Retro-Mukaiyama Aldol Reaction-Driven Silicon Catalysis

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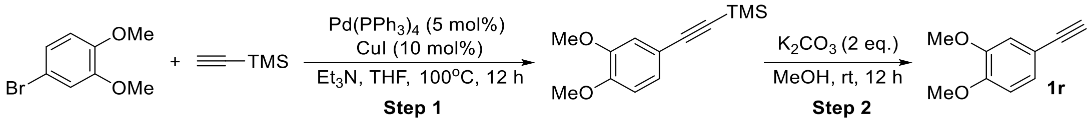
1. General Information

All experiments were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glove box equipped with an MO 40-2 inert gas purifier or using standard Schlenk techniques. Deuterated solvents were used as received. GC analysis was performed on an Agilent 8860 with Hp-5 column, flame ionization detector, and N_2 as carrier gas. GS-MS analysis was performed on Agilent 8860/5977B GCMS system with MS detector, and helium as carrier gas. NMR spectra were recorded on BRUKER Avance III (600 or 400 MHz) spectrometers. High-resolution mass spectra (HRMS) were recorded on Bruker MicroTOF-QII mass instrument (APCI). Unless otherwise noted, the alkynes and aldehydes were purchased from Bidepharm or Energy Chemical and used as received.

2. General Procedure for the Synthesis of Substrates or Silicon-Containing Reagents

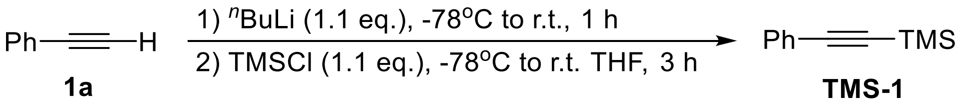
Synthesis of 1r[1]



Step 1: To a 25 mL Young-type tube was charged with a magnetic stir-bar, $Pd(PPh_3)_4$ (115.6 mg, 0.1 mmol), CuI (63.4 mg, 0.2 mmol), 4-bromo-1,2-dimethoxybenzene (434.1 mg, 2 mmol, 1.0 eq.), dry THF (1.0 mL) and triethylamine (0.8 mL) under nitrogen atmosphere. Then trimethylsilyl acetylene (0.35 mL, 2.4 mmol, 1.2 eq.) was added slowly and the reaction mixture was stirred at 100 ºC for 12 hours. After the reaction was completed, the solvent was concentrated under reduced pressure. The crude product was purified via flash chromatography on silica gel and eluted with petroleum ether/ ethyl acetate (20/1) to afford ((3,4-dimethoxyphenyl) ethynyl) trimethyl silane as a white solid (418.8 mg, 89% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.09 – 7.06 (m, 1H), 6.97 – 6.96 (m, 1H), 6.78 (d, J = 12.4 Hz, 1H), 3.88 – 3.87 (m, 6H), 0.24 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.8, 148.6, 125.5, 115.4, 114.7, 110.9, 105.4, 92.5, 56.0, 0.2.

Step 2: To a solution of ((3,4-dimethoxyphenyl) ethynyl) trimethyl silane (418.0 mg, 1.8 mmol, 1.0 eq.) in methanol (1.8 mL) was added K_2CO_3 (496.8 mg, 3.6 mmol, 2.0 eq.). The mixture was stirred at room temperature for 12 hours. After the reaction was completed, the reaction mixture was filtered through a short pad of celite and eluted with ethyl acetate. The solvent was removed under reduced pressure, affording **1r** as a brown solid[1] (263.2 mg, 90% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.11 – 7.09 (m, 1H), 6.99 (s, 1H), 6.81 – 6.79 (m, 1H), 3.89 – 3.87 (m, 6H), 3.01 – 3.00 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.1, 148.8, 125.6, 114.9, 114.4. 111.1, 83.9, 75.8, 56.0.

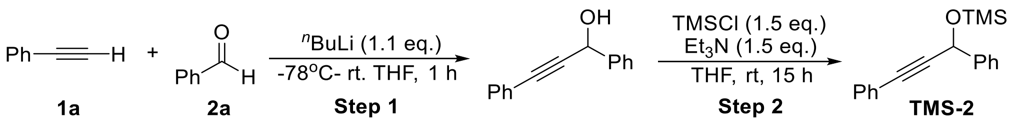
Synthesis of TMS-1[2]



1a **TMS-1**

To a THF solution of **1a** (1.1 mL, 10.0 mmol, 1.0 eq.) at -78°C was added ^{n}BuLi (2.4 M, 4.6 mL, 11.0 mmol, 1.1 eq.) under nitrogen atmosphere. The reaction mixture was warmed to room temperature and stirred for 1 hour. Then trimethylchlorosilane (1.4 mL, 11.0 mmol, 1.1 eq.) was added at -78 °C and the resulting mixture was warmed to room temperature and stirred for 3 hours, followed by quenching with a saturated aqueous NH_4Cl solution. The resulting solution was extracted by Et_2O (3 x 15 mL) and the organic solution was combined and dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified via flash chromatography on silica gel and eluted with petroleum ether to afford **TMS-1** as the colorless liquid[2] (1.3 g, 75% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.47 – 7.46 (m, 2H), 7.30 – 7.29 (m, 3H), 0.25 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 132.1, 128.6, 128.3, 123.3. 105.3, 94.3, 0.1.

Synthesis of TMS-2[3-4]



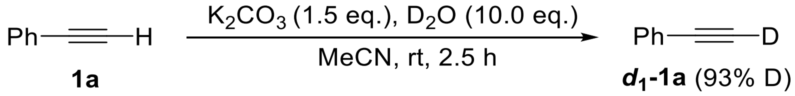
Step 1: To a THF solution of **1a** (1.4 mL, 13.0 mmol, 1.3 eq.) at -78°C was added ^{n}BuLi (2.4 M, 4.6 mL, 11.0 mmol, 1.1 eq.) under nitrogen atmosphere. The reaction mixture was warmed to room temperature and stirred for 1 hour. Then **2a** (1.0 mL, 10.0 mmol, 1.0 eq.) was added to the solution at -78 °C and the resulting mixture was warmed to room temperature and stirred for 1 hour, followed by quenching with a saturated aqueous NH_4Cl solution. The resulting solution was extracted by EtOAc (3 x 15 mL) and the organic solution was combined and dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified via flash chromatography on silica gel and eluted with petroleum ether/ethyl acetate (20/1) to afford 1,3-diphenylprop-2-yn-1-ol as the colorless liquid[3] (1.98 g, 95% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.64 – 7.63 (m, 2H), 7.50 – 7.48 (m, 2H), 7.43 – 7.41 (m, 2H), 7.38 – 7.31 (m, 4H), 5.71 (s, 1H), 2.37 (s, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.8, 131.9, 128.8, 128.8, 128.6, 128.4, 126.9, 122.5, 88.8, 86.8, 65.3.

Step 2: To a stirred solution of 1,3-diphenyl-2-propyn-1-ol (2.3 g, 11 mmol, 1.0 eq.) and triethylamine (2.3 mL, 16.5 mmol, 1.5 eq.) in THF (20.0 mL) was added trimethylsilyl chloride (2.1 mL, 16.5 mmol, 1.5 eq.) at room temperature and stirred for 15 hours. After the reaction was completed, the solvent and excess trimethylsilyl chloride were removed under reduced pressure. The residue was diluted by Et_2O (20 mL) and filtrated. The solvent was evaporated and the residue was purified by distillation under reduced pressure to give **TMS-2** as the orange liquid[4] (2.67 g, 87% yield): b.p. 123°C/ 0.15 mm Hg. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.57 (m, 2H), 7.47 – 7.45 (m, 2H), 7.41 – 7.37 (m, 2H), 7.33 – 7.29 (m, 4H), 5.72 (s, 1H), 0.26 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.6, 131.8, 128.6, 128.5, 128.4, 128.0, 126.7, 123.0, 89.9, 86.1, 65.3, 0.5; **^{29}Si NMR** (80 MHz, $CDCl_3$) δ 20.3.

Synthesis of TMS-3

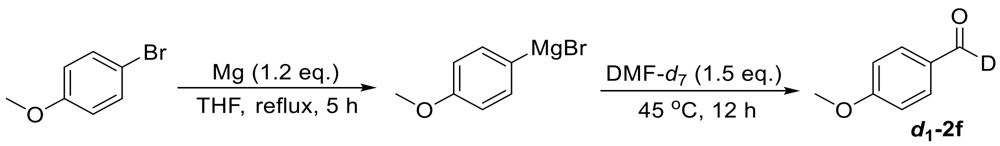
To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (406.0 mg, 7.0 mmol), DMSO (30 mL), **TMS-1** (3.03 g, 17.4 mmol, 1.0 eq.) and **2a** (3.7 g, 34.8 mmol, 2.0 eq.) under nitrogen atmosphere. The resulting solution was allowed to stir at 50 °C for 12 hours. Then H_2O (20.0 mL) was added to the mixture and the solution was extracted by ethyl acetate (10 mL x 3). The organic layer was dried over anhydrous Na_2SO_4. After concentrating, the crude product was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1) to give **TMS-3** as a white solid (3.46 g, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 5.1 Hz, 2H), 7.41 (d, J = 5.0 Hz, 2H), 7.32 – 7.27 (m, 3H), 7.22 – 7.20 (m, 1H), 7.17 – 7.15 (m, 2H), 7.08 – 7.01 (m, 5H), 6.80 (s, 1H), 5.77 (s, 1H), 0.01 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 200.2, 144.4, 141.8, 136.9, 135.6, 132.9, 129.6, 129.5, 129.0, 128.3, 128.1, 128.1, 127.8, 127.8, 127.1, 76.4; **^{29}Si NMR** (80 MHz, $CDCl_3$) δ 19.6; **HRMS** (APCI) calcd for $C_{25}H_{27}O_2Si$ [M+H]: 387.1780, found: 387.1743.

Synthesis of *d*1-1a[1]



To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added K_2CO_3 (2.0 g, 15.0 mmol, 1.5 eq.), **1a** (1.1 mL, 10.0 mmol, 1.0 eq.) and dry CH_3CN (10.0 mL). The reaction mixture was stirred under N_2 atmosphere for 30 minutes. Then D_2O (2.0 mL, 20.0 mmol 10.0 eq.) was added and the mixture was allowed to stir for additional 2 hours. The resulting crude reaction mixture was diluted with dry dichloromethane (10.0 mL) and transferred to an oven dried separatory funnel. The organic layer was dried over anhydrous Na_2SO_4. After concentrating, the crude product was purified by flash column chromatography on silica gel and eluted with petroleum ether to afford deuterated phenylacetylene as colorless liquid[1] (334.0 mg, 32% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.3 Hz, 2H), 7.37 – 7.31 (m, 3H), 3.08 (s, 0.07H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 132.3, 128.9, 128.5, 122.3, 83.8, 83.4 (t, *J* = 7.6 Hz).

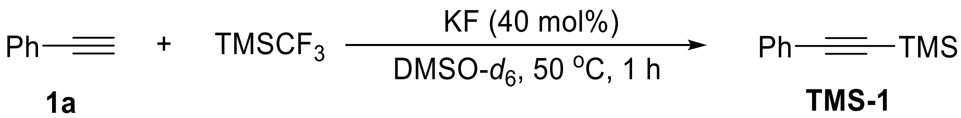
Synthesis of *d*1-2f[5]



I_2 (10.0 mg) was added to the mixture of Mg (144.0 mg, 6.0 mmol, 1.2 eq.) and THF (5.0 mL) in a 100 mL two-neck flask under nitrogen atmosphere and the reaction mixture was stirred until the solution become colorless. Then a solution of 1-bromo-4-methoxybenzene (935.0 mg, 5.0 mmol, 1.0 eq.) in THF (10.0 mL) was added slowly to the reaction mixture. The reaction mixture was then stirred under reflux for additional 5 hours. Subsequently, the reaction mixture was cooled to 45 °C and *N*,*N*-dimethylformamide-d_7 (0.6 mL, 7.5 mmol, 1.5 eq.) was added dropwise to the solution. The reaction mixture was then stirred overnight and cooled to room temperature. The reaction was quenched by aqueous saturated ammonium chloride solution (20.0 mL). THF was removed under reduced pressure and the residue was extracted by dichloromethane (20 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the crude product was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (20/1) to afford 4-methoxybenzaldehyde as colorless liquid[5] (546.7 mg, 80% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.90 – 5.88 (m, 2H), 5.07 – 5.04 (m, 2H), 1.94 (d, *J* = 7.8 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.7 (t, *J* = 26.3 Hz), 164.8, 132.1, 130.1, 114.5, 55.7.

3. Initial Studies on Reaction Design

(a) The reaction of 1a and TMSCF3



To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (4.6 mg, 0.08 mmol), DMSO-d_6 (1.5 mL, 0.13 M), **1a** (20.4 mg, 0.2 mmol, 1 eq.) and $TMSCF_3$ (28.4 mg, 0.2 mmol, 1 eq.) under nitrogen atmosphere. The resulting solution was allowed to stir at 50 °C for 1 hour. After cooling to room temperature, mesitylene (16.3 mg, as the internal standard) was added into the mixture and the yield of **TMS-1** (72% yield) was determined by NMR.

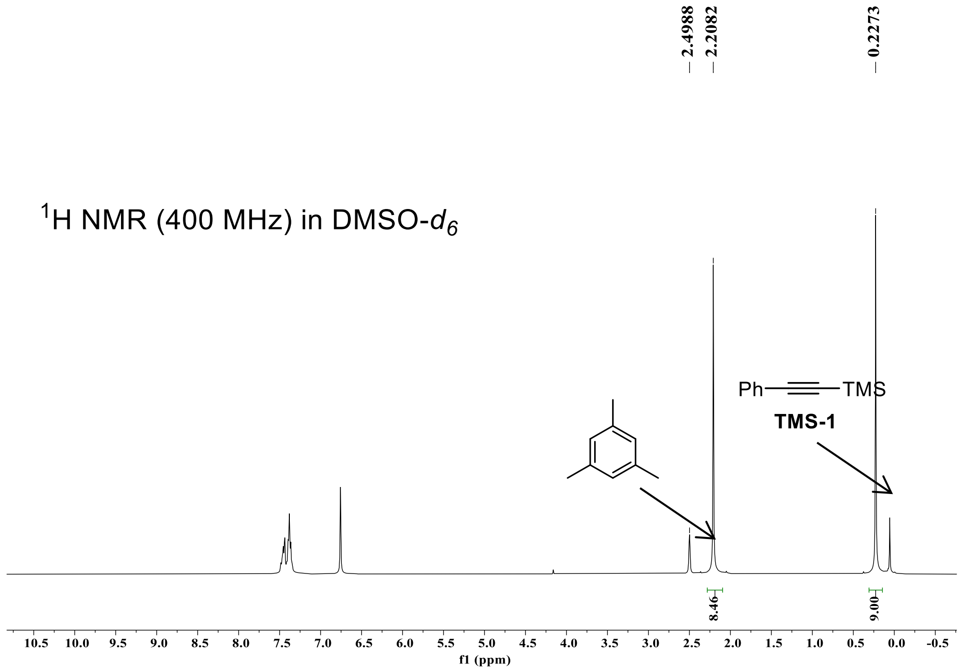
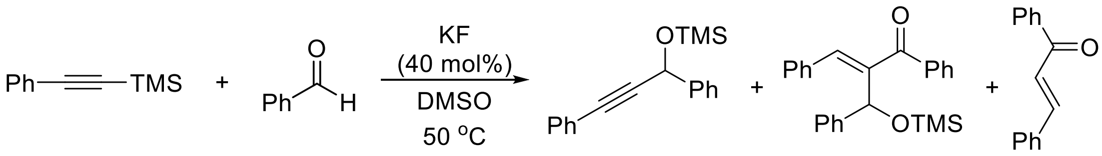


Figure S1. ^{1}H NMR spectrum of the crude reaction mixture of **1a** with $TMSCF_3$

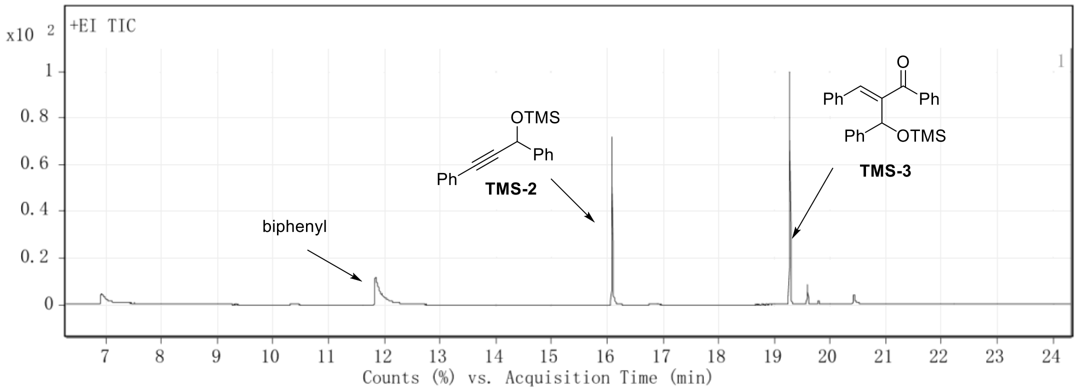
(b) The reaction of TMS-1 and 2a

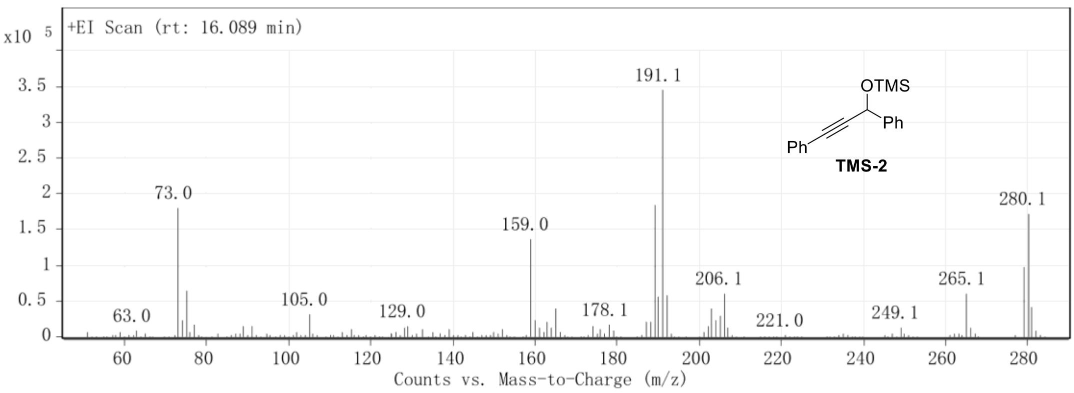


			TMS-1	2a		TMS-2	TMS-3	3aa
Condition A	3 h	43%	36%	0%
Condition B	w/o KF, 12 h	0%	0%	0%

For Condition A:

To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (4.6 mg, 0.08 mmol), DMSO (1.5 mL, 0.13 M), **TMS-1** (34.8 mg, 0.2 mmol, 1 eq.) and **2a** (42.4 mg, 0.4 mmol, 2 eq.) under nitrogen atmosphere. The resulting solution was allowed to stir at 50 ºC for 3 hours. The reaction mixture was then subjected to GC and GC-MS analysis using biphenyl as the internal standard. The product **TMS-2** and **TMS-3** were obtained in 43% and 36% yields, respectively, while **3aa** was not observed.





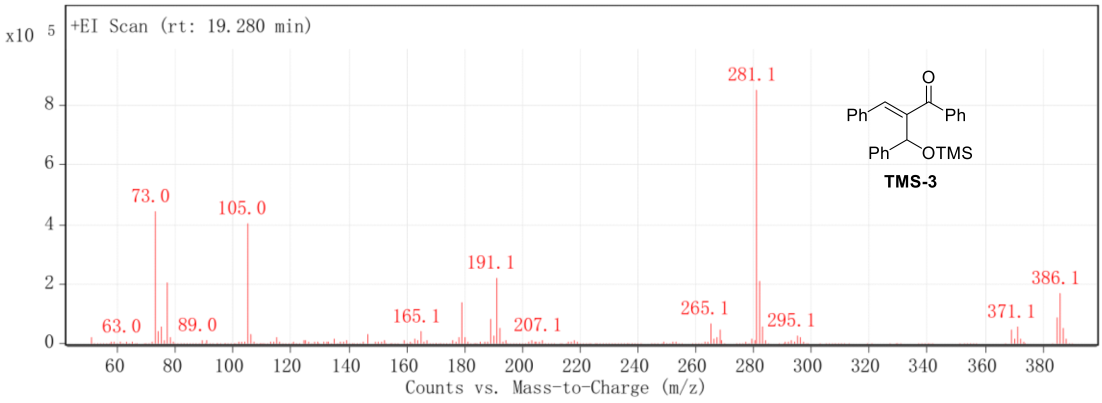
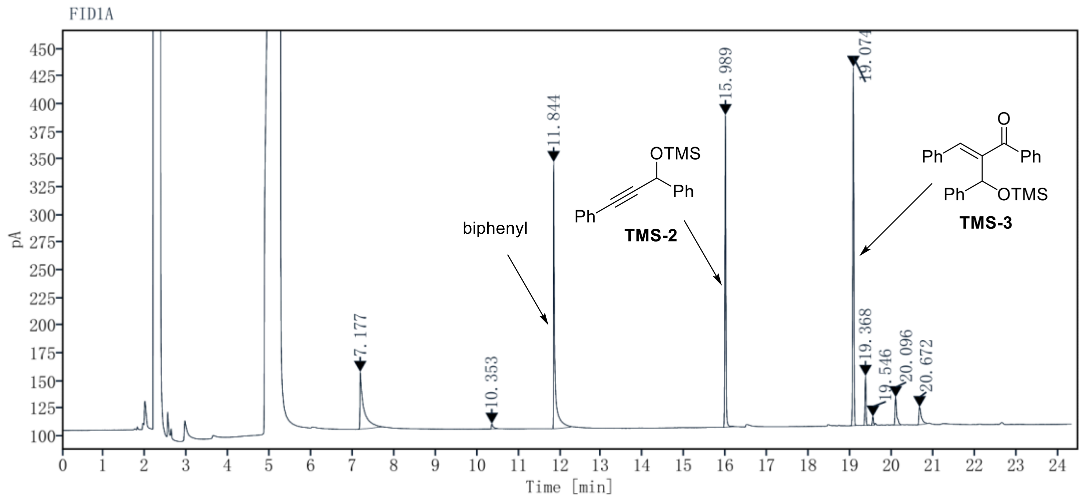


Figure S2. GC-MS spectra of the reaction mixture of **TMS-1** with **2a** under condition A



Illustrate FID1A

Retention Time [min]	Peak Area	Peak Area %
7.177	327.27094	14.95
10.353	14.67410	0.67
11.844	533.58456	24.37
15.989	497.96979	22.74
19.074	582.04845	26.58
19.368	80.36263	3.67
19.546	15.87366	0.72
20.096	71.07055	3.25
20.672	66.93297	3.06

Figure S3. GC spectrum of the reaction mixture of **TMS-1** with **2a** under condition A

For Condition B:

To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added DMSO (1.5 mL, 0.13 M), **TMS-1** (34.8 mg, 0.2 mmol, 1 eq.) and **2a** (42.4 mg, 0.4 mmol, 2 eq.) under nitrogen atmosphere. The resulting solution was allowed to stir at 50 °C for 12 hours. The reaction mixture was subjected to GC-MS analysis, indicating that the reaction of **TMS-1** with **2a** did not proceed in the absence of KF.

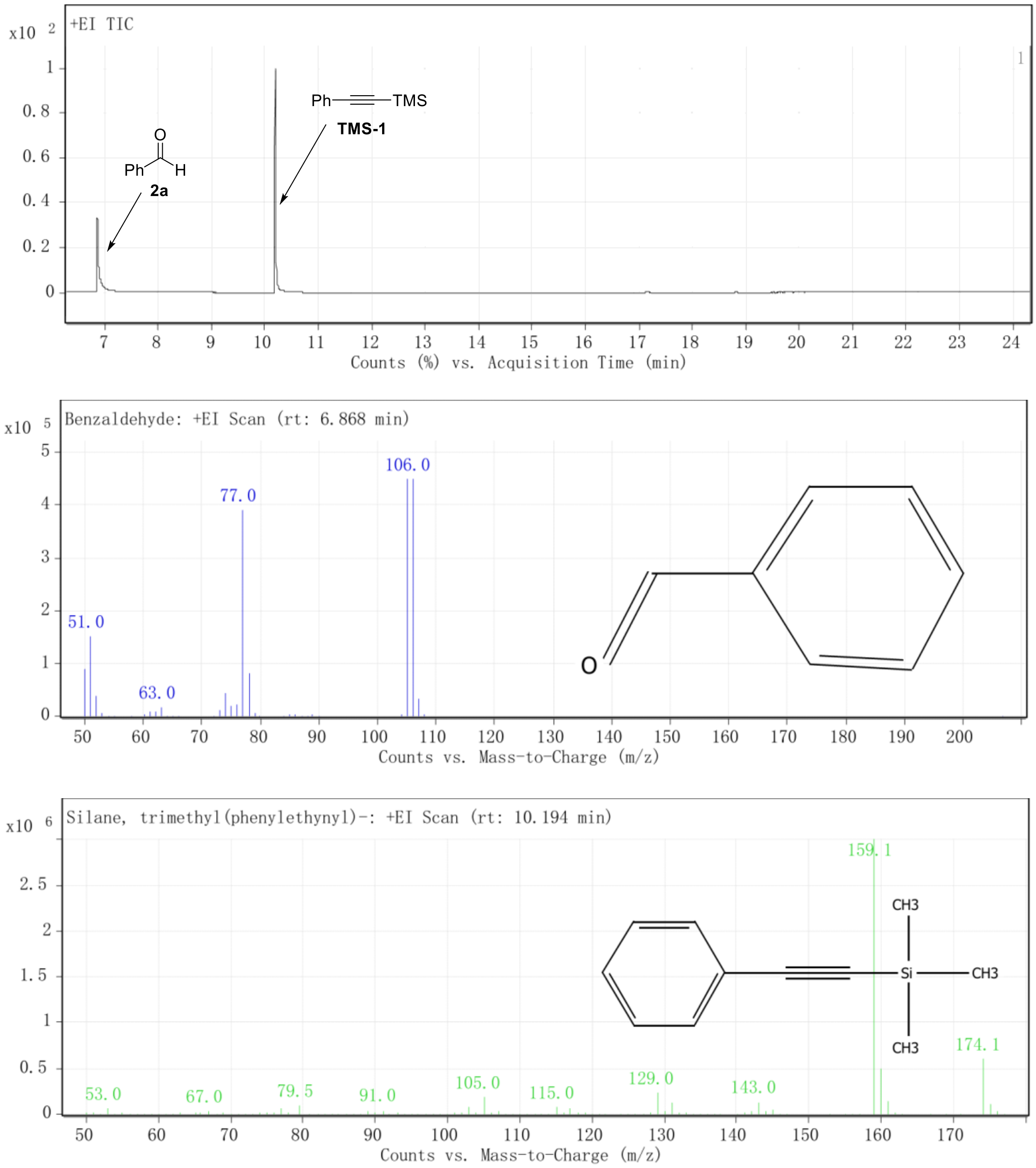
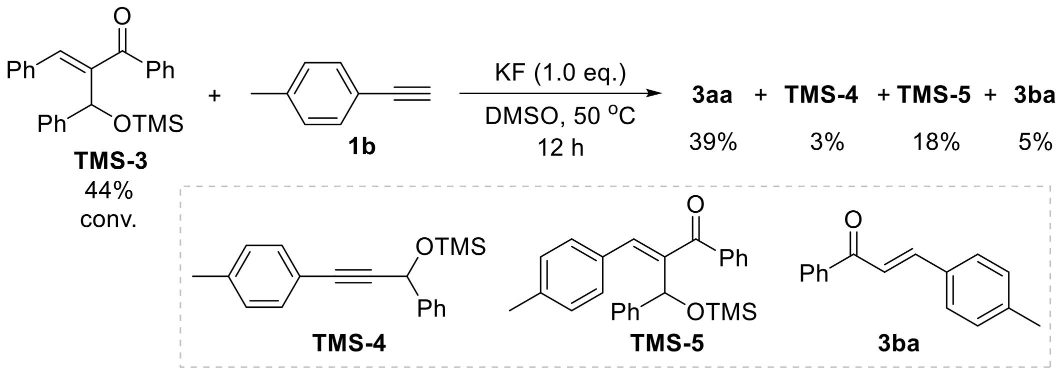
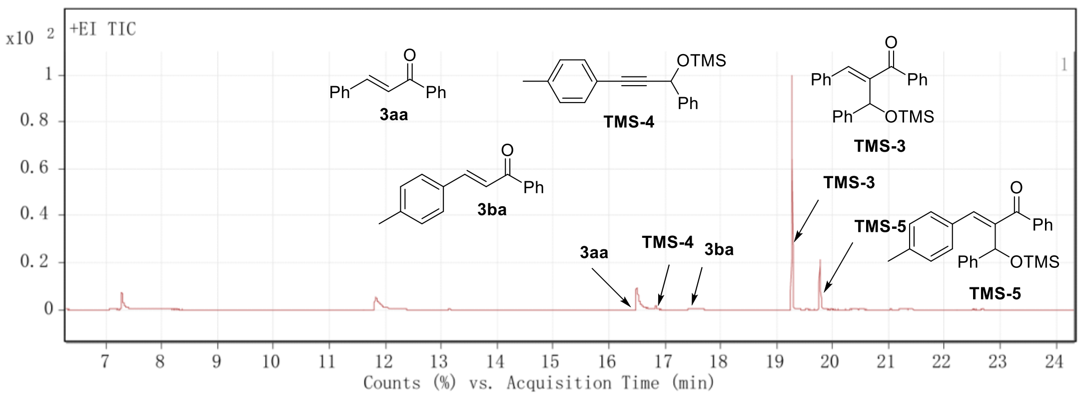


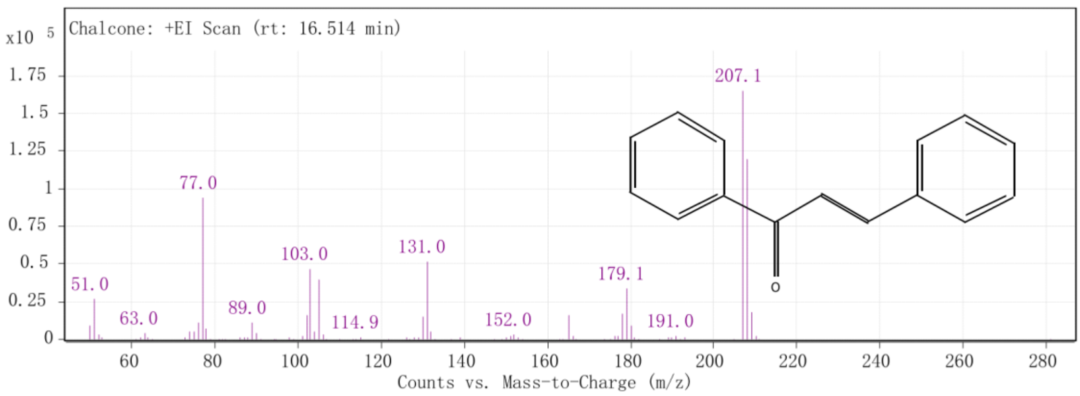
Figure S4. GC-MS spectra of the reaction mixture of **TMS-1** with **2a** under condition B

(c) The reaction of TMS-3 and 1b



To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (11.6 mg, 0.2 mmol), DMSO (1.5 mL, 0.13 M), **TMS-3** (77.2 mg, 0.2 mmol, 1 eq.) and **1b** (23.2 mg, 0.4 mmol, 2 eq.) under nitrogen atmosphere. The resulting solution was allowed to stir at 50 °C for 12 hours. The reaction mixture was subjected to GC and GS-MS analysis using biphenyls as the internal standard. The product **3aa** was obtained in 39% yield, together with 3% yield of **TMS-4**. In addition, **TMS-5** and 3ba were also observed in 18% and 5% yields, respectively.





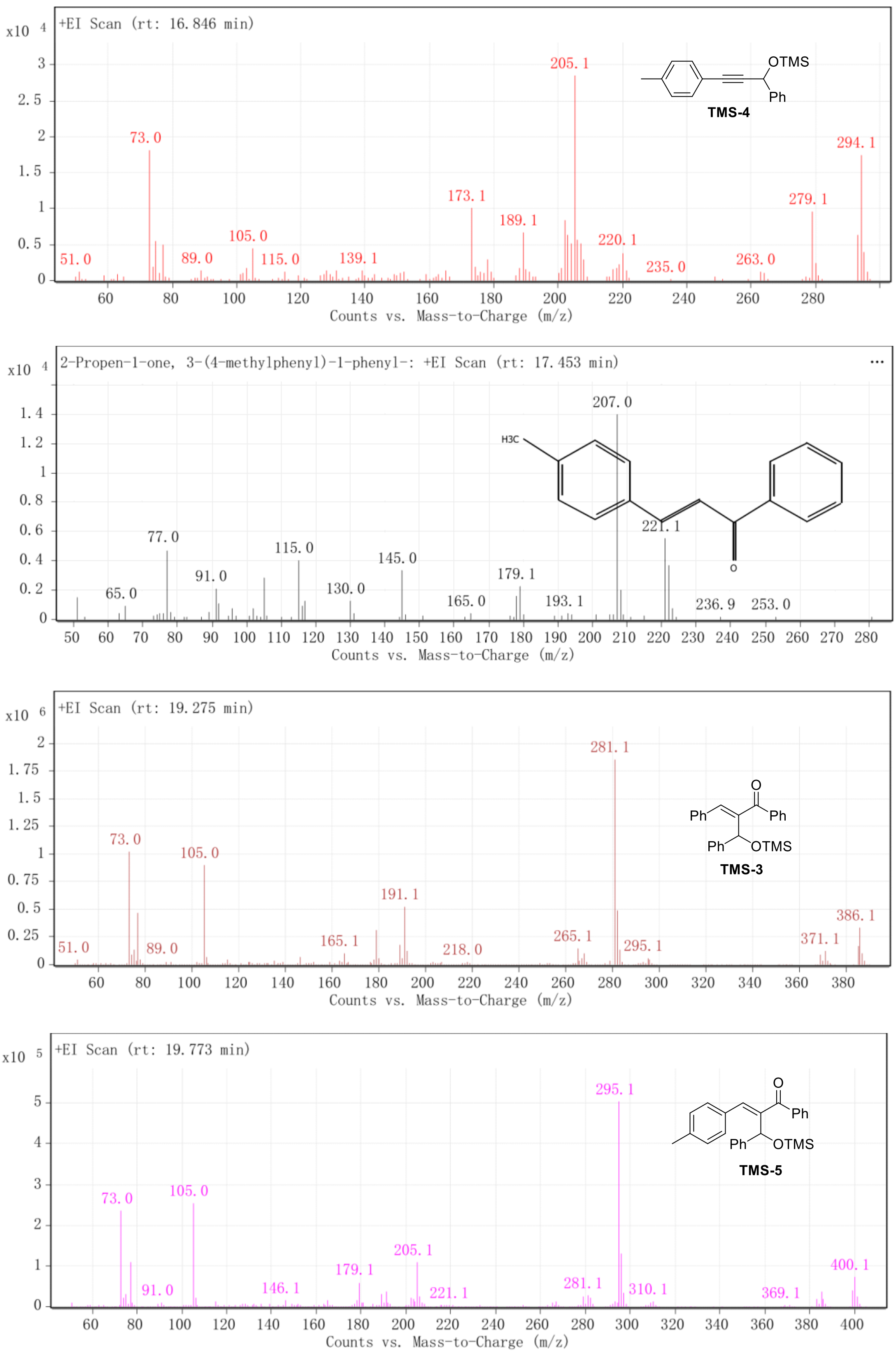
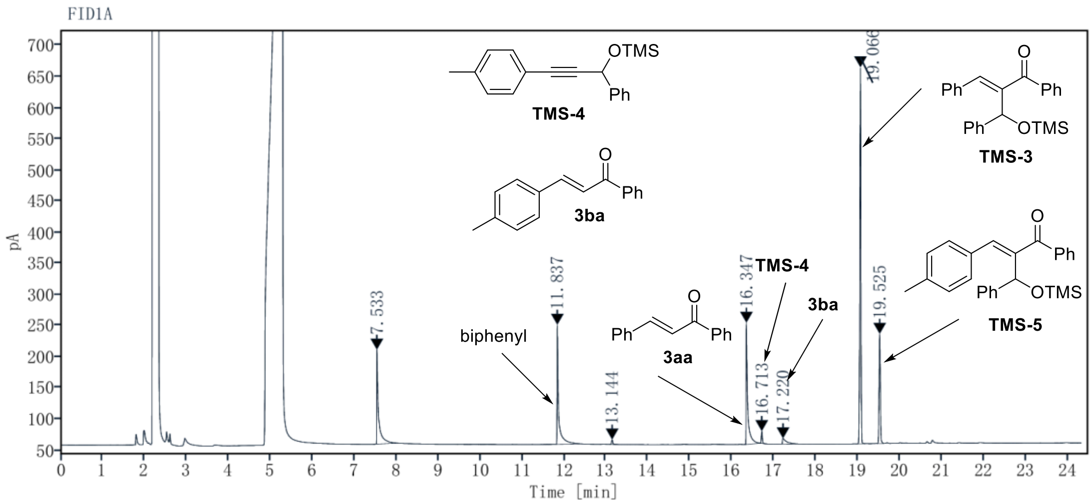


Figure S5. GC-MS spectra of the reaction mixture of **TMS-3** with **1b**

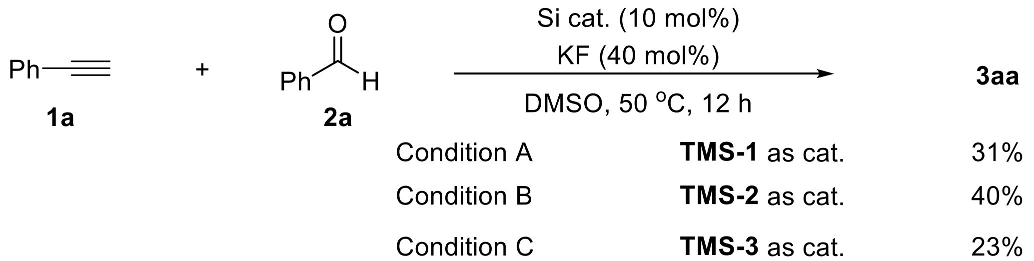


Illustrate FID1A

Retention Time [min]	Peak Area	Peak Area %
7.533	445.10868	14.83
11.837	479.64359	15.98
13.144	13.38931	0.45
16.347	482.46290	16.07
16.713	35.38674	1.18
17.220	61.29192	2.04
19.066	1123.30353	37.42
19.525	361.11739	12.03

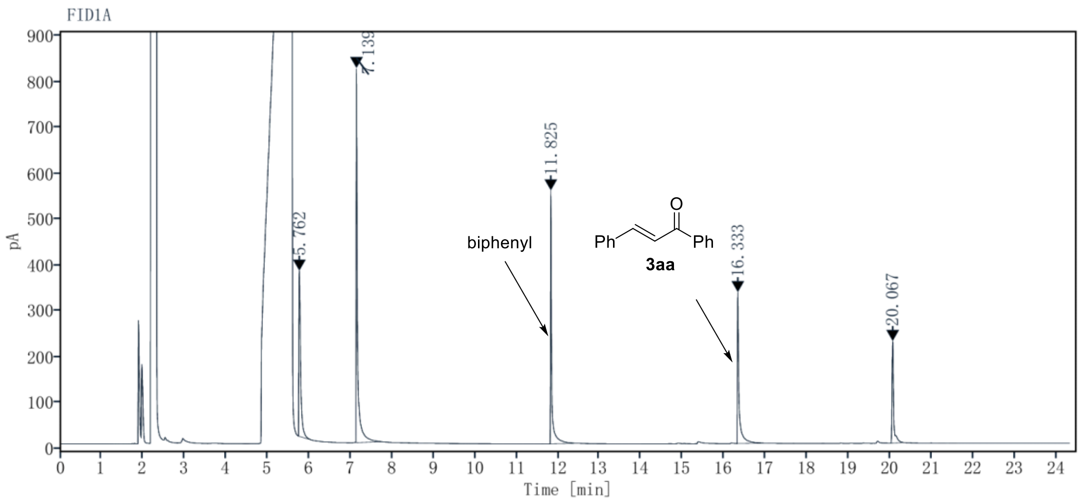
Figure S6. GC spectra of the reaction mixture of **TMS-3** with **1b**

(d) The reaction of 1a and 2a under different Si catalysts



For Condition A:

To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (4.6 mg, 0.08 mmol) and DMSO (1.5 mL, 0.13 M) under nitrogen atmosphere. Then **1a** (20.4 mg, 0.2 mmol, 1.0 eq.), **TMS-1** (1.8 mg, 0.02 mmol) and **2a** (42.4 mg, 0.4 mmol, 2 eq.) were added to the mixture. The resulting solution was allowed to stir at 50 °C for 12 hours. The reaction mixture was then subjected to GC analysis using biphenyl as the internal standard. The product **3aa** was obtained in 31% yield.



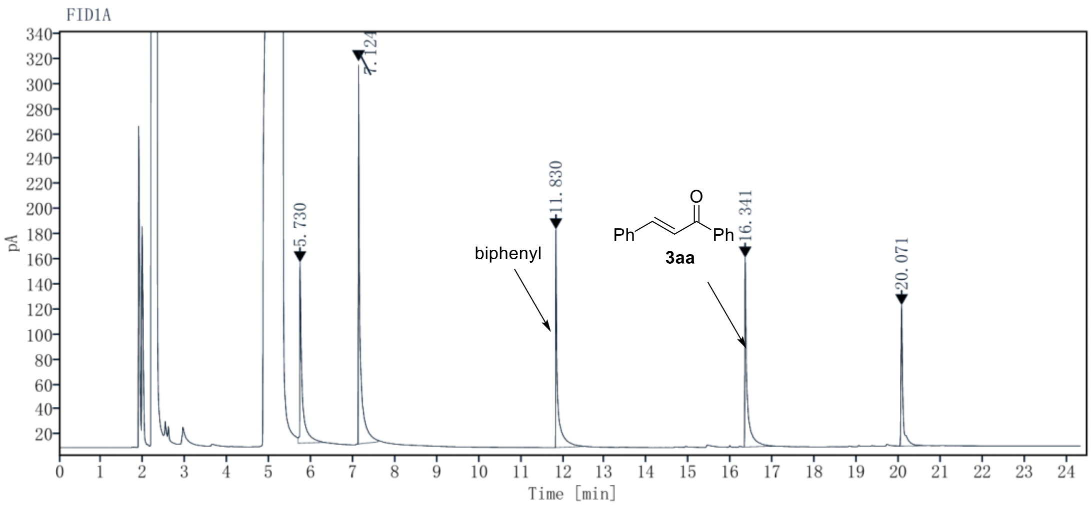
Illustrate FID1A

Retention Time [min]	Peak Area	Peak Area %
5.762	1038.20058	19.37
7.139	1800.16339	33.59
11.825	1081.01343	20.17
16.333	846.78399	15.80
20.067	593.47129	11.07

Figure S7. GC spectrum of the reaction mixture of **1a** with **1b** under condition A

For Condition B:

To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (4.6 mg, 0.08 mmol) and DMSO (1.5 mL, 0.13 M) under nitrogen atmosphere. Then **1a** (20.4 mg, 0.2 mmol, 1.0 eq.), **TMS-2** (5.6 mg, 0.02 mmol, 10 mol%) and **2a** (42.4 mg, 0.4 mmol, 2 eq.) were added to the mixture. The resulting solution was allowed to stir at 50 °C for 12 hours. The reaction mixture was then subjected to GC analysis using biphenyl as the internal standard. The product **3aa** was obtained in 40% yield.



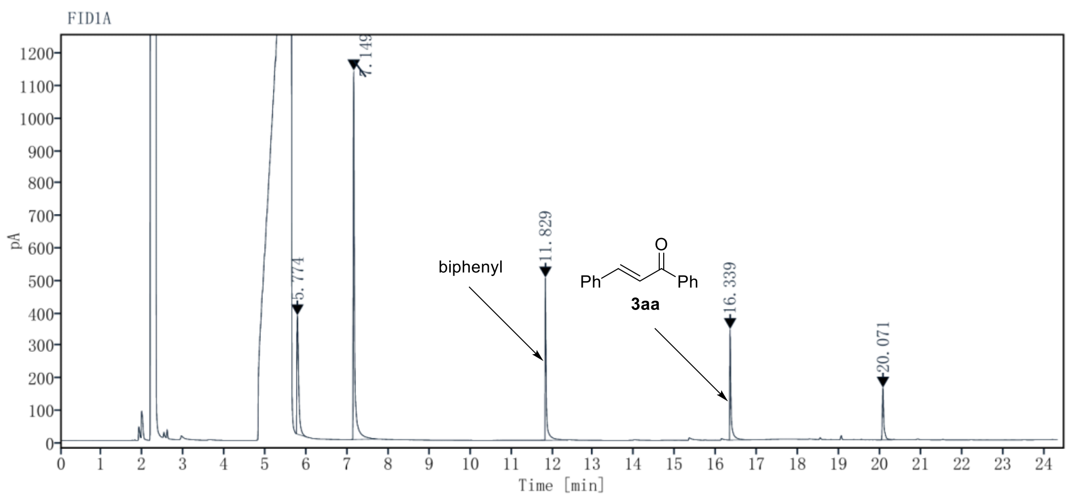
Illustrate FID1A

Retention Time [min]	Peak Area	Peak Area %
5.730	532.74377	19.13
7.124	843.79946	30.29
11.830	507.26069	18.21
16.341	537.59638	19.30
20.071	364.09799	13.07

Figure S8. GC spectrum of the reaction mixture of **1a** with **1b** under condition B

For Condition C:

To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (4.6 mg, 0.08 mmol) and DMSO (1.5 mL, 0.13 M) under nitrogen atmosphere. Then **1a** (20.4 mg, 0.2 mmol, 1.0 eq.), **TMS-3** (7.7 mg, 0.02 mmol, 20 mol%) and **2a** (42.4 mg, 0.4 mmol, 2 eq.) were added to the mixture. The resulting solution was allowed to stir at 50 ºC for 12 hours. The reaction mixture was subjected to GC analysis using biphenyl as the internal standard. The product **3aa** was obtained in 23% yield.



Illustrate FID1A

Retention Time [min]	Peak Area	Peak Area %
5.774	1134.88231	19.52
7.149	2585.48092	44.46
11.829	952.12423	16.37
16.339	725.21934	12.47
20.071	417.52662	7.18

Figure S9. GC spectrum of the reaction mixture of **1a** with **1b** under condition C

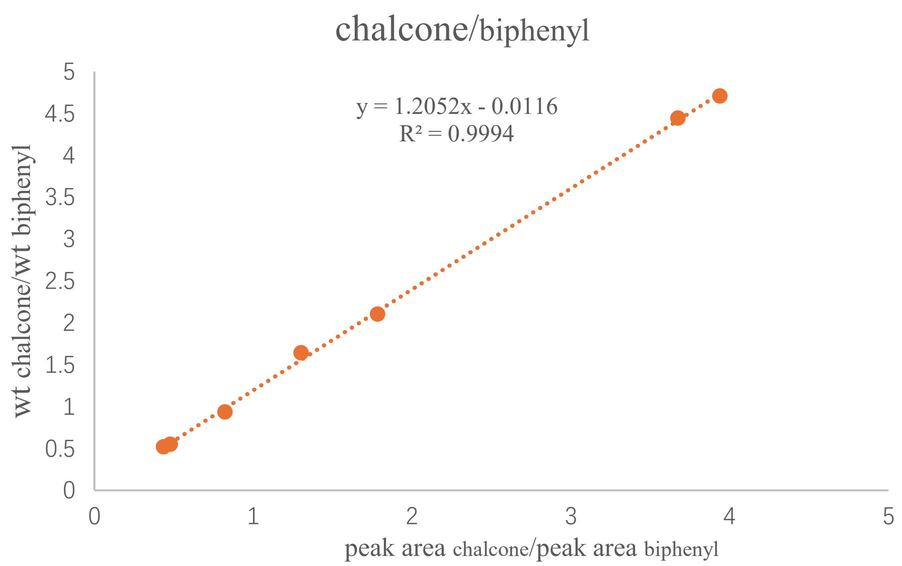
4. Standard curve plot

GC acquisition method: Agilent 8860 GC system; Column: HP-5, 30 m x 320 μm x 0.25 μm, Inlets: 280 °C; Detector: FID 300 °C; Carrier Gas: N_2; Flow: 1.0 mL/min; Oven: 50 °C, hold 4 min; 15 °C/min to 280 °C, hold 5 min.

a) Standard curve plot for chalcone and biphenyl

Table S1. Measurement of the relative GC response factors of chalcone and biphenyl

Entry	biphenyl (mg)	chalcone (mg)	biphenyl (peak area)	chalcone (peak area)
1	0.9	4.0	87.350	321.044
2	1.9	4.0	112.454	200.454
3	2.8	4.6	211.872	275.828
4	3.1	2.9	241.754	198.807
5	4.1	19.3	328.486	1293.866
6	5.1	2.8	293.637	140.504
7	11.9	6.2	959.472	417.389



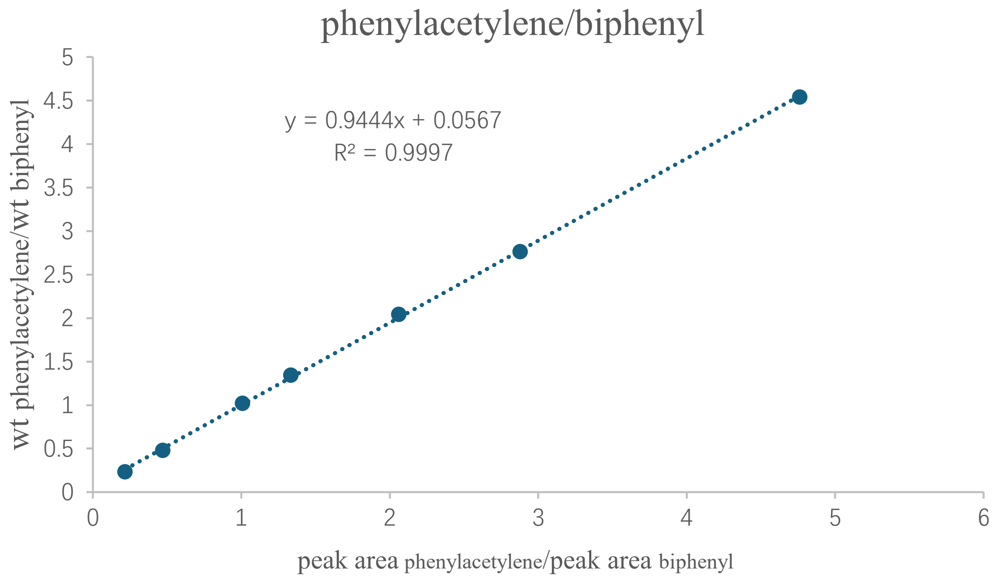
$$M_{chalcone} = (1.2052 * \text{Peak area}_{chalcone} \,/\, \text{Peak area}_{biphenyl}) * M_{biphenyl}$$

Figure S10. Standard curve plot of chalcone and biphenyl

b) Standard curve plot for phenylacetylene and biphenyl

Table S2. Measurement of the relative GC response factors of phenylacetylene and biphenyl

Entry	biphenyl (mg)	phenylacetylene (mg)	biphenyl (peak area)	phenylacetylene (peak area)
1	10.4	47.2	1781.801	8485.577
2	20.5	41.9	3562.890	7344.693
3	30.4	31.0	5311.567	5359.218
4	42.3	20.3	7267.942	3417.775
5	50.1	11.7	8747.486	1894.197
6	29.7	39.9	5624.324	7499.915
7	10.9	30.1	1860.473	5354.495



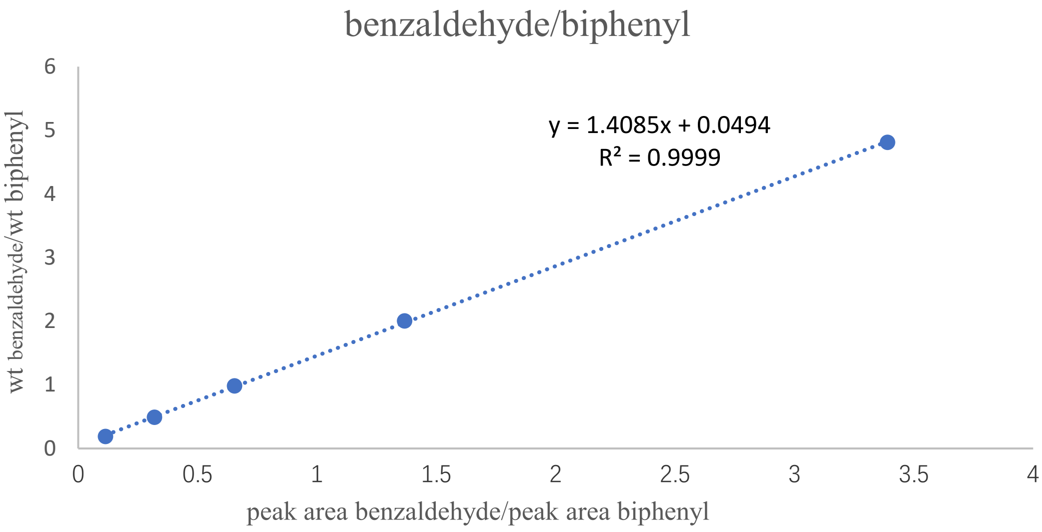
$$M_{phenylacetylene} = (0.9444 * \text{Peak area}_{phenylacetylene} / \text{Peak area}_{biphenyl}) * M_{biphenyl}$$

Figure S11. Standard curve plot of phenylacetylene and biphenyl

c) Standard curve plot for benzaldehyde and biphenyl

Table S3. Measurement of the relative GC response factors of benzaldehyde and biphenyl

Entry	biphenyl (mg)	benzaldehyde (mg)	biphenyl (peak area)	benzaldehyde (peak area)
1	10.1	48.6	994.610	3372.185
2	20.1	40.3	1849.441	2527.996
3	30.5	30.0	3225.035	2112.444
4	40.4	19.8	4825.549	1540.802
5	50.5	9.6	8535.603	974.435



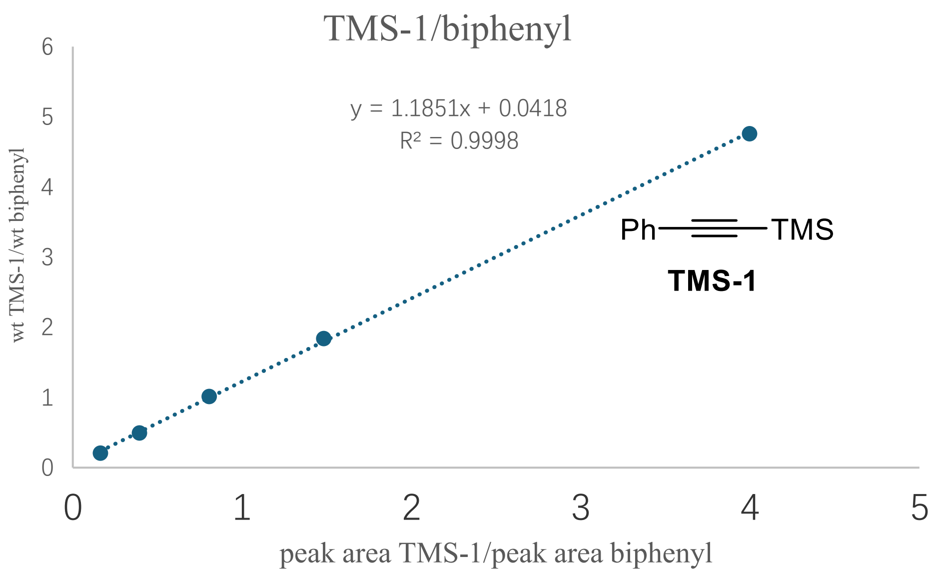
$$M_{benzaldehyde} = (1.4085 * \text{Peak area}_{benzaldehyde} / \text{Peak area}_{biphenyl}) * M_{biphenyl}$$

Figure S12. Standard curve plot of benzaldehyde and biphenyl

d) Standard curve plot for TMS-1 and biphenyl

Table S4. Measurement of the relative GC response factors of TMS-1 and biphenyl

Entry	biphenyl (mg)	TMS-1 (mg)	biphenyl (peak area)	TMS-1 (peak area)
1	10.9	51.9	2836.928	11336.949
2	22.4	41.2	5785.020	8572.704
3	30.0	30.4	7267.182	5859.832
4	40.5	20.1	9932.278	3917.218
5	49.7	10.3	12567.959	2054.961



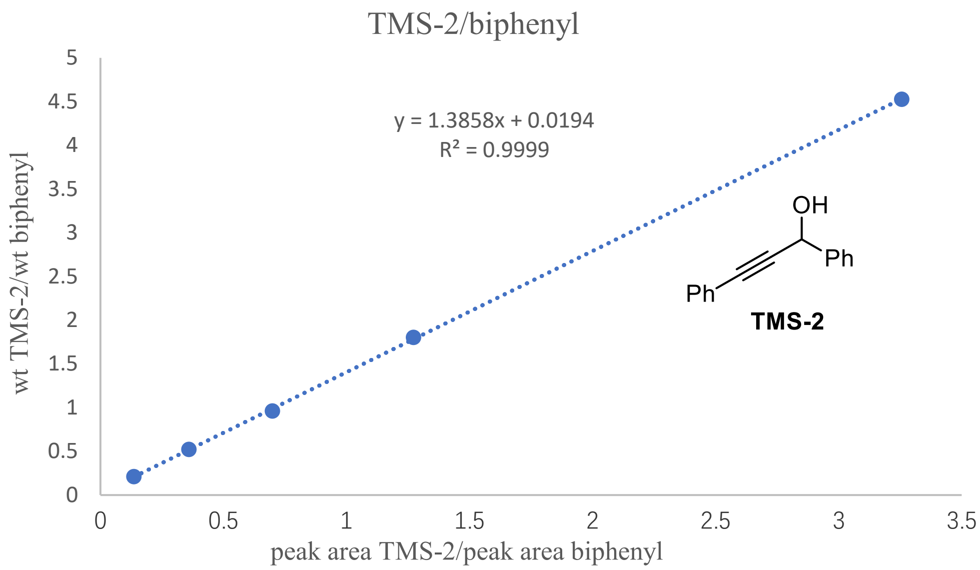
$M_{TMS-1} = (1.1851 * \text{Peak area}_{TMS-1} / \text{Peak area}_{biphenyl}) * M_{biphenyl}$

Figure S13. Standard curve plot of **TMS-1** and biphenyl

e) Standard curve plot for TMS-2 and biphenyl

Table S5. Measurement of the relative GC response factors of TMS-2 and biphenyl

Entry	biphenyl (mg)	TMS-2 (mg)	biphenyl (peak area)	TMS-2 (peak area)
1	10.8	48.9	2216.271	7215.711
2	21.3	38.4	4350.991	5533.440
3	29.8	28.7	6743.169	4717.956
4	41.9	21.9	8171.732	2937.570
5	51.3	10.8	11534.263	1566.524



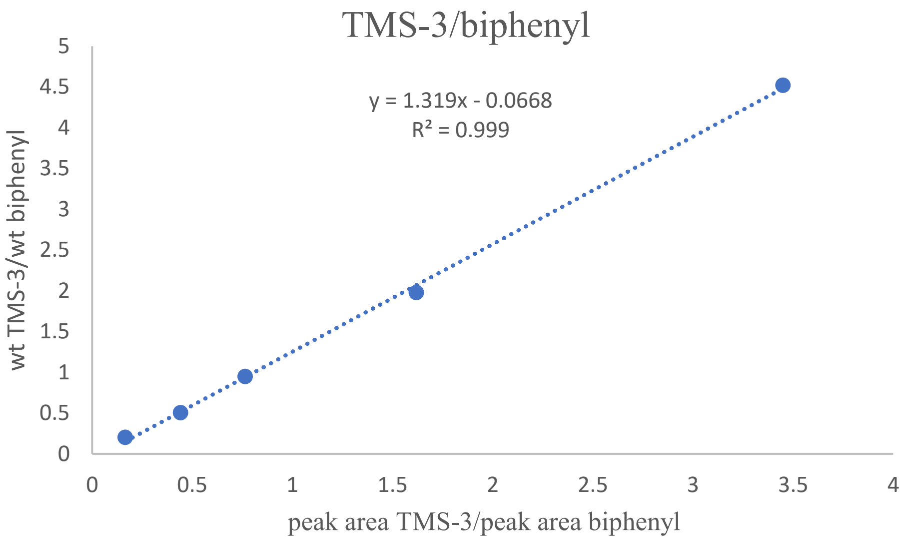
$M_{TMS\text{-}2} = (1.3858 * \text{Peak area}_{TMS\text{-}2} / \text{Peak area}_{biphenyl}) * M_{biphenyl}$

Figure S14. Standard curve plot of **TMS-2** and biphenyl

f) Standard curve plot for TMS-3 and biphenyl

Table S6. Measurement of the relative GC response factors of TMS-3 and biphenyl

Entry	biphenyl (mg)	TMS-3 (mg)	biphenyl (peak area)	TMS-3 (peak area)
1	11.1	50.2	2143.020	7393.370
2	20.6	40.8	3396.553	5499.995
3	31.2	29.6	4967.652	3795.669
4	40.5	20.4	8416.976	3716.784
5	49.8	10.2	9115.124	1504.658



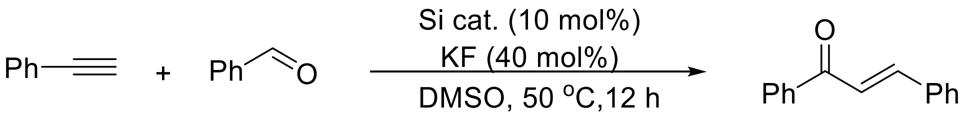
$$M_{TMS\text{-}3} = (1.319 * \text{Peak area}_{TMS\text{-}3} / \text{Peak area}_{biphenyl}) * M_{biphenyl}$$

Figure S15. Standard curve plot of **TMS-3** and biphenyl

5. Optimization of the Reaction Conditions

To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added base (0.08 mmol, 40 mol%) and solvent (1.5 mL, 0.13 M) under nitrogen atmosphere. Then **1a** (20.4 mg, 0.2 mmol, 1.0 eq.), silane (0.04 mmol, 20 mol%) and **2a** (42.4 mg, 0.4 mmol, 2 eq.) was added to the mixture. The resulting solution was allowed to stir at 50 °C for 12 hours. After the reaction finished, the reaction mixture was subjected to GC and GC-MS analysis using biphenyls as the internal standard. The solvents with high boiling points required the addition of H_2O (20 mL) to the mixture and the solution was extracted by ethyl acetate (10 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4. After concentrating, the crude product was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-20/1) to give the desired product **3aa**.

Table S7. Screening of silicon catalyst[a]



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

Entry	Silane	Yield (%)[b]
1	$TMSCF_3$	73
2	Ph_2MeSiH	28
3	Et_3SiH	47
4	$PhSiH_3$	69
5	$PhMe_2SiH$	26
6	Ph_2SiH_2	63
7	TMSCl	0
8	TMSBr	0
9	$Me_2PhSiCl$	0

[a]Reaction conditions: **1a** (20.4 mg, 0.2 mmol, 1 eq.), **2a** (42.4 mg, 0.4 mmol, 2 eq.), silicon catalyst (0.02 mmol, 10 mol%), KF (4.6 mg, 0.08 mmol, 40 mol%), DMSO (1.5 mL, 0.13 M), 50 °C, 12 h. [b]Yields were determined by GC using biphenyl as the internal standard.

Table S8. Screening of base[a]

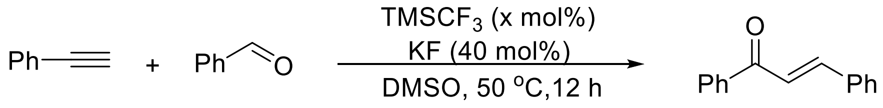
1a **2a** **3aa**

Entry	base	Yield (%)[b]
1	KF	73
2	K_2CO_3	61
3	Cs_2CO_3	51
4	KOH	33
5	CsF	53
6	K_3PO_4	65
7	MeOK	16
8	MeONa	24
9	EtONa	29
10	^{t}BuOK	6
11	^{t}BuONa	20

12	^{t}BuOLi	29
13	Na_2CO_3	NR
14	DBU	NR
15	Et_3N	NR
16	^{i}Pr_2NH	NR
17	DIPEA	NR
18	DMAP	NR
19	DABCO	NR
20	NaOAc	NR

[a]Reaction conditions: **1a** (20.4 mg, 0.2 mmol, 1 eq.), **2a** (42.4 mg, 0.4 mmol, 2 eq.), $TMSCF_3$ (2.8 mg, 0.02 mmol, 10 mol%), base (0.08 mmol, 40 mol%), DMSO (1.5 mL, 0.13 M), 50 ℃, 12 h. [b]Yields were determined by GC using biphenyl as the internal standard.

Table S9. Screening of the loading of $TMSCF_3$[a]



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

Entry	$TMSCF_3$(x mol%)	Yield (%)[b]
1	5	10
2	10	73
3	20	83
4	40	79
5	80	58
6	100	46

[a]Reaction conditions: **1a** (20.4 mg, 0.2 mmol, 1 eq.), **2a** (42.4 mg, 0.4 mmol, 2 eq.), $TMSCF_3$ (x mol%), KF (4.6 mg, 0.08 mmol, 40 mol%), DMSO (1.5 mL, 0.13 M), 50 °C, 12 h. [b]Yields were determined by GC using biphenyl as the internal standard.

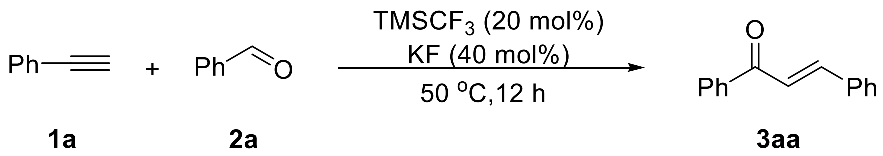
Table S10. Screening of the loading of KF[a]

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

Entry	KF (x mol%)	Yield (%)[b]
1	10	22
2	20	66
3	40	83
4	60	64

[a]Reaction conditions: **1a** (20.4 mg, 0.2 mmol, 1 eq.), **2a** (42.4 mg, 0.4 mmol, 2 eq.), $TMSCF_3$ (5.7 mg, 0.04 mmol, 20 mol%), KF (x mol%), DMSO (1.5 mL, 0.13 M), 50 °C, 12 h. [b]Yields were determined by GC using biphenyl as the internal standard.

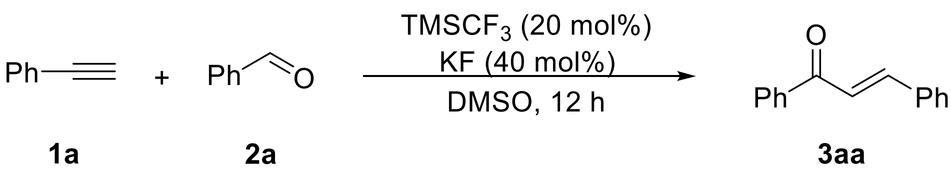
Table S11. Screening of solvent[a]



Entry	Solvent	Yield (%)[b]
1	DMSO	83
2	DMAc	13
3	DMF	26
4	DCM	NR
5	MeOH	NR
6	THF	NR
7	Toluene	NR
8	Dioxane	NR
9	CH_3CN	NR
10	*n*-hexane	NR

[a]Reaction conditions: **1a** (20.4 mg, 0.2 mmol, 1 eq.), **2a** (42.4 mg, 0.4 mmol, 2 eq.), $TMSCF_3$ (5.7 mg, 0.04 mmol, 20 mol%), KF (4.6 mg, 0.08 mmol, 40 mol%), solvent (1.5 mL, 0.13 M), 50 °C, 12 h. [b]Yields were determined by GC using biphenyl as the internal standard.

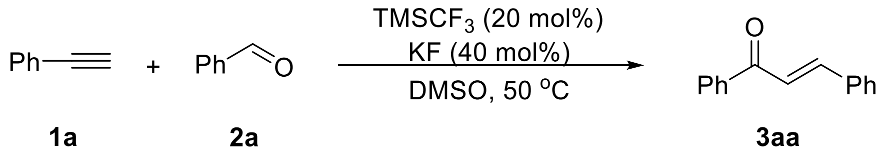
Table S12. Screening of temperature[a]



Entry	T(°C)	Yield (%)[b]
1	rt	18
2	40	50
3	50	83
4	60	70
5	80	72

[a]Reaction conditions: **1a** (20.4 mg, 0.2 mmol, 1 eq.), **2a** (42.4 mg, 0.4 mmol, 2 eq.), $TMSCF_3$ (5.7 mg, 0.04 mmol, 20 mol%), KF (4.6 mg, 0.08 mmol, 40 mol%), DMSO (1.5 mL, 0.13 M), 12 h. [b]Yields were determined by GC using biphenyl as the internal standard.

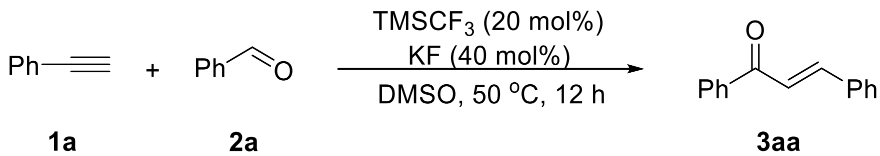
Table S13. Screening of time[a]



Entry	t(h)	Yield (%)[b]
1	3	34
2	6	52
3	9	63
5	12	83
4	24	75

[a]Reaction conditions: **1a** (20.4 mg, 0.2 mmol, 1 eq.), **2a** (42.4 mg, 0.4 mmol, 2 eq.), $TMSCF_3$ (5.7 mg, 0.04 mmol, 20 mol%), KF (4.6 mg, 0.08 mmol, 40 mol%), DMSO (1.5 mL, 0.13 M), 50 °C. [b]Yields were determined by GC using biphenyl as the internal standard.

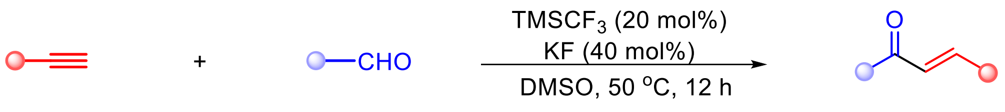
Gram-Scale Synthesis of 3aa



To a 100 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (232 mg, 4.0 mmol) and DMSO (30 mL, 0.33 M) under nitrogen atmosphere. Then **1a** (1.02 g, 10.0 mmol, 1.0 eq.), $TMSCF_3$ (284.4 mg, 2 mmol) and **2a** (2.12 g, 20 mmol, 2 eq.) was added to the mixture. The resulting solution was allowed to stir at 50

°C for12 hours. After the reaction finished, H_2O (80 mL) was added to the mixture and the solution was extracted by ethyl acetate (60 mL x 3). The organic layer was dried over anhydrous Na_2SO_4. After concentrating, the crude product was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50/1-20/1) to give the desired product **3aa** (1.53 g, 74% yield).

