Supporting Information

Photocatalytic *E*→*Z* isomerization of *gem*-bromofluoroalkenes: Stereoselective synthesis of β-fluorostyrene derivatives

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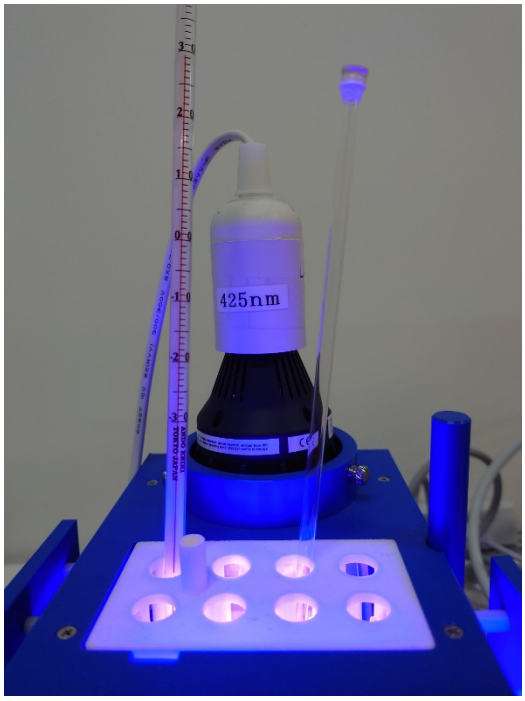
Materials and methods

All the chemicals for synthesis of the substrates and catalysts and the coupling reactions were commercially available (Aldrich or Tokyo Chemical Industry Co., Ltd. (TCI), FUJIFILM Wako Pure Co., Lt, Kanto Chemical Co., Inc.) unless otherwise noted. All *gem*-bromofluoroalkenes and photocatalysts were prepared according to the reported procedures.[1] All the reactions were carried out by standard Schlenk techniques unless otherwise noted. Anhydrous organic solvents and deuterated solvents were purchased from Kanto Chemical Co., Inc. Thin-layer chromatography was performed on TLC plates with 60 F_{254} (Merck).

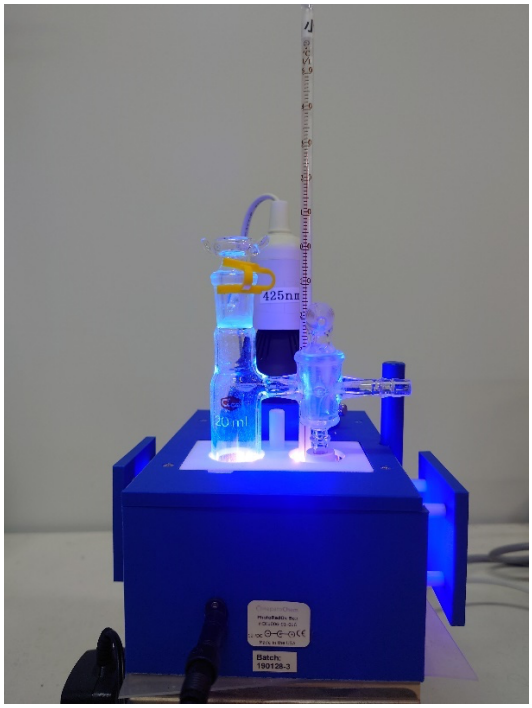
The following apparatuses were used for experiments and measurements.

Photoreactor: EvoluChem PhotoRedOx Box (425 nm). Flow reactor: DFC (56 mL in 15 borosilica-glass tubes (2.7 mm in diameter, 65 cm in length) around 405 nm LEDs). Automated column chromatography: Biotage Isolera Prime (Biotage SNAP Ultra cartrideges, particle size 25 μm). Recycling preparative HPLC (GPC): Japan Analytical Industry Co., Ltd. (JAI) LC-9201 (columns: JAIGEL-1H and JAIGEL-2H, eluent: $CHCl_3$). NMR spectra: JEOL JNM-ECX400 spectrometer (400 MHz for ^1H, 376 MHz for ^{19}F, 101 MHz for ^{13}C) and Magritek Spinsolve 60 Ultra (62 MHz for ^1H, 58 MHz for ^{19}F). The chemical shifts were referenced to an external tetramethylsilane signal (0.0 ppm) by using the solvent resonance for ^1H and $^{13}C\{^1H\}$ NMR and referenced to an external CF_3COOH (−76.5 ppm) or an internal $C_6H_5CF_3$ (–63.7 ppm) signals for ^{19}F NMR. The coupling constants were quoted in Hz (*J*). The splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). The splitting patterns that could not be interpreted or easily visualized were designated as apparent patterns or broad (br). High-resolution mass spectra (HRMS) (ESI/APCI/APPI Mass spectra): Thermo Fisher Exactive at Center for Analytical Instrumentation, Chiba University and Hitachi High-Tech Nano Frontier LD at Instrumental Analysis Center at Yokohama National University. Elemental analyses: PerkinElmer PE2400II at Center for Analytical Instrumentation, Chiba University. DFT calculations: Gaussian 16, Revision C.02 program package.

Apparatus for photoreaction



NMR-scale experiments

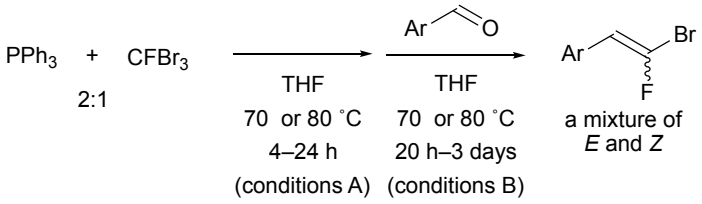


Preparative-scale experiments

Flow experiments

Preparation of *gem*-bromofluoroalkene 1

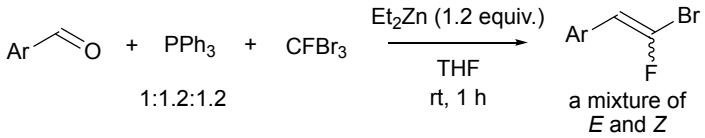
General procedures A



According to the reported procedures,[1a] *gem*-bromofluoroalkenes **1a**–**d**, **g–j** were prepared.

To a THF solution (24-60 mL) of PPh_3 (2 equiv.) in a two-necked flask, $CFBr_3$ (1 equiv.) was added under Ar atmosphere. The reaction mixture was stirred at 70 or 80 ºC (Al block) for 4–24 h. Then, the slurry mixture was allowed to cool down to room temperature. The corresponding aldehyde (1 equiv.) was slowly added to the reaction mixture and was stirred at 70 or 80 ºC (Al block) for 20 h–3 days. After the reaction, the mixture was filtered, washed with diethyl ether, and concentrated under reduced pressure. The product was obtained after purification by automated column chromatography.

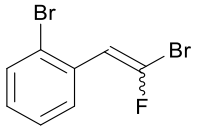
General procedures B



According to the reported procedures,[1b] *gem*-bromofluoroalkenes **1e** and **f** were prepared.

To a THF solution (30 mL) of PPh_3 (1.2 equiv.) in a two-neck flask, $CFBr_3$ (1.2 equiv.) and the corresponding aldehyde (1 equiv.) were added under Ar atmosphere. After that a hexane solution of Et_2Zn (1.09 mol/L, 1.2 equiv.) was added dropwise over 30 min. at room temperature. The reaction mixture was stirred at room temperature for 1 h. After the reaction, the mixture was quenched with MeOH (10 mL), stirred for 1 h, and concentrated under reduced pressure. The product was obtained after purification by automated column chromatography.

1-Bromo-2-(2-bromo-2-fluoroethenyl)benzene (**1a**)



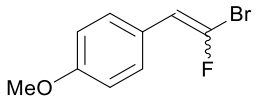
1a

According to the general procedures A, the use of PPh_3 (2.99 g, 11.4 mmol), $CFBr_3$ (1.54 g, 5.69 mmol), THF (20.0 mL), and 2-bromobenzaldehyde (1.08 g, 5.84 mmol) under conditions A (80 ˚C, 24 h) and conditions B (80 ˚C, 3 days) afforded **1a** as a colorless liquid (0.803 g, 2.87 mmol, 50% yield, *E*/*Z* = 60:40). Column eluent: hexane/EtOAc = 99:1.

The data are in agreement with those reported in the literature.[2]

^{1}H NMR (62 MHz, $CDCl_3$, rt): δ 7.66-7.20 (Ar-*H*), 6.66 (d, $^3J_{HF}$ = 15 Hz; *H*C=CBrF in *Z* isomer), 6.32 (d, $^3J_{HF}$=32 Hz; *H*C=CBrF in *E* isomer). **^{19}F NMR** (58 MHz, CD_3CN): δ –68.9 (d, $^3J_{HF}$ = 16 Hz; *Z* isomer), –71.6 (d, $^3J_{HF}$ = 32 Hz; *E* isomer).

1-(2-Bromo-2-fluoroethenyl)-4-methoxybenzene (**1b**)



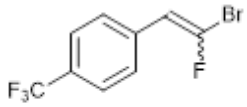
1b

According to the general procedures A, the use of PPh_3 (2.96 g, 11.3 mmol), $CFBr_3$ (1.76 g, 6.49 mmol), THF (60.0 mL), and *p*-anisaldehyde (0.863 g, 6.34 mmol) under conditions A (70 ˚C, 4 h) and conditions B (70 ˚C, 20 h) afforded **1b** as a colorless liquid (0.303 g, 1.31 mmol, 22% yield, *E*/*Z* = 51:49). Column eluent: hexane/EtOAc = 8:2.

The data are in agreement with those reported in the literature.[3]

^{1}H NMR (62 MHz, $CDCl_3$, rt): δ 7.53-7.6.81 (Ar-*H*), 6.63 (d, $^3J_{HF}$ = 15 Hz; *H*C=CBrF in *Z* isomer), 5.93 (d, $^3J_{HF}$=32 Hz; *H*C=CBrF in *E* isomer), 3.84 (s; OC*H*$_3$). **^{19}F NMR** (58 MHz, CD_3CN): δ –64.7 (d, $^3J_{HF}$ = 15 Hz; *Z* isomer), –67.3 (d, $^3J_{HF}$ = 33 Hz; *E* isomer).

1-(2-Bromo-2-fluoroethenyl)-4-(trifluoromethyl)benzene (**1c**)



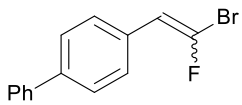
1c

According to the general procedures A, the use of PPh_3 (2.99 g, 11.4 mmol), $CFBr_3$ (1.50 g, 5.54 mmol), THF (60.0 mL), and 4-(trifluoromethyl) benzaldehyde (0.761 g, 4.36 mmol) under conditions A (70 ˚C, 4 h) and conditions B (70 ˚C, 20 h) afforded **1c** as a colorless liquid (0.472 g, 1.76 mmol, 31% yield, *E*/*Z* = 53:47). Column eluent: hexane/EtOAc = 99:1.

The data are in agreement with those reported in the literature.[4]

^{1}H NMR (62 MHz, $CDCl_3$, rt): δ 7.60-7.45 (Ar-*H*), 6.59 (d, $^3J_{HF}$ = 15 Hz; *H*C=CBrF in *Z* isomer), 5.94 (d, $^3J_{HF}$ = 32 Hz; *H*C=CBrF in *E* isomer). **^{19}F NMR** (58 MHz, CD_3CN): δ –60.7 (d, $^3J_{HF}$ = 15 Hz; *Z* isomer), –62.7 (s, CF_3), –65.2 (d, $^3J_{HF}$ = 32 Hz; *E* isomer).

4-(2-Bromo-2-fluoroethenyl)-1,1'-biphenyl (**1d**)

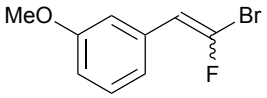


1d

According to the general procedures A, the use of PPh_3 (2.98 g, 11.4 mmol), $CFBr_3$ (1.78 g, 6.13 mmol), THF (60.0 mL), and biphenyl-4-carboxaldehyde (0.810 g, 4.71 mmol) under conditions A (70 ˚C, 4 h) and conditions B (70 ˚C, 20 h) afforded **1d** as a white solid (0.351 g, 1.26 mmol, 31% yield, *E*/*Z* = 60:40). Column eluent: hexane/EtOAc = 9:1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.65-7.37 (Ar-*H*), 6.73 (d, $^3J_{HF}$ = 16 Hz; *H*C=CBrF in *Z* isomer), 6.05 (d, $^3J_{HF}$ = 32 Hz; *H*C=CBrF in *E* isomer). **^{19}F NMR** (376 MHz, CD_3CN): δ –64.6 (d, $^3J_{HF}$ = 15 Hz; *Z* isomer), –67.3 (d, $^3J_{HF}$ = 34 Hz; *E* isomer). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 140.9 (d, J_{CF} = 2 Hz), 140.7 (d, $^1J_{CF}$ = 3 Hz), 140.52, 140.47, 135.0 (d, $^1J_{CF}$ = 317 Hz), 134.1 (d, $^1J_{CF}$ = 332 Hz), 131.6 (d, J_{CF} = 5 Hz), 130.5 (d, J_{CF} = 9 Hz), 129.0, 128.91, 128.88, 128.62,128.55, 127.6, 127.4, 127.3, 127.2, 127.1, 112.9 (apparent dd), 111.5 (d, J_{CF} = 24 Hz). **HRMS** (APCI) calcd m/z for $[C_{14}H_{10}BrF]^+$ 275.9944, found 275.9947 $[M]^+$.

1-(2-Bromo-2-fluoroethenyl)-3-methoxybenzene (**1e**)

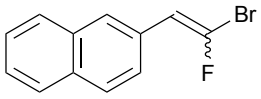


1e

According to the general procedures B, use of PPh_3 (0.629 g, 2.40 mmol), $CFBr_3$ (0.651 g, 2.41 mmol), THF (30.0 mL), *m*-anisaldehyde (0.284 g, 2.08 mmol) and Et_2Zn (2.30 mL, 2.51 mmol) afforded **1e** as a colorless liquid (0.241 g, 1.04 mmol, 50% yield, *E*/*Z* =42/58). Column eluent: hexane/EtOAc = 95:5.
The data are in accordance with the reported literature.[5]

^{1}H NMR (62 MHz, $CDCl_3$, rt): δ 7.32-6.88 (Ar-*H*), 6.59 (d, $^3J_{HF}$ = 16 Hz; *H*C=CBrF in *Z* isomer), 6.15 (d, $^3J_{HF}$ = 33 Hz; *H*C=CBrF in *E* isomer), 3.76 (s; OCH3). **^{19}F NMR** (58 MHz, CD_3CN): δ –63.0 (d, $^3J_{HF}$ = 15 Hz; *Z* isomer), –65.1 (d, $^3J_{HF}$ = 32 Hz; *E* isomer).

2-(2-Bromo-2-fluoroethenyl)naphthalene (**1f**)

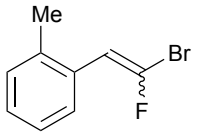


1f

According to the general procedures B, use of PPh_3 (0.629 g, 2.40 mmol), $CFBr_3$ (0.651 g, 2.41 mmol), THF (30.0 mL), 2-naphtalaldehyde (0.312 g, 2.00 mmol) and Et_2Zn (2.30 mL, 2.51 mmol) afforded **1f** as a white solid (0.269 g, 1.07 mmol, 54% yield, *E*/*Z* = 45:55). Column eluent: hexane.
The data are in accordance with the reported literature.[1b]

^{1}H NMR (62 MHz, $CDCl_3$, rt): δ 7.95-7.43 (Ar-*H*), 6.84 (d, $^3J_{HF}$ = 15 Hz; *H*C=CBrF in *Z* isomer), 6.15 (d, $^3J_{HF}$ = 33 Hz; *H*C=CBrF in *E* isomer). **^{19}F NMR** (58 MHz, CD_3CN): δ –62.7 (d, $^3J_{HF}$ = 15 Hz; *Z* isomer), –65.5 (d, $^3J_{HF}$ = 33 Hz; *E* isomer).

1-(2-Bromo-2-fluoroethenyl)-2-methylbenzene (**1g**)



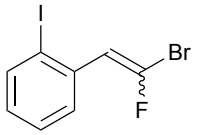
1g

According to the general procedures A, the use of PPh_3 (5.98 g, 22.8 mmol), $CFBr_3$ (2.93 g, 11.5 mmol), THF (48.0 mL), and 2-methylbenzaldehyde (1.37 g, 11.4 mmol) under conditions A (80 ˚C, 24 h) and conditions B (80 ˚C, 3 days) afforded **1g** as a colorless liquid (0.773 g, 3.59 mmol, 31% yield, *E*/*Z* = 64:36). Column eluent: hexane. Further purification by recycling preparative HPLC (GPC) afforded the analytically pure product.

The data are in agreement with those reported in the literature.[6]

^{1}H NMR (62 MHz, $CDCl_3$, rt): δ 8.43-7.32 (Ar-*H*), 7.05 (d, $^3J_{HF}$ = 13 Hz; *H*C=CBrF in *Z* isomer), 6.51 (d, $^3J_{HF}$=26 Hz; *H*C=CBrF in *E* isomer). **^{19}F NMR** (58 MHz, CD_3CN): δ –69.5 (d, $^3J_{HF}$ = 13 Hz; *Z* isomer), –72.5 (d, $^3J_{HF}$ = 26 Hz; *E* isomer).

1-(2-Bromo-2-fluoroethenyl)-2-iodobenzene (**1h**)



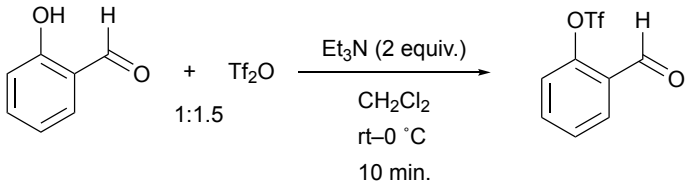
1h

According to the general procedures A, use of PPh_3 (2.09 g, 7.96 mmol), $CFBr_3$ (1.25 g, 4.61 mmol), THF (60.0 mL), and 2-iodobenzaldehyde (1.05 g, 4.53 mmol) under conditions A (80 ˚C, 24 h) and conditions B (80 ˚C, 24 h) afforded **1h** as a colorless liquid (0.501 g, 1.53 mmol, 33% yield, *E*/*Z* = 44:56). Column eluent: hexane/EtOAc = 99:1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.89–7.85 (Ar-*H*), 7.61 (m; Ar-*H*), 7.51 (m; Ar-*H*), 7.39–7.32 (Ar-*H*), 7.02 (m; Ar-*H*), 6.97 (m; Ar-*H*), 6.66 (d, $^3J_{HF}$ = 12 Hz; *H*C=CBrF in *Z* isomer), 6.27 (d, $^3J_{HF}$ = 28 Hz; *H*C=CBrF in *E* isomer). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –65.4 (d, $^3J_{HF}$ = 11 Hz; *Z* isomer), –68.5 (d, $^3J_{HF}$ = 30 Hz; *E* isomer). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 139.6, 139.2, 137.6 (d, $^1J_{CF}$ = 320 Hz), 136.4 (d, $^3J_{CF}$ = 9 Hz), 135.8 (d, $^3J_{CF}$ = 5 Hz), 135.4 (d, $^1J_{CF}$ = 334 Hz), 130.2 (d, $^4J_{CF}$ = 2 Hz), 129.7, 129.6, 129.5, 128.5, 128.2, 116.8 ($^2J_{CF}$ = 5 Hz), 115.9 ($^2J_{CF}$ = 25 Hz), 100.3 ($^4J_{CF}$ = 4 Hz), 98.8. **EA** calcd for C_8H_5BrFI: C 29.39; H 1.54, found: C 29.47; H 1.52.

2-(2-Bromo-2-fluoroethenyl)phenyl trifluoromethanesulfonate (**1i**)

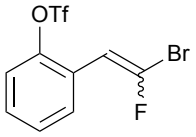
The title compound was prepared from the reaction of 2-formylphenyl trifluoromethanesulfonate, which was obtained from the following method.



A 50 mL two-necked flask under argon was charged with salicylaldehyde (1.02 g, 8.35 mmol), CH_2Cl_2 (20 mL), Et_3N (1.71 g, 0.0169 mol) and the solution was stirred at room temperature for 10 min. The reaction mixture was cooled to 0 °C. Then, Tf_2O (1.71 mL, 11.9 mmol) was added dropwise over 10 min. The reaction mixture was stirred for 10 min at 0 °C while being monitored by TLC (hexane/EtOAc = 9:1). Then, the reaction was quenched by $NaHCO_3$ aq. (20 mL). The aqueous layer was extracted with CH_2Cl_2 (20 mL). The organic layer was washed with 1 M HCl (25 mL), and the aqueous layer was again extracted with CH_2Cl_2 (20 mL). The combined organic layer was washed with brine (20 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Automated column chromatography (hexane/EtOAc = 9:1) afforded 2-formylphenyl trifluoromethanesulfonate (1.55 g, 6.11 mmol, 75% yield) as yellow oil.

The data are in agreement with those reported in the literature.[7]

^{1}H NMR (62 MHz, $CDCl_3$, rt): δ 10.3 (s, 1H; CO*H*), 8.08-7.43 (4H; Ar-*H*). **^{19}F NMR** (58 MHz, $CDCl_3$): δ –70.9 (s; OSO_2CF_3).

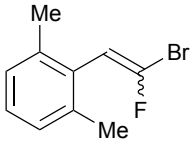


1i

According to the general procedures A, the use of PPh_3 (3.09 g, 11.7 mmol), $CFBr_3$ (1.60 g, 5.91 mmol), THF (24.0 mL), and 2-formylphenyl trifluoromethanesulfonate (1.42 g, 5.59 mmol) under conditions A (80 ˚C, 24 h) and conditions B (80 ˚C, 3 days) afforded **1i** as a colorless liquid (0.245 g, 1.14 mmol, 27% yield, *E*/*Z* = 61:39). Column eluent: hexane.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.75‑7.68 (Ar-*H*), 7.43–7.30 (Ar–*H*), 6.70 (d, $^3J_{HF}$ = 12 Hz; *H*C=CBrF in *Z* isomer), 6.21 (d, $^3J_{HF}$ = 32 Hz; *H*C=CBrF in *E* isomer). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –60.4 (d, $^3J_{HF}$ = 11 Hz; HC=CBr*F* in *Z* isomer), –64.0 (d, $^3J_{HF}$ = 30 Hz; HC=CBr*F* in *E* isomer), -73.3 (s; C*F*$_3$SO$_2$O in *E* isomer), -73.4 (s; C*F*$_3$SO$_2$O in *Z* isomer). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 147.2 (d, $^4J_{CF}$ = 3 Hz), 145.9, 138.8 (d, $^1J_{CF}$ = 321 Hz), 136.8 (d, $^1J_{CF}$ = 335 Hz), 130.9 (d, $^4J_{CF}$ = 2 Hz), 130.5 (d, $^4J_{CF}$ = 11 Hz), 130.1, 129.7, 128.7, 128.5, 126.1 (d, $^3J_{CF}$ = 8 Hz), 125.9 (d, $^3J_{CF}$ = 5 Hz), 121.90, 121.88, 118.7 (q, $^1J_{CF}$ = 304 Hz; 2C), 105.7 (d, $^2J_{CF}$ = 27 Hz), 105.4 (d, $^2J_{CF}$ = 6 Hz). **EA** calcd for $C_9H_5BrF_4SO_3$: C 30.97; H 1.44, found: C 30.66; H 1.34.

2-(2-Bromo-2-fluoroethenyl)-1,3-dimethylbenzene (**1j**)

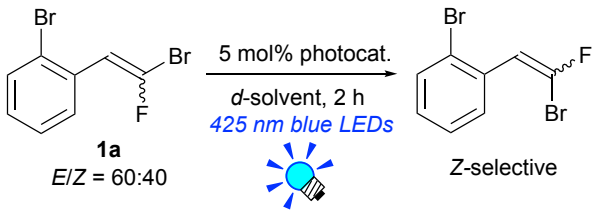


1j

According to the general procedures A, the use of PPh_3 (5.98 g, 22.8 mmol), $CFBr_3$ (2.89 g, 11.7 mmol), THF (48.0 mL), and 2,6-dimethylbenzaldehyde (1.57 g, 11.7 mmol) under conditions A (80 ˚C, 24 h) and conditions B (80 ˚C, 3 days) afforded **1j** as a colorless liquid (1.11 g, 4.83 mmol, 42% yield, *E*/*Z* = 57:43). Column eluent: hexane. Further purification by recycling preparative HPLC (GPC) afforded the analytically pure product.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.19–7.06 (Ar–*H*), 6.54 (d, $^3J_{HF}$ = 12 Hz; *H*C=CBrF in *Z* isomer), 6.05 (d, $^3J_{HF}$ = 36 Hz; *H*C=CBrF in *E* isomer), 2.30 (s; C*H*$_3$ in *E* isomer), 2.28 (s; C*H*$_3$ in *Z* isomer). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –66.1 (d, $^3J_{HF}$ = 34 Hz; *E* isomer), –68.5 (d, $^3J_{HF}$ = 11 Hz; *Z* isomer). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 137.5 (d, $^1J_{CF}$ = 321 Hz), 137.0 (d, $^4J_{CF}$ = 3 Hz), 136.8, 132.1 (d, $^1J_{CF}$ = 326 Hz), 131.1 (d, $^3J_{CF}$ = 7 Hz), 131.0, 128.2, 128.1, 127.6 (2C), 111.1 (d, $^2J_{CF}$ = 12 Hz), 109.7 (d, $^2J_{CF}$ = 20 Hz), 20.5 (d, J_{CF} = 2 Hz), 20.3. **HRMS** (APPI) calcd m/z for $[C_{10}H_{10}BrF]^+$ 227.9944, found 227.9946 $[M]^+$.

General procedures for NMR experiment (Table 1)



An NMR tube was charged with photocatalyst (0.0120 mmol). Then, **1a** (72.1 mg, 0.224 mmol), deuterated solvent (0.50 mL in total), and an internal standard, $C_6H_5CF_3$ (0.00300 mmol) or dimethyl sulfone (0.00300 mmol) were added under Ar atmosphere and the mixture was degassed by three freeze-pump-thaw cycles. The tube was placed at a distance of –1 cm away from LED lamps (λ = 425 nm) under wind blowing. The reaction was carried out under visible light irradiation at room temperature (25 – 27˚C) and monitored by NMR spectroscopy.

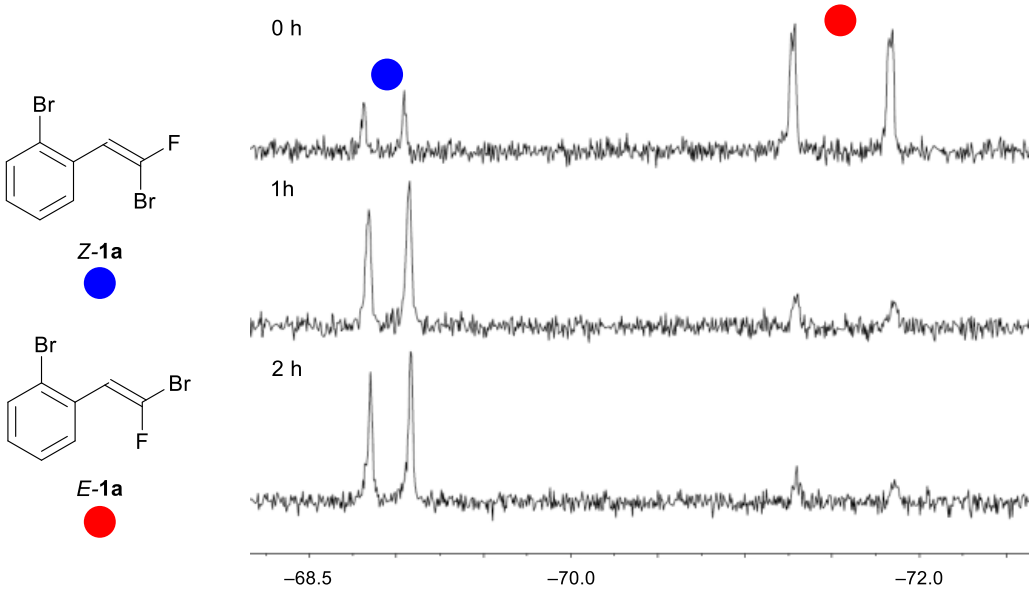
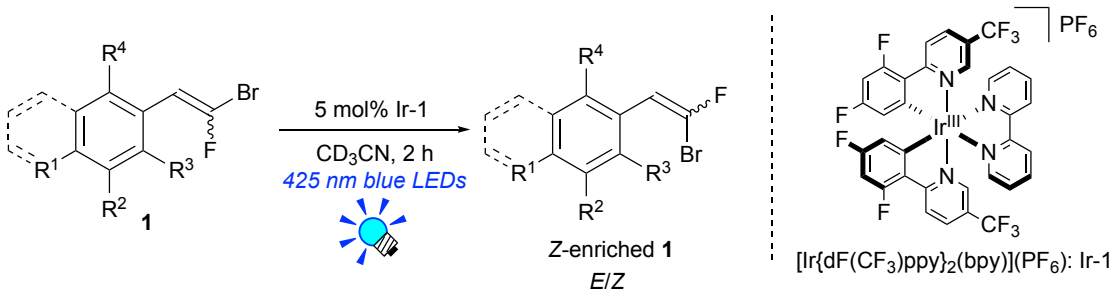


Figure S1. ^{19}F NMR spectra (58 MHz) of the photocatalytic isomerization of **1a** using Ir-1 in CD_3CN.

Procedures for isomerization reactions of 1 (Table 2)



Photocatalytic isomerization of **1a** (R^1, R^2 = H, R^3 = Br, R^4 = H)

Reaction mixture of Ir-1 (0.0122 g, 0.0122 mmol), **1a** (*E*/*Z* = 60:40) (0.0753 g, 0.269 mmol), benzotrifluoride (0.00741 g, 0.00507 mmol), and CD_3CN (0.5 mL) under visible light irradiation at room temperature (26 – 27 ˚C) attained to *E*/*Z* =16:84 in 2 h in 93% NMR yield.

For preparative-scale spectral data of *Z*-**1a**, see page S27.

Photocatalytic isomerization of **1b** (R^1 = MeO, R^2, R^3, R^4 = H)

Reaction mixture of Ir-1 (0.0210 g, 0.0210 mmol), **1b** (*E*/*Z* = 51:49) (0.0610 g, 0.260 mmol), dimethyl sulfone (0.00388 g, 0.00412 mmol), and CD_3CN (0.5 mL) under visible light irradiation at room temperature (26– 27 ˚C) attained to *E*/*Z* = 29:71 in 2 h in 95% NMR yield.

Photocatalytic isomerization of **1c** (R^1 = CF_3, R^2, R^3, R^4 = H)

Reaction mixture of Ir-1 (0.0250 g, 0.0250 mmol), **1c** (*E*/*Z* = 53:47) (0.0601 g, 0.220 mmol), dimethyl sulfone (0.00357 g, 0.00379 mmol), and CD_3CN (0.5 mL) under visible light irradiation at room temperature (26 – 27 ˚C) attained to *E*/*Z* = 30:70 in 2 h in 91% NMR yield.

Photocatalytic isomerization of **1d** (R^1 = Ph, R^2, R^3, R^4 = H)

Reaction mixture of Ir-1 (0.0120 g, 0.0120 mmol), **1d** (*E*/*Z* = 60:40) (0.0604 g, 0.217 mmol), dimethyl sulfone (0.00387 g, 0.00411 mmol), and CD_3CN (0.5 mL) under visible light irradiation at room temperature (26 – 27 ˚C) attained to *E*/*Z* = 36:64 in 2 h in 94% NMR yield.

Photocatalytic isomerization of **1e** (R^1 = H, R^2 = MeO, R^3, R^4 = H)

Reaction mixture of Ir-1 (0.0120 g, 0.0120 mmol), **1e** (*E*/*Z* = 47:53) (0.0550 g, 0.238 mmol), benzotrifluoride (0.00640 g, 0.00438 mmol), and CD_3CN (0.5 mL) under visible light irradiation at room temperature (26 – 27 ˚C) attained to *E*/*Z* = 35:65 in 2 h in 91% NMR yield.

Photocatalytic isomerization of **1f**

Reaction mixture of Ir-1 (0.0121 g, 0.0121 mmol), **1f** (*E*/*Z* = 50:50) (0.0617 g, 0.246 mmol), benzotrifluoride (0.00820 g, 0.00561 mmol), and CD_3CN (0.5 mL) under visible light irradiation at room temperature (26 – 27 ˚C) attained to *E*/*Z* = 40:60 in 2 h in 94% NMR yield.

Photocatalytic isomerization of **1g** (R^1, R^2 = H, R^3 = Me, R^4 = H)
Reaction mixture of Ir-1 (0.0130 g, 0.0130 mmol), **1g** (*E*/*Z* = 64:36) (0.0530 g, 0.246 mmol), benzotrifluoride (0.00251 g, 0.00172 mmol), and CD_3CN (0.5 mL) under visible light irradiation at room temperature (25 – 26 ˚C) attained to *E*/*Z* =17:83 in 2 h in 92% NMR yield.

Photocatalytic isomerization of **1h** (R^1, R^2 = H, R^3 = I, R^4 = H)
Reaction mixture of Ir-1 (0.0250 g, 0.0250 mmol), **1h** (*E*/*Z* = 44:56) (0.0754 g, 0.234 mmol), benzotrifluoride (0.00632 g, 0.00433 mmol), and CD_3CN (0.5 mL) under visible light irradiation at room temperature (26– 27 ˚C) attained to *E*/*Z* =10:90 in 2 h in 95% NMR yield.
For preparative-scale spectral data of *Z*-**1h**, see page S36.

Photocatalytic isomerization of **1i** (R^1, R^2 = H, R^3 = TfO, R^4 = H)
Reaction mixture of Ir-1 (0.0130 g, 0.0130 mmol), **1i** (*E*/*Z* = 61:39) (0.0871 g, 0.249 mmol), benzotrifluoride (0.00255 g, 0.00176 mmol), and CD_3CN (0.5 mL) under visible light irradiation at room temperature (25 – 26 ˚C) attained to *E*/*Z* =14:86 in 2 h in 94% NMR yield.
For preparative-scale spectral data of *Z*-**1i**, see page S42.

Photocatalytic isomerization of **1j** (R^1, R^2 = H, R^3, R^4 = Me)

Reaction mixture of Ir-1 (0.0160 g, 0.0160 mmol), **1j** (*E*/*Z* = 57:43) (0.0581 g, 0.254 mmol), benzotrifluoride (0.00250 g, 0.00170 mmol), and CD_3CN (0.5 mL) under visible light irradiation at room temperature (25 – 26 ˚C) attained to *E*/*Z* = <5:>99 in 22 h in 94% NMR yield.

For preparative-scale spectral data of *Z*-**1j**, see page S48.

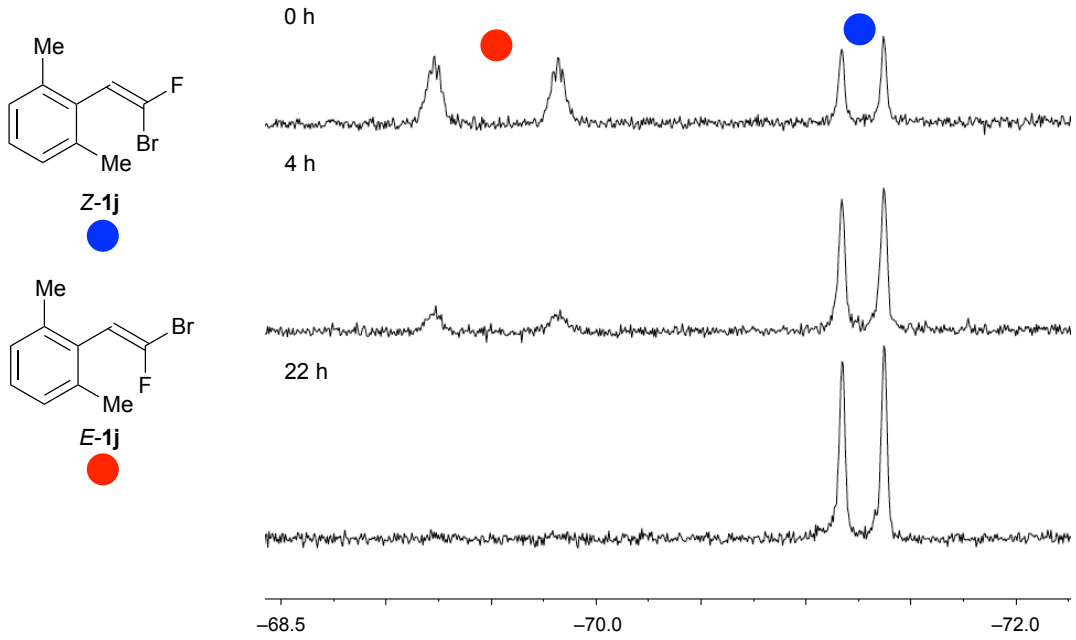
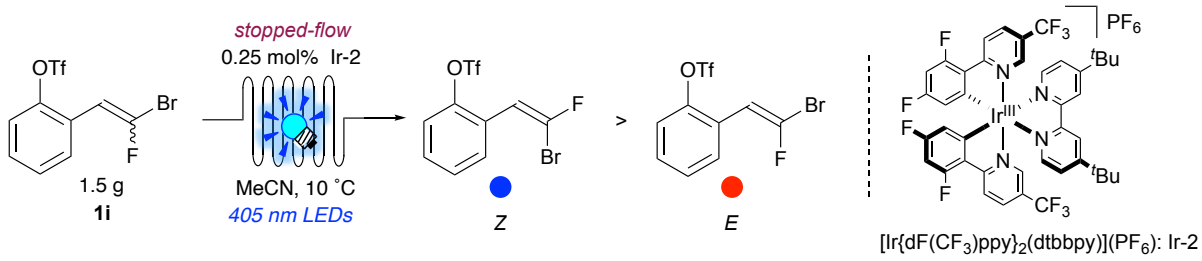


Figure S2. ^{19}F NMR spectra (58 MHz) of the photocatalytic isomerization of **1j**.

Gram-scale photocatalytic flow isomerization of 1i (Figure 2)



A 100 mL-Schlenk tube was charged with [Ir{dF(CF_3)ppy}$_2$(dtbbpy)](PF_6) (11 mg, 9.8 μmol), **1i** (1.47 g, 4.20 mmol), $C_6H_5CF_3$ (internal standard) (0.155 g) and dry MeCN (25.0 mL) under Ar. The reaction mixture was evacuated and refilled with Ar three times. The flow reactor was purged with N_2. Then, the reaction mixture was placed in a disposal syringe (50 mL), and pumped into the flow reactor (DFC: 2.7 mm in diameter, 65 cm in length x 15 → volume 56 mL). The flow reactor was irradiated with blue LED lamps ($h\nu$ = 405 nm) at 10 ˚C. Monitoring the reaction by in-line ^{19}F NMR spectroscopy confirmed the photostationary state. The product mixture was concentrated *in vacuo*. Without further purification, the residue was applied to the next reaction (see S15).

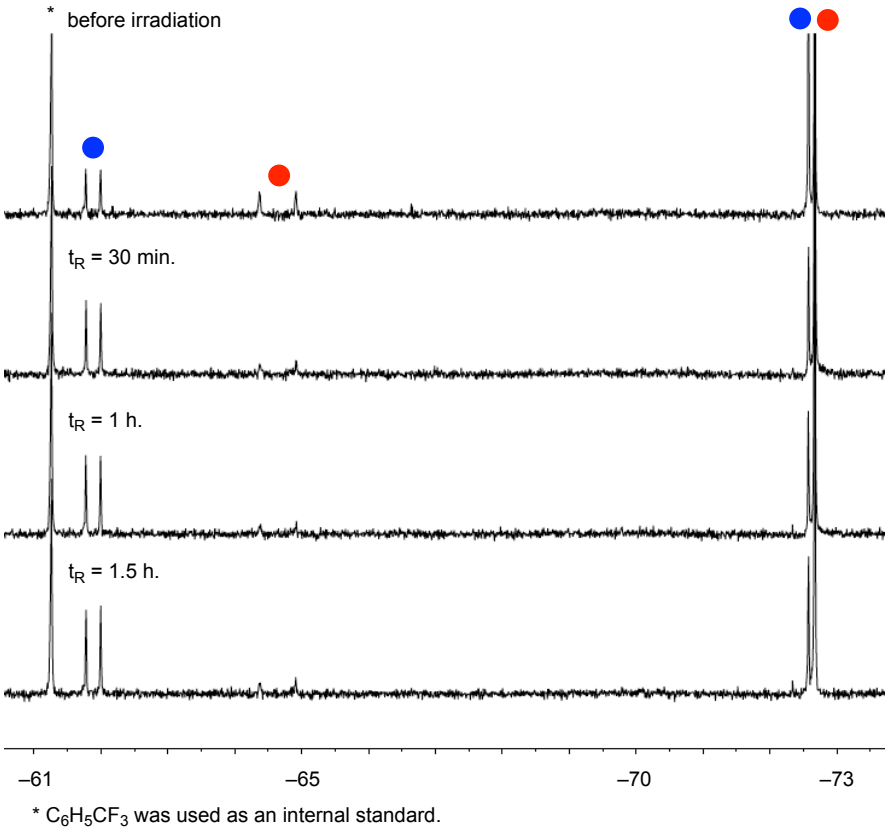
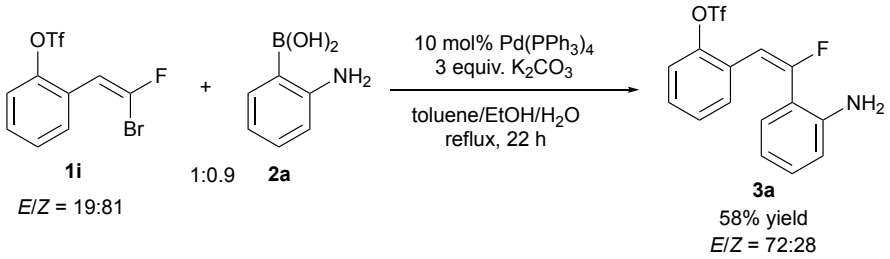


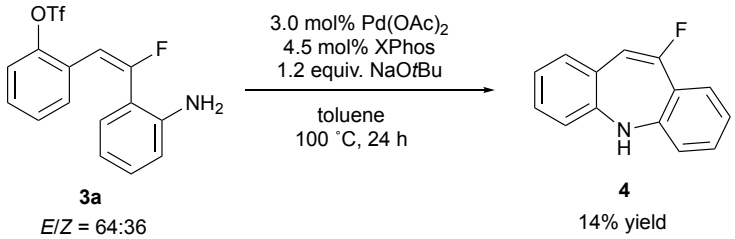
Figure S3. In-line ^{19}F NMR spectra (58 MHz) of the photocatalytic isomerization of **1i**.

Synthetic procedures and characterization for fluorinated 5*H*-dibenz[*b*,*f*]azepine (4) (Figure 2)

The title compound was prepared from the reaction of (*E*)-2-(2-(2-aminophenyl)-2-fluorovinyl)phenyl trifluoromethanesulfonate (*E*-**3a**), which was obtained from the following method.



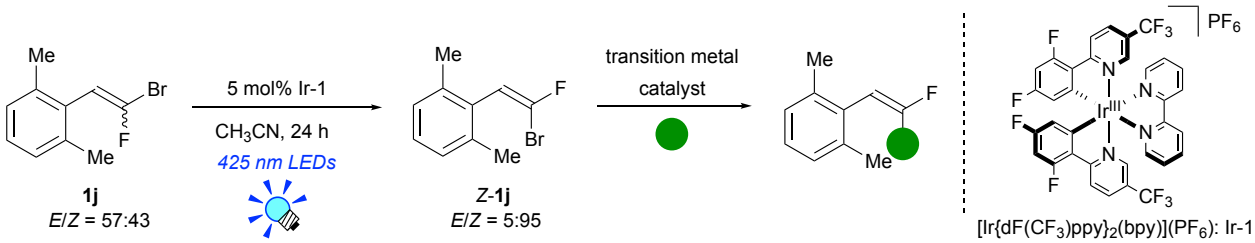
A 50 mL two-necked flask was charged with $Pd(PPh_3)_4$ (0.177 g, 0.153 mmol), K_2CO_3 (0.594 g, 4.30 mmol), **1i** (0.508 g, 1.45 mmol), which was obtained by the photocatalytic isomerization (see S14), toluene (15 mL), nitrogen bubbled EtOH/H_2O = 1:1 (6 mL), **2a** (0.174 g, 1.27 mmol) under Ar. The solution was refluxed for 22 h. Then, the reaction was quenched by H_2O (10 mL). The aqueous layer was extracted with Et_2O (10 m L × 3). The organic layer was washed with H_2O (10 mL×3) and brine (10 mL × 3), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Automated column chromatography (hexane/EtOAc = 8:2) afforded **3a** (0.345 g, 0.955 mmol, 58% yield, *E*/*Z* = 64:36) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$, rt): δ 8.02 (apparent dd; Ar–*H*), 7.42–6.66 (Ar–*H*), 6.58 (d, $^3J_{HF}$ = 20 Hz; *H*C=CF in *E* isomer), 6.31(d, $^3J_{HF}$ = 40 Hz; *H*C=CF in *Z* isomer), 4.04 (br. s; N–*H*). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –73.3 (C*F*$_3$SO$_2$O in *E* isomer), –73.4 (C*F*$_3$SO$_2$O in *Z* isomer), –84.2 (d, $^3J_{HF}$ = 19 Hz), –98.2 (d, $^3J_{HF}$ = 38 Hz). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): 160.1 (d, $^1J_{CF}$ = 266 Hz), 160.0 (d, $^1J_{CF}$ = 257 Hz), 147.2 (d, J_{CF} = 4 Hz), 146.6, 145.2, 145.0, 131.8 (d, J_{CF} = 3 Hz), 131.4, 131.1 (d, J_{CF} = 13 Hz), 130.9 (d, J_{CF} = 3 Hz), 130.3, 129.1 (d, J_{CF} = 6 Hz), 129.0, 128.8, 129.6, 128.3, 127.7 (d, J_{CF} = 13 Hz), 127.5 (d, J_{CF} = 3 Hz), 121.7, 121.6, 118.80 (q, $^1J_{CF}$ = 321 Hz), 118.75 (q, $^1J_{CF}$ = 321 Hz), 118.5, 118.2, 117.5 (d, J_{CF} = 25 Hz), 116.9, 116.3, 115.8 (d, J_{CF} = 25 Hz), 103.9 (d, $^2J_{CF}$ = 37 Hz), 100.8 (d, $^2J_{CF}$ = 10 Hz). **HRMS** (APCI) calcd m/z for $[C_{14}H_{10}FN+H]^+$ 212.0870, found 212.0871 $[M+H]^+$.



A 30 mL two-necked flask was charged with **3a** (0.255 g, 0.706 mmol), $Pd(OAc)_2$ (0.00670 g, 0.0298 mmol), XPhos (0.0207 g, 0.0434 mmol), NaO*t*Bu (0.111 g, 1.14 mmol), toluene (0.5 mL) under Ar. The solution was stirred at 100 °C for 24 h. Then, the reaction was diluted with ethyl acetate (5 mL). The organic layer was washed with $NaHCO_3$ (10 mL × 3), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Automated column chromatography (hexane/EtOAc = 85:15) afforded **4** (0.0212 g, 0.100 mmol, 14% yield) as a yellow solid.

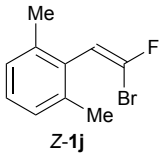
^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.27 (d, J_{HH} = 8 Hz, 1H; Ar–*H*), 7.17 (apparent td, 1H; Ar–*H*), 7.06 (m, 1H; Ar–*H*), 6.93 (apparent br. t, 1H; Ar–*H*), 6.90 (d, J_{HH} = 4 Hz, 2H; Ar–*H*), 6.59 (apparent br. t, 2H; Ar–*H*), 6.27 (d, $^{3}J_{HF}$ = 20 Hz, 1H; *H*C=CF), 5.10 (br. s, 1H; N–*H*). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –102.5 (d, $^{3}J_{HF}$ = 19 Hz). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): 158.0 (d, $^{1}J_{CF}$ = 248 Hz), 148.7 (d, J_{CF} = 7 Hz), 146.4, 131.5, 130.2 (d, J_{CF} = 4 Hz), 129.1, 126.24, 126.17 (d, J_{CF} = 7 Hz), 124.7 (d, $^{2}J_{CF}$ = 29 Hz), 123.8, 123.0, 119.7, 119.68 (d, J_{CF} = 3 Hz), 111.5 (d, $^{2}J_{CF}$ = 31 Hz). **HRMS** (APCI) calcd m/z for $[C_{14}H_{10}FN+H]^{+}$ 212.0870, found 212.0871 $[M+H]^{+}$.

Pot-economical procedures and characterization for monofluoroalkenes (3b–e) (Scheme 2)



General procedures for photocatalytic isomerization: A Schlenk tube was charged with Ir-1 (5.0 mol%). To the tube, **1j** (1.0 equiv.) and CH_3CN were added under Ar atmosphere. The mixture was degassed by three freeze-pump-thaw cycles. The tube was placed at a distance of –1 cm away from LED lamps (λ = 425 nm) under wind blowing. The reaction was carried out under light irradiation for 24 h at room temperature (25 – 27˚C). After then, the solution was concentrated *in vacuo.* The isomer ratio was confirmed by ^{19}F NMR spectroscopy. The residue was applied to the following transition-metal-catalyzed reactions without any purification.

2-((*Z*)-2-Bromo-2-fluoroethenyl)-1,3-dimethylbenzene (*Z*-**1j**)

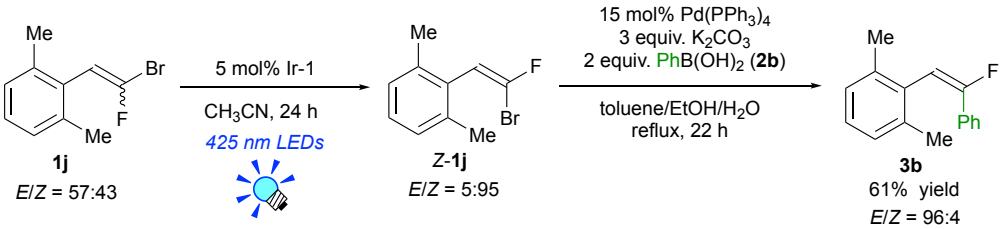


Z-**1j**

A reaction mixture of Ir-1 (0.0213 g 0.0211 mmol), **1j** (0.0721 g, 0.315 mmol), CH_3CN (1.50 mL) in a 10 mL Schlenk tube afforded *Z*-enriched **1j** (*E*/*Z* = 5:95).

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.2-7.1 (3H; Ar–*H*), 6.52 (d, $^3J_{HF}$ = 8 Hz, 1H; *H*C=CBrF), 2.26 (s, 6H; C*H*$_3$). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –68.6 (d, $^3J_{HF}$ = 11 Hz). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): 137.5 (d, $^1J_{CF}$ = 322 Hz), 137.1 (d, J_{CF} = 3 Hz), 131.2 (d, J_{CF} = 6 Hz), 128.2, 127.6, 126.1 (d, $^2J_{CF}$ = 19 Hz), 20.3.

2-((*E*)-2-Fluoro-2-phenylethenyl)-1,3-dimethylbenzene (**3b**)



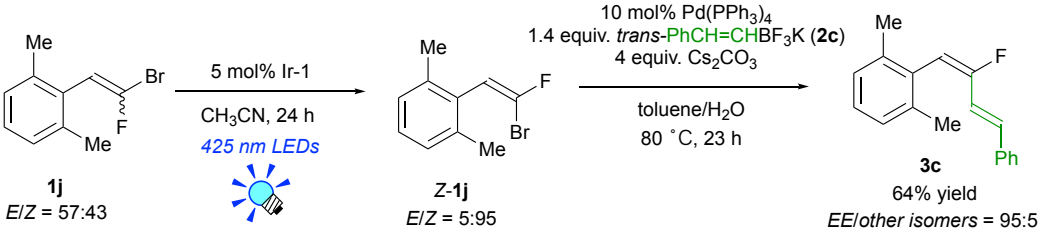
A reaction mixture of Ir-1 (0.0213 g 0.0211 mmol), **1j** (0.0721 g, 0.315 mmol), CH_3CN (1.50 mL) in a 10 mL Schlenk tube afforded *Z*-enriched **1j** (*E*/*Z* = 5:95), which was confirmed by ^{19}F NMR spectroscopy (58 MHz).

The tube was charged with $Pd(PPh_3)_4$ (0.0562 g, 0.0486 mmol), K_2CO_3 (0.119 g, 0.861 mmol), toluene (4.00 mL), N_2-bubbled mixed solvent (EtOH:H_2O = 1:1, 2.00 mL), phenylboronic acid (**2b**) (0.0776 g,

0.636 mmol) under Ar. The reaction mixture was stirred for 22 h at reflux. Then, the reaction was quenched by H_2O (10 mL). The aqueous layer was extracted with Et_2O (10 mL × 3). The organic layer was washed with H_2O (10 mL × 3) and brine (10 mL × 3), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Automated column chromatography afforded **3b** as a white solid (0.0430 g, 0.191 mmol, 61% yield, *E*/*Z* = 96:4). Column eluent: hexane.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.3–7.1 (8H; Ar–*H*), 6.42 (d, $^3J_{HF}$ = 20 Hz, 1H; *H*C=CF), 2.24 (s, 6H; C*H*$_3$). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –105.8 (d, $^3J_{HF}$ = 23 Hz). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): 156.6 (d, $^1J_{CF}$ = 245 Hz), 136.9 (d, J_{CF} = 2 Hz), 132.4, 132.36 (d, $^2J_{CF}$ = 41 Hz), 129.1, 128.4 (d, J_{CF} = 2 Hz), 127.9, 127.6, 126.1 (d, J_{CF} = 7 Hz), 106.8 (d, $^2J_{CF}$ = 29 Hz), 20.5. **HRMS** (APPI) calcd m/z for $[C_{16}H_{15}F]^+$ 226.1152, found 226.1151 $[M]^+$.

2-((1*E*,3*E*)-2-Fluoro-4-phenylbuta-1,3-dien-1-yl)-1,3-dimethylbenzene (**3c**)

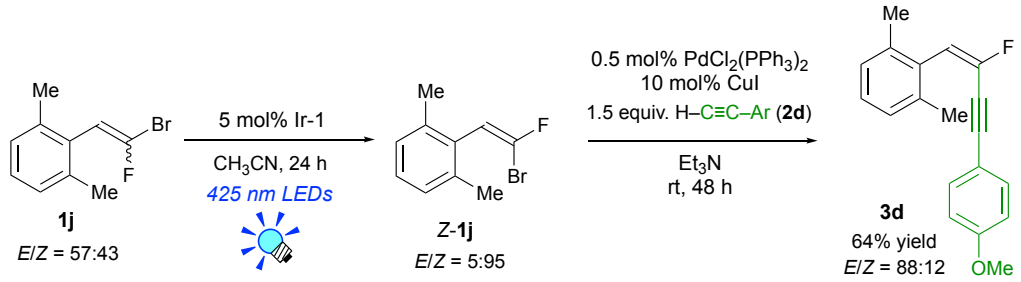


A reaction mixture of Ir-1 (0.0221 g 0.0219 mmol), **1j** (0.0801 g, 0.349 mmol), CH_3CN (1.45 mL) in a 10 mL Schlenk tube afforded *Z*-enriched **1j** (*E*/*Z* = 5:95), which was confirmed by ^{19}F NMR spectroscopy (58 MHz).

The tube was charged with $Pd(PPh_3)_4$ (0.0542 g, 0.0469 mmol), Cs_2CO_3 (0.259 g, 1.34 mmol), potassium *trans*-styryltrifluoroborate (**2c**) (0.105 g, 0.499 mmol), toluene (3 mL), N_2-bubbled H_2O (1 mL) under Ar. The reaction mixture was stirred for 23 h at 80 °C. Then, the reaction was quenched by H_2O (5 mL). The aqueous layer was extracted with Et_2O (5 mL × 3). The organic layer was washed with H_2O (5 mL × 3) and brine (5 mL × 3), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Automated column chromatography afforded **3c** as a white solid (0.0565 g, 0.224 mmol, 64% yield, *EE*/*other stereoisomers* = 95:5). Column eluent: hexane/EtOAc = 99:1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.5–7.2 (8H; Ar–*H*), 7.11 (d, $^3J_{HH}$ = 20 Hz, 1H; HC=C*H*Ph), 6.38 (dd, $^3J_{HF}$ = 24 Hz, $^3J_{HH}$ = 16 Hz; CF–*H*C=CHPh), 6.32 (br. d, $^3J_{HF}$ = 20 Hz, 1H; *H*C=CF), 2.40 (s, 6H; C*H*$_3$). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –117.5 (dd, $^3J_{HF}$ = 19 Hz, $^3J_{HF}$ = 26 Hz). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): 157.1 (d, $^1J_{CF}$ = 248 Hz), 137.5 (d, J_{CF} = 3 Hz),136.2, 132.0 (d, J_{CF} = 12 Hz), 131.0 (d, J_{CF} = 4 Hz), 128.8, 128.6, 127.7, 127.6, 127.1, 117.1 (d, $^2J_{CF}$ = 23 Hz),, 108.5 (d, $^2J_{CF}$ = 27 Hz), 20.9. **HRMS** (APPI) calcd m/z for $[C_{18}H_{17}F]^+$ 252.1309, found 252.1306 $[M]^+$.

2-((*E*)-2-Fluoro-4-(4-methoxyphenyl)but-1-en-3-yn-1-yl)-1,3-dimethylbenzene (**3d**)

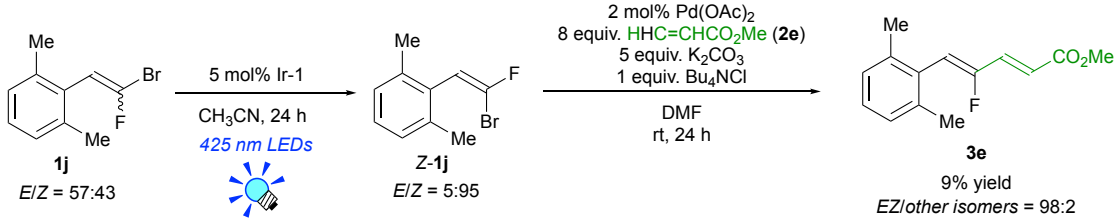


A reaction mixture of Ir-1 (0.0231 g 0.0229 mmol), **1j** (0.104 g, 0.453 mmol), CH_3CN (1.45 mL) in a 10 mL Schlenk tube afforded *Z*-enriched **1j** (*E*/*Z* = 5:95), which was confirmed by ^{19}F NMR spectroscopy (58 MHz).

