

Supporting Information

Stereospecific hydrodehalogenation of alkenyl bromides: a new approach to the synthesis of (*E*)-alkenes

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1. General information

All reactions were carried out under nitrogen in oven-dried glassware with magnetic stirring. Unless otherwise noted, all materials were obtained from commercial suppliers and were used without further purification. All solvents were reagent grade. THF was distilled from sodium-benzophenone ketyl and degassed thoroughly with dry nitrogen directly before use. Unless otherwise noted, organic extracts were dried with Na₂SO₄, filtered through a fritted glass funnel, and concentrated with a rotary evaporator (20-30 mmHg). Flash chromatography was performed with silica gel (200-300 mesh) using the mobile phase indicated. Melting points were determined on a Büchi 510 capillary apparatus and are uncorrected. The NMR spectra were obtained with a Varian VXR-300 spectrometer at 300 for ¹H and 75.4 MHz for ¹³C or with a Bruker Ascend 400 MHz spectrometer at 400.1 for ¹H and 100.6 MHz for ¹³C in CDCl₃ solution with TMS as internal standard. Chemical shifts are reported in ppm downfield from internal Me₄Si in CDCl₃. The following abbreviations were used to describe peak patterns where appropriate: singlet (s), doublet (d), triplet (t), multiplet (m) and broad resonances (br).

2. Known 1,2-disubstituted 1-bromoalkenes

Analytical and spectra data of the products (*Z*)-1-(2-bromo-2-phenylvinyl)-4-methoxybenzene (**1a**),¹ (*Z*)-methyl 4-(2-bromo-2-phenylvinyl)benzoate (**1f**),² ((1*Z*,3*E*)-1-bromobuta-1,3-diene-1,4-diyl)dibenzene (**1n**),³ ((1*Z*,3*E*)-2-bromobuta-1,3-diene-1,4-diyl)dibenzene (**1o**)⁴ and (*Z*)-(2-bromobut-1-en-3-yne-1,4-diyl)dibenzene (**1p**)⁵ were identical to those reported in the literature.

3. Known 1,2-disubstituted alkenes

Analytical and spectra data of the products (*E*)-1-methoxy-4-styrylbenzene (**2a**),⁶ (*E*)-1-methyl-3-styrylbenzene (**2b**),⁷ (*E*)-1-chloro-4-styrylbenzene (**2c**),⁸ (*E*)-1-chloro-3-styrylbenzene (**2d**),⁹ (*E*)-1-nitro-4-styrylbenzene (**2e**),⁹ (*E*)-methyl 4-styrylbenzoate (**2f**),¹⁰ (*E*)-1-bromo-4-styrylbenzene (**2g**),¹¹ (*E*)-3-styrylbenzotrile (**2h**),¹² (*E*)-3-(3-methylstyryl)pyridine (**2i**),¹³ (1*E*,3*E*)-1,4-diphenylbuta-1,3-diene (**2l**),¹⁴ (*Z*)-but-1-en-3-yne-1,4-diyl)dibenzene (**2m**)¹⁵ and (*Z*)-but-1-en-3-yne-1,4-diyl)dibenzene (**2n**)¹⁶ were identical to those reported in the literature.

4. General procedure for the Suzuki-Miyaura cross-couplings of 1,1-dibromo-1-alkenes with boronic acids.

A mixture of 1,1-dibromo-1-alkene (2.4 mmol), phenyl boronic acid (317.3 mg, 2.6 mmol), cesium carbonate (2.25 g, 6.9 mmol), 1,4-dioxane (15 mL) and H₂O (6 mL) was degassed by bubbling argon for few minutes and then Pd₂(dba)₃ (57.0 mg, 0.062 mmol) e tri(2-furyl)phosphine (TFP) (86.0 mg, 0.37 mmol) were added. The mixture was heated at 65 °C for the proper time under argon. After cooling, the mixture was taken up in ethyl acetate (60 mL) and washed two times with

brine. The organic layer was dried over anhydrous Na_2SO_4 , filtered, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography by using as the eluent petroleum ether or mixtures of petroleum ether and ethyl acetate.

(Z)-1-(2-bromo-2-phenylvinyl)-3-methylbenzene (1b): This compound was purified by flash chromatography by using petroleum ether as the eluent: 71% yield, pale yellow oil, ^1H NMR (400.1 MHz, CDCl_3): δ 7.62-7.59 (m, 2H), 7.51 (d, $J = 7.9$ Hz, 1H), 7.46 (s, 1H), 7.35-7.23 (m, 4H), 7.14 (s, 1H), 7.10 (d, $J = 7.9$ Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 141.2, 139.9, 130.3, 130.1, 129.0, 128.8, 128.5, 128.3, 128.0, 126.5, 124.0, 21.7. Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{Br}$: C, 65.27; H, 40.80. Found: C, 65.74; H, 40.55.

(Z)-1-(2-bromo-2-phenylvinyl)-4-chlorobenzene (1c): This compound was purified by flash chromatography by using petroleum ether as the eluent: 75% yield, white solid mp 55-56 °C; ^1H NMR (400.1 MHz, CDCl_3): δ 7.67-7.60 (m, 4H), 7.41-7.32 (m, 5H), 7.15 (s, H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 140.8, 134.7, 133.8, 130.5, 129.0, 128.7, 128.4 (2C), 127.8, 124.9. Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{BrCl}$: C, 57.27; H, 3.43. Found: C, 57.89; H, 3.47.

Z)-1-(2-bromo-2-phenylvinyl)-3-chlorobenzene (1d): This compound was purified by flash chromatography by using petroleum ether as the eluent: 69% yield, pale yellow oil; ^1H NMR (400.1 MHz, CDCl_3): δ 7.70 (s, 1H), 7.62 (d, $J = 6.8$, 2H), 7.55 (d, $J = 6.8$, 1H), 7.42-7.27 (m, 5H), 7.14 (s, 1H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 140.7, 130.1, 134.1, 129.4, 129.1, 129.0, 128.6, 128.5, 128.0, 127.8, 127.4, 125.6. Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{BrCl}$: C, 57.27; H, 3.43. Found: C, 56.72; H, 3.39.

(Z)-1-(2-bromo-2-phenylvinyl)-4-nitrobenzene (1e): This compound was purified by flash chromatography by using petroleum ether as the eluent: 80% yield, white solid, mp 112-113 °C; ^1H NMR (400.1 MHz, CDCl_3): δ 8.24 (d, $J = 8.8$, 2H), 7.84 (d, $J = 8.8$, 2H), 7.68-7.63 (m, 2H), 7.46-7.37 (m, 3H), 7.26 (s, 1H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 146.9, 142.8, 140.2, 130.0, 129.6, 128.6, 128.2, 127.9, 127.8, 123.5. Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{BrNO}_2$: C, 55.29; H, 3.31; N, 4.61. Found: C, 55.44; H, 3.34; N, 4.59.

(Z)-1-bromo-4-(2-bromo-2-phenylvinyl)benzene (1g): This compound was purified by flash chromatography by using petroleum ether as the eluent: white solid, mp 53-54 °C; ^1H NMR (400.1 MHz, CDCl_3): δ 7.62 (d, $J = 7.8$ Hz, 2H), 7.53 (d, $J = 8.4$ Hz, 1H), 7.50 (d, $J = 7.8$ Hz, 1H), 7.40-7.30 (m, 3H), 7.11 (s, 1H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 140.7, 135.1, 131.3, 130.7, 128.9, 128.7, 128.4, 127.7, 124.9, 122.0. Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{Br}_2$: C, 49.74; H, 2.98. Found: C, 49.73; H, 2.96.

(Z)-1-(1-bromo-2-phenylvinyl)-4-methoxybenzene (1h): This compound was purified by flash chromatography by using petroleum ether/AcOEt = 95/5 as the eluent: 73% yield, white solid, mp 71-73 °C; ¹H NMR (400.1 MHz, CDCl₃): δ 7.68 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.13 (s, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H). ¹³C NMR (100.6 MHz, CDCl₃): δ 160.1, 136.6, 133.6, 129.3, 129.2, 128.5, 128.2, 127.9, 124.0, 113.7, 55.5. Anal. Calcd for C₁₅H₁₃BrO: C, 62.30; H, 4.53; Br, 27.63; O, 5.53. Found: C, 62.88; H, 4.47.

(Z)-3-(1-bromo-2-phenylvinyl)benzotrile (1i): This compound was purified by flash chromatography by using petroleum ether/AcOEt = 95/5 as the eluent: 73% yield, yellow-orange solid, mp 71-73 °C; ¹H NMR (400.1 MHz, CDCl₃): δ 7.96-7.94 (m, 1H), 7.88 (ddd, *J* = 8.0, 2.0, 1.2 Hz, 1H), 7.73-7.70 (m, 2H), 7.63 (ddd, *J* = 7.6, 1.8, 1.2 Hz, 1H), 7.51 (dt, *J* = 8.0, 0.4 Hz, 1H), 7.45-7.34 (m, 3H), 7.26 (s, 1H). ¹³C NMR (100.6 MHz, CDCl₃): δ 142.3, 135.5, 132.1, 132.0, 131.4, 129.3 (2C), 129.2, 128.7, 128.4, 121.0, 118.4, 112.8. Anal. Calcd for C₁₅H₁₀BrN: C, 63.40; H, 3.55; N 4.93. Found: C, 63.17; H, 3.49; N 4.88.

(Z)-1-(1-bromo-2-phenylvinyl)-3-chlorobenzene (1j): This compound was purified by flash chromatography by using petroleum ether as the eluent: 73% yield, pale yellow oil; ¹H NMR (300 MHz, CDCl₃): δ 7.69-7.62 (m, 2H), 7.60 (s, 1H), 7.49-7.44 (m, 1H), 7.39-7.21 (m, 5H), 7.15 (s, 1H). ¹³C NMR (75.4 MHz, CDCl₃): δ 142.6, 135.7, 134.2, 130.9, 129.4, 129.2, 128.6, 128.3, 128.2, 127.8, 125.9, 122.0. Anal. Calcd for C₁₄H₁₀BrCl: C, 57.27; H, 3.43. Found: C, 57.62; H, 3.41.

(Z)-3-(2-bromo-2-*m*-tolylvinyl)pyridine (1k): This compound was purified by flash chromatography by using petroleum ether as the eluent: 42% yield, pale yellow oil, ¹H NMR (400.1 MHz, CDCl₃): δ 8.78 (d, *J* = 2.4, 1H), 8.50 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.43-7.41 (m, 2H), 7.28-7.20 (m, 2H), 7.15-7.11 (m, 2H), 2.35 (s, 3H). ¹³C NMR (100.6 MHz, CDCl₃): δ 150.2, 148.2, 139.8, 137.6, 135.2, 131.9, 129.5, 127.9, 127.8, 126.5, 125.6, 124.5, 122.5, 20.9. Anal. Calcd for C₁₄H₁₂BrN: C, 61.33; H, 4.41; N, 5.11. Found: C, 61.66; H, 4.39; N, 5.10.

(Z)-1-(1-bromo-4-phenylbut-1-enyl)-3-methylbenzene (1l): This compound was purified by flash chromatography by using petroleum ether as the eluent: 43% yield, pale yellow oil, ^1H NMR (400.1 MHz, CDCl_3): δ 7.30-7.08 (m, 8H), 6.99 (d, $J = 11.2$ Hz, 1H), 6.13 (t, $J = 9.2$ Hz, 1H), 2.77-2.68 (m, 2H), 2.65-2.58 (m, 2H), 2.26 (s, 3H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 141.4, 140.0, 137.9, 130.5, 129.3, 128.3 (2C), 128.0, 126.4, 126.2, 124.9, 34.7, 34.5, 21.5. Anal. Calcd for $\text{C}_{17}\text{H}_{17}\text{Br}$: C, 67.78; H, 5.69. Found: C, 67.40; H, 5.64.

(Z)-1-(1-bromo-2-cyclohexylvinyl)-3-methylbenzene (1m): This compound was purified by flash chromatography by using petroleum ether as the eluent: 30% yield, pale yellow oil, ^1H NMR: δ 7.32-7.02 (m, 2H), 7.25-7.10 (m, 1H), 7.55-7.03 (m, 1H), 6.00 (d, $J = 8.8$ Hz, 1H), 2.60-2.52 (m, 1H), 2.34 (s, 3H), 1.85-1.66 (m, 5H), 1.45-1.12 (m, 5H). ^{13}C NMR: δ 140.2, 137.9, 136.8, 129.0, 128.3, 128.1, 124.80, 123.4, 41.6, 31.8, 26.0, 25.7, 21.4. Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{Br}$: C, 64.52; H, 6.86. Found: C, 64.86; H, 6.83.

5. General procedure for the hydrodehalogenation of alkenyl bromides

5.1. General procedure for the hydrodehalogenation of halogenated alkenyl bromides using Bu_3SnH and $\text{Pd}(\text{PPh}_3)_4$

A mixture of (Z)-1-(2-bromo-2-phenylvinyl)-4-methoxybenzene (144.6 mg, 0.5 mmol) and anhydrous toluene (5 mL) was degassed by bubbling argon for few minutes. Then, Bu_3SnH (174.6 mg, 0.6 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (28.9 mg, 0.025 mmol) were added. The resulting mixture was heated at 60 °C under argon for 48 h. The residue was taken up in brine and extracted three times with ethyl ether. The organic phase was dried and the solvent was evaporated. The ^1H NMR of the residue showed that it contains only the starting material **1a**.

5.2. General procedure for the hydrodehalogenation of halogenated alkenyl bromides using $n\text{-Bu}_3\text{N-HCOOH}$ and $\text{PdCl}_2(\text{PPh}_3)_2$

A mixture of (Z)-1-(2-bromo-2-phenylvinyl)-4-methoxybenzene (101.2 mg, 0.35 mmol) and anhydrous DMF (3 mL) was degassed by bubbling argon for few minutes. Then, $\text{PdCl}_2(\text{PPh}_3)_2$ (24.6 mg, 0.035 mmol), $n\text{-Bu}_3\text{N}$ (38 mg, 48.7 mL), HCOOH (40 mg, 32.8 mL) were added. The mixture was heated at 60 °C under argon for 16 h. The residue was taken up in brine and extracted three times with ethyl ether. The organic phase was washed with 10% Na_2CO_3 , separated, dried, the solvent was evaporated and the residue was purified by flash chromatography using of petroleum ether/ethyl acetate = 95% as the eluent, to give 48.6 mg (66% yield) of pure **2a**.

5.3. General procedure for the hydrodehalogenation of halogenated alkenyl bromides using HCOONa–DMF and Pd(PPh₃)₄

A mixture of (*Z*)-1-(2-bromo-2-phenylvinyl)-4-methoxybenzene (289.2 mg, 1.0 mmol) and anhydrous DMF (8 mL) was degassed by bubbling argon for few minutes. Then, Pd(PPh₃)₄ (57.8 mg, 0.05 mmol) and HCOONa (102.0 mg, 1.5 mmol) were added. The resulting mixture was heated at 60 °C under argon for 14 h. The mixture was taken up in brine and extracted three times with ethyl ether. The organic phase was washed with 10% Na₂CO₃, separated and dried. The solvent was evaporated and the residue was purified by flash chromatography using petroleum ether/ethyl acetate = 95/5 as the eluent, to give 168.2 mg (80% yield) of pure **2a**.

5.4. General procedure for the hydrodehalogenation of halogenated alkenyl bromides using HCOONH₄–MeOH and PdCl₂(PPh₃)₂

A mixture of (*Z*)-1-(2-bromo-2-phenylvinyl)-4-methoxybenzene (112.8 mg, 0.39 mmol) and anhydrous MeOH (3 mL) was degassed by bubbling argon for few minutes. Then, PdCl₂(PPh₃)₂ (14.0 mg, 0.02 mmol), HCOONH₄ (34.6 mg, 0.55 mmol) were added. The resulting mixture was heated at 60 °C under argon for 48 h. The residue was taken up in brine and extracted three times with ethyl ether. The organic phase was washed with 10% Na₂CO₃, separated, dried and the solvent was evaporated. The ¹H NMR of this residue showed that it contains the starting material **1a** and the product **2a** in a ratio of 67:33.

5.5. General procedure for the hydrodehalogenation of halogenated alkenyl bromides using NaOMe–DMF and Pd(PPh₃)₄

A mixture of (*Z*)-1-(2-bromo-2-phenylvinyl)-4-methoxybenzene (101.2 mg, 0.35 mmol) and anhydrous DMF (3 mL) was degassed by bubbling argon for few minutes. Then, Pd(PPh₃)₄ (31.2 mg, 0.027 mmol) and NaOMe (0.4 g) were added. The resulting mixture was heated at 60 °C under argon for 36 h. The residue was taken up in brine and extracted three times with ethyl ether. The organic phase was washed with 10% NH₄Cl, separated, dried, the solvent was evaporated and the residue was purified by flash chromatography using of petroleum ether/ethyl acetate = 95/% as the eluent, to give 24.3 mg (33% yield) of pure **2a**.

5.6. General procedure for the hydrodehalogenation of halogenated alkenyl bromides using Et₃SiH–MeCN and PdCl₂(PPh₃)₂

A mixture of (*Z*)-1-(2-bromo-2-phenylvinyl)-4-methoxybenzene (144.6 mg, 0.5 mmol) and anhydrous MeCN (4 mL) was degassed by bubbling argon for few minutes. Then, PdCl₂(PPh₃)₂ (14.0 mg, 0.02 mmol), Et₃SiH (80.1 mg, 0.11 ml) were added. The resulting mixture was heated at 60 °C under argon for 24 h. The mixture was taken up in brine and extracted three times with ethyl acetate. The organic phase was dried and the solvent was evaporated. The ¹H NMR of this residue showed no signal attributable to both the starting material **1a** and the product **2a**.

5.7. General procedure for the hydrodehalogenation of halogenated alkenyl bromides using NaBH₄-TMEDA and Pd(OAc)₂-PPh₃

A mixture of (*Z*)-1-(2-bromo-2-phenylvinyl)-4-methoxybenzene (144.6 mg, 0.5 mmol) in anhydrous THF (10 mL) was degassed by bubbling argon for few minutes. Then, Pd(OAc)₂ (5.6 mg, 0.025 mmol, 5.0 mol%) and PPh₃ (26.2 mg, 0.1 mmol, 20 mol%) were added. After 15 minutes TMEDA (0.215 g, 1.82 mmol, 3.64 equiv) and finally NaBH₄ (53.0 mg, 1.40 mmol, 2.8 equiv) were introduced in sequence. The mixture was stirred at room temperature under argon for 20 h. The residue was taken up in brine and extracted with ethyl acetate. The organic phase was separated, dried, the solvent was evaporated and the residue was purified by flash chromatography using of petroleum ether/ethyl acetate = 95/5 as the eluent, to give 92.5 mg (88% yield) of pure **2a**.

5.8. General procedure for the hydrodehalogenation of halogenated alkenyl bromides by using NaBH₄-TMEDA and PdCl₂(PPh₃)₂

A mixture of (*Z*)-1-(2-bromo-2-phenylvinyl)-4-methoxybenzene (145 mg, 0.5 mmol) in anhydrous THF (10 mL) was degassed by bubbling argon for few minutes. Then, PdCl₂(PPh₃)₂ (17.6 mg, 0.025 mmol, 5.0 mol%), TMEDA (0.215 g, 1.82 mmol, 3.64 equiv) and finally NaBH₄ (53.0 mg, 1.40 mmol, 2.8 equiv) were introduced in sequence. The mixture was stirred at room temperature or heated at 65 °C under argon for 20 h. The residue was taken up in brine and extracted with ethyl acetate. The organic phase was separated, dried, the solvent was evaporated and the residue was purified by flash chromatography using of petroleum ether/ethyl acetate = 95/5 as the eluent, to give 96.7 mg (92% yield) of pure **2a**.

6. Characterization data of new alkenes

(*E*)-1-methyl-3-(4-phenylbut-1-enyl)benzene (2j): This compound was purified by flash chromatography by using petroleum ether as the eluent: 64% yield, white solid 44-46 °C, ¹H NMR (400.1 MHz, CDCl₃): δ 7.31-7.11 (m, 8H), 7.01 (d, 1H, *J* = 7.2 Hz), 6.38 (d, 1H, *J* = 16.0 Hz), 6.28-

6.20 (m, 1H), 2.82-2.74 (m, 2H), 2.55-2.49 (m, 2H), 2.33 (s, 3H). ¹³C NMR (100.6 MHz, CDCl₃): δ 141.8, 138.0, 137.7, 130.4, 129.8, 128.5, 128.4, 127.7, 126.7, 125.9, 123.1, 35.9, 34.9, 21.4. Anal. Calcd for C₁₇H₁₈: C, 91.84; H, 8.16. Found: C, 91.29; H, 8.19.

(E)-1-(2-cyclohexylvinyl)-3-methylbenzene (2k): This compound was purified by flash chromatography by using petroleum ether as the eluent: 75% yield, pale yellow oil, ¹H NMR: δ 7.21-6.90 (m, 4H), 6.30 (d, 1H, *J* = 16.0 Hz), 6.15 (dd, 1H, *J* = 16.0, 6.8 Hz), 2.32 (s, 3H), 2.16-2.07 (m, 1H), 1.81-1.62 (m, 4H), 1.34-1.20 (m, 6H). ¹³C NMR: δ 143.3, 138.1, 138.0, 136.7, 128.4, 127.6, 127.4, 126.7, 123.2, 41.2, 33.1, 26.3, 26.1, 21.5. Anal. Calcd for C₁₅H₂₀Br: C, 89.94; H, 10.06. Found: C, 90.55; H, 10.02.

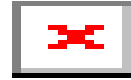
7. References

- (1) C. Muthiah, K. P. Kumar, S. Kumaraswamy, K. C. K. Swamy, *Tetrahedron* 1998, **54**, 14315–14326.
- (2) W. Shen, L. Wang, *J. Org. Chem.*, 1999, **64**, 8873–8879.
- (3) H. Klein, T. Roisnel, C. Bruneau, S. Derien, *Chem. Commun.*, 2012, **48**, 11032–11034.
- (4) J.-X. Wang, K. Wang, L. Zhao, H. Li, Y. Fu, Y. Hu, *Adv. Synth. Catal.*, 2006, **348**, 1262–1270.
- (5) J.-c. Shi, X. Zeng, E.-i. Negishi, *Org. Lett.*, 2003, **5**, 1825–1828.
- (6) E. Alacid, C. Najera, *J. Org. Chem.*, 2009, **74**, 8191–8195.
- (7) J. Zhang, W. Zhang, Y. Wang, M. Zhang, *Adv. Synth. Catal.*, 2008, **350**, 2065–2076.
- (8) C. Belger, B. Plietker, *Chem. Comm.*, 2012, **48**, 5419–5421.
- (9) A. R. Hajipour, K. Karami, G. Tavakoli, *Appl. Organometal. Chem.*, 2010, **24**, 798–804.
- (10) E. Shirakawa, H. Otsuka, T. Hayashi, *Chem. Commun.* 2005, **47**, 5885–5886.
- (11) R. Frei, A. S. Breitbach, H. E. Blackwell, *Angew. Chem.* 2012, **51**, 5226–5229.
- (12) X. Cui, Z. Li, C.-Z. Tao, Y. Xu, J. Li, L. Liu, Q.-X. Guo, *Org. Lett.*, 2006, **8**, 2467–2470.
- (13) H. F. Sore, C. M. Boehner, L. Laraia, P. Logoteta, C. Prestinari, M. Scott, K. Williams, W. R. Galloway, D. R. Spring, *Org. Biomol. Chem.*, 2011, **9**, 504–515.
- (14) Z.-Y. Peng, F.-F. Ma, L.-F. Zhu, X.-M. Xie, Z. Zhang, *J. Org. Chem.*, 2009, **74**, 6855–6858.
- (15) C. Jahier, O. L. Zatolochnaya, V. Gevorgyan, N. V. Zvyagintsev, V. P. Ananikov, *Org. Lett.*, 2012, **14**, 2846–2849.
- (16) T. Li, J. Mao, X. Qu, P. Sun, H. Yang, Y. Zhu, *Org. Biomol. Chem.*, 2011, **9**, 7309-7312.

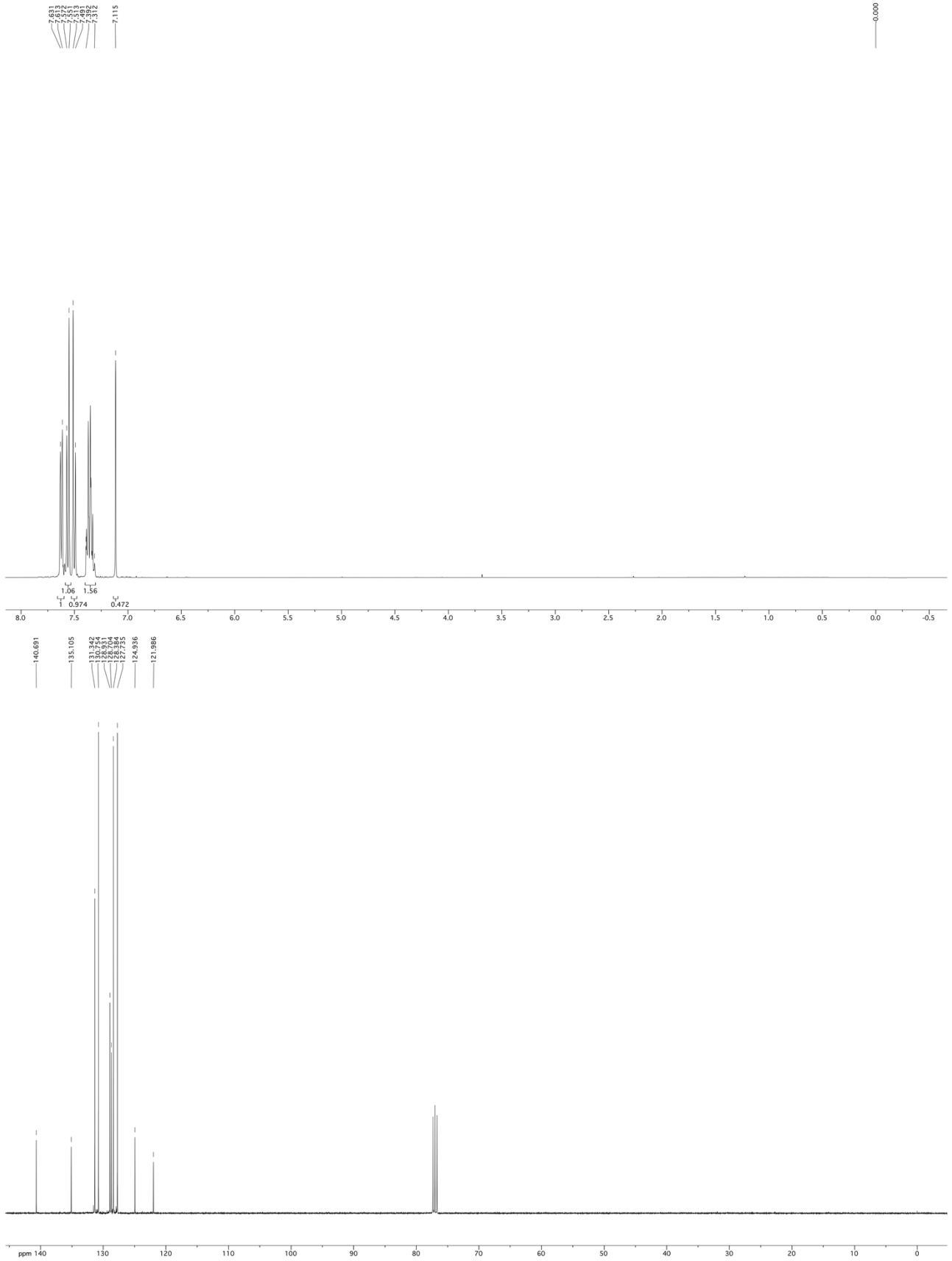
8. NMR spectra of the new products

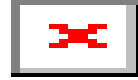


(Z)-1-(2-bromo-2-phenylvinyl)-3-methylbenzene (1b):

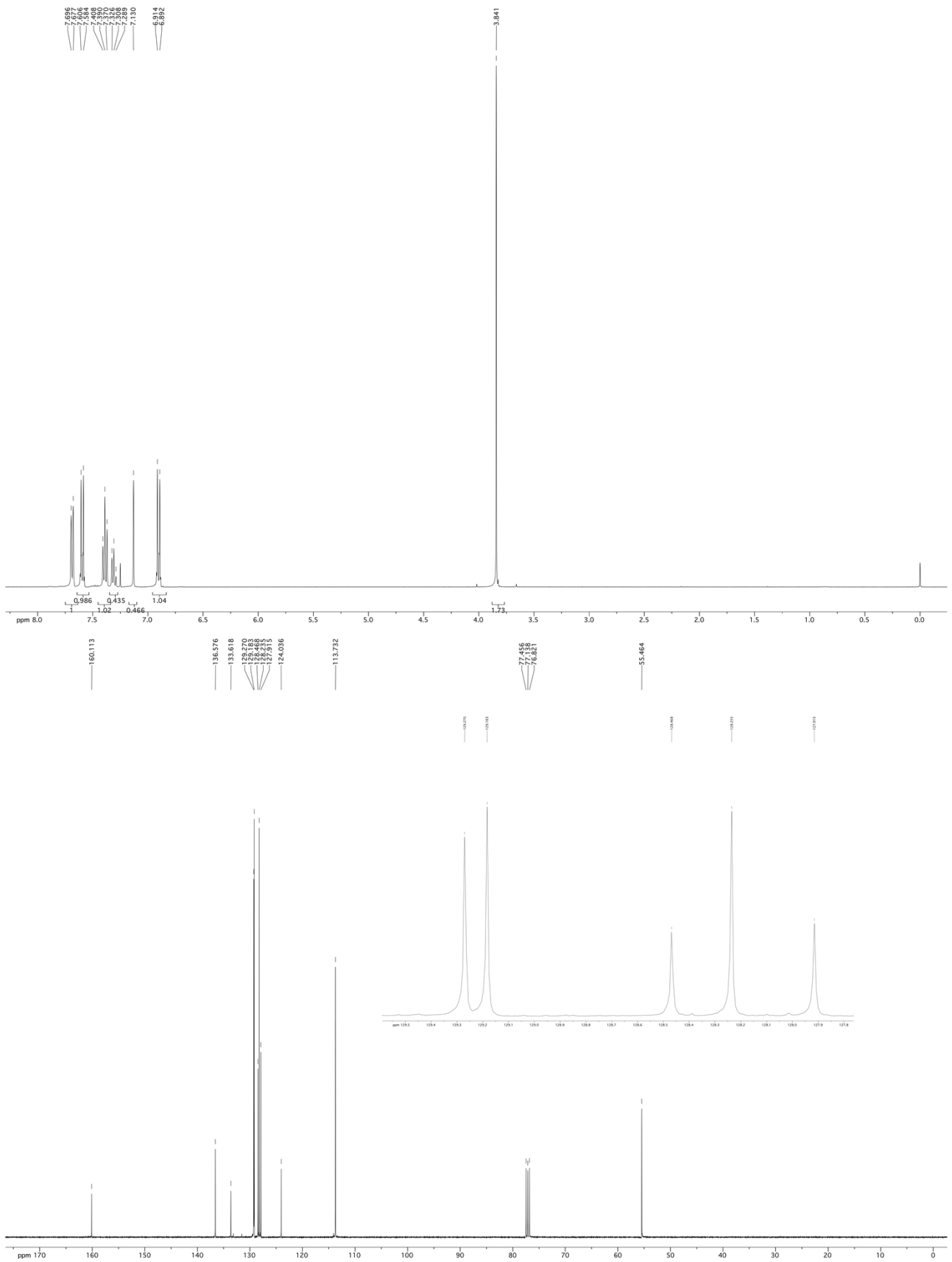


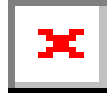
(Z)-1-bromo-4-(2-bromo-2-phenylvinyl)benzene (1g):



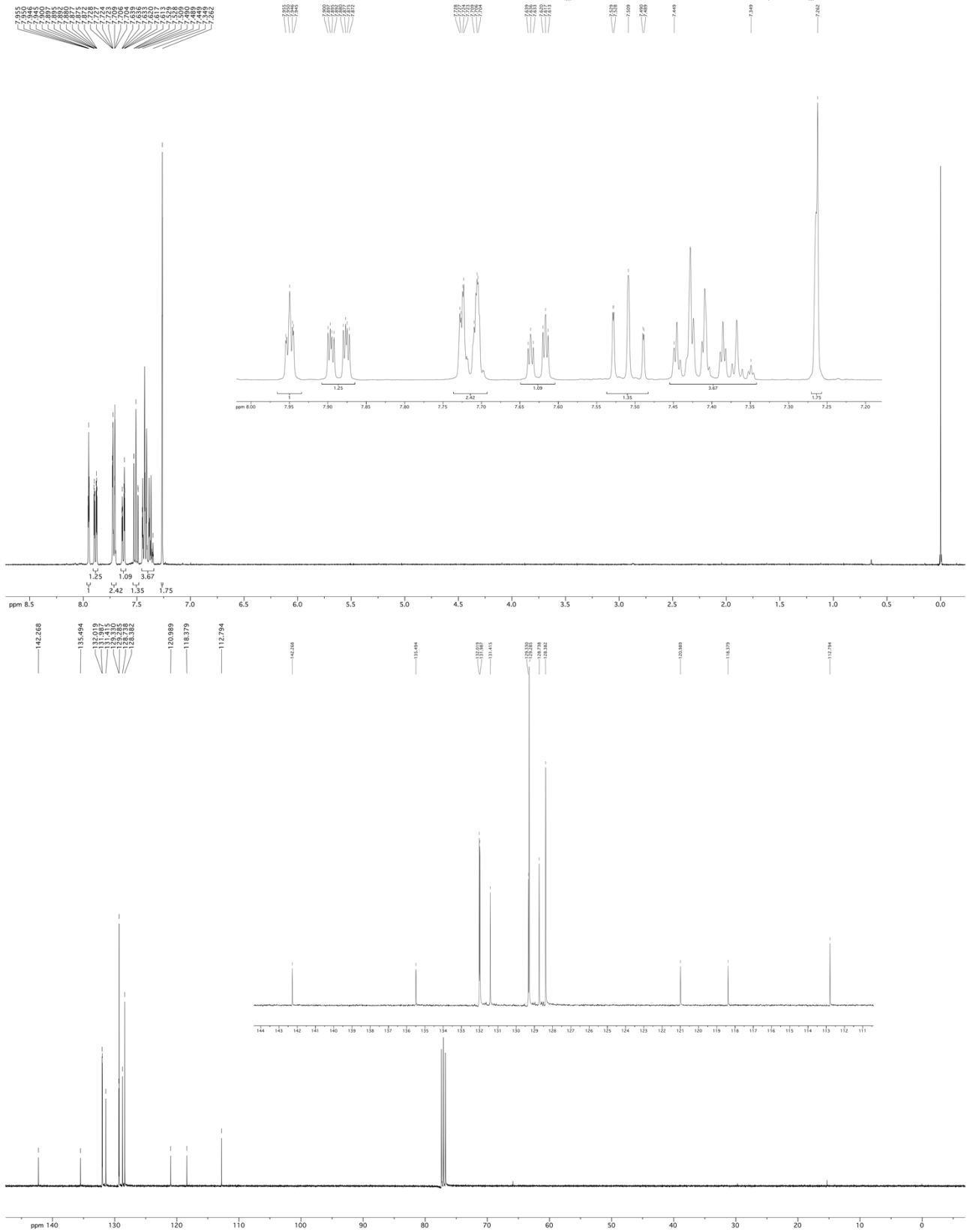


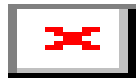
(Z)-1-(1-bromo-2-phenylvinyl)-4-methoxybenzene (1h):



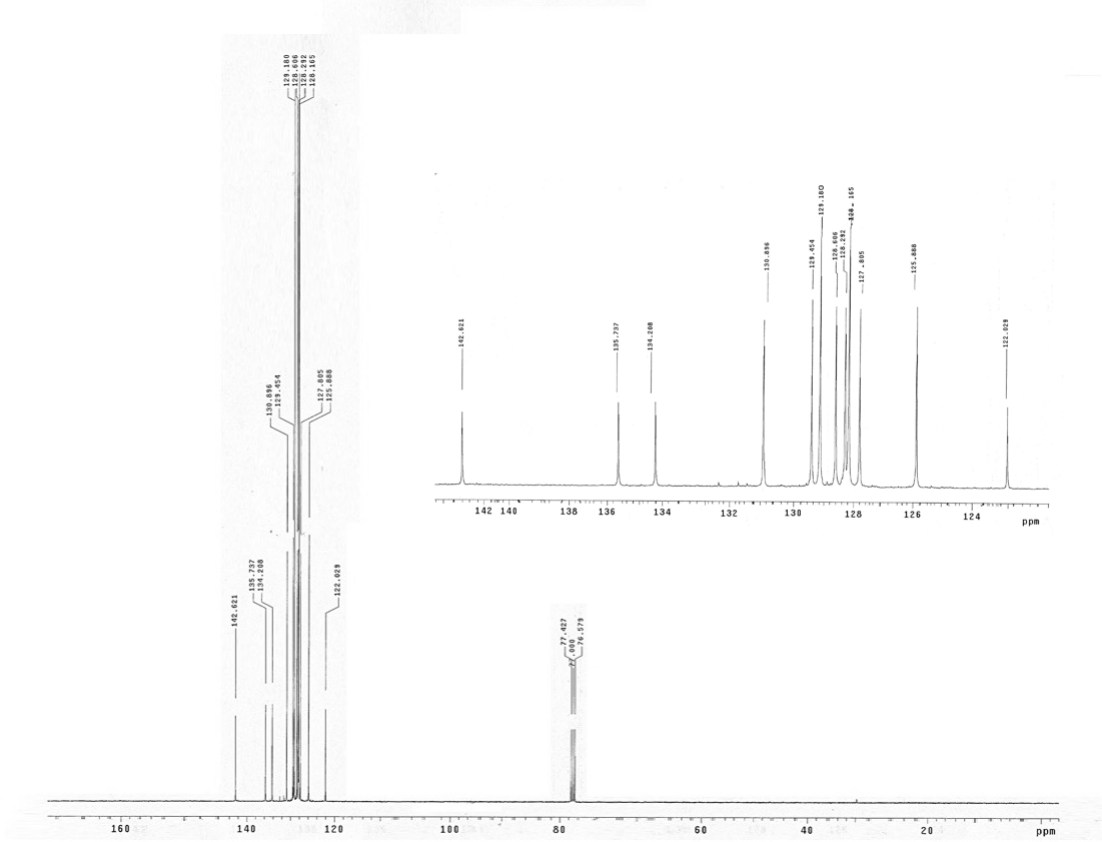
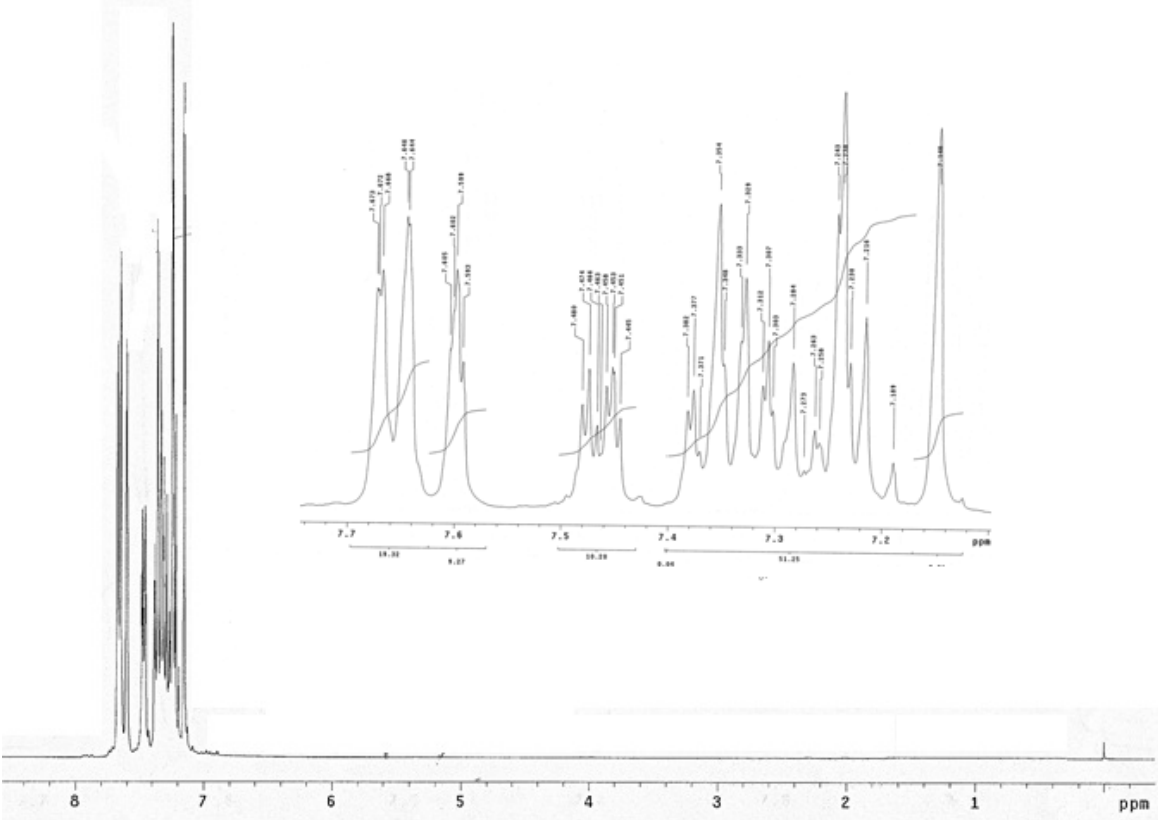


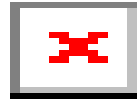
(Z)-3-(1-bromo-2-phenylvinyl)benzonitrile (1i):



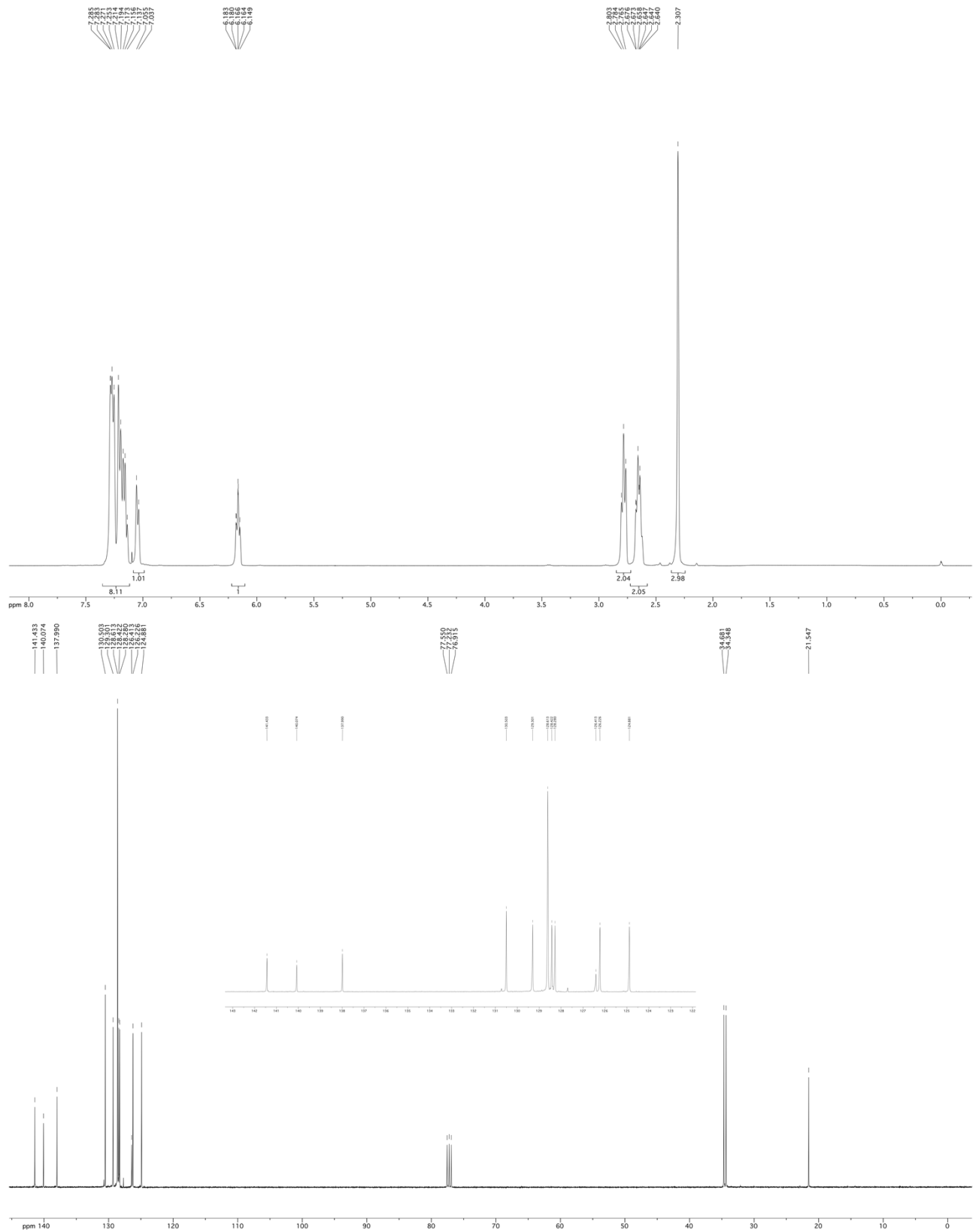


(Z)-1-(1-bromo-2-phenylvinyl)-3-chlorobenzene (1j):



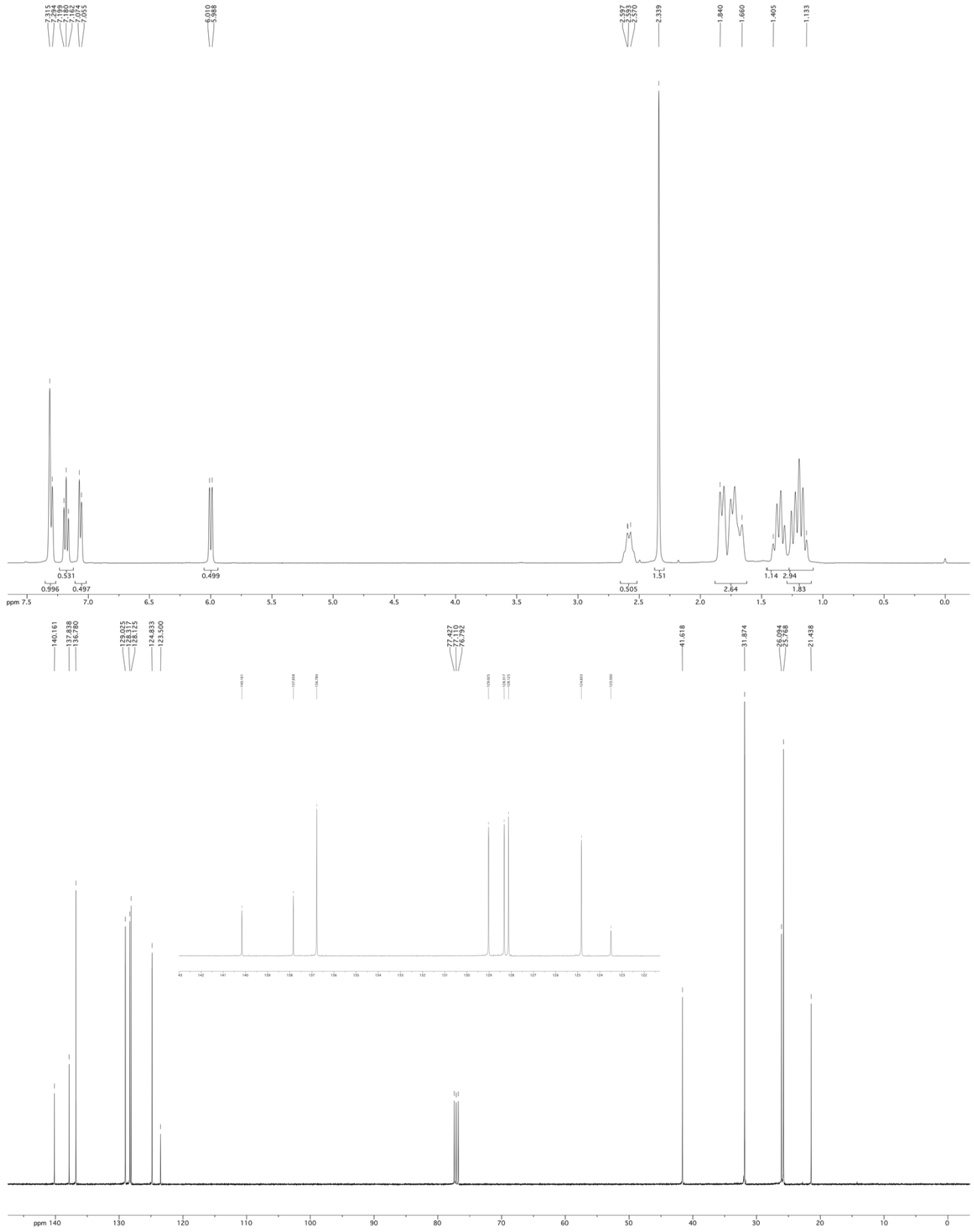


(Z)-1-(1-bromo-4-phenylbut-1-enyl)-3-methylbenzene (11):



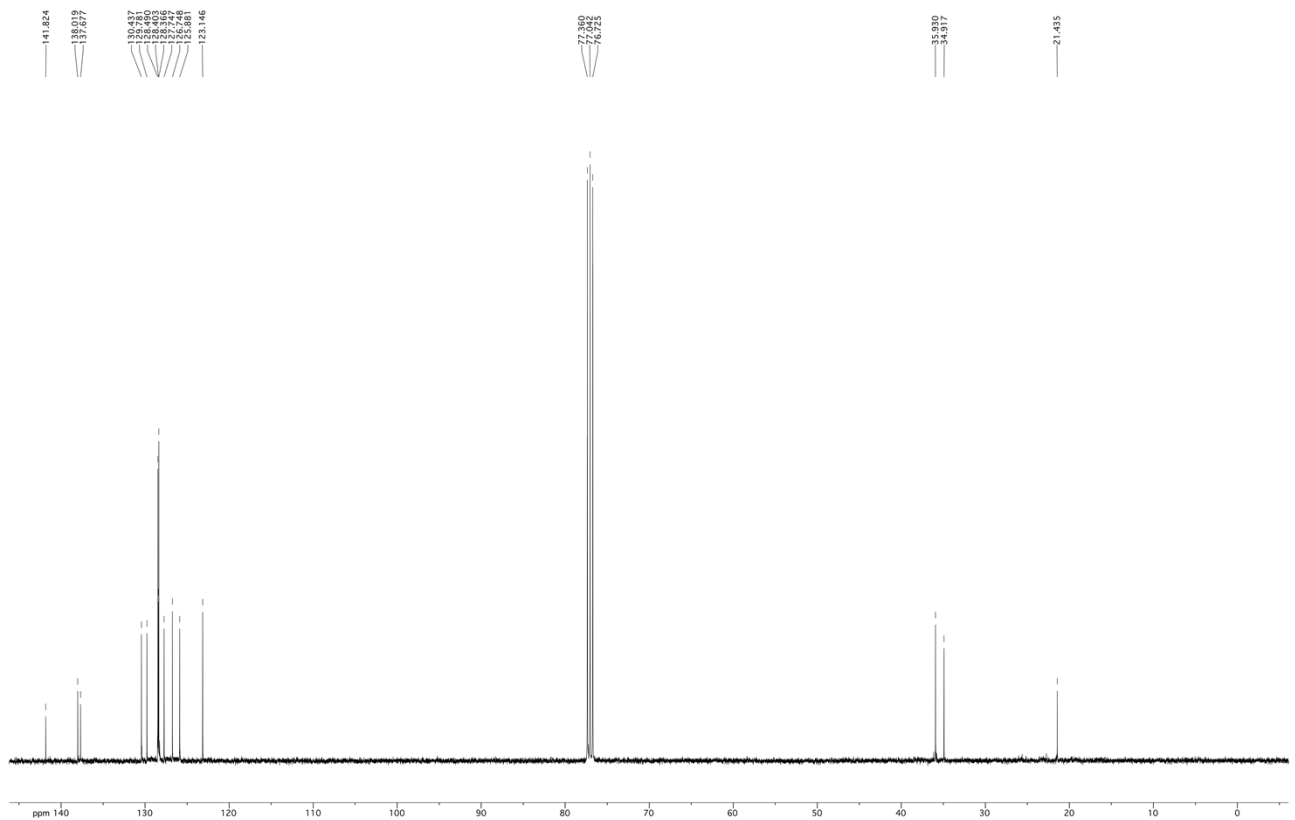
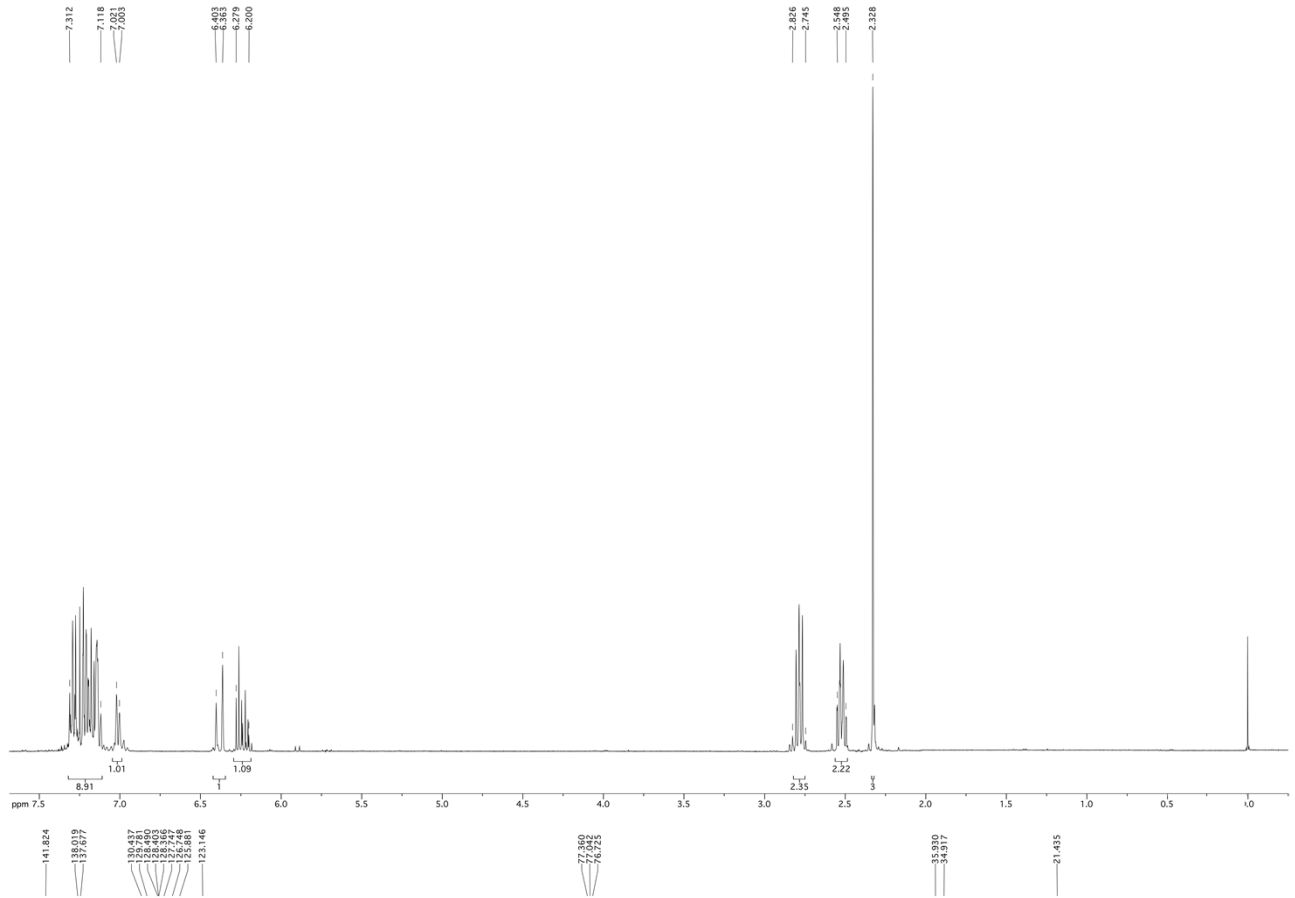


(Z)-1-(1-bromo-2-cyclohexylvinyl)-3-methylbenzene (1m):





(E)-1-methyl-3-(4-phenylbut-1-enyl)benzene (2j):





(E)-1-(2-cyclohexylvinyl)-3-methylbenzene (2k):

