


¹H NMR 3g

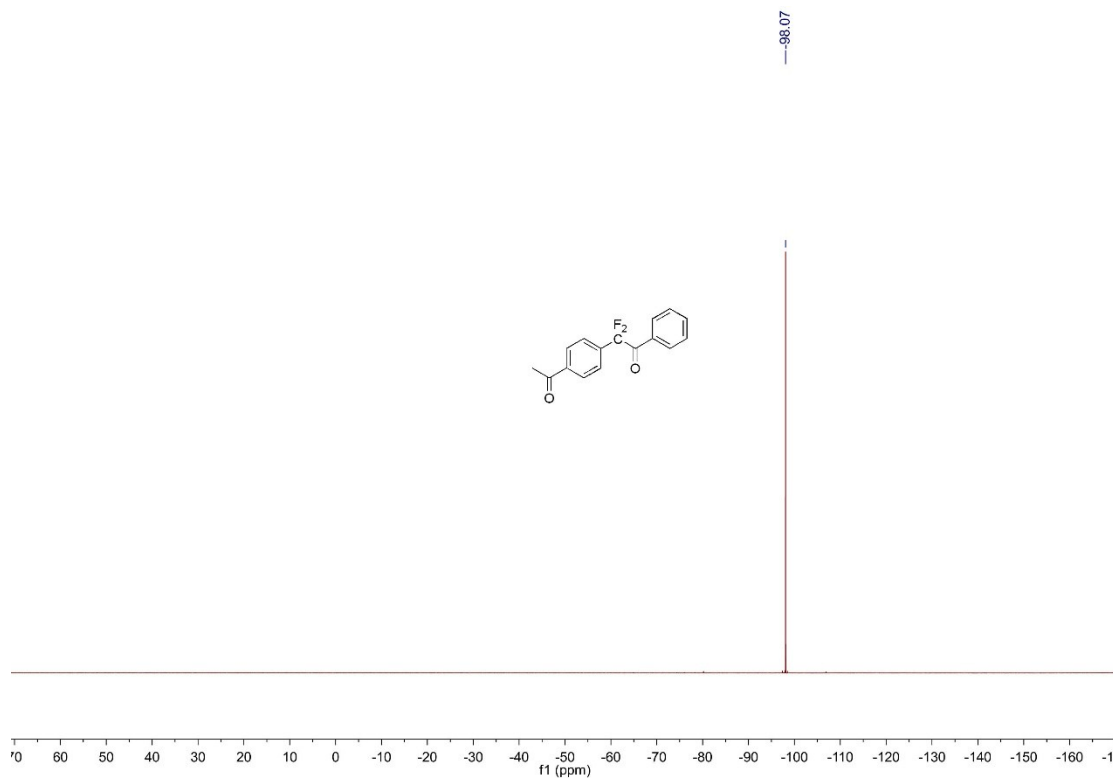


¹³C NMR 3g

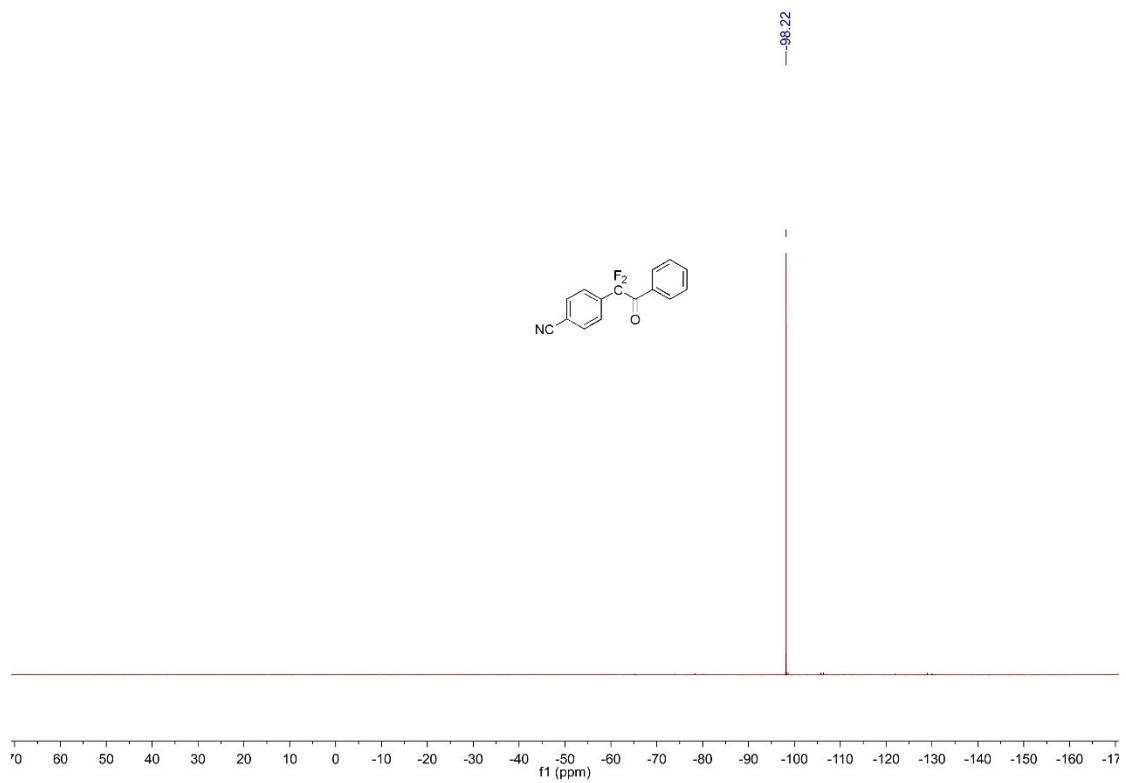




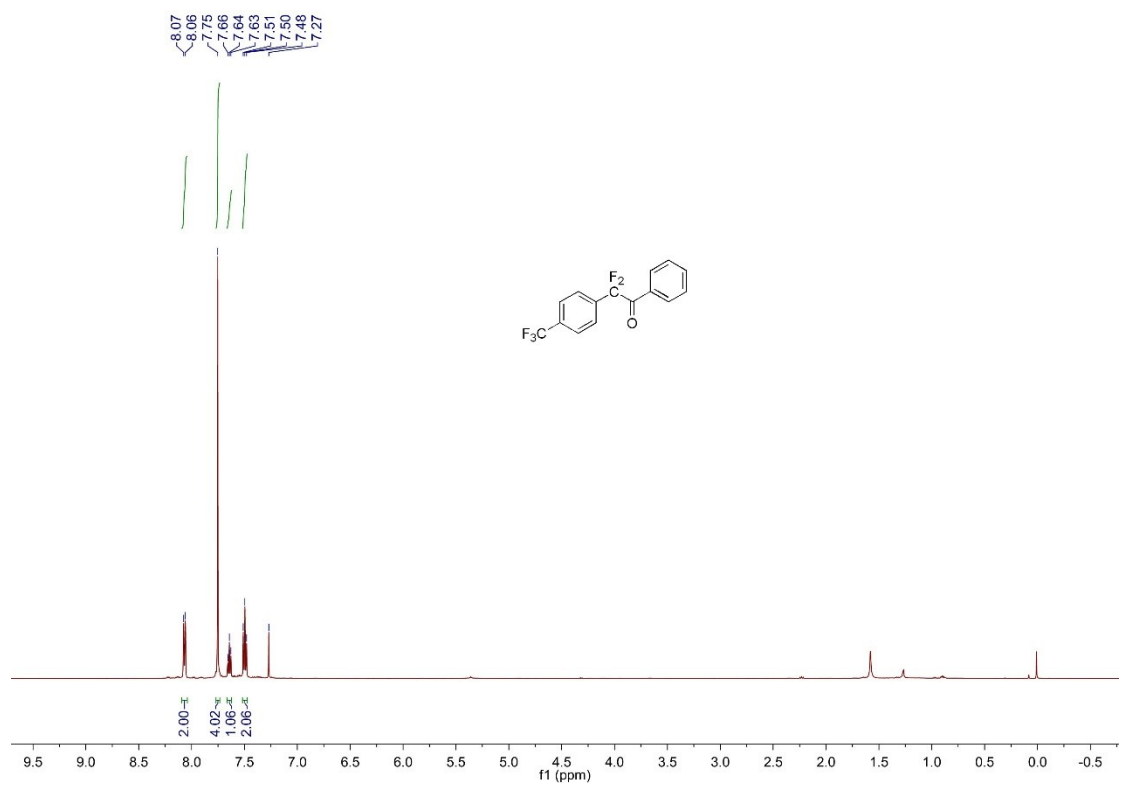
¹³C NMR 3h



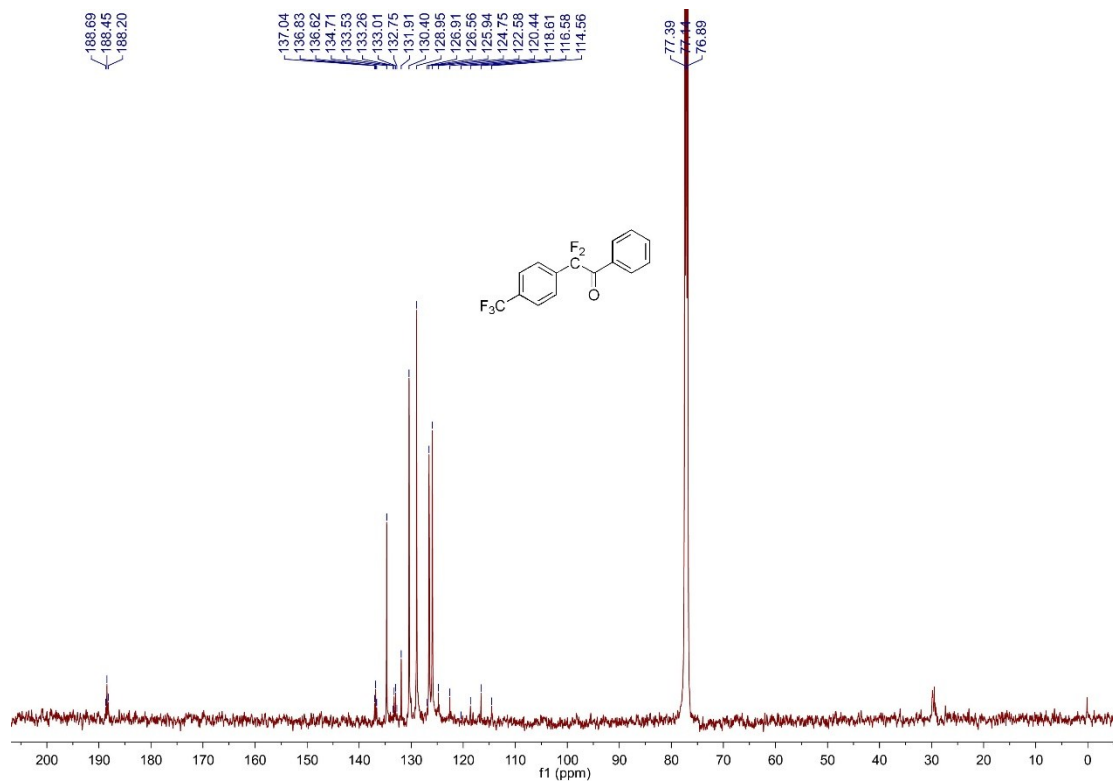
¹⁹F NMR 3h



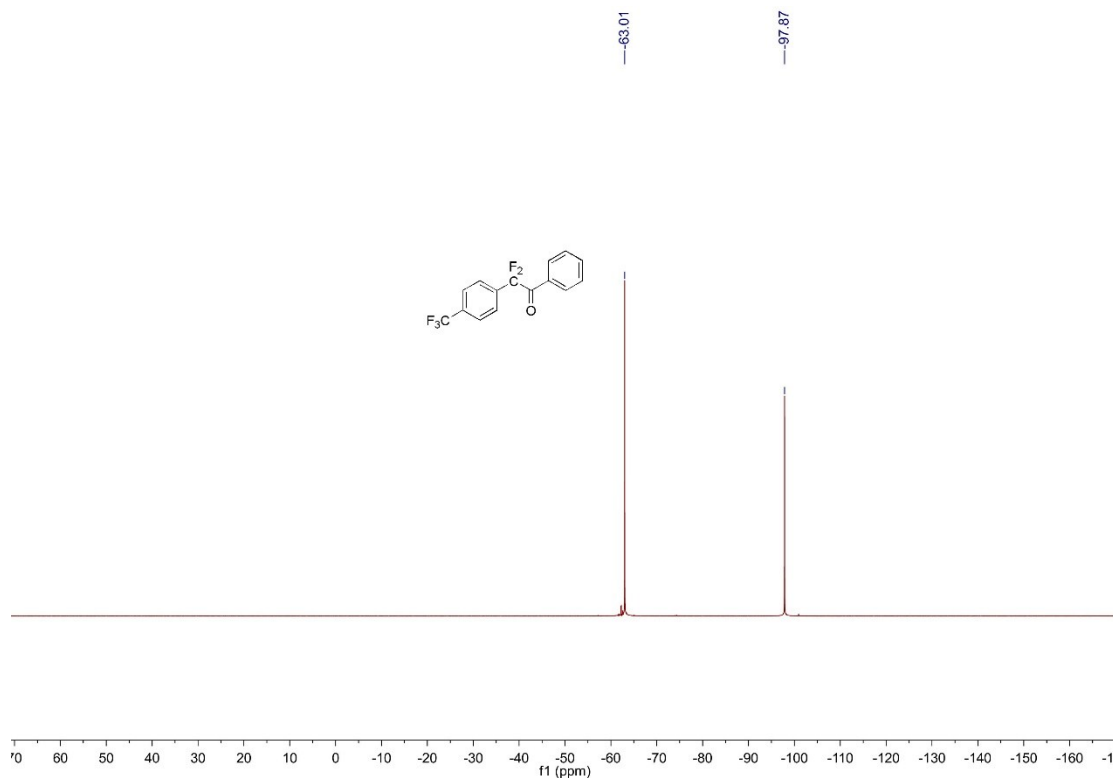
^{19}F NMR **3i**



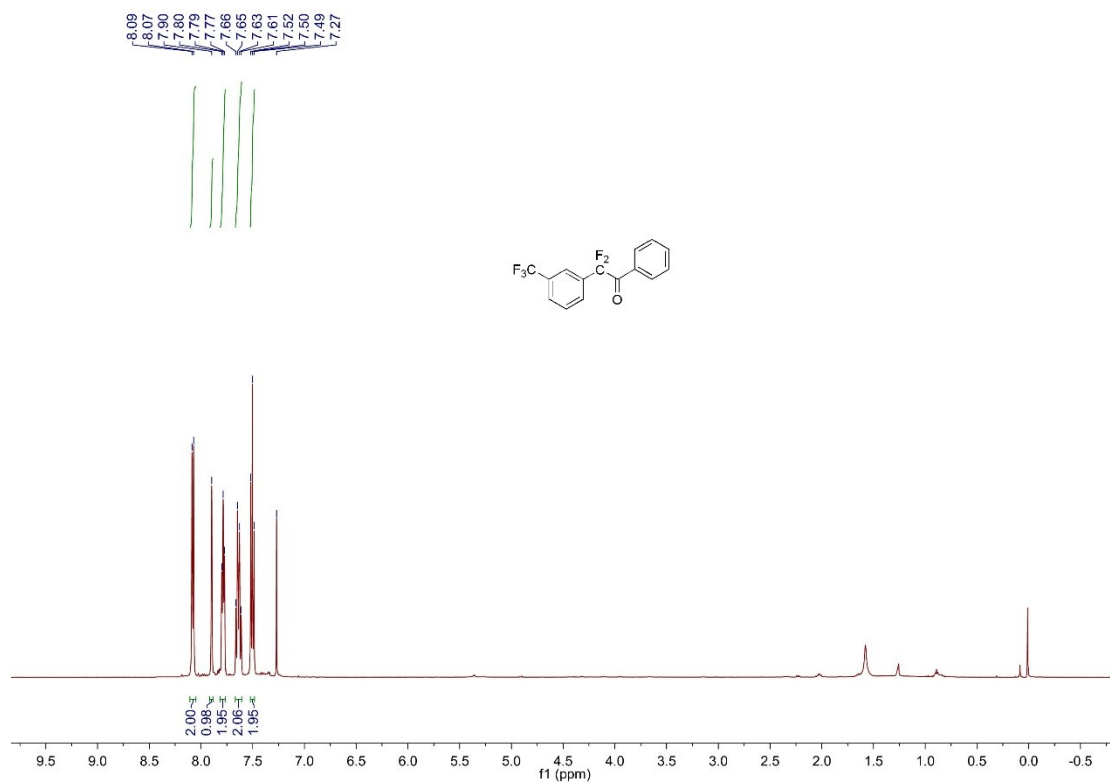
^1H NMR **3j**



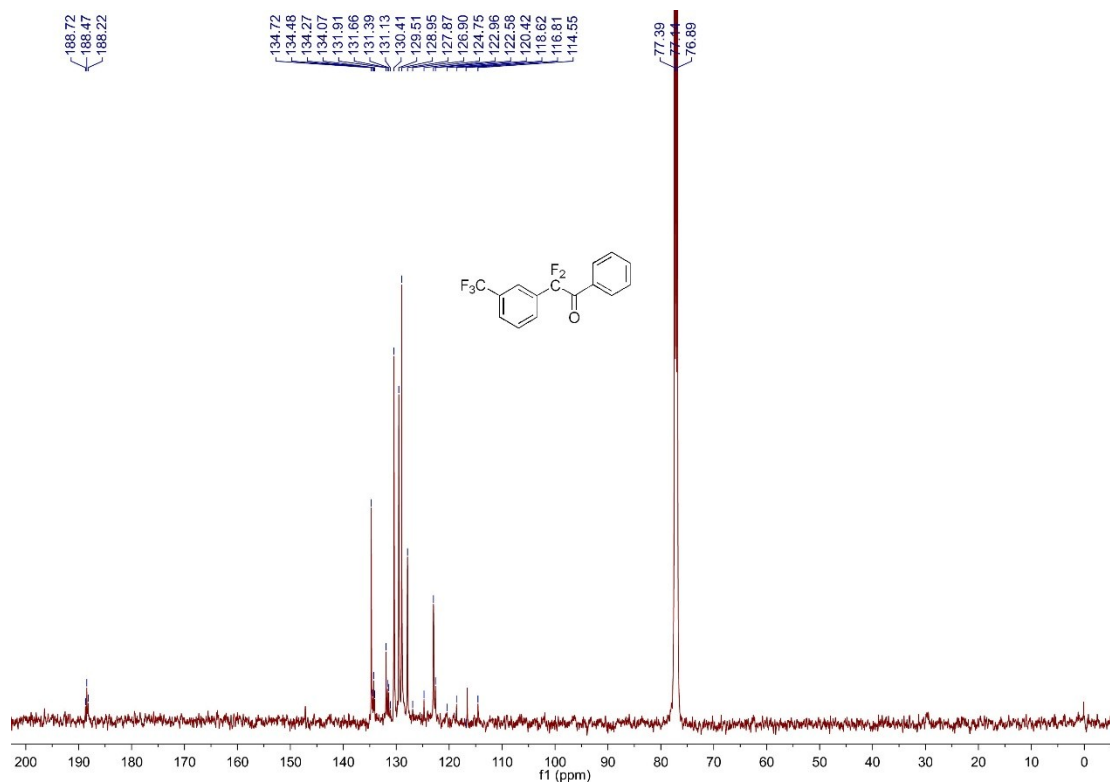
^{13}C NMR 3j



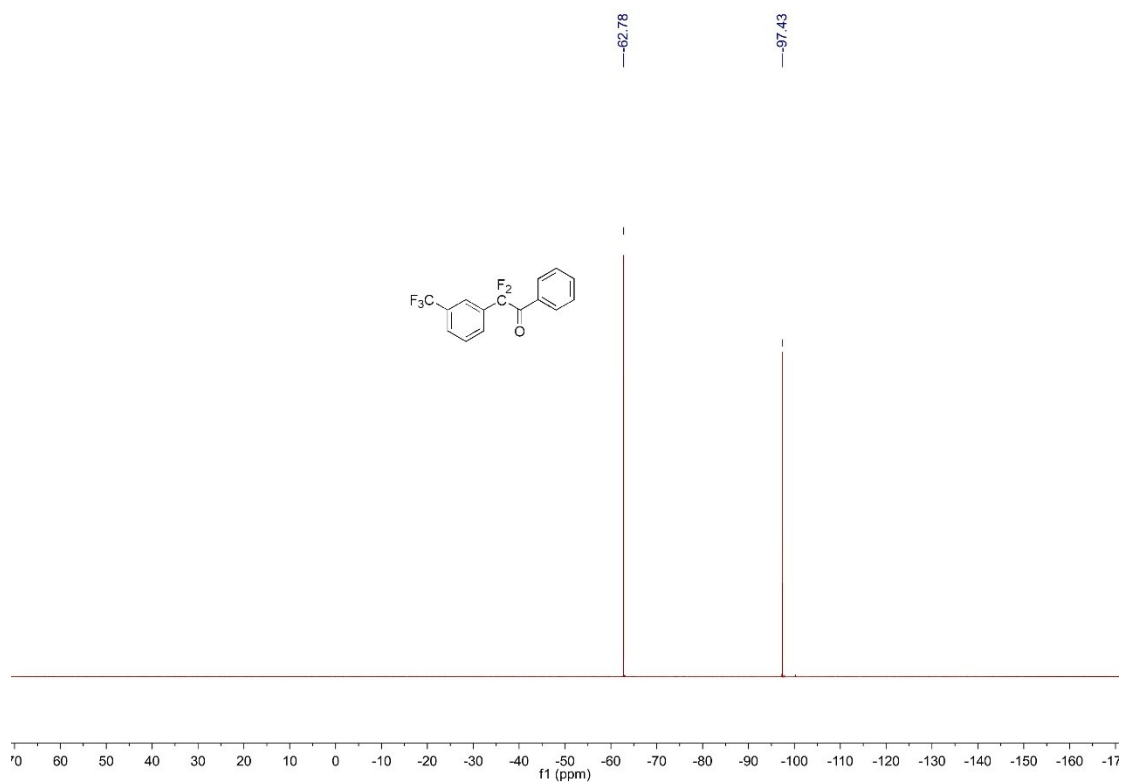
^{19}F NMR 3j



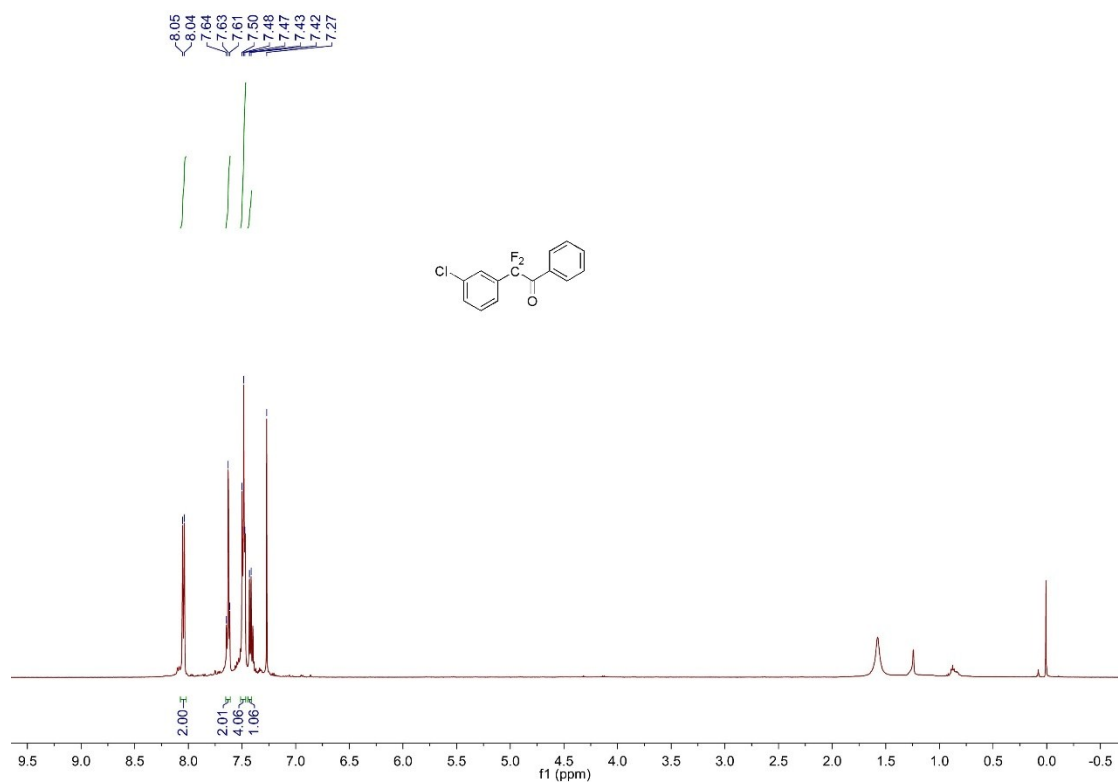
¹H NMR 3k



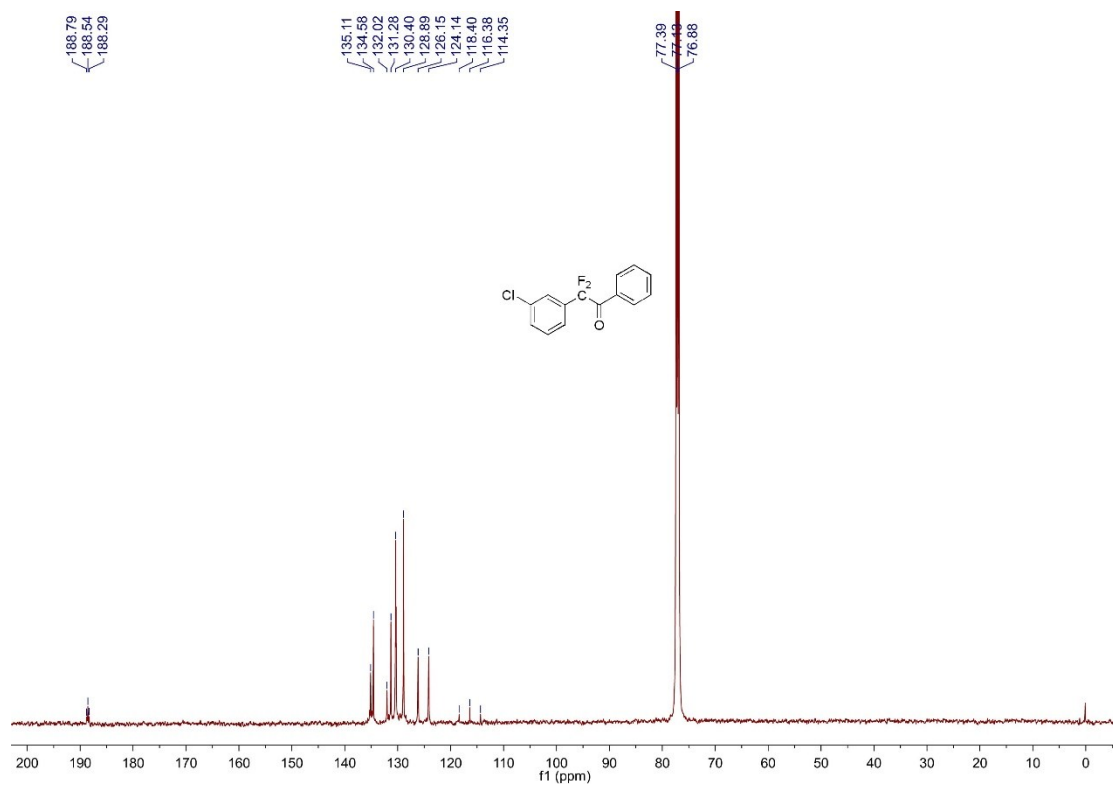
¹³C NMR 3k



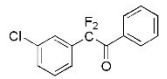
^{19}F NMR 3k



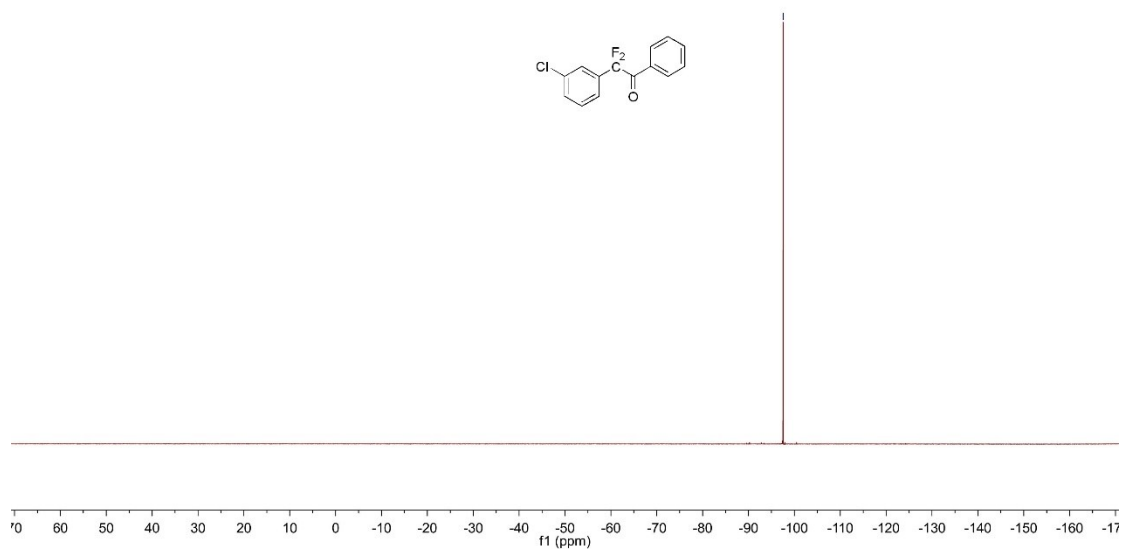
^1H NMR 3l



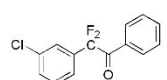
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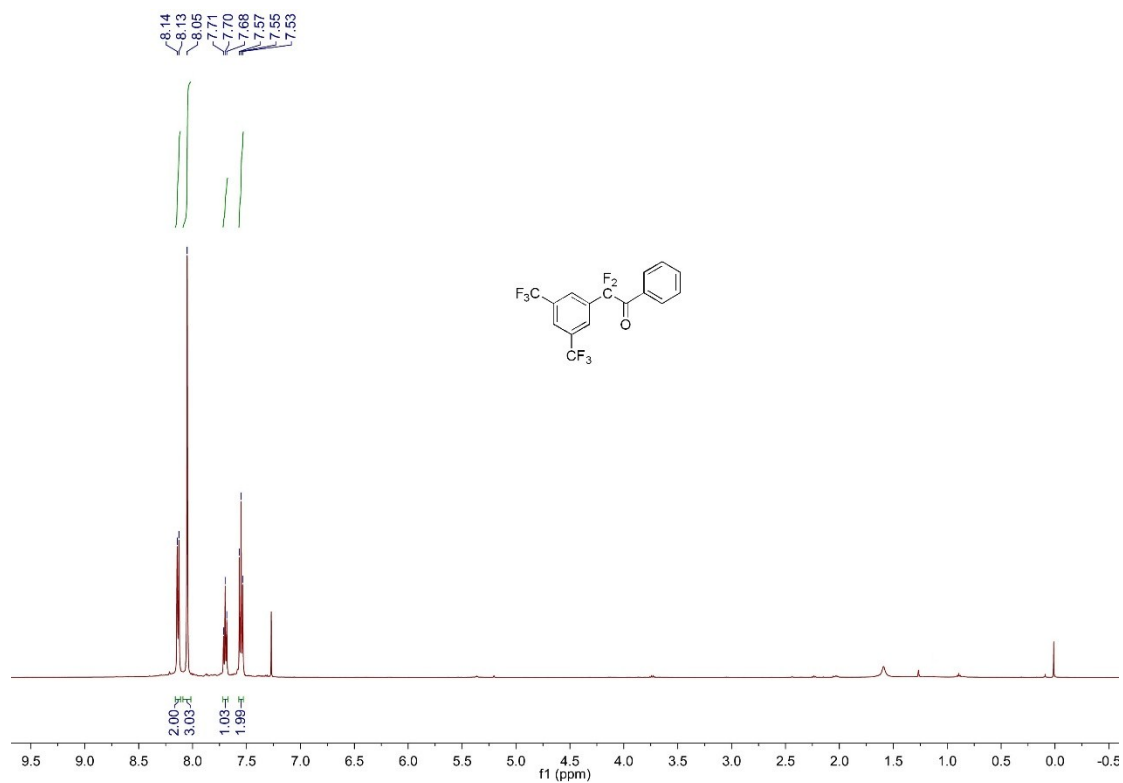


