

Supporting Information

Base Promoted *gem*-Difluoroolefination of Alkyl Triflones

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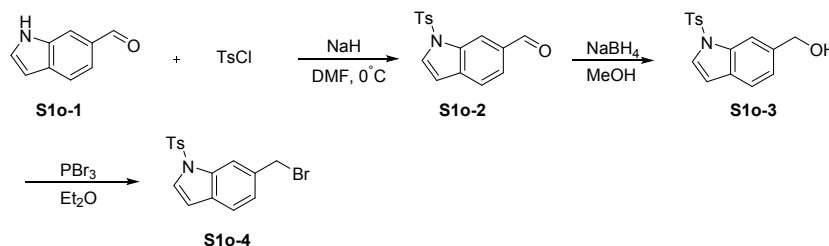
1. General

^1H NMR (400 MHz, 600 MHz), ^{13}C NMR (100 MHz, 150 MHz) and ^{19}F NMR (376 MHz, 564 MHz) spectra were recorded on a Bruker NMR apparatus. The chemical shifts are reported in δ (ppm) values (^1H and ^{13}C NMR relative to CHCl_3 , δ 7.26 ppm for ^1H NMR and δ 77.0 ppm for ^{13}C NMR). Or alternatively, ^1H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm). Multiplicities are recorded by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet) and br (broad). Coupling constants (J) are reported in Hertz (Hz). TLC was developed on silica gel 60 F254 glassplates. The products were purified using a commercial flash chromatography system or a regular glass column. The High-Resolution Mass measurements were conducted using an Agilent 7250 GC/Q-TOF equipment.

Commercial reagents and solvents were obtained from the commercial providers and used without further purification. Work-ups and purifications were performed using commercial reagent-grade solvents. Most benzyl bromides were commercially available from Sigma-Aldrich, TCI and Bidepharm. Starting materials **2d**¹ and **1ac**², **2ac**² are known compounds.

2. Synthesis of benzyl bromide

Procedure for the synthesis of S1o-4:



Procedure for the synthesis of S1o-2:

Under nitrogen atmosphere, to a solution of 1H-indole-6-carbaldehyde (**S1o-1**) (1.0 equiv) and TsCl (1.05 equiv) in dry DMF (0.2 M/L) was added NaH (1.2 equiv) slowly at 0 °C. After stirring at 0 °C to room temperature for 12 hours, the mixture was quenched by NH_4Cl (aq.) at 0 °C. The mixture was extracted with EtOAc, combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure to afford residue, which was further purified by silica-gel column chromatography eluting with a mixture of EA and PE to give methyl 1-tosyl-1H-indole-6-carbaldehyde (**S1o-2**).

Procedure for the synthesis of S1o-3:

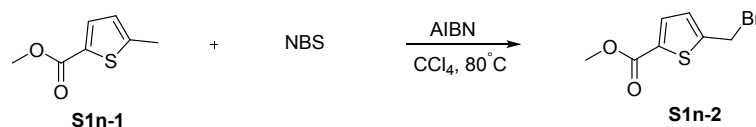
Under nitrogen atmosphere, to a solution of 1-tosyl-1H-indole-6-carbaldehyde (**S1o-2**) (1.0 equiv) in MeOH (0.1 M/L) was added NaBH_4 (1.0 equiv) slowly at 0 °C. After stirring at room temperature for 1 h, water was added at 0 °C. The mixture was extracted with EtOAc, combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure to afford methyl 6-hydroxymethyl-1-tosylindole (**S1o-3**), which was used in the next step without further purification.

Procedure for the synthesis of S1o-4:

Under nitrogen atmosphere, to a solution of 6-hydroxymethyl-1-tosylindole (**S1o-3**) (1.0 equiv) in dry Et₂O (0.1 M/L) was added PBr_3 (1.0 equiv) slowly at 0 °C. After stirring at room temperature for 2 h, water and saturated NaHCO_3 (aq.) were added at 0 °C. The mixture was extracted with Et₂O, combined

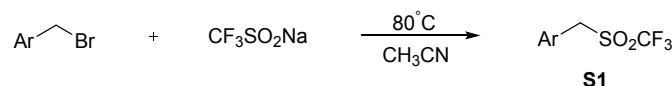
organic layer were dried over Na₂SO₄ and evaporated under reduced pressure to afford methyl 6-bromomethyl-1-tosylindole (**S1o-4**), which was used without further purification.

Procedure for the synthesis of **S1n-2**



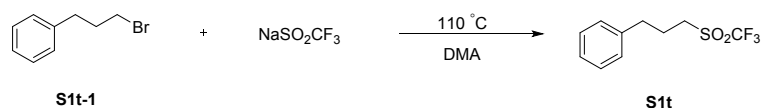
To a solution of methyl 5-methylthiophene-2-carboxylate (**S1n-1**) (1.0 equiv) in carbon tetrachloride (0.2 M/L) at room temperature was added NBS (1.2 equiv) and AIBN (10 mol%). The resulting mixture was heated to 80 °C and stirred at this temperature for 12 h under a nitrogen atmosphere. The mixture was filtered, and the filtrate was concentrated in a vacuum to give the crude product methyl 5-(bromomethyl)thiophene-2-carboxylate (**S1n-2**) as a yellow oil. The product was used in the next step without further purification.

3. General procedure for the synthesis of **S1**



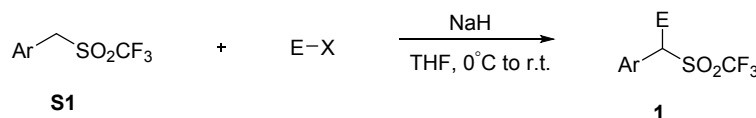
Under a nitrogen atmosphere, a mixture of benzyl bromide **1** (1.0 equiv.) and NaSO₂CF₃ **2** (2.0 equiv.) in acetonitrile (0.2 M/L) was heated at 80 °C for about 12 to 24 h. After completed the reaction was monitored by TLC and GC-MS, the reaction mixture was cooled down to room temperature; the reaction mixture was concentrated in a vacuum to give a residue. The residue was washed with dichloromethane and filtered through Celite to give the crude product. The crude product was purified by silica gel chromatography eluted with PE: EtOAc = 20:1 or recrystallization from a mixture of hexane and dichloromethane to give product **S1**.

Procedure for the synthesis of **S1t**



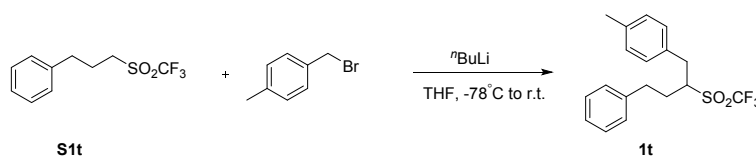
Under a nitrogen atmosphere, a mixture of (3-bromopropyl)benzene **1** (1.0 equiv.) and NaSO₂CF₃ **2** (2.0 equiv.) in DMA (0.2 M/L) was heated at 110 °C for 3 days. After completed the reaction was monitored by TLC and GC-MS, the reaction mixture was cooled down to room temperature; the reaction mixture was concentrated in a vacuum to give a residue. The residue was washed with dichloromethane and filtered through Celite to give the crude product. The crude product was purified by recrystallization from a mixture of hexane and dichloromethane to give the product (3-((trifluoromethyl)sulfonyl)propyl)benzene **S1t**.

4. General procedure for the synthesis of **1**



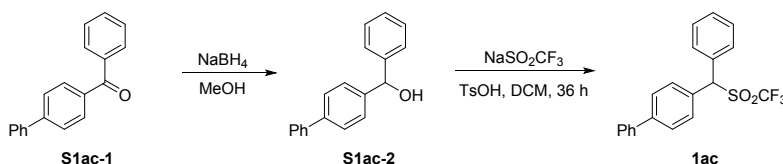
To a solution of **S1** (1.0 equiv.) in THF (0.2 M/L) was added NaH (1.1 equiv.) under nitrogen atmosphere at 0 °C. The mixture was stirred at 0 °C for 10 minutes, and then benzyl bromide or alkyl iodide in THF was added via syringe. The mixture was stirred at 0 °C to room temperature for several hours. After completion of the reaction (monitored by TLC), the mixture was diluted with NH₄Cl (aq.), and extracted with ethyl acetate; combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, filtered, concentrated under vacuum to give a residue. The residue was purified by silica gel column chromatography eluting with a mixture of ethyl acetate and petroleum ether to give the **1**.

Procedure for the synthesis of **1t**



Under nitrogen atmosphere, to a solution of 3-((trifluoromethyl)sulfonyl)propyl)benzene **S1t** (1.0 equiv.) in THF (0.1 M/L) was added ⁿBuLi (1.2 equiv., 1.6 M/L) at -78°C. The mixture was stirred at -78 °C for 30 minutes, and then 1-(bromomethyl)-4-methylbenzene in THF was added via syringe. The mixture was stirred at -78 °C to room temperature for 16 hours. After completion of the reaction (monitored by TLC), the mixture was diluted with NH₄Cl (aq.), and extracted with ethyl acetate; combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, filtered, concentrated under vacuum to give a residue. The residue was purified by silica gel column chromatography eluting with a mixture of ethyl acetate and petroleum ether (V_{EA}/V_{PE} = 1/100) to give 1-methyl-4-(4-phenyl-2-((trifluoromethyl)sulfonyl)butyl)benzene **1t**.

Procedure for the synthesis of **1ac**:



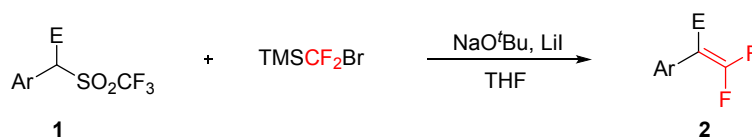
Procedure for the synthesis of **S1ac-2**:

Under nitrogen atmosphere, to a solution of [1,1'-biphenyl]-4-yl(phenyl)methanone (**S1ac-1**) (1.0 equiv) in MeOH (0.1 M/L) was added NaBH₄ (1.0 equiv) slowly at 0 °C. After stirring at room temperature for 1 h, water was added at 0 °C. The mixture was extracted with EtOAc, combined organic layers were dried over Na₂SO₄ and evaporated under reduced pressure to afford [1,1'-biphenyl]-4-yl(phenyl)methanol (**S1ac-2**), which was used in the next step without further purification.

Procedure for the synthesis of **1ac**:

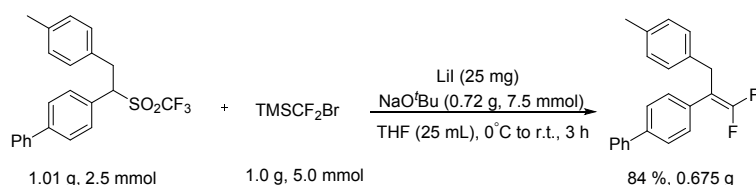
A mixture of [1,1'-biphenyl]-4-yl(phenyl)methanol (**S1ac-2**) (1.0 equiv), NaSO₂CF₃ (1.5 equiv) and TsOH·H₂O (1.5 equiv) in DCM (0.4 M/L) was stirred at room temperature for 36 h. The mixture was directly filtered and purified by recrystallization from a mixture of DCM and PE to give pure product **1ac**.

5. General procedure for the synthesis of *gem*-difluoroalkenes **2**



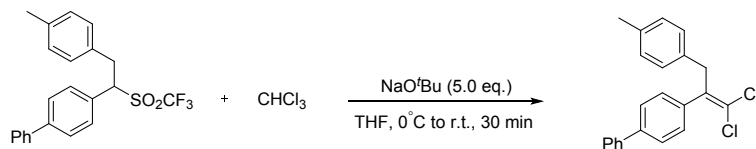
To a Schlenk tube was added **1** (0.1 mmol, 1.0 equiv), NaO^tBu (0.3 mmol, 3.0 equiv, 28.0 mg) and LiI (5 mmol%, 1 mg) in the glove box. The tube was evacuated/backfilled with N₂ three times, THF (1.0 mL) was added. The reaction mixture was stirred at 0 °C for 30 minutes, and then TMSCF₂Br (0.2 mmol, 2.0 equiv, 40.0 mg) was added via syringe. Then the reaction mixture was allowed to warm to room temperature and stirred for 30-60 minutes. After completion of the reaction (monitored by TLC), the mixture was concentrated under vacuum to give a residue. The residue was purified by column chromatography on silica gel eluting with a mixture of ethyl acetate and petroleum ether (or 100 % petroleum ether) to give the desired product *gem*-difluoroalkenes **2**.

6. Gram scale synthesis of **2a**



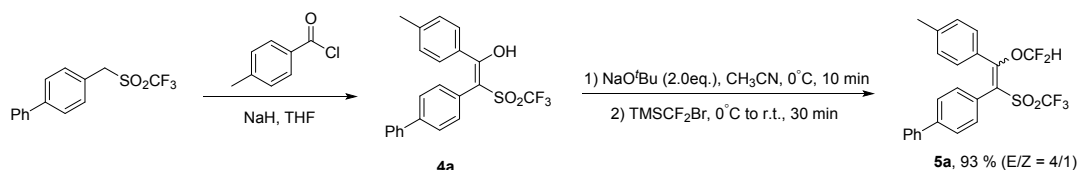
To a Schlenk tube was added **1a** (2.5 mmol, 1.0 equiv, 1.01 g), NaO^tBu (7.5 mmol, 3.0 equiv, 0.72 g) in the glove box. The tube was evacuated/backfilled with N₂ three times, THF (25 mL) was added. The reaction mixture was stirred at 0 °C for 30 minutes, and then TMSCF₂Br (5.0 mmol, 2.0 equiv, 1.0 g) was added via syringe within 5 minutes. Then the reaction mixture was allowed to warm to room temperature and stirred for 3 hours. The mixture was concentrated under a vacuum to give a residue. The residue was purified by column chromatography on silica gel eluting with 100 % petroleum ether to give **2a** (0.675 g, 84%).

7. Procedure for the synthesis of *gem*-dichloroalkene **3a**



To a Schlenk tube was added **1a** (0.1 mmol, 1.0 equiv, 41.0 mg), NaO^tBu (0.5 mmol, 5.0 equiv, 48.0 mg) in the glove box. The tube was evacuated/backfilled with N₂ three times, THF (1.0 mL) was added. The reaction mixture was stirred at 0 °C for 30 minutes, and then CHCl₃ (0.2 mmol, 2.0 equiv, 24.0 mg) was added via syringe. Then the reaction mixture was allowed to warm to room temperature and stirred for 30 minutes. The mixture was concentrated under a vacuum to give a residue. The residue was purified by column chromatography on silica gel eluting with 100 % petroleum ether to give the desired product *gem*-dichloroalkene **3a**.

8. Procedure for the synthesis of 5a



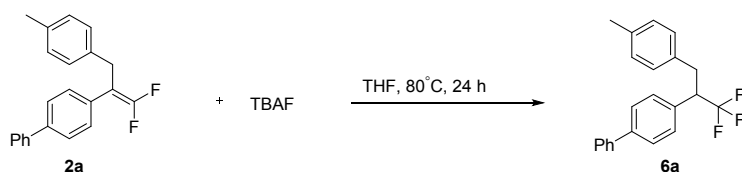
Procedure for the synthesis of 4a

Under nitrogen atmosphere, to a solution of 4-(((trifluoromethyl)sulfonyl)methyl)-1,1'-biphenyl **1ah** (1.0 equiv.) in THF (0.1 M/L) was added NaH (2.0 equiv.) at 0 °C. The mixture was stirred for 5-10 minutes, then *p*-tolchloride (1.0 equiv.) was added at 0 °C. The mixture was stirred at this temperature for 20 minutes. After completion of the reaction (monitored by TLC), the reaction mixture was quenched by water, extracted with ethyl acetate, and combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, filtered, concentrated under vacuum to give a residue. The residue was purified by silica gel column chromatography eluting with a mixture of ethyl acetate and petroleum ether (EA/PE = 1/3) to give **4a**.

Procedure for the synthesis of 5a

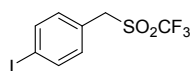
To a Schlenk tube was added **4a** (0.1 mmol, 1.0 equiv), NaO^tBu (0.2 mmol, 2.0 equiv, 19.0 mg) in the glove box. The tube was evacuated/backfilled with N₂ three times, CH₃CN (1.0 mL) was added. The reaction mixture was stirred at 0 °C for 10 minutes, and then TMSCF₂Br (0.2 mmol, 2.0 equiv, 40.0 mg) was added via syringe. Then the reaction mixture was allowed to warm to room temperature and stirred for 30 minutes. After completion of the reaction (monitored by TLC), the mixture was concentrated under vacuum to give a residue. The residue was purified by thin-layer chromatography on silica gel (EA/PE = 1/10) to give the mixture isomer of **5a**. Note: one of the isomer **5a'** was obtained after purification by thin-layer chromatography on silica gel (EA/PE = 1/10), again.

9. Procedure for the synthesis of 6a

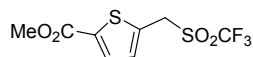


Under nitrogen atmosphere, a mixture of **2a** (0.1 mmol, 1.0 equiv.) and tetrabutylammonium fluoride (2.0 equiv., 1.0 M/L in THF) was heated at 80 °C for 24 hours. After completion of the reaction (monitored by TLC and GC-MS), the reaction mixture was cooled down to room temperature; the reaction mixture was concentrated in a vacuum to give a residue. The residue was purified by silica gel column chromatography eluting with a mixture of ethyl acetate and petroleum ether (EA/PE = 1/100) to give **6a**.

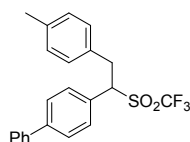
10. The characterization data of compounds:

1-Iodo-4-(((trifluoromethyl)sulfonyl)methyl)benzene (S1g)

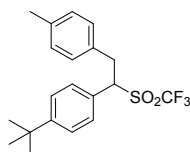
White solid, m.p. 159-161°C; ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.80 – 7.78 (m, 2H), 7.17 – 7.15 (m, 2H), 4.41 (s, 2H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: -76.3. ¹³C NMR (150 MHz, Chloroform-*d*) δ: 138.5, 132.9, 122.7, 119.6 (q, *J* = 327.0 Hz), 96.6, 55.6. HRMS (ESI) calcd. for C₈H₅F₃O₂IS [M-H]⁻: 348.9013, found: 348.9014.

Methyl 5-(((trifluoromethyl)sulfonyl)methyl)thiophene-2-carboxylate (S1n)

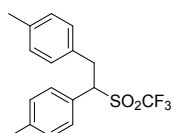
Yellow solid, m.p. 85-87°C; ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.76 (d, *J* = 3.8 Hz, 1H), 7.23 (d, *J* = 3.8 Hz, 1H), 4.71 (s, 2H), 3.91 (s, 3H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: -75.5. ¹³C NMR (100 MHz, Chloroform-*d*) δ: 161.7, 136.9, 133.6, 132.2, 129.8, 119.6 (q, *J* = 326.0 Hz), 52.5, 51.2. HRMS (EI⁺) calcd. for C₈H₇F₃O₄S₂ [M]⁺: 287.9732, found: 287.9735.

4-(2-(*p*-tolyl)-1-(((trifluoromethyl)sulfonyl)ethyl)-1,1'-biphenyl (1a)

White solid, m.p. 120-122°C; ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.52 (dd, *J* = 8.0, 2.8 Hz, 4H), 7.39 – 7.30 (m, 5H), 6.92 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 7.8 Hz, 2H), 4.50 (dd, *J* = 11.6, 3.2 Hz, 1H), 3.68 (dd, *J* = 13.8, 3.2 Hz, 1H), 3.33 (dd, *J* = 13.7, 11.6 Hz, 1H), 2.18 (s, 3H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: -73.2. ¹³C NMR (100 MHz, Chloroform-*d*) δ: 142.7, 139.8, 137.1, 131.9, 130.7, 129.5, 129.1, 129.0, 128.0, 127.6, 127.4, 127.1, 120.1 (q, *J* = 330.4 Hz), 68.8, 33.9, 21.1. HRMS (EI⁺) calcd. for C₂₂H₁₉F₃O₂S [M]⁺: 404.1052, found: 404.1048.

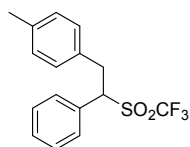
1-(*tert*-Butyl)-4-(2-(*p*-tolyl)-1-(((trifluoromethyl)sulfonyl)ethyl)benzene (1b)

Viscous oil, ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.25 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.85 (d, *J* = 7.8 Hz, 2H), 6.74 (d, *J* = 7.8 Hz, 2H), 4.44 (dd, *J* = 11.3, 3.2 Hz, 1H), 3.60 (dd, *J* = 13.8, 3.2 Hz, 1H), 3.27 (dd, *J* = 13.8, 11.4 Hz, 1H), 2.11 (s, 3H), 1.18 (s, 9H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: -73.3. ¹³C NMR (100 MHz, Chloroform-*d*) δ: 153.2, 136.9, 132.1, 129.9, 129.4, 129.0, 126.0, 125.3, 120.1 (q, *J* = 330.5 Hz), 68.8, 34.7, 33.8, 31.2, 21.0. HRMS (EI⁺) calcd. for C₂₀H₂₃F₃O₂S [M]⁺: 384.1365, found: 384.1362.

4,4'-(1-((Trifluoromethyl)sulfonyl)ethane-1,2-diyl)bis(methylbenzene) (1c)

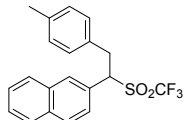
White solid, m.p. 60-62°C; ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.22 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 7.6 Hz, 2H), 6.84 (d, *J* = 7.6 Hz, 2H), 4.49 (dd, *J* = 11.6, 3.1 Hz, 1H), 3.70 (dd, *J* = 13.7, 3.1 Hz, 1H), 3.35 (t, *J* = 12.6 Hz, 1H), 2.33 (s, 3H), 2.24 (s, 3H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: -73.3. ¹³C NMR (100 MHz, Chloroform-*d*) δ: 140.0, 136.9, 132.0, 130.0, 129.8, 129.4, 129.0, 125.3, 120.0 (q, *J* = 330.3 Hz), 68.8, 33.8, 21.3, 21.0. HRMS (FI⁺) calcd. for C₁₇H₁₇F₃O₂S [M]⁺: 342.0896, found: 342.0902.

1-Methyl-4-(2-phenyl-2-((trifluoromethyl)sulfonyl)ethyl)benzene (1d)



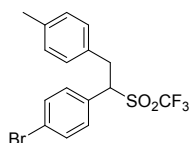
White solid, m.p. 61-63°C; ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.37 – 7.33 (m, 5H), 6.96 (d, *J* = 7.7 Hz, 2H), 6.83 (d, *J* = 7.7 Hz, 2H), 4.52 (dd, *J* = 11.6, 3.2 Hz, 1H), 3.73 (dd, *J* = 13.7, 3.2 Hz, 1H), 3.36 (dd, *J* = 13.6, 11.6 Hz, 1H), 2.23 (s, 3H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: -73.3. ¹³C NMR (100 MHz, Chloroform-*d*) δ: 137.0, 131.8, 130.2, 129.9, 129.4, 129.0, 129.0, 128.6, 120.0 (q, *J* = 330.2 Hz), 69.0, 33.8, 21.0. HRMS (EI⁺) calcd. for C₁₆H₁₅F₃O₂S [M]⁺: 328.0739, found: 328.0743.

2-(2-(*p*-Tolyl)-1-((trifluoromethyl)sulfonyl)ethyl)naphthalene (1e)

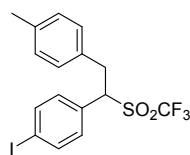


White solid, m.p. 98-100°C; ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.87 – 7.76 (m, 4H), 7.55 – 7.49 (m, 3H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.85 (d, *J* = 7.7 Hz, 2H), 4.70 (dd, *J* = 11.6, 3.1 Hz, 1H), 3.80 (dd, *J* = 13.8, 3.1 Hz, 1H), 3.50 (dd, *J* = 13.8, 11.6 Hz, 1H), 2.20 (s, 3H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: -73.2. ¹³C NMR (100 MHz, Chloroform-*d*) δ: 137.0, 133.7, 133.0, 131.8, 130.7, 129.4, 129.0, 128.9, 128.3, 127.8, 127.3, 126.7, 126.2, 125.9, 120.0 (q, *J* = 330.4 Hz), 69.2, 33.8, 21.0. HRMS (EI⁺) calcd. for C₂₀H₁₇F₃O₂S [M]⁺: 378.0896, found: 378.0903.

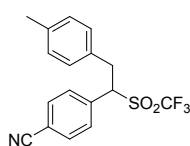
1-Bromo-4-(2-(*p*-tolyl)-1-((trifluoromethyl)sulfonyl)ethyl)benzene (1f)



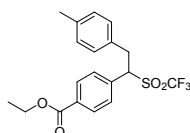
White solid, m.p. 57-59°C; ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.49 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.82 (d, *J* = 7.6 Hz, 2H), 4.49 (dd, *J* = 11.8, 3.2 Hz, 1H), 3.72 (dd, *J* = 13.8, 3.1 Hz, 1H), 3.29 (dd, *J* = 13.7, 11.7 Hz, 1H), 2.25 (s, 3H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: -73.8. ¹³C NMR (100 MHz, Chloroform-*d*) δ: 136.9, 133.8, 132.4, 131.7, 130.6, 129.3, 129.2, 128.7, 127.9, 127.2, 126.0, 125.2, 124.5, 121.5, 120.1 (q, *J* = 330.2 Hz), 62.1, 35.3, 20.9. HRMS (EI⁺) calcd. for C₁₆H₁₄F₃O₂SBr [M]⁺: 405.9844, found: 405.9848.

1-Iodo-4-(2-(*p*-tolyl)-1-((trifluoromethyl)sulfonyl)ethyl)benzene (1g)

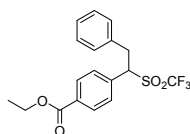
White solid, m.p. 65-67°C; ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.69 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.83 (d, *J* = 7.6 Hz, 2H), 4.46 (dd, *J* = 11.9, 3.2 Hz, 1H), 3.72 (dd, *J* = 13.9, 3.1 Hz, 1H), 3.29 (dd, *J* = 13.8, 11.6 Hz, 1H), 2.26 (s, 3H), 1.55 (s, 2H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: -73.2. ¹³C NMR (100 MHz, Chloroform-*d*) δ: 138.3, 137.2, 131.8, 131.4, 129.6, 128.9, 128.4, 119.9 (q, *J* = 330.1 Hz), 96.4, 68.4, 33.7, 21.1. HRMS (EI⁺) calcd. for C₁₆H₁₄F₃O₂SI [M]⁺: 453.9706, found: 453.9699.

4-(2-(*p*-Tolyl)-1-((trifluoromethyl)sulfonyl)ethyl)benzonitrile (1h)

White solid, m.p. 104-106°C; ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.65 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 7.7 Hz, 2H), 6.80 (d, *J* = 7.7 Hz, 2H), 4.57 (dd, *J* = 11.8, 3.3 Hz, 1H), 3.78 (dd, *J* = 13.8, 3.3 Hz, 1H), 3.31 (dd, *J* = 13.7, 11.8 Hz, 1H), 2.25 (s, 3H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: -73.3. ¹³C NMR (100 MHz, Chloroform-*d*) δ: 137.5, 134.1, 132.6, 130.8, 130.7, 129.6, 128.8, 119.8 (d, *J* = 330.1 Hz), 117.8, 114.0, 68.2, 33.8, 21.0. HRMS (EI⁺) calcd. for C₁₇H₁₄F₃NO₂S [M]⁺: 353.0692, found: 353.0693.

Ethyl 4-(2-(*p*-tolyl)-1-((trifluoromethyl)sulfonyl)ethyl)benzoate (1i)

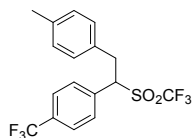
White solid, m.p. 97-99°C; ¹H NMR (400 MHz, Chloroform-*d*) δ: 8.02 (d, *J* = 7.9 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 7.7 Hz, 2H), 6.81 (d, *J* = 7.7 Hz, 2H), 4.57 (dd, *J* = 11.7, 3.2 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.76 (dd, *J* = 13.7, 3.2 Hz, 1H), 3.35 (dd, *J* = 13.7, 11.7 Hz, 1H), 2.24 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: -73.3. ¹³C NMR (100 MHz, Chloroform-*d*) δ: 165.8, 137.2, 133.5, 131.9, 131.2, 130.1, 130.1, 129.5, 128.9, 119.8 (q, *J* = 330.2 Hz), 68.5, 61.3, 33.8, 21.0, 14.3. HRMS (EI⁺) calcd. for C₁₉H₁₉F₃O₄S [M]⁺: 400.0951, found: 400.0945.

Ethyl 4-(2-phenyl-1-((trifluoromethyl)sulfonyl)ethyl)benzoate (1j)

White solid, m.p. 96-98°C; ¹H NMR (400 MHz, Chloroform-*d*) δ: 8.02 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.17-7.13 (m, 3H), 6.96-6.93 (m, 2H), 4.67 (dd, *J* = 11.8, 3.2 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.80 (dd, *J* = 13.7, 3.2 Hz, 1H), 3.40 (dd, *J* = 13.6, 11.7 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H). ¹⁹F

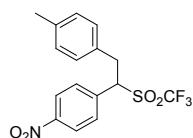
NMR (376 MHz, Chloroform-*d*) δ : -73.3. ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 165.7, 134.4, 133.4, 131.9, 130.2, 130.1, 129.1, 128.8, 127.5, 119.9 (q, $J = 330.1$ Hz), 68.4, 61.3, 34.1, 14.2. HRMS (EI⁺) calcd. for $\text{C}_{18}\text{H}_{17}\text{F}_3\text{O}_4\text{S}$ [M]⁺: 386.0794, found: 386.0796.

1-Methyl-4-(2-(4-(trifluoromethyl)phenyl)-2-((trifluoromethyl)sulfonyl)ethyl)benzene (1k)



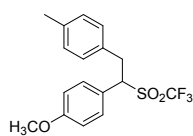
White solid, m.p. 42-44°C; ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.62 (d, $J = 8.1$ Hz, 2H), 7.47 (d, $J = 8.0$ Hz, 2H), 6.99 (d, $J = 7.7$ Hz, 2H), 6.82 (d, $J = 7.6$ Hz, 2H), 4.59 (dd, $J = 11.7, 3.2$ Hz, 1H), 3.77 (dd, $J = 13.8, 3.2$ Hz, 1H), 3.34 (dd, $J = 13.7, 11.7$ Hz, 1H), 2.25 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -63.0, -73.3. ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 137.3, 132.9, 132.0 (q, $J = 32.9$ Hz), 131.1, 130.5, 129.6, 128.8, 126.0 (q, $J = 3.8$ Hz), 123.6 (q, $J = 272.4$ Hz), 119.8 (q, $J = 330.0$ Hz), 68.3, 33.8, 21.0. HRMS (EI⁺) calcd. for $\text{C}_{17}\text{H}_{14}\text{F}_6\text{O}_2\text{S}$ [M]⁺: 396.0613, found: 396.0612.

1-Methyl-4-(2-(4-nitrophenyl)-2-((trifluoromethyl)sulfonyl)ethyl)benzene (1l)

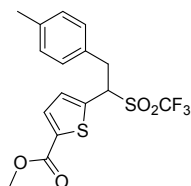


White solid, m.p. 100-102°C; ^1H NMR (400 MHz, Chloroform-*d*) δ : 8.22 – 8.19 (m, 2H), 7.55 – 7.52 (m, 2H), 6.98 (d, $J = 7.8$ Hz, 2H), 6.82 (d, $J = 7.8$ Hz, 2H), 4.67 (dd, $J = 11.8, 3.4$ Hz, 1H), 3.81 (dd, $J = 13.7, 3.4$ Hz, 1H), 3.35 (dd, $J = 13.8, 11.8$ Hz, 1H), 2.24 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -73.2. ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 148.7, 137.5, 136.0, 131.1, 130.6, 129.7, 128.8, 124.1, 119.8 (q, $J = 329.9$ Hz), 67.9, 33.8, 21.0. HRMS (EI⁺) calcd. for $\text{C}_{16}\text{H}_{14}\text{F}_3\text{NO}_4\text{S}$ [M]⁺: 373.0590, found: 373.0585.

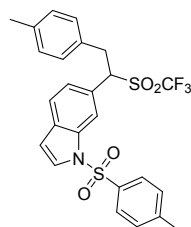
1-Methoxy-4-(2-(*p*-tolyl)-1-((trifluoromethyl)sulfonyl)ethyl)benzene (1m)



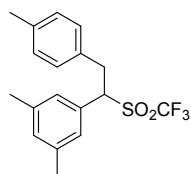
White solid, m.p. 75-77°C; ^1H NMR (600 MHz, Chloroform-*d*) δ : 7.25 (d, $J = 8.6$ Hz, 2H), 6.96 (d, $J = 7.8$ Hz, 2H), 6.85 – 6.83 (m, 4H), 4.51 (dd, $J = 11.7, 3.2$ Hz, 1H), 3.74 (s, 3H), 3.68 (dd, $J = 13.7, 3.2$ Hz, 1H), 3.32 (dd, $J = 13.7, 11.7$ Hz, 1H), 2.22 (s, 3H). ^{19}F NMR (564 MHz, Chloroform-*d*) δ : -73.2. ^{13}C NMR (150 MHz, Chloroform-*d*) δ : 160.8, 136.9, 132.0, 131.5, 129.4, 129.0, 120.1 (q, $J = 330.4$ Hz), 120.0, 114.5, 68.6, 55.2, 33.7, 21.0. HRMS (EI⁺) calcd. for $\text{C}_{17}\text{H}_{17}\text{F}_3\text{O}_3\text{S}$ [M]⁺: 358.0845, found: 358.0852.

Methyl 5-(2-(p-tolyl)-1-((trifluoromethyl)sulfonyl)ethyl)thiophene-2-carboxylate (1n)

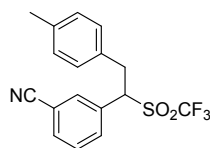
White solid, m.p. 83-85°C; ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.64 (d, J = 3.9 Hz, 1H), 7.09 (d, J = 3.9 Hz, 1H), 7.02 (d, J = 7.7 Hz, 2H), 6.92 (d, J = 7.7 Hz, 2H), 4.87 (dd, J = 11.8, 3.2 Hz, 1H), 3.89 – 3.75 (m, 4H), 3.28 (dd, J = 13.6, 11.7 Hz, 1H), 2.25 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -72.7. ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 161.8, 137.5, 136.8, 136.2, 133.2, 131.2, 130.8, 129.6, 128.9, 119.9 (q, J = 330.5 Hz), 64.7, 52.4, 34.9, 21.0. HRMS (EI $^+$) calcd. for $\text{C}_{16}\text{H}_{15}\text{F}_3\text{O}_4\text{S}_2$ [M] $^+$: 392.0358, found: 392.0365.

6-(2-(p-Tolyl)-1-((trifluoromethyl)sulfonyl)ethyl)-1-tosyl-1H-indole (1o)

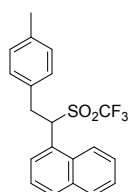
Off-white solid, m.p. 131-133°C; ^1H NMR (400 MHz, Chloroform-*d*) δ : ^1H NMR (400 MHz, Chloroform-*d*) δ : 8.15 (s, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 3.7 Hz, 1H), 7.45 (d, J = 8.2 Hz, 1H), 7.16 (d, J = 8.4 Hz, 3H), 6.93 (d, J = 7.8 Hz, 2H), 6.85 (d, J = 7.9 Hz, 2H), 6.59 (d, J = 3.6 Hz, 1H), 4.73 (dd, J = 11.7, 3.3 Hz, 1H), 3.79 (dd, J = 13.8, 3.2 Hz, 1H), 3.48 (dd, J = 13.8, 11.7 Hz, 1H), 2.29 (s, 3H), 2.21 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -73.2. ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 145.3, 136.9, 134.9, 134.7, 132.2, 131.7, 129.9, 129.4, 129.0, 128.1, 126.9, 125.4, 124.4, 121.9, 120.0 (q, J = 330.5 Hz), 115.7, 109.1, 69.4, 33.9, 21.5, 21.0. HRMS (ESI $^+$) calcd. for $\text{C}_{25}\text{H}_{26}\text{F}_3\text{N}_2\text{O}_4\text{S}_2$ [$\text{M}+\text{NH}_4$] $^+$: 539.1281, found: 539.1285.

1,3-Dimethyl-5-(2-(p-tolyl)-1-((trifluoromethyl)sulfonyl)ethyl)benzene (1p)

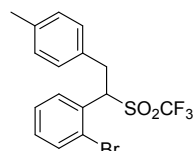
White solid, m.p. 102-104°C; ^1H NMR (400 MHz, Chloroform-*d*) δ : 6.99 (d, J = 7.5 Hz, 3H), 6.94 (brs, 2H), 6.85 (d, J = 7.7 Hz, 2H), 4.44 (dd, J = 11.3, 3.2 Hz, 1H), 3.67 (dd, J = 13.8, 3.1 Hz, 1H), 3.36 (dd, J = 13.8, 11.3 Hz, 1H), 2.29 (s, 6H), 2.25 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -73.3. ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 138.6, 136.9, 132.1, 131.7, 129.3, 128.9, 128.2, 127.9, 120.0 (d, J = 330.3 Hz), 69.0, 33.9, 21.3, 21.0. HRMS (EI $^+$) calcd. for $\text{C}_{18}\text{H}_{19}\text{F}_3\text{O}_2\text{S}$ [M] $^+$: 356.1052, found: 356.1049.

3-(2-(*p*-Tolyl)-1-((trifluoromethyl)sulfonyl)ethyl)benzonitrile (1q)

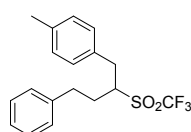
White solid, m.p. 111-113°C; ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.67 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.62 – 7.59 (m, 2H), 7.50 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.81 (d, *J* = 7.6 Hz, 2H), 4.56 (dd, *J* = 11.8, 3.3 Hz, 1H), 3.78 (dd, *J* = 13.9, 3.3 Hz, 1H), 3.30 (dd, *J* = 13.8, 11.7 Hz, 1H), 2.25 (s, 3H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: -73.2. ¹³C NMR (100 MHz, Chloroform-*d*) δ: 137.5, 134.3, 133.5, 133.5, 130.7, 130.7, 130.0, 129.7, 128.9, 119.8 (q, *J* = 330.1 Hz), 117.8, 113.4, 67.8, 33.7, 21.0. HRMS (FI⁺) calcd. for C₁₇H₁₄NF₃O₂S [M]⁺: 353.0692, found: 353.0699.

1-(2-(*p*-Tolyl)-1-((trifluoromethyl)sulfonyl)ethyl)naphthalene (1r)

White solid, m.p. 82-84°C; ¹H NMR (400 MHz, Chloroform-*d*) δ: 8.01 (d, *J* = 7.3 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.84 – 7.82 (m, 1H), 7.71 – 7.68 (m, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.47 – 7.44 (m, 2H), 6.86 (brs, 4H), 5.63 (dd, *J* = 11.2, 3.4 Hz, 1H), 3.89 (dd, *J* = 13.9, 3.4 Hz, 1H), 3.56 (dd, *J* = 13.8, 11.1 Hz, 1H), 2.14 (s, 3H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: -73.8. ¹³C NMR (100 MHz, Chloroform-*d*) δ: 136.9, 133.8, 132.4, 131.7, 130.6, 129.3, 129.2, 128.7, 127.9, 127.2, 126.0, 125.2, 124.5, 121.5, 120.1 (q, *J* = 330.2 Hz), 62.1, 35.3, 20.9. HRMS (EI⁺) calcd. for C₂₀H₁₇F₃O₂S [M]⁺: 378.0896, found: 378.0900.

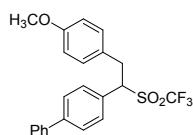
1-Bromo-2-(2-(*p*-tolyl)-1-((trifluoromethyl)sulfonyl)ethyl)benzene (1s)

Colorless oil, ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.77 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.44 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.37 (td, *J* = 7.7, 1.3 Hz, 1H), 7.15 (td, *J* = 7.8, 1.6 Hz, 1H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.86 (d, *J* = 8.1 Hz, 2H), 5.52 (dd, *J* = 11.5, 3.7 Hz, 1H), 3.76 (dd, *J* = 13.8, 3.7 Hz, 1H), 3.30 (dd, *J* = 13.8, 11.5 Hz, 1H), 2.21 (s, 3H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: -74.5. ¹³C NMR (100 MHz, Chloroform-*d*) δ: 137.1, 133.4, 131.1, 130.8, 130.3, 129.4, 129.1, 128.8, 128.1, 127.0, 119.9 (q, *J* = 329.7 Hz), 65.8, 34.8, 21.1. HRMS (EI⁺) calcd. for C₁₆H₁₄F₃BrO₂S [M]⁺: 405.9844, found: 405.9846.

1-Methyl-4-(4-phenyl-2-((trifluoromethyl)sulfonyl)butyl)benzene (1t)

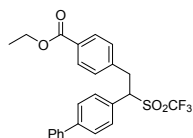
Colorless oil, ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.24 – 7.16 (m, 3H), 7.14 (d, J = 7.8 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 6.97 – 6.95 (m, 2H), 3.52–3.45 (m, 1H), 3.41 (dd, J = 14.0, 3.8 Hz, 1H), 2.91 (dd, J = 14.1, 10.5 Hz, 1H), 2.70–2.65 (m, 2H), 2.35 (s, 3H), 2.31 – 2.20 (m, 1H), 2.12 – 2.02 (m, 1H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -74.4. ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 139.6, 137.4, 132.2, 129.8, 129.1, 128.7, 128.5, 126.6, 120.2 (q, J = 329.7 Hz), 61.8, 33.4, 32.5, 28.2, 21.1. HRMS (EI^+) calcd. for $\text{C}_{18}\text{H}_{19}\text{F}_3\text{O}_2\text{S}$ [M] $^+$: 356.1052, found: 356.1057.

4-(2-(4-Methoxyphenyl)-1-((trifluoromethyl)sulfonyl)ethyl)-1,1'-biphenyl (1aa)



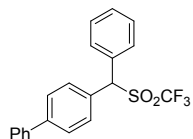
White solid, m.p. 117–119°C; ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.60 – 7.57 (m, 4H), 7.46 – 7.35 (m, 5H), 6.91 – 6.88 (m, 2H), 6.72 – 6.70 (m, 2H), 4.56 – 4.52 (m, 1H), 3.76–3.71 (m, 4H), 3.38 (dd, J = 13.8, 11.5 Hz, 1H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -73.2. ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 158.8, 142.6, 139.8, 130.6, 130.2, 128.9, 127.9, 127.6, 127.4, 127.1, 126.8, 120.0 (q, J = 330.4 Hz), 114.1, 68.8, 55.2, 33.5. HRMS (EI^+) calcd. for $\text{C}_{22}\text{H}_{19}\text{F}_3\text{O}_3\text{S}$ [M] $^+$: 420.1002, found: 420.1005.

Ethyl 4-(2-([1,1'-biphenyl]-4-yl)-2-((trifluoromethyl)sulfonyl)ethyl)benzoate (1ab)



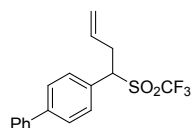
White solid, m.p. 95–97°C; ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.88 – 7.85 (m, 2H), 7.59 – 7.55 (m, 4H), 7.45 – 7.34 (m, 5H), 7.09 – 7.07 (m, 2H), 4.62 (dd, J = 11.7, 3.3 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 3.83 (dd, J = 13.7, 3.3 Hz, 1H), 3.50 (dd, J = 13.7, 11.7 Hz, 1H), 1.34 (t, J = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -73.1. ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 166.1, 142.9, 140.0, 139.6, 130.4, 130.0, 129.7, 129.2, 128.9, 128.0, 127.7, 127.1, 126.8, 120.0 (q, J = 330.2 Hz), 68.2, 61.1, 34.2, 14.3. HRMS (ESI^+) calcd. for $\text{C}_{24}\text{H}_{22}\text{F}_3\text{O}_2\text{S}$ [$\text{M}+\text{H}$] $^+$: 463.1185, found: 463.1184.

4-(Phenyl((trifluoromethyl)sulfonyl)methyl)-1,1'-biphenyl (1ac)²



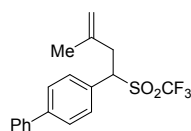
White solid, m.p. 121–123°C; ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.72 – 7.62 (m, 6H), 7.56 – 7.55 (m, 2H), 7.46 – 7.33 (m, 6H), 5.68 (d, J = 2.2 Hz, 1H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -72.8. ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 142.7, 139.9, 130.5, 130.0, 129.9, 129.6, 129.3, 129.0, 128.3, 128.0, 127.9, 127.2, 120.2 (q, J = 330.7 Hz), 71.8.

4-(1-((Trifluoromethyl)sulfonyl)but-3-en-1-yl)-1,1'-biphenyl (1ad)



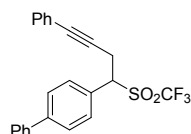
White solid, m.p. 136-138°C; ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.61 (dd, J = 19.5, 7.7 Hz, 4H), 7.45 (dd, J = 13.8, 7.5 Hz, 4H), 7.36 (t, J = 7.3 Hz, 1H), 5.54 (dq, J = 16.7, 7.4 Hz, 1H), 5.11 (dd, J = 29.6, 13.6 Hz, 2H), 4.47 (dd, J = 11.4, 4.0 Hz, 1H), 3.17 (dt, J = 11.7, 4.9 Hz, 1H), 3.00 (td, J = 13.5, 12.8, 6.7 Hz, 1H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -73.3. ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 142.9, 139.9, 131.1, 130.5, 129.0, 128.0, 127.8, 127.2, 120.1, 120.0 (q, J = 330.2 Hz), 66.8, 32.1. HRMS (EI $^+$) calcd. for $\text{C}_{17}\text{H}_{15}\text{F}_3\text{O}_2\text{S}$ [M] $^+$: 340.0739, found: 340.0745.

4-(3-Methyl-1-((trifluoromethyl)sulfonyl)but-3-en-1-yl)-1,1'-biphenyl (1ae)



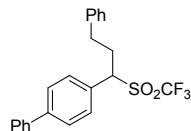
White solid, m.p. 117-119°C; ^1H NMR (600 MHz, Chloroform-*d*) δ : 7.63 (d, J = 7.9 Hz, 1H), 7.59 (d, J = 7.4 Hz, 1H), 7.49 – 7.43 (m, 4H), 7.36 (t, J = 7.4 Hz, 1H), 4.84 – 4.68 (m, 2H), 4.60 (dt, J = 11.9, 3.0 Hz, 1H), 3.14 – 3.11 (m, 1H), 2.99- 2.94 (m, 1H), 1.65 (s, 3H). ^{19}F NMR (564 MHz, Chloroform-*d*) δ : -73.1. ^{13}C NMR (150 MHz, Chloroform-*d*) δ : 142.8, 139.8, 138.2, 130.5, 128.9, 127.9, 127.6, 127.3, 127.1, 120.0 (q, J = 330.0 Hz), 115.9, 65.9, 35.5, 22.1. HRMS (EI $^+$) calcd. for $\text{C}_{18}\text{H}_{17}\text{F}_3\text{O}_2\text{S}$ [M] $^+$: 354.0896, found: 354.0901.

4-(4-Phenyl-1-((trifluoromethyl)sulfonyl)but-3-yn-1-yl)-1,1'-biphenyl (1af)



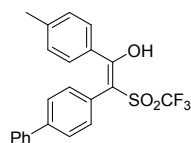
White solid, m.p. 120-122°C; ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.68 (d, J = 8.0 Hz, 2H), 7.64 – 7.55 (m, 4H), 7.47-7.44 (m, 2H), 7.38 (t, J = 7.2 Hz, 1H), 7.27 – 7.19 (m, 5H), 4.71 (dd, J = 10.4, 4.6 Hz, 1H), 3.53 (dd, J = 17.0, 4.6 Hz, 1H), 3.40 (dd, J = 16.9, 10.4 Hz, 1H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -73.5. ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 143.1, 139.9, 131.6, 130.4, 129.0, 128.5, 128.3, 128.0, 127.8, 127.2, 127.1, 122.4, 119.9 (d, J = 329.7 Hz), 84.6, 82.5, 65.6, 20.6. HRMS (EI $^+$) calcd. for $\text{C}_{23}\text{H}_{17}\text{F}_3\text{O}_2\text{S}$ [M] $^+$: 414.0896, found: 414.0893.

4-(3-Phenyl-1-((trifluoromethyl)sulfonyl)propyl)-1,1'-biphenyl (1ag)



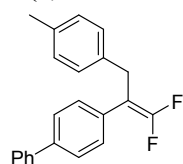
White solid, m.p. 81-83°C; ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.67 – 7.65 (m, 2H), 7.62 – 7.59 (m, 2H), 7.46-7.42 (m, 4H), 7.39 – 7.34 (m, 1H), 7.31-7.27 (m, 2H), 7.24 – 7.19 (m, 1H), 7.08-7.06 (m, 2H), 4.35 (dd, J = 11.6, 3.0 Hz, 1H), 2.76 – 2.69 (m, 2H), 2.62 – 2.53 (m, 1H), 2.50 – 2.42 (m, 1H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -73.2. ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 143.0, 139.9, 139.0, 130.6, 129.0, 128.9, 128.5, 128.04, 127.96, 127.3, 127.2, 126.9, 120.0 (d, J = 330.2 Hz), 66.2, 31.9, 29.0. HRMS (EI $^+$) calcd. for $\text{C}_{22}\text{H}_{19}\text{F}_3\text{O}_2\text{S}$ [M] $^+$: 404.1052, found: 404.1055.

2-([1,1'-Biphenyl]-4-yl)-1-(*p*-tolyl)-2-((trifluoromethyl)sulfonyl)ethen-1-ol (4a)



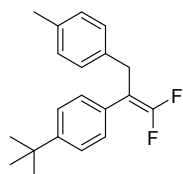
White solid, m.p. 114-116°C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.82 (m, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.56 – 7.53 (m, 2H), 7.45 – 7.41 (m, 2H), 7.38 – 7.34 (m, 1H), 7.26 – 7.24 (m, 2H), 6.40 (s, 1H), 2.38 (s, 3H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: -73.1. ¹³C NMR (100 MHz, Chloroform-*d*) δ: 187.0, 146.2, 143.6, 139.6, 132.0, 131.1, 129.9, 129.2, 128.9, 128.3, 128.1, 127.2, 123.8, 119.9 (q, *J* = 330.5 Hz), 72.1, 21.8. HRMS (EI⁺) calcd. for C₂₂H₁₇F₃O₃S [M]⁺: 418.0845, found: 418.0843.

4-(1,1-Difluoro-3-(*p*-tolyl)prop-1-en-2-yl)-1,1'-biphenyl (2a)



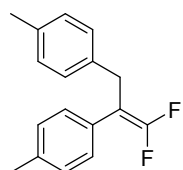
White solid, 25.9 mg, 81%, m.p. 68-70°C; ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.49 – 7.42 (m, 4H), 7.36-7.32 (m, 2H), 7.29 – 7.23 (m, 3H), 7.02 – 6.98 (m, 4H), 3.65 (t, *J* = 2.2 Hz, 2H), 2.22 (s, 3H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: -89.9 (dt, *J* = 39.9, 2.7 Hz), -90.4 (d, *J* = 39.6 Hz). ¹³C NMR (100 MHz, Chloroform-*d*) δ: 154.5 (dd, *J* = 292.4, 287.8 Hz), 140.5, 140.0, 136.0, 135.4 (t, *J* = 2.6 Hz), 132.6 (t, *J* = 4.0 Hz), 129.2, 128.8, 128.6 (t, *J* = 3.6 Hz), 128.1, 127.4, 127.03, 126.97, 91.5 (dd, *J* = 21.5, 13.0 Hz), 33.3, 21.0. HRMS (EI⁺) calcd. for C₂₂H₁₈F₂ [M]⁺: 320.1372, found: 320.1373.

1-(*tert*-Butyl)-4-(1,1-difluoro-3-(*p*-tolyl)prop-1-en-2-yl)benzene (2b)



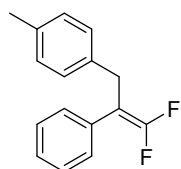
Colorless oil, 24.8 mg, 83%, ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.31 – 7.28 (m, 2H), 7.24 – 7.21 (m, 2H), 7.09 – 7.04 (m, 4H), 3.68 (t, *J* = 2.3 Hz, 2H), 2.29 (s, 3H), 1.28 (s, 9H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: -90.3 (dt, *J* = 41.0, 3.0 Hz), -90.9 (d, *J* = 39.6 Hz). ¹³C NMR (100 MHz, Chloroform-*d*) δ: 154.5 (dd, *J* = 292.1, 287.0 Hz), 150.1, 135.8, 135.6 (t, *J* = 2.6 Hz), 130.7 (t, *J* = 3.8 Hz), 129.2, 128.1, 127.7 (t, *J* = 3.6 Hz), 125.3, 91.3 (dd, *J* = 21.1, 13.0 Hz), 34.5, 33.3, 31.3, 21.0. HRMS (EI⁺) calcd. for C₂₀H₂₂F₂ [M]⁺: 300.1684, found: 300.1682.

4,4'-(3,3-Difluoroprop-2-ene-1,2-diyl)bis(methylbenzene) (2c)



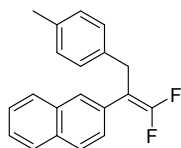
Colorless oil, 20.6 mg, 80%, ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.17 – 7.14 (m, 2H), 7.08 (d, J = 8.0 Hz, 2H), 7.04 (brs, 4H), 3.67 (t, J = 2.3 Hz, 2H), 2.29 (s, 3H), 2.27 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -91.0 (dt, J = 41.6, 3.0 Hz), -91.4 (d, J = 41.6 Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 154.3 (dd, J = 290.0, 285.0 Hz), 137.0, 135.8, 135.5 (t, J = 2.7 Hz), 130.6 (t, J = 3.8 Hz), 129.2, 129.1, 128.2, 128.1 (t, J = 3.0 Hz), 91.6 (dd, J = 21.2, 13.5 Hz), 33.5, 21.1, 21.0. HRMS (EI^+) calcd. for $\text{C}_{17}\text{H}_{16}\text{F}_2$ $[\text{M}]^+$: 258.1215, found: 258.12171.

1-(3,3-Difluoro-2-phenylallyl)-4-methylbenzene (2d)



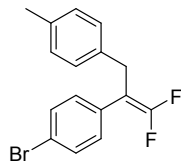
Colorless oil, 16.8 mg, 69%, ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.30 – 7.19 (m, 5H), 7.04 (brs, 4H), 3.69 (t, J = 2.2 Hz, 2H), 2.28 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -90.5 (dt, J = 40.5, 2.4 Hz), -91.1 (d, J = 40.5 Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 154.4 (dd, J = 290.0, 285.5 Hz), 135.9, 135.4 (t, J = 2.5 Hz), 133.7 (t, J = 3.8 Hz), 129.2, 128.4, 128.3 (t, J = 3.5 Hz), 128.2, 127.3, 91.8 (dd, J = 21.4, 13.2 Hz), 33.5, 21.0. (known)

2-(1,1-Difluoro-3-(*p*-tolyl)prop-1-en-2-yl)naphthalene (2e)

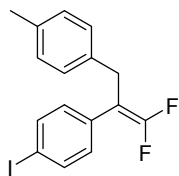


Colorless oil, 23.2 mg, 79%, ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.78 – 7.72 (m, 4H), 7.45 – 7.38 (m, 3H), 7.08 – 7.01 (m, 4H), 3.79 (t, J = 2.2 Hz, 2H), 2.26 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -90.0 (dt, J = 39.5, 3.0 Hz), -90.8 (d, J = 39.6 Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 154.6 (dd, J = 292.2, 287.8 Hz), 136.0, 135.4 (t, J = 2.5 Hz), 133.2, 132.4, 131.1 (t, J = 4.0 Hz), 129.2, 128.2, 128.0, 128.0, 127.6, 127.5 (t, J = 3.6 Hz), 126.2, 126.16 – 126.07 (m, 2C), 92.1 (dd, J = 21.5, 13.1 Hz), 33.6, 21.0. HRMS (EI^+) calcd. for $\text{C}_{20}\text{H}_{16}\text{F}_2$ $[\text{M}]^+$: 294.1221, found: 294.1215.

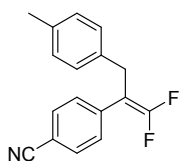
1-Bromo-4-(1,1-difluoro-3-(*p*-tolyl)prop-1-en-2-yl)benzene (2f)



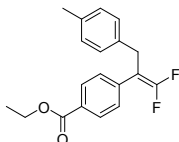
Colorless oil, 24.6 mg, 76%, ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.41 – 7.37 (m, 2H), 7.14 – 7.10 (m, 2H), 7.06-7.00 (m, 4H), 3.66 (t, J = 2.2 Hz, 2H), 2.28 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -89.7 (dt, J = 38.8, 2.7 Hz), -90.1 (d, J = 38.7 Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 154.3 (dd, J = 292.2, 288.2 Hz), 136.1, 134.9 (t, J = 2.6 Hz), 132.5 (t, J = 3.9 Hz), 131.5, 129.9 (t, J = 3.6 Hz), 129.3, 128.1, 121.3, 91.2 (dd, J = 22.0, 13.3 Hz), 33.3, 21.0. HRMS (EI^+) calcd. for $\text{C}_{16}\text{H}_{13}\text{F}_2\text{Br}$ $[\text{M}]^+$: 322.0163, found: 322.0160.

1-(3,3-Difluoro-2-(4-iodophenyl)allyl)-4-methylbenzene (2g)

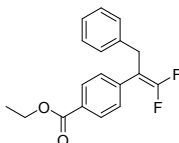
Colorless oil, 30.1 mg, 81%, ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.61 – 7.57 (m, 2H), 7.06 – 6.98 (m, 6H), 3.65 (t, J = 2.2 Hz, 2H), 2.28 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -89.5 (dt, J = 38.3, 2.8 Hz), -89.9 (d, J = 38.3 Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 154.3 (dd, J = 292.5, 288.3 Hz), 137.5, 136.1, 134.9 (t, J = 2.6 Hz), 133.2 (t, J = 3.9 Hz), 130.1 (t, J = 3.6 Hz), 129.3, 128.1, 92.8, 91.3 (dd, J = 22.0, 13.0 Hz), 33.2, 21.0. HRMS (EI $^+$) calcd. for $\text{C}_{16}\text{H}_{13}\text{F}_2\text{I}$ [M] $^+$: 370.0025, found: 370.0022.

4-(1,1-Difluoro-3-(*p*-tolyl)prop-1-en-2-yl)benzonitrile (2h)

Colorless oil, 23.0 mg, 86%, ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.57 – 7.54 (m, 2H), 7.39 – 7.36 (m, 2H), 7.06 (d, J = 7.9 Hz, 2H), 7.01 (d, J = 8.1 Hz, 2H), 3.71 (t, J = 2.1 Hz, 2H), 2.29 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -87.1 (dt, J = 33.1, 2.7 Hz), -87.7 (d, J = 33.2 Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 154.8 (dd, J = 294.9, 290.0 Hz), 138.6 (t, J = 4.3 Hz), 136.4, 134.4 (t, J = 2.7 Hz), 132.1, 129.4, 128.9 (dd, J = 4.3, 3.4 Hz), 128.0, 118.6, 110.9, 91.3 (dd, J = 22.8, 12.2 Hz), 32.9, 21.0. HRMS (EI $^+$) calcd. for $\text{C}_{17}\text{H}_{13}\text{F}_2\text{N}$ [M] $^+$: 269.1011, found: 269.1015.

Ethyl 4-(1,1-difluoro-3-(*p*-tolyl)prop-1-en-2-yl)benzoate (2i)

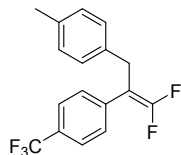
Colorless oil, 27.5 mg, 87%, ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.95 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.03 (d, J = 1.9 Hz, 4H), 4.34 (q, J = 7.1 Hz, 2H), 3.71 (d, J = 2.5 Hz, 2H), 2.28 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -88.5 (d, J = 35.8 Hz), -88.9 (d, J = 35.6 Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 166.2, 154.6 (dd, J = 292.0, 287.0 Hz), 138.3 (t, J = 4.1 Hz), 136.1, 134.9 (t, J = 2.6 Hz), 129.6, 129.3, 129.2, 128.2 (t, J = 3.7 Hz), 128.1, 91.7 (dd, J = 22.0, 12.6 Hz), 61.0, 33.2, 21.0, 14.3. HRMS (EI $^+$) calcd. for $\text{C}_{19}\text{H}_{18}\text{F}_2\text{O}_2$ [M] $^+$: 316.1269, found: 316.1267.

Ethyl 4-(1,1-difluoro-3-phenylprop-1-en-2-yl)benzoate (2j)

Colorless oil, 26.5 mg, 88%, ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.97 – 7.94 (m, 2H), 7.36 – 7.32 (m, 2H), 7.26 – 7.21 (m, 2H), 7.19 – 7.13 (m, 3H), 4.35 (q, J = 7.1 Hz, 2H), 3.76 (t, J = 2.3 Hz, 2H),

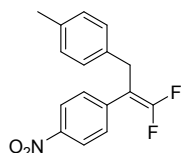
1.36 (t, $J = 7.1$ Hz, 3H). ^{19}F NMR (376 MHz, Chloroform- d) δ : -88.3 (dt, $J = 35.5, 3.0$ Hz), -88.8 (d, $J = 35.4$ Hz). ^{13}C NMR (100 MHz, Chloroform- d) δ : 166.2, 154.6 (dd, $J = 293.9, 288.9$ Hz), 138.2 (t, $J = 4.1$ Hz), 138.0 (t, $J = 2.6$ Hz), 129.6, 129.3, 128.6, 128.2, 128.2 (t, $J = 3.5$ Hz), 126.6, 91.5 (dd, $J = 22.0, 12.9$ Hz), 61.0, 33.6, 14.3. HRMS (EI $^{+}$) calcd. for $\text{C}_{18}\text{H}_{16}\text{F}_2\text{O}_2$ $[\text{M}]^{+}$: 302.1113, found: 302.1108.

1-(3,3-Difluoro-2-(4-(trifluoromethyl)phenyl)allyl)-4-methylbenzene (2k)



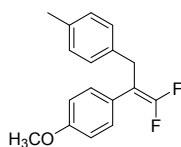
Colorless oil, 26.3 mg, 84%, ^1H NMR (400 MHz, Chloroform- d) δ : 7.53 (d, $J = 8.2$ Hz, 2H), 7.37 (d, $J = 8.2$ Hz, 2H), 7.07 – 7.02 (m, 4H), 3.71 (t, $J = 2.2$ Hz, 2H), 2.29 (s, 3H). ^{19}F NMR (376 MHz, Chloroform- d) δ : -62.7 (s, 3F), -88.5 (dt, $J = 35.8, 2.8$ Hz), -89.2 (d, $J = 36.2$ Hz). ^{13}C NMR (150 MHz, Chloroform- d) δ : 154.7 (dd, $J = 293.5, 288.9$ Hz), 137.4, 136.3, 134.7 (t, $J = 2.7$ Hz), 129.4, 129.2, 128.6 (t, $J = 3.6$ Hz), 128.1, 125.3 (q, $J = 3.8$ Hz), 124.0 (q, $J = 272.0$ Hz), 91.3 (dd, $J = 22.4, 12.5$ Hz), 33.2, 21.0. HRMS (EI $^{+}$) calcd. for $\text{C}_{17}\text{H}_{13}\text{F}_5$ $[\text{M}]^{+}$: 312.0932, found: 312.0933.

1-(3,3-Difluoro-2-(4-nitrophenyl)allyl)-4-methylbenzene (2l)



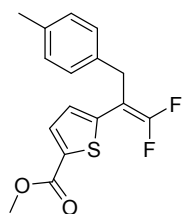
Pale yellow oil, 22.0 mg, 76%, m.p. 120-122°C; ^1H NMR (400 MHz, Chloroform- d) δ : 8.15 – 8.11 (m, 2H), 7.45 – 7.43 (m, 2H), 7.07-7.01 (m, 4H), 3.74 (t, $J = 2.2$ Hz, 2H), 2.29 (s, 3H). ^{19}F NMR (376 MHz, Chloroform- d) δ : -86.6 (dt, $J = 31.8, 2.8$ Hz), -87.2 (d, $J = 31.5$ Hz). ^{13}C NMR (100 MHz, Chloroform- d) δ : 154.8 (dd, $J = 293.0, 288.0$ Hz), 146.7, 140.6 (t, $J = 4.5$ Hz), 136.5, 134.5 (t, $J = 2.6$ Hz), 129.5, 129.0 (dd, $J = 5.0, 4.0$ Hz), 128.0, 123.6, 91.2 (dd, $J = 23.0, 12.0$ Hz), 33.0, 21.0. HRMS (EI $^{+}$) calcd. for $\text{C}_{16}\text{H}_{13}\text{ONF}_2$ $[\text{M}]^{+}$: 289.0909, found: 289.0905.

1-(3,3-Difluoro-2-(4-methoxyphenyl)allyl)-4-methylbenzene (2m)



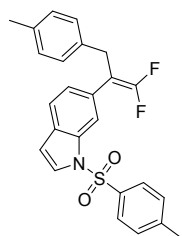
Colorless oil, 26.0 mg, 95%, ^1H NMR (400 MHz, Chloroform- d) δ : 7.19 – 7.17 (m, 2H), 7.04 (brs, 4H), 6.82-6.80 (m, 2H), 3.76 (s, 3H), 3.65 (t, $J = 2.3$ Hz, 2H), 2.28 (s, 3H). ^{19}F NMR (376 MHz, Chloroform- d) δ : -91.7 (dt, $J = 43.1, 2.9$ Hz), -92.1 (d, $J = 43.3$ Hz). ^{13}C NMR (100 MHz, Chloroform- d) δ : 158.6, 154.2 (dd, $J = 290.5, 286.7$ Hz), 135.9, 135.5 (t, $J = 2.6$ Hz), 129.41 (t, $J = 3.6$ Hz), 129.2, 128.2, 125.8 (t, $J = 3.6$ Hz), 113.8, 91.3 (dd, $J = 21.3, 13.6$ Hz), 55.2, 33.6, 21.0. HRMS (EI $^{+}$) calcd. for $\text{C}_{17}\text{H}_{16}\text{F}_2\text{O}$ $[\text{M}]^{+}$: 374.1164, found: 374.1171.

Methyl 5-(1,1-difluoro-3-(*p*-tolyl)prop-1-en-2-yl)thiophene-2-carboxylate (2n)



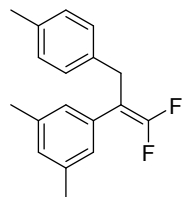
White solid, 22.3 mg, 72%, m.p. 29-31°C; ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.61 (dd, *J* = 4.0, 1.1 Hz, 1H), 7.13 – 7.08 (m, 4H), 6.97 (d, *J* = 4.0 Hz, 1H), 3.85 (s, 3H), 3.73 (t, *J* = 2.2 Hz, 2H), 2.30 (s, 3H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: -81.0 (d, *J* = 24.0 Hz), -87.4 (dt, *J* = 23.9, 2.5 Hz). ¹³C NMR (100 MHz, Chloroform-*d*) δ: 162.5, 155.0 (dd, *J* = 297.0, 289.4 Hz), 142.8 (dd, *J* = 7.7, 3.8 Hz), 136.5, 134.2 (t, *J* = 2.6 Hz), 133.5, 132.1 – 131.9 (m), 129.4, 128.0, 126.3 (t, *J* = 5.5 Hz), 88.3 (dd, *J* = 26.2, 12.4 Hz), 52.2 32.9, 21.0. HRMS (EI⁺) calcd. for C₁₆H₁₄F₂O₂S [M]⁺: 308.0677, found: 308.0684.

6-(1,1-Difluoro-3-(*p*-tolyl)prop-1-en-2-yl)-1-tosyl-1*H*-indole (2o)

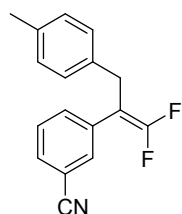


White solid, 39.8 mg, 91%, m.p. 109-111°C; ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.93 (dd, *J* = 1.6, 0.9 Hz, 1H), 7.59 – 7.56 (m, 2H), 7.51 (d, *J* = 3.6 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.17 (dt, *J* = 8.3, 1.6 Hz, 1H), 7.13 – 7.05 (m, 6H), 6.56 (dd, *J* = 3.7, 0.8 Hz, 1H), 3.77 (t, *J* = 2.2 Hz, 2H), 2.31 (d, *J* = 4.7 Hz, 6H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: -90.2 (dt, *J* = 40.5, 2.7 Hz), -90.8 (d, *J* = 40.2 Hz). ¹³C NMR (100 MHz, Chloroform-*d*) δ: 154.5 (dd, *J* = 290.0, 285.5 Hz), 144.9, 135.9, 135.4 (t, *J* = 2.6 Hz), 135.0, 134.8, 130.0 (t, *J* = 4.0 Hz), 129.8, 129.3, 128.2, 126.9, 126.8, 123.6 (dd, *J* = 4.7, 2.8 Hz), 121.1, 113.4 (t, *J* = 3.7 Hz), 108.8, 92.1 (dd, *J* = 21.7, 12.8 Hz), 33.8, 21.6, 21.1. HRMS (EI⁺) calcd. for C₂₅H₂₁O₂NF₂S [M]⁺: 437.1256, found: 437.1263.

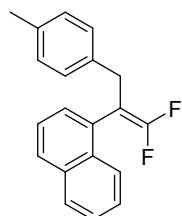
1-(1,1-Difluoro-3-(*p*-tolyl)prop-1-en-2-yl)-3,5-dimethylbenzene (2p)



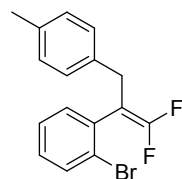
Colorless oil, 21.2 mg, 78%, ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.04 (brs, 4H), 6.88 – 6.85 (m, 3H), 3.66 (t, *J* = 2.3 Hz, 2H), 2.28 (s, 3H), 2.25 (s, 6H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: -90.8 (dt, *J* = 41.0, 2.7 Hz), -91.2 (d, *J* = 41.1 Hz). ¹³C NMR (100 MHz, Chloroform-*d*) δ: 154.3 (dd, *J* = 289.4, 285.2 Hz), 137.8, 135.8, 135.6 (t, *J* = 2.8 Hz), 133.5 (t, *J* = 3.5 Hz), 129.1, 129.0, 128.2, 126.1 (t, *J* = 3.3 Hz), 91.9 (dd, *J* = 20.8, 13.4 Hz), 33.5, 21.4, 21.0. HRMS (EI⁺) calcd. for C₁₈H₁₈F₂ [M]⁺: 272.1371, found: 272.1378.

3-(1,1-Difluoro-3-(*p*-tolyl)prop-1-en-2-yl)benzonitrile (2q)

Colorless oil, 25.6 mg, 95%, ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.54 (q, J = 1.4 Hz, 1H), 7.49 (tt, J = 7.0, 1.5 Hz, 2H), 7.38 (t, J = 7.8 Hz, 1H), 7.06 (d, J = 7.9 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 3.69 (t, J = 2.2 Hz, 2H), 2.29 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -88.4 (dt, J = 35.8, 2.7 Hz), -89.1 (d, J = 35.9 Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 154.7 (dd, J = 293.4, 289.3 Hz), 136.4, 135.0 (t, J = 4.1 Hz), 134.3 (t, J = 2.7 Hz), 132.7 (t, J = 3.5 Hz), 131.8 (t, J = 3.7 Hz), 130.8, 129.4, 129.3, 128.1, 118.6, 112.7, 90.8 (dd, J = 22.9, 12.7 Hz), 33.1, 21.0. HRMS (EI^+) calcd. for $\text{C}_{17}\text{H}_{13}\text{F}_2\text{N}$ [M] $^+$: 269.1011, found: 269.1017.

