Engaging Alkenyl Halides with Alkylsilicates via Photoredox Dual Catalysis

Niki R. Patel, Christopher B. Kelly, Matthieu Jouffroy, and Gary A. Molander*

Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

*To whom correspondence should be addressed. E-mail: gmolandr@sas.upenn.edu

Supporting Information

Key to Abbreviated Terms:

bpy: 2,2'-bipyridyl
CFL: Compact fluorescent light
dtbbpy: 4,4'-di-*tert*-butyl-2,2'-dipyridyl
LED: Light-emitting diode
TMG: 1,1,3,3-Tetramethylguanidine

General Considerations:

General:

All chemical transformations requiring inert atmospheric conditions or vacuum distillation utilized Schlenk line techniques with a 4- or 5-port dual-bank manifold. Argon or nitrogen was used to provide such an atmosphere. NMR Spectra (^{1}H, ^{13}C) were performed at 298 K. ^{1}H NMR spectra obtained in $CDCl_3$ were referenced to residual non-deuterated chloroform (δ 7.26) in the deuterated solvent. Spectra obtained in DMSO-d_6 were referenced to residual DMSO-d_5 (δ 2.50) in the deuterated solvent. ^{13}C NMR spectra obtained in $CDCl_3$ were referenced to chloroform (δ 77.3). ^{13}C NMR spectra obtained in DMSO-d_6 were referenced to DMSO (δ 39.5). Reactions were monitored by GC/MS, ^{1}H NMR, and/or by TLC on silica gel plates (60Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/EtOAc as the eluant and visualized using permanganate stain, Seebach's stain,[1] ninhydrin stain, and/or UV light. Silica plugs utilized flash silica gel (60Å porosity, 32-63 μm). Flash chromatography was accomplished using an automated system (visualizing at 254 nm, monitoring at 280 nm) with silica cartridges (60Å porosity, 20-40 μm). Solvents were purified either by distillation over sodium or CaH_2 or by use of drying cartridges through a solvent delivery system. Melting points (°C) are uncorrected.

Chemicals:

Deuterated NMR solvents were either used as purchased (DMSO-d_6) or were stored over 4Å molecular sieves and K_2CO_3 ($CDCl_3$). Na_2SO_4, $MgSO_4$, MeOH, CH_2Cl_2, $CHCl_3$, MeCN, pentane, Et_2O, and pyridine, were used as purchased. Et_3N and *i*-Pr_2NH, were purchased from commercial suppliers and distilled from CaH_2 prior to use. THF was purchased from commercial suppliers and dried *via* a solvent delivery system. Catechol was purchased and recrystallized from refluxing hexanes or heptanes. DMF (99.8%, extra dry) was stored over 4 Å molecular sieves. $NiCl_2$•dme (min. 97%) and $RuCl_3$•$3H_2O$ were purchased commercially. Alkenyl halides were either purchased from commercial suppliers or prepared in-house. In the case of the latter, syntheses of these halides are provided. The alkenyl halides *trans*-1-iodo-1-octene (**2a**), β-bromostyrene (**2b**), 2-bromoindene (**2e**), ethyl *cis*-3-bromoacrylate (**2f**), bromomethylenecyclohexane (**2h**), 1-bromo-2-methyl-propene (**2i**), and 1-chloro-1-cyclopentene (**2l**) were purchased from commercial suppliers and used without further purification. $Ru(bpy)_3(PF_6)_2$ was prepared in-house by the procedure outlined here. Silicates were prepared according to the representative procedure outlined here from their corresponding

[1] Seebach, D.; Imwinkelried, R; Stucky, G. *Helv. Chim. Acta.* **1987**, *70*, 448.

alkyltrimethoxysilanes. Characterization data for new silicates is provided. Information (preparation protocols, characterization etc.) for silicates **1c**, **1d**, **1e**, **1h**, **1i**, **1l**, and **1m** can be found in our previous report.[2]

Photochemistry:

Irradiation of reaction vessels was accomplished either using standard 26 W CFLs or LEDs (blue or white). The choice of light source did not seem to have any effect on reaction success. In most cases either CFL or blue LEDs were employed for irradiation. LEDs were configured as outlined in the *Photochemical Reactor Design* section. A fan was employed to ensure reactions remained at or near room temperature when using either CFLs or LEDs.

Information for LED-based Photoreactor Components:

- *Blue LEDs*: 39.4 inch strips, 470 nm blue light, 32918 mcd ft^{-1}
- *Natural White LEDs*: 39.4 inch strips, 380-700 nm, CCT rating: 4000K
- *Power Supply*: 12V DC CPS series Power Supply - 15 Watt
- *Connectors* (links power supply to LEDs): LC2 Locking Male Connector CPS Adapter Cable
- *Clip Fan*: 2-Speed Clip Fan, 6-Inch
- Pyrex crystallizing dishes (125 X 65 mm)
- Aluminum foil
- Duct tape

[2] Jouffroy, M.; Primer, D.; Molander, G. A. *J. Am. Chem. Soc.,* **2015**, ASAP DOI: 10.1021/jacs.5b10963

Photochemical Reactor Design (LEDs only)

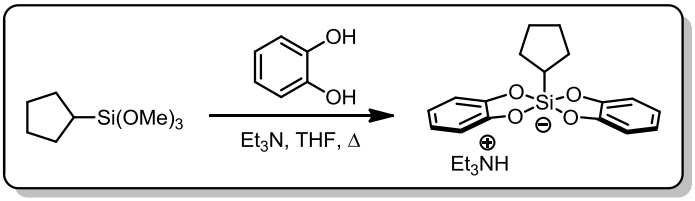
Protocol for reactor setup

Remove the protective layer on the sticky side of the LED strip and carefully wrap the LED strips on the inside of a clean Pyrex dish.[3] Four bands of LEDs can fit into a 125 X 65 mm Pyrex crystallizing dish.[4] Once the LEDs are securely wrapped, place a layer of aluminium foil around the outside of the dish (including the bottom). Tape the connector wires as well as the foil with duct tape to secure both in place. For vial-scale reactions, cut a sample vial rack using a saw and place it inside. For larger vessels (e.g., round bottom flasks), simply lower the flask into the irradiation bay.[5] Place the reactor on top of a stirring place. Position a fan about 6-12 inches above the reactor for cooling and set it to its maximum setting. Turn on the lights and fan. Allow 15 min to pass for temperature equilibration. Temperature should be monitored in real time using a temperature probe to determine the ambient temperature within the reactor. Place a double layer of aluminum foil in front of the reactor to reflect light back into the reactor. ***CAUTION:*** Given the brightness of the reactor, it is recommended that impact-resistant sunglasses are used when working with the reactor for eye protection.

[3] Starting from the bottom upward affords the easiest approach.
[4] If smaller lengths of LED strips are used, they can be linked together. Most LED strips are able to be cut (at specified locations) and powered by either end. The appropriate connector is required (male or female) for each end.
[5] This design can accommodate up to a 250 mL round bottom flask. However, if desired, a larger reactor can be assembled by using larger recrystallization dish and additional LEDs.

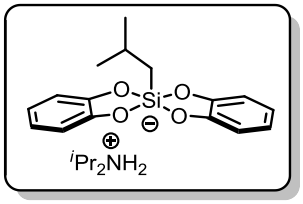
Representative Synthesis of Silicates

Preparation of triethylammonium bis(catecholato)cyclopentylsilicate (1b)



To an oven-dried 100 mL round bottom flask equipped with a stir bar, reflux condenser, and gas inlet adapter was added catechol[6] (3.99 g, 0.0362 mol, 1.95 equiv) followed by anhyd THF (35 mL) and anhyd Et_3N (2.26 g, 3.1 mL, 0.223 mol, 1.2 equiv). The mixture was placed under an argon atmosphere and was allowed to stir at rt for 5 min. The solution became a pale reddish brown. After this time, the cyclopentyltrimethoxysilane (3.54 g, 0.0186 mol, 1 equiv) dissolved in a minimal amount of THF (5 mL) was added all at once. The solution immediately lightened to a golden yellow. The solution was then heated to reflux in an oil bath and allowed to stir at this temperature overnight.[7] Once the reaction was judged to be complete by crude ^{1}H NMR analysis,[8] the solvent was removed *in vacuo* by rotary evaporation. The crude solid was dissolved in CH_2Cl_2 (~60 mL), and a minimum amount of pentane (~10 mL) was added as an anti-solvent, resulting in precipitation of a fine white powder. The powder was collected *via* filtration through a medium porosity fritted funnel. The powder was washed with a minimal amount of Et_2O (~10 mL) followed by a copious amount of pentane (~125 mL). The solid was collected and dried further *in vacuo* to give the pure silicate (5.23 g, 68%) as a powdery off-white solid (mp = 201 °C).

^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.81 - 0.90 (m, 1H), 1.16 (t, J = 7.2 Hz, 9H), 1.20 - 1.26 (m, 2H), 1.26 - 1.40 (m, 4H), 1.40 - 1.50 (m, 2H), 3.08 (q, J = 7.3 Hz, 6H), 6.39 - 6.44 (m, 4H), 6.48 - 6.52 (m, 4H), 8.82 (br s, 1H). **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 8.6 (CH_3), 25.9 (CH_2), 28.5 (CH_2), 29.8 (CH), 45.8 (CH_2), 109.2 (C), 116.9 (CH), 150.9 (CH). **FT-IR** (cm^{-1}, neat, ATR) 3040 (w, br), 2950 (w, b), 1486 (vs), 1243 (vs), 1015 (w), 818 (vs), 732 (vs), 522 (vs). **HRMS** (ES-) calcd for $C_{23}H_{33}NO_4Si$ $[M]^-$: 313.0896, found: 313.0902.

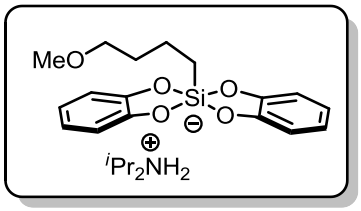


Diisopropylammonium Bis(catecholato)isobutylsilicate, 1g (4.86 g, 86%) was prepared according to the general procedure for silicate synthesis from isobutyltrimethoxysilane (2.50 g, 0.014 mol) ***with the following modification:*** *i*-Pr_2NH (1.70 g, 2.35 mL, 0.0168 mol, 1.2 equiv) was used in place of Et_3N. The desired silicate **1g** was isolated as a powdery white solid (mp = 216 °C).

^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.50 (d, J = 6.8 Hz, 2H), 0.75 (d, J = 6.4 Hz, 6H), 1.20 (d, J = 6.6 Hz, 12H), 1.68 (sept, J = 6.6 Hz, 1H), 3.35 (dt, J = 12.9, 6.4 Hz, 2H), 6.39 - 6.45 (m, 4H),

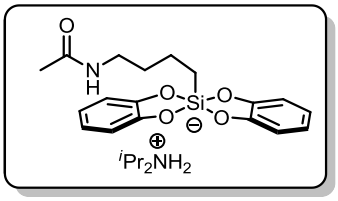
[6] Recrystallized from hexane or heptane prior to use.
[7] Depending on the nature of the silicate and its solubility in THF, precipitation of the product would occur.
[8] For DIPA silicates, it is advisable to use deuterated acetone as the NMR solvent, as they have poor solubility in most other deuterated solvents.

6.47 - 6.55 (m, 4H), 8.02 (br s, 2H). **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 18.8 (CH_3), 24.4 (CH), 26.3 (CH_3), 29.4 (CH_2), 46.4 (CH), 109.4 (C), 117.0 (CH), 150.6 (CH). **FT-IR** (cm^{-1}, neat, ATR) 3047 (w, br), 2948 (w), 1484 (vs), 1238 (vs), 1014 (w), 812 (w), 734 (vs), 498 (m). **HRMS** (ES-) calcd for $C_{16}H_{17}O_4Si$ [M]$^-$: 301.0896, found: 301.0899.



Diisopropylammonium Bis(catecholato)(3-methoxypropyl)silicate, 1j (5.39 g, 86%) was prepared according to the general procedure for silicate synthesis from (3-methoxypropyl)trimethoxysilane (2.91 g, 0.015 mol) ***with the following modification:*** *i*-Pr_2NH (1.82 g, 2.52 mL, 0.018 mol, 1.2 equiv) was used in place of Et_3N. The desired silicate **1j** was isolated as a powdery off-white solid (mp = 208 °C).

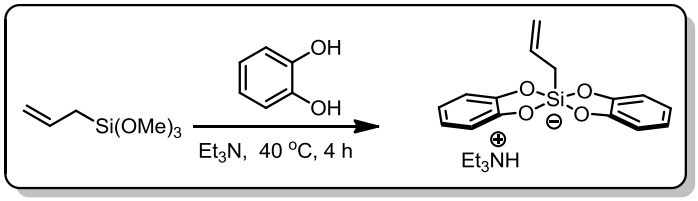
^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.39 - 0.51 (m, 2H), 1.19 (d, J = 6.4 Hz, 12H), 1.34 - 1.49 (m, 2H), 3.08 (s, 3H), 3.10 (t, J = 6.8 Hz, 2H), 3.35 (sept, J = 6.4 Hz, 2H), 6.41 - 6.48 (m, 4H), 6.49 - 6.59 (m, 4H), 8.03 (br s, 2H). **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 13.9 (CH_2), 18.8 (CH), 24.4 (CH_2), 46.4 (CH), 57.5 (CH_3), 75.1 (CH_2), 109.5 (C), 117.1 (CH), 150.5 (CH). **FT-IR** (cm^{-1}, neat, ATR) 3045 (w, br), 2872 (w, br), 1582 (w), 1484 (s), 1237 (s), 810 (s), 734 (s). **HRMS** (ES-) calcd for $C_{22}H_{33}NO_5Si$ [M]$^-$: 317.0845, found: 317.0849.



Diisopropylammonium Bis(catecholato)(3-acetamidopropyl)silicate, 1k (4.84 g, 66%) was prepared according to the general procedure for silicate synthesis from (3-acetamidopropyl)trimethoxysilane (3.32 g, 0.015 mol) ***with the following modification:*** *i*-Pr_2NH (1.82 g, 2.52 mL, 0.018 mol, 1.2 equiv) was used in place of Et_3N. The desired silicate **1k** was isolated as a powdery off-white solid (mp = 174 °C).

^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.36 - 0.51 (m, 2H), 1.19 (d, J = 6.6 Hz, 12H), 1.23 - 1.34 (m, 2H), 1.71 (s, 3H), 2.80 (q, J = 6.8 Hz, 2H), 3.35 (sept, J = 6.6 Hz, 2H), 6.40 - 6.46 (m, 4H), 6.48 - 6.55 (m, 4H), 7.62 (br s, 1H), 8.01 (br s, 2H). **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 15.8 (CH_2), 18.8 (CH_3), 22.6 (CH_3), 24.8 (CH_2), 42.0 (CH_2), 46.3 (CH), 109.5 (C), 117.0 (CH), 150.5 (CH), 168.5 (C). **FT-IR** (cm^{-1}, neat, ATR) 3339 (w, br), 3092 (vw, br.), 2880 (vw, br.), 1487 (s), 1242 (s), 1015 (w), 818 (vs), 736 (vs), 595 (m). **HRMS** (ES-) calcd for $C_{23}H_{34}N_2O_5Si$ [M]$^-$: 344.0954, found: 344.0966.

Preparation of Triethylammonium Bis(catecholato)allylsilicate (1f)



Allyl silicate **1f** was prepared according to the procedure outlined by Hosomi.[9] To a 25 mL round bottom flask equipped with a stir bar was added anhyd Et_3N (2.15 g, 2.96 mL, 0.0213 mol,

[9] Hosomi, A.; Kohra, S.; Ogata, K.; Yanagi, T.; Tominaga, Y. *J. Org. Chem.*, **1990**, *55*, 2415.

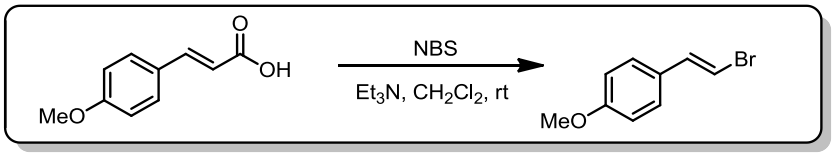
4.25 equiv) and catechol[10] (1.13 g, 0.01025 mol, 2.05 equiv) followed by allyltrimethoxysilane (0.811 g, 0.005 mol, 1 equiv). The flask was sealed with a septum and placed under an argon atmosphere *via* an inlet needle. The solution was heated to 40 ^{o}C *via* an oil bath and stirred at this temp for 4 h. Formation of a light pink precipitate was observed during the course of the reaction. After this time, the flask was cooled to rt, and the solid was filtered and washed with pentane (~100 mL). The crude solid was dissolved in CH_2Cl_2 (~40 mL), and a minimum amount of pentane (~ 5 mL) was added as an anti-solvent, resulting in precipitation of a fine light pink powder. The powder was collected via filtration through a medium porosity fritted funnel. The powder was with pentane (~100 mL). The solid was collected and dried further *in vacuo* to give the pure silicate (1.06 g, 55%) as a powdery pale pink solid (mp = 128 °C).

^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.15 (t, J = 7.3 Hz, 9H), 1.50 (d, J = 8.1 Hz, 2H), 3.08 (q, J = 7.2 Hz, 6H), 4.47 (dt, J = 10.0, 1.2 Hz, 1H), 4.58 (dt, J = 17.1, 1.1 Hz, 1H), 5.67 (tdd, J = 17.4, 8.1, 1.8 Hz, 1 H)), 6.40 - 6.46 (m, 4H), 6.49 - 6.55 (m, 4H), 8.76 (br s, 1H). **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 8.6 (CH_3), 26.2 (CH_2), 45.8 (CH_2), 109.5 (C), 110.8 (s, 1 C), 117.1 (CH_2), 137.5 (CH), 150.4 (C). **FT-IR** (cm^{-1}, neat, ATR) 3065 (vw, br), 2952 (vw, b), 1486 (s), 1245 (s), 1013 (w), 855 (w), 827 (vs), 732 (s), 664 (m). **HRMS** (ES-) calcd for $C_{21}H_{29}NO_4Si$ $[M]^-$: 285.0583, found: 285.0587.

[10] Recrystallized from hexane or heptane prior to use

Synthesis of Alkenyl Halides

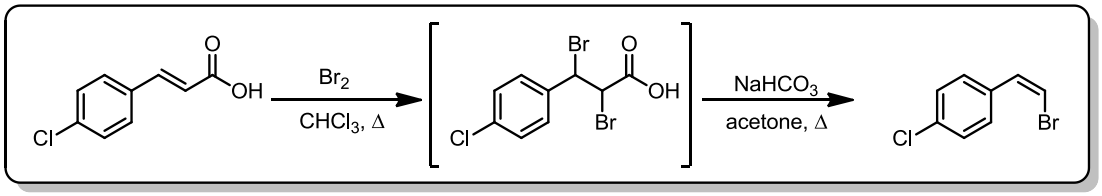
Preparation of (*E*)-1-(2-bromovinyl)-4-methoxybenzene[11] (2c)



This procedure is a modification of the procedure outlined by Alexakis.[11] To a 100 mL round bottom flask equipped with a stir bar was added (*E*)-3-(4-methoxyphenyl)acrylic acid (1.78 g, 0.010 mol, 1 equiv) and CH_2Cl_2 (35 mL). Et_3N (0.051 g, 0.0005 mol, 0.05 equiv) was added to the suspension and was stirred for 5 min at rt. At this time NBS (2.14 g, 0.012 mol, 1.2 equiv) was added all at once, and the reaction was stirred at rt. After 5 min, the suspension began to clear and, after 20 min, it became a clear, pale yellow solution.[12] CO_2 evolution was observed during this time. The now clear solution was allowed to stir overnight. After this time, the solvent was removed *in vacuo* by rotary evaporation, resulting in a crude tan solid. The solid was transferred to a medium porosity fritted funnel and washed with pentane (~200 mL). The pentane was then removed *in vacuo* by rotary evaporation, resulting in a semi-solid, which was taken up in a minimum amount of pentane (~5 mL). Filtration through a short pad of silica followed by eluting with 95:5 hexane/EtOAc afforded a clear, pale yellow solution. Removal of the solvent *in vacuo* gave the desired alkenyl bromide, **2c**, as an off-white, powdery solid (1.52 g, 71%). mp = 51 °C

^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.81 (s, 3H), 6.61 (d, *J* = 13.7 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 13.7 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 55.5 (CH_3), 104.2 (CH), 114.4 (CH), 127.5 (CH), 129.0 (C), 136.8 (CH), 159.9 (C). **GC-MS** (EI) 214 ($[M]^+$, ^{81}Br 99%), 212 ($[M]^+$, ^{79}Br 100%), 199 (^{81}Br 44%), 197 (^{79}Br 44%), 171 (^{81}Br 17%), 169 (^{79}Br 18%), 133 (31%), 118 (21%), 90 (39%), 99 (9%), 63 (20%), 51 (6%).

Preparation of (*Z*)-1-(2-bromovinyl)-4-chlorobenzene[13] (2d)



Stage One: Bromination

The following procedure is a modification of the procedure outlined by Stille.[13] To a 250 mL round bottom flask equipped with a stir bar and reflux condenser was added (*E*)-3-(4-chlorophenyl)acrylic acid (9.13 g, 0.050 mol, 1 equiv) and $CHCl_3$ (72 mL). After stirring for 5

[11] Mueller, D.; Alexakis, A. *Chem. Eur. J.* **2013**, *19*, 15226.
[12] If this induction period does not occur an additional 0.1-0.2 equiv of Et_{3N} should be added.
[13] Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174.

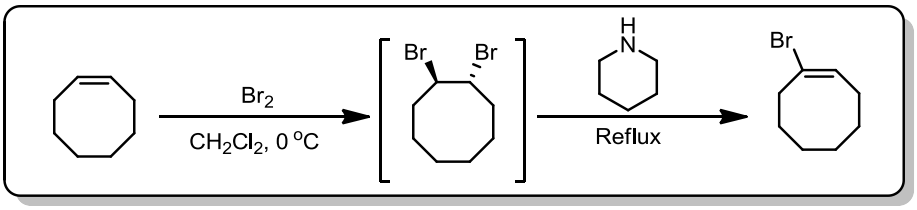
min, Br_2 (8.31 g, 2.66 mL, 1.04 equiv) was added dropwise to the flask. After complete addition of Br_2, the solution was heated to reflux and allowed to stir overnight. The solution became clear, and then the formation of a precipitate was observed. After stirring overnight, the solution was cooled to rt, and the solvent was removed *in vacuo* by rotary evaporation. The solid was transferred to a medium porosity fritted funnel and washed with a minimum amount of cold Et_2O (~25 mL) followed by a copious amount of pentane (~200 mL). The solid was dried *in vacuo*, giving the crude dibromide as a white solid (13.1 g, 77%), which was used directly in the next step.

Stage Two: Elimination

The crude dibromide (12.5 g, 0.0365 mol) from the previous step was transferred to a 250 mL round bottom flask equipped with a stir bar and reflux condenser. HPLC grade acetone (140 mL) followed by $NaHCO_3$ (13.15 g, 0.124 mol, 3.4 equiv) was added to the flask, and the solution was heated to reflux *via* an oil bath. The solution was stirred at reflux overnight. After this time, the solution was cooled to rt, and the solvent was removed *in vacuo* by rotary evaporation. The resulting slurry was dissolved in a mixture of Et_2O (~100 mL) and deionized H_2O (~100 mL) and transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with Et_2O (2 × ~125 mL). The combined organic layers were washed with saturated aq $NaHCO_3$ (~100 mL), deionized H_2O (~100 mL), and brine (~150 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Filtration through a short pad of silica followed by eluting with pentane afforded a clear, pale yellow solution. Removal of the pentane *in vacuo* gave the desired alkenyl bromide, **2d**, as a pale yellow oil (6.98 g, 88%).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.46 (d, J = 8.2 Hz, 1H), 7.03 (d, J = 8.2 Hz, 1H), 7.35 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.2 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 107.4 (CH), 128.6 (CH), 130.4 (CH), 131.4 (CH), 133.5 (C), 134.2 (CH). **GC-MS** (EI) 220 ($[M]^+$, ^{81}Br, ^{37}Cl 31%), 218 ($[M]^+$, ^{81}Br, ^{35}Cl & ^{79}Br, ^{37}Cl 100%), 216 ($[M]^+$, ^{79}Br, ^{35}Cl 85%), 139 (31%), 137 (82%), 111 (6%), 101 (61%), 75 (36%), 50 (18%).

Preparation of (*E*)-1-bromocyclooct-1-ene[14] (2g)



Stage One: Bromination

This procedure is a modification of the procedure outlined by Gassman.[14] To a 50 mL round bottom flask equipped with a stir bar was added cyclooctene (5.00 g, 0.045 mol, 1 equiv) and CH_2Cl_2 (10 mL). The solution was cooled to 0 °C *via* an ice bath and stirred for 10 min. Br_2 (7.2 g, 2.32 mL, 1 equiv) was added to the flask dropwise *via* a disposable syringe. After complete

[14] Gassman, P. G.; Macomber, D. W.; Willging, S. M. *J. Am. Chem. Soc.* **1985**, *107*, 2380.

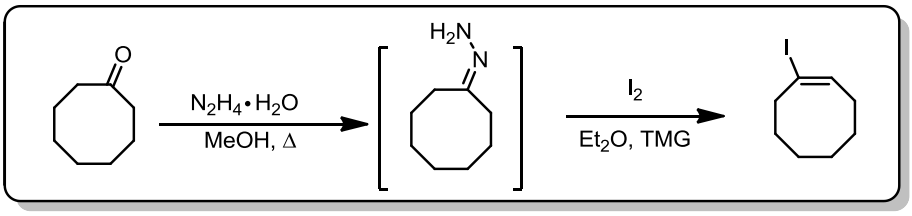
addition of Br_2, the solution was allowed to stir at 0 °C for 5 min. The solution was then warmed to rt and stirred for 1 h. At this time the solvent was removed *in vacuo* by rotary evaporation, and the crude bromide (12.15 g, assumed quantitative) was carried on directly to the next step.

Stage Two: Elimination

The crude bromide from the previous step was transferred to a 50 mL round bottom flask equipped with a stir bar and reflux condenser. The bromide was dissolved in piperidine (20 mL), and the solution was heated to reflux *via* an oil bath. Formation of a voluminous precipitate was observed. After stirring overnight, the crude solution was cooled to rt and filtered through a medium porosity fritted funnel. The crude solids were washed with pentane (≈ 250 mL). The filtrate was transferred to a separatory funnel and washed sequentially with 1 M H_2SO_4 (2 × ≈ 75 mL), saturated $NaHCO_3$ (2 × ≈ 75 mL), deionized H_2O (≈ 100 mL), and brine (≈ 100 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by vacuum distillation (94-96 °C @ 22 mm Hg) to give the desired alkenyl halide, **2g**, as a clear, pale yellow oil (5.32 g, 63% over 2 steps).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.47 - 1.57 (m, 6H), 1.60 - 1.66 (m, 2H), 2.06 - 2.13 (m, 2H), 2.58 - 2.64 (m, 2H), 6.03 (t, J = 8.5 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 25.7 (CH_2), 26.6 (CH_2), 27.7 (CH_2), 28.8 (CH_2), 30.1 (CH_2), 35.3 (CH_2), 125.0 (CH), 131.8 (C). **GC-MS** (EI) 190 ($[M]^+$, ^{81}Br 32%), 188 ($[M]^+$, ^{79}Br 32%), 162 (^{81}Br 14%), 160 (^{79}Br 14%), 148 (^{81}Br 4%), 146 (^{79}Br 4%), 134 (^{81}Br 10%), 132 (^{79}Br 10%), 109 (77%), 81 (48%), 79 (28%), 67 (100%), 65 (16%), 55 (20%), 53 (33%).

Preparation of (*E*)-1-iodocyclooct-1-ene[15] *via* the Barton method (2g′)



Stage One: Hydrazone formation

This procedure is a modification of the procedure outlined by Yudin.[16] To a 50 mL round bottom flask equipped with reflux condenser and stir bar was added cyclooctanone (6.31 g, 0.050 mol, 1 equiv) followed by MeOH (8 mL). Hydrazine hydrate (3.5 g, 3.4 mL, 0.070 mol, 1.4 equiv) was added to the flask, and the reaction mixture was heated to reflux for 2 h. After this time, the solution was cooled to rt and transferred to a separatory funnel. CH_2Cl_2 (100 mL) and deionized H_2O (150 mL) were added, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 75 mL), and the combined organic layers were washed with brine (200 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed by rotary evaporation to give the crude hydrazine (5.53 g), which was used directly in the next step.

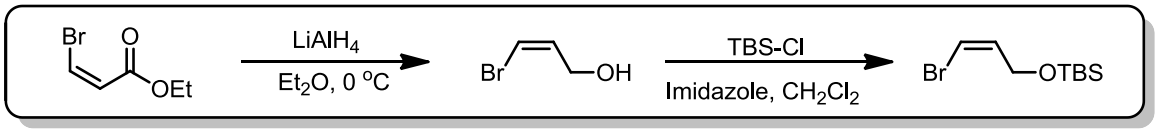
[15] Kropp, P. J.; McNeely, S. A. Davis, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 6907.
[16] Cheung, L. L. W.; Yudin, A. K. *Chem. Eur. J.* **2010**, *16*, 4100.

Stage Two: Iodination

To a 250 mL flame dried, round bottom flask equipped with a stir bar was added I_2 (13.01 g, 0.0573 mol, 2.05 equiv) and anhyd Et_2O (25 mL). The flask was sealed with a septum and placed under an argon atmosphere *via* an inlet needle. The solution was cooled to 0 °C for 10 min. After this time, TMG (13.53g, 0.117 mol, 4.7 equiv) dissolved in Et_2O (16 mL) was added to the flask dropwise. Upon complete addition of TMG, the solution was stirred at 0 °C for 15 min. After this time, the crude hydrazone (3.51 g, 0.025 mol, 1 equiv) from the previous step dissolved in Et_2O (16 mL) was added dropwise to the solution *via* a syringe. Upon complete addition of the hydrazone, the solution was stirred at 0 °C for 15 min. The reaction was quenched with 2 M HCl (50 mL) and stirred for 10 min. After this time, saturated $Na_2S_2O_3$ (50 mL) was added, and the solution was stirred for an additional 10 min. The now quenched solution was transferred to a separatory funnel, and the layers were separated. The aqueous layer was extracted with pentane (3 × 75 mL), and the combined organic layers were washed with 2 M HCl (~100 mL), saturated aq $Na_2S_2O_3$ (2 × ~100 mL), deionized H_2O (~150 mL), and brine (~150 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by vacuum distillation (80-82 °C @ 2 mm Hg) to give the alkenyl iodide, **2g′** as a clear, yellow oil (3.00 g, 51%).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.44 - 1.62 (m, 8H), 2.02 - 2.12 (m, 2H), 2.57 - 2.70 (m, 2H), 6.36 (t, *J* = 8.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 25.5 (CH_2), 26.8 (CH_2), 27.6 (CH_2), 30.0 (CH_2), 30.3 (CH_2), 38.7 (CH_2), 101.0 (C), 141.2 (CH). **GC-MS** (EI) 236 ($[M]^+$, 80%), 109 (55%), 91 (7%), 81 (25%), 79 (26%), 67 (100%), 65 (12%), 55 (28%), 53 (19%).

Preparation of (*Z*)-3-bromoprop-2-en-1-ol (2j) &
(*Z*)-((3-bromoallyl)oxy)(tert-butyl)dimethylsilane (2k)



(*Z*)-3-Bromoprop-2-en-1-ol[17] (2j)

This procedure is a modification of the procedure outlined by Taylor.[17] To a 250 mL round bottom flask equipped with a stir bar was added $LiAlH_4$ (1.14 g, 0.030 mol, 0.75 equiv) and anhyd Et_2O (80 mL). The flask was sealed with a septum and placed under an argon atmosphere *via* an inlet needle. The flask was cooled to 0 °C for 10 min *via* an ice bath. At this time, (*Z*)-ethyl 3-bromoacrylate **2f** (7.16 g, 0.040 mol, 1 equiv) was dissolved in anhyd Et_2O (20 mL) and added dropwise to the flask *via* a syringe. After complete addition of the bromide, the solution was allowed to stir at 0 °C for 90 min. At this time the reaction was quenched by sequential addition of deionized H_2O (1.15 mL), 2 M NaOH (2.30 mL), and again with deionized H_2O (3.45 mL). ***CAUTION*** *Evolves excess H_2 gas!* The solution of the resulting heterogeneous

[17] Wei, X.; Taylor, R. J. K. *J. Org. Chem.*, **2000**, *65*, 616.

mixture was decanted, and the solids were washed with Et_2O (2 × ~100 mL). The combined ethereal extracts were transferred to a separatory funnel and washed with deionized H_2O (~100 mL) followed by brine (~150 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by vacuum distillation (70-72 ^oC @ 5 mm Hg) to give the desired alcohol, **2j**, as a clear, colorless oil (2.52 g, 46%).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.32 (dd, *J* = 6.1, 1.5 Hz, 2H), 6.27 (dt, *J* = 7.3, 1.5 Hz, 1H), 6.35 (dt, *J* = 7.3, 5.8 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 61.2 (CH_2), 109.1 (CH), 134.1 (CH). **GC-MS** (EI) 137 ($[M]^+$, ^{81}Br 4%), 135 ($[M]^+$, ^{79}Br 5%), 107 (^{81}Br 4%), 105 (^{79}Br 3%), 81 (4%), 57 (100%).

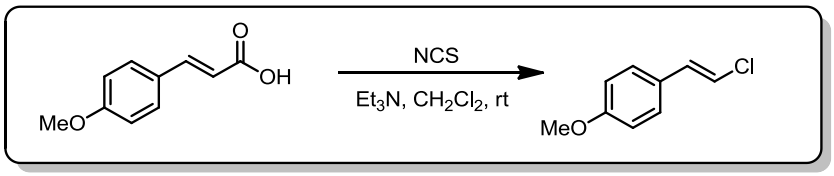
(*Z*)-((3-Bromoallyl)oxy)(*tert*-butyl)dimethylsilane[18] (2k)

This procedure is a modification of the procedure outlined by Davies.[19] To a 100 mL round bottom flask equipped with a stir bar was added (*Z*)-3-bromoprop-2-en-1-ol (0.685 g, 0.005 mol, 1 equiv), *tert*-butyldimethylsilyl chloride (0.791 g, 0.00525 mol, 1.05 equiv), and CH_2Cl_2 (25 mL). The solution was stirred for 15 min, at which point the solution was homogeneous. At this time, imidazole (0.374 g, 0.0055 mol, 1.1 equiv) was added to the flask, resulting in the immediate formation of a white precipitate. The resulting suspension was stirred overnight at rt. After this time, the solution was quenched with pentane and stirred for an additional 15 min. The resulting heterogeneous solution was filtered through a pad of silica, eluting with Et_2O (~250 mL). The solvent was removed *in vacuo*, affording the pure silyl ether, **2k**, as a clear, colorless oil (1.22 g, 97%).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.07 - 0.11 (m, 6H), 0.89 - 0.92 (m, 9H), 4.33 (dd, *J* = 5.5, 1.8 Hz, 2H), 6.16 (dt, *J* = 7.3, 1.8 Hz, 1H), 6.27 (dt, *J* = 7.3, 5.5 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ -4.96 (CH_3), 18.5 (C), 26.1 (CH_3), 62.2 (CH_2), 106.9 (CH), 135.5 (CH). **GC-MS** (EI) 252 ($[M]^+$, ^{81}Br 0.1%), 250 ($[M]^+$, ^{79}Br 0.1%), 195 (^{81}Br 100%), 193 (^{79}Br 99%), 169 (^{81}Br 83%), 167 (^{79}Br 81%), 139 (^{81}Br 65%), 137 (^{79}Br 62%), 99 (13%), 85% (11%), 73 (25%), 59 (10%).

[18] Gallagher, W. P.; Maleczka, R. E., Jr. *J. Org. Chem.* **2005**, *70*, 841.
[19] Davies, H. M. L.; Hedley, S. J.; Bohall, B. R. *J. Org. Chem.* **2005**, *70*, 10737.

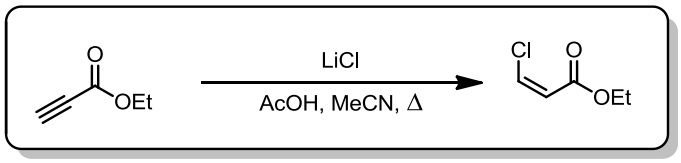
Preparation of (*E*)-1-(2-chlorovinyl)-4-methoxybenzene[20] (2m)



This procedure is a modification of the procedure outlined by Alexakis.[21] To a 250 mL round bottom flask equipped with a stir bar was added (*E*)-3-(4-methoxyphenyl)acrylic acid (3.56 g, 0.020 mol, 1 equiv) and CH_2Cl_2 (67 mL). Et_3N (0.506 g, 0.005 mol, 0.25 equiv) was added to the suspension and was stirred for 5 min at rt. At this time NCS (3.20 g, 0.024 mol, 1.2 equiv) was added all at once, and the reaction was stirred at rt. After 5 min the suspension began to clear and, after 20 min, it became a clear, pale yellow solution.[22] CO_2 evolution was observed during this time. The now clear solution was allowed to stir overnight. After this time, the solvent was removed *in vacuo* by rotary evaporation, resulting in a crude tan solid. The solid was transferred to a medium porosity fritted funnel and washed with pentane (~200 mL). The pentane was then removed *in vacuo* by rotary evaporation, resulting in a semi-solid, which was taken up in a minimum amount of pentane (~5 mL). Filtration through a short pad of silica followed by eluting with 95:5 hexane/EtOAc afforded a clear pale yellow. Removal of the solvent *in vacuo* gave the desired alkenyl chloride, **2m**, as a clear, pale yellow oil (2.17 g, 64%).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.81 (s, 3H), 6.50 (d, *J* = 13.7 Hz, 1H), 6.77 (d, *J* = 13.7 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 55.5 (CH_3), 114.4 (CH), 116.6 (CH), 127.6 (CH), 127.8 (C), 132.93 (CH), 159.83 (C). **GC-MS** (EI) 170 ($[M]^+$, ^{37}Cl 49%), 168 ($[M]^+$, ^{35}Cl 100%), 155 (^{37}Cl 28%), 153 (^{35}Cl 72%), 133 (17%), 127 (^{37}Cl 28%), 125 (^{35}Cl 50%), 118 (6%), 118 (6%), 101 (10%), 99 (12%), 89 (37%), 77 (6%). 75 (9%), 63 (20%).

Preparation of (*Z*)-ethyl 3-chloroacrylate[23] (2n)



This procedure is a modification of the procedure outlined by Ma.[24] To a 100 mL round bottom flask equipped with a stir bar and reflux condenser was added ethyl propiolate (4.90 g, 0.050 mol, 1 equiv), LiCl (2.33 g, 0.055 mol, 1.1 equiv), and MeCN (50 mL). The heterogeneous solution was allowed to stir for 5 min and, after this time, AcOH (3.30 g, 0.055 mol, 1.1 equiv),

[20] Bull, J. A.; Mousseau, J. J.; Charette, A. B. *Org. Lett.* **2008** , *10*, 5484.
[21] Mueller, D.; Alexakis, A. *Chem. Eur. J.* **2013**, *19*, 15226.
[22] If this induction period does not occur, an additional 0.1-0.2 equiv of Et_3N should be added.
[23] Reetz, M. T.; Sommer, K. *Eur. J. Org. Chem.* **2003**, 3485.
[24] Ma, S.; Lu, X.; Li, Z. *J. Org. Chem.* **1992**, *57*, 709

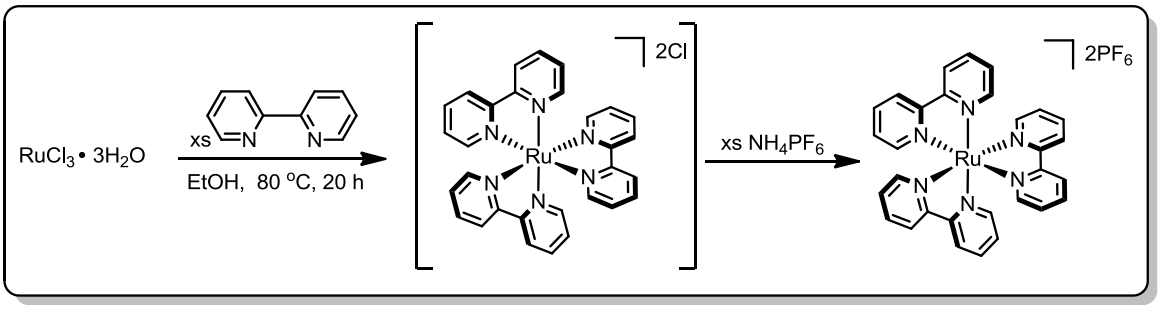
dissolved in a minimal amount of MeCN (≈ 5 mL), was added. The solution was heated to reflux and stirred for 36 h. Analysis by crude ^{1}H NMR over time indicated that the reaction stalled, and thus additional LiCl (0.639 g, 0.015 mol, 0.3 equiv) and AcOH (0.901 g, 0.015 mol, 0.3 equiv) were added. The solution was allowed to stir for 12 h, and at this time the reaction was still incomplete. Additional LiCl (0.639 g, 0.015 mol, 0.3 equiv) and AcOH (0.901 g, 0.015 mol, 0.3 equiv) were added, and the reaction mixture was stirred at reflux for another 24 h. At this time, the reaction was deemed complete and was cooled to rt. The crude reaction mixture was transferred to a separatory funnel and dissolved in pentane (~100 mL), and saturated aq $NaHCO_3$ (~100 mL) was added. The layers were separated, and the aqueous layer was extracted with pentane (3 × ~50 mL). The combined organic layers were washed with saturated aq $NaHCO_3$ (~150 mL), deionized H_2O (2 × ~75 mL), and brine (~100 mL). The organic layer was dried (Na_2SO_4), and the solvent was carefully[25] removed *in vacuo* by rotary evaporation, giving the desired alkenyl chloride, **2n**, as a clear, pale yellow oil (4.53 g, 67%).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.30 (t, *J* = 7.6 Hz, 3H), 4.23 (q, *J* = 7.6 Hz, 2H), 6.18 (d, *J* = 8.2 Hz, 1H), 6.69 (d, *J* = 8.2 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 14.3 (CH_3), 60.8 (CH_2), 121.6 (CH), 132.5 (CH), 163.6 (C). **GC-MS** (EI) 135 ([M]+, 0.1%), 106 (17%), 99 (72%) 91 (54%), 89 (100%), 71 (10%), 63 (12%), 61 (33%).

[25] Note that the alkenyl chloride is highly volatile. Pressures lower than 50 mm Hg are not advised.

Synthesis of $Ru(bpy)_3(PF_6)_2$

Preparation of the Photocatalyst

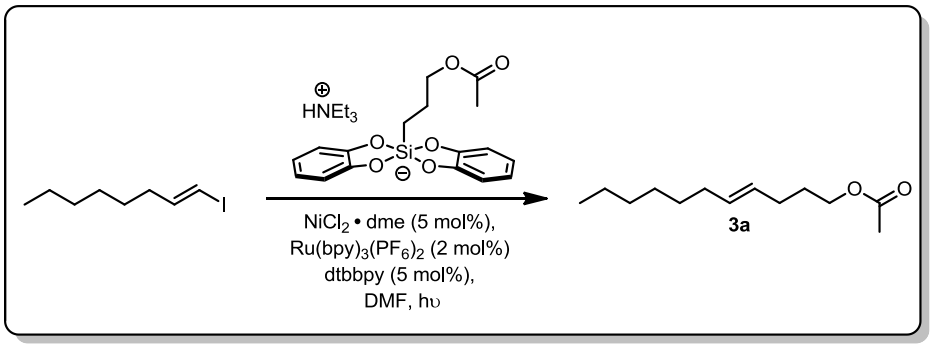


This procedure is a modification of the procedure outlined by Wrighton.[26] To a 500 mL round bottom flask equipped with a stir bar and reflux condenser was added 2,2'-bipyridyl (9.68 g, 62.0 mmol, 5.1 equiv) and $RuCl_3 \bullet 3H_2O$ (3.16 g, 12.1 mmol, 1.0 equiv). The system was sealed with a rubber septum and evacuated four times *via* an inlet needle and purged with N_2. Freshly distilled and degassed EtOH (300 mL) was then added, and the solution was heated to reflux *via* an oil bath. The solution was allowed to stir at reflux for 16 h. The flask was then cooled to rt, and NH_4PF_6 (16.30 g, 100 mmol, 8.3 equiv) was added, resulting in the formation of a voluminous orange precipitate. The reflux condenser was removed, and the solution was heated 15 min at 40 °C. After this time, the solution was cooled to rt and then chilled in a refrigerator (≈ 5 °C) overnight. The precipitate was collected by vacuum filtration and washed thoroughly with H_2O (~1 L), EtOH (~300 mL), and finally Et_2O (~200 mL) to afford a bright red powder.[27] NMR analysis of the solid revealed the presence of a small amount of 2,2'-bipyridyl. To purify the photocatalyst further, the red solid was taken up in hot acetone (400 mL) and filtered through a pad of Celite® (10 x 3 cm), eluting with hot acetone (~300 mL). The resulting pumpkin orange filtrate was concentrated *in vacuo* by rotary evaporation to *ca.* 400 mL, then reagent grade MeOH (~200 mL) was added. Rapidly, an orange solid formed, and addition of Et_2O (~300 mL) further enhances precipitation of the solid. The precipitate was collected by vacuum filtration, and the pumpkin orange cake was washed thoroughly with EtOH (~300 mL) and finally Et_2O (~200 mL) to afford the title compound as a fluffy powder (8.07 g, 78%). Characterization data for this compound matched that reported in the literature.[25]

[26] Mabrouk, P. A.; Wrighton, M. S. *Inorg. Chem.* **1986**, *25*, 526.

[27] In some cases, NMR analysis of the intermediate brick red solid shows the presence of other complexes, namely $Ru(bpy)_3(Cl)_2$ and $Ru(bpy)_3(PF_6)Cl$. In these cases, the solid was retaken up in H_2O (~200 mL), and NH_4PF_6 (~2 equiv) was added. The resulting suspension was sonicated at rt for 30 min then filtered, affording a brick red cake that was purified using the above mentioned procedure.