—97.54

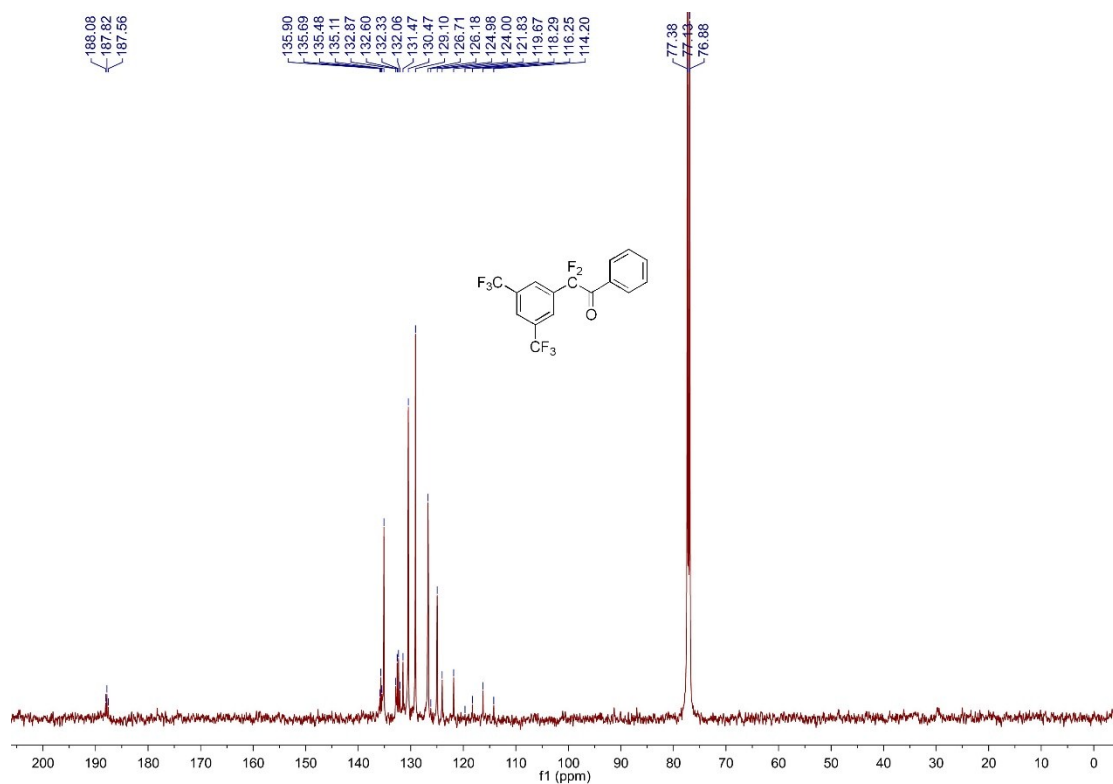


¹⁹F NMR 31

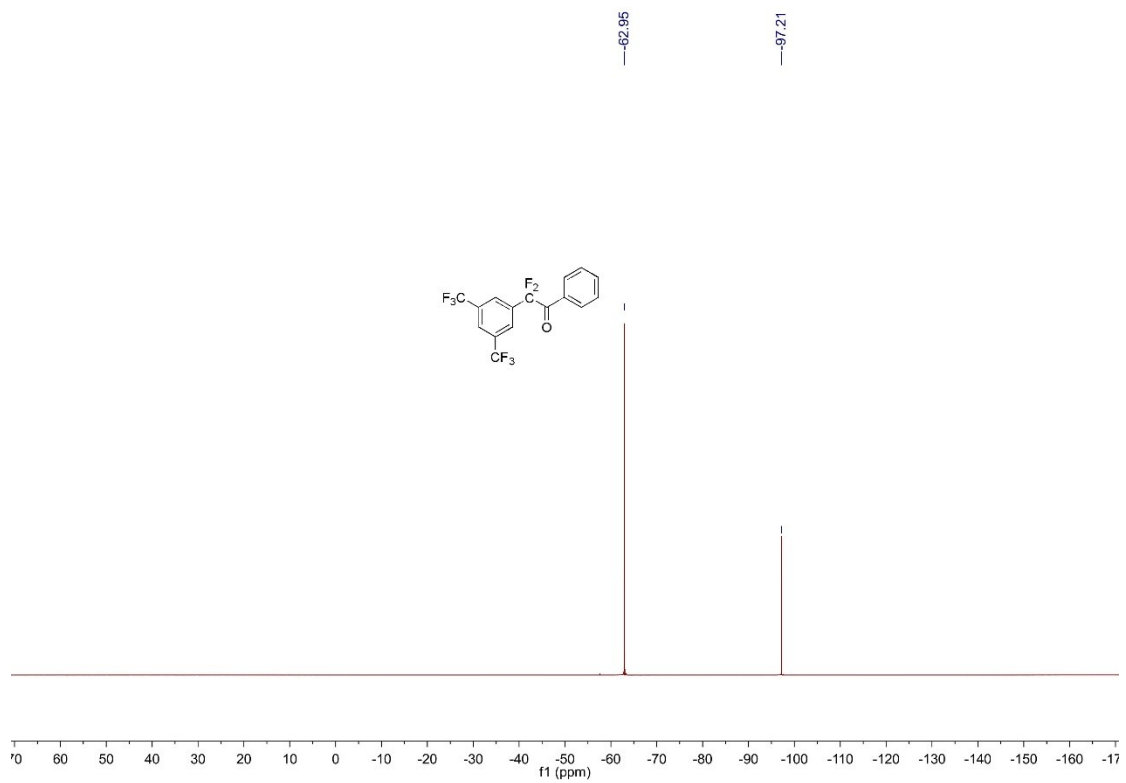




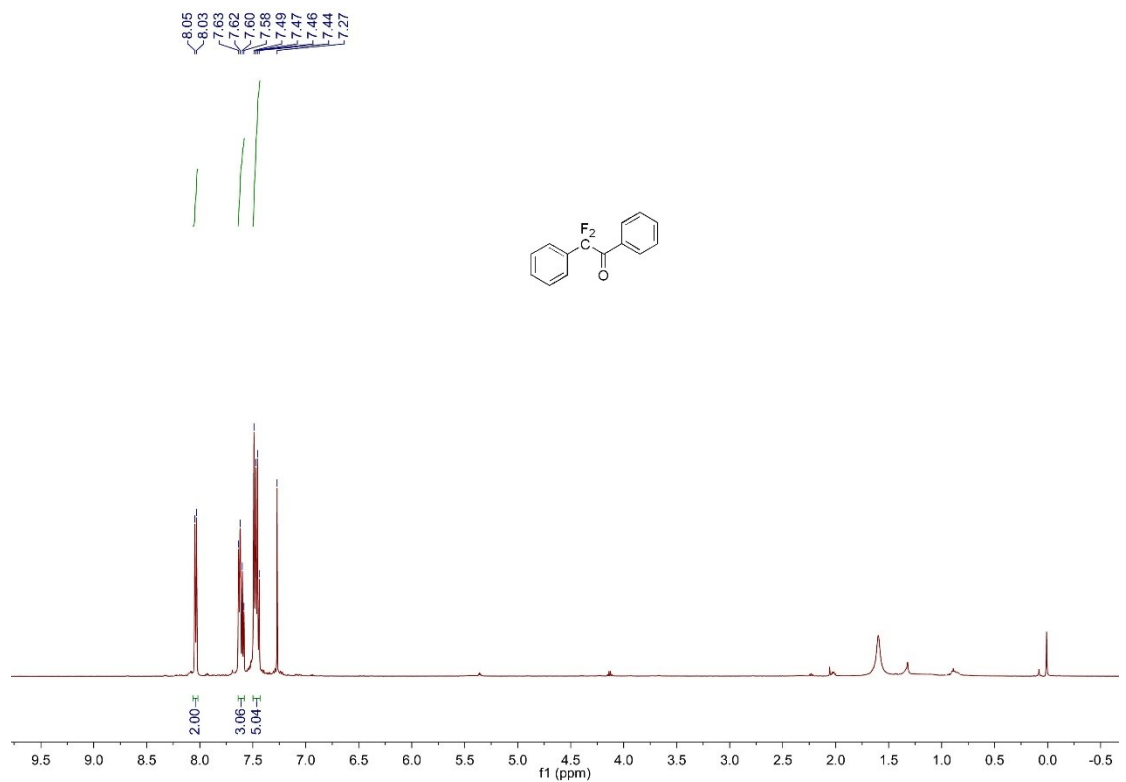
¹H NMR **3m**



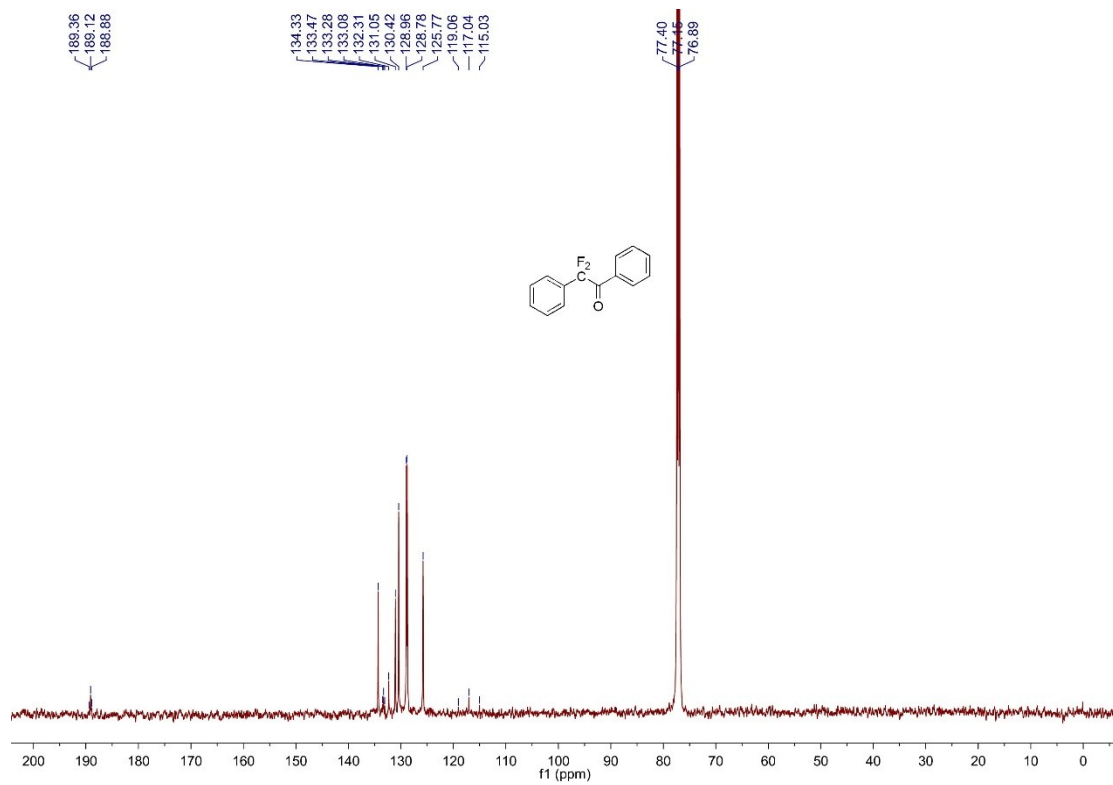
¹³C NMR **3m**



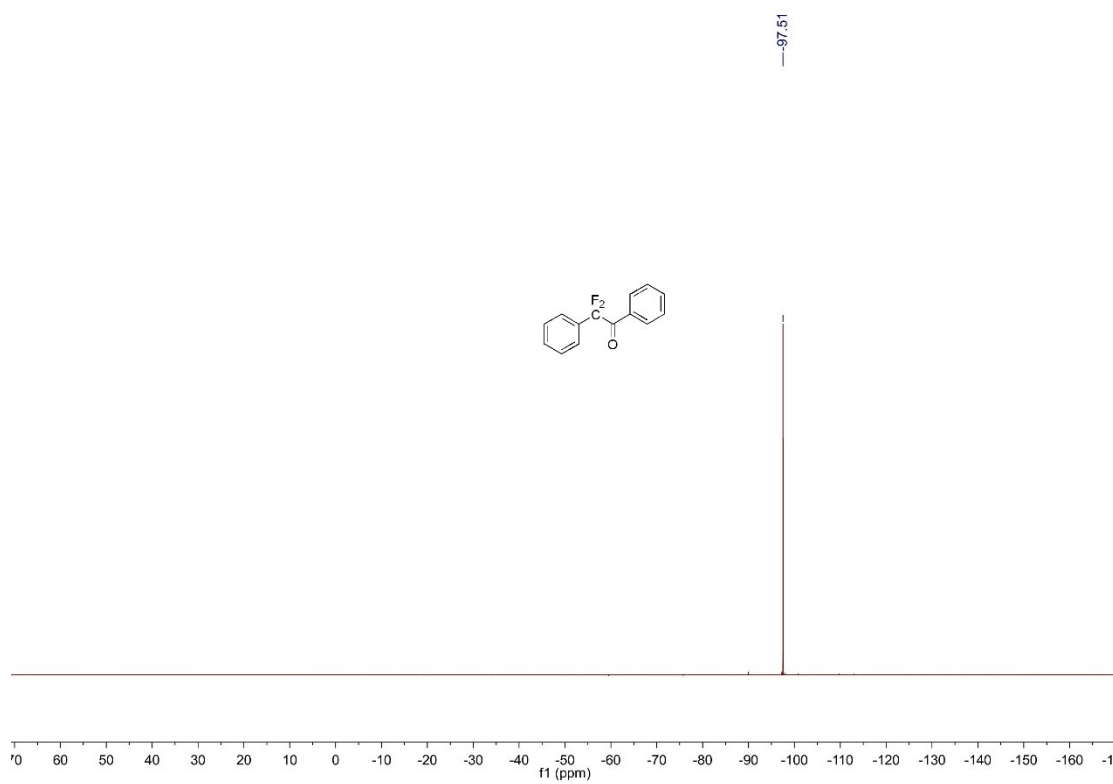
^{19}F NMR **3m**



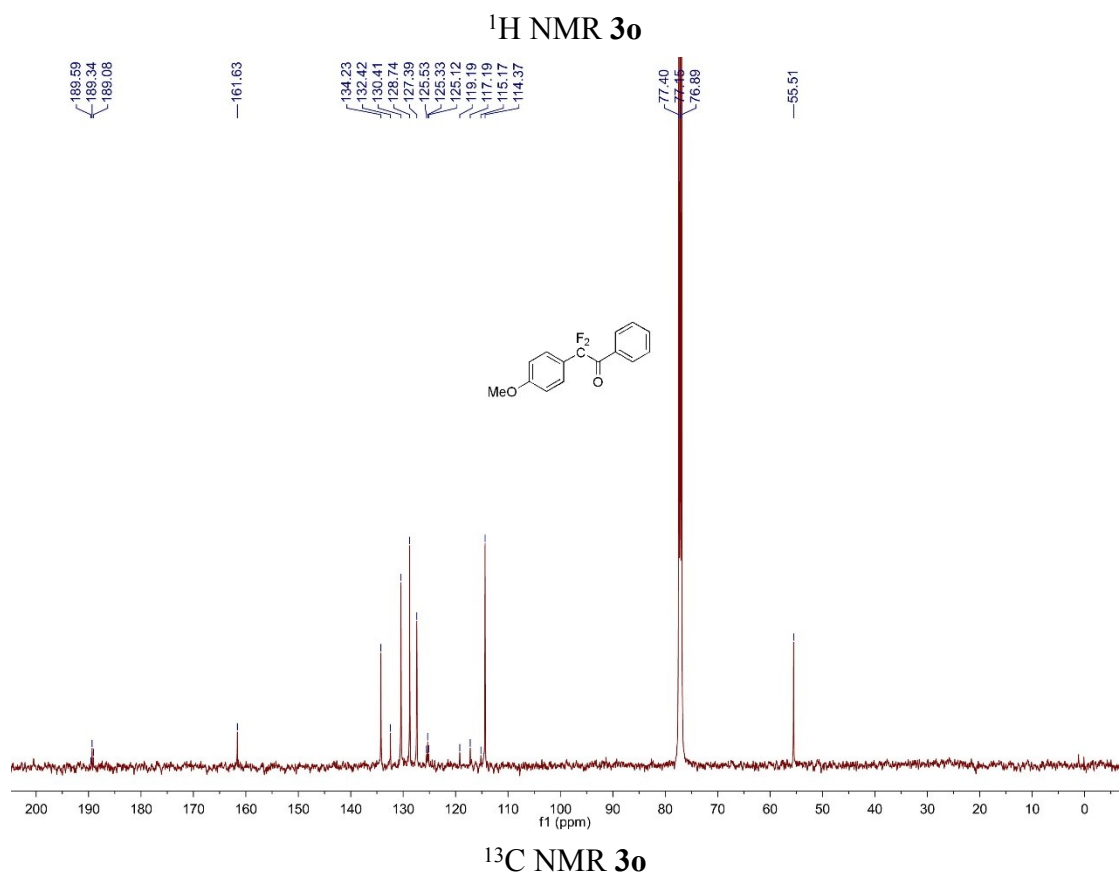
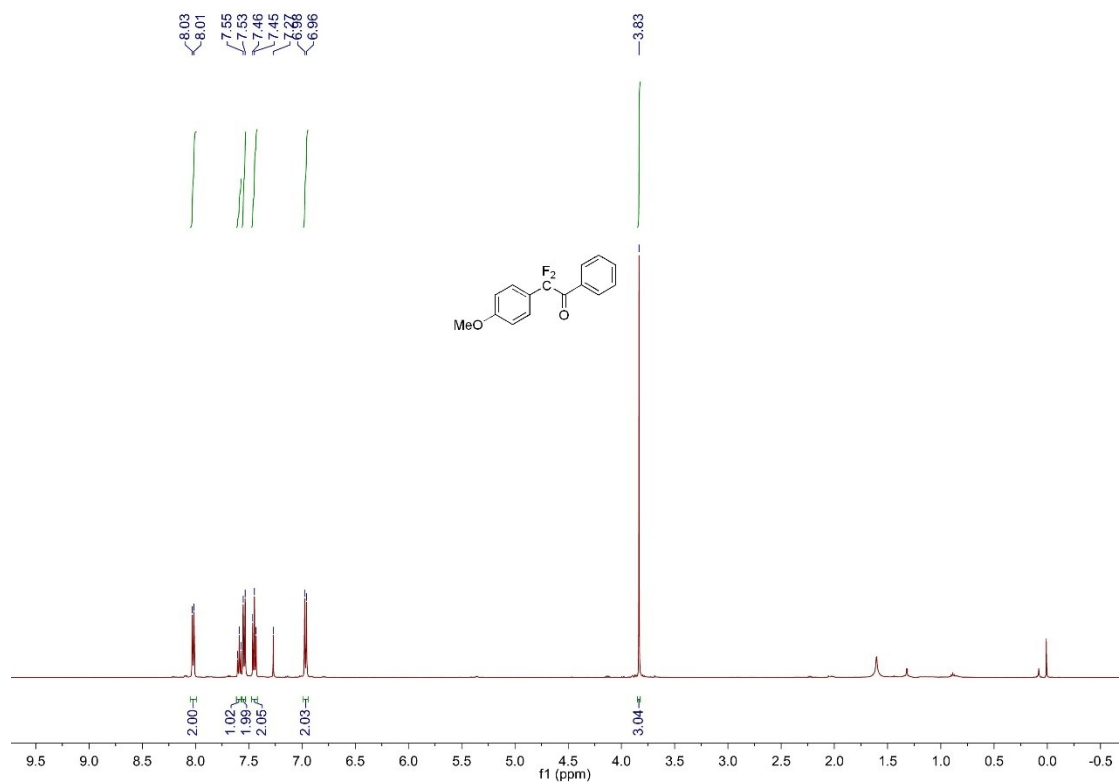
^1H NMR **3n**