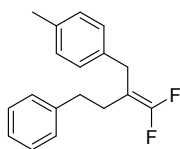
1-(1,1-Difluoro-3-(*p*-tolyl)prop-1-en-2-yl)naphthalene (2r)

Colorless oil, 6.5 mg, 22%, ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.86 – 7.81 (m, 2H), 7.78 (dt, J = 8.3, 1.0 Hz, 1H), 7.50-7.46 (m, 2H), 7.34 (dd, J = 8.3, 7.1 Hz, 1H), 7.04 (dd, J = 7.1, 1.2 Hz, 1H), 6.99 (d, J = 7.8 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 3.67 (brs, 2H), 2.27 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -89.3 (d, J = 42.1 Hz), -92.9 (dt, J = 41.7, 2.7 Hz). ^{13}C NMR (150 MHz, Chloroform-*d*) δ : 153.6 (dd, J = 288.0, 286.5 Hz), 136.0, 135.2 (t, J = 2.8 Hz), 133.7, 131.5 (d, J = 3.0 Hz), 130.9 (d, J = 4.4 Hz), 129.0, 128.7, 128.5, 128.3, 127.8 (d, J = 3.4 Hz), 126.3, 125.8, 125.2, 124.9, 90.6 (dd, J = 22.0, 17.7 Hz), 35.3, 21.0. HRMS (EI^+) calcd. for $\text{C}_{20}\text{H}_{16}\text{F}_2$ [M] $^+$: 294.1215, found: 294.1218.

1-Bromo-2-(1,1-difluoro-3-(*p*-tolyl)prop-1-en-2-yl)benzene (2s)

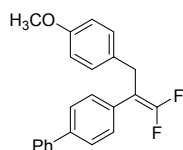
Colorless oil, 9.7 mg, 30%, ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.58 – 7.56 (m, 1H), 7.16 – 7.09 (m, 2H), 7.02 (d, J = 7.8 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 6.85 – 6.83 (m, 1H), 3.61 (s, 2H), 2.29 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -88.6 (d, J = 39.5 Hz), -93.9 (dt, J = 40.3, 2.7 Hz). ^{13}C NMR (150 MHz, Chloroform-*d*) δ : 153.5 (t, J = 286.5 Hz), 136.0, 134.7 (t, J = 2.6 Hz), 134.1 (dd, J = 6.0, 1.5 Hz), 132.8, 132.4 – 131.8 (m), 129.4, 129.0, 128.8, 127.1, 124.3 (dd, J = 3.3, 1.3 Hz), 92.5 (dd, J = 24.2, 16.7 Hz), 34.1, 21.1. HRMS (EI^+) calcd. for $\text{C}_{16}\text{H}_{13}\text{F}_2\text{Br}$ [M] $^+$: 322.0163, found: 322.0162.

1-(2-(Difluoromethylene)-4-phenylbutyl)-4-methylbenzene (2t)



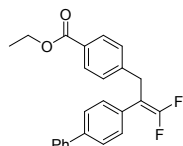
Colorless oil, 11.7 mg, 43%, ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.28 – 7.23 (m, 3H), 7.20 – 7.16 (m, 1H), 7.12 – 7.05 (m, 6H), 3.26 (t, J = 2.0 Hz, 2H), 2.64 – 2.60 (m, 2H), 2.32 (s, 3H), 2.20 – 2.16 (m, 2H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -95.5 (dt, J = 53.2, 2.0 Hz), -95.8 (dt, J = 53.5, 2.6 Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 153.9 (t, J = 282.0 Hz), 141.2, 136.1, 135.4 (t, J = 2.6 Hz), 129.2, 128.6, 128.4, 128.3, 126.0, 88.6 (t, J = 17.1 Hz), 33.8 (t, J = 2.7 Hz), 32.0 (dd, J = 2.7, 1.1 Hz), 27.7 (d, J = 2.1 Hz), 21.1. HRMS (EI^+) calcd. for $\text{C}_{18}\text{H}_{18}\text{F}_2$ [M] $^+$: 272.1371, found: 272.1372.

4-(1,1-Difluoro-3-(4-methoxyphenyl)prop-1-en-2-yl)-1,1'-biphenyl (2aa)



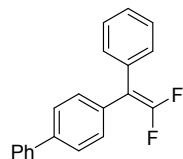
White solid, 30.8 mg, 92%, m.p. 65-67°C; ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.57 – 7.50 (m, 4H), 7.43-7.39 (m, 2H), 7.35 – 7.30 (m, 3H), 7.12 – 7.08 (m, 2H), 6.85 – 6.73 (m, 2H), 3.75 (s, 3H), 3.70 (t, J = 2.3 Hz, 2H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -90.1 (dt, J = 39.9, 2.7 Hz), -90.5 (d, J = 39.9 Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 158.2, 154.5 (dd, J = 292.2, 287.7 Hz), 140.5, 140.0, 132.6 (t, J = 3.8 Hz), 130.5 (t, J = 2.0 Hz), 129.3, 128.8, 128.6 (t, J = 3.6 Hz), 127.4, 127.0, 127.0, 114.0, 91.7 (dd, J = 21.3, 12.9 Hz), 55.2, 33.0. HRMS (EI^+) calcd. for $\text{C}_{22}\text{H}_{18}\text{F}_2\text{O}$ [M] $^+$: 336.1320, found: 336.1318.

Ethyl 4-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)benzoate (2ab)



Colorless oil, 29.9 mg, 79%, ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.96 – 7.92 (m, 2H), 7.56 – 7.50 (m, 4H), 7.44 – 7.39 (m, 2H), 7.35-7.31 (m, 3H), 7.27 – 7.24 (m, 2H), 4.34 (q, J = 7.1 Hz, 2H), 3.82 (t, J = 2.2 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -89.2 (dt, J = 38.0, 2.5 Hz), -89.7 (d, J = 38.1 Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 166.5, 154.6 (dd, J = 290.0, 286.3 Hz), 143.7 (t, J = 2.7 Hz), 140.4, 140.2, 132.0 (t, J = 3.8 Hz), 129.9, 128.9, 128.8, 128.5 (t, J = 3.6 Hz), 128.3, 127.5, 127.2, 127.0, 91.0 (dd, J = 21.3, 14.0 Hz), 60.9, 33.8, 14.4. HRMS (EI^+) calcd. for $\text{C}_{24}\text{H}_{20}\text{F}_2\text{O}_2$ [M] $^+$: 378.1426, found: 378.1422.

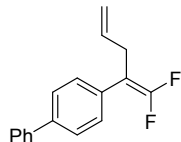
4-(2,2-Difluoro-1-phenylvinyl)-1,1'-biphenyl (2ac)²



White solid, 19.0 mg, 65%, m.p. 69-71°C; ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.61 – 7.56 (m, 4H), 7.46 – 7.42 (m, 2H), 7.40 – 7.30 (m, 8H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -87.3 (d, J = 31.9 Hz),

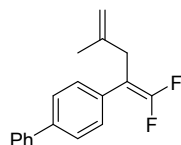
-87.5 (d, $J = 31.6$ Hz). ^{13}C NMR (150 MHz, Chloroform- d) δ : 153.8 (t, $J = 293.6$ Hz), 140.5, 140.4, 134.2 (t, $J = 3.5$ Hz), 133.3 (t, $J = 3.7$ Hz), 130.0 (t, $J = 3.5$ Hz), 129.8 (t, $J = 3.3$ Hz), 128.9, 128.5, 127.7, 127.5, 127.1, 127.1, 96.0 (t, $J = 18.1$ Hz).

4-(1,1-Difluoropenta-1,4-dien-2-yl)-1,1'-biphenyl (2ad)



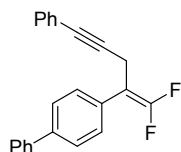
Colorless oil, 16.4 mg, 64%, ^1H NMR (400 MHz, Chloroform- d) δ : 7.53 – 7.49 (m, 4H), 7.39 – 7.33 (m, 4H), 7.29 – 7.25 (m, 1H), 5.81-5.71 (m, 1H), 5.09 – 4.92 (m, 2H), 3.12-3.09 (m, 2H). ^{19}F NMR (376 MHz, Chloroform- d) δ : -89.44 (dt, $J = 39.5, 2.9$ Hz), -90.07 (d, $J = 39.3$ Hz). ^{13}C NMR (100 MHz, Chloroform- d) δ : 153.0 (dd, $J = 290.9, 286.4$ Hz), 139.5, 138.9, 133.5 (t, $J = 2.7$ Hz), 131.5 (t, $J = 4.1$ Hz), 127.8, 127.3 (t, $J = 3.7$ Hz), 126.3, 126.0, 126.0, 115.4, 89.1 (dd, $J = 21.6, 15.5$ Hz), 30.9. HRMS (FI^+) calcd. for $\text{C}_{17}\text{H}_{14}\text{F}_2$ [M] $^+$: 256.1058, found: 256.1062.

4-(1,1-Difluoro-4-methylpenta-1,4-dien-2-yl)-1,1'-biphenyl (2ae)



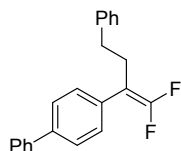
White solid, 18.9 mg, 70%, m.p. 34-36°C; ^1H NMR (600 MHz, Chloroform- d) δ : 7.60 – 7.55 (m, 4H), 7.45 – 7.41 (m, 4H), 7.35 – 7.33 (m, 1H), 4.79 (d, $J = 17.7$ Hz, 2H), 3.12 (s, 2H), 1.75 (s, 3H). ^{19}F NMR (564 MHz, Chloroform- d) δ : -89.2 (d, $J = 38.9$ Hz), -89.9 (d, $J = 38.7$ Hz). ^{13}C NMR (100 MHz, Chloroform- d) δ : 154.4 (dd, $J = 292.7, 287.8$ Hz), 141.9 (t, $J = 3.0$ Hz), 140.6, 139.9, 132.8 (t, $J = 4.0$ Hz), 128.8, 128.4 (t, $J = 3.7$ Hz), 127.4, 127.0 (2C), 112.2, 90.0 (dd, $J = 21.6, 12.7$ Hz), 36.0, 22.3. HRMS (EI^+) calcd. for $\text{C}_{18}\text{H}_{16}\text{F}_2$ [M] $^+$: 270.1215, found: 270.1220.

4-(1,1-Difluoro-5-phenylpent-1-en-4-yn-2-yl)-1,1'-biphenyl (2af)



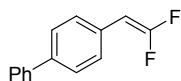
Viscous oil, 12.2 mg, 37%, ^1H NMR (400 MHz, Chloroform- d) δ : 7.64 – 7.56 (m, 6H), 7.46-7.43 (m, 2H), 7.37 – 7.33 (m, 3H), 7.27 – 7.24 (m, 4H), 3.54 (t, $J = 2.1$ Hz, 2H). ^{19}F NMR (376 MHz, Chloroform- d) δ : -88.0 (dt, $J = 37.5, 3.0$ Hz), -88.9 (d, $J = 37.0$ Hz). ^{13}C NMR (100 MHz, Chloroform- d) δ : 154.0 (dd, $J = 290.8, 287.4$ Hz), 140.5, 140.4, 131.8 (t, $J = 3.8$ Hz), 131.6, 128.8, 128.5 (t, $J = 3.8$ Hz), 128.2, 128.0, 127.5, 127.1, 127.1, 123.3, 89.0 (dd, $J = 20.8, 15.3$ Hz), 85.9 (t, $J = 3.8$ Hz), 81.8, 19.0. HRMS (EI^+) calcd. for $\text{C}_{23}\text{H}_{16}\text{F}_2$ [M] $^+$: 330.1215, found: 330.1213.

4-(1,1-Difluoro-4-phenylbut-1-en-2-yl)-1,1'-biphenyl (2ag)



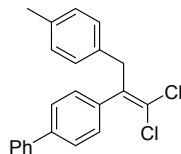
Colorless oil, 16.1 mg, 50%, ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.63 – 7.59 (m, 4H), 7.48 – 7.43 (m, 2H), 7.42 – 7.34 (m, 3H), 7.31 – 7.26 (m, 3H), 7.22 – 7.14 (m, 3H), 2.77 – 2.69 (m, 4H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -90.4 (dd, J = 41.9, 2.0 Hz), -90.9 (d, J = 41.6 Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 153.8 (dd, J = 289.5, 285.5 Hz), 141.0, 140.6, 140.1, 132.4 (t, J = 3.8 Hz), 128.8, 128.6 (t, J = 3.4 Hz), 128.4, 128.4, 127.4, 127.2, 127.0, 126.1, 91.6 (dd, J = 21.8, 13.1 Hz), 34.1 (t, J = 2.6 Hz), 29.6 (d, J = 1.6 Hz). HRMS (EI $^+$) calcd. for $\text{C}_{22}\text{H}_{18}\text{F}_2$ $[\text{M}]^+$: 320.1371, found: 320.1374.

4-(2,2-Difluorovinyl)-1,1'-biphenyl (2ah)¹



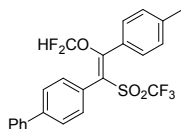
White solid, 6.3 mg, 29%, ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.61 – 7.57 (m, 4H), 7.46 – 7.40 (m, 4H), 7.37 – 7.33 (m, 1H), 5.32 (dd, J = 26.3, 3.8 Hz, 1H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -81.9 (dd, J = 30.7, 26.1 Hz), -83.8 (dd, J = 30.7, 3.9 Hz). ^{13}C NMR (150 MHz, Chloroform-*d*) δ : 156.4 (dd, J = 298.5, 288.6 Hz), 140.5, 139.8, 129.4 (t, J = 6.5 Hz), 128.9, 128.1 (dd, J = 6.4, 3.5 Hz), 127.5, 127.4, 127.0, 82.0 (dd, J = 29.2, 13.5 Hz).

4-(1,1-Dichloro-3-(*p*-tolyl)prop-1-en-2-yl)-1,1'-biphenyl (3a),



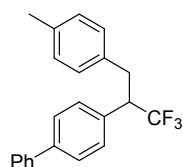
White solid, 11.3 mg, 32%, m.p. 74-76°C; ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.60 – 7.56 (m, 2H), 7.54 – 7.50 (m, 2H), 7.46 – 7.40 (m, 2H), 7.36 – 7.31 (m, 1H), 7.18 – 7.15 (m, 2H), 7.06-7.04 (m, 2H), 7.02-7.00 (m, 2H), 3.93 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 140.5, 140.4, 138.9, 137.7, 136.2, 133.9, 129.2, 128.8, 128.8, 128.6, 127.5, 127.0, 126.9, 118.8, 41.9, 21.1. HRMS (EI $^+$) calcd. for $\text{C}_{22}\text{H}_{18}\text{Cl}_2$ $[\text{M}]^+$: 352.0780, found: 352.0777.

(*E*)-4-(2-(Difluoromethoxy)-2-(*p*-tolyl)-1-((trifluoromethyl)sulfonyl)vinyl)-1,1'-biphenyl (5a')



White solid, 33.2 mg, 70%, m.p. 139-141°C; ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.55 – 7.53 (m, 2H), 7.50 – 7.48 (m, 2H), 7.43-7.40 (m, 2H), 7.36-7.32 (m, 1H), 7.25 (d, J = 2.9 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.1 Hz, 2H), 6.35 (t, J = 71.9 Hz, 1H), 2.30 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -75.1, -83.1 (d, J = 71.8 Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 162.8 (t, J = 3.5 Hz), 142.8, 142.0, 139.8, 132.6, 129.9, 129.6, 128.9, 128.5, 127.9, 127.2, 127.0, 126.9, 123.1, 120.4 (q, J = 328.9 Hz), 115.3 (t, J = 264.6 Hz), 21.5. HRMS (EI $^+$) calcd. for $\text{C}_{23}\text{H}_{17}\text{F}_5\text{O}_3\text{S}$ $[\text{M}]^+$: 468.0813, found: 468.0813.

4-(1,1,1-Trifluoro-3-(*p*-tolyl)propan-2-yl)-1,1'-biphenyl (6a)



Viscous oil, 17.2 mg, 51%, ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.60 – 7.56 (m, 2H), 7.54 – 7.50 (m, 2H), 7.42 (dd, J = 8.4, 6.8 Hz, 2H), 7.36 – 7.31 (m, 1H), 7.29 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 7.8 Hz, 2H), 6.89 (d, J = 8.0 Hz, 2H), 3.61 – 3.47 (m, 1H), 3.36 (dd, J = 14.0, 4.0 Hz, 1H), 3.11 (dd, J = 13.9, 10.9 Hz, 1H), 2.25 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -69.3 (d, J = 9.0 Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 140.8, 140.4, 136.1, 134.5, 133.4, 129.6, 129.1, 128.8, 128.8, 127.5, 127.2, 127.1, 126.8 (q, J = 280.5 Hz), 51.9 (q, J = 26.1 Hz), 35.1 (d, J = 2.6 Hz), 21.0. HRMS (EI $^+$) calcd. for $\text{C}_{22}\text{H}_{19}\text{F}_3$ $[\text{M}]^+$: 340.1433, found: 340.1430.

11. References

1. M. Tomoya, I. Yoshiteru, M. Masahiro, *Chem. Lett.* 2008, 37, 1006-1007.
2. Y. Maekawa, M. Nambo, D. Yokogawa, C. M. Crudden, *J. Am. Chem. Soc.* **2020**, 142, 15667-15672.
3. M. Nambo, J. C. Yim, L. B. O. Freitas, Y. Tahara, Z. T. Ariki, Y. Maekawa, D. Yokogawa, C. M. Crudden, *Nat. Commun.* **2019**, 10, 4528-4535.

12. Copies of NMR spectra

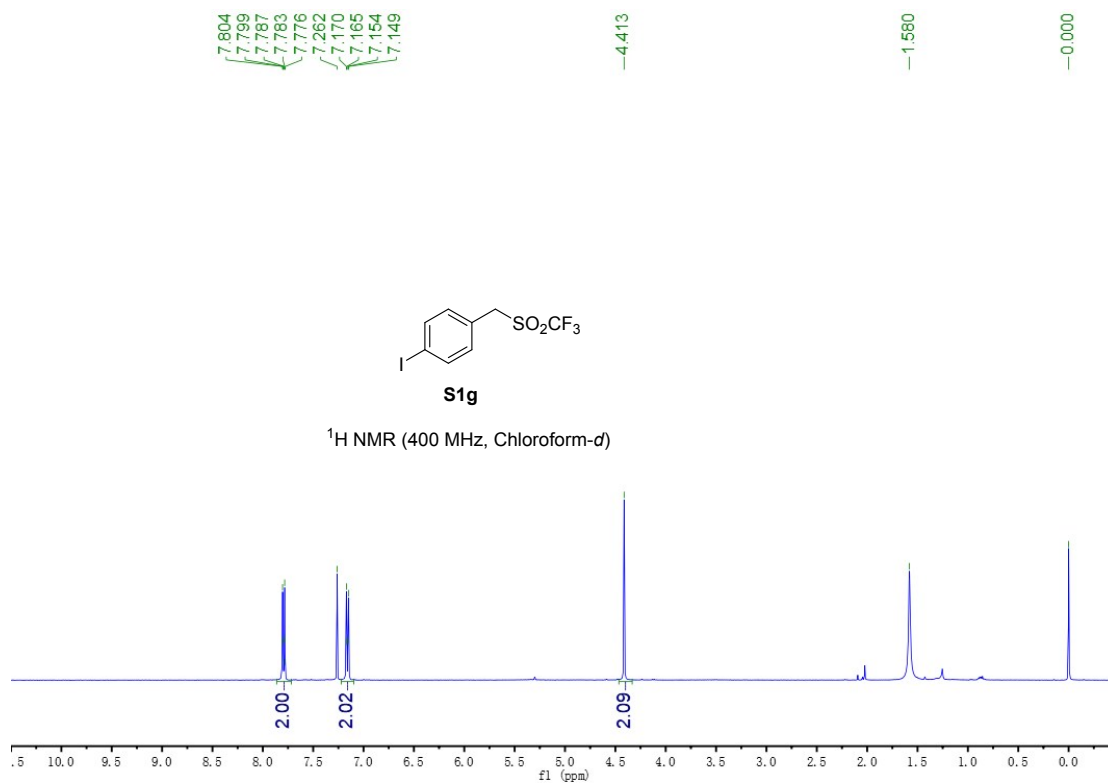


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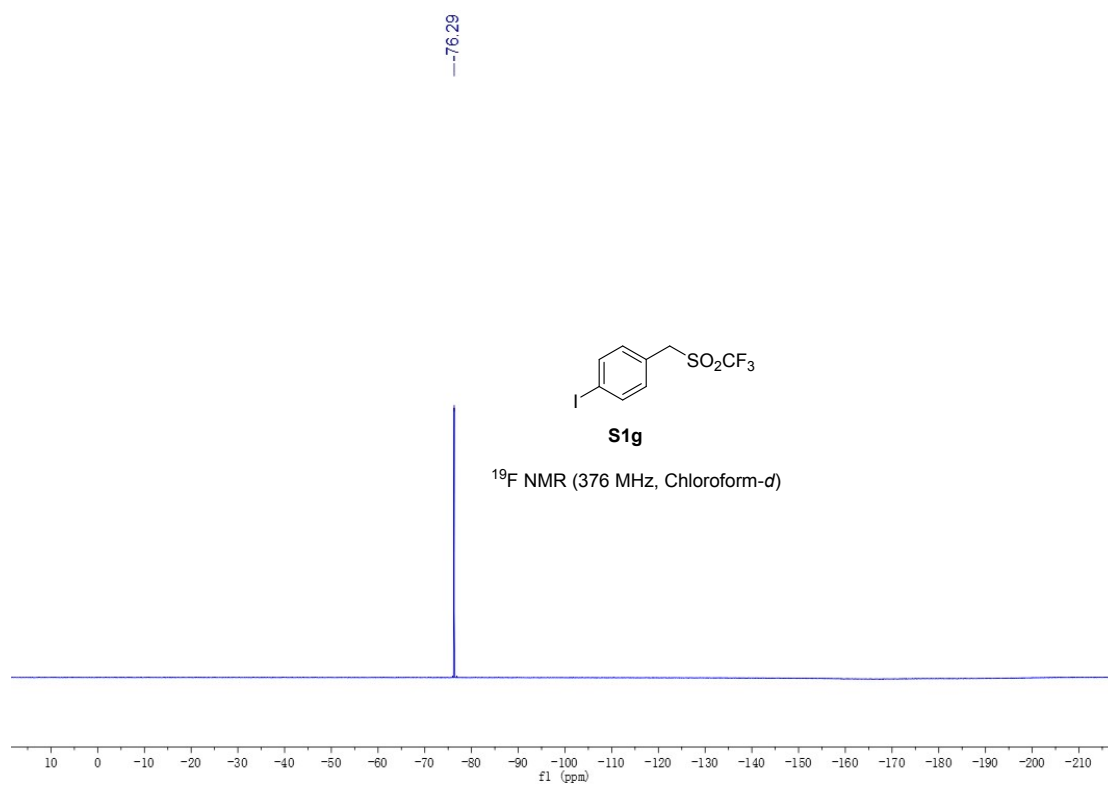


Figure S 2

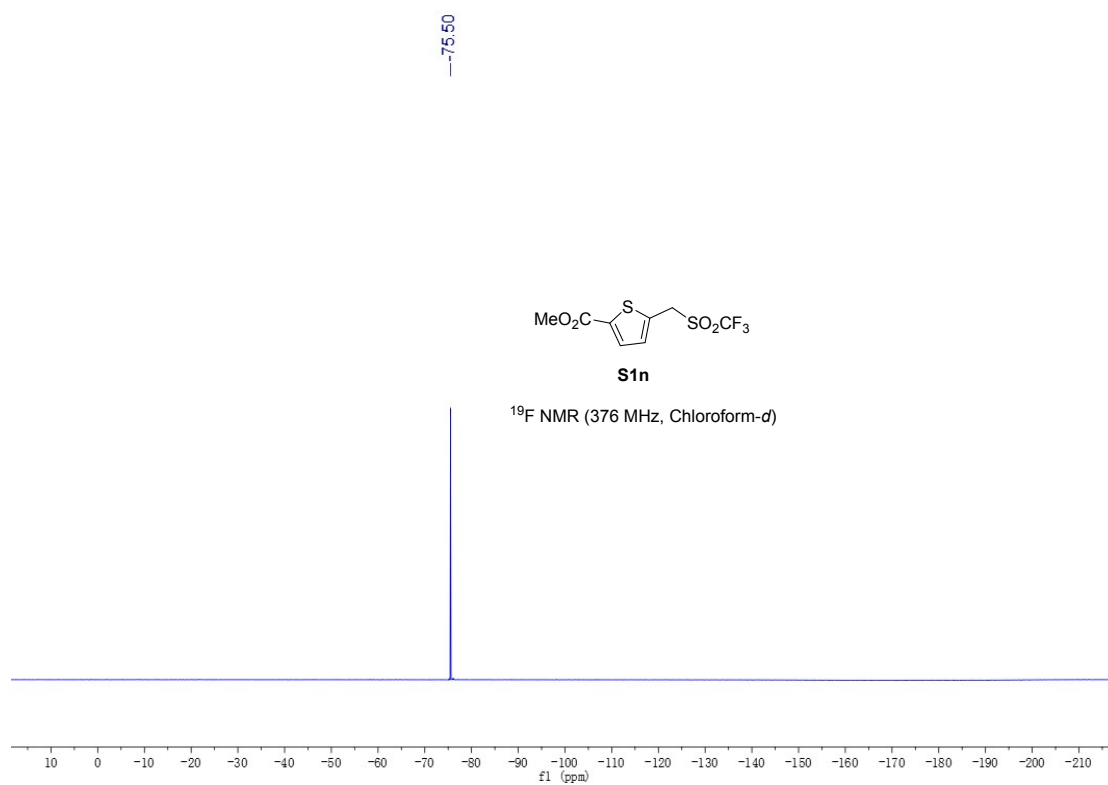


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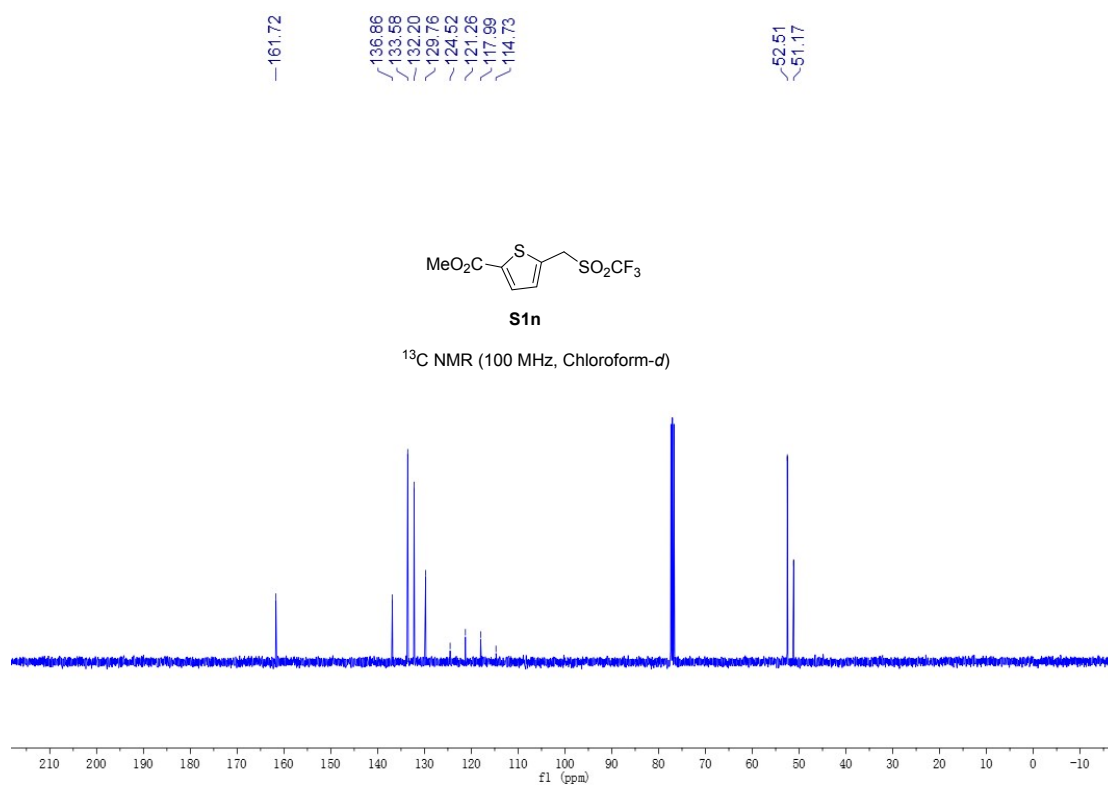


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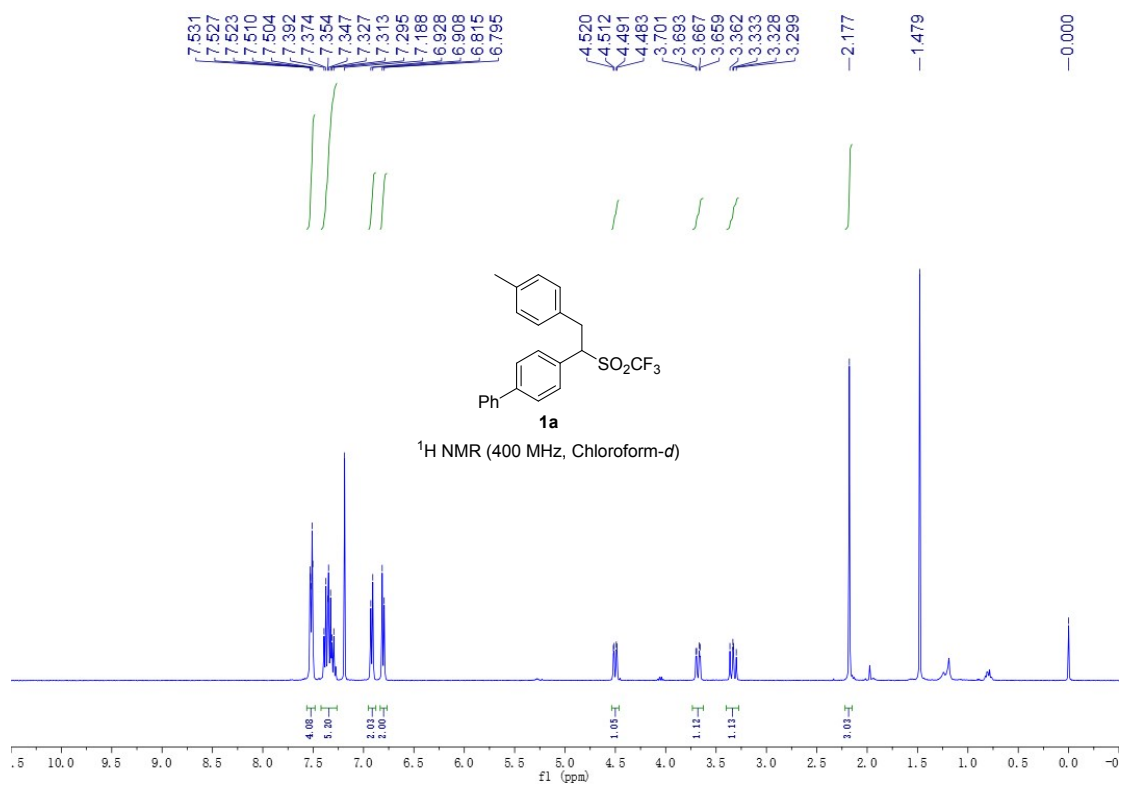


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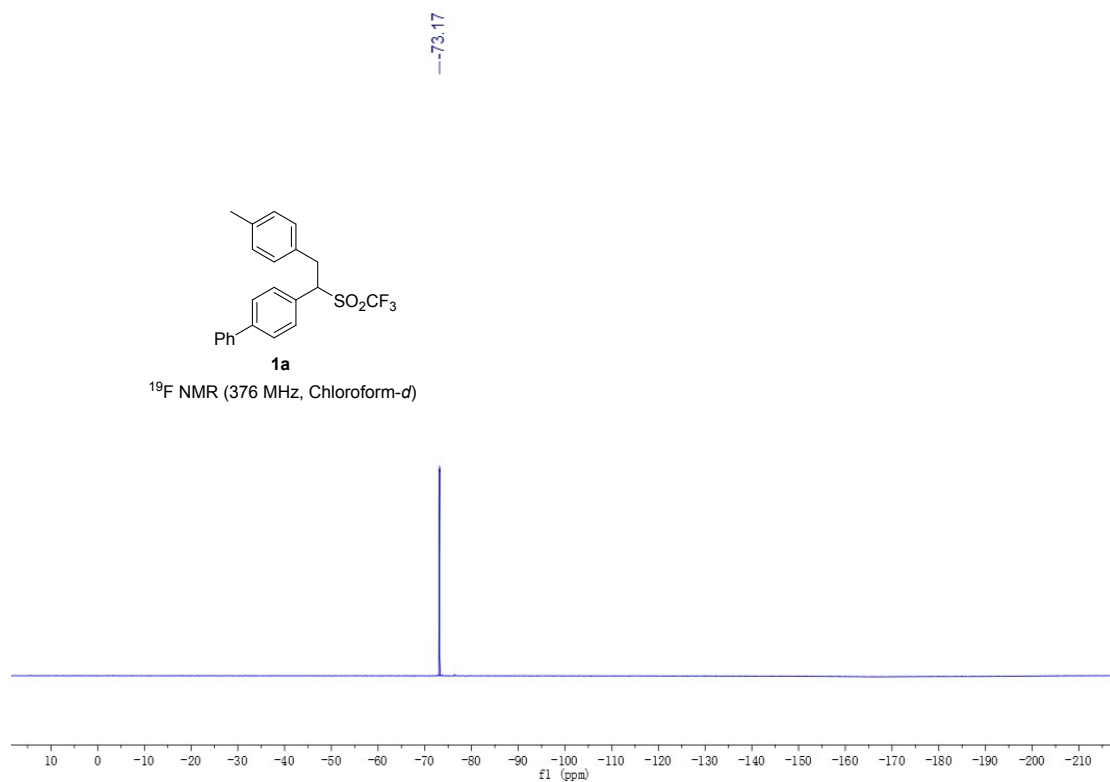


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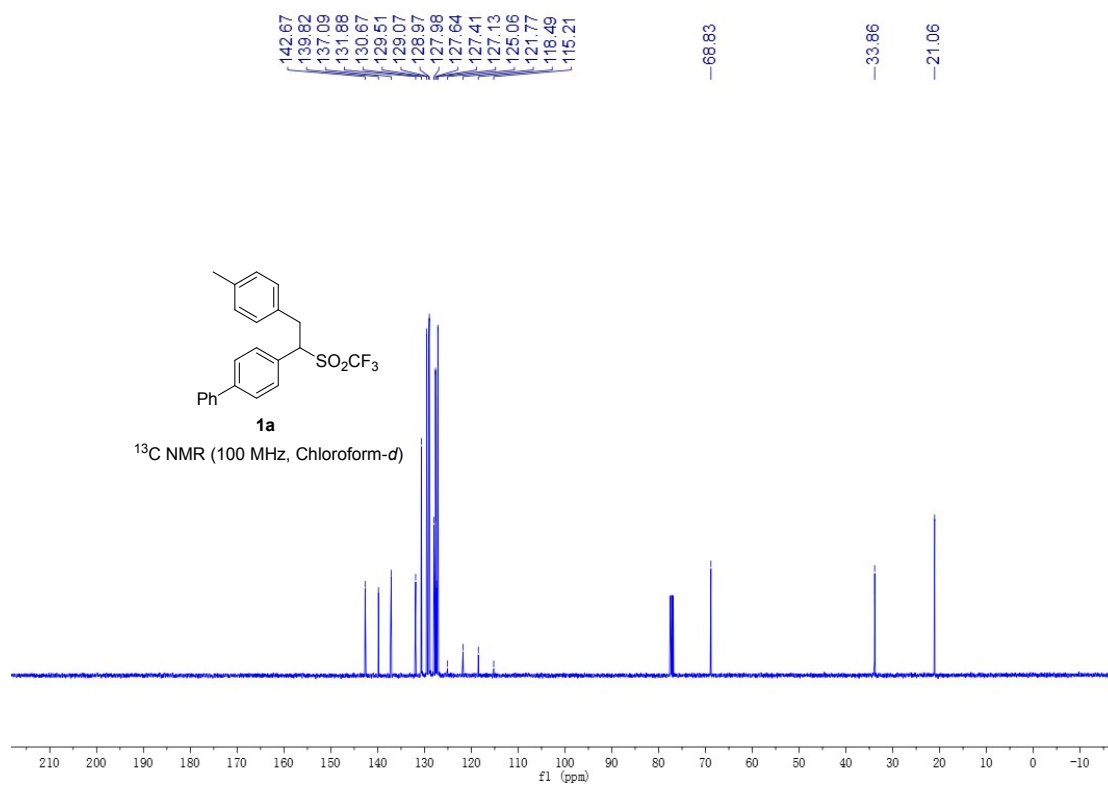


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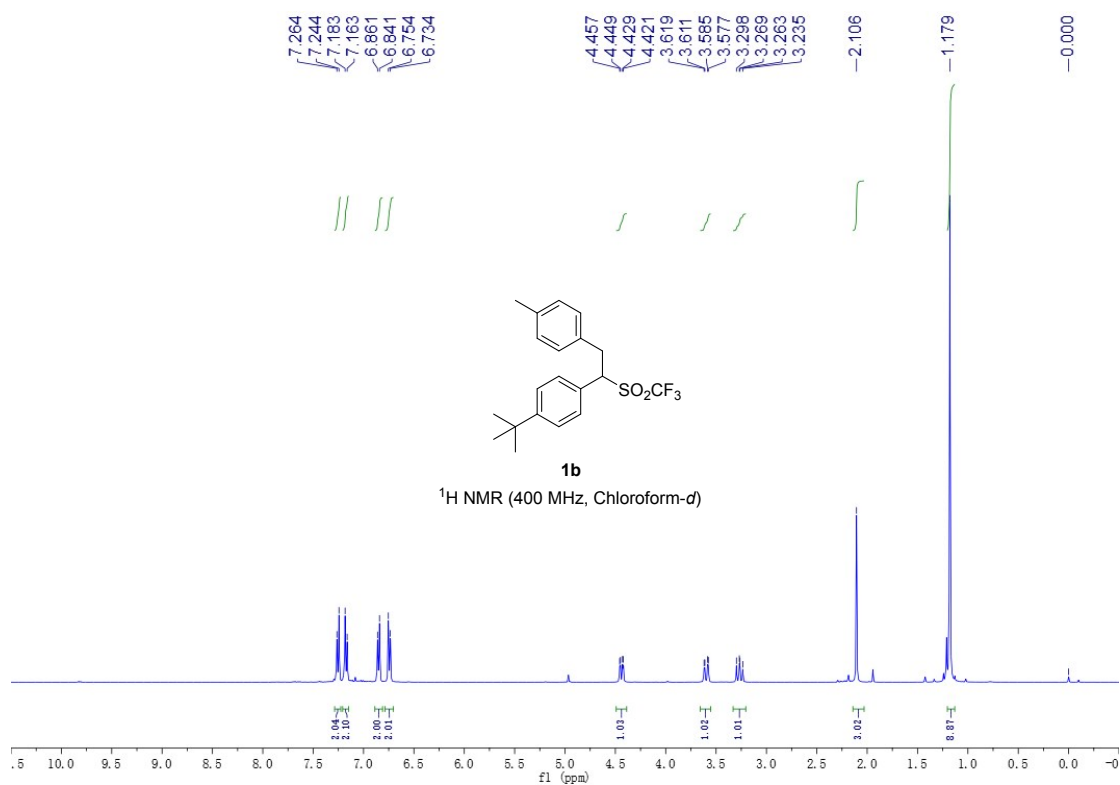


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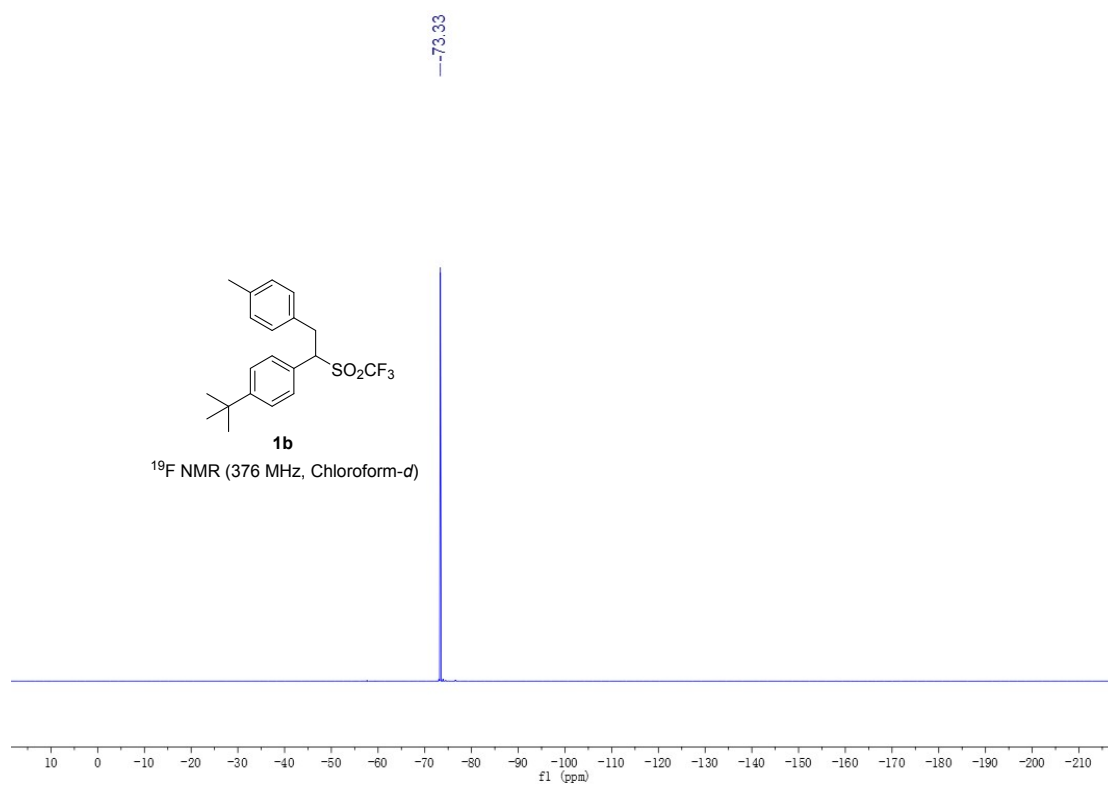


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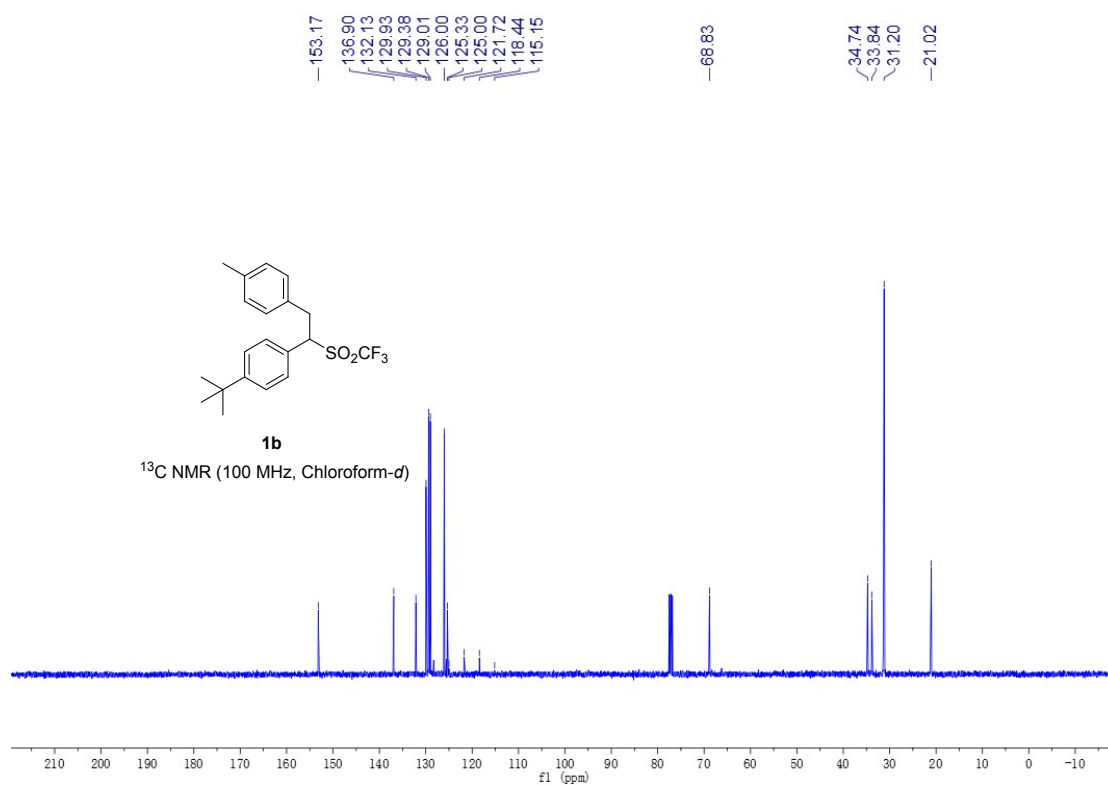


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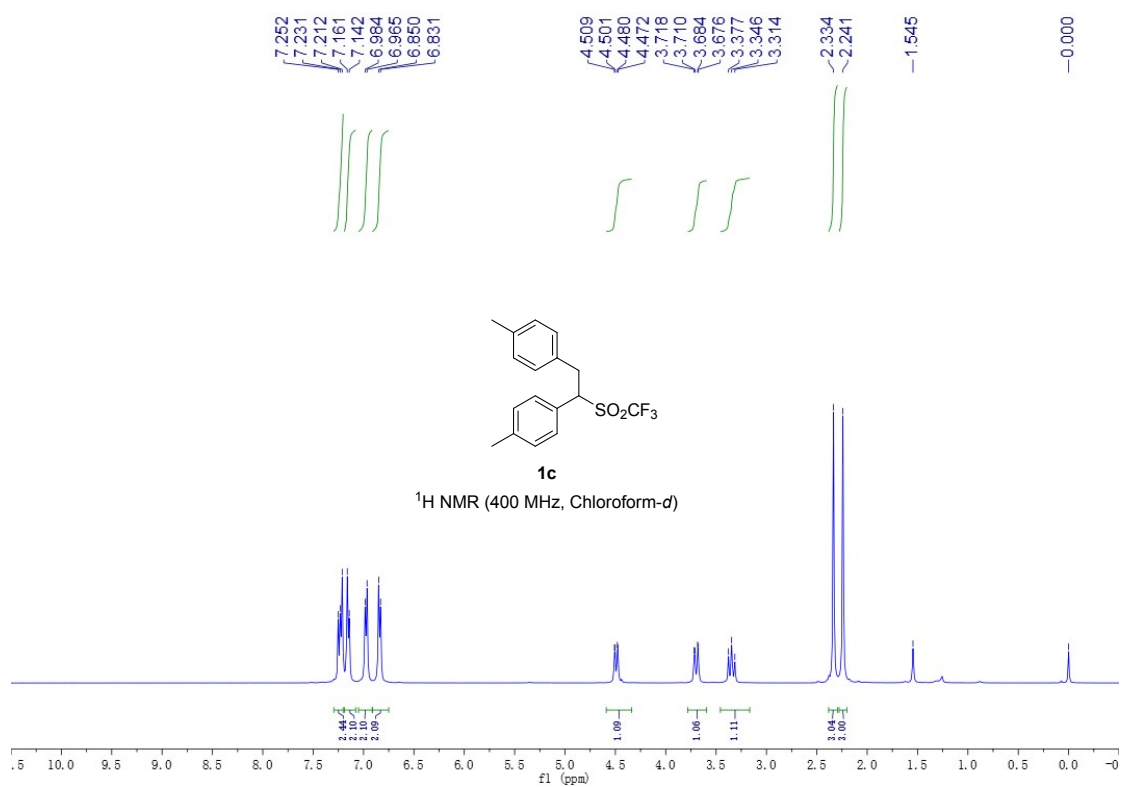


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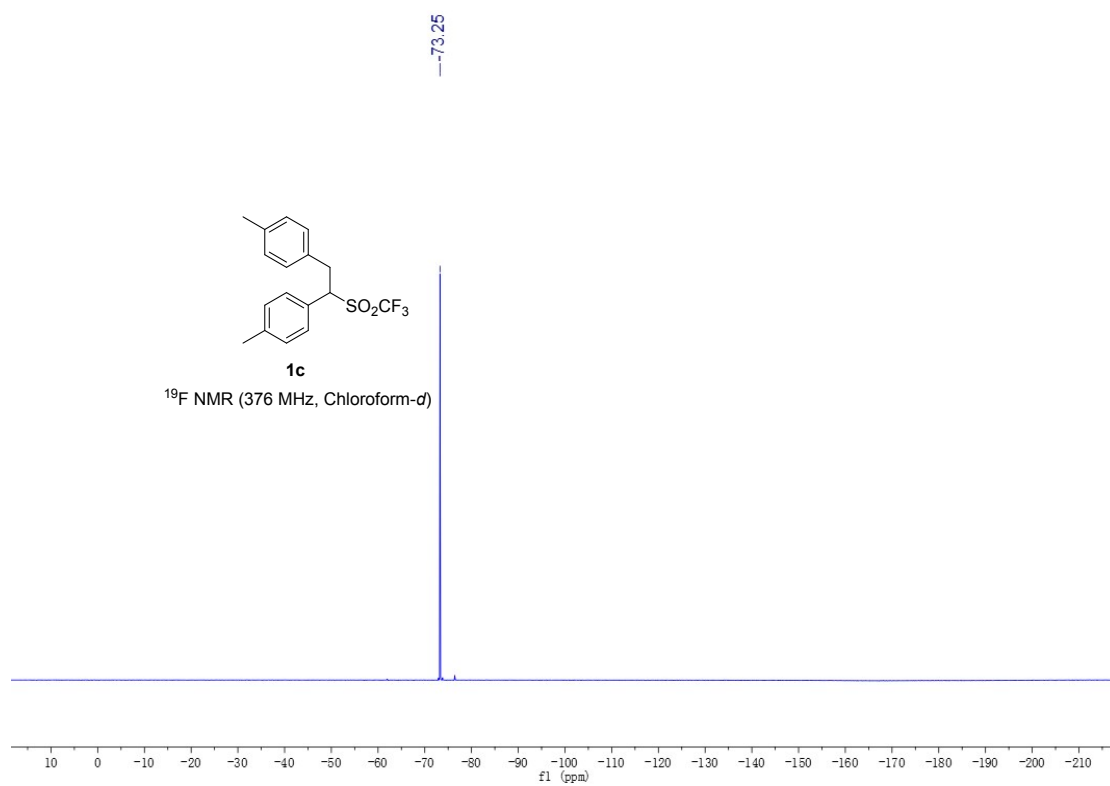


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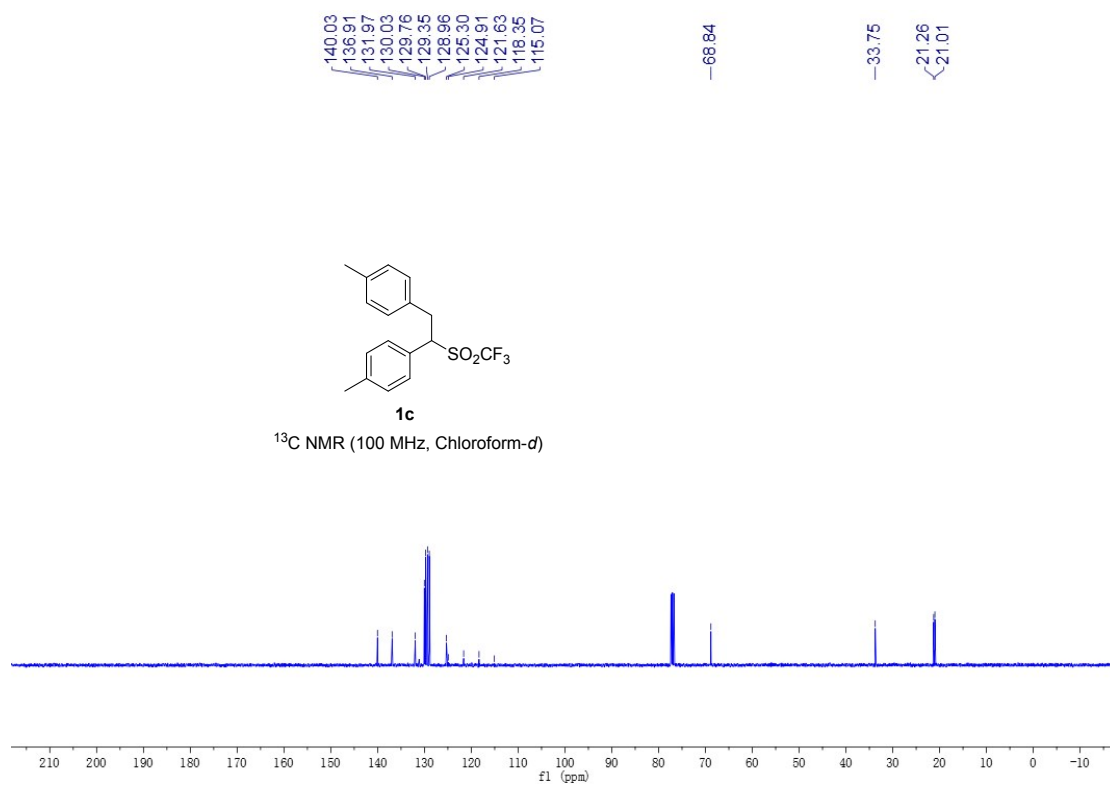


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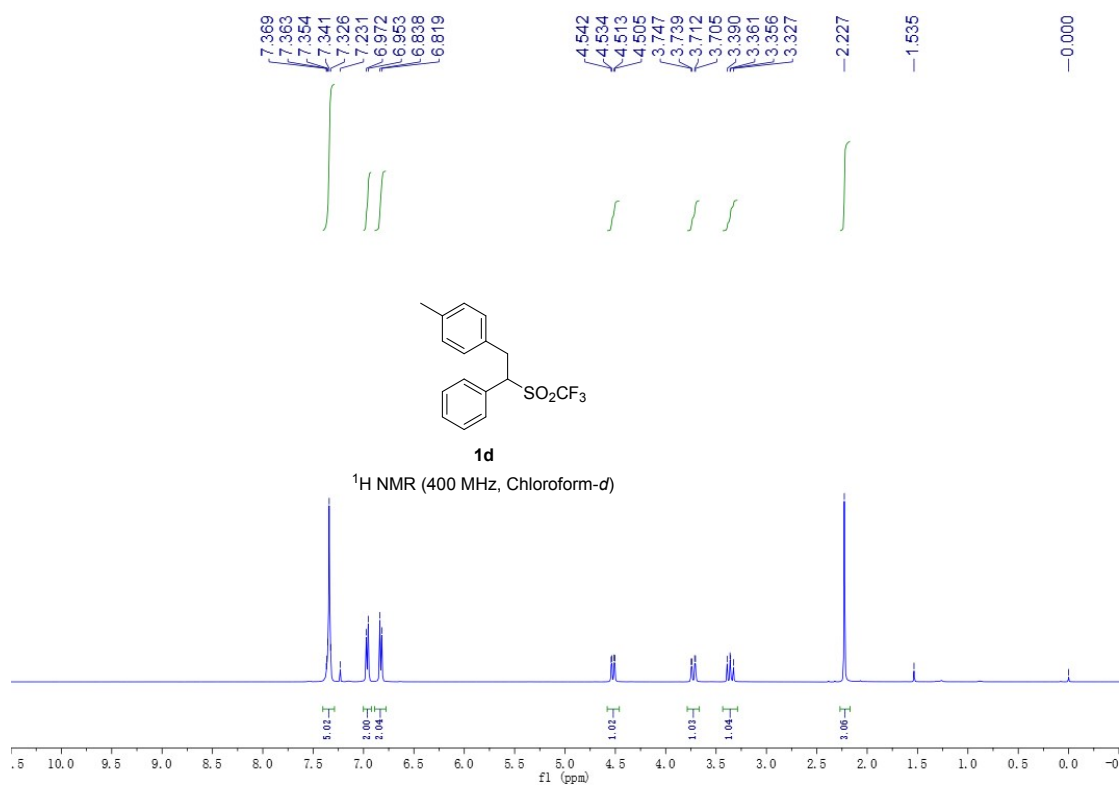


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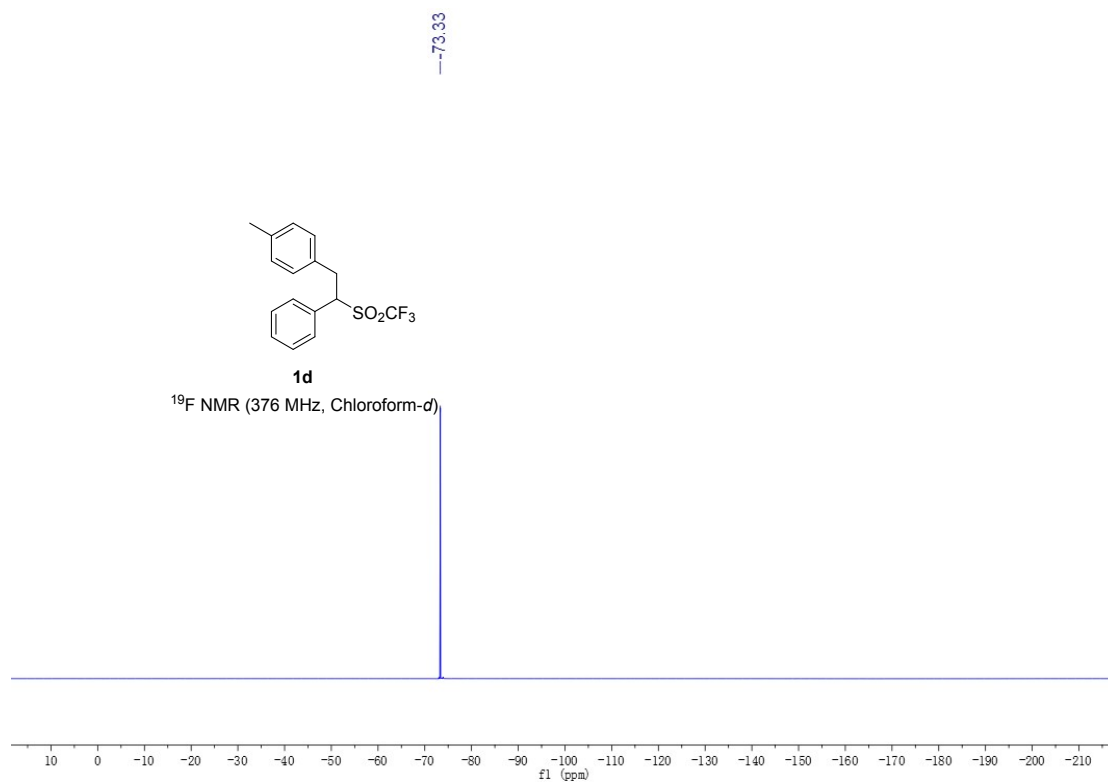


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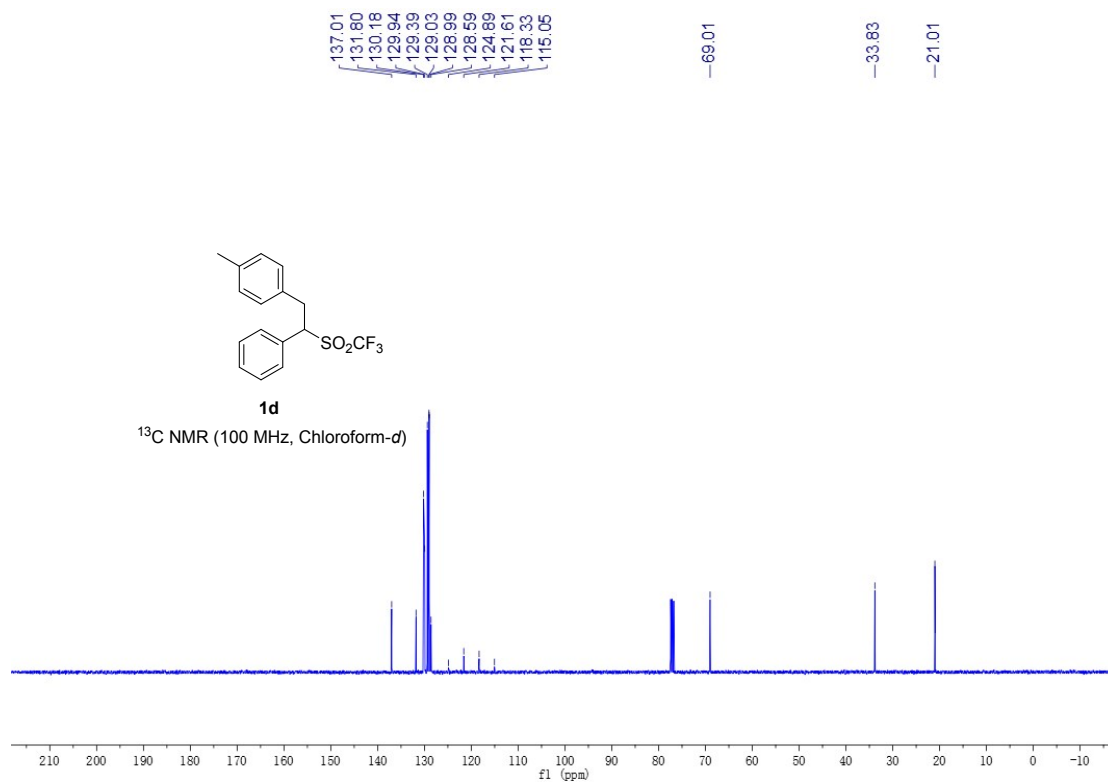


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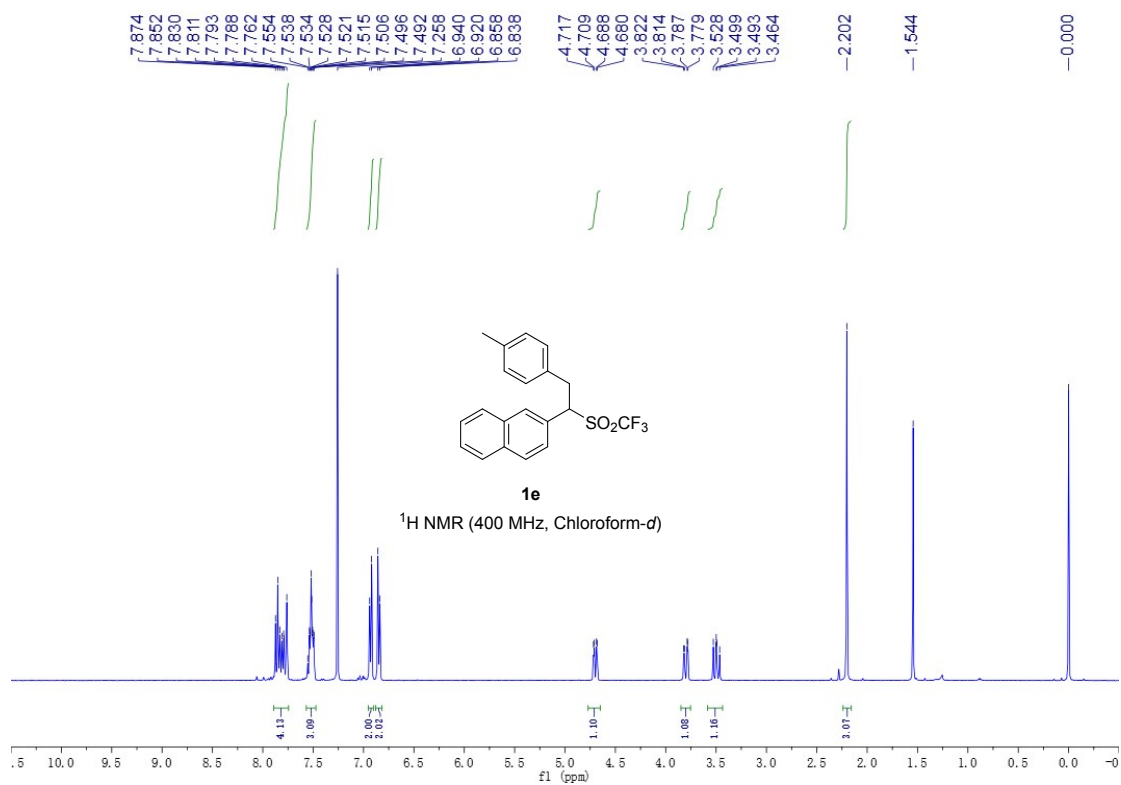


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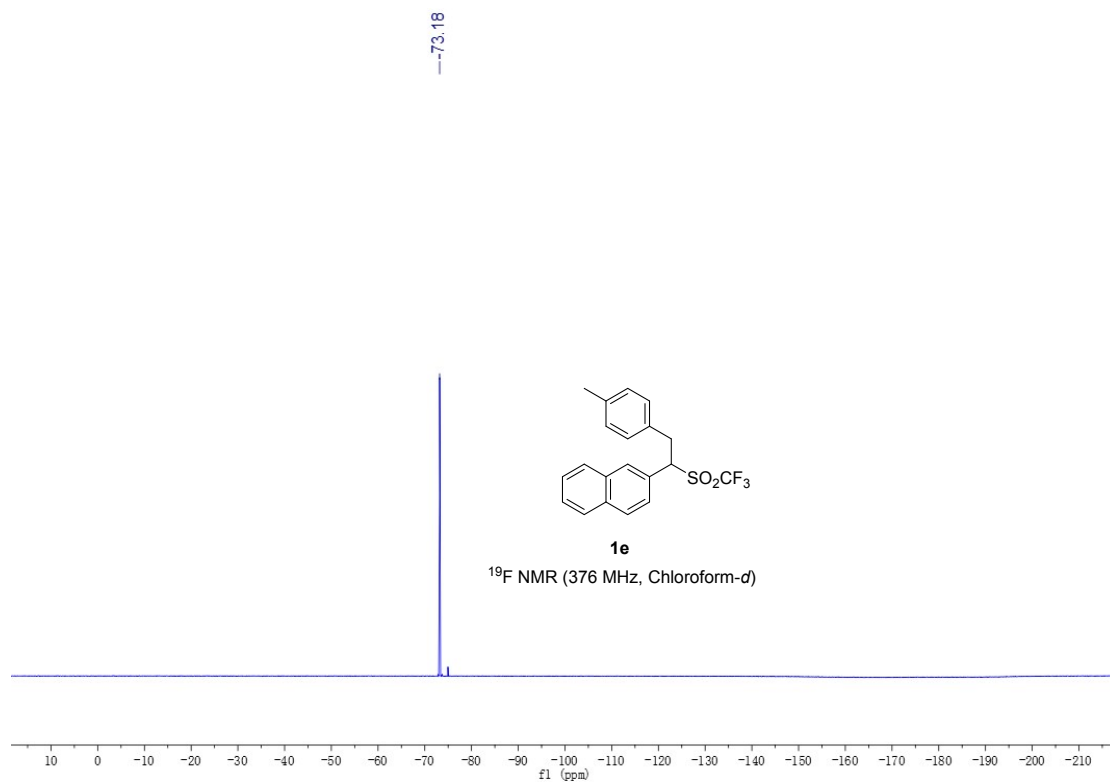


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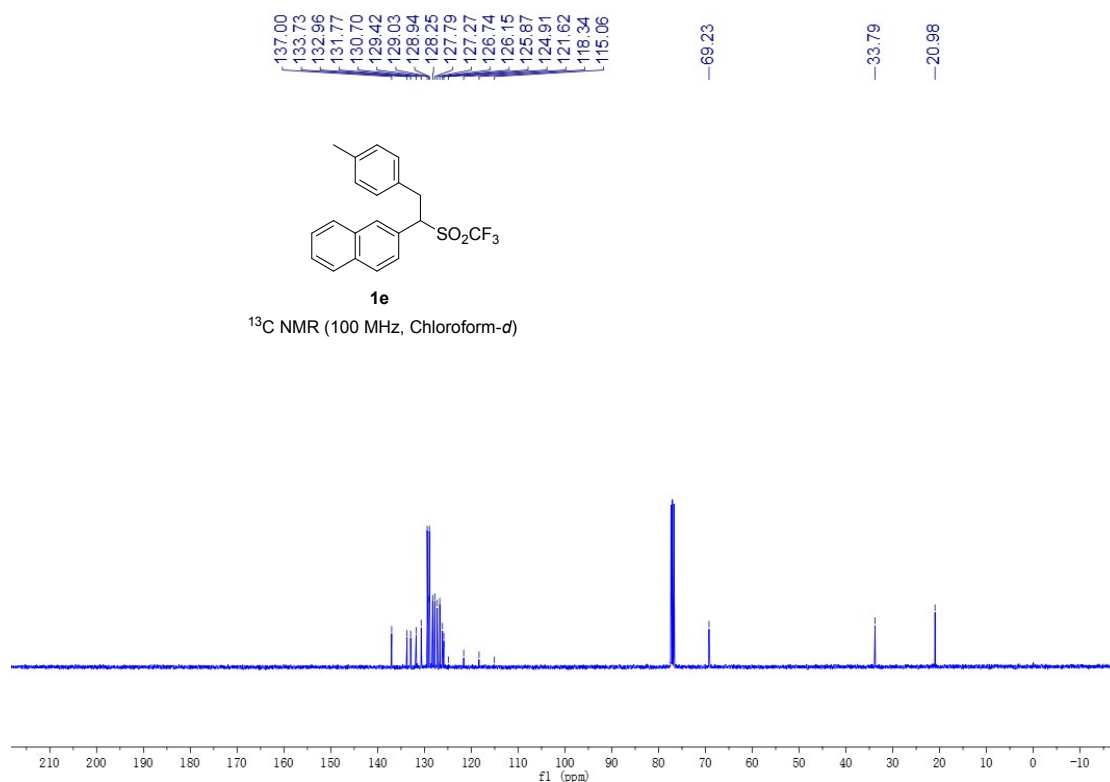


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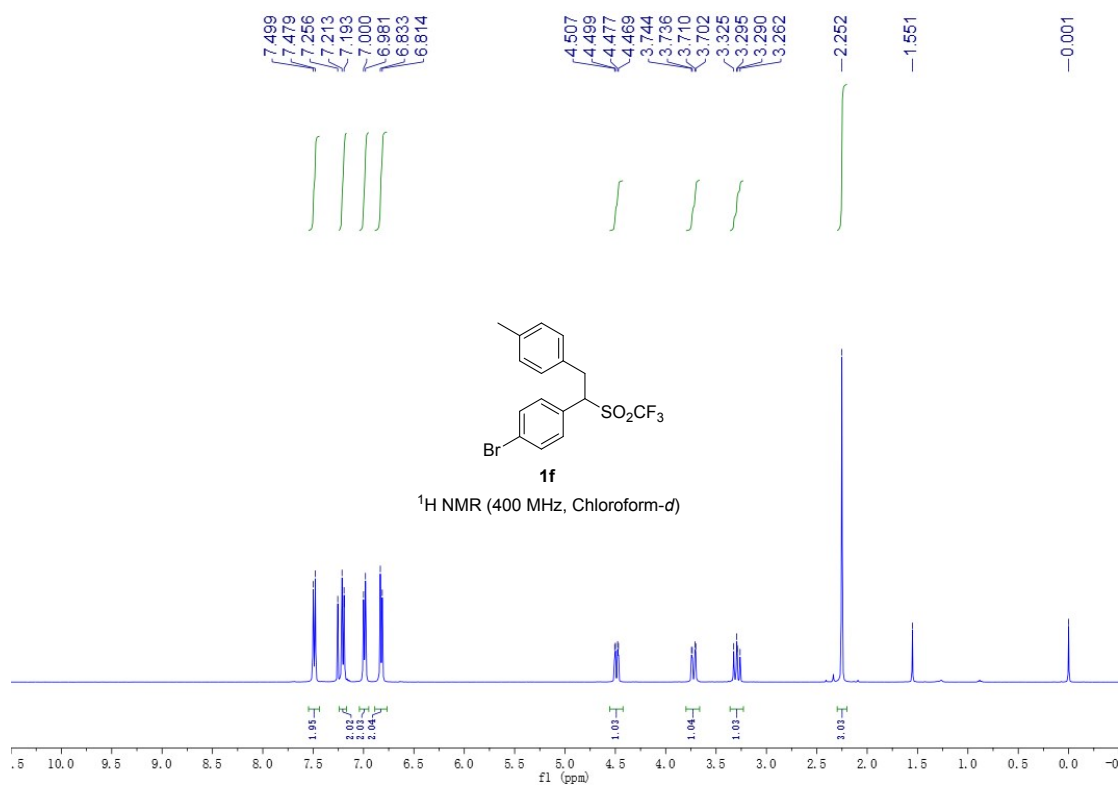