6. General Procedure for the Synthesis of α,β-Unsaturated Ketones

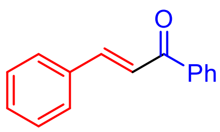


1 2 3

To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (4.6 mg, 0.08 mmol, 40 mol%) and DMSO (1.5 mL, 0.13 M) under nitrogen atmosphere. Then **1** (0.2 mmol, 1.0 eq.), $TMSCF_3$ (5.7 mg, 0.04 mmol, 20 mol%) and **2** (0.4 mmol, 2 eq.) was added to the mixture. The resulting solution was allowed to stir at 50 °C for 12 hours. After the reaction finished, H_2O (20 mL) was added to the mixture and the solution was extracted by ethyl acetate (10 mL x 3). The organic layer was dried over anhydrous Na_2SO_4. After concentrating, the crude product was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1-20/1) to give the desired product **3**.

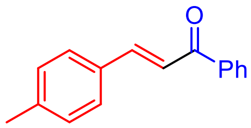
7. Experimental characterization data for products

(*E*)-Chalcone (3aa)[6]**：** The title compound was prepared according to the general procedure to give a white solid, 33.4 mg, 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 – 8.02 (m, 2H), 7.84 (d, J = 15.7 Hz, 1H), 7.66 – 7.64 (m, 2H), 7.61 – 7.49 (m, 4H), 7.43 – 7.42 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.7, 145.0, 138.4, 135.1, 132.9, 130.7, 129.1, 128.8, 128.7, 128.6, 122.3.



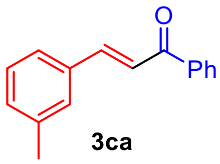
3aa

(*E*)-1-Phenyl-3-(p-tolyl)prop-2-en-1-one (3ba)[7]: The title compound was prepared according to the general procedure to give a white solid, 32.2 mg, 73% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 – 8.01 (m, 2H), 7.82 (d, J = 15.7 Hz, 1H), 7.61 – 7.54 (m, 3H), 7.52 – 7.48 (m, 3H), 7.24 – 7.22 (m, 2H), 2.40 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.8, 145.1, 141.2, 138.6, 132.8, 132.4, 129.9, 128.7, 128.6, 121.3, 21.7.



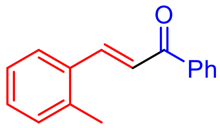
3ba

(*E*)-1-Phenyl-3-(m-tolyl)prop-2-en-1-one (3ca)[7]: The title compound was prepared according to the general procedure to give a white solid, 30.9 mg, 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 – 8.02 (m, 2H), 7.81 (d, J = 15.8 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.54 – 7.49 (m, 3H), 7.46 – 7.45 (m, 2H), 7.34 – 7.30 (m, 1H), 7.24 – 7.23 (m, 1H), 2.40 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.7, 145.2, 138.7, 138.4, 135.0, 132.8, 131.5, 129.2, 129.0, 128.7, 128.6, 125.8, 122.1, 21.5.



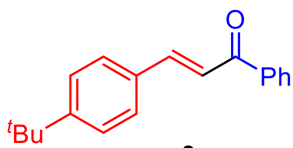
3ca

(*E*)-1-Phenyl-3-(o-tolyl)prop-2-en-1-one (3da)[7]: The title compound was prepared according to the general procedure to give a white solid, 28.7 mg, 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, J = 15.5 Hz, 1H), 8.05 – 8.03 (m, 2H), 7.72 (d, J = 7.4 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.53 – 7.45 (m, 3H), 7.34 – 7.29 (m, 1H), 7.27 – 7.23 (m, 2H) 2.49 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.6, 142.6, 138.5, 138.4, 134.1, 132.9, 131.1, 130.4, 128.8, 128.7, 126.6, 126.5, 123.3, 20.0.



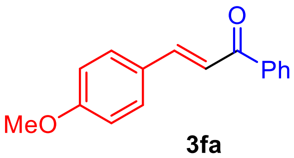
3da

(*E*)-3-(4-(Tert-butyl)phenyl)-1-phenylprop-2-en-1-one (3ea)[8]: The title compound was prepared according to the general procedure to give a white solid, 33.9 mg, 64% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 – 8.01 (m, 2H), 7.83 (d, J = 15.7 Hz, 1H), 7.60 – 7.57 (m, 3H), 7.53 – 7.48 (m, 3H), 7.46 – 7.44 (m, 2H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.9, 154.4, 145.0, 138.6, 132.8, 132.3, 128.7, 128.6, 128.5, 126.1, 121.5, 35.1, 31.3.



3ea

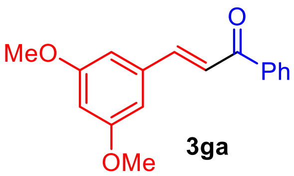
(*E*)-3-(4-Methoxyphenyl)-1-phenylprop-2-en-1-one (3fa)[7]**:** The title compound was



3fa

prepared according to the general procedure to give a white solid, 35.9 mg, 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 – 8.00 (m, 2H), 7.81 (d, *J* = 15.7 Hz, 1H), 7.61 – 7.55 (m, 3H), 7.51 – 7.48 (m, 2H), 7.43 (d, *J* = 15.6 Hz, 1H), 6.95 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.7, 161.8, 144.8, 138.7, 132.7, 130.3, 128.7, 128.5, 127.8, 120.0, 114.6, 55.5.

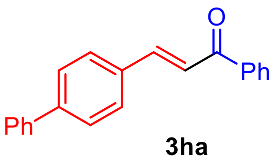
(*E*)- 3-(3,5-Dimethoxyphenyl)-1-phenylprop-2-en-1-one (3ga)[9]**:** The title compound



3ga

was prepared according to the general procedure to give a white solid, 38.3 mg, 71% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.73 (d, *J* = 15.6 Hz, 1H), 7.60 – 7.58 (m, 1H), 7.52 – 7.46 (m, 3H), 6.78 (s, 2H), 6.53 (s, 1H), 3.84 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.7, 161.2, 145.0, 138.3, 136.9, 132.9, 128.8, 128.7, 122.8, 106.5, 102.9, 55.6.

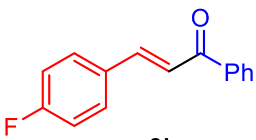
(*E*)-3-([1,1'-Biphenyl]-4-yl)-1-phenylprop-2-en-1-one (3ha)[7]**:** The title compound



3ha

was prepared according to the general procedure to give a white solid, 39.6 mg, 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.4 Hz, 2H), 7.88 (d, *J* = 15.7 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.68 – 7.63 (m, 4H), 7.60 – 7.45 (m, 6H), 7.41 – 7.37 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.7, 144.6, 143.5, 140.3, 138.4, 134.0 132.9, 129.1, 129.1, 128.8, 128.7, 128.1, 127.8, 127.2, 122.1.

(*E*)-3-(4-Fluorophenyl)-1-phenylprop-2-en-1-one (3ia)[7]**:** The title compound was

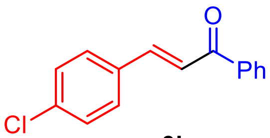


3ia

prepared according to the general procedure to give a white solid, 29.9 mg, 66% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 – 8.00 (m, 2H), 7.80 (d, *J* = 15.7 Hz, 1H), 7.65 – 7.57 (m, 3H), 7.53 – 7.44 (m, 3H), 7.14 – 7.09 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.4, 165.5 (d, *J* = 252.7 Hz), 143.6, 138.3, 133.0, 131.3 (d, *J* = 3.1 Hz), 130.5 (d, *J* = 8.6 Hz), 128.8 (d, *J* = 17.2 Hz), 122.0, 116.4 (d, *J* = 22.0 Hz); **^{19}F NMR**

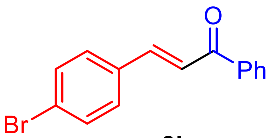
(377 MHz, $CDCl_3$) δ -109.06.

(*E*)-3-(4-Chlorophenyl)-1-phenylprop-2-en-1-one (3ja)[7]: The title compound was prepared according to the general procedure to give a white solid, 30.4 mg, 63% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 – 8.00 (m, 2H), 7.80 (d, *J* = 15.8 Hz, 1H), 7.65 – 7.57 (m, 3H), 7.53 – 7.44 (m, 3H), 7.13 – 7.09 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.3, 143.4, 138.2, 136.5, 133.5, 133.0, 129.7, 129.4, 128.8, 128.6, 122.6.



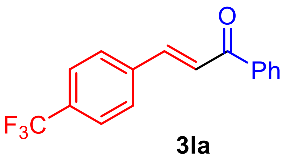
3ja

(*E*)-3-(4-Bromophenyl)-1-phenylprop-2-en-1-one (3ka)[8]: The title compound was prepared according to the general procedure to give a white solid, 37.6 mg, 66% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 – 8.00 (m, 2H), 7.76 (d, *J* = 15.7 Hz, 1H), 7.62 – 7.49 (m, 8H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.4, 143.5, 138.2, 134.0, 133.1, 132.4, 129.9, 128.8, 128.7, 124.9, 122.8.



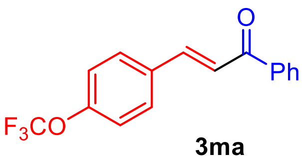
3ka

(*E*)-1-Phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (3la)[7]: The title compound was prepared according to the general procedure to give a white solid, 17.3 mg, 31% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.04 – 8.02 (m, 2H), 7.82 (d, *J* = 15.7 Hz, 1H), 7.75 – 7.67 (m, 4H), 7.61 – 7.58 (m, 2H), 7.54 – 7.52 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.2, 142.9, 138.5, 138.0, 133.3, 132.2 (q, *J* = 32.3 Hz), 128.9, 128.7, 128.6, 126.1 (q, *J* = 2.6 Hz), 124.9 (q, *J* = 181.9 Hz), 124.4; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.86.



3la

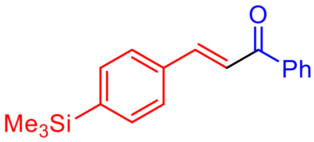
(*E*)-1-Phenyl-3-(4-(trifluoromethoxy)phenyl)prop-2-en-1-one (3ma)[8]: The title compound was prepared according to the general procedure to give a white solid, 43.2 mg, 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 – 8.01 (m, 2H), 7.80 (d, *J* = 15.7 Hz, 1H), 7.69 (d, *J* = 8.7 Hz, 2H), 7.62 – 7.58 (m, 1H), 7.53 – 7.48 (m, 3H), 7.28 (d, *J* = 7.6 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.3, 150.7, 143.1, 138.1, 133.6, 133.1, 130.0, 128.8, 128.7, 123.0, 121.3, 119.7; **^{19}F NMR** (377



3ma

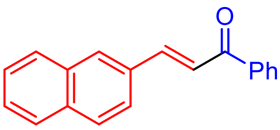
MHz, $CDCl_3$) δ -57.73.

(*E*)-1-Phenyl-3-(4-(trimethylsilyl)phenyl)prop-2-en-1-one (3na): The title compound was prepared according to the general procedure to give a white solid, 35.4 mg, 63% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 – 8.01 (m, 2H), 7.83 (d, *J* = 15.7 Hz, 1H), 7.64 – 7.49 (m, 8H), 0.3 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.8, 145.1, 144.2, 138.4, 135.3, 134.0, 132.9, 128.8, 128.7, 127.7, 122.4, -1.1; **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -3.6; **HRMS** (APCI) calcd for $C_{18}H_{21}OSi$ [M+H]: 281.1362, found: 281.1365.



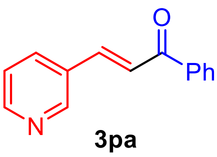
3na

(*E*)-3-(Naphthalen-2-yl)-1-phenylprop-2-en-1-one (3oa)[7]: The title compound was prepared according to the general procedure to give a white solid, 35.6 mg, 69% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.08 – 8.04 (m, 3H), 8.00 (d, *J* = 15.7 Hz, 1H), 7.89 – 7.84 (m, 3H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.67 (d, *J* = 15.7 Hz, 1H), 7.62 – 7.59 (m, 1H), 7.54 – 7.53 (m, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.7, 145.1, 138.4, 134.5, 133.5, 132.9, 132.5, 130.8, 128.9, 128.8, 128.7, 127.9, 127.5, 126.9, 123.8, 122.4.



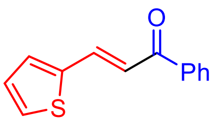
3oa

(*E*)-1-Phenyl-3-(pyridin-3-yl)prop-2-en-1-one (3pa)[8]: The title compound was prepared according to the general procedure to give a white solid, 31.2 mg, 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.2 Hz, 1H), 8.15 – 8.09 (m, 3H), 7.80 – 7.73 (m, 2H), 7.62 – 7.58 (m, 1H), 7.53 – 7.48 (m, 3H), 7.32 – 7.29 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.6, 153.4, 150.3, 142.8, 138.0, 137.1, 133.2, 128.9, 128.8, 125.8, 125.5, 124.5.



3pa

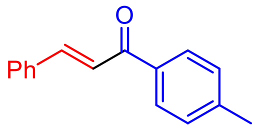
(*E*)-1-Phenyl-3-(thiophen-2-yl)prop-2-en-1-one (3qa)[8]: The title compound was prepared according to the general procedure to give a white solid, 30.7 mg, 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 – 8.00 (m, 2H), 8.00 (d, *J* = 15.3 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.52 – 7.48 (m, 2H), 7.42 (d, *J* = 5.0 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.10 – 7.08 (m,



3qa

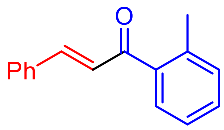
1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.0, 140.5, 138.3, 137.3, 132.9, 132.1, 128.9, 128.7, 128.5, 128.5, 121.0.

(*E*)-3-Phenyl-1-(p-tolyl)prop-2-en-1-one (3ab)[6]**:** The title compound was prepared according to the general procedure to give a white solid, 29.6 mg, 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.83 (d, *J* = 15.6 Hz, 1H), 7.66 – 7.64 (m, 2H), 7.56 (d, *J* = 15.6 Hz, 1H), 7.42 – 7.41 (m, 3H), 7.32 (d, *J* = 7.6 Hz, 2H), 2.44 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.1, 144.5, 143.8, 135.8, 135.1, 130.5, 129.5, 129.1, 128.8, 128.5, 122.2, 21.8.



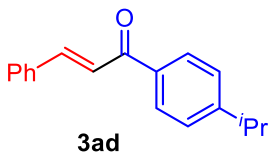
3ab

(*E*)-3-Phenyl-1-(o-tolyl)prop-2-en-1-one (3ac)[6]**:** The title compound was prepared according to the general procedure to give a white solid, 30.3 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 2H), 7.51 – 7.45 (m, 2H), 7.42 – 7.37 (m, 4H), 7.30 – 7.28 (m, 2H), 7.16 (d, *J* =16.0 Hz, 1H), 2.46 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.7, 146.0, 139.2, 137.1, 134.8, 131.4, 130.8, 130.6, 129.1, 128.5, 128.2, 126.9, 125.6, 20.3.



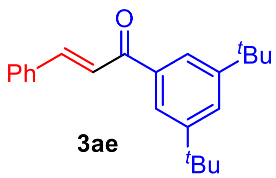
3ac

(*E*)-1-(4-Isopropylphenyl)-3-phenylprop-2-en-1-one (3ad)[6]**:** The title compound was prepared according to the general procedure to give a white solid, 32.2 mg, 64% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.83 (d, *J* = 15.7 Hz, 1H), 7.66 – 7.65 (m, 2H), 7.57 (d, *J* = 15.7 Hz, 1H), 7.43 – 7.42 (m, 3H), 7.37 (d, *J* = 7.9 Hz, 2H), 3.03– 2.96 (m, 1H), 1.30 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.2, 154.5, 144.5, 136.2, 135.2, 130.6, 129.1, 128.9, 128.5, 126.9, 122.3, 34.4, 23.8.



3ad

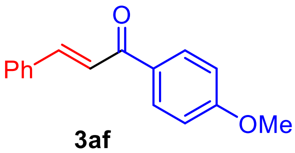
(*E*)-1-(3,5-Di-tert-butylphenyl)-3-phenylprop-2-en-1-one (3ae): The title compound was prepared according to the general procedure to give a white solid, 45.7 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.85 (m, 2H), 7.83 (d, *J* = 15.8 Hz, 1H), 7.69 – 7.64



3ae

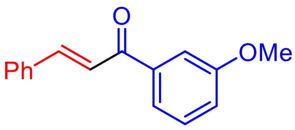
(m, 3H), 7.54 (d, *J* = 15.7 Hz, 1H), 7.46 – 7.41 (m, 3H), 1.4 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.7, 151.4, 144.6, 138.1, 135.2, 130.5, 129.1, 128.5, 127.1, 123.0, 122.9, 35.1, 31.5; **HRMS** (APCI) calcd for $C_{23}H_{29}O$ [M+H]: 321.2218, found: 321.2221.

(*E*)-1-(4-Methoxyphenyl)-3-phenylprop-2-en-1-one (3af)[6]**:** The title compound was prepared according to the general procedure to give a white solid, 35.7 mg, 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 – 8.03 (m, 2H), 7.82 (d, *J* = 15.6 Hz, 1H), 7.65 – 7.63 (m, 2H), 7.56 (d, *J* =15.7 Hz, 1H), 7.44 – 7.40 (m, 3H), 6.99 – 6.97 (m, 2H), 3.88 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.8, 163.6, 144.1, 135.2, 131.3, 130.9, 130.4, 129.0, 128.5, 122.1, 114.0, 55.6.



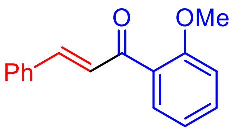
3af

(*E*)-1-(3-Methoxyphenyl)-3-phenylprop-2-en-1-one (3ag)[6]**:** The title compound was prepared according to the general procedure to give a white solid, 33.5 mg, 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 15.8 Hz, 1H), 7.65 – 7.60 (m, 3H), 7.56 – 7.49 (m, 2H), 7.43 – 7.41 (m, 4H), 7.15 – 7.12 (m, 1H), 3.88 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.4, 160.1, 145.0, 139.7, 135.0, 130.7, 129.7, 129.1, 128.6, 122.3, 121.2, 119.4, 113.0, 55.6.



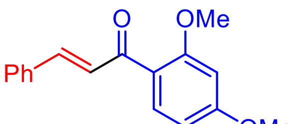
3ag

(*E*)-1-(2-Methoxyphenyl)-3-phenylprop-2-en-1-one (3ah)[10]**:** The title compound was prepared according to the general procedure to give a white solid, 32.2 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 4H), 7.49 – 7.46 (m, 1H), 7.40 – 7.36 (m, 4H), 7.06 – 6.99 (m, 2H), 3.90 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.1, 158.3, 143.3, 135.3, 133.0, 130.5, 130.3, 129.0, 128.5, 127.2, 120.9, 111.8, 55.9.



3ah

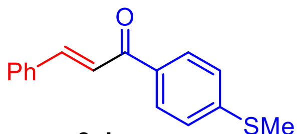
***(E)*-1-(2,4-Dimethoxyphenyl)-3-phenylprop-2-en-1-one (3ai)**[10]**:** The title compound was prepared according to the general procedure to give a white solid, 38.0 mg, 71% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 – 7.76 (m, 1H), 7.69 (d, *J* = 15.8 Hz, 1H), 6.60 – 6.59



3ai

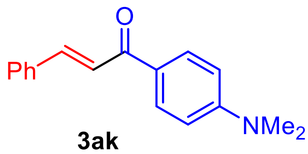
(m, 2H), 7.54 (d, *J* = 15.9 Hz, 1H), 7.39 (s, 3H), 6.58 – 6.50 (m, 2H), 3.91 (s, 3H), 3.87 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.7, 164.3, 160.6, 142.1, 135.6, 133.0, 129.0, 128.4, 127.3, 122.3, 105.3, 98.8, 55.9, 55.7.

(*E*)-1-(4-(Methylthio)phenyl)-3-phenylprop-2-en-1-one (3aj)[10]**:** The title compound was prepared according to the general procedure to give a white solid, 39.6 mg, 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 15.6 Hz, 1H), 7.65 – 7.63 (m, 2H), 7.54 (d, *J* = 15.7 Hz, 1H), 7.42 – 7.41 (m, 3H), 7.32 (d, *J* = 8.2 Hz, 2H), 2.53 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 189.3, 145.8, 144.6, 135.0, 134.5, 130.6, 129.1, 128.5, 125.2, 121.8, 14.9.



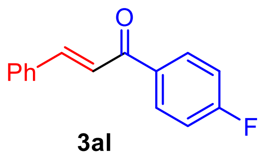
3aj

(*E*)-1-(4-(Dimethylamino)phenyl)-3-phenylprop-2-en-1-one (3ak)[11] **:** The title compound was prepared according to the general procedure to give a white solid, 38.4 mg, 76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 – 8.00 (m, 2H), 7.81 (d, *J* = 15.5 Hz, 1H), 7.65 – 7.57 (m, 3H), 7.43 – 7.39 (m, 3H), 6.73 – 6.70 (m, 2H), 3.14 – 3.03 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 187.9, 153.5, 142.6, 135.6, 131.0, 129.0, 128.3, 126.1, 122.3, 110.9, 40.2.



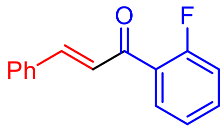
3ak

(*E*)-1-(4-Fluorophenyl)-3-phenylprop-2-en-1-one (3al)[11]**:** The title compound was prepared according to the general procedure to give a white solid, 29.7 mg, 66% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 2H), 7.84 (d, *J* = 15.7 Hz, 1H), 7.66 – 7.63 (m, 2H), 7.52 (d, *J* = 15.7 Hz, 1H), 7.43 – 7.42 (m, 3H), 7.20 – 7.15 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 189.0, 167.0 (d, *J* = 255.4 Hz), 145.2, 134.9, 134.7 (d, *J* = 3.0 Hz), 131.3 (d, *J* = 10.1 Hz), 130.8, 129.1, 128.6, 121.8, 116.0 (d, *J* = 22.2 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ -105.59.



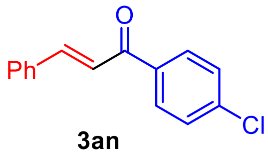
3al

(*E*)-1-(2-Fluorophenyl)-3-phenylprop-2-en-1-one (3am)[12]**:** The title compound was prepared according to the general procedure to give a white solid, 27.9 mg, 62% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 – 7.79 (m, 1H), 7.74 (d, *J* = 15.7 Hz, 1H), 7.61 – 7.60 (m, 2H), 7.53 – 7.49 (m, 1H), 7.40 – 7.36 (m, 4H), 7.25 – 7.24 (m, 1H), 7.17 – 7.14 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 189.3, 162.2 (d, *J* = 253.1 Hz), 145.0, 134.8, 134.1 (d, *J* = 8.5 Hz), 131.1 (d, *J* = 42.3 Hz), 130.8, 129.1, 128.7, 127.3 (d, *J* =13.1 Hz), 125.8 (d, *J* = 6.3 Hz), 124.7 (d, *J* = 3.3 Hz), 116.8 (d, *J* = 23.1 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ -110.86.



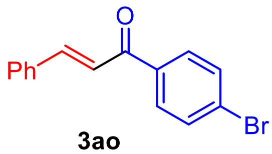
3am

(*E*)-1-(4-Chlorophenyl)-3-phenylprop-2-en-1-one (3an)[6]**:** The title compound was prepared according to the general procedure to give a white solid, 32.3 mg, 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 – 7.96 (m, 2H), 7.84 (d, *J* = 15.7 Hz, 1H), 7.64 (s, 2H), 7.49 – 7.43 (m, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 189.3, 145.5, 139.3, 136.6, 134.8, 130.0, 129.1, 129.1, 128.6, 121.6.



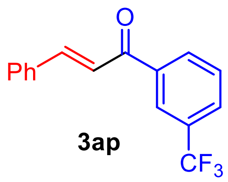
3an

(*E*)-1-(4-Bromophenyl)-3-phenylprop-2-en-1-one (3ao)[6]**:** The title compound was prepared according to the general procedure to give a white solid, 38.7 mg, 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.87 (m, 2H), 7.84 (d, *J* = 15.7 Hz, 1H), 7.66 – 7.62 (m, 4H), 7.49 – 7.41 (m, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 189.4, 145.5, 136.9, 134.7, 132.0, 130.8, 130.1, 129.0, 128.5, 127.9, 121.5.



3ao

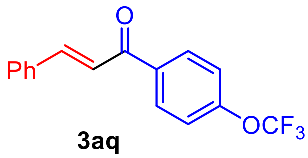
(*E*)-3-Phenyl-1-(3-(trifluoromethyl)phenyl)prop-2-en-1-one (3ap)[12]**:** The title compound was prepared according to the general procedure to give a white solid, 18.5 mg, 34% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 7.88 – 7.83 (m, 2H), 7.68 – 7.63 (m, 3H), 7.53 (d, *J* = 15.8 Hz, 1H), 7.45 – 7.44 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 189.2, 146.2, 138.9, 134.6, 131.5 (q, *J* = 21.9 Hz), 131.1, 129.4, 129.3 (q, *J* = 2.2 Hz), 129.2, 128.8, 125.4 (q, *J* = 2.4 Hz), 124.8, 123.0, 121.3;



3ap

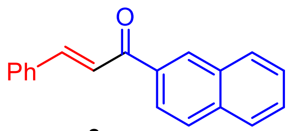
^{19}**F NMR** (377 MHz, $CDCl_3$) δ -62.73.

(***E***)**-3-Phenyl-1-(4-(trifluoromethoxy)phenyl)prop-2-en-1-one (3aq)**[12]**:** The title compound was prepared according to the general procedure to give a white solid, 37.8 mg, 65% yield. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.09 – 8.06 (m, 2H), 7.85 (d, *J* = 15.7 Hz, 1H), 7.66 – 7.64 (m, 2H), 7.51 – 7.47 (m, 1H), 7.44 – 7.42 (m, 3H), 7.35 – 7.32 (m, 2H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 189.1, 152.6, 145.7, 136.6, 134.8, 130.9, 130.6, 129.2, 128.7, 121.7, 120.6, 119.2; ^{19}**F NMR** (377 MHz, $CDCl_3$) δ -57.59.



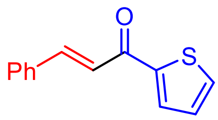
3aq

(***E***)**-1-(Naphthalen-2-yl)-3-phenylprop-2-en-1-one (3ar)**[6]**:** The title compound was prepared according to the general procedure to give a white solid, 34.4 mg, 67% yield. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.55 – 8.54 (m, 1H), 8.13 – 8.10 (m, 1H), 8.01(d, *J* = 7.9 Hz, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.91 – 7.87 (m, 2H), 7.72 – 7.68 (m, 3H), 7.64 – 7.55 (m, 2H). 7.48 – 7.43 (m, 3H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 190.4, 144.9, 135.7, 135.6, 135.1, 132.7, 130.7, 130.1, 129.7, 129.1, 128.7, 128.6, 128.5, 128.0, 126.9, 124.6, 122.3.



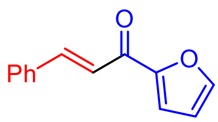
3ar

(***E***)**-3-Phenyl-1-(thiophen-2-yl)prop-2-en-1-one (3as)**[6]**:** The title compound was prepared according to the general procedure to give a white solid, 29.7 mg, 69% yield. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 2H), 7.69 – 7.63 (m, 3H), 7.44 – 7.41 (m, 4H), 7.20 – 7.17 (m, 1H); ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 182.2, 145.6, 144.2, 134.8, 134.0, 131.9, 130.7, 129.1, 128.6, 128.4, 121.7.



3as

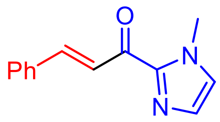
(***E***)**-1-(Furan-2-yl)-3-phenylprop-2-en-1-one (3at)**[6]**:** The title compound was prepared according to the general procedure to give a white solid, 28.6 mg, 72% yield. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 15.8 Hz, 1H), 7.66 – 7.64 (m, 3H), 7.47 – 7.41 (m, 4H), 7.34 (d, *J* = 3.5 Hz, 1H), 6.60 – 6.59 (m, 1H); ^{13}**C NMR** (151 MHz, $CDCl_3$)



3at

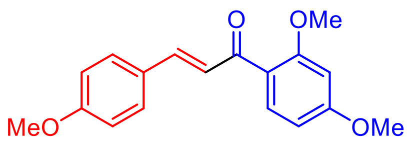
δ 178.2, 153.8, 146.7, 144.1, 134.8, 130.7, 129.1, 128.7, 121.3, 117.7, 112.7.

(*E*)-1-(1-Methyl-1H-imidazol-2-yl)-3-phenylprop-2-en-1-one (3au)[13]**:** The title compound was prepared according to the general procedure to give a white solid, 30.2 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 16.0 Hz, 1H), 7.85 (d, *J* = 16.0 Hz, 1H), 7.71 – 7.68 (m, 2H), 7.40 – 7.38 (m, 3H), 7.22 (s, 1H), 7.07 (s, 1H), 4.09 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.6, 144.1, 143.6, 135.1, 130.6, 129.4, 129.0, 128.9, 127.4, 122.9, 36.5.



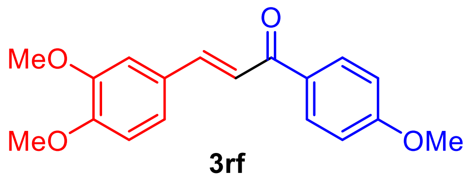
3au

Metochalcone (3fi)[10]**:** The title compound was prepared according to the general procedure to give a yellow solid, 27.2 mg, 46% yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.75 – 7.72 (m, 1H), 7.66 – 7.63 (m, 1H), 7.56 – 7.53 (m, 2H), 7.41 – 7.37 (m, 1H), 6.92 – 6.90 (m, 2H), 6.56 – 6.54 (m, 1H), 6.50 – 6.49 (m, 1H), 3.90 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 190.8, 164.1, 161.4, 160.4, 142.2, 132.8, 130.1, 128.3, 125.2, 122.7, 114.4, 105.3, 98.9, 55.9, 55.7, 55.5.



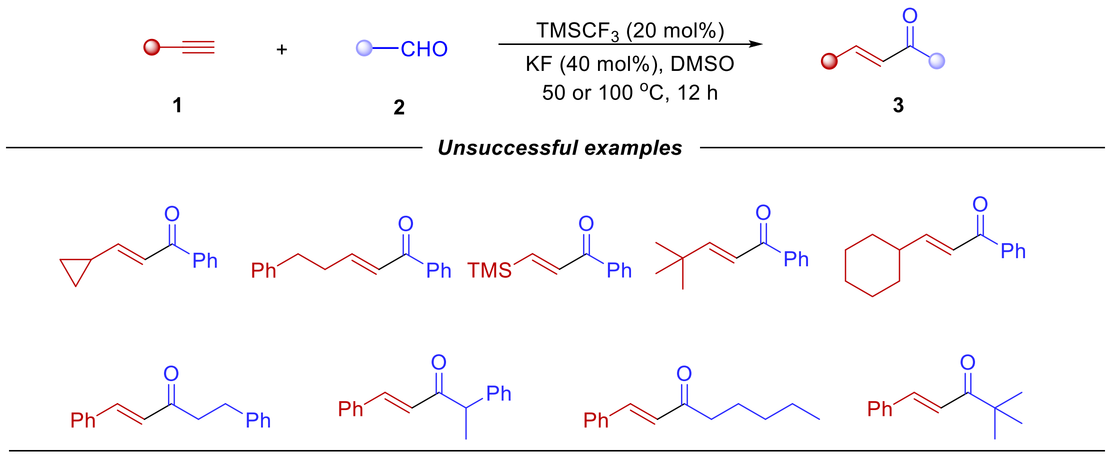
3fi

Antineoplastic agent (3rf)[14]**:** The title compound was prepared according to the general procedure to give a white solid, 23.7 mg, 40% yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.04 – 8.03 (m, 2H), 7.77 (d, *J* = 15.7 Hz, 1H), 7.42 – 7.39 (m, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.00 – 6.98 (m, 2H), 6.91 – 6.89 (m, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 3.89 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$): δ 188.9, 163.5, 151.5, 149.4, 144.3, 131.5, 130.9, 128.3, 123.1, 120.1, 114.0, 111.3, 110.3, 56.1, 55.6.

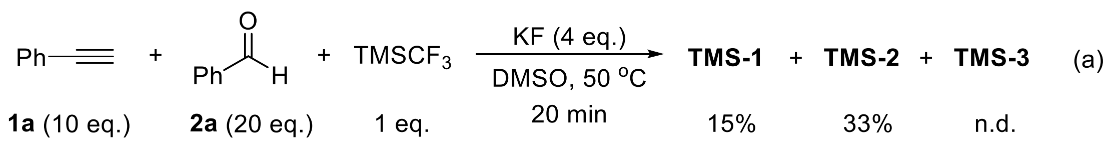


3rf

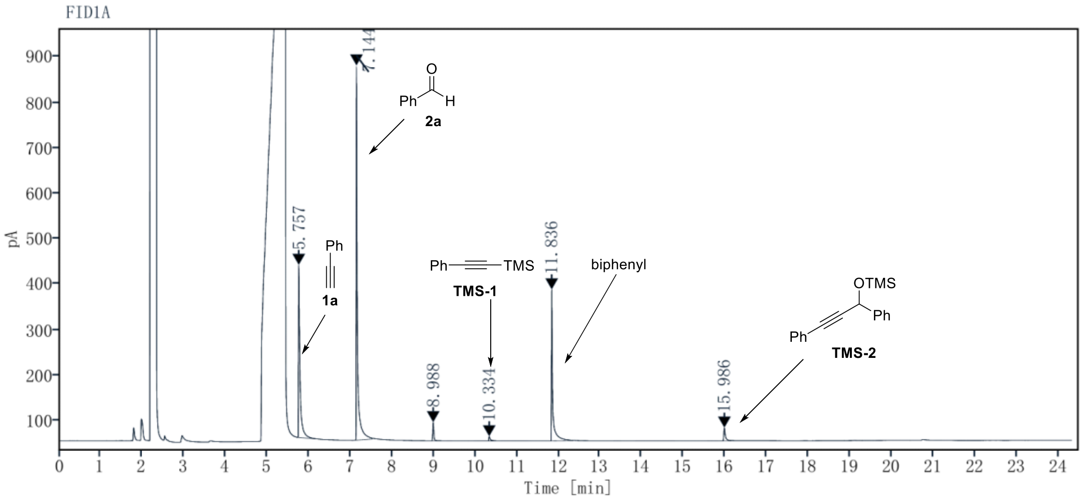
The synthesis of α,β-unsaturated ketones using aliphatic alkynes and aldehydes



8. Mechanism Studies



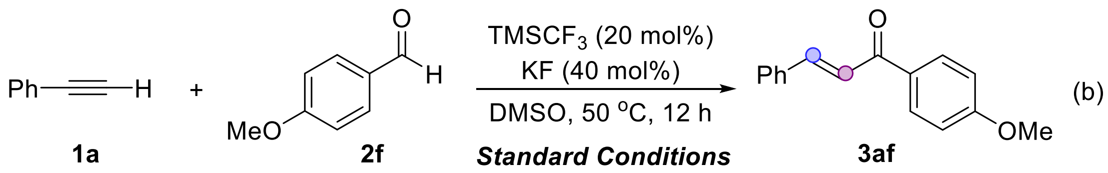
To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (4.6 mg, 0.08 mmol) and DMSO (1.5 mL, 0.33 M) under nitrogen atmosphere. Then **1a** (20.6 mg, 0.2 mmol), $TMSCF_3$ (2.9 mg, 0.02 mmol) and **2a** (42.4 mg, 0.4 mmol) was added to the mixture. The resulting solution was allowed to stir at 50 °C for 20 minutes. Then biphenyl (12.4 mg) was added to the solution as internal standard and the resulting mixture was subjected to GC analysis.

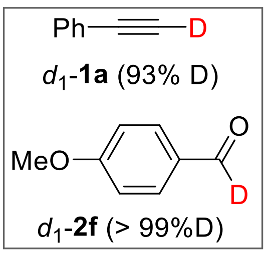


Illustrate FID1A

Retention Time [min]	Peak Area	Peak Area %
5.757	982.47688	27.80
7.144	1667.22096	47.17
8.988	73.44714	2.08
10.334	25.19756	0.71
11.836	708.71992	20.05
15.986	77.13361	2.18

Figure S16. GC spectrum of the crude reaction mixture of **1a** with **2a** in the presence of $TMSCF_3$





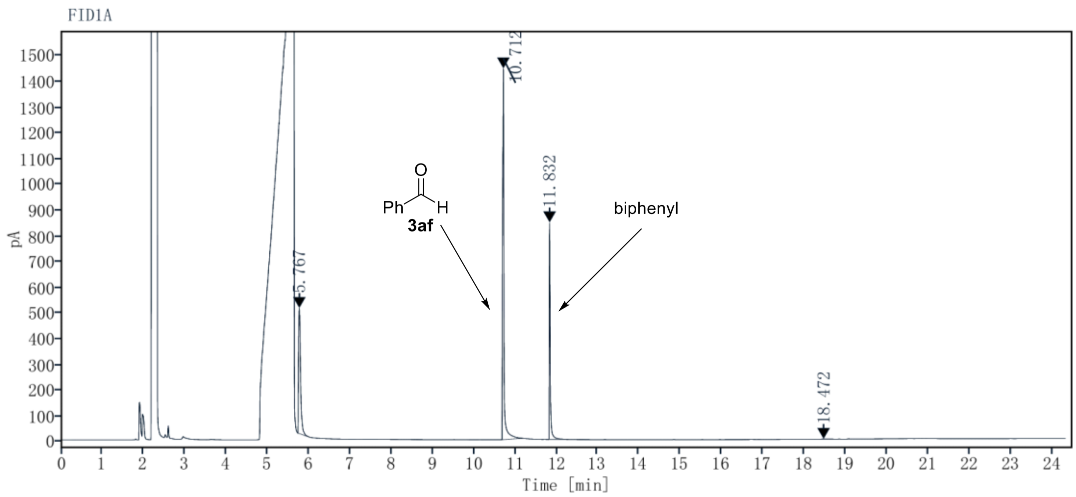
	variation from standard conditions	yield of **3af**
Condition A	none	75%
Condition B	d_1-**1a** (93% D) instead of **1a**	n.r.
Condition C	d_1-**2f** (> 99%D) instead of **2f**	trace
Condition D	DMSO-d_6 instead of DMSO	trace

For Condition A:

To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (4.6 mg, 0.08 mmol) and DMSO (1.5 mL, 0.33 M) under nitrogen atmosphere. Then **1a** (20.6 mg, 0.2 mmol, 1.0 eq.), $TMSCF_3$ (5.7 mg, 0.04 mmol, 20 mol%) and **2f** (54.4 mg, 0.4 mmol, 2 eq.) was added to the mixture. The resulting solution was allowed to stir at 50 °C for 12 hours. After the reaction finished, the solvents required the addition of H_2O (20 mL) to the mixture and the solution was extracted by ethyl acetate (10 mL x 3). The organic layer was dried over anhydrous Na_2SO_4. After concentrating, the crude product was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (30/1-15/1) to give the desired product **3af** (35.7 mg, 75% yield).

For Condition B:

To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (4.6 mg, 0.08 mmol) and DMSO (1.5 mL, 0.33 M) under nitrogen atmosphere. Then ***d*₁-1a** (20.8 mg, 0.2 mmol, 1.0 eq.), $TMSCF_3$ (5.7 mg, 0.04 mmol) and **2f** (54.4 mg, 0.4 mmol, 2 eq.) was added to the mixture. The resulting solution was allowed to stir at 50 °C for 12 hours. The reaction mixture was subjected to GC analysis using biphenyl as the internal standard and no reaction was observed.



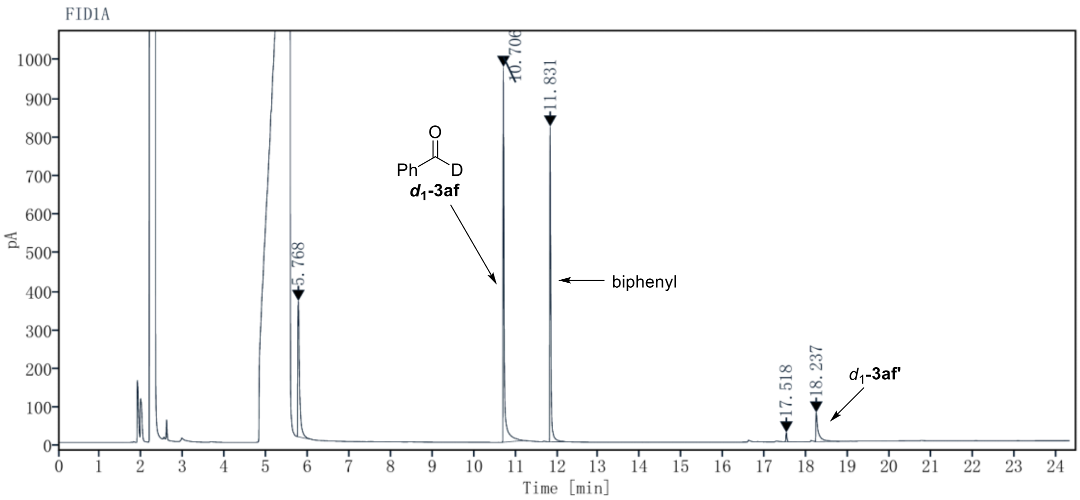
Illustrate FID1A

Retention Time [min]	Peak Area	Peak Area %
5.767	1627.29673	25.81
10.712	3277.50251	51.99
11.832	1387.55112	22.01
18.472	11.79149	0.19

Figure S17. GC spectrum of the crude reaction mixture of ***d*₁-1a** with **2f** at 50 °C

For Condition C:

To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (4.6 mg, 0.08 mmol) and DMSO (1.5 mL, 0.33 M) under nitrogen atmosphere. Then **1a** (20.6 mg, 0.2 mmol, 1 eq.), $TMSCF_3$ (5.7 mg, 0.04 mmol) and ***d*₁-2f** (54.8 mg, 0.4 mmol, 2 eq.) was added to the mixture. The resulting solution was allowed to stir at 50 °C for 12 hours. The reaction mixture was subjected to GC analysis using biphenyl as the internal standard and only trance amount of ***d*₁-3af'** (<10%) was observed.



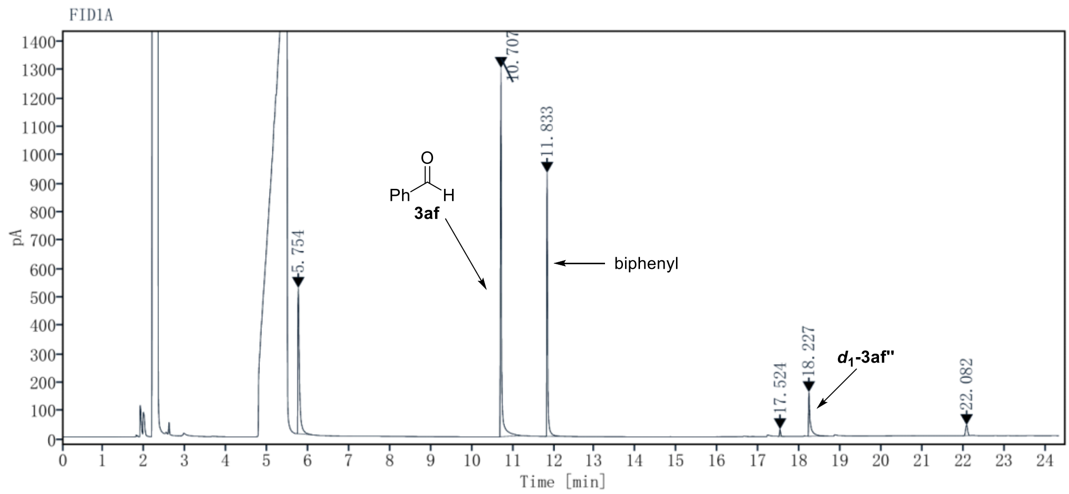
Illustrate FID1A

Retention Time [min]	Peak Area	Peak Area %
5.768	1028.37689	22.45
10.706	1863.01228	40.67
11.831	1343.12123	29.32
17.518	41.97247	0.92
18.237	304.20764	6.64

Figure S18. GC spectrum of the crude reaction mixture of **1a** with ***d*₁-2f** at 50 °C

For Condition D:

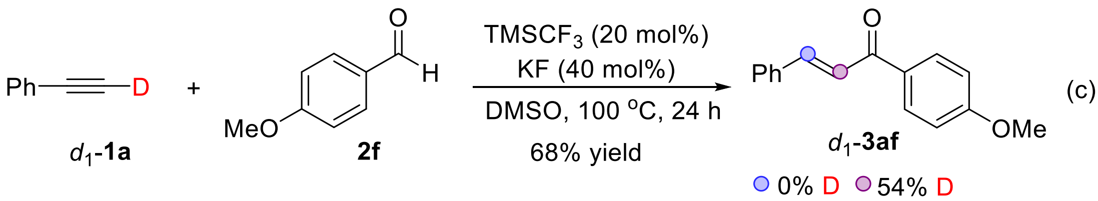
To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (4.6 mg, 0.08 mmol) and DMSO-d_6 (1.5 mL, 0.33 M) under nitrogen atmosphere. Then **1a** (20.6 mg, 0.2 mmol, 1 eq.), $TMSCF_3$ (5.7 mg, 0.04 mmol) and **2f** (54.4 mg, 0.4 mmol, 2 eq.) was added to the mixture. The resulting solution was allowed to stir at 50 °C for 12 hours. The reaction mixture was subjected to GC analysis using biphenyl as the internal standard and only trance amount of ***d*₁-3af''** (<10%) was observed.



Illustrate FID1A

Retention Time [min]	Peak Area	Peak Area %
5.754	1405.25793	22.35
10.707	2723.74264	43.32
11.833	1506.04464	23.95
17.524	46.81182	0.74
18.227	476.71539	7.58
22.082	128.68216	2.05

Figure S19. GC spectrum of the reaction mixture for condition D



To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (4.6 mg, 0.08 mmol) and DMSO (1.5 mL, 0.33 M) under nitrogen atmosphere. Then *d*$_1$-**1a** (20.6 mg, 0.2 mmol, 1 eq.), TMSCF$_3$ (5.7 mg, 0.04 mmol) and **2f** (54.4 mg, 0.4 mmol, 2 eq.) was added to the mixture. The resulting solution was allowed to stir at 100 °C for 24 hours. After the reaction finished, H_2O (20 mL) was added to the mixture and the solution was extracted by ethyl acetate (10 mL x 3). The organic layer was dried over anhydrous Na_2SO_4. After concentrating, the crude product was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (30/1-10/1) to give the desired product *d*$_1$-**3af** (32.3 mg, 68% yield).

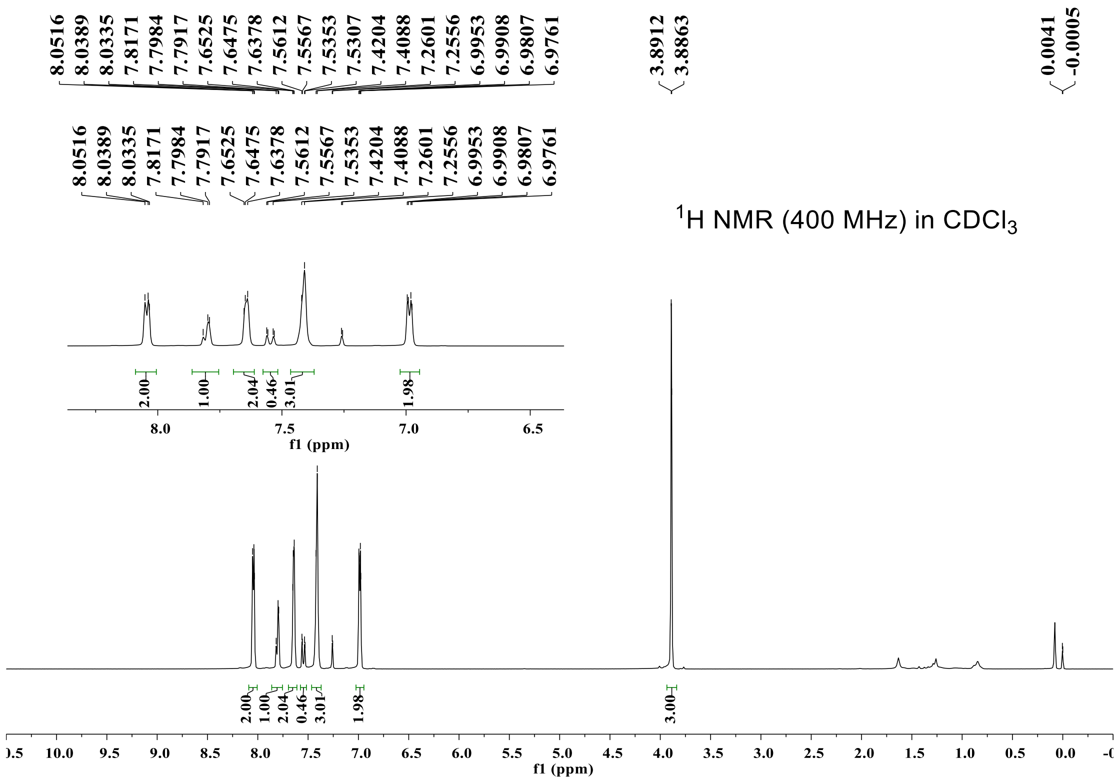
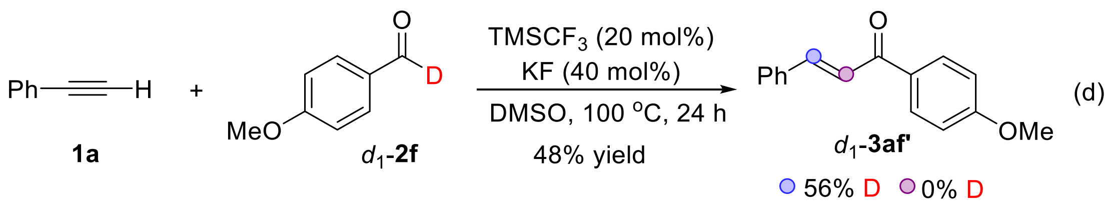


Figure S20. NMR spectrum of the reaction mixture of d_1-**2a** and **2f**



To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (4.6 mg, 0.08 mmol) and DMSO (1.5 mL, 0.33 M) under nitrogen atmosphere. Then **1a** (20.4 mg, 0.2 mmol, 1 eq.), $TMSCF_3$ (5.7 mg, 0.04 mmol) and d_1-**2f** (54.8 mg, 0.4 mmol, 2 eq.) was added to the mixture. The resulting solution was allowed to stir at 100 °C for 24 hours. After the reaction finished, H_2O (20 mL) was added to the mixture and the solution was extracted by ethyl acetate (10 mL x 3). The organic layer was dried over anhydrous Na_2SO_4. After concentrating, the crude product was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (30/1-10/1) to give the desired product d_1-**3af'** (23.1 mg, 48% yield).

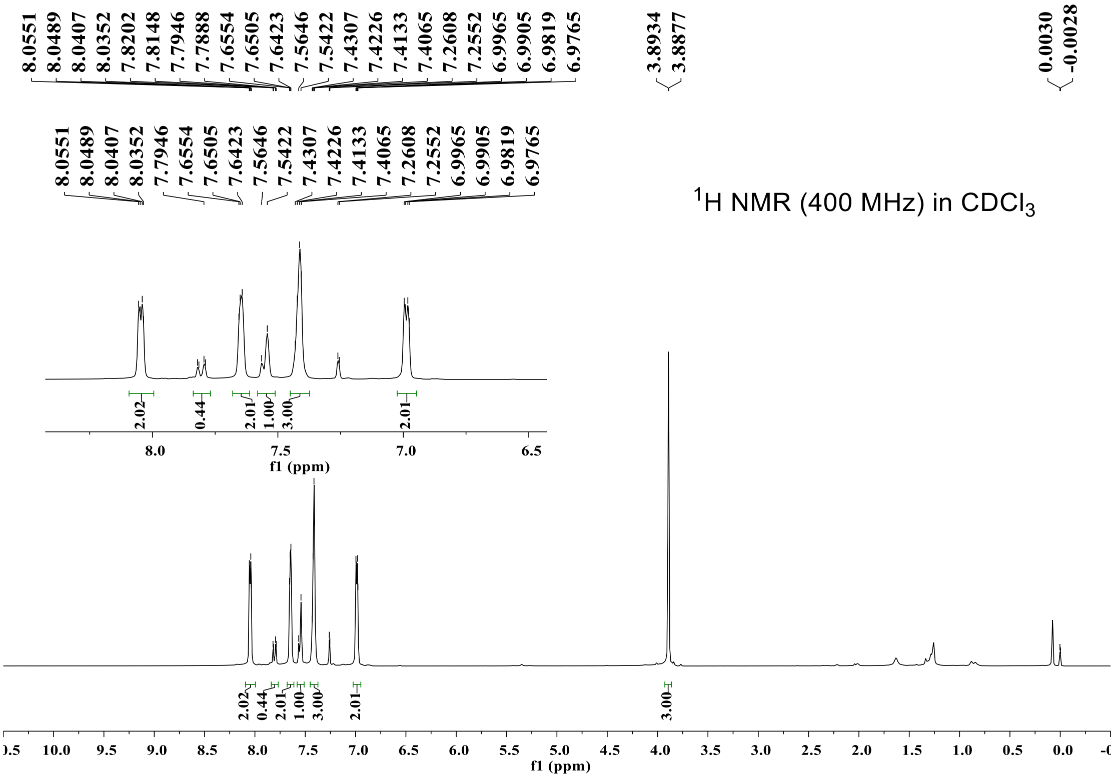
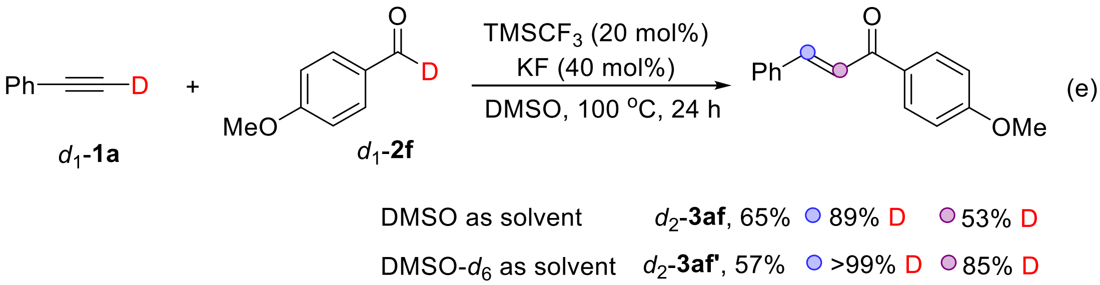


Figure S21. NMR spectrum of the reaction mixture of **1a** and d_1-**2f**



To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (4.6 mg, 0.08 mmol) and DMSO or DMSO-d_6 (1.5 mL, 0.33 M) under nitrogen atmosphere. Then d_1-**1a** (20.6 mg, 0.2 mmol, 1 eq.), TMSCF$_3$ (5.7 mg, 0.04 mmol) and d_1-**2f** (54.8 mg, 0.4 mmol, 2 eq.) was added to the mixture. The resulting solution was allowed to stir at 100 °C for 24 hours. After the reaction finished, H_2O (20 mL) was added to the mixture and the solution was extracted by ethyl acetate (10 mL x 3). The organic layer was dried over anhydrous Na_2SO_4. After concentrating, the crude product was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (30/1-10/1) to give the desired product d_2-**3af** (30.9 mg, 65% yield) or d_2-**3af'** (27.4 mg, 57% yield).

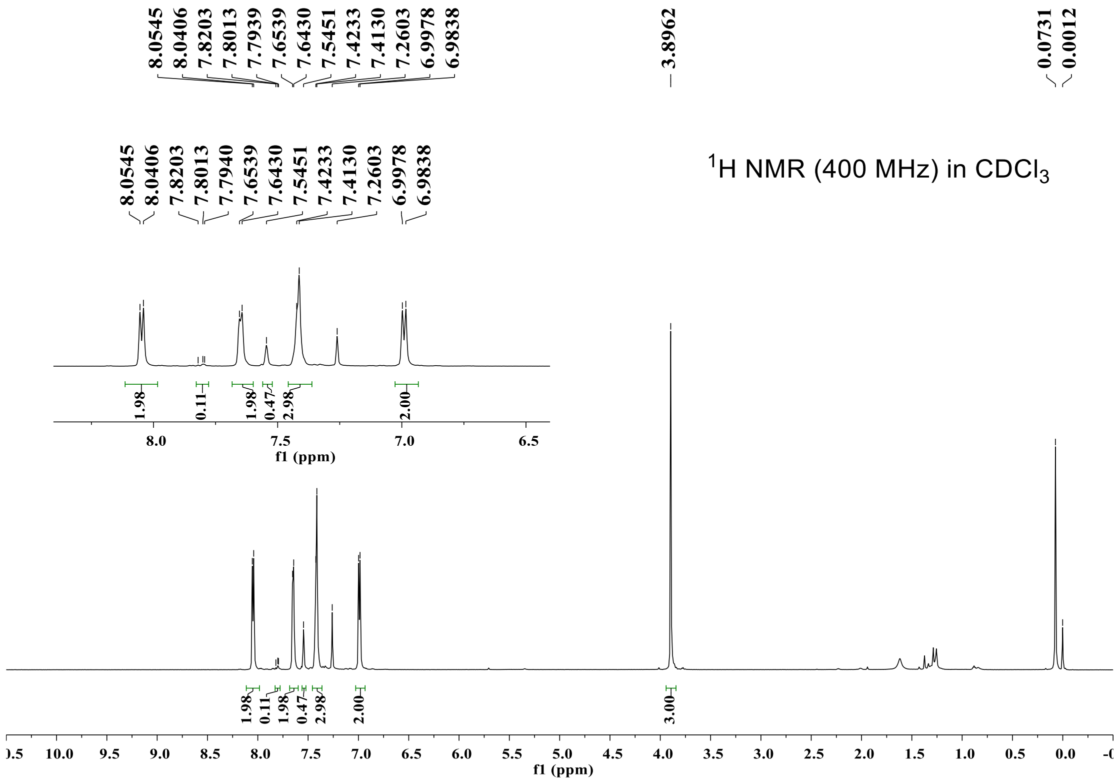


Figure S22. NMR spectrum of the reaction mixture of d_1-**1a** and d_1-**2f** in DMSO

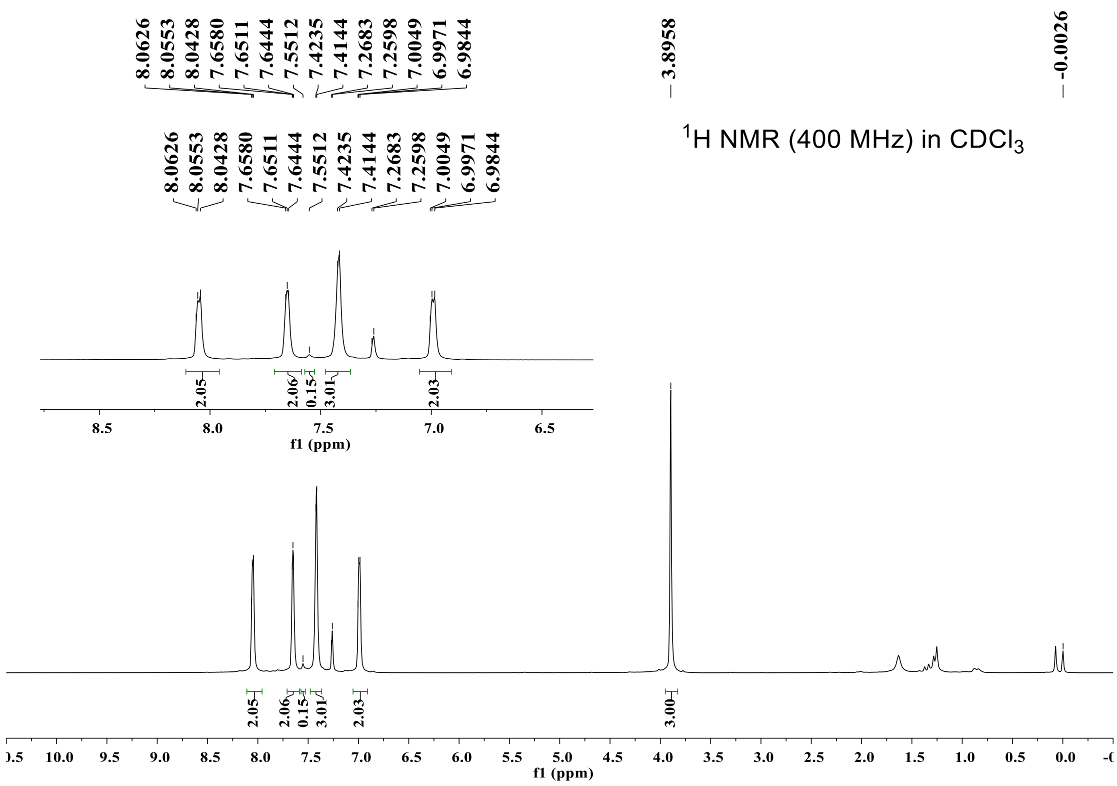
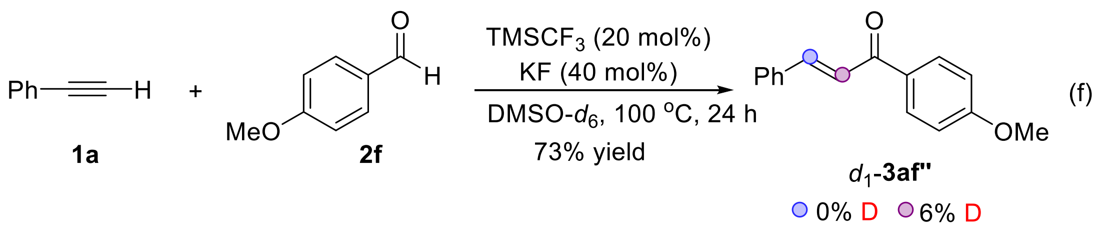


Figure S23. NMR spectrum of the reaction mixture of d_1-**1a** and d_1-**2f** in DMSO-d_6



To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (4.6 mg, 0.08 mmol) and DMSO-d_6 (1.5 mL, 0.33 M) under nitrogen atmosphere. Then **1a** (20.4 mg, 0.2 mmol, 1 eq.), $TMSCF_3$ (5.7 mg, 0.04 mmol) and **2f** (54.4 mg, 0.4 mmol, 2 eq.) was added to the mixture. The resulting solution was allowed to stir at 100 °C for 24 hours. After the reaction finished, the solvents required the addition of H_2O (20 mL) to the mixture and the solution was extracted by ethyl acetate (10 mL x 3). The organic layer was dried over anhydrous Na_2SO_4. After concentrating, the crude product was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (30/1-10/1) to give the desired product d_1-**3af''** (34.7 mg, 73% yield).

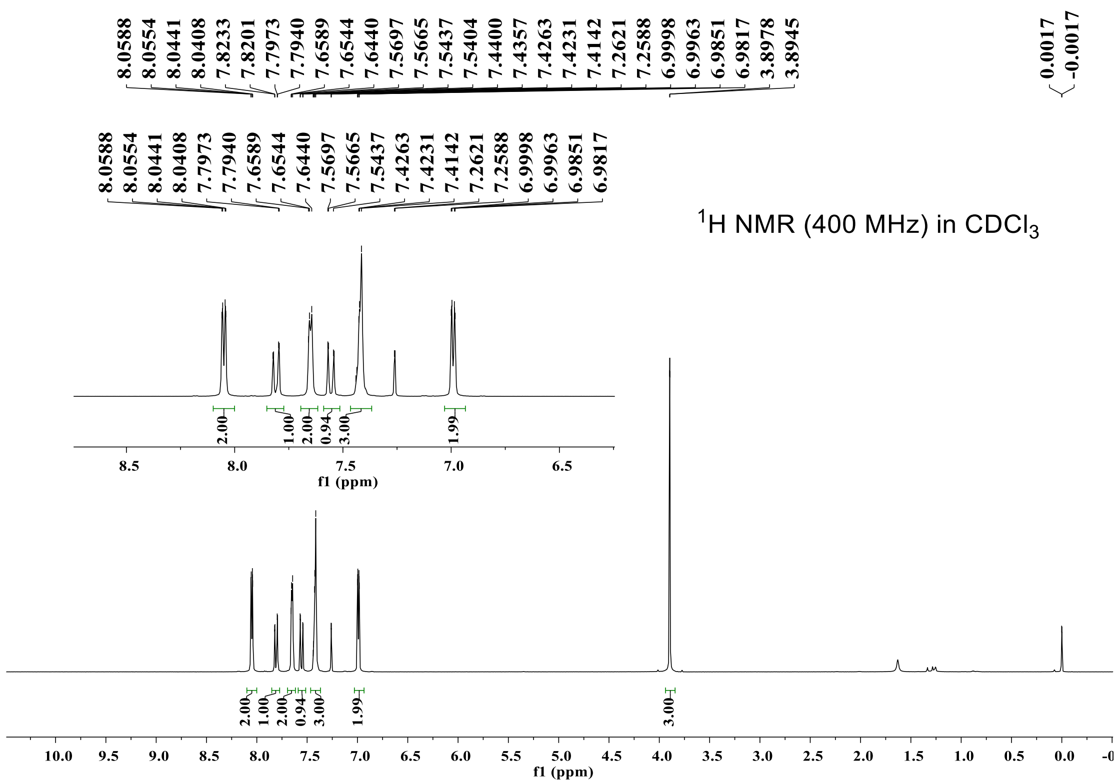
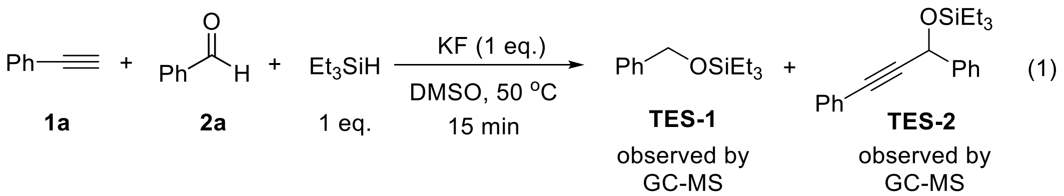


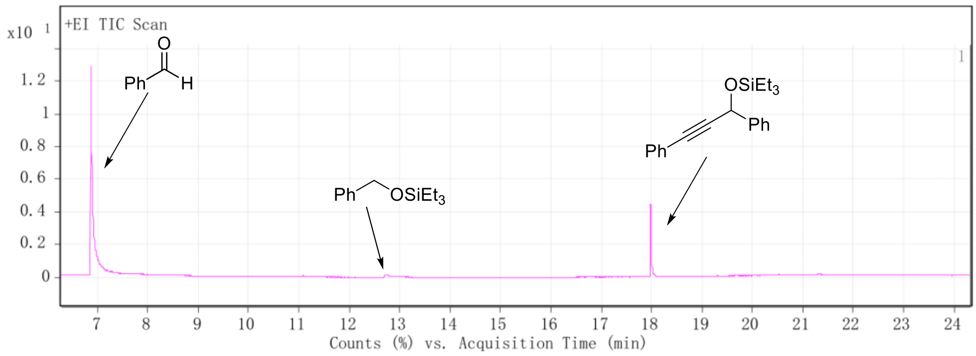
Figure S24. NMR spectrum of the reaction mixture of **1a** and **2f** in DMSO-d_6

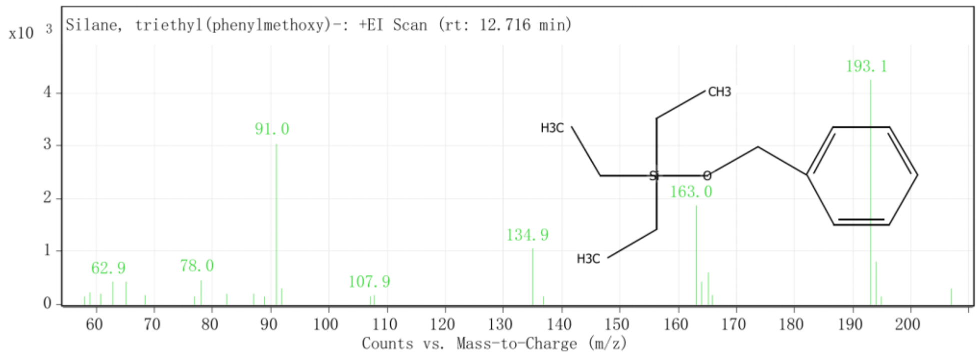
The mechanistic study of Si-H species

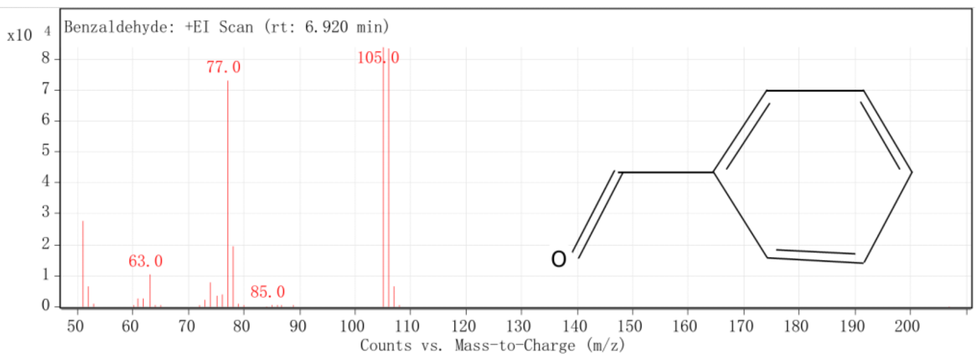
(1) The rection of 1a, 2a and Et3SiH



To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (11.6 mg, 0.2 mmol), DMSO (1.5 mL, 0.13 M), **1a** (20.4 mg, 0.2 mmol, 1 eq.), Et_3SiH (23.2 mg, 0.2 mol, 1 eq.) and **2a** (21.2 mg, 0.2 mmol, 1 eq.) under nitrogen atmosphere. The resulting solution was allowed to stir at 50 °C for 15 minutes. Then the reaction mixture was subjected to GS-MS analysis.