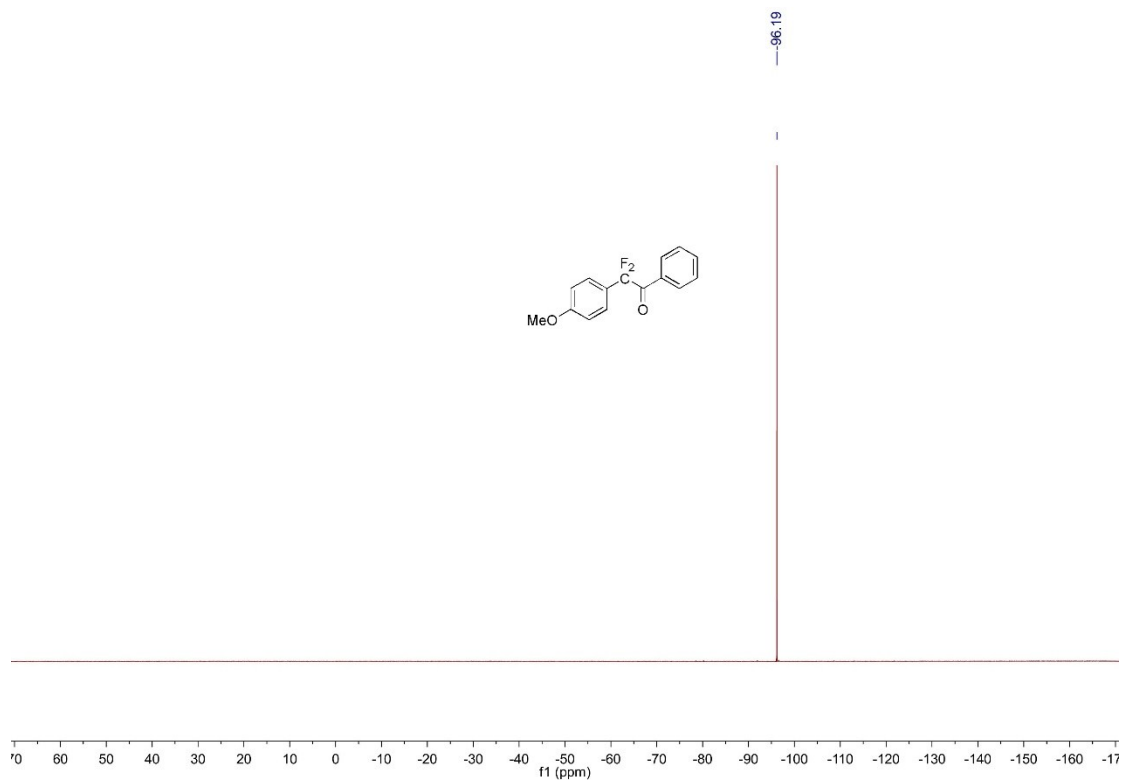


¹³C NMR 3n

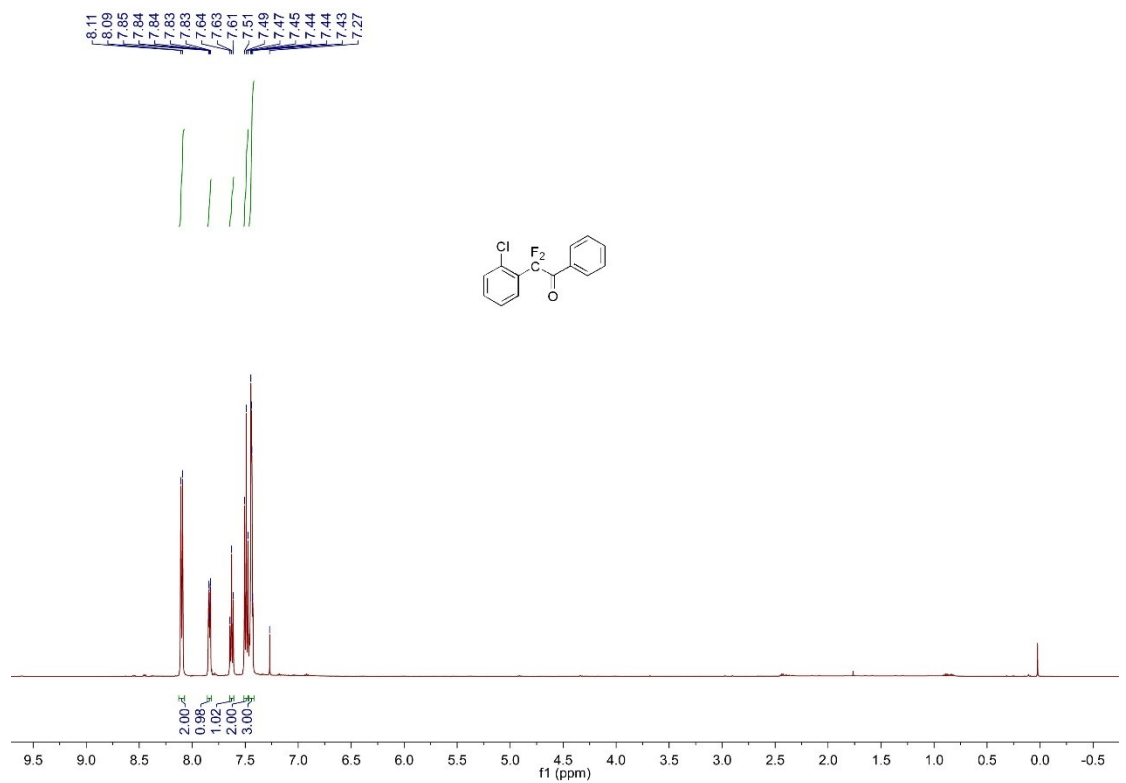


¹⁹F NMR 3n

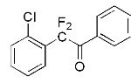
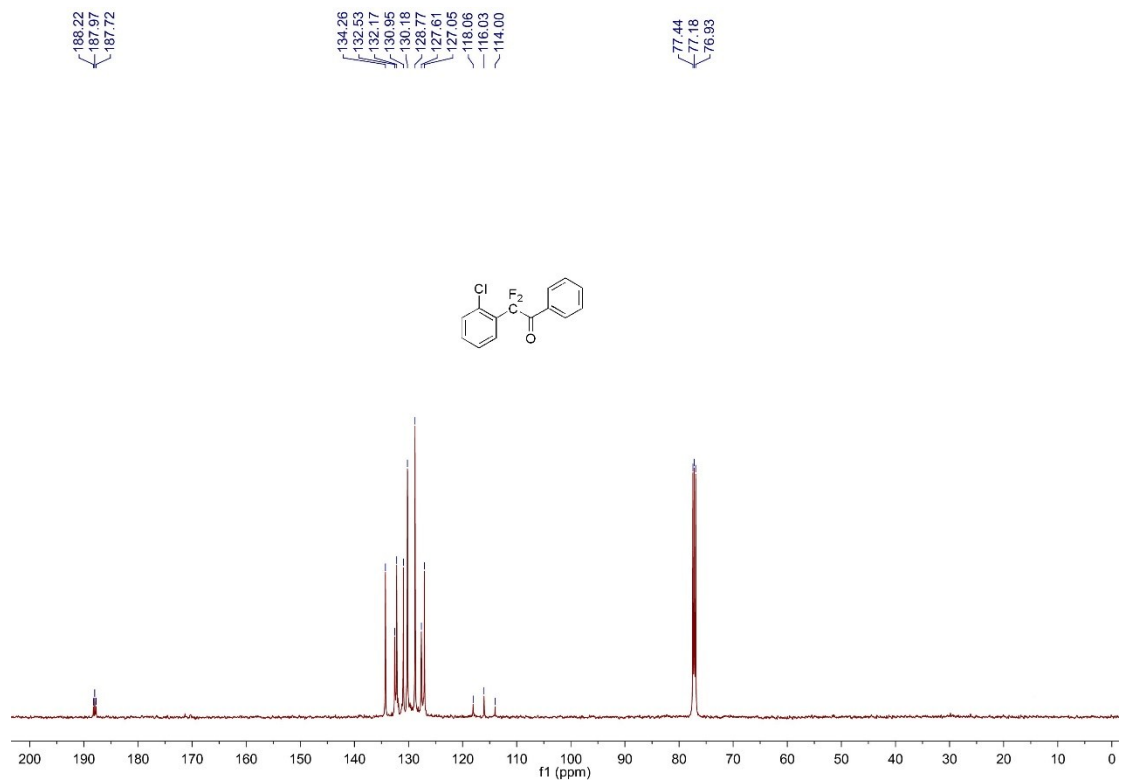




^{19}F NMR **3o**

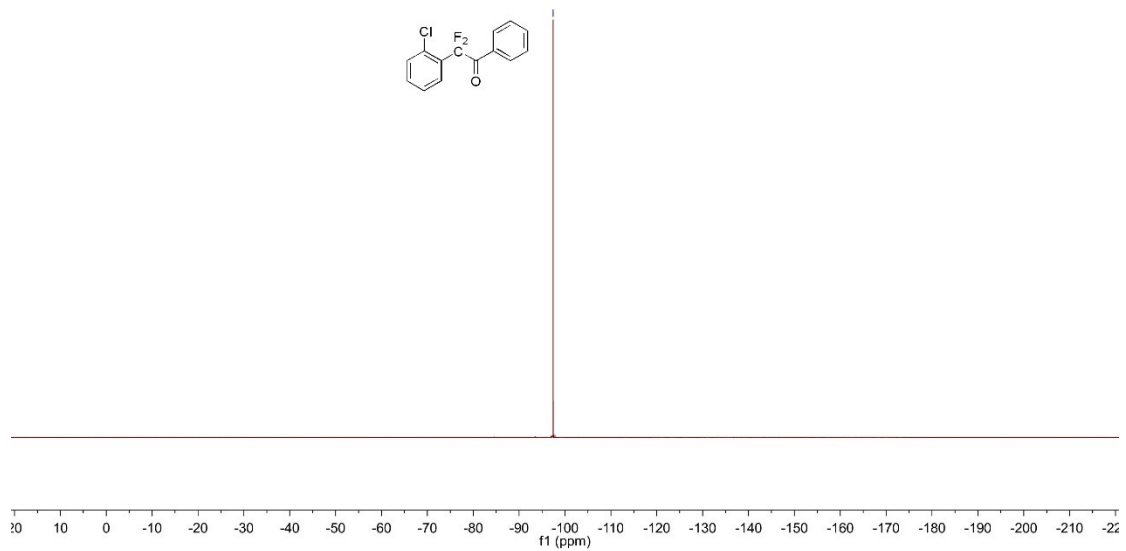


^1H NMR **3p**

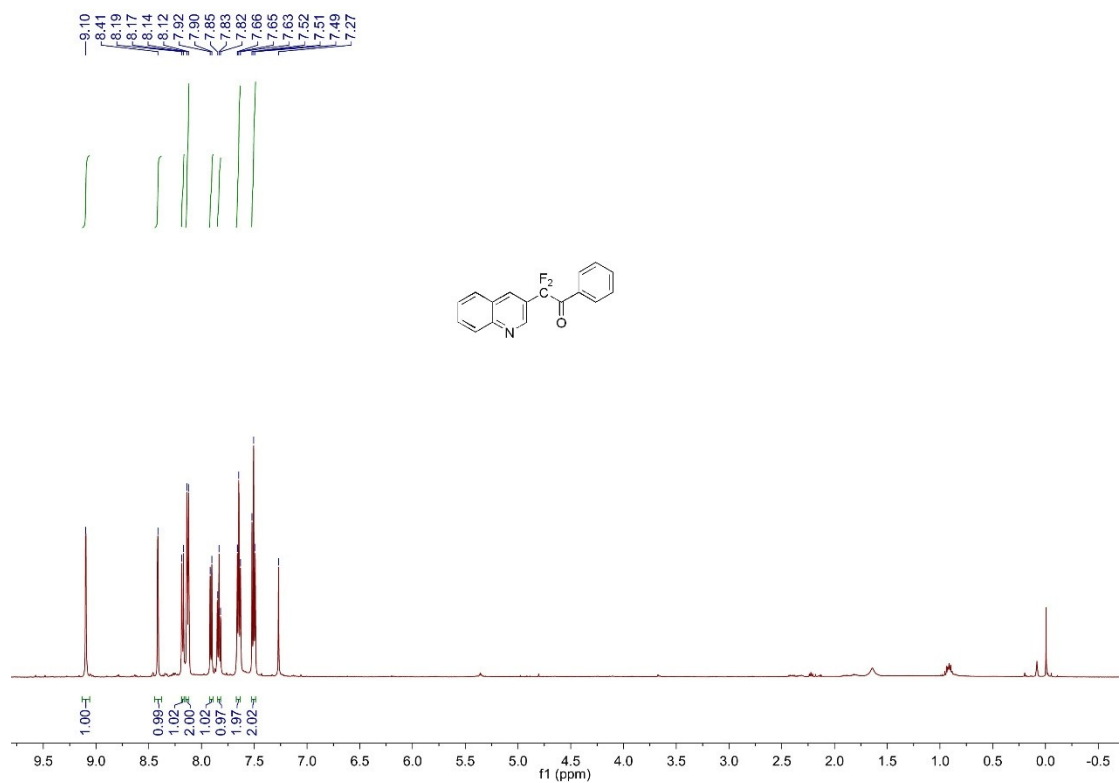


¹³C NMR 3p

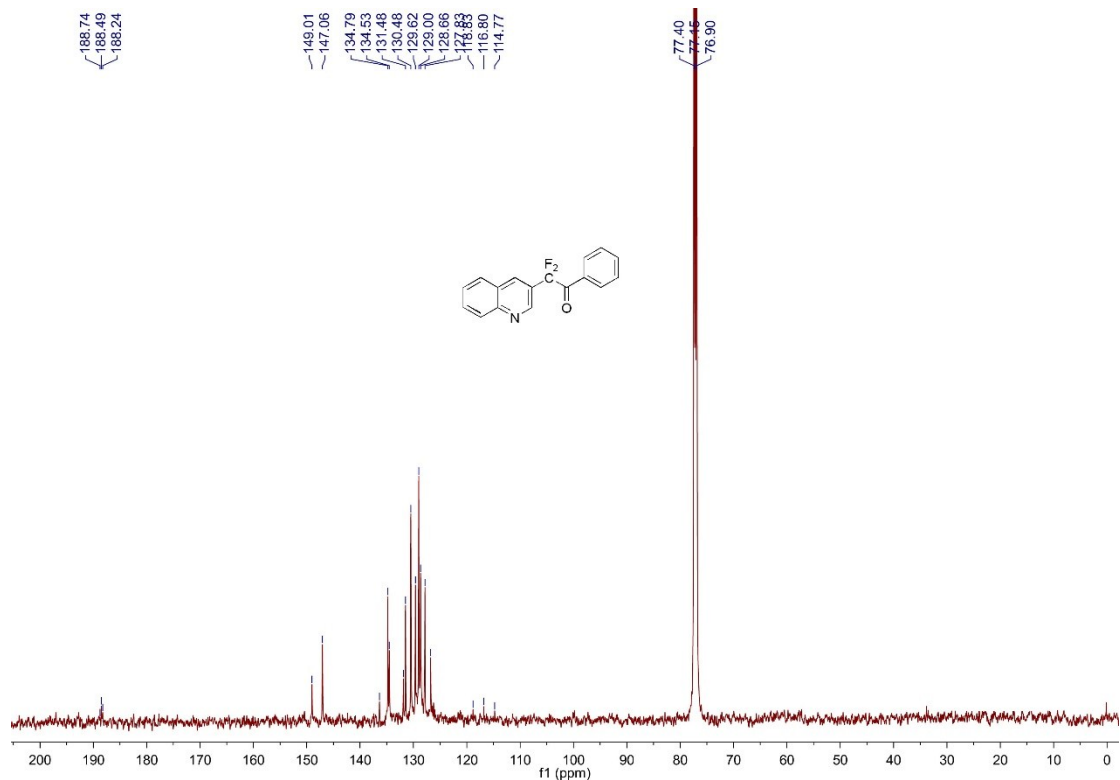
—97.42



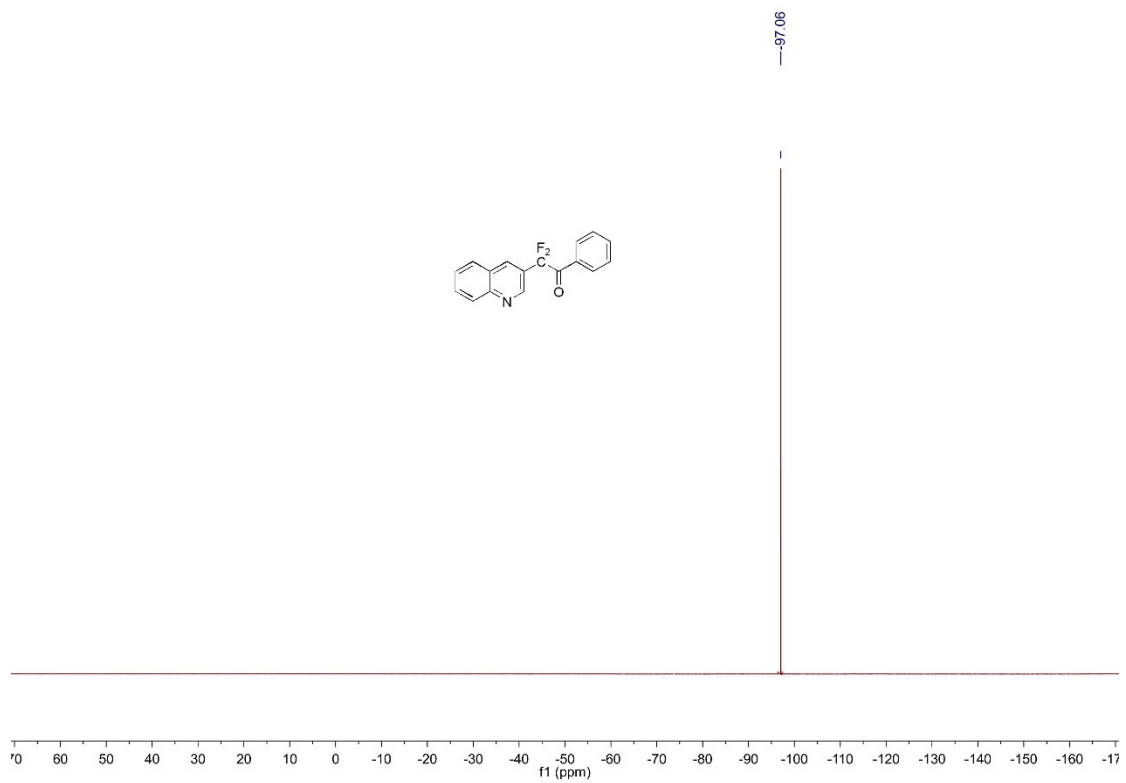
¹⁹F NMR 3p



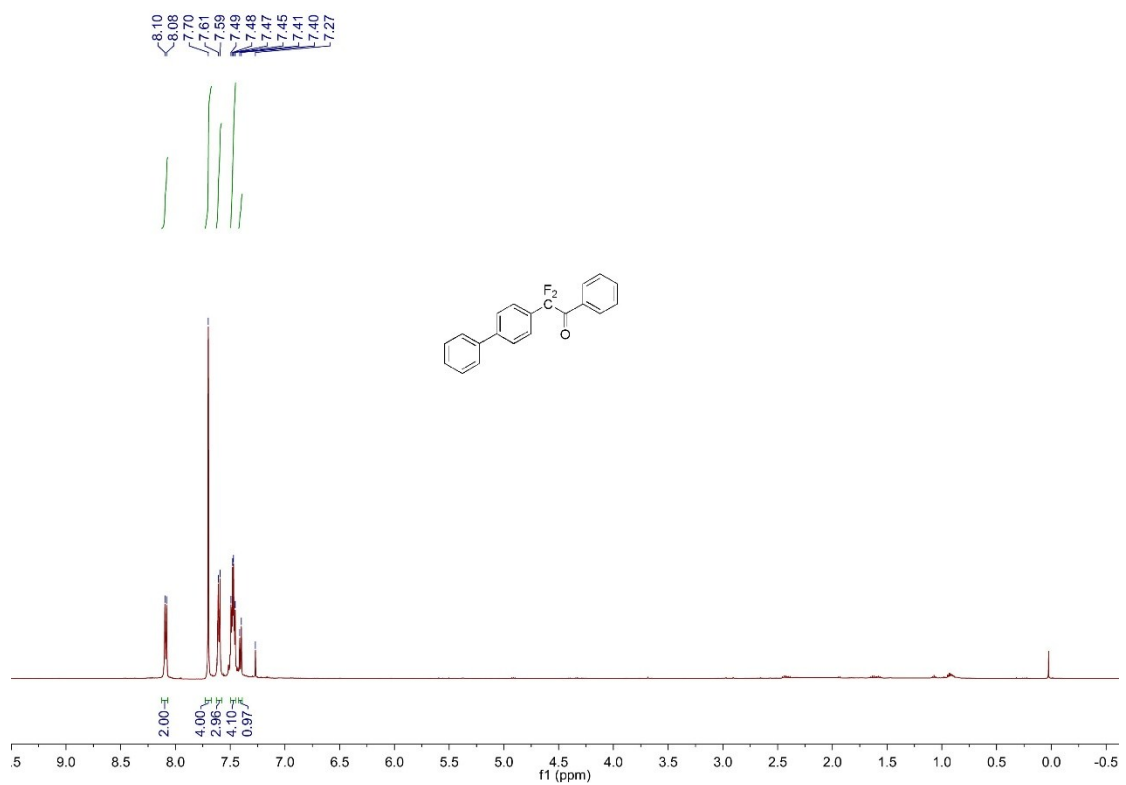
¹H NMR 3r



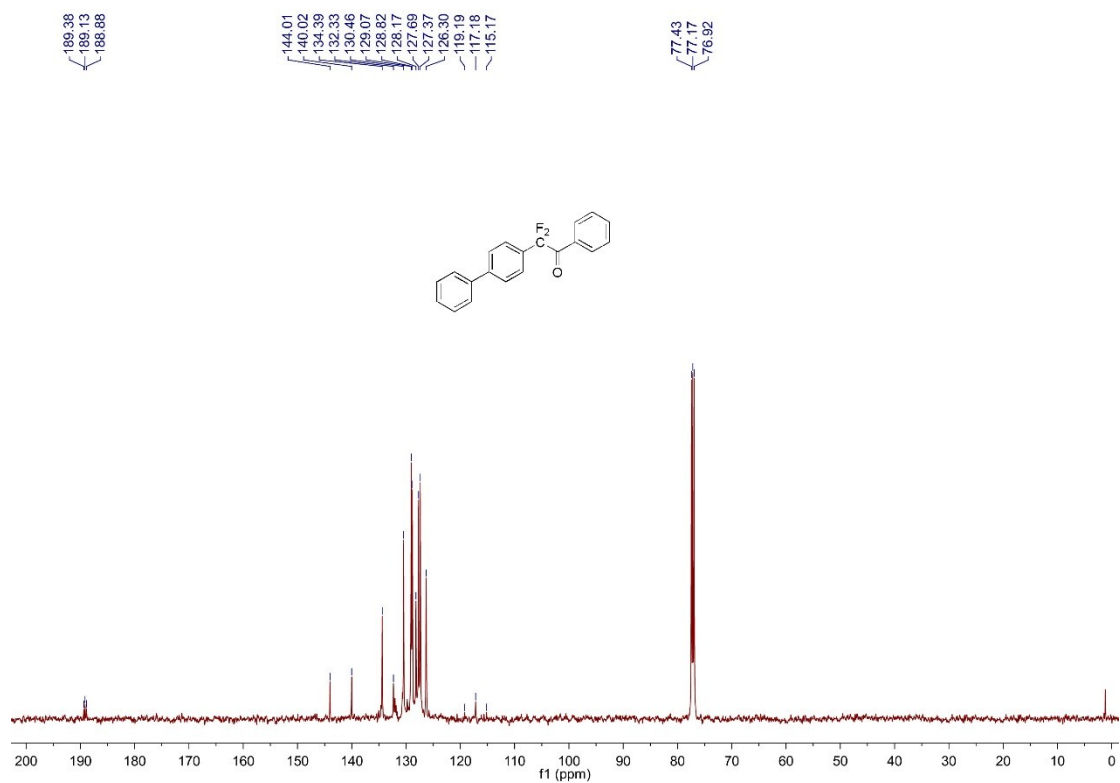
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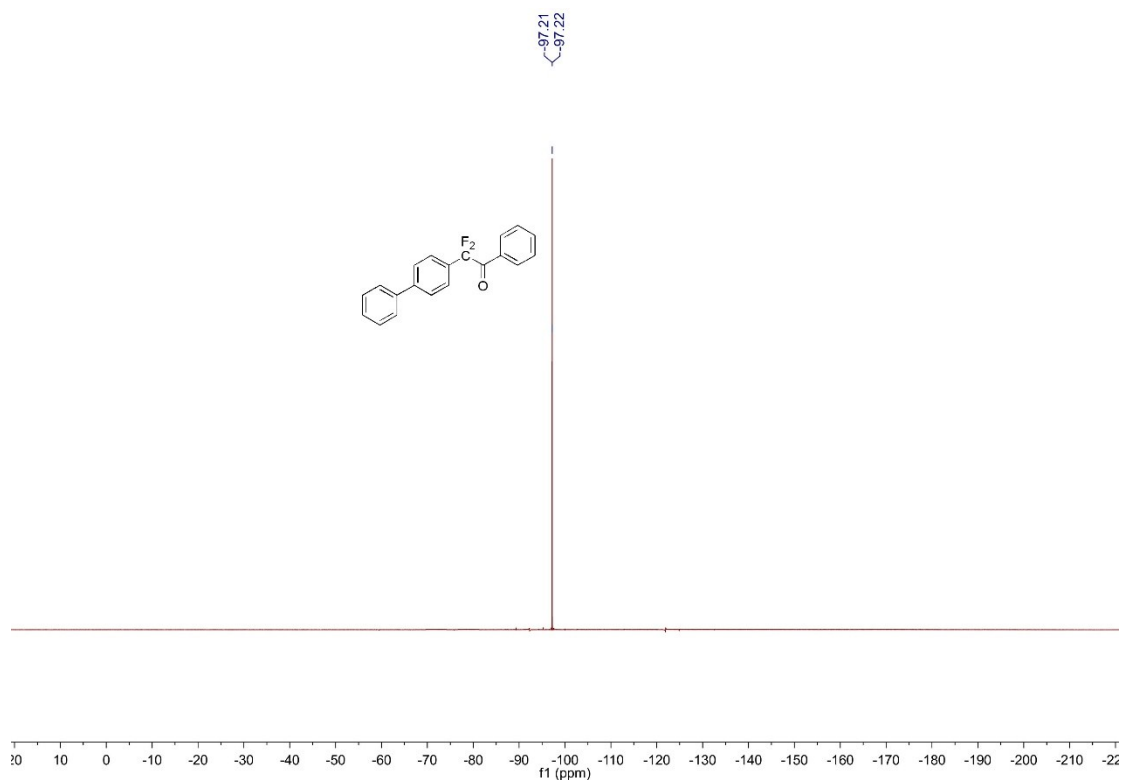
^{19}F NMR 3r



