

Supporting information

Ring opening of methylenecyclopropanes with halides in liquid sulfur dioxide

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General experimental details

Reagents purchased from *Alfa Aesar*, *Acros Organics*, *Sigma Aldrich* were used as received. All solvents were distilled prior to use. THF was distilled from Na under Ar atmosphere.

GC analysis were performed on *Hewlett Packard Agilent Technologies 6890*, connected to *Agilent Technologies 5975B* mass spectrometer (electron ionization (EI) methods described below). Sample injected in manual mode.

For column chromatography *ROCC Silica Gel* (40-60 μm , 60 \AA) was used. Chromatography was monitored by TLC (*E.Merck Kieselgel 60 F₂₅₄*), visualized with UV light or permanganate stain.

High-resolution mass (HRMS) (electrospray ionization (ESI)) were recorded with an *Agilent 1290 Infinity* series ultra-high pressure liquid chromatography connected to an *Agilent 6230* time-of-flight mass spectrometer or (atmospheric pressure chemical ionization (APCI)) on *7 T solariX XR* (*Bruker Daltonik GmbH*) Fourier transform ion cyclotron resonance mass spectrometer equipped with an APCI source.

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra recorded on *Bruker Avance 300* or *Bruker Avance 500* spectrometers in CDCl_3 . Chemical shifts (δ) reported in *ppm* and coupling constants (*J*) in *Hz*. Residual solvent peaks used as reference ($^1\text{H-NMR} = 7.26$ ppm and $^{13}\text{C-NMR} \delta = 77.2$ ppm). Multiplicities are reported as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), dd (double dublet), dt (double triplet), m (multiplet), bs (broad signal). For quantitative NMR 1,2,3-trimethoxybenzene or diphenylmethane were used as internal standards.

Methods used for GC:

Method a:

Column	Agilent Technologies J&W 123-0132 DB-1ms capillary column, 30m x 0.32 mmID, 0.25 μm .
Column temperature	50 °C (4 min hold) to 290 °C (3 min hold) ; Ramp - 50 °C /min
Injector / detector temperature	250 °C / 230 °C
Carrier gas	Helium 2 mL/min
Injection mode	<i>Split</i> 1:10 ; solvent delay 4 min.
Injection volume	1 μL

Method b:

Column	Agilent Technologies J&W 123-0132 DB-1ms capillary column, 30m x 0.32 mmID, 0.25 μm .
Column temperature	50 °C (3 min hold) to 270 °C (3 min hold) ; Ramp - 50 °C /min
Injector / detector temperature	250 °C / 230 °C
Carrier gas	Helium 2 mL/min
Injection mode	<i>Split</i> 1:50 ; solvent delay 3 min.
Injection volume	1 μL

Method c:

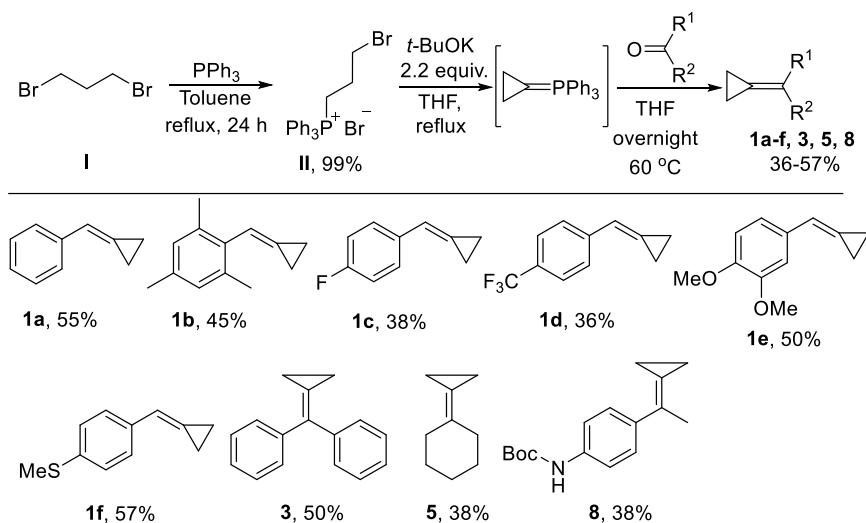
Column	Agilent Technologies J&W 123-0132 DB-1ms capillary column, 30m x 0.32 mmID, 0.25µm.
Column temperature	50 °C (3 min hold) to 270 °C (3 min hold) ; Ramp - 50 °C /min
Injector / detector temperature	250 °C / 230 °C
Carrier gas	Helium 1.2 mL/min
Injection mode	<i>Split</i> 1:20 ; solvent delay 3 min.
Injection volume	1 µL

Experimental procedures

General method methylenecyclopropane preparation

Methylenecyclopropanes **1af**, **3**, **5** and **8** were prepared according to previously reported method.¹

1,3-Dibromopropane (**I**) (5 g, 25 mmol, 1 equiv.) and triphenylphosphine (6.5 g, 25 mmol, 1 equiv.) is heated in toluene at reflux for 24 hours. After cooling the reaction mixture is filtered off and the precipitate is washed with additional toluene and dried under vacuum giving phosphonium salt **II** in quantitative yield. The phosphonium salt **II** (5 g, 10.77 mmol, 1.1 equiv.) is weighed in oven dried round bottom 2-neck 100 mL flask with condenser and rubber septum. Flask is degassed under vacuum and filled with inert N₂ atmosphere. Phosphonium salt **II** is suspended in anh. THF (40 mL) and KO*t*-Bu (dried under reduced pressure in 150 °C oil bath) (2.417 g, 21.54 mmol, 2.2 equiv.) is added in 3 portions over 30 minutes. The resulting yellowish reaction mixture is refluxed for 2 h. Aldehyde or ketone (9.79 mmol, 1 equivalent) is added to the brown-yellowish suspension and stirred overnight at 60 °C. The mixture is poured into ice water (20 mL) and extracted with hexanes (3 x 15 mL). The combined organic layer is washed with saturated NaCl solution and dried over anhydrous Na₂SO₄. Sulphate is filtered off and solvent evaporated under reduced pressure. Crude product is purified by column chromatography over silica gel (Hex) to give pure products **1af**, **3**, **5** and **8**.



¹ Xie, H.; Xu, B. *Eur. J. Org. Chem.* **2016**, 2594–2598.

General method for methylenecyclopropane ring opening in liquid SO₂

Glass test tube containing a stirring bar, methylenecyclopropane (50 mg, 1 equiv.), group I or II metal salt (MX) or ammonium salt (3 equiv.) and water (1.2 equiv. (except for NH₄⁺ salts)) was placed in a stainless steel pressure reactor (150 mL). The reactor is cooled in dry ice-ethanol bath to -78 °C. From reservoir SO₂ (~20 g) is distilled to the steel reactor and the reactor is sealed. The reactor is warmed to room temperature and heated with stirring in oil bath to desired temperature: 60 °C (~8 atm), 100 °C (~16 atm) or room temperature (~3 atm). After reaction is complete SO₂ is distilled back to reservoir for solvent recovery or the gas flow is neutralized with aqueous NaOH. The solid residue is washed with water (10 mL) or aqueous Na₂S₂O₃ solution (10 mL) (in reactions with iodides for neutralization of I₂ traces) and extracted with DCM (3 x 5 mL). The combined organic layer is dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. The obtained crude product is purified with column chromatography over silica gel (Hex, Hex/DCM or Hex/EtOAc) to give pure product.

Method for synthesis of product 4b at SO₂ reflux temperature (-10 °C)

Methylenecyclopropane **3** (50mg, 0.242 mmol, 1 equiv.), LiBr (63 mg, 0.726 mmol, 3 equiv.) and water (6 mg, 0.290 mmol, 1.2 equiv.) are weighed in oven-dried 2-neck 100 mL flask equipped with dry ice condenser. Sulfur dioxide (~ 15 mL) from storage tank is distilled to reaction flask and the reaction mixture is stirred for 1 h at -10 °C. Dry ice condenser is removed and the evaporated SO₂ gas is neutralized in aqueous NaOH solution. The solid residue is washed with water (10 mL) and extracted with DCM (3 x 5 mL). The combined organic layer is dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. The obtained crude product is purified by column chromatography over silica gel (Hex) to give pure product.

Method for methylenecyclopropane ring opening in solution of SO₂ in THF

MCP (50 mg, 1 equiv.), LiX (3 equivalents) and water (1.2 equiv.) is weighed in a pressure vial (10 mL) [*Ace pressure tube or similar*] and freshly prepared 3M solution of SO₂ in THF (1 mL) is added. The pressure vial is sealed and heated in oil bath at 70 °C for 1 h (*use safety shield: glass tube under pressure!*). After cooling, the resulting solution is filtered through silica gel layer and the solvent evaporated under reduced pressure. The obtained crude product is purified by column chromatography over silica gel (Hex or Hex/EtOAc) to give pure product.

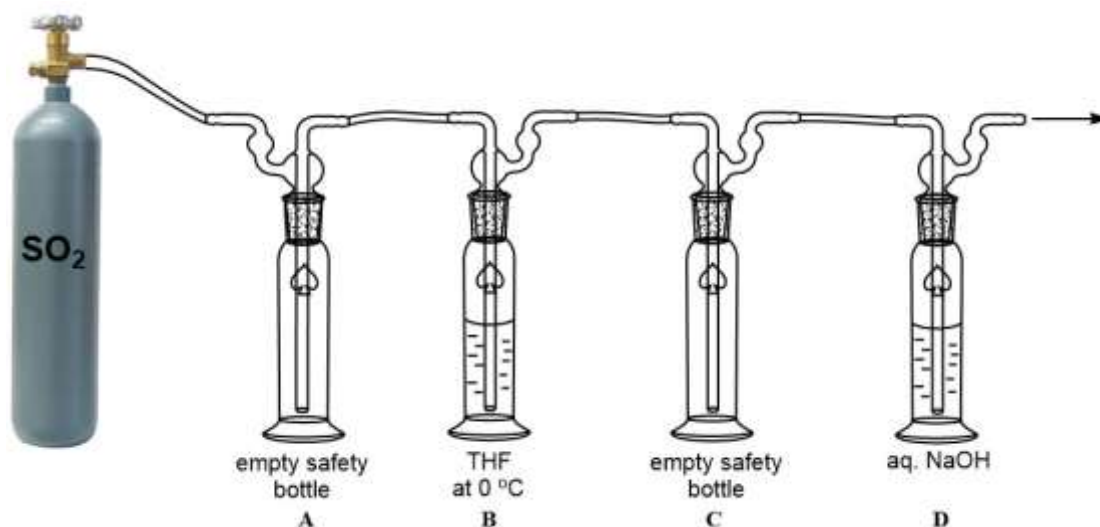
Method for methylenecyclopropane ring opening with catalytic amount of H₃PO₄

MCP (50 mg, 1 equiv.), LiX (3 equiv.) is weighed in a pressure vial (10 mL) and THF (1mL) is added. Freshly prepared 4% aqueous solution of H₃PO₄ that corresponded to both 1.2 equivalents of water and 1 mol% of H₃PO₄ is added. The pressure vial is sealed and heated in oil bath at 70 °C for 1 h (*use safety shield: glass tube under pressure!*). After cooling, the resulting solution is filtered through silica gel layer and the solvent evaporated under reduced pressure. The obtained crude product is purified by column chromatography over silica gel (Hex or Hex/EtOAc) to give pure product.

Preparation of SO₂ solution in THF

SO₂ reservoir is connected to empty gas wash bottle (A) that is connected to the gas wash bottle (B) filled with freshly distilled THF (100 mL), This is further connected to empty gas wash bottle (C) and bottle (D) filled with diluted aqueous NaOH solution (300 mL). While cooling THF containing wash bottle in ice bath (0 °C), SO₂ gas is slowly run through the system until THF solution starts to bubble vigorously (~15 min) and about 150 mL of solution is obtained. Its concentration was determined by iodometric titration and was found to be 7 M in SO₂.

The aforementioned saturated solution is diluted with THF in a volumetric flask to obtain 3 M solution of SO₂ in THF.



The saturated solution of SO₂ in THF is iodometrically titrated.²

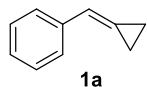
In 100 mL Erlenmeyer flask I₂ (254 mg, 1mmol) and KI (232 mg, 1.4 mmol) is weighed and diluted with THF (10 mL). Aforementioned saturated solution of SO₂ in THF (1 mL) is diluted in volumetric flask (100 mL) with distilled water to obtain 1:100 dilution. From the diluted solution 1 mL is added to Erlenmeyer flask with I₂ solution and the residual I₂ is back-titrated with standardized aqueous solution of Na₂S₂O₃. As indicator to determine titration endpoint 1% starch solution is added.

According to formula (1) residual I₂ after addition of SO₂ solution in THF is calculated and SO₂ is further calculated from equation (2).



² J. B. Ferguson, *J. Am. Chem. Soc.* **1917**, 39, 364-373.

Characterization of products



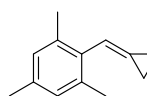
(cyclopropylidenemethyl)benzene (1a):

GC/MS (Method a) (70eV, EI) m/z = 130.1 ([M⁺]), t_r = 6.40 min.

R_f = 0.50 (Hex)

¹H-NMR (300 MHz, CDCl₃): δ = 7.54 (d, 2H), 7.34 (t, 2H), 7.22 (t, 1H), 6.77 (quint, 1H, ⁴J = 1.8 Hz), 1.44 (dt, 2H, ³J = 7.7 Hz, ⁴J = 1.8 Hz), 1.19 (dt, 2H, ³J = 7.7 Hz, ⁴J = 1.8 Hz) ppm. Correspond to literature data.³

¹³C-NMR (75 MHz, CDCl₃): δ = 138.43, 128.62, 126.86, 126.78, 124.48, 118.43, 4.39, 0.69 ppm. Correspond to literature data.³



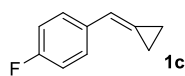
2-(cyclopropylidenemethyl)-1,3,5-trimethylbenzene (1b):

GC/MS (Method c) (70eV, EI) m/z = 172.0 ([M⁺]), t_r = 6.42 min.

R_f = 0.70 (Hex)

¹H-NMR (500 MHz, CDCl₃): δ = 6.88 (s, 2H), 6.78 (s, 1H), 2.28 (s, 3H), 2.24 (s, 6H), 1.25 (t, 2H, ³J = 7.8 Hz), 1.10 (t, 2H, ³J = 7.8 Hz) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 136.04, 135.90, 134.10, 128.32, 126.44, 116.83, 20.91, 20.84, 4.91, 2.70 ppm.

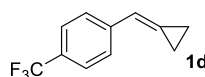


1-(cyclopropylidenemethyl)-4-fluorobenzene (1c):

R_f = 0.55 (Hex)

¹H-NMR (500 MHz, CDCl₃): δ = 7.49 (dd, ³J = 8.7 Hz, ⁴J_{H-F} = 5.6 Hz), 7.01 (dd, 2H, ³J = 8.7 Hz, ³J_{H-F} = 8.7 Hz), 6.71 (s, 1H), 1.40 (t, 2H, ³J = 7.7 Hz), 1.18 (t, 2H, ³J = 7.7 Hz) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 161.76 (d, ¹J_{C-F} = 245 Hz), 134.40 (d, ⁴J_{C-F} = 3 Hz), 127.97 (d, ³J_{C-F} = 8 Hz), 123.82, 117.13, 115.28 (d, ²J_{C-F} = 22 Hz), 4.02, 0.58 ppm.



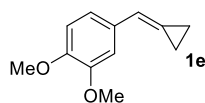
1-(cyclopropylidenemethyl)-4-(trifluoromethyl)benzene (1d):

GC/MS (Method c) (70eV, EI) m/z = 149.0 ([M⁺]), t_r = 7.52 min.

R_f = 0.55 (Hex)

¹H-NMR (500 MHz, CDCl₃): δ = 7.61 (d, 2H, ³J = 8.2 Hz), 7.56 (d, 2H, ³J = 8.2 Hz), 6.79 (t, 1H, ⁴J = 2.1 Hz), 1.46 (ddd, ³J = 8.1 Hz, ³J = 7.9 Hz, ⁴J = 2.1 Hz), 1.23 (dd, 2H, ³J = 8.1 Hz, ³J = 7.9 Hz) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 141.64, 128.45 (q, ²J = 33 Hz), 127.79, 126.62, 125.39 (q, ³J_{C-F} = 4 Hz), 124.37 (q, ¹J_{C-F} = 272 Hz), 117.28, 4.32, 0.73 ppm.



4-(cyclopropylidenemethyl)-1,2-dimethoxybenzene (1e):

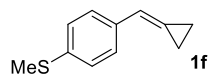
GC/MS (Method c) (70eV, EI) m/z = 190.1 ([M⁺]), t_r = 7.00 min.

R_f = 0.45 (20% Hex / EtOAc)

³ Makosza, M.; Bujok, R. *Synlett* **2008**, *4*, 586-588.

¹H-NMR (500 MHz, CDCl₃): δ = 7.15 (s, 1H), 7.04 (d, 1H, ³J = 8.2 Hz), 6.84 (d, 1H, ³J = 8.2 Hz), 6.69 (t, 1H, ³J = 1.9 Hz), 3.91 (s, 3H), 3.89 (s, 3H), 1.40 (td, 2H, ³J = 7.5 Hz, ⁴J = 1.9 Hz), 1.17 (t, 2H, ³J = 7.5 Hz) ppm. Correspond to literature data.⁴

¹³C-NMR (126 MHz, CDCl₃): δ = 148.96, 148.11, 131.56, 122.00, 119.39, 117.83, 111.15, 109.29, 55.92, 55.74, 3.95, 0.51 ppm. Correspond to literature data.⁴



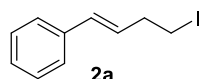
(4-(cyclopropylidenemethyl)phenyl)(methyl)sulfane (1f):

GC/MS (Method c) (70eV, EI) m/z = 176.1 ([M⁺]), t_r = 6.97 min.

R_f = 0.30 (Hex)

¹H-NMR (500 MHz, CDCl₃): δ = 7.45 (d, 2H, ³J = 8.3 Hz), 7.24 (d, 2H, ³J = 8.3 Hz), 6.71 (bs, 1H), 2.49 (s, 3H), 1.41 (t, 2H, ³J = 7.7 Hz), 1.17 (t, 2H, ³J = 7.7 Hz) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 136.45, 135.45, 126.99, 126.91, 123.86, 117.66, 16.10, 4.15, 0.54 ppm.



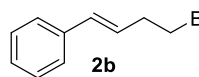
(E)-(4-iodobut-1-en-1-yl)benzene (2a):

GC/MS (Method a) (70eV, EI) m/z = 258.0 ([M⁺]), t_r = 7.57 min.

R_f = 0.40 (Hex)

¹H-NMR (300 MHz, CDCl₃): δ = 7.23-7.41 (m, 5H), 6.49 (d, 1H, ³J = 15.8 Hz), 6.16 (dt, 1H, ³J = 15.8 Hz, ³J = 6.9 Hz), 3.25 (t, 2H, ³J = 6.8 Hz), 2.80 (q, 2H, ³J = 6.8 Hz) ppm.

¹³C-NMR (75 MHz, CDCl₃): δ = 137.26, 132.47, 128.76, 128.68, 127.62, 126.37, 37.17, 5.13 ppm.



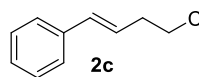
(E)-(4-bromobut-1-en-1-yl)benzene (2b):

GC/MS (Method a) (70eV, EI) m/z = 212.0 / 210.0 ([M⁺]), t_r = 7.30 min.

R_f = 0.40 (Hex)

¹H-NMR (300 MHz, CDCl₃): δ = 7.23-7.41 (m, 5H), 6.53 (d, 1H, ³J = 16.0 Hz), 6.23 (dt, 1H, ³J = 16.0 Hz, ³J = 7.0 Hz), 3.51 (t, 2H, ³J = 7.0 Hz), 2.80 (q, 2H, ³J = 7.0 Hz) ppm.

¹³C-NMR (75 MHz, CDCl₃): δ = 137.19, 132.87, 128.75, 127.63, 126.82, 126.36, 36.47, 32.45 ppm.



(E)-(4-chlorobut-1-en-1-yl)benzene (2c):

GC/MS (Method a) (70eV, EI) m/z = 168.1 / 166.1 ([M⁺]), t_r = 7.04 min.

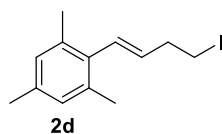
R_f = 0.40 (Hex)

¹H-NMR (300 MHz, CDCl₃): δ = 7.23-7.41 (m, 5H), 6.52 (d, 1H, ³J = 16.0 Hz), 6.22 (dt, 1H, ³J = 16.0 Hz, ³J = 7.0 Hz), 3.64 (t, 2H, ³J = 7.0 Hz), 2.70 (q, 2H, ³J = 7.0 Hz) ppm. Correspond to literature data.⁵

¹³C-NMR (75 MHz, CDCl₃): δ = 137.11, 132.83, 128.56, 127.43, 126.19, 125.83, 44.03, 36.19 ppm. Correspond to literature data.⁵

⁴ Furstner, A.; Aissa, C. *J. Am. Chem. Soc.* **2006**, *128*, 6306-6307.

⁵ Kabalka, G. W.; Yao, M. L.; Borella, S.; Wu, Z. Z. *Org. Lett.* **2005**, *7*, 2865-2867.



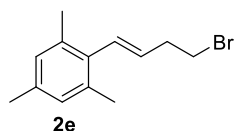
(E)-2-(4-iodobut-1-en-1-yl)-1,3,5-trimethylbenzene (2d):

GC/MS (Method c) (70eV, EI) m/z = 300.1 ([M⁺]), t_r = 7.43 min.

R_f = 0.70 (30% Hex / DCM)

¹H-NMR (500 MHz, CDCl₃): δ = 6.86 (s, 2H), 6.42 (d, 1H, ³J = 16.1 Hz), 5.60 (dt, 1H, ³J = 16.1 Hz, ³J = 6.9 Hz), 3.28 (t, 2H, ³J = 6.9 Hz), 2.81 (q, 2H, ³J = 6.9 Hz), 2.28 (s, 6H), 2.27 (s, 3H) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 136.07, 135.82, 133.91, 133.10, 130.13, 128.48, 37.33, 21.00, 20.90, 5.63 ppm.



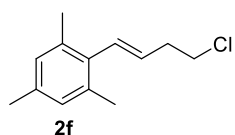
(E)-2-(4-bromobut-1-en-1-yl)-1,3,5-trimethylbenzene (2e):

GC/MS (Method c) (70eV, EI) m/z = 252.1 / 254.1 ([M⁺]), t_r = 7.19 min.

R_f = 0.70 (30% Hex / DCM)

¹H-NMR (500 MHz, CDCl₃): δ = 6.86 (s, 2H), 6.42 (d, 1H, ³J = 16.1 Hz), 5.63 (dt, 1H, ³J = 16.1 Hz, ³J = 6.9 Hz), 3.50 (t, 2H, ³J = 6.9 Hz), 2.80 (q, 2H, ³J = 6.9 Hz), 2.27 (s, 9H) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 136.08, 135.83, 133.95, 131.38, 130.55, 128.46, 36.61, 32.62, 20.90, 20.88 ppm.



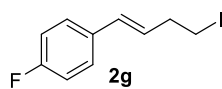
(E)-2-(4-chlorobut-1-en-1-yl)-1,3,5-trimethylbenzene (2f):

GC/MS (Method c) (70eV, EI) m/z = 208.1 ([M⁺]), t_r = 6.96 min.

R_f = 0.65 (30% Hex / DCM)

¹H-NMR (500 MHz, CDCl₃): δ = 6.86 (s, 2H), 6.43 (d, 1H, ³J = 16.1 Hz), 5.63 (dt, 1H, ³J = 16.1 Hz, ³J = 6.8 Hz), 3.64 (t, 2H, ³J = 6.8 Hz), 2.70 (q, 2H, ³J = 6.8 Hz), 2.26 (s, 9H) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 136.05, 135.83, 134.00, 130.64, 130.59, 128.44, 44.28, 36.50, 20.90, 20.83 ppm.



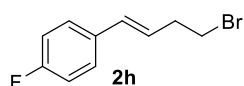
(E)-1-fluoro-4-(4-iodobut-1-en-1-yl)benzene (2g):

GC/MS (Method c) (70eV, EI) m/z = 276.0 ([M⁺]), t_r = 6.84 min.

R_f = 0.30 (Hex)

¹H-NMR (500 MHz, CDCl₃): δ = 7.33 (dd, 2H, ³J = 8.6 Hz, ⁴J_{H-F} = 5.5 Hz), 7.00 (dd, 2H, ³J = 8.6 Hz, ³J_{H-F} = 8.6 Hz), 6.43 (d, 1H, ³J = 15.8 Hz), 6.06 (dt, 1H, ³J = 15.7 Hz, ³J = 7.0 Hz), 3.24 (t, 2H, ³J = 7.0 Hz), 2.77 (q, 2H, ³J = 7.0 Hz) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 162.25 (d, ¹J_{C-F} = 247 Hz), 133.21 (d, ⁴J_{C-F} = 3 Hz), 131.12, 128.25 (d, ⁵J_{C-F} = 2 Hz), 127.69 (d, ³J_{C-F} = 8 Hz), 115.47 (d, ²J_{C-F} = 22 Hz), 36.86, 4.95 ppm.



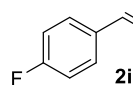
(E)-1-(4-bromobut-1-en-1-yl)-4-fluorobenzene (2h):

GC/MS (Method c) (70eV, EI) m/z = 228.0 / 230.0 ([M⁺]), t_r = 6.57 min.

R_f = 0.30 (Hex)

¹H-NMR (500 MHz, CDCl₃): δ = 7.32 (dd, 2H, ³J = 8.6 Hz, ⁴J_{H-F} = 5.5 Hz), 7.00 (dd, 2H, ³J = 8.6 Hz, ³J_{H-F} = 8.6 Hz), 6.45 (d, 1H, ³J = 15.8 Hz), 6.11 (dt, 1H, ³J = 15.8 Hz, ³J = 7.0 Hz), 3.47 (t, 2H, ³J = 7.0 Hz), 2.77 (q, 2H, ³J = 7.0 Hz) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 162.25 (d, ¹J_{C-F} = 247 Hz), 133.21 (d, ⁴J_{C-F} = 3 Hz), 131.53, 127.66 (d, ³J_{C-F} = 8 Hz), 126.41 (d, ⁵J_{C-F} = 2 Hz), 115.44 (d, ²J_{C-F} = 22 Hz), 36.17, 32.19 ppm.



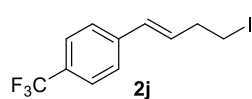
(E)-1-(4-chlorobut-1-en-1-yl)-4-fluorobenzene (2i):

GC/MS (Method c) (70eV, EI) m/z = 184.0 ([M⁺]), t_r = 6.32 min.

R_f = 0.25 (Hex)

¹H-NMR (500 MHz, CDCl₃): δ = 7.33 (dd, 2H, ³J = 8.6 Hz, ³J_{H-F} = 5.6 Hz), 7.00 (dd, 2H, ³J = 8.6 Hz, ³J_{H-F} = 8.6 Hz), 6.46 (d, 1H, ³J = 15.9 Hz), 6.12 (dt, 1H, ³J = 15.9 Hz, ³J = 6.9 Hz), 3.62 (t, 2H, ³J = 6.9 Hz), 2.67 (q, 2H, ³J = 6.9 Hz) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 162.23 (d, ¹J_{C-F} = 247 Hz), 133.21 (d, ⁴J_{C-F} = 3 Hz), 131.63, 127.67 (d, ³J_{C-F} = 8 Hz), 125.58 (d, ⁵J_{C-F} = 2 Hz), 115.43 (d, ²J_{C-F} = 22 Hz), 44.01, 36.07 ppm.



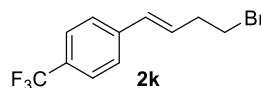
(E)-1-(4-iodobut-1-en-1-yl)-4-(trifluoromethyl)benzene (2j):

GC/MS (Method c) (70eV, EI) m/z = 326.0 ([M⁺]), t_r = 6.87 min.

R_f = 0.70 (30% Hex / DCM)

¹H-NMR (500 MHz, CDCl₃) δ = 7.56 (d, 2H, ³J = 8.1 Hz), 7.46 (d, 2H, ³J = 8.1 Hz), 6.51 (d, 1H, ³J = 15.9 Hz), 6.25 (dt, 1H, ³J = 15.9 Hz, ⁴J = 7.0 Hz), 3.26 (t, 2H, ³J = 7.0 Hz), 2.82 (q, 2H, ³J = 7.0 Hz) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 140.51, 131.29, 131.05, 129.27 (q, ²J_{C-F} = 33 Hz), 126.33, 125.54 (q, ³J_{C-F} = 4 Hz), 124.19 (q, ¹J_{C-F} = 272 Hz), 36.76, 4.36 ppm.



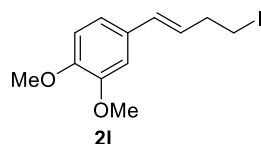
(E)-1-(4-bromobut-1-en-1-yl)-4-(trifluoromethyl)benzene (2k):

GC/MS (Method c) (70eV, EI) m/z = 278.0 / 280.0 ([M⁺]), t_r = 6.62 min.

R_f = 0.60 (30% Hex / DCM)

¹H-NMR (500 MHz, CDCl₃): δ = 7.56 (d, 2H, ³J = 8.2 Hz), 7.45 (d, 2H, ³J = 8.2 Hz), 6.53 (d, 1H, ³J = 15.9 Hz), 6.30 (dt, 1H, ³J = 15.9 Hz, ³J = 6.9 Hz), 3.50 (t, 2H, ³J = 6.9 Hz), 2.82 (q, 2H, ³J = 6.9 Hz) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 140.47, 131.46, 129.50, 129.29 (q, ²J_{C-F} = 33 Hz), 126.34, 125.53 (q, ³J_{C-F} = 4 Hz), 124.19 (q, ¹J_{C-F} = 272 Hz), 36.12, 31.81 ppm.



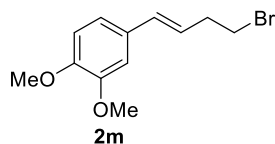
(E)-4-(4-iodobut-1-en-1-yl)-1,2-dimethoxybenzene (2l):

GC/MS (Method c) (70eV, EI) m/z = 318.0 ([M⁺]), t_r = 7.86 min.