The tube was charged with $PdCl_2(PPh_3)_2$ (0.0161 g, 0.00229 mmol), CuI (0.00780 g, 0.0410 mmol), 4-ethynylanisole (**2d**) (0.0881 g, 0.661 mmol), Et_3N (0.500 mL) under Ar. The reaction mixture was stirred for 48 h at room temperature. Then, the reaction was quenched by H_2O (5 mL). The aqueous layer was extracted with Et_2O (10 mL). The organic layer was washed with brine (10 mL × 3), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Automated column chromatography afforded **3d** as a clear green solid (0.0731 g, 0.292 mmol, 64% yield, *E*/*Z* = 88:12). Column eluent: hexane/EtOAc = 9/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.5-6.8 (Ar-*H*), 6.57 (d, $^3J_{HF}$ = 12 Hz; *H*C=CF in *E* isomer), 6.22 (d, $^3J_{HF}$ = 36 Hz; *H*C=CF in *Z* isomer), 3.84 (s; OC*H*$_3$ in *Z* isomer), 3.79 (s; OC*H*$_3$ in *E* isomer), 2.35 (s; C*H*$_3$ in *E* isomer), 2.32 (br. s; C*H*$_3$ in *Z* isomer). **^{19}F NMR** (376 MHz, CD_3CN): δ -99.7 (d, $^3J_{HF}$ = 38 Hz; in *Z* isomer), –102.3 (d, $^3J_{HF}$ = 11 Hz; in *E* isomer). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 160.5, 143.1 (d, $^1J_{CF}$ = 237 Hz), 137. 4 (d, J_{CF} = 2 Hz), 133.4 (d, J_{CF} = 2 Hz), 131.1 (d, J_{CF} = 8 Hz), 127.7, 127.5, 114.8 (d, $^2J_{CF}$ = 30 Hz), 114.2, 113. 5 (d, J_{CF} = 2 Hz), 95.7 (d, $^3J_{CF}$ = 7 Hz), 79.3 (d, $^2J_{CF}$ = 43 Hz), 55.5, 20.7. **HRMS** (APCI) calcd m/z for $[C_{19}H_{17}FO+H]^+$ 281.1336, found 281.1334 $[M+H]^+$.

Methyl (2*E*,4*Z*)-5-(2,6-dimethylphenyl)-4-fluoropenta-2,4-dienoate (**3e**)



A reaction mixture of Ir-1 (0.0221 g 0.0219 mmol), **1j** (0.104 g, 0.454 mmol), CH_3CN (1.45 mL) in a 10 mL Schlenk tube afforded *Z*-enriched **1j** (*E*/*Z* = 5:95), which was confirmed by ^{19}F NMR spectroscopy (58 MHz).

The tube was charged with $PdOAc_2$ (0.00210 g, 0.0102mmol) and DMF (5 mL) under Ar. The mixture was stirred for 15 min at room temperature. Then, to the mixture, K_2CO_3 (0.167 g, 1.21 mmol), Bu_4NCl

(0.121 g, 0.437 mmol), and methyl acrylate (**2e**) (0.227 g, 3.78 mmol) were added under Ar. The reaction mixture was stirred for 24 h at room temperature. After then, the mixture was concentrated *in vacuo*. Automated column chromatography afforded **3e** as a light brown liquid (0.0098 g, 0.0418 mmol, 9% yield, *EZ*/*other isomers* = 98:2). Stereochemistry was determined by coupling constants and NOESY. Column eluent: hexane/EtOAc = 9/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.26 (dd, $^{3}J_{HH}$ = 16 Hz, $^{3}J_{HF}$ = 24 Hz, 1H; CFC*H*), 7.14 (m, 1H; Ar-*H*), 7.06 (d, $^{3}J_{HH}$ = 8 Hz, 2H; Ar-*H*), 6.24 (apparent dt, $^{3}J_{HH}$ = 16 Hz; HC=C*H*CO), 6.16 (d, $^{3}J_{HF}$ = 40 Hz; *H*C=CF), 3.81 (s, 3H; OCH_3), 2.26 (apparent d, 6H; CH_3). **^{19}F NMR** (376 MHz, CD_3CN): δ –115.3 (dd, $^{3}J_{HF}$ = 38 Hz, 26 Hz). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 167.0, 154.4 (d, $^{1}J_{CF}$ = 258 Hz), 137.0, 136.0 (d, J_{CF} = 24 Hz), 130.7, 128.2, 127.6, 119.1, 115.8 (d, J_{CF} = 16 Hz), 52.1, 20.6 (d, J_{CF} = 2 Hz). **HRMS** (APCI) calcd m/z for $[C_{14}H_{15}FO_2+H]^+$ 235.1129, found 235.1129 $[M+H]^+$.

DFT calculation studies (Figure 1)

Quantum chemical calculations were performed by using Gaussian 16, Revision C.02 program package.[8] The geometry optimizations were carried out at the BLYP/def2-TZVP[9,10] level of theory. Gibbs free energies were calculated as a sum of the single-point electronic energy and thermal correction to the Gibbs free energy. Singlet and triplet excitation energies were calculated with TD-DFT using the BLYP functional.

(1) Optimized structure of *E*-**1j**

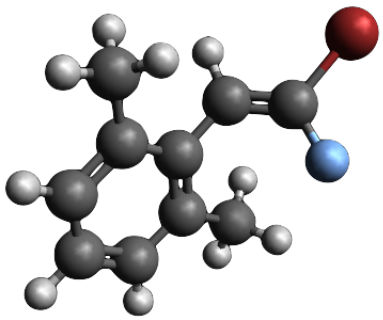


Table S1. Cartesian coordinates and electronic energies after geometry optimization of *E*-**1j**

C	-3.99140	-0.20040	0.17050
C	-3.17380	-1.31060	-0.04060
C	-1.78880	-1.17370	-0.23720
C	-1.22320	0.12870	-0.21090
C	-2.05700	1.26590	-0.01840
C	-3.43210	1.08030	0.17580
H	-5.06250	-0.33030	0.32100
H	-3.61300	-2.30780	-0.06720
H	-4.06850	1.95080	0.33510
C	1.24630	-0.16790	0.23630
C	-1.47900	2.66800	-0.00220
H	-0.68960	2.77450	0.75480
H	-1.02860	2.93640	-0.97010
H	-2.25950	3.40660	0.21370
C	-0.96290	-2.41770	-0.50130
H	-0.18950	-2.24110	-1.25930
H	-0.44960	-2.76400	0.40650
H	-1.60460	-3.23520	-0.85090
Br	3.09810	0.18630	-0.11080
F	1.09400	-1.02900	1.26710

C	0.22520	0.36900	-0.44020
H	0.50470	1.09940	-1.19840

Sum of electronic and zero-point Energies= -3060.919544 hartree
Sum of electronic and thermal Energies= -3060.907238 hartree
Sum of electronic and thermal Enthalpies= -3060.906294 hartree
Sum of electronic and thermal Free Energies= -3060.959344 hartree

Table S2 TDDFT-calculated vertical excitation energies of *E*-**1j** (BLYP/def2-TZVP).

First triplet excitation

Excited State 1: 3.3565 eV (323.86 kJ/mol) 369.39 nm f=0.0000 <S**2>=2.000

55 -> 61	-0.11330
56 -> 60	-0.16662
57 -> 58	0.66399
57 -> 59	-0.12539

First singlet excitation

Excited State 4: 4.3283 eV (417.62 kJ/mol) 286.45 nm f=0.0117 <S**2>=0.000

56 -> 58	0.60170
56 -> 59	0.12622
57 -> 58	0.12955
57 -> 59	0.16968
57 -> 60	0.26027

(2) Optimized structure of *Z*-**1j**

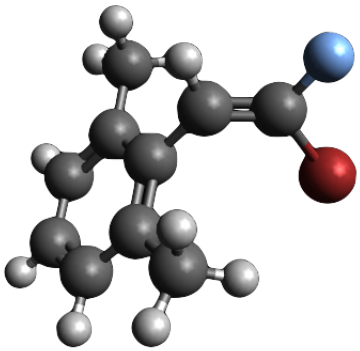


Table S3. Cartesian coordinates and electronic energies after geometry optimization of *Z*-**1j**

C	3.41520	0.42200	-0.70930
C	2.65160	1.45060	-0.15400
C	1.42860	1.18400	0.48310
C	0.97230	-0.15630	0.54730
C	1.75060	-1.20840	0.00110
C	2.96650	-0.89820	-0.62710
H	4.36170	0.64780	-1.19930
H	3.00810	2.47930	-0.20660
H	3.56430	-1.70310	-1.05460
C	1.28500	-2.64950	0.08060
H	2.01820	-3.32090	-0.38120
H	1.14120	-2.97420	1.12160
H	0.32300	-2.79320	-0.43050
C	0.63510	2.32540	1.09030
H	-0.28850	2.52150	0.52790
H	0.33820	2.10950	2.12540
H	1.22680	3.24840	1.09140
C	-0.30140	-0.49070	1.24760
H	-0.24520	-0.91150	2.25690
C	-1.54000	-0.36700	0.76940
F	-2.62830	-0.70890	1.50310
Br	-2.03930	0.26870	-0.96440

Sum of electronic and zero-point Energies= -3060.918090 hartree

Sum of electronic and thermal Energies= -3060.905602 hartree

Sum of electronic and thermal Enthalpies= -3060.904658 hartree

Sum of electronic and thermal Free Energies= -3060.958956 hartree

Table S4 TDDFT-calculated vertical excitation energies of *Z*-**1j** (BLYP/def2-TZVP).

First triplet excitation

Excited State	1:	3.7499 eV (361.81 kJ/mol)	330.63 nm	f=0.0000	<S**2>=2.000
55 -> 58	-0.11776				
55 -> 61	-0.16352				
56 -> 58	0.48655				
56 -> 59	-0.20833				
56 -> 60	-0.13693				
57 -> 58	-0.13744				
57 -> 59	0.10065				
57 -> 60	-0.33136				
57 -> 61	-0.10758				

First singlet excitation

Excited State	4:	4.5345 eV (437.52 kJ/mol)	273.42 nm	f=0.0039	<S**2>=0.000
56 -> 58	0.11594				
56 -> 60	0.14338				
57 -> 58	0.56168				
57 -> 59	0.36777				
57 -> 61	-0.10765				

(3) Optimized structure of the biradical intermediate

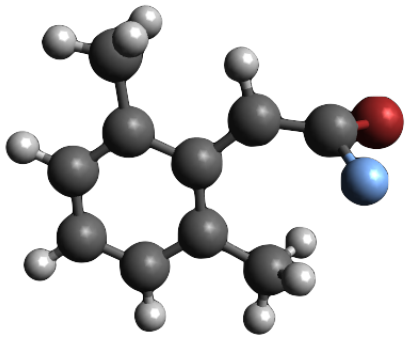


Table S5. Cartesian coordinates and electronic energies after geometry optimization of the biradical intermediate

C	3.63640	0.95620	-0.46300
C	2.50580	1.75620	-0.26430
C	1.25980	1.21490	0.05880
C	1.13050	-0.22350	0.19420
C	2.31430	-1.04210	-0.02520
C	3.52680	-0.43500	-0.34130
H	4.59350	1.41180	-0.71260
H	2.59380	2.83780	-0.36360
H	4.40560	-1.05940	-0.50010
C	2.27360	-2.55370	0.08270
H	3.26470	-2.97330	-0.12290
H	1.97250	-2.88950	1.08580
H	1.56890	-3.00110	-0.63330
C	0.10560	2.17380	0.25180
H	-0.72360	1.96780	-0.43690
H	-0.30250	2.12710	1.26870
H	0.44050	3.20160	0.07150
C	-0.06800	-0.91130	0.54600
H	0.00690	-1.99840	0.57460
C	-1.42820	-0.48110	0.82190
F	-1.68760	0.33070	1.88750
Br	-2.69060	-0.15220	-0.63970

Sum of electronic and zero-point Energies= -3060.840031 hartree

Sum of electronic and thermal Energies= -3060.827494 hartree

Sum of electronic and thermal Enthalpies= -3060.826549 hartree

Sum of electronic and thermal Free Energies= -3060.881199 hartree

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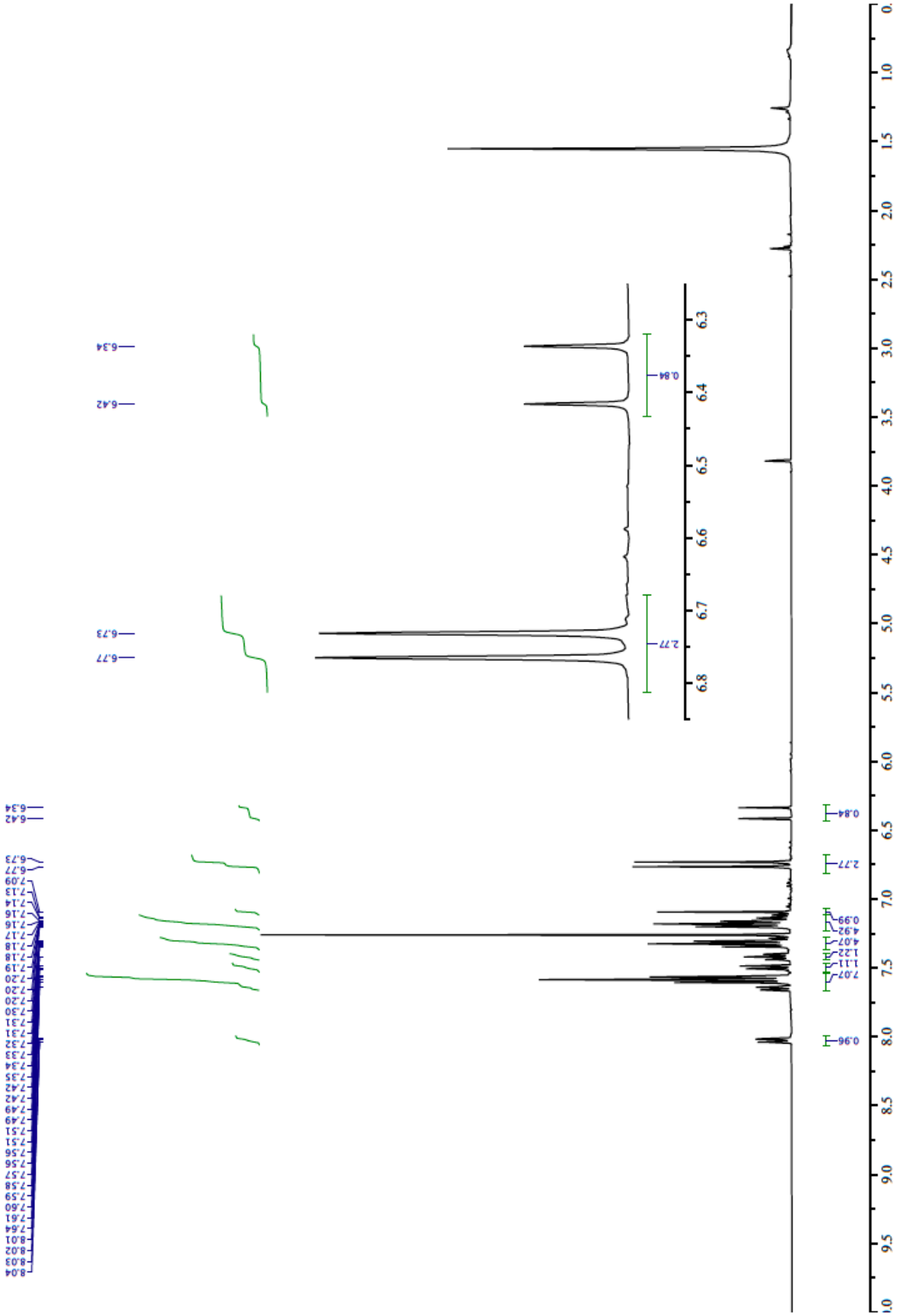
NMR spectra

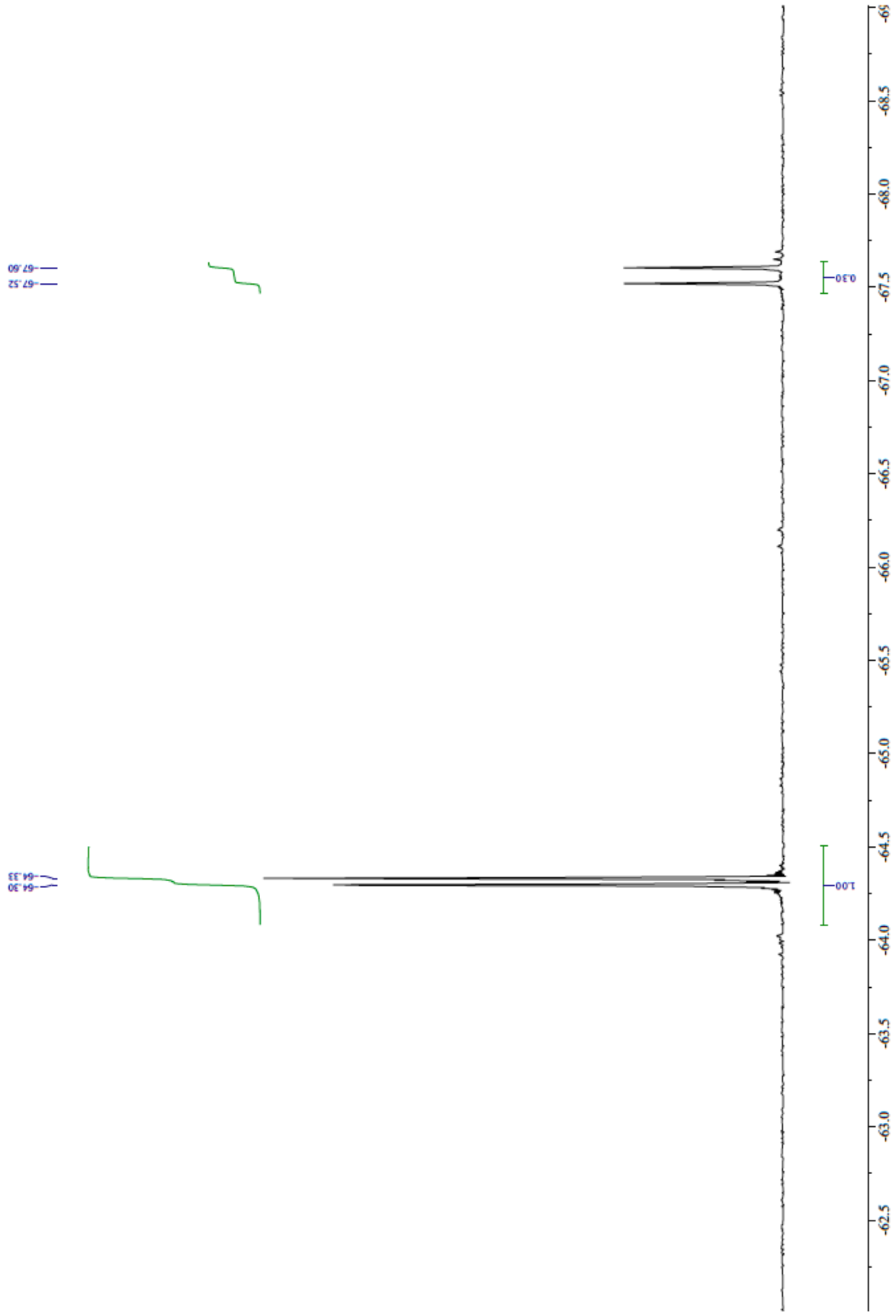
Z-enriched 1-bromo-2-(2-bromo-2-fluoroethenyl)benzene (**1a**) (*Z*-**1a**)

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



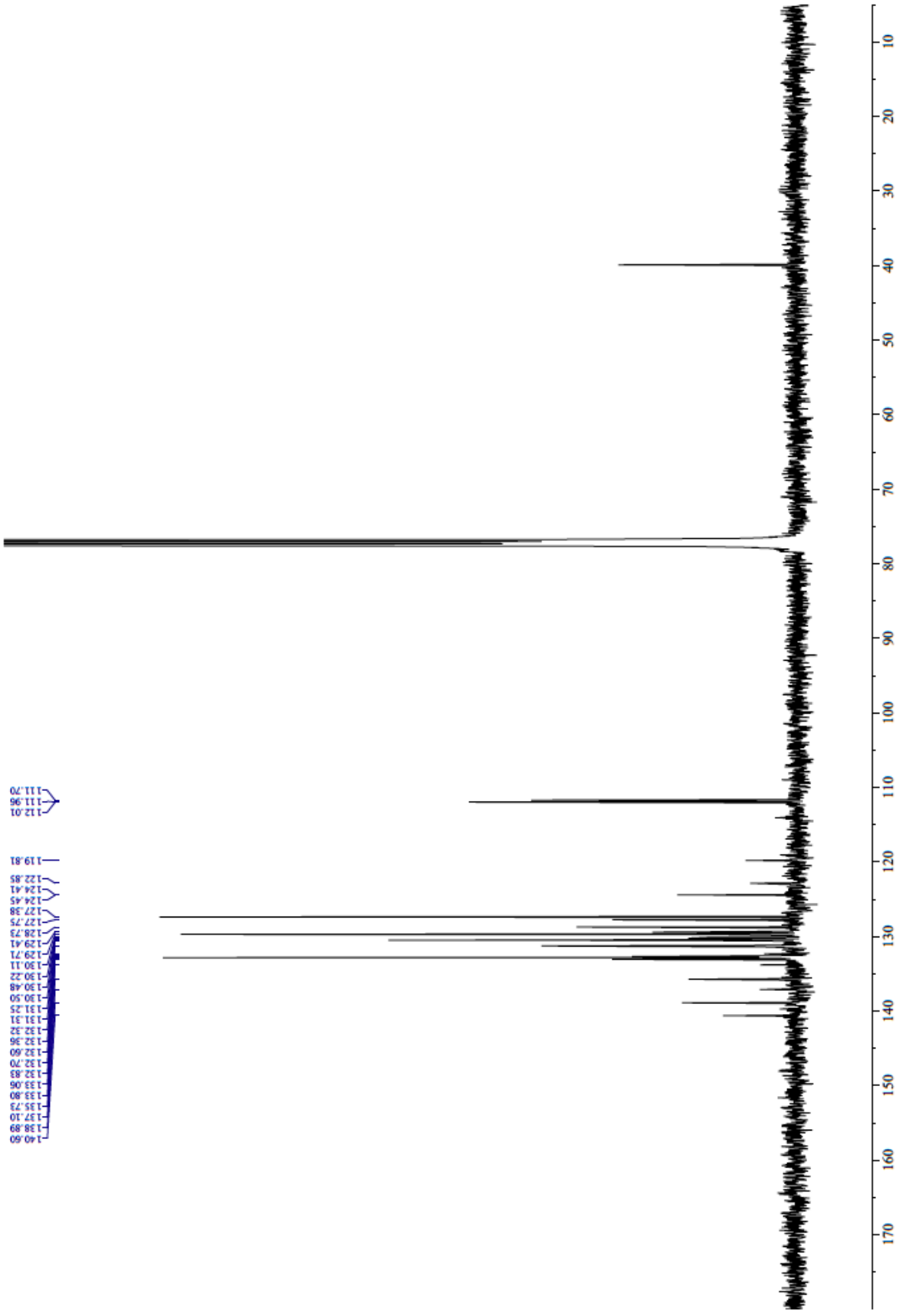
Z-enriched 1-bromo-2-(2-bromo-2-fluoroethenyl)benzene (**1a**) (*Z*-**1a**)

^{19}F NMR (376 MHz, $CDCl_3$, rt)



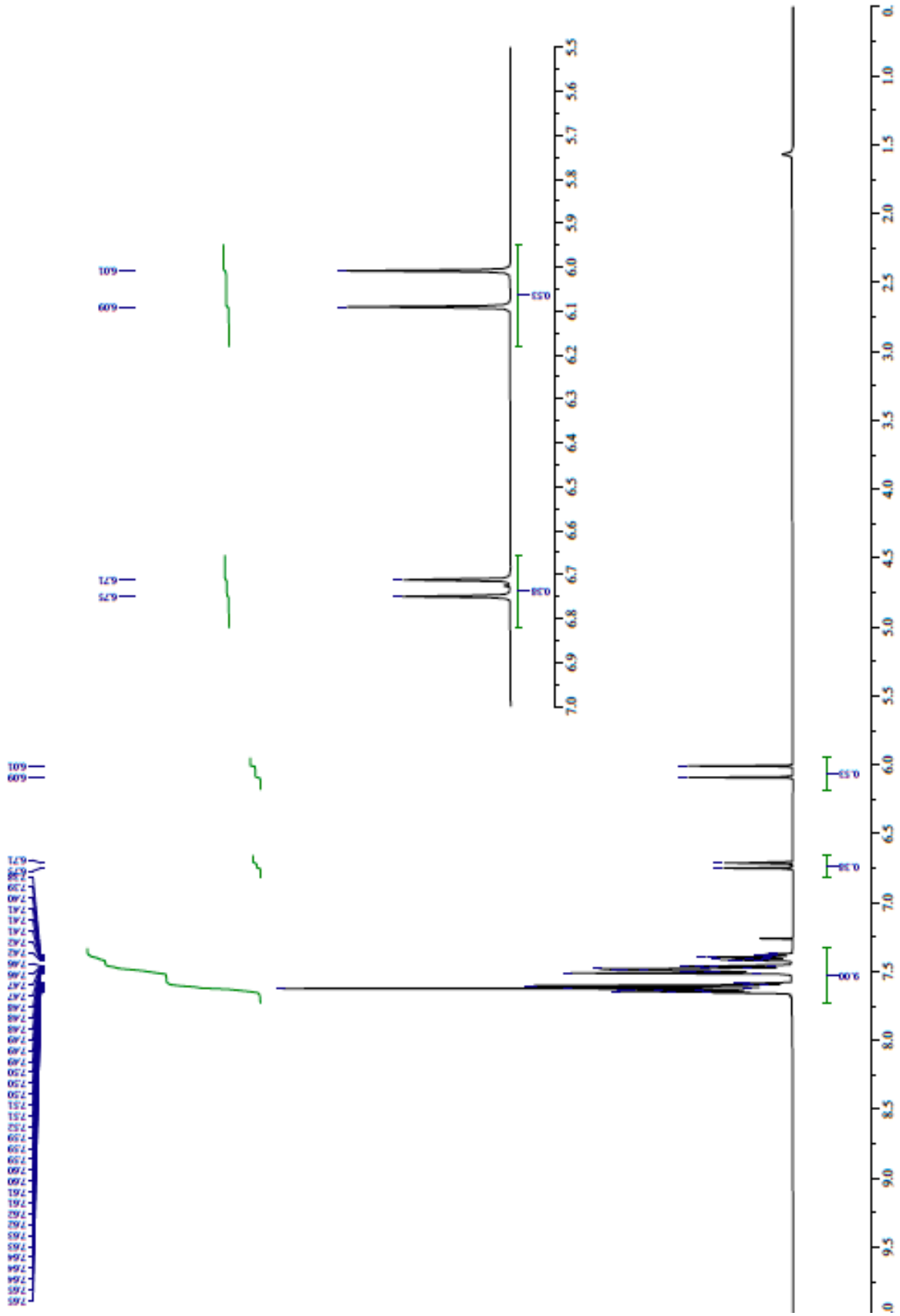
Z-enriched 1-bromo-2-(2-bromo-2-fluoroethenyl)benzene (**1a**) (*Z*-**1a**)

^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)



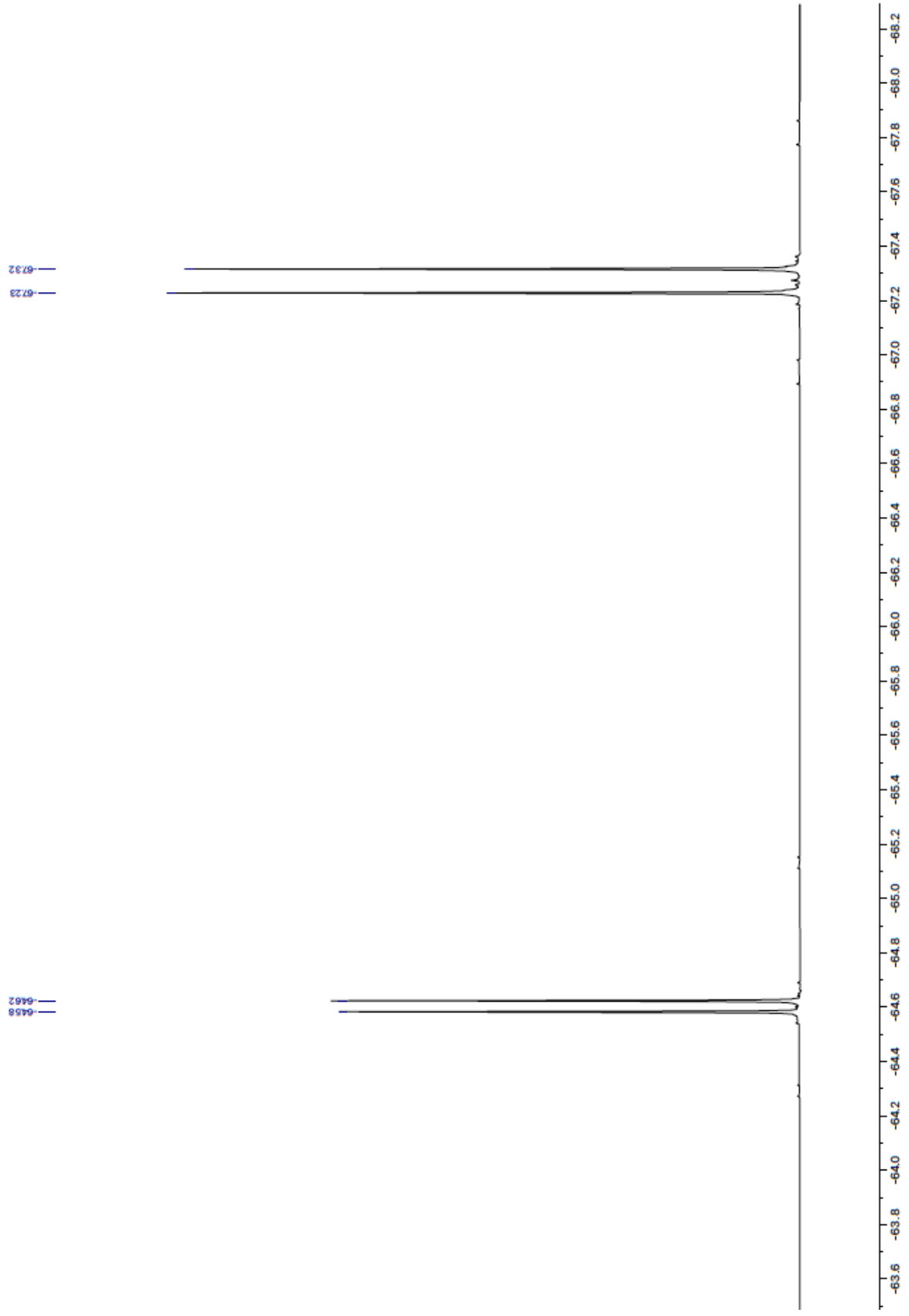
4-(2-Bromo-2-fluoroethenyl)-1,1'-biphenyl (**1d**)

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



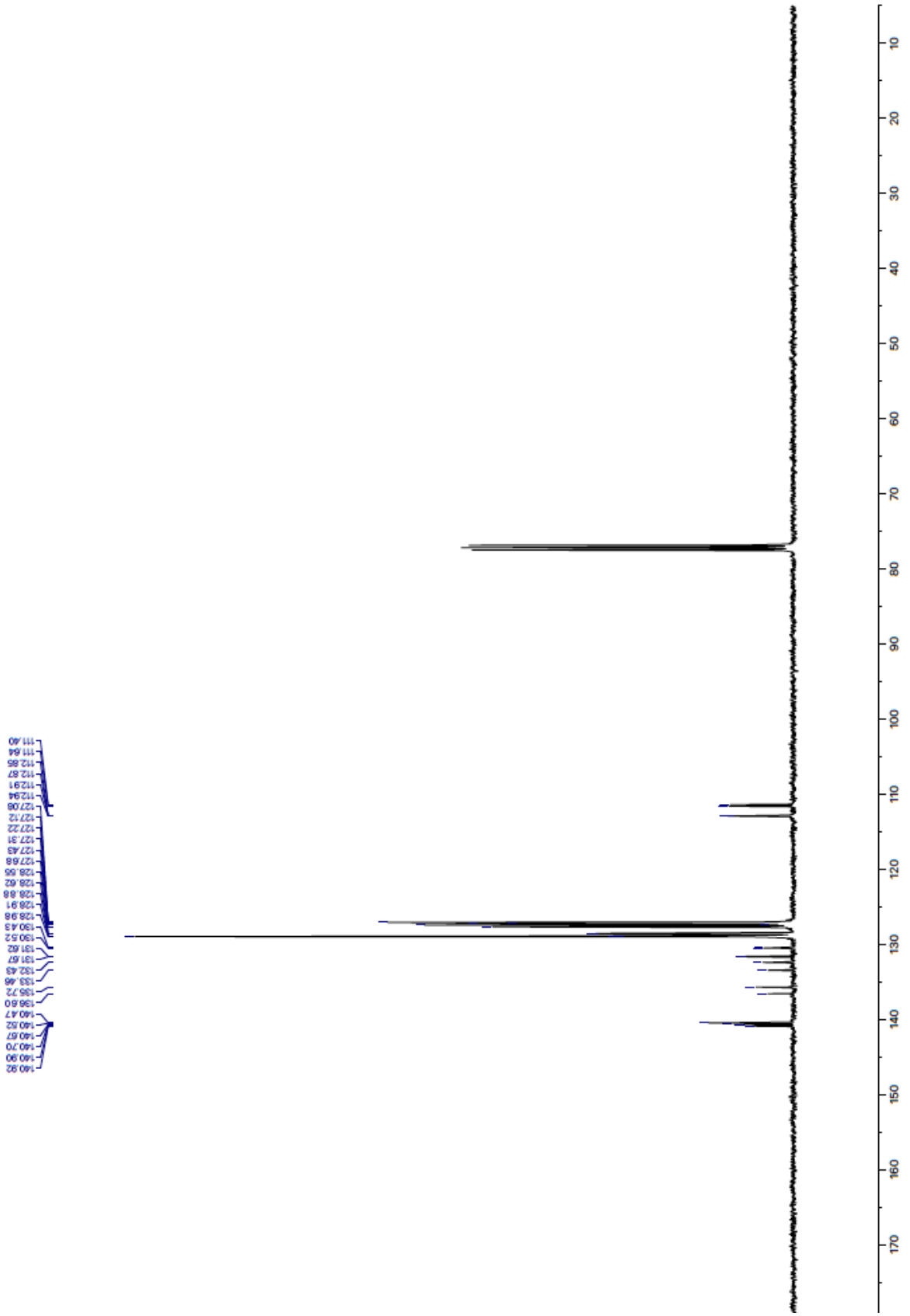
4-(2-Bromo-2-fluoroethenyl)-1,1'-biphenyl (**1d**)

^{19}F NMR (376 MHz, $CDCl_3$, rt)



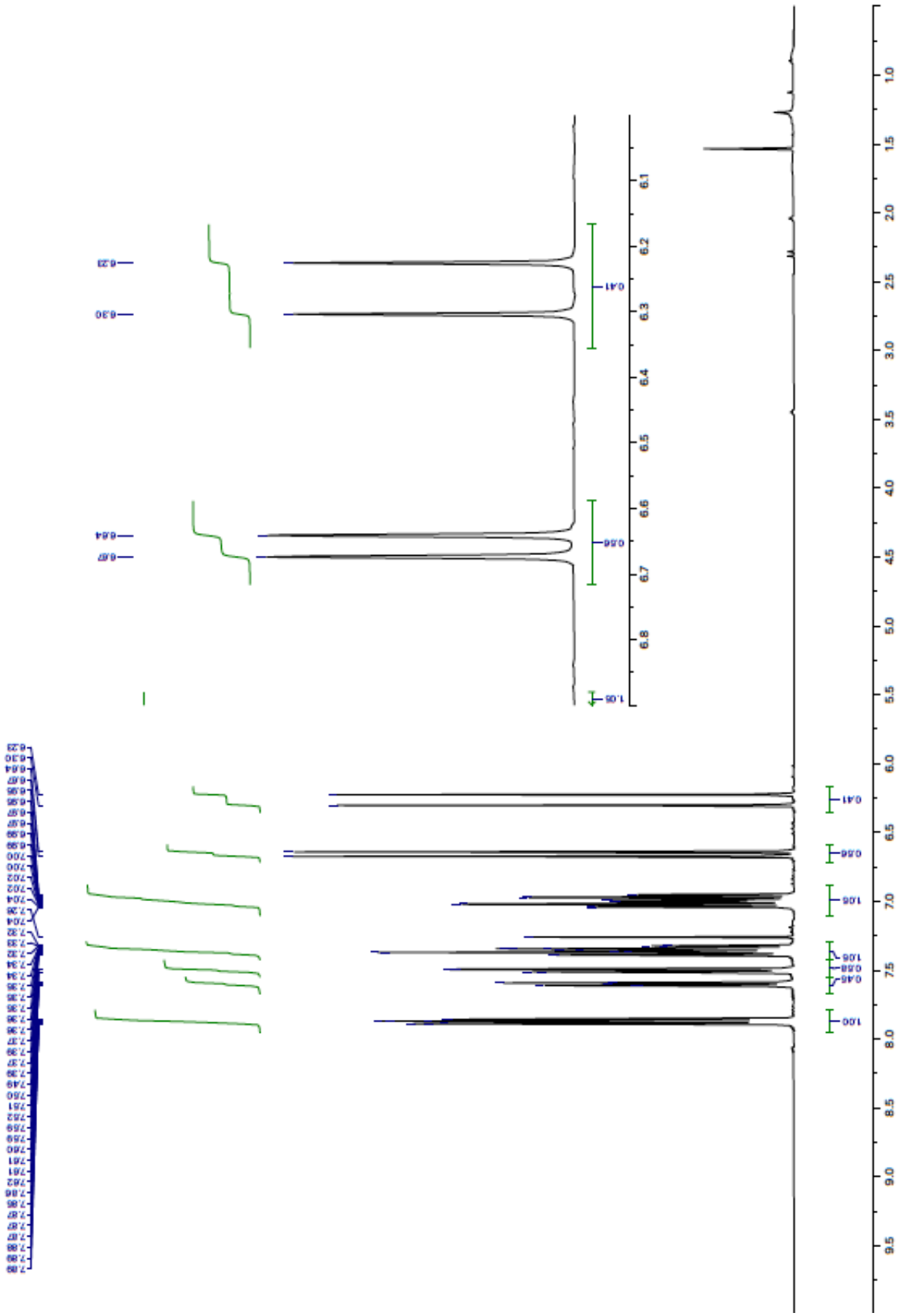
4-(2-Bromo-2-fluoroethenyl)-1,1'-biphenyl (**1d**)

^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)



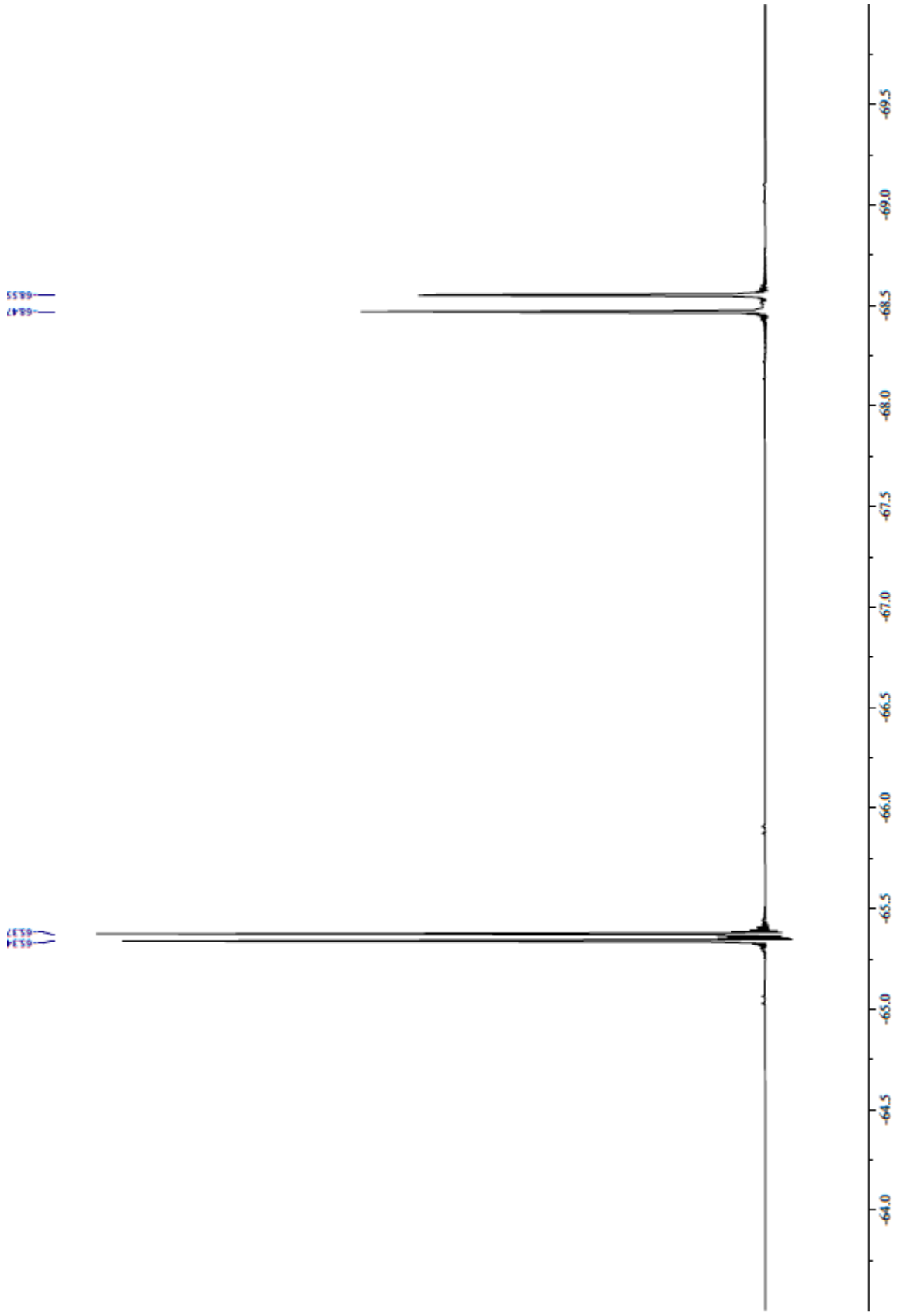
1-(2-Bromo-2-fluoroethenyl)-2-iodobenzene (**1h**)

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



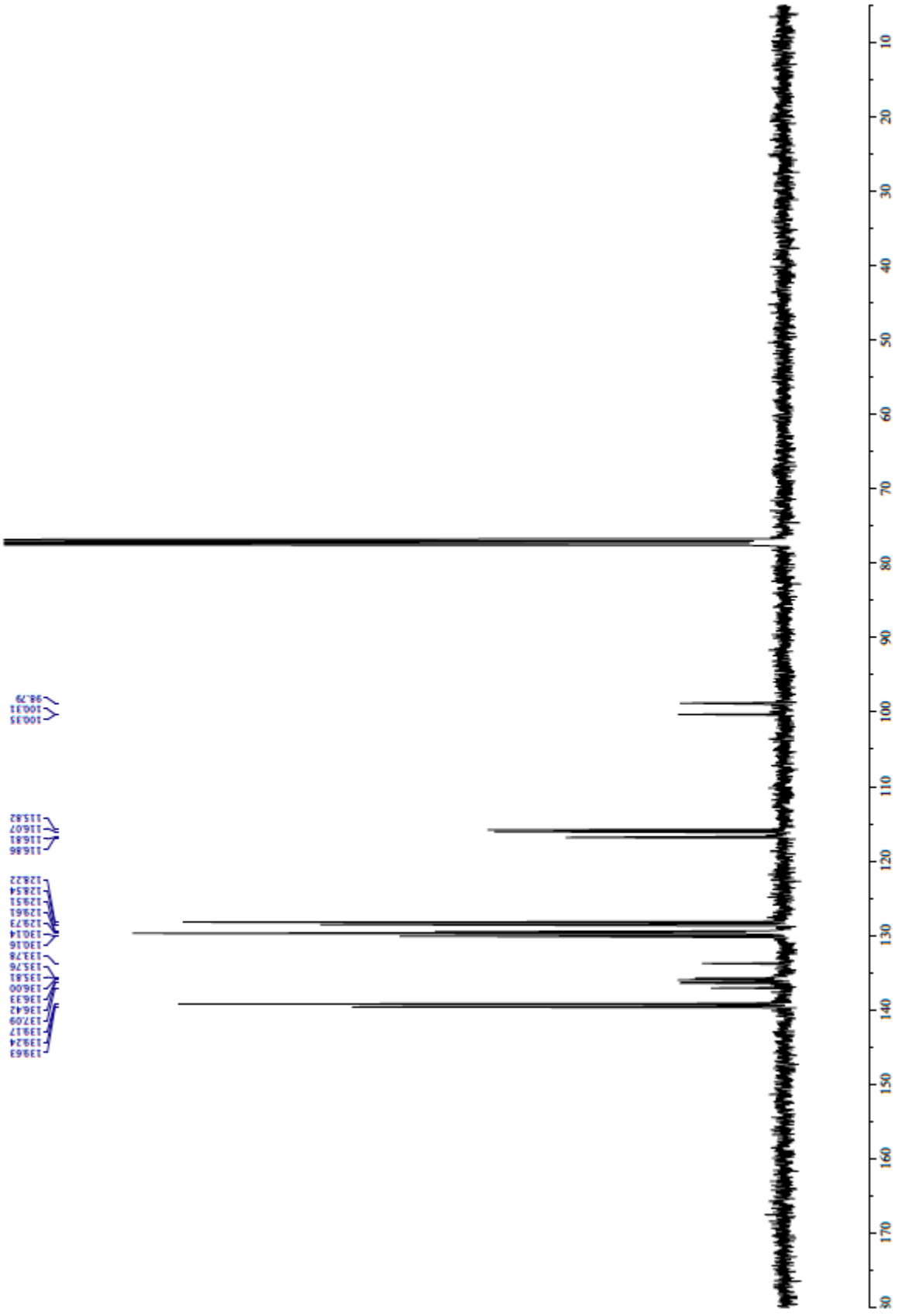
1-(2-Bromo-2-fluoroethenyl)-2-iodobenzene (**1h**)

^{19}F NMR (376 MHz, $CDCl_3$, rt)



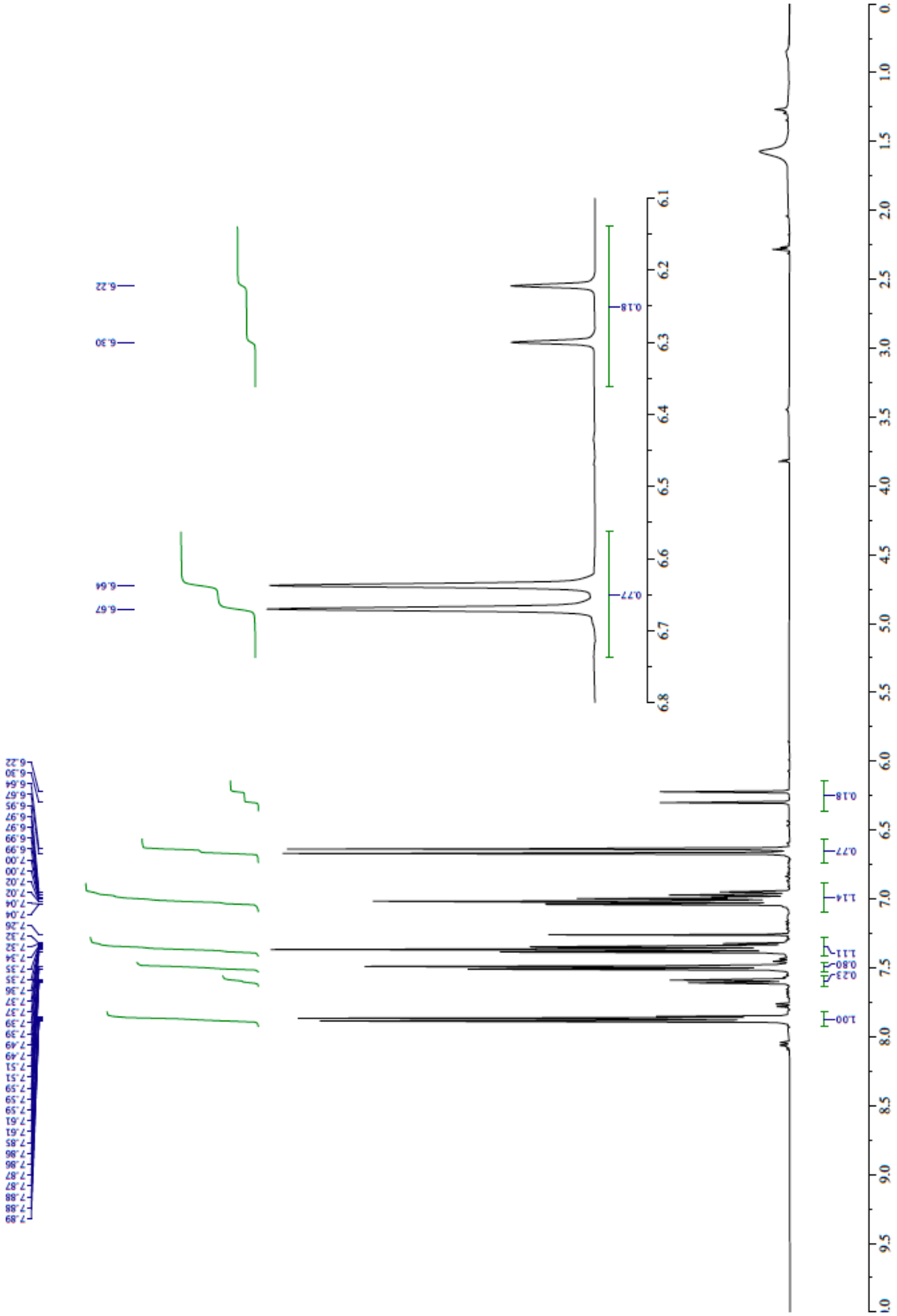
1-(2-Bromo-2-fluoroethenyl)-2-iodobenzene (**1h**)

^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)



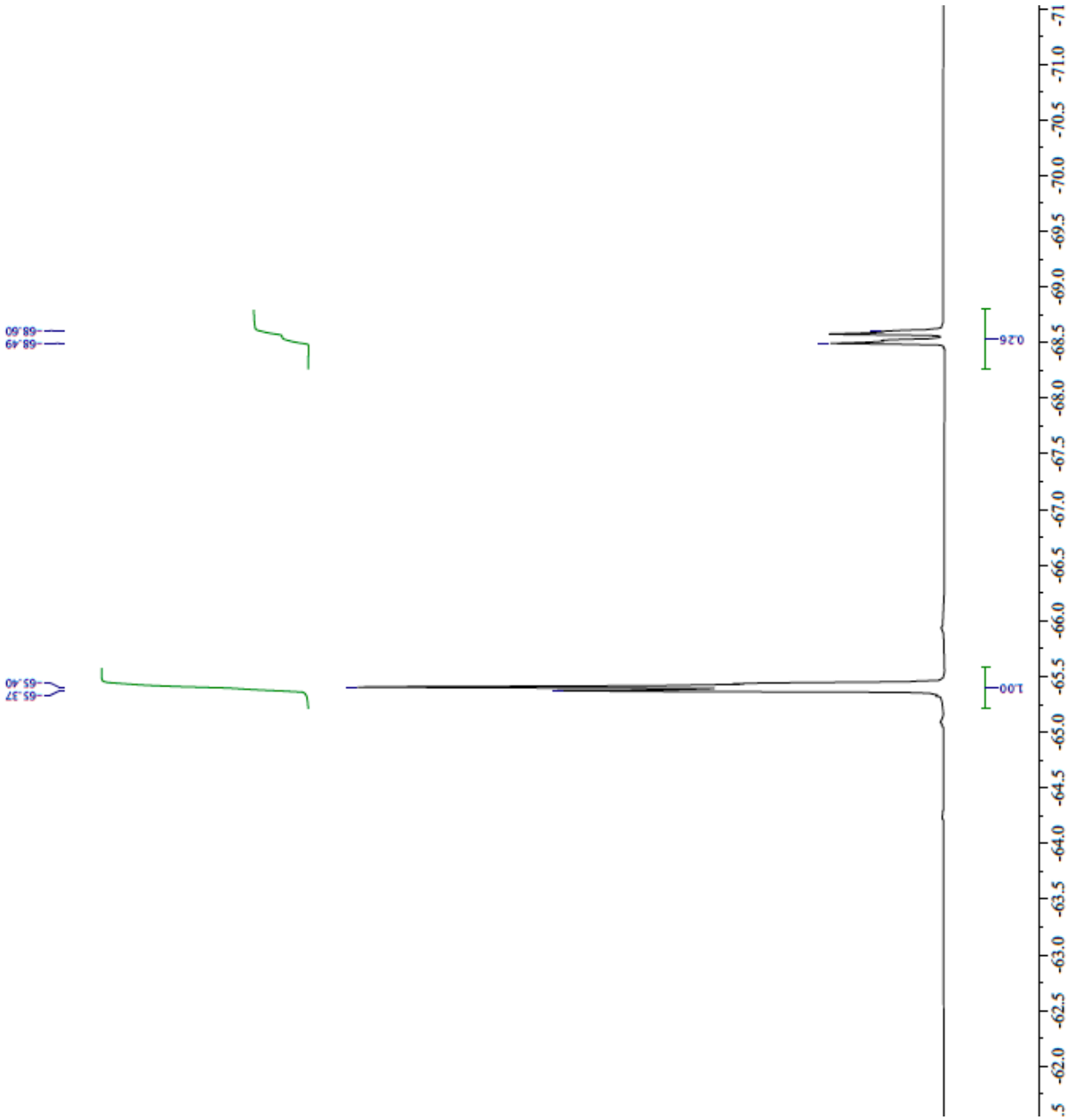
Z-enriched 1-(2-bromo-2-fluoroethenyl)-2-iodobenzene (*Z*-**1h**)

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



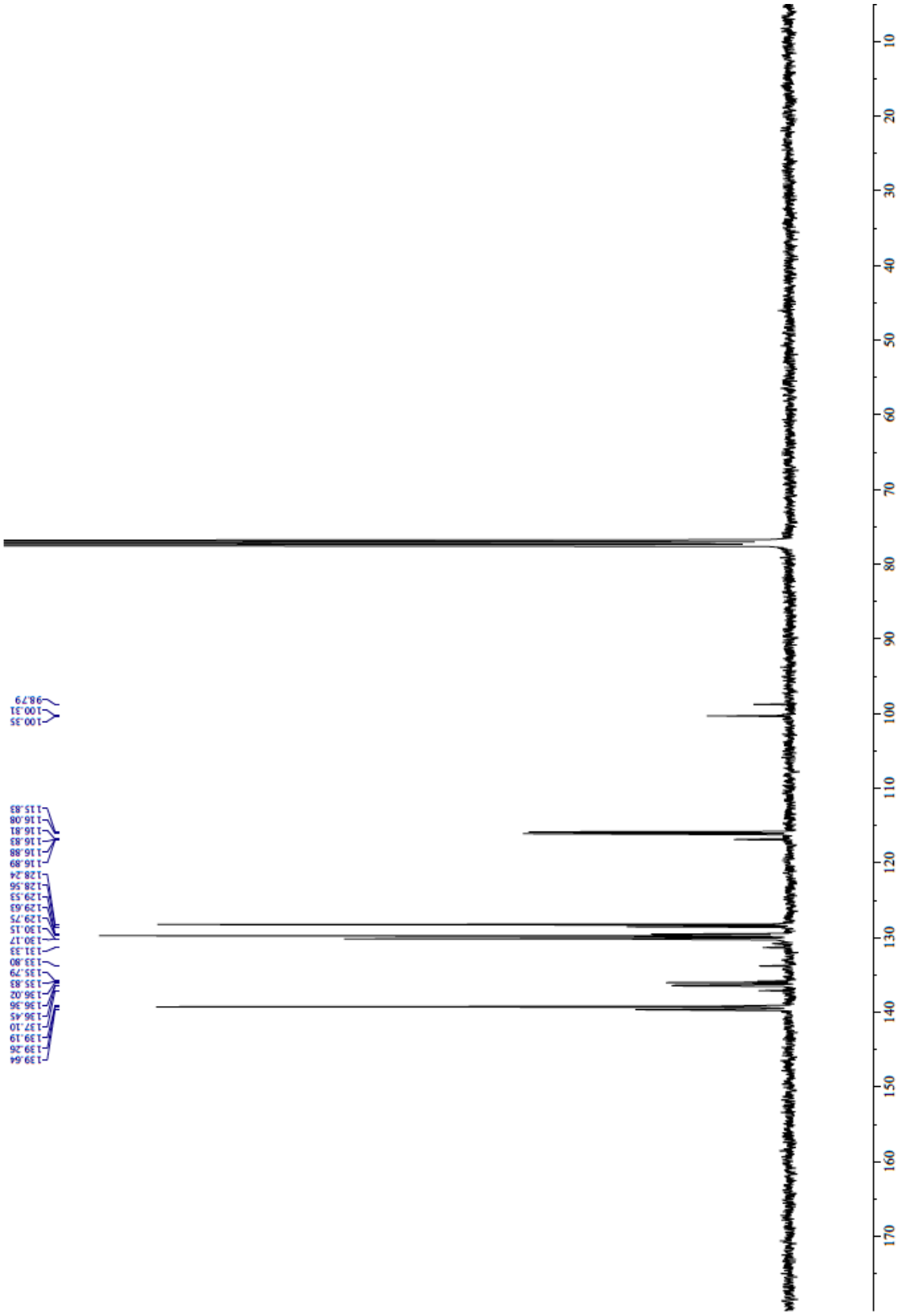
Z-enriched 1-(2-bromo-2-fluoroethenyl)-2-iodobenzene (*Z*-**1h**)

^{19}F NMR (376 MHz, $CDCl_3$, rt)