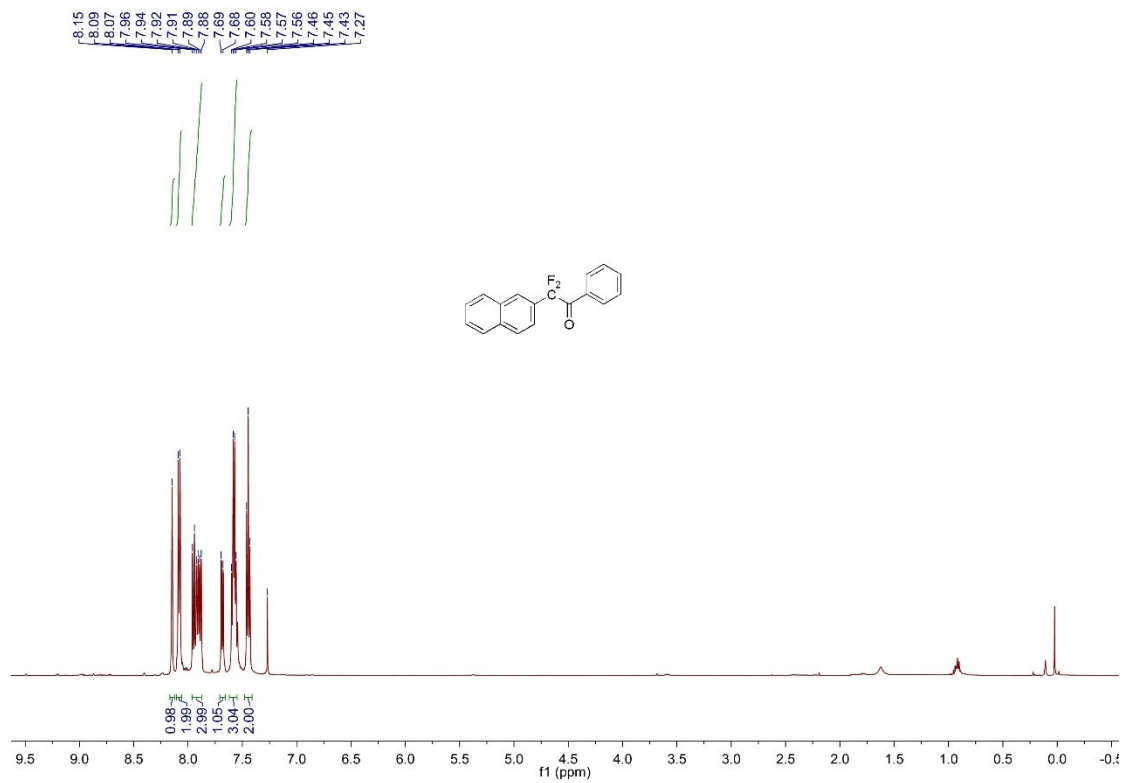
^1H NMR 3s



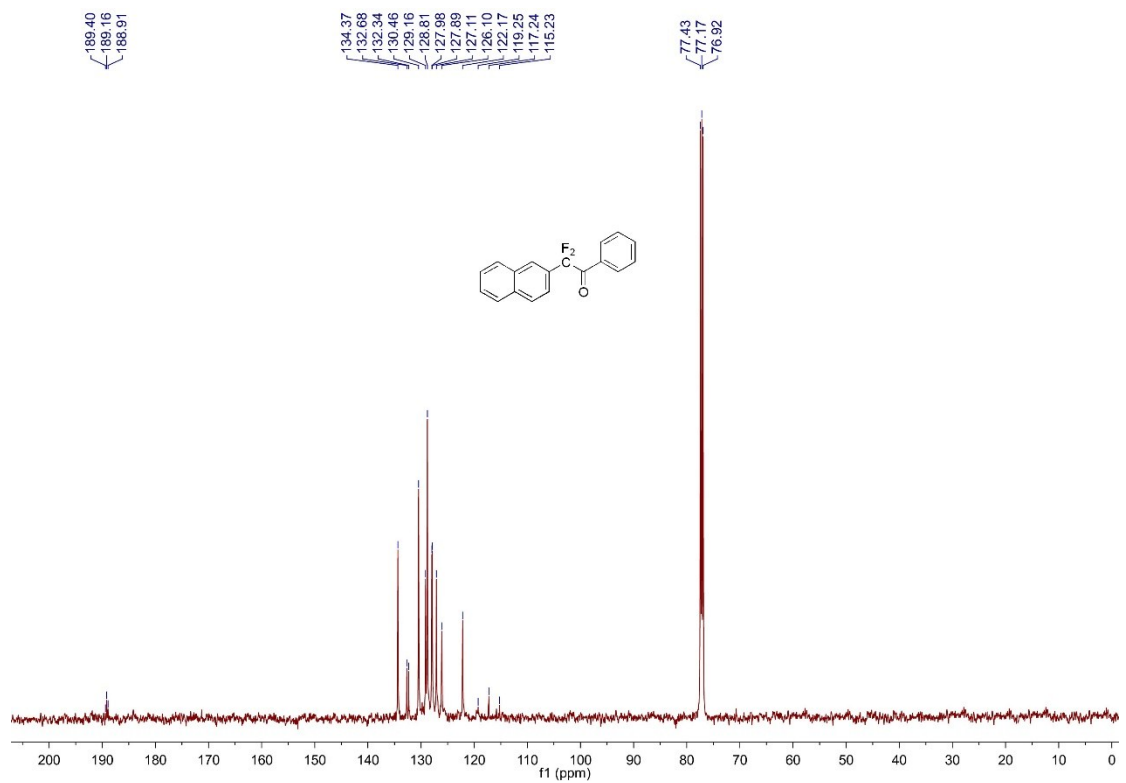
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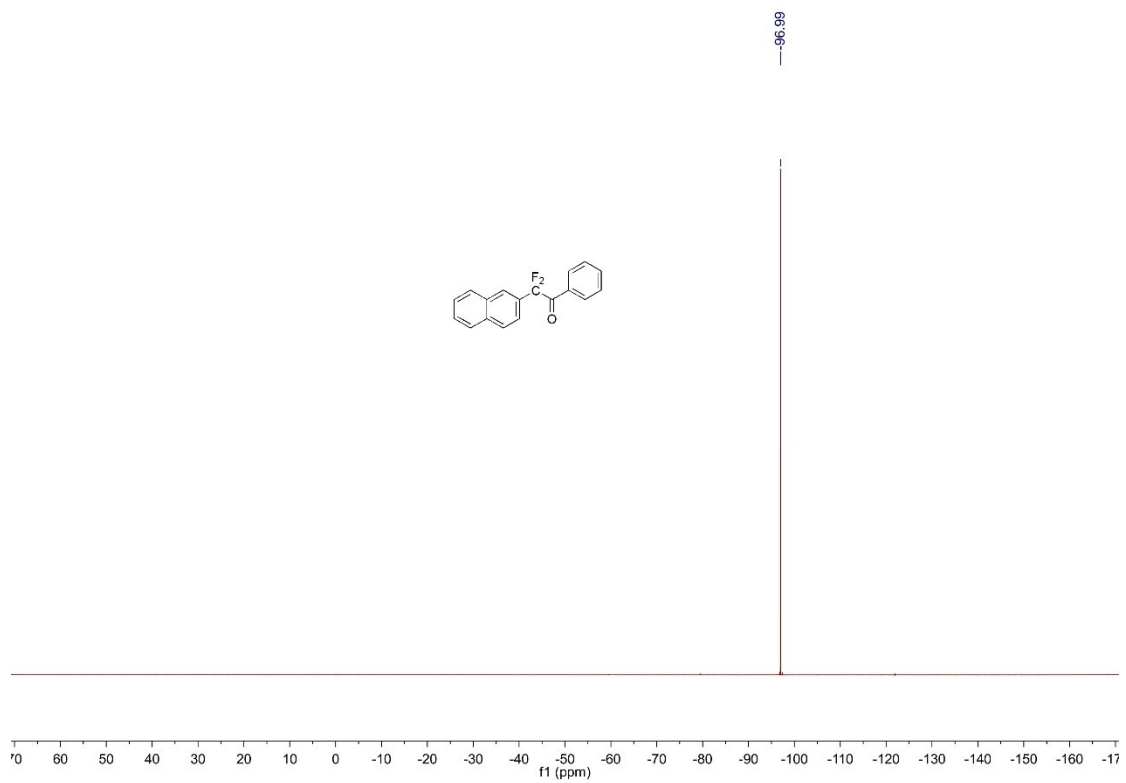
¹⁹F NMR 3s



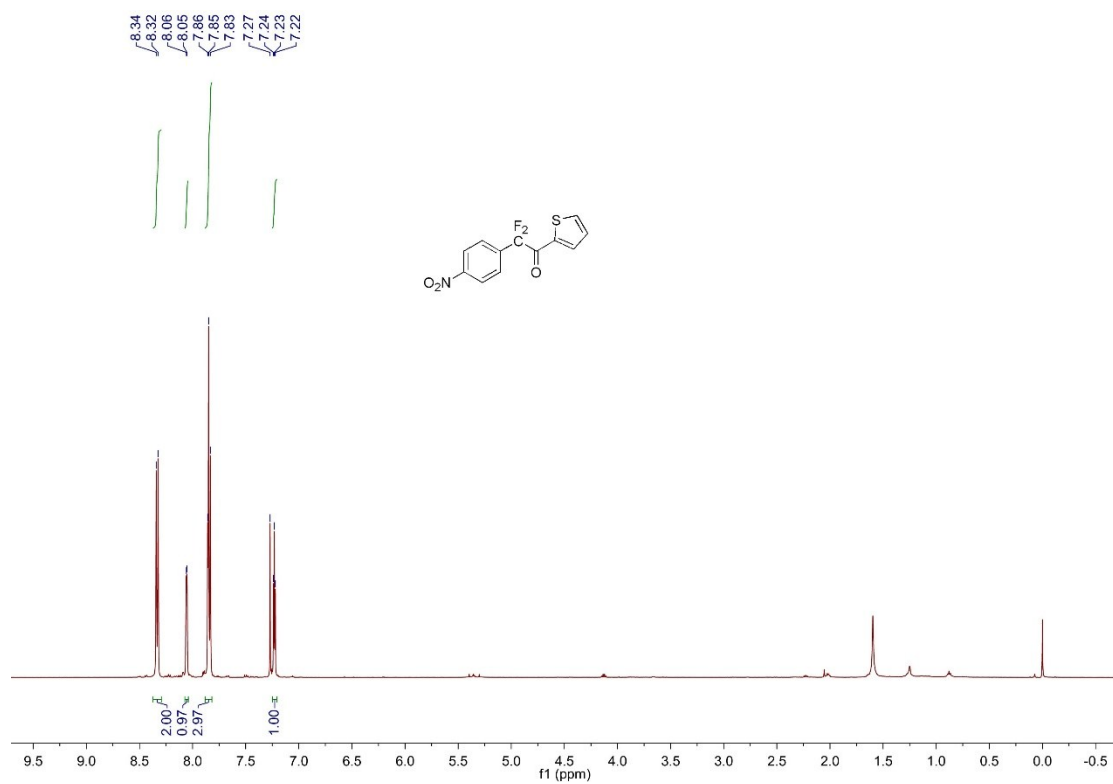
¹H NMR 3t



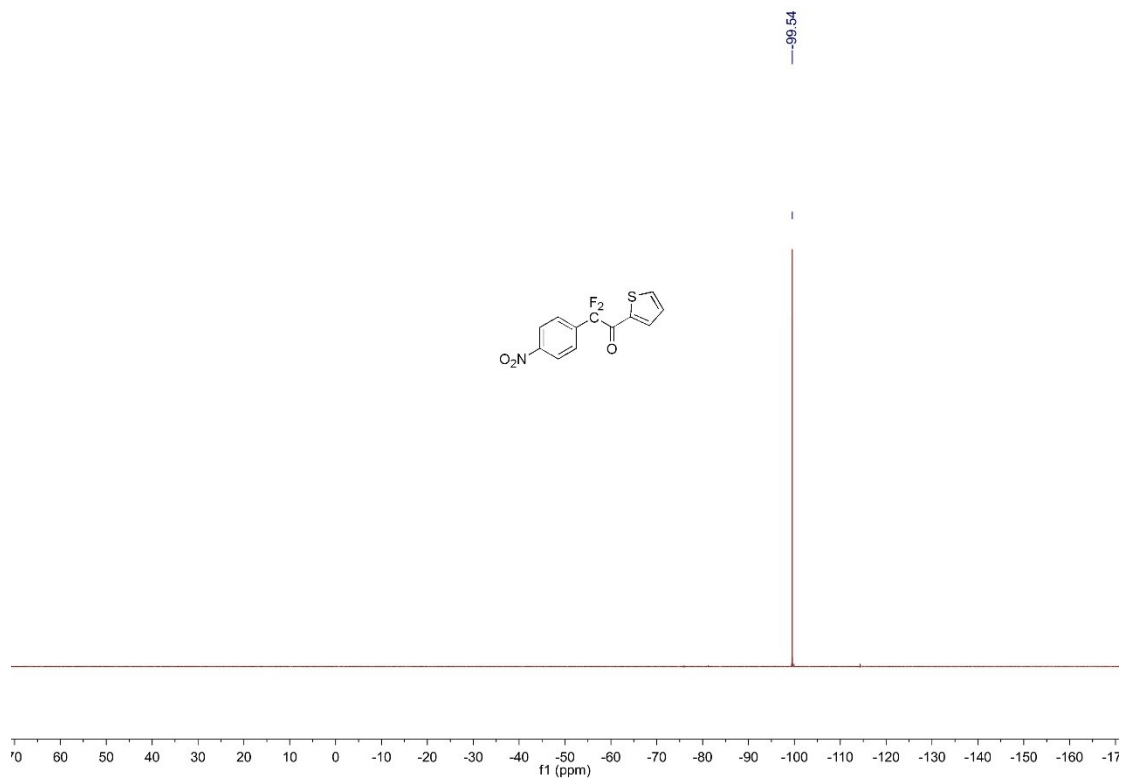
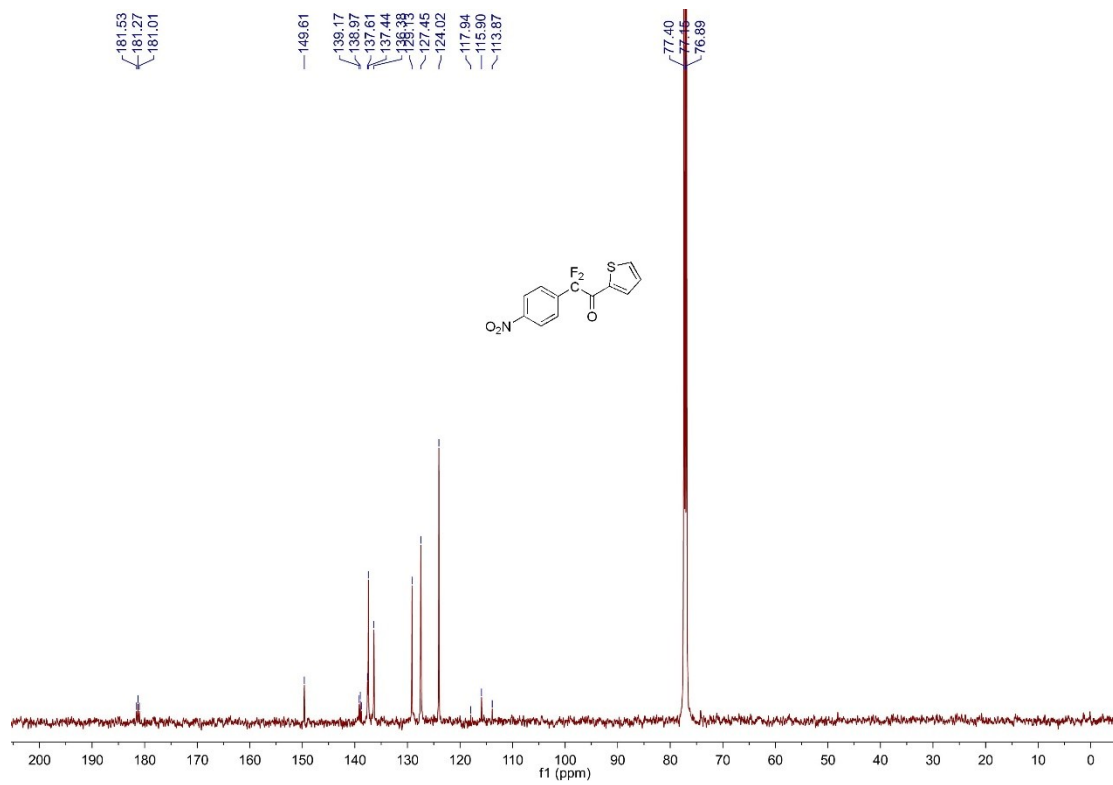
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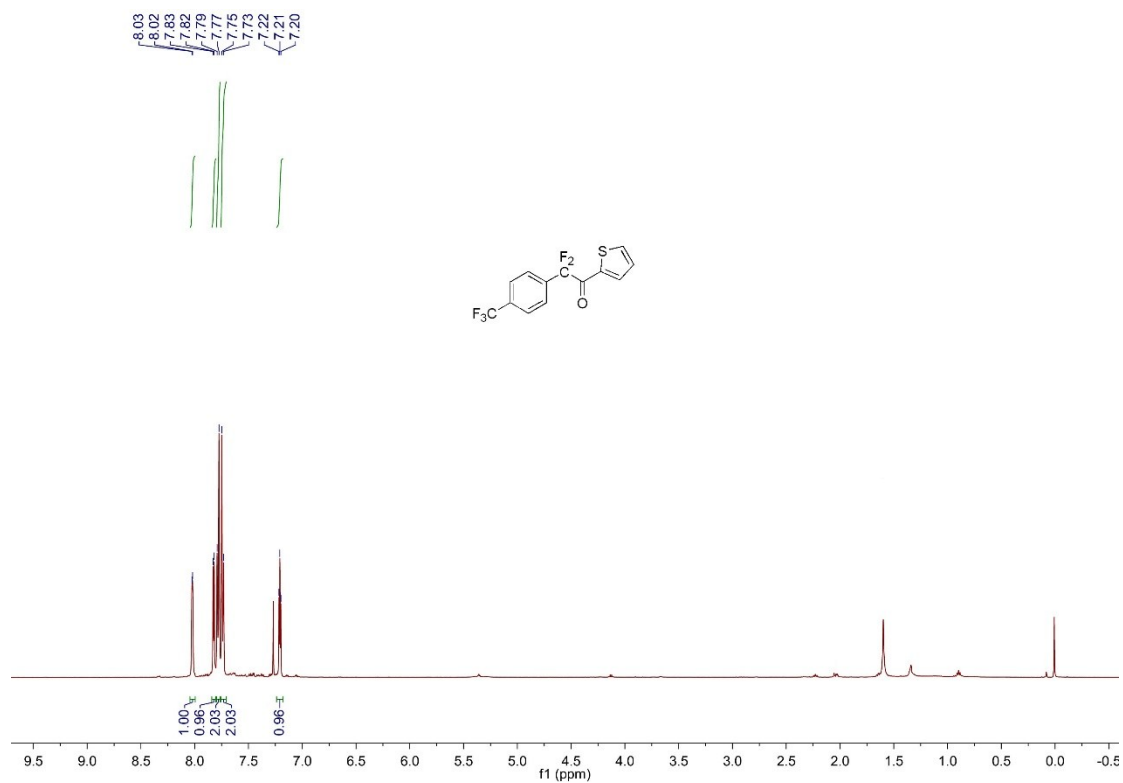


