Micro-Electro-Flow Catalyzed (μ-EFC) Ultra-fast Cross-Electrophile Coupling of Activated C(sp^3)-O Bonds

Sanjeev Kumar,[a,b] Ajay K. Singh*[a,b]

[a]Department of Organic Synthesis & Process Chemistry, CSIR-Indian Institute of Chemical Technology, Hyderabad-500007, India.

[b]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, Uttar Pradesh, India.

E-mail: ajaysingh015@gmail.com; ajaysingh015@iict.res.in

Table of Contents

1. General information.

1.1 Material and method used in experiments.

Most of the reagents and chemicals were purchased from Sigma-Aldrich and AVRA chemicals, which were used without further purification, and demineralized water (18.2 mS conductivity) was used in all experiments. All work-up and purification procedures were carried out with the reagent-grade solvents. Analytical thin-layer chromatography (TLC) was performed using analytical chromatography silica gel 60 F254 precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm). Polytetrafluoroethylene (PTFE) (id = 100-1000 μm) tubing, T-junction, and high-purity Perfluoro alkoxy alkanes (PFA) tubing were also purchased from Upchurch IDEX HEALTH & SCIENCE. The syringe pump, heating system, back pressure controller (BPR), valve, catalytic reactor, and Asia Manager PC software system were all purchased from Syrris Asia System. Platinum electrode, Aluminium electrode, graphite electrode, platinum electrode, zinc electrode, bought from the SmartChemSynth Pvt. Ltd. Hyderabad, India and catalytic reactor were all purchased from Smart Chem. Synth. Pvt. Ltd. Hyderabad, India.

1.2 Measurement method.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker, 500, 400 or 300 MHz in $CDCl_3$, DMSO-d_6, solvent. Chemical shifts for ^1H NMR were expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm). Chemical shifts for ^{13}C NMR were expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm) or DMSO-d_6 (39.5 ppm) and data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, quin = quintet, sext = sextet, m = multiplet), coupling constants (Hz), and integration. High-resolution mass spectra (HRMS) were obtained from a JMS-T100TD instrument (DART) and Thermo Fisher Scientific Exactive (APCI). Power-Sonic 405 sonication instrument was used for washing the metal surface. ATR analysis was conducted on a portable FTIR spectrometer

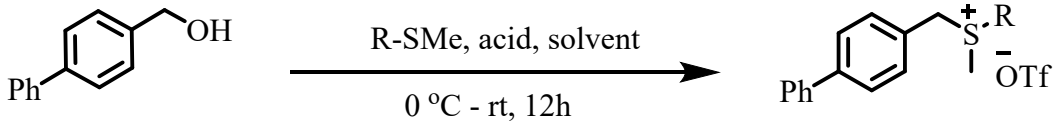
Bruker ALPHA and Datalog model DCS-PS-6401 power supply system was used to supply the constant current. The melting point was conducted on POLMAN MP-96. Han's Yueming laser series (model CMA0604-B-A, Carbon dioxide based, laser power 60W), Inline IR study were conducted with React IR^{TM} 15, mettler Toledo 7.1 Instrument, and iC IR 7.1.84.0 software.

2. A general procedure for the preparation of starting materials.

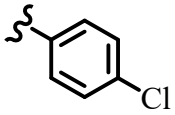
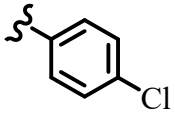
2.1 General procedure for the synthesis of benzyl sulfonium salts.

To an oven-dried 250 mL round-bottomed flask equipped with a Teflon coated magnetic stir bar, [1,1'-biphenyl]-4-ylmethanol **(1a)** (20.0 mmol), solvent (50 mL), and R-SMe (40.0 mmol) were added. Further reaction mixture was cooled to 0 ^{o}C and corresponding acid (20 mmol) were added using a syringe. Then the tube was sealed by a septum and with additional nitrogen gas balloon. Further reaction mixture was placed in magnetic stirrer for 12h at room temperature. After reaction for 12 h, the solvent was removed under the reduced pressure. Further reaction mixture was precipitated in additional 50 mL of ether (diethyl ether or methyl tetra butyl ether MTBE) was filtered through a short plug of silica gel and washed with ether (20 mL). The product was washed using flash column chromatography on 200–300-mesh silica gel with MeOH/$CHCl_3$ as an eluent.

Table S1: Reaction optimization under the various condition.

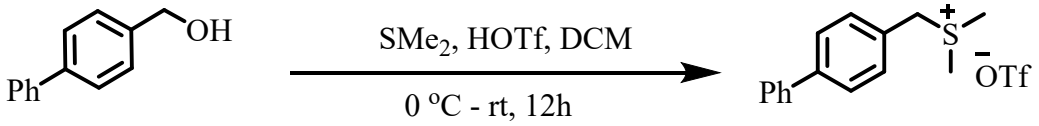


1a **2**

Entry	R	Solvent	Acid	% Yield
1	Me	ACN	HOTf	89
2	Me	Acetone	HOTf	86
3	Me	DCM	HOTf	92
4	Me	Ethyl acetate	HOTf	NA
5		DCM	HOTf	77
6		ACN	HOTf	75
7	Me	DCM	PTSA	NA
8	Me	DCM	$HClO_4$	65

Reaction condition: [1,1'-biphenyl]-4-ylmethanol **(1a)** (20.0 mmol), R-SMe (3.0 mL, 40.0 mmol) acid (1.8 mL, 20.0 mmol), solvent (50 mL), Yields are based on isolated yield.

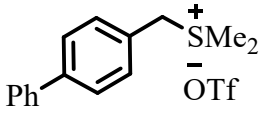
Table S2: Solvent optimization for the precipitating the sulfonium salt



1a **2a**

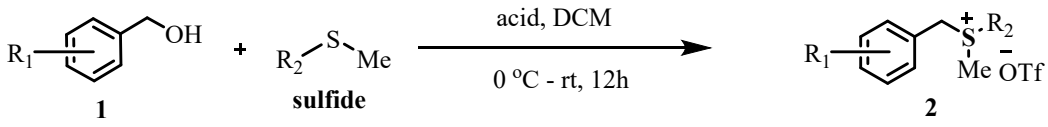
Entry	Washing solvent	% Yield
1	Et_2O	92
2	MTBE	91

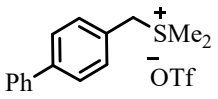
Reaction condition: [1,1'-biphenyl]-4-ylmethanol **(1a)** (20.0 mmol), R-SMe (3.0 mL, 40.0 mmol) acid (1.8 mL, 20.0 mmol), DCM (50 mL), yields are based on isolated yield.



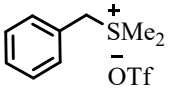
([1,1'-Biphenyl]-4-ylmethyl) dimethyl sulfonium trifluoromethanesulfonate (2a): A 250 mL round-bottomed flask was charged with **1a** (3.68 g, 20.0 mmol), DCM (50 mL), and Me_2S (2.95 mL, 40.0 mmol). The solution was cooled to 0 ℃ in an ice bath and treated with a dropwise addition of HOTf (1.8 mL, 20.0 mmol). The resulting mixture was slowly warmed up to room temperature and stirred for extra 12 hours. The solvent was removed under reduced pressure. Then, Et_2O (50 mL) was added and stirred violently for ten minutes. The precipitated solids were filtered off and washed with Et_2O (3×20 mL) to afford **2a** salts as white solids. The crude mixture after evaporation was washed by flash column chromatography on silica gel (CH_2Cl_2: MeOH = 10:1), the product was isolated in 6.95 g, 92% yield **2a** as a white solid melting point: 166-169 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.80 (d, J = 8.3 Hz, 2H), 7.71 (dd, J = 5.2, 3.3 Hz, 2H), 7.57 – 7.47 (m, 4H), 7.42 (dd, J = 4.9, 3.7 Hz, 1H), 4.68 (s, 2H), 2.82 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 141.36, 139.14, 131.38, 129.16, 128.08, 127.57, 127.30, 126.82, 45.58, 23.91. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.75 (s). IR (ν_{max}): 3027, 1247, 1157, 1025, 743, 633 cm^{-1}. HRMS (ESI): *m/z* calcd

for $C_{15}H_{17}S$, $[M\text{-}OTf]^+$: 229.1045, found: 183.1041. Verified the analytical data with those reported in the literature.[1]

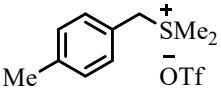




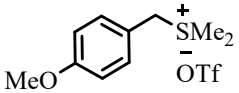
2a: 92 %



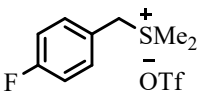
2b: 81%



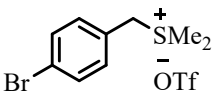
2c: 75 %



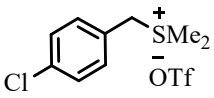
2d: 77%



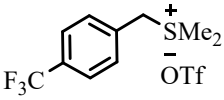
2e: 65%



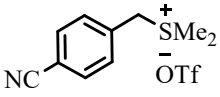
2f: 76%



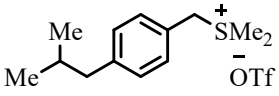
2g: 75%



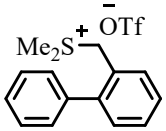
2h: 68%



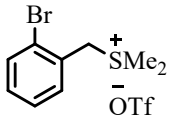
2i: 70%



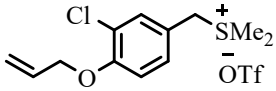
2j: 70%



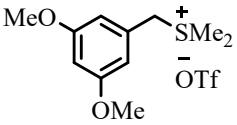
2k: 68%



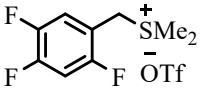
2l: 71 %



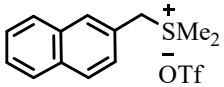
2m: 72%



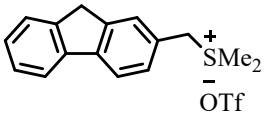
2n: 75%



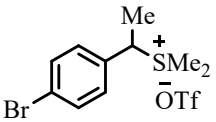
2o: 76%



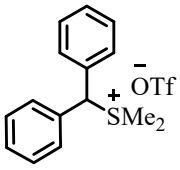
2p: 73%



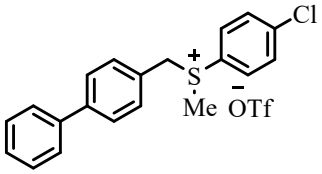
2q: 75%



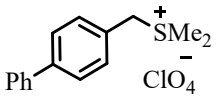
2r: 76%



2s: 71%

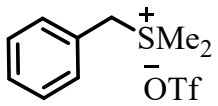


2t: 77%

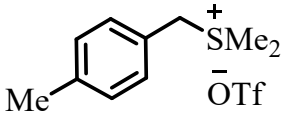


2u: 65 %

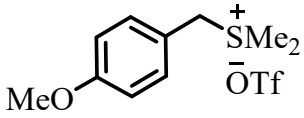
Fig. S1. Reaction condition: benzyl alcohol **(1a)** (20.0 mmol), R^2-SMe (40.0 mmol), acid (20.0 mmol), DCM (50 mL), yields are based on isolated yield.



Benzyl dimethyl sulfonium trifluoromethanesulfonate (2b): This starting compound **2b** was prepared according to the procedure mentioned in section **2a.** The product was isolated in 4.89 g, 81% yield **2b** as a white solid, melting point 54-56 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.52 – 7.41 (m, 5H), 4.64 (s, 2H), 2.78 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 130.63, 129.65, 129.34, 128.19, 122.27, 119.07, 45.73, 39.50, 23.78. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.75 (s). IR (ν_{max})**:** 3030, 1428, 1231, 1155, 1017, 766, 700, 627, 572 cm^{-1}. HRMS (ESI)**:** *m/z* calcd for $C_9H_{13}S$ [M-OTf] $^{+}$:] 153.0732, found: 153.0736. Verified the analytical data with those reported in the literature.[1]



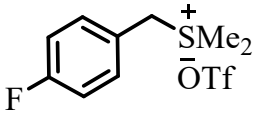
Dimethyl(4-methylbenzyl) sulfonium trifluoromethanesulfonate (2c): This starting compound **2c** was prepared according to the procedure mentioned in section **2a.** The product was isolated in in 4.74 g, 75% yield **2c** as a white solid, melting point 72-74 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.36 – 7.27 (m, 4H), 4.59 (s, 2H), 2.76 (s, 6H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 139.31, 130.59, 129.90, 124.98, 121.95, 119.39, 45.55, 23.65, 20.82. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.75 (s). IR (ν_{max}): 3470, 1426, 1239, 1153, 1017, 820, 737, 626 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{10}H_{15}S$ [M-OTf] $^{+}$:] 167.0889, found: 153.0893.



4-Methoxybenzyl) dimethyl sulfonium trifluoromethanesulfonate (2d): This starting compound **2d** was prepared according to the procedure mentioned in section **2a.** The product was isolated in 5.11 g, 77% yield **2d** as a white solid, melting point 72-74℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.6 Hz, 2H), 4.64 (s, 2H), 3.78 (s, 3H), 2.81 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.02, 132.28, 122.04, 118.86, 117.90, 115.01, 77.00, 55.33, 46.53, 23.38. ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.43 (s). IR (ν_{max}): 3026, 1609, 1510, 1432, 1236, 1156, 1018, 831, 749,

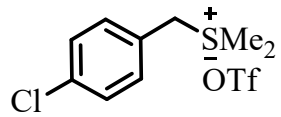
628 cm^{-1}. HRMS (ESI**):** *m/z* calcd for $C_{10}H_{15}S$, $[M\text{-}OTf]^+$: 183.0838, found: 183.0839. Verified the analytical data with those reported in the literature.[1]

(4-Fluorobenzyl)dimethylsulfonium trifluoromethanesulfonate (2e): This starting compound



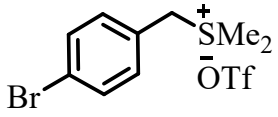
2e was prepared according to the procedure mentioned in section **2a.** The product was isolated in 4.16 g, 65% yield **2e** as a white solid, melting point 42-46 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.51 (dd, J = 8.5, 5.5 Hz, 2H), 7.30 (t, J = 8.1 Hz, 2H), 4.63 (s, 1H), 2.78 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.16, 161.70, 133.13, 133.05, 124.55, 124.53, 122.38, 119.18, 116.55, 116.34, 45.05, 23.74. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.82 (s), -111.62 (s). IR (ν_{max}): 3028, 1605, 1510, 1428, 1229, 1155, 1017, 840, 753, 628, 575, 522cm^{-1}. HRMS (ESI): *m/z* calcd for $C_9H_{12}FS$, $[M\text{-}OTf]^+$: 171.0638, found: 171.0633. Verified the analytical data with those reported in the literature.[1]

(4-Chlorobenzyl)dimethylsulfonium trifluoromethanesulfonate (2f): This starting compound



2f was prepared according to the procedure mentioned in section **2a.** The product was isolated in 5.76 g, 75% yield **2f** as a white solid, melting point 84-86 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.63 – 7.51 (m, 2H), 7.50 – 7.44 (m, 2H), 4.63 (s, 1H), 2.79 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 134.54, 132.54, 129.39, 127.25, 122.27, 119.07, 44.94, 23.78. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.76 (s). IR (ν_{max}): 3030, 1424, 1234, 1155,1094, 1015, 826, 625 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_9H_{12}ClS$, $[M\text{-}OTf]^+$: 187.0343, found: 187.03438.

(4-Bromobenzyl)dimethylsulfonium trifluoromethanesulfonate (2g):



This starting compound **2g** was prepared according to the procedure mentioned in section **2a.** The product was isolated in 5.02 g, 76% yield **2g** as a white solid, melting point 78-80 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.70 (d, J = 8.4 Hz,

2H), 7.41 (d, J = 8.4 Hz, 2H), 4.61 (s, 1H), 2.79 (s, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 132.78, 132.30, 127.65, 123.22, 121.94, 119.38, 44.99, 23.78. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.75 (s). IR (ν_{max}): 3425, 1241,1158, 1017, 826, 627 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_9H_{12}BrS$, [M-OTf]$^+$: 230.9837, found: 230.9840.

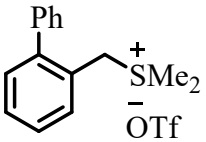
Dimethyl(4-(trifluoromethyl)benzyl)sulfonium trifluoromethanesulfonate (2h): This starting compound **2h** was prepared according to the procedure mentioned in section **2a.** The product was isolated in 5.03 g, 68% yield **2h** as a white solid, melting point 85-87 ℃. ^{1}H NMR (500 MHz DMSO-d_6) δ 7.72 – 7.60 (m, 4H), 4.75 (s, 2H), 2.88 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 133.18, 131.67, 130.21, 129.89, 126.30, 126.27, 125.53, 125.41, 122.70, 122.33, 119.13, 45.11, 26.25, 24.06. ^{19}F NMR (376 MHz, DMSO-d_6) δ -62.21 (s), -78.15 (s). IR (ν_{max}): 3430, 1246, 1159, 1023, 628, 574 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{10}H_{12}F_3S$, [M-OTf]$^+$: 221.0606, found: 221.0604.

(4-Cyanobenzyl)dimethylsulfonium trifluoromethanesulfonate (2i): This starting compound **2i** was prepared according to the procedure mentioned in section **2a.** The product was isolated in 5.03 g, 77% yield **2i** as a white solid, melting point 144-146 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.97 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 4.73 (s, 2H), 2.84 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 133.92, 133.14, 131.64, 118.33, 112.33, 45.12, 24.02. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.78 (s). IR (ν_{max}): 3030, 1426, 1241, 1156, 1019, 842, 754, 627, 566 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{10}H_{12}NS$, [M-OTf]$^+$: 178.0685, found: 178.0681.

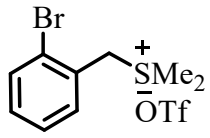
(4-Isobutylbenzyl) dimethyl sulfonium trifluoromethanesulfonate (2j): This starting compound **2j** was prepared according to the procedure mentioned in section **2a.** The

product was isolated in 5.01 g, 70% yield **2j** as a white solid, melting point 72-74 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.36 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 4.59 (s, 2H), 2.76 (s, 6H), 2.48 (d, J = 7.2 Hz, 2H), 1.84 (dt, J = 13.5, 6.8 Hz, 1H), 0.86 (d, J = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 143.08, 130.60, 130.03, 128.76, 126.51, 125.41, 45.74, 44.33, 29.69, 23.83, 22.24. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.77 (s). IR (ν_{max}): 3434, 1238, 1156, 1018, 627 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{13}H_{21}S$, $[M\text{-}OTf]^+$: 209.1358, found: 209.1356.

([1,1'-Biphenyl]-2-ylmethyl)dimethylsulfonium trifluoromethanesulfonate (2k): This starting compound **2k** was prepared according to the procedure mentioned in section **2a.** The product was isolated in 5.14 g, 68% yield **2k** as a white solid, melting point 70-72 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.62 (dd, J = 7.2, 1.l7 Hz, 1H), 7.50 (tdd, J = 7.0, 6.1, 2.1 Hz, 5H), 7.42 – 7.33 (m, 3H), 4.65 (s, 2H), 2.66 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 142.98, 139.19, 131.76, 131.07, 129.84, 129.23, 128.87, 128.36, 128.00, 126.08, 122.33, 119.13, 44.74, 24.25. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.74 (s). IR (ν_{max}): 3458, 1247, 1150, 1019, 753, 704, 626 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{15}H_{17}S$, $[M\text{-}OTf]^+$: 229.1045, found: 229.1041.

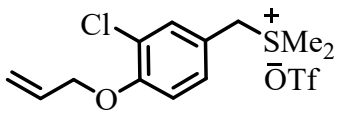


(2-Bromobenzyl)dimethylsulfonium trifluoromethanesulfonate (2l): This starting compound **2l** was prepared according to the procedure mentioned in section **2a.** The product was isolated in 5.38 g, 71% yield **2l** as a white solid, melting point 60-62 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.78 (dd, J = 8.0, 1.1 Hz, 1H), 7.61 (dd, J = 7.6, 1.7 Hz, 1H), 7.51 (td, J = 7.5, 1.2 Hz, 1H), 7.43 (td, J = 7.7, 1.7 Hz, 1H), 4.78 (s, 2H), 2.92 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 133.54 (d, $J_{C–F}$ = 19.2 Hz), 131.98, 128.71, 128.44, 124.67, 120.70 (d, $J_{C–F}$ = 323 Hz), 46.63, 24.48. ^{19}F NMR (376 MHz, DMSO-d_6) δ -73.00 (s). IR



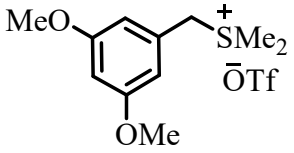
(ν_{max}): 3446, 3018, 1427, 1234, 1153, 1018, 762, 628, 571 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_9H_{12}BrS$, $[M\text{-}OTf]^+$: 230.9838, found: 230.9835.

(4-(Allyloxy)-3-chlorobenzyl)dimethylsulfonium trifluoromethanesulfonate (2m): This



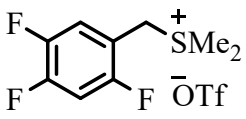
starting compound **2m** was prepared according to the procedure mentioned in section **2a.** The product was isolated in 5.64 g, 72% yield **2m** as a white solid, melting point 75-77 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.57 (d, J = 2.1 Hz, 1H), 7.39 (dd, J = 8.5, 2.2 Hz, 1H), 7.25 (d, J = 8.6 Hz, 1H), 6.05 (ddt, J = 17.2, 10.4, 5.1 Hz, 1H), 5.45 (dq, J = 17.2, 1.6 Hz, 1H), 5.30 (dd, J = 10.6, 1.5 Hz, 1H), 4.70 (d, J = 5.1 Hz, 2H), 4.56 (s, 2H), 2.78 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.40, 132.81, 131.98, 130.88, 121.90, 121.11, 117.91, 114.50, 69.13, 44.89, 23.70. ^{19}F NMR (376 MHz, DMS- d_6) δ -77.76 (s). IR (ν_{max}): 3021, 1601, 1493, 1425, 1242, 1152, 1006, 924, 812, 742, 625, 573 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{12}H_{16}ClOS$ $[M\text{-}OTf]^+$: 243.0605, found: 243.0602.

3, 5-Dimethoxybenzyl)dimethylsulfonium



trifluoromethanesulfonate (2n): This starting compound **2n** was prepared according to the procedure mentioned in section **2a.** The product was isolated in 4.43 g, 75% yield **2n** as a white solid, melting point 71-73 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.63 – 6.56 (m, 3H), 4.52 (s, 2H), 3.76 (s, 6H), 2.78 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.96, 130.28, 122.30, 119.09, 108.53, 101.16, 55.42, 45.95, 24.02. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.74 (s). IR (ν_{max}): 3458, 3020, 1599, 1239, 1150, 1017, 837, 626 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{11}H_{17}O_2S$, $[M\text{-}OTf]^+$: 213.0943, found: 213.0940.

Dimethyl(2,4,5-trifluorobenzyl)sulfonium trifluoromethanesulfonate.



(2o): This starting compound **2o** was prepared according to the procedure mentioned in section **2a.** The product was isolated in 5.41 g, 76% yield **2o**

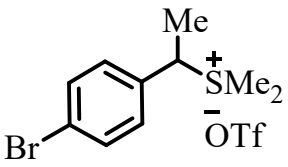
as a white solid, melting point 63-65 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.77 – 7.30 (m, 2H), 4.64 (d, J = 17.4 Hz, 2H), 2.83 (d, J = 21.0 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.46, 158.36, 156.00, 155.90, 152.24, 152.08, 151.93, 151.28, 151.14, 149.74, 149.58, 149.44, 148.81, 148.66, 147.98, 147.83, 145.56, 145.43, 128.56, 128.50, 128.46, 126.18, 126.13, 126.08, 125.83, 122.64, 121.21, 121.18, 121.01, 120.38, 120.34, 120.23, 120.20, 119.44, 118.97, 118.82, 116.24, 112.98, 112.93, 112.81, 107.61, 107.39, 107.33, 107.11, 45.04, 24.35, 24.15. ^{19}F NMR (376 MHz, DMSO) δ -77.89 (s), -114.85 (d, J = 12.4 Hz), -131.17 (d, J = 21.9 Hz), -136.95 (t, J = 14.9 Hz), -141.71 (d, J = 17.1 Hz). IR (ν_{max}): 3028, 1516, 1427, 1229, 1155, 1017, 885, 837, 628 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_9H_{10}F_3S$ [M-OTf]$^+$: 207.0455 found: 207.0450.

Dimethyl(naphthalen-2-ylmethyl)sulfonium trifluoromethanesulfonate (2p): This starting compound **2p** was prepared according to the procedure mentioned in section **2a.** The product was isolated in 5.13 g, 73% yield **2p** as a white solid, melting point 58-60 °C. ^{1}H NMR (400 MHz, DMS-d_6) δ 8.02 (s, 1H), 7.97 (dd, J = 6.1, 3.3 Hz, 2H), 7.60 (dd, J = 6.2, 3.2 Hz, 2H), 7.55 (dd, J = 8.5, 1.4 Hz, 1H), 4.79 (s, 2H), 2.82 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 133.63, 133.44, 131.97, 128.70, 128.44, 124.67, 122.30, 119.10, 46.62, 24.47. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.75 (s). IR (ν_{max}): 3469, 3030, 1427, 1233, 1155, 1019, 822, 752, 627, 571 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{13}H_{15}S$ [M-OTf]$^+$: 203.0889 found: 203.0885. Verified the analytical data with those reported in the literature[1]

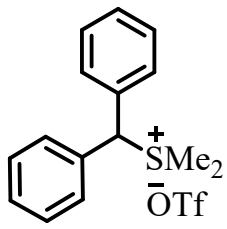
(9H-Fluoren-2-yl)methyl)dimethylsulfonium trifluoromethanesulfonate (2q): This starting compound **2q** was prepared according to the procedure mentioned in section **2a.** The product was isolated in 5.85 g, 75% yield **2q** as a white solid, melting point 168-170 °C. ^{1}H NMR

(400 MHz, DMS-d_6) δ 7.99 (dd, J = 23.0, 7.5 Hz, 2H), 7.68 – 7.59 (m, 2H), 7.51 – 7.31 (m, 3H), 4.71 (s, 2H), 3.99 (s, 2H), 2.81 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.03, 143.36, 142.49, 140.17, 129.45, 127.52, 127.44, 126.97, 126.26, 125.28, 120.70, 120.49, 46.20, 36.39, 23.76. ^{19}F NMR (376 MHz, DMSO-d_6) δ -73.01 (s). IR (ν_{max}): 1425, 1245, 1151, 1021, 742, 630, cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{16}H_{17}S$ [M-OTf]$^+$: 241.1045 found: 241.1040.

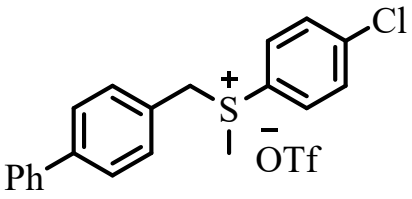
(1-(4-Bromophenyl)ethyl)dimethylsulfonium trifluoromethanesulfonate (2r): This starting compound **2r** was prepared according to the procedure mentioned in section **2a.** The product was isolated in 5.97 g, 76% yield **2r** as a white solid, melting point 101-103 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.33 – 7.29 (m, 2H), 7.24 (d, J = 8.0 Hz, 2H), 4.90 (q, J = 7.1 Hz, 1H), 2.94 (s, 3H), 2.62 (s, 3H), 1.84 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 132.74, 132.37, 131.08, 123.48, 122.31, 119.11, 53.48, 22.78, 22.31, 15.59. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.75 (s). IR (ν_{max}): 3010, 1422, 1238, 1157, 1018, 824, 766, 627, 574 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{10}H_{14}BrS$ [M-OTf]$^+$: 244.9994 found: 244.9990.



Benzhydryldimethylsulfonium trifluoromethanesulfonate (2s): This starting compound **2s** was prepared according to the procedure mentioned in section **2a.** The product was isolated in 5.36 g, 71% yield **2s** as a white solid, melting point 116-118 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.66 (d, J = 1.5 Hz, 1H), 7.64 (d, J = 1.0 Hz, 1H), 7.52 (d, J = 1.5 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.37 (dd, J = 8.1, 1.0 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.20 (dt, J = 9.3, 4.3 Hz, 31H), 6.12 (s, 1H), 2.79 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.16, 128.53, 127.17, 126.68, 122.74, 119.54, 74.73, 17.74. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.75 (s). IR (ν_{max}): 3023, 14285, 1246, 1147, 1019, 703, 624, 571 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{15}H_{17}S$ [M-OTf]$^+$: 229.1045 found: 229.1040.

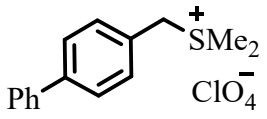


([1,1'-biphenyl]-4-ylmethyl) (4-chlorophenyl) (methyl)sulfonium trifluoromethanesulfonate



(2t): A 250 mL round-bottomed flask was charged with **1a** (3.68 g, 20.0 mmol), DCM (50 mL), and (4-chlorophenyl)(methyl)sulfane (5.18 mL, 40.0 mmol). The solution was cooled to 0 ℃ in an ice bath and treated with a dropwise addition of HOTf (1.8 mL, 20.0 mmol). The resulting mixture was slowly warmed up to room temperature and stirred for extra 12 hours. The solvent was removed under reduced pressure. Then, Et_2O (50 mL) was added and stirred violently for ten minutes. The precipitated solids were filtered off and washed with Et_2O (3×20 mL) to afford **2t** salts as white solids. The product was isolated in 7.29 g, 77% yield **2t** as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.75 (d, J = 8.2 Hz, 2H), 7.69 (dd, J = 8.2, 1.0 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H), 7.48 (t, J = 7.7 Hz, 2H), 7.39 (s, 1H), 7.36 – 7.33 (m, 2H), 7.28 – 7.24 (m, 2H), 5.35 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 141.64, 139.44, 137.44, 133.08, 132.53, 130.35, 129.46, 129.24, 129.17, 129.05, 128.91, 128.05, 127.77, 127.64, 127.21, 126.92, 126.66, 126.51, 76.70, 14.88. IR (ν_{max}): 3009, 1574, 1477, 1417, 1249, 1157, 1093, 1021, 823, 750, 630 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{20}H_{18}ClS$ $[M\text{-}OTf]^+$: 325.0812 found: 325.0818.

([1,1'-Biphenyl]-4-ylmethyl) dimethyl sulfonium perchlorate (2u): A 250 mL round-bottomed flask was charged with **1a** (3.68 g, 20.0 mmol), DCM (50 mL), and Me_2S (2.95 mL, 40.0 mmol). The solution was cooled to 0 ℃ in an ice bath and treated with a dropwise addition of $HClO_4$ (1.2 mL, 20.0 mmol). The resulting mixture was slowly warmed up to room temperature and stirred for extra 12 hours. The solvent was removed under reduced pressure. Then, Et_2O (50 mL) was added and stirred violently for ten minutes. The precipitated solids were filtered off and washed with Et_2O (3×20 mL) to afford **2u** salts as white



solids. The product was isolated in 4.3 g, 65% yield **2u** as a white solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.79 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 7.4 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.49 (t, J = 7.7 Hz, 2H), 7.41 (d, J = 7.4 Hz, 1H), 4.67 (s, 2H), 2.81 (s, 6H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 141.44, 139.19, 131.45, 129.23, 128.15, 127.64, 127.31, 126.89, 45.67, 23.96. IR (ν_{max}): 3021, 1417, 1079, 1000, 738, 691 cm^{-1}.

3. General reaction procedure and fabrication of micro electro flow reactor (μ-EFR).

Electro-flow reactor (μ-EFR) outer body was fabricated with a Bakelite body Fig. S2. (60 mm length x 60 mm width x 10 mm thickness). The second layer was fabricated with PTFE film (60 mm length x 60 mm width x 1 mm thickness) layer made with a laser cutter. Next, platinum electrode was customized as per the reactor size (60 mm length x 60 mm width 0.2 mm thickness) and the solution flow under the constant current, the fourth layer incorporated of a laser scratch PTFE flexible plastic (60 mm x 60 mm x 2 mm thickness) zig-zag groove with a rectangular shape. Aluminium (Al) electrode was customized as per the reactor size (60 mm length x 60 mm width x 2 mm thickness) and the solution flow under the constant current. After construction of each layer and to align the patterns, the 4-corners of each two PTFE Teflon films were instructed to make a hole (1 mm diameter). Eventually, both the platinum and aluminium electrodes were sandwiched by teflon zig-zag channel sheets with identical dimension to fit groove channels and integrate by inserting metal pins through the holes at the film corners Fig. S2. Bakelite holders, the set was aligned by inserting metal pins through the holes at the film corners. Finally, the Bakelite holder was tightly pressed by screw to seal the device with no leak Fig. S2.

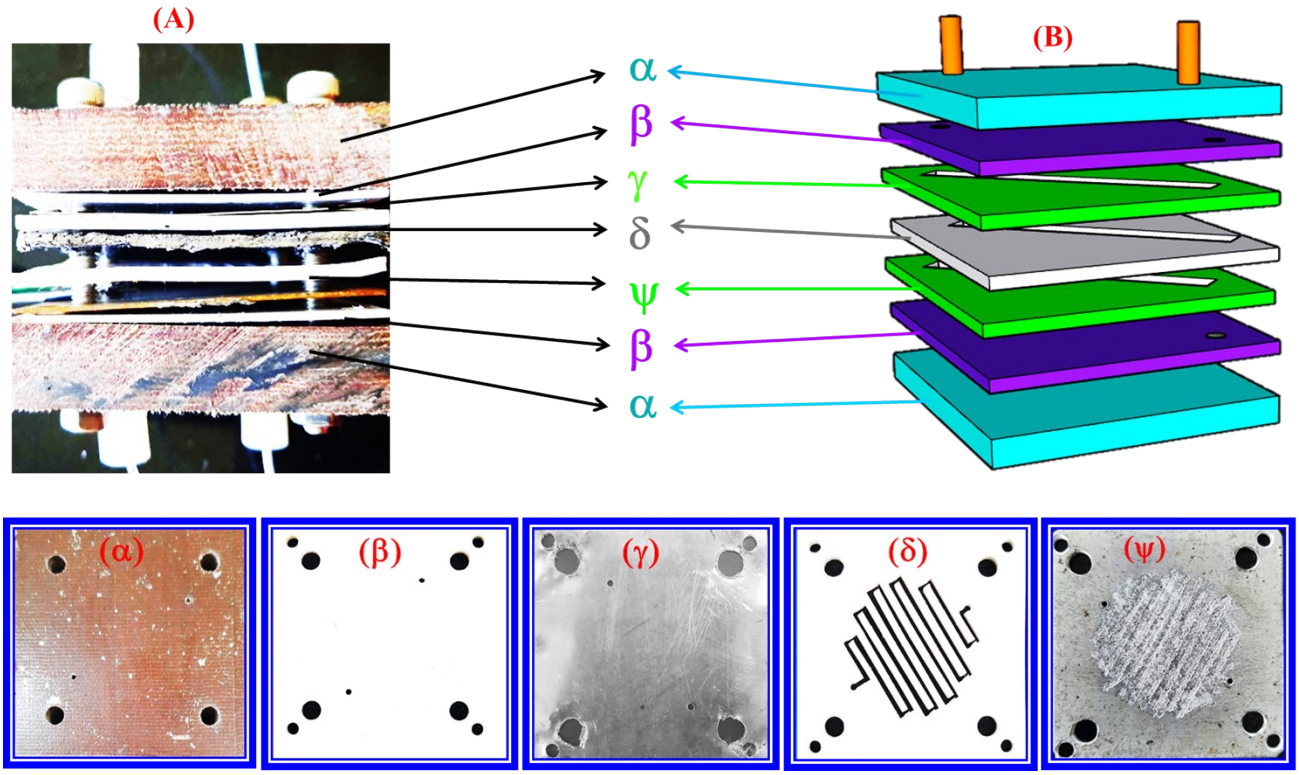


Fig. S2. Schematic graphic presentation of micro electro-flow reactor; (A) original photograph (B) 3D model; (α) customized Bakelite (polyoxybenzylmethylenglycolanhydride) plate; (β) metal protecting PTFE; (γ) Pt electrode; (δ) laser grooved PTFE channel; (ψ) aluminium electrode.

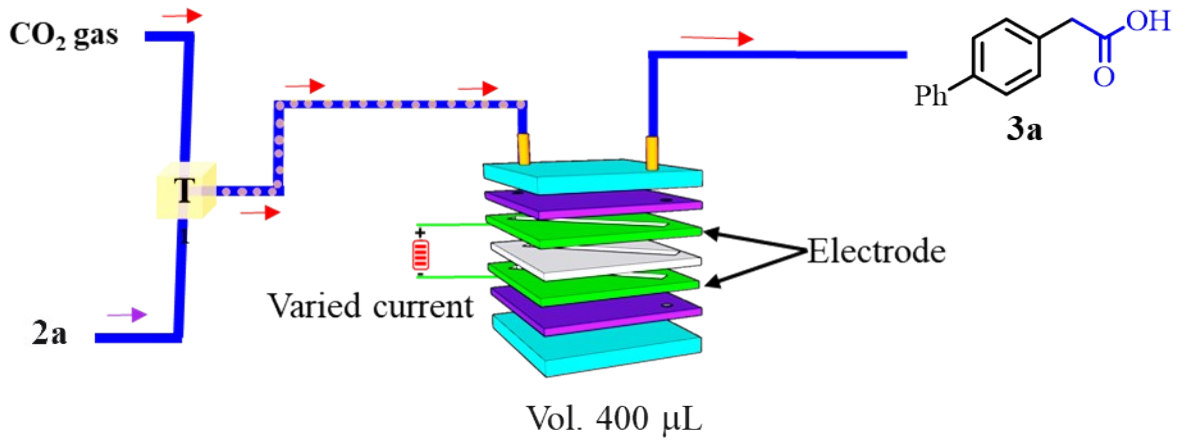


Fig. S3. Schematic set-up for the electrolysis reaction.

4. General procedure for the serial extraction, phase separation, batch process and an integrated electro-flow platform.

4.1 Fabrication of a dual channel micro-separator: As illustrated in figure S4, laser ablation on PTFE film was employed to fabricate the proposed dual channel device. First of all, layers of 1000 µm thick PTFE films were ablated by UV laser 355 nm, to form serpentine microchannel (1000 µm width, 1000 µm depth and 80 cm length) as per our previously reported procedure.[2-4] The 4-corners of each film were holed (1 mm dia.) to align the film patterns. After laser ablation, the films were cleaned by washing with acetone under ultrasonic and dried. Polytetrafluoroethylene (PTFE) membrane (Whatmann, 0.45 µm pore, 47 mm dia.) sandwiched by two sheets of PTFE film with identical dimension of microchannel were placed between metal holder, which were aligned each other by inserting metal pins through the holes at the film corners. Finally, metal holder was tightly pressed by screw to seal the device with no leak.

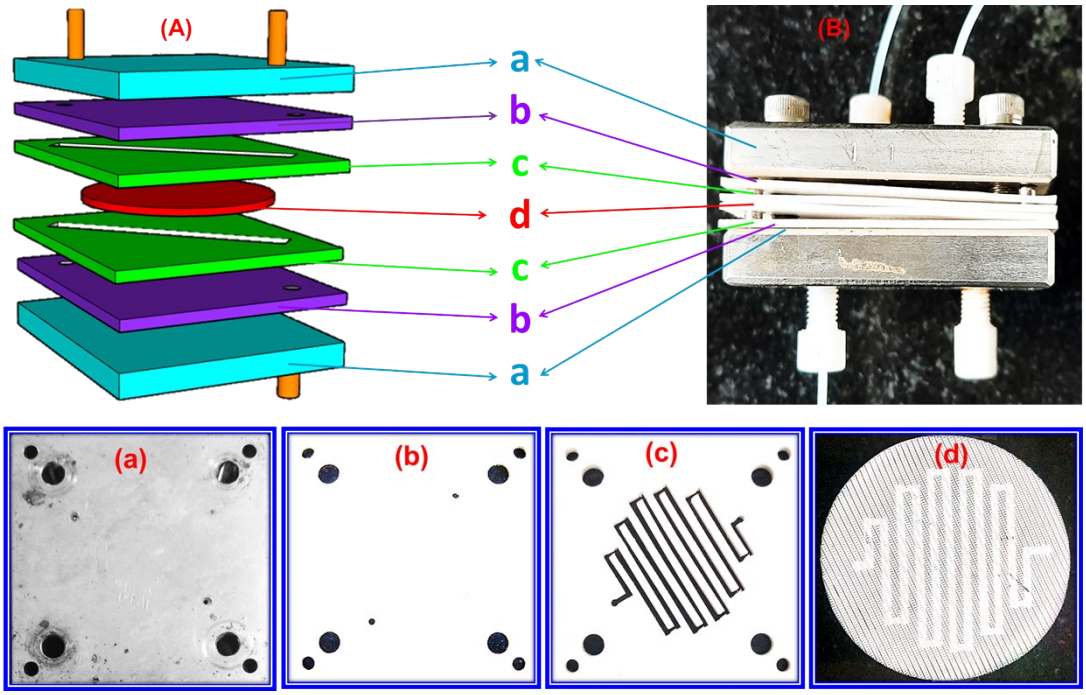


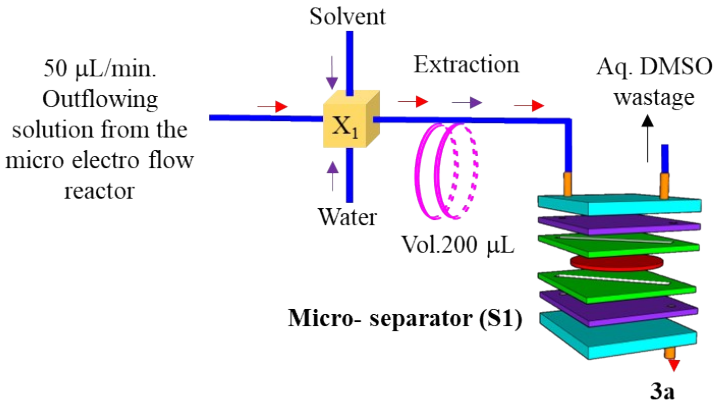
Fig. S4. Illustration of a fluoropolymer PTFE membrane based micro separator; **(A)** 3D model; **(B)** original photograph; **(a)** SS-metal body; **(b)** metal protecting PTFE layer; **(c)** laser grooved PTFE channel; **(d)** propylene coated PTFE membrane.

Stage 1: In-line solvent exchange, extraction and separation of product 3a

To exchange the solvent by extracting the product from DMSO to low volatile solvent (diethyl ether (DEE)/ *t*-butyl methyl ether (MTBE)/ dichloromethane (DCM)/ ethyl acetate/ toluene/ hexane) the additional PTFE membrane embedded phase separator was connected to the outlet of the electro flow reactor as shown in (Table S3). A sequential process of droplet formation, extraction and separation for purification of the product was conducted in droplet microfluidics equipped with the PTFE membrane micro separator, as explained in a step-wise manner at the below. At first, alternating organic-aqueous droplets was formed by introducing water into the product mixture in DMSO through X-junction. Then, the extraction was carried out by passing through a length of 0.5 m capillary during 1.3 min. Finally, the mixture of organic phase containing **3a** was selectively separated by wetting and penetrating through the PTFE membrane into the bottom channel of the separator, whereas the aq.

DMSO containing aqueous phase did not wet the membrane to stay at the upper channel, and gone to the waste (Table S3).

Table S3. Solvent exchange through the micro-separator S1 for **3a** separation.

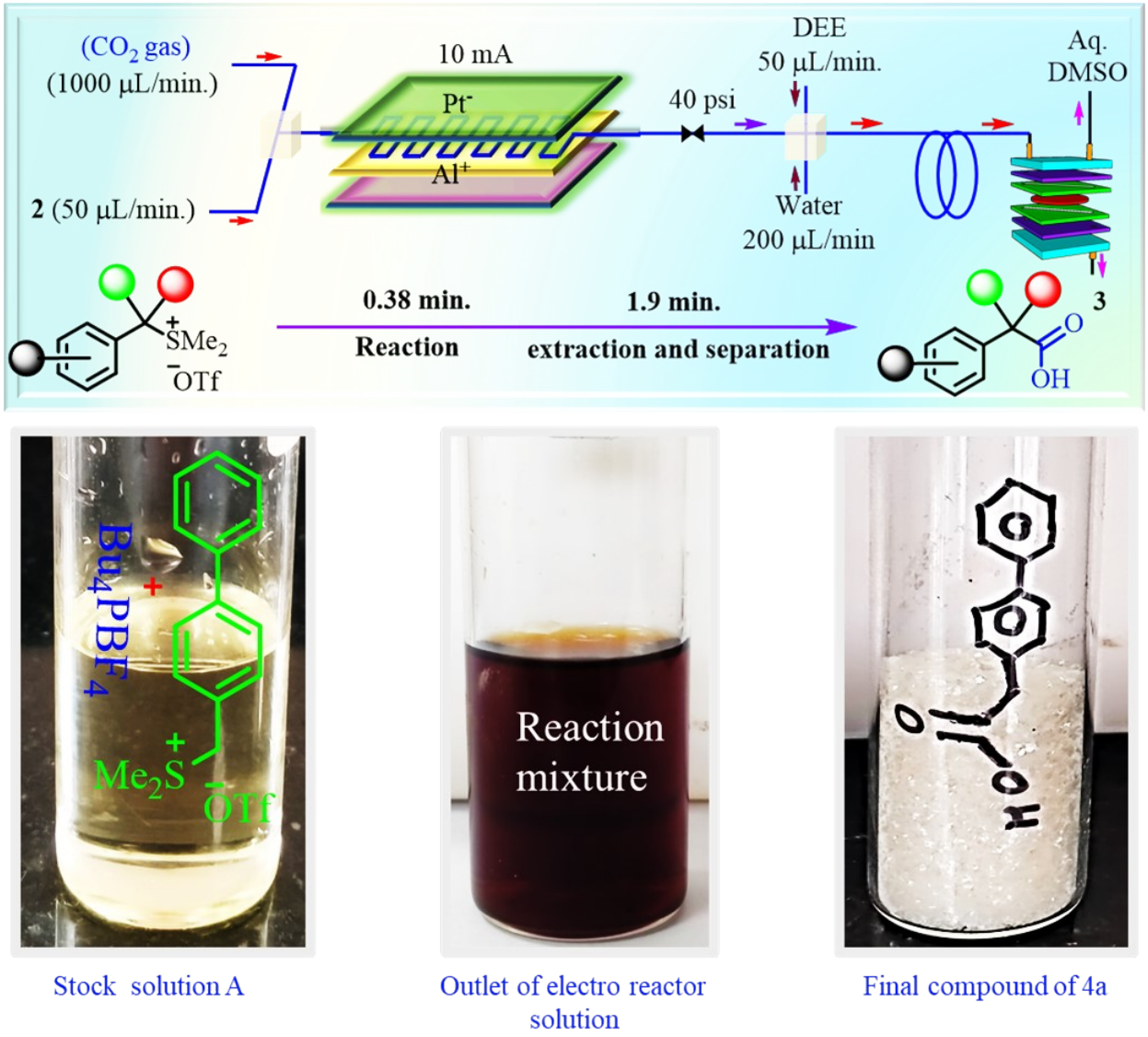


Entry	Solvent	Solvent Flow rate (µL/min.)	Water Flow rate (µL/min.)	Extraction time (min.)	Separation time (min.)	% Yield 3a
1	DEE	200	300	0.36	0.36	87
2	DEE	100	500	0.30	0.30	84
3	DEE	100	300	0.44	0.44	90
4	DEE	150	200	0.50	0.50	93
5	DEE	50	200	0.66	0.66	99
6	MTBE	50	200	0.66	0.66	98
7	DCM	50	200	0.66	0.66	95
8	Ethyl acetate	50	200	0.66	0.66	91
9	Toluene	50	200	0.66	0.66	67
10	Hexane	50	200	0.66	0.66	NA

Yields are based on isolated yield.

4.2. General procedure for the integrated one-flow synthesis, extraction and separation of 3a.

The stock solution (**A**) containing benzyl sulfoniumtrifluoromethanesulfonate salt (**2**): Bu_4PBF_4: DMSO in a molar ratio (1:1:468) was taken in bottle and carbon dioxide gas balloon was connected with syringe pump. Two reactants were introduced through T-junction in to maintain the stoichiometry (Table 1 entry 1), and then passed through a micro electro flow reactor for the synthesis of carboxylate product during 0.38 min of residence time and 40 psi pressure at 10 mA current as an electrode platinum and aluminum. And the excess amount of remaining gas was removed by collecting reaction mixture in open flask. From the quenched reaction mixture, solvent exchange (from high boiling solvent DMSO to low boiling solvent diethyl ether DEE) was carried out by introducing water and low boiling solvent DEE through additional X_1-junction to form organic-aqueous droplets (Table S3). Complete extraction between organic-aqueous segments was accomplished for 1.3 min retention time by flowing through a PTFE capillary (id = 1000 μm, length = 0.5 m, vol. = 400 μL). The complete separation was achieving by passing through the micro separator under the optimized reaction condition. The extracted waste aqueous layer was further extracted with ethyl acetate and analyzed by NMR and confirmed by the absence of the corresponding peaks in the crude NMR analysis (^1H and ^{13}C NMR spectra) which showed no product. The ethyl acetate layer was concentrated under vacuum to give the product and subsequent purification by column chromatography.



Stock solution A

Outlet of electro reactor solution

Final compound of 4a

Fig. S5. Integrated continuous flow set-up for synthesis of **3a.**

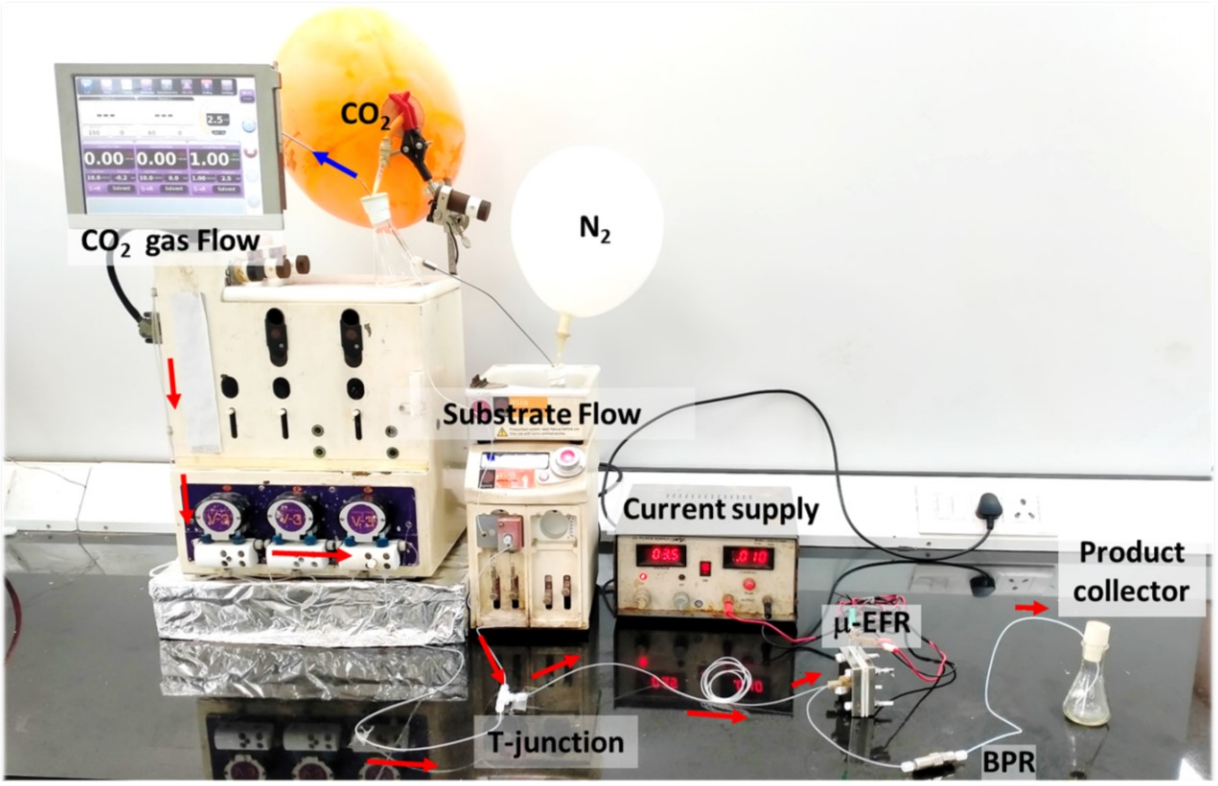
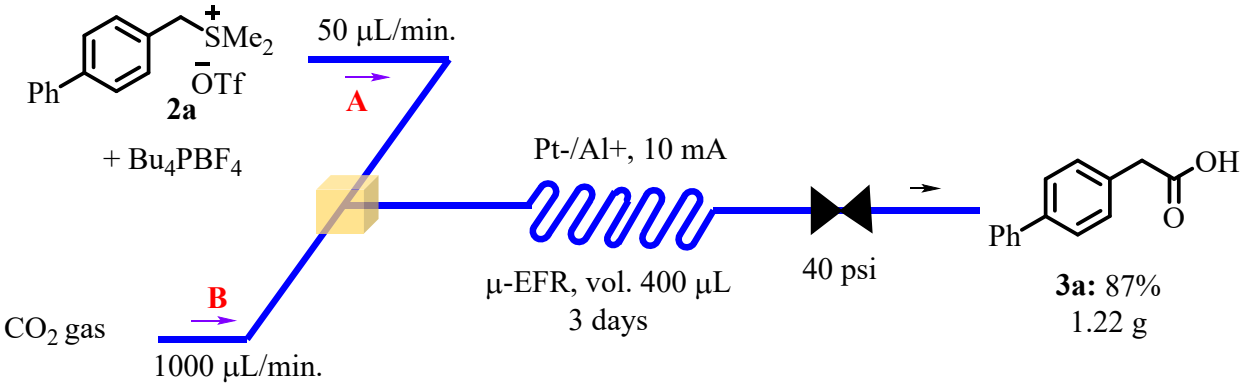


Fig. S6. Snapshot of real-experimental set-up for the control electro-flow optimization for the cross-electrophile coupling reaction.

4.3 Gram scale synthesis of Felbinac (3a).



Reaction condition: stock solution A, **2a** (2.84 g): Bu_4PBF_4 (2.5 g): DMSO (250 mL) in a molar ratio (1:1:468). Yields are based on isolated yield.

The stock solution (A) containing benzyl sulfoniumtrifluoromethanesulfonate salt **2a** (2.84 g): Bu_4PBF_4 (2.5 g): DMSO (250 mL) in a molar ratio (1:1:468) was taken in bottle and carbon dioxide gas balloon was connected with flow rate of 50 and 1000 µl/min. respectively. Two reactants were introduced through T-junction in to maintain the stoichiometry (1:29), and then passed through a micro electro flow reactor for the synthesis of carboxylate product during 0.38 min. of residence time and 40 psi pressure at 10 mA constant current as an electrode platinum and aluminum. And the excess amount of remaining gas was removed by collecting reaction mixture in an open flask. Out-flowing product mixture solution further connected with the X-junction. Exchanging of the high boiling solvent DMSO to low boiling solvent diethyl ether DEE was carried out by introducing water (200 µL/min.) and low boiling solvent DEE (50 µL/min.) through additional X_1-junction to form organic-aqueous droplets. Complete extraction between organic-aqueous segments was accomplished in 1.3 min. retention time by flowing through a PTFE capillary (id = 1000 mm, length = 0.5 m, vol. = 400 mL). The complete separation was achieved by passing through the above designed dual channel micro separator (vol 200 ml) under the 0.66 min. of retention time. The organic layer solution of 220 mL was collected under the stable condition (it may take ~0.2-0.5h) for the next 72 h of the time. Regular batch protocol has been applied for the further purification to obtain the 1.22 g isolated product, 88% yield of **3a** as a white solid and a melting point is 161–162 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 4H), 7.46 – 7.40 (m, 2H), 7.39 – 7.29 (m, 3H), 3.70 (s, 2H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.31, 140.68, 140.35, 132.23, 129.78, 128.75, 127.40, 127.31, 127.07, 40.60. IR (ν_{max}): 2925, 1679, 1408, 1336, 1238, 921, 748, 672 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{14}H_{12}O_2$ $[M+H]^+$: 4213.0910, found: 213.0904. Verified the analytical data with those reported in the literature.[5-8]

Productivity under optimized condition

Molar solution = 0.03 M

Flow rate = 50 μL/min

Product molecular weight = 212

Product yield = 88 %

$$Productivity\ g/day\ = \frac{0.03_X 0.05_X 60_X 24_X 212_X 0.88}{1000}$$

Productivity = 0.403 g day^{-1}

Faradaic efficiency (ϕ) calculation in flow process

Experimental Charge (Q) = Mol × n × F

Experimental Charge (Q) = product mol × 2 × 96485.33

= 0.0019 × 2 × 96485.33

Experimental Charge = 366.82 C

Theoretical charge (Q) = 0.01 × 86400

= 864 C

$$Faradaic\ efficiency(\phi)\ = \frac{experimental\ charge(Qe)}{theoretical\ charge(Qt)}\ X\ 100$$

$$Faradaic\ efficiency(\phi) = \frac{366.82}{864}\ X\ 100$$

Faradic efficiency (ϕ) = 42.5%

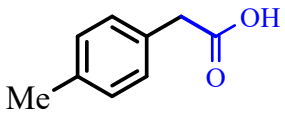
Space-time yield (STY) for the formation of compound 3a in the flow process.

$$Space - time\ yield\ (STY) = \frac{0.403}{0.4}$$

Space-time yield (STY) =1.0 g day^{-1} mL^{-1}

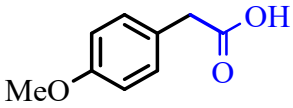
2-Phenylacetic acid (3b): The stock solution (A) containing benzyl sulfoniumtrifluoromethanesulfonate salt **2b** (228 mg): Bu_4PBF_4 (207 mg): DMSO (20 mL) in a molar ratio (1:1:468) was taken in bottle and carbon dioxide gas balloon was connected with flow rate of 50 and 1000 µL/min. respectively. Two reactants were introduced through T-junction in to maintain the stoichiometry (1:29), and then passed through a micro electro flow reactor for the synthesis of carboxylate product during 0.38 min. of residence time and 40 psi pressure at 10 mA constant current as an electrode platinum and aluminium. And the excess amount of remaining gas was removed by collecting reaction mixture in an open flask. Out-flowing product mixture solution further connected with the X-junction. Exchanging of the high boiling solvent DMSO to low boiling solvent diethyl ether DEE was carried out by introducing water (200 µL/min.) and low boiling solvent DEE (50 µL/min.) through additional X_1-junction to form organic-aqueous droplets. Complete extraction between organic-aqueous segments was accomplished for 1.3 min. retention time by flowing through a PTFE capillary (id = 1000 mm, length = 0.5 m, vol. = 400 mL). The complete separation was achieved by passing through the above designed dual channel micro separator (vol 200 µl) under the 0.66 min. of retention time. The organic layer solution of 10 mL was collected under the stable condition (it may take ~0.2-0.5h) for the next 200 min. of the time at the end of the micro-separator. Regular batch protocol has been applied for the further purification to obtain the 27.6 mg isolated product, 70% yield of **3b** as a white solid and a melting point is 73-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.10 (s, 2H), 7.37 – 7.23 (m, 12H), 3.63 (s, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.11, 133.20, 129.34, 128.61, 127.32, 41.05. IR (ν_{max}): 2930, 2874, 1654, 1589, 1448, 1367, 1227, 986, 794, 654 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_8H_8O_2$ $[M+H]^+$: 137.0593, found: 137.0597. Verified the analytical data with those reported in the literature.[5, 7]

2-(p-Tolyl) acetic acid (3c): The electrolysis product **(3c)** was conducted following preparation



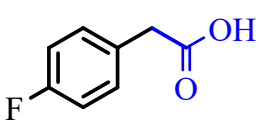
according to the procedure as described in section **3b** for electrochemical carboxylation. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 34.65 mg, 77% yield of **3c** as a white solid and a melting point is 89-91 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (q, J = 8.2 Hz, 4H), 3.61 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.05, 137.01, 130.21, 129.34, 129.21, 77.32, 77.00, 77.00, 76.68, 40.47, 21.08. IR (ν_{max}): 3019, 2924, 1699, 1415, 125, 923, 808, 765 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_9H_{10}O_2$ [M-H] $^{+}$: 150.0680, found: found: 149.0610. Verified the analytical data with those reported in the literature[9-11]

2-(4-Methoxyphenyl) acetic acid (3d): The electrolysis product **(3d)** was conducted following



preparation according to the procedure as described in section **3b** for electrochemical carboxylation. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 42.33 mg, 85% yield of **3d** as a white solid and a melting point is 83-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.69 (s, 1H), 7.19 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 3.78 (s, 3H), 3.57 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.31, 158.80, 130.38, 125.28, 114.04, 55.22, 40.12. IR (ν_{max}): 2954, 1692, 1506, 1411, 1228, 1168, 1015, 902, 812, 762, 666 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_9H_{10}O_3$ [M+H] 167.0708, found: found: 167.0697. Verified the analytical data with those reported in the literature.[5, 10]

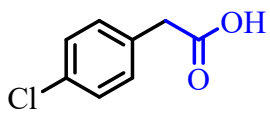
2-(4-Fluorophenyl) acetic acid (3e): The electrolysis product **(3e)** was conducted following



preparation according to procedure as described in section **3b** for electrochemical carboxylation. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 32.81 mg, 71% yield of **3e** as a white

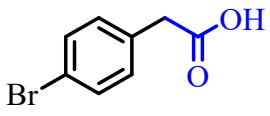
solid and a melting point is 81-83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 7.02 (t, J = 8.7 Hz, 2H), 3.63 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.91, 162.12 (d, $^{1}J_{C\text{-}F}$ = 246 Hz), 130.94 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 129.04, 115.51 (d, $^{1}J_{C\text{-}F}$ = 22 Hz), 40.12. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.35 (s). IR (ν_{max}): 3059, 1716, 1513, 1417, 1241, 1161, 1095, 1032, 809 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_8H_7FO_2$ [M+H] $^{+}$: 155.0508, found: 155.0512. Verified the analytical data with those reported in the literature.[5]

2-(4-Chlorophenyl) acetic acid (3f): The electrolysis product **(3f)** was conducted following



preparation according to the procedure as described in section **3b** for electrochemical carboxylation. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 40.29 mg, 79% yield of **3f** as a white solid and a melting point is 106-108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 1H), 7.24 – 7.17 (m, 1H), 3.62 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.03, 133.39, 131.61, 130.72, 128.79, 40.25 IR (ν_{max}): 2919, 1686, 1487, 1408, 1329, 1236,1166, 1079, 908, 800, 727 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_8H_7ClO_2$ [M+H] $^{+}$: 71.02073, found: 171.02019. Verified the analytical data with those reported in the literature.[12, 13]

2-(4-Bromophenyl) acetic acid (3g): The electrolysis product **(3g)** was conducted following



preparation according to the procedure as described in section **3b** for electrochemical carboxylation. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 48.14 mg, 75% yield of **3g** as a white solid and a melting point is 121-123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.4 Hz, 1H), 7.16 (d, J = 8.4 Hz, 1H), 3.60 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.87, 132.22, 131.73, 131.09, 121.42, 40.38. IR (ν_{max}): 2923, 1692, 14078, 1319, 1240, 1163, 1106, 1059, 1009, 921,

795, 721 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_8H_7BrO_2$ $[M+H]^+$: 213.9707, found 14.9702. Verified the analytical data with those reported in the literature.[5]

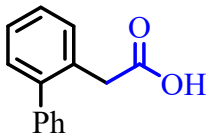
2-(4-(Trifluoromethyl) phenyl) acetic acid (3h): The electrolysis product **(3h)** was conducted following preparation according to procedure as described in section **3b** for electrochemical carboxylation. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 42.23 mg, 69% yield of **3h** as a white solid and a melting point is 79-81 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 3.72 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.26, 137.11, 129.79, 125.58 (d, $^1J_{C\text{-}F}$ = 3.6 Hz), 122.68, 40.62. ^{19}F NMR (376 MHz, CDCl3) δ -62.64 (s). IR (ν_{max}): 2926, 1707, 1414, 1321, 1238, 1161, 1115, 1064, 1017, 817 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_9H_7O_2F_3$, $[M-H]^-$: 203.0314, found: 203.0308. Verified the analytical data with those reported in the literature.[5]

2-(4-Cyanophenyl) acetic acid (3i): The electrolysis product **(3i)** was conducted following preparation according to the procedure as described in section **3b** for electrochemical carboxylation. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 37.20 mg, 77% yield of **3i** as a white solid and a melting point is 150-152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 3.73 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.44, 138.48, 132.39, 130.26, 118.53, 111.47, 40.80. IR (ν_{max}): 2911, 2221, 1681, 1410, 1325, 1238, 1187, 901, 812, 751, 664 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_9H_7NO_2$ $[M+H]^+$: 162.055, found: 162.0560. Verified the analytical data with those reported in the literature.[12]

2-(4-Isobutylphenyl) acetic acid (Ibufenac) (3j): The electrolysis product **(3j)** was conducted following preparation according to the procedure as described in section **3b** for electrochemical carboxylation. Finally, the organic layer solution

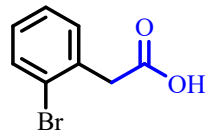
was concentrated under vacuum and the product was isolated in 46.65 mg, 81% yield of **3j** as a white solid and a melting point is 85-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 14H), 7.11 (d, *J* = 8.0 Hz, 15H), 3.62 (s, 14H), 2.46 (d, *J* = 7.2 Hz, 15H), 1.85 (dt, *J* = 13.5, 6.8 Hz, 8H), 0.90 (d, *J* = 6.6 Hz, 51H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.71, 140.77, 130.48, 129.36, 129.04, 45.04, 40.65, 30.15, 22.36. IR (ν_{max}): 2934, 1699, 1403, 1278, 1223, 903, 765, 667 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{12}H_{16}O_2$ $[M]^+$: 192.1150, found: 192.1144. Verified the analytical data with those reported in the literature[10]

2-([1,1'-Biphenyl]-2-yl) acetic acid (3k): The electrolysis product **(3k)** was conducted following



preparation according to the procedure as described in section **3b** for electrochemical carboxylation. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 41.35 mg, 65% yield of **3k** as a white solid and a melting point is 111-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.23 (m, 19H), 3.63 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.48, 142.57, 140.87, 131.01, 130.36, 130.26, 129.19, 128.25, 127.58, 127.39, 127.24, 38.39. IR (ν_{max}): 2914, 1693, 1422, 1312, 1265, 1151, 931, 748, 691, 617 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{14}H_{12}O_2$ $[M+H]^+$: 213.0908 found: 213.0902. Verified the analytical data with those reported in the literature.[7]

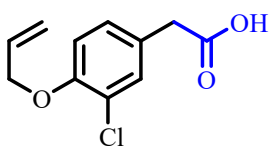
2-(2-Bromophenyl) acetic acid (3l): The electrolysis product **(3l)** was conducted following



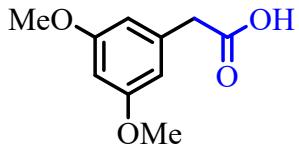
preparation according to the procedure as described in section **3b** for electrochemical carboxylation. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 43.45 mg, 68% yield of **3l** as a white solid and a melting point is 103-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 0.8 Hz, 1H), 7.30 – 7.28 (m, 1H), 7.16 (ddd, *J* = 8.0, 5.6, 3.6 Hz, 1H), 3.85 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.67, 133.53, 132.87, 131.54, 129.13, 127.60,

125.07, 41.22. IR (ν_{max}): 2894, 1696, 1408, 1292, 1230, 1017, 922, 755, 663 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_8H_7BrO_2$ $[M+H]^+$: 216.9707, found: 216.96751. Verified the analytical data with those reported in the literature.[12]

2-(4-(Allyloxy)-3-chlorophenyl) acetic acid (3m): The electrolysis product **(3m)** was conducted following preparation according to procedure as described in section **3b** for electrochemical carboxylation. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 49.50 mg, 73% yield of **3m** as a white solid and a melting point is 91-143 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 2.1 Hz, 1H), 7.11 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.12 – 6.00 (m, 1H), 5.50 – 5.42 (m, 1H), 5.34 – 5.26 (m, 1H), 4.60 (dt, *J* = 5.0, 1.4 Hz, 2H), 3.57 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.41, 153.39, 132.55, 131.18, 128.52, 126.45, 123.08, 117.93, 113.75, 69.77, 39.63. IR (ν_{max}): 2922, 1689, 1499, 1414, 1242, 1159, 1056, 1008, 920, 800, 723 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{11}H_{11}ClO_3$ $[M+H]^+$: 227.0475, found: 227.0461.



2-(3,5-Dimethoxyphenyl) acetic acid (3n): The electrolysis product **(3n)** was conducted following preparation according to the procedure as described in section **3b** for electrochemical carboxylation. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 40.00 mg, 68% yield of **3n** as a white solid and a melting point is 101-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.44 (d, *J* = 2.2 Hz, 2H), 6.39 (s, 1H), 3.78 (s, 6H), 3.58 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.85, 160.87, 135.26, 107.44, 99.41, 55.32, 41.19. IR (ν_{max}): 2923, 1691, 1593, 1459, 1416, 1295, 1199, 1137, 1049, 901, 817, 731, 649 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{10}H_{12}O_3$ $[M+H]^+$: 197.0813, found: 197.0815. Verified the analytical data with those reported in the literature.[14]



2-(2,4,5-Trifluorophenyl) acetic acid (3o): The electrolysis product **(3o)** was conducted following preparation according to procedure as described in section **3b** for electrochemical carboxylation. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 39.90 mg, 70% yield of **3o** as a white solid and a melting point is 122-124 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (ddd, *J* = 10.0, 8.6, 6.9 Hz, 1H), 6.95 (td, *J* = 9.5, 6.6 Hz, 1H), 3.66 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.01, 157.35, 157.28, 154.91, 154.84, 150.96, 150.83, 150.70, 148.46, 148.32, 148.20, 147.95, 147.86, 145.55, 145.39, 119.26, 119.22, 119.07, 119.02, 116.86, 116.68, 105.86, 105.65, 105.59, 105.38, 33.47. ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.37 (d, *J* = 17.5 Hz), -134.10 (d, *J* = 24.3 Hz), -142.52 (dd, *J* = 21.4, 18.0 Hz). IR (ν_{max}): 2926, 1685, 1510, 1415, 1319, 1217, 1151, 1085, 916, 844, 765, 684, 618 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{12}H_{10}O_2$ [M+H]$^+$: 190.0241 found: 190.0245. Verified the analytical data with those reported in the literature.[15]

2-(Naphthalen-2-yl) acetic acid (3p): The electrolysis product **(3p)** was conducted following preparation according to the procedure as described in section **3b** for electrochemical carboxylation. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 48.00 mg, 86% yield of **3p** as a white solid and a melting point is 140-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 3H), 7.73 (s, 1H), 7.50 – 7.43 (m, 2H), 7.40 (dd, *J* = 8.4, 1.8 Hz, 1H), 3.81 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.96, 133.39, 132.54, 130.71, 128.33, 128.16, 127.66, 127.28, 126.23, 125.94, 41.09. IR (ν_{max}): 2906, 1691, 1405, 1328, 1216, 902, 824, 753, 676 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{12}H_{10}O_2$ [M+H]$^+$: 187.0759, found: 187.0765. Verified the analytical data with those reported in the literature.[5]

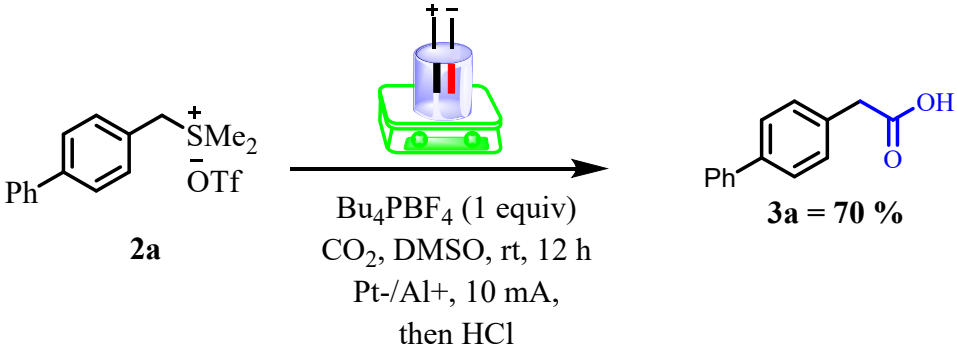
2-(9H-Fluoren-2-yl) acetic acid (3q): The electrolysis product **(3q)** was conducted following preparation according to the procedure as described in section **3b** for electrochemical carboxylation. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 55.12 mg, 82% yield of **3q** as a white solid and a melting point is 128-130 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 11.3, 7.7 Hz, 2H), 7.60 – 7.50 (m, 1H), 7.47 (s, 1H), 7.36 (dd, *J* = 7.5, 0.8 Hz, 1H), 7.32 – 7.27 (m, 2H), 3.89 (s, 2H), 3.73 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.36, 143.75, 143.25, 141.01, 131.68, 127.98, 126.74, 126.05, 125.00, 119.96, 119.88, 40.94, 36.82. IR (ν_{max}): 3035, 1694, 1414, 1342, 1236, 929, 738, 677 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{15}H_{12}O_2$ $[M+H]^+$: 225.0915, found: 225.0903.

2-(4-Bromophenyl) propanoic acid (3r): The electrolysis product **(3r)** was conducted following preparation according to the procedure as described in section **3b** for electrochemical carboxylation. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 38.98 mg, 57% yield of **3r** as a white solid and a melting point is 66-68 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 2H), 7.21 – 7.18 (m, 2H), 3.70 (q, *J* = 7.2 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.14, 138.68, 131.78, 129.34, 121.39, 44.67, 18.04. IR (ν_{max}): 2926, 1696, 1472, 1405, 1273, 1223, 1069, 1001, 925, 830, 743, 656 cm^{-1} HRMS (ESI): *m/z* calcd for $C_9H_9BrO_2$ $[M+H]^+$: 228.9864, found: 228.9870. Verified the analytical data with those reported in the literature.[16]

2,2-Diphenyl acetic acid (3s): The electrolysis product **(3s)** was conducted following preparation according to the procedure as described in section **3b** for electrochemical carboxylation. Finally, the organic layer solution was

concentrated under vacuum and the product was isolated in 43.24 mg, 68% yield of **3s** as a white solid and a melting point is 146-148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 3H), 7.32 (s, 5H), 7.31 – 7.27 (m, 2H), 5.05 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.80, 137.90, 128.65, 127.48, 56.87. IR (ν_{max}): 2896, 1691, 1493, 1406, 1306, 1214, 1027, 926, 736, 685, 629 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{14}H_{12}O_2$ $[M+H]^+$: 213.0915, found: 213.0920. Verified the analytical data with those reported in the literature.[13]

4.4 General procedure for the synthesis of 2-([1,1'-biphenyl]-4-yl) acetic acid (3a) in batch process.



An oven dried 50 mL test tube or round bottom flask charged with magnetic stirrer was added **2a (**114 mg**):** Bu_4PBF_4 (106 mg): DMSO (10 mL) in molar ratio (1: 1: 468) under N_2. The flask was evacuated and kept with CO_2 balloon (approx. 1 atm). The reaction mixture was kept under electrolysis (10 mA current) at room temperature for 12 hours. The crude residue was purified by normal phase silica gel chromatography eluted with the mixture to afforded the corresponding 2-([1,1'-biphenyl]-4-yl) acetic acid **(3a)** in 70 % (45.5 mg) of yield.

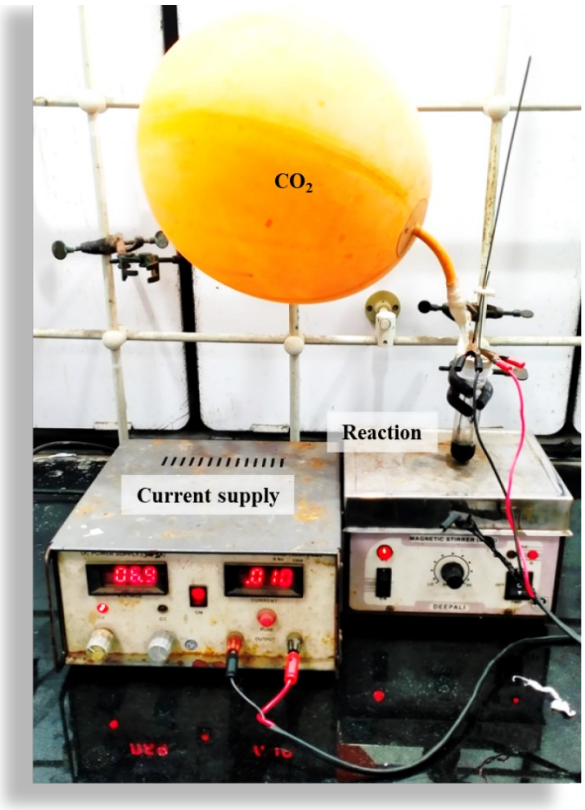


Fig. S7. Snapshot of real-experimental set-up for deoxy-carboxylation in batch process.

Faradaic efficiency (ϕ) calculation in batch process

Experimental Charge = 0.00021 × 2 × 0.70 × 96485.33

= 28.991 C

Theoretical charge (Q) = 0.01×720× 60

= 420 C

$$Faradaic\ efficiency(\phi) = \frac{experimental\ charge(Qe)}{theoretical\ charge(Qt)} X\ 100$$

$$Faradaic\ efficiency(\phi) = \frac{28.991}{420} X\ 100$$

Faradic efficiency (ϕ) = 6.9%

Space-time yield (STY) for the formation of compound 3a in the batch process.

$$Space - time\ yield\ (STY)\ = \frac{Product\ mol}{reactor\ volume\ \times\ operation\ time}$$

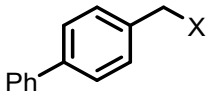
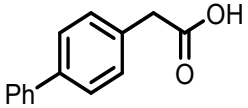
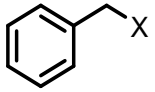
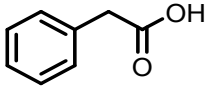
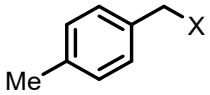
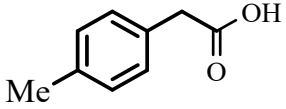
Reaction time 12 h, Reactor volume = 50 mL

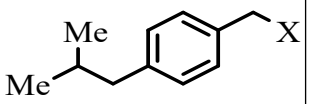
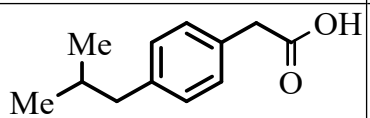
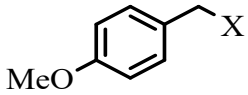
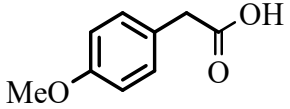
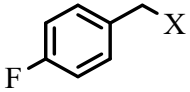
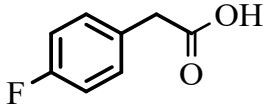
$$Space - time\ yield\ (STY) = \frac{0.00022}{50\ X\ .5}$$

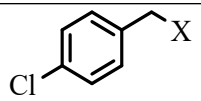
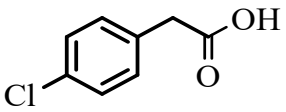
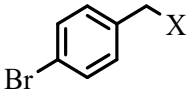
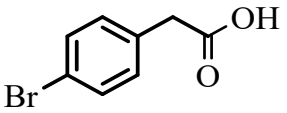
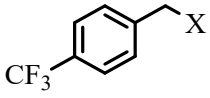
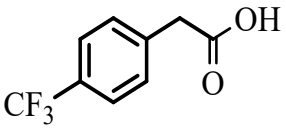
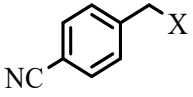
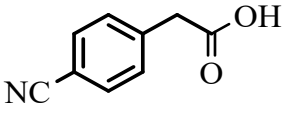
$= 0.0000088$ mol day^{-1} mL^{-1}

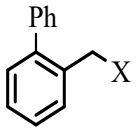
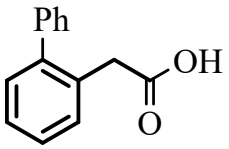
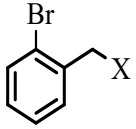
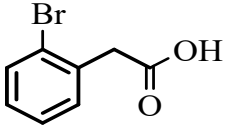
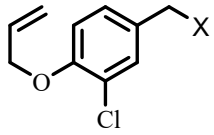
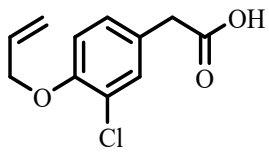
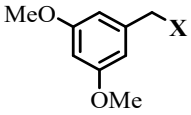
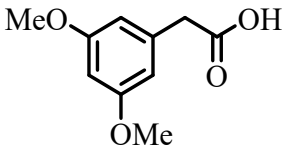
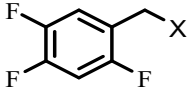
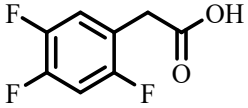
Space-time yield (STY) = 0.00186 g day^{-1} mL^{-1}

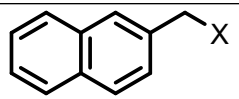
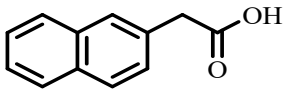
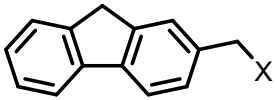
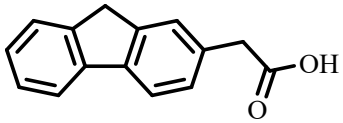
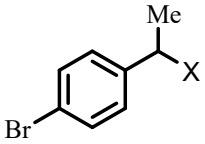
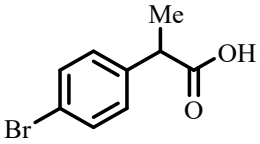
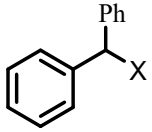
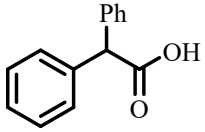
Table S4. Comparative table for synthesis of carboxylic acid.

Entry	Substrate formula	Product formula 1	X	Comparative result
1			OH or SMe_2OTf	88%, 0.38 min. (our study)
			F	4CzIPN, Et_3SiH, Cs_2CO_3, 87%, rt, 16 h, (Ref. [6])
			Br	[Ir] cat, DABCO, HCO_2K, 90% rt, 24 h (Ref. [13])
			NMe_3OTf	[Ir]-cat, Cs_2CO_3, Na_2CO_3, 80% 36 h, (Ref. [7])
				$^tBu_4PBF_4$, 72%, 20 h, rt (Ref. [5])
			OPiv	[Ni] cat, PMe_3, Mn, 61% 100 °C, 24 h. (Ref. [17])
			OH, OAc	DPA_2FBN, Cs_2CO_3, DIPEA, 89%, 48 h, (Ref.[18])
2			OH or SMe_2OTf	70%, 0.38 min. (our study)
			NMe_3OTf	[Ir]-cat, Cs_2CO_3, Na_2CO_3, 80% 36 h, (Ref. [7])
			NMe_3OTf	$^tBu_4PBF_4$, 72%, 20 h, (Ref. [5])
			NMe_3I	[Ni] cat, ligand, Mn, 51%, 90°C, 72 h, (Ref. [8])
3			OH or SMe_2OTf	77%, 0.38 min. (our study)
			OAc	DPA_2FBN, Cs_2CO_3, DIPEA, 89%, 48 h, (Ref.[18])
			H	[Ni] cat, $(2\text{-py})_2CH_2$, xanthone, t-BuOK, 75%, 4

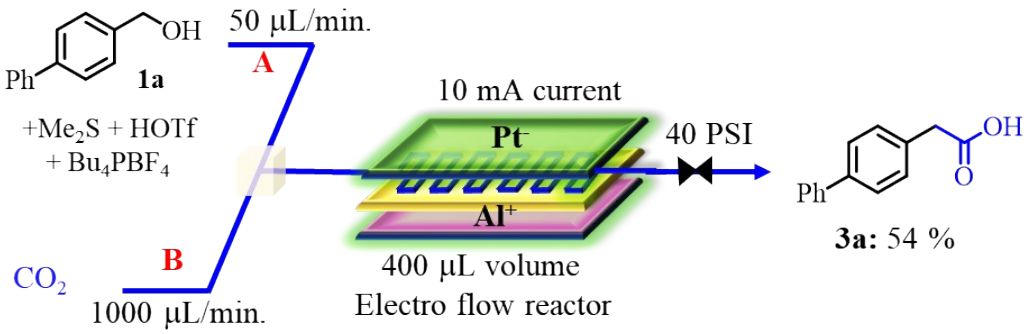
				h, (Ref.[9])
4			OH or SMe_2OTf Ethylene glycol ketal Acetophenones	81%, 0.38 min. (our study) 9-BBN-H, [O], 100 °C, 18 h $Pd(PPh_3)_4$TEMPO, $NaClO_2$, 60%, 35 °C, 6-8 h, Multistep synthesis Ref. [19]) Sulfer, PTS, morpholine, 130 °C, 8 h, NaOH, TEBA, HCl, 78%, 100 °C, 8 h Multistep synthesis (Ref.[20])
5			OH or SMe_2OTf OAc X = NMe_3OTf	81%, 0.38 min. (our study) DPA_2FBN, Cs_2CO_3, DIPEA, 89%, 48 h, (Ref.[18]) $^tBu_4PBF_4$, 72%, 20 h, (Ref. [5]) ACS Catal. 2019, 9, 4699−4705
6			OH or SMe_2OTf	81%, 0.38 min. (our study)
			NMe_3I NMe_3OTf NMe_3OTf	[Ni] cat, ligand, Mn, 51%, 90°C, 72 h, (Ref. [8]) Ir]-cat, Cs_2CO_3, Na_2CO_3, 80% 36 h, (Ref. [7]) $^tBu_4PBF_4$, 72%, 20 h, (Ref. [5])

7			OH or SMe_2OTf H Br	79%, 0.38 min. rt (our study) [Ni] cat, $(2\text{-py})_2CH_2$, xanthone, t-BuOK, 33%, 4 h, (Ref.[9]) [Ni] cat, DPPO, DTBP, Bu_4NI, CO, 59%, 140 °C, 14 h (Ref. [12]) [Ir] cat, DABCO, HCO_2K, 48% rt, 24 h (Ref. [13])
8			OH or SMe_2OTf NMe_3OTf	75%, 0.38 min. rt (our study) $^tBu_4PBF_4$, 56%, 20 h, (Ref. [5])
9			OH or SMe_2OTf OAc NMe_3OTf	69%, 0.38 min. rt (our study) DPA_2FBN, Cs_2CO_3, DIPEA, 58%, 48 h, (Ref.[18]) Ir]-cat, Cs_2CO_3, Na_2CO_3, 80% 36 h, (Ref. [7]) Bu_4PBF_4, 56%, 20 h, (Ref. [5])
10			OH or SMe_2OTf OAc NMe_3OTf NMe_3OTf	77%, 0.38 min. (our study) DPA_2FBN, Cs_2CO_3, DIPEA, 82%, 48 h, (Ref.[18]) Ir]-cat, Cs_2CO_3, Na_2CO_3, 84% 36 h, (Ref. [7]) Bu_4PBF_4, 67%, 20 h, (Ref. [5])

11			OH or SMe_2OTf NMe_3OTf	65%, 0.38 min. rt (our study) Ir]-cat, Cs_2CO_3, Na_2CO_3, 84% 36 h, (Ref. [7])
12			OH or SMe_2OTf H	68%, 0.38 min. (our study) [Ni] cat, DPPO, DTBP, Bu_4NI, 59%, 140 °C, 14 h (Ref. [12])
12			OH or SMe_2OTf $ClCH(SEt)CO_2Et$	73%, 0.38 min. (our study) Yb(OTf), $ZnCl_2$ 85%, 50 °C, 5 h, (Ref.[21])
13			OH or SMe_2OTf SO_2Ph	68%, 0.38 min. (our study) TBAI, 99 %, 6-12 h Pt/Mg (Ref.[14])
14			OH or SMe_2OTf COOH	70%, 0.38 min. (our study) NEt_3, $ClCO_2Et$, CH_2N_2, Homologation, 58%, rt, 80 min. (Ref. [15])

13			OH or SMe_2OTf NMe_3I NMe_3OTf OAc	86%, 0.38 min. (our study) [Ni] cat, ligand, Mn, 63%, 90°C, 72 h, (Ref. [8]) Ir]-cat, Cs_2CO_3, Na_2CO_3, 84% 36 h, (Ref. [7]) Bu_4PBF_4, 72%, 20 h, (Ref. [5]) DPA2FBN, Cs_2CO_3, DIPEA, 84%, 48 h,(Ref.[18])
17			OH or SMe_2OTf	82%, 0.38 min. (our study)
18			OH or SMe_2OTf Styrene	57%, 0.38 min. (our study) [Pd], $FeCl_3$, PPh_3, CO, 85%, 80 °C 15 h (Ref. [16])
19			OH or SMe_2OTf NMe_3OTf Br	68%, 0.38 min. (our study) [Ir]-cat, Cs_2CO_3, Na_2CO_3, 79% 36 h, (Ref. [7]) Bu_4PBF_4, 54%, 20 h, (Ref. [5]) [Ni] cat, PCy_3 TBAI, Zn, 47%, 12h, rt-50 °C, (Ref. [22])

4.5 One pot reaction to generate carboxylation 3a.



The stock solution of **2a:** Me_2S: HOTf: DCM in molar ratio (1: 2: 1: 57) under N_2 and stirrer in 10 min., after dry to DCM solvent in vacuum then adding of Bu_4PBF_4: DMSO (molar ratio 1: 260) and carbon dioxide gas balloon was connected with pump. Two reactants were introduced through T-junction in a flow rate to maintain the stoichiometry and then passed through an electro flow reactor (reactor volume 400 µL, 10 mA current) for the synthesis of carboxylate product during 0.38 min. of residence time and 40 psi pressure and the crude residue to analyzed to ^{1}H-NMR spectrums were provided as below Fig. S8.

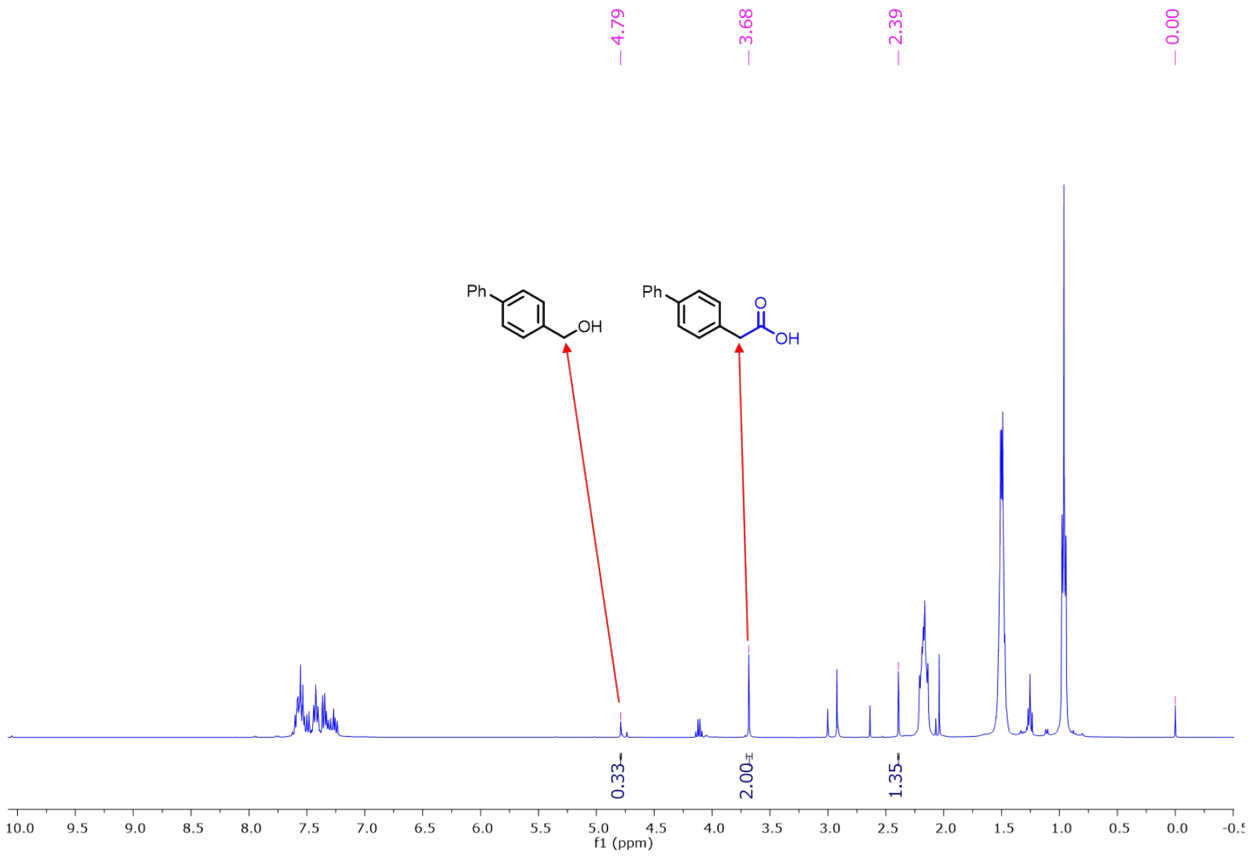
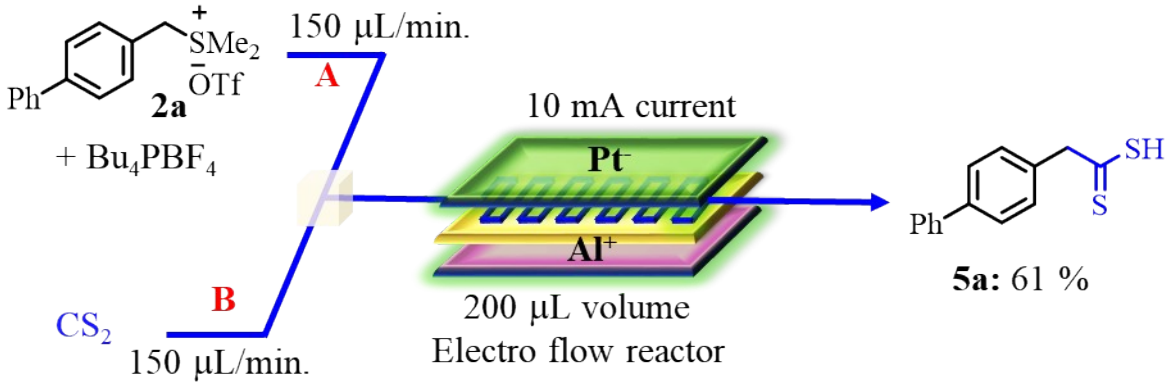


Fig. S8. Crude ^{1}H NMR spectra of one pot reaction in $CDCl_3$

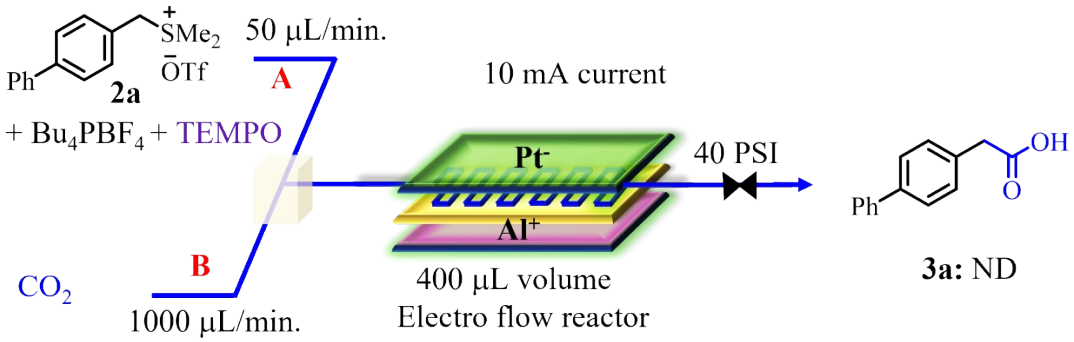
4.6 General procedure for the synthesis of 2-([1,1'-biphenyl]-4-yl)ethanedithioic acid (5a)



The stock solution **(A)** containing **2a:** Bu_4PBF_4: DMSO in a molar ratio (1:1:468) and the stock solution **(B)** containing $\mathbf{CS_2}$: DMSO in molar ratio (1:94) was taken in two separate syringes and connected with designed µ-EFR to perform the reaction. Two reactants were introduced into capillary micro-reactor through T- junction in a flow rate to maintain the stoichiometry and then passed through a µ-EFR (reactor volume 200 µL) for the synthesis of crass coupling reaction product during 0.66 min. of residence time at 10 mA current as an electrode platinum and aluminium. The Outlet organic layer of µ-EFR was concentrated under vacuum to give the product and subsequent purification by column chromatography on silica gel afforded the corresponding product was isolated in 61% yield of **5a** as a black solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.50 (m, 4H), 7.43 (dd, J = 15.6, 7.9 Hz, 2H), 7.38 – 7.23 (m, 3H), 4.02 (s, 1H), 3.96 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.66 (d, J = 279.7 Hz), 140.82 (d, J = 5.1 Hz), 140.23 (d, J = 5.6 Hz), 134.89 (d, J = 30.4 Hz), 132.87 (s), 129.38 (s), 129.34 (s), 127.79 (dd, J = 72.2, 67.5 Hz), 126.97 (s), 41.07, (d, J = 54.5 Hz). IR (ν_{max}): 2921, 1482, 1406, 1232, 1056, 949, 878, 833, 750, 693, 658 cm^{-1}.

