Supplementary Information

DDQ-catalyzed oxidative α-allylation of isochromans under aerobic condition

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Table of Contents

I. Experimetnal Procedures

General: All reactions were conducted using oven-dried glassware under an atmosphere of argon (Ar). All commercially available reagents and anhydrous solvents were obtained from Sigma Aldrich, TCI, Alfa, Junsei, Samchun, DaeJung Chemical and were used without further purification. Solvents CH_2Cl_2 was dried and distilled following usual protocols. Organic solvents were evaporated with reduced pressure using a rotary evaporator. Reactions were followed by TLC analysis using silica gel 60 F_{254} with fluorescent indicator using UV lamp and ninhydrin solution with heat as visualizing agents. Flash chromatography was carried out using Merck silica gel 60 (0.063-0.200 mm) and KANTO silica gel 60N (spherical, neutral). The ^{1}H NMR spectra and ^{13}C NMR spectra were measured with Bruker AVANCE III HD 400. ^{1}H NMR chemical shifts are expressed in parts per million (δ) downfield to $CHCl_3$ (δ = 7.26), ^{13}C NMR chemical shifts are expressed in parts per million (δ) relative to the central $CDCl_3$ resonance (δ = 77.0). Coupling constants in ^{1}H NMR are in Hz. The following abbreviations were used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet. $CDCl_3$ was used as NMR solvent and standard material TMS (tetramethylsilane) wasn't contained. Low-resolution mass spectral analyses (LRMS) were performed on Agilent 6125 SQ LCMS system. High-resolution mass spectral analysis (HRMS) data was acquired on a Bruker Compact Ultra High Resolution ESI Q-TOF mass spectrometer at the OCRC (Organic Chemistry Research Center), Sogang University (Seoul, Republic of Korea).

1-Allylisochromane (8a).[1] Dichloroethane (3.7 mL) was bubbled with O_2 for 1 h. To a solution of isochroman **6a** (50 mg, 0.37 mmol) in dichloroethane was added DDQ (17 mg, 0.074 mol) and TBN (8.86 µL, 0.074 mmol). The reaction mixture was allowed to stir at room temperature for 36 h. The solvent was removed under reduced pressure, and dichloroethane (3.7 mL) was

added to the crude oil again. To this solution was added $LiPF_6$ (28 mg, 0.18 mmol) and methanesulfonic acid (6.7 µL, 0.074 mmol). Allyltributyl stannane (0.23 mL, 0.74 mmol) was added dropwise to the above mixture. The reaction mixture was allowed to stir at 80 °C for 24 h. After completion of the reaction (monitored by TLC), it was quenched with saturated aqueous $NaHCO_3$ (10 mL), extracted with CH_2Cl_2 (3 x 10 mL) and washed with brine. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (ether/*n*-hexane = 1:50) to afford compound **8a** (49 mg, 76%) as colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.18–7.16 (m, 2H), 7.11–7.10 (m, 2H), 5.96–5.85 (m, 1H), 5.17–5.07 (m, 2H), 4.84 (dd, J = 7.8, 3.0 Hz, 1H), 4.19–4.14 (m, 1H), 3.81–3.75 (m, 1H), 3.02–2.96 (m, 1H), 2.71–2.66 (m, 2H), 2.62–2.55 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.5, 135.0, 134.0, 129.0, 126.3, 126.1, 124.8, 117.2, 75.5, 63.6, 40.3, 29.0.

1-Allyl-7-methylisochromane (8b) and 7-methylisochroman-1-one (8b′). Following the same procedure used for the synthesis of **8a**, the reaction of isochroman **6b** (55 mg, 0.37 mmol), DDQ (17 mg, 0.074 mol), TBN (8.86 µL, 0.074 mmol), $LiPF_6$ (28 mg, 0.18 mmol), methanesulfonic acid (6.7 µL, 0.074 mmol) and allyltributyl stannane (0.23 mL, 0.74 mmol) in dichloroethane (3.7 mL) afforded compound **8b** (53 mg, 76%) as colorless oil after purification by flash column chromatography on silica gel (ether/n-hexane = 1:50) along with lactone **8b'** (4.8 mg, 8%).

8b: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.01–6.98 (m, 2H), 6.91 (s, 1H), 5.95–5.88 (m, 1H), 5.18–5.07 (m, 2H), 4.80 (dd, J = 8.2, 3.3 Hz, 1H), 4.17–4.12 (m, 1H), 3.78–3.72 (m, 1H), 2.94 (m, 1H), 2.70–2.55 (m, 3H), 2.31 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.5, 135.5, 135.2, 130.9, 128.8, 127.1, 125.3, 116.8, 75.5, 63.4, 40.4, 28.7, 21.2. HRMS (ESI) calcd for $C_{13}H_{16}NaO$ $[M+Na]^+$ 211.1098, found 211.1096.

8b′: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.34 (dd, J = 7.7, 1.4 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 4.51 (t, J = 6.0 Hz, 2H), 3.01 (t, J = 6.0 Hz, 2H), 2.38 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 165.4, 137.5, 136.5, 134.5, 130.6, 127.1, 125.0, 67.4, 27.4, 21.0.

1-Allyl-4-methylisochromane (8c) and 4-methylisochroman-1-one (8c′). Following the same procedure used for the synthesis of **8a**, the reaction of isochroman **6c** (55 mg, 0.37 mmol), DDQ (17 mg, 0.074 mol), TBN (8.86 µL, 0.074 mmol), $LiPF_6$ (28 mg, 0.18 mmol), methanesulfonic acid (6.7 µL, 0.074 mmol) and allyltributyl stannane (0.23 mL, 0.74 mmol) in dichloroethane (3.7 mL) afforded a 2.2:1 diasteromeric mixture of compound **8c** (56 mg, 80%) as colorless oil after purification by flash column chromatography on silica gel (ether/n-hexane = 1:50) along with lactone **8c'** (4.2 mg, 7%). Each isomer was partially separated for characterization.

8c (Major isomer): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29–7.10 (m, 4H), 5.99–5.87 (m, 1H), 5.19–5.10 (m, 2H), 4.84 (dd, J = 7.6, 3.4 Hz, 1H), 4.12–4.08 (m, 0.5H), 3.92–3.85 (m, 1H), 3.49–3.45 (m, 0.5H), 3.08–2.58 (m, 3H), 1.38 (d, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 139.6, 139.3, 137.1, 137.0, 135.1, 134.9, 128.4, 126.9, 126.5, 126.4, 126.0, 125.9, 124.7, 124.6, 117.0, 116.9, 75.9, 75.8, 69.2, 69.1, 40.3, 40.2, 32.9, 31.9, 21.1, 17.4. HRMS (ESI) calcd for $C_{13}H_{16}NaO$ $[M+Na]^+$ 211.1092, found 211.1098. **8c** (Minor isomer): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29–7.10 (m, 4H), 5.99–5.87 (m, 1H), 5.19–5.10 (m, 2H), 4.89 (dd, J = 8.0, 3.6 Hz, 1H), 4.12–4.08 (m, 0.5H), 3.92–3.85 (m, 1H), 3.49–3.45 (m, 0.5H), 3.08–2.58 (m, 3H), 1.26 (d, J = 7.0 Hz, 3H).

8c': ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, J = 7.8, 1.2 Hz, 1H), 7.57 (td, J = 7.6, 1.4 Hz, 1H), 7.39 (td, J = 7.6, 0.7 Hz, 1H), 7.30-7.28 (m, 1H), 4.51 (dd, J = 10.9, 4.1 Hz, 1H), 4.24 (dd, J = 10.9, 6.6 Hz, 1H), 3.15 (m, 1H), 1.37 (d, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 165.1, 144.5, 133.9, 130.4, 127.5, 125.7, 124.3, 72.4, 31.7, 16.6.

1-Allyl-3-methylisochromane (8d) and 3-methylisochroman-1-one (8d'). Following the

same procedure used for the synthesis of **8a**, the reaction of isochroman **6d** (55 mg, 0.37 mmol), DDQ (17 mg, 0.074 mol), TBN (8.86 μL, 0.074 mmol), $LiPF_6$ (28 mg, 0.18 mmol), methanesulfonic acid (6.7 μL, 0.074 mmol) and allyltributyl stannane (0.23 mL, 0.74 mmol) in dichloroethane (3.7 mL) afforded a 2.9:1 diastereomeric mixture of compound **8d** (50 mg, 72%) as colorless oil after purification by flash column chromatography on silica gel (ether/n-hexane = 1:50) along with lactone **8d'** (5.9 mg, 10%). Each isomer was partially separated for characterization.

8d (Major isomer): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.17–7.13 (m, 2H), 7.09–7.04 (m, 2H), 6.05–5.94 (m, 1H), 5.16–5.11 (m, 2H), 4.89 (dd, J = 9.8, 3.9 Hz, 1H), 4.11–4.03 (m, 1H), 2.7–2.61 (m, 3H), 2.52–2.46 (m, 1H), 1.30 (d, J = 6.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.7, 135.6, 133.5, 128.9, 126.5, 125.9, 125.4, 116.9, 74.6, 63.9, 40.6, 36.0, 21.4. HRMS (ESI) calcd for $C_{13}H_{16}NaO$ $[M+Na]^+$ 211.1098, found 211.1091. **8d** (Minor isomer): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.20–7.08 (m, 4H), 5.94–5.84 (m, 1H), 5.13 (dd, J = 17.2, 1.5 Hz, 1H), 5.05 (d, J = 10.2 Hz, 1H), 4.88–4.87 (m, 1H), 3.83–3.77 (m, 1H), 2.8–2.53 (m, 4H), 1.35 (d, J = 6.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.7, 135.1, 134.7, 128.8, 126.3, 126.1, 124.6, 116.8, 76.4, 70.5, 40.3, 36.8, 21.9.

8d′: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, J = 7.8, 1.0 Hz, 1H), 7.52 (td, J = 7.5, 1.4 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 4.67 (m, 1H), 2.95-2.92 (m, 2H), 1.51 (d, J = 6.3 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 165.6, 139.1, 133.6, 130.2, 127.6, 127.3, 124.9, 75.0, 34.8, 20.9.

1-Allyl-7-methoxyisochromane (8e) and 7-methoxyisochroman-1-one (8e′). Following the same procedure used for the synthesis of **8a**, the reaction of isochroman **6e** (53.6 mg, 0.33 mmol), DDQ (15 mg, 0.067 mol), TBN (8.0 μL, 0.067 mmol), $LiPF_6$ (25 mg, 0.16 mmol), methanesulfonic acid (6.7 μL, 0.074 mmol) and allyltributyl stannane (0.21 mL, 0.67 mmol) in dichloroethane (3.3 mL) afforded compound **8e** (34 mg, 50%) as colorless oil by purification

by flash column chromatography on silica gel (ether/n-hexane = 1:50) along with lactone **8e'** (8.1 mg, 14%).

8e: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.03 (d, J = 8.3 Hz, 1H), 6.75 (dd, J = 8.4, 2.5 Hz, 1H), 6.64 (d, J = 2.3 Hz, 1H), 5.96–5.85 (m, 1H), 5.16 (dd, J = 17.2, 1.6 Hz, 1H), 5.10 (d, J = 10.2 Hz, 1H), 4.80 (dd, J = 7.7, 3.3 Hz, 1H), 4.17–4.12 (m, 1H), 3.78 (s, 3H), 3.76–3.71 (m, 1H), 2.96–2.88 (m, 1H), 2.71–2.54 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 157.9, 138.8, 135.1, 129.9, 126.2, 117.1, 112.3, 110.2, 75.6, 63.7, 55.4, 40.4, 28.3. HRMS (ESI) calcd for $C_{13}H_{16}NaO_2$ $[M+Na]^+$ 227.1047, found 227.1046.

8e′: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, J = 2.7 Hz, 1H), 7.16 (d, J = 8.1 Hz, 1H), 7.09 (dd, J = 8.4, 2.7 Hz, 1H), 4.51 (t, J = 6.0, 2H), 3.83 (s, 3H), 2.99 (t, J = 6.0 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 165.2, 159.0, 131.8, 128.4, 126.0, 121.6, 112.9, 67.6, 55.6, 27.0.

1-Allyl-6-methoxyisochromane (8f). Following the same procedure used for the synthesis of **8a**, the reaction of isochroman **6f** (53.6 mg, 0.32 mmol), DDQ (14.8 mg, 0.065 mol), TBN (7.8 µL, 0.065 mmol), $LiPF_6$ (25 mg, 0.16 mmol), methanesulfonic acid (4.2 µL, 0.065 mmol) and allyltributyl stannane (0.21 mL, 0.65 mmol) in dichloroethane (3.3 mL) afforded compound **8f** (44 mg, 66%) as colorless oil by purification by flash column chromatography on silica gel (ether/n-hexane = 1:50). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.18–7.16 (m, 2H), 7.11–7.10 (m, 2H), 5.96–5.85 (m, 1H), 5.17–5.07 (m, 2H), 4.84 (dd, J = 7.8, 3.0 Hz, 1H), 4.19–4.14 (m, 1H), 3.81–3.75 (m, 1H), 3.02–2.96 (m, 1H), 2.71–2.66 (m, 2H), 2.62–2.55 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.0, 135.5, 135.2, 130.1, 126.0, 117.0, 113.5, 112.5, 75.4, 63.5, 55.3, 40.5, 29.5. HRMS (ESI) calcd for $C_{13}H_{16}NaO_2$ $[M+Na]^+$ 227.1047, found 227.1045.

1-Allyl-6,7-dimethoxyisochromane (8g) and 6,7-dimethoxyisochroman-1-one (8g′). Following the same procedure used for the synthesis of **8a**, the reaction of isochroman **6g** (72.4 mg, 0.37 mmol), DDQ (17 mg, 0.074 mol), TBN (8.86 µL, 0.074 mmol), $LiPF_6$ (28 mg, 0.18 mmol), methanesulfonic acid (6.7 µL, 0.074 mmol) and allyltributyl stannane (0.23 mL, 0.74

mmol) in dichloroethane (3.7 mL) afforded compound **8g** (42 mg, 48%) as colorless oil by purification by flash column chromatography on silica gel (ether/n-hexane = 1:50) along with lactone **8g'** (33 mg, 42%).

8g: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.59 (d, J = 4.8, 2H), 5.93–5.86 (m, 1H), 5.17–5.08 (m, 2H), 4.77 (dd, J = 7.6, 3.4 Hz, 1H), 4.16–4.11 (m, 1H), 3.78–3.72 (m, 1H), 2.95–2.87 (m, 1H), 2.71–2.52 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 147.5, 147.4, 135.1, 129.5, 126.1, 116.9, 111.4, 107.9, 75.1, 63.4, 56.0, 55.8, 40.5, 28.5. HRMS (ESI) calcd for $C_{14}H_{18}NaO_3$ $[M+Na]^+$ 257.1153, found 257.1149.

8g′: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 6.67 (s, 1H), 4.50 (t, J = 6.0 Hz, 2H), 3.92 (s, 3H), 3.89 (s, 3H), 2.97 (t, J = 6.0 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 165.2, 153.6, 148.4, 133.9, 117.4, 111.8, 109.1, 67.3, 56.1, 56.1, 27.4.

1-Allyl-7-fluoroisochromane (8h). Following the same procedure used for the synthesis of **8a**, the reaction of isochroman **6h** (56.7 mg, 0.37 mmol), DDQ (17 mg, 0.074 mol), TBN (8.86 µL, 0.074 mmol) $LiPF_6$ (28 mg, 0.18 mmol), methanesulfonic acid (6.7 µL, 0.074 mmol) and allyltributyl stannane (0.23 mL, 0.74 mmol) in dichloroethane (3.7 mL) afforded compound **8h** (16 mg, 18%) as colorless oil after purification by flash column chromatography on silica gel (ether/n-hexane = 1:50). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.08–7.04 (m, H), 6.87 (td, J = 8.5, 2.5 Hz, 1H), 6.81 (dd, J = 9.8, 24 Hz, 1H), 5.93–5.83 (m, 1H), 5.15 (dd, J = 17.2, 1.6 Hz, 1H), 5.10 (d, J = 10.2 Hz, 1H), 4.79 (dd, J = 7.5, 3.3 Hz, 1H), 4.18–4.13 (m, 1H), 3.77–3.71 (m, 1H), 2.98–2.90 (m, 1H), 2.71 – 2.66 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.2 (d, ^{1}J = 243.5 Hz), 139.6 (d, ^{3}J = 6.1 Hz), 134.6, 130.4 (d, ^{3}J = 7.7 Hz), 129.7 (d, ^{4}J = 3.0 Hz), 117.4, 113.6 (d, ^{2}J = 21.2 Hz), 111.6 (d, ^{2}J = 22.0 Hz), 75.4 (d, ^{4}J = 2.2 Hz), 63.6, 40.2, 28.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.2. HRMS (ESI) calcd for $C_{12}H_{13}FNaO$ $[M+Na]^+$ 215.0847, found 215.0837.

1-Allyl-7-chloroisochromane (8i). Following the same procedure used for the synthesis of **8a**, the reaction of isochroman **6i** (62.8 mg, 0.37 mmol), DDQ (17 mg, 0.074 mol), TBN (8.86 µL, 0.074 mmol), $LiPF_6$ (28 mg, 0.18 mmol), methanesulfonic acid (6.7 µL, 0.074 mmol) and allyltributyl stannane (0.23 mL, 0.74 mmol) in dichloroethane (3.7 mL) afforded compound **8i** (25 mg, 33%) as colorless oil after purification by flash column chromatography on silica gel (ether/n-hexane = 1:50). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.14–7.03 (m, 3H), 5.91–5.84 (m, 1H), 5.17–5.09 (m, 2H), 4.78 (dd, J = 7.8, 3.3 Hz, 1H), 4.17–4.12 (m, 1H), 3.77–3.70 (m, 1H), 2.96–2.90 (m, 1H), 2.71–2.54 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 139.6, 134.6, 132.6, 131.7, 130.3, 126.6, 125.0, 117.4, 75.3, 63.4, 40.2, 28.5. HRMS (ESI) calcd for $C_{12}H_{13}ClNaO$ $[M+Na]^+$ 231.0552, found 231.0550.

1-Allyl-7-bromoisochromane (8j). Following the same procedure used for the synthesis of **8a**, the reaction of isochroman **6j** (79.4 mg, 0.37 mmol), DDQ (17 mg, 0.074 mol), TBN (8.86 µL, 0.074 mmol), $LiPF_6$ (28 mg, 0.18 mmol), methanesulfonic acid (6.7 µL, 0.074 mmol), and allyltributyl stannane (0.23 mL, 0.74 mmol) in dichloroethane (3.7 mL) afforded compound **8j** (32 mg, 34%) as colorless oil after purification by flash column chromatography on silica gel (ether/n-hexane = 1:50). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29–7.25 (m, 2H), 6.99 (d, J = 8.1 Hz, 1), 5.91–5.84 (m, 1H), 5.18–5.08 (m, 2H), 4.78 (dd, J = 7.9, 3.4 Hz, 1H), 4.17–4.12 (m, 1H), 3.76–3.70 (m, 1H), 2.95–2.88 (m, 1H), 2.72–2.52 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 140.0, 134.6, 133.1, 130.7, 129.5, 127.9, 119.7, 117.5, 75.2, 63.3, 40.2, 28.6. HRMS (ESI) calcd for $C_{12}H_{13}BrNaO$ $[M+Na]^+$ 275.0047, found 275.0046.

1-Allyl-6-fluoroisochromane (8k). Following the same procedure used for the synthesis of **8a**, the reaction of isochroman **6k** (56.7 mg, 0.37 mmol), DDQ (17 mg, 0.074 mol), TBN (8.86 µL, 0.074 mmol), $LiPF_6$ (28 mg, 0.18 mmol), methanesulfonic acid (6.7 µL, 0.074 mmol) and allyltributyl stannane (0.23 mL, 0.74 mmol) in dichloroethane (3.7 mL) afforded compound **8k** (30 mg, 41%) as colorless oil after purification by flash column chromatography on silica gel

(ether/n-hexane = 1:50). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.06 (q, J = 4.7 Hz, 1H), 6.88 (td, J = 8.5, 2.6 Hz, 1H), 6.81 (dd, J = 9.3, 2.5 Hz, 1H), 5.93–5.83 (m, 1H), 5.16–5.07 (m, 2H), 4.80 (dd, J = 7.3, 2.9 Hz, 1H), 4.17–4.12 (m, 1H), 3.78–3.72 (m, 1H), 3.02–2.95 (m, 1H), 2.72–2.63 (m, 2H), 2.60–2.52 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.2 (d, ^{1}J = 244.9 Hz), 136.4 (d, ^{3}J = 7.3 Hz), 134.8, 133.5 (d, ^{4}J = 2.9 Hz), 126.5 (d, ^{3}J = 8.2 Hz), 117.2, 115.2 (d, ^{2}J = 20.5 Hz), 113.3 (d, ^{2}J = 21.2 Hz), 75.2, 63.1, 40.3, 29.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.8. HRMS (ESI) calcd for $C_{12}H_{13}FNaO$ $[M+Na]^+$ 215.0847, found 215.0860.

1-Allyl-6-chloroisochromane (8l). Following the same procedure used for the synthesis of **8a**, the reaction of isochroman **6l** (62.8 mg, 0.37 mmol), DDQ (17 mg, 0.074 mol), TBN (8.86 µL, 0.074 mmol), $LiPF_6$ (28 mg, 0.18 mmol), methanesulfonic acid (6.7 µL, 0.074 mmol) and allytributyl stannane (0.23 mL, 0.74 mmol) in dichloroethane (3.7 mL) after compound **8l** (29 mg, 37%) as colorless oil purification by flash column chromatography on silica gel (ether/n-hexane = 1:50). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.15-7.10 (m, 2H), 7.03 (dd, J = 8.5, 2.6 Hz, 1H), 5.92–5.82 (m, 1H), 5.15–5.07 (m, 2H), 4.79 (dd, J = 7.6, 3.4 Hz, 1H), 4.17–4.12 (m, 1H), 3.77–3.71 (m, 1H), 3.00–2.93 (m, 1H), 2.71–2.52 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 136.3, 136.1, 134.6, 132.0, 128.8, 126.4, 126.4, 117.4, 75.3, 63.2, 40.3, 29.0. HRMS (ESI) calcd for $C_{12}H_{13}ClNaO$ $[M+Na]^+$ 231.0552, found 231.0548.

1-Allylisochroman-7-yl acetate (8m). Following the same procedure used for the synthesis of **8a**, the reaction of isochroman **6m** (71.6 mg, 0.37 mmol), DDQ (17 mg, 0.074 mol), TBN (8.86 µL, 0.074 mmol), $LiPF_6$ (28 mg, 0.18 mmol), methanesulfonic acid (6.7 µL, 0.074 mmol) and allyltributyl stannane (0.23 mL, 0.74 mmol) in dichloroethane (3.7 mL) afforded compound **8m** (10 mg, 12%) as colorless oil after purification by flash column chromatography on silica gel (ether/n-hexane = 1:50). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.2 Hz, 1H), 6.89 (dd, J = 8.2, 2.1 Hz, 1H), 6.84 (d, J = 2.0 Hz, 1H), 5.94–5.83 (m, 1H), 5.16–5.08 (m, 2H), 4.81 (dd, J = 7.7, 3.3 Hz, 1H), 4.18–4.13 (m, 1H), 3.78–3.72 (m, 1H), 3.00–2.93 (m, 1H), 2.71–2.53 (m,

3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 169.7, 148.8, 139.1, 134.7, 131.8, 130.0, 119.8, 117.9, 117.3, 75.5, 63.5, 40.2, 28.6, 21.2. HRMS (ESI) calcd for $C_{14}H_{16}NaO_3$ $[M+Na]^+$ 255.0996, found 255.0995.

4-Allyl-1,4-dihydro-2*H*-benzo[f]isochromene (8p) and 1,2-dihydro-4*H*-benzo [f]isochromen-4-one (8p′). Following the same procedure used for the synthesis of **8a**, the reaction of isochroman **6p** (68.6 mg, 0.37 mmol), DDQ (17 mg, 0.074 mol), TBN (8.86 µL, 0.074 mmol), $LiPF_6$ (28 mg, 0.18 mmol), methanesulfonic acid (6.7 µL, 0.074 mmol) and allyltributyl stannane (0.23 mL, 0.74 mmol) in dichloroethane (3.7 mL) afforded compound **8p** (72 mg, 86%) as colorless oil after purification by flash column chromatography on silica gel (ether/n-hexane = 1:50) along with lactone **8p'** (5.9 mg, 8%).

8p: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.3 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 8.5 Hz, 1H), 7.54 (td, J = 11.9, 1.2 Hz, 1H), 7.49 (d, J = 7.4, 1.0 Hz, 1H), 7.24 (d, J = 8.6 Hz, 1H), 5.97–5.87 (m, 1H), 5.17 (dd, J = 17.2, 1.7 Hz, 1H), 5.09 (d, J = 10.2 Hz, 1H), 5.0–4.9 (m, 1H), 4.37–4.32 (m, 1H), 3.95–3.89 (m, 1H), 3.28–3.20 (m, 1H), 3.13–3.07 (m, 1H), 2.83–2.77 (m, 1H), 2.69–2.62 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 135.0, 134.8, 132.1, 132.0, 129.5, 128.5, 126.4, 125.6, 123.2, 122.9, 117.1, 75.8, 63.0, 40.3, 25.7. HRMS (ESI) calcd for $C_{16}H_{16}NaO$ $[M+Na]^+$ 247.1098, found 247.1092.

8p′: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.6 Hz, 1H), 8.04-8.02 (s, 1H), 7.92-7.90 (m, 1H), 7.84 (d, J = 8.6 Hz, 1H), 7.67-7.60 (m, 2H), 4.68 (t, J = 6.1 Hz, 2H), 3.45 (t, J = 6.1 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 165.4, 138.5, 135.6, 129.8, 128.9, 128.6, 127.7, 127.2, 125.2, 124.3, 122.4, 66.6, 24.2.

1-Allyl-7-(*p*-tolyl)isochroman (8q) and 7-(p-tolyl)isochroman-1-one (8q′). Following the same procedure used for the synthesis of **8a**, the reaction of isochroman **6q** (83.6 mg, 0.37 mmol), DDQ (17 mg, 0.074 mol), TBN (8.86 µL, 0.074 mmol), $LiPF_6$ (28 mg, 0.18 mmol), methanesulfonic acid (6.7 µL, 0.074 mmol) and allyltributyl stannane (0.23 mL, 0.74 mmol)

in dichloroethane (3.7 mL) afforded compound **8q** (48.2 mg, 57%) as colorless oil after purification by flash column chromatography on silica gel (ether/n-hexane = 1:50) along with lactone **8q'** (19 mg, 21%).

8q: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.1 Hz, 2H), 7.39 (dd, J = 7.9, 1.4 Hz, 1H), 7.31 (s, 1H), 7.25 (dd, J = 8.7, 0.8 Hz, 2H), 7.18 (d, J = 7.9 Hz, 1H), 6.00-5.90 (m, 1H), 5.20-5.09 (m, 2H), 4.90 (dd, J = 8.0, 3.5 Hz, 1H), 4.22-4.17 (m, 1H), 3.84-3.78 (m, 1H), 3.07-2.99 (m, 1H), 2.82-2.61 (m, 3H), 2.40 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 138.4, 138.2, 137.2, 135.2, 129.6, 129.4, 127.0, 125.2, 123.5, 75.8, 63.5, 40.6, 28.9, 21.2. HRMS-ESI (m/z): $[M+Na]^+$ calcd. for $C_{19}H_{20}NaO$ 287.1406, found 287.1409.

8q′: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 1.9 Hz, 1H), 7.76 (dd, J = 7.9, 2.0 Hz, 1H), 7.52-7.50 (m, 2H), 7.32 (dd, J = 7.9, 0.4 Hz, 1H), 7.27-7.25 (m, 2H), 4.57 (t, J = 6.0 Hz, 2H), 3.09 (t, J = 6.0 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 165.2, 140.8, 137.9, 137.8, 136.5, 132.0, 129.6, 128.5, 127.7, 126.8, 125.6, 67.3, 27.5, 21.1.

1-Allyl-7-(4-(trifluoromethoxy)phenyl)isochroman (8r) and 7-(4-(trifluoromethoxy) phenyl)isochroman-1-one (8r′). Following the same procedure used for the synthesis of **8a**, the reaction of isochroman **6r** (109.6 mg, 0.37 mmol), DDQ (17 mg, 0.074 mol), TBN (8.86 µL, 0.074 mmol), $LiPF_6$ (28 mg, 0.18 mmol), methanesulfonic acid (6.7 µL, 0.074 mmol) and allyltributyl stannane (0.23 mL, 0.74 mmol) in dichloroethane (3.7 mL) afforded compound **8r** (39.7 mg, 40%) as colorless oil after purification by flash column chromatography on silica gel (ether/n-hexane = 1:50) along with lactone **8r'** (20 mg, 17%).

8r: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.6 Hz, 2H), 7.33 (d, J = 7.7 Hz, 1H), 7.25 (d, J = 7.7 Hz, 2H), 7.17 (d, J = 7.9 Hz, 1H), 5.97-5.87 (m, 1H), 5.17-5.08 (m, 2H), 4.87 (d, 4 J = 4.6 Hz, 1H), 4.20-4.15 (m, 1H), 3.81-3.75 (m, 1H), 3.05-2.99 (m, 1H), 2.77-2.59 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 140.0, 138.5, 137.9, 135.0, 133.9, 129.6, 128.5, 125.3, 123.7,

121.4, 119.4, 117.3, 75.7, 63.4, 40.5, 28.9. HRMS-ESI (m/z): $[M+Na]^+$ calcd. for $C_{19}H_{17}F_3NaO_2$ 357.1073, found 357.1072.

8r': ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 1.8 Hz, 1H), 7.74 (dd, J = 7.9, 2.0 Hz, 1H), 7.63-7.61 (m, 2H), 7.36 (dd, J = 7.9, 0.5 Hz, 1H), 7.31-7.29 (m, 2H), 4.58 (t, J = 6.0 Hz, 2H), 3.11 (t, J = 6.0 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 164.9, 149.1, 139.5, 138.7, 138.2, 132.0, 128.7, 128.4, 127.9, 125.8, 121.4, 67.3, 27.5.

1-Allyl-1,3-dihydroisobenzofuran (8s).[2] Following the same procedure used for the synthesis of **8a**, the reaction of isochroman **6q** (44.8 mg, 0.37 mmol), DDQ (17 mg, 0.074 mol), TBN (8.86 µL, 0.074 mmol), $LiPF_6$ (28 mg, 0.18 mmol), methanesulfonic acid (6.7 µL, 0.074 mmol) and allyltributyl stannane (0.23 mL, 0.37 mmol) in dichloroethane (3.7 mL) afforded compound **8q** (17.9 mg, 30%) as colorless oil after purification by flash column chromatography on silica gel (ether/n-hexane = 1:50). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.28–7.18 (m, 2H), 5.92–5.82 (m, 1H), 5.31–5.28 (m, 1H), 5.18–5.17 (m, 0.5H), 5.15–5.10 (m, 2H), 5.09–5.08 (m, 0.5H), 5.07–5.04 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.6, 139.5, 134.2, 127.5, 127.2, 121.4, 121.0, 117.7, 83.3, 72.7, 40.8.

7-Allyl-4,7-dihydro-5H-thieno[2,3-c]pyran (8t). Following the same procedure used for the synthesis of **8a**, the reaction of isochroman **6s** (52.2 mg, 0.37 mmol), DDQ (17 mg, 0.074 mol), TBN (8.86 µL, 0.074 mmol), $LiPF_6$ (28 mg, 0.18 mmol), methanesulfonic acid (6.7 µL, 0.074 mmol) and allyltributyl stannane (0.23 mL, 0.74 mmol) in dichloroethane (3.7 mL) afforded compound **8s** (19.5 mg, 29%) as yellow oil after purification by flash column chromatography on silica gel (ether/*n*-hexane = 1:50). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J = 5.0 Hz, 1H), 6.81 (d, J = 5.0 Hz, 1H), 5.98–5.88 (m, 1H), 5.22–5.13 (m, 2H), 4.85 (td, J = 4.6, 2.1 Hz, 1H), 4.23 (qd, J = 5.7, 2.0 Hz, 1H), 3.76 (td, J = 14.0, 7.8 Hz, 1H), 2.92–2.83 (m, 1H), 2.67–2.52 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 134.7, 134.0, 133.6, 127.1, 122.7, 117.8, 74.7, 64.5, 41.4, 26.2. HRMS (ESI) calcd for $C_{10}H_{12}NaOS$ $[M+Na]^+$ 203.0506, found 203.0504.

***tert*-Butyl 4-(4-fluorophenyl)piperazine-1-carboxylate (15a).**[3] A solution of 1-bromo-4-fluorobenzene **14** (0.57 mmol), N-Boc-piperazine **13** (0.85 mmol), sodium tert-butoxide (1.66 mmol), tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$, 0.017 mmol), and 2-dicyclohexylphosphino-2',6'-diisopropoxy-1,1'-biphenyl (0.05 mmol) in toluene (1.0 mL) was stirred at 105°C for 4 hours. After the reaction was completed, the mixture was diluted with ethyl acetate and washed with water and saturated aqueous NaCl. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude residue was then purified by column chromatography on silica gel (*n*-hexane/EtOAc = 10:1) to afford the desired compound **15a** (0.17 g, quant) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96-6.92 (m, 2H), 6.87-6.83 (m, 2H), 3.55 (t, J = 5.1 Hz, 4H), 3.01 (t, J = 5.1 Hz, 4H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5 (d, ^1J = 238 Hz), 154.6, 148.0 (d, ^4J = 2 Hz), 118.5 (d, ^3J = 8 Hz), 115.6 (d, ^2J = 22 Hz), 79.8, 50.4, 28.4. LRMS (ESI) calcd for $C_{15}H_{22}FN_2O_2$ $[M+H]^+$ 281.2, found 281.1.

1-(4-Fluorophenyl)piperazine (15). A solution of *tert*-butyl 4-(4-fluorophenyl)piperazine-1-carboxylate **15a** (0.17 mmol) was added to HCl (2.0 M in diethyl ether, 0.8 mL) and the reaction mixture was stirred for 23 hours at room temperature. After completion, the mixture was washed with a small amount of methanol and excess diethyl ether to obtain a white solid. The product was then washed with 2M NaOH and extracted with EtOAc. The organic layer was dried over $MgSO_4$, evaporated under reduced pressure, and 1-(4-fluorophenyl)piperazine **15** was obtained without further purification as yellow liquid in 68% yield. R_f = 0.11 (DCM:MeOH = 2:1). ^{1}H NMR (400 MHz, MeOH-d_4) HCl salt form. δ 7.42-7.39 (m, 2H), 7.17-7.12 (m, 2H), 3.64 (dd, J = 6.9, 3.5 Hz, 4H), 3.57 (dd, J = 6.8, 3.4 Hz, 4H), 3.26 (m, 1H). ^{13}C NMR (100 MHz, MeOH-d_4) δ 160.3 (d, ^1J = 243 Hz), 142.5, 121.0 (d, ^3J = 8 Hz), 116.1 (d, ^2J = 23 Hz), 115.6 (d, ^2J = 22 Hz), 49.3, 42.4. LRMS (ESI) calcd for $C_{10}H_{14}FN_2$ $[M+H]^+$ 181.1, found 181.1.

2-(6,7-Dimethoxyisochroman-1-yl)acetaldehyde (16).[4] To a solution of 1-allyl-6,7-dimethoxyisochromane **8g** (15.0 mg, 0.064 mmol) in a 4:1 mixture of dioxane and water (1.0 mL) were added 2,6-lutidine (37.0 μL, 0.32 mmol), OsO_4 (40 μL, 4% solution in H_2O), and $NaIO_4$ (68.0 mg, 0.32 mmol) sequentially at 35°C. The mixture was stirred for 22 hours. Once the reaction was completed, the dioxane was removed under reduced pressure and the remaining aqueous layer was extracted with DCM. The combined organic layer was washed with 1 N HCl to remove excess 2,6-lutidine, followed by treatment with brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude residue was then purified by column chromatography on silica gel (n-hexane/EtOAc = 2:1) to afford aldehyde **16** (9.8 mg, 65%) as clear oil. R_f = 0.42 (n-hexane/EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (t, J = 2.4 Hz, 1H), 6.61 (s, 1H), 6.49 (s, 1H), 5.22 (t, J = 5.8 Hz, 1H), 4.13 (m, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 3.78 (m, 1H), 2.94 (m, 1H), 2.87 (dd, J = 5.8, 2.4 Hz, 2H), 2.61 (dt, J = 16.0, 3.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5, 148.0, 147.7, 127.9, 126.1, 111.7, 107.4, 71.4, 63.7, 56.0, 55.9, 49.5, 28.3. LRMS (ESI) calcd for $C_{13}H_{17}O_4$ $[M+H]^+$ 237.1, found 237.1.

1-(2-(6,7-Dimethoxyisochroman-1-yl)ethyl)-4-(4-fluorophenyl)piperazine (2).[5] To a solution of 2-(6,7-dimethoxyisochroman-1-yl)acetaldehyde **16** (5.0 mg, 0.021 mmol) in DCM (0.2 mL), 1-(4-fluorophenyl)piperazine **15** (4.5 mg, 0.025 mmol) and $NaBH(OAc)_3$ (6.0 mg, 0.028 mmol) were added, and the mixture was stirred at room temperature for 2 hours. Once the reaction was completed, the aqueous layer was extracted with DCM. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude residue was then purified by column chromatography on silica gel (EtOAc Only) to afford compound **2** (5.8 mg, 68%) as yellowish oil. R_f = 0.43 (n-hexane/EtOAc = 1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97-6.93 (m, 2H), 6.88-6.85 (m, 2H), 6.59 (d, J = 3.2 Hz, 2H), 4.78 (d, J = 6.2 Hz, 1H), 4.11 (m, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.74 (m, 1H), 3.15 (t, J = 4.8, 4H), 2.90

(m, 1H), 2.68-2.57 (m, 7H), 2.16-2.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2 (d, ^1J = 245 Hz), 147.9, 147.6, 147.5, 129.7, 125.9, 117.9 (d, ^3J = 8 Hz), 115.5 (d, ^2J = 22 Hz), 111.5, 107.7, 74.4, 63.2, 56.0, 55.8, 54.9, 53.3, 50.0, 33.2, 28.5. ^{19}F NMR (400 MHz, $CDCl_3$) δ -124.6. LRMS (ESI) calcd for $C_{23}H_{30}FN_2O_3$ $[M+H]^+$ 401.2, found 401.2.