R_f = 0.40 (20% Hex / EtOAc)

¹H-NMR (500 MHz, CDCl₃): δ = 6.92 (s, 1H), 6.91 (d, 1H, ³J = 8.0 Hz), 6.81 (d, 1H, ³J = 8.0 Hz), 6.41 (d, 1H, ³J = 15.7 Hz), 6.01 (dt, 1H, ³J = 15.7 Hz, ³J = 7.1 Hz), 3.90 (s, 3H), 3.88 (s, 3H), 3.24 (t, 2H, ³J = 7.1 Hz), 2.77 (q, 2H, ³J = 7.1 Hz) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 149.09, 148.75, 131.95, 130.20, 126.56, 119.26, 111.22, 108.73, 55.94, 55.88, 37.04, 5.21 ppm.



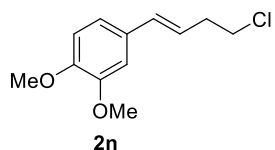
(E)-4-(4-bromobut-1-en-1-yl)-1,2-dimethoxybenzene (2m):

GC/MS (Method c) (70eV, EI) $m/z = 270.1 / 272.1$ ($[M^+]$), $t_r = 7.63$ min.

$R_f = 0.40$ (20% Hex / EtOAc)

$^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta = 6.92$ (s, 1H), 6.90 (d, 1H, $^3J = 8.3$ Hz), 6.81 (d, 1H, $^3J = 8.3$ Hz), 6.42 (d, 1H, $^3J = 15.8$ Hz), 6.05 (dt, 1H, $^3J = 15.8$, $^3J = 7.0$ Hz), 3.90 (s, 3H), 3.88 (s, 3H), 3.47 (t, 2H, $^3J = 7.0$ Hz), 2.76 (q, 2H, $^3J = 7.0$ Hz) ppm.

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): $\delta = 149.07, 148.76, 132.37, 130.17, 124.67, 119.28, 111.19, 108.71, 55.94, 55.84, 36.30, 32.39$ ppm.



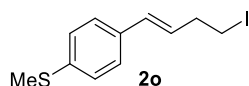
(E)-4-(4-chlorobut-1-en-1-yl)-1,2-dimethoxybenzene (2n):

GC/MS (Method c) (70eV, EI) $m/z = ([M^+])$, $t_r =$ min.

$R_f = 0.35$ (20% Hex / EtOAc)

$^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta = 6.92$ (s, 1H), 6.89 (d, 1H, $^3J = 8.3$ Hz), 6.81 (d, 1H, $^3J = 8.3$ Hz), 6.43 (d, 1H, $^3J = 15.8$ Hz), 6.07 (dt, 1H, $^3J = 15.8$ Hz, $^3J = 7.0$ Hz), 3.90 (s, 3H), 3.88 (s, 3H), 3.62 (t, 2H, $^3J = 7.0$ Hz), 2.67 (q, 2H, $^3J = 7.0$ Hz) ppm.

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): $\delta = 149.06, 148.73, 132.47, 130.21, 123.84, 119.28, 111.17, 108.67, 55.95, 55.85, 44.21, 36.19$ ppm.



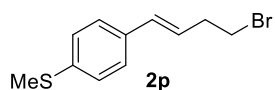
(E)-(4-(4-iodobut-1-en-1-yl)phenyl)(methyl)sulfane (2o):

GC/MS (Method c) (70eV, EI) $m/z = 304.0$ ($[M^+]$), $t_r = 7.91$ min.

$R_f = 0.30$ (30% Hex / DCM)

$^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta = 7.29$ (d, 2H, $^3J = 8.4$ Hz), 7.20 (d, 2H, $^3J = 8.4$ Hz), 6.42 (d, 1H, $^3J = 15.8$ Hz), 6.11 (dt, 1H, $^3J = 15.8$ Hz, $^3J = 7.3$ Hz), 3.24 (t, 2H, $^3J = 7.3$ Hz), 2.77 (q, 2H, $^3J = 7.3$ Hz), 2.48 (s, 3H) ppm.

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): $\delta = 137.56, 134.09, 131.65, 127.98, 126.80, 126.59, 36.98, 15.93, 4.98$ ppm.



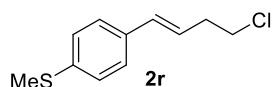
(E)-(4-(4-bromobut-1-en-1-yl)phenyl)(methyl)sulfane (2p):

GC/MS (Method c) (70eV, EI) $m/z = 256.0 / 258.0$ ($[M^+]$), $t_r = 7.66$ min.

$R_f = 0.30$ (30% Hex / DCM)

$^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta = 7.28$ (d, 2H, $^3J = 8.3$ Hz), 7.20 (d, 2H, $^3J = 8.3$ Hz), 6.44 (d, 1H, $^3J = 15.8$ Hz), 6.15 (dt, 1H, $^3J = 15.8$ Hz), 3.47 (t, 2H, $^3J = 7.0$ Hz), 2.77 (q, 2H, $^3J = 7.0$ Hz), 2.48 (s, 3H) ppm.

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): $\delta = 137.57, 134.06, 132.06, 126.78, 126.59, 126.12, 36.28, 32.22, 15.93$ ppm.



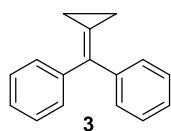
(E)-(4-(4-chlorobut-1-en-1-yl)phenyl)(methyl)sulfane (2r):

GC/MS (Method c) (70eV, EI) $m/z = 212.0$ ($[M^+]$), $t_r = 7.43$ min.

$R_f = 0.25$ (30% Hex / DCM)

¹H-NMR (500 MHz, CDCl₃): δ = 7.28 (d, 2H, ³J = 8.4 Hz), 7.20 (d, 2H, ³J = 8.4 Hz), 6.44 (d, 1H, ³J = 15.9 Hz), 6.17 (dt, 1H, ³J = 15.9 Hz, ³J = 7.0 Hz), 3.62 (t, 2H, ³J = 7.0 Hz), 2.67 (q, 2H, ³J = 7.0 Hz), 2.48 (s, 3H) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 137.52, 134.10, 132.16, 126.78, 126.58, 125.29, 44.04, 36.17, 15.94 ppm.



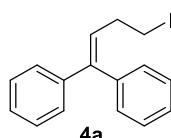
(cyclopropylidene)methylene)dibenzene (3):

GC/MS (Method b) (70eV, EI) m/z = 206.1 ([M⁺]), t_r = 6.96 min.

R_f = 0.45 (Hex)

¹H-NMR (300 MHz, CDCl₃): δ = 7.47 (d, 4H, ³J = 7Hz), 7.27 – 7.40 (m, 6H), 1.44 (s, 4H) ppm. Correspond to literature data.³

¹³C-NMR (126 MHz, CDCl₃): δ = 141.12, 130.17, 128.55, 128.26, 127.04, 124.58, 3.77 ppm. Correspond to literature data.³



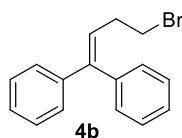
(4-iodobut-1-ene-1,1-diyl)dibenzene (4a):

GC/MS (Method b) (70eV, EI) m/z = 333.9 ([M⁺]), t_r = 7.70 min.

R_f = 0.20 (Hex)

¹H-NMR (300 MHz, CDCl₃): δ = 7.15-7.42 (m, 10H), 6.03 (t, 1H, ³J = 7.2 Hz), 3.20 (t, 2H, ³J = 7.2 Hz), 2.71 (q, 2H, ³J = 7.2 Hz) ppm. Correspond to literature data.⁶

¹³C-NMR (126 MHz, CDCl₃): δ = 144.00, 142.29, 139.80, 129.85, 128.49, 128.33, 127.85, 127.47, 127.46, 127.44, 33.53, 5.70 ppm. Correspond to literature data.⁶



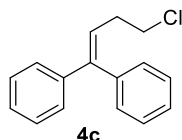
(4-bromobut-1-ene-1,1-diyl)dibenzene (4b):

GC/MS (Method b) (70eV, EI) m/z = 286.1 / 288.1 ([M⁺]), t_r = 7.45 min.

R_f = 0.20 (Hex)

¹H-NMR (500 MHz, CDCl₃): δ = 7.18-7.42 (m, 10H), 6.10 (t, 1H, ³J = 7.2Hz), 3.44 (t, 2H, ³J = 6.9 Hz), 2.69 (q, 2H, ³J = 7.0 Hz). Correspond to literature data.⁶

¹³C-NMR (126 MHz, CDCl₃): δ = 144.45, 142.26, 139.77, 129.87, 128.52, 128.33, 127.49, 127.46, 127.45, 125.86, 33.09, 32.84 ppm. Correspond to literature data.⁶



(4-chlorobut-1-ene-1,1-diyl)dibenzene (4c):

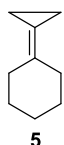
GC/MS (Method b) (70eV, EI) m/z = 242.1 / 244.1 ([M⁺]), t_r = 7.27 min.

R_f = 0.20 (Hex)

¹H-NMR (500 MHz, CDCl₃): δ = 7.17-7.41 (m, 10H), 6.12 (t, 1H, ³J = 7.3 Hz), 3.58 (t, 2H, ³J = 6.9 Hz), 2.60 (q, 2H, ³J = 6.9 Hz) ppm. Correspond to literature data.⁶

¹³C-NMR (126 MHz, CDCl₃): δ = 144.62, 142.30, 139.80, 129.91, 128.53, 128.34, 127.49, 127.47, 127.44, 124.96, 44.55, 33.09 ppm. Correspond to literature data.⁶

⁶ Xu, B.; Shi, M. *Org. Lett.* **2003**, *5*, 1415-1418.



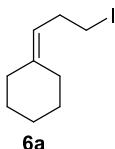
cyclopropylidenecyclohexane (5):

GC/MS (Method b) (70eV, EI) $m/z = 122.1$ ($[M^+]$), $t_r = 4.47$ min.

$R_f = 0.90$ (Hex)

$^1\text{H-NMR}$ (300 MHz, CDCl_3): $\delta = 2.26$ (bs, 4H), 1.57 (bs, 6H), 0.99 (bs, 4H) ppm.

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3): $\delta = 128.31, 111.82, 33.73, 27.98, 26.92, 1.77$ ppm.



(3-iodopropylidene)cyclohexane (6a):

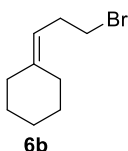
GC/MS (Method b) (70eV, EI) $m/z = 250.1$ ($[M^+]$), $t_r = 6.08$ min.

$R_f = 0.65$ (Hex)

HRMS: calculated $[\text{C}_9\text{H}_{15}\text{I} + \text{H}]^+$ 251.0291, found 251.0297

$^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta = 5.45$ (bs, 1H), 3.16 (t, 2H, $^3J = 7.0$ Hz), 2.02 (t, 2H, $^3J = 7.1$ Hz), 1.95-2.00 (m, 2H), 1.87-1.95 (m, 4H), 1.58-1.64 (m, 2H), 1.52-1.57 (m, 2H) ppm.

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): $\delta = 135.86, 122.45, 38.69, 31.68, 28.37, 25.41, 23.14, 22.66, 7.01$ ppm.



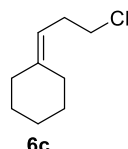
(3-bromopropylidene)cyclohexane (6b):

GC/MS (Method b) (70eV, EI) $m/z = 202.0 / 204.0$ ($[M^+]$), $t_r = 5.75 / 7.78$ min.

$R_f = 0.65$ (Hex)

$^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta = 5.09$ (t, 1H, $^3J = 7.2$ Hz), 3.35 (t, 2H, $^3J = 7.4$ Hz), 2.59 (q, 2H, $^3J = 7.4$ Hz), 2.13-2.17 (m, 2H), 2.09-2.13 (m, 2H), 1.51-1.60 (m, 6H) ppm.

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): $\delta = 143.43, 117.63, 37.27, 33.34, 31.10, 29.06, 28.73, 27.99, 26.96$ ppm.



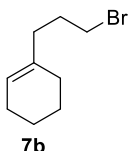
(3-chloropropylidene)cyclohexane (6c):

GC/MS (Method b) (70eV, EI) $m/z = 158.1 / 160.1$ ($[M^+]$), $t_r = 5.46$ min.

$R_f = 0.65$ (Hex)

$^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta = 5.08$ (t, 1H, $^3J = 7.3$ Hz), 3.46 (t, 2H, $^3J = 7.3$ Hz), 2.46 (q, 2H, $^3J = 7.3$ Hz), 2.11-2.15 (m, 2H), 2.06-2.10 (m, 2H), 1.48-1.58 (m, 6H) ppm.

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): $\delta = 143.47, 116.64, 44.86, 37.28, 30.92, 29.04, 28.75, 28.00, 26.97$ ppm.



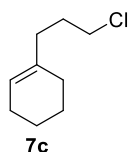
1-(3-bromopropyl)cyclohex-1-ene (7b):

GC/MS (Method b) (70eV, EI) $m/z = 202.0 / 204.0$ ($[M^+]$), $t_r = 5.75 / 5.78$ min.

$R_f = 0.65$ (Hex)

$^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta = 5.45$ -5.48 (m, 1H), 3.41 (t, 2H, $^3J = 6.8$ Hz), 2.07-2.11 (m, 2H), 1.95-2.04 (m, 4H), 1.90-1.95 (m, 2H), 1.61-1.67 (m, 2H), 1.56-1.61 (m, 2H) ppm.

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): $\delta = 136.01, 122.36, 36.46, 33.83, 30.92, 28.36, 25.39, 23.12, 22.65$ ppm.



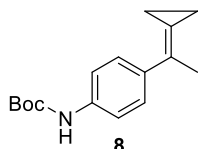
1-(3-chloropropyl)cyclohex-1-ene (7c):

GC/MS (Method b) (70eV, EI) $m/z = 158.1 / 160.1$ ($[M^+]$), $t_r = 5.46$ min.

$R_f = 0.65$ (Hex)

$^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta = 5.42\text{-}5.45$ (m, 1H), 3.51 (t, 2H, $^3J = 6.7$ Hz), 1.96-2.00 (m, 2H), 1.83-1.92 (m, 4H), 1.59-1.64 (m, 2H), 1.48-1.57 (m, 4H) ppm.

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): $\delta = 136.18, 122.23, 44.94, 35.23, 30.76, 28.38, 25.39, 23.13, 22.66$ ppm.



tert-butyl (4-(1-cyclopropylideneethyl)phenyl)carbamate (8):

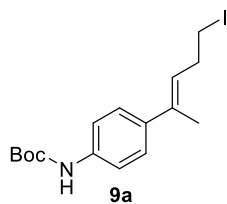
GC/MS (Method b) (70eV, EI) $m/z = 259.1$ ($[M^+]$), $t_r = 7.67$ min.

$R_f = 0.70$ (20% Hex/EtOAc)

HRMS: calculated $[\text{C}_{16}\text{H}_{21}\text{NO}_2 + \text{H}]^+ 260.1645$, found 260.1645

$^1\text{H-NMR}$ (300 MHz, CDCl_3): $\delta = 7.57$ (d, 2H, $^3J = 8.7$ Hz), 7.34 (d, 2H, $^3J = 8.7$ Hz), 6.45 (s, 1H), 2.20 (s, 3H), 1.52 (s, 9H), 1.42 (t, 2H, $^3J = 6.7$ Hz), 1.10 (t, 2H, $^3J = 6.7$ Hz) ppm.

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): $\delta = 152.91, 136.94, 135.73, 126.14, 122.07, 119.45, 118.40, 80.63, 28.55, 19.89, 5.93, 0.63$ ppm.



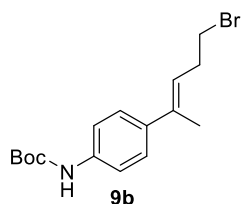
tert-butyl (E)-(4-(5-iodopent-2-en-2-yl)phenyl)carbamate (9a):

GC/MS (Method b) (70eV, EI) $m/z = 387.1$ ($[M^+]$), $t_r = 8.77$ min.

$R_f = 0.60$ (20% Hex/EtOAc)

$^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta = 7.28\text{-}7.34$ (m, 4H), 6.46 (s, 1H), 5.66 (t, 1H, $^3J = 7.2$ Hz), 3.21 (t, 2H, $^3J = 7.2$ Hz), 2.80 (q, 2H, $^3J = 7.2$ Hz), 2.01 (s, 3H), 1.52 (s, 9H).

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): $\delta = 152.84, 138.18, 137.40, 136.74, 126.36, 125.59, 118.43, 80.68, 33.08, 28.49, 16.20, 5.41$ ppm.



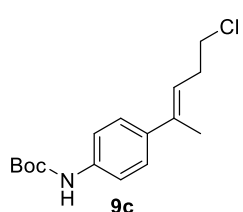
tert-butyl (E)-(4-(5-bromopent-2-en-2-yl)phenyl)carbamate (9b):

GC/MS (Method b) (70eV, EI) $m/z = 340.8$ ($[M^+]$), $t_r = 8.42$ min.

$R_f = 0.65$ (20% Hex/EtOAc)

$^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta = 7.28\text{-}7.35$ (m, 4H), 6.45 (s, 1H), 5.71 (t, 1H, $^3J = 7.2$ Hz), 3.45 (t, 2H, $^3J = 7.2$ Hz), 2.77 (q, 2H, $^3J = 7.2$ Hz), 2.02 (s, 3H), 1.52 (s, 9H) ppm.

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): $\delta = 152.83, 138.13, 137.42, 137.20, 126.37, 123.50, 118.41, 80.70, 32.50, 32.44, 28.49, 16.17$ ppm.



tert-butyl (E)-(4-(5-chloropent-2-en-2-yl)phenyl)carbamate (9c):

GC/MS (Method b) (70eV, EI) $m/z = 295.1$ ($[M^+]$), $t_r = 8.14$ min.

$R_f = 0.60$ (20% Hex/EtOAc)

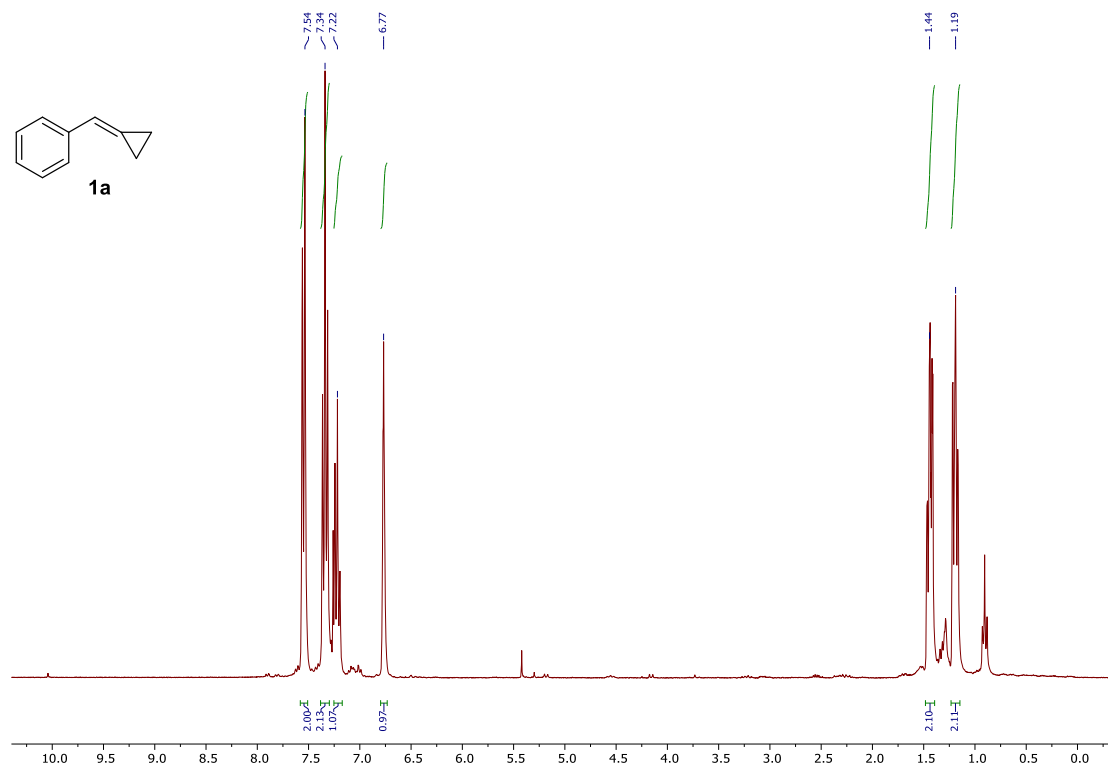
HRMS: calculated $[\text{C}_{16}\text{H}_{22}\text{NO}_2\text{Cl} + \text{H}]^+ 296.1412$, found 296.1395

¹H-NMR (500 MHz, CDCl₃): δ = 7.28-7.34 (m, 4H), 6.46 (s, 1H), 5.73 (t, 1H, ³*J* = 7.1 Hz), 3.59 (t, 2H, ³*J* = 7.1 Hz), 2.67 (q, 2H, ³*J* = 7.1 Hz), 2.03 (s, 3H), 1.52 (s, 9H) ppm.

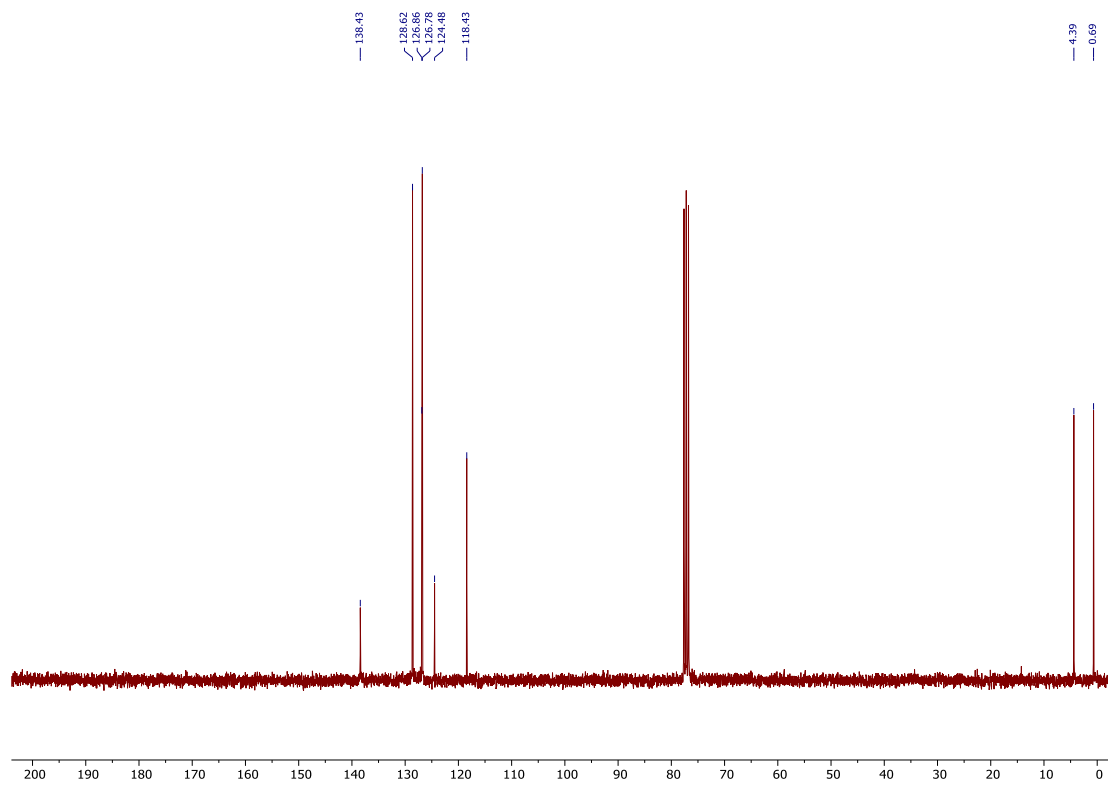
¹³C-NMR (126 MHz, CDCl₃): δ = 152.83, 138.16, 137.40, 137.29, 126.40, 122.51, 118.37, 81.80, 44.22, 32.37, 28.47, 16.12 ppm.

NMR Spectra

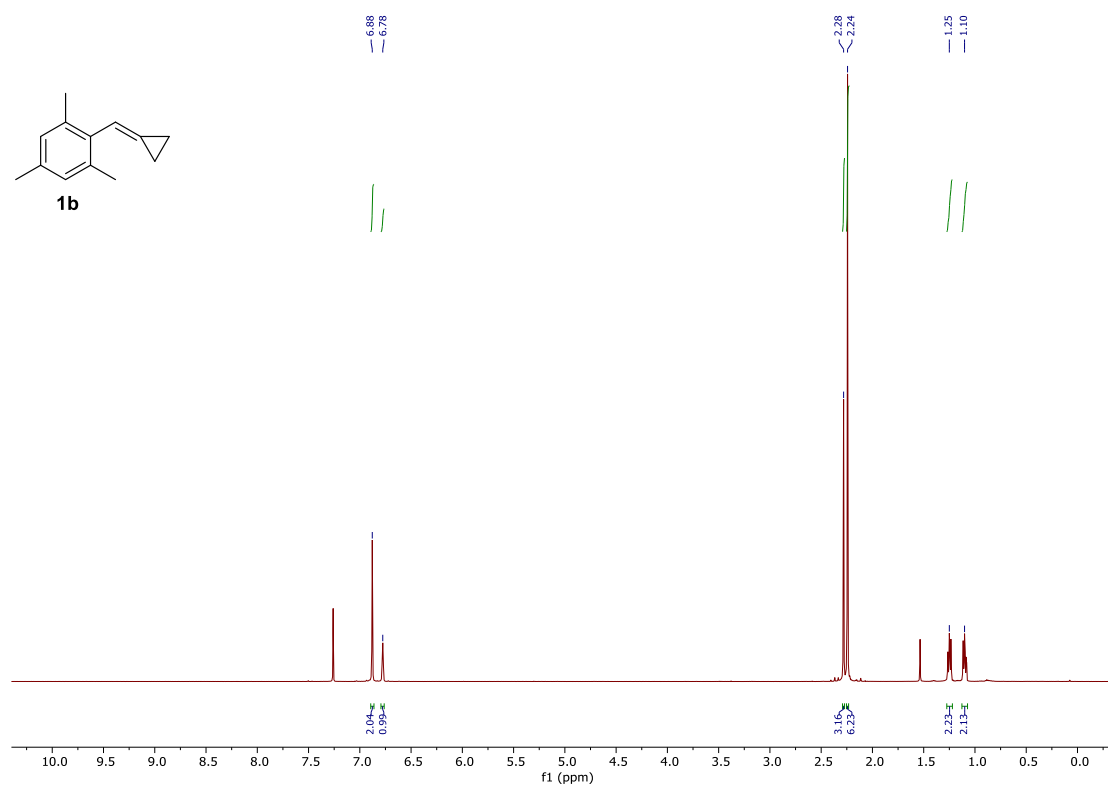
1a $^1\text{H-NMR}$ (300 MHz, CDCl_3) spectrum:



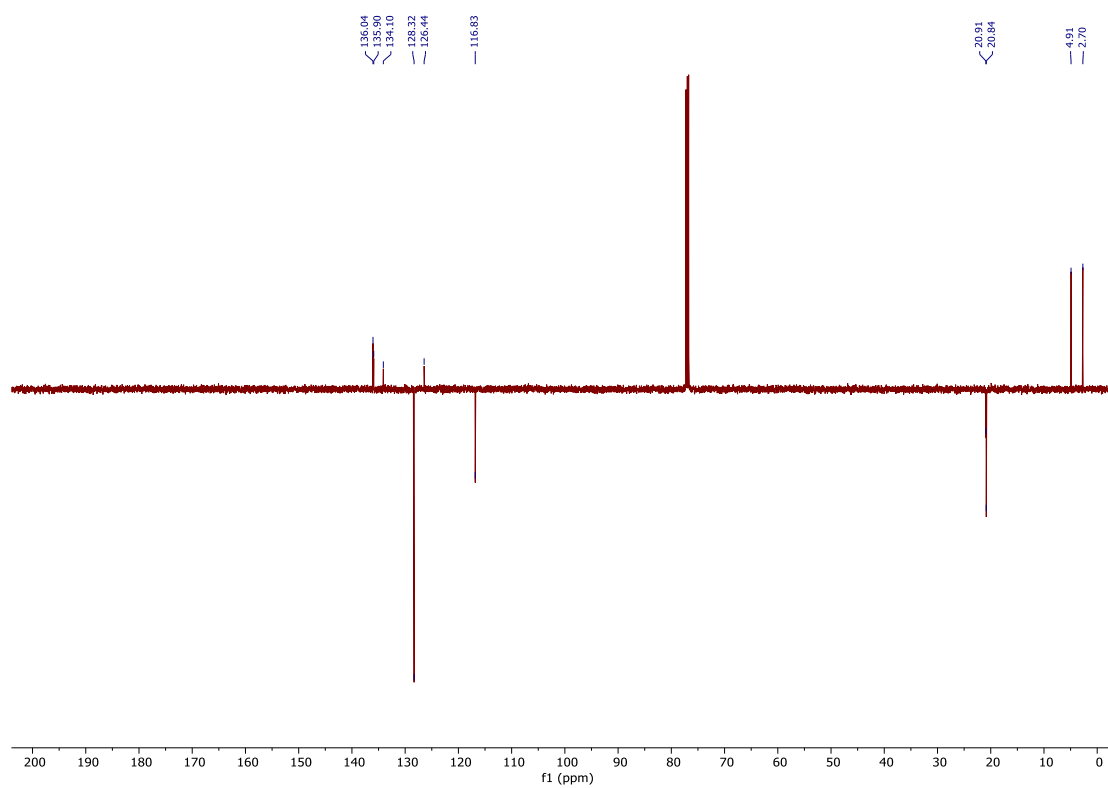
1 $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) spectrum:



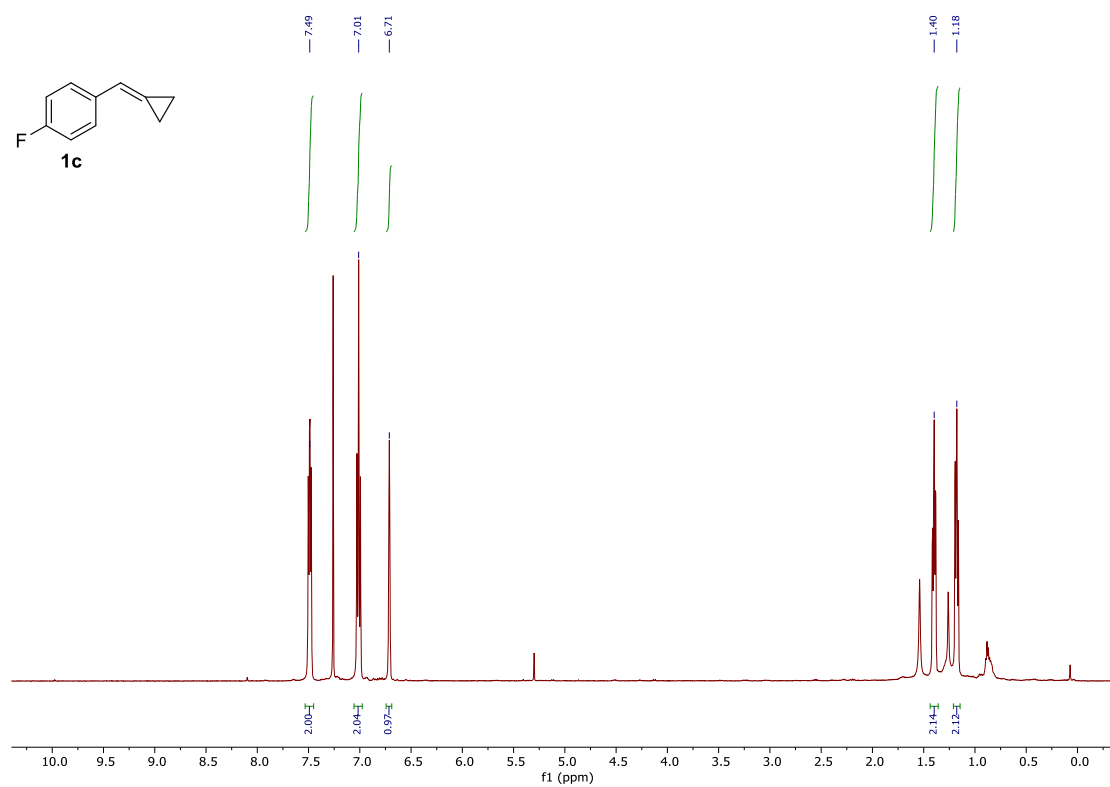
1b ¹H-NMR (500 MHz, CDCl₃) spectrum:



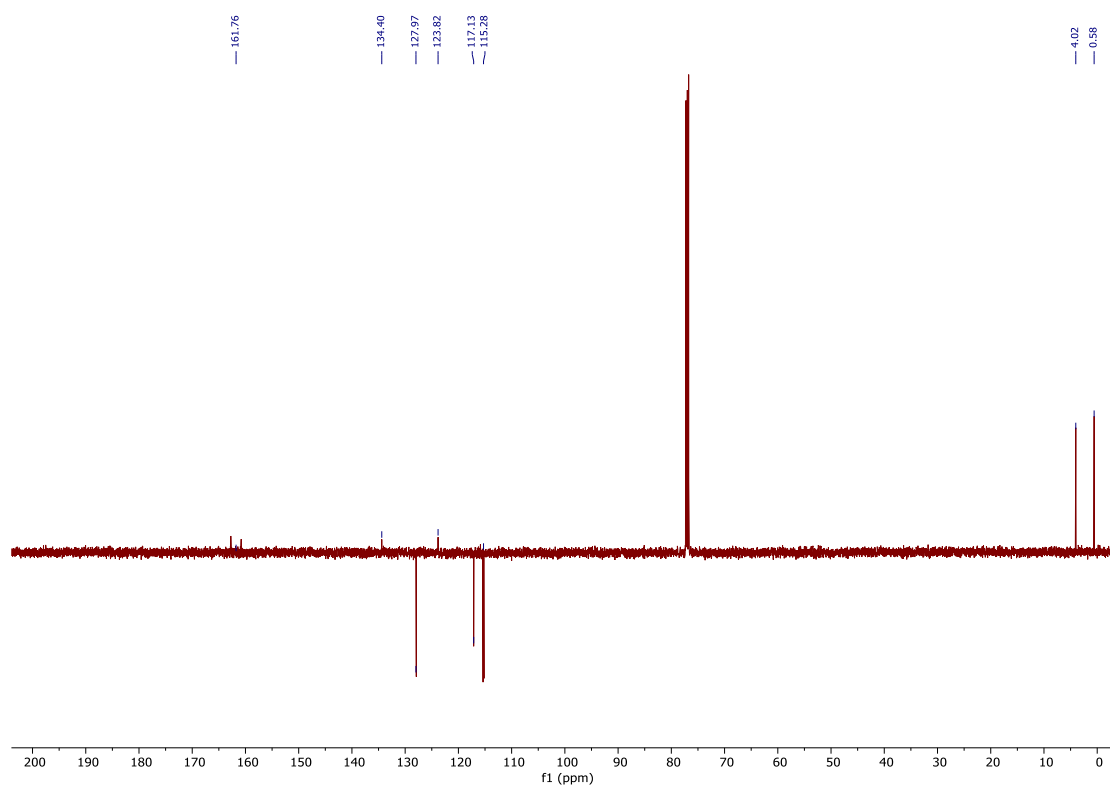
1b ¹³C-NMR (126 MHz, CDCl₃) spectrum:



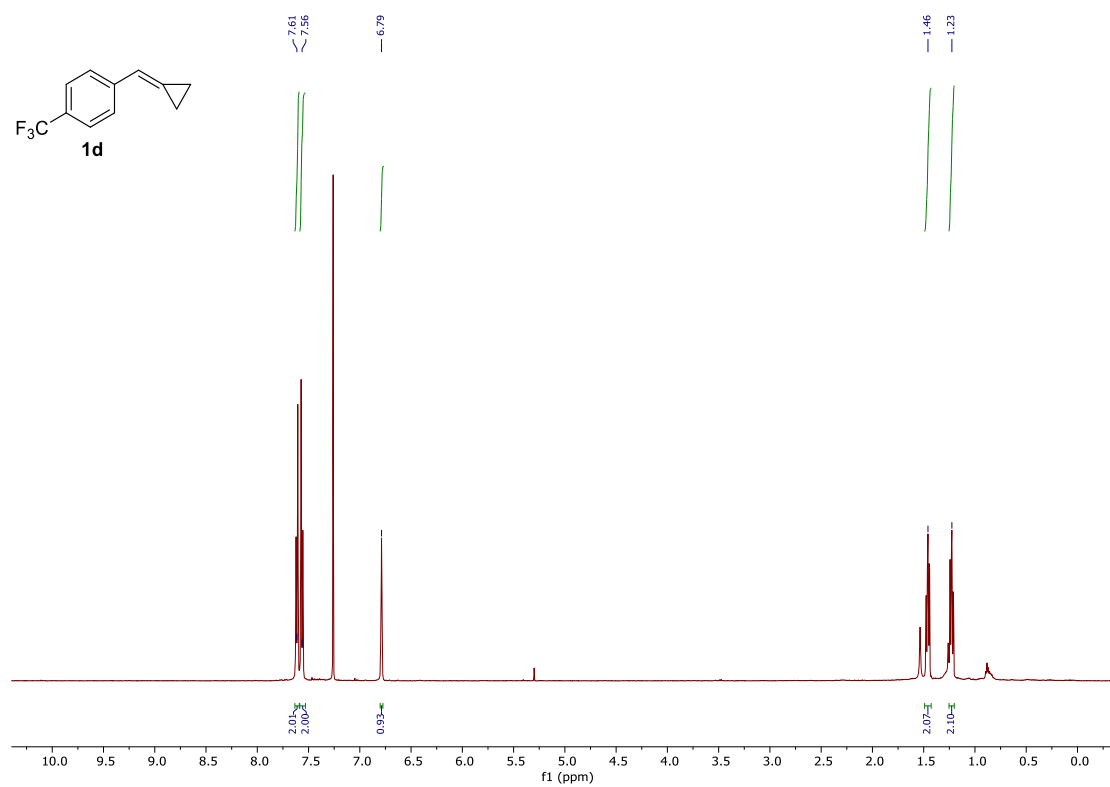
1c ¹H-NMR (500 MHz, CDCl₃) spectrum:



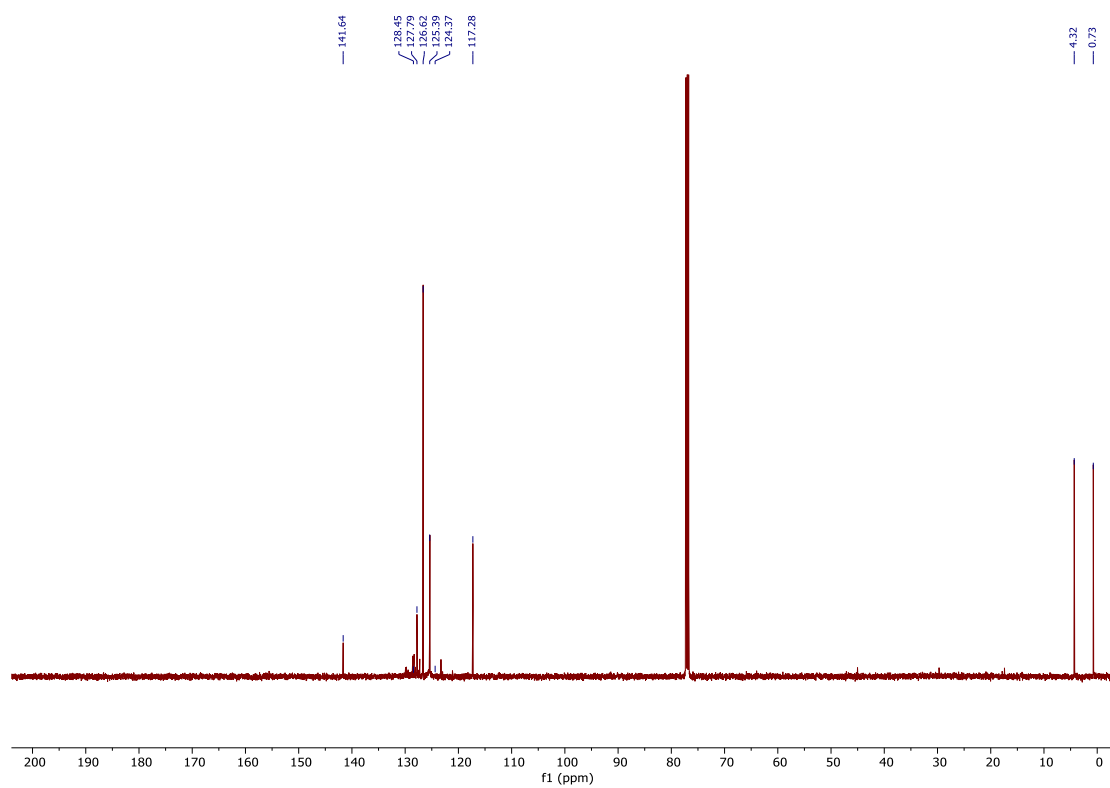
1c ¹³C-NMR (126 MHz, CDCl₃) spectrum:



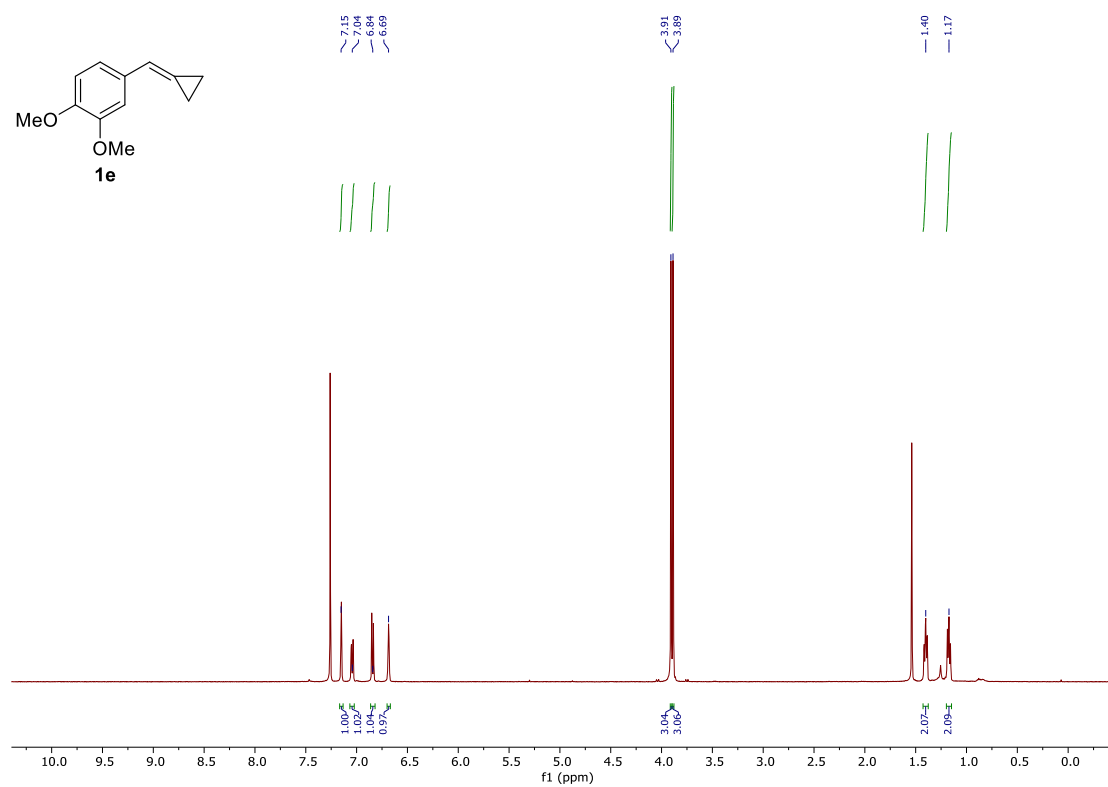
1d ¹H-NMR (500 MHz, CDCl₃) spectrum:



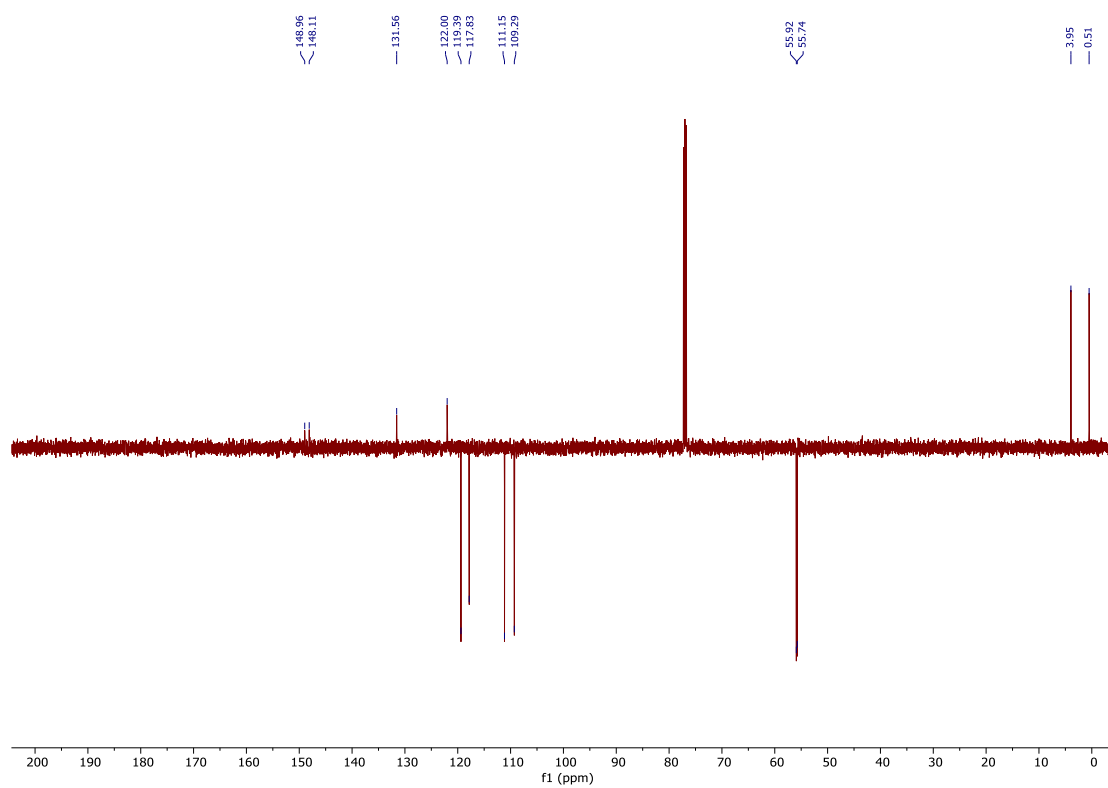
1d ¹³C-NMR (126 MHz, CDCl₃) spectrum:



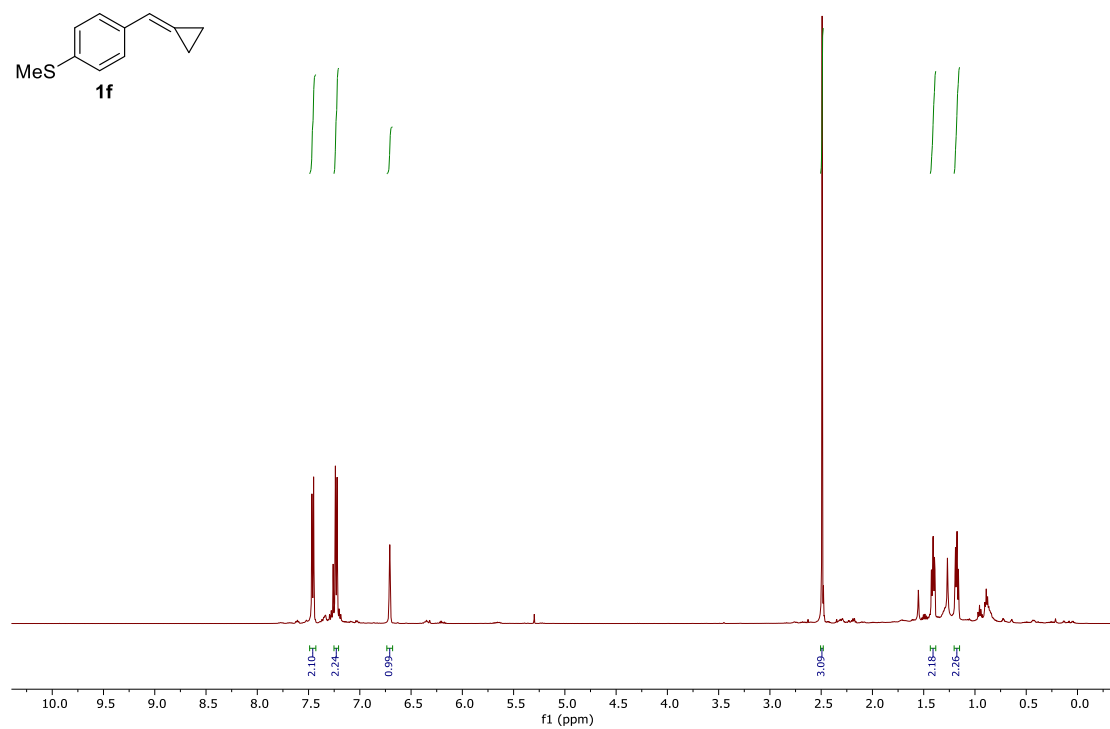
1e ¹H-NMR (500 MHz, CDCl₃) spectrum:



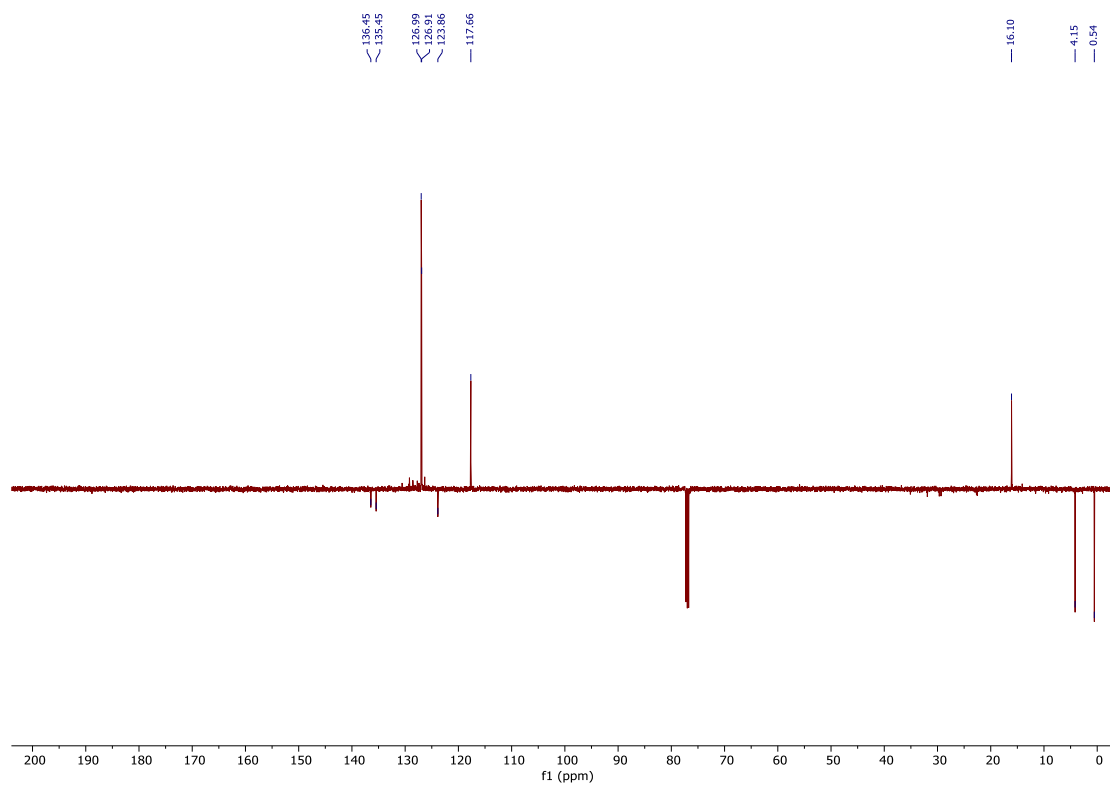
1e ¹³C-NMR (126 MHz, CDCl₃) spectrum:



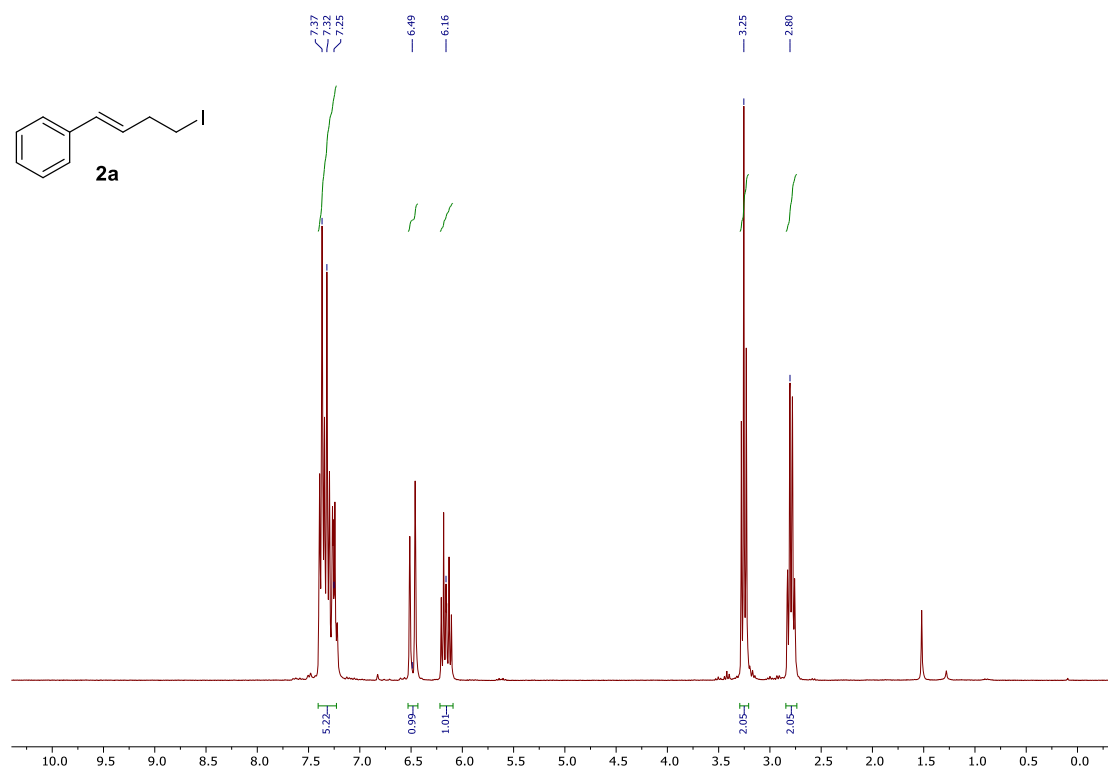
1f ¹H-NMR (500 MHz, CDCl₃) spectrum:



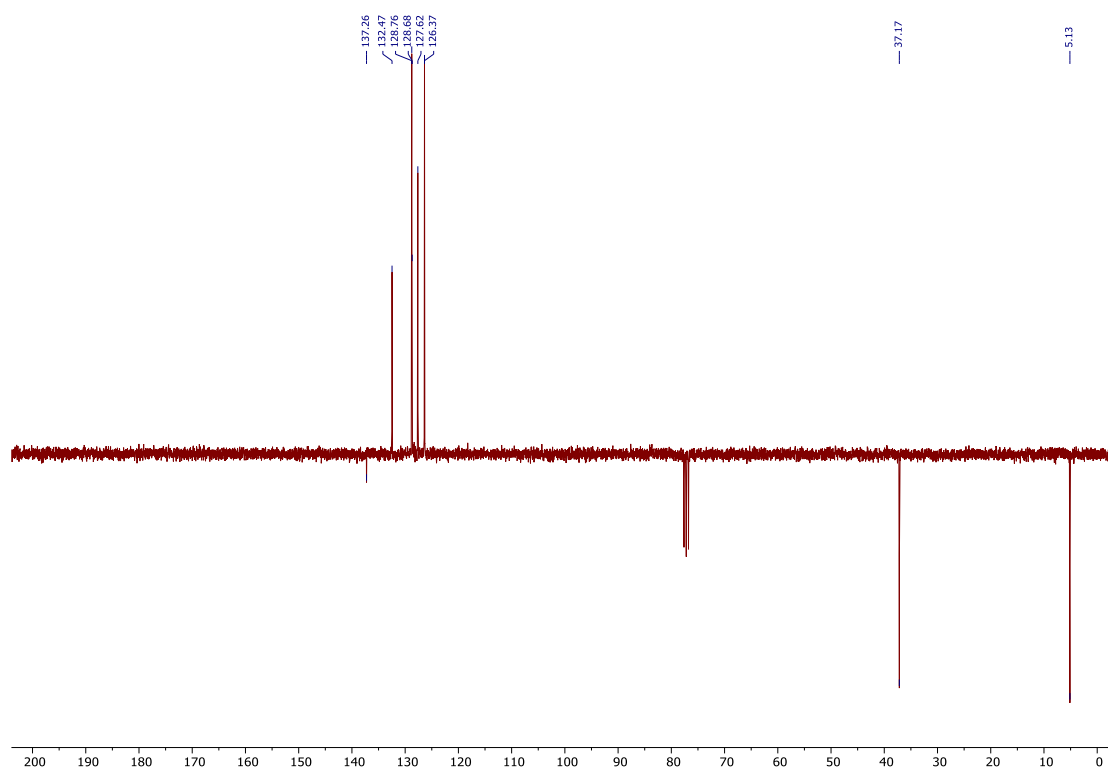
1f ¹³C-NMR (126 MHz, CDCl₃) spectrum:



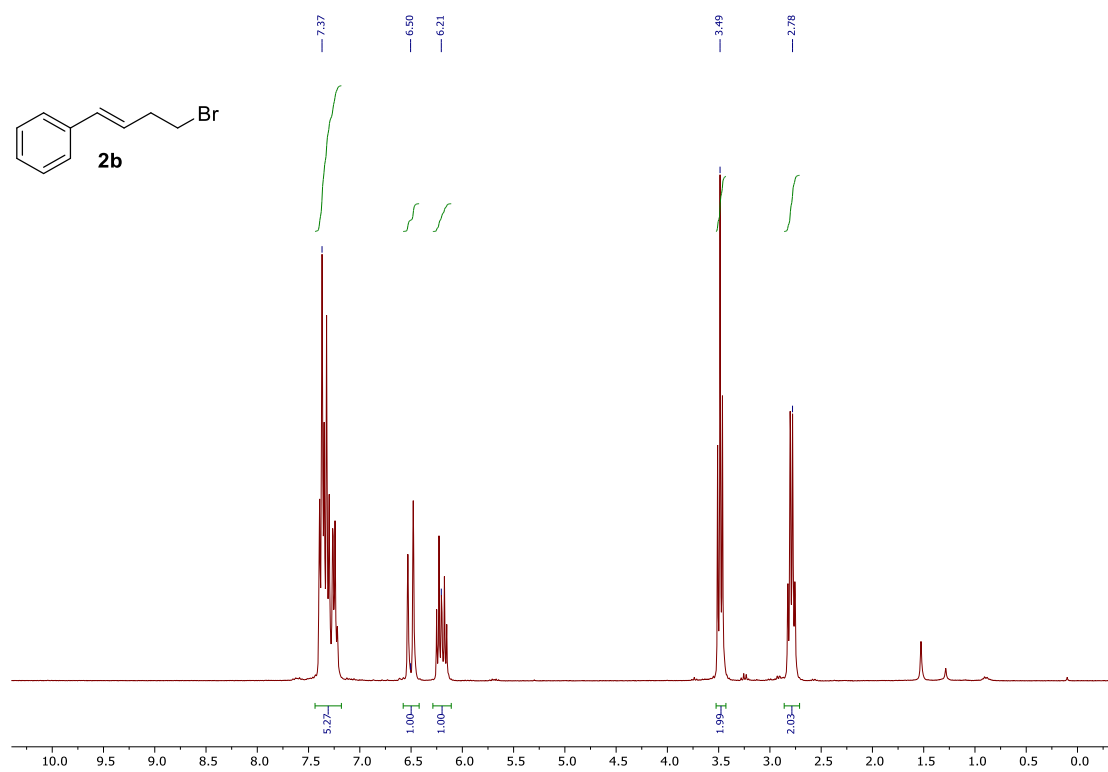
2a $^1\text{H-NMR}$ (300 MHz, CDCl_3) spectrum:



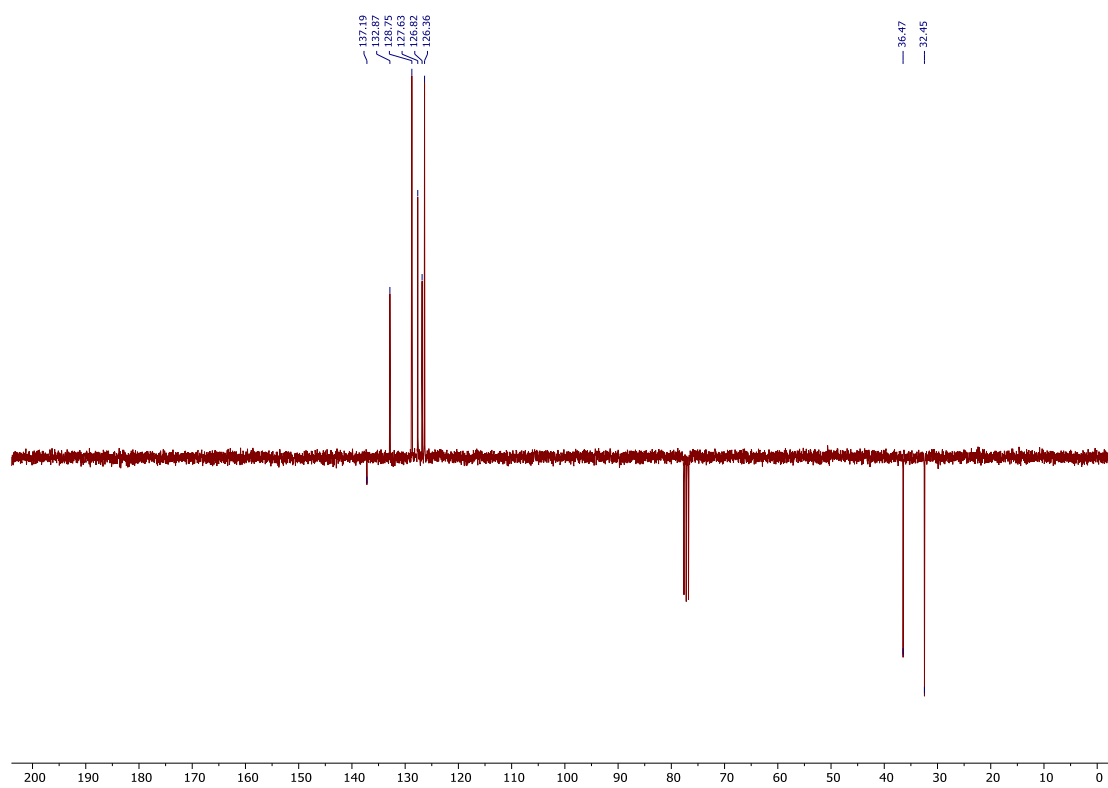
2a $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) spectrum:



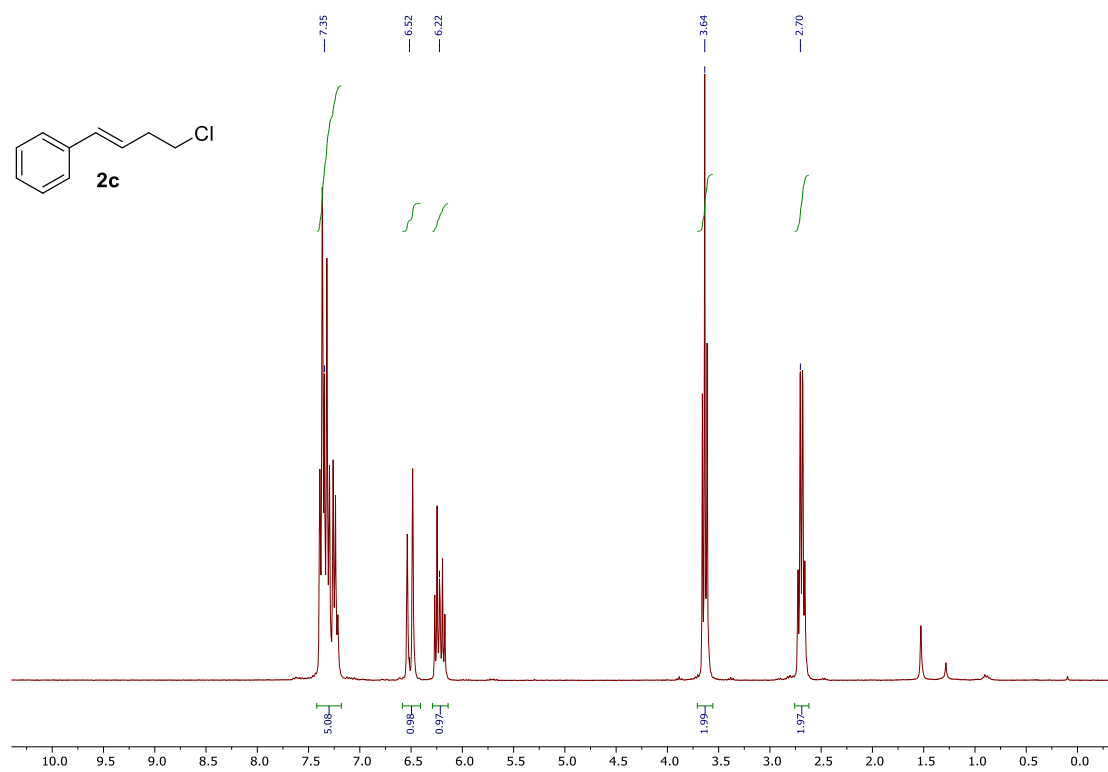
2b $^1\text{H-NMR}$ (300 MHz, CDCl_3) spectrum:



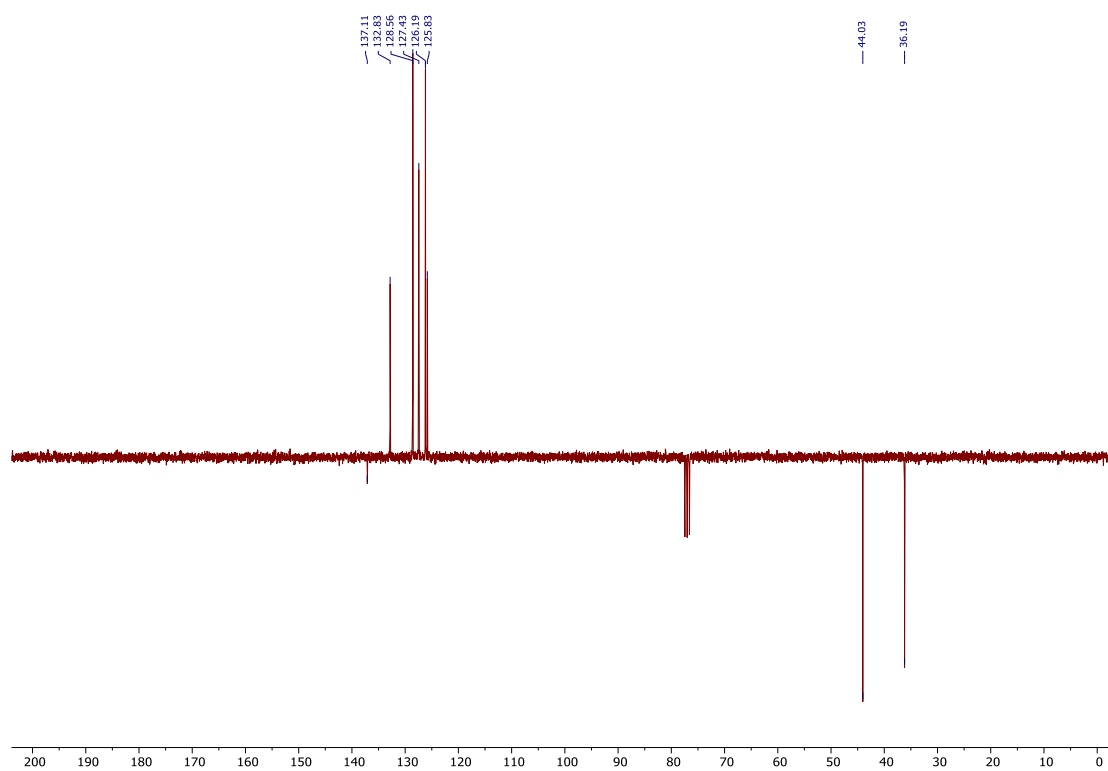
2b $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) spectrum:



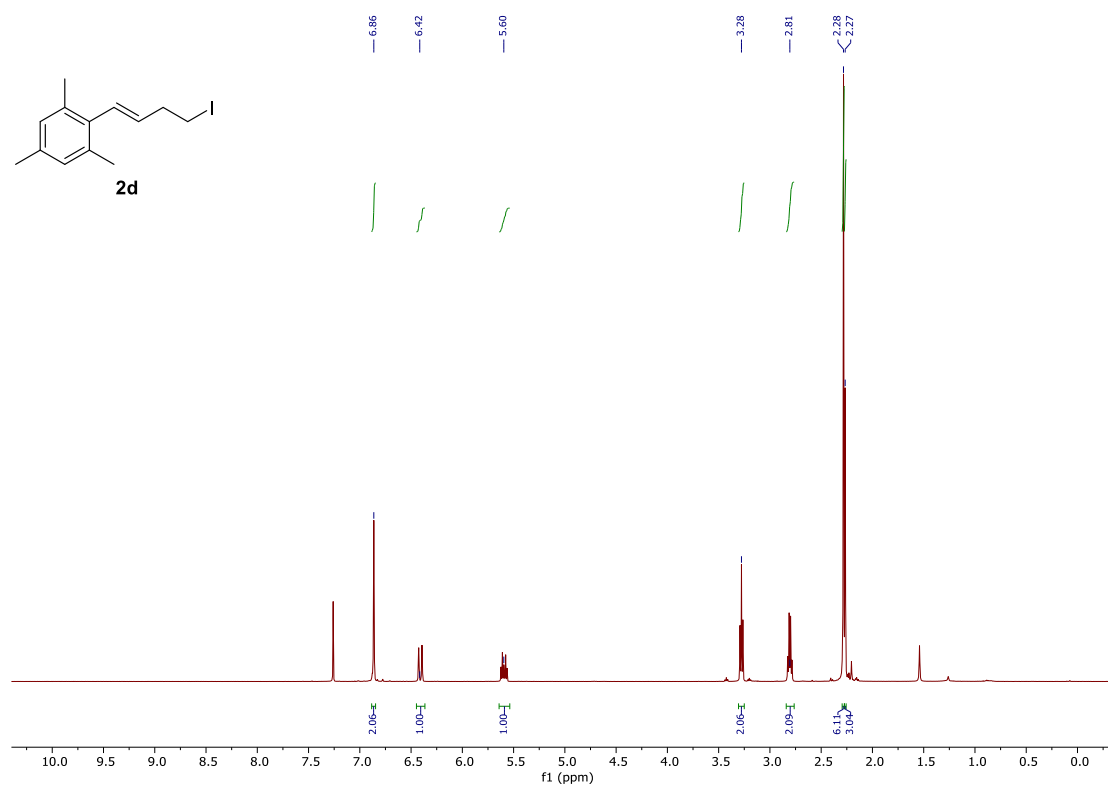
2c $^1\text{H-NMR}$ (300 MHz, CDCl_3) spectrum:



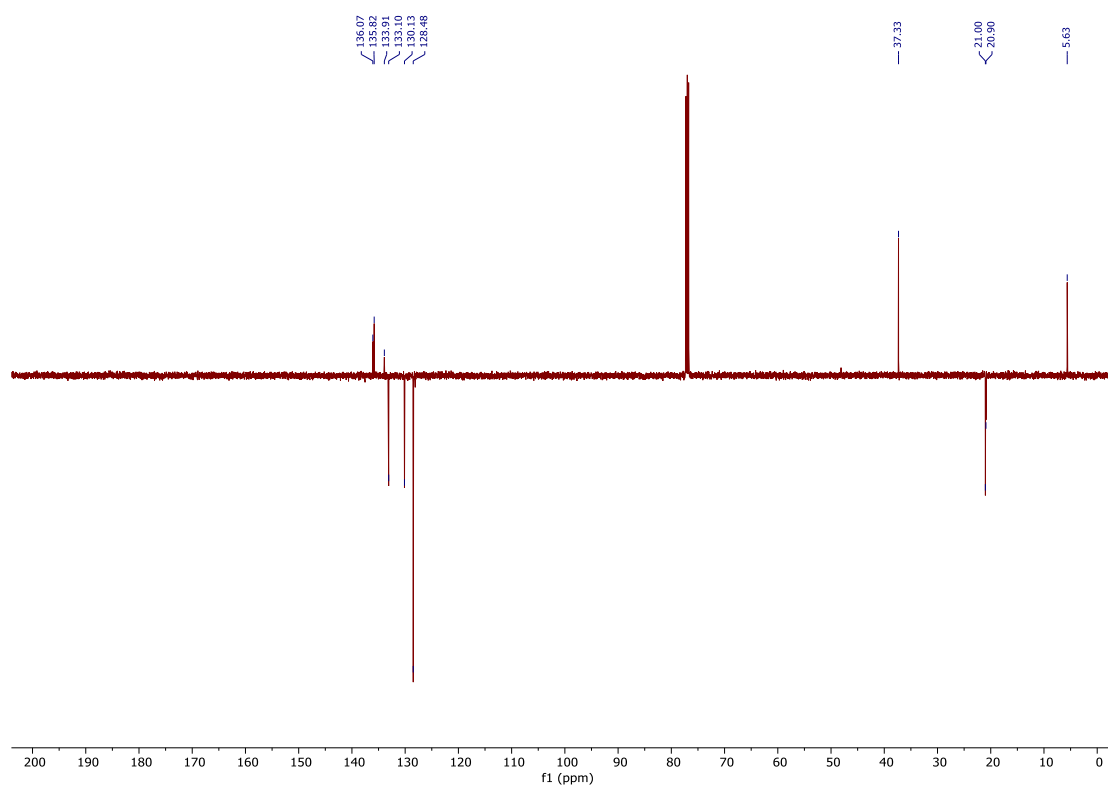
2c $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) spectrum:



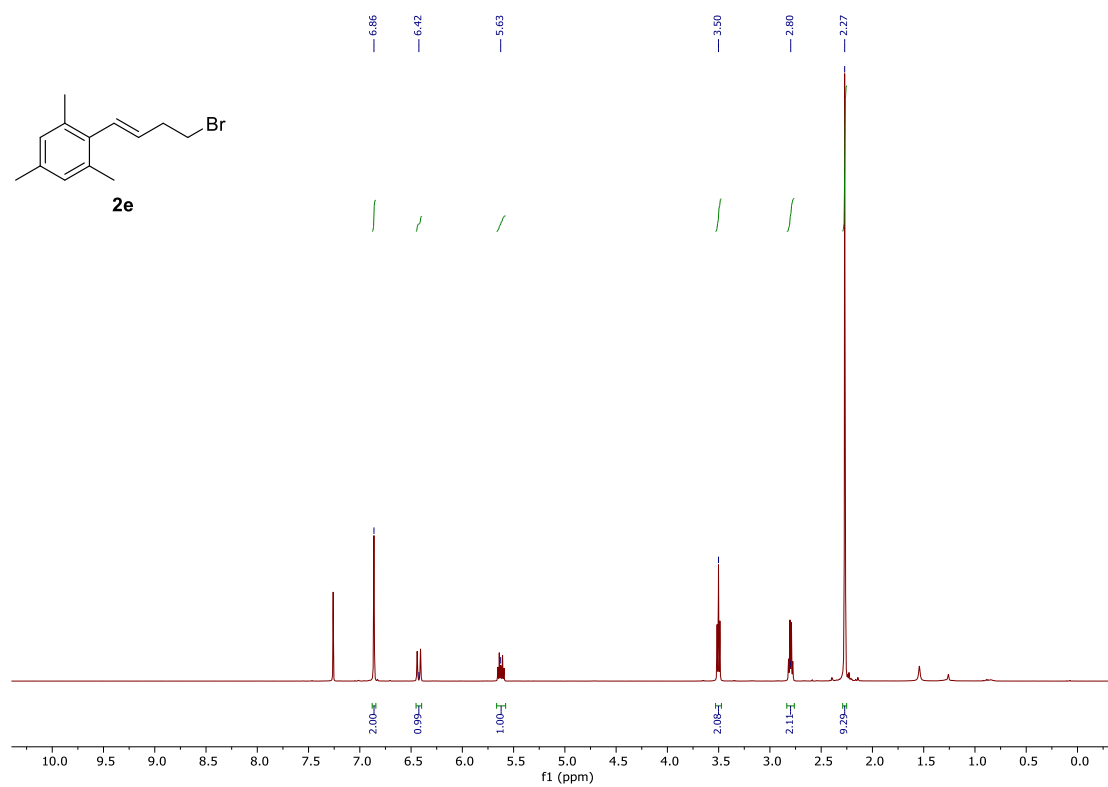
2d $^1\text{H-NMR}$ (500 MHz, CDCl_3) spectrum:



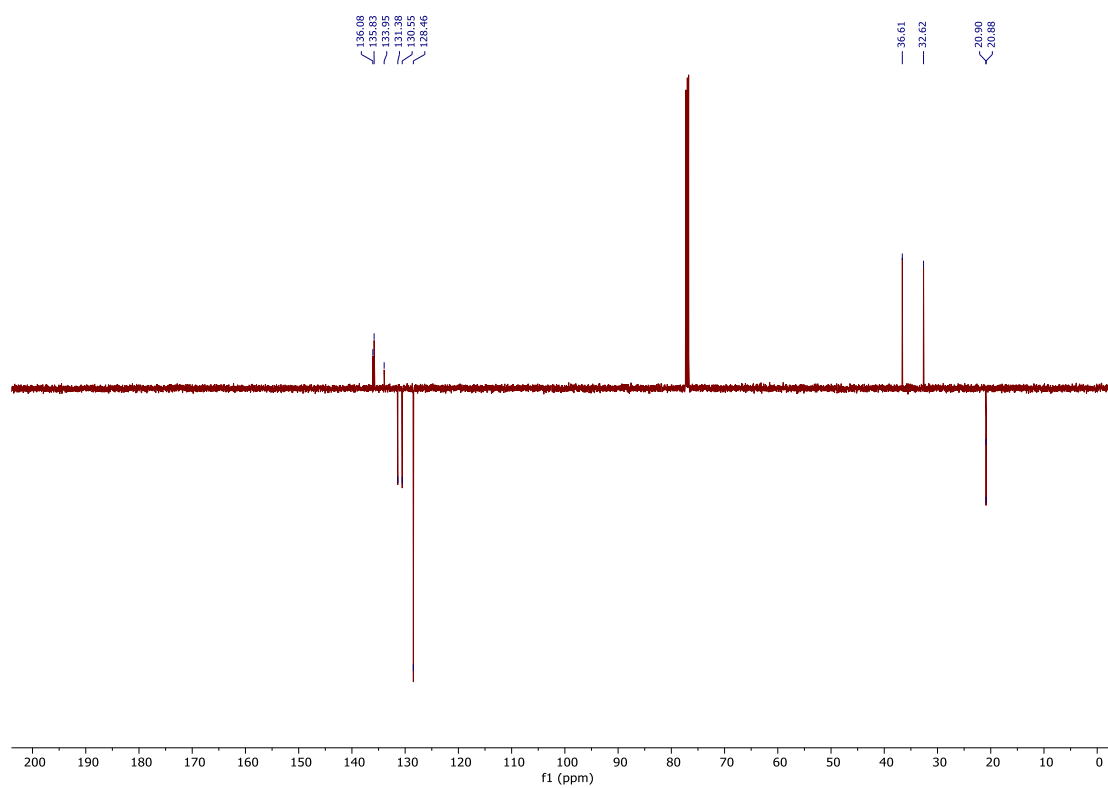
2d $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) spectrum:



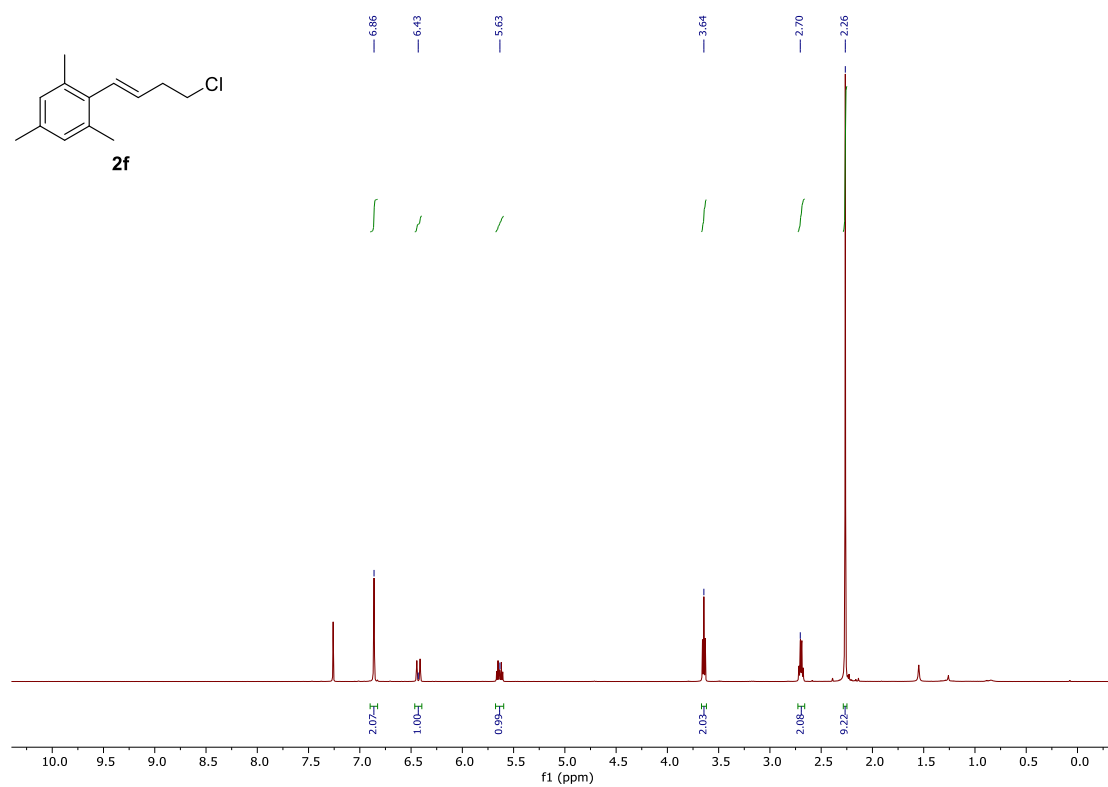
2e $^1\text{H-NMR}$ (500 MHz, CDCl_3) spectrum:



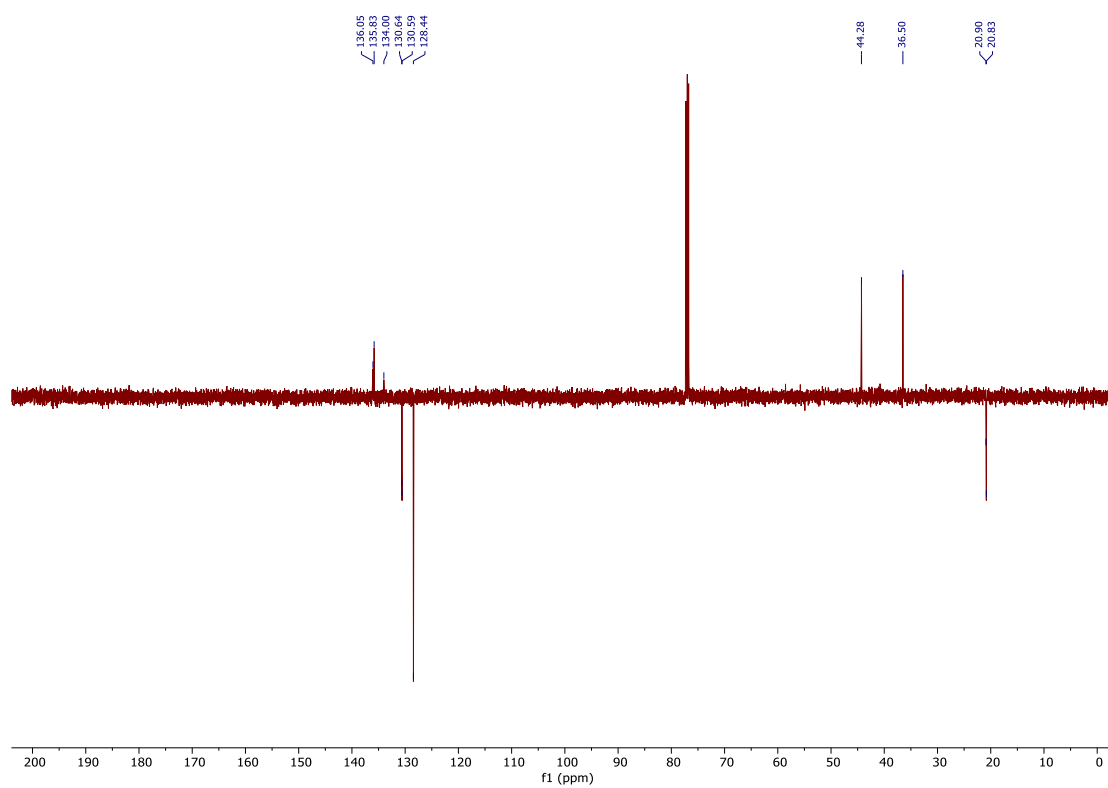
2e $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) spectrum:



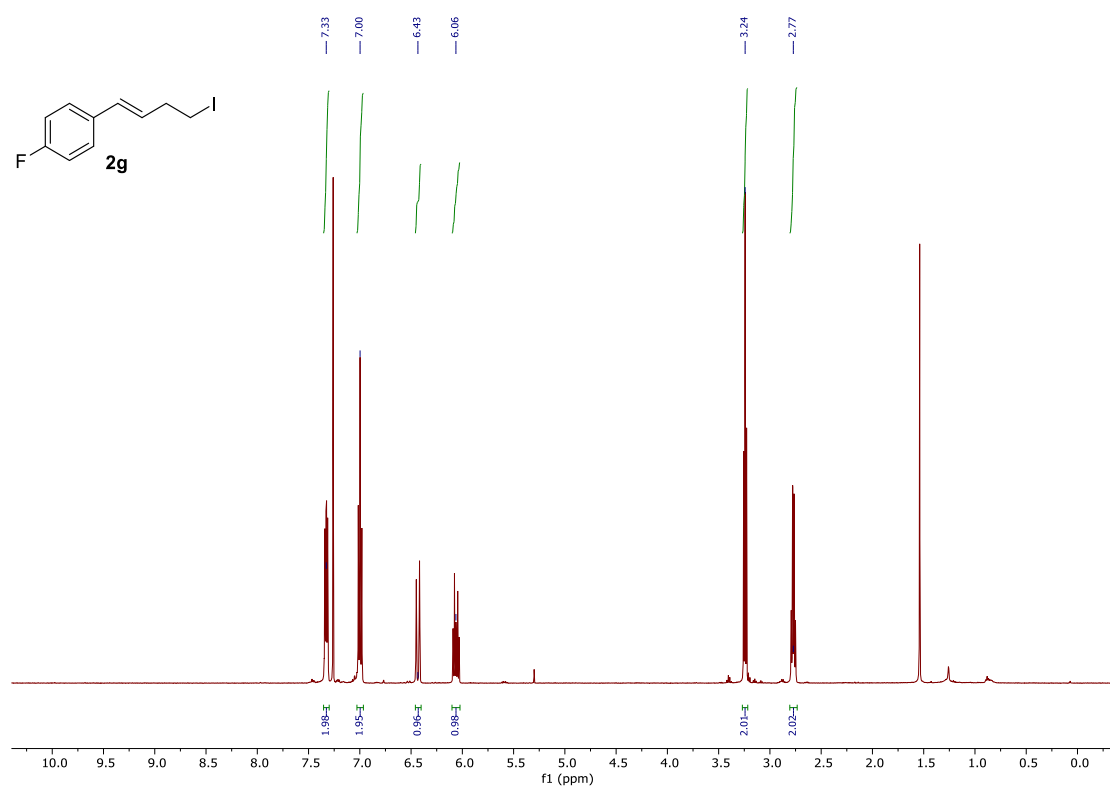
2f $^1\text{H-NMR}$ (500 MHz, CDCl_3) spectrum:



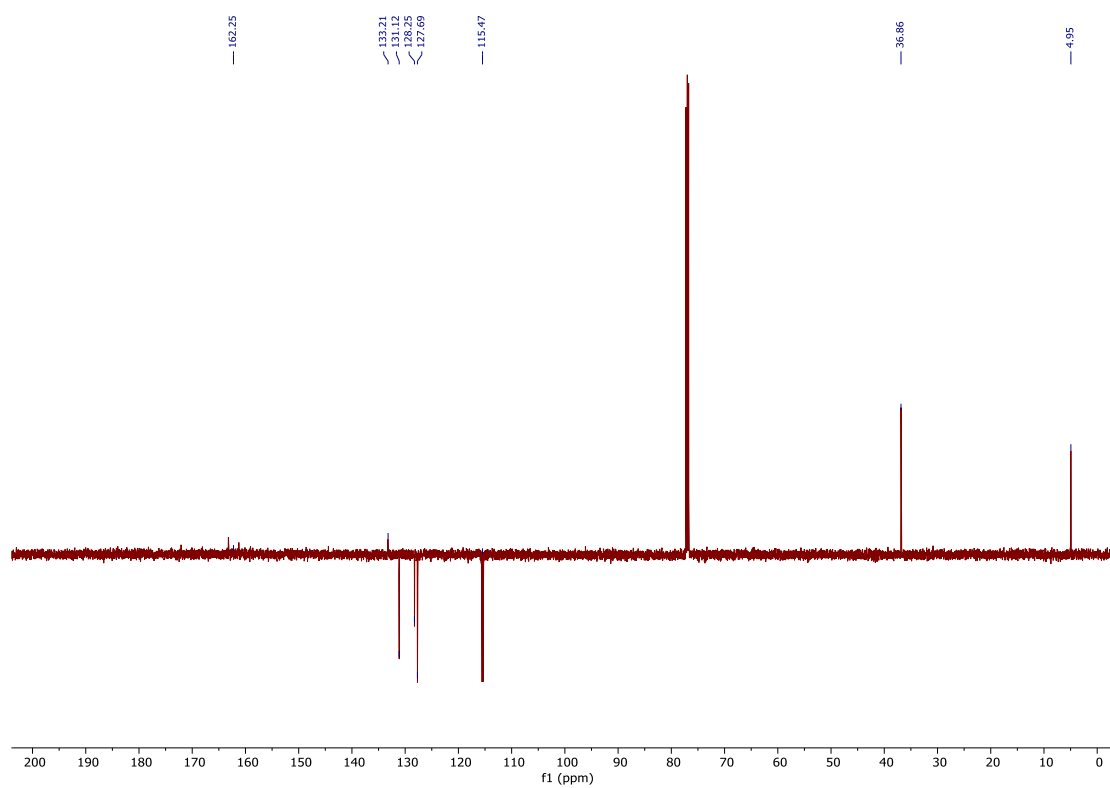
2f $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) spectrum:



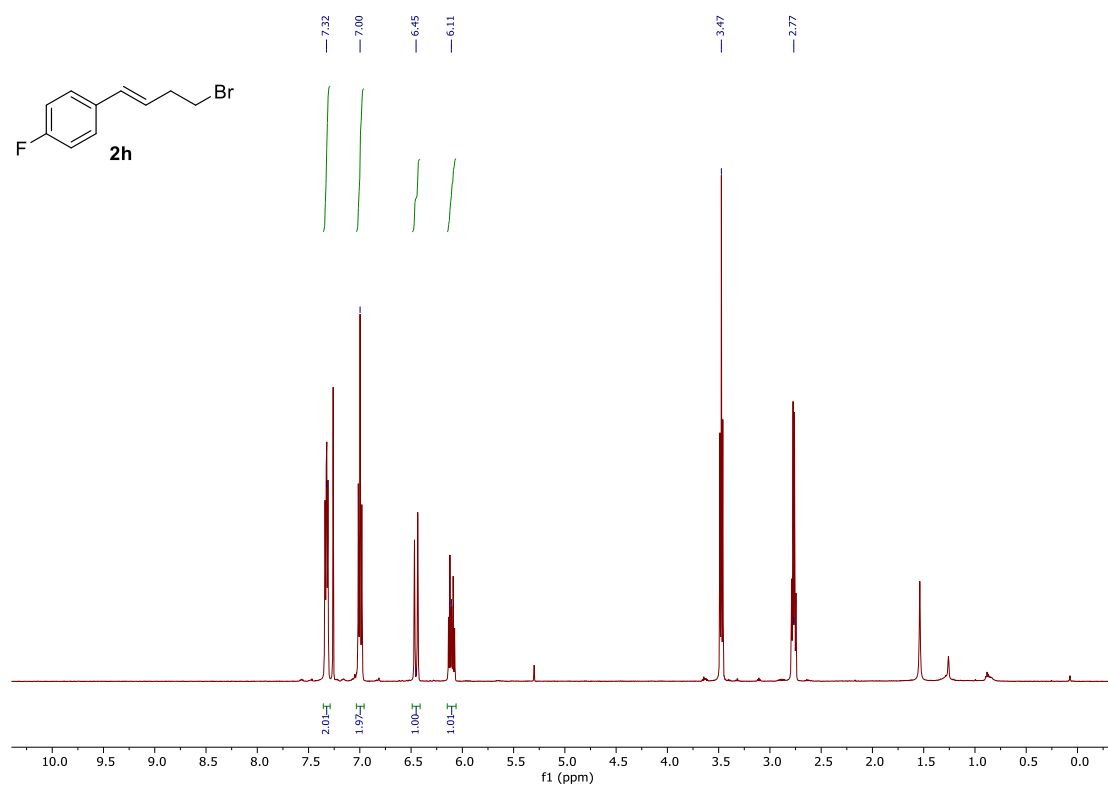
2g ¹H-NMR (500 MHz, CDCl₃) spectrum:



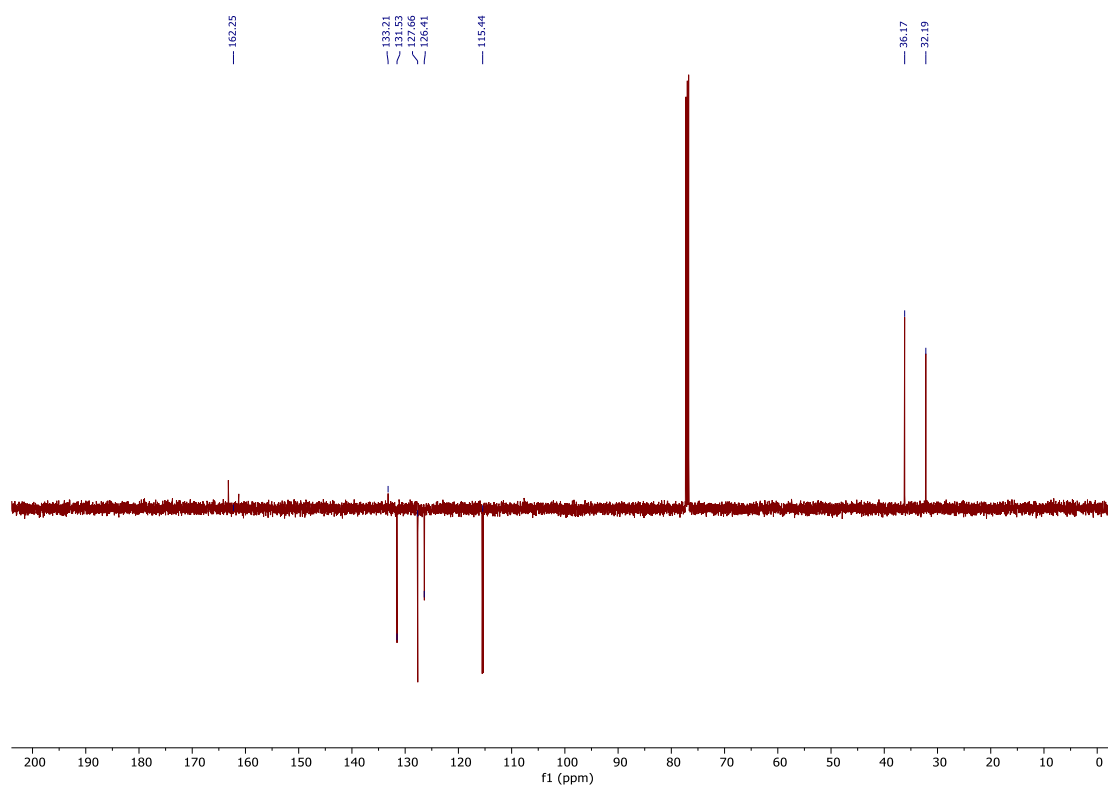
2g ¹³C-NMR (126 MHz, CDCl₃) spectrum:



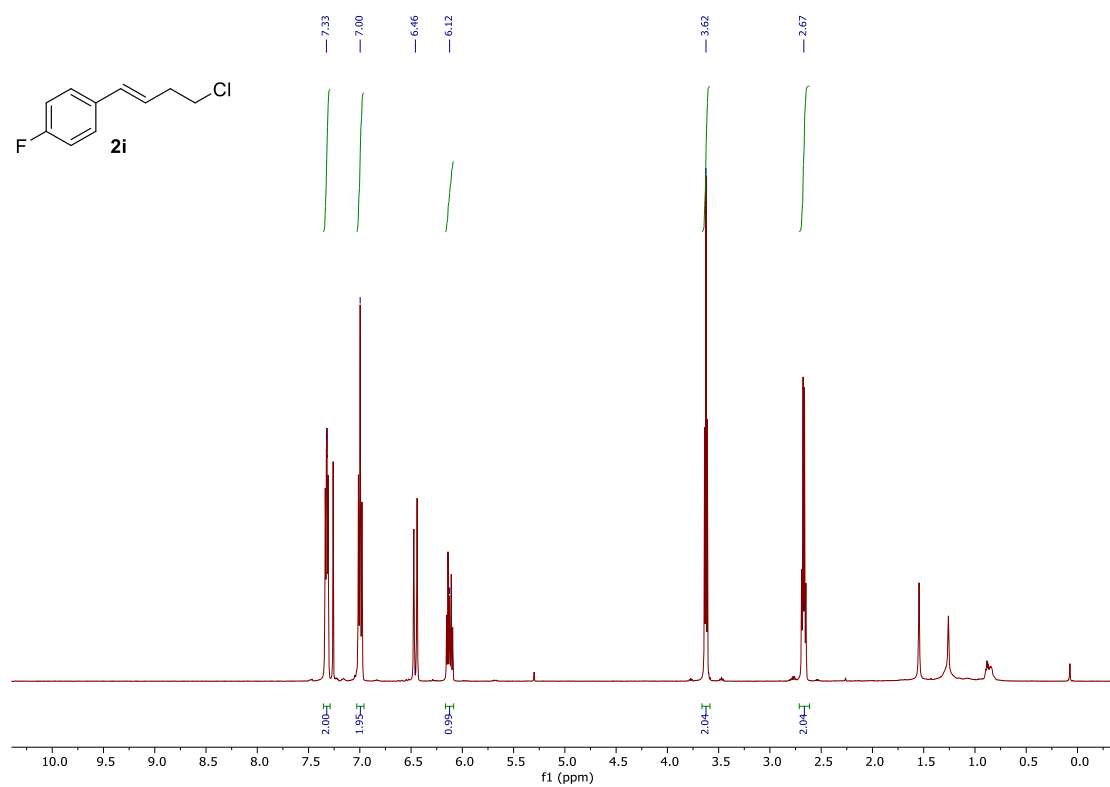
2h ¹H-NMR (500 MHz, CDCl₃) spectrum:



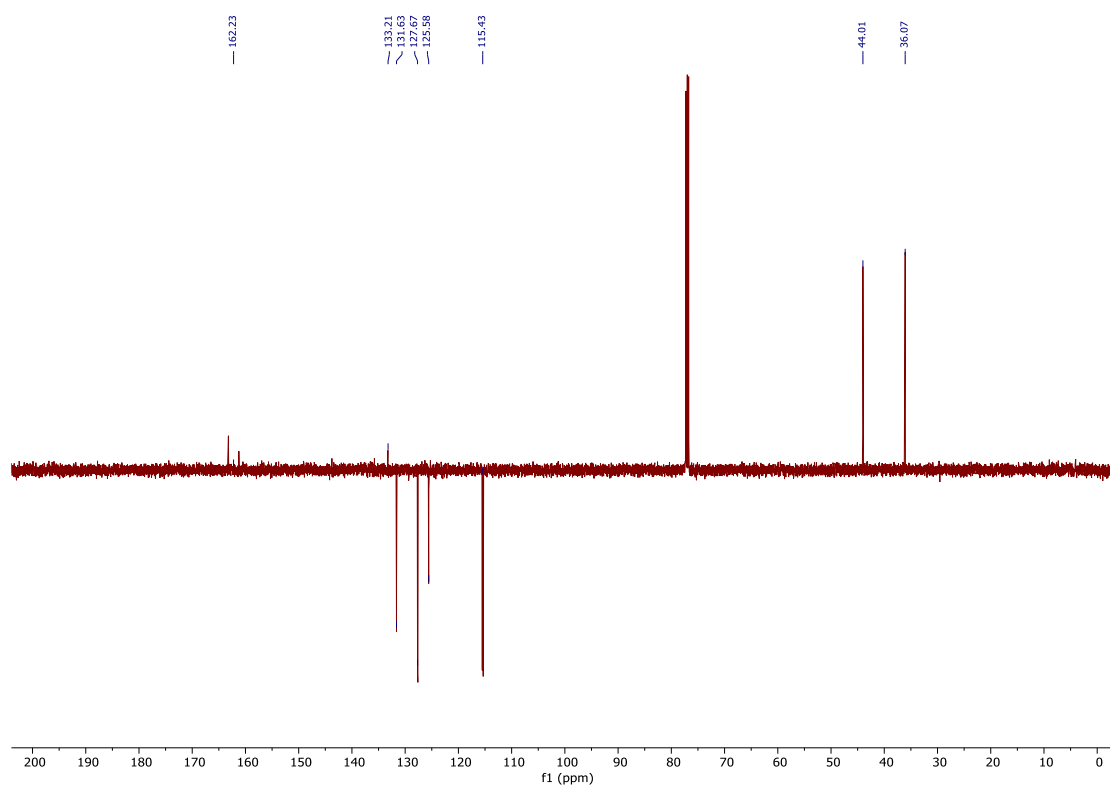
2h ¹³C-NMR (126 MHz, CDCl₃) spectrum:



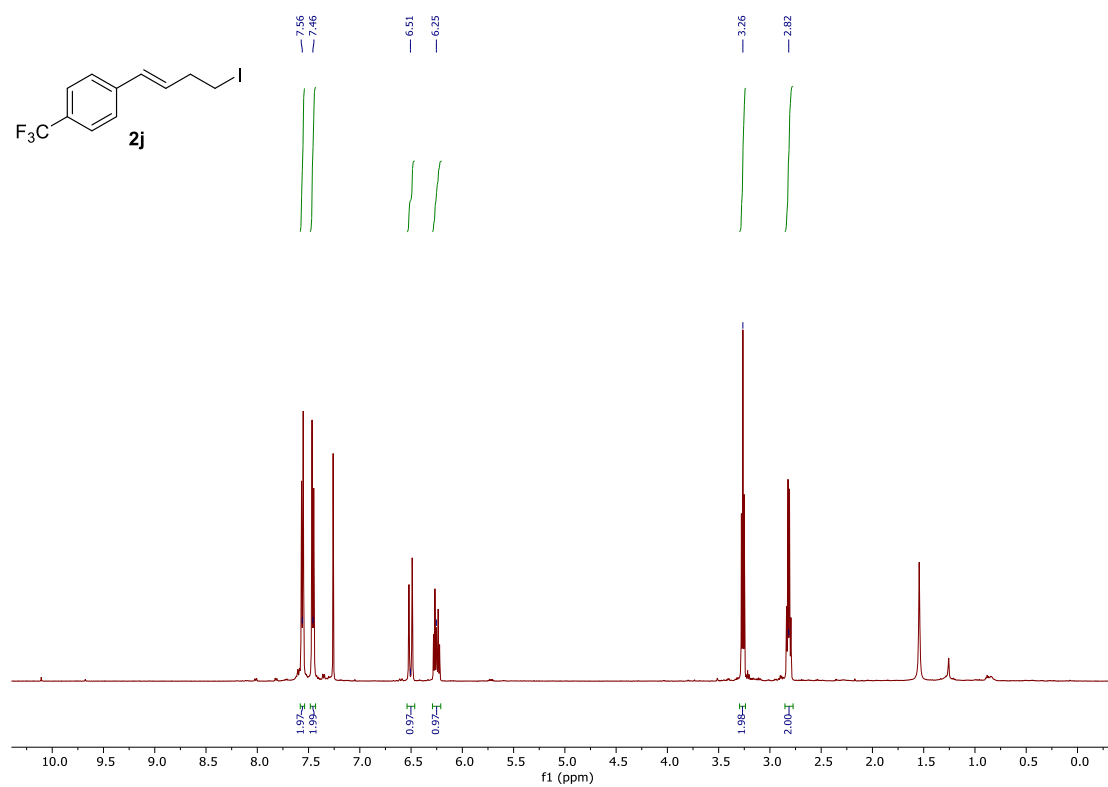
2i $^1\text{H-NMR}$ (500 MHz, CDCl_3) spectrum:



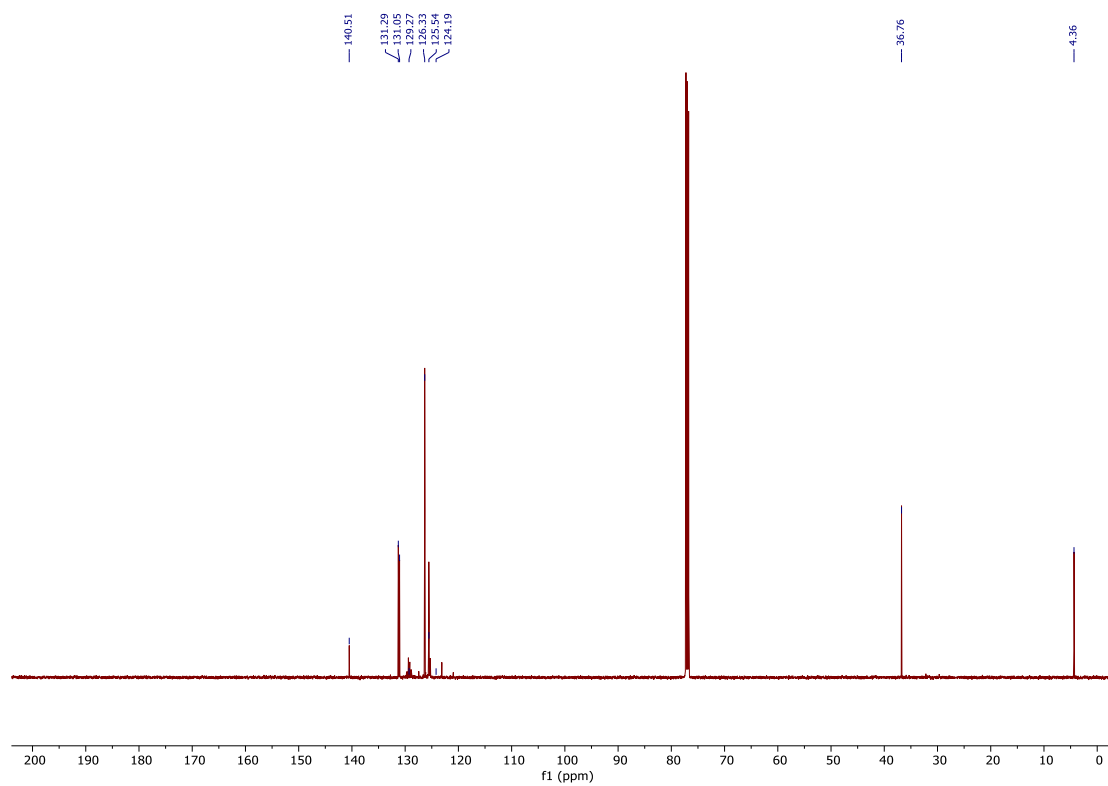
2i $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) spectra:



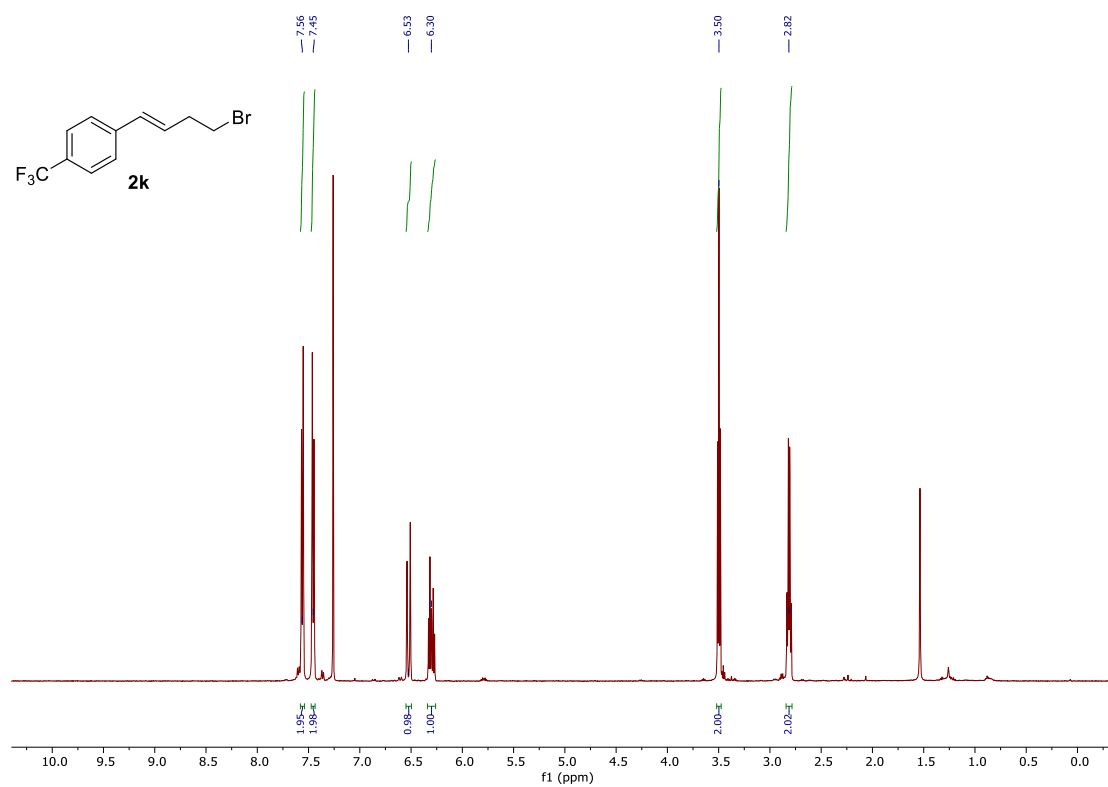
2j $^1\text{H-NMR}$ (500 MHz, CDCl_3) spectrum:



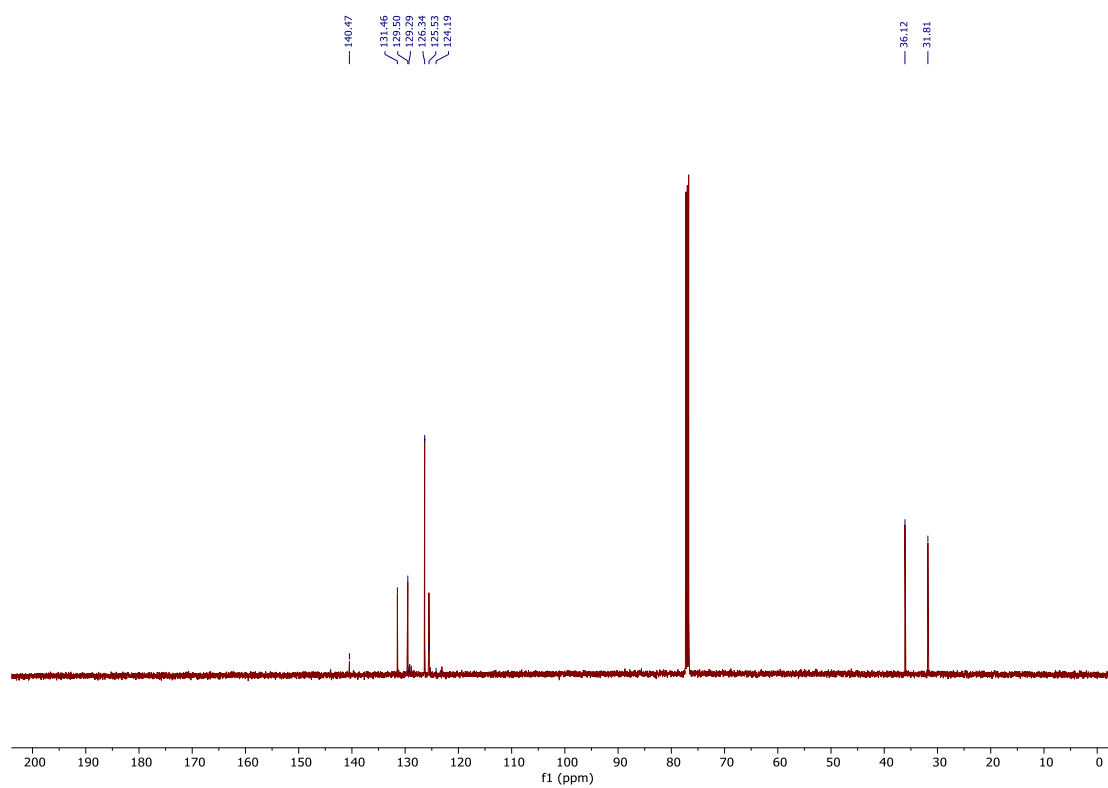
2j $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) spectrum:



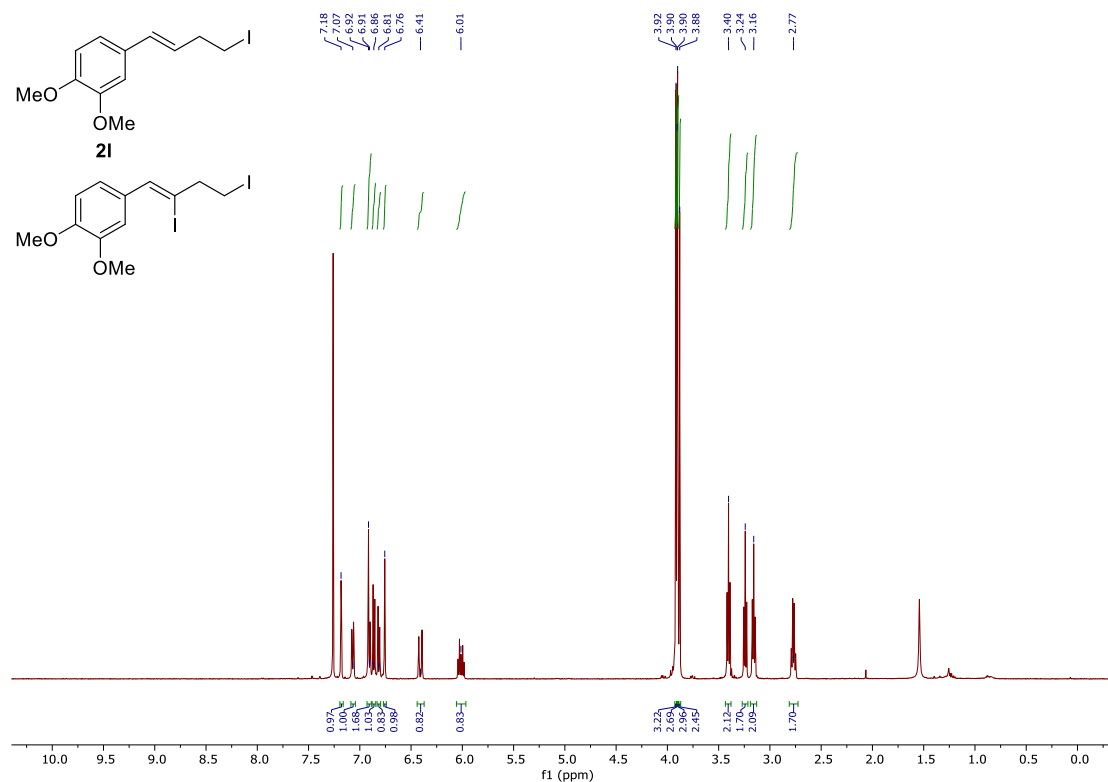
2k ¹H-NMR (500 MHz, CDCl₃) spectrum:



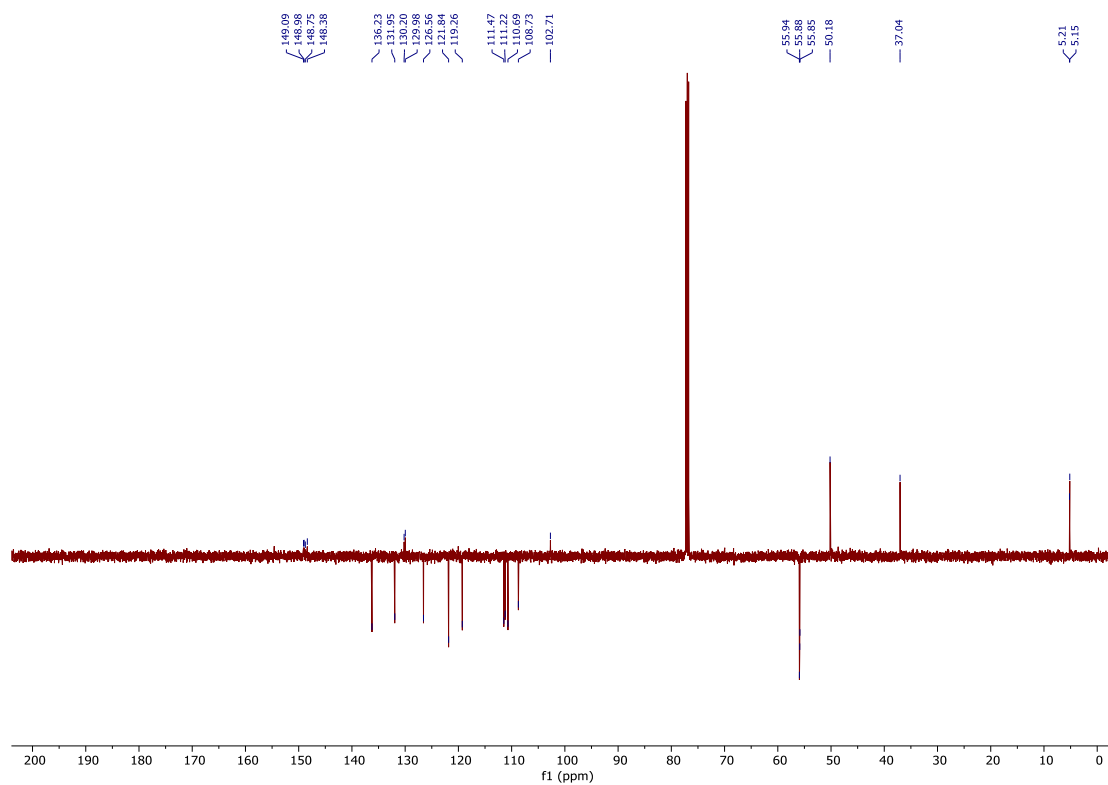
2k ¹³C-NMR (126 MHz, CDCl₃) spectrum:



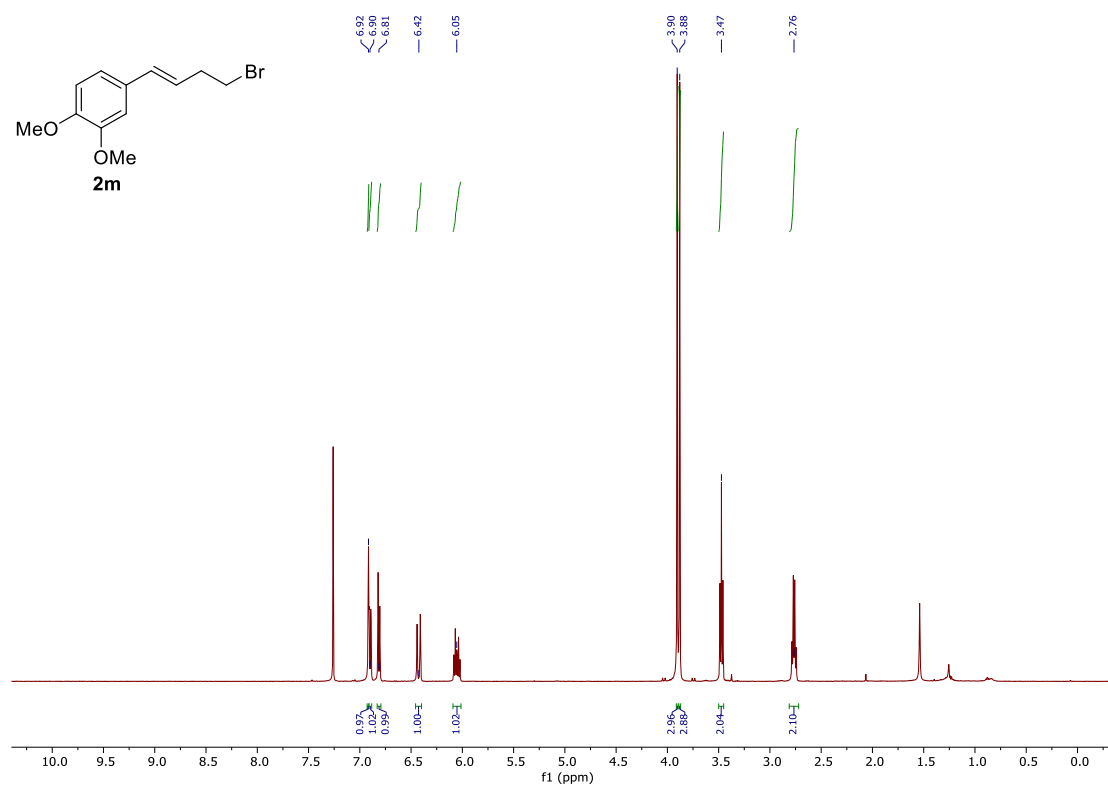
2I and (*Z*)-4-(2,4-diiodobut-1-en-1-yl)-1,2-dimethoxybenzene mixture ¹H-NMR (500 MHz, CDCl₃) spectrum:



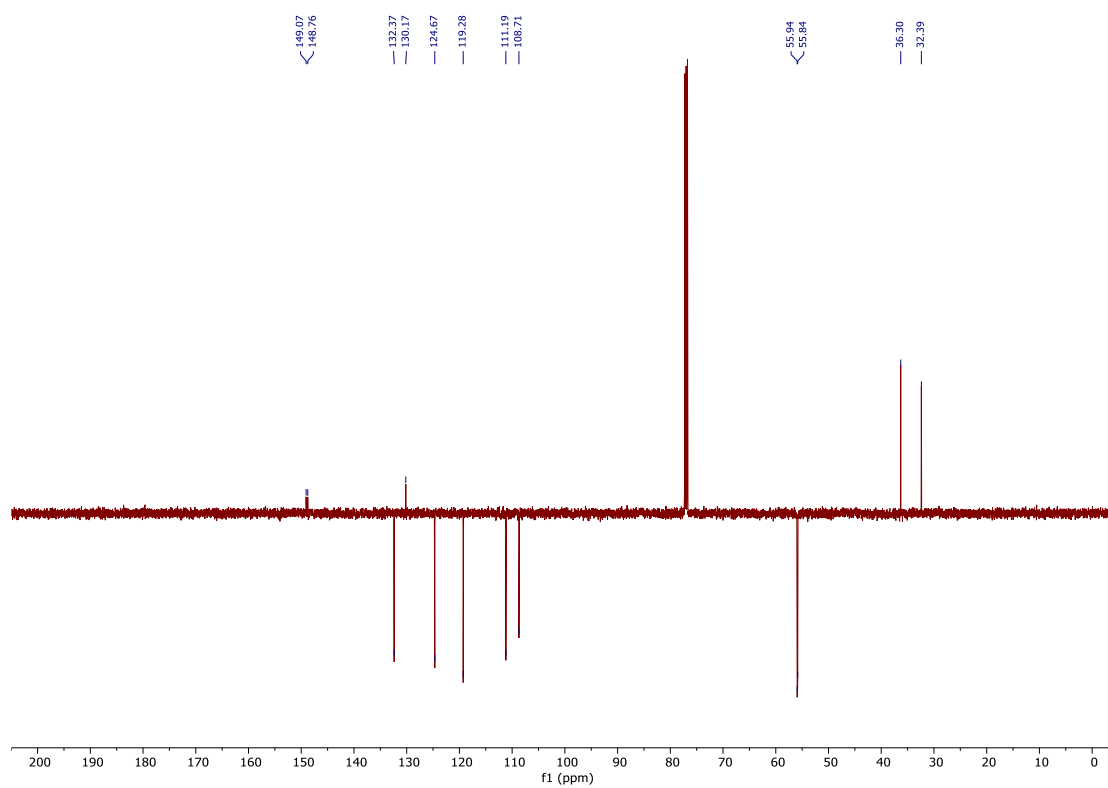
2I and (*Z*)-4-(2,4-diiodobut-1-en-1-yl)-1,2-dimethoxybenzene mixture ¹³C-NMR (126 MHz, CDCl₃) spectrum:



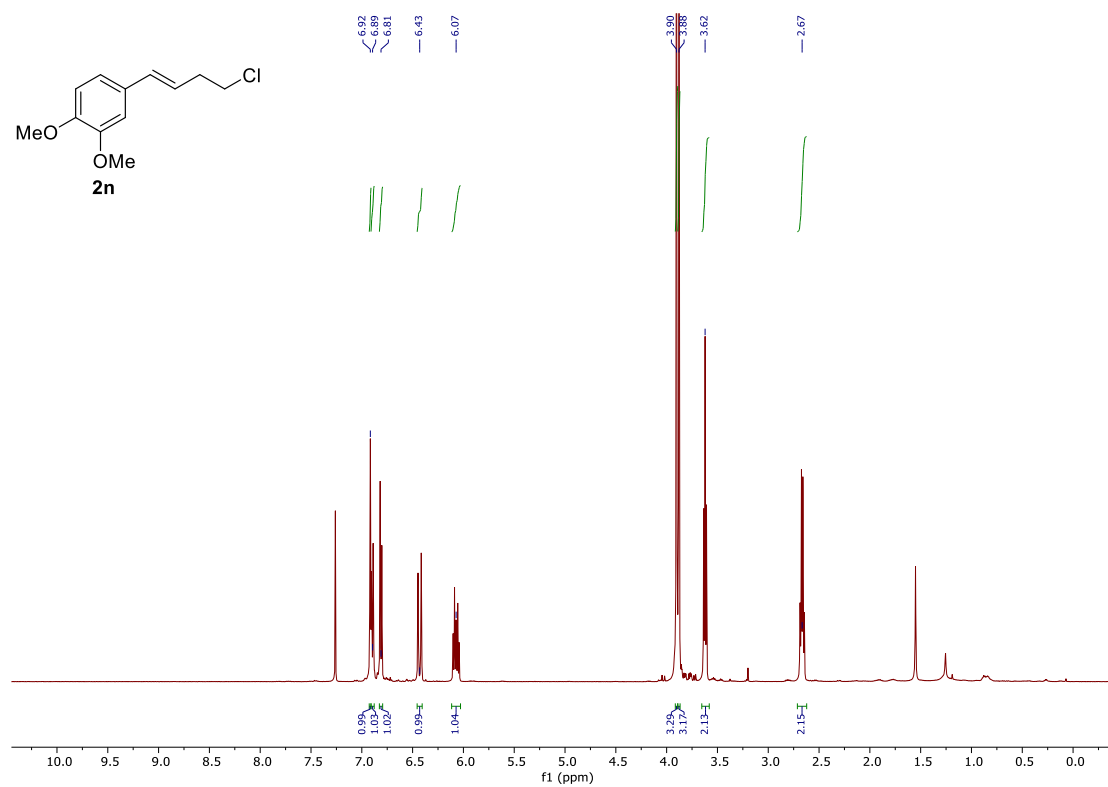
2m $^1\text{H-NMR}$ (500 MHz, CDCl_3) spectrum:



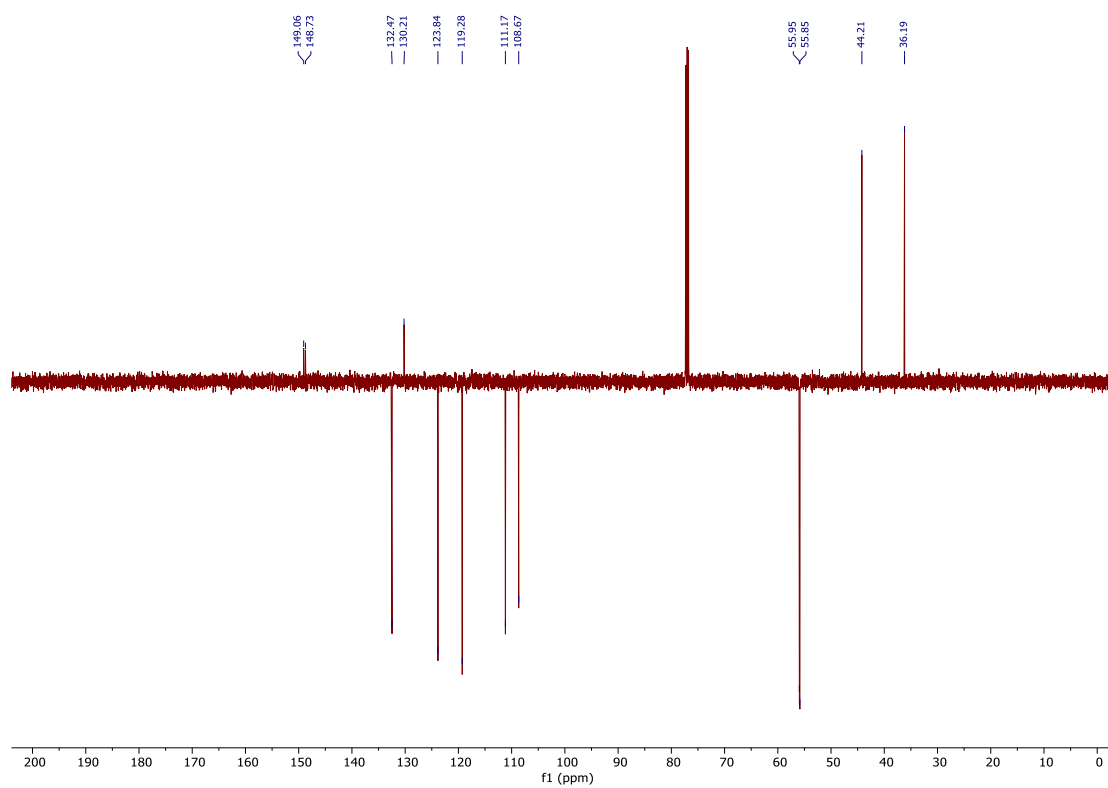
2m $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) spectrum:



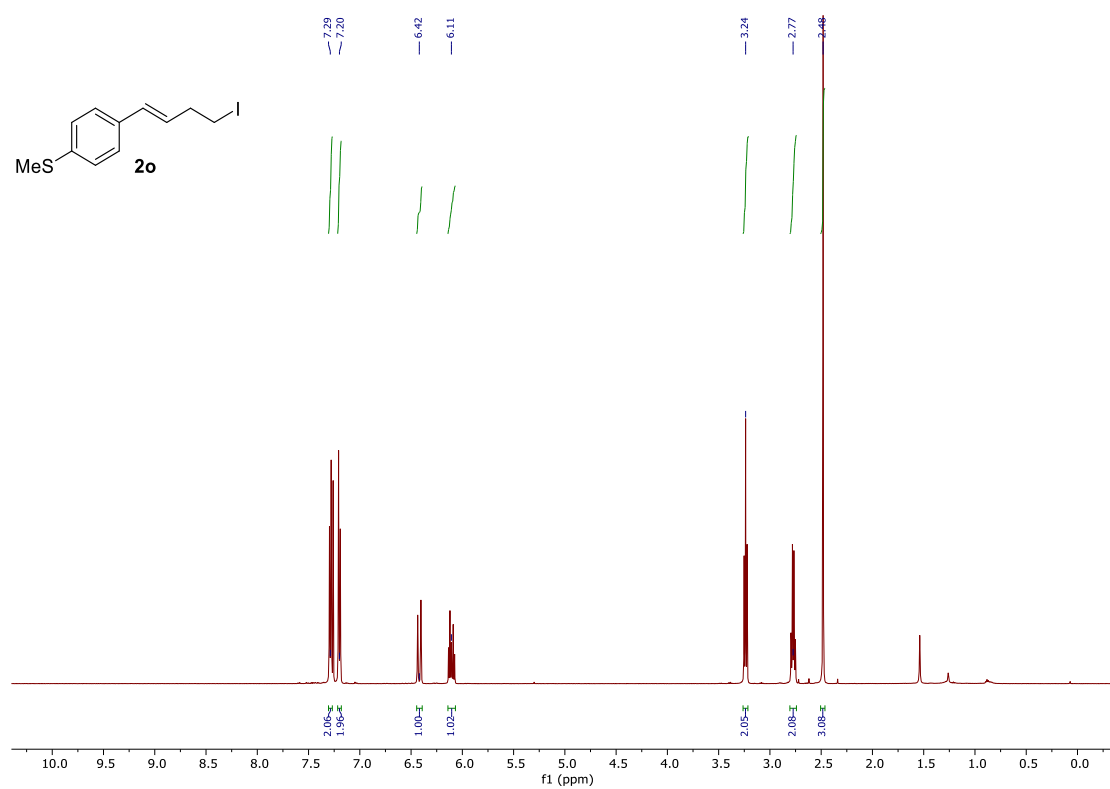
2n ¹H-NMR (500 MHz, CDCl₃) spectrum:



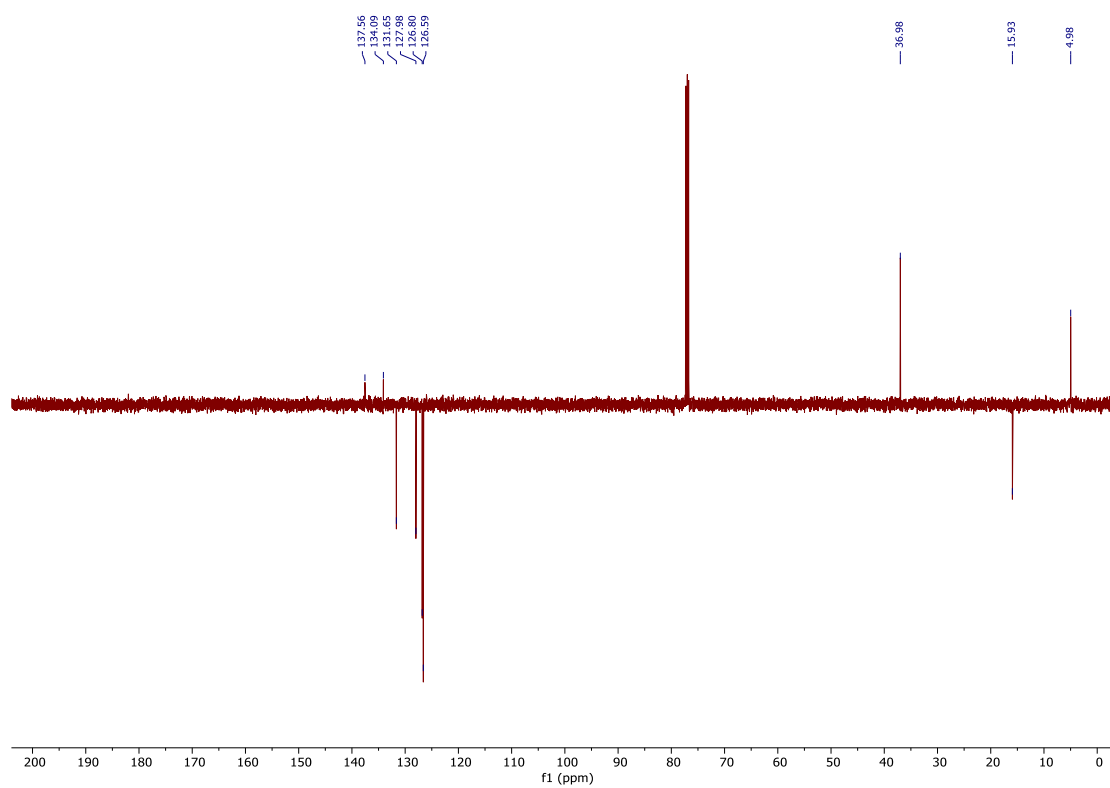
2n ¹³C-NMR (126 MHz, CDCl₃) spectrum:



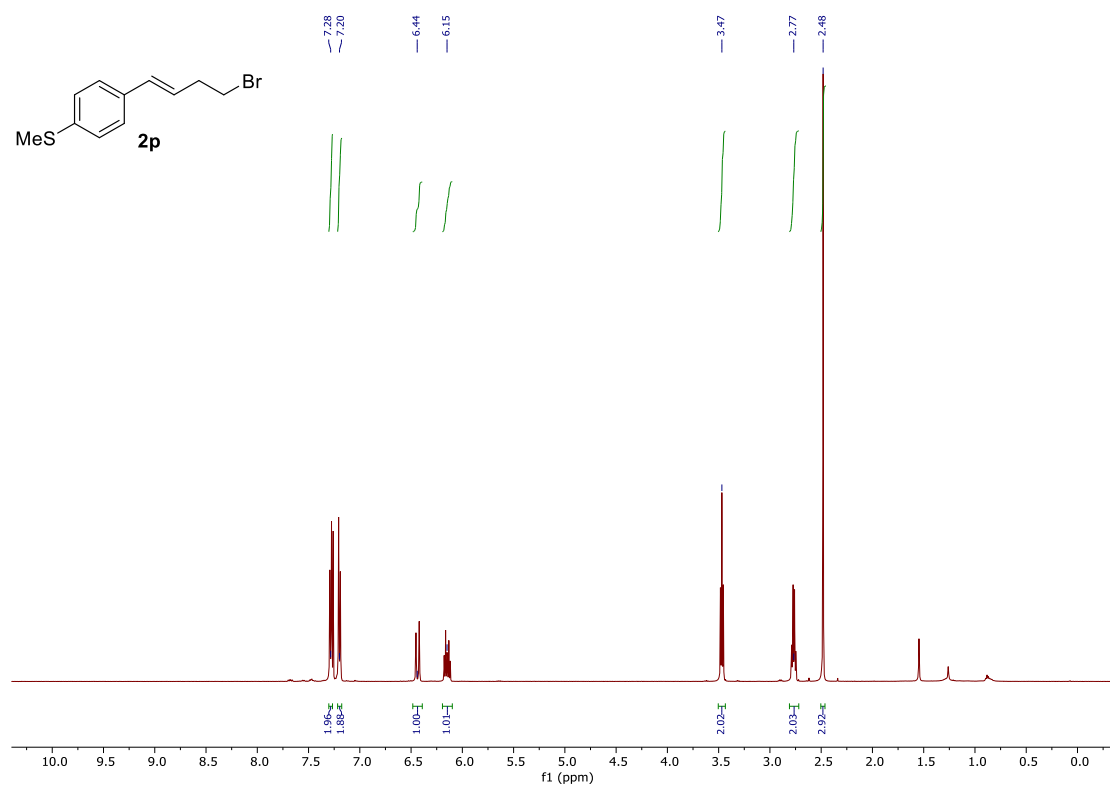
2o $^1\text{H-NMR}$ (500 MHz, CDCl_3) spectrum:



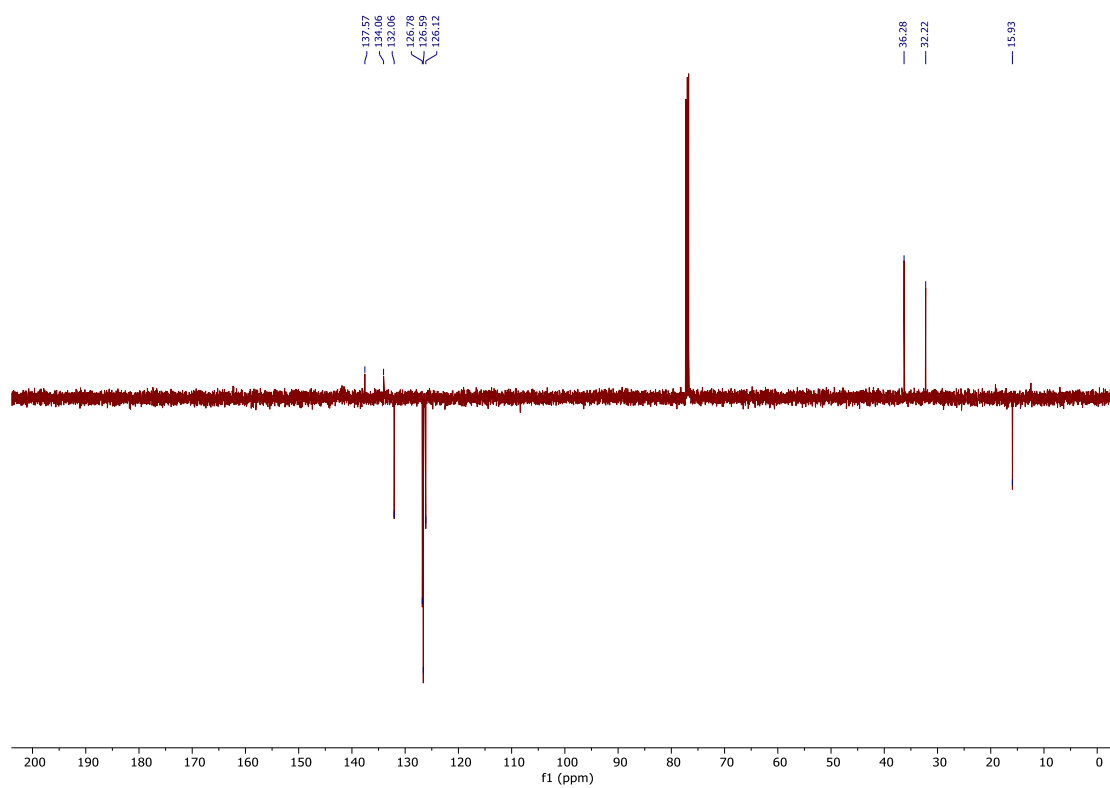
2o $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) spectrum:



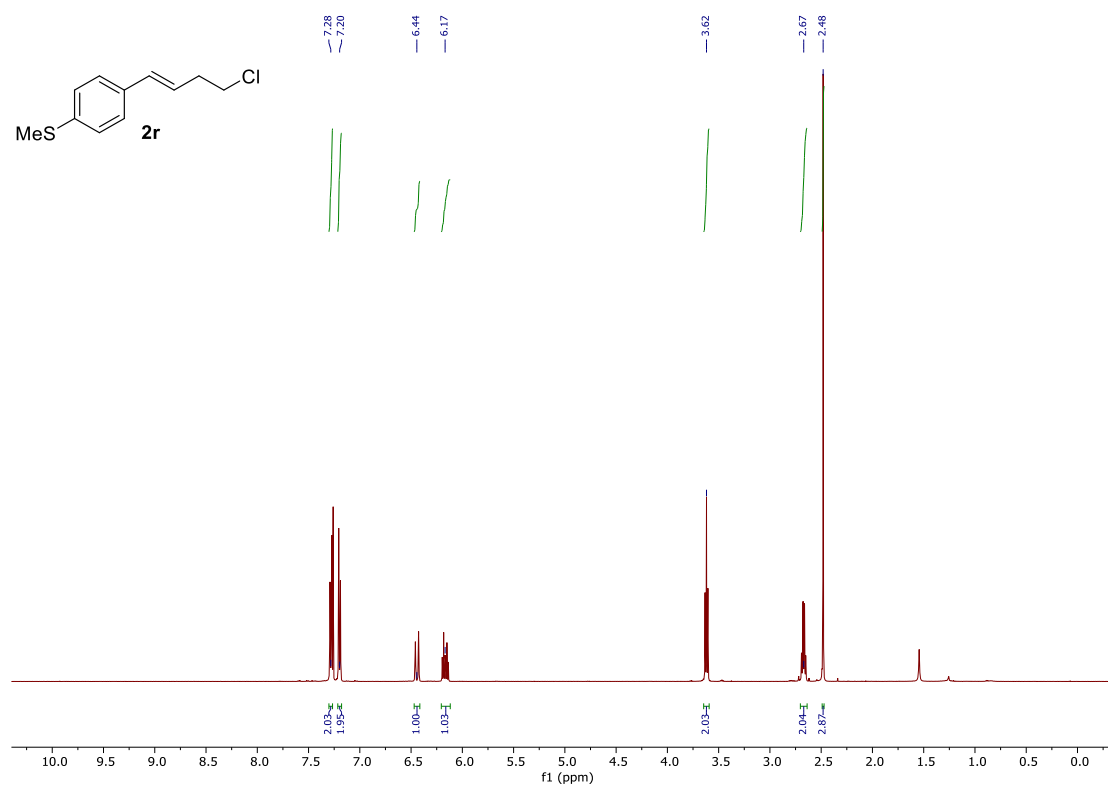
2p $^1\text{H-NMR}$ (500 MHz, CDCl_3) spectrum:



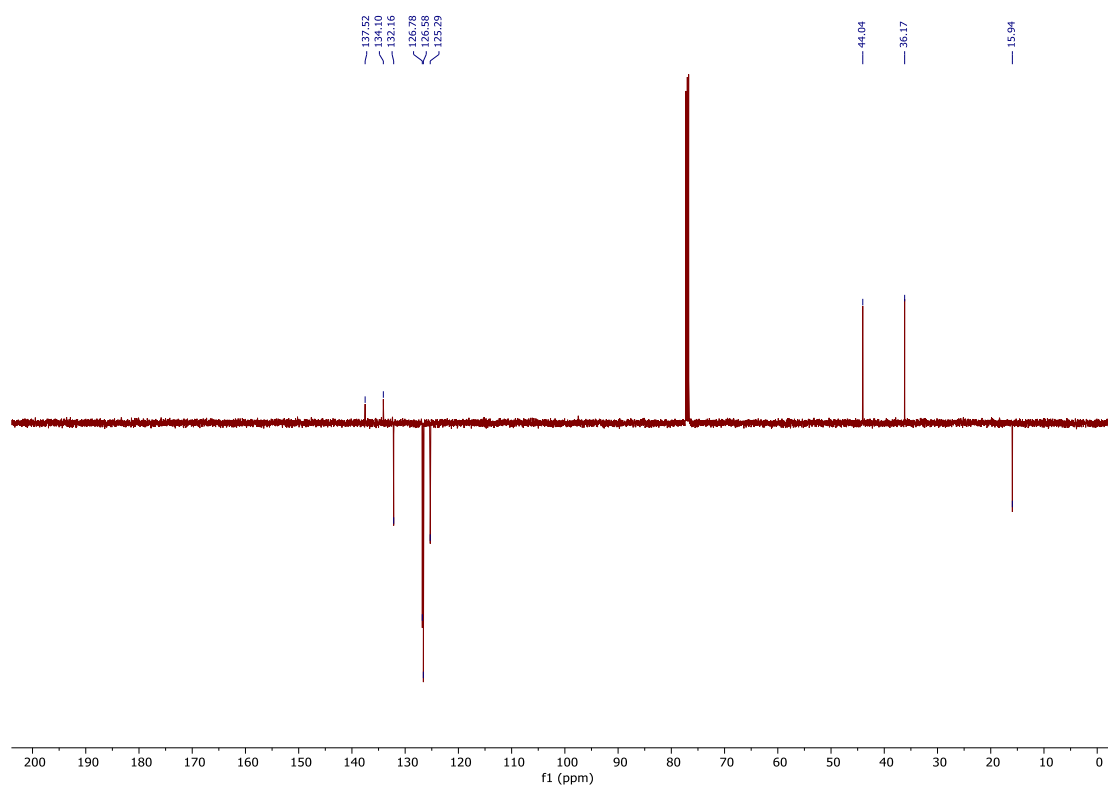
2p $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) spectrum:



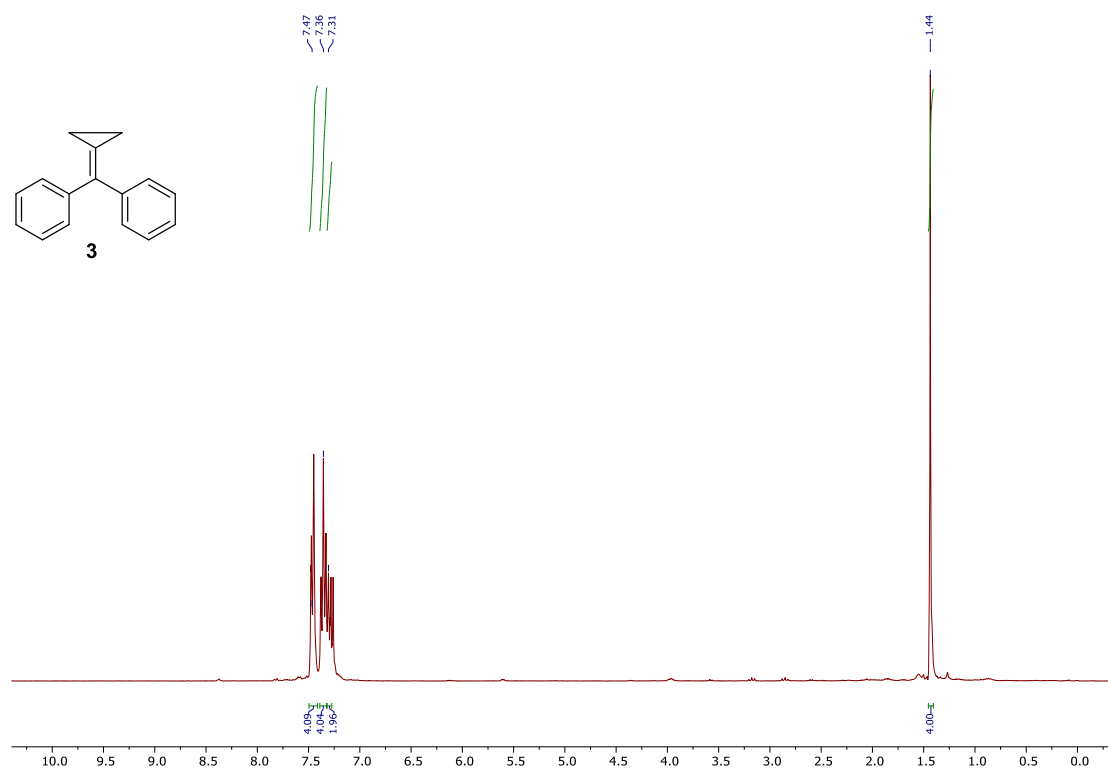
2r $^1\text{H-NMR}$ (500 MHz, CDCl_3) spectrum:



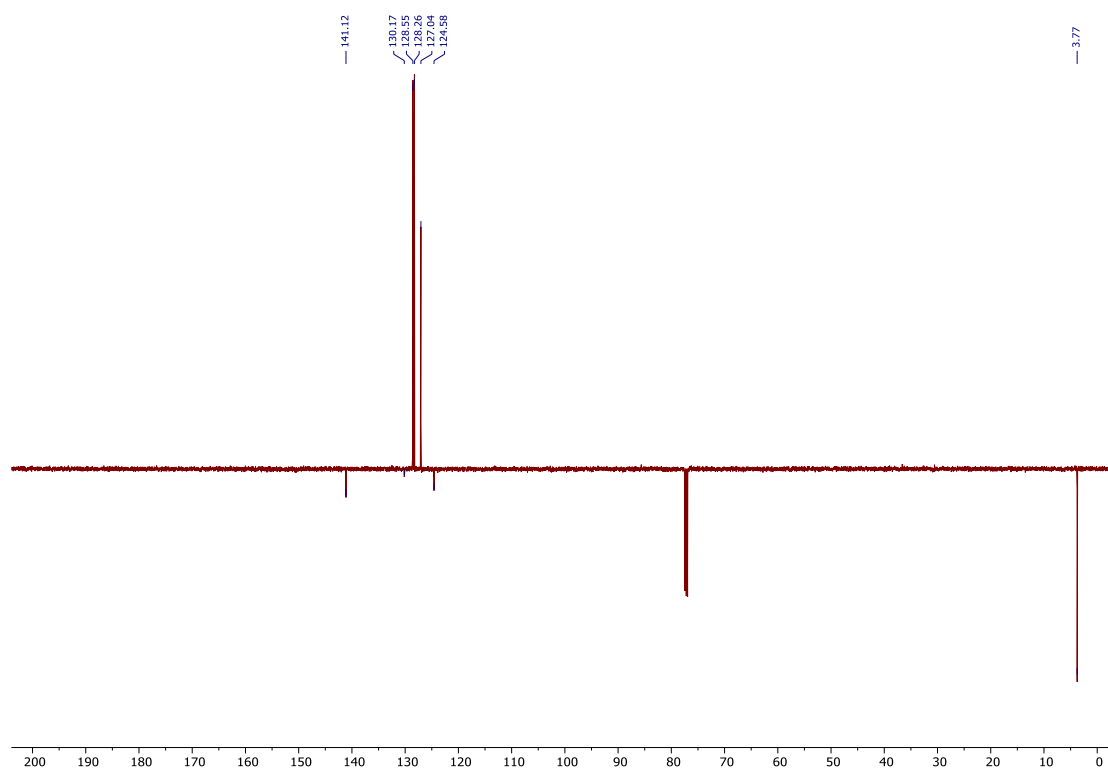
2r $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) spectrum:



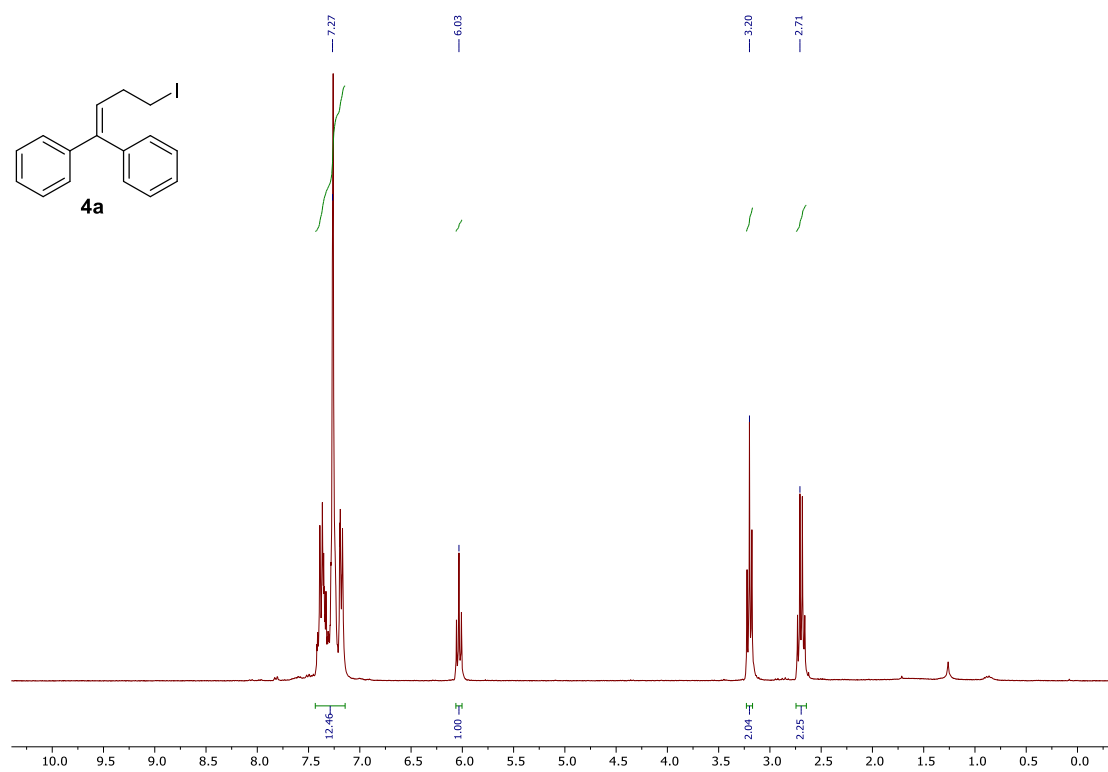
3 $^1\text{H-NMR}$ (300 MHz, CDCl_3) spectrum:



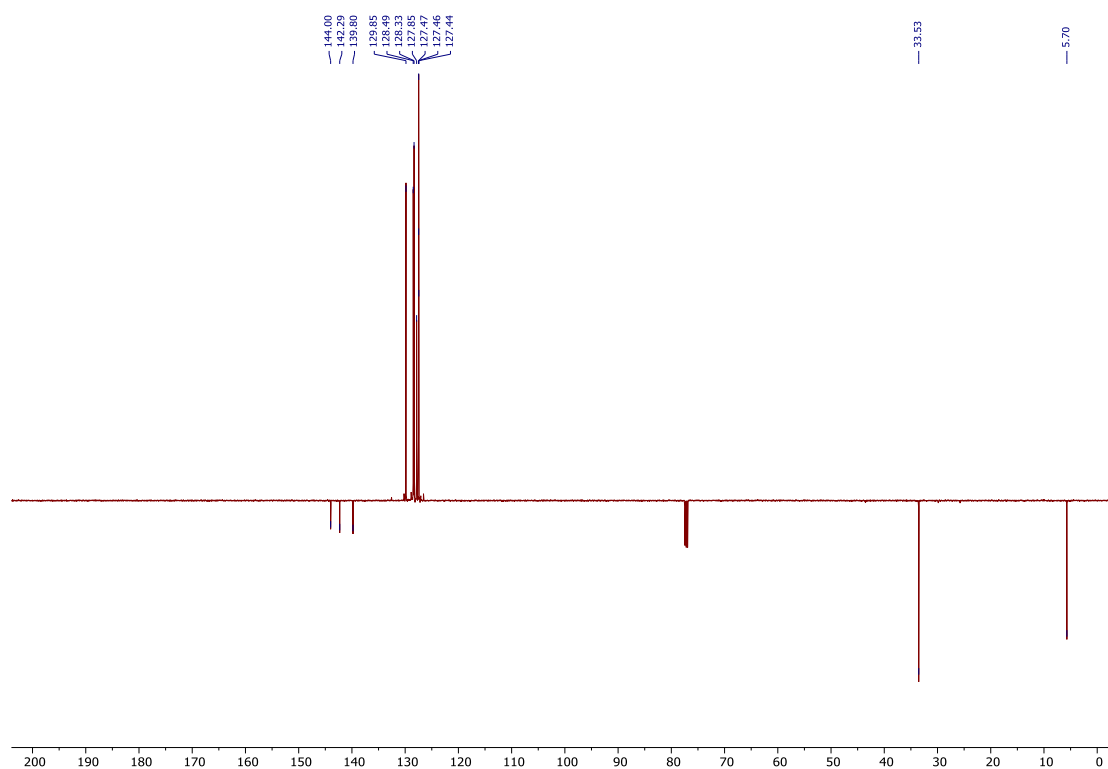
3 $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) spectrum:



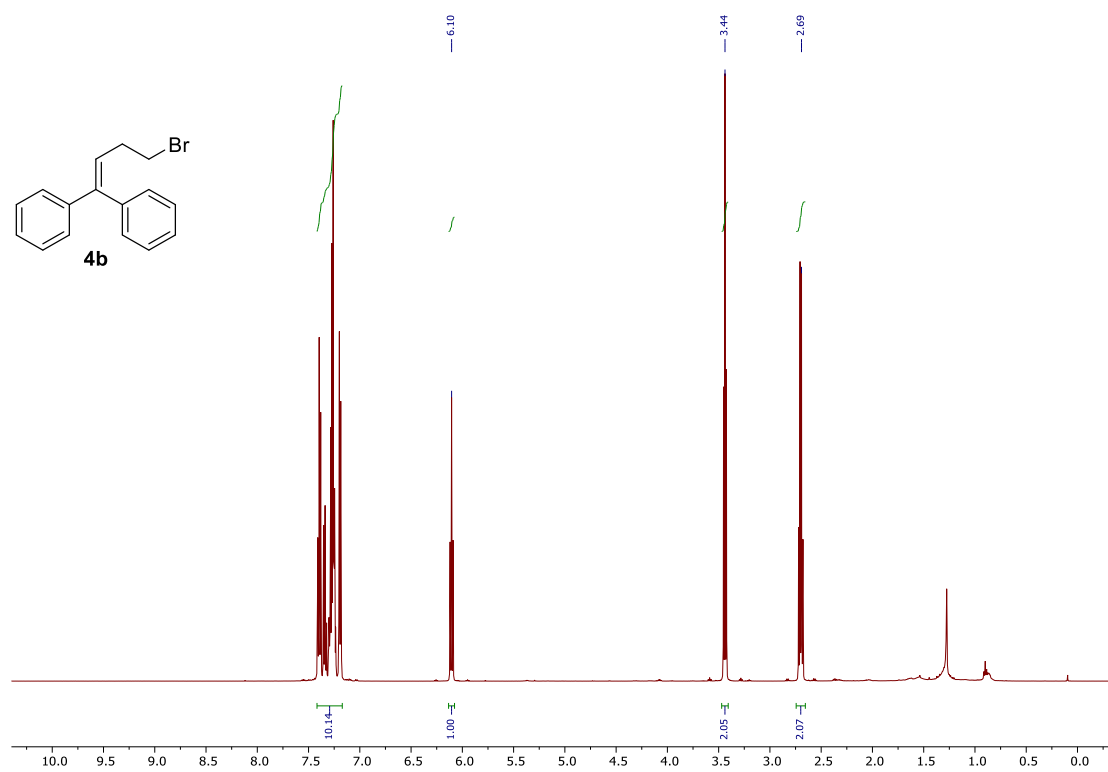
4a $^1\text{H-NMR}$ (300 MHz, CDCl_3) spectrum:



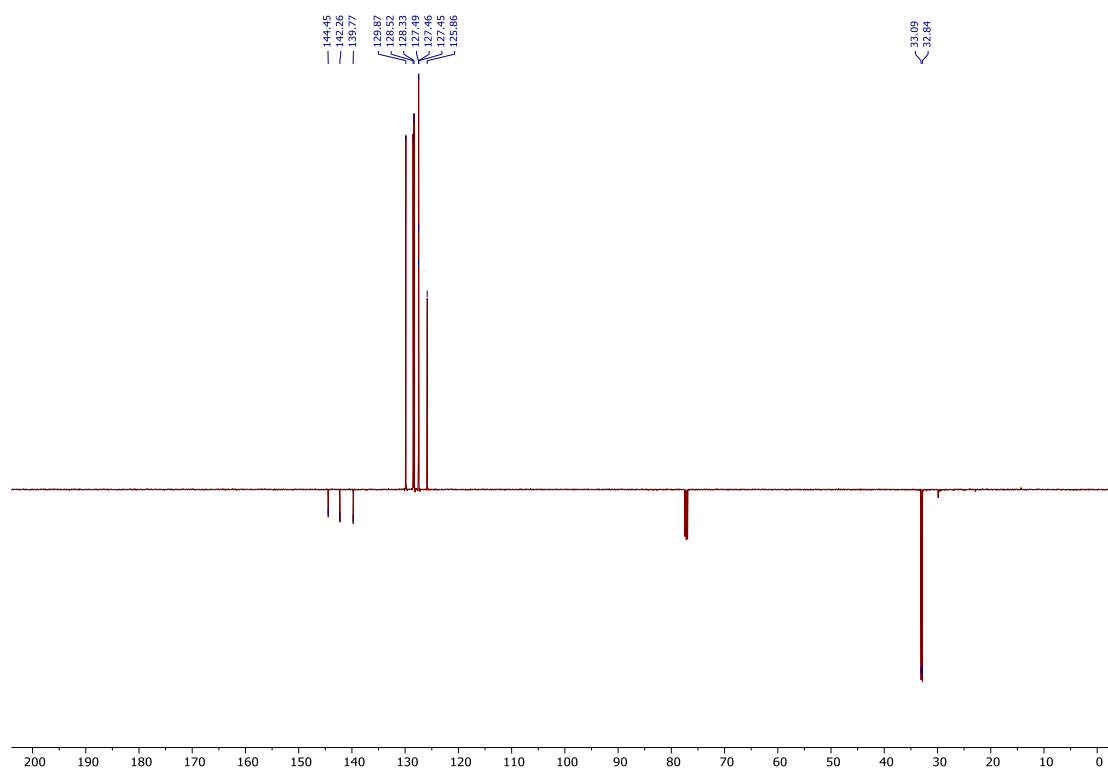
4a $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) spectrum:



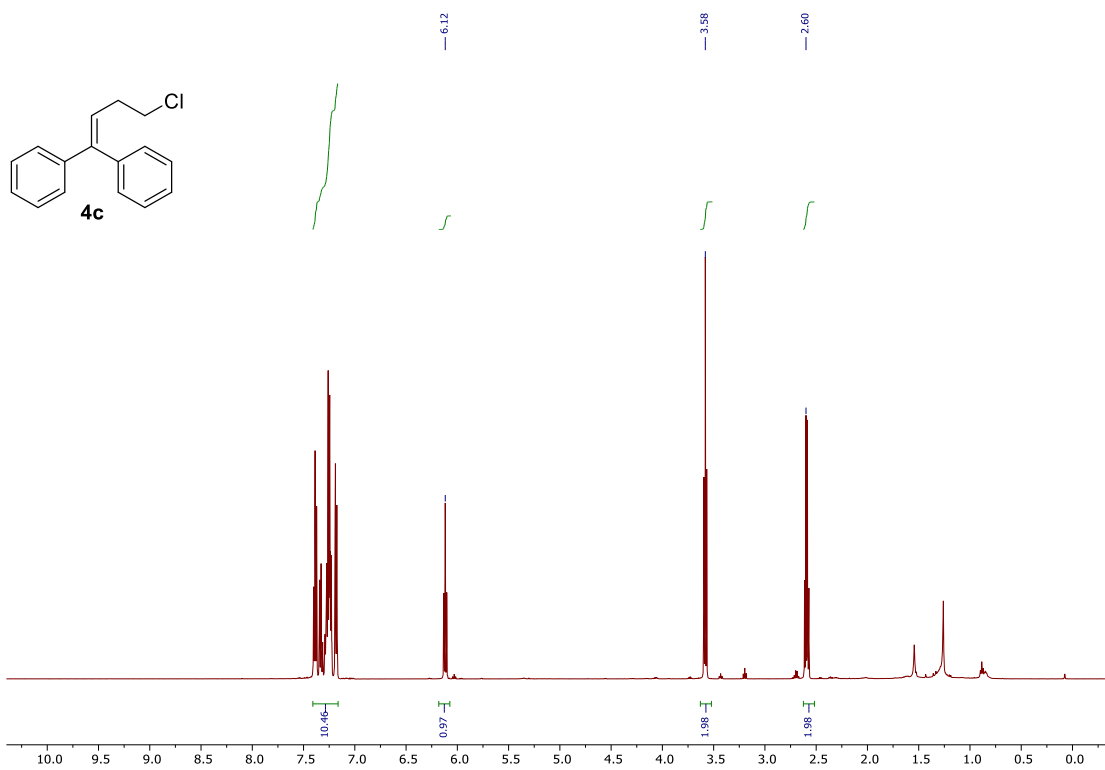
4b $^1\text{H-NMR}$ (500 MHz, CDCl_3) spectrum:



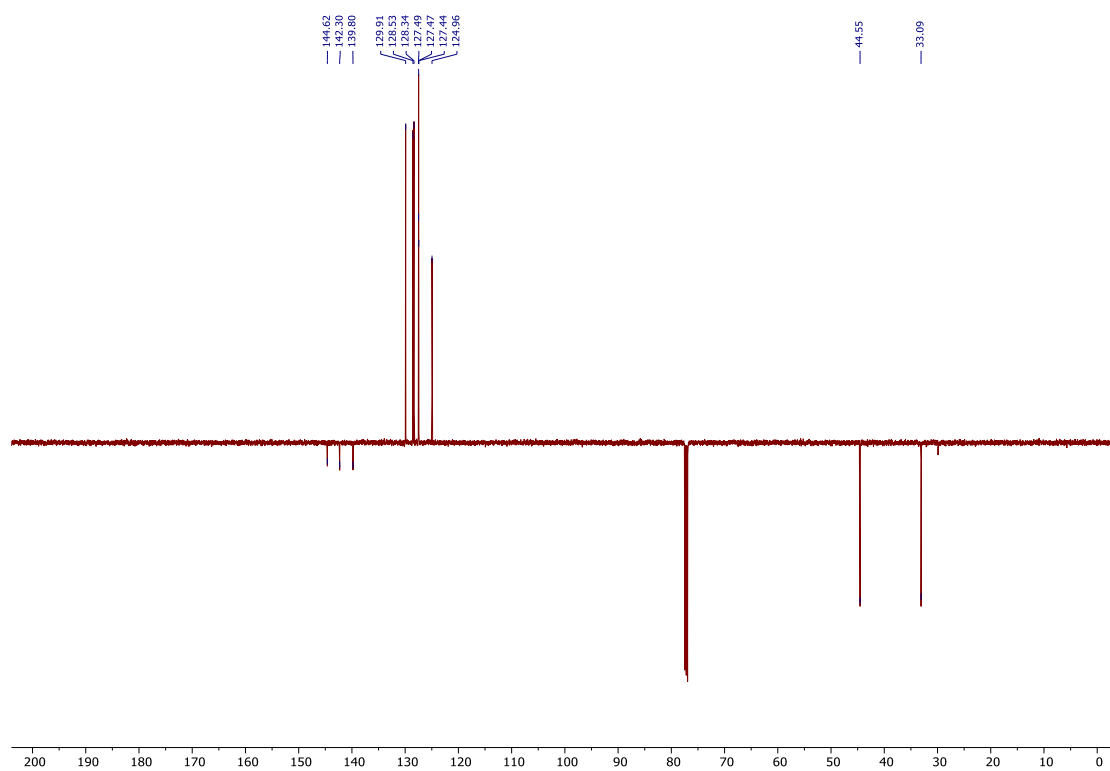
4b $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) spectrum:



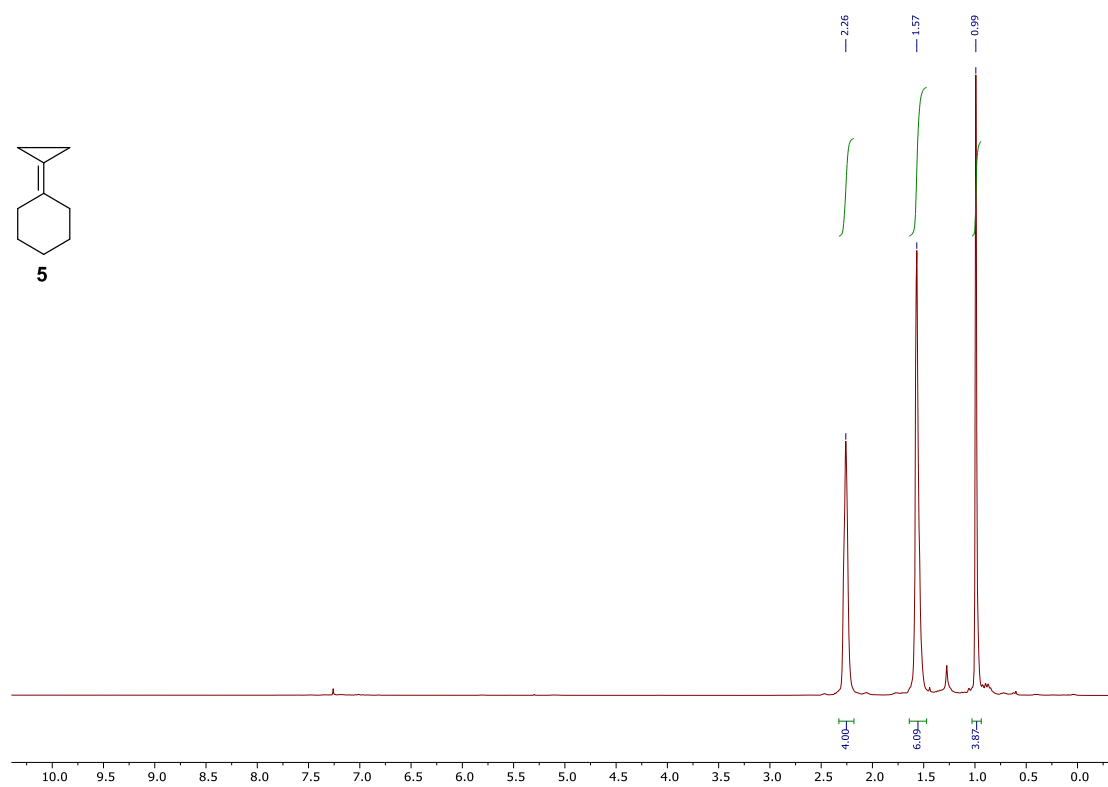
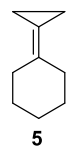
4c $^1\text{H-NMR}$ (500 MHz, CDCl_3) spectrum:



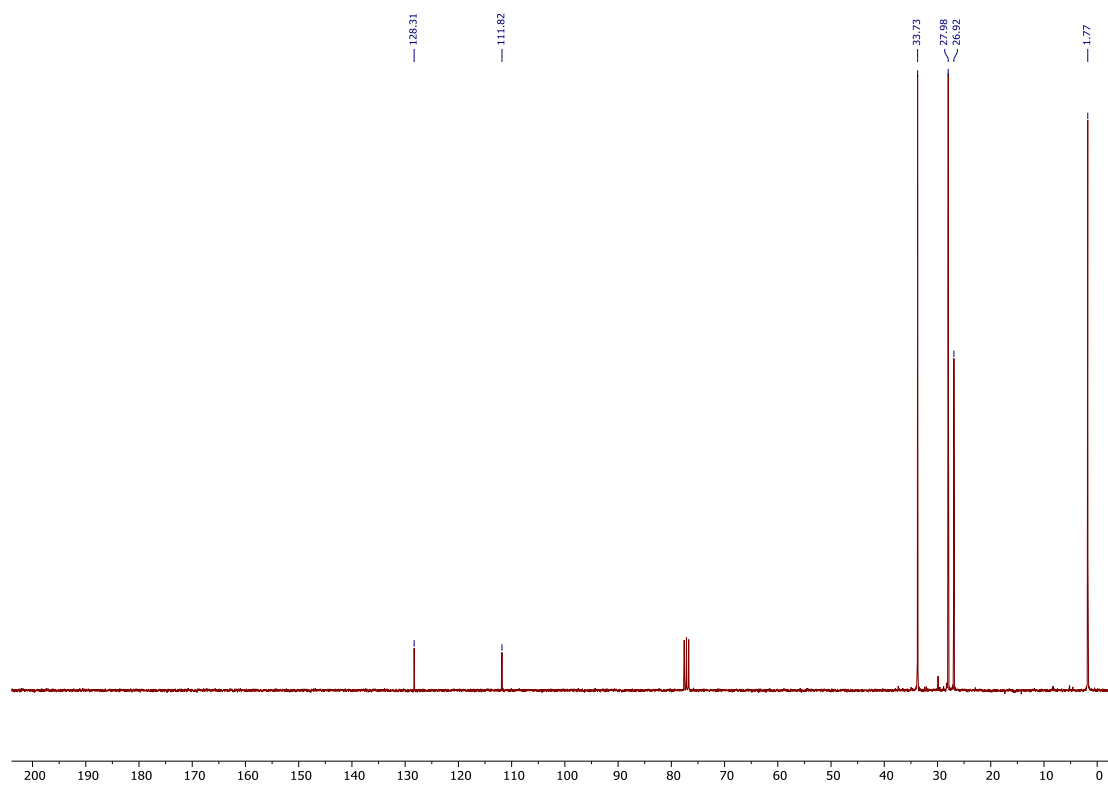
4c $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) spectrum:



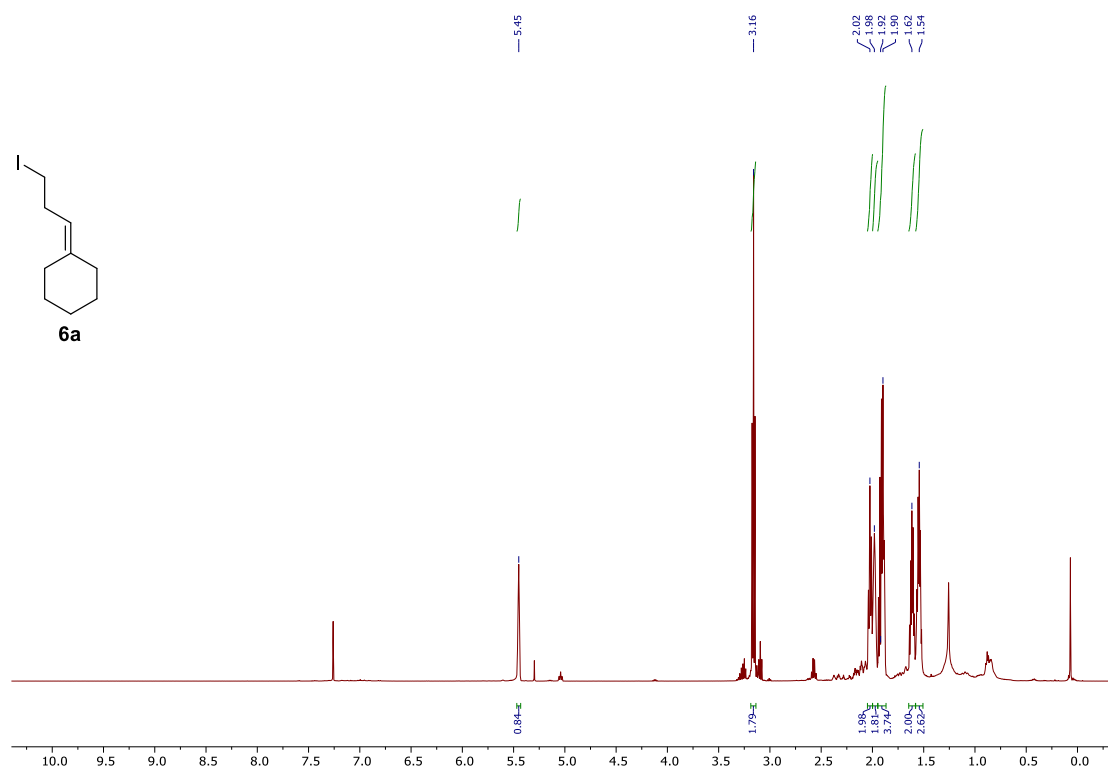
5 $^1\text{H-NMR}$ (300 MHz, CDCl_3) spectrum:



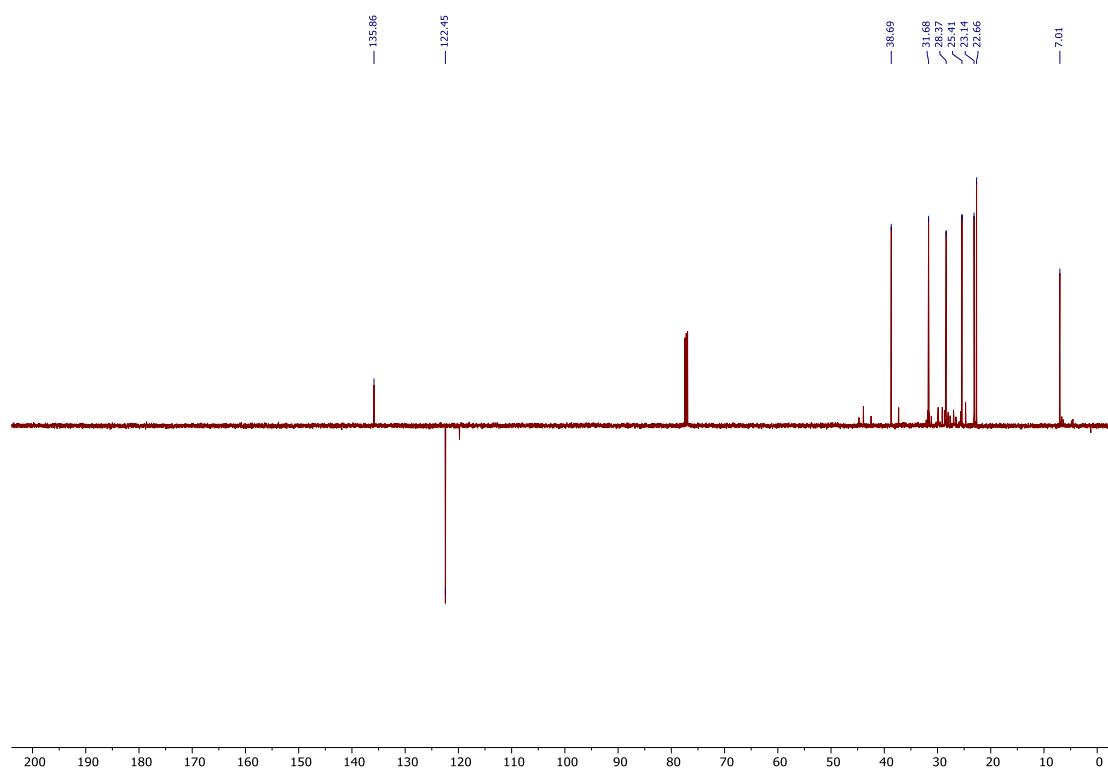
5 $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) spectrum:



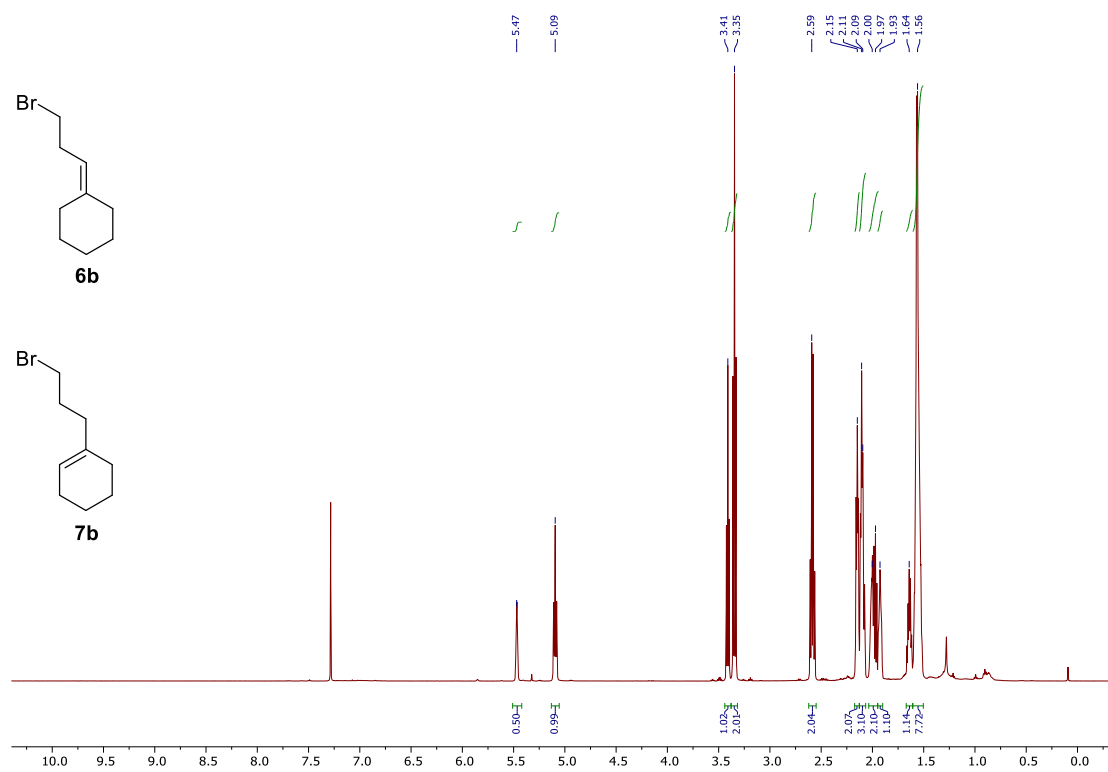
6a $^1\text{H-NMR}$ (300 MHz, CDCl_3) spectrum:



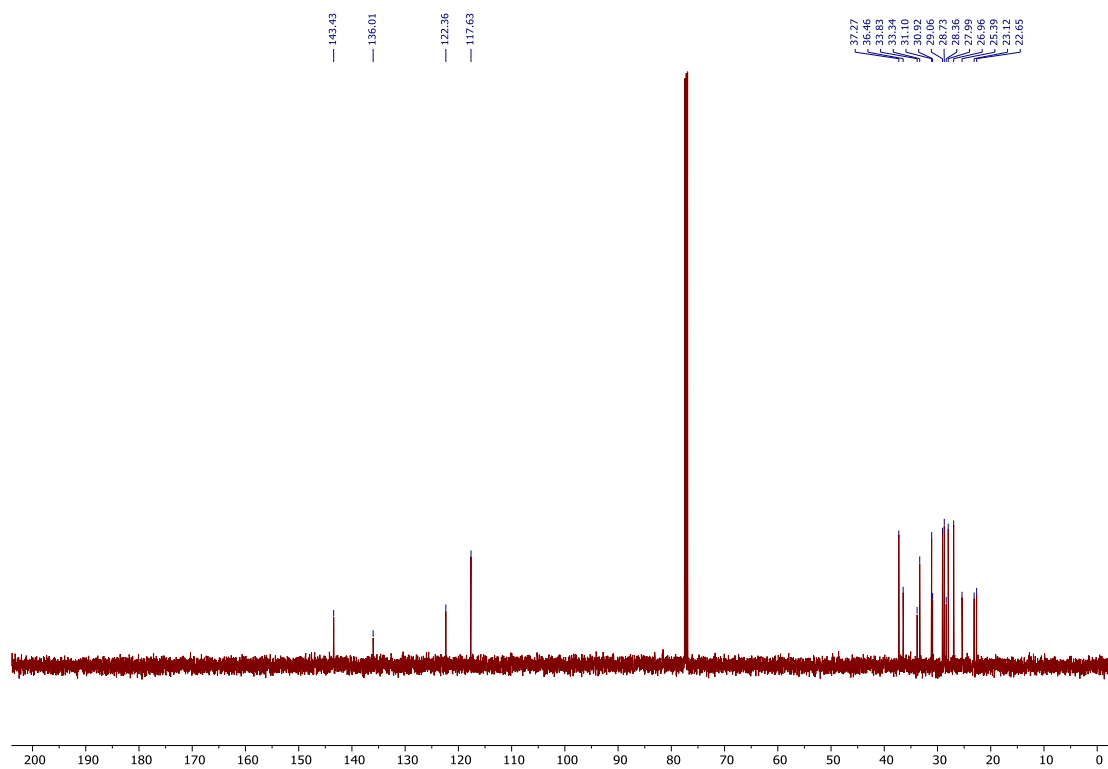
6a $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) spectrum:



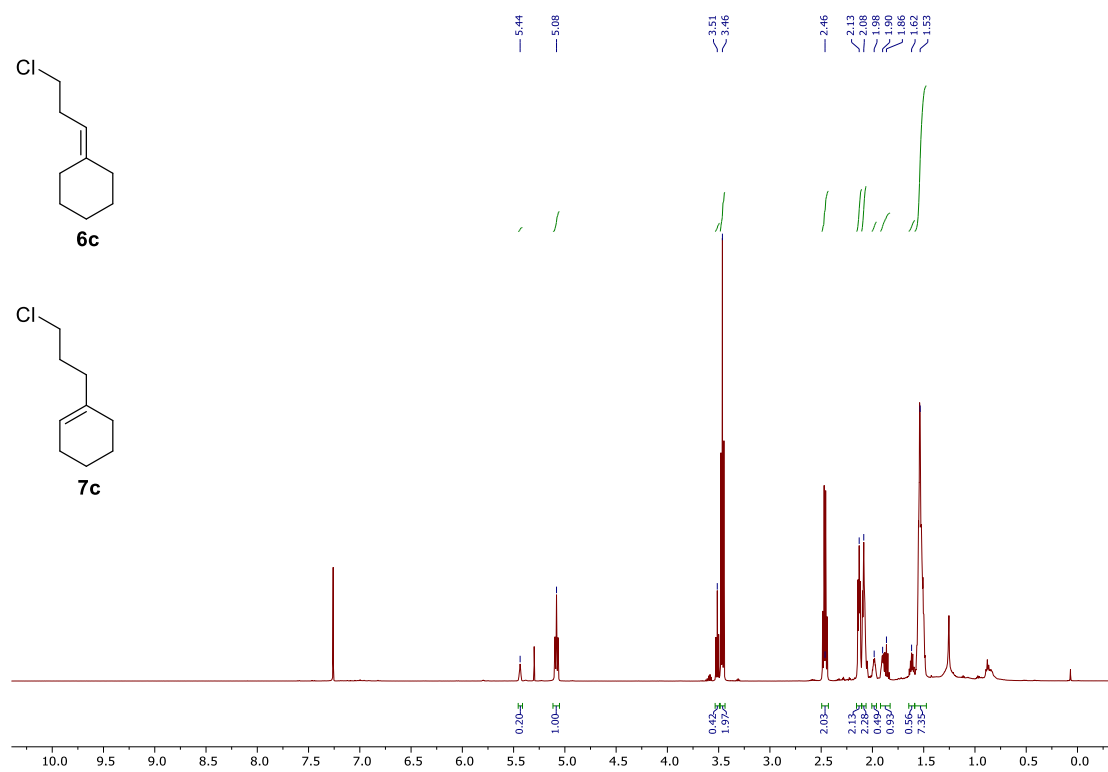
$^1\text{H-NMR}$ (300 MHz, CDCl_3) spectrum of **6b** and **7b** mixture:



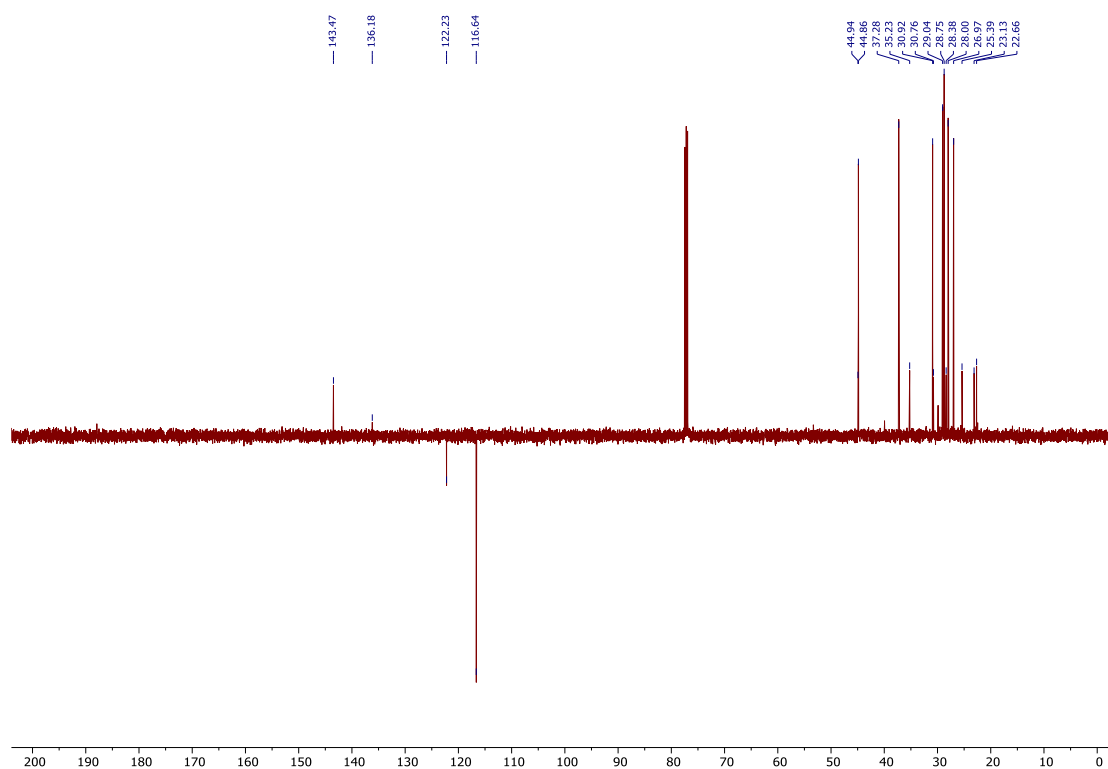
$^{13}\text{C-NMR}$ (75 MHz, CDCl_3) spectrum of **6b** and **7b** mixture:



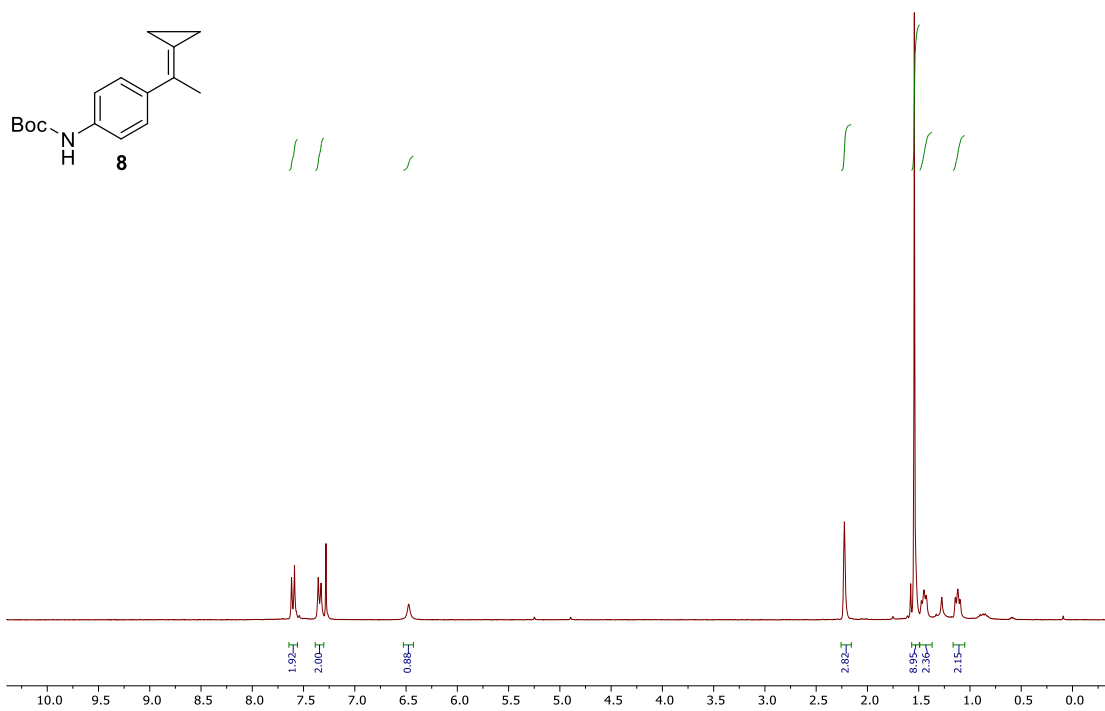
$^1\text{H-NMR}$ (300 MHz, CDCl_3) spectrum of **6c** and **7c** mixture:



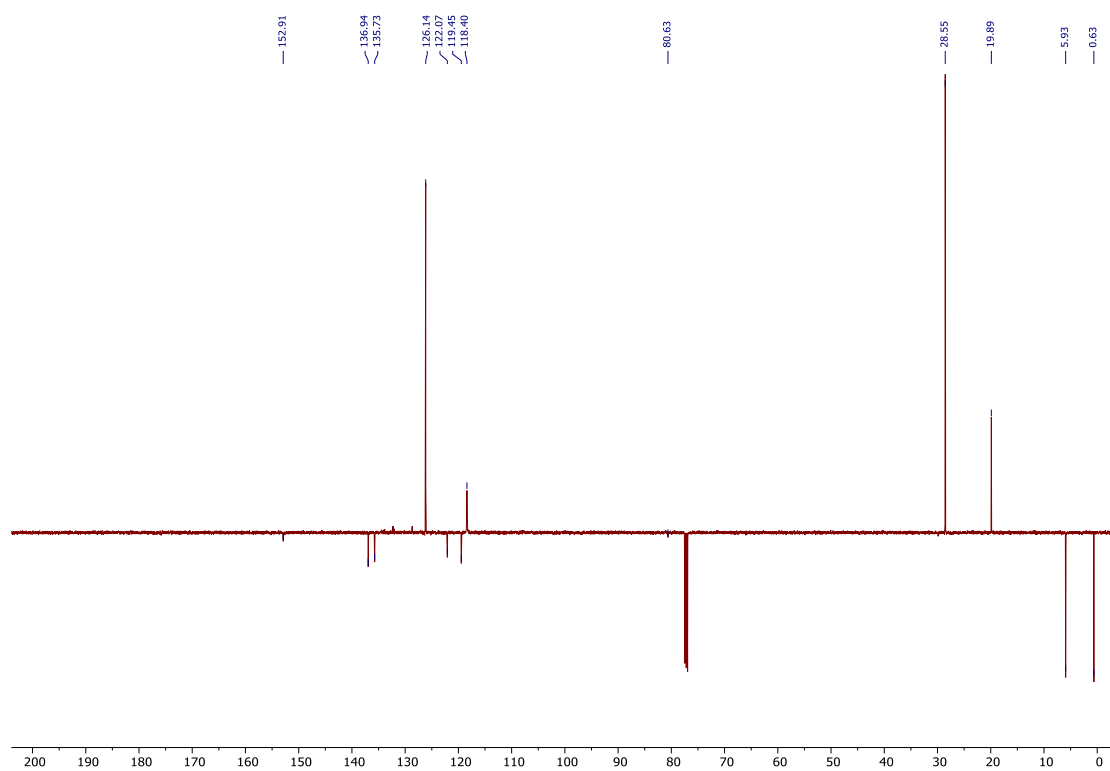
$^{13}\text{C-NMR}$ (75 MHz, CDCl_3) spectrum of **6c** and **7c** mixture:



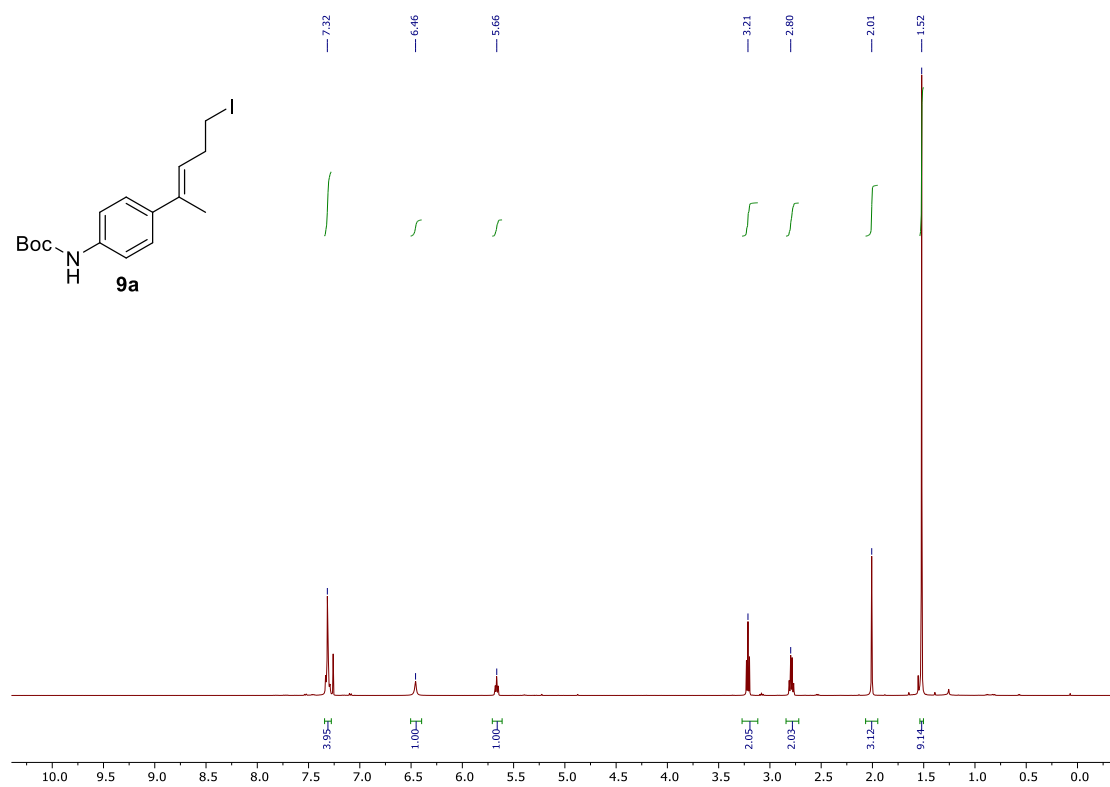
8 $^1\text{H-NMR}$ (300 MHz, CDCl_3) spectrum:



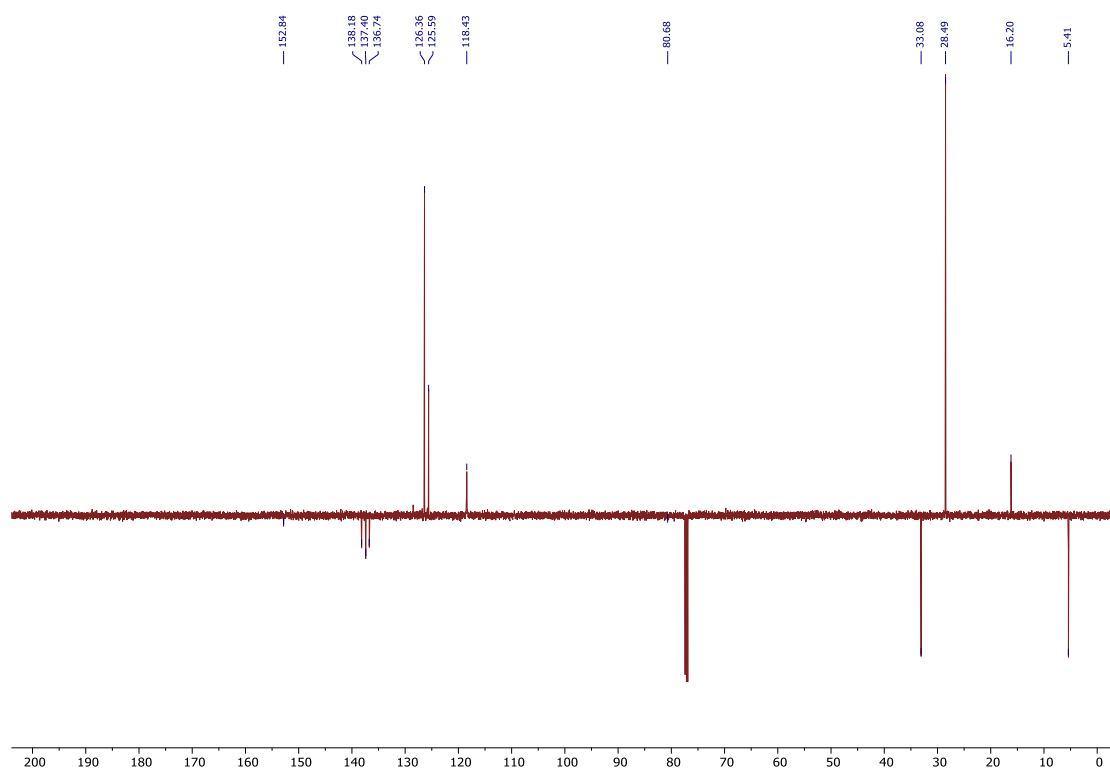
8 $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) spectrum:



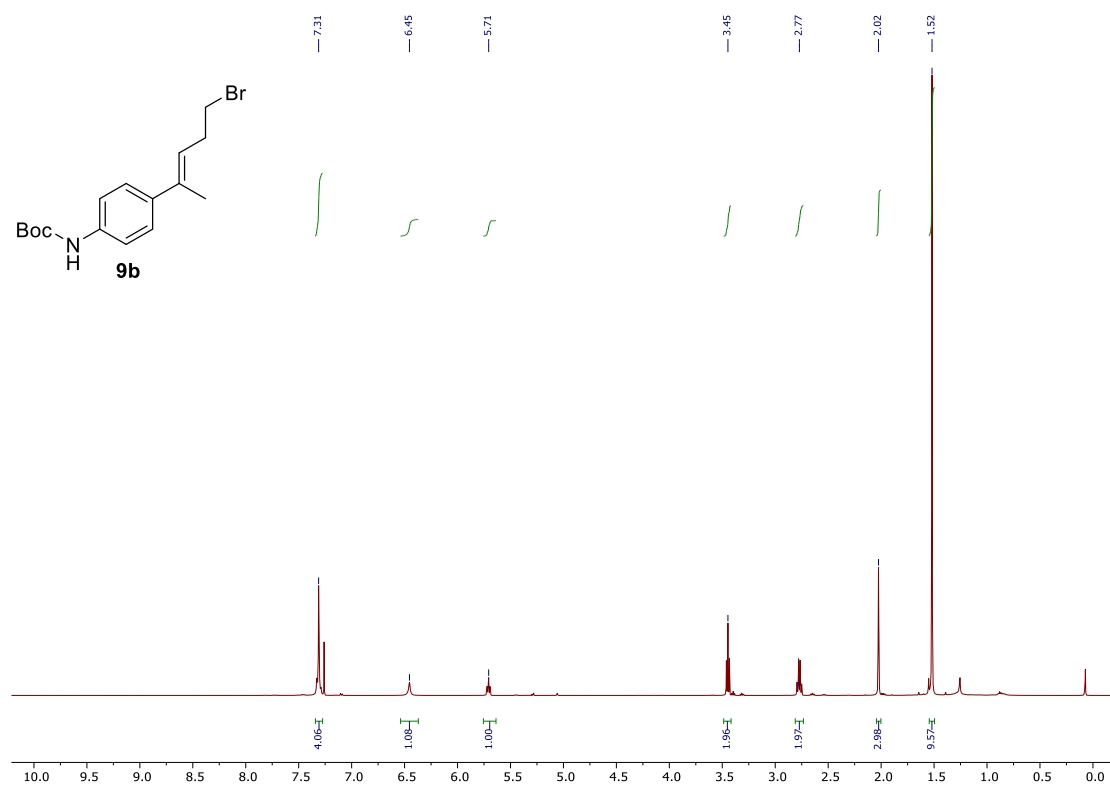
9a ¹H-NMR (500 MHz, CDCl₃) spectrum:



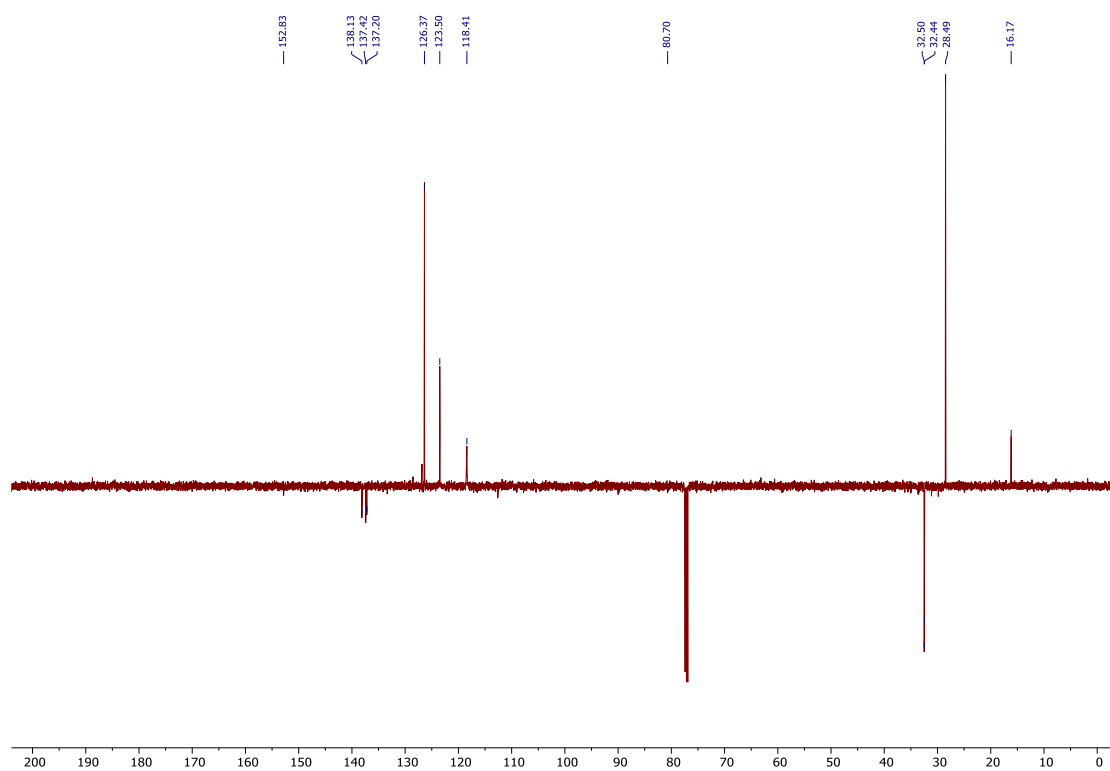
9a ¹³C-NMR (126 MHz, CDCl₃) spectrum:



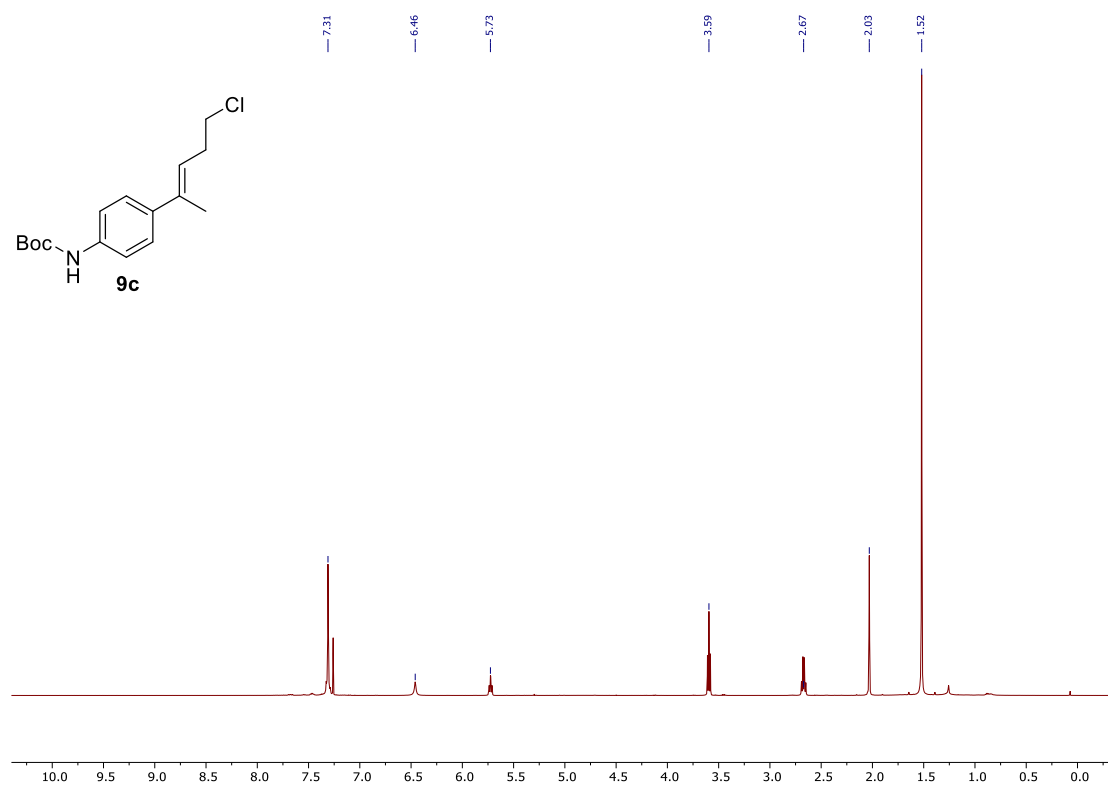
9b $^1\text{H-NMR}$ (500 MHz, CDCl_3) spectrum:



9b $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) spectrum:



9c $^1\text{H-NMR}$ (500 MHz, CDCl_3) spectrum:



9c $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) spectrum:

