

Ligands Effects on Negishi Couplings of Alkenyl Halides

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Supporting Information

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Instrumentation and Chemicals

General. Reactions were performed in a 5 mL round bottom flask under an argon atmosphere containing a Teflon coated stir bar and septum. All commercially available reagents were used without further purification. Zinc dust 98.0% was purchased from Strem Chemicals (catalog #93-3060) or from Across and was stored in the glove box, as was (Amphos)₂PdCl₂ (CAS #887919-35-9) obtained from Johnson Matthey ((Amphos)₂PdCl₂ = dichloro-bis(*p*-dimethylaminophenyl-di-*t*-butylphosphine)palladium(II); Pd-132, catalog #C4138). *Z*-Vinyl iodides and *Z*-vinyl bromides were prepared following literature procedures.¹ Organozinc halides, such as *n*-C₁₀H₂₁ZnI, *n*-C₇H₂₁ZnI, IZn(CH₂)₃CO₂Et, and PhCH₂CH₂ZnI were prepared as 1 M solutions in THF according to known procedures.² PhZnI·LiCl was prepared as a 1 M solution in THF according to a known procedure.³

Column chromatography was performed using Silicycle Silia-P 60 Å flash silica gel. GC analyses were recorded on a Hewlett-Packard HP 6890 chromatograph equipped with a capillary column HP-1 (30 m × 0.25 mm × 0.25 μm). ¹H and ¹³C NMR spectra were measured on a Varian Inova-400 (400 and 100 MHz, respectively) spectrometer at ambient temperature. Proton NMR data were recorded as follows: chemical shift in ppm referenced from residual solvent peak (CDCl₃, 7.26 ppm), multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; p = pentet, h = heptet, m = multiplet), coupling constant (Hz), and integration. ¹³C Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (CDCl₃, 77.00 ppm). Mass spectral data were acquired on either a VF Autospec or an analytical VG-70-250 HF instrument.

Experimental Procedures and Characterization Data

General Procedure (Table 1). To a 5 mL round-bottom flask under argon equipped with a magnetic stir bar and charged with a palladium catalyst (2 mol %, 0.02 mmol) or PdCl₂ (2 mol %, 0.02 mmol) and the corresponding ligand (6 mol %, 0.06 mmol), dry THF (2 mL) was added followed by (*Z*)-1-iodooct-1-ene (1 mmol). For entries 10 and 11 TMEDA (1.1 equiv) or Et₃N (2.2 equiv) was added. Pre-formed *n*-C₁₀H₂₁ZnI (1 M in THF, 1.1 mmol, 1.1 equiv) was then added dropwise at rt. The resulting solution was stirred 4 h at rt (24 h for entries 10 and 11). The reaction was then quenched with saturated NH₄Cl solution; the product was extracted with EtOAc and concentrated *in vacuo*. NMR experiments in support of GC/GCMS data were performed on crude, unpurified product. In all cases the results obtained by both methods were within 5%.

General Procedure A (Table 2). To a 5 mL round-bottom flask under argon equipped with a magnetic stir bar and charged with PdCl₂(PPh₃)₂ (2 mol %, 0.02 mmol), dry THF (2 mL) was added followed by corresponding alkenyl halide (1 mmol). Pre-formed organozinc halide (1 M in THF, 1.1 mmol, 1.1 equiv) was added dropwise at rt. The resulting solution was stirred at rt until determined to be complete by GC analysis. The reaction was then quenched with saturated NH₄Cl solution; the product was extracted with EtOAc and concentrated *in vacuo*. NMR experiments in support of GC/GCMS data were performed on crude, unpurified product. In all cases the results obtained by both methods were within 5%.

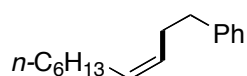
General Procedure B (Table 2). To a 5 mL round-bottom flask under argon equipped with a magnetic stir bar and charged with PdCl₂(PPh₃)₂ (2 mol %, 0.02 mmol), dry THF (2 mL) was added followed by TMEDA (1.1 mmol, 1.1 equiv) and then the alkenyl halide (1 mmol). Pre-formed organozinc halide (1 M in THF, 1.1 mmol, 1.1 equiv) was added dropwise at rt. The resulting solution was stirred at rt until the reaction was determined to be complete by GC analysis. The reaction was then quenched with saturated NH₄Cl solution; the product was extracted with EtOAc and concentrated *in vacuo*. NMR experiments in support of GC/GCMS data were performed on crude, unpurified product. In all cases the results obtained by both methods were within 5%.

General Procedure C (Table 2). To a 5 mL round-bottom flask under argon equipped with a magnetic stir bar and charged with PdCl₂(PPh₃)₂ (1 mol %, 0.01 mmol), dry THF (2 mL) was added followed by TMEDA (1.1 mmol, 1.1 equiv) and the alkenyl halide (1 mmol). Pre-formed organozinc halide (1 M in THF, 1.1 mmol, 1.1 equiv) was added dropwise at rt. The resulting solution was stirred at 60 °C until the reaction was determined to be complete by GC analysis (normally 2-3 hours). The reaction was then quenched with saturated NH₄Cl solution; the product was extracted with EtOAc and concentrated *in vacuo*. NMR experiments in support of GC/GCMS data were performed on crude, unpurified product. In all cases the results obtained by both methods were within 5%.

General Procedure D (Table 2). To a 5 mL round-bottom flask under argon equipped with a magnetic stir bar and charged with PdCl₂(Amphos)₄ (2 mol %, 0.02 mmol), dry THF (2 mL) was added followed by corresponding alkenyl halide (1 mmol). Pre-formed organozinc halide (1 M in THF, 1.1 mmol, 1.1 equiv) was added dropwise at rt. The resulting solution was stirred at rt until the isomerization was determined to be complete by GC analysis. The reaction was then quenched with saturated NH₄Cl solution; the product was extracted with EtOAc and concentrated *in vacuo*. NMR experiments in support of GC/GCMS data were performed on crude, unpurified product. In all cases the results obtained by both methods were within 5%.

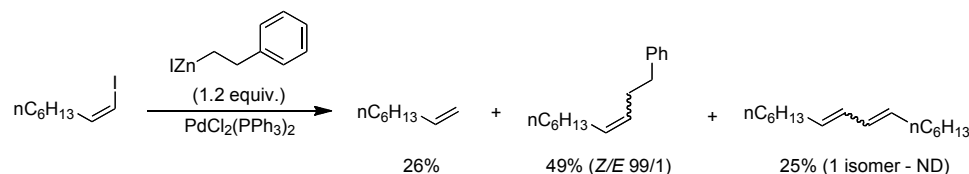
General Procedure E (Table 2): To a 5 mL round-bottom flask under argon equipped with a magnetic stir bar and charged with PdCl₂(Amphos)₄ (2 mol %, 0.02 mmol), dry THF (2 mL) was added followed by TMEDA (1.1 mmol, 1.1 equiv) and corresponding alkenyl halide (1 mmol). Pre-formed organozinc halide (1 M in THF, 1.1 mmol, 1.1 equiv) was added dropwise at rt. The resulting solution was stirred at rt until it was determined to be complete by GC analysis. The reaction was then quenched with saturated NH₄Cl solution; the product was extracted with EtOAc and concentrated *in vacuo*. NMR experiments in support of GC/GCMS data were performed on crude, unpurified product. In all cases the results obtained by both methods were within 5%.

1-((Z)-Dec-3-enyl)benzene (5)

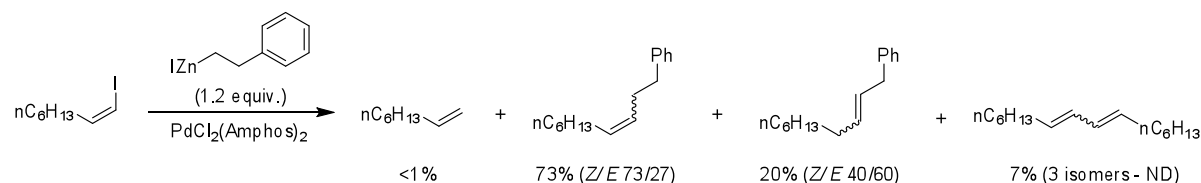


From (Z)-1-iodooct-1-ene (238 mg, 1 mmol, *Z/E* – 99/1) and phenethylzinc iodide (1.1 mmol, 1 M in THF), the product was obtained in

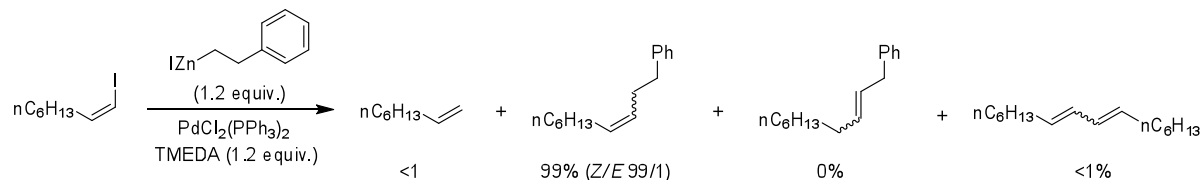
- 49% GC yield (*Z/E* 99/1) following **General Procedure A**



- 73% GC yield (*Z/E* 73/27) following **General Procedure A** with PdCl₂(Amphos)₂ (2 mol %, 0.02 mmol), instead of PdCl₂(PPh₃)₂

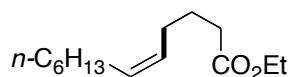


- 92% isolated yield (200 mg, *Z/E* 99/1) following **General Procedure B**



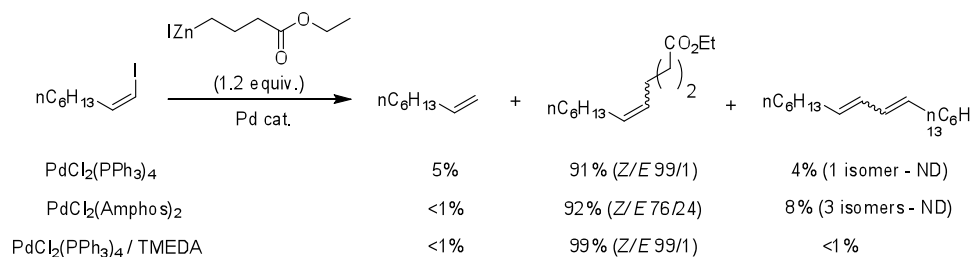
¹H NMR (400 MHz): δ 7.28 (t, *J* = 7.4 Hz, 2H), 7.20-7.17 (m, 3H), 5.42-5.31 (m, 2H), 2.66 (t, *J* = 6.9 Hz, 2H), 2.38-2.34 (m, 2H), 2.00-1.97 (m, 2H), 1.31-1.26 (m, 8H), 0.89 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz): δ 142.4, 131.0, 128.8, 128.7, 128.5, 126.0, 36.3, 32.0, 29.8, 29.4, 29.2, 27.5, 22.9, 14.3. HRMS (C₁₆H₂₄) calcd. 216.1878, found 216.1873.

(Z)-Ethyl dodec-5-enoate (6)



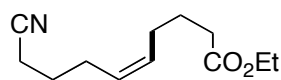
From (Z)-1-iodooct-1-ene (238 mg, 1 mmol, *Z/E* – 99/1) and (4-ethoxy-4-oxobutyl)zinc iodide (1.1 mmol, 1 M in THF), the product was obtained in

- 91% GC yield (*Z/E* 99/1) following **General Procedure A**
- 92% GC yield (*Z/E* 76/24) following **General Procedure A** with PdCl₂(Amphos)₂ (2 mol %, 0.02 mmol), instead of PdCl₂(PPh₃)₂
- 95% isolated yield (214 mg, *Z/E* 99/1) following **General Procedure B**



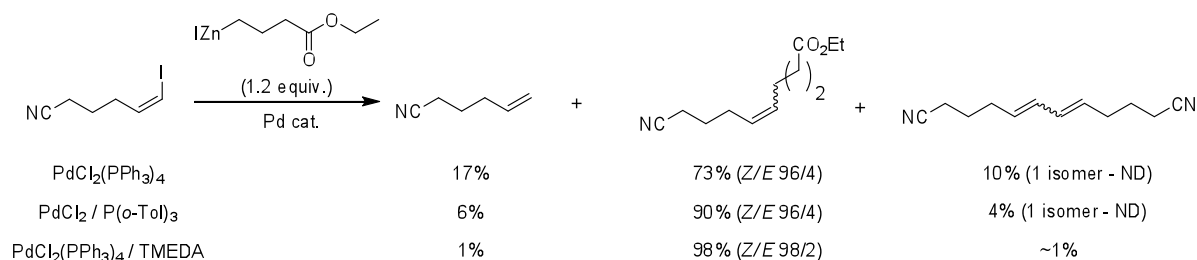
¹H NMR (400 MHz): δ 5.43-5.38 (m, 1H), 5.34-5.29 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.30 (q, *J* = 7.6 Hz, 2H), 2.06 (q, *J* = 7.4 Hz, 2H), 2.00 (q, *J* = 7.7 Hz, 2H), 1.70-1.65 (m, 2H), 1.34-1.24 (m, 11H), 0.88 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz): δ 173.6, 131.0, 128.3, 60.2, 33.8, 31.8, 29.7, 29.0, 27.2, 26.5, 24.9, 22.6, 14.3, 14.1. HRMS (C₁₄H₂₆O₂); calcd. 226.1933, found 226.1934.

(Z)-Ethyl 9-cyanonon-5-enoate (7)



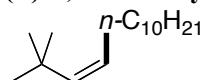
From (Z)-6-iodohex-5-enitrile (221 mg, 1 mmol, *Z/E* – 98/2) and (4-ethoxy-4-oxobutyl)zinc iodide (1.1 mmol, 1 M in THF), the product was obtained in

- 73% GC yield (*Z/E* 96/4) following **General Procedure A**
- 90% GC yield (*Z/E* 96/4) following **General Procedure A** with PdCl₂ (2 mol %, 0.02 mmol) and P(*o*-Tol)₃ (6 mol %, 0.06 mmol), instead of PdCl₂(PPh₃)₂
- 94% isolated yield (214 mg, *Z/E* 98/2) following **General Procedure B**



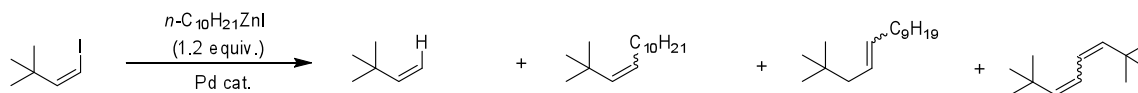
¹H NMR (400 MHz): δ 5.48-5.43 (m, 1H), 5.35-5.30 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.33 (t, *J* = 7.2 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 2.19 (q, *J* = 7.2 Hz, 2H), 2.09 (q, *J* = 7.3 Hz, 2H), 1.75-1.66 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz): δ 173.7, 131.3, 128.1, 119.9, 60.5, 33.9, 26.8, 26.2, 25.5, 25.0, 16.7, 14.5. HRMS (C₁₂H₁₉NO₂); calcd. 209.1416, found 209.1419.