General Procedures for Photoredox Cross-coupling of Alkenes



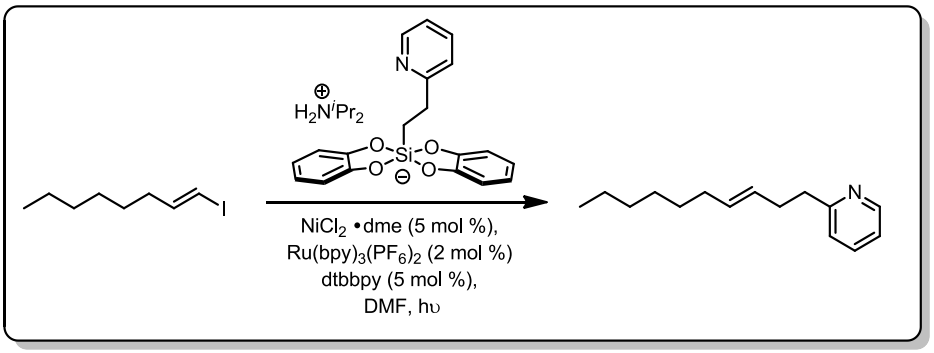
General Procedure A: ***Systems lacking Lewis basic functional groups and/or possessing low polarity***

(*E*)-Undec-4-en-1-yl Acetate (3a)

To an 8 mL reaction vial equipped with an appropriately sized stir bar were added the silicate **1a** (268 mg, 0.6 mmol, 1.2 equiv), $NiCl_2$•dme (5.5 mg, 0.025 mmol, 0.05 equiv), dtbbpy (6.7 mg, 0.025, 0.05 equiv), and $Ru(bpy)_3(PF_6)$ (8.6 mg, 0.01 mmol, 0.02 equiv). The vial was sealed with a cap containing a TFE-lined silicone septa and was evacuated three times *via* an inlet needle and purged with argon. The vial was then charged *via* a syringe with the iodide **2a** (119 mg, 0.5 mmol, 1 equiv) dissolved in anhyd, degassed DMF (5 mL). The cap was sealed with Parafilm, and the now bright red solution was irradiated in the aforementioned LED reactor. The temperature of the reaction was maintained at approximately 27 ^{o}C *via* a fan. The solution was stirred vigorously while being irradiated. Reaction progress was monitored by GC/MS. Once judged to be complete, the now opaque, milky-brown solution was transferred to a separatory funnel and diluted with deionized H_2O (~20 mL) and Et_2O (~20 mL). The layers were separated,[28] and the aqueous layer was extracted with Et_2O (3 × ~20 mL). The combined organic layers were washed with 2 M NaOH (2 × ~30 mL), 2 M HCl (~30 mL), deionized H_2O (~30 mL), and brine (~50 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by passing the crude material over a pad of silica, eluting with two volumes of hexane and discarding the eluate followed by 95:5 to 9:1 hexane/EtOAc to give the desired alkene, **3a**, as a clear, colorless oil (62 mg, 58%).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.88 (t, *J* = 7.1 Hz, 3H), 1.22 - 1.35 (m, 8H), 1.64 - 1.72 (m, 2H), 1.97 (q, *J* = 6.7 Hz, 2H), 2.04 (s, 3H), 2.05 (q, *J* = 6.7 Hz, 2H), 4.06 (t, *J* = 6.7 Hz, 2H), 5.31 - 5.50 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 14.4 (CH_3), 21.3 (CH_3), 22.9 (CH_2), 28.7 (CH_2), 29.1 (CH_2), 29.8 (CH_2), 32.0 (CH_2), 32.8 (CH_2), 64.3 (CH_2), 128.9 (CH), 131.9 (CH_2), 171.5 (C). **GC-MS** (EI) 212 ($[M]^+$,0.1 %), 152 (38%), 124 (10%), 110 (17%), 95 (31%), 81 (80%), 79 (20%), 68 (100%), 55 (30%). **HRMS** (CI+) calcd for $C_{13}H_{25}O_2$ $[M+H]^+$: 213.1855, found: 213.1845.

[28] Note that a precipitate will often form and rest at the interface between the organic and aqueous layers. It can be discarded during the washes without compromising yield.



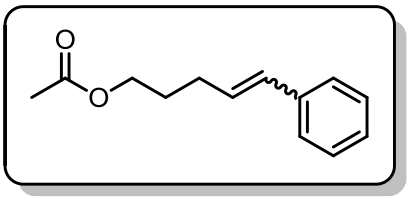
General Procedure B: ***Systems with Lewis basic functional groups***

(*E*)-2-(Dec-3-en-1-yl)pyridine (3v)

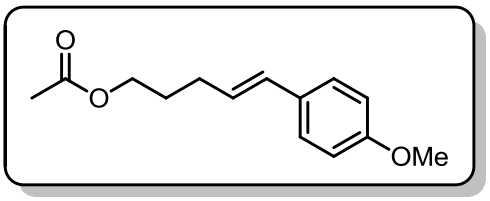
To an 8 mL reaction vial equipped with an appropriately sized stir bar were added the silicate **1l** (272 mg, 0.6 mmol, 1.2 equiv), $NiCl_2$•dme (5.5 mg, 0.025 mmol, 0.05 equiv), dtbbpy (6.7 mg, 0.025, 0.05 equiv), and $Ru(bpy)_3(PF_6)$ (8.6 mg, 0.01 mmol, 0.02 equiv). The vial was sealed with a cap containing a TFE-lined silicone septa and was evacuated three times *via* an inlet needle and purged with argon. The vial was then charged *via* a syringe with the iodide, **2a** (119 g, 0.5 mmol, 1 equiv) dissolved in anhyd, degassed DMF (5 mL). The cap was sealed with Parafilm, and the now bright red solution was irradiated in the aforementioned LED reactor. The temperature of the reaction was maintained at approximately 27 °C *via* a fan. The solution was stirred vigorously while being irradiated. Reaction progress was monitored by GC/MS. Once judged to be complete, the now opaque, milky-brown solution was transferred to a separatory funnel and diluted with 2 M NaOH (~20 mL) and Et_2O (~20 mL). The layers were separated,[29] and the aqueous layer was extracted with Et_2O (3 × ~20 mL). The combined organic layers were washed with 2 M NaOH (~30 mL), deionized H_2O (~30 mL), and brine (~50 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by passing the crude material over a pad of silica, eluting with two volumes of hexane and discarding the eluate followed by 95:5 to 9:1 hexane/EtOAc to give the desired alkene, **3v**, as a clear, colorless oil (78 mg, 72%).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.17 - 1.34 (m, 8H), 1.89 - 2.01 (m, 2H), 2.36 - 2.46 (m, 2H), 2.84 (t, *J* = 7.9 Hz, 2H), 5.35 - 5.50 (m, 2H), 7.08 (dd, *J* = 7.3, 4.8 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.57 (td, *J* = 7.7, 1.6 Hz, 1H), 8.52 (dt, *J* = 4.8, 0.9 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 14.3 (CH_3), 22.9 (CH_2), 29.0 (CH_2), 29.7 (CH_2), 32.0 (CH_2), 32.8 (CH_2), 33.0 (CH_2), 38.7 (CH_2), 121.1 (CH), 123.1 (CH), 129.1 (CH), 131.7 (CH), 136.3 (CH), 149.5 (CH), 162.0 (C). **GC-MS** (EI) 217 ($[M]^+$, 7%) 188 (7%), 160 (6%), 146 (100%), 132 (46%), 130 (11%), 119 (20%), 117 (23%), 93 (43%), 79 (4%) 65 (7%), 55 (3%). **HRMS** (ES+) calcd for $C_{15}H_{24}N$ $[M+H]^+$: 218.1909, found: 218.1917.

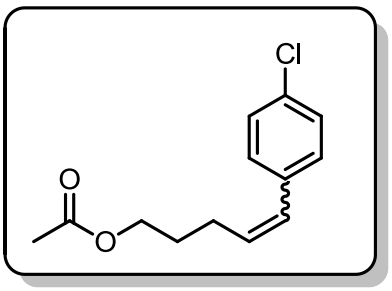
[29] Note that a precipitate will often form and rest at the interface between the organic and aqueous layers. It can be discarded during the washes without compromising yield.



5-Phenylpent-4-en-1-yl Acetate,[30] **3b** (65 mg, 63%) was prepared according to General Procedure A for photoredox cross-coupling of bromoalkene **2b** (92 mg, 0.5 mmol, *cis:trans* ratio 1:13.3). The desired cross-coupled alkene was obtained as a clear, light yellow oil (*cis:trans* ratio 1:11.1). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.78 - 1.86 (m, 2H), 2.06 (s, 3H), 2.29 (q, *J* = 7.6 Hz, 2H), 4.12 (t, *J* = 6.6 Hz, 2H), 6.20 (dt, *J* = 15.7, 7.0 Hz, 1H), 6.41 (d, *J* = 15.9 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.26 - 7.36 (m, 4H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.2 (CH_3), 28.6 (CH_2), 29.6 (CH_2), 64.2 (CH_2), 126.2 (CH), 127.3 (CH), 128.8 (CH), 129.6 (CH), 130.9 (CH), 137.8 (C), 171.4 (C). **GC-MS** (EI) 204 ($[M]^+$, 0.4%), 144 (54%), 129 (100%), 117 (18%), 115 (27%), 91 (20%), 77 (4%), 66 (4%), 51 (3%). **HRMS** (ES+) calcd for $C_{13}H_{16}O_2Na$ $[M+Na]^+$: 227.1048, found: 227.1050.

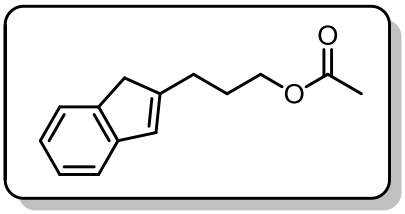


(*E*)-5-(4-Methoxyphenyl)pent-4-en-1-yl Acetate, 3c (99 mg, 84%) was prepared according to General Procedure A for photoredox cross-coupling of bromoalkene **2c** (107 mg, 0.5 mmol). The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.76 - 1.84 (m, 2H), 2.05 (s, 3H), 2.26 (q, *J* = 7.3 Hz, 2H), 3.80 (s, 3H), 4.11 (t, *J* = 6.6 Hz, 2H), 6.05 (dt, *J* = 15.6, 7.1 Hz, 1H), 6.35 (d, *J* = 15.6 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.2 (CH_3), 28.7 (CH_2), 29.6 (CH_2), 55.5 (CH_3), 64.2 (CH_2), 114.2 (CH), 127.3 (CH), 127.4 (CH), 130.3 (CH), 130.6 (C), 159.0 (C), 171.43 (C). **GC-MS** (EI) 234 ($[M]^+$, 88%), 174 (100%), 159 (87%), 147 (84%), 143 (71%), 131 (29%), 128 (20%), 121 (29%), 115 (39%), 103 (17%), 91 (43%), 77 (14%), 65 (6%), 55 (3%), 53 (3%). **HRMS** (ES+) calcd for $C_{14}H_{19}O_3$ $[M+H]^+$: 235.1334, found: 235.1344.

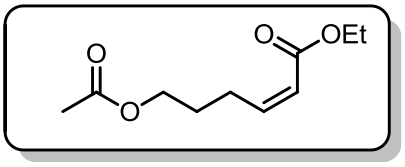


(*Z*)-5-(4-Chlorophenyl)pent-4-en-1-yl Acetate, 3d (105 mg, 87%) was prepared according to General Procedure A for photoredox cross-coupling of bromoalkene **2d** (109 mg, 0.5 mmol). The desired cross-coupled alkene was obtained as a clear, yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.74 - 1.82 (m, 2H), 2.00 (s, 3H), 2.37 (qd, *J* = 7.4, 1.8 Hz, 2H), 4.07 (t, *J* = 6.6 Hz, 2H), 5.66 (dt, *J* = 11.7, 7.3 Hz, 1H), 6.41 (d, *J* = 11.7 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.0 (CH_3), 25.1 (CH_2), 28.9 (CH_2), 63.9 (CH_2), 128.5 (CH), 128.9 (CH), 130.2 (CH), 132.2 (CH), 132.6 (C), 136.0 (C), 171.2 (C). **GC-MS** (EI) 240 ($[M]^+$, ^{37}Cl 1%), 238 ($[M]^+$, ^{35}Cl 2%), 180 (^{37}Cl 10%), 178 (^{35}Cl 29%), 165 (^{37}Cl, 5%), 163 (^{35}Cl 13%), 151 (8%), 143 (100%), 128 (40%), 115 (25%), 89 (4%), 75 (3%). **HRMS** (CI+) calcd for $C_{13}H_{15}ClO_2$ [M]+: 238.0761, found: 238.0762.

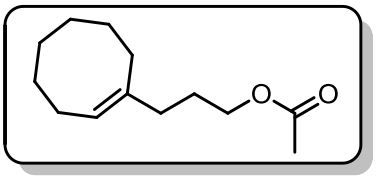
[30] Roman,S. A.; Closson,W. D. *J. Am. Chem. Soc.* **1969** , *91*, 1701.



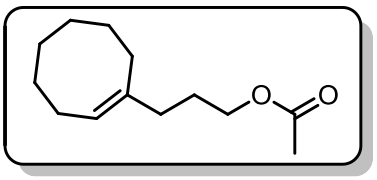
3-(1H-Inden-2-yl)propyl Acetate, 3e (98 mg, 90%) was prepared according to General Procedure A for photoredox cross-coupling of bromoalkene **2e** (98 mg, 0.5 mmol). The desired cross-coupled alkene was obtained as a clear, pale yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.96 (dt, *J* = 15.2, 6.6 Hz, 2H), 2.05 (s, 3H), 2.56 (t, *J* = 7.5 Hz, 2H), 3.32 (s, 2H), 4.13 (t, *J* = 6.6 Hz, 2H), 6.53 (s, 1H), 7.10 (td, *J* = 7.4, 1.2 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.37 (dd, *J* = 7.3, 0.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.2 (CH_3), 27.8 (CH_2), 28.2 (CH_2), 41.3 (CH_2), 64.3 (CH_2), 120.3 (CH), 123.7 (CH), 124.0 (CH), 126.6 (CH), 127.0 (CH), 143.2 (C), 145.6 (C), 149.3 (C), 171.4 (C). **GC-MS** (EI) 216 ($[M]^+$, 35%), 156 (87%), 141 (81%), 128 (100%), 115 (52%), 102 (5%), 91 (5%), 77 (5%), 63 (4%), 51 (3%). **HRMS** (ES+) calcd for $C_{14}H_{16}O_2Na$ $[M+Na]^+$: 239.1048, found: 239.1055.



(*Z*)-Ethyl 6-Acetoxyhex-2-enoate, 3f (66 mg, 66%) was prepared according to General Procedure A for photoredox cross-coupling of bromoalkene **2f** (90 mg, 0.5 mmol). The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.29 (td, *J* = 7.1, 0.9 Hz, 3H), 1.75 - 1.83 (m, *J* = 7.1 Hz, 2H), 2.05 (d, *J* = 0.9 Hz, 3H), 2.74 (q, *J* = 7.3 Hz, 2H), 4.09 (t, *J* = 6.5 Hz, 2H), 4.17 (qd, *J* = 7.1, 0.9 Hz, 2H), 5.78 - 5.82 (m, 1H), 6.21 (dt, *J* = 11.6, 7.6 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 14.5 (CH_3), 21.2 (CH_3), 25.7 (CH_2), 28.2 (CH_2), 60.1 (CH_2), 64.1 (CH_2), 120.9 (CH), 148.8 (CH), 166.5 (C), 171.4 (C). **GC-MS** (EI) 200 ($[M]^+$, 0.1%), 158 (12%), 140 (38%), 127 (16%), 125 (14%), 113 (100%), 99 (21%), 97 (63%), 94 (84%), 86 (10%), 84 (50%), 81 (15%), 71 (10%), 67 (74%), 55 (16%), 53 (13%). **HRMS** (ES+) calcd for $C_{10}H_{17}O_4$ $[M+H]^+$: 201.1127, found: 201.1122.

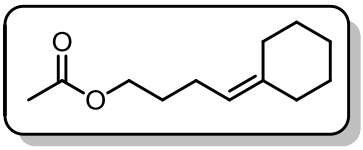


(*E*)-3-(Cyclooct-1-en-1-yl)propyl Acetate, 3g (83 mg, 77%) was prepared according to General Procedure A for photoredox cross-coupling of bromoalkene **2g** (95 mg, 0.5 mmol). The desired cross-coupled alkene was obtained as a clear, pale yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.43 - 1.54 (m, 8H), 1.74 (dt, *J* = 14.9, 6.7 Hz, 2H), 2.01 - 2.10 (m, 4H), 2.05 (s, 3H), 2.12 - 2.16 (m, 2H), 4.06 (t, *J* = 6.7 Hz, 2H), 5.35 (t, *J* = 8.2 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.3 (CH_3), 26.5 (CH_2), 26.5 (CH_2), 26.8 (CH_2), 27.2 (CH_2), 29.1 (CH_2), 29.1 (CH_2), 30.2 (CH_2), 33.8 (CH_2), 64.7 (CH_2), 124.6 (CH), 139.7 (C), 171.5 (C). **GC-MS** (EI) 210 ($[M]^+$,0.1 %), 150 (58%), 135 (24%), 122 (100%), 109 (29%), 107 (44%), 95 (35%) 93 (59%), 91 (17%), 81 (54%), 79 (62%), 77 (16%), 67 (70%), 55 (25%), 53 (12%). **HRMS** (CI+) calcd for $C_{13}H_{23}O_2$ $[M+H]^+$: 211.1698, found: 211.1707.

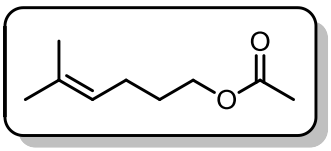


(*E*)-3-(Cyclooct-1-en-1-yl)propyl Acetate, 3g (71 mg, 70%) was prepared according to General Procedure A for photoredox cross-coupling of iodoalkene **2g′** (118 mg, 0.5 mmol). The desired cross-coupled alkene was obtained as a clear, pale yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.43 - 1.54 (m, 8H), 1.74 (dt, *J* = 14.9, 6.7 Hz, 2H), 2.01 - 2.10 (m, 4H), 2.05 (s, 3H),

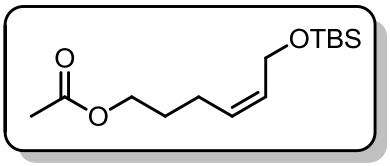
2.12 - 2.16 (m, 2H), 4.06 (t, *J* = 6.7 Hz, 2H), 5.35 (t, *J* = 8.2 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.3 (CH_3), 26.5 (CH_2), 26.5 (CH_2), 26.8 (CH_2), 27.2 (CH_2), 29.1 (CH_2), 29.1 (CH_2), 30.2 (CH_2), 33.8 (CH_2), 64.7 (CH_2), 124.6 (CH), 139.7 (C), 171.5 (C). **GC-MS** (EI) 210 ($[M]^+$,0.1 %), 150 (58%), 135 (24%), 122 (100%), 109 (29%), 107 (44%), 95 (35%) 93 (59%), 91 (17%), 81 (54%), 79 (62%), 77 (16%), 67 (70%), 55 (25%), 53 (12%) **HRMS** (CI+) calcd for $C_{13}H_{23}O_2$ $[M+H]^+$: 211.1698, found: 211.1707.



4-Cyclohexylidenebutyl Acetate, 3h (73 mg, 74%) was prepared according to General Procedure A for photoredox cross-coupling of bromoalkene **2h** (88 mg, 0.5 mmol). The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.44 - 1.57 (m, 6H), 1.61 - 1.69 (m, 2H), 2.03 - 2.08 (m, 4H), 2.04 (s, 3H), 2.10 (t, *J* = 5.8 Hz, 2H), 4.05 (t, *J* = 6.7 Hz, 2H), 5.04 (t, *J* = 7.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.3 (CH_3), 23.5 (CH_2), 27.1 (CH_2), 28.0 (CH_2), 28.9 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 37.4 (CH_2), 64.3 (CH_2), 119.9 (CH), 141.0 (C), 171.5 (C). **GC-MS** (EI) 196 ($[M]^+$, 1%), 136 (89%), 121 (48%), 107 (100%), 93 (72%), 91 (22%), 81 (64%), 79 (98%), 77 (20%), 67 (80%), 65 (10%), 55 (28%). **HRMS** (ES+) calcd for $C_{12}H_{20}O_2Na$ $[M+Na]^+$: 219.1361, found: 219.1361.

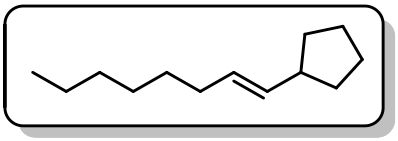


5-Methylhex-4-en-1-yl Acetate,[31] **3i** (31 mg, 48%) was prepared according to General Procedure A for photoredox cross-coupling of bromoalkene **2i** (68 mg, 0.5 mmol). The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.60 (s, 3H), 1.62 - 1.70 (m, 2H), 1.69 (s, 3H), 2.05 (q, *J* = 7.6 Hz, 2H), 2.05 (s, 3H), 4.05 (t, *J* = 6.7 Hz, 2H), 5.07 - 5.12 (m, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 17.8 (CH_3), 21.3 (CH_3), 24.5 (CH_2), 25.9 (CH_3), 28.9 (CH_2), 64.3 (CH_2), 123.4 (CH), 132.8 (C), 171.5 (C). **GC-MS** (EI) 156 ($[M]^+$,0.1%), 96 (49%), 81 (100%), 79 (10%), 69 (14%), 67 (12%), 55 (10%), 53 (6%).

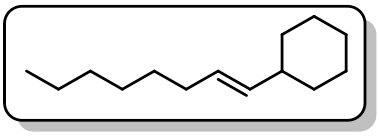


(*Z*)-6-((*tert*-Butyldimethylsilyl)oxy)hex-4-en-1-yl Acetate, 3k (121 mg, 88%) was prepared according to General Procedure A for photoredox cross-coupling of bromoalkene **2k** (126 mg, 0.5 mmol). The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.07 (s, 6H), 0.90 (s, 9H), 1.66 - 1.74 (m, 2H), 2.05 (s, 3H), 2.12 (q, *J* = 7.3 Hz, 2H), 4.06 (t, *J* = 6.6 Hz, 2H), 4.22 (dt, *J* = 6.1, 0.8 Hz, 2H), 5.37 - 5.46 (m, 1H), 5.52 - 5.61 (m, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ -4.9 (CH_3), 18.6 (C), 21.2 (CH_3), 24.2 (CH_2), 26.2 (CH_3), 28.7 (CH_2), 59.5 (CH_2), 64.1 (CH_2), 129.5 (CH), 130.9 (CH), 171.3 (C). **GC-MS** (EI) 272 ($[M]^+$, 0.1%), 215 (22%), 173 (9%), 159 (4%), 117 (100%), 99 (6%), 81 (69%), 79 (18%), 75 (55%), 73 (19%), 59 (5%), 53 (5%). **HRMS** (ES+) calcd for $C_{14}H_{28}O_3SiNa$ $[M+Na]^+$: 295.1705, found: 295.1704.

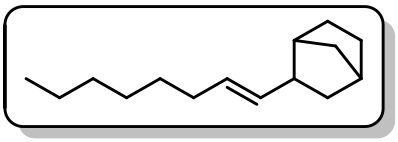
[31] Wang, Z. J.; Jackson, W. R.; Robinson, A. J. *Org. Lett.* **2013**, *15*, 3006.



(*E*)-Oct-1-en-1-ylcyclopentane,[32] **3l** (62 mg, 68%) was prepared according to General Procedure A for photoredox cross-coupling of iodoalkene **2a** (119 mg, 0.5 mmol) and cyclopentylsilicate **1b** (249 mg, 0.006 mol, 1.2 equiv) ***with the following modifications***: 1) Pentane was used in place of Et_2O during the extraction. 2) Pentane was used as the eluant for the SiO_2 plug. The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.20 - 1.38 (m, 10H), 1.49 - 1.58 (m, 2H), 1.58 - 1.68 (m, 2H), 1.70 - 1.79 (m, 2H), 1.92 - 2.00 (m, 2H), 2.32 - 2.43 (m, 1H), 5.30 - 5.46 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 14.4 (CH_3), 22.9 (CH_2), 25.4 (CH_2), 29.1 (CH_2), 29.9 (CH_2), 32.0 (CH_2), 32.8 (CH_2), 33.5 (CH_2), 43.6 (CH), 128.7 (CH), 135.2 (CH). **GC-MS** (EI) 180 ([M]$^+$, 23%),123 (10%), 109 (11%), 85 (87%), 82 (67%), 79 (18%), 67 (100%), 55 (24%). **HRMS** (CI+) calcd for $C_{13}H_{24}$ [M]$^+$: 180.1878, found: 180.1871

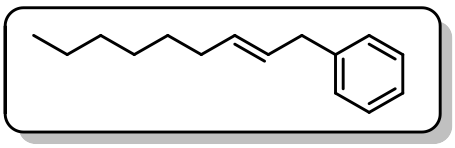


(*E*)-Oct-1-en-1-ylcyclohexane,[33] **3m** (72 mg, 74%) was prepared according to General Procedure A for photoredox cross-coupling of iodoalkene **2a** (119 mg, 0.5 mmol) and cyclohexylsilicate **1c** (258 mg, 0.006 mol, 1.2 equiv) ***with the following modifications***: 1) Pentane was used in place of Et_2O during the extraction 2) Pentane was used as the eluant for the SiO_2 plug. The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.88 (t, *J* = 7.3 Hz, 3H), 1.04 (qd, *J* = 12.4, 4.0 Hz, 2H), 1.15 (tt, *J* = 12.3, 3.2 Hz, 1H), 1.20 - 1.35 (m, 10H), 1.60 - 1.65 (m, 1H), 1.66 - 1.73 (m, 4H), 1.88 (t, *J* = 11.1 Hz, 1H), 1.93 - 1.99 (m, 2H), 5.28 - 5.40 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 14.3 (CH_3), 22.9 (CH_2), 26.4 (CH_2), 26.5 (CH_2), 29.1 (CH_2), 29.9 (CH_2), 32.0 (CH_2), 32.9 (CH_2), 33.6 (CH_2), 40.9 (CH), 128.0 (CH), 136.6 (CH). **GC-MS** (EI) 194 ([M]$^+$, 40%), 166 (4%), 138 (4%) 124 (7%), 109 (68%), 96 (100%), 81 (95%), 79 (20%), 67 (93%), 55 (36%). **HRMS** (CI+) calcd for $C_{14}H_{26}$ [M]$^+$: 194.2035, found: 194.2034.

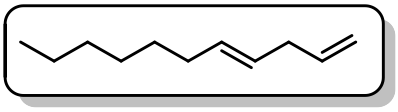


(*E*)-2-(Oct-1-en-1-yl)bicyclo[2.2.1]heptane, (±)-3n (78 mg, 76%) was prepared according to General Procedure A for photoredox cross-coupling of iodoalkene **2a** (119 mg, 0.5 mmol) and bicycloheptylsilicate **1d** (265 mg, 0.006 mol, 1.2 equiv) ***with the following modifications***: 1) Pentane was used in place of Et_2O during the extraction. 2) Pentane was used as the eluant for the SiO_2 plug. The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.88 (t, *J* = 6.9 Hz, 3 H), 1.05 - 1.17 (m, 2 H), 1.18 - 1.36 (m, 11 H), 1.41 - 1.53 (m, 3 H), 1.89 - 2.08 (m, 4 H), 2.20 (br s, 1 H), 5.29 - 5.32 (m, 2 H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 14.3 (CH_3), 22.9 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.9 (CH_2), 30.0 (CH_2), 32.0 (CH_2), 32.8 (CH_2), 35.8 (CH_2), 36.9 (CH), 38.3 (CH_2), 43.1 (CH), 45.2 (CH), 128.0 (CH), 136.3 (CH). **GC-MS** (EI) 206 ([M]$^+$, 28%), 178 (8%), 149 (18%), 135 (13%), 121 (63%), 110 (10%), 108 (13%), 95 (56%), 91 (19%), 82 (18%), 80 (100%), 77 (16%), 67 (78%), 55 (22%). **HRMS** (CI+) calcd for $C_{15}H_{26}$ [M]$^+$: 206.2035, found: 206.2038.

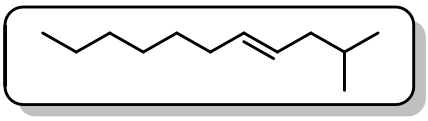
[32] Brown, H. C.; Basavaiah, D. *J. Org. Chem.* **1982**, *47*, 754.
[33] Noble, A.; McCarver, S. J.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2015**, *137*, 624.



(*E*)-Non-2-en-1-ylbenzene,[33] **3o** (71 mg, 70%) was prepared according to General Procedure A for photoredox cross-coupling of iodoalkene **2a** (119 mg, 0.5 mmol) and benzylpentylsilicate **1e** (263 mg, 0.006 mol, 1.2 equiv) ***with the following modifications***: 1) Pentane was used in place of Et_2O during the extraction. 2) Pentane was used as the eluant for the SiO_2 plug. The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.89 (t, *J* = 6.7 Hz, 3H), 1.21 - 1.33 (m, 6H), 1.33-1.41 (m, 2H), 2.03 (q, *J* = 6.8 Hz, 2H), 3.34 (d, *J* = 6.1 Hz, 2H), 5.44 - 5.62 (m, 2H), 7.17 - 7.21 (m, 3H), 7.29 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 14.3 (CH_3), 22.9 (CH_2), 29.1 (CH_2), 29.7 (CH_2), 32.0 (CH_2), 32.8 (CH_2), 39.3 (CH_2), 126.1 (CH), 128.6 (CH), 128.7 (CH), 128.9 (CH), 132.4 (CH), 141.4 (C). **GC-MS** (EI) 202 ($[M]^+$, 31%), 131 (11%), 129 (10%), 117 (70%), 115 (18%), 104 (100%) 91 (53%),77 (5%),69 (8%), 55 (5%). **HRMS** (CI+) calcd for $C_{15}H_{22}$ $[M]^+$: 202.1722, found: 202.1724.

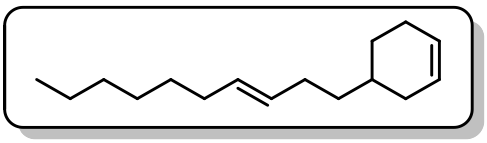


(*E*)-Undeca-1,4-diene,[34] **3p** (26 mg, 32%) was prepared according to General Procedure A for photoredox cross-coupling of iodoalkene **2a** (119 mg, 0.5 mmol) and benzylpentylsilicate **1f** (233 mg, 0.006 mol, 1.2 equiv) ***with the following modifications***: 1) Pentane was used in place of Et_2O during the extraction. 2) Pentane was used as the eluant for the SiO_2 plug. The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.88 (t, *J* = 7.1 Hz, 3H), 1.16 - 1.43 (m, 8H), 2.00 (q, *J* = 7.1 Hz, 2H), 2.67 - 2.78 (m, 2H), 4.97 (ddt, *J* = 10.1, 2.1, 1.1 Hz, 1H), 5.02 (dq, *J* = 17.1, 1.7 Hz, 1H), 5.33 - 5.52 (m, 2H), 5.83 (ddt, *J* = 16.9, 10.2, 6.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 14.3 (CH_3), 22.9 (CH_2), 29.1 (CH_2), 29.7 (CH_2), 32.0 (CH_2), 32.8 (CH_2), 37.0 (CH_2), 114.9 (CH_2), 127.7 (s, 4 C), 132.1 (s, 4 C), 137.8 (s, 3 C). **GC-MS** (EI) 152 ($[M]^+$, 16%), 124 (13%), 110 (14%), 95 (29%), 81 (83%), 79 (44%), 67 (100%), 54 (84%). **HRMS** (APCI) calcd for $C_{11}H_{20}$ $[M]^+$: 152.1565, found: 152.1559.

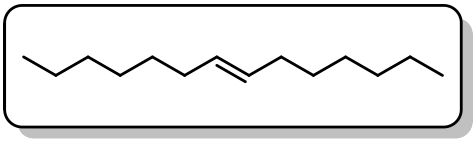


(*E*)-2-Methylundec-4-ene, 3q (72 mg, 86%) was prepared according to General Procedure A for photoredox cross-coupling of iodoalkene **2a** (119 mg, 0.5 mmol) and isobutylpentylsilicate **1g** (242 mg, 0.006 mol, 1.2 equiv) ***with the following modifications***: 1) Pentane was used in place of Et_2O during the extraction. 2) Pentane was used as the eluant for the SiO_2 plug. The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.87 (d, *J* = 6.4 Hz, 6H), 0.88 (t, *J* = 6.7 Hz, 3H), 1.17 - 1.38 (m, 8H), 1.57 (sept, *J* = 6.8 Hz, 1H), 1.86 (t, *J* = 5.6 Hz, 2H), 1.98 (q, *J* = 5.2 Hz, 2H), 5.32 - 5.43 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 14.3 (CH_3), 22.5 (CH_3), 22.9 (CH_2), 28.8 (CH_2), 29.1 (CH_2), 29.9 (CH), 32.0 (CH_2), 32.9 (CH_2), 42.3 (CH_2), 129.2 (CH), 131.9 (CH). **GC-MS** (EI) 168 ($[M]^+$, 34%), 153 (3%), 112 (9%), 97 (20%), 83 (48%), 69 (100%), 56 (93%) **HRMS** (CI+) calcd for $C_{12}H_{25}$ $[M+H]^+$: 169.1956, found: 169.1950.

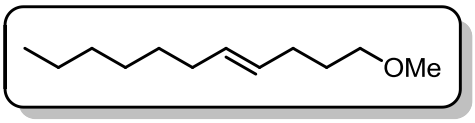
[34] Wilson, S. R.; Zucker, P. A. *J. Org. Chem.* **1988**, *53*, 4682.



(*E*)-4-(Dec-3-en-1-yl)cyclohex-1-ene, 3r (88 mg, 80%) was prepared according to General Procedure A for photoredox cross-coupling of iodoalkene **2a** (119 mg, 0.5 mmol) and (2-(3-cyclohexenyl)ethyl)silicate **1h** (263 mg, 0.006 mol, 1.2 equiv) ***with the following modifications***: 1) Pentane was used in place of Et_2O during the extraction. 2) Pentane was used as the eluant for the SiO_2 plug. The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.17 - 1.38 (m, 11H), 1.50 - 1.59 (m, 1H), 1.60 - 1.68 (m, 1H), 1.70 - 1.77 (m, 1H), 1.94 - 1.99 (m, 2H), 2.00 - 2.06 (m, 4H), 2.06 - 2.13 (m, 1H), 5.34 - 5.46 (m, 2H), 5.65 (s, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 14.3 (CH_3), 22.9 (CH_2), 25.5 (CH_2), 29.1 (CH_2, CH overlapping), 29.9 (CH_2), 30.2 (CH_2), 32.0 (CH_2), 32.1 (CH_2), 32.9 (CH_2), 33.2 (CH_2), 36.9 (CH_2), 126.9 (CH), 127.3 (CH), 130.6 (CH), 130.6 (CH). **GC-MS** (EI) 220 ($[M]^+$, 14%), 178 (14%), 135 (31%), 121 (64%),107 (18%), 94 (45%), 91 (12%), 79 (100%), 69 (13%), 67 (44%), 55 (27%). **HRMS** (CI+) calcd for $C_{16}H_{28}$ $[M]^+$: 220.2191, found: 220.2182.

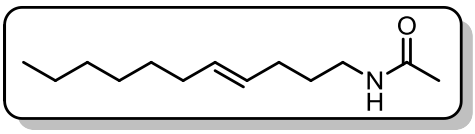


(*E*)-Tetradec-7-ene,[35] 3s (61 mg, 62%) was prepared according to General Procedure A for photoredox cross-coupling of iodoalkene **2a** (119 mg, 0.5 mmol) and (2-hexylsilicate **1i** (263 mg, 0.006 mol, 1.2 equiv) ***with the following modifications***: 1) Pentane was used in place of Et_2O during the extraction. 2) Pentane was used as the eluant for the SiO_2 plug. The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.88 (t, *J* = 7.0 Hz, 6H) 1.18 - 1.41 (m, 16H) 1.85 - 2.06 (m, 4H) 5.39 (tt, *J* = 3.5, 1.6 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 14.4 (CH_3), 23.0 (CH_2), 29.1 (CH_2), 29.9 (CH_2), 32.1 (CH_2), 32.9 (CH_2), 130.7 (CH). **GC-MS** (EI) 196 ($[M]^+$, 24%), 125 (6%), 111 (22%), 97 (51%), 83 (72%), 69 (100%), 55 (92%) **HRMS** (CI+) calcd for $C_{14}H_{28}$ $[M]^+$: 196.2191, found: 196.2182.

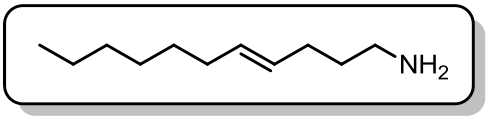


(*E*)-1-Methoxyundec-4-ene, 3t (78 mg, 85%) was prepared according to General Procedure A for photoredox cross-coupling of iodoalkene **2a** (119 mg, 0.5 mmol) and (3-methoxypropyl)silicate **1j** (252 mg, 0.006 mol, 1.2 equiv). The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.21 - 1.37 (m, 8H), 1.59 - 1.67 (m, 2H), 1.97 (q, *J* = 6.8 Hz, 2H), 2.04 (q, *J* = 6.8 Hz, 2H), 3.33 (s, 3H), 3.37 (t, *J* = 6.7 Hz, 2H), 5.30 - 5.48 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 14.3 (CH_3), 22.9 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 32.0 (CH_2), 32.8 (CH_2), 58.8 (CH_3), 72.5 (CH_2), 129.6 (CH), 131.3 (CH). **GC-MS** (EI) 184 ($[M]^+$,1 %), 152 (31%), 110 (15%), 95 (30%), 81 (80%), 79 (22%), 71 (36%), 68 (100%), 58 (36%), 55 (36%). **HRMS** (CI+) calcd for $C_{12}H_{22}$ $[M\text{-}H_2O]^+$: 166.1711, found: 166.1706.

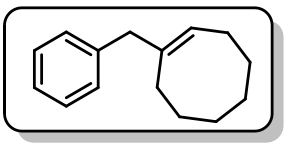
[35] Collazo, L. R.; Guziec, F. S. *J. Org. Chem.* **1993**, *58*, 43.



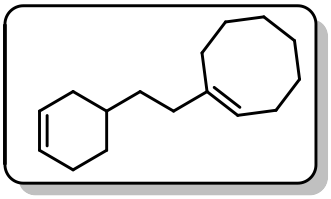
(*E*)-*N*-(Undec-4-en-1-yl)acetamide, 3u (78 mg, 74%) was prepared according to General Procedure A for photoredox cross-coupling of iodoalkene **2a** (119 mg, 0.5 mmol) and (3-acetamidopropyl)silicate **1k** (268 mg, 0.006 mol, 1.2 equiv) ***with the following modifications***: 1) EtOAc and saturated Na_2CO_3 were used in place of Et_2O and 2 M NaOH during the extraction. 2) Further purification was accomplished by SiO_2 column chromatography (gradient hexane to 50:50 hexane/EtOAc). The desired cross-coupled alkene was obtained as a clear, light brown oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.18 - 1.35 (m, 8H), 1.51 - 1.59 (m, 2H), 1.90 - 1.97 (m, 5H), 2.00 (dt, *J* = 13.8, 6.6 Hz, 2H), 3.22 (q, *J* = 6.6 Hz, 2H), 5.27 - 5.48 (m, 2H), 5.74 (br s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 14.3 (CH_3), 22.8 (CH_3), 23.5 (CH_2), 29.0 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 30.2 (CH_2), 31.9 (CH_2), 32.7 (CH_2), 39.5 (CH_2), 129.1 (CH), 131.7 (CH), 170.2 (C). **GC-MS** (EI) 211 ($[M]^+$, 28%), 168 (7%), 154 (7%), 140 (13%), 126 (8%), 112 (9%), 110 (10%), 98 (20%), 95 (23%), 87 (21%), 85 (10%), 81 (58%), 73 (100%), 68 (40%), 60 (69%), 55 (28%), **HRMS** (CI+) calcd for $C_{13}H_{26}NO$ $[M+H]^+$: 212.2014, found: 212.2012.



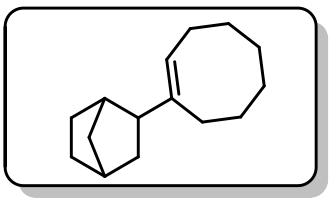
(*E*)-Undec-4-en-1-amine, 3w (25 mg, 27%) was prepared according to General Procedure B for photoredox cross-coupling of iodoalkene **2a** (119 mg, 0.5 mmol) and ammonium propylsilicate **1j** (182 mg, 0.006 mol, 1.2 equiv) ***with the following modifications***: 1) EtOAc and saturated Na_2CO_3 were used in place of Et_2O and 2 M NaOH during the extraction. 2) Saturated Na_2CO_3 in deionized H_2O was used in place of deionized H_2O at the start of the workup. 3) Further purification was accomplished by SiO_2 column chromatography [gradient 99:1 to 90:10 CH_2Cl_2/MeOH containing NH_4OH (1 %, *v*/*v*)]. The desired cross-coupled alkene was obtained as a clear, light brown oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.20 - 1.36 (m, 9H), 1.39 - 1.55 (br. m, 3H), 1.96 (q, *J* = 6.3 Hz, 2H), 1.98 - 2.05 (m, 2H), 2.68 (t, *J* = 6.9 Hz, 2H), 5.30 - 5.47 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 14.3 (CH_3), 22.9 (CH_2), 29.1 (CH_2), 29.8 (CH_2), 30.1 (CH_2), 32.0 (CH_2), 32.8 (CH_2), 33.8 (CH_2), 42.0 (CH_2), 129.8 (CH), 131.2 (CH). **HRMS** (ES+) calcd for $C_{11}H_{23}N$ $[M+H]^+$: 170.1909, found: 170.1914. **FT-IR** (cm^{-1}, neat, ATR) 3357 (vw br) 3027 (vw br) 1812 (vs) 2853 (s) 1558 (s br) 1487 (s) 1467 (s) 1251 (m) 965 (s) 740 (s).



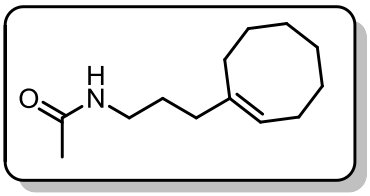
(*E*)-1-Benzylcyclooct-1-ene, 3x (55 mg, 54%) was prepared according to General Procedure A for photoredox cross-coupling of bromoalkene **2g** (95 mg, 0.5 mmol) and benzylsilicate **1e** (263 mg, 0.006 mol, 1.2 equiv) ***with the following modifications***: 1) Pentane was used in place of Et_2O during the extraction. 2) Pentane was used as the eluant for the SiO_2 plug. The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.37 - 1.53 (m, 8 H), 2.08 - 2.15 (m, 4 H), 3.30 (s, 2 H), 5.39 (t, *J* = 8.2 Hz, 1 H), 7.17 - 7.21 (m, 3 H), 7.26 - 7.30 (m, 2 H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 26.6 (CH_2), 26.7 (CH_2), 26.8 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 30.3 (CH_2), 126.1 (CH), 126.2 (CH), 128.4 (CH), 129.5 (CH), 140.5 (C), 140.8 (C). **GC-MS** (EI) 200 ($[M]^+$, 67%) 172 (63%), 143 (22%), 129 (52%), 117 (55%), 115 (35%), 109 (96%), 104 (39%), 91 (100%), 81 (27%), 77 (15%), 67 (69%), 65 (21%), 55 (13%), 51 (7%) **HRMS** (APCI) calcd for $C_{15}H_{21}$ $[M+H]^+$: 201.1643, found: 201.1637.



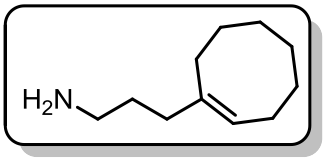
(*E*)-1-(2-(Cyclohex-3-en-1-yl)ethyl)cyclooct-1-ene, 3y (98 mg, 88%) was prepared according to General Procedure A for photoredox cross-coupling of bromoalkene **2g** (95 mg, 0.5 mmol) and (2-(3-cyclohexenyl)ethyl)silicate **1h** (273 mg, 0.006 mol, 1.2 equiv) ***with the following modifications***: 1) Pentane was used in place of Et_2O during the extraction. 2) Pentane was used as the eluant for the SiO_2 plug. The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.12 - 1.42 (m, 4H), 1.41 - 1.56 (m, 9H), 1.58 - 1.79 (m, 2H), 1.95 - 2.17 (m, 8H), 5.33 (t, *J* = 8.2 Hz, 1H), 5.65 (s, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 25.6 (CH_2), 26.6 (CH_2), 26.8 (CH_2), 29.2 (CH), 29.2 (CH_2), 29.2 (CH_2), 30.3 (CH_2), 32.2 (CH_2), 33.7 (CH_2), 35.1 (CH_2), 35.5 (CH_2), 123.7 (CH), 127.0 (CH), 127.3 (CH), 141.4 (C). **GC-MS** (EI) 218 ($[M]^+$, 41%), 175 (11%), 147 (7%), 137 (16%), 121 (12%), 109 (15%), 94 (58%), 91 (21%), 81 (75%), 79 (100%), 69 (26%), 67 (48%), 55 (27%), 53 (15%). **HRMS** (CI+) calcd for $C_{16}H_{26}$ $[M]^+$: 218.2035, found: 218.2030.



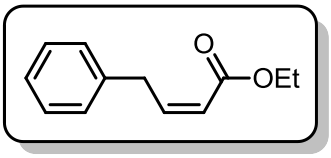
(*E*)-2-(Cyclooct-1-en-1-yl)bicyclo[2.2.1]heptane, 3z (76 mg, 75%) was prepared according to General Procedure A for photoredox cross-coupling of bromoalkene **2g** (95 mg, 0.5 mmol) and bicycloheptylsilicate **1d** (265 mg, 0.006 mol, 1.2 equiv) ***with the following modifications***: 1) Pentane was used in place of Et_2O during the extraction. 2) Pentane was used as the eluant for the SiO_2 plug. The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.01 - 1.10 (m, 1H), 1.13 - 1.21 (m, 2H), 1.33 - 1.38 (m, 1H), 1.40 (d, *J* = 7.0 Hz, 2H), 1.43 - 1.56 (m, 10H), 1.99 (t, *J* = 7.2 Hz, 1H), 2.06 - 2.23 (m, 6H), 5.28 (td, *J* = 8.1, 1.2 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 26.5 (CH_2), 26.7 (CH_2), 26.9 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 29.7 (CH_2), 30.3 (CH_2), 30.8 (CH_2), 36.1 (CH_2), 36.8 (CH_2), 36.9 (CH), 40.3 (CH), 48.2 (CH), 120.7 (CH), 144.7 (C). **GC-MS** (EI) 204 ($[M]^+$, 39 %), 176 (29%), 161 (15%), 147 (15%), 121 (32%), 108 (17%), 95 (42%), 93 (34%), 91 (33%), 80 (100%),77 (22%), 67 (51%) 55 (16%). **HRMS** (CI+) calcd for $C_{15}H_{24}$ $[M]^+$: 204.1878, found: 204.1873.



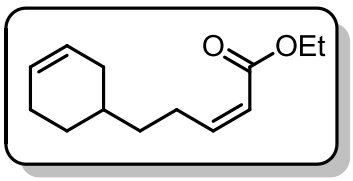
(*E*)-*N*-(3-(Cyclooct-1-en-1-yl)propyl)acetamide, 3aa (99 mg, 94%) was prepared according to General Procedure A for photoredox cross-coupling of bromoalkene **2g** (95 mg, 0.5 mmol) and (3-acetamidopropyl)silicate **1k** (268 mg, 0.006 mol, 1.2 equiv) ***with the following modifications***: 1) EtOAc and saturated Na_2CO_3 were used in place of Et_2O and 2 M NaOH during the extraction. 2) Further purification was accomplished by SiO_2 column chromatography (gradient hexane to 50:50 hexane/EtOAc). The desired cross-coupled alkene was obtained as a clear, pale yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.37 - 1.52 (m, 8H), 1.55 - 1.63 (m, 2H), 1.94 (s, 3H), 1.98 (t, *J* = 7.9 Hz, 2H), 2.02 - 2.08 (m, 2H), 2.08 - 2.15 (m, 2H), 3.21 (q, *J* = 6.8 Hz, 2H), 5.32 (t, *J* = 8.1 Hz, 1H), 5.75 (br s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 23.5 (CH_3), 26.4 (CH_2), 26.5 (CH_2), 26.7 (CH_2), 28.1 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 30.1 (CH_2), 34.9 (CH_2), 39.8 (CH_2), 124.6 (CH), 140.0 (C), 170.2 (C). **GC-MS** (EI) 209 ($[M]^+$, 8%), 150 (100%), 135 (34%), 122 (68%), 109 (21%), 107 (20%), 95 (27%), 93 (29%), 86 (15%), 81 (31%), 79 (32%), 73 (36%), 67 (33%), 60 (22%), 55 (15%). **HRMS** (ES+) calcd for $C_{13}H_{24}NO$ $[M+H]^+$: 210.1858, found: 210.1857.