II. Spectral Data

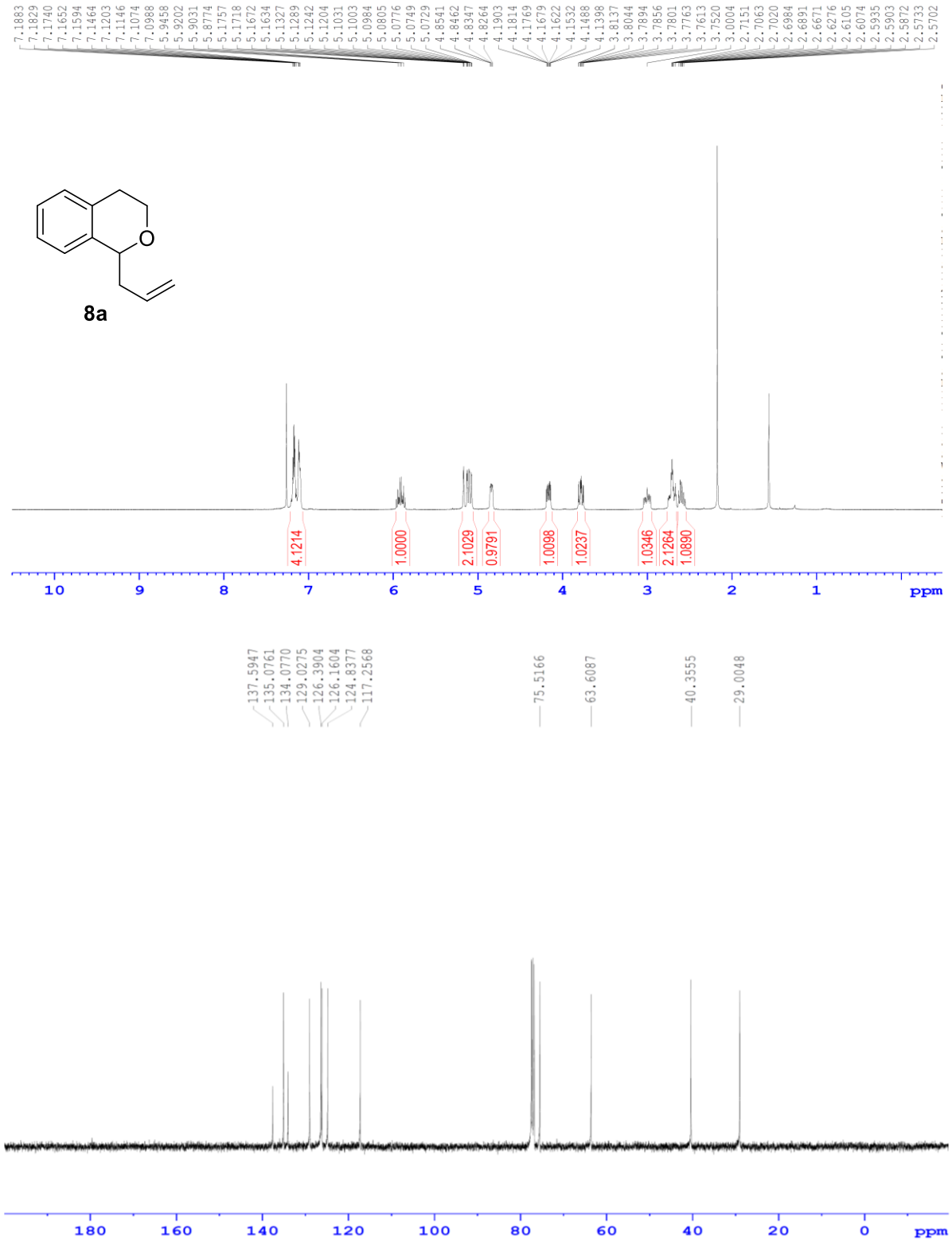


Figure S1. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8a** in $CDCl_3$.

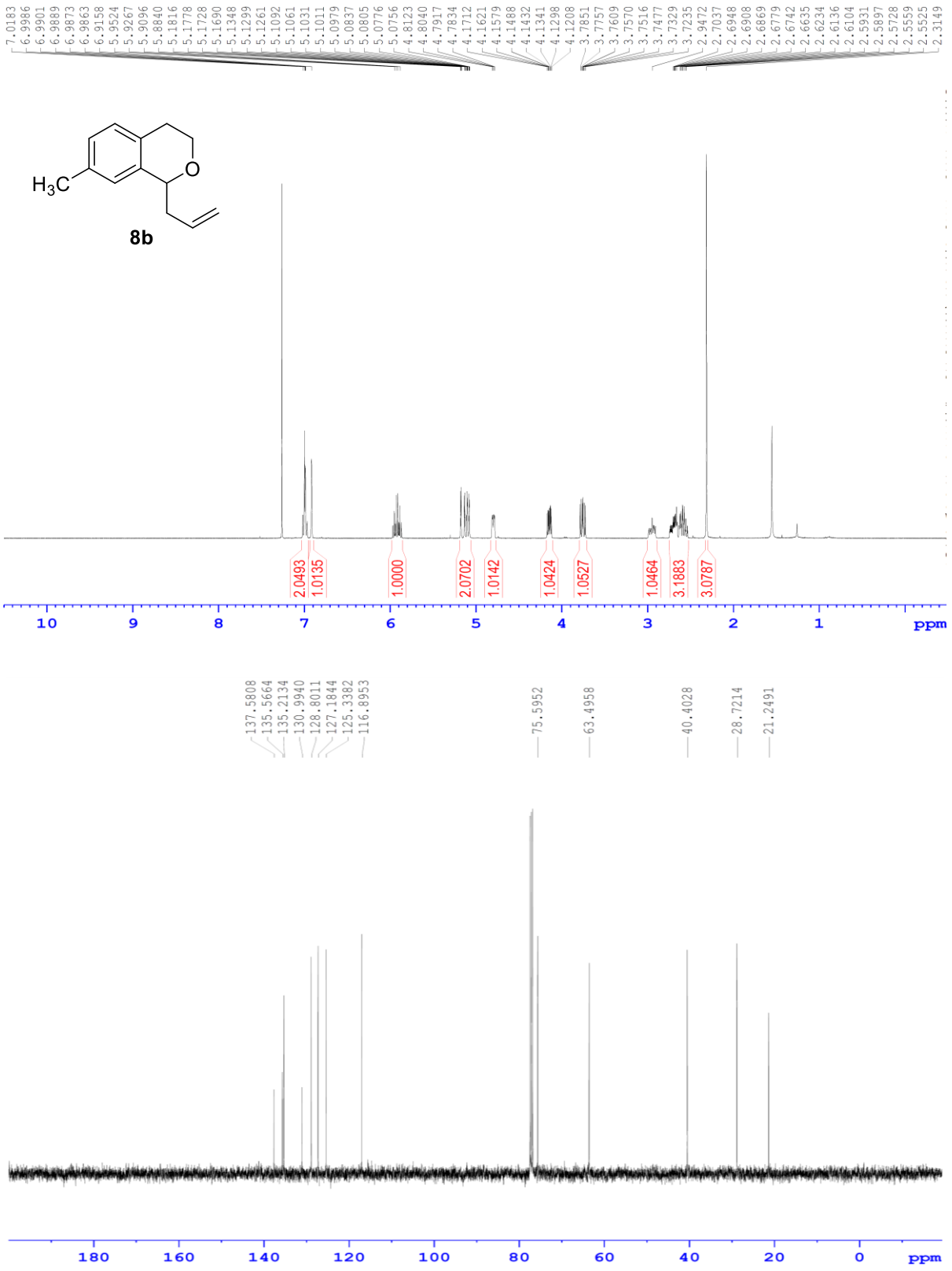


Figure S2. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8b** in $CDCl_3$.

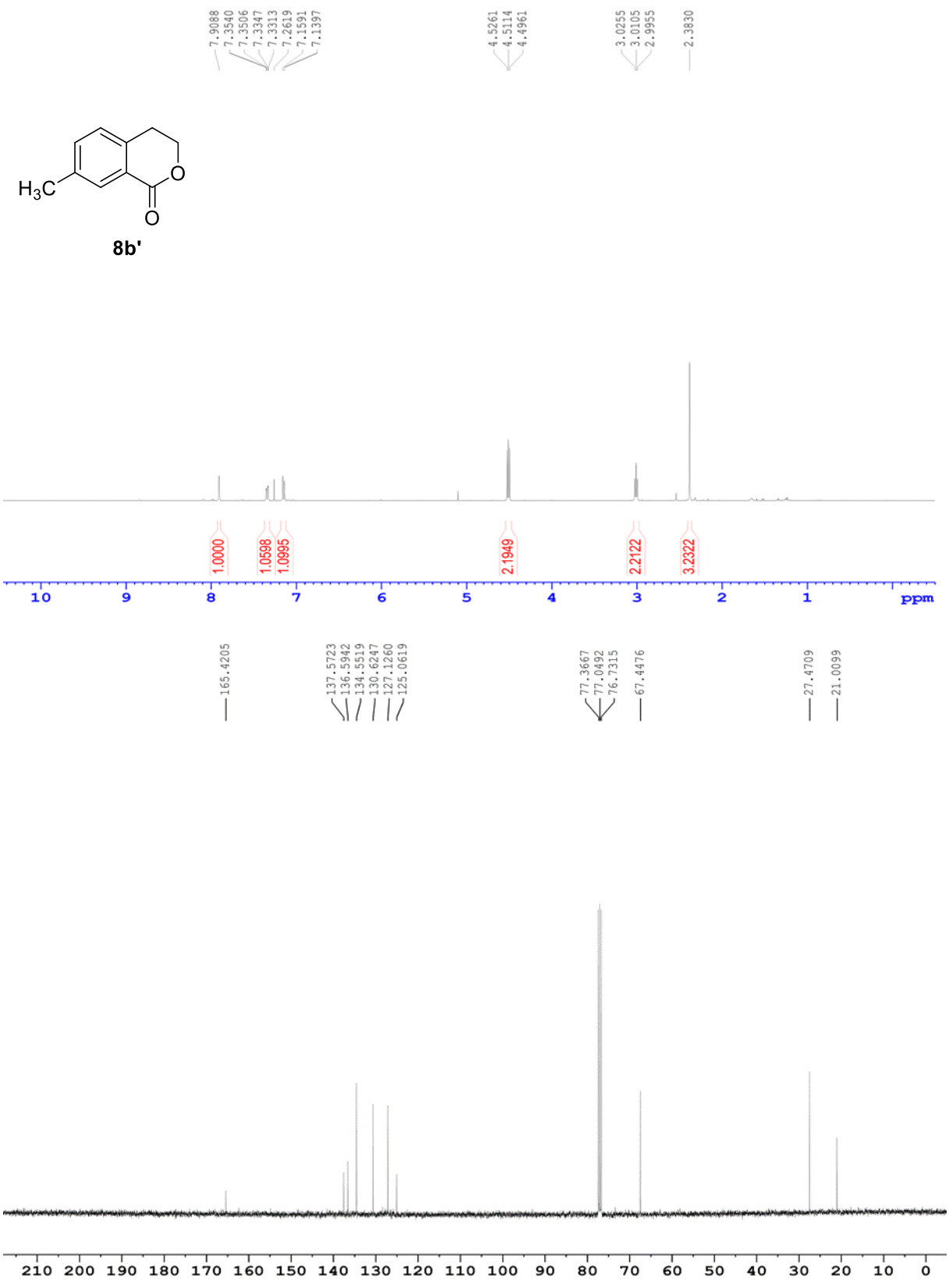


Figure S3. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8b′** in $CDCl_3$.

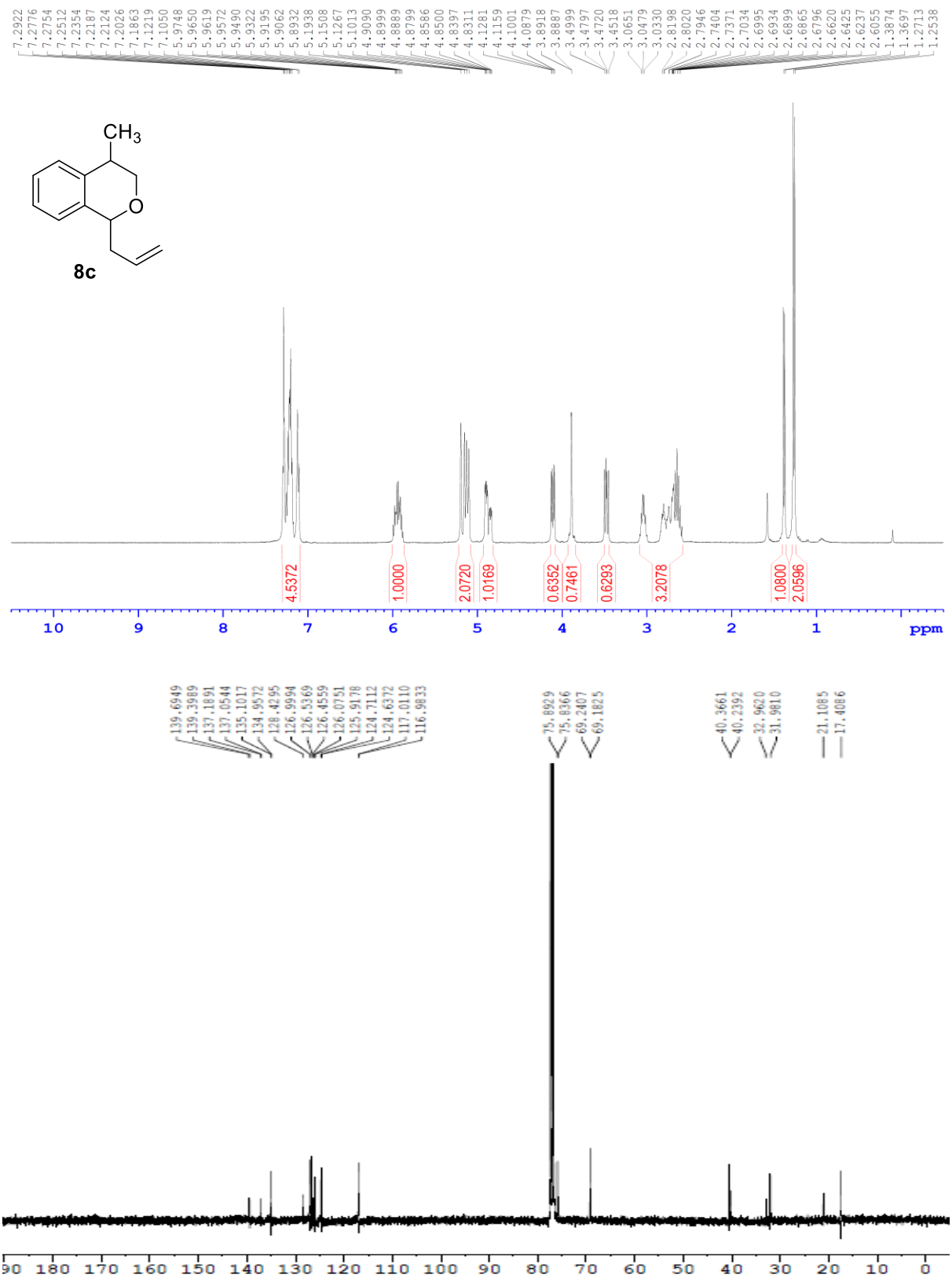


Figure S4. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8c** in $CDCl_3$.

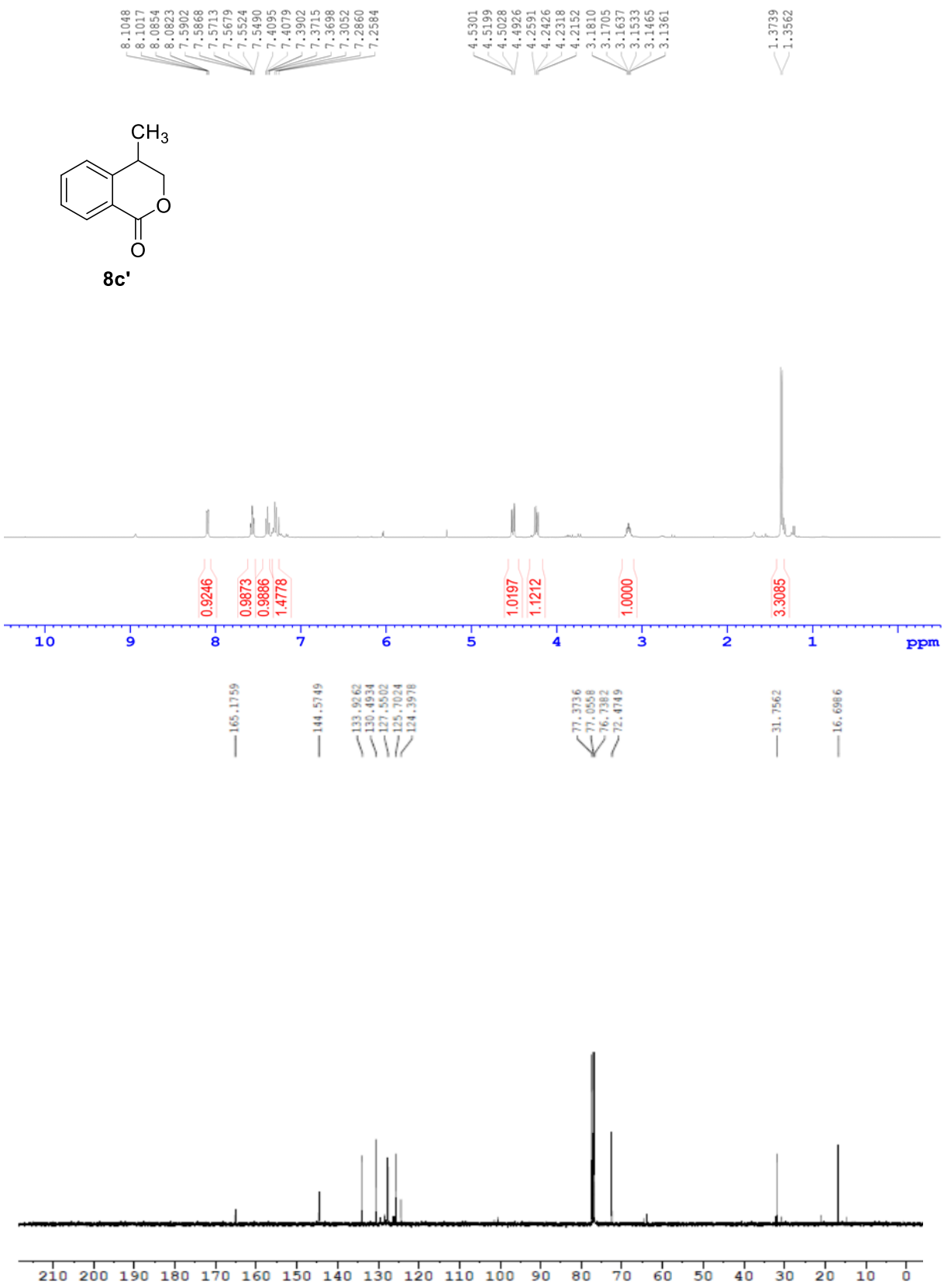


Figure S5. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8c′** in $CDCl_3$.

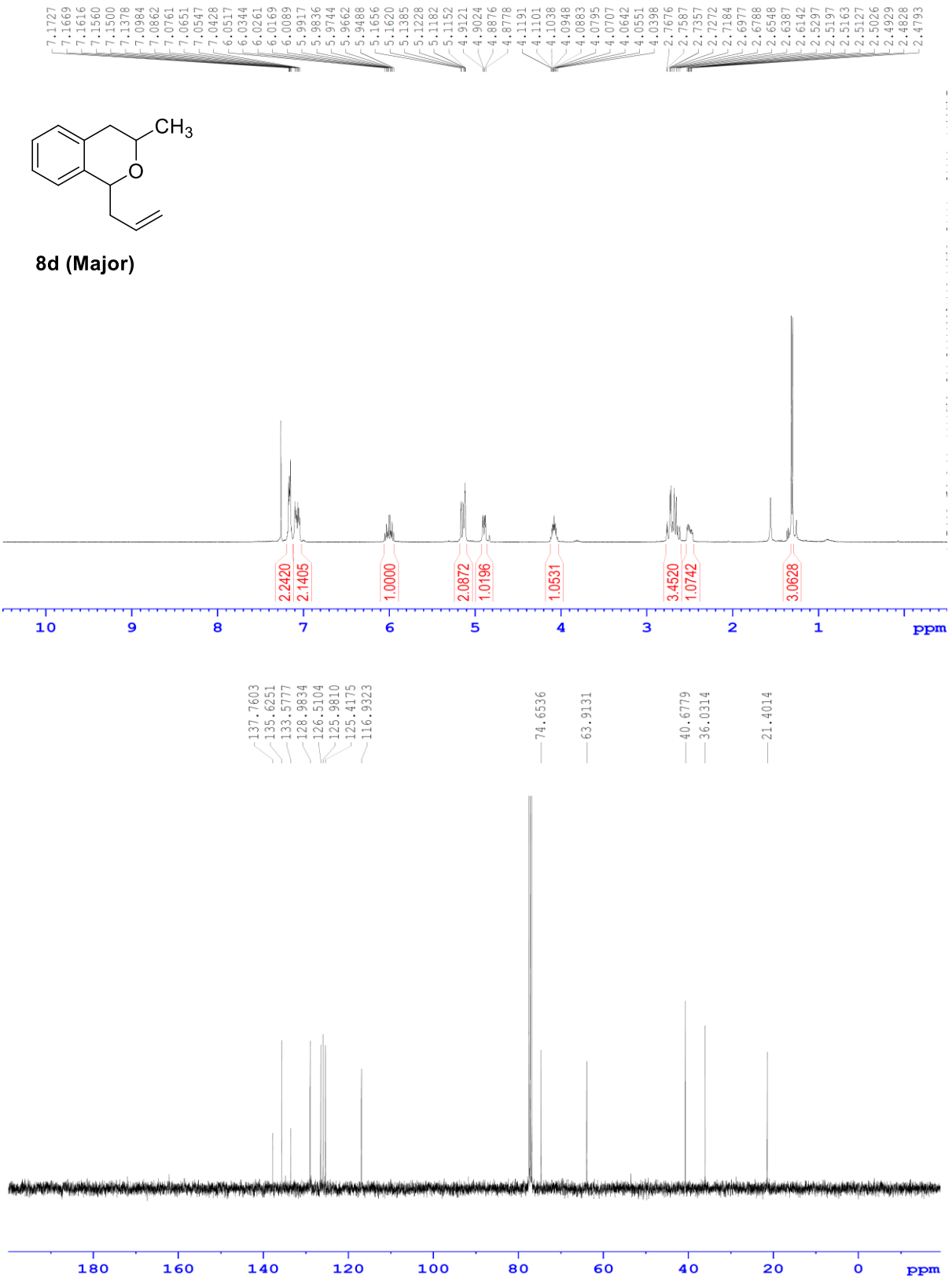


Figure S6. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8d** in $CDCl_3$.