(Z)-2,2-Dimethyltetradec-3-ene (8)



From (Z)-1-iodo-3,3-dimethylbut-1-ene (210 mg, 1 mmol, *Z/E* >99/1) and *n*-decylzinc iodide (1.1 mmol, 1 M in THF), the product was obtained in

- <20% GC yield (*Z/E* 90/10) following **General Procedure A**
- 61% GC yield (*Z/E* 92/8) following **General Procedure A** with PdCl₂ (2 mol %, 0.02 mmol) and P(*o*-Tol)₃ (6 mol %, 0.06 mmol), instead of PdCl₂(PPh₃)₂
- 63% isolated yield (141 mg, *Z/E* 99/1) following **General Procedure B**

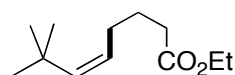


conversion

PdCl ₂ (PPh ₃) ₄	<20%	ND	77% (<i>Z/E</i> 90/10)	23 % (1 isomer - ND)	0%
PdCl ₂ / P(<i>o</i> -Tol) ₃	~80%	ND	76% (<i>Z/E</i> 92/8)	24% (2 isomers - ND)	0%
PdCl ₂ (PPh ₃) ₄ / TMEDA	~80%	ND	100% (<i>Z/E</i> 99/1)	0%	0%

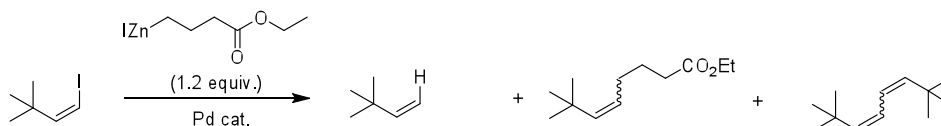
¹H NMR (400 MHz): δ 5.30 (dt, *J* = 12.1 Hz, *J* = 1.7 Hz, 1H), 5.15 (dt, *J* = 12.1 Hz, *J* = 7.4 Hz, 1H), 2.15 (dq, *J* = 7.5 Hz, *J* = 1.7 Hz, 2H), 1.32-1.27 (m, 16H), 1.10 (s, 9H), 0.88 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz): δ 139.8, 129.4, 32.2, 32.1, 31.6, 31.4, 31.2, 29.9, 29.9, 29.9, 29.6, 29.6, 22.9, 14.3. HRMS (C₁₆H₃₂); calcd. 224.2504, found 224.2509

(Z)-Ethyl 7,7-dimethyloct-5-enoate (9)



From (Z)-1-iodo-3,3-dimethylbut-1-ene (210 mg, 1 mmol, *Z/E* >99/1) and (4-ethoxy-4-oxobutyl)zinc iodide (1.1 mmol, 1 M in THF), the product was obtained in

- <20% GC yield (*Z/E* 94/6) following **General Procedure A**
- 60% GC yield (*Z/E* 94/6) following **General Procedure A** with PdCl₂ (2 mol %, 0.02 mmol) and P(*o*-Tol)₃ (6 mol %, 0.06 mmol), instead of PdCl₂(PPh₃)₂
- 84% isolated yield (166 mg, *Z/E* 99/1) following **General Procedure B**

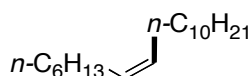


conversion

PdCl ₂ (PPh ₃) ₄	<20%	ND	<i>Z/E</i> 94/6	0%
PdCl ₂ / P(<i>o</i> -Tol) ₃	~60%	ND	<i>Z/E</i> 94/6	0%
PdCl ₂ (PPh ₃) ₄ / TMEDA	~90%	ND	<i>Z/E</i> 99/1	0%

¹H NMR (400 MHz): δ 5.30 (brt, *J* = 12.0 Hz, 1H), 5.15 (dt, *J* = 12.0 Hz, *J* = 7.4 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 2.22 (dq, *J* = 7.5 Hz, *J* = 1.2 Hz, 2H), 1.69 (p, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.10 (s, 9H). ¹³C NMR (100 MHz): δ 173.9, 140.9, 127.8, 60.4, 34.1, 33.8, 31.3, 27.9, 25.6, 14.5. HRMS (C₁₂H₂₂O₂); calcd. 198.1620, found 198.1616.

(Z)-Octadec-7-ene (10)



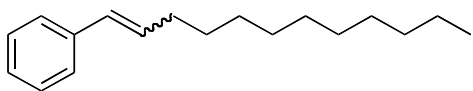
From (Z)-1-iodooct-1-ene (238 mg, 1 mmol, *Z/E* – 99/1) or (Z)-1-bromooct-1-ene (see Table 2) and *n*-decylzinc iodide (1.1 mmol, 1 M in THF), the product was obtained in

- 64% GC yield (*Z/E* 98/2) following **General Procedure A**
- 91% isolated yield (*Z/E* 99/1) following **General Procedure B**

- 98% isolated yield (247 mg, *Z/E* 99/1) following **General Procedure C** – The reaction was then quenched with saturated NH₄Cl solution; the product was extracted with *n*-hexane and concentrated *in vacuo*. NMR experiments in support of GC/GCMS data were performed on crude (filtrated through 1 cm short plug of silica gel) unpurified product and showed >99% purity – no purification needed.

¹H NMR (400 MHz): δ 5.37-5.35 (m, 2H), 2.03 (m, 4H), 1.34-1.28 (m, 24H), 0.90 (t, *J* = 7.1 Hz, 6H), 1.10 (s, 9H). ¹³C NMR (100 MHz): δ 129.8, 129.7, 31.9, 31.8, 29.8, 29.8, 29.7, 29.7, 29.6, 29.4, 29.3, 29.0, 27.2, 27.2, 22.7, 22.7, 14.1, 14.1. HRMS (C₁₈H₃₆); calcd. 252.2817, found 252.2815.

Dodec-1-en-1-ylbenzene (11)



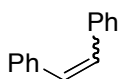
From (*Z*)-(2-bromovinyl)benzene (183 mg, 1 mmol, *Z/E* >99/1) for entries 14-18, or from (2-bromovinyl)benzene (183 mg, 1 mmol, *Z/E* 13/87) for entry 19, and *n*-decylzinc iodide (1.1 mmol, 1 M in THF), the product was obtained in

- 37% GC yield (*Z/E* 90/10) following **General Procedure A**
- 94% GC yield (*Z/E* 98/2) following **General Procedure B**
- 96% isolated yield (*Z/E* 99/1) following **General Procedure C**. The reaction was then quenched with saturated NH₄Cl solution; the product was extracted with *n*-hexane and concentrated *in vacuo*. NMR experiments in support of GC/GCMS data were performed on crude (filtrated through 1 cm short plug of silica gel) unpurified product and showed 98-99% purity – no purification needed.
- 85% isolated yield (*Z/E* 2/98) following **General Procedure D**. After reaction completion (20-30 min) reaction mixture was stirred for additional 24 h at rt to ensure full isomerization of *cis*- to *trans*- product. Checking the reaction during first 30 min by GC aliquots showed constant ~70/30 *Z/E* ratio of formed dodec-1-en-1-ylbenzene independent of the extent of conversion.
- 90% GC yield (*Z/E* 96/4) following **General Procedure E**
- 88% isolated yield (*Z/E* 1/99) following **General Procedure D** and starting from (2-bromovinyl)benzene (*Z/E* 13/87). After reaction was complete (20-30 min), the mixture was stirred for additional 24 h at room temperature to ensure full isomerization of *cis*- to *trans*- product.

cis- ¹H NMR (400 MHz): δ 7.34 (t, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 6.9 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.40 (brd, *J* = 11.7 Hz, 1H), 5.67 (dt, *J* = 11.7 Hz, *J* = 7.3 Hz, 1H), 2.32 (dq, *J* = 7.5 Hz, *J* = 1.5 Hz, 2H), 1.47-1.42 (m, 2H), 1.31-1.26 (m, 14H), 0.88 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz): δ 137.7, 133.2, 128.6, 128.5, 128.0, 126.3, 31.9, 30.0, 29.6, 29.6, 29.5, 29.4, 29.3, 28.6, 22.7, 14.1. HRMS (C₁₈H₂₈); calcd. 244.2191, found 244.2186.

trans- ¹H NMR (400 MHz): δ 7.34 (d, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 6.23 (dt, *J* = 15.9 Hz, *J* = 6.9 Hz, 1H), 2.20 (q, *J* = 7.1 Hz, 2H), 1.50-1.45 (m, 2H), 1.34-1.27 (m, 14H), 0.89 (t, *J* = 7.1 Hz, 3H). C NMR (100 MHz): δ 137.8, 131.2, 129.5, 128.3, 126.6, 125.8, 33.1, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 22.7, 14.1. HRMS (C₁₈H₂₈); calcd. 244.2191, found 244.2187.

1,2-Diphenylethene (12)

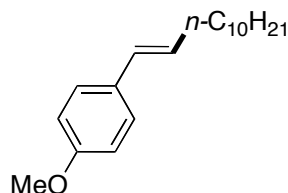


From (*Z*)-(2-bromovinyl)benzene (183 mg, 1 mmol, *Z/E* >99/1) for entries 20-22, or from (2-bromovinyl)benzene (183 mg, 1 mmol, *Z/E* 13/87) for entry 23, and PhZnI·LiCl (1.1 mmol, 1 M in THF), the product was obtained in

- 78% GC yield (*Z/E* 97/3) following **General Procedure A**
- 93% isolated yield (*Z/E* 98/2) following **General Procedure B**
- 85% isolated yield (*Z/E* 1/99) following **General Procedure D**. After the reaction reached completion (20-30 min), it was stirred for additional 24 h at rt to ensure full isomerization of *cis*- to *trans*- product.

- 94% isolated yield (*Z/E* 1/99) following **General Procedure D** and starting from (2-bromovinyl)benzene (*Z/E* 13/87). After the reaction reached completion (20-30 min), it was stirred for additional 24 h at rt to ensure full isomerization of *cis*- to *trans*- product.

(*E*)-1-(Dodec-1-en-1-yl)-4-methoxybenzene (13)

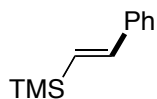


From 1-(2-bromovinyl)-4-methoxybenzene (213 mg, 1 mmol, *Z/E* 33/67) and *n*-decylzinc iodide (1.1 mmol, 1 M in THF), the product was obtained in

- 96% isolated yield (*Z/E* 1/99) following **General Procedure D**. After the reaction reached completion (20-30 min), it was stirred for additional 24 h at rt to ensure full isomerization of *cis*- to *trans*- product. The reaction was then quenched with saturated NH₄Cl solution; the product was extracted with *n*-hexane and concentrated *in vacuo*. NMR experiments in support of GC/GCMS data were performed on crude (filtered through a 1 cm plug of silica gel) unpurified product which showed ~98% purity – no purification needed!

¹H NMR (400 MHz): δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.32 (d, *J* = 15.8 Hz, 1H), 6.08 (dt, *J* = 15.8 Hz, *J* = 6.9 Hz, 1H), 3.80 (s, 3H), 2.17 (q, *J* = 7.0 Hz, 2H), 1.47-1.42 (m, 2H), 1.32-1.27 (m, 14H), 0.88 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz): δ 158.4, 130.7, 129.0, 128.9, 126.8, 113.8, 55.3, 33.0, 31.9, 29.6, 29.6, 29.5, 29.5, 29.3, 29.2, 22.7, 14.1. HRMS (C₁₉H₃₀O); calcd. 274.2297, found 374.2295.

(*E*)-Trimethyl(styryl)silane (14)

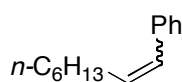


From (2-bromovinyl)trimethylsilane (179 mg, 1 mmol, *Z/E* 8/92) and PhZnI·LiCl (1.1 mmol, 1 M in THF), the product was obtained in

- 89% isolated yield (*Z/E* 1/99) following **General Procedure D**. After the reaction reached completion (20-30 min), it was stirred for additional 24 h at rt to ensure full isomerization of *cis*- to *trans*- product.

¹H NMR (400 MHz): δ 7.43 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 19.2 Hz, 1H), 6.48 (d, *J* = 19.2 Hz, 1H), 0.16 (s, 9H). ¹³C NMR (100 MHz): δ 143.4, 138.2, 129.4, 128.4, 127.8, 126.2, -1.2. HRMS (C₁₂H₂₂O₂); calcd. 198.1620, found 198.1616.

(*E*)-Oct-1-en-1-ylbenzene (15)



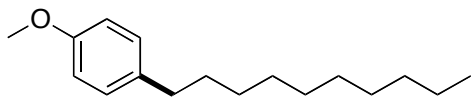
From (*Z*)-1-iodooct-1-ene (238 mg, 1 mmol, *Z/E* – 99/1) and PhZnI·LiCl (1.1 mmol, 1 M in THF), the product was obtained in

- 92% GC yield (*Z/E* 96/4) following **General Procedure A**
- 93% isolated yield (*Z/E* 99/1) following **General Procedure B**
- 90% isolated yield (*Z/E* 4/96) following **General Procedure D**. After the reaction reached completion (20-30 min), it was stirred for additional 24 h at rt to ensure full isomerization of *cis*- to *trans*- product.

cis- ¹H NMR (400 MHz): δ 7.34 (t, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 7.0 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.40 (brd, *J* = 11.7 Hz, 1H), 5.67 (dt, *J* = 11.7 Hz, *J* = 7.3 Hz, 1H), 2.32 (dq, *J* = 7.5 Hz, *J* = 1.5 Hz, 2H), 1.46-1.42 (m, 2H),

1.32-1.26 (m, 6H), 0.88 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz): δ 137.7, 133.2, 128.6, 128.5, 128.0, 126.3, 31.7, 30.0, 29.0, 28.7, 22.6, 14.1. HRMS ($\text{C}_{14}\text{H}_{20}$); calcd. 188.1565, found 188.1560.

1-Decyl-4-methoxybenzene (20a)

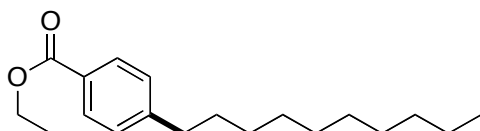


From 1-bromo-4-methoxybenzene (187 mg, 1 mmol) and *n*-decylzinc iodide (1.1 mmol, 1 M in THF) at 40 °C, 12 h, the product was obtained in

- <5% conv. by GC following **General Procedure A**
- 91% GC yield (**19a/20a/21a** - 7/91/2) following **General Procedure A** with $\text{PdCl}_2(\text{dppf})$ (2 mol %, 0.02 mmol), instead of $\text{PdCl}_2(\text{PPh}_3)_2$
- 95% isolated yield following **General Procedure B**

^1H NMR (400 MHz): δ 7.09 (d, $J = 8.6$ Hz, 2H), 6.82 (d, $J = 8.6$ Hz, 2H), 3.79 (s, 3H), 2.54 (t, $J = 7.7$ Hz, 2H), 1.59-1.54 (m, 2H), 1.29-1.26 (m, 14H), 0.88 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz): δ 157.4, 135.0, 129.1, 113.5, 55.2, 35.0, 31.9, 31.8, 29.6, 29.6, 29.5, 29.3, 29.3, 22.7, 14.1. HRMS ($\text{C}_{17}\text{H}_{28}\text{O}$); calcd. 248.2140, found 248.2138.