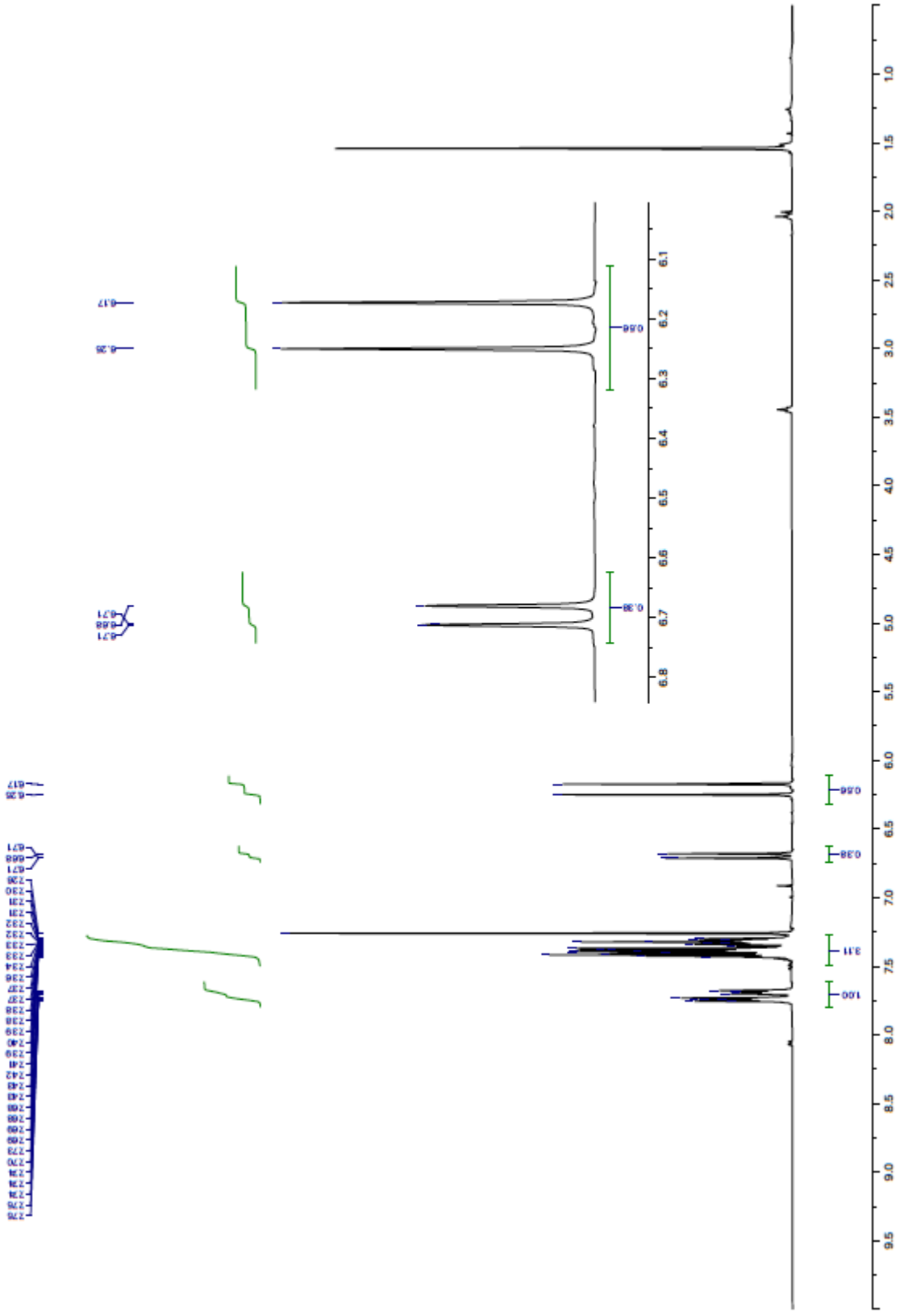
Z-enriched 1-(2-bromo-2-fluoroethenyl)-2-iodobenzene (*Z*-**1h**)

^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)



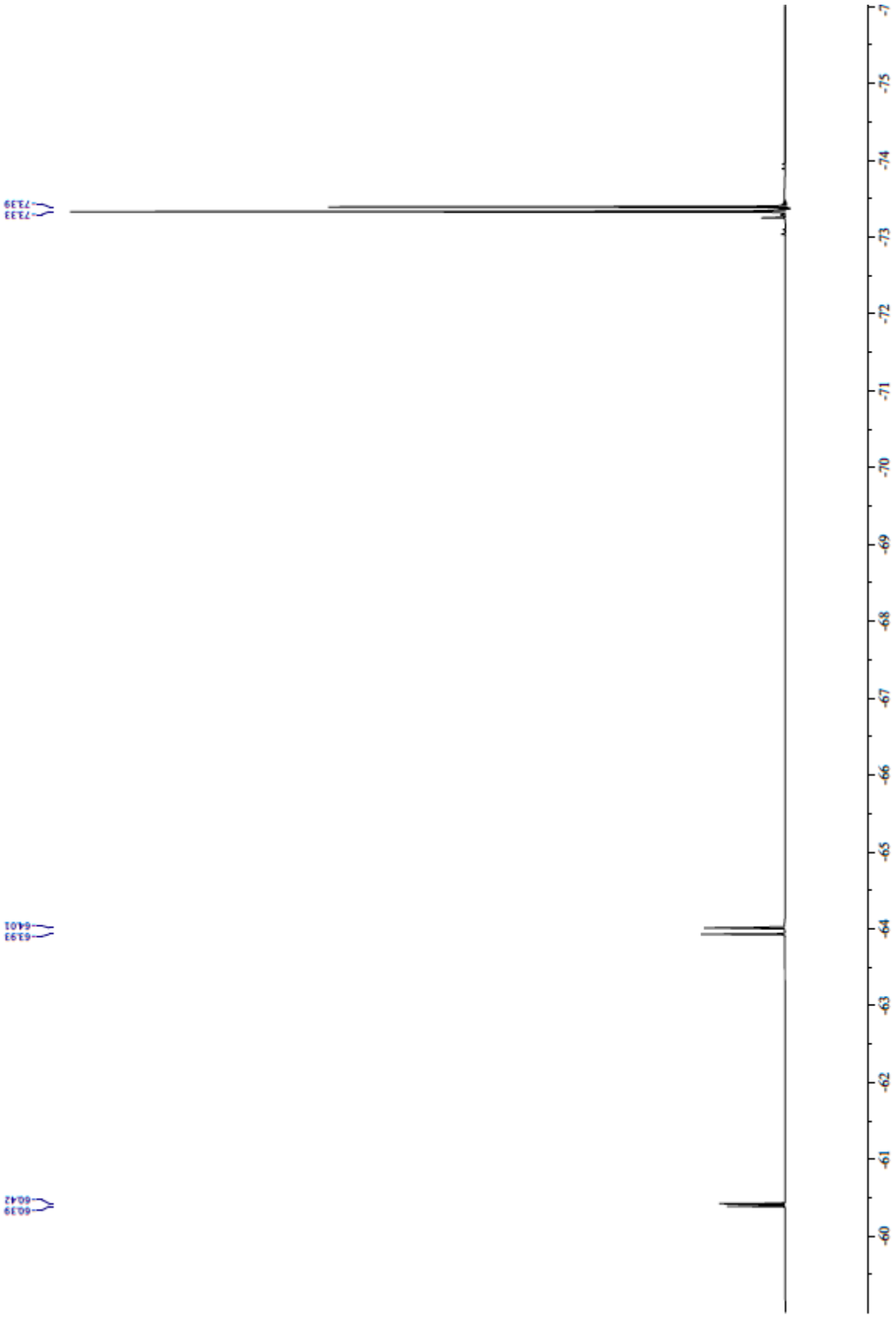
2-(2-Bromo-2-fluoroethenyl)phenyl trifluoromethanesulfonate (**1i**)

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



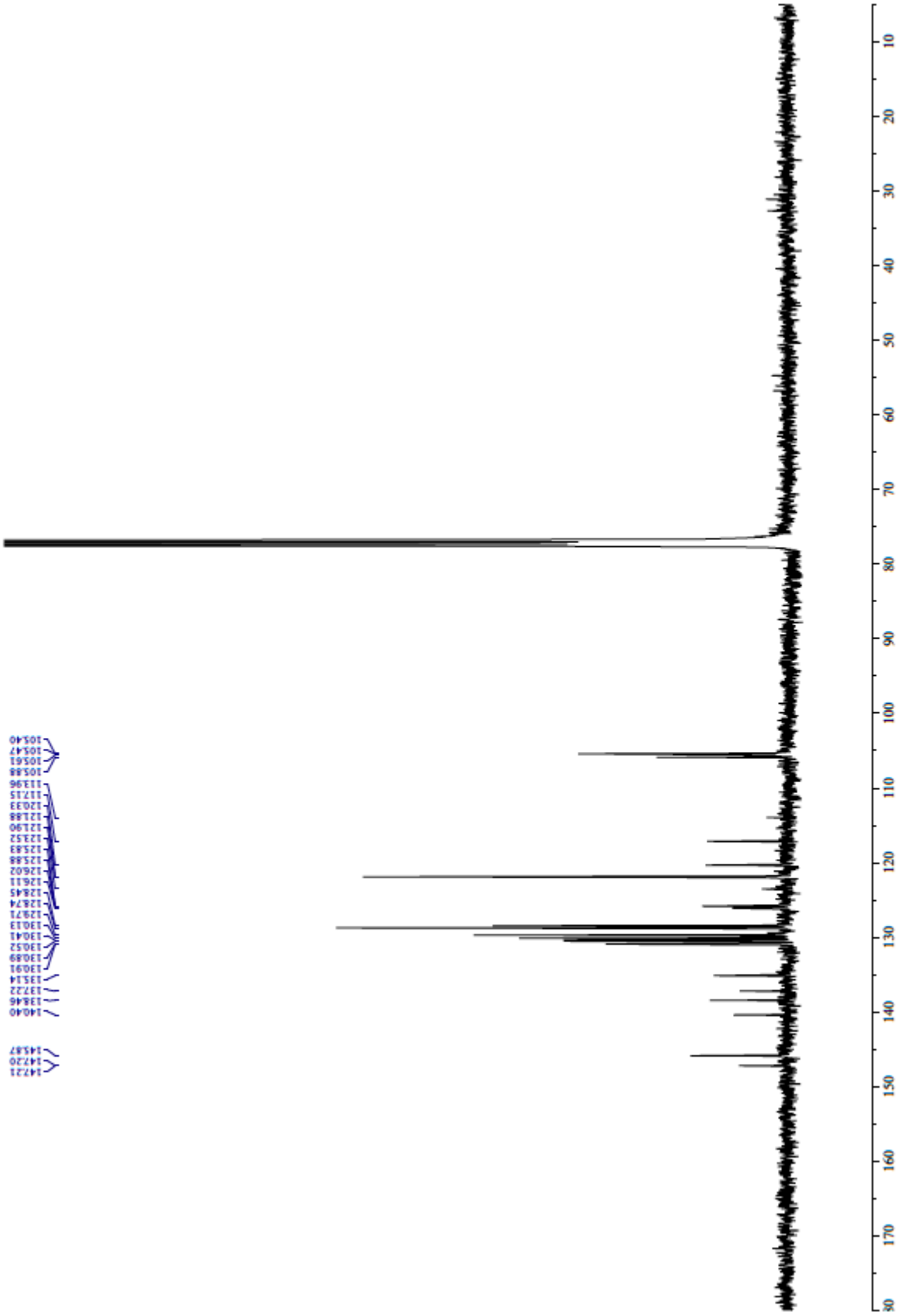
2-(2-Bromo-2-fluoroethenyl)phenyl trifluoromethanesulfonate (**1i**)

^{19}F NMR (376 MHz, $CDCl_3$, rt)



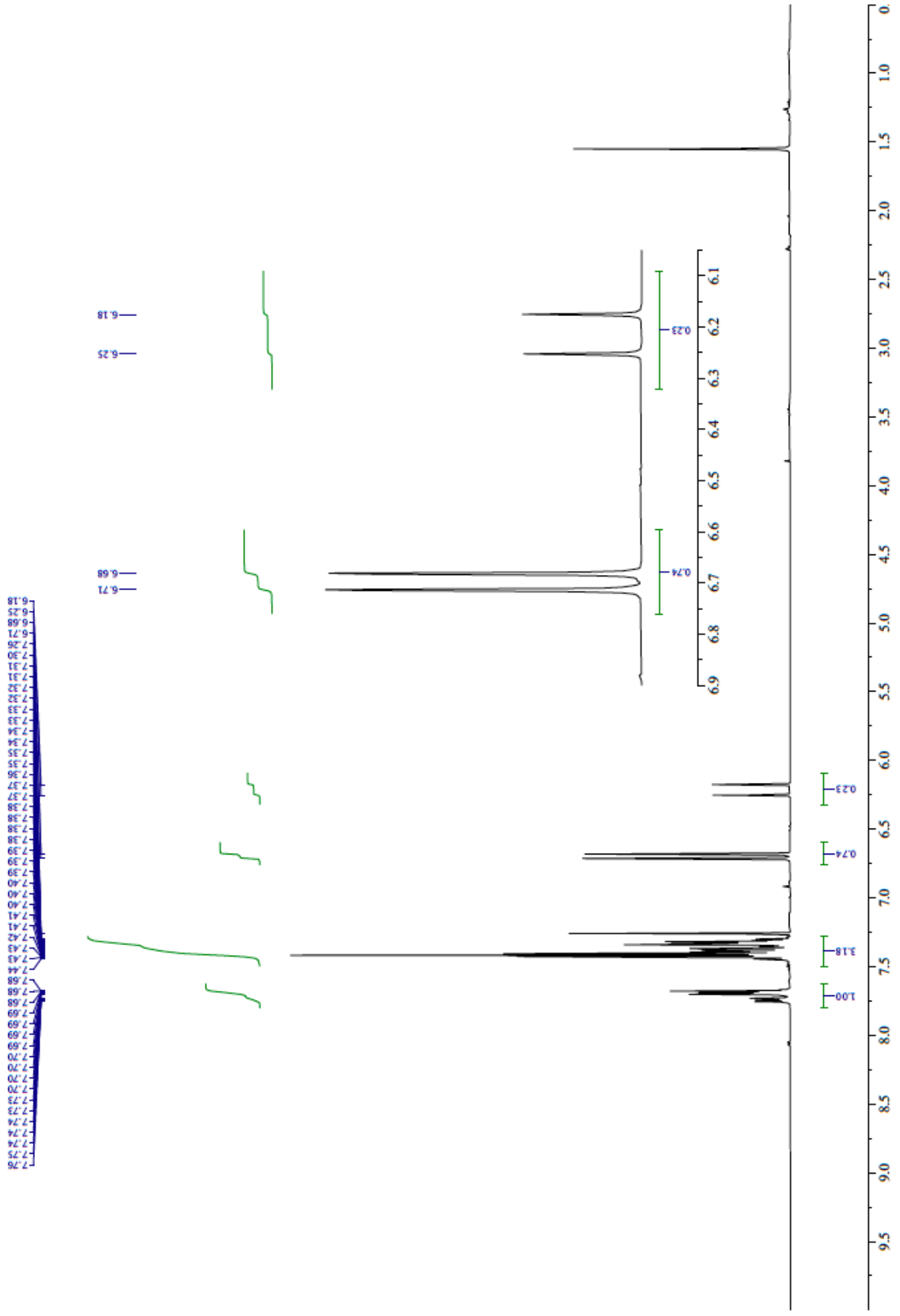
2-(2-Bromo-2-fluoroethenyl)phenyl trifluoromethanesulfonate (**1i**)

^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)



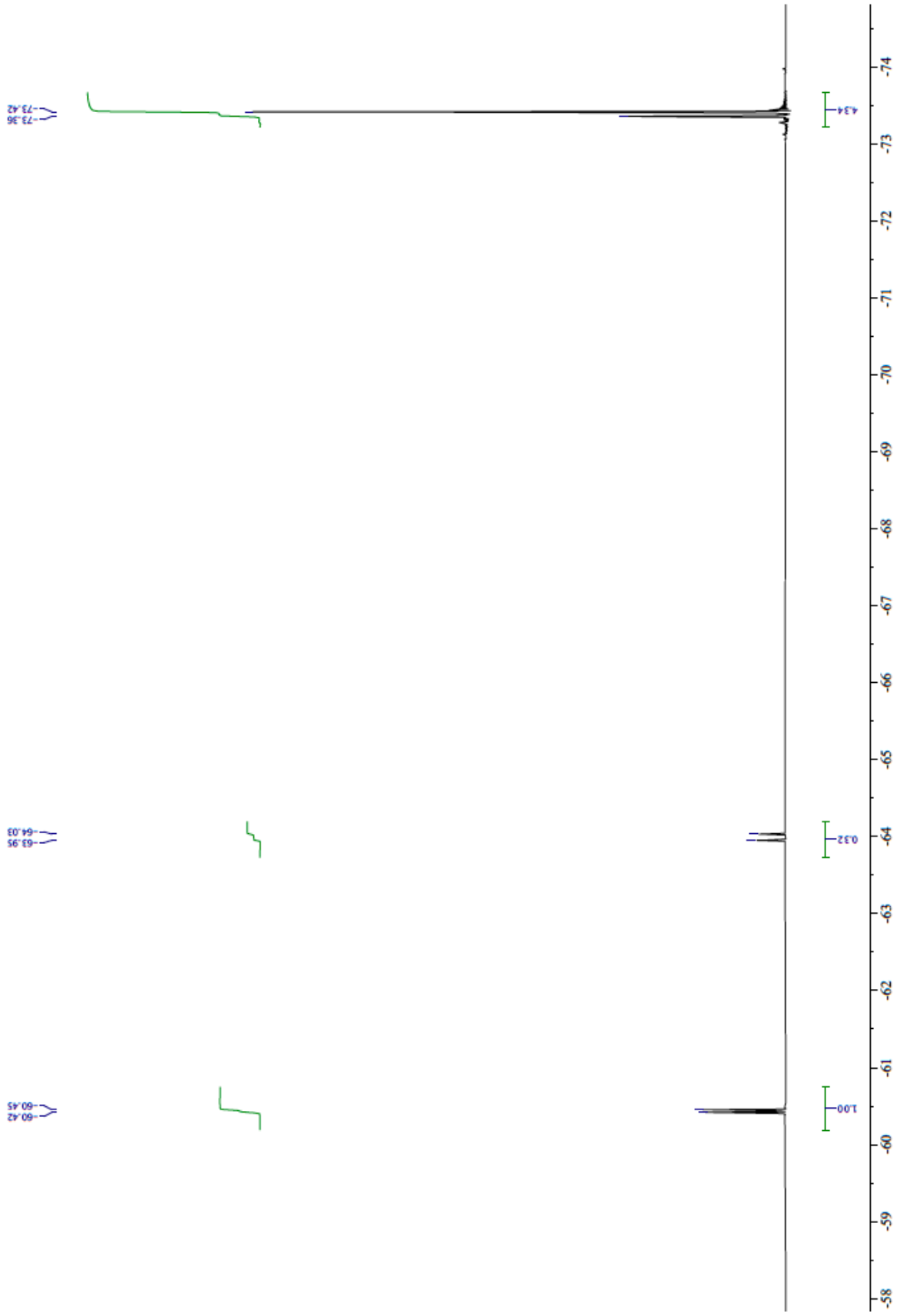
Z-enriched 2-(2-bromo-2-fluoroethenyl)phenyl trifluoromethanesulfonate (*Z*-**1i**)

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



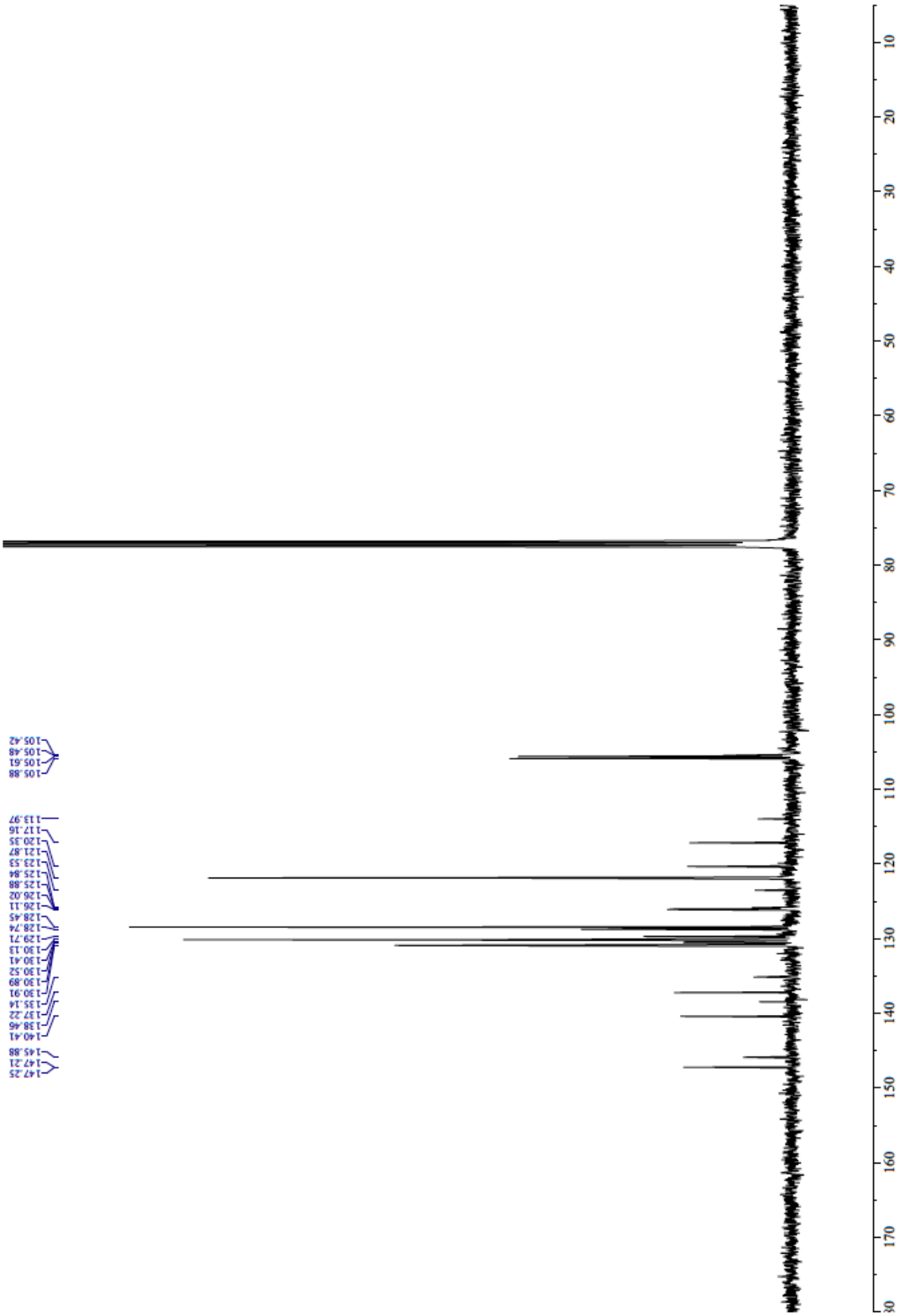
Z-enriched 2-(2-bromo-2-fluoroethenyl)phenyl trifluoromethanesulfonate (*Z*-**1i**)

^{19}F NMR (376 MHz, $CDCl_3$, rt)



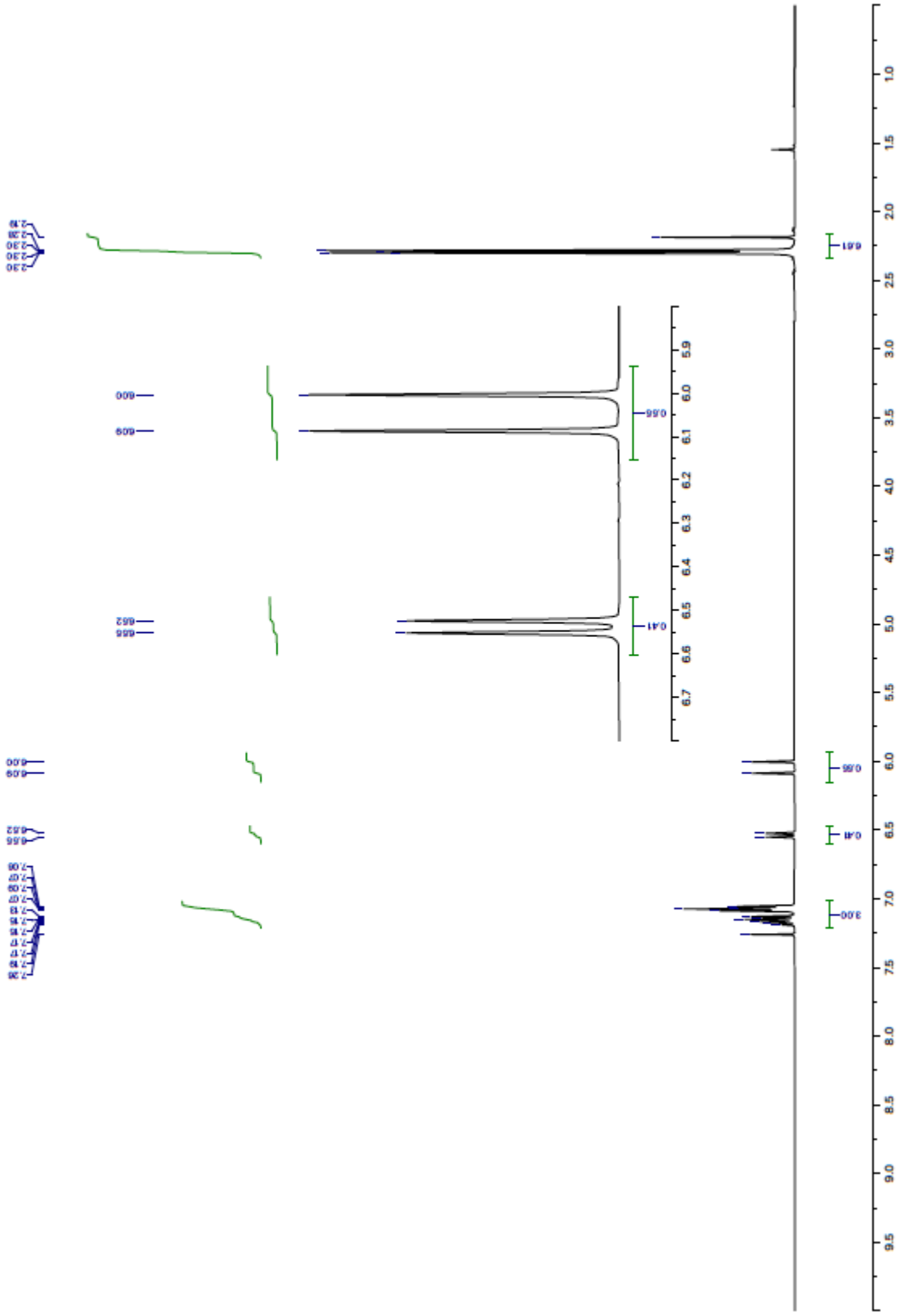
Z-enriched 2-(2-bromo-2-fluoroethenyl)phenyl trifluoromethanesulfonate (*Z*-**1i**)

^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)



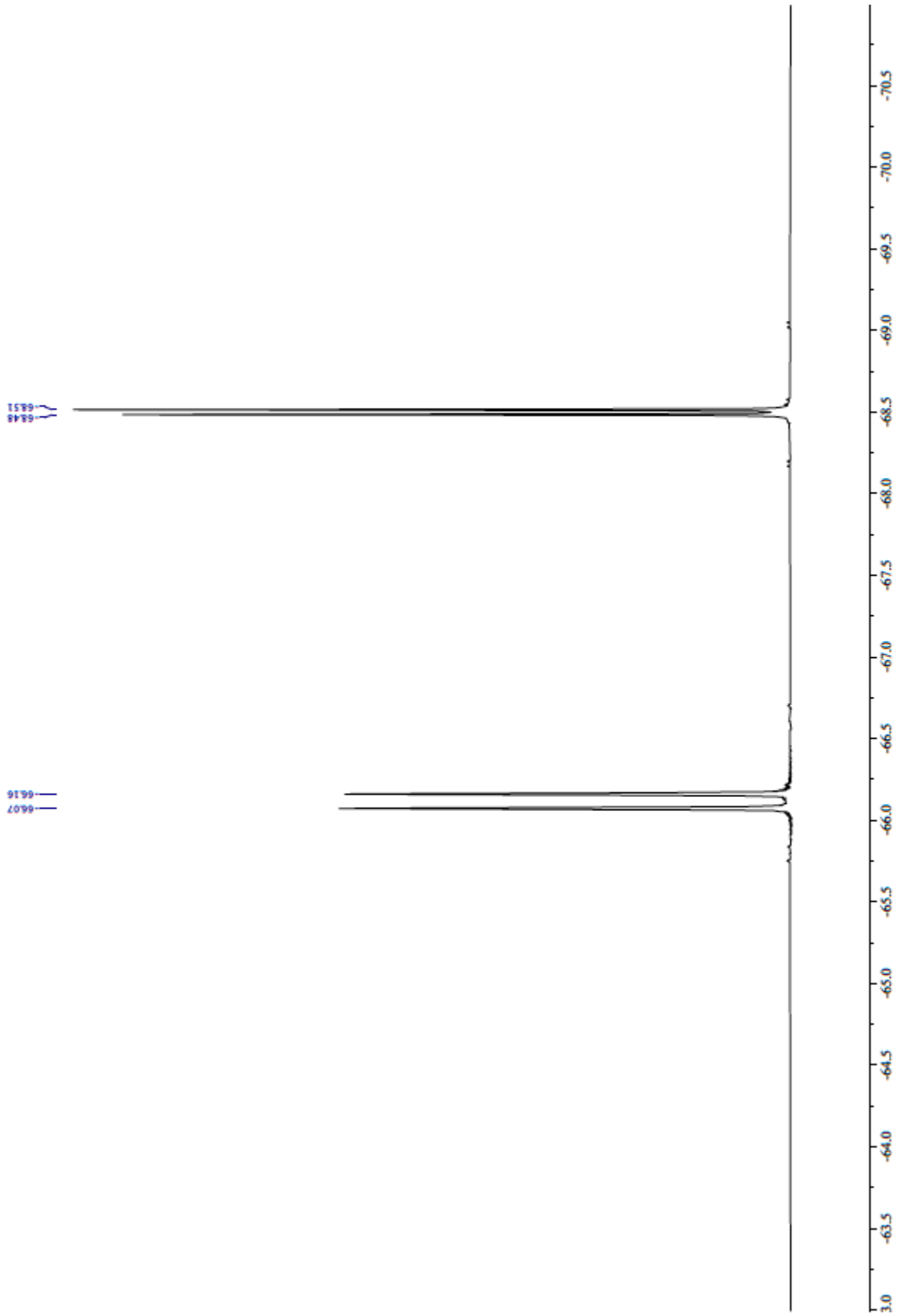
2-(2-Bromo-2-fluoroethenyl)-1,3-dimethylbenzene (**1j**)