^{19}F NMR 3t

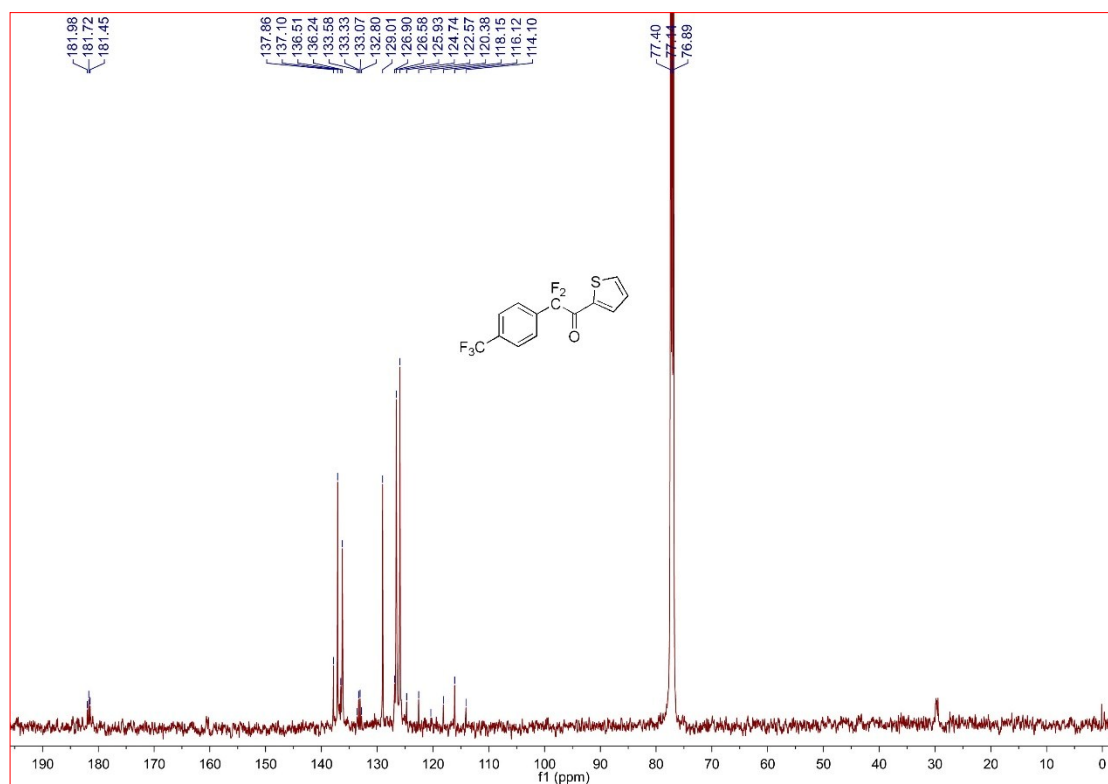


^1H NMR 3u

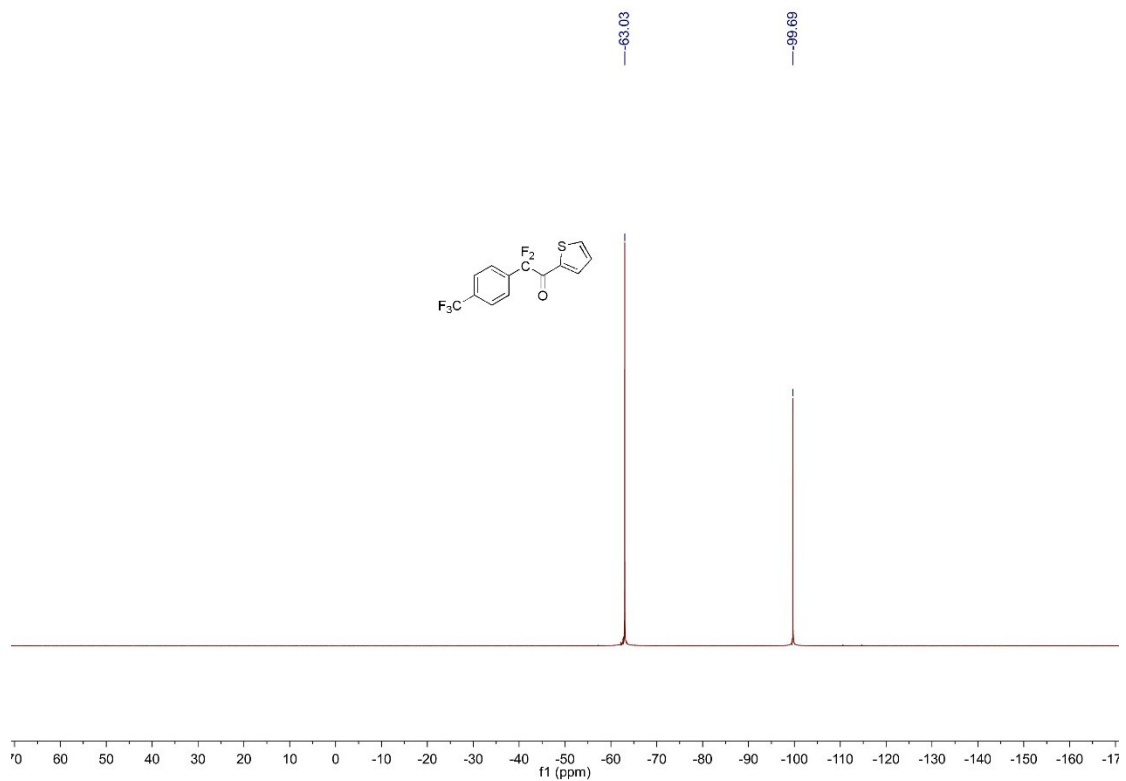




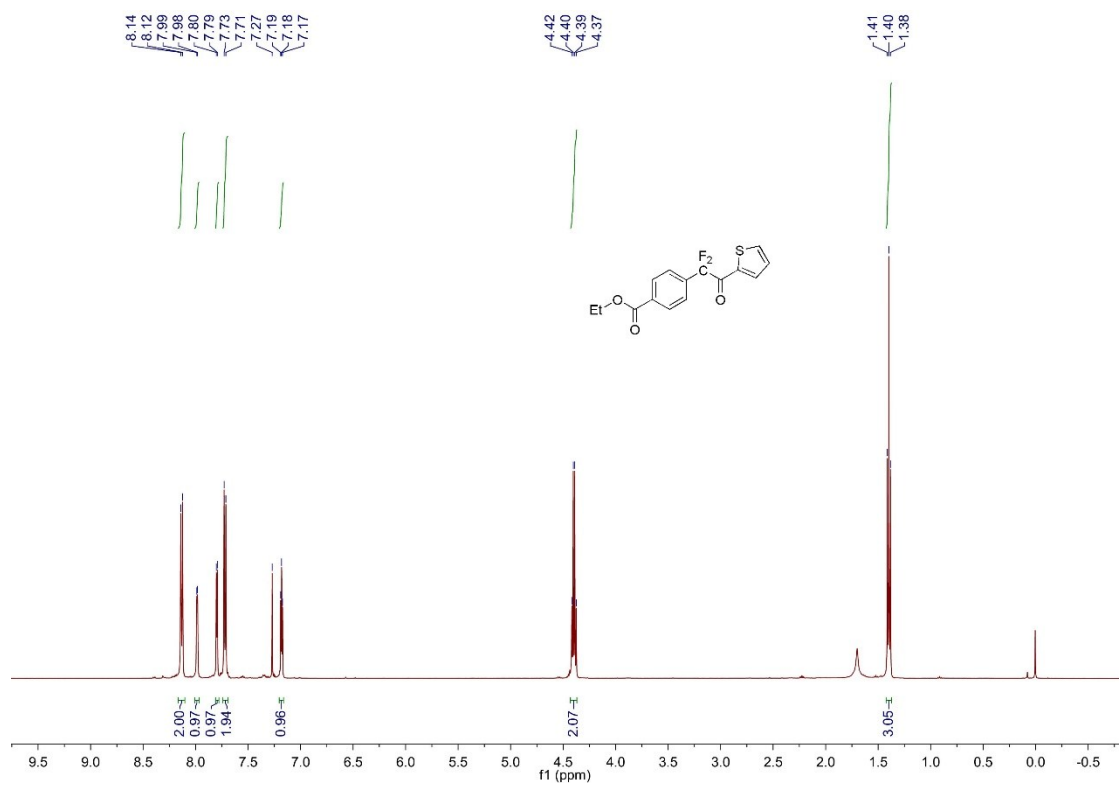
$^1\text{H NMR}$ 3v



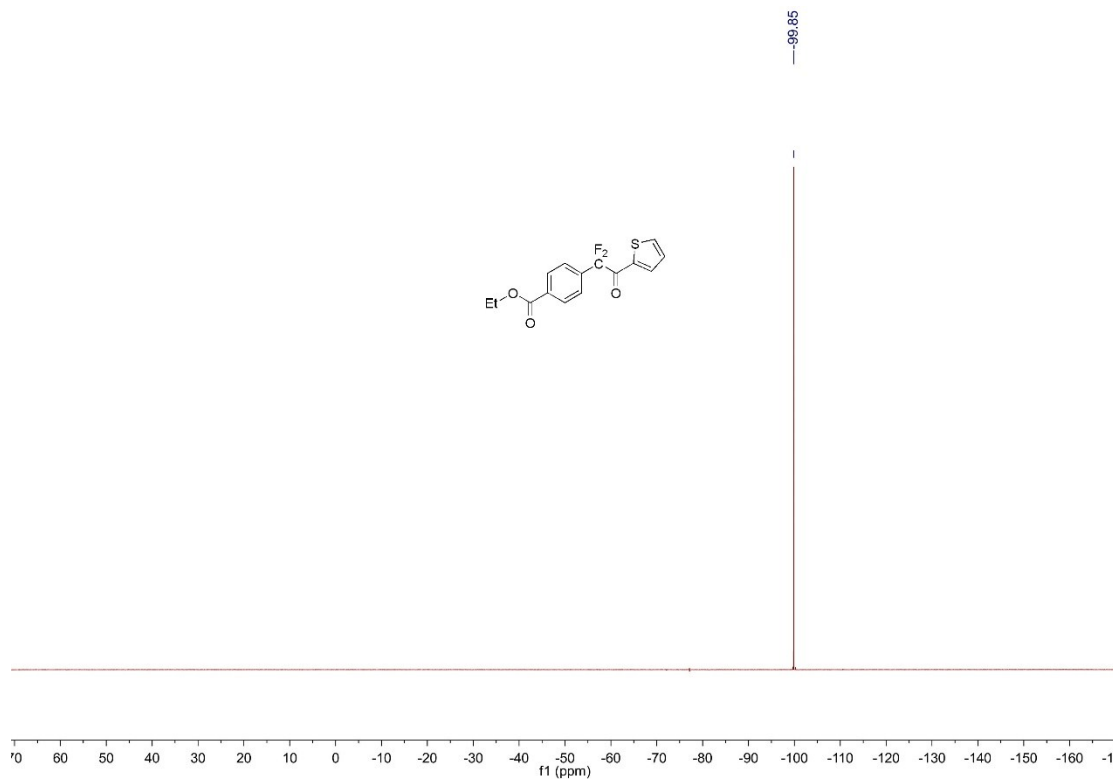
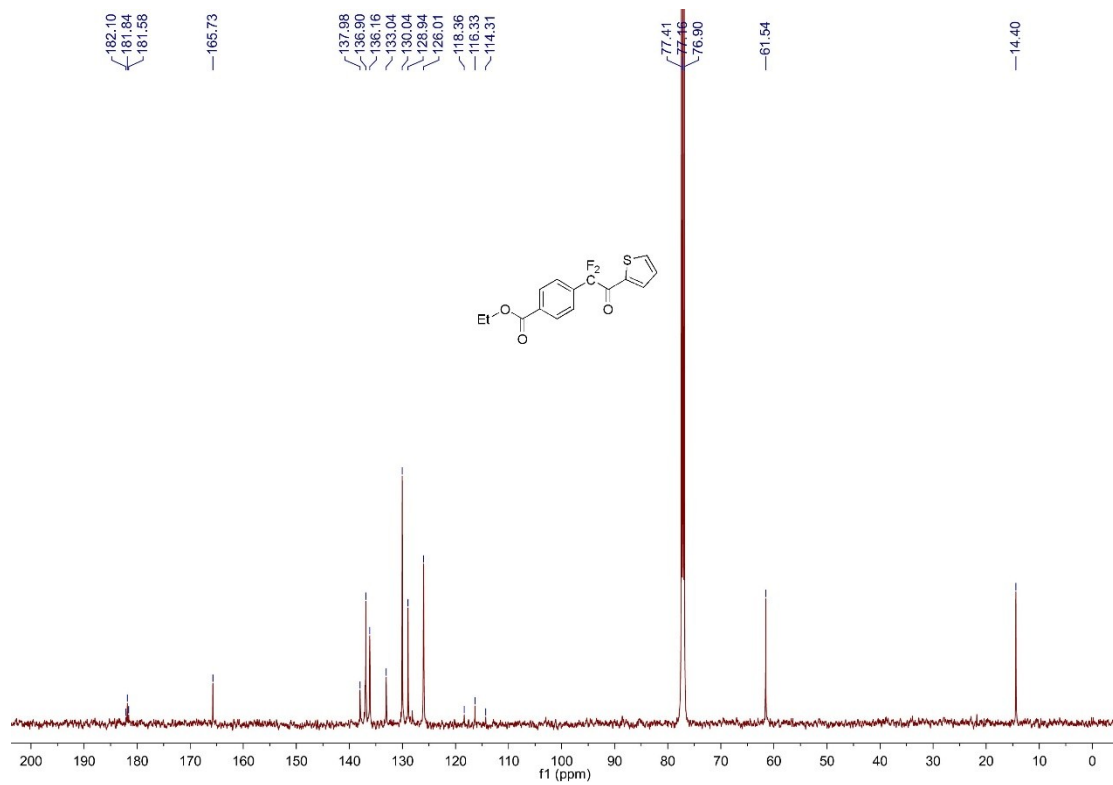
$^{13}\text{C NMR}$ 3v

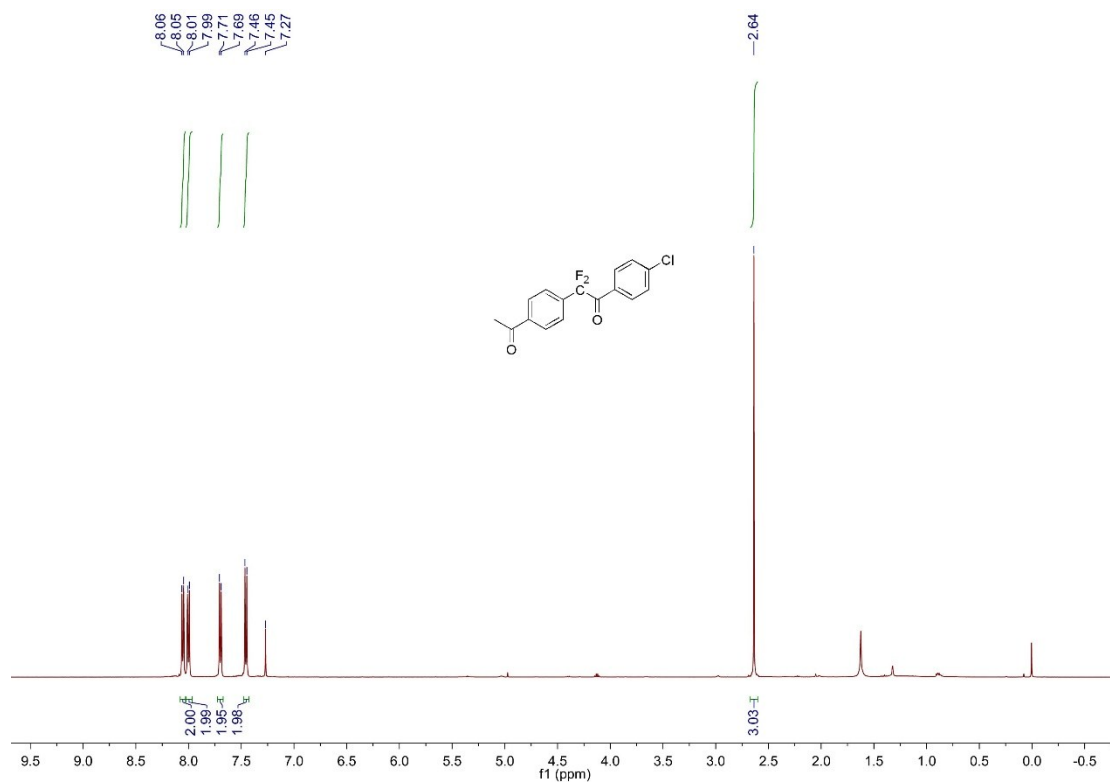


^{19}F NMR **3v**

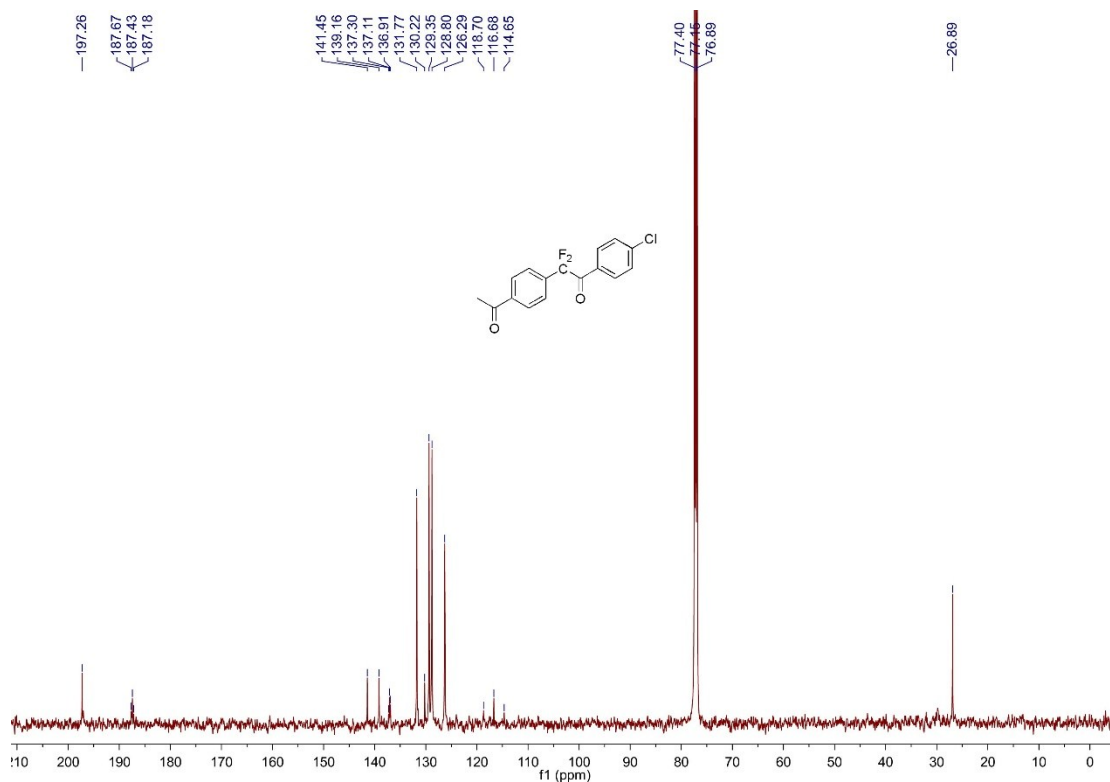


^1H NMR **3w**

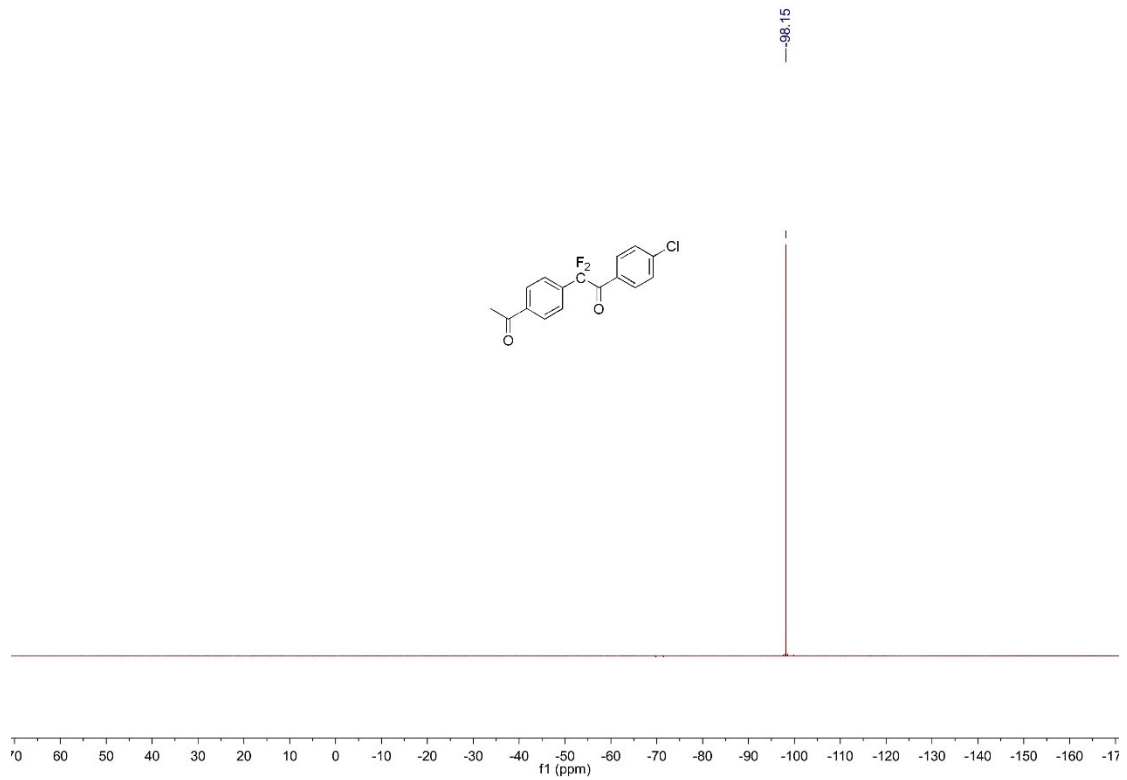




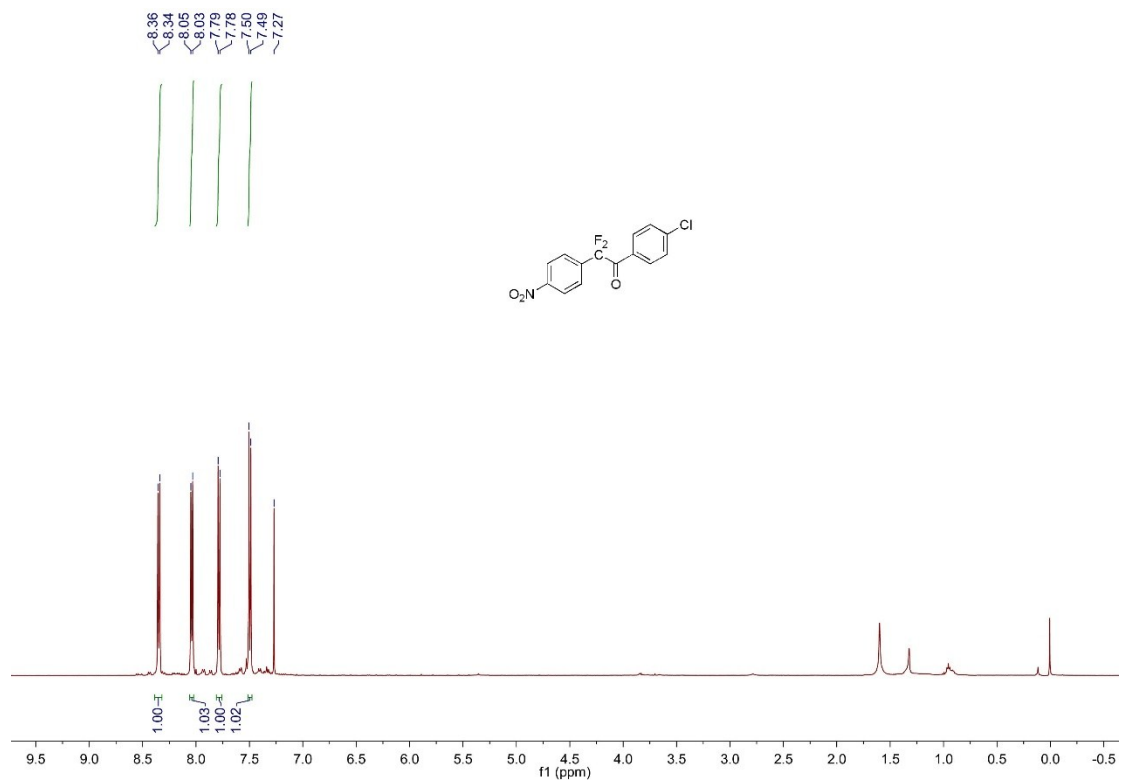
¹H NMR 3x



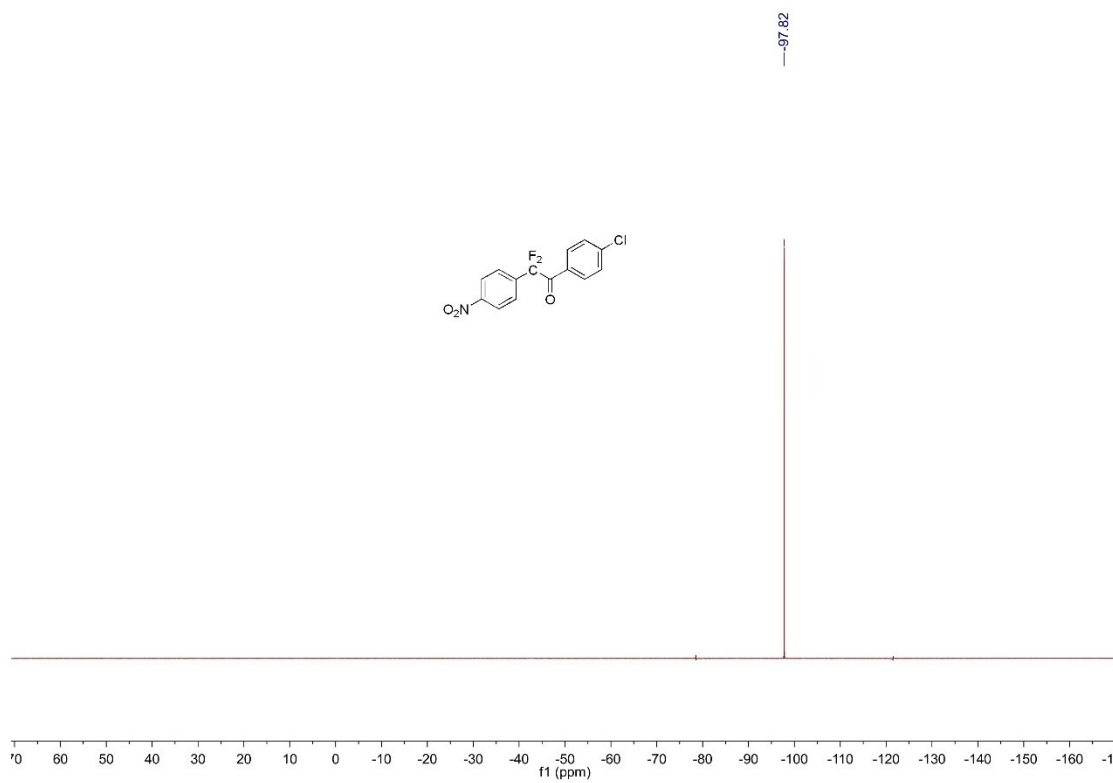
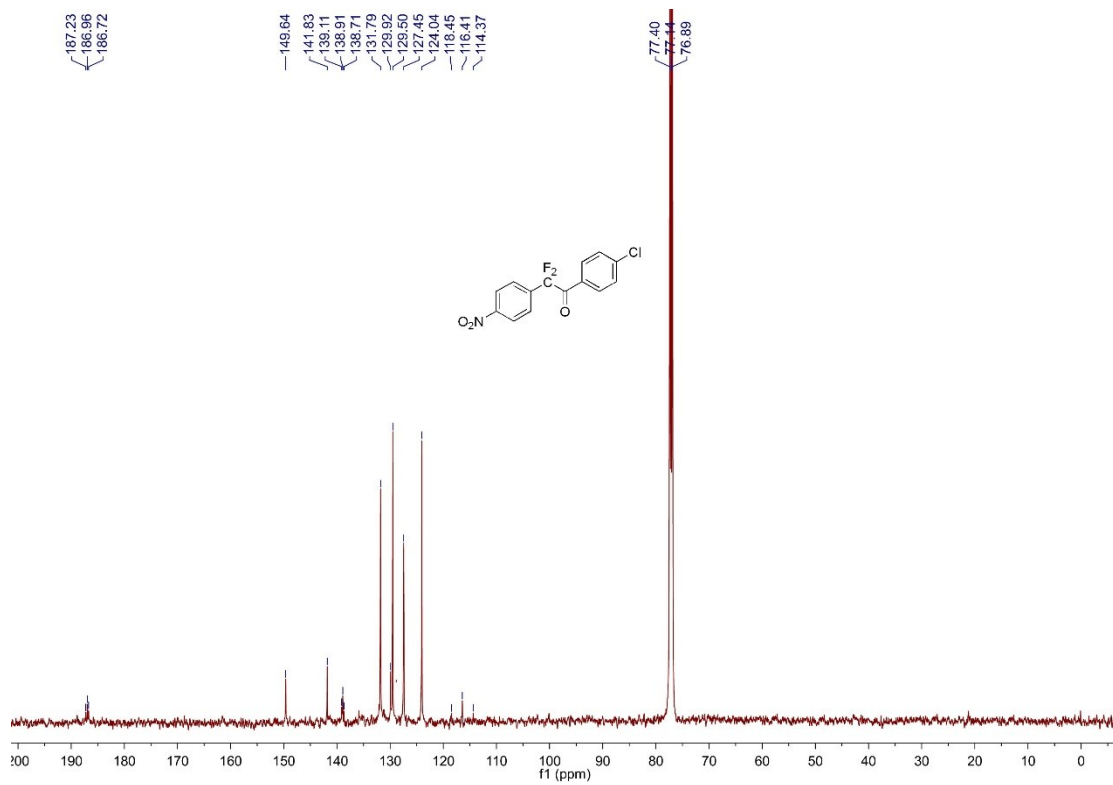
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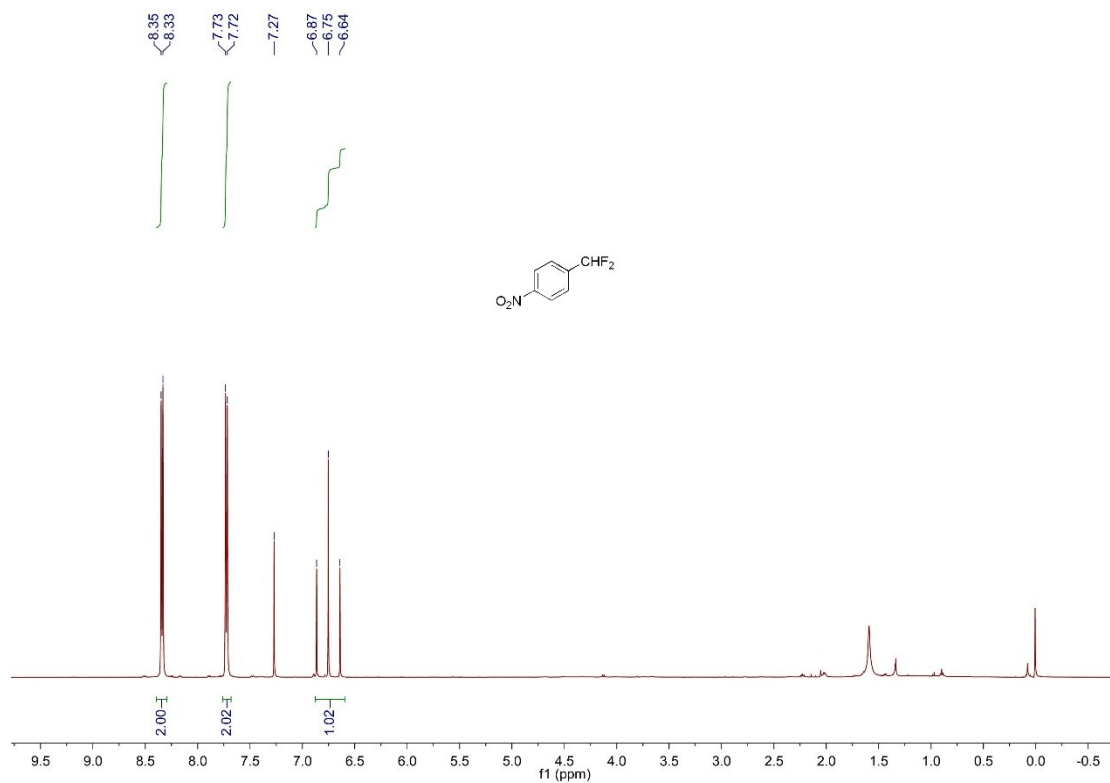