Ethyl 4-decylbenzoate (20b)



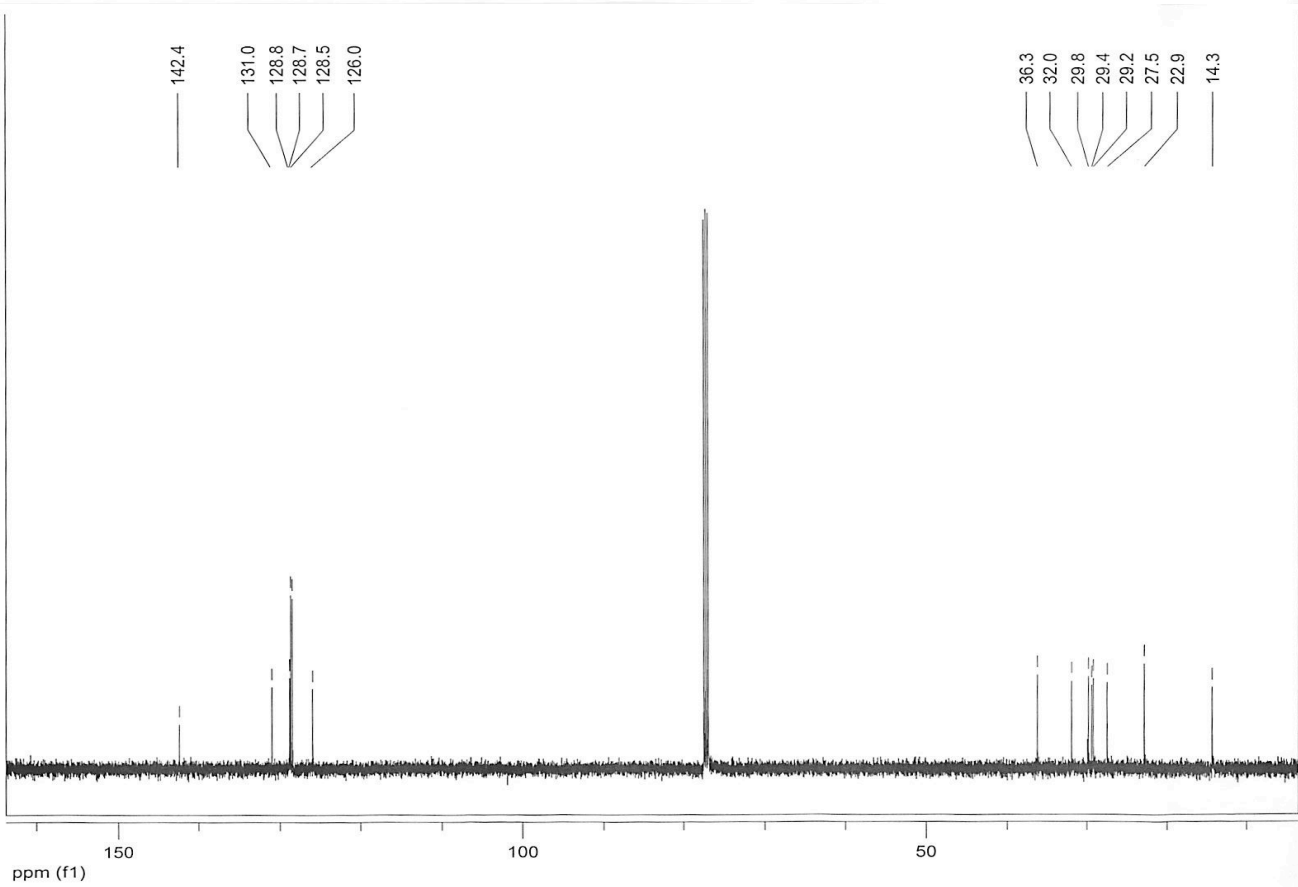
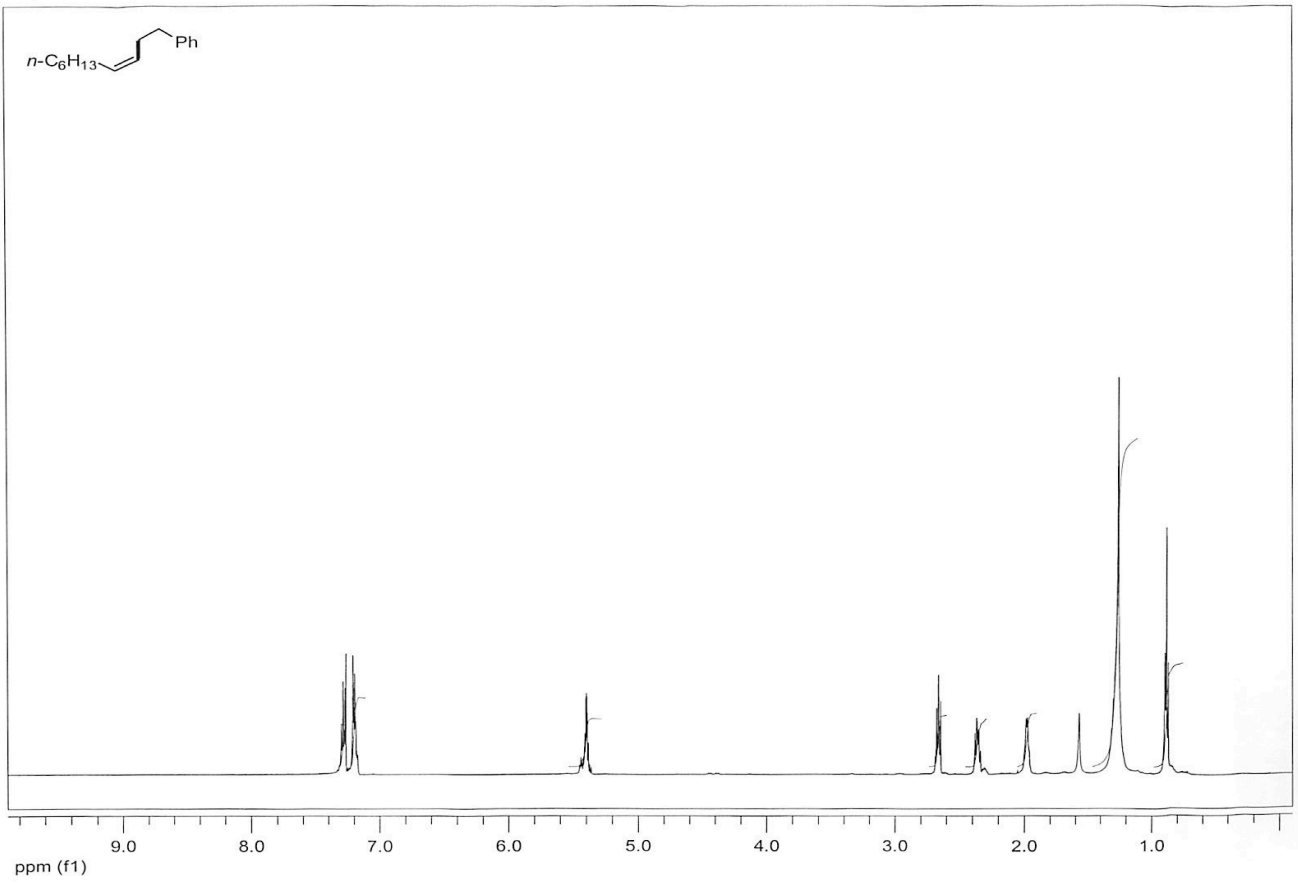
From ethyl 4-bromobenzoate (229 mg, 1 mmol) and *n*-decylzinc iodide (1.1 mmol, 1 M in THF) at rt, 20 h, the product was obtained in

- 26% GC yield (**19b/20b/21b** - 4/26/70) following **General Procedure A**
- 91% GC yield (**19a/20a/21a** - 5/91/4) following **General Procedure A** with $\text{PdCl}_2(\text{dppf})$ (2 mol %, 0.02 mmol), instead of $\text{PdCl}_2(\text{PPh}_3)_2$
- 93% isolated yield following **General Procedure B**

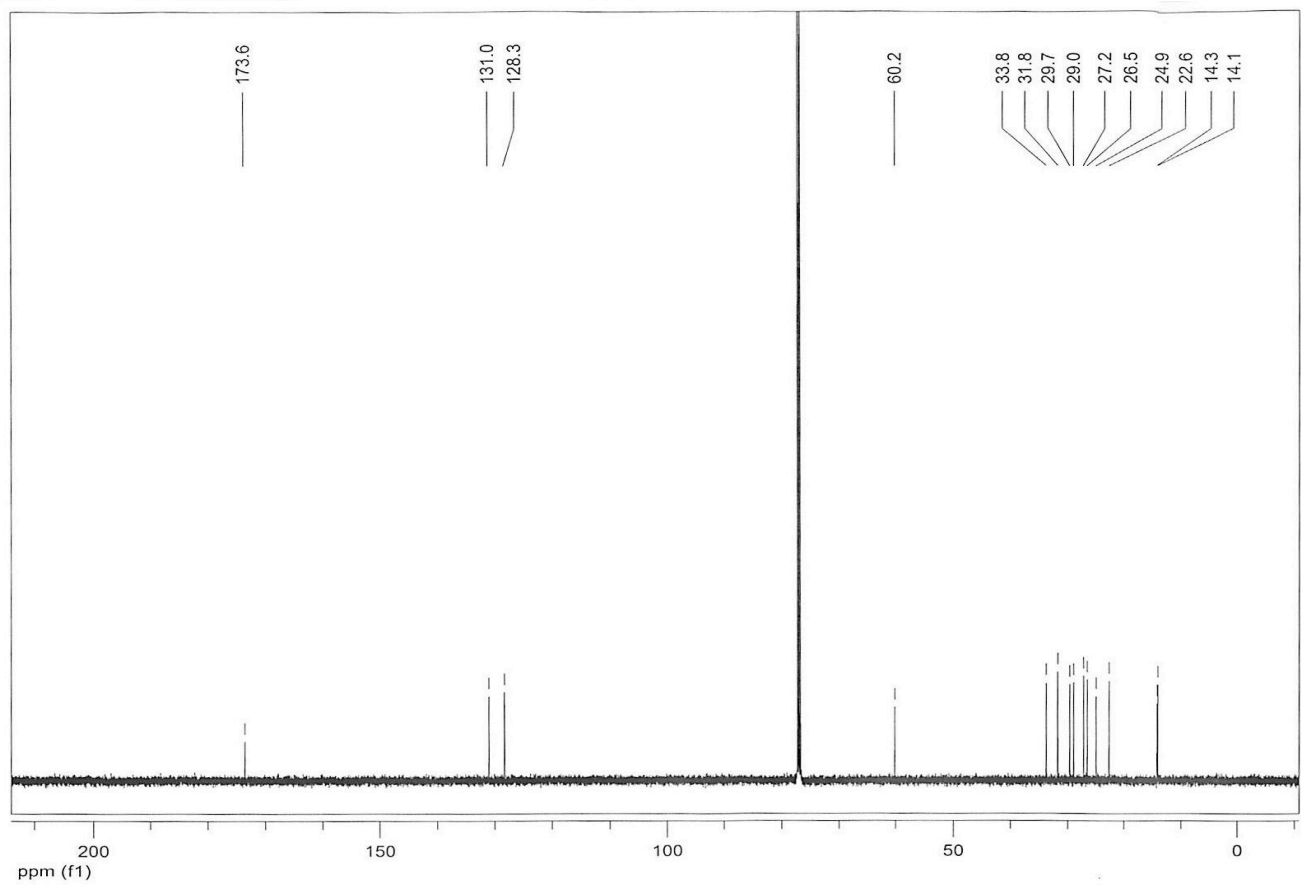
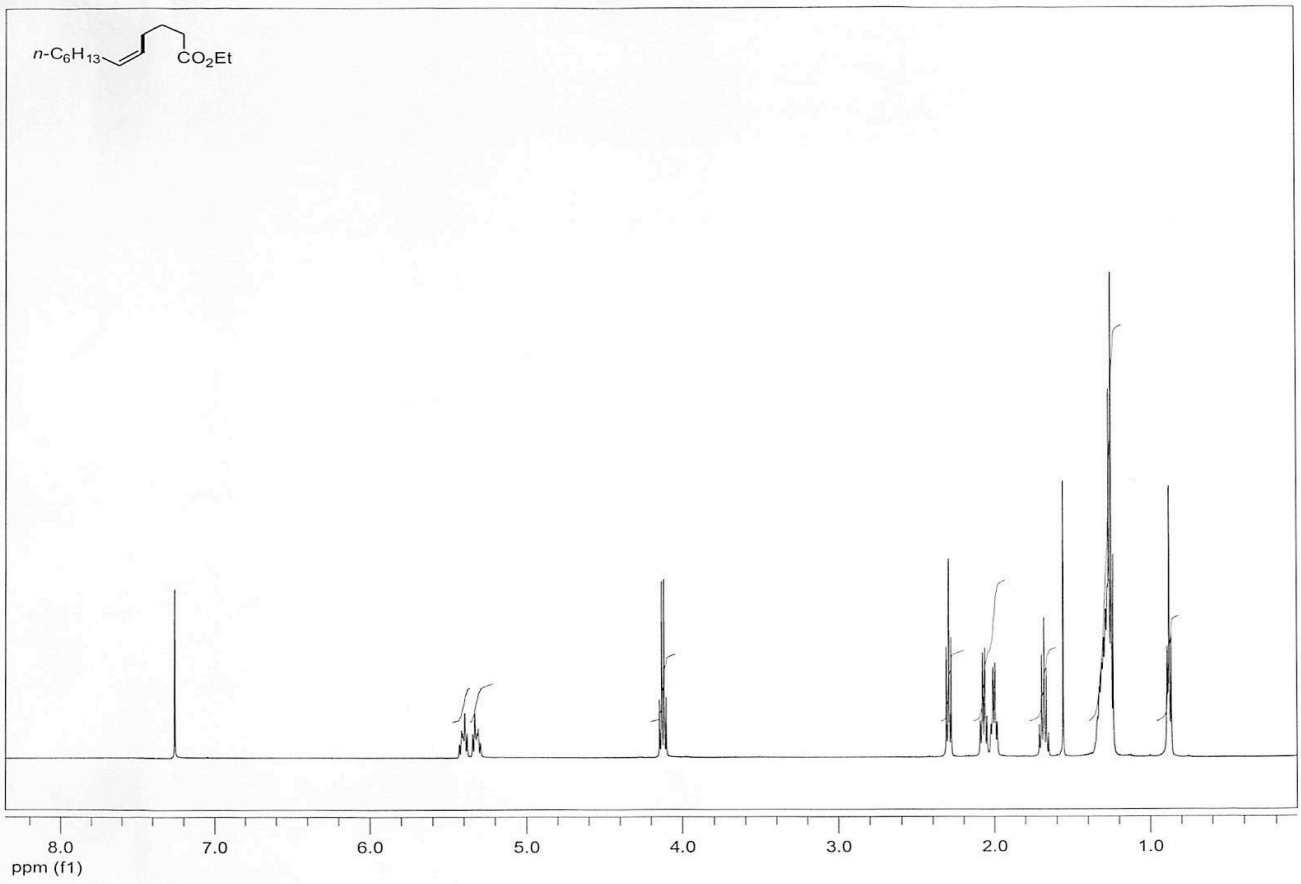
^1H NMR (400 MHz): δ 7.95 (d, $J = 8.3$ Hz, 2H), 7.25 (d, $J = 8.3$ Hz, 2H), 4.36 (q, $J = 7.1$ Hz, 2H), 2.65 (t, $J = 7.7$ Hz, 2H), 1.63-1.60 (m, 2H), 1.38 (t, $J = 7.1$ Hz, 3H), 1.29-1.25 (m, 14H), 0.88 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz): δ 166.6, 148.3, 129.4, 128.3, 127.8, 60.7, 36.0, 31.9, 31.2, 29.6, 29.5, 29.4, 29.3, 29.2, 22.7, 14.4, 14.1. HRMS ($\text{C}_{19}\text{H}_{30}\text{O}_2$); calcd. 290.2246, found 290.2241.