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



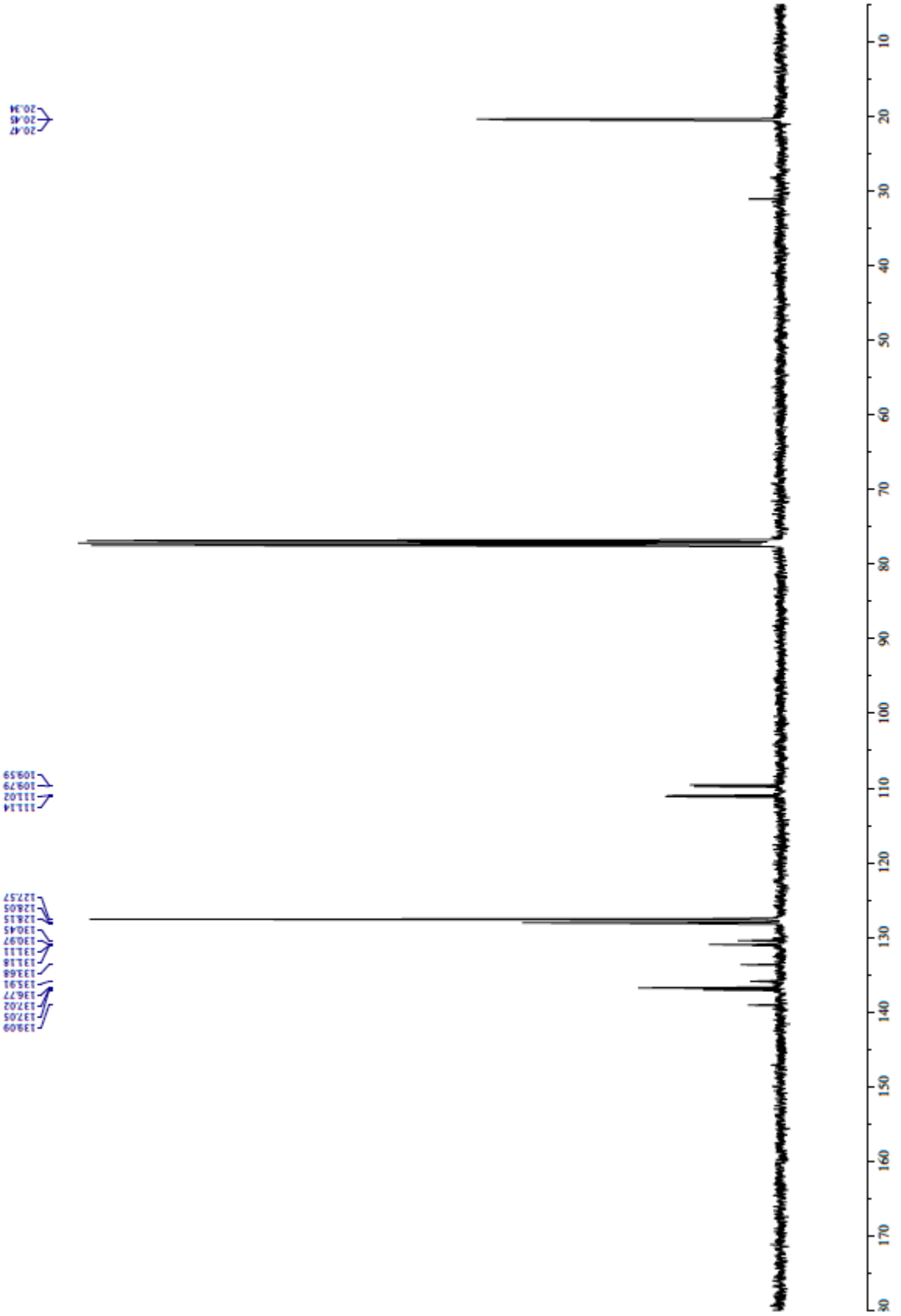
2-(2-Bromo-2-fluoroethenyl)-1,3-dimethylbenzene (**1j**)

^{19}F NMR (376 MHz, $CDCl_3$, rt)



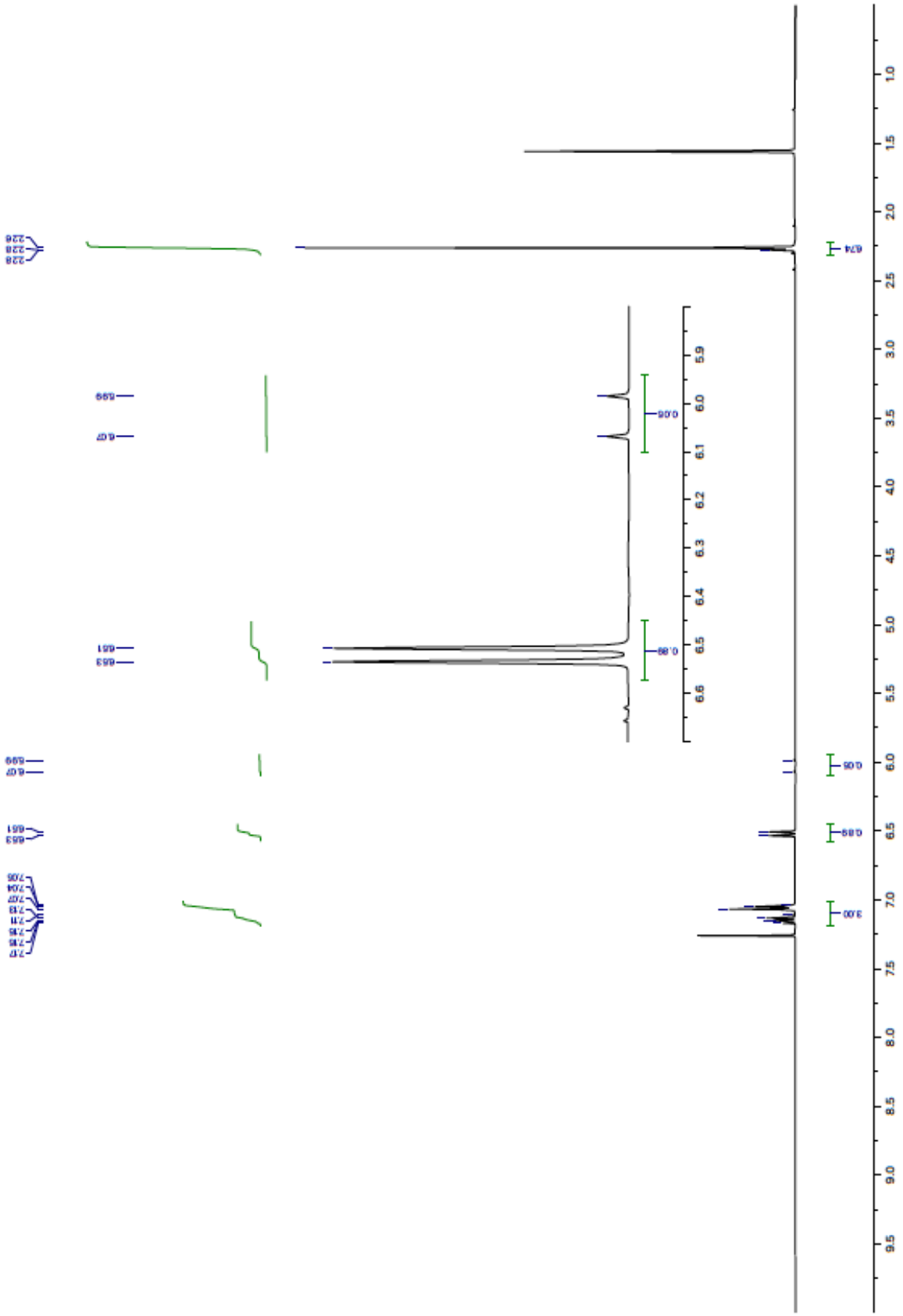
2-(2-Bromo-2-fluoroethenyl)-1,3-dimethylbenzene (**1j**)

^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)



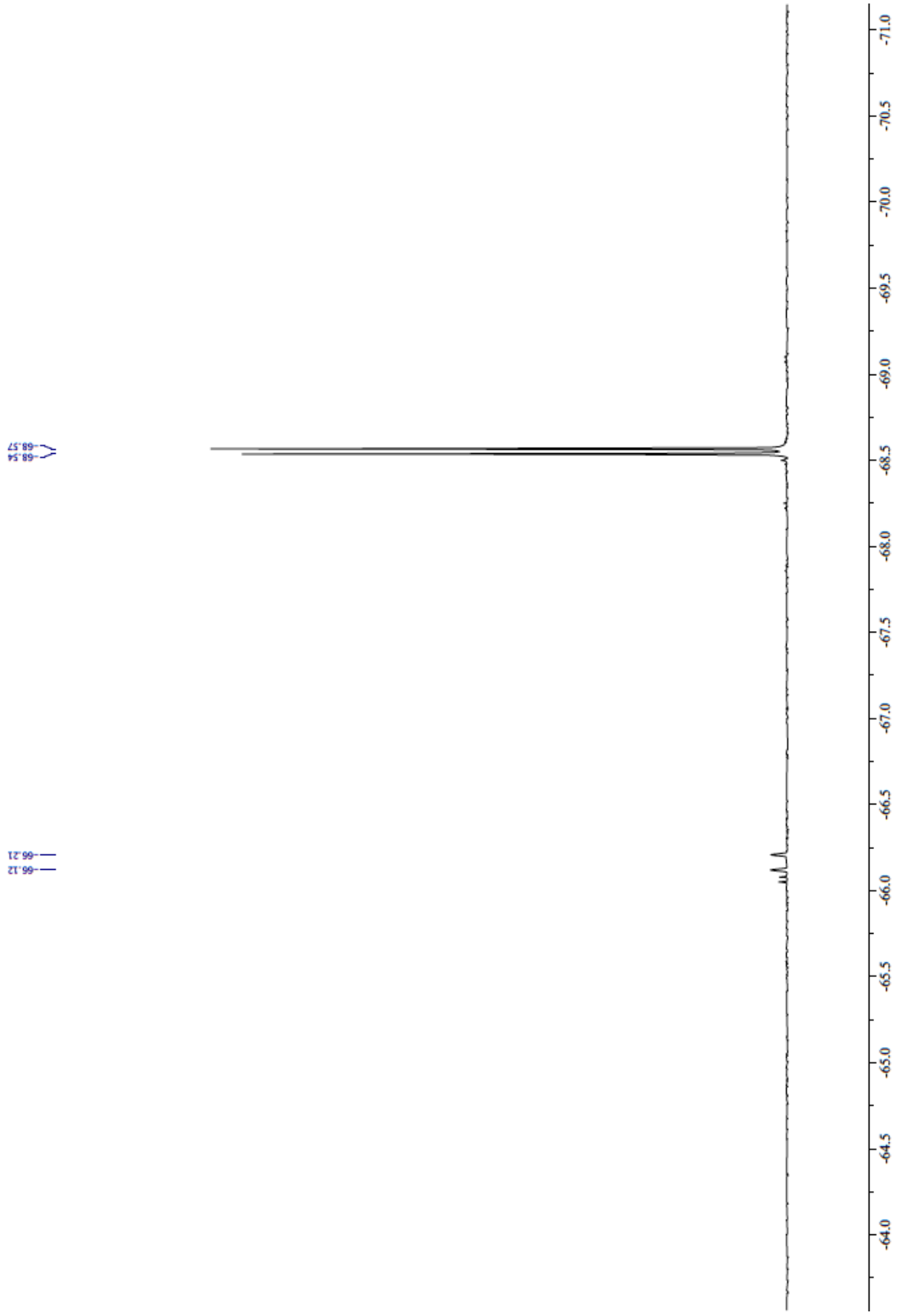
2-((*Z*)-2-Bromo-2-fluoroethenyl)-1,3-dimethylbenzene (*Z*-**1j**)

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



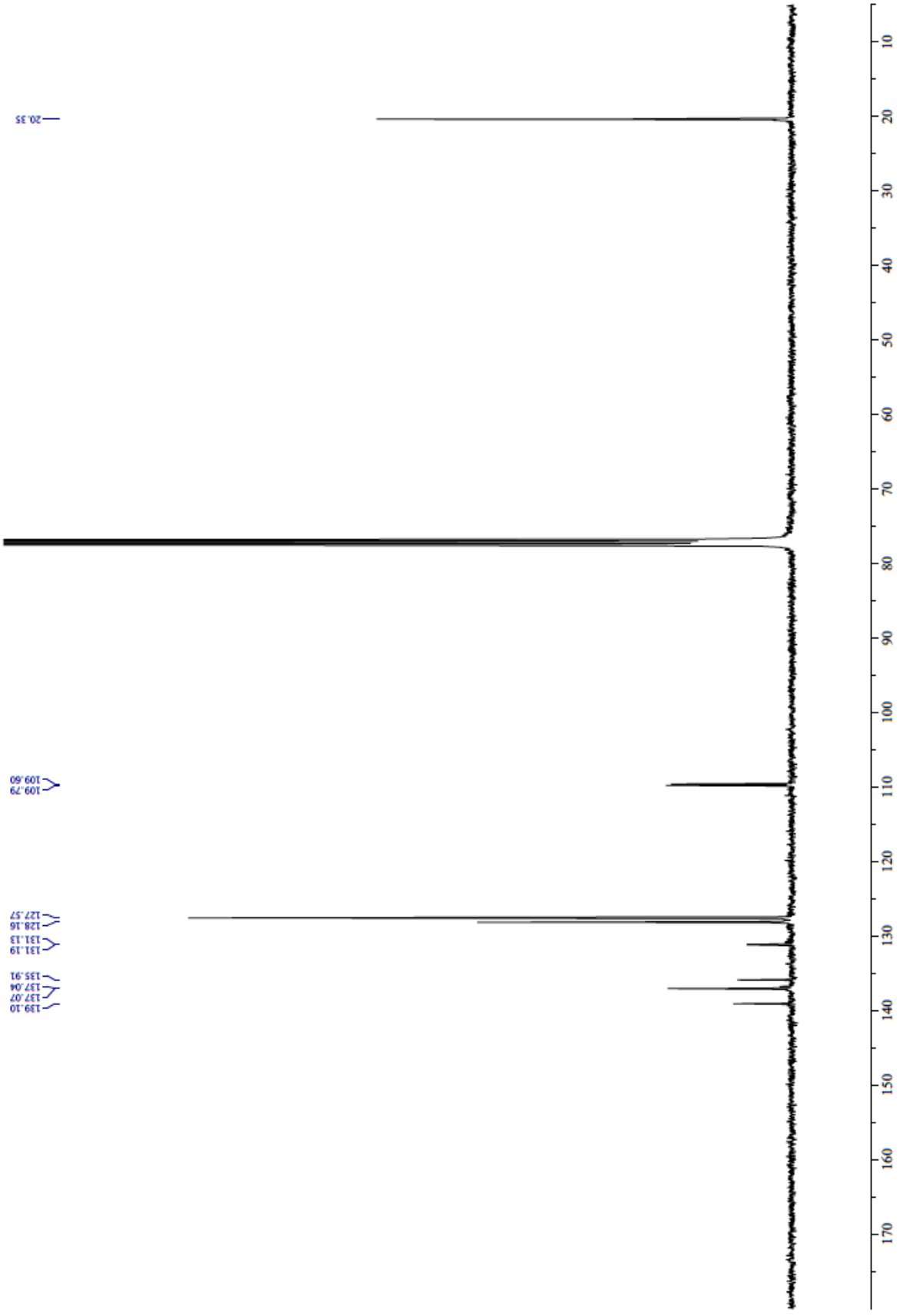
2-((*Z*)-2-Bromo-2-fluoroethenyl)-1,3-dimethylbenzene (*Z*-**1j**)

^{19}F NMR (376 MHz, $CDCl_3$, rt)



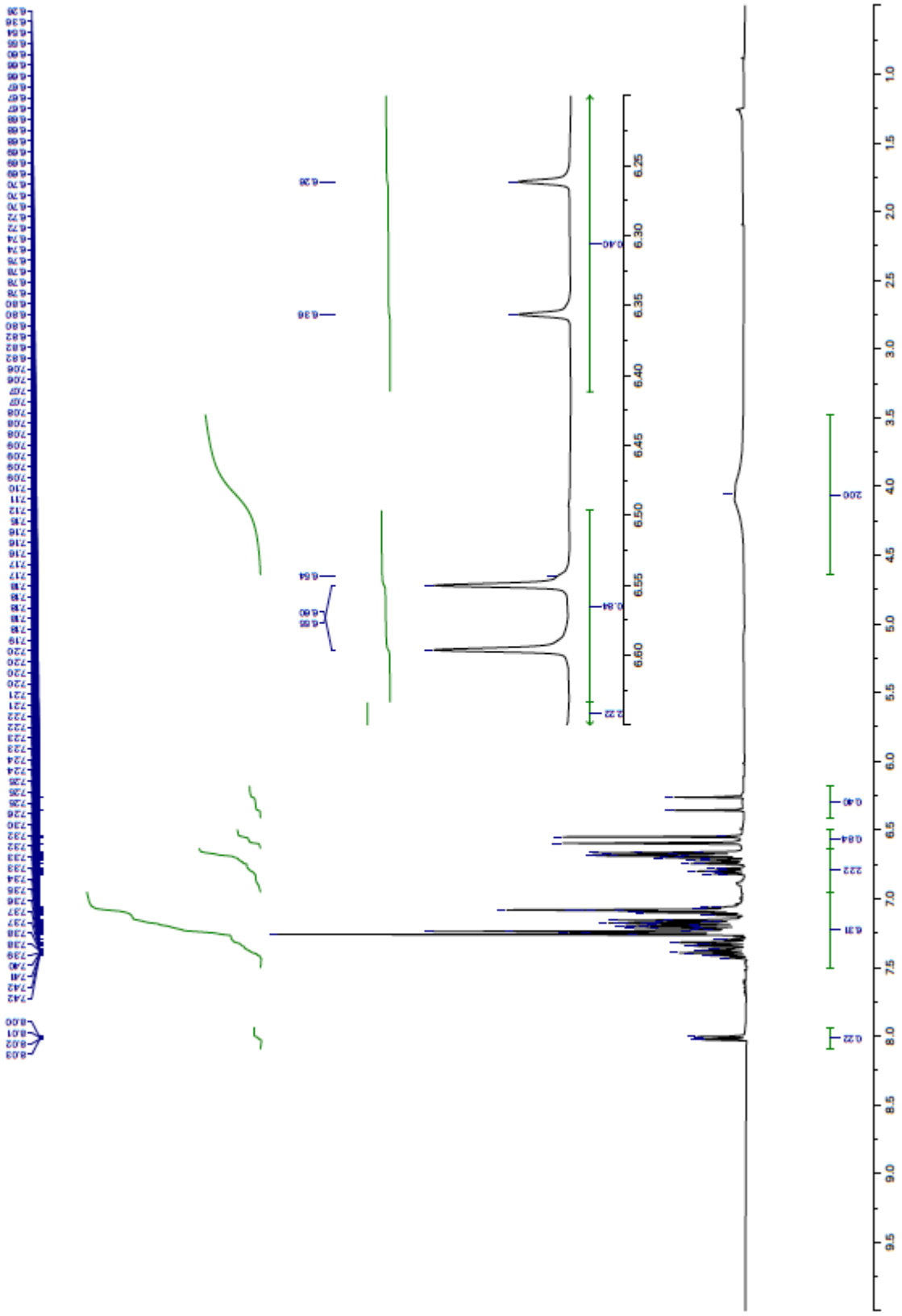
2-((*Z*)-2-Bromo-2-fluoroethenyl)-1,3-dimethylbenzene (*Z*-**1j**)

^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)



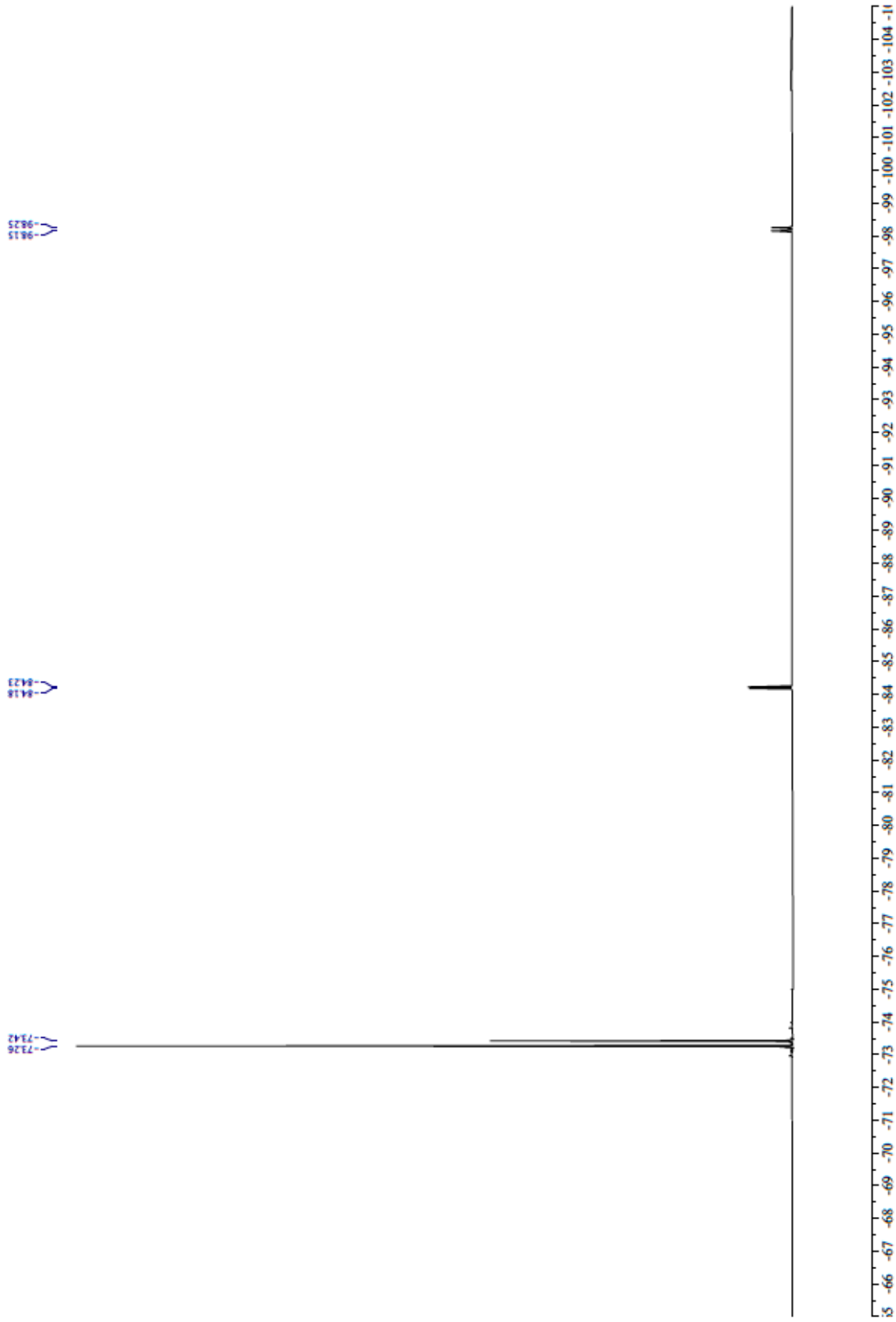
2-(2-(2-Aminophenyl)-2-fluorovinyl)phenyl trifluoromethanesulfonate (**3a**)

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



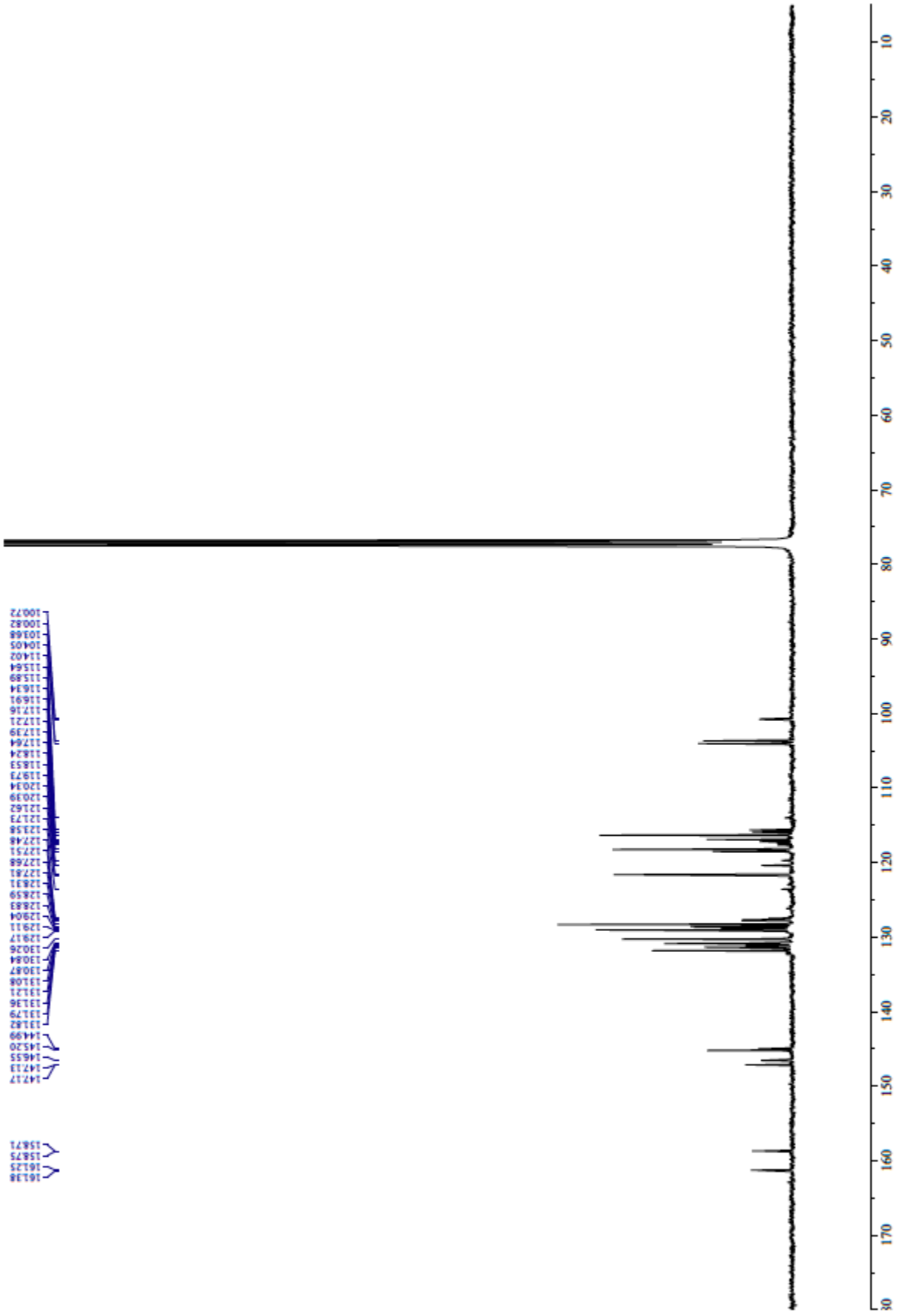
2-(2-(2-Aminophenyl)-2-fluorovinyl)phenyl trifluoromethanesulfonate (**3a**)

^{19}F NMR (376 MHz, $CDCl_3$, rt)