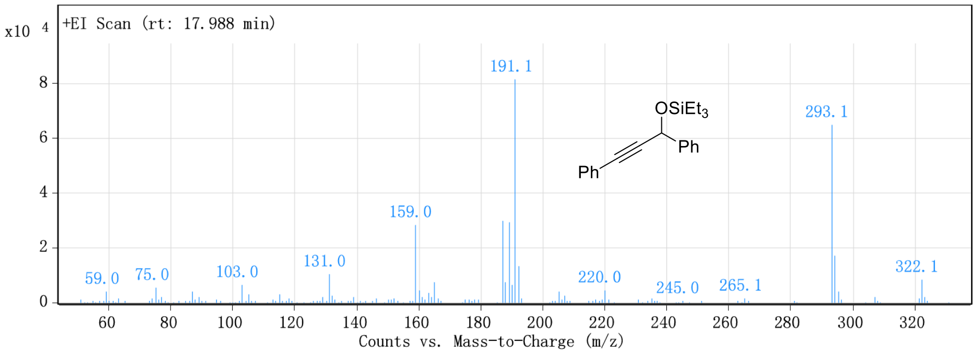
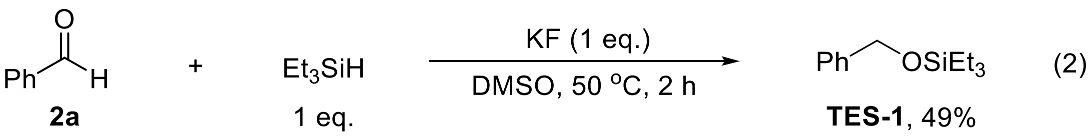
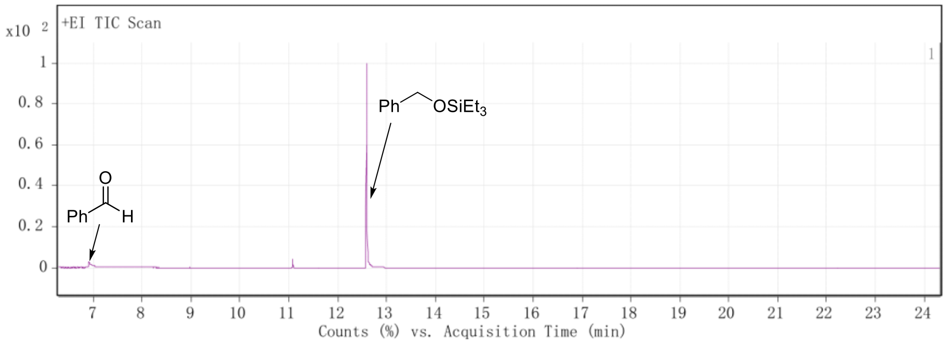


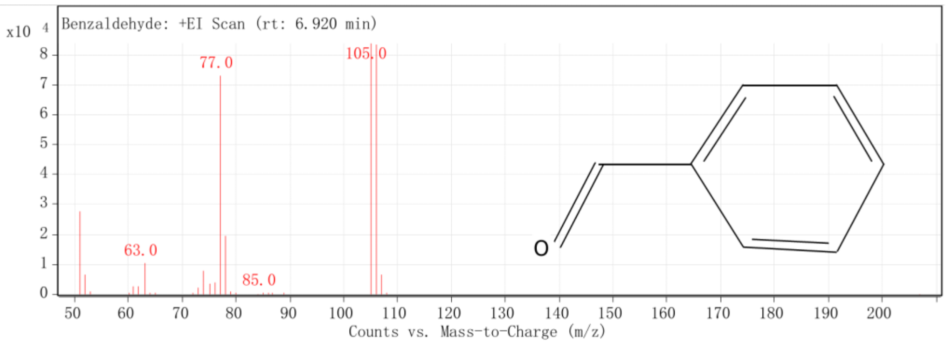
Figure 25. GC-MS spectra of the reaction mixture of **1a**, **2a** and Et_3SiH after 15 min

(2) The rection of 2a and Et3SiH



To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (11.6 mg, 0.2 mmol), DMSO (1.5 mL, 0.13 M), Et_3SiH (23.2 mg, 0.2 mol, 1 eq.) and **2a** (21.2 mg, 0.2 mmol, 1 eq.) under nitrogen atmosphere. The resulting solution was allowed to stir at 50 °C for 2 hours. The reaction mixture was subjected to GS-MS and GC analysis using biphenyls as the internal standard. The product **TES-1** was obtained in 49% yield.





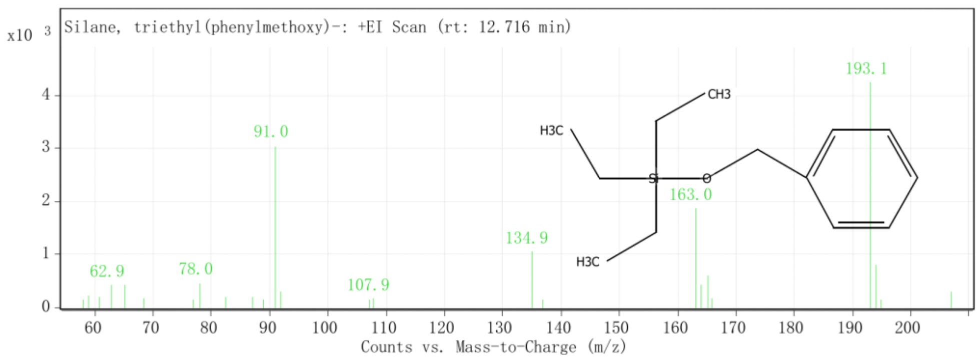
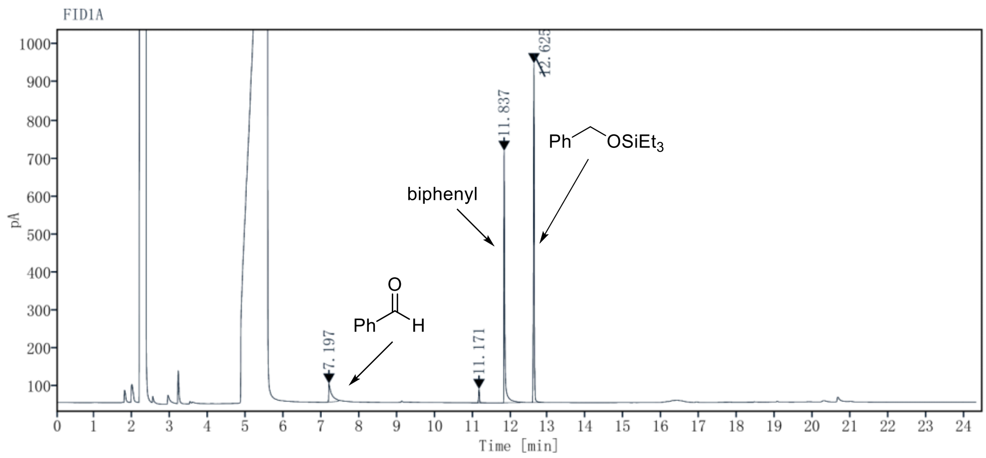


Figure 26. GC-MS spectra of the reaction mixture of **2a** and Et_3SiH

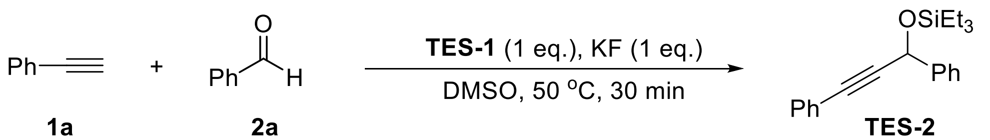


Illustrate FID1A

Retention Time [min]	Peak Area	Peak Area %
7.197	266.06351	8.96
11.171	59.88624	2.02
11.837	1174.81805	39.56
12.625	1468.99580	49.47

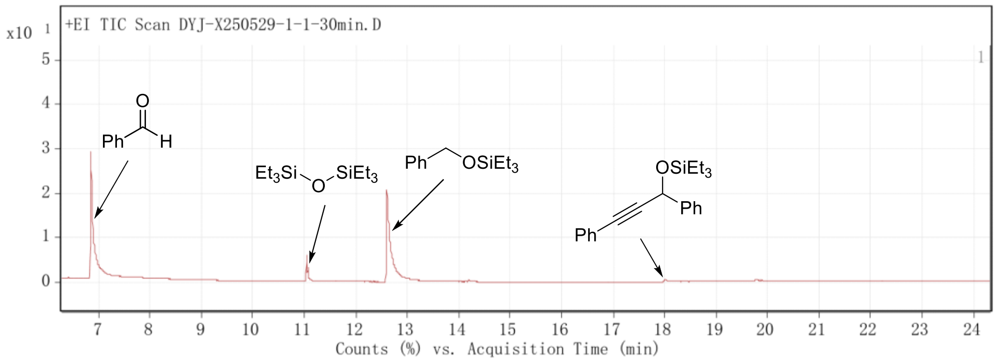
Figure 27. GC spectrum of the reaction mixture of **2a** and Et_3SiH

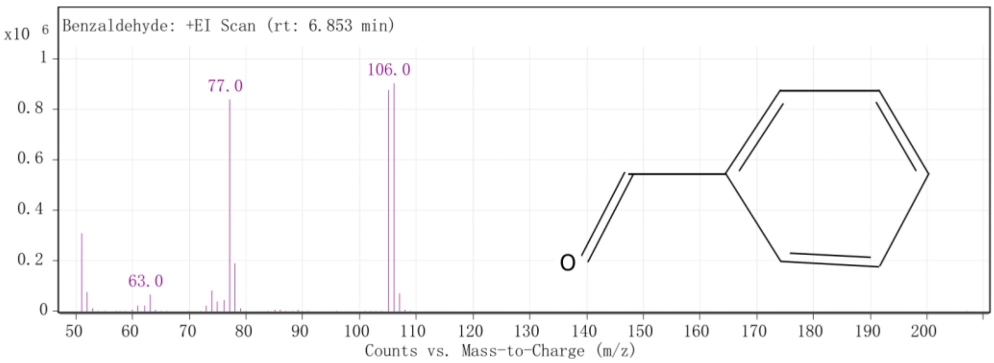
(3) The rection of 1a, 2a and TES-1

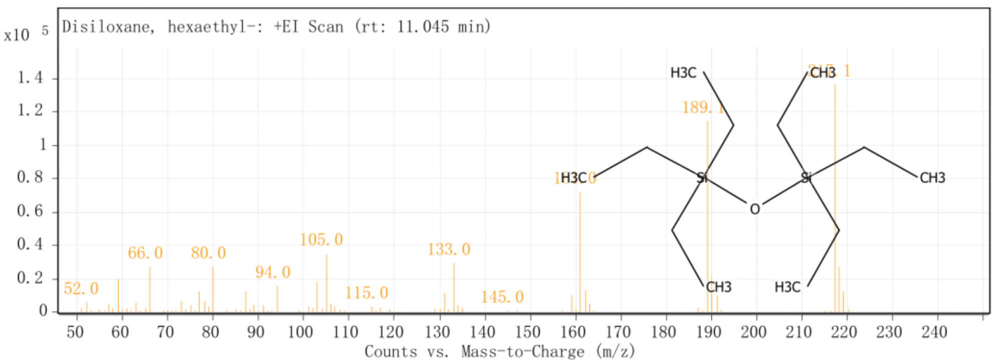


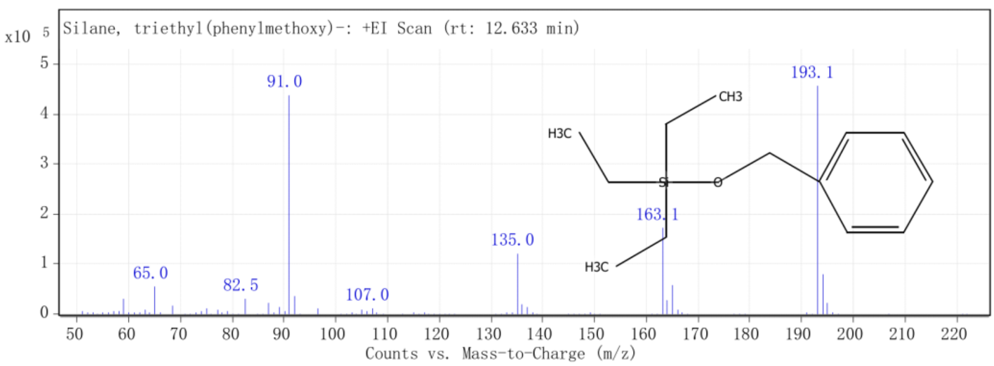
1a **2a** **TES-2** observed by GC-MS (3)

To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (5.8 mg, 0.1 mmol), DMSO (0.8 mL), **1a** (10.2 mg, 0.1 mmol, 1 eq.), **TES-1** (20.6 mg, 0.1 mol, 1 eq.) and **2a** (21.2 mg, 0.2 mmol, 2 eq.) under nitrogen atmosphere. The resulting solution was allowed to stir at 50 °C for 30 minutes. The reaction mixture was subjected to GS-MS analysis.









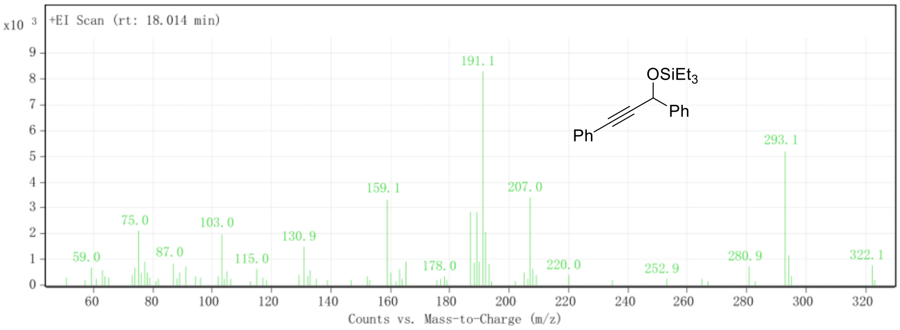
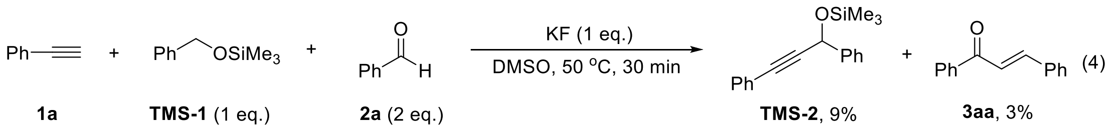
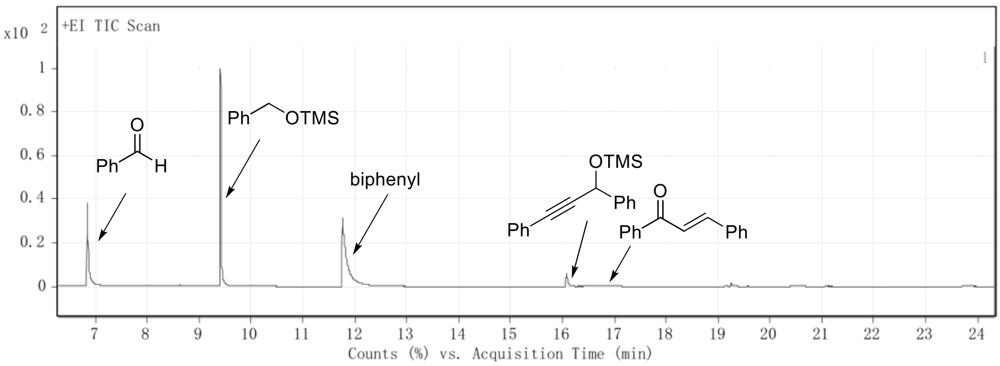


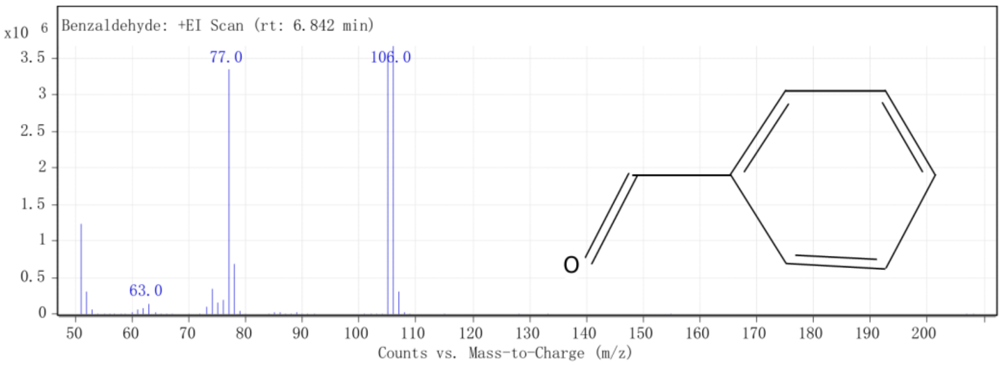
Figure 28. GC-MS spectra of the reaction mixture of **1a, 2a** and **TES-1**

(4) The rection of 1a, 2a and TMS-1



To a 25 mL flame-dried Young-type tube equipped with a magnetic stirring bar was added KF (5.8 mg, 0.1 mmol), DMSO (0.8 mL), **1a** (10.2 mg, 0.1 mmol, 1 eq.), **TMS-1** (18.0 mg, 0.1 mmol, 1 eq.), and **2a** (21.2 mg, 0.2mmol, 2 eq.) under nitrogen atmosphere. The resulting solution was allowed to stir at 50 ºC for 30 minutes. The reaction mixture was then subjected to GC-MS and GC analysis using biphenyl as the internal standard.





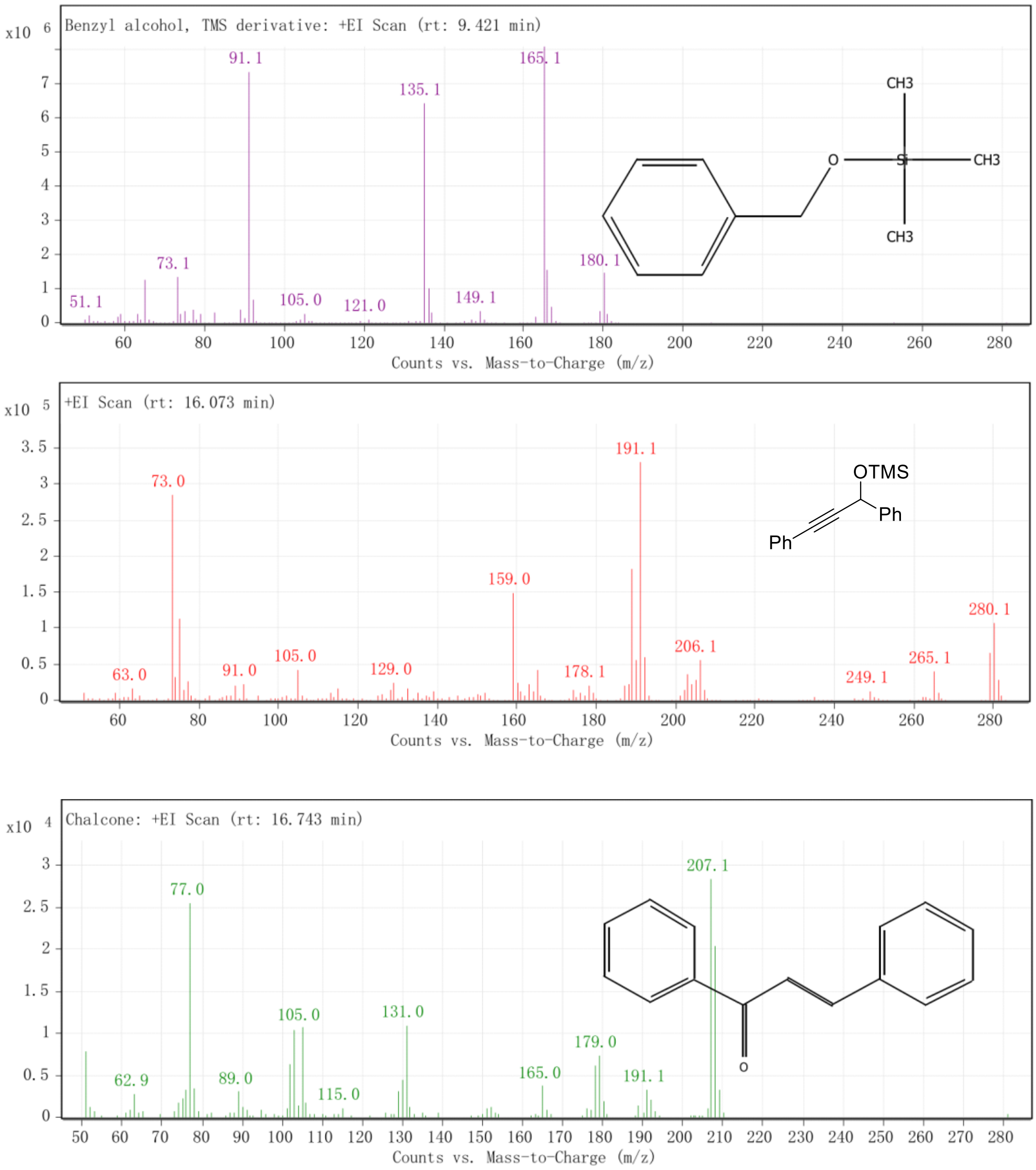
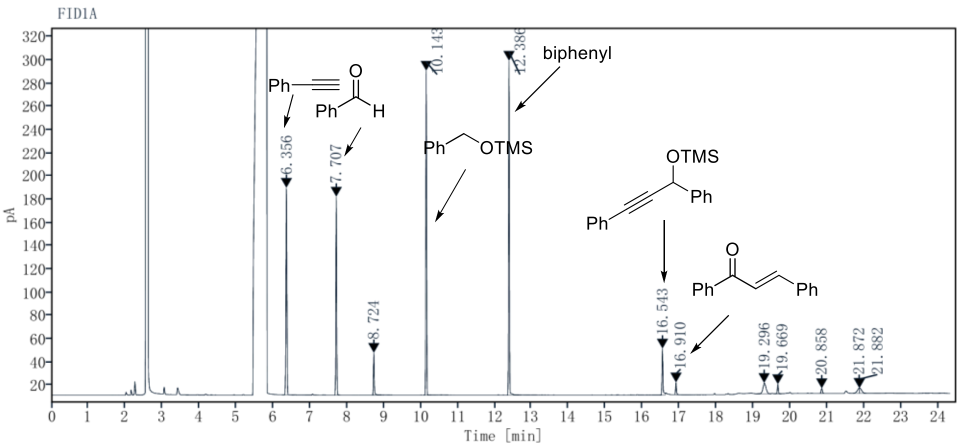


Figure 29. GC-MS spectra of the reaction mixture of **1a, 2a** and **TMS-1**



Illustrate FID1A

Retention Time [min]	Peak Area	Peak Area %
6.356	330.69061	19.41
7.707	264.60062	15.53
8.724	60.09958	3.53
10.143	414.67182	24.34
12.386	426.37787	25.02
16.543	69.88550	4.10
16.910	19.14223	1.12
19.296	55.57794	3.26
19.669	15.70613	0.92
20.858	11.13035	0.65

Figure 30. GC spectrum of the reaction mixture of **1a, 2a** and **TMS-1**

(5) Proposed mechanism catalyzed by Si-H species

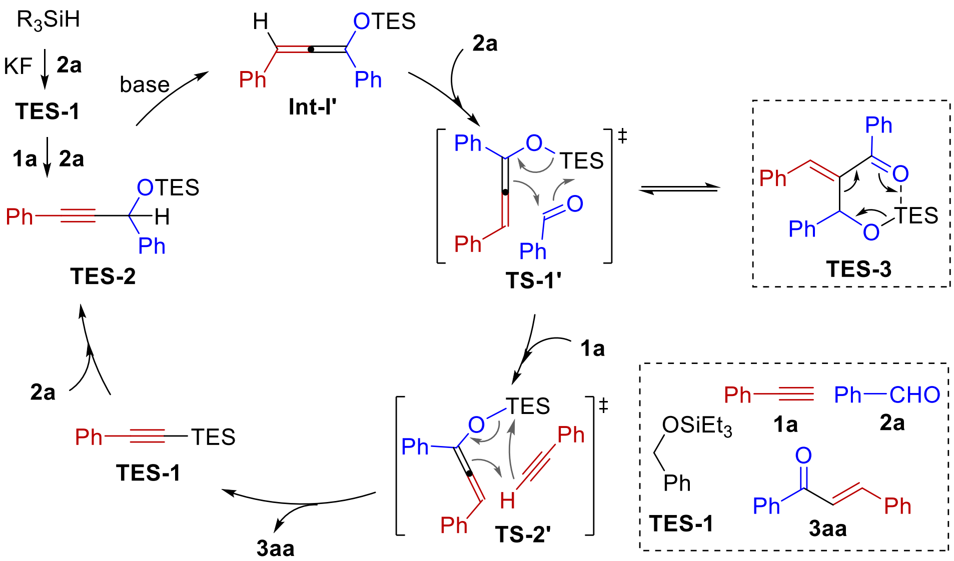


Figure 31. Proposed mechanism catalyzed by Si-H species

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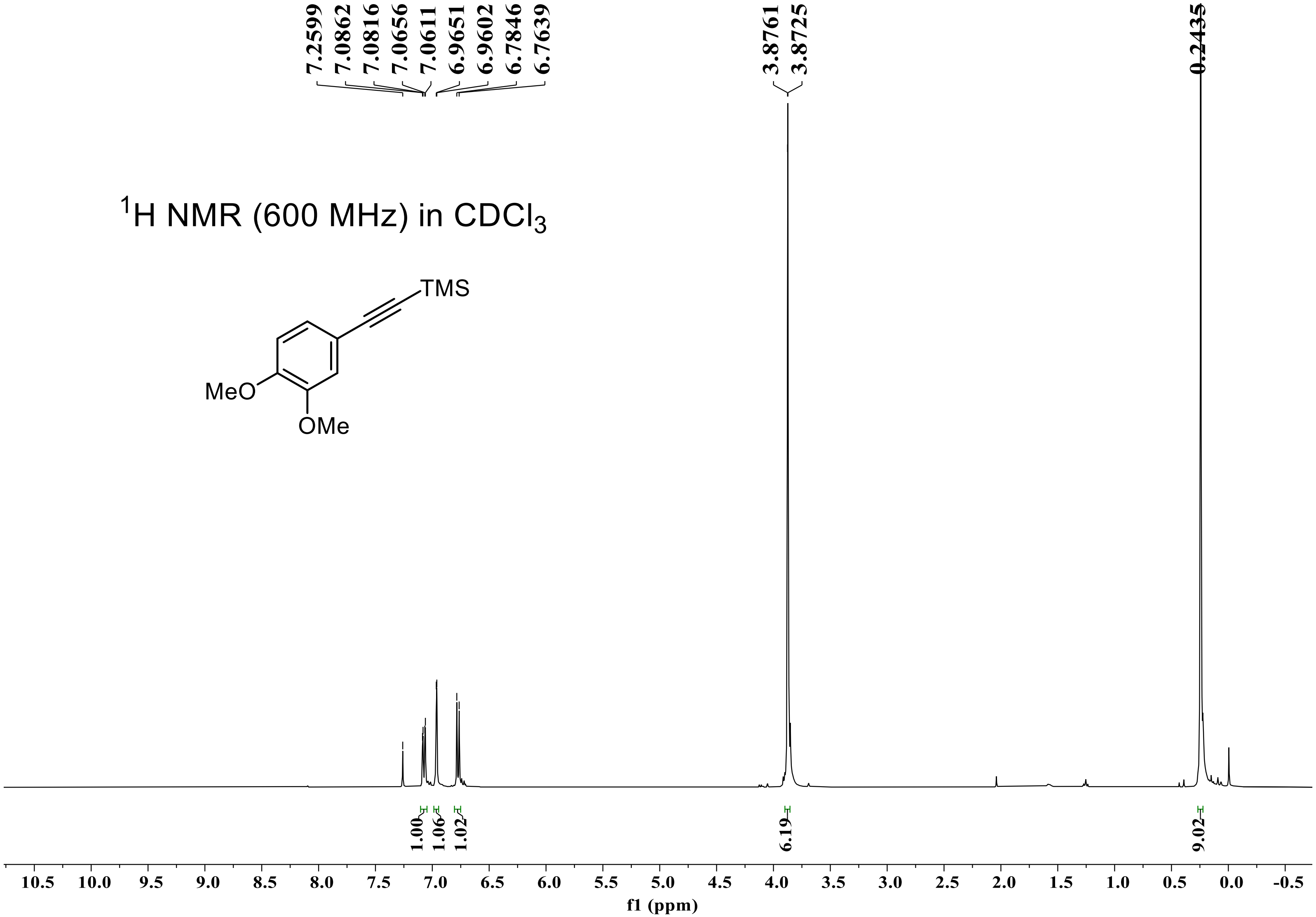
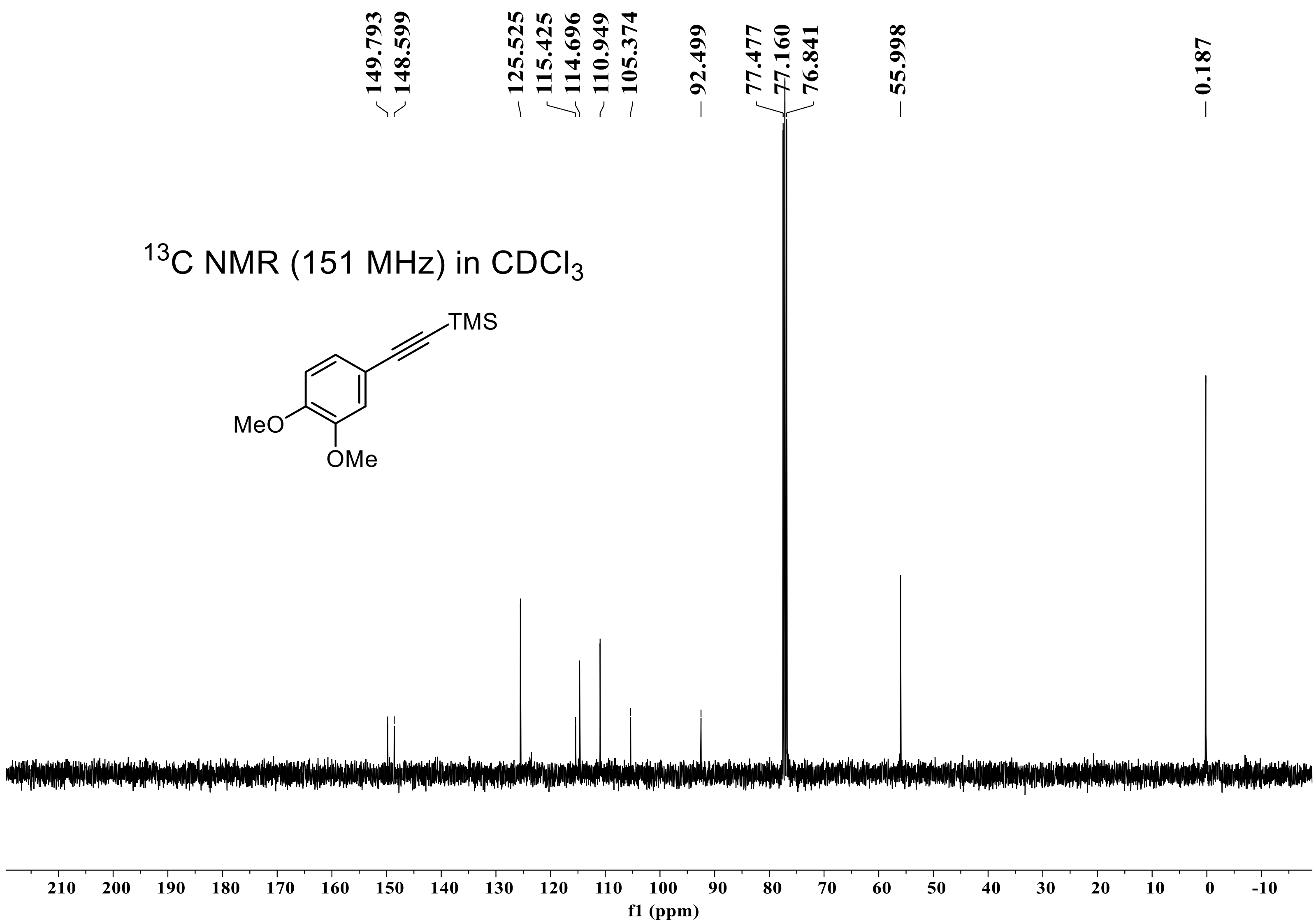
10. Copies for NMR Spectra

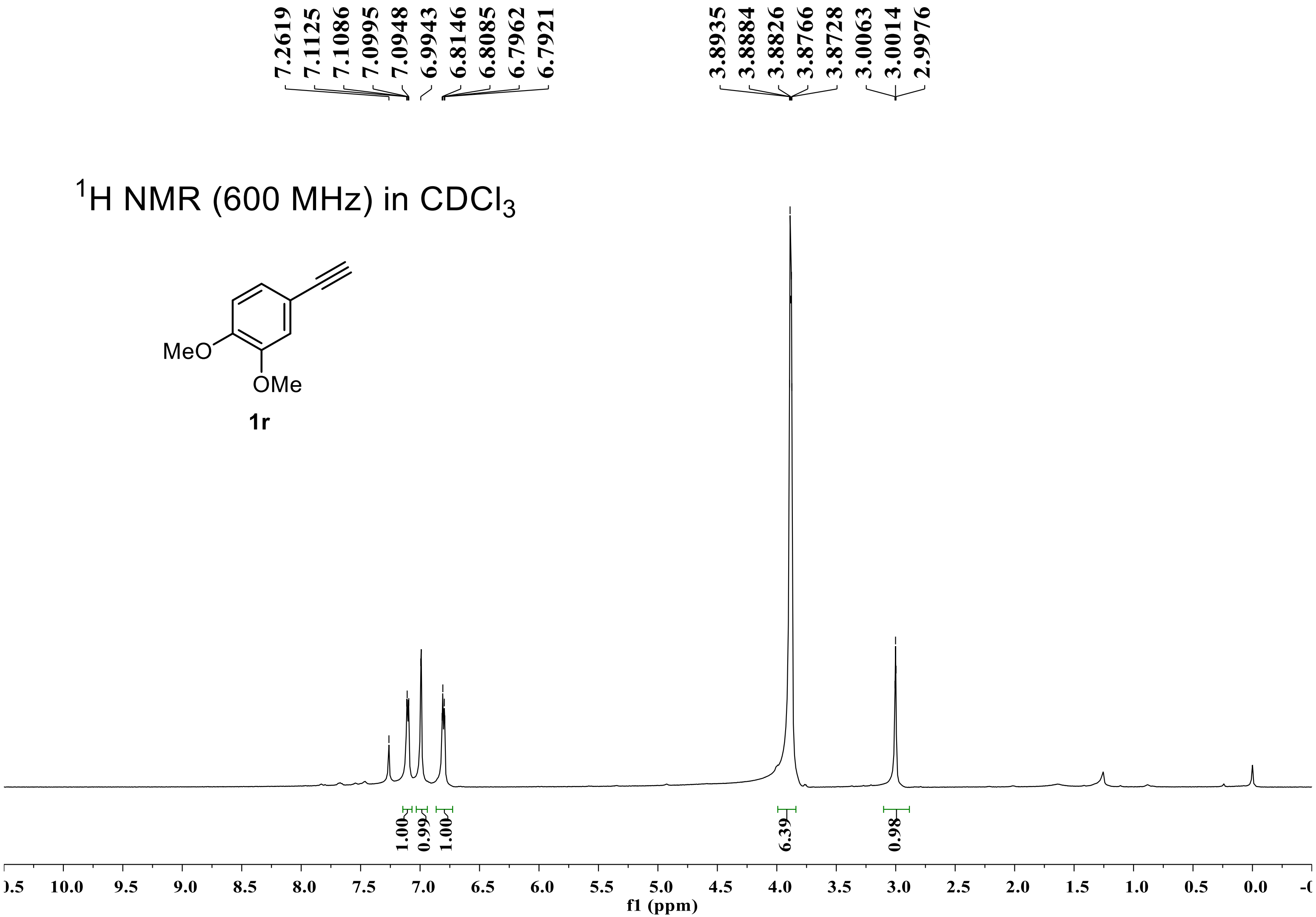


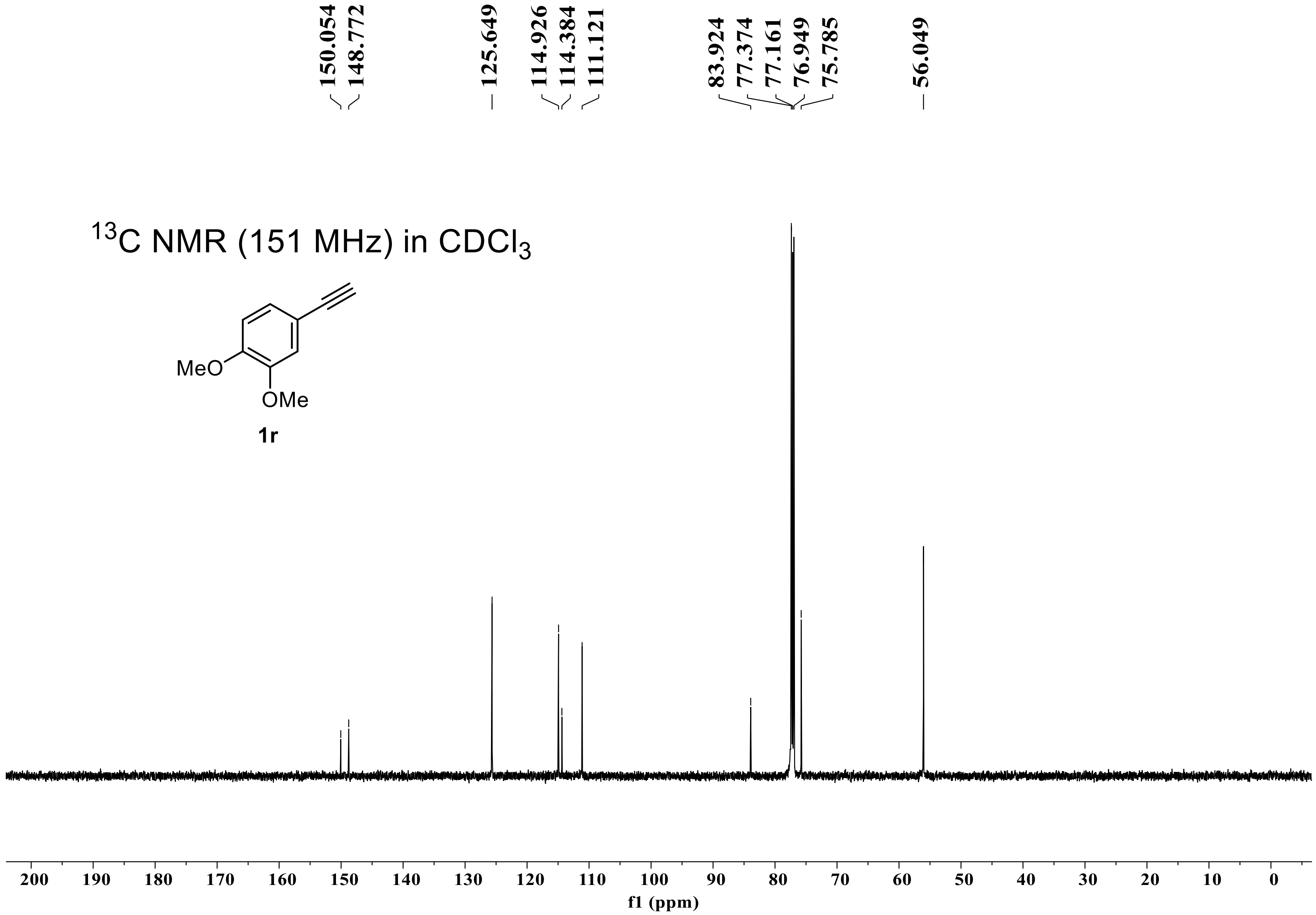
7.2599
7.0862
7.0816
7.0656
7.0611
6.9651
6.9602
6.7846
6.7639
3.8761
3.8725
0.2435
^{1}H NMR (600 MHz) in $CDCl_3$
TMS
MeO
OMe
1.00
1.06
1.02
6.19
9.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

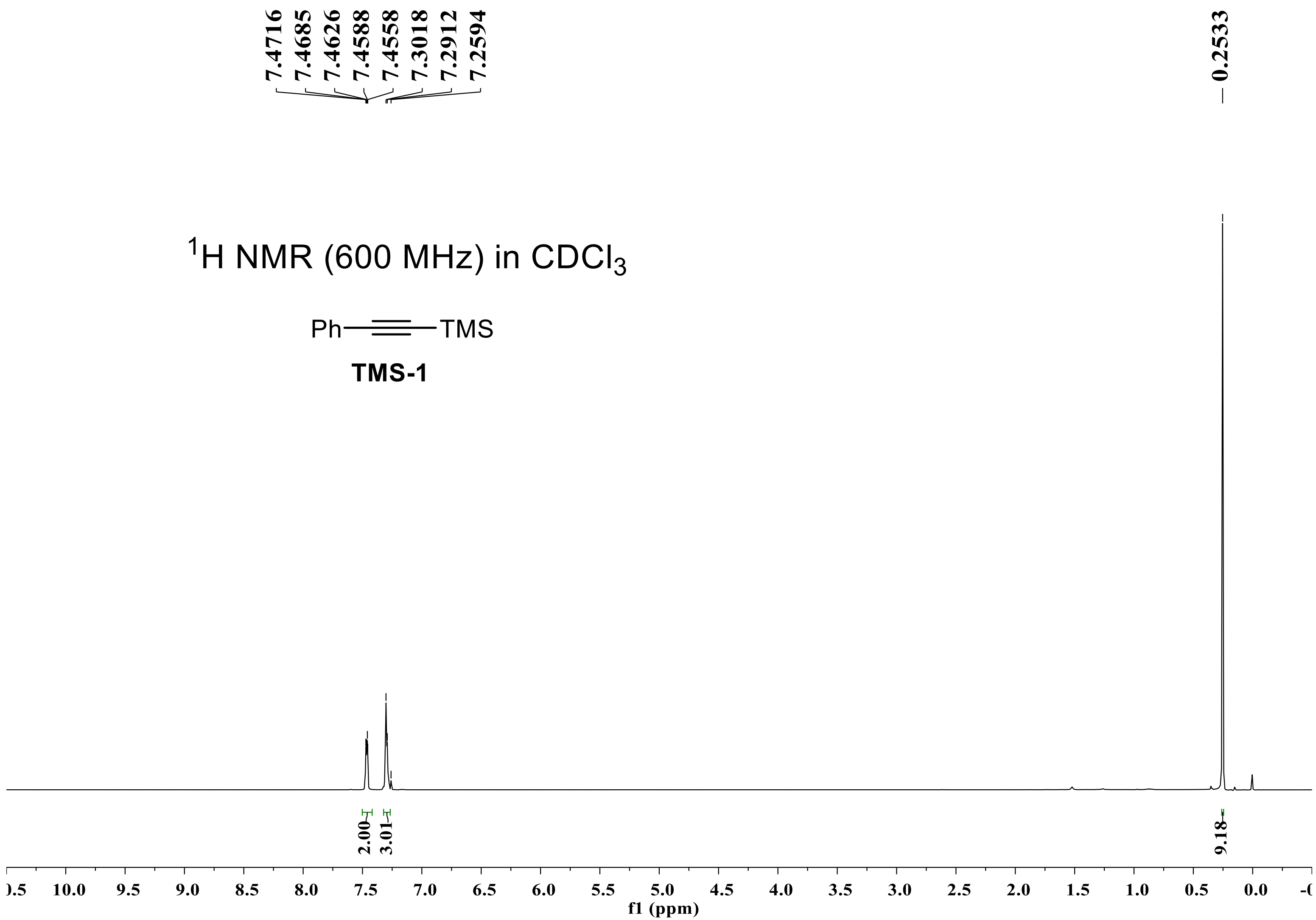
^{13}C NMR (151 MHz) in $CDCl_3$



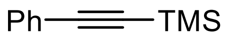
^{1}H NMR (600 MHz) in $CDCl_3$



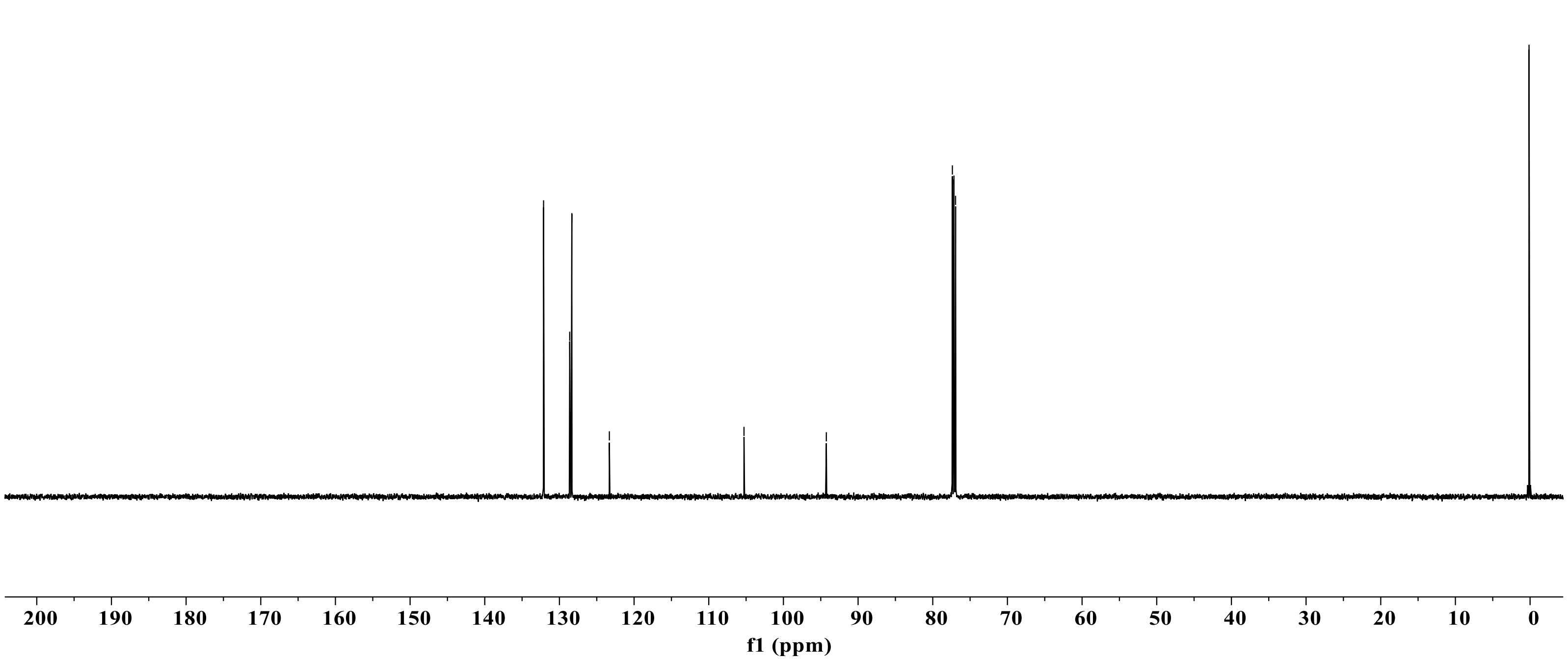

150.054
148.772
125.649
114.926
114.384
111.121
83.924
77.374
77.161
76.949
75.785
56.049
13C NMR (151 MHz) in CDCl3
MeO
OMe
1r
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

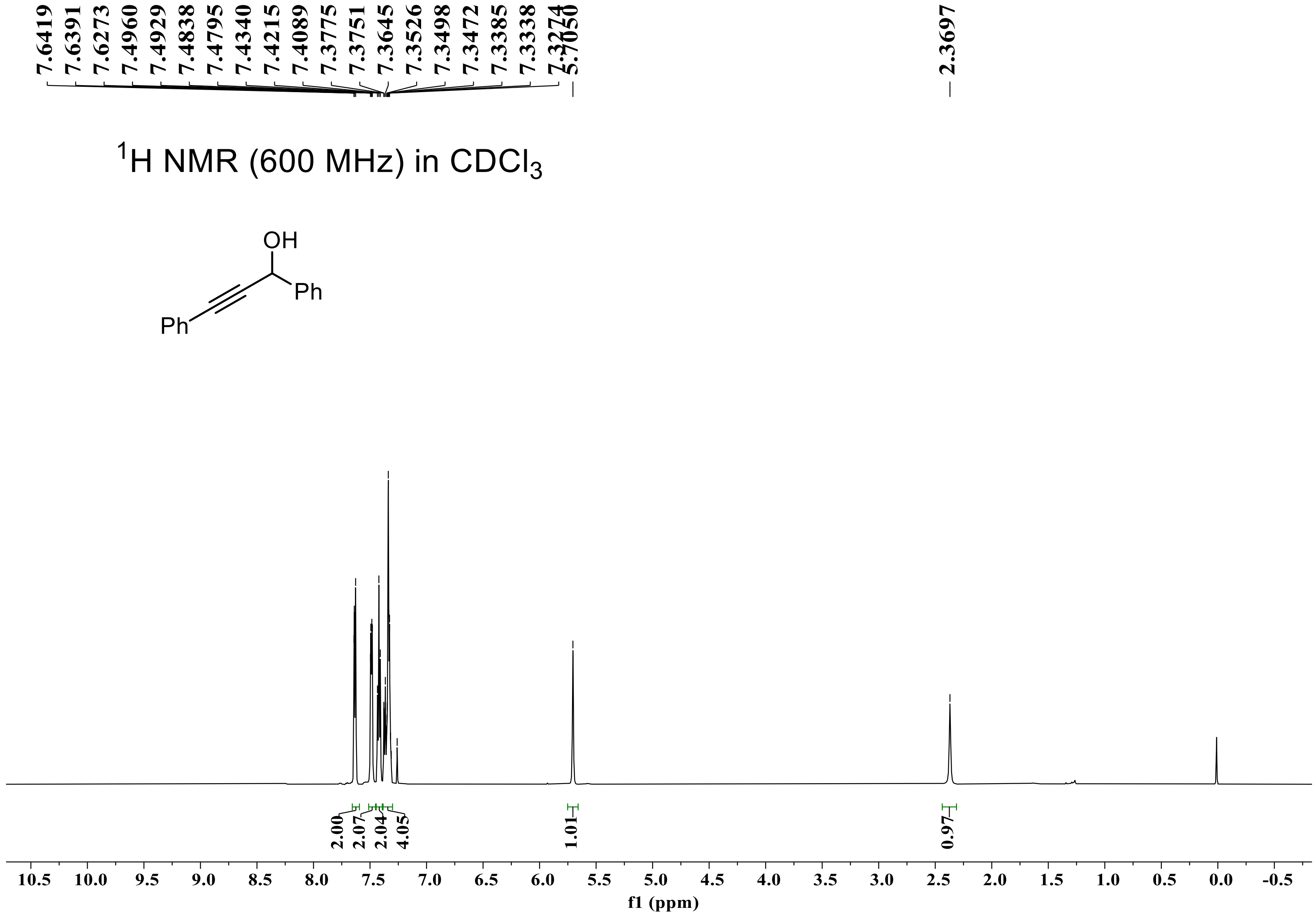

7.4716
7.4685
7.4626
7.4588
7.4558
7.3018
7.2912
7.2594
0.2533
1H NMR (600 MHz) in CDCl3
Ph—≡—TMS
TMS-1
2.00
3.01
9.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

^{13}C NMR (151 MHz) in $CDCl_3$

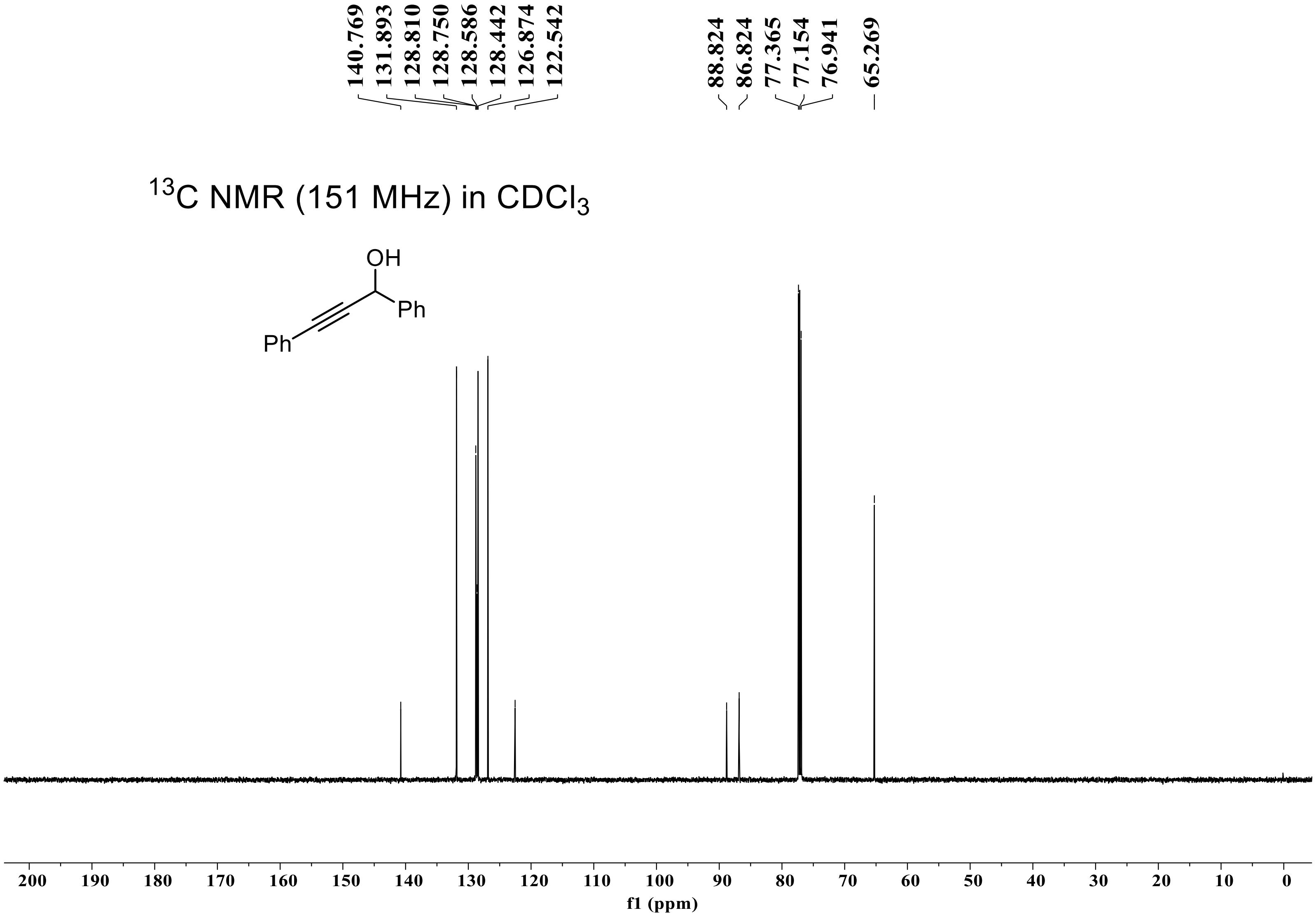


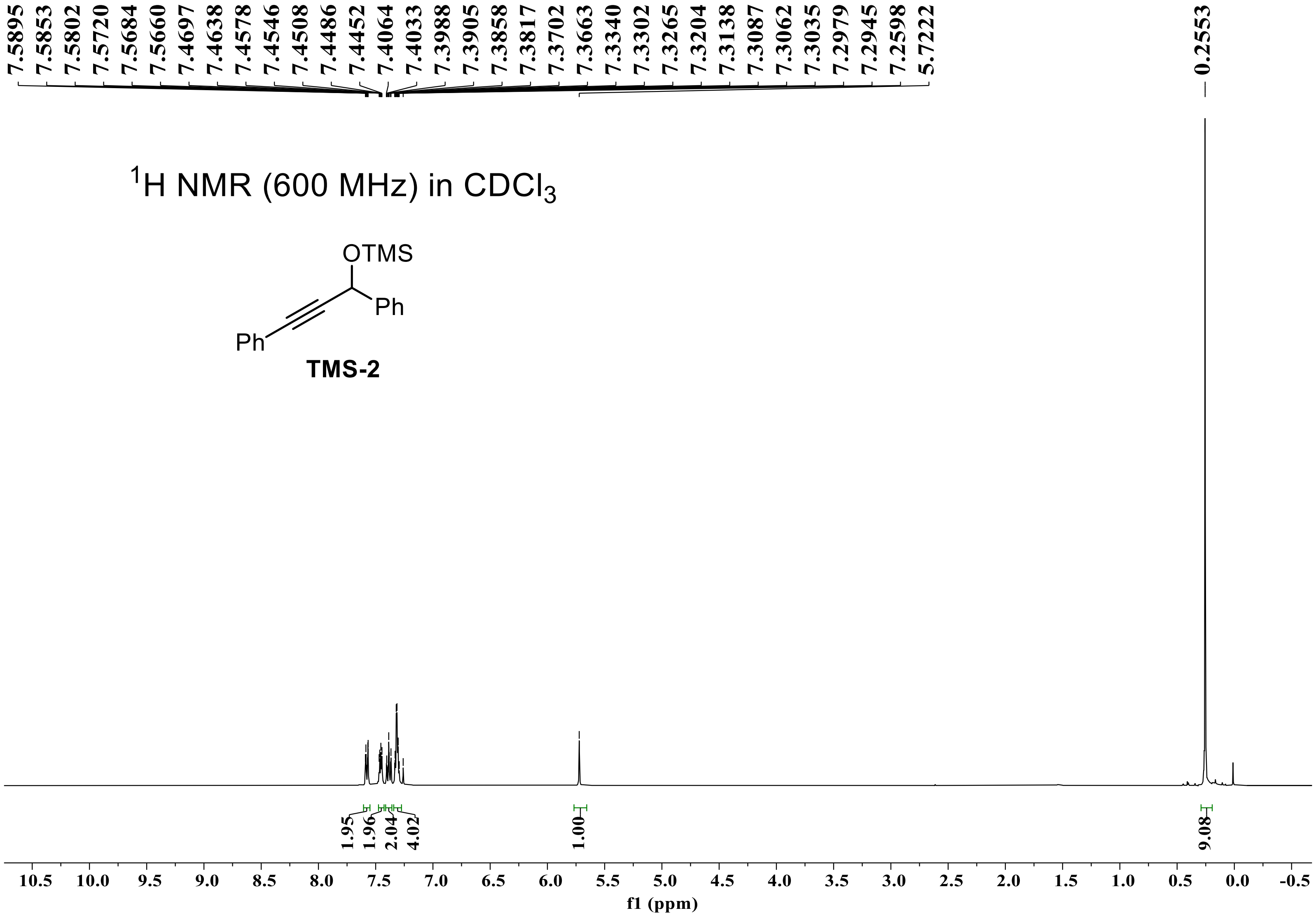
TMS-1




7.6419
7.6391
7.6273
7.4960
7.4929
7.4838
7.4795
7.4340
7.4215
7.4089
7.3775
7.3751
7.3645
7.3526
7.3498
7.3472
7.3385
7.3338
7.3274
5.7050
2.3697
^{1}H NMR (600 MHz) in $CDCl_3$
OH
Ph
Ph
2.00
2.07
2.04
4.05
1.01
0.97
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

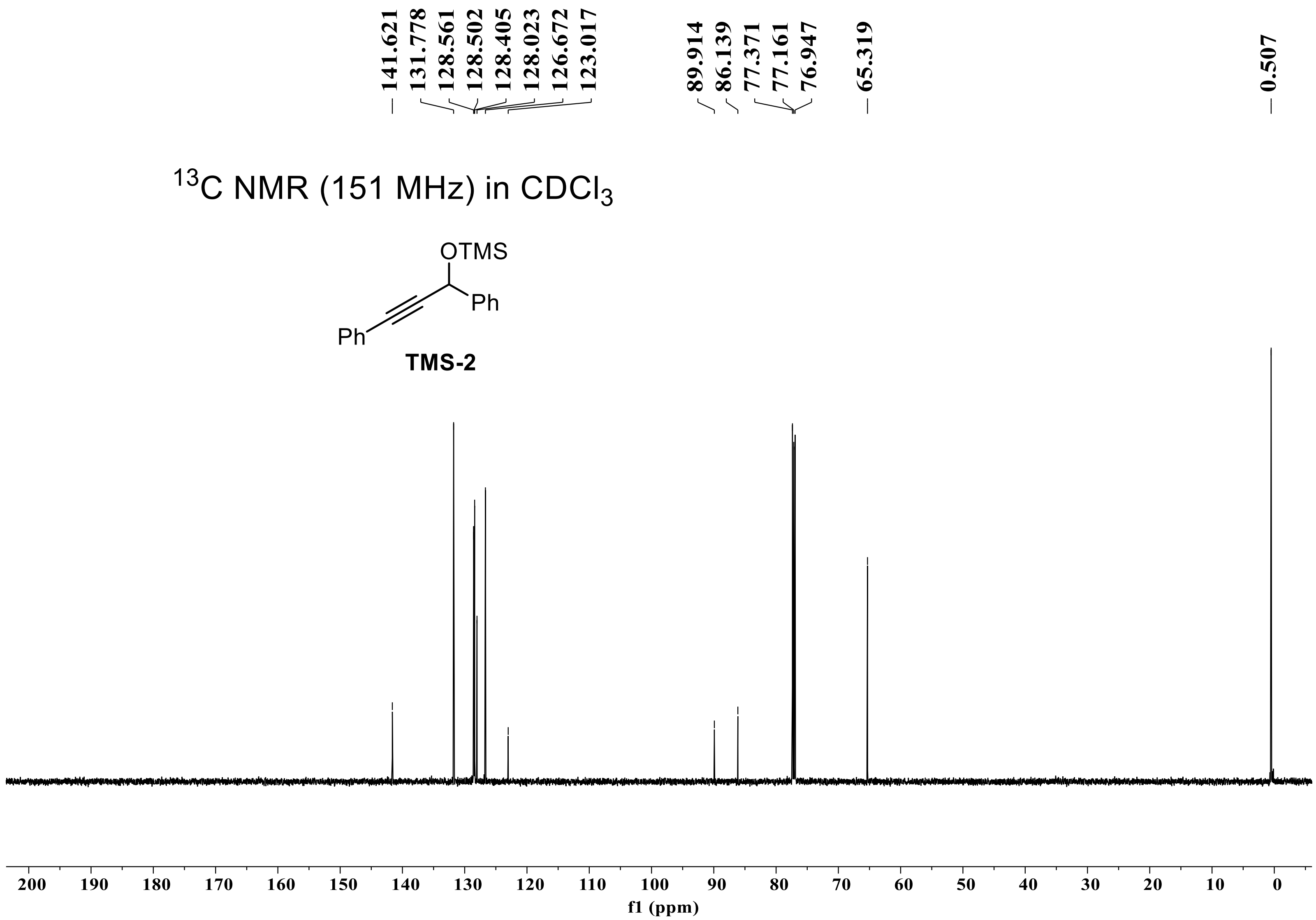
^{13}C NMR (151 MHz) in $CDCl_3$





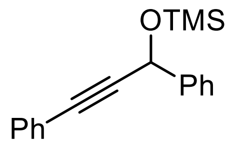
7.5895
7.5853
7.5802
7.5720
7.5684
7.5660
7.4697
7.4638
7.4578
7.4546
7.4508
7.4486
7.4452
7.4064
7.4033
7.3988
7.3905
7.3858
7.3817
7.3702
7.3663
7.3340
7.3302
7.3265
7.3204
7.3138
7.3087
7.3062
7.3035
7.2979
7.2945
7.2598
5.7222
0.2553
^{1}H NMR (600 MHz) in $CDCl_3$
OTMS
Ph
Ph
TMS-2
1.95
1.96
2.04
4.02
1.00
9.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

^{13}C NMR (151 MHz) in $CDCl_3$

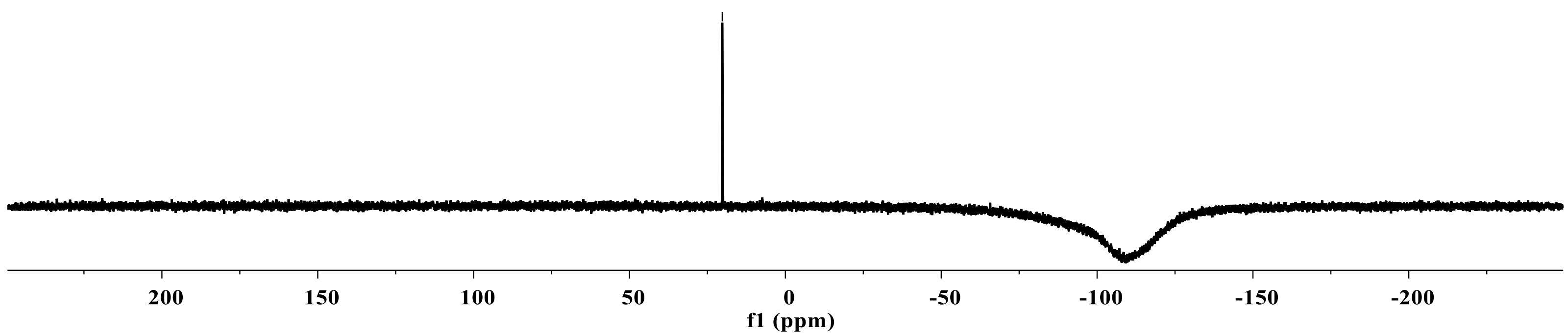


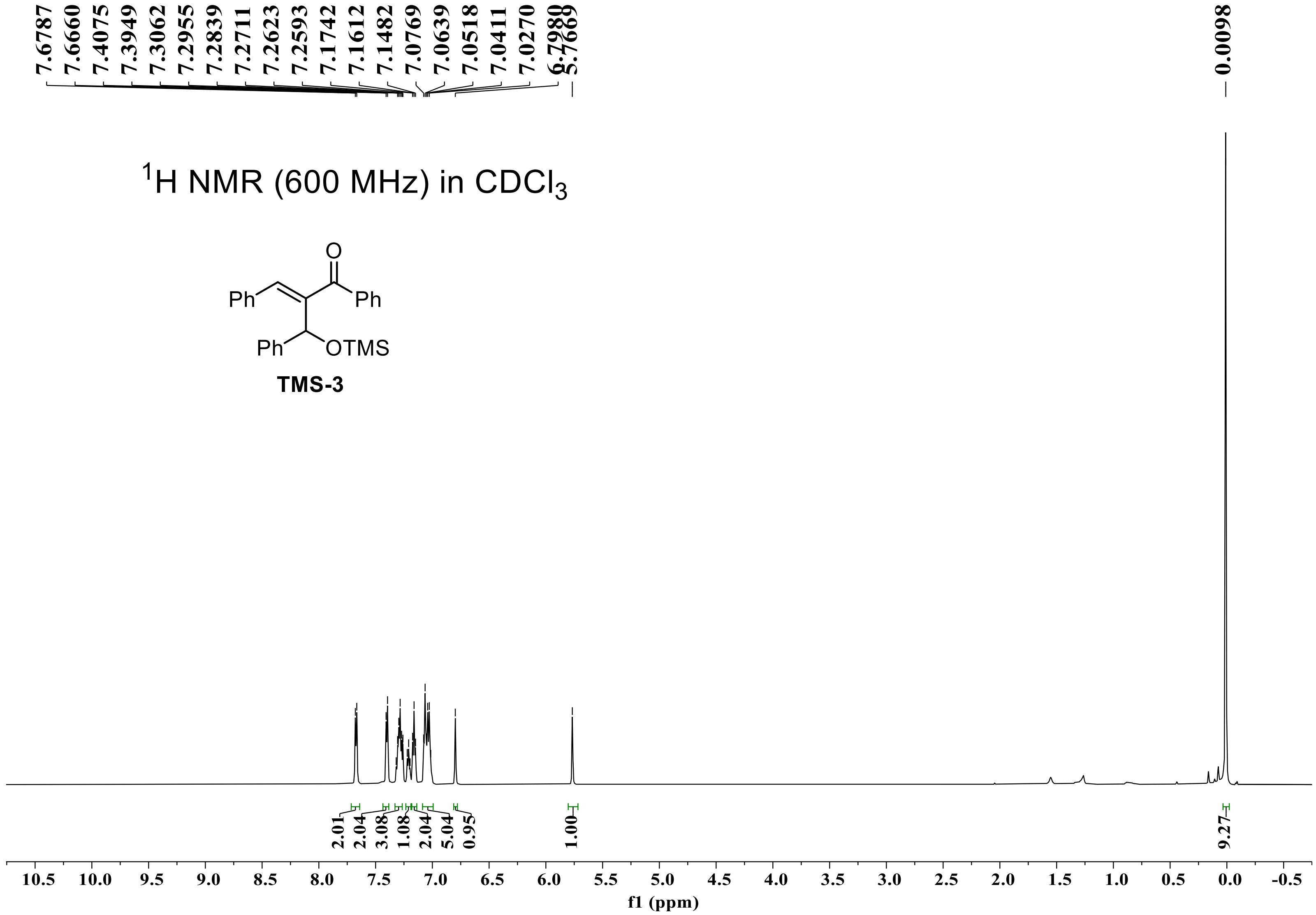
TMS-2

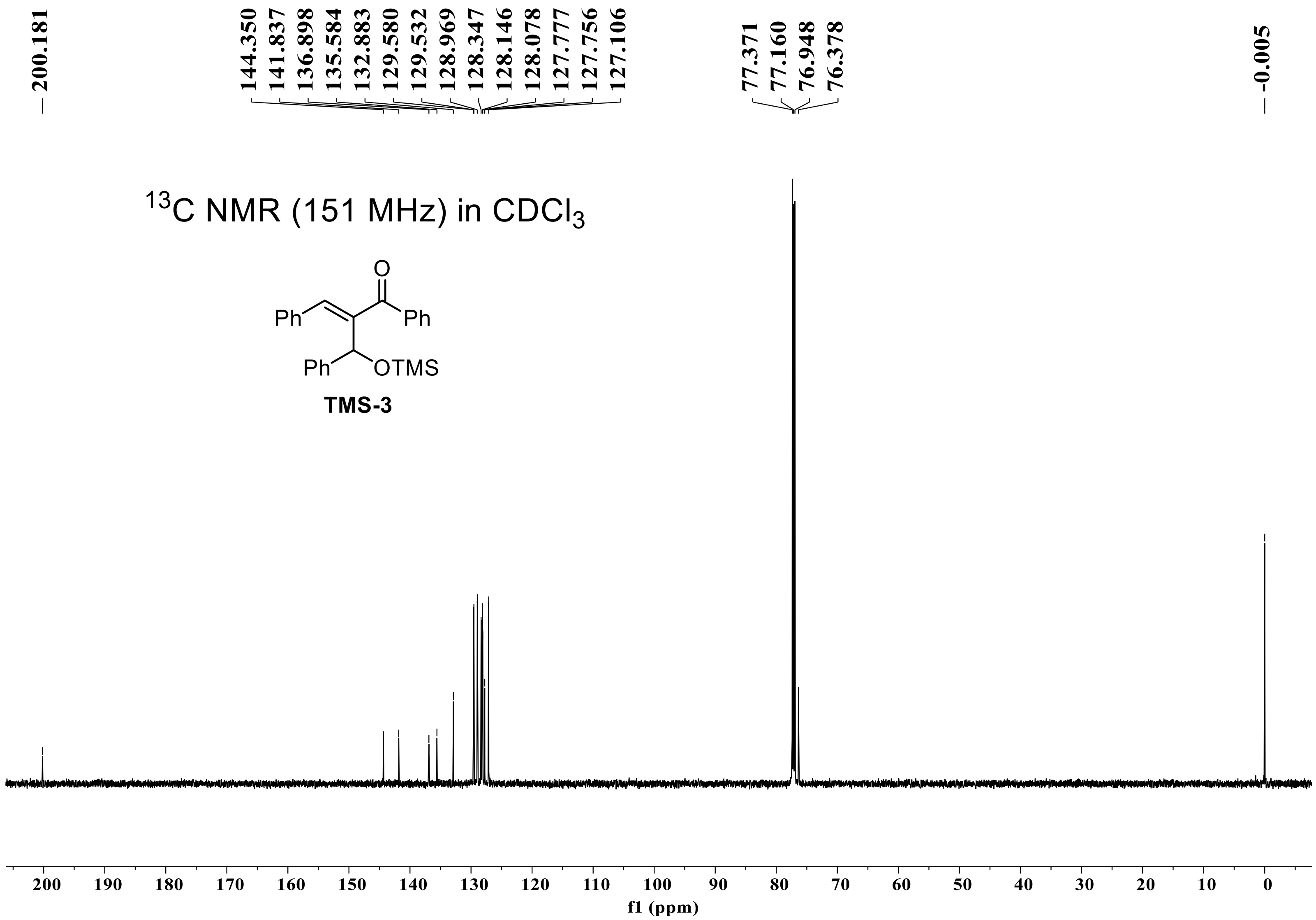
^{29}Si NMR (80 MHz, $CDCl_3$)