5. Mechanistic studies.

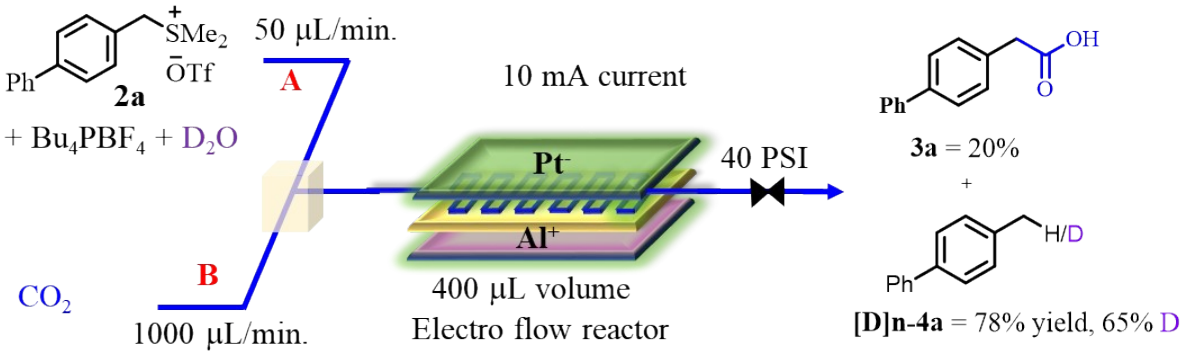
5.1 Radical scavenger experiments.



The stock solution **of 2a:** Bu_4PBF_4: TEMPO: DMSO in molar ratio (1:1:5:468) and carbon dioxide gas balloon was connected with pump. Two reactants were introduced through T-junction in a flow rate to maintain the stoichiometry and then passed through an electro flow reactor (reactor volume 400 µL, 10 mA current) for the synthesis of carboxylate product during 0.38 min. of residence time and 40 psi pressure. Though we were failed to detect TEMPO-alkyl radical adduct by HRMS, this reaction afforded no desired product **3a**, which might support the existence of a benzyl radical.

5.2 Deuterium-labelling experiments (Kinetic Isotope Effects).

Step 1. H/D Exchange Experiment.



The stock solution **of 2a:** Bu_4PBF_4: D_2O: DMSO in molar ratio (1:1:20:468) and carbon dioxide gas balloon was connected with pump. Two reactants were introduced through T-junction in a flow rate to maintain the stoichiometry and then passed through an electro flow reactor (reactor volume 400 μL, 10 mA current) for the synthesis of carboxylate product during 0.38 min of residence time and 40 psi pressure and the solvent was removed under reduced pressure to give the residue and purified by column chromatography, yield $[D]_n$-**3a** (20%) as a white solid and $[D]_n$-**4a** (78%) as a white solid. The D-incorporation was estimated by ^1H NMR spectroscopy. This result indirectly confirmed the existence of benzylic carbanion. The 1H-NMR spectrums were provided as below Fig. S9.

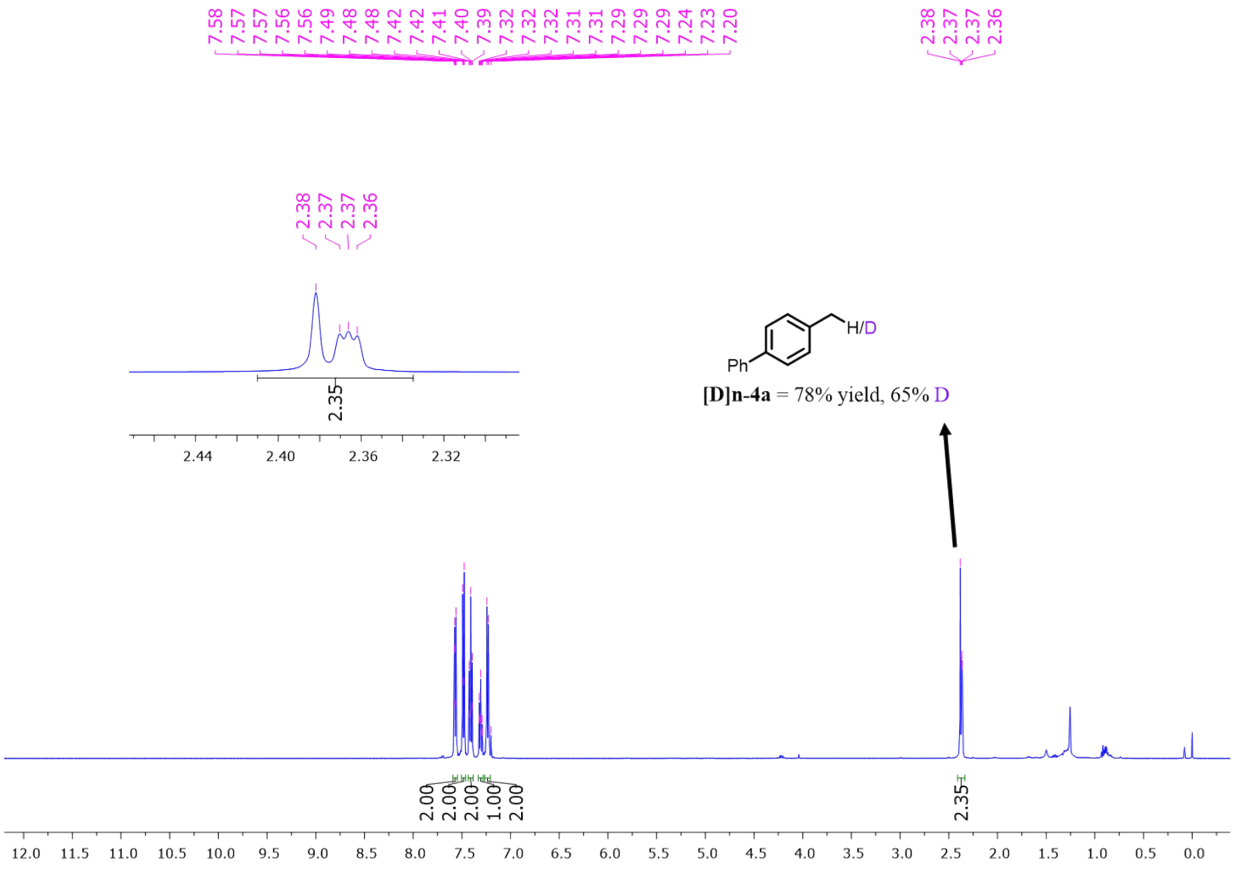
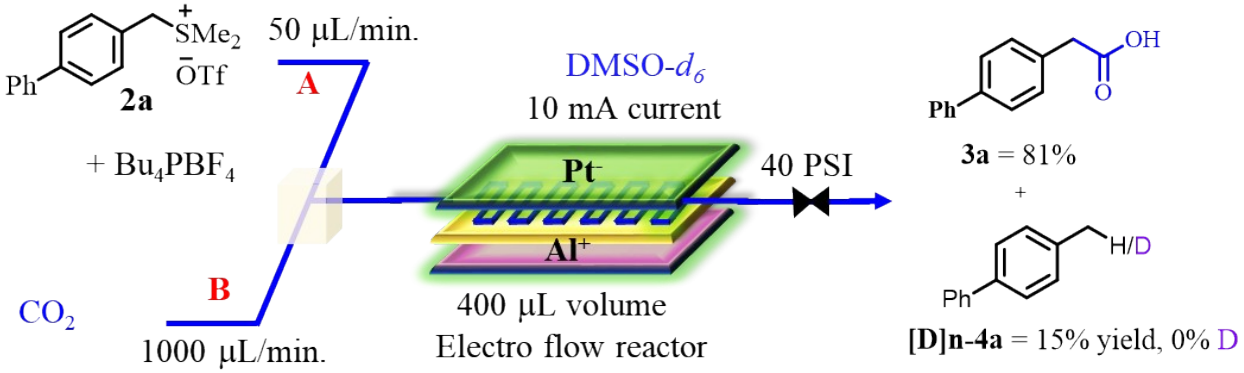


Fig. S9. ^1H NMR spectra of 4-(methyl-d)-1,1'-biphenyl, in $CDCl_3$.

Step 2. DMSO-d_6 Experiment.



The stock solution of **2a:** Bu_4PBF_4: DMSO-d_6 in molar ratio (1:1:471) and carbon dioxide gas balloon was connected with pump. Two reactants were introduced through T-junction in a flow rate to maintain the stoichiometry and then passed through an electro flow reactor (reactor volume 400 µL, 10 mA current) for the synthesis of carboxylate product during 0.38 min of residence time and 45 psi pressure and the solvent was removed under reduced pressure to give the residue and purified by column chromatography, yield $[D]_n$-**3a** (81%) as a white solid and $[D]_n$-**4a** (15%) as a white solid. The D-incorporation was estimated by ^{1}H NMR spectroscopy. This result indirectly confirmed the existence of benzylic carbanion. The ^{1}H-NMR spectrums were provided as below Fig. S10.

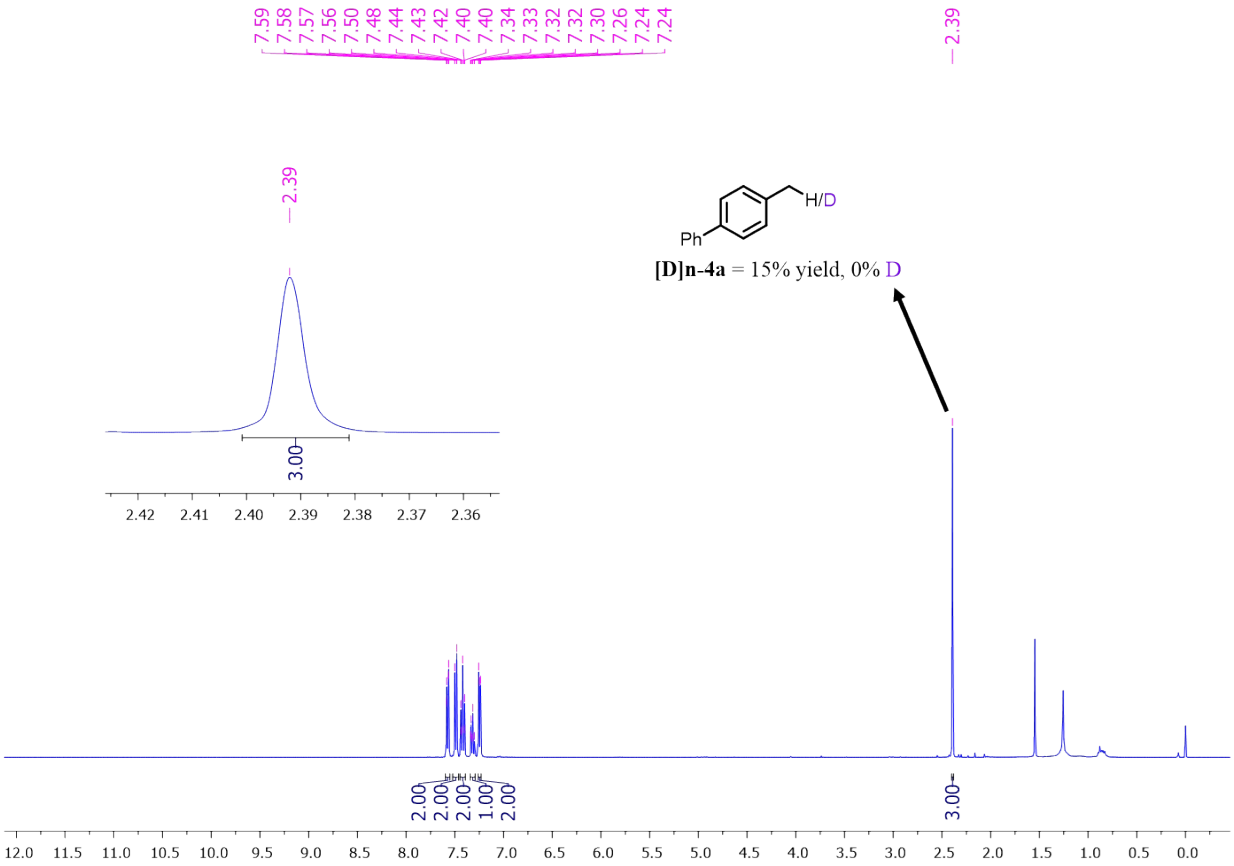
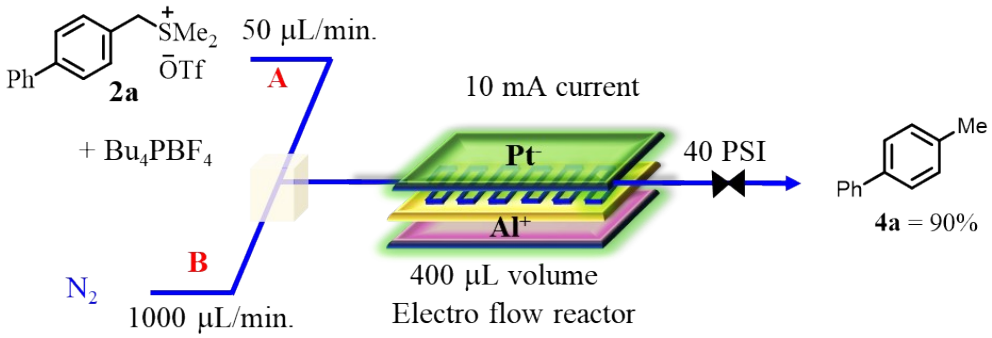


Fig. S10. ^{1}H NMR spectra of 4-(methyl-d)-1,1'-biphenyl, in $CDCl_3$.

5.3 Side reaction of 3a



The stock solution of **2a:** Bu_4PBF_4: DMSO in molar ratio (1:1: 468) and nitrogen gas balloon was connected with pump. Two reactants were introduced through T-junction in a flow rate to maintain the stoichiometry and then passed through an electro flow reactor (reactor volume 400 µL, 10 mA current) for the synthesis of 4-methyl-1,1'-biphenyl product during 0.38 min. of residence time and 40 psi pressure and the solvent was removed under reduced pressure to give the residue and purified by column chromatography, yield **4a** (90%) as a white solid. The ^{1}H-NMR spectrums were provided as below Fig. S11.

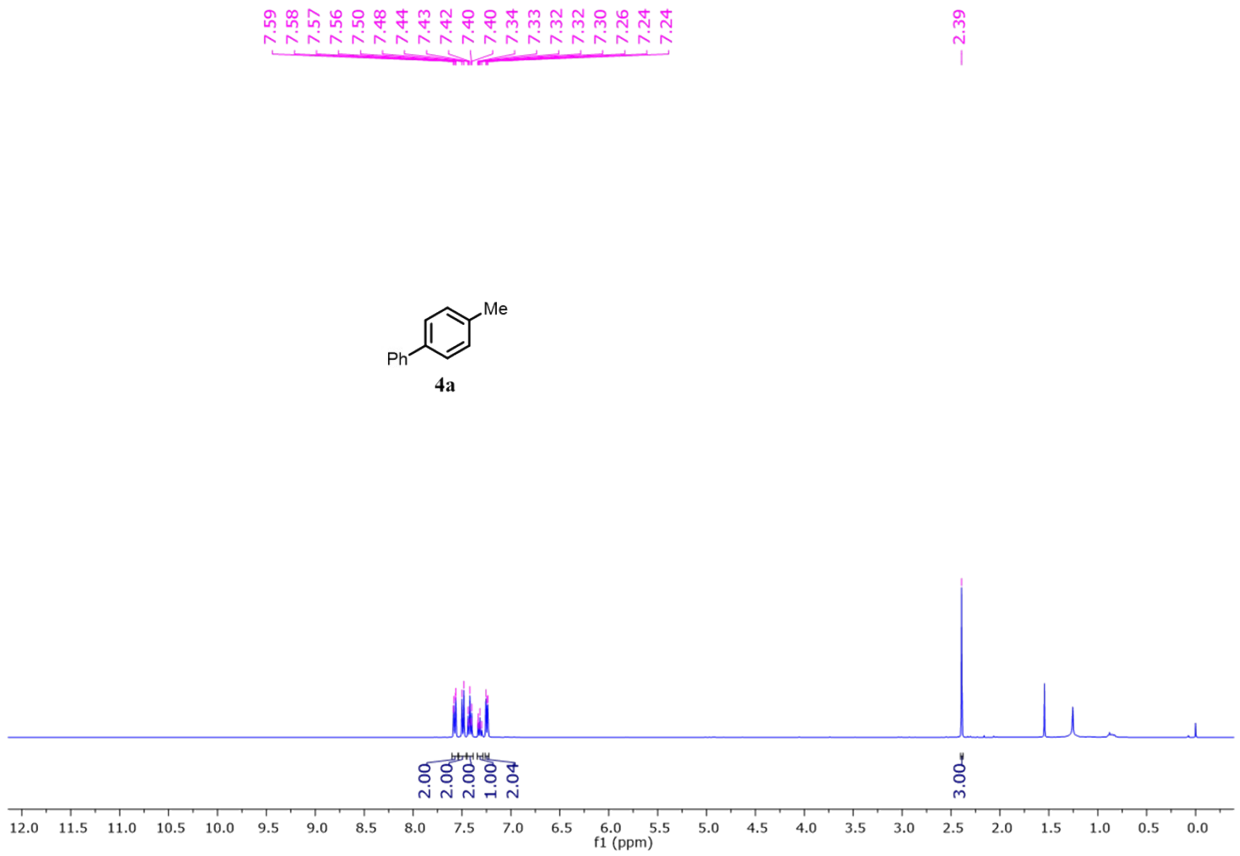


Fig. S11. ^{1}H NMR spectra of 4-methyl-1,1'-biphenyl in $CDCl_3$

5.4 Cyclic voltammetry (CV) analysis.

Cyclic voltammetry (CV) measurement was conducted with HCH Instrument Model: CHI6005E electrochemical Workstation and CH Instr. ChI6005E software. For below the all experiments, a platinum working electrode (disk, diameter: 2 mm), a platinum wire counter electrode (disk, diameter 1.5), and a saturated Ag/AgCl reference electrode (disk, diameter: 2 mm), were operating. The voltammograms were recorded at room temperature in a DMSO at a substrate the concentration of 5 mmol/L and with 0.1 mol/L Bu_4PBF_4 as supporting electrolyte. All solutions were saturated with N_2 before the measurement and an over-pressure of N_2 was maintained throughout the experiment. The scan rate is 100 mV/s. and Sensitivity (A/V) = $1e^{-4}$.

A variety of cyclic voltammetric (CV) studies were conducted in order to investigate the redox potentials of chemicals. As shown in Fig. S12, when testing compound **2a** in the presence of 0.1 M Bu_4PBF_4 as supporting electrolyte, we found the reduction potential of (E_P^{Ox} = -0.54 V and -1.25 V vs Ag/AgCl in DMSO) generated in-situ after reduction of sulfonium salts. All the CVs showed the same or similar reductive peaks around -2.0 V, which might arise from anion exchange between benzyl sulfonium salts with Bu_4PBF_4. As reported by serval researchers group, the benzyl radical might be easier to be reduced to an anion in the case of reduction of sulfonium salts[23] and benzyltrimethylammonium salts.[5, 7] The potential we observed was near to the reductive potential of benzyl radical reported before, from which we proposed a pathway of two single-electron reductions to form benzyl anion via benzyl radical. After testing the CV of sulfonium salts, we noticed there was always a strong smell of sulphur, which might be Me_2S.[5] The cyclic voltammetric (CV) for a solution of Me_2S` in DMSO as supporting electrolyte (Bu_4PBF_4] is shown in Fig. S12.[24, 25]

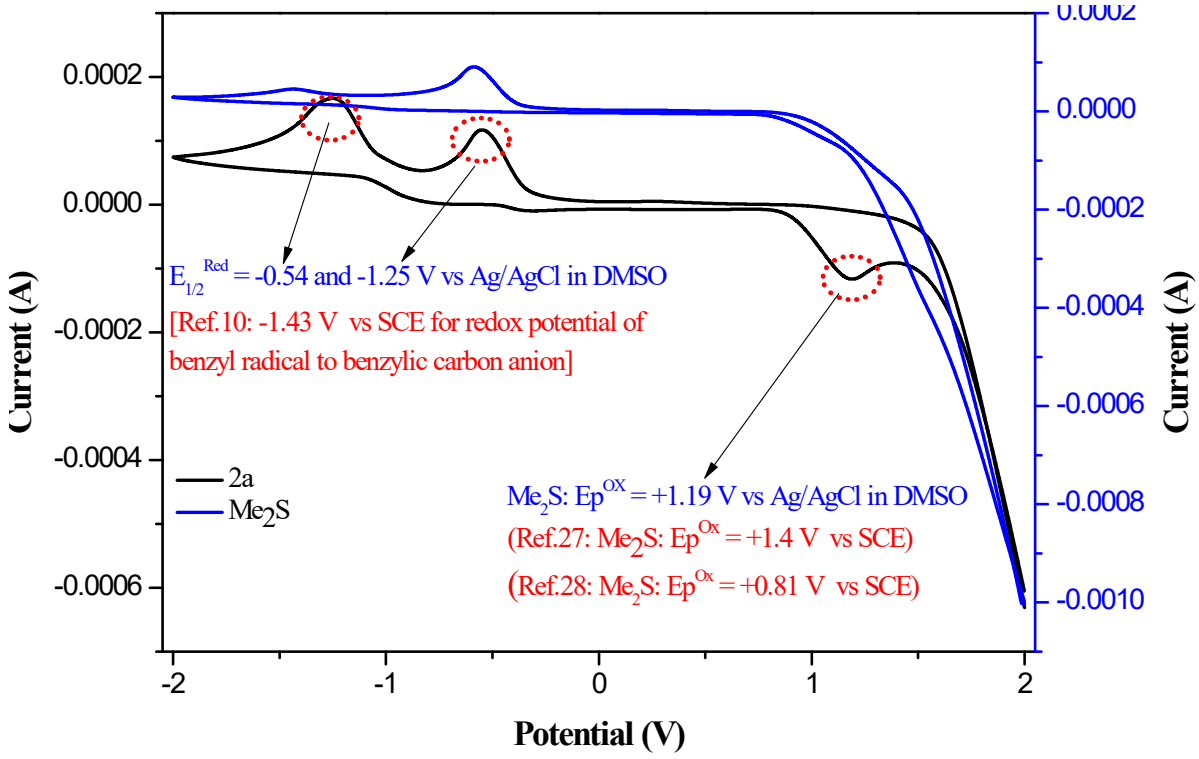
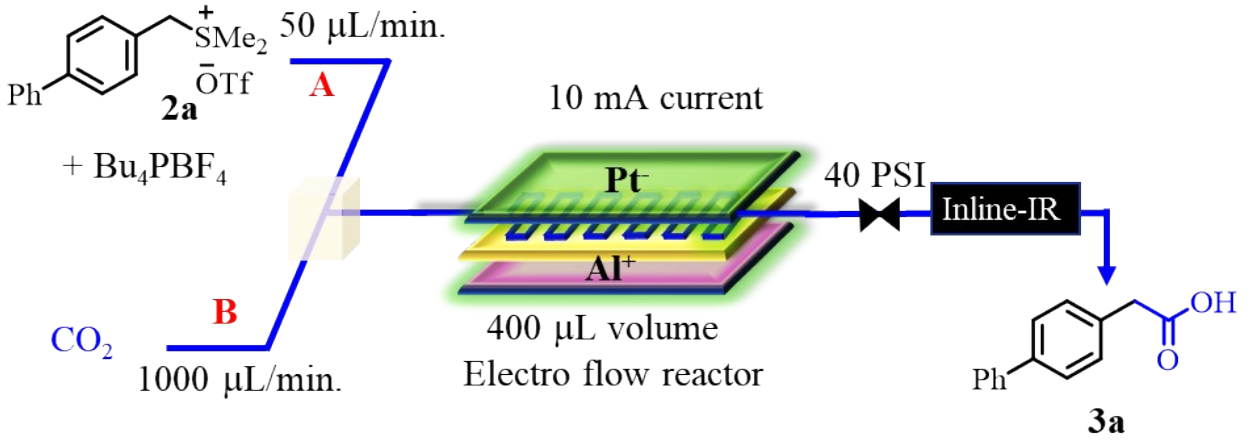


Fig. S12. Cyclic voltammograms of compound **3a** and Me_2S in DMSO under N_2 at scan rate 100 mV/s

5.5 Continuous flow IR study:



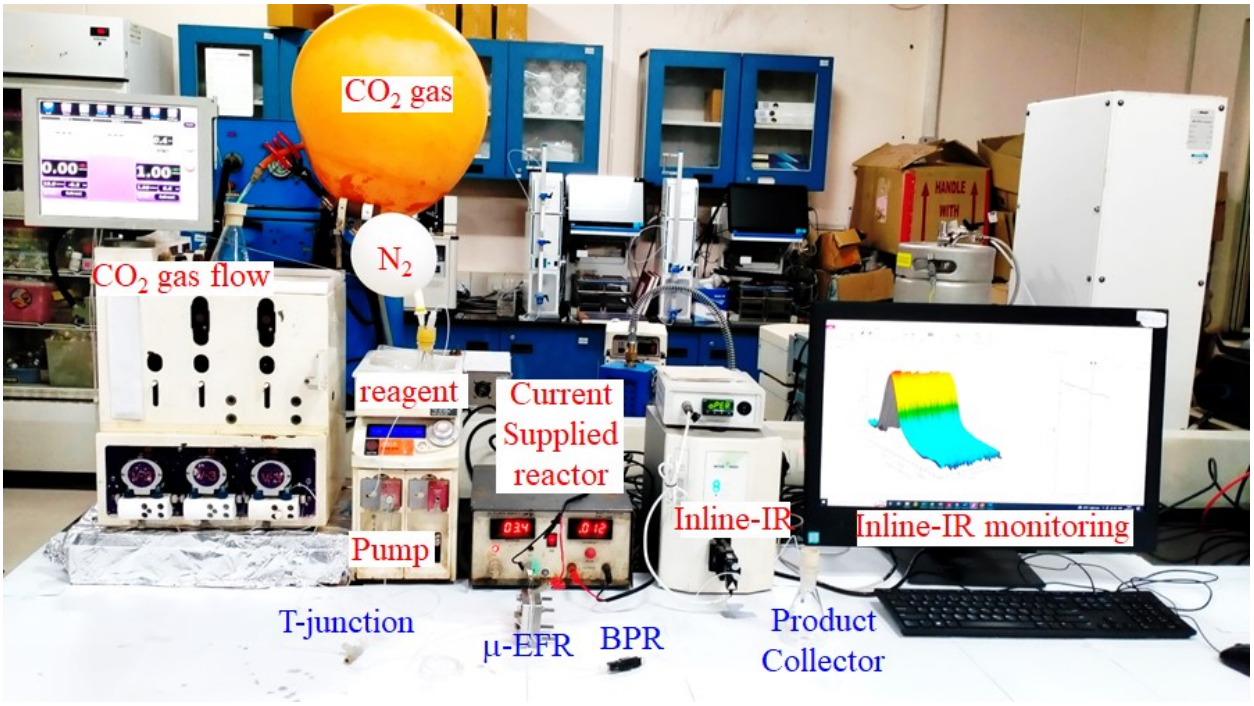


Fig. S13. Flow diagram set and snapshot of the basic set up for the inline IR analysis.

The stock solution of **2a:** Bu_4PBF_4: DMSO in molar ratio (1:1: 468) and carbon dioxide gas balloon was connected with pump. Two reactants were introduced through T-junction in a flow rate to maintain the stoichiometry and then passed through an electro flow reactor (reactor volume 400 μL). After the reactor inline IR instrument were connected (Fig. 13) for analysis the reaction progress. At first, reaction mixture and carbon dioxide were pumping with standard condition without passing the current and inline IR spectra was recorded (Fig.14a). Under the stable flow condition CO_2 stretching band was observed at around 2335 cm^{-1} but once we started to flow the current the peak intensity of the carbon dioxide was decreased (Fig. 14b). Further to check the carbon dioxide adduct formation or transformation of some function group we were compare the peak intensity of carbon dioxide with reference carbon dioxide peak (Fig. 14b), shows that under the electrolysis condition the carbon dioxide concentration was decreased. After the confirmation of the carbon dioxide participation in reaction, next we were interested to see the what new functional group transformation has been happened during the electrolysis. After the electrolysis, the new peak 1716 cm^{-1} was appeared, which is correspond to -C=O(OH) group (Fig. 14d-f)

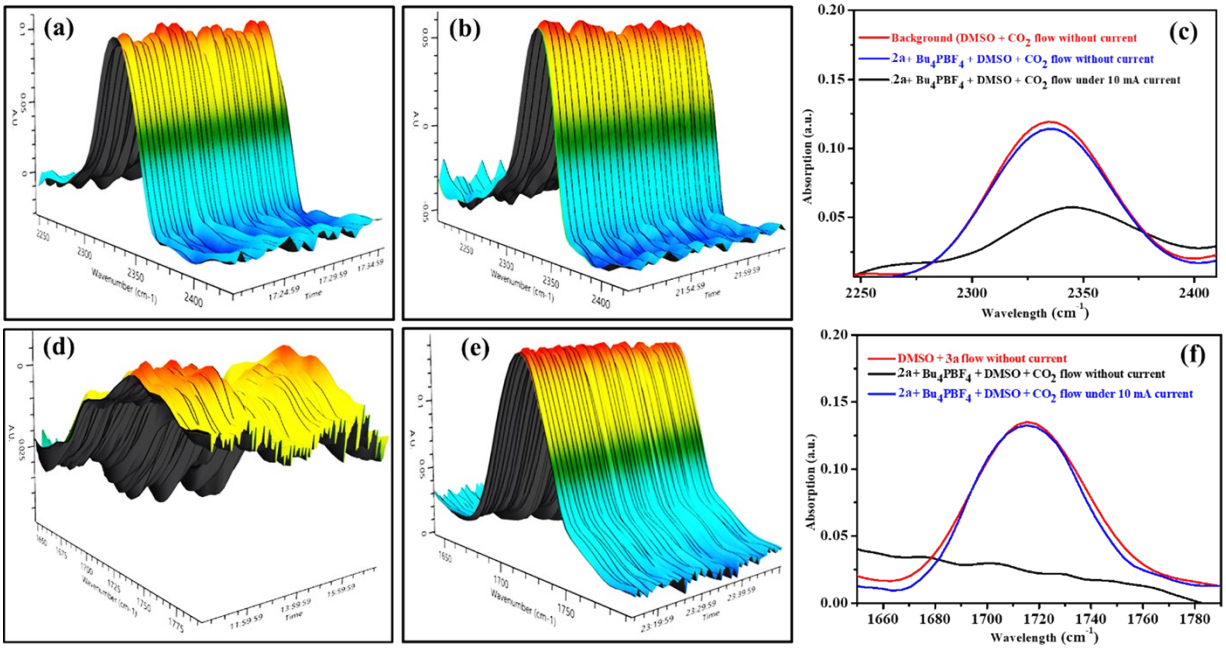
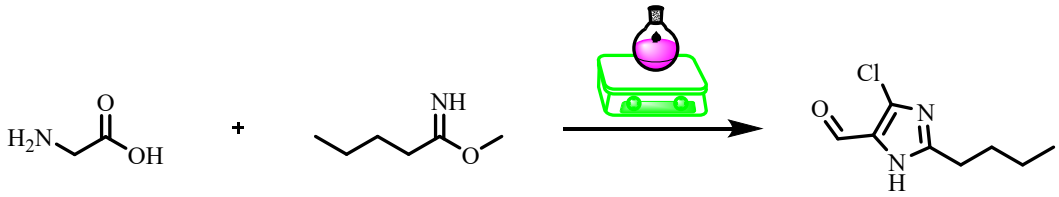


Fig. S14. Qualitative analysis of the in-situ functional group transformation of carbon dioxide to carboxylic acid analyzed by time-resolved in-line IR absorption spectroscopy; **(a)** $\nu_{asymmetrical}$ = 2335 cm^{-1}, CO_2 gas mixed with starting materials and passing without current; **(b)** with current; **(c)** comparative consumption of carbon dioxide with and without current; **(d)** raw data of reaction mixture passing through μ-EFR without current ($\nu_{C=O(OH)}$ = 1716 cm^{-1}); **(e)** raw data of reaction mixture passing through μ-EFR with current ($\nu_{C=O(OH)}$ = 1716 cm^{-1}); **(f)** comparative deconvoluted inline IR absorption spectrum of with and without current.

6. General processor for the synthesis of aldehyde and an integrated one-flow synthesis of carbonylation alcohol.

6.1 General procedure for the synthesis of 2-Butyl-5-chloro-3H-imidazole-4-carbaldehyde.

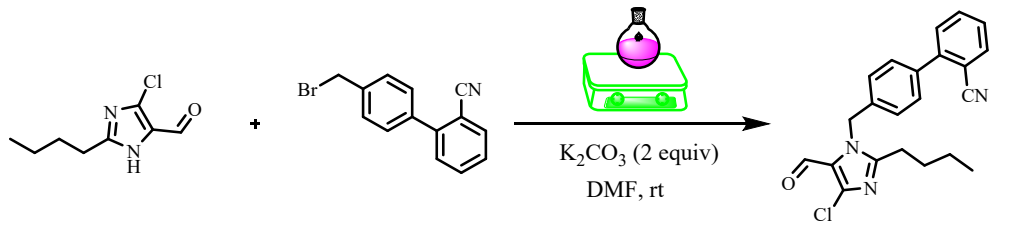


Methyl Pentanimidate **glycine** **2-butyl-4-chloro-1*H*-imidazole-5-carbaldehyde**

The glycine (2.6 g, 0.50 mol) in MeOH (11 mL) and water (0.6 mL) at 0 °C was adjusted from 8.0 to 9.5 by the addition of 2 drops of 30% NaOH before the addition of a solution of imidate methyl pentanimidate (4 g, 0.50 mol) in toluene (7 mL). The suspension was stirred overnight at room temperature, and the pH was adjusted from 10.1 to 7.0 by the addition of a few drops of the con. H_2SO_4 before the addition of toluene and removal of the solvent by vacuum. The resulting suspension was cooled to 0 °C, then added with $POCl_3$ (15 g), and heated to 80 °C before the addition of DMF (7 g) at such a rate that the temperature rose to 96 °C (HCl evolution). The dark brown reaction mixture was heated for 2 h at 100 °C, cooled to room temperature, and poured into water (17 mL) with the maintenance of the temperature at <30 °C. The reaction flask was rinsed with water and toluene, and to the combined reaction mixture and wash, liquors were added Celite (1.3 g). The pH of the mixture was adjusted from -1.2 to +1.2 by the addition of 30% NaOH (20 mL), and the Celite was filtered and washed with water and toluene. The phases were separated, and the organic phase was washed twice with water. The organic phase was concentrated to vacuum, added 2 ml toluene was, heated to 65 °C, and cooled to -10 °C. The precipitate was filtered and washed with toluene. The product was isolated in 52% yield of 2-Butyl-5-chloro-3H-imidazole-4-carbaldehyde as a white solid, melting point 92–93 °C. ^{1}H NMR (400 MHz, DMSO)

δ 13.32 (s, 1H), 9.57 (s, 1H), 2.63 (t, *J* = 7.5 Hz, 2H), 1.62 (ddd, *J* = 13.3, 8.3, 6.7 Hz, 2H), 1.26 (dq, *J* = 14.6, 7.4 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 177.01, 153.75, 138.57, 125.59, 29.39, 27.52, 21.58, 13.54. HRMS (ESI): *m/z* calcd for $C_8H_{11}ClN_2O$, $[M+H]^+$: 187.0638, found: 187.0637.

6.2 General procedure for the synthesis of 1-([1,1'-biphenyl]-4-ylmethyl)- 2-butyl-4-chloro-1H-imidazole- 5-carbaldehyde.



2-Butyl-4-chloro-1*H*-imidazole-5-carbaldehyde

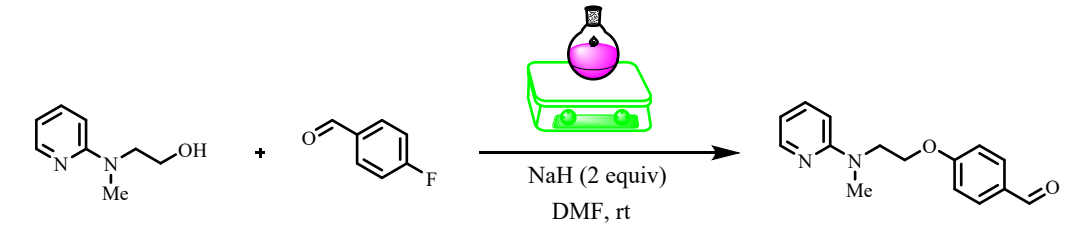
4'-(Bromomethyl)-[1,1'-biphenyl]-2-carbonitrile

4'-((2-Butyl-4-chloro-5-formyl-1*H*-imidazol-1-yl)methyl)-[1,1'-biphenyl]-2-carbonitrile

To a solution of 2-butyl-4-chloro-1H-imidazole-5-carbaldehyde (1.0 equiv.) in dry DMF, anhydrous K_2CO_3 (2.0 equiv.) was added and stirred for 15 min. at the ice. To this reaction mixture 4-(bromomethyl)-1,1'-biphenyl (1.2 equiv.) was added and stirred at ambient temperature overnight. After completion of the reaction, water (200 mL) was added to the reaction mixture and extracted with EtOAc. The organic layer was washed with water and brine solution. The organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by flash column chromatography hexane/ethyl acetate; 80:20). The product was isolated in 90% yield 1-([1,1'-biphenyl]-4-ylmethyl)- 2-butyl-4-chloro-1H-imidazole- 5-carbaldehyde as a white solid, melting point 92–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 – 9.74 (m, 1H), 7.76 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.64 (td, *J* = 7.7, 1.4 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.50 – 7.40 (m, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 5.62 (s, 2H), 2.68 (dd, *J* = 9.4, 6.2 Hz, 2H), 1.71 (ddd, *J* = 11.5, 8.9, 6.6 Hz, 2H), 1.37 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.90, 154.58, 144.50, 143.13, 137.83, 136.09, 133.73, 132.86, 129.93, 129.29, 127.74, 126.68,

124.24, 118.47, 111.11, 47.88, 29.20, 26.47, 22.32, 13.62. IR (ν_{max}): 2924, 2857, 1658, 1513, 1376, 1265, 825, 759 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{21}H_{21}ClN_2O$, $[M+H]^+$: 378.1373, found: 378.1391.

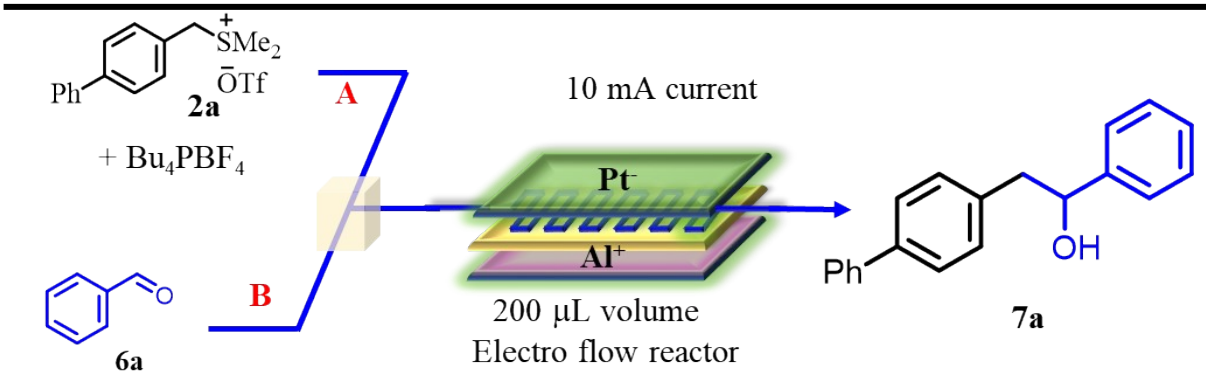
6.3 General procedure for the Synthesis of 4-(2-(methyl(pyridin-2-yl) amino)ethoxy)benzaldehyde.



2-(methyl(pyridin-2-yl) amino)ethan-1-ol **4-fluorobenzaldehyde** **4-(2-(methyl(pyridin-2-yl) amino)ethoxy)benzaldehyde**

To a solution of 2-(methyl(pyridin-2-yl) amino) ethan-1-ol (1.0 equiv.) in dry DMF, anhydrous NaH (2.0 equiv.) was added and stirred for 15 min. at the 0 °C. To this reaction mixture, 4-fluoro benzaldehyde (1.2 equiv.) was added and stirred at ambient temperature overnight. After completion of the reaction, water was added to the reaction mixture and extracted with EtOAc. The organic layer was washed with water and brine solution. The organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by flash column chromatography (hexane/ethyl acetate; 85:15). The product was isolated in 65% yield 4-(2-(methyl(pyridin-2-yl) amino) ethoxy) benzaldehyde as a yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 8.15 (ddd, *J* = 4.9, 2.0, 0.8 Hz, 1H), 7.80 – 7.75 (m, 2H), 7.47 – 7.41 (m, 1H), 7.00 – 6.96 (m, 2H), 6.55 (ddd, *J* = 7.1, 5.0, 0.8 Hz, 1H), 6.52 – 6.48 (m, 1H), 4.25 (t, *J* = 5.7 Hz, 2H), 3.99 (t, *J* = 5.7 Hz, 2H), 3.12 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.47, 163.67, 157.94, 147.60, 137.12, 131.69, 129.68, 114.56, 111.70, 105.49, 66.44, 49.01, 37.60. HRMS (ESI): *m/z* calcd for $C_{15}H_{17}N_2O_2$, $[M+H]^+$: 257.1290, found: 257.1284. Verified the analytical data with those reported in the literature.[26]

6.4 General procedure for the optimization table S5.



Entry	Deviation of flow rate (µL/min.)		Residence time (min.)	%Yield (7a)
	A	B		
1	1000	1000	0.1	10
2	500	500	0.4	25
3	400	400	0.25	40
4	300	300	0.33	55
5	200	200	0.5	70
6	150	150	0.66	75

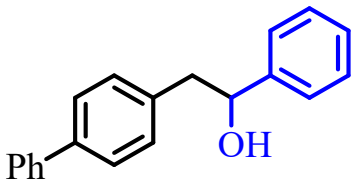
A stock solution (A) containing ([1,1'-biphenyl]-4-ylmethyl)dimethylsulfonium trifluoromethanesulfonate (**2a**), Bu4PBF$_4$: DMSO in a molar ratio (1:1:468) and benzaldehyde aldehyde (**6a**): DMSO in molar ratio (1:468) in separate leak-proof syringe were connected to the newly fabricated micro-electro flow reactor (µ-PFR). The solution was passed through 200 µL PTFE reactor volume under 10 mA current (Table S5, entry 1,) at a flow rate of 1000 µL/min. (stock solution A and B) with a residence time of 0.1 min., which led to 10% yield. Next, we investigated the effect of variation in the flow rate (Table S5 entries 2-7), which resulted in product **7a** being obtained in 75% good yield (Table S5 entry 6).

7	100	100	1	75

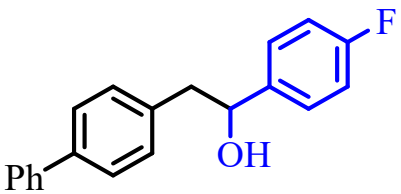
Table S5. Optimization of cross-electrophile coupling reaction

Reaction condition: 2a: Bu_4PBF_4: DMSO in molar ratio (1:1:468) and 1a: DMSO in molar ratio (1:468). Yields are based on isolated yield.

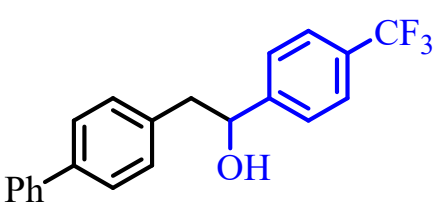
6.5 General procedure for the integrated one-flow synthesis of 7a: The stock solution (**A**) containing benzyl sulfoniumtrifluoromethanesulfonate salt (**2**): Bu_4PBF_4: DMSO in a molar ratio (1:1:468) was taken in bottle and aldehyde/ketone (**6**): DMSO in molar ratio (1:468) was connected with syringe pump. Two reactants A and B were introduced through T-junction in to maintain the stoichiometry (Table S5), and then passed through a micro electro flow reactor for the synthesis of alcohols product during 0.66 min. of residence time at 10 mA current as an electrode platinum and aluminium. Under the stable condition the out-flowing solution from the electro-flow reactor collected for 66 min. and regular batch process extraction separation and purification protocols have been applied to afforded the corresponding 61.68 mg, 75% yield of **7a**, as a white solid and melting point is 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 4H), 7.49 – 7.33 (m, 7H), 7.32 – 7.27 (m, 3H), 4.95 (dd, *J* = 8.4, 4.9 Hz, 1H), 3.07 (qd, *J* = 13.7, 6.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.81, 140.87, 139.55, 137.13, 129.91, 128.74, 128.46, 127.67, 127.22, 127.16, 127.01, 125.90, 75.34, 45.70. IR (ν_{max}): 3275, 1484, 1443, 1264, 1021, 814, 752, 692 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{20}H_{18}O$ $[M+H]^+$: 275.1836, found: 275.1840. Verified the analytical data with those reported in the literature.[7, 27]



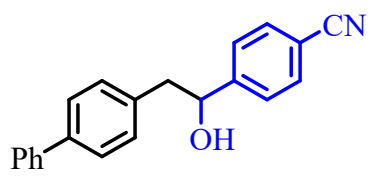
2-([1,1'-Biphenyl]-4-yl)-1-(4-fluorophenyl) ethan-1-ol (7b): The electrolysis product **(7b)** was conducted following preparation according to the general procedure as described in section **6.5** for electrochemical cross coupling reaction. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 63.09 mg, 72% yield of **7a** as a white solid and a melting point is 150-152 °C**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 2H), 7.55 – 7.51 (m, 2H), 7.46 – 7.41 (m, 2H), 7.36 – 7.30 (m, 3H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.06 – 7.01 (m, 2H), 4.92 (dd, *J* = 8.1, 5.2 Hz, 1H), 3.03 (t, *J* =



7.0 Hz, 2H), 2.05 (t, J = 13.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.42, 160.98, 140.77, 139.54 (d, J = 15.6 Hz), 136.76, 129.90, 128.75, 127.55 (d, J = 8.0 Hz), 127.23, 126.98, 115.33, 115.22 (d, J = 21.3 Hz), 74.67, 45.77. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.95. IR (ν_{max}): 3378, 2917, 1600, 1496, 1214, 1154, 1037, 827, 750, 687 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{20}H_{17}FO$ $[M]^+$: 315.1161, found: 315.1165. Verified the analytical data with those reported in the literature.[7]

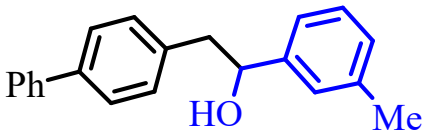


2-([1,1'-Biphenyl]-4-yl)-1-(4-(trifluoromethyl) phenyl) ethan-1-ol (7c): The electrolysis product **(7c)** was conducted following preparation according to the general procedure as described in section **6.5** for electrochemical cross coupling reaction. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 74.92 mg, 73% yield of **7c** as a white solid and a melting point is 134-136 °C**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.53 (m, 6H), 7.50 (d, J = 8.4 Hz, 2H), 7.44 (ddd, J = 9.2, 4.2, 2.5 Hz, 3H), 7.38 – 7.31 (m, 1H), 7.28 (s, 1H), 5.01 (dd, J = 8.6, 4.7 Hz, 1H), 3.05 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.62, 140.69, 139.83, 136.32, 129.91, 129.71, 129.00, 128.78, 128.08, 127.3 (m, J = 18.18 Hz), 127.00, 126.17, 125.36 (d, J = 3.6 Hz), 74.64, 45.75. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.60 (d, J = 116.9 Hz). IR (ν_{max}): 3310, 2923, 1682, 1604, 1480, 1414, 1317, 1166, 1118, 1057, 1005, 834, 749, 691 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{21}H_{15}F_3$ $[M\text{-}H_2O]^-$: 325.12, found: 325.18. Verified the analytical data with those reported in the literature.[27]

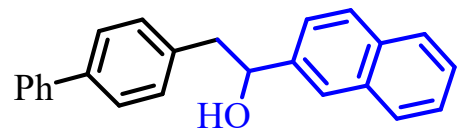


4-(2-([1,1'-Biphenyl]-4-yl)-1-hydroxyethyl) benzo nitrile (7d): The electrolysis product **(7d)** was conducted following preparation according to the general procedure as described in section **6.5** for electrochemical cross coupling reaction. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 62.82 mg, 70% yield of **7d** as a white solid and a melting point is 133-135 °C**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m,

6H), 7.48 – 7.42 (m, 2H), 7.39 – 7.33 (m, 3H), 7.30 (d, J = 8.3 Hz, 2H), 4.96 (dd, J = 7.7, 5.4 Hz, 1H), 3.11 (dd, J = 13.6, 8.1 Hz, 2H), 2.04 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.74, 142.23, 140.93, 140.51, 132.06, 130.38, 128.81, 127.44, 127.27, 127.03, 126.26, 118.94, 110.40, 74.71, 45.68. IR (ν_{max}): 3469, 2918, 2221, 1481, 1400, 1223, 1174, 1050, 1001, 829, 752, 688 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{21}H_{18}NO$ [M+H] $^+$: 300.1383, found 300.1384. Verified the analytical data with those reported in the literature.[27]



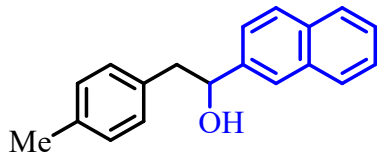
2-([1,1'-Biphenyl]-4-yl)-1-(m-tolyl) ethan-1-ol (7e): The electrolysis product **(7e)** was conducted following preparation according to the general procedure as described in section **6.5** for electrochemical cross coupling reaction. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 64.00 mg, 74% yield of **7a** as a white solid and a melting point is 102-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (ddt, J = 8.3, 3.8, 1.7 Hz, 4H), 7.46 – 7.41 (m, 2H), 7.36 – 7.27 (m, 3H), 7.25 – 7.02 (m, 4H), 4.96 – 4.85 (m, 1H), 3.05 (qd, J = 13.7, 6.6 Hz, 2H), 2.37 (s, 3H), 1.97 (d, J = 2.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.80, 140.90, 139.53, 138.13, 137.30, 129.90, 128.73, 128.37 (d, J = 4.0 Hz), 127.18 (d, J = 8.0 Hz), 127.01, 126.55, 122.95, 75.34, 45.69, 21.47. IR (ν_{max}): 3422, 2903, 1593, 1472, 1232, 1047, 996, 821, 752, 693 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{21}H_{21}O$ [M+H] $^+$: 289.1592, found: 289.1595.



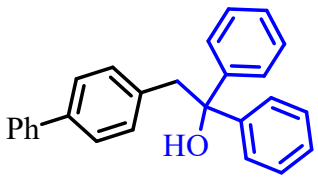
2-([1,1'-Biphenyl]-4-yl)-1-(naphthalen-2-yl) ethan-1-ol (7f): The electrolysis product **(7f)** was conducted following preparation according to the general procedure as described in section **6.5** for electrochemical cross coupling reaction. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 69.09 mg, 71% yield of **7f** as a white solid and a melting point is 165-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.71 (m, 5H), 7.65 – 7.38 (m, 8H), 7.37 – 7.28 (m, 2H), 5.22 – 5.01 (m, 1H), 3.35 – 3.06 (m, 2H), 2.14 – 2.02 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.19, 129.95, 128.74, 128.24, 128.11, 127.98, 127.75, 127.68, 127.56, 127.25, 127.17, 127.01, 126.14, 126.08, 125.86, 125.56, 124.62, 124.08, 75.37 (d, J = 11.5 Hz), 45.92 (d, J = 60.6 Hz). IR (ν_{max}): 3396, 2916, 1485, 1410, 1362, 1267, 119, 1047, 825, 745, 693 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{24}H_{21}O$ [M+H] $^{+}$: 325.1592, found: 325.1597. Verified the analytical data with those reported in the literature.[27]

1-(Naphthalen-2-yl)-2-(p-tolyl) ethan-1-ol (7g): The electrolysis product **(7g)** was conducted following preparation according to the general procedure as described in section **6.5** for electrochemical cross coupling reaction. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 44.82 mg, 57% yield of **7g** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.64 (m, 4H), 7.47 (dddd, J = 9.8, 6.6, 6.1, 1.7 Hz, 2H), 7.34 – 7.23 (m, 2H), 7.16 (d, J = 7.8 Hz, 1H), 7.11 (s, 2H), 5.00 (ddd, J = 29.9, 8.1, 5.0 Hz, 1H), 3.23 – 2.94 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.27, 140.84, 137.29, 136.21, 135.68, 134.78, 133.50, 133.27, 132.95, 132.29, 129.37, 129.26, 129.11, 128.14, 128.07, 128.02, 127.96, 127.77, 127.66, 127.61, 127.54, 126.07, 126.00, 125.83, 125.77, 125.47, 124.55, 124.11, 75.43, 75.07, 46.20, 45.60, 21.13, 21.04. IR (ν_{max}): 3021, 1215, 1010, 907, 723, 663 cm^{-1}. Verified the analytical data with those reported in the literature.[28]

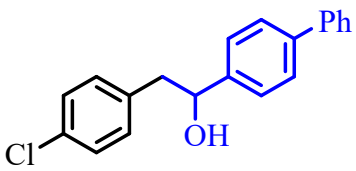


22-([1,1'-Biphenyl]-4-yl)-1,1-diphenylethan-1-ol (7h): The electrolysis product **(7h)** was conducted following preparation according to the general procedure as described in section **6.5** for electrochemical cross coupling reaction. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 74.58 mg, 71% yield of **7h** as a white solid and a melting point is 150-152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 2H), 7.48 – 7.36 (m, 8H), 7.31 (dd, J = 10.1, 4.9 Hz, 5H), 7.26 – 7.20 (m, 2H), 6.96 (d, J = 8.2 Hz, 2H), 3.68 (s, 2H), 2.35 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.52, 140.68, 139.52,



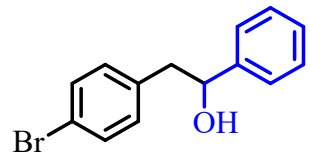
134.87, 131.26, 128.69, 128.10, 127.16, 126.91, 126.68, 126.18, 77.95, 47.61. IR (ν_{max}): 3541, 2921, 1484, 1343, 1184, 1043, 1003, 910, 834, 751, 692, 597 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{26}H_{22}O$ $[M\text{-}OH]^-$: 333.16487, found: 333.1646. Verified the analytical data with those reported in the literature.[7]

1-([1,1'-Biphenyl]-4-yl)-2-(4-chlorophenyl) ethan-1-ol (7i): The electrolysis product **(7i)**

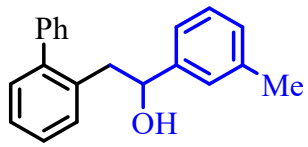


was conducted following preparation according to the general procedure as described in section **6.5** for electrochemical cross coupling reaction. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 68.40 mg, 74% yield of **7i** as a white solid and a melting point is 101-103 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.51 (m, 4H), 7.47 – 7.30 (m, 6H), 7.28 – 7.22 (m, 2H), 7.16 – 7.10 (m, 1H), 4.92 (t, *J* = 6.5 Hz, 1H), 3.08 – 2.97 (m, 2H), 2.03 – 1.94 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.69, 136.58, 130.89, 129.91, 128.78, 128.55, 127.29, 127.23, 127.19, 127.05, 127.00, 126.32, 74.82 (d, *J* = 38.38 Hz), 45.44 (d, *J* = 56.56 Hz), IR (ν_{max}): 2931, 2858, 1729, 1475, 1403, 1281, 1185, 1073, 997, 823, 749, 692, cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{20}H_{17}ClO$ $[M\text{-}OH]^-$: 291.0946, found: 91.0958.

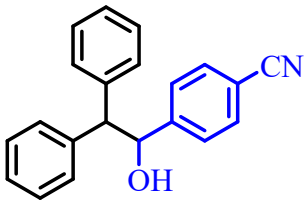
1-([1,1'-Biphenyl]-4-yl)-2-(4-bromophenyl) ethan-1-ol (7j): The



electrolysis product **(7j)** was conducted following preparation according to the general procedure as described in section **6.5** for electrochemical cross coupling reaction. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 62.10 mg, 75% yield of **7j** as a colorless liquid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.34 – 7.30 (m, 2H), 7.30 – 7.25 (m, 3H), 7.00 (d, *J* = 8.3 Hz, 2H), 4.81 (t, *J* = 6.6 Hz, 1H), 2.94 (d, *J* = 6.6 Hz, 2H), 2.07 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.47, 136.96, 131.37, 131.23, 128.41, 127.72, 125.83, 120.39, 75.11, 45.15. IR (ν_{max}): 2921, 1482, 1406, 1232, 1056, 878, 833, 750, 698, 658 cm^{-1}.

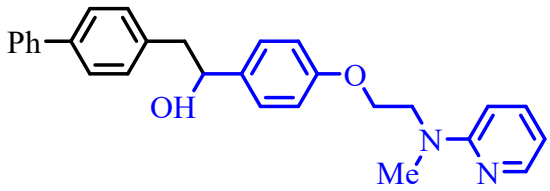


2-([1,1'-Biphenyl]-2-yl)-1-(m-tolyl)ethan-1-ol (7k): The electrolysis product **(7k)** was conducted following preparation according to the general procedure as described in section **4.5** for electrochemical cross-electrophile coupling reaction. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 62.24 mg, 72% yield of **7k** as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.19 (m, 9H), 7.09 (t, J = 7.5 Hz, 1H), 6.99 (d, J = 7.5 Hz, 1H), 6.83 (s, 1H), 6.78 (d, J = 7.6 Hz, 1H), 4.58 (dd, J = 9.0, 4.3 Hz, 1H), 3.10 (dd, J = 13.9, 4.3 Hz, 1H), 2.88 (dd, J = 13.9, 9.0 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.90, 142.55, 141.52, 137.76, 135.73, 130.44, 130.19, 129.29, 128.09, 128.03, 127.96, 127.33, 126.83, 126.46, 126.11, 122.51, 74.55, 43.28, 21.33. IR (ν_{max}): 3016, 1480, 1441, 1215, 1044, 742, 666 cm^{-1} HRMS (ESI): *m/z* calcd for $C_{21}H_{20}O$ [M-H]$^{-}$: 287.1592, found: 287.1448.



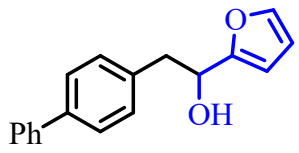
4-(1-Hydroxy-2,2-diphenylethyl) benzonitrile (7l): The electrolysis product **(7l)** was conducted following preparation according to the general procedure as described in section **6.5** for electrochemical cross coupling reaction. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 63.71 mg, 71% yield of **7l** as a white solid and a melting point is 106-108 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.42 (m, 2H), 7.41 – 7.30 (m, 4H), 7.29 – 7.19 (m, 3H), 7.19 – 7.09 (m, 3H), 7.09 – 7.00 (m, 2H), 5.42 (d, J = 8.7 Hz, 1H), 4.21 – 4.07 (m, 1H), 2.34 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.55, 140.52, 139.82, 131.71, 128.93, 128.77, 128.47, 128.39, 127.50, 127.29, 126.82, 118.77, 111.13, 60.41. IR (ν_{max}): 3484, 2927, 2222, 1484, 1384, 1286, 1179, 1039, 829, 750, 693 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{21}H_{17}NO$ [M+H]$^{+}$: 300.1388, found: 300.1408.

2-([1,1'-Biphenyl]-4-yl)-1-(4-(2-(methyl(pyridin-2-yl)amino)ethoxy)phenyl)ethan-1-ol

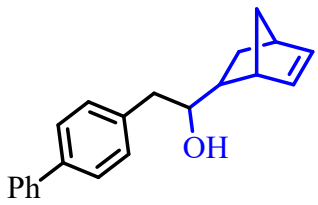


(7m): The electrolysis product **(7m)** was conducted following preparation according to the general procedure as described in section **6.5** for electrochemical cross coupling reaction. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 86.5 mg, 68% yield of **7m** as a white solid and a melting point is 110-112 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 4.0 Hz, 1H), 7.57 (d, *J* = 7.4 Hz, 2H), 7.54 – 7.46 (m, 3H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.26 (dd, *J* = 11.8, 8.8 Hz, 4H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.57 (dd, *J* = 10.5, 6.7 Hz, 2H), 4.94 – 4.82 (m, 1H), 4.20 (t, *J* = 5.6 Hz, 2H), 3.99 (t, *J* = 5.6 Hz, 2H), 3.17 (s, 3H), 3.03 (d, *J* = 6.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.31, 147.06, 140.92, 139.48, 137.82, 137.26, 136.18, 129.94, 128.77, 127.20, 127.03, 114.40, 111.80, 106.25, 99.84, 74.98, 66.27, 49.70, 45.65, 37.99. IR (ν_{max}): 2922, 2860, 1601, 1496, 1427, 1234, 1160, 1040, 824, 754, 699, 625 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{28}H_{28}N_2O_2$ $[M+H]^+$: 425.2230, found: 425.2230.

2-([1,1'-Biphenyl]-4-yl)-1-(furan-2-yl)ethan-1-ol (7n): The electrolysis product **(7n)** was conducted following preparation according to the general procedure as described in section **5.5** for electrochemical cross coupling reaction. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 47.54 mg, 60% yield of **7n** as a yellow solid and a melting point is 53-55 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 7.55 – 7.50 (m, 2H), 7.45 – 7.38 (m, 3H), 7.35 – 7.30 (m, 1H), 7.27 – 7.24 (m, 2H), 6.34 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.25 (d, *J* = 3.2 Hz, 1H), 4.95 (dd, *J* = 8.1, 5.4 Hz, 1H), 3.19 (ddd, *J* = 21.8, 13.7, 6.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.71, 141.98, 140.82, 139.59, 136.42, 129.81, 128.71, 127.19, 127.15, 126.98, 110.24, 106.44, 68.71, 41.79. IR (ν_{max}): 2924, 1488, 1150, 1010, 808, 821, 744 cm^{-1}. Verified the analytical data with those reported in the literature.[27]

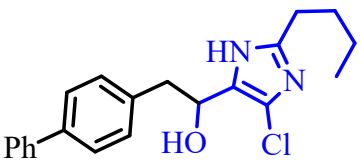


2-([1,1'-Biphenyl]-4-yl)-1-((1R,4R)-bicyclo[2.2.1]hept-5-en-2-yl)ethan-1-ol (7o): The



electrolysis product **(7o)** was conducted following preparation according to the general procedure as described in section **6.5** for electrochemical cross coupling reaction. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 42.65 mg, 49% yield of **7o** as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.51 (m, 4H), 7.42 (ddd, *J* = 6.5, 5.4, 1.8 Hz, 2H), 7.36 – 7.25 (m, 3H), 6.26 – 5.97 (m, 2H), 3.26 – 2.99 (m, 2H), 2.86 (ddd, *J* = 54.9, 26.3, 2.1 Hz, 2H), 2.68 – 2.52 (m, 1H), 2.26 – 2.00 (m, 1H), 1.89 (ddd, *J* = 11.5, 9.2, 3.8 Hz, 1H), 1.55 – 1.42 (m, 2H), 1.39 – 1.33 (m, 1H), 1.28 (dd, *J* = 8.2, 4.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.89 (d, J = 3.5 Hz), 139.37 (d, J = 8.5 Hz), 137.97 – 137.30 (m), 137.04 (d, J = 8.9 Hz), 136.63 (d, J = 5.5 Hz), 132.60, 129.88, 128.72, 127.13 (dd, J = 19.3, 10.1 Hz), 76.32, 49.25, 45.81 (d, J = 19.4 Hz), 45.39 (d, J = 20.8 Hz), 45.10, 44.80, 43.99, 42.97 (d, J = 14.8 Hz), 42.79 – 42.19 (m), 41.95 (d, J = 14.6 Hz), 30.44, 29.72, 29.28. IR (ν_{max}): 2952, 1216, 752 cm^{-1}.

2-([1,1'-Biphenyl]-4-yl)-1-(2-butyl-4-chloro-1H-imidazol-5-yl)ethan-1-ol (7p): The



electrolysis product **(7p)** was conducted following preparation according to the general procedure as described in section **6.5** for electrochemical cross coupling reaction. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 73.30 mg, 69% yield of **7p** as a white solid and a melting point is 141-143 °C. ^{1}H NMR (400 MHz, DMSO) δ 12.05 (s, 1H), 7.56 – 7.51 (m, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.36 (dd, *J* = 10.4, 4.8 Hz, 2H), 7.26 (dt, *J* = 9.1, 4.2 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 5.44 (s, 1H), 4.70 (t, *J* = 7.2 Hz, 1H), 3.00 (dd, *J* = 13.4, 7.2 Hz, 1H), 2.88 (dd, *J* = 13.4, 7.1 Hz, 1H), 2.48 – 2.45 (m, 1H), 1.50 (dd, *J* = 14.9, 7.4 Hz, 2H), 1.17 (dd, *J* = 8.9, 5.8 Hz, 2H), 0.79 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 146.88, 140.45, 138.35, 137.94, 130.17, 129.38, 127.68, 127.11, 126.91, 126.72,

123.20, 65.12, 42.67, 30.52, 27.91, 21.98, 14.11. IR (ν_{max}): 2928, 2860, 1421, 1244, 1060, 1013, 816, 753, 693 cm^{-1}.

4'-((5-(2-([1,1'-Biphenyl]-4-yl)-1-hydroxyethyl)-2-butyl-4-chloro-1H-imidazol-1-yl)methyl)-[1,1'-biphenyl]-2-carbonitrile (7q): The electrolysis product **(7q)** was conducted following preparation according to the general procedure as described in section **6.5** for electrochemical cross coupling reaction. Finally, the organic layer solution was concentrated under vacuum and the product was isolated in 83.41 mg, 51% yield of **7q** as a white solid and a melting point is 92-94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.60 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.54 (t, *J* = 1.7 Hz, 1H), 7.53 (s, 1H), 7.50 (d, *J* = 2.3 Hz, 2H), 7.48 (d, *J* = 2.2 Hz, 2H), 7.45 – 7.38 (m, 4H), 7.33 (d, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 5.17 (s, 2H), 4.99 (t, *J* = 6.7 Hz, 1H), 3.12 (qd, *J* = 13.5, 7.1 Hz, 2H), 2.53 (td, *J* = 7.3, 1.8 Hz, 2H), 2.09 (s, 1H), 1.72 – 1.64 (m, 2H), 1.34 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.55, 140.69, 137.71, 137.06, 136.24, 133.83, 132.93, 129.95, 129.81, 129.43, 128.79, 127.81, 127.31, 127.26, 126.97, 126.25, 126.03, 125.97, 125.64, 118.58, 111.25, 67.27, 47.23, 42.28, 29.80, 26.79, 22.44, 13.78. IR (ν_{max}): 2926, 1454, 1247, 1040, 824, 755, 697, cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{35}H_{32}ClN_3O$ $[M+H]^+$: 546.2312, found: 546.2334.

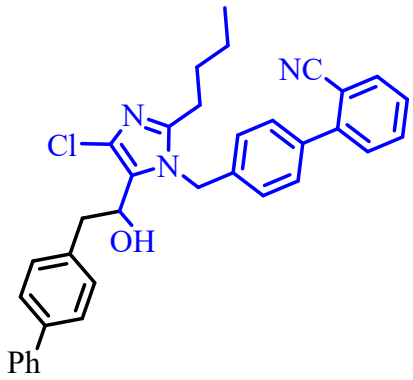
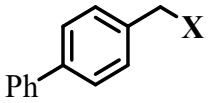
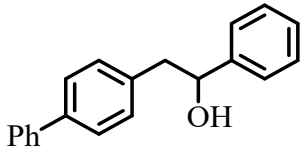
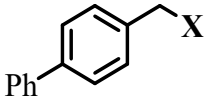
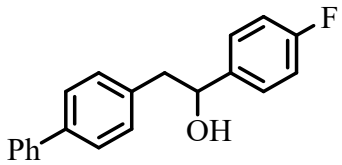
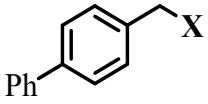
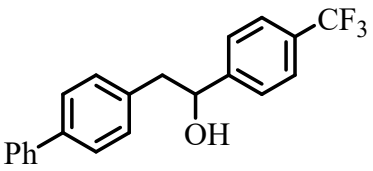
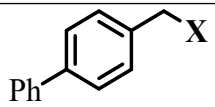
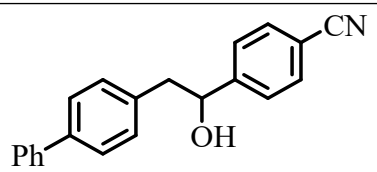
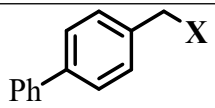
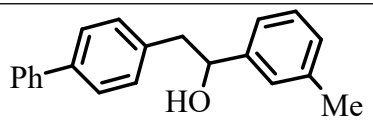
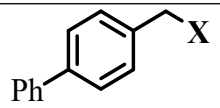
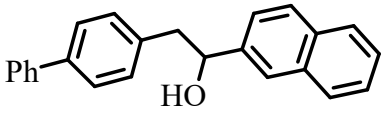
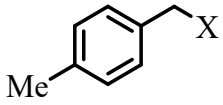
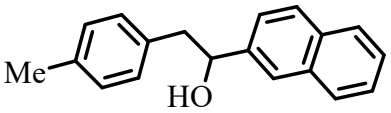
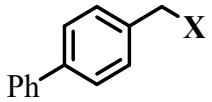
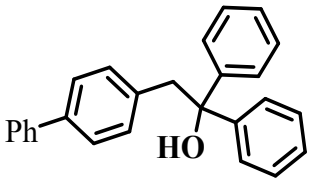
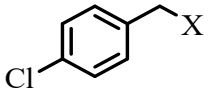
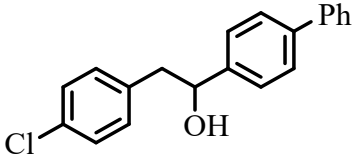
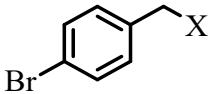
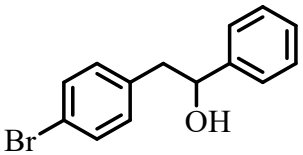
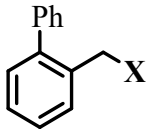
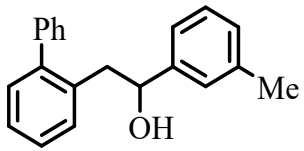
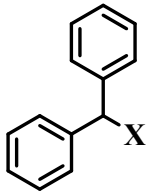
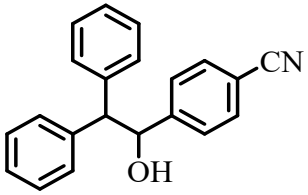
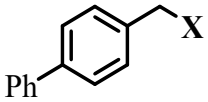
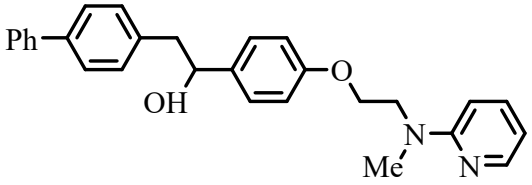
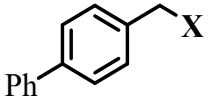
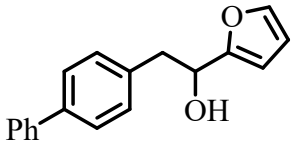
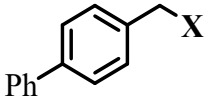
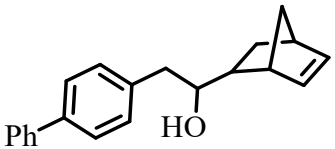
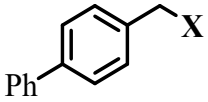
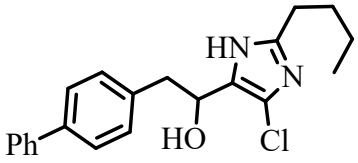
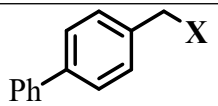
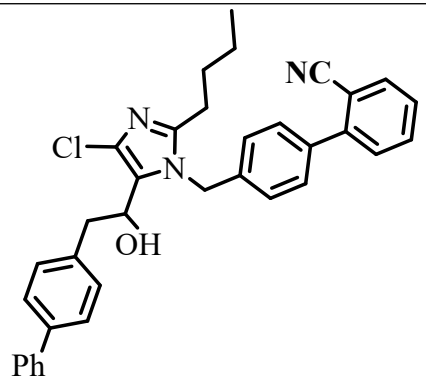


Table S6. Comparative results of cross-electrophile coupling reaction.

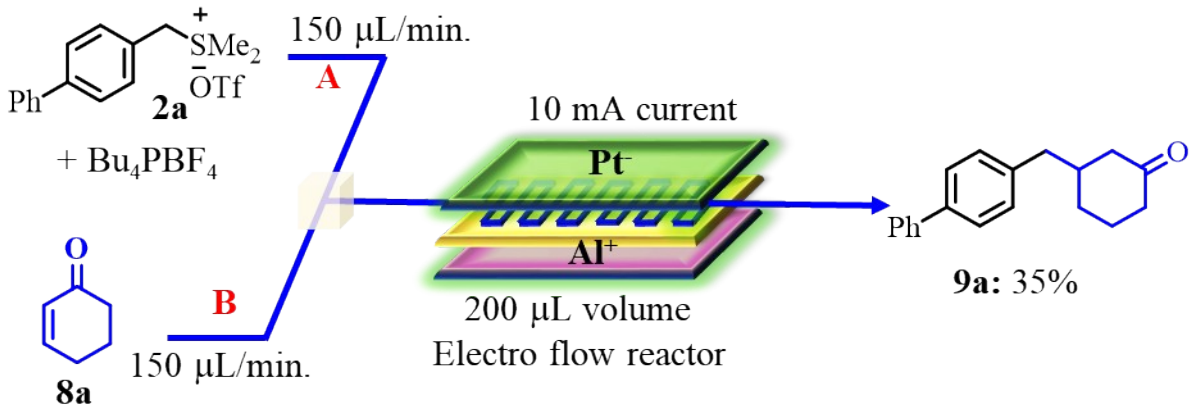
Entry	Substrate formula	Product formula	X	Comparative result
1			OH or SMe_2OTf NMe_3OTf $OPO(OPH)_2$	75%, 0.40 min. (our study) [Ir]-cat, Cs_2CO_3, Na_2CO_3, 70% 36 h,(Ref. [7]) $^nBu_4NI$, 70%, 4 h, rt, SST/C 20 mA, (Ref. [27])
2			OH or SMe_2OTf NMe_3OTf COOH	72%, 0.40 min. (our study) [Ir]-cat, Cs_2CO_3, Na_2CO_3, 76% 36 h,(Ref. [7]) 4CzIPN, CsF, 65%, 36 h, (Ref. [29])
3			OH or SMe_2OTf COOH	72%, 0.40 min. (our study) 4-CzIPN, CsF, 65%, 36 h, (Ref. [29])
4			OH or SMe_2OTf $OPO(OPH)_2$	70%, 0.40 min. (our study) $^nBu_4NI$, 76%, 4 h, SST/C 20 mA, (Ref. [27])
5			OH or SMe_2OTf	74%, 0.40 min. (our study)

6			OH or SMe_2OTf $OPO(OPH)_2$	71%, 0.40 min. (our study) $^nBu_4NI$, 62%, 4 h, SST/C 20 mA, (Ref. [27])
7			OH or SMe_2OTf Epoxide	71%, 0.40 min. (our study) $[Ni(cod)_2]$, BrettPhos, $PhB(OH)_2$, K_3PO_4, 74%, 100°C, 4 h, (Ref. [28])
8			OH or SMe_2OTf NMe_3OTf	71%, 0.40 min. (our study) [Ir]-cat, Cs_2CO_3, Na_2CO_3, 44% 36 h, rt, (Ref.[7])
9			OH or SMe_2OTf	74%, 0.40 min. (our study)
10			OH or SMe_2OTf	75%, 0.40 min. (our study)
11			OH or SMe_2OTf	74%, 0.40 min. (our study)

12			OH or SMe_2OTf	71%, 0.40 min. (our study)
13			OH or SMe_2OTf	68%, 0.40 min. (our study)
14			OH or SMe_2OTf $OPO(OPH)_2$	71%, 0.40 min. (our study) $^{n}Bu_4NI$, 62%, 4 h, SST/C 20 mA, (Ref. [27])
15			OH or SMe_2OTf	49%, 0.40 min. (our study)
16			OH or SMe_2OTf	69%, 0.40 min. (our study)

17			OH or SMe_2OTf	69%, 0.40 min. (our study)

6.6 General procedure for the synthesis of 3-([1,1'-biphenyl]-4-ylmethyl)cyclohexan-1-one (9a)



The stock solution **(A)** containing **2a:** Bu_4PBF_4: DMSO in a molar ratio (1:1:468) and the stock solution **(B)** containing **8a**: DMSO in molar ratio (1:234) was taken in two separate syringes and connected with designed µ-EFR to perform the reaction. Two reactants were introduced into capillary micro-reactor through T-junction in a flow rate to maintain the stoichiometry and then passed through a µ-EFR (reactor volume 200 µL) for the synthesis of cross coupling reaction product during 0.66 min. of residence time at 10 mA current as an electrode platinum and aluminium. The outlet organic layer of µ-EFR was concentrated under vacuum to give the product and subsequent purification by column chromatography on silica gel afforded the corresponding product was isolated in 35% yield of **9a** as a colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.4 Hz, 1H), 7.20 (d, J = 8.1 Hz, 2H), 2.67 (t, J = 5.4 Hz, 2H), 2.46 – 2.23 (m, 3H), 2.16 – 2.01 (m, 3H), 1.92 (d, J = 13.7 Hz, 1H), 1.67 (ddd, J = 17.2, 8.8, 3.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.66, 139.74, 132.81, 129.55, 129.40, 128.76, 127.13, 127.03, 113.11, 47.90, 42.64, 41.46, 40.93, 30.97, 29.74, 25.17. IR (ν_{max}): 2923, 2856, 1709, 1670, 1478, 1453, 1272, 1232, 760, 699 cm^{-1}.

7. Supporting references.

S1. W. Wang, K. Yao and F. Wu, *Synlett*, 2022, **33**, 361-366.

S2. S. Kumar, B. Mahajan, B. K. Malviya, G. Sukumar, P. Srihari and A. K. Singh, *React. Chem. Eng.*, 2021, **6**, 1801-1805.

S3. S. Kumar, D. Aand, S. Pabbaraja, D.-P. Kim and A. K. Singh, *ACS Sustain. Chem. Eng.* 2019, **7**, 19605-19611.

S4. S. Kumar and A. K. Singh, *Chem. Comm.*, 2022, DOI: 10.1039/D2CC03713K.

S5. D.-T. Yang, M. Zhu, Z. J. Schiffer, K. Williams, X. Song, X. Liu and K. Manthiram, *ACS Catal.*, 2019, **9**, 4699-4705.

S6. S.-S. Yan, S.-H. Liu, L. Chen, Z.-Y. Bo, K. Jing, T.-Y. Gao, B. Yu, Y. Lan, S.-P. Luo and D.-G. Yu, *Chem*, 2021, **7**, 3099-3113.

S7. L.-L. Liao, G.-M. Cao, J.-H. Ye, G.-Q. Sun, W.-J. Zhou, Y.-Y. Gui, S.-S. Yan, G. Shen and D.-G. Yu, *J. Am. Chem. Soc.*, 2018, **140**, 17338-17342.

S8. T. Moragas, M. Gaydou and R. Martin, *Angew. Chem. Int. Ed.*, 2016, **55**, 5053-5057.

S9. N. Ishida, Y. Masuda, Y. Imamura, K. Yamazaki and M. Murakami, *J. Am. Chem. Soc.*, 2019, **141**, 19611-19615.

S10. C. Li, P. Zhao, R. Li, B. Zhang and W. Zhao, *Angew. Chem. Int. Ed.*, 2020, **59**, 10913-10917.

S11. T. Tanaka, R. Yazaki and T. Ohshima, *J. Am. Chem. Soc.*, 2020, **142**, 4517-4524.

S12. Y. Ding, R. Huang, W. Zhang and H. Huang, *Org. Lett.*, 2022, **24**, 7972-7977.

S13. W. Hang, D. Li, S. Zou and C. Xi, *J. Org. Chem.*, 2022, DOI: 10.1021/acs.joc.2c01840.

S14. J.-S. Zhong, Z.-X. Yang, C.-L. Ding, Y.-F. Huang, Y. Zhao, H. Yan and K.-Y. Ye, *J. Org. Chem.*, 2021, **86**, 16162-16170.

S15. A. Rana, B. K. Malviya, D. K. Jaiswal, P. Srihari and A. K. Singh, *Green Chem.*, 2022, **24**, 4794-4799.

S16. Z. Huang, Y. Cheng, X. Chen, H.-F. Wang, C.-X. Du and Y. Li, *Chem.Comm.*, 2018, **54**, 3967-3970.

S17. A. Correa, T. León and R. Martin, *J. Am. Chem. Soc.*, 2014, **136**, 1062-1069.

S18. C.-K. Ran, Y.-N. Niu, L. Song, M.-K. Wei, Y.-F. Cao, S.-P. Luo, Y.-M. Yu, L.-L. Liao and D.-G. Yu, *ACS Catal.*, 2022, **12**, 18-24.

S19. J. A. Soderquist, I. Kock and M. E. Estrella, *Org. Process Res. Dev.* 2006, **10**, 1076-1079.

S20. M. M. A. m. S. R. Adapa, *Synth. Commun.*, 2006, **33**, Pages 59-63.

S21. S. Sinha, B. Mandal and S. Chandrasekaran, *Tetrahedron Lett.*, 2000, **41**, 9109-9112.

S22. T. León, A. Correa and R. Martin, *J. Am. Chem. Soc.*, 2013, **135**, 1221-1224.

S23. F. D. Saeva and B. P. Morgan, *J. Am. Chem. Soc.*, 1984, **106**, 4121-4125.

S24. E. Alfonzo and S. M. Hande, *ACS Catal.*, 2020, **10**, 12590-12595.

S25. X. Wang, W.-Y. Tong, B. Huang, S. Cao, Y. Li, J. Jiao, H. Huang, Q. Yi, S. Qu and X. Wang, *J. Am. Chem. Soc.*, 2022, **144**, 4952-4965.

S26. M. Purwa, A. Rana and A. K. Singh, *React. Chem. Eng.*, 2022, **7**, 2084-2092.

S27. H. Wang, Z. Wang, G. Zhao, V. Ramadoss, L. Tian and Y. Wang, *Org. Lett.*, 2022, **24**, 3668-3673.

S28. D. K. Nielsen and A. G. Doyle, *Angew. Chem. Int. Ed.*, 2011, **50**, 6056-6059.

S29. G. Liu, Y. Gao and W. Su, *J. Org. Chem.*, 2023, **88**, 6322–6332.

8. NMR spectra.

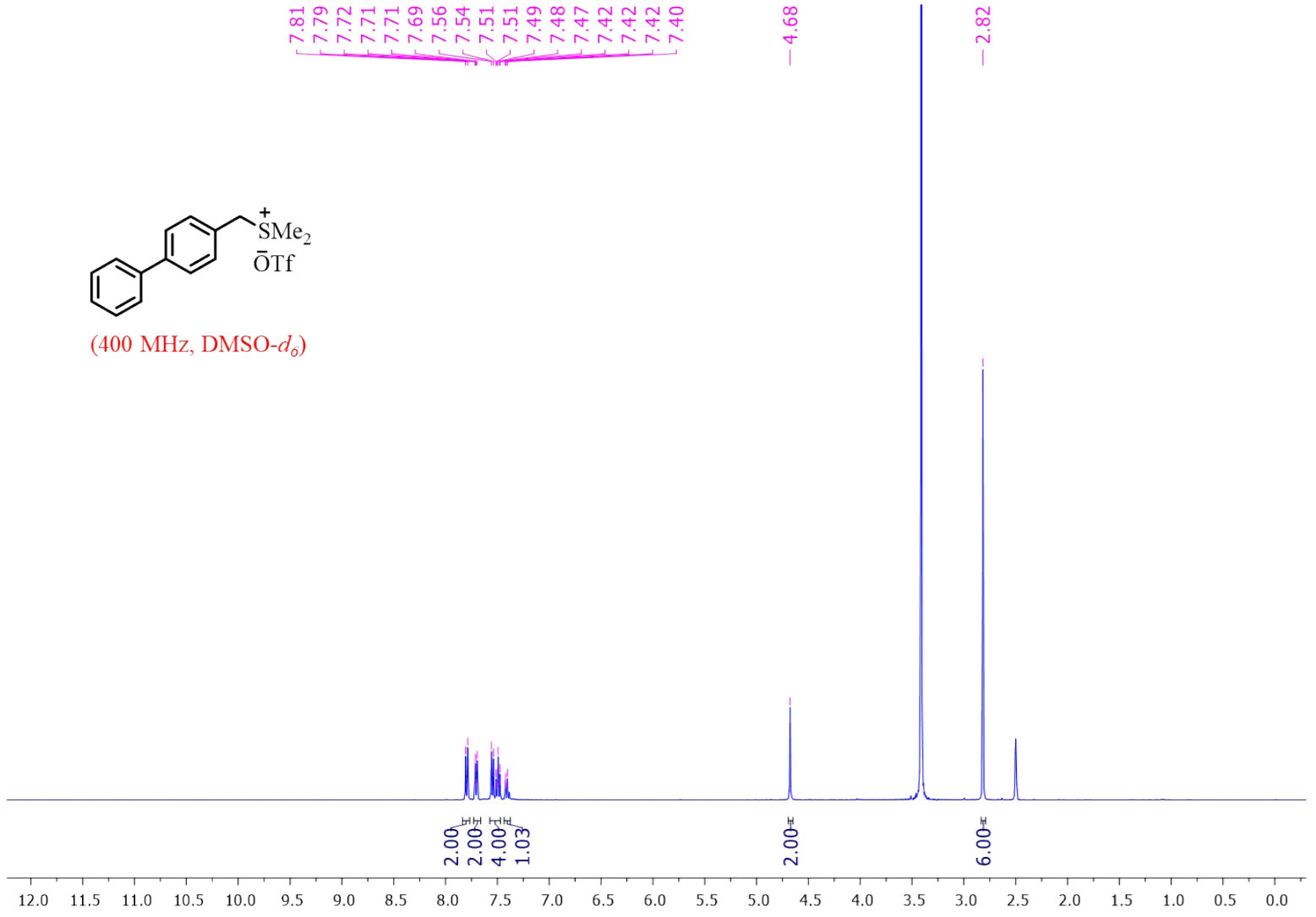


Fig. S15. ^{1}H NMR spectra of ([1,1'-Biphenyl]-4-ylmethyl) dimethyl sulfonium trifluoromethanesulfonate (**2a**) in DMSO-d_6.

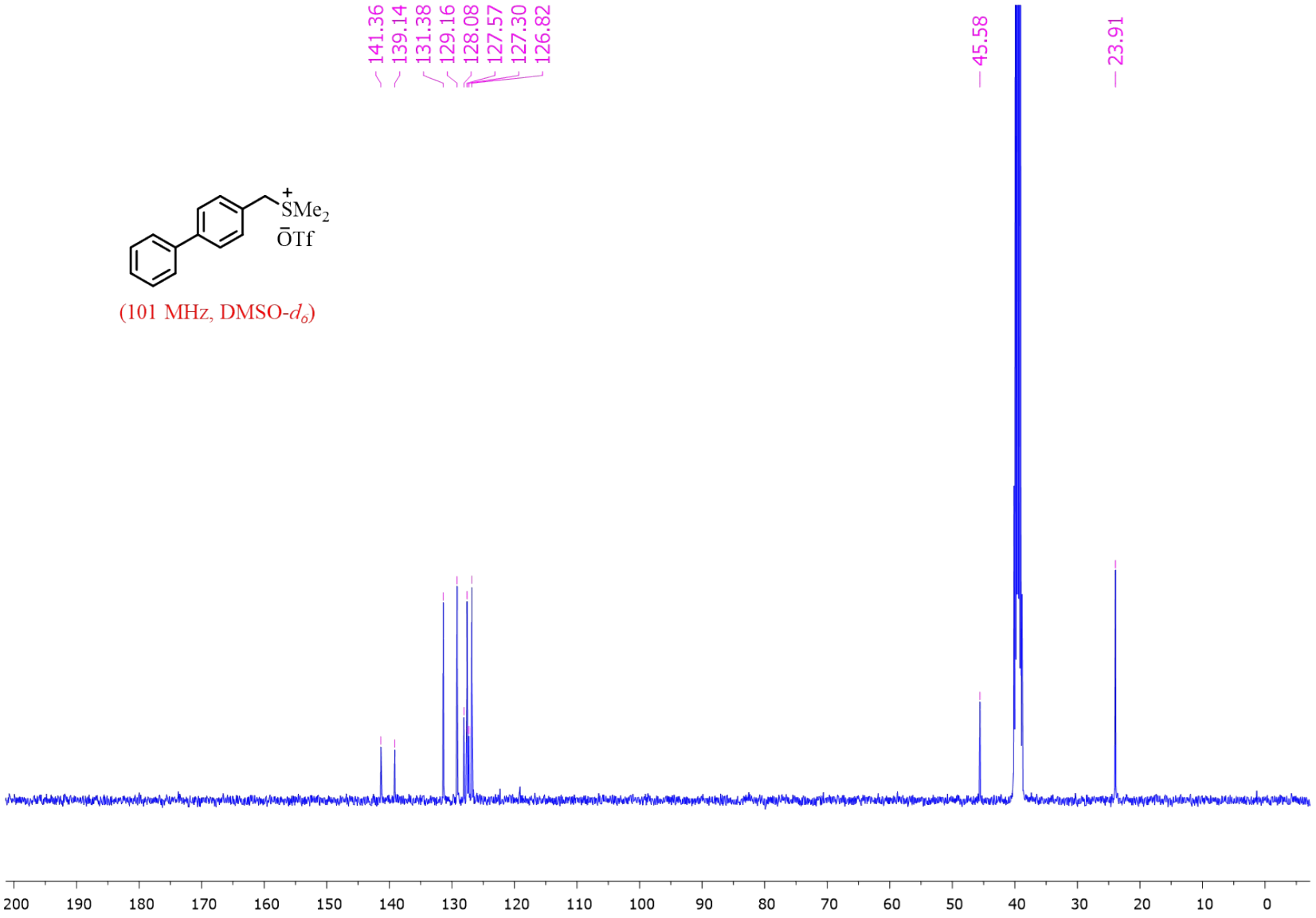


Fig. S16. ^{19}C NMR spectra of ([1,1'-Biphenyl]-4-ylmethyl) dimethyl sulfonium trifluoromethanesulfonate (**2a**) in DMSO-d_6.