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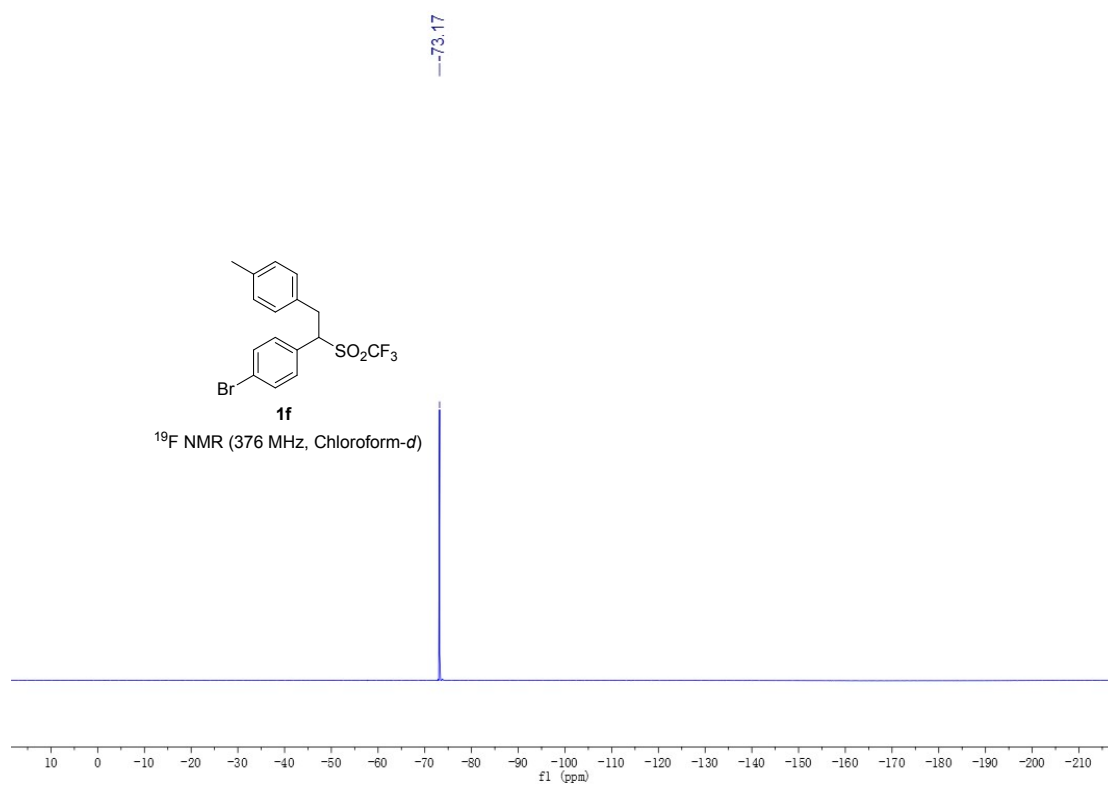


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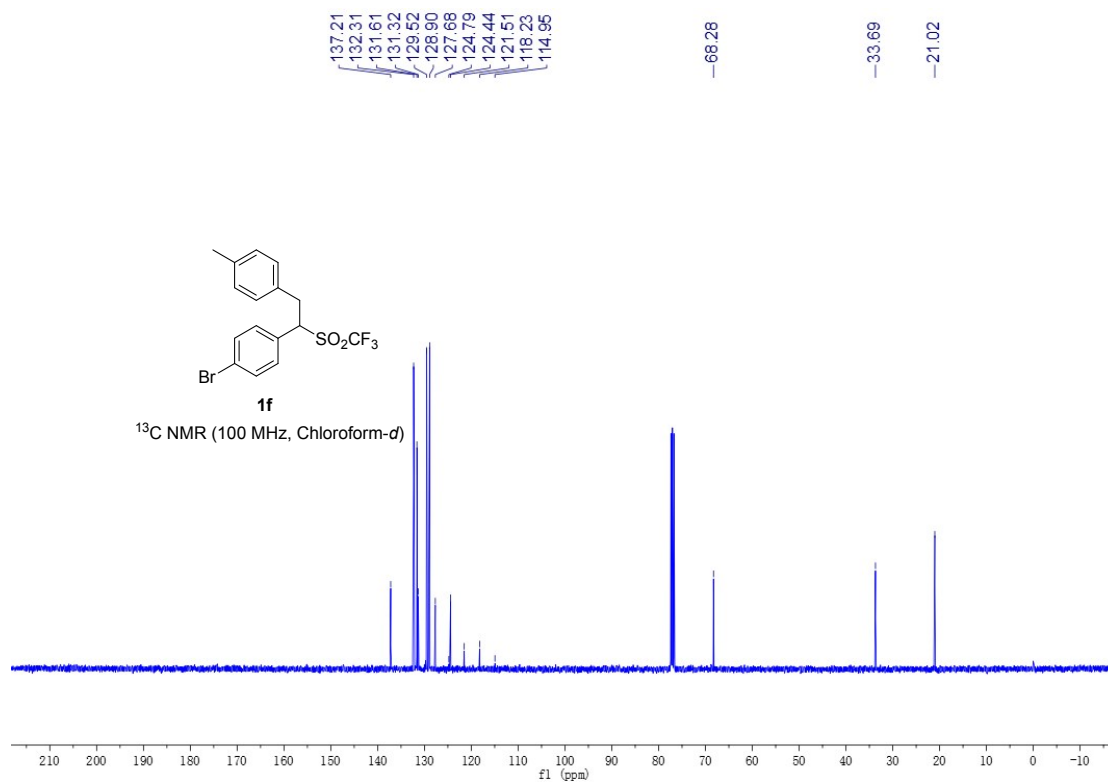


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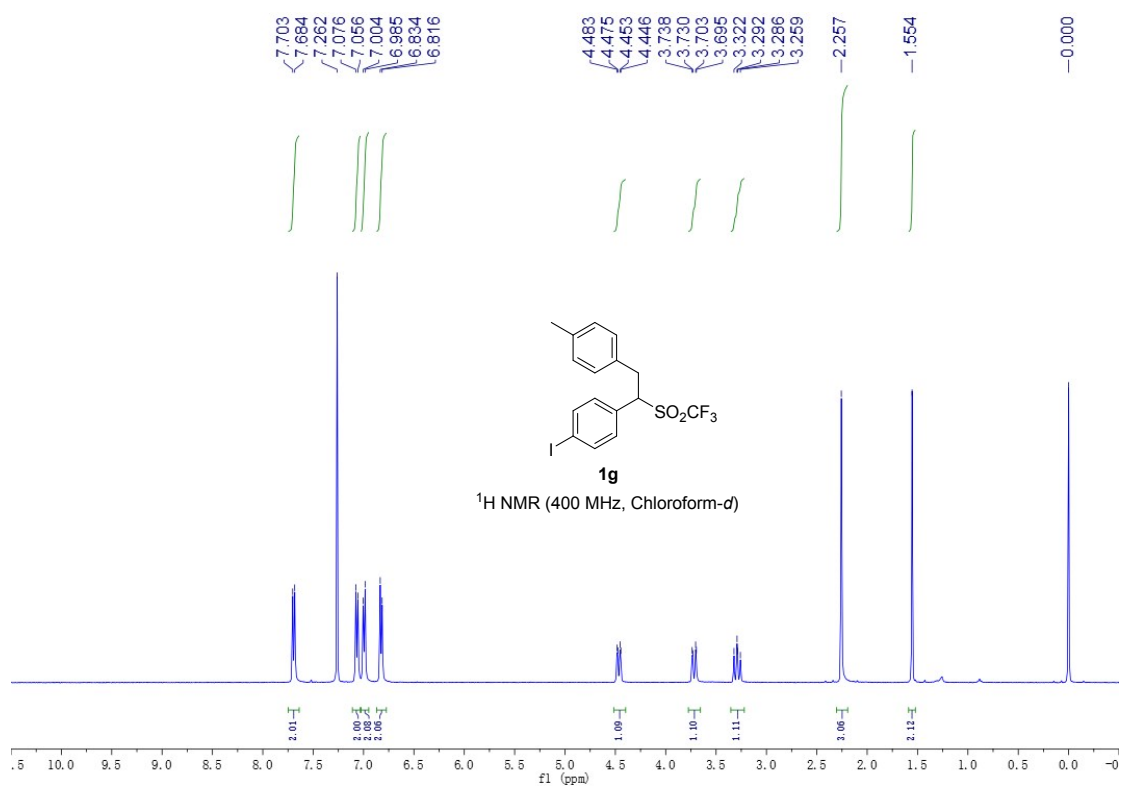


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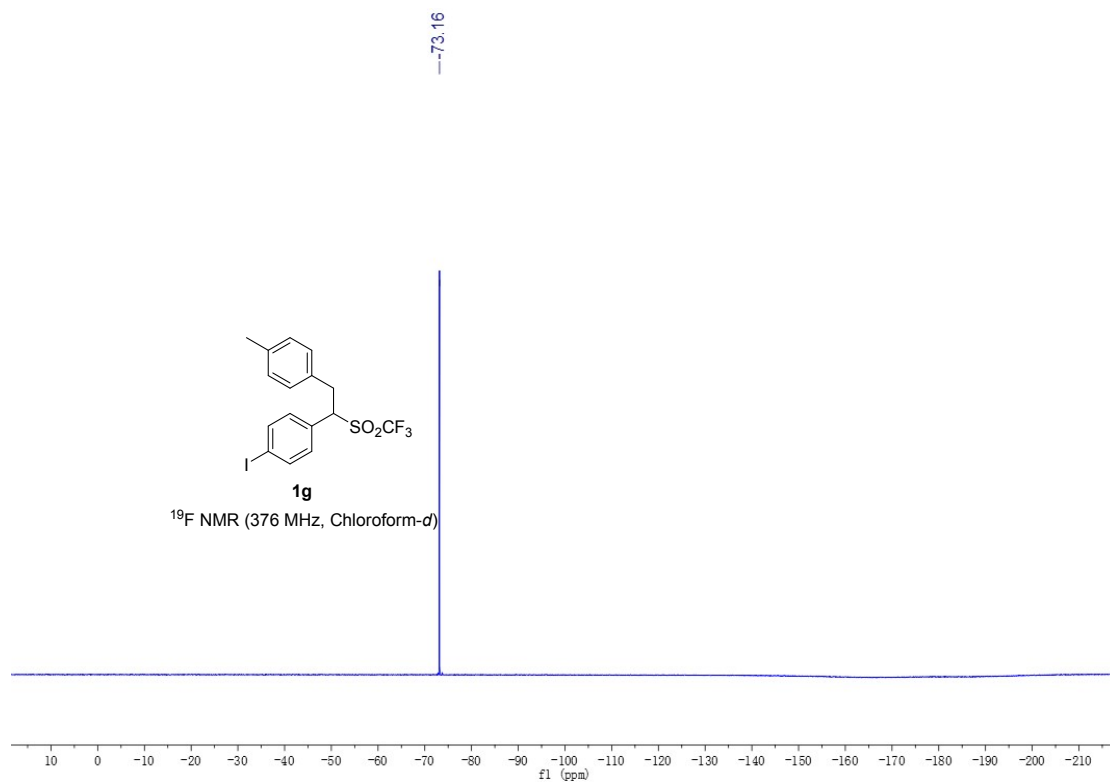


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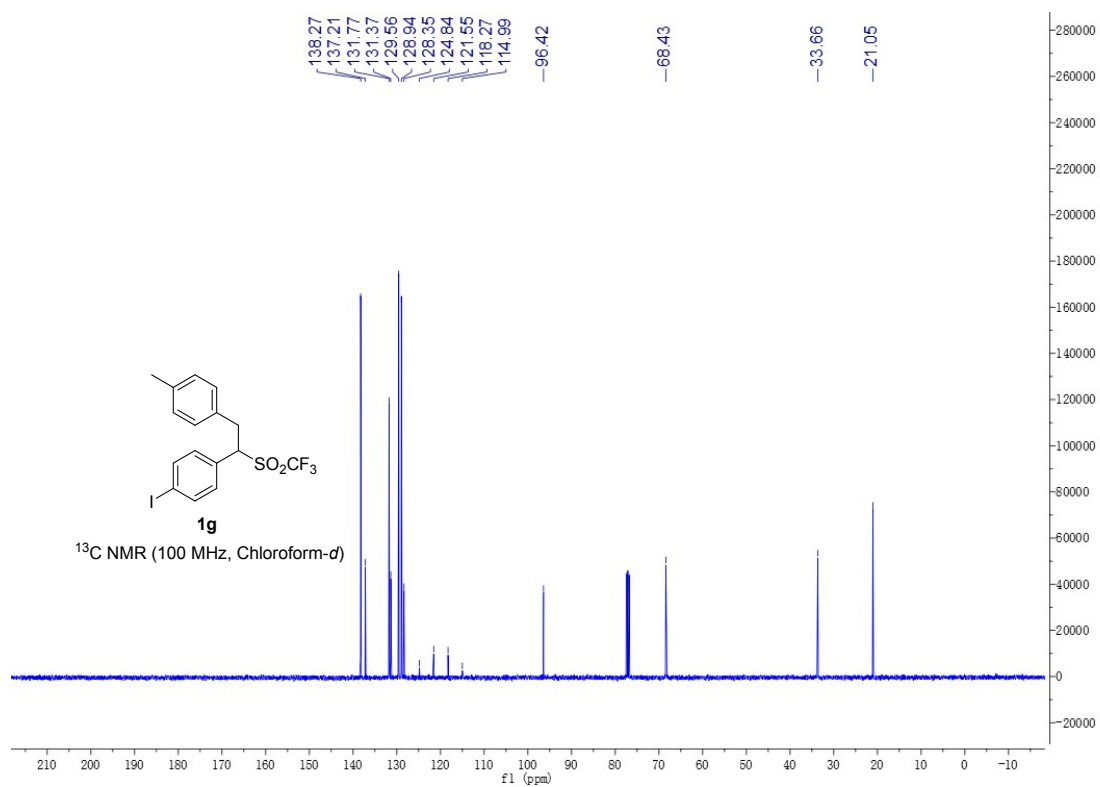


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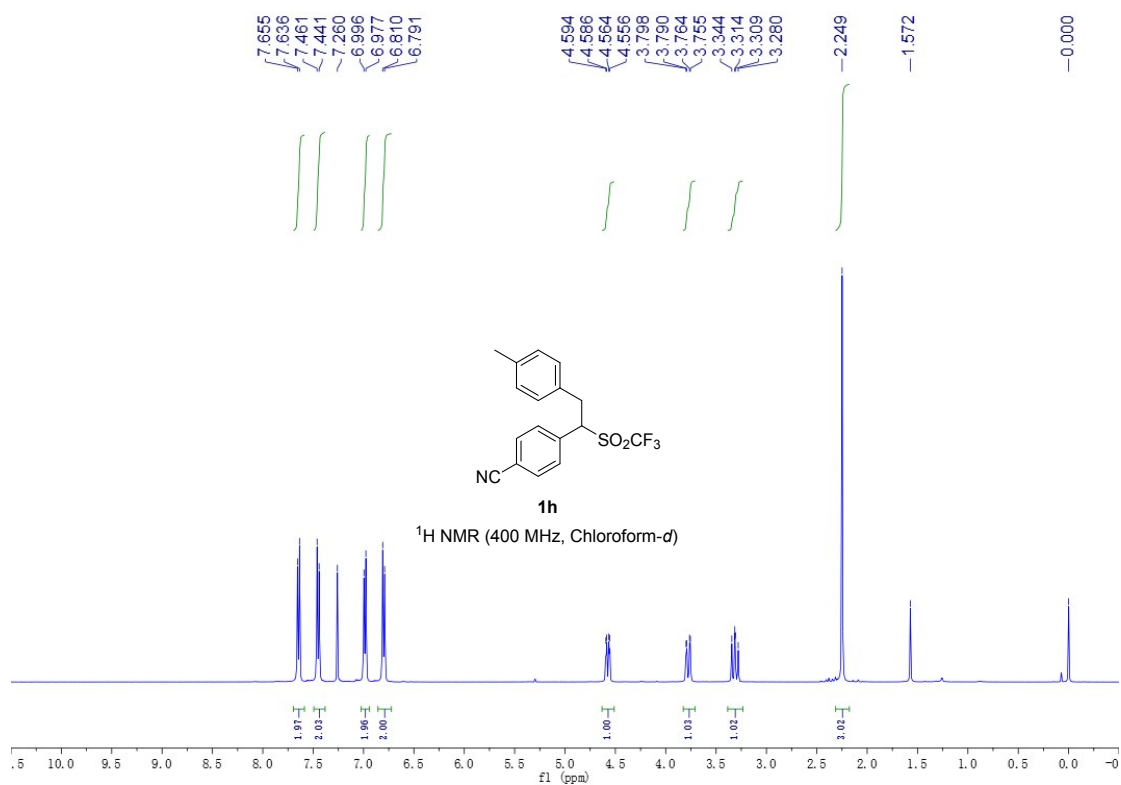


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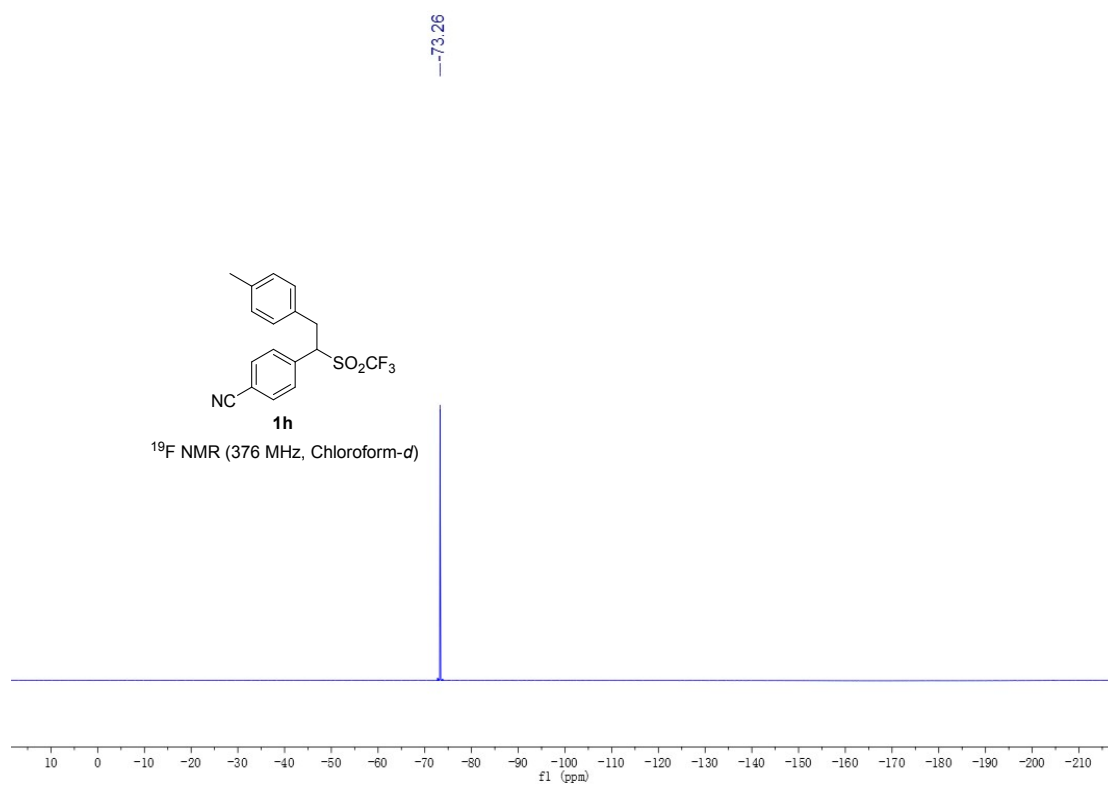


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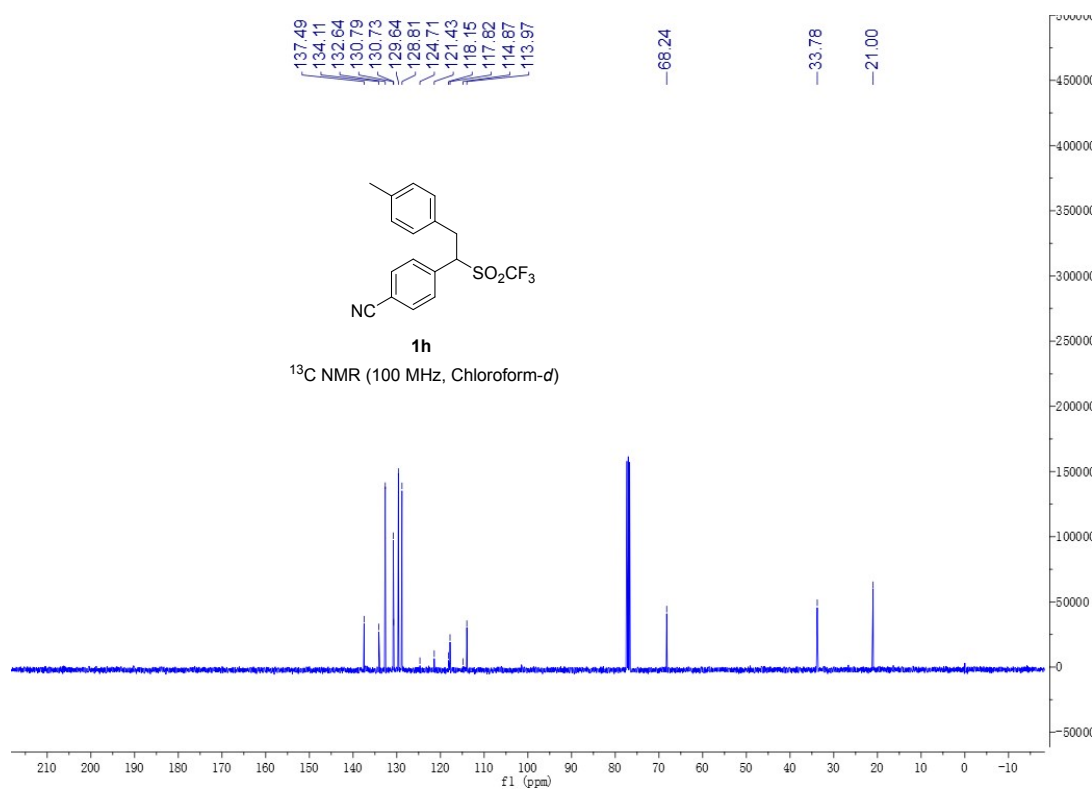


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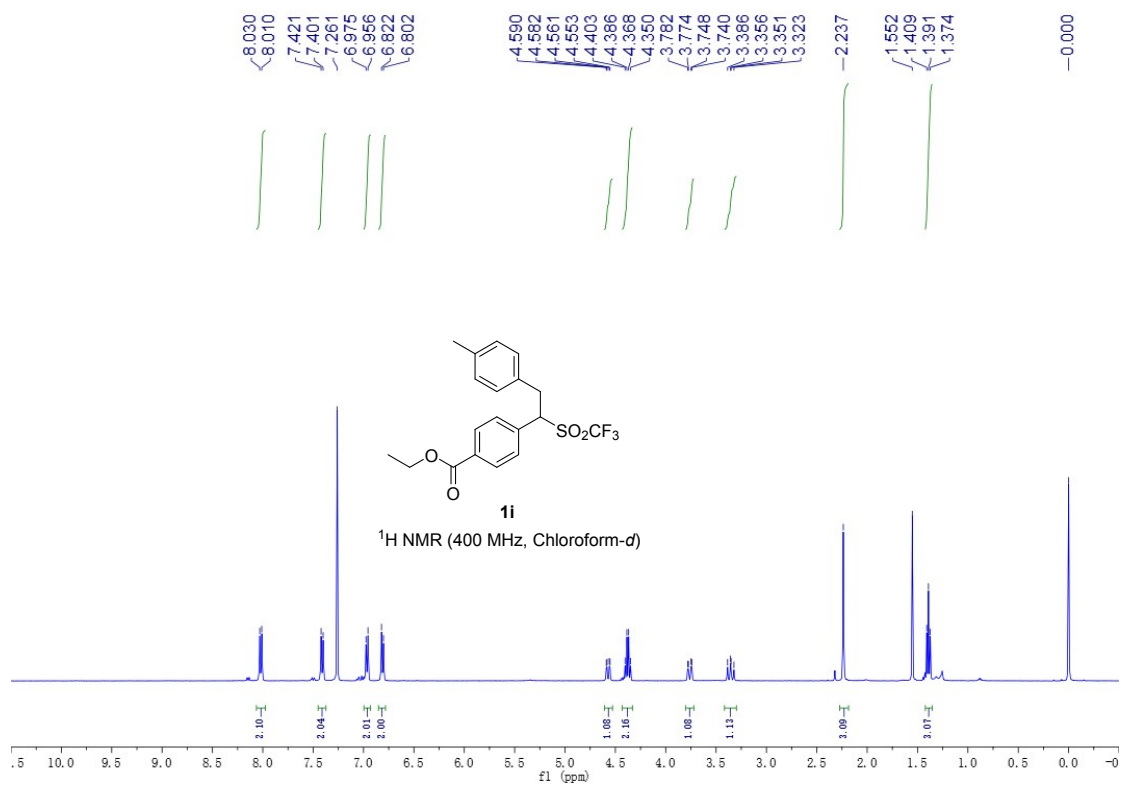


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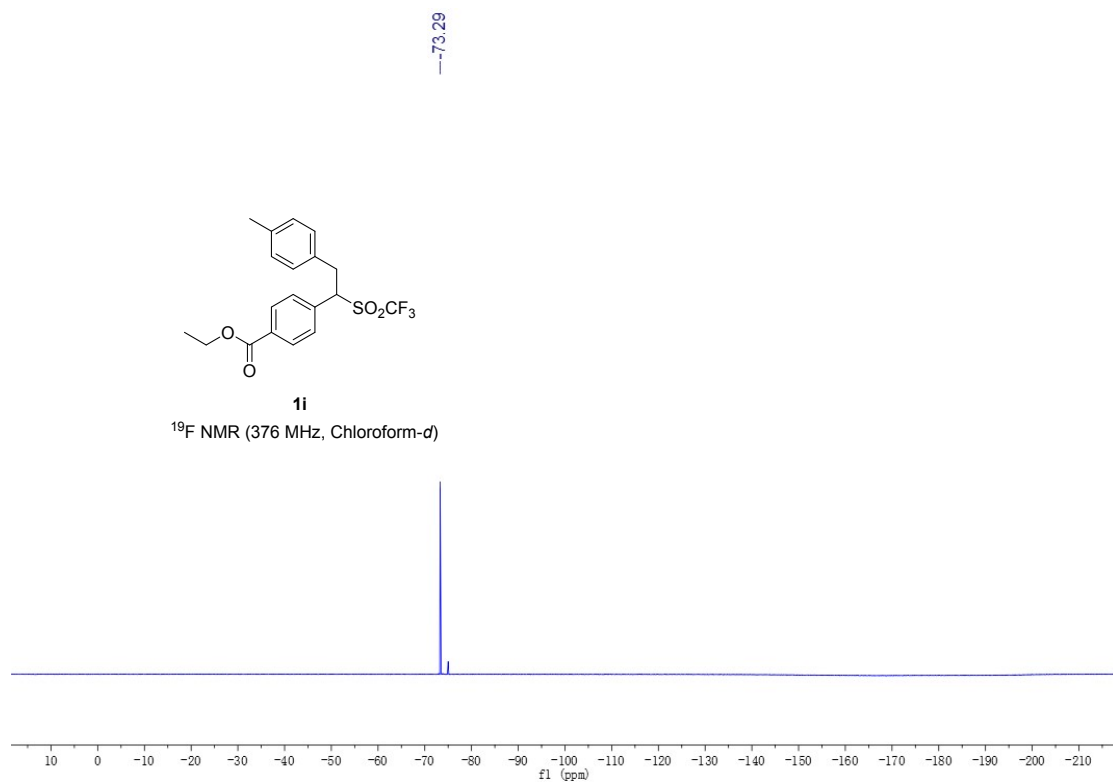


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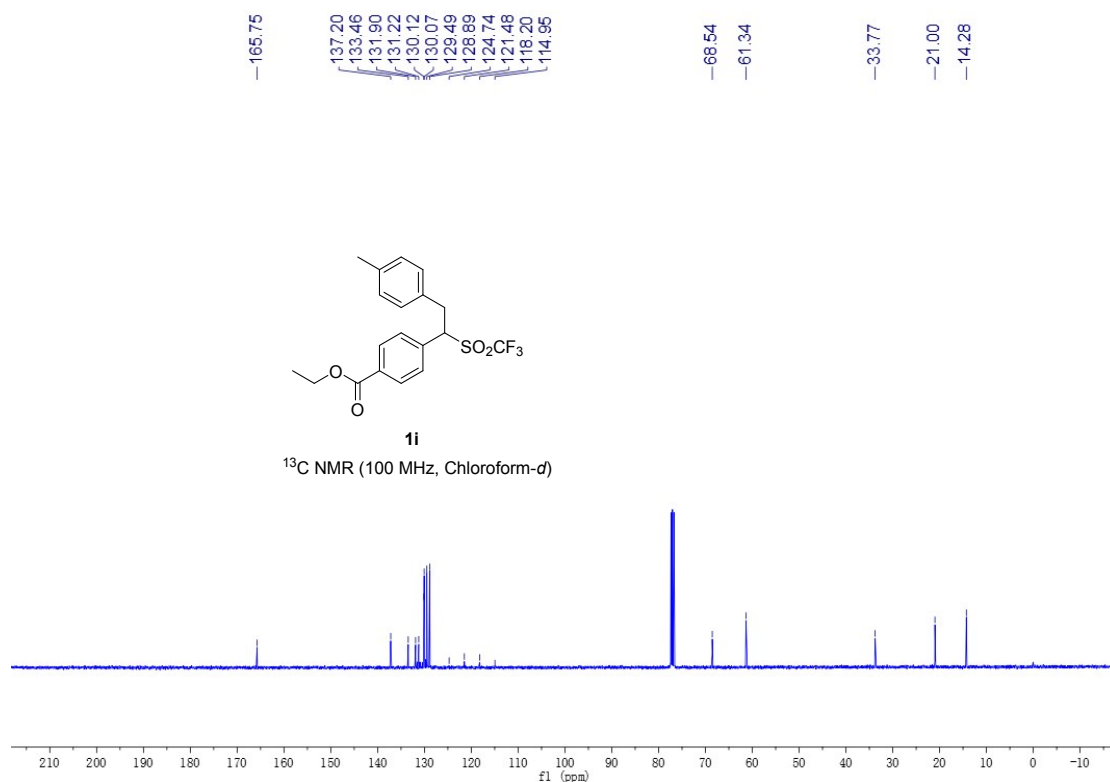


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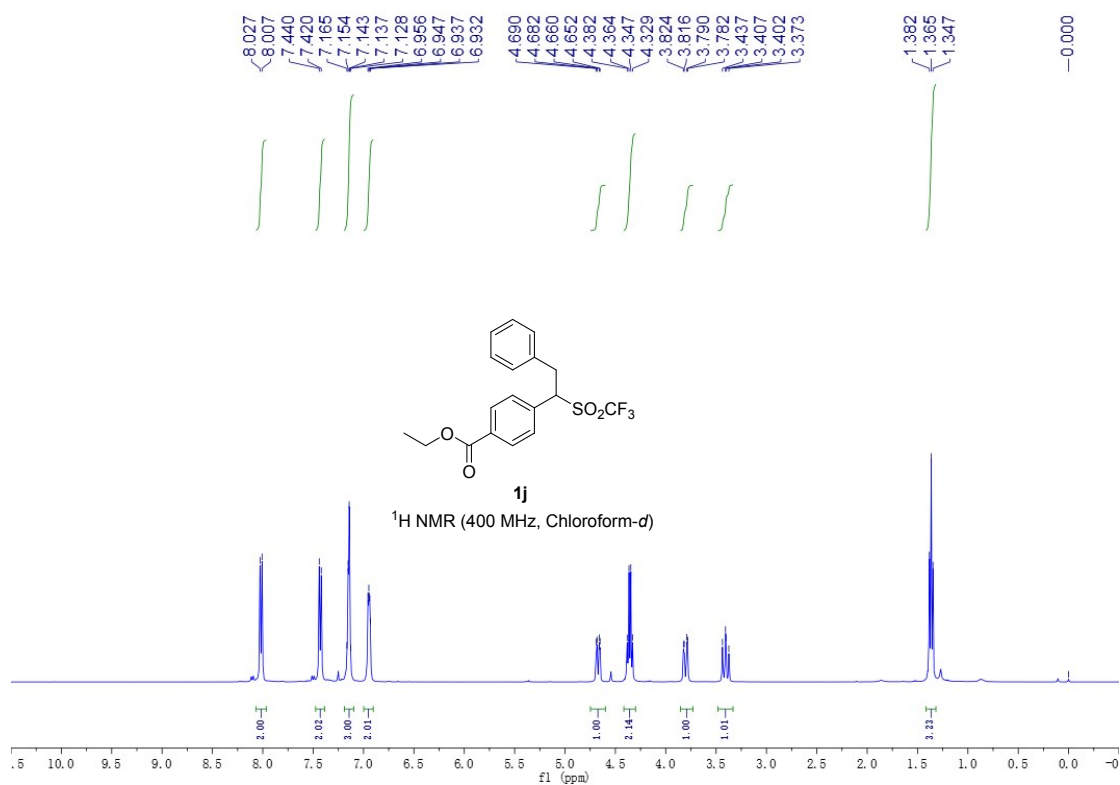


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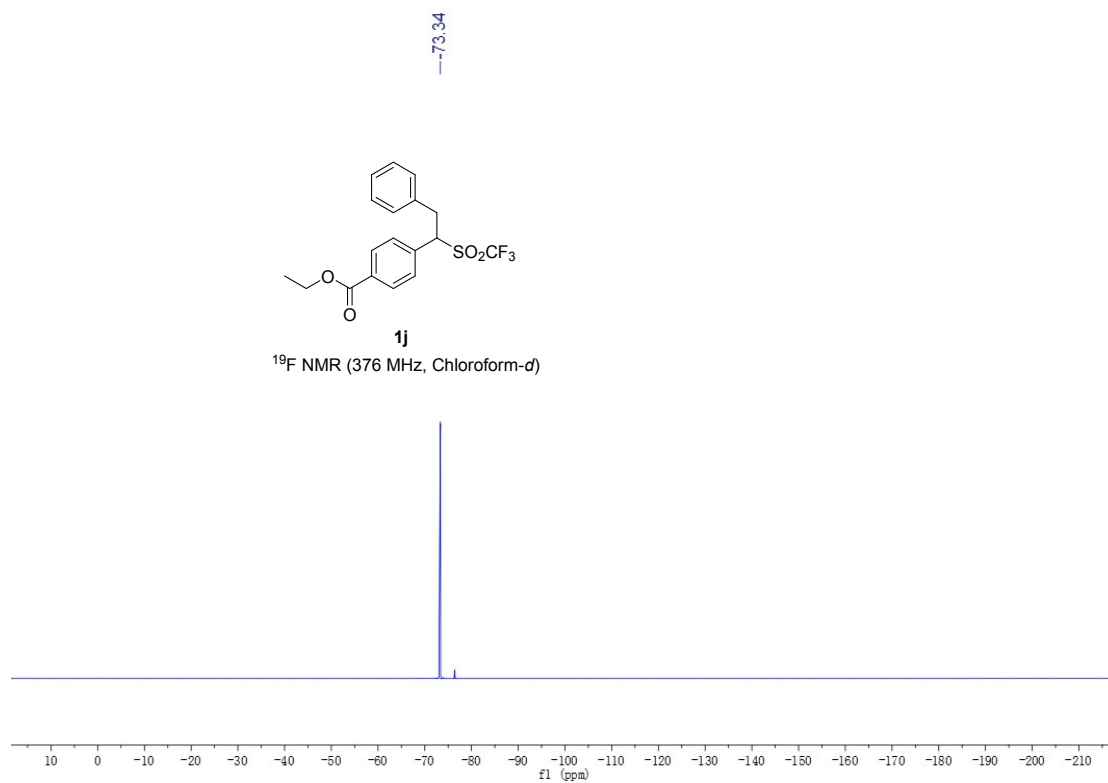


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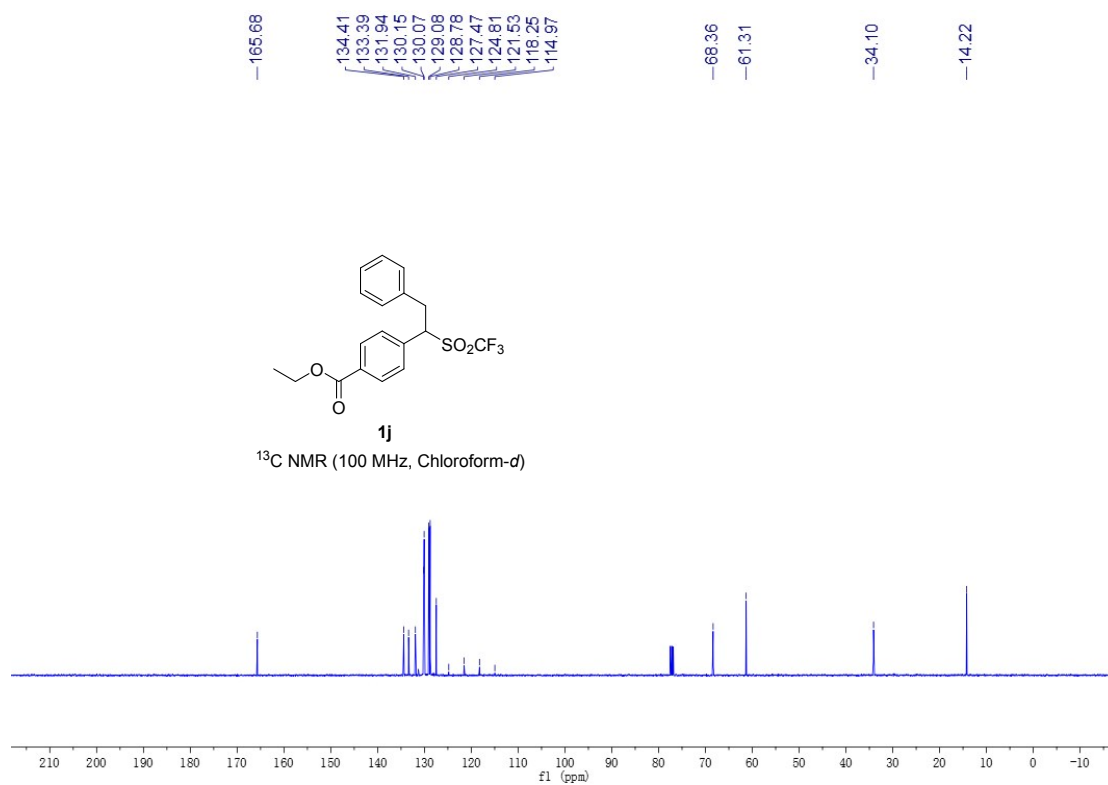


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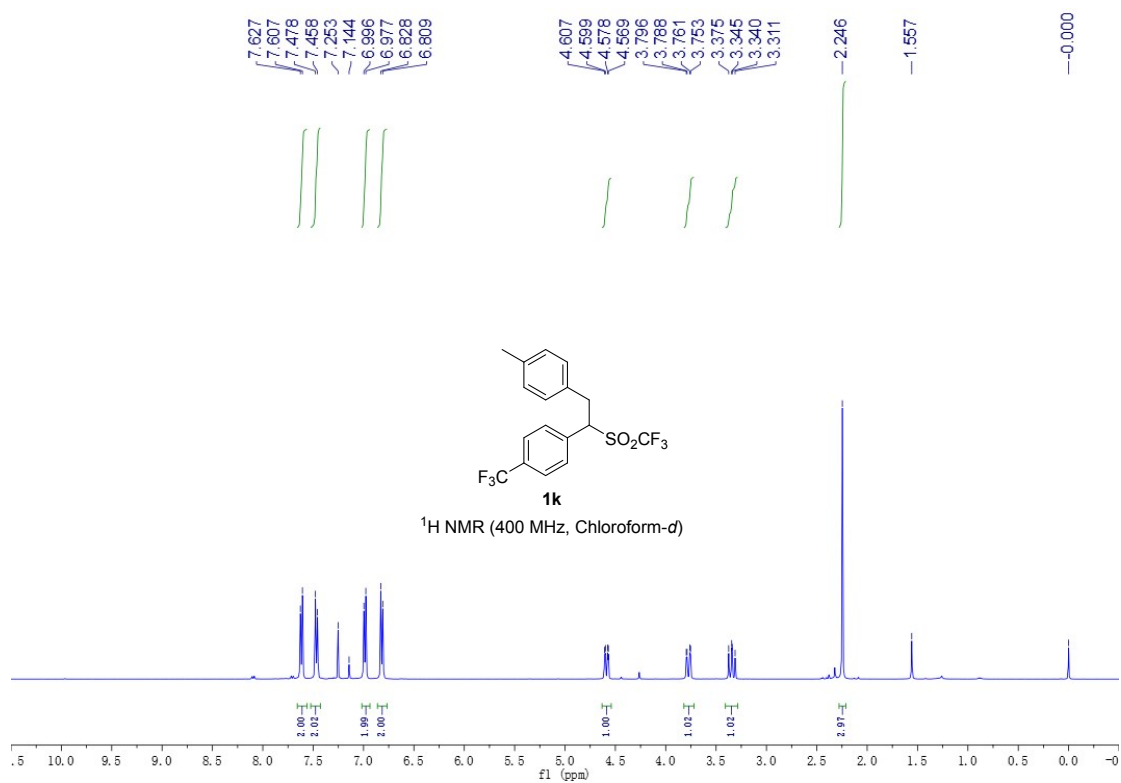


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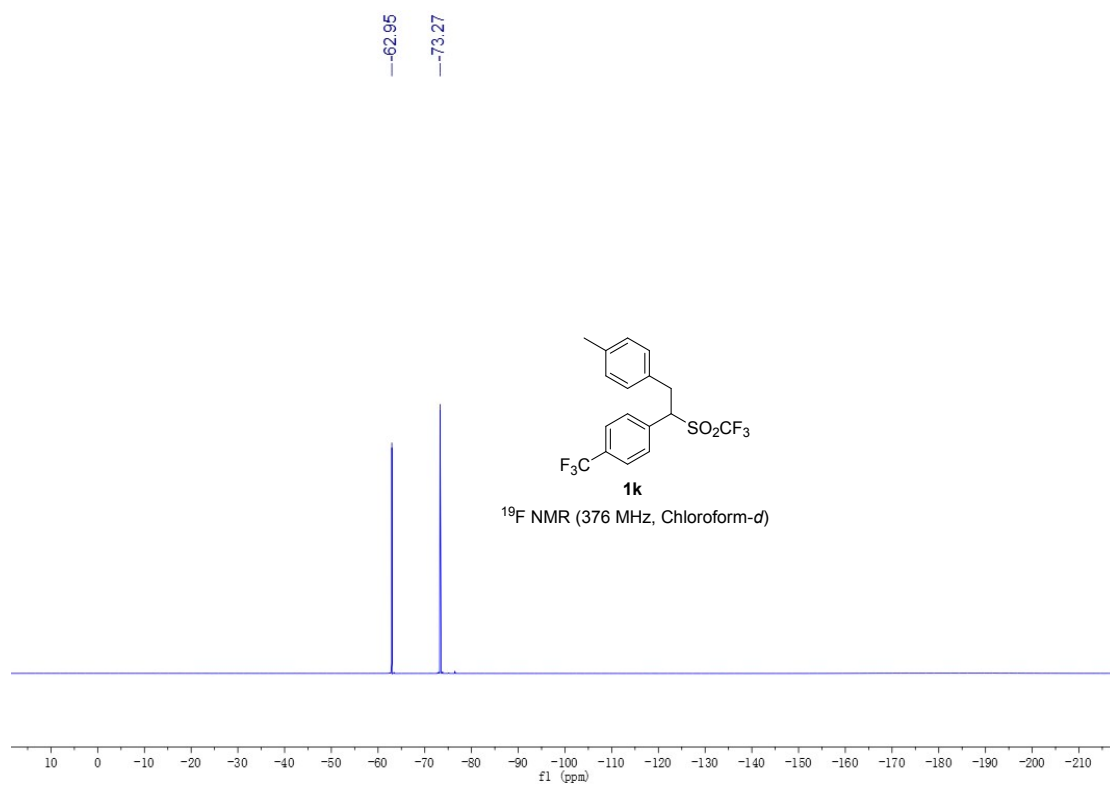


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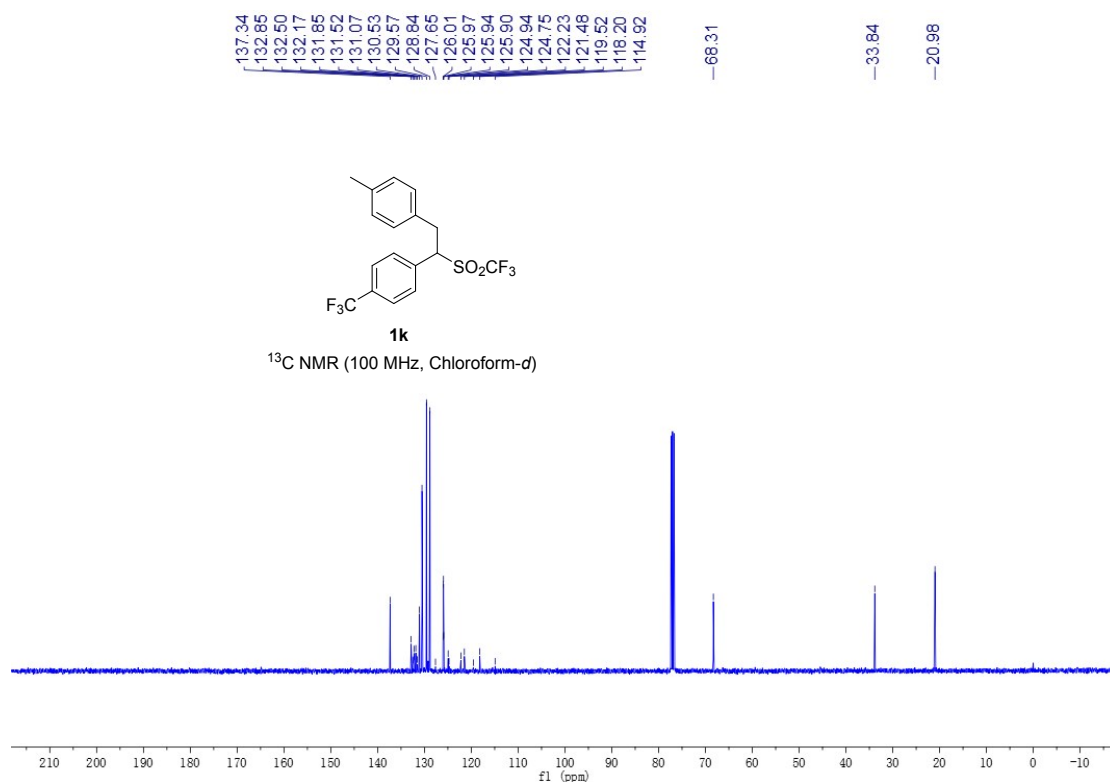


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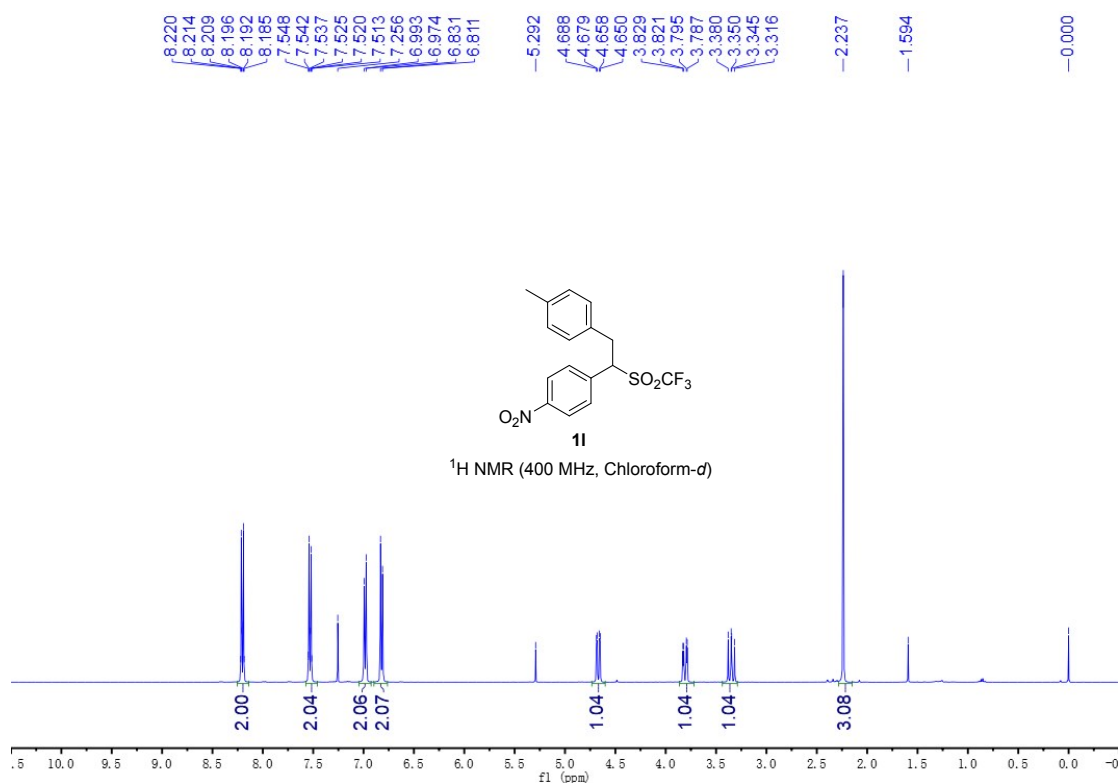


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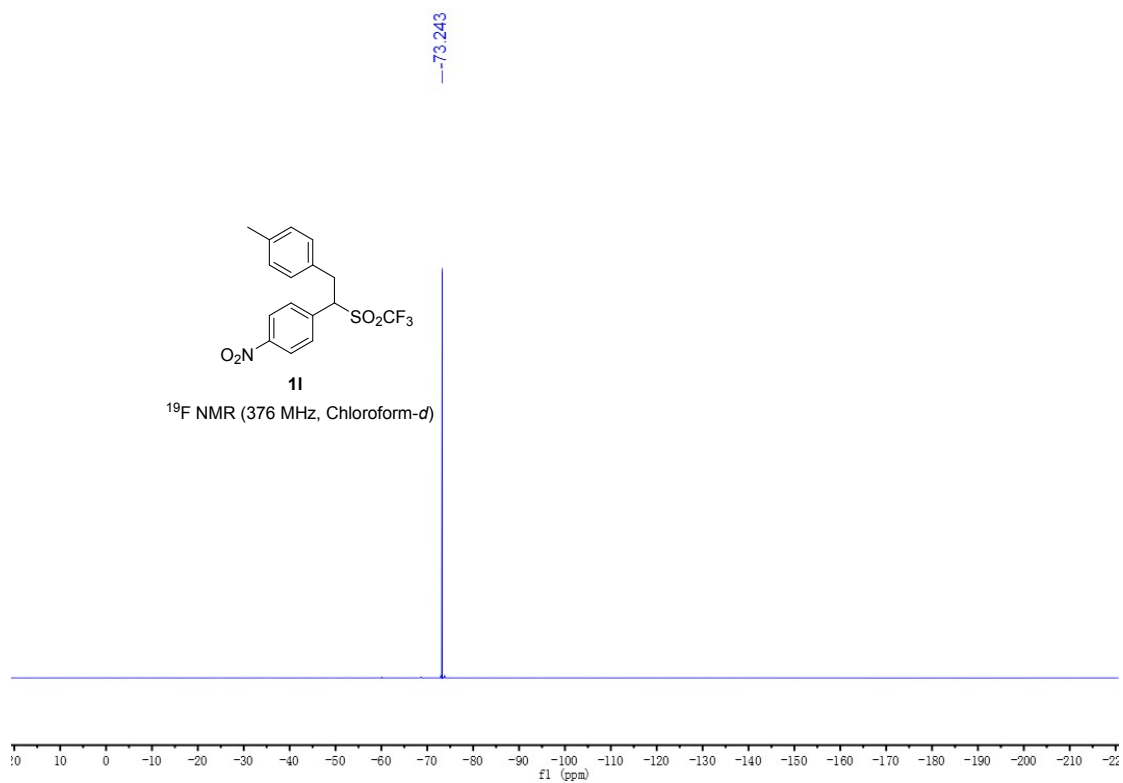


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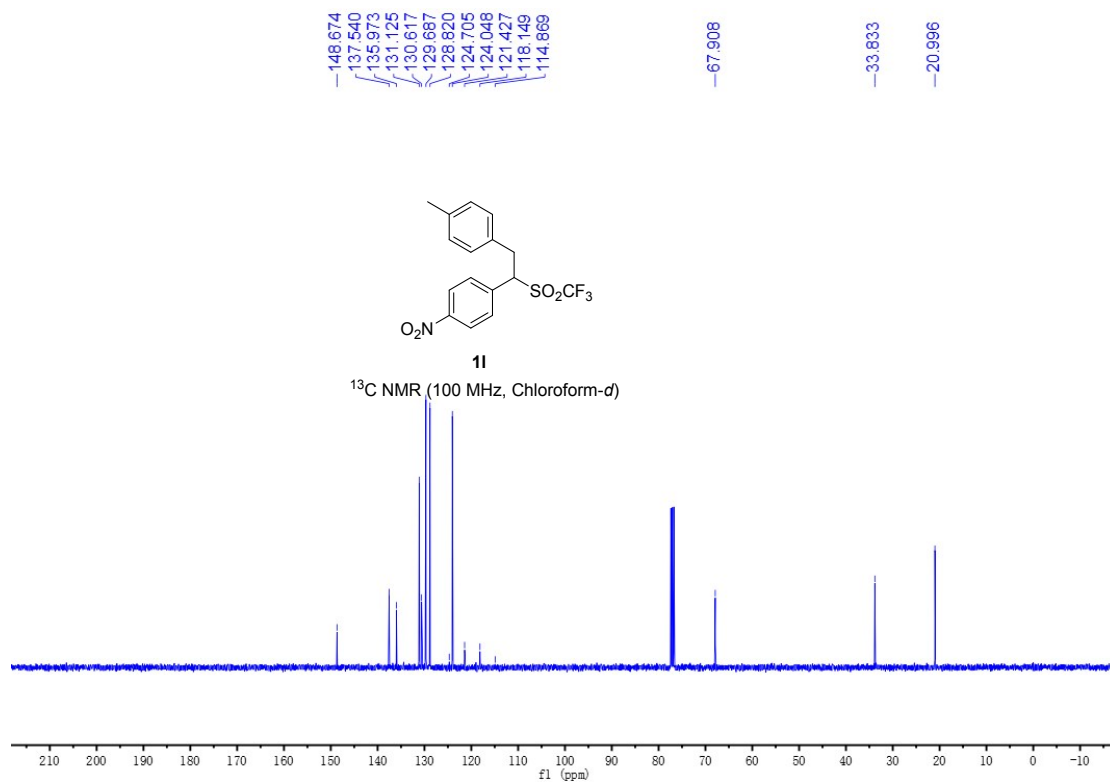


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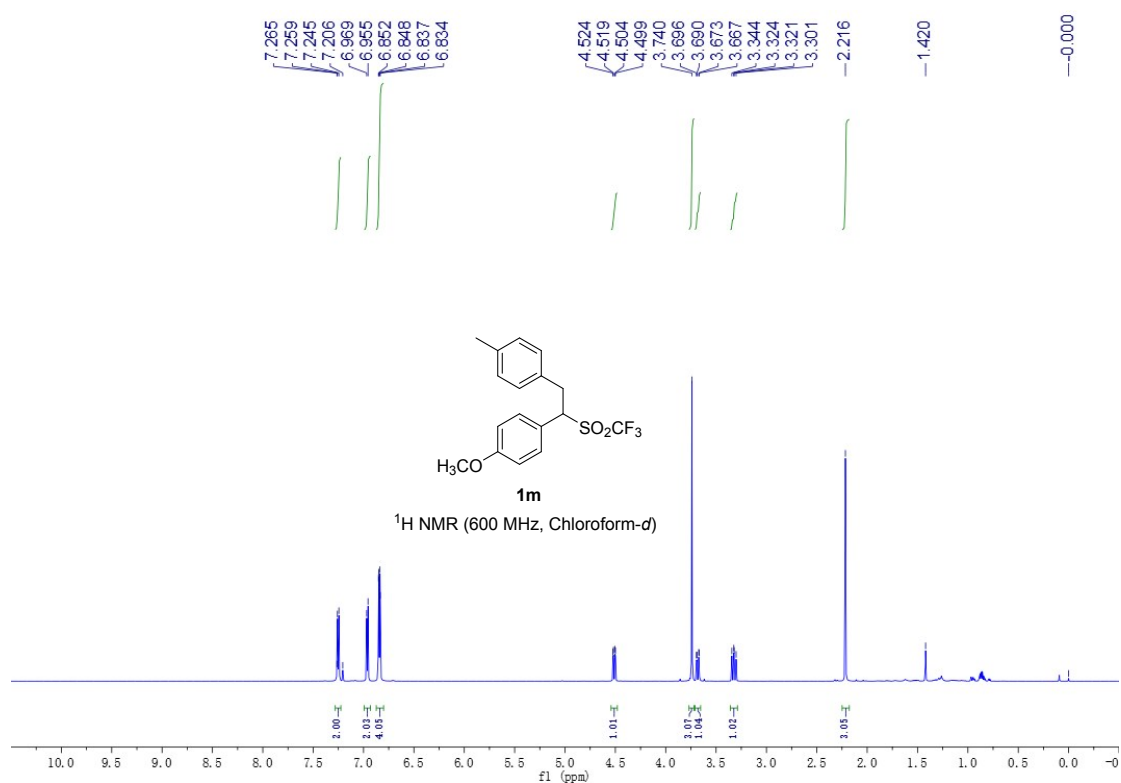


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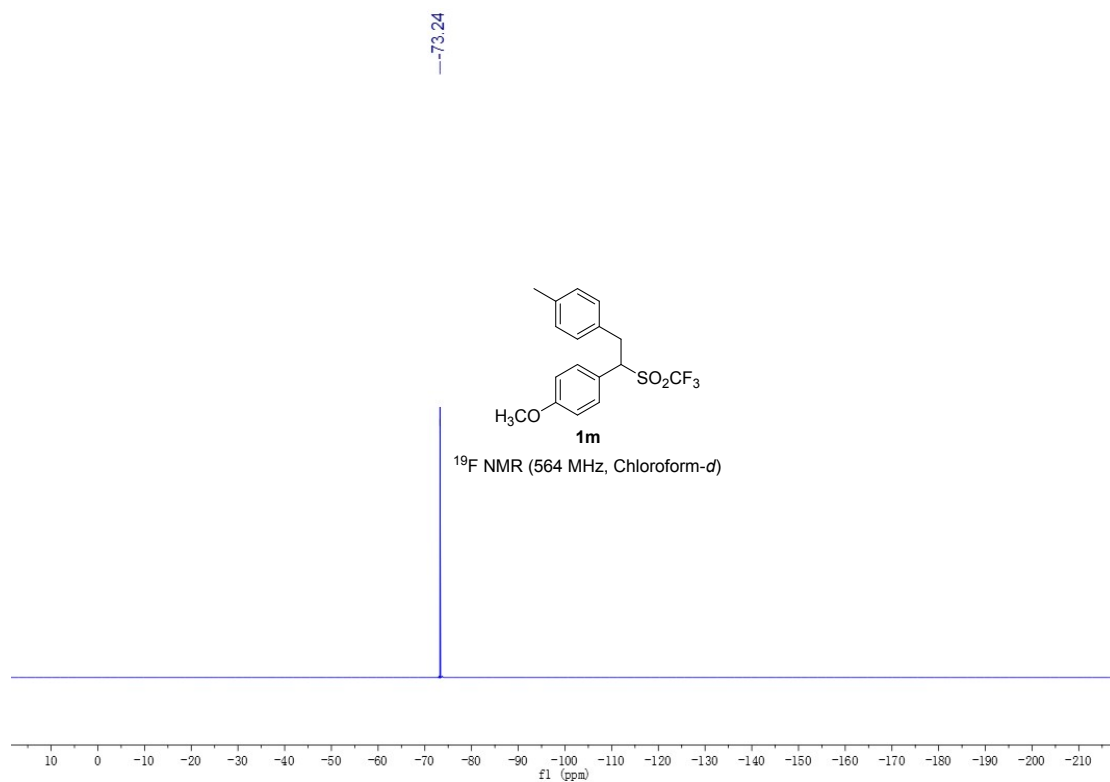


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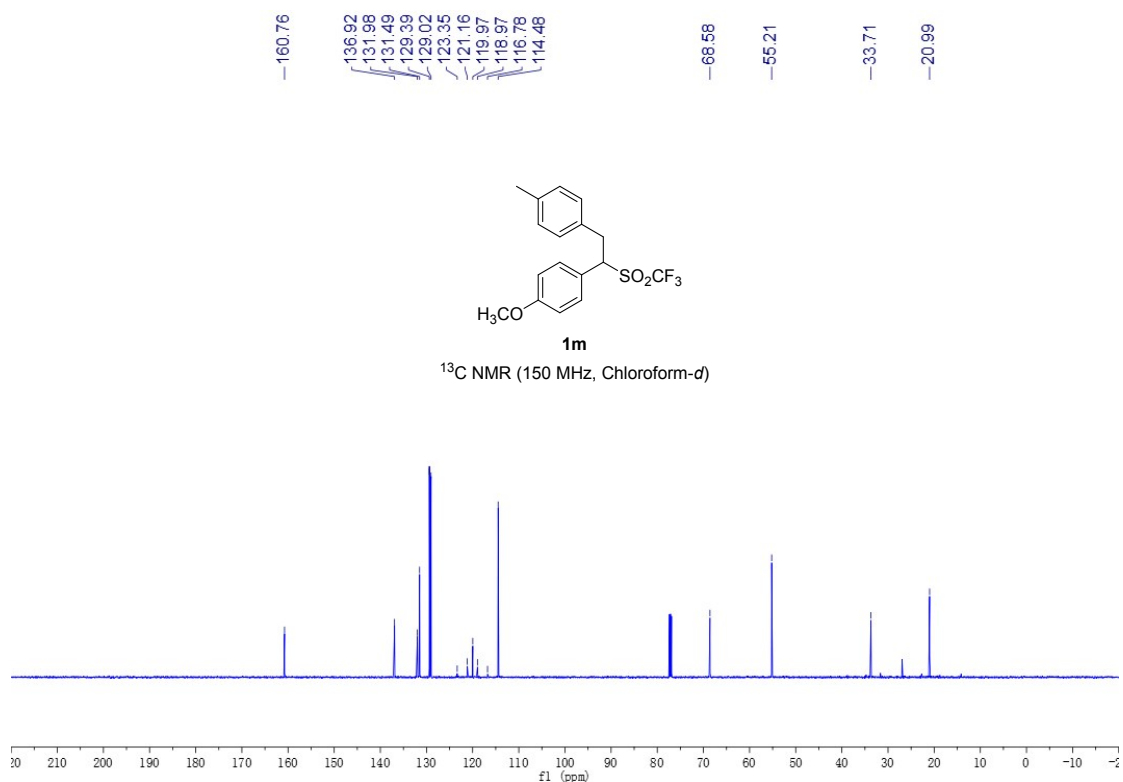


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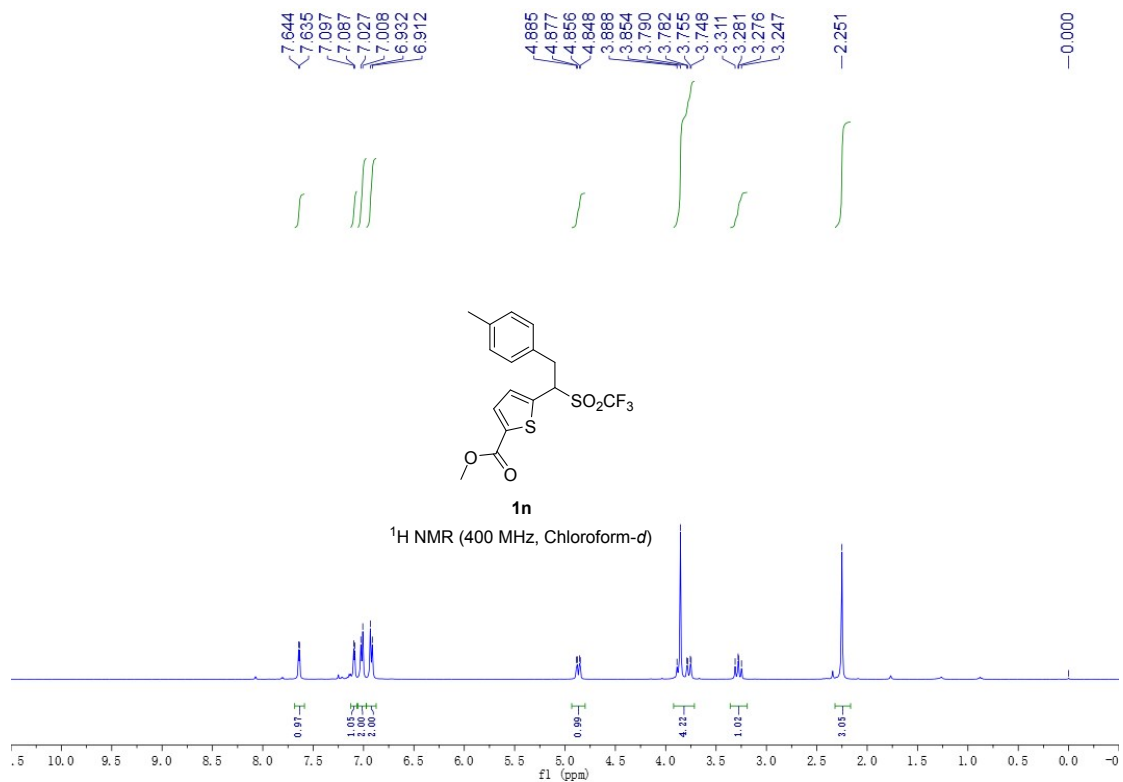


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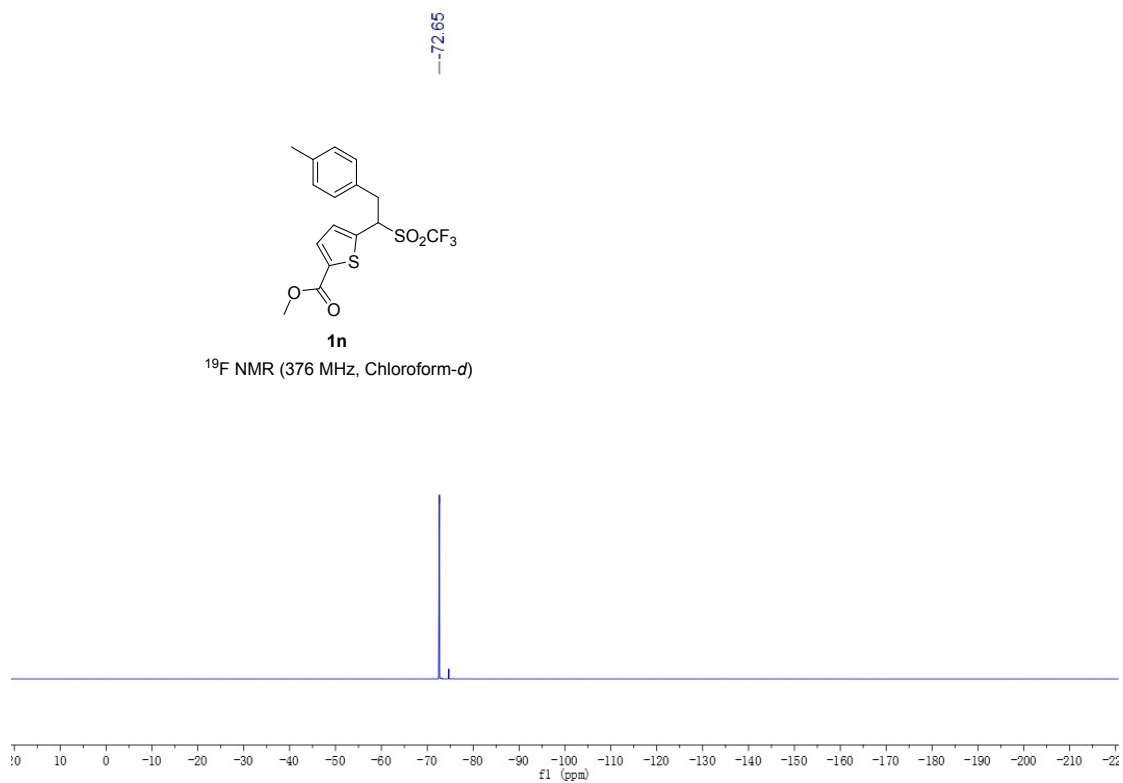