TMS-2



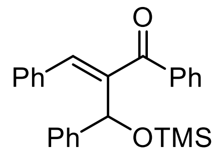

7.6787
7.6660
7.4075
7.3949
7.3062
7.2955
7.2839
7.2711
7.2623
7.2593
7.1742
7.1612
7.1482
7.0769
7.0639
7.0518
7.0411
7.0270
6.7980
5.7669
0.0098
^{1}H NMR (600 MHz) in $CDCl_3$
O
Ph
Ph
Ph
OTMS
TMS-3
2.01
2.04
3.08
1.08
2.04
5.04
0.95
1.00
9.27
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



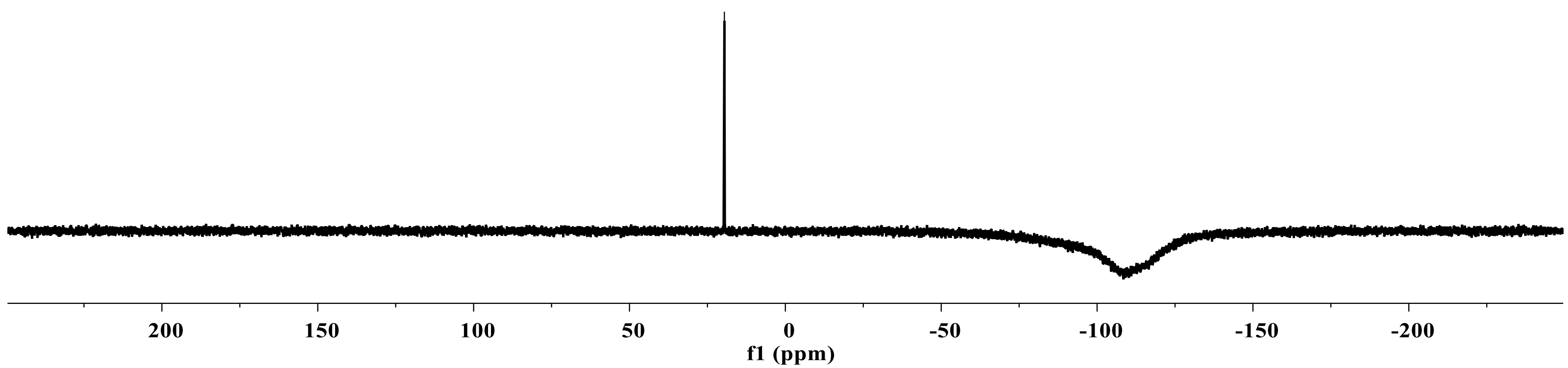
200.181
144.350
141.837
136.898
135.584
132.883
129.580
129.532
128.969
128.347
128.146
128.078
127.777
127.756
127.106
77.371
77.160
76.948
76.378
-0.005
13C NMR (151 MHz) in CDCl3
O
Ph
Ph
Ph
OTMS
TMS-3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

— 19.562

^{29}Si NMR (80 MHz, $CDCl_3$)

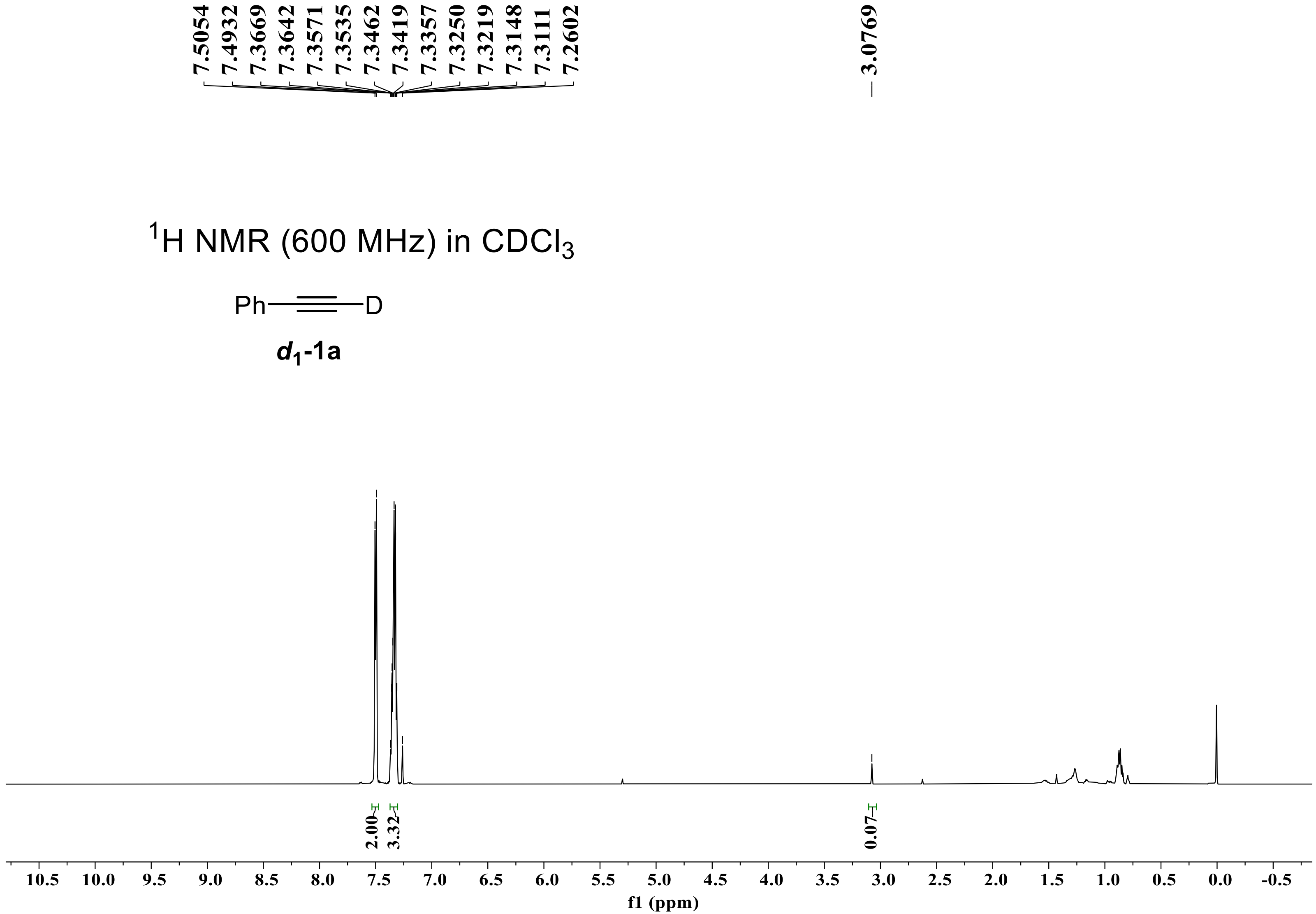


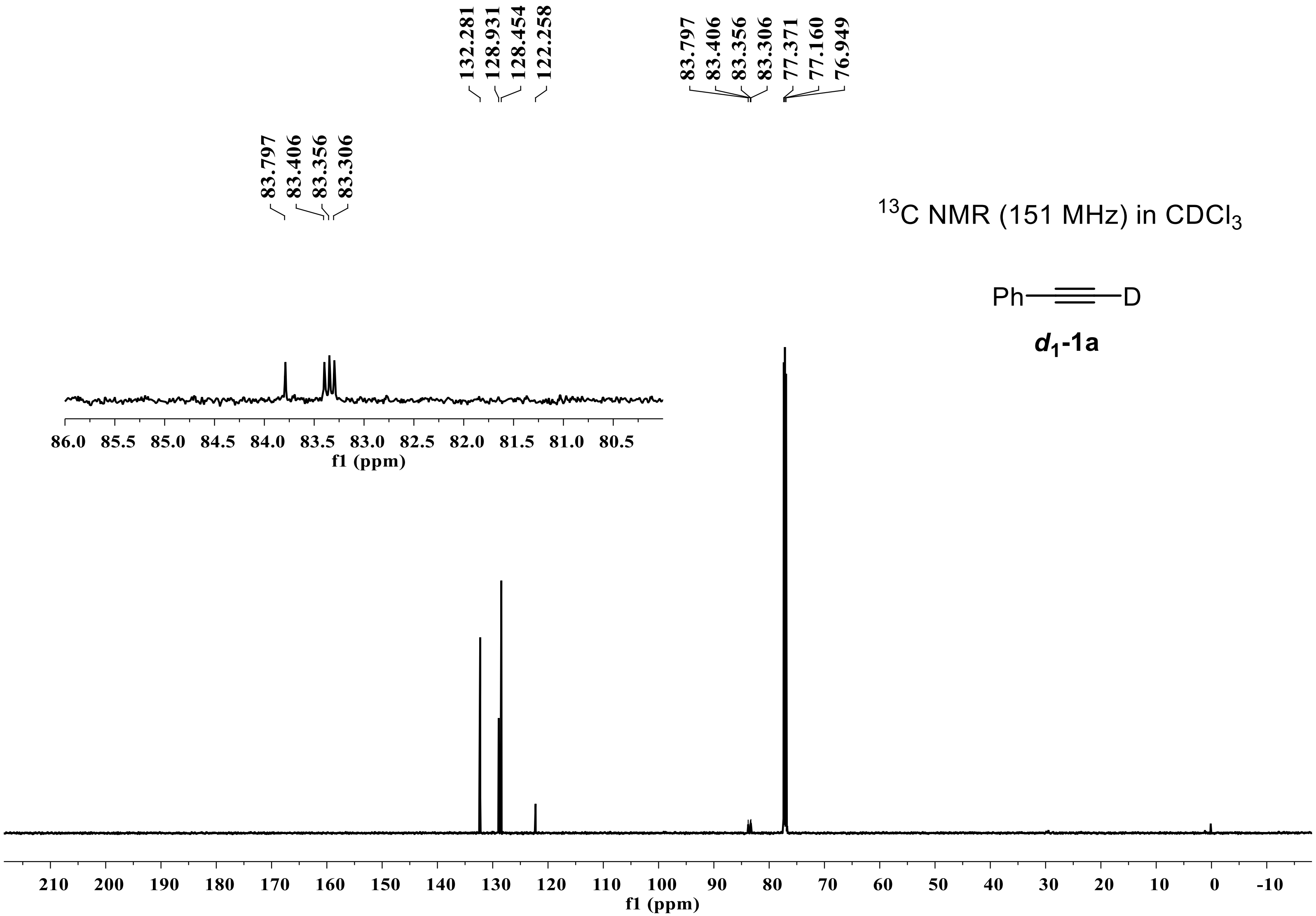
TMS-3



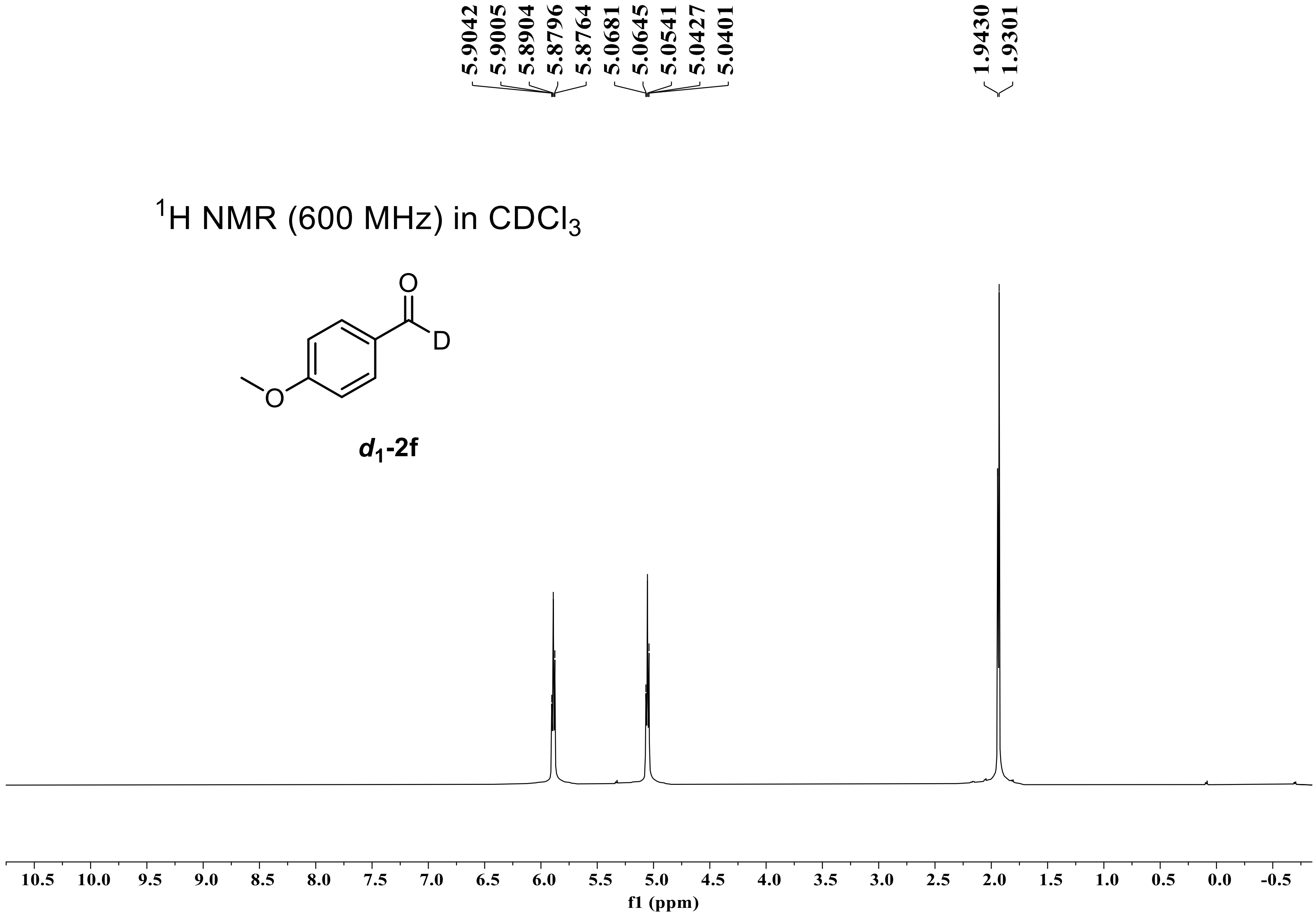
^{1}H NMR (600 MHz) in $CDCl_3$

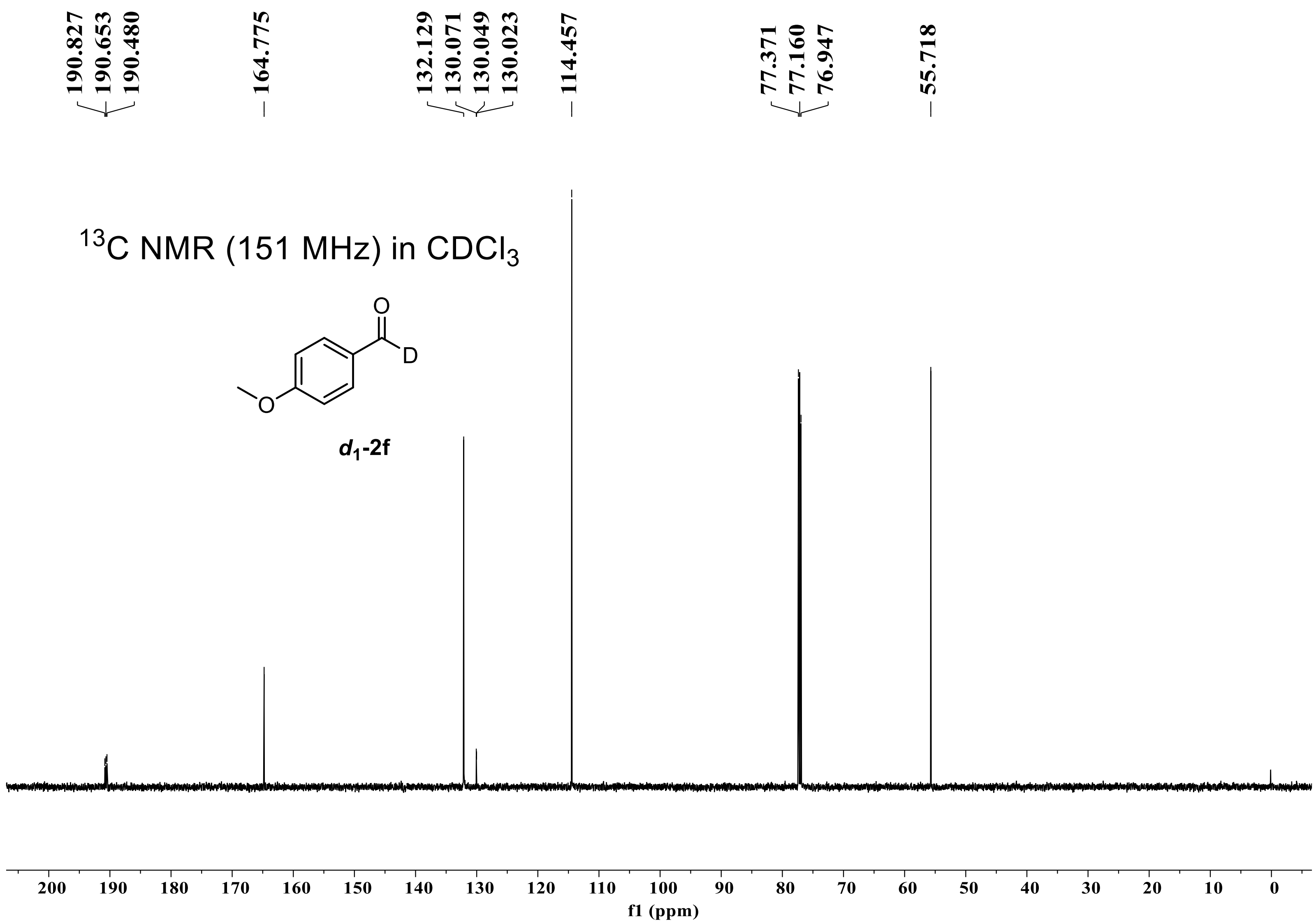
***d*$_1$-1a**





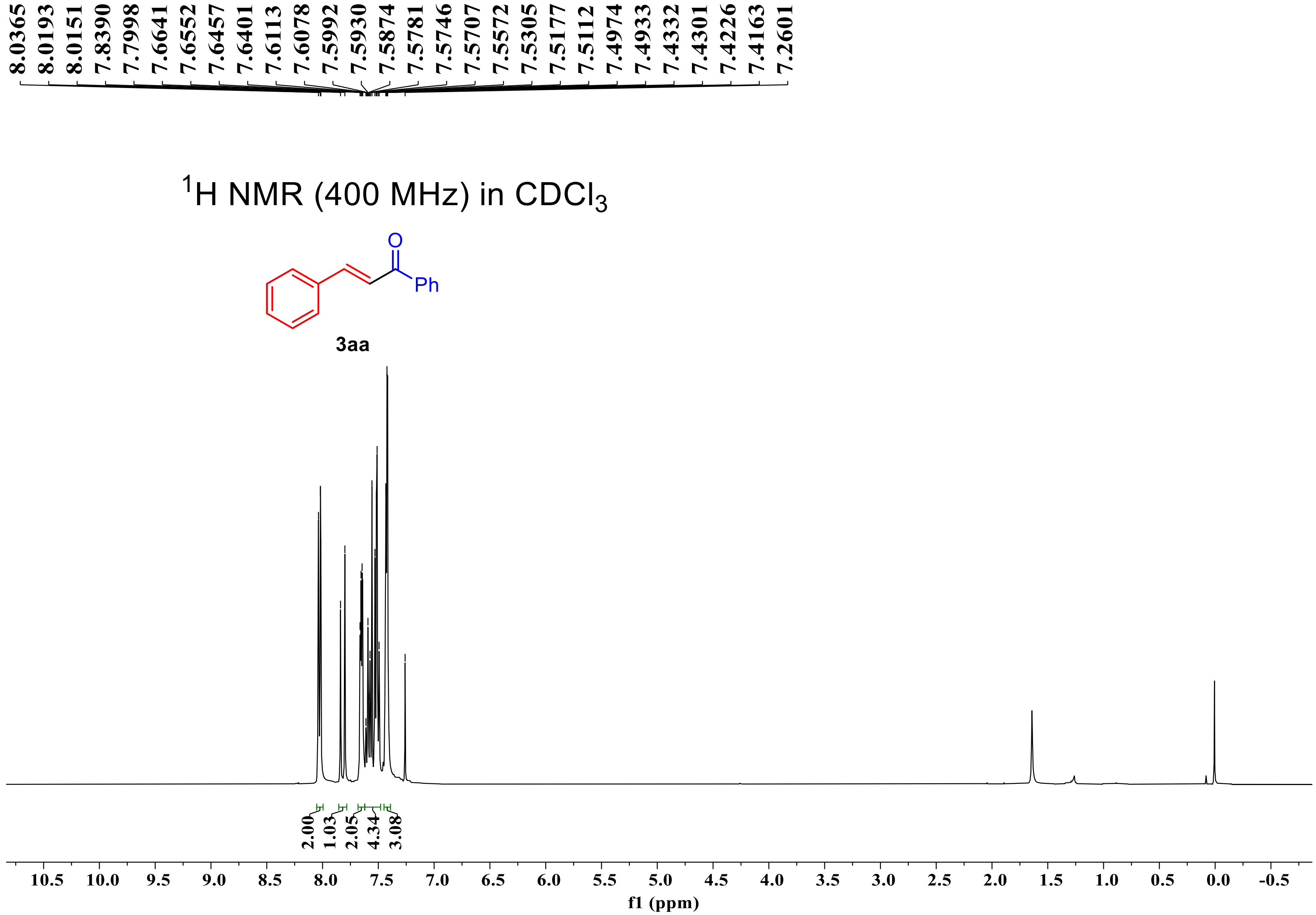
132.281
128.931
128.454
122.258
83.797
83.406
83.356
83.306
77.371
77.160
76.949
83.797
83.406
83.356
83.306
^{13}C NMR (151 MHz) in CDCl$_3$
Ph—≡—D
d$_1$-1a
86.0 85.5 85.0 84.5 84.0 83.5 83.0 82.5 82.0 81.5 81.0 80.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

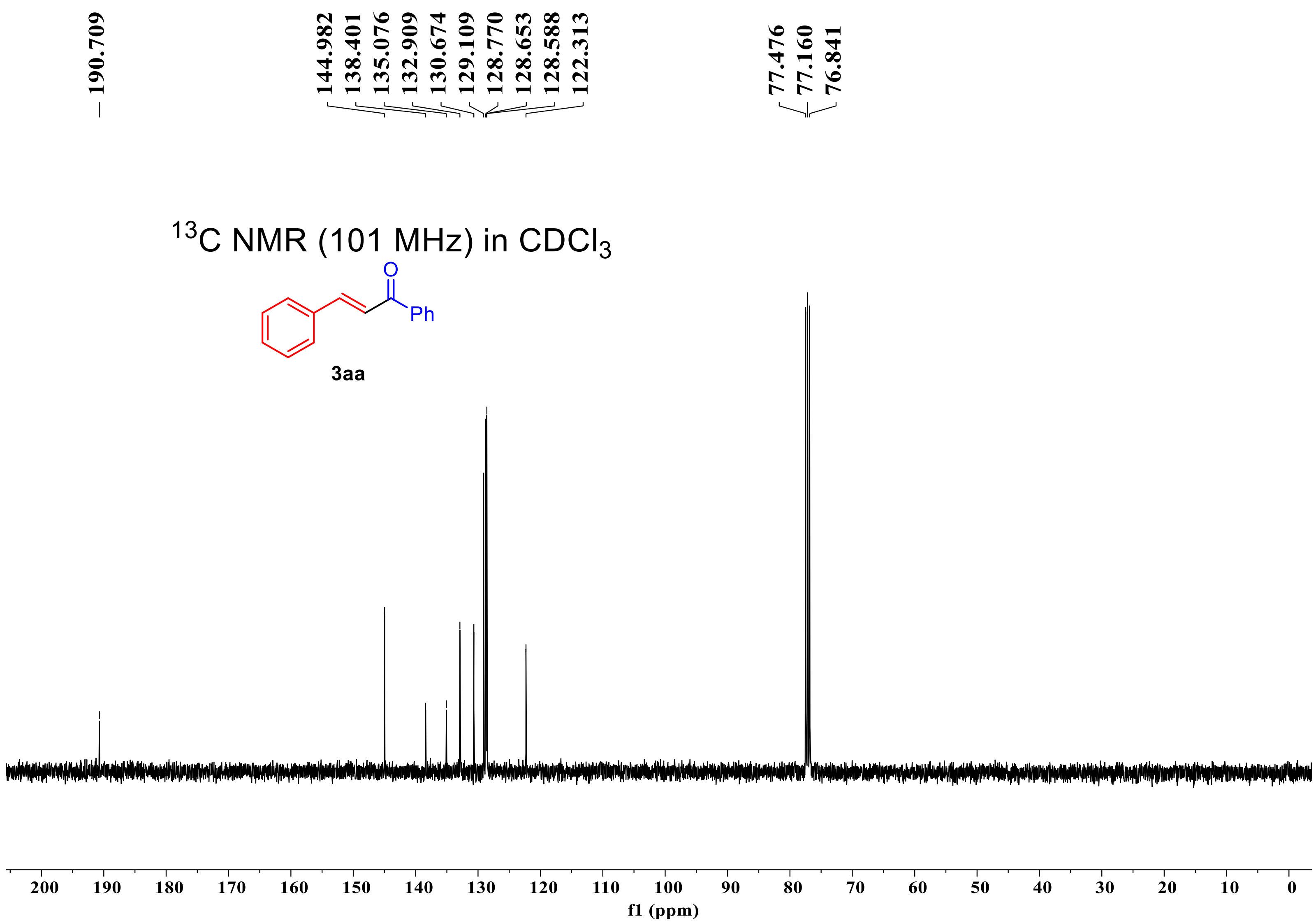

5.9042
5.9005
5.8904
5.8796
5.8764
5.0681
5.0645
5.0541
5.0427
5.0401
1.9430
1.9301
^{1}H NMR (600 MHz) in $CDCl_3$
O
D
O
d$_1$-**2f**
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

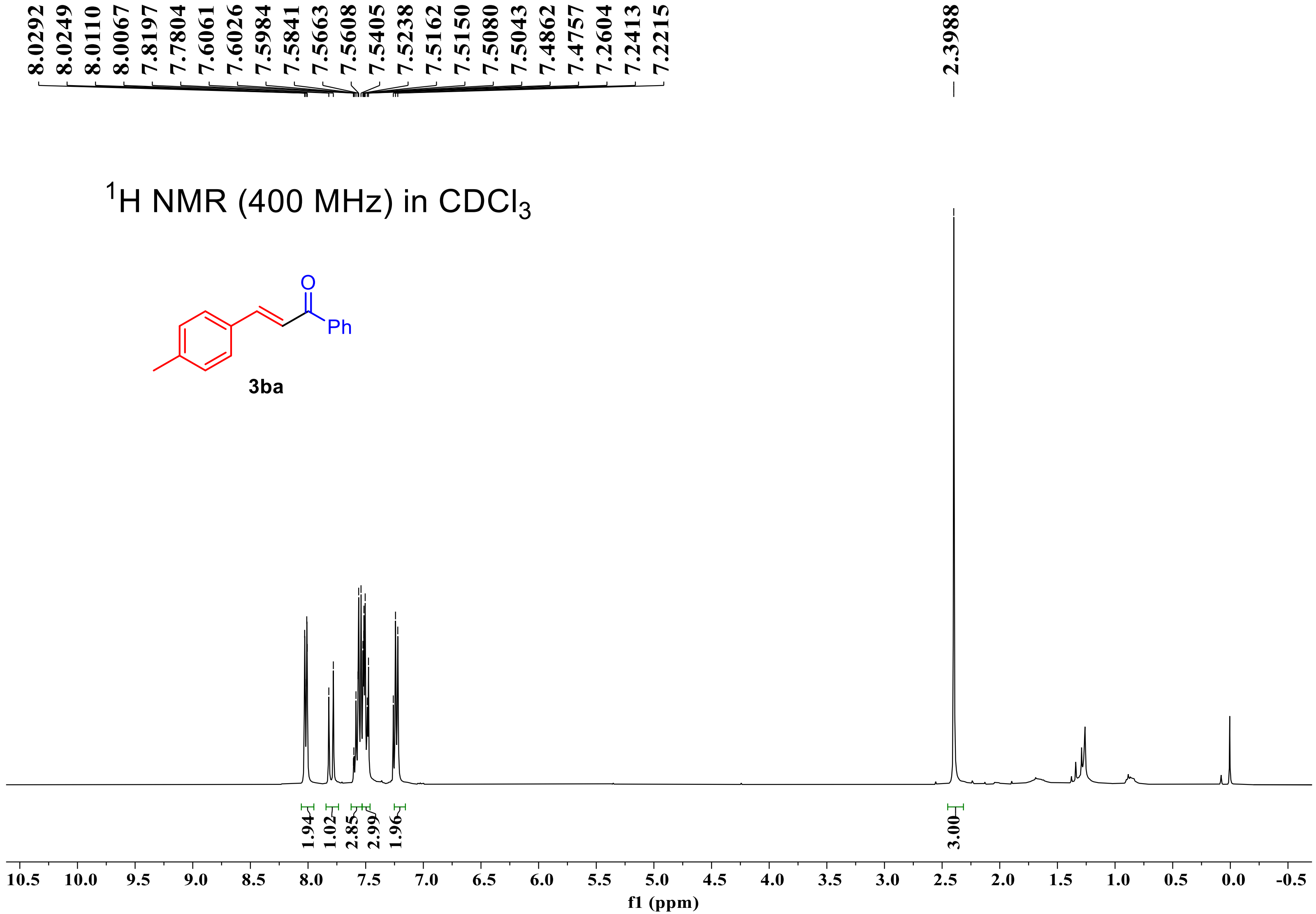


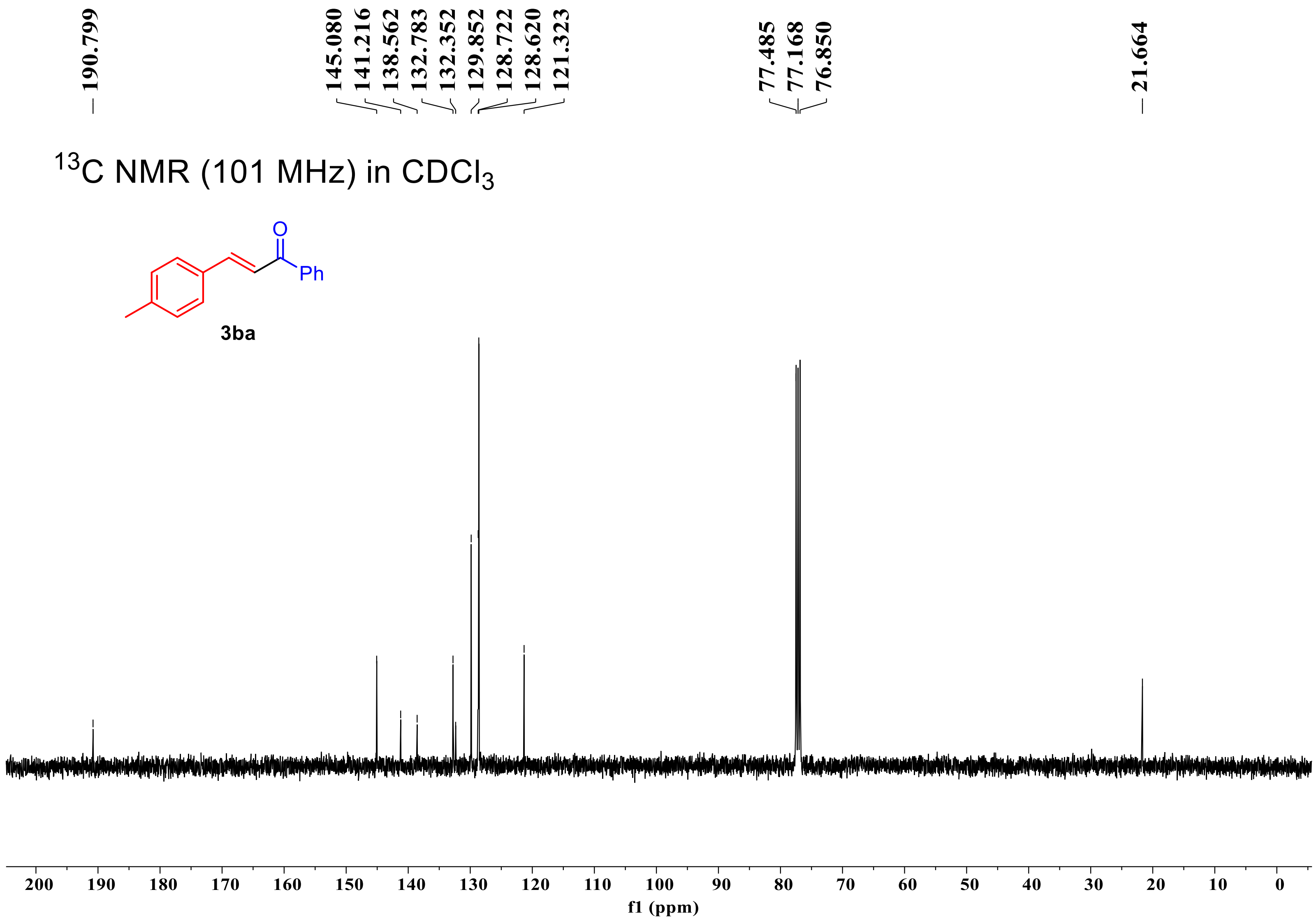
^{13}C NMR (151 MHz) in $CDCl_3$

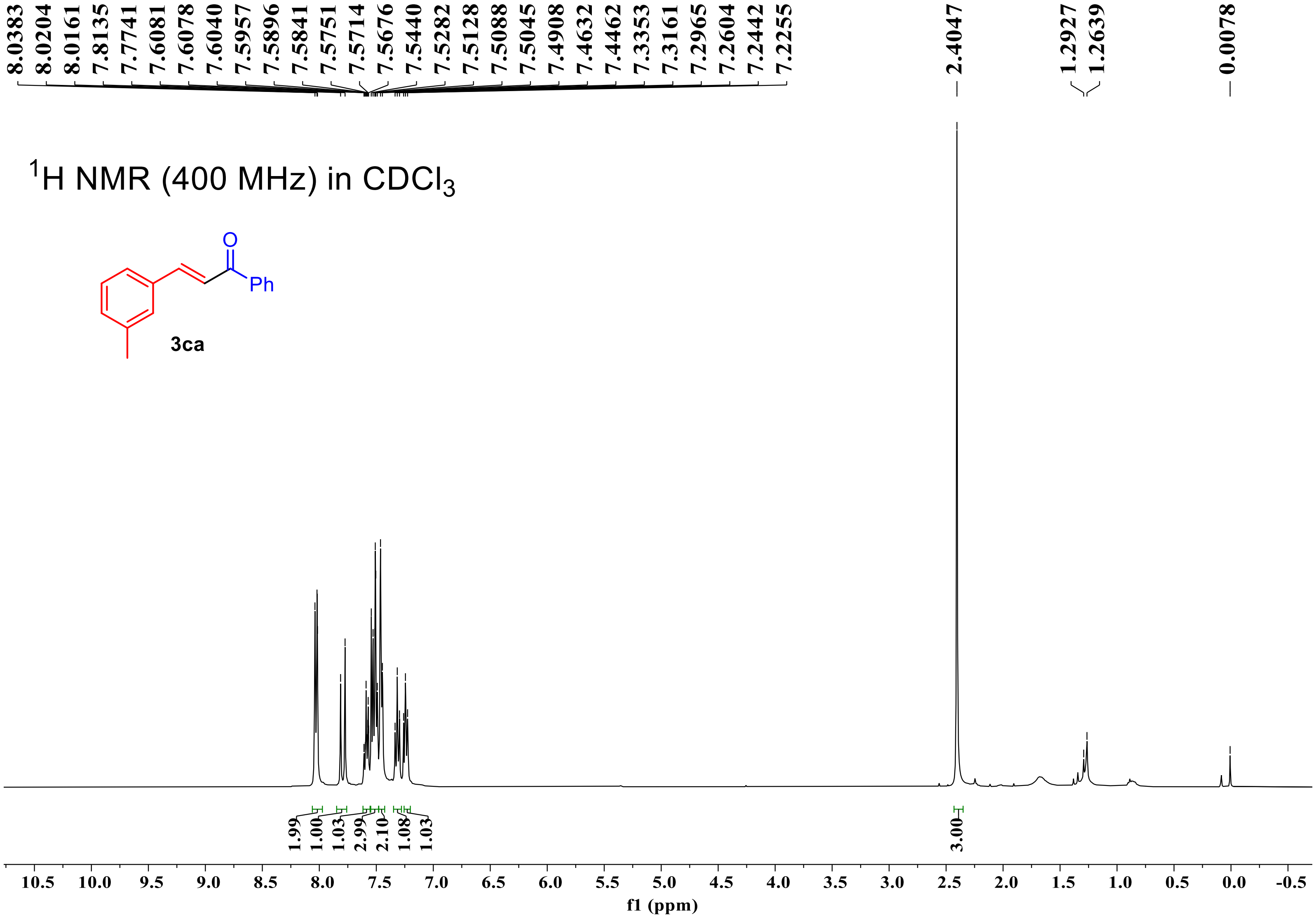
***d*$_1$-2f**

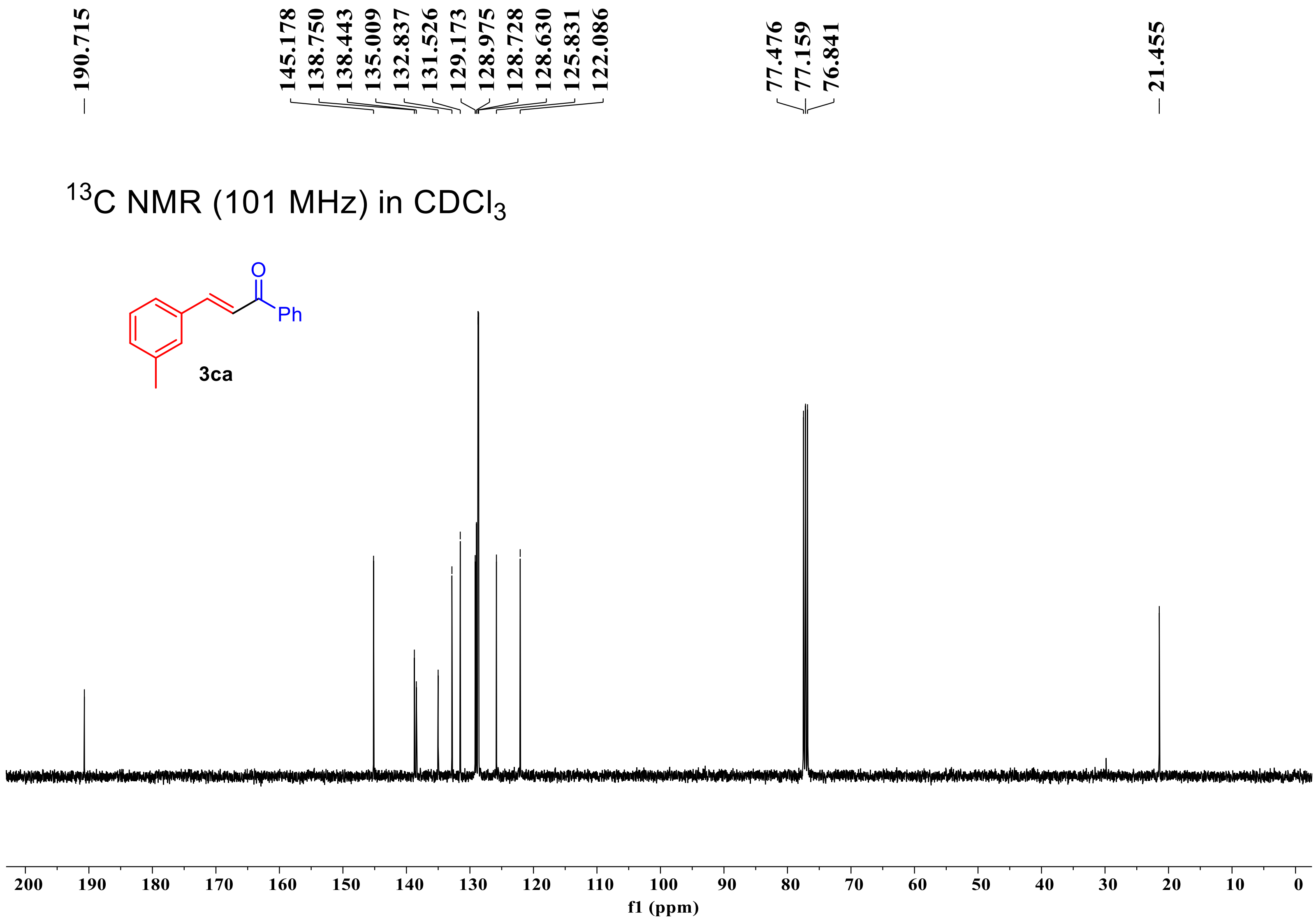

8.0365
8.0193
8.0151
7.8390
7.7998
7.6641
7.6552
7.6457
7.6401
7.6113
7.6078
7.5992
7.5930
7.5874
7.5781
7.5746
7.5707
7.5572
7.5305
7.5177
7.5112
7.4974
7.4933
7.4332
7.4301
7.4226
7.4163
7.2601
^{1}H NMR (400 MHz) in $CDCl_3$
O
Ph
3aa
2.00
1.03
2.05
4.34
3.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

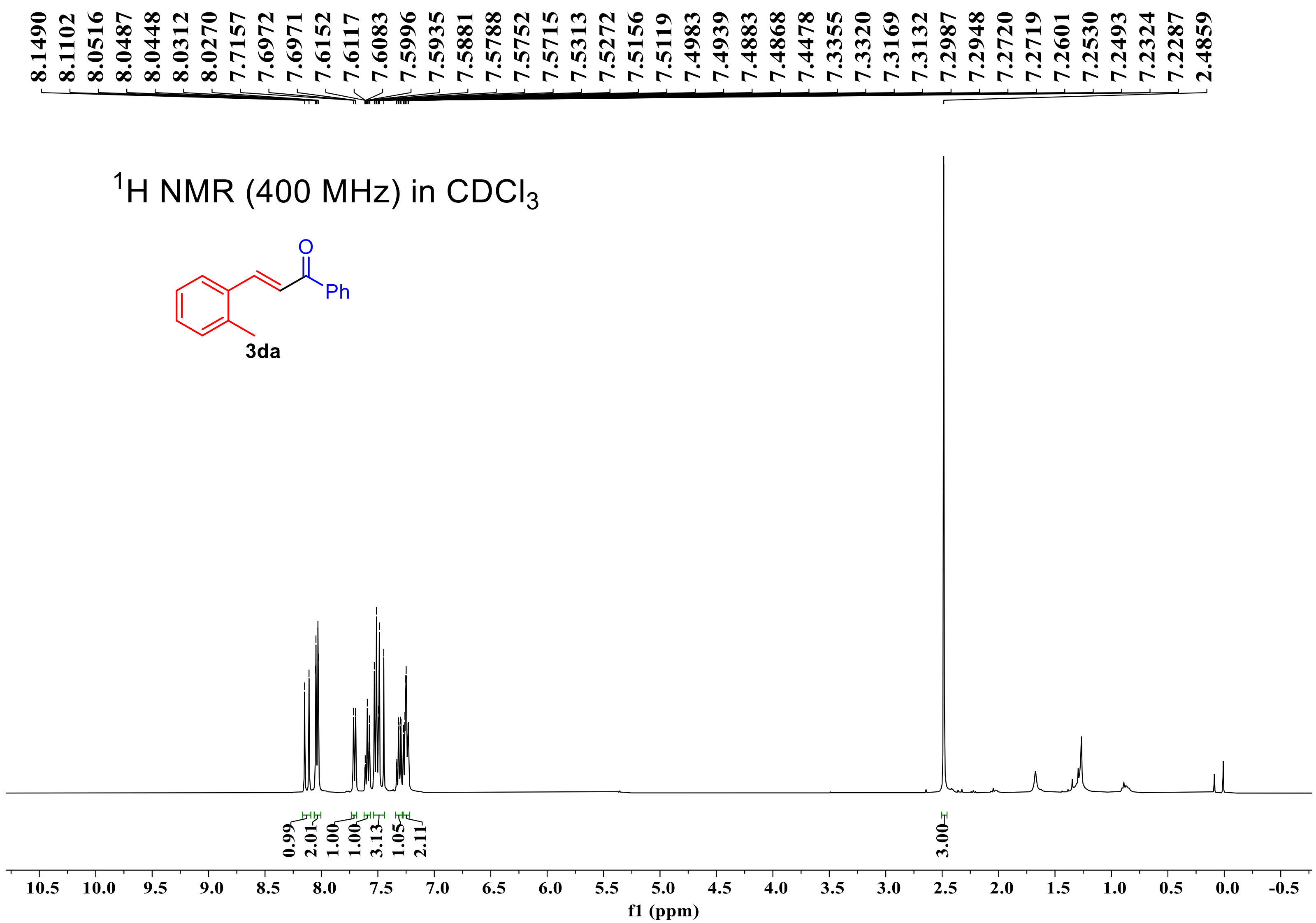

190.709
144.982
138.401
135.076
132.909
130.674
129.109
128.770
128.653
128.588
122.313
77.476
77.160
76.841
^{13}C NMR (101 MHz) in $CDCl_3$
O
Ph
3aa
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

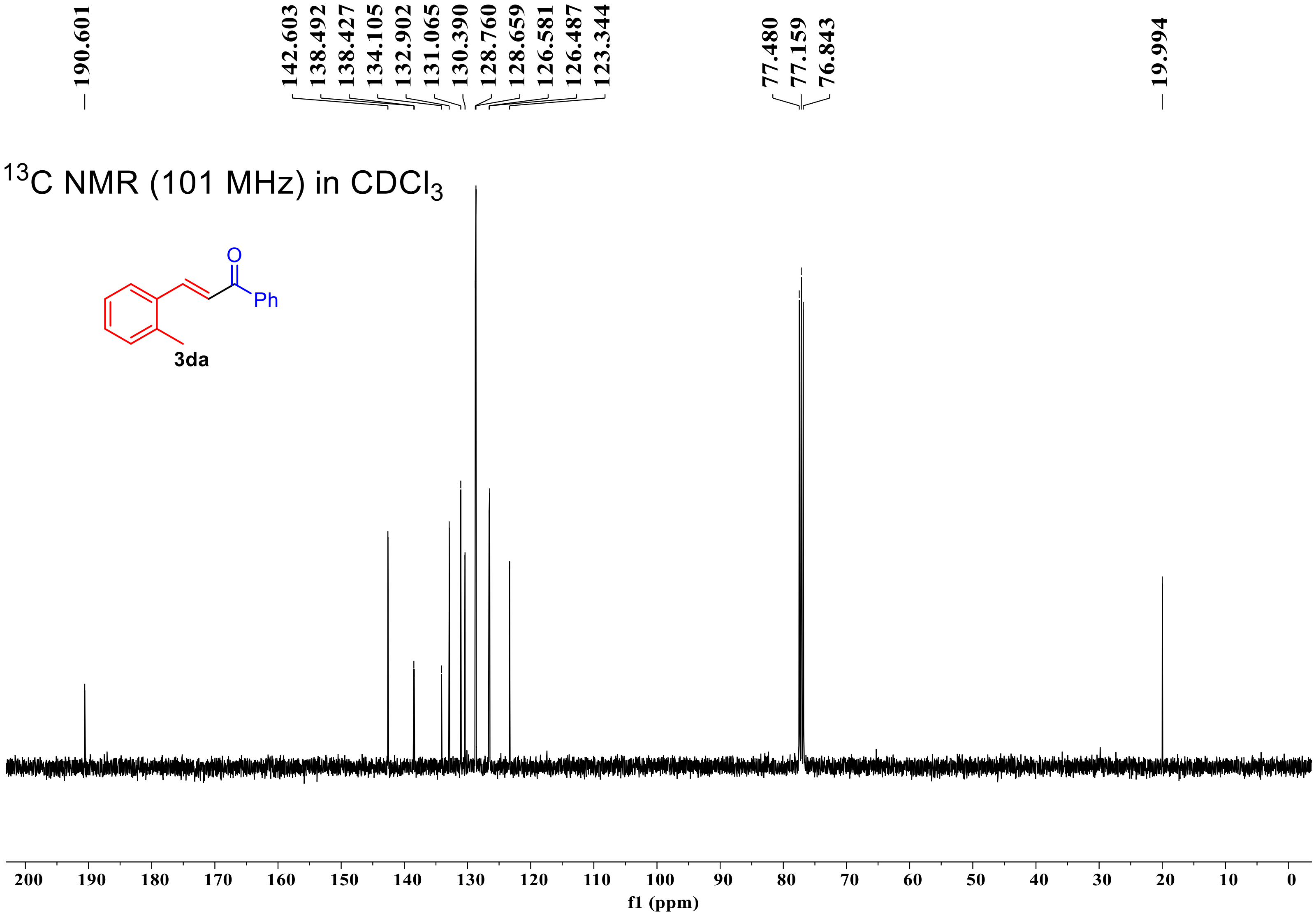

8.0292
8.0249
8.0110
8.0067
7.8197
7.7804
7.6061
7.6026
7.5984
7.5841
7.5663
7.5608
7.5405
7.5238
7.5162
7.5150
7.5080
7.5043
7.4862
7.4757
7.2604
7.2413
7.2215
2.3988
^{1}H NMR (400 MHz) in $CDCl_3$
O
Ph
3ba
1.94
1.02
2.85
2.99
1.96
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

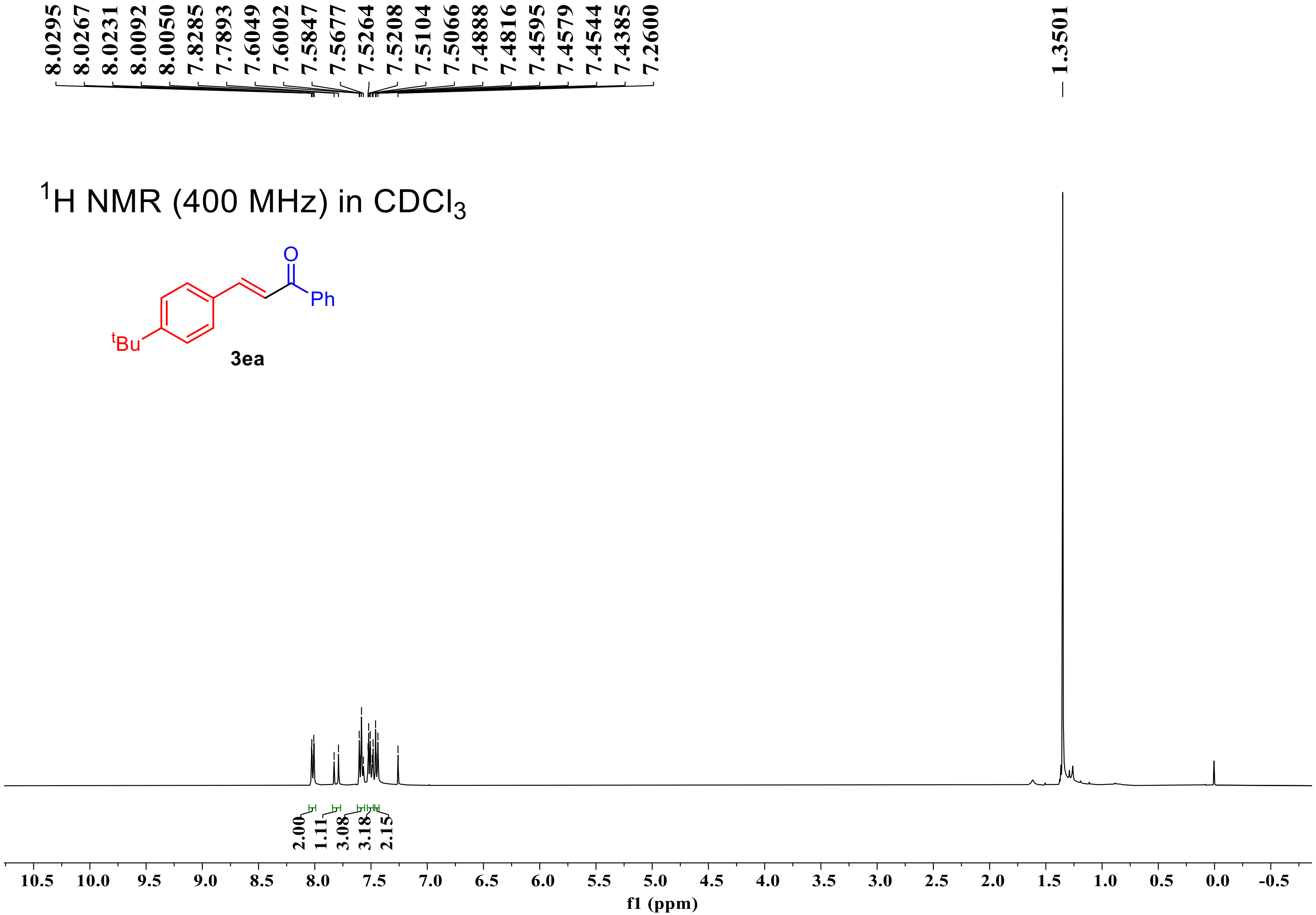

190.799
145.080
141.216
138.562
132.783
132.352
129.852
128.722
128.620
121.323
77.485
77.168
76.850
21.664
13C NMR (101 MHz) in CDCl3
O
Ph
3ba
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

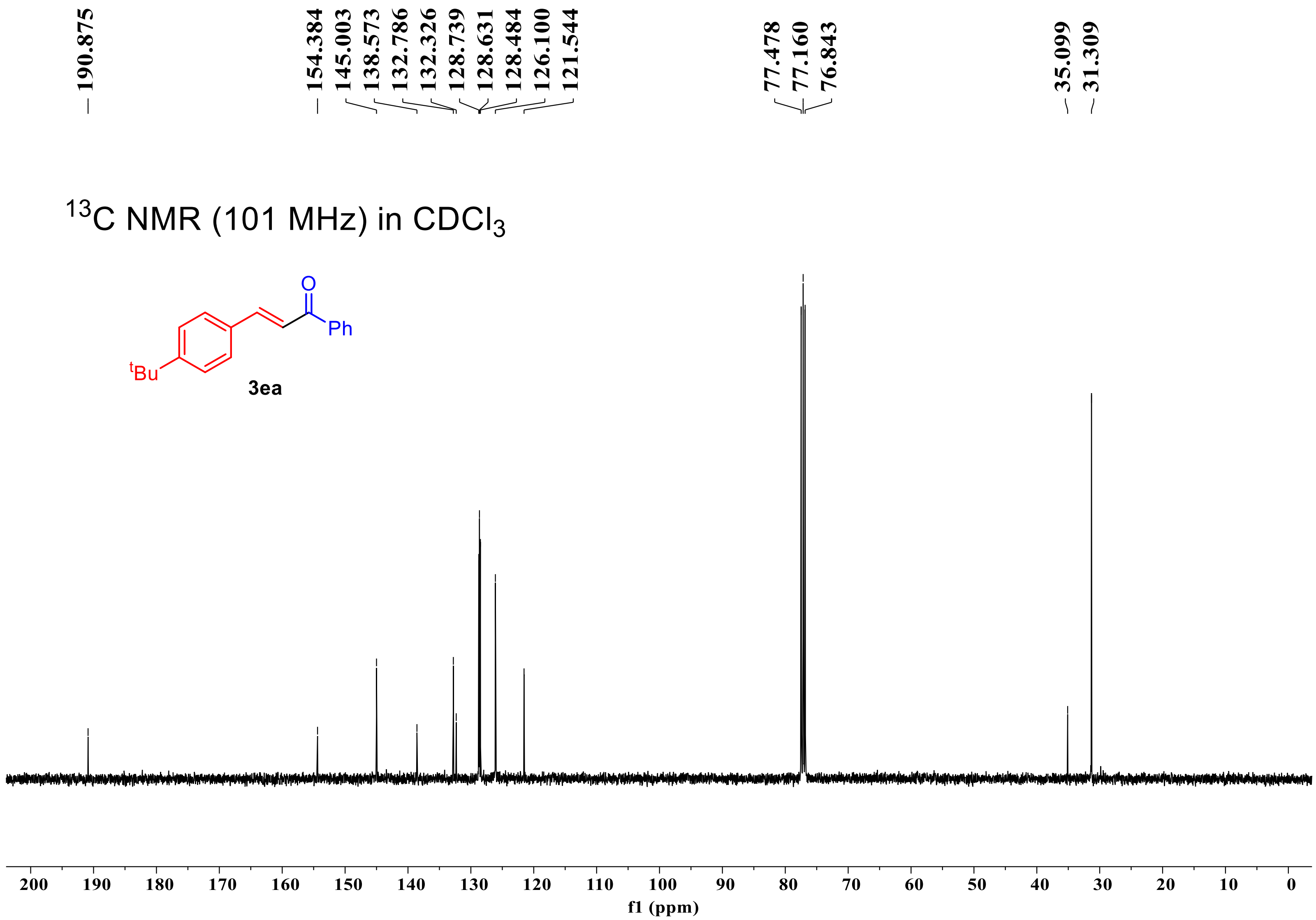

8.0383
8.0204
8.0161
7.8135
7.7741
7.6081
7.6078
7.6040
7.5957
7.5896
7.5841
7.5751
7.5714
7.5676
7.5440
7.5282
7.5128
7.5088
7.5045
7.4908
7.4632
7.4462
7.3353
7.3161
7.2965
7.2604
7.2442
7.2255
2.4047
1.2927
1.2639
0.0078
^{1}H NMR (400 MHz) in $CDCl_3$
O
Ph
3ca
1.99
1.00
1.03
2.99
2.10
1.08
1.03
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


190.715
145.178
138.750
138.443
135.009
132.837
131.526
129.173
128.975
128.728
128.630
125.831
122.086
77.476
77.159
76.841
21.455
^{13}C NMR (101 MHz) in $CDCl_3$
O
Ph
3ca
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

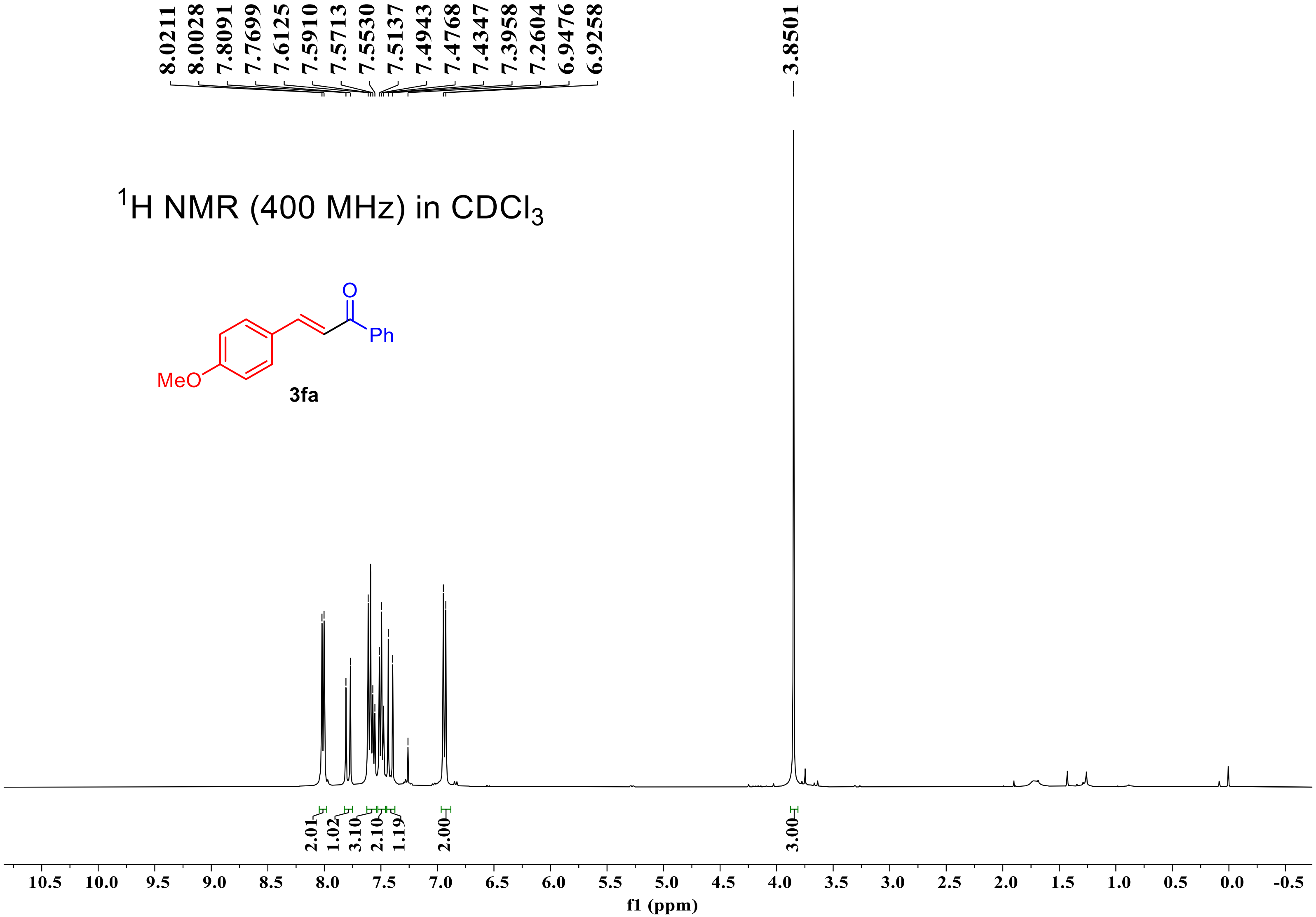

8.1490
8.1102
8.0516
8.0487
8.0448
8.0312
8.0270
7.7157
7.6972
7.6971
7.6152
7.6117
7.6083
7.5996
7.5935
7.5881
7.5788
7.5752
7.5715
7.5313
7.5272
7.5156
7.5119
7.4983
7.4939
7.4883
7.4868
7.4478
7.3355
7.3320
7.3169
7.3132
7.2987
7.2948
7.2720
7.2719
7.2601
7.2530
7.2493
7.2324
7.2287
2.4859
^{1}H NMR (400 MHz) in $CDCl_3$
O
Ph
3da
0.99
2.01
1.00
1.00
3.13
1.05
2.11
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


190.601
142.603
138.492
138.427
134.105
132.902
131.065
130.390
128.760
128.659
126.581
126.487
123.344
77.480
77.159
76.843
19.994
13C NMR (101 MHz) in CDCl3
O
Ph
3da
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.0295
8.0267
8.0231
8.0092
8.0050
7.8285
7.7893
7.6049
7.6002
7.5847
7.5677
7.5264
7.5208
7.5104
7.5066
7.4888
7.4816
7.4595
7.4579
7.4544
7.4385
7.2600
1.3501
1H NMR (400 MHz) in CDCl3
O
Ph
tBu
3ea
2.00
1.11
3.08
3.18
2.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

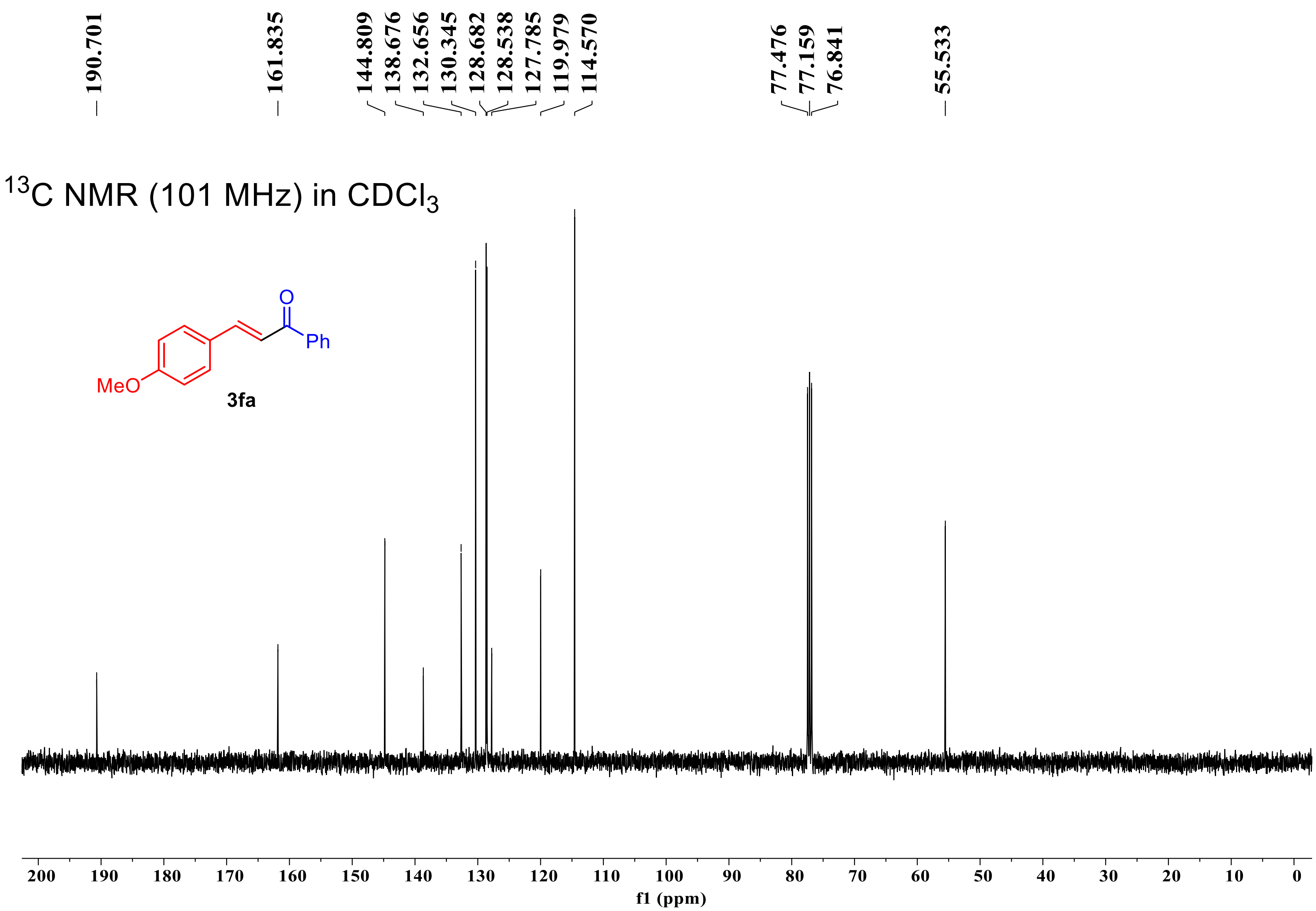


190.875
154.384
145.003
138.573
132.786
132.326
128.739
128.631
128.484
126.100
121.544
77.478
77.160
76.843
35.099
31.309
^{13}C NMR (101 MHz) in $CDCl_3$
O
Ph
^{t}Bu
3ea
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