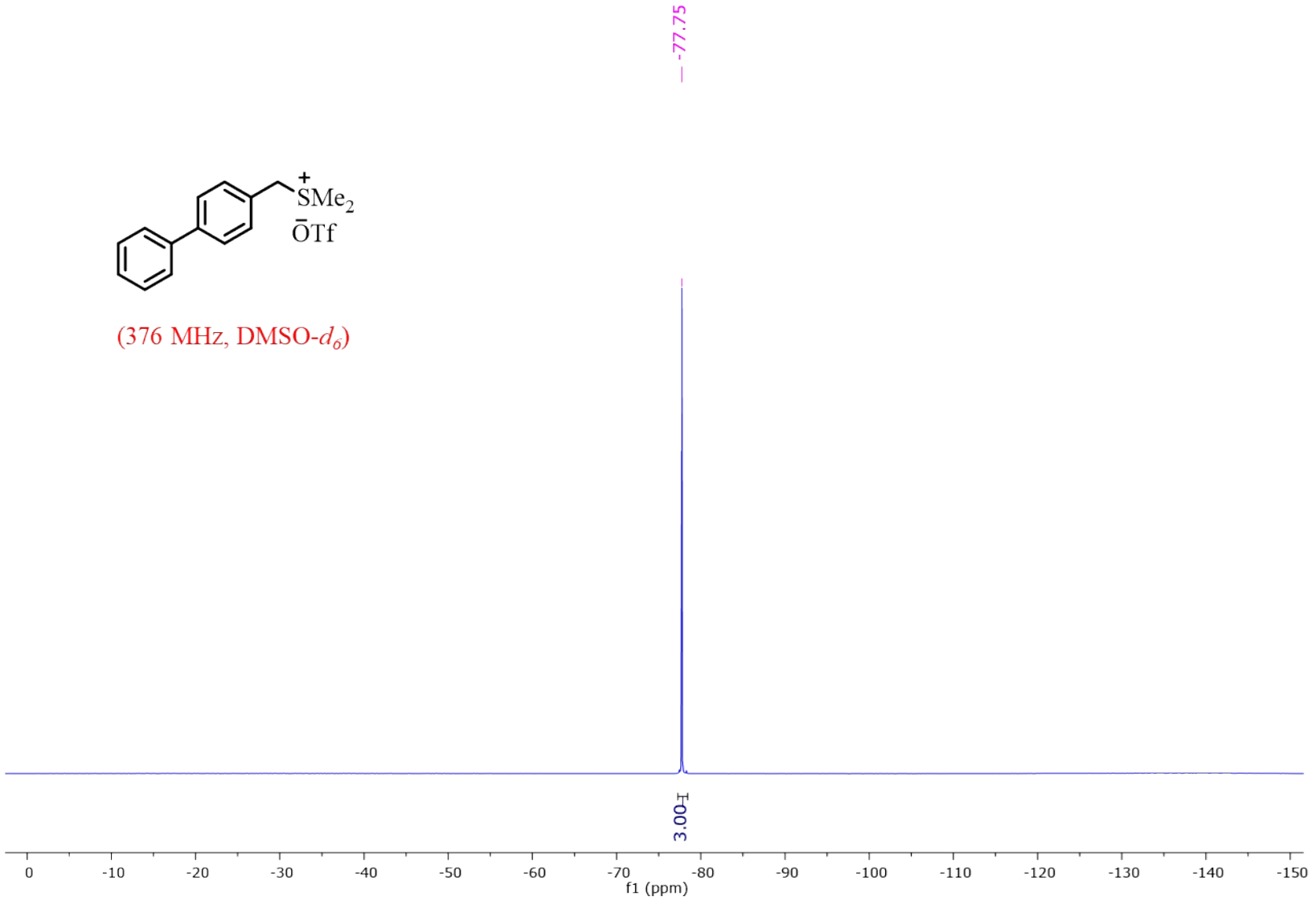


Fig. S17. ^{9}F NMR spectra of ([1,1'-Biphenyl]-4-ylmethyl) dimethyl sulfonium trifluoromethanesulfonate (**2a**) in DMSO-d_6.

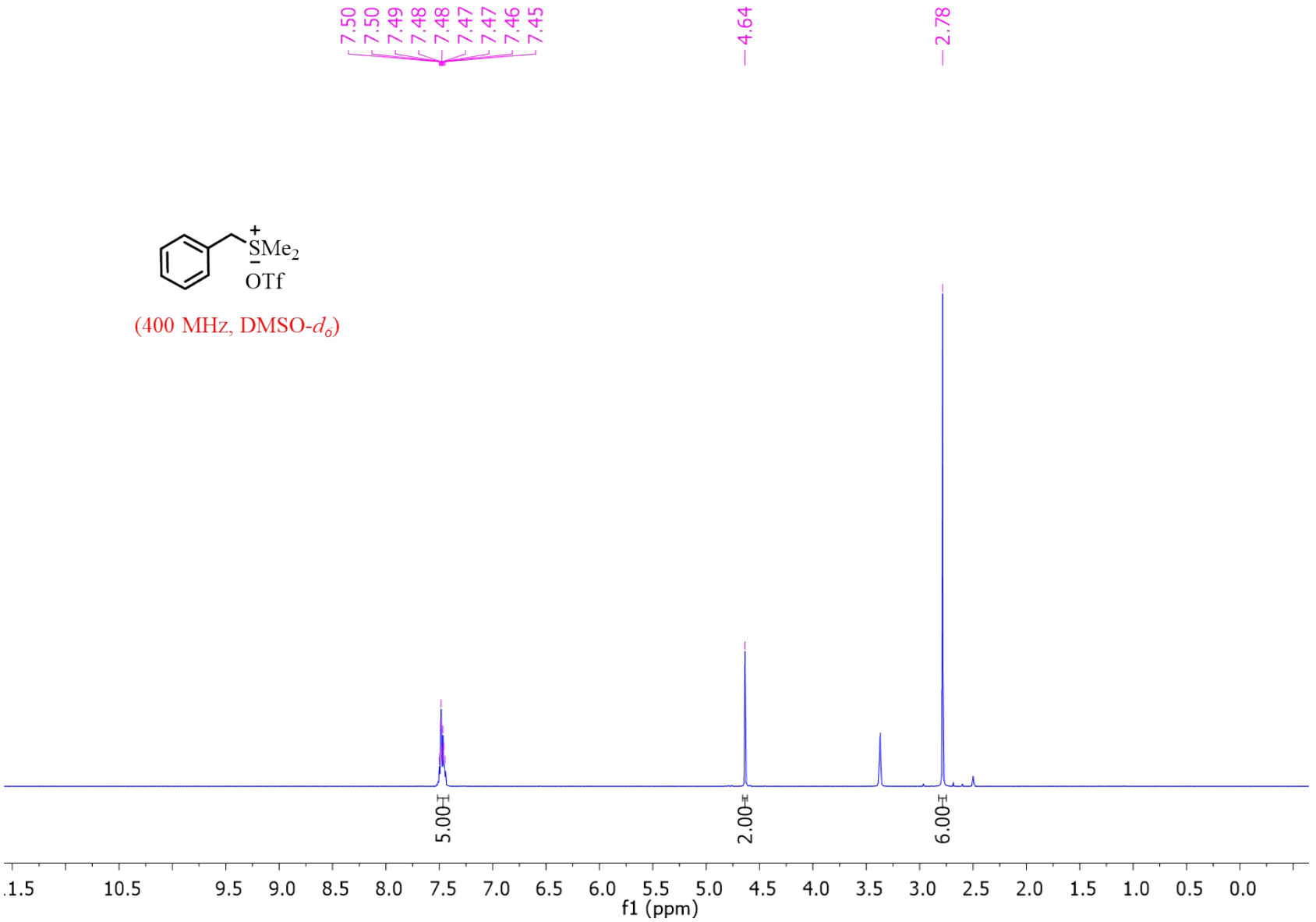


Fig. S18. ^{1}H NMR spectra of benzyl dimethyl sulfonium trifluoromethanesulfonate (**2b**) in DMSO-d_6.

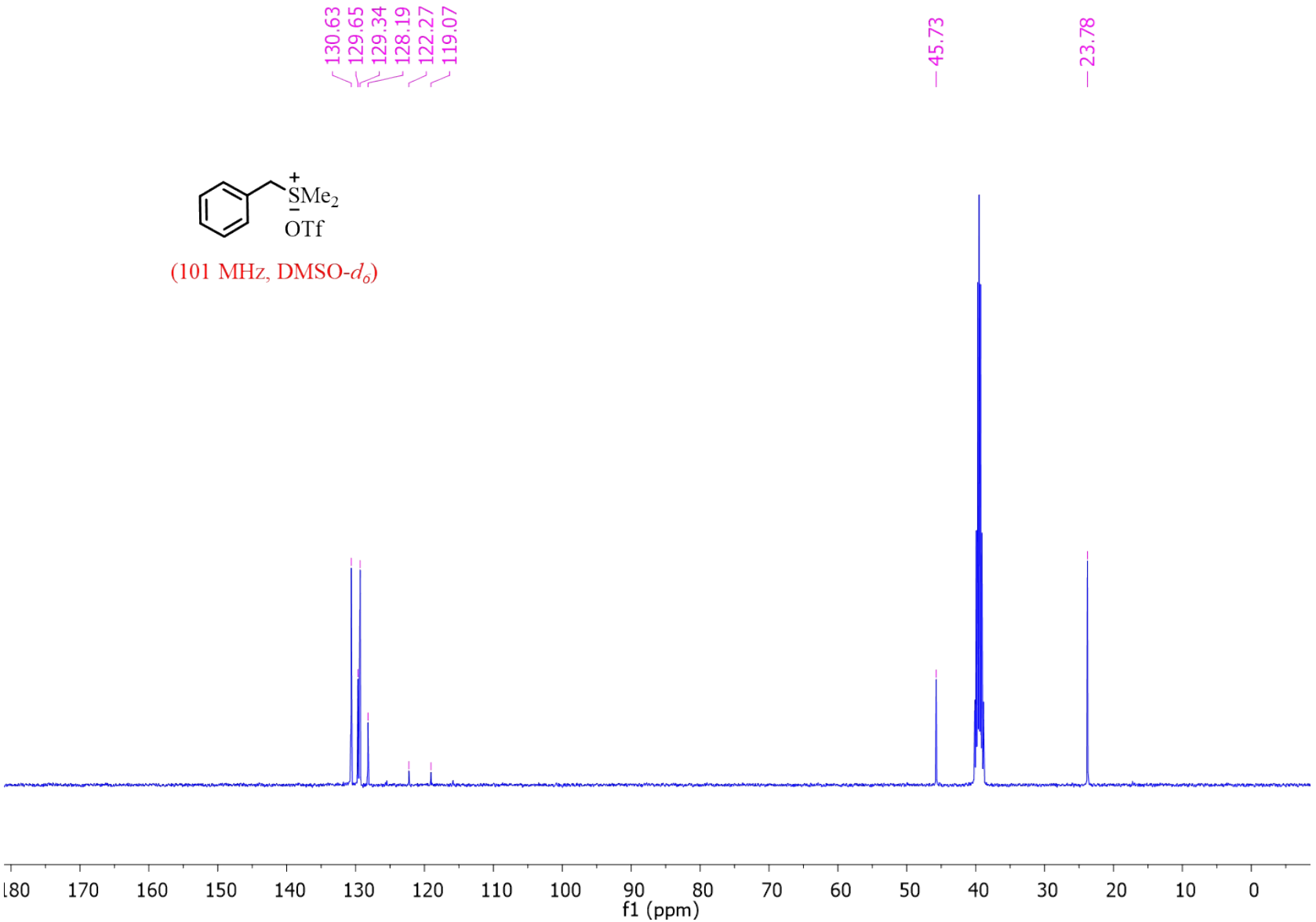


Fig. S19. ^{13}C NMR spectra of benzyl dimethyl sulfonium trifluoromethanesulfonate (**2b**) in DMSO-d_6.

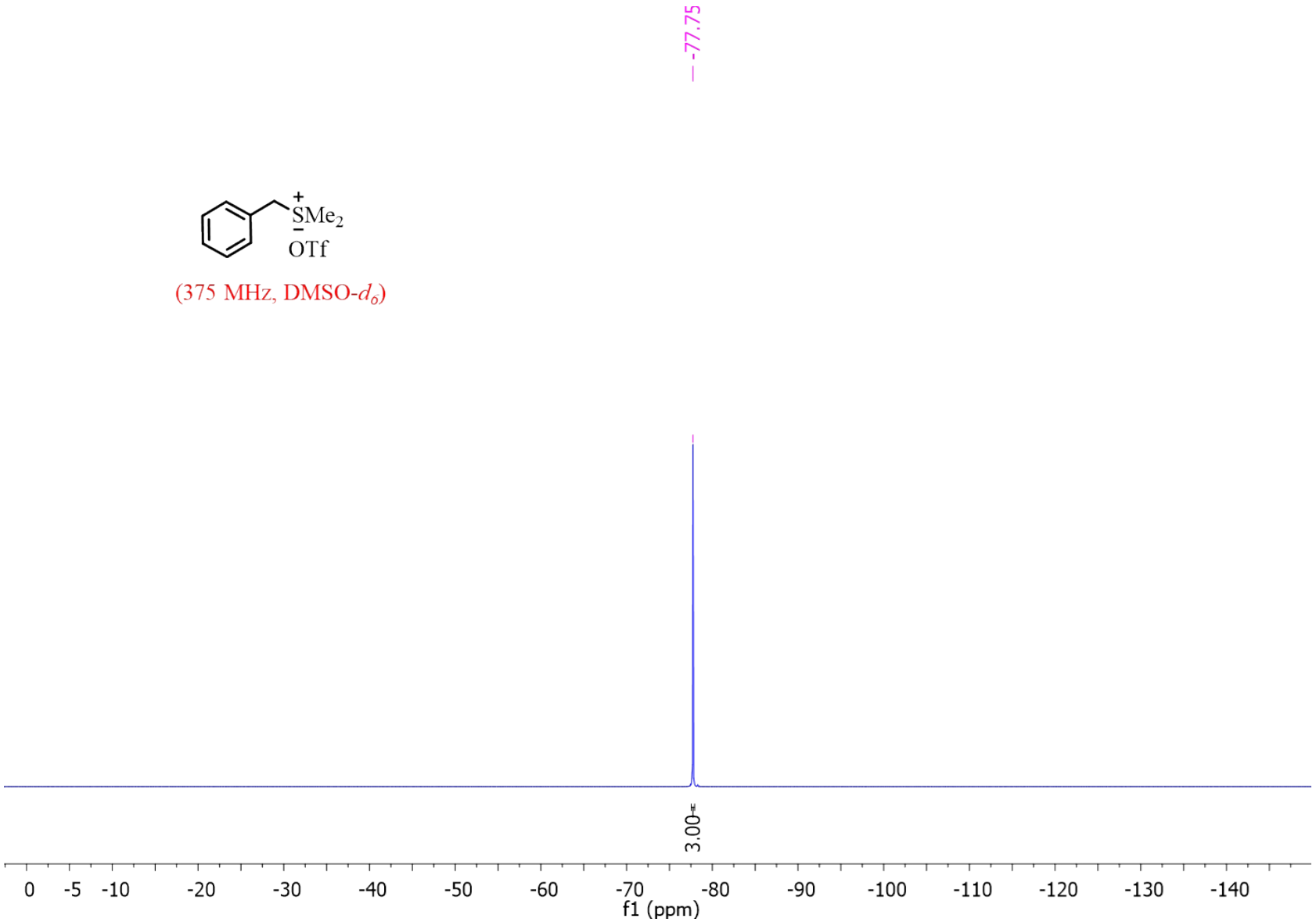


Fig. S20. ^{19}F NMR spectra of benzyl dimethyl sulfonium trifluoromethanesulfonate (**2b**) in DMSO-d_6.

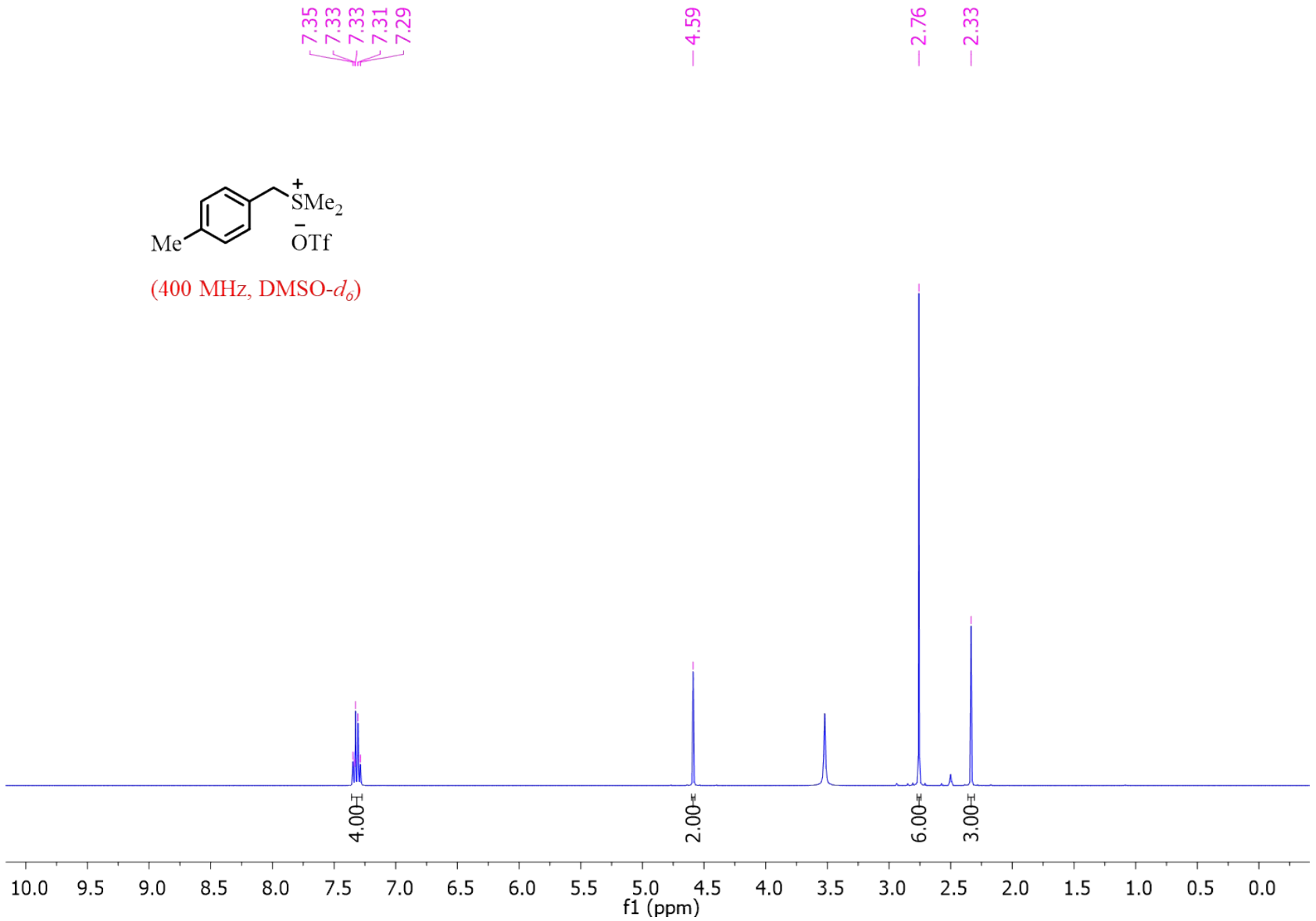


Fig. S21. ^{1}H NMR spectra of dimethyl(4-methylbenzyl) sulfonium trifluoromethanesulfonate (**2c**) in DMSO-d_6.

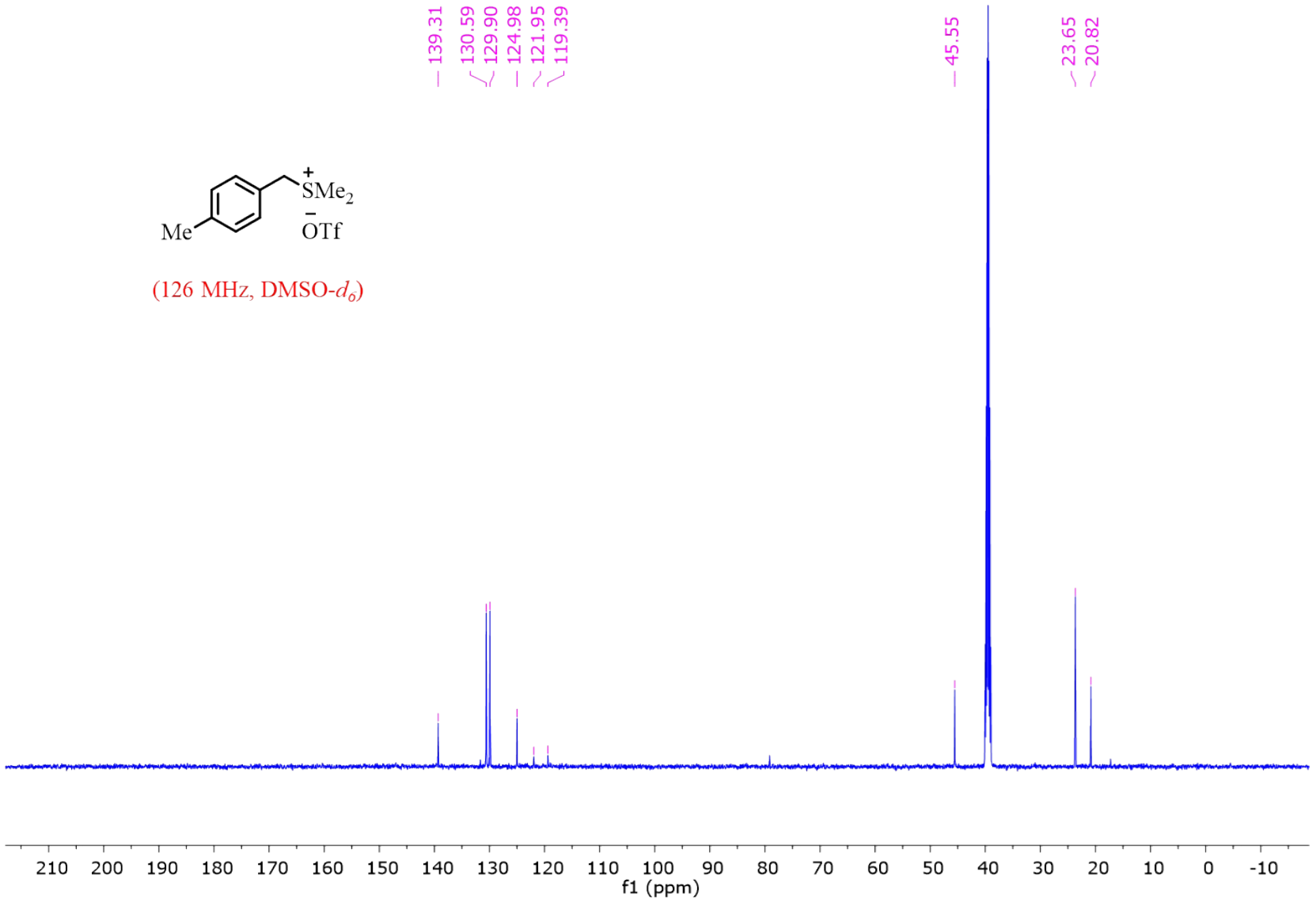


Fig. S22. ^{13}C NMR spectra of dimethyl(4-methylbenzyl) sulfonium trifluoromethanesulfonate (**2c**) in DMSO-d_6.

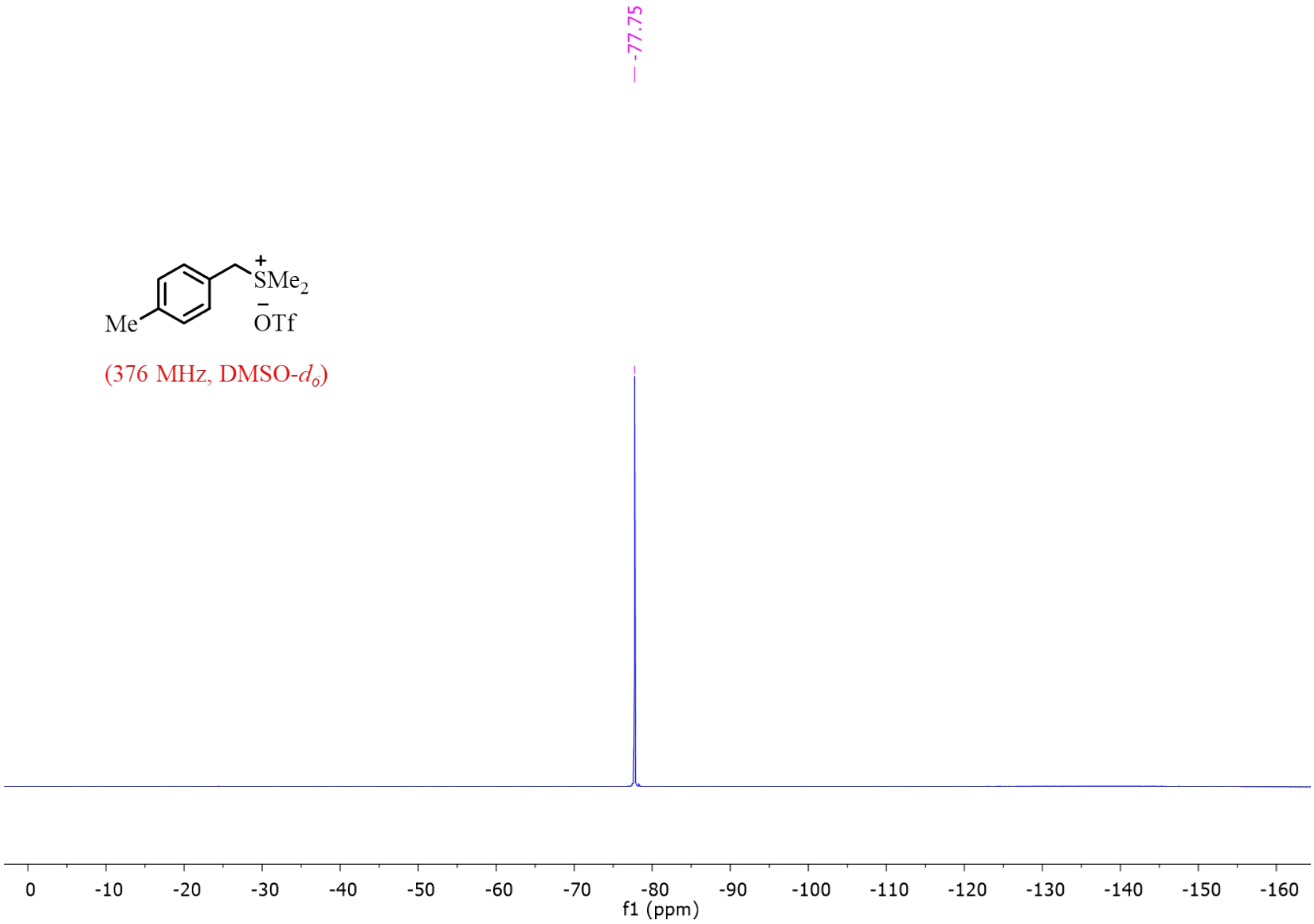


Fig. S23. ^{19}F NMR spectra of dimethyl(4-methylbenzyl) sulfonium trifluoromethanesulfonate (**2c**) in DMSO-d_6.

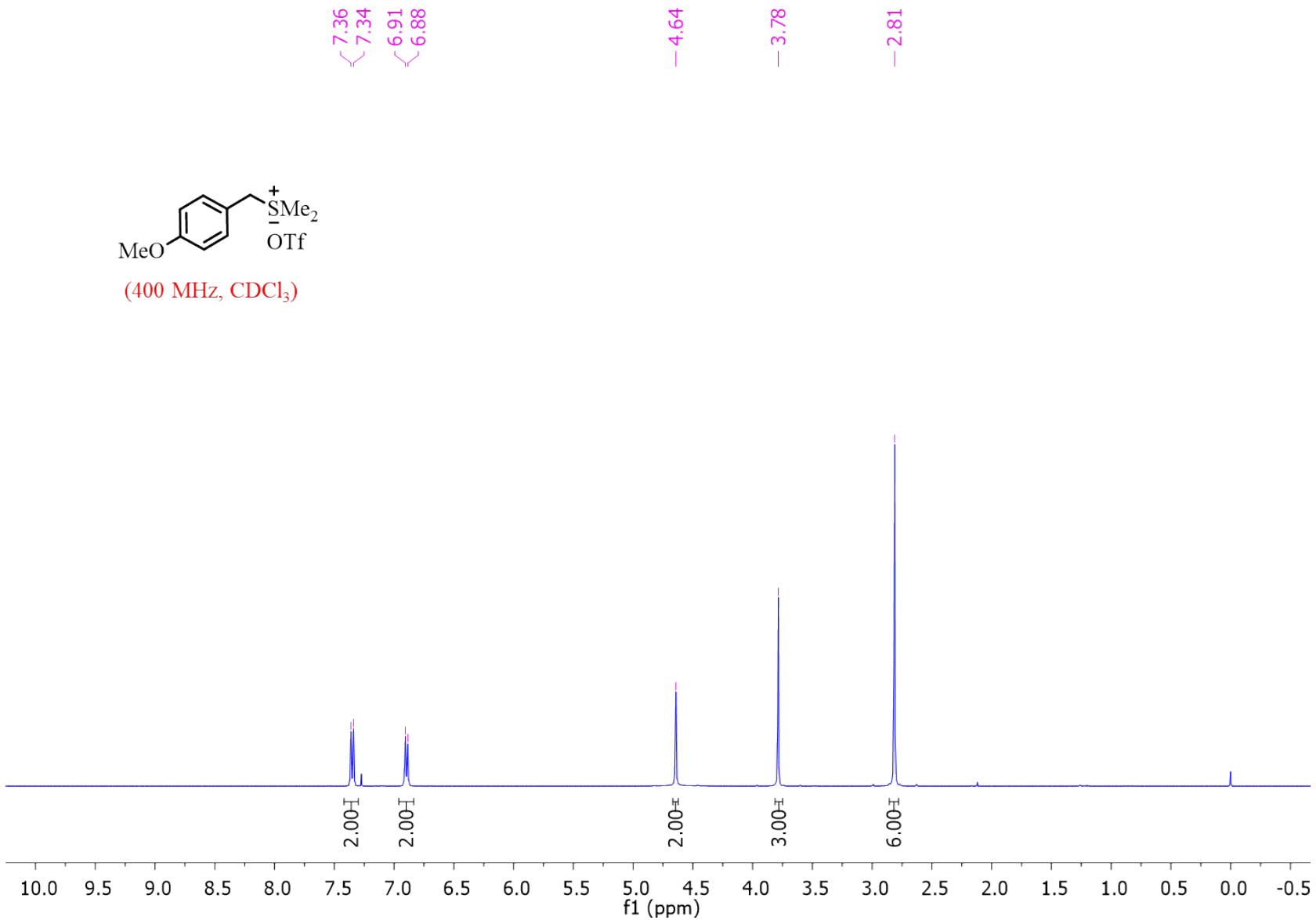


Fig. S24. ^{1}H NMR spectra of 4-methoxybenzyl) dimethyl sulfonium trifluoromethanesulfonate (**2d**) in $CDCl_3$.

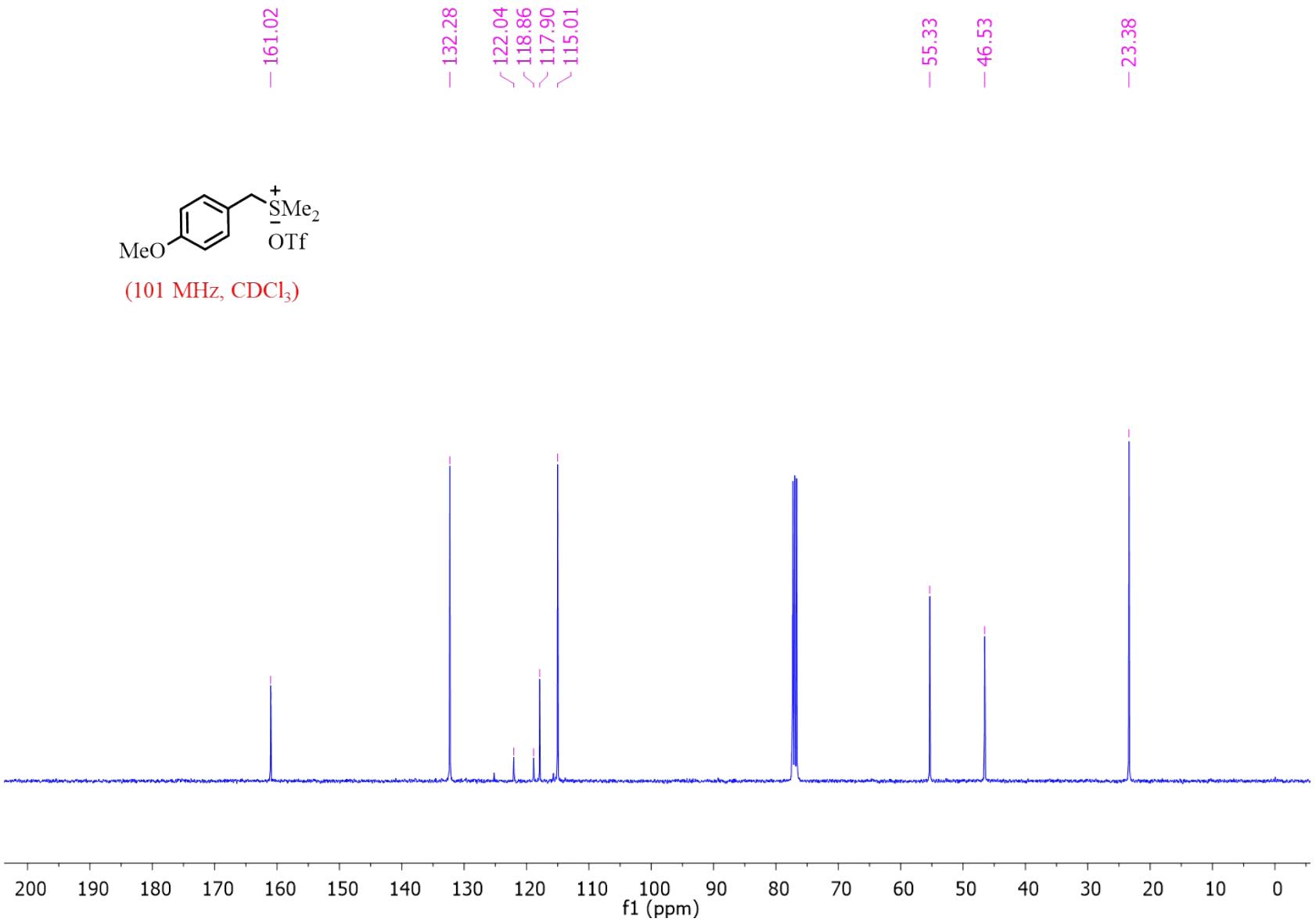


Fig. S25. ^{13}C NMR spectra of 4-methoxybenzyl) dimethyl sulfonium trifluoromethanesulfonate (**2d**) in $CDCl_3$.

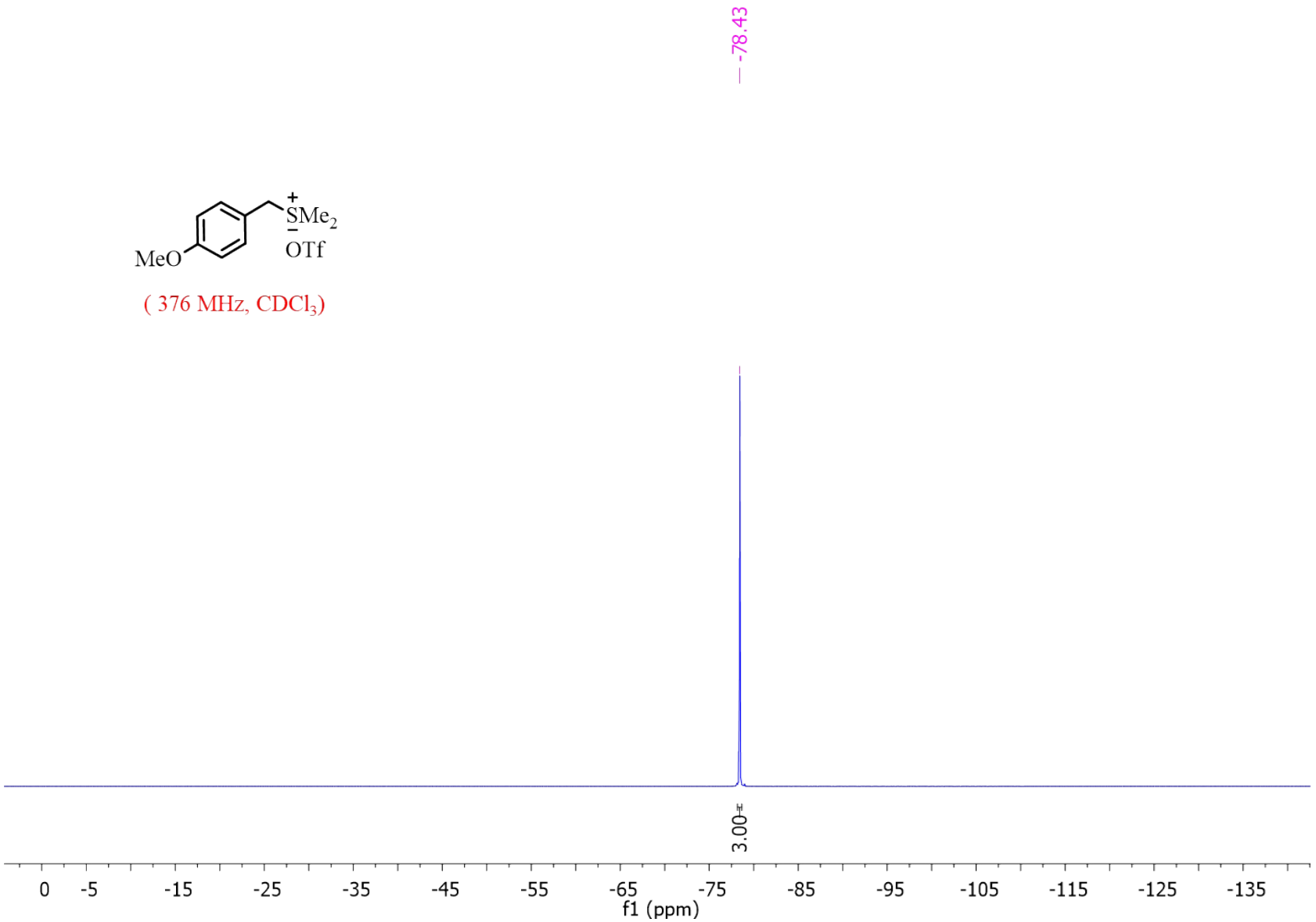


Fig. S26. ^{19}F NMR spectra of 4-methoxybenzyl) dimethyl sulfonium trifluoromethanesulfonate (**2d**) in $CDCl_3$.

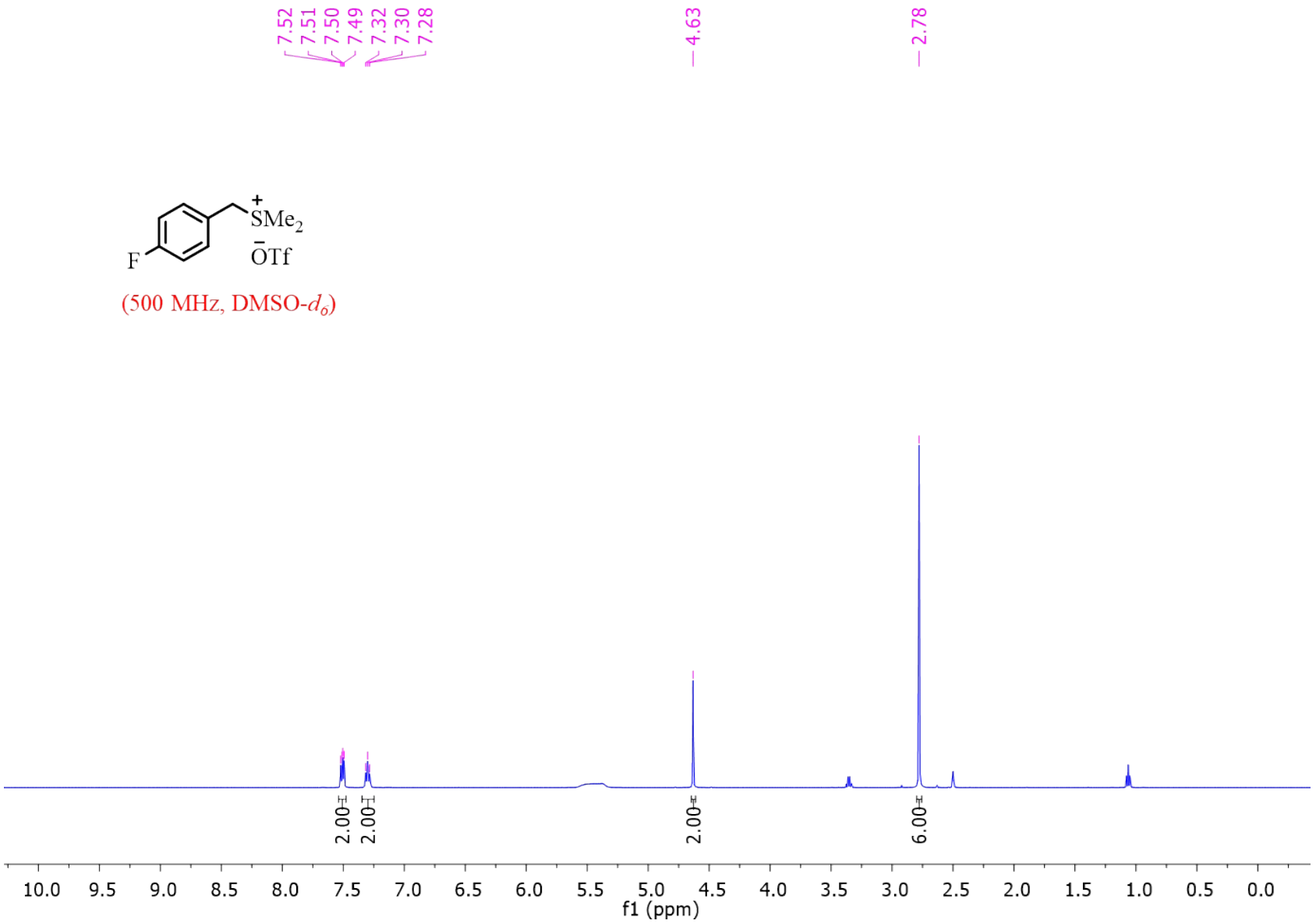


Fig. S27. ^{1}H NMR spectra of (4-Fluorobenzyl)dimethylsulfonium trifluoromethanesulfonate (**2e**) in DMSO-d_6.

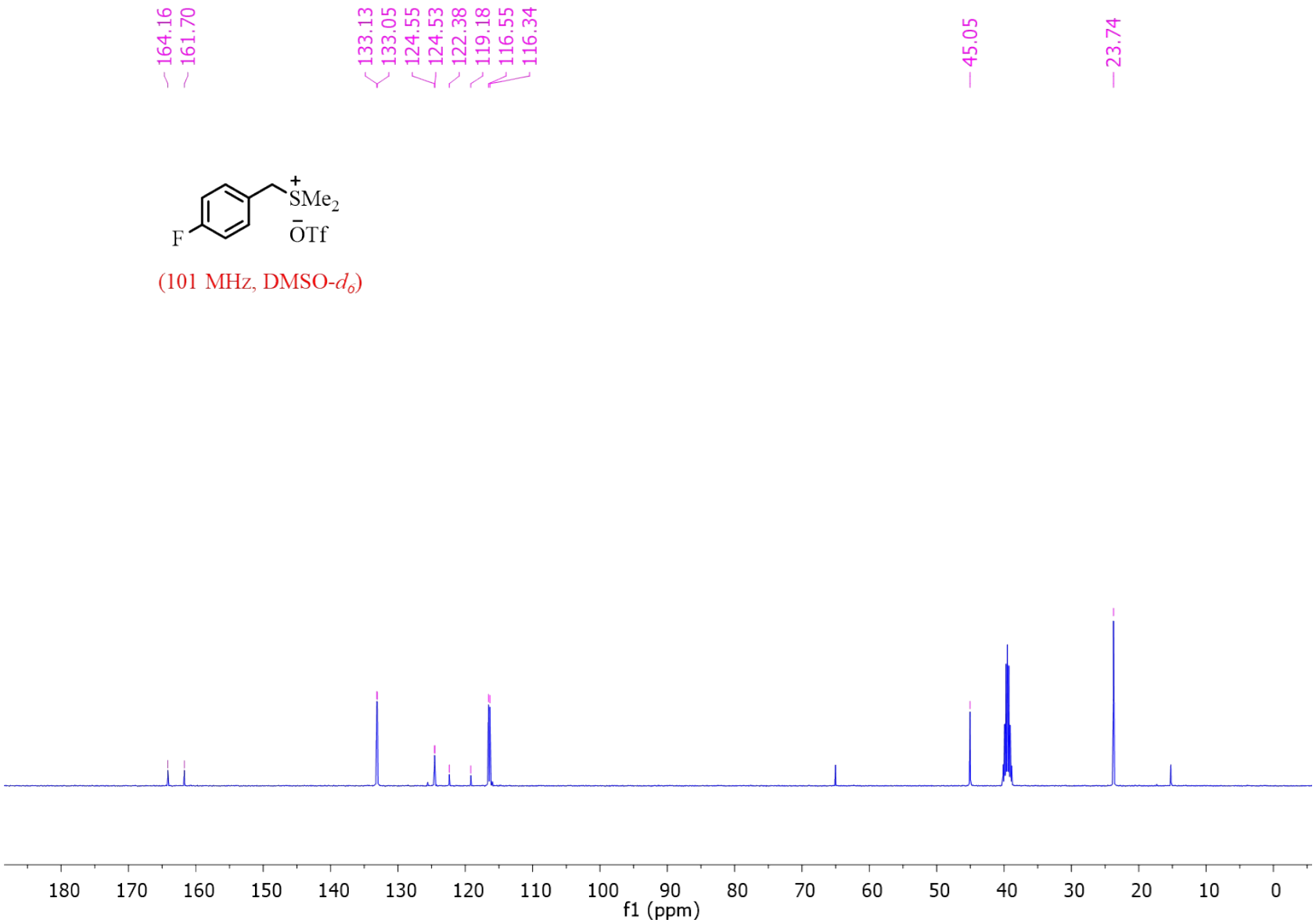


Fig. S28. ^{13}C NMR spectra of (4-Fluorobenzyl)dimethylsulfonium trifluoromethanesulfonate (**2e**) in DMSO-d_6.

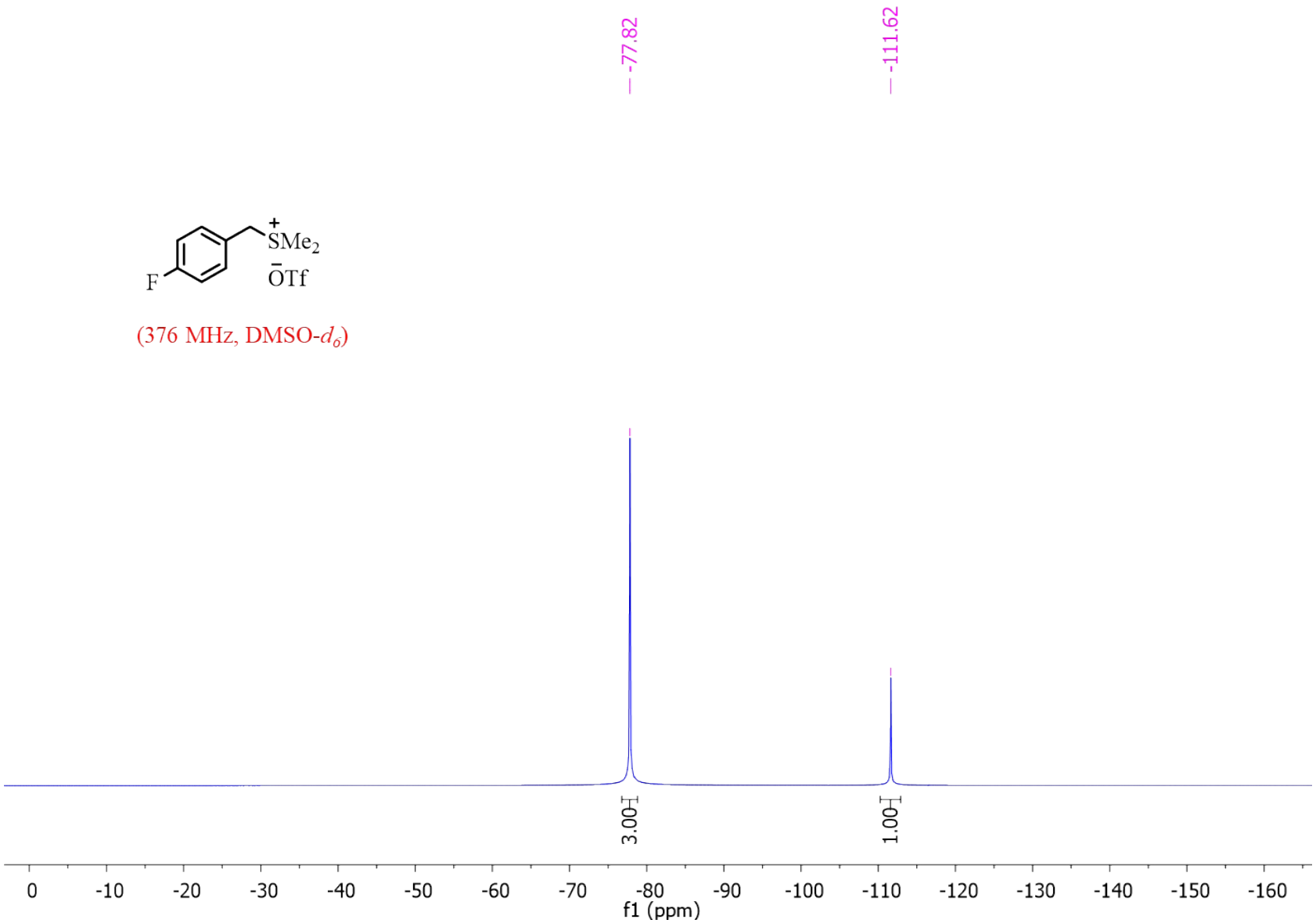


Fig. S29. ^{19}F NMR spectra of (4-Fluorobenzyl) dimethylsulfonium trifluoromethanesulfonate (**2e**) in DMSO-d_6.

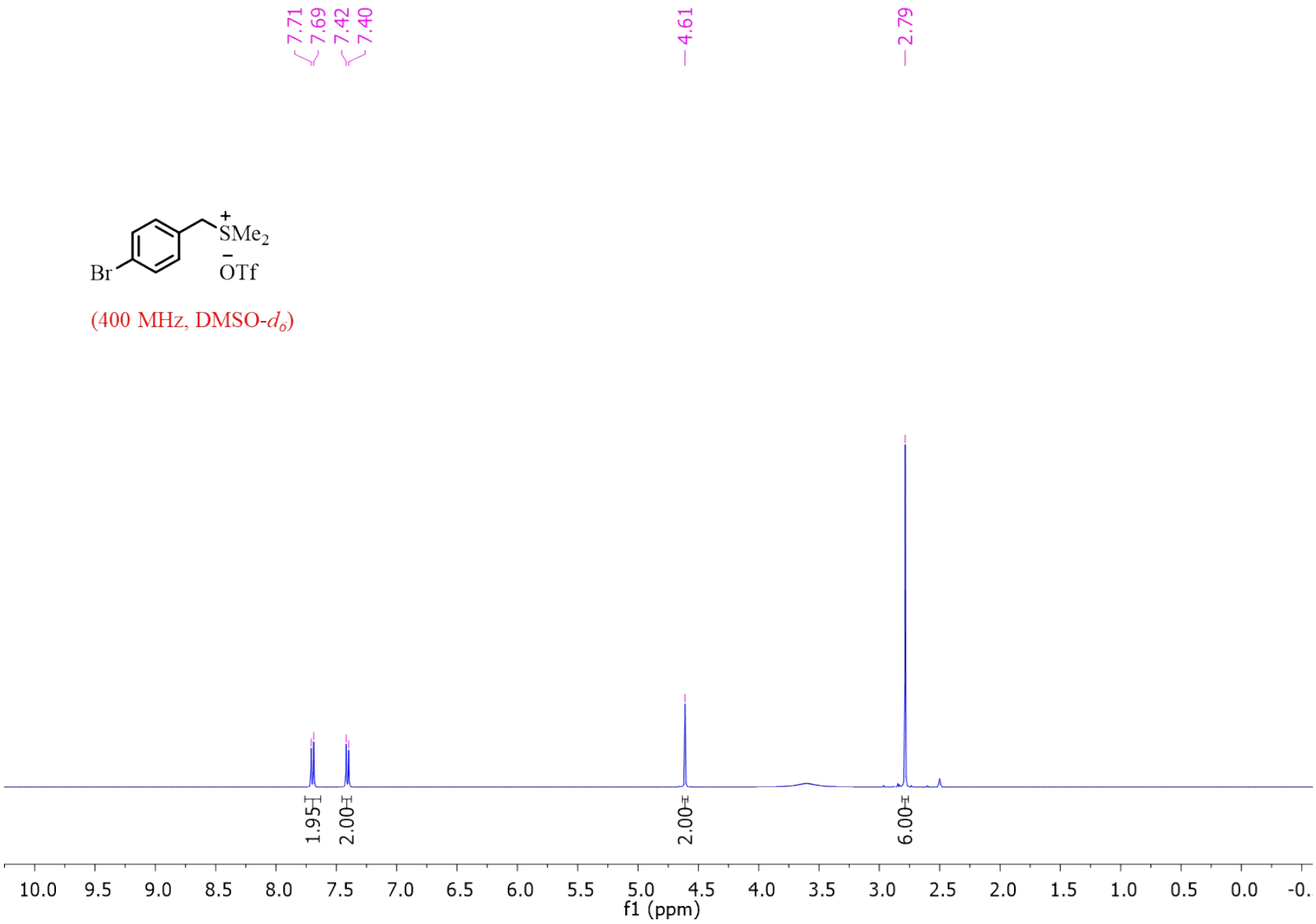


Fig. S30. [1]FH NMR spectra of (4-bromobenzyl) dimethylsulfonium trifluoromethanesulfonate (**2f**) in DMSO-d_6.

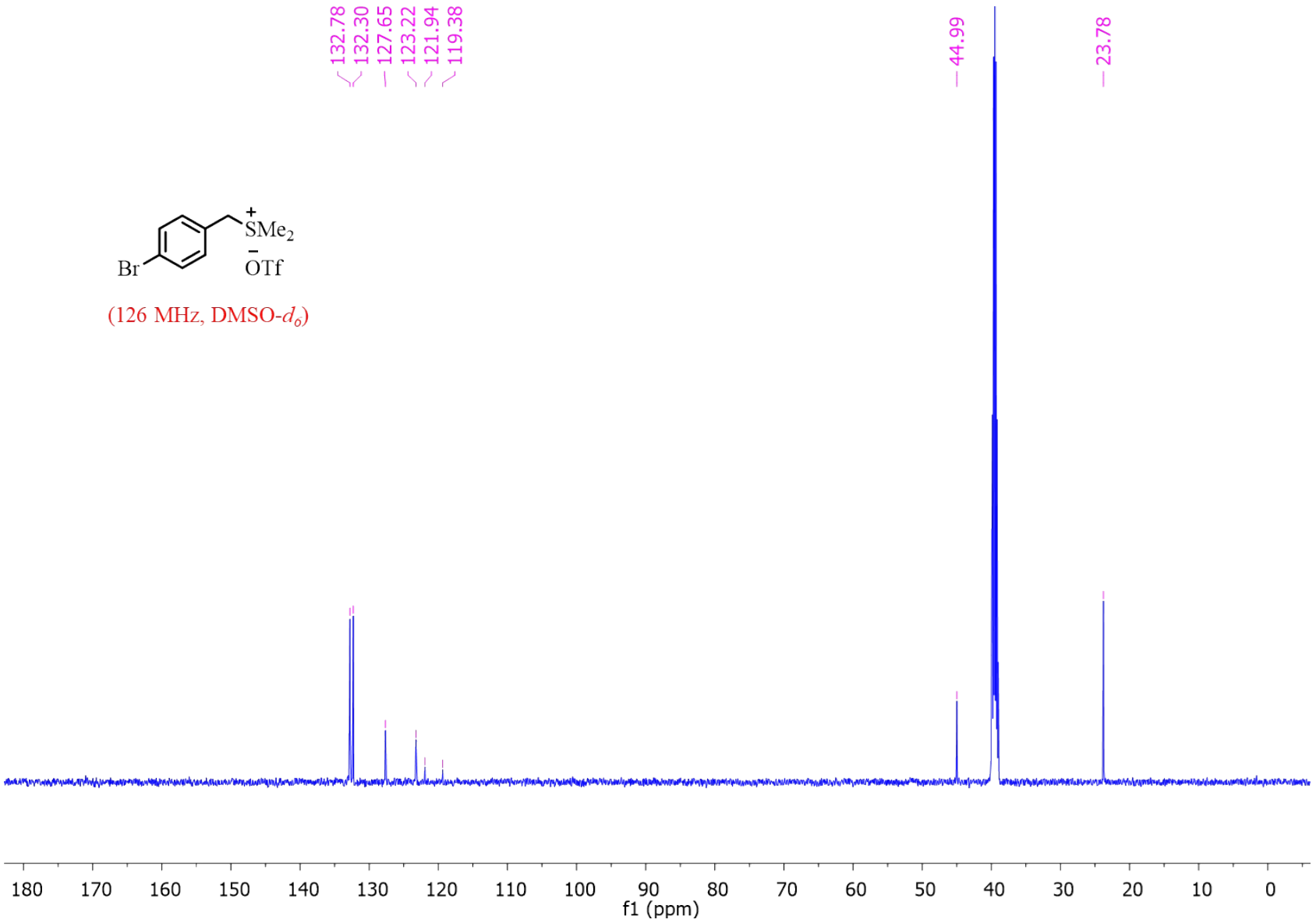


Fig. S31. ^{13}C NMR spectra of (4-bromobenzyl) dimethylsulfonium trifluoromethanesulfonate (**2f**) in DMSO-d_6.

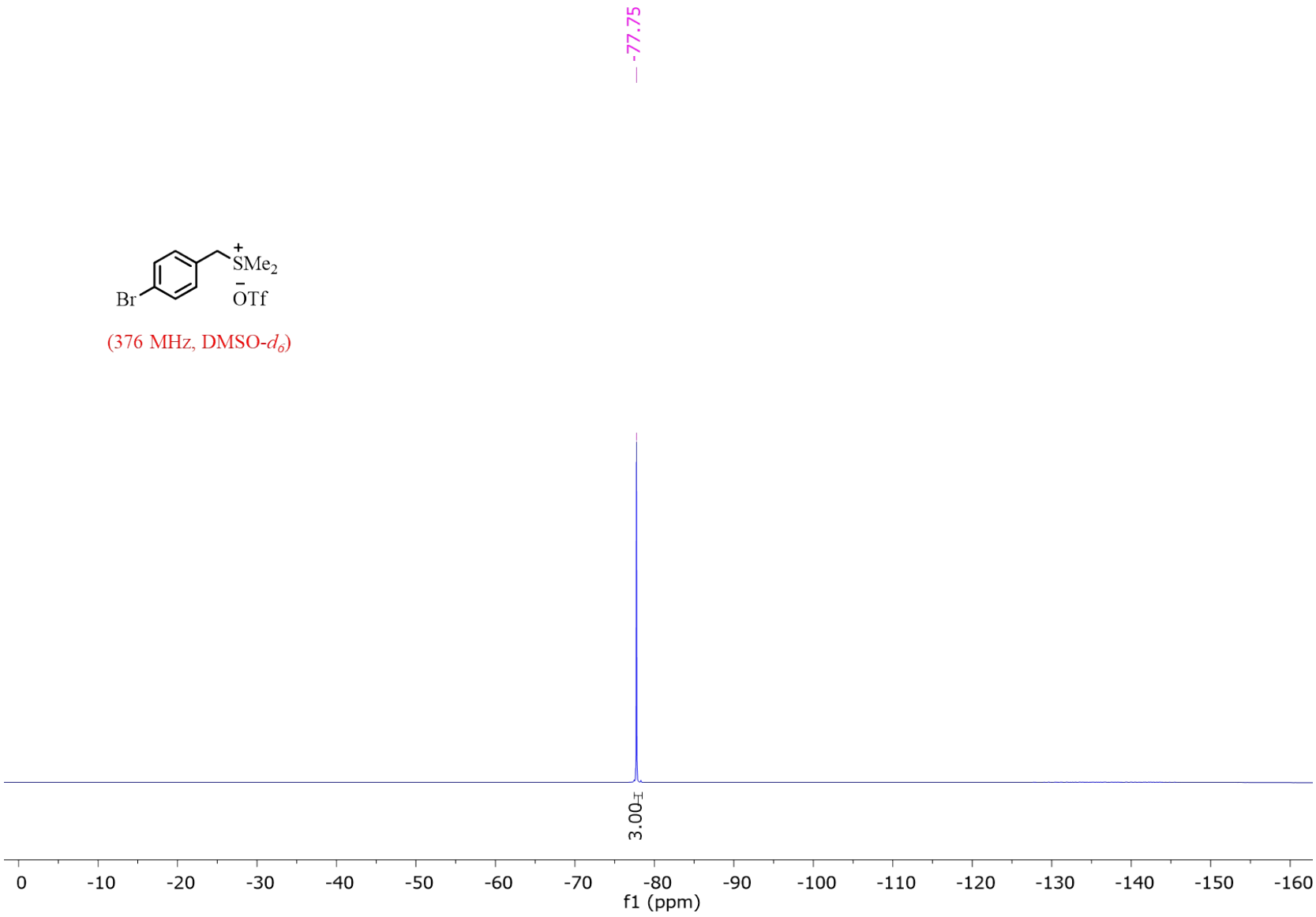


Fig. S32. ^{19}F NMR spectra of (4-bromobenzyl) dimethylsulfonium trifluoromethanesulfonate (**2f**) in DMSO-d_6.

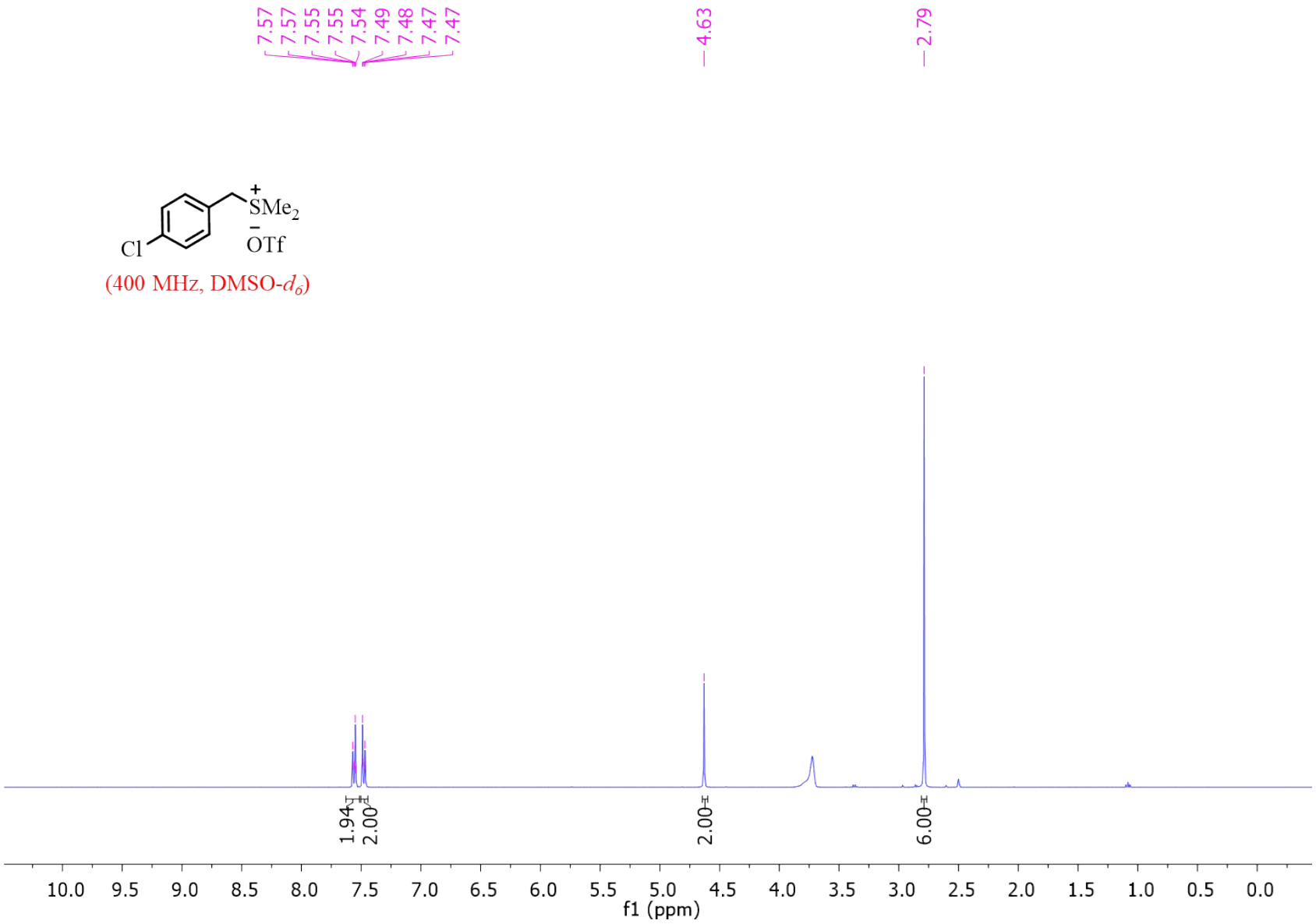


Fig. S33. ^{1}H NMR spectra of (4-Chlorobenzyl) dimethylsulfonium trifluoromethanesulfonate (**2g**) in DMSO-d_6.

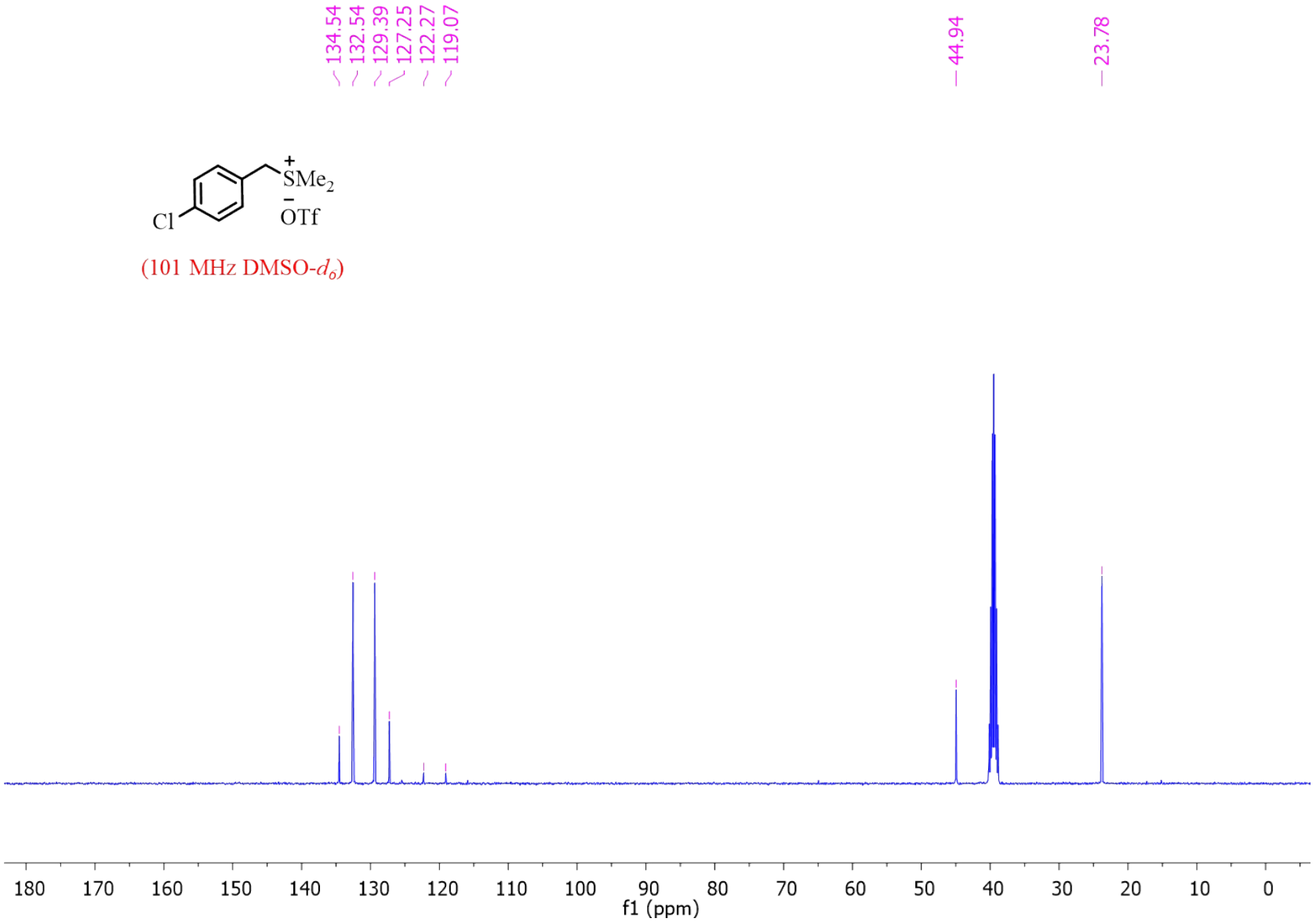


Fig. S34. ^{13}C NMR spectra of (4-Chlorobenzyl) dimethylsulfonium trifluoromethanesulfonate (**2g**) in DMSO-d_6.

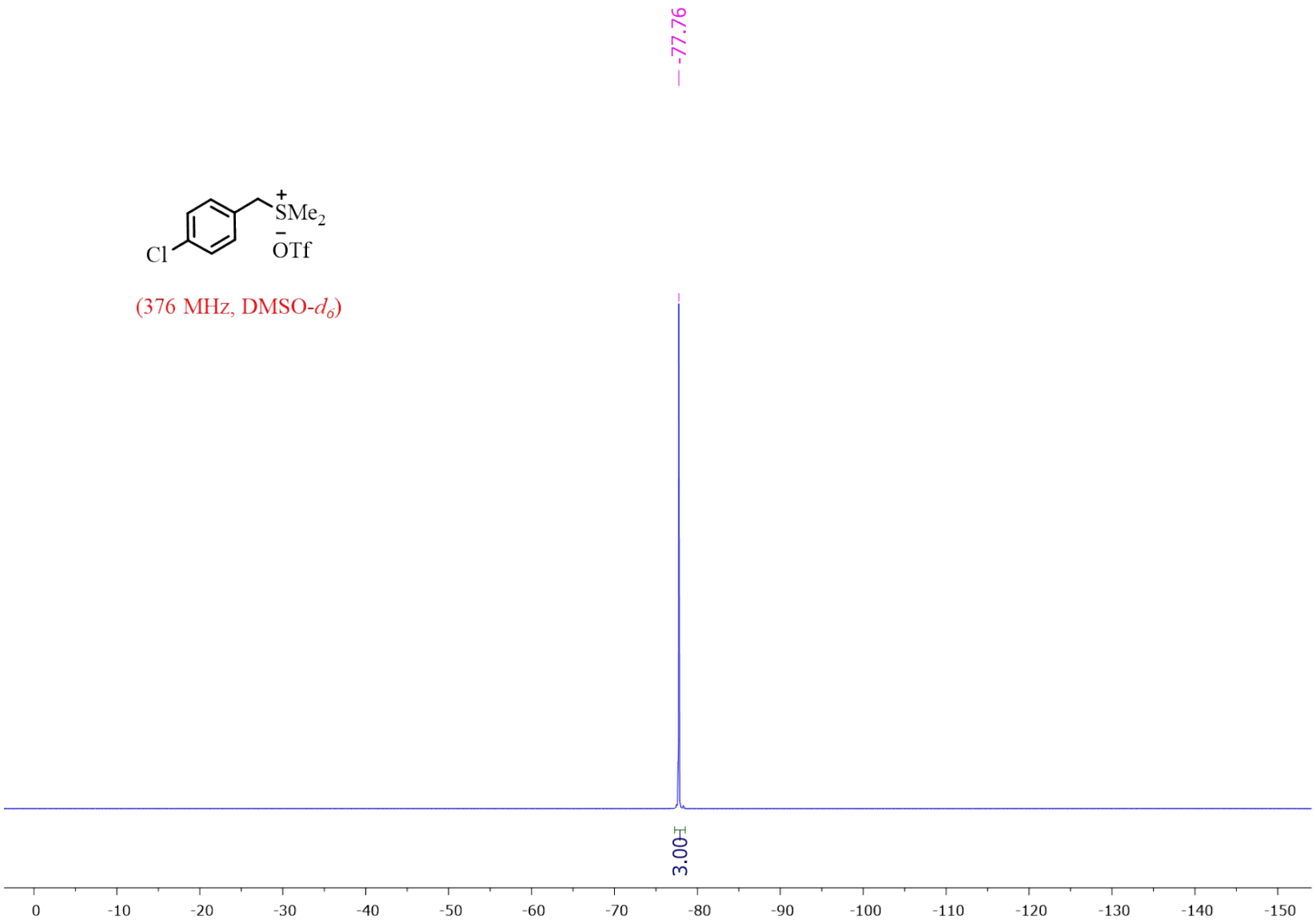


Fig. S35. ^{19}F NMR spectra of (4-Chlorobenzyl) dimethylsulfonium trifluoromethanesulfonate (**2g**) in DMSO-d_6.

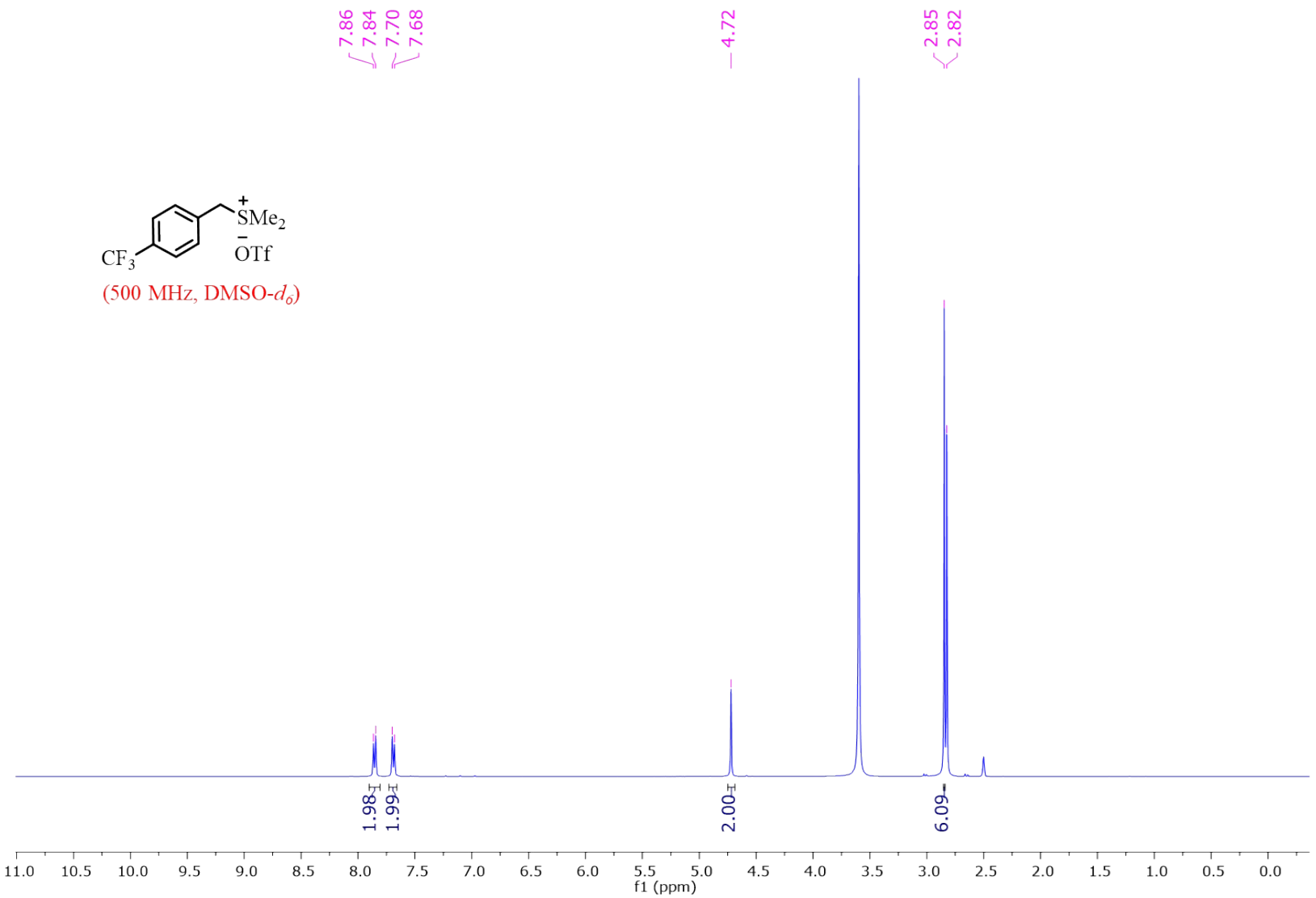


Fig. S36. ^{1}H NMR spectra of dimethyl(4-(trifluoromethyl) benzyl) sulfonium trifluoromethanesulfonate (**2h**) in DMSO-d_6.

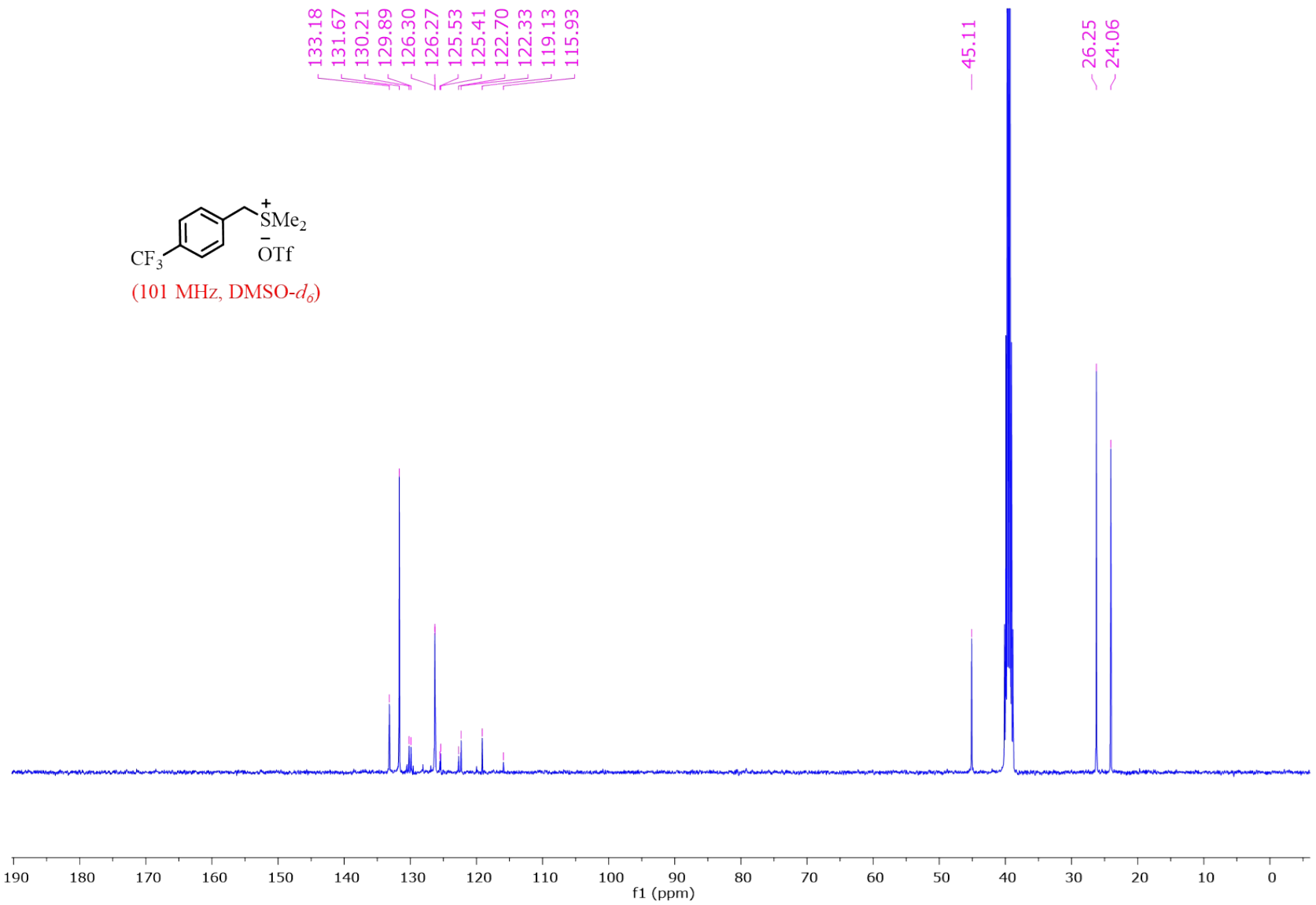


Fig. S37. ^{13}C NMR spectra of dimethyl(4-(trifluoromethyl) benzyl) sulfonium trifluoromethanesulfonate (**2h**) in DMSO-d_6.

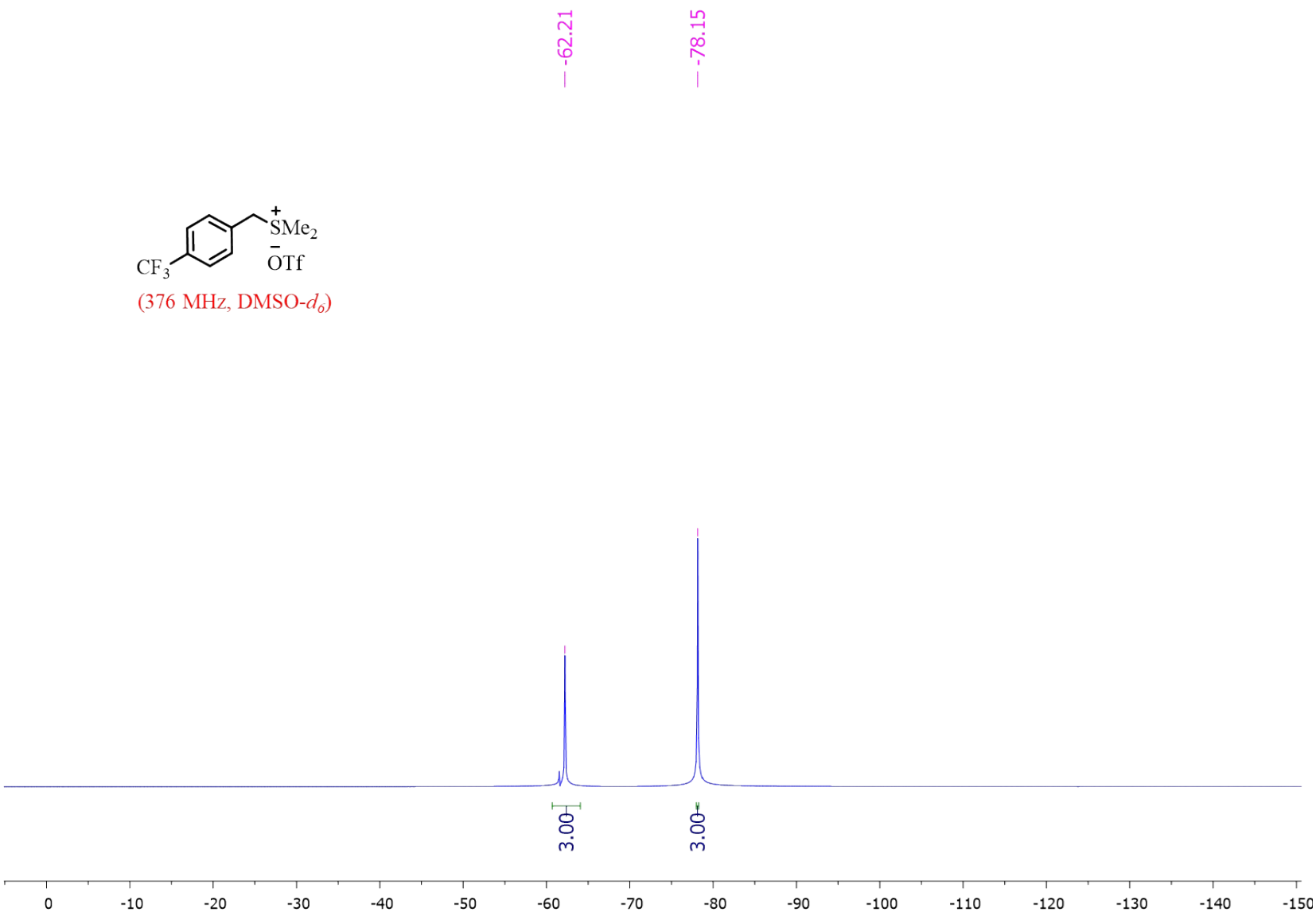


Fig. S38. ^{19}F NMR spectra of dimethyl(4-(trifluoromethyl) benzyl) sulfonium trifluoromethanesulfonate (**2h**) in DMSO-d_6.

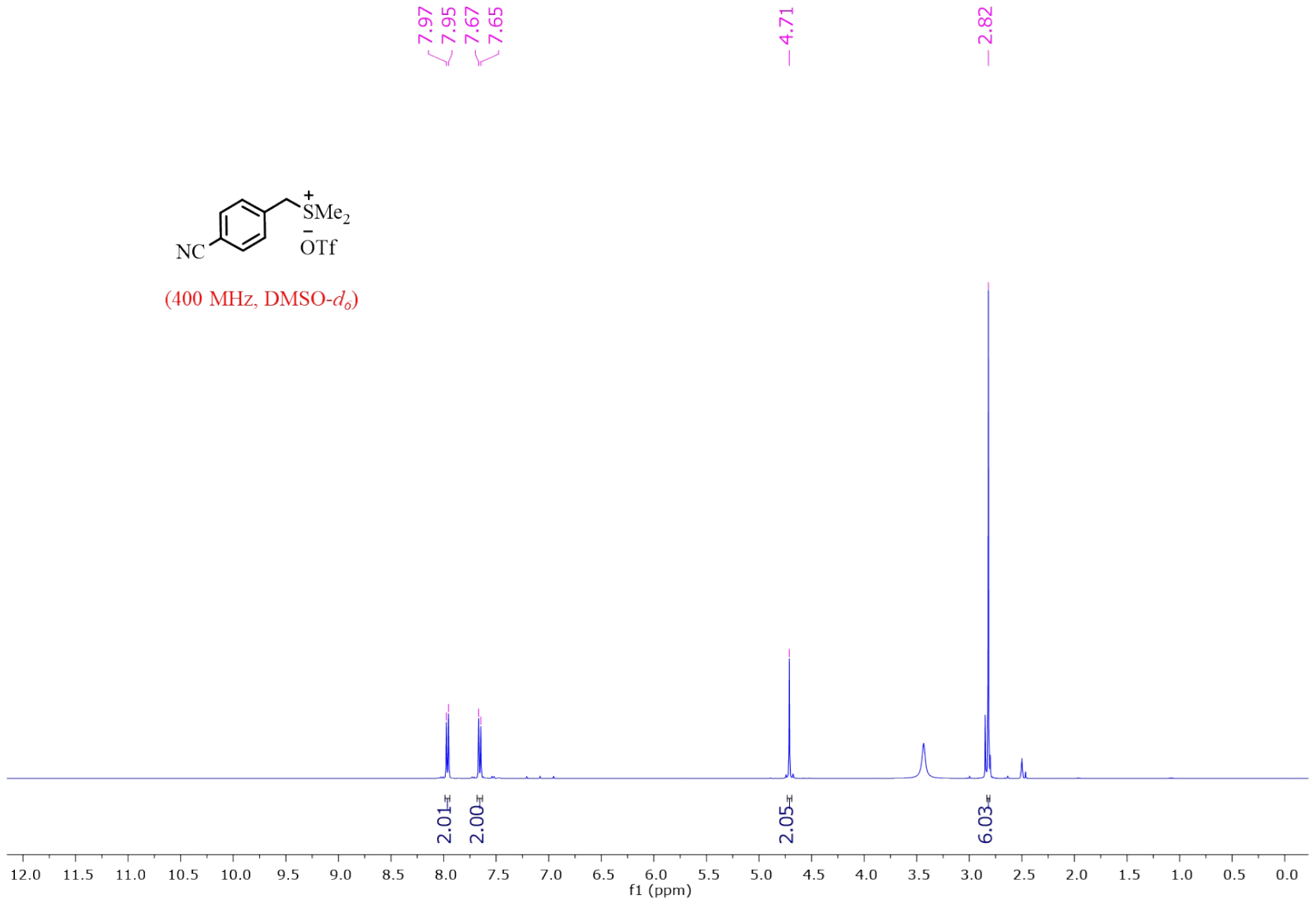


Fig. S39. ^{1}H NMR spectra of (4-cyanobenzyl)dimethylsulfonium trifluoromethanesulfonate (**2i**) in DMSO-d_6.

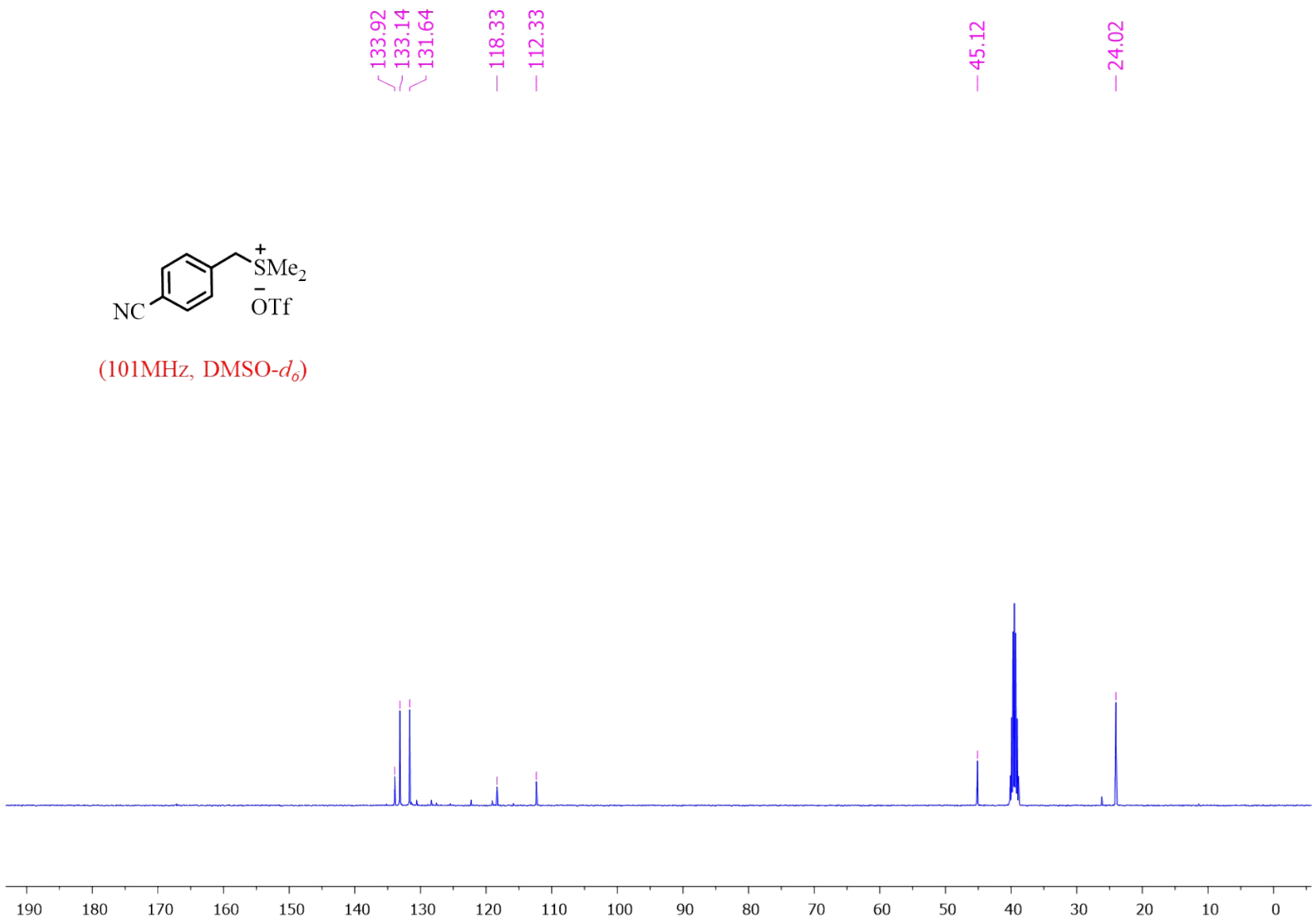


Fig. S40. ^{13}C NMR spectra of (4-cyanobenzyl)dimethylsulfonium trifluoromethanesulfonate (**2i**) in DMSO-d_6.

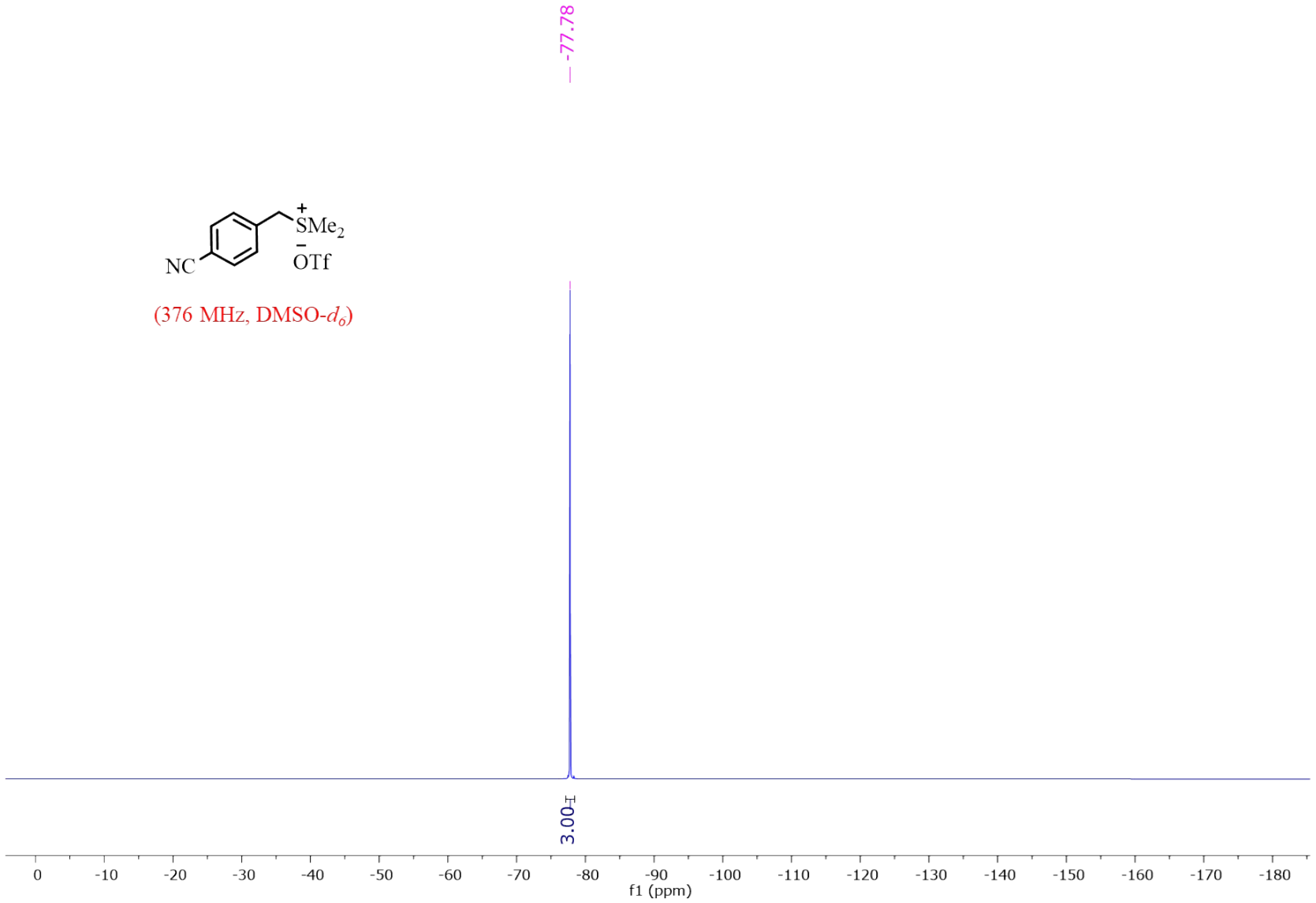


Fig. S41. ^{19}F NMR spectra of (4-cyanobenzyl)dimethylsulfonium trifluoromethanesulfonate (**2i**) in DMSO-d_6.