¹⁹F NMR 3x

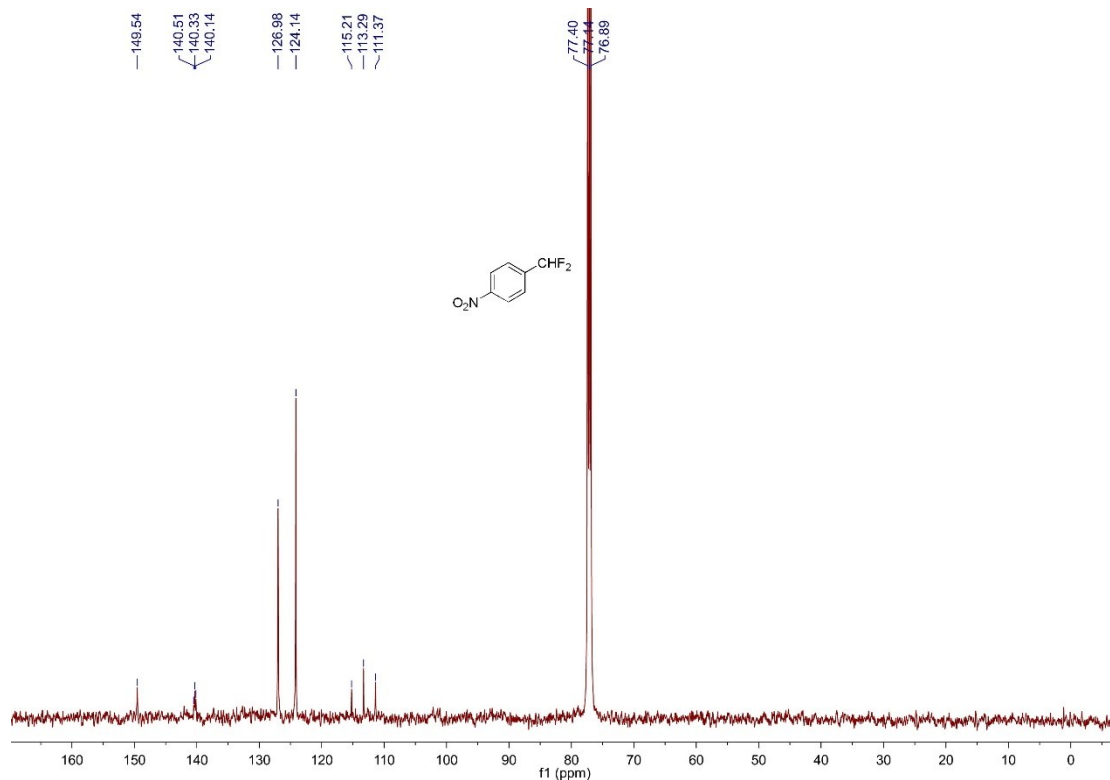


¹H NMR 3y

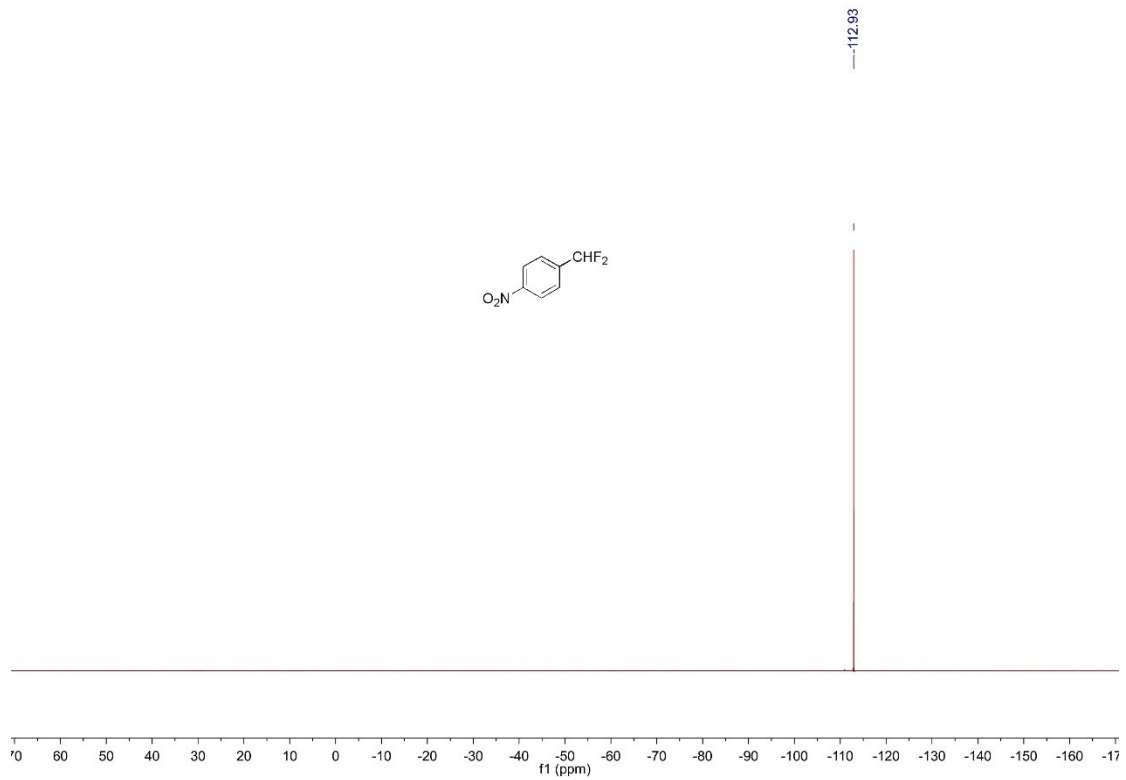




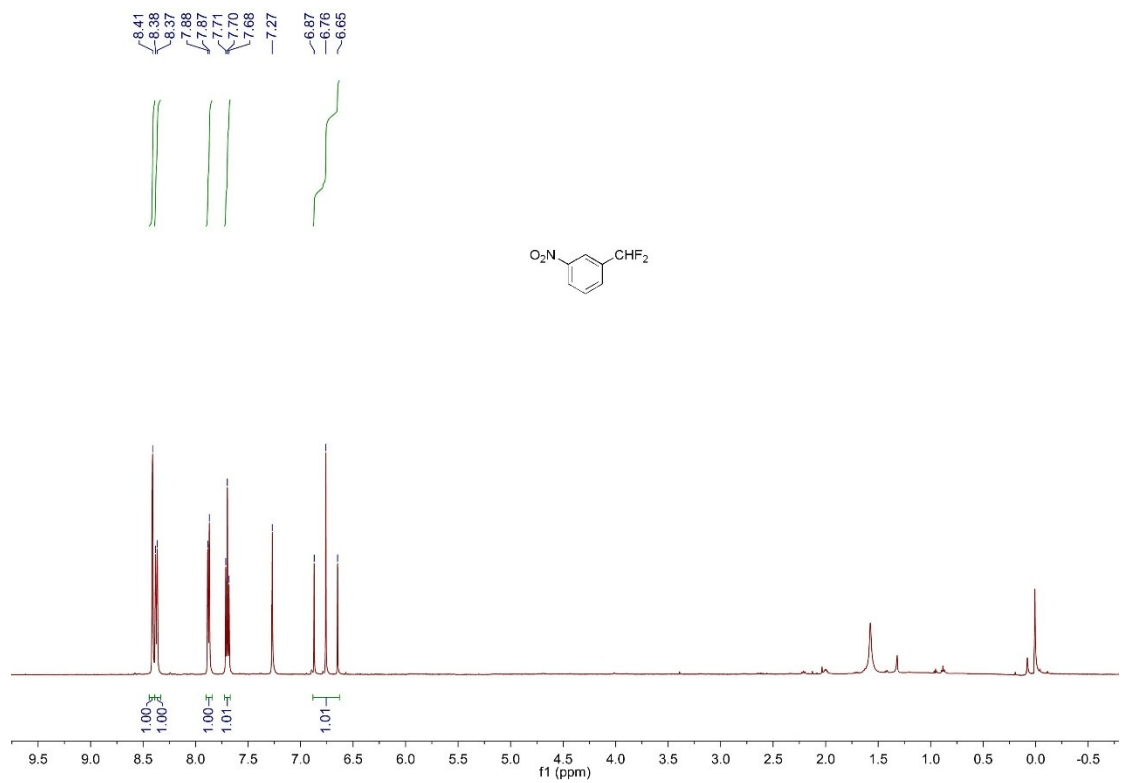
¹H NMR 4a



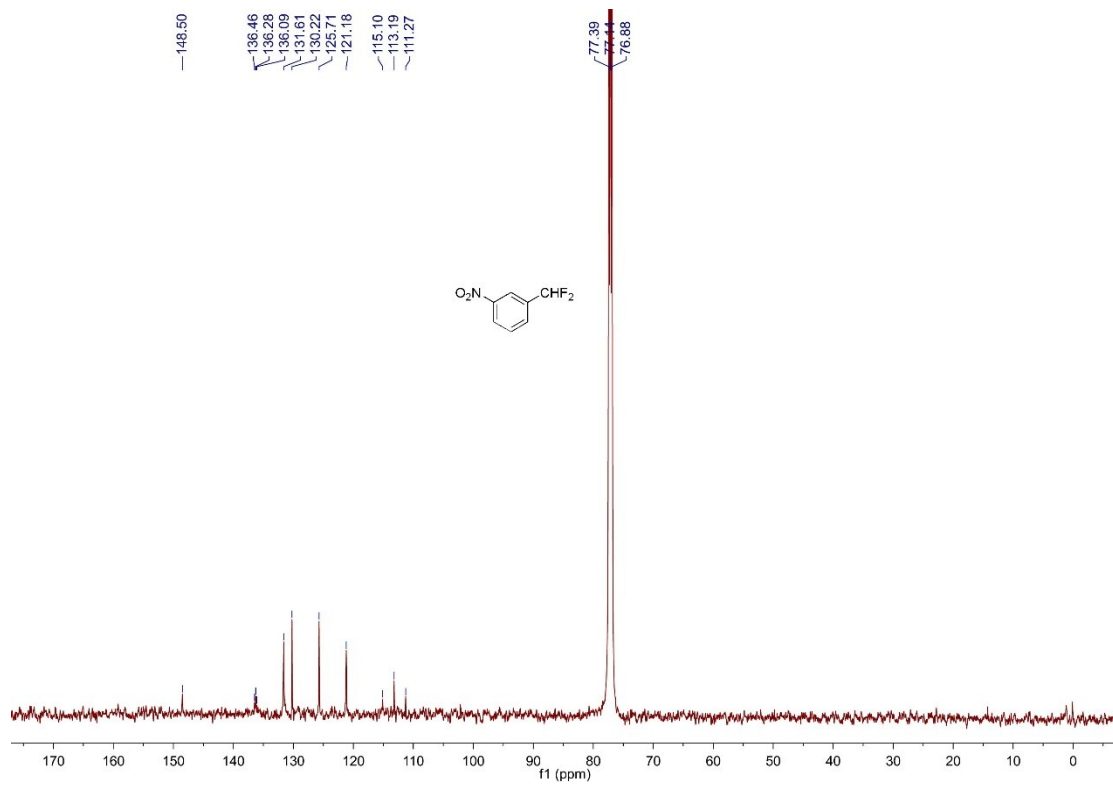
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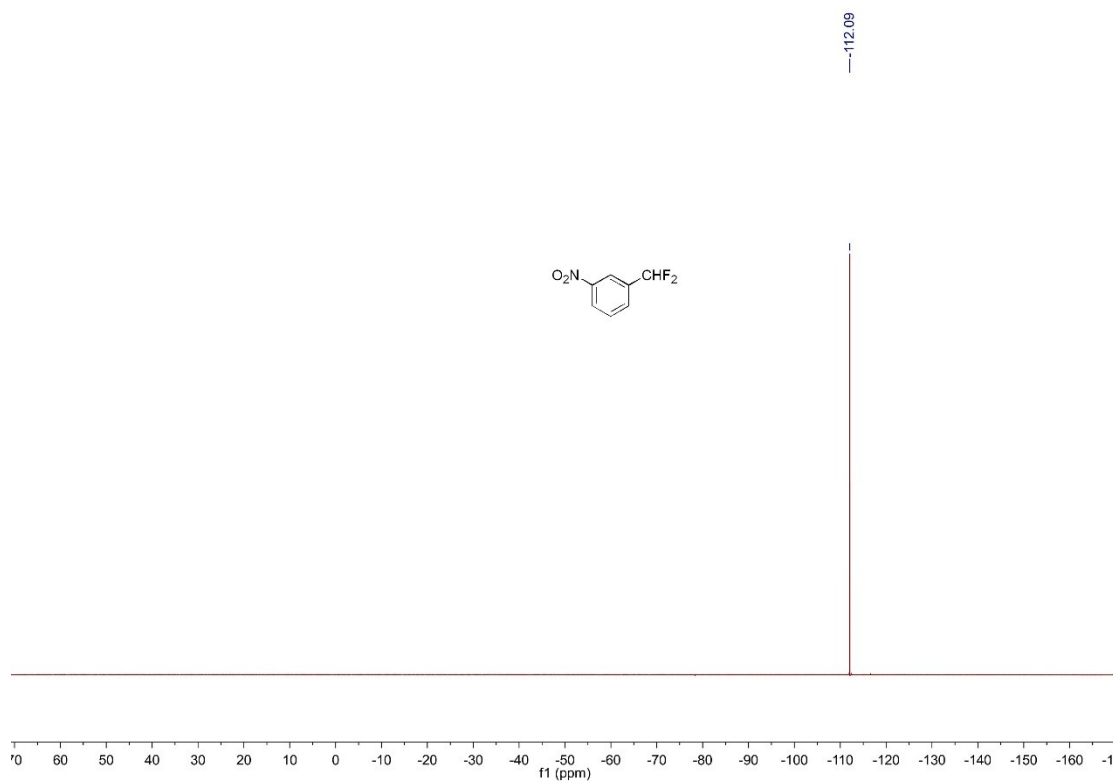
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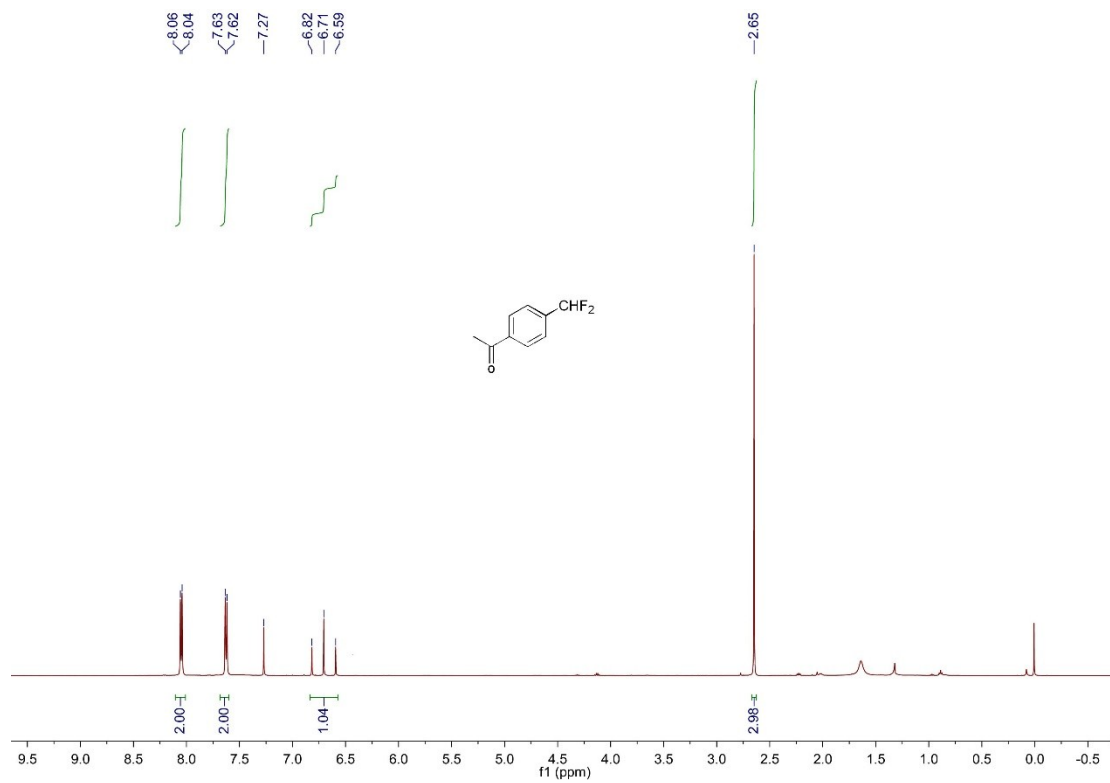
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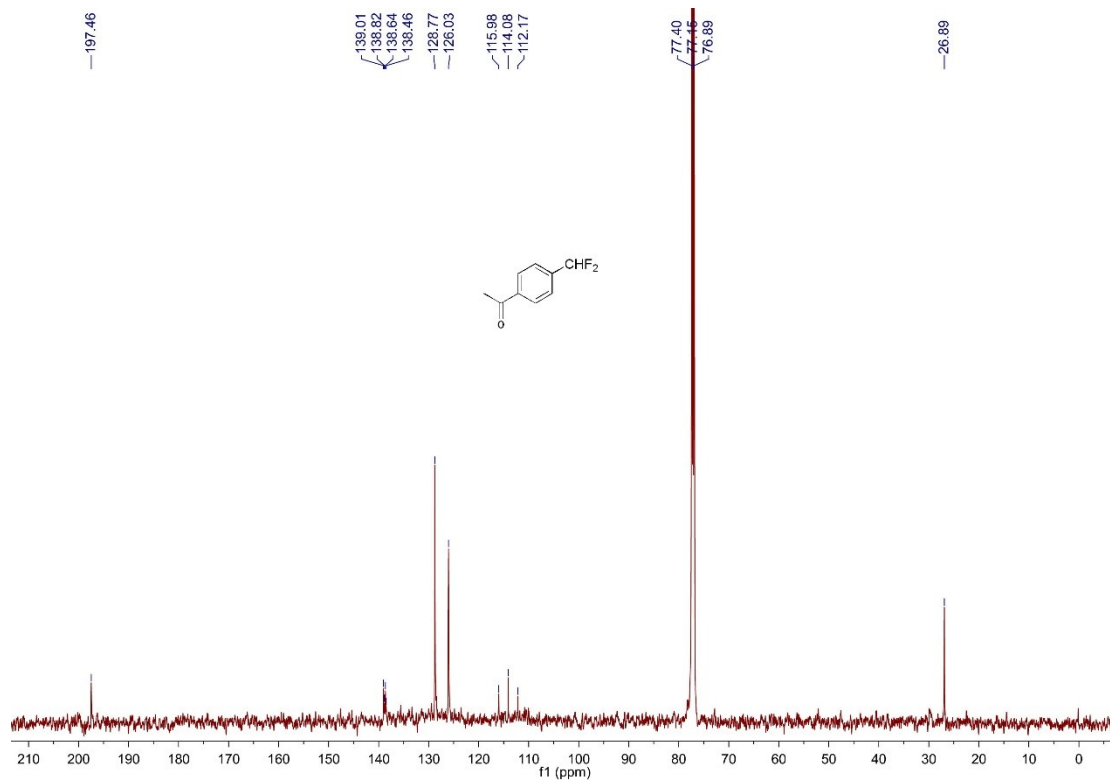
¹³C NMR **4b**



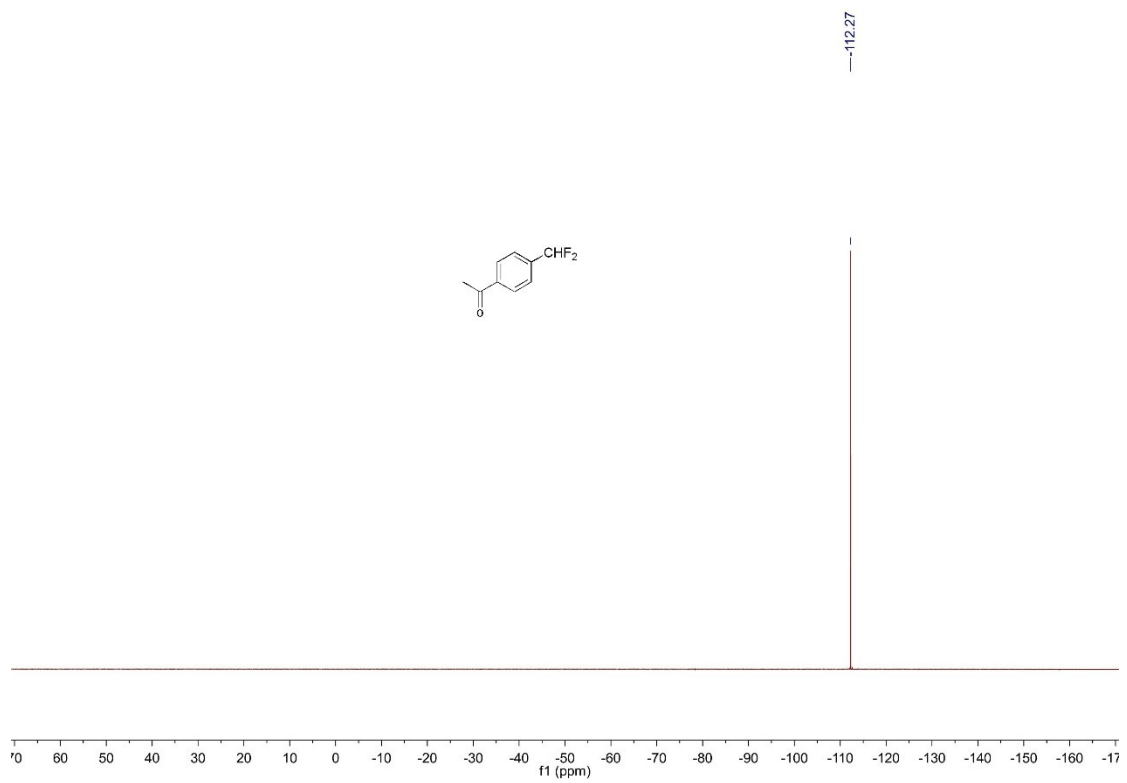
¹⁹F NMR **4b**



¹H NMR 4c



¹³C NMR 4c



^{19}F NMR **4c**