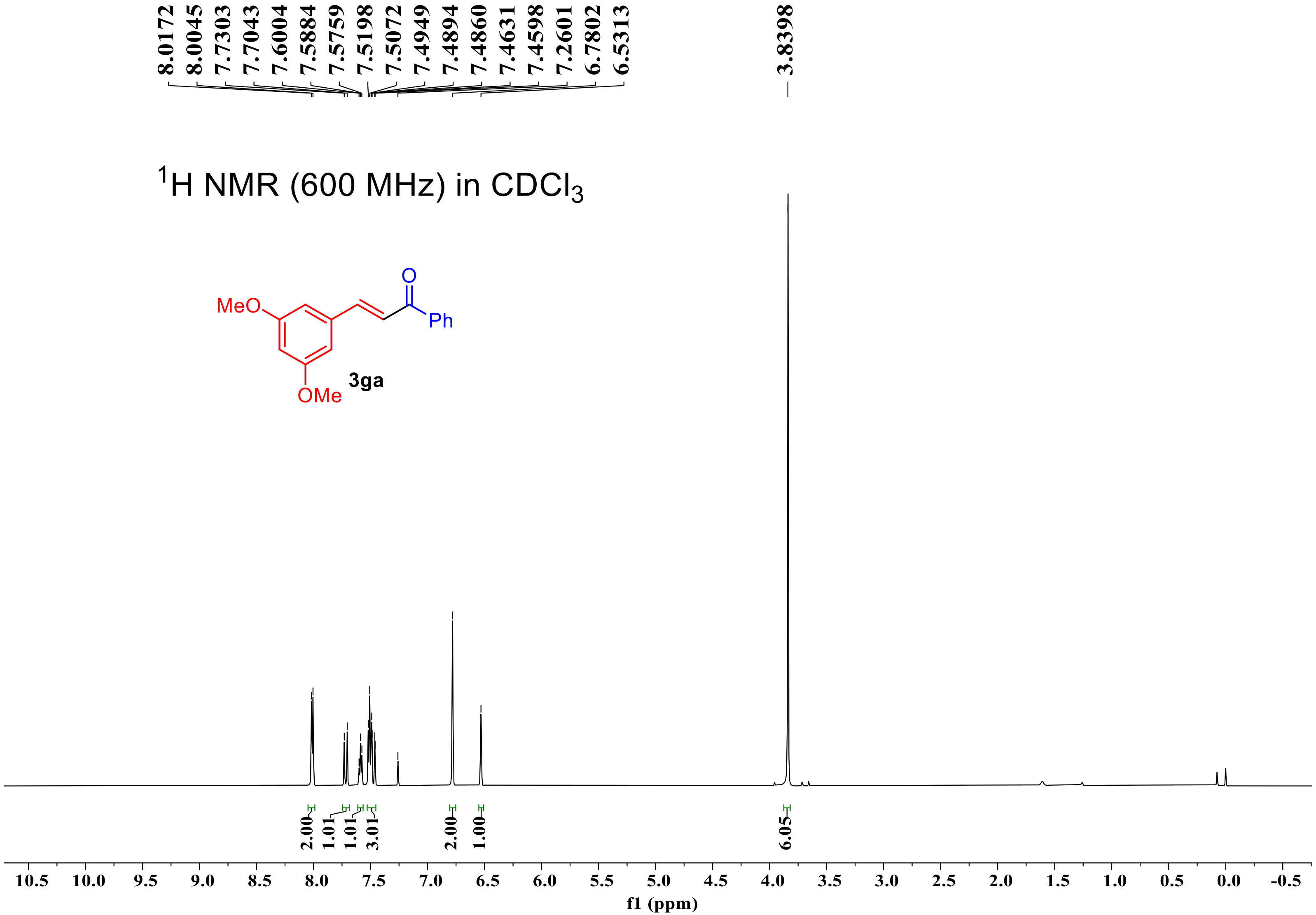


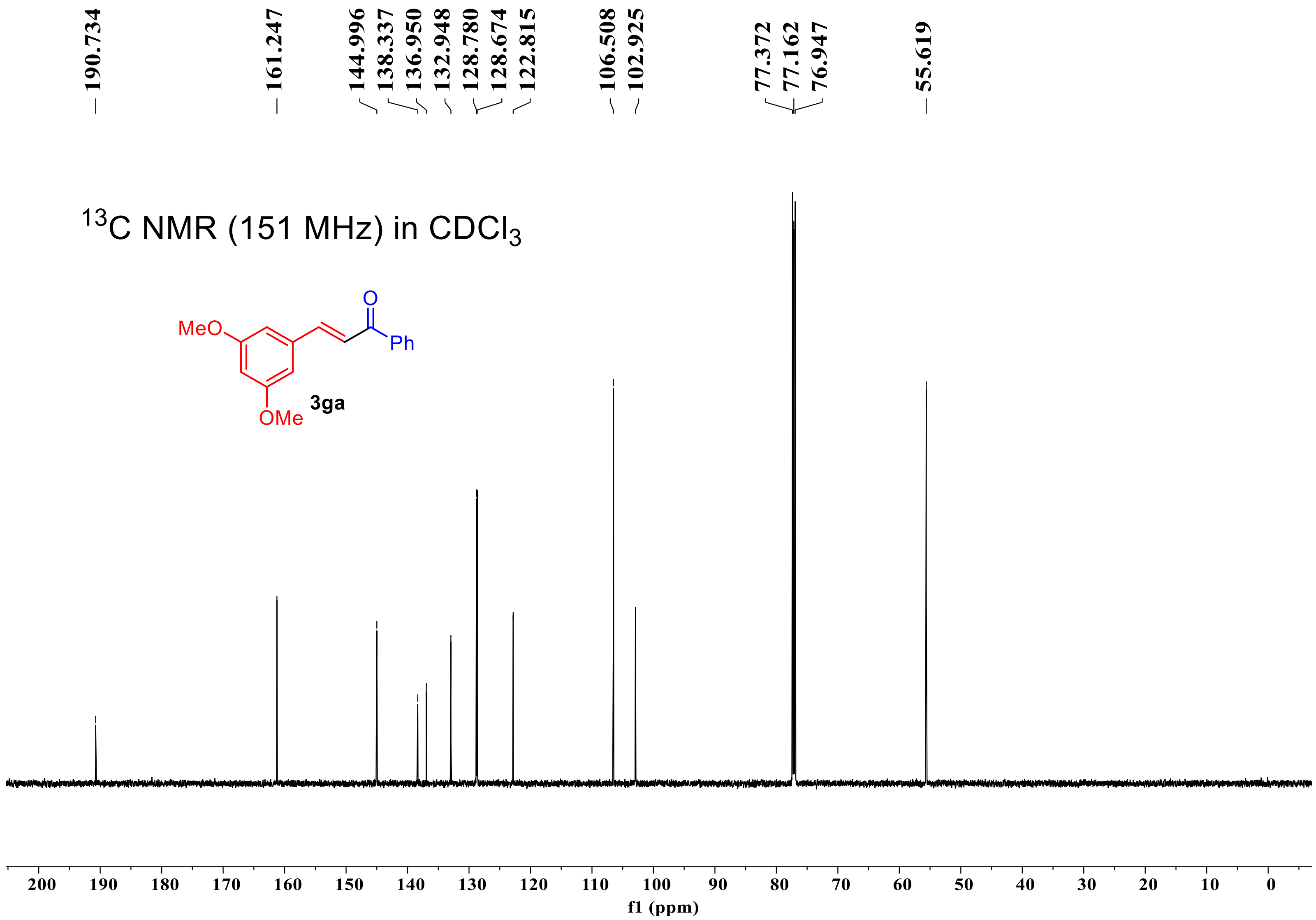
[1]H NMR (400 MHz) in $CDCl_3$

3fa

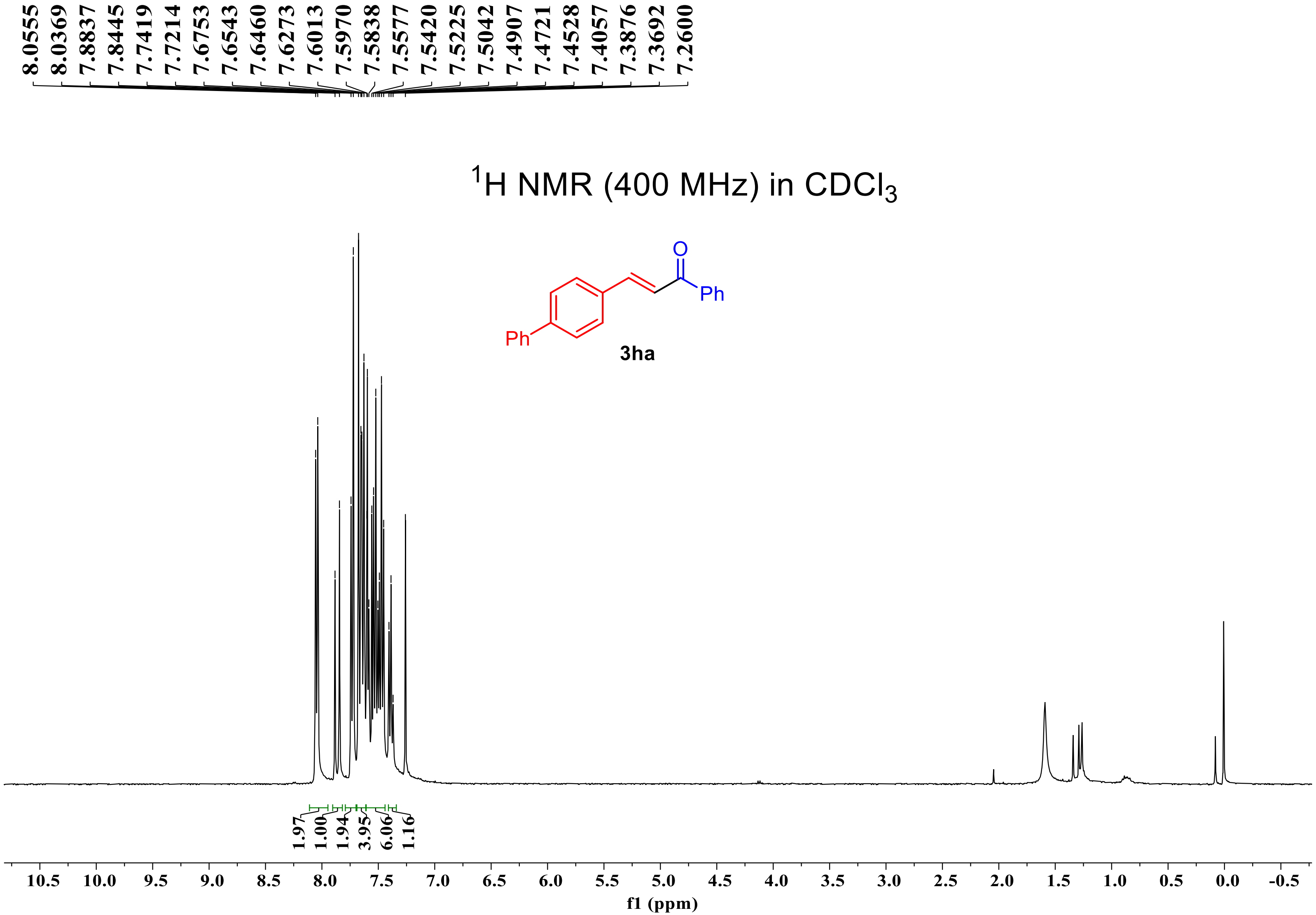


190.701
161.835
144.809
138.676
132.656
130.345
128.682
128.538
127.785
119.979
114.570
77.476
77.159
76.841
55.533
13C NMR (101 MHz) in CDCl3
O
Ph
MeO
3fa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

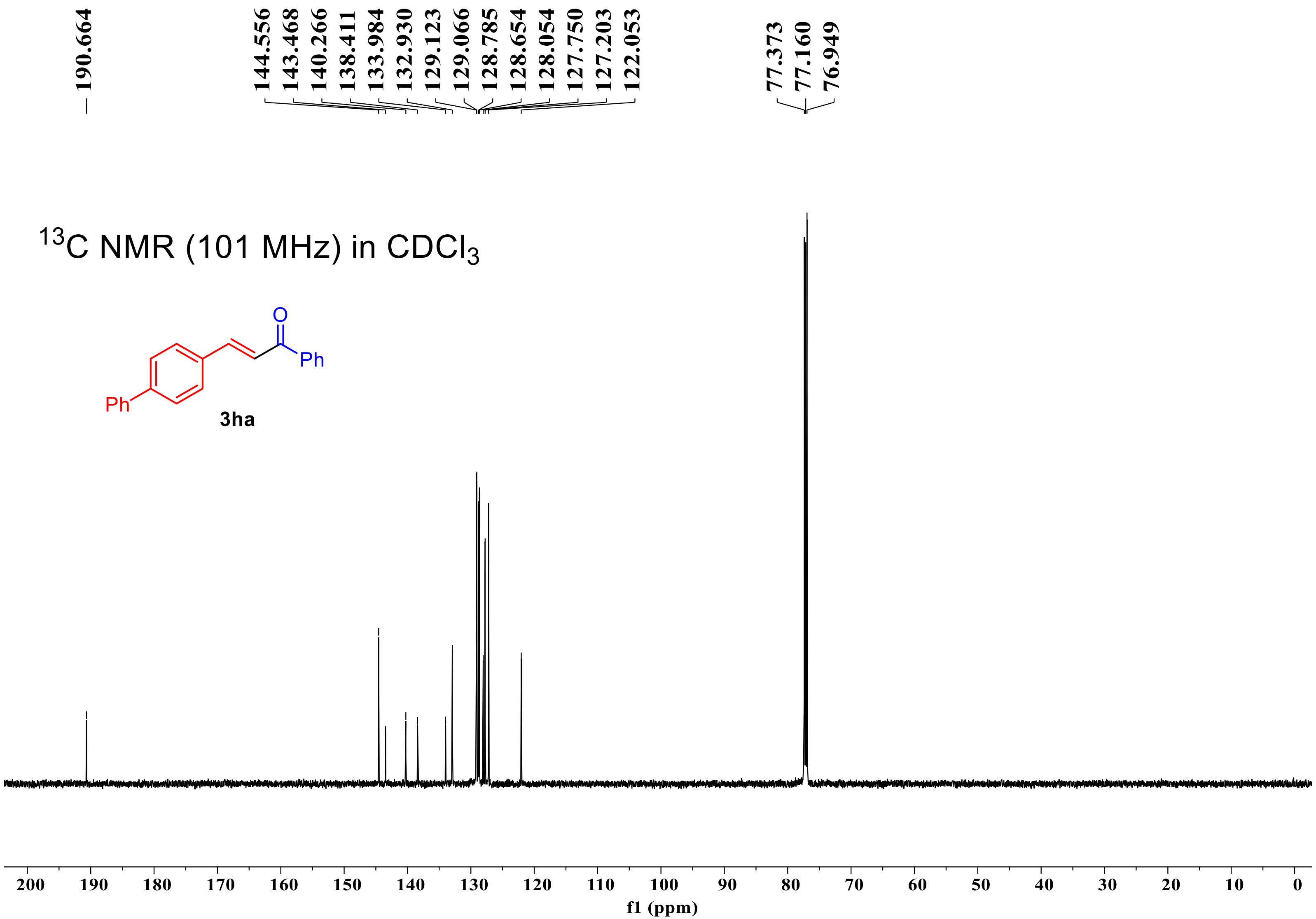

8.0172
8.0045
7.7303
7.7043
7.6004
7.5884
7.5759
7.5198
7.5072
7.4949
7.4894
7.4860
7.4631
7.4598
7.2601
6.7802
6.5313
3.8398
1H NMR (600 MHz) in CDCl3
MeO
O
Ph
OMe
3ga
2.00
1.01
1.01
3.01
2.00
1.00
6.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

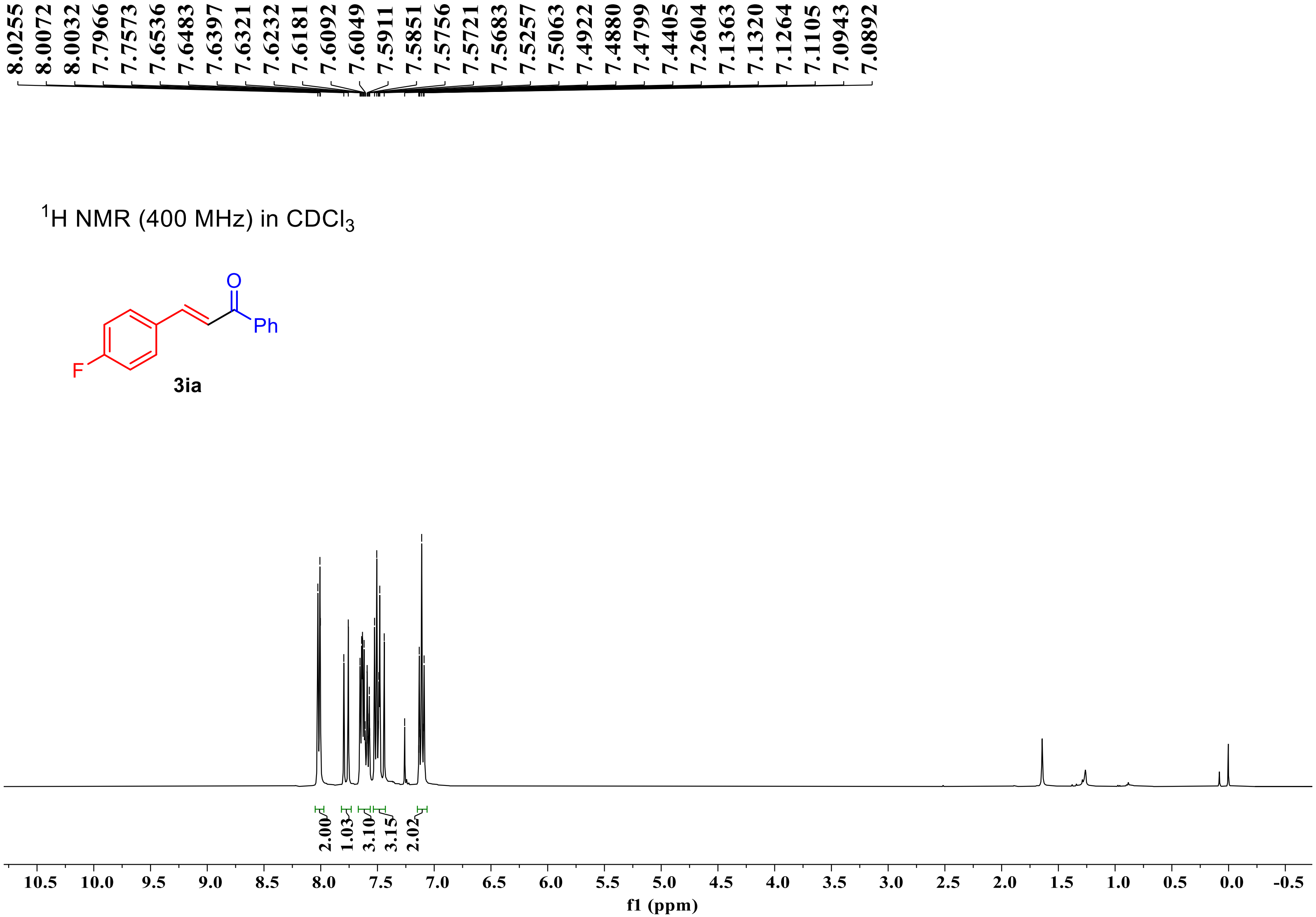

190.734
161.247
144.996
138.337
136.950
132.948
128.780
128.674
122.815
106.508
102.925
77.372
77.162
76.947
55.619
13C NMR (151 MHz) in CDCl3
MeO
O
Ph
3ga
OMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

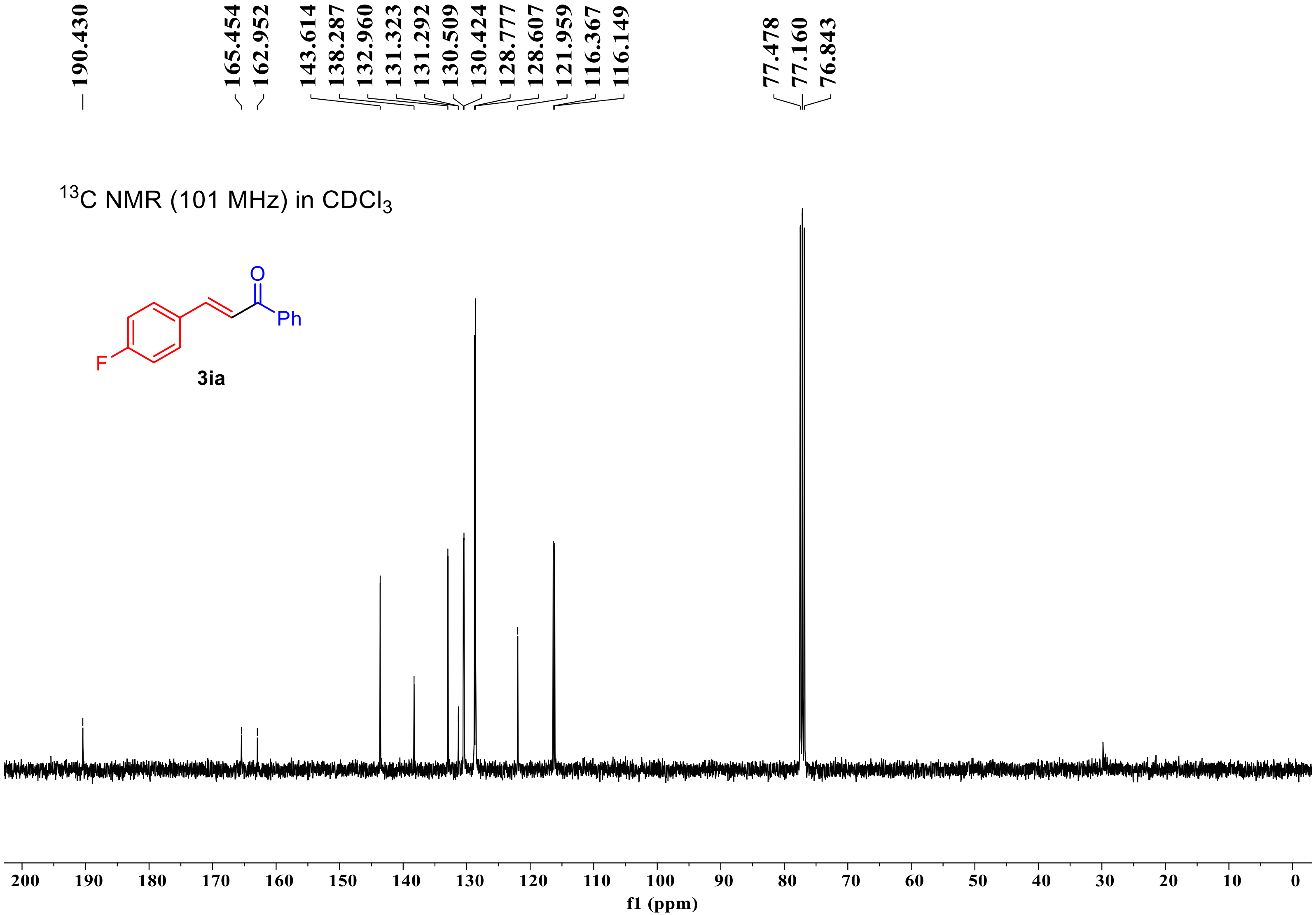
^1H NMR (400 MHz) in $CDCl_3$



^{13}C NMR (101 MHz) in $CDCl_3$



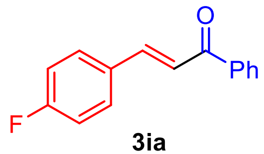

8.0255
8.0072
8.0032
7.7966
7.7573
7.6536
7.6483
7.6397
7.6321
7.6232
7.6181
7.6092
7.6049
7.5911
7.5851
7.5756
7.5721
7.5683
7.5257
7.5063
7.4922
7.4880
7.4799
7.4405
7.2604
7.1363
7.1320
7.1264
7.1105
7.0943
7.0892
^{1}H NMR (400 MHz) in $CDCl_3$
O
Ph
F
3ia
2.00
1.03
3.10
3.15
2.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



^{13}C NMR (101 MHz) in $CDCl_3$

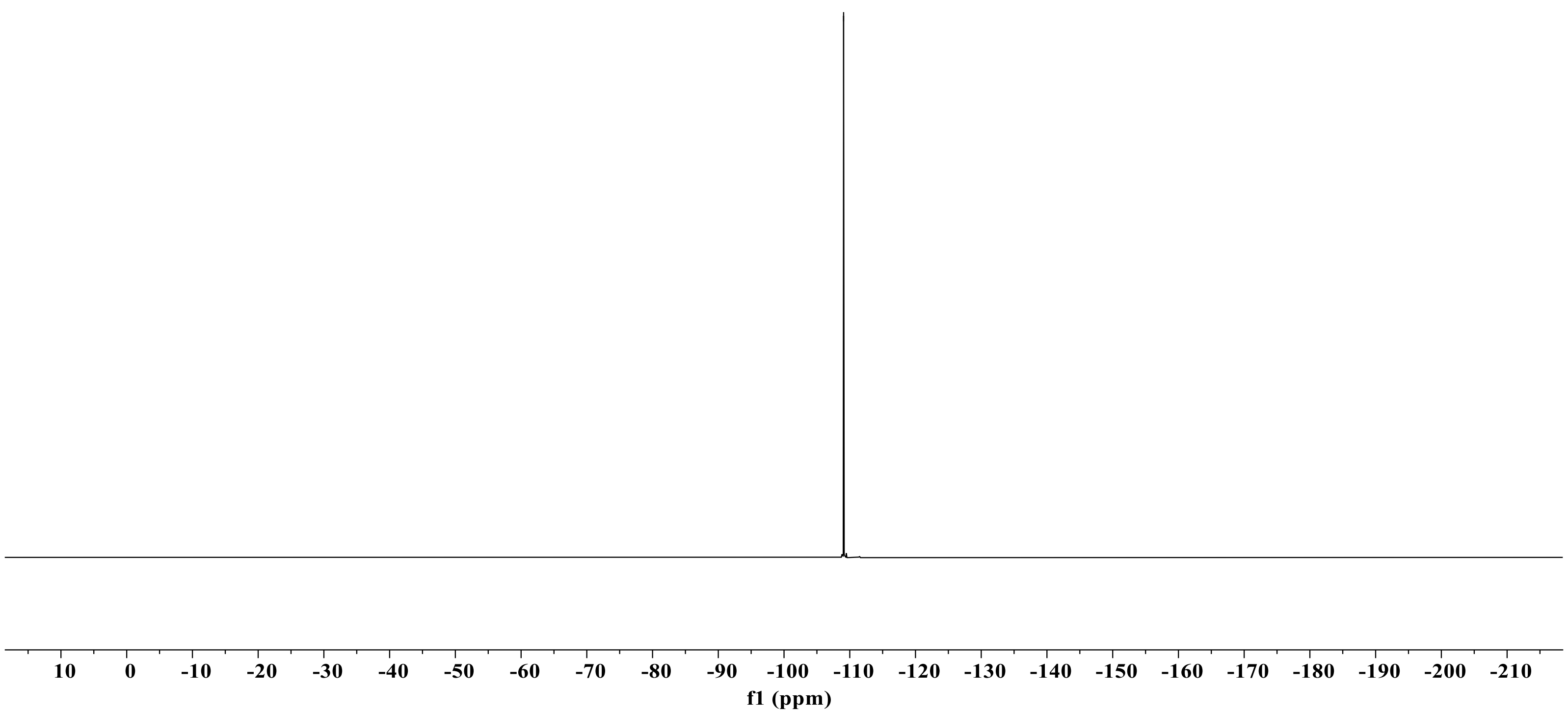
3ia

^{19}F NMR (377 MHz) in $CDCl_3$

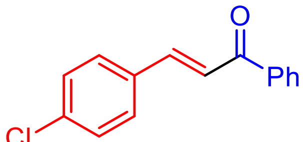


3ia

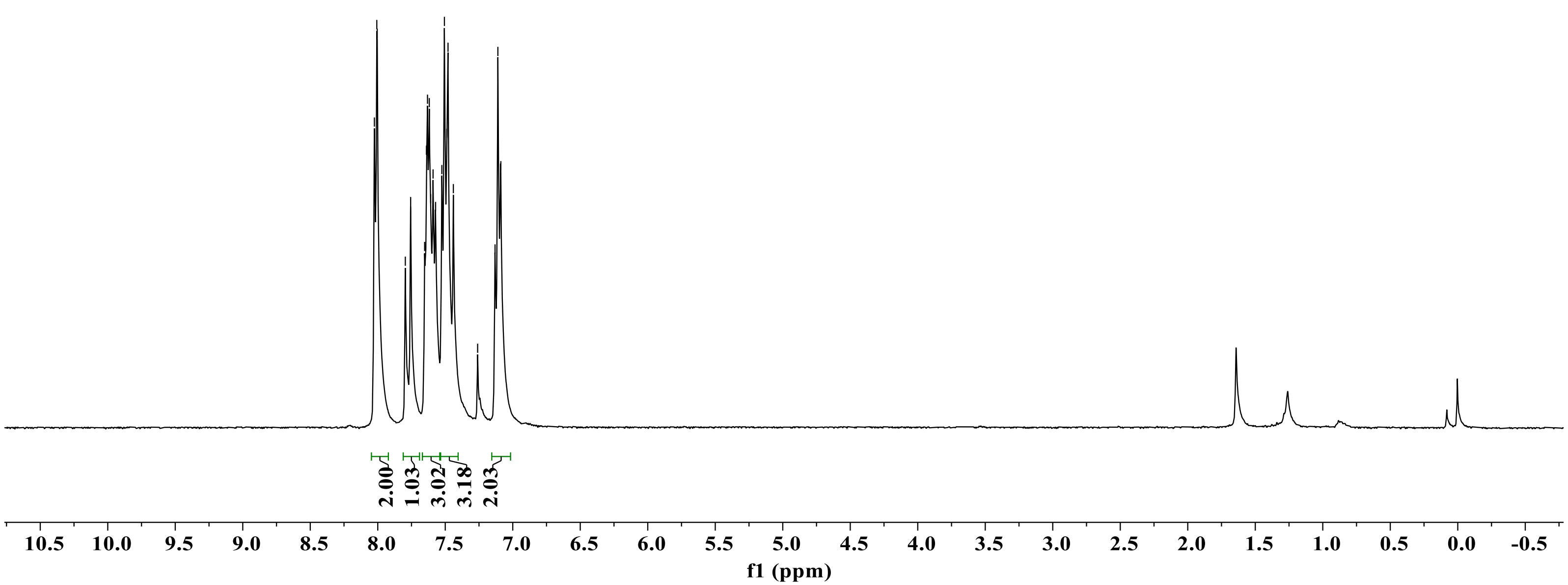
-109.0616



^1H NMR (400 MHz) in $CDCl_3$



3ja

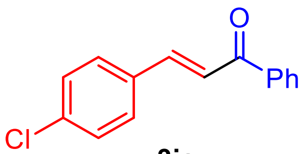


190.317

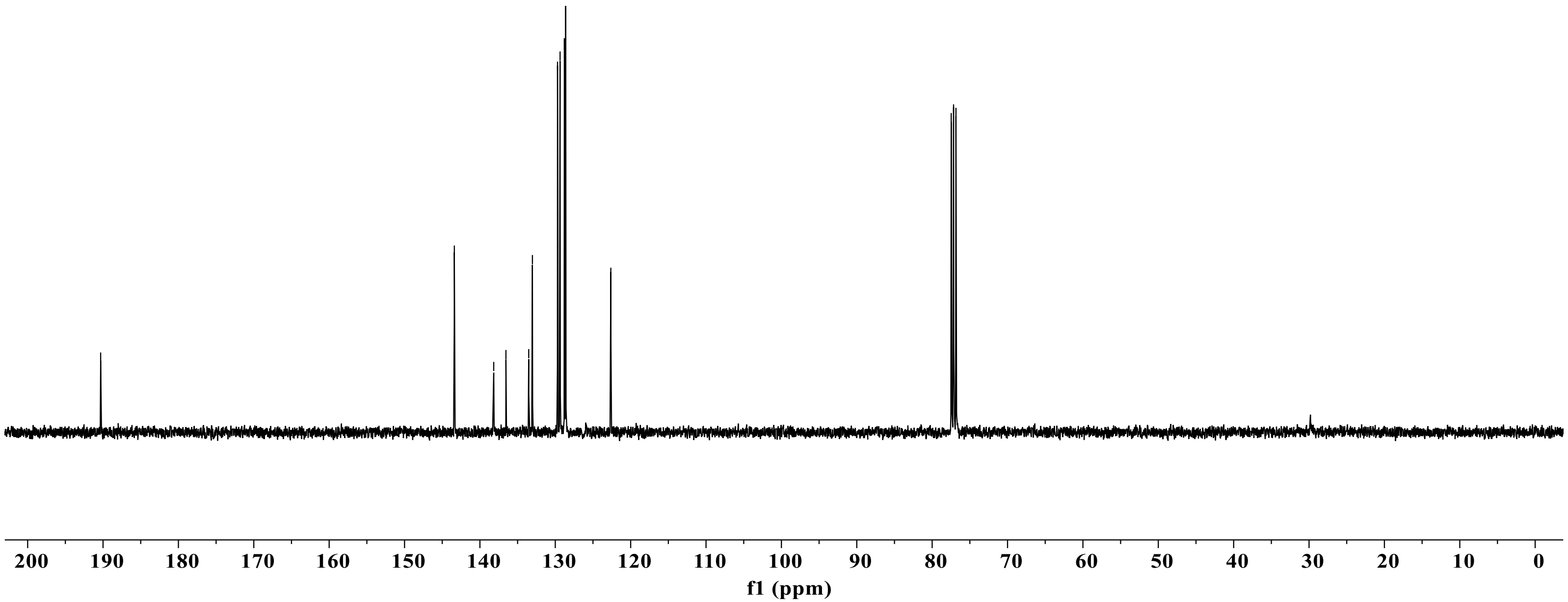
143.392
138.169
136.548
133.529
133.033
129.702
129.364
128.791
128.617
122.631

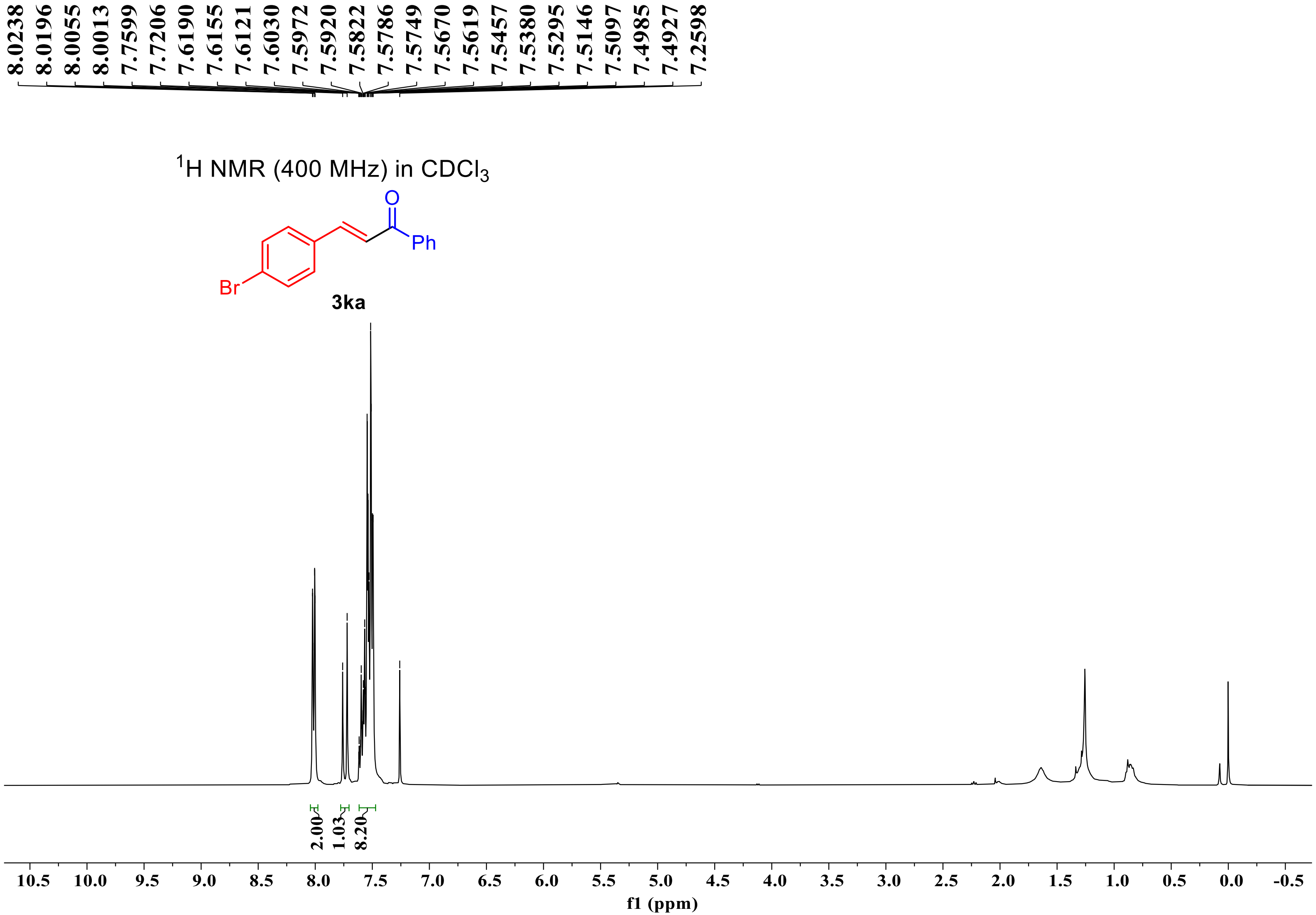
77.476
77.159
76.841

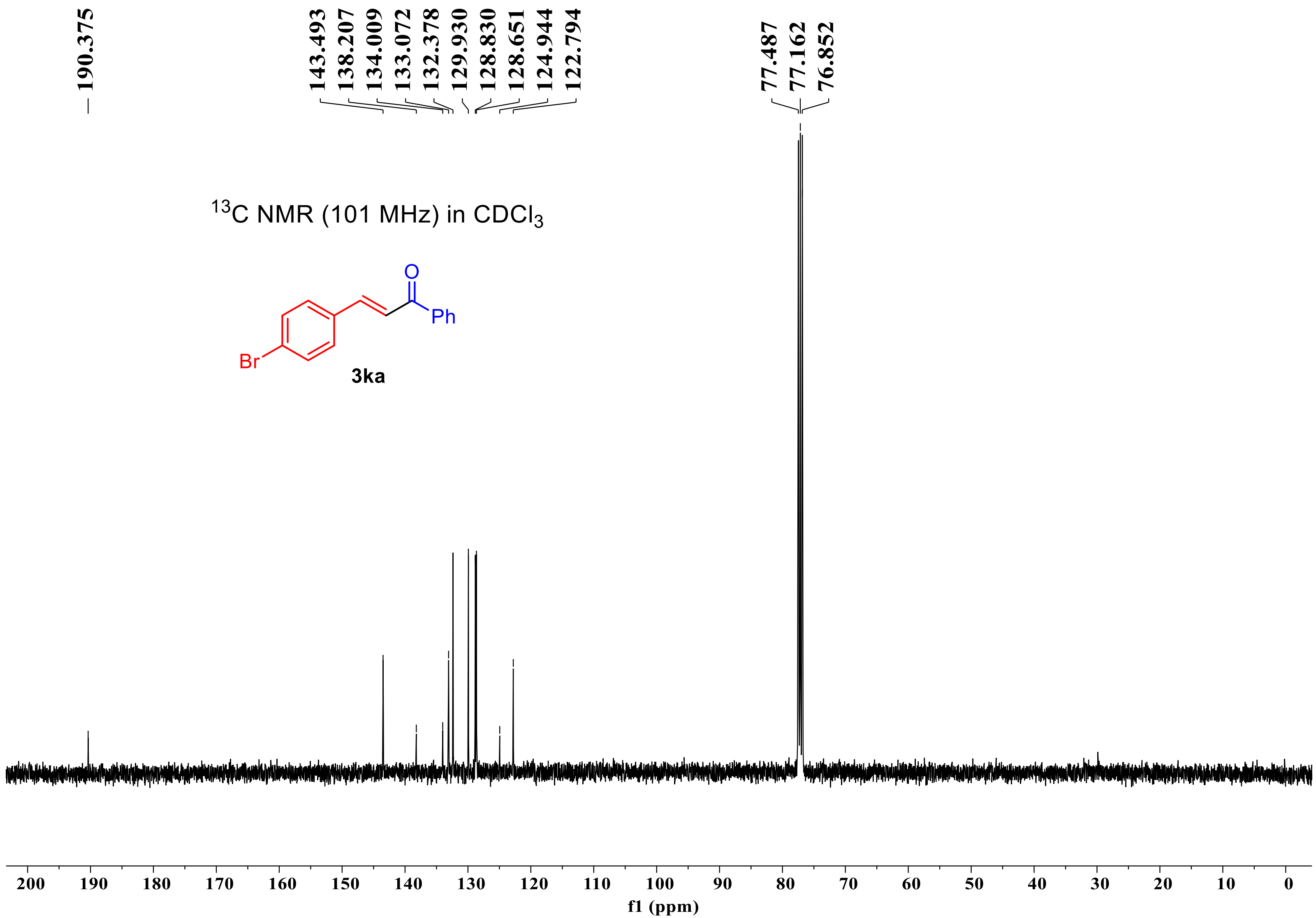
^{13}C NMR (101 MHz) in $CDCl_3$

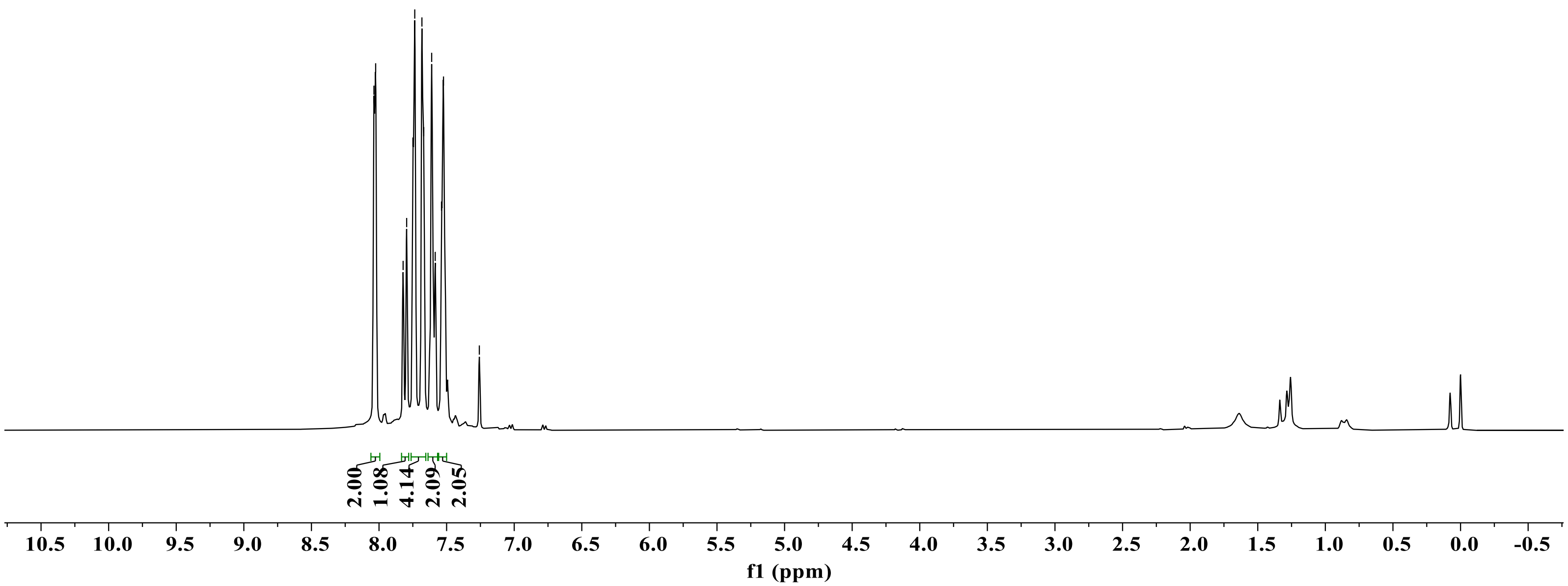


3ja

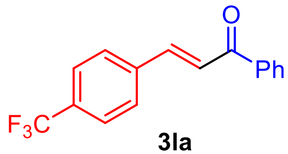



8.0238
8.0196
8.0055
8.0013
7.7599
7.7206
7.6190
7.6155
7.6121
7.6030
7.5972
7.5920
7.5822
7.5786
7.5749
7.5670
7.5619
7.5457
7.5380
7.5295
7.5146
7.5097
7.4985
7.4927
7.2598
^{1}H NMR (400 MHz) in $CDCl_3$
O
Ph
Br
3ka
2.00
1.03
8.20
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

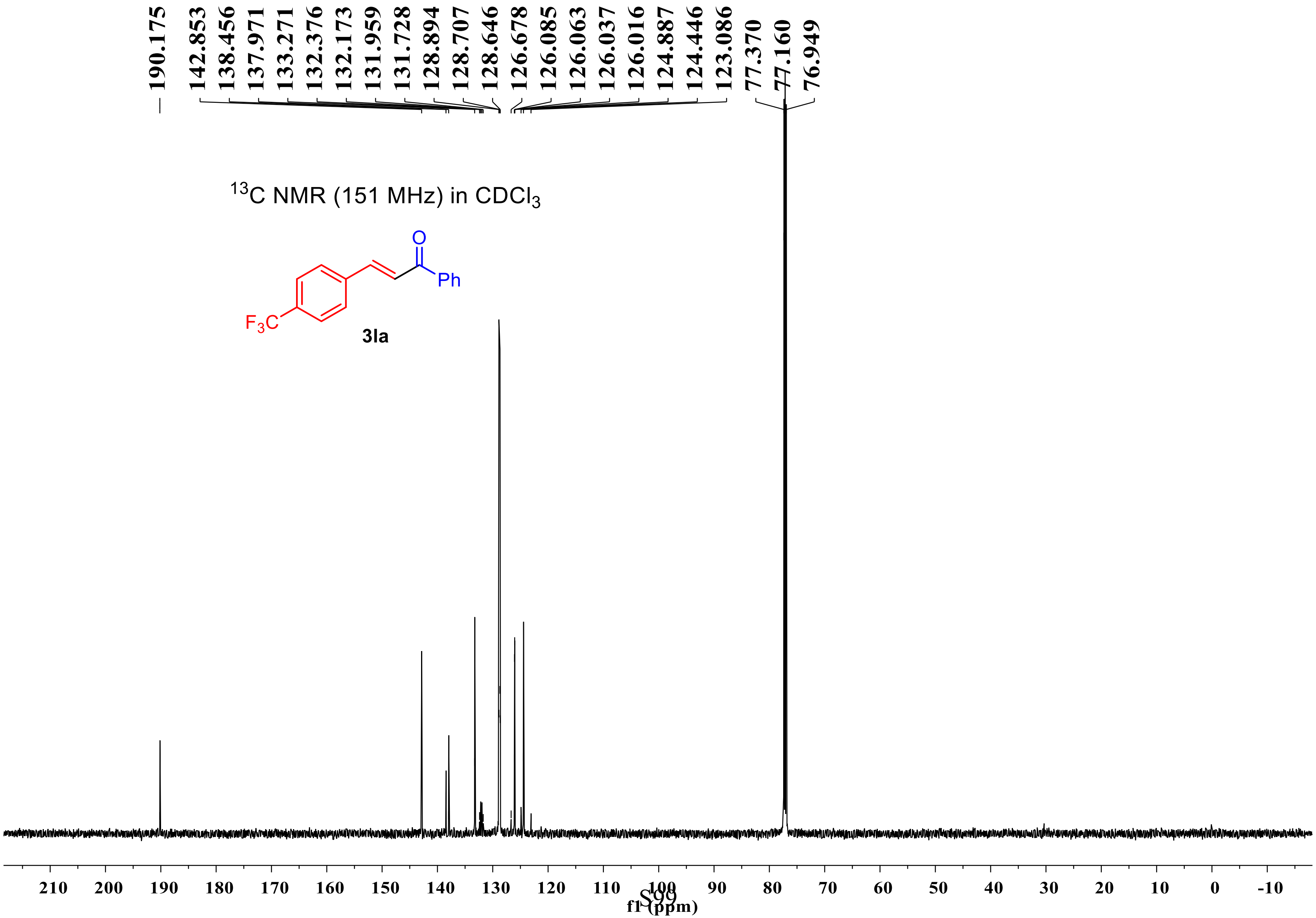

190.375
143.493
138.207
134.009
133.072
132.378
129.930
128.830
128.651
124.944
122.794
77.487
77.162
76.852
^{13}C NMR (101 MHz) in CDCl$_3$
O
Ph
Br
3ka
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



^{1}H NMR (600 MHz) in $CDCl_3$

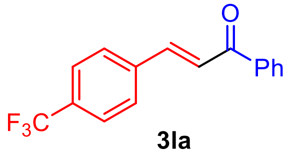


3la

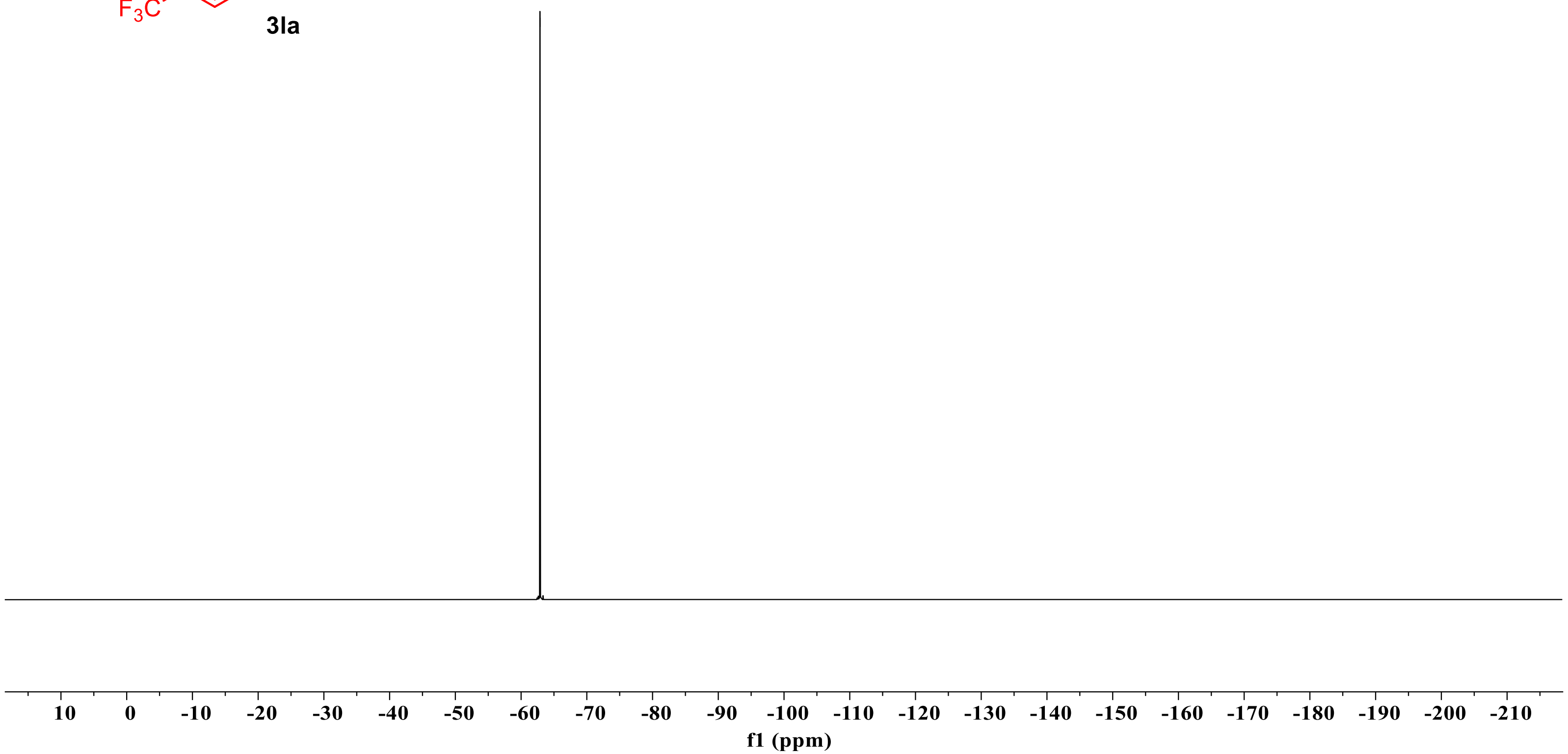

190.175
142.853
138.456
137.971
133.271
132.376
132.173
131.959
131.728
128.894
128.707
128.646
126.678
126.085
126.063
126.037
126.016
124.887
124.446
123.086
77.370
77.160
76.949
^{13}C NMR (151 MHz) in $CDCl_3$
O
Ph
F_3C
3la
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

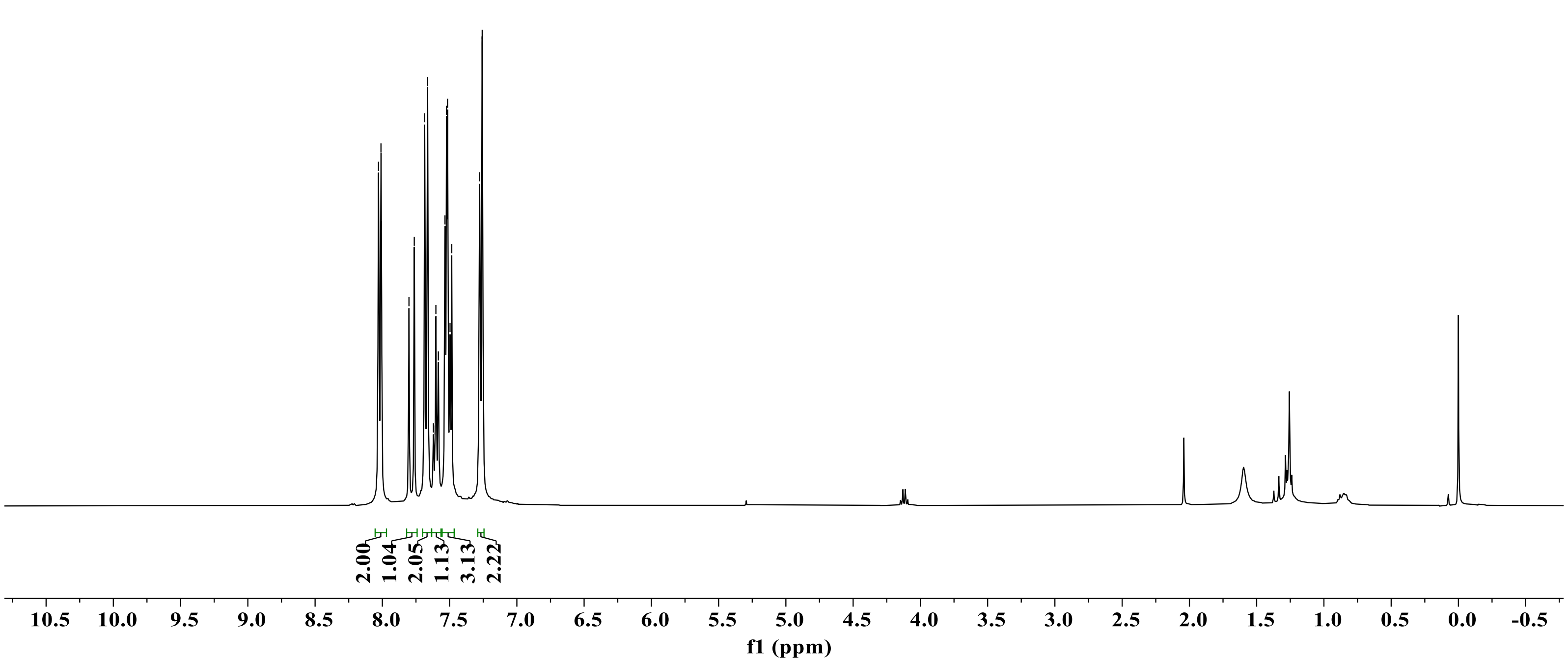
-62.8634

^{19}F NMR (377 MHz) in $CDCl_3$

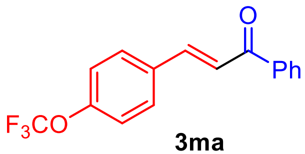


3la

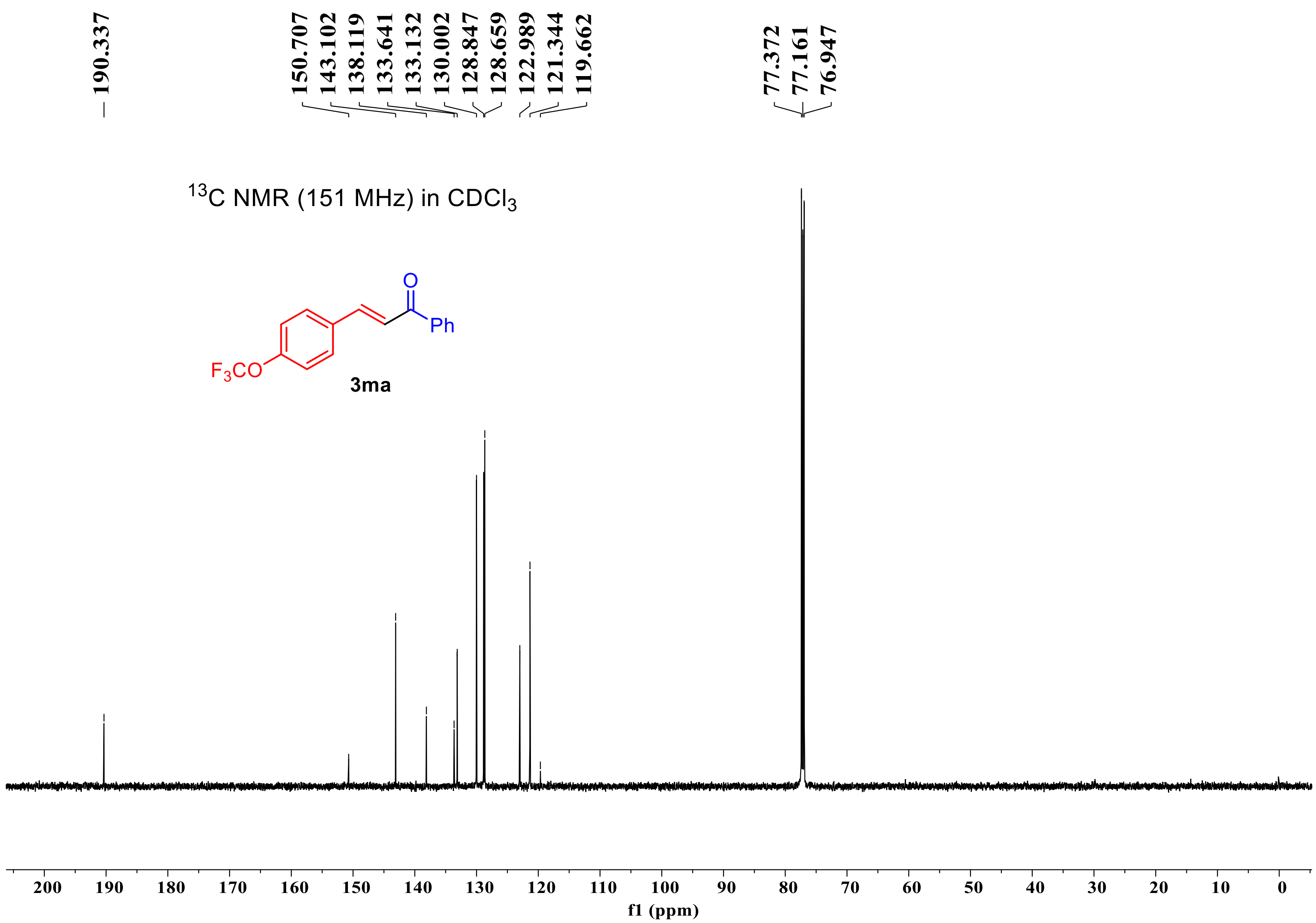




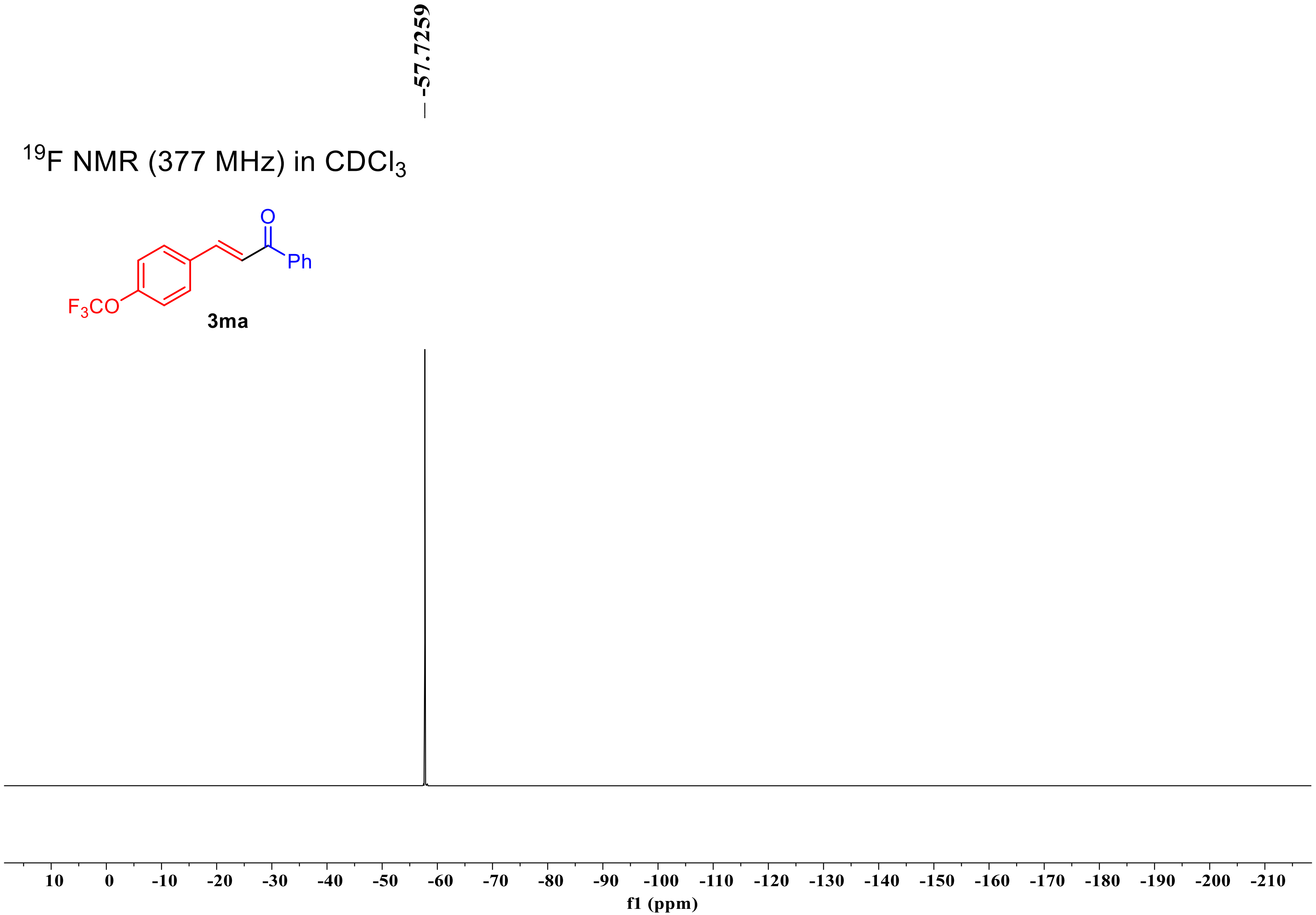
^{1}H NMR (400 MHz) in $CDCl_3$

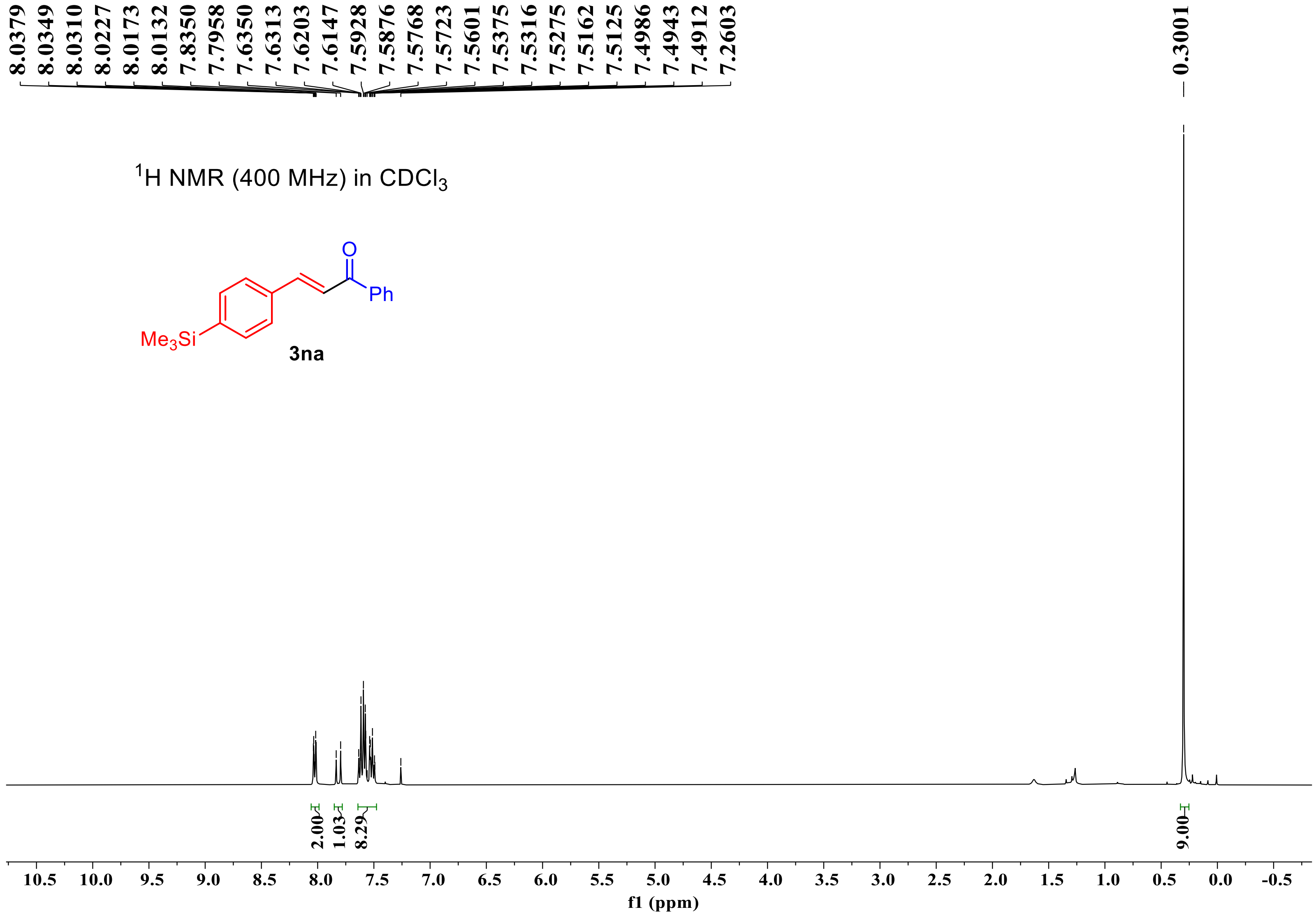


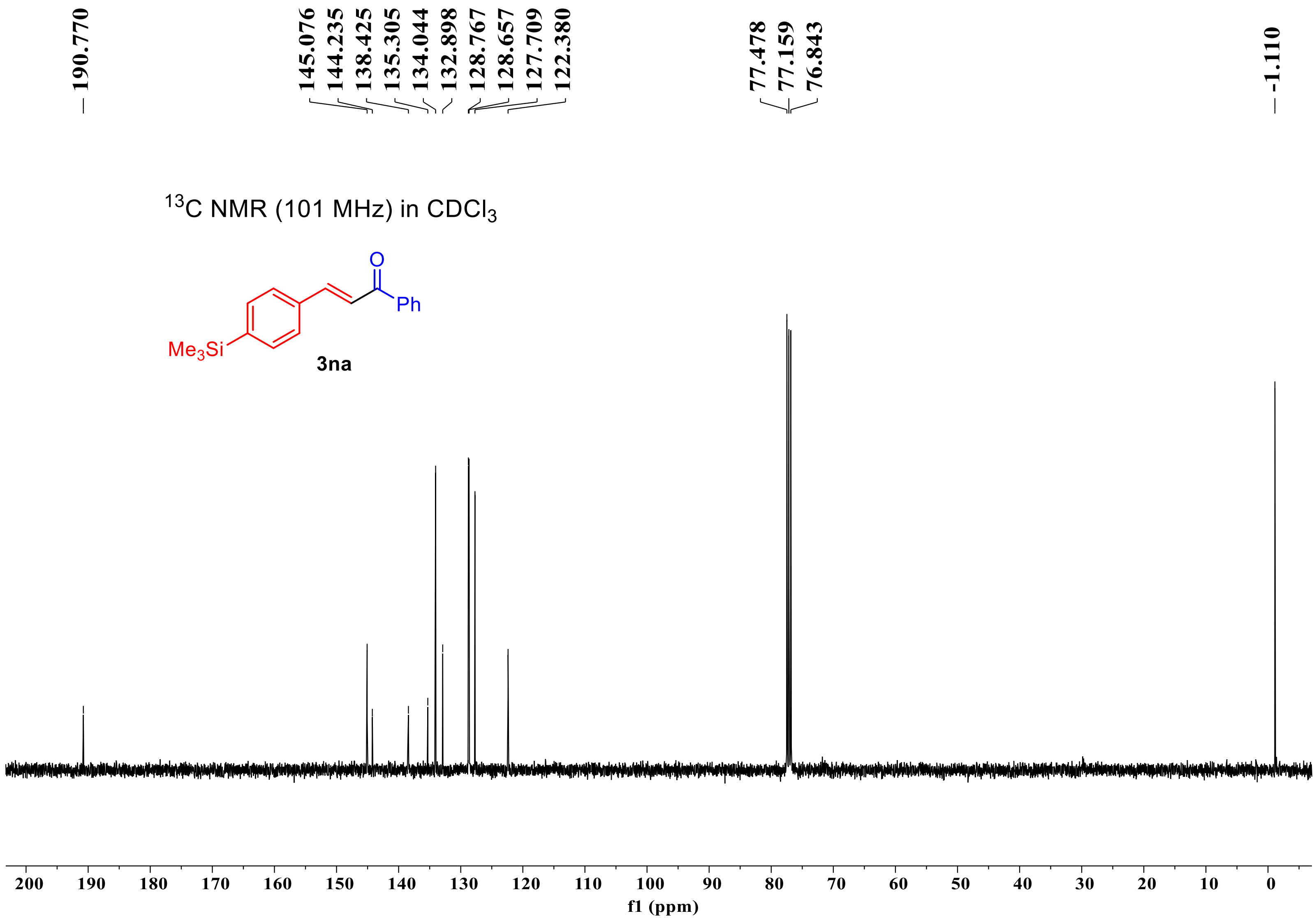
3ma



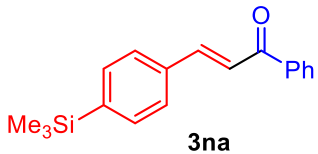
190.337
150.707
143.102
138.119
133.641
133.132
130.002
128.847
128.659
122.989
121.344
119.662
77.372
77.161
76.947
13C NMR (151 MHz) in CDCl3
O
Ph
F3CO
3ma
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-57.7259
19F NMR (377 MHz) in CDCl3
O
Ph
F3CO
3ma
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

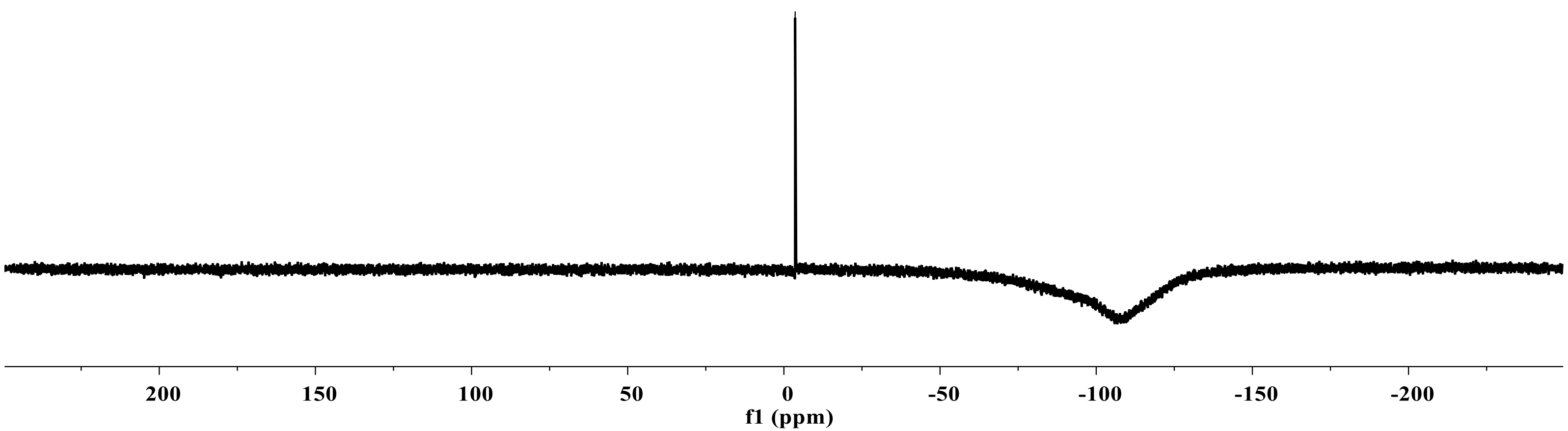

8.0379
8.0349
8.0310
8.0227
8.0173
8.0132
7.8350
7.7958
7.6350
7.6313
7.6203
7.6147
7.5928
7.5876
7.5768
7.5723
7.5601
7.5375
7.5316
7.5275
7.5162
7.5125
7.4986
7.4943
7.4912
7.2603
0.3001
¹H NMR (400 MHz) in CDCl3
O
Ph
Me3Si
3na
2.00
1.03
8.29
9.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