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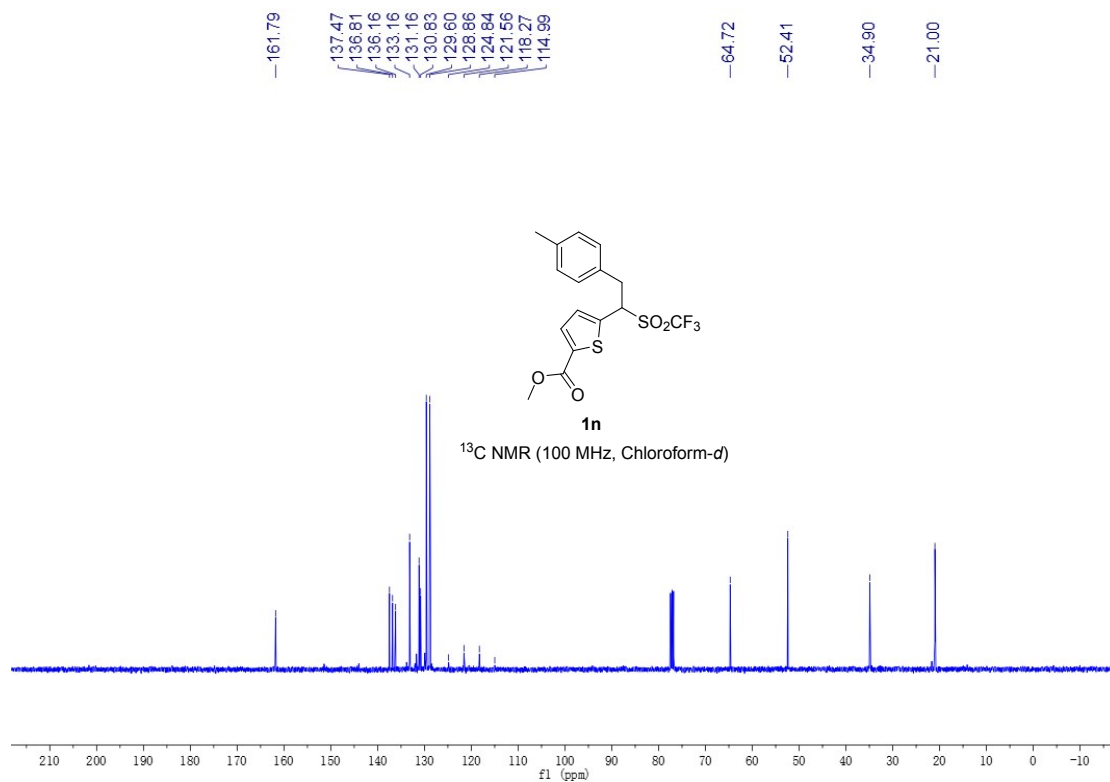


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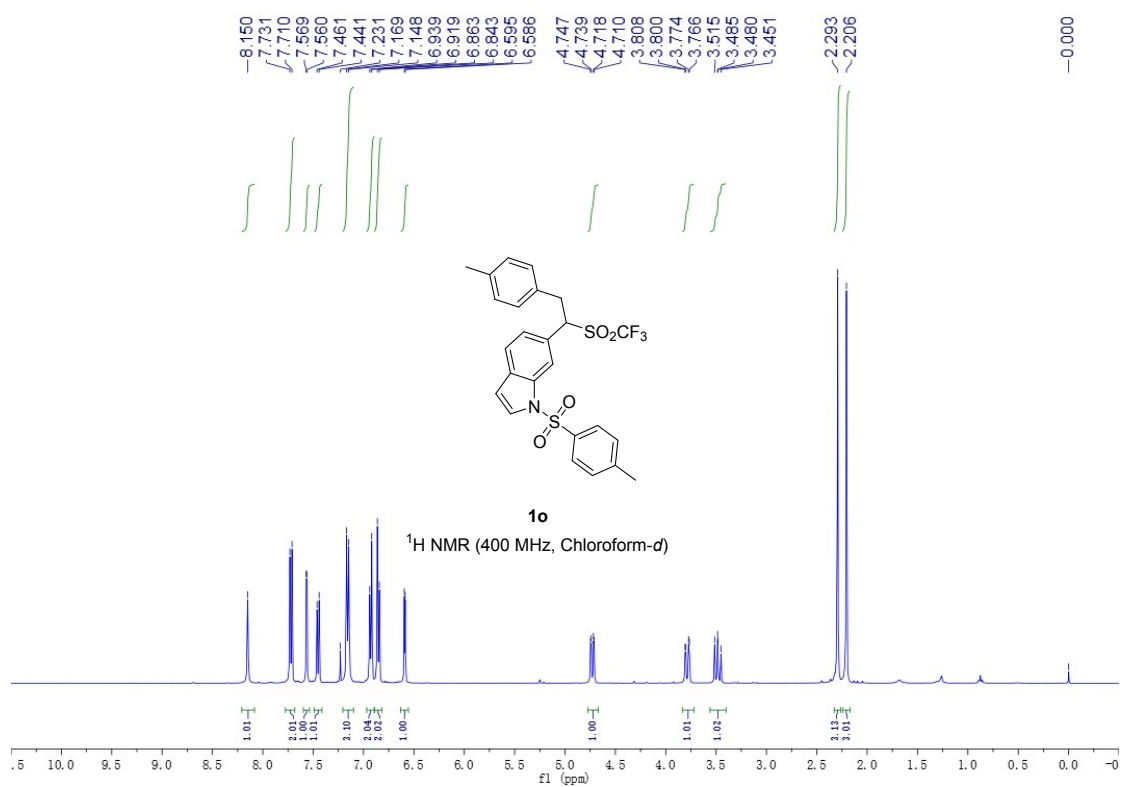


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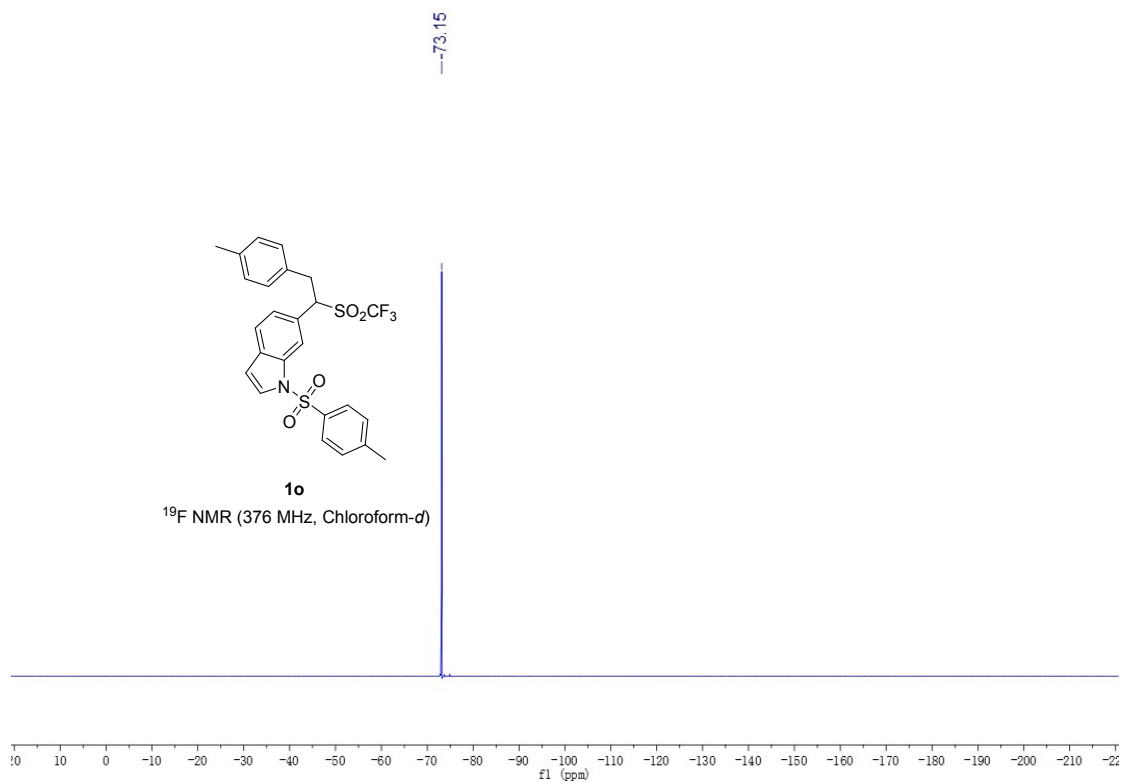


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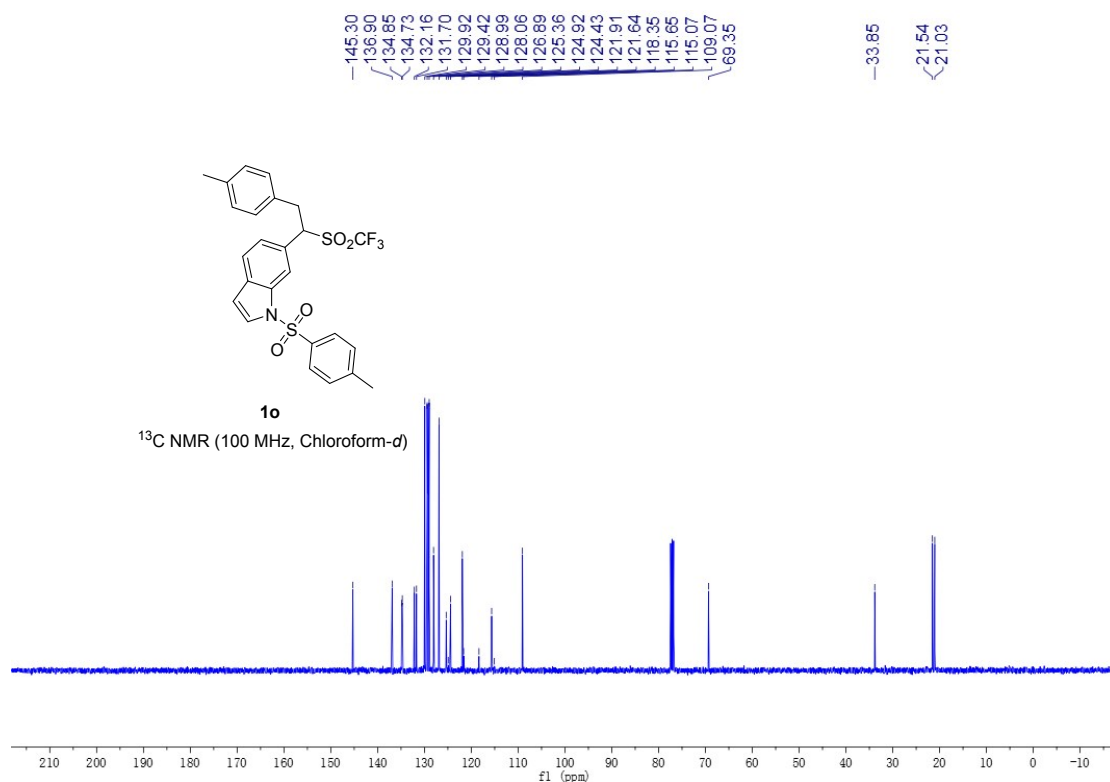


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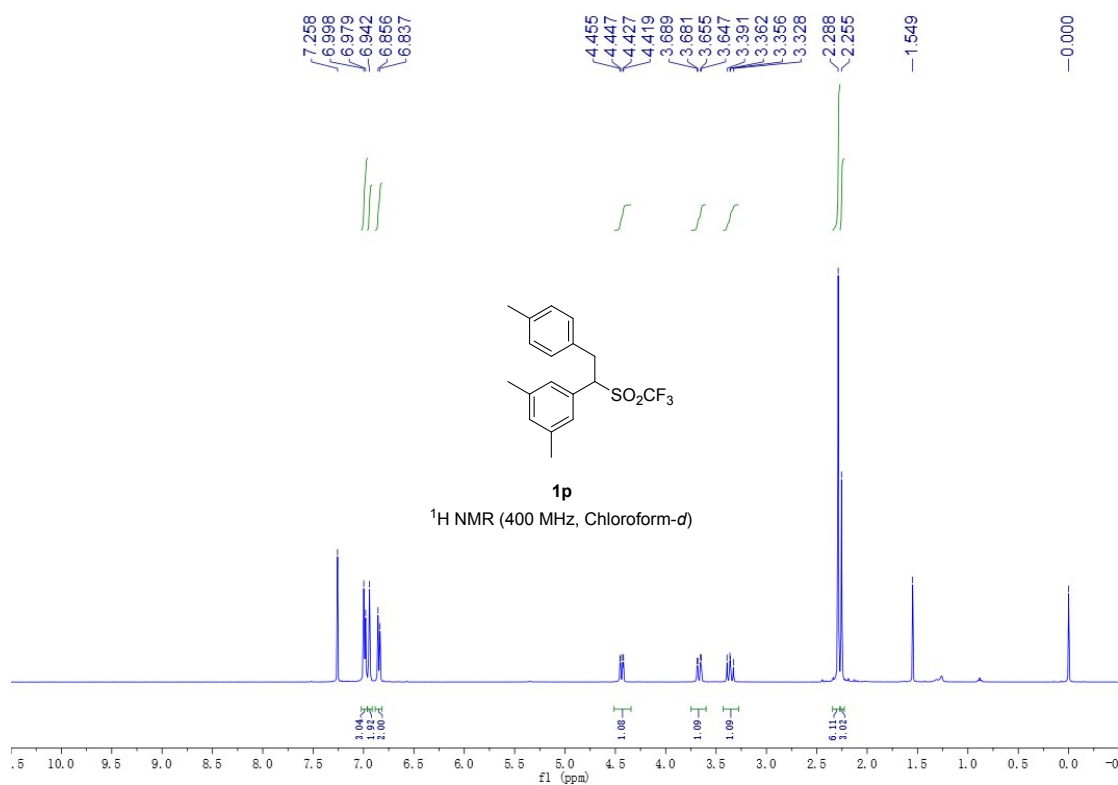


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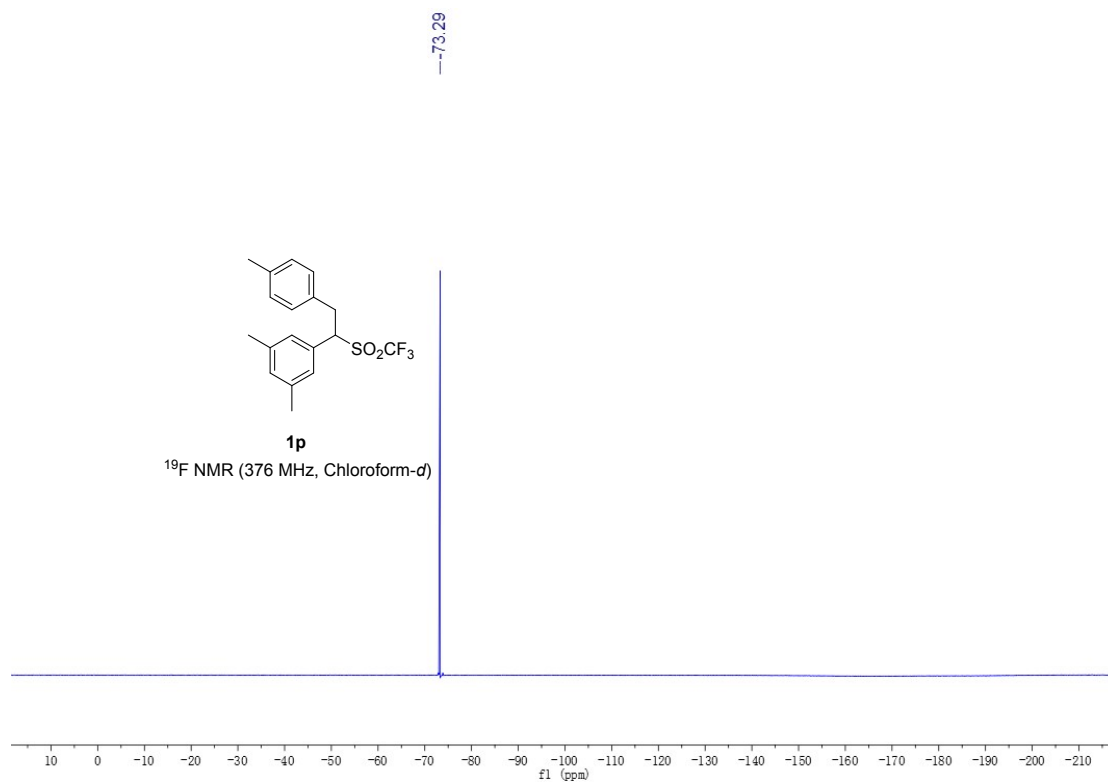


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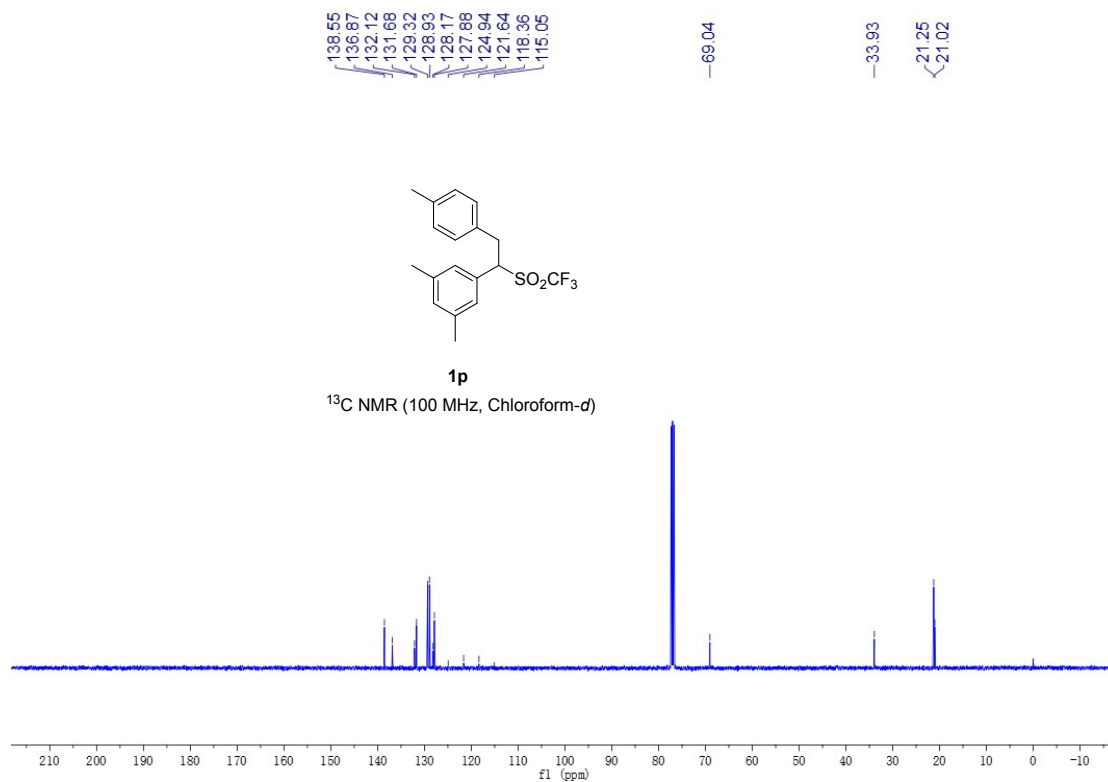


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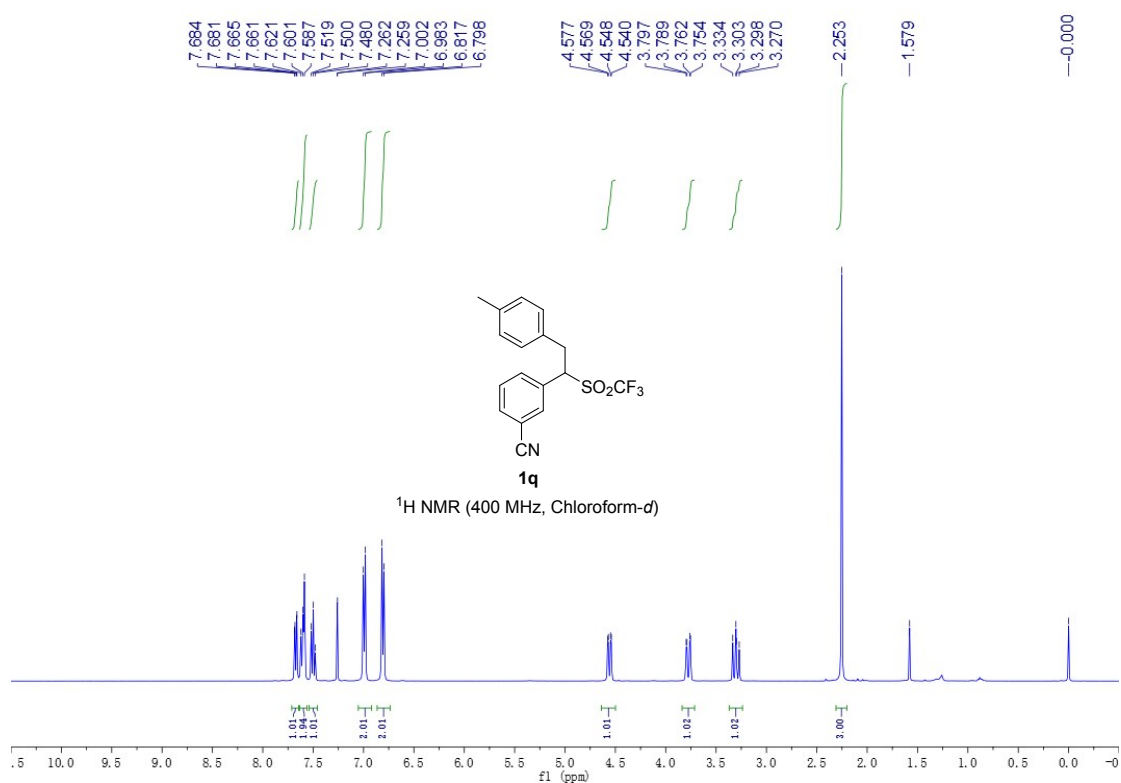


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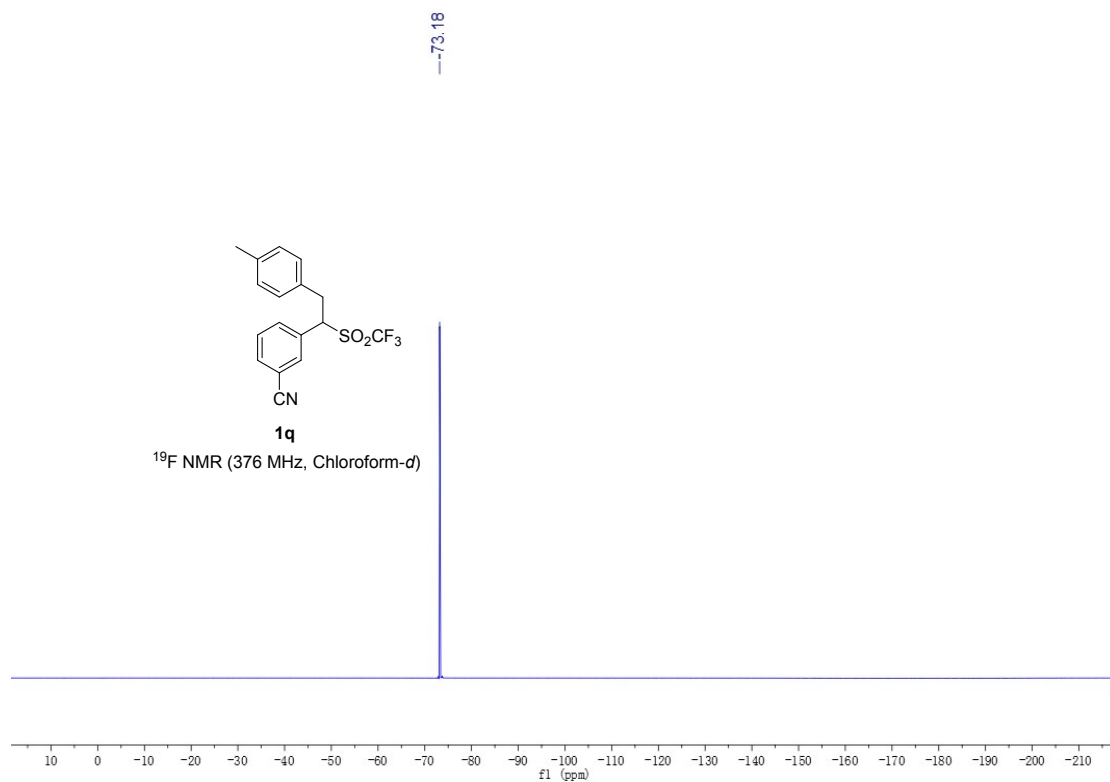


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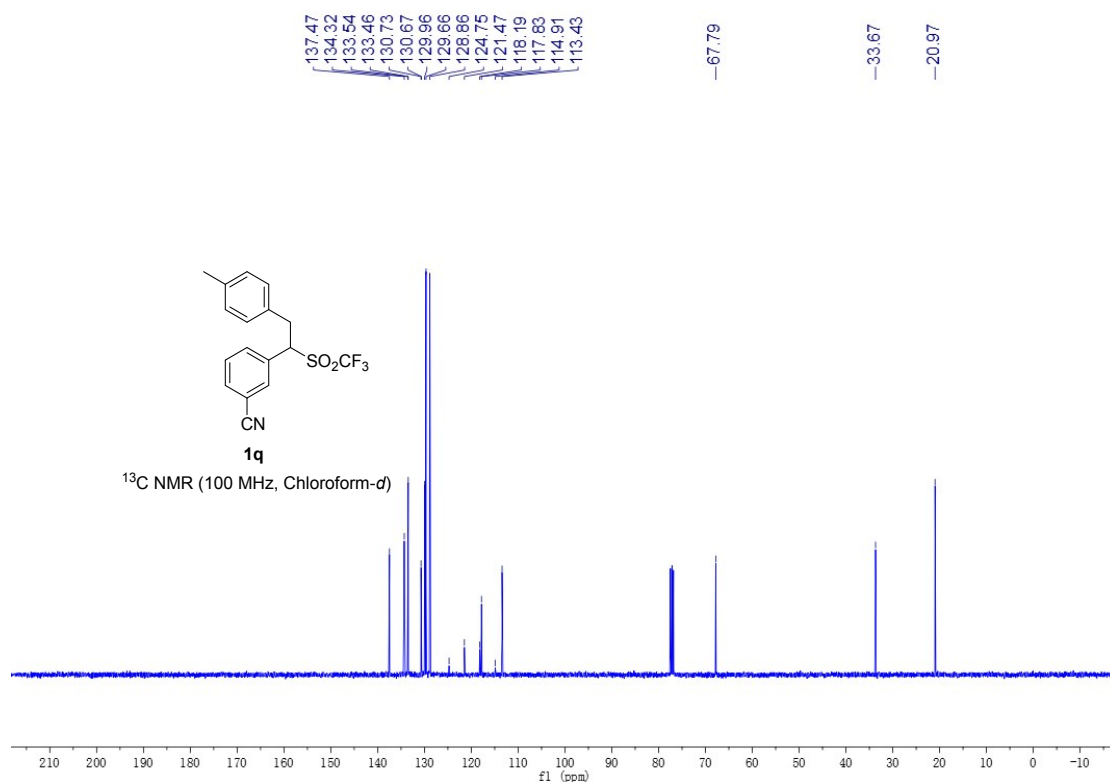


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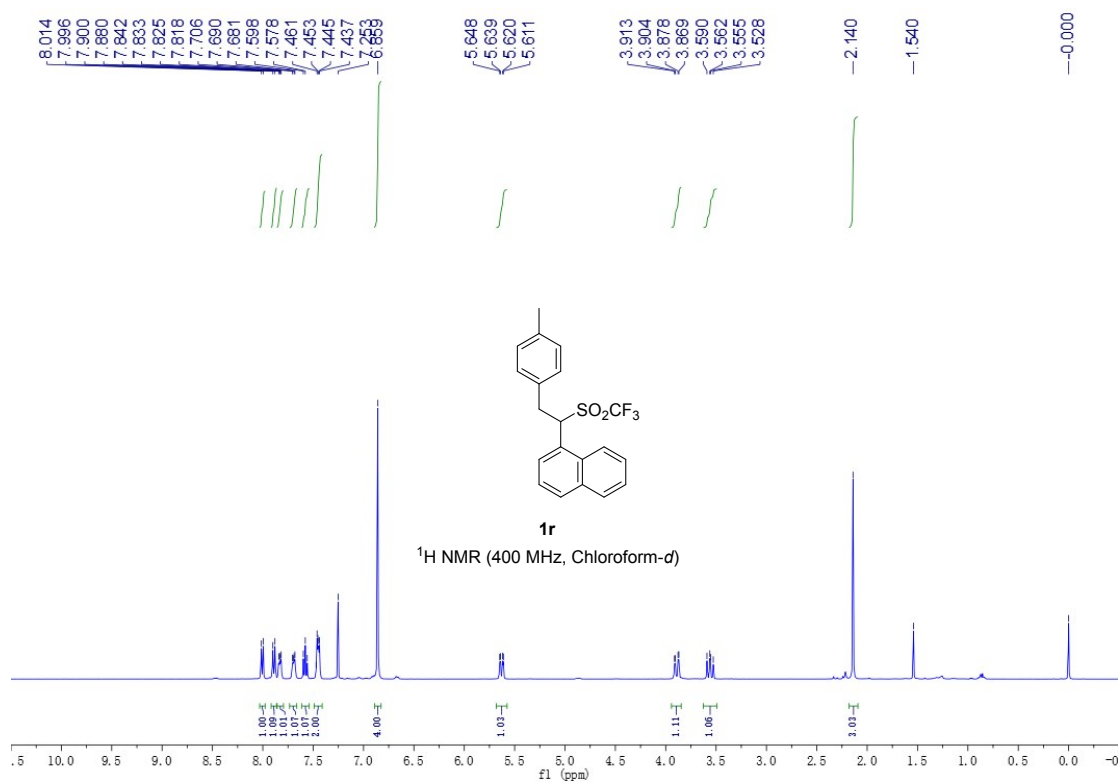


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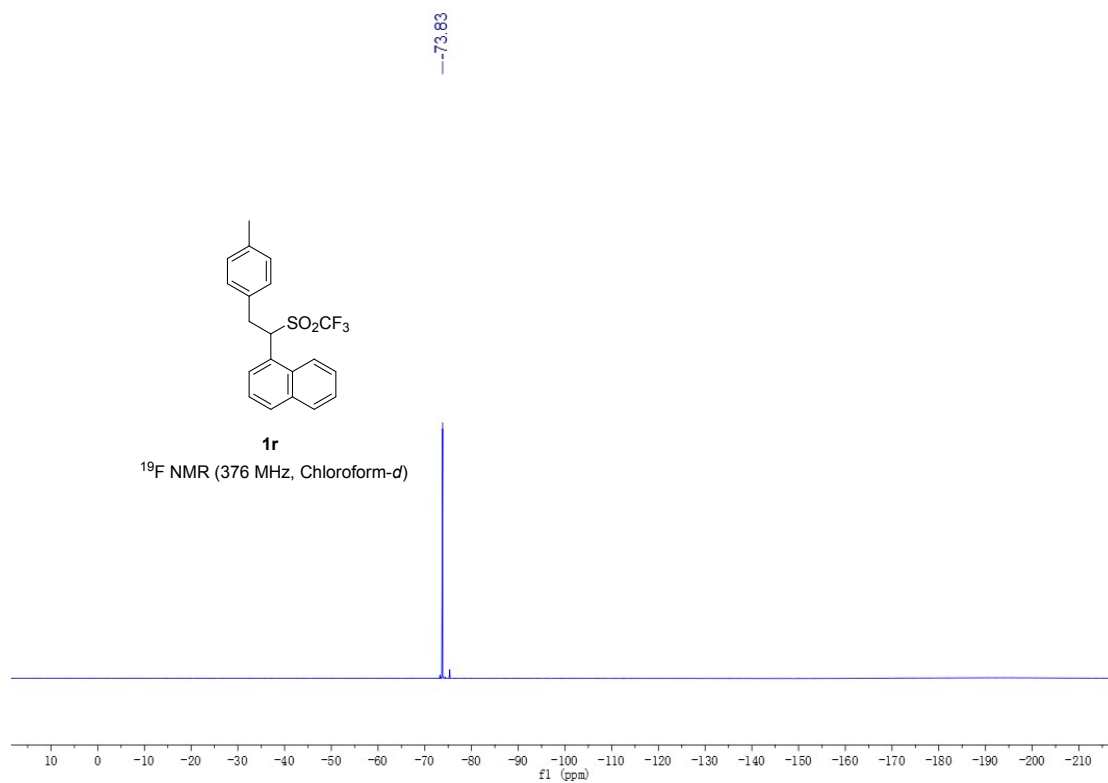


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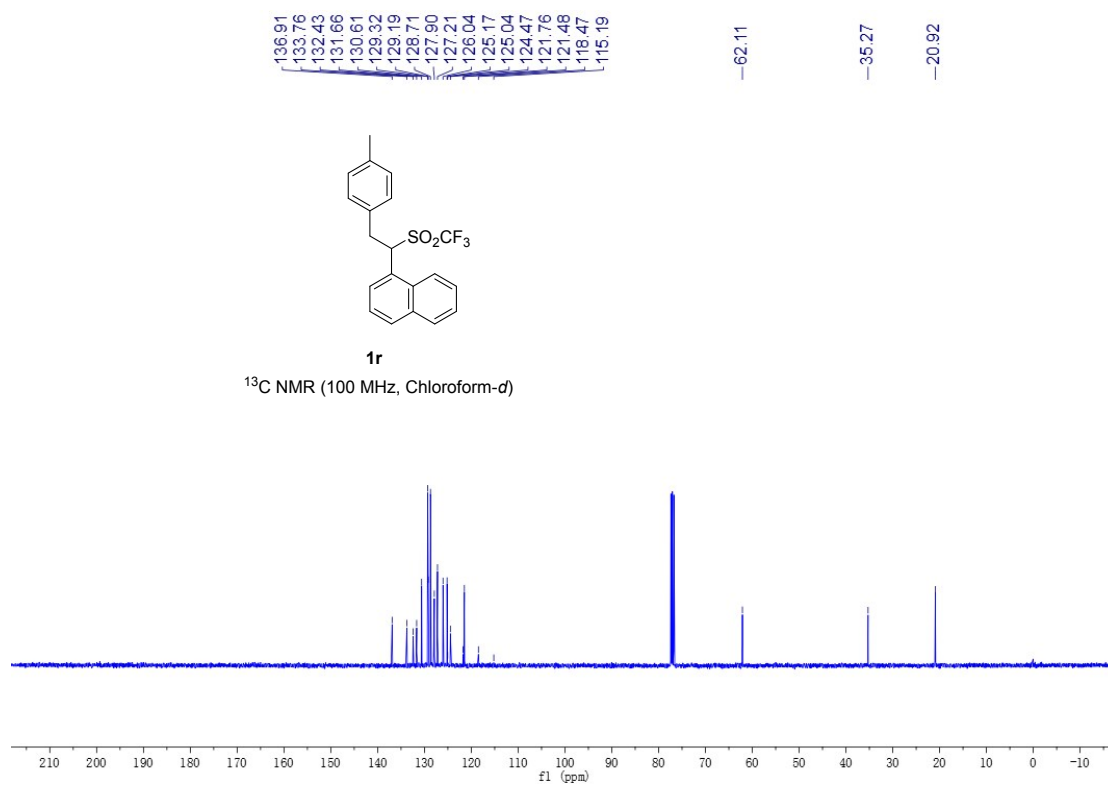


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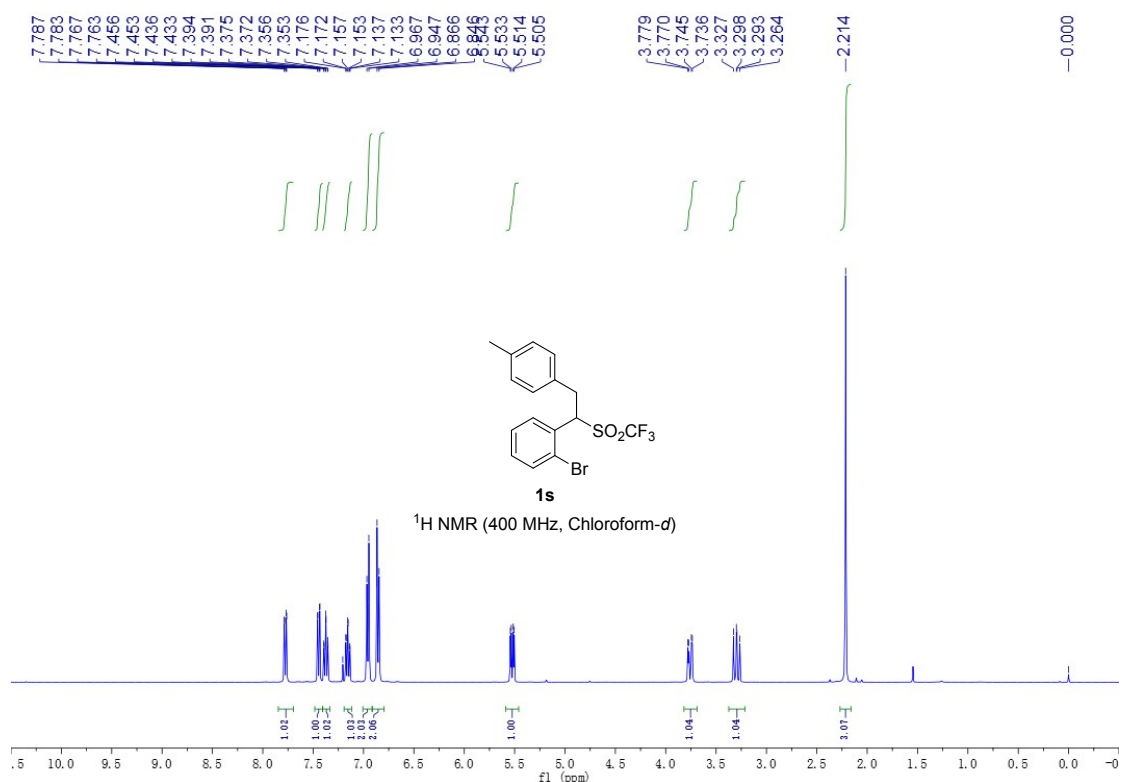


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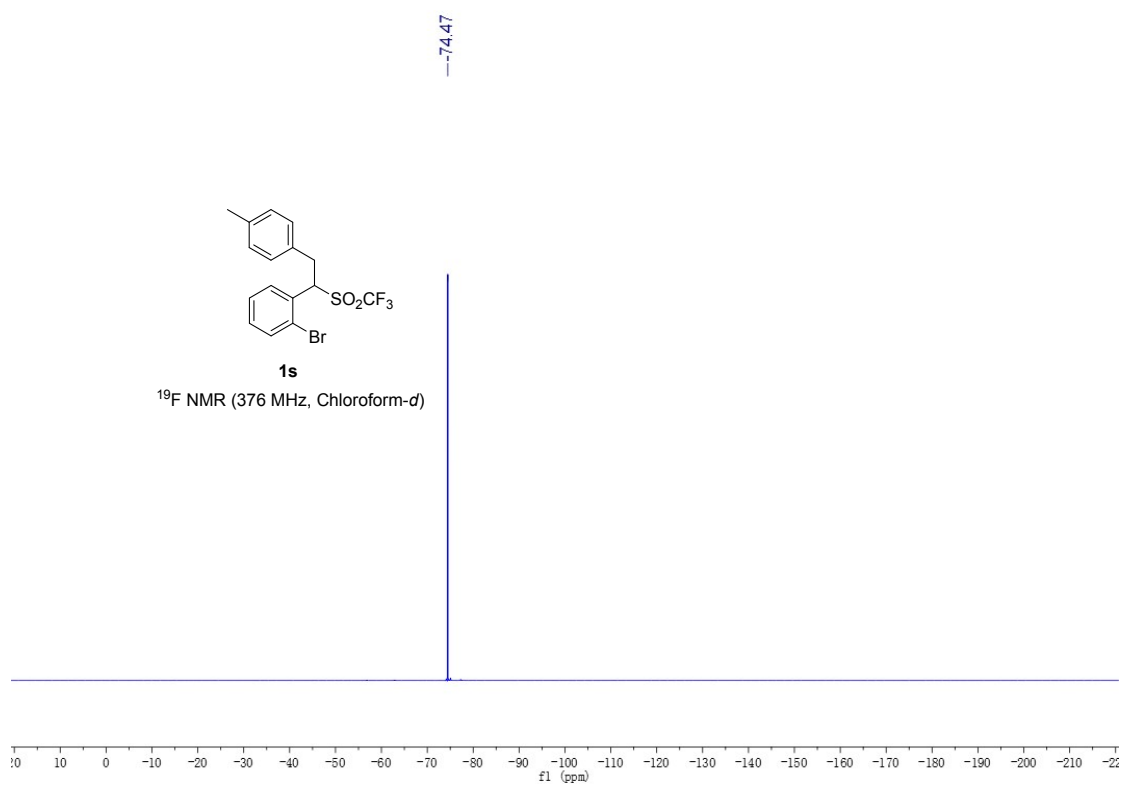


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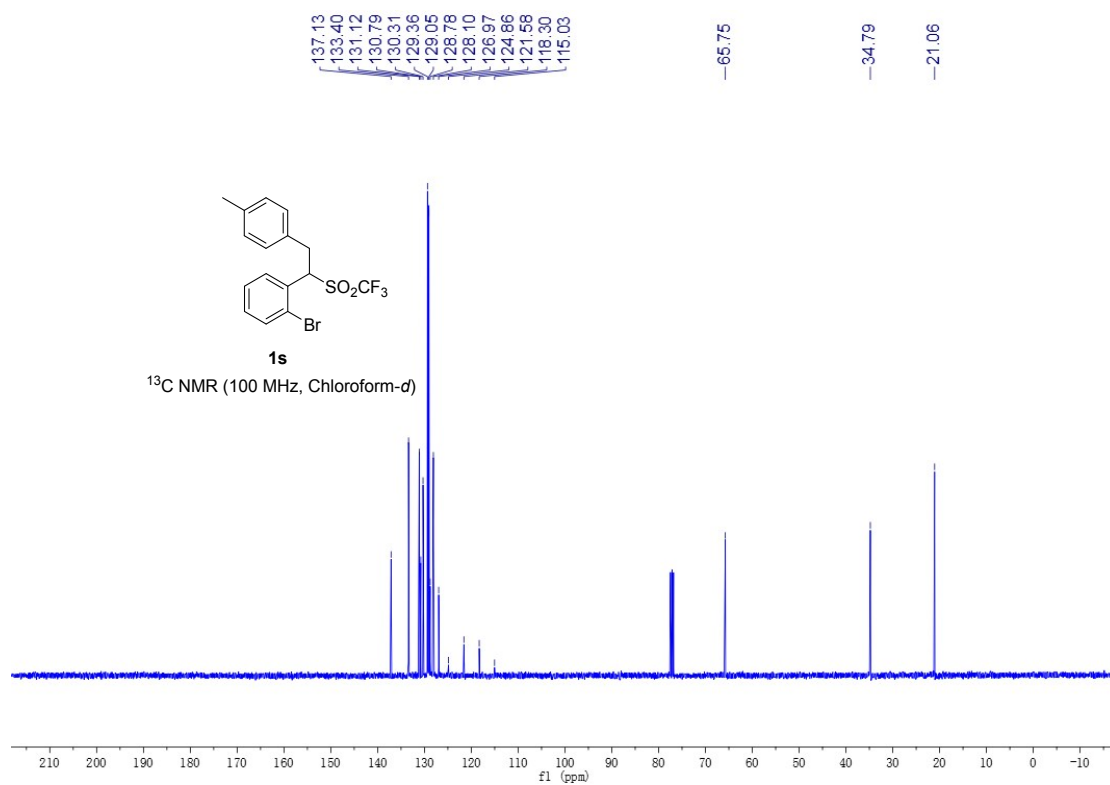


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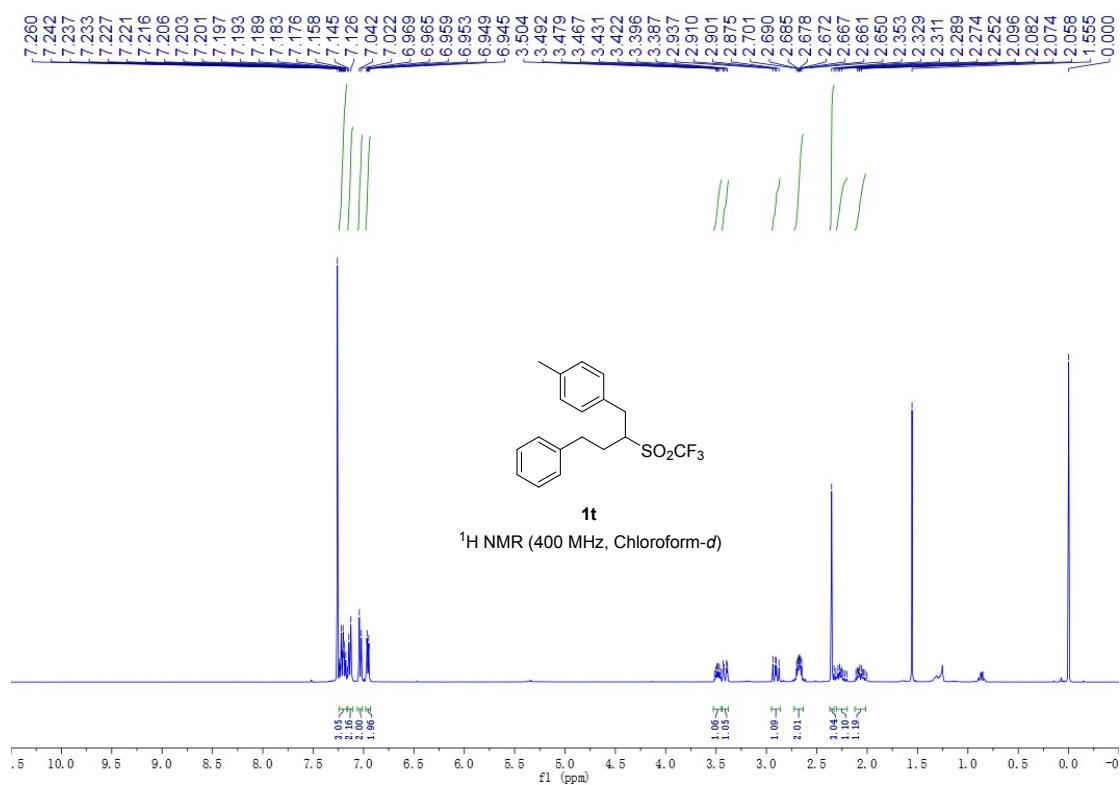


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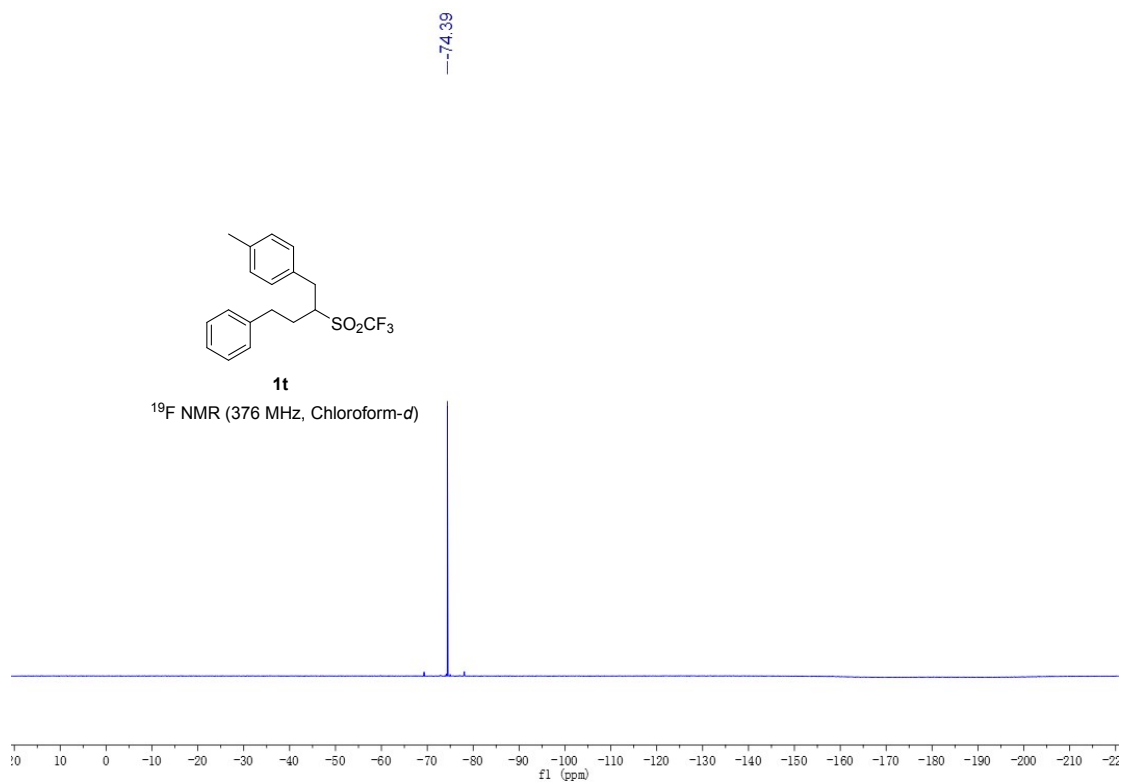


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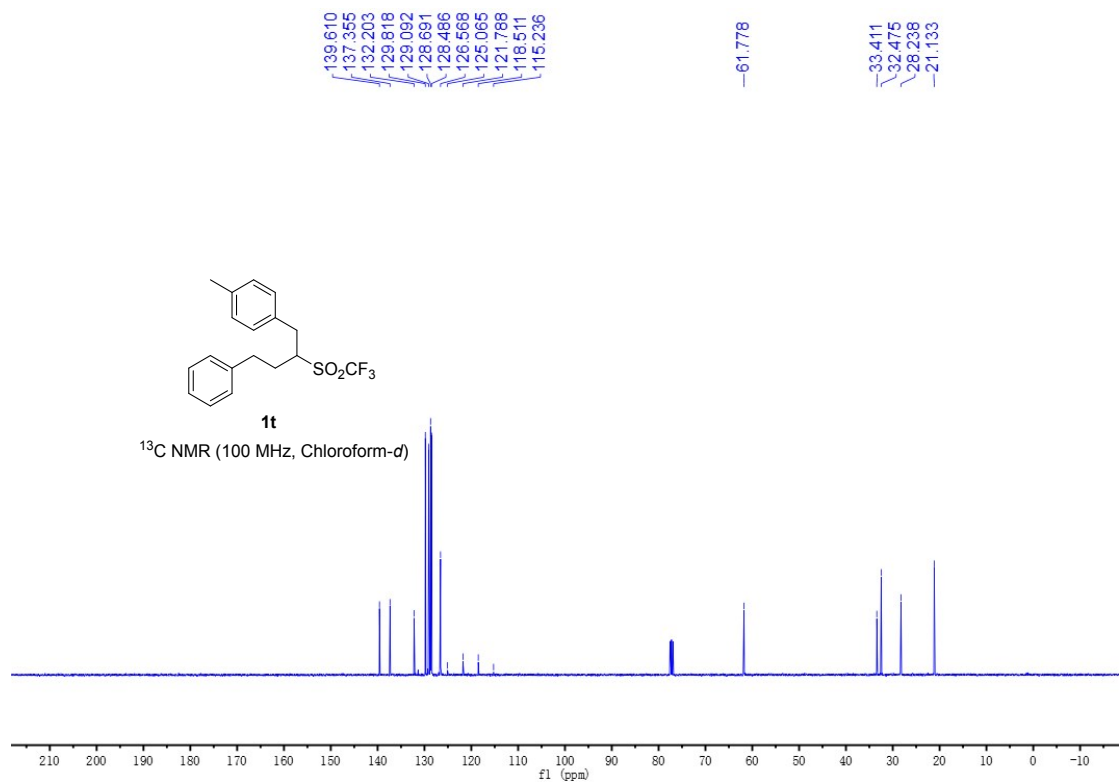


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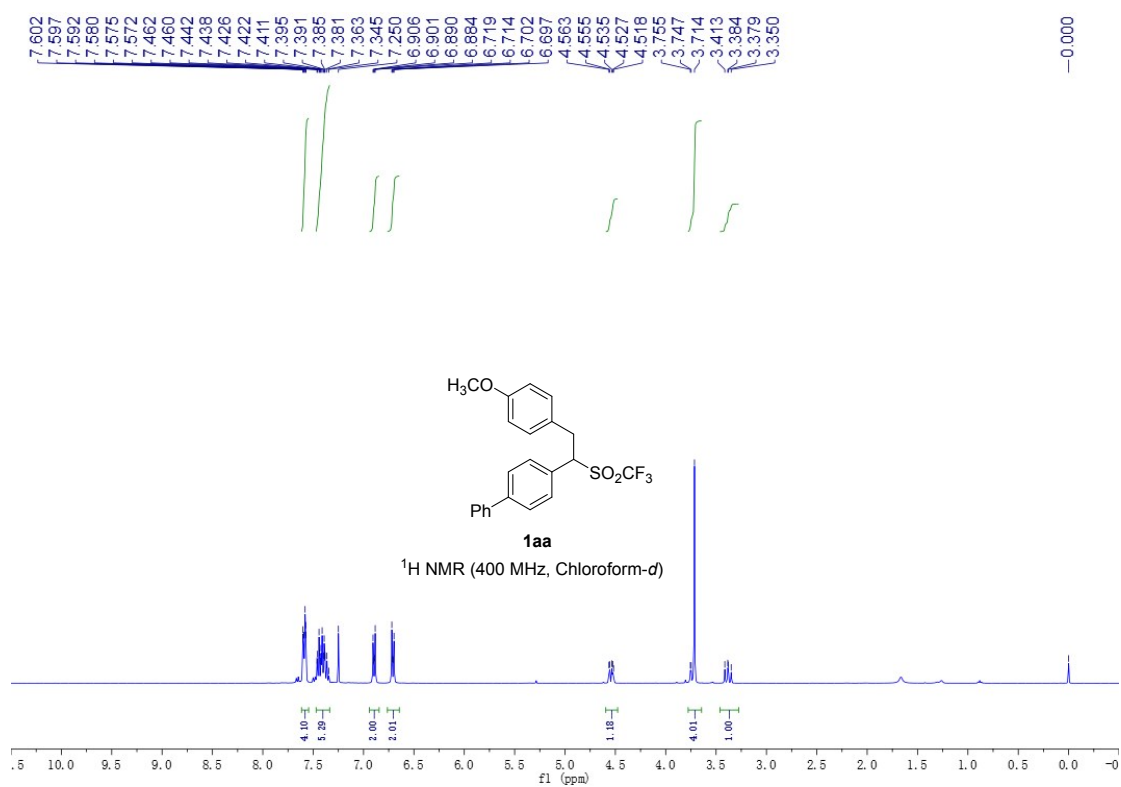


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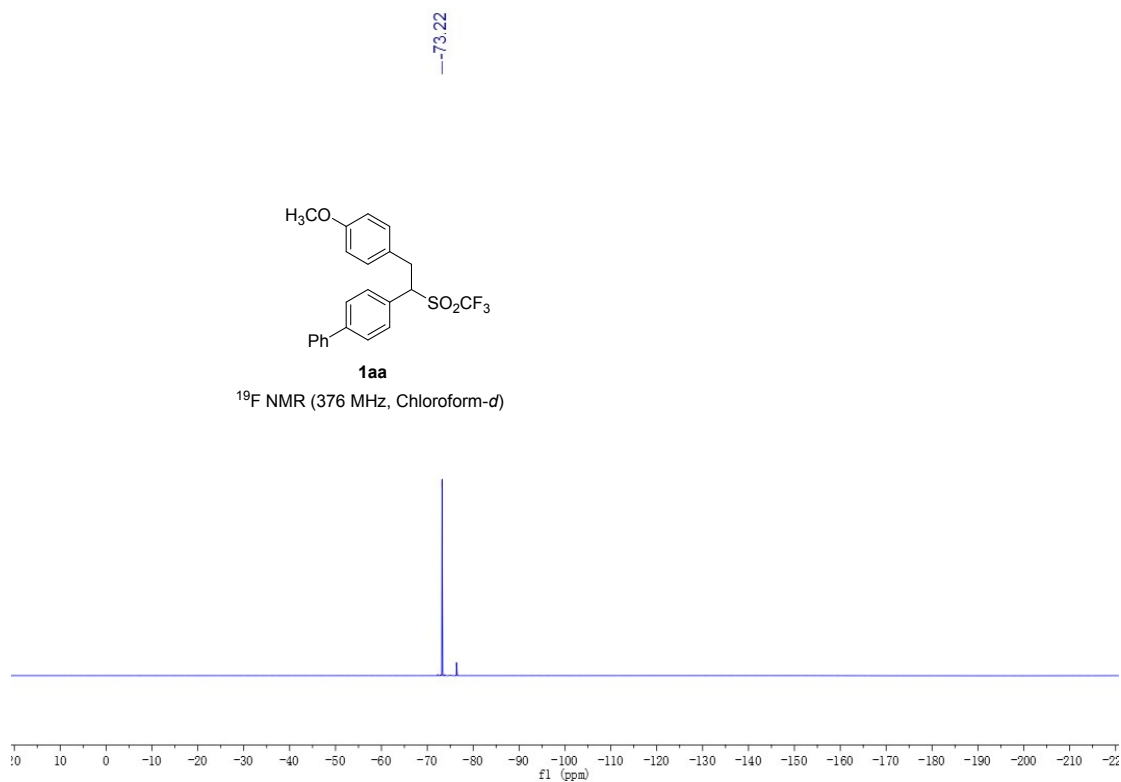


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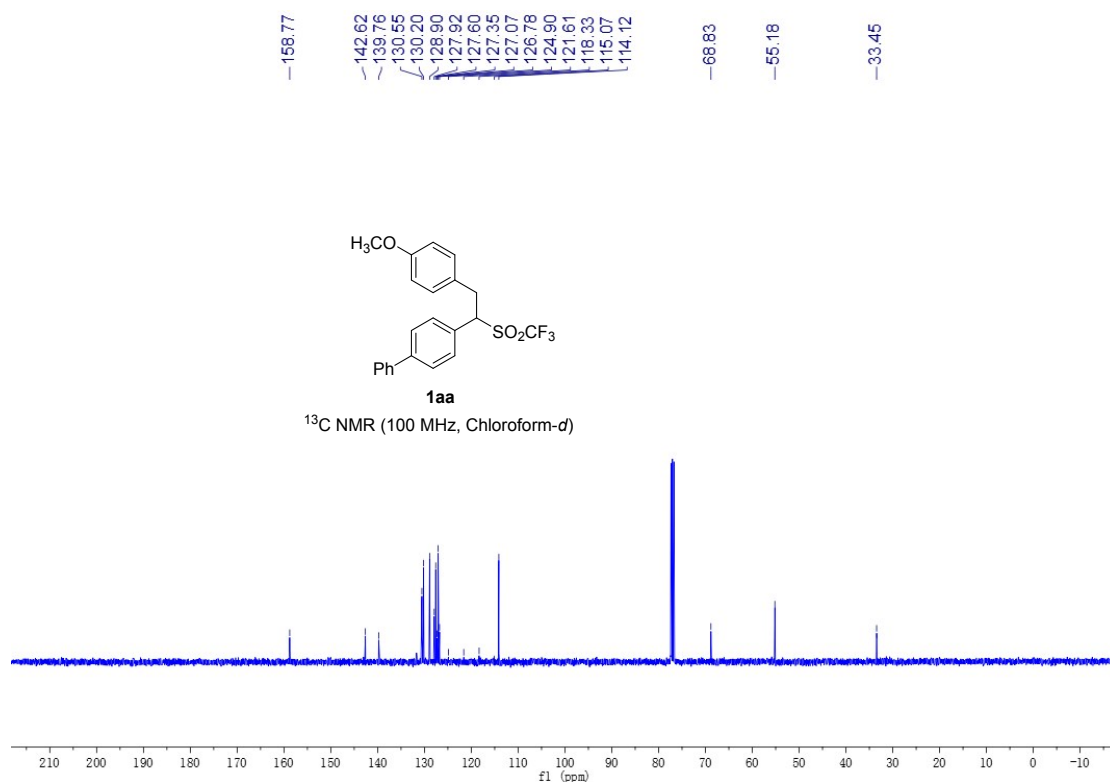


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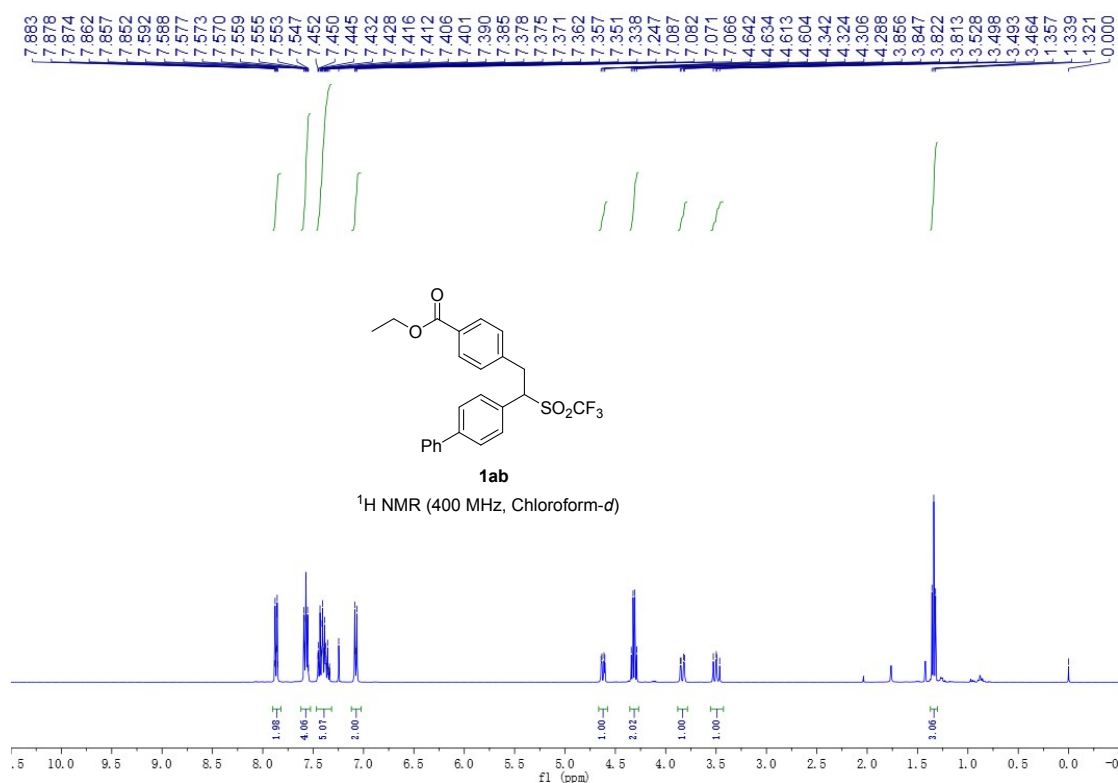


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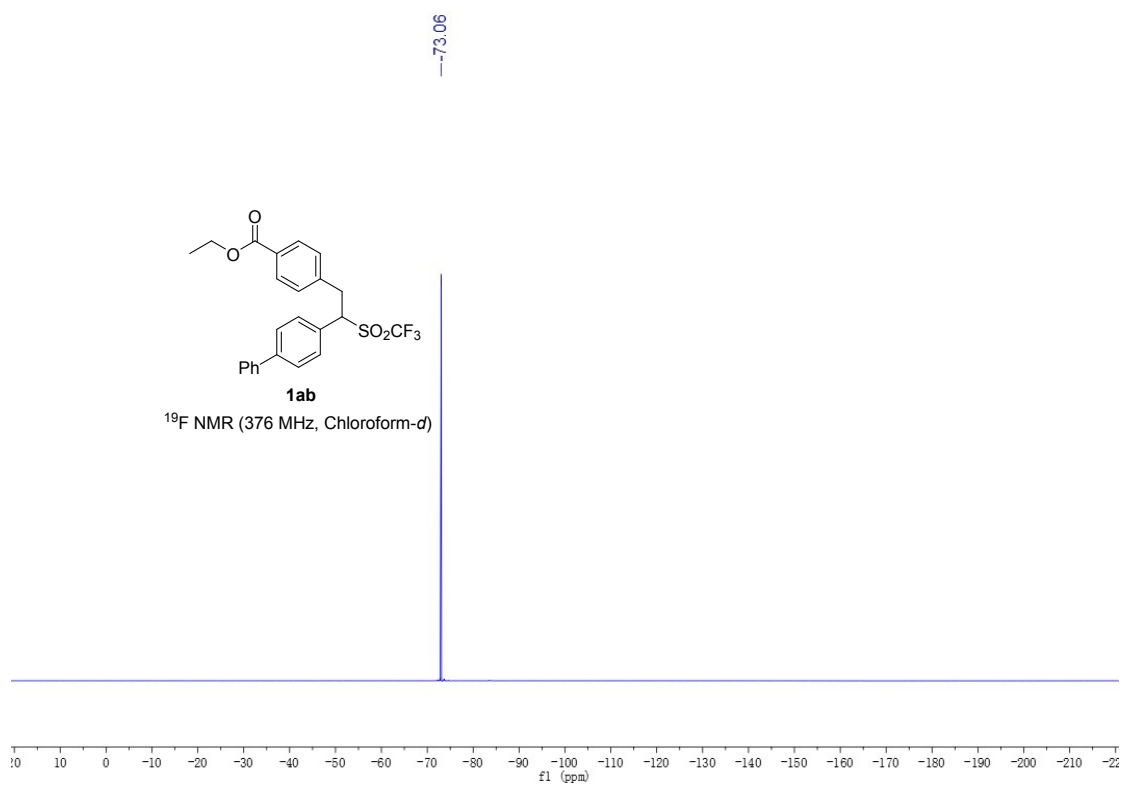


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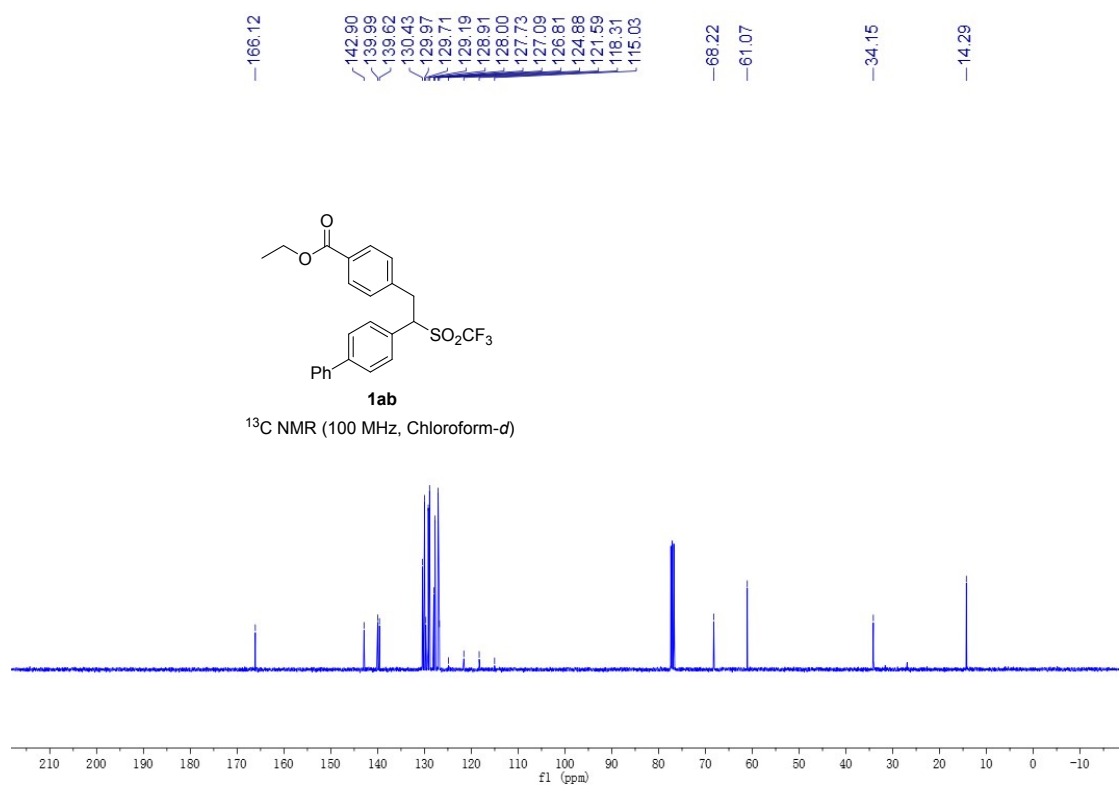


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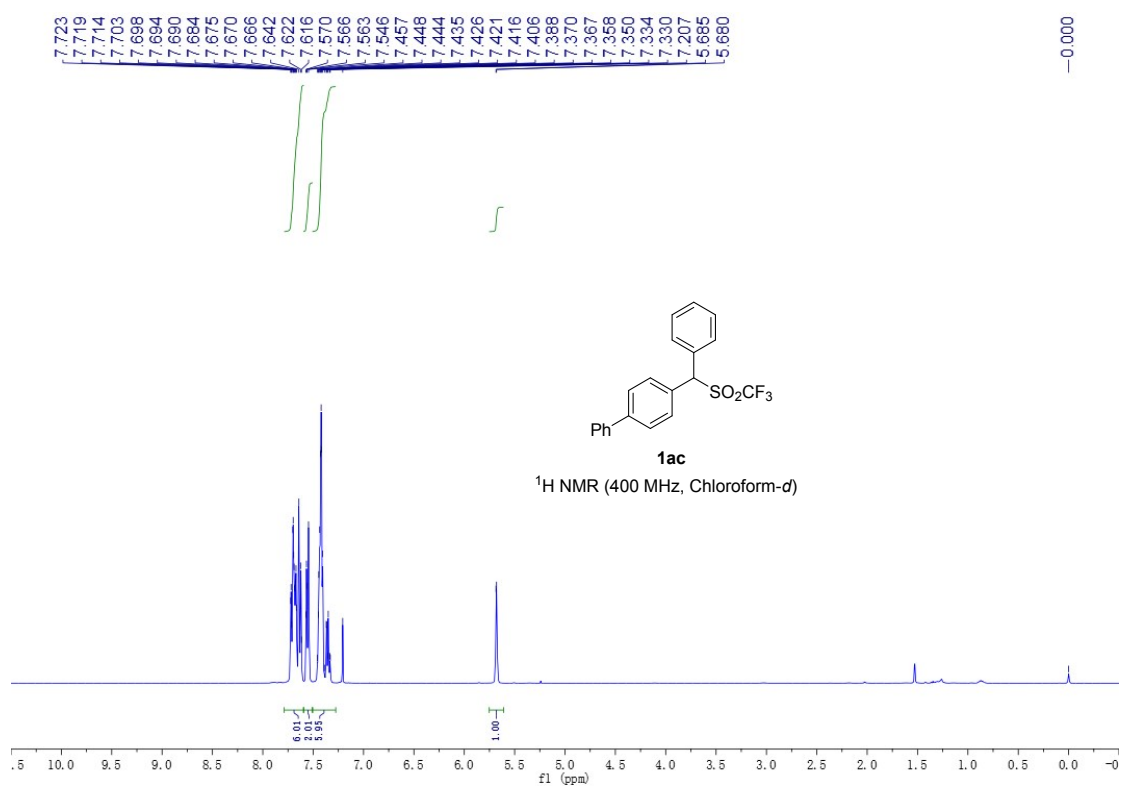


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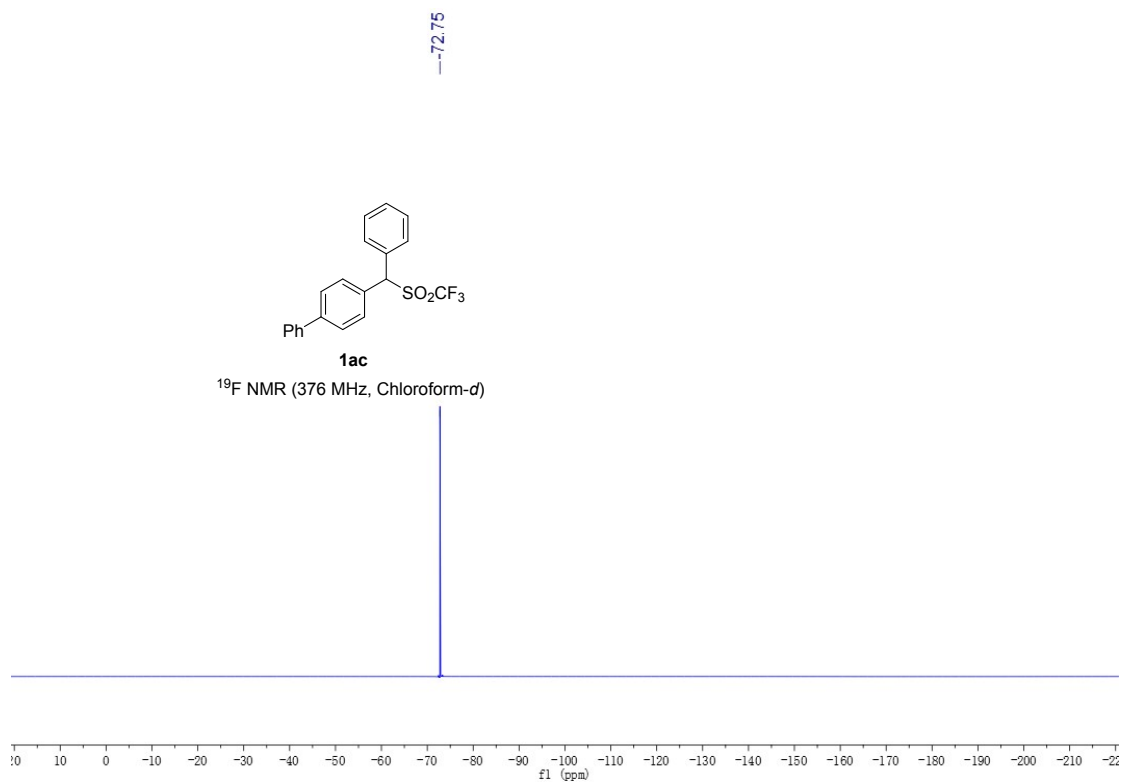


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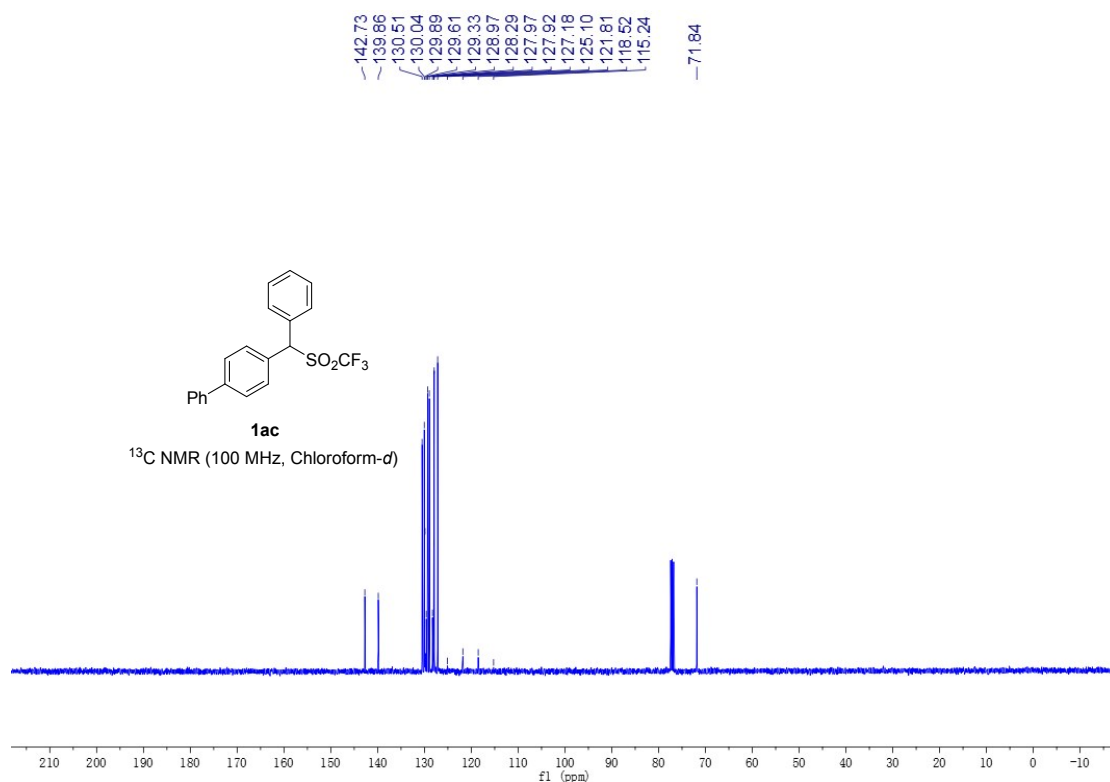


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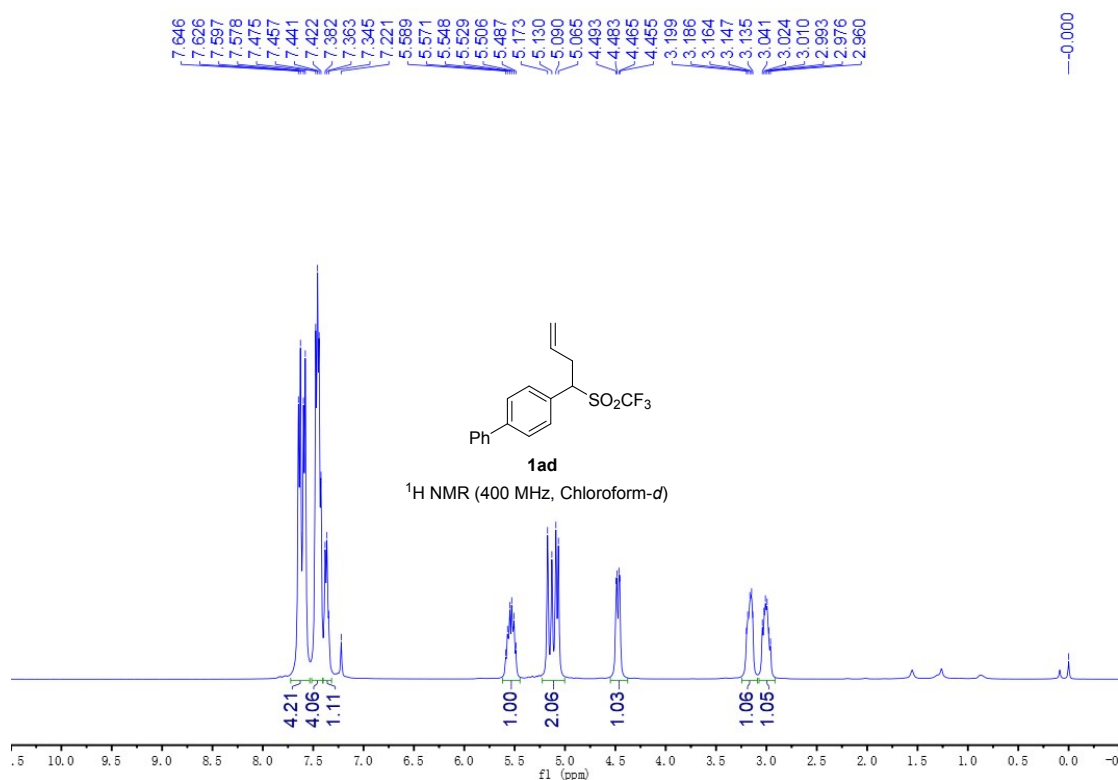


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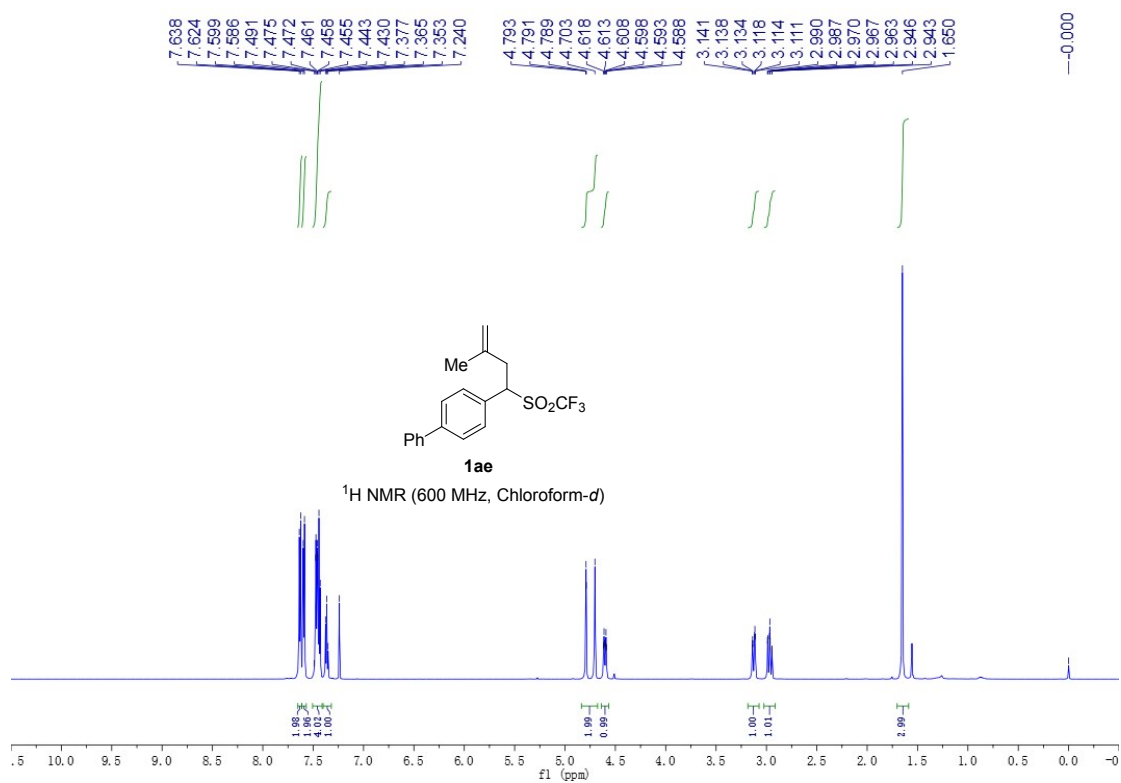


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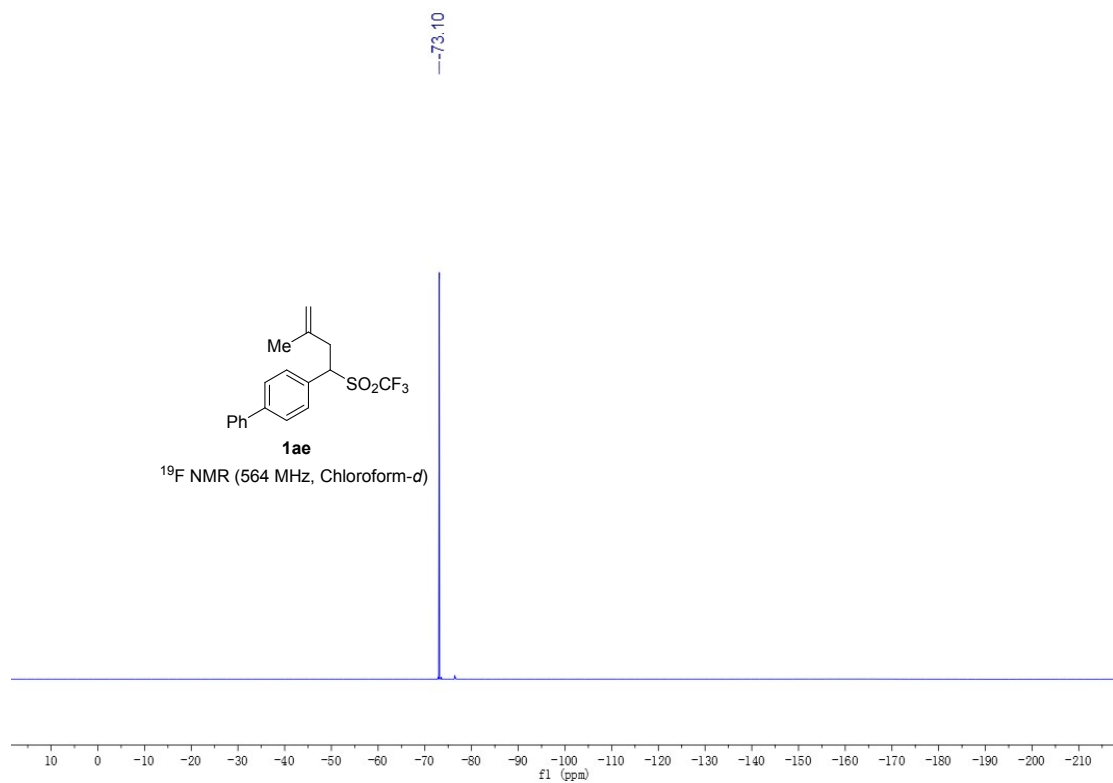


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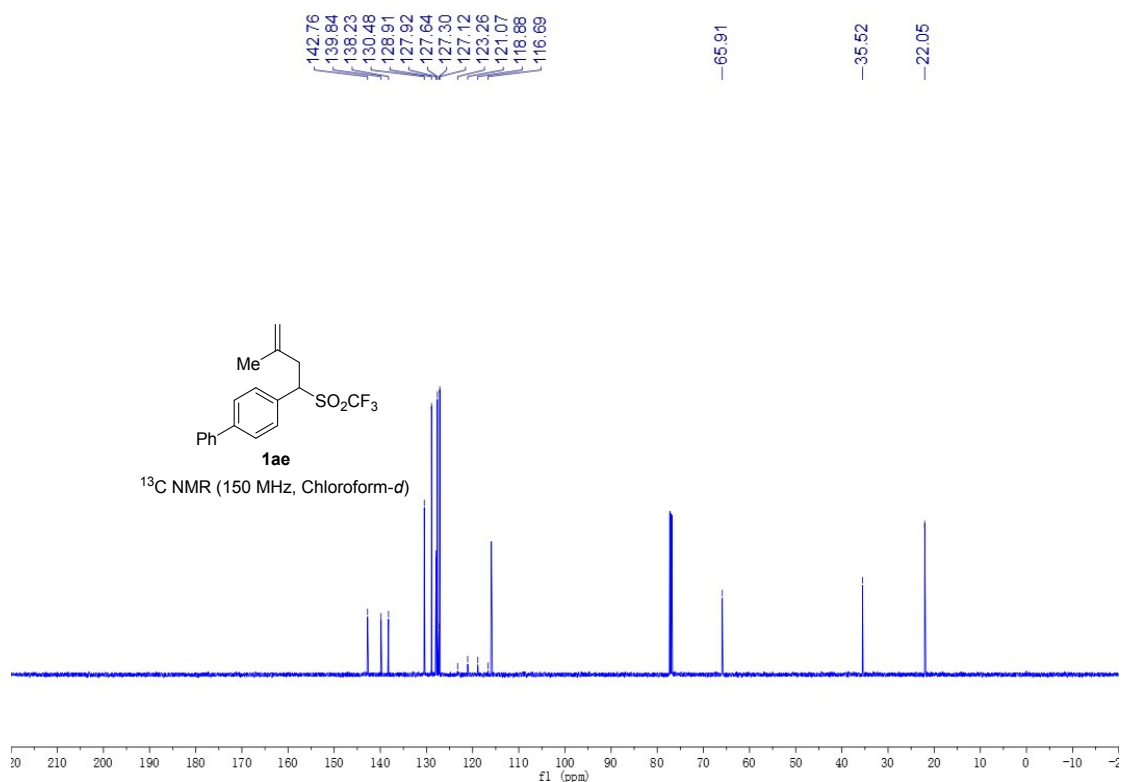


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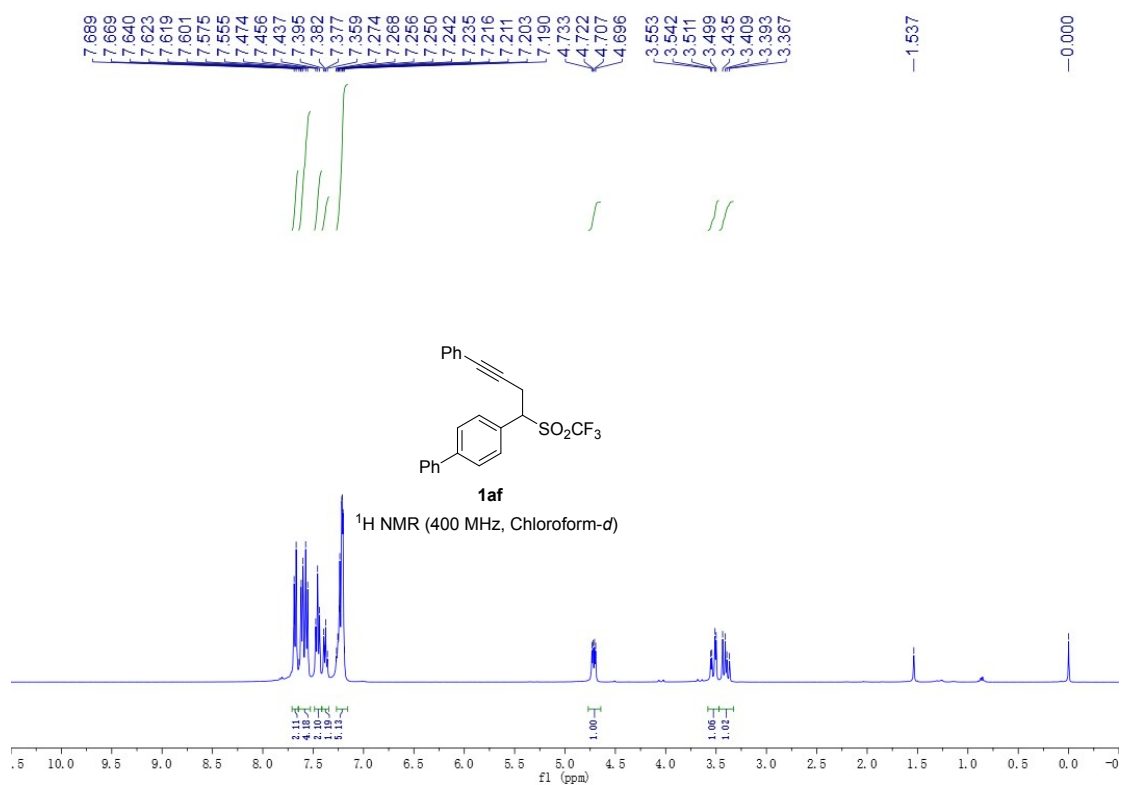


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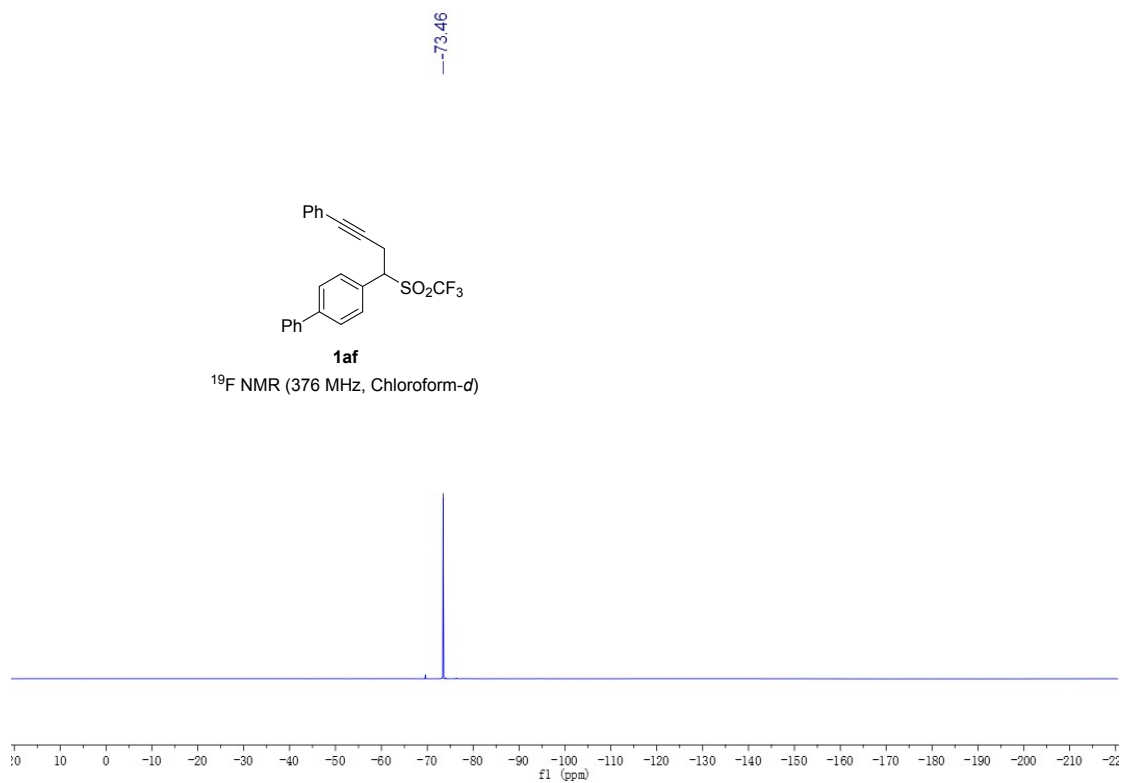


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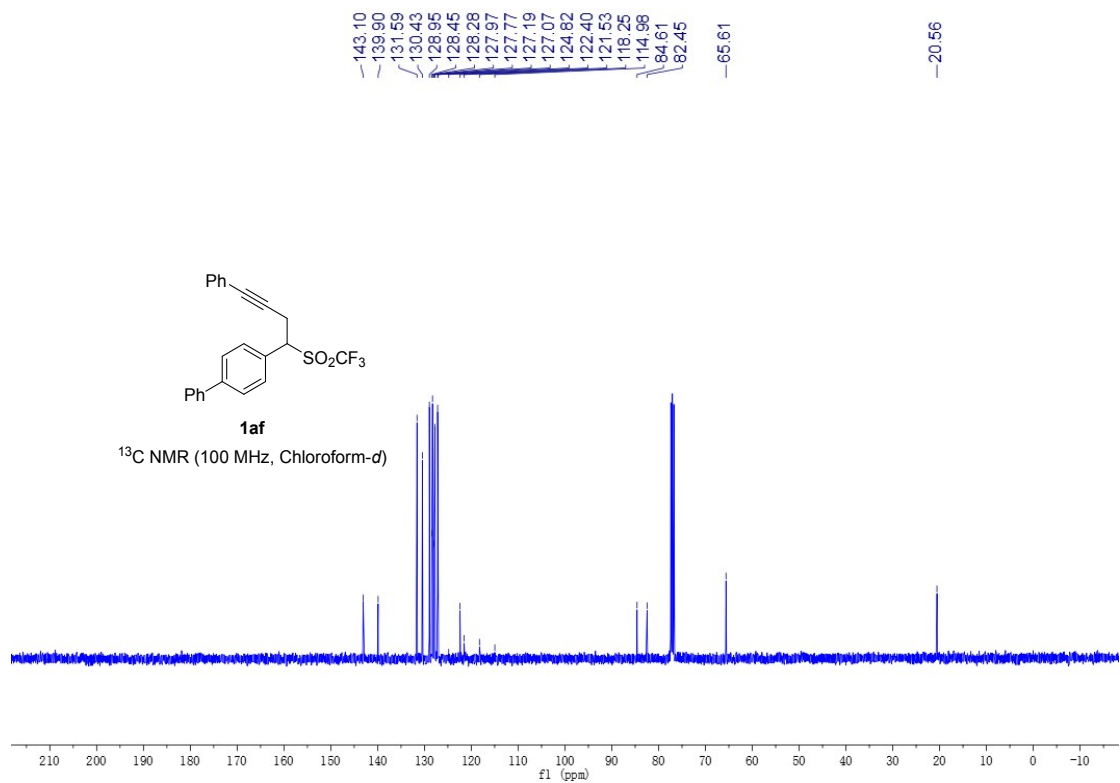


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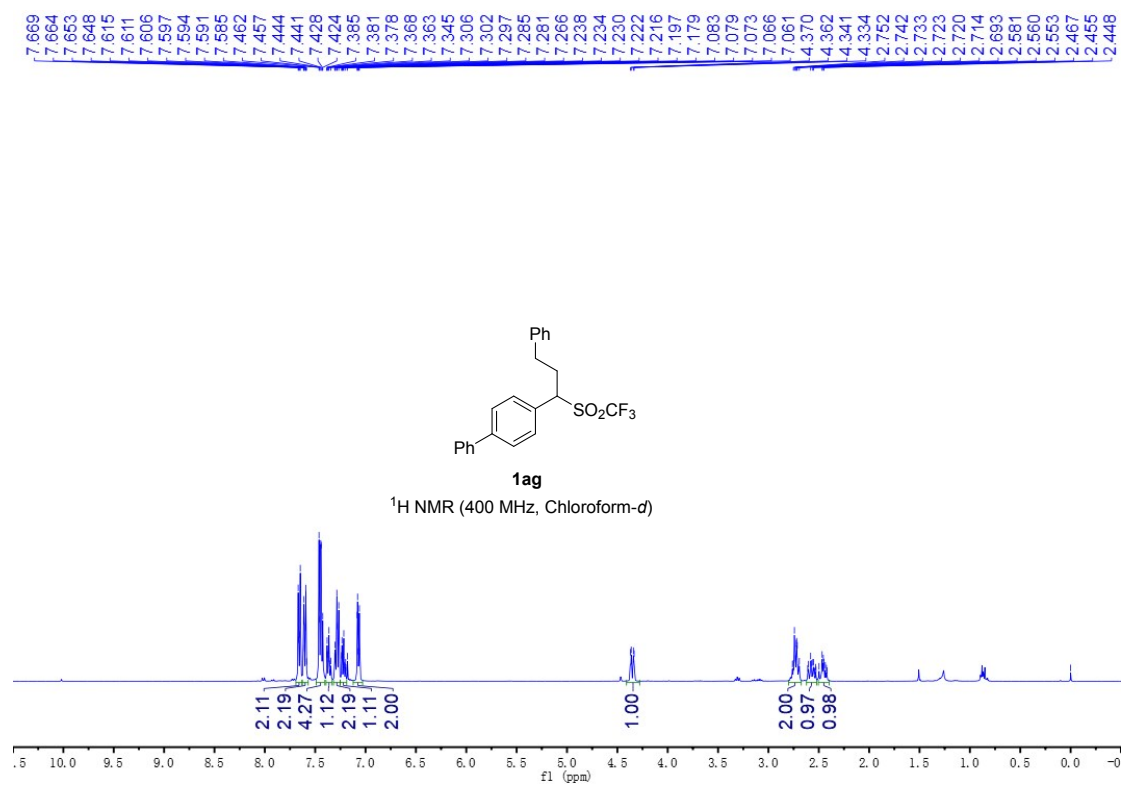


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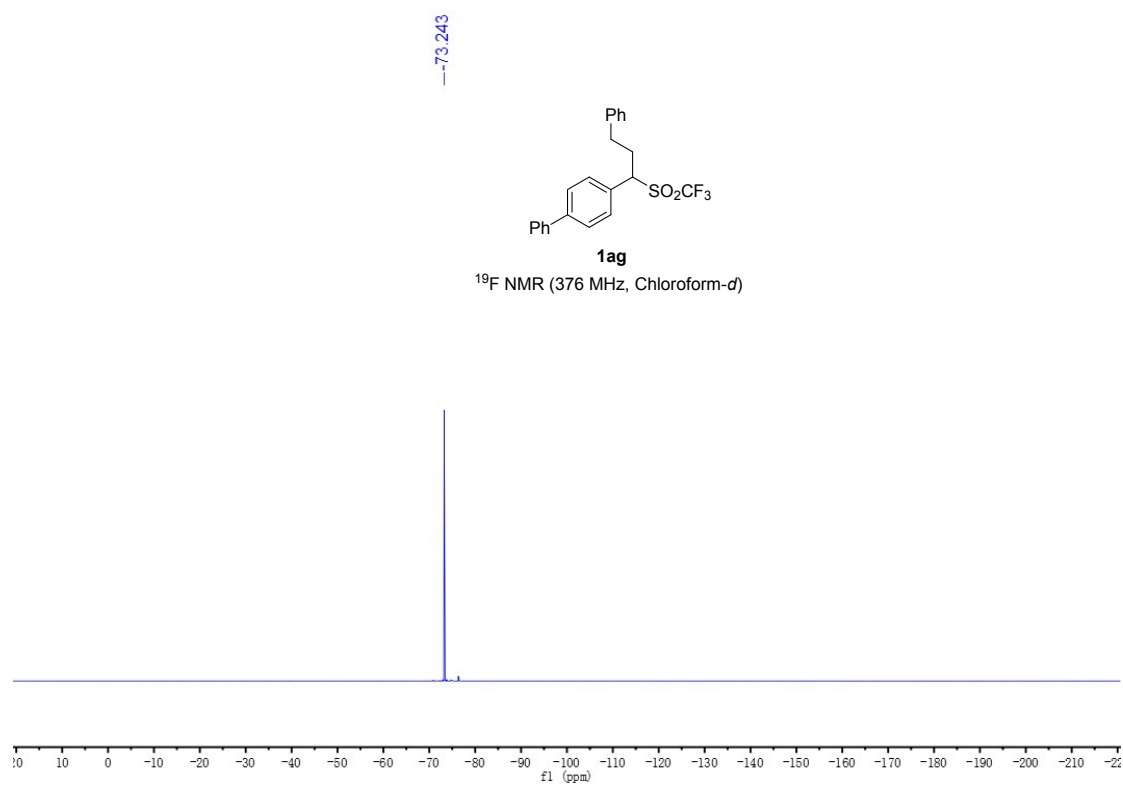


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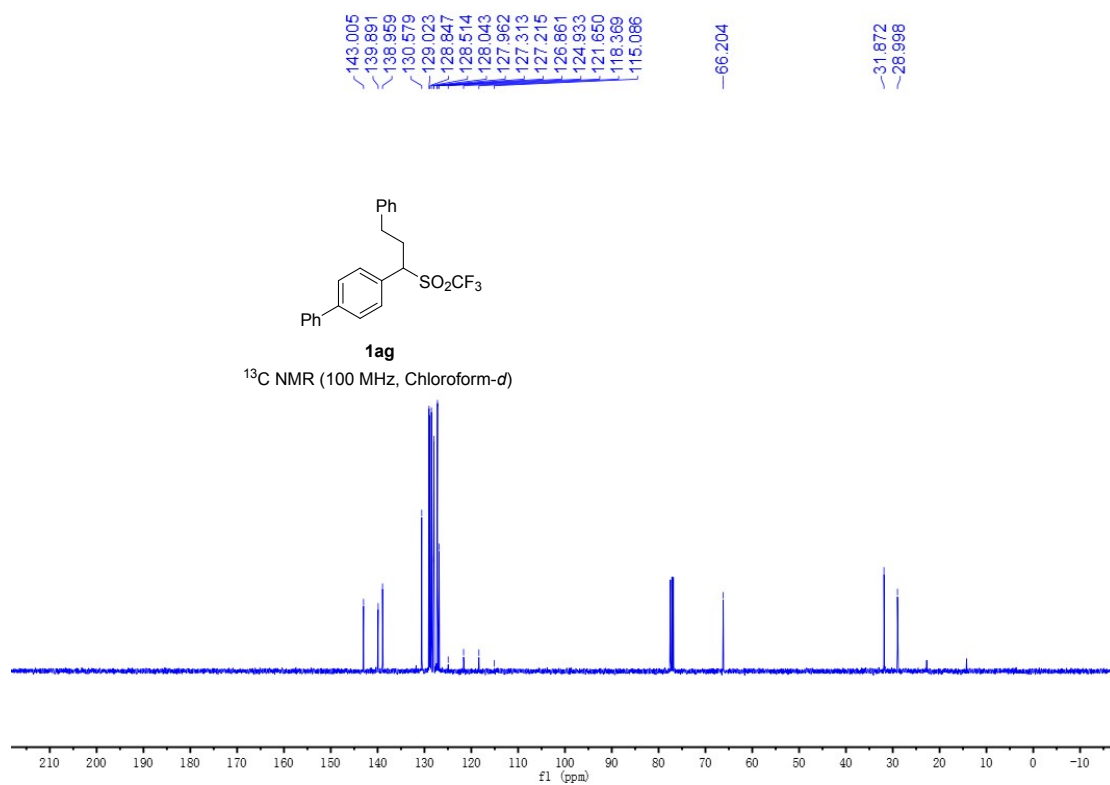


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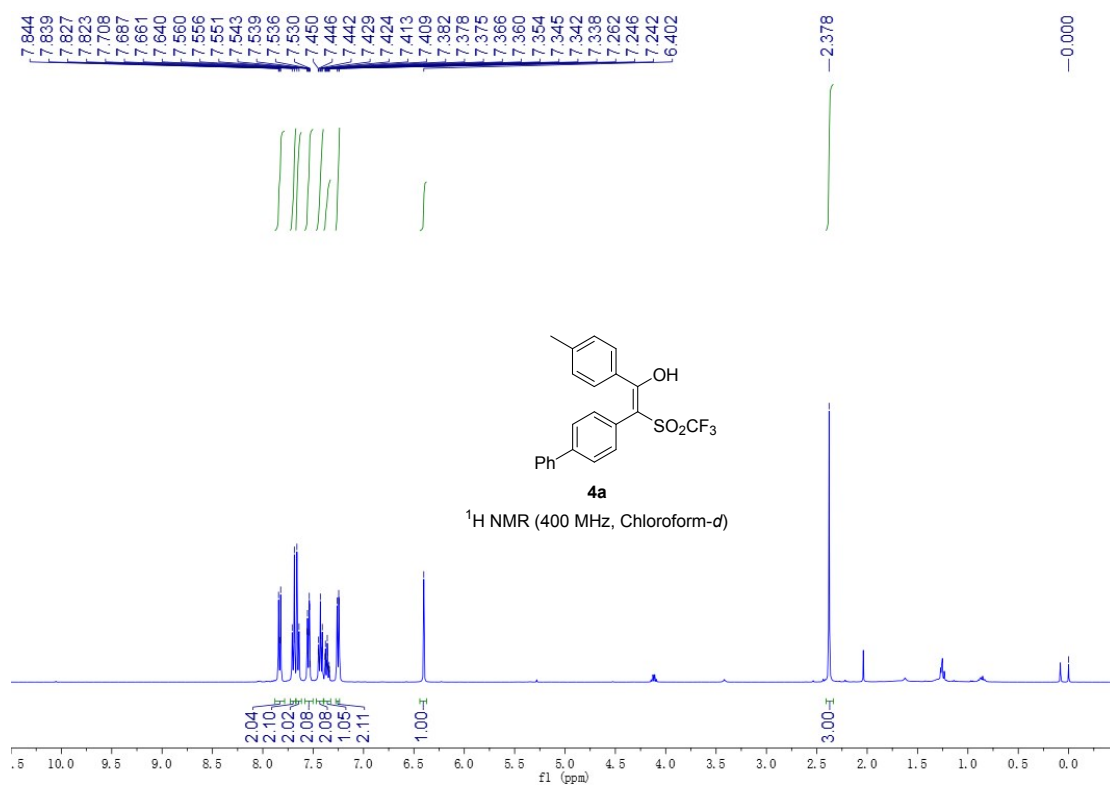


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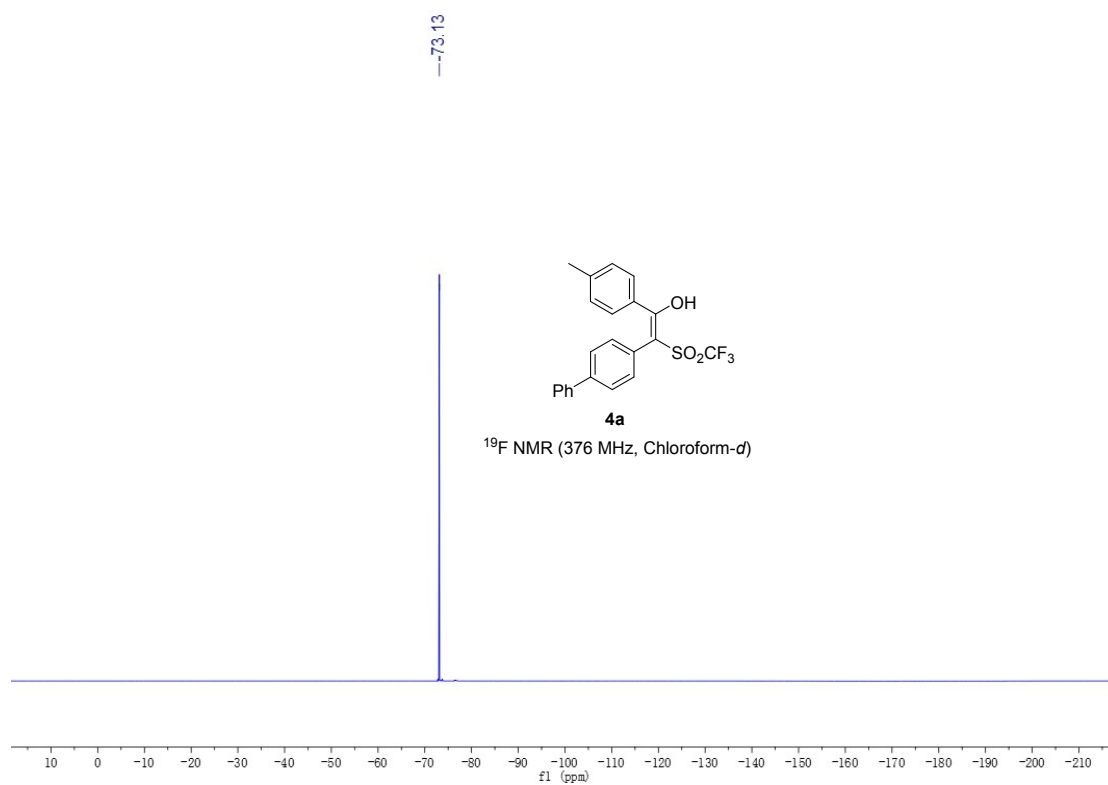


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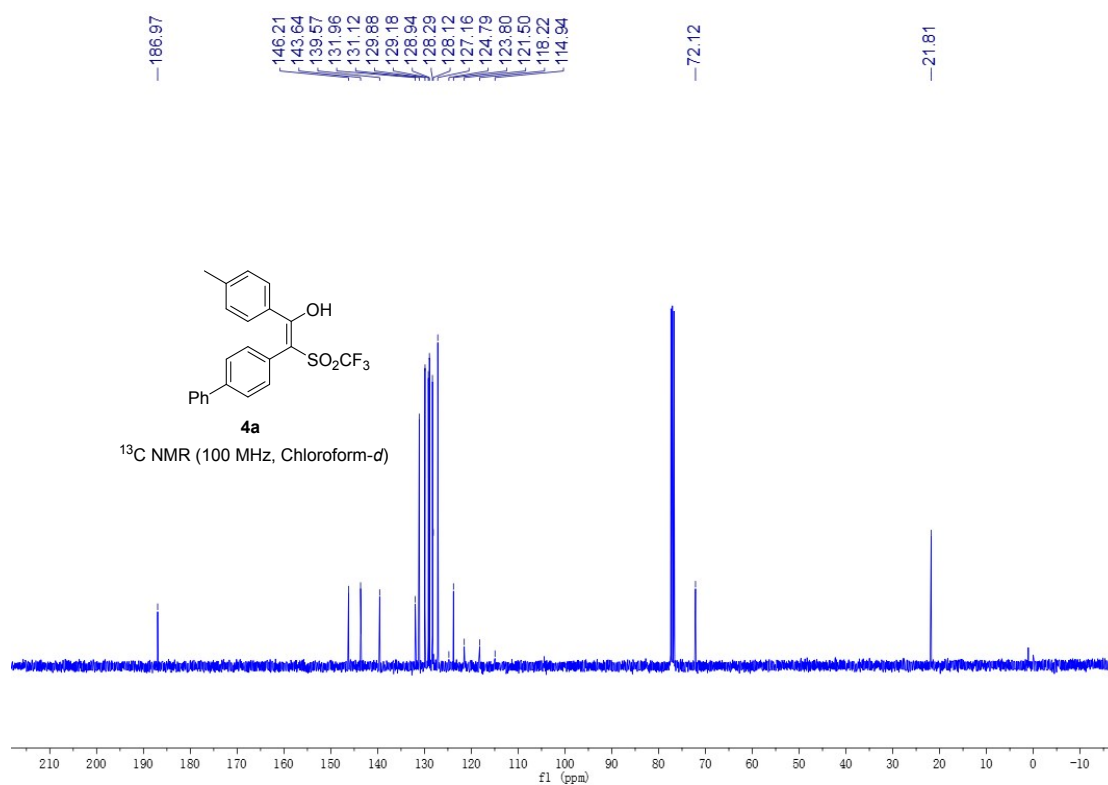


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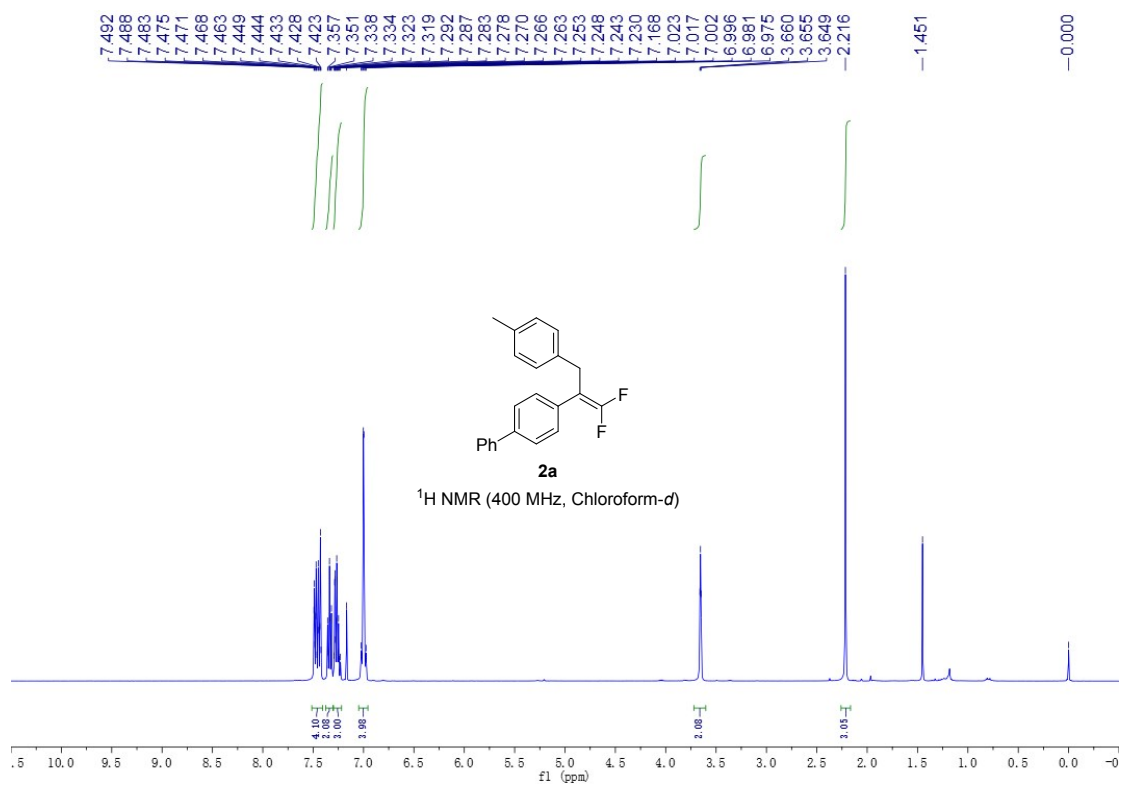


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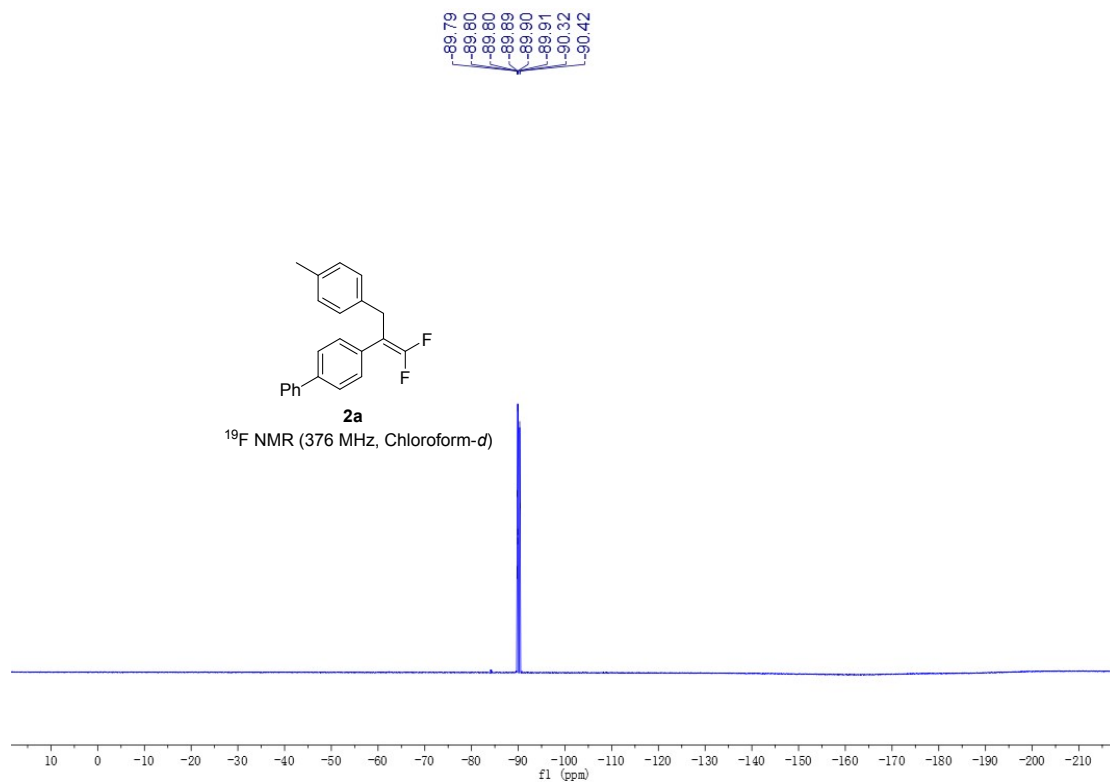


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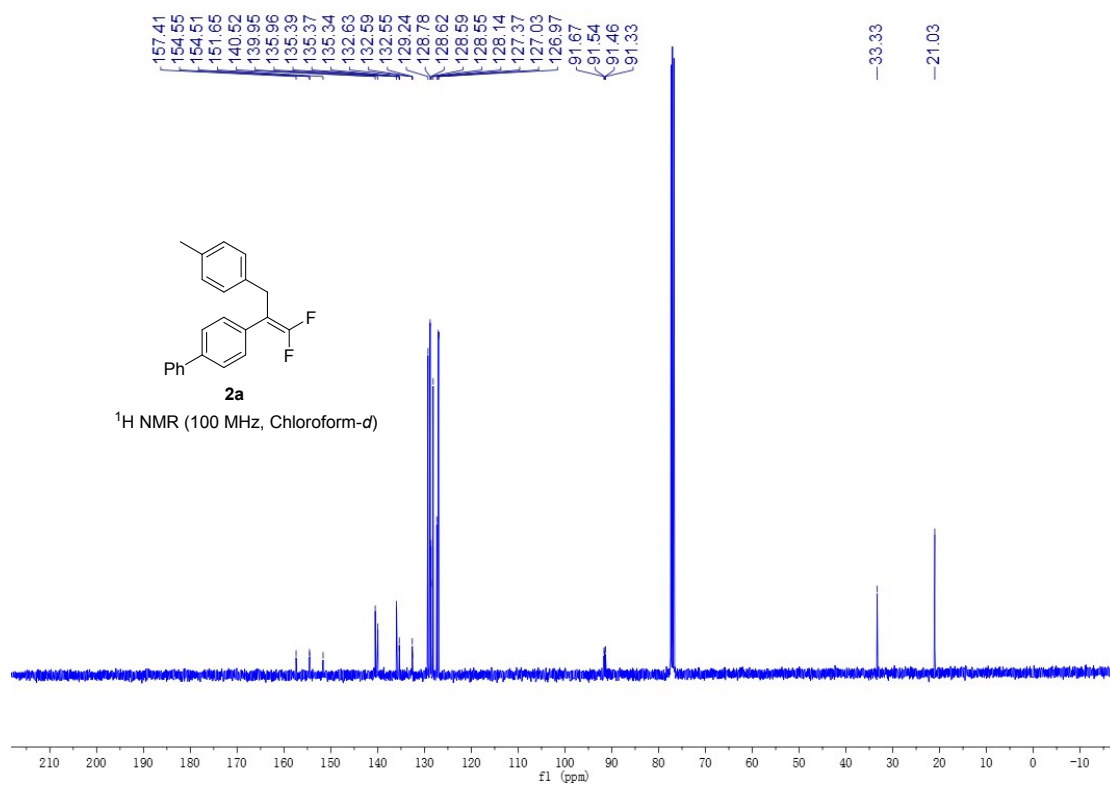


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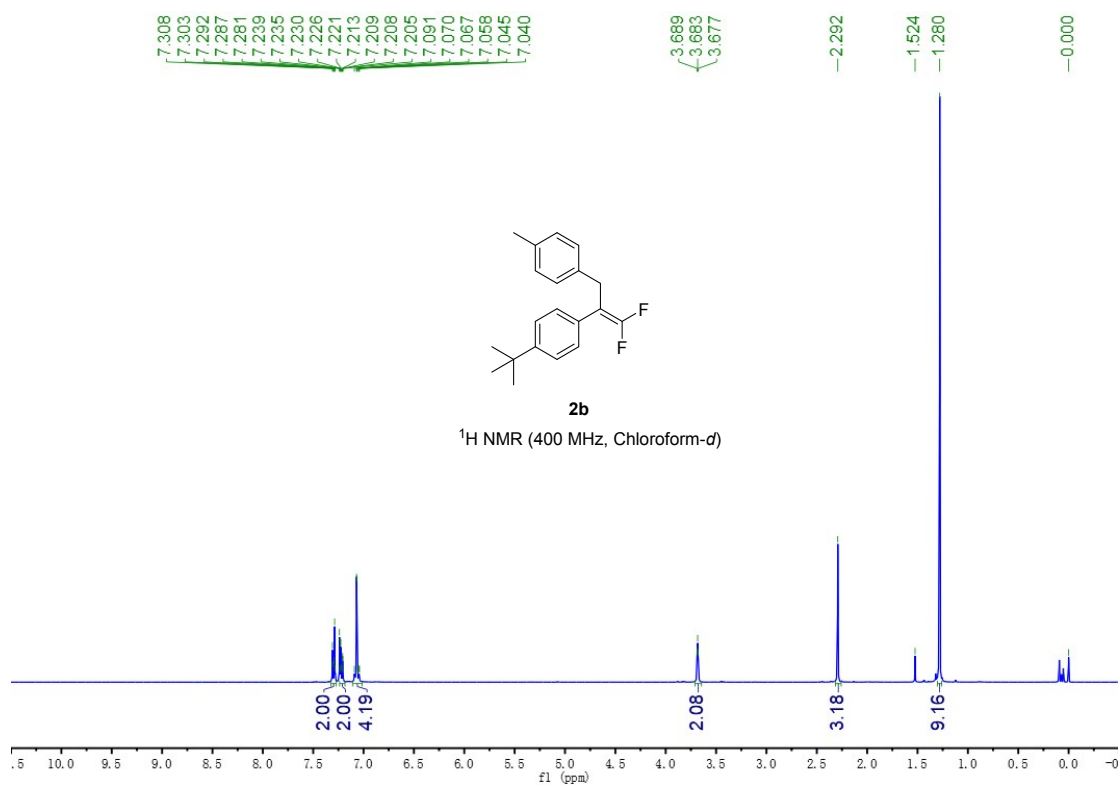


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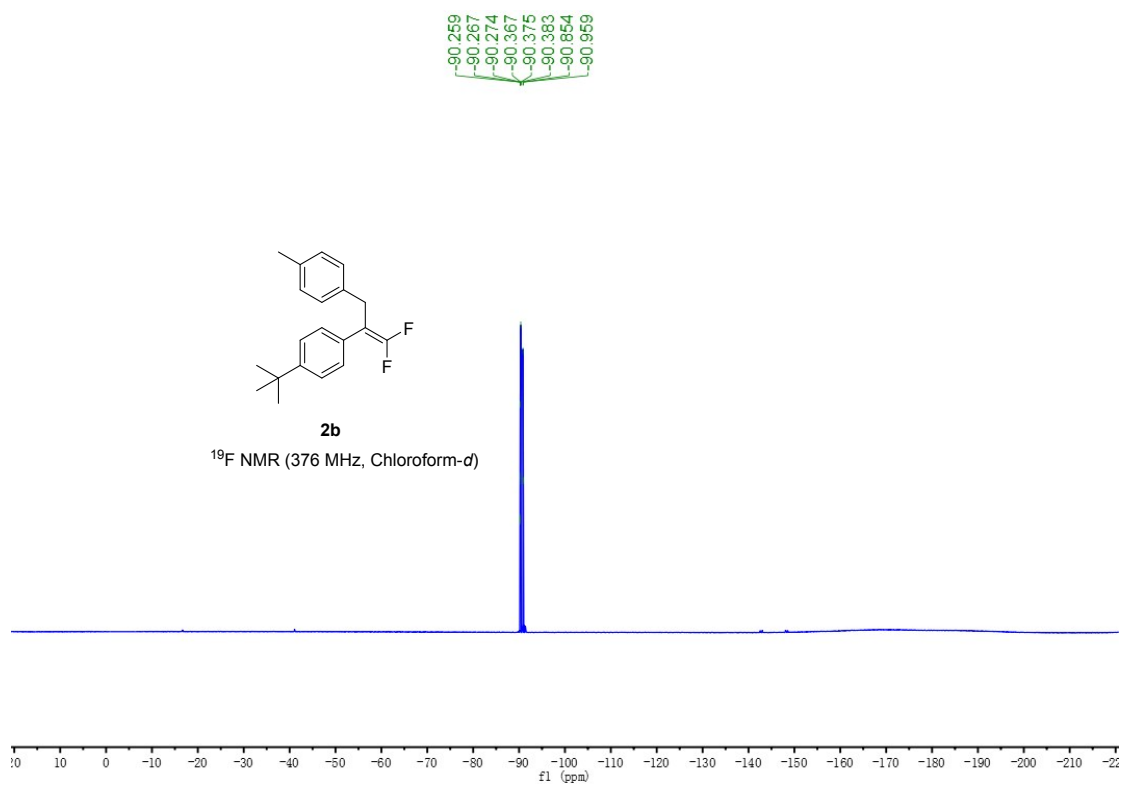


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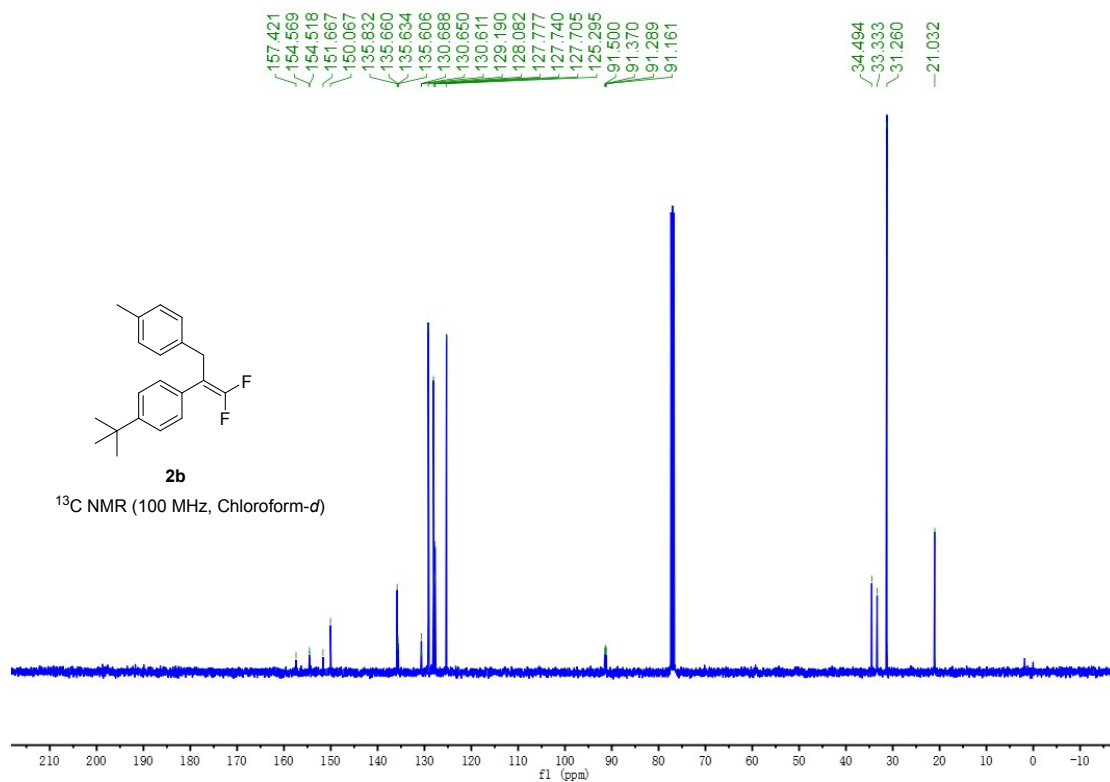


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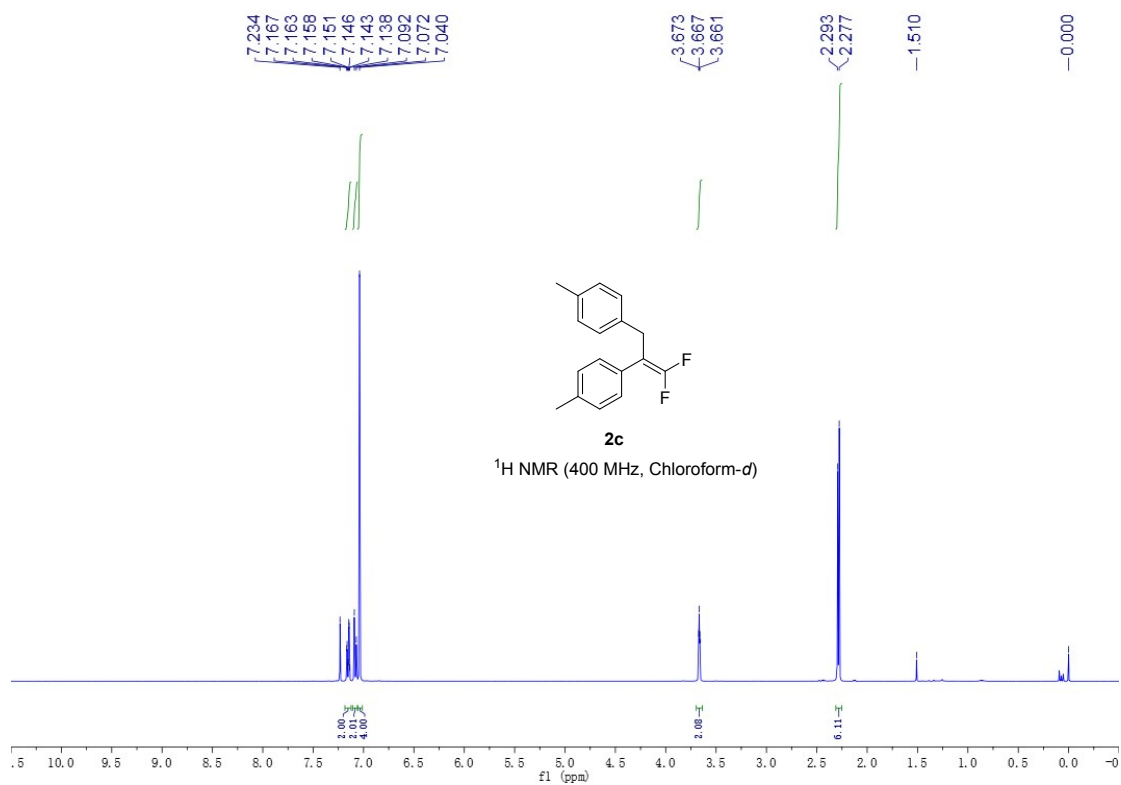


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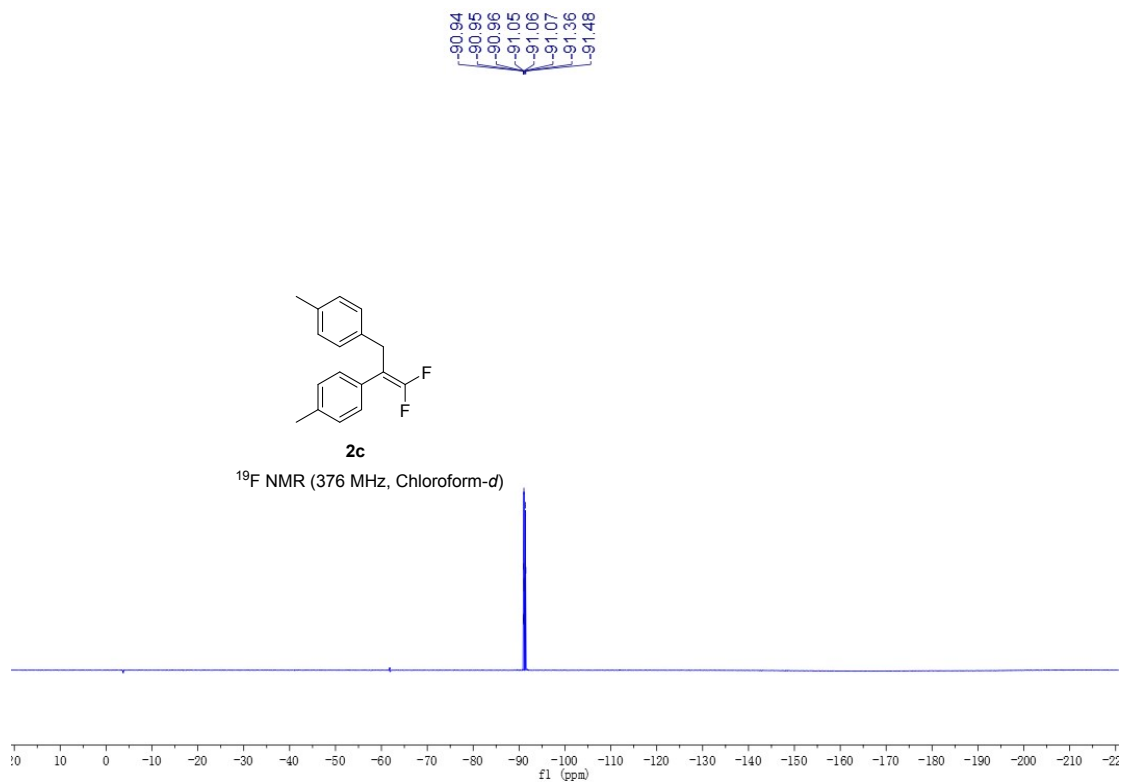


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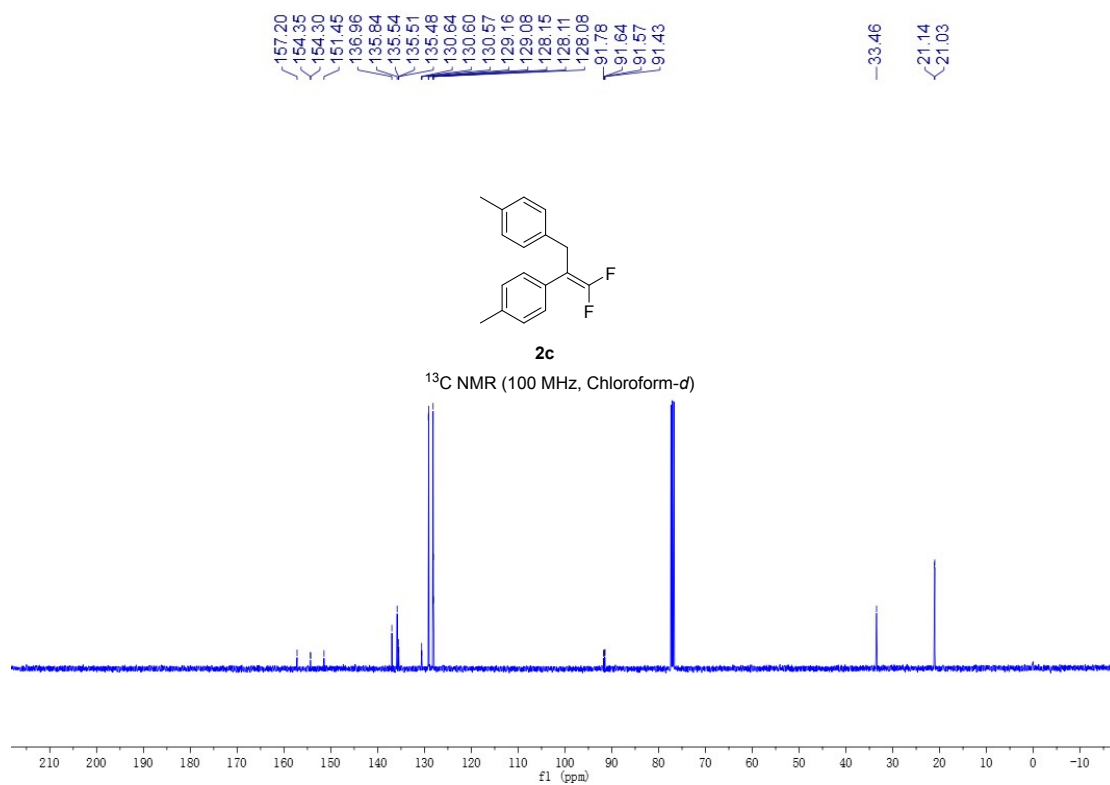


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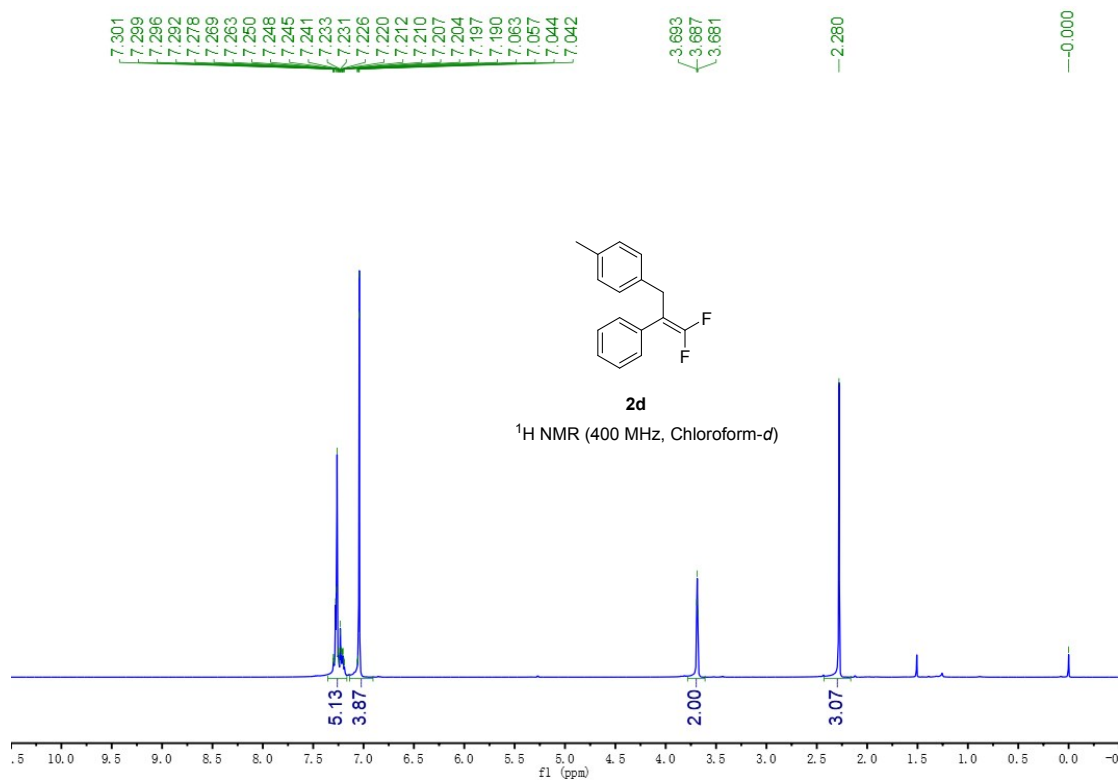


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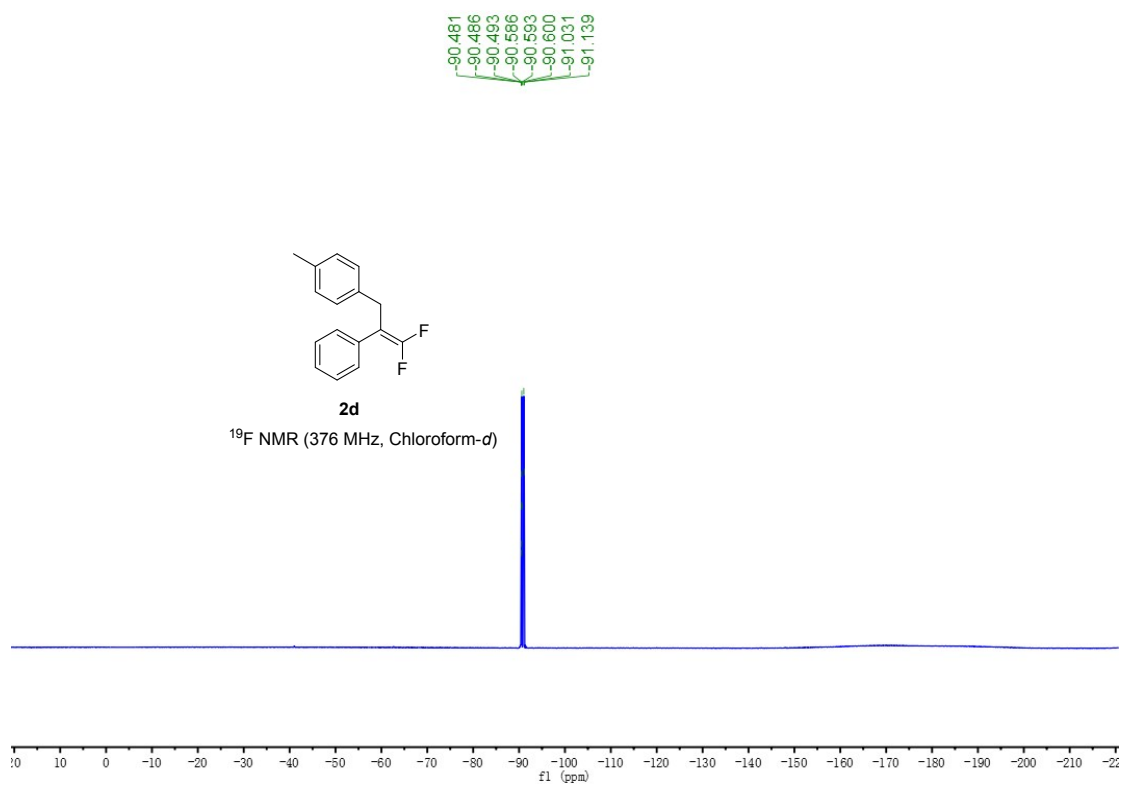


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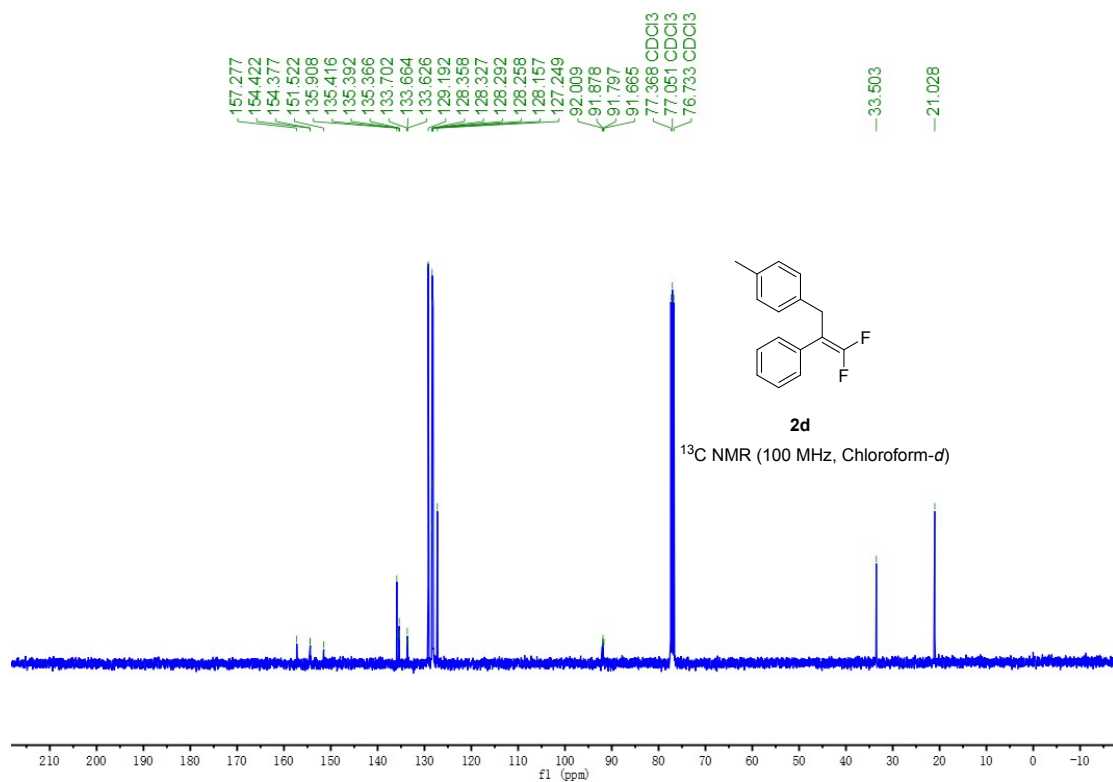


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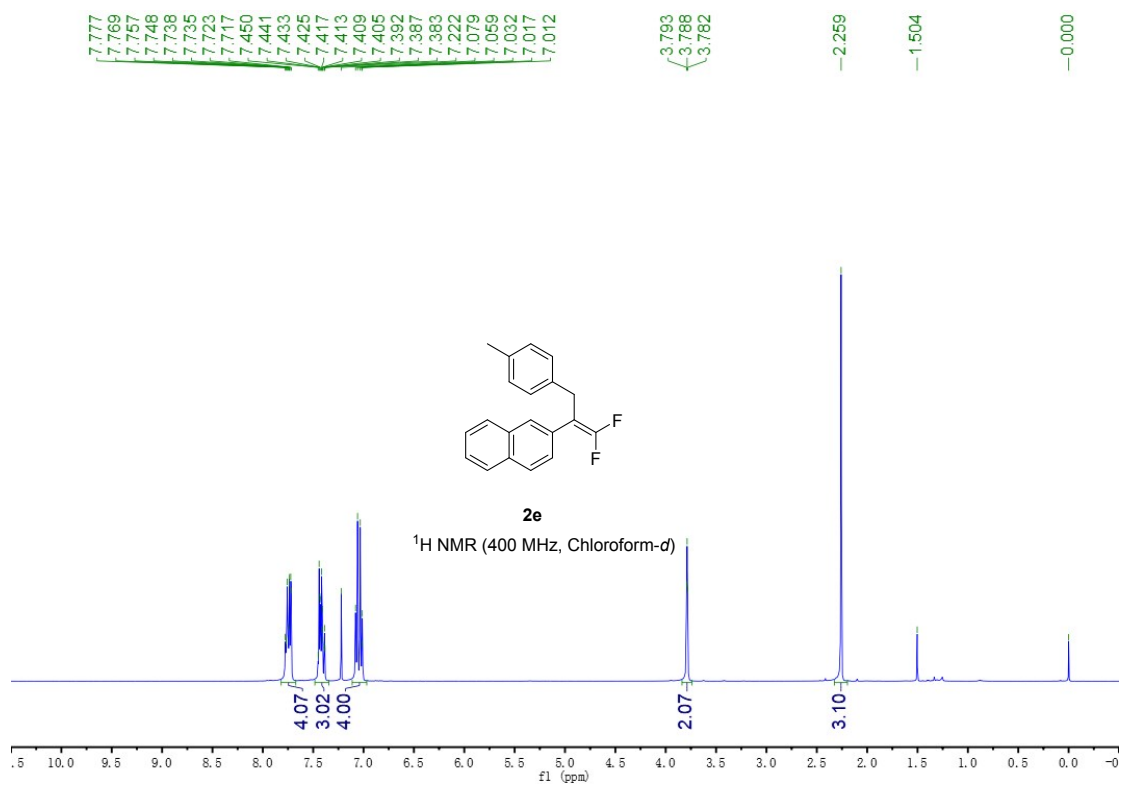


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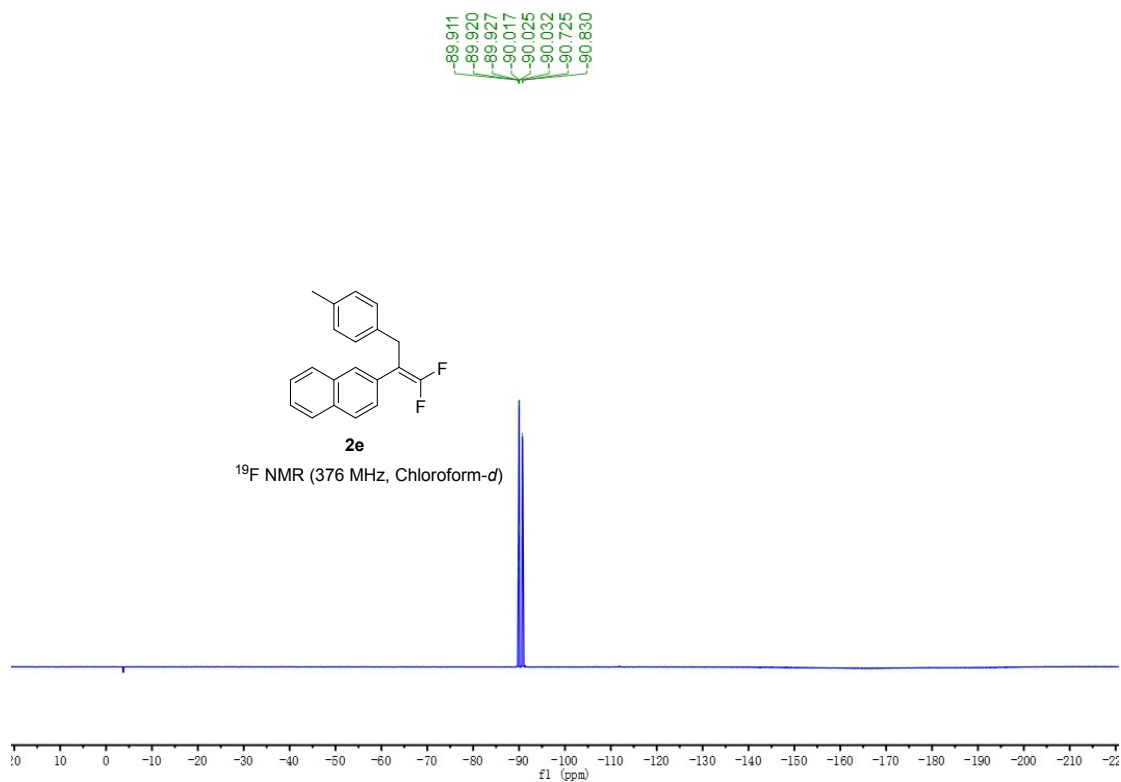


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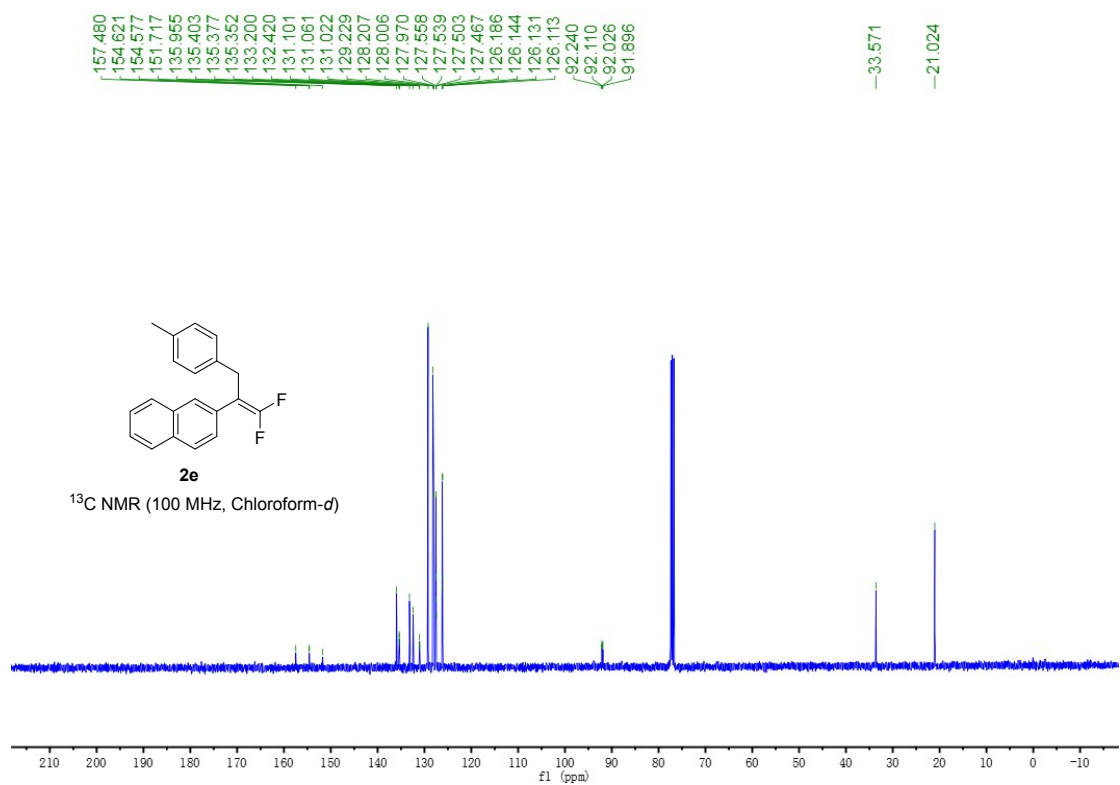


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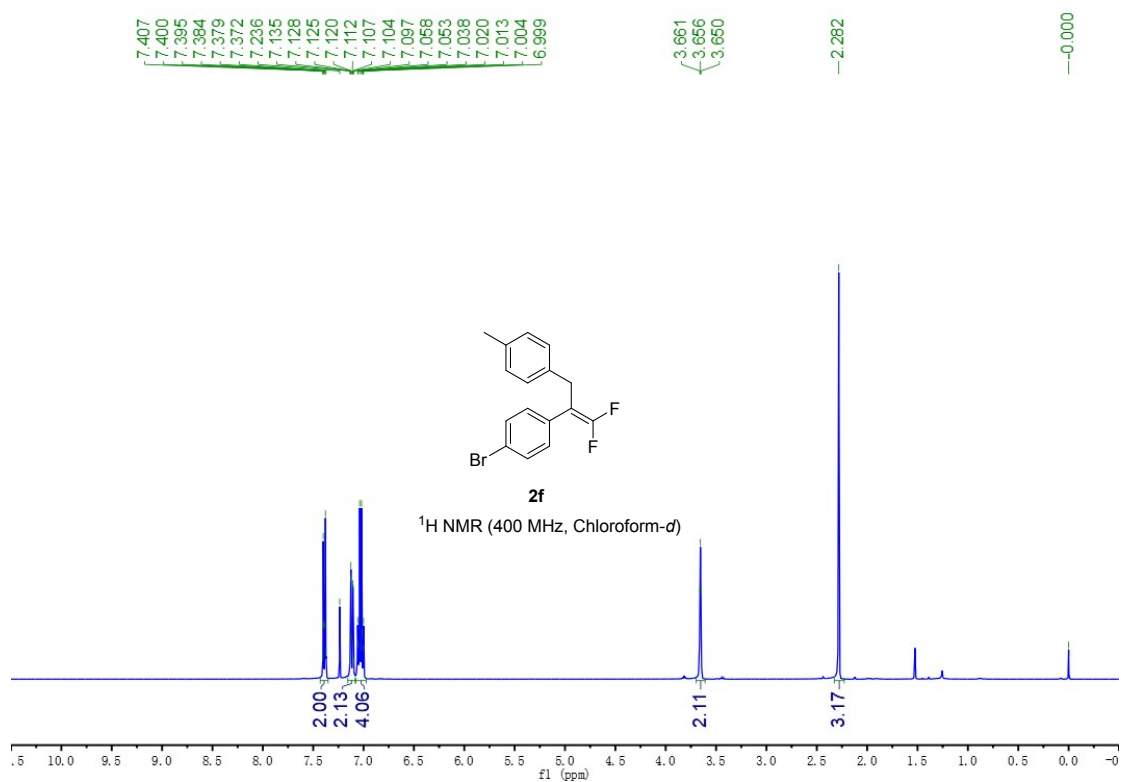


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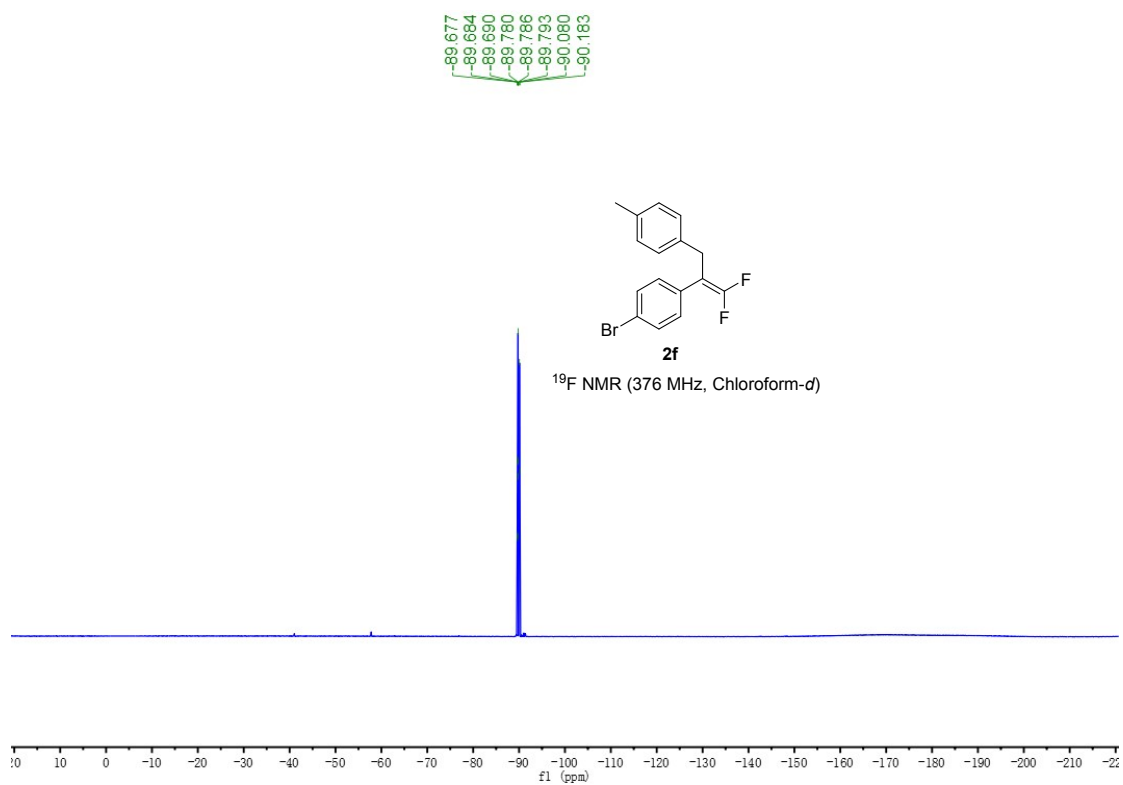


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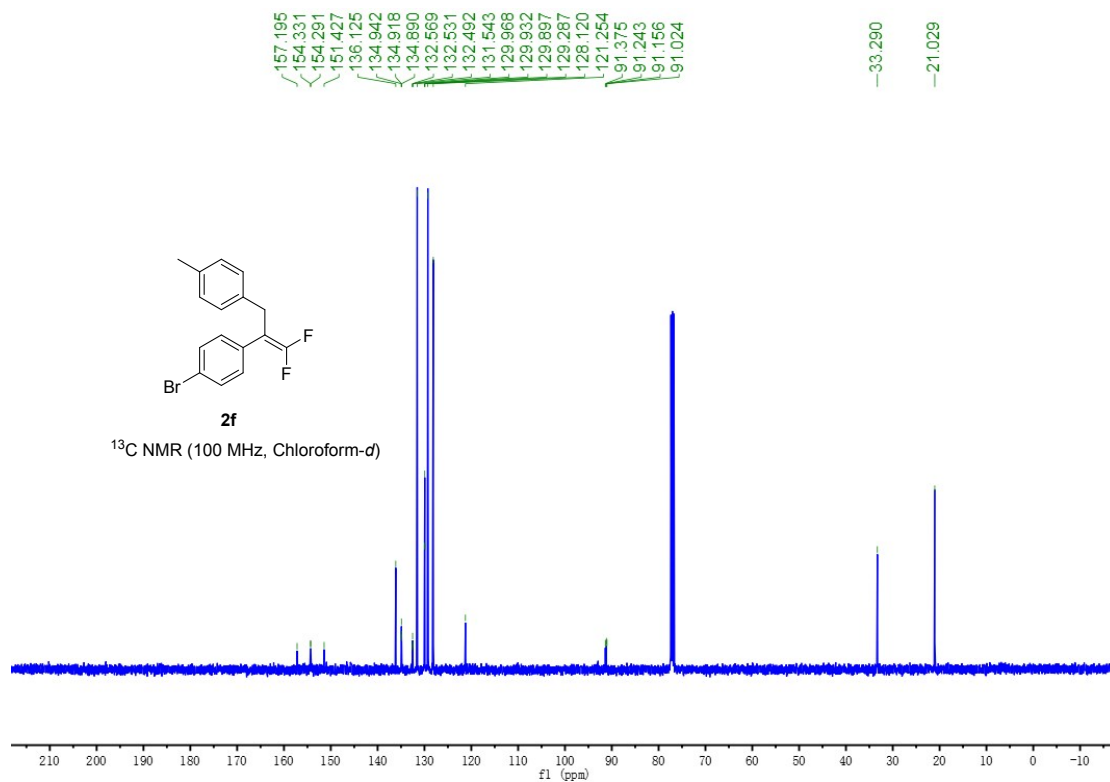


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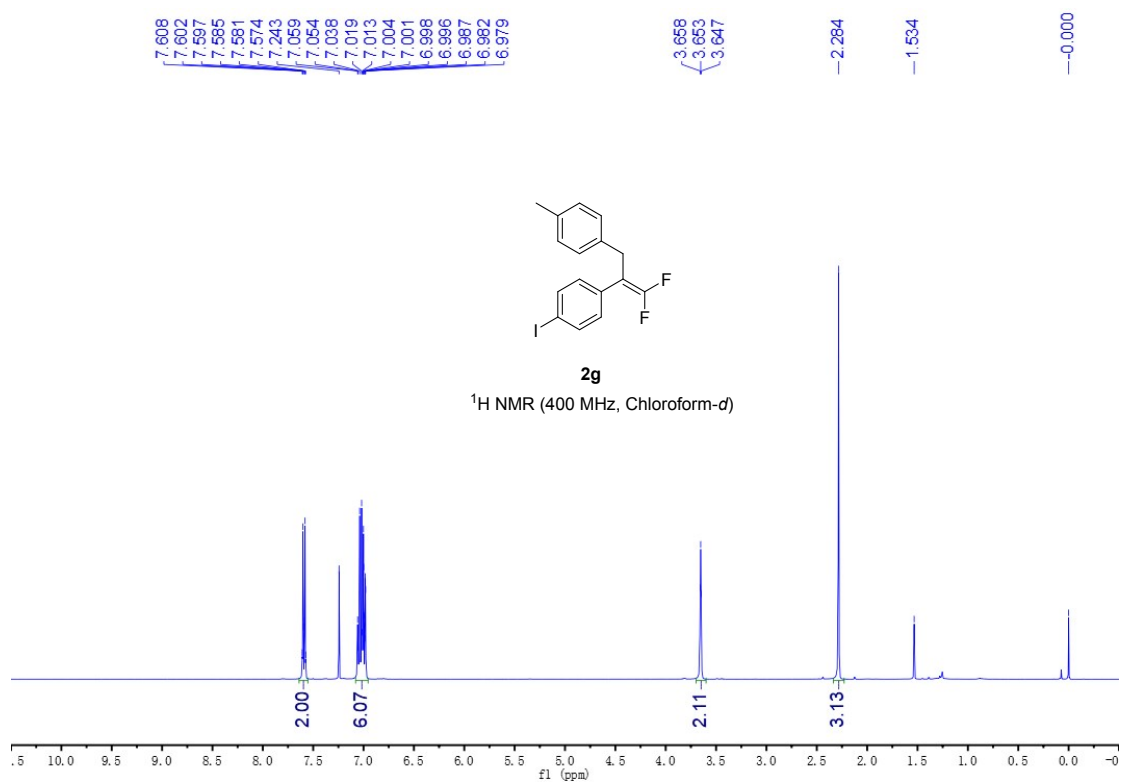


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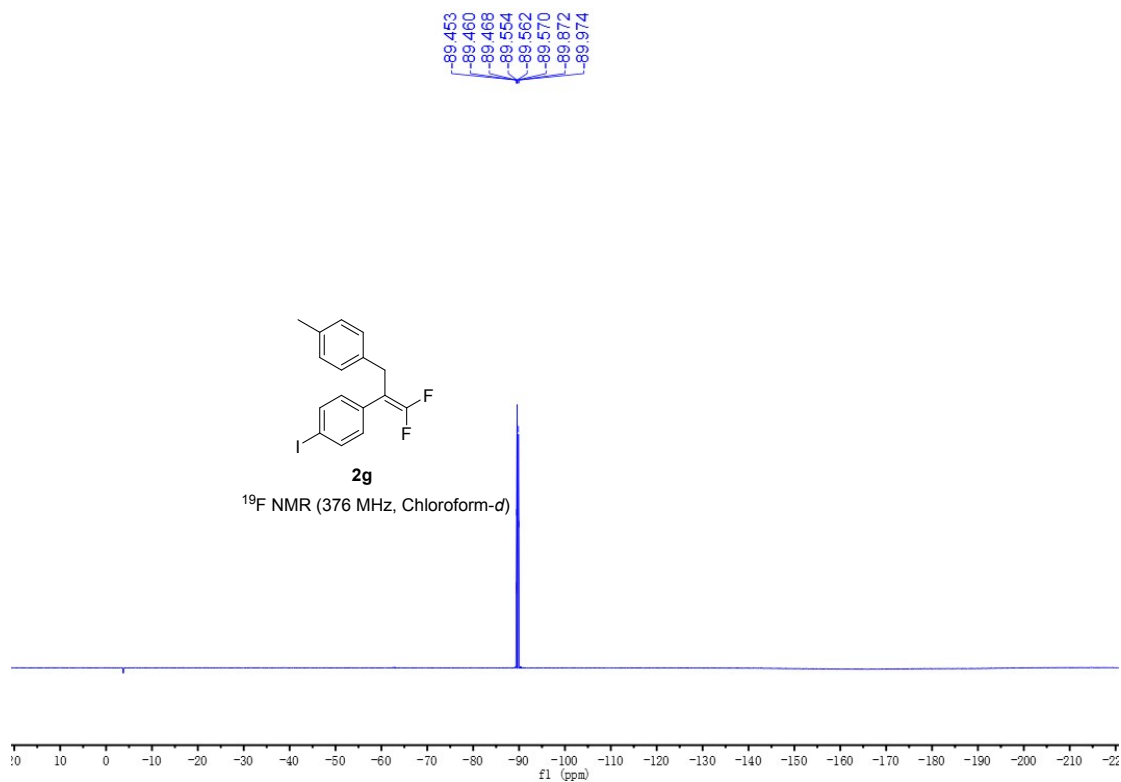


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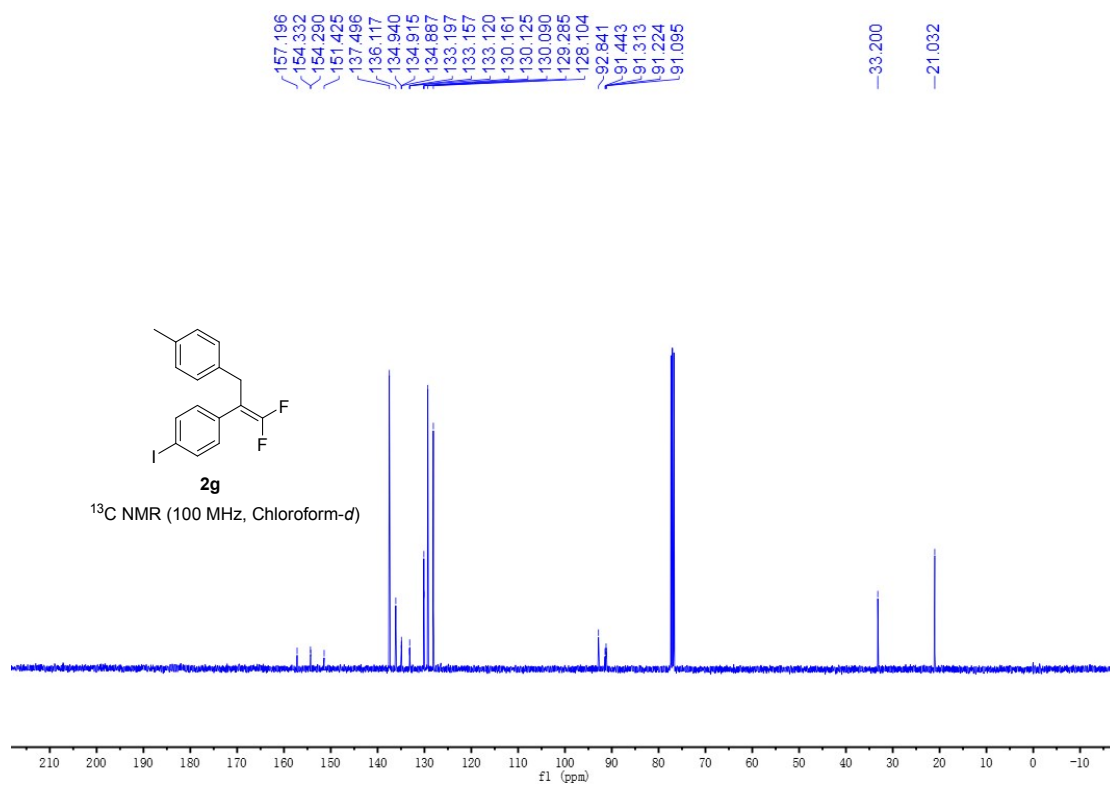


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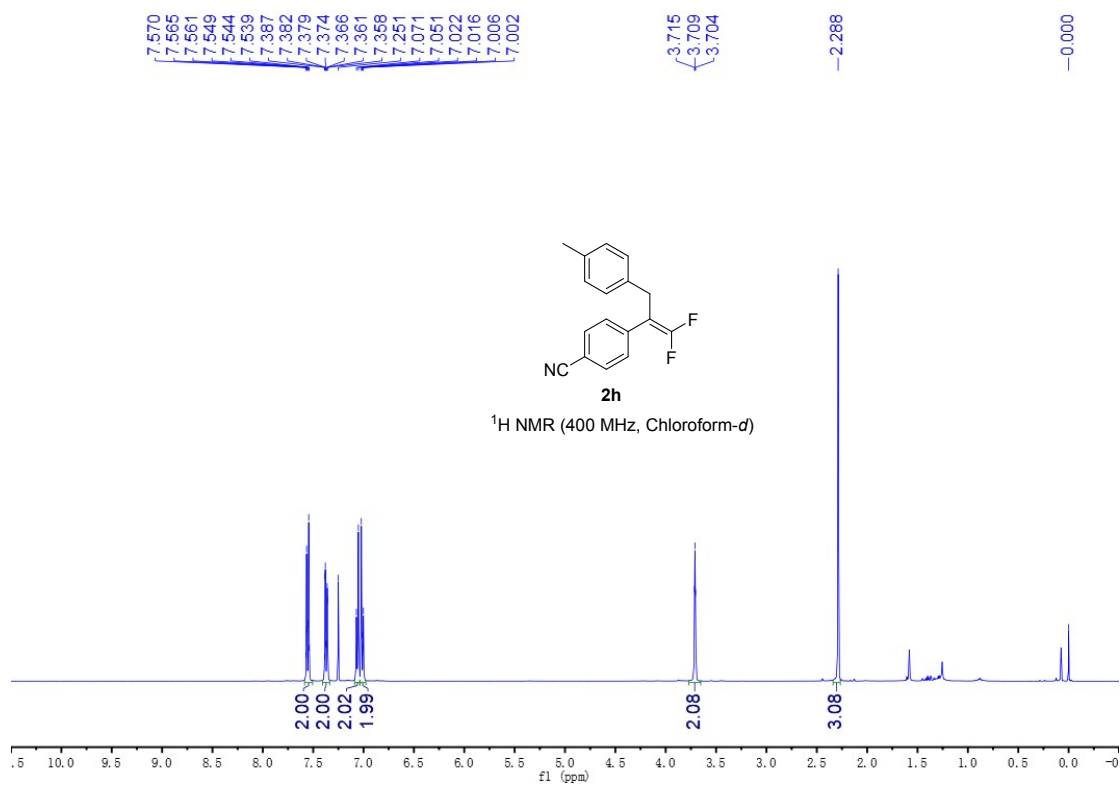


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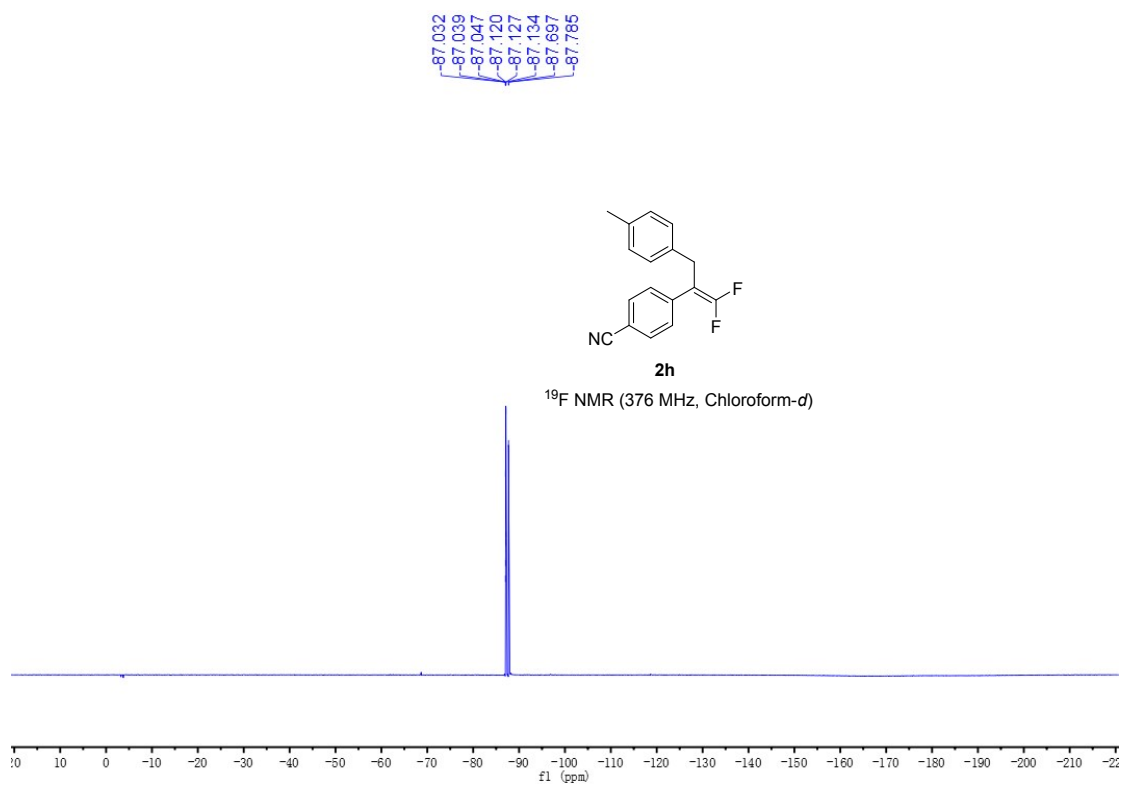


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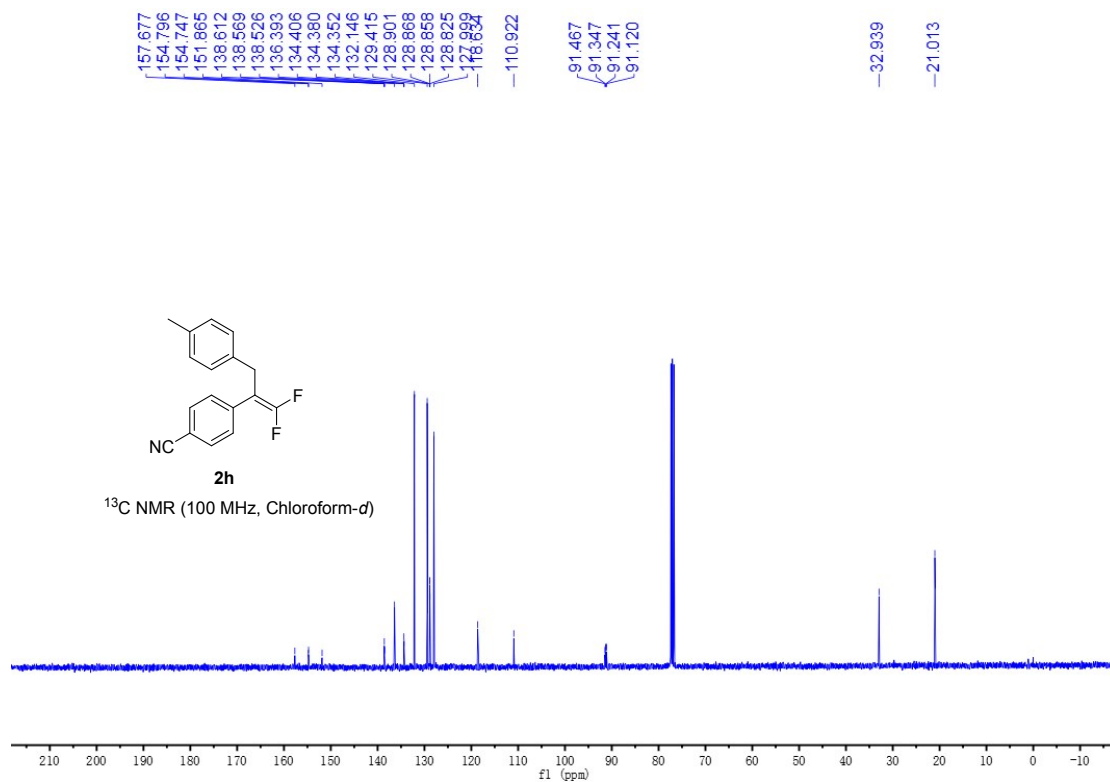


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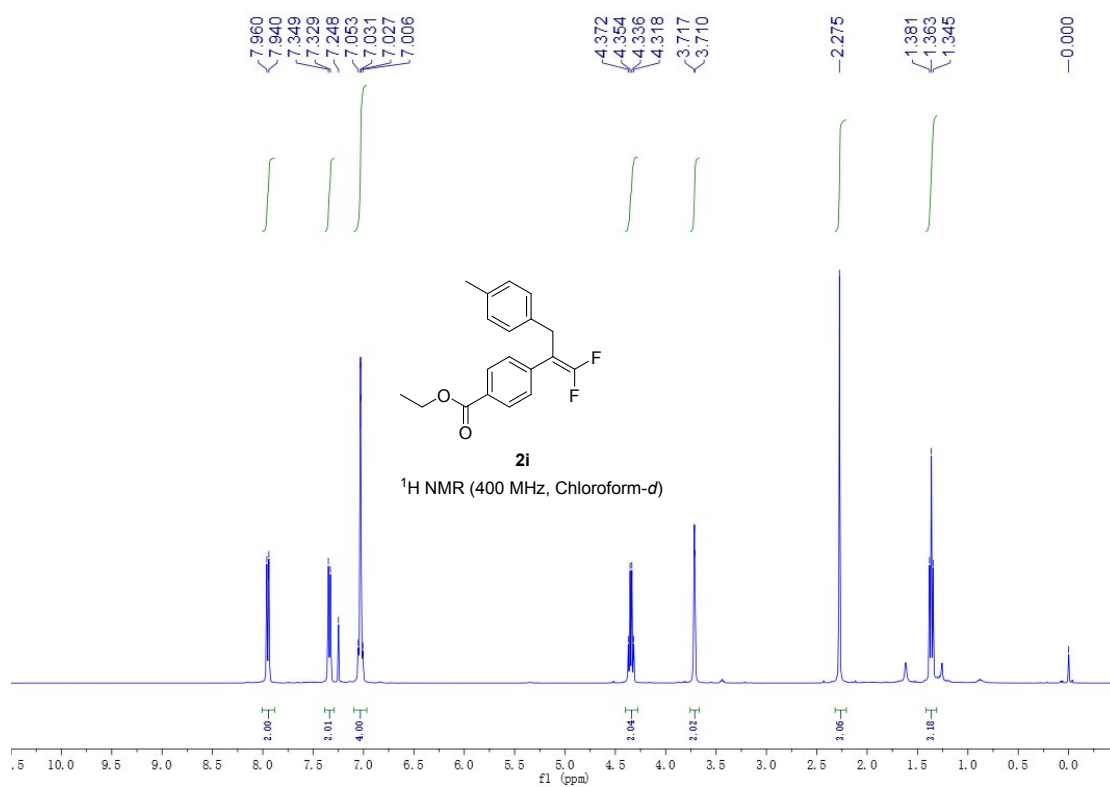


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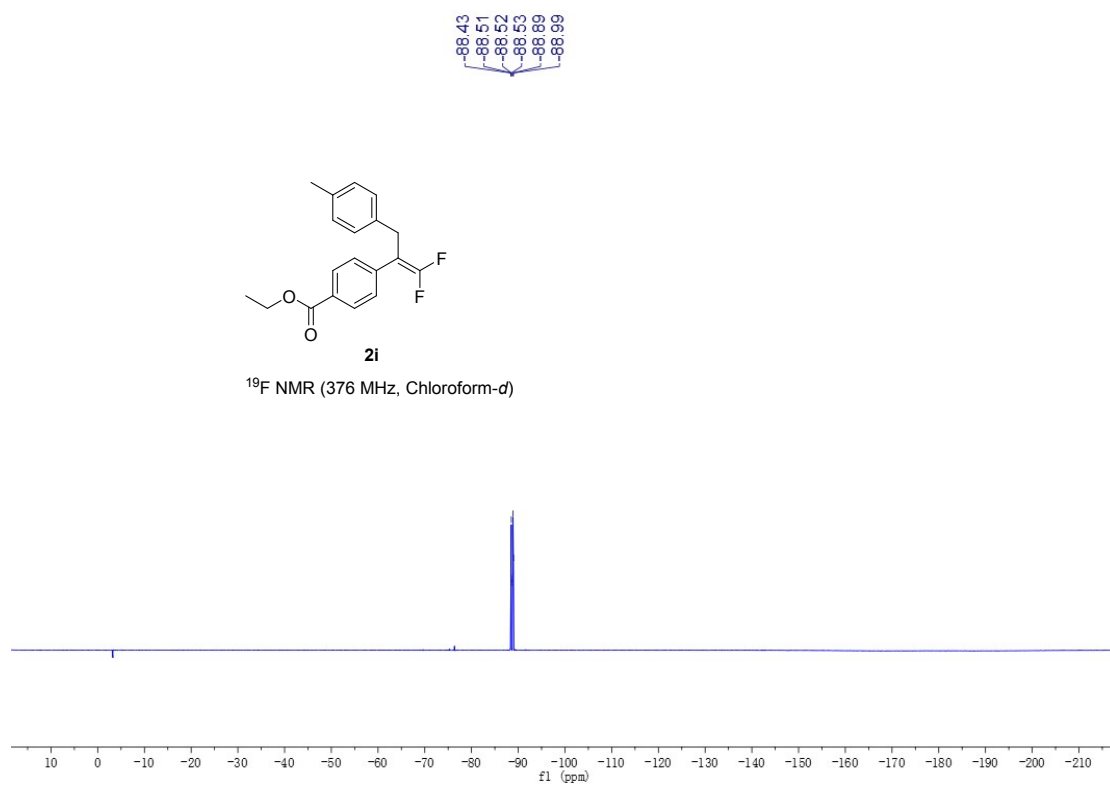


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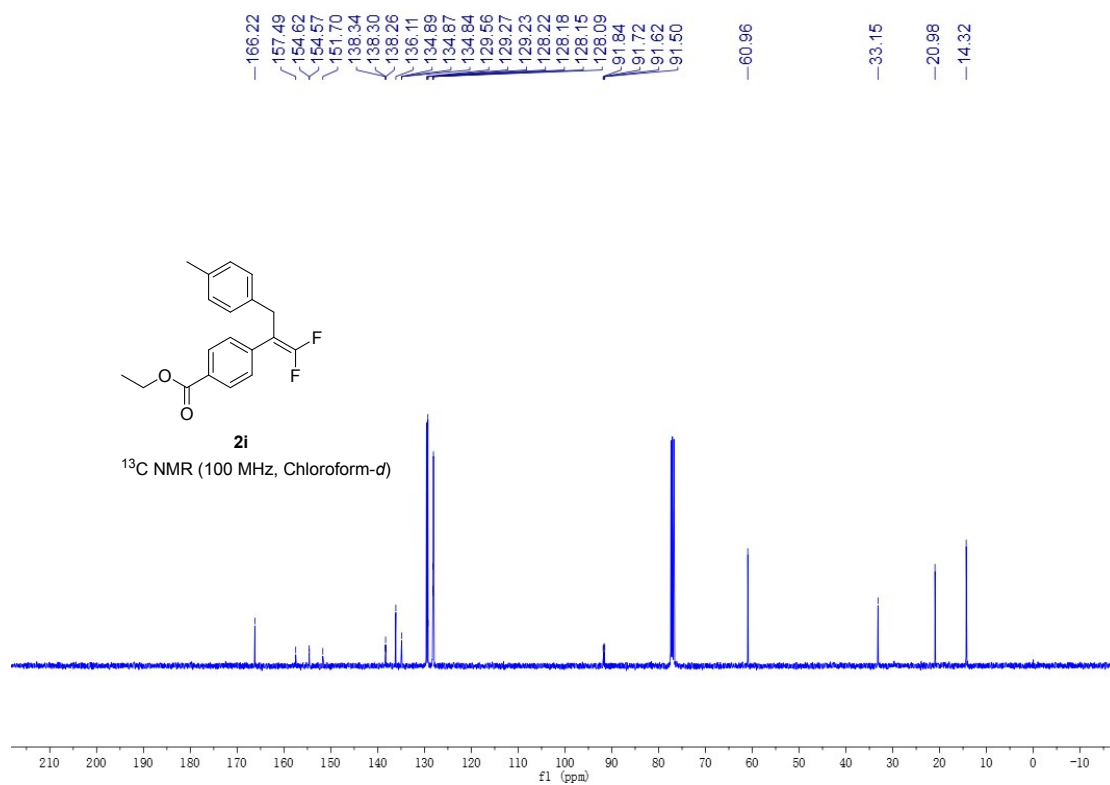


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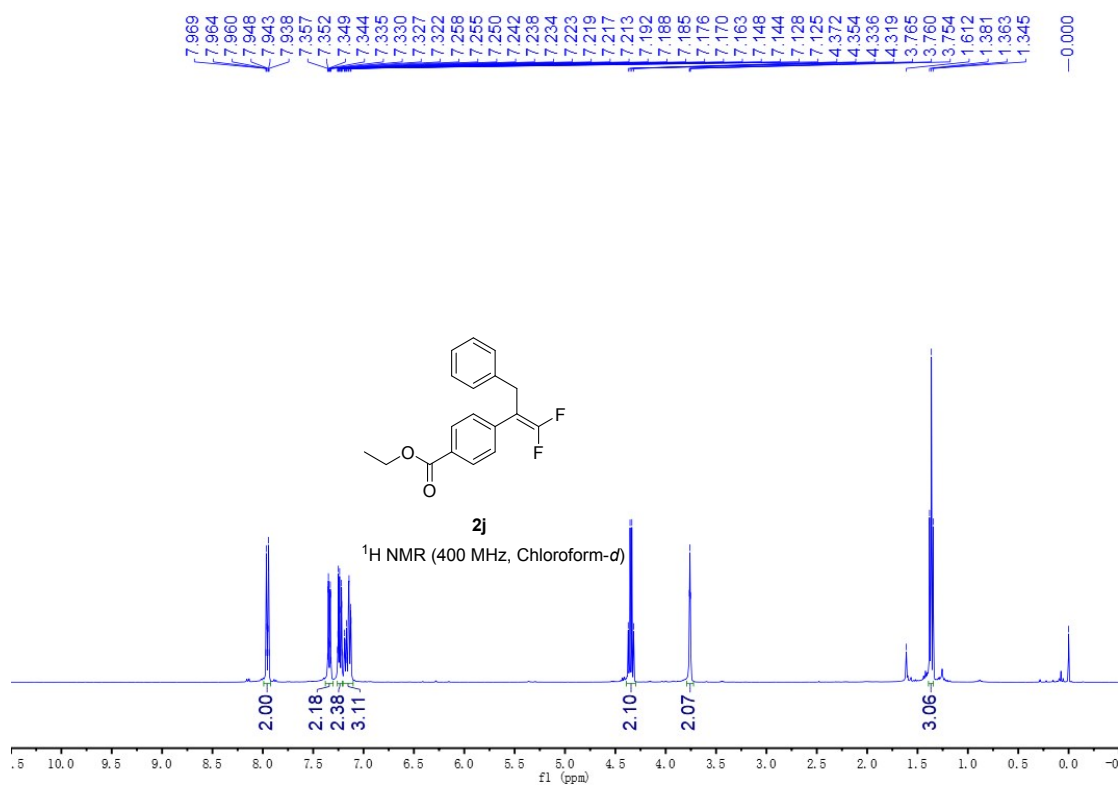


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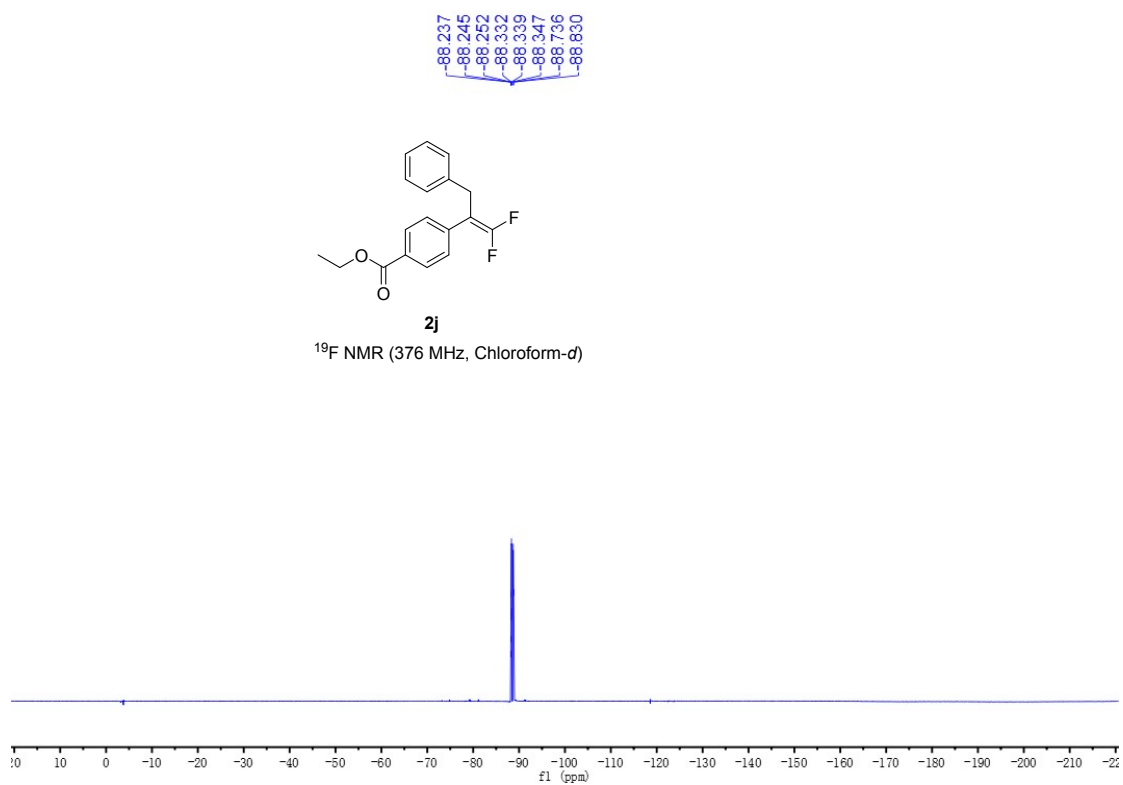


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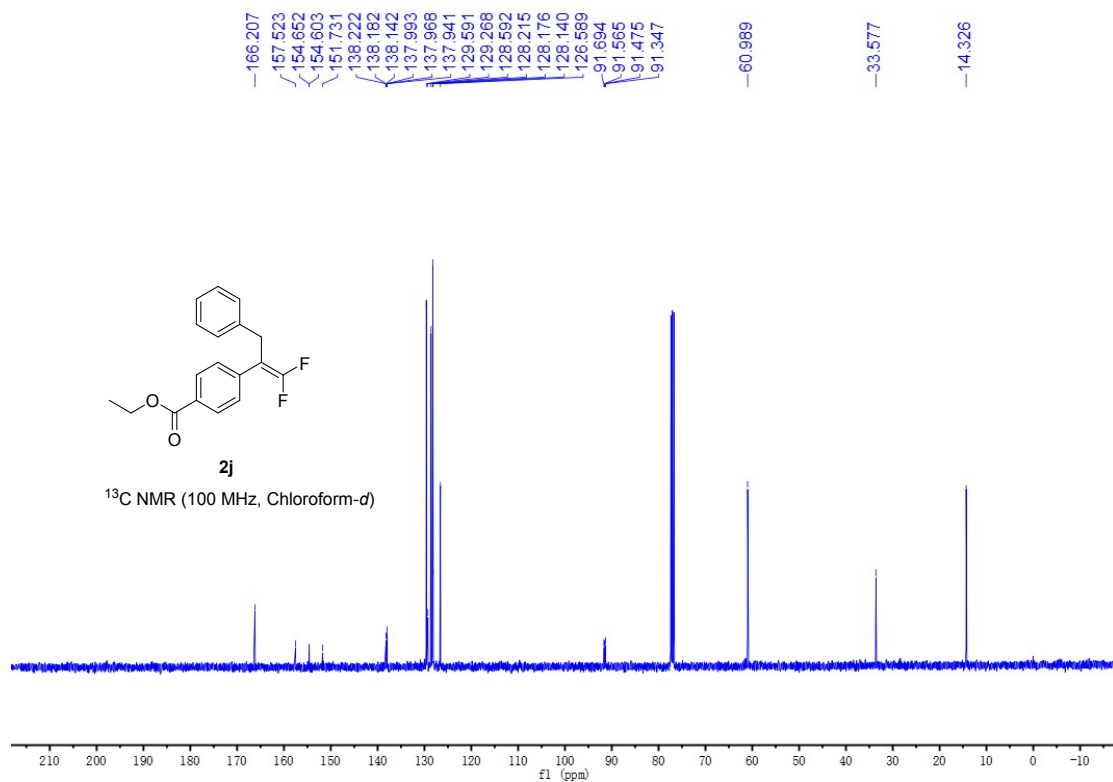


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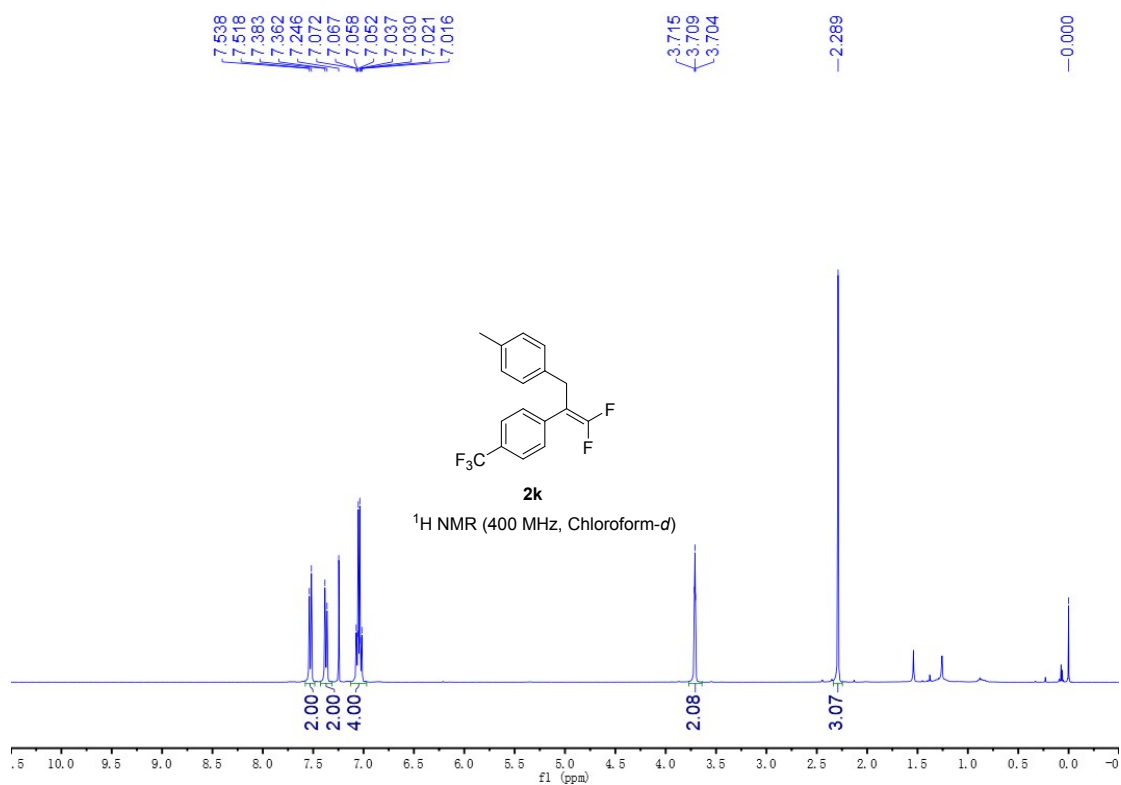


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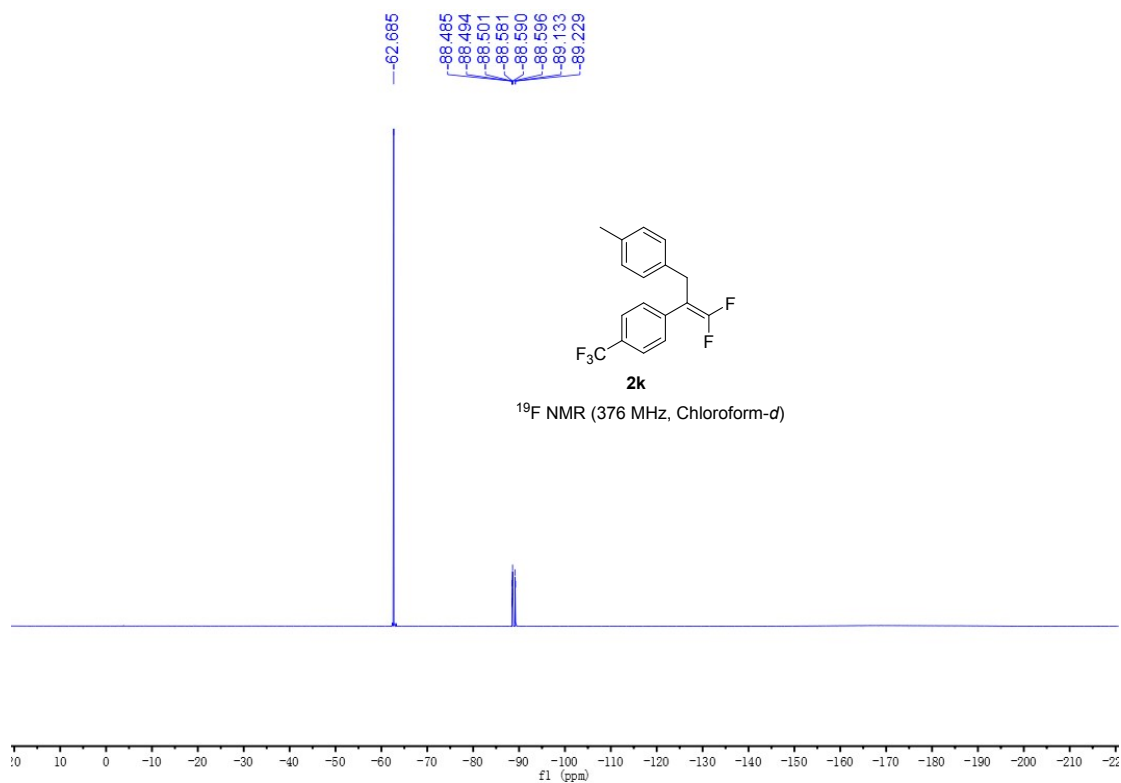


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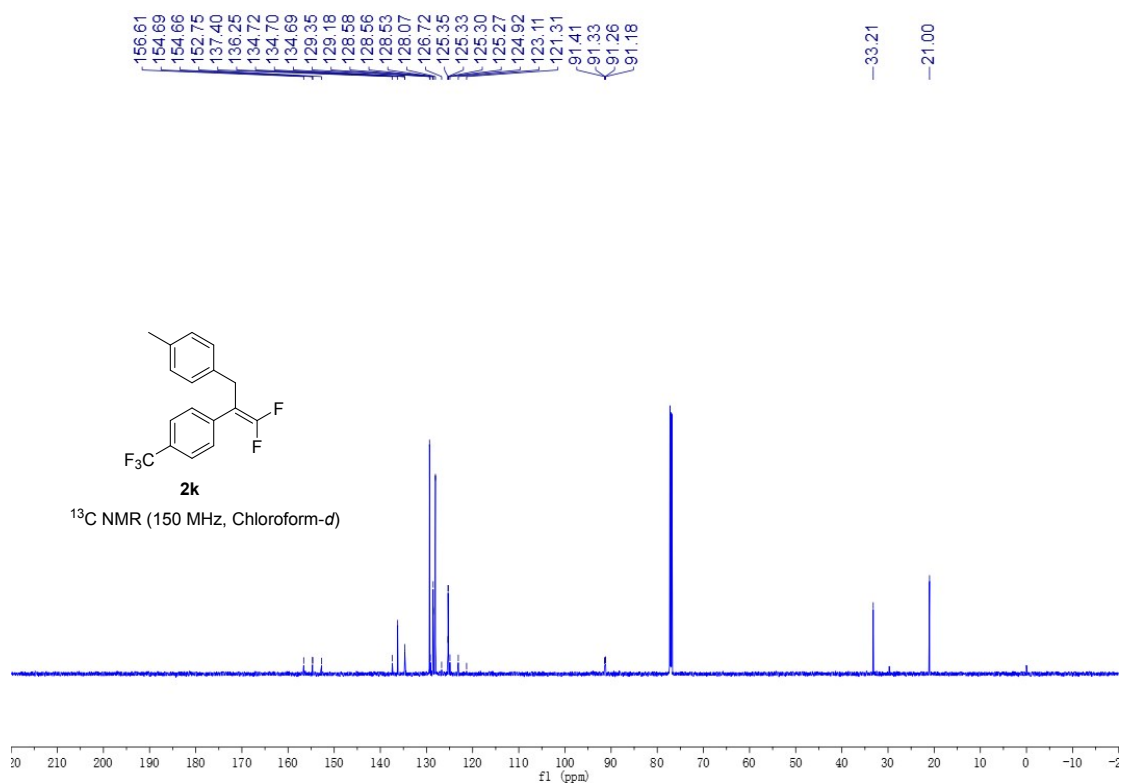


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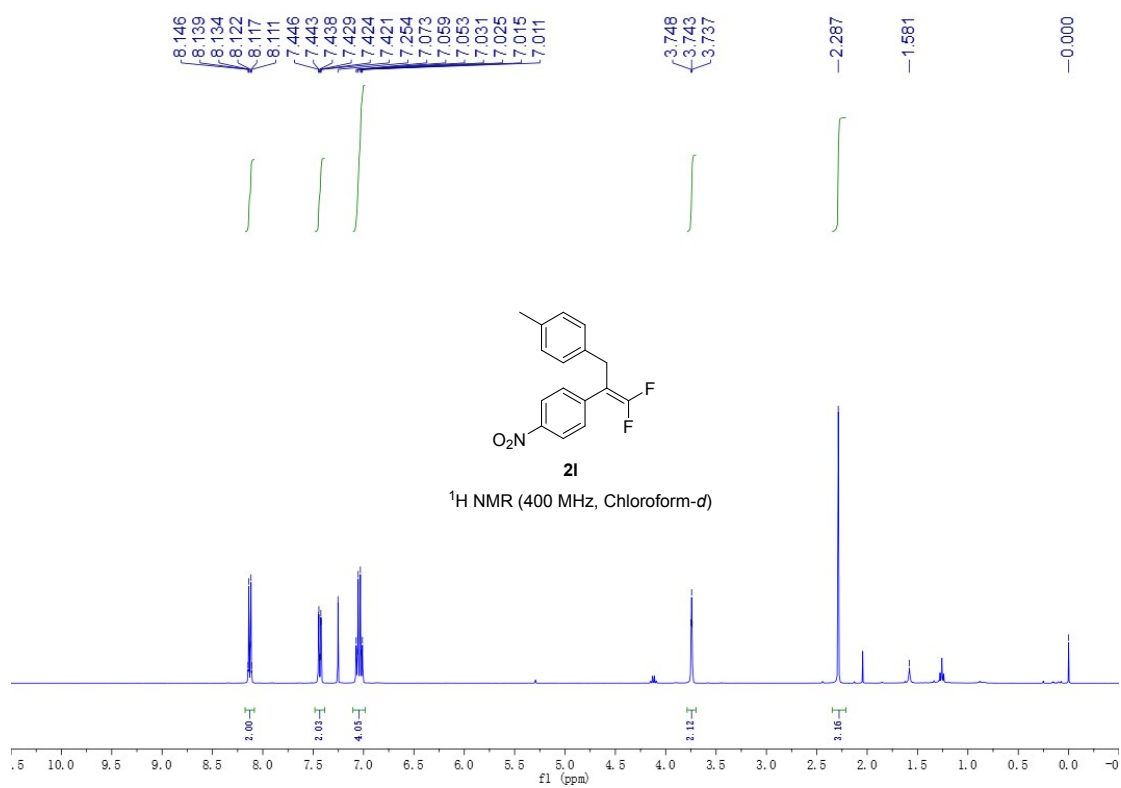


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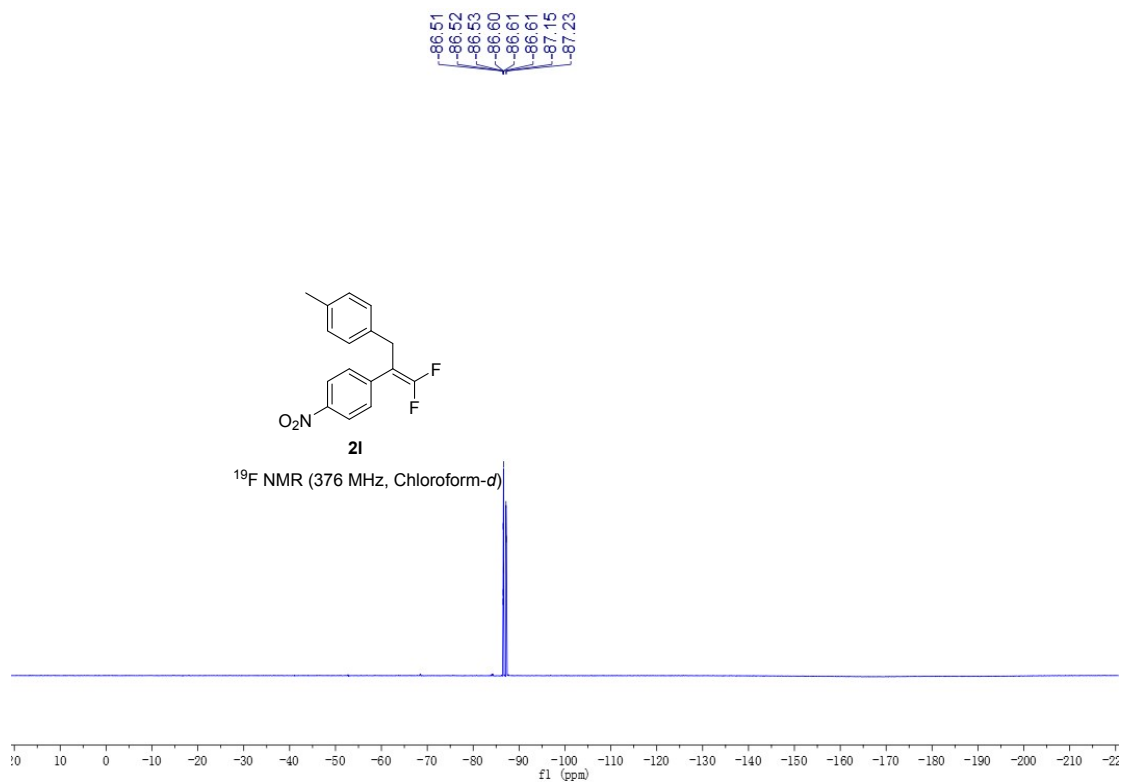


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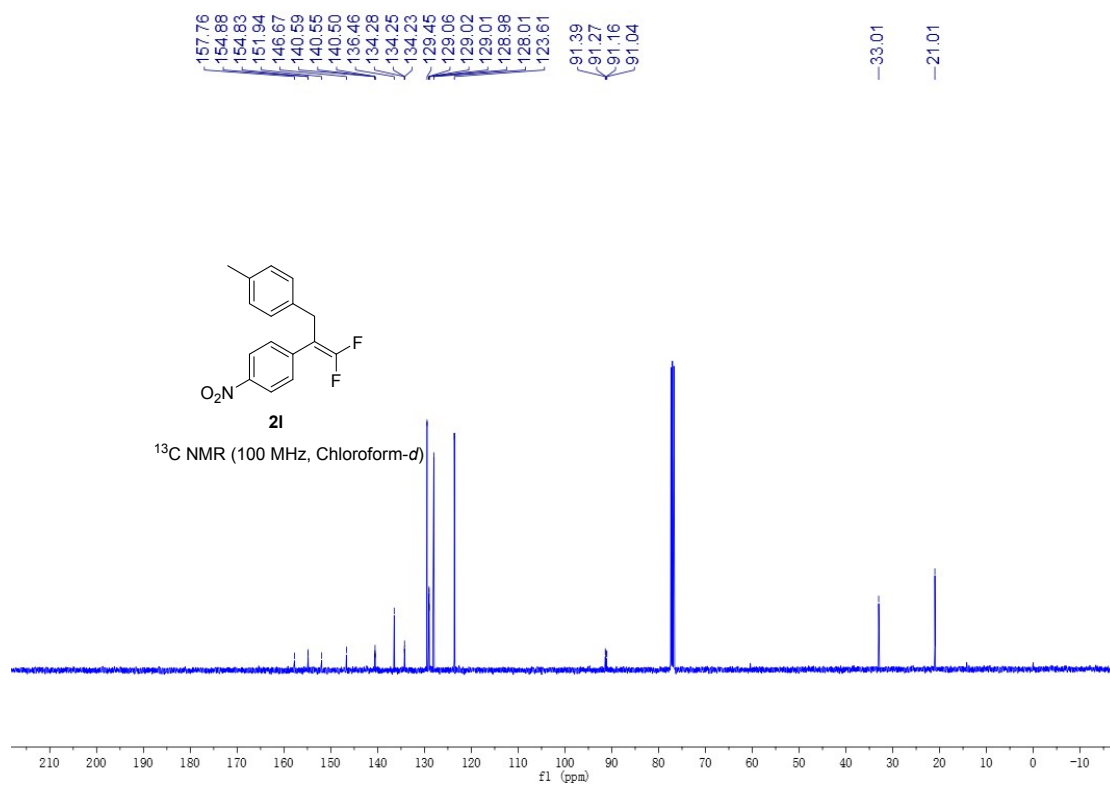


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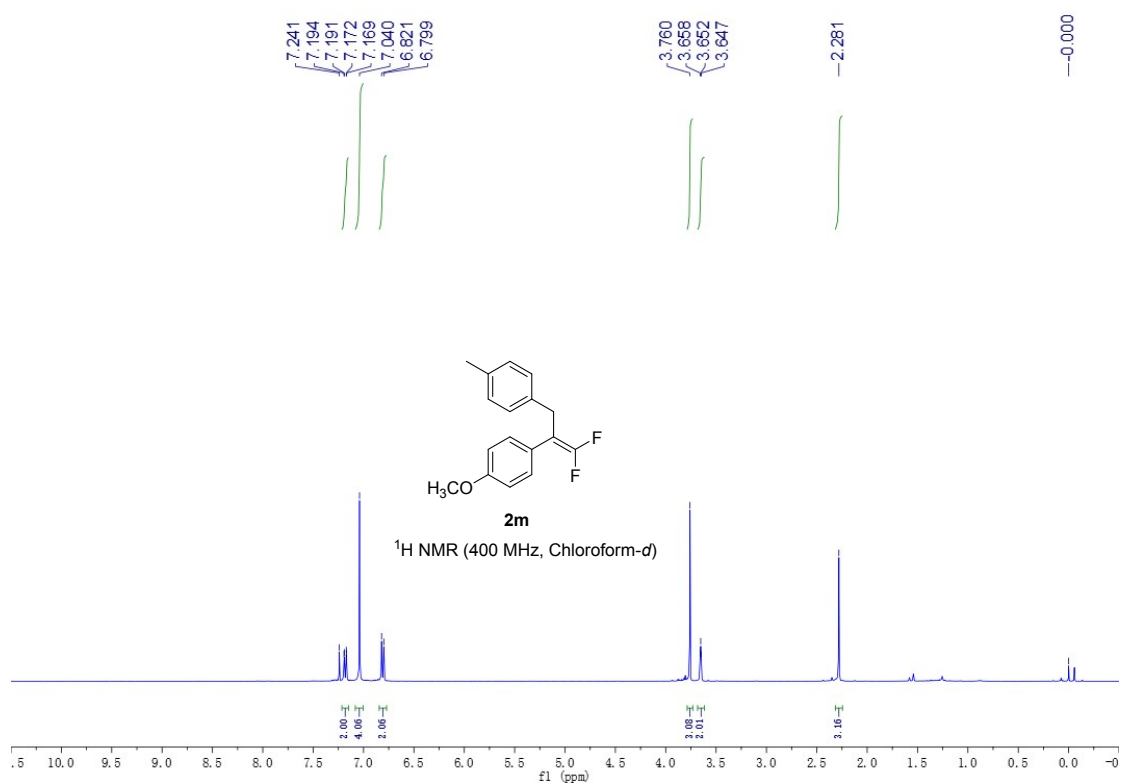