(*E*)-3-(Cyclooct-1-en-1-yl)propan-1-amine, 3ab (84 mg, 25%) was prepared according to General Procedure B for photoredox cross-coupling of bromoalkene **2g** (95 mg, 0.5 mmol) and ammonium propylsilicate **1j** (182 mg, 0.006 mol, 1.2 equiv) ***with the following modifications***: 1) EtOAc and saturated aq Na_2CO_3 were used in place of Et_2O and 2 M NaOH during the extraction. 2) Saturated aq Na_2CO_3 was used in place of deionized H_2O at the start of the workup. 3) Further purification was accomplished by SiO_2 column chromatography (gradient 99:1 to 90:10 CH_2Cl_2/MeOH containing NH_4OH (1 %, *v*/*v*). The desired cross-coupled alkene was obtained as a clear, light brown oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.41 - 1.56 (m, 9H), 1.56 - 1.67 (m, 2H), 1.99 - 2.05 (m, 2H), 2.04 - 2.12 (m, 3H), 2.12 - 2.23 (m, 2H), 2.50 (br s, 1H), 2.68 - 2.82 (m, 1H), 5.35 (t, *J* = 7.8 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 26.5 (CH_2), 26.8 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 30.2 (CH_2), 31.7 (CH_2), 34.9 (CH_2), 38.8 (CH_2), 42.1 (CH_2), 124.3 (CH), 140.4 (C). **HRMS** (ES+) calcd for $C_{11}H_{21}N$ $[M+H]^+$: 168.1752, found:168.1754. **FT-IR** (cm^{-1}, neat, ATR) 3303 (w, br) 3036 (vw) 2919 (vs) 2848 (s) 1573 (s) 1467 (s), 1304 (s) 818 (w).



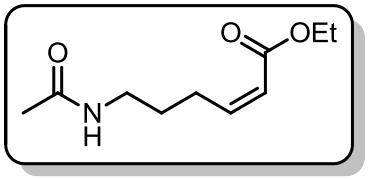
(*Z*)-Ethyl 4-Phenylbut-2-enoate,[36] 3ac (91 mg, 90%) was prepared according to General Procedure A for photoredox cross-coupling of bromoalkene **2f** (90 mg, 0.5 mmol) and benzylsilicate **1d** (263mg, 0.006 mol, 1.2 equiv). The desired cross-coupled alkene was obtained as a clear, yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.32 (t, *J* = 7.0 Hz, 3H), 4.03 (dd, *J* = 7.6, 1.5 Hz, 2H), 4.22 (q, *J* = 7.6 Hz, 2H), 5.85 (dt, *J* = 11.3, 1.5 Hz, 1H), 6.35 (dt, *J* = 11.3, 7.6 Hz, 1H), 7.21 - 7.25 (m, 3H), 7.30 (t, *J* = 7.3 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 14.5 (CH_3), 35.4 (CH_2), 60.3 (CH_2), 120.2 (CH), 126.6 (CH), 128.8 (CH), 139.7 (C), 148.2 (CH), 166.7 (C). **GC-MS** (EI) 190 ($[M]^+$, 76%), 162 (14%), 144 (55%), 133 (38%), 127 (16%), 117 (72%), 115 (100%), 105 (11%), 91 (40%), 89 (12%), 77 (10%), 65 (19%), 58 (8%), 51 (9%). **HRMS** (ES+) calcd for $C_{12}H_{14}O_2Na$ $[M+Na]^+$: 213.0891, found: 213.0896.



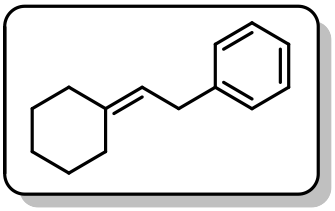
(*Z*)-Ethyl 5-(Cyclohex-3-en-1-yl)pent-2-enoate, 3ad (98 mg, 93%) was prepared according to General Procedure A for photoredox cross-coupling of bromoalkene **2f** (90 mg, 0.5 mmol) and (2-(3-cyclohexenyl)ethyl)silicate **1h** (273 mg, 0.006 mol, 1.2 equiv). The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.19 - 1.34 (m, 1H), 1.30 (t, *J* = 6.8 Hz, 3H), 1.39 - 1.46 (m, 2H), 1.54 - 1.62 (m, 1H), 1.64 - 1.73 (m, 1H), 1.74 - 1.82 (m, 1H), 2.01 - 2.09 (m, 2H), 2.10 - 2.17 (m, 1H), 2.71 (qt, *J* = 7.7, 1.7 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 5.66 (s, 2H), 5.76 (dt, *J* = 11.5, 1.6 Hz, 1H), 6.23 (dt, *J* = 11.5, 7.5 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 14.5 (CH_3), 25.4 (CH_2), 26.8 (CH_2), 29.0 (CH), 31.9 (CH_2), 33.5 (CH_2), 36.1 (CH_2), 60.0 (CH_2), 119.9 (CH), 126.7 (CH), 127.3 (CH), 150.9 (CH), 166.7 (C). **GC-MS** (EI) 208 ($[M]^+$, 7%), 162 (26%), 144 (13%), 134 (61%), 127 (61%), 120 (85%), 114 (51%), 105 (16%), 101 (40%), 99 (79%), 93 (47%), 91 (53%), 86 (48%), 81 (61%), 79 (100%), 73 (21%), 67

[36] Ghosh, A. K.; Nicponski, D. R. *Org. Lett.* **2011**, *13*, 4328.

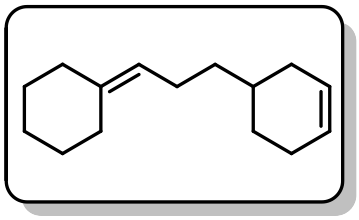
(53%) 55 (32%), 53 (37%). **HRMS** (ES+) calcd for $C_{13}H_{21}O_2$ $[M+H]^+$: 209.1542, found: 209.1545.



(*Z*)-Ethyl 6-Acetamidohex-2-enoate, 3af (63 mg, 63%) was prepared according to General Procedure A for photoredox cross-coupling of bromoalkene **2f** (90 mg, 0.5 mmol) and 3-acetamidopropyl)silicate **1k** (268 mg, 0.006 mol, 1.2 equiv) ***with the following modifications***: 1) EtOAc and saturated Na_2CO_3 were used in place of Et_2O and 2 M NaOH during the extraction. 2) Further purification was accomplished by SiO_2 column chromatography (gradient hexane to 40:60 hexane/EtOAc). The desired cross-coupled alkene was obtained as a clear, yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.26 (t, *J* = 7.1 Hz, 3H), 1.59 - 1.67 (m, 2H), 1.94 (s, 3H), 2.64 (q, *J* = 7.3 Hz, 2H), 3.20 (q, *J* = 6.2 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 5.81 (dt, *J* = 11.3, 1.2 Hz, 1H), 6.17 (dt, *J* = 11.5, 8.2 Hz, 1H), 6.37 (br s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 14.4 (CH_3), 23.5 (CH_3), 26.0 (CH_2), 28.3 (CH_2), 38.3 (CH_2), 60.2 (CH_2), 121.1 (CH), 149.0 (CH), 167.0 (C), 170.4 (C). **GC-MS** (EI) 199 ($[M]^+$, 1%), 156 (79%), 125 (30%), 112 (100%), 100 (24%), 94 (42%), 86 (64%), 82 (21%), 72 (28%), 67 (31%), 60 (21%), 55 (12%). 53 (10%). **HRMS** (ES+) calcd for $C_{10}H_{18}NO_3$ $[M+H]^+$: 200.1287, found: 200.1288.



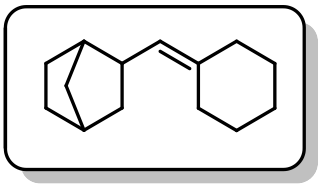
(2-Cyclohexylideneethyl)benzene,[37] 3ah (57 mg, 60%) was prepared according to General Procedure A for photoredox cross-coupling of bromoalkene **2h** (88 mg, 0.5 mmol) and benzylsilicate **1e** (263 mg, 0.006 mol, 1.2 equiv) ***with the following modifications***: 1) Pentane was used in place of Et_2O during the extraction. 2) Pentane was used as the eluant for the SiO_2 plug. The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.54 - 1.63 (m, 6H), 2.11 - 2.17 (m, 2H), 2.27 (t, *J* = 5.2 Hz, 2H), 3.38 (d, *J* = 7.3 Hz, 2H), 5.29 (tt, *J* = 7.4, 1.1 Hz, 1H), 7.16 - 7.22 (m, 3H), 7.27 - 7.32 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 27.2 (CH_2), 28.1 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 33.6 (CH_2), 37.4 (CH_2), 120.0 (CH), 125.9 (CH), 128.6 (CH), 128.6 (CH), 140.8 (C), 142.2 (C). **GC-MS** (EI) 186 ($[M]^+$, 57%), 143 (13%), 129 (28%), 117 (13%), 115 (15%), 104 (100%), 95 (17%), 91 (32%), 79 (10%), 67 (11%), 55 (3%), 51 (4%). **HRMS** (APCI) calcd for $C_{14}H_{19}$ $[M+H]^+$: 187.1487, found: 187.1481.



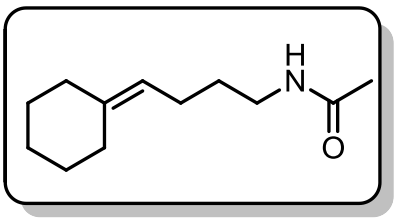
4-(3-Cyclohexylidenepropyl)cyclohex-1-ene, 3ai (80 mg, 78%) was prepared according to General Procedure A for photoredox cross-coupling of bromoalkene **2h** (88 mg, 0.5 mmol) and (2-(3-cyclohexenyl)ethyl)silicate **1h** (273 mg, 0.006 mol, 1.2 equiv) ***with the following modifications***: 1) Pentane was used in place of Et_2O during the extraction. 2) Pentane was used as the eluant for the SiO_2 plug. The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.17 - 1.33 (m, 4H), 1.46 - 1.58 (m, 7H), 1.59 - 1.69 (m, 1H), 1.70 - 1.78 (m, 1H), 1.98 - 2.09 (m, 6H), 2.09 - 2.14 (m, 2H), 5.06 (t, *J* = 7.2 Hz,

[37] Perez-Aguilar, M. C.; Valdes, C. *Angew. Chem., Int. Ed.* **2012**, *51*, 5953.

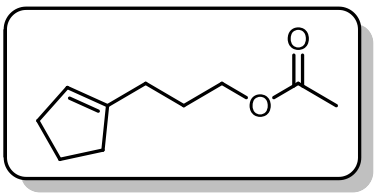
1H), 5.61 - 5.69 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 24.6 (CH_2), 25.6 (CH_2), 27.2 (CH_2), 28.1 (CH_2), 28.9 (CH_2), 29.0 (CH), 29.1 (CH_2), 32.2 (CH_2), 33.3 (CH_2), 37.4 (CH_2), 37.5 (CH_2), 121.7 (CH), 127.0 (CH), 127.3 (CH), 139.7 (CH). **GC-MS** (EI) 204 ($[M]^+$, 40%), 161 (10%), 148 (6%), 135 (5%), 121 (21%), 108 (21%), 94 (53%), 91 (16%), 79 (100%), 67 (58%), 65 (9%), 55 (24%), 53 (14%). **HRMS** (CI+) calcd for $C_{15}H_{24}$ $[M]^+$: 204.1878, found: 204.1870.



2-(Cyclohexylidenemethyl)bicyclo[2.2.1]heptane, 3aj (85 mg, 90%) was prepared according to General Procedure A for photoredox cross-coupling of bromoalkene **2h** (88 mg, 0.5 mmol) and bicycloheptylsilicate **1d** (265 mg, 0.006 mol, 1.2 equiv) ***with the following modifications***: 1) Pentane was used in place of Et_2O during the extraction. 2) Pentane was used as the eluant for the SiO_2 plug. The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.06 - 1.24 (m, 4H), 1.33-1.41 (m, 1H), 1.44 - 1.57 (m, 9H), 1.91 (br s, 1H), 2.02 (t, *J* = 5.3 Hz, 2H), 2.12 (t, *J* = 5.9 Hz, 2H), 2.18 - 2.28 (m, 2H), 4.96 (d, *J* = 8.5 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 27.2 (CH_2), 28.1 (CH_2), 29.0 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 30.0 (CH_2), 36.2 (CH_2), 36.8 (CH_2), 37.3 (CH_2), 39.9 (CH), 40.2 (CH), 43.8 (CH), 129.1 (CH), 137.8 (C). **GC-MS** (EI) 190 ($[M]^+$, 56%), 161 (12%), 149 (10%), 147 (19%), 134 (7%), 122 (20%), 107 (30%), 105 (12%), 95 (25%), 93 (52%), 91 (34%), 80 (100%), 77 (26%), 67 (55%), 55 (16%) 53 (13%). **HRMS** (CI+) calcd for $C_{14}H_{22}$ $[M]^+$: 190.1722, found: 190.1716.

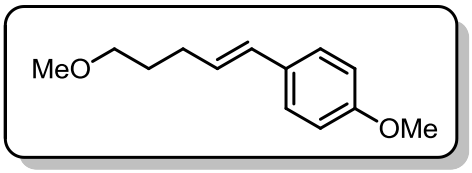


N*-(4-Cyclohexylidenebutyl)acetamide, 3ak** (77 mg, 78%) was prepared according to General Procedure A for photoredox cross-coupling of bromoalkene **2h** (88 mg, 0.5 mmol) and 3-(acetamidopropyl)silicate **1k** (268 mg, 0.006 mol, 1.2 equiv) ***with the following modifications: 1) EtOAc and saturated Na_2CO_3 were used in place of Et_2O and 2 M NaOH during the extraction. 2) Further purification was accomplished by SiO_2 column chromatography (gradient hexane to 50:50 hexane/EtOAc). The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.43 - 1.59 (m, 8H), 1.95 (s, 3H), 1.98 - 2.07 (m, 4H), 2.07 - 2.12 (m, 2H), 3.21 (q, *J* = 6.6 Hz, 2H), 5.03 (t, *J* = 7.2 Hz, 1H), 5.76 (br s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 23.5 (CH_3), 24.7 (CH_2), 27.1 (CH_2), 28.0 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 30.1 (CH_2), 37.3 (CH_2), 39.6 (CH_2), 120.3 (CH), 140.7 (C), 170.2 (C). **GC-MS** (EI) 195 ($[M]^+$, 84%), 152 (12%), 136 (80%), 121 (33%), 107 (53%), 100 (32%), 93 (40%), 91 (19%), 86 (38%), 81 (54%), 79 (58%), 73 (100%), 67 (60%), 60 (48%), 55 (23%). **HRMS** (ES+) calcd for $C_{12}H_{22}NO$ $[M+H]^+$: 196.1701, found: 196.1703.

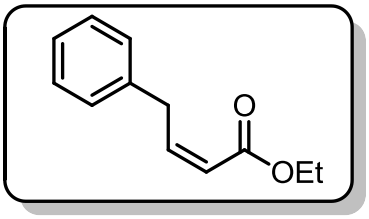


3-(Cyclopent-1-en-1-yl)propyl Acetate, 3am (42 mg, 50%) was prepared according to General Procedure A for photoredox cross-coupling of chloroalkene **2l** (51 mg, 0.5 mmol) and (3-acetoxypropylsilicate **1a** (273 mg, 0.006 mol, 1.2 equiv). The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.75 - 1.83 (m, 2H), 1.82-1.90 (m, 2H), 2.05 (s, 3H), 2.13 (t, *J* = 7.4 Hz, 2H), 2.23 (t, *J* = 7.2 Hz, 2H), 2.27 - 2.33 (m, 2H), 4.06 (t, *J* = 6.7 Hz, 2H), 5.31 - 5.39 (m, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.2 (CH_3), 23.7

(CH_2), 27.0 (CH_2), 27.7 (CH_2), 32.7 (CH_2), 35.3 (CH_2), 64.6 (CH_2), 124.2 (CH), 143.7 (C), 171.4 (C). **GC-MS** (EI) 168 ($[M]^+$, 0.1%), 108 (52%), 93 (100%), 91 (19%), 79 (57%), 77 (18%), 67 (36%) 53 (6%). **HRMS** (CI+) calcd for $C_{10}H_{17}O_2$ $[M+H]^+$: 169.1229, found: 169.1228.

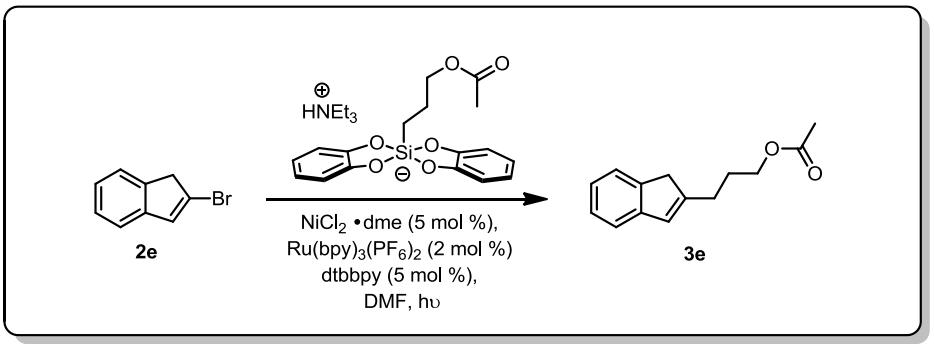


(*E*)-1-Methoxy-4-(5-methoxypent-1-en-1-yl)benzene, 3an (79 mg, 77%) was prepared according to General Procedure A for photoredox cross-coupling of chloroalkene **2m** (84 mg, 0.5 mmol) and (3-methoxypropyl)silicate **1j** (252 mg, 0.006 mol, 1.2 equiv). The desired cross-coupled alkene was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.70 - 1.78 (m, 2H), 2.26 (q, *J* = 7.3 Hz, 2H), 3.35 (s, 3H), 3.42 (t, *J* = 6.6 Hz, 2H), 3.80 (s, 3H), 6.07 (dt, *J* = 15.7, 7.0 Hz, 1H), 6.35 (d, *J* = 15.6 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 29.7 (CH_2), 29.7 (CH_2), 55.5 (CH_3), 58.8 (CH_3), 72.4 (CH_2), 114.2 (CH), 127.2 (CH), 128.2 (CH), 129.8 (CH), 130.8 (C), 159.0 (C). **GC-MS** (EI) 206 ($[M]^+$, 100%), 174 (75%), 159 (62%), 147 (85%), 143 (50%), 134 (15%), 131 (26%), 128 (19%), 121 (44%) 117 (20%), 115 (43%), 103 (20%), 91 (48%), 77 (17%), 71 (10%), 65 (8%) 51 (6%). **HRMS** (ES+) calcd for $C_{13}H_{19}O_2$ $[M+H]^+$: 207.1388, found: 207.1385.



(*Z*)-Ethyl 4-Phenylbut-2-enoate,[36] 3ac (76 mg, 80%) was prepared according to General Procedure A for photoredox cross-coupling of chloroalkene **2n** (67 mg, 0.5 mmol) and benzylsilicate **1e** (263 mg, 0.006 mol, 1.2 equiv). The desired cross-coupled alkene was obtained as a clear, yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.32 (t, *J* = 7.0 Hz, 3H) 4.03 (dd, *J* = 7.6, 1.5 Hz, 2H) 4.22 (q, *J* = 7.6 Hz, 2H) 5.85 (dt, *J* = 11.3, 1.5 Hz, 1H) 6.35 (dt, *J* = 11.3, 7.6 Hz, 1H) 7.21 - 7.25 (m, 3H) 7.30 (t, *J* = 7.3 Hz, 2H) **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 14.5 (CH_3), 35.4 (CH_2), 60.3 (CH_2), 120.2 (CH), 126.6 (CH), 128.9 (CH), 139.7 (C), 148.2 (CH), 166.7 (C). **GC-MS** (EI) 190 ($[M]^+$, 76%), 162 (14%), 144 (55%), 133 (38%), 127 (16%), 117 (72%), 115 (100%), 105 (11%), 91 (40%), 89 (12%), 77 (10%), 65 (19%), 58 (8%), 51 (9%). **HRMS** (ES+) calcd for $C_{12}H_{14}O_2Na$ $[M+Na]^+$: 213.0891, found: 213.0896.

Modified Procedure for Large Scale Cross-Coupling

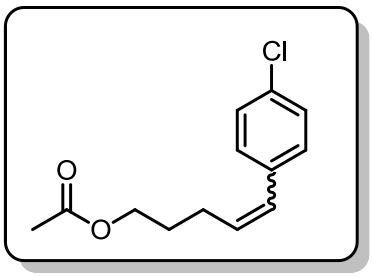


3-(1H-Inden-2-yl)propyl Acetate (3e)

To a Schlenk flask[38] equipped with an appropriately sized stir bar was added the (3-acetoxypropyl)silicate **1a** (3.05 g, 6.6 mmol, 1.2 equiv), $NiCl_2$•dme (60.4 mg, 0.025 mmol, 0.275 equiv), dtbbpy (73.8 mg, 0.025, 0.275 equiv), and $Ru(bpy)_3(PF_6)$ (94.6 mg, 0.11 mmol, 0.02 equiv). The flask was sealed with a rubber septum and evacuated three times *via* its inlet valve and purged with argon. The flask was then charged *via* a syringe with the bromide **2e** (1.07 g, 5.5 mmol, 1 equiv) dissolved in anhyd, degassed DMF (55 mL). The now bright red solution was irradiated in the aforementioned LED reactor.[39] The reaction was maintained at approximately 27 ^{o}C *via* a fan. The solution was stirred vigorously while being irradiated. Reaction progress was monitored by HPLC (or GC/MS). Once judged to be complete, the now opaque, milky-brown solution was transferred to a separatory funnel and diluted with deionized H_2O (~150 mL) and Et_2O (~100 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 × ~100 mL). The combine organic layers were washed with 2 M NaOH (2 × ~100 mL), 2 M HCl (~100 mL), deionized H_2O (~100 mL), and brine (~100 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by passing the crude material over a pad of silica, eluting with two volumes of hexane and discarding the eluate followed by 95:5 to 9:1 hexane/EtOAc to give the desired alkene, **3e**, as a clear colorless oil (0.898 g, 75%).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.96 (dt, *J* = 15.2, 6.6 Hz, 2H), 2.05 (s, 3H), 2.56 (t, *J* = 7.5 Hz, 2H), 3.32 (s, 2H), 4.13 (t, *J* = 6.6 Hz, 2H), 6.53 (s, 1H), 7.10 (td, *J* = 7.4, 1.2 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.37 (dd, *J* = 7.3, 0.5 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.2 (CH_3), 27.8 (CH_2), 28.2 (CH_2), 41.3 (CH_2), 64.3(CH_2), 120.3 (CH), 123.7 (CH), 124.0 (CH), 126.6 (CH), 127.0 (CH), 143.2 (C), 145.6 (C), 149.3 (C), 171.4 (C). **GC-MS** (EI) 216 ($[M]^+$, 35%), 156 (87%), 141 (81%), 128 (100%), 115 (52%), 102 (5%), 91 (5%), 77 (5%), 63 (4%), 51 (3%). **HRMS** (ES+) calcd for $C_{14}H_{16}O_2Na$ $[M+Na]^+$: 239.1048, found: 239.1055.

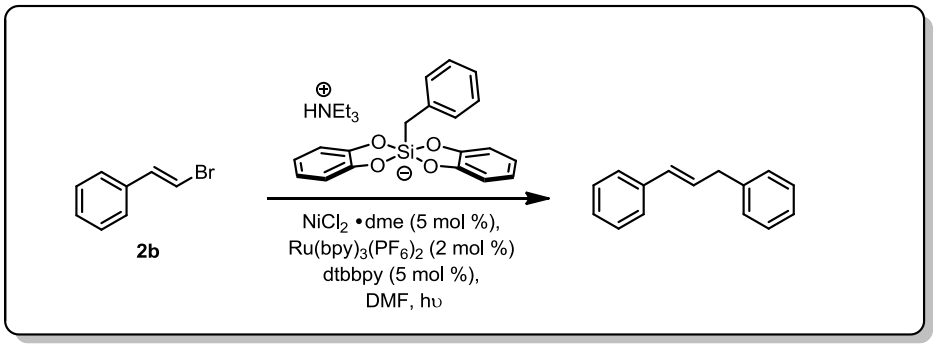
[38] Note that Schlenk flask or round bottom flask could interchangeably be used with no difference in reaction yield.
[39] Note that both blue and white LEDs can be used interchangeably with no difference in reaction yield.



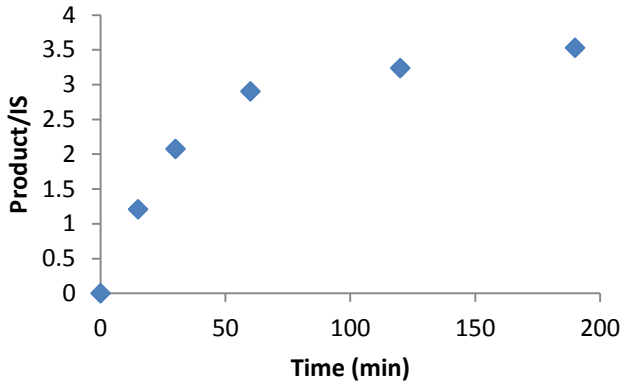
(*Z*)-5-(4-Chlorophenyl)pent-4-en-1-yl Acetate, 3d (0.833 g, 76%) was prepared according to a modified procedure for large scale photoredox cross-coupling of **2d** (1.00 g, 4.60 mmol) and (3-acetoxypropyl)silicate **1a** (2.47 g, 5.52 mmol, 1.2 equiv). The desired cross-coupled alkene was obtained as a pale yellow semi-solid. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.74 - 1.82 (m, 2H), 2.00 (s, 3H), 2.37 (qd, *J* = 7.4, 1.8 Hz, 2H), 4.07 (t, *J* = 6.6 Hz, 2H), 5.66 (dt, *J* = 11.7, 7.3 Hz, 1H), 6.41 (d, *J* = 11.7 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.1 (CH_3), 25.1 (CH_2), 28.8 (CH_2), 63.9 (CH_2), 128.5 (CH), 128.9 (CH), 130.2 (CH), 132.2 (CH), 132.6 (C), 136.0 (C), 171.2 (C). **GC-MS** (EI) 240 ($[M]^+$, ^{37}Cl 1%), 238 ($[M]^+$, ^{35}Cl 2%), 180 (^{37}Cl 10%), 178 (^{35}Cl 29%), 165 (^{37}Cl, 5%), 163 (^{35}Cl 13%), 151 (8%), 143 (100%), 128 (40%), 115 (25%), 89 (4%), 75 (3%). **HRMS** (CI+) calcd for $C_{13}H_{15}ClO_2$ [M]+: 238.0761, found: 238.0762.

Reaction Monitoring and Control Studies

Reaction Monitoring



To an 8 mL reaction vial equipped with an appropriately sized stir bar were added the silicate **1e** (268 mg, 0.6 mmol, 1.2 equiv), $NiCl_2$•dme (5.5 mg, 0.025 mmol, 0.05 equiv), dtbbpy (6.7 mg, 0.025, 0.05 equiv), $Ru(bpy)_3(PF_6)$ (8.6 mg, 0.01 mmol, 0.02 equiv), and 4,4'-di-*tert*-butylbiphenyl (internal standard, 13.3 mg, 0.05 mmol, 0.1 equiv). The vial was sealed with a cap containing a TFE-lined silicone septa and was evacuated three times *via* an inlet needle and purged with argon. The vial was then charged with the iodide **2b** (91.5 mg, 0.5 mmol, 1 equiv) dissolved in anhyd, degassed DMF (5 mL) *via* a syringe. The cap was sealed with Parafilm, and the now bright red solution was irradiated in front of a CFL. The reaction was maintained at approximately 27 ^{o}C *via* a fan. The solution was stirred vigorously while being irradiated. At each time point, 0.5 mL aliquots were taken from the reaction vessel via a syringe. Aliquots were diluted with 1.5 mL of MeCN. The reaction progress was monitored by HPLC and GC-MS. Depending on the combination of silicate and alkenyl halide, reaction times varied.



Control studies

Experiment 1

To a 2 dram reaction vial equipped with an appropriately sized stir bar were added the silicate **1e** (52 mg, 0.12 mmol, 1.2 equiv), $NiCl_2$•dme (1.1 mg, 0.005 mmol, 0.05 equiv), dtbbpy

(1.34 mg, 0.005, 0.05 equiv), and $Ru(bpy)_3(PF_6)$ (1.7 mg, 0.002 mmol, 0.02 equiv). The vial was sealed with a cap containing a TFE-lined silicone cap and was evacuated three times *via* an inlet needle and purged with argon. The vial was then charged with the iodide **2b** (91.5 mg, 0.5 mmol, 1 equiv) dissolved in anhyd, degassed DMF (5 mL) *via* a syringe. The cap was sealed with Parafilm, and the reaction vial was covered with aluminum foil. The solution was stirred vigorously in the dark. After 24 h, the reaction progress was monitored by HPLC and GC-MS, showing no formation of cross-coupled product.

Experiment 2

To a 2 dram reaction vial equipped with an appropriately sized stir bar were added the silicate **1e** (52 mg, 0.12 mmol, 1.2 equiv), $NiCl_2$•dme (1.1 mg, 0.005 mmol, 0.05 equiv), and dtbbpy (1.34 mg, 0.005, 0.05 equiv). The vial was sealed with a cap containing a TFE-lined silicone cap and was evacuated three times *via* an inlet needle and purged with argon. The vial was then charged *via* a syringe with the iodide **2b** (91.5 mg, 0.5 mmol, 1 equiv) dissolved in anhyd, degassed DMF (5 mL). The cap was sealed with Parafilm, and the now bright red solution was irradiated in front of a CFL. The reaction was maintained at approximately 27 ^{o}C *via* a fan. The solution was stirred vigorously while being irradiated. After 24 h, reaction progress was monitored by HPLC and GC-MS, showing no formation of cross-coupled product.

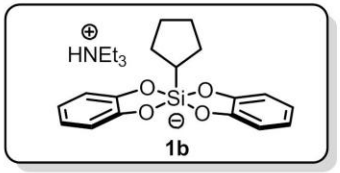
Experiment 3

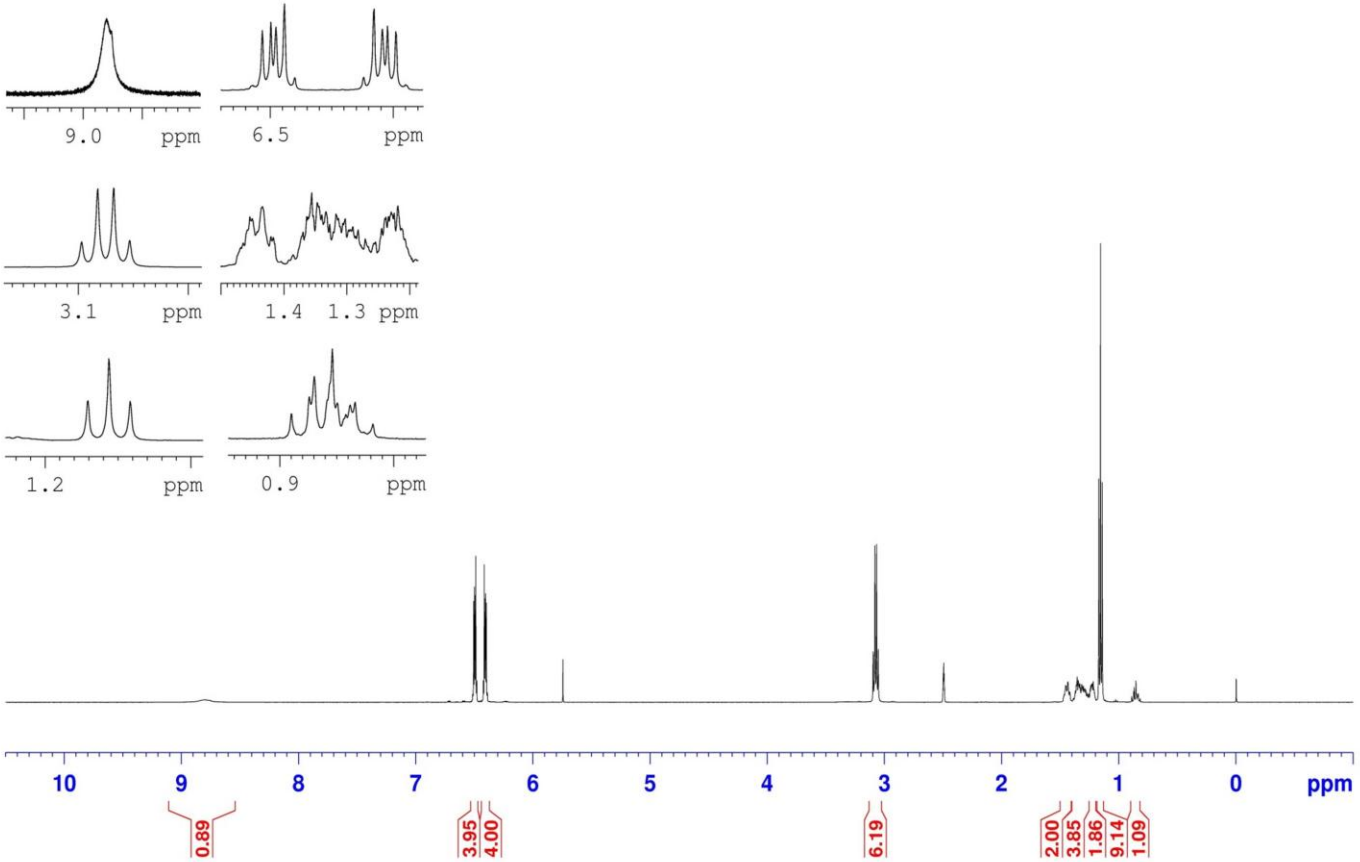
To a 2 dram reaction vial equipped with an appropriately sized stir bar were added the silicate **1e** (52 mg, 0.12 mmol, 1.2 equiv) and $Ru(bpy)_3(PF_6)$ (1.7 mg, 0.002 mmol, 0.02 equiv). The vial was sealed with a cap containing a TFE-lined silicone cap and was evacuated three times *via* an inlet needle and purged with argon. The vial was then charged *via* a syringe with the iodide **2b** (91.5 mg, 0.5 mmol, 1 equiv) dissolved in anhyd, degassed DMF (5 mL). The cap was sealed with Parafilm, and the now bright red solution was irradiated in front of a CFL. The reaction was maintained at approximately 27 ^{o}C *via* a fan. The solution was stirred vigorously while being irradiated. After 24 h, reaction progress was monitored by HPLC and GC-MS, showing trace conversion to cross-coupled product.

experiment #	conditions	yield (determined by HPLC)
1	no light	0%
2	no Ru photocatalyst	0%
3	no $NiCl_2$·dme	<5%

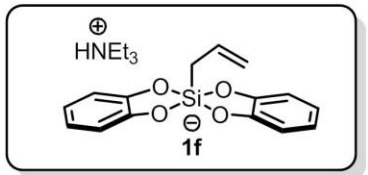
^{1}H NMR Spectra of Synthesized Compounds

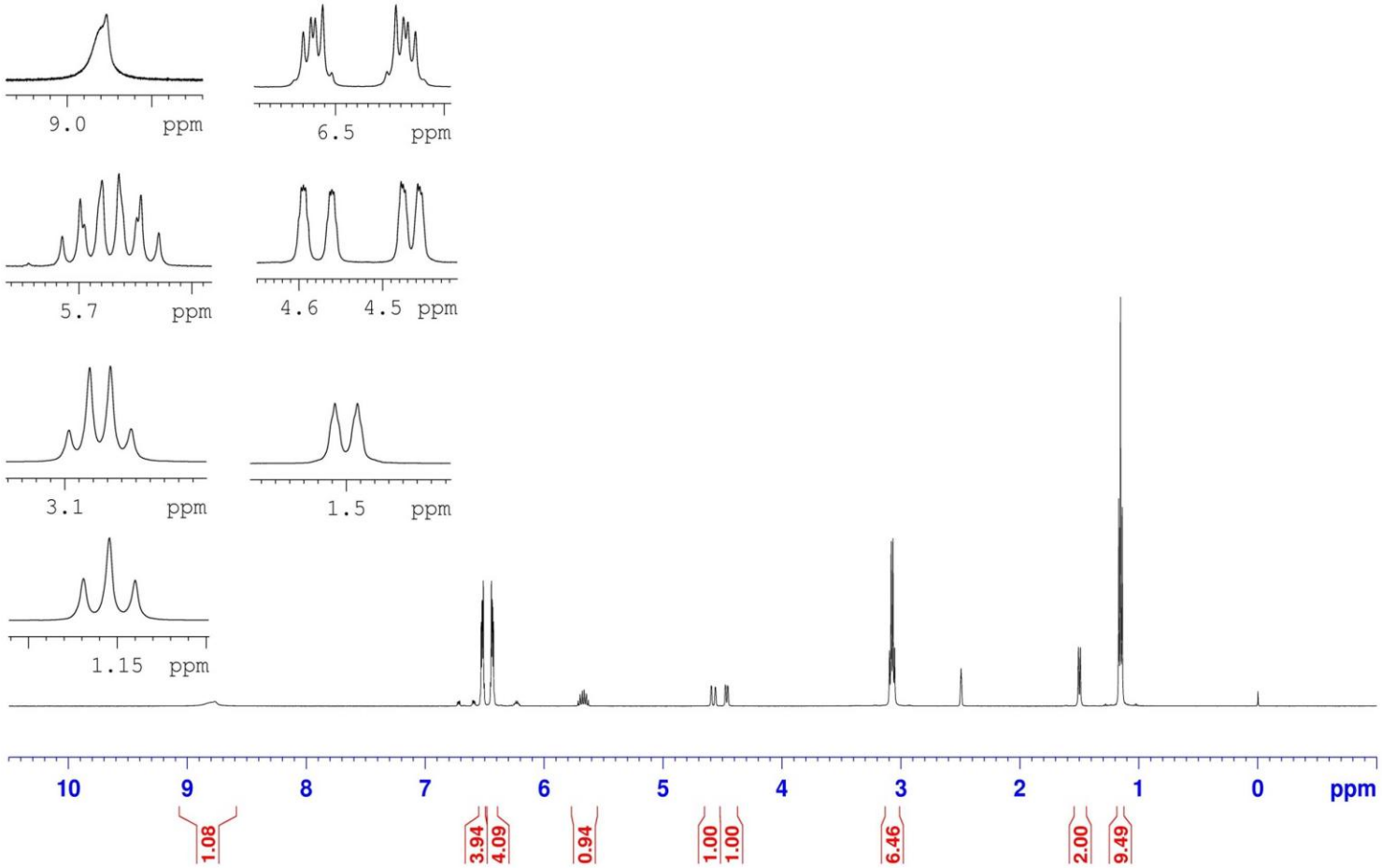
triethylammonium bis(catecholato)cyclopentylsilicate
500 MHz, DMSO–d6



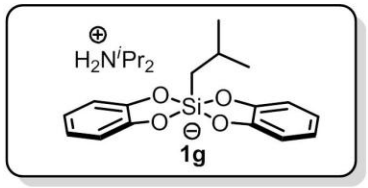


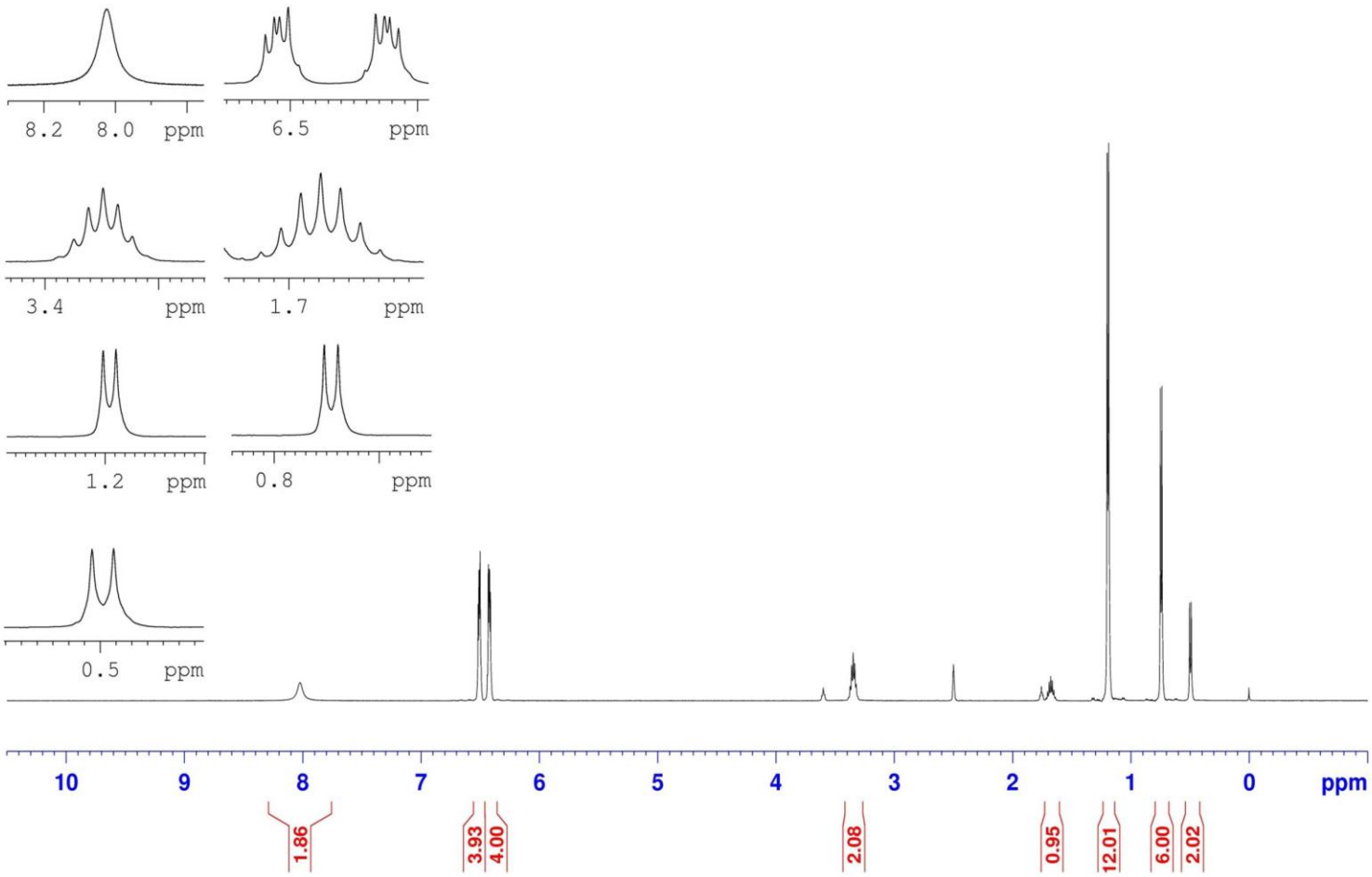
triethylammonium bis(catecholato)allylsilicate
500 MHz, DMSO–d6



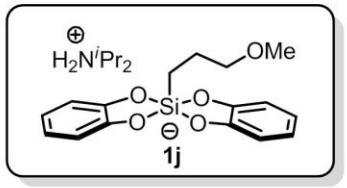


diisopropylammonium bis(catecholato)isobutylsilicate
500 MHz, DMSO–d6





diisopropylammonium bis(catecholato)(3−methoxypropyl)silicate
500 MHz, DMSO−d6



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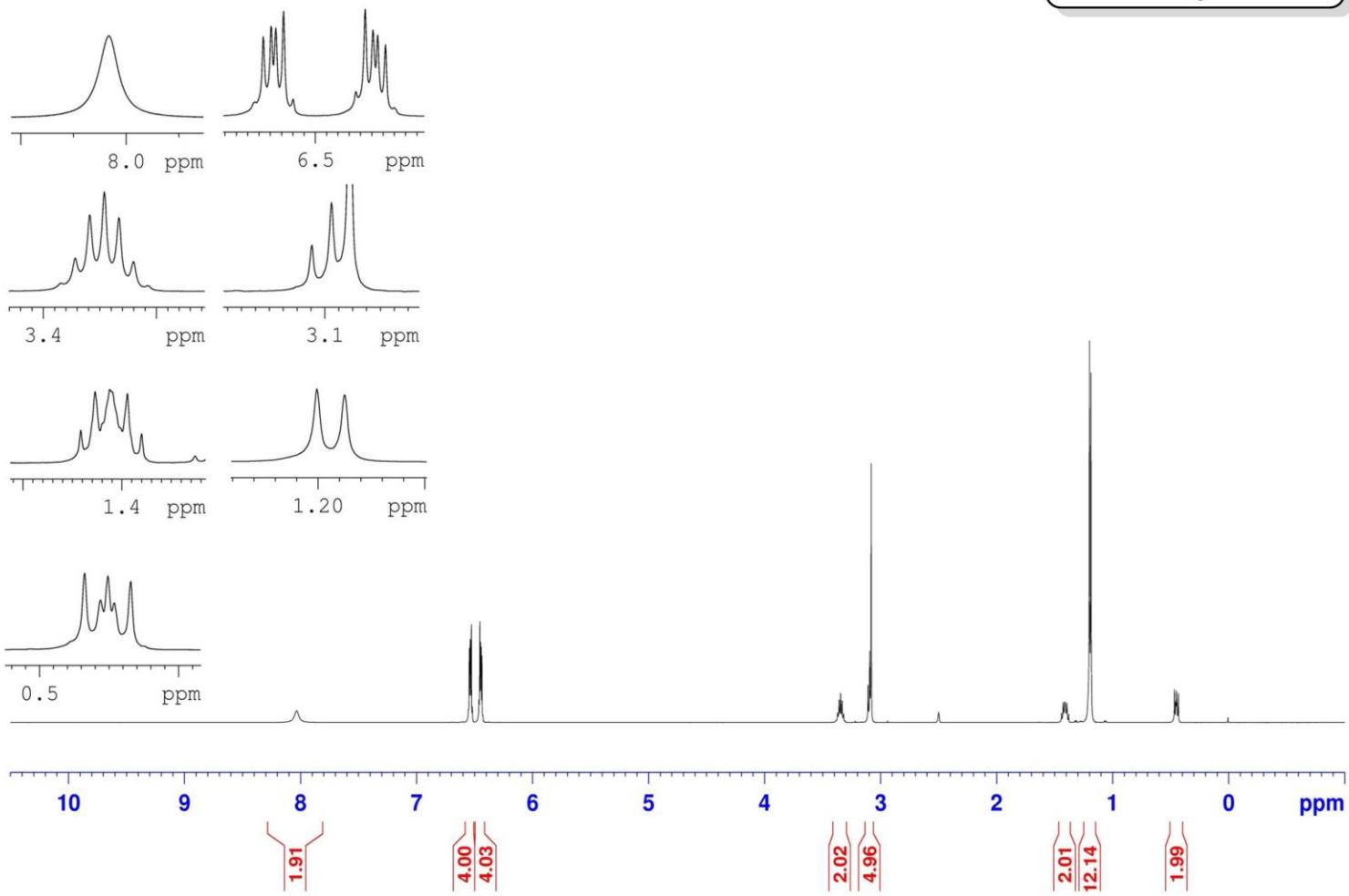
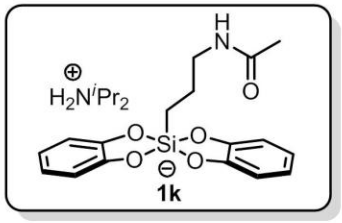
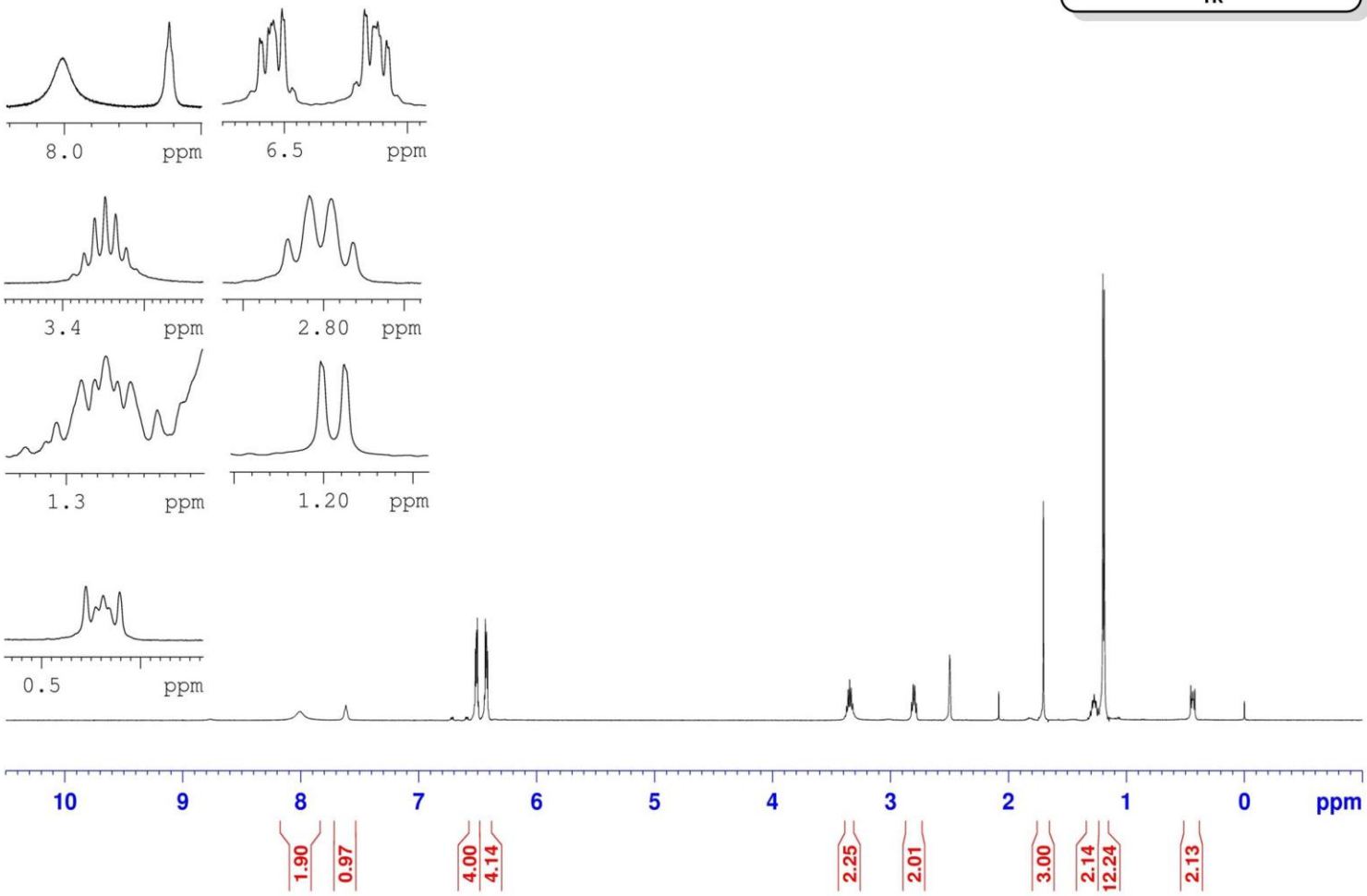
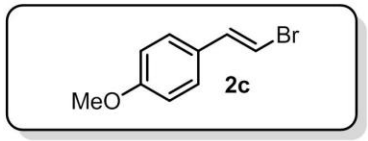