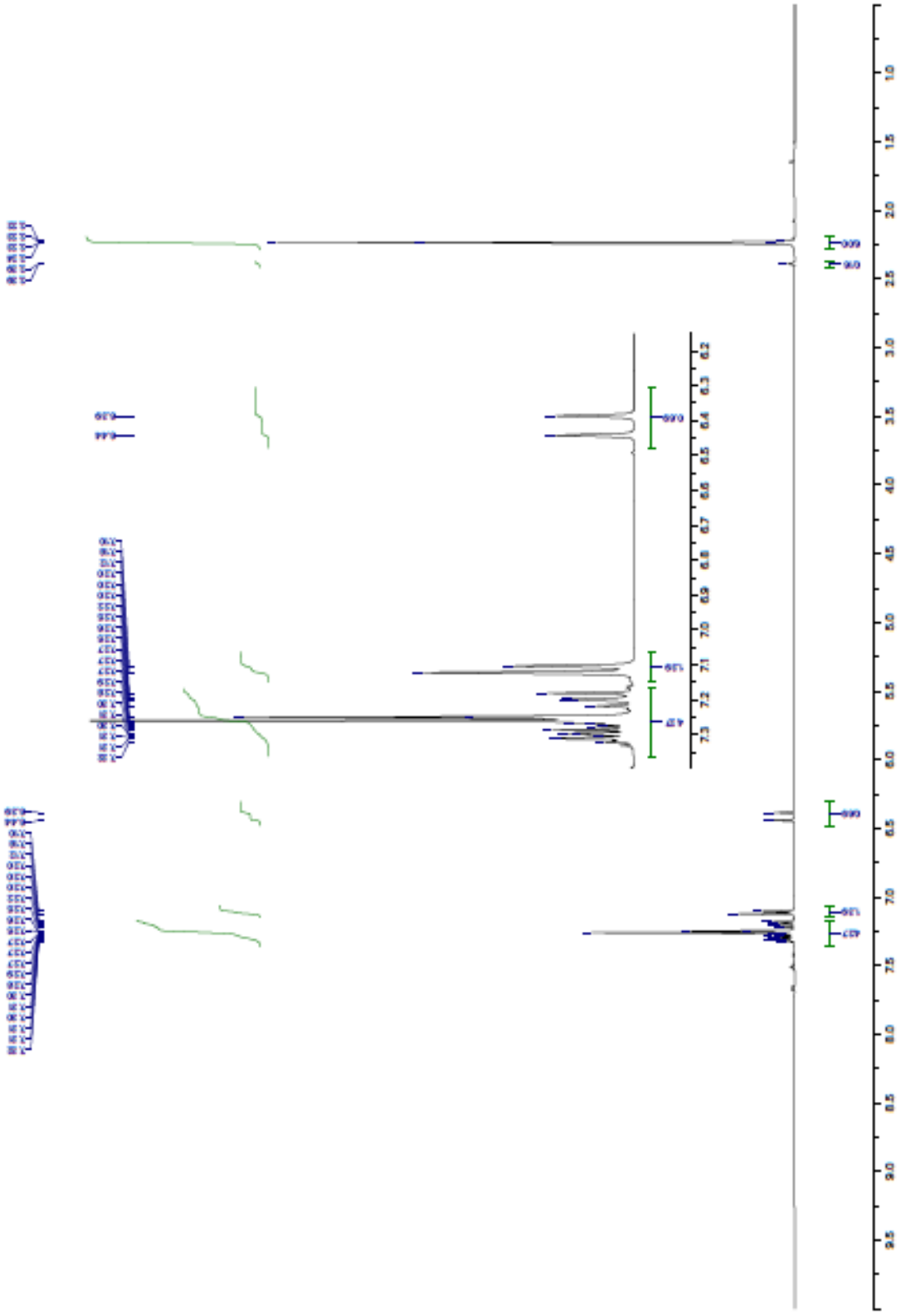
2-(2-(2-Aminophenyl)-2-fluorovinyl)phenyl trifluoromethanesulfonate (**3a**)

^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)



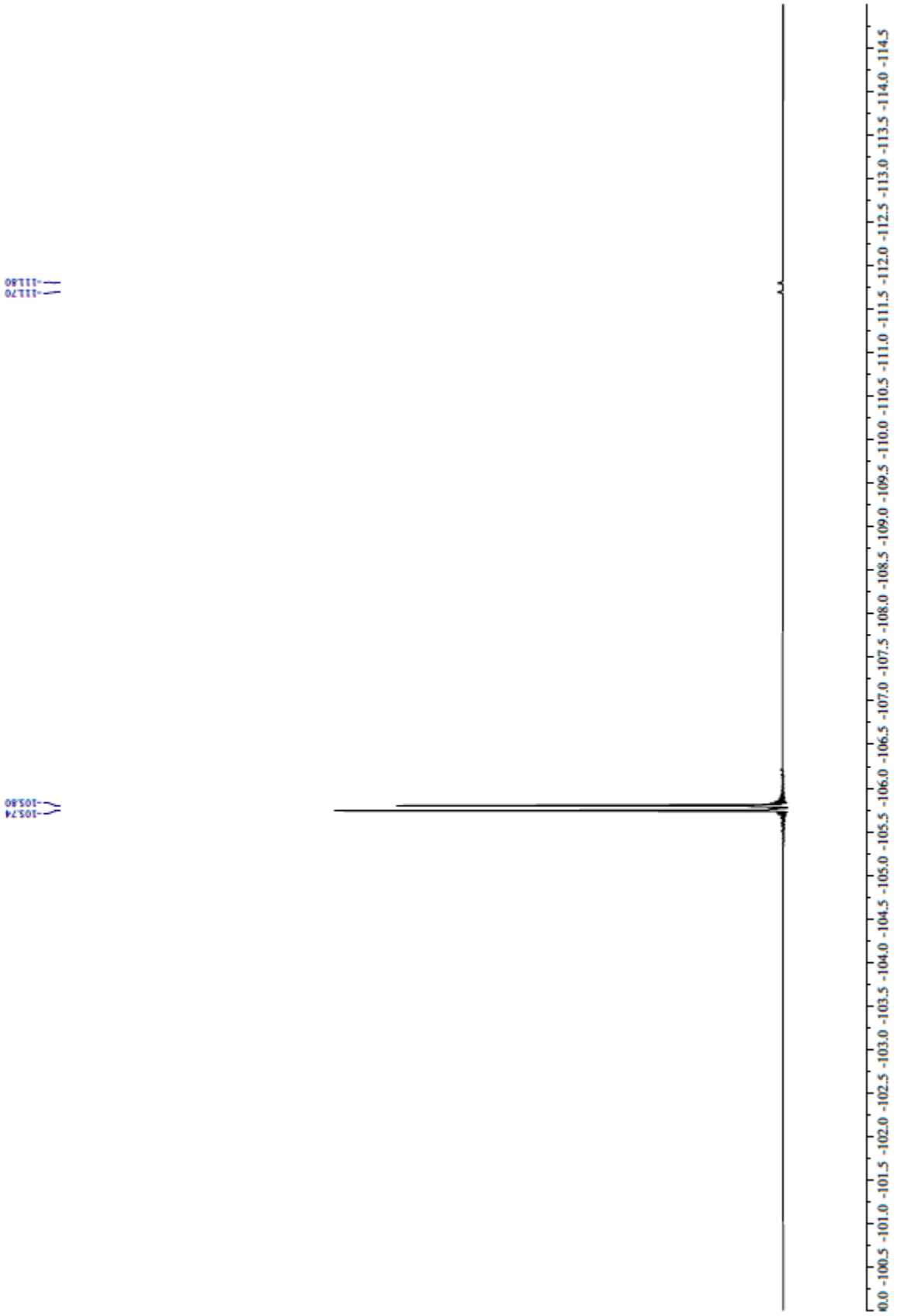
2-((*E*)-2-Fluoro-2-phenylethenyl)-1,3-dimethylbenzene (**3b**)

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



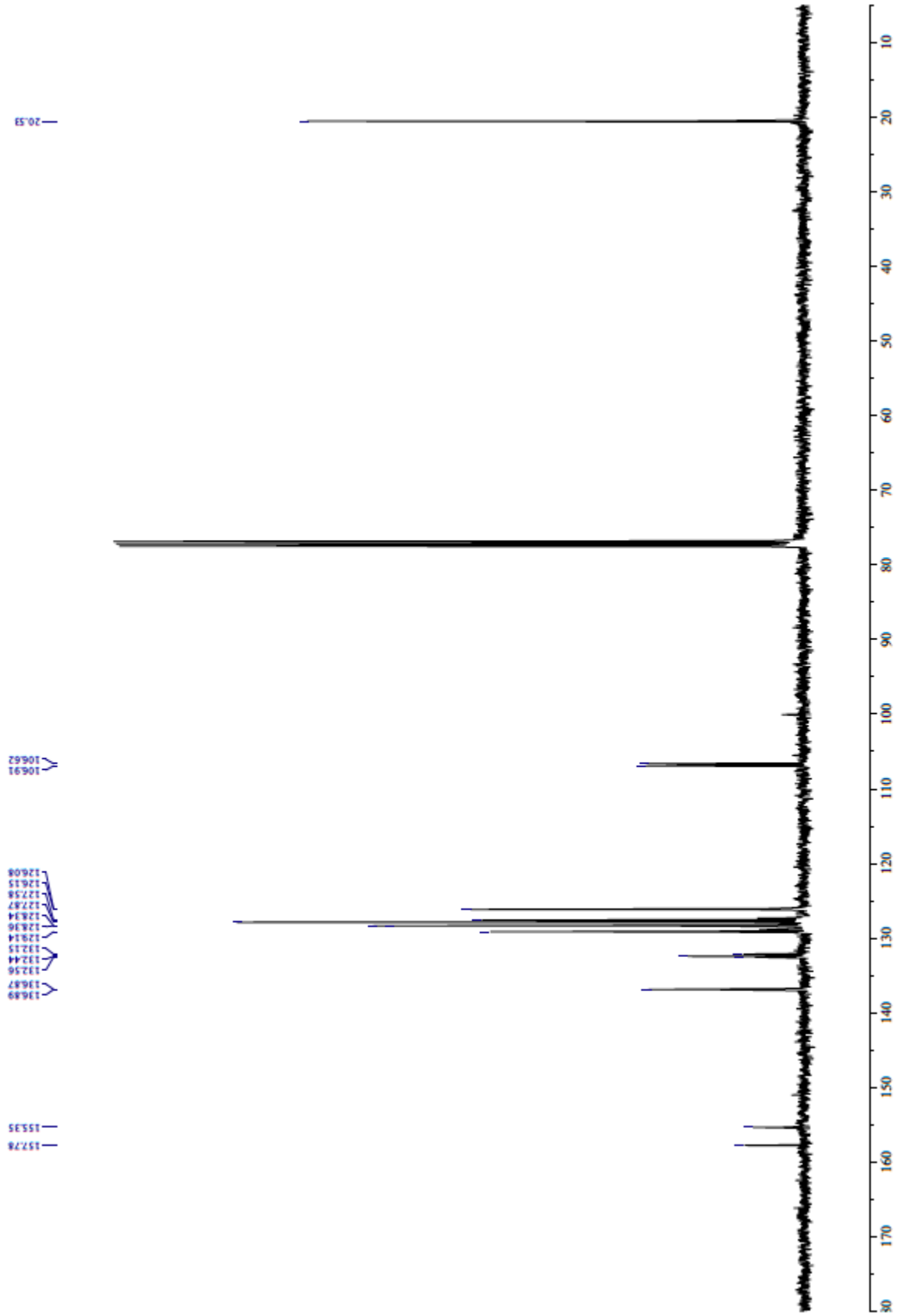
2-((*E*)-2-Fluoro-2-phenylethenyl)-1,3-dimethylbenzene (**3b**)

^{19}F NMR (376 MHz, $CDCl_3$, rt)



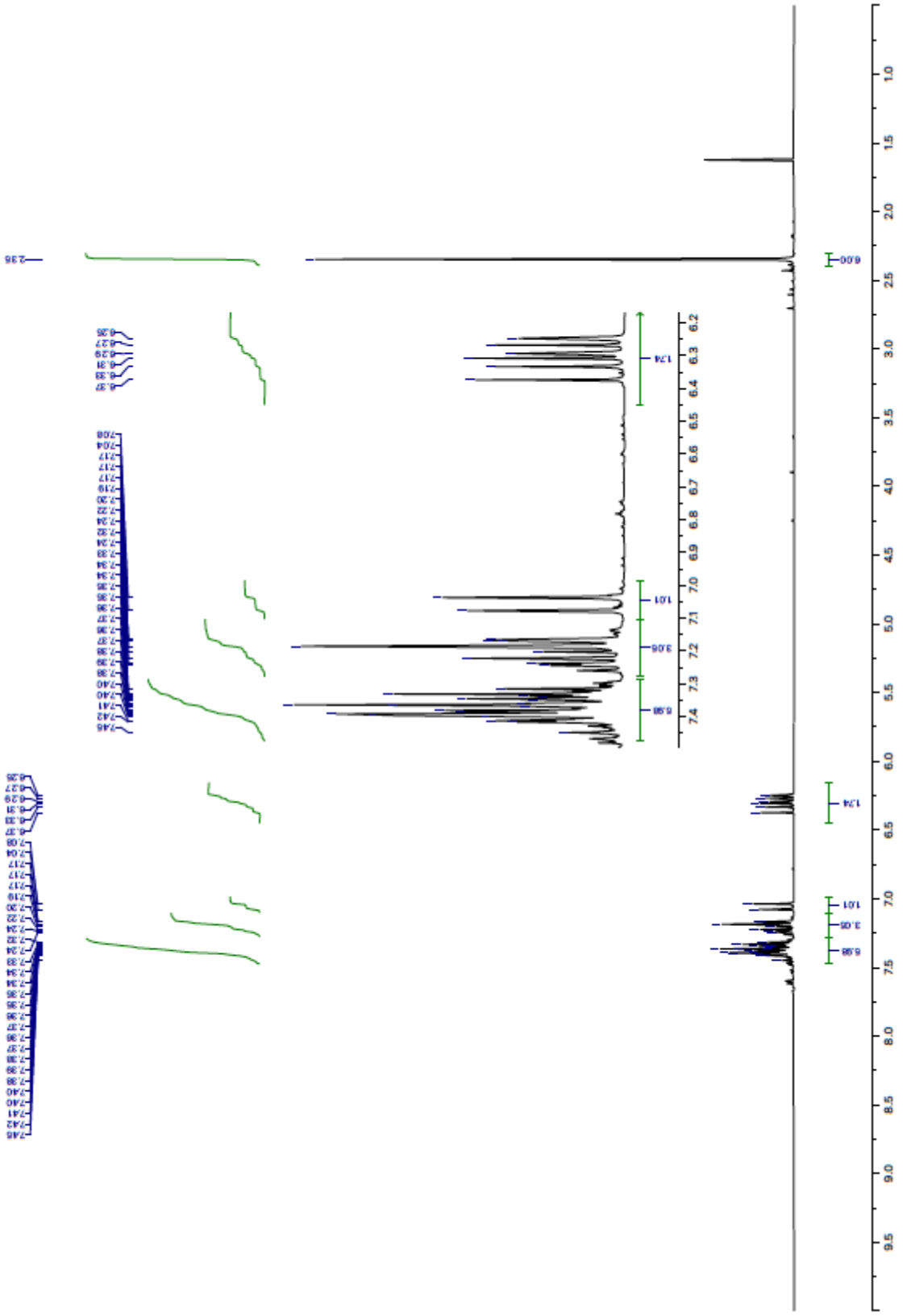
2-((*E*)-2-Fluoro-2-phenylethenyl)-1,3-dimethylbenzene (**3b**)

^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)



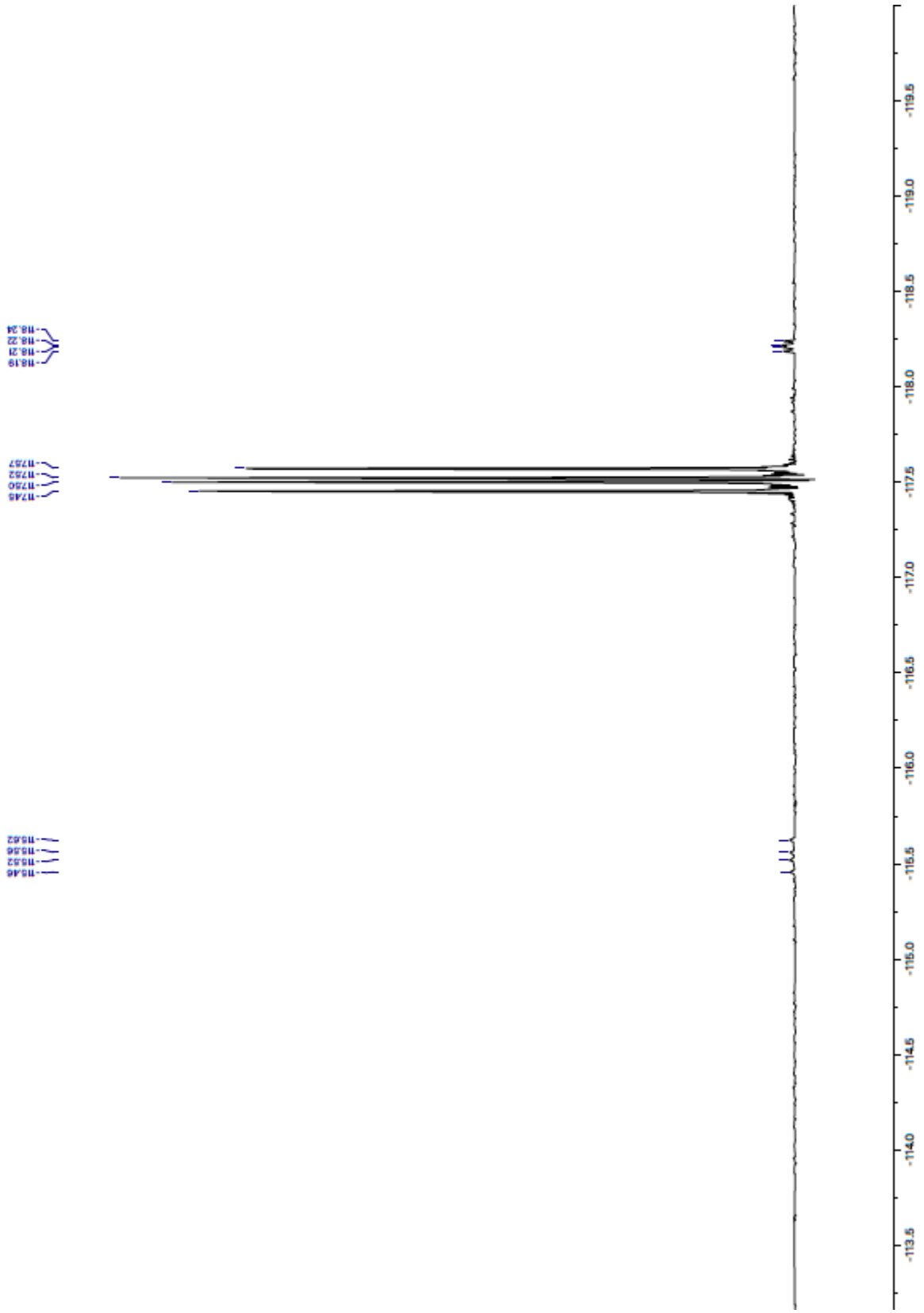
2-((1*E*,3*E*)-2-Fluoro-4-phenylbuta-1,3-dien-1-yl)-1,3-dimethylbenzene (**3c**)

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



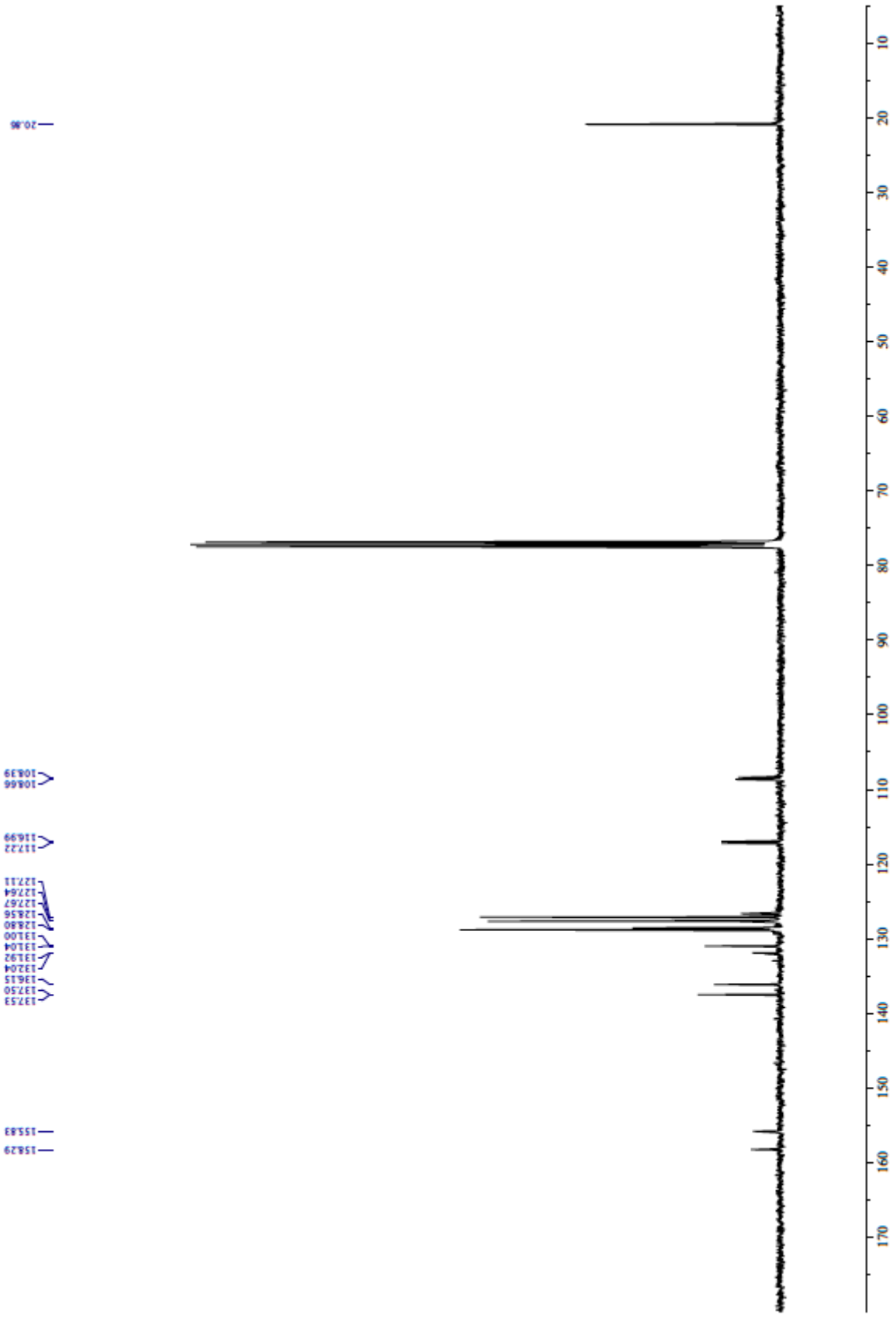
2-((1*E*,3*E*)-2-Fluoro-4-phenylbuta-1,3-dien-1-yl)-1,3-dimethylbenzene (**3c**)

^{19}F NMR (376 MHz, $CDCl_3$, rt)



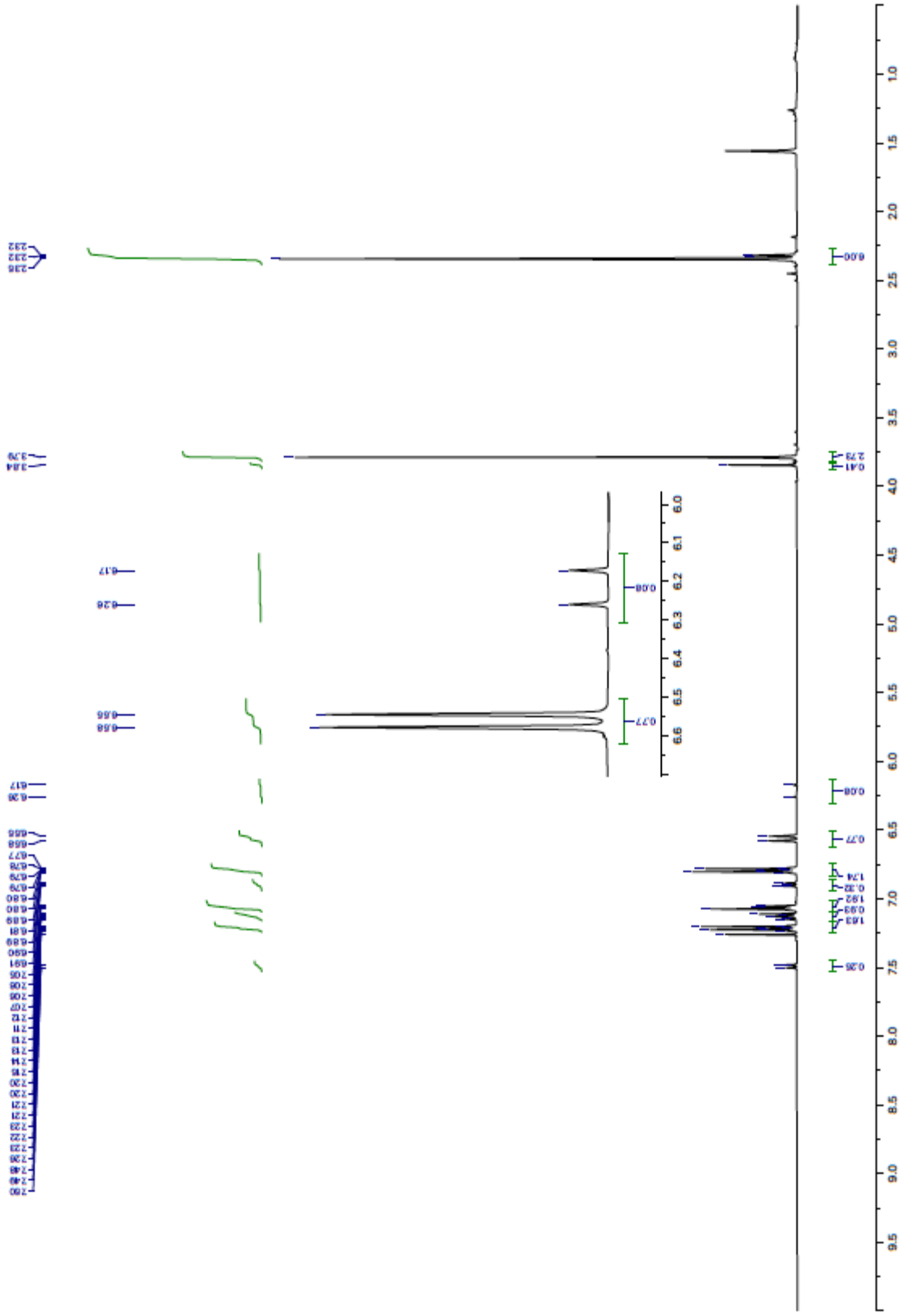
2-((1*E*,3*E*)-2-Fluoro-4-phenylbuta-1,3-dien-1-yl)-1,3-dimethylbenzene (**3c**)

^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)



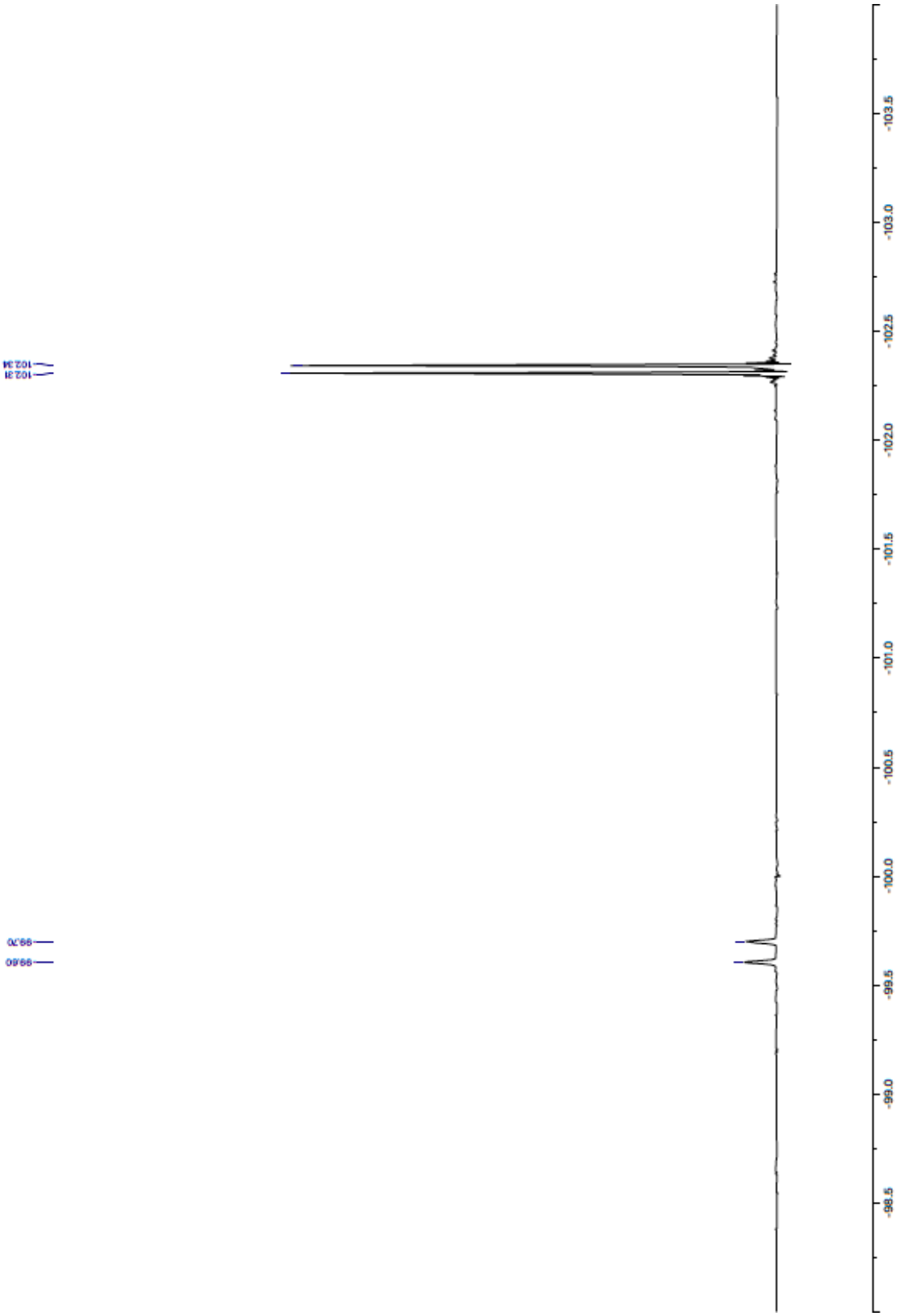
2-((*E*)-2-Fluoro-4-(4-methoxyphenyl)but-1-en-3-yn-1-yl)-1,3-dimethylbenzene (**3d**)