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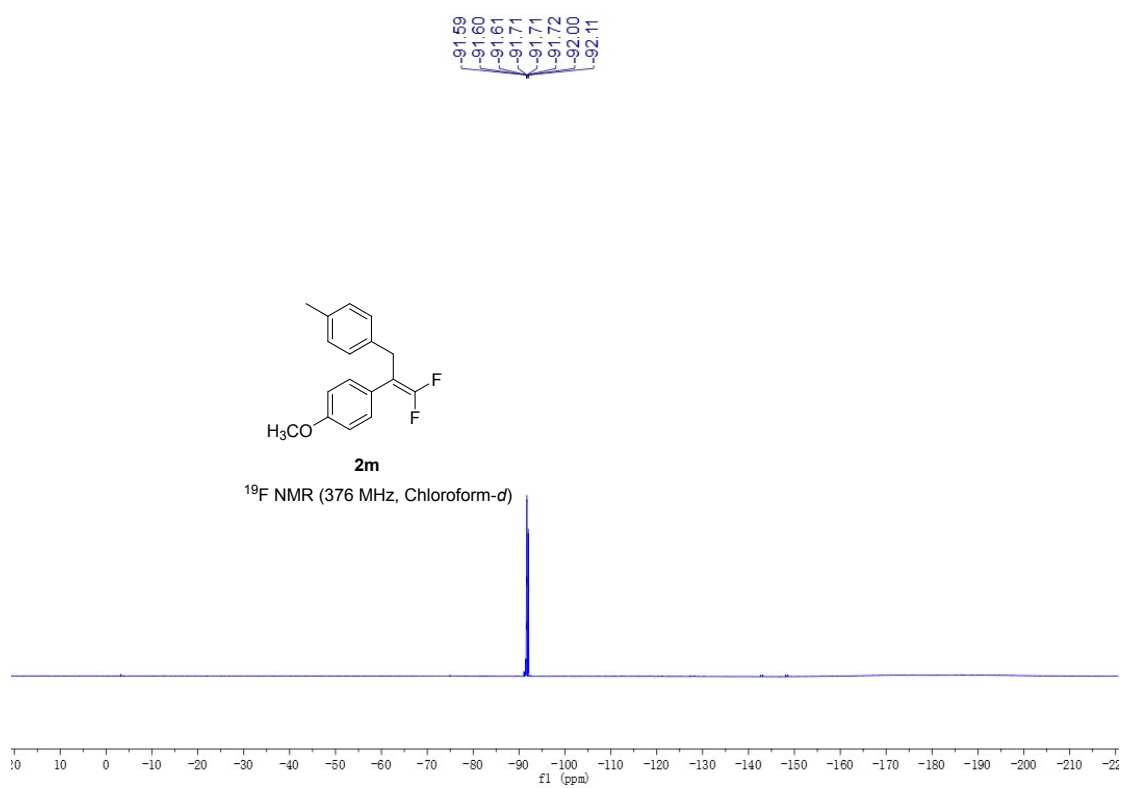


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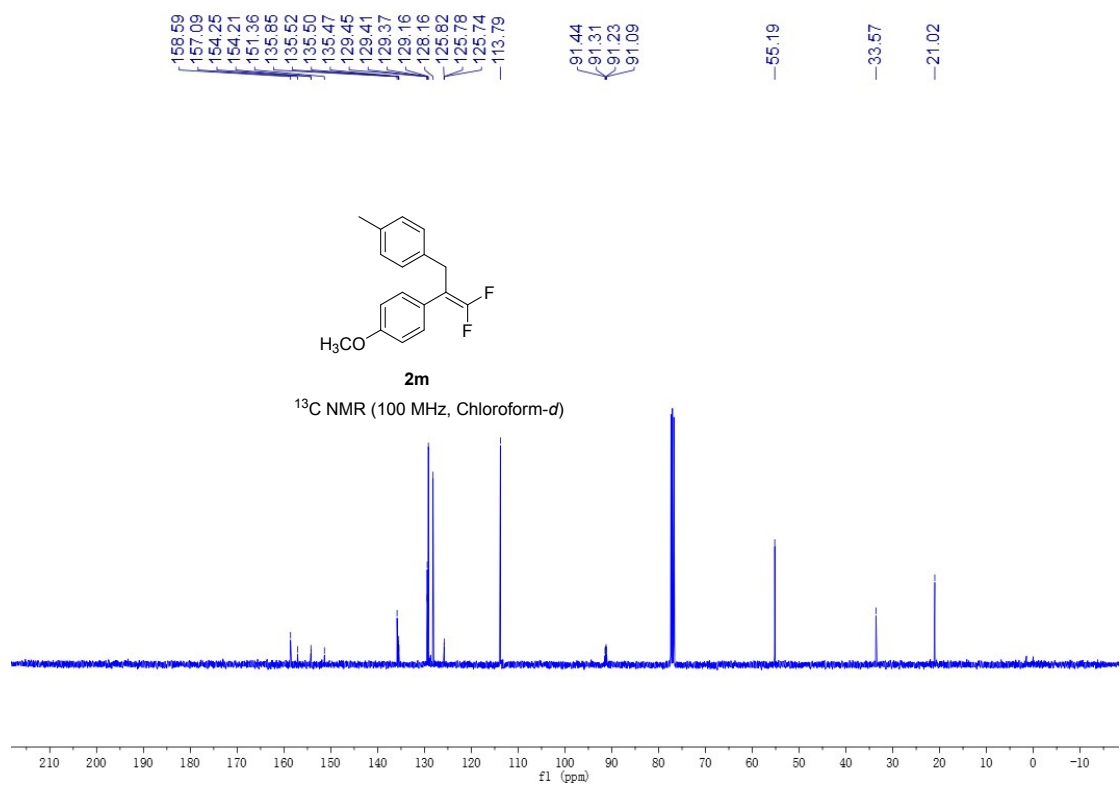


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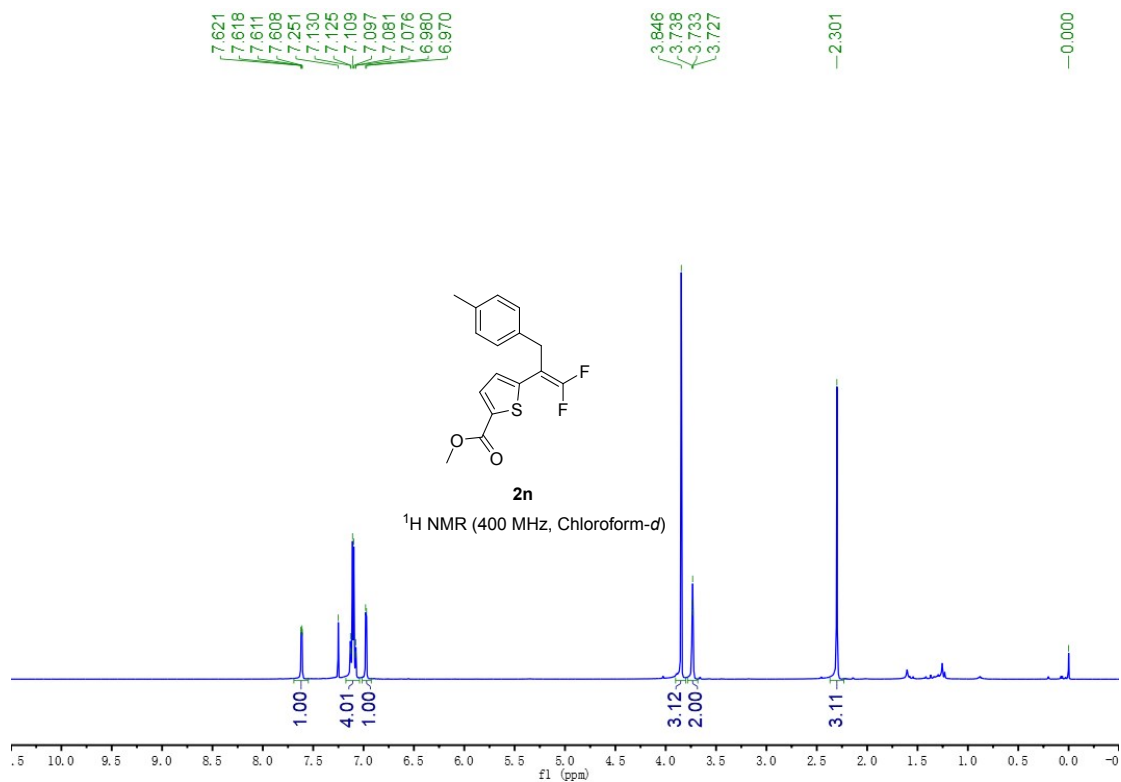


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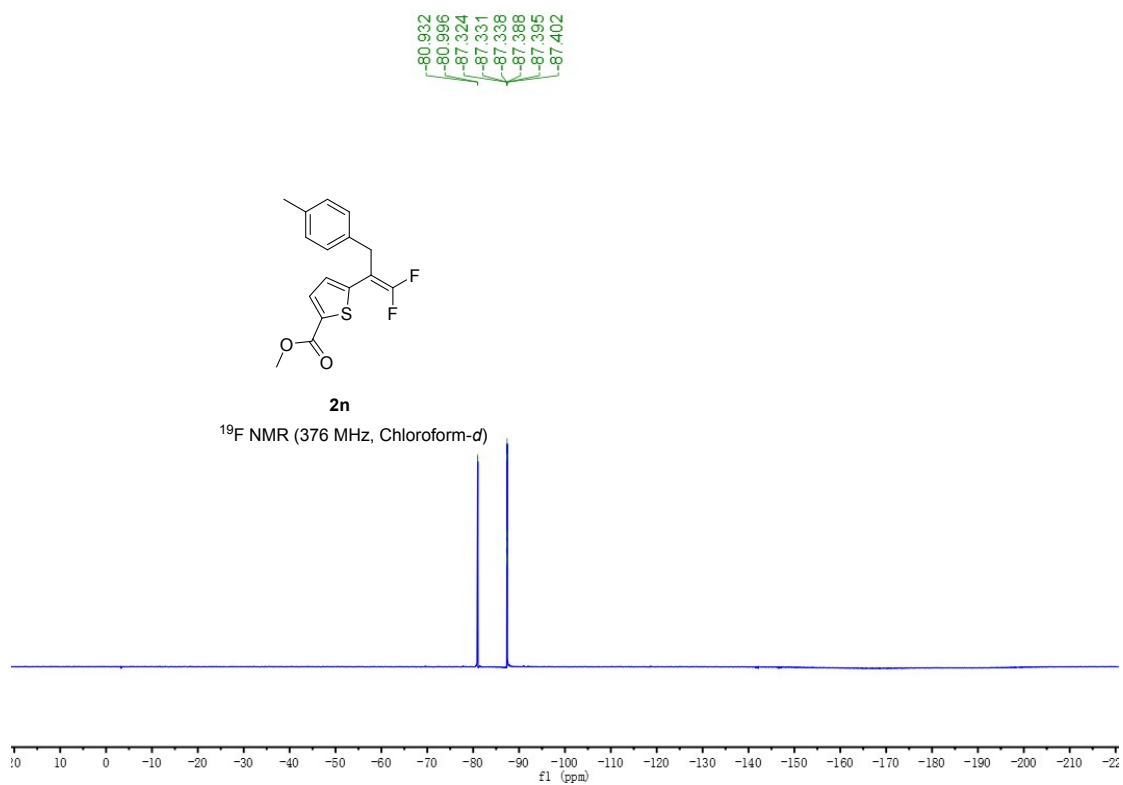


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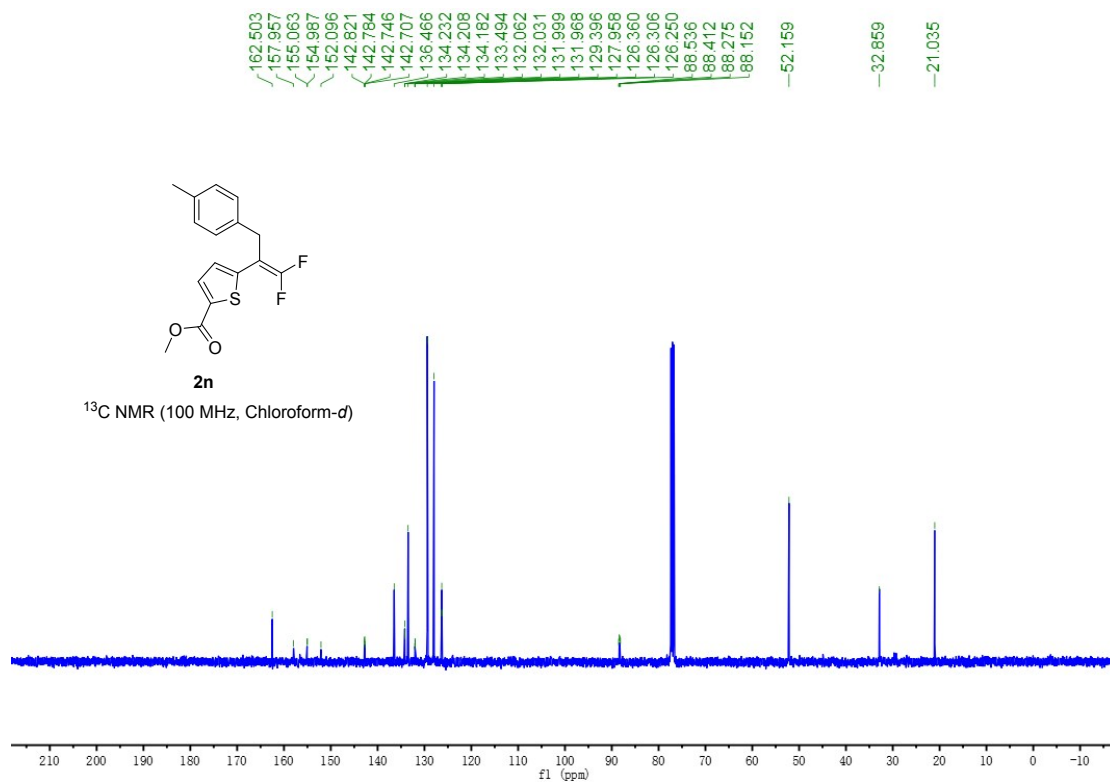


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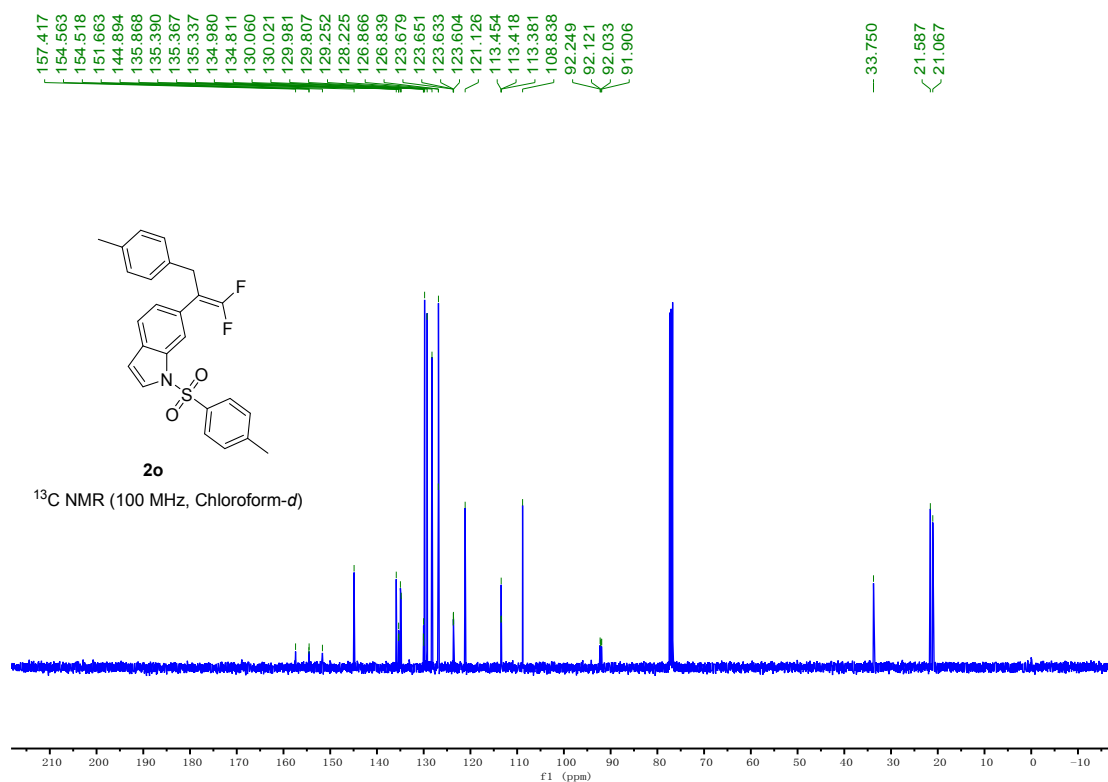


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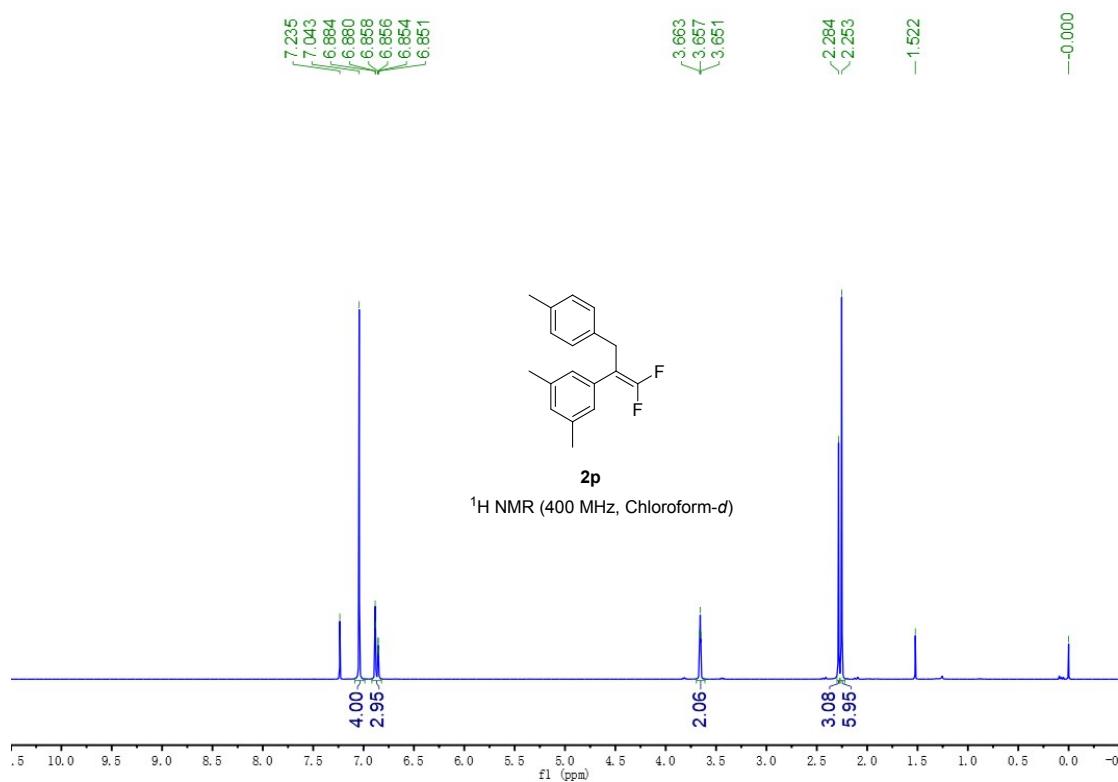


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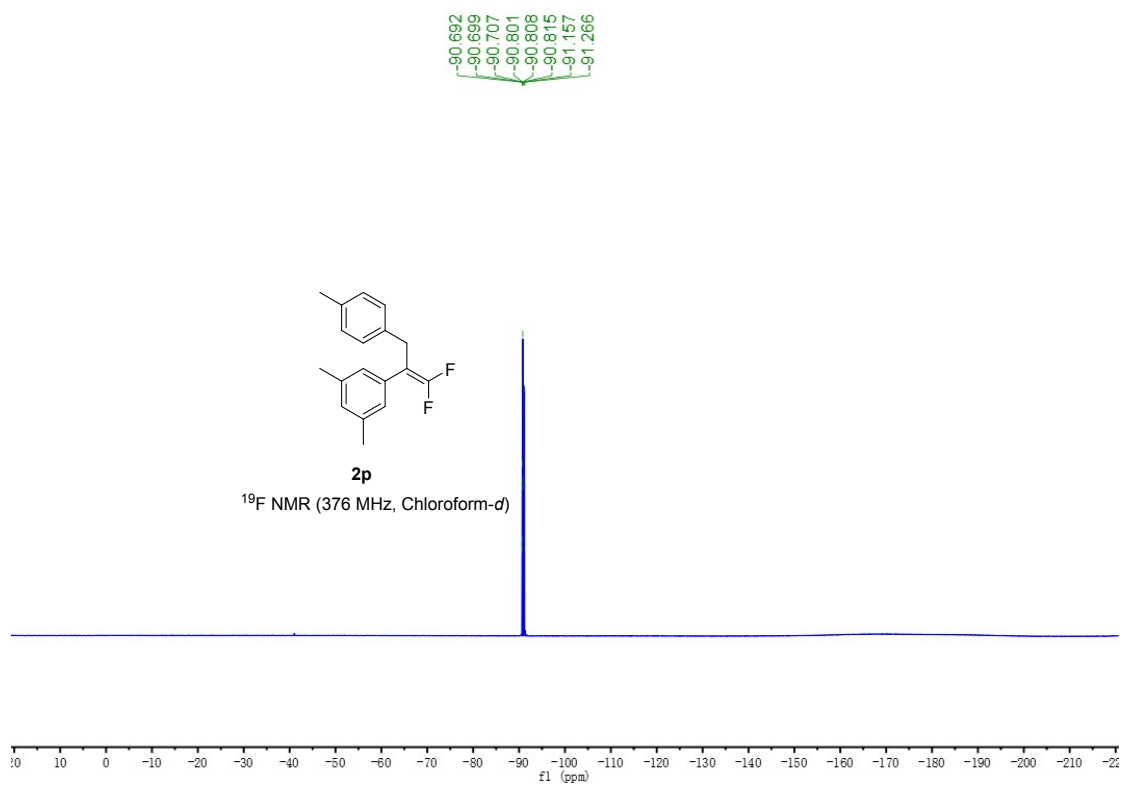


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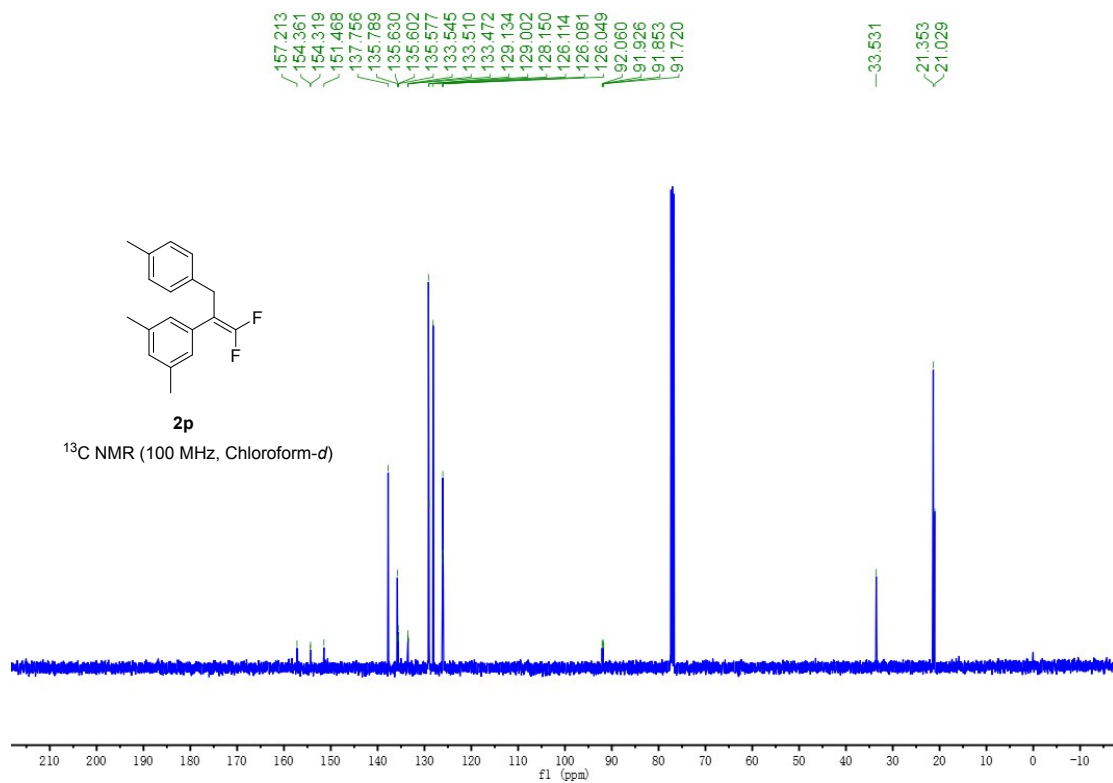


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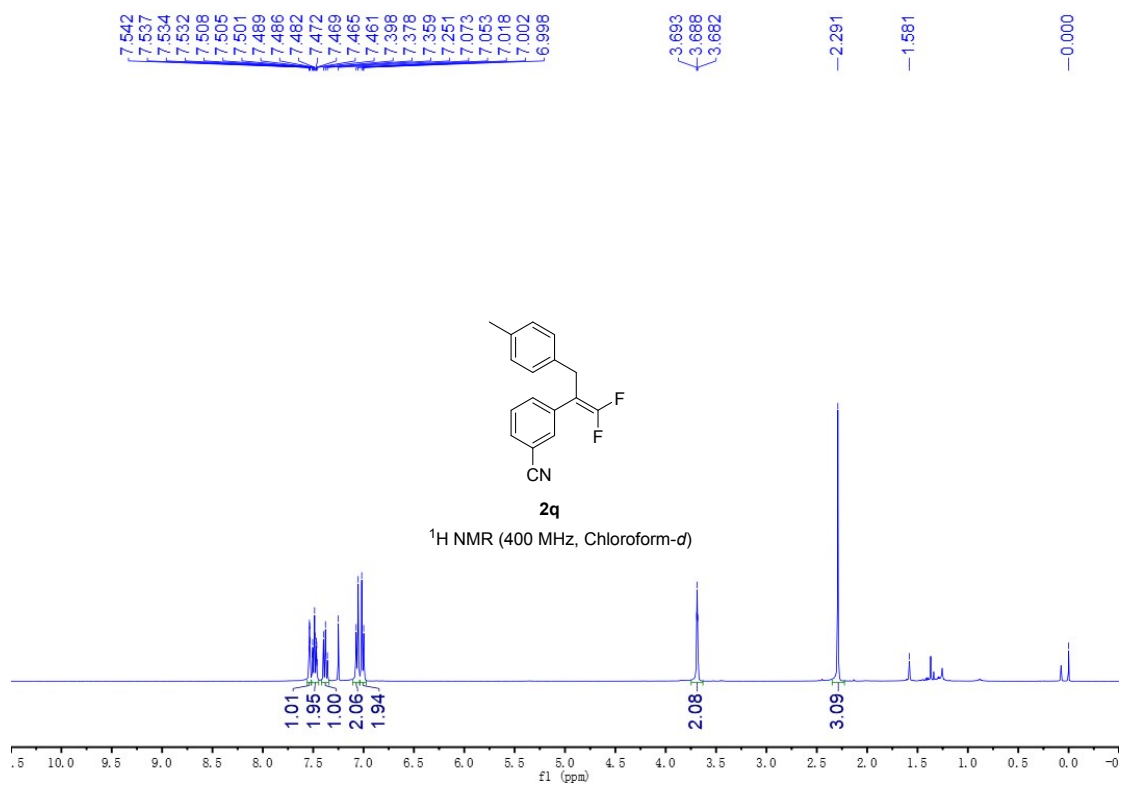


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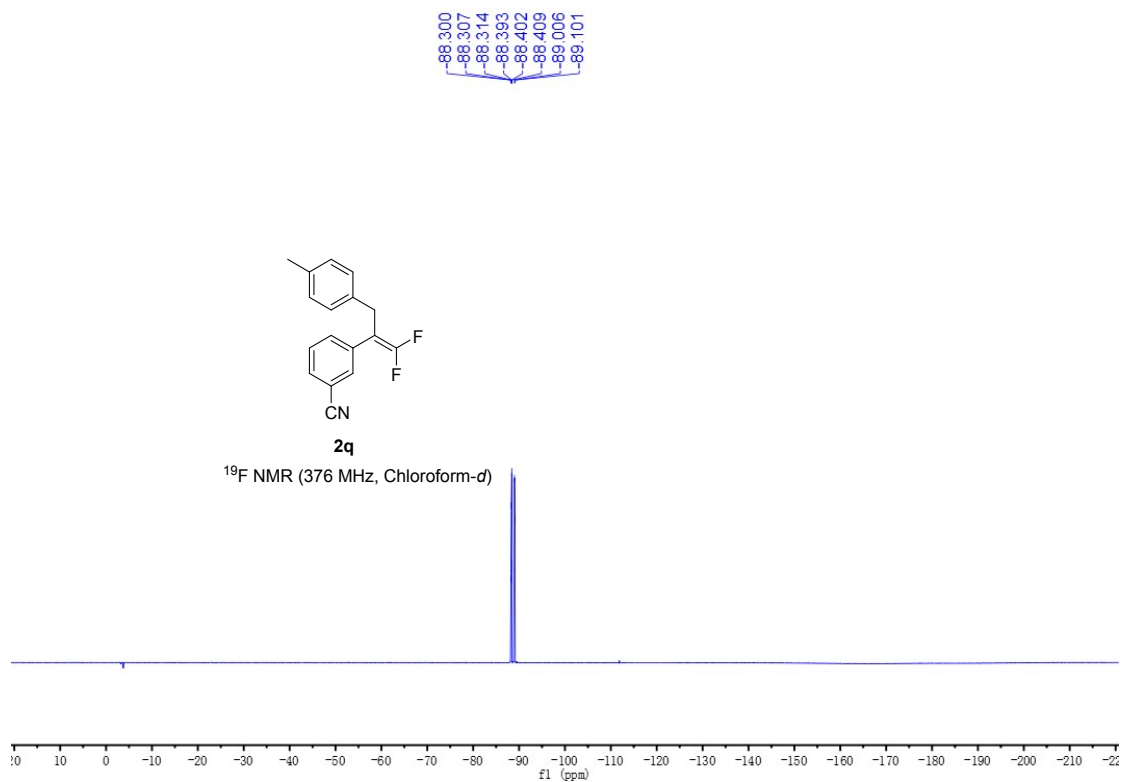


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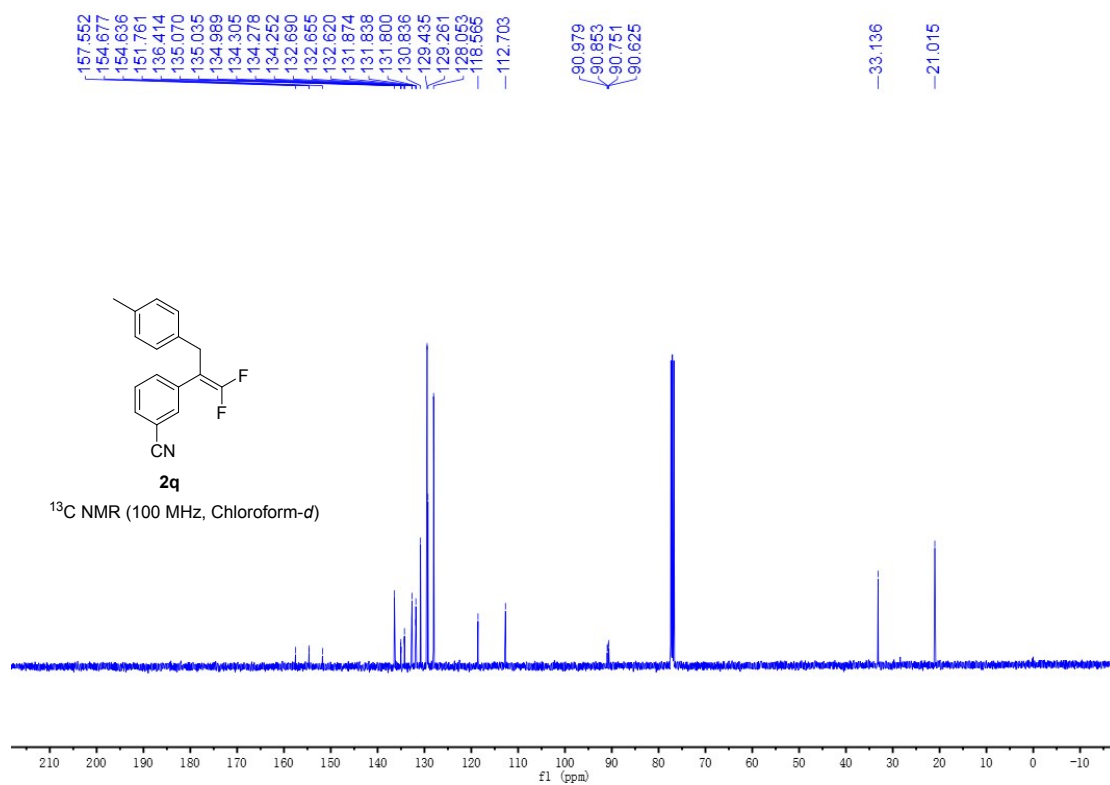


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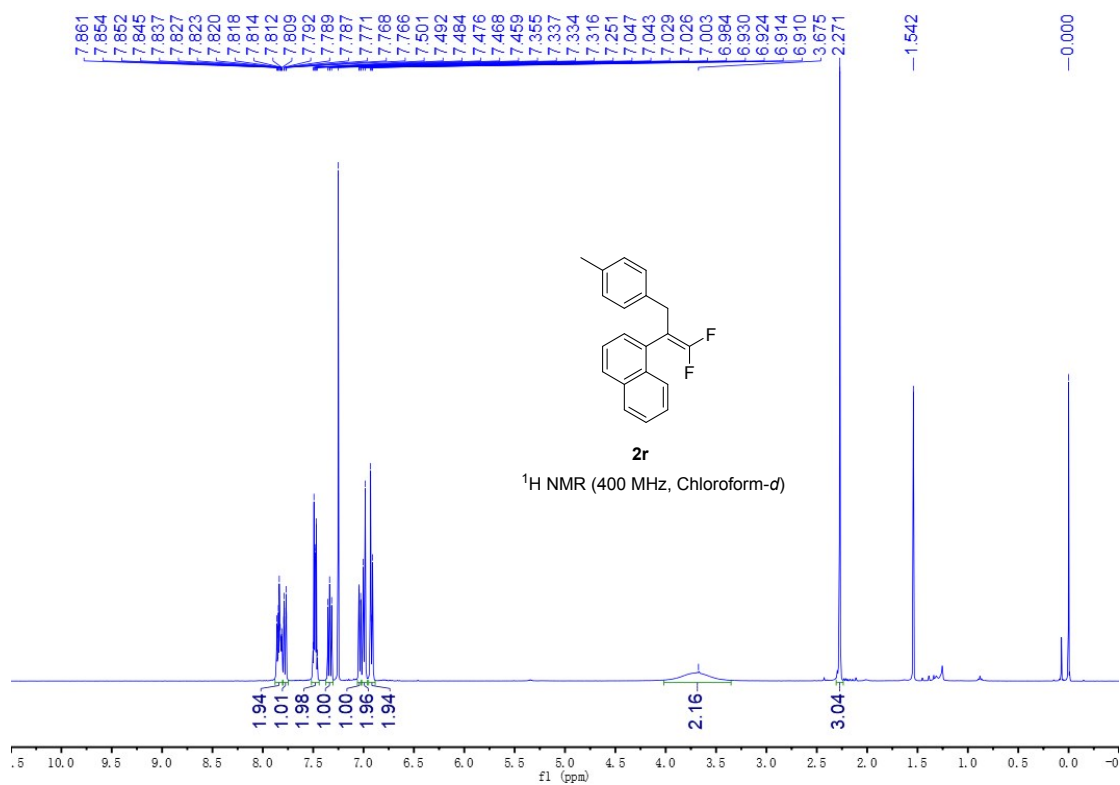


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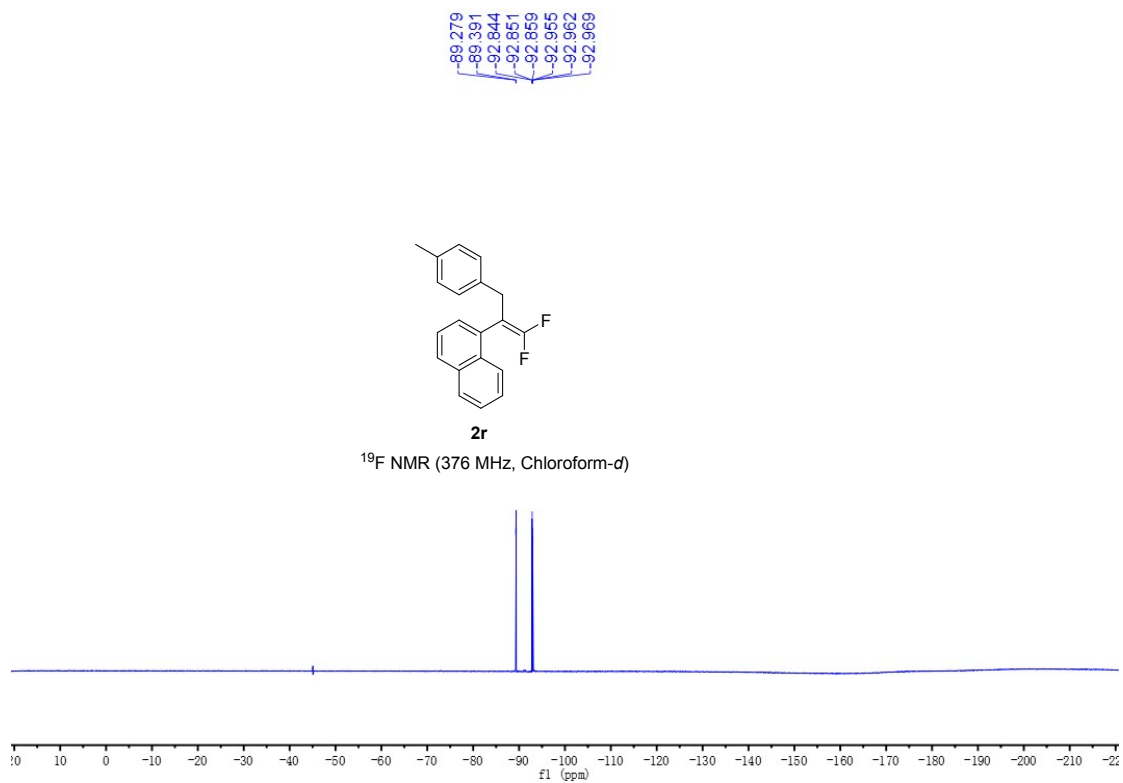


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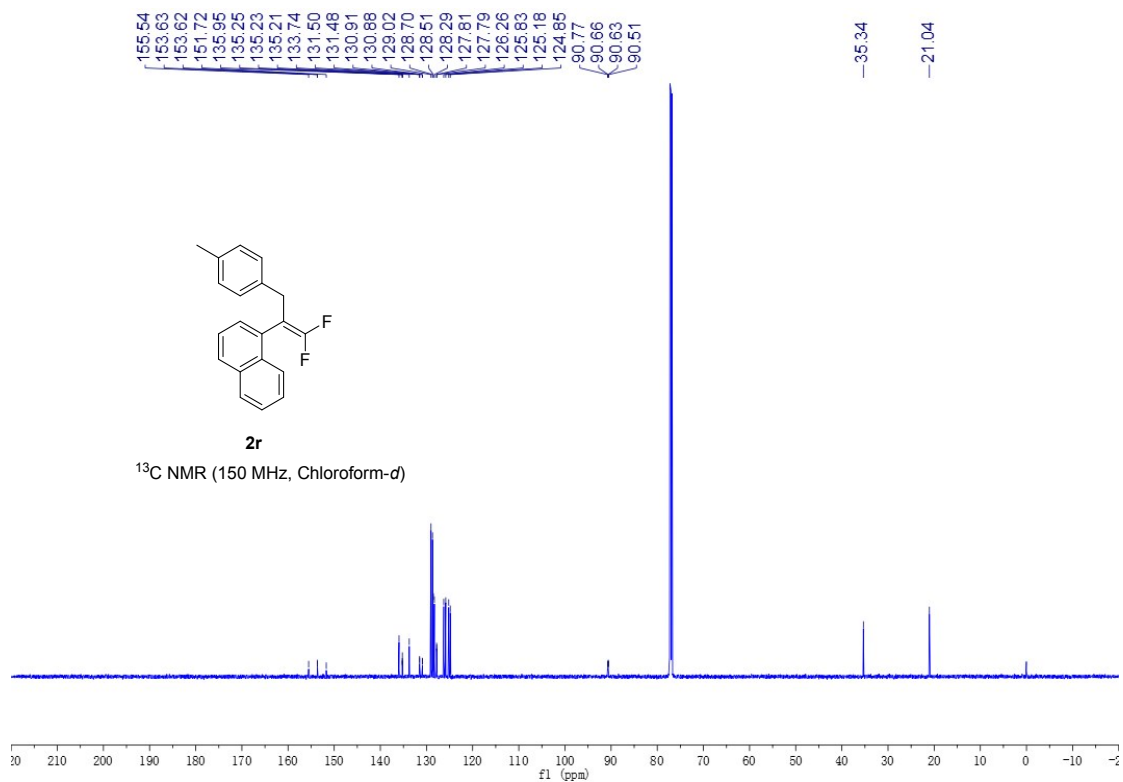


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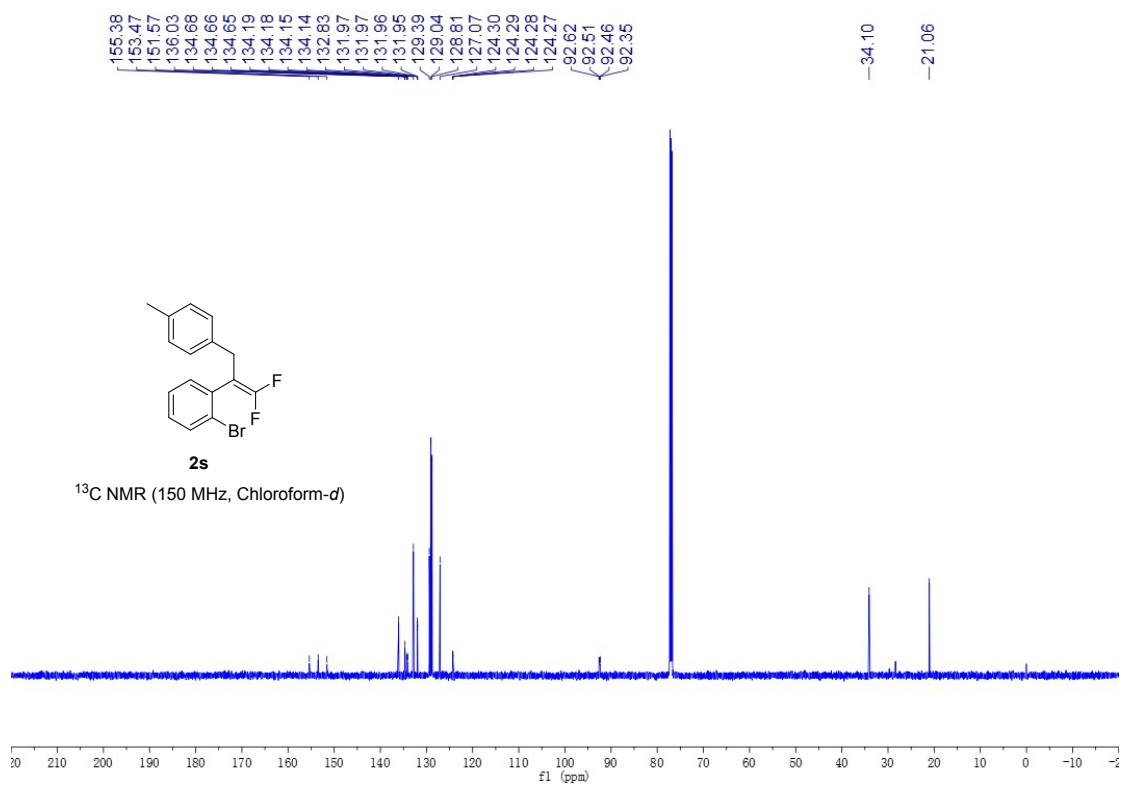


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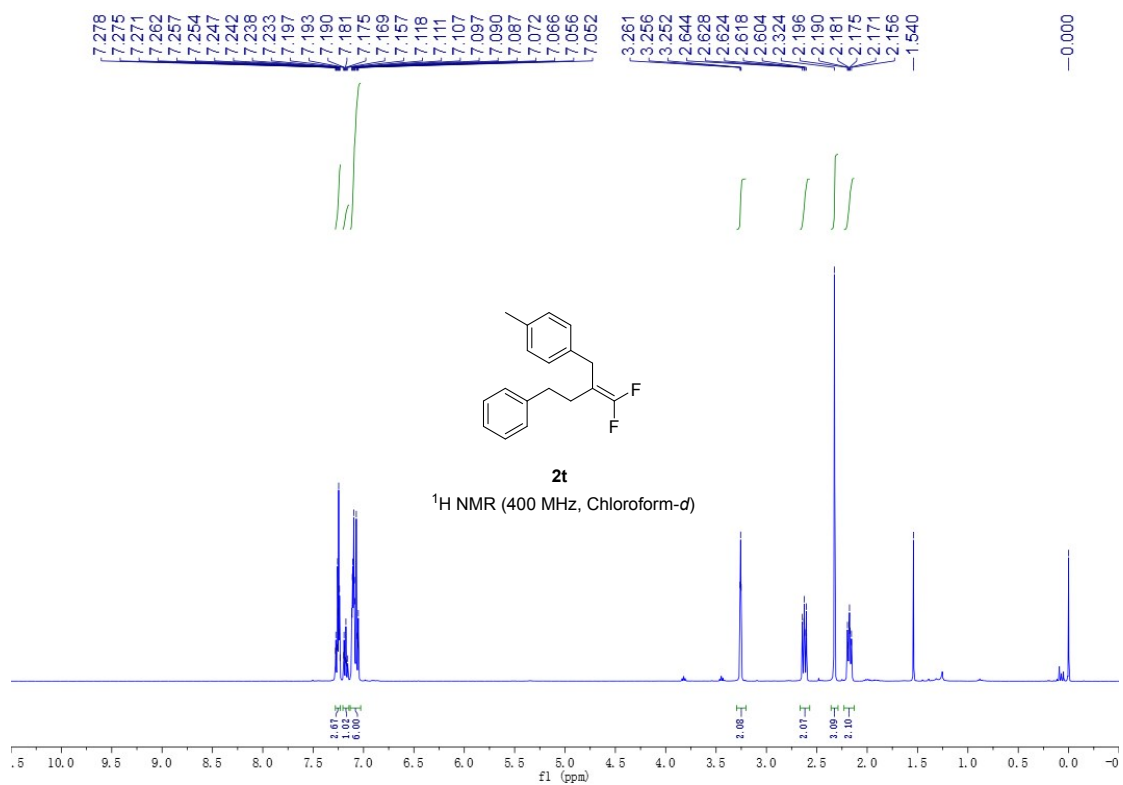


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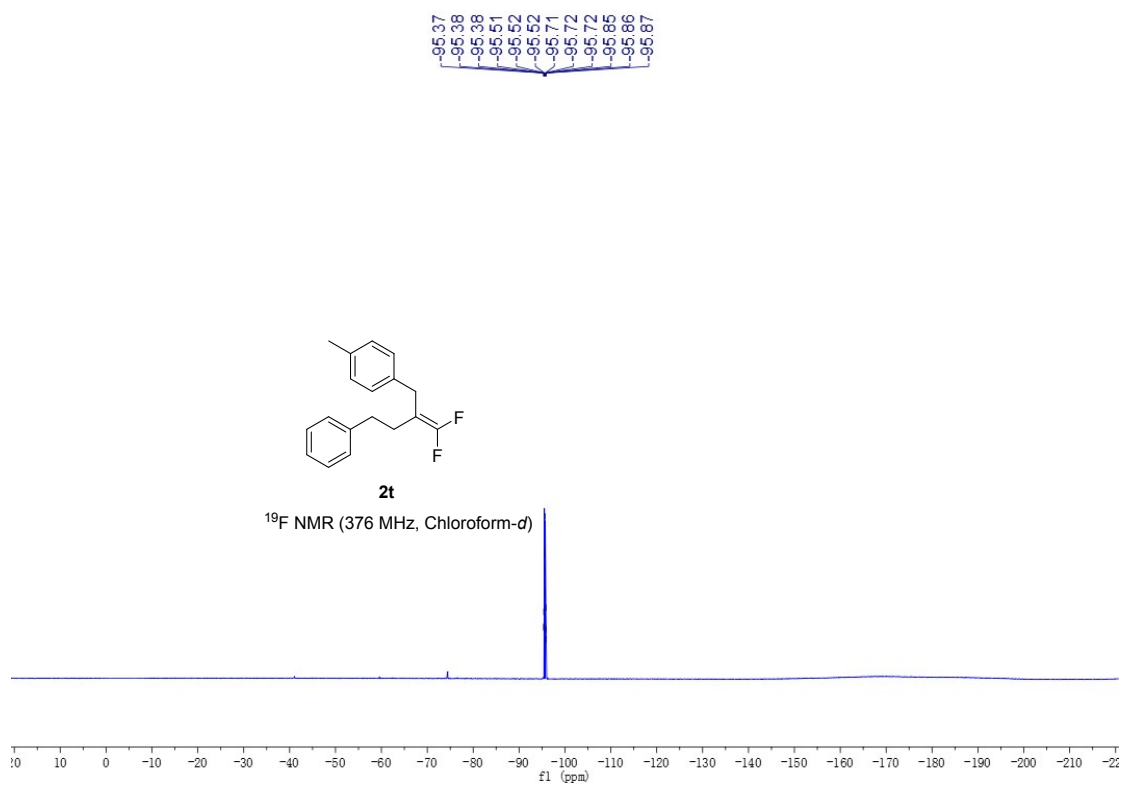


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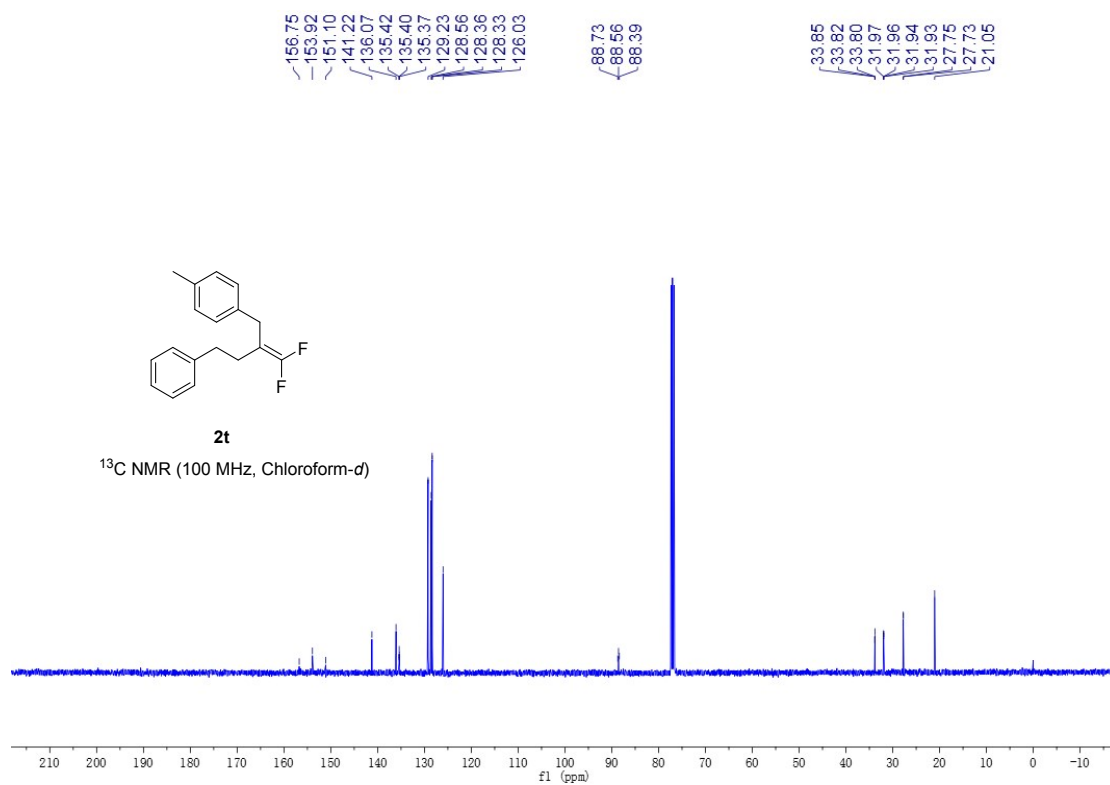


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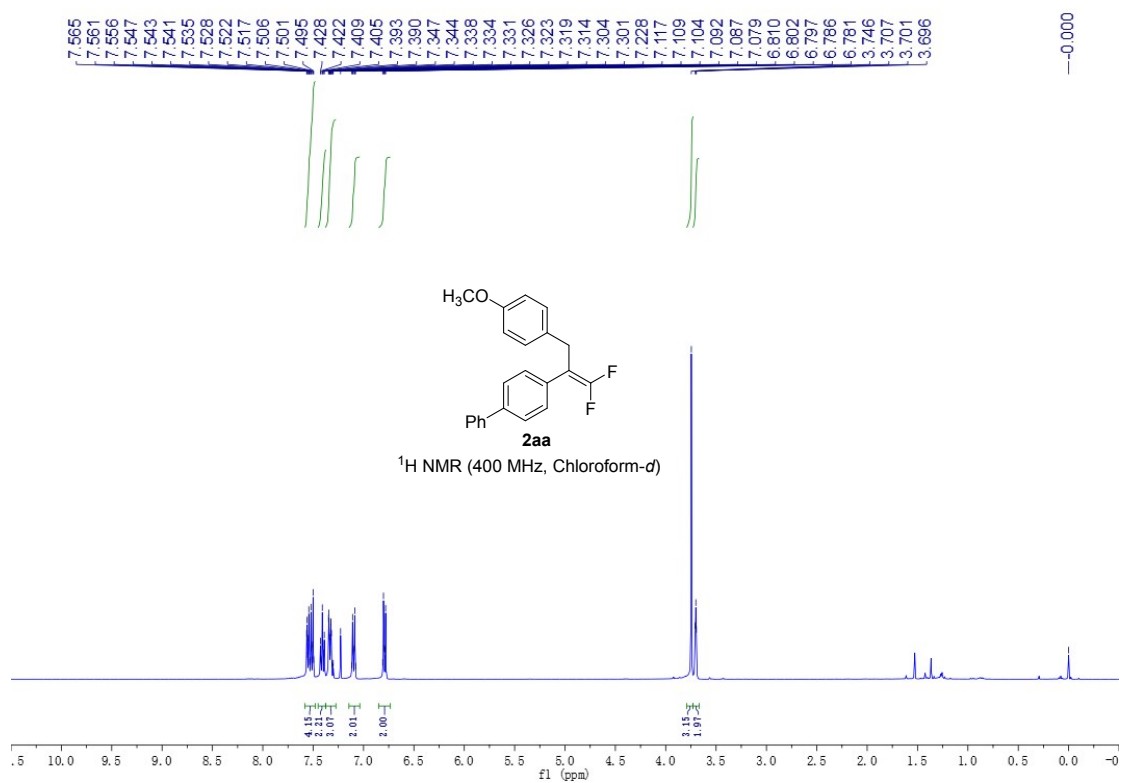


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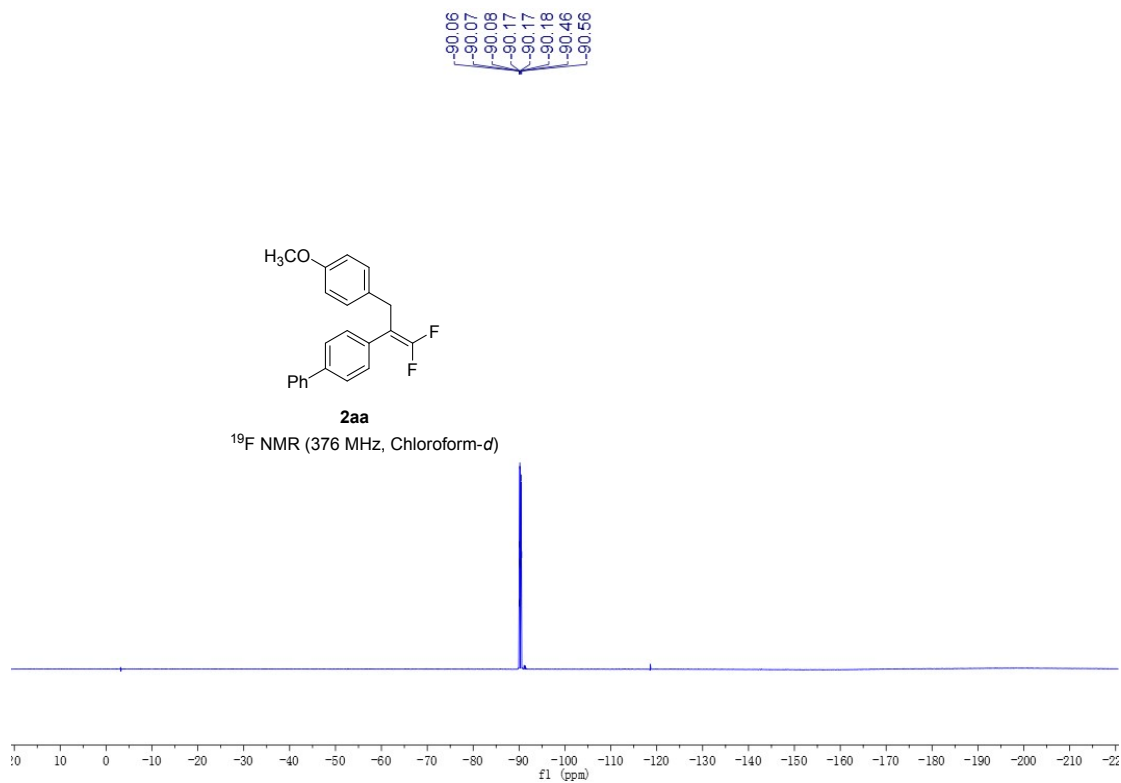


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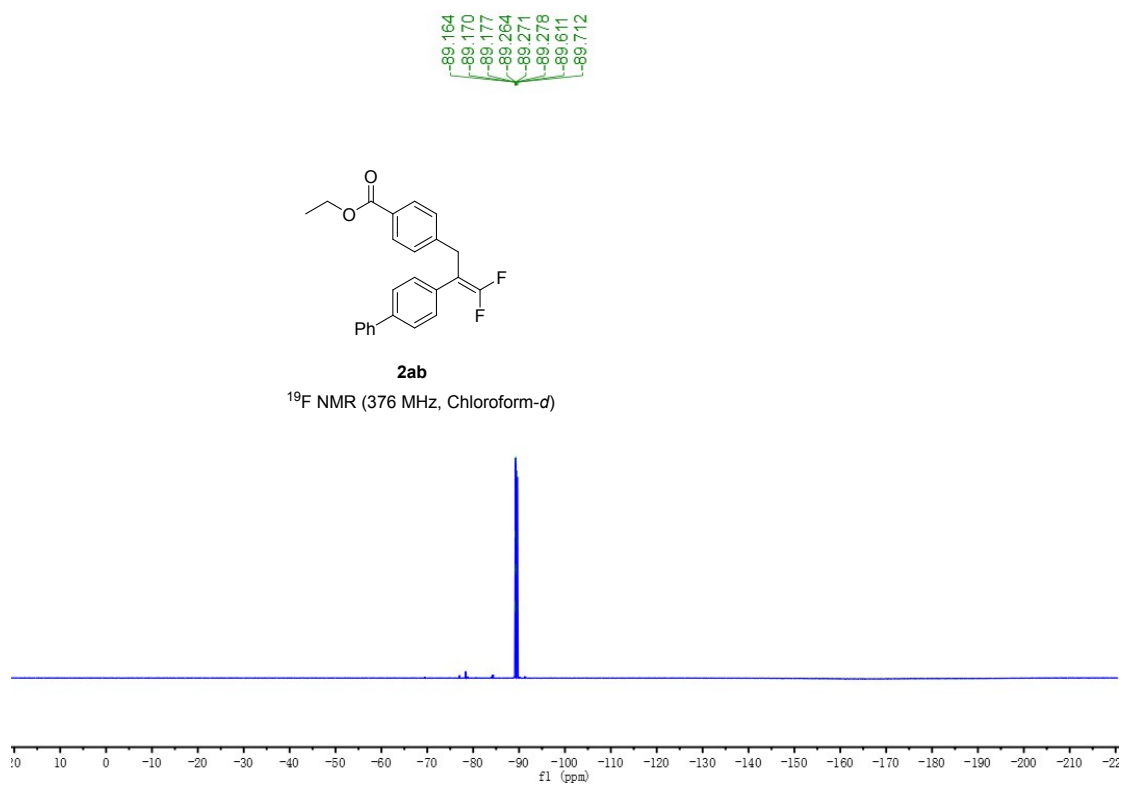


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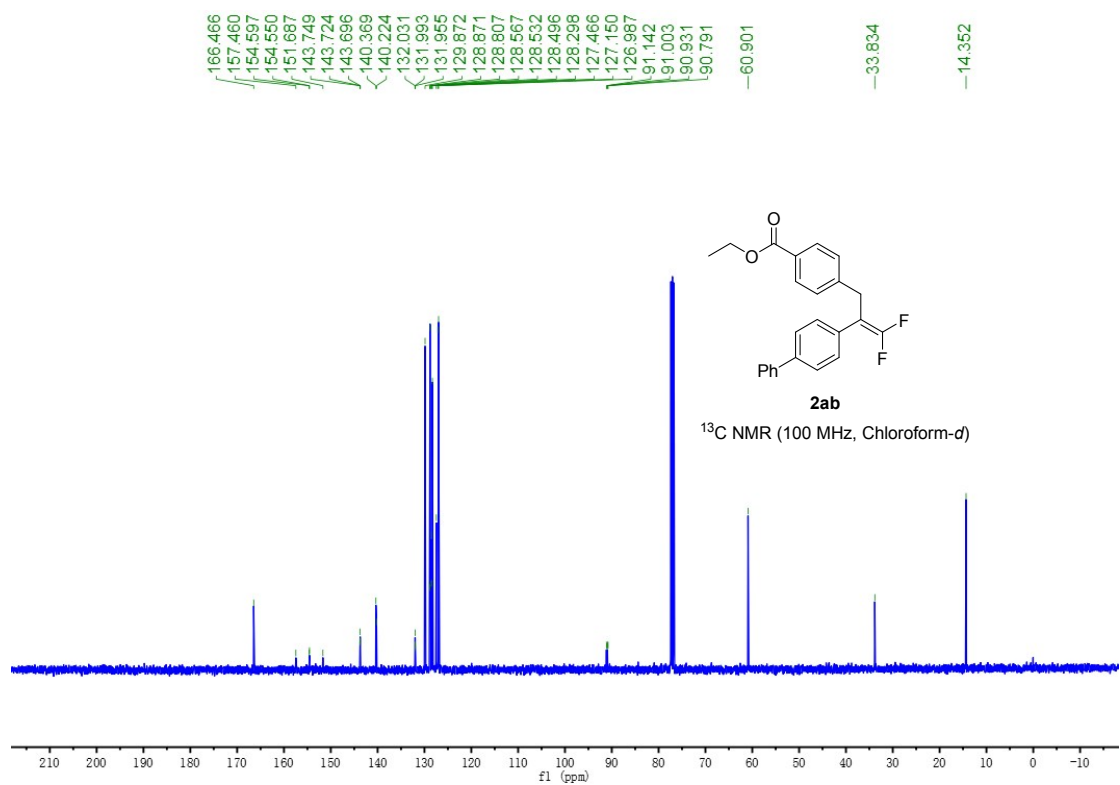


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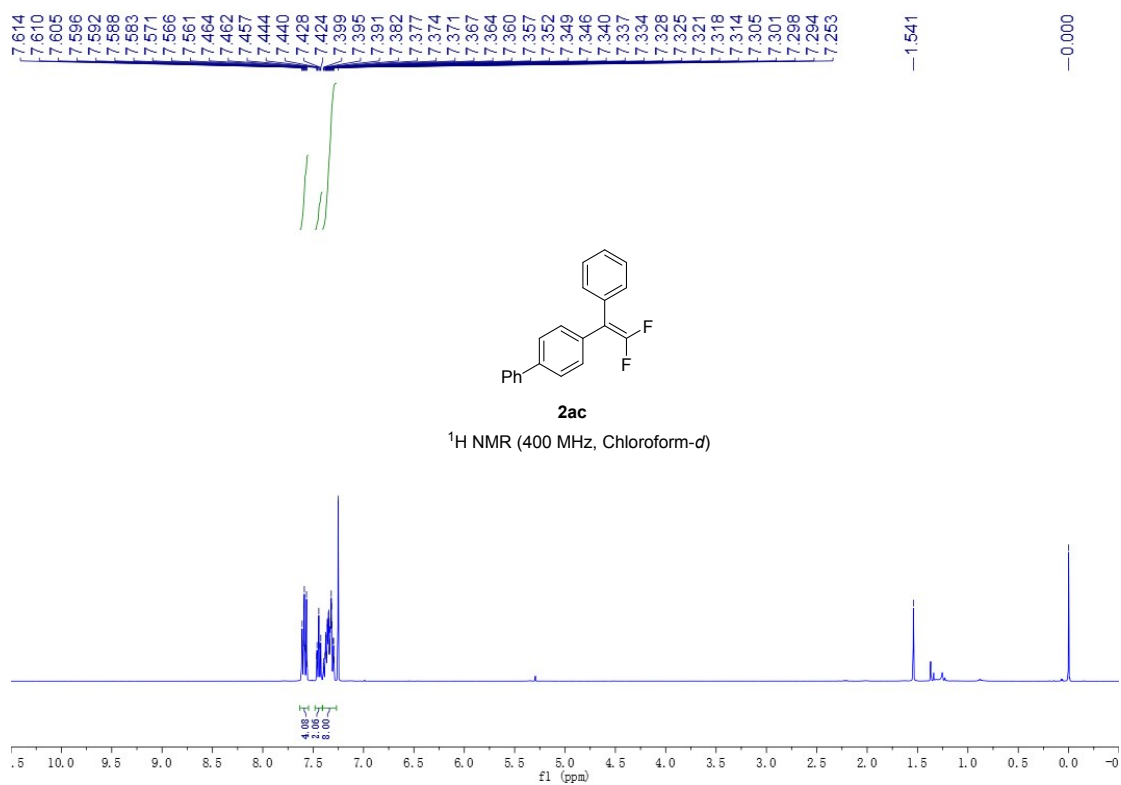


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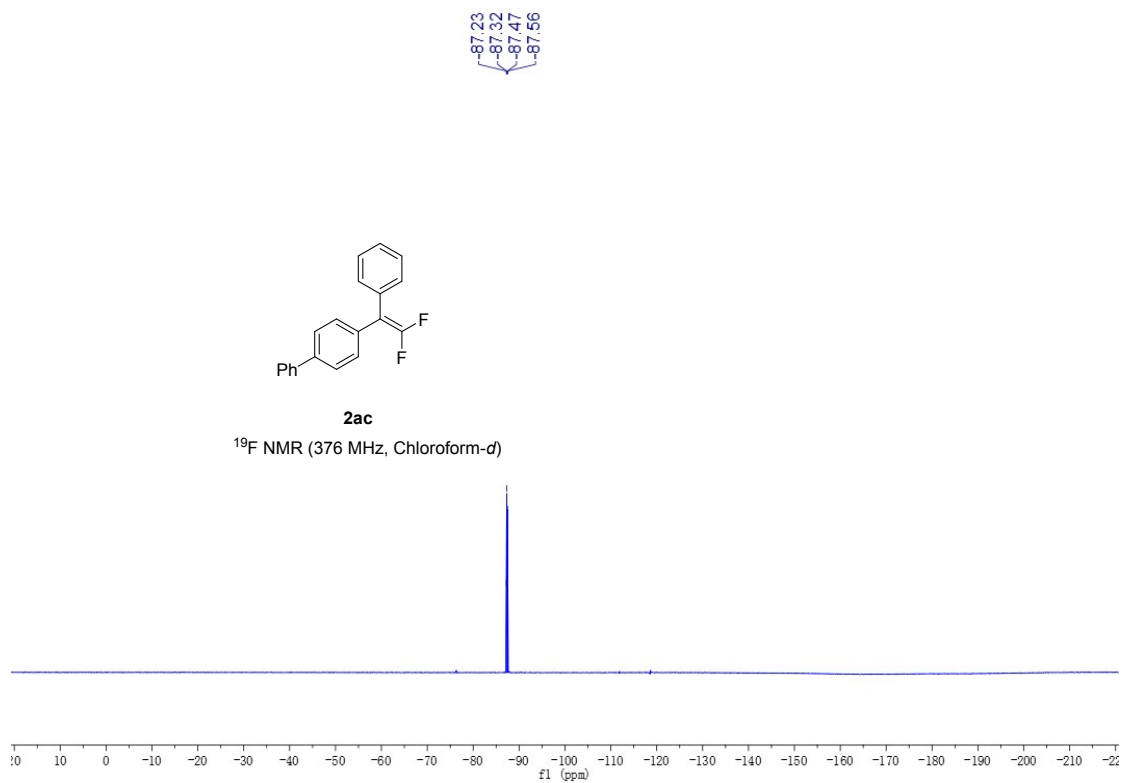