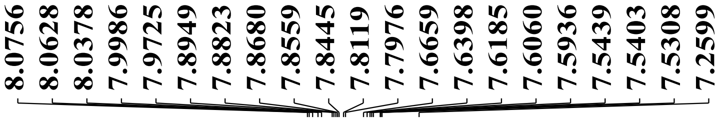

190.770
145.076
144.235
138.425
135.305
134.044
132.898
128.767
128.657
127.709
122.380
77.478
77.159
76.843
-1.110
^{13}C NMR (101 MHz) in $CDCl_3$
O
Ph
Me_3Si
3na
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{29}Si NMR (80 MHz, $CDCl_3$)

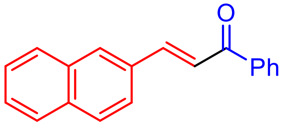


3na

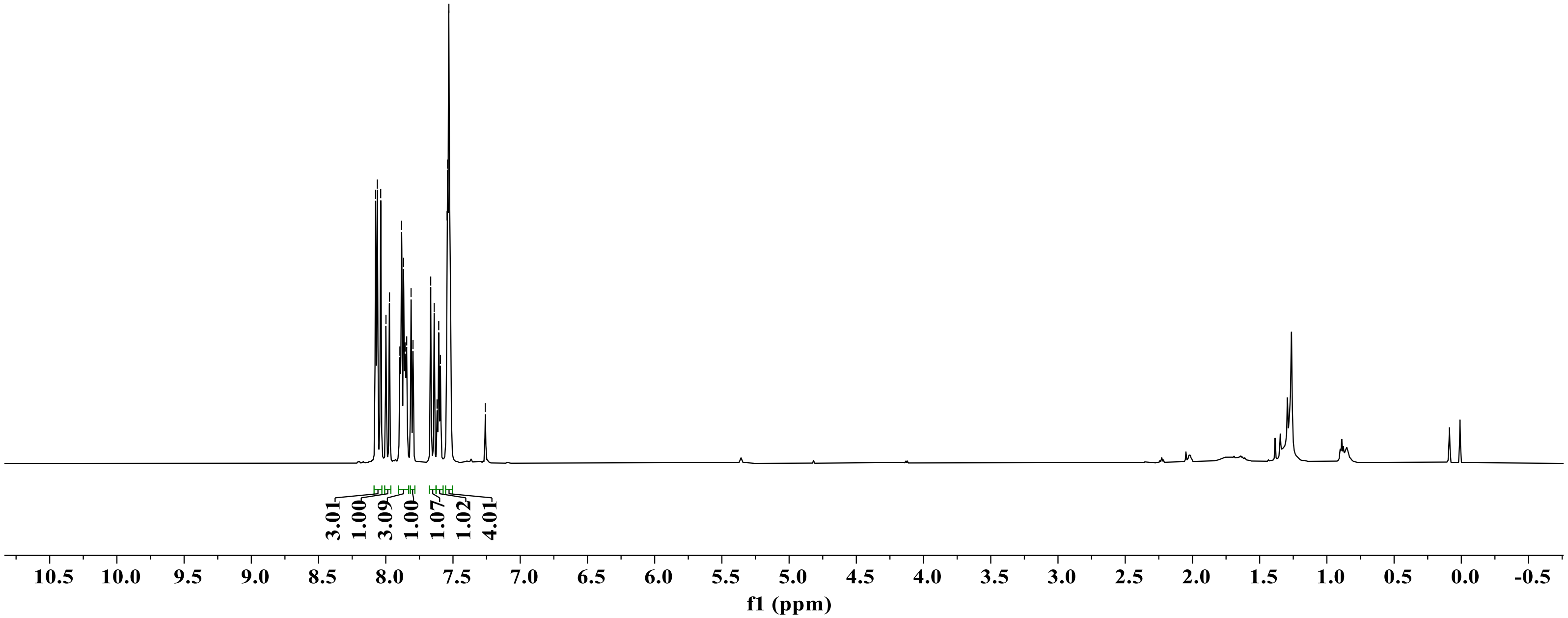




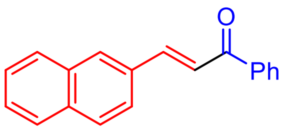
^{1}H NMR (600 MHz) in $CDCl_3$



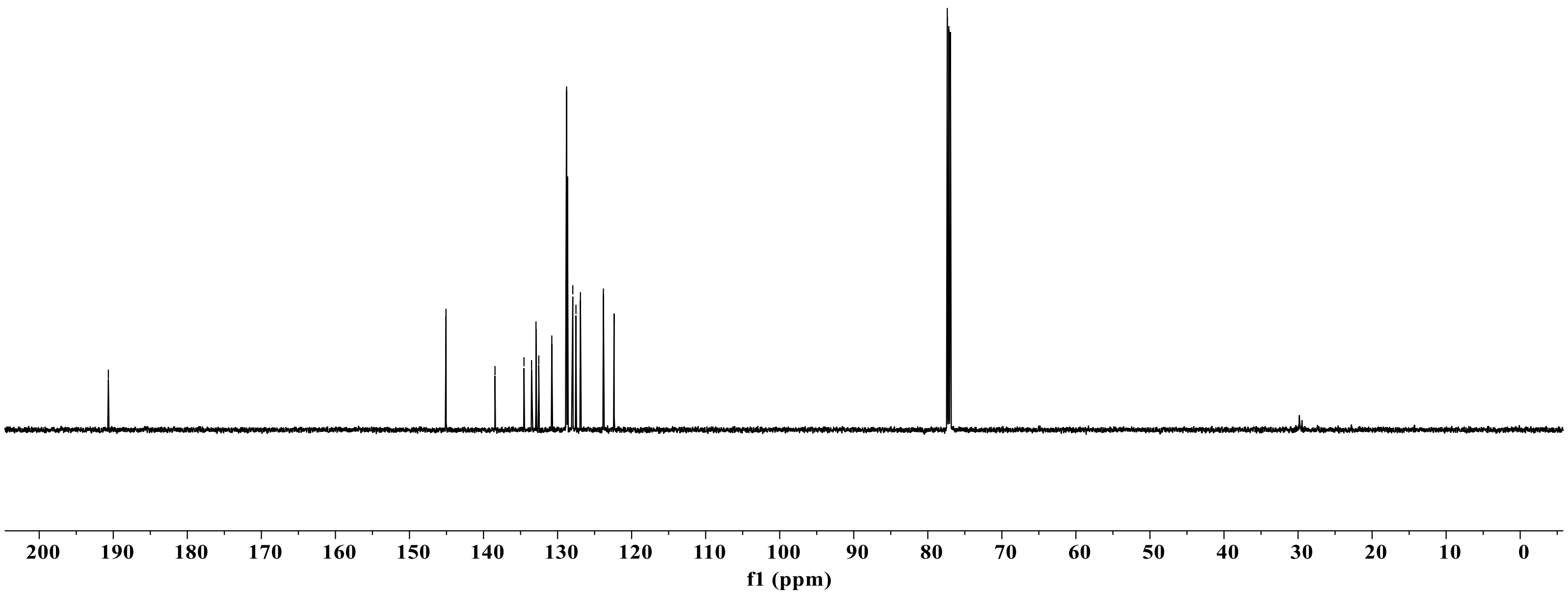
3oa

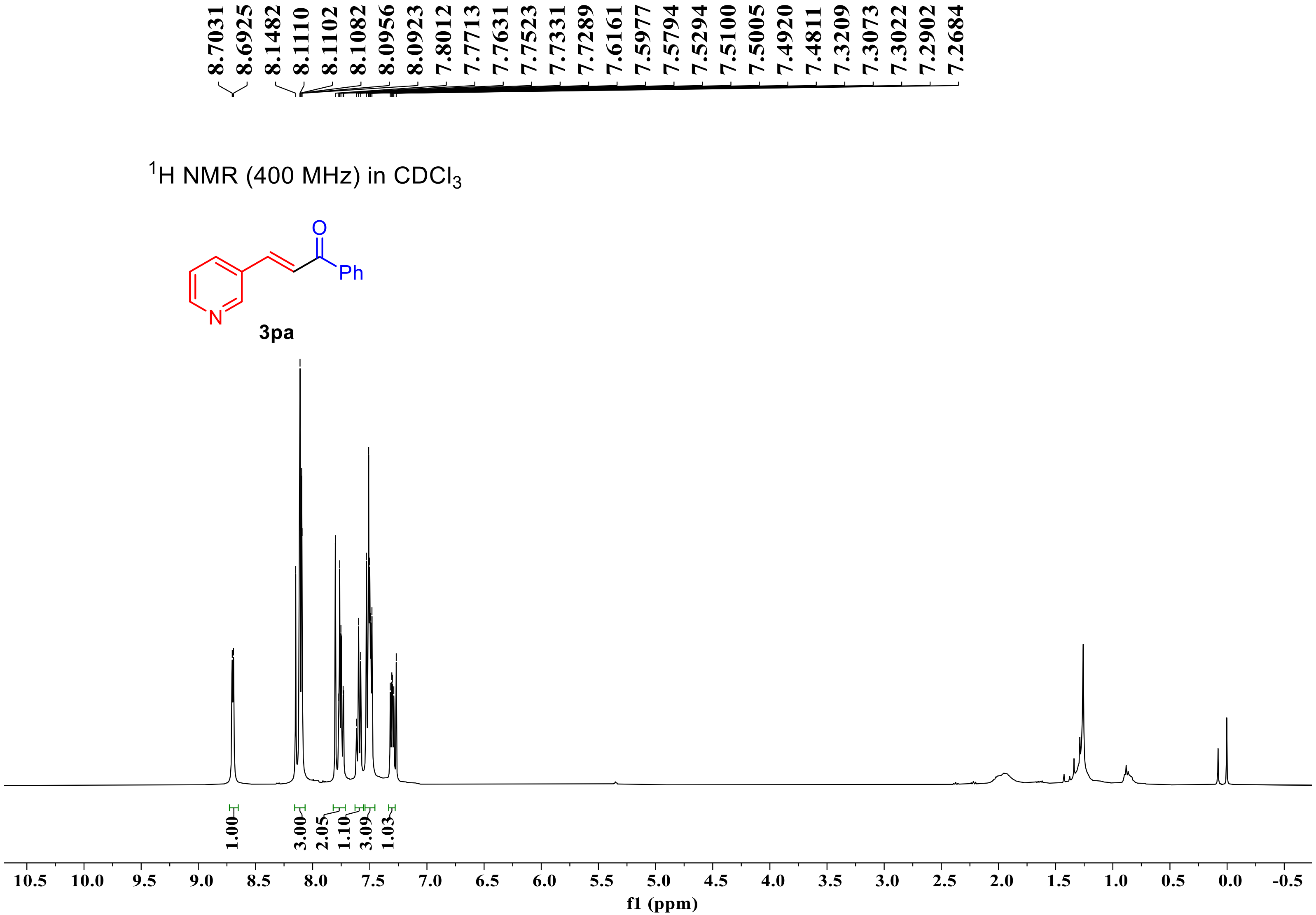


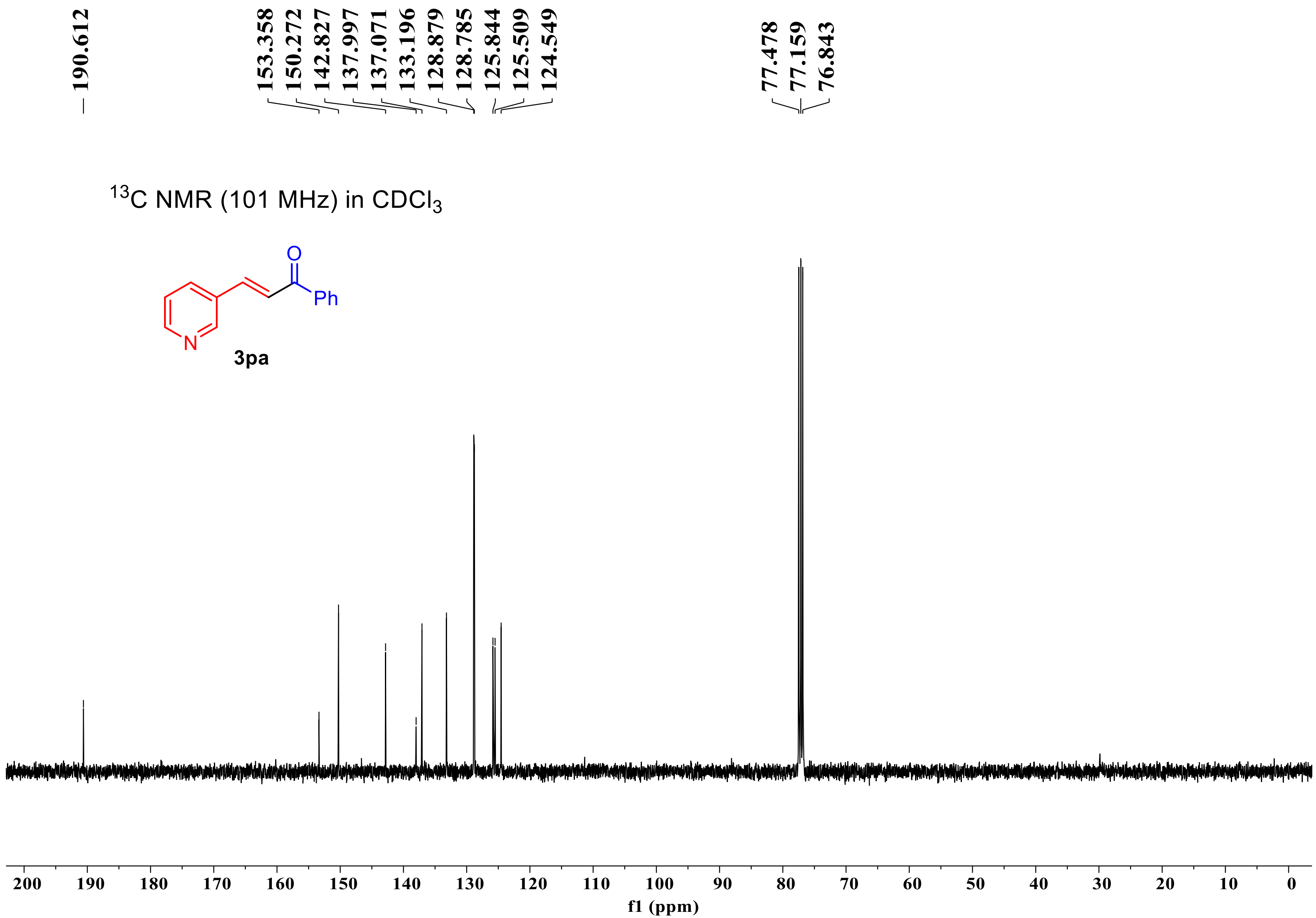
^{13}C NMR (151 MHz) in $CDCl_3$

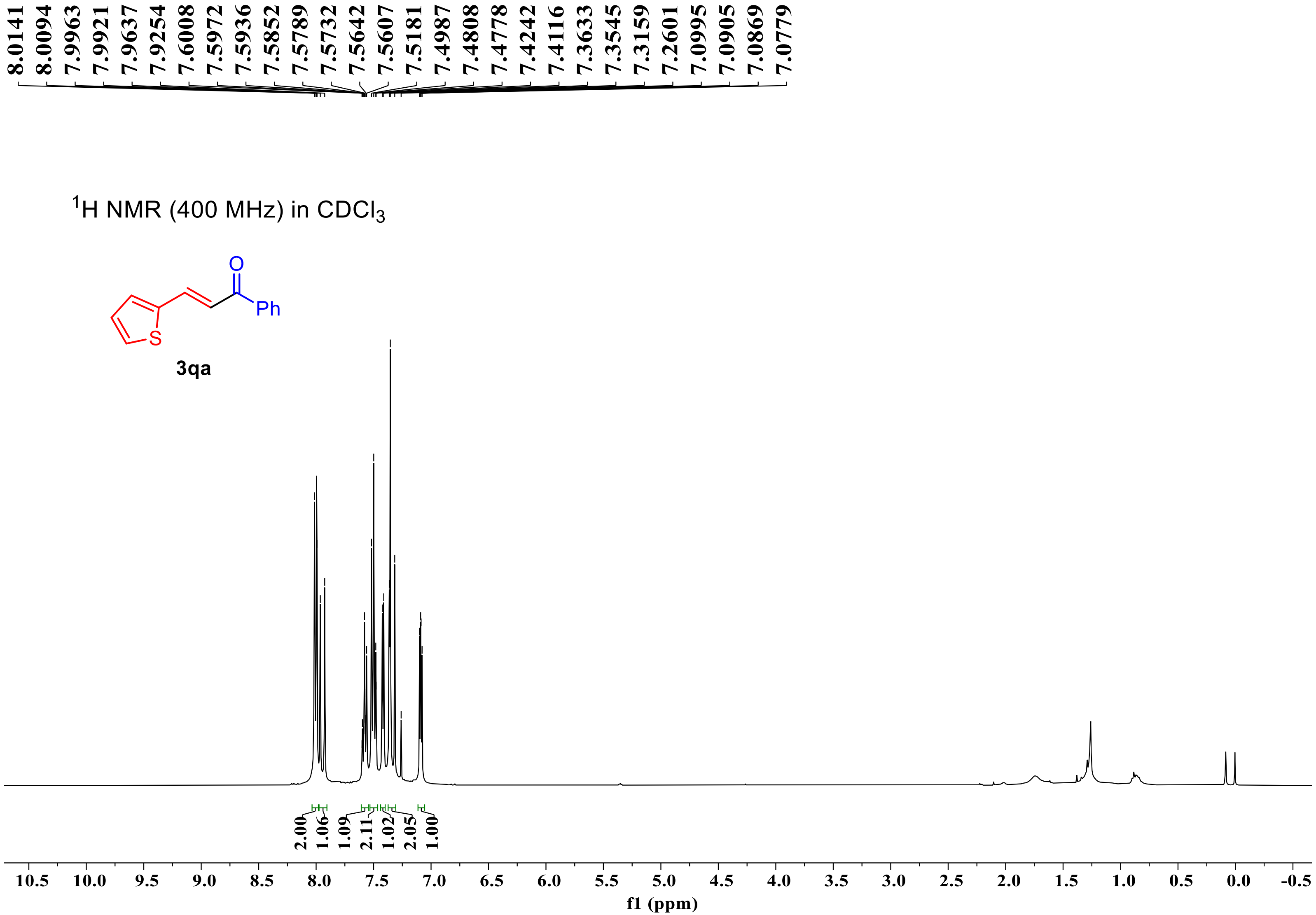


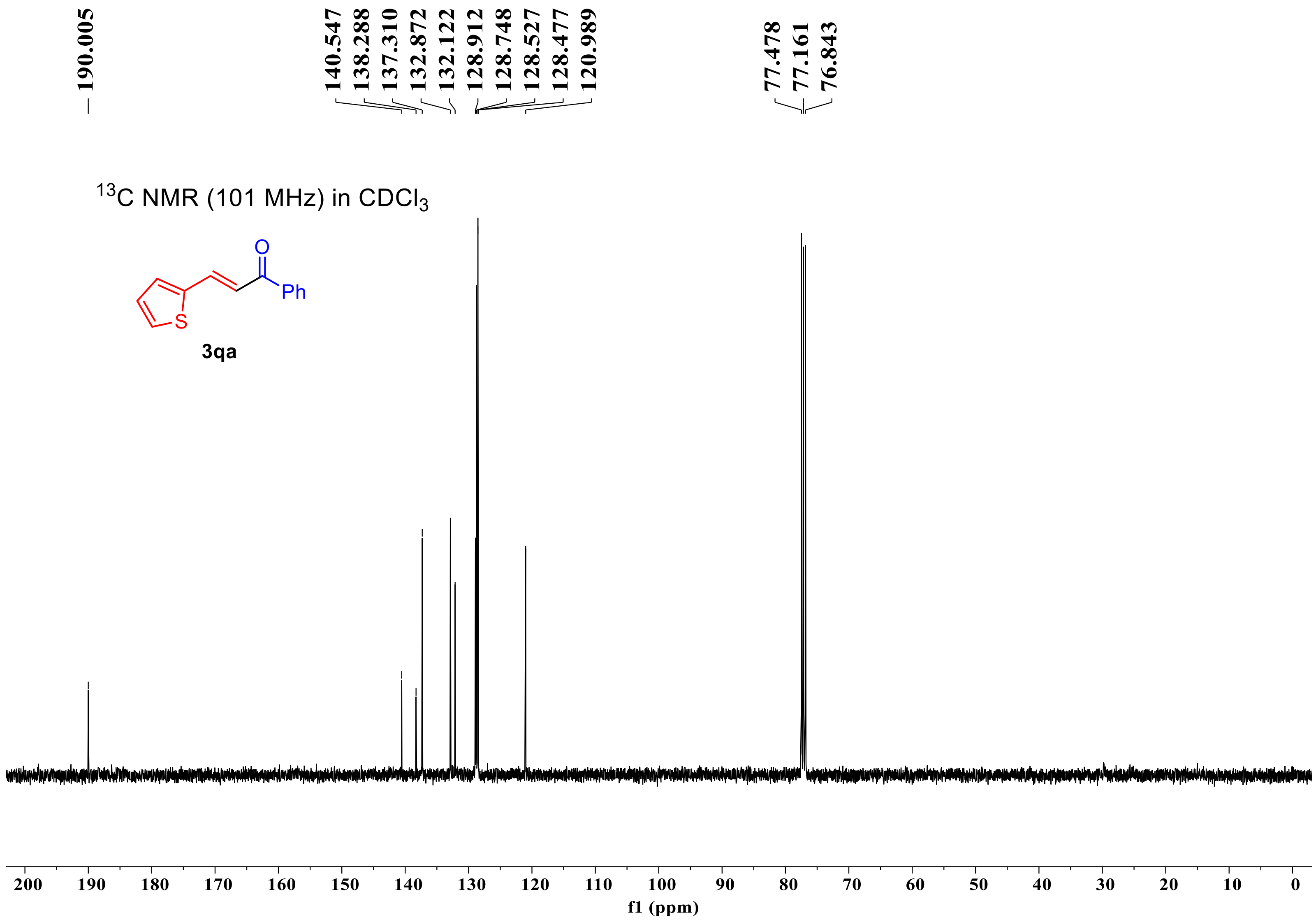
3oa

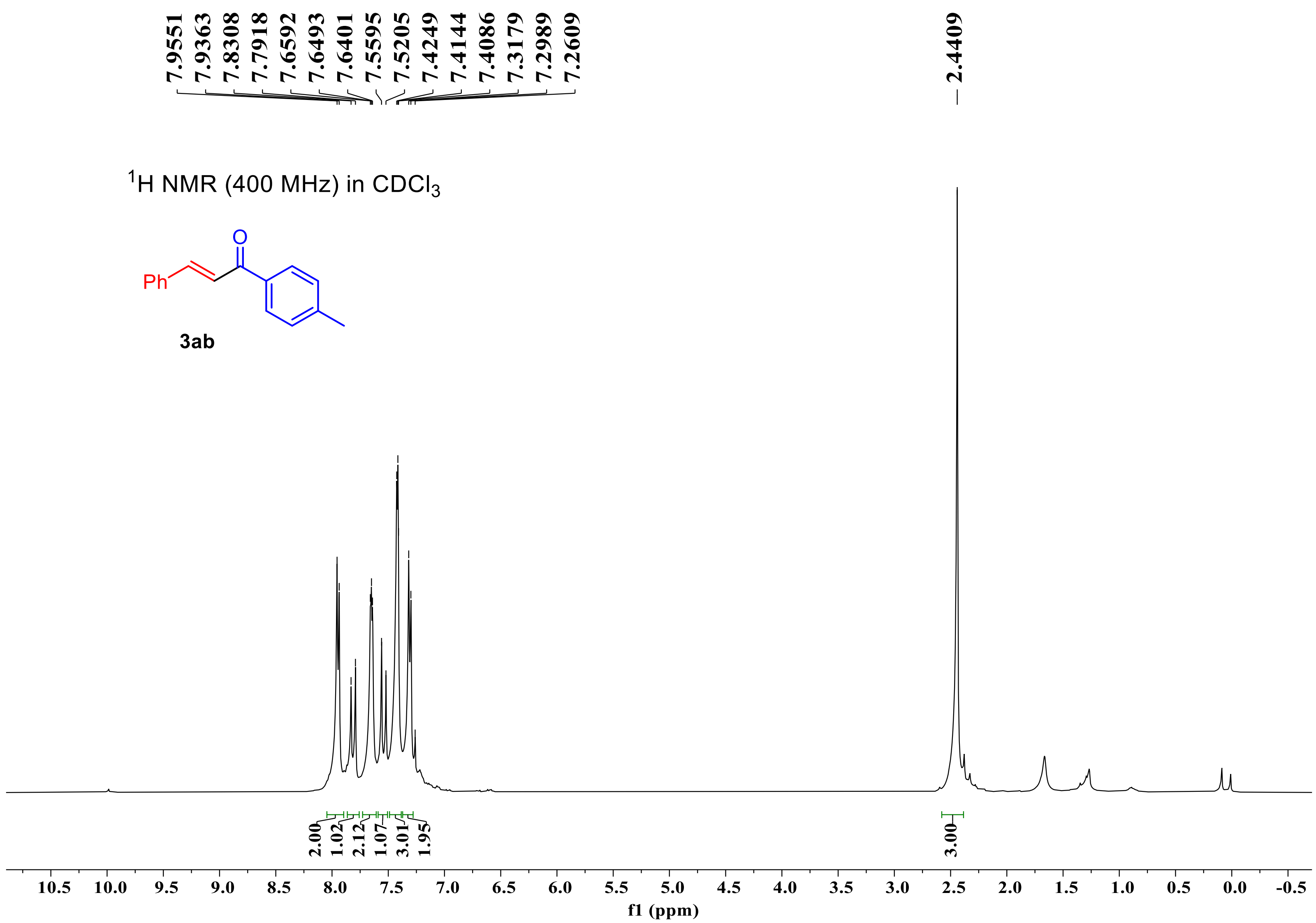


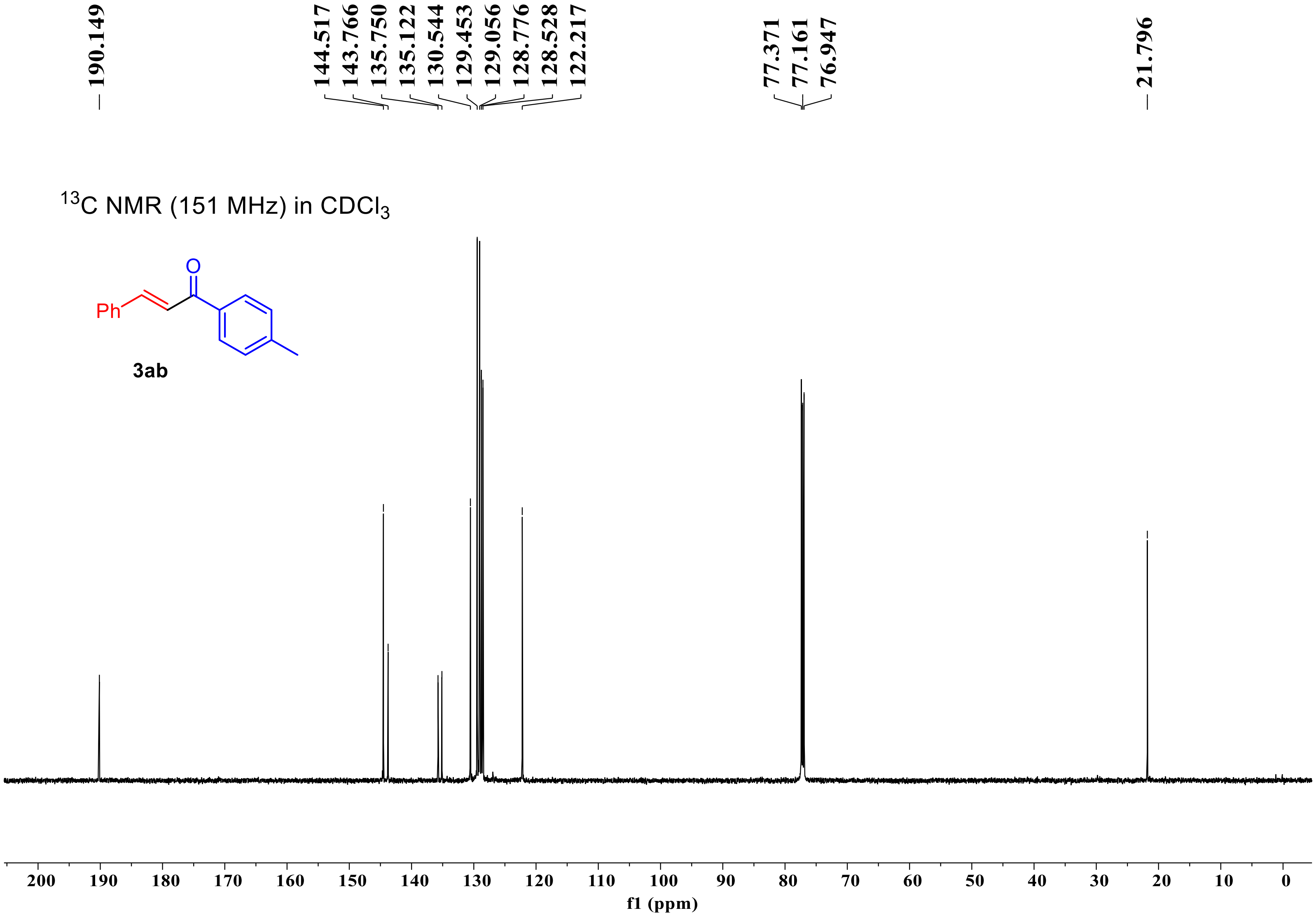

8.7031
8.6925
8.1482
8.1110
8.1102
8.1082
8.0956
8.0923
7.8012
7.7713
7.7631
7.7523
7.7331
7.7289
7.6161
7.5977
7.5794
7.5294
7.5100
7.5005
7.4920
7.4811
7.3209
7.3073
7.3022
7.2902
7.2684
1H NMR (400 MHz) in CDCl3
O
Ph
N
3pa
1.00
3.00
2.05
1.10
3.09
1.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

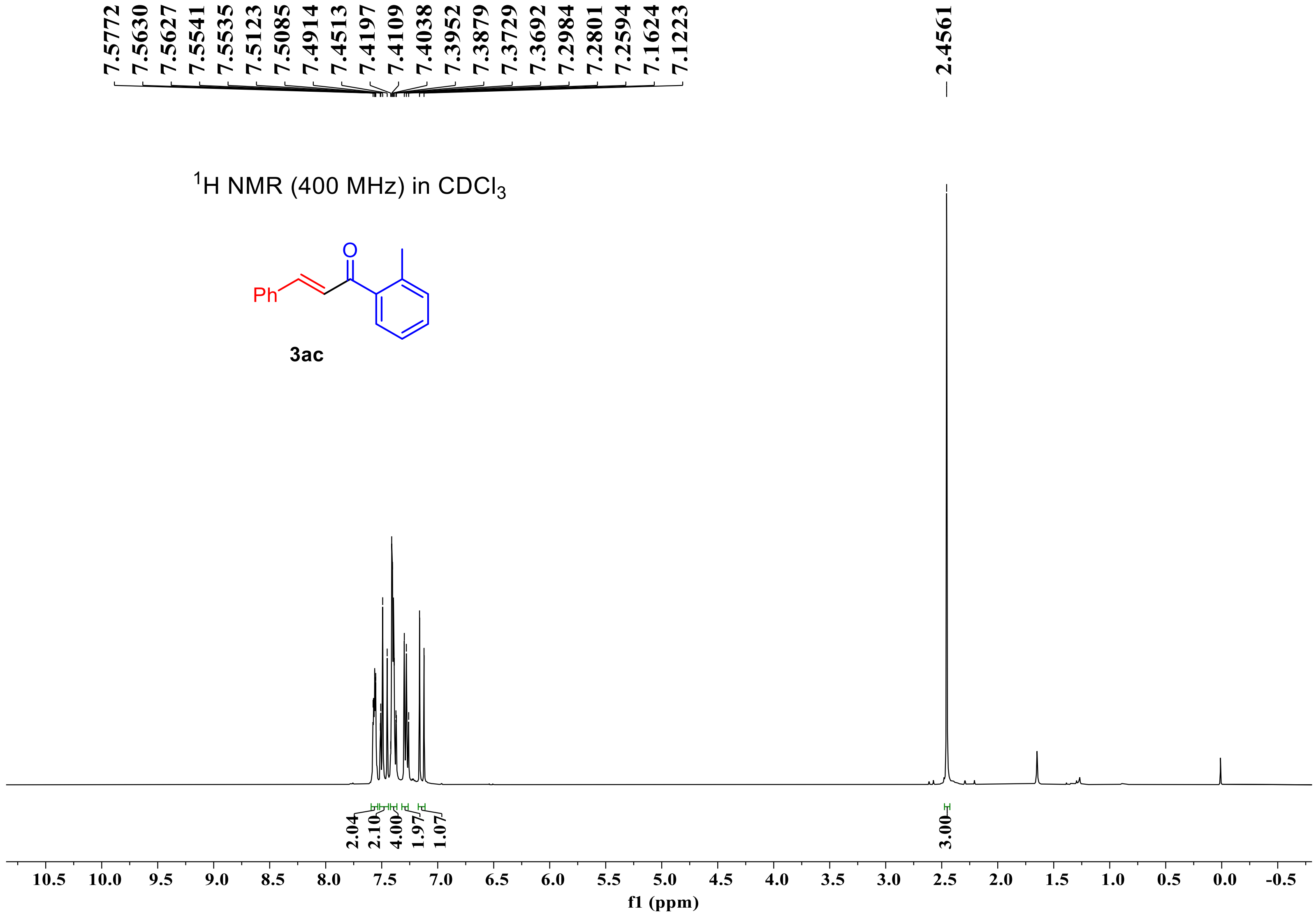

190.612
153.358
150.272
142.827
137.997
137.071
133.196
128.879
128.785
125.844
125.509
124.549
77.478
77.159
76.843
^{13}C NMR (101 MHz) in $CDCl_3$
O
Ph
N
3pa
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

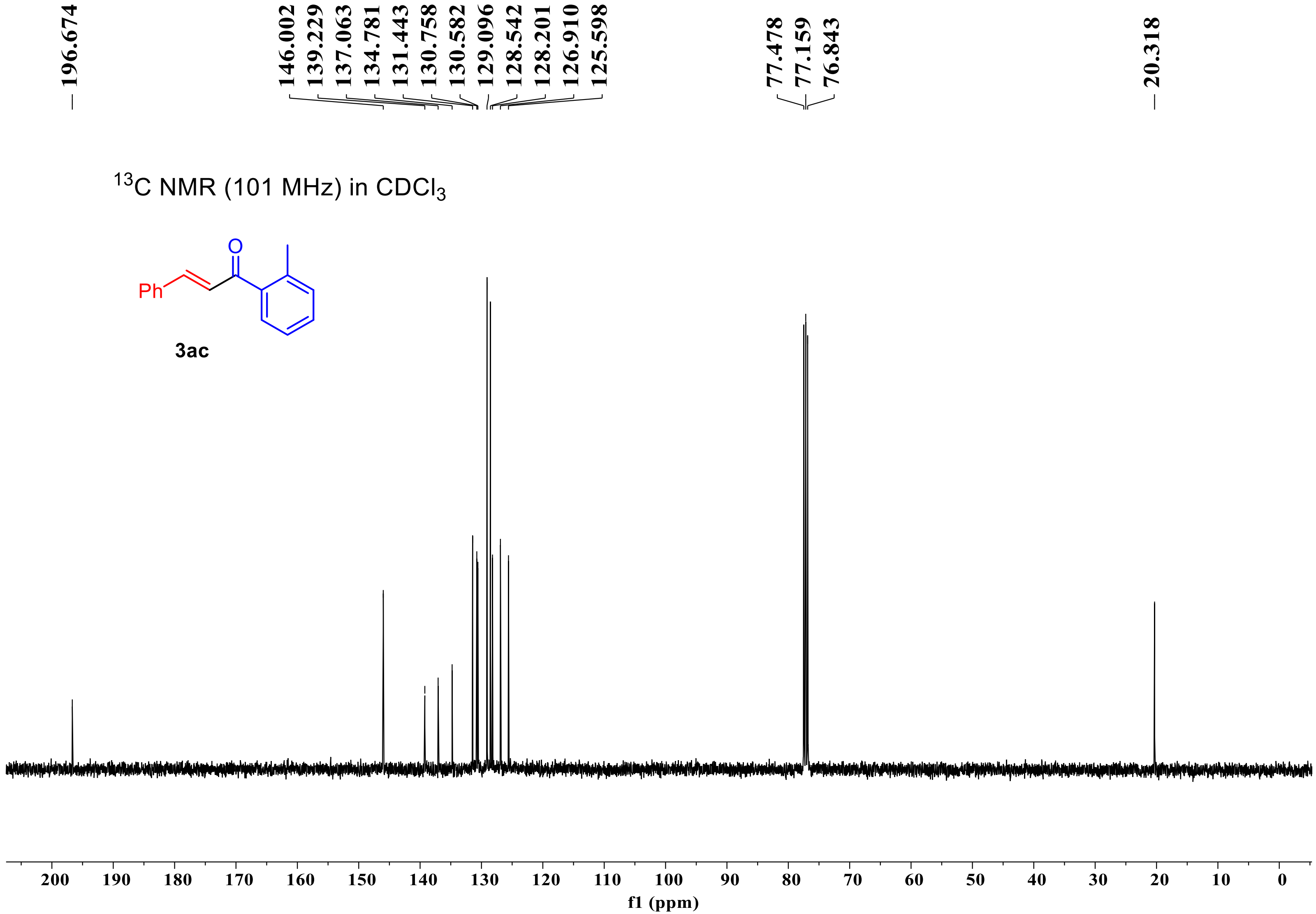

8.0141
8.0094
7.9963
7.9921
7.9637
7.9254
7.6008
7.5972
7.5936
7.5852
7.5789
7.5732
7.5642
7.5607
7.5181
7.4987
7.4808
7.4778
7.4242
7.4116
7.3633
7.3545
7.3159
7.2601
7.0995
7.0905
7.0869
7.0779
^{1}H NMR (400 MHz) in $CDCl_3$
O
Ph
S
3qa
2.00
1.06
1.09
2.11
1.02
2.05
1.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


190.005
140.547
138.288
137.310
132.872
132.122
128.912
128.748
128.527
128.477
120.989
77.478
77.161
76.843
13C NMR (101 MHz) in CDCl3
O
Ph
S
3qa
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

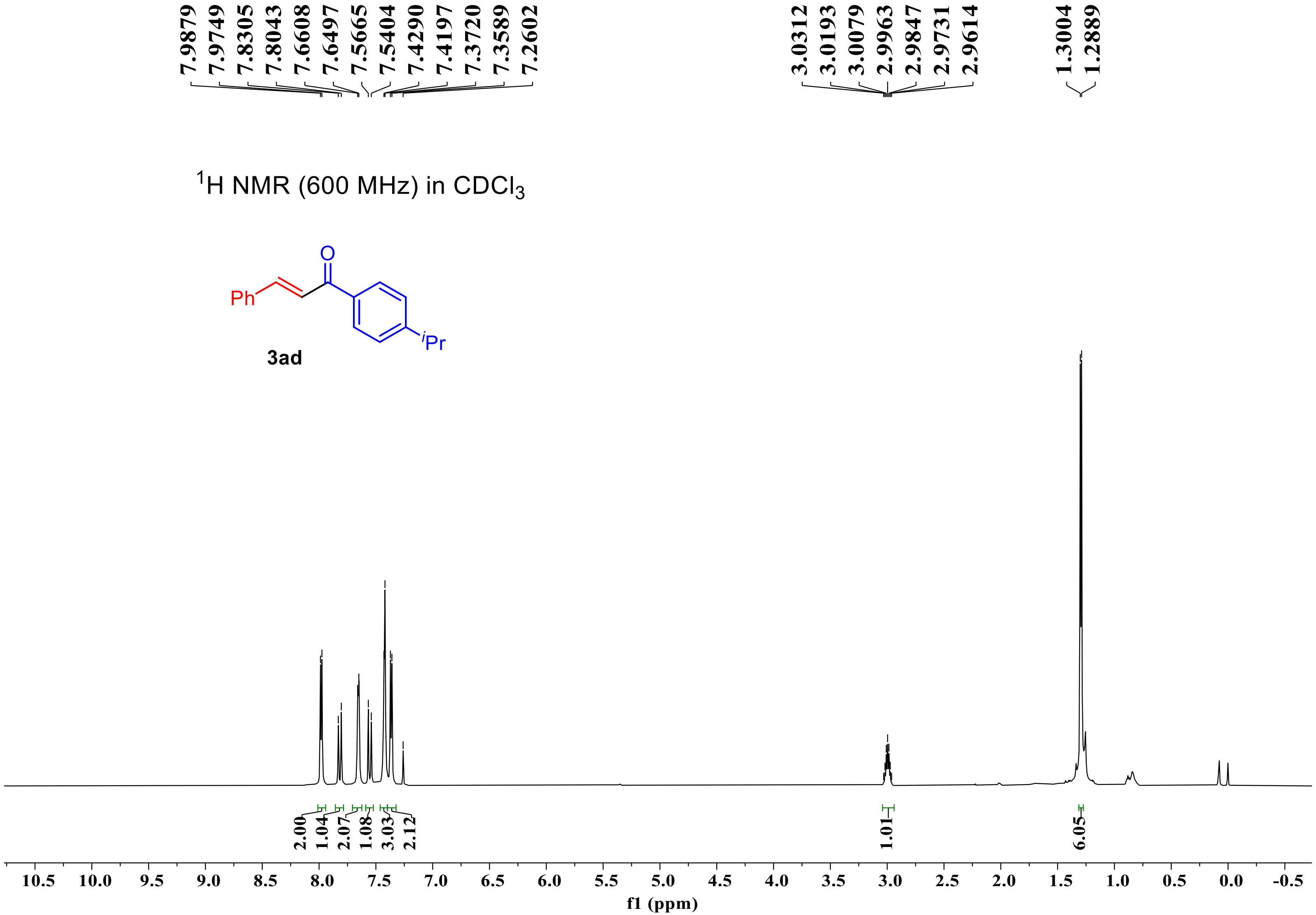

7.9551
7.9363
7.8308
7.7918
7.6592
7.6493
7.6401
7.5595
7.5205
7.4249
7.4144
7.4086
7.3179
7.2989
7.2609
2.4409
^{1}H NMR (400 MHz) in CDCl$_3$
O
Ph
3ab
2.00
1.02
2.12
1.07
3.01
1.95
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

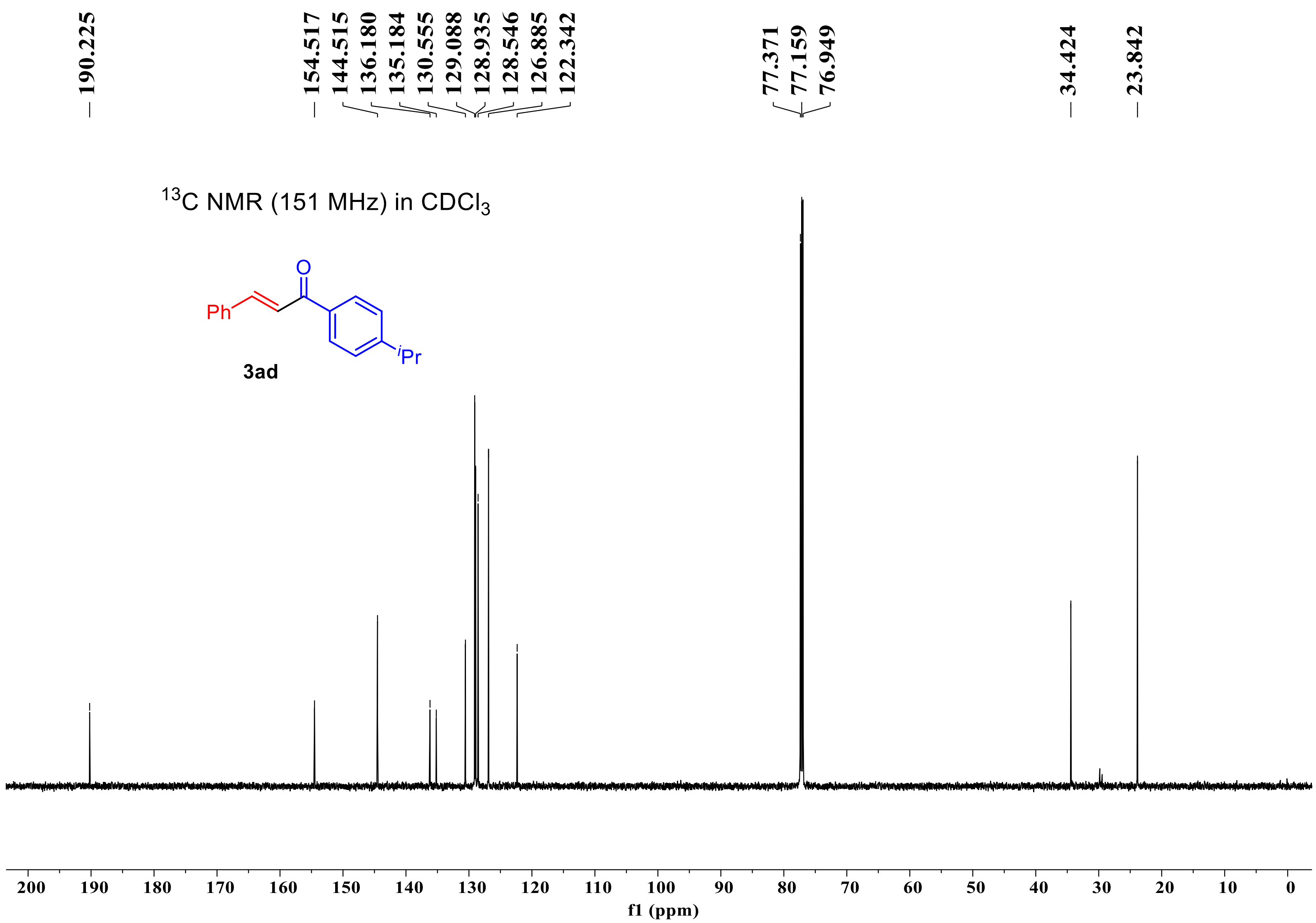

190.149
144.517
143.766
135.750
135.122
130.544
129.453
129.056
128.776
128.528
122.217
77.371
77.161
76.947
21.796
^{13}C NMR (151 MHz) in $CDCl_3$
Ph
O
3ab
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

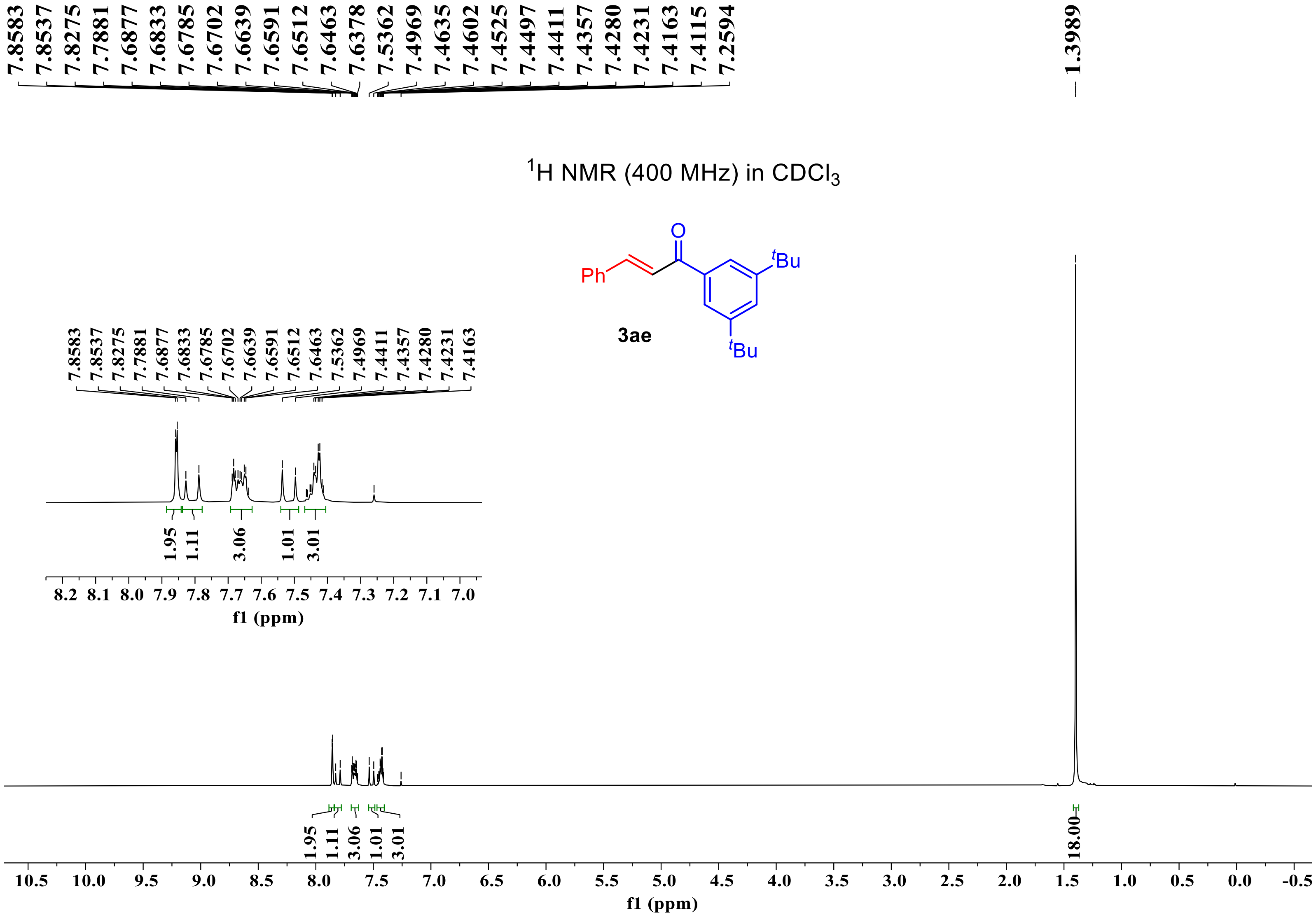

7.5772
7.5630
7.5627
7.5541
7.5535
7.5123
7.5085
7.4914
7.4513
7.4197
7.4109
7.4038
7.3952
7.3879
7.3729
7.3692
7.2984
7.2801
7.2594
7.1624
7.1223
2.4561
^{1}H NMR (400 MHz) in $CDCl_3$
O
Ph
3ac
2.04
2.10
4.00
1.97
1.07
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

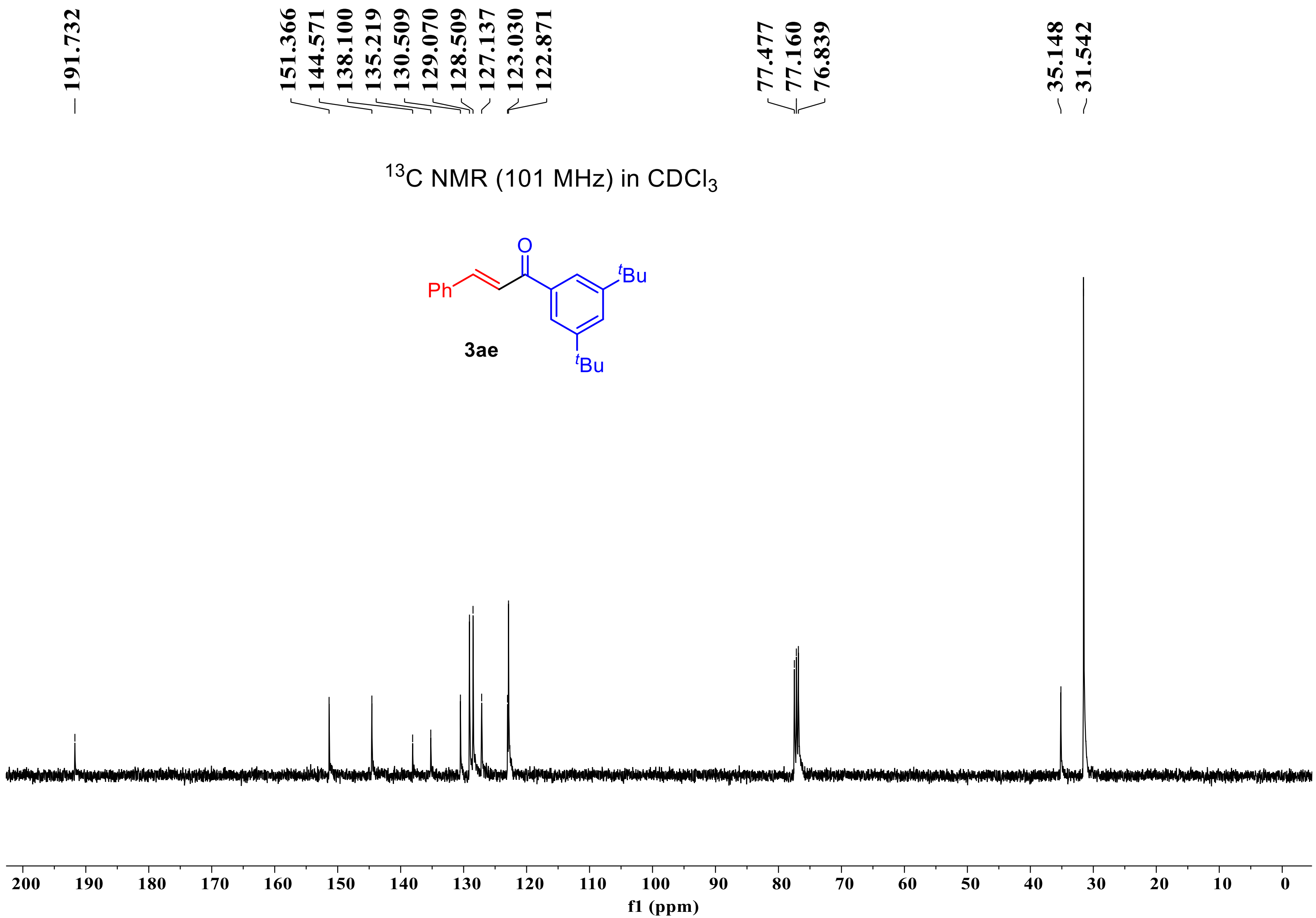


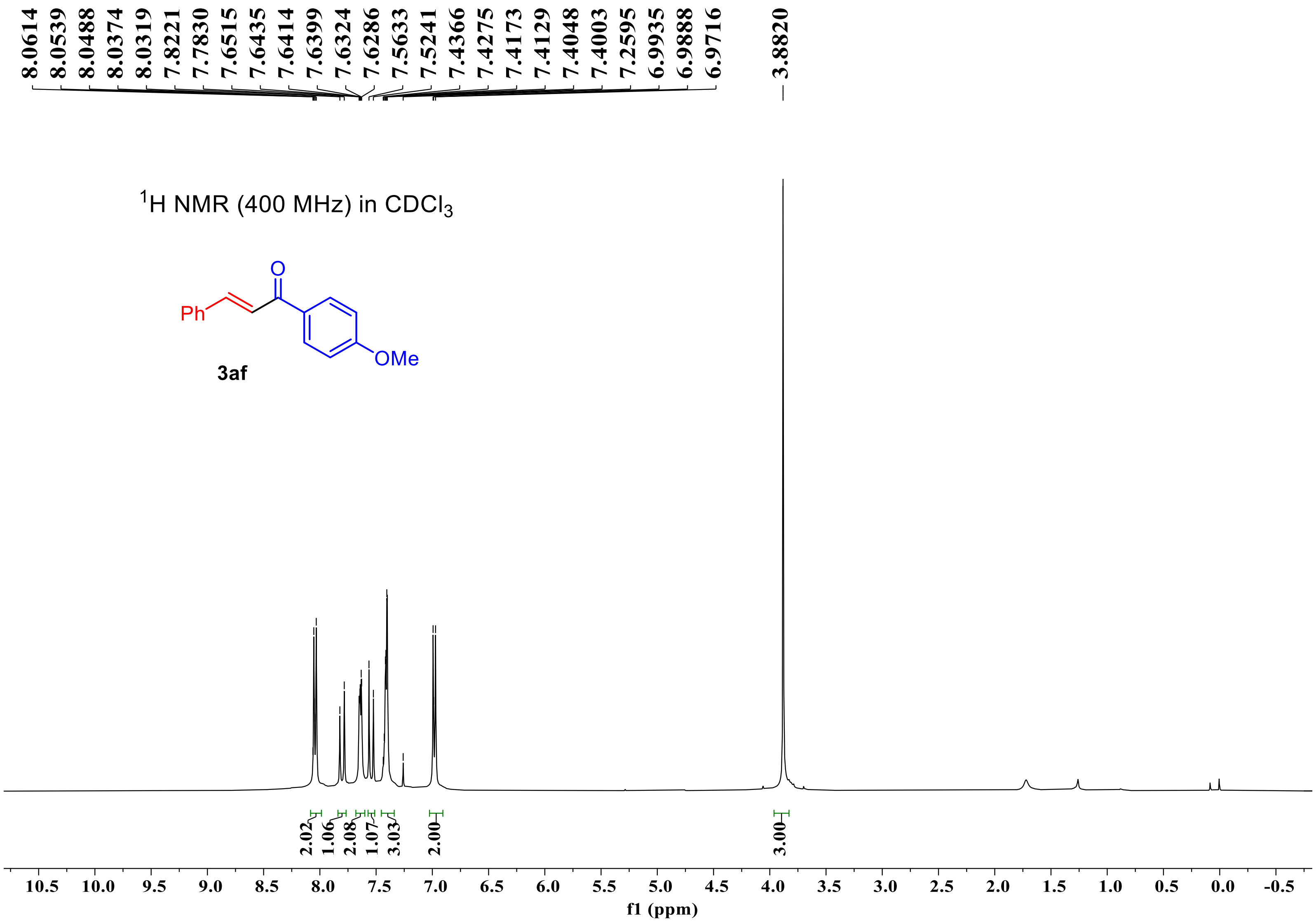
196.674
146.002
139.229
137.063
134.781
131.443
130.758
130.582
129.096
128.542
128.201
126.910
125.598
77.478
77.159
76.843
20.318
^{13}C NMR (101 MHz) in CDCl$_3$
Ph
O
3ac
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

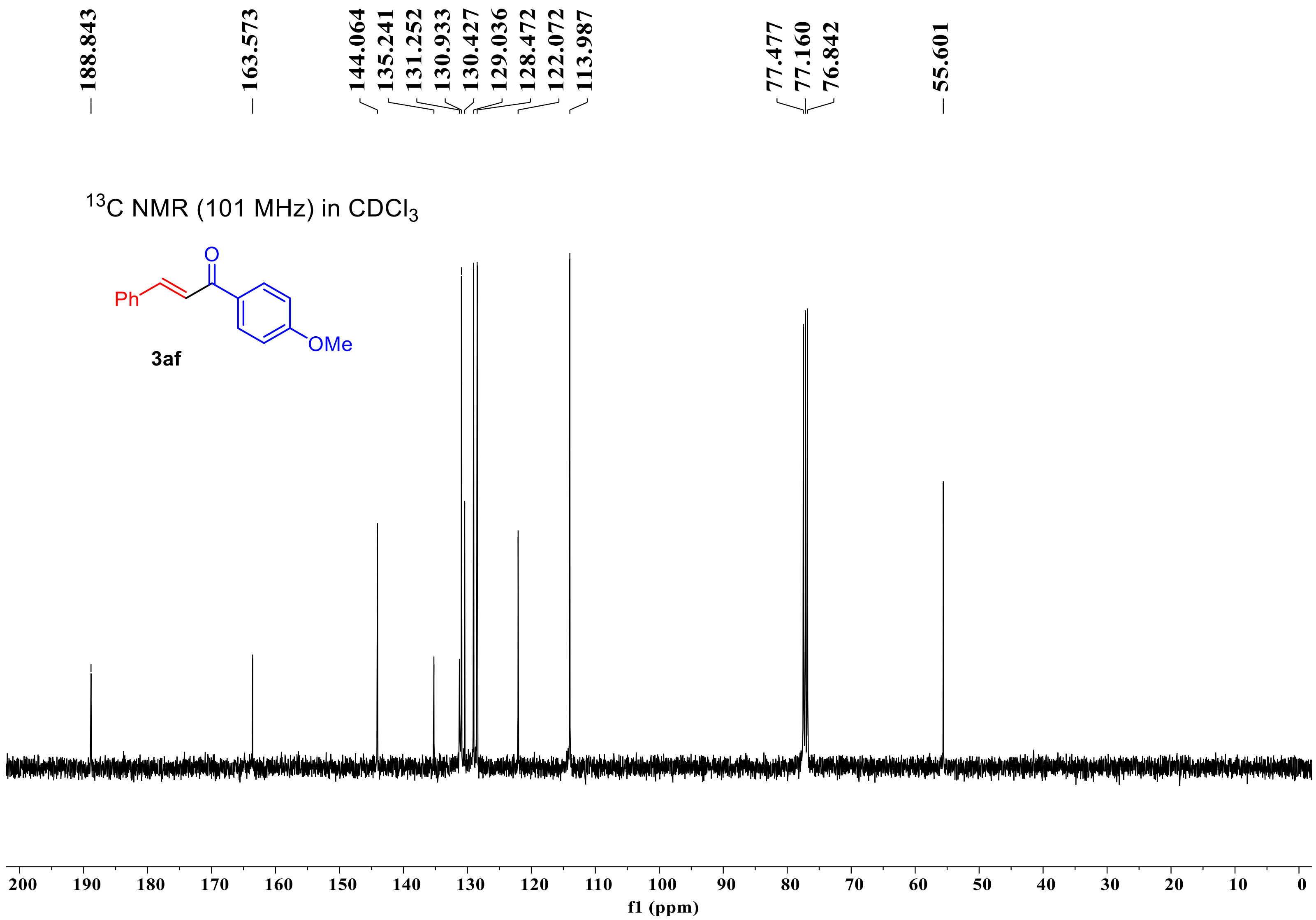

7.9879
7.9749
7.8305
7.8043
7.6608
7.6497
7.5665
7.5404
7.4290
7.4197
7.3720
7.3589
7.2602
3.0312
3.0193
3.0079
2.9963
2.9847
2.9731
2.9614
1.3004
1.2889
¹H NMR (600 MHz) in CDCl₃
O
Ph
ⁱPr
3ad
2.00
1.04
2.07
1.08
3.03
2.12
1.01
6.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


190.225
154.517
144.515
136.180
135.184
130.555
129.088
128.935
128.546
126.885
122.342
77.371
77.159
76.949
34.424
23.842
^{13}C NMR (151 MHz) in $CDCl_3$
O
Ph
^{i}Pr
3ad
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

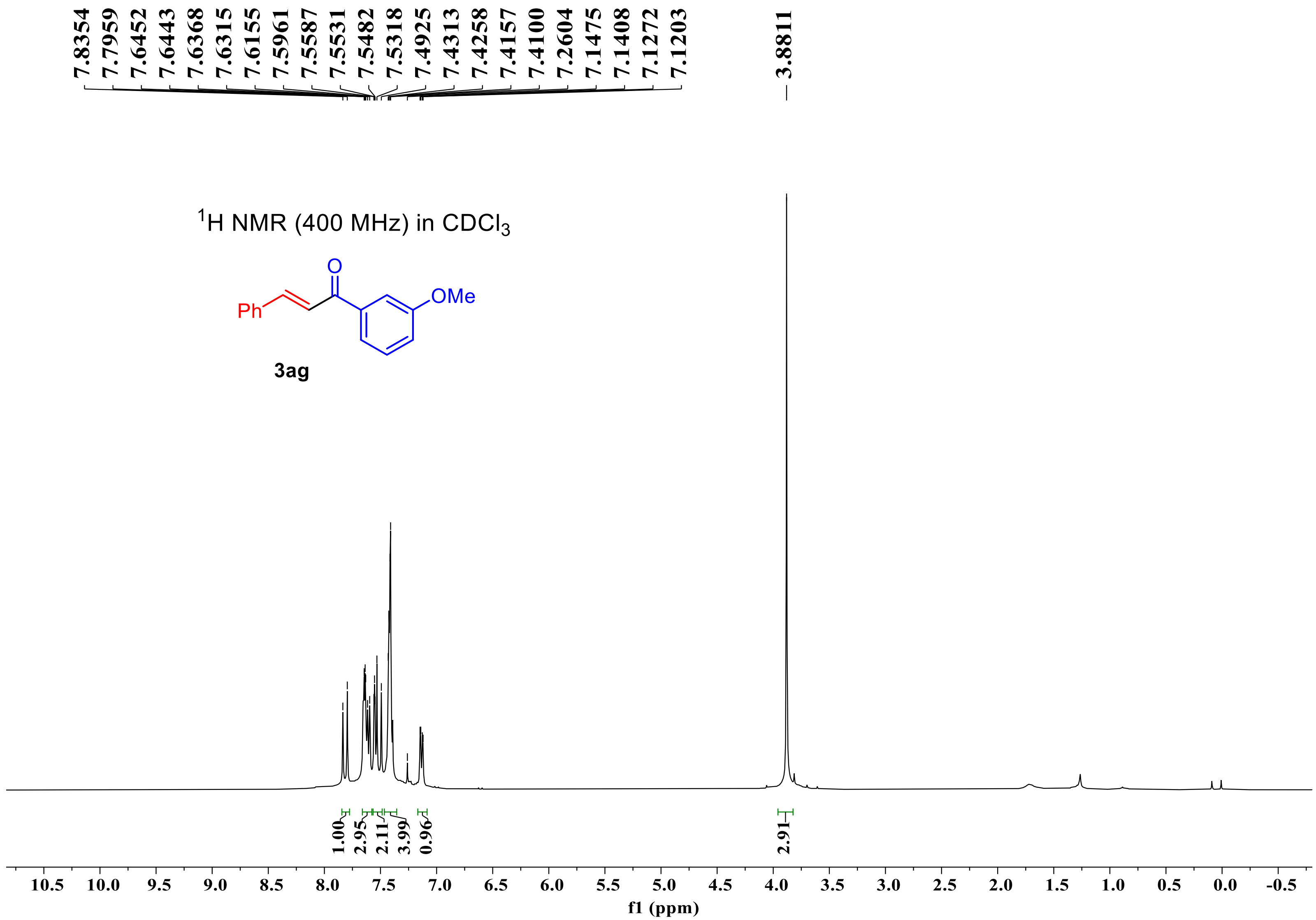

7.8583
7.8537
7.8275
7.7881
7.6877
7.6833
7.6785
7.6702
7.6639
7.6591
7.6512
7.6463
7.6378
7.5362
7.4969
7.4635
7.4602
7.4525
7.4497
7.4411
7.4357
7.4280
7.4231
7.4163
7.4115
7.2594
1.3989
^{1}H NMR (400 MHz) in $CDCl_3$
O
Ph
^{t}Bu
^{t}Bu
3ae
1.95
1.11
3.06
1.01
3.01
18.00
f1 (ppm)


191.732
151.366
144.571
138.100
135.219
130.509
129.070
128.509
127.137
123.030
122.871
77.477
77.160
76.839
35.148
31.542
^{13}C NMR (101 MHz) in $CDCl_3$
O
Ph
^{t}Bu
^{t}Bu
3ae
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

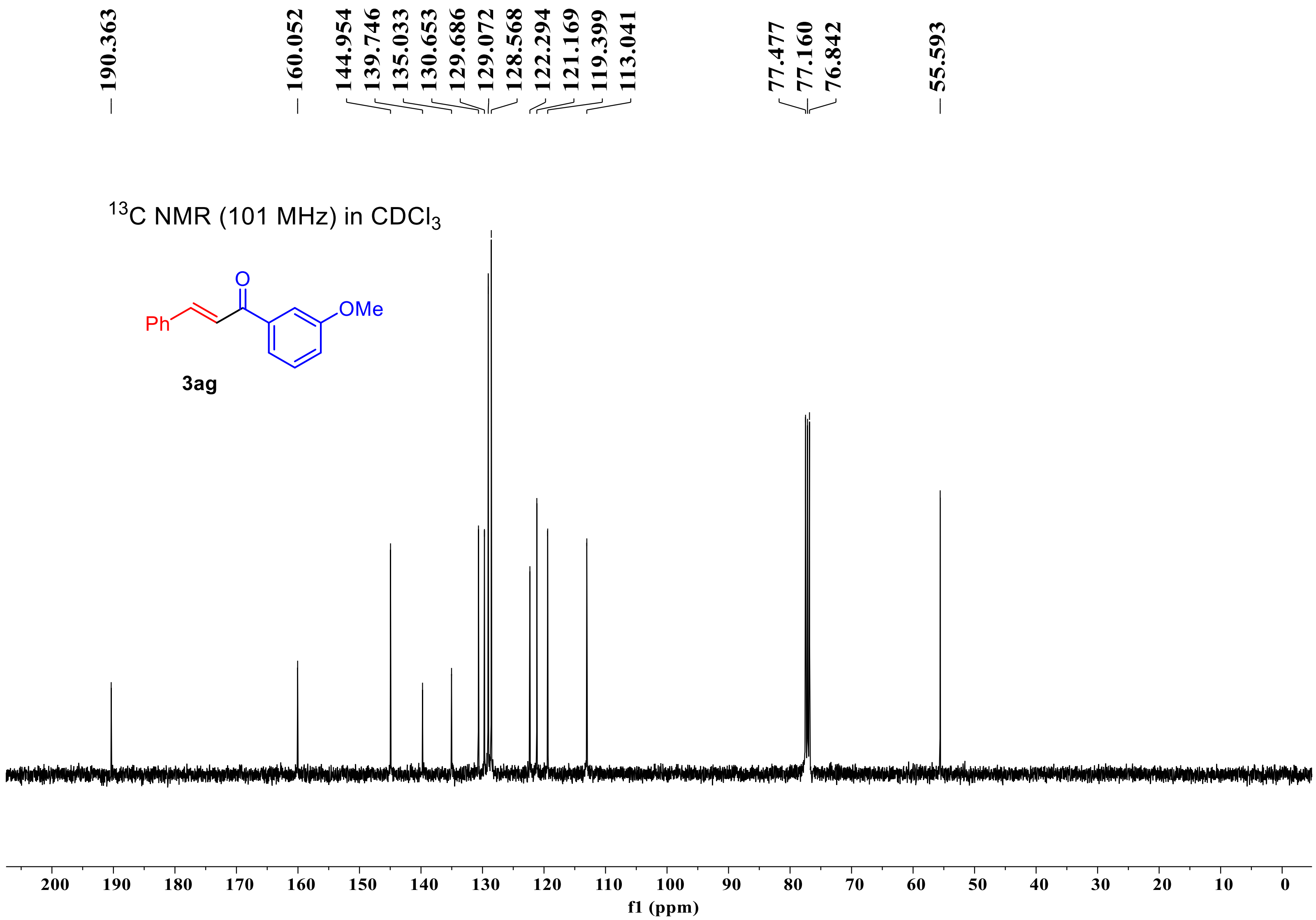

8.0614
8.0539
8.0488
8.0374
8.0319
7.8221
7.7830
7.6515
7.6435
7.6414
7.6399
7.6324
7.6286
7.5633
7.5241
7.4366
7.4275
7.4173
7.4129
7.4048
7.4003
7.2595
6.9935
6.9888
6.9716
3.8820
1H NMR (400 MHz) in CDCl3
O
Ph
OMe
3af
2.02
1.06
2.08
1.07
3.03
2.00
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