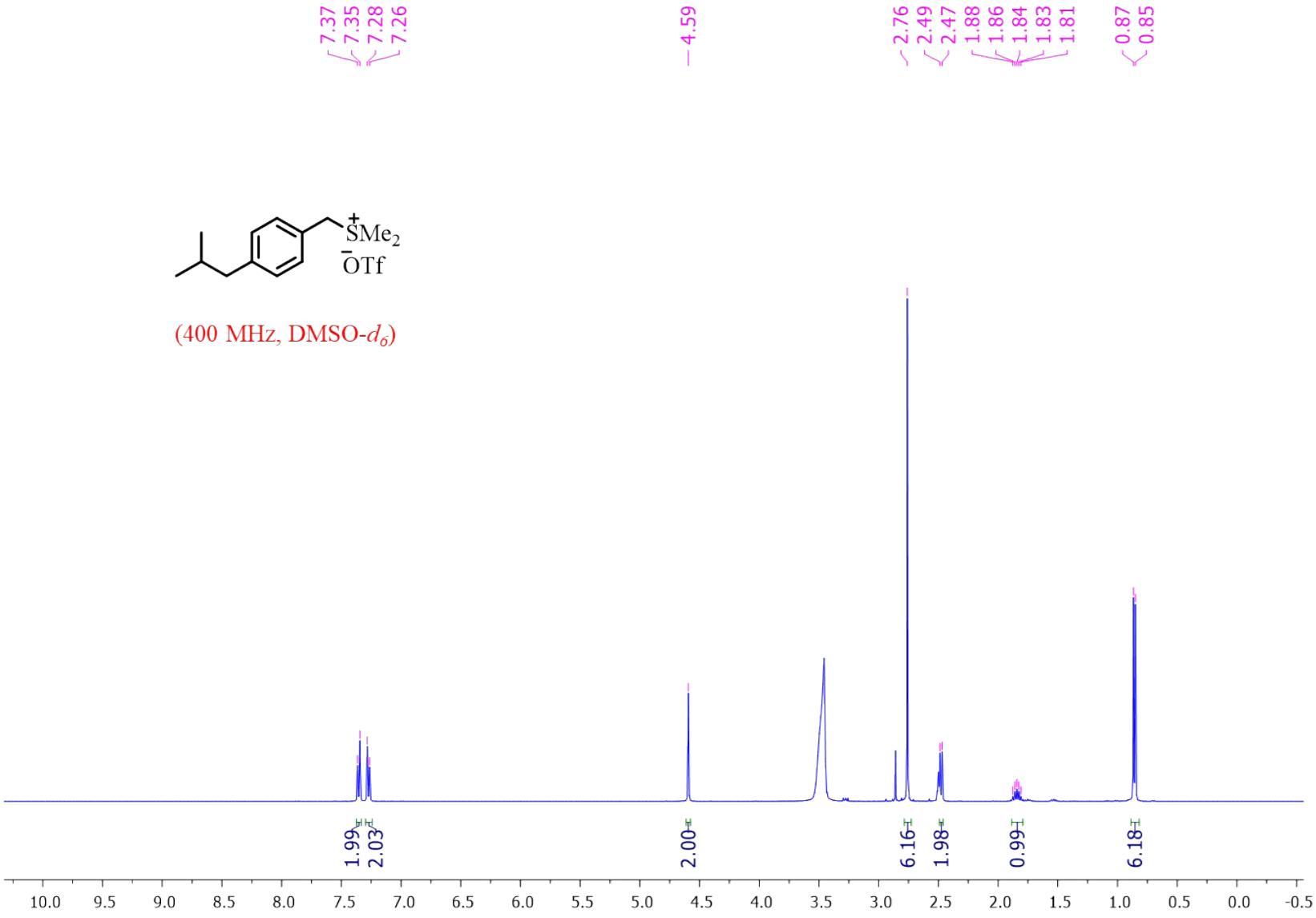


Fig. S42. ^{1}H NMR spectra of (4-Isobutylbenzyl) dimethyl sulfonium trifluoromethanesulfonate (**2j**) in DMSO-d_6.

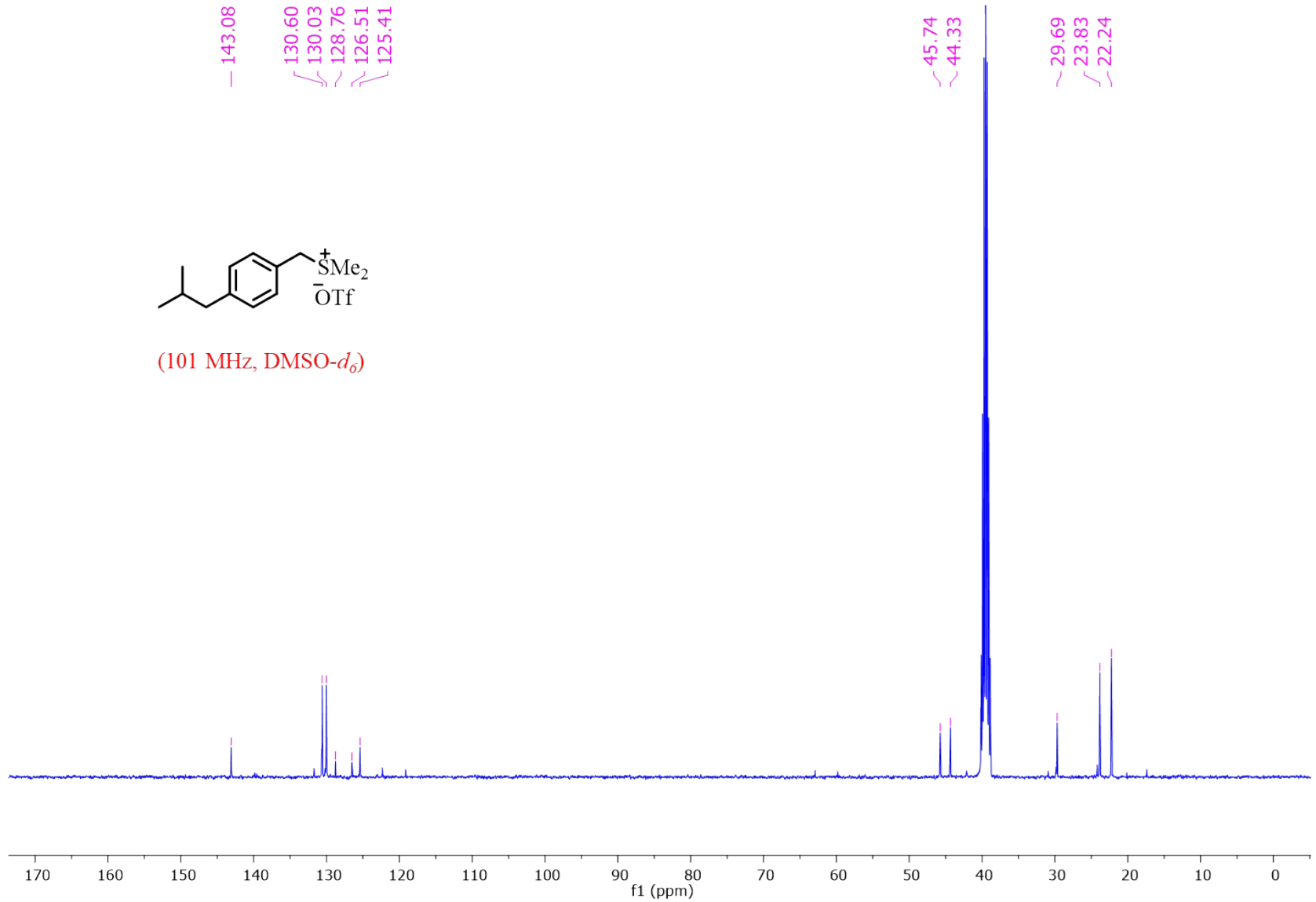


Fig. S43. ^{13}C NMR spectra of (4-Isobutylbenzyl) dimethyl sulfonium trifluoromethanesulfonate (**2j**) in DMSO-d_6.

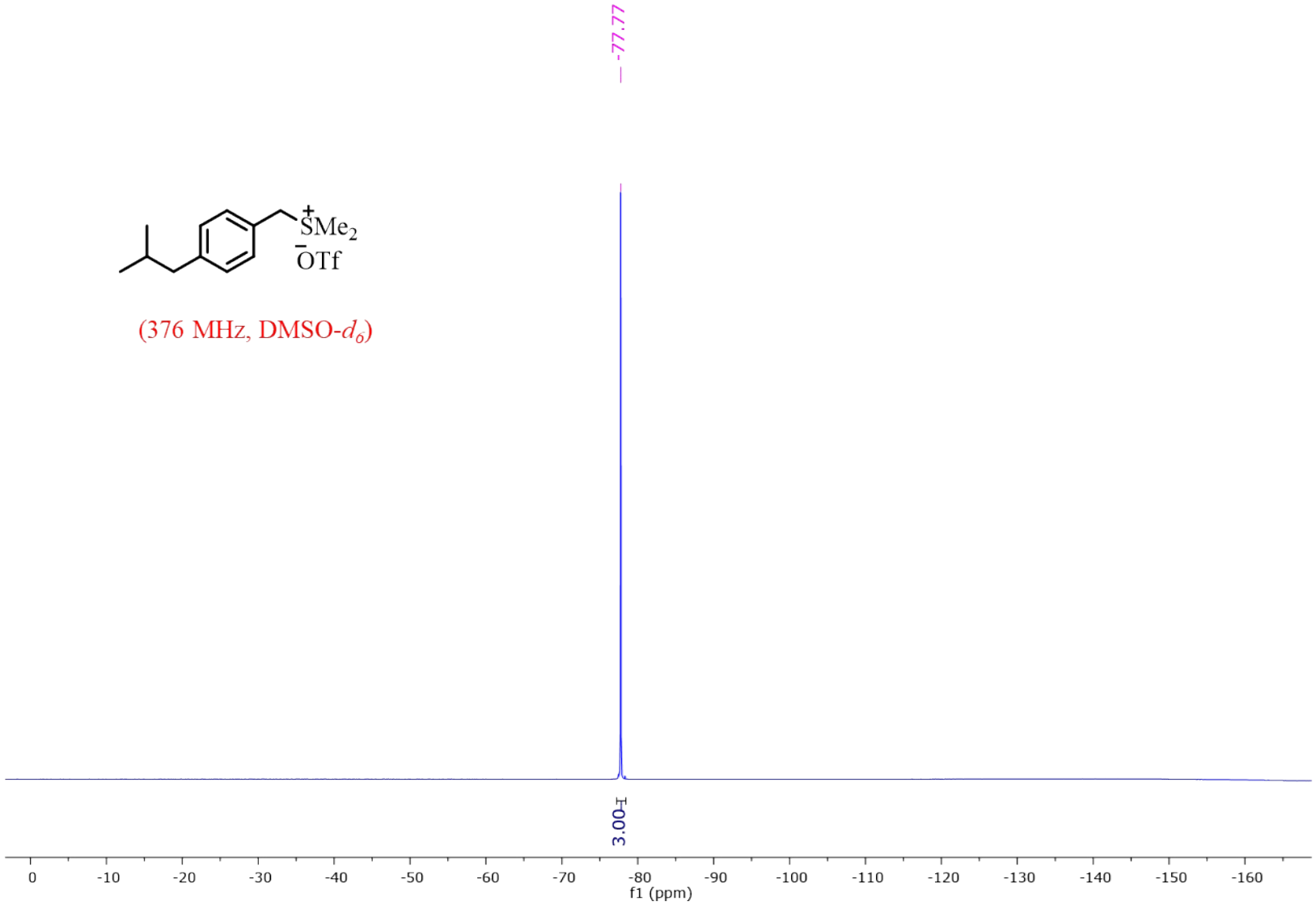


Fig. S44. ^{19}F NMR spectra of (4-Isobutylbenzyl) dimethyl sulfonium trifluoromethanesulfonate (**2j**) in DMSO-d_6.

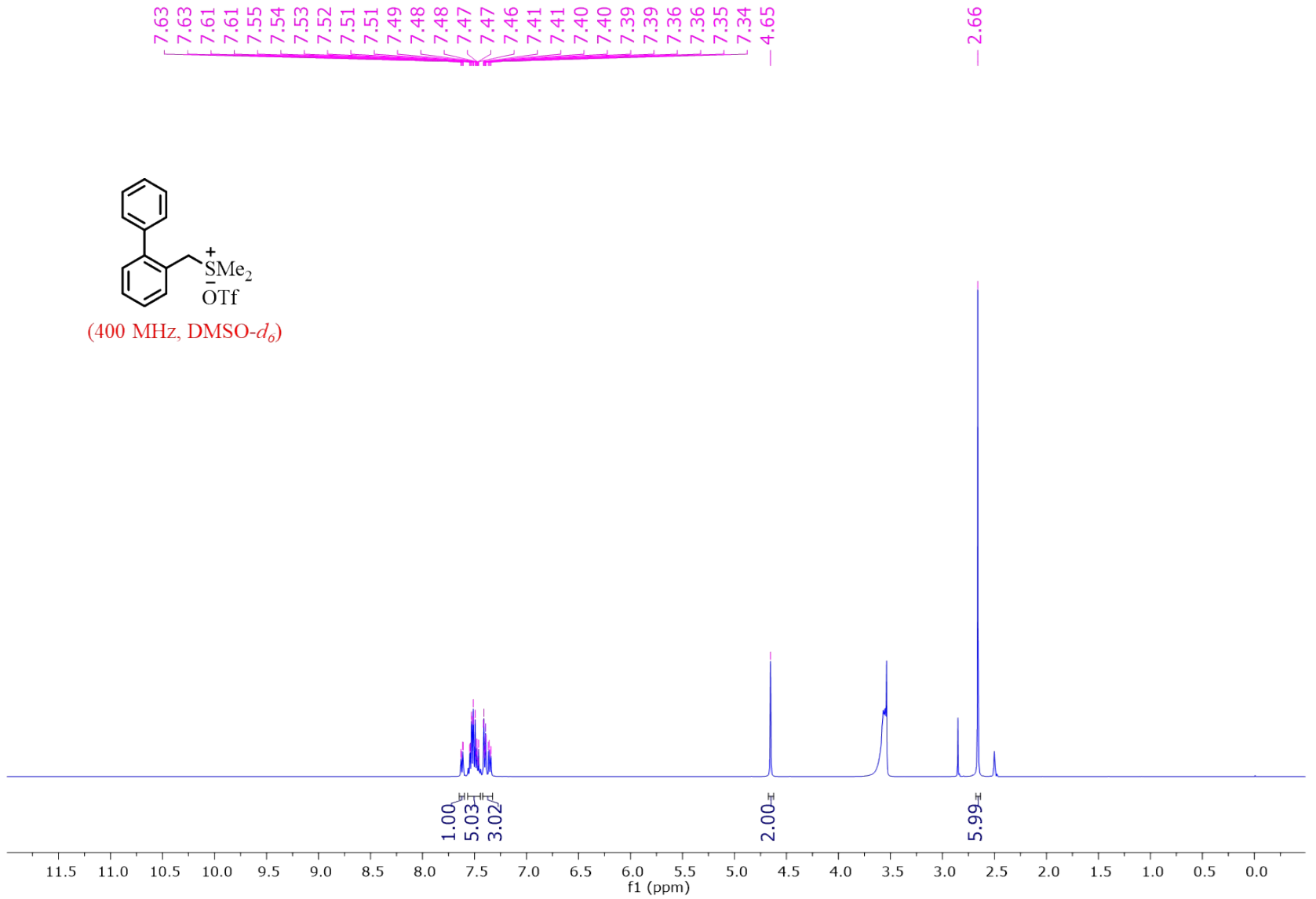


Fig. S45. ^{1}H NMR spectra of ([1,1'-Biphenyl]-2-ylmethyl)dimethylsulfonium trifluoromethanesulfonate (**2k**) in DMSO-d_6.

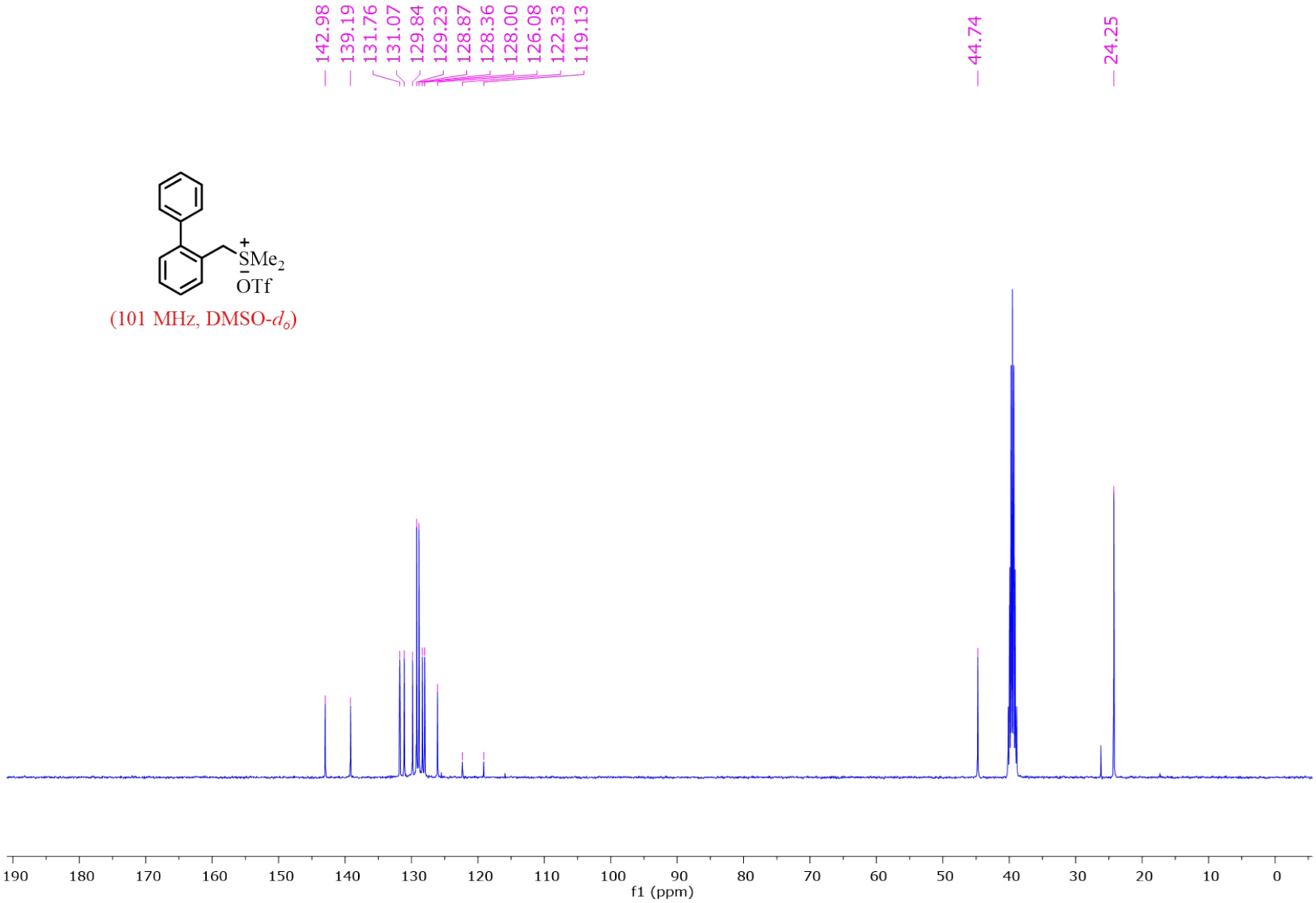


Fig. S46. ^{13}C NMR spectra of ([1,1'-biphenyl]-2-ylmethyl)dimethylsulfonium trifluoromethanesulfonate (**2k**) in DMSO-d_6.

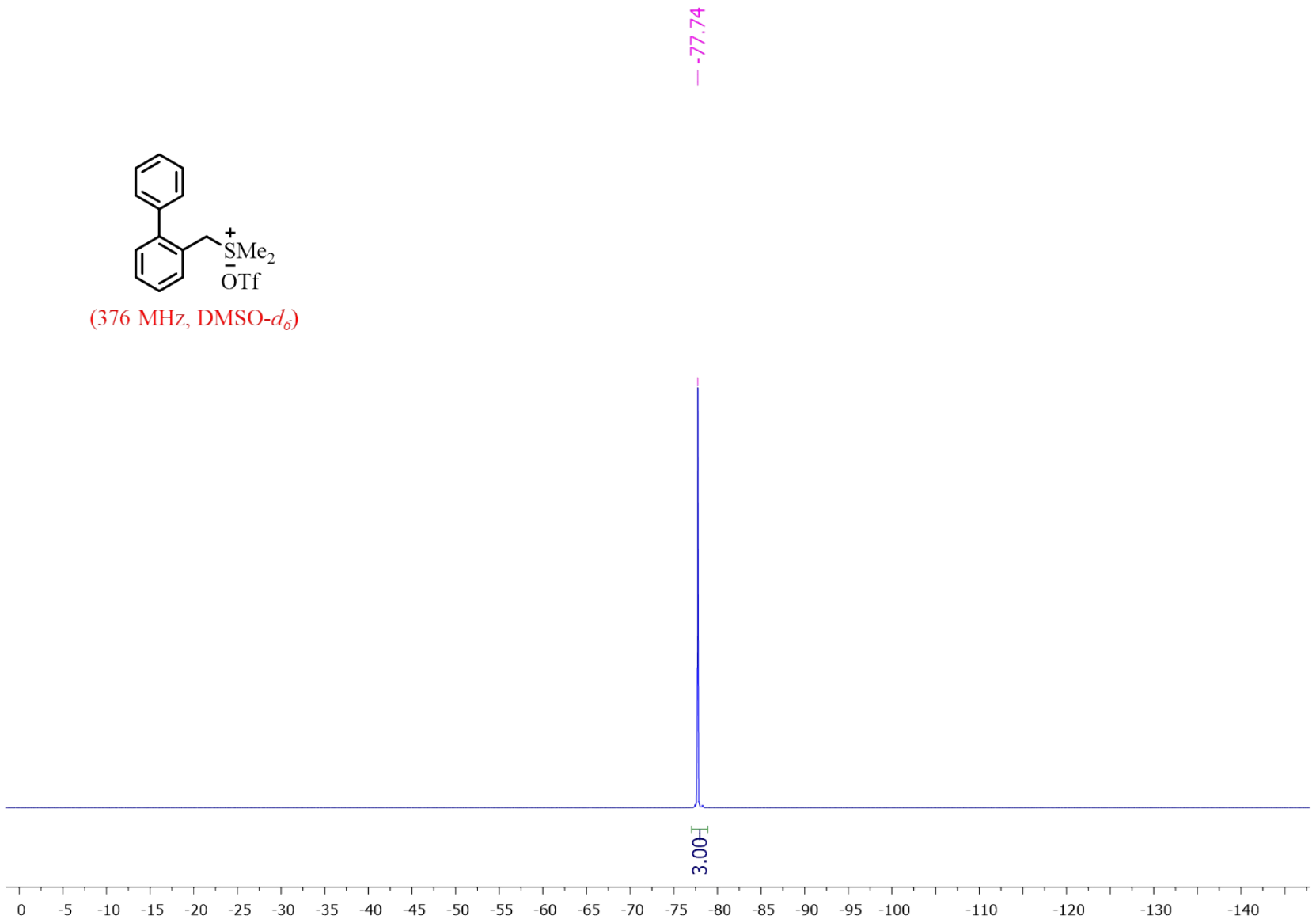


Fig. S47. ^{19}F NMR spectra of ([1,1'-biphenyl]-2-ylmethyl)dimethylsulfonium trifluoromethanesulfonate (**2k**) in DMSO-d_6.

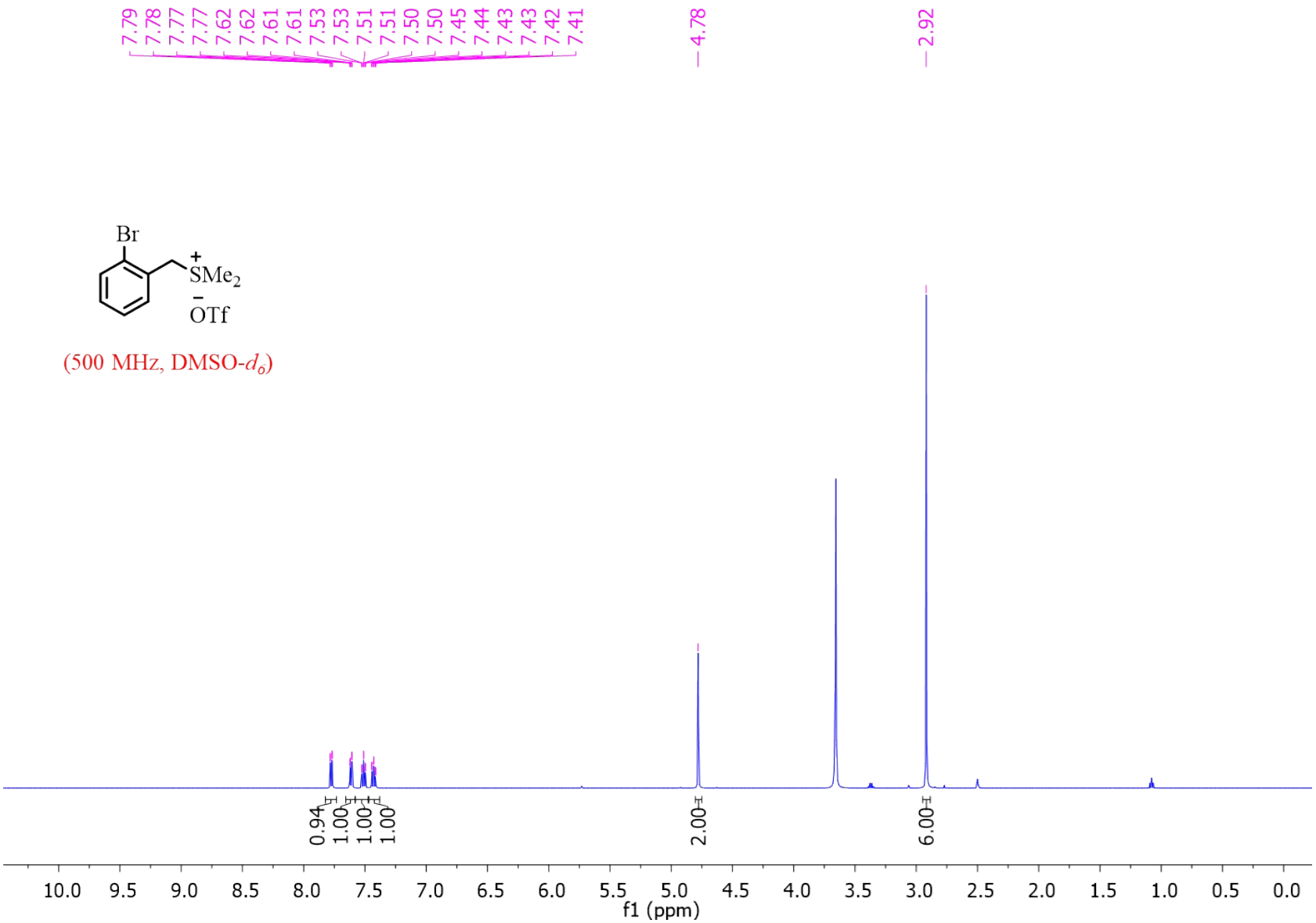


Fig. S48. ^{1}H NMR spectra of (2-bromobenzyl)dimethylsulfonium trifluoromethanesulfonate (**2l**) in DMSO-d_6.

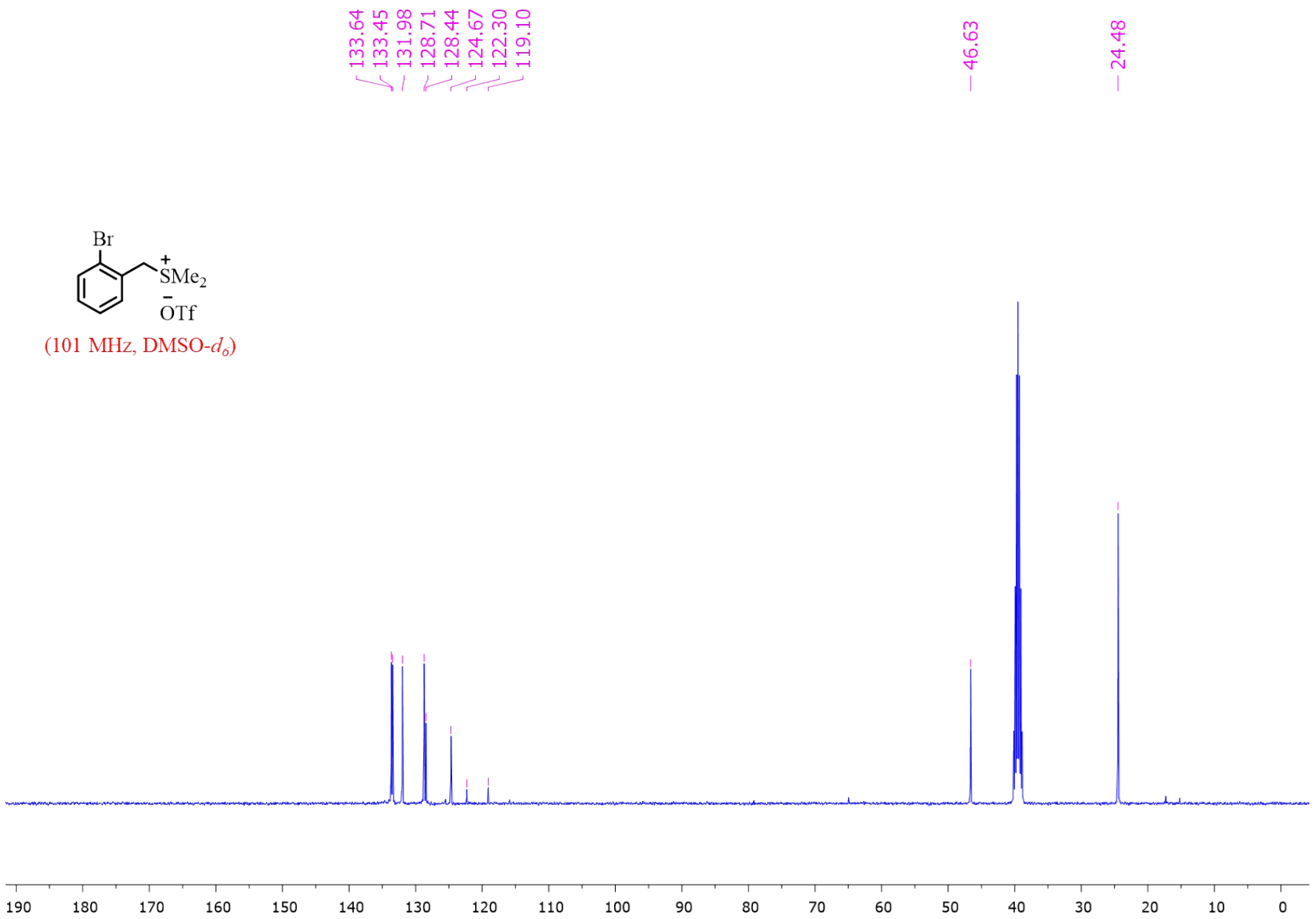


Fig. S49. ^{13}C NMR spectra of (2-bromobenzyl)dimethylsulfonium trifluoromethanesulfonate (**2l**) in DMSO-d_6.

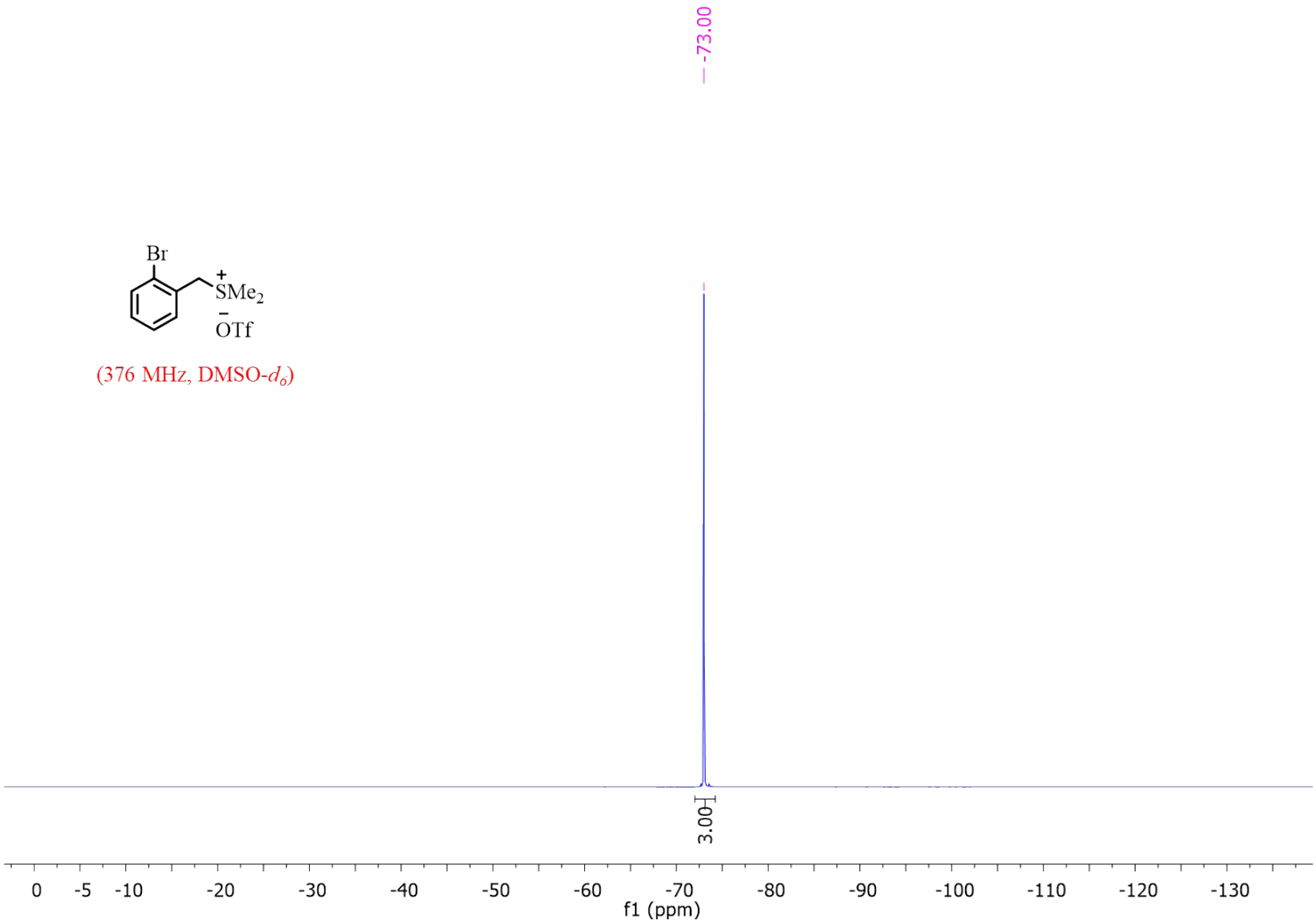


Fig. S50. ^{19}F NMR spectra of (2-bromobenzyl)dimethylsulfonium trifluoromethanesulfonate (**2l**) in DMSO-d_6.

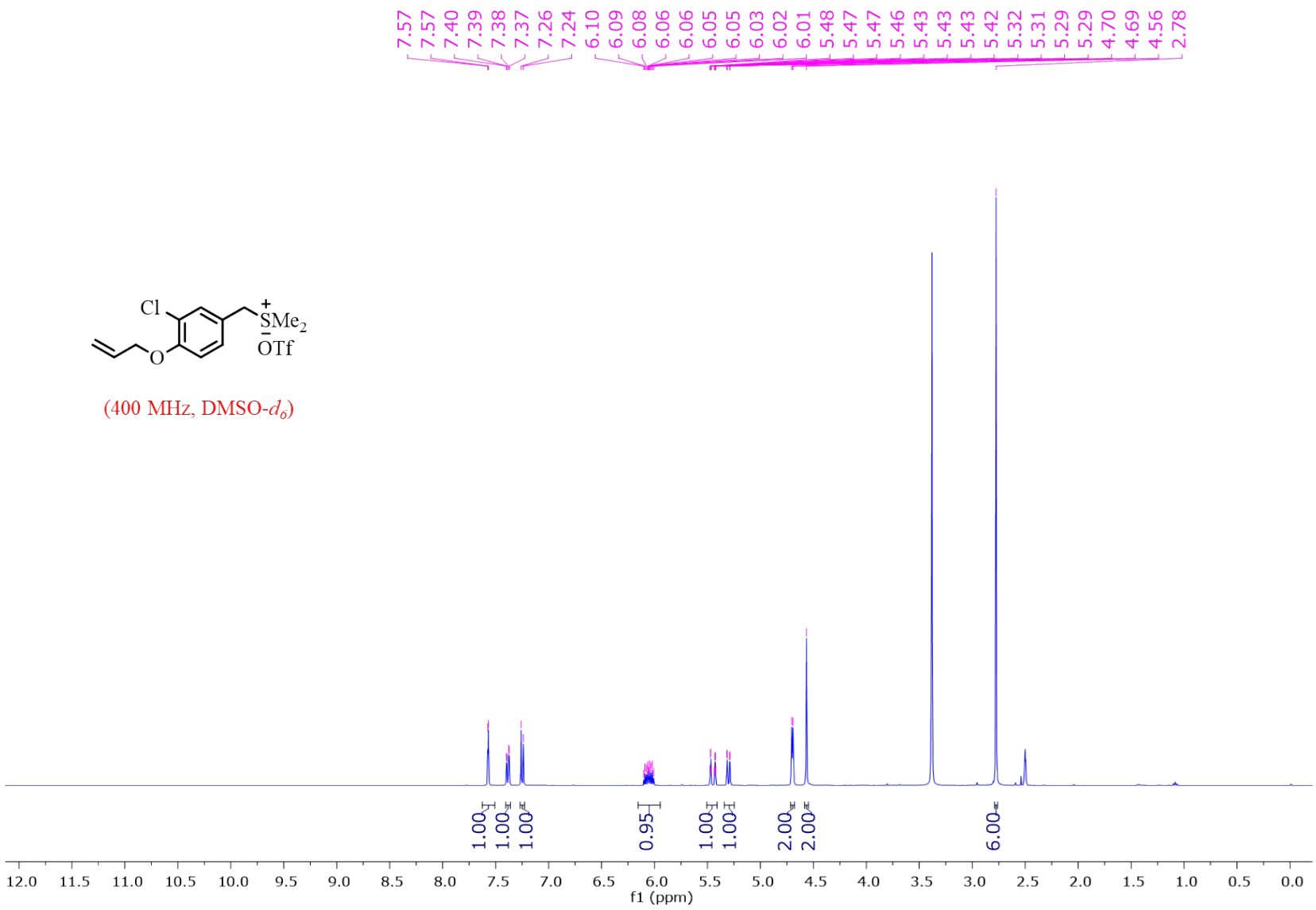


Fig. S51. ^{1}H NMR spectra of (4-(allyloxy)-3-chlorobenzyl)dimethylsulfonium trifluoromethanesulfonate (**2m**) in DMSO-d_6.

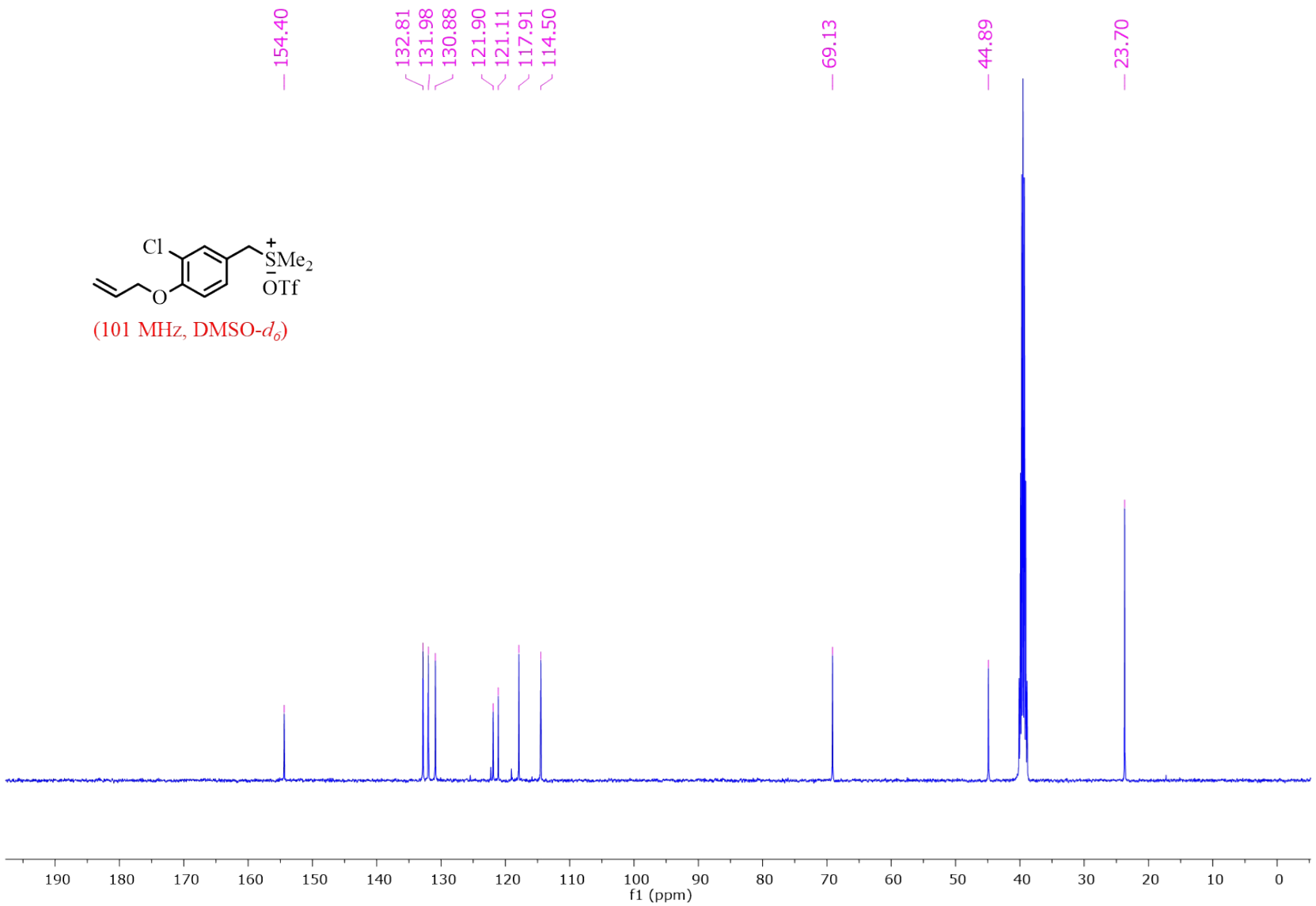


Fig. S52. ^{13}C NMR spectra of (4-(allyloxy)-3-chlorobenzyl)dimethylsulfonium trifluoromethanesulfonate (**2m**) in DMSO-d_6.

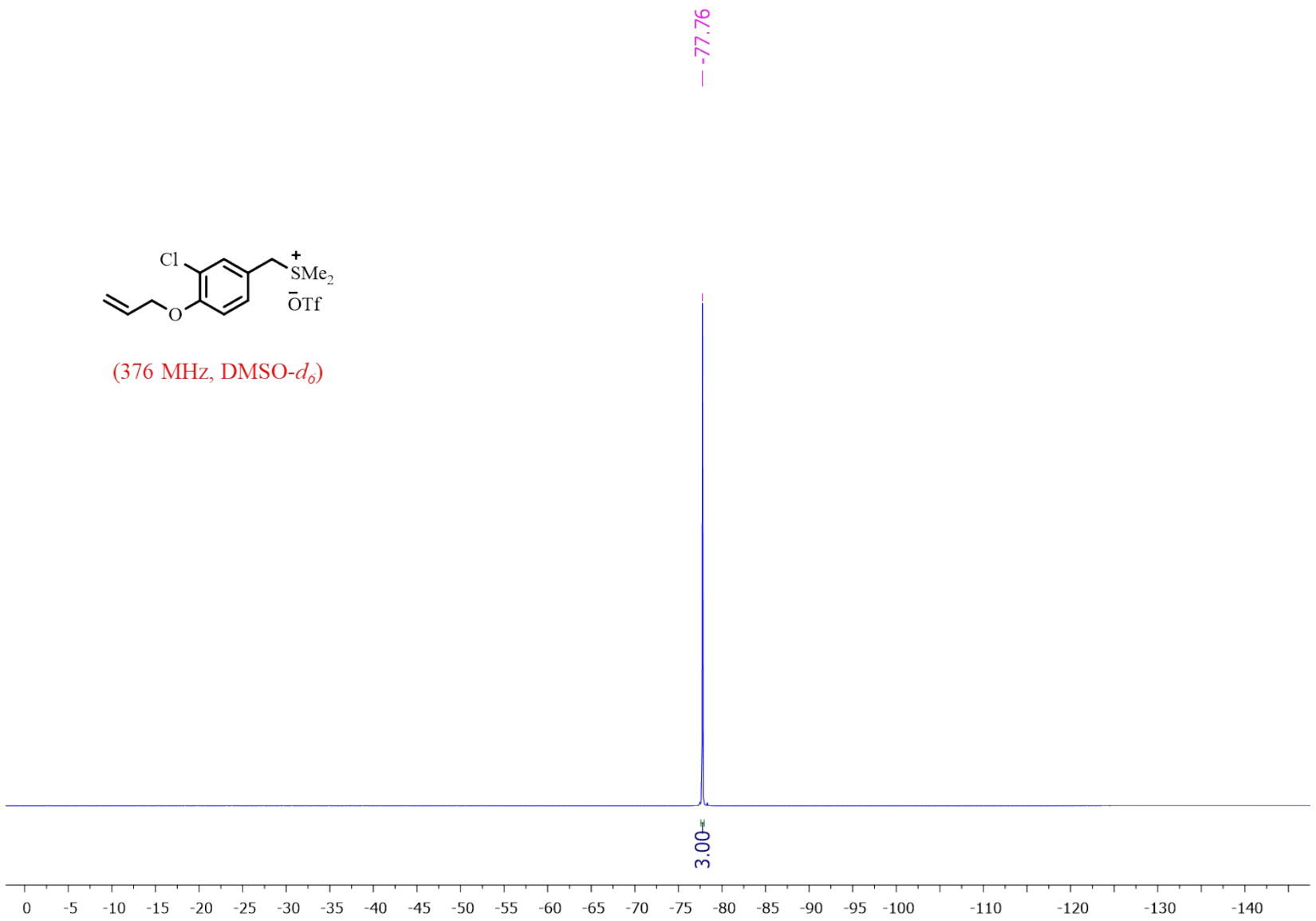


Fig. S53. ^{19}F NMR spectra of (4-(allyloxy)-3-chlorobenzyl)dimethylsulfonium trifluoromethanesulfonate (**2m**) in DMSO-d_6.

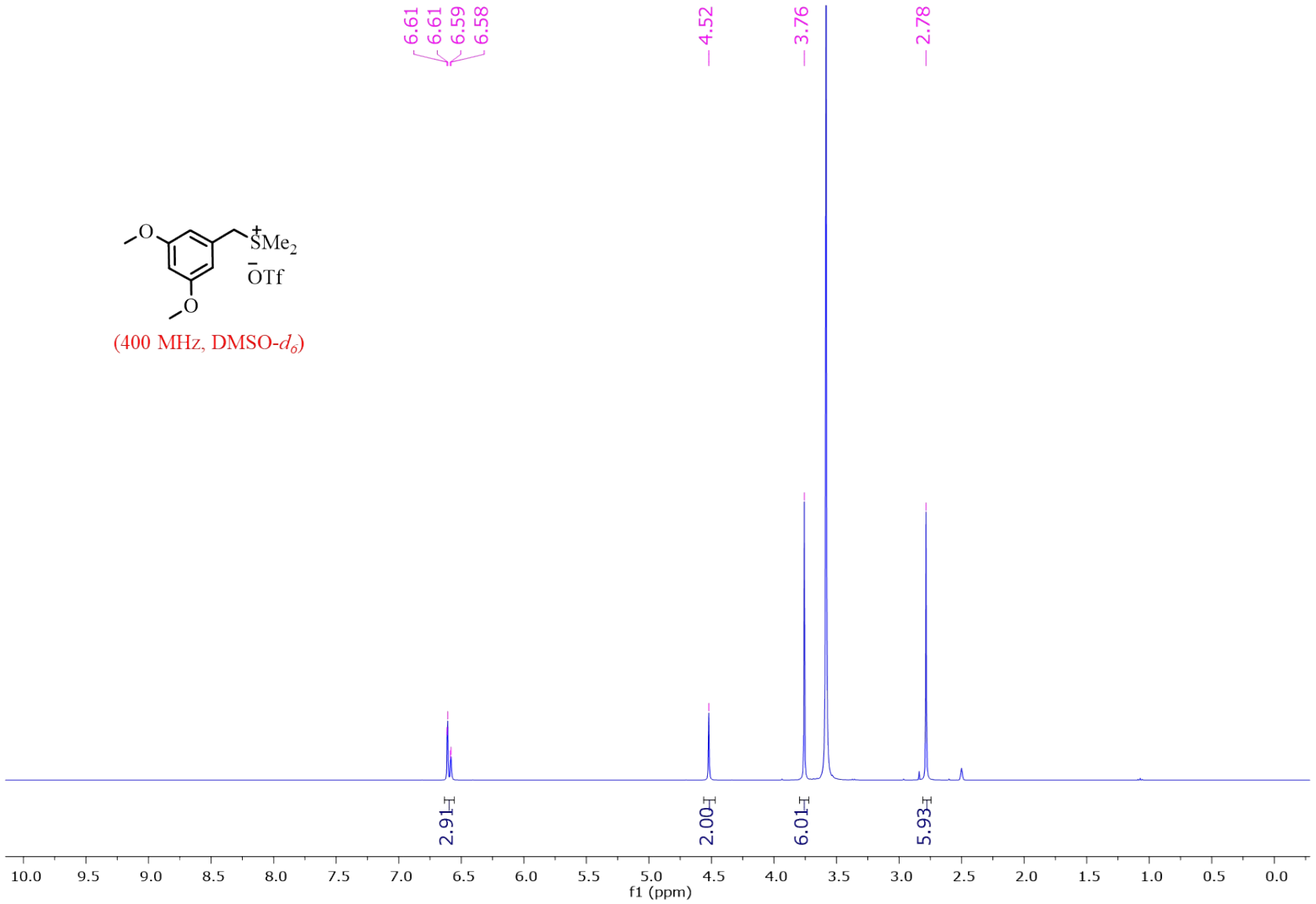


Fig. S54. ^{1}H NMR spectra of (3,5-dimethoxybenzyl)dimethylsulfonium trifluoromethanesulfonate (**2n**) in DMSO-d_6.

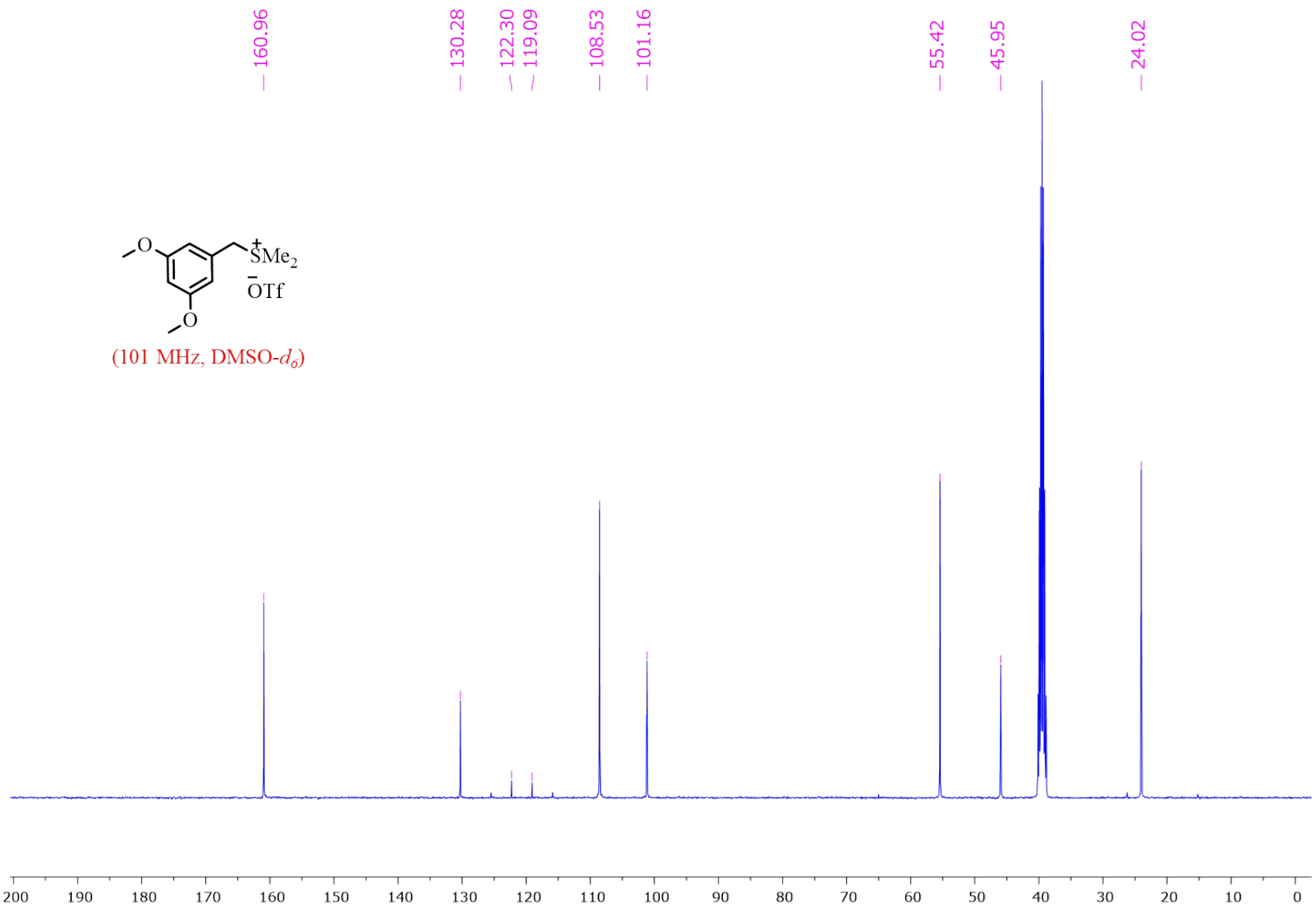


Fig. S55. ^{13}C NMR spectra of (3,5-dimethoxybenzyl)dimethylsulfonium trifluoromethanesulfonate (**2n**) in DMSO-d_6.

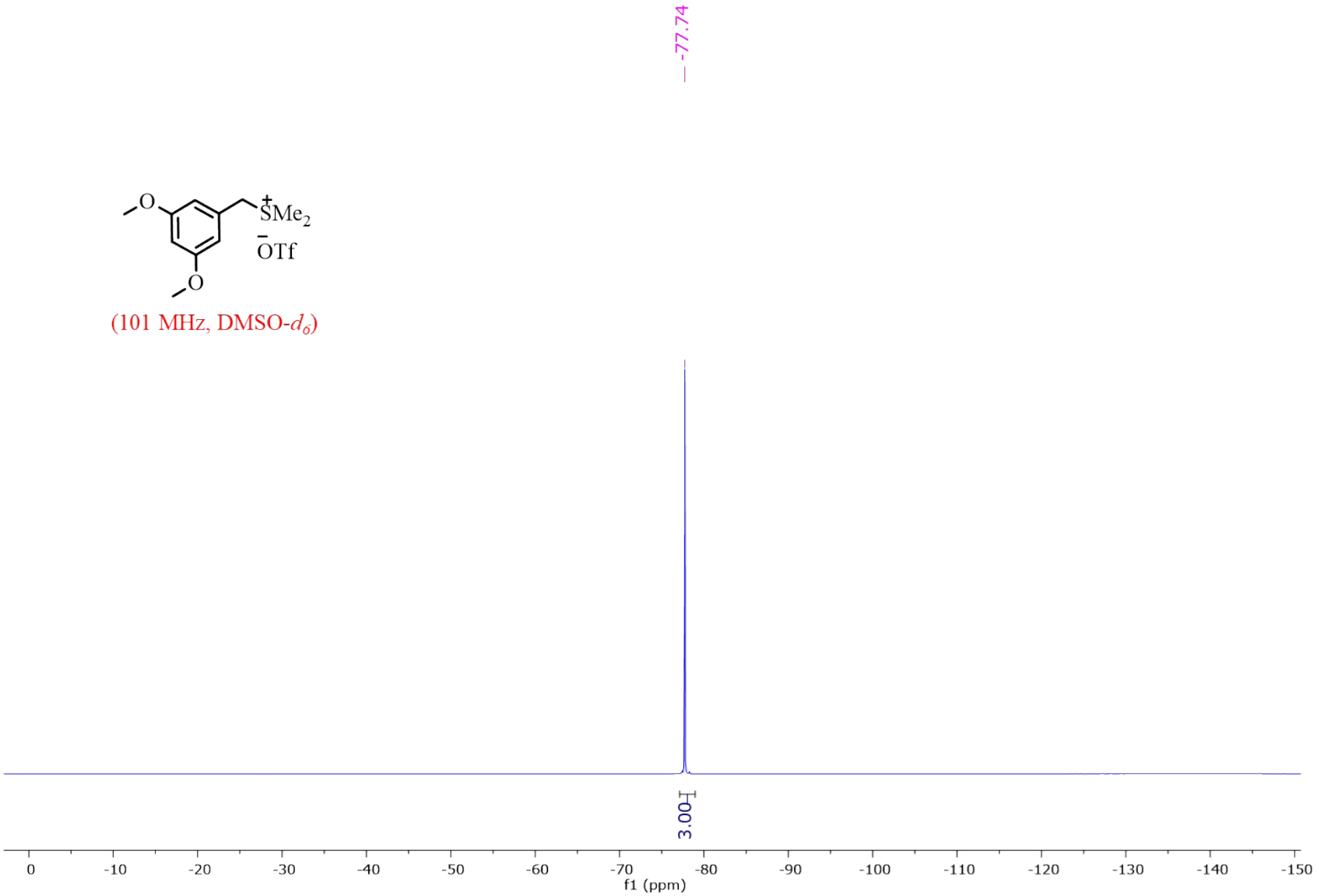


Fig. S56. ^{19}F NMR spectra of (3,5-dimethoxybenzyl)dimethylsulfonium trifluoromethanesulfonate (**2n**) in DMSO-d_6.

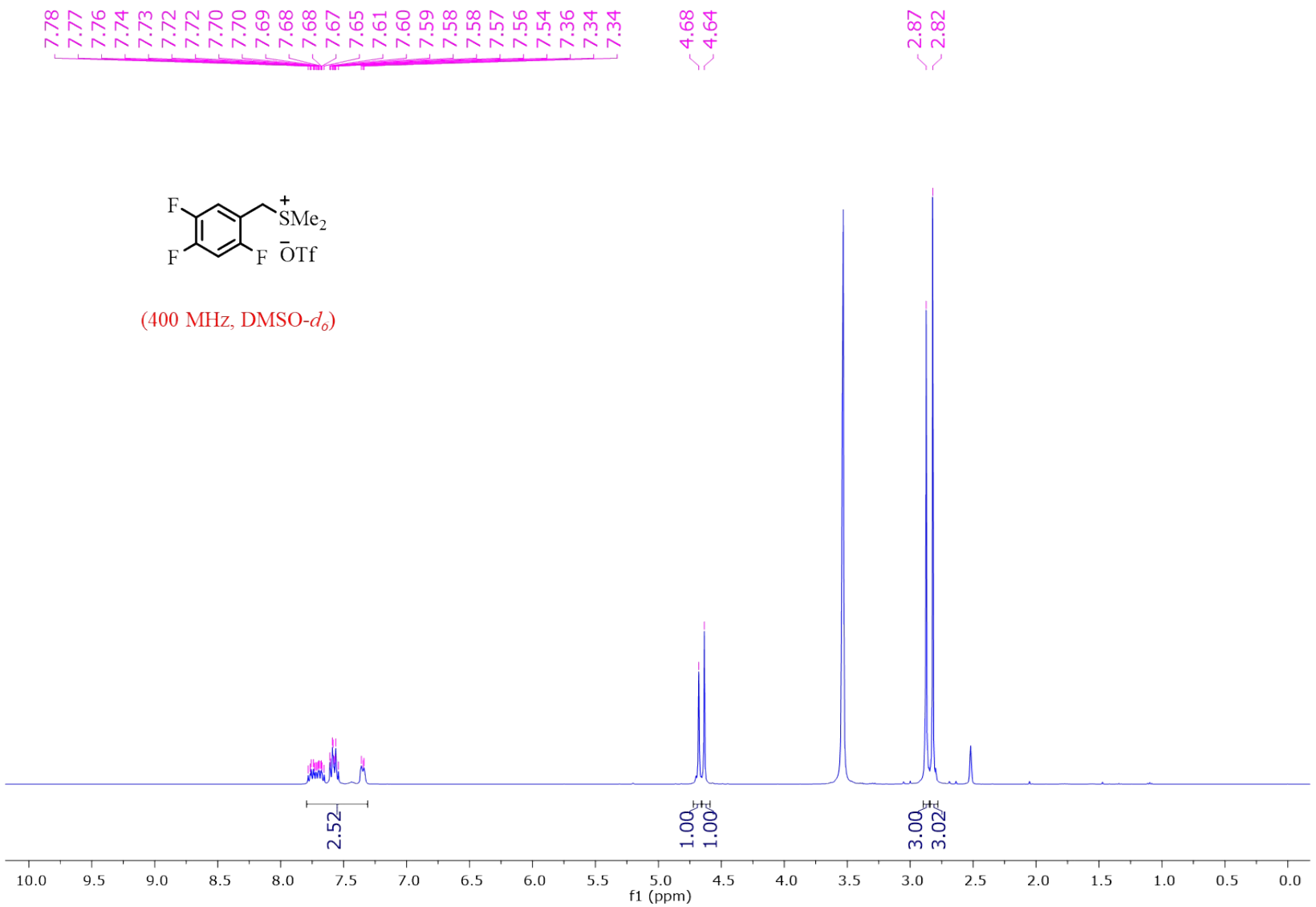


Fig. S57. ^{1}H NMR spectra of dimethyl(2,4,5-trifluorobenzyl)sulfonium trifluoromethanesulfonate (**2o**) in DMSO-d_6.

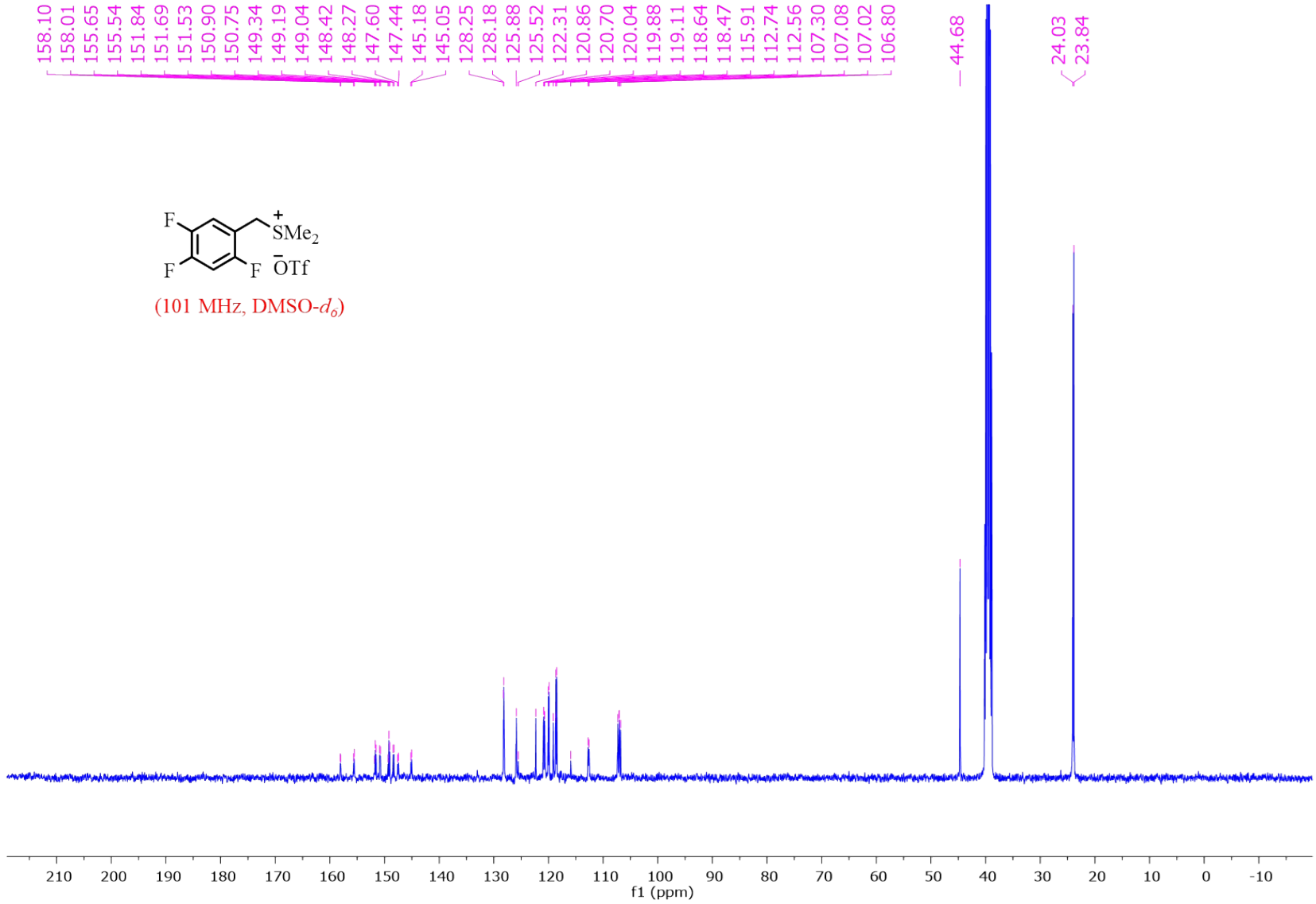


Fig. S58. ^{13}C NMR spectra of dimethyl(2,4,5-trifluorobenzyl)sulfonium trifluoromethanesulfonate (**2o**) in DMSO-d_6.

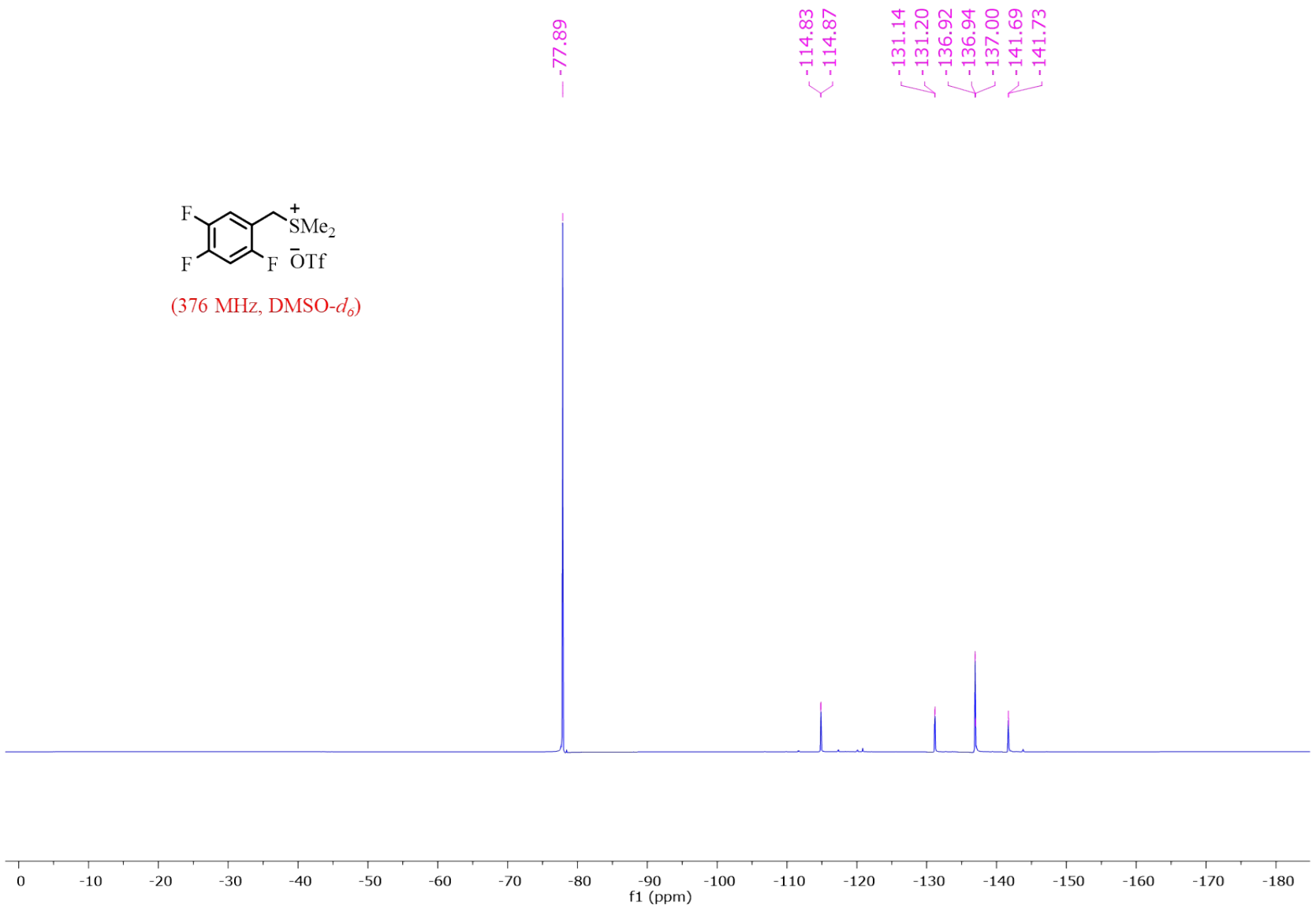


Fig. S59. ^{19}F NMR spectra of dimethyl(2,4,5-trifluorobenzyl)sulfonium trifluoromethanesulfonate (**2o**) in DMSO-d_6.

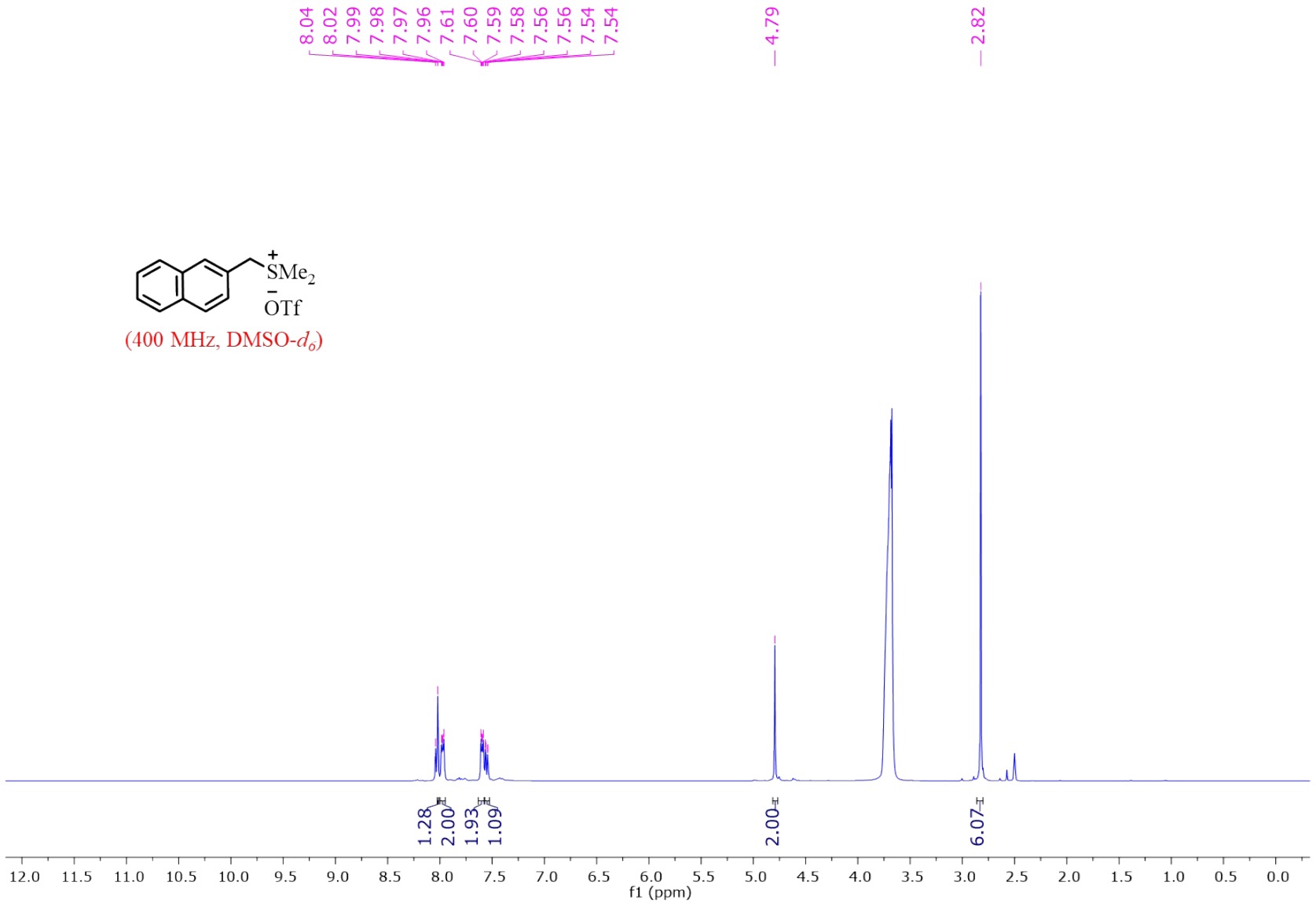


Fig. S60. ^{1}H NMR spectra of dimethyl(naphthalen-2-ylmethyl)sulfonium trifluoromethanesulfonate (**2p**) in DMSO-d_6.

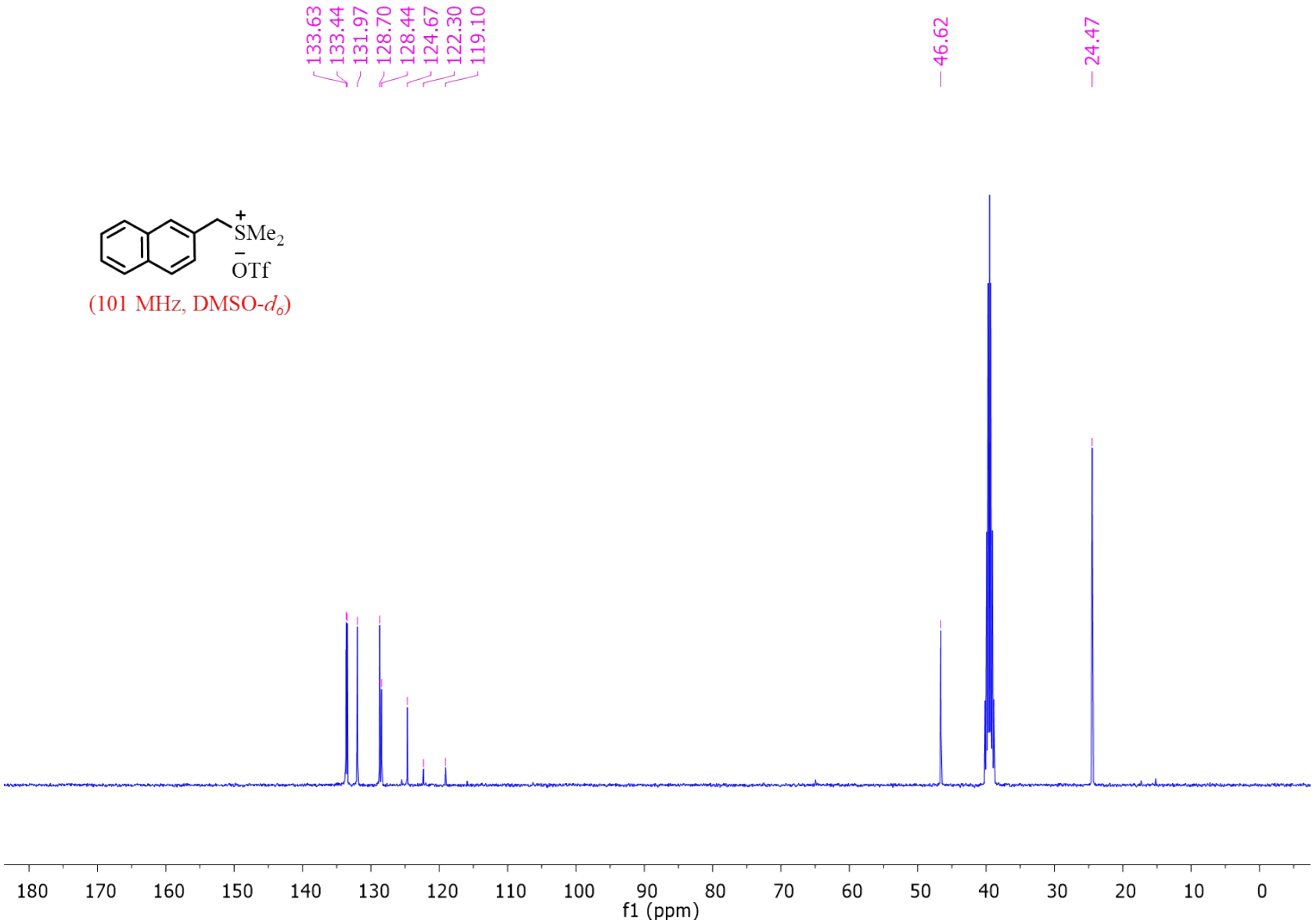


Fig. S61. ^{13}C NMR spectra of dimethyl(naphthalen-2-ylmethyl)sulfonium trifluoromethanesulfonate (**2p**) in DMSO-d_6.

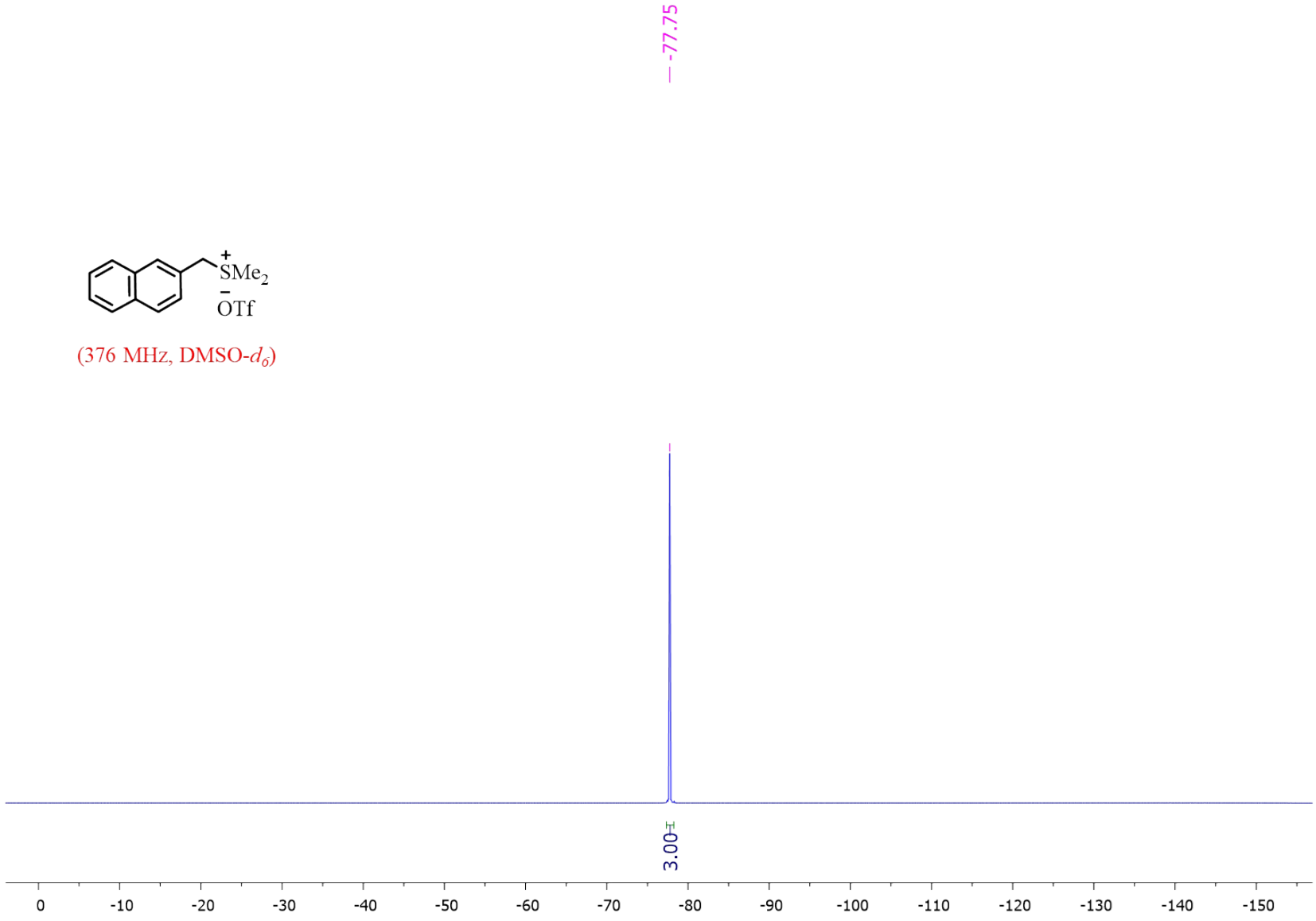


Fig. S62. ^{19}F NMR spectra of dimethyl(naphthalen-2-ylmethyl)sulfonium trifluoromethanesulfonate (**2p**) in DMSO-d_6.

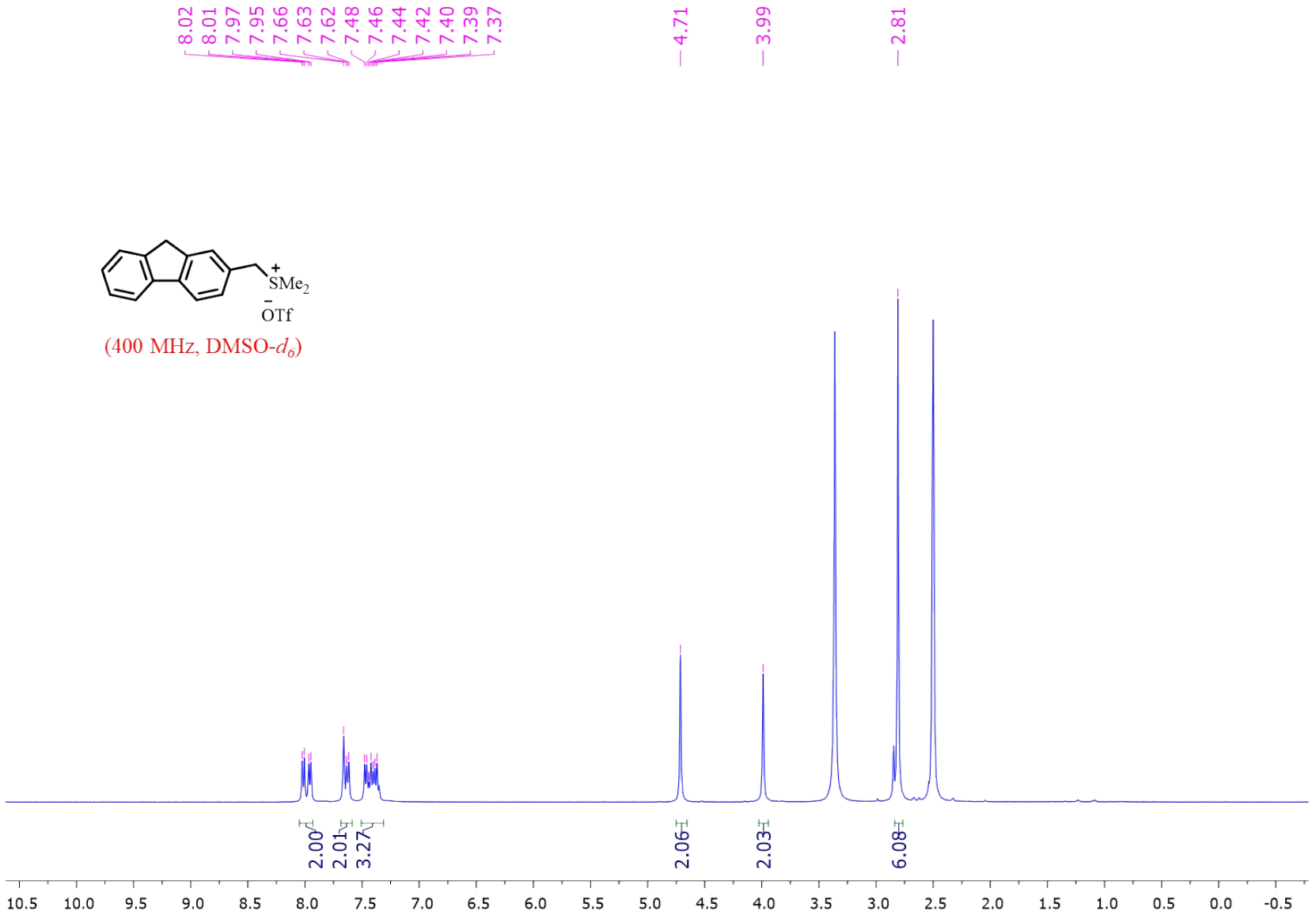


Fig. S63. ^{1}H NMR spectra of (9H-Fluoren-2-yl)methyl)dimethylsulfonium trifluoromethanesulfonate (**2q**) in DMSO-d_6.

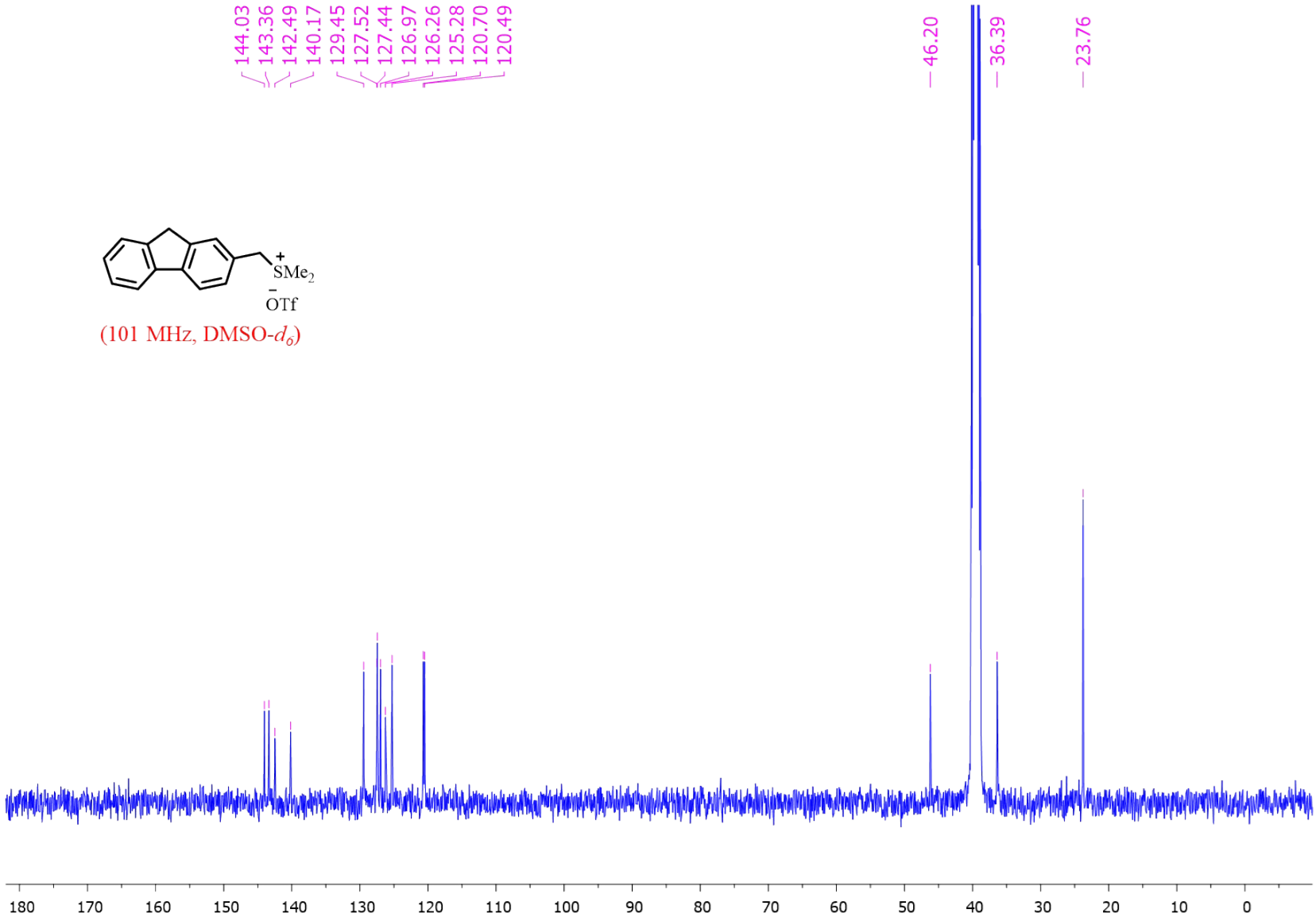


Fig. S64. ^{13}C NMR spectra of (9H-Fluoren-2-yl)methyl)dimethylsulfonium trifluoromethanesulfonate (**2q**) in DMSO-d_6.

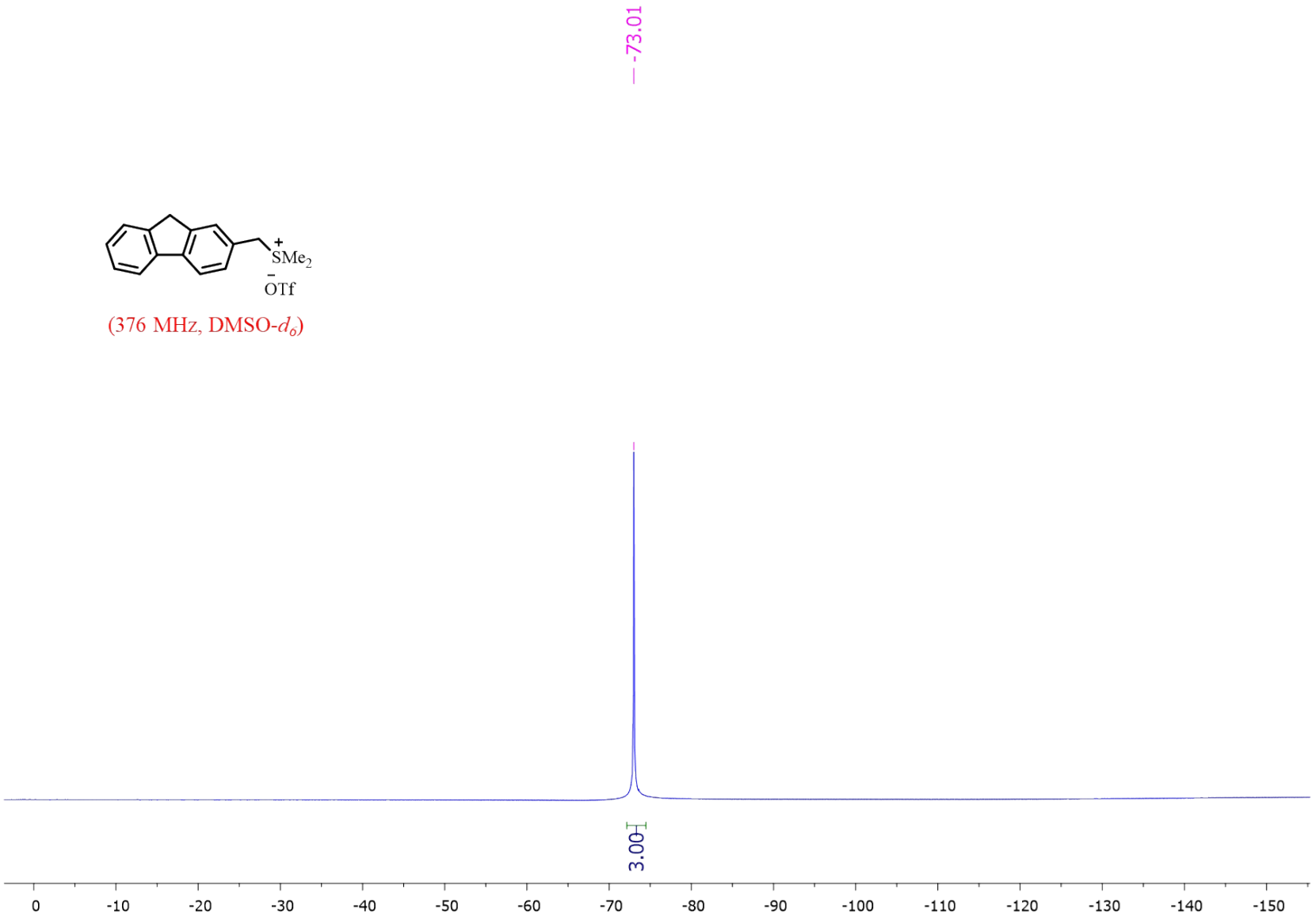


Fig. S65. ^{19}F NMR spectra of (9H-Fluoren-2-yl)methyl)dimethylsulfonium trifluoromethanesulfonate (**2q**) in DMSO-d_6.

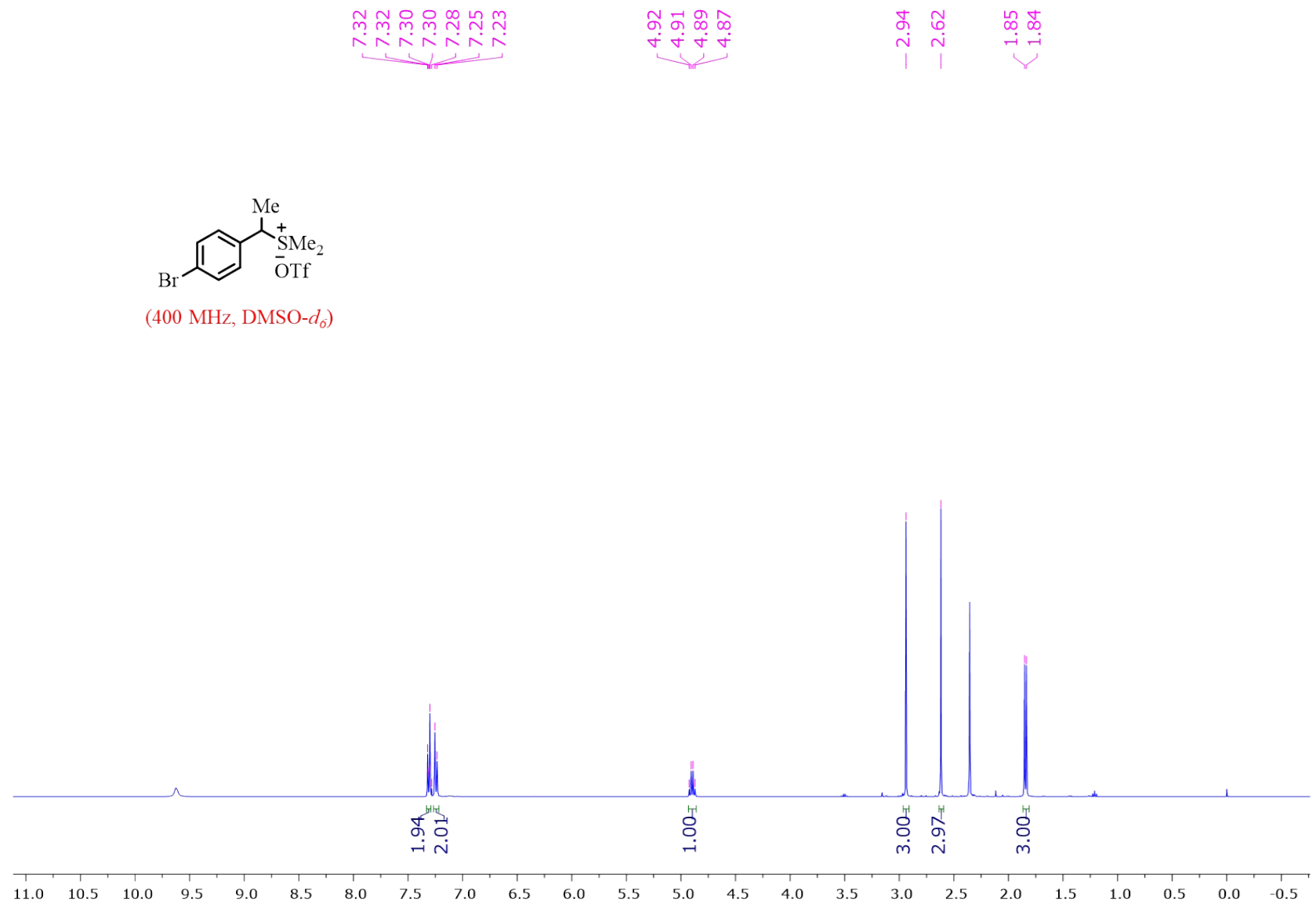


Fig. S66. ^{1}H NMR spectra of (1-(4-Bromophenyl)ethyl)dimethylsulfonium trifluoromethanesulfonate (**2r**) in DMSO-d_6.

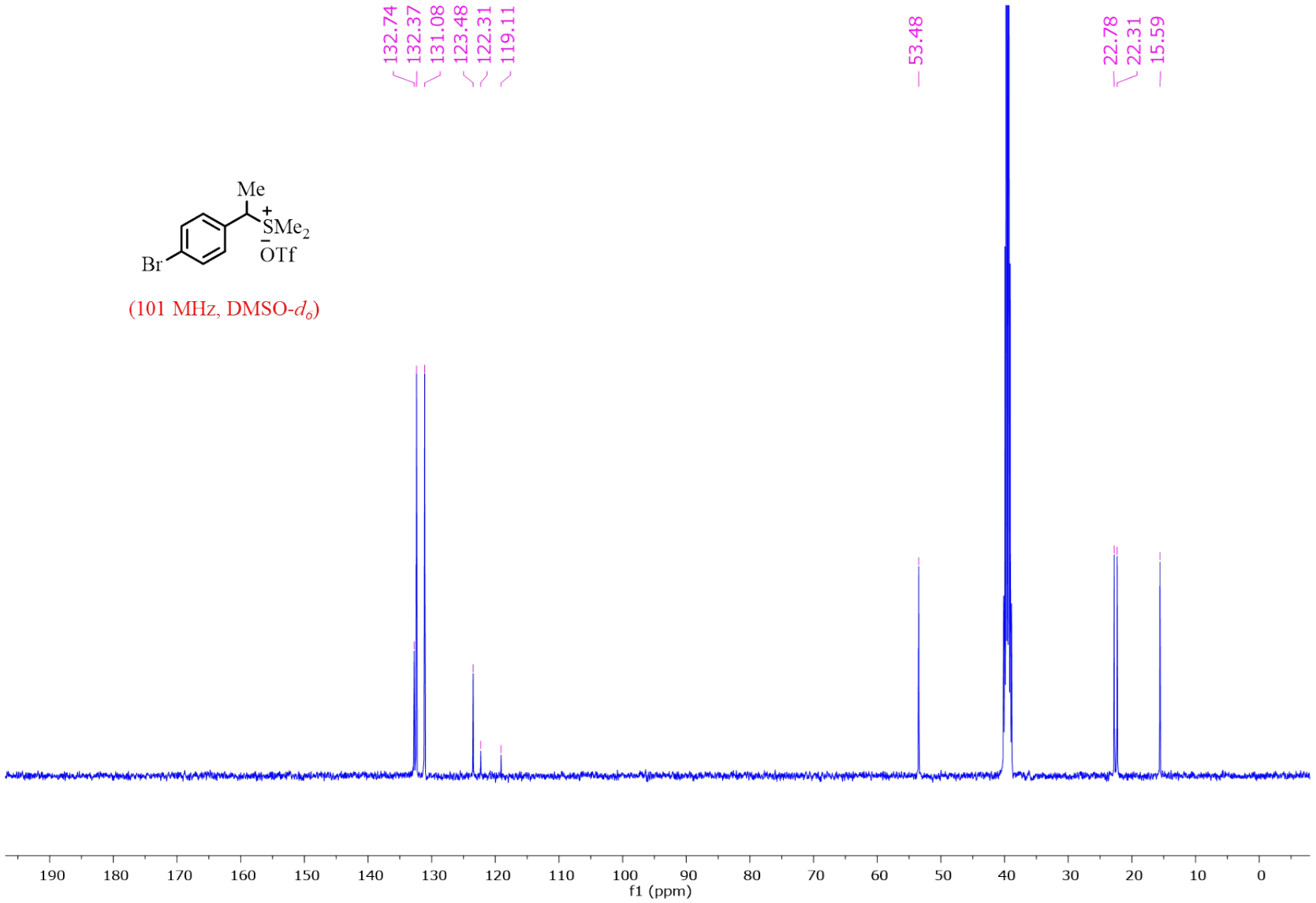


Fig. S67. ^{13}C NMR spectra of (1-(4-Bromophenyl)ethyl)dimethylsulfonium trifluoromethanesulfonate (**2r**) in DMSO-d_6.

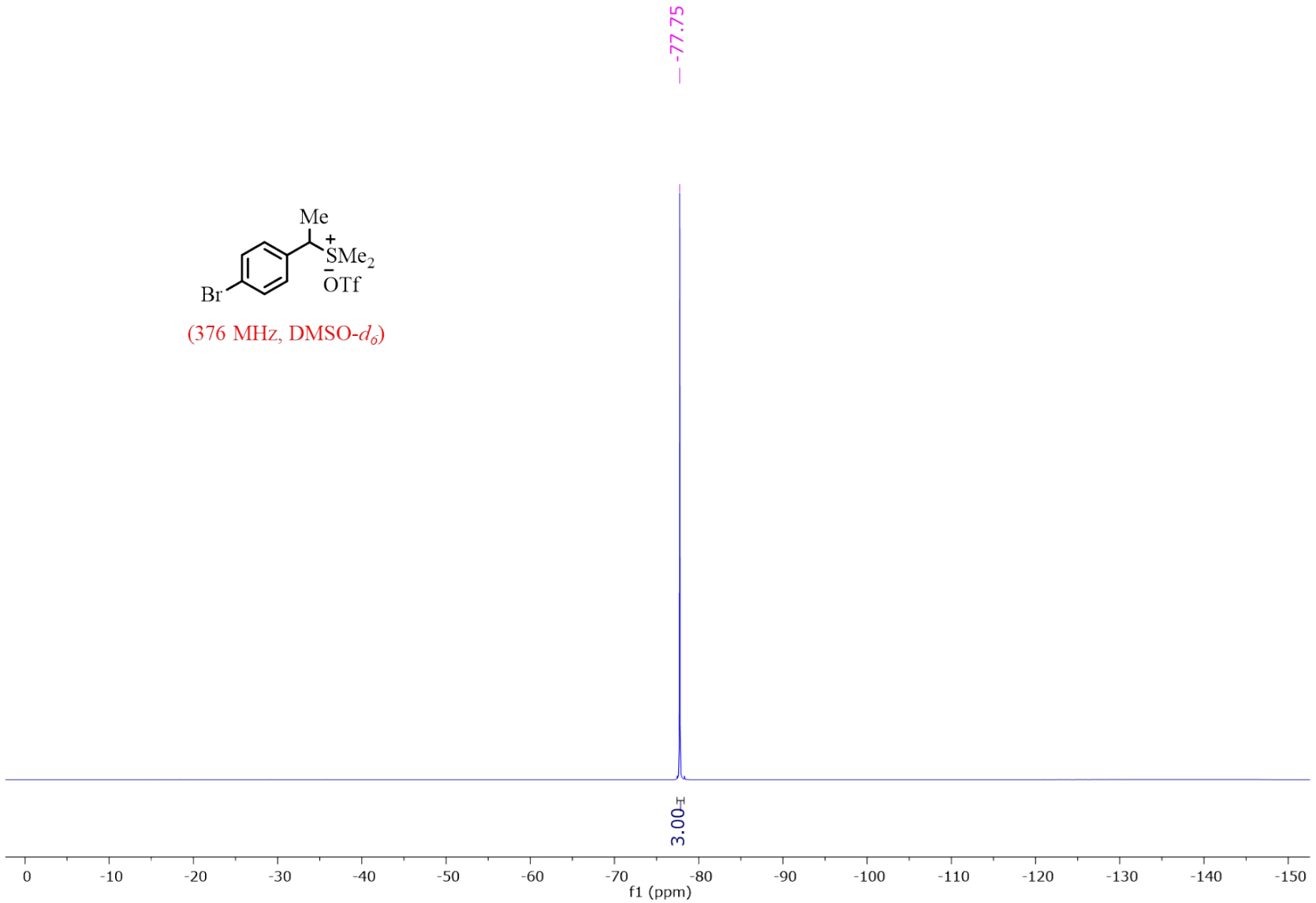


Fig. S68. ^{19}F NMR spectra of (1-(4-Bromophenyl)ethyl)dimethylsulfonium trifluoromethanesulfonate (**2r**) in DMSO-d_6.

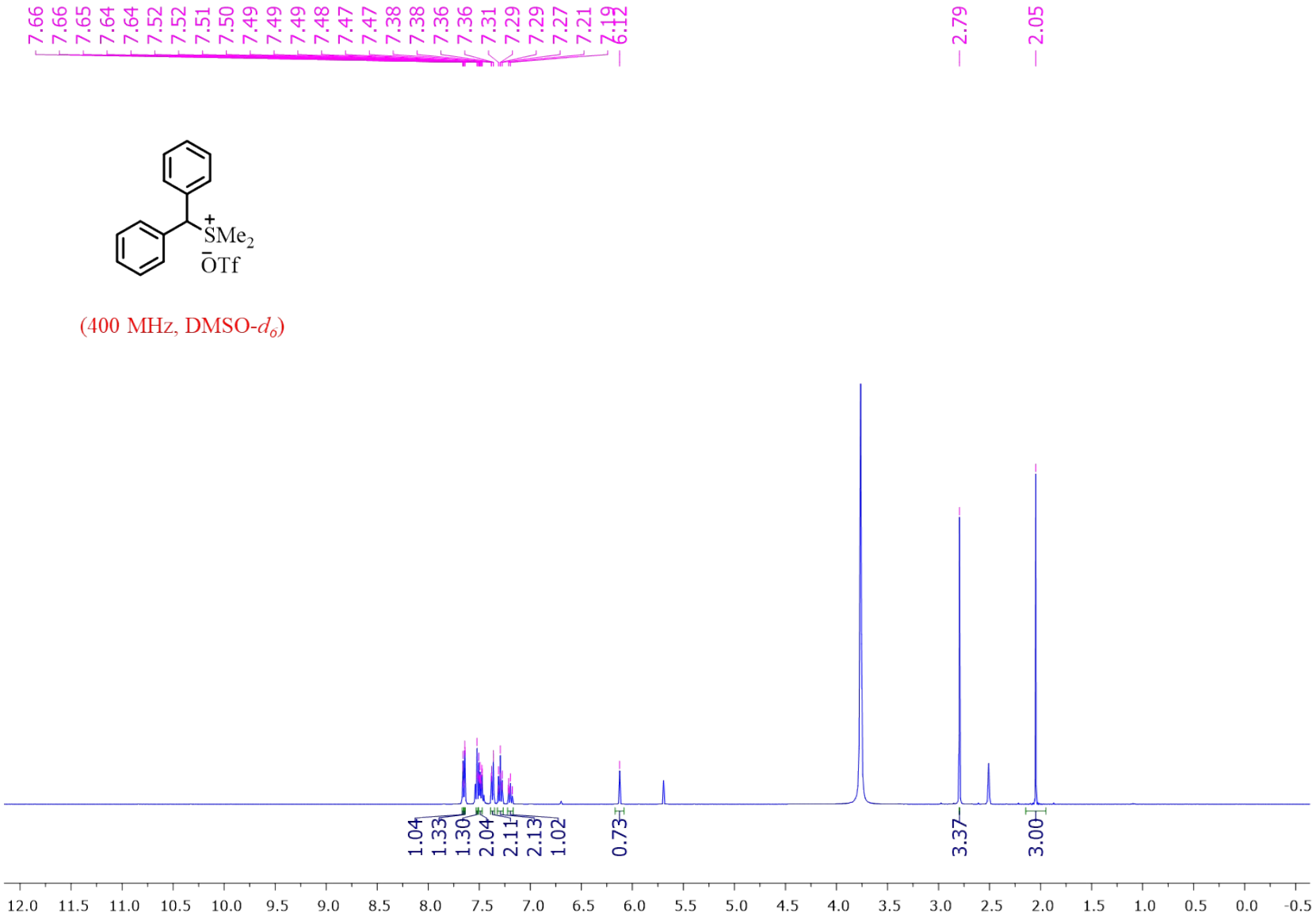


Fig. S69. ^{1}H NMR spectra of benzhydryldimethylsulfonium trifluoromethanesulfonate (**2s**) in DMSO-d_6.

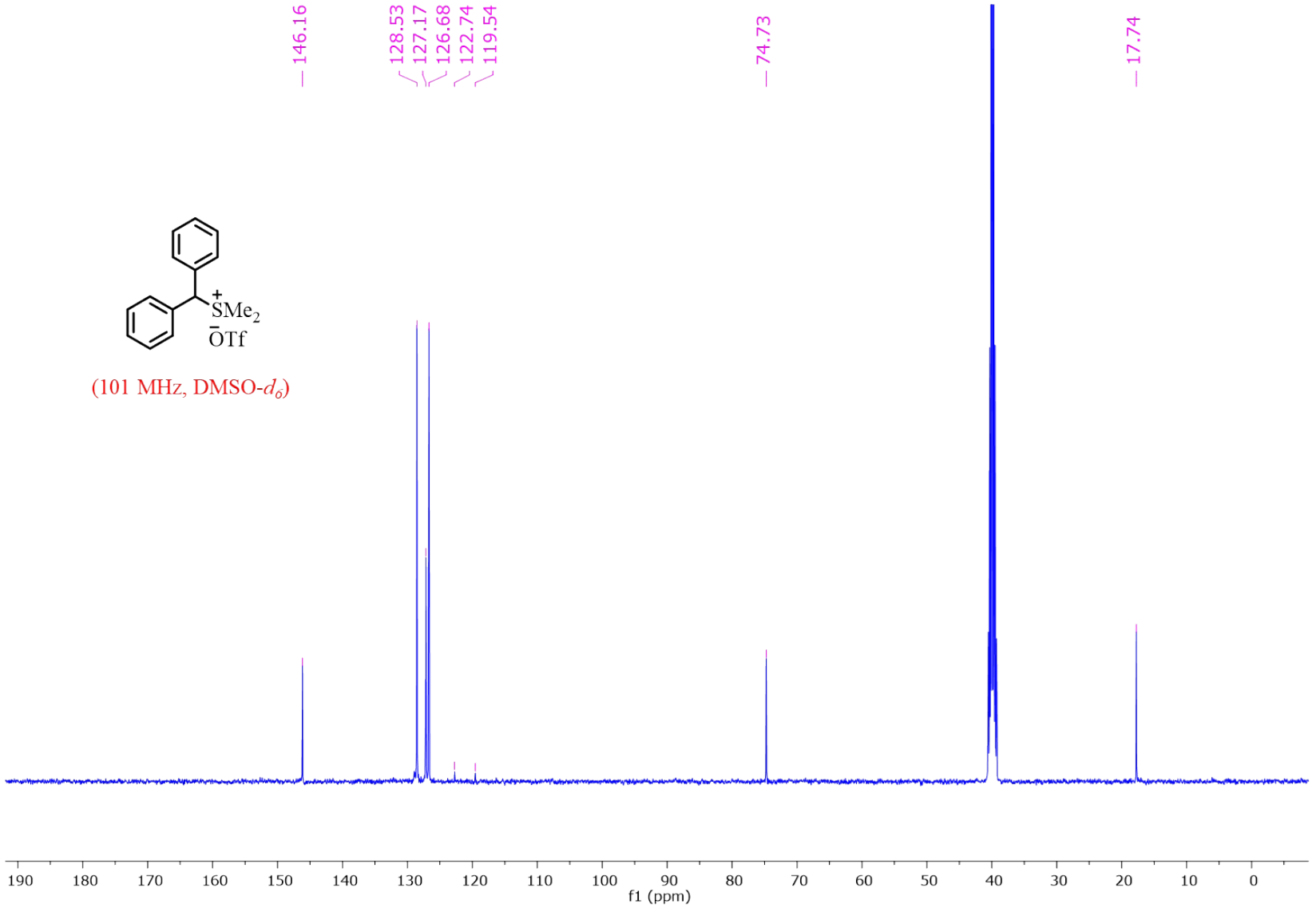


Fig. S70. ^{13}C NMR spectra of benzhydryldimethylsulfonium trifluoromethanesulfonate (**2s**) in DMSO-d_6.

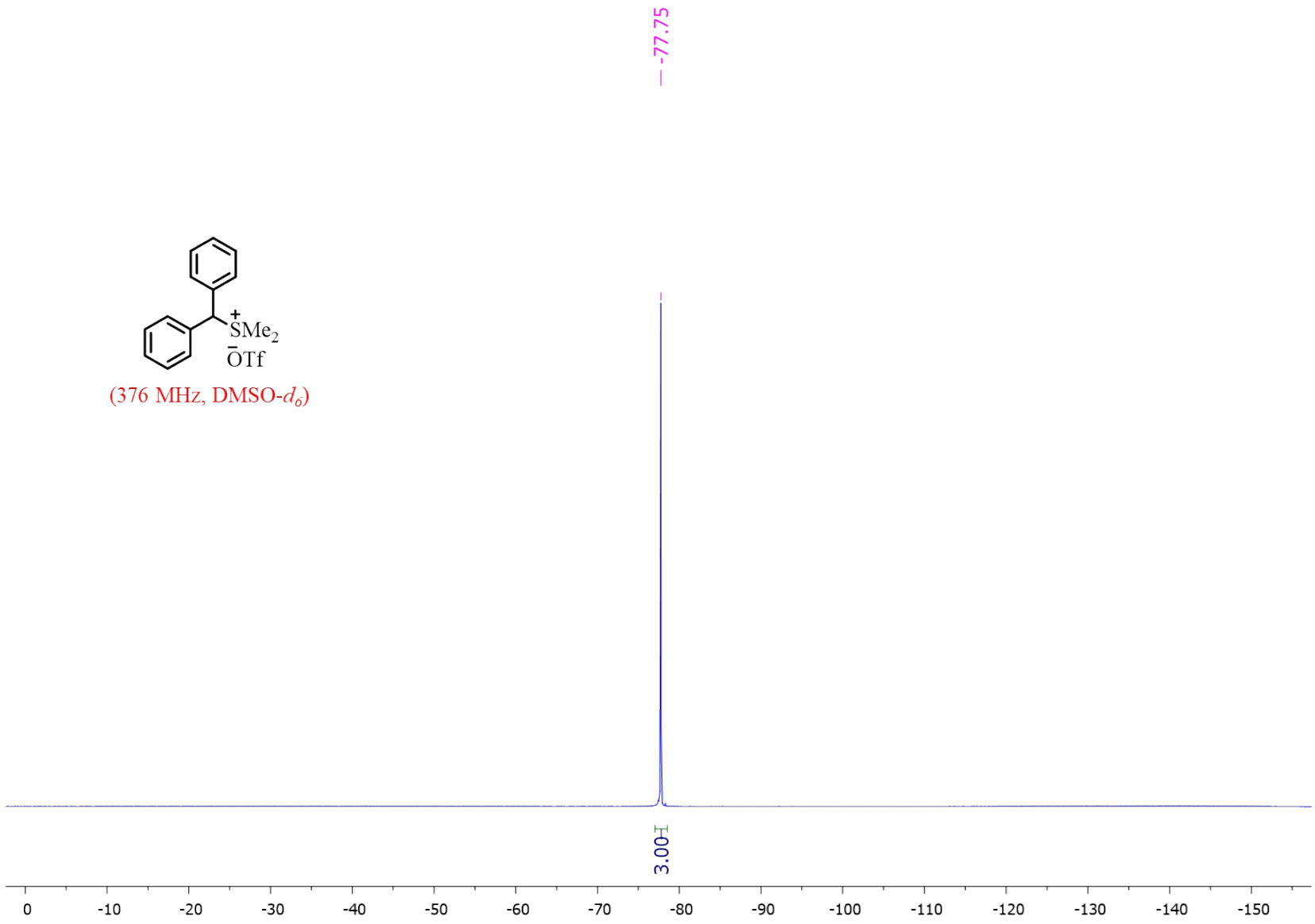


Fig. S71. ^{19}F NMR spectra of benzhydryldimethylsulfonium trifluoromethanesulfonate (**2s**) in DMSO-d_6.

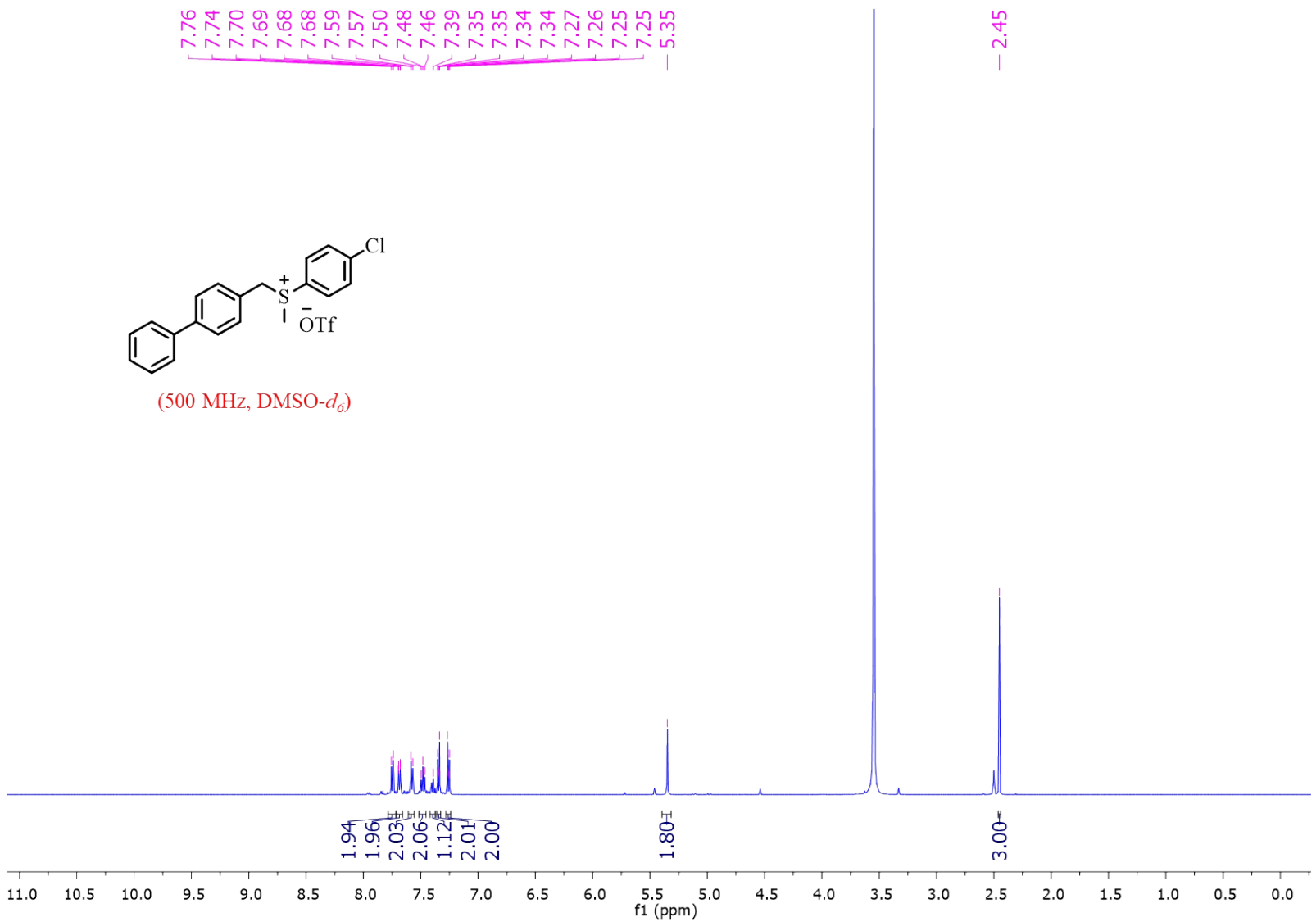


Fig. S72. ^{1}H NMR spectra of ([1,1'-biphenyl]-4-ylmethyl)(4-chlorophenyl)(methyl)sulfonium trifluoromethanesulfonate (**2t**) in DMSO-d_6.

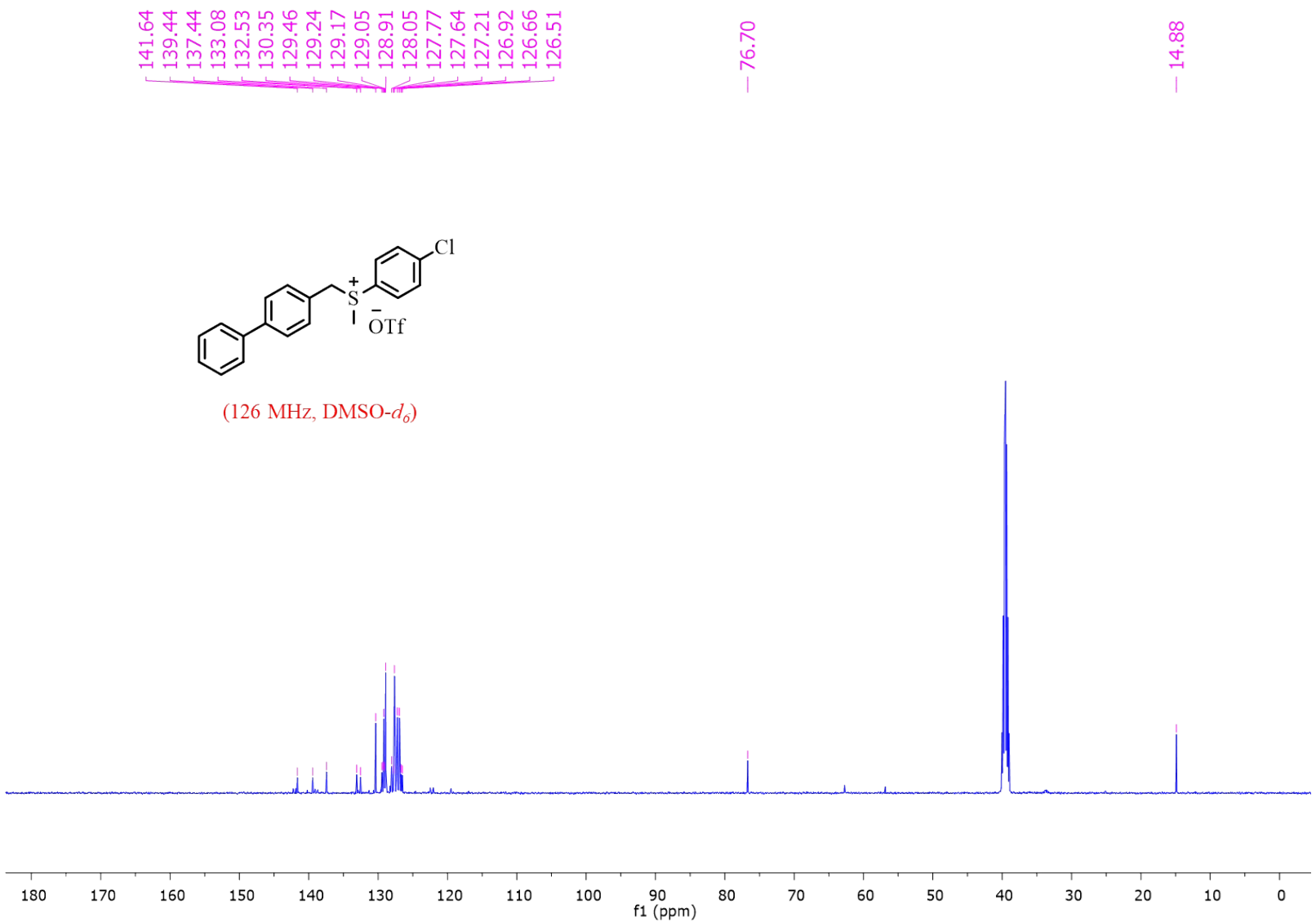


Fig. S73. ^{13}C NMR spectra of ([1,1'-biphenyl]-4-ylmethyl)(4-chlorophenyl)(methyl)sulfonium trifluoromethanesulfonate (**2t**) in DMSO-d_6.

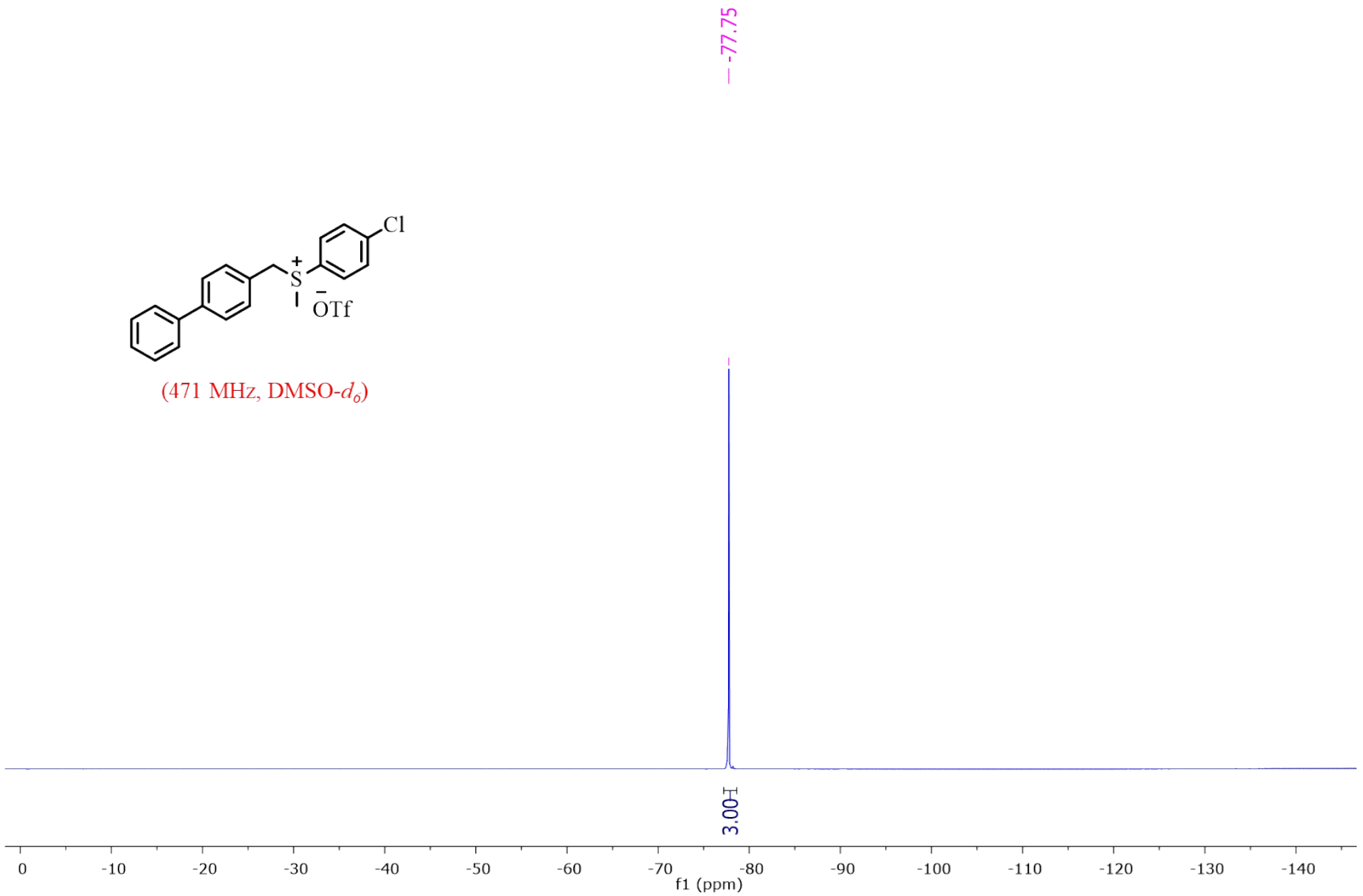


Fig. S74. ^{19}F NMR spectra of ([1,1'-biphenyl]-4-ylmethyl)(4-chlorophenyl)(methyl)sulfonium trifluoromethanesulfonate (**2t**) in DMSO-d_6.

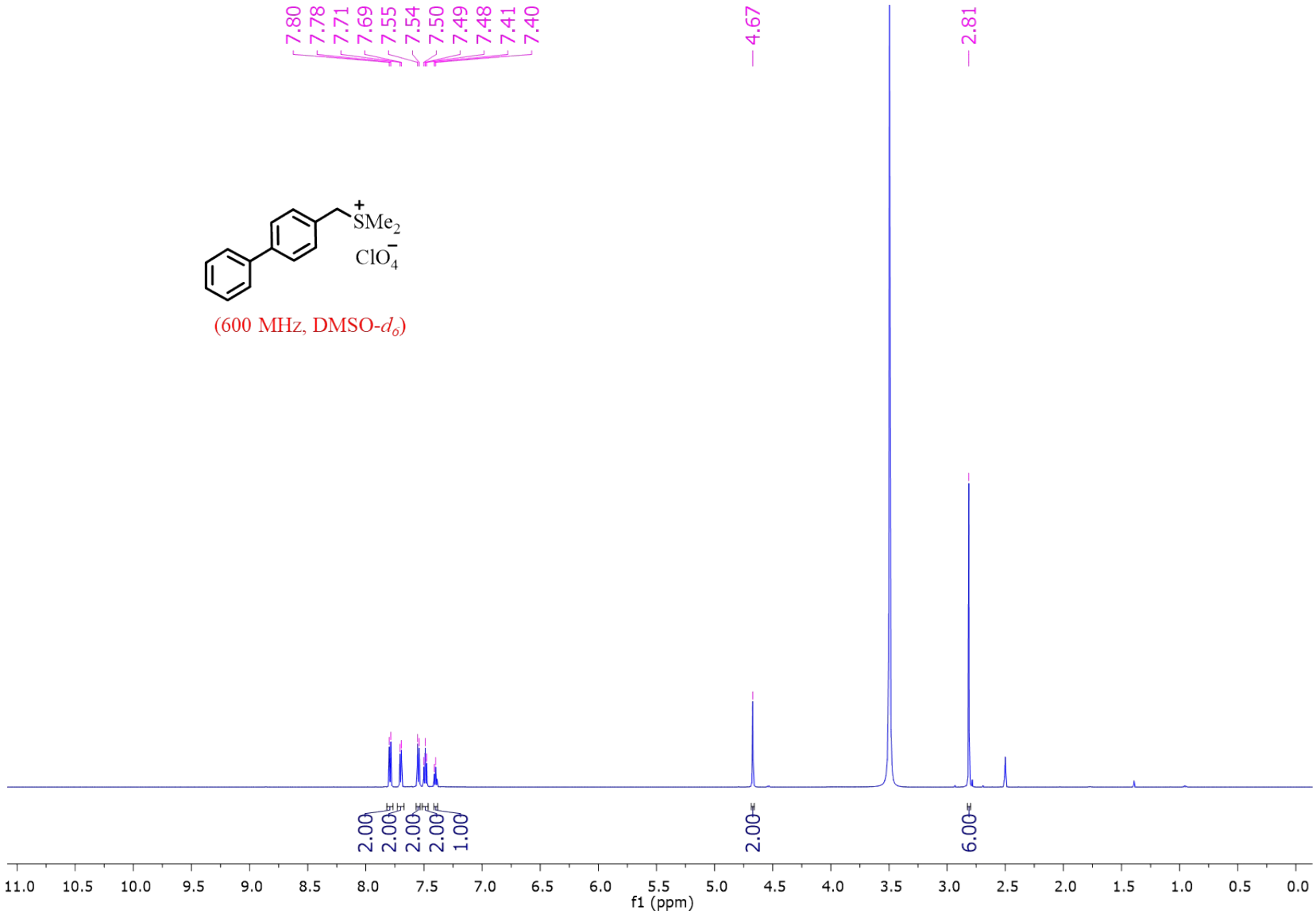


Fig. S75. ^{1}H NMR spectra of ([1,1'-biphenyl]-4-ylmethyl) dimethyl sulfonium perchlorate (**2u**) in DMSO-d_6.

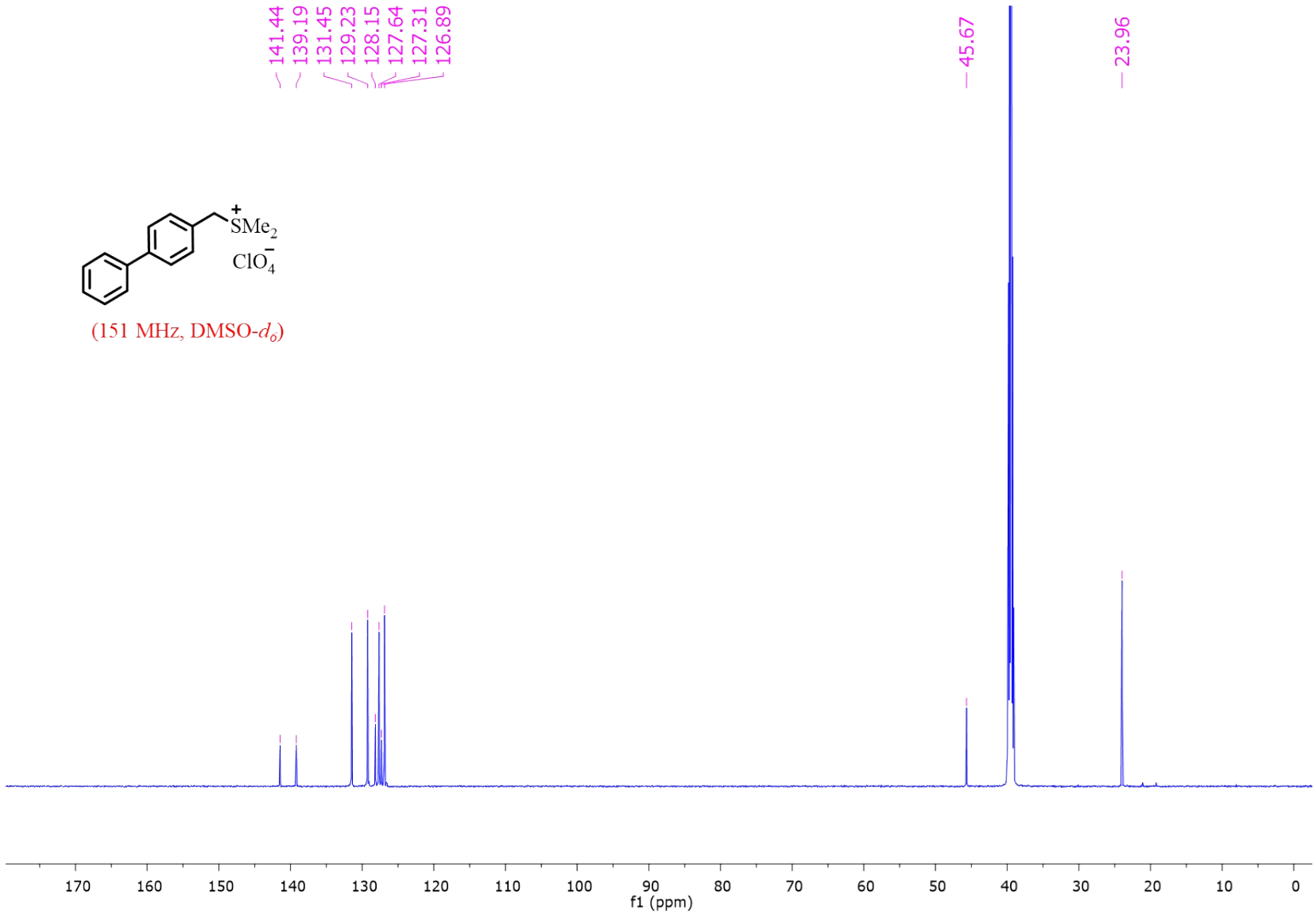


Fig. S76. ^{13}C NMR spectra of ([1,1'-biphenyl]-4-ylmethyl) dimethyl sulfonium perchlorate (**2u**) in DMSO-d_6.

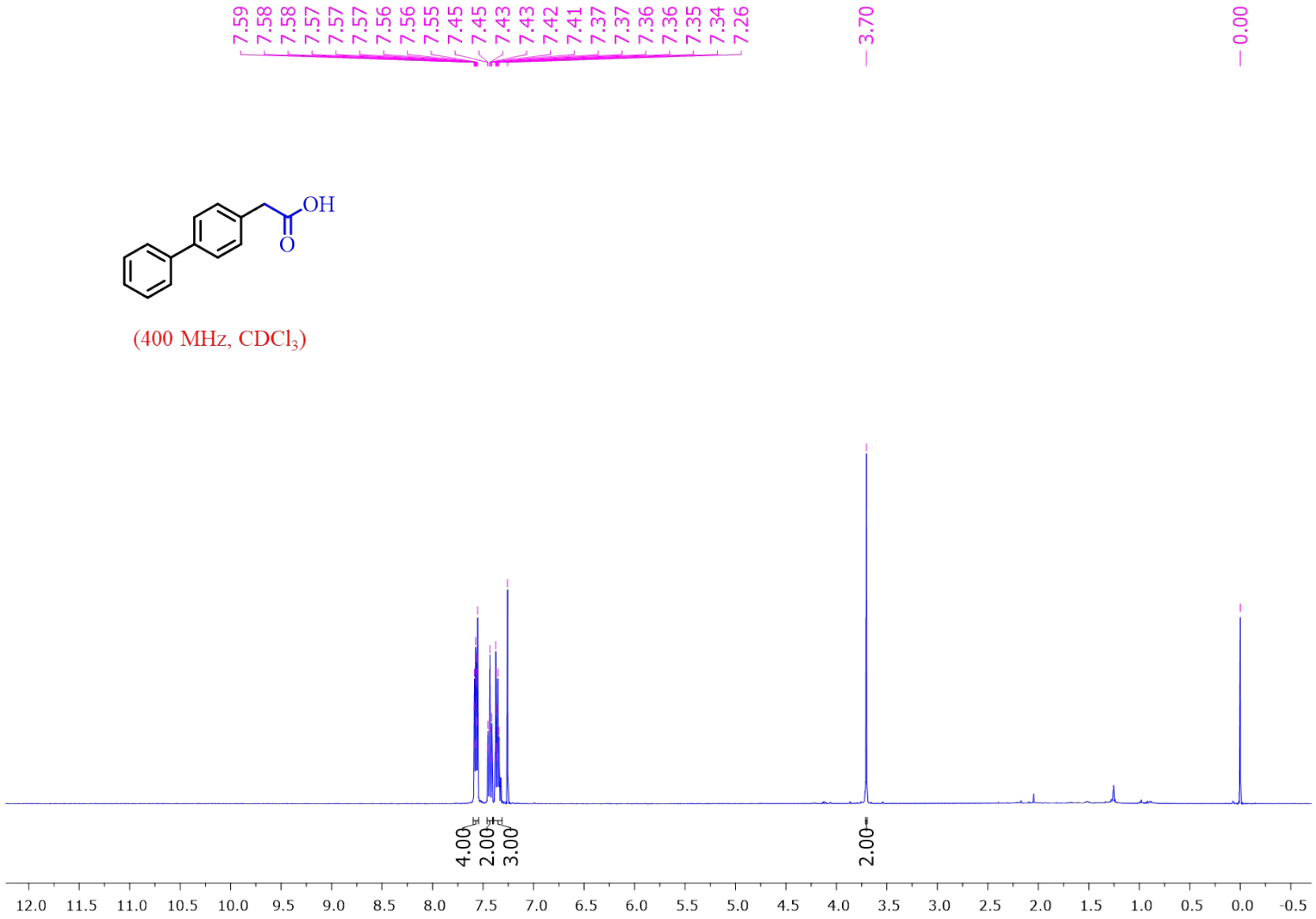


Fig. S77. ^{1}H NMR spectra of 2-([1,1'-biphenyl]-4-yl) acetic acid (felbinac) (**3a**) in $CDCl_3$.

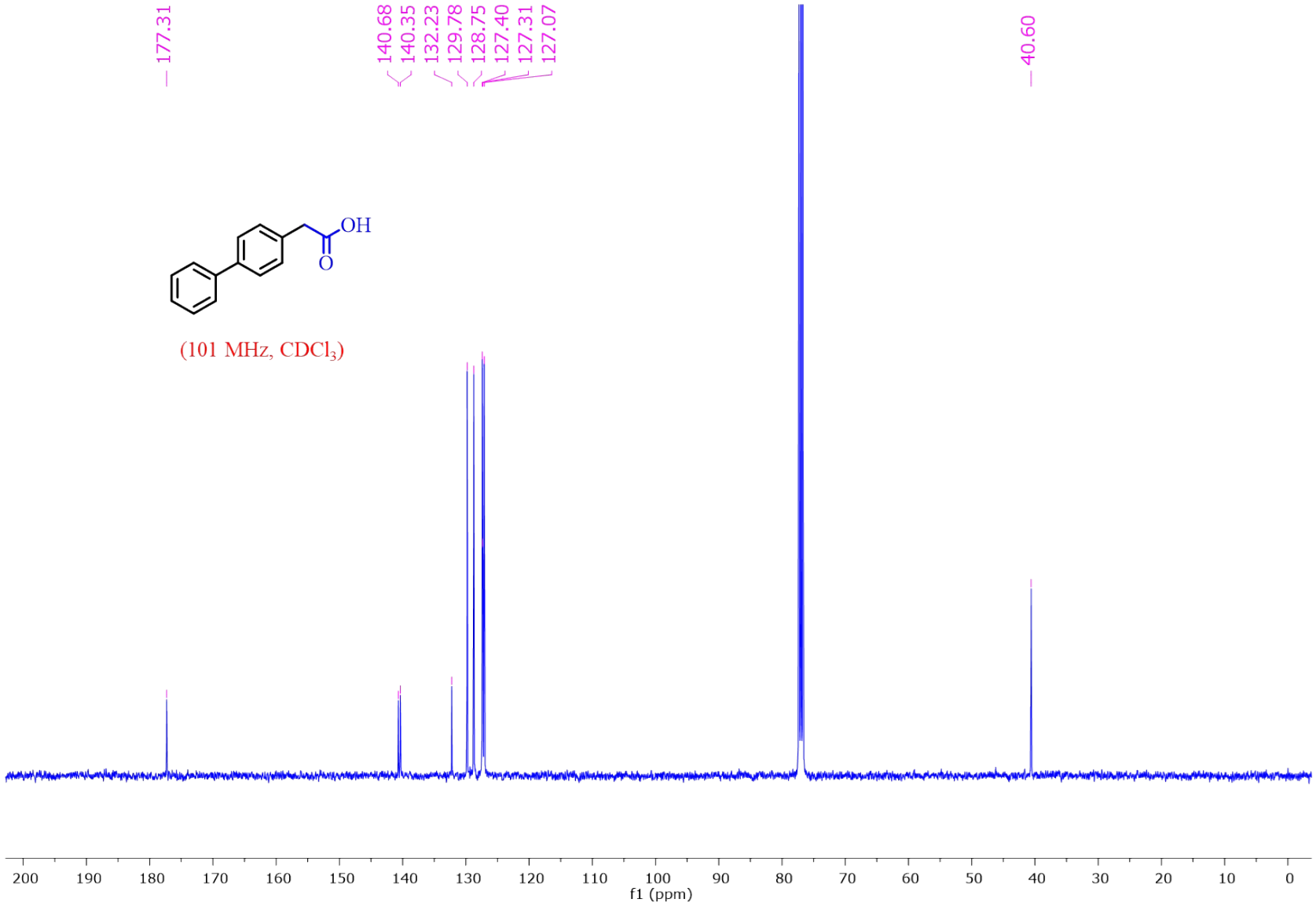


Fig. S78. ^{13}C NMR spectra of 2-([1,1'-biphenyl]-4-yl) acetic acid (felbinac) (**3a**) in $CDCl_3$.

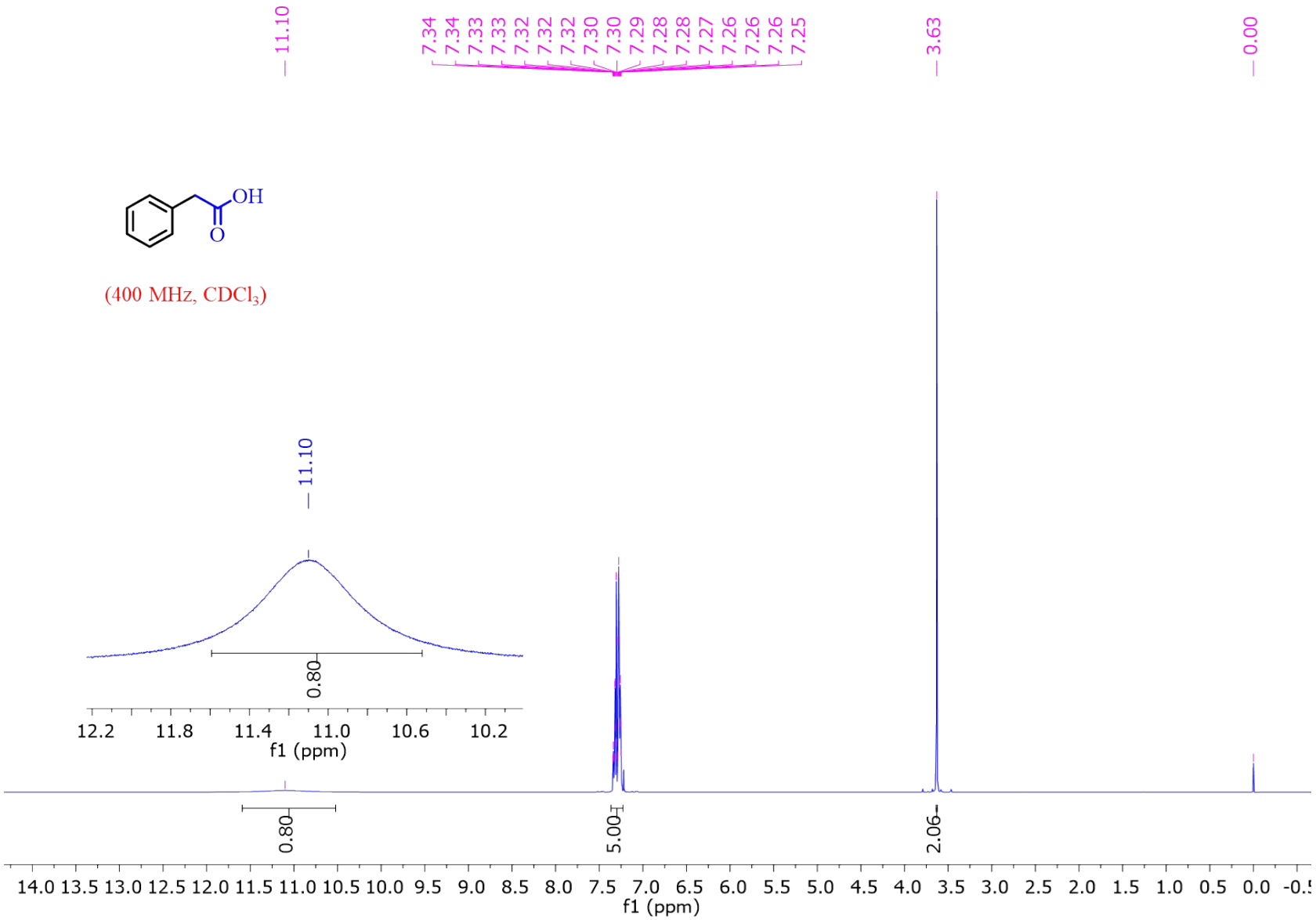


Fig. S79. ^{1}H NMR spectra of 2-phenylacetic acid (**3b**) in $CDCl_3$.

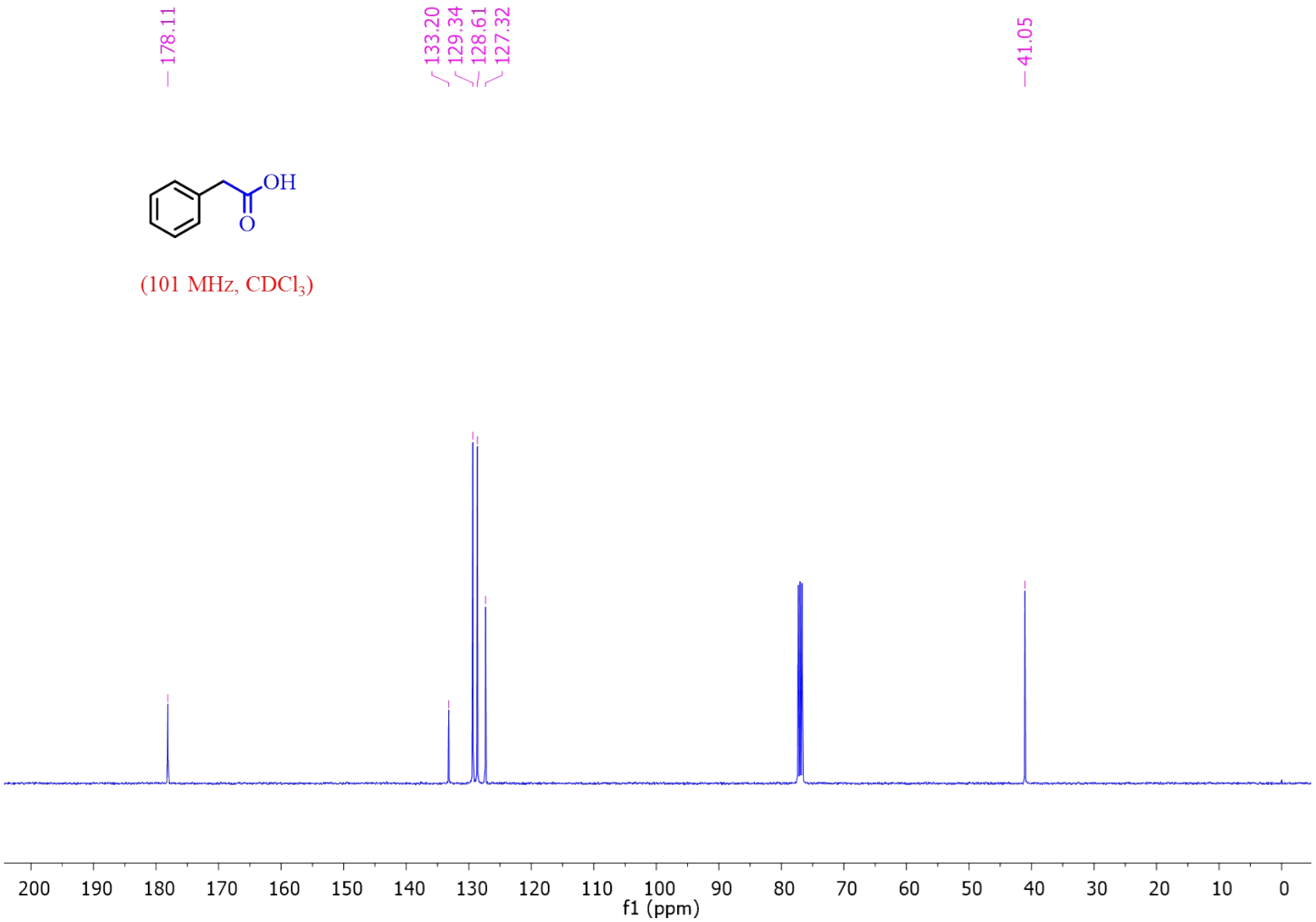


Fig. S80. ^{13}C NMR spectra of 2-phenylacetic acid (**3b**) in $CDCl_3$.

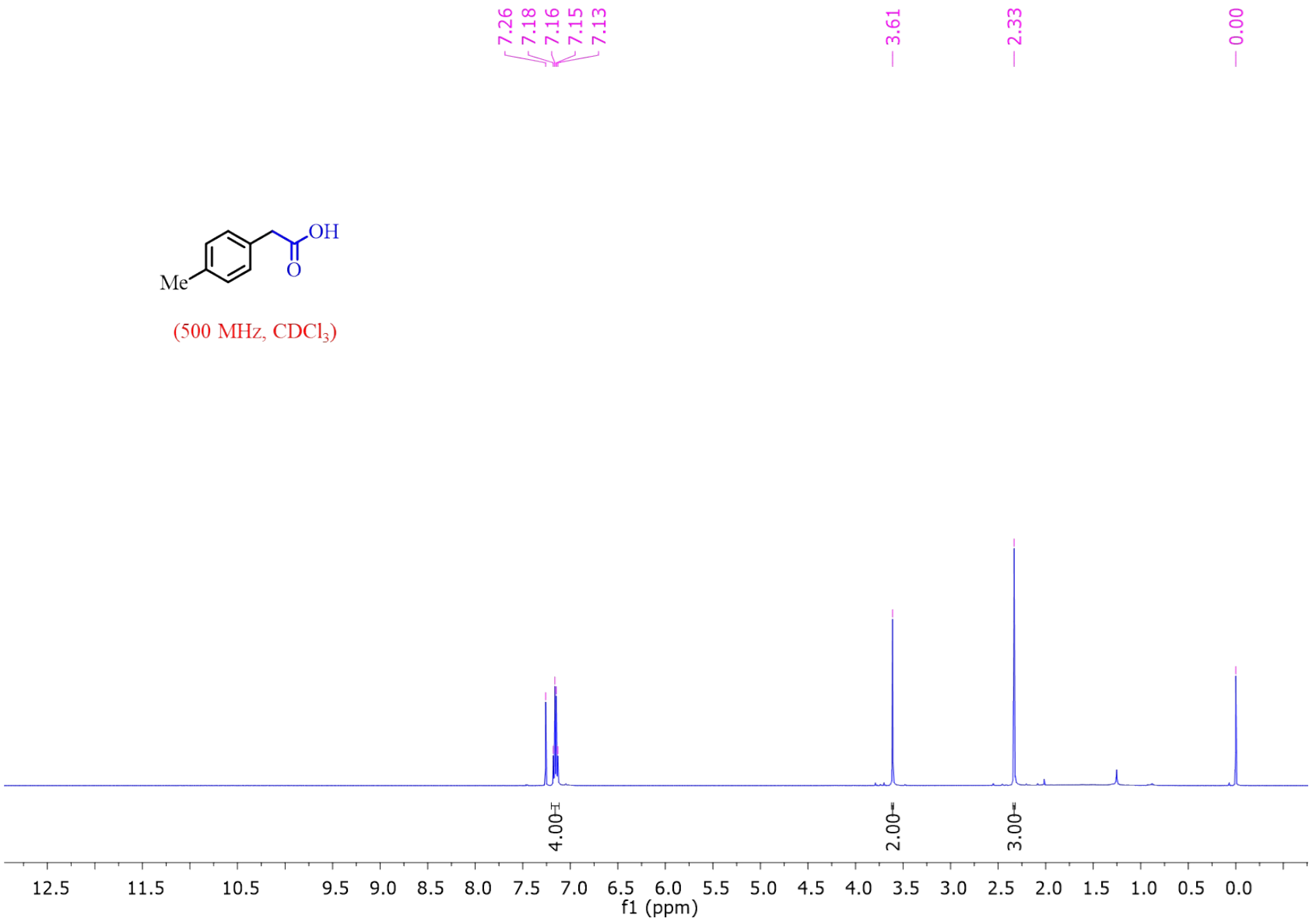


Fig. S81. ^{1}H NMR spectra of 2-(p-tolyl) acetic acid (**3c**) in $CDCl_3$.

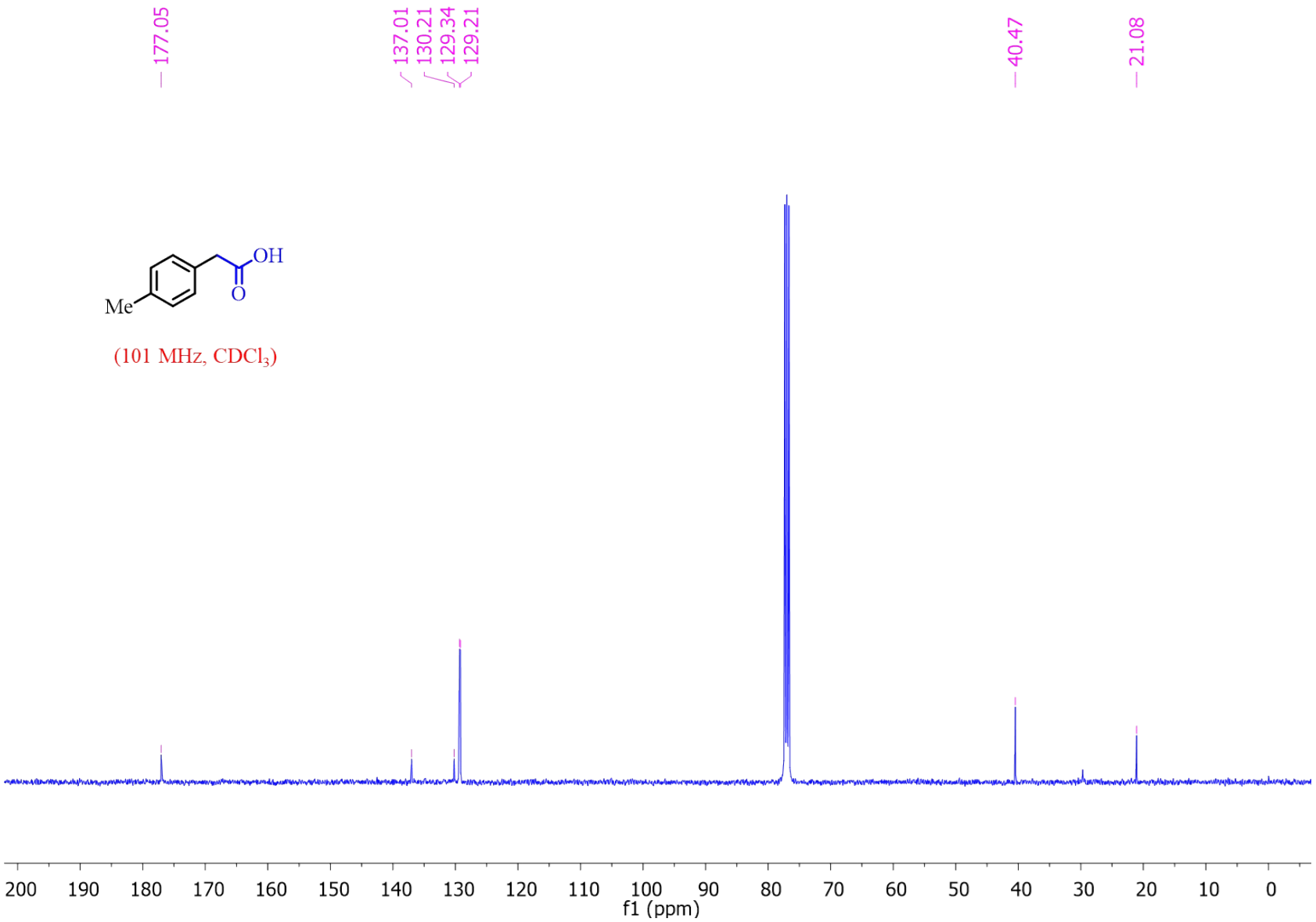


Fig. S82. ^{13}C NMR spectra of 2-(p-tolyl) acetic acid (**3c**) in $CDCl_3$.

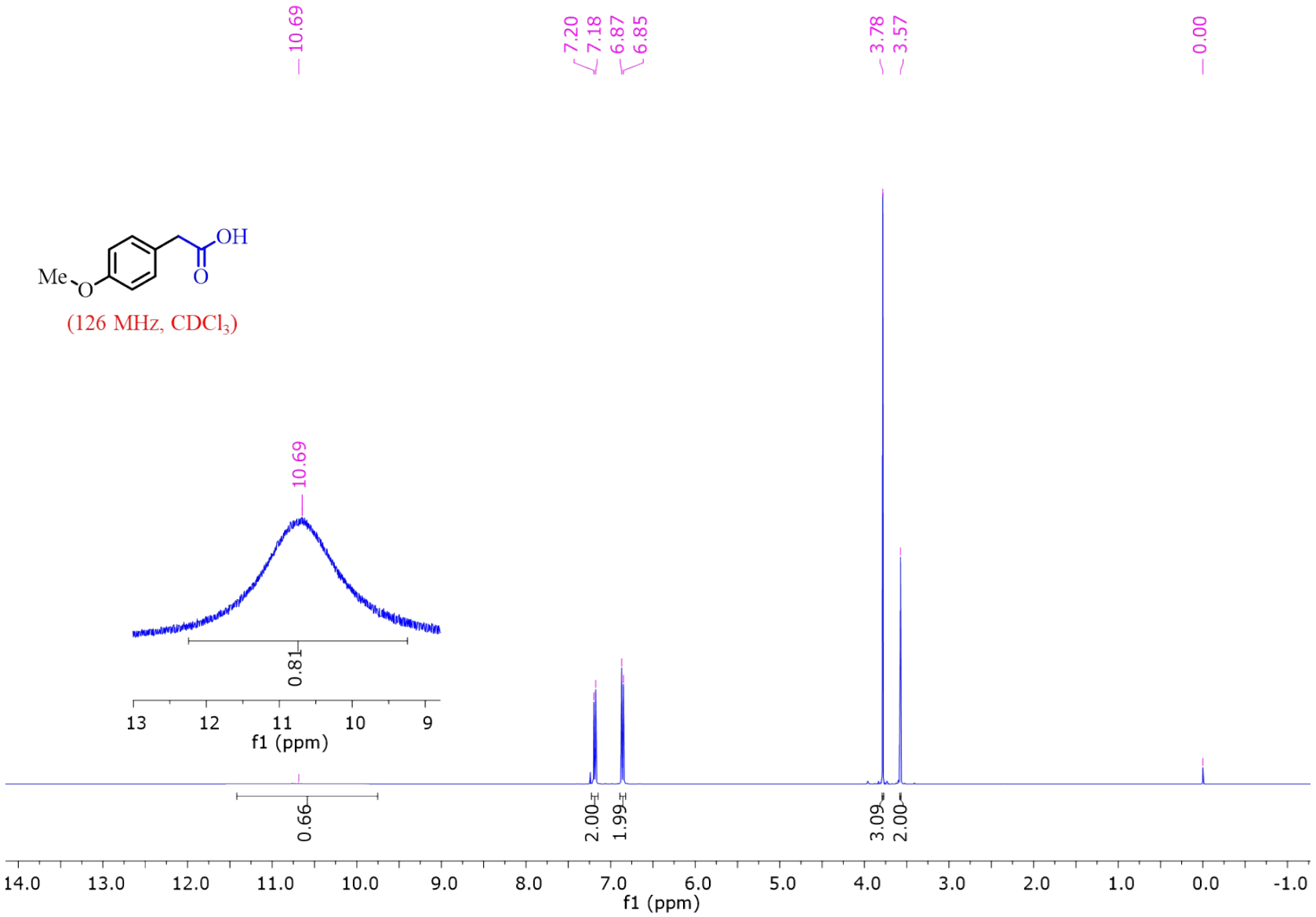


Fig. S83. ^{1}H NMR spectra of 2-(4-Methoxyphenyl) acetic acid (**3d**) in $CDCl_3$.

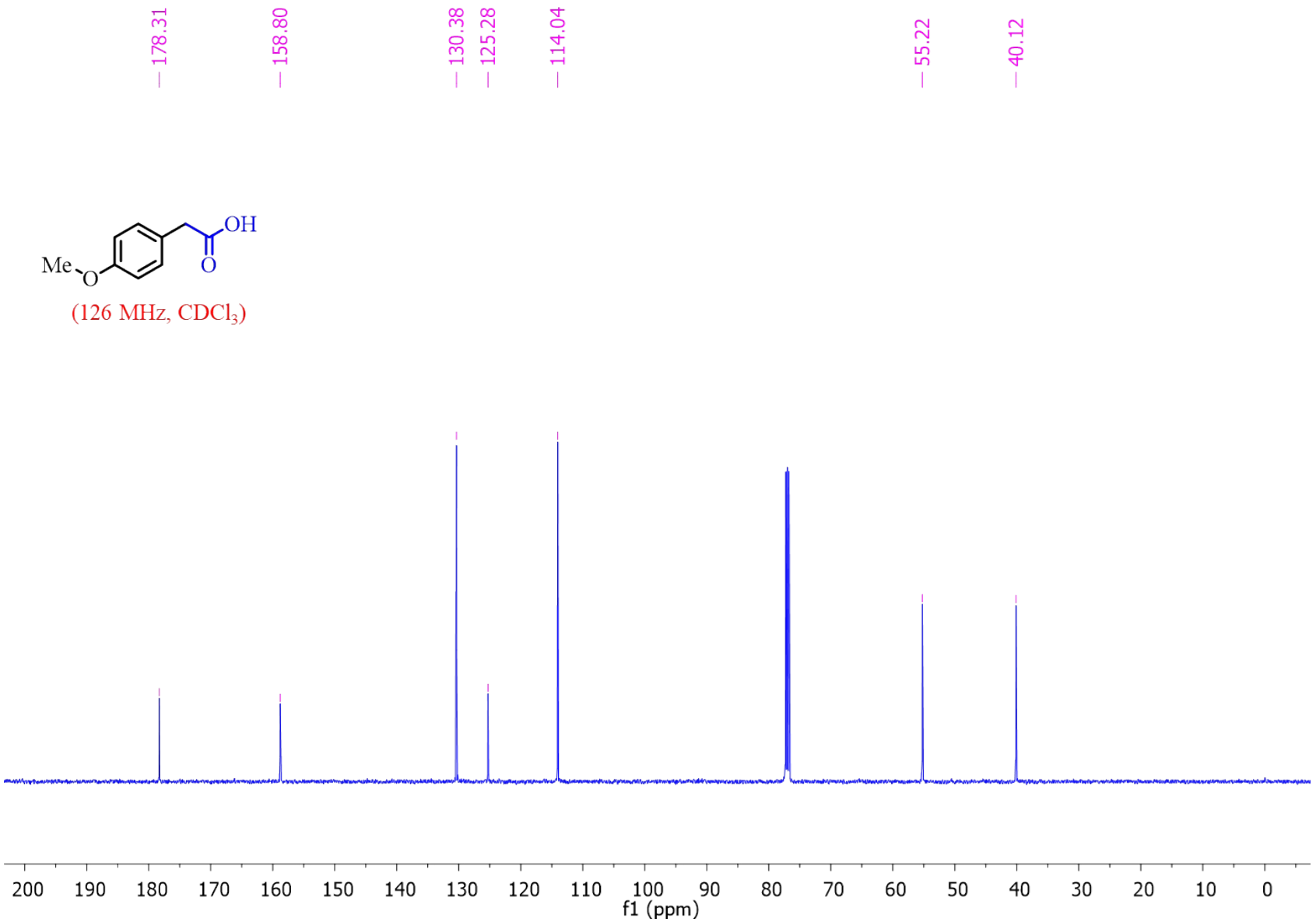


Fig. S84. ^{13}C NMR spectra of 2-(4-Methoxyphenyl) acetic acid (**3d**) in $CDCl_3$.

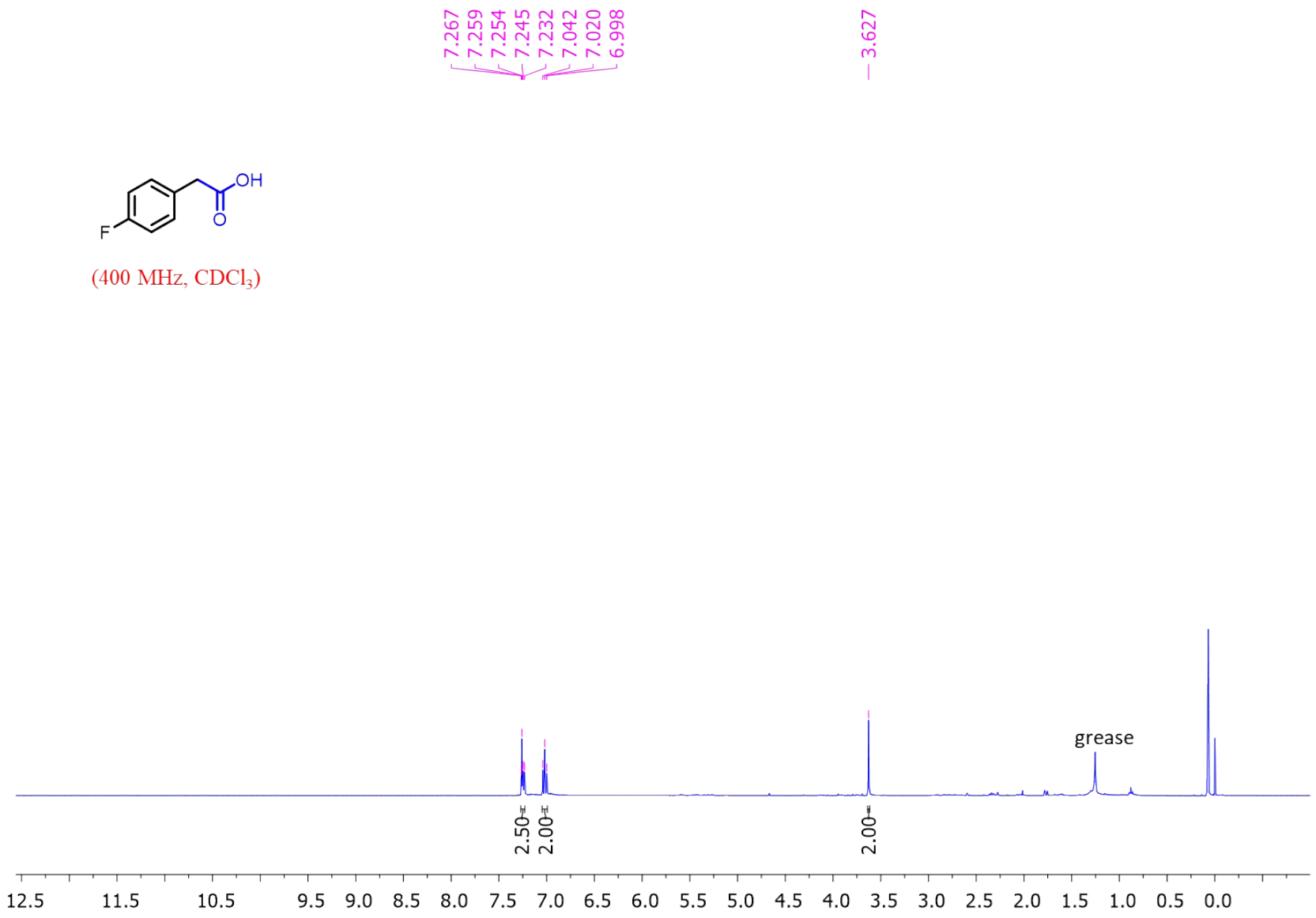


Fig. S85. ^{1}H NMR spectra of 2-(4-Fluorophenyl) acetic acid (**3e**) in $CDCl_3$.

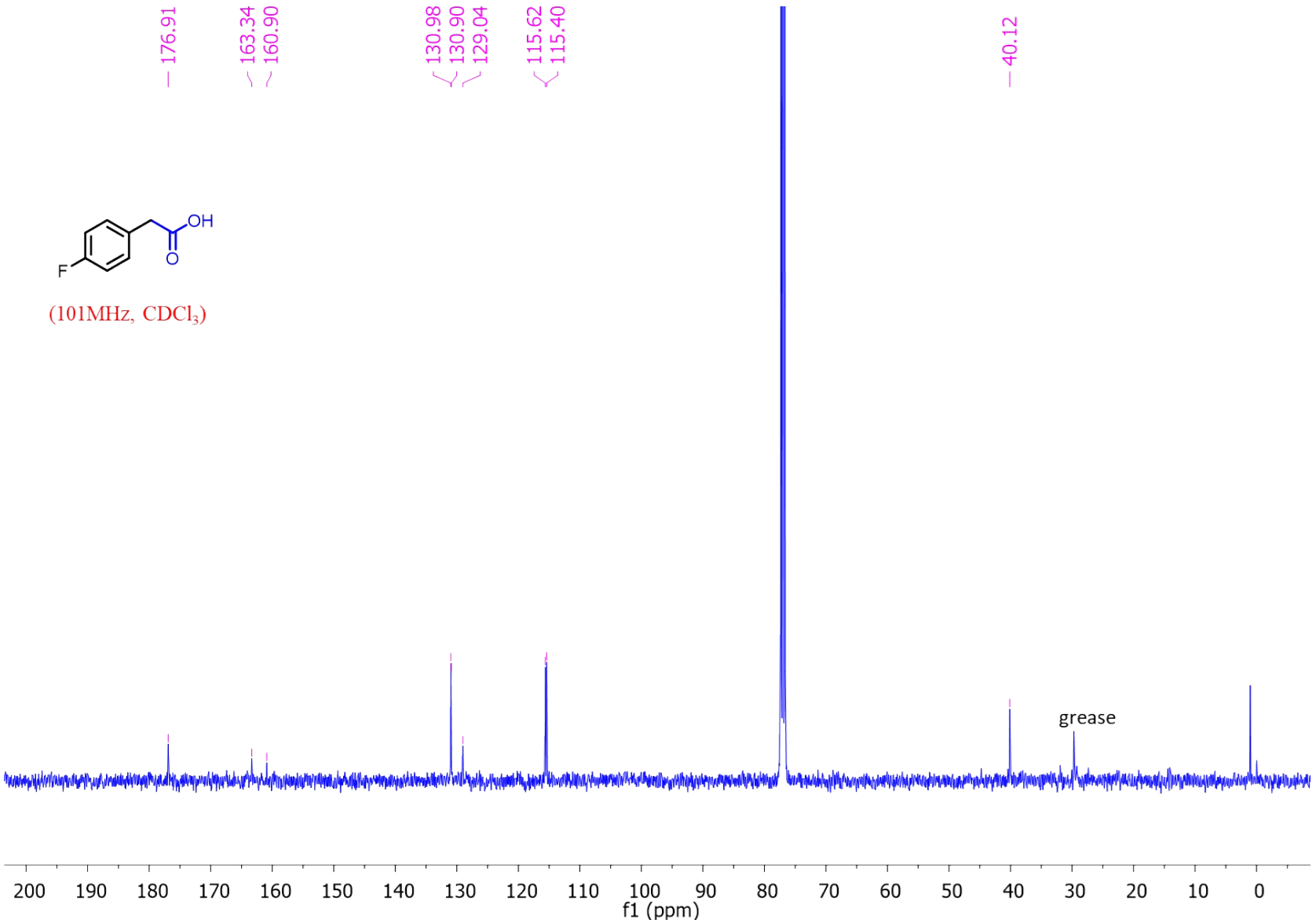


Fig. S86. ^{13}C NMR spectra of 2-(4-Fluorophenyl) acetic acid (**3e**) in $CDCl_3$.

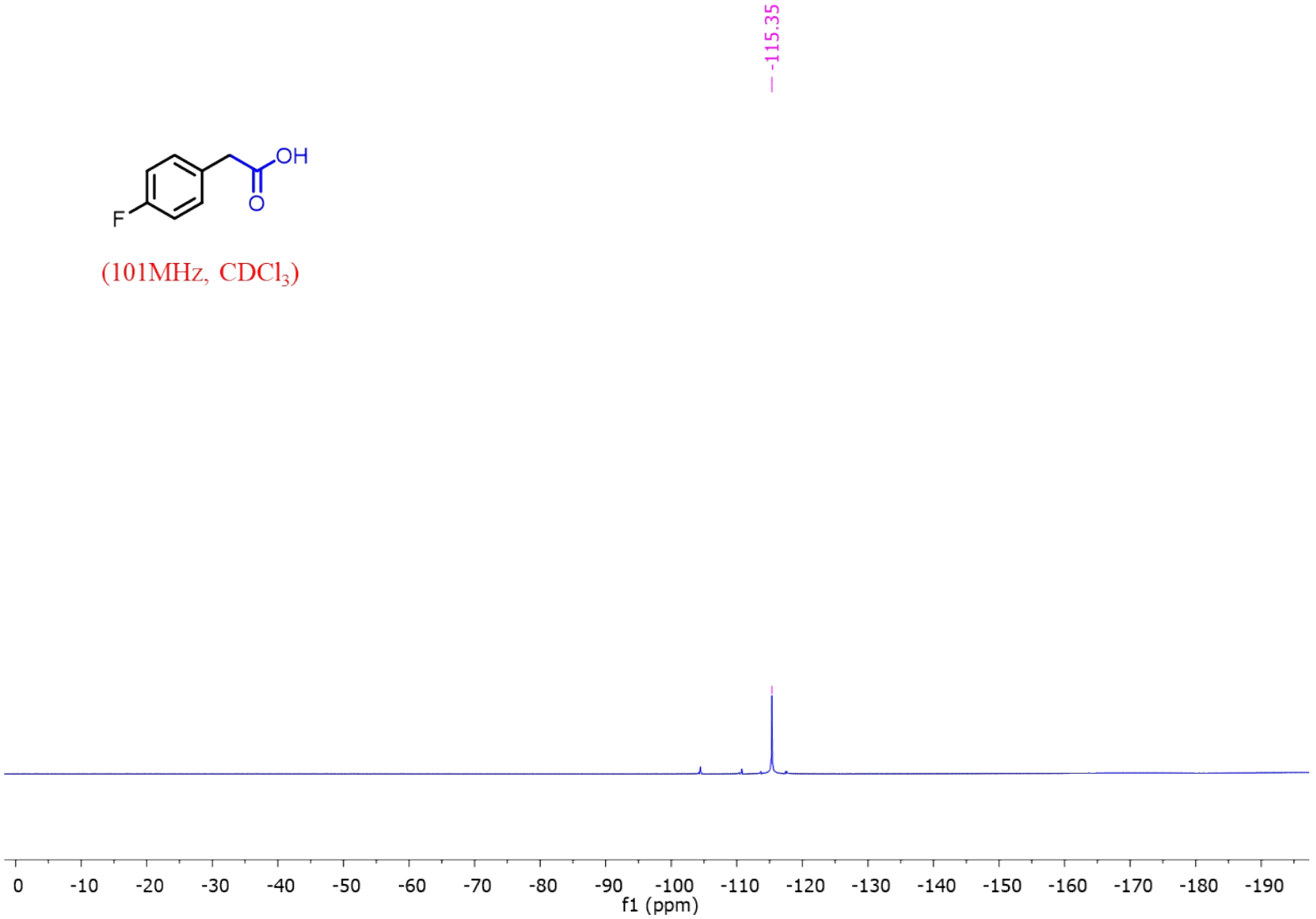


Fig. S87. ^{19}F NMR spectra of 2-(4-Fluorophenyl) acetic acid (**3e**) in $CDCl_3$.

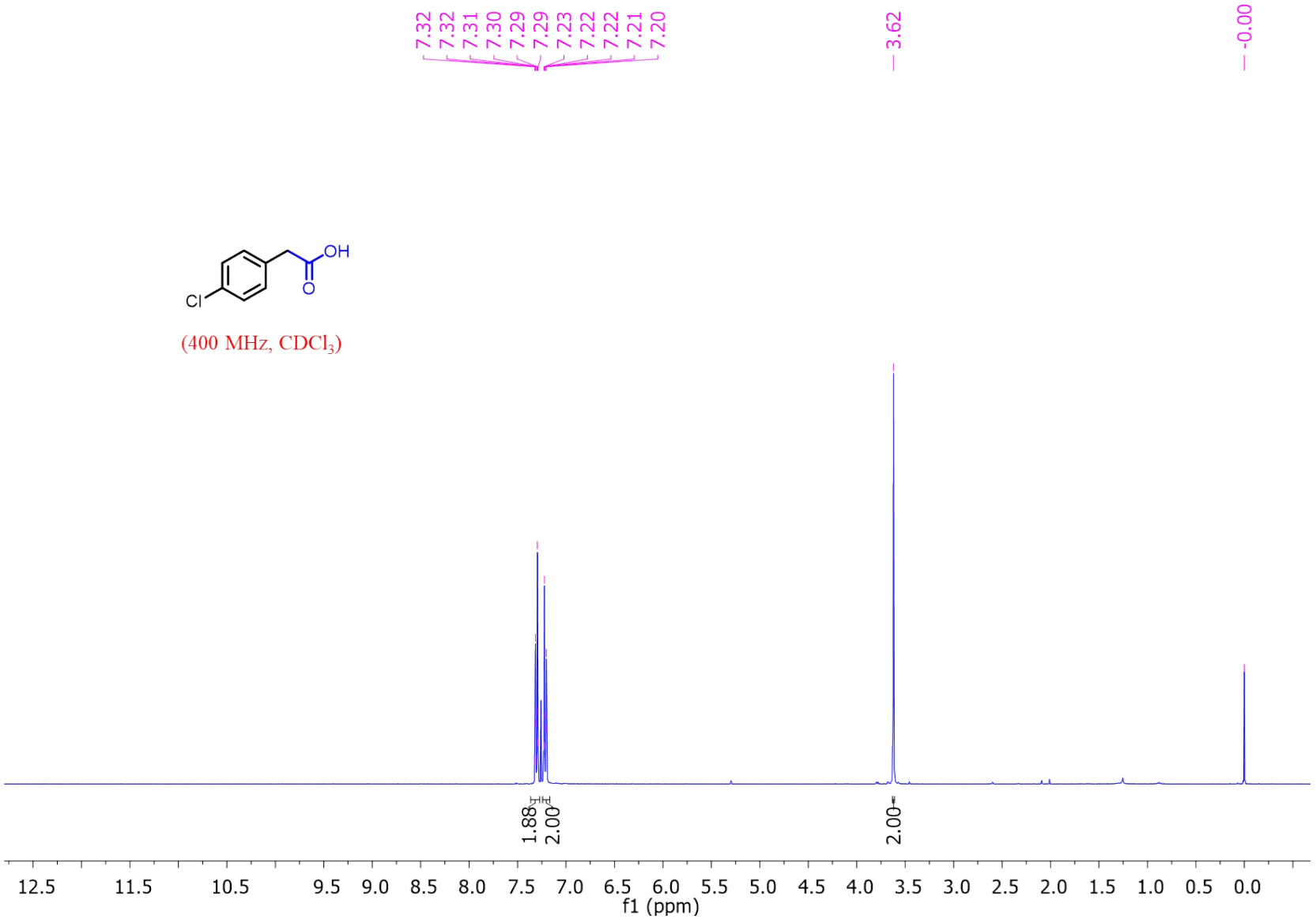


Fig. S88. ^{1}H NMR spectra of 2-(4-chlorophenyl) acetic acid (**3e**) in $CDCl_3$.

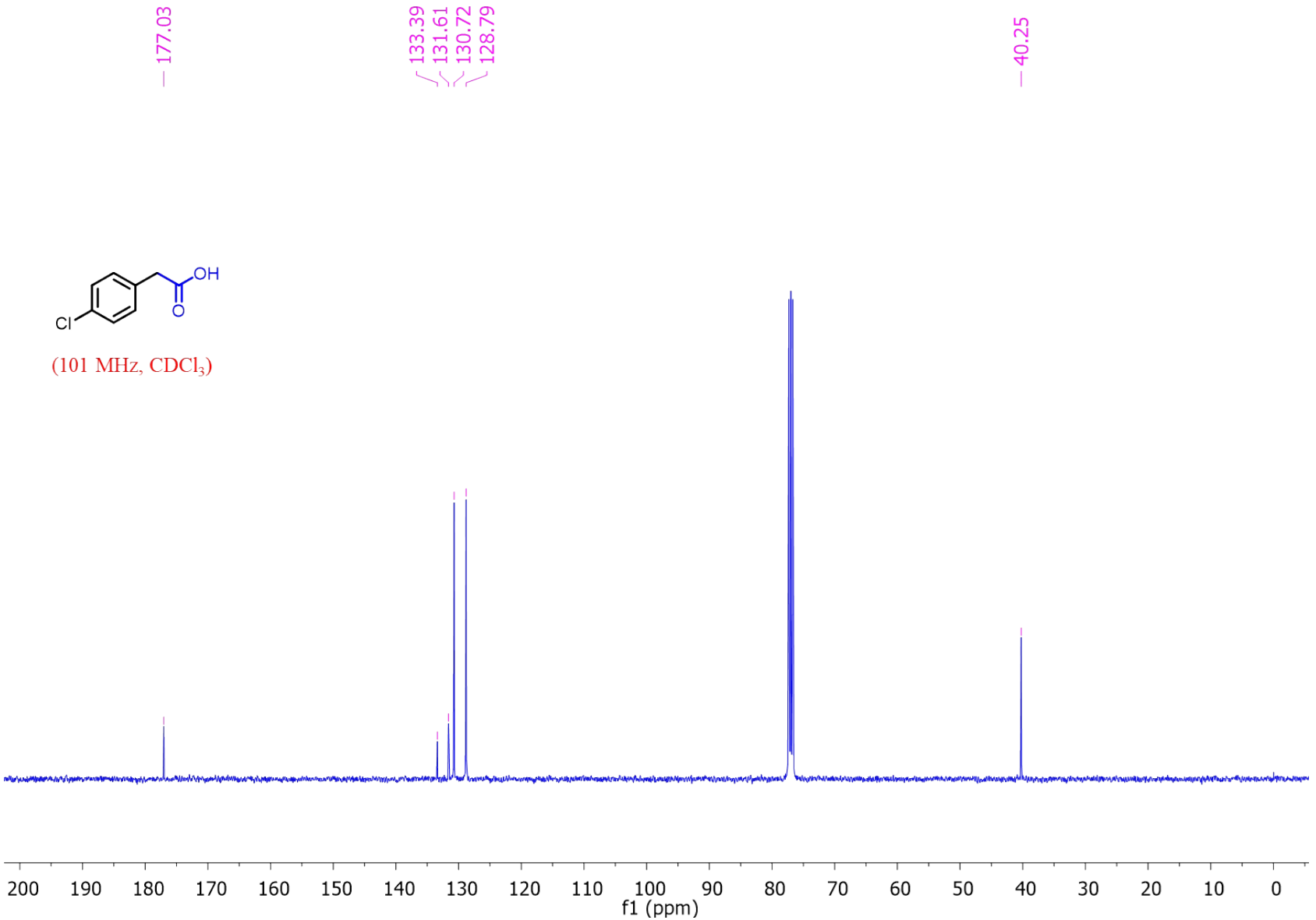


Fig. S89. ^{13}C NMR spectra of 2-(4-chlorophenyl) acetic acid (**3e**) in $CDCl_3$.

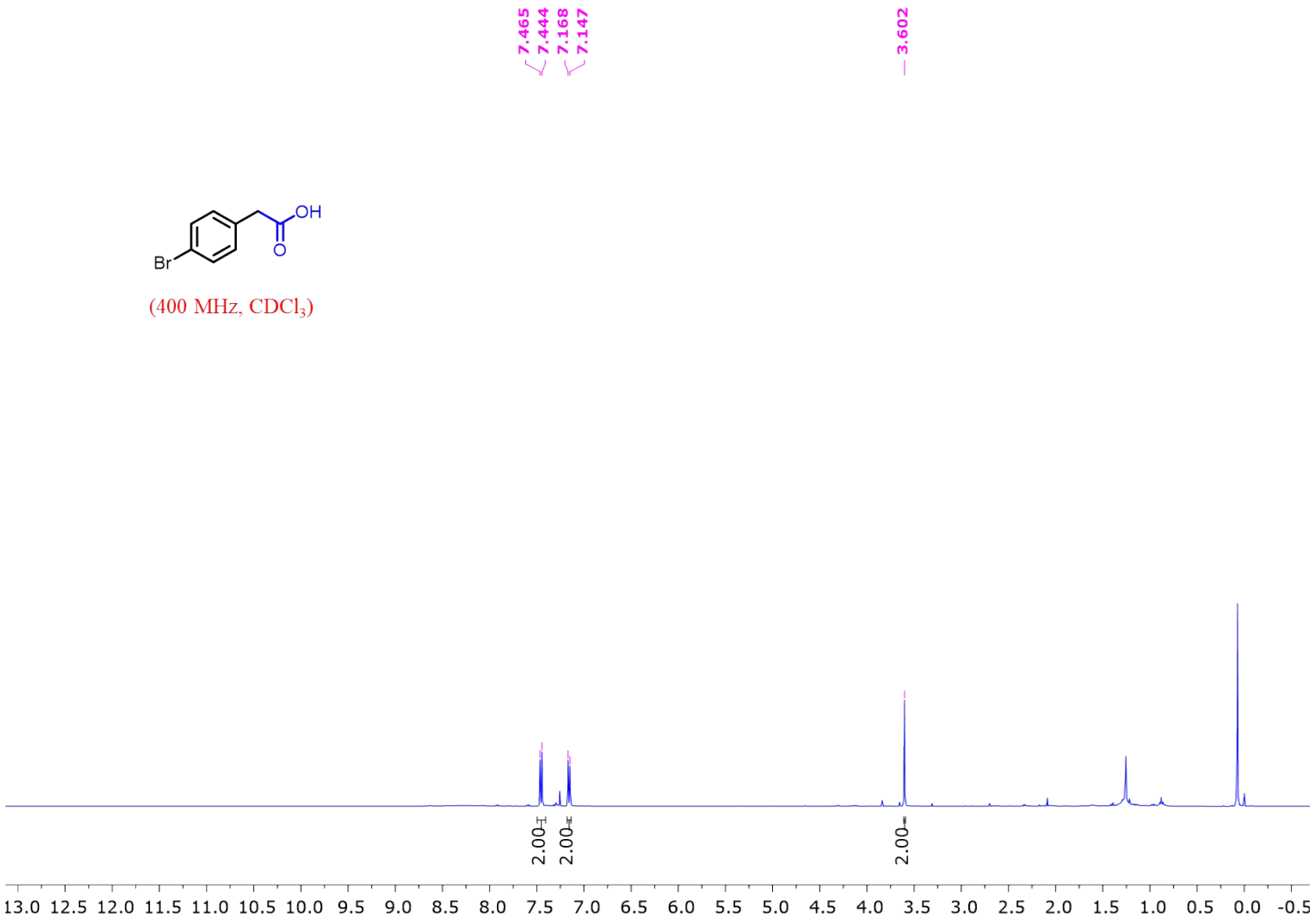


Fig. S90. ^{1}H NMR spectra of 2-(4-Bromophenyl) acetic acid (**3f**) in $CDCl_3$.

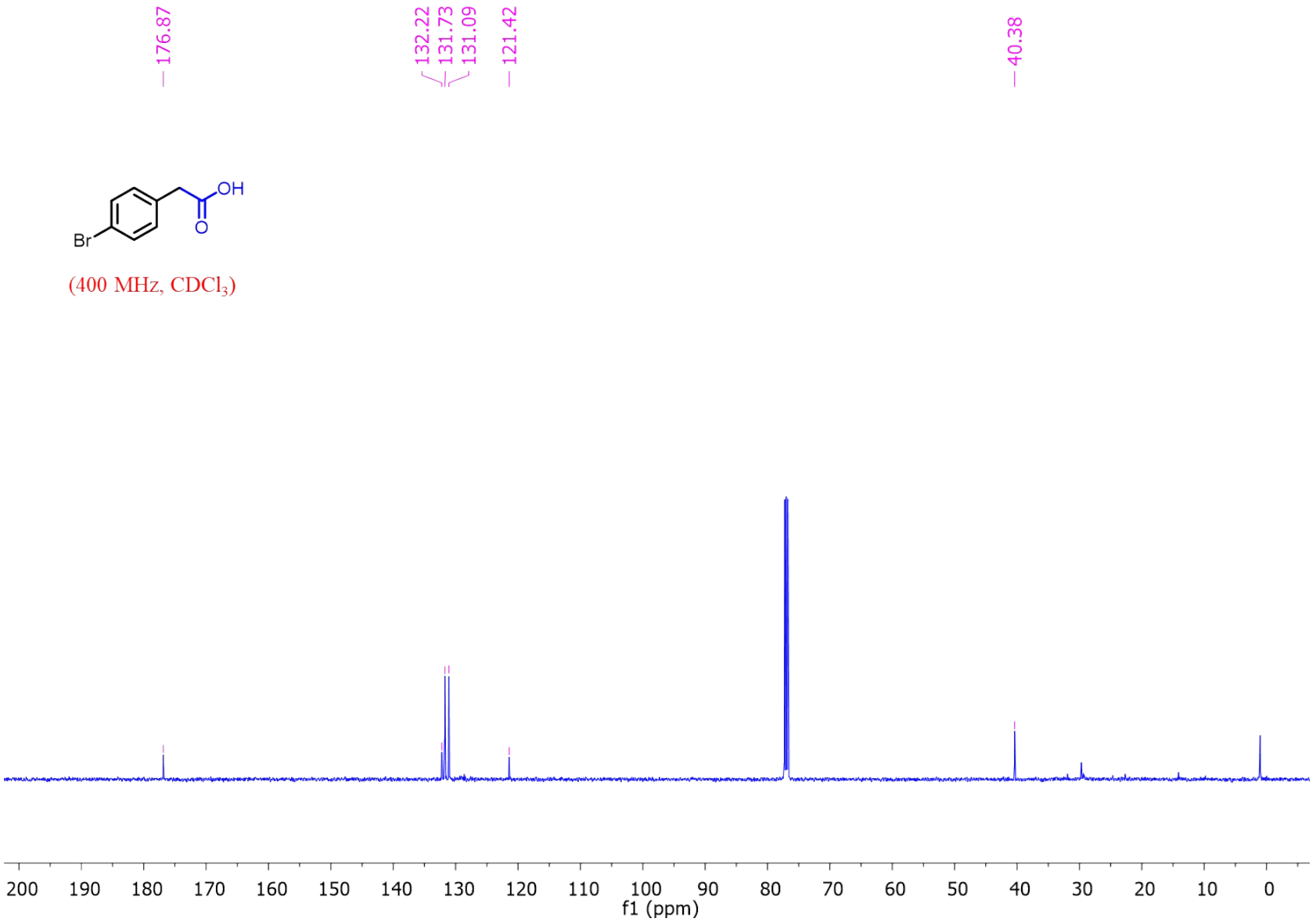


Fig. S91. ^{13}C NMR spectra of 2-(4-Bromophenyl) acetic acid (**3f**) in $CDCl_3$.

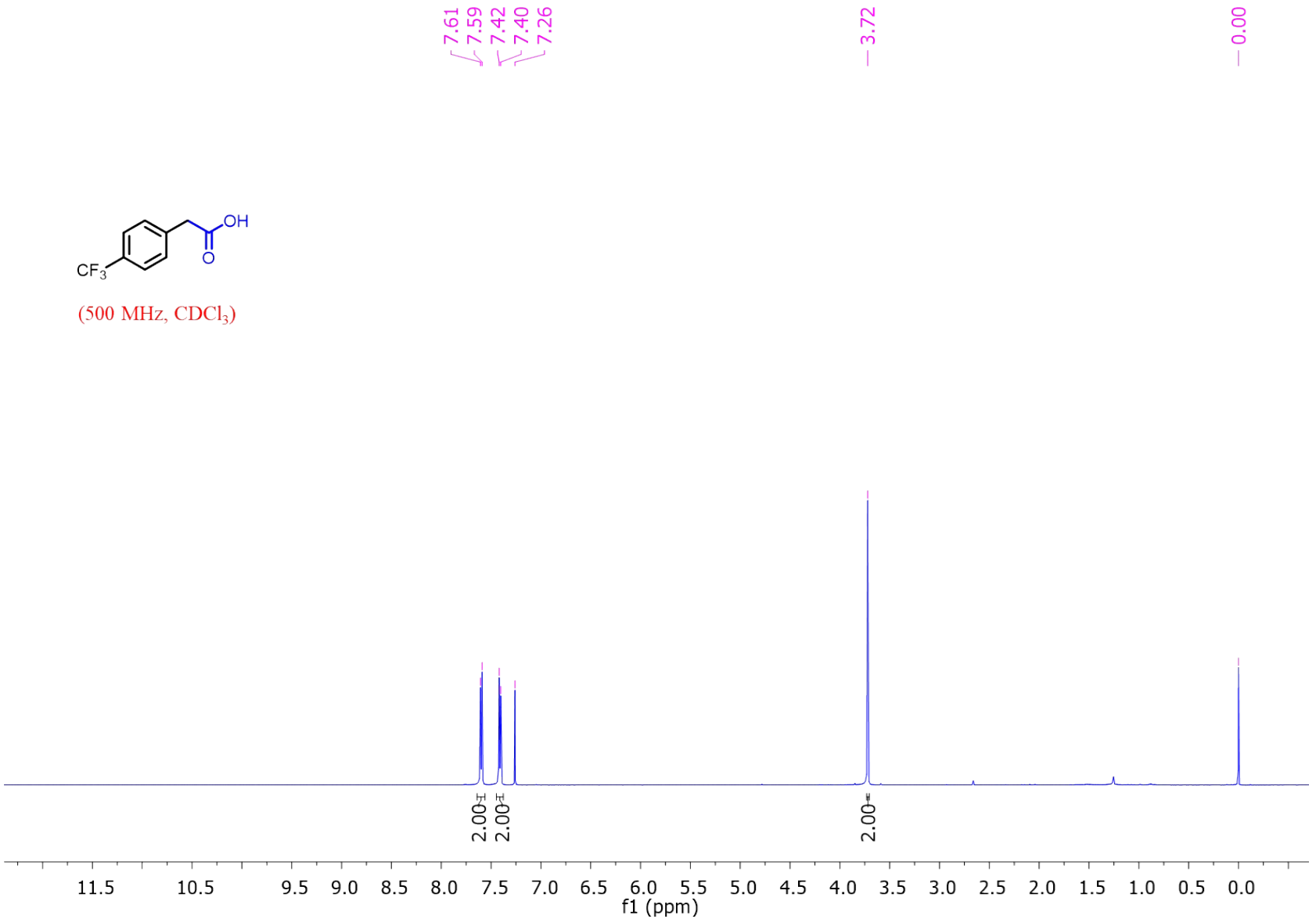


Fig. S92. ^{1}H NMR spectra of 2-(4-(trifluoromethyl)phenyl) acetic acid (**3g**) in $CDCl_3$.

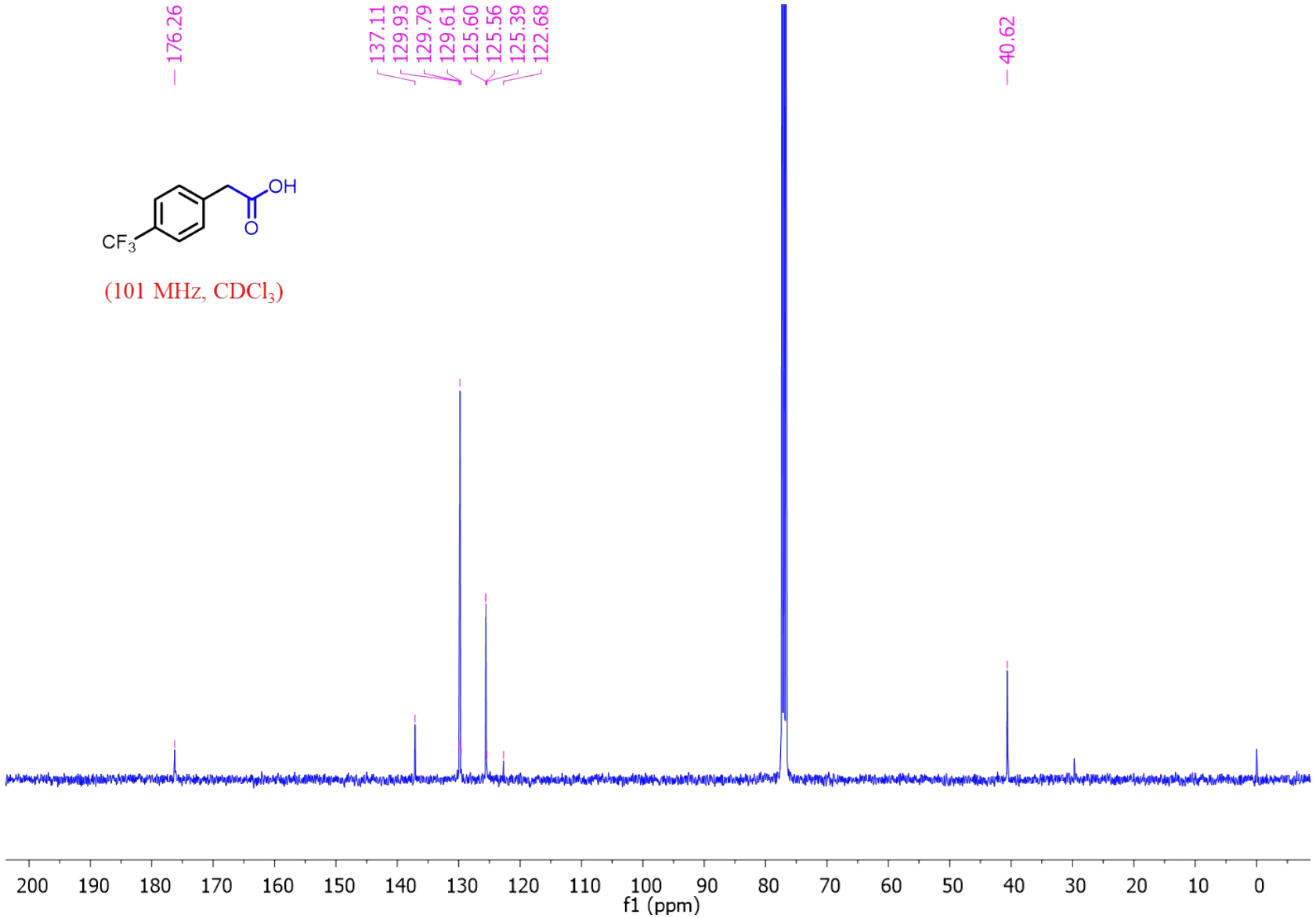


Fig. S93. ^{13}C NMR spectra of 2-(4-(trifluoromethyl)phenyl) acetic acid (**3g**) in $CDCl_3$

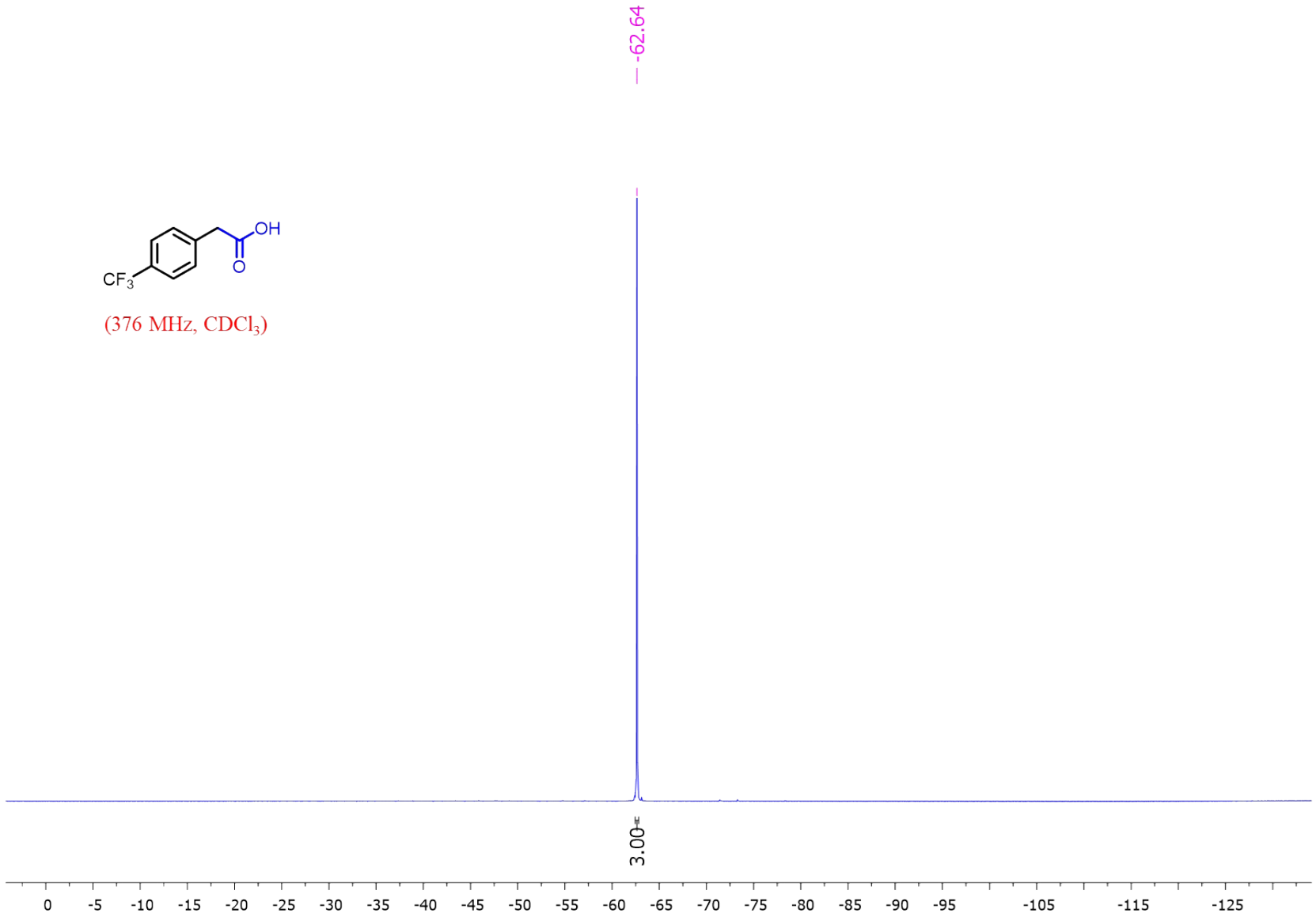


Fig. S94. ^{19}F NMR spectra of 2-(4-(trifluoromethyl)phenyl) acetic acid (**3g**) in $CDCl_3$.

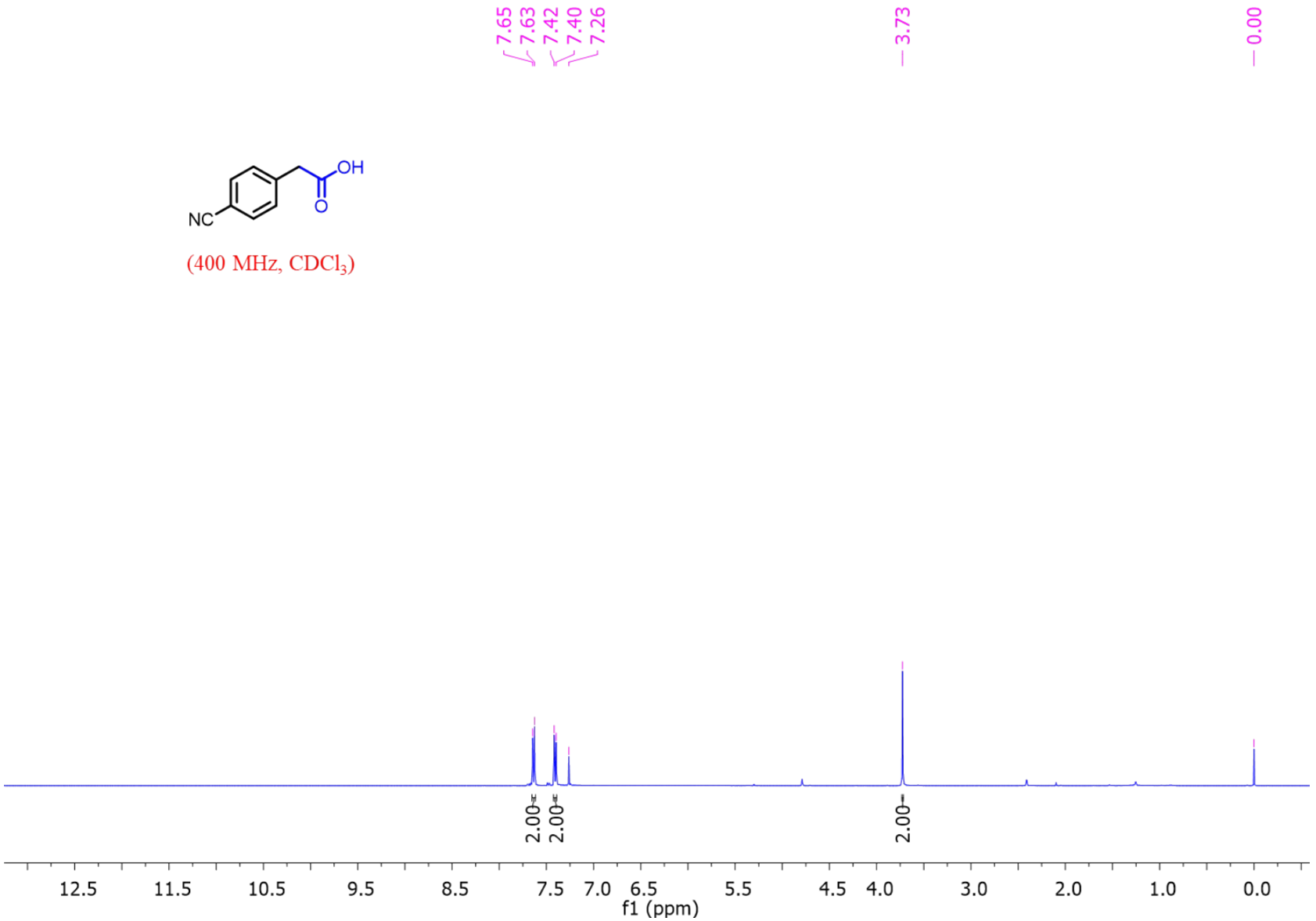


Fig. S95. ^{1}H NMR spectra of 2-(4-cyanophenyl) acetic acid (**3i**) in $CDCl_3$.

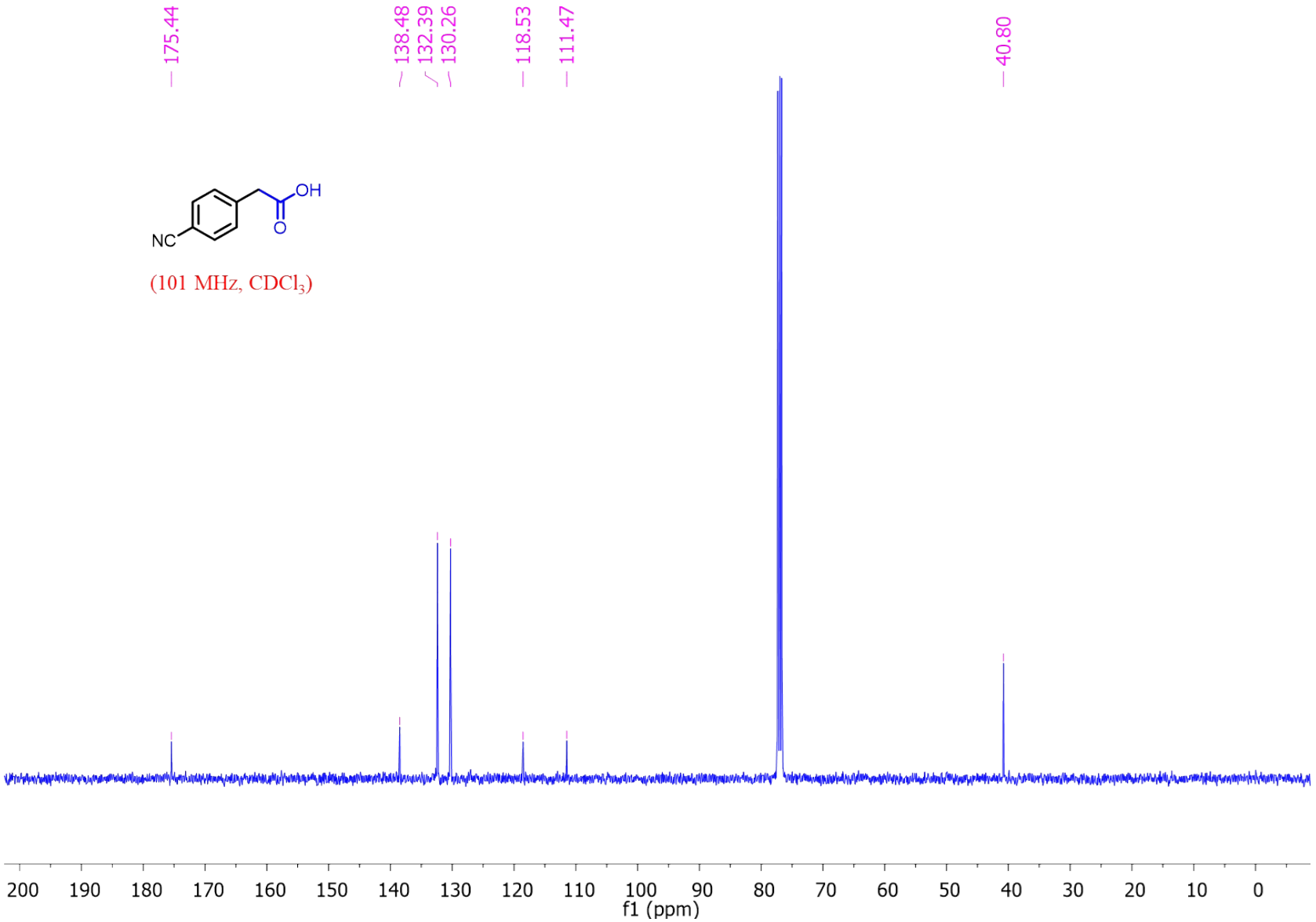


Fig. S96. ^{13}C NMR spectra of 2-(4-cyanophenyl) acetic acid (**3i**) in $CDCl_3$.

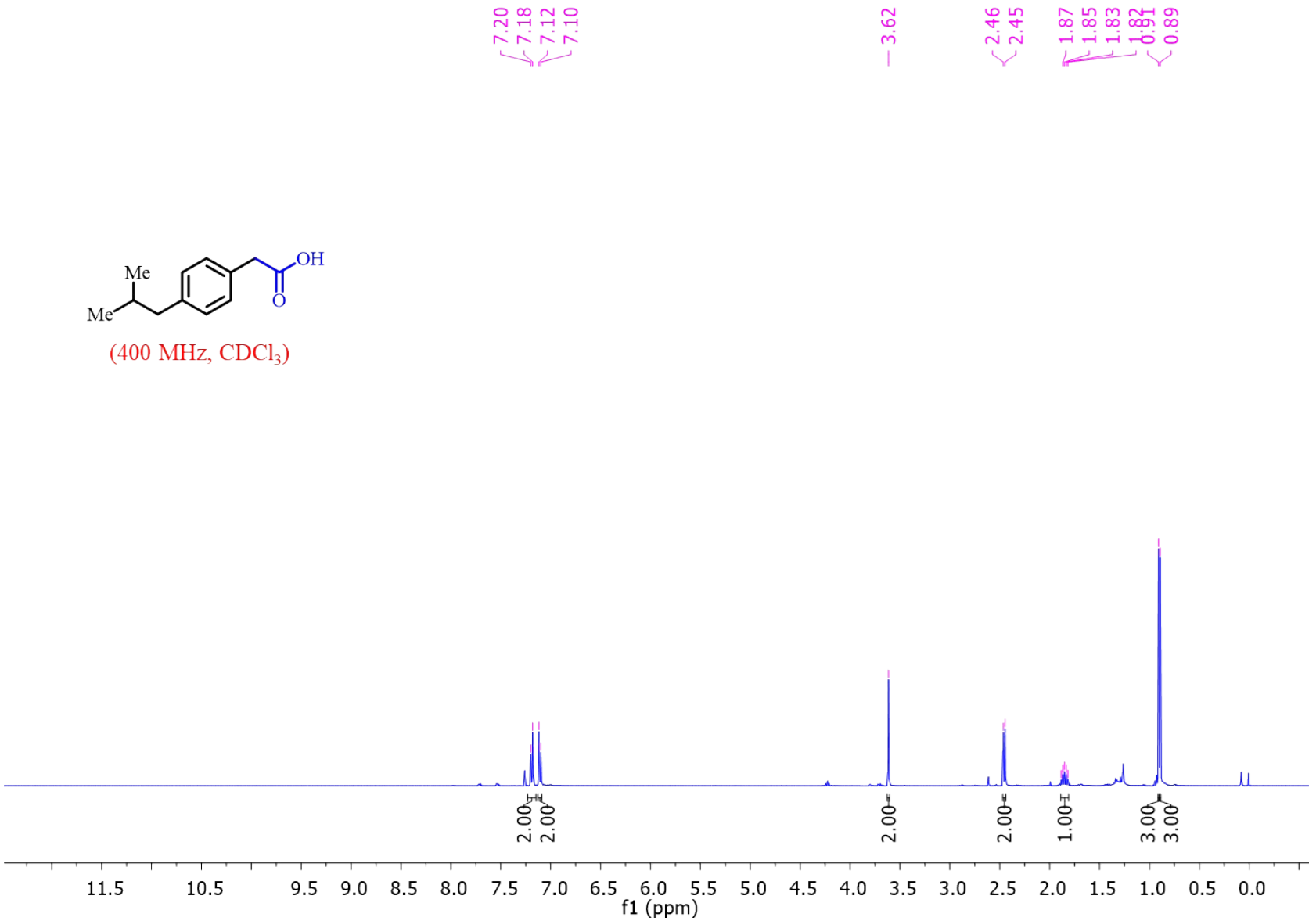


Fig. S97. ^{1}H NMR spectra of 2-(4-Isobutylphenyl) acetic acid (Ibufenac) (**3j**) in $CDCl_3$.

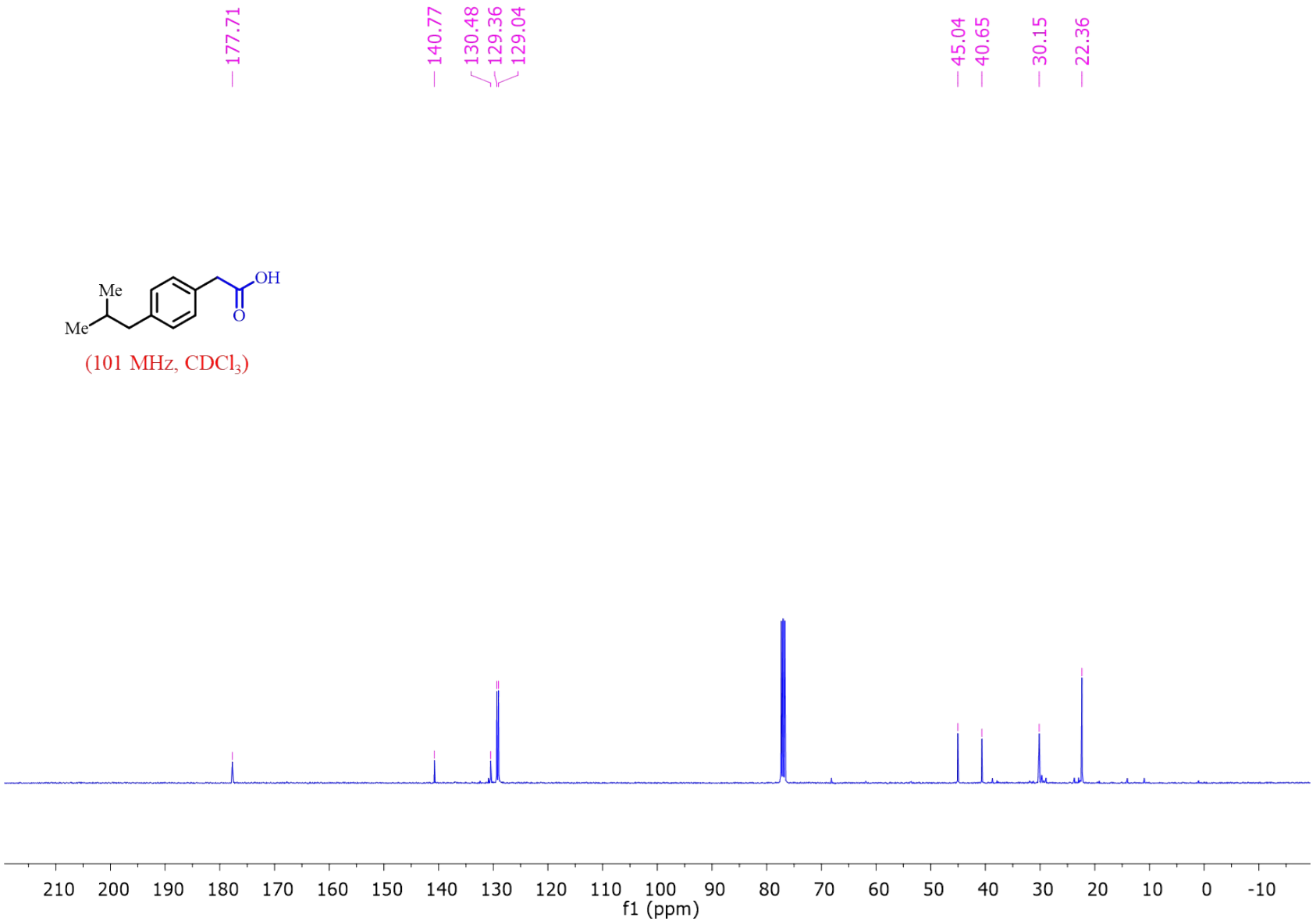


Fig. S98. ^{13}C NMR spectra of 2-(4-Isobutylphenyl) acetic acid (Ibufenac) (**3j**) in $CDCl_3$.

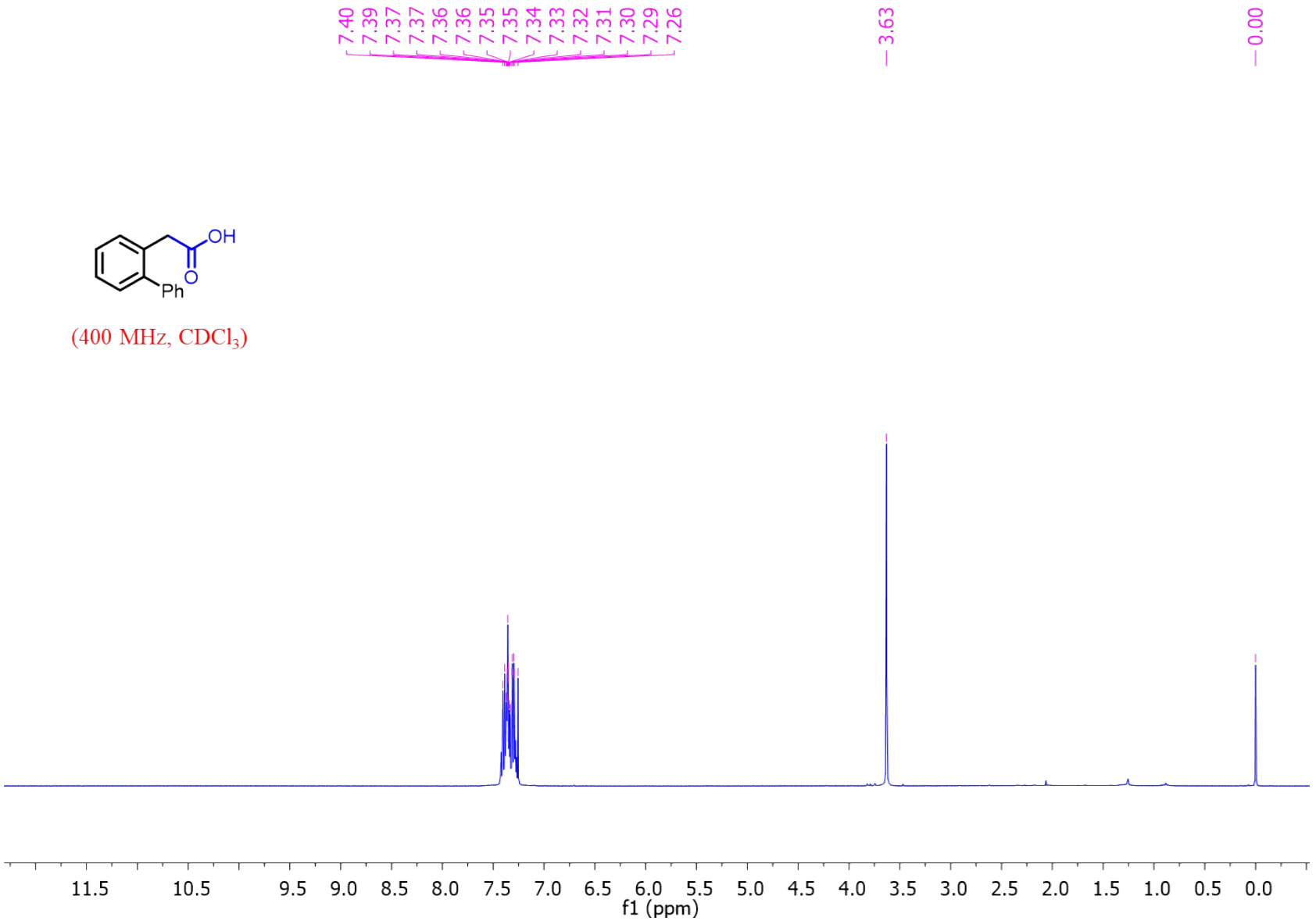


Fig. S99. ^{1}H NMR spectra of 2-([1,1'-Biphenyl]-2-yl) acetic acid (**3k**) in $CDCl_3$.

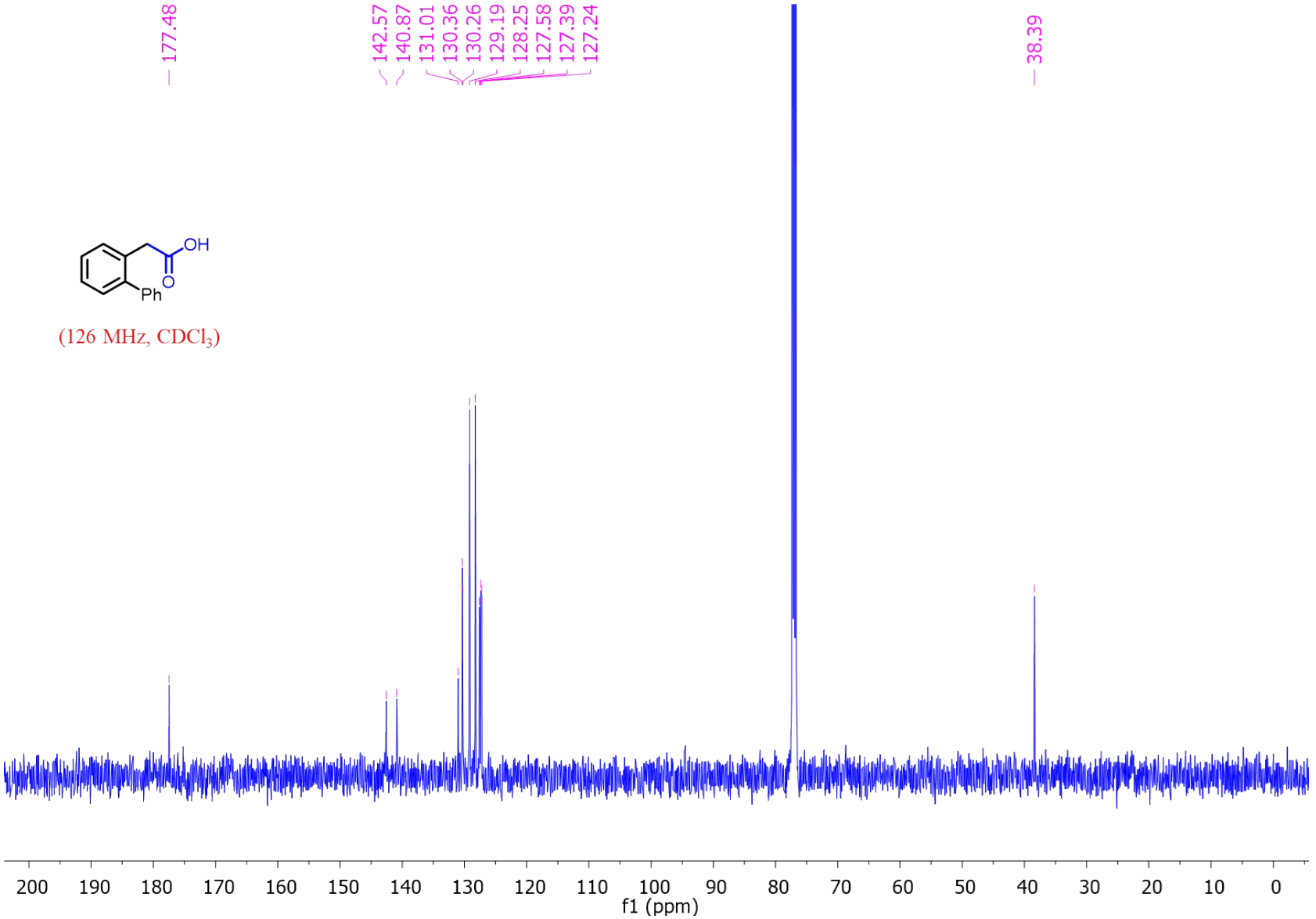


Fig. S100. ^{13}C NMR spectra of 2-([1,1'-Biphenyl]-2-yl) acetic acid (**3k**) in $CDCl_3$.

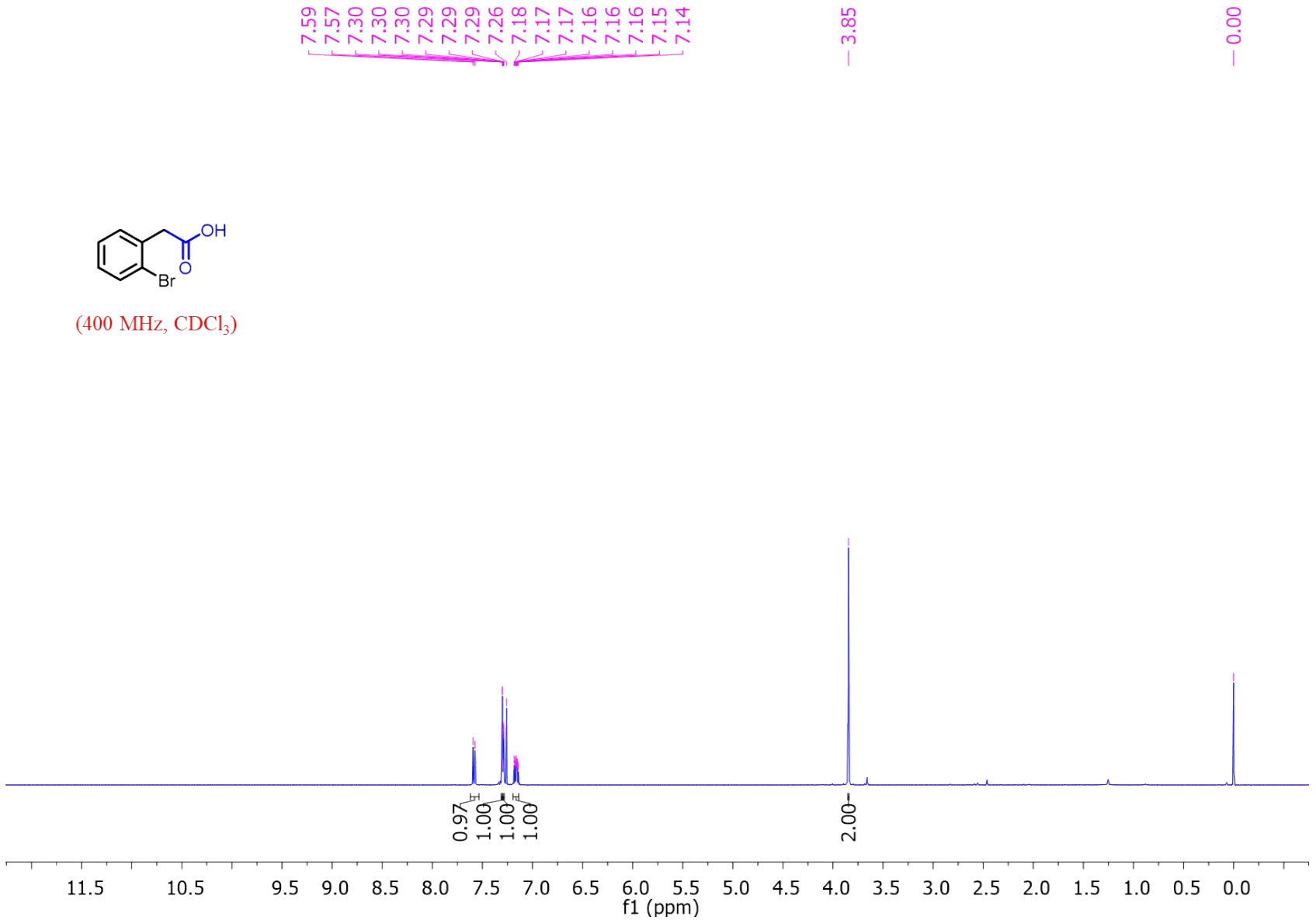


Fig. S101. ^{1}H NMR spectra of 2-(2-Bromophenyl) acetic acid (**3l**) in $CDCl_3$.

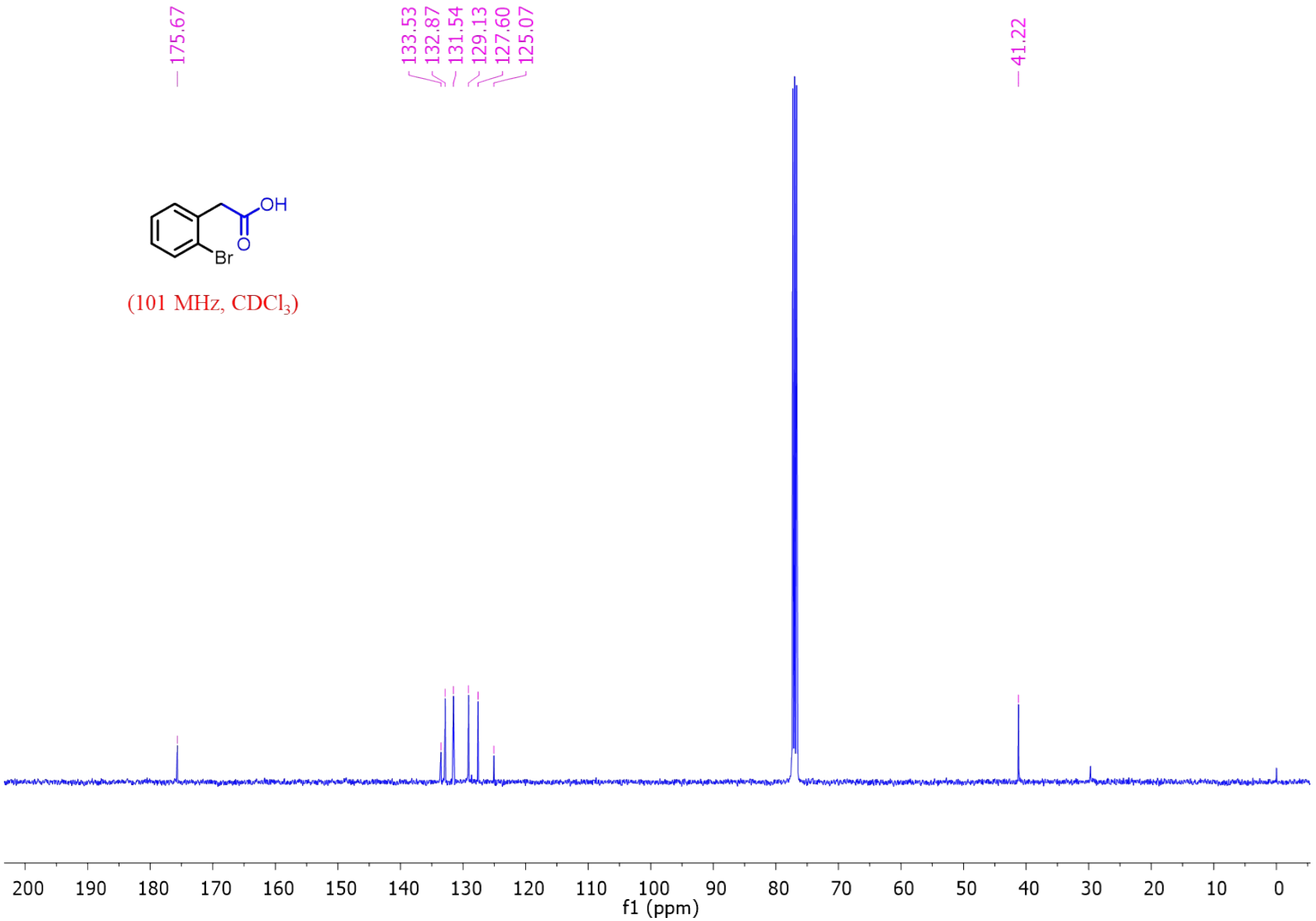


Fig. S102. ^{13}C NMR spectra of 2-(2-Bromophenyl) acetic acid (**3l**) in $CDCl_3$.

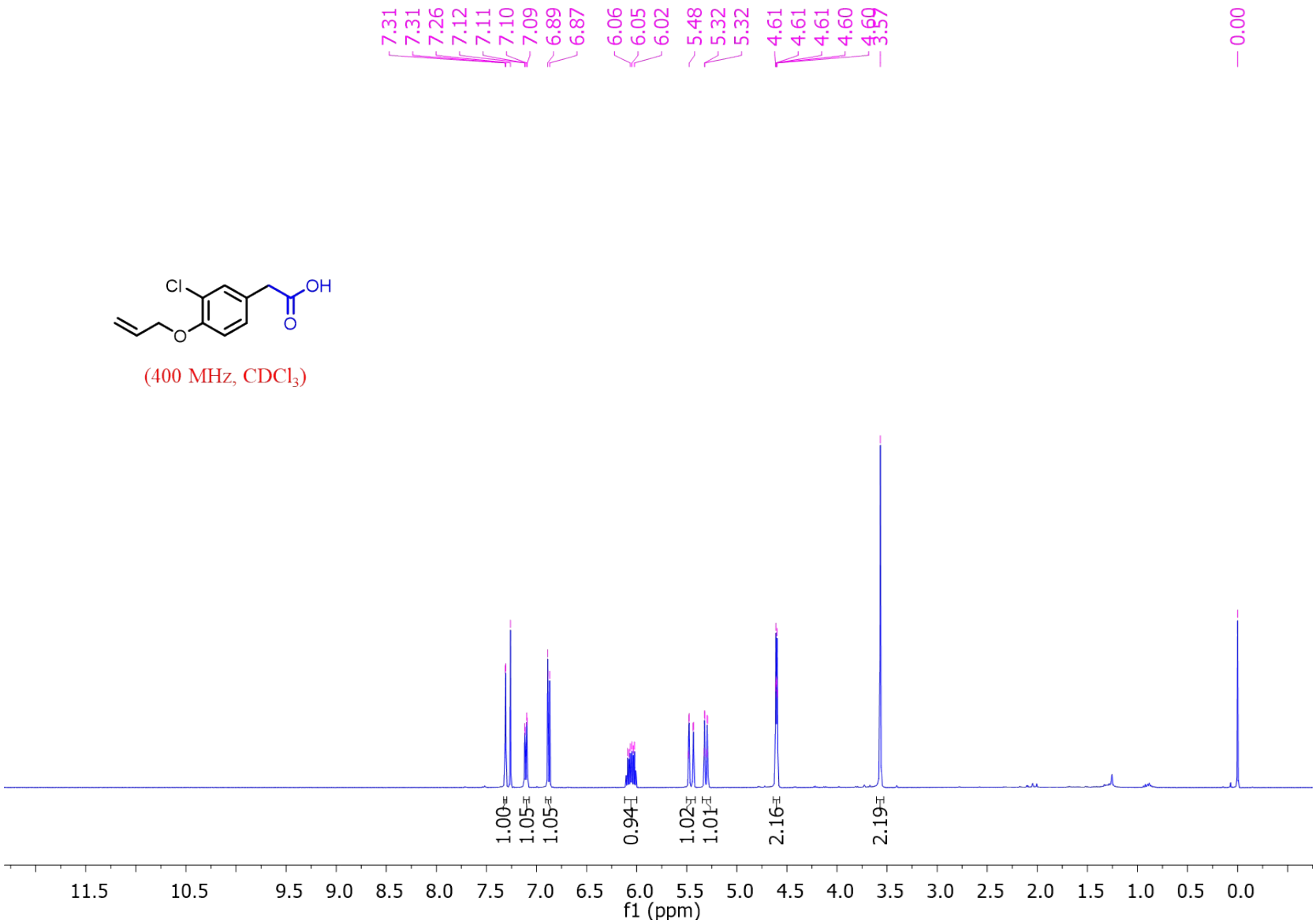


Fig. S103. ^{13}C NMR spectra of 2-(4-(allyloxy)-3-chlorophenyl) acetic acid (**3m**) in $CDCl_3$.

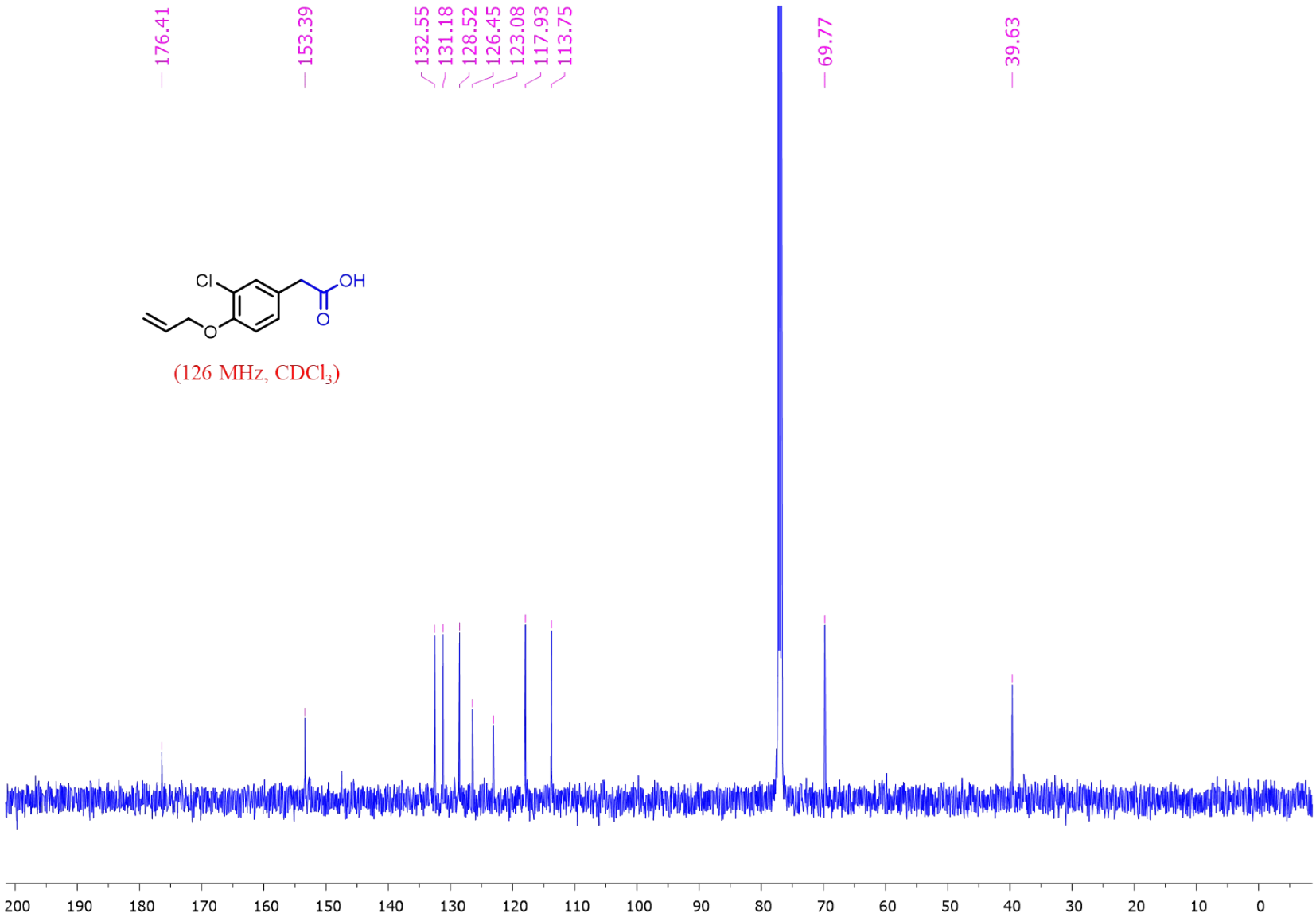


Fig. S104. ^{13}C NMR spectra of 2-(4-(allyloxy)-3-chlorophenyl) acetic acid (**3m**) in $CDCl_3$.

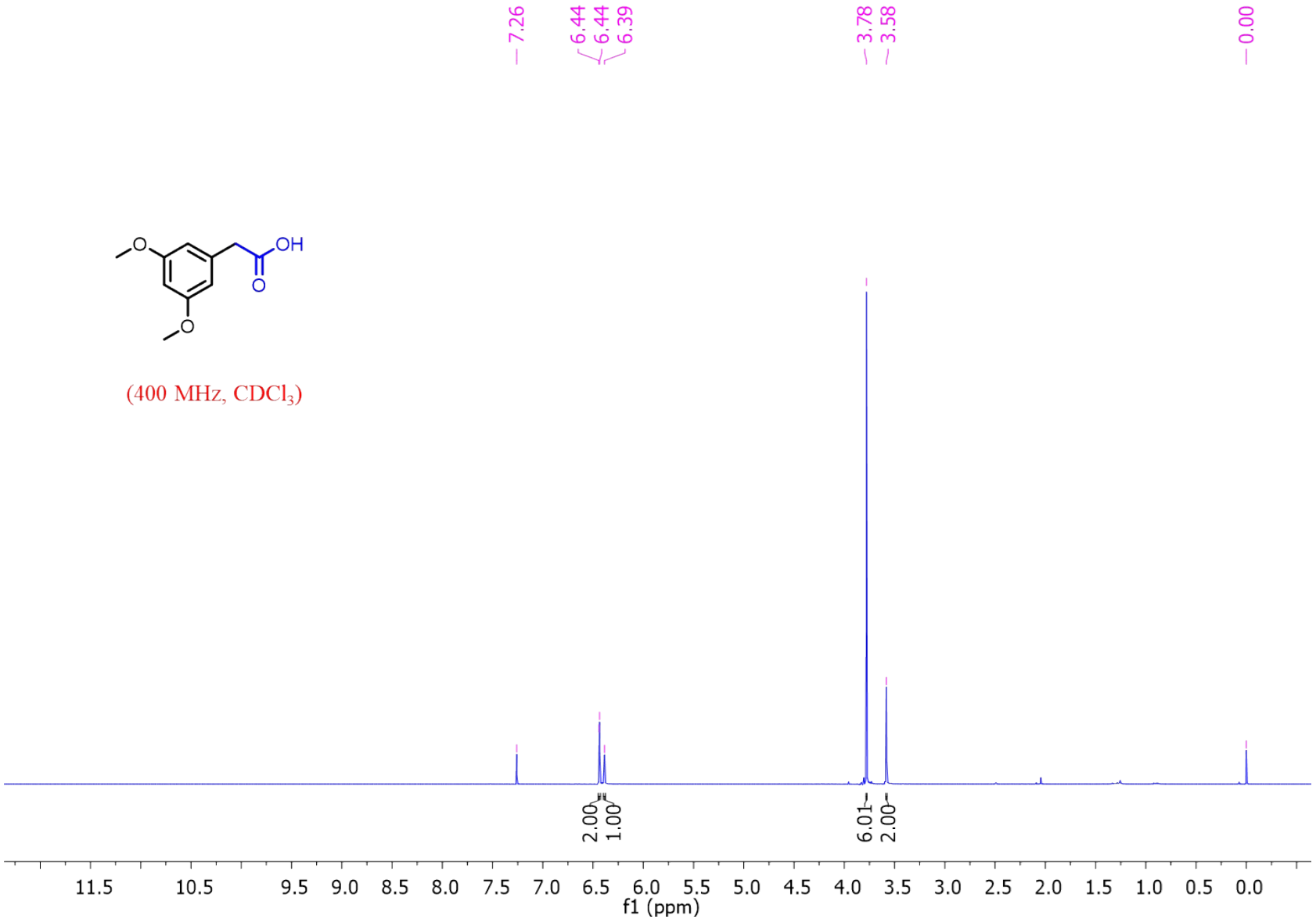


Fig. S105. ^{1}H NMR spectra of 2-(3,5-Dimethoxyphenyl) acetic acid (**3n**) in $CDCl_3$.

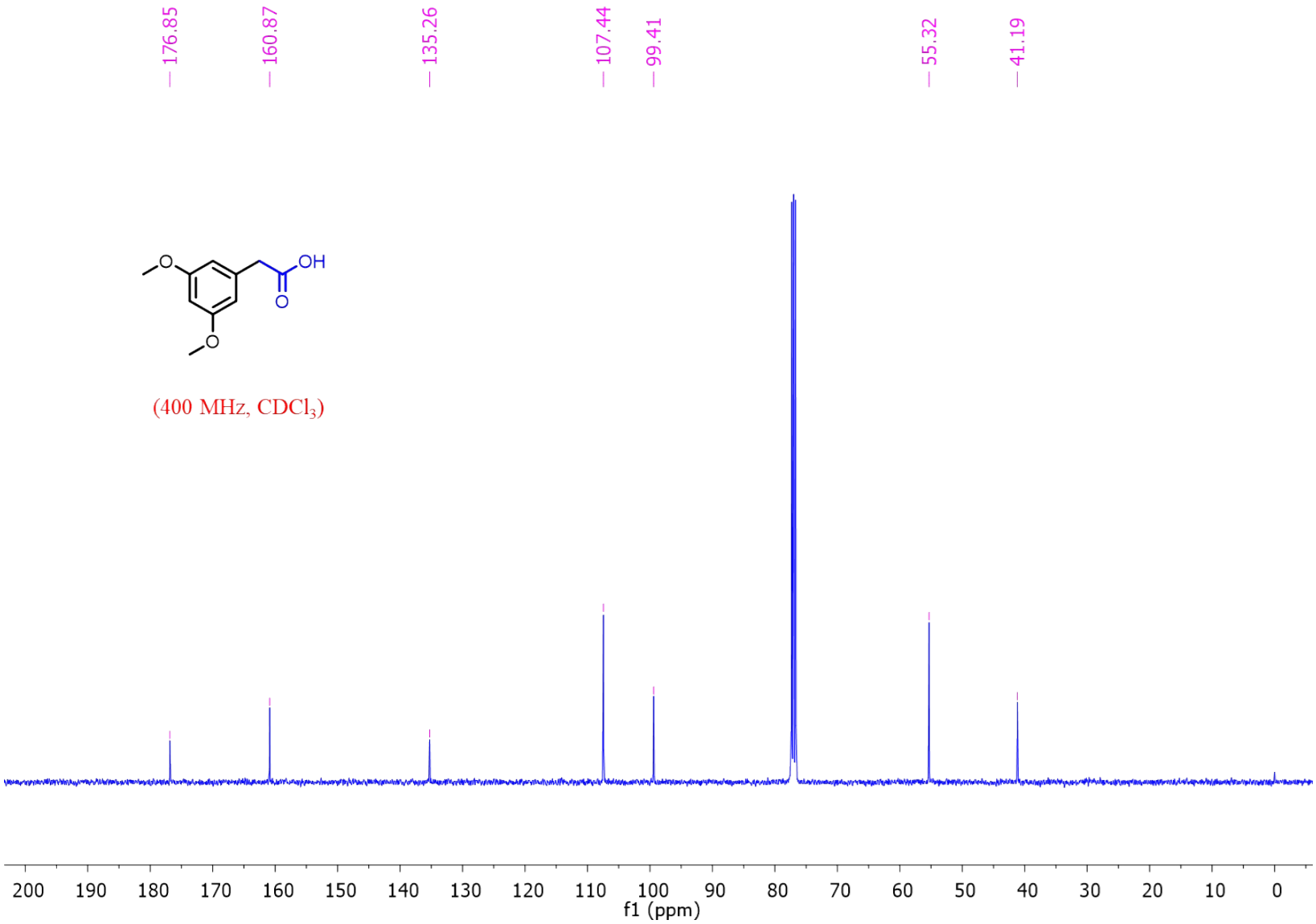


Fig. S106. ^{13}C NMR spectra of 2-(3,5-Dimethoxyphenyl) acetic acid (**3n**) in $CDCl_3$.

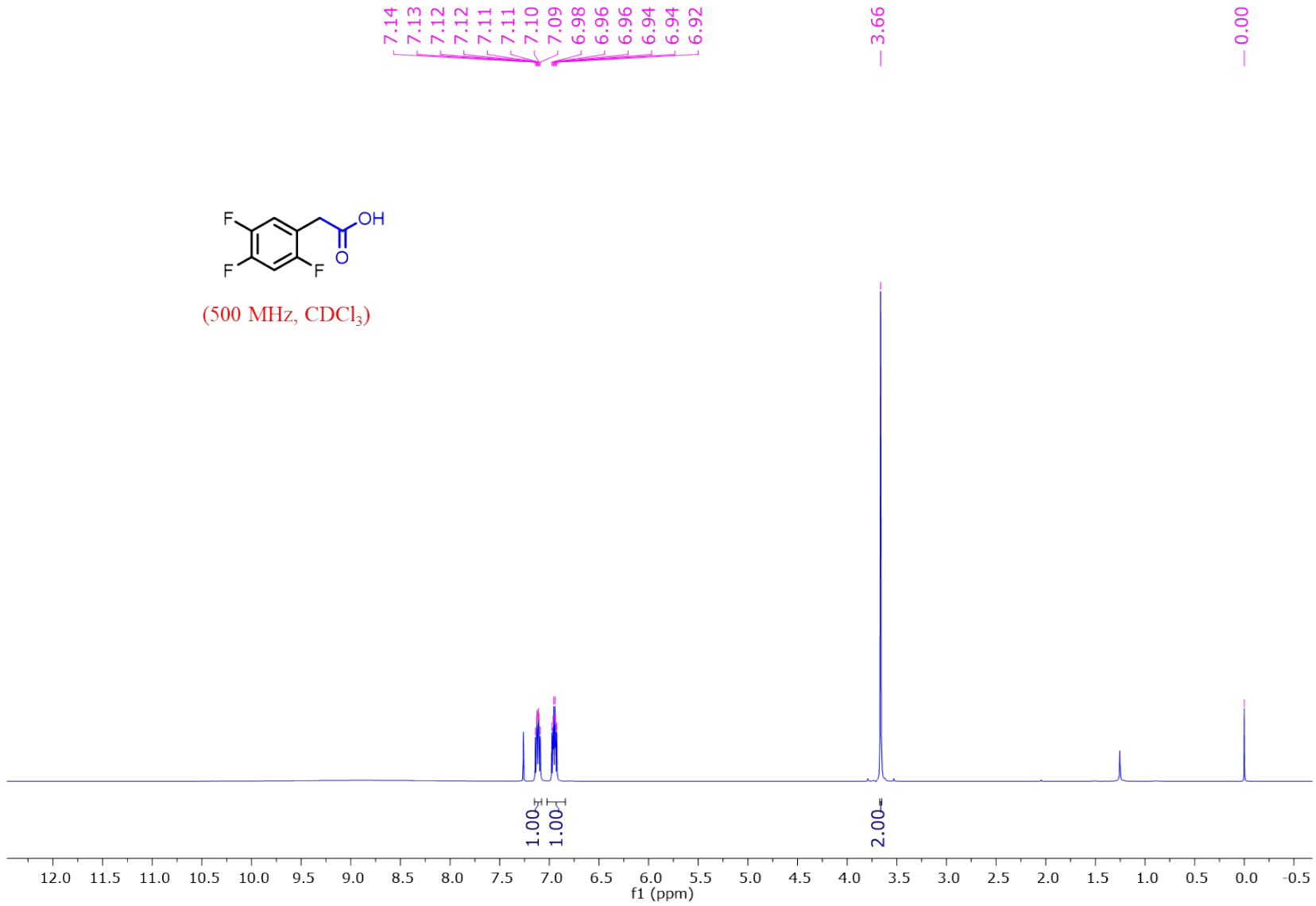


Fig. S107. ^{13}H NMR spectra of 2-(2,4,5-trifluorophenyl)acetic acid (**3o**) in $CDCl_3$.

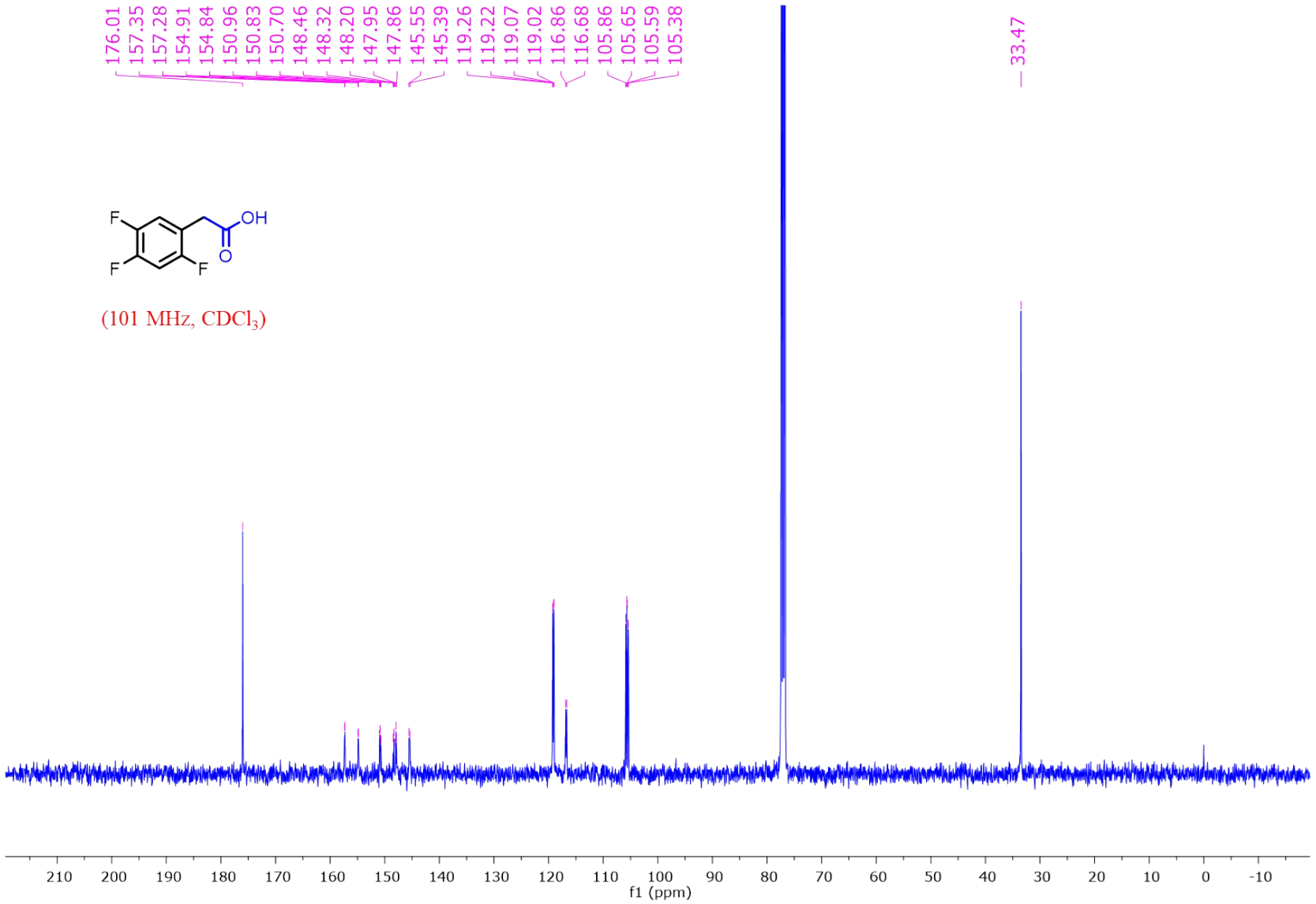


Fig. S108. ^{13}C NMR spectra of 2-(2,4,5-trifluorophenyl)acetic acid (**3o**) in $CDCl_3$.

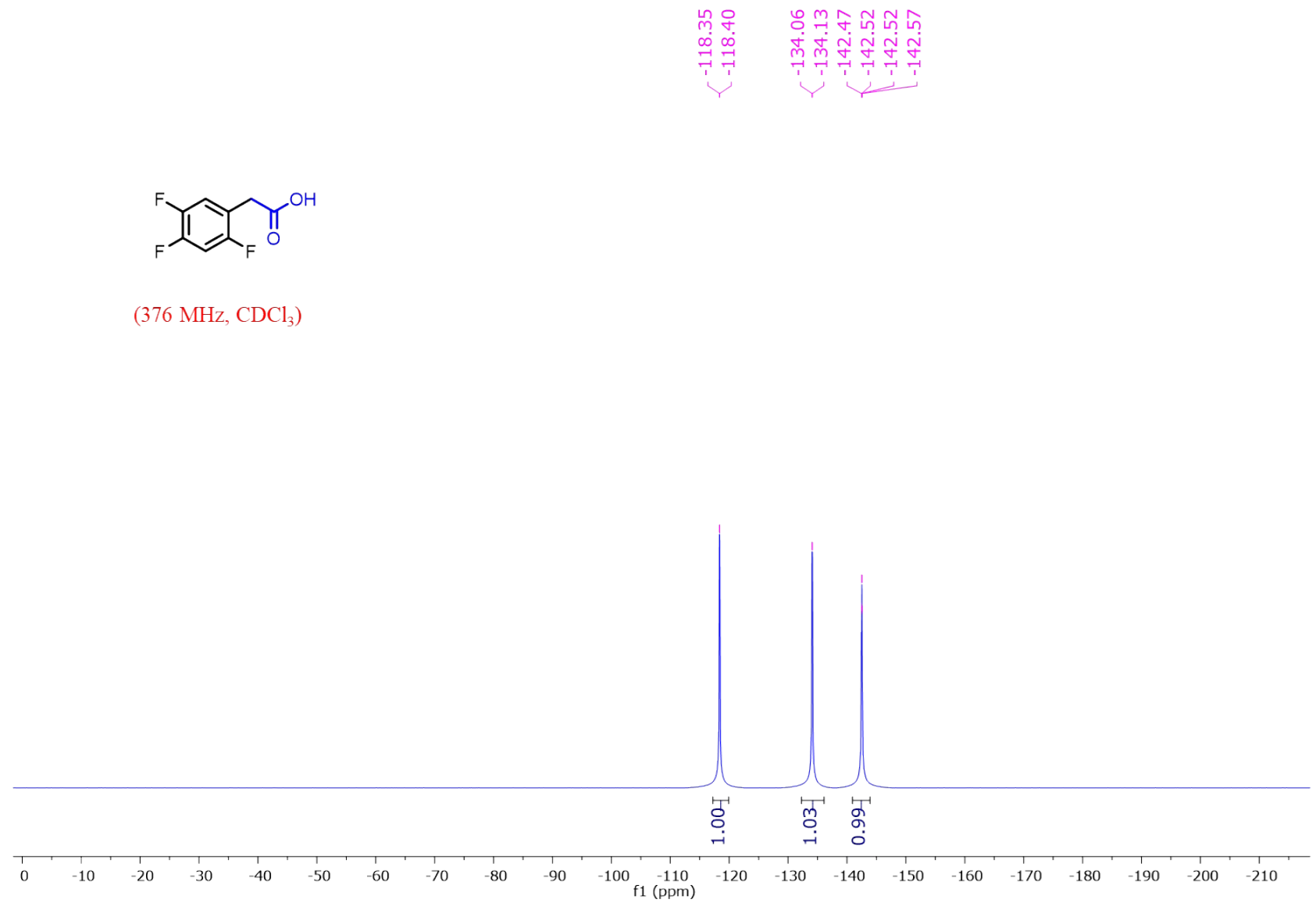


Fig. S109. ^{19}F NMR spectra of 2-(2,4,5-trifluorophenyl)acetic acid (**3o**) in $CDCl_3$.

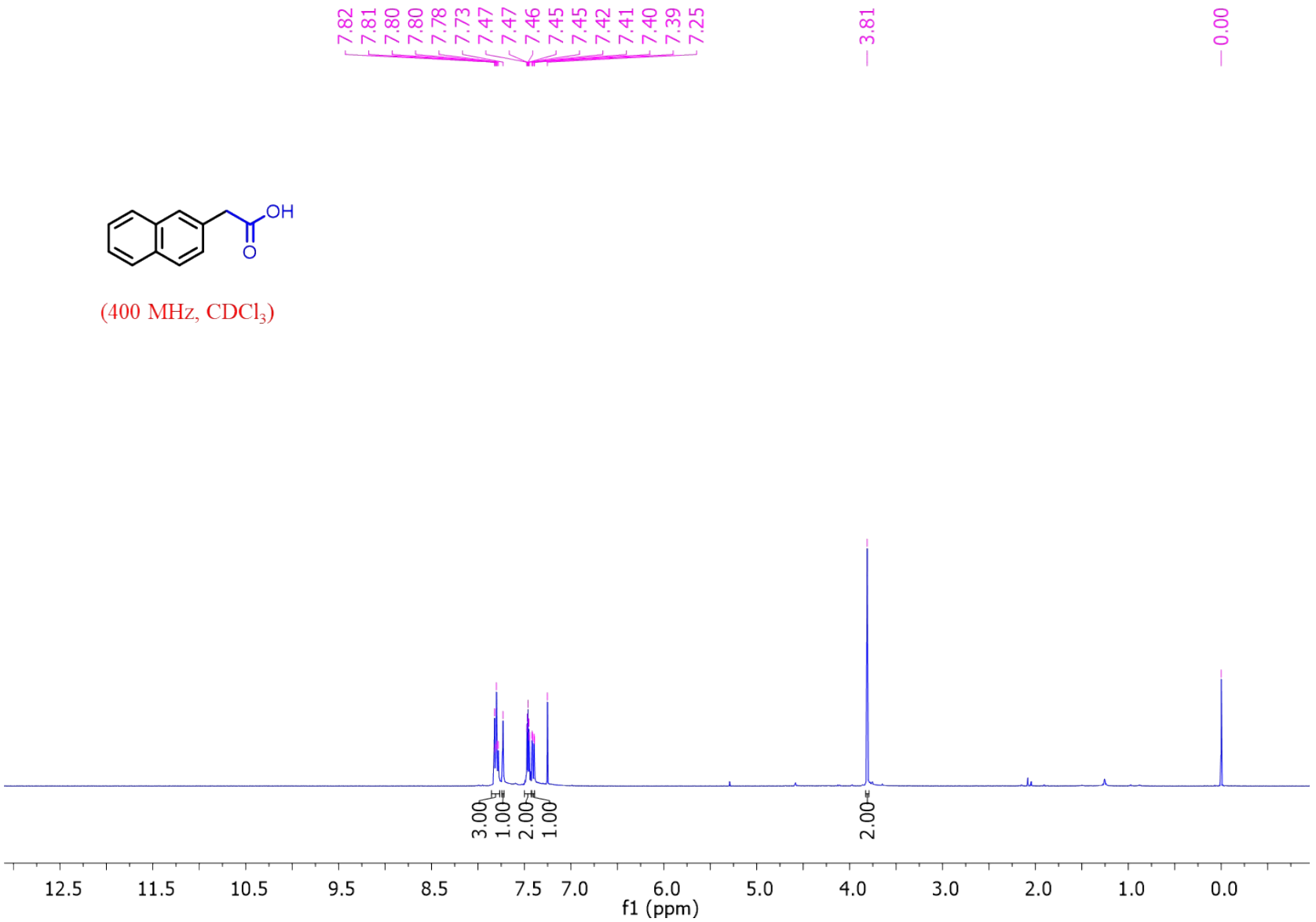


Fig. S110. ^{1}H NMR spectra of 2-(naphthalen-2-yl) acetic acid (**3p**) in $CDCl_3$.

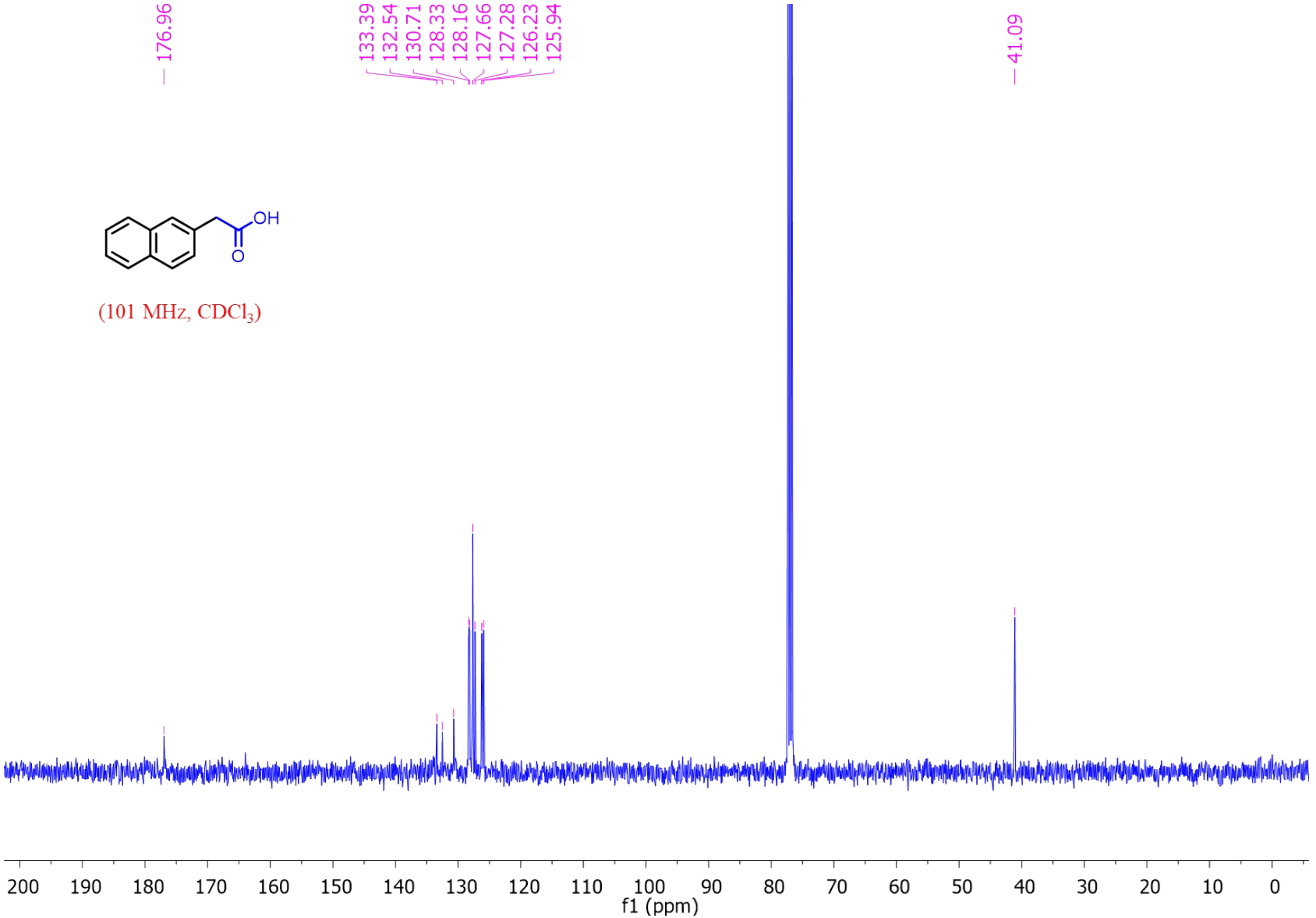


Fig. S111. ^{13}C NMR spectra of 2-(naphthalen-2-yl) acetic acid (**3p**) in $CDCl_3$.

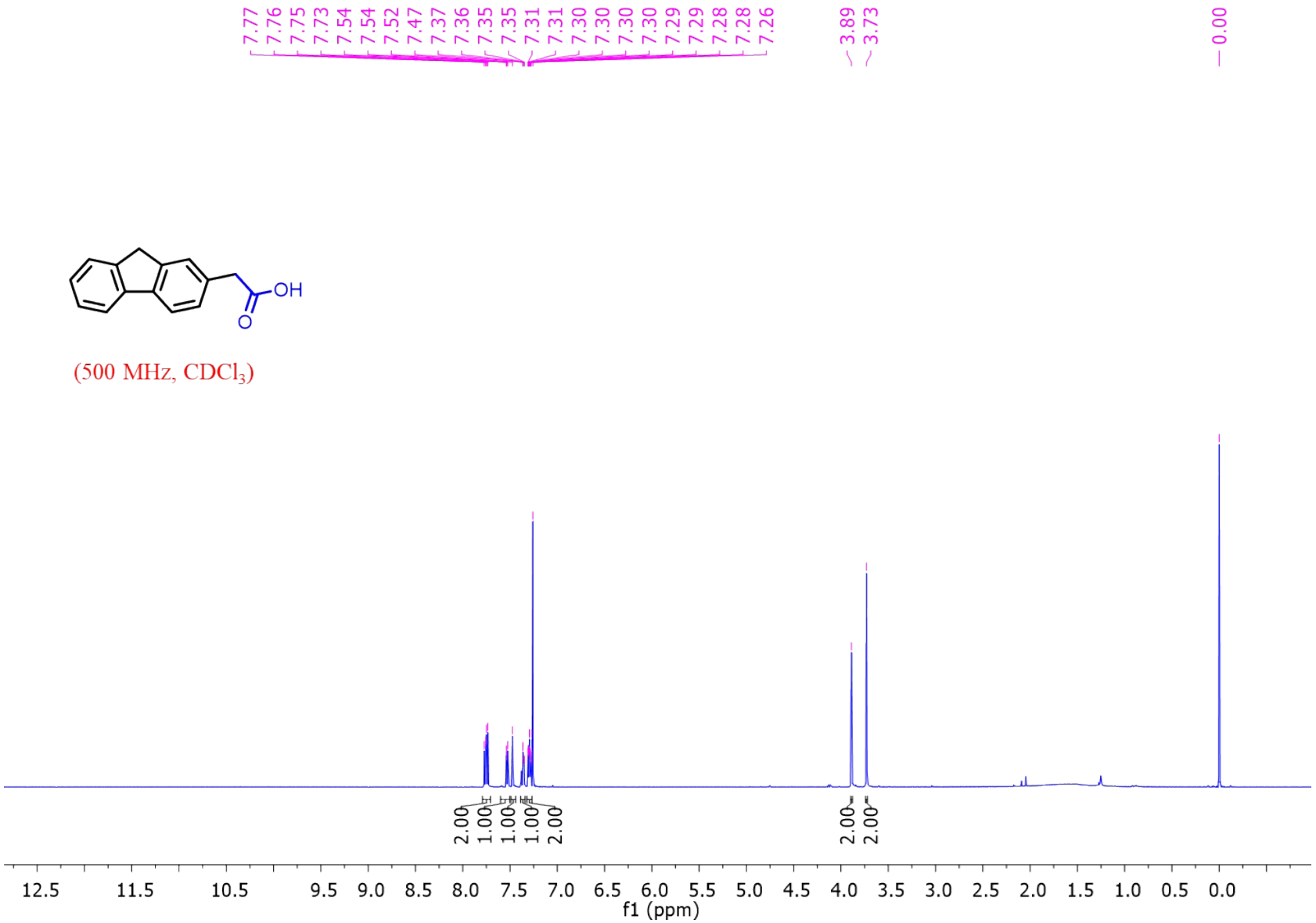


Fig. S112. ^{13}C NMR spectra of 2-(9H-fluoren-2-yl) acetic acid (**3q**) in $CDCl_3$.

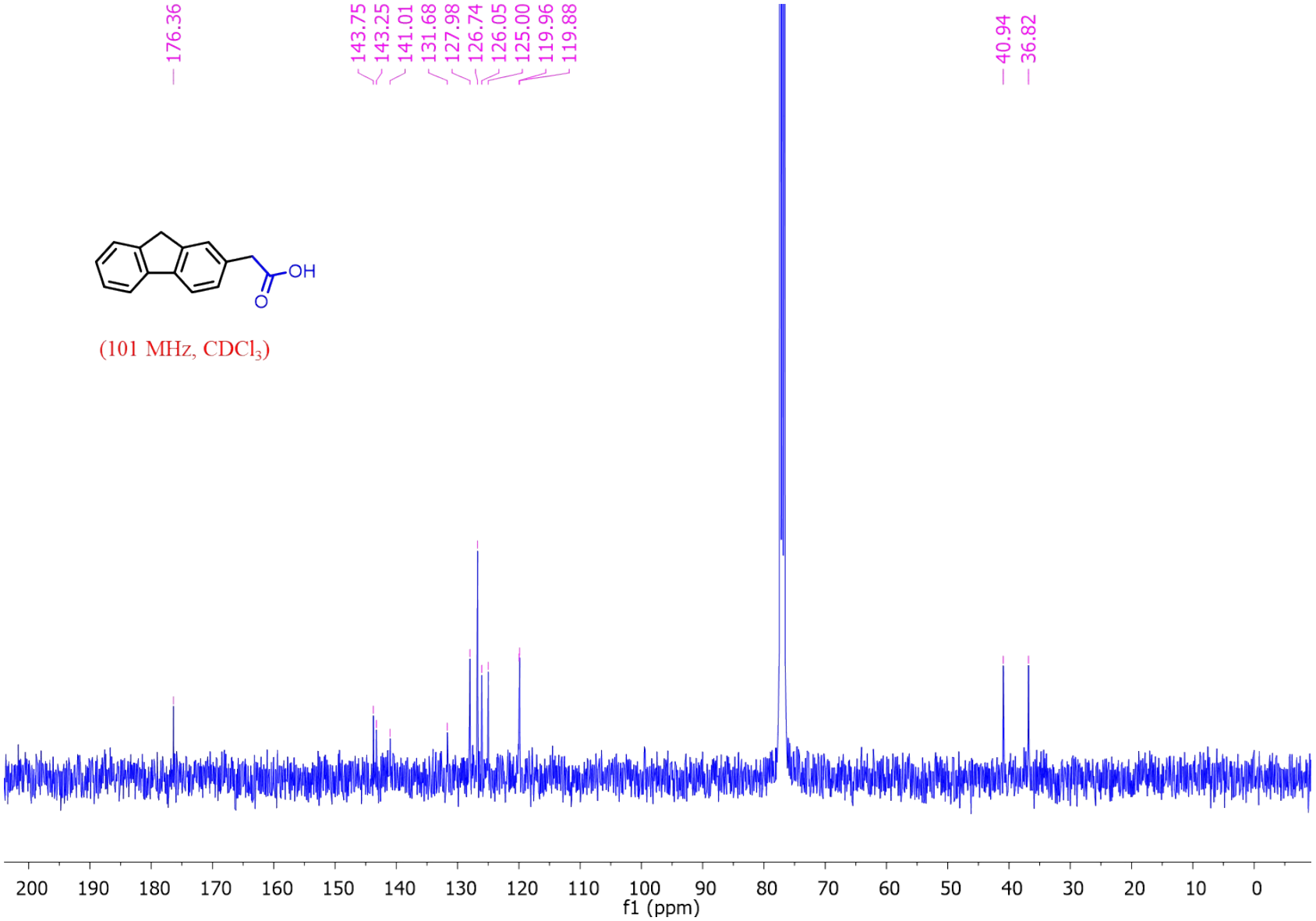


Fig. S113. ^{13}C NMR spectra of 2-(9H-fluoren-2-yl) acetic acid (**3q**) in $CDCl_3$.

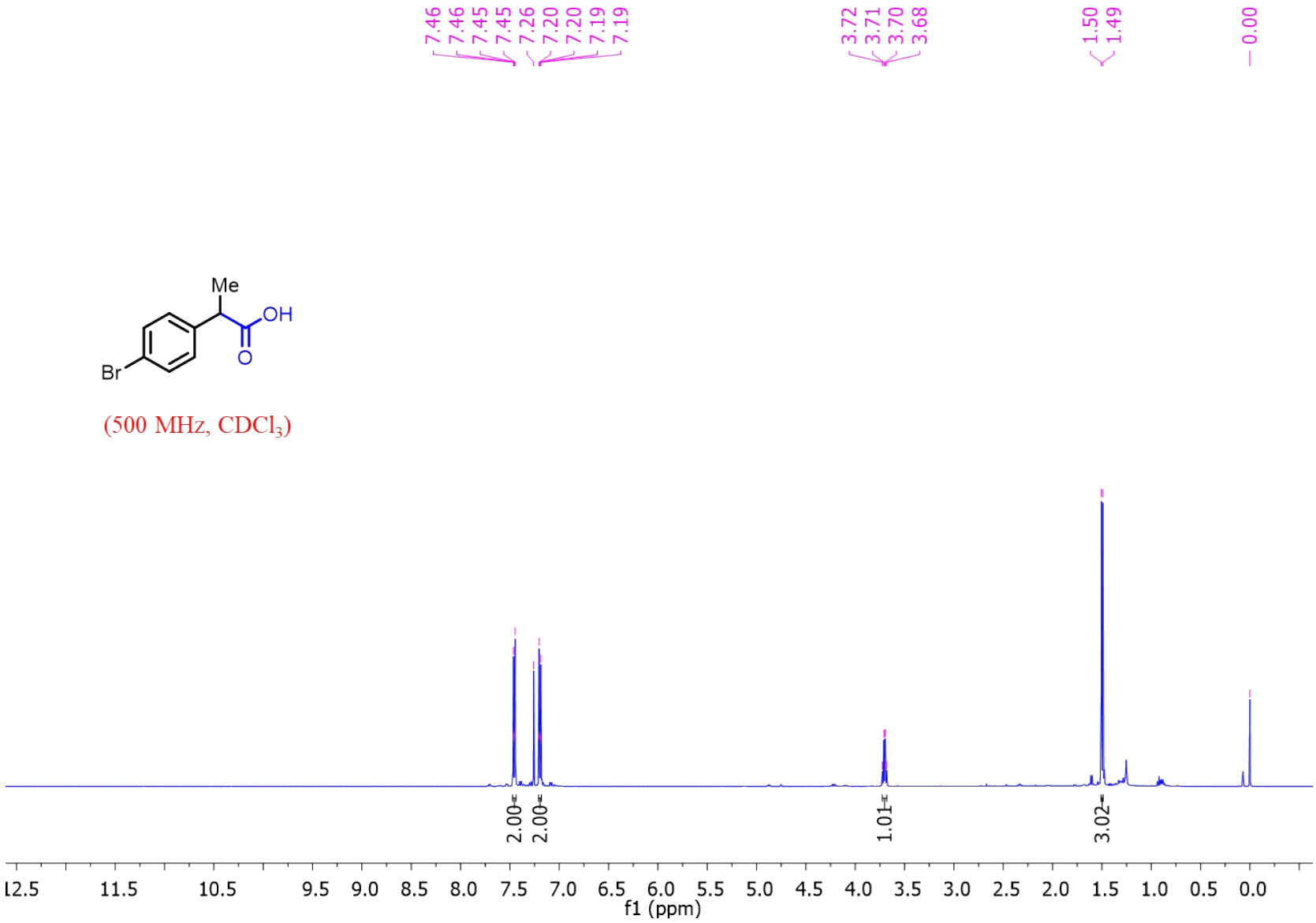


Fig. S114. ^{13}C NMR spectra of 2-(4-bromophenyl) propanoic acid (**3r**) in $CDCl_3$.

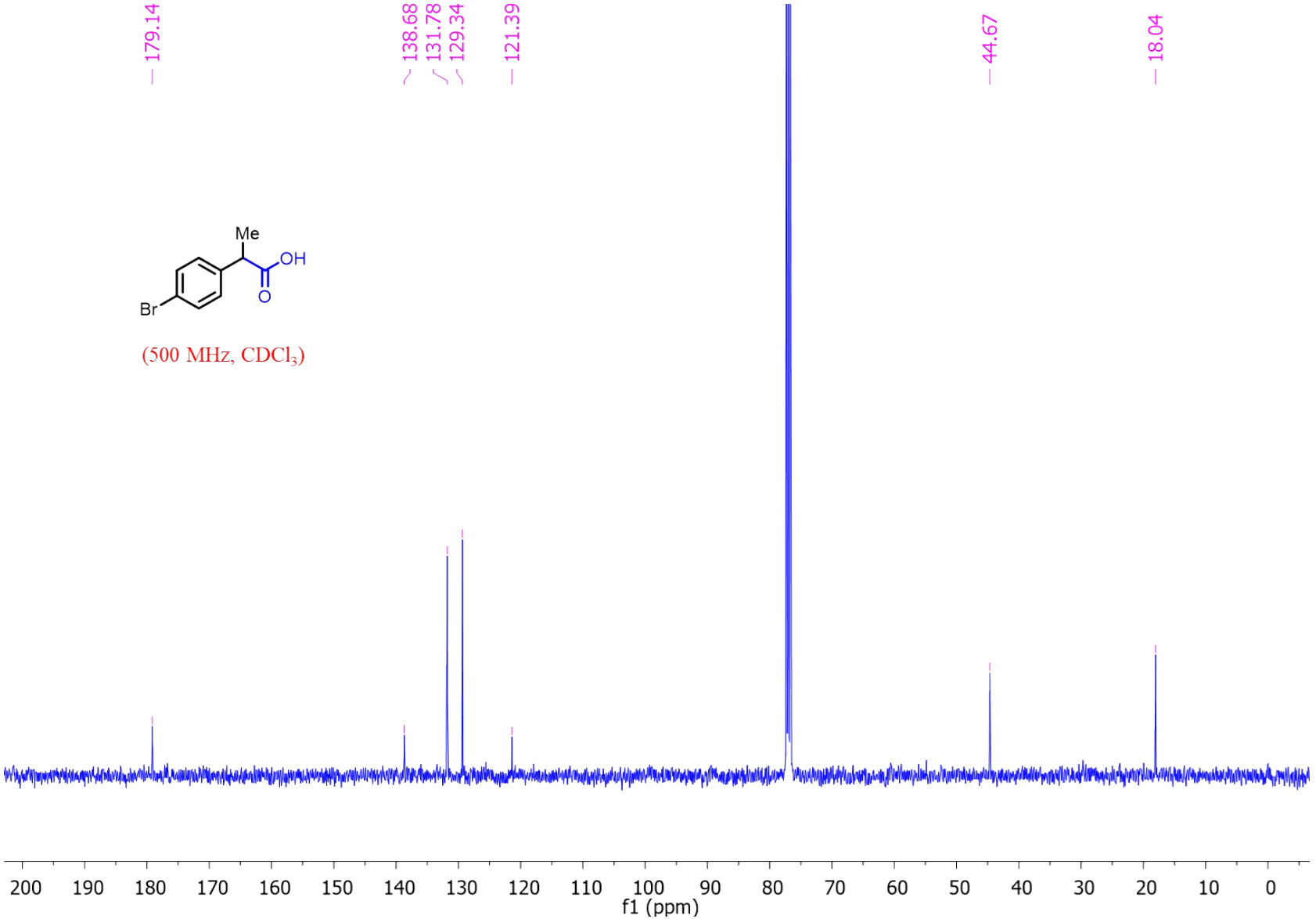


Fig. S115. ^{13}C NMR spectra of 2-(4-bromophenyl) propanoic acid (**3r**) in $CDCl_3$.

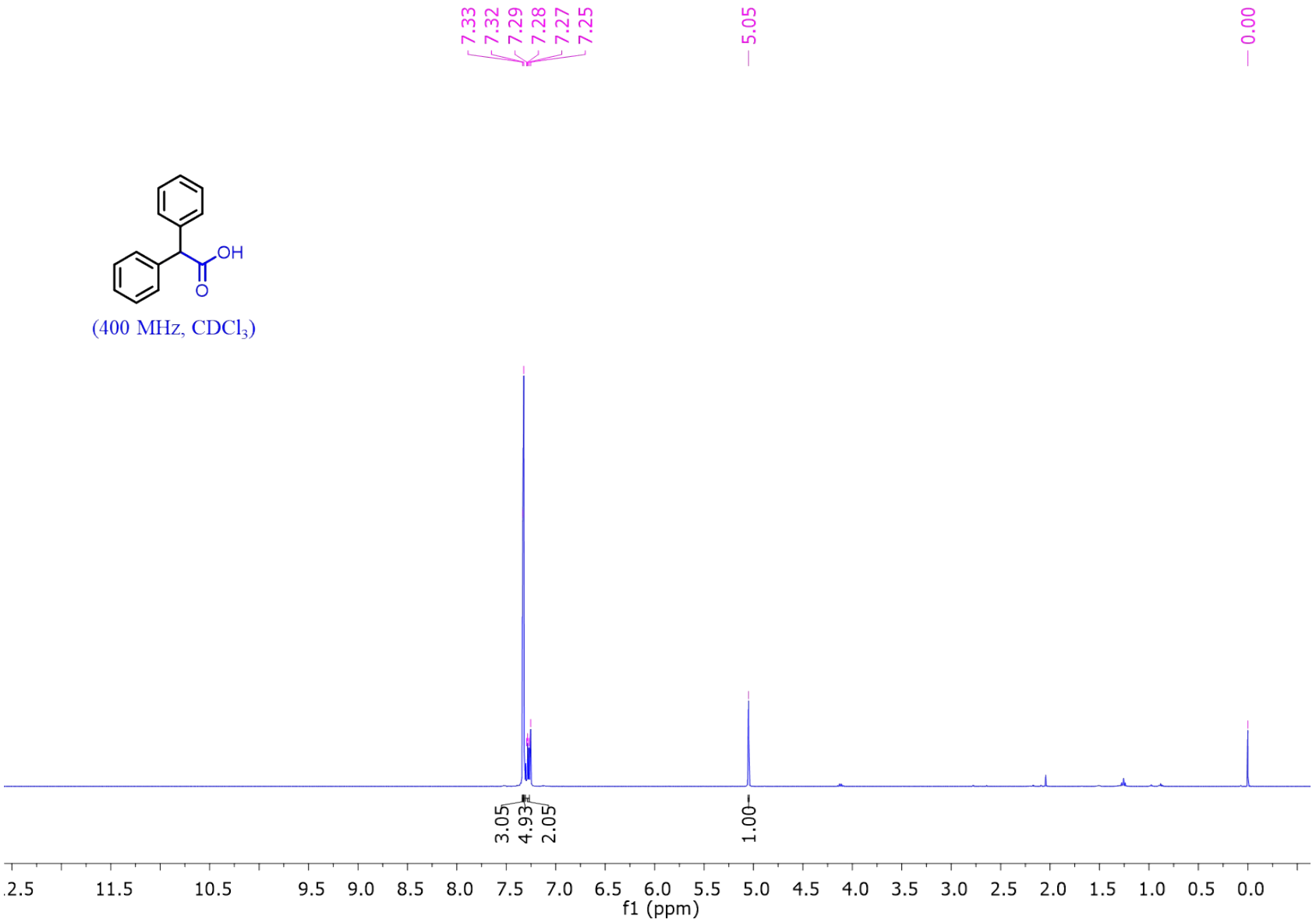


Fig. S116. ^{1}H NMR spectra of 2,2-diphenyl acetic acid (**3s**) in $CDCl_3$.

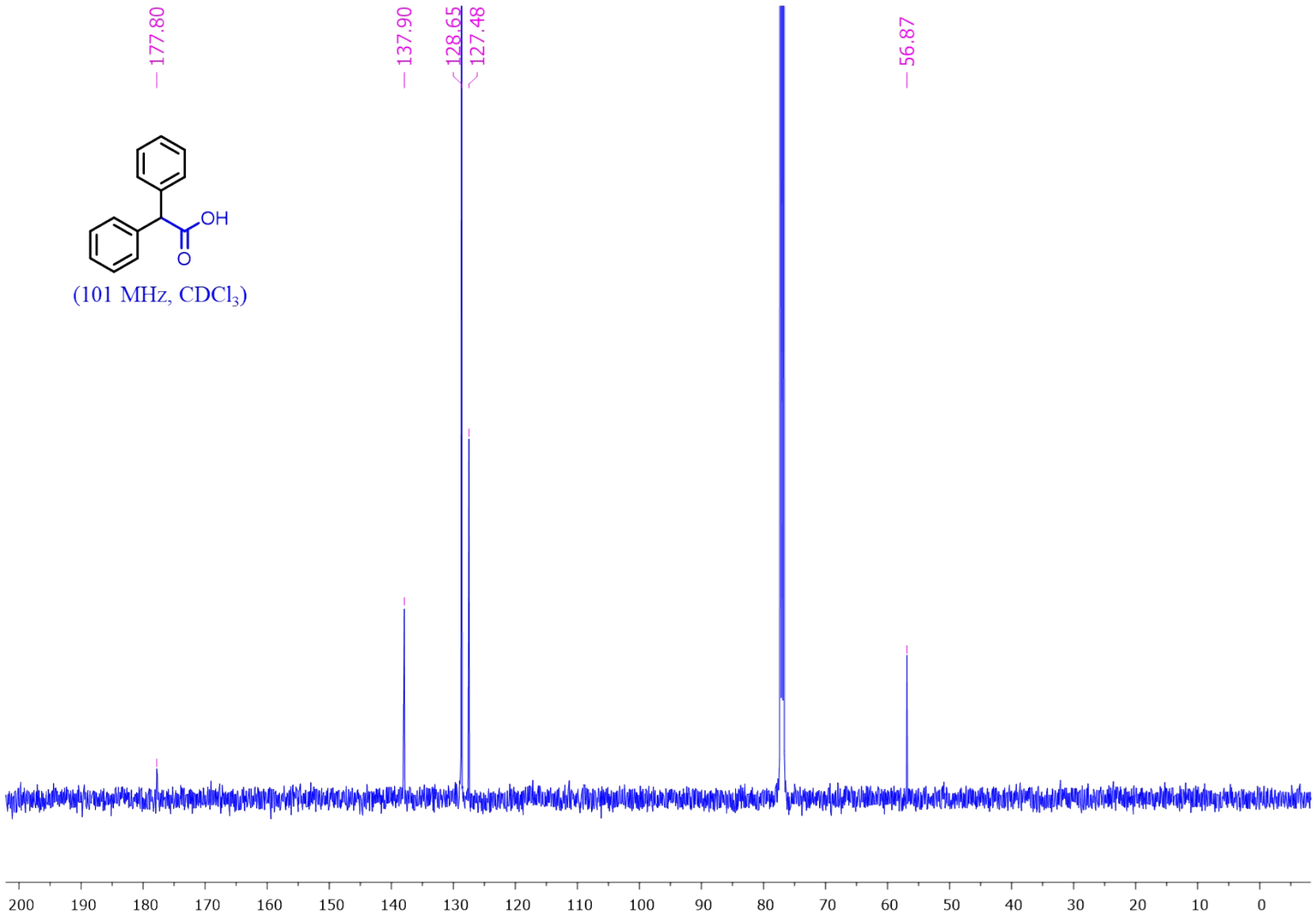


Fig. S117. ^{13}C NMR spectra of 2,2-diphenyl acetic acid (**3s**) in $CDCl_3$.

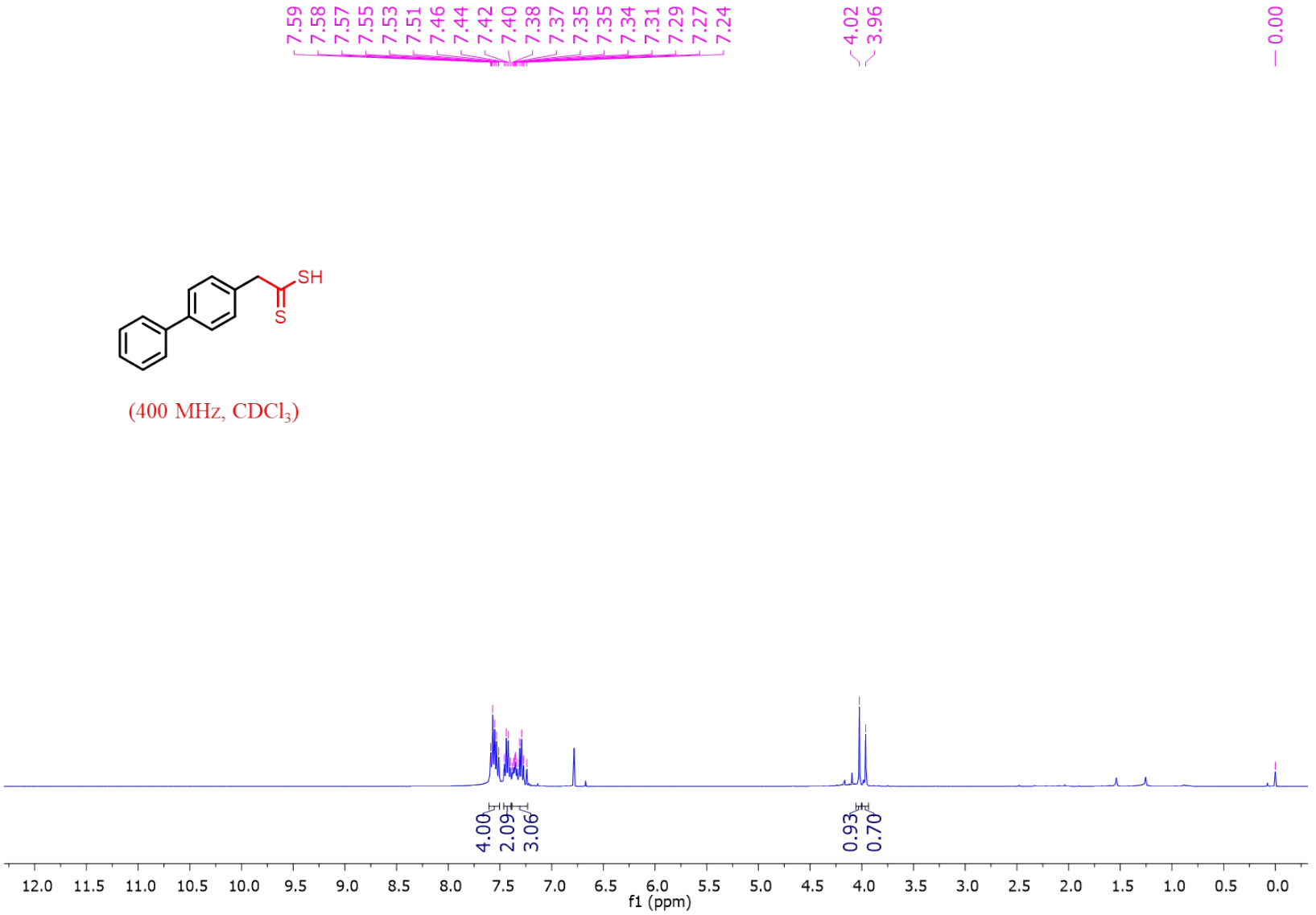


Fig. S118. ^{1}H NMR spectra of 2-([1,1'-biphenyl]-4-yl)ethanedithioic acid (**5a**) in $CDCl_3$.

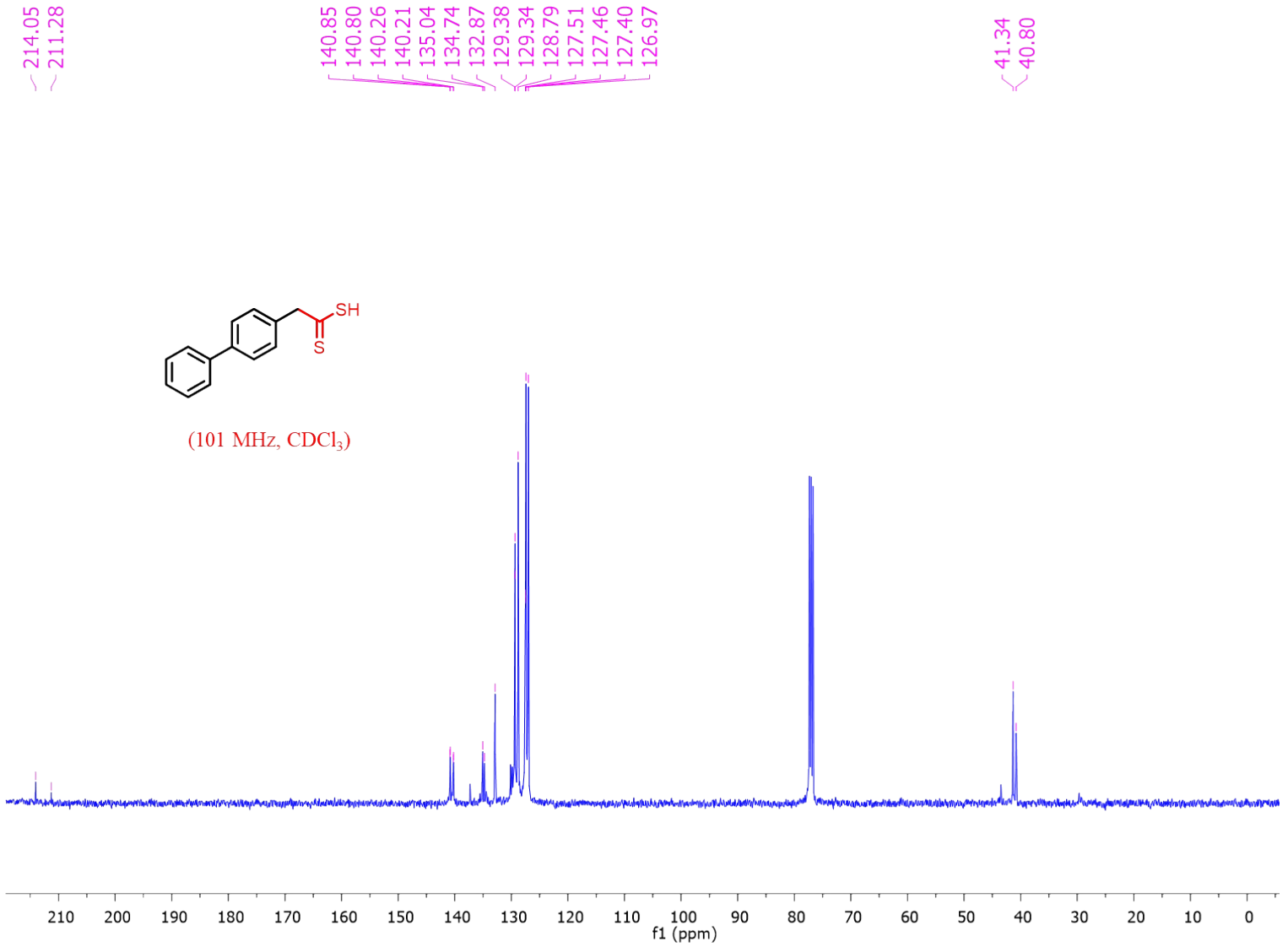


Fig. S119. ^{13}C NMR spectra of 2-([1,1'-biphenyl]-4-yl)ethanedithioic acid (**5a**) in $CDCl_3$.

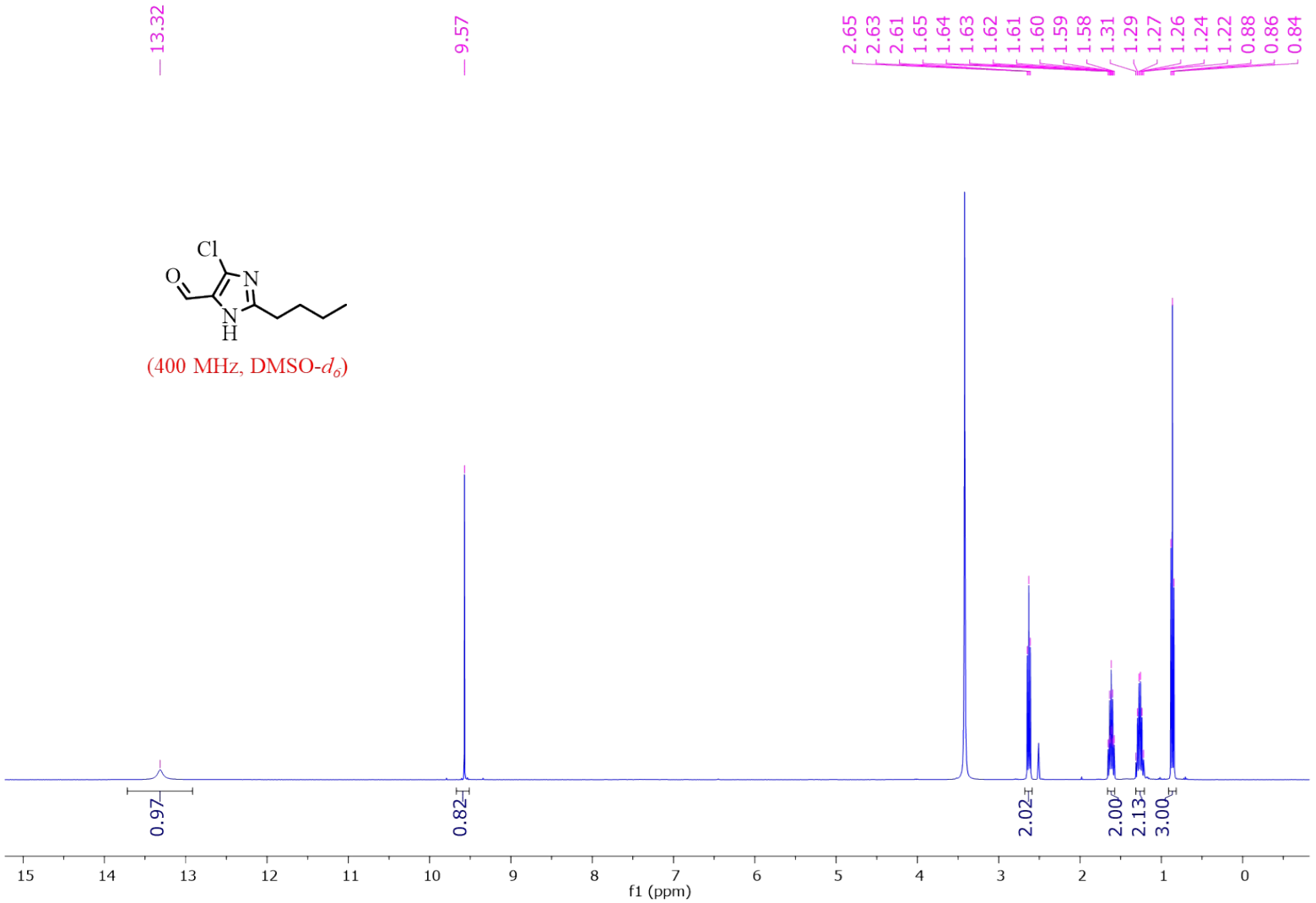


Fig. S120. ^{1}H NMR spectra of 2-Butyl-5-chloro-3H-imidazole-4-carbaldehyde in DMSO-*d6*.

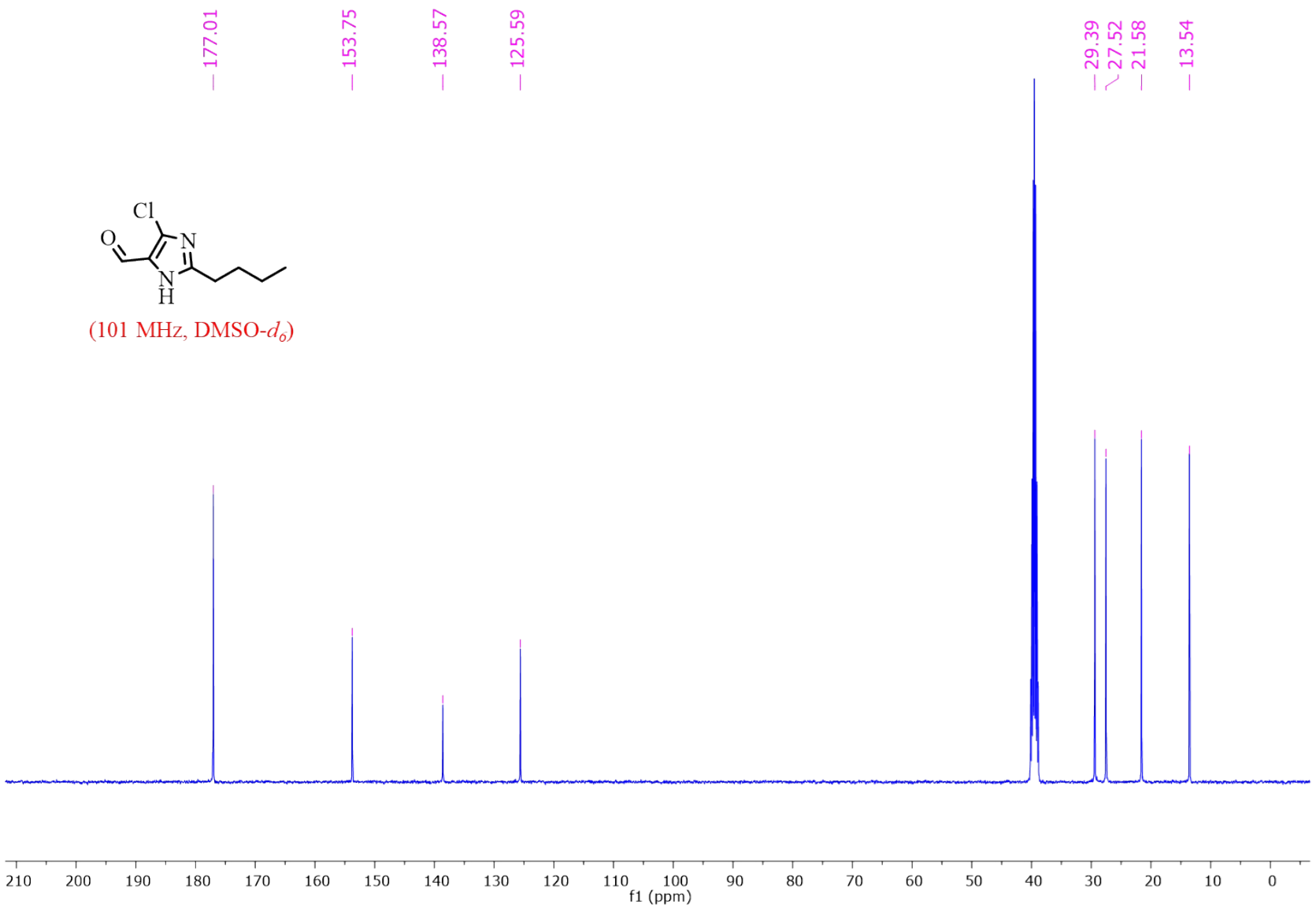


Fig. S121. ^{13}C NMR spectra of 2-Butyl-5-chloro-3H-imidazole-4-carbaldehyde in DMSO-d_6.

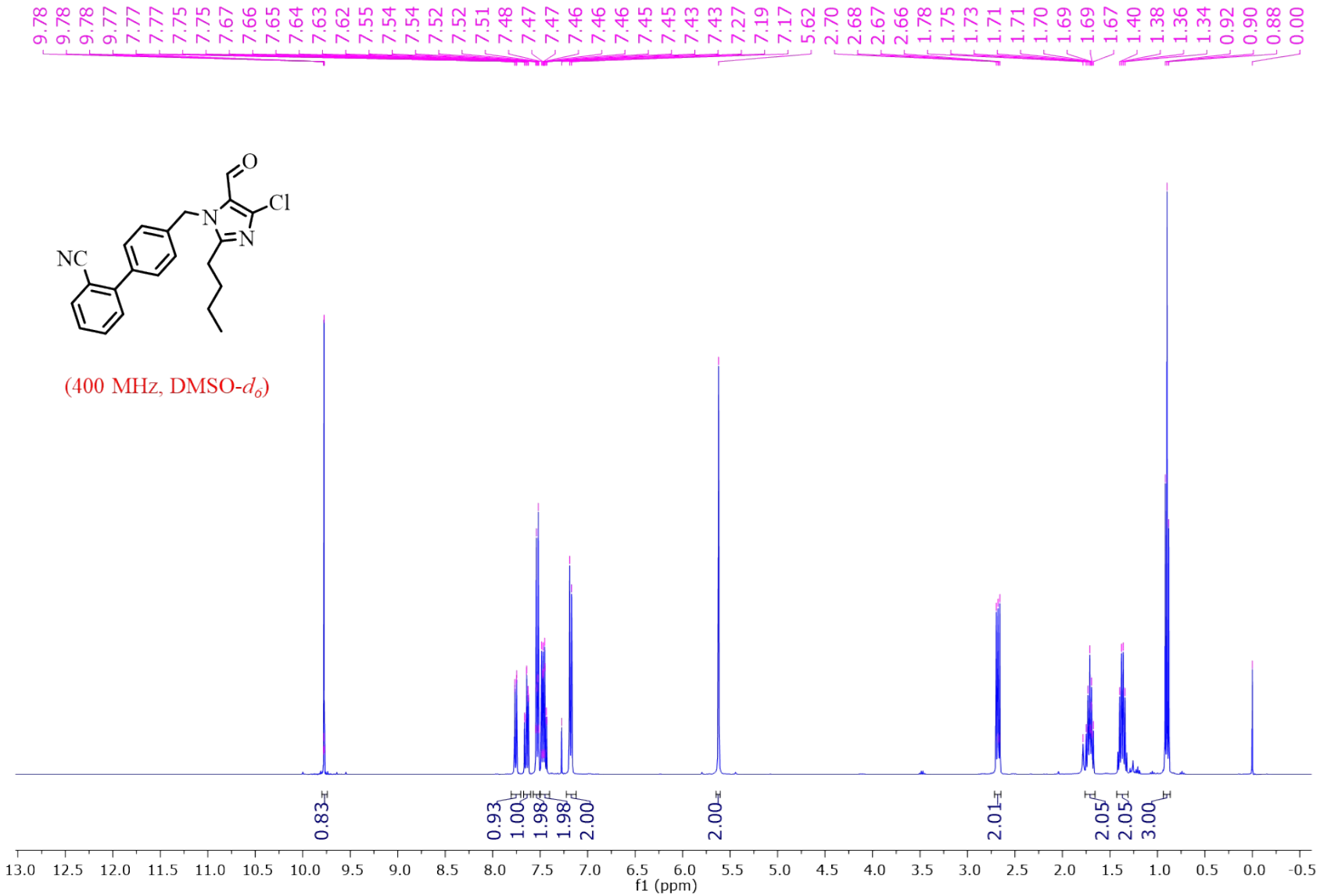


Fig. S122. ^{1}H NMR spectra of 1-([1,1'-biphenyl]-4-ylmethyl)- 2-butyl-4-chloro-1H-imidazole- 5-carbaldehyde $CDCl_3$.

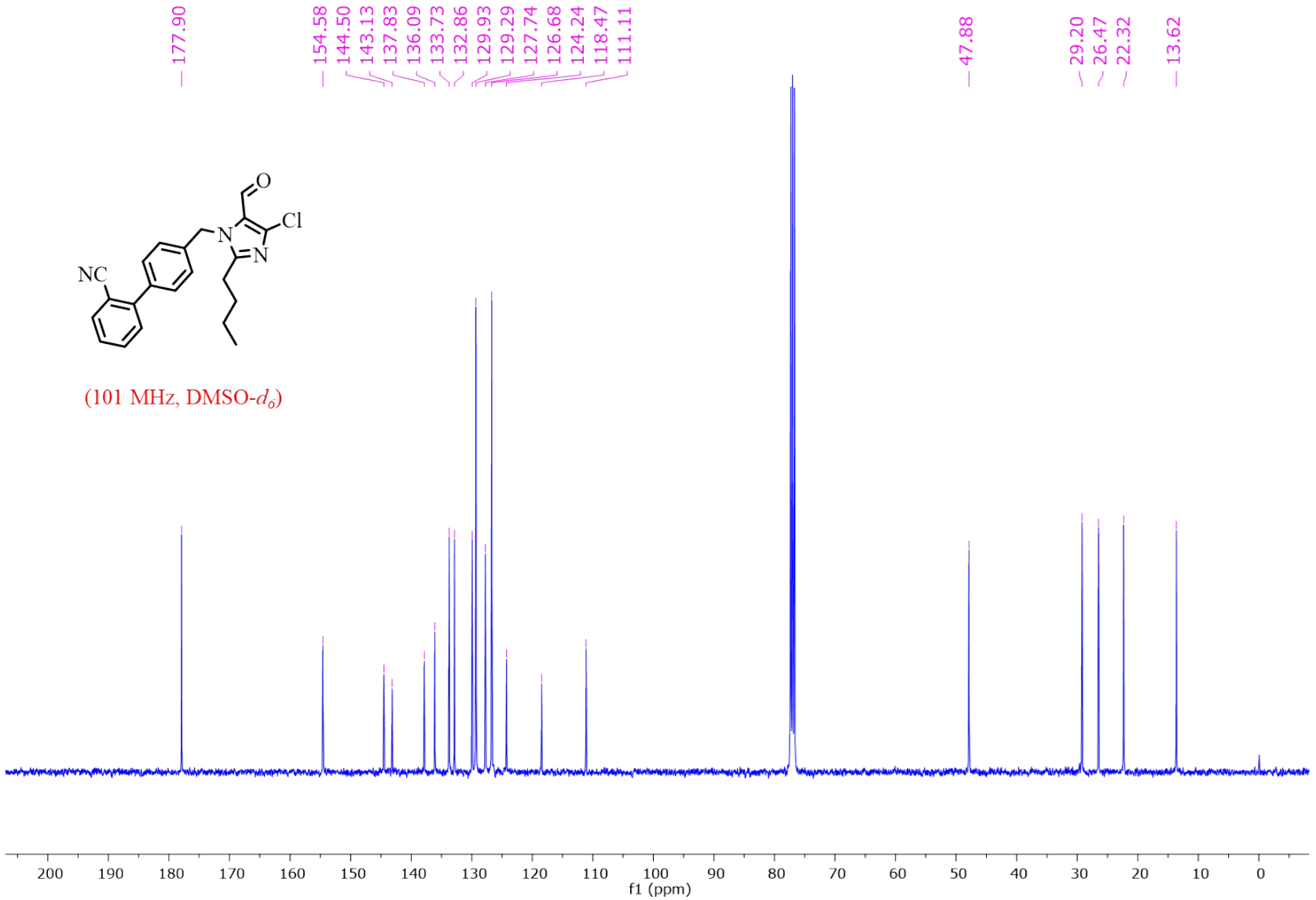


Fig. S123. ^{13}C NMR spectra of 1-([1,1'-biphenyl]-4-ylmethyl)- 2-butyl-4-chloro-1H-imidazole- 5-carbaldehyde in $CDCl_3$.

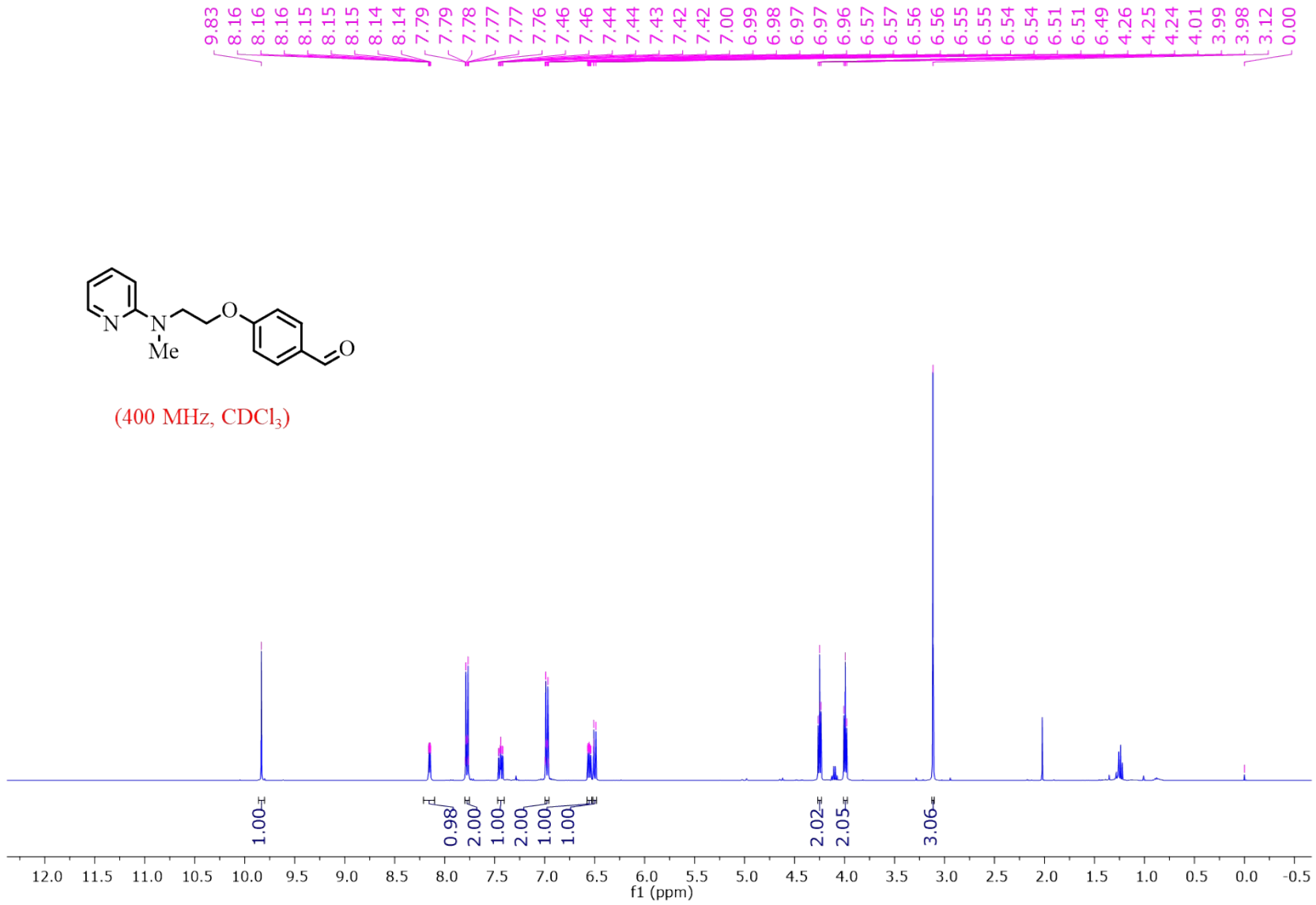


Fig. S124. ^{1}H NMR spectra of 4-(2-(methyl(pyridin-2-yl) amino) ethoxy) benzaldehyde in $CDCl_3$.

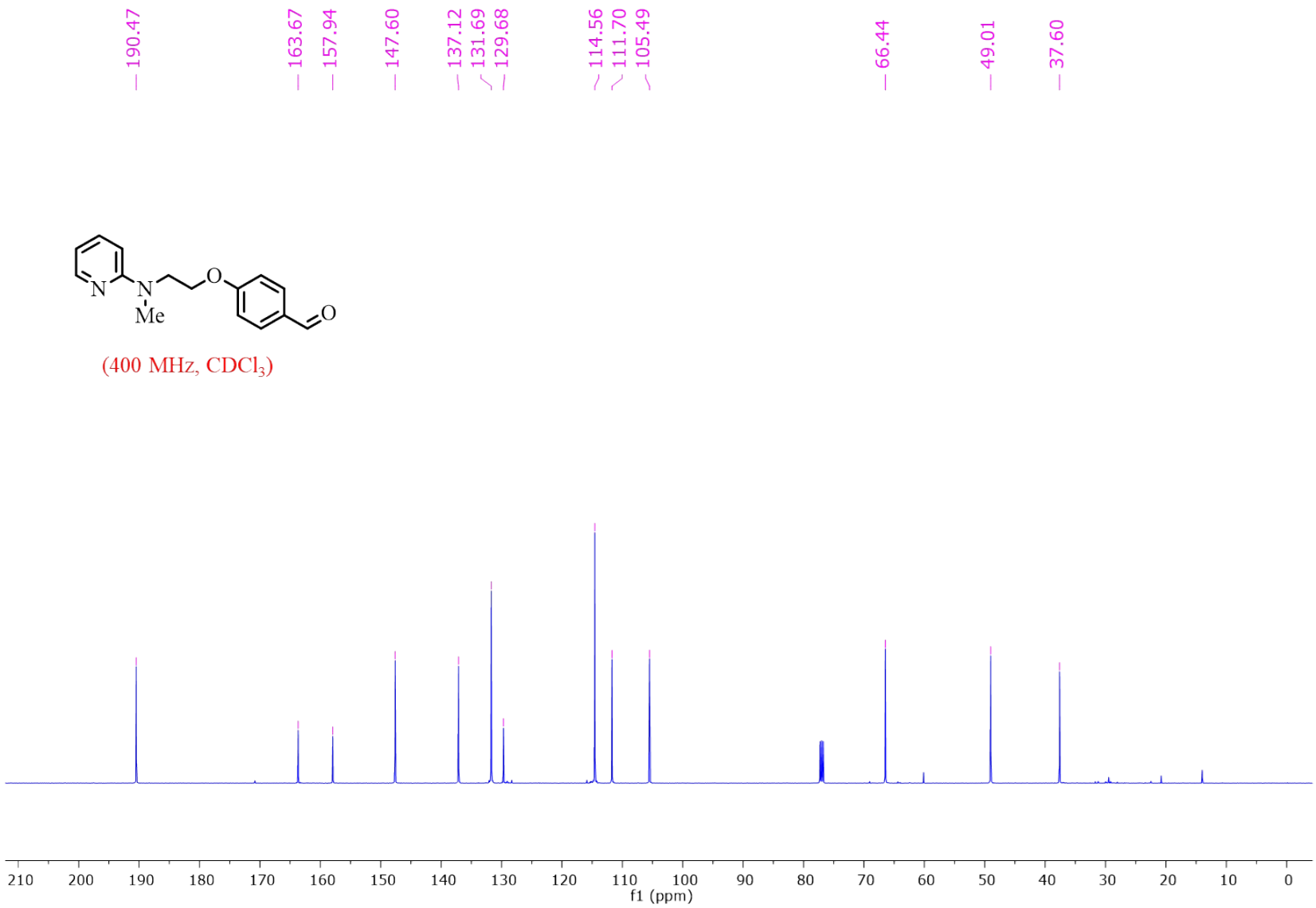


Fig. S125. ^{13}C NMR spectra of 4-(2-(methyl(pyridin-2-yl) amino) ethoxy) benzaldehyde in $CDCl_3$.

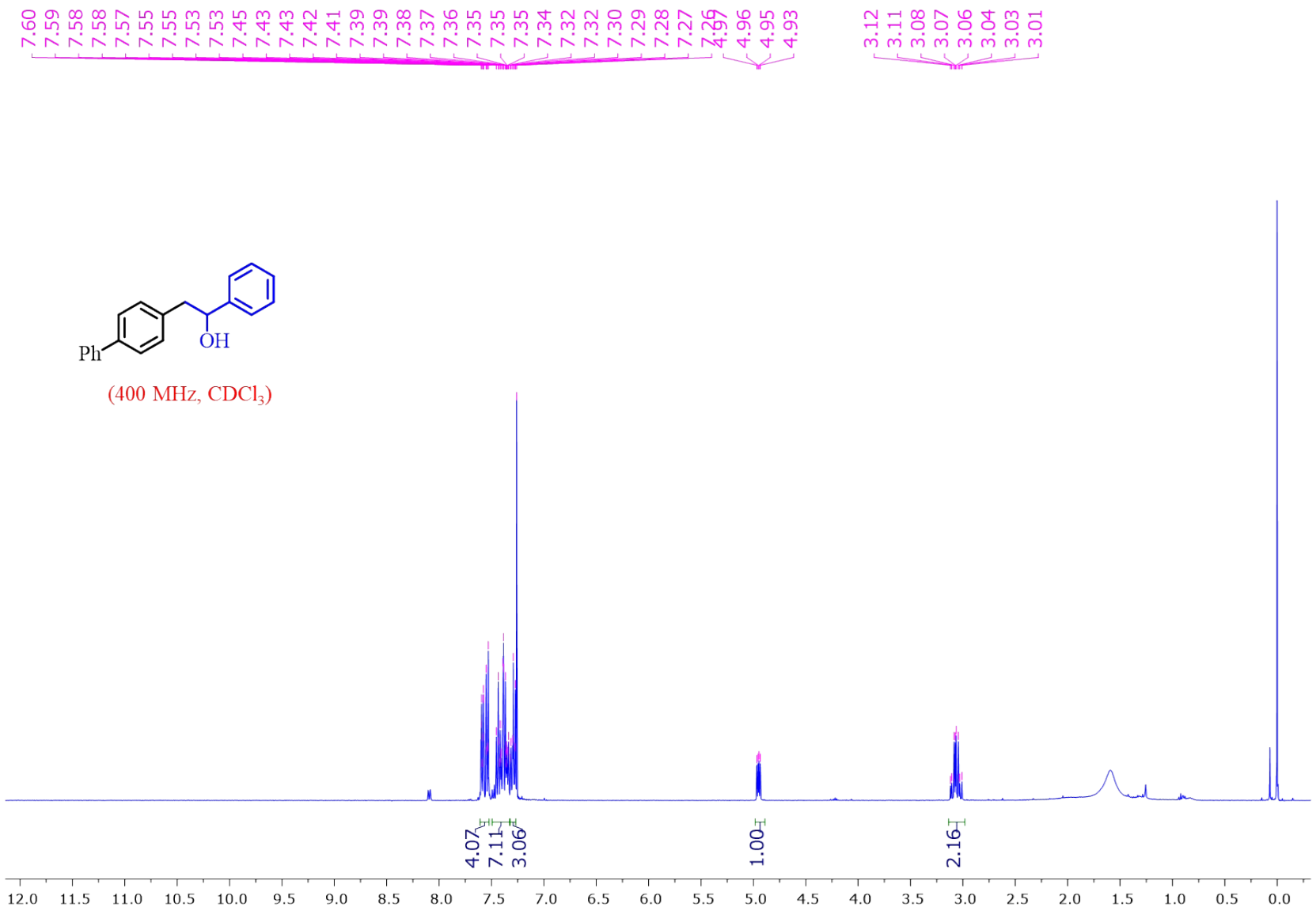


Fig. S126. ^{13}C NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1-phenylethan-1-ol (**7a**) in $CDCl_3$.

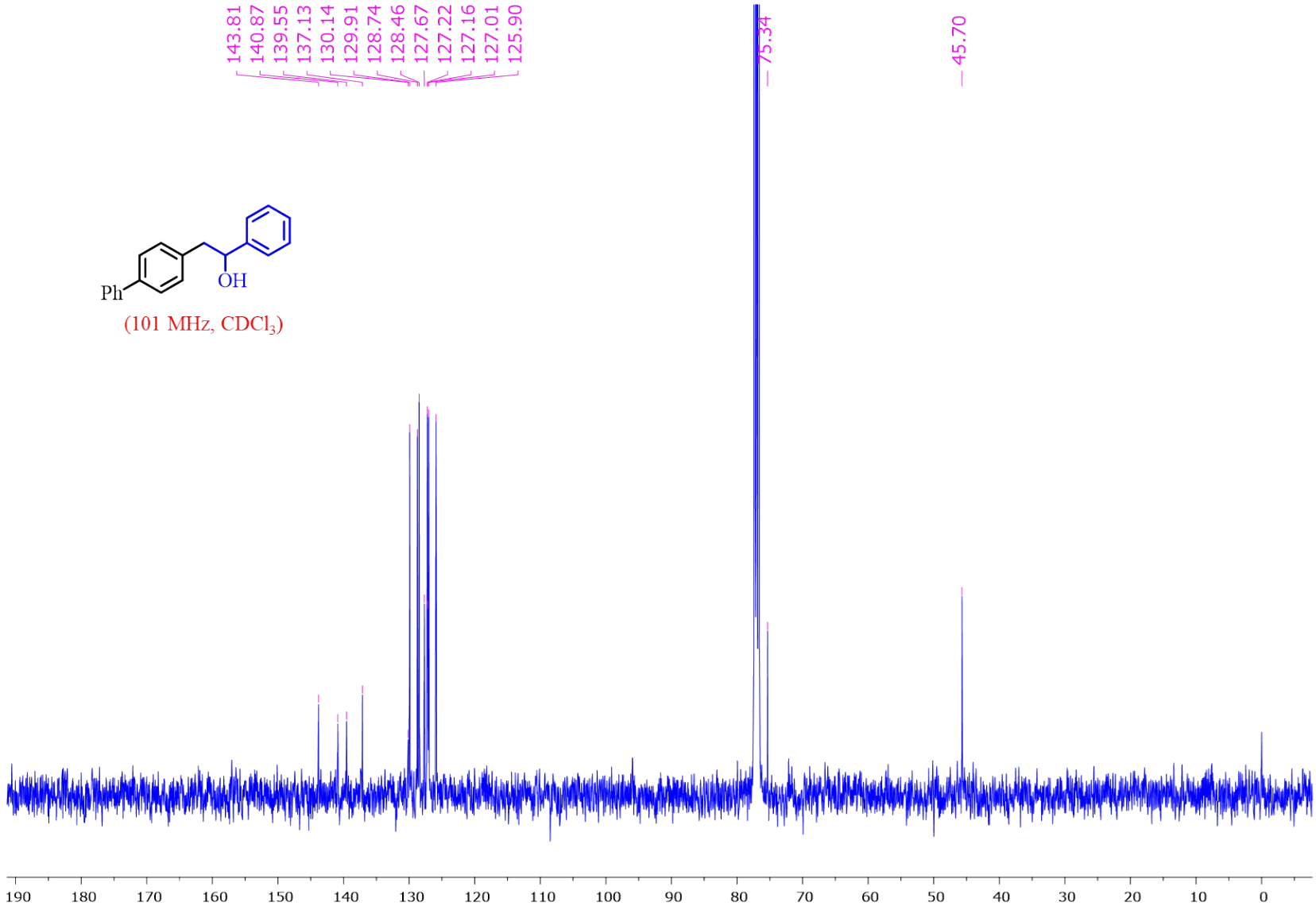


Fig. S127. ^{13}C NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1-phenylethan-1-ol (**7a**) in $CDCl_3$.

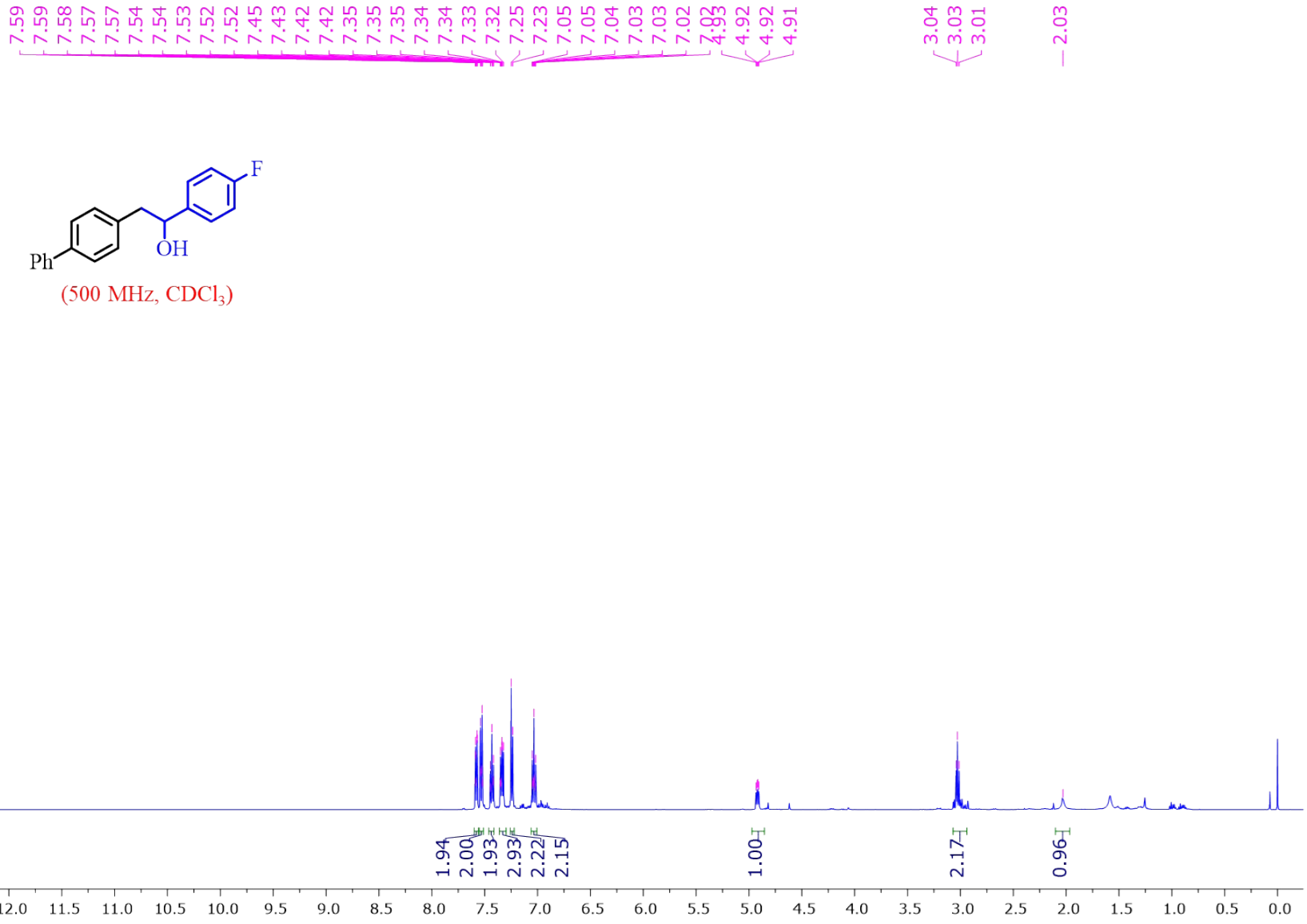


Fig. S128. ^{1}H NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1-(4-fluorophenyl)ethan-1-ol (**7b**) in $CDCl_3$.

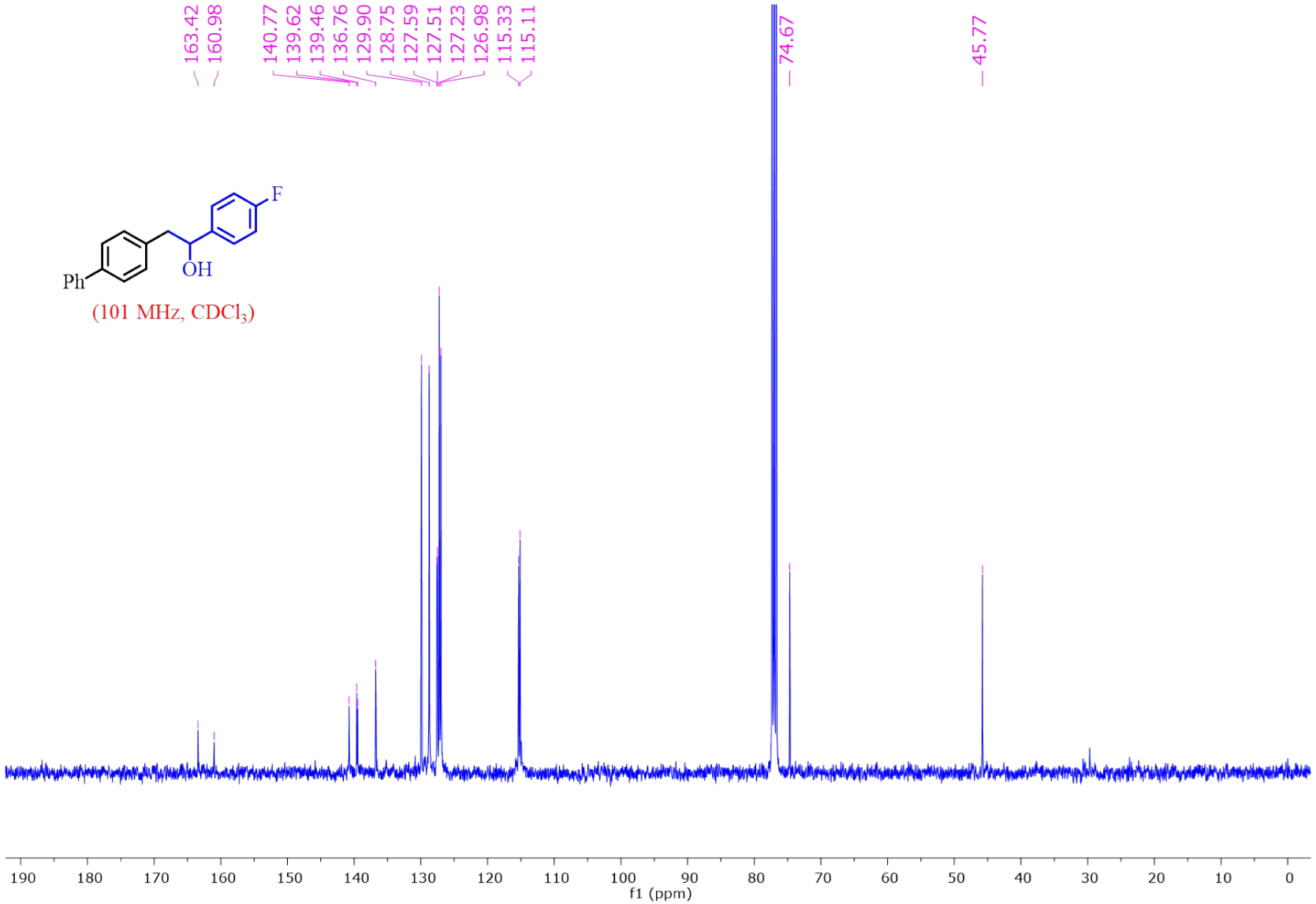


Fig. S129. ^{13}C NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1-(4-fluorophenyl)ethan-1-ol (**7b**) in $CDCl_3$.

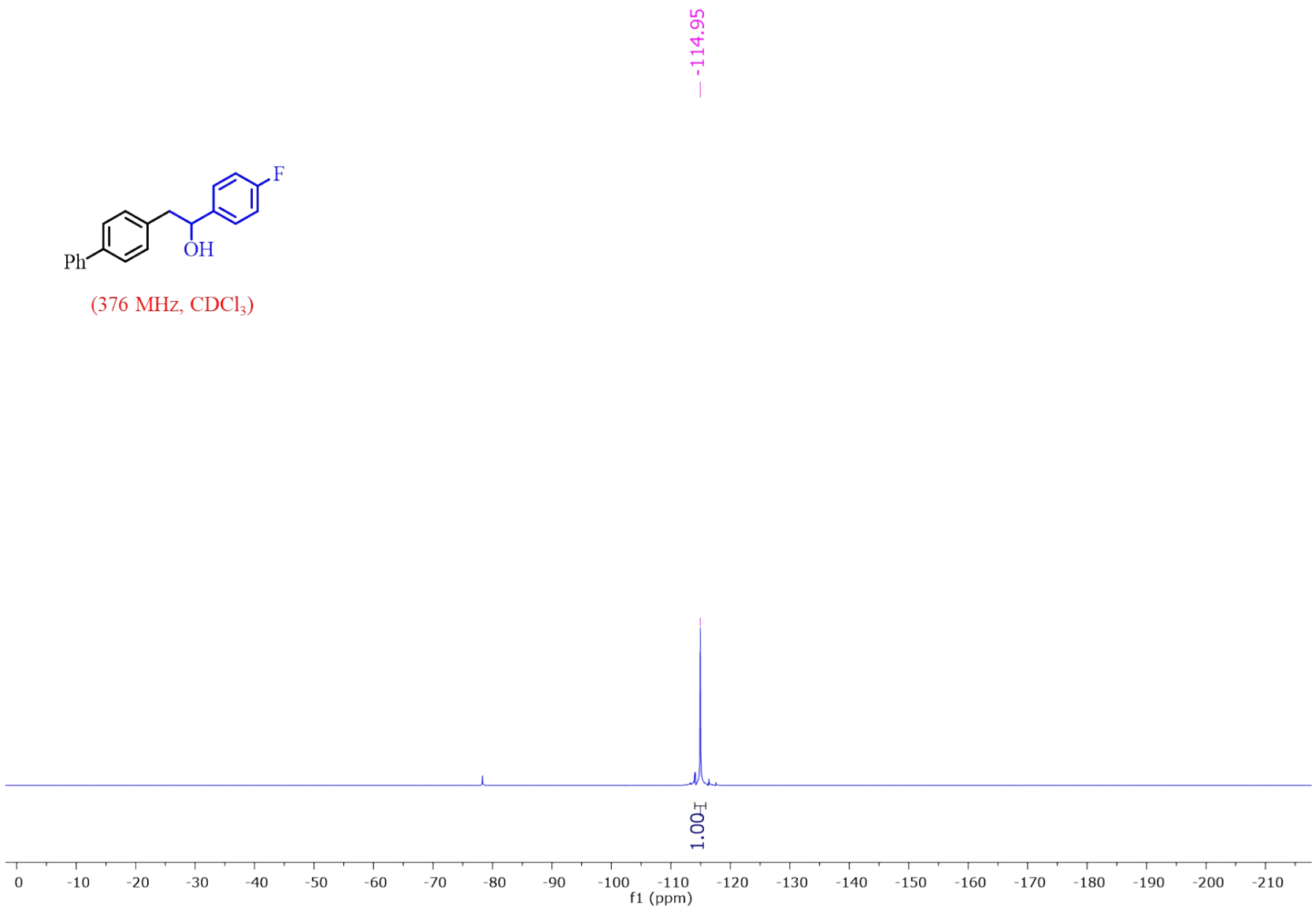


Fig. S130. ^{19}F NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1-(4-fluorophenyl)ethan-1-ol (**7b**) in $CDCl_3$.

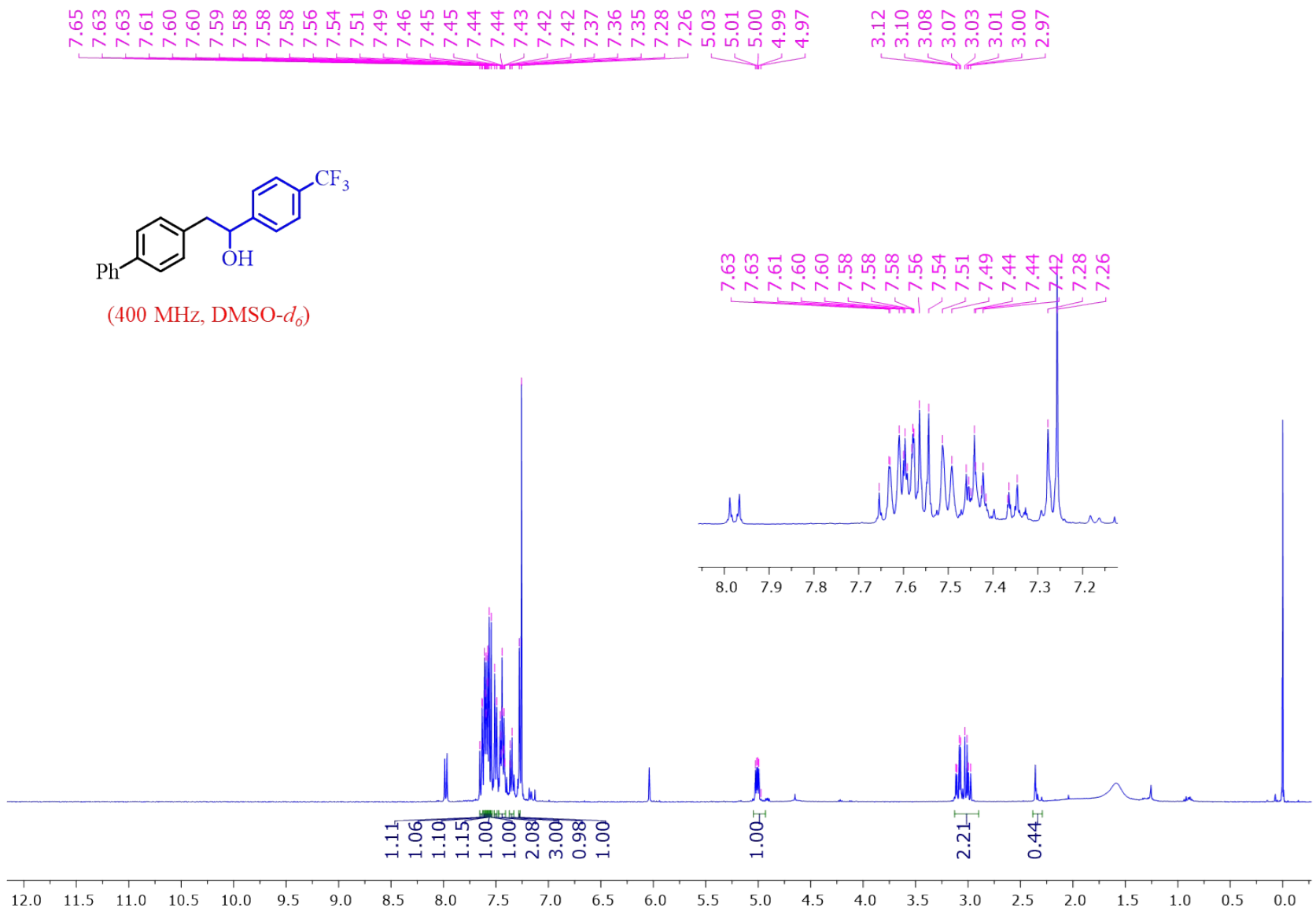


Fig. S131. ^{1}H NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1-(4-(trifluoromethyl)phenyl)ethan-1-ol (**7c**) in $CDCl_3$.

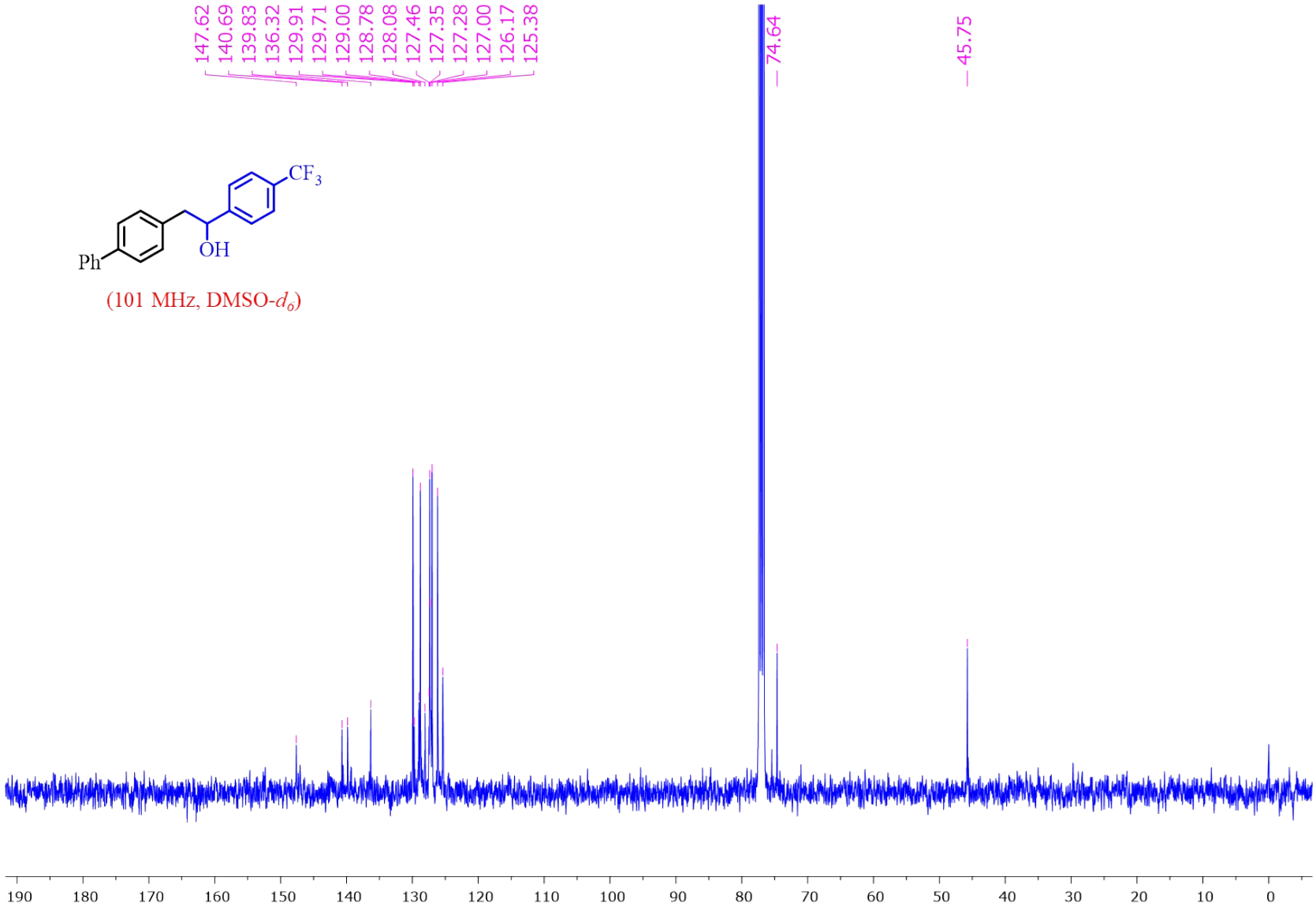


Fig. S132. ^{13}C NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1-(4-(trifluoromethyl)phenyl)ethan-1-ol (**7c**) in $CDCl_3$.

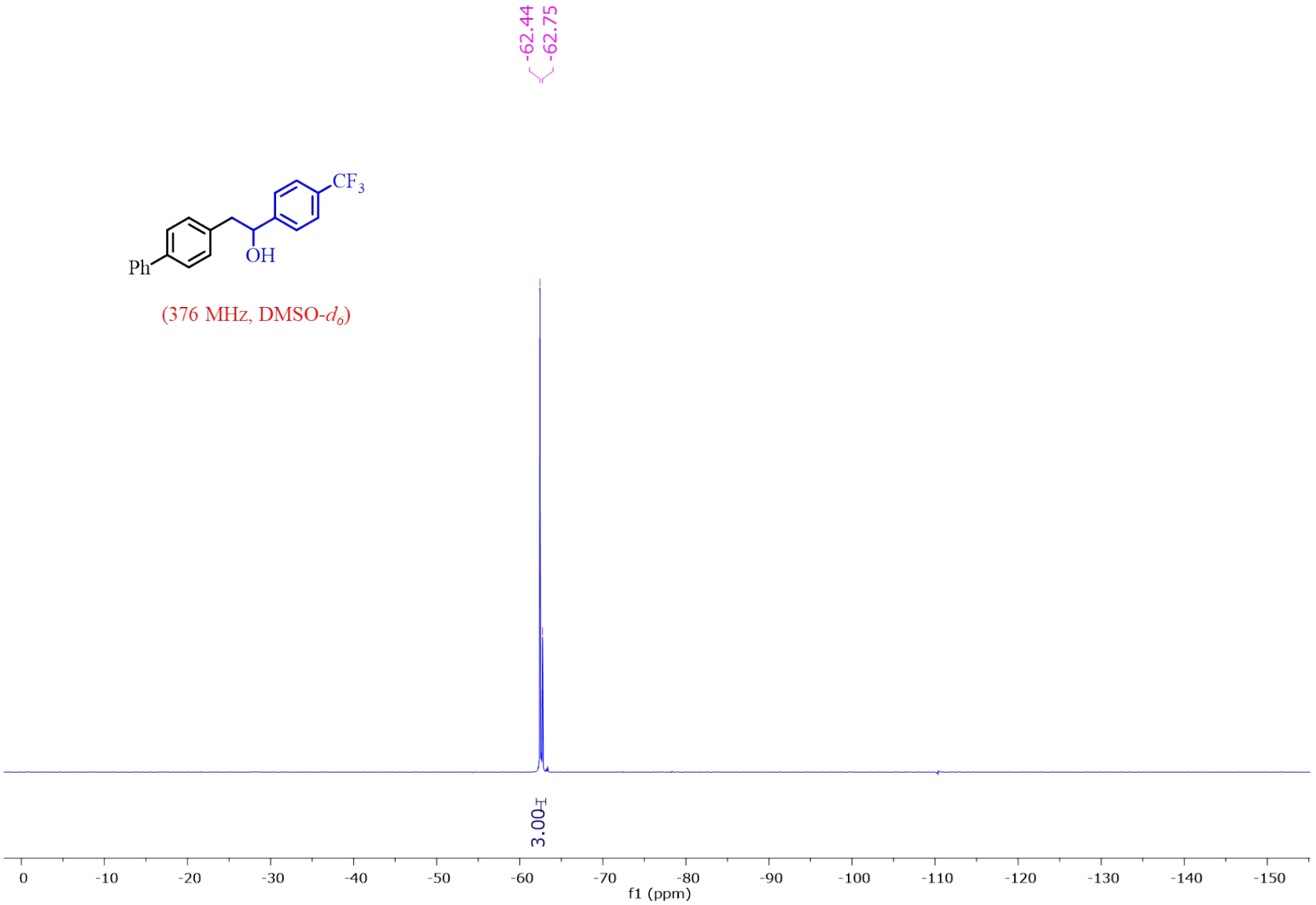


Fig. S133. ^{19}F NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1-(4-(trifluoromethyl)phenyl)ethan-1-ol (**7c**) in $CDCl_3$.

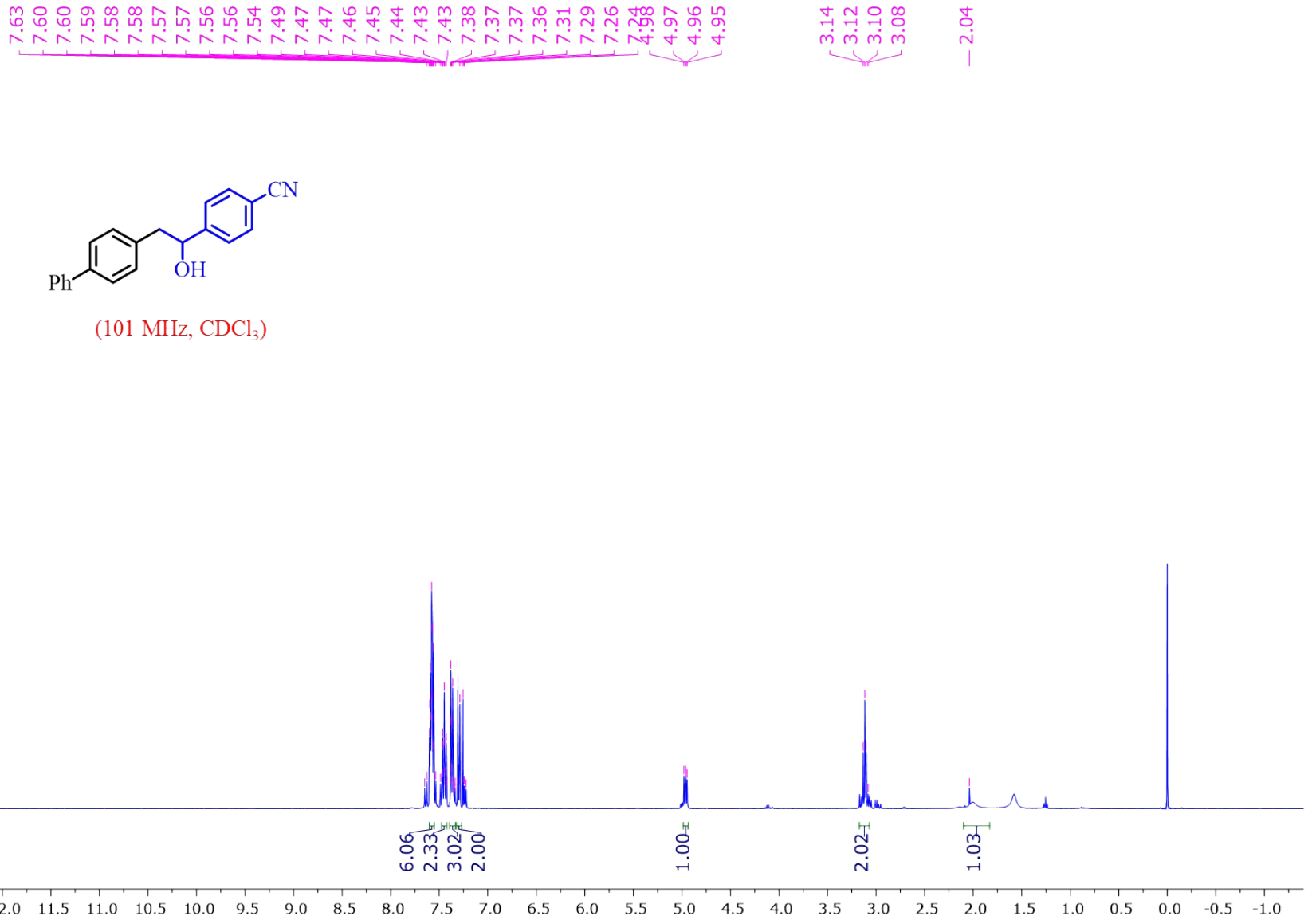


Fig. S134. ^{1}H NMR spectra of 4-(2-([1,1'-biphenyl]-4-yl)-1-hydroxyethyl)benzonitrile (**7d**) in $CDCl_3$.

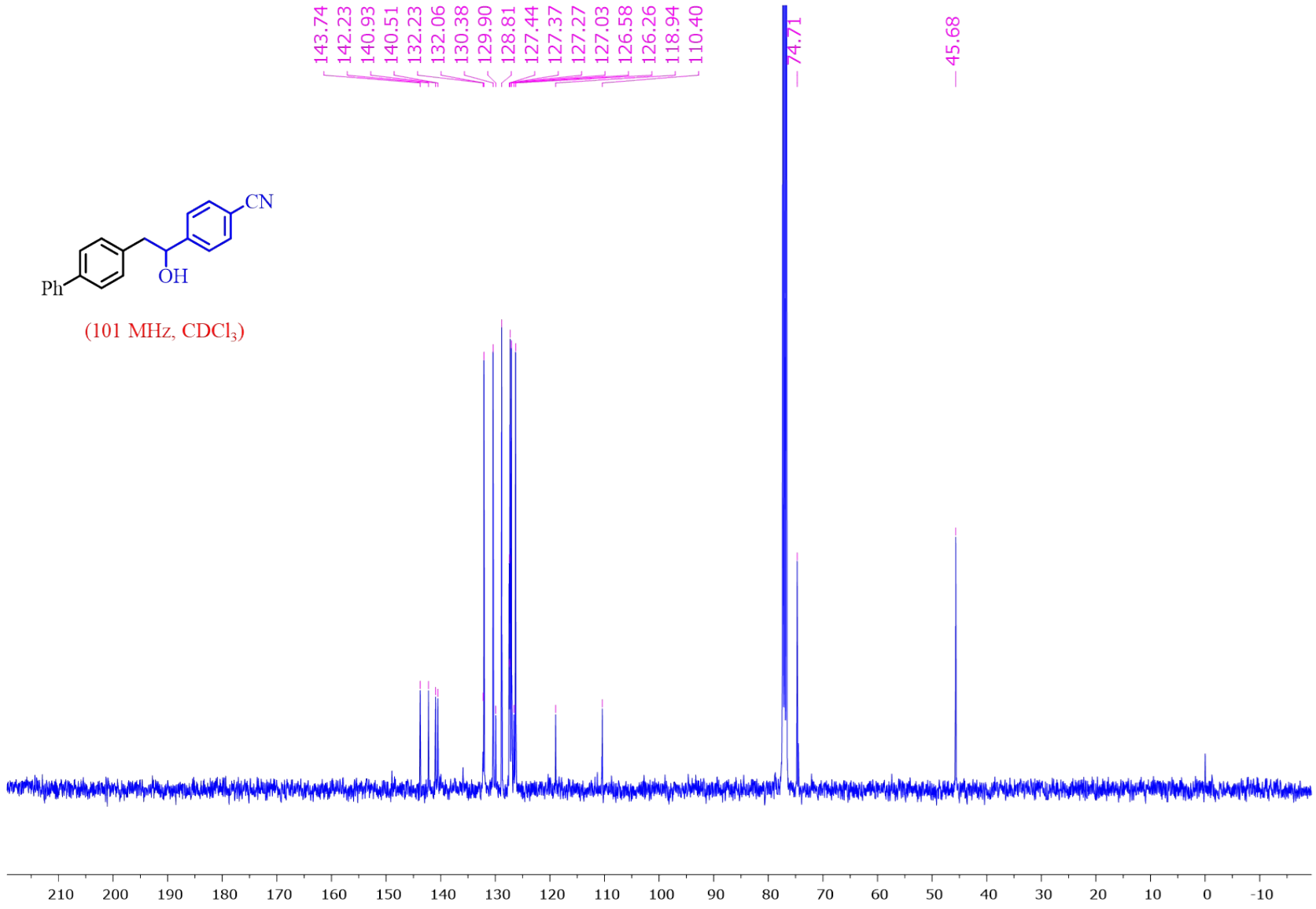


Fig. S135. ^{1}3C NMR spectra of 4-(2-([1,1'-biphenyl]-4-yl)-1-hydroxyethyl)benzonitrile (**7d**) in $CDCl_3$.

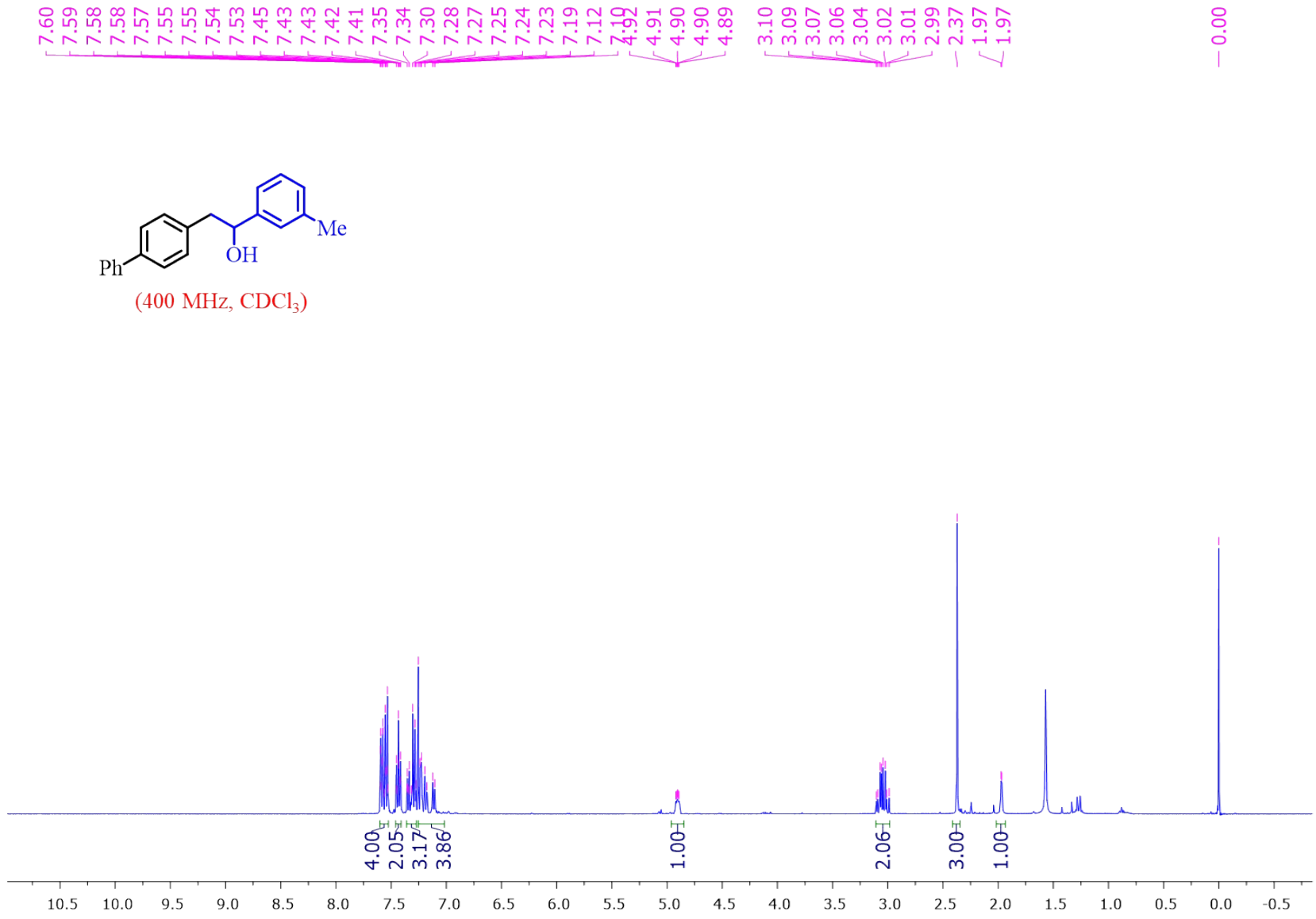


Fig. S136. ^{1}H NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1-(m-tolyl)ethan-1-ol (**7e**) in $CDCl_3$.

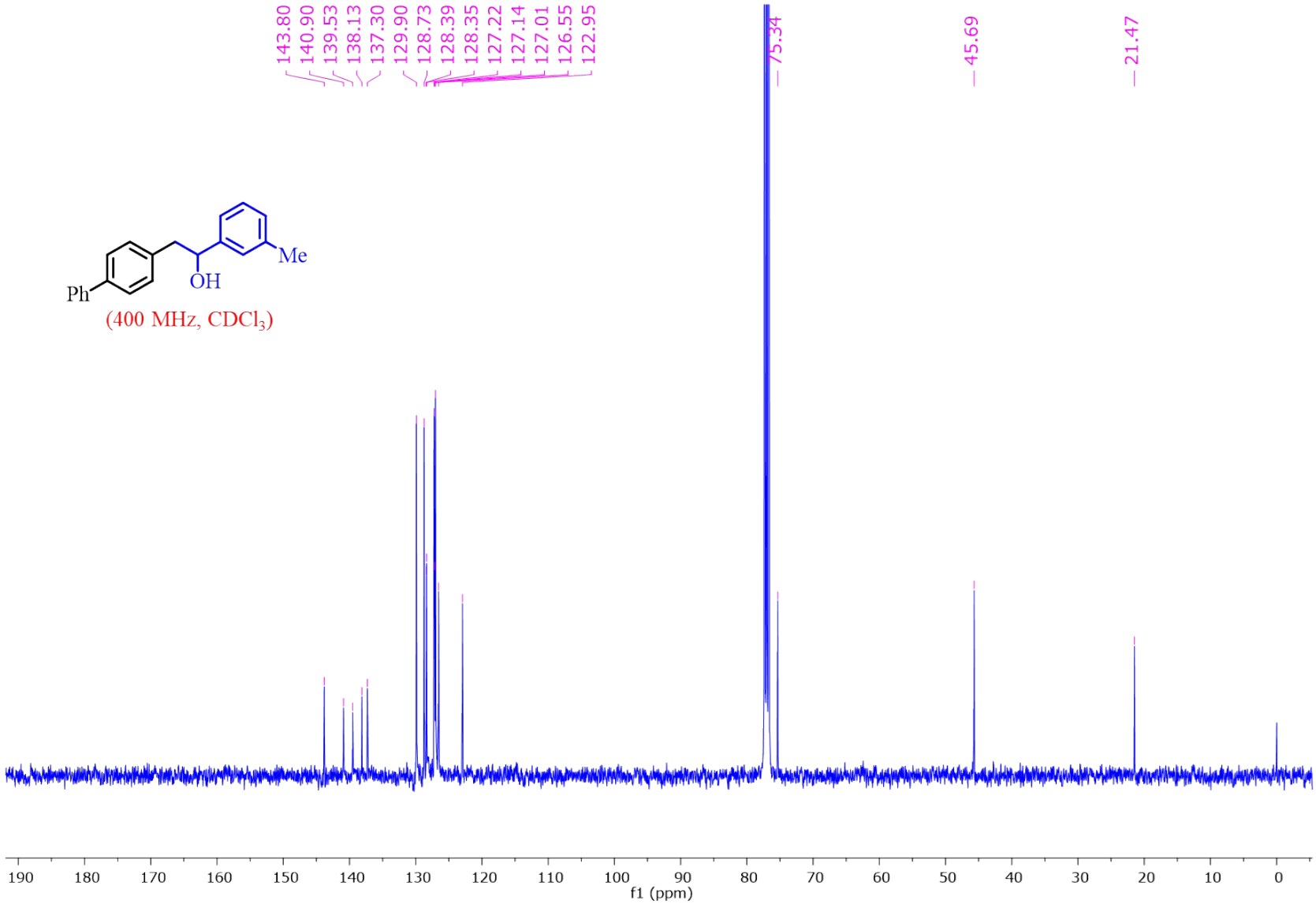


Fig. S137. ^{13}C NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1-(m-tolyl)ethan-1-ol (**7e**) in $CDCl_3$.

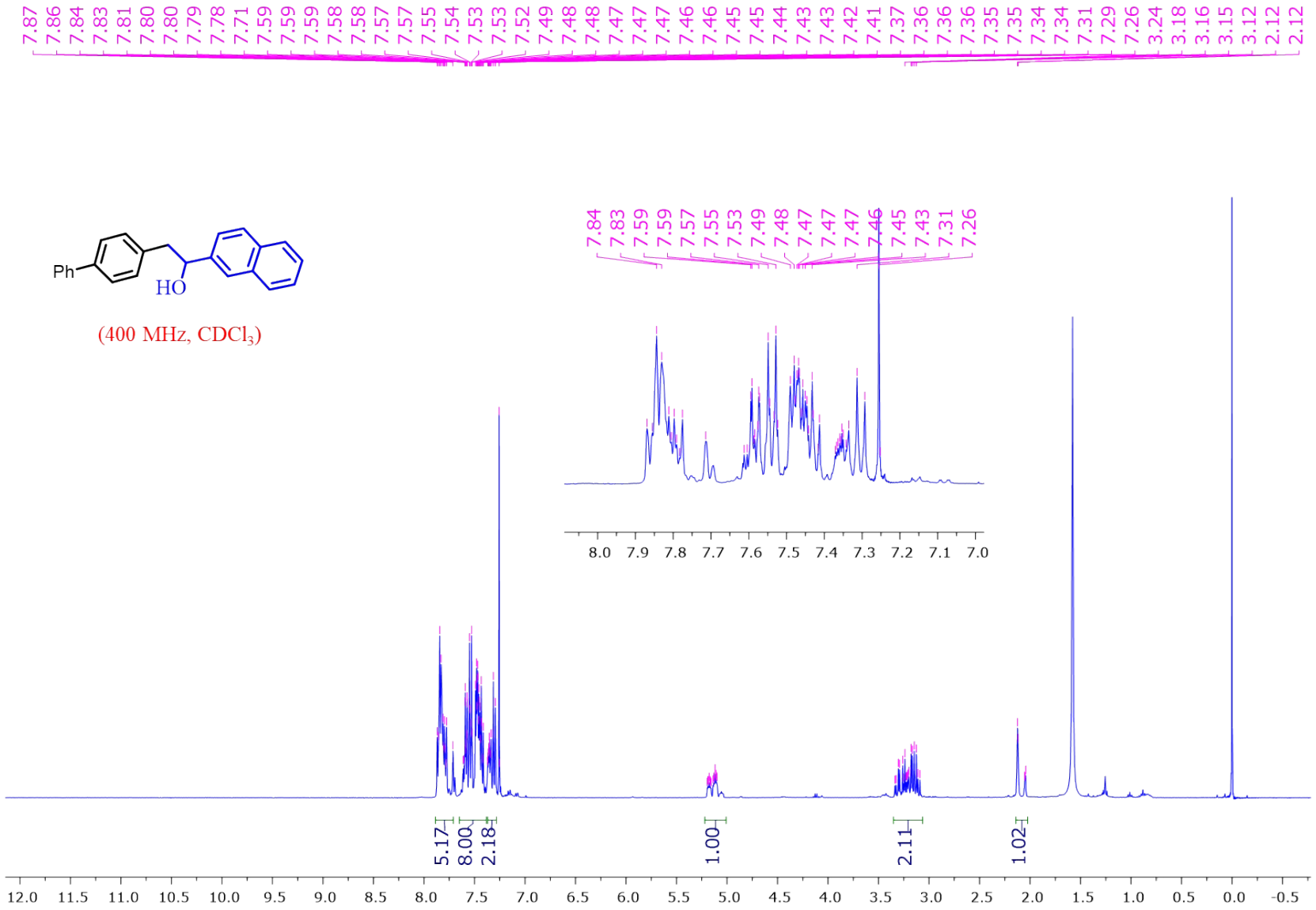


Fig. S138. ^{1}H NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1-(naphthalen-2-yl)ethan-1-ol (**7f**) in $CDCl_3$.

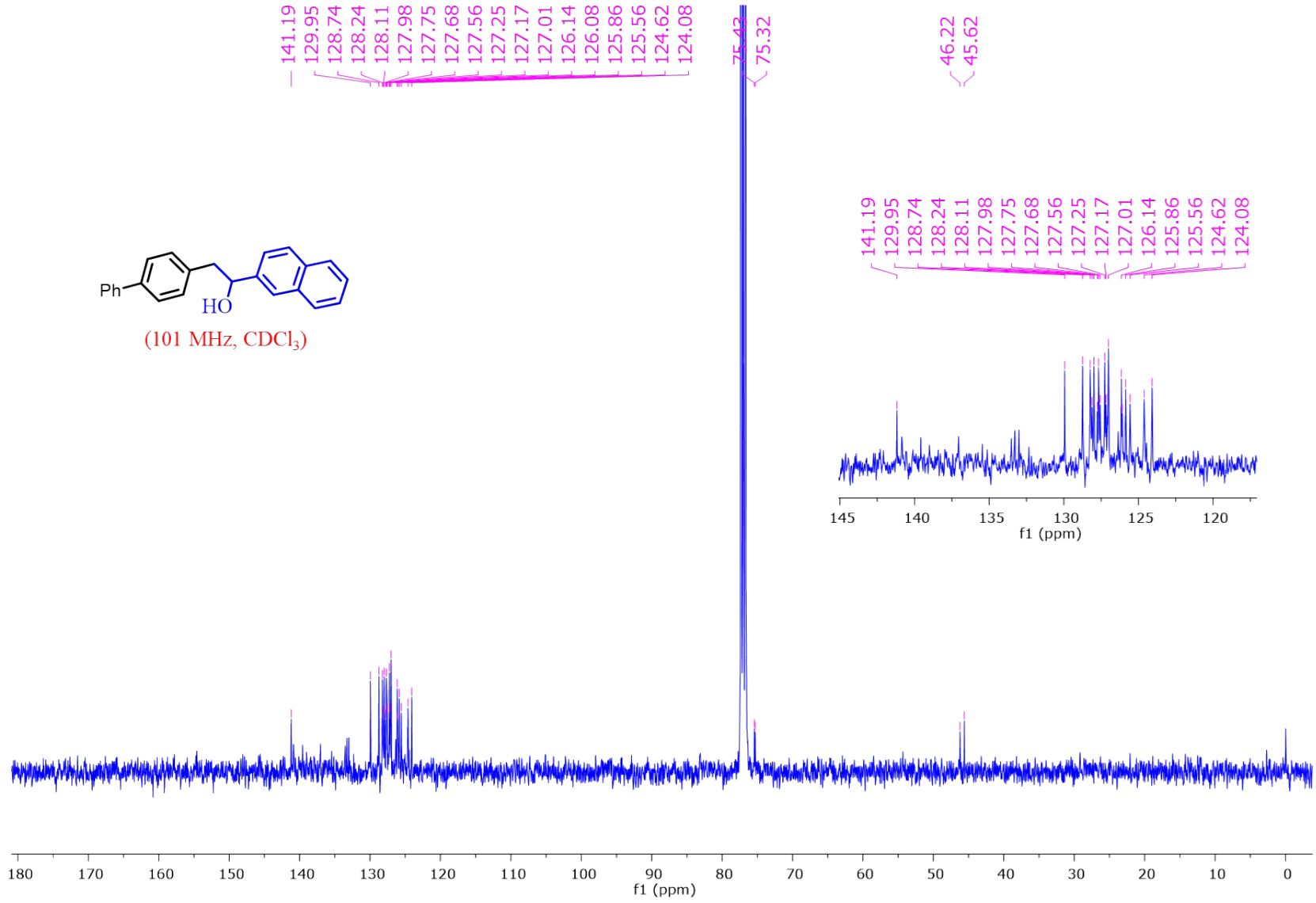


Fig. S139. ^{13}C NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1-(naphthalen-2-yl)ethan-1-ol (**7f**) in $CDCl_3$.