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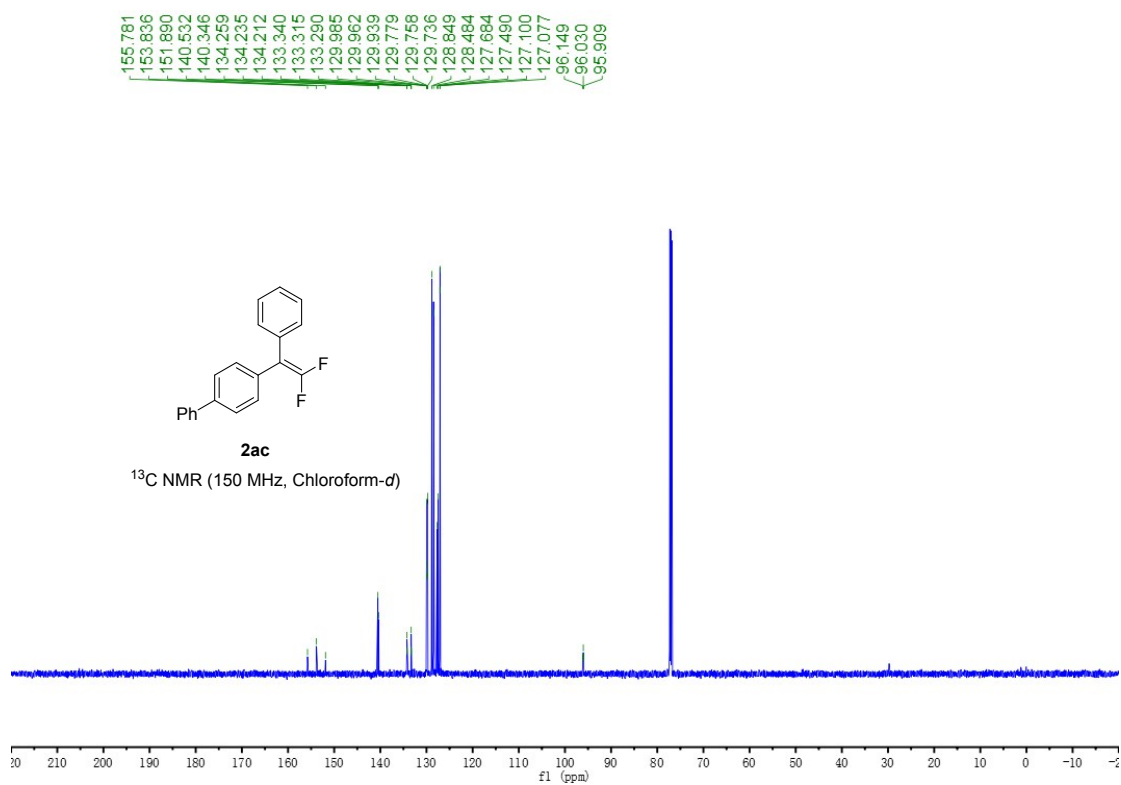


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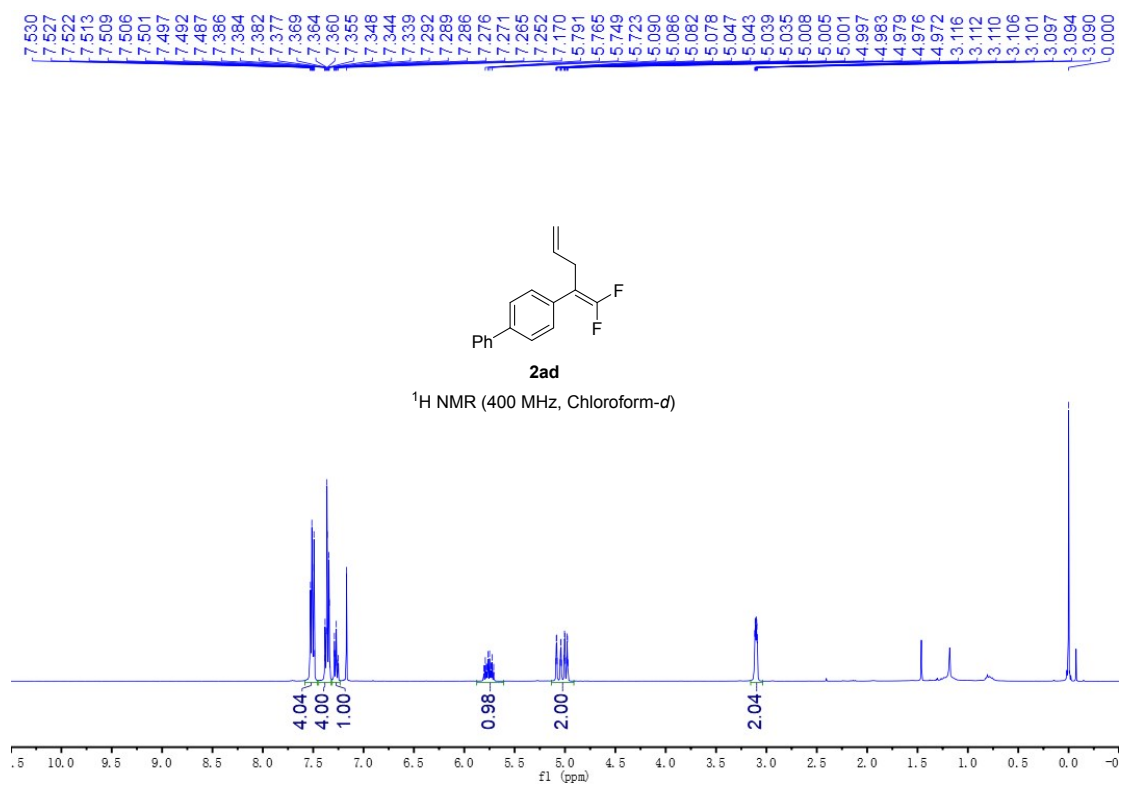


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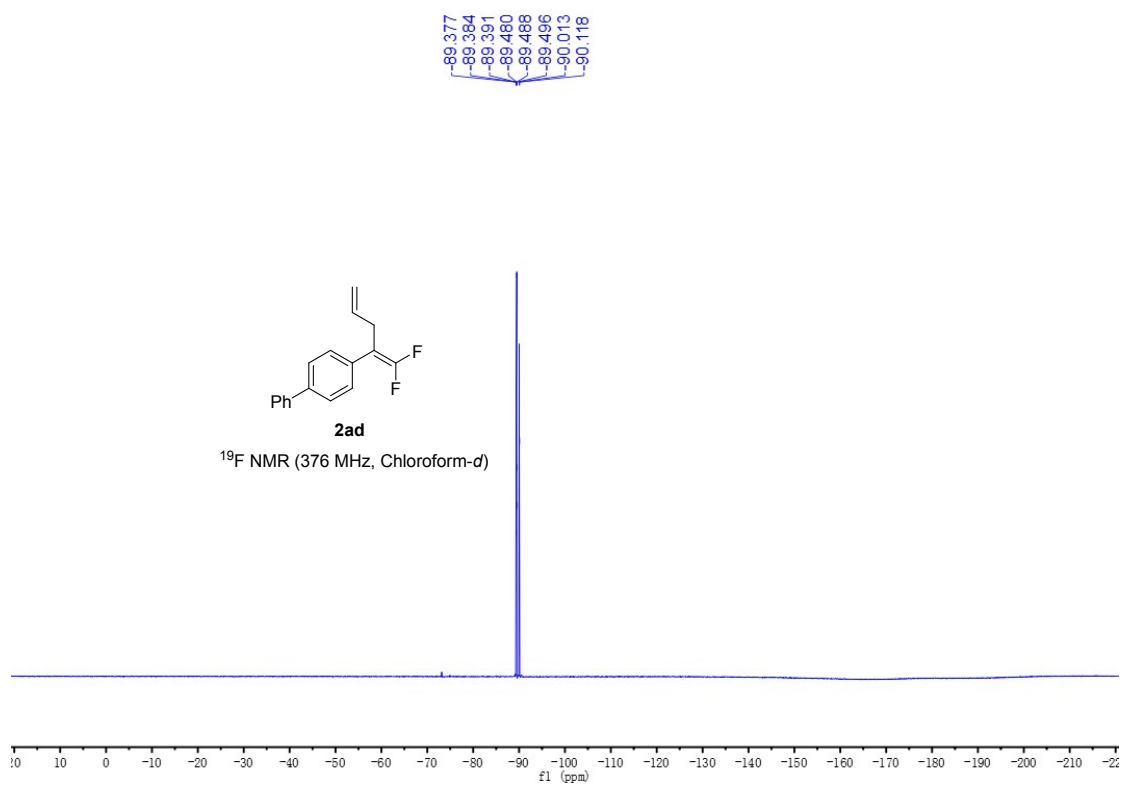


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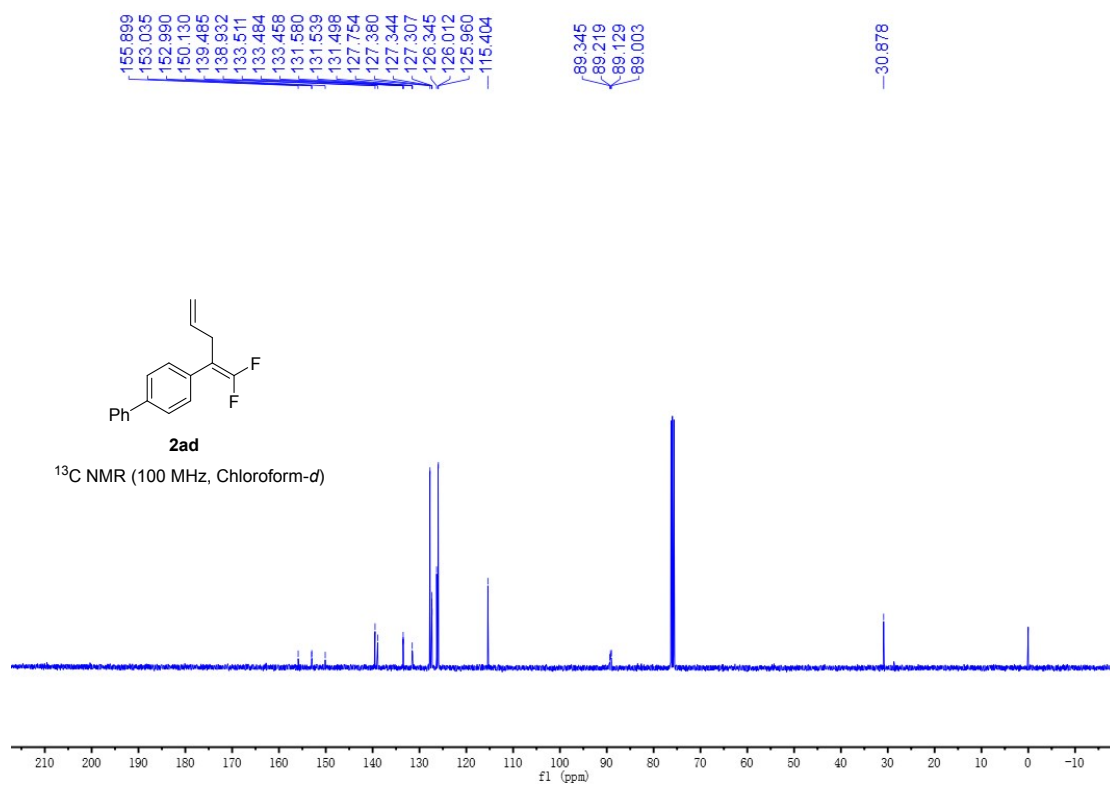


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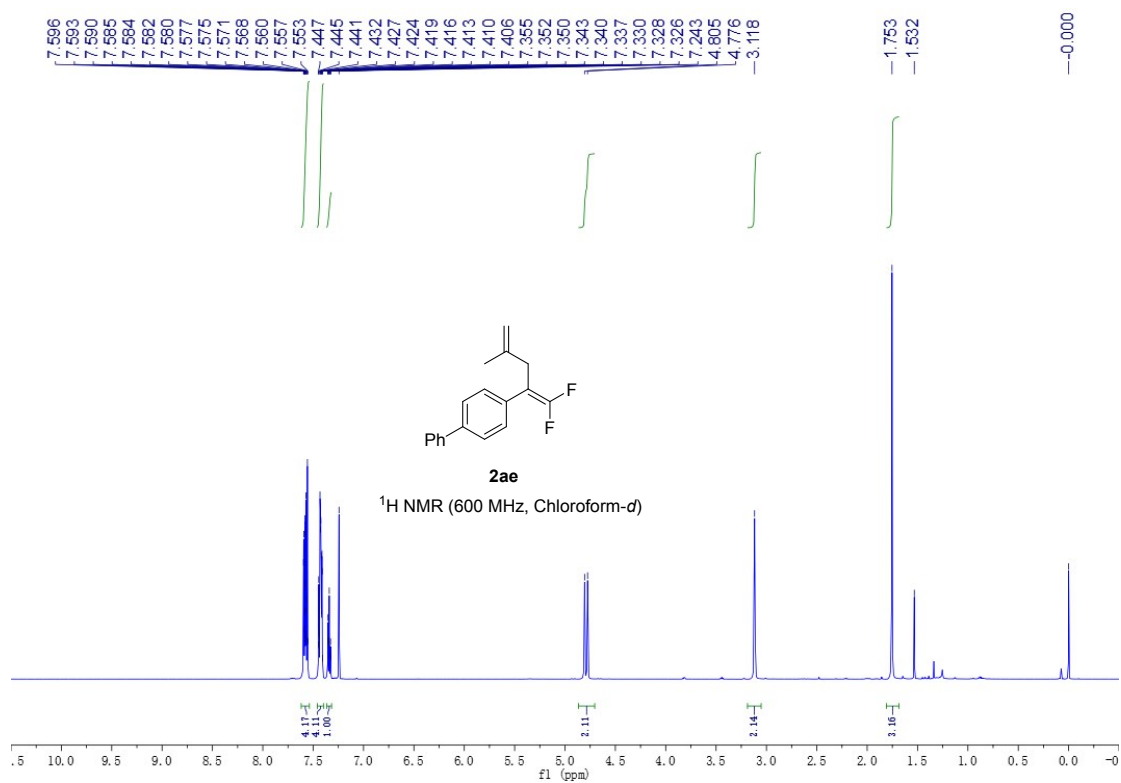


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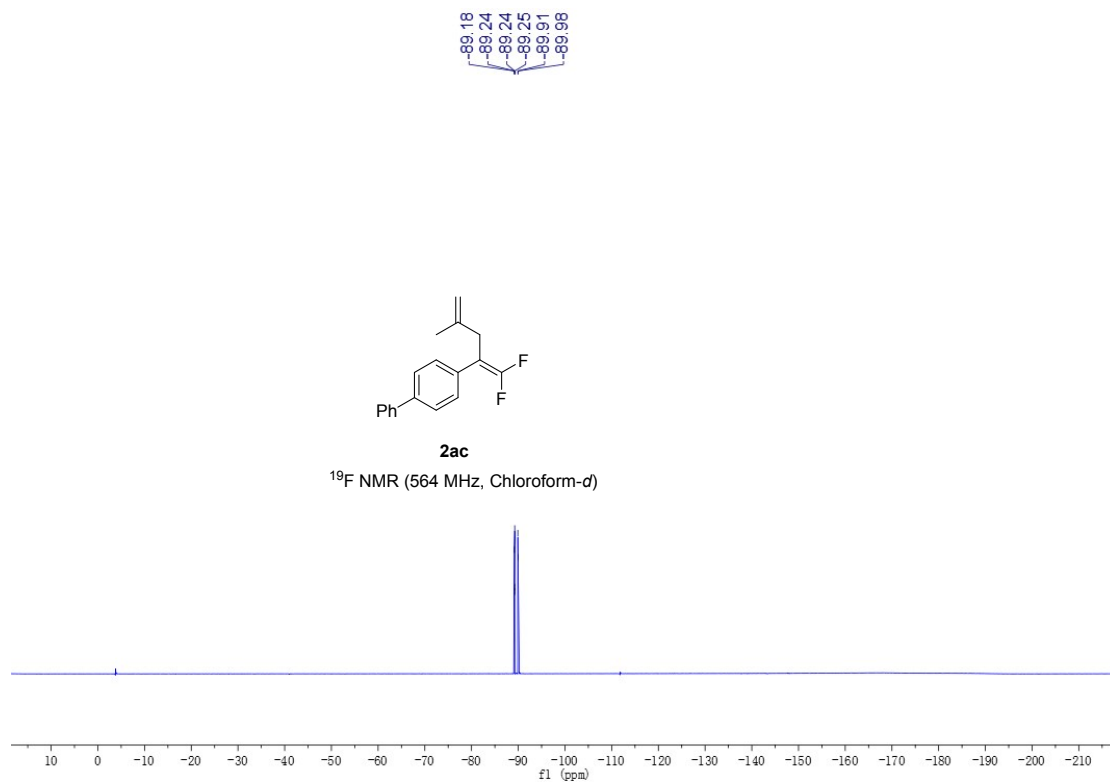


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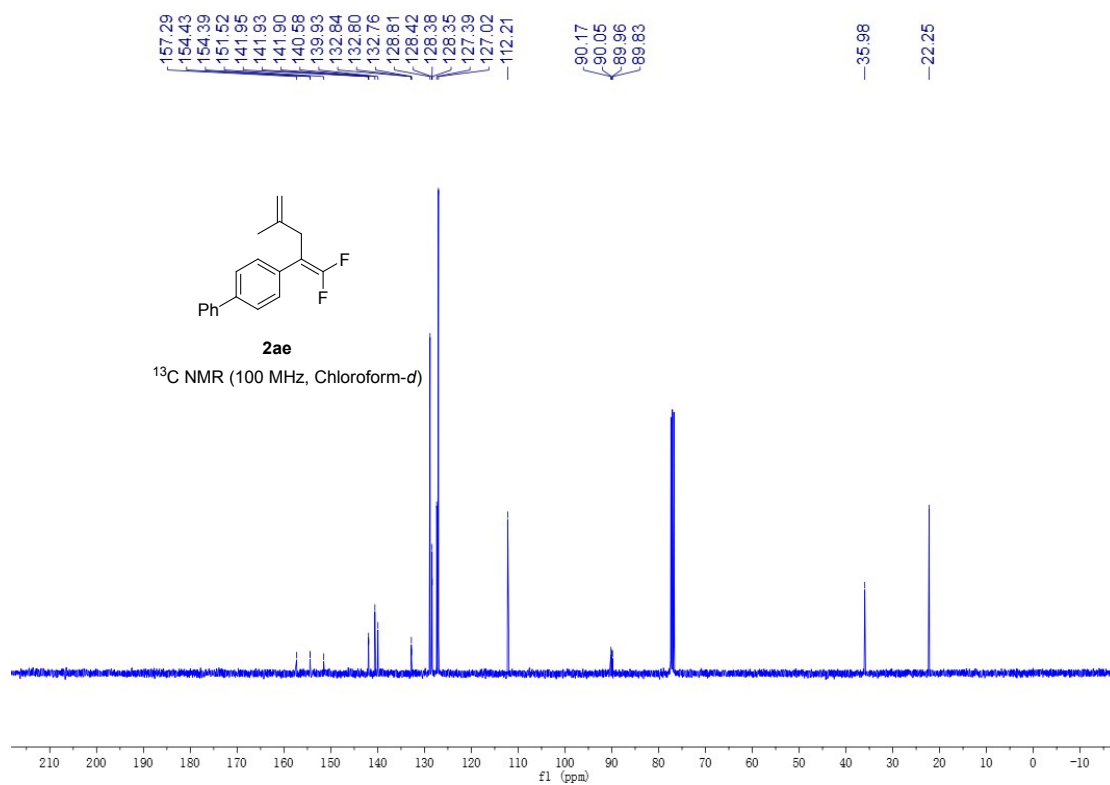


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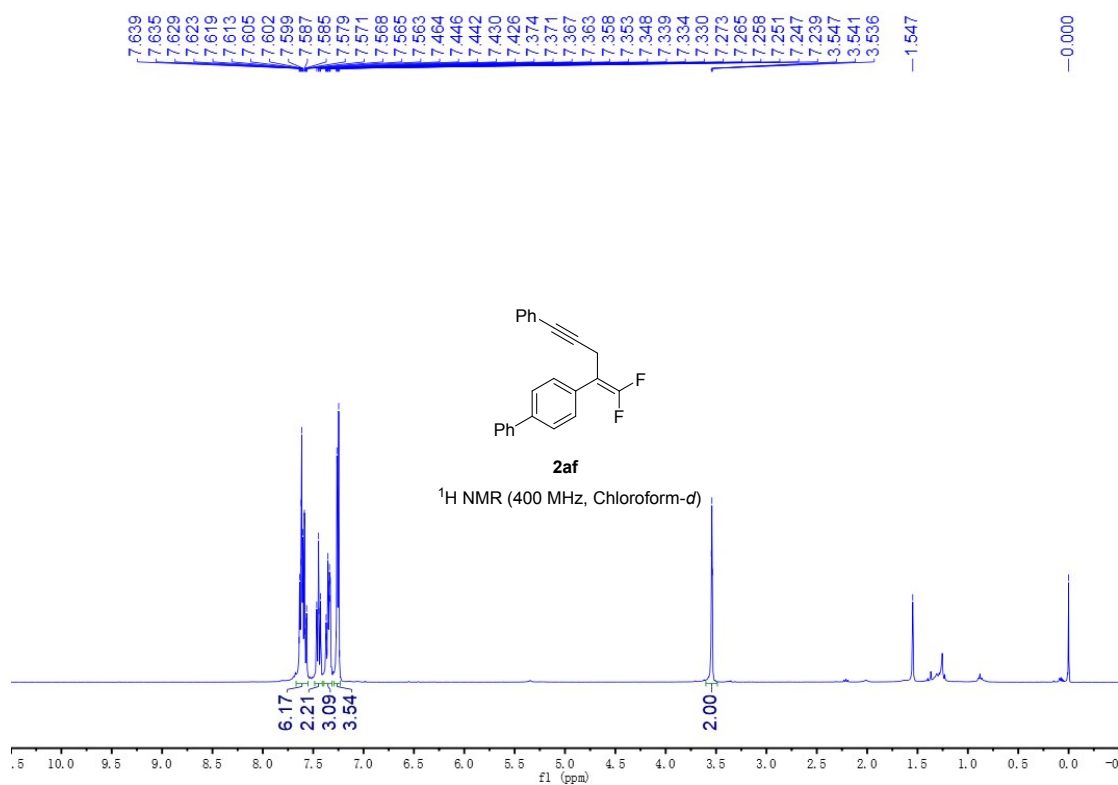


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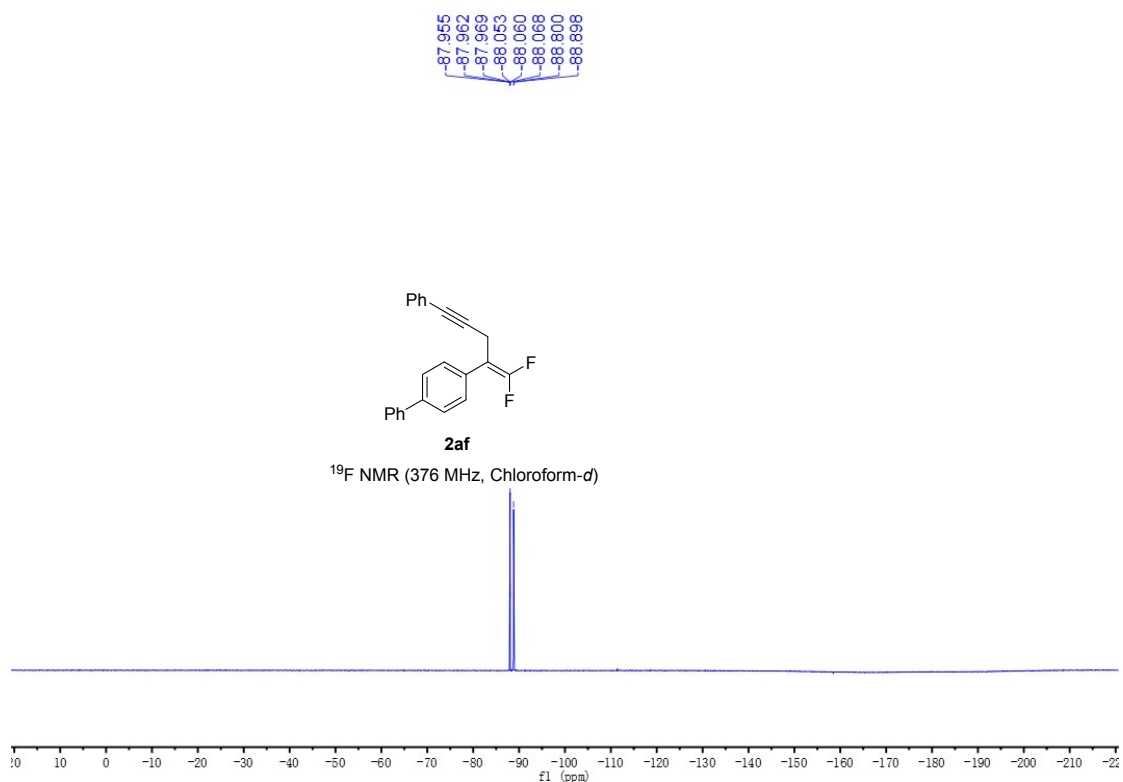


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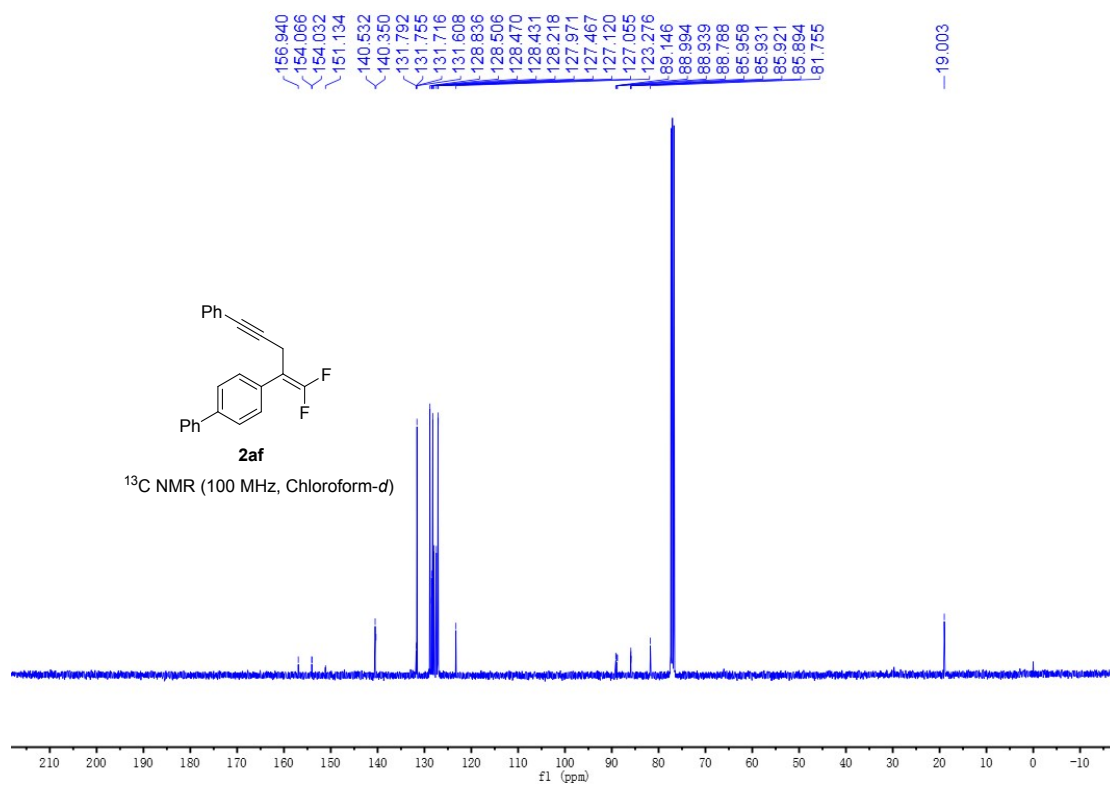
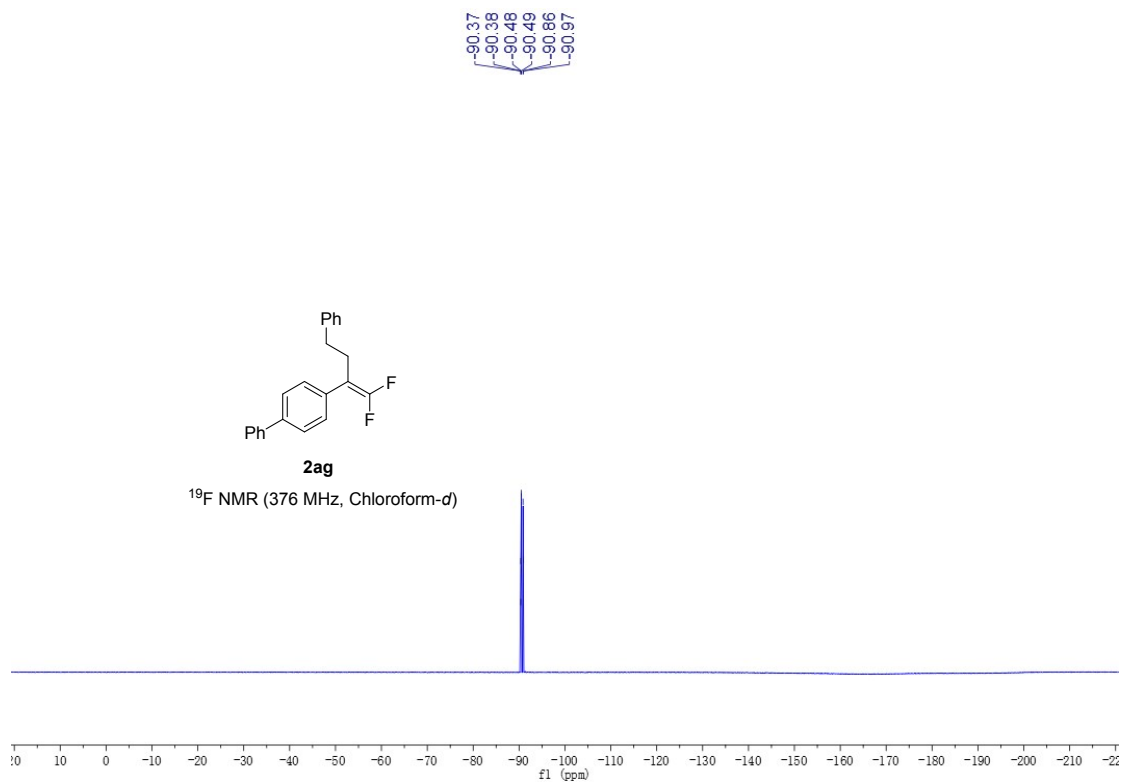
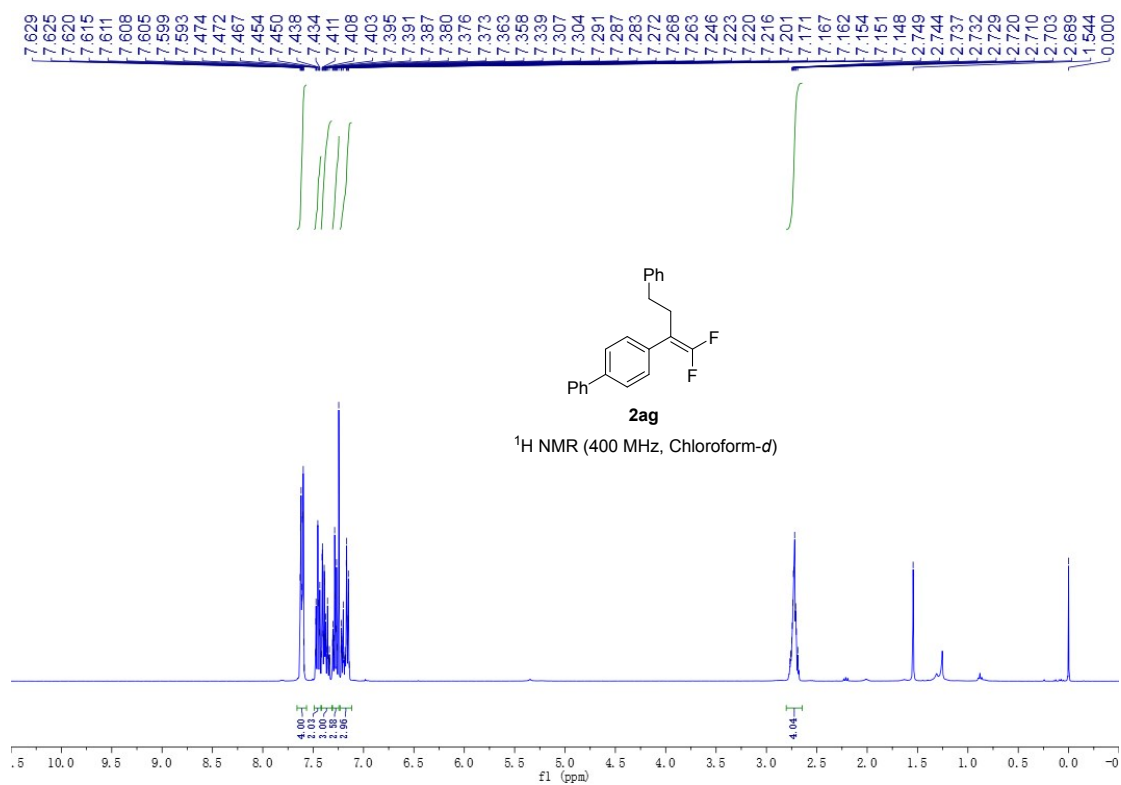


Figure S 168



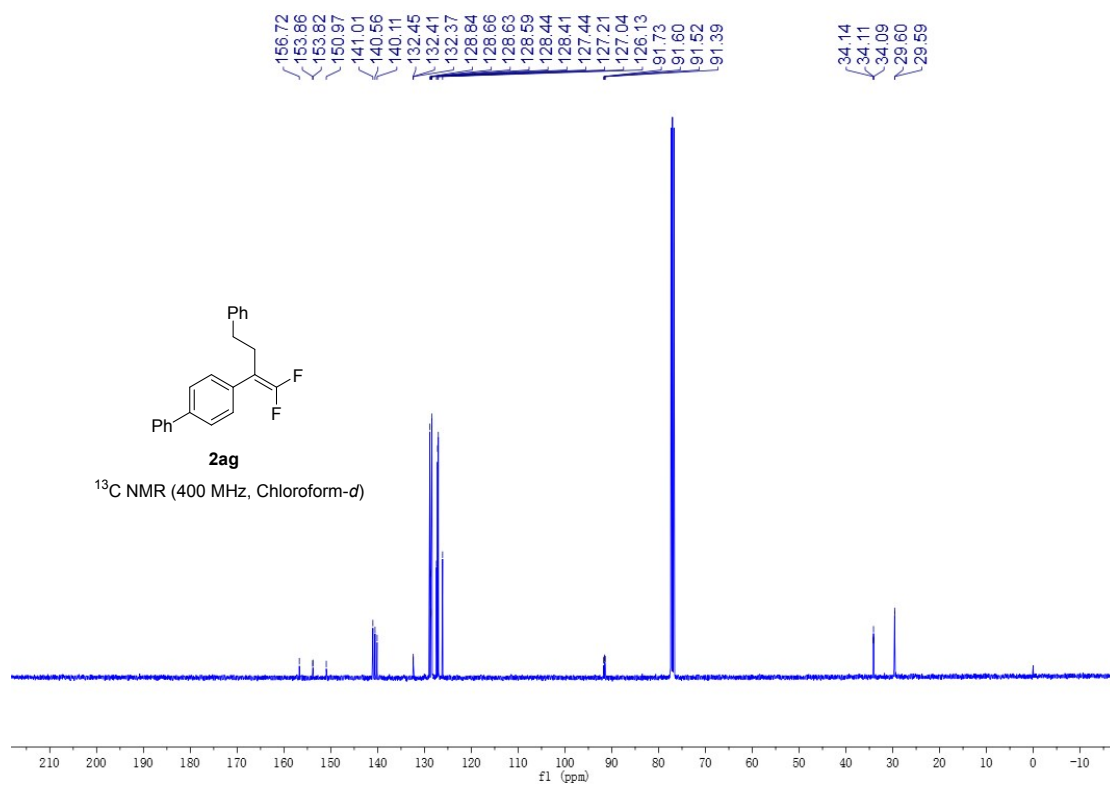


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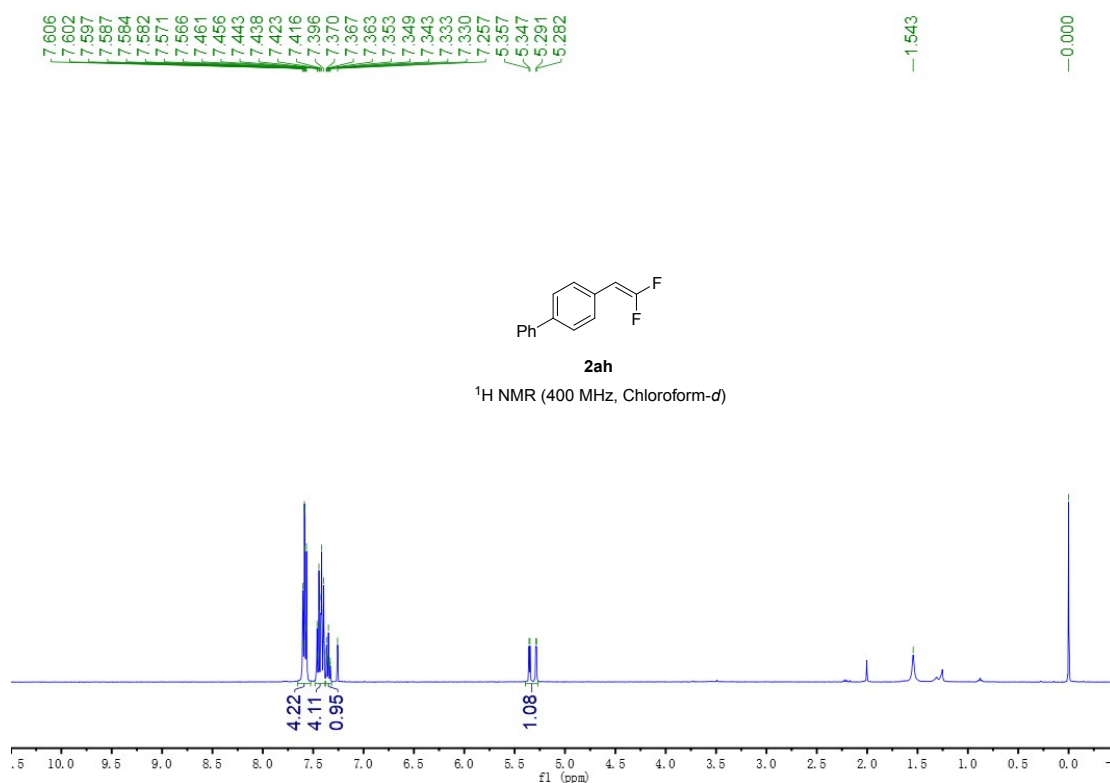


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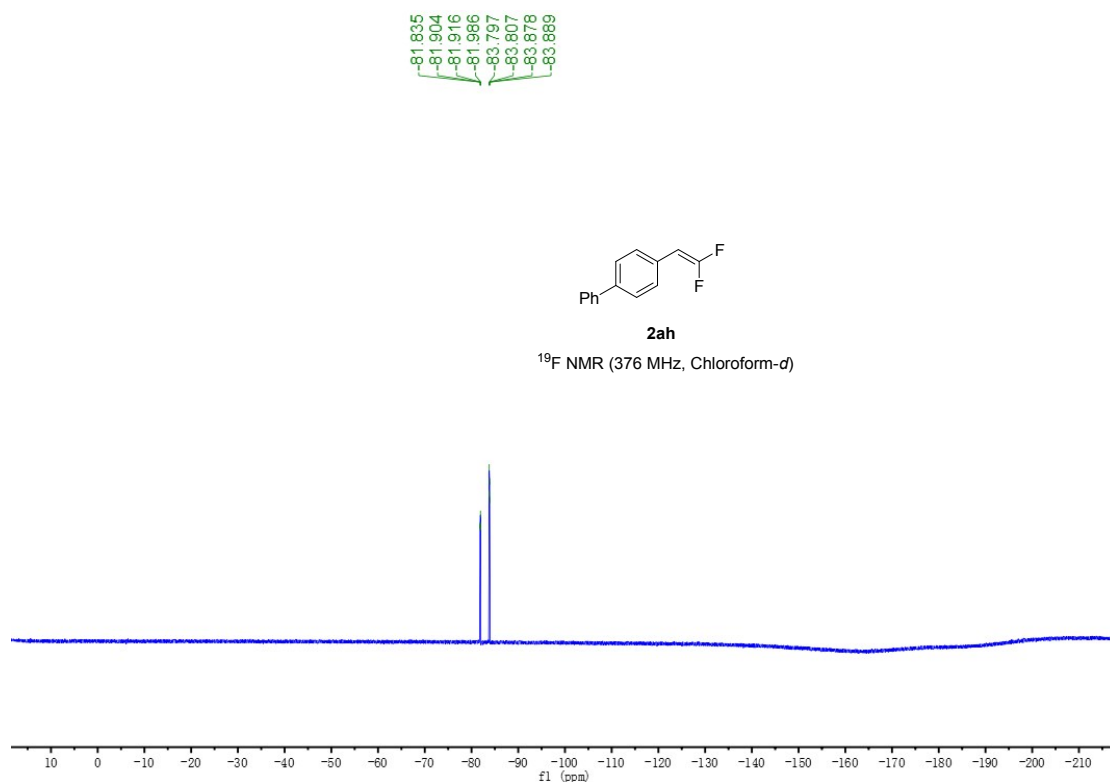


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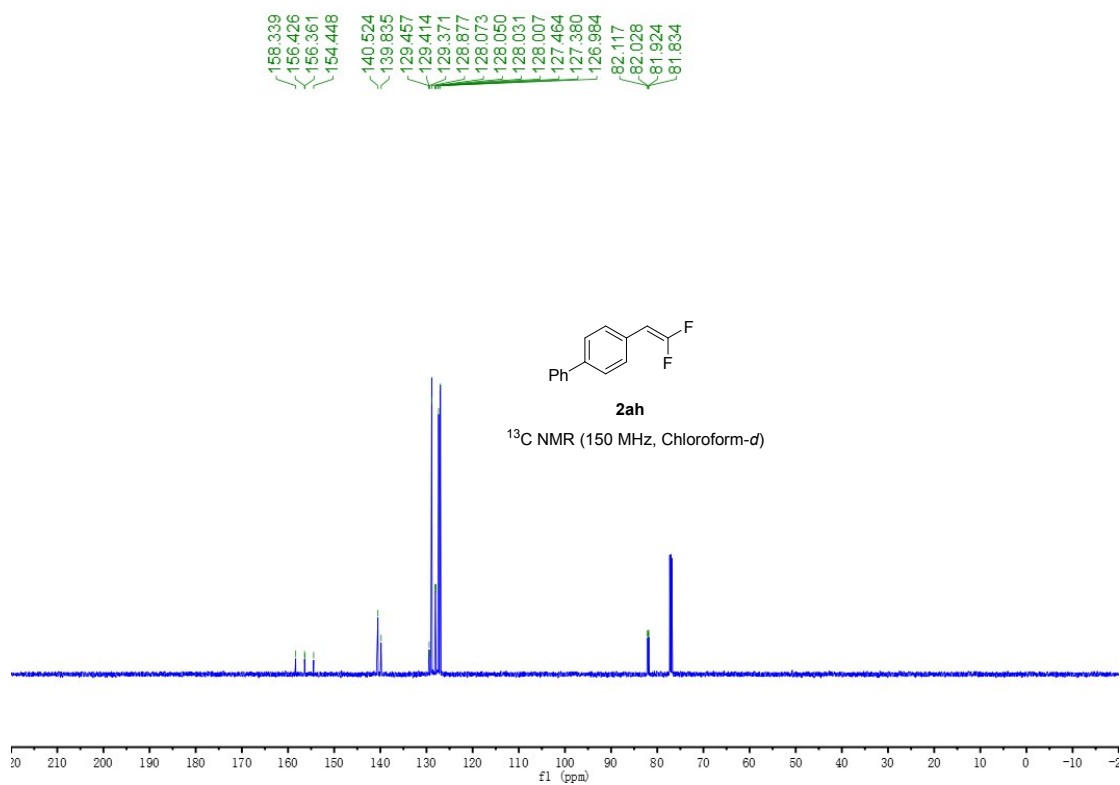


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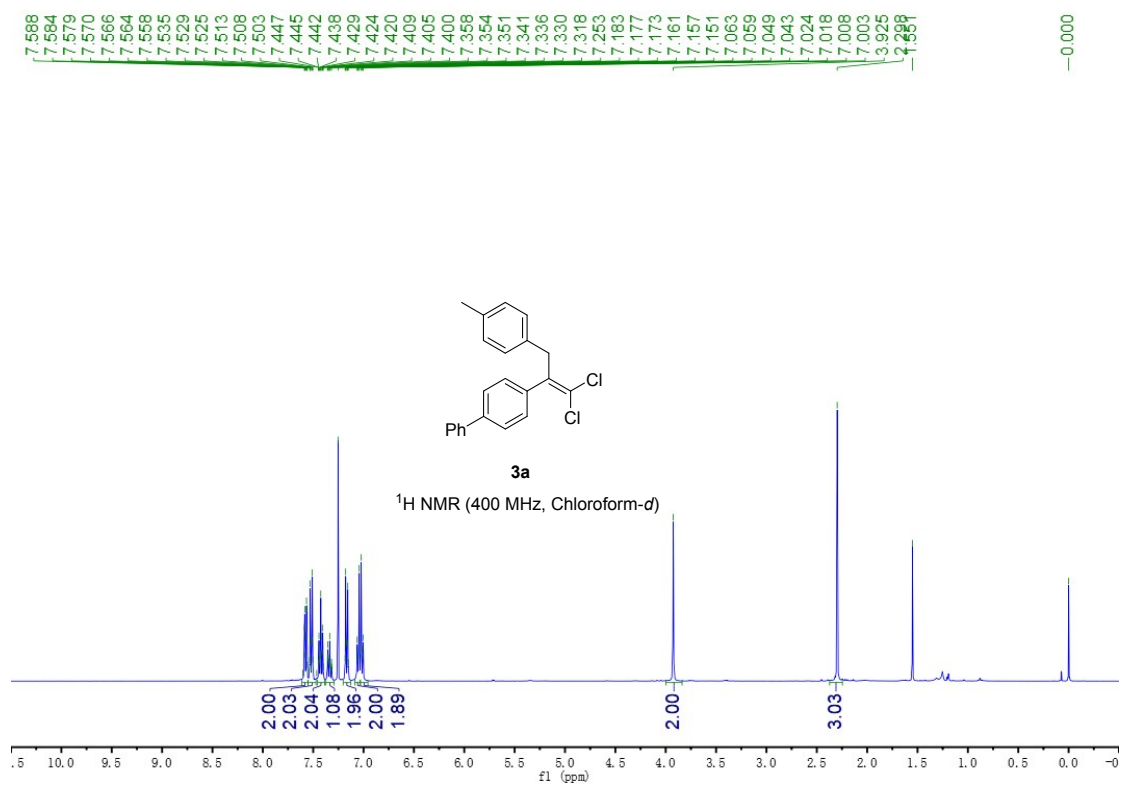


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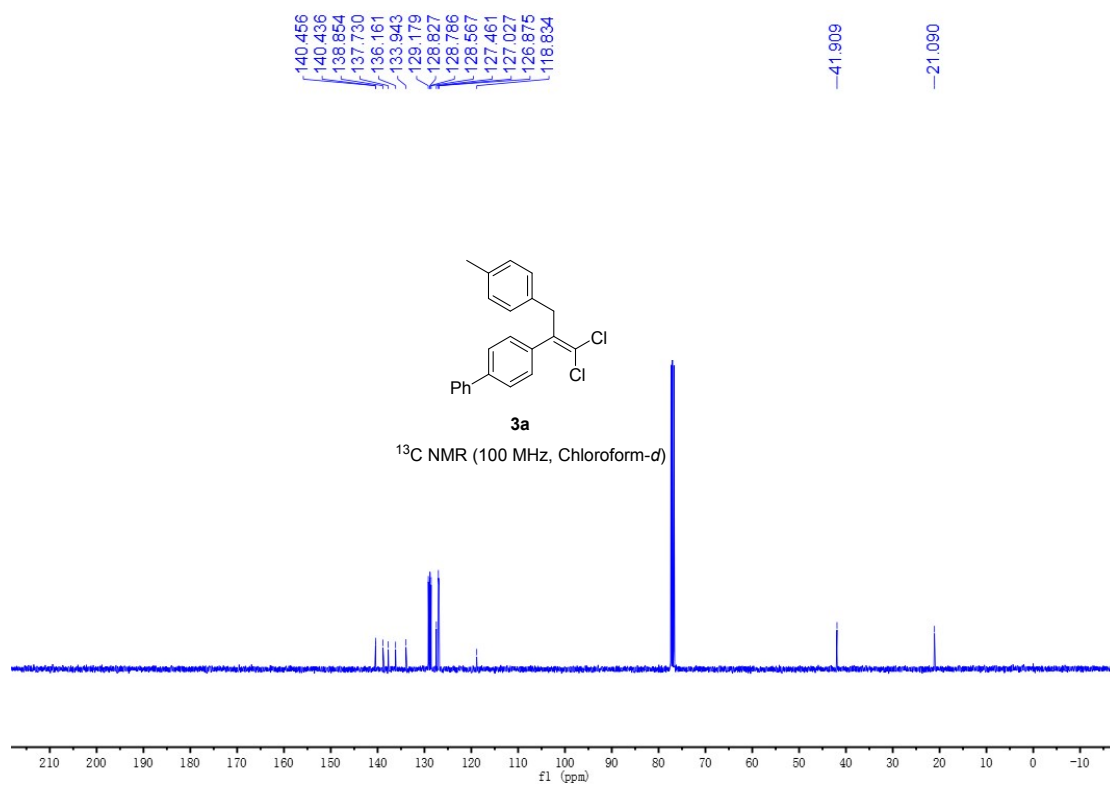


Figure S 176

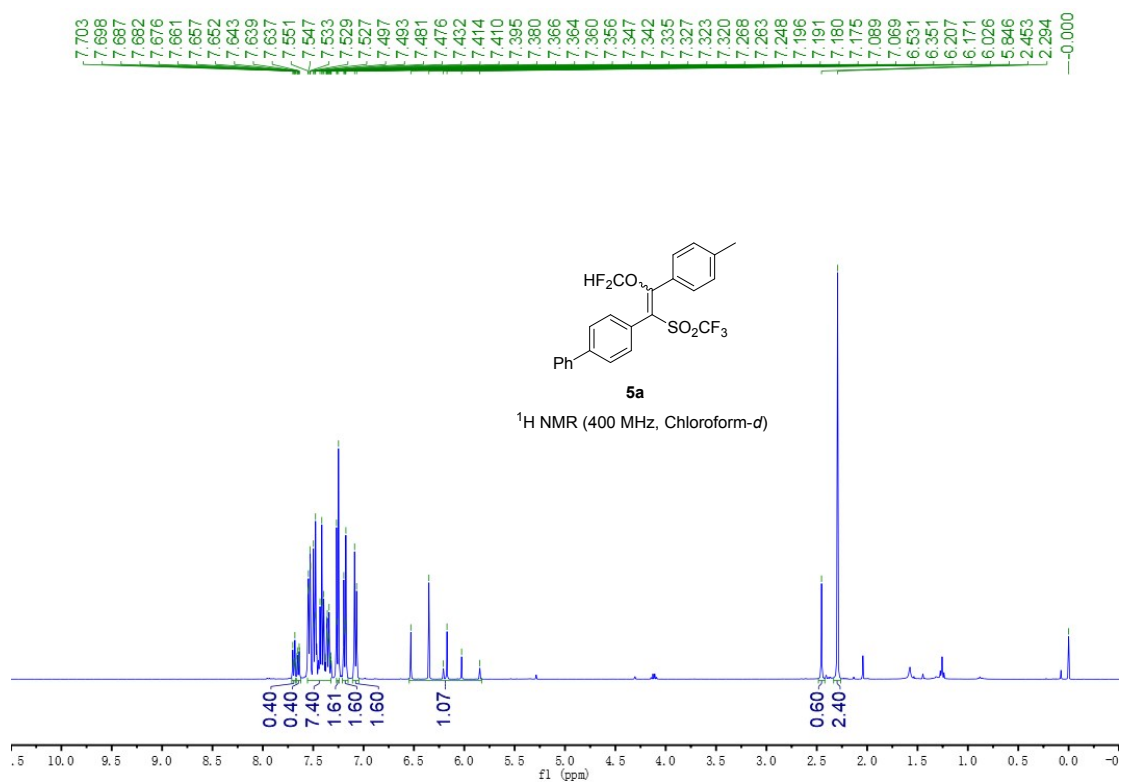


Figure S 177

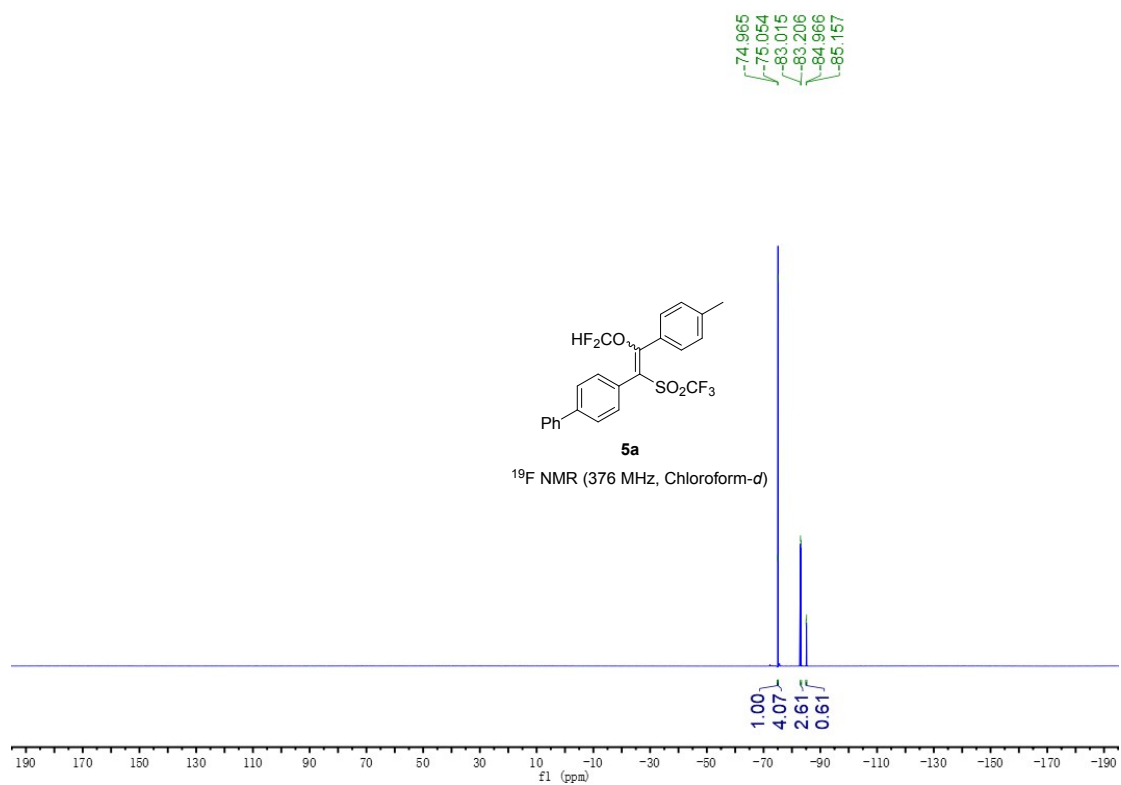


Figure S 178

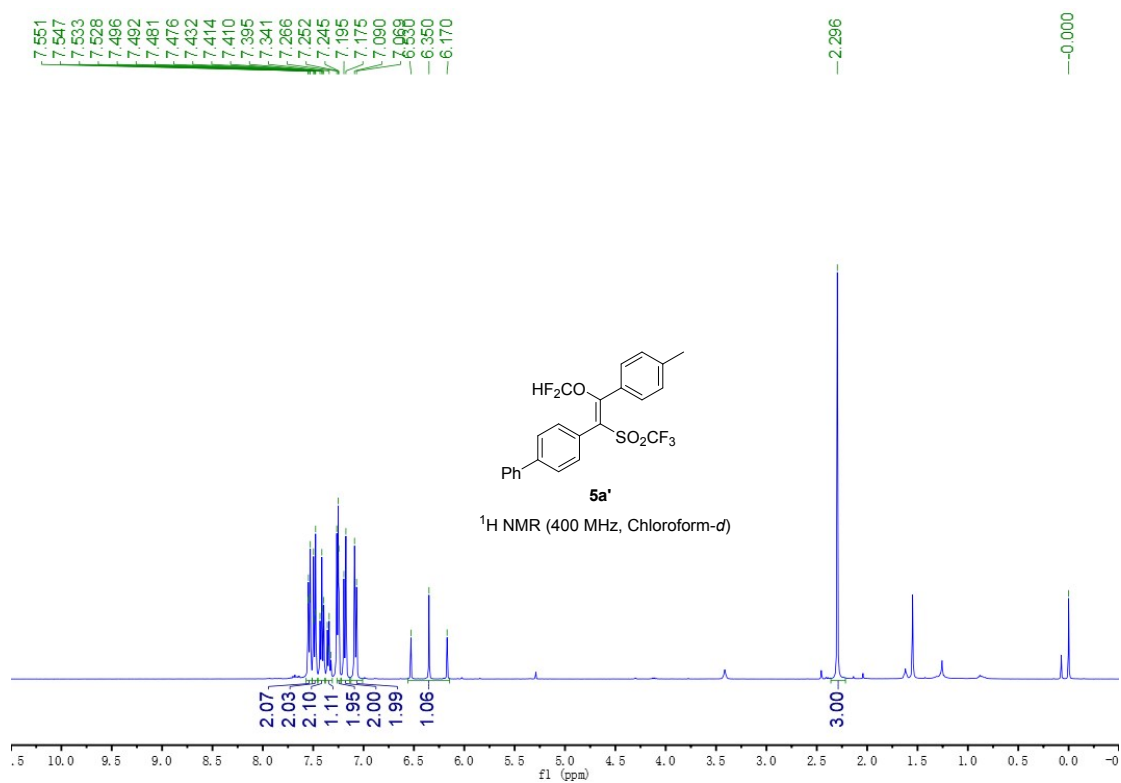


Figure S 179

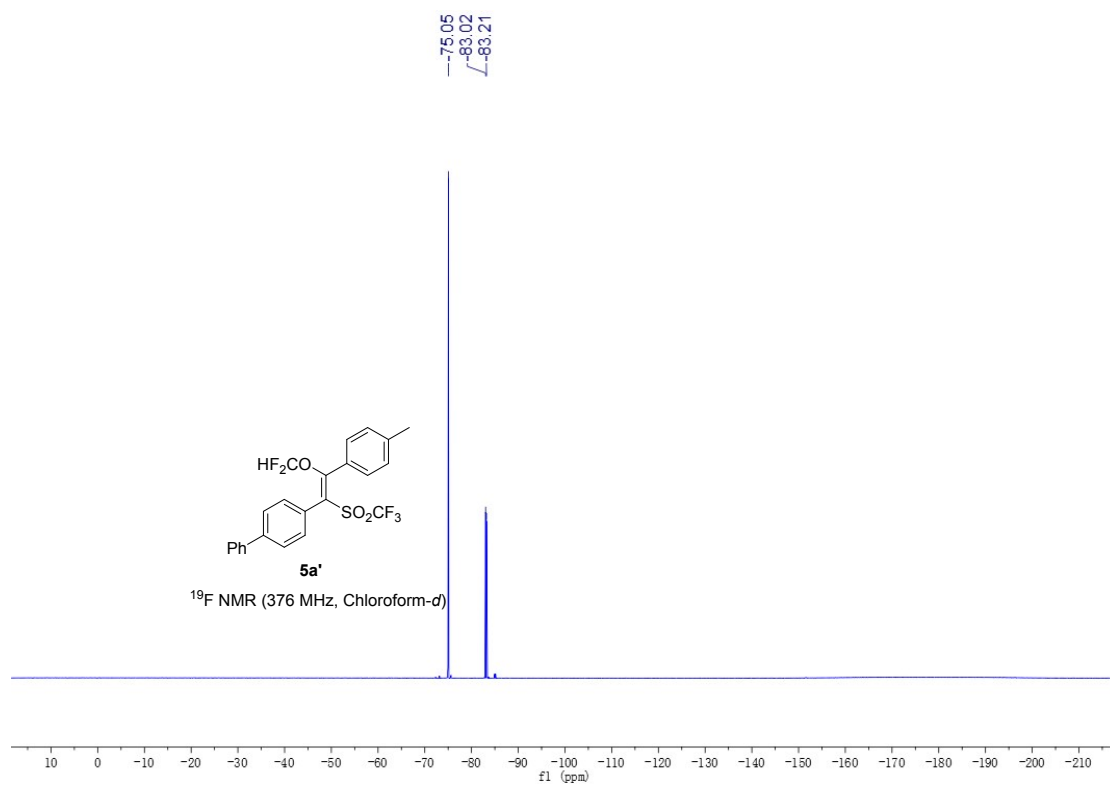


Figure S 180

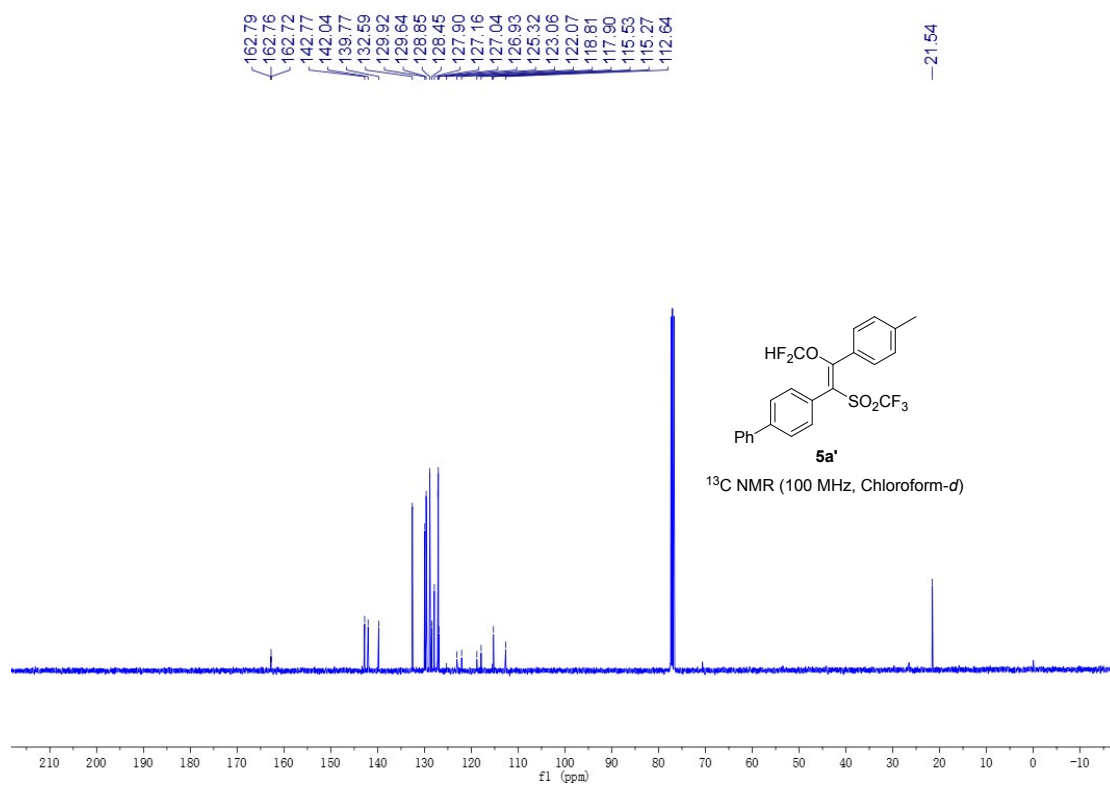


Figure S 181

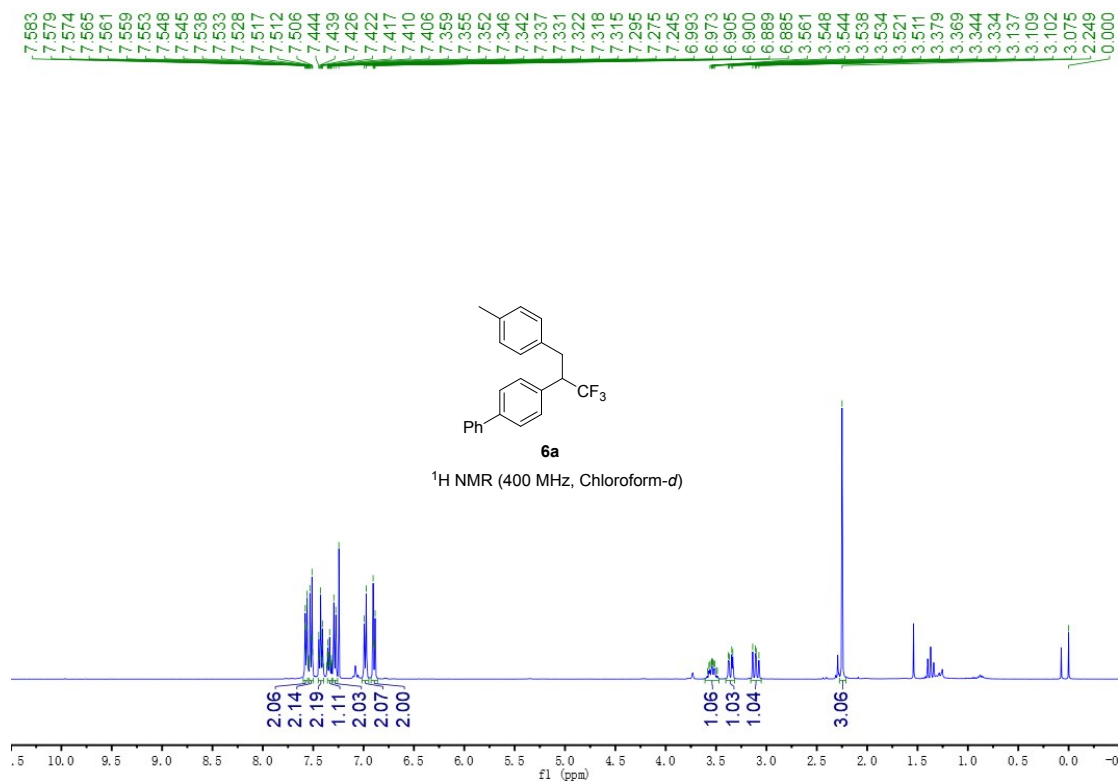


Figure S 182

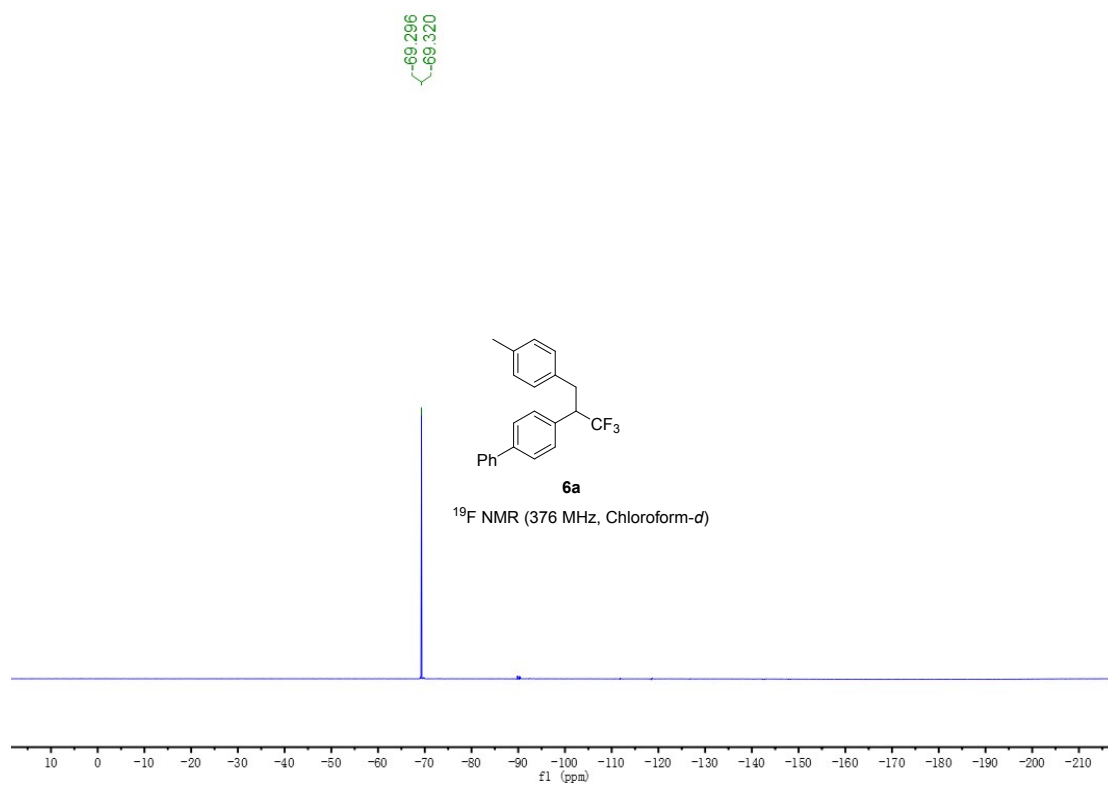


Figure S 183

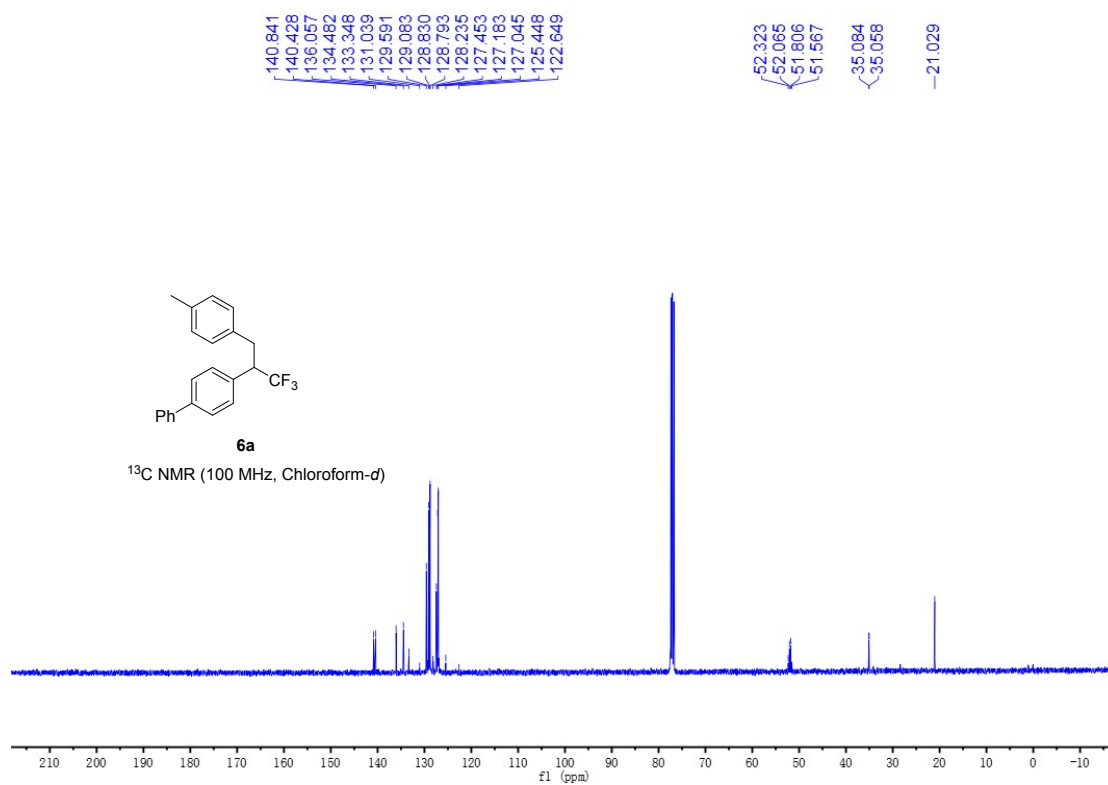


Figure S 184