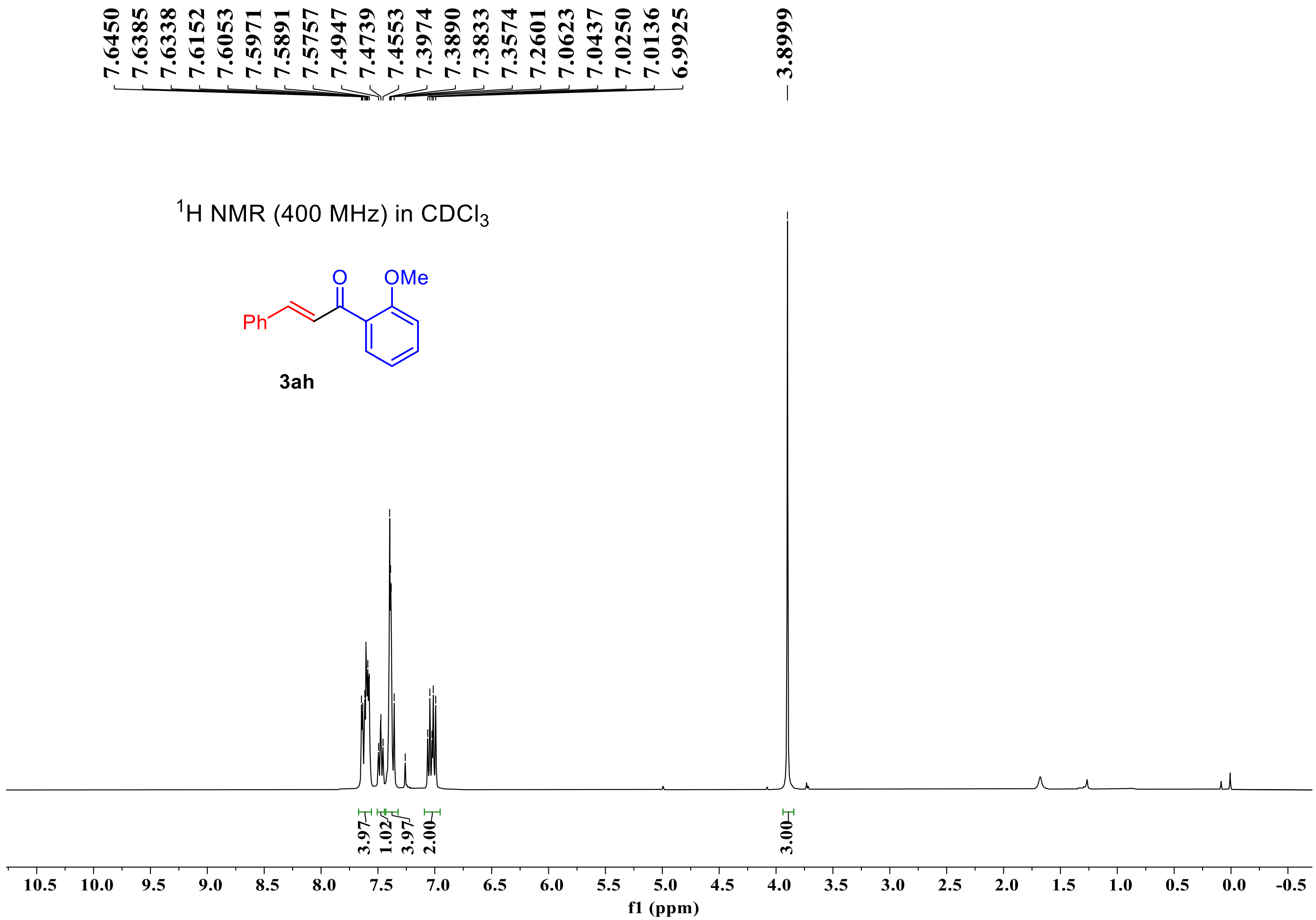


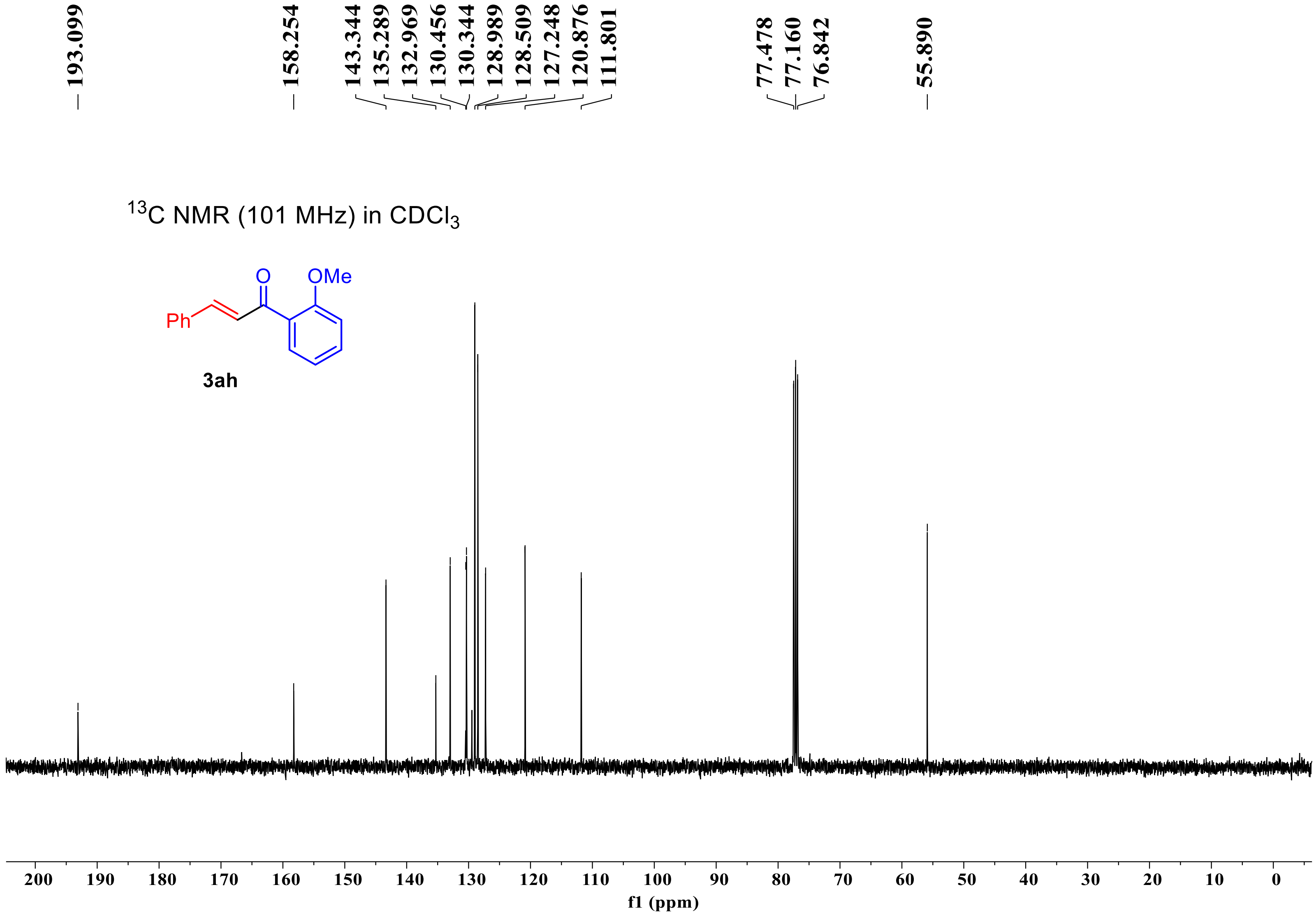
188.843
163.573
144.064
135.241
131.252
130.933
130.427
129.036
128.472
122.072
113.987
77.477
77.160
76.842
55.601
13C NMR (101 MHz) in CDCl3
O
Ph
OMe
3af
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



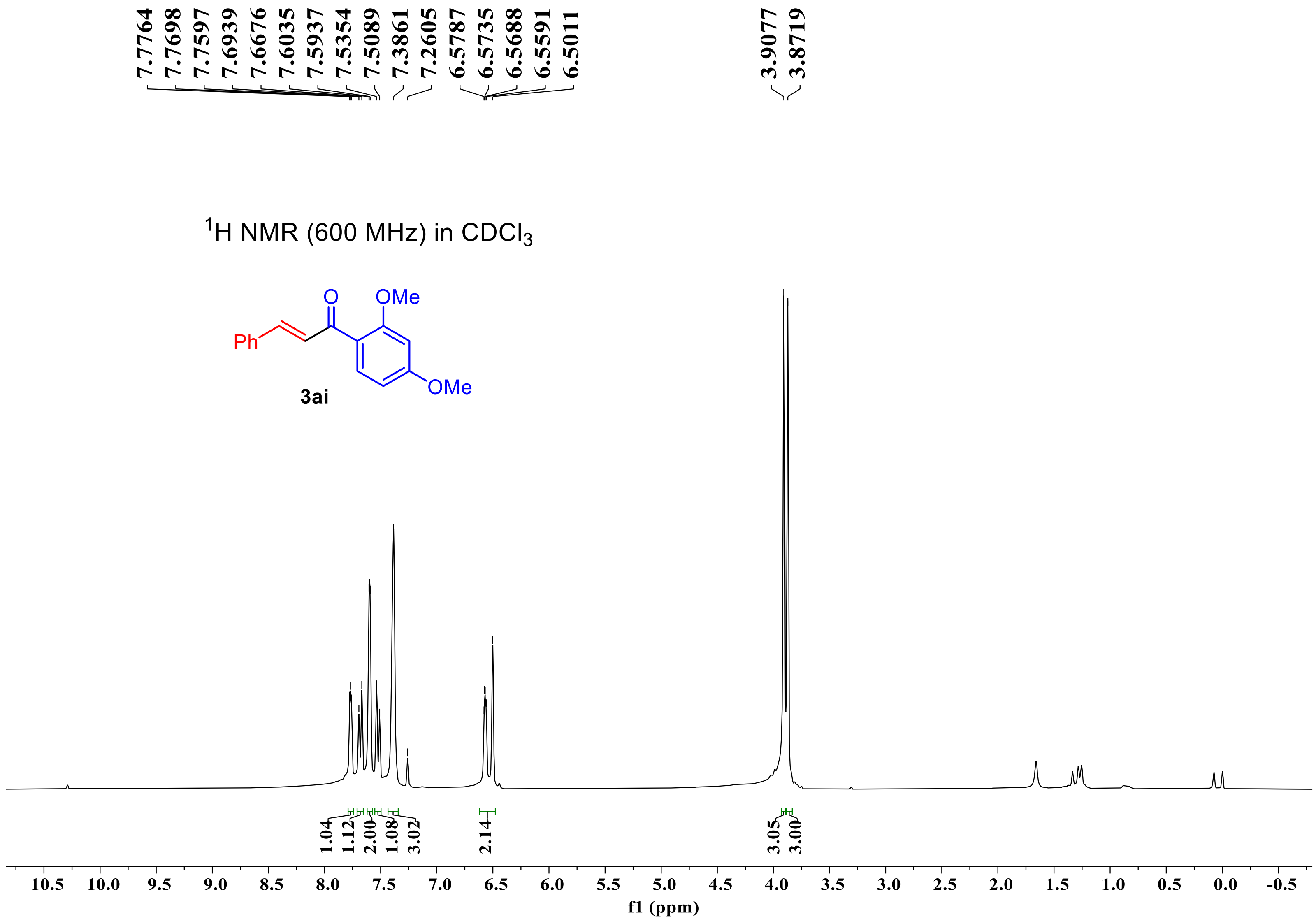
7.8354
7.7959
7.6452
7.6443
7.6368
7.6315
7.6155
7.5961
7.5587
7.5531
7.5482
7.5318
7.4925
7.4313
7.4258
7.4157
7.4100
7.2604
7.1475
7.1408
7.1272
7.1203
3.8811
1H NMR (400 MHz) in CDCl3
O
OMe
Ph
3ag
1.00
2.95
2.11
3.99
0.96
2.91
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

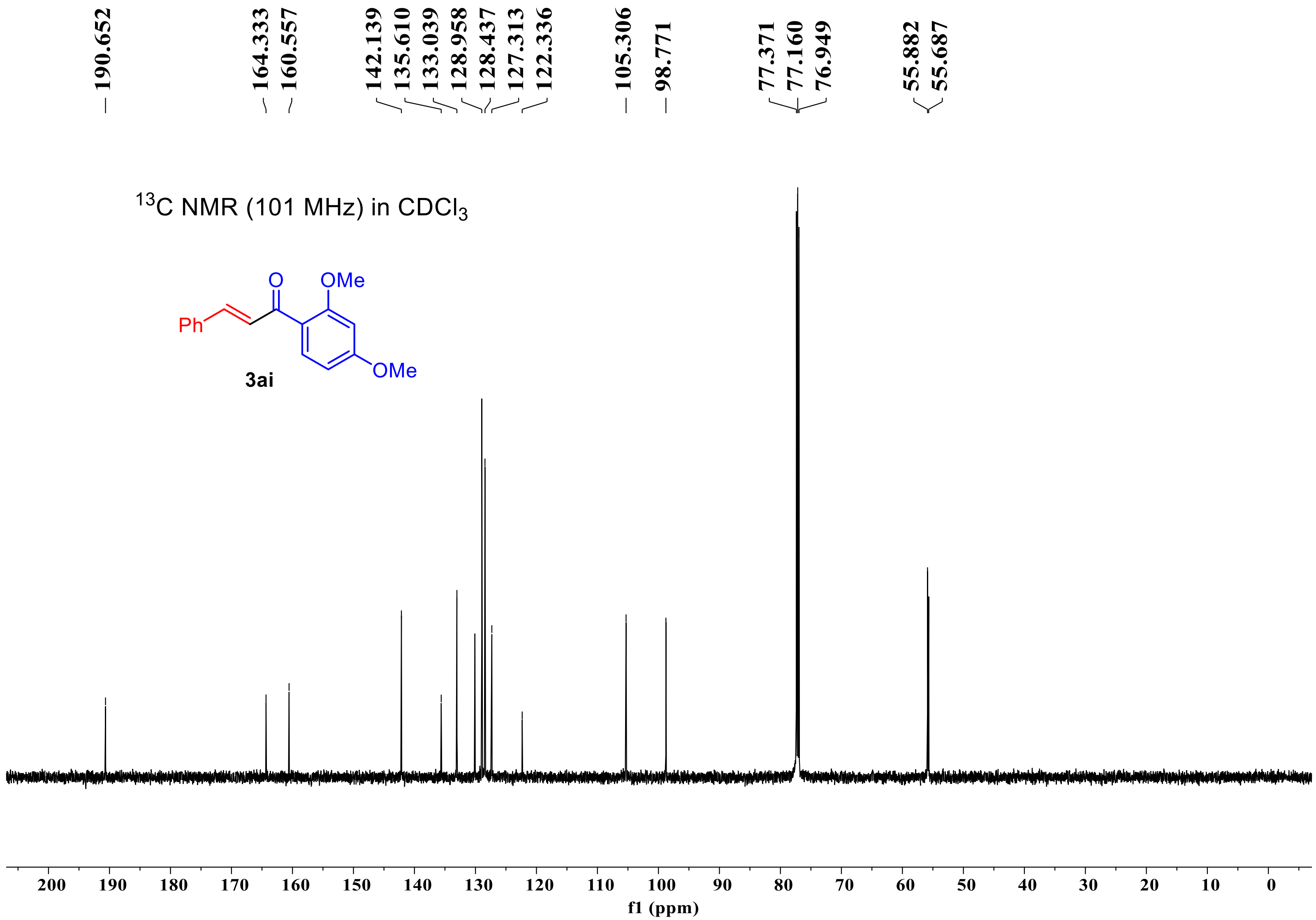

190.363
160.052
144.954
139.746
135.033
130.653
129.686
129.072
128.568
122.294
121.169
119.399
113.041
77.477
77.160
76.842
55.593
^{13}C NMR (101 MHz) in CDCl$_3$
O
Ph
OMe
3ag
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

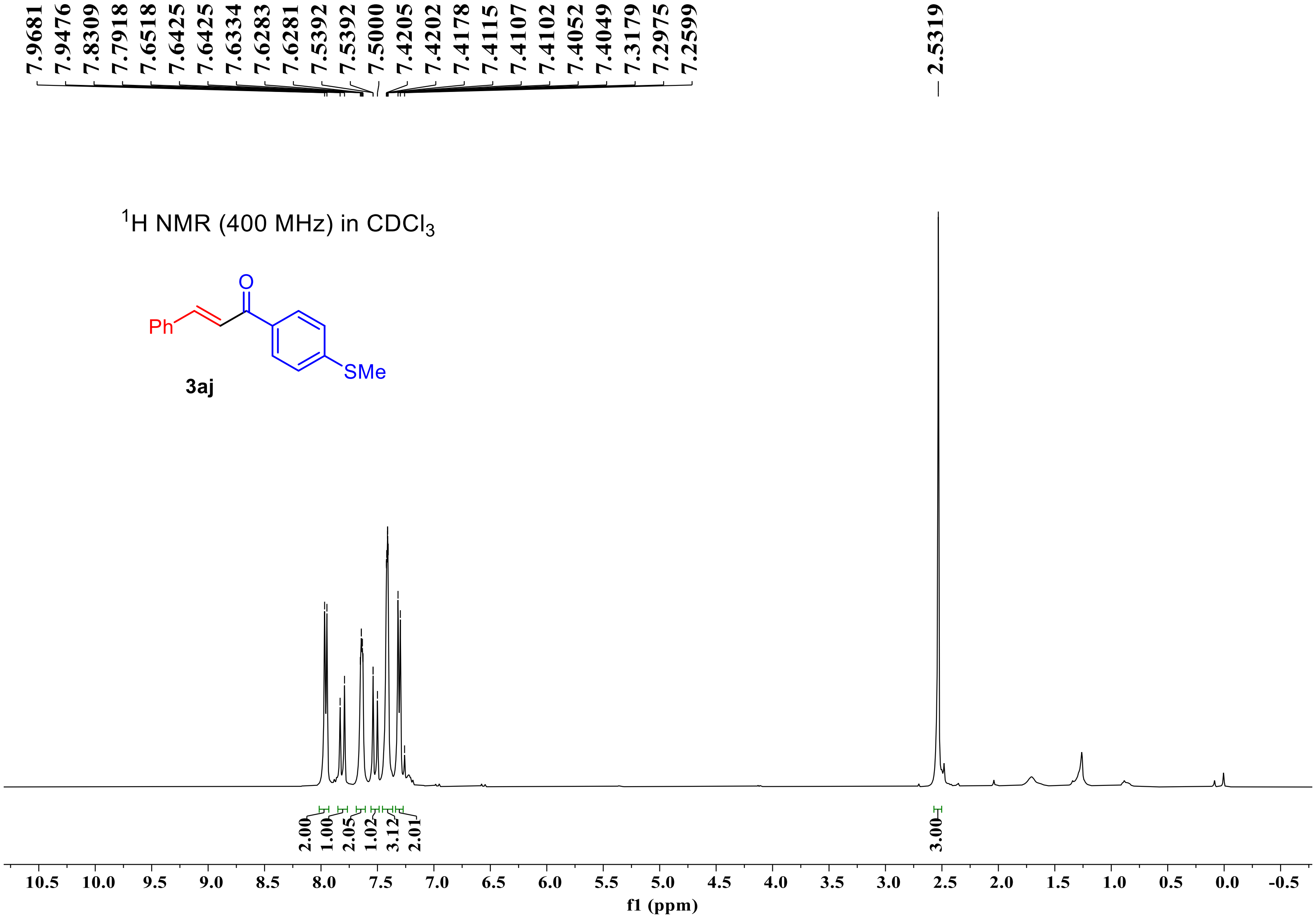

7.6450
7.6385
7.6338
7.6152
7.6053
7.5971
7.5891
7.5757
7.4947
7.4739
7.4553
7.3974
7.3890
7.3833
7.3574
7.2601
7.0623
7.0437
7.0250
7.0136
6.9925
3.8999
1H NMR (400 MHz) in CDCl3
O
OMe
Ph
3ah
3.97
1.02
3.97
2.00
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

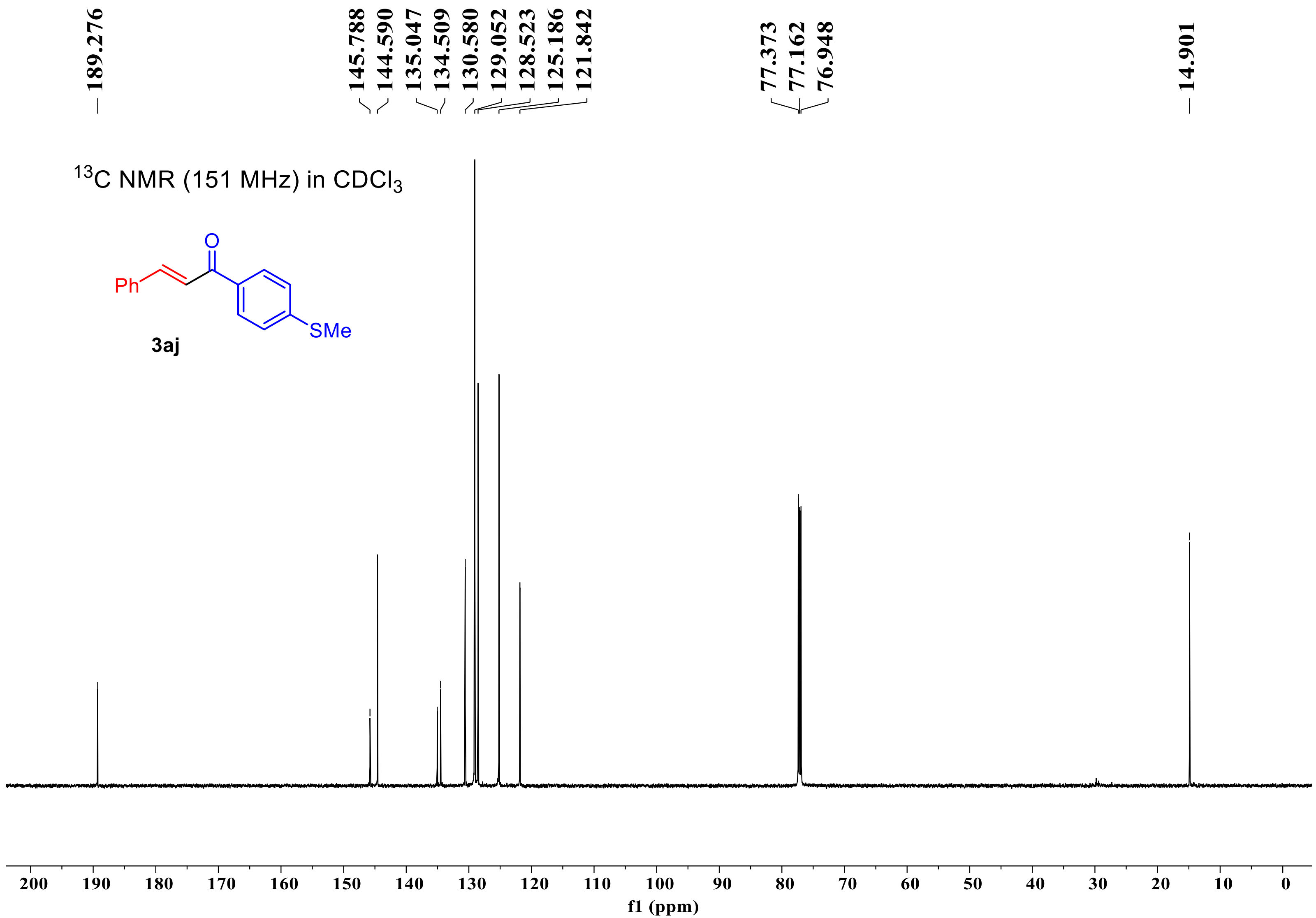


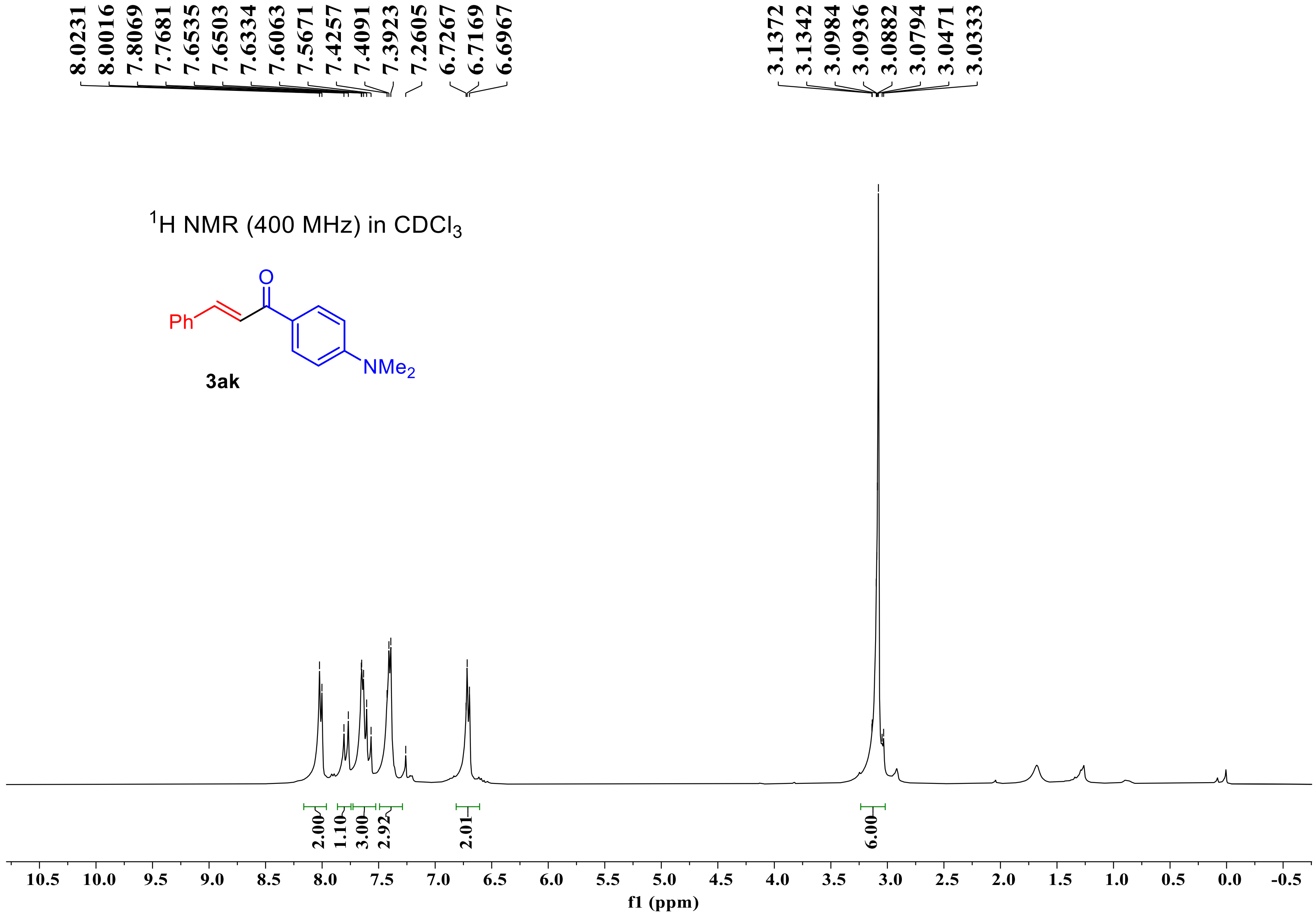
193.099
158.254
143.344
135.289
132.969
130.456
130.344
128.989
128.509
127.248
120.876
111.801
77.478
77.160
76.842
55.890
^{13}C NMR (101 MHz) in $CDCl_3$
O
OMe
Ph
3ah
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

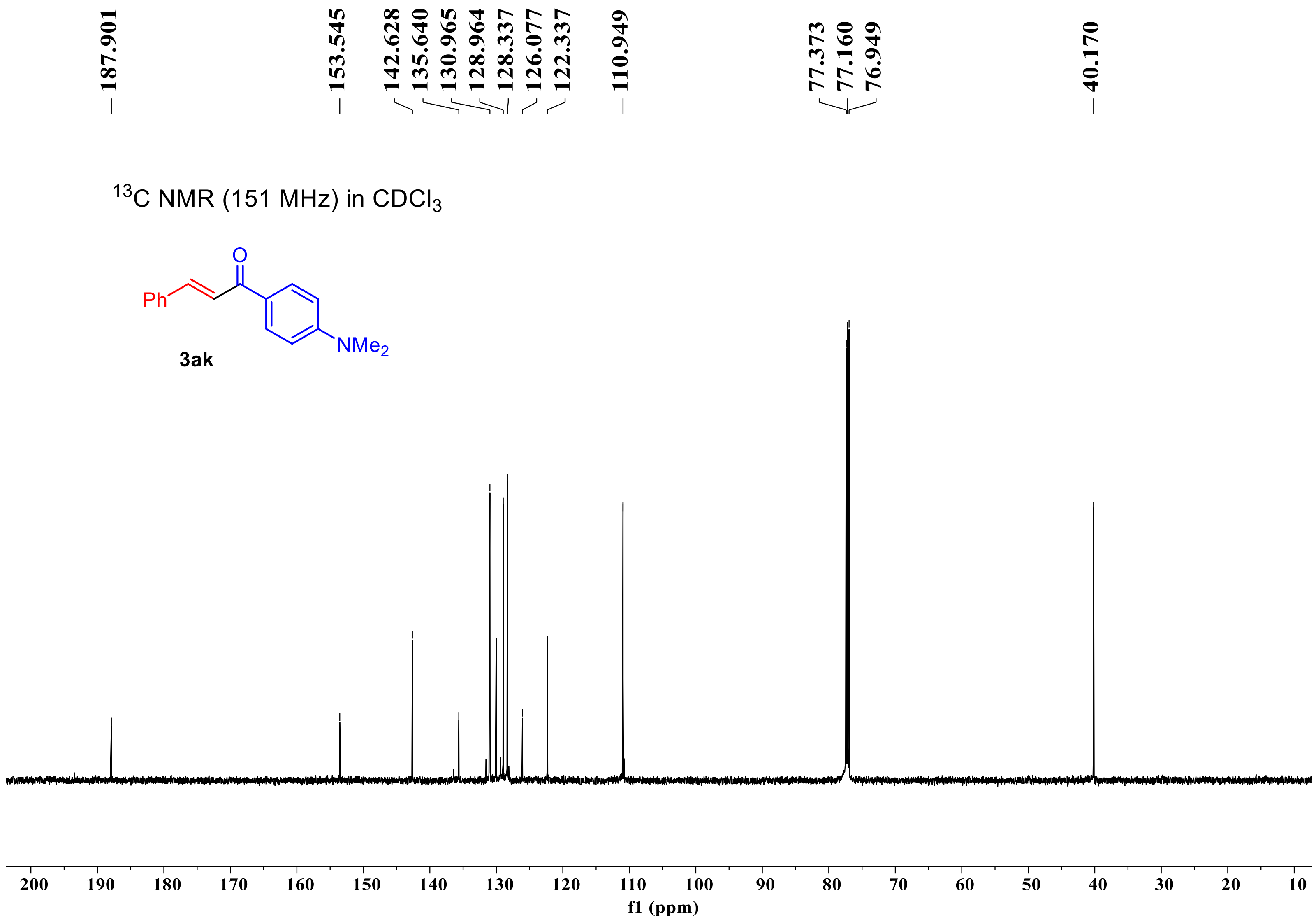

7.7764
7.7698
7.7597
7.6939
7.6676
7.6035
7.5937
7.5354
7.5089
7.3861
7.2605
6.5787
6.5735
6.5688
6.5591
6.5011
3.9077
3.8719
¹H NMR (600 MHz) in CDCl3
O
OMe
Ph
OMe
3ai
1.04
1.12
2.00
1.08
3.02
2.14
3.05
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

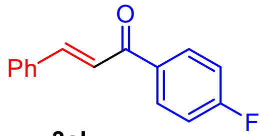

190.652
164.333
160.557
142.139
135.610
133.039
128.958
128.437
127.313
122.336
105.306
98.771
77.371
77.160
76.949
55.882
55.687
13C NMR (101 MHz) in CDCl3
O
OMe
Ph
OMe
3ai
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.9681
7.9476
7.8309
7.7918
7.6518
7.6425
7.6425
7.6334
7.6283
7.6281
7.5392
7.5392
7.5000
7.4205
7.4202
7.4178
7.4115
7.4107
7.4102
7.4052
7.4049
7.3179
7.2975
7.2599
2.5319
^{1}H NMR (400 MHz) in $CDCl_3$
O
Ph
SMe
3aj
2.00
1.00
2.05
1.02
3.12
2.01
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

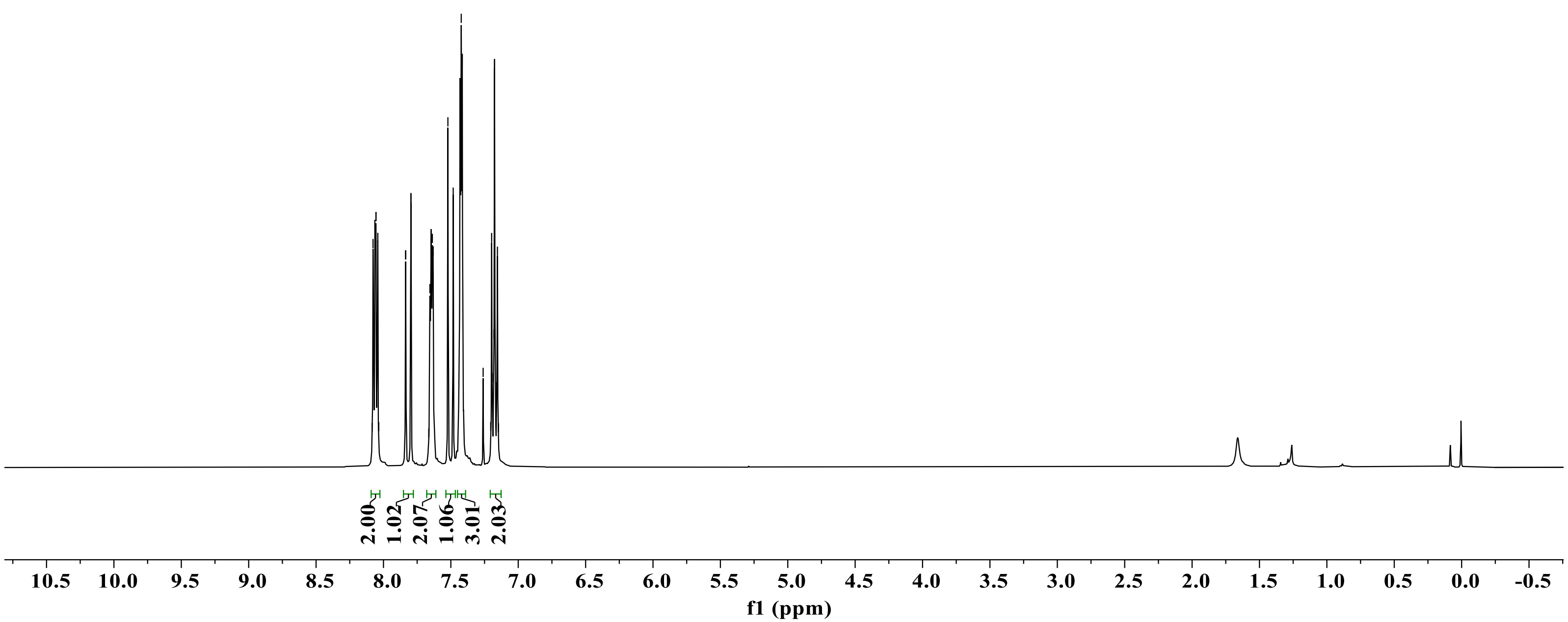

189.276
145.788
144.590
135.047
134.509
130.580
129.052
128.523
125.186
121.842
77.373
77.162
76.948
14.901
^{13}C NMR (151 MHz) in $CDCl_3$
O
Ph
SMe
3aj
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.0231
8.0016
7.8069
7.7681
7.6535
7.6503
7.6334
7.6063
7.5671
7.4257
7.4091
7.3923
7.2605
6.7267
6.7169
6.6967
3.1372
3.1342
3.0984
3.0936
3.0882
3.0794
3.0471
3.0333
1H NMR (400 MHz) in CDCl3
O
Ph
NMe2
3ak
2.00
1.10
3.00
2.92
2.01
6.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


187.901
153.545
142.628
135.640
130.965
128.964
128.337
126.077
122.337
110.949
77.373
77.160
76.949
40.170
13C NMR (151 MHz) in CDCl3
O
Ph
NMe2
3ak
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

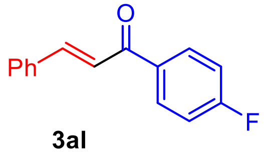


3al

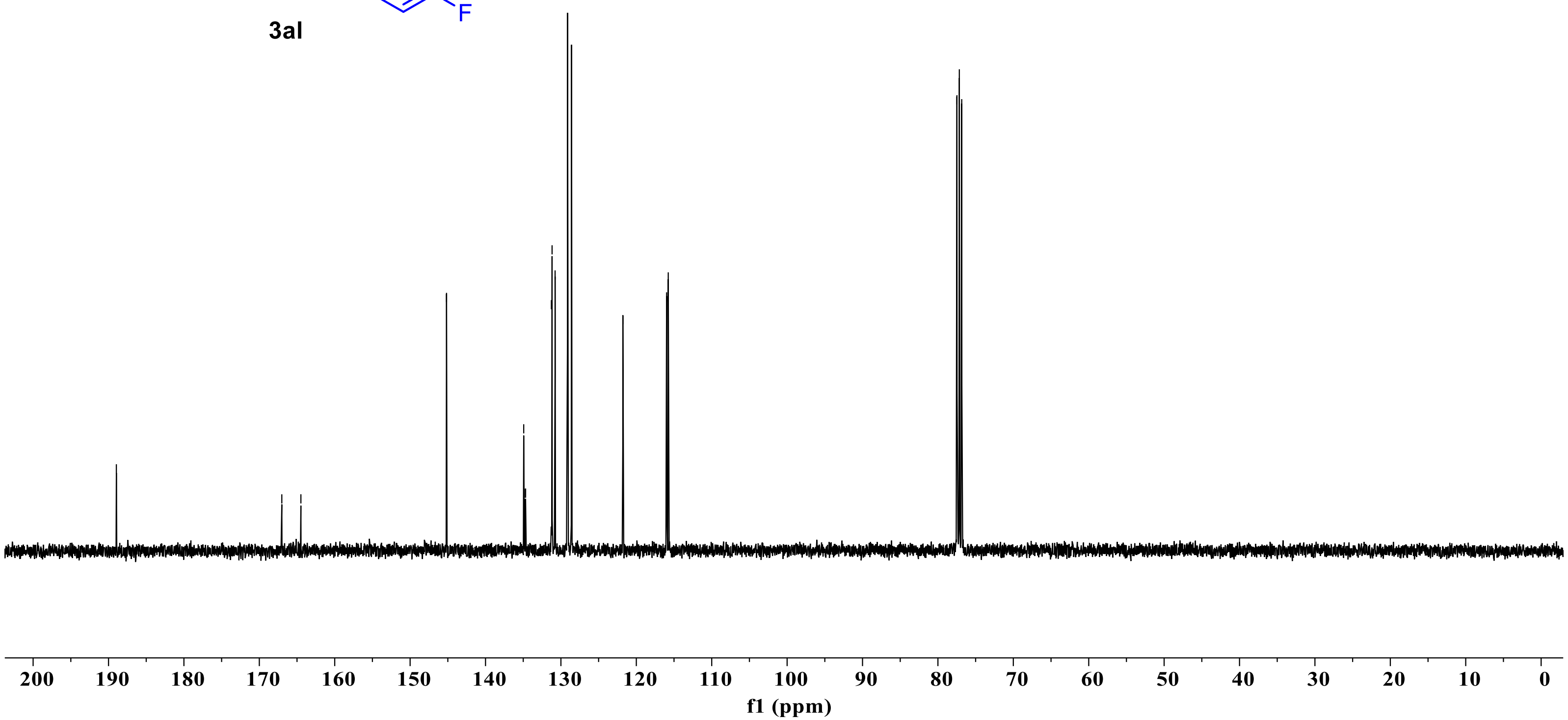

8.0844
8.0774
8.0723
8.0639
8.0555
8.0555
8.0470
8.0419
8.0348
7.8353
7.8353
7.7961
7.7960
7.6638
7.6553
7.6463
7.6463
7.6426
7.6373
7.6329
7.6312
7.5218
7.4825
7.4302
7.4228
7.4155
7.2604
7.2041
7.1972
7.1923
7.1799
7.1758
7.1758
7.1544
7.1471
^{1}H NMR (400 MHz) in $CDCl_3$
2.00
1.02
2.07
1.06
3.01
2.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

188.961
167.016
164.487
145.171
134.936
134.717
134.687
131.267
131.174
130.774
129.125
128.595
121.784
115.982
115.764
77.478
77.160
76.844

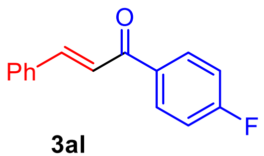
^{13}C NMR (101 MHz) in $CDCl_3$



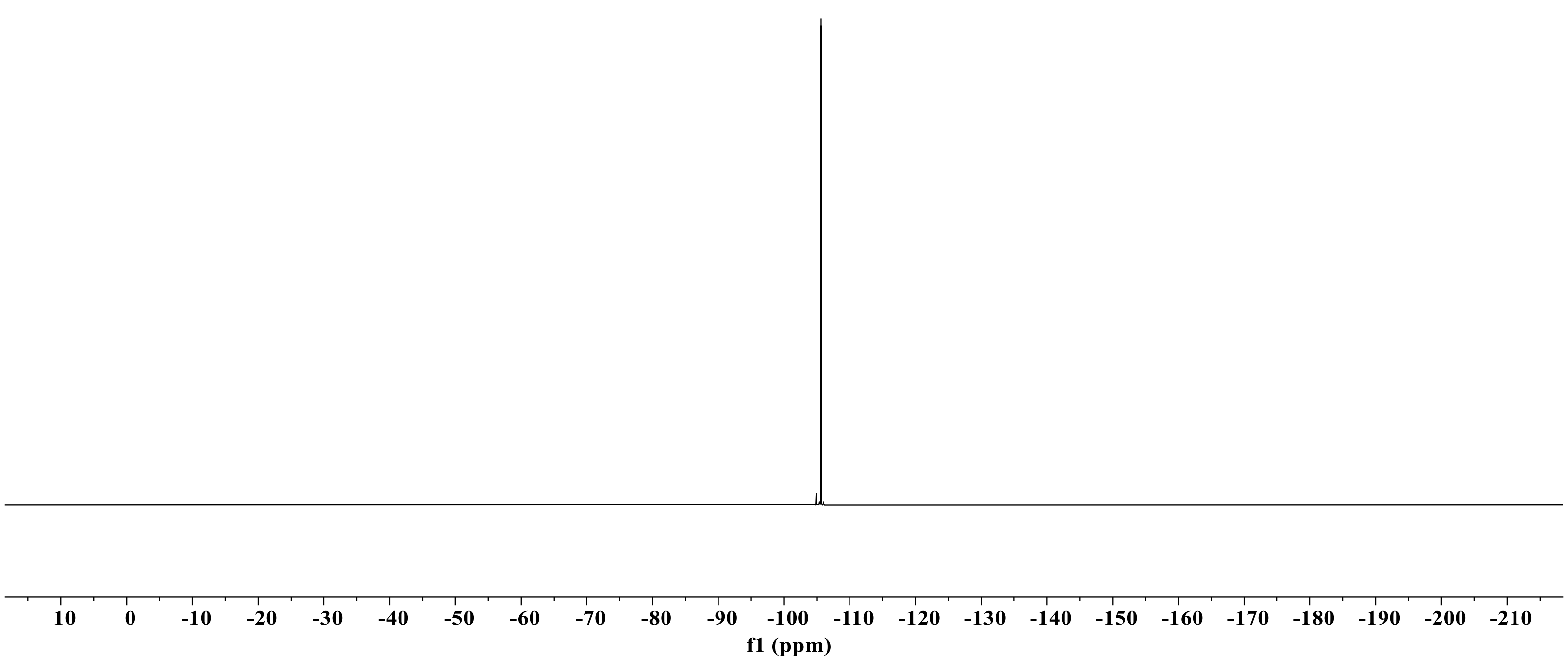
3al

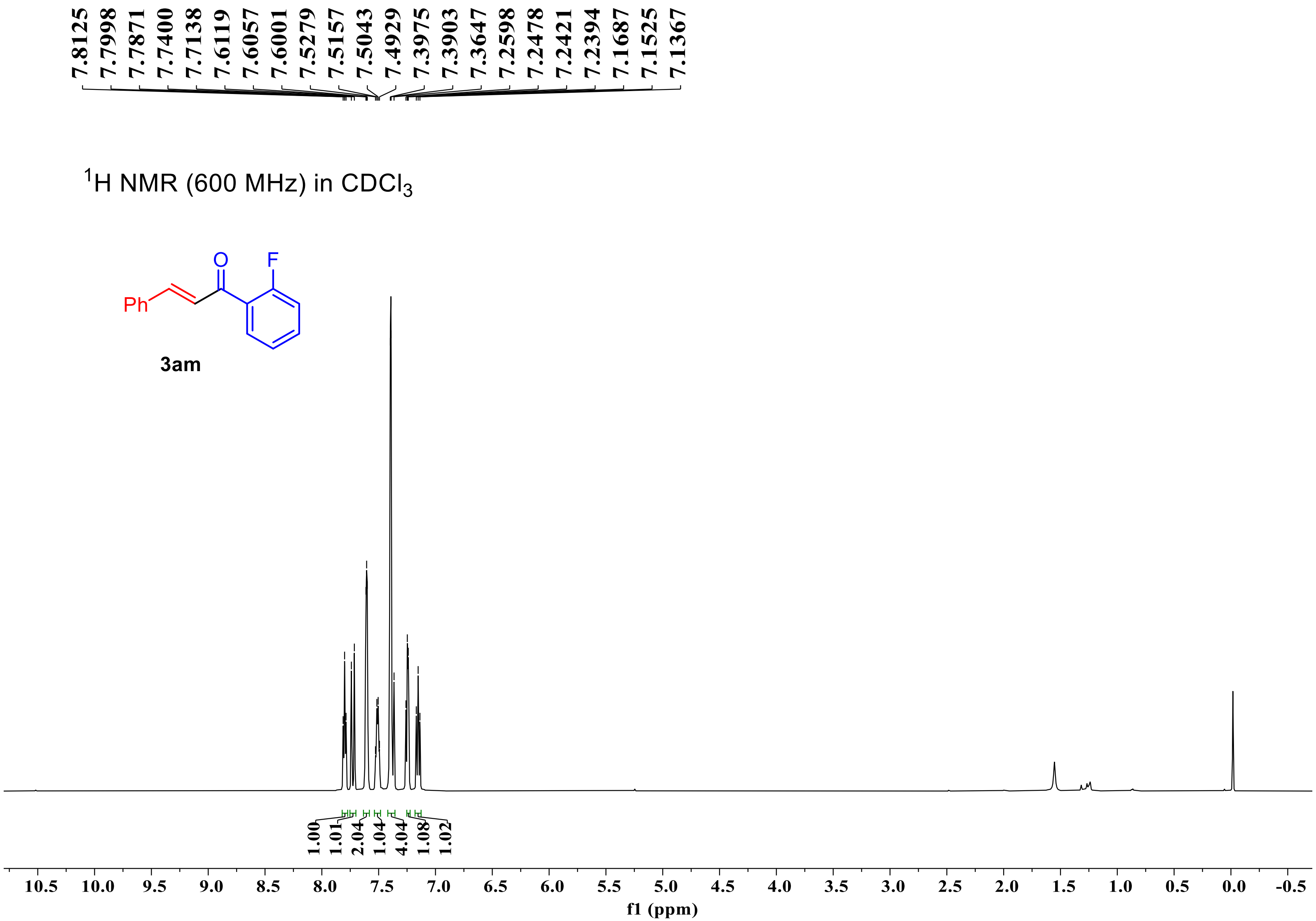


^{19}F NMR (377 MHz) in $CDCl_3$

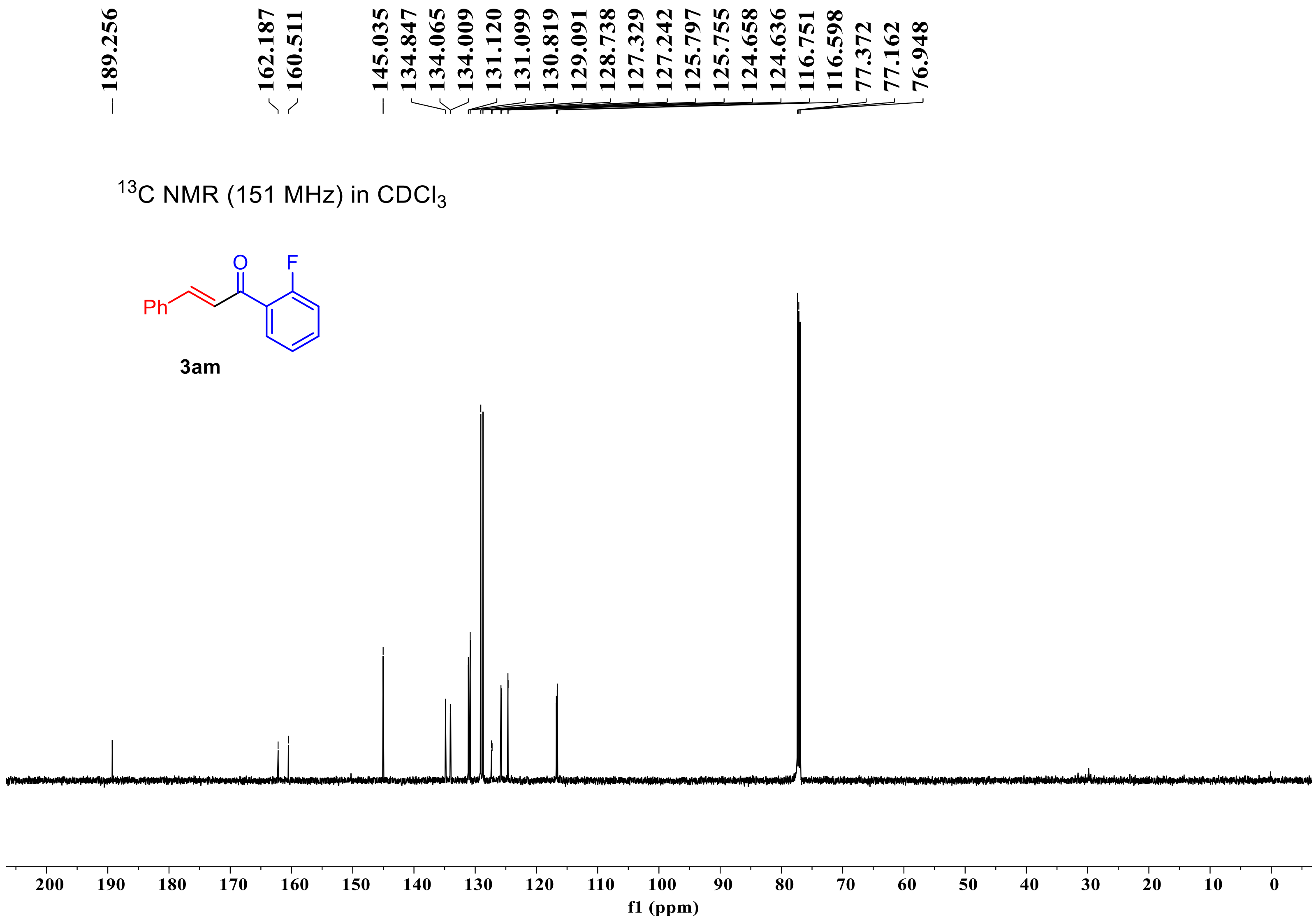


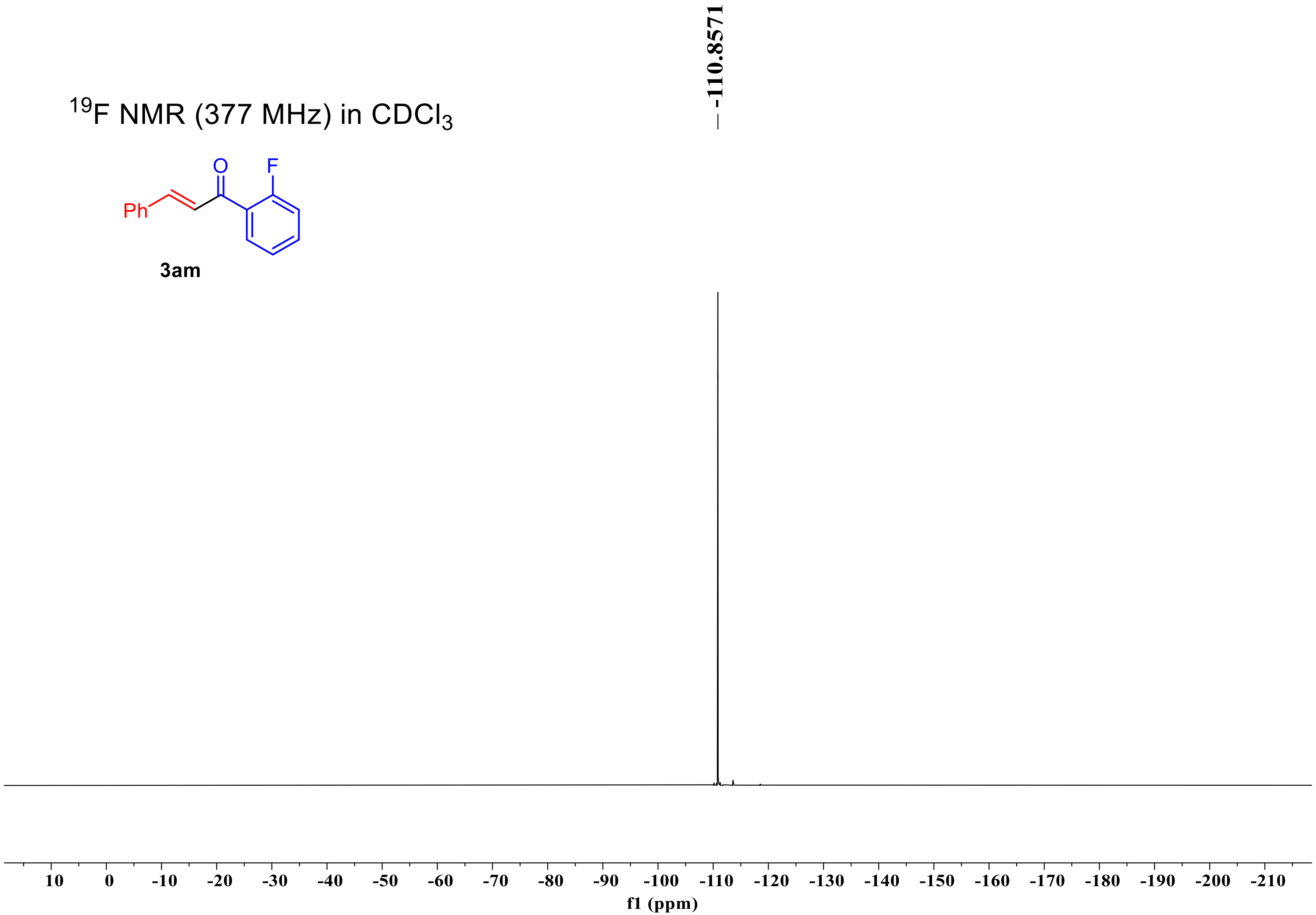
3al



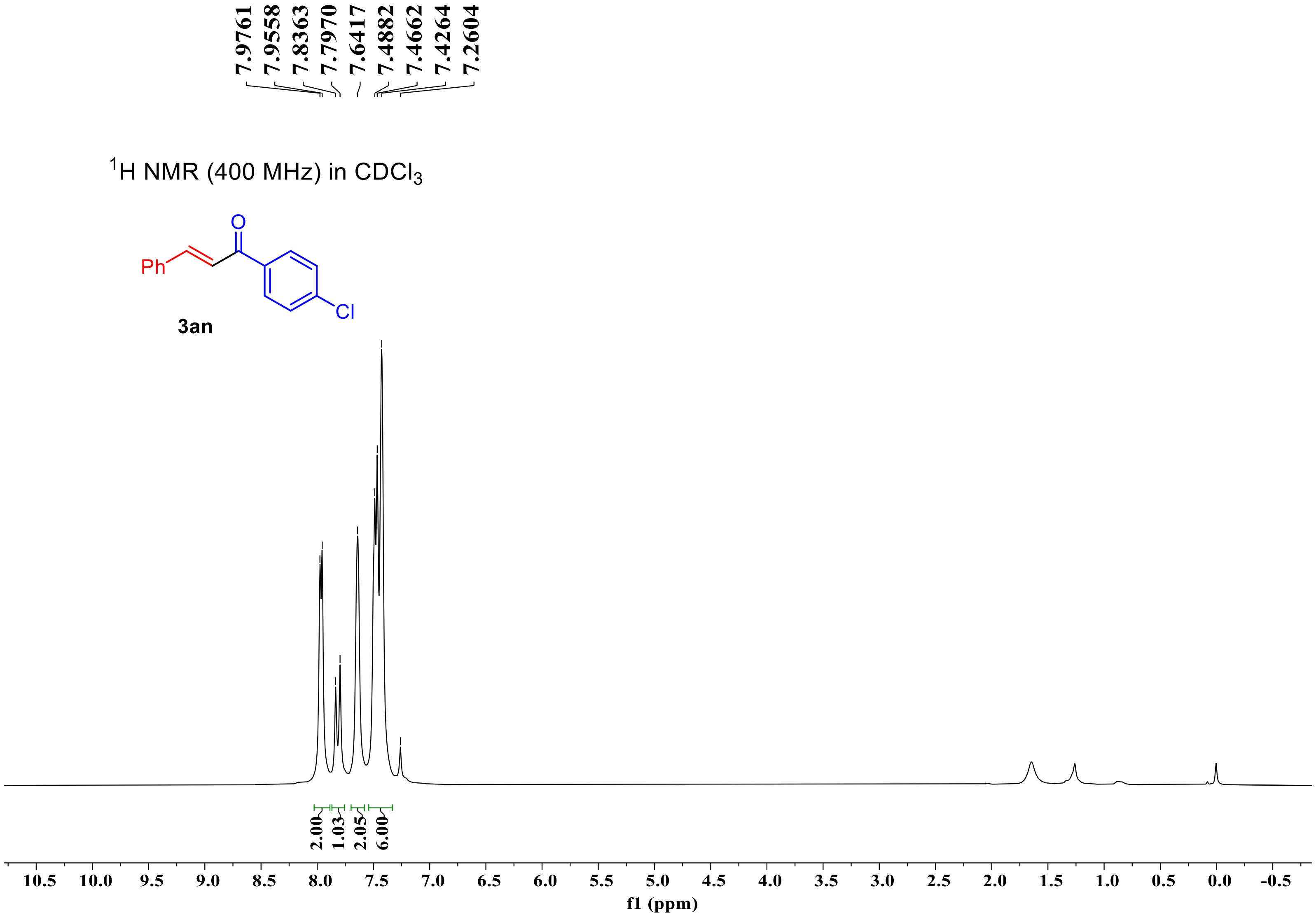


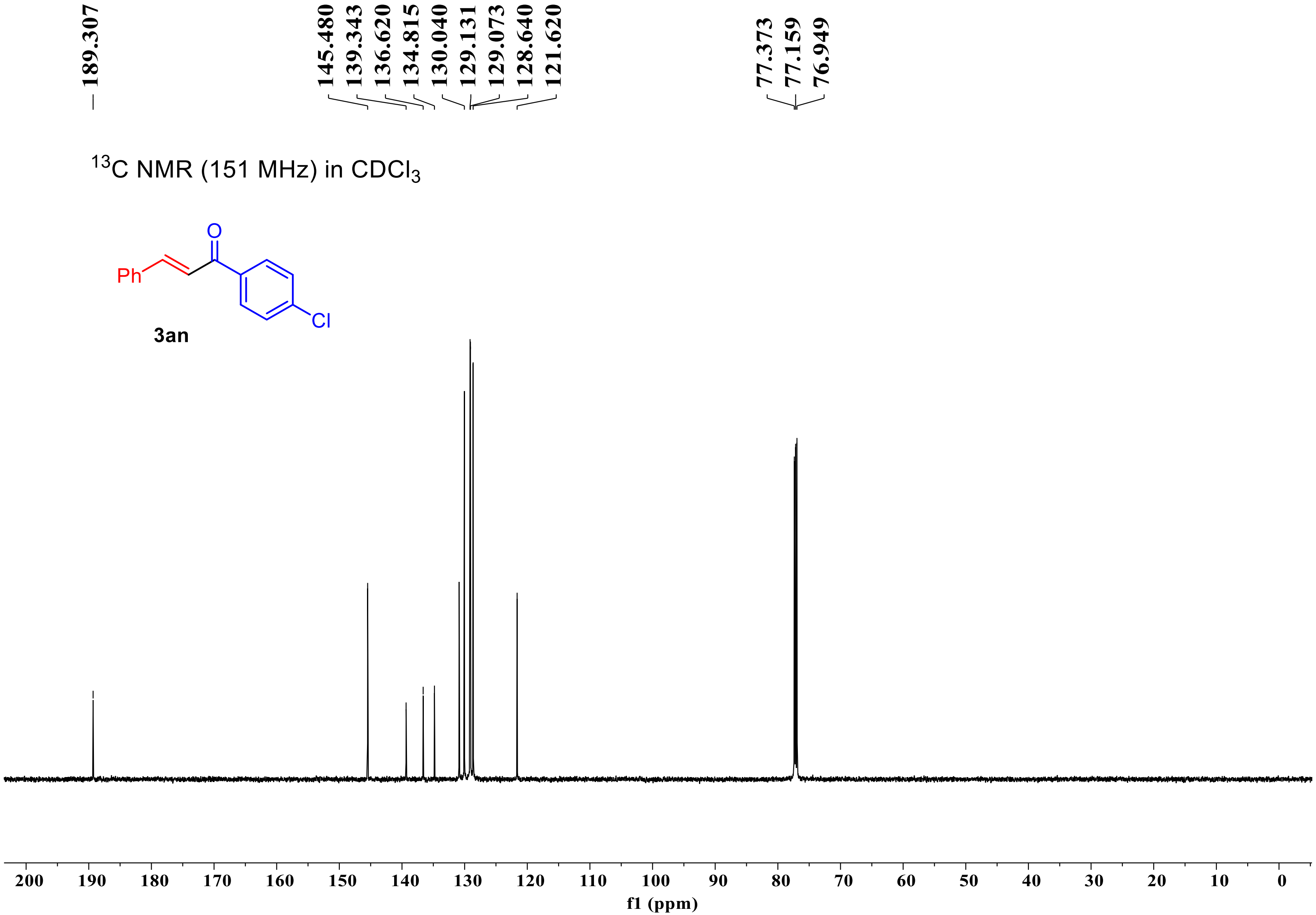
7.8125
7.7998
7.7871
7.7400
7.7138
7.6119
7.6057
7.6001
7.5279
7.5157
7.5043
7.4929
7.3975
7.3903
7.3647
7.2598
7.2478
7.2421
7.2394
7.1687
7.1525
7.1367
^{1}H NMR (600 MHz) in $CDCl_3$
O
F
Ph
3am
1.00
1.01
2.04
1.04
4.04
1.08
1.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


189.256
162.187
160.511
145.035
134.847
134.065
134.009
131.120
131.099
130.819
129.091
128.738
127.329
127.242
125.797
125.755
124.658
124.636
116.751
116.598
77.372
77.162
76.948
13C NMR (151 MHz) in CDCl3
O
F
Ph
3am
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

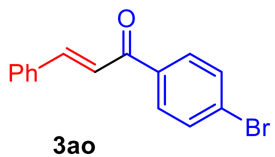


-110.8571
^{19}F NMR (377 MHz) in $CDCl_3$
O
F
Ph
3am
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

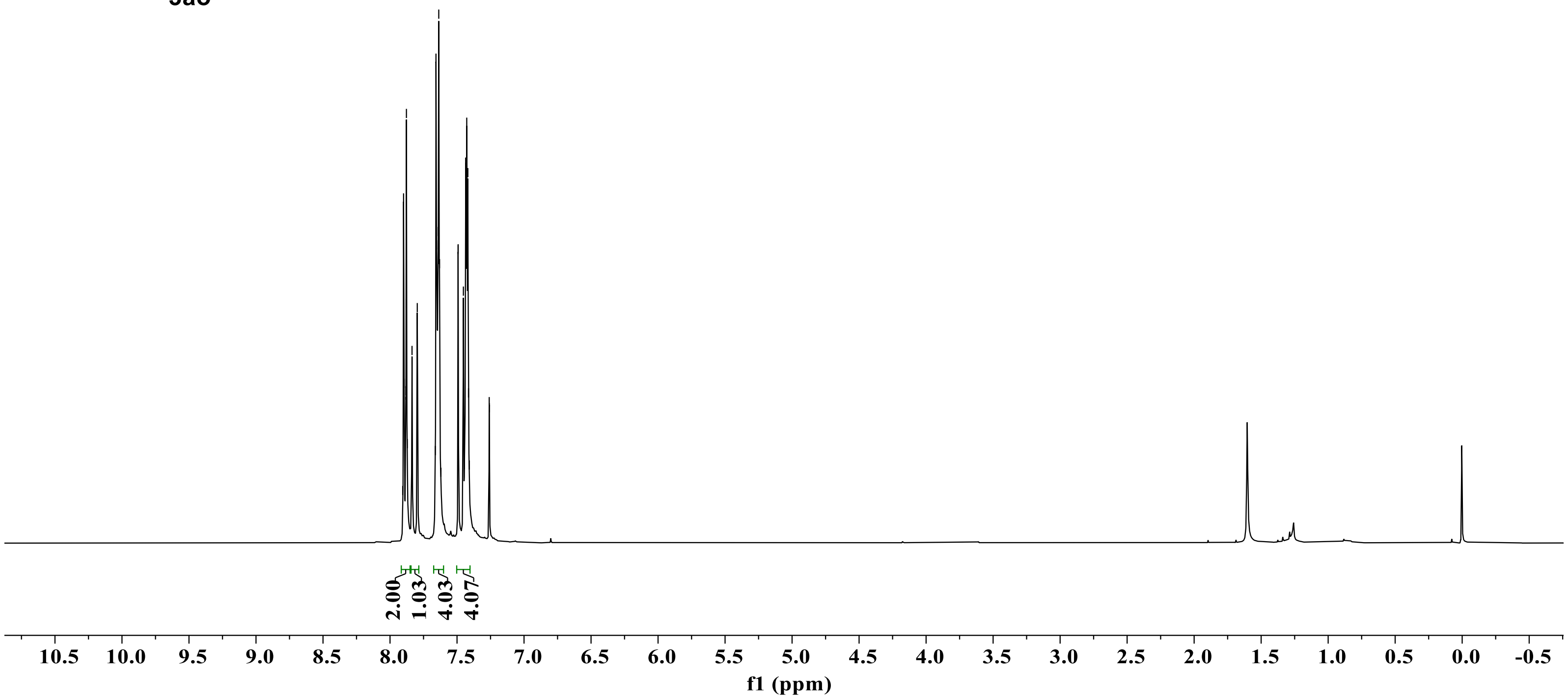

7.9761
7.9558
7.8363
7.7970
7.6417
7.4882
7.4662
7.4264
7.2604
1H NMR (400 MHz) in CDCl3
Ph
O
Cl
3an
2.00
1.03
2.05
6.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


189.307
145.480
139.343
136.620
134.815
130.040
129.131
129.073
128.640
121.620
77.373
77.159
76.949
13C NMR (151 MHz) in CDCl3
O
Ph
Cl
3an
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