1. (a) Denmark, S. E.; Yang S.-M. *Tetrahedron* **2004**, *60*, 9695; (b) Ren, H.; Krasovskiy, A.; Knochel P. *Org. Lett.*, **2004**, *6*, 4215; (c) Brown, H. C.; Blue, C. D.; Nelson, D. J.; Bhat N. G. *J. Org. Chem.* **1989**, *54*, 6064.
2. Knochel, P.; Singer R. D. *Chem. Rev.* **1993**, *93*, 2117.
3. Krasovskiy, A.; Malakhov, V.; Gavryushin, A.; Knochel, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 6040.

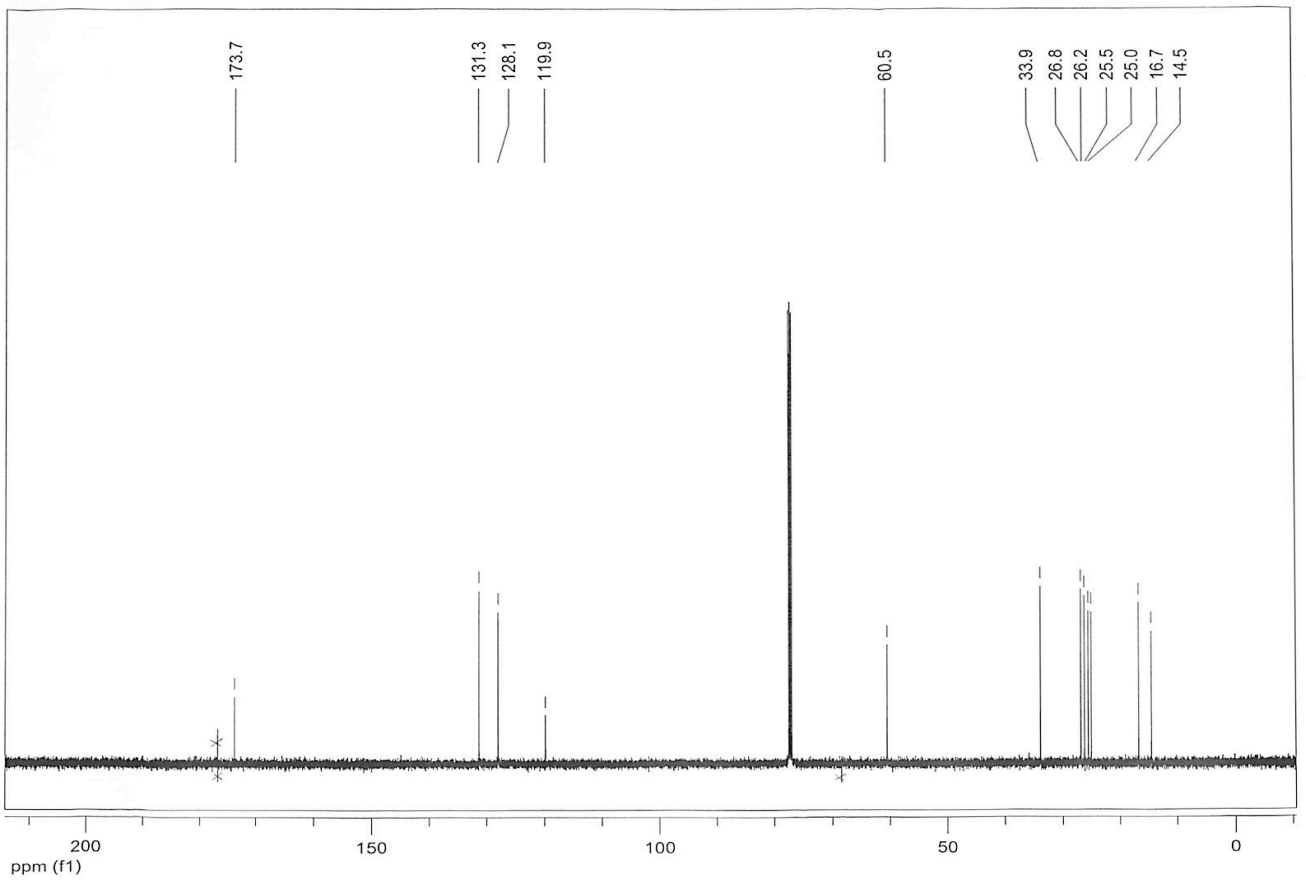
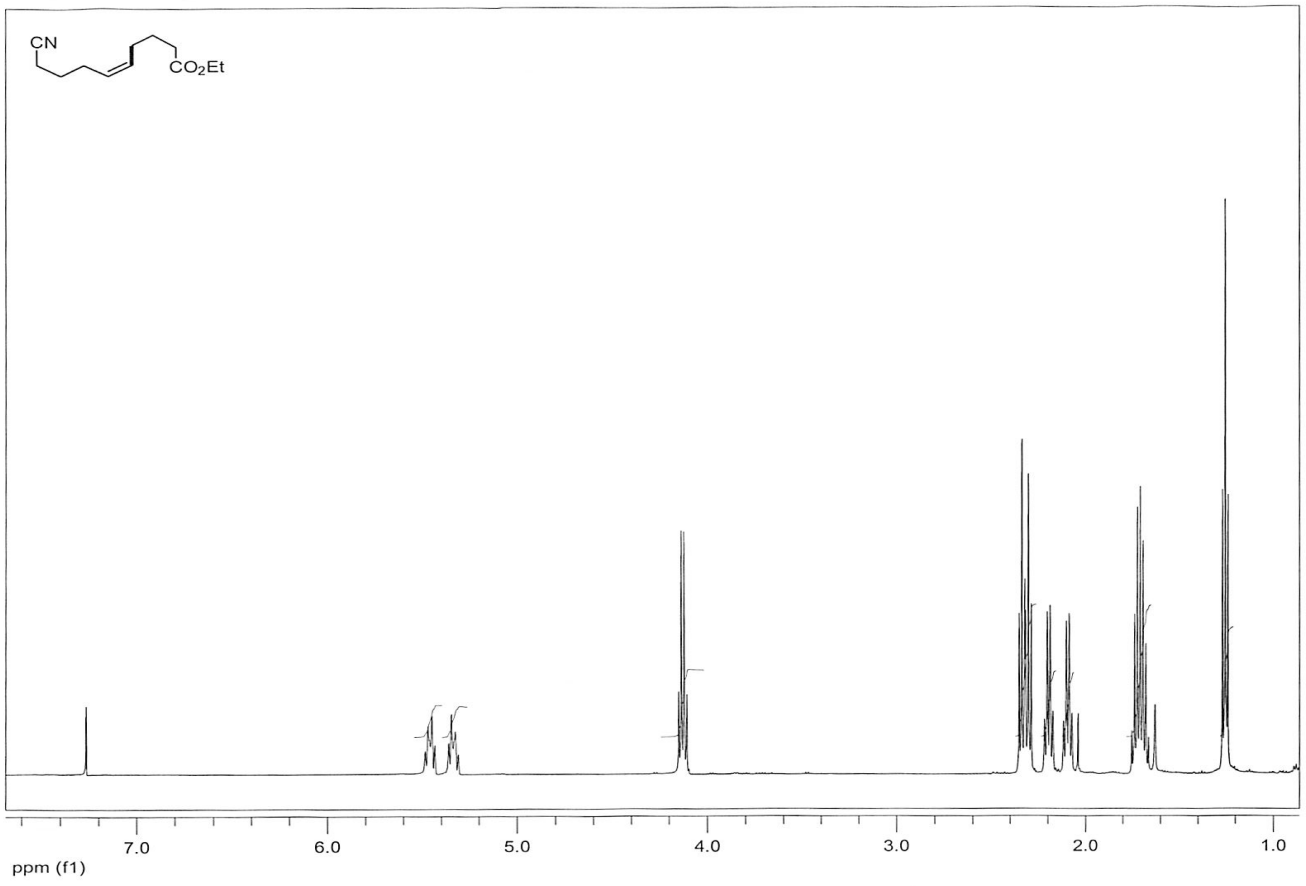
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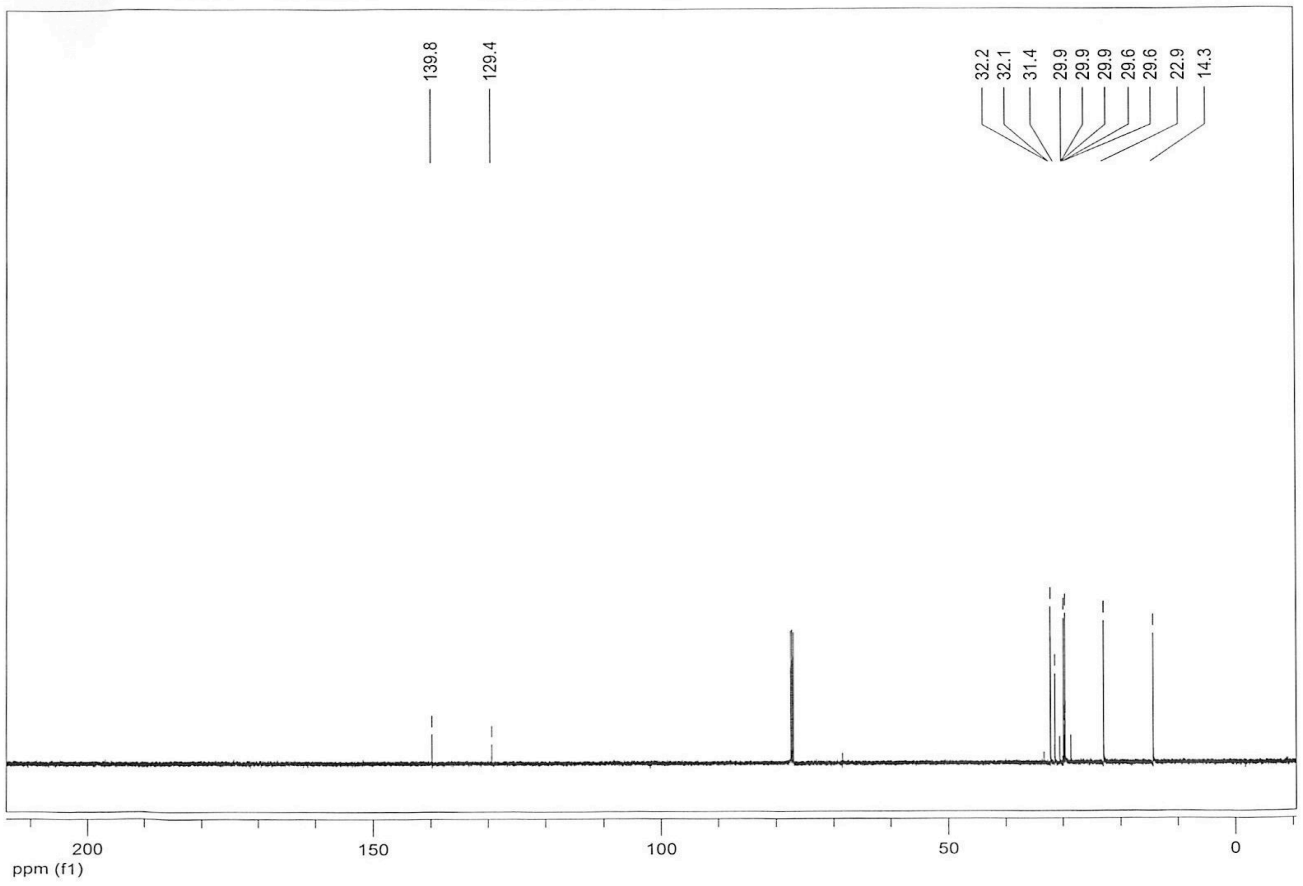
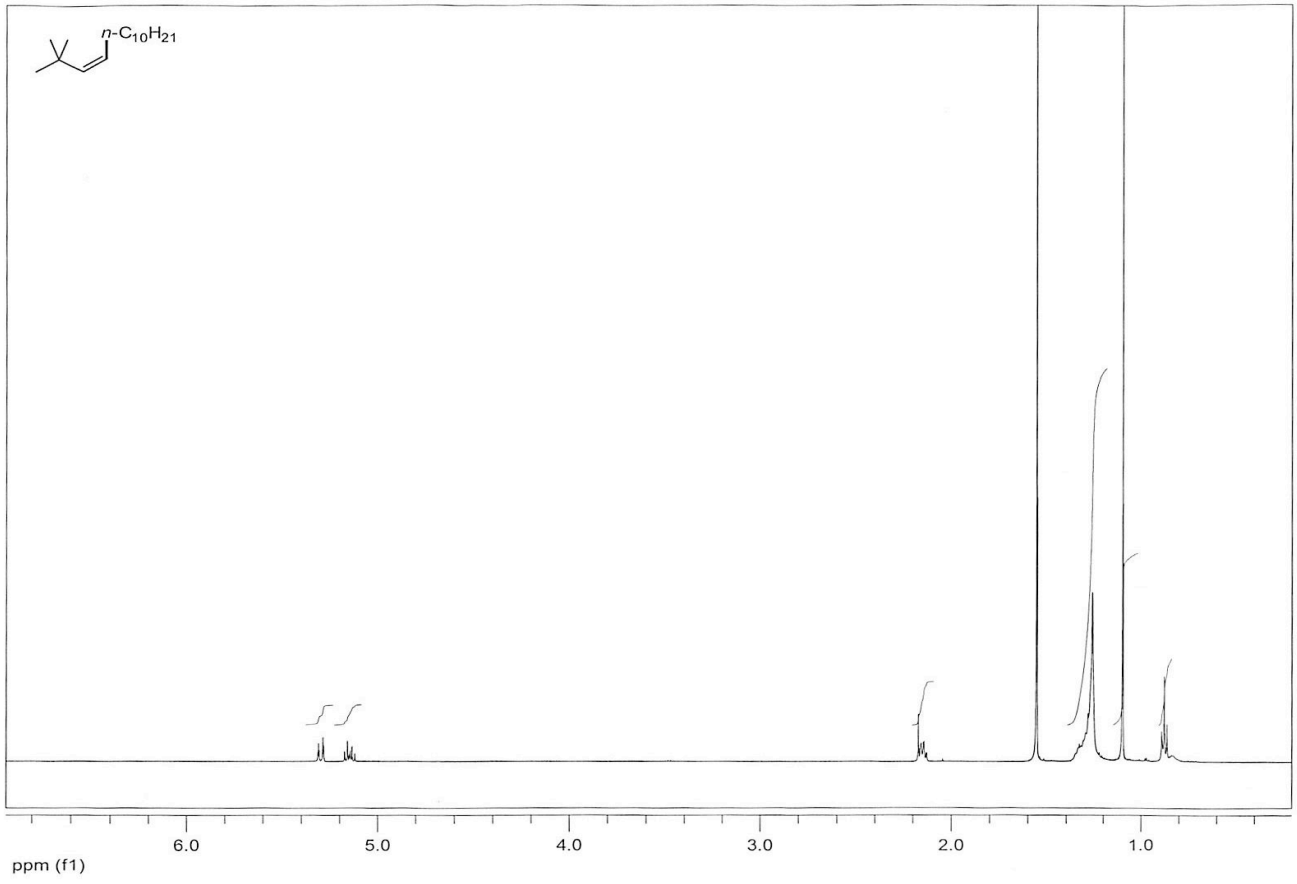
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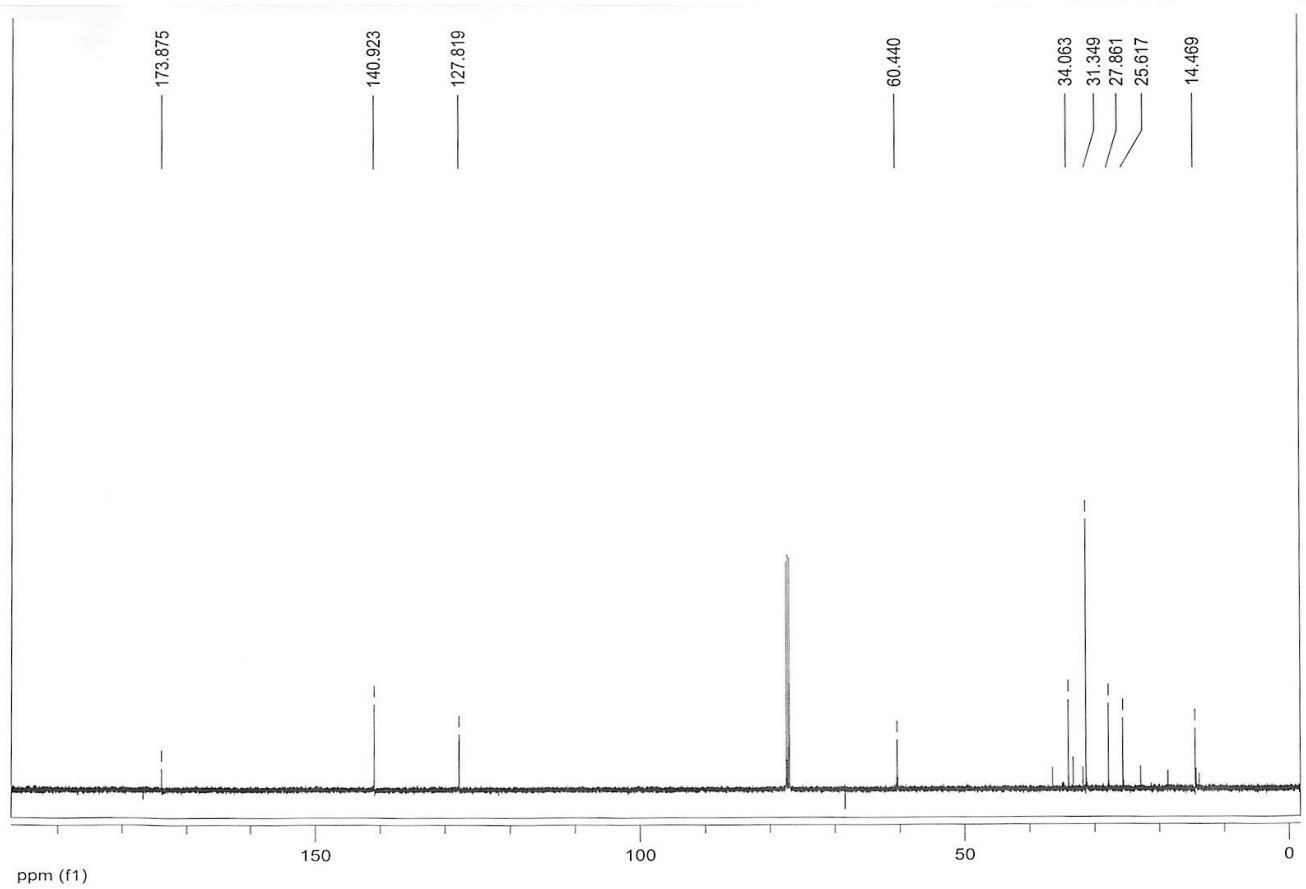
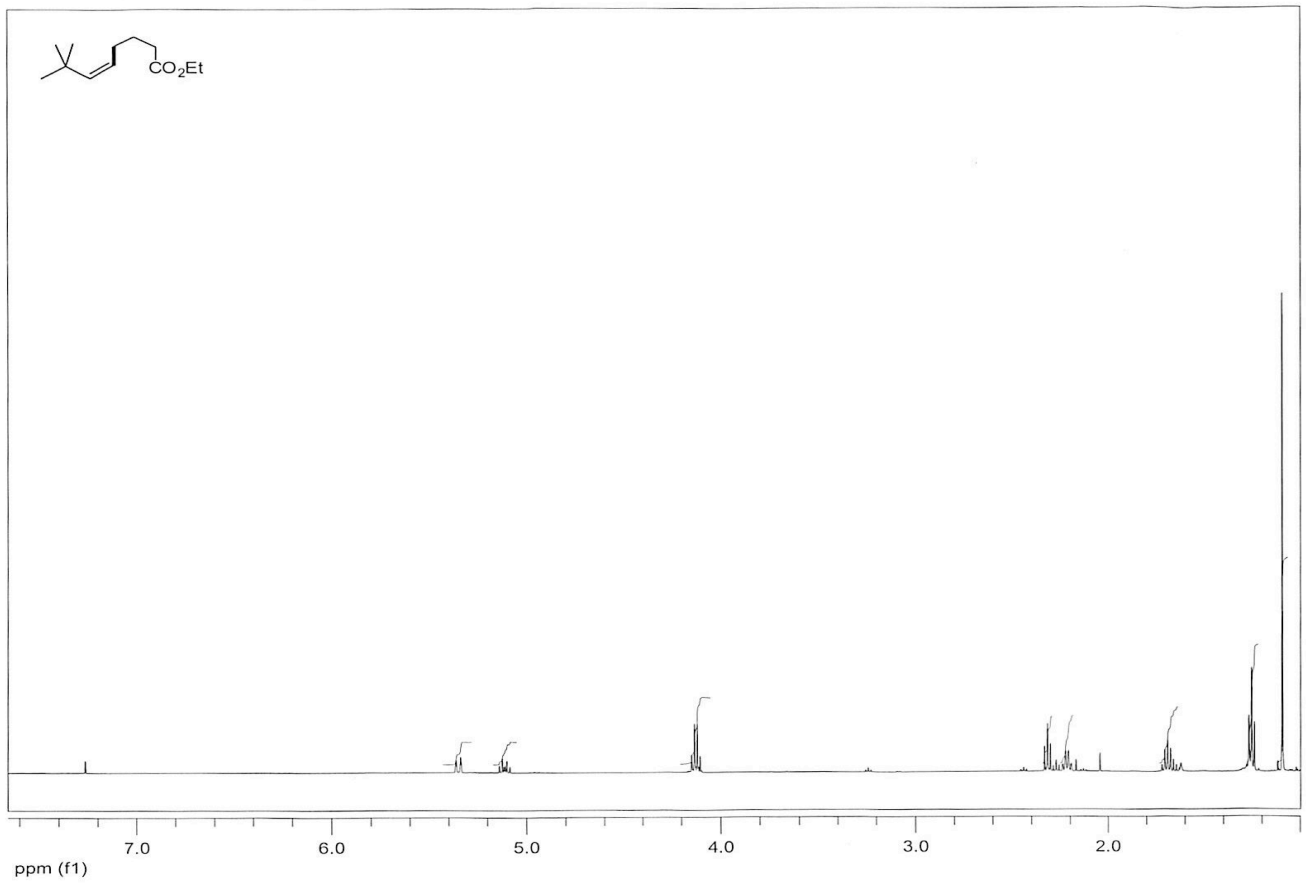


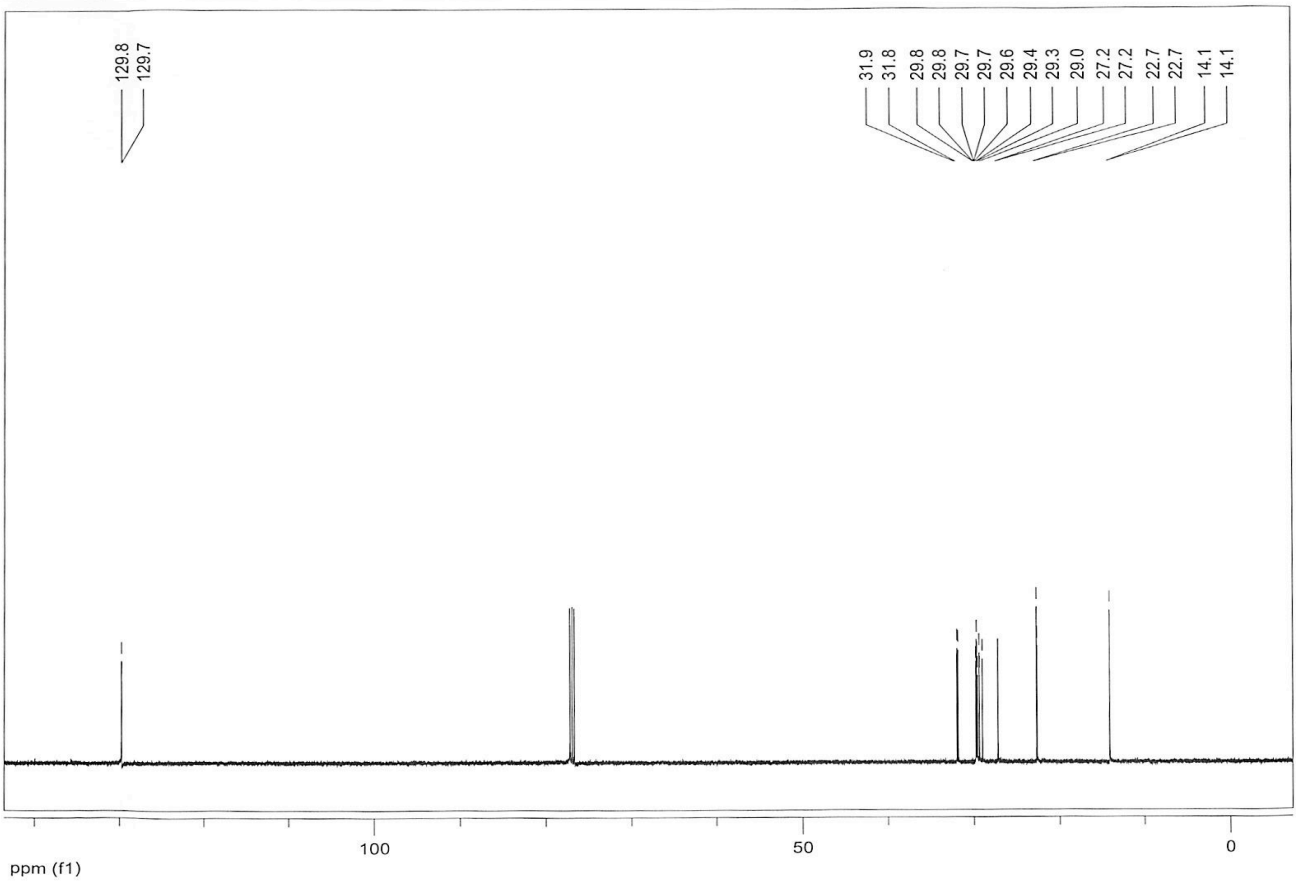
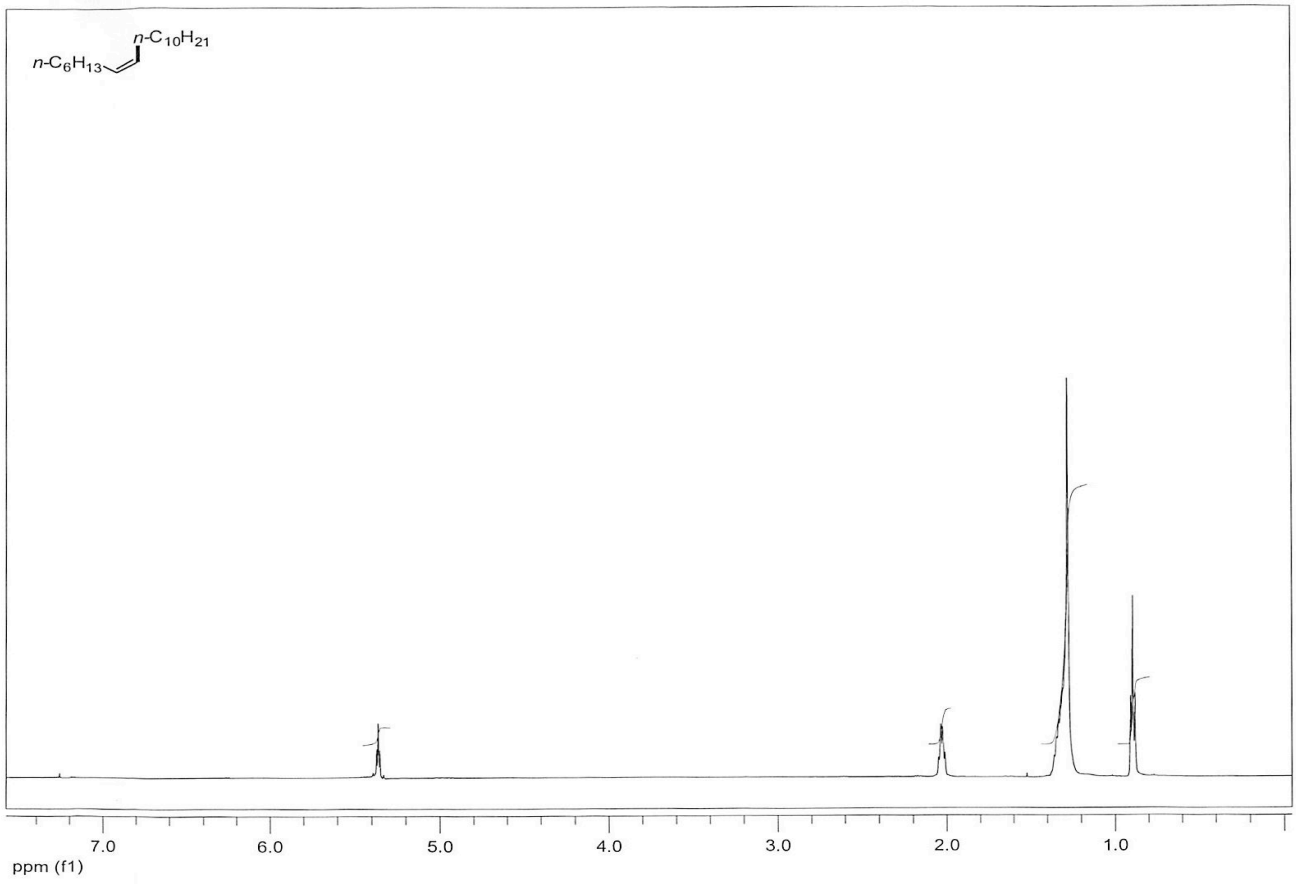
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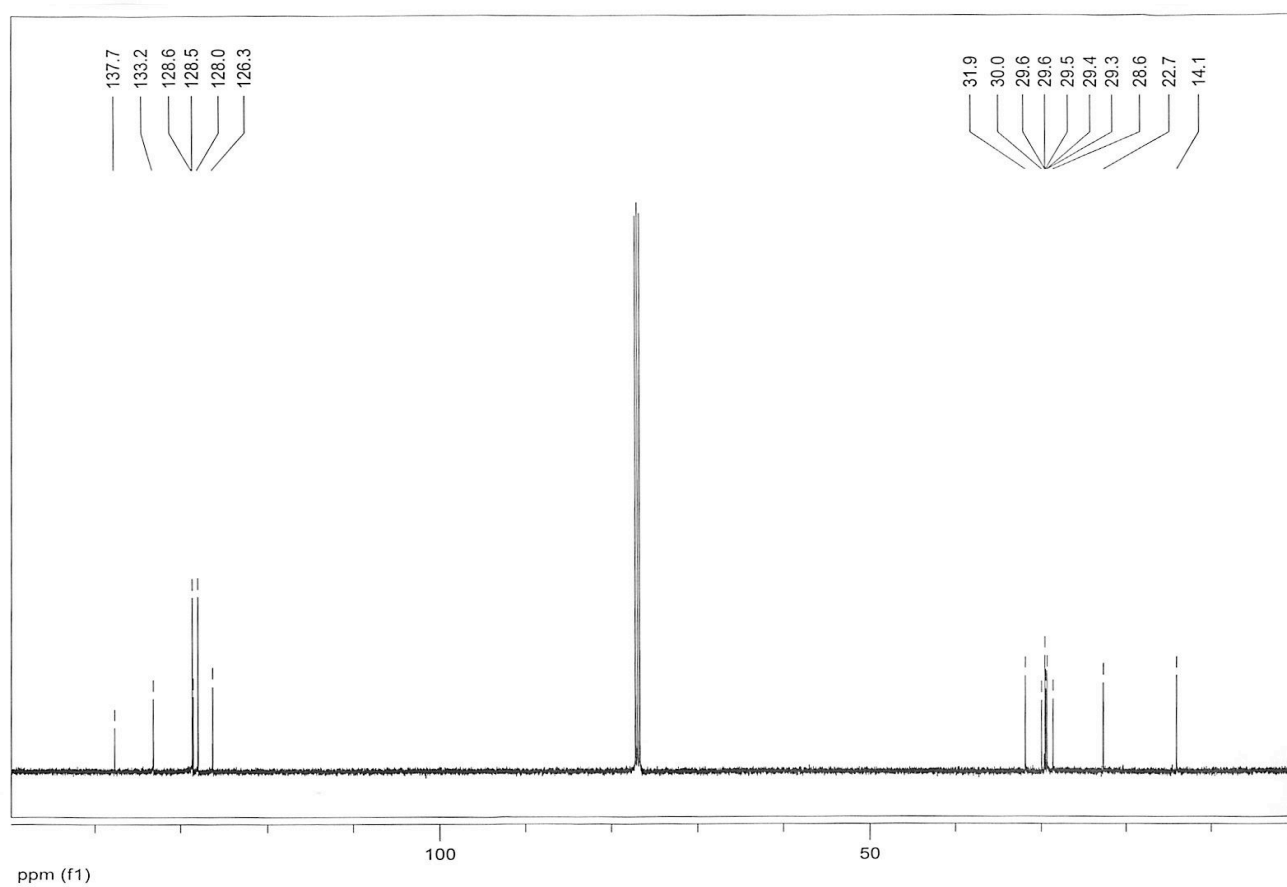
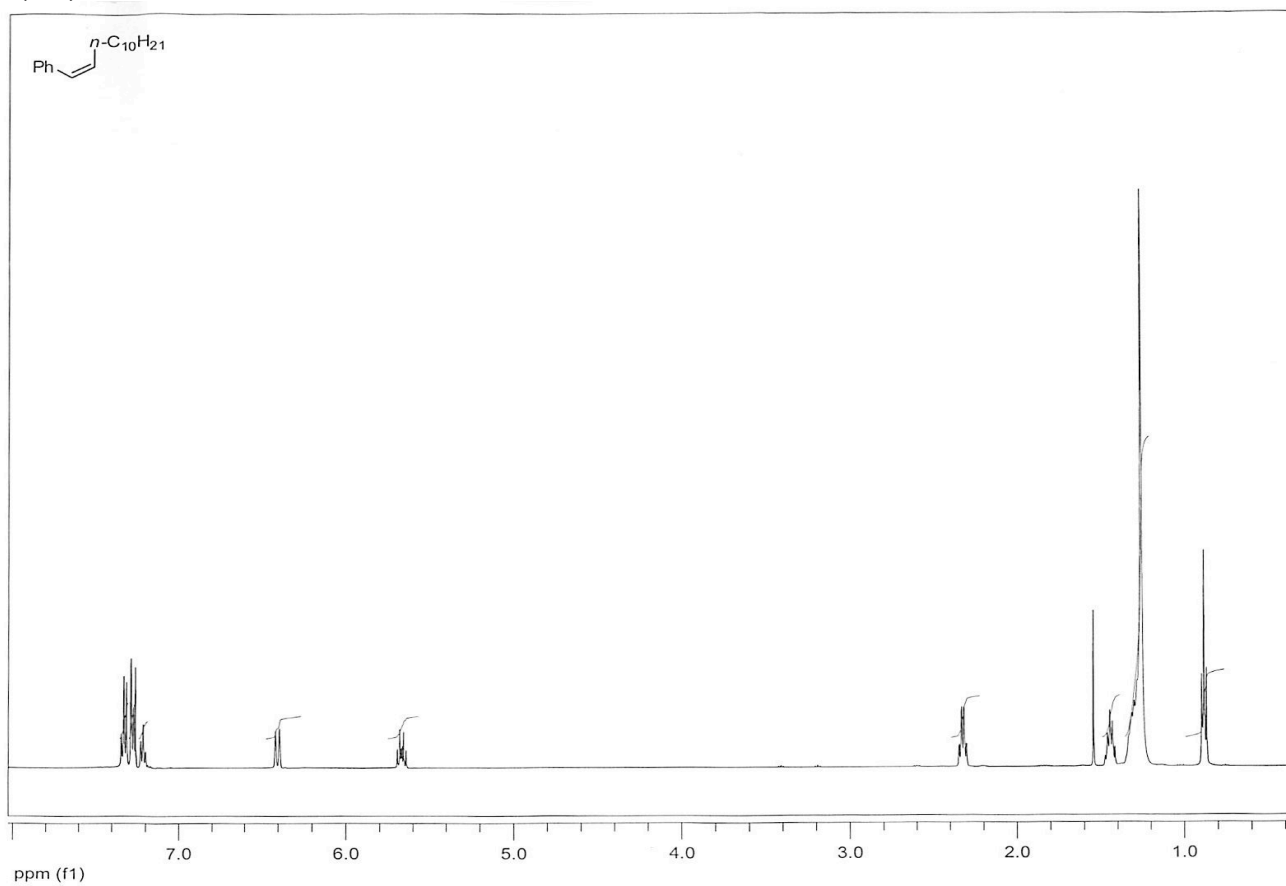
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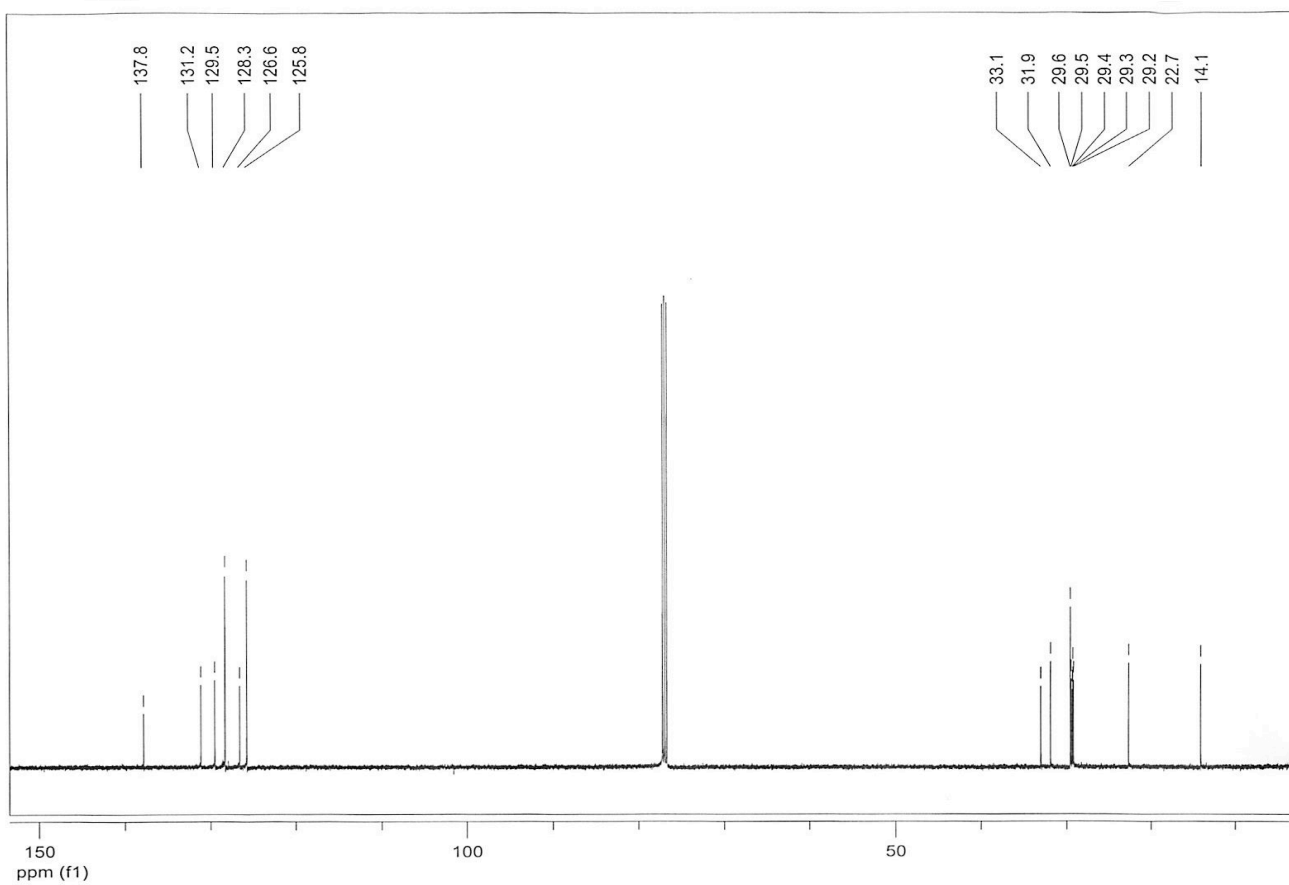
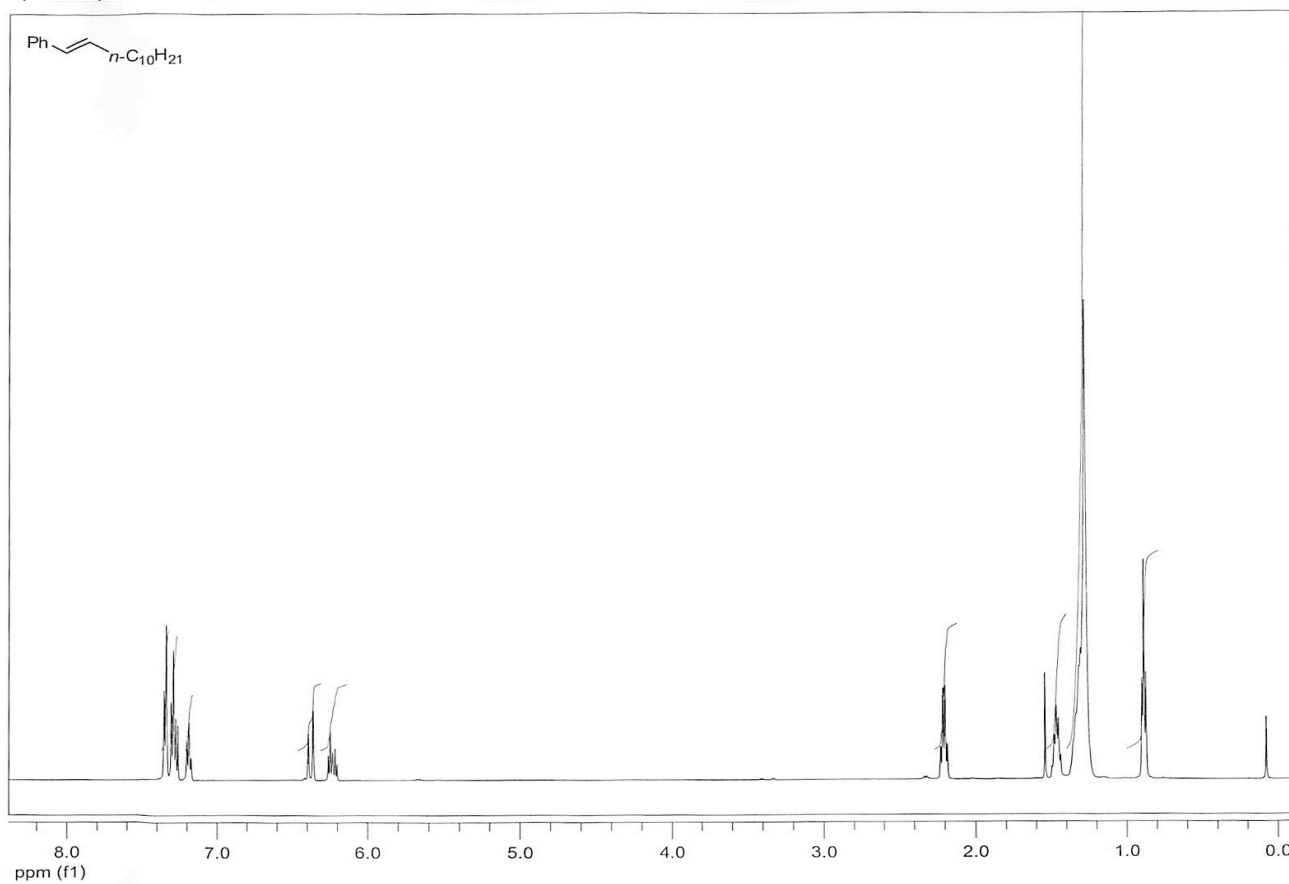