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



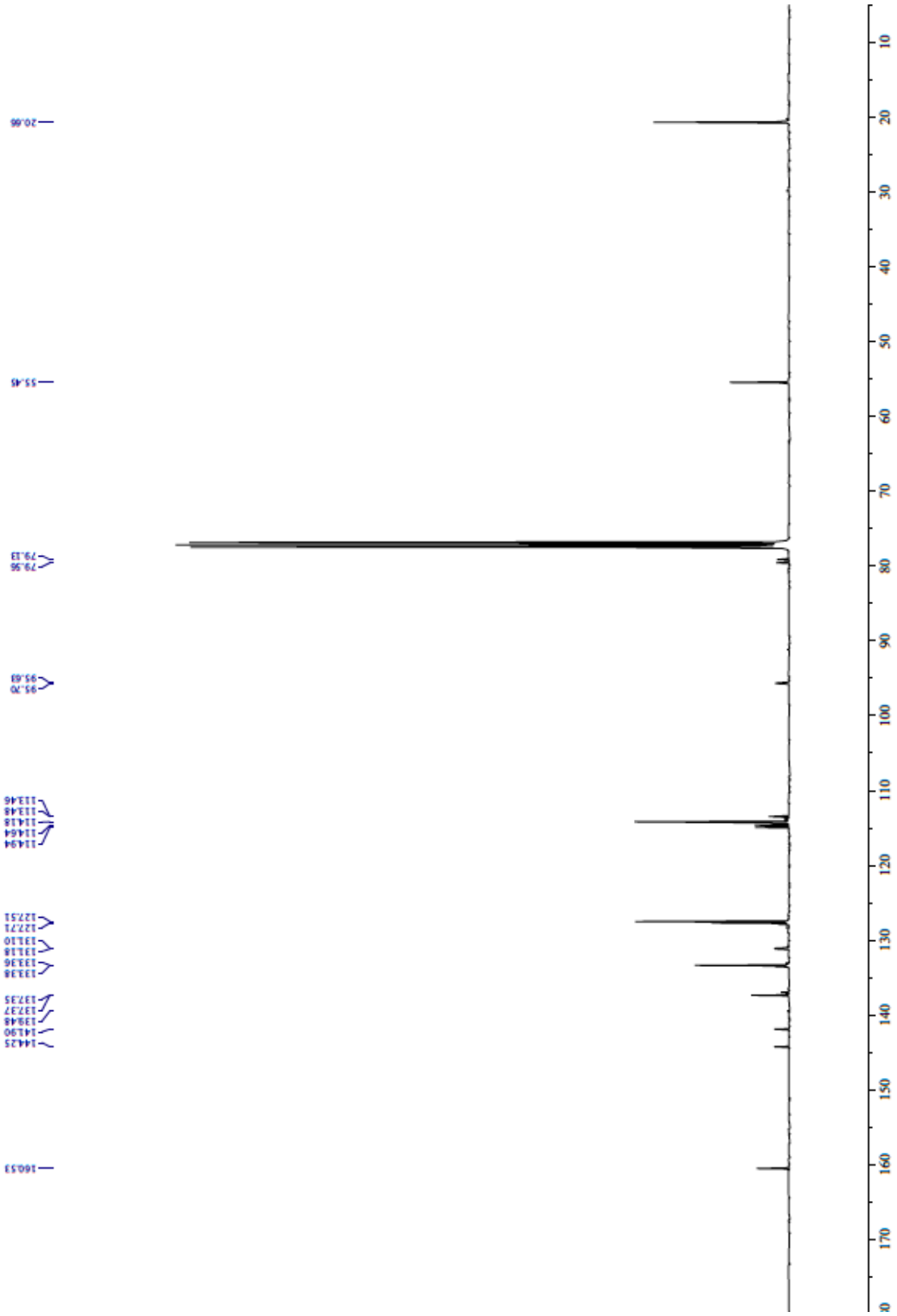
2-((*E*)-2-Fluoro-4-(4-methoxyphenyl)but-1-en-3-yn-1-yl)-1,3-dimethylbenzene (**3d**)

^{19}F NMR (376 MHz, $CDCl_3$, rt)



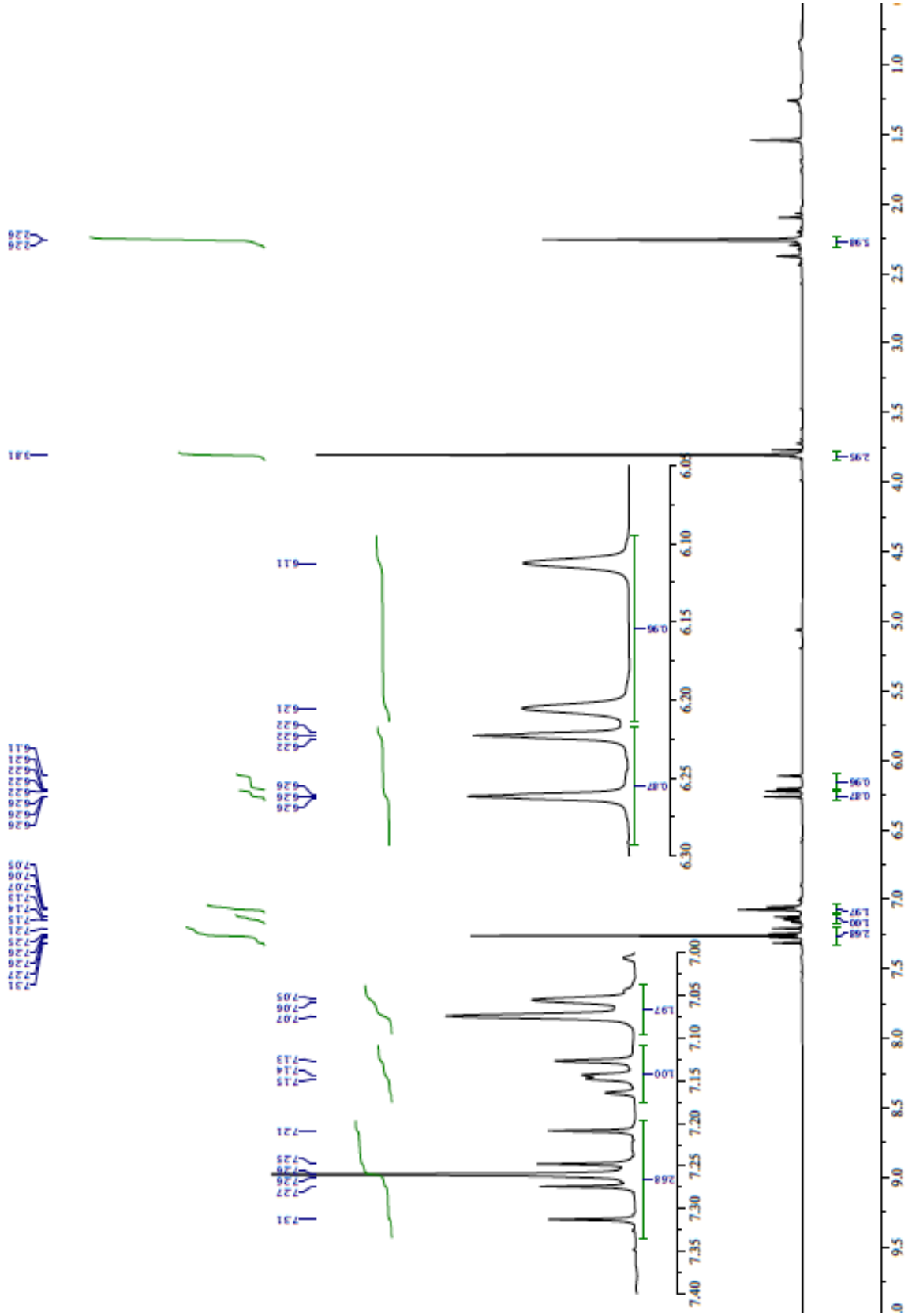
2-((*E*)-2-Fluoro-4-(4-methoxyphenyl)but-1-en-3-yn-1-yl)-1,3-dimethylbenzene (**3d**)

^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)



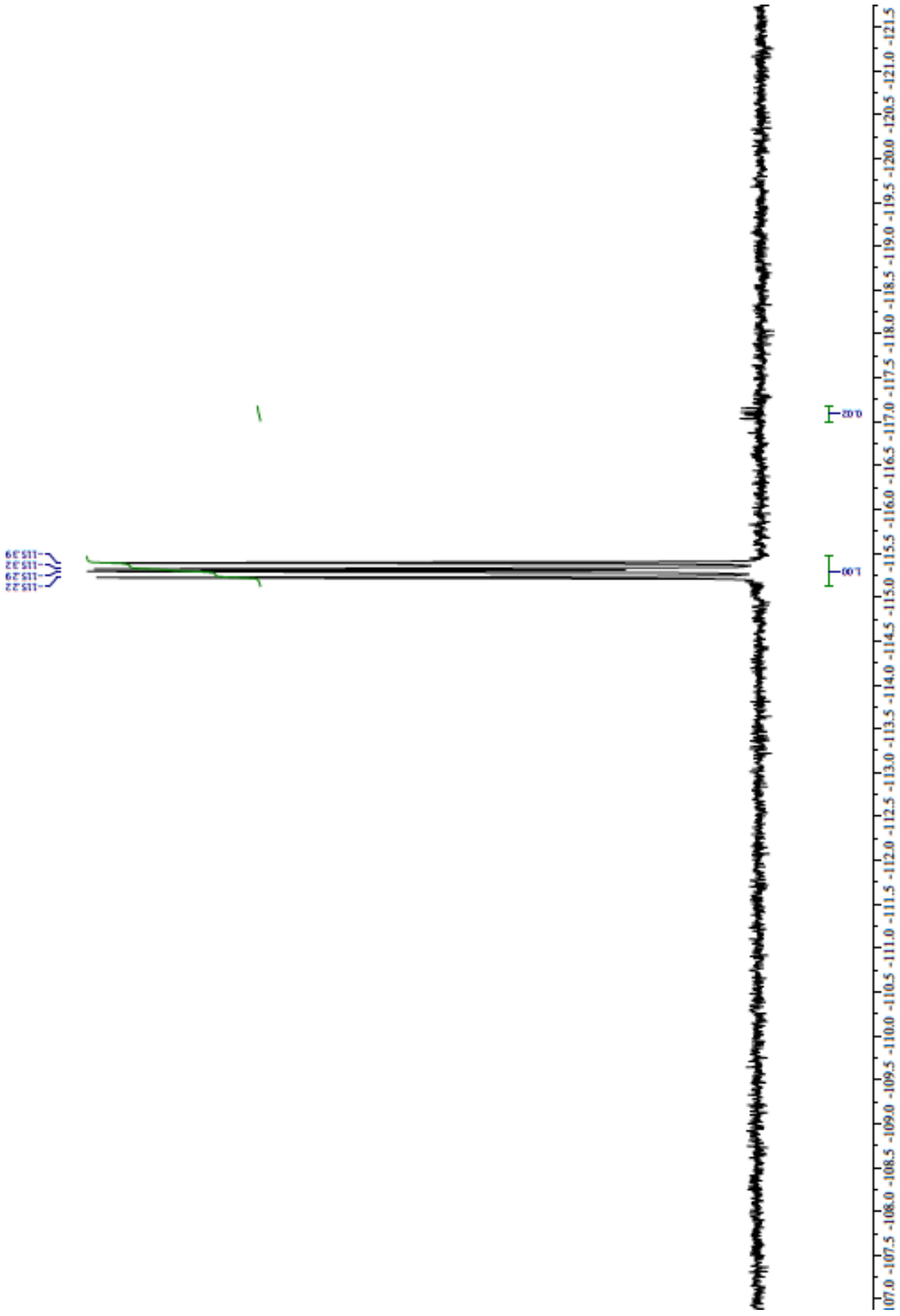
Methyl (2*E*,4*Z*)-5-(2,6-dimethylphenyl)-4-fluoropenta-2,4-dienoate (**3e**)

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



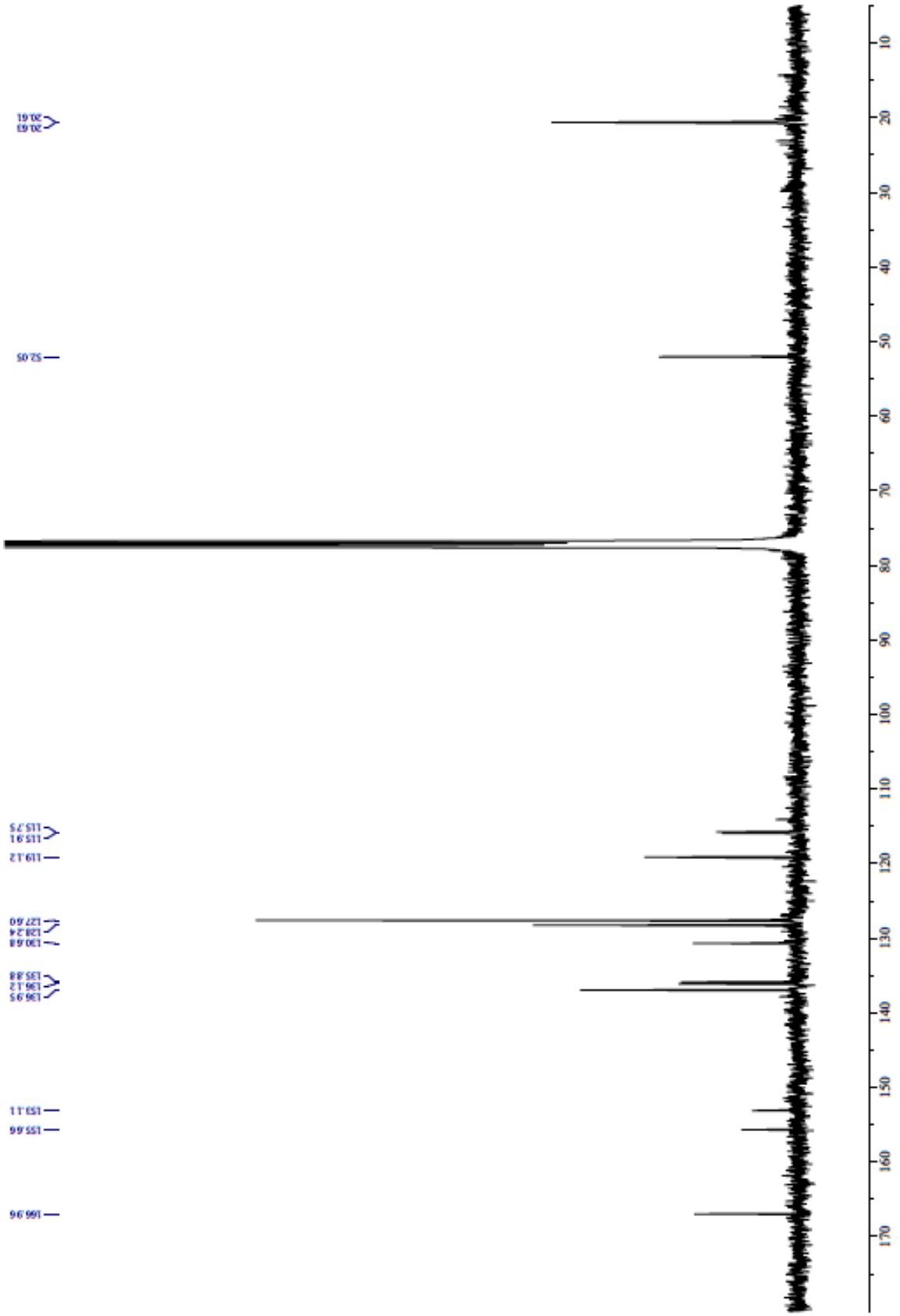
Methyl (2*E*,4*Z*)-5-(2,6-dimethylphenyl)-4-fluoropenta-2,4-dienoate (**3e**)

^{19}F NMR (376 MHz, $CDCl_3$, rt)



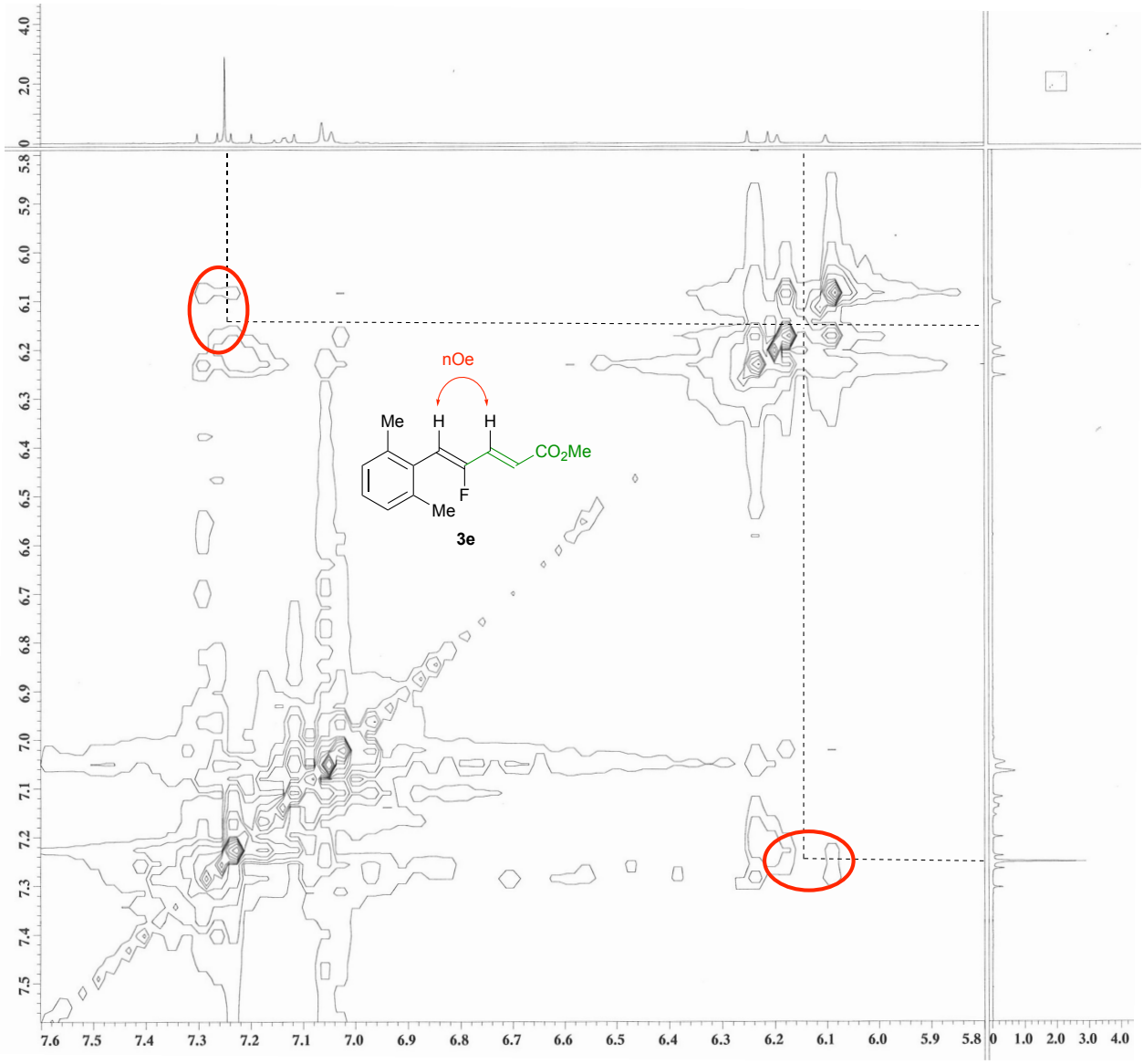
Methyl (2*E*,4*Z*)-5-(2,6-dimethylphenyl)-4-fluoropenta-2,4-dienoate (**3e**)

^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)



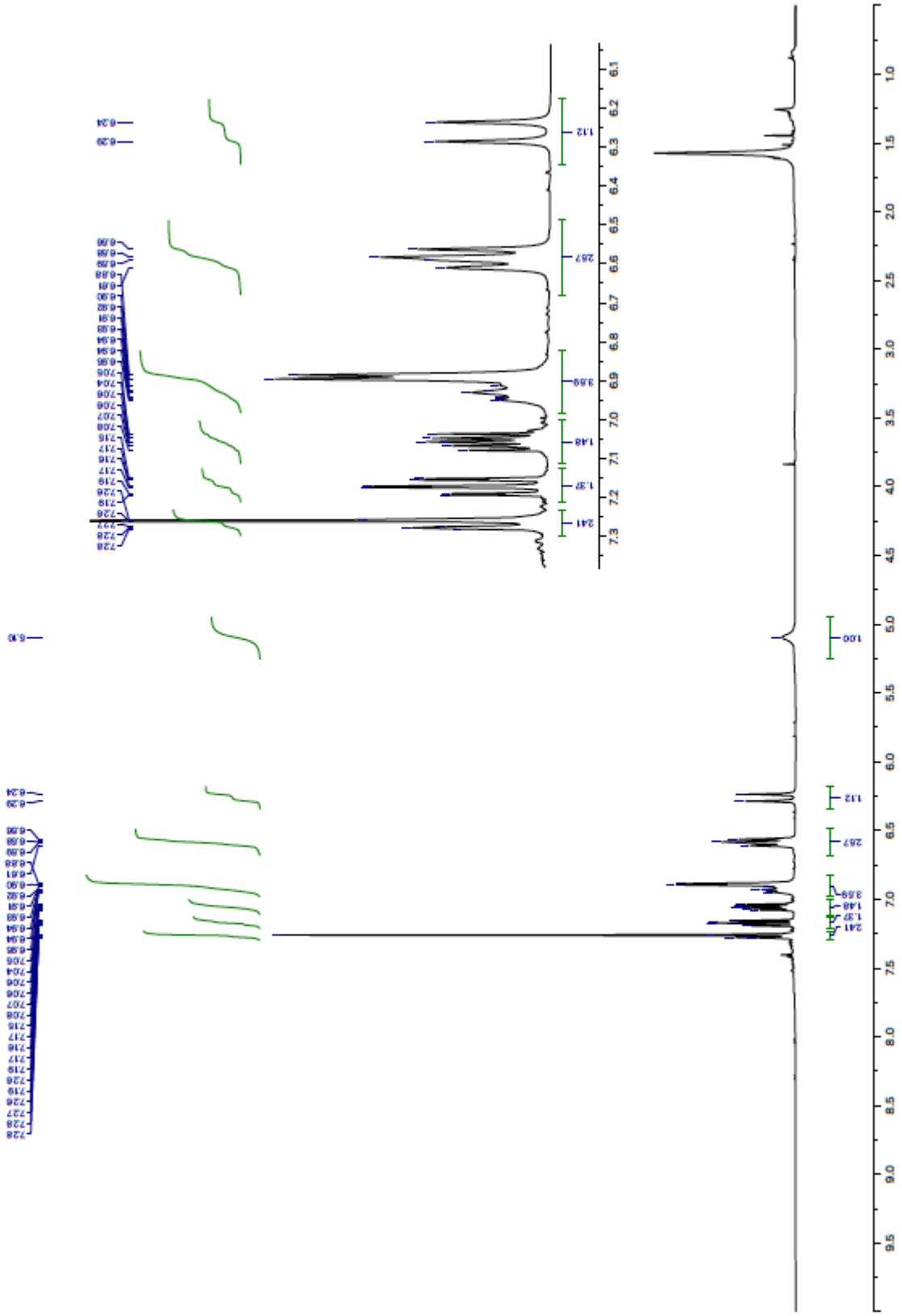
Methyl (2*E*,4*Z*)-5-(2,6-dimethylphenyl)-4-fluoropenta-2,4-dienoate (**3e**)

NOESY



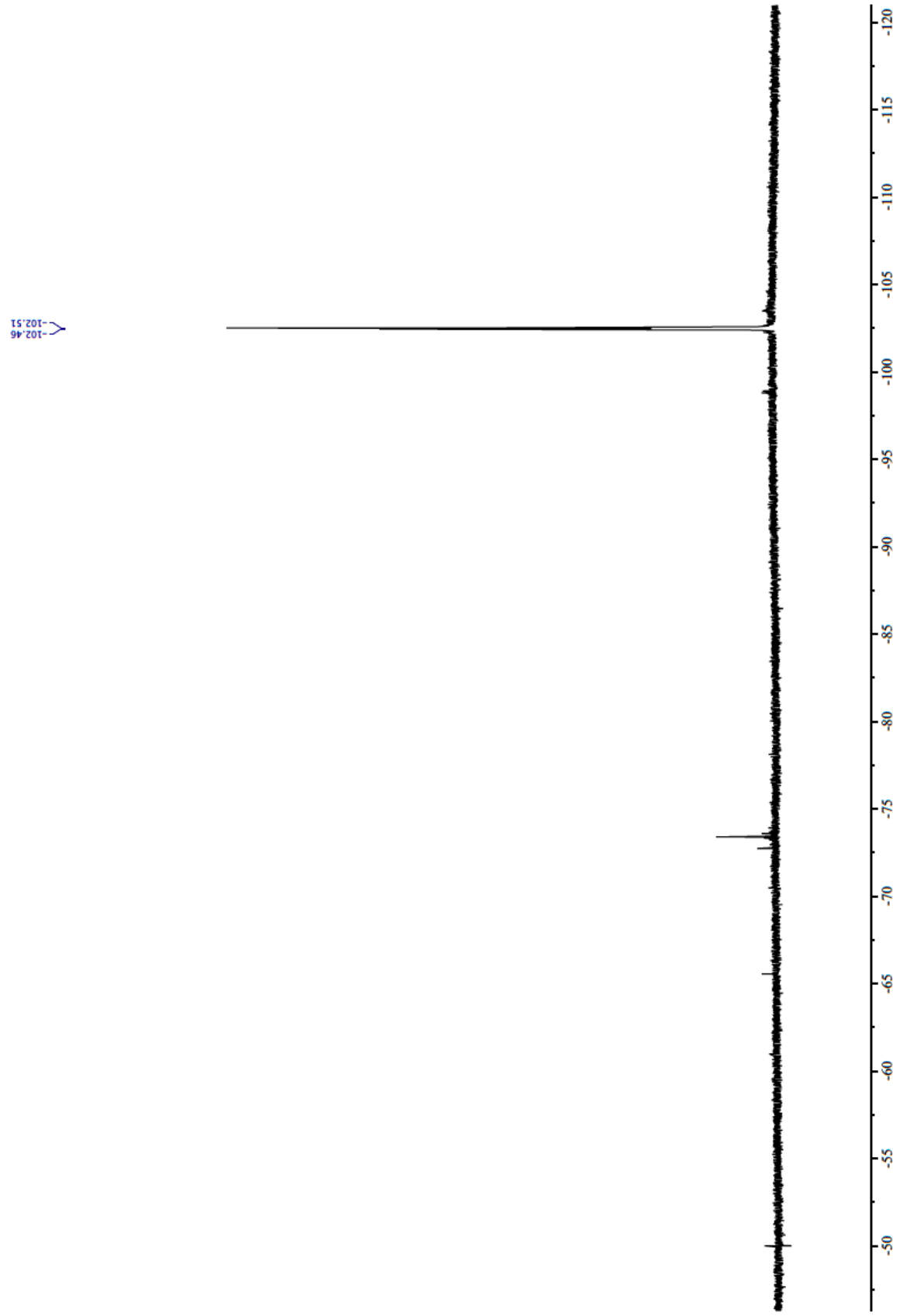
Fluorinated 5*H*-dibenz[*b*,*f*]azepine (**4**)

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



Fluorinated 5*H*-dibenz[*b*,*f*]azepine (**4**)

^{19}F NMR (376 MHz, $CDCl_3$, rt)



Fluorinated 5*H*-dibenz[*b*,*f*]azepine (**4**)

^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)