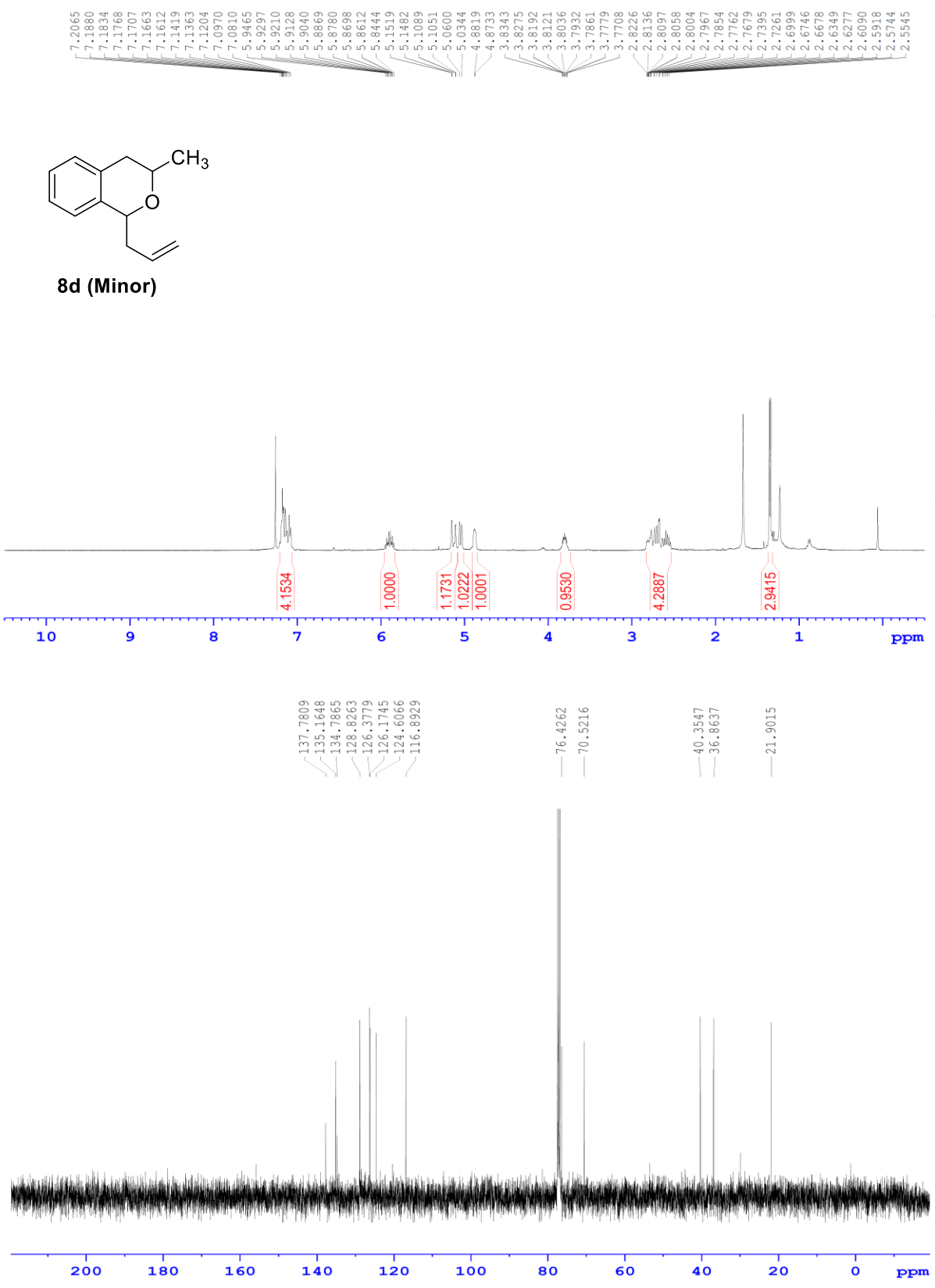


Figure S7. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8d** in $CDCl_3$.

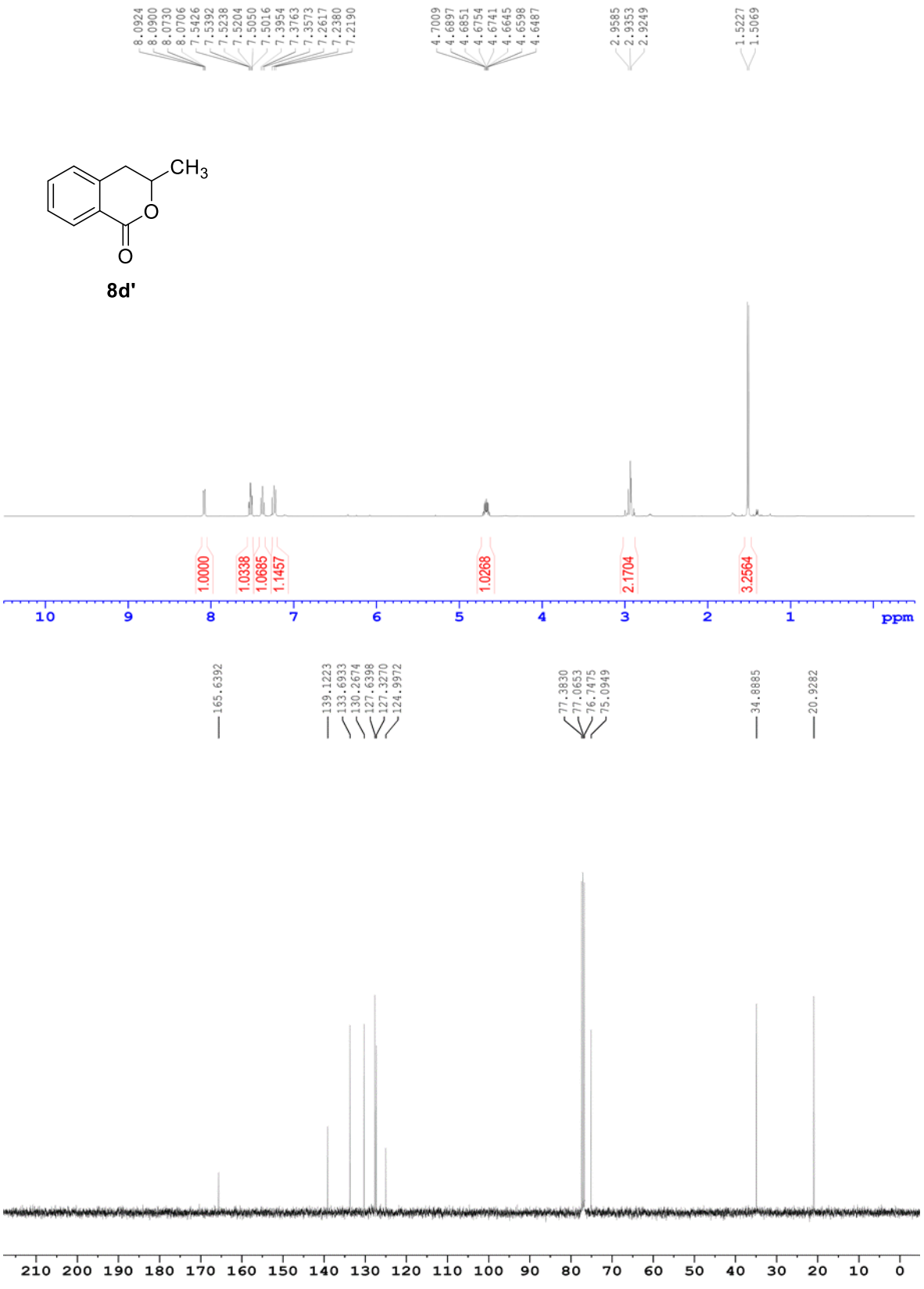


Figure S8. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8d′** in $CDCl_3$.

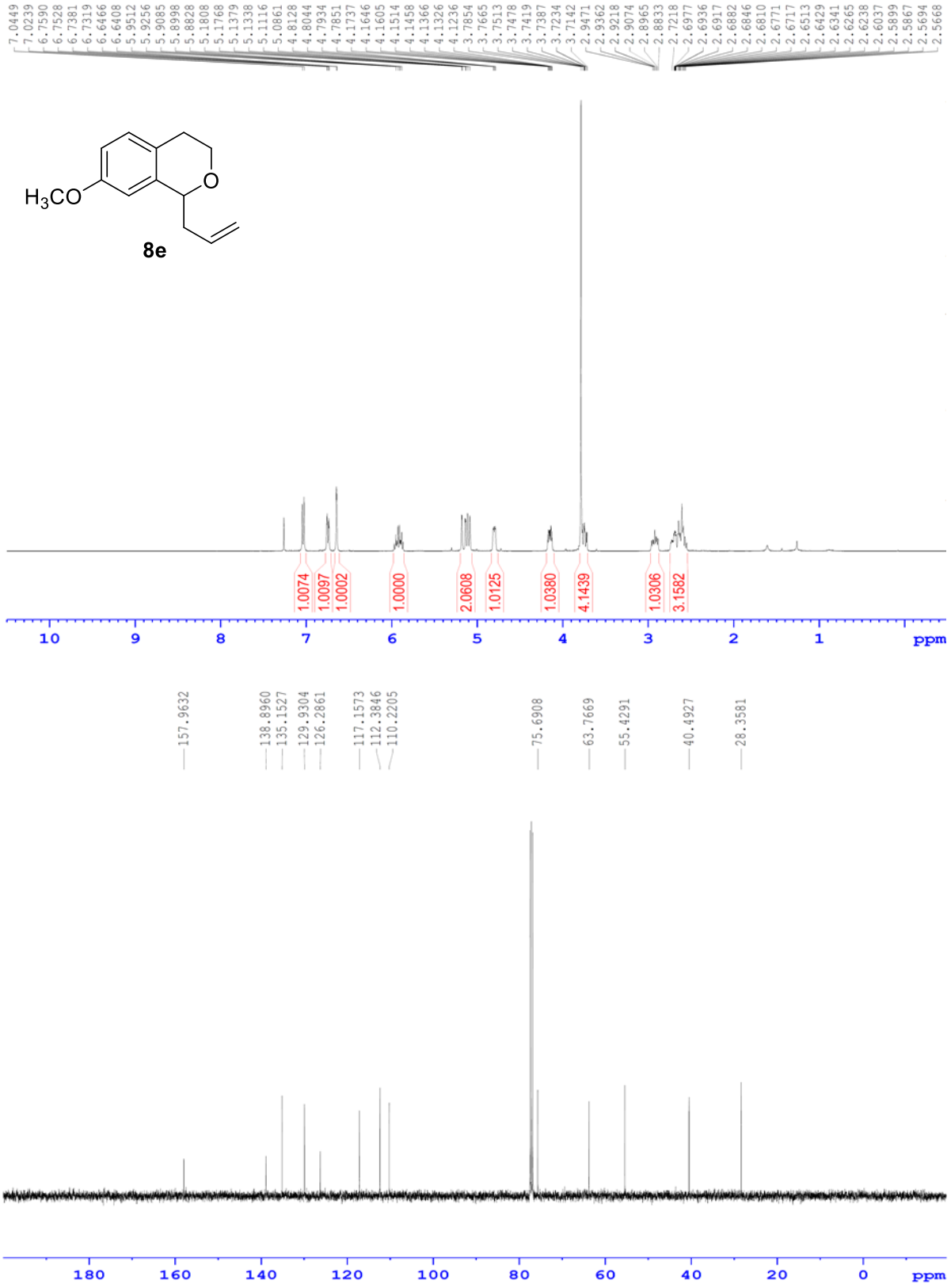


Figure S9. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8e** in $CDCl_3$.

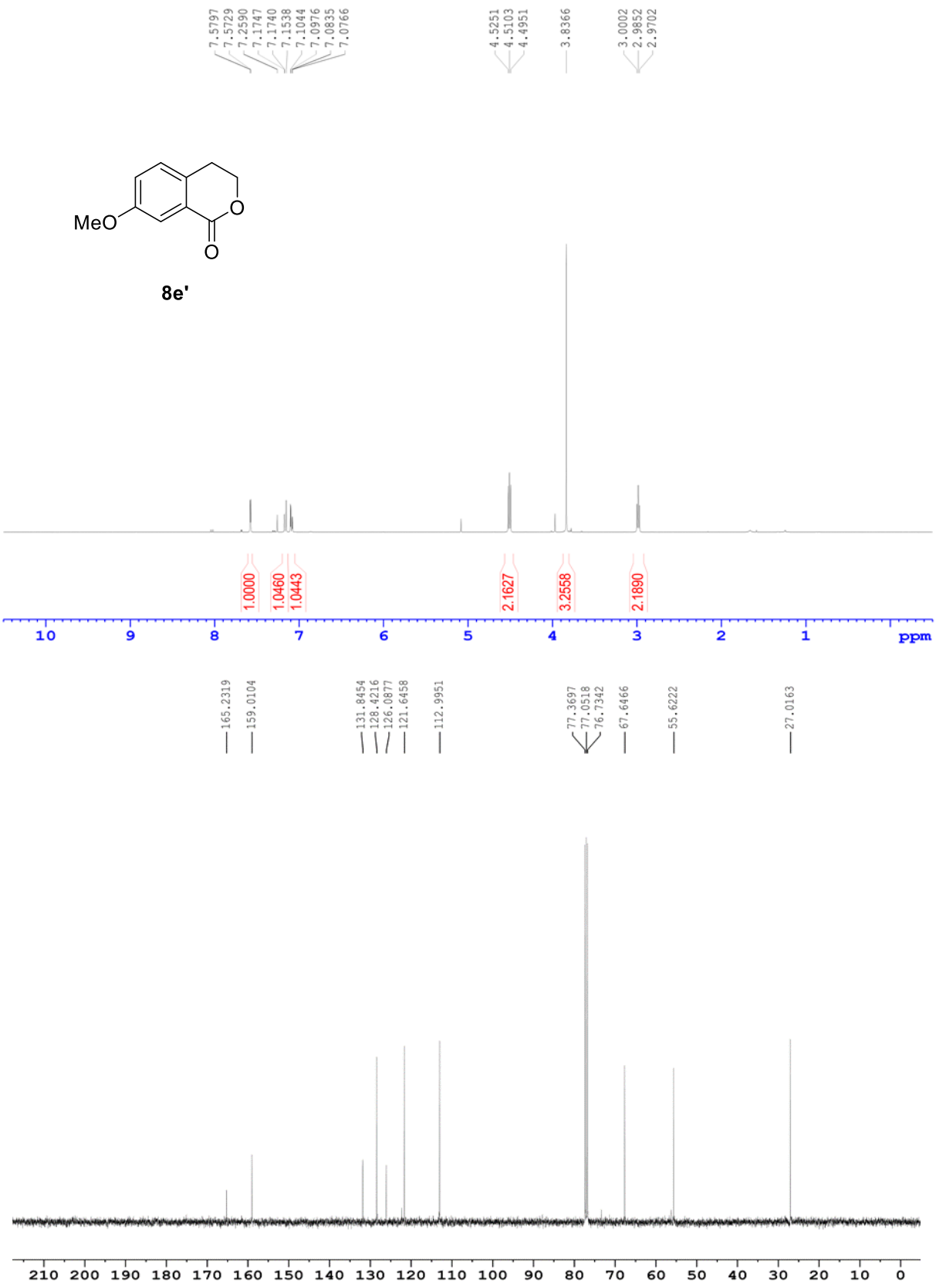


Figure S10. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8e′** in $CDCl_3$.

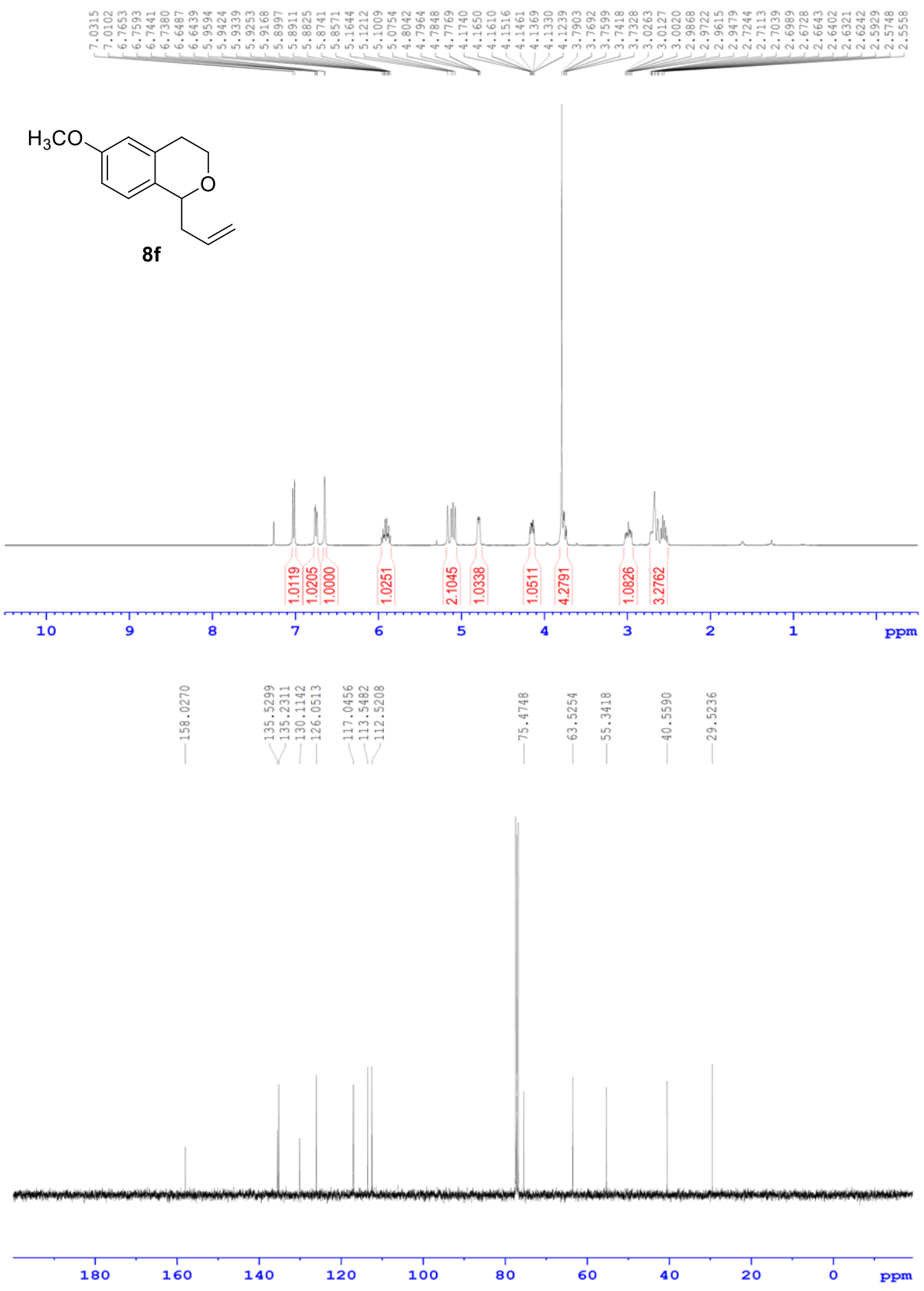


Figure S11. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8f** in $CDCl_3$.