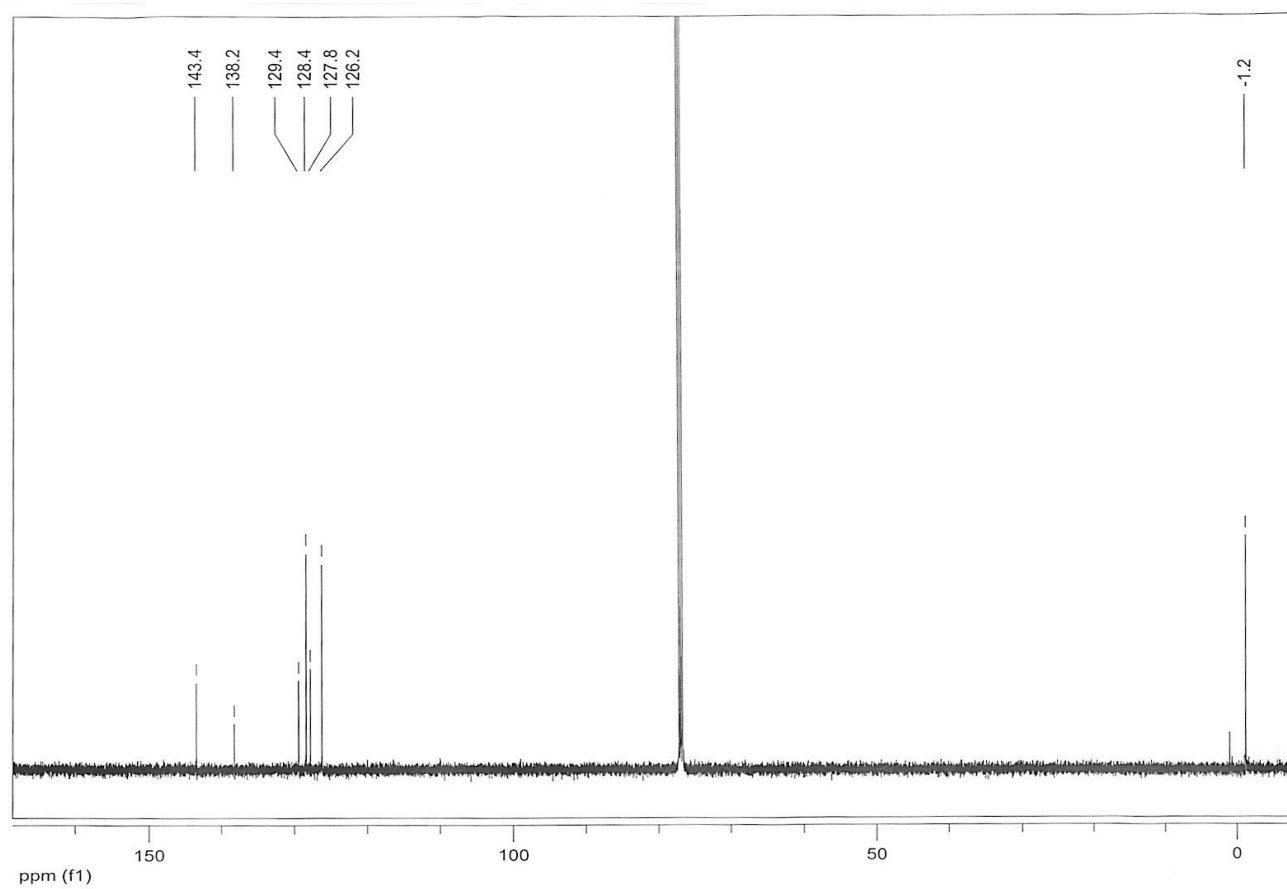
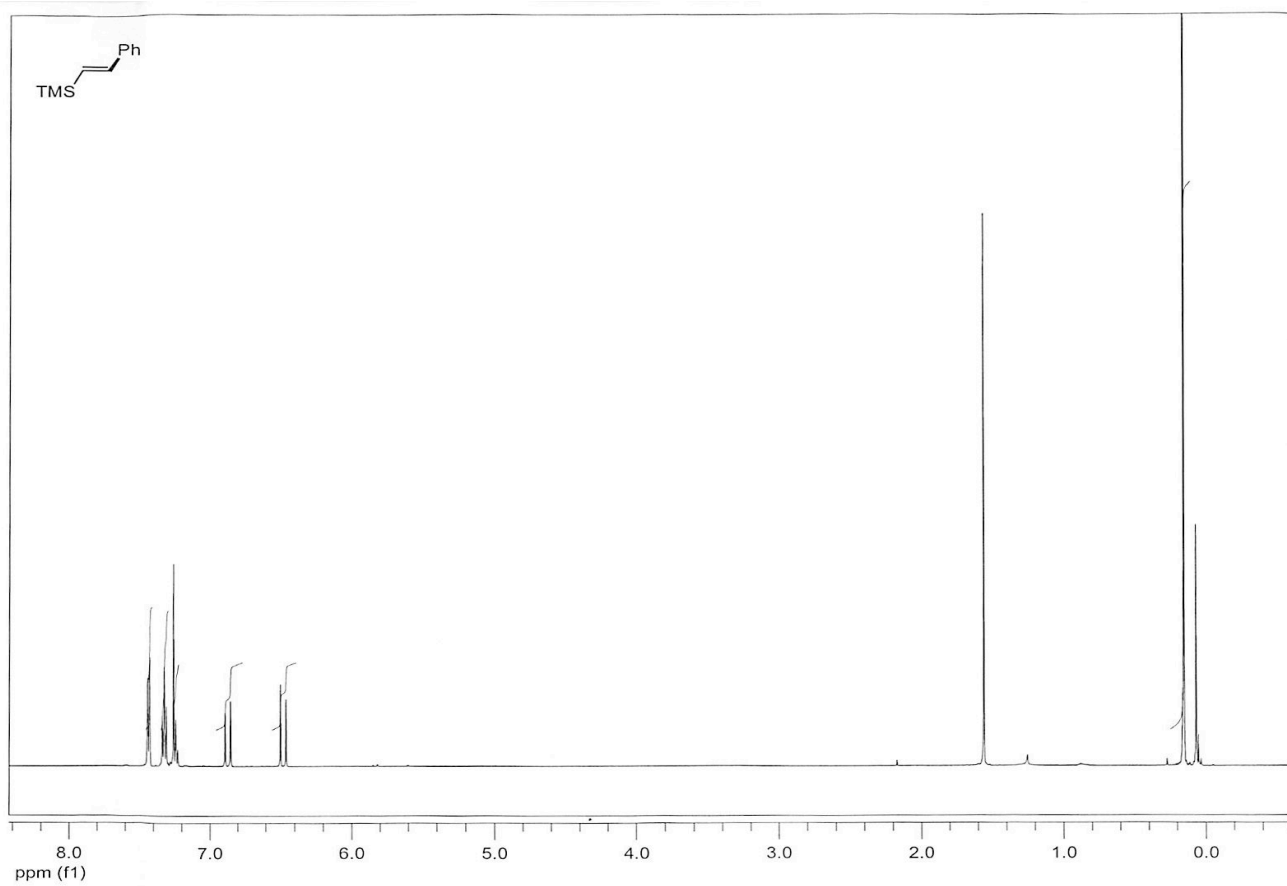