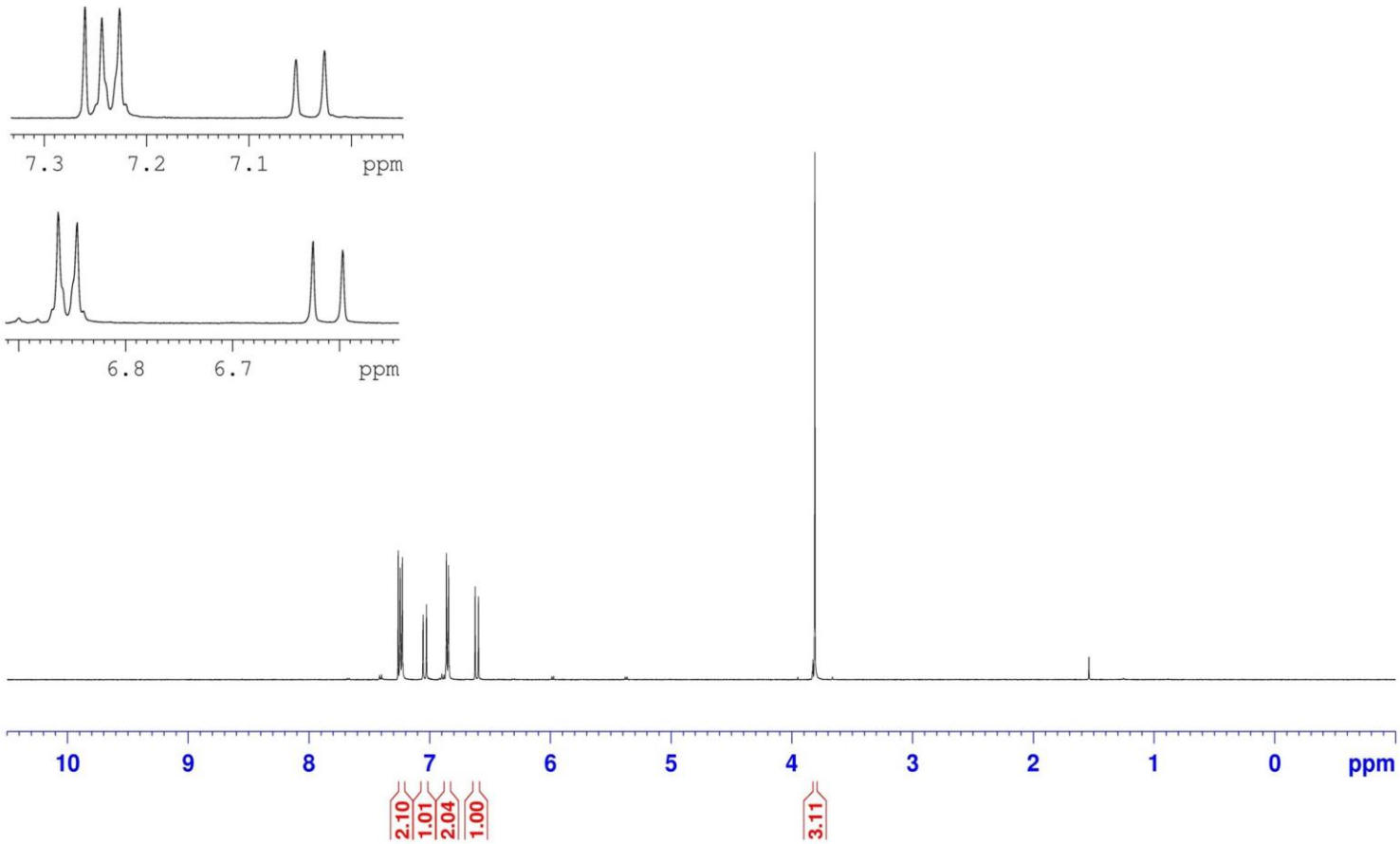
diisopropylammonium bis(catecholato)(3–acetamidopropyl)silicate
500 MHz, DMSO–d6



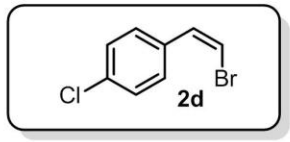


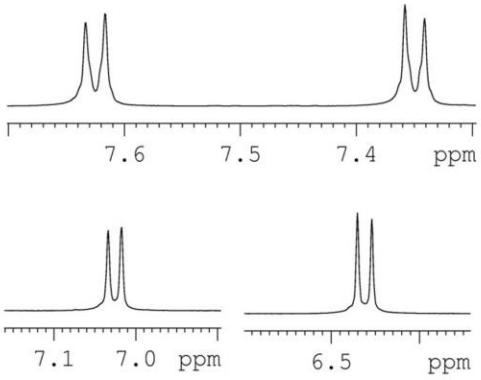
(E)−1−(2−bromovinyl)−4−methoxybenzene
500 MHz, CDCl3

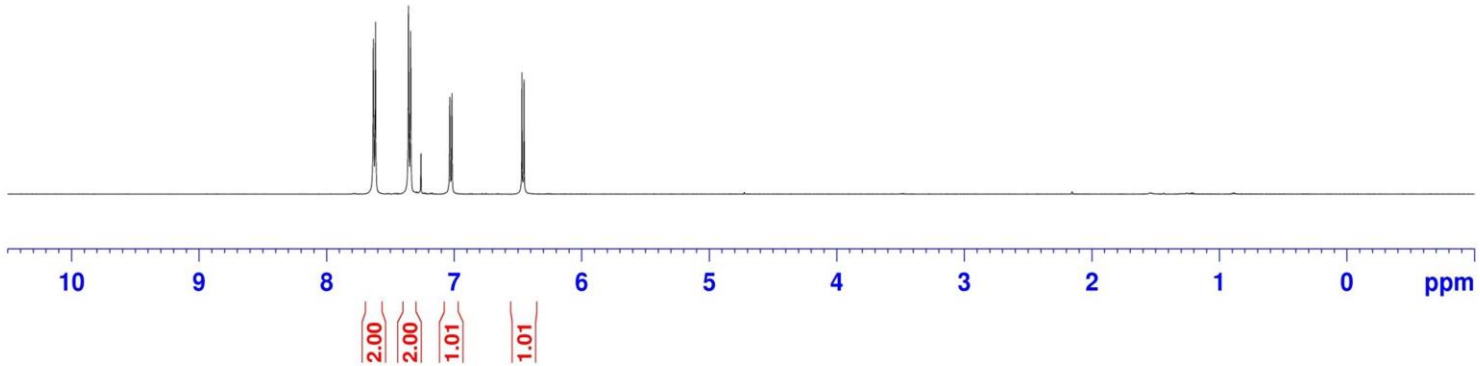




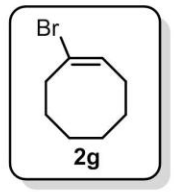
(Z)−1−(2−bromovinyl)−4−chlorobenzene
500 MHz, CDCl3

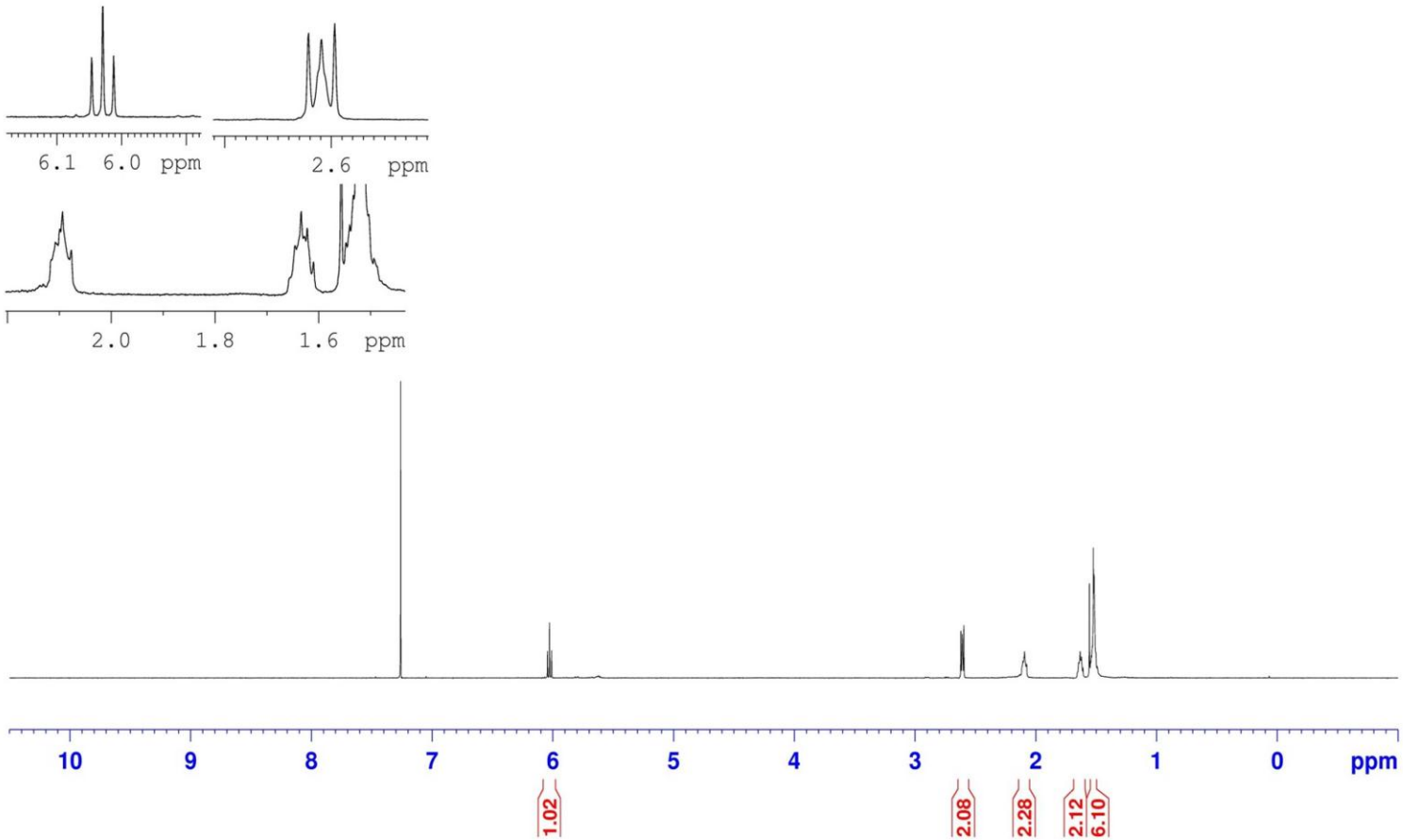




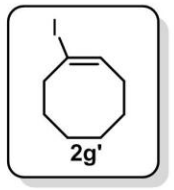


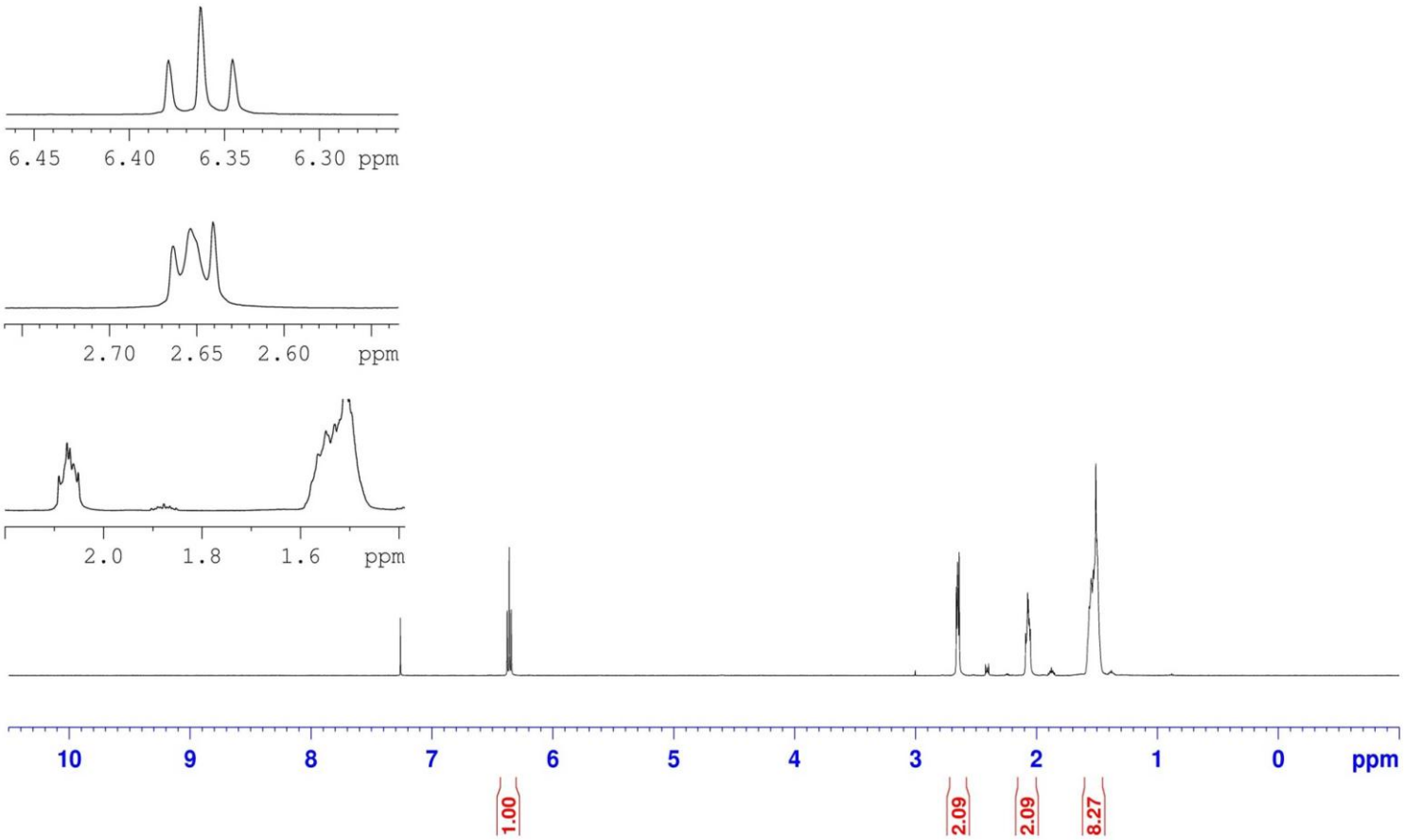
(E)−1−bromocyclooct−1−ene
500 MHz, CDCl3



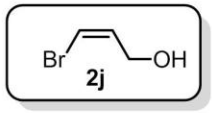


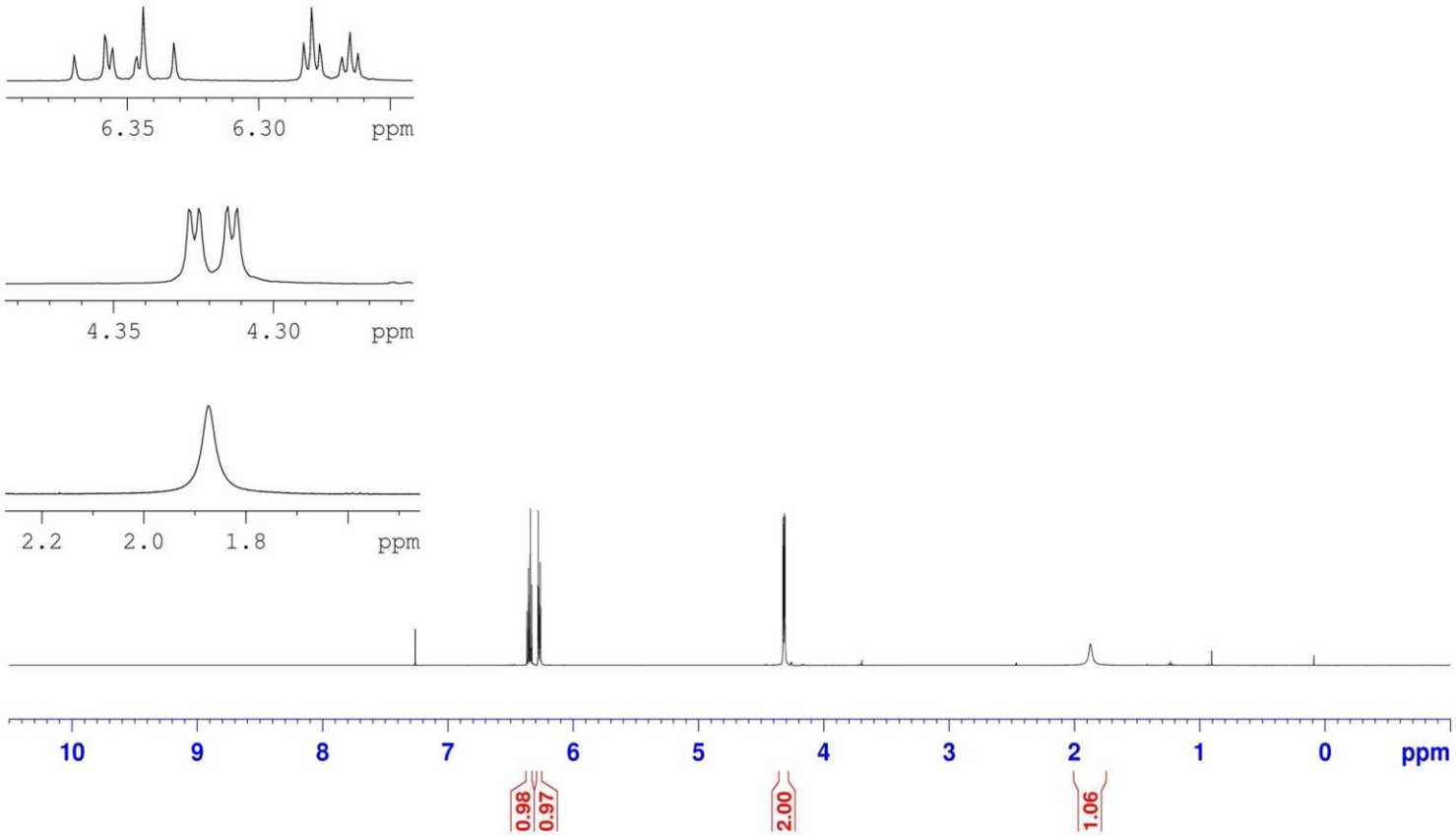
(E)−1−iodocyclooct−1−ene
500 MHz, CDCl3



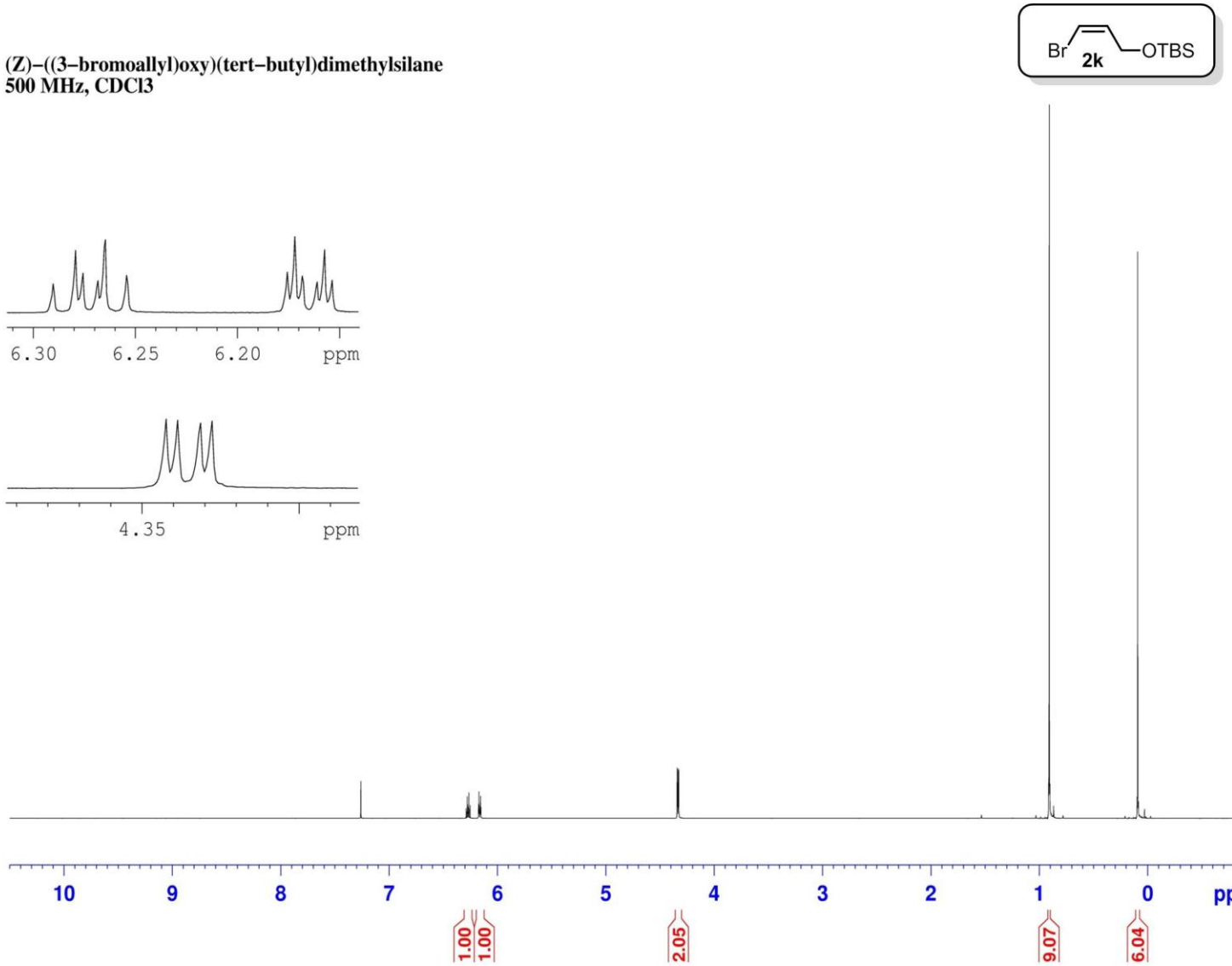


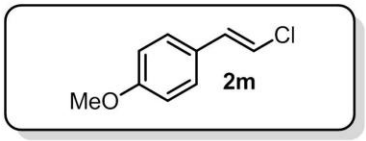
(Z)−3−bromoprop−2−en−1−ol
500 MHz, CDCl3



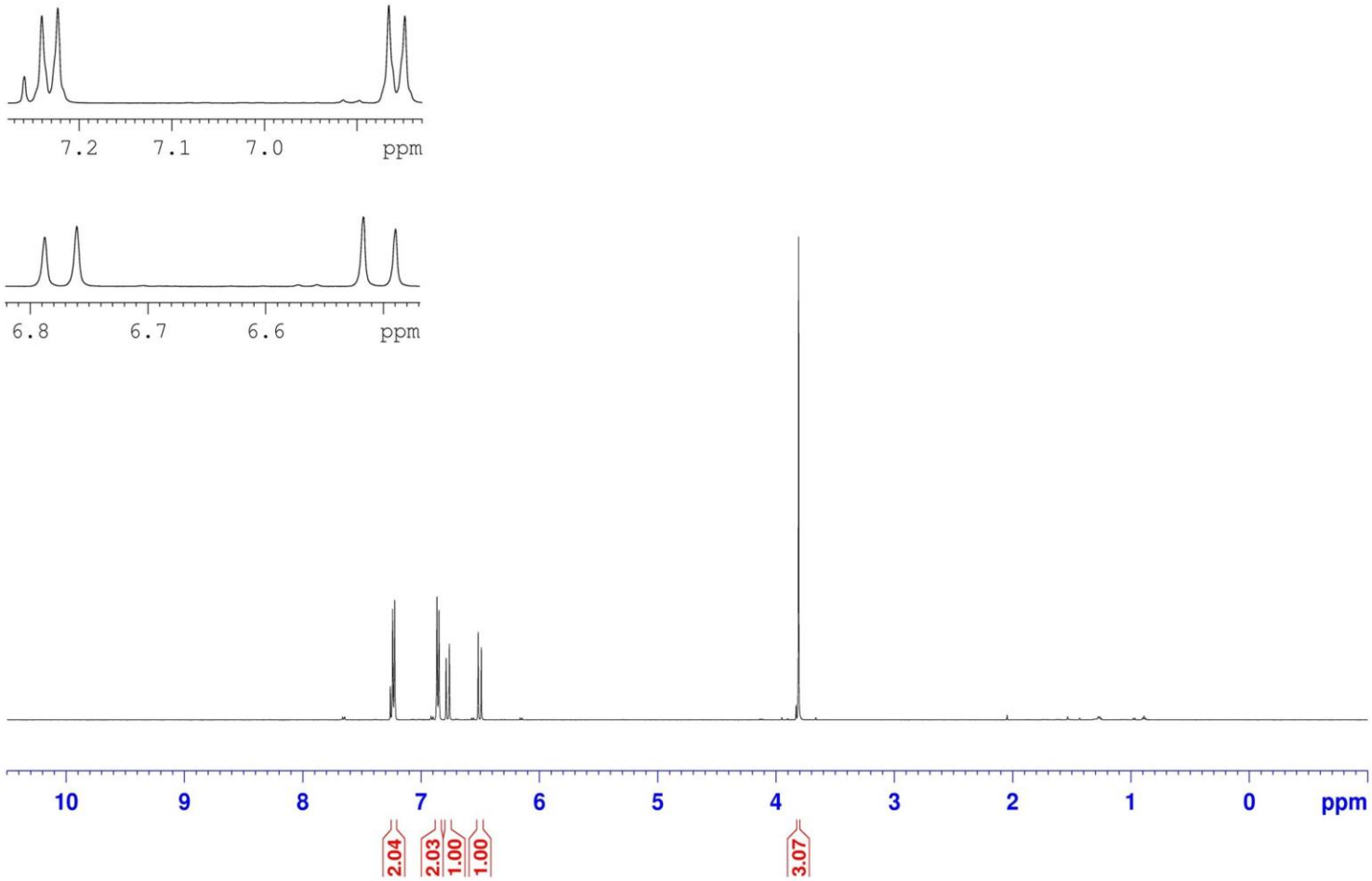


(Z)−((3−bromoallyl)oxy)(tert−butyl)dimethylsilane
500 MHz, CDCl3

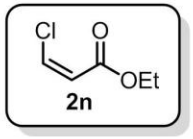


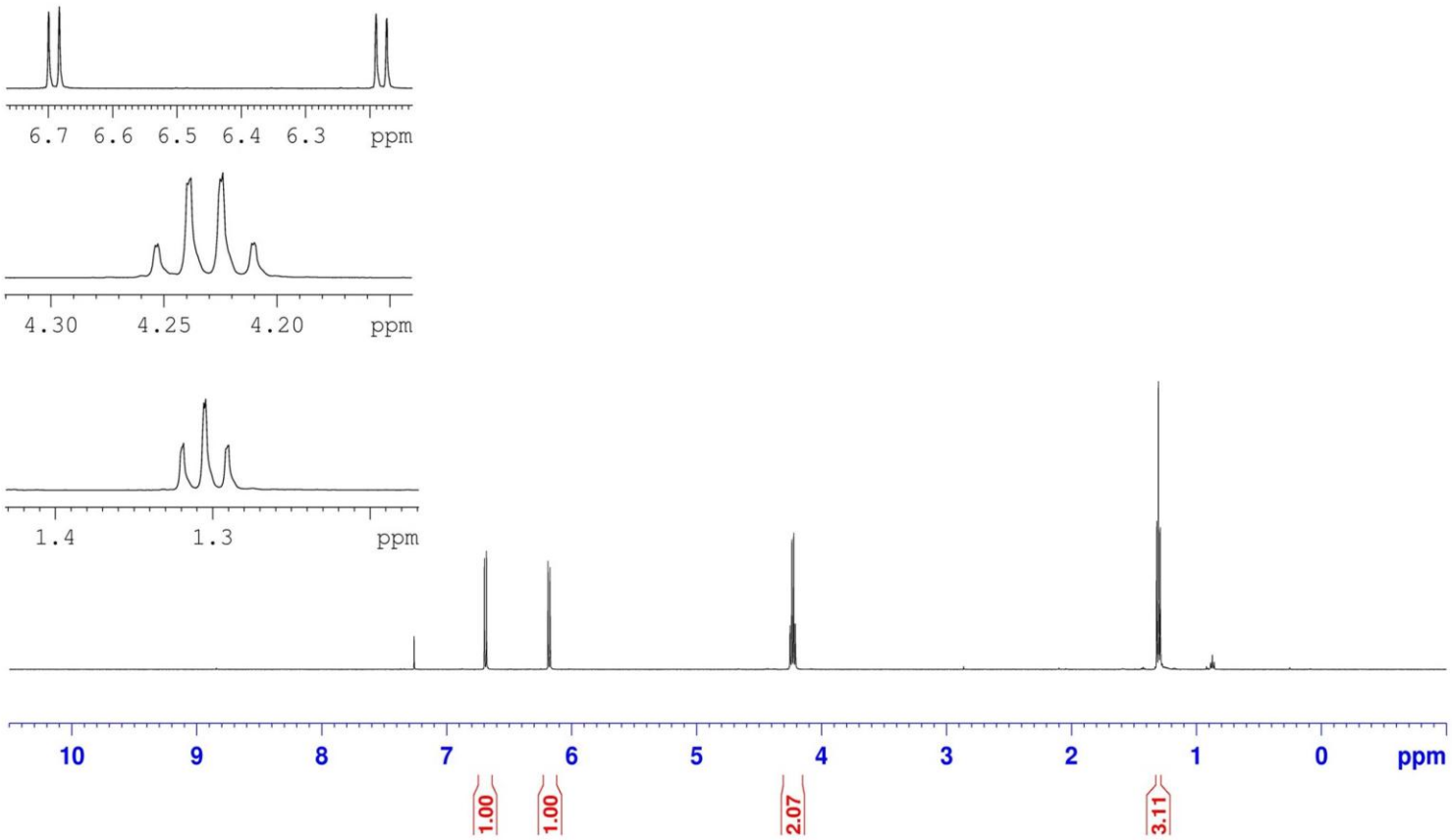


(E)−1−(2−chlorovinyl)−4−methoxybenzene
500 MHz, CDCl3

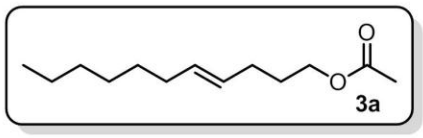


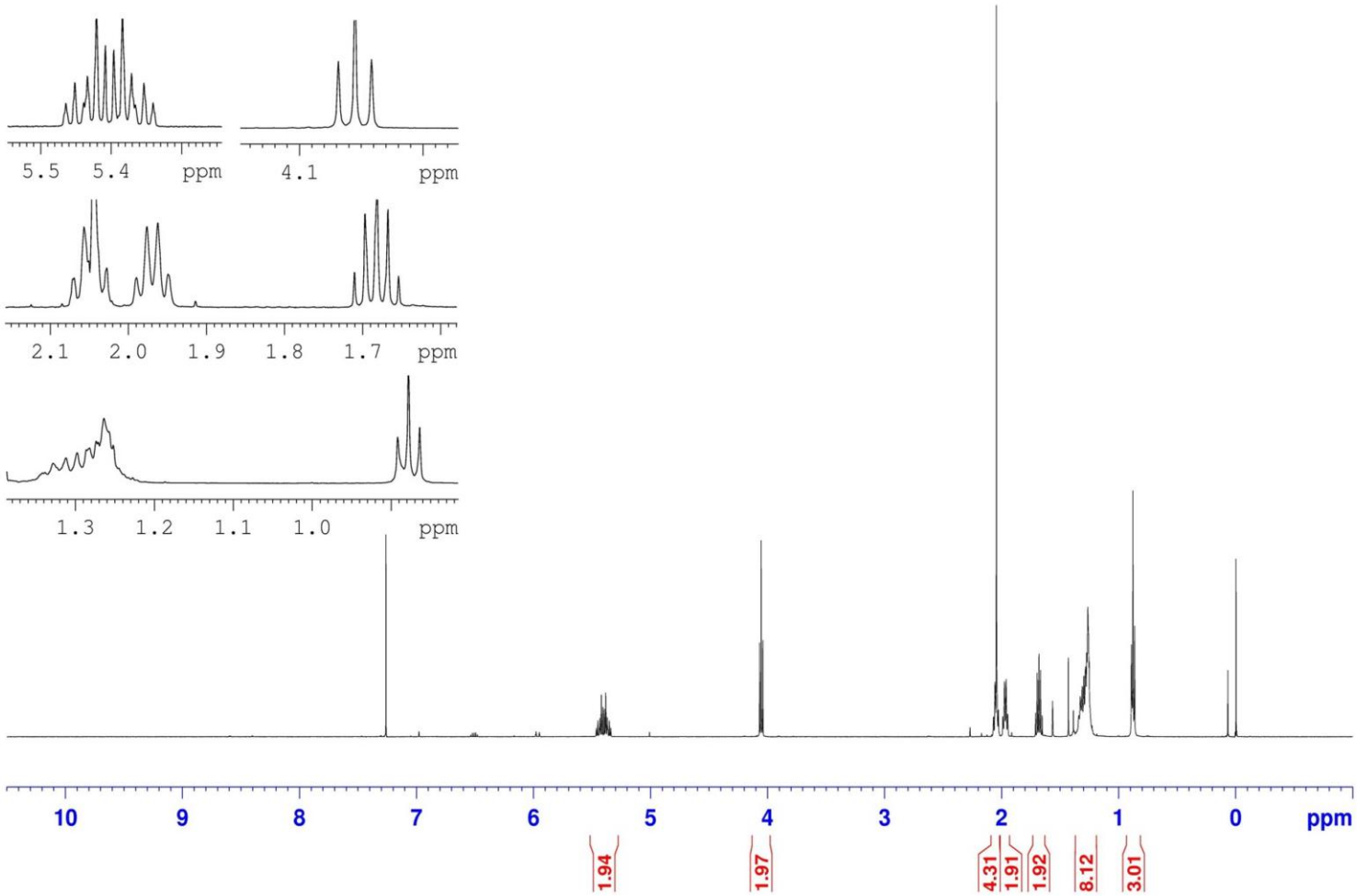
(Z)–ethyl 3–chloroacrylate
500 MHz, CDCl3



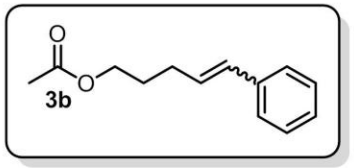


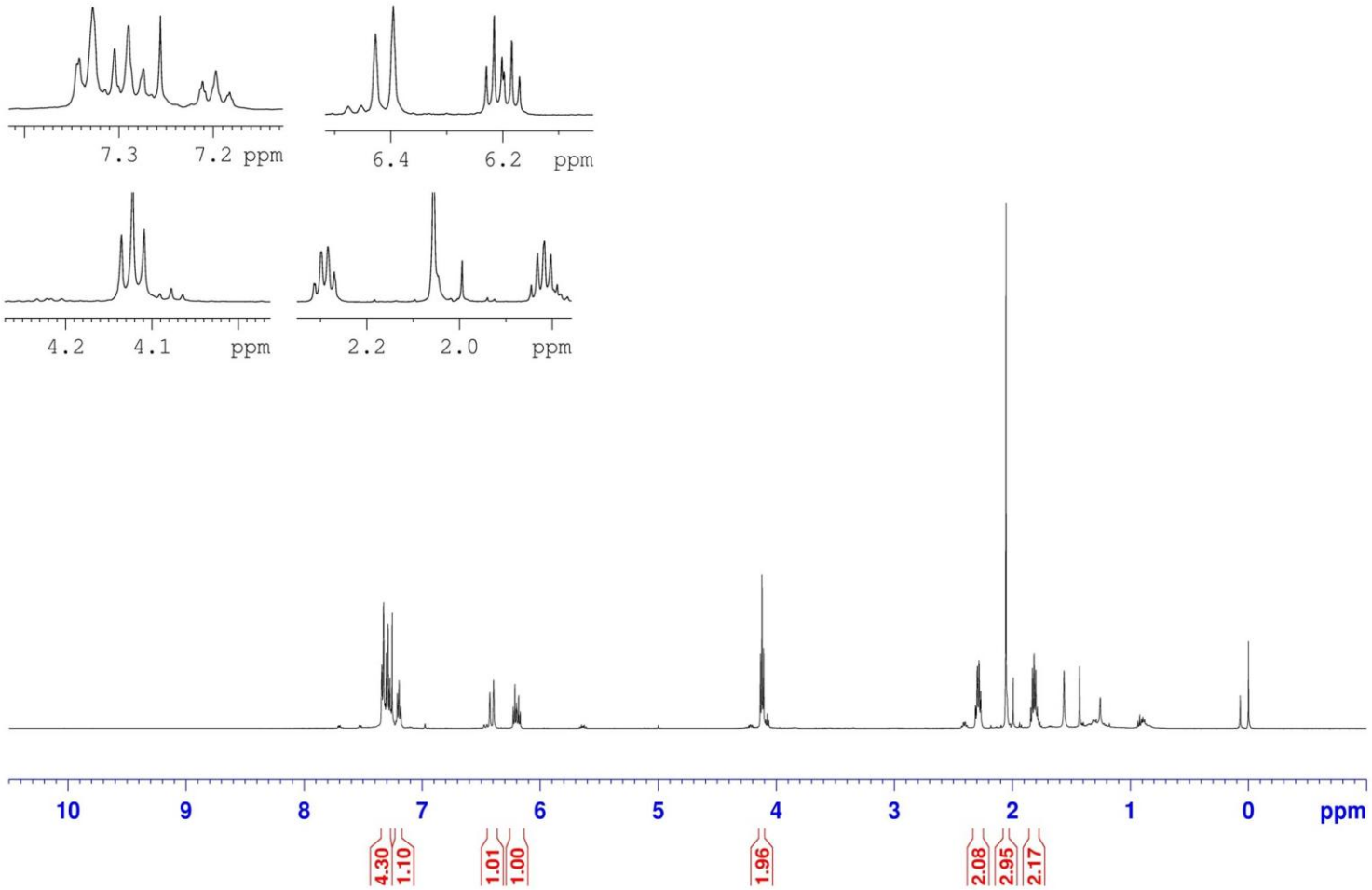
(E)–undec–4–en–1–yl acetate
500 MHz, CDCl3



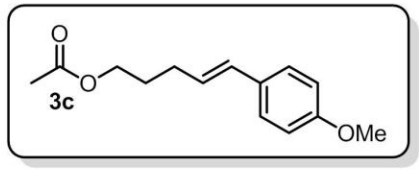


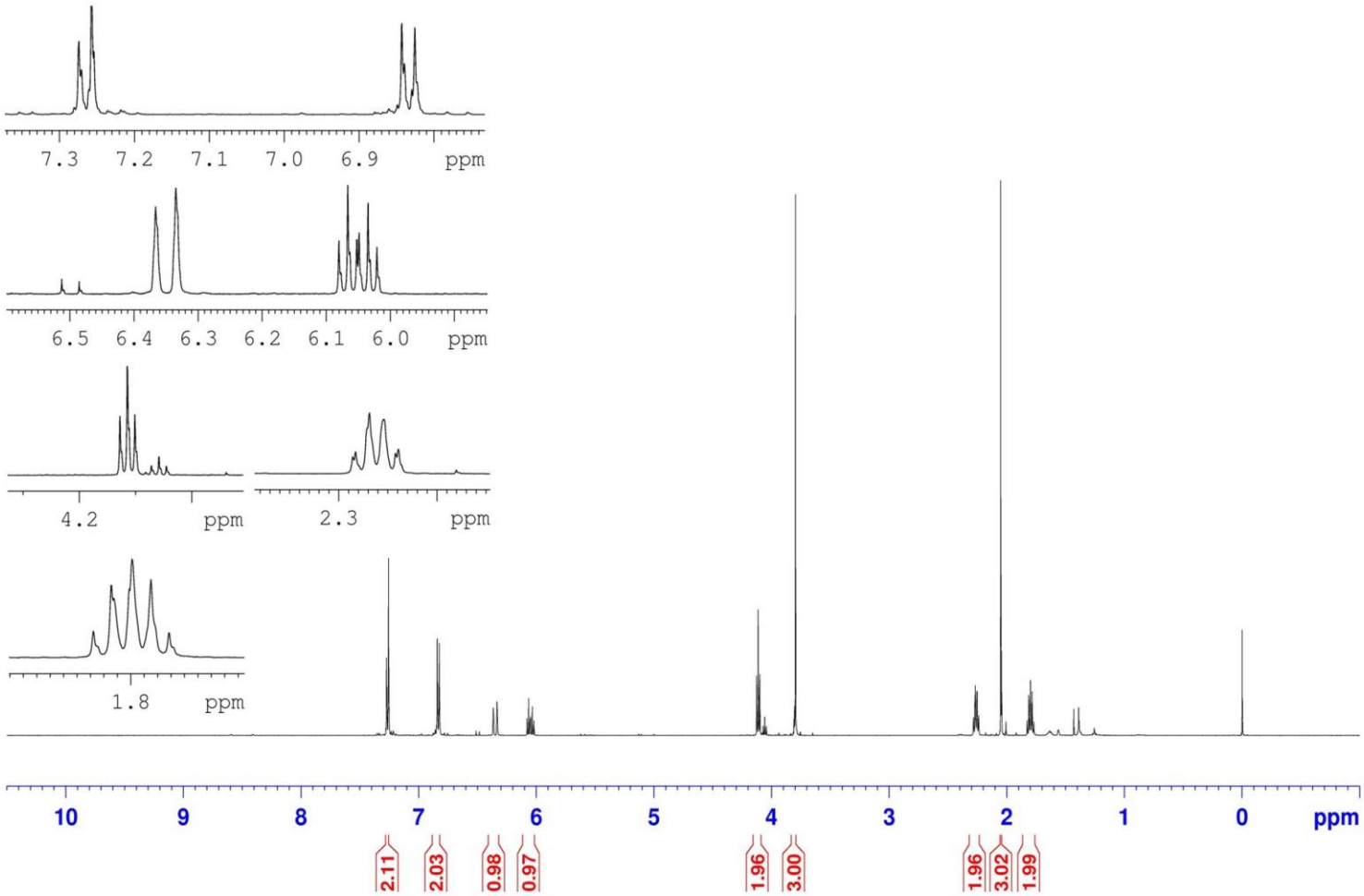
5–phenylpent–4–en–1–yl acetate
500 MHz, CDCl3

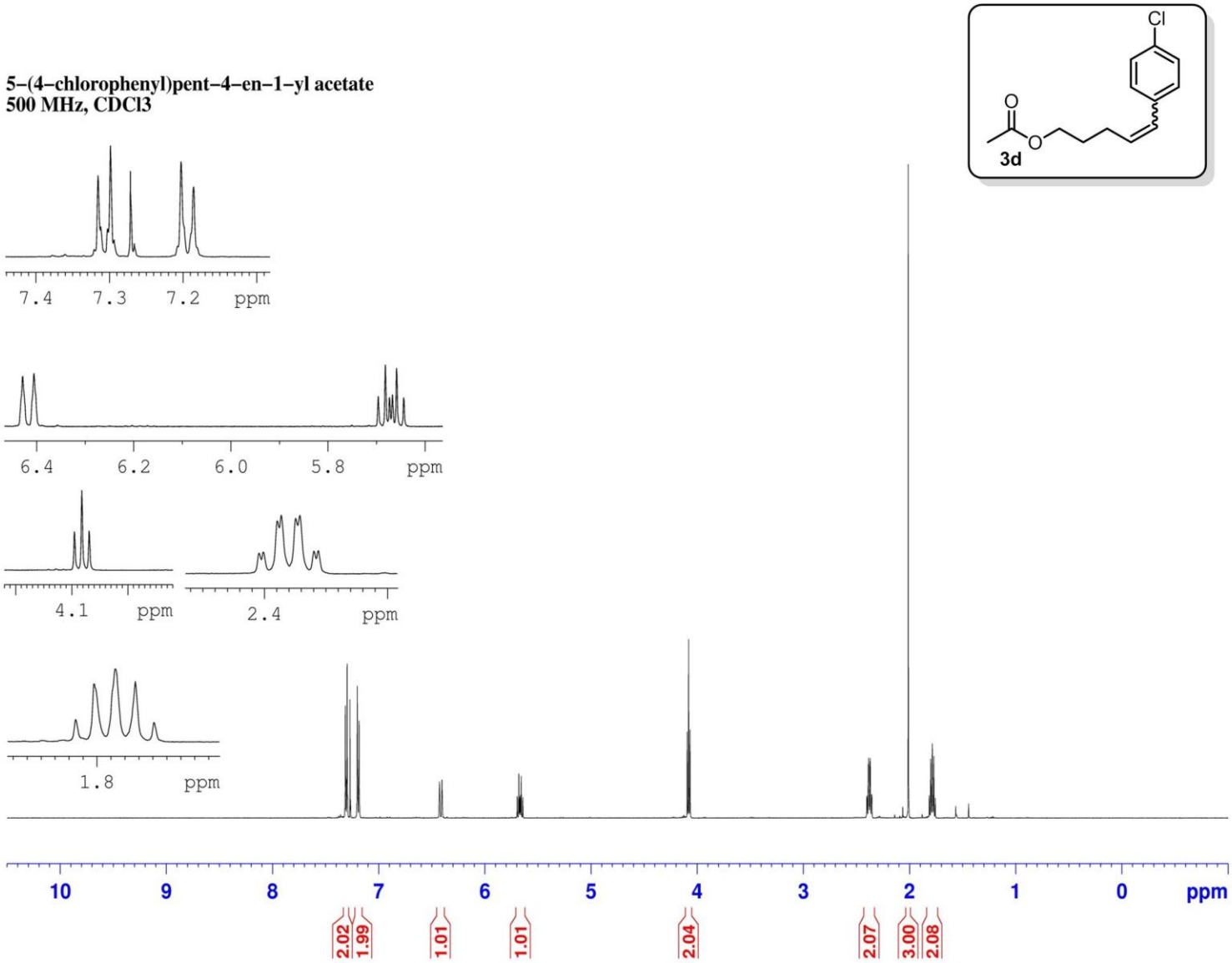




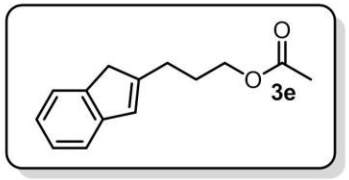
(E)–5–(4–methoxyphenyl)pent–4–en–1–yl acetate
500 MHz, CDCl3

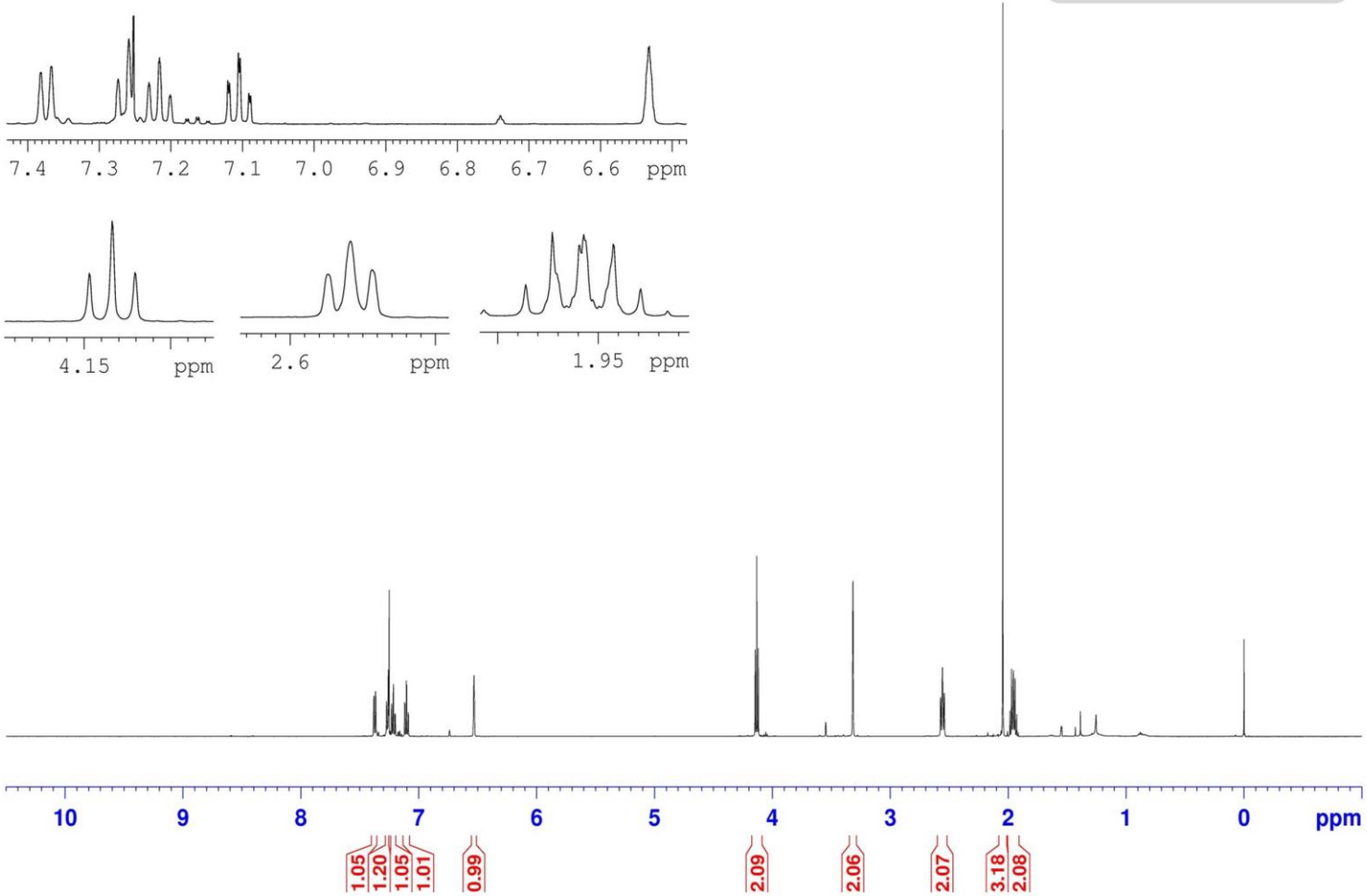




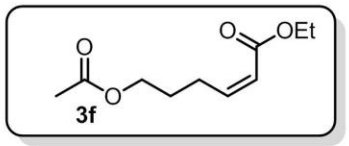

5–(4–chlorophenyl)pent–4–en–1–yl acetate
500 MHz, CDCl3
Cl
O
O
3d
7.4
7.3
7.2
ppm
6.4
6.2
6.0
5.8
ppm
4.1
ppm
2.4
ppm
1.8
ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
2.02
1.99
1.01
1.01
2.04
2.07
3.00
2.08

3–(1H–inden–2–yl)propyl acetate
500 MHz, CDCl3

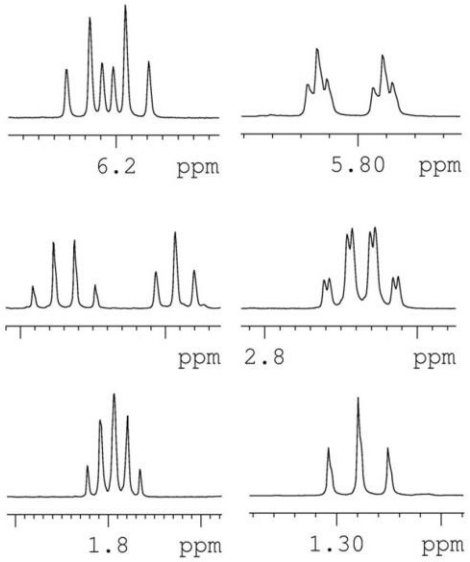




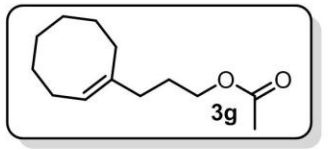
(Z)–ethyl 6–acetoxyhex–2–enoate
500 MHz, CDCl3

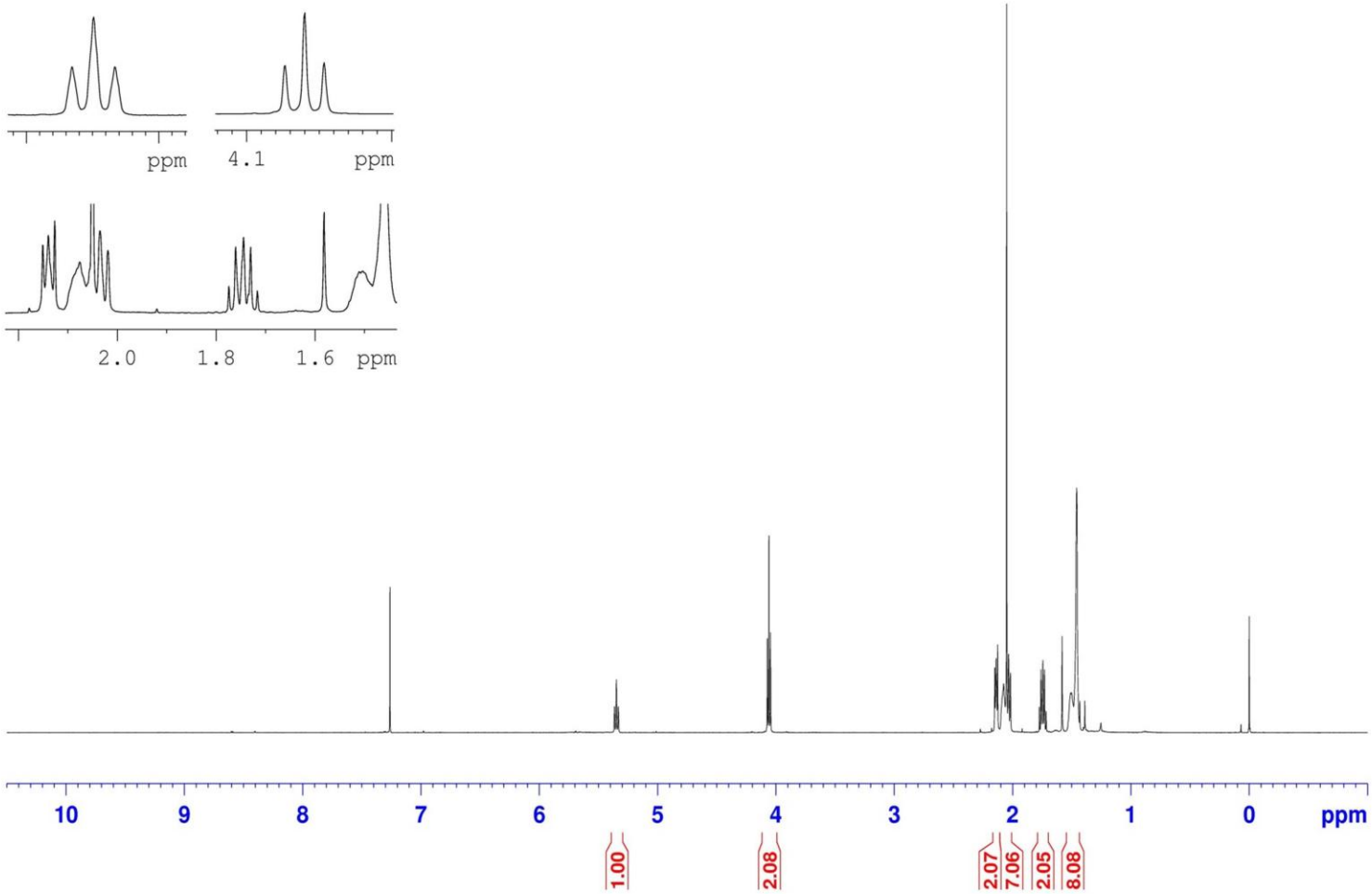


3f

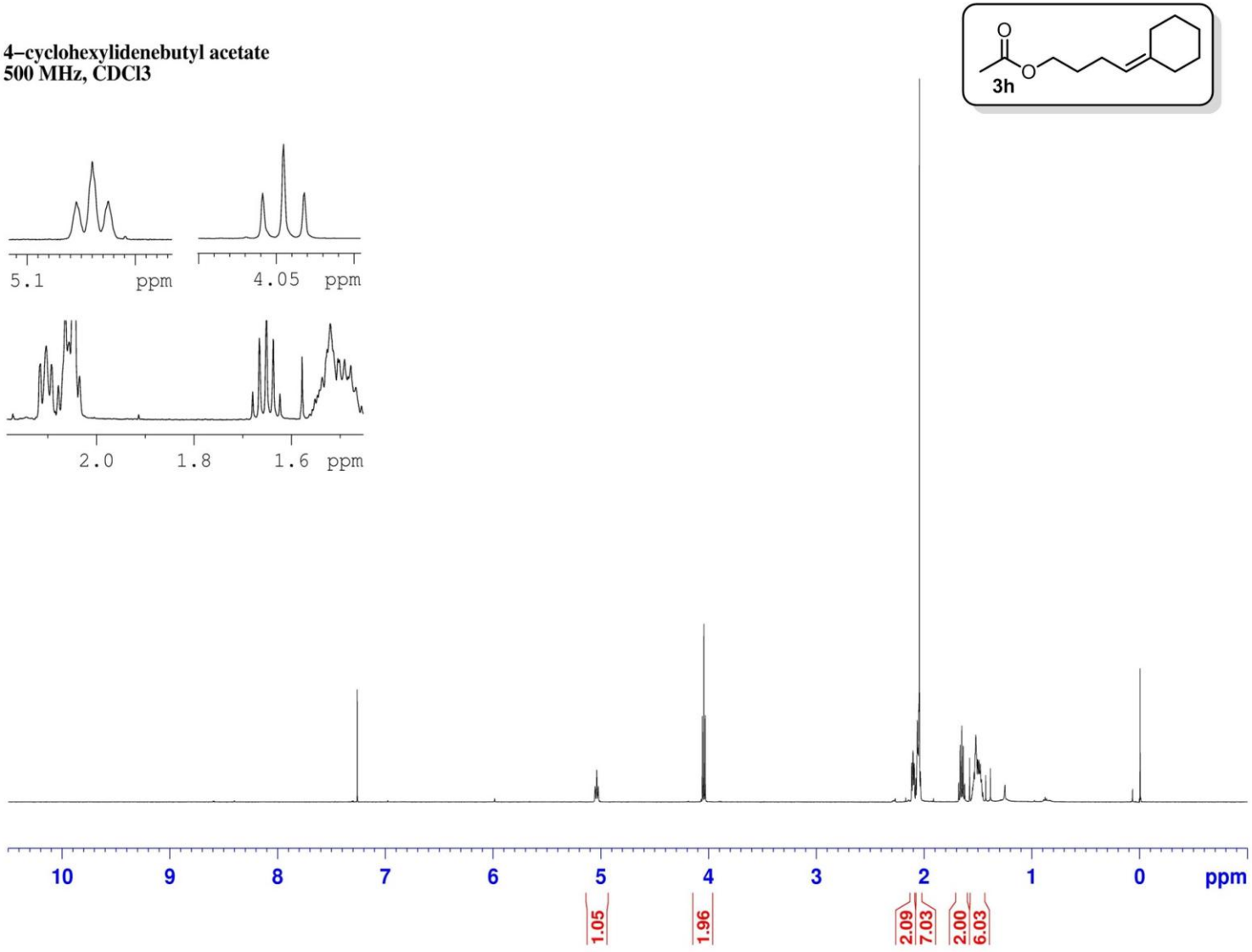


(E)−3−(cyclooct−1−en−1−yl)propyl acetate
500 MHz, CDCl3

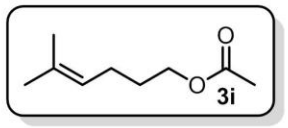


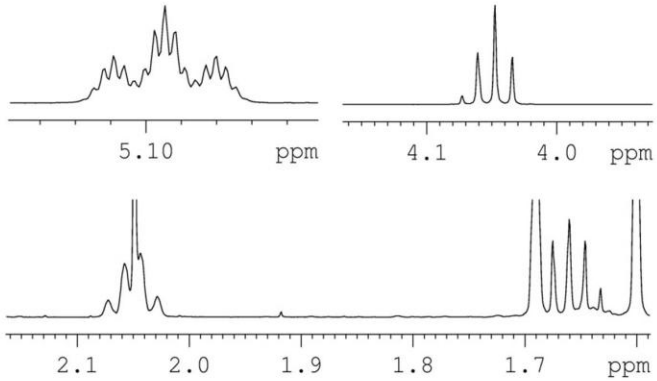


4–cyclohexylidenebutyl acetate
500 MHz, CDCl3

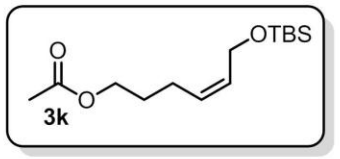


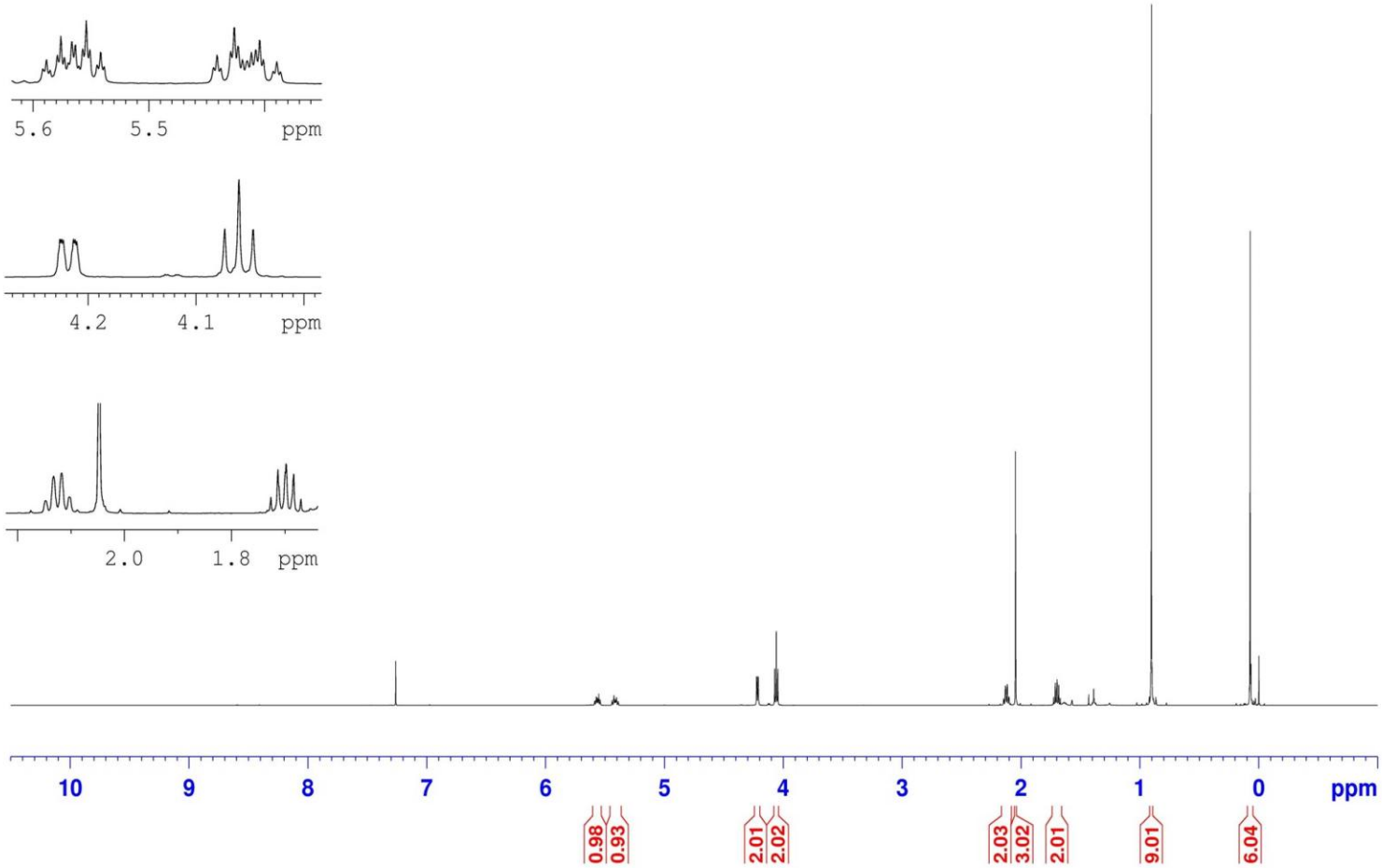
5–methylhex–4–en–1–yl acetate
500 MHz, CDCl3



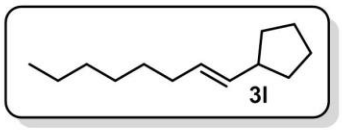


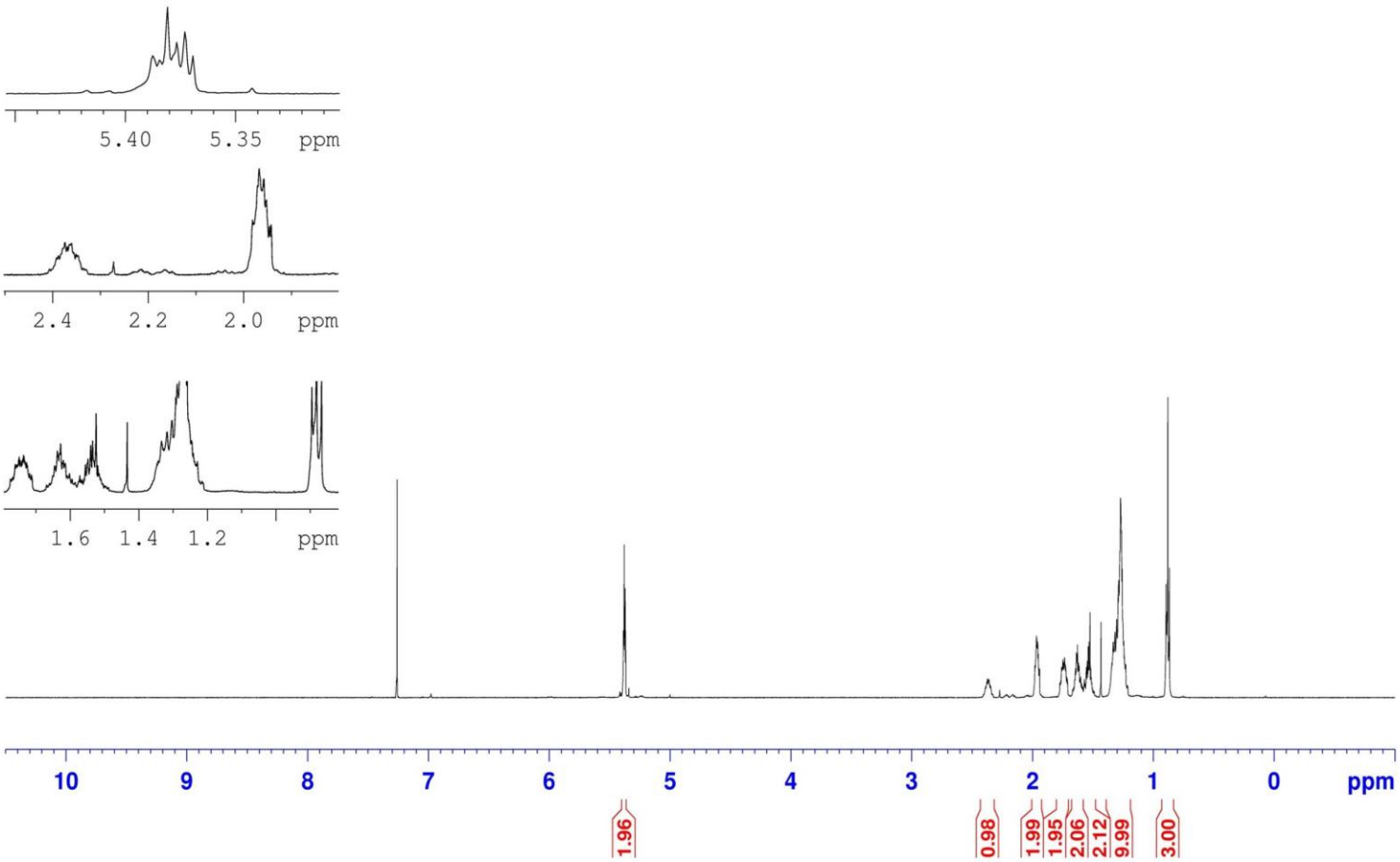
(Z)−6−((tert−butyldimethylsilyl)oxy)hex−4−en−1−yl acetate
500 MHz, CDCl3



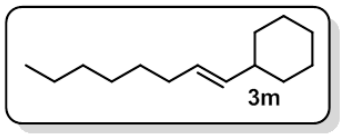


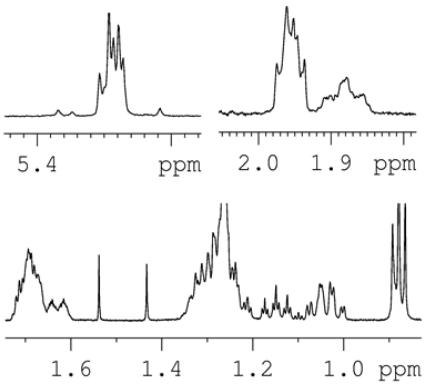
(E)–oct–1–en–1–ylcyclopentane
500 MHz, CDCl3

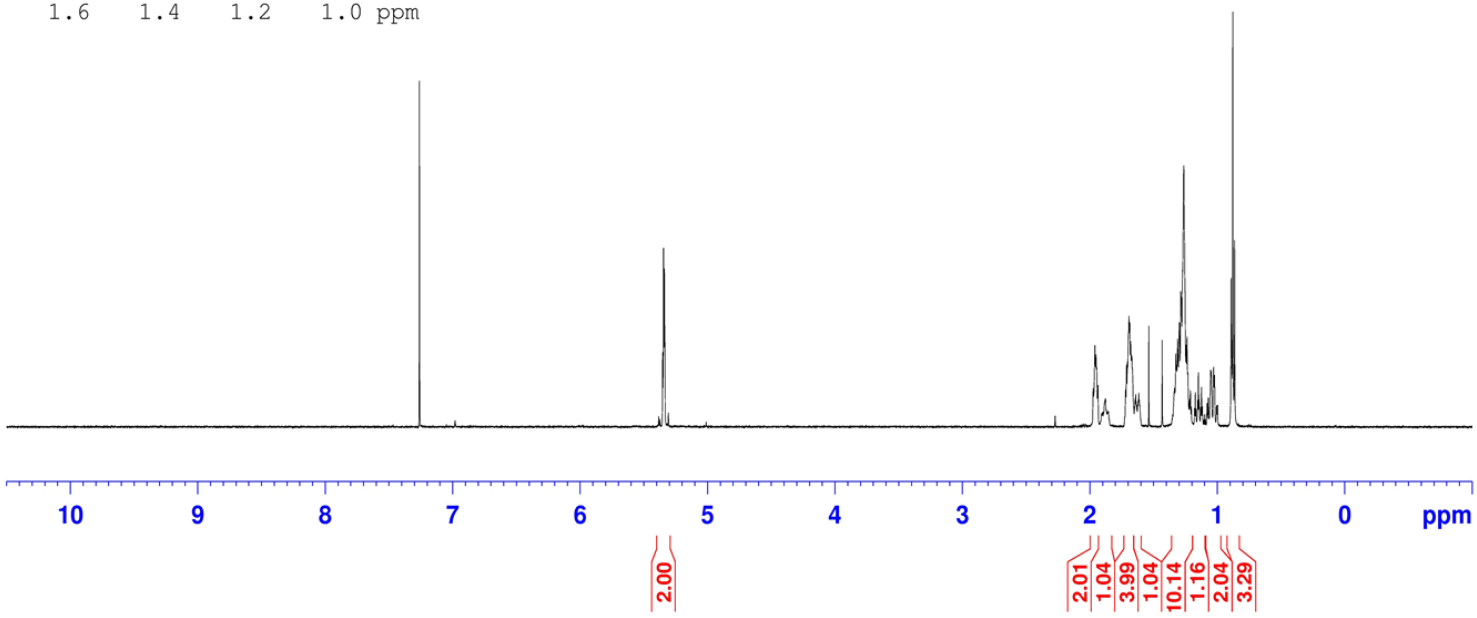




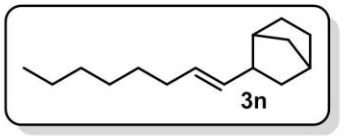
(E)−oct−1−en−1−ylcyclohexane
500 MHz, CDCl3

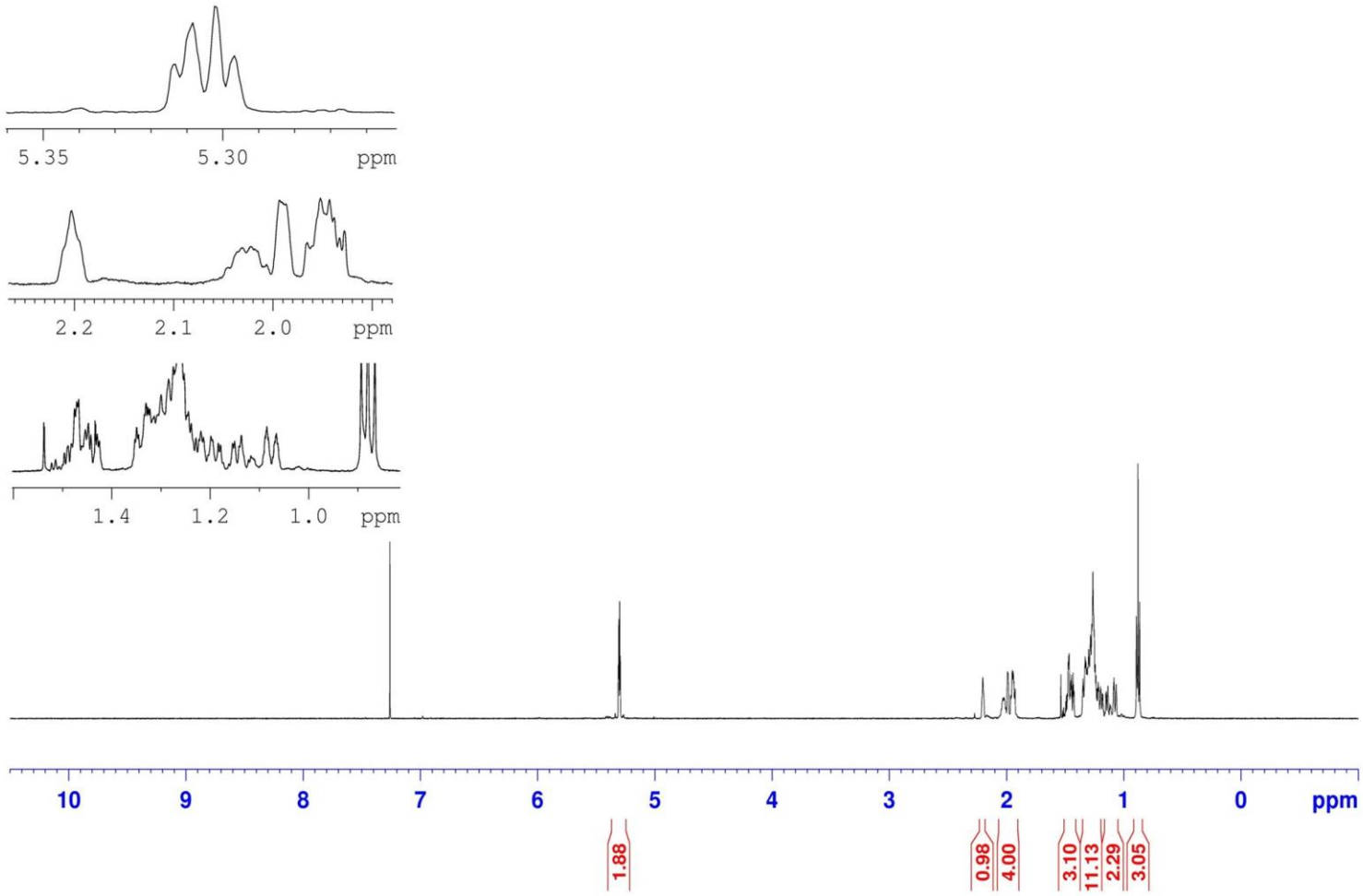




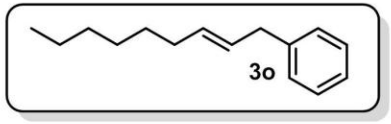


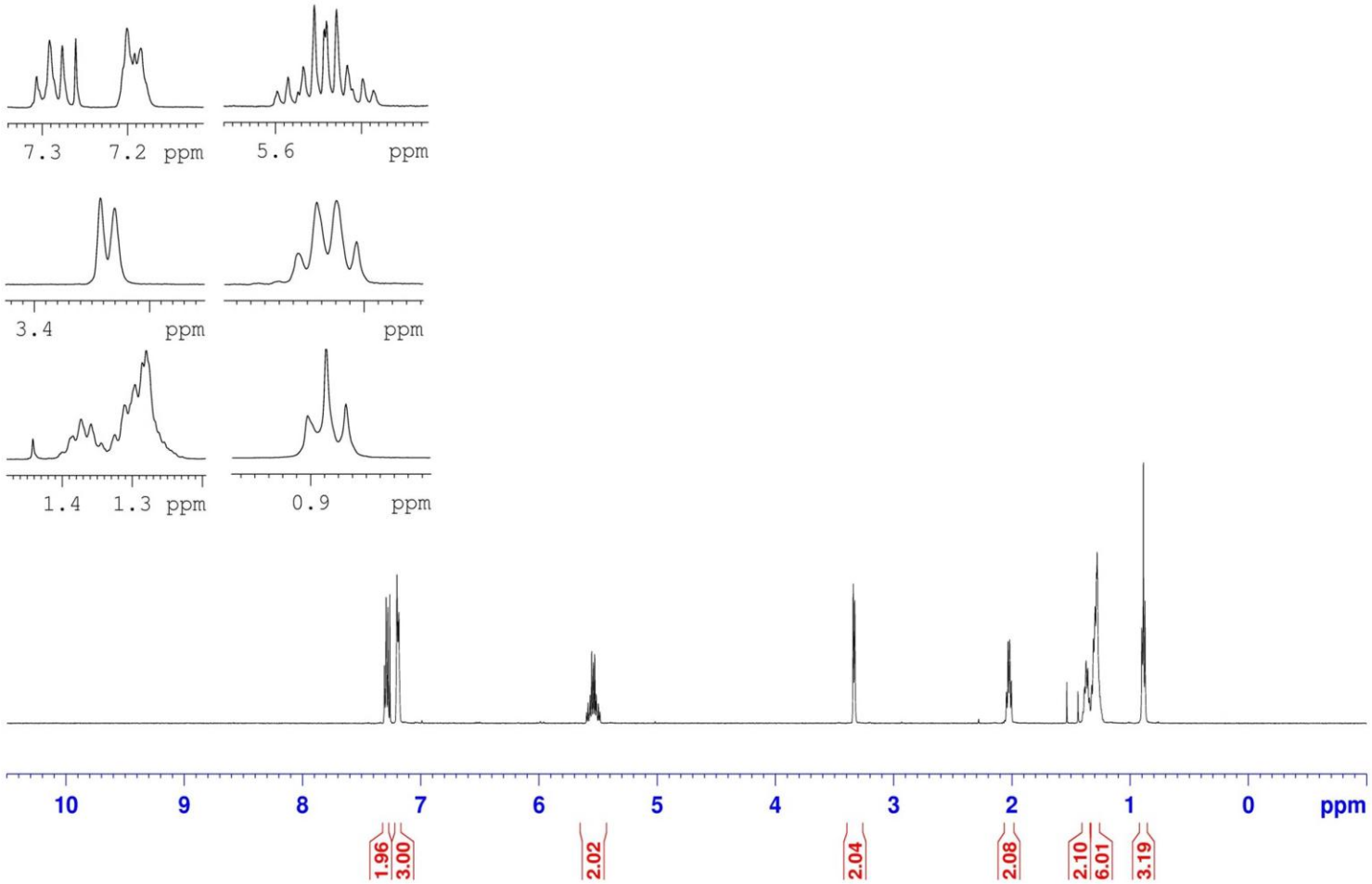
(E)−2−(oct−1−en−1−yl)bicyclo[2.2.1]heptane
500 MHz, CDCl3



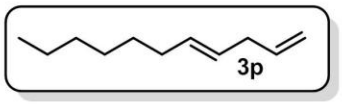


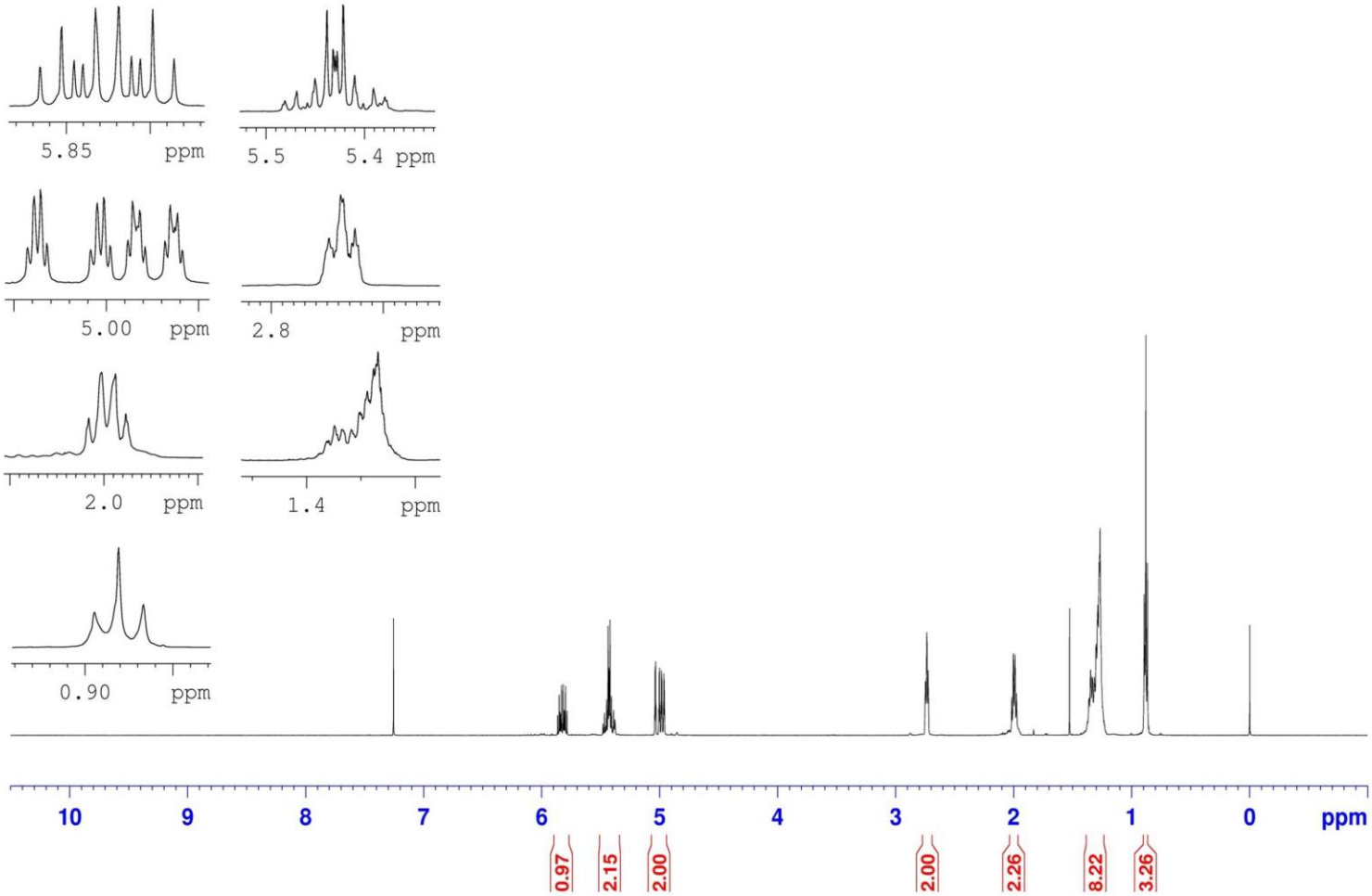
(E)–non–2–en–1–ylbenzene
500 MHz, CDCl3

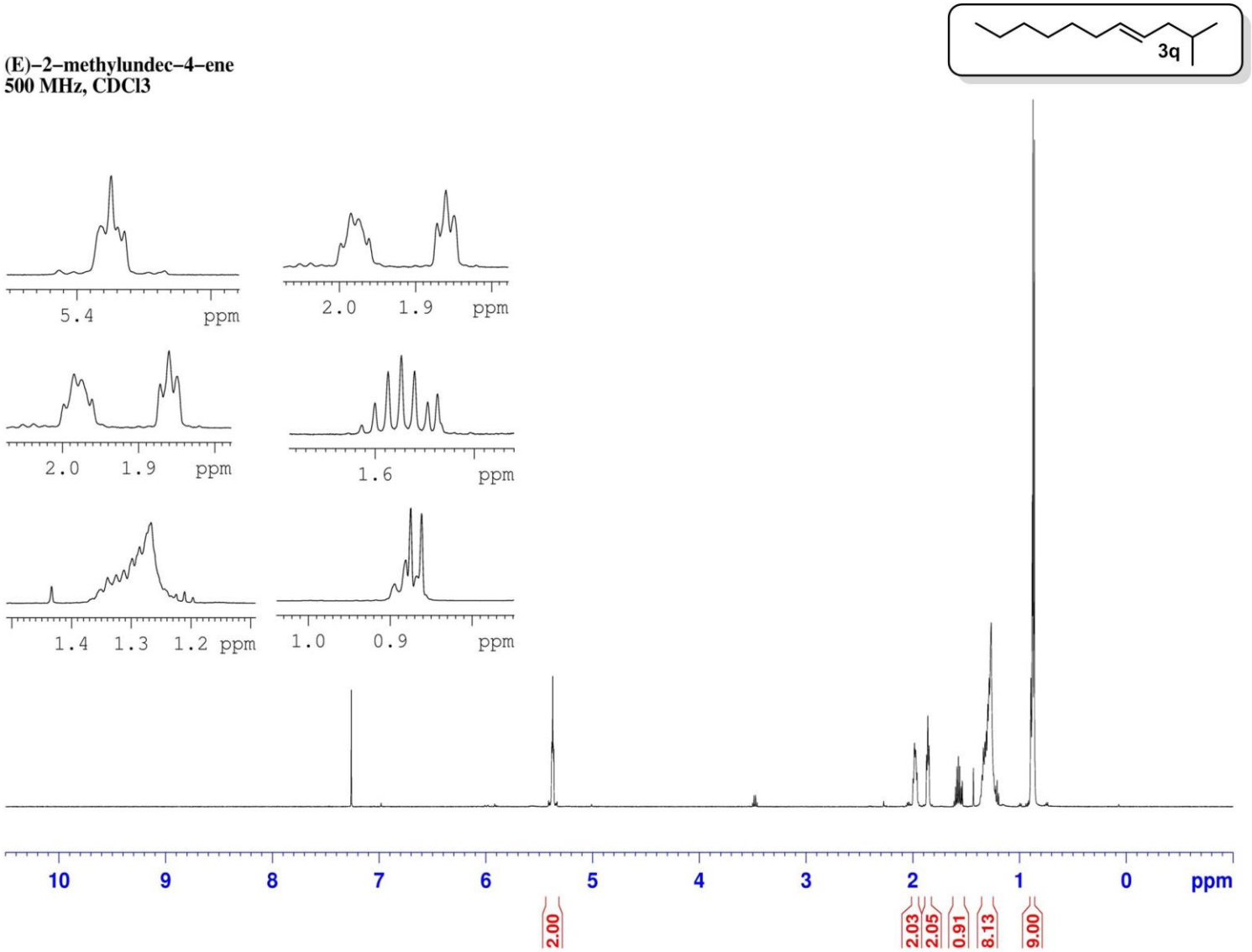




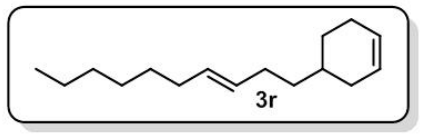
(E)–undeca–1,4–diene
500 MHz, CDCl3

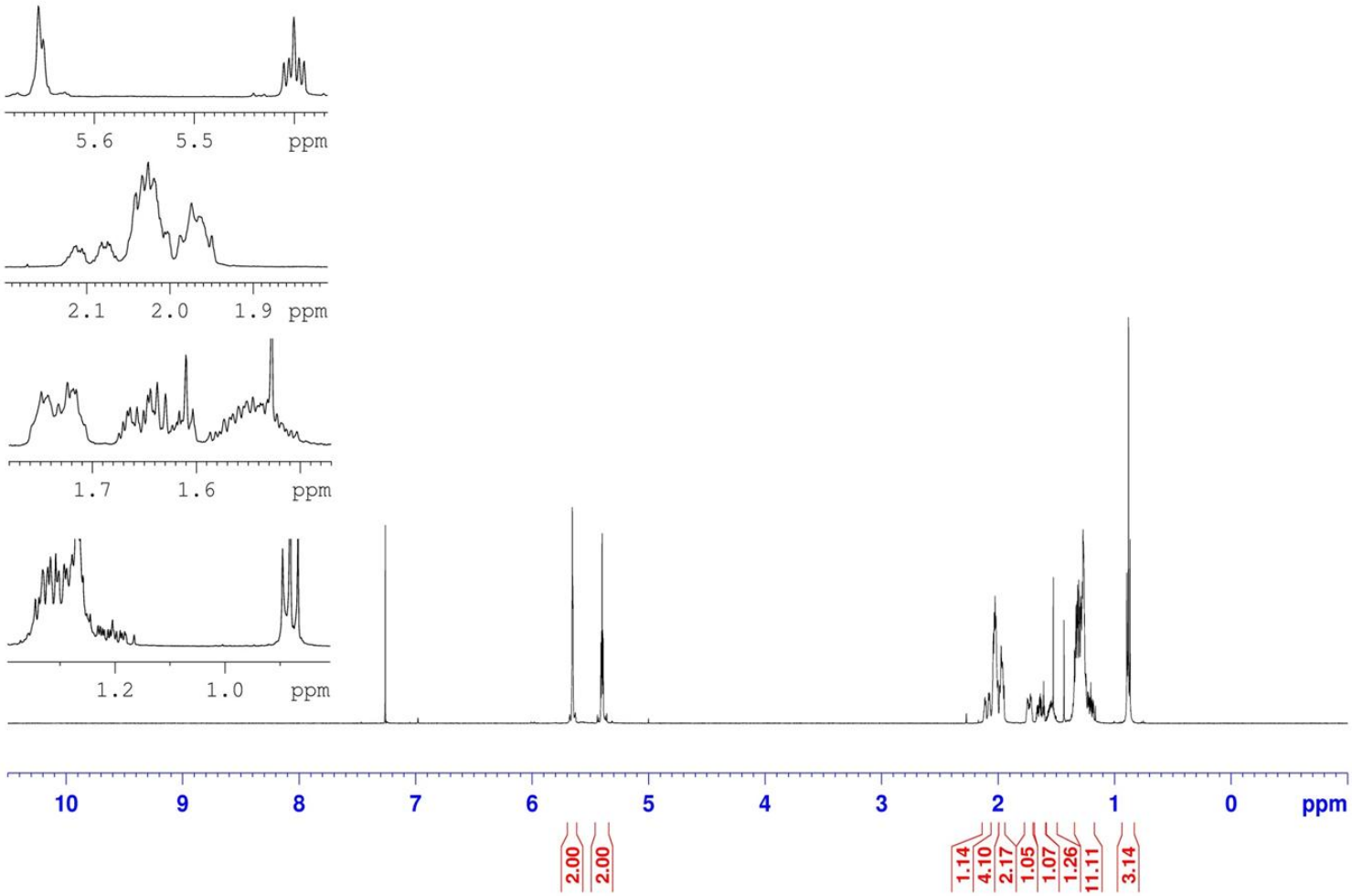




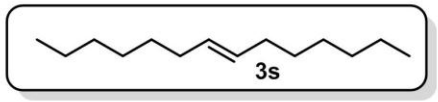

(E)–2–methylundec–4–ene
500 MHz, CDCl3
3q
5.4
ppm
2.0
1.9
ppm
2.0
1.9
ppm
1.6
ppm
1.4
1.3
1.2
ppm
1.0
0.9
ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.03
2.05
0.91
8.13
9.00

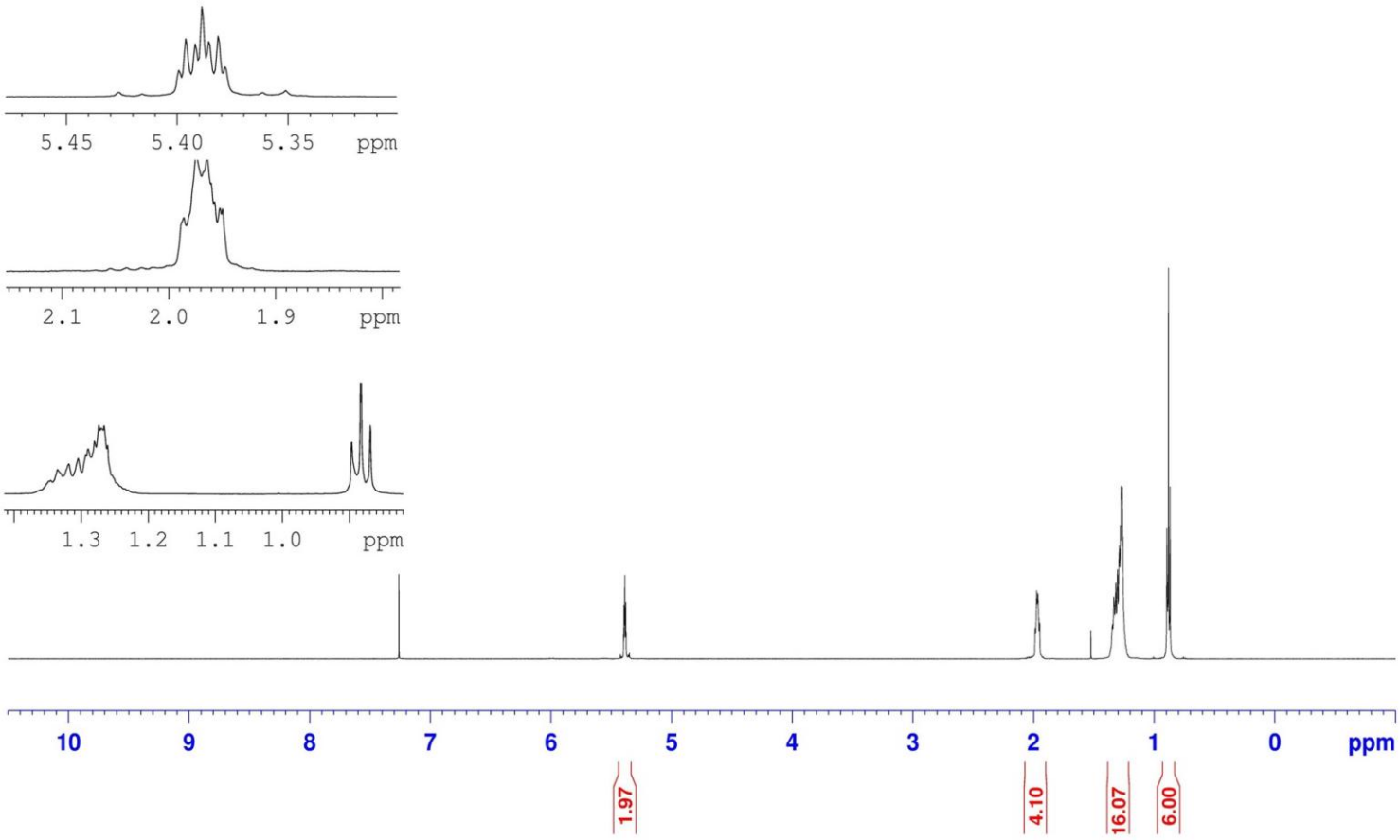
(E)–4–(dec–3–en–1–yl)cyclohex–1–ene
500 MHz, CDCl3



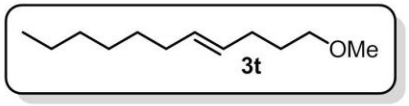


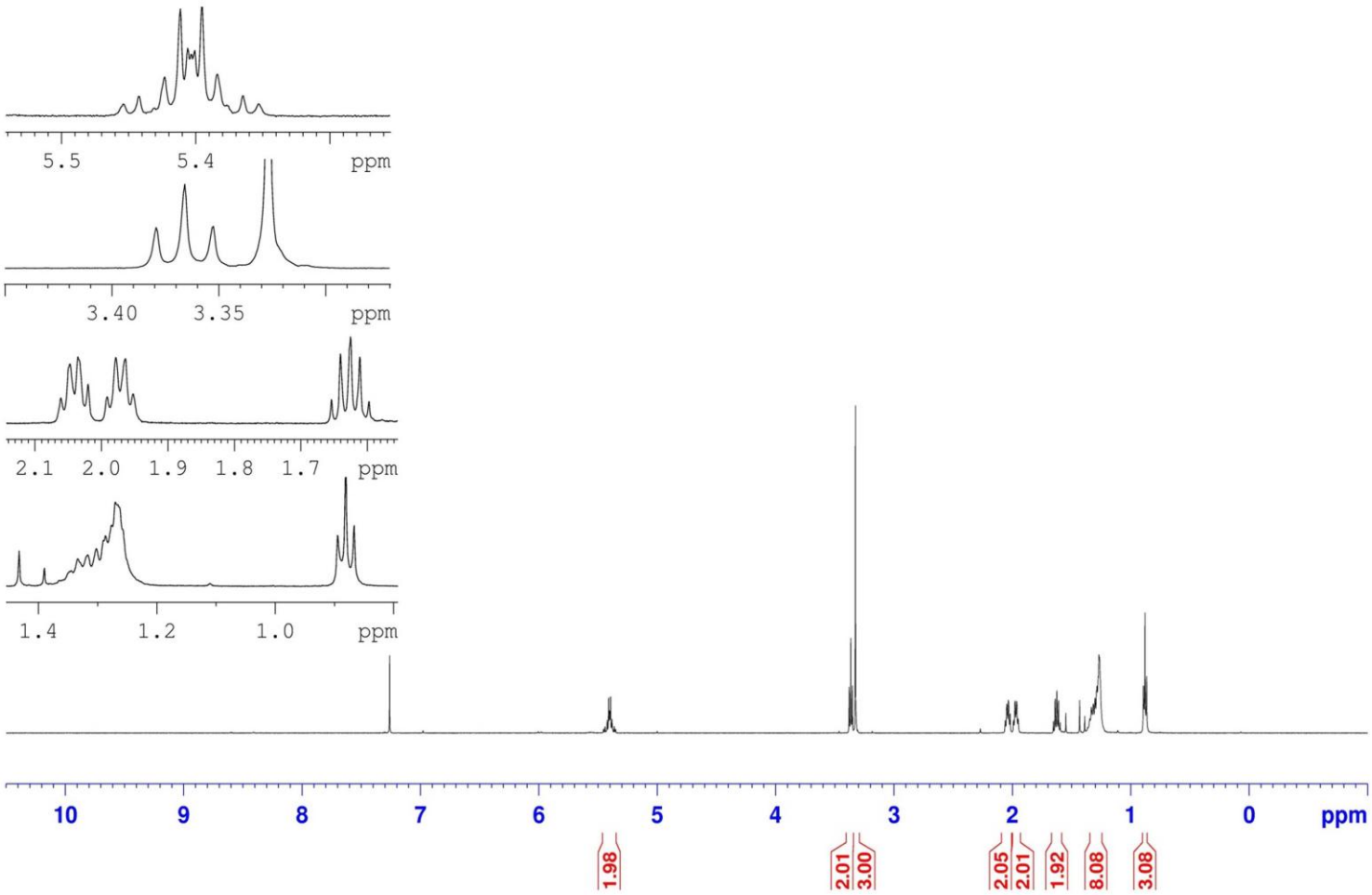
(E)−tetradec−7−ene
500 MHz, CDCl3

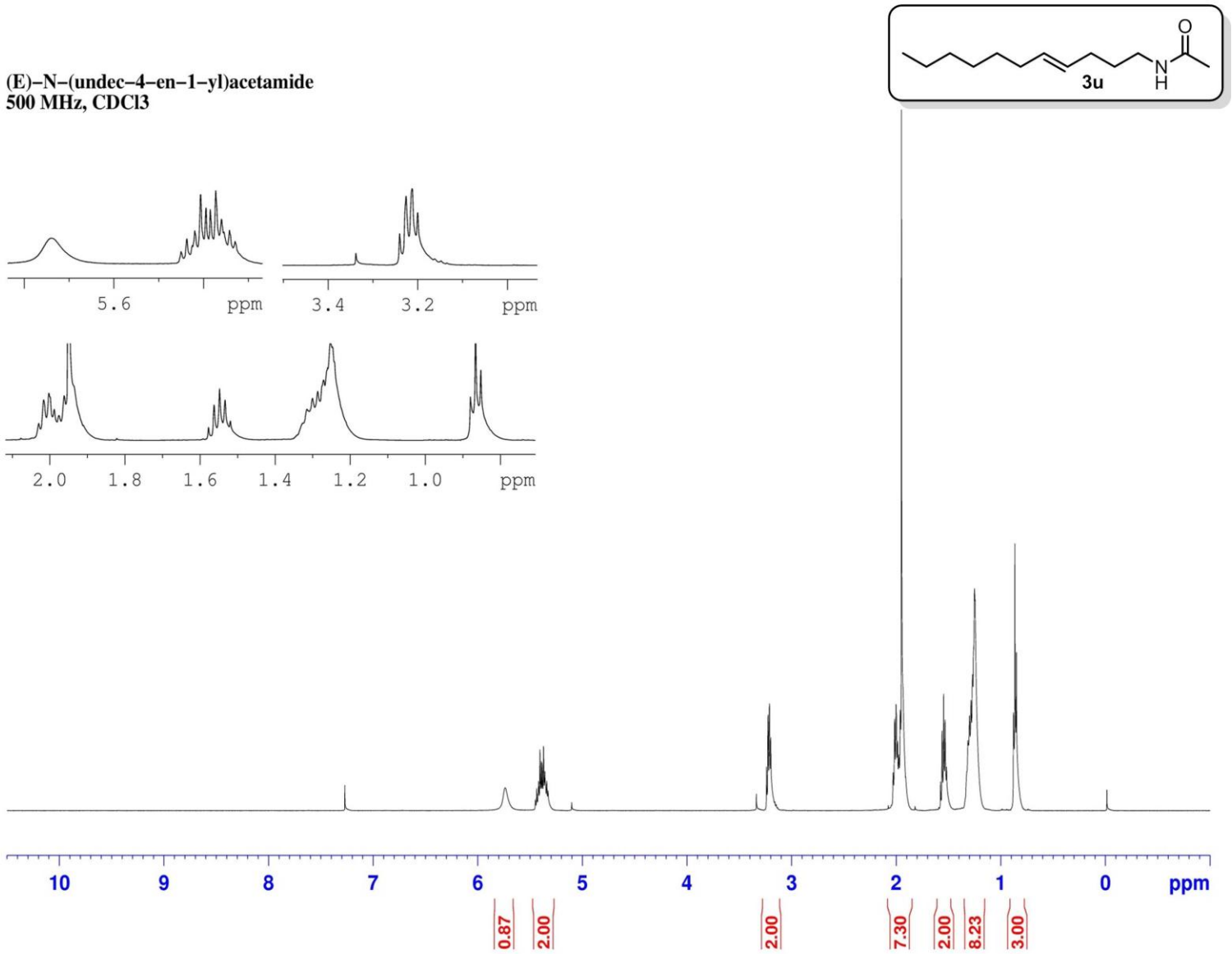




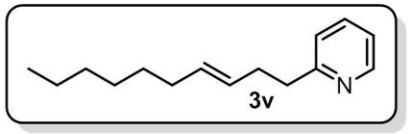
(E)−1−methoxyundec−4−ene
500 MHz, CDCl3

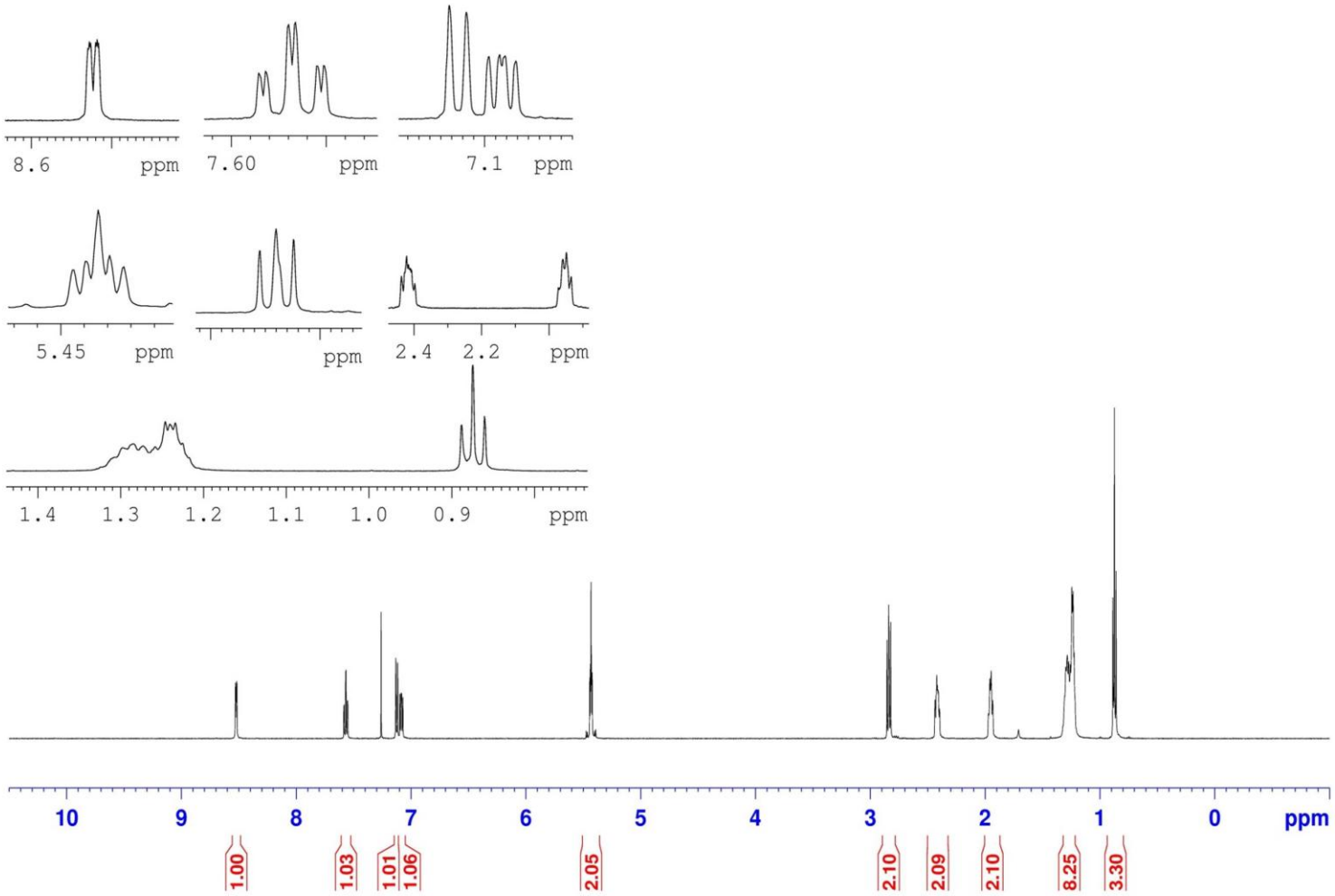




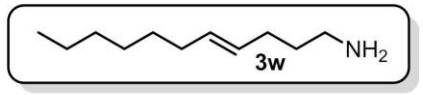

(E)–N–(undec–4–en–1–yl)acetamide
500 MHz, CDCl3
3u
O
N
H
5.6
ppm
3.4
3.2
ppm
2.0
1.8
1.6
1.4
1.2
1.0
ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
0.87
2.00
2.00
7.30
2.00
8.23
3.00

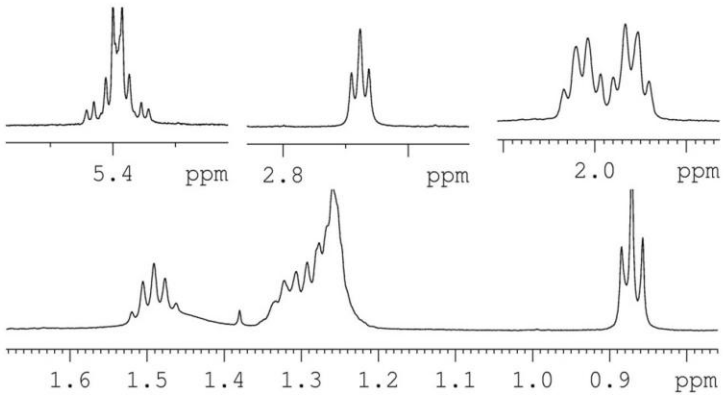
(E)−2−(dec−3−en−1−yl)pyridine
500 MHz, CDCl3

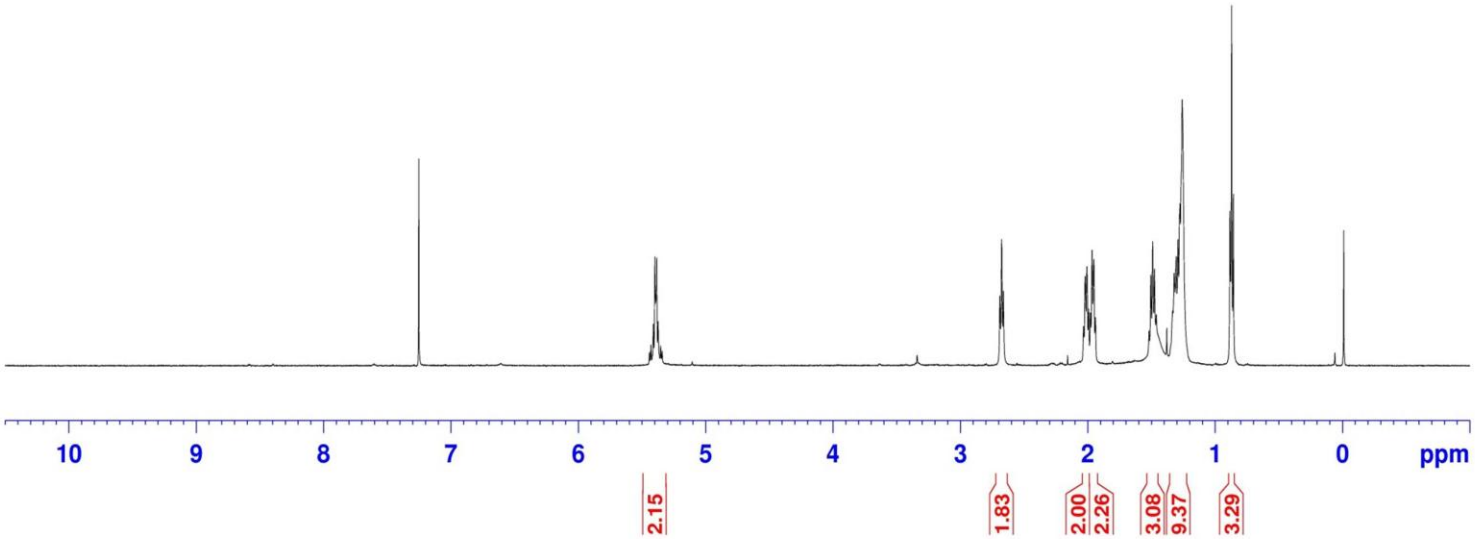




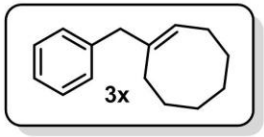
(E)–undec–4–en–1–amine
500 MHz, CDCl3

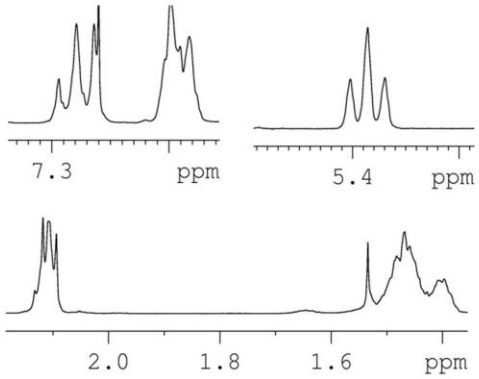


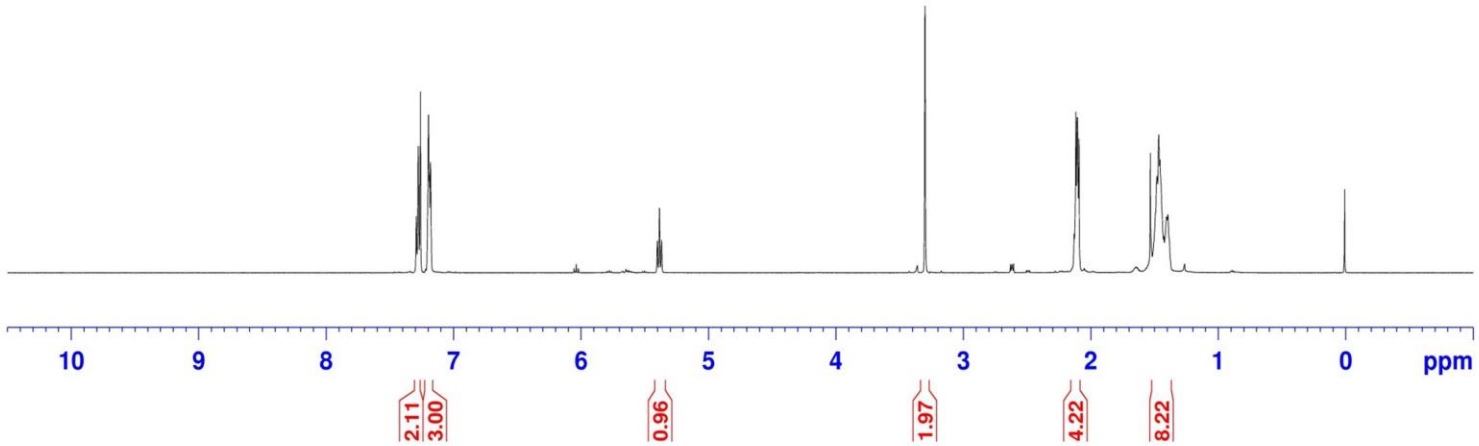




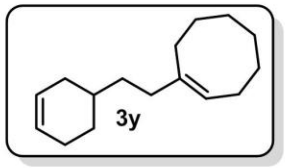
(E)–1–benzylcyclooct–1–ene
125 MHz, CDCl3

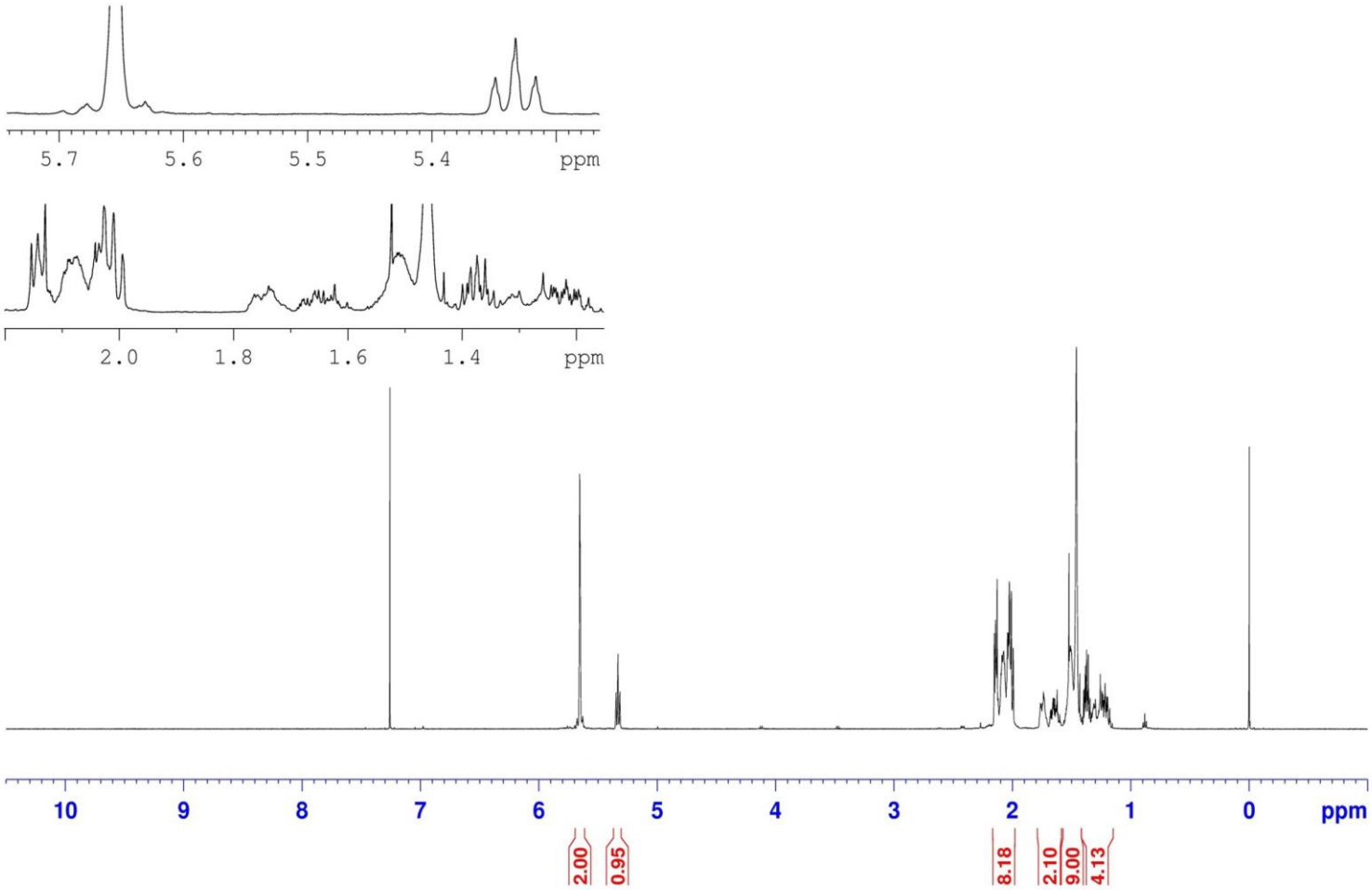




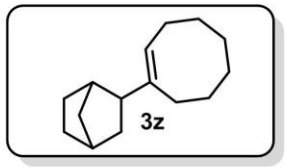


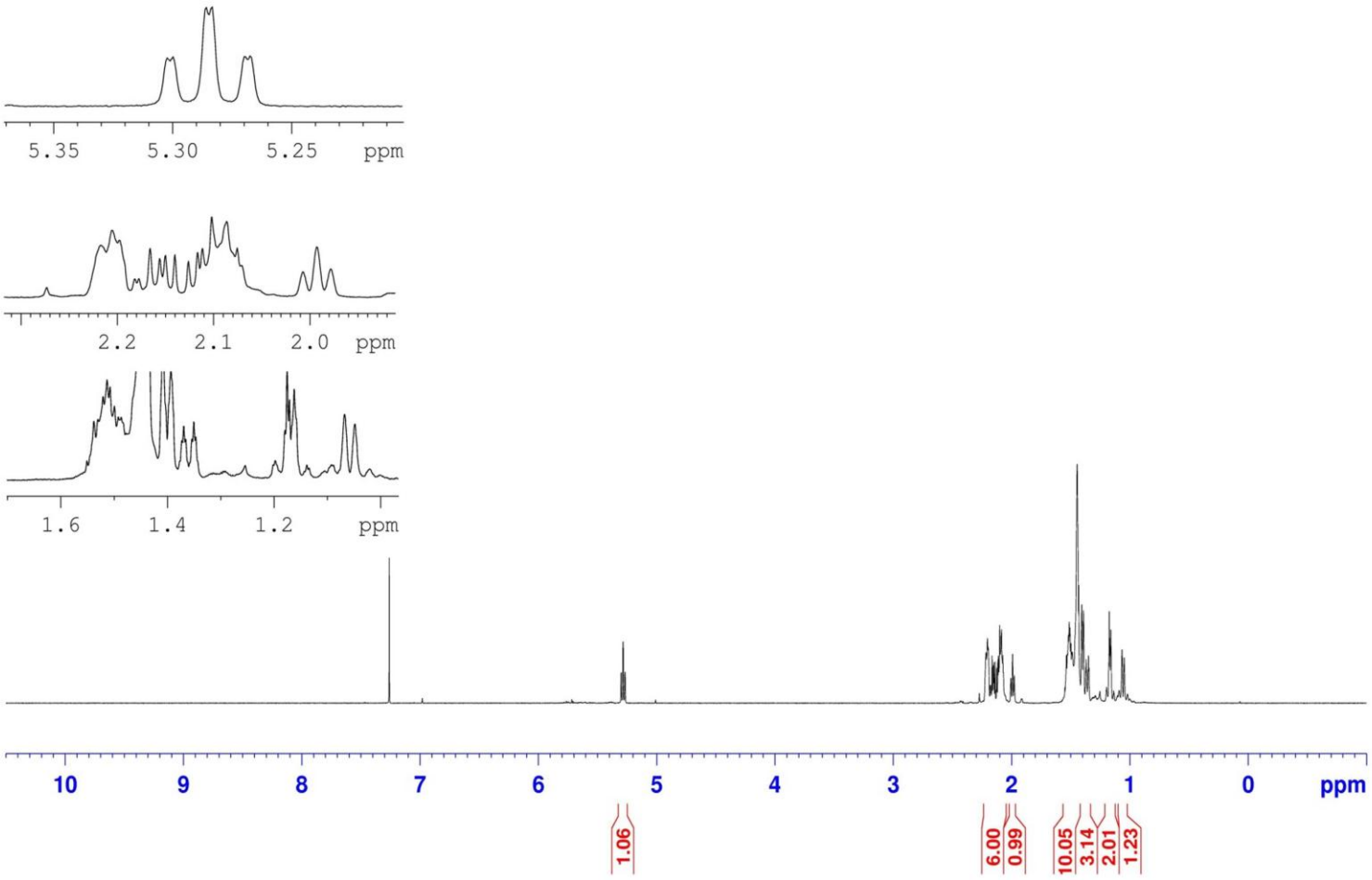
(E)−1−(2−(cyclohex−3−en−1−yl)ethyl)cyclooct−1−ene
500 MHz, CDCl3



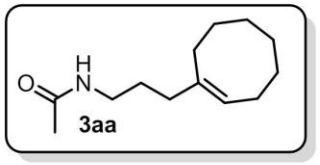


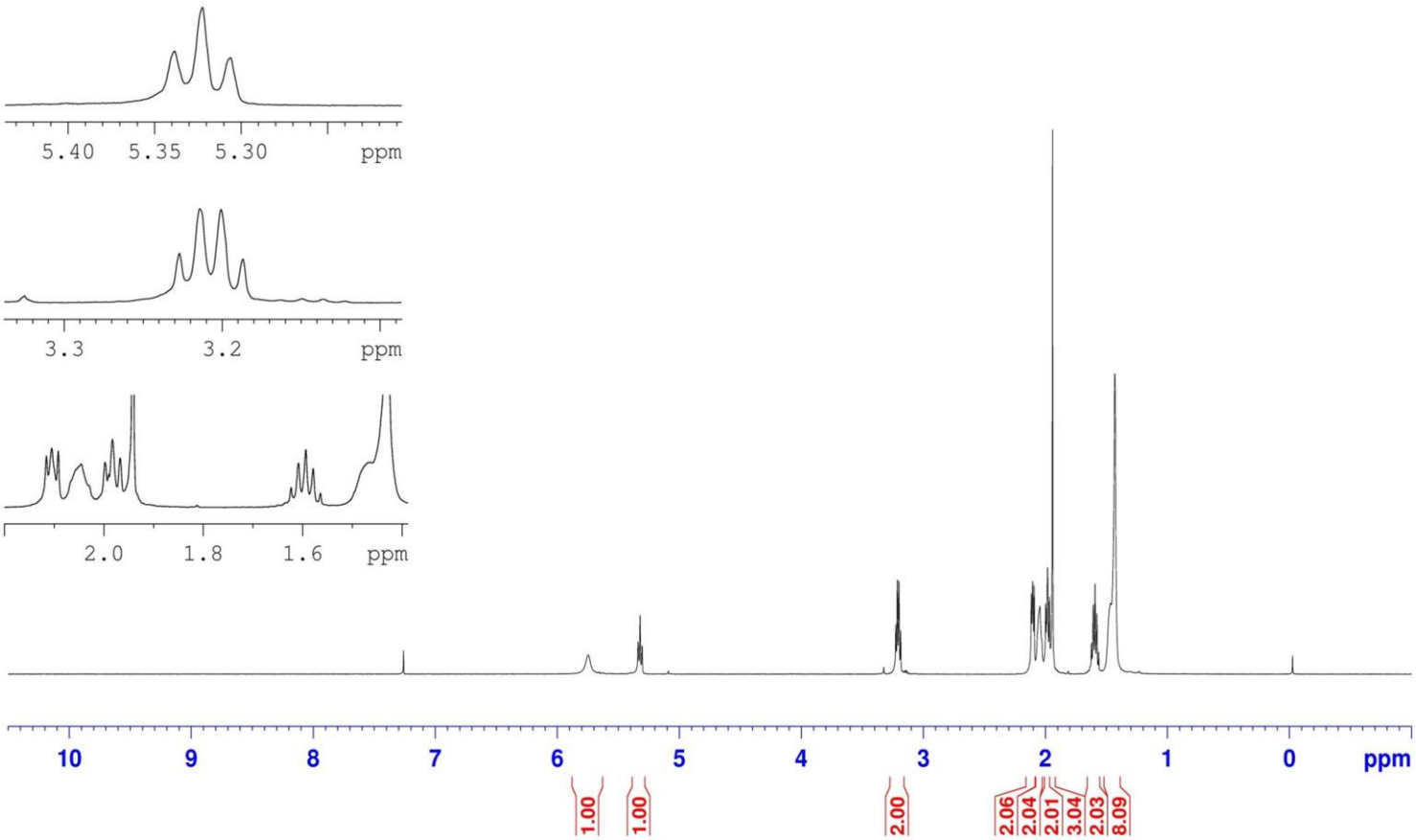
(E)−2−(cyclooct−1−en−1−yl)bicyclo[2.2.1]heptane
500 MHz, CDCl3



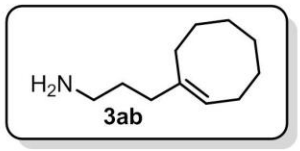


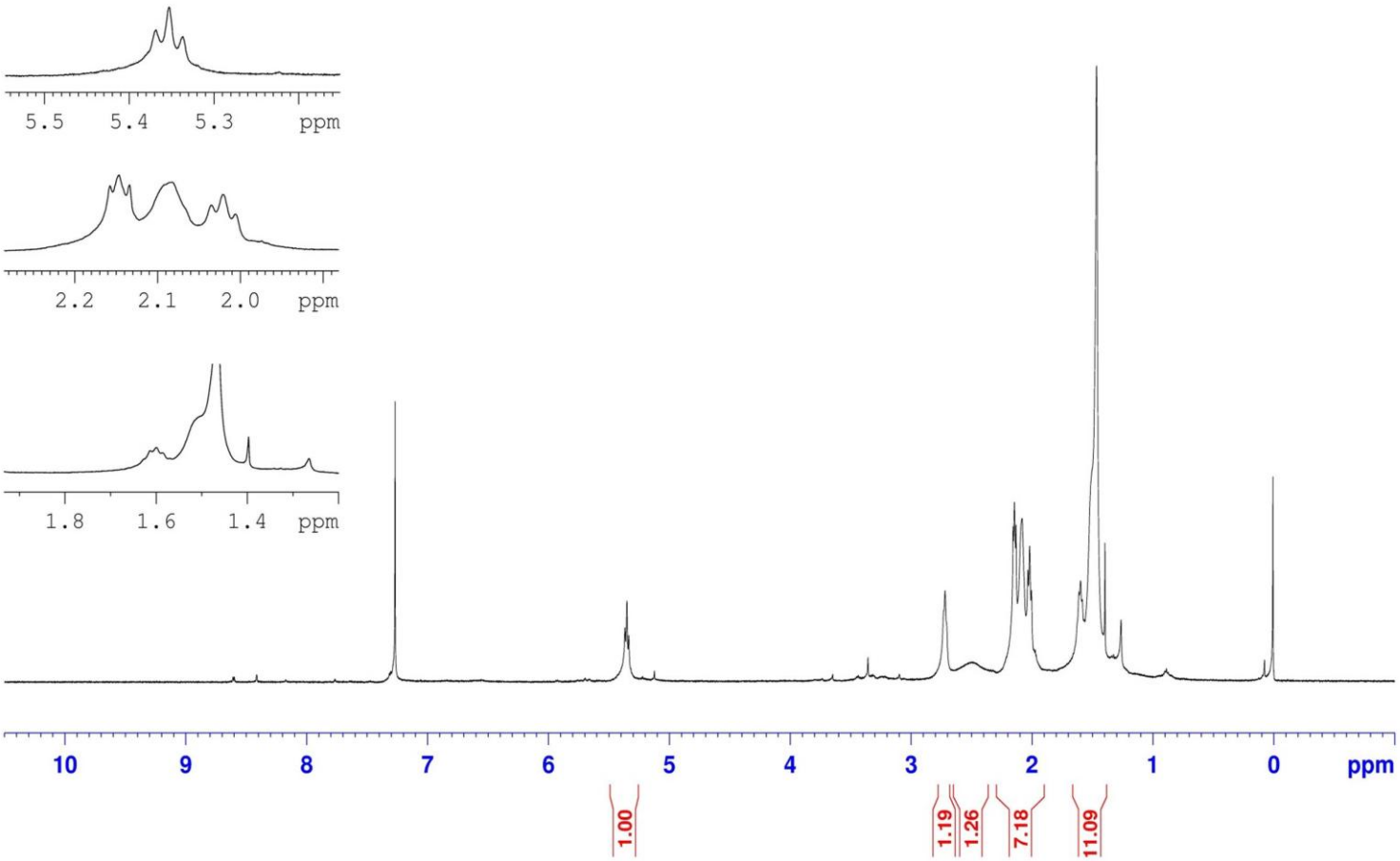
(E)−N−(3−(cyclooct−1−en−1−yl)propyl)acetamide
500 MHz, CDCl3



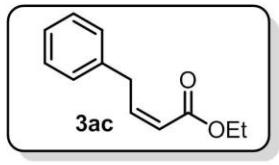


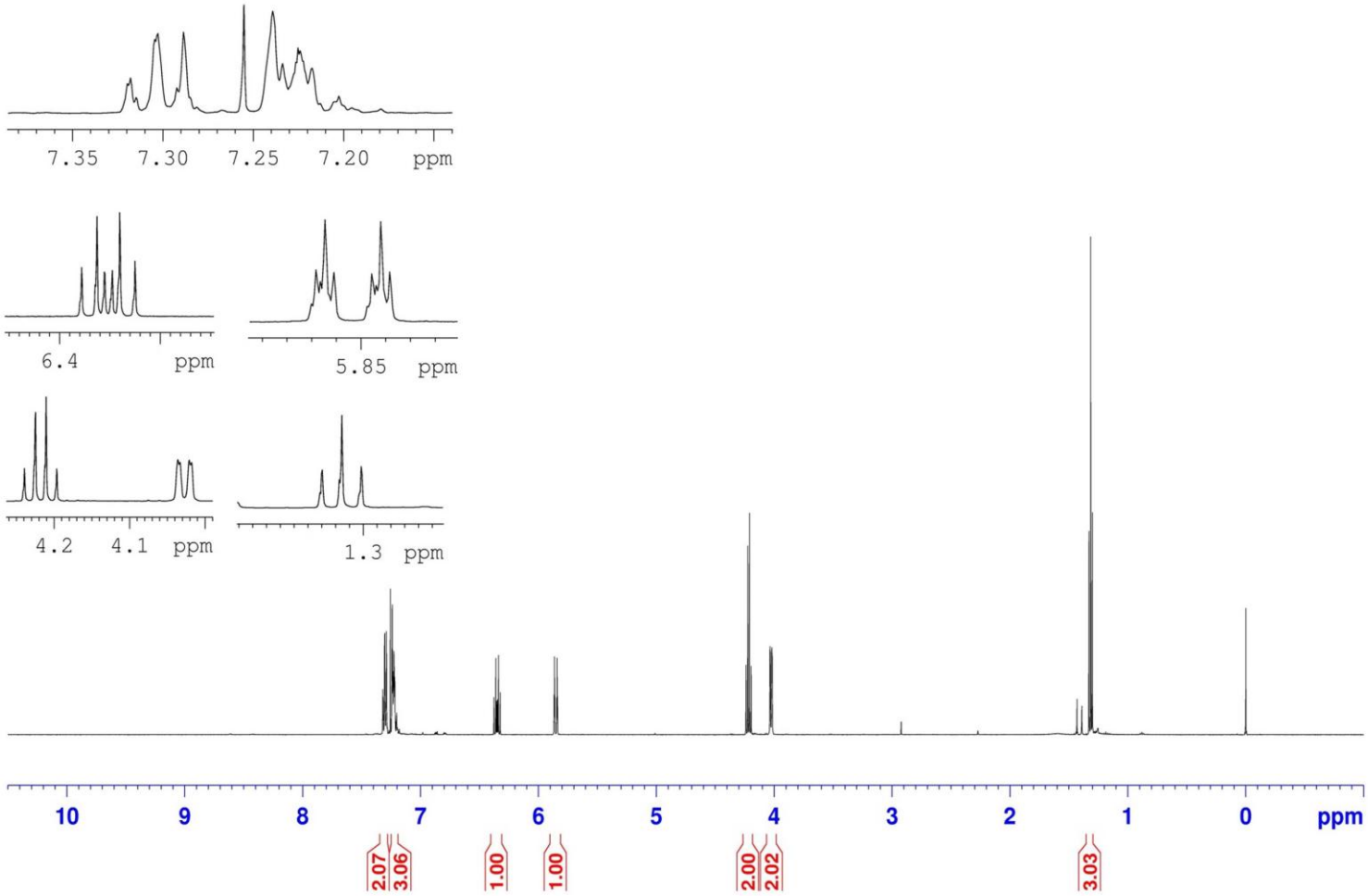
(E)–3–(cyclooct–1–en–1–yl)propan–1–amine
500 MHz, CDCl3



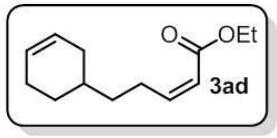


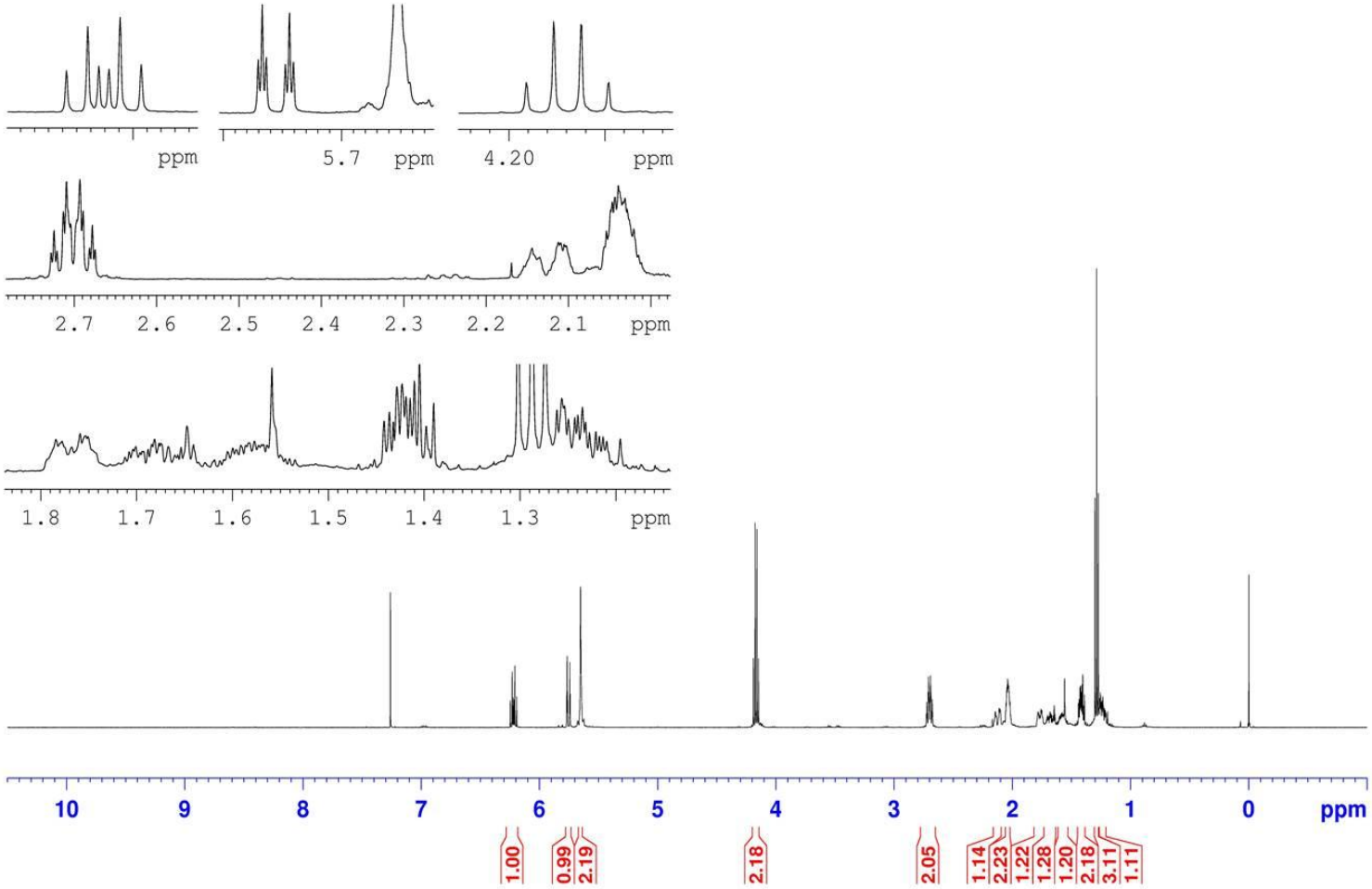
(Z)−ethyl 4−phenylbut−2−enoate
500 MHz, CDCl3