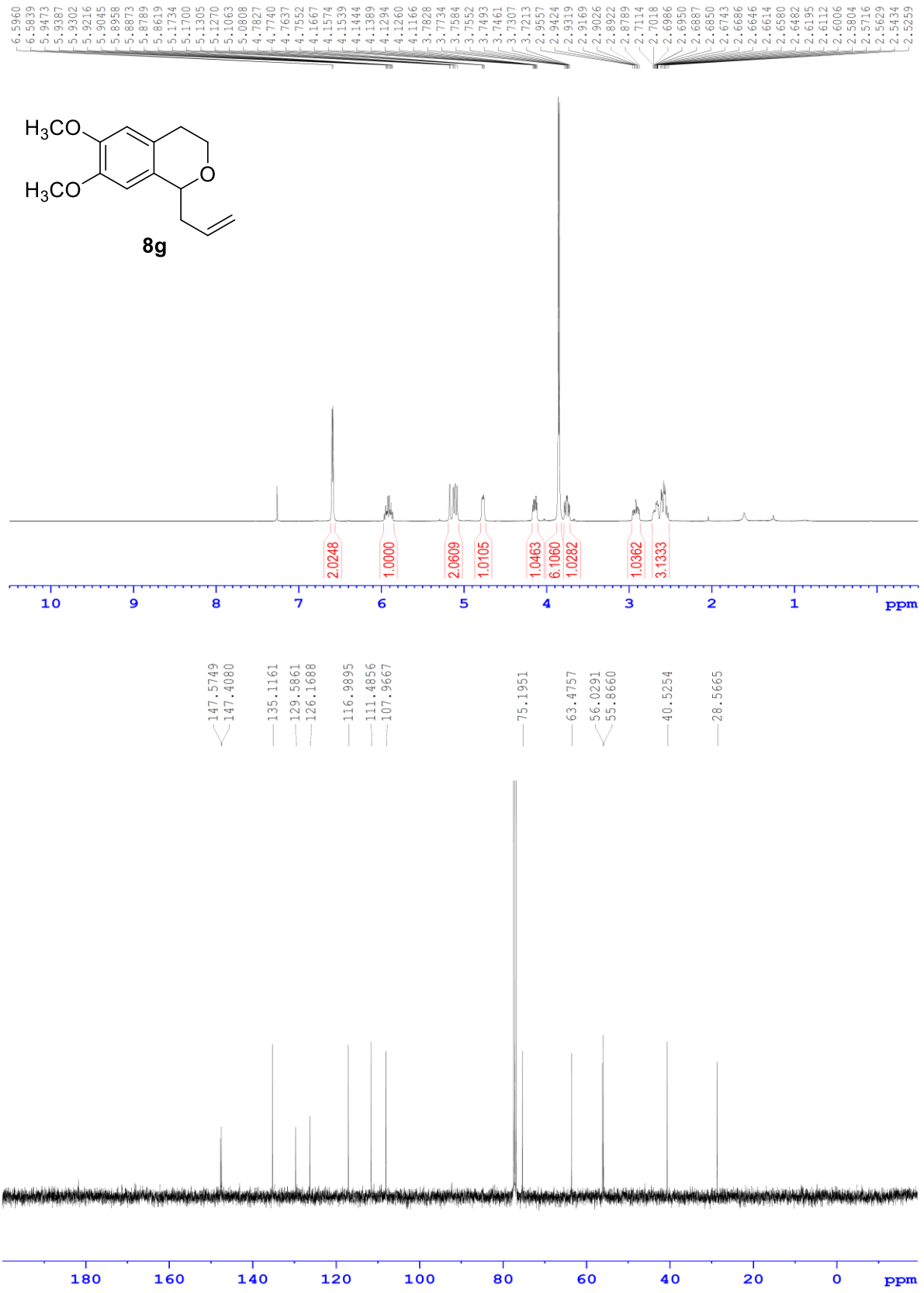


Figure S12. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8g** in $CDCl_3$.

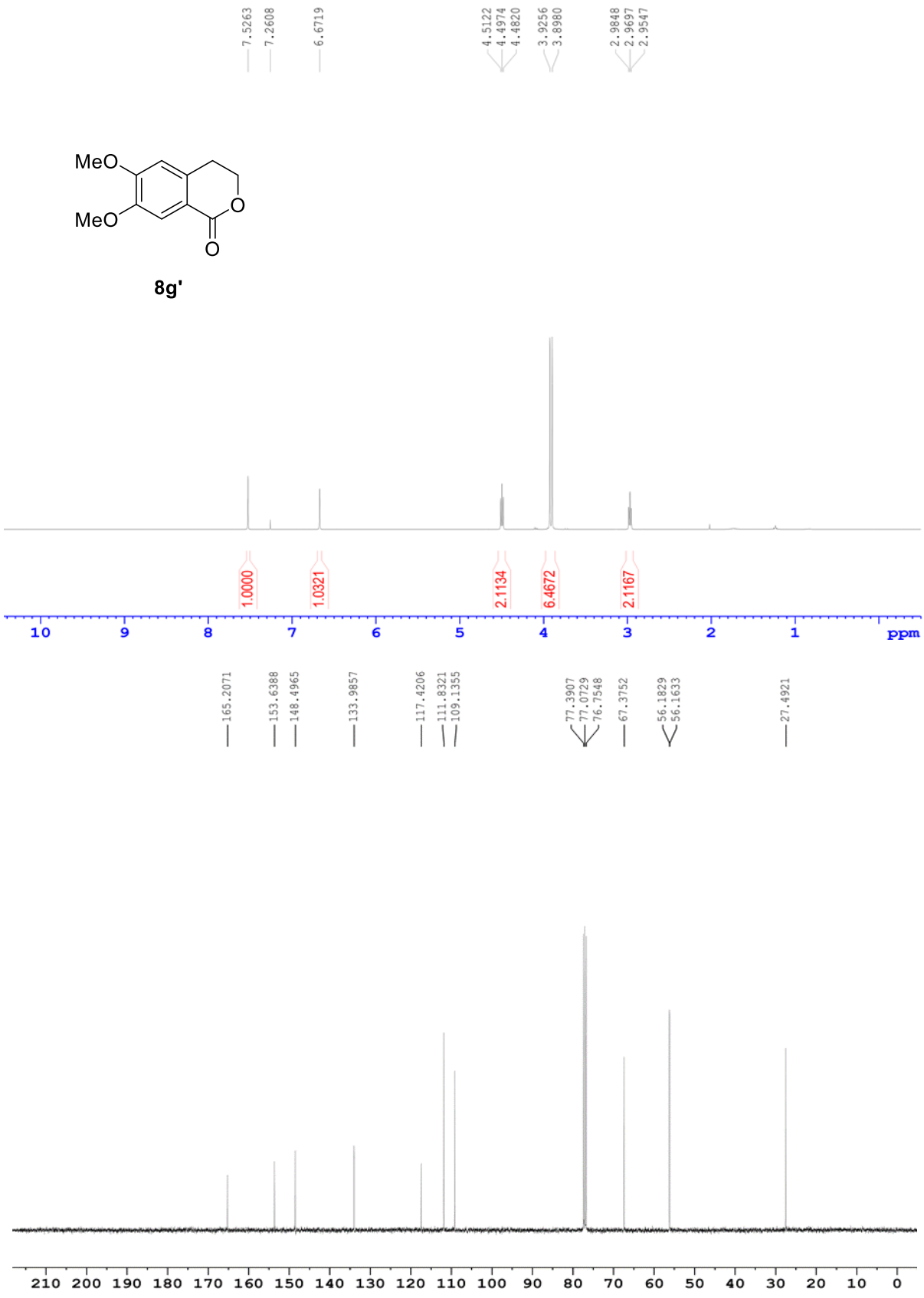


Figure S13. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8g′** in $CDCl_3$

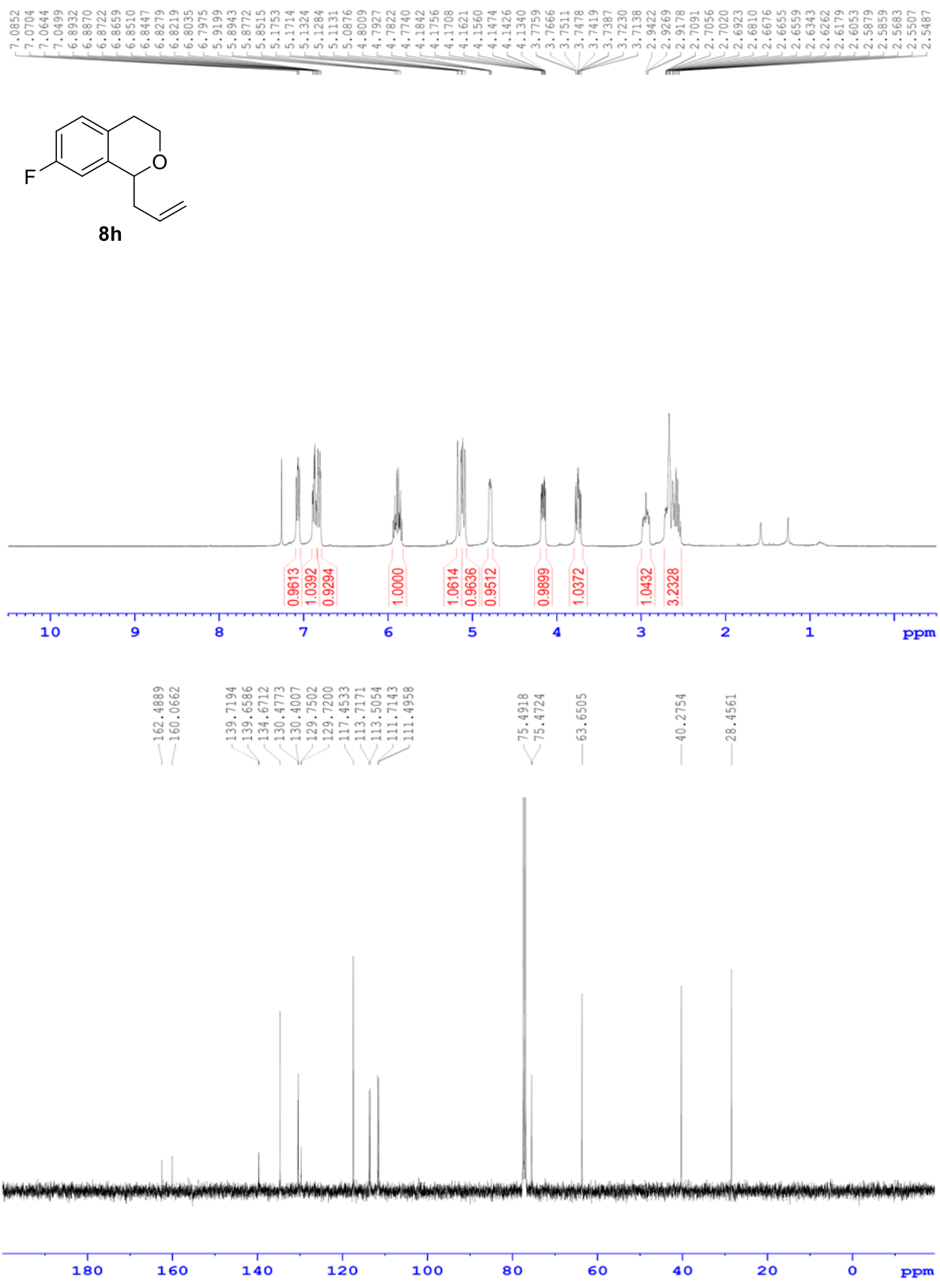


Figure S14. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8h** in $CDCl_3$.

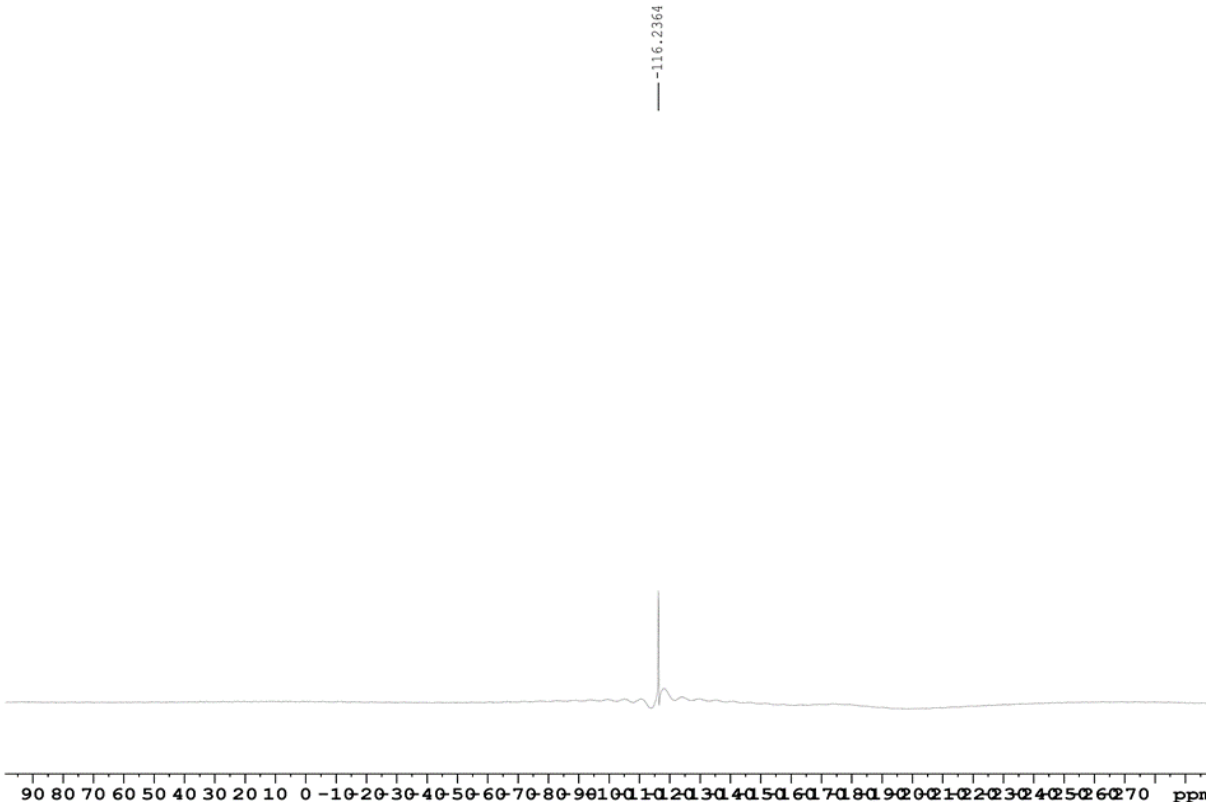


Figure S15. 376 MHz ^{19}F NMR spectrum of **8h** in $CDCl_3$.

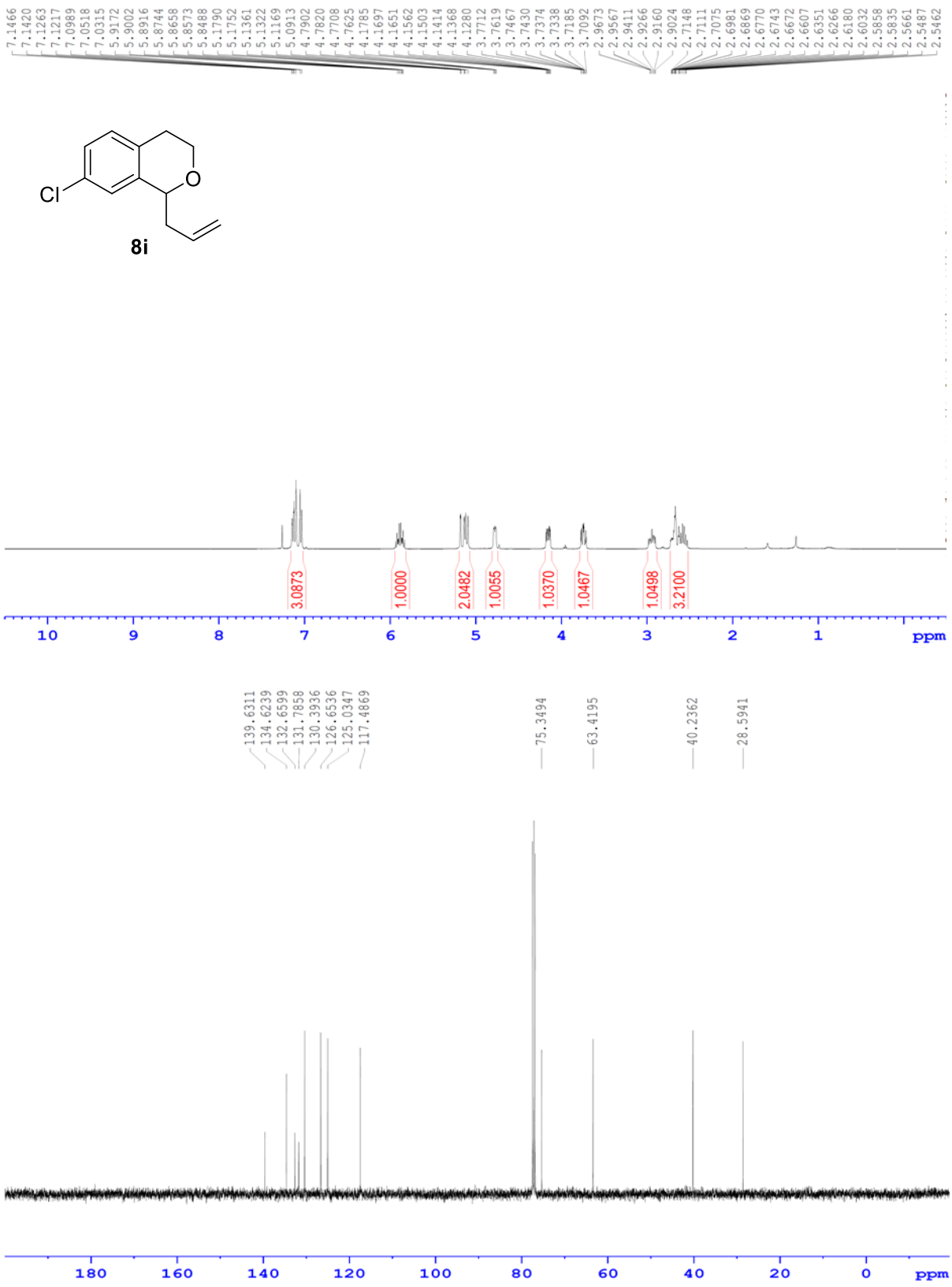


Figure S16. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8i** in $CDCl_3$.