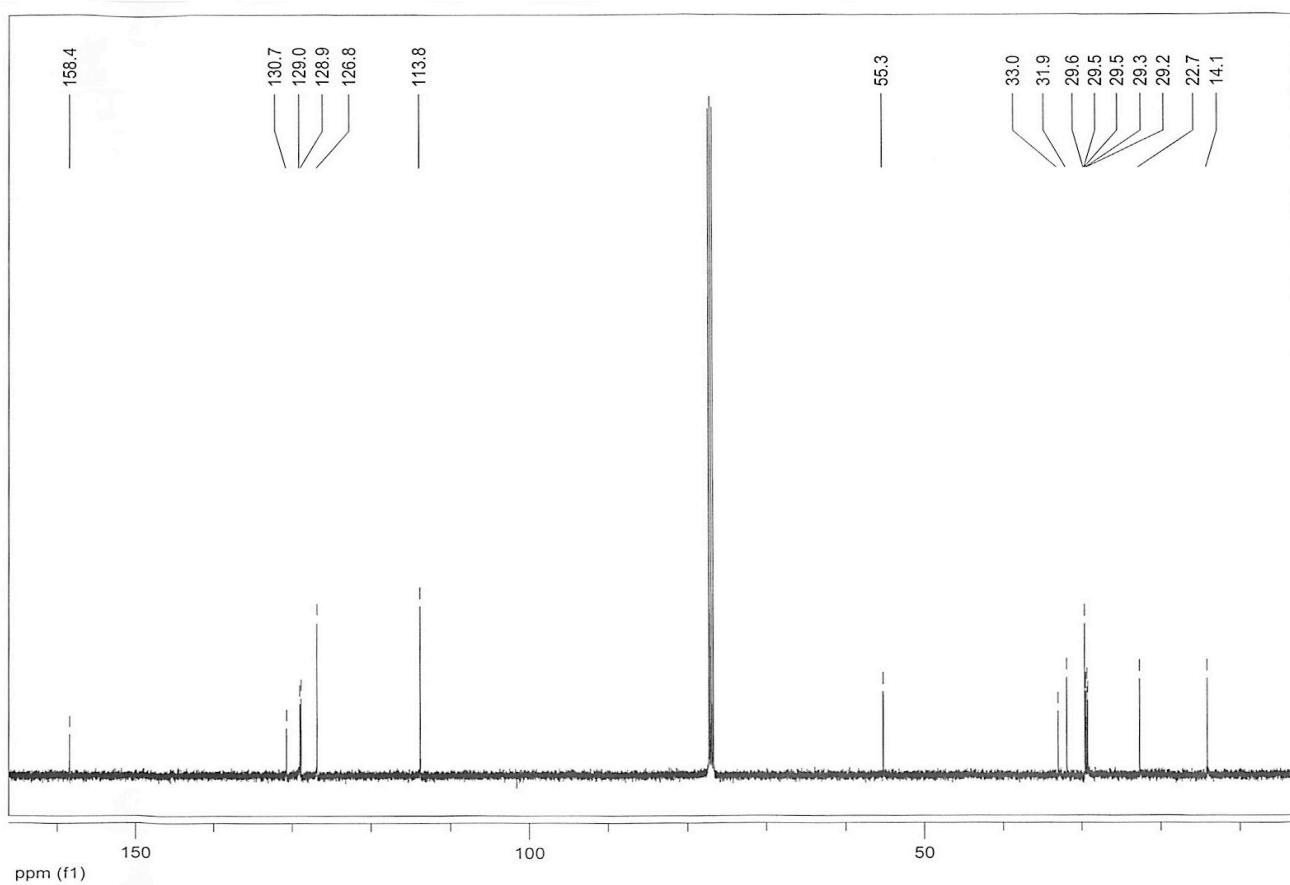
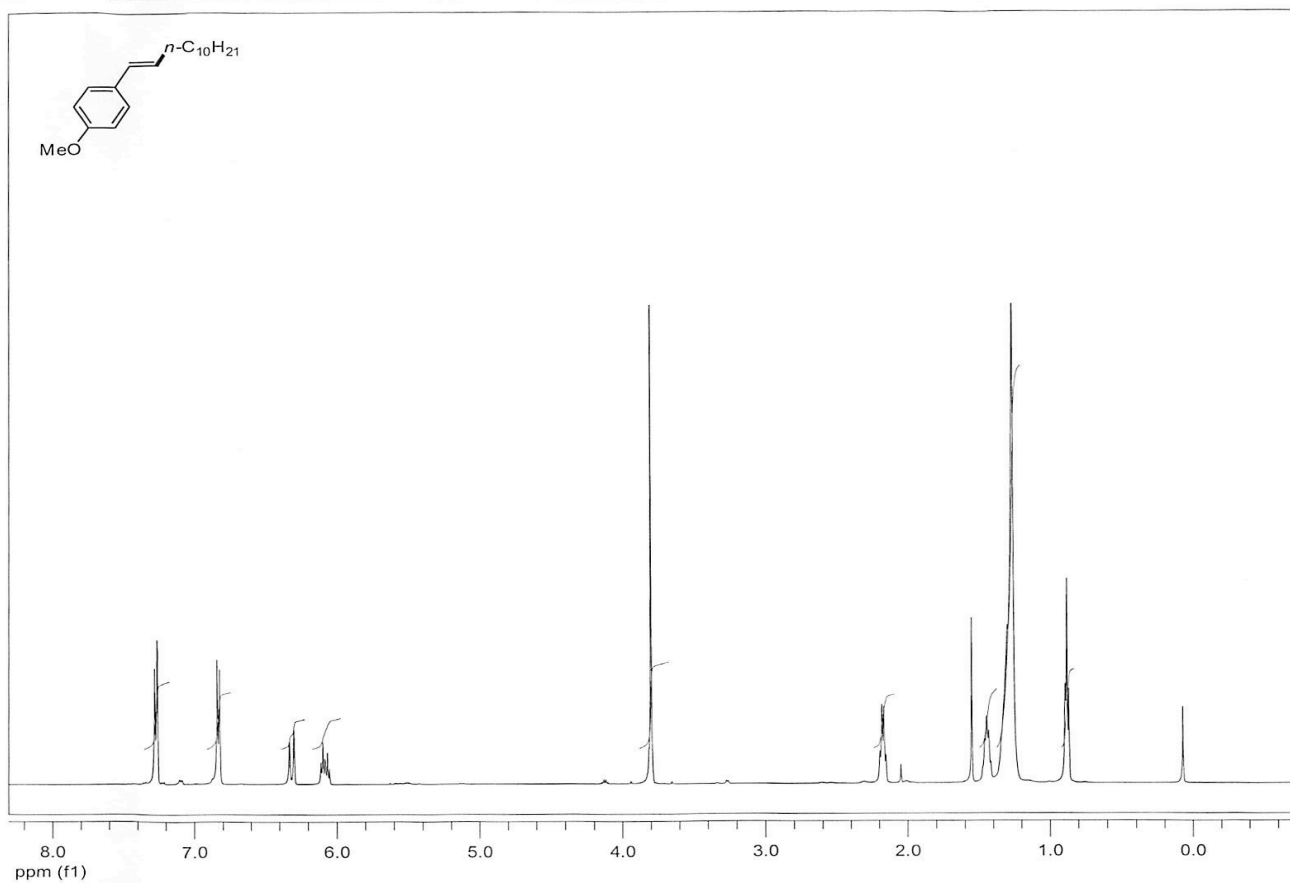
11 (*cis*-)