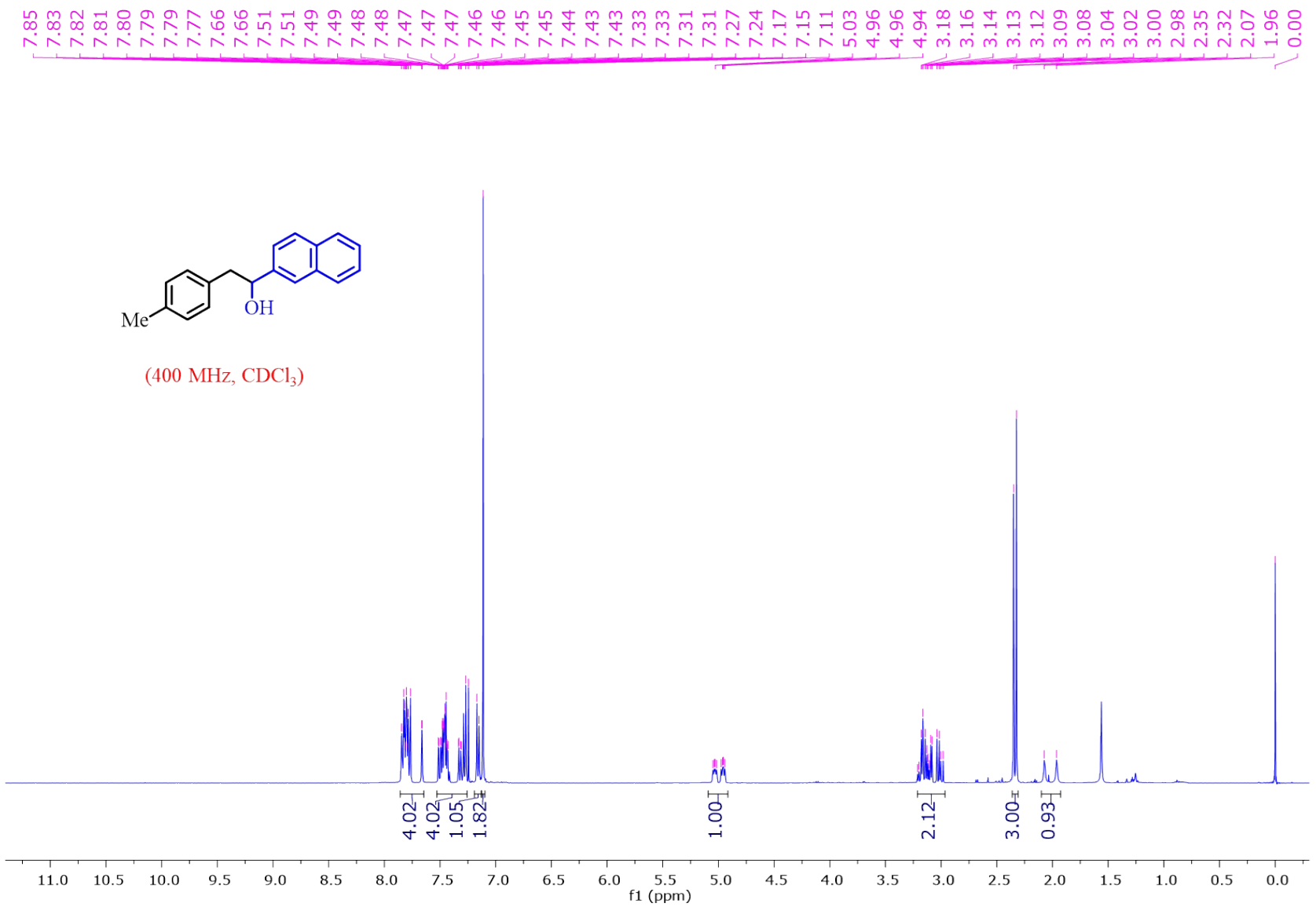


Fig. S140. ^{1}H NMR spectra of 1-(naphthalen-2-yl)-2-(p-tolyl)ethan-1-ol (**7g**) in $CDCl_3$.

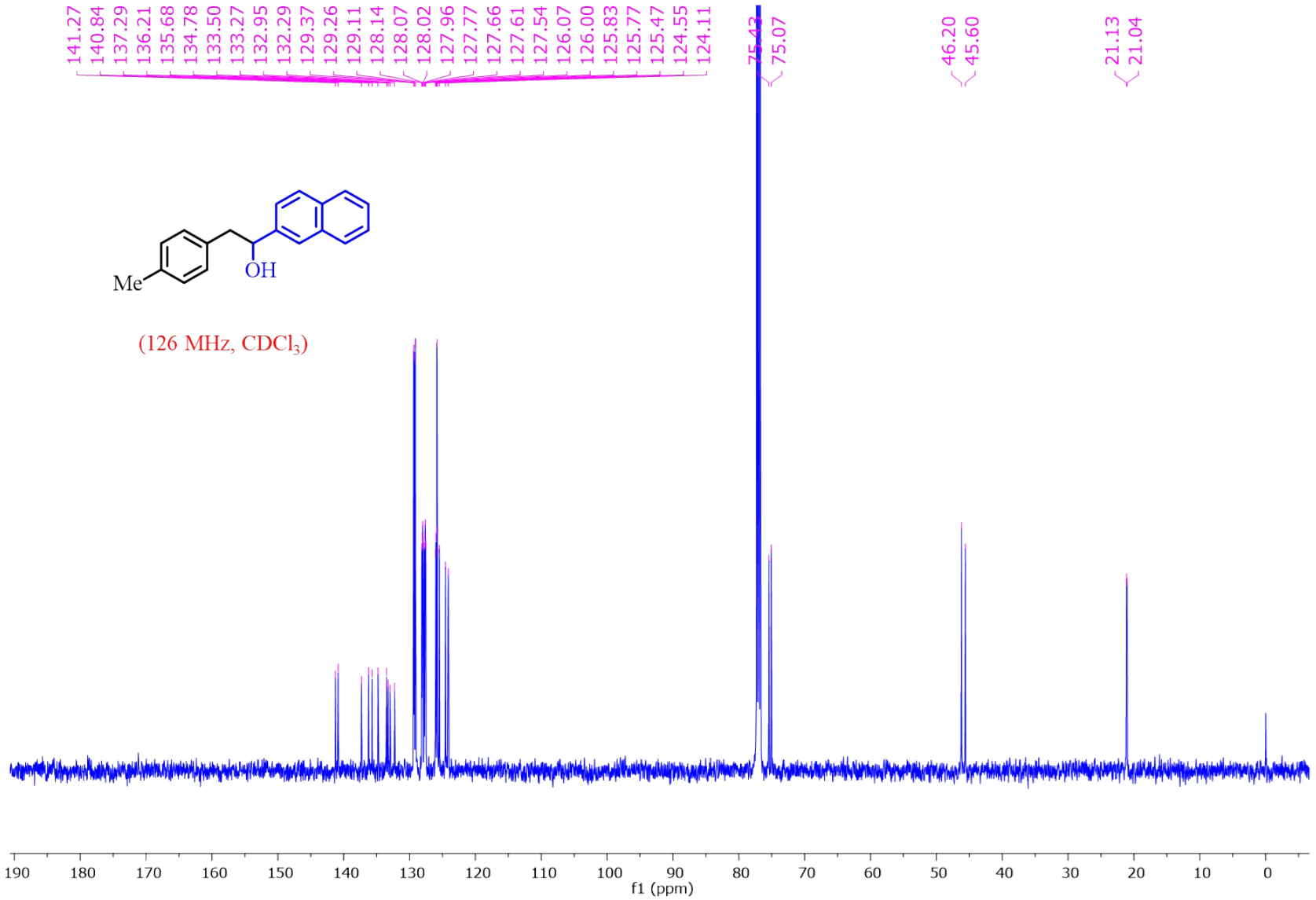


Fig. S141. ^{13}C NMR spectra of 1-(naphthalen-2-yl)-2-(p-tolyl)ethan-1-ol (**7g**) in $CDCl_3$.

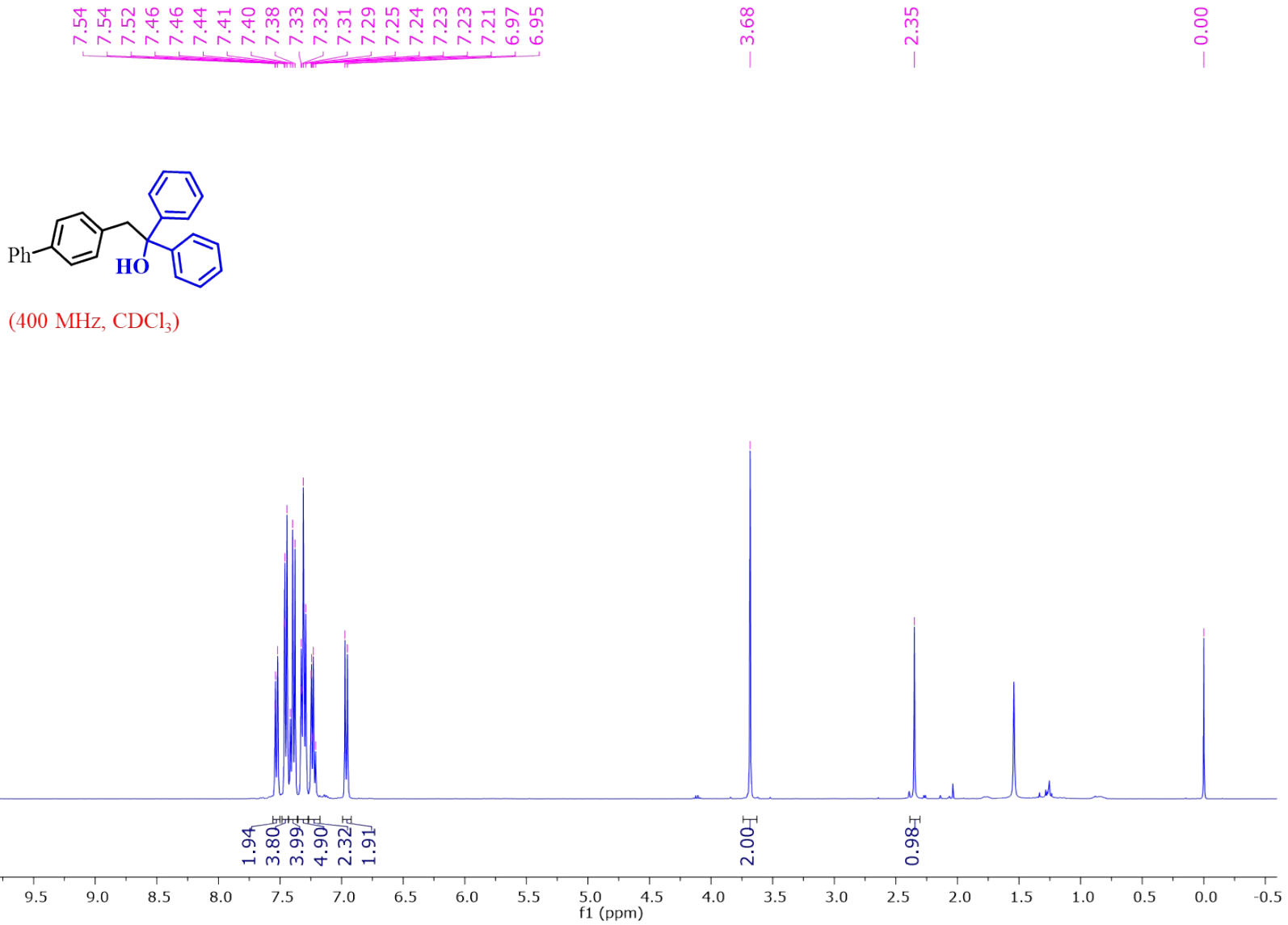


Fig. S142. ^{1}H NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1,1-diphenylethan-1-ol (**7h**) in $CDCl_3$.

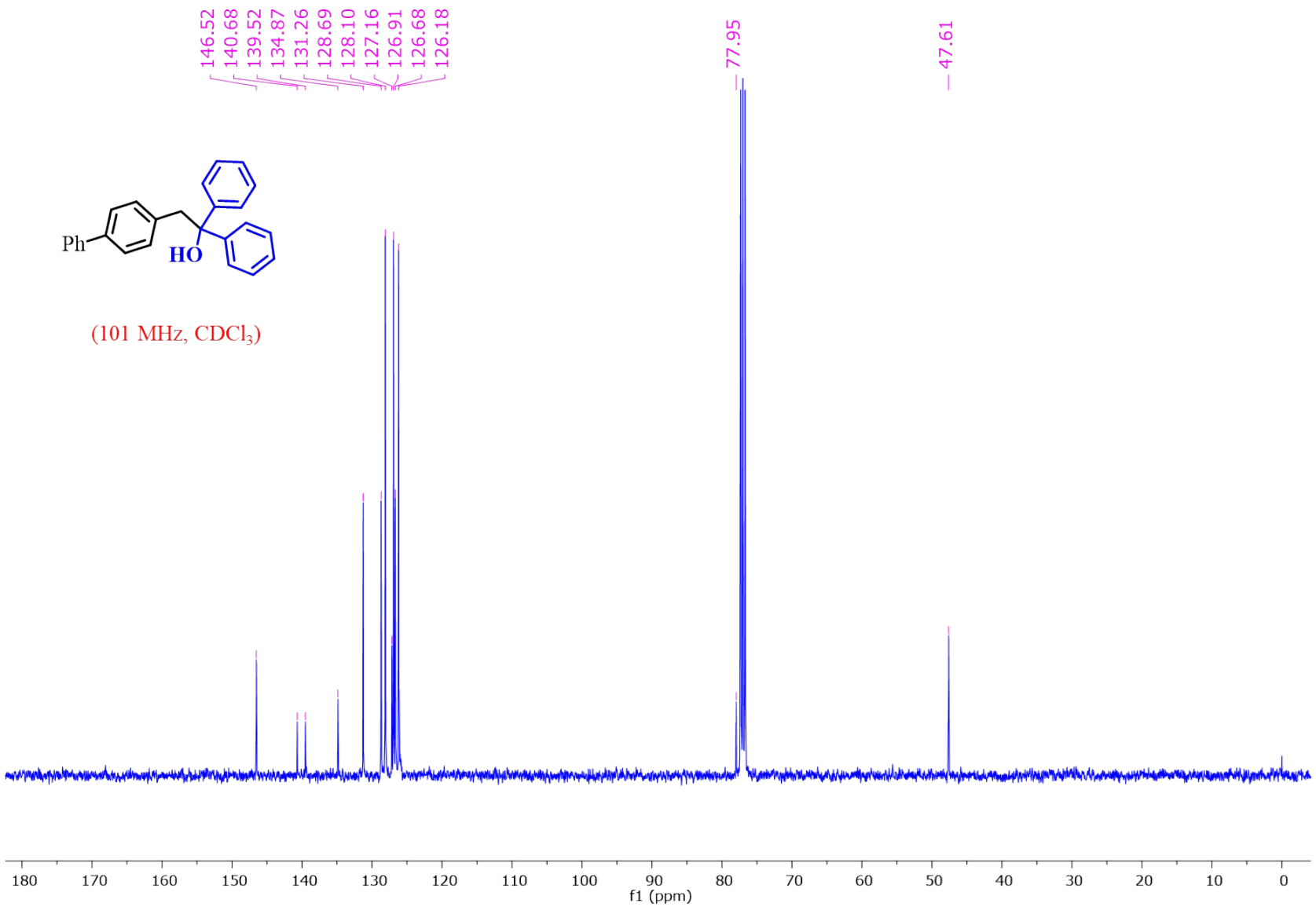


Fig. S143. ^{13}C NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1,1-diphenylethan-1-ol (**7h**) in $CDCl_3$.

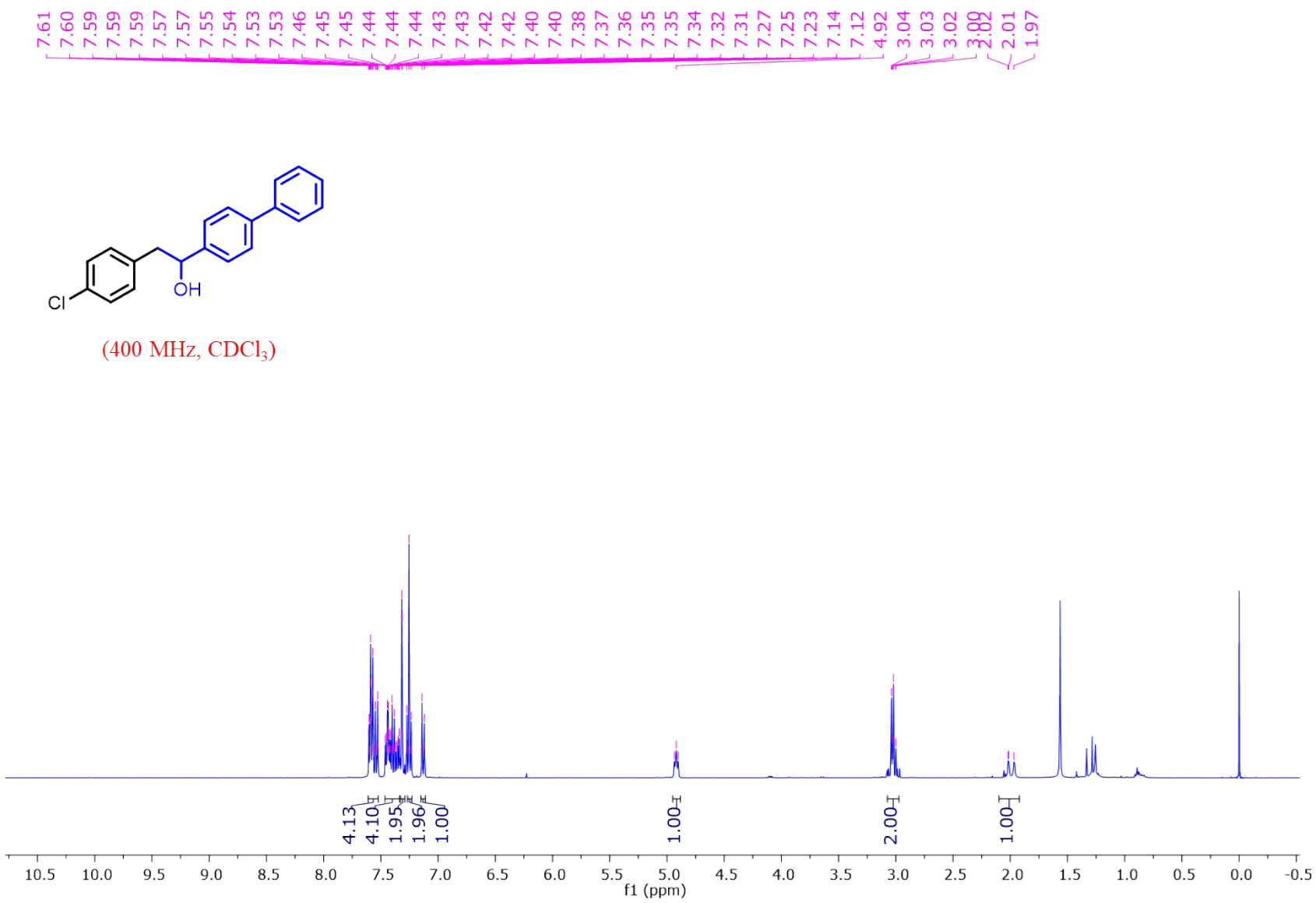


Fig. S144. ^{1}H NMR spectra of 1-([1,1'-biphenyl]-4-yl)-2-(4-chlorophenyl) ethan-1-ol (**7i**) in $CDCl_3$.

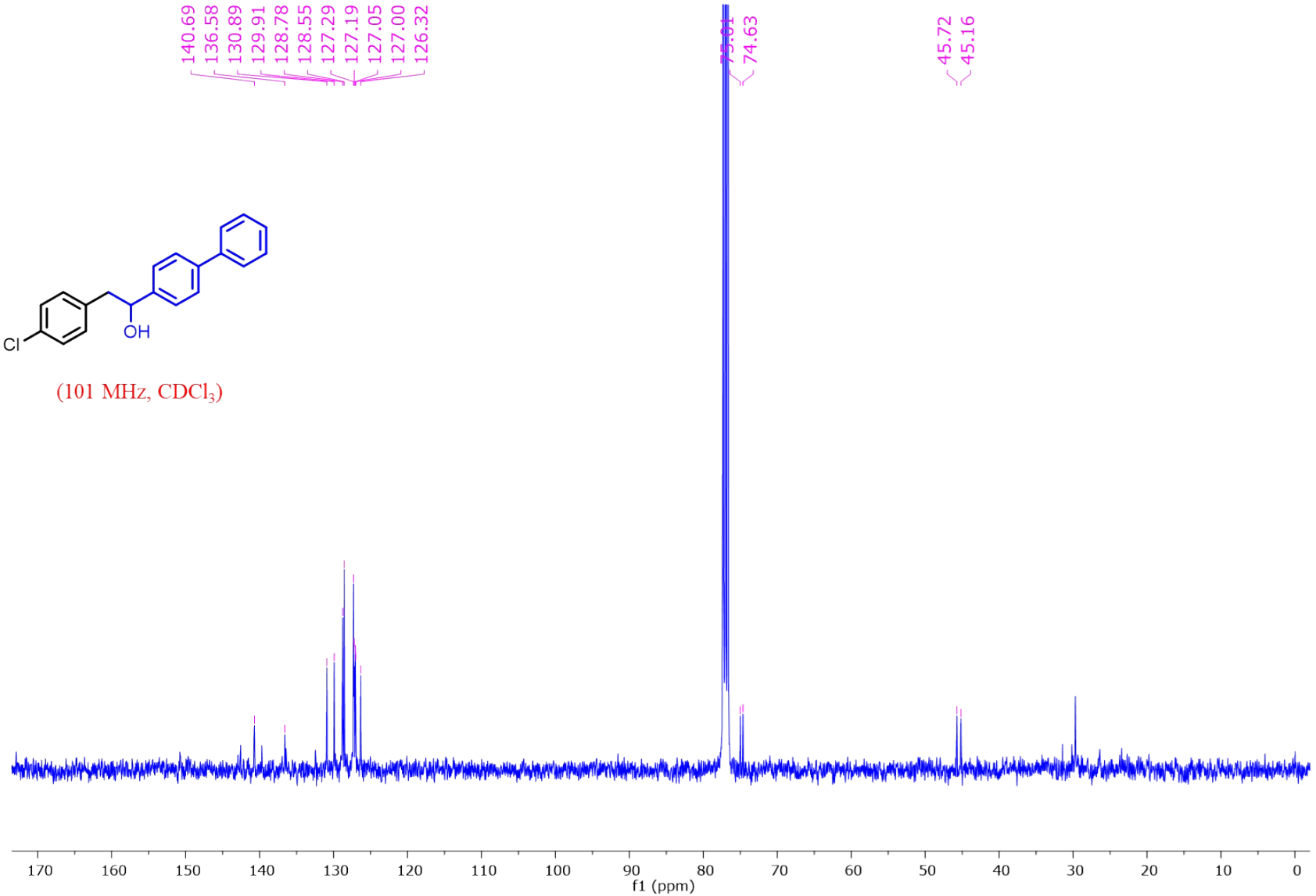


Fig. S145. ^{13}C NMR spectra of 1-([1,1'-biphenyl]-4-yl)-2-(4-chlorophenyl) ethan-1-ol (**7i**) in $CDCl_3$.

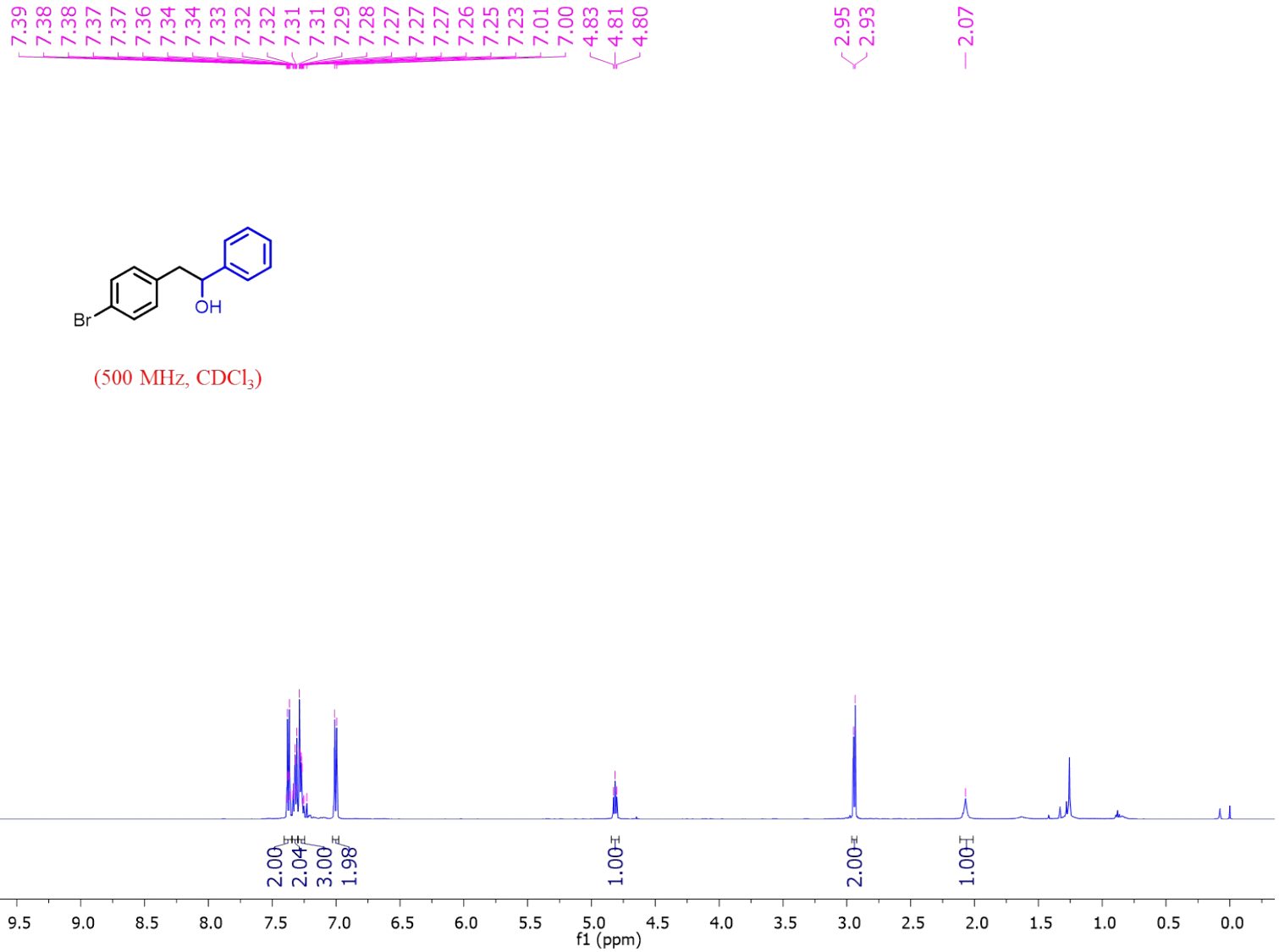


Fig. S146. ^{1}H NMR spectra of 2-(4-bromophenyl)-1-phenylethan-1-ol (**7j**) in $CDCl_3$.

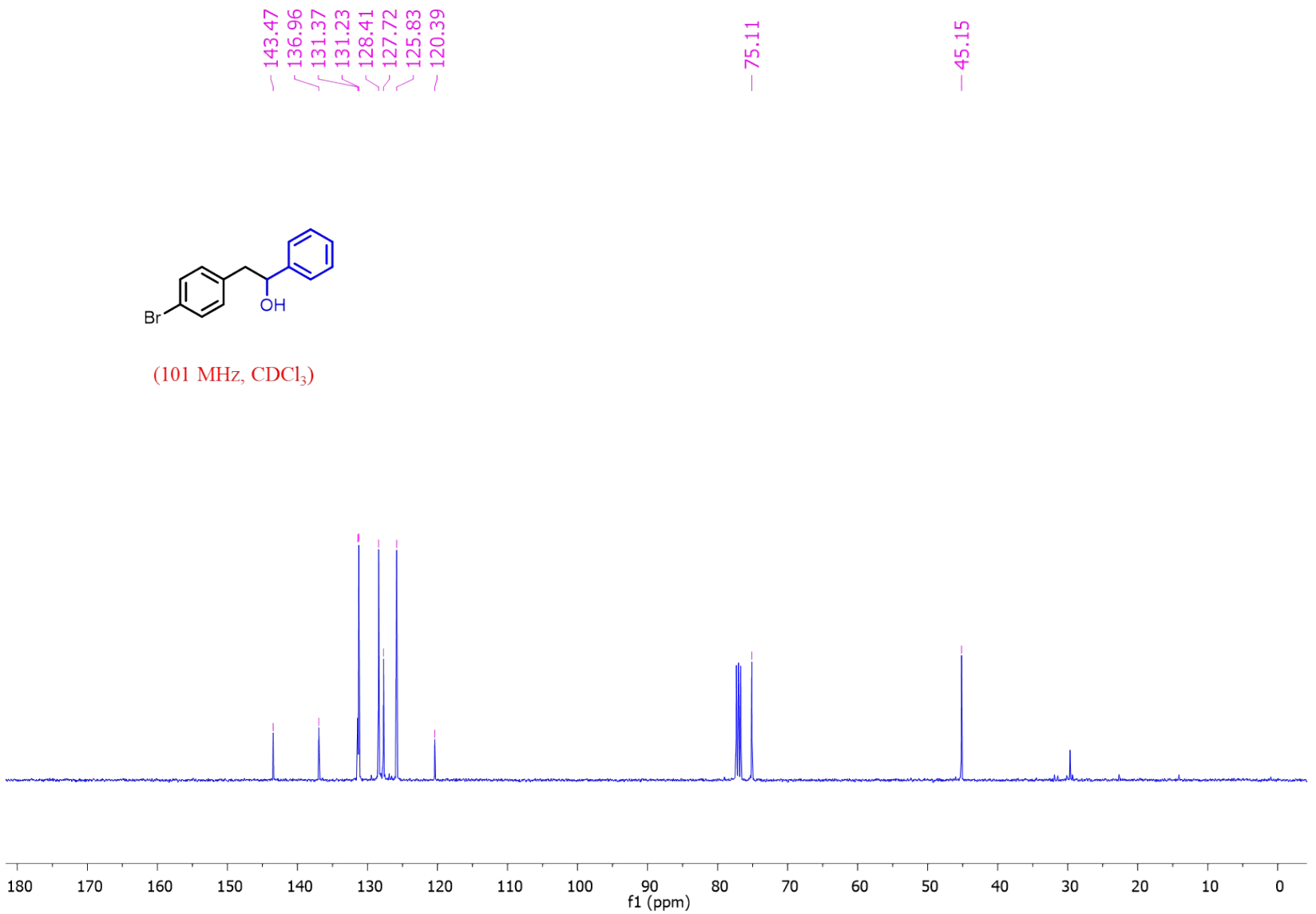


Fig. S147. ^{13}C NMR spectra of 2-(4-bromophenyl)-1-phenylethan-1-ol (**7j**) in $CDCl_3$.

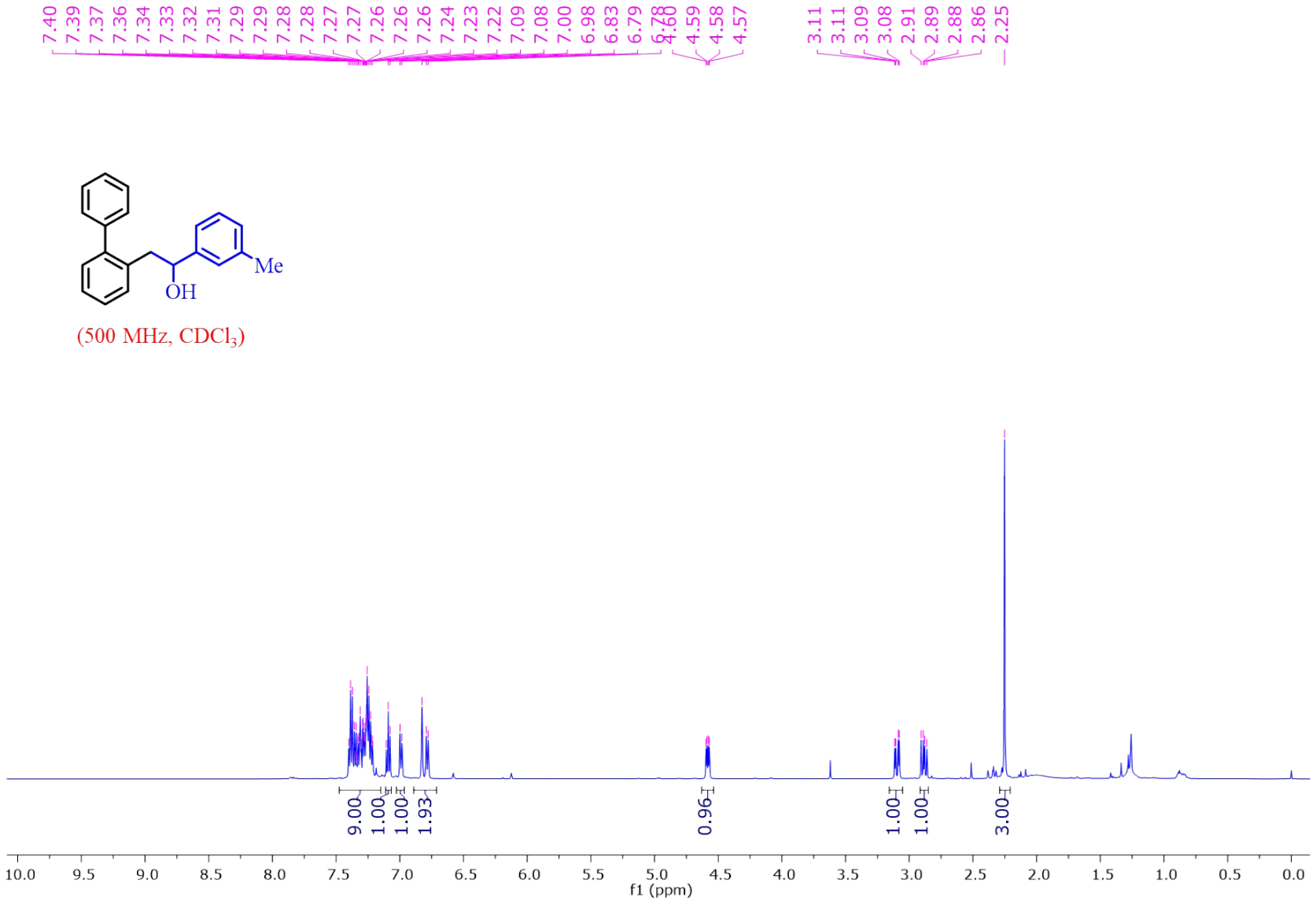


Fig. S148. ^{1}H NMR spectra of 2-([1,1'-biphenyl]-2-yl)-1-(m-tolyl)ethan-1-ol (**7k**) in $CDCl_3$.

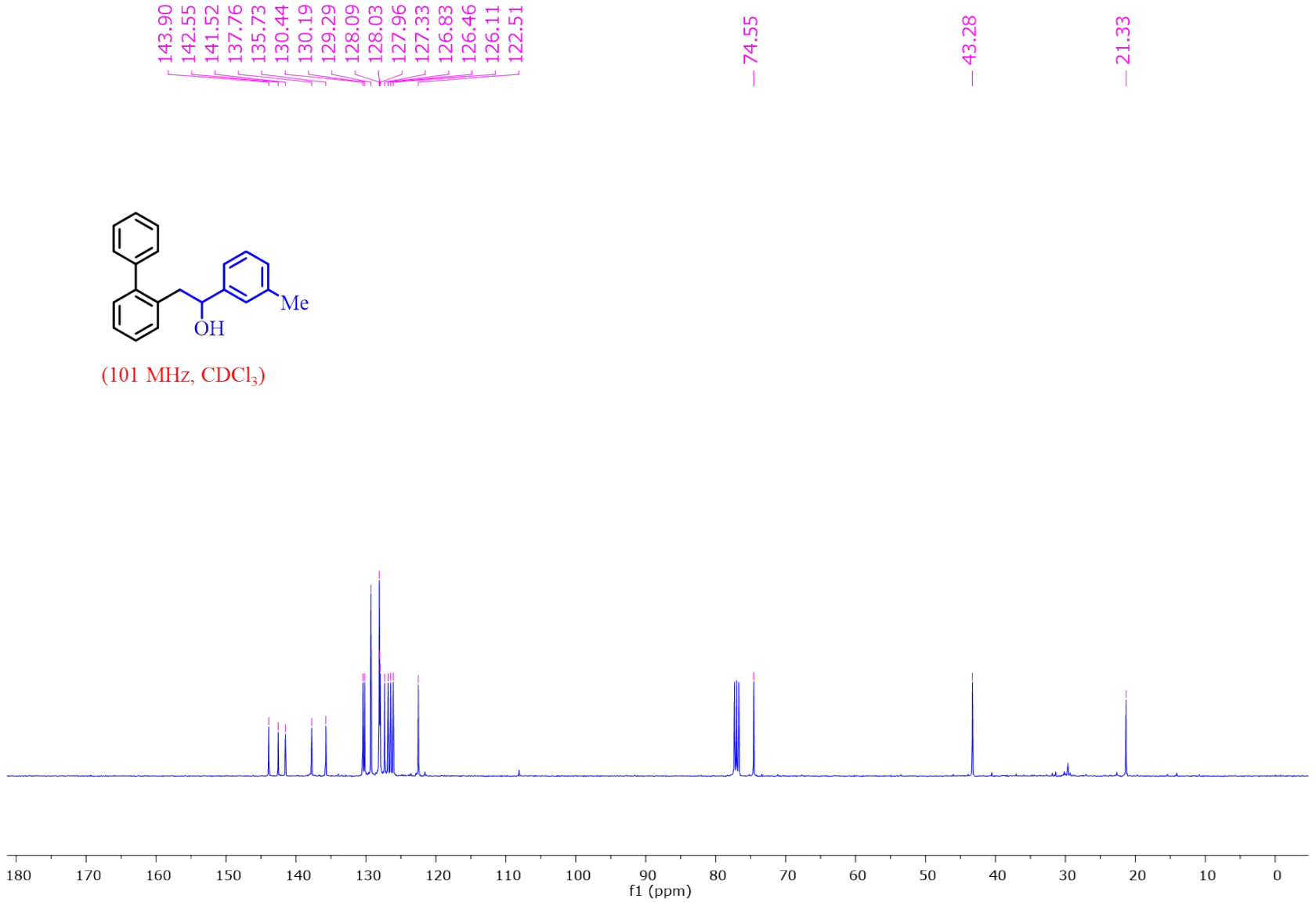


Fig. S149. ^{13}C NMR spectra of 2-([1,1'-biphenyl]-2-yl)-1-(m-tolyl)ethan-1-ol (**7k**) in $CDCl_3$.

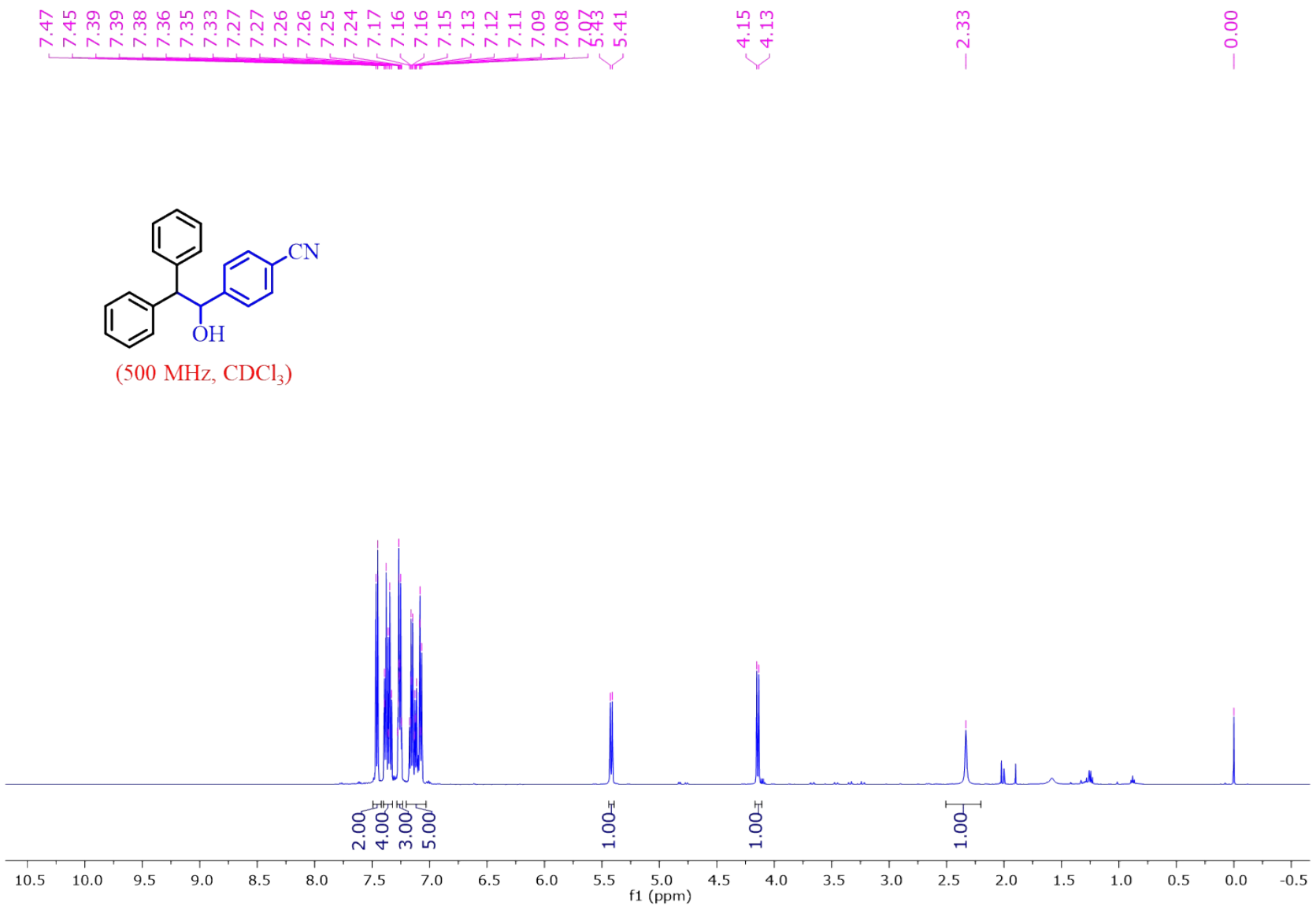


Fig. S150. ^{1}H NMR spectra of 4-(1-hydroxy-2,2-diphenylethyl)benzonitrile (**7l**) in $CDCl_3$.

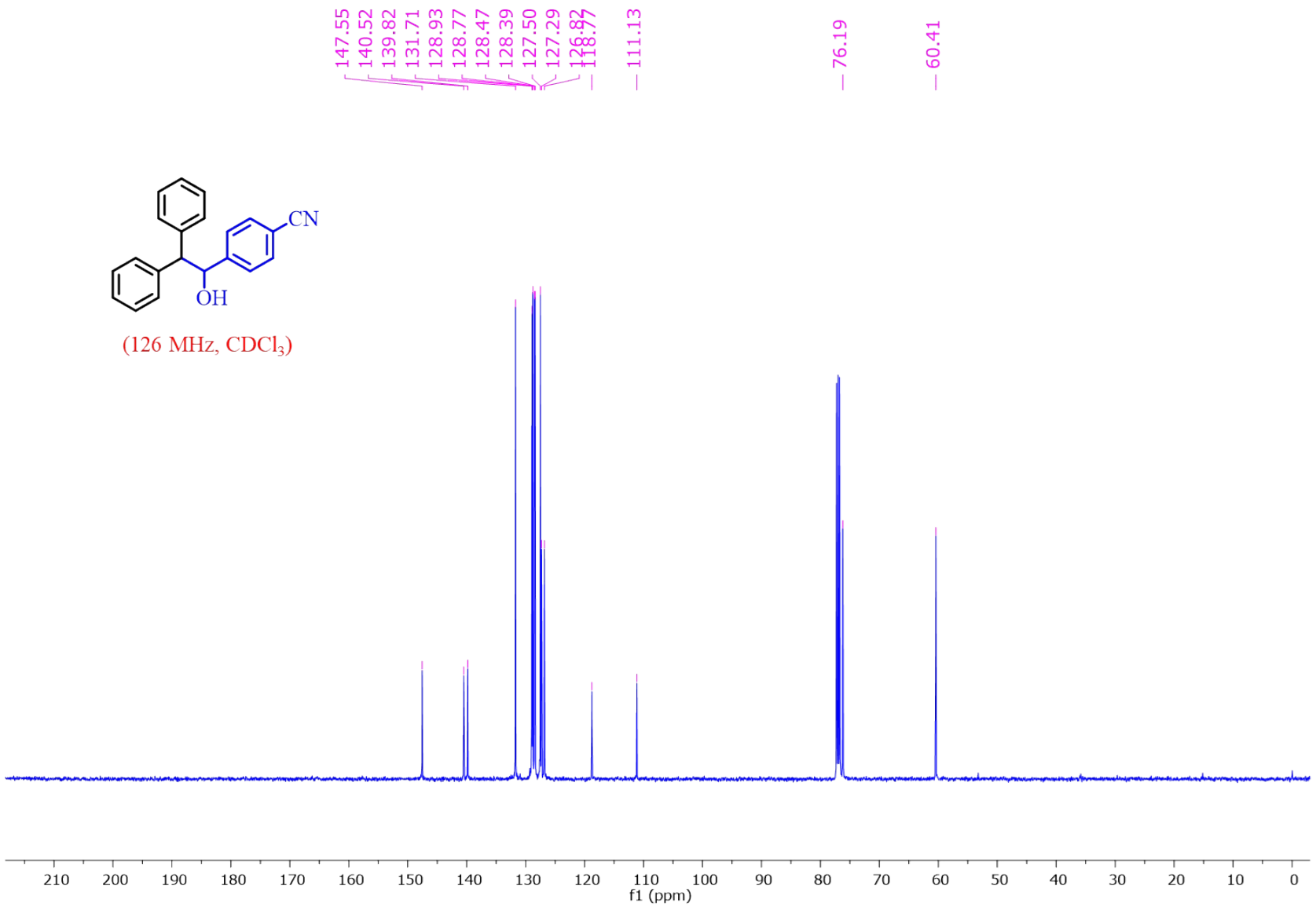


Fig. S151. ^{13}C NMR spectra of 4-(1-hydroxy-2,2-diphenylethyl)benzonitrile (**7l**) in $CDCl_3$.

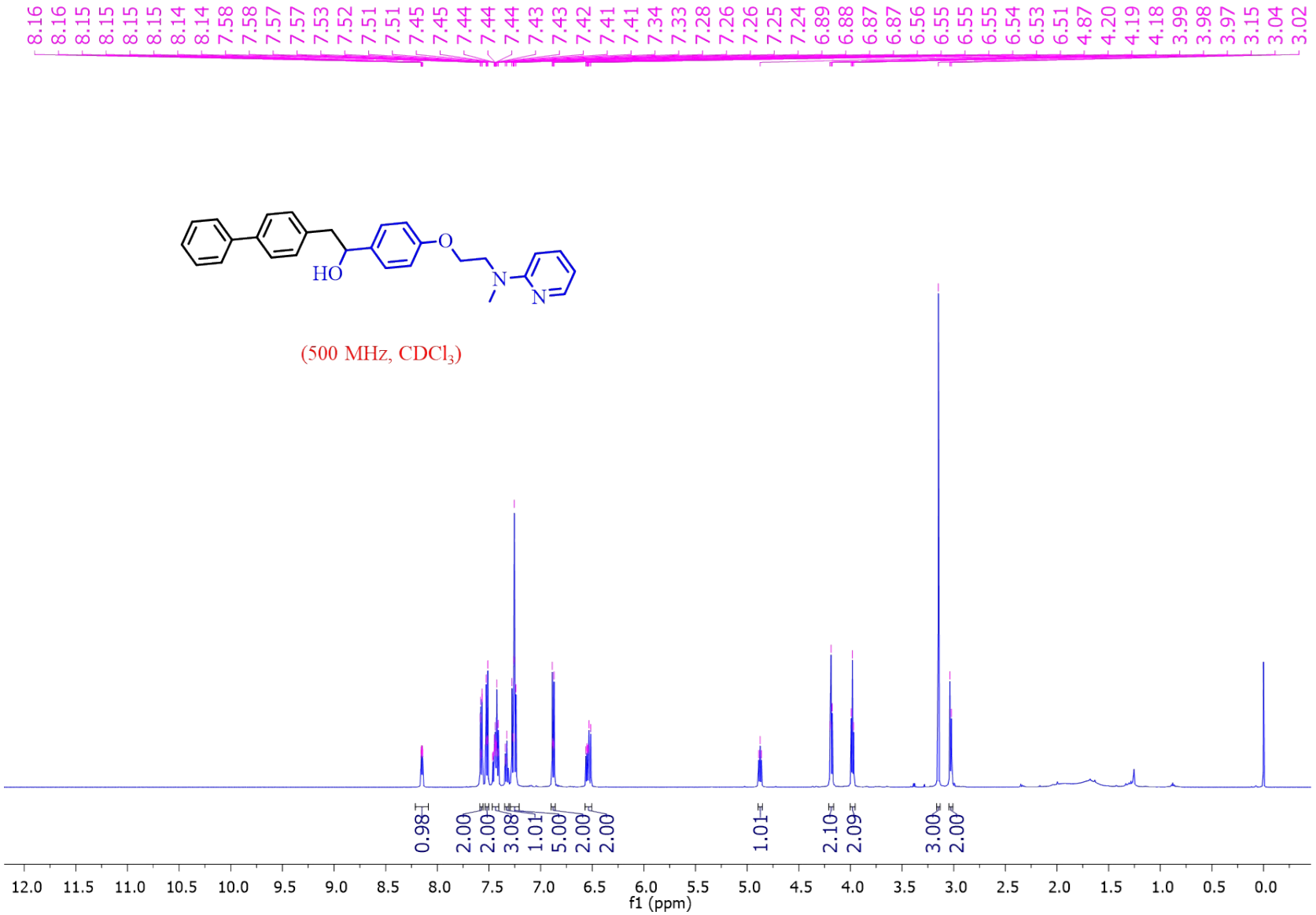


Fig. S152. ^{1}H NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1-(4-(2-(methyl(pyridin-2-yl)amino)ethoxy)phenyl)ethan-1-ol (**7m**) in $CDCl_3$.

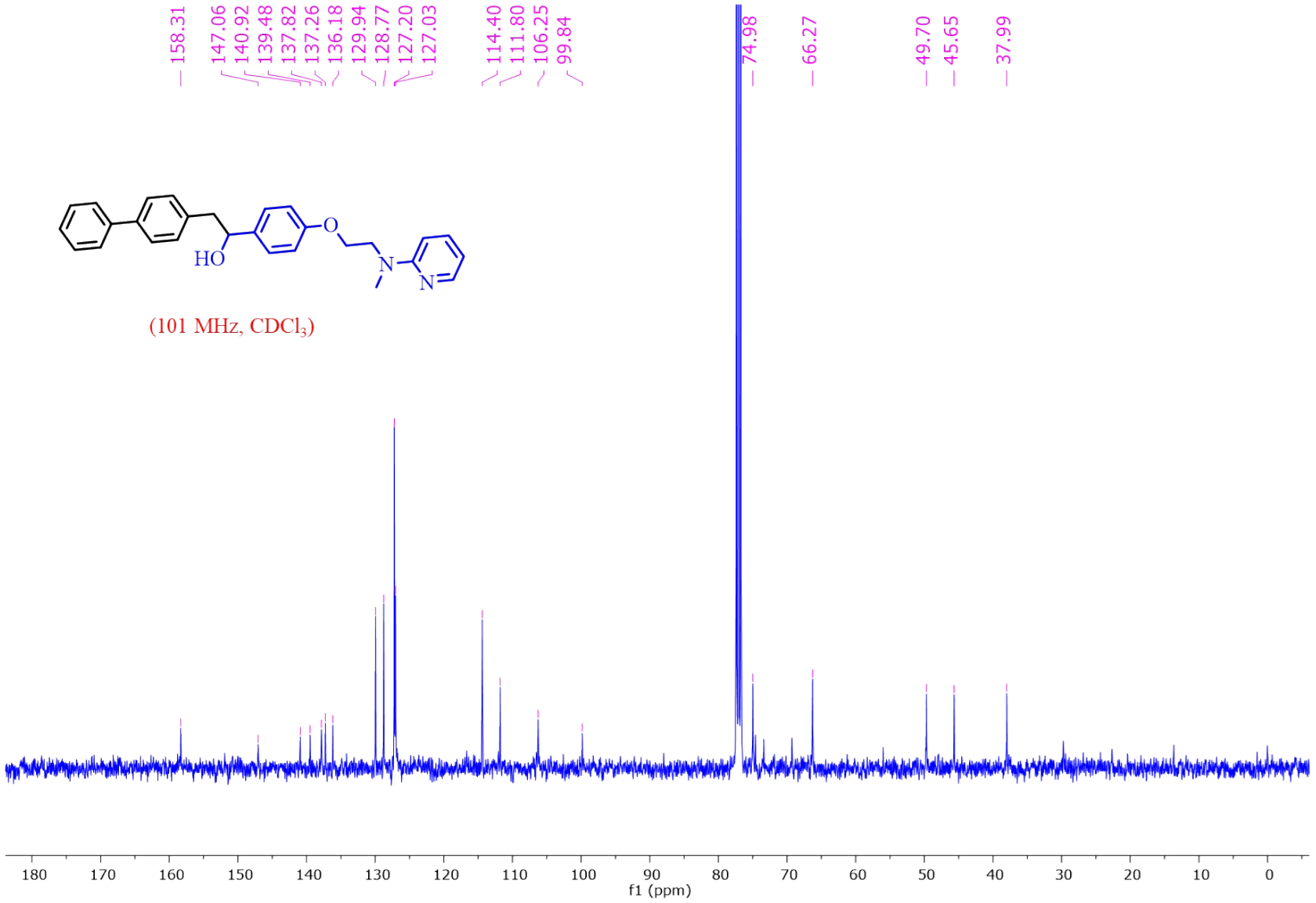


Fig. S153. ^{13}C NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1-(4-(2-(methyl(pyridin-2-yl)amino)ethoxy)phenyl)ethan-1-ol (**7m**) in $CDCl_3$.

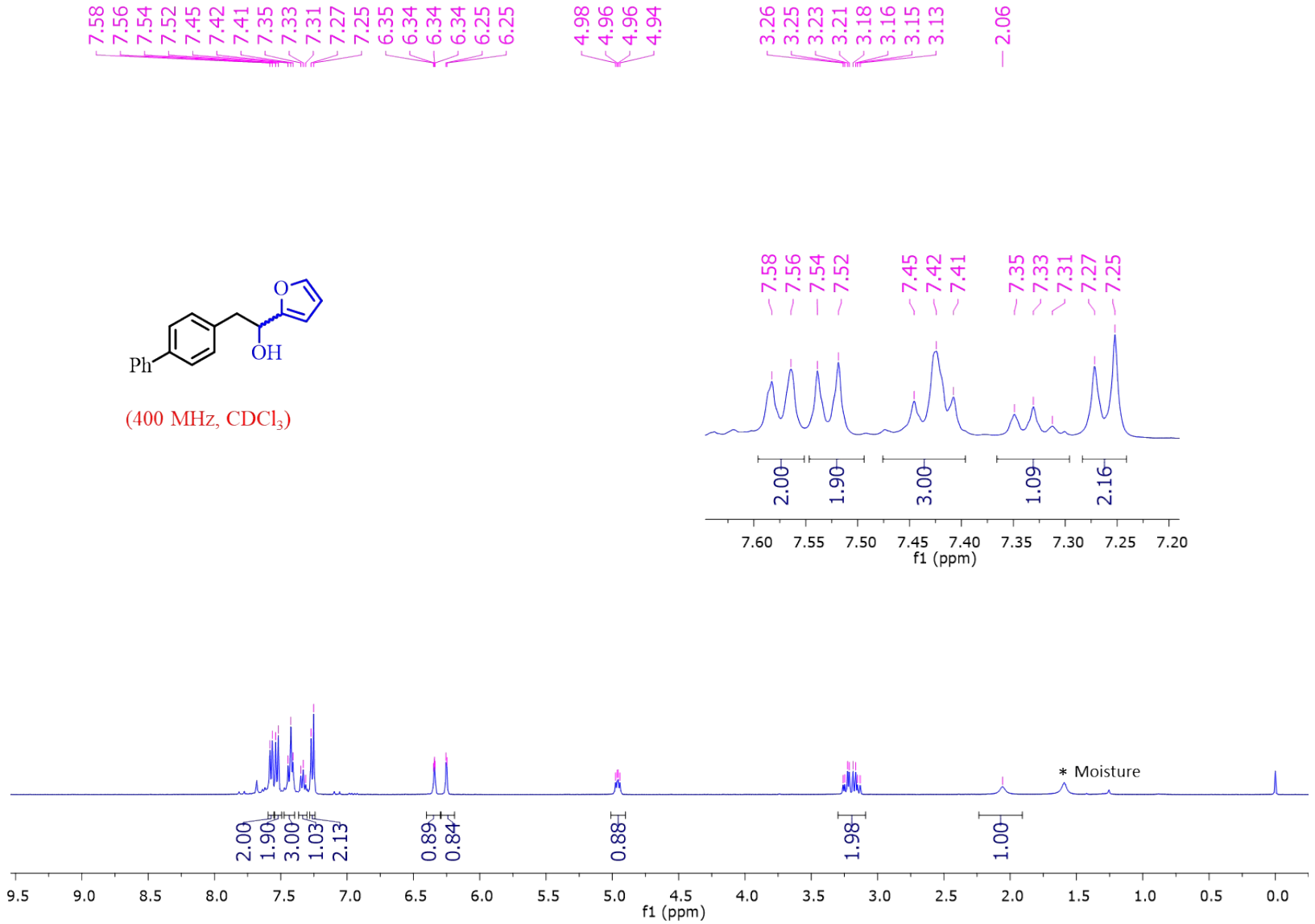


Fig. S154. ^{1}H NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1-(furan-2-yl)ethan-1-ol (**7n**) in $CDCl_3$.

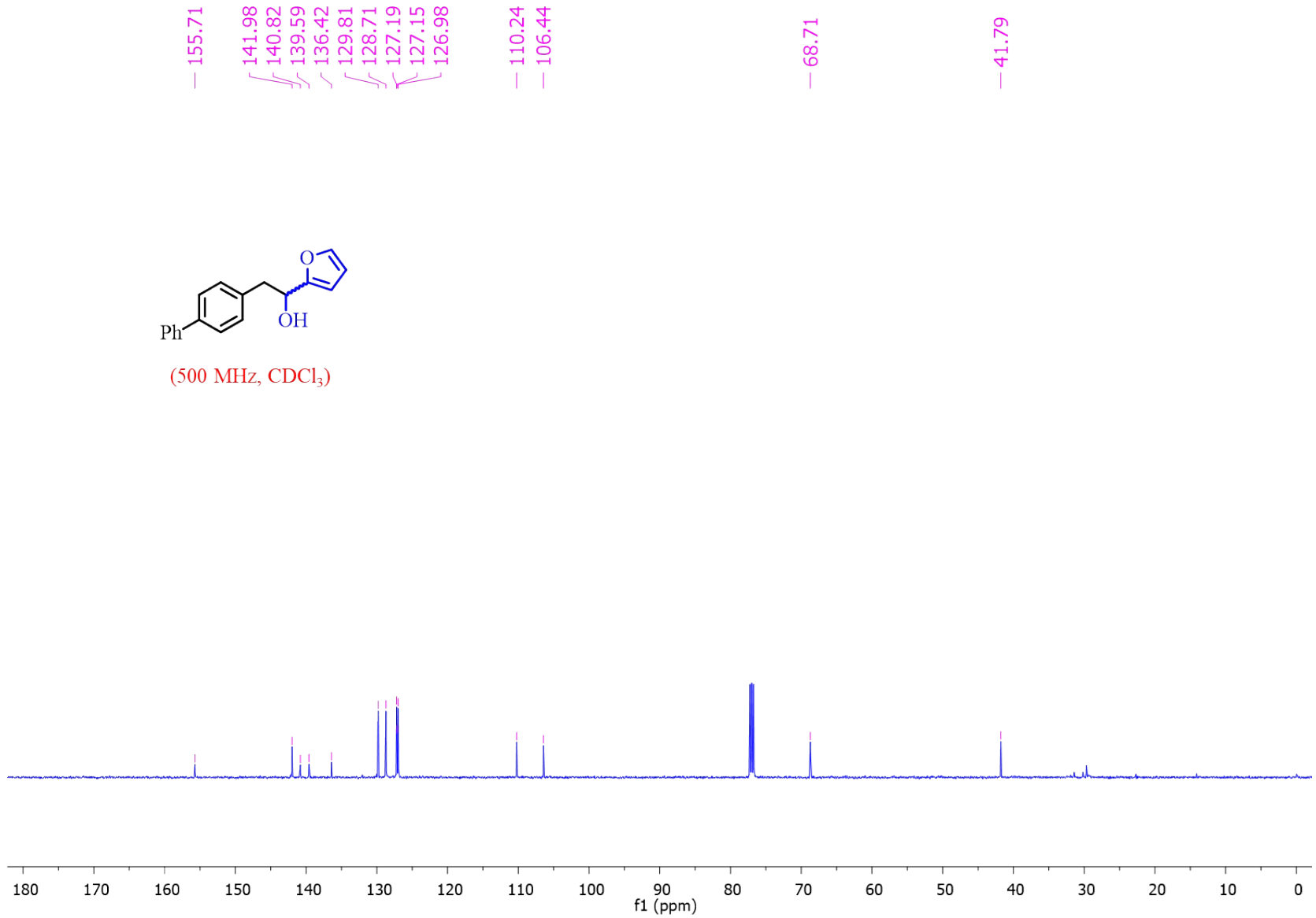


Fig. S155. ^{13}C NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1-(furan-2-yl)ethan-1-ol (**7n**) in $CDCl_3$.

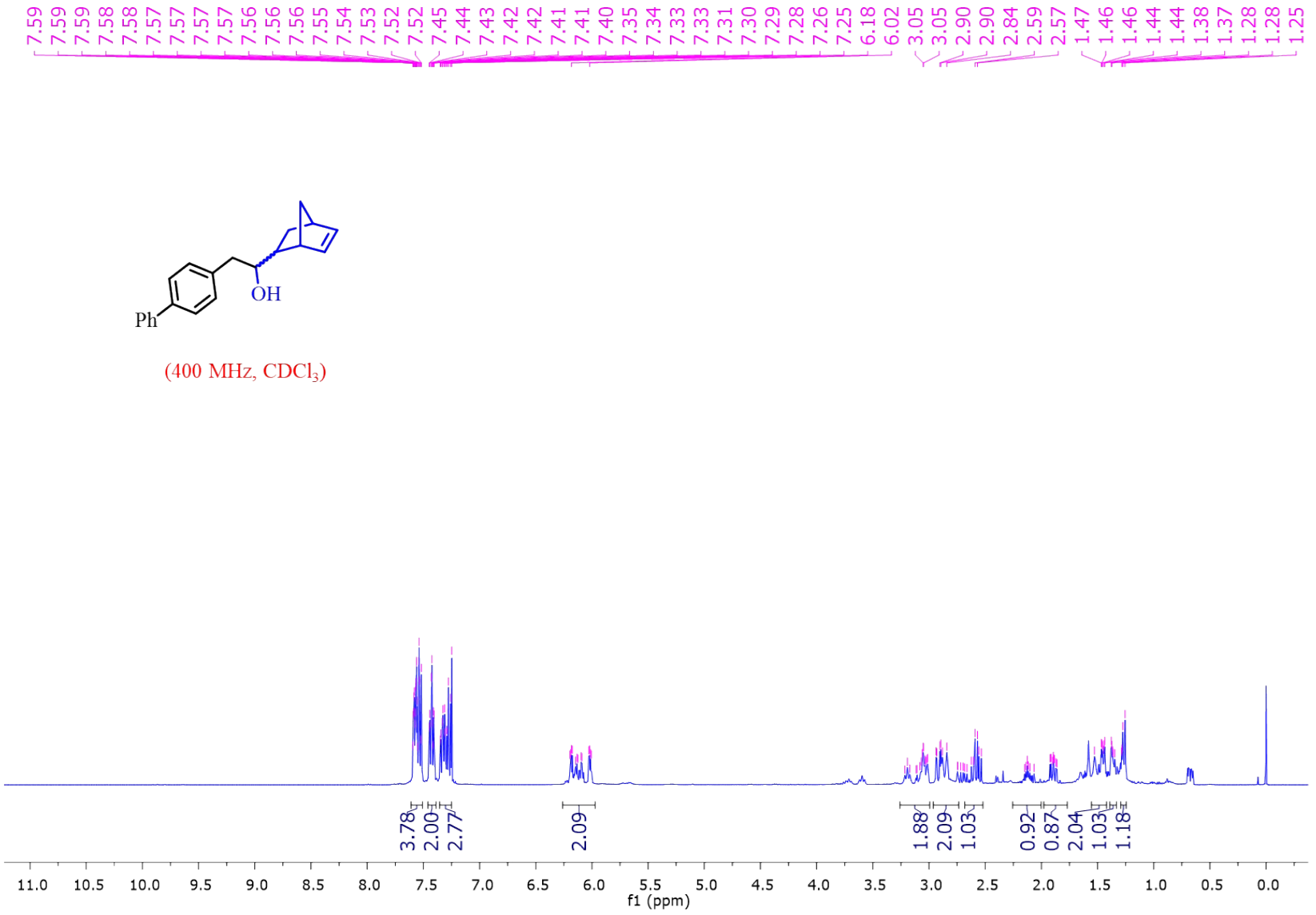


Fig. S156. ^{1}H NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1-((1R,4R)-bicyclo[2.2.1]hept-5-en-2-yl)ethan-1-ol (**7o**) in $CDCl_3$.

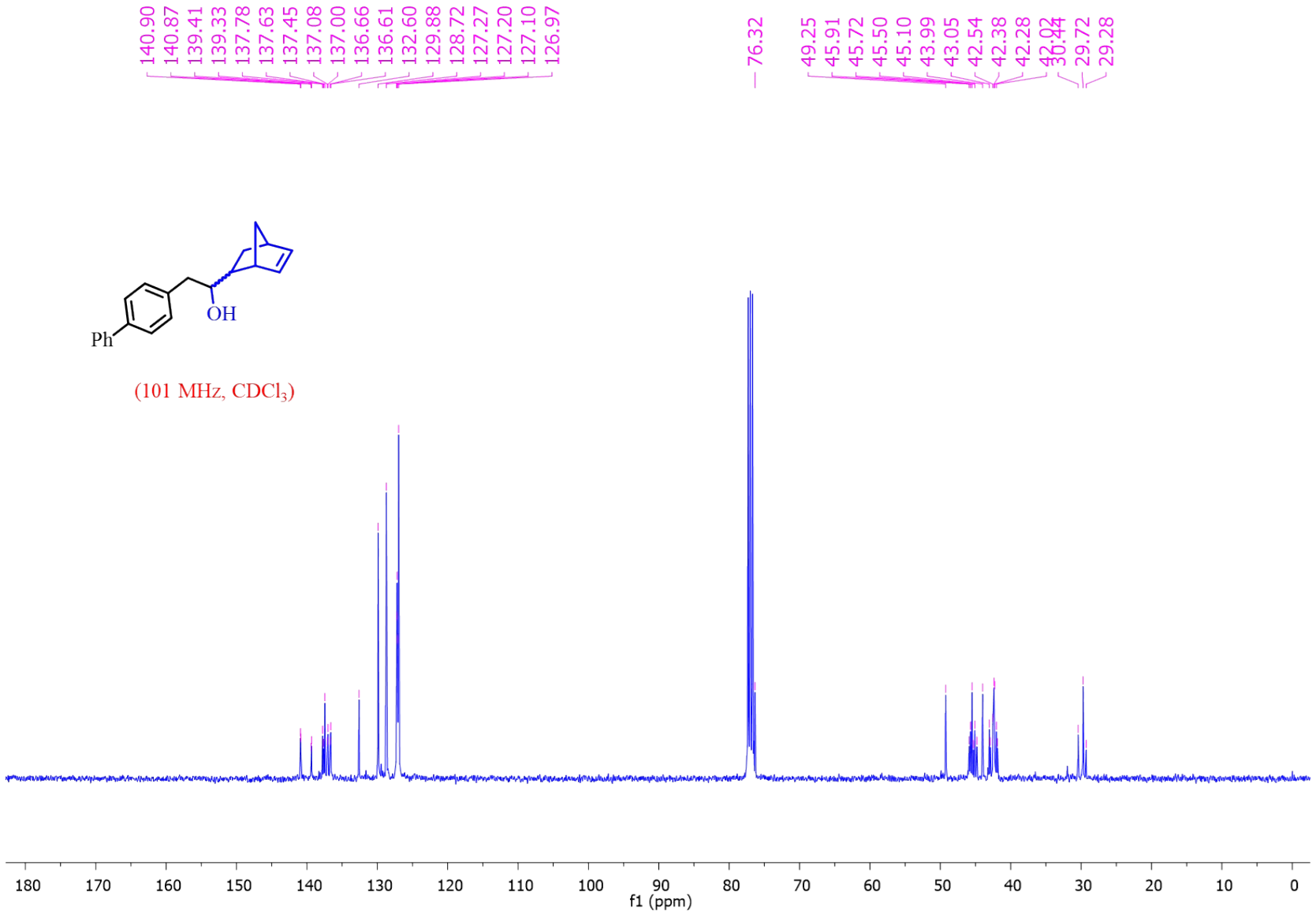


Fig. S157. ^{13}C NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1-((1R,4R)-bicyclo[2.2.1]hept-5-en-2-yl)ethan-1-ol (**7o**) in $CDCl_3$.

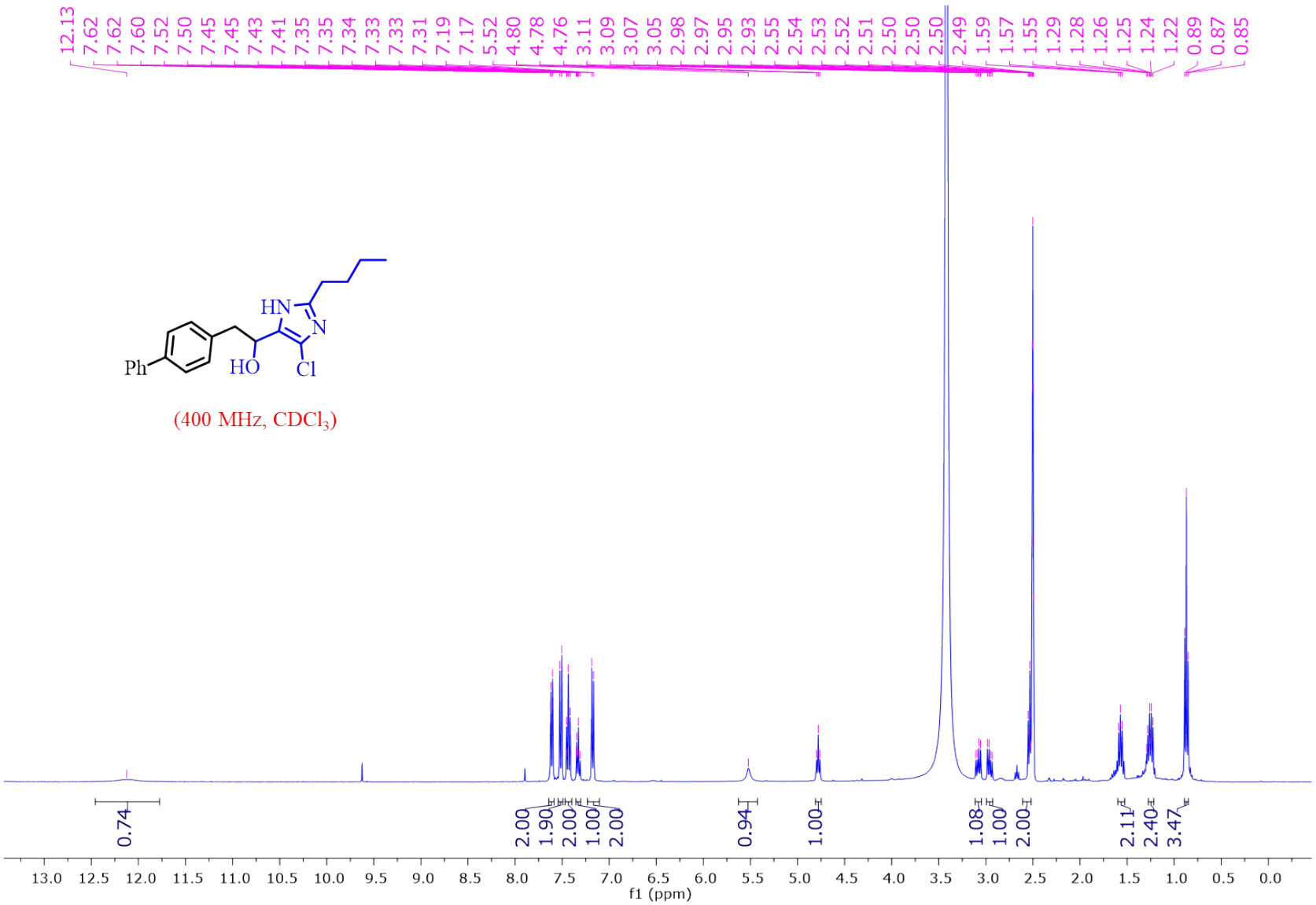


Fig. S158. ^{1}H NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1-(2-butyl-4-chloro-1H-imidazol-5-yl)ethan-1-ol (**7p**) in $CDCl_3$.

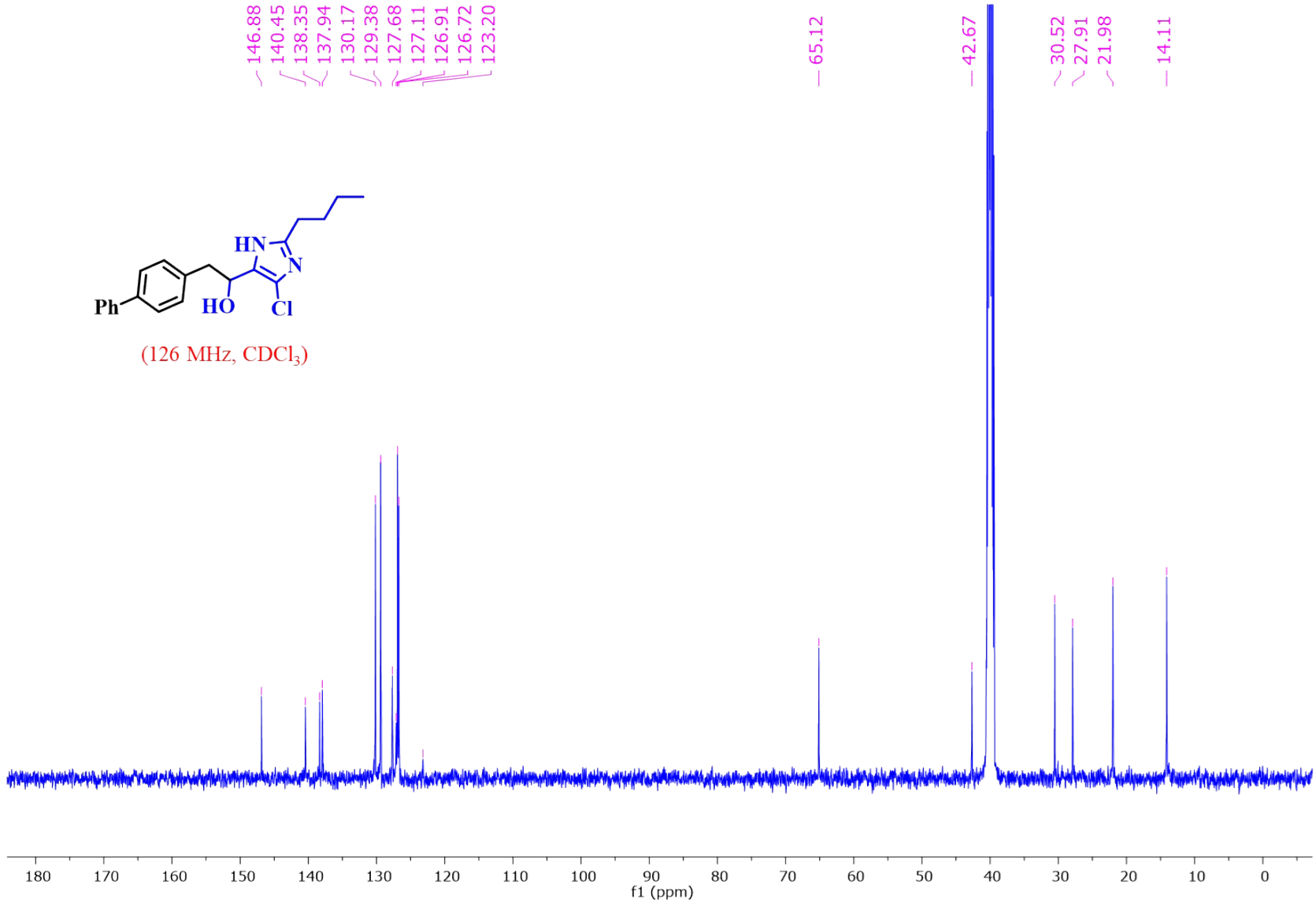


Fig. S159. ^{13}C NMR spectra of 2-([1,1'-biphenyl]-4-yl)-1-(2-butyl-4-chloro-1H-imidazol-5-yl)ethan-1-ol (**7p**) in $CDCl_3$.

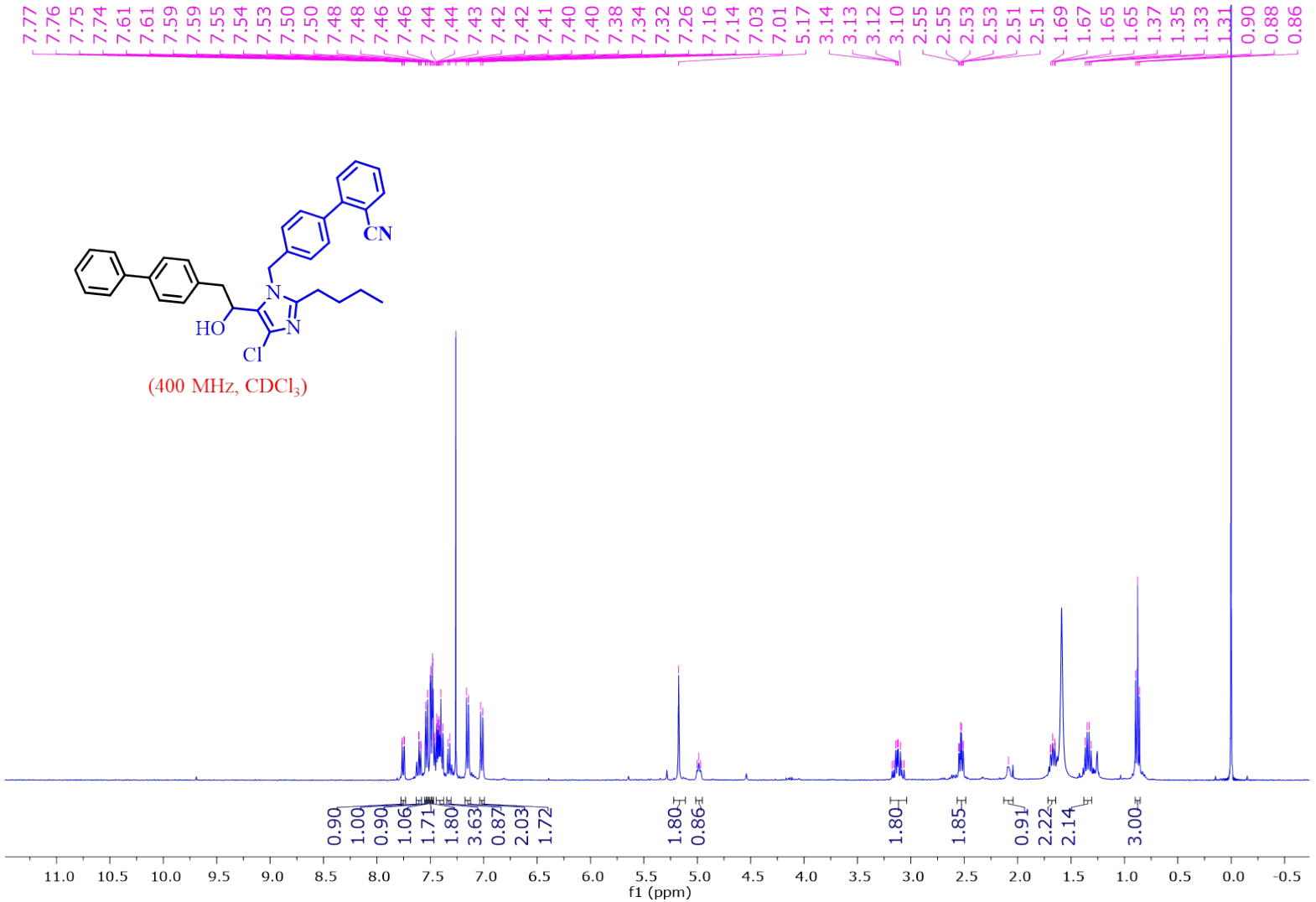


Fig. S160. ^{1}H NMR spectra of 4'-((5-(2-([1,1'-biphenyl]-4-yl)-1-hydroxyethyl)-2-butyl-4-chloro-1H-imidazol-1-yl)methyl)-[1,1'-biphenyl]-2-carbonitrile (**7q**) in $CDCl_3$.

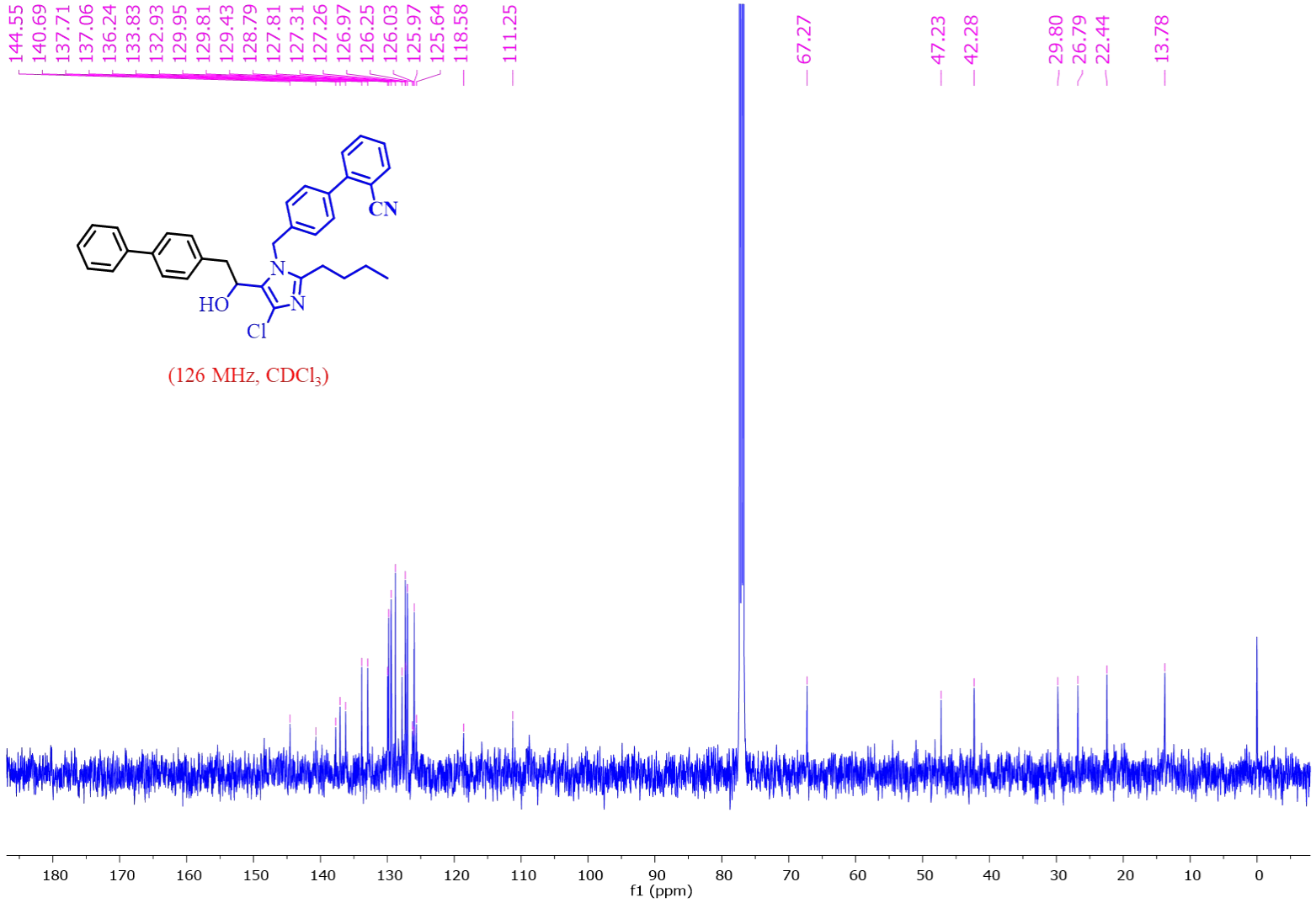


Fig. S161. ^{13}C NMR spectra of 4'-((5-(2-([1,1'-biphenyl]-4-yl)-1-hydroxyethyl)-2-butyl-4-chloro-1H-imidazol-1-yl)methyl)-[1,1'-biphenyl]-2-carbonitrile (**7q**) in $CDCl_3$.

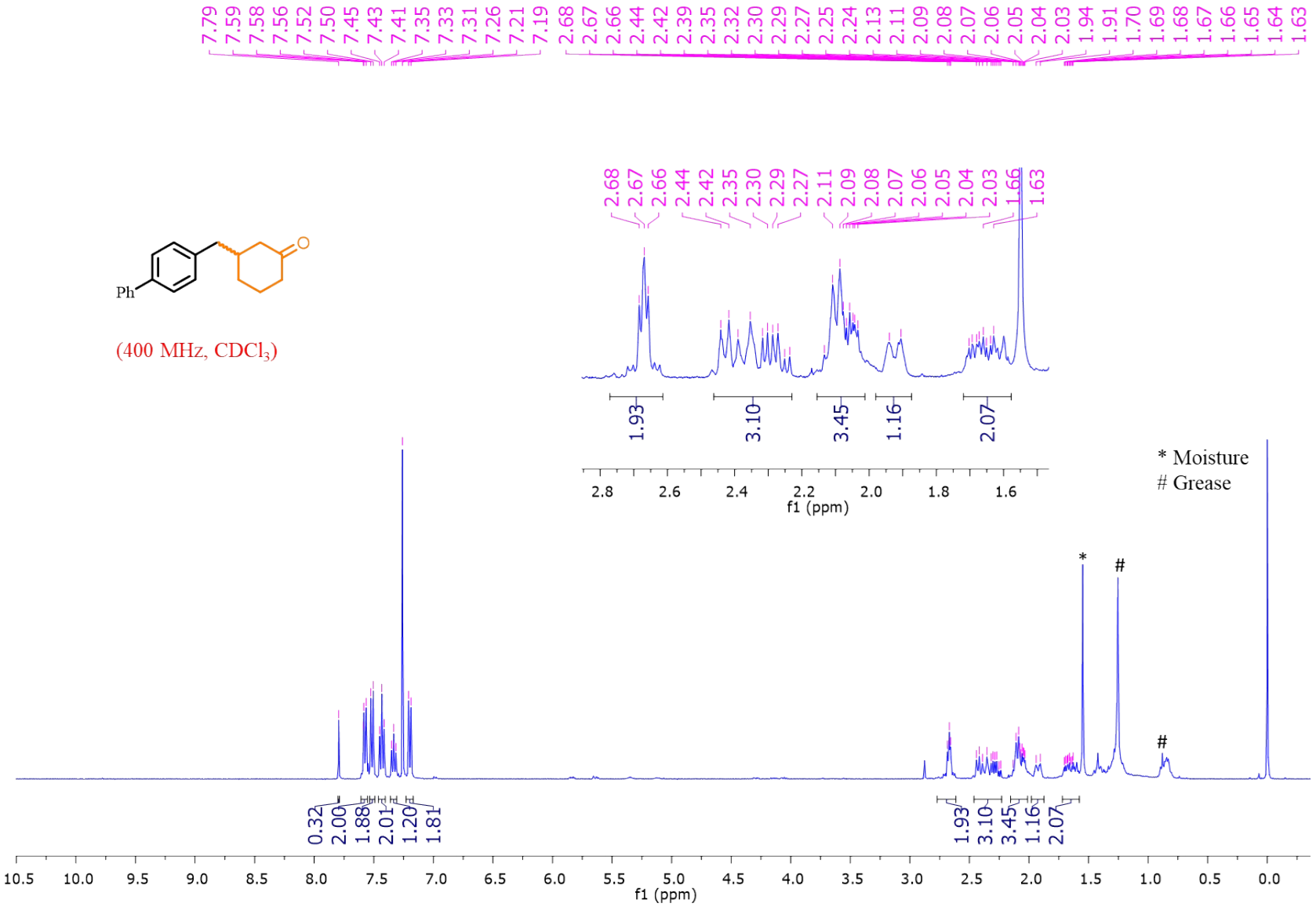


Fig. S162. ^{1}H NMR spectra of 3-([1,1'-biphenyl]-4-ylmethyl)cyclohexan-1-one (**9a**) in $CDCl_3$.

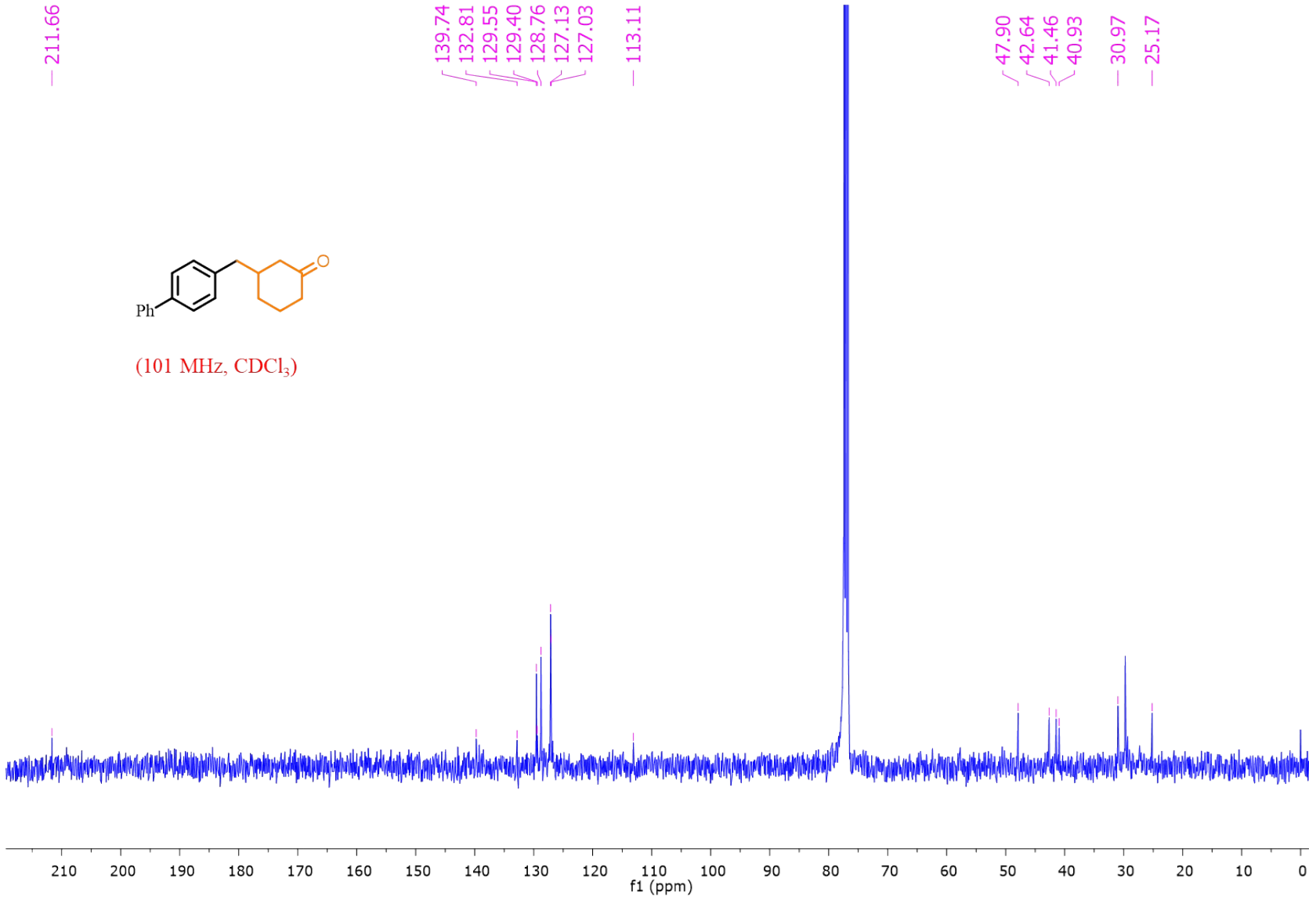


Fig. S163. ^{13}C NMR spectra of 3-([1,1'-biphenyl]-4-ylmethyl)cyclohexan-1-one (**9a**) in $CDCl_3$.