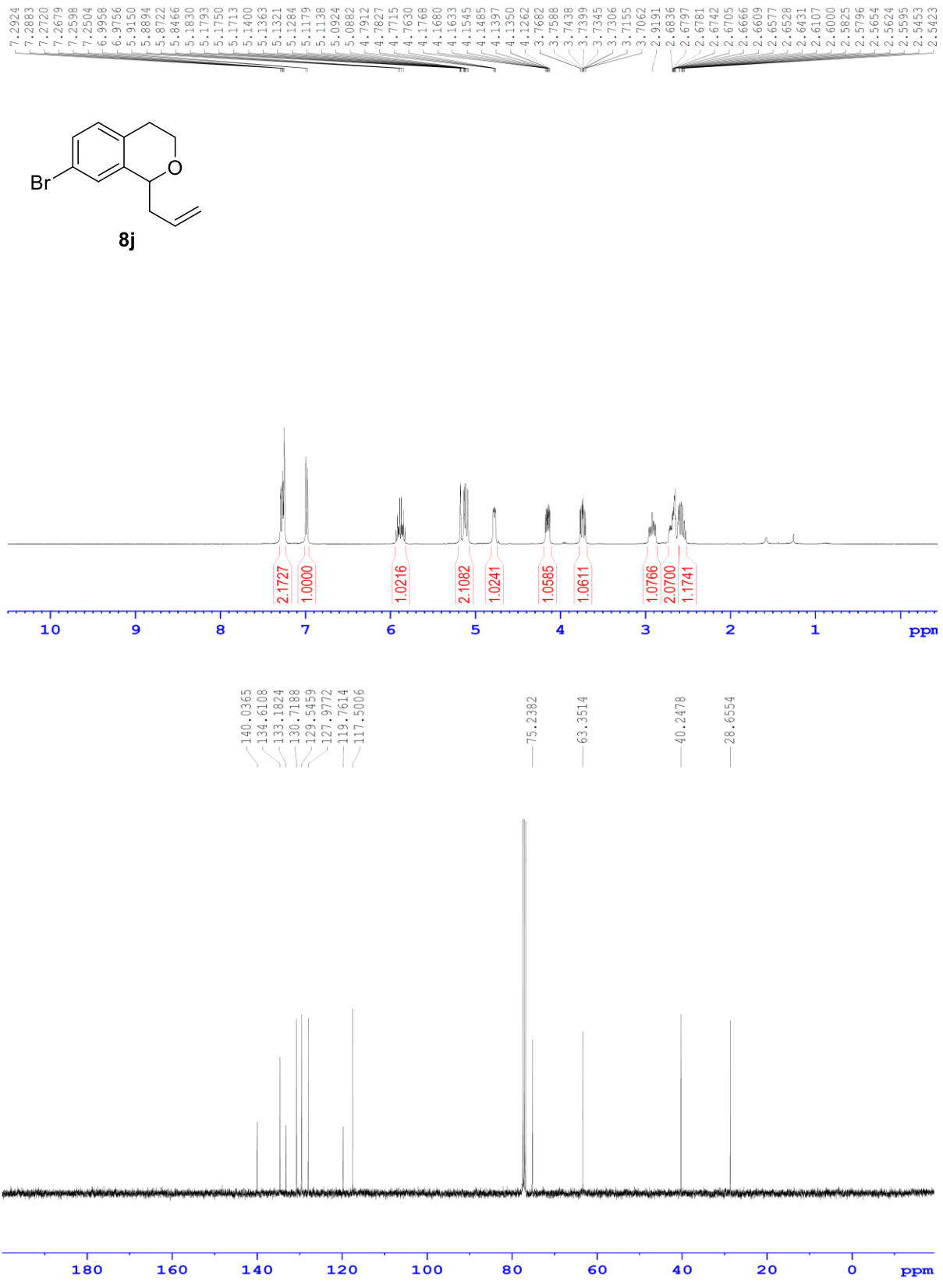
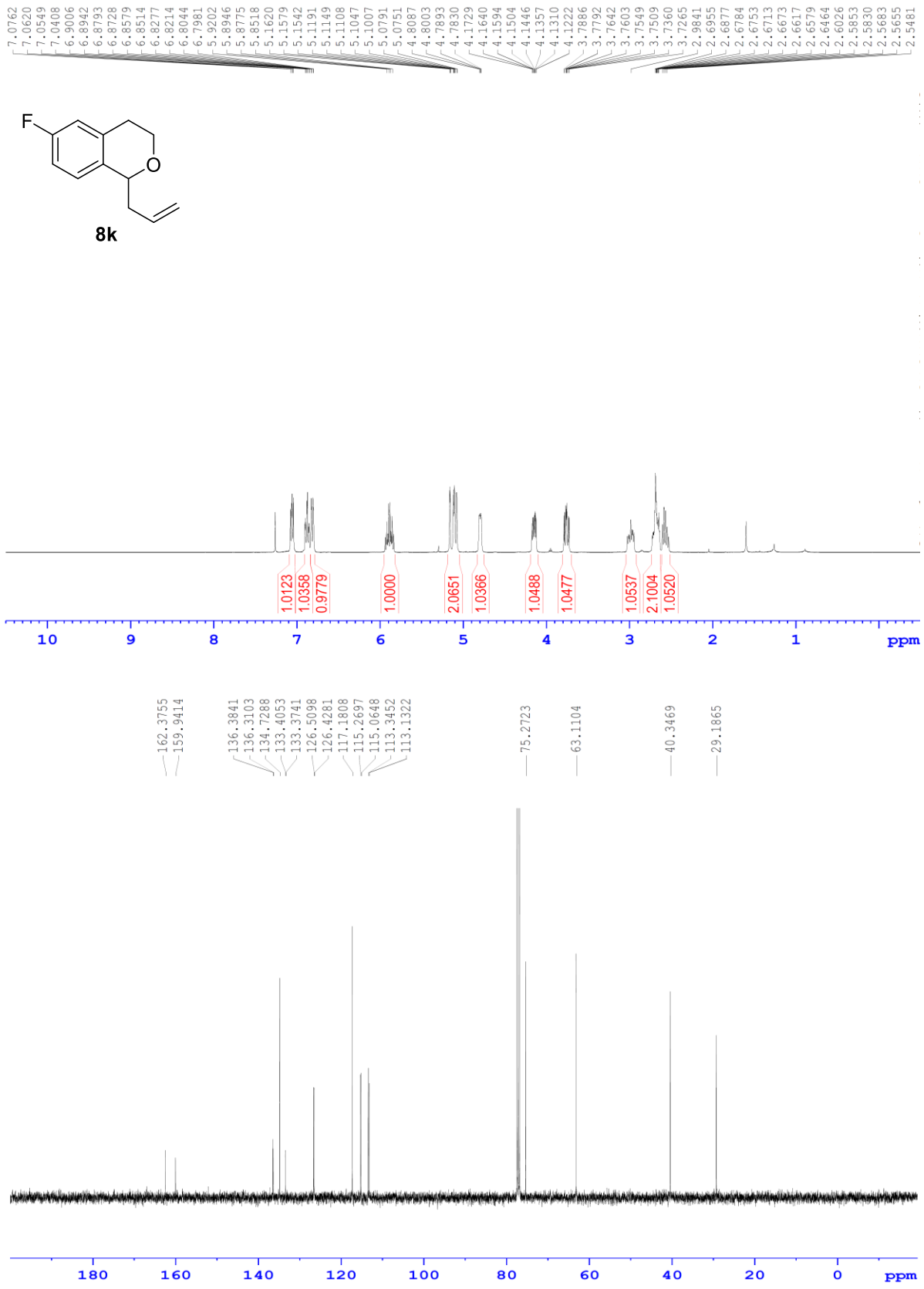


Figure S17. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8j** in $CDCl_3$.



. **Figure S18.** 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8k** in $CDCl_3$.

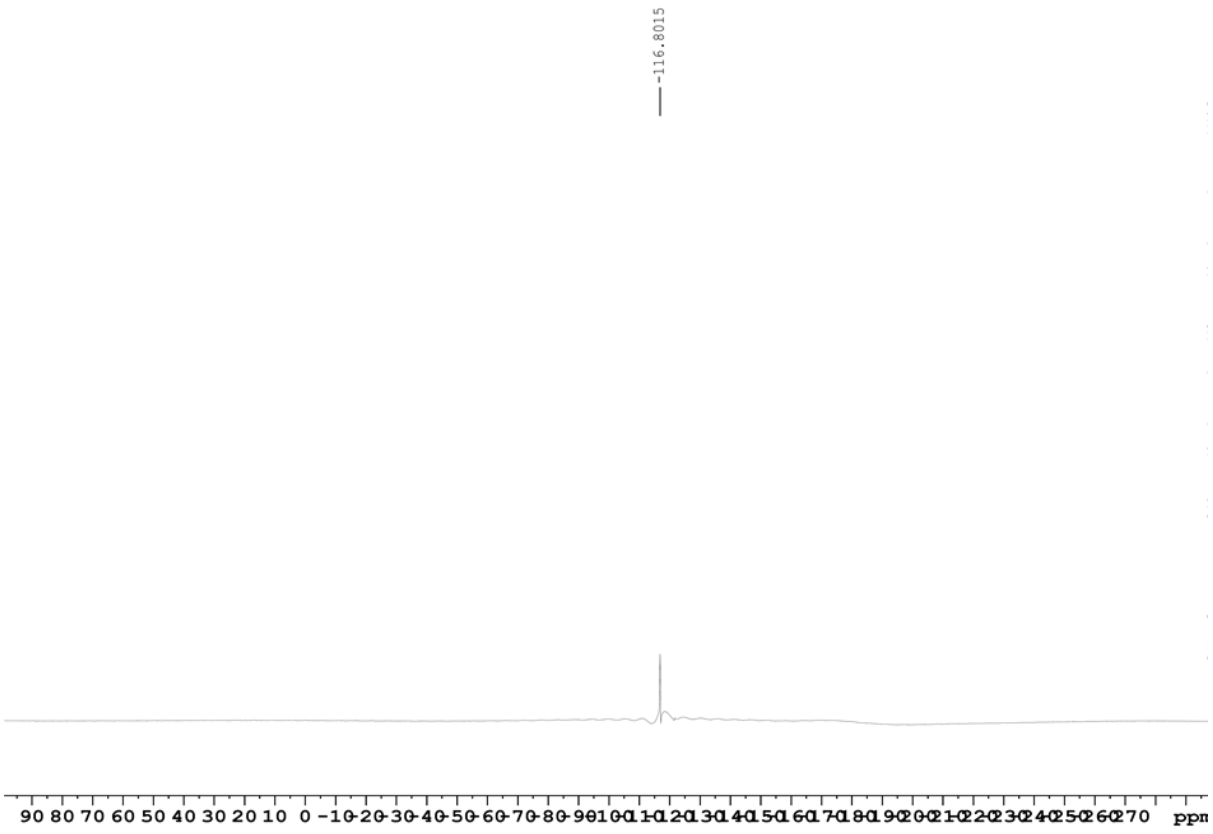


Figure S19. 376 MHz ^{19}F NMR spectrum of **8k** in $CDCl_3$.

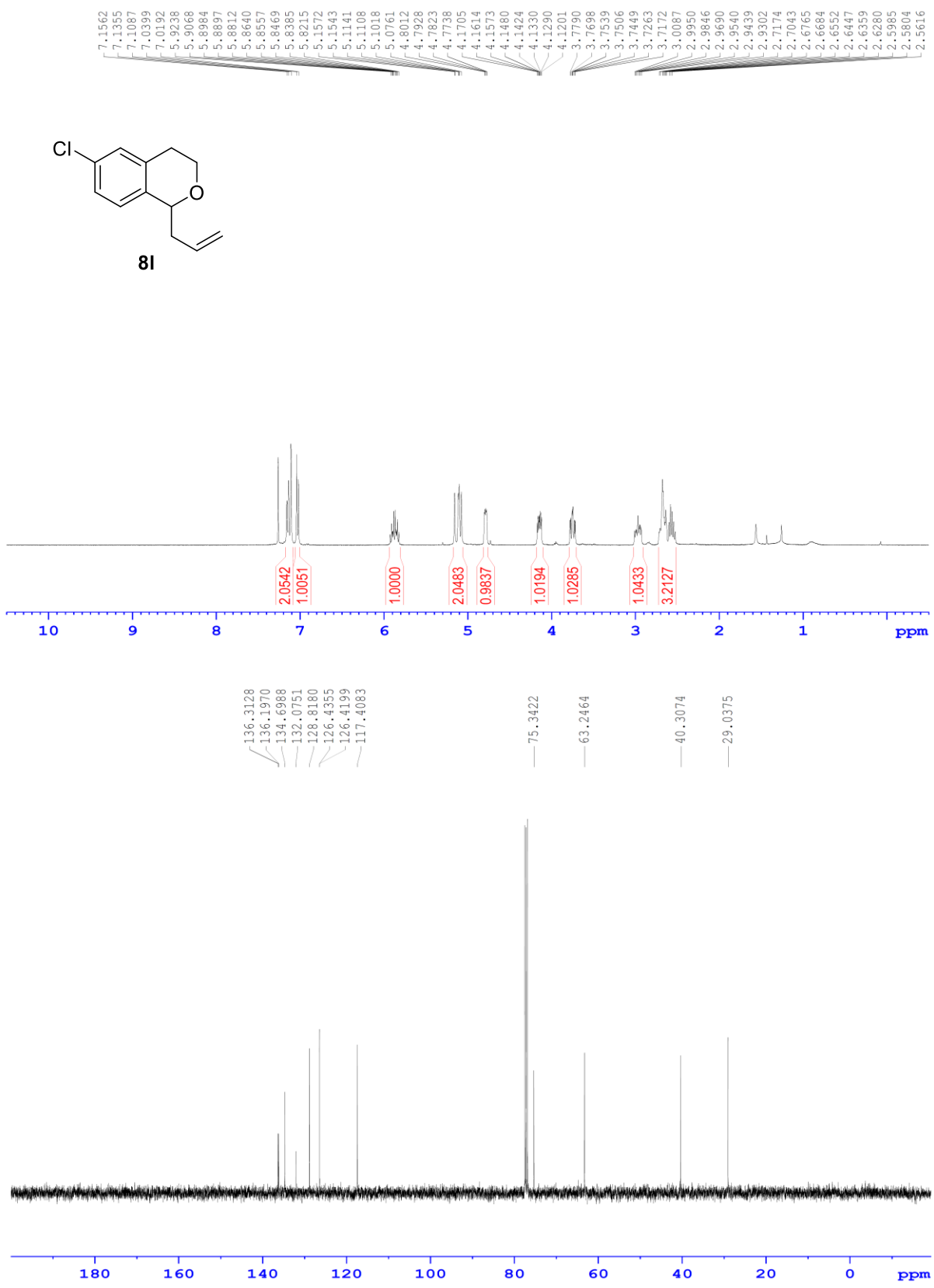


Figure S20. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8l** in $CDCl_3$.

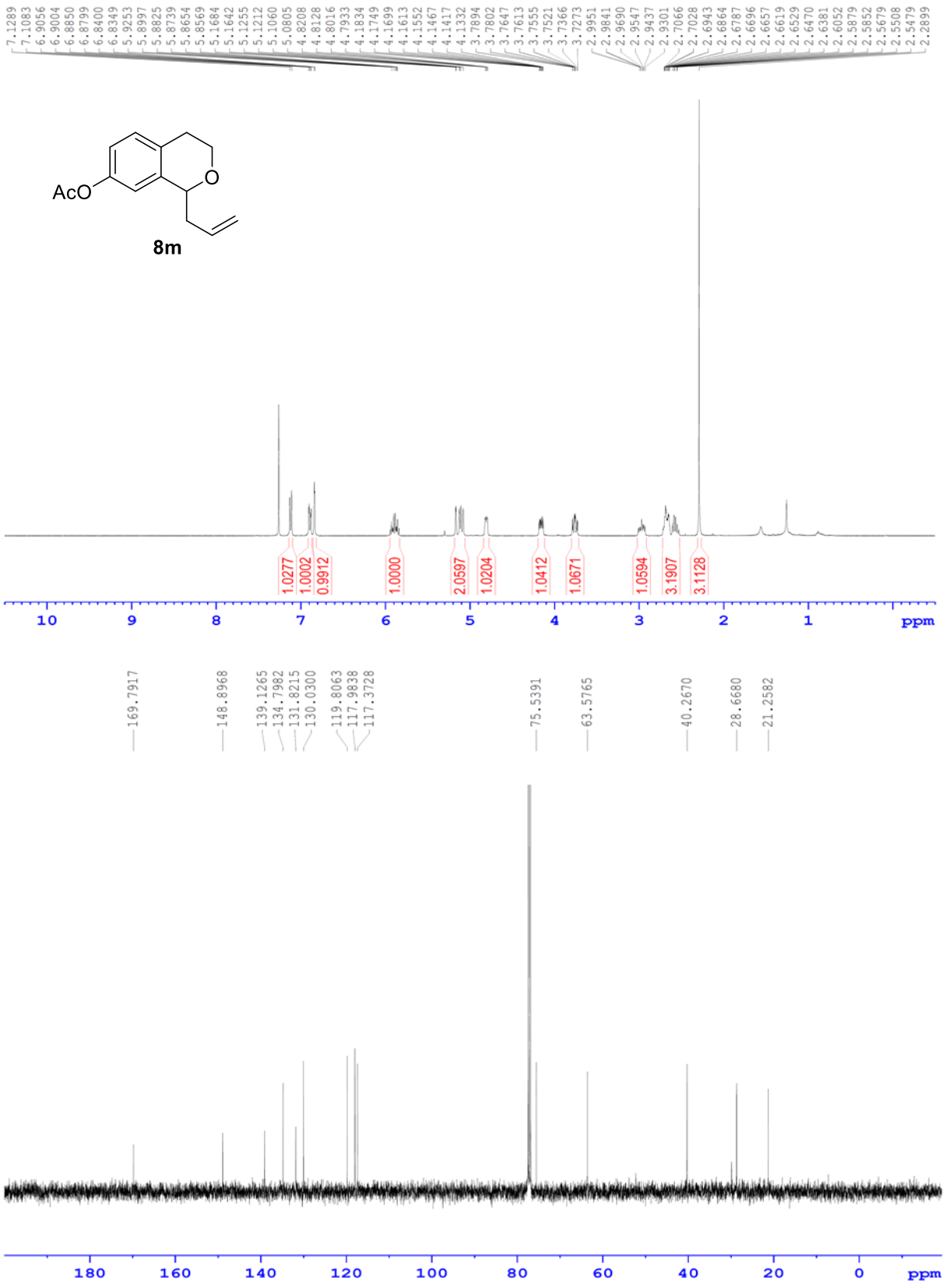


Figure S21. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8m** in $CDCl_3$.