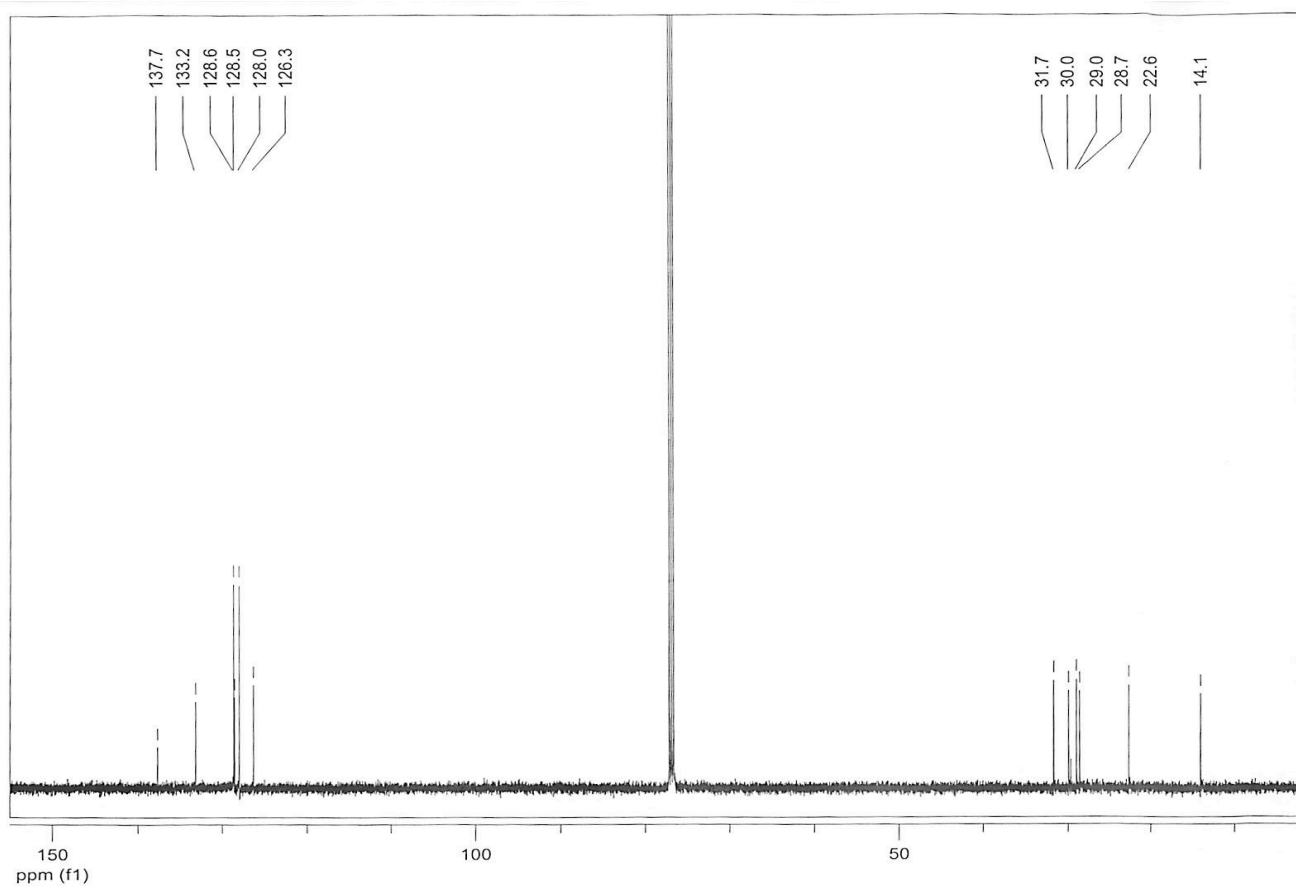
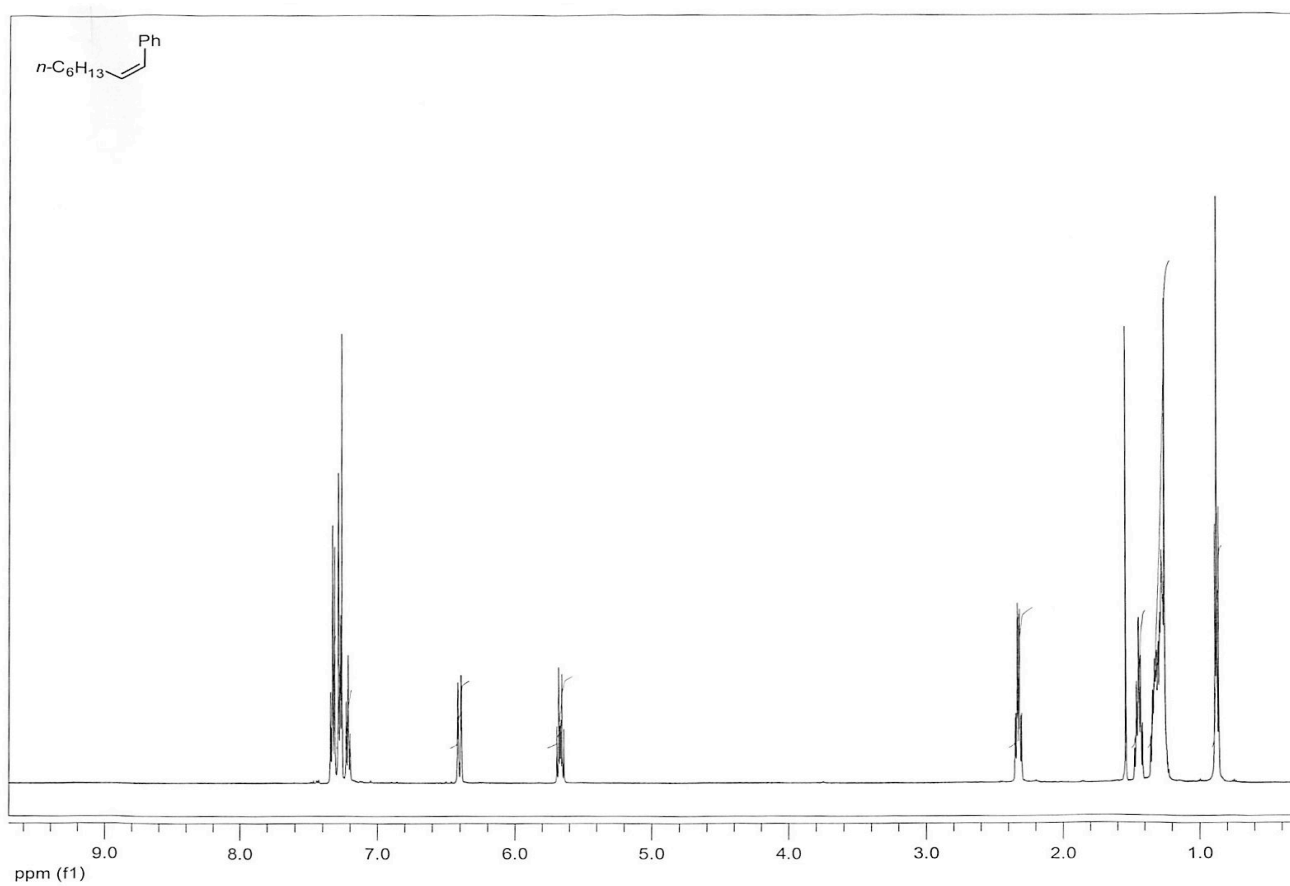


11 (*trans*-)

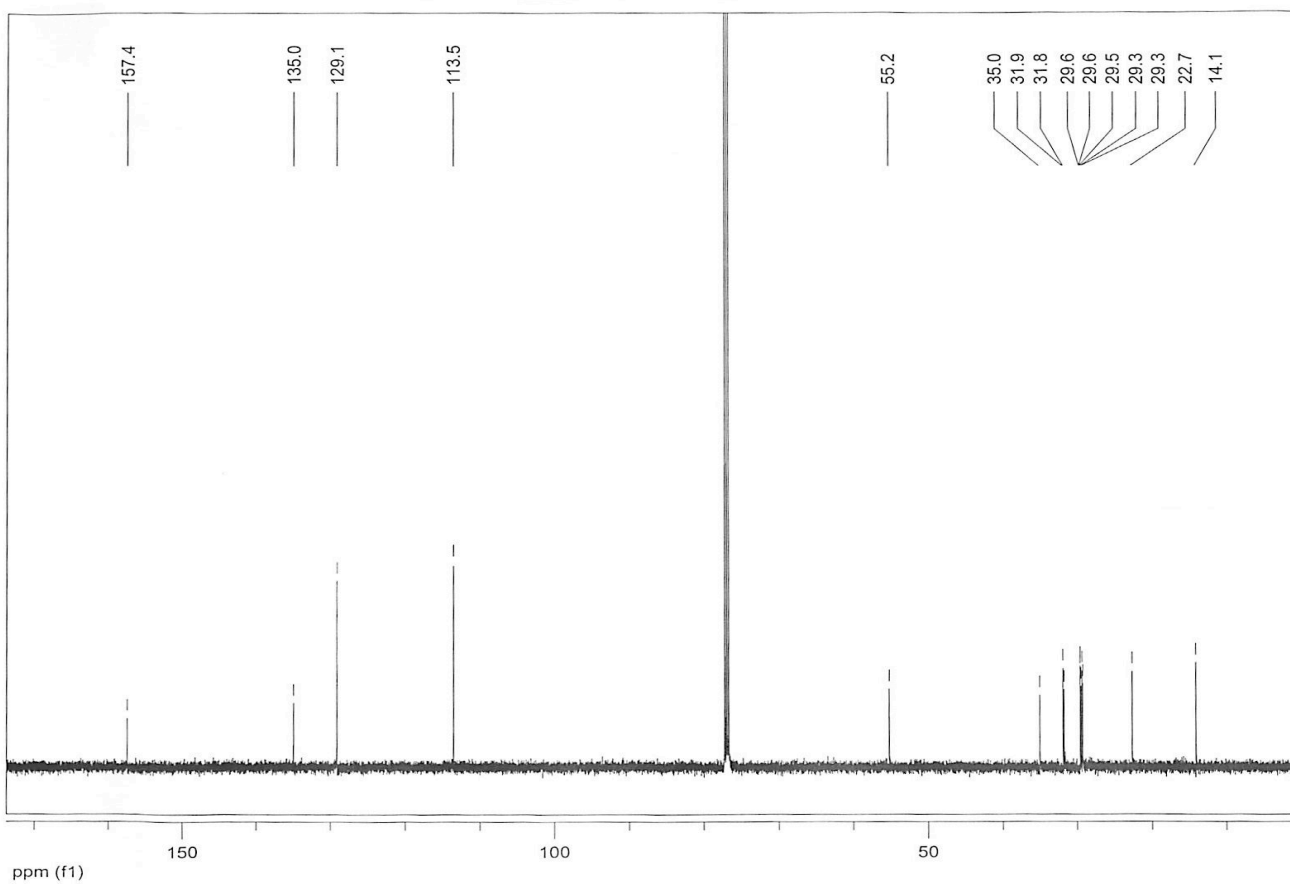
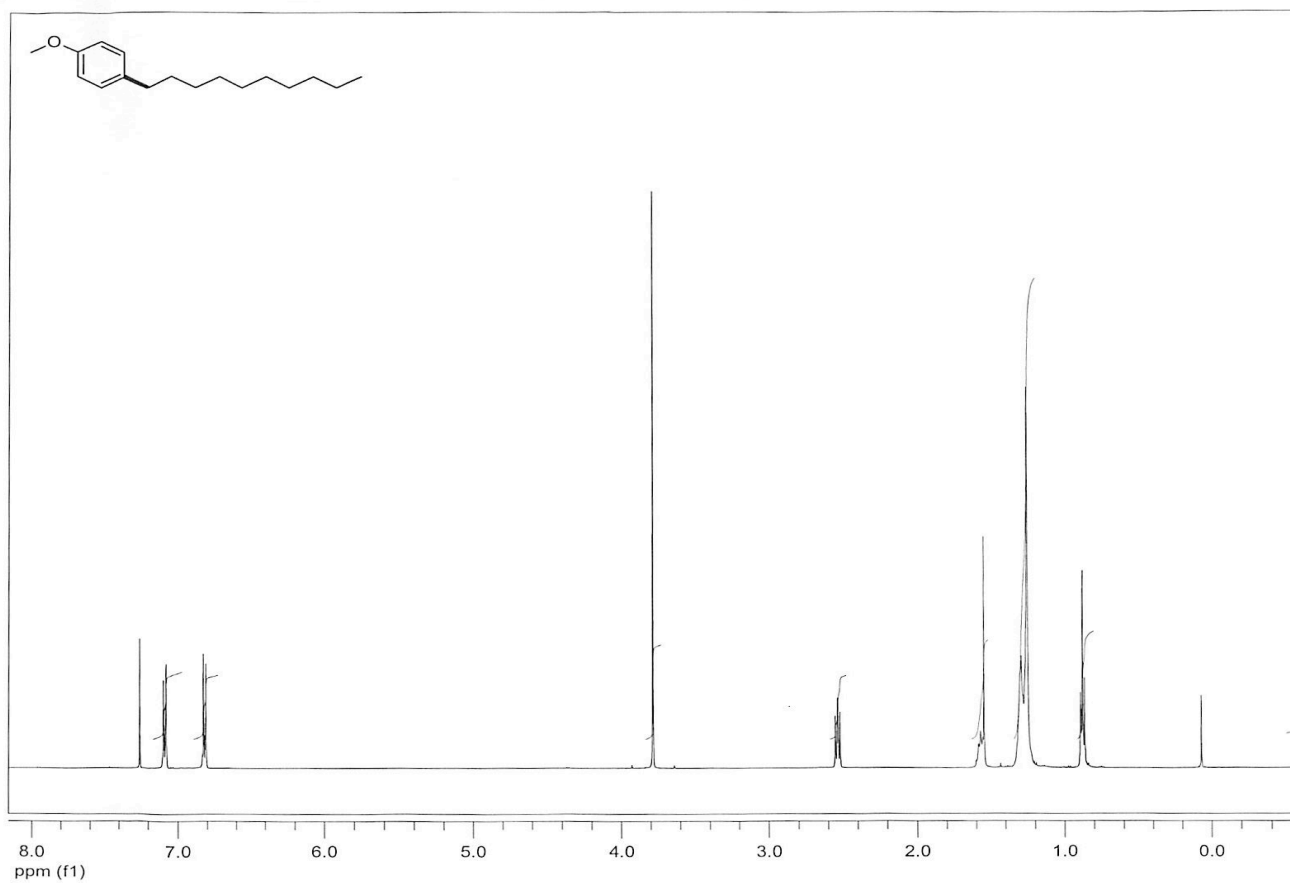








20a



20b