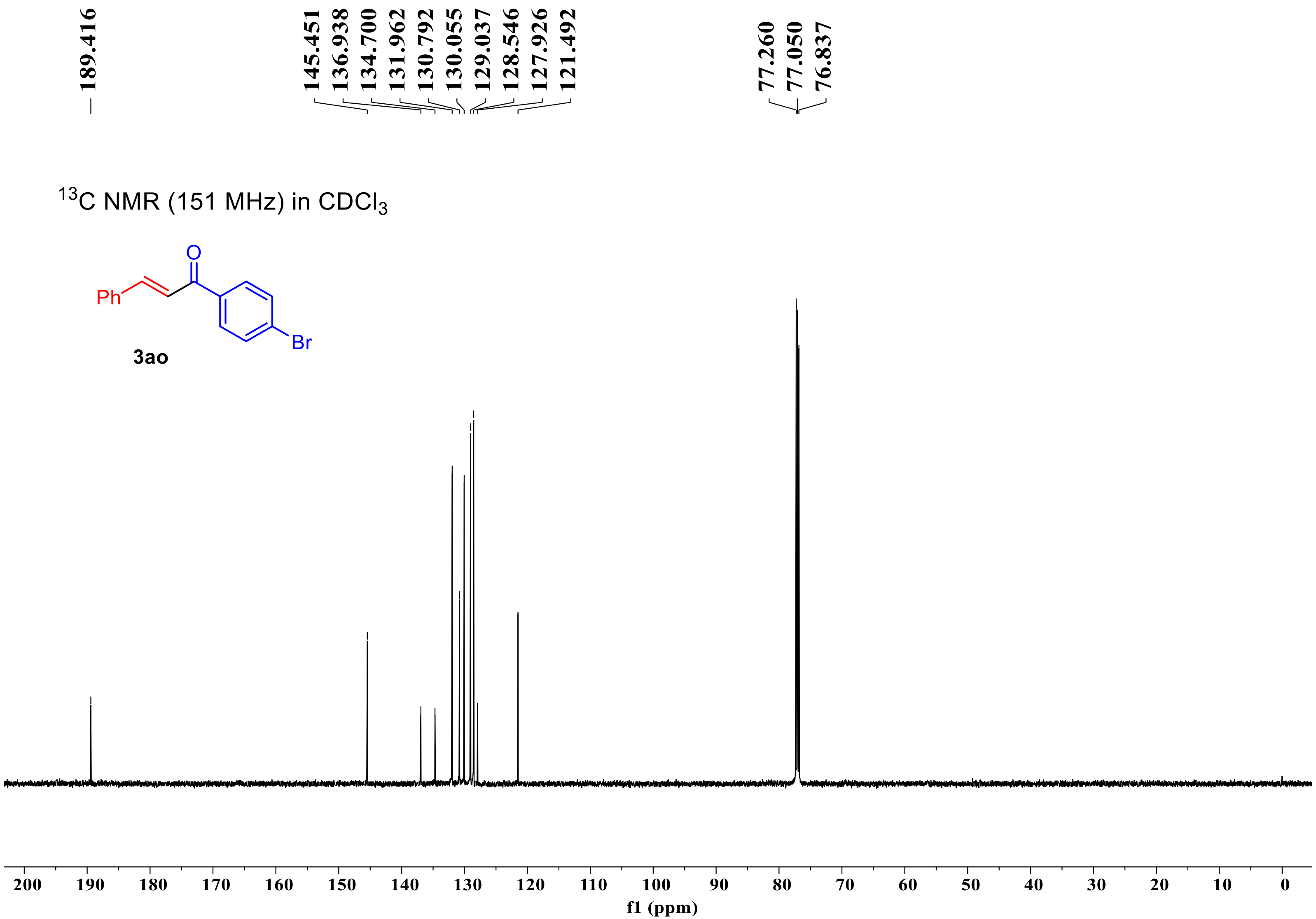
^{1}H NMR (400 MHz) in $CDCl_3$



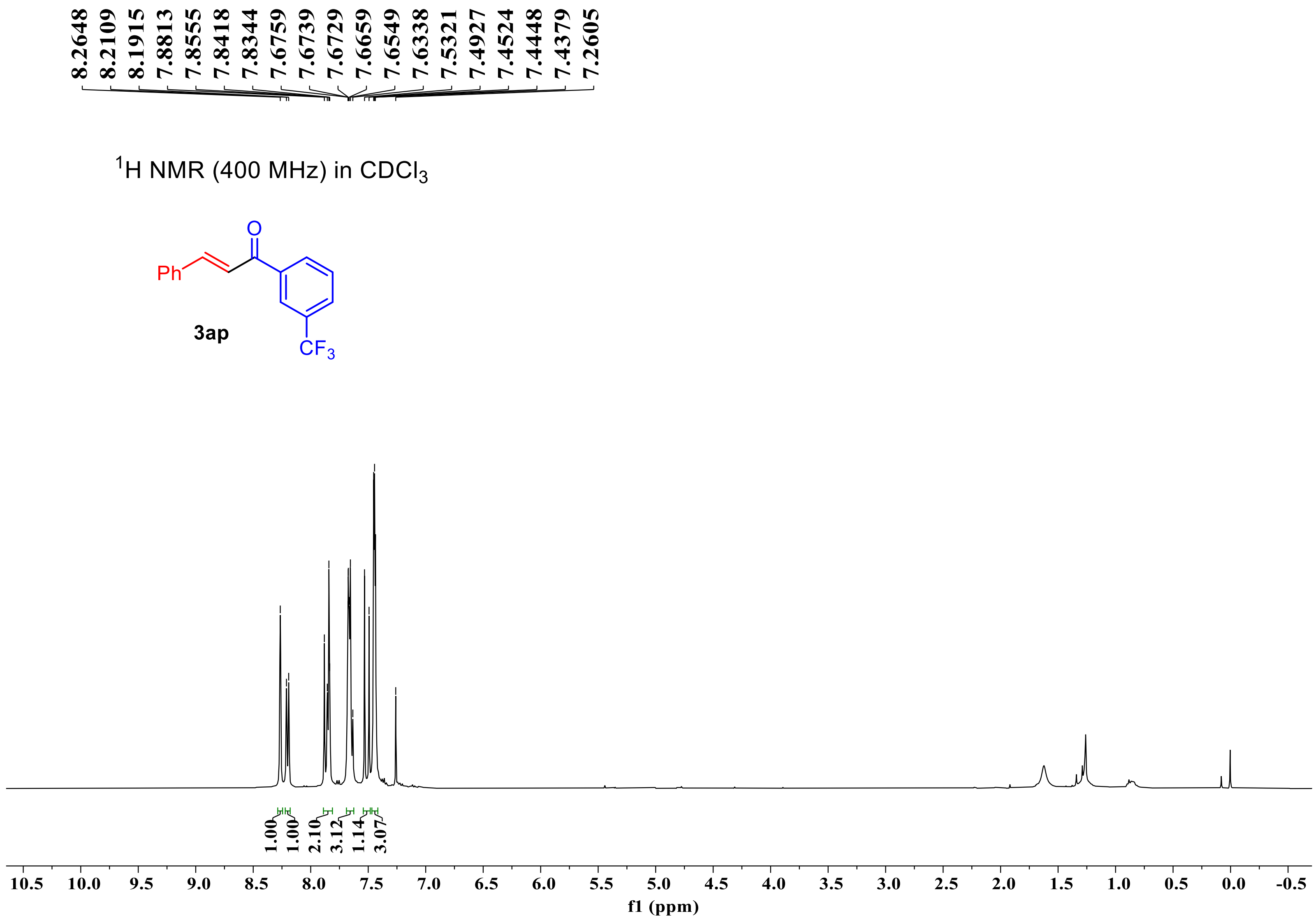
3ao

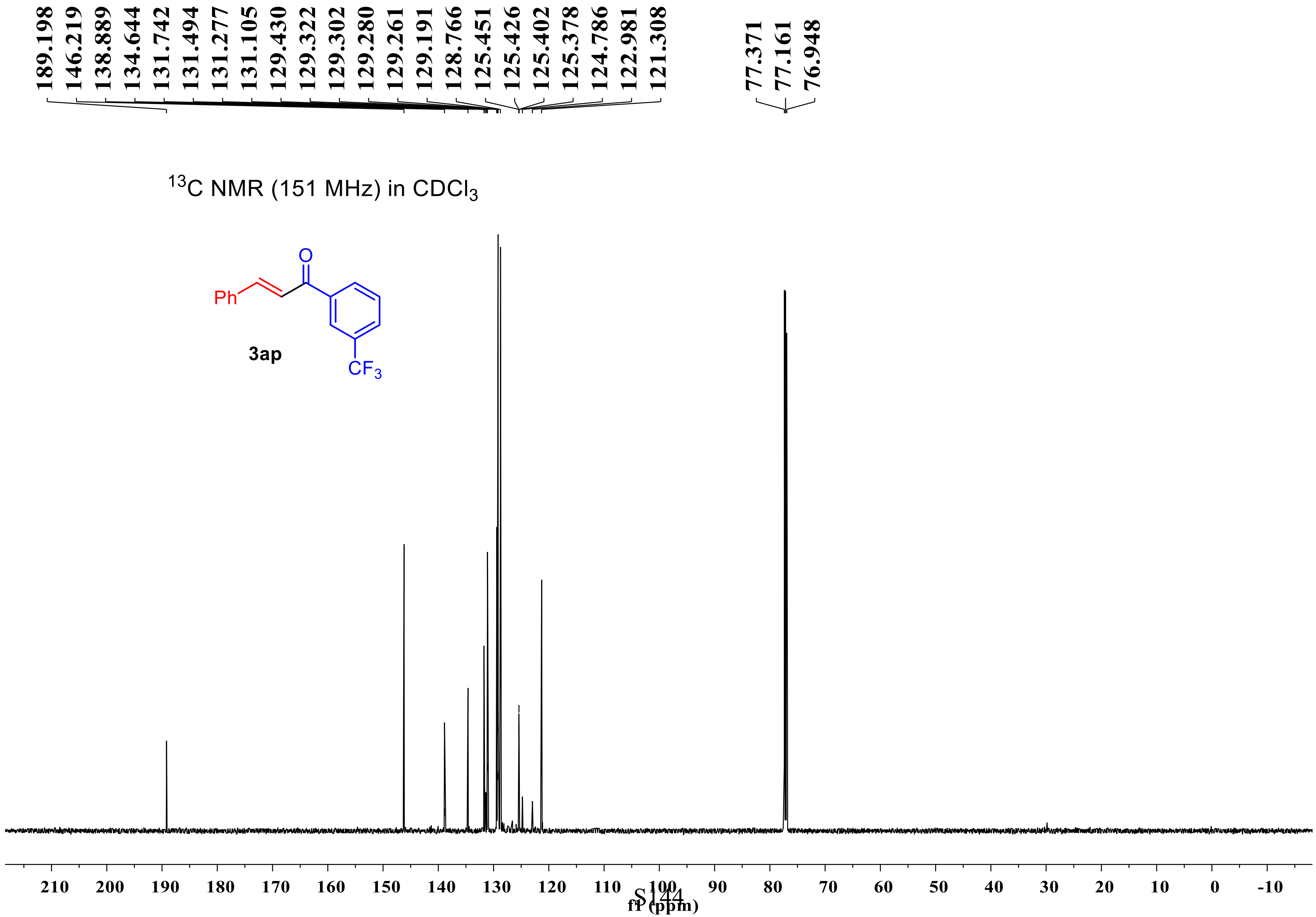


^{13}C NMR (151 MHz) in $CDCl_3$

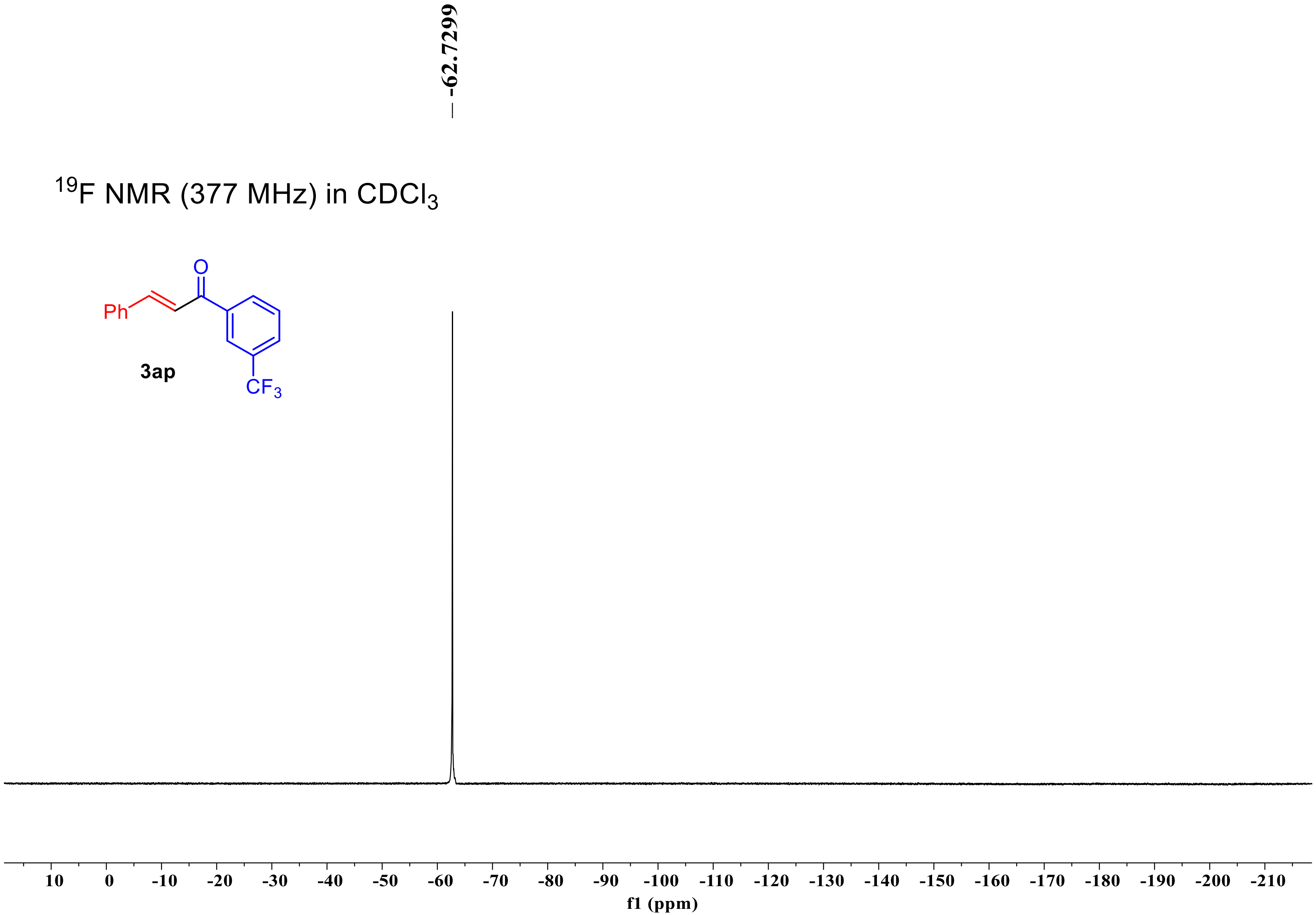


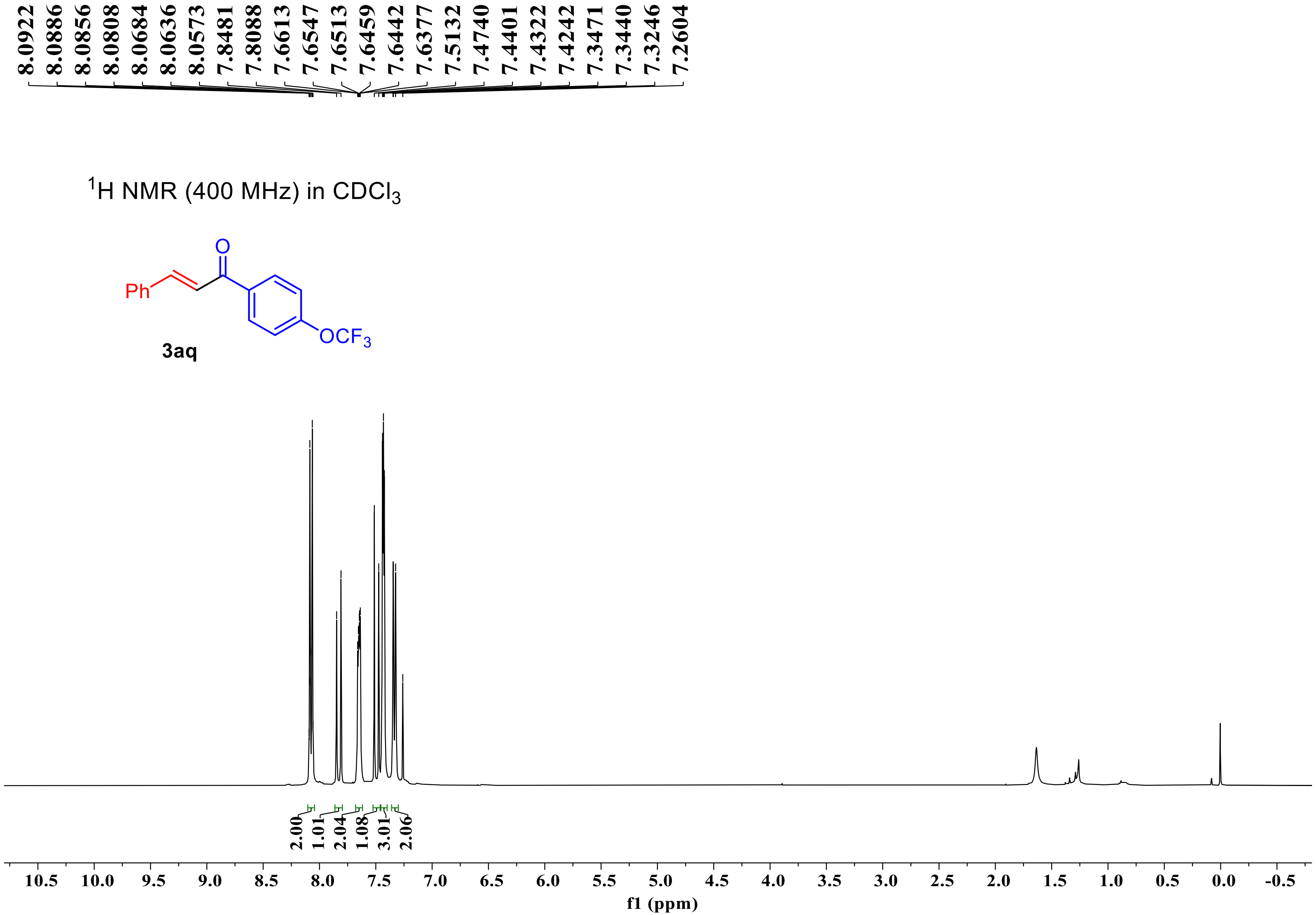
3ao

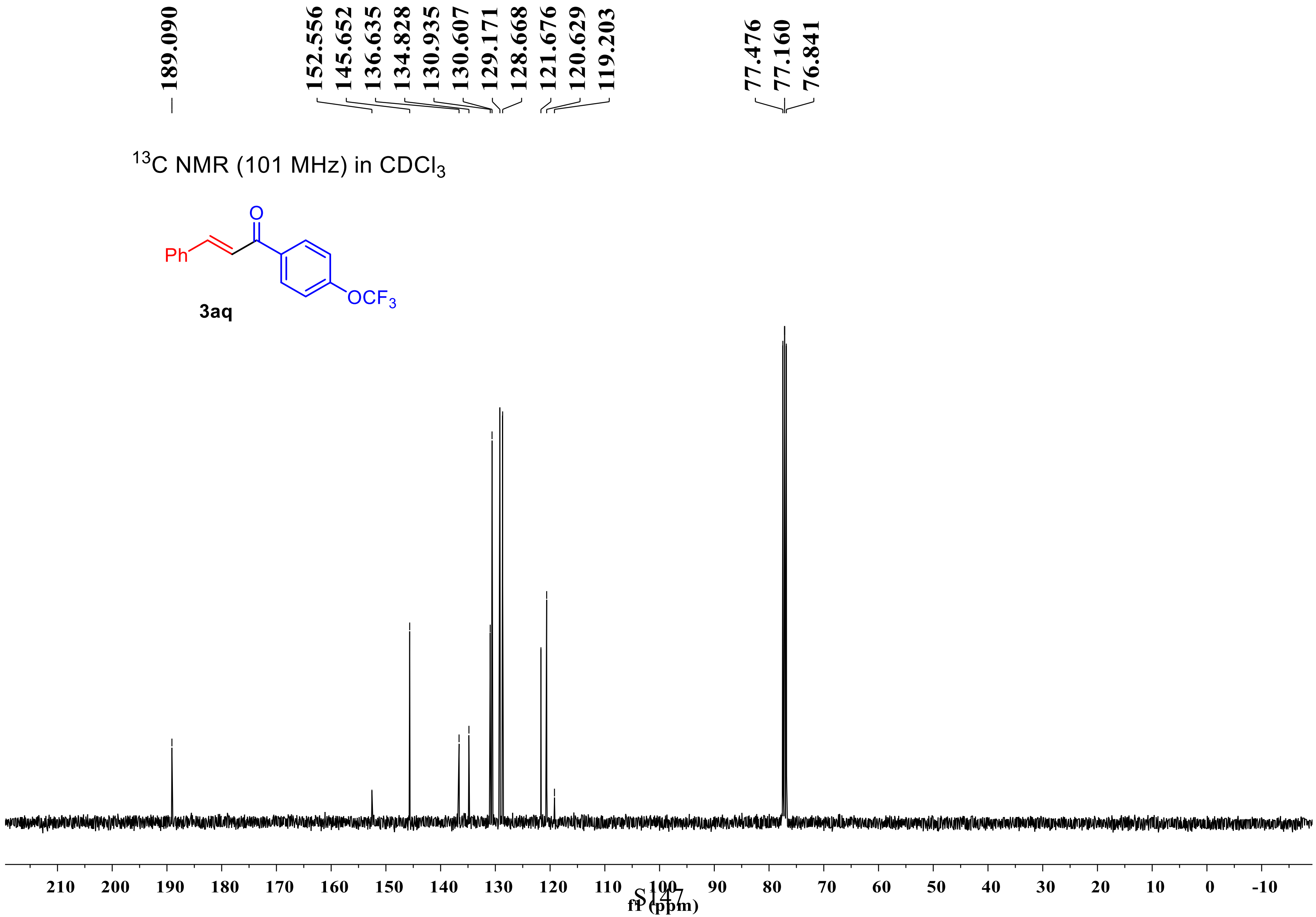

8.2648
8.2109
8.1915
7.8813
7.8555
7.8418
7.8344
7.6759
7.6739
7.6729
7.6659
7.6549
7.6338
7.5321
7.4927
7.4524
7.4448
7.4379
7.2605
^{1}H NMR (400 MHz) in $CDCl_3$
O
Ph
3ap
CF_3
1.00
1.00
2.10
3.12
1.14
3.07
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


189.198
146.219
138.889
134.644
131.742
131.494
131.277
131.105
129.430
129.322
129.302
129.280
129.261
129.191
128.766
125.451
125.426
125.402
125.378
124.786
122.981
121.308
77.371
77.161
76.948
^{13}C NMR (151 MHz) in $CDCl_3$
O
Ph
3ap
CF_3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{19}F NMR (377 MHz) in $CDCl_3$

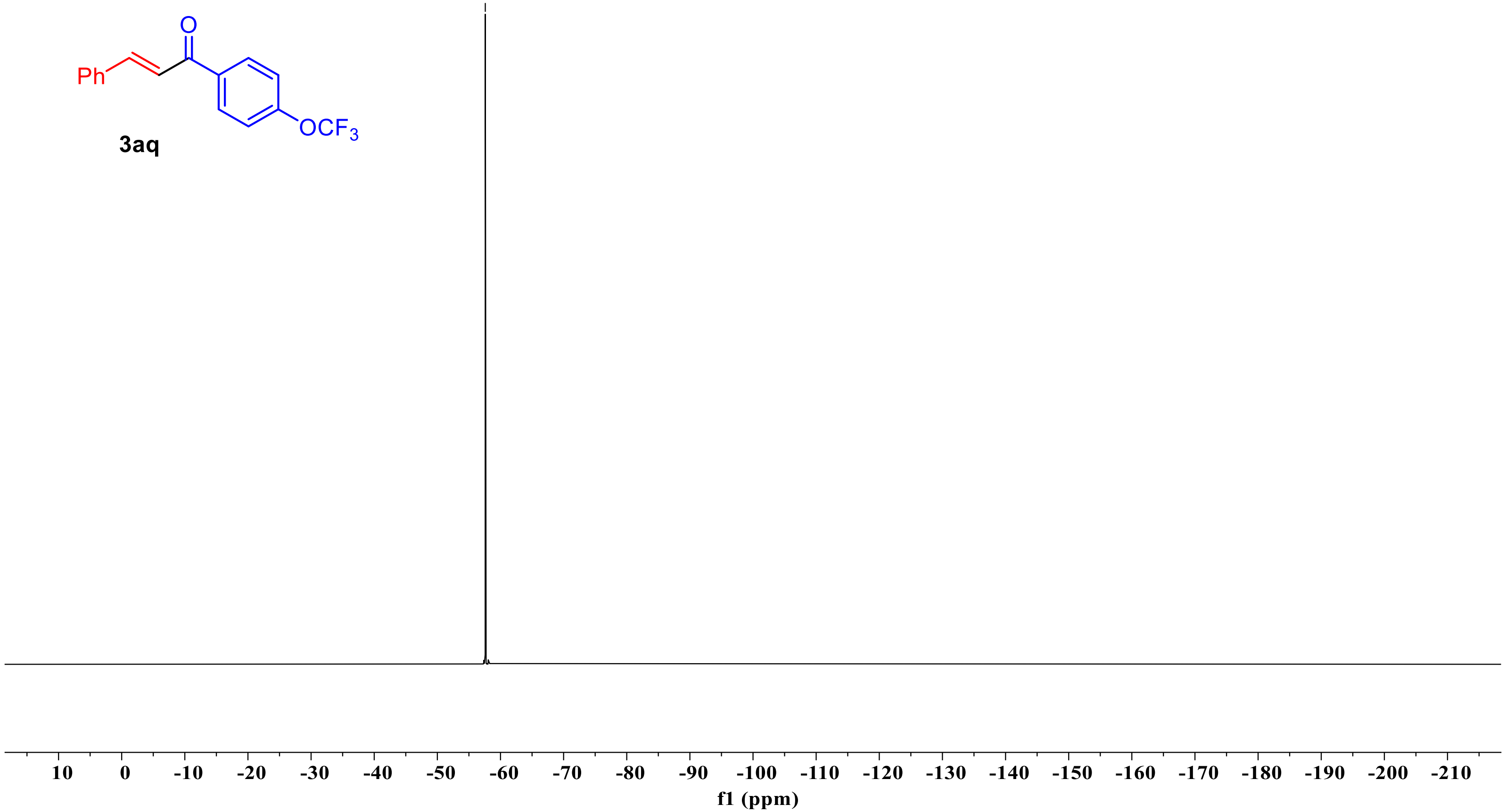


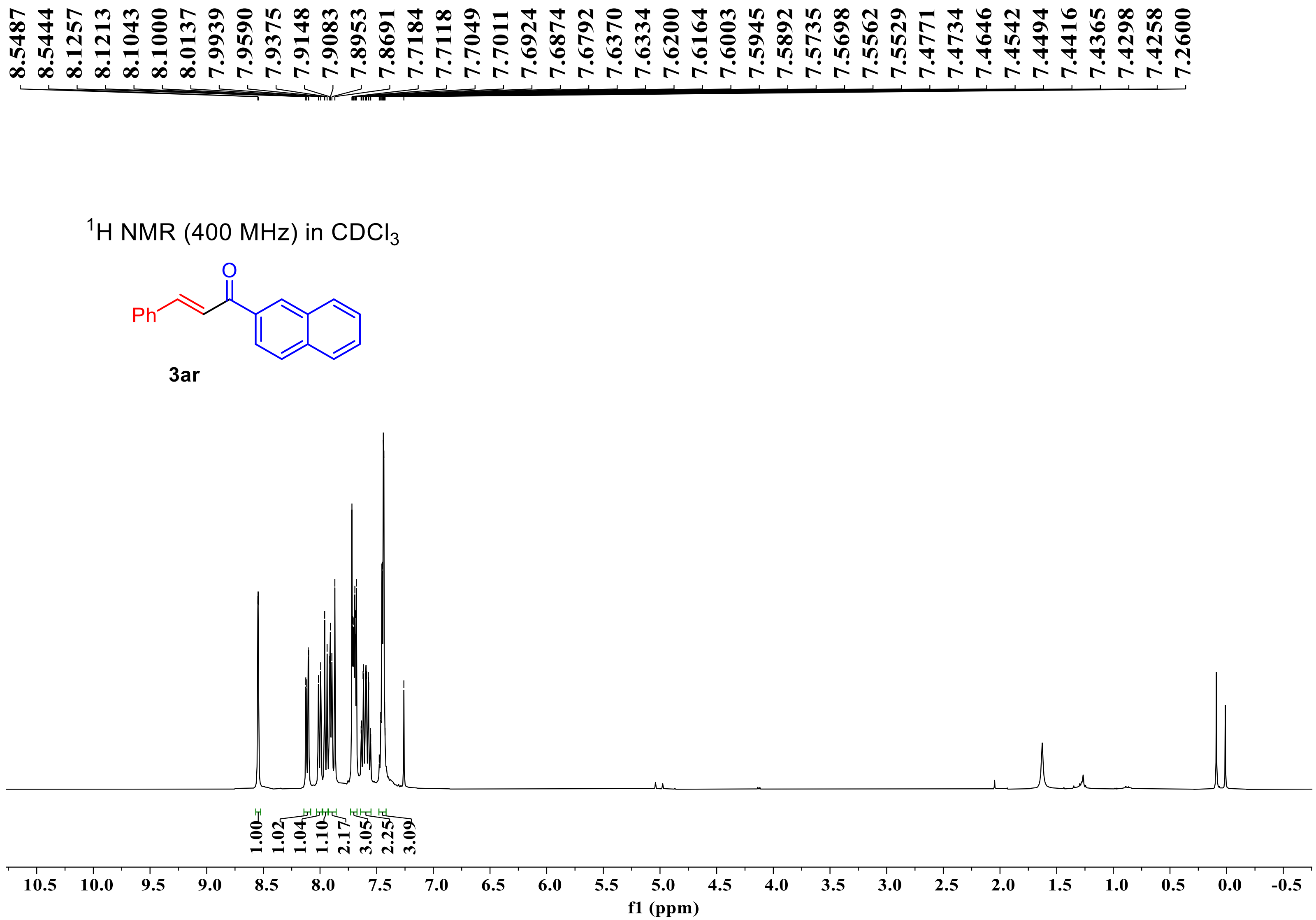

8.0922
8.0886
8.0856
8.0808
8.0684
8.0636
8.0573
7.8481
7.8088
7.6613
7.6547
7.6513
7.6459
7.6442
7.6377
7.5132
7.4740
7.4401
7.4322
7.4242
7.3471
7.3440
7.3246
7.2604
1H NMR (400 MHz) in CDCl3
O
Ph
OCF3
3aq
2.00
1.01
2.04
1.08
3.01
2.06
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


189.090
152.556
145.652
136.635
134.828
130.935
130.607
129.171
128.668
121.676
120.629
119.203
77.476
77.160
76.841
^{13}C NMR (101 MHz) in $CDCl_3$
Ph
O
OCF_3
3aq
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

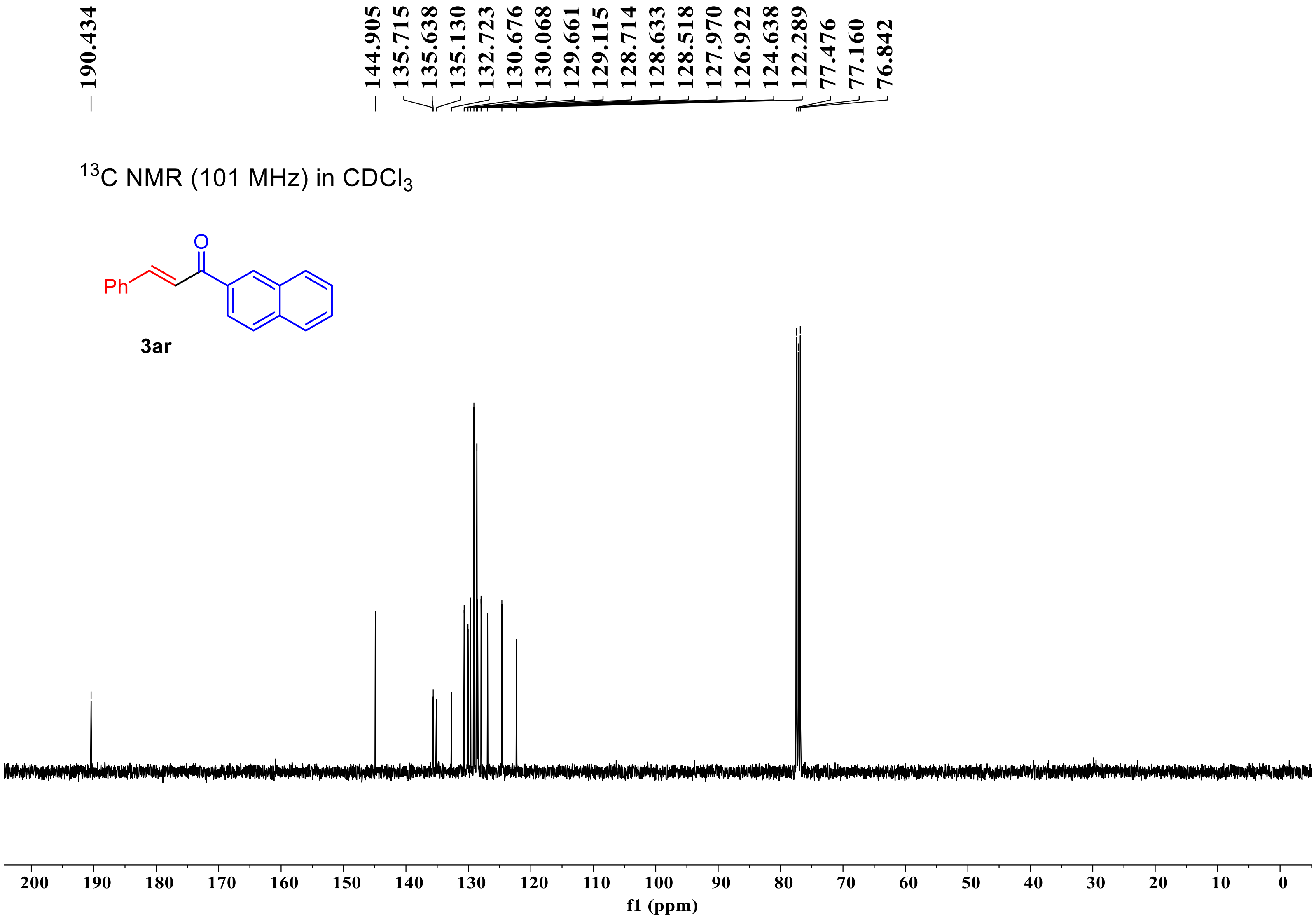
-57.5929

^{19}F NMR (377 MHz) in $CDCl_3$

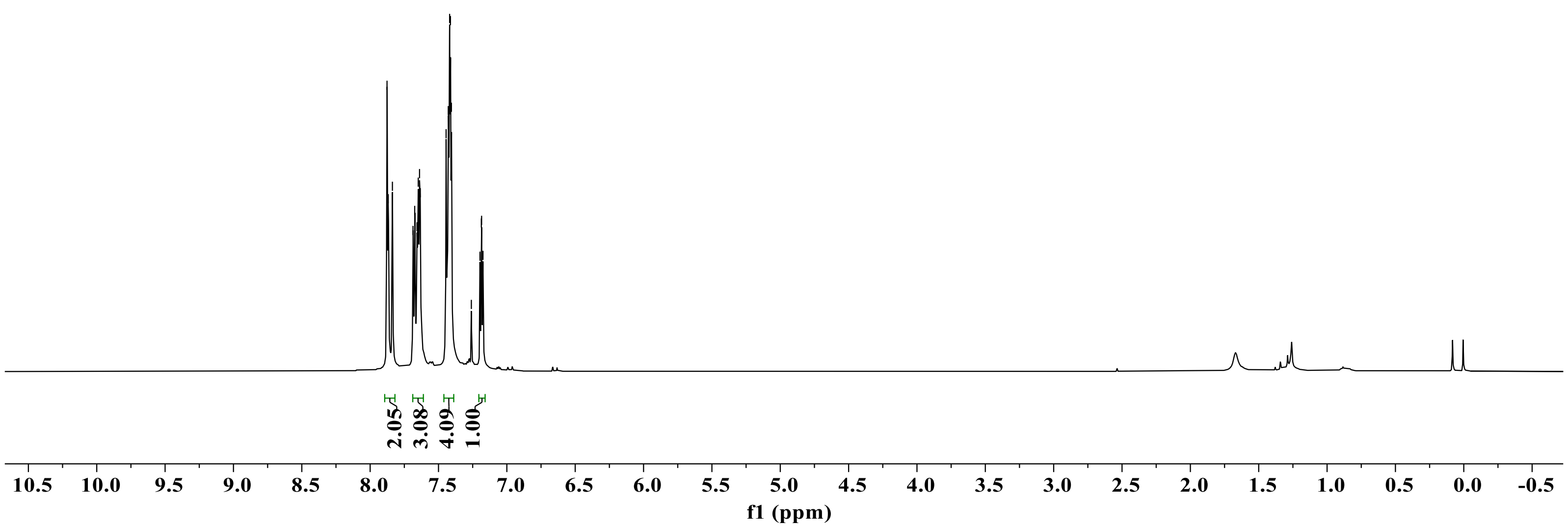



8.5487
8.5444
8.1257
8.1213
8.1043
8.1000
8.0137
7.9939
7.9590
7.9375
7.9148
7.9083
7.8953
7.8691
7.7184
7.7118
7.7049
7.7011
7.6924
7.6874
7.6792
7.6370
7.6334
7.6200
7.6164
7.6003
7.5945
7.5892
7.5735
7.5698
7.5562
7.5529
7.4771
7.4734
7.4646
7.4542
7.4494
7.4416
7.4365
7.4298
7.4258
7.2600
1H NMR (400 MHz) in CDCl3
Ph
O
3ar
1.00
1.02
1.04
1.10
2.17
3.05
2.25
3.09
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

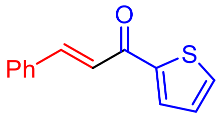
^{13}C NMR (101 MHz) in $CDCl_3$



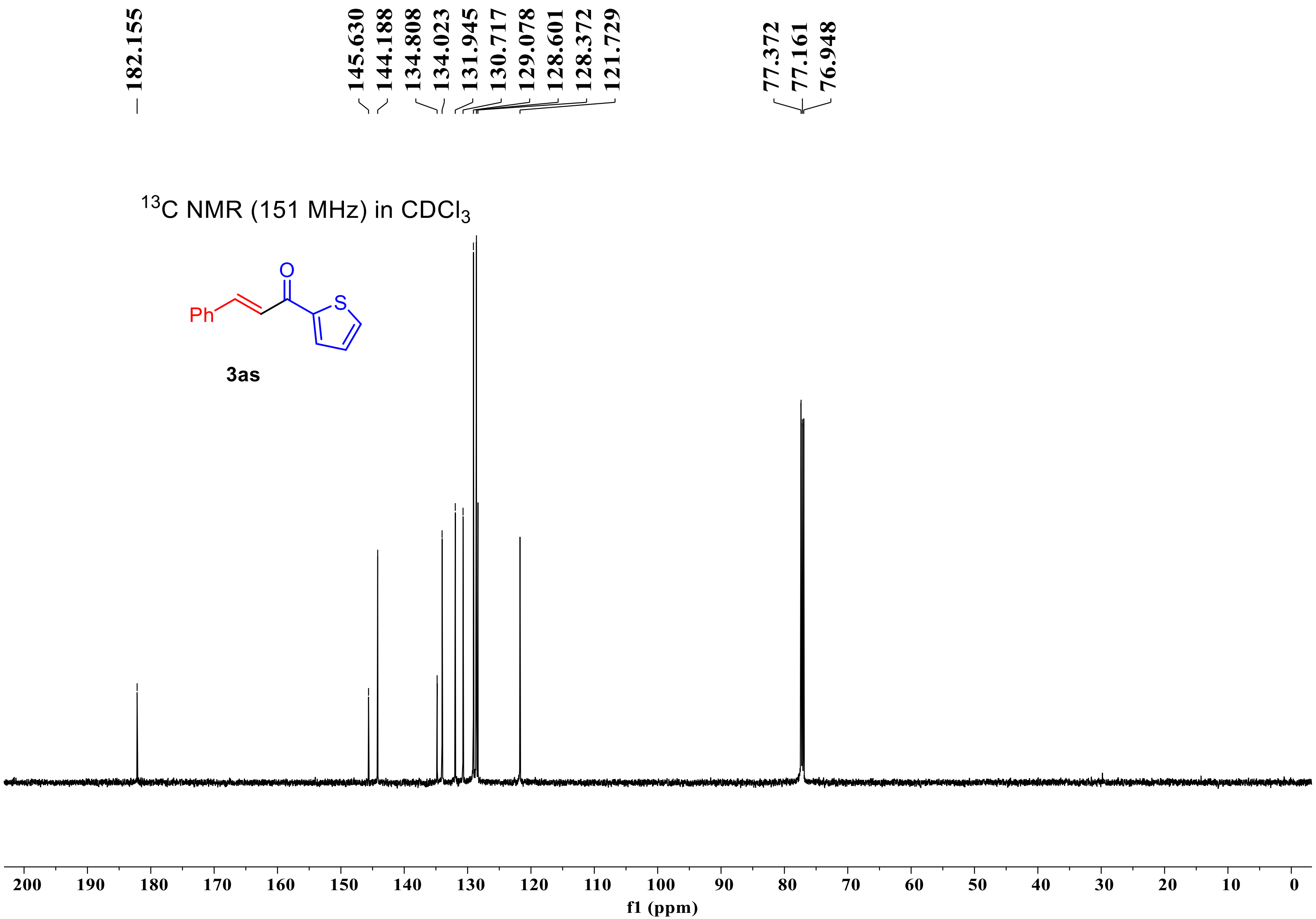
3ar



^{1}H NMR (400 MHz) in $CDCl_3$

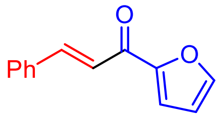


3as

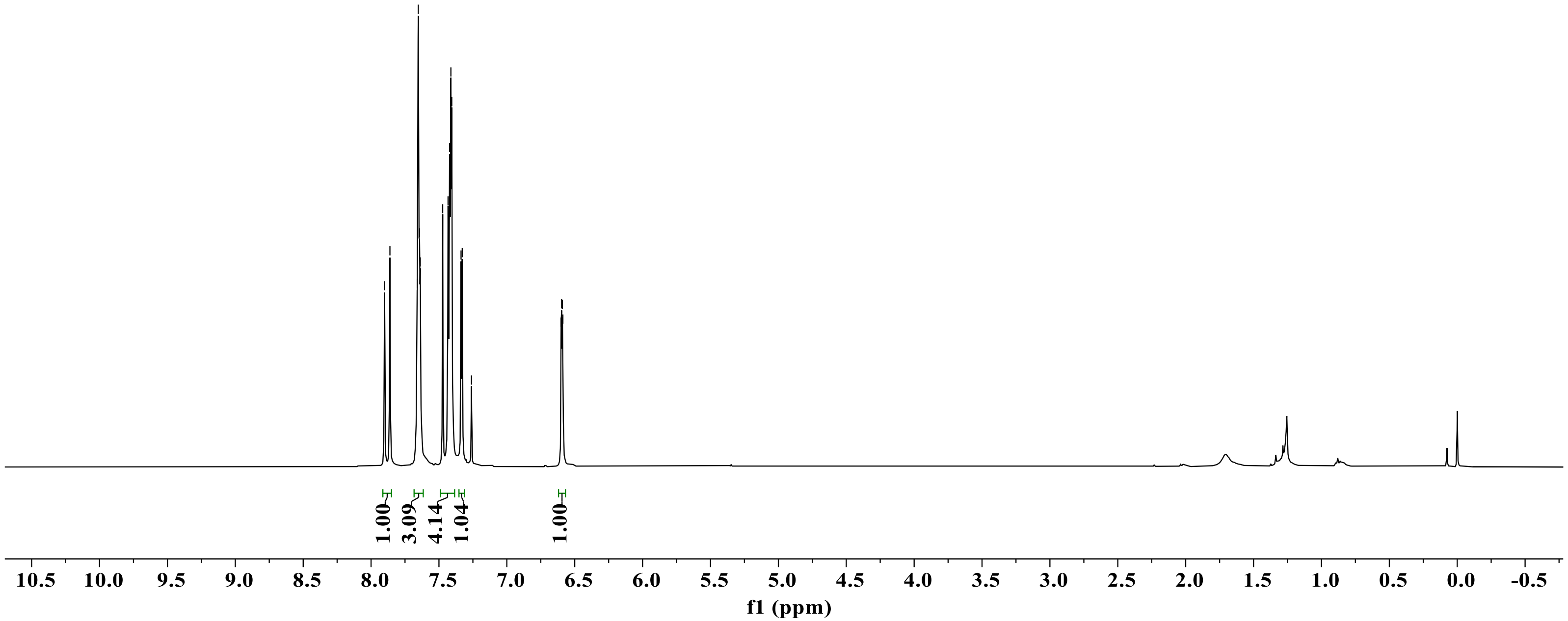


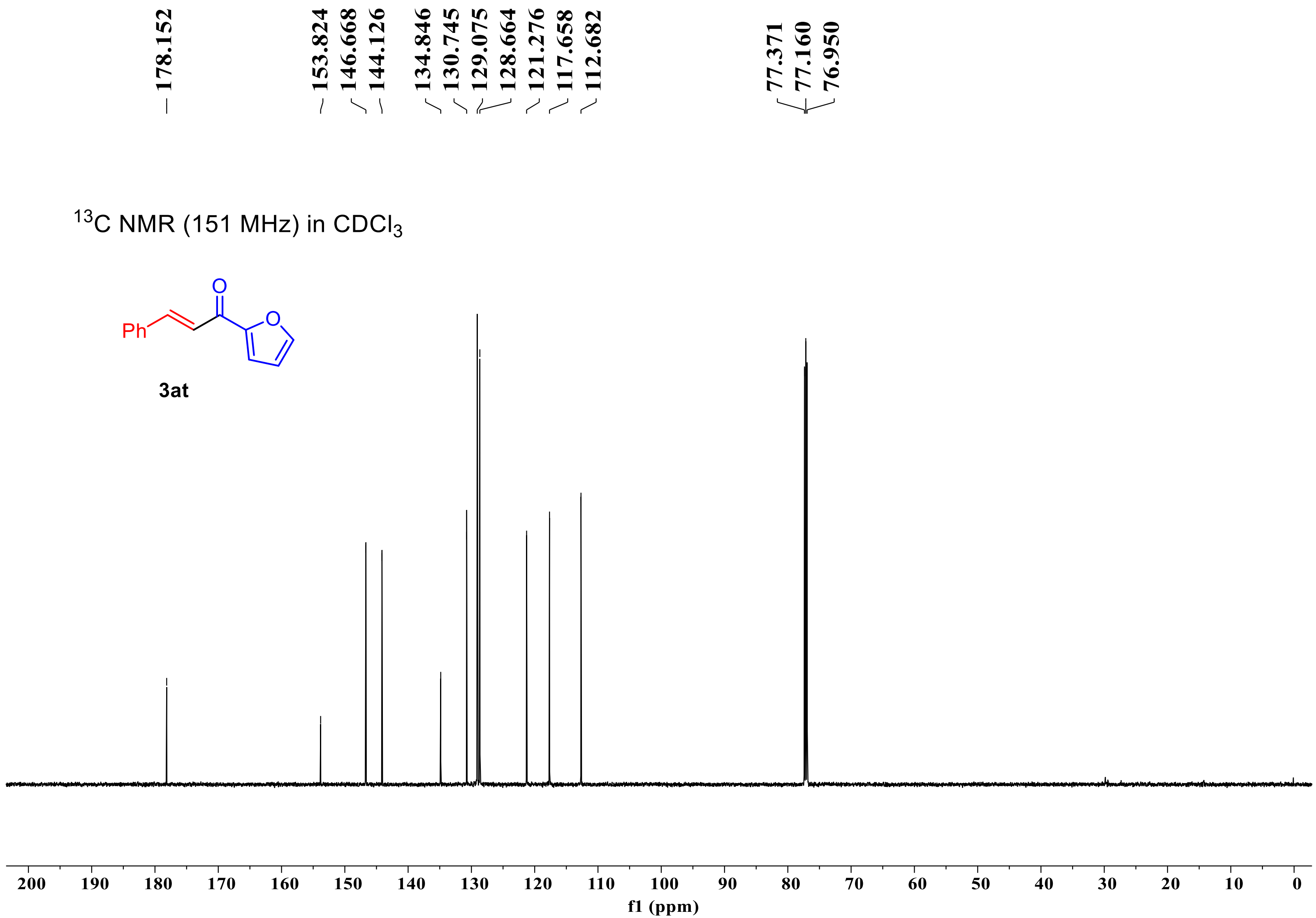
182.155
145.630
144.188
134.808
134.023
131.945
130.717
129.078
128.601
128.372
121.729
77.372
77.161
76.948
^{13}C NMR (151 MHz) in CDCl$_3$
O
S
Ph
3as
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

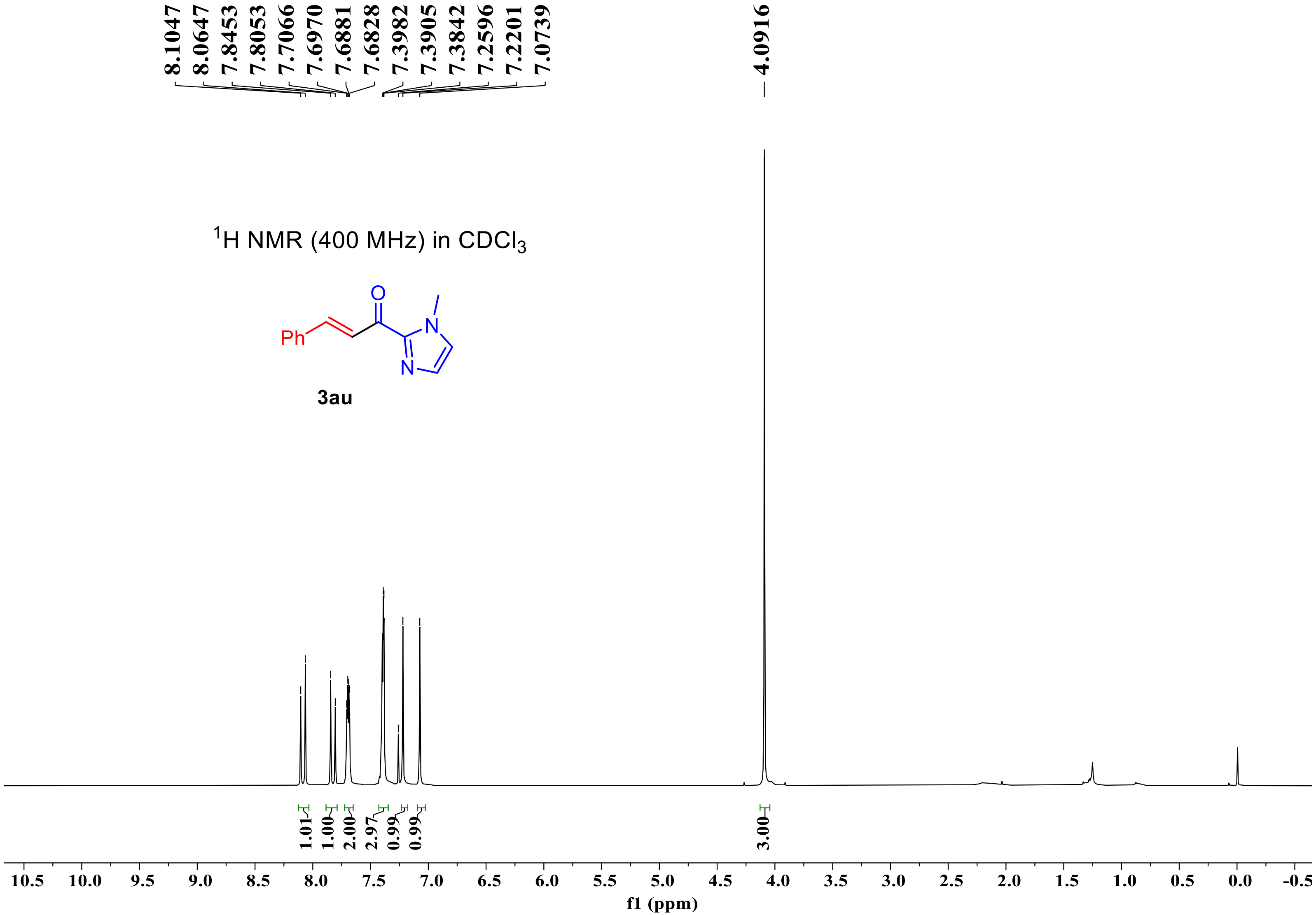
^{1}H NMR (400 MHz) in $CDCl_3$



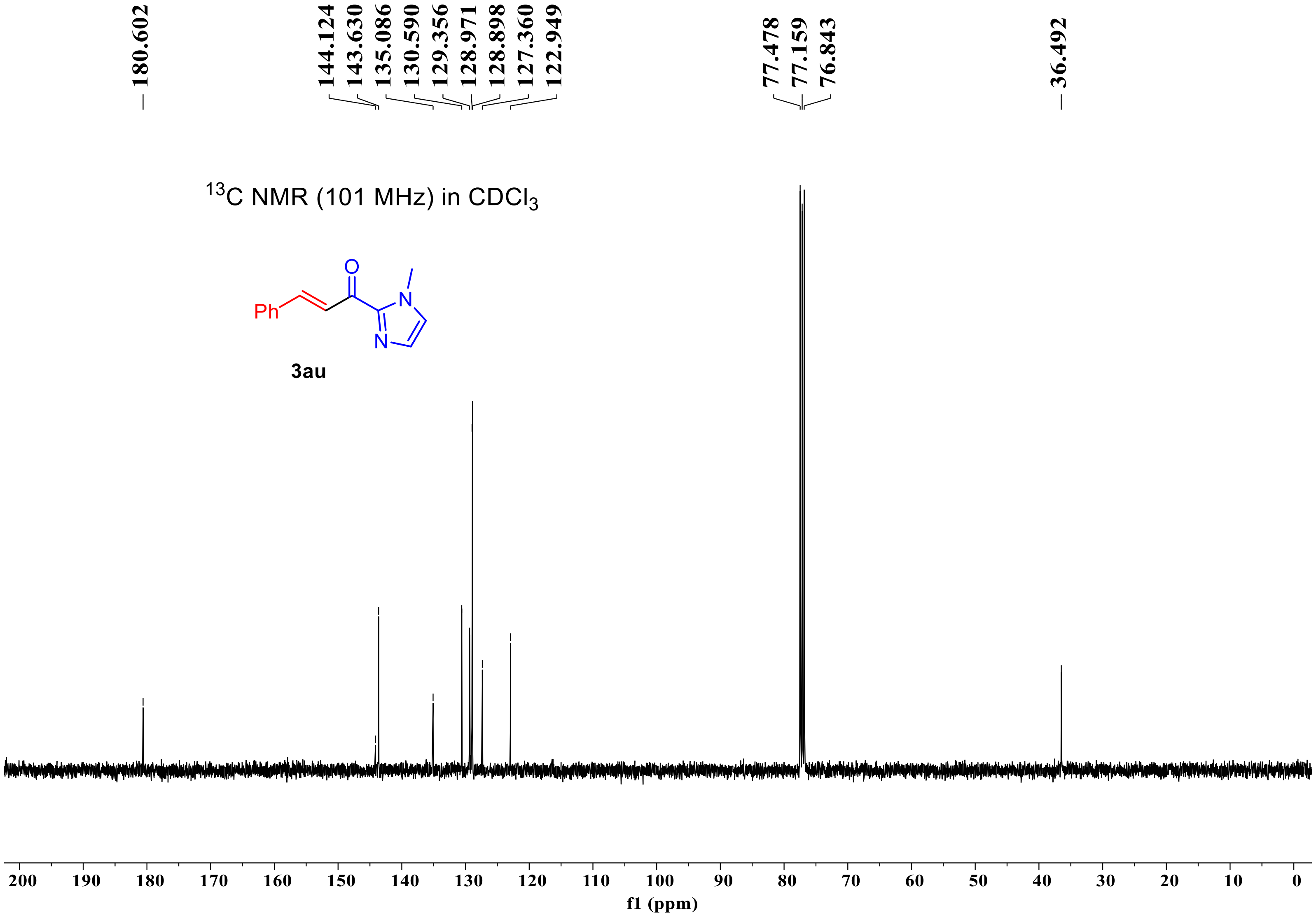
3at



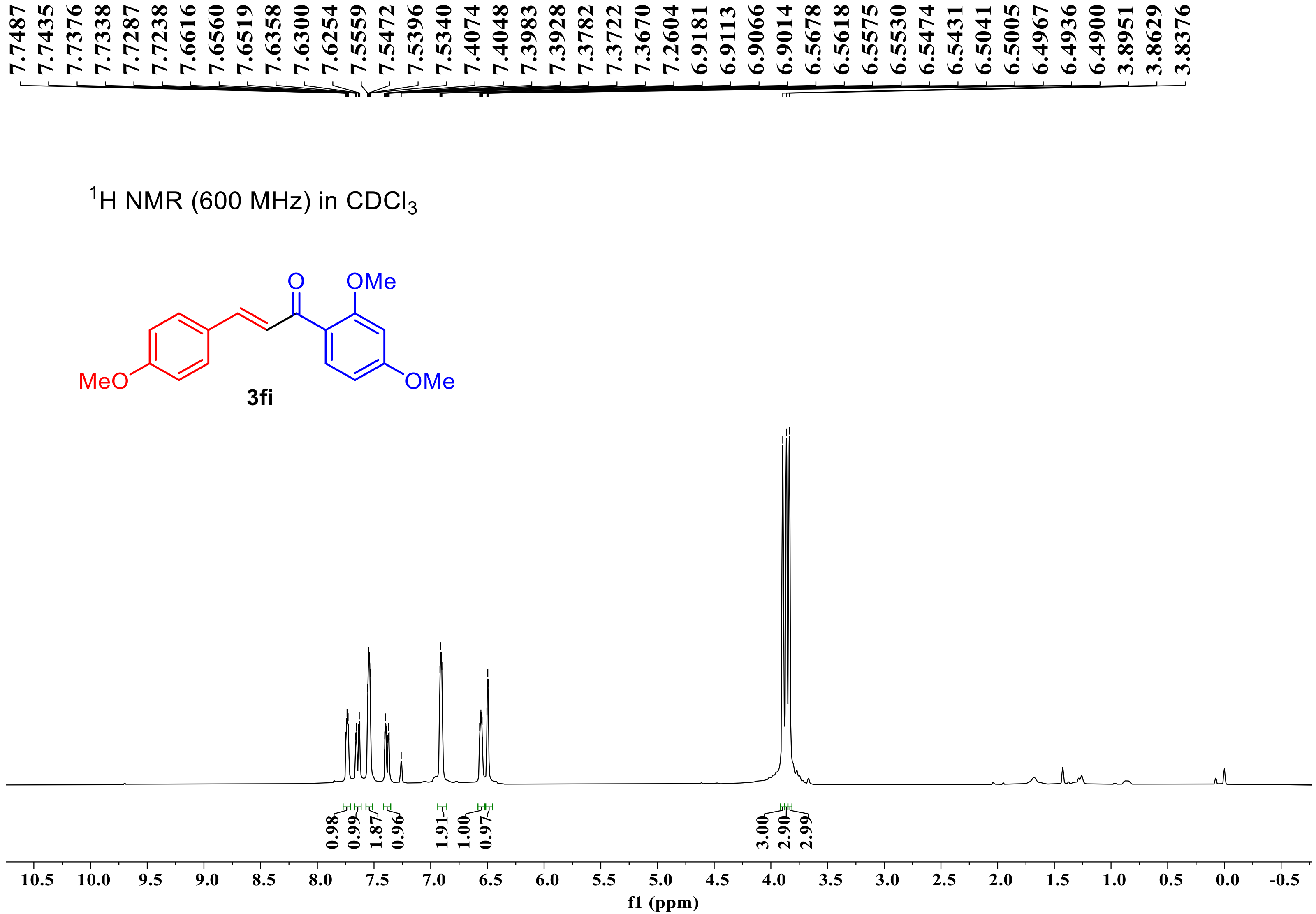

178.152
153.824
146.668
144.126
134.846
130.745
129.075
128.664
121.276
117.658
112.682
77.371
77.160
76.950
13C NMR (151 MHz) in CDCl3
Ph
O
O
3at
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

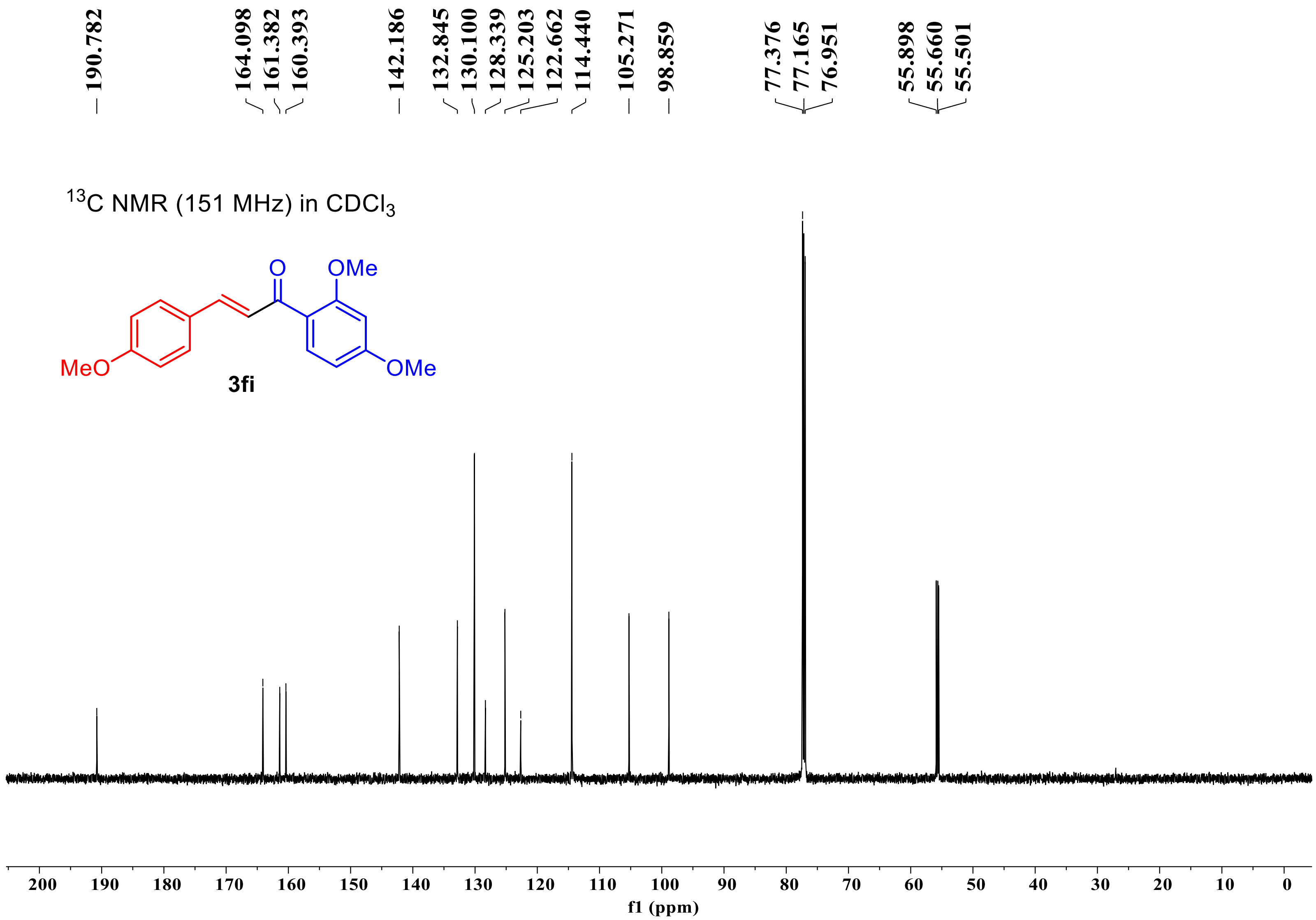

8.1047
8.0647
7.8453
7.8053
7.7066
7.6970
7.6881
7.6828
7.3982
7.3905
7.3842
7.2596
7.2201
7.0739
4.0916
^{1}H NMR (400 MHz) in $CDCl_3$
O
N
Ph
N
3au
1.01
1.00
2.00
2.97
0.99
0.99
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

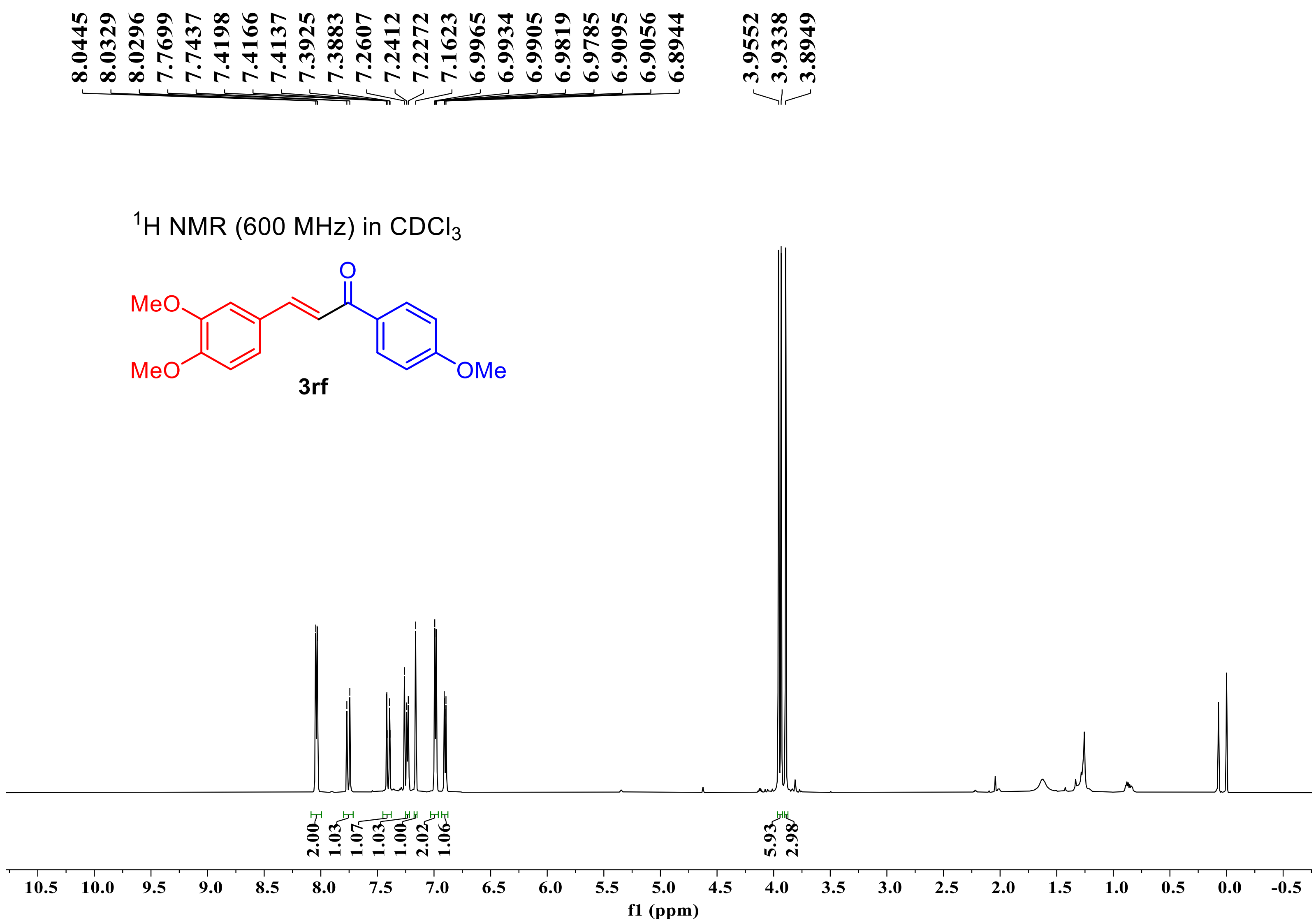
^{13}C NMR (101 MHz) in $CDCl_3$

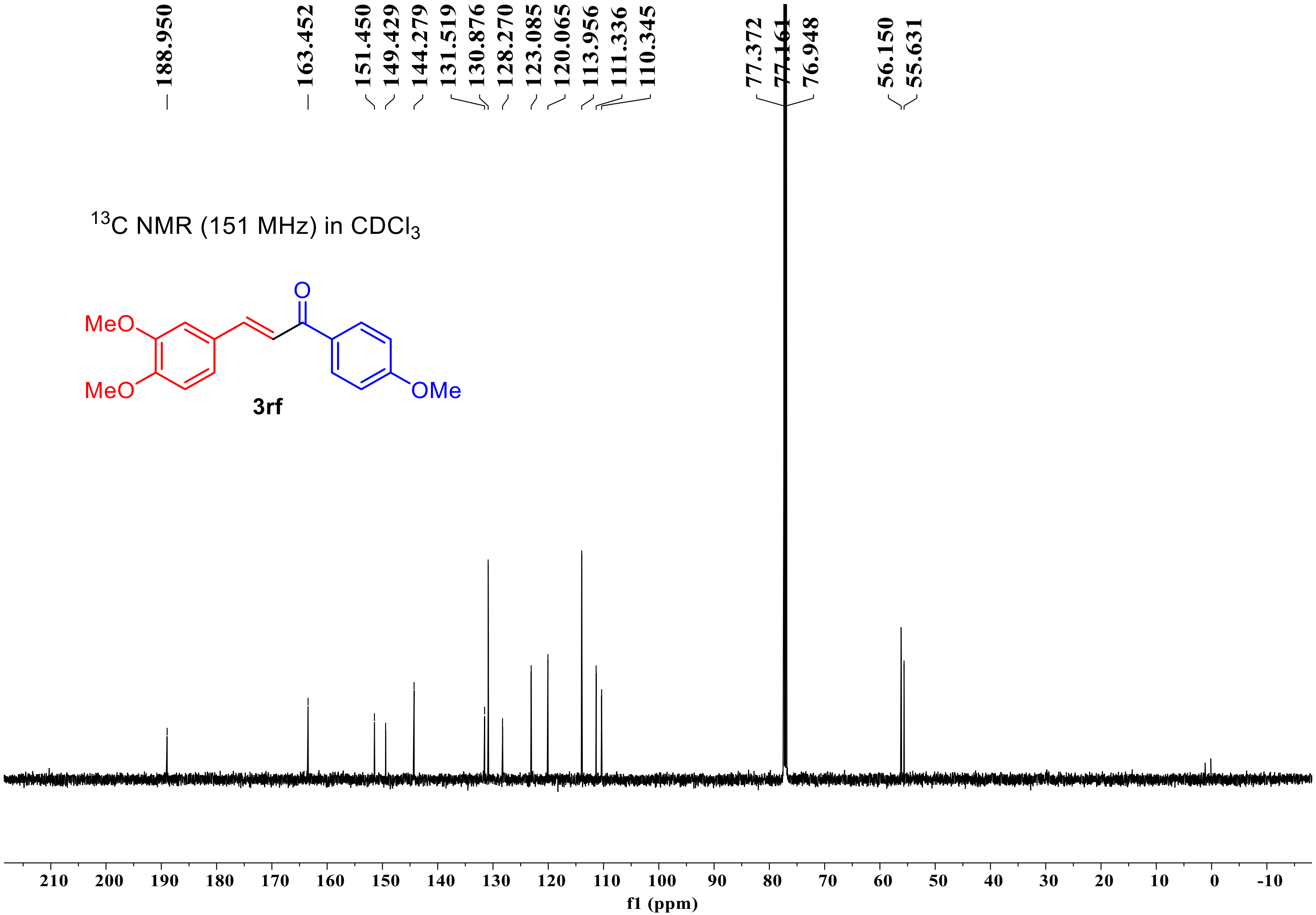


3au


7.7487
7.7435
7.7376
7.7338
7.7287
7.7238
7.6616
7.6560
7.6519
7.6358
7.6300
7.6254
7.5559
7.5472
7.5396
7.5340
7.4074
7.4048
7.3983
7.3928
7.3782
7.3722
7.3670
7.2604
6.9181
6.9113
6.9066
6.9014
6.5678
6.5618
6.5575
6.5530
6.5474
6.5431
6.5041
6.5005
6.4967
6.4936
6.4900
3.8951
3.8629
3.8376
[1]H NMR (600 MHz) in $CDCl_3$
O
OMe
MeO
OMe
3fi
0.98
0.99
1.87
0.96
1.91
1.00
0.97
3.00
2.90
2.99
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


190.782
164.098
161.382
160.393
142.186
132.845
130.100
128.339
125.203
122.662
114.440
105.271
98.859
77.376
77.165
76.951
55.898
55.660
55.501
13C NMR (151 MHz) in CDCl3
O
OMe
MeO
OMe
3fi
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.0445
8.0329
8.0296
7.7699
7.7437
7.4198
7.4166
7.4137
7.3925
7.3883
7.2607
7.2412
7.2272
7.1623
6.9965
6.9934
6.9905
6.9819
6.9785
6.9095
6.9056
6.8944
3.9552
3.9338
3.8949
1H NMR (600 MHz) in CDCl3
MeO
MeO
O
OMe
3rf
2.00
1.03
1.07
1.03
1.00
2.02
1.06
5.93
2.98
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


188.950
163.452
151.450
149.429
144.279
131.519
130.876
128.270
123.085
120.065
113.956
111.336
110.345
77.372
77.161
76.948
56.150
55.631
^{13}C NMR (151 MHz) in $CDCl_3$
MeO
MeO
O
OMe
3rf
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)