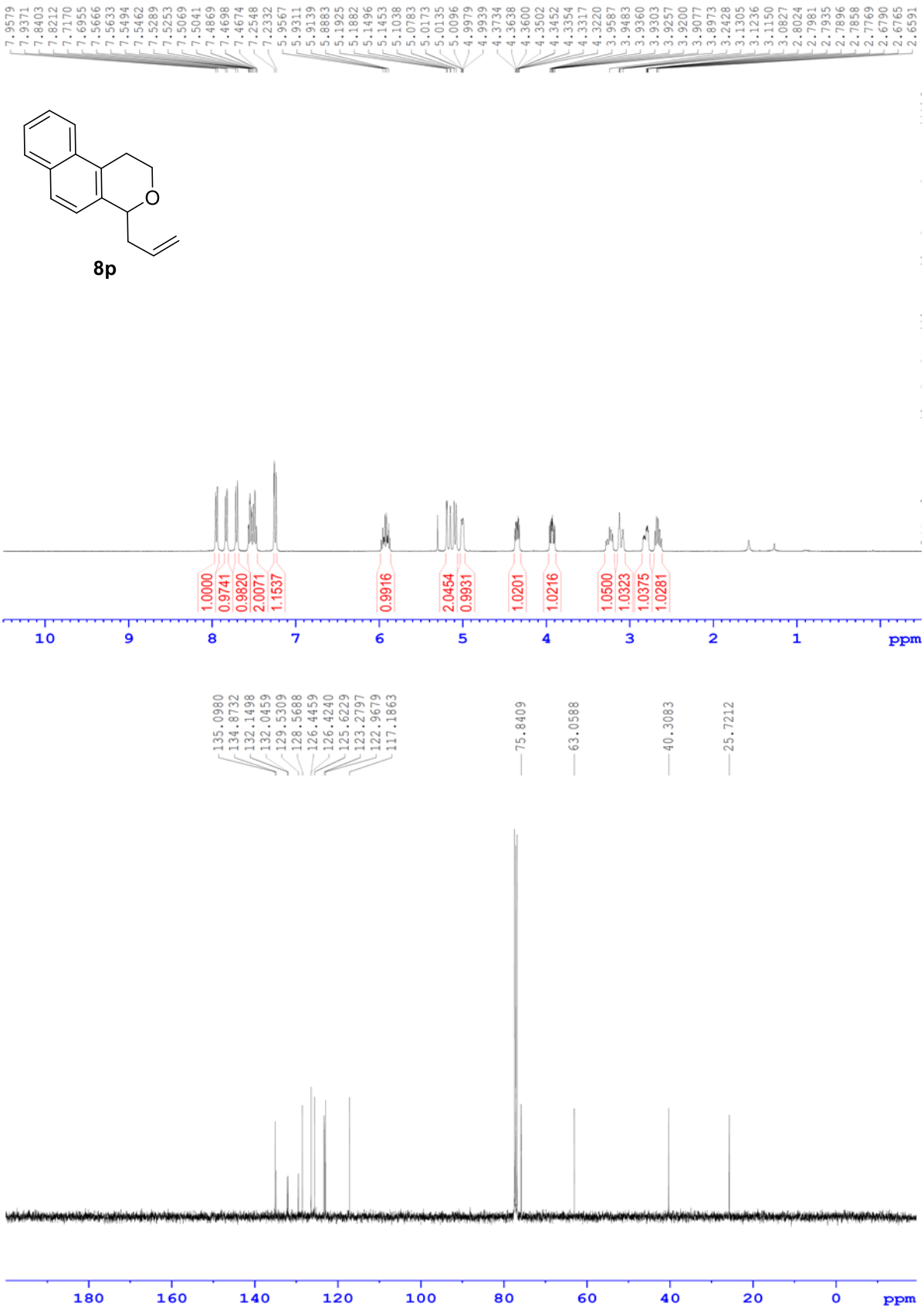


Figure S22. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8p** in $CDCl_3$.

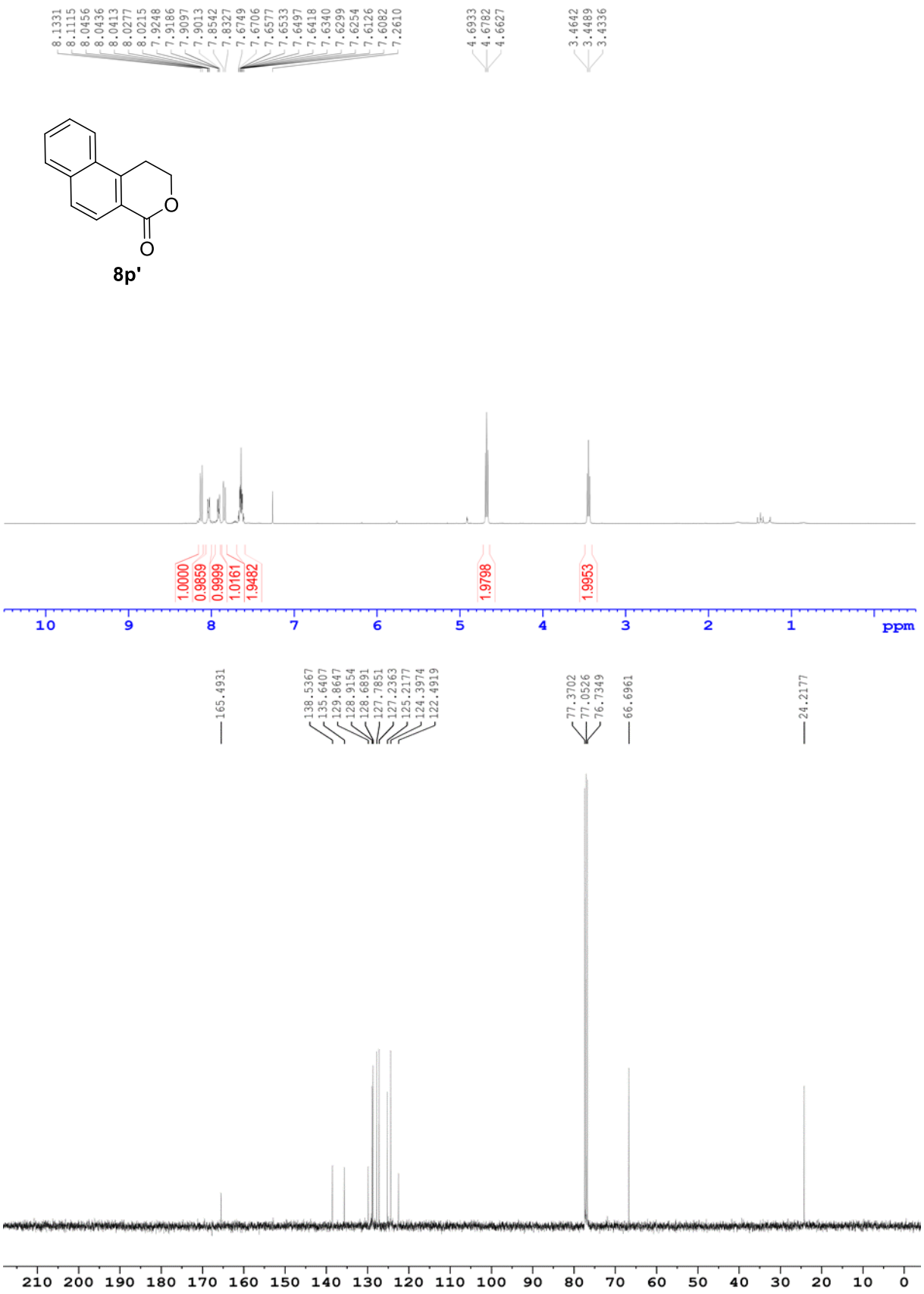


Figure S23. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8p′** in $CDCl_3$

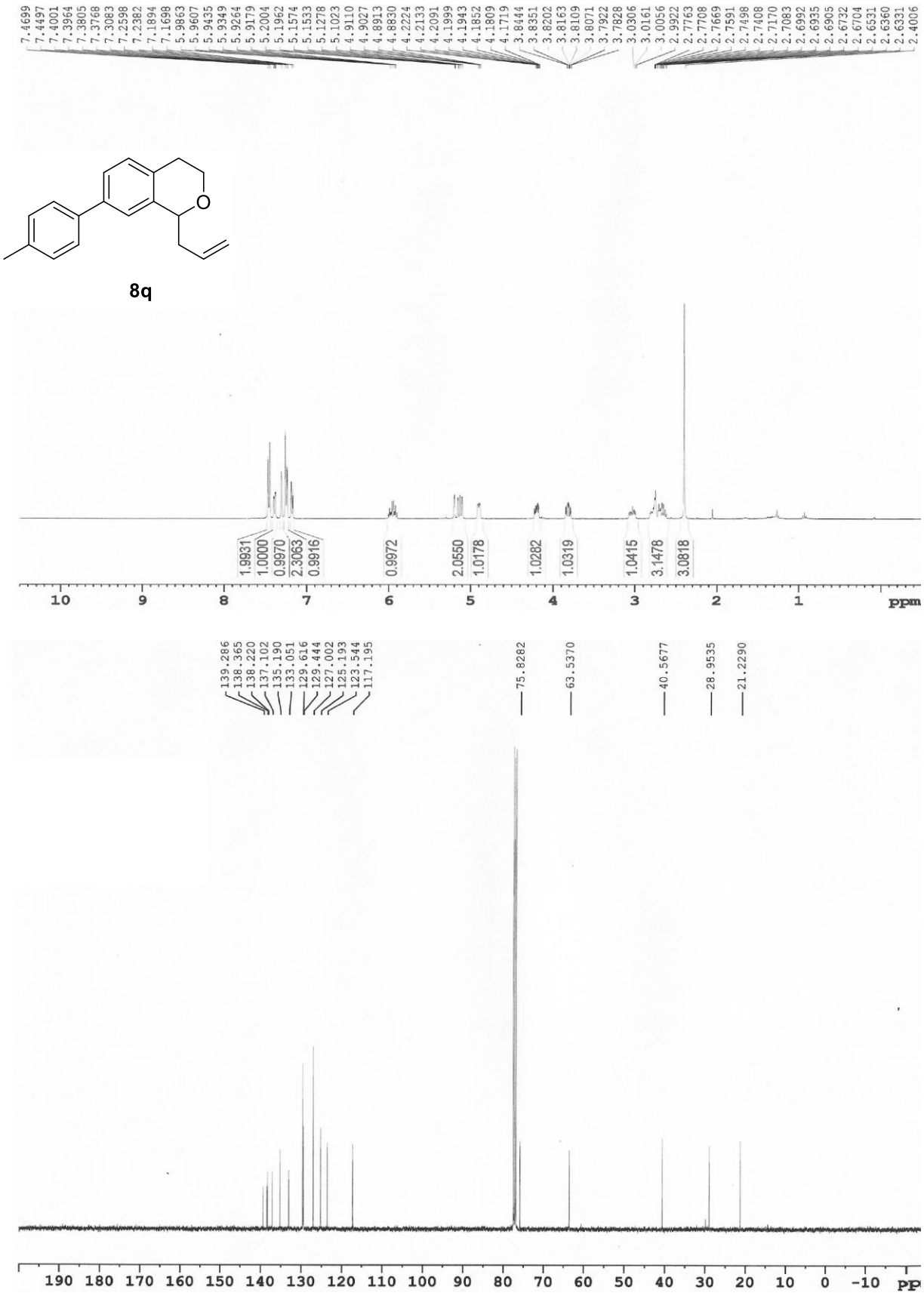


Figure S24. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8q** in $CDCl_3$.

Figure S25. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8q′** in $CDCl_3$

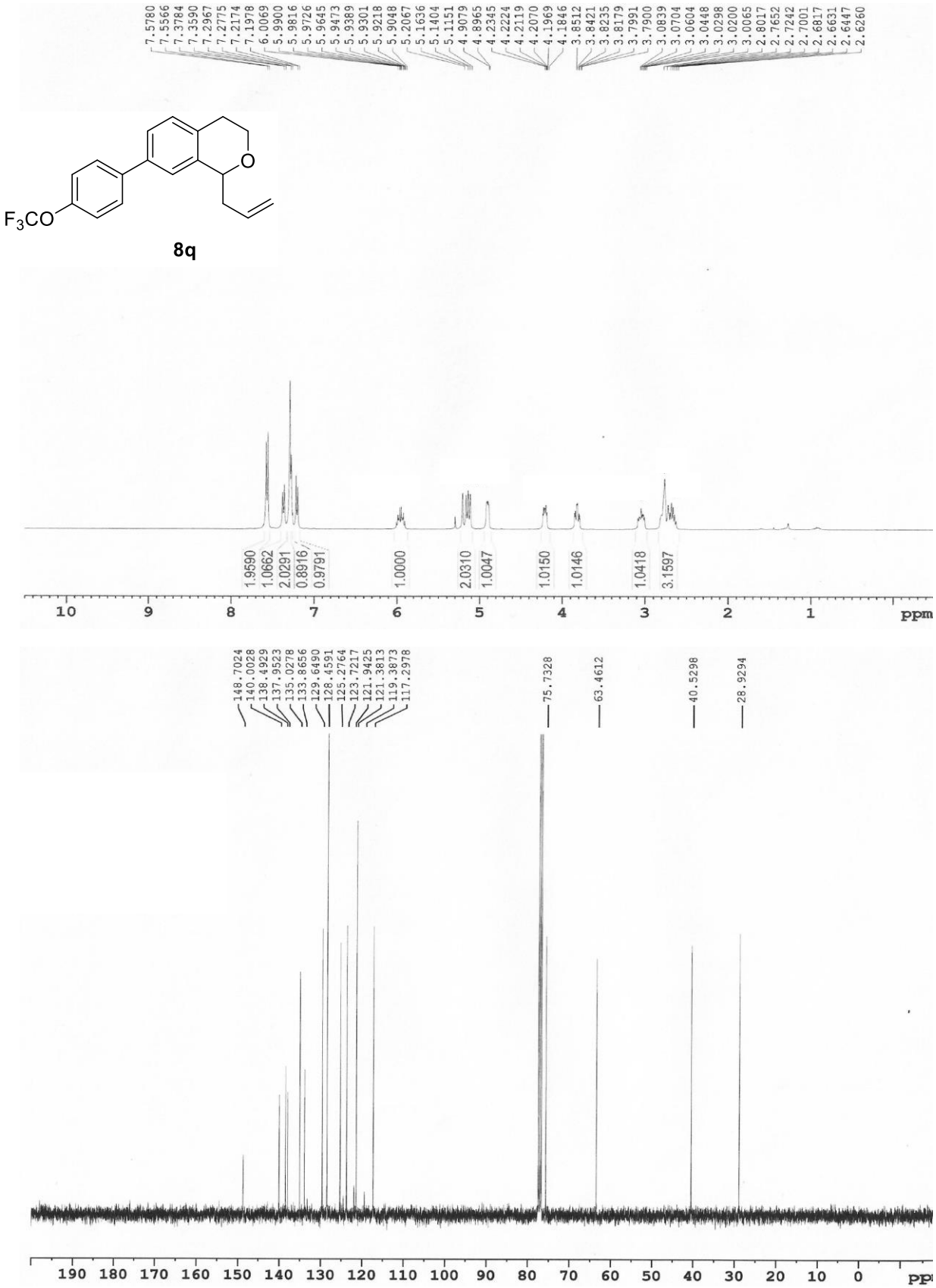


Figure S26. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8r** in $CDCl_3$.

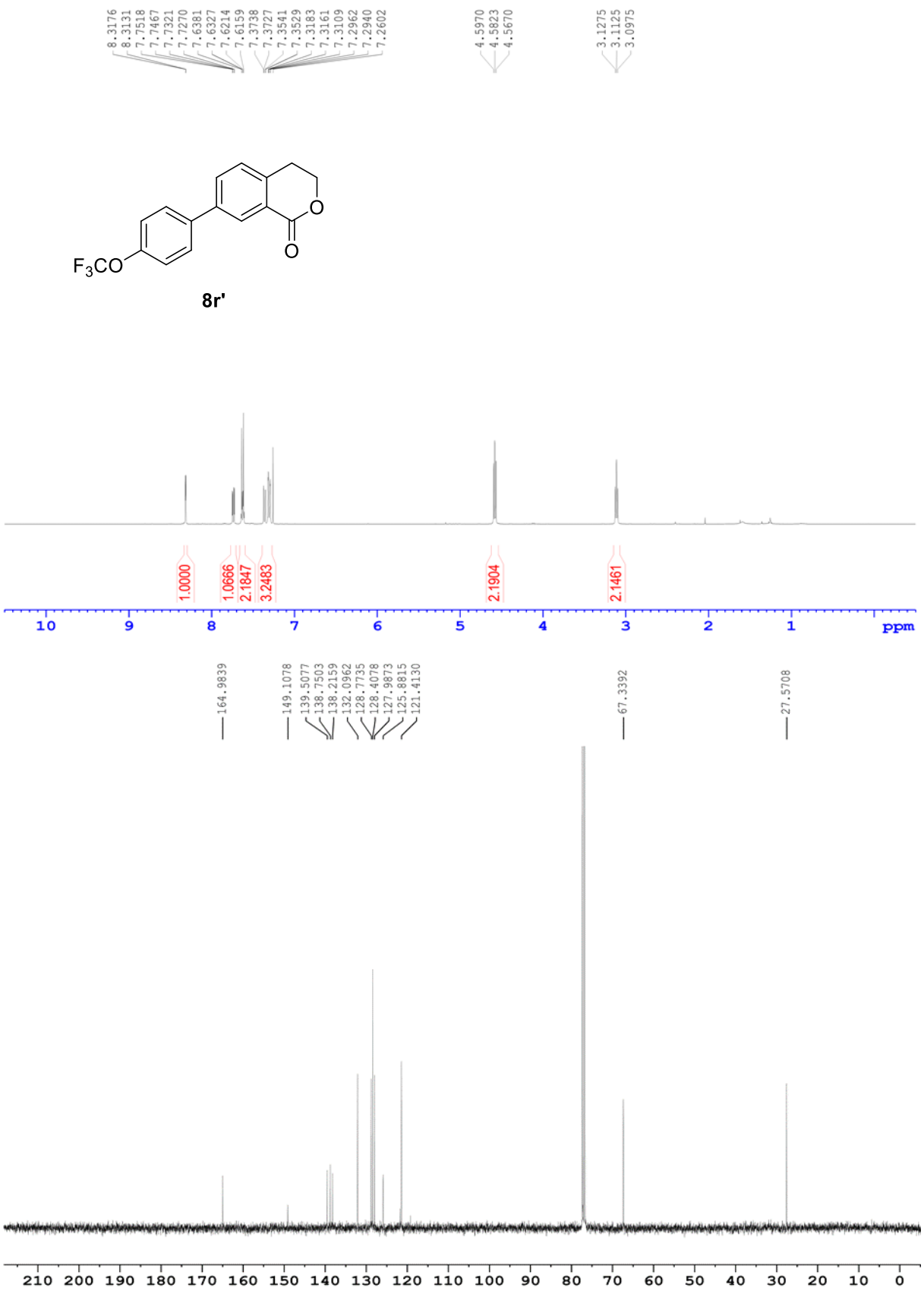


Figure S27. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8r′** in $CDCl_3$.

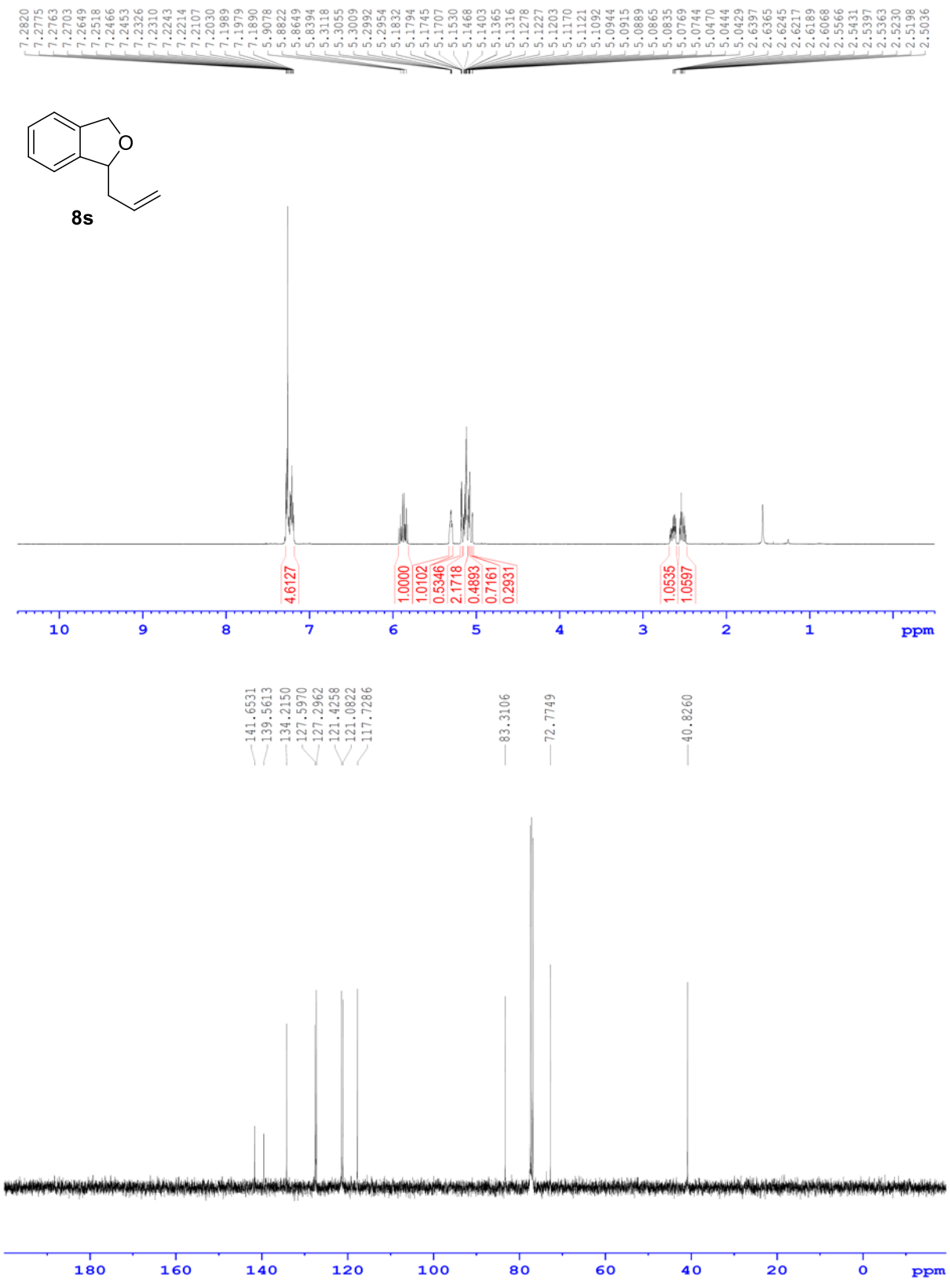


Figure S28. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8s** in $CDCl_3$.

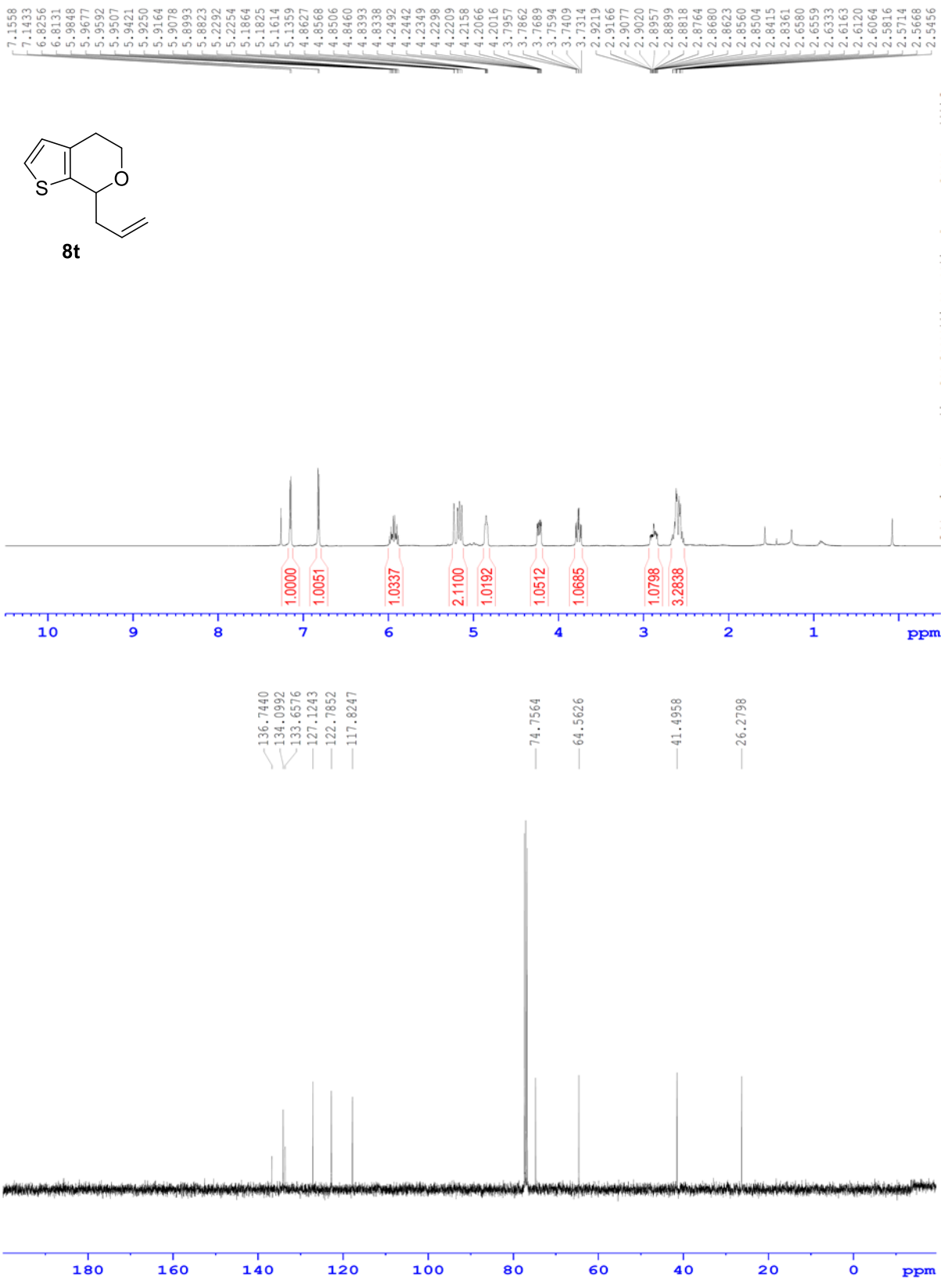


Figure S29. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **8t** in $CDCl_3$.

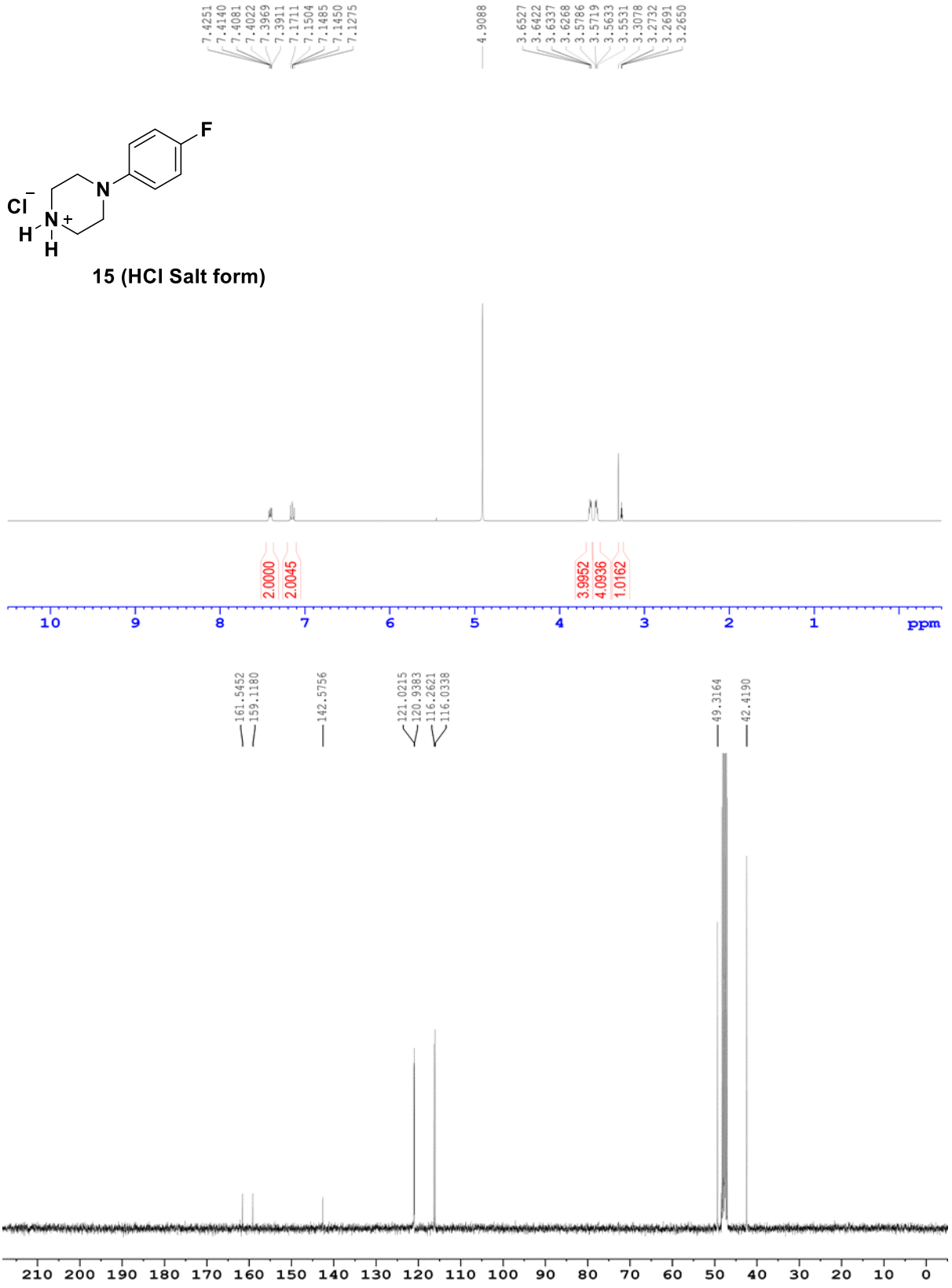


Figure S30. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **15** in MeOD.

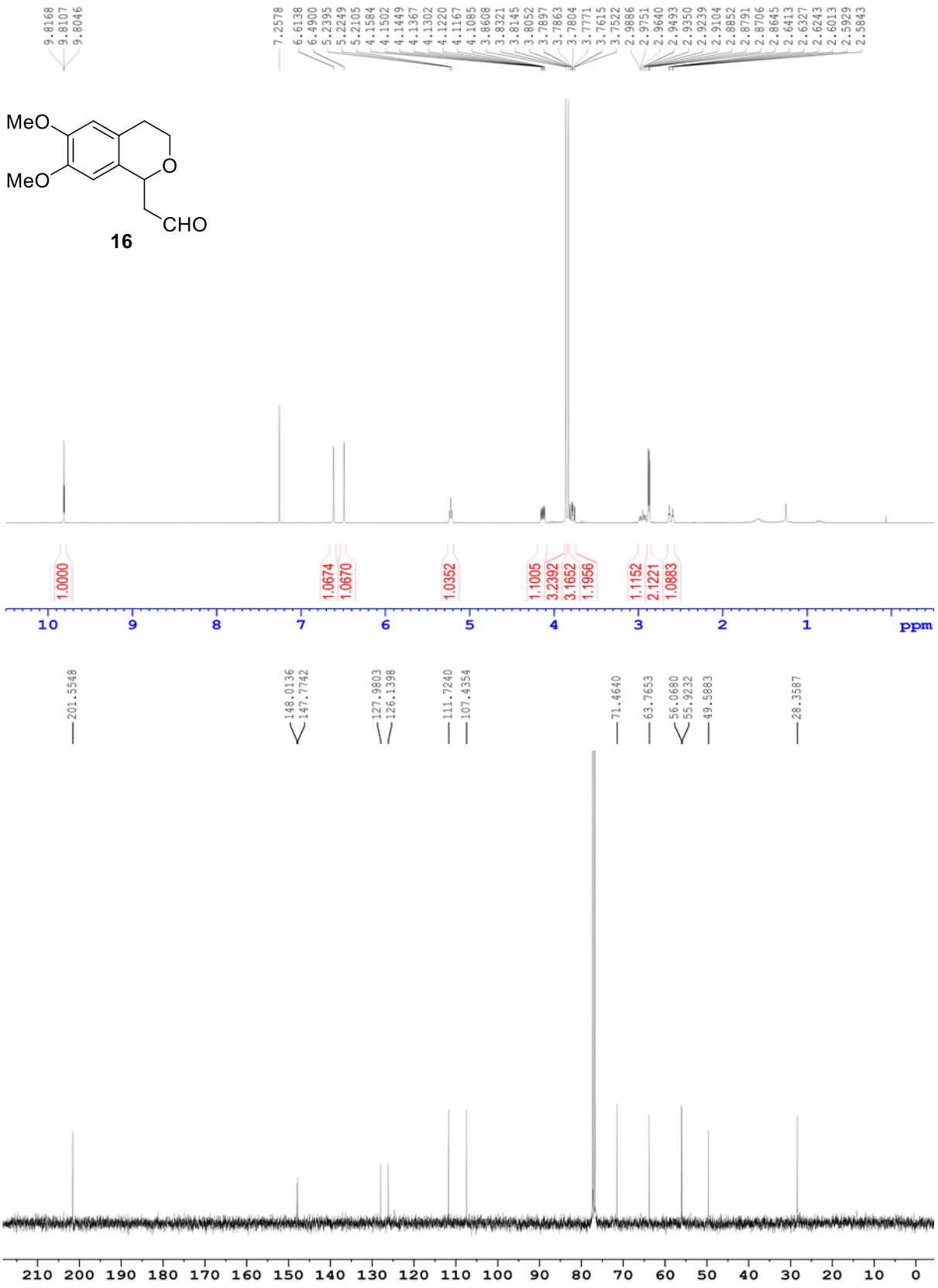


Figure S31. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **16** in $CDCl_3$.

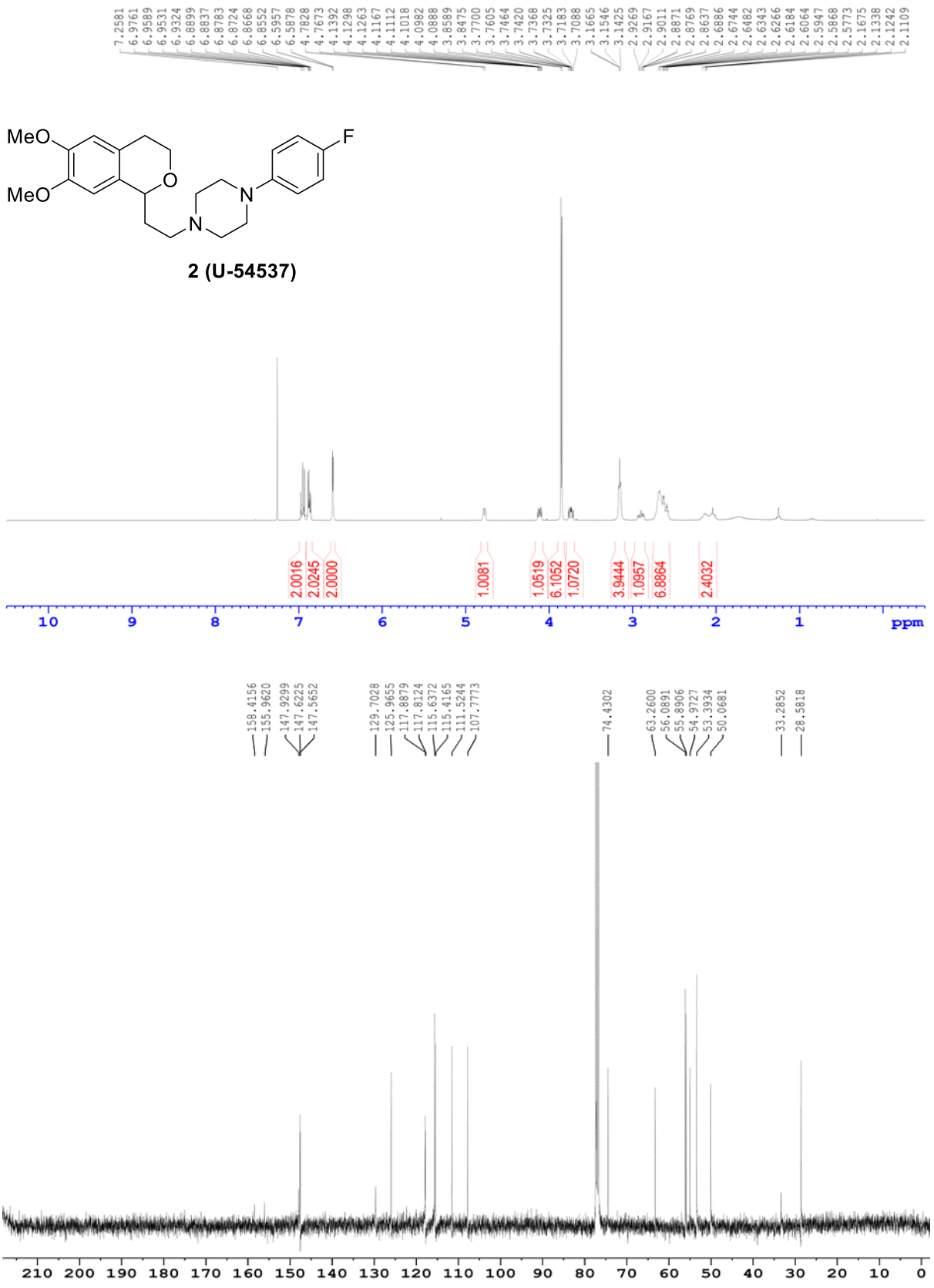


Figure S32. 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **2** in $CDCl_3$.

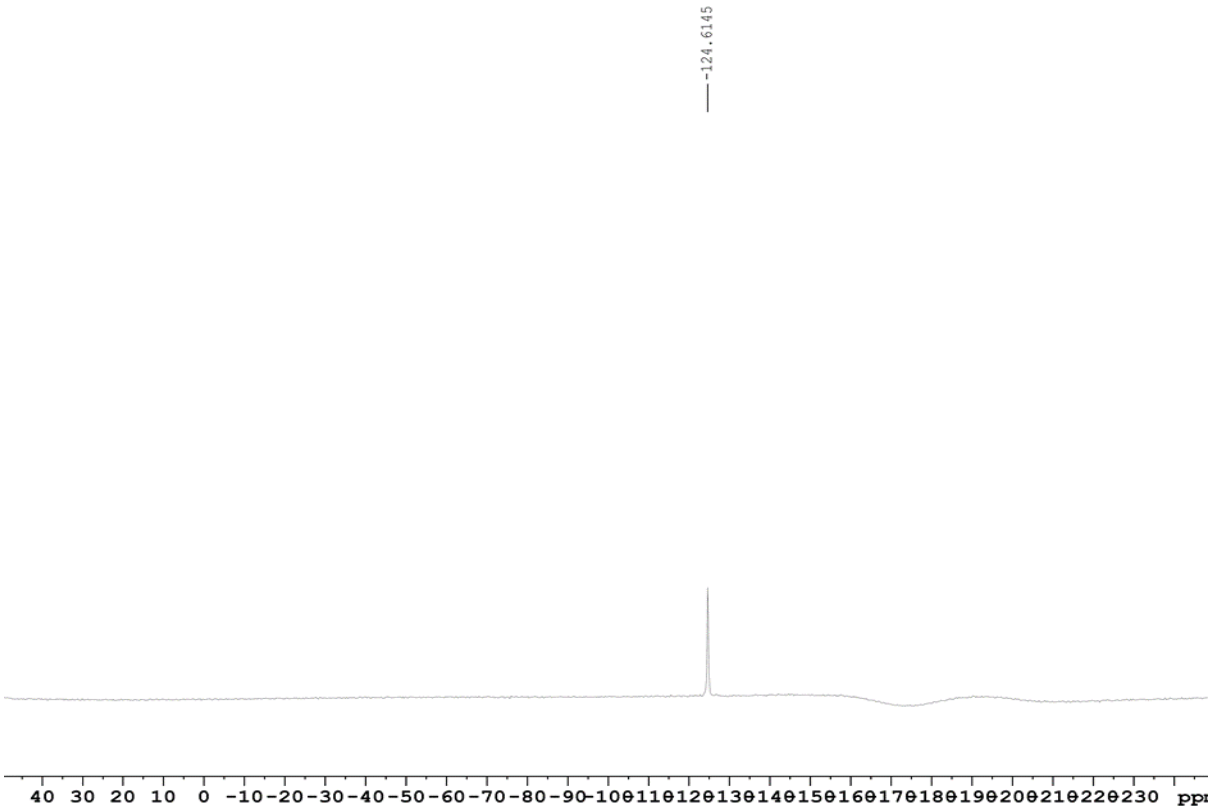


Figure S33. 376 MHz ^{19}F NMR spectrum of **2** in $CDCl_3$.

III. References

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