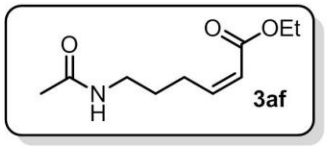


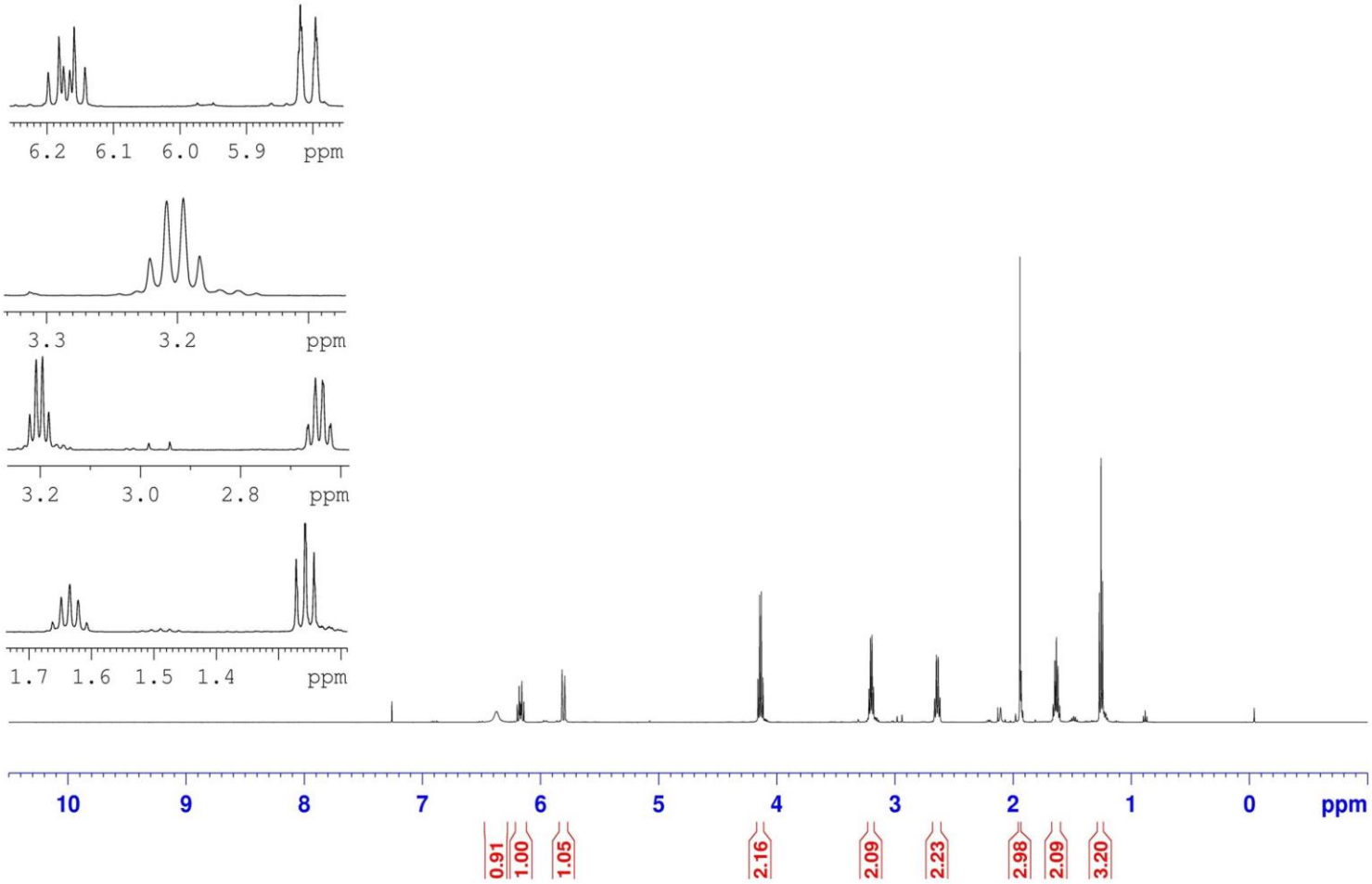
(Z)–Ethyl 5–(Cyclohex–3–en–1–yl)pent–2–enoate
500 MHz, CDCl3



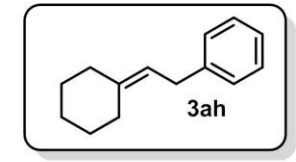


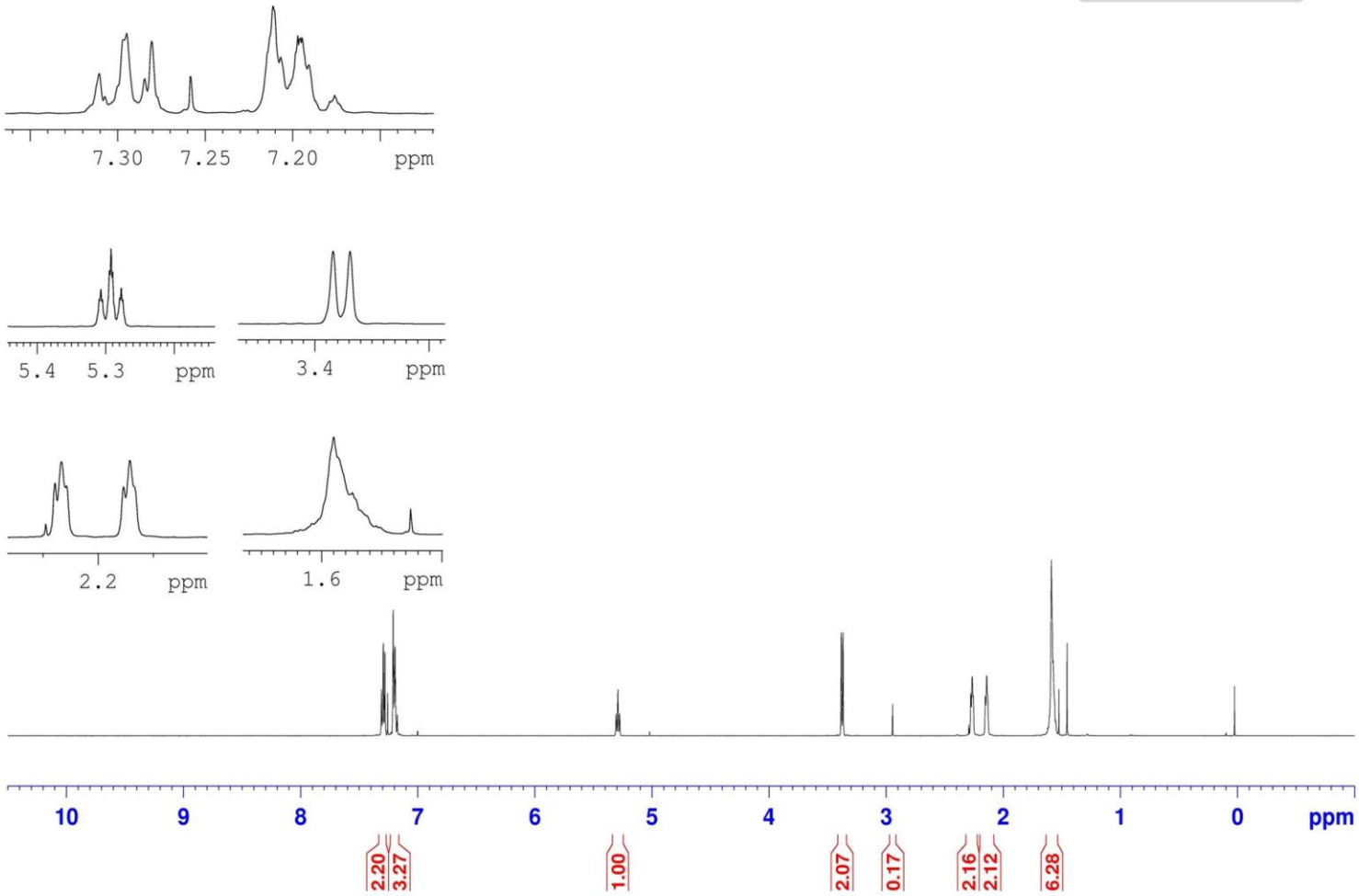
(Z)–ethyl 6–acetamidohex–2–enoate
500 MHz, CDCl3



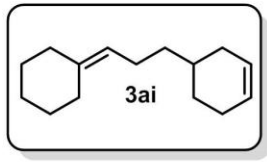


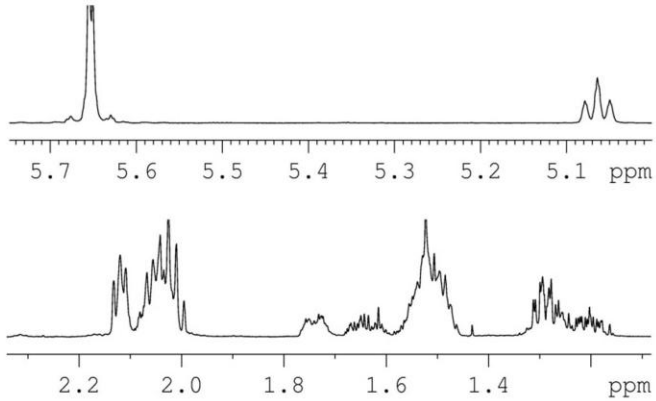
(2−cyclohexylideneethyl)benzene
500 MHz, CDCl3

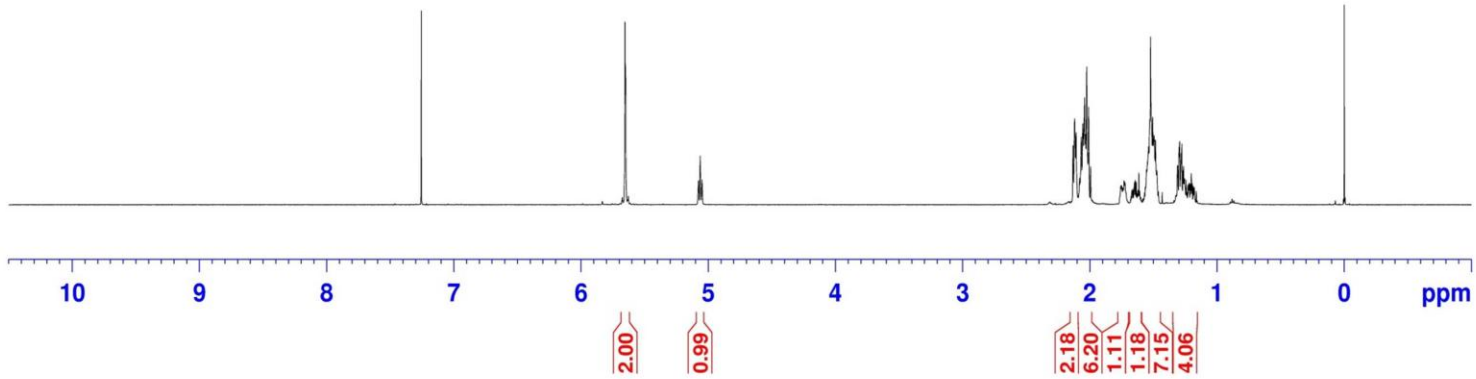




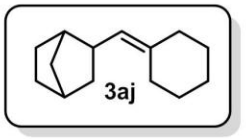
4–(3–cyclohexylidenepropyl)cyclohex–1–ene
500 MHz, CDCl3

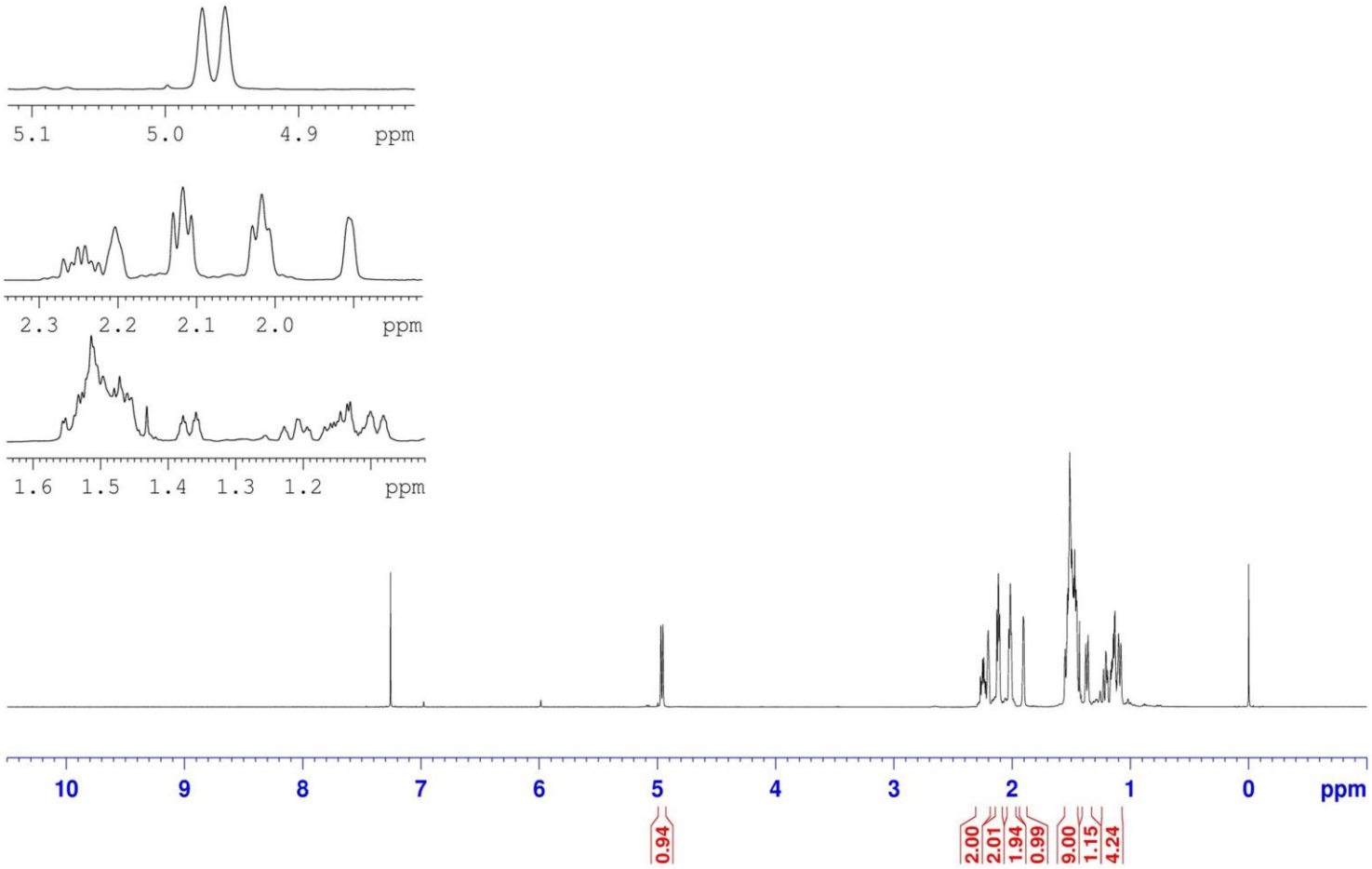




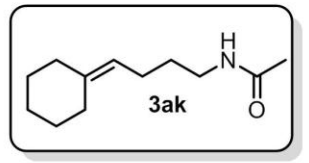


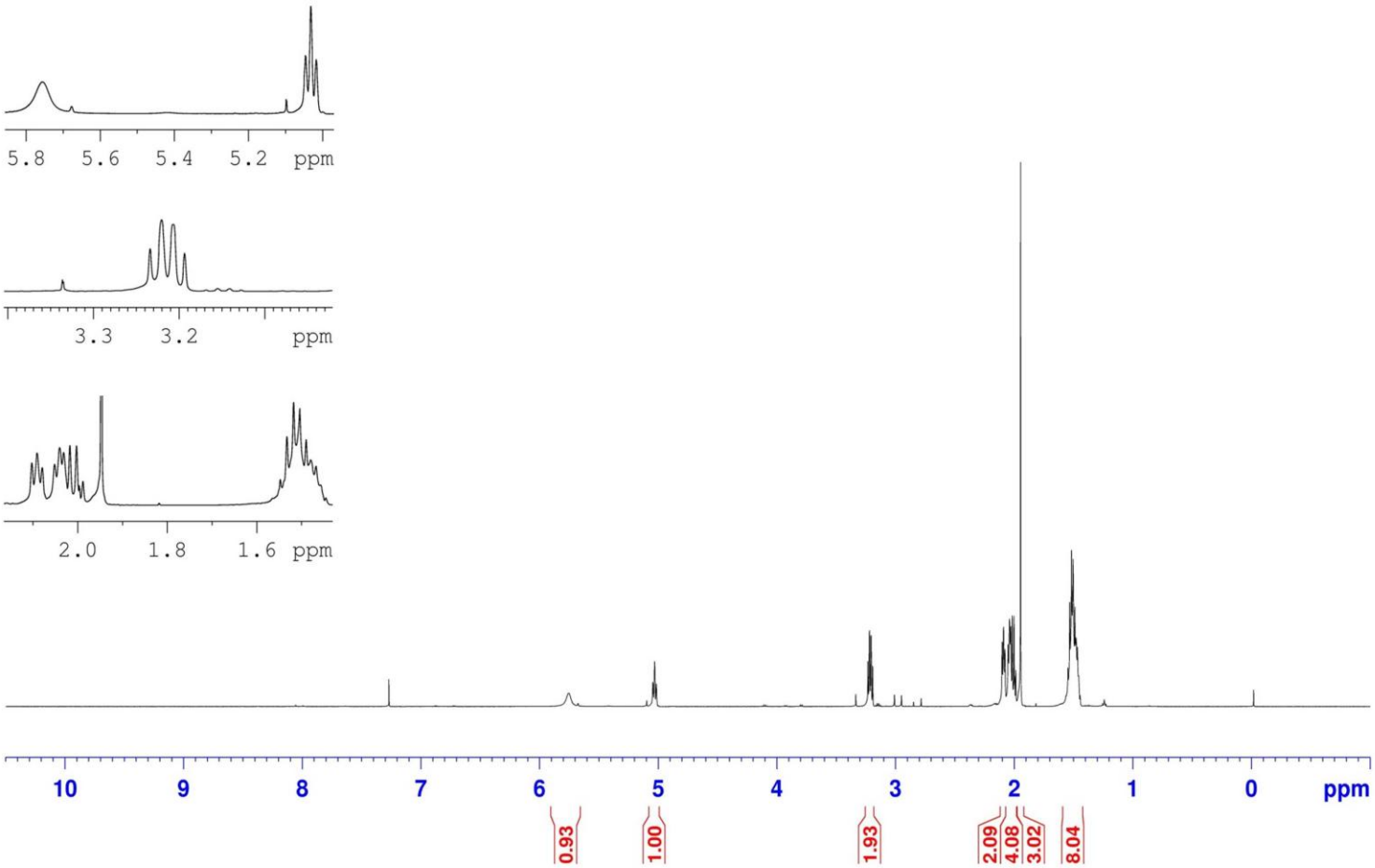
2–(cyclohexylidenemethyl)bicyclo[2.2.1]heptane
500 MHz, CDCl3



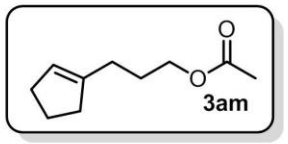


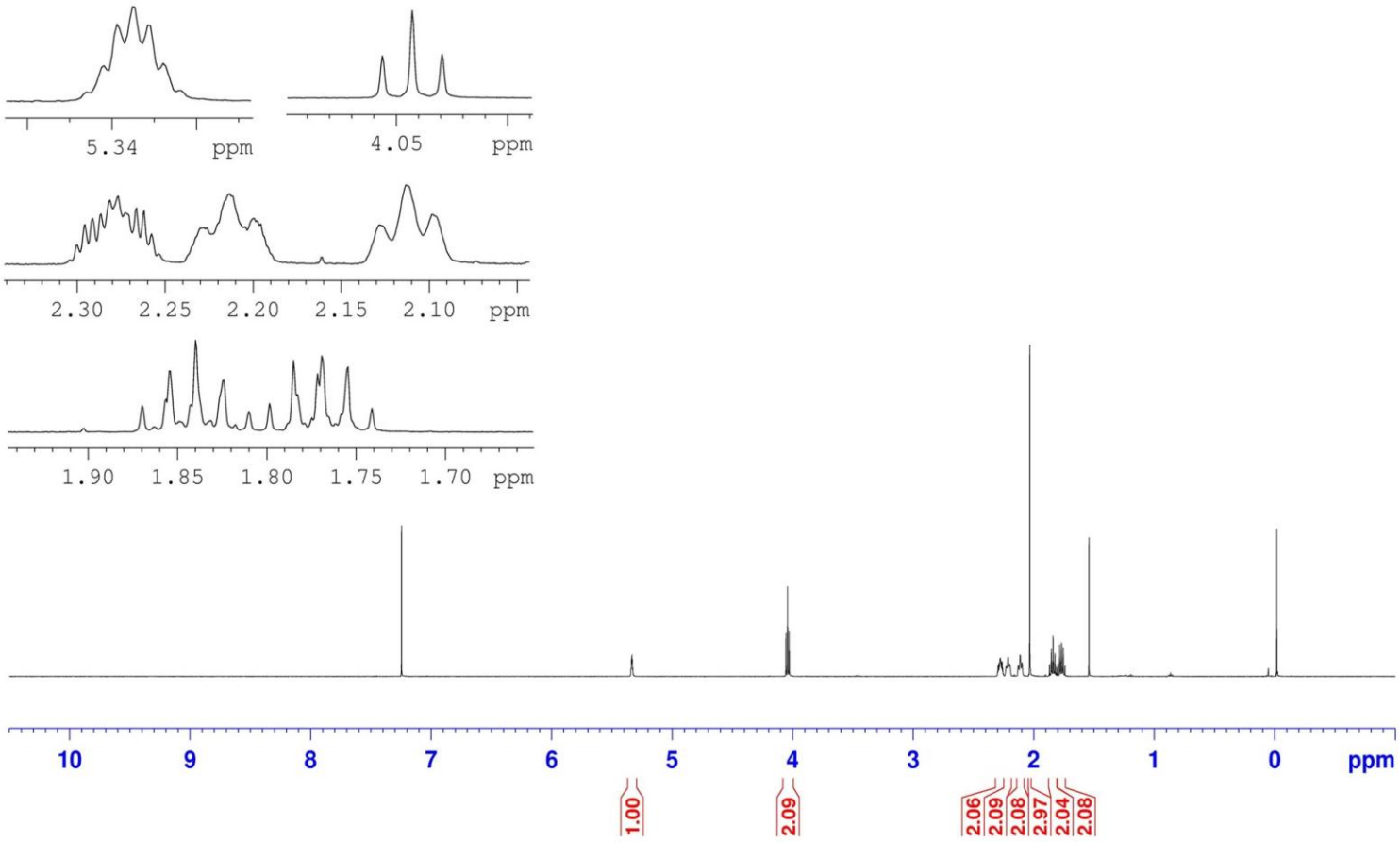
N–(4–cyclohexylidenebutyl)acetamide
500 MHz, CDCl3



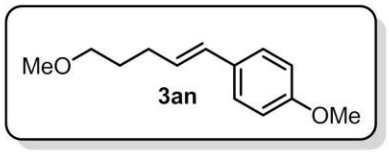


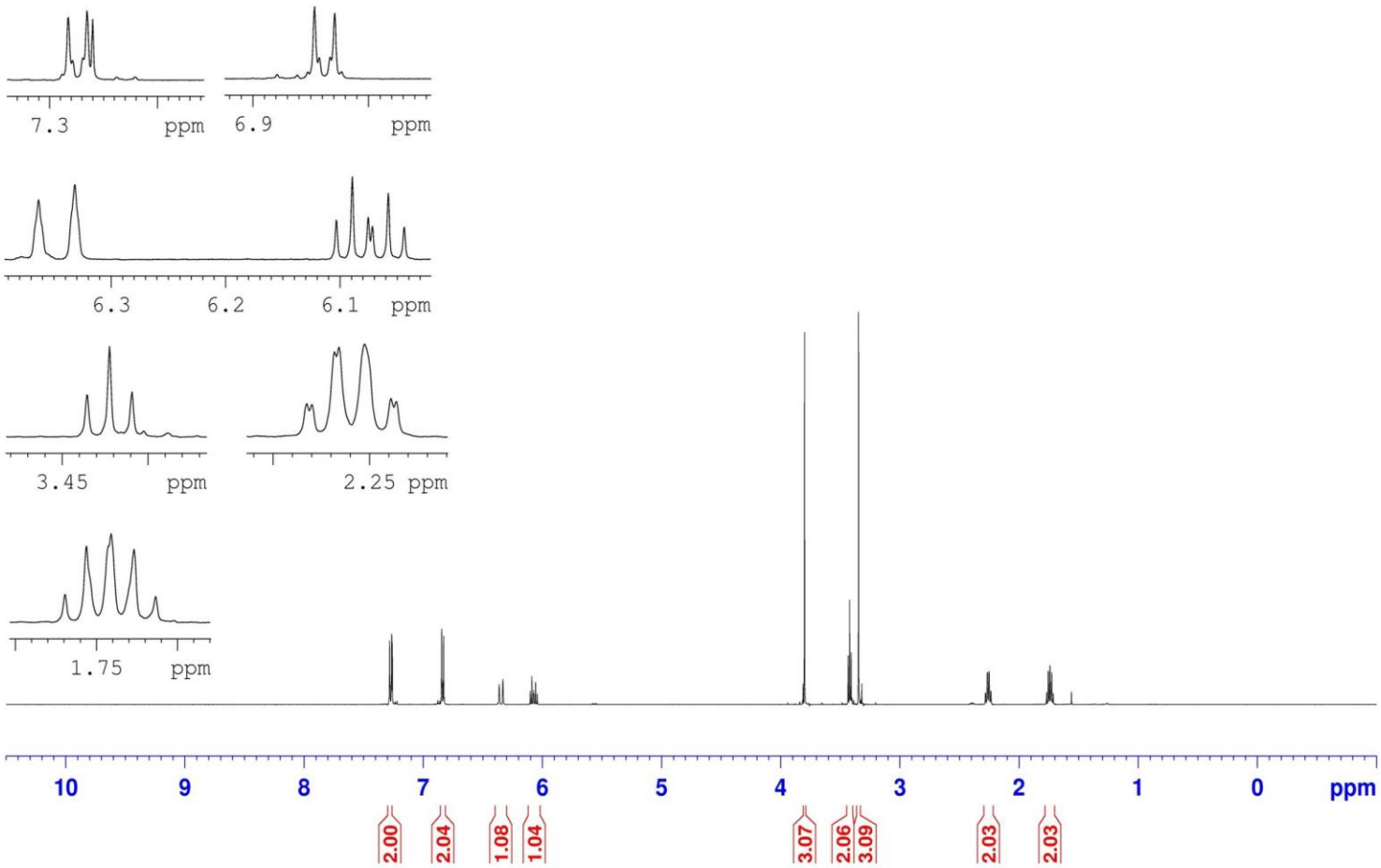
3–(cyclopent–1–en–1–yl)propyl acetate
500 MHz, CDCl3



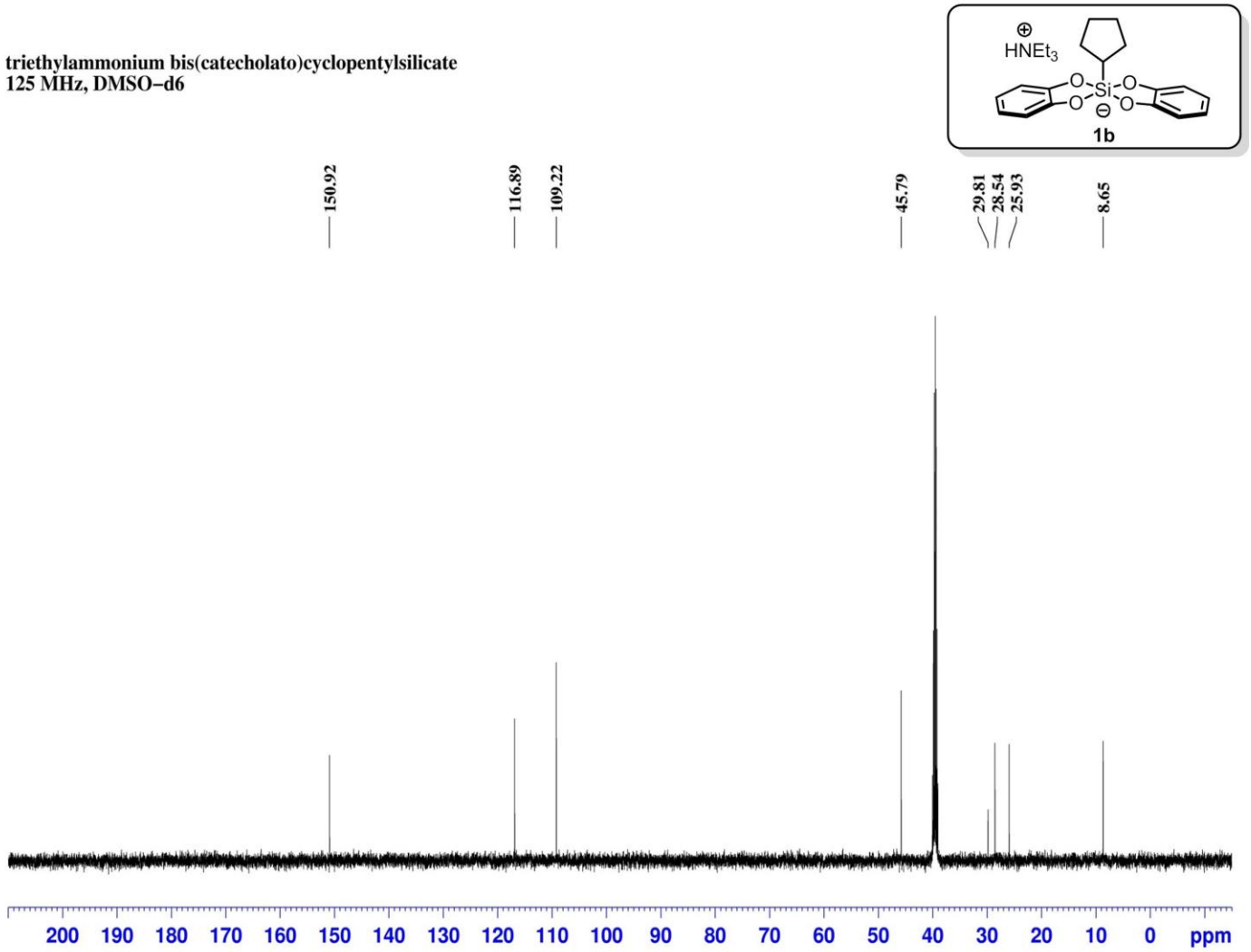


(E)−1−methoxy−4−(5−methoxypent−1−en−1−yl)benzene
500 MHz, CDCl3

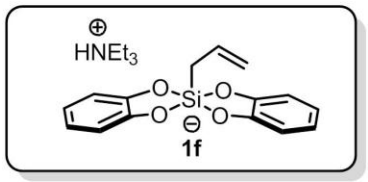


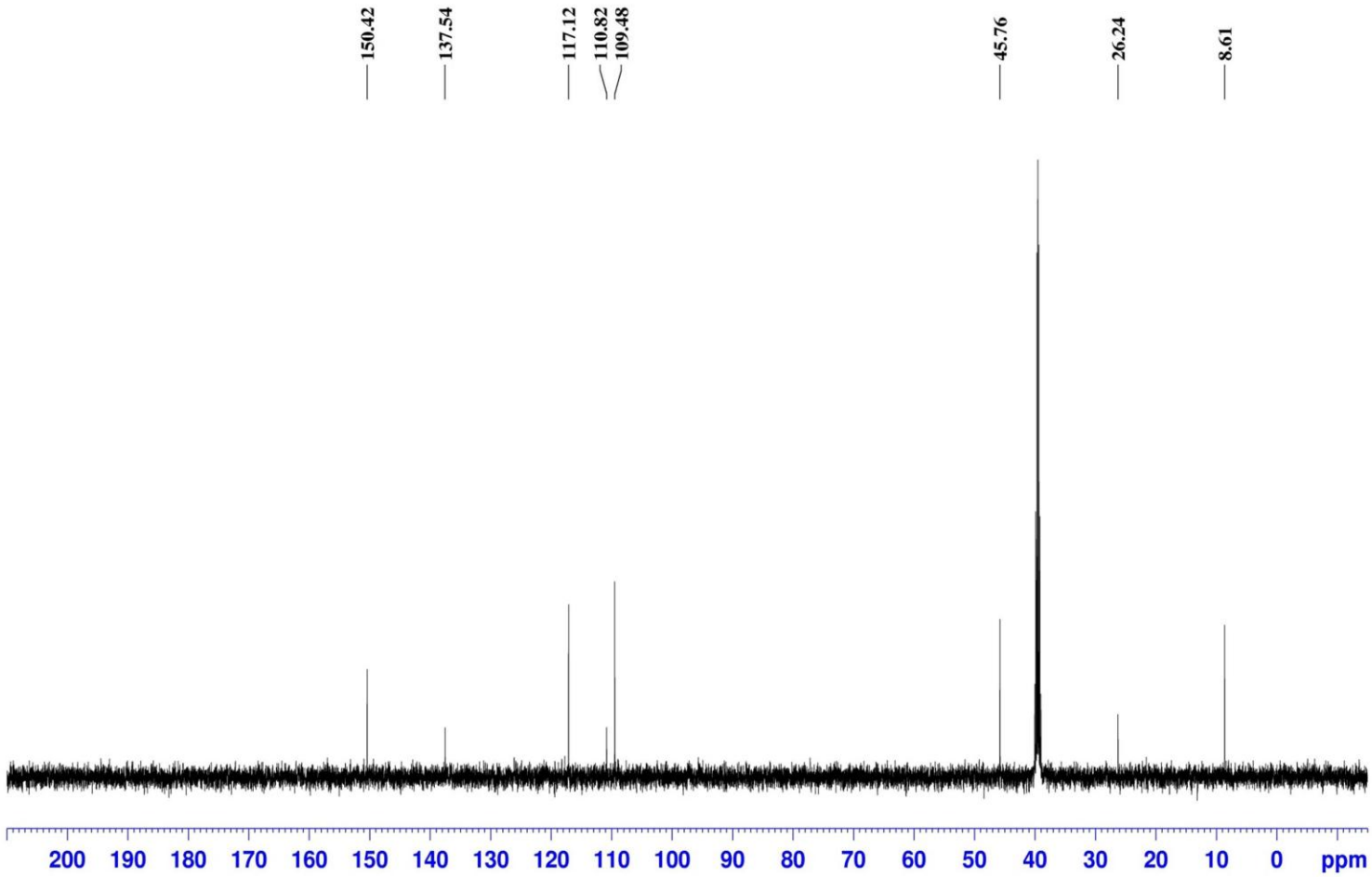


^{13}C NMR Spectra of Synthesized Compounds

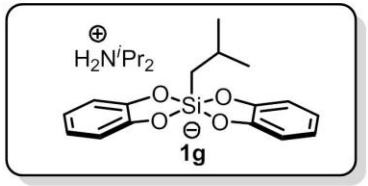


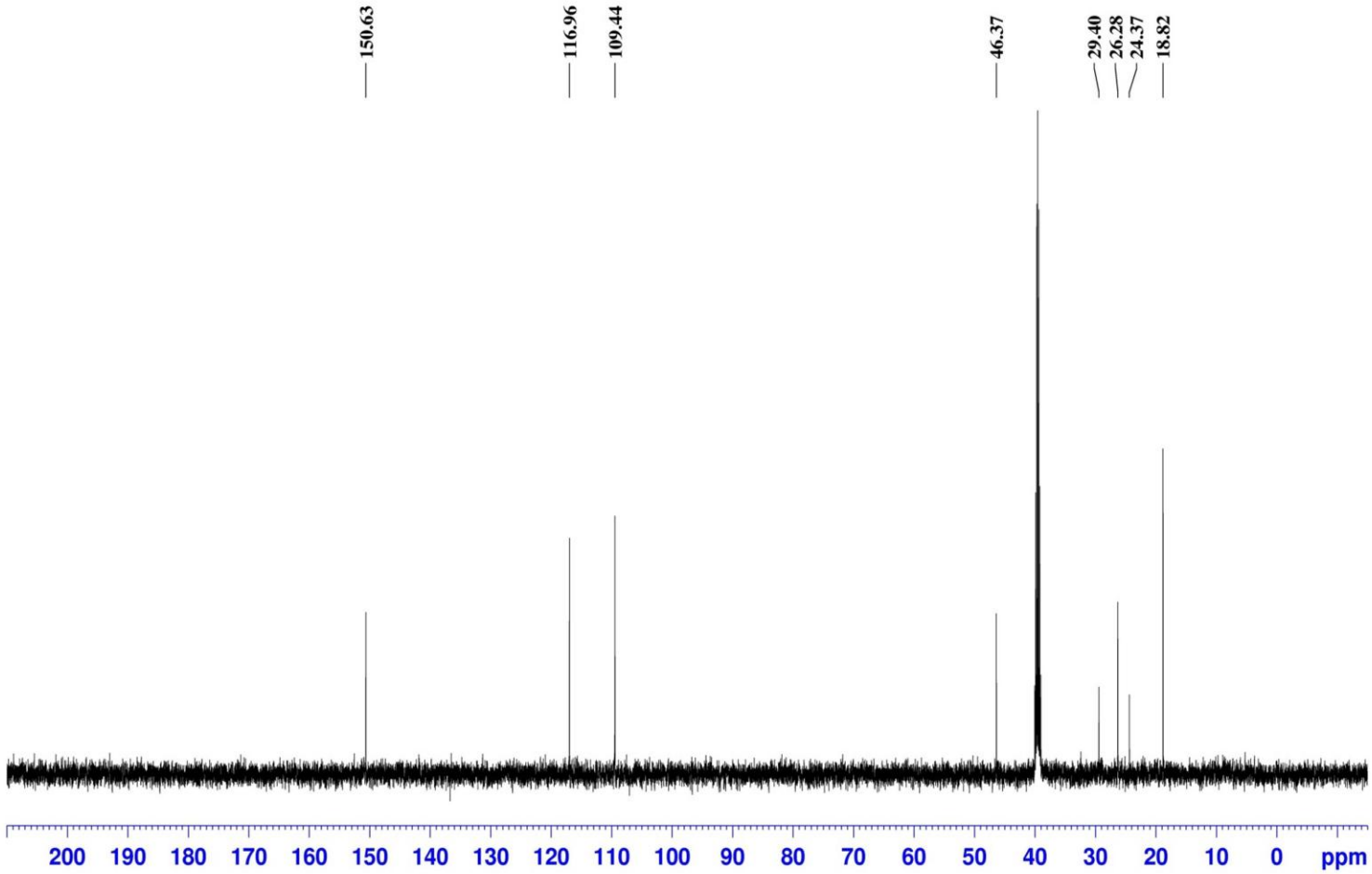
triethylammonium bis(catecholato)allylsilicate
125 MHz, DMSO–d6



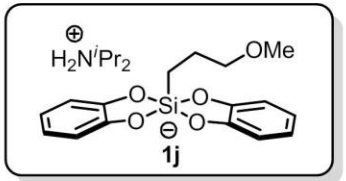


diisopropylammonium bis(catecholato)isobutylsilicate
125 MHz, DMSO–d6

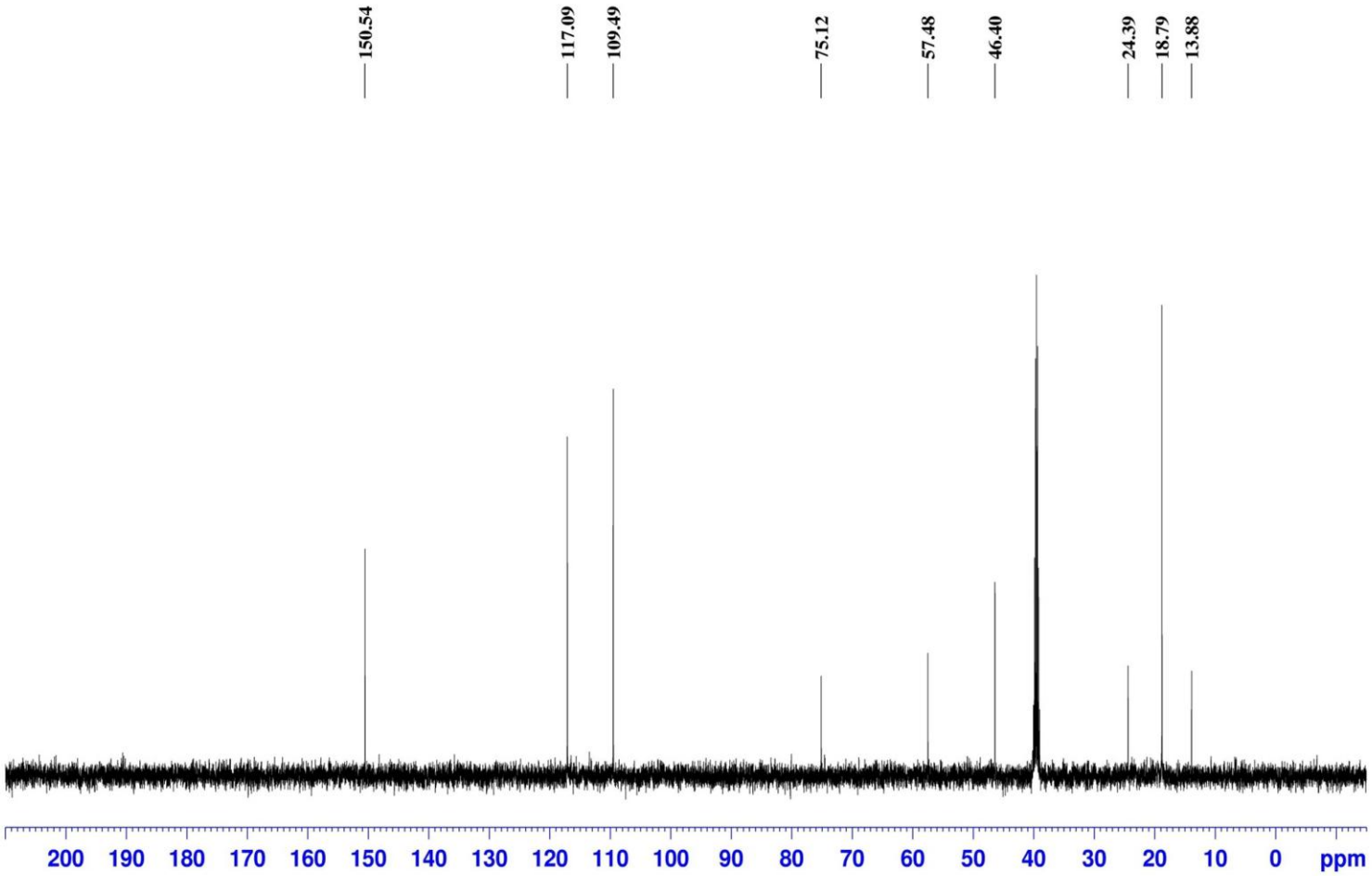




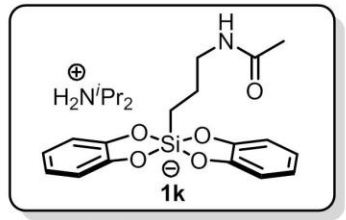
diisopropylammonium bis(catecholato)(3−methoxypropyl)silicate
125 MHz, DMSO−d6

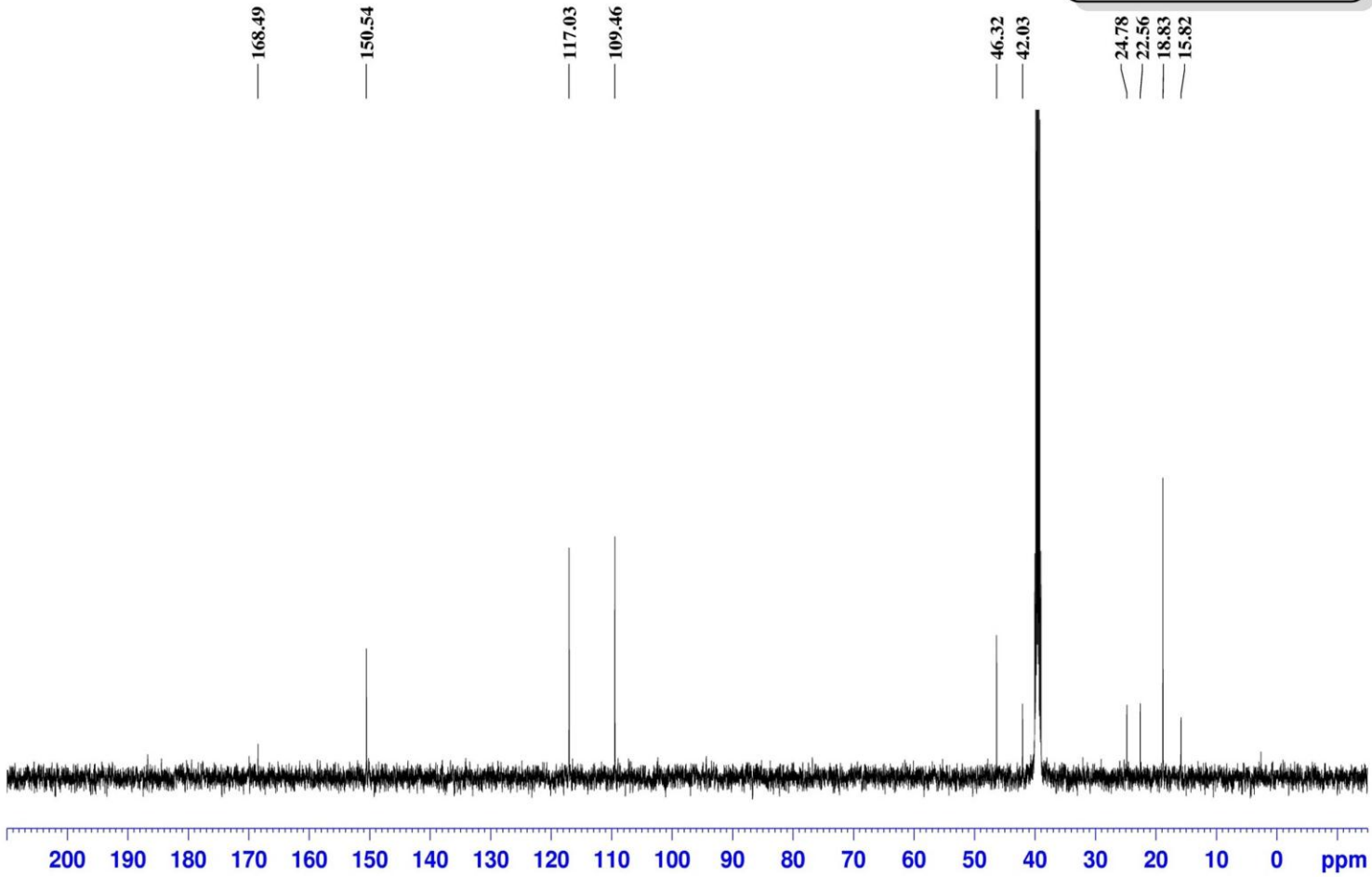


1j

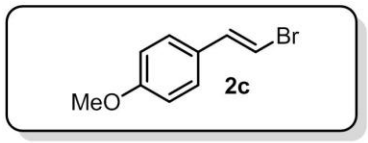


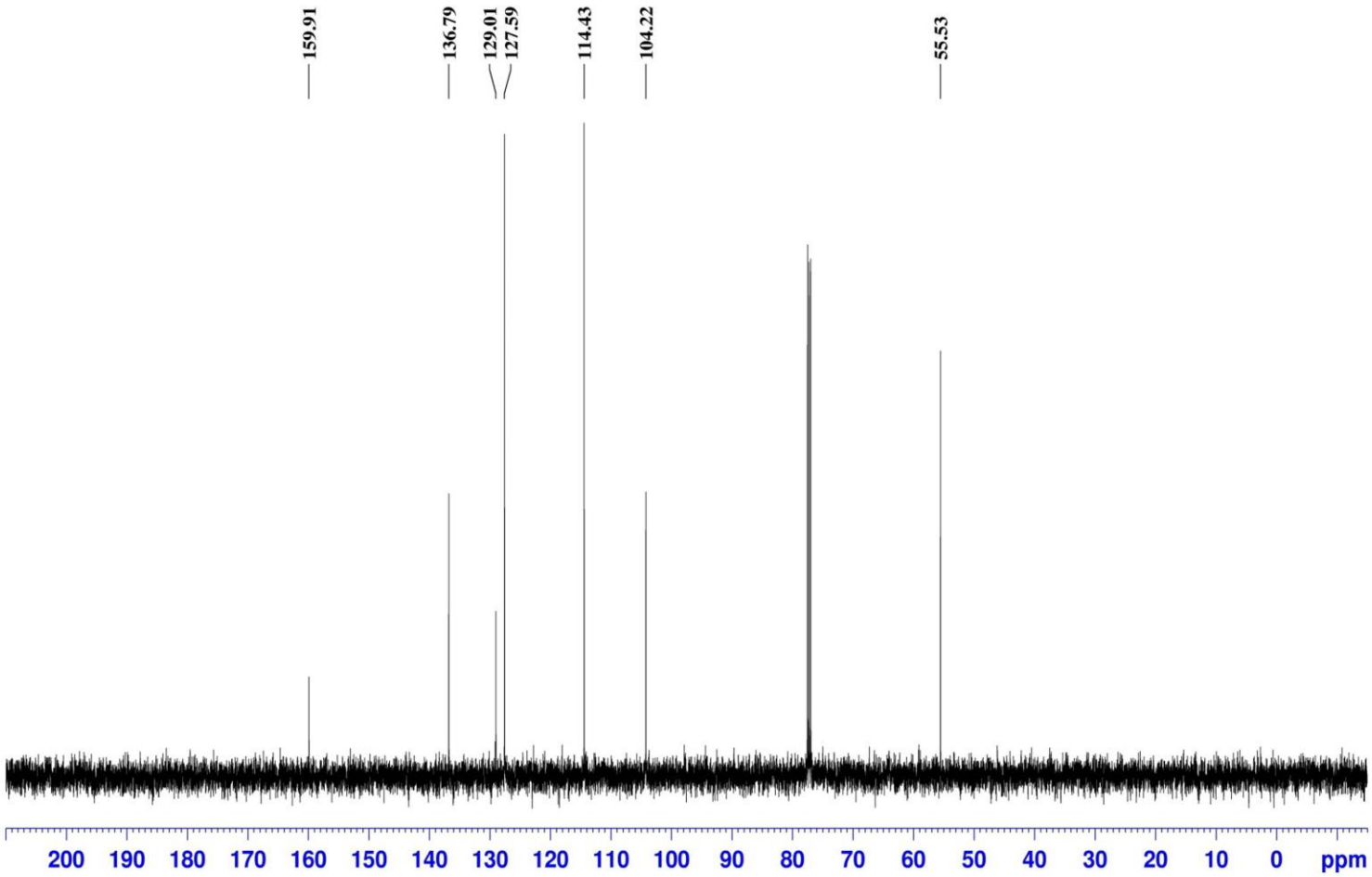
diisopropylammonium bis(catecholato)(3−acetamidopropyl)silicate
125 MHz, DMSO−d6



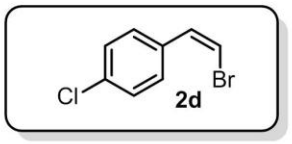


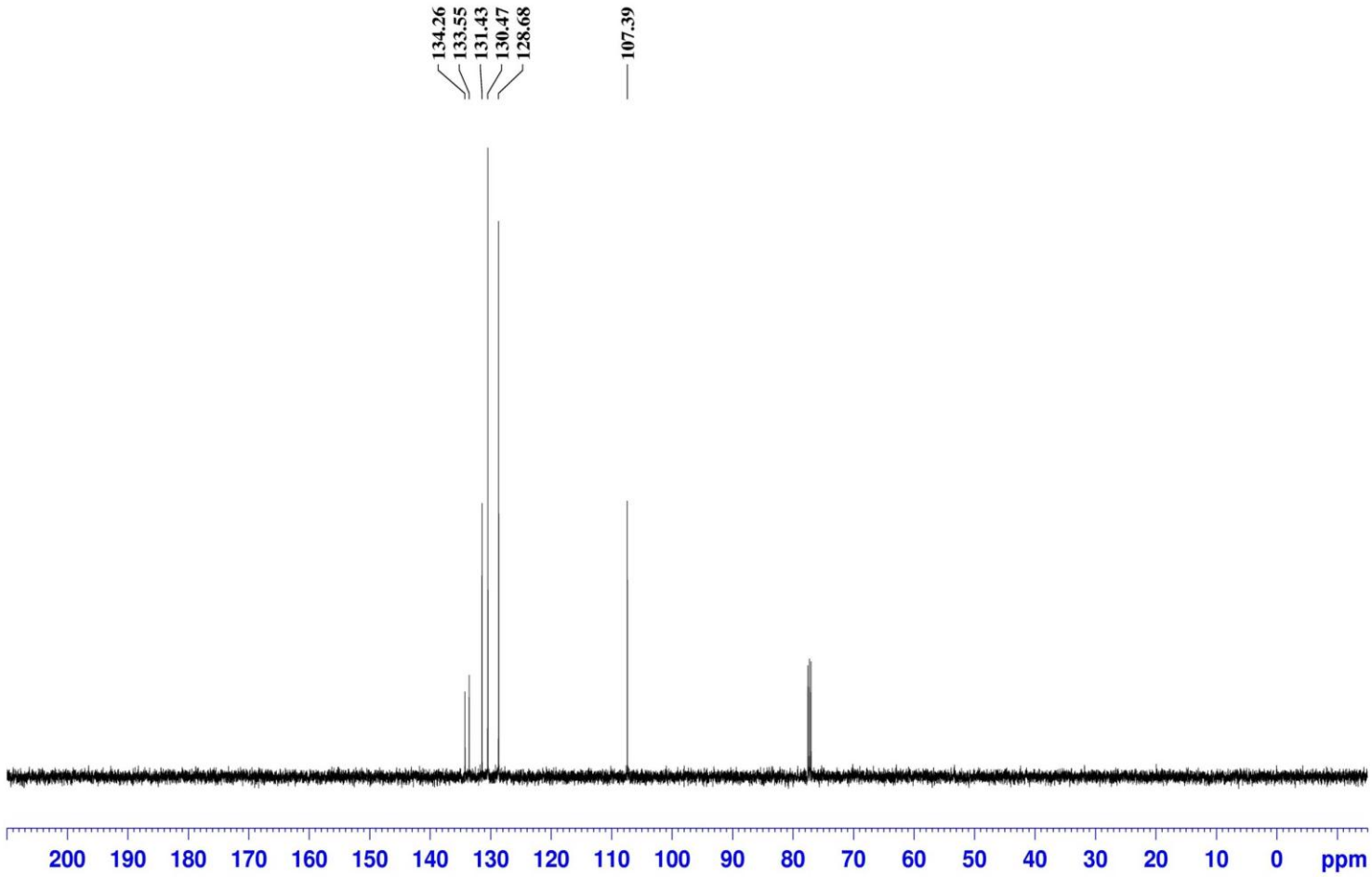
(E)−1−(2−bromovinyl)−4−methoxybenzene
125 MHz, CDCl3



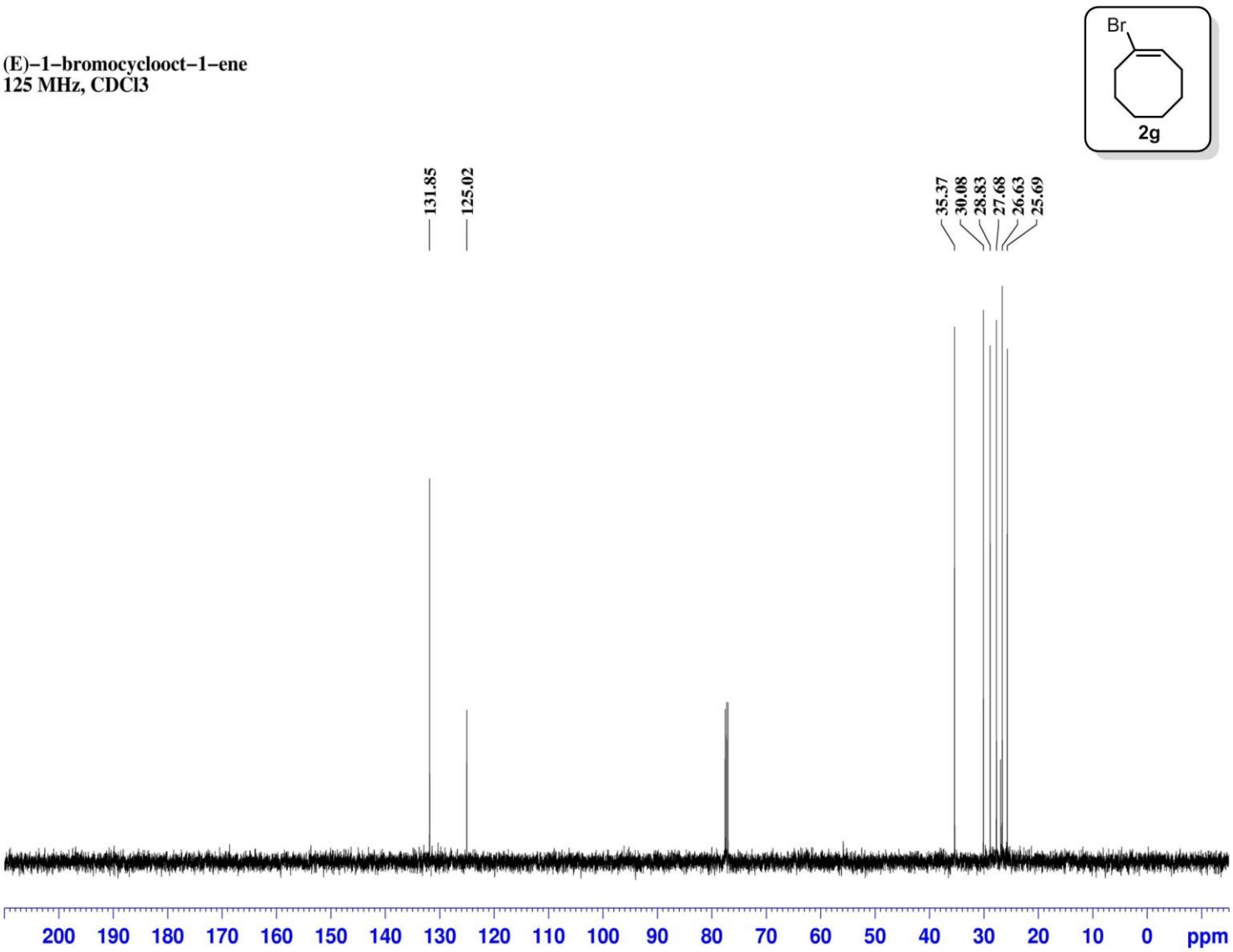


(Z)−1−(2−bromovinyl)−4−chlorobenzene
125 MHz, CDCl3

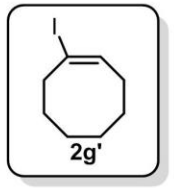


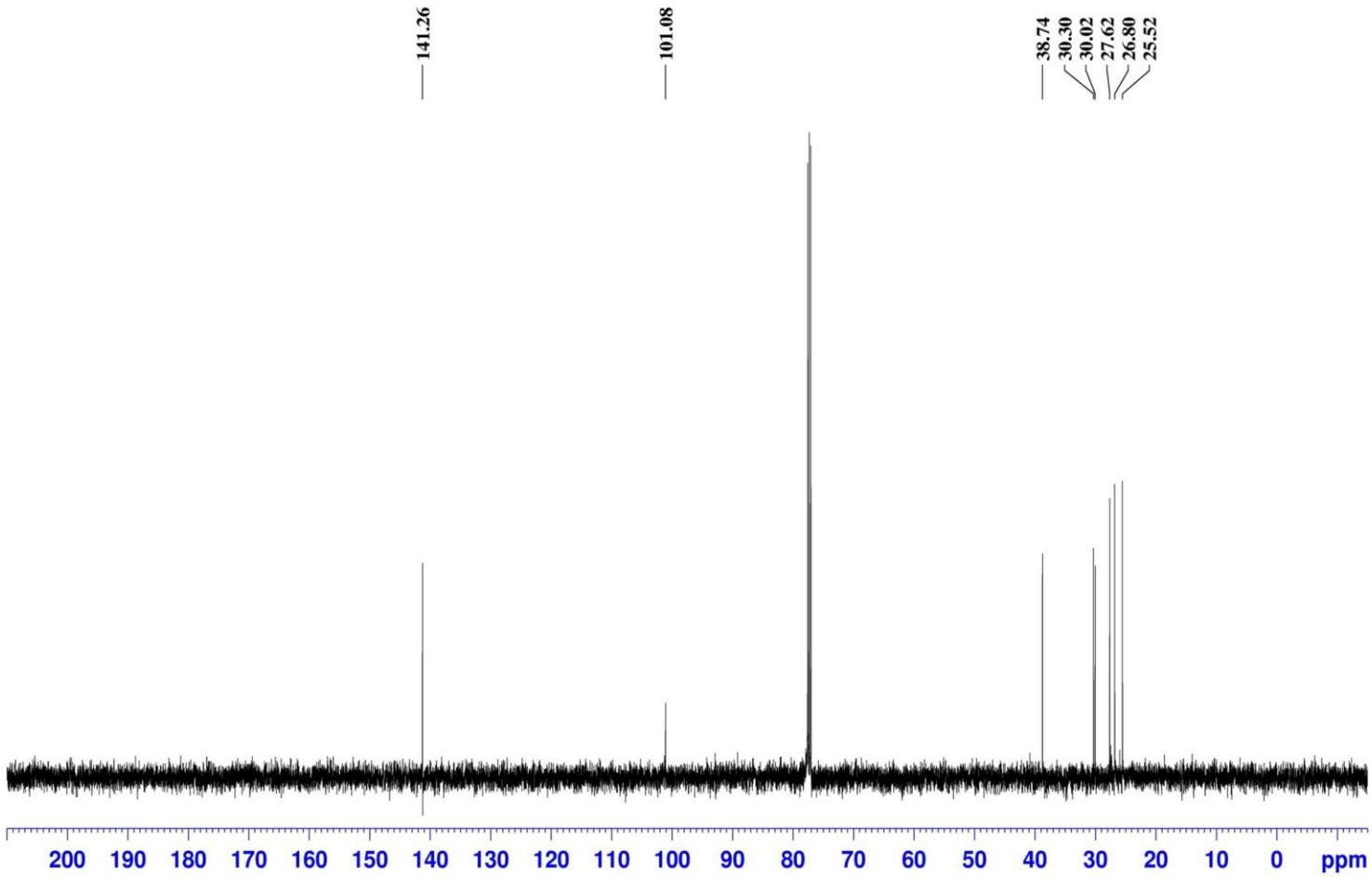


(E)−1−bromocyclooct−1−ene
125 MHz, CDCl3

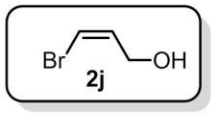


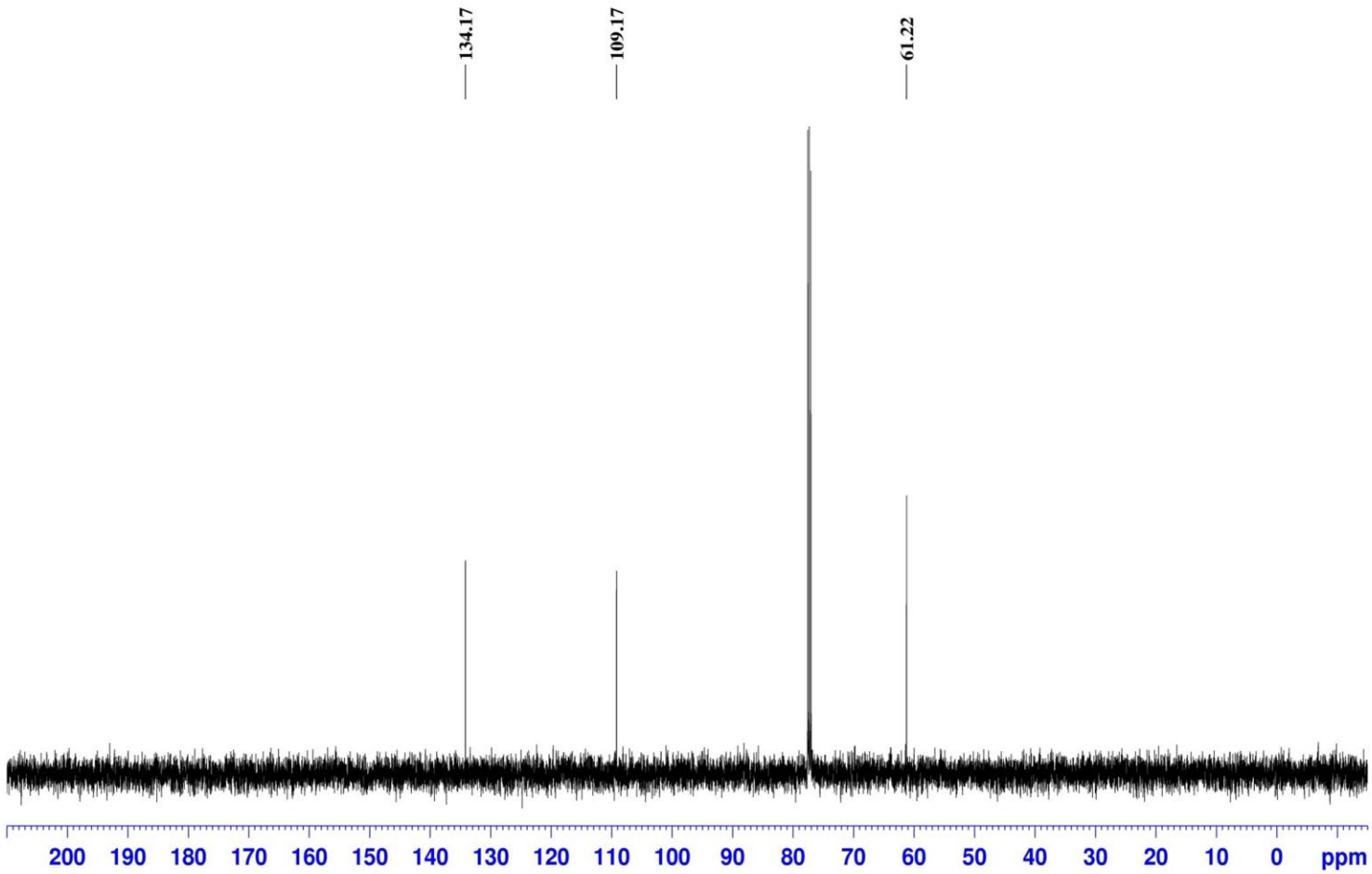
(E)−1−iodocyclooct−1−ene
125 MHz, CDCl3



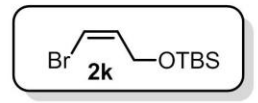


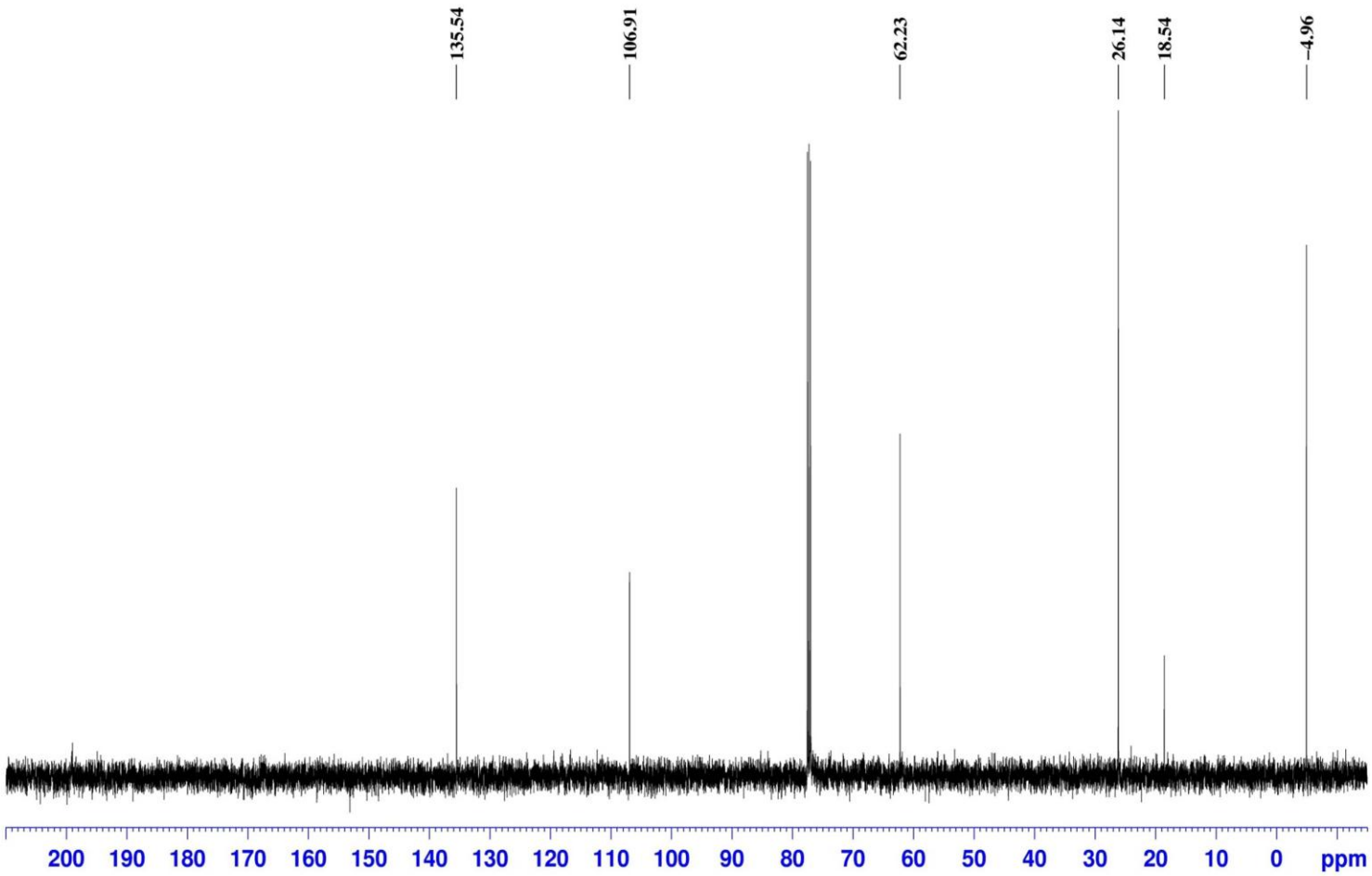
(Z)–3–bromoprop–2–en–1–ol
125 MHz, CDCl3



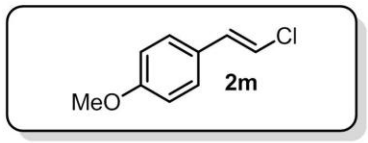


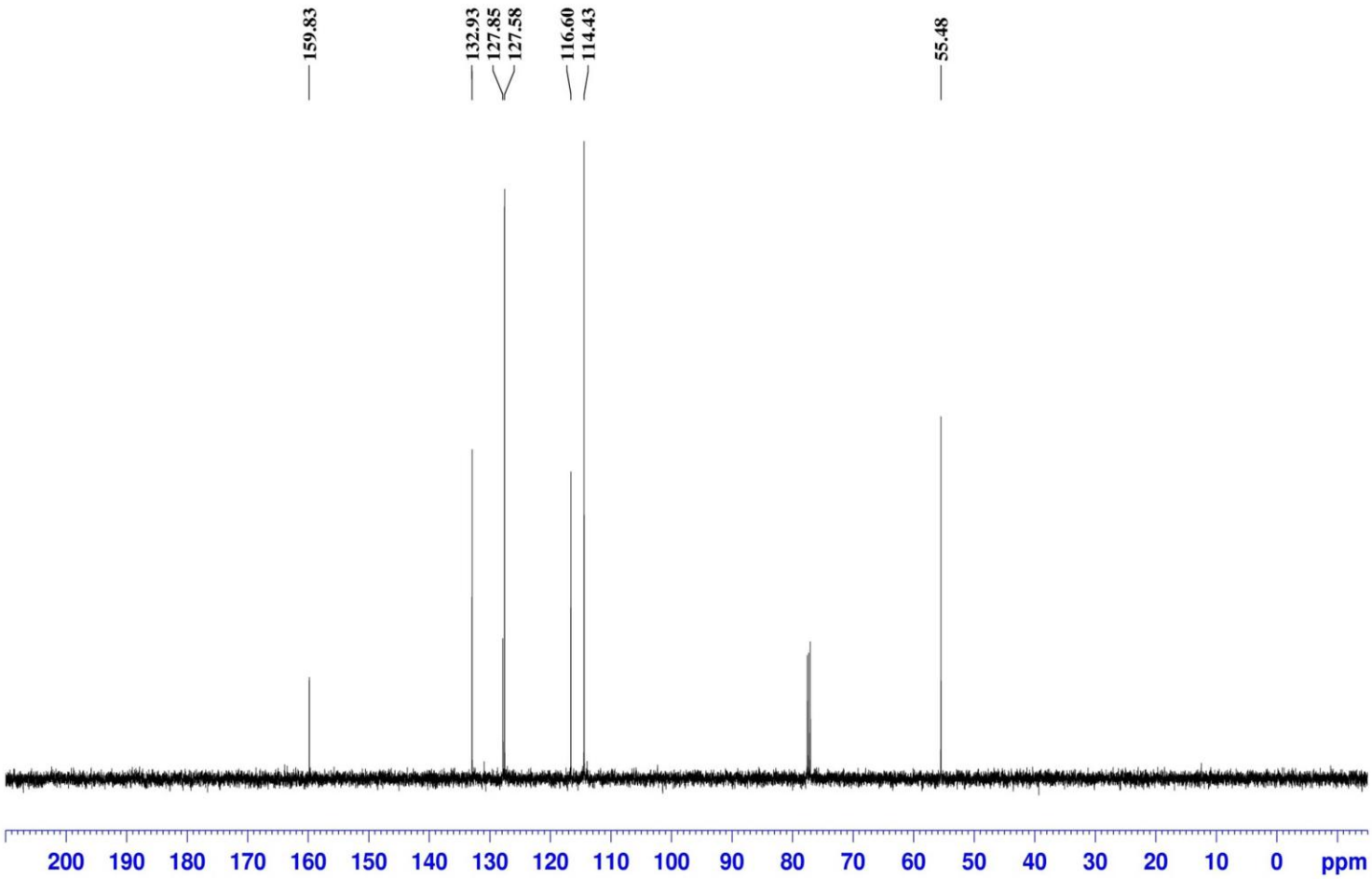
(Z)−((3−bromoallyl)oxy)(tert−butyl)dimethylsilane
125 MHz, CDCl3



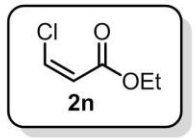


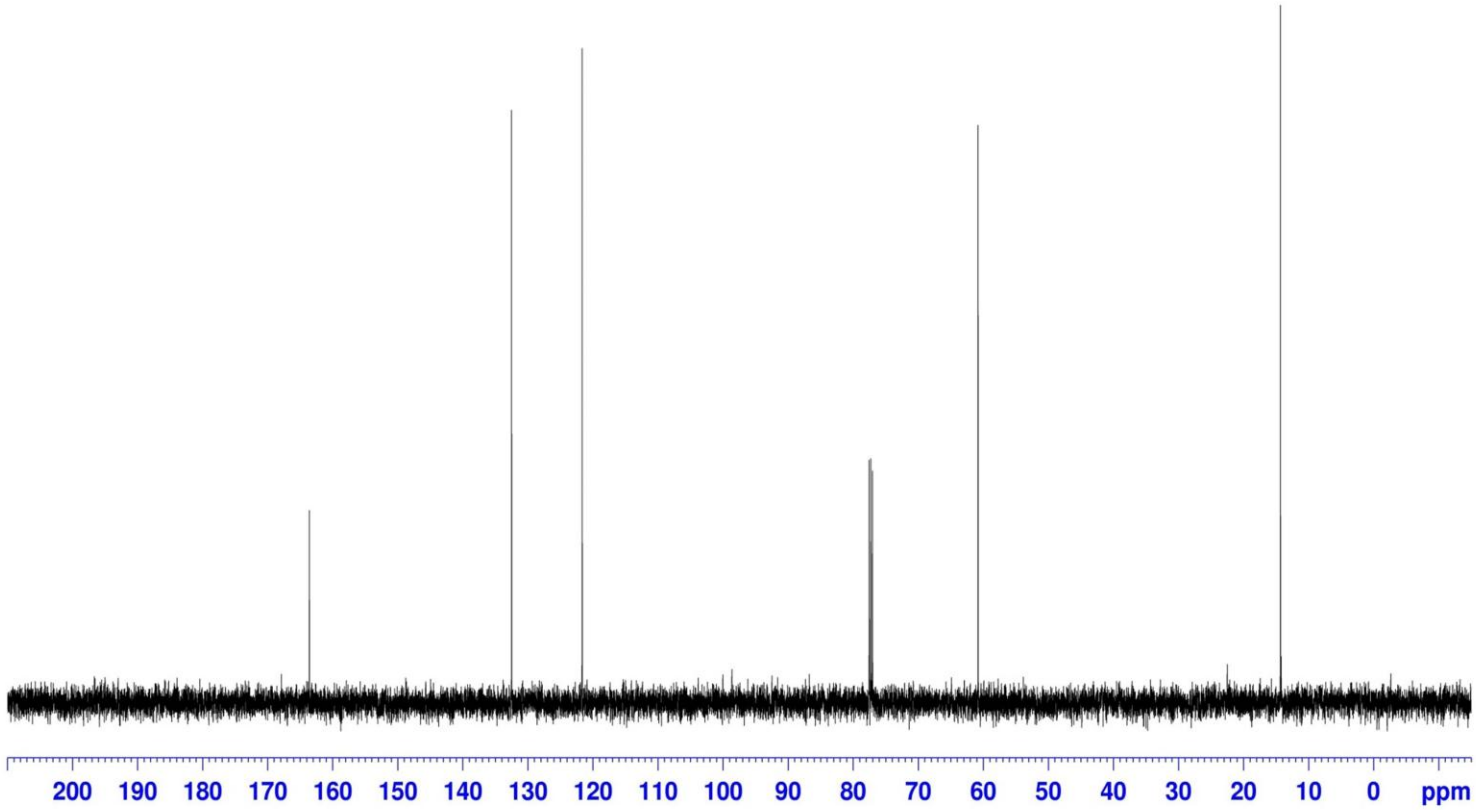
(E)−1−(2−chlorovinyl)−4−methoxybenzene
125 MHz, CDCl3



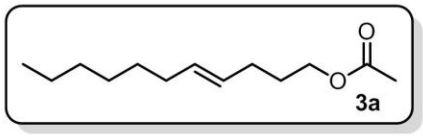


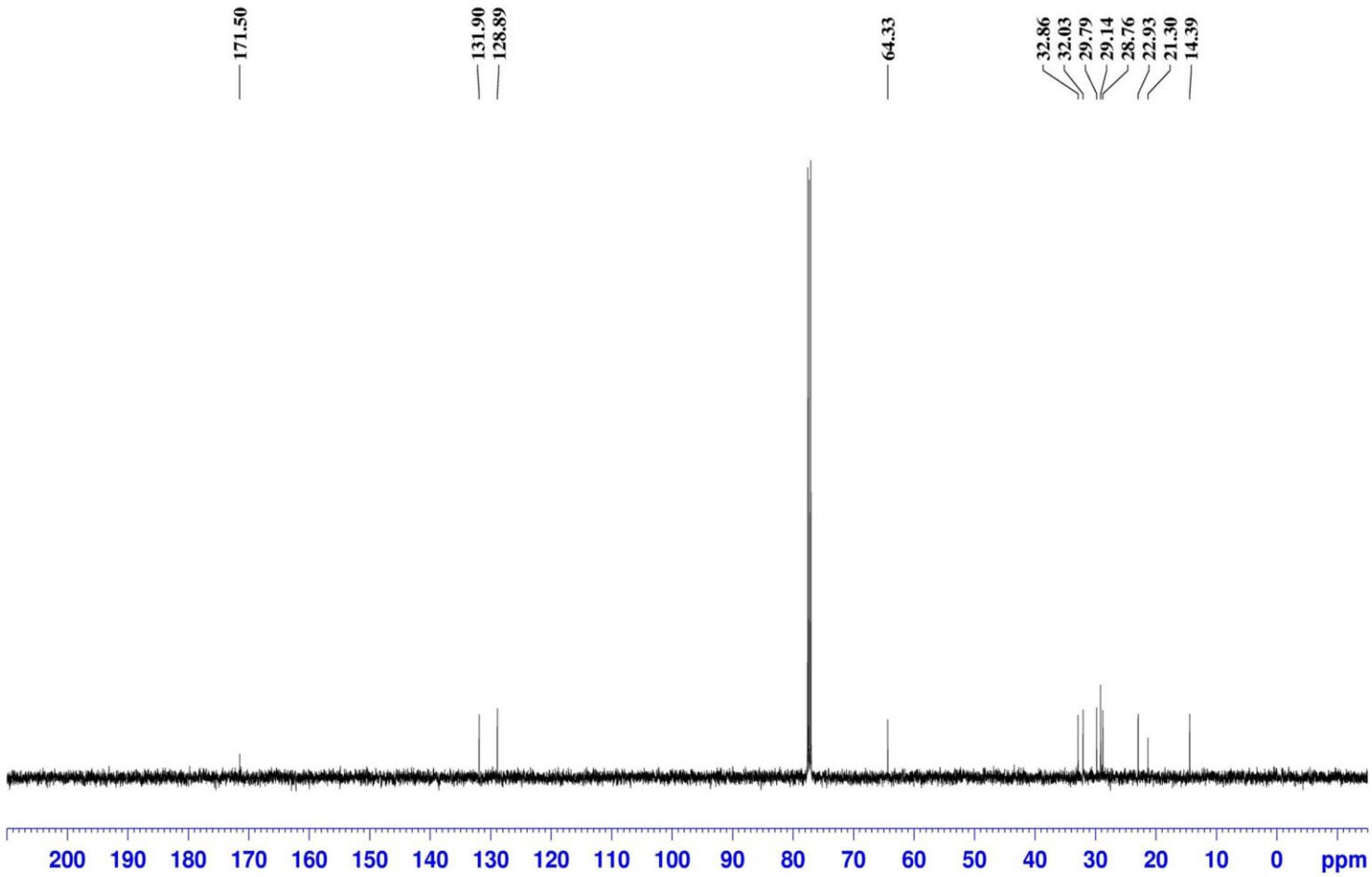
(Z)–ethyl 3–chloroacrylate
125 MHz, CDCl3



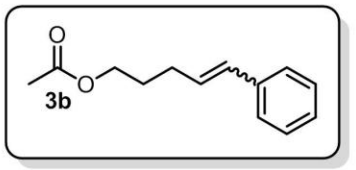


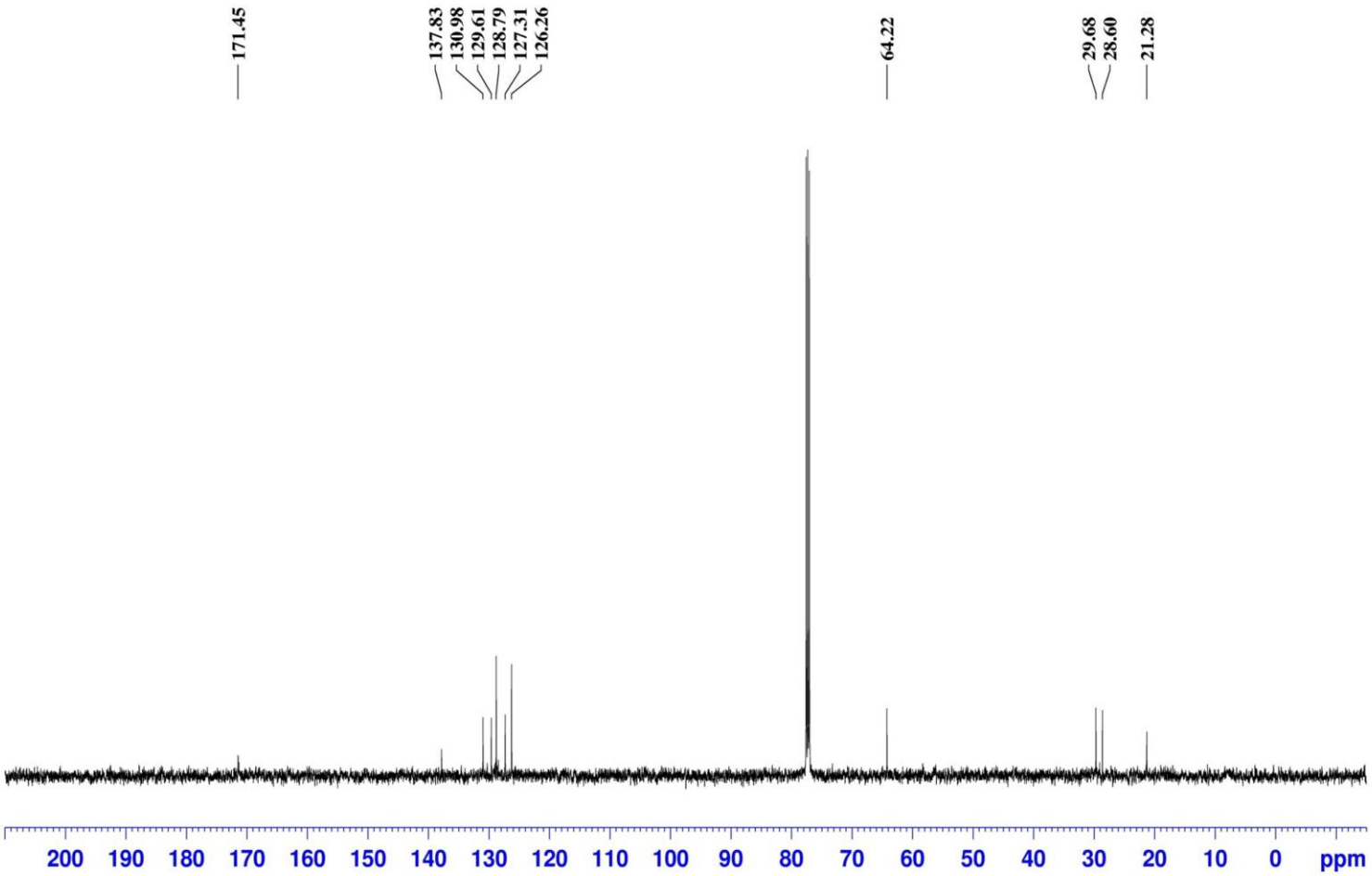
(E)–undec–4–en–1–yl acetate
125 MHz, CDCl3



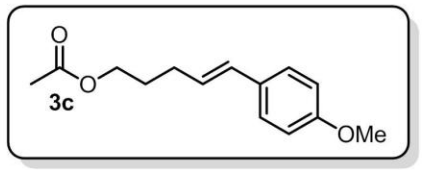


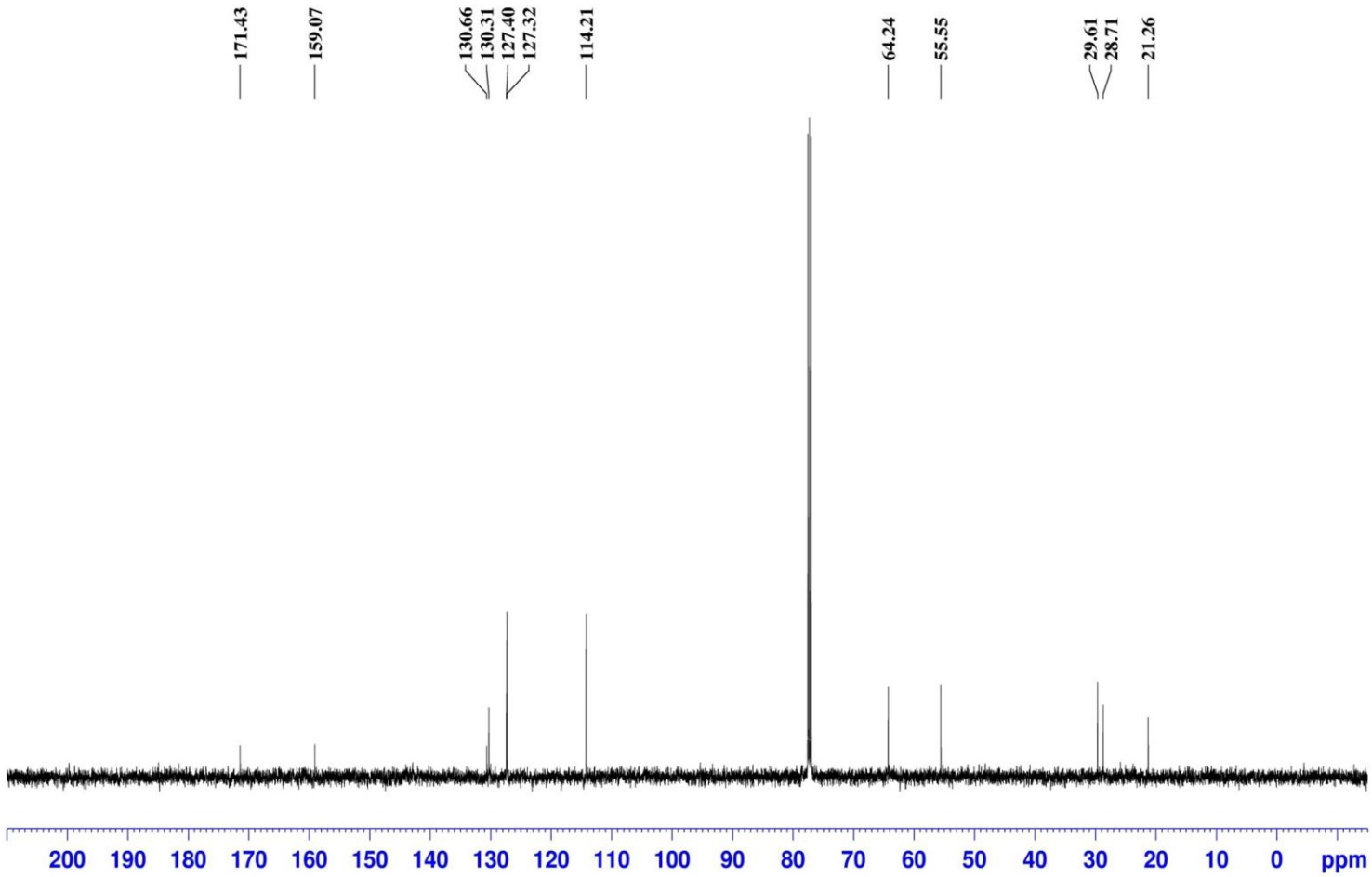
5–phenylpent–4–en–1–yl acetate
125 MHz, CDCl3



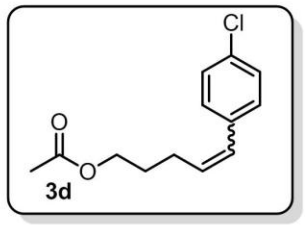


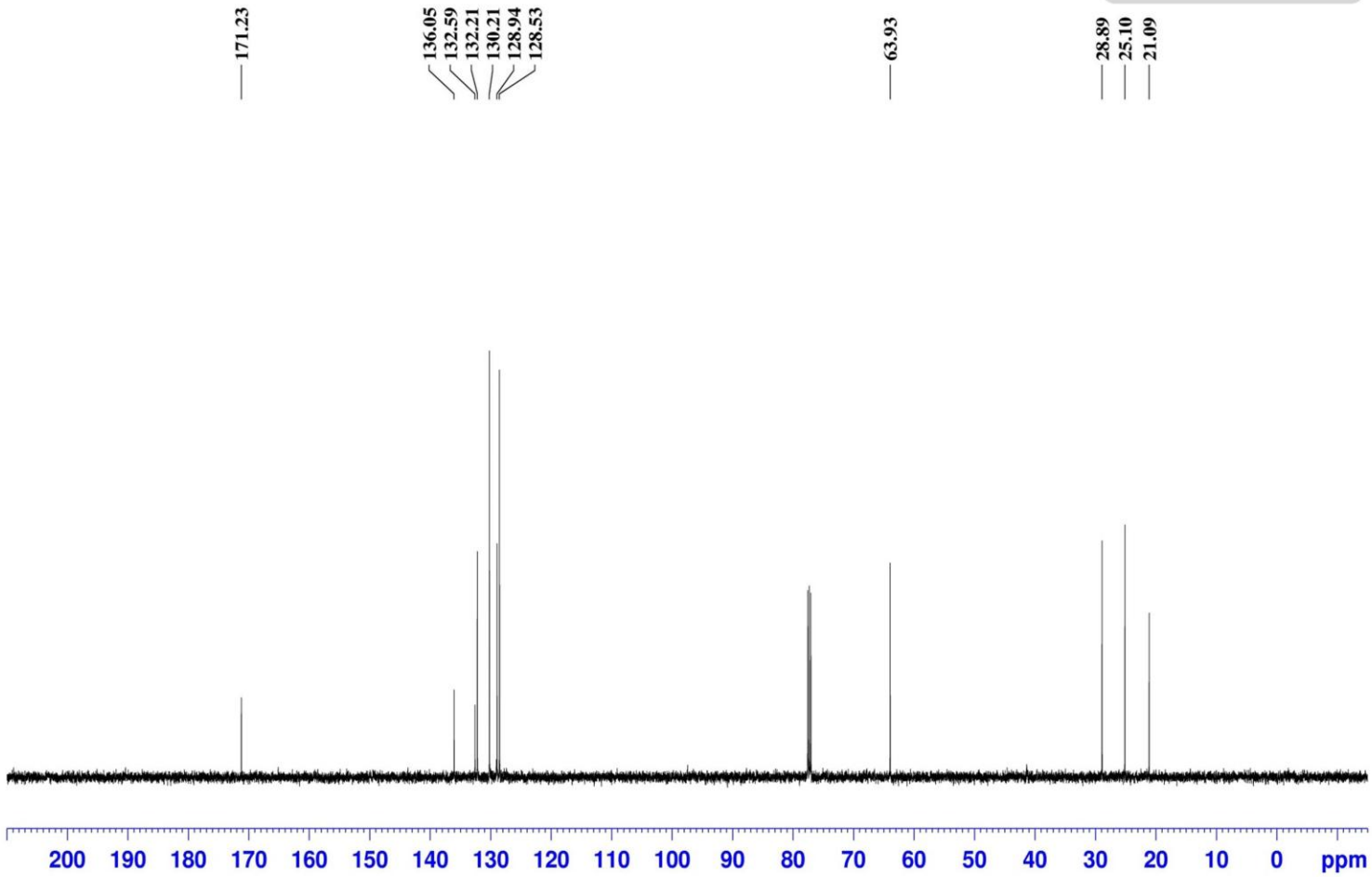
(E)−5−(4−methoxyphenyl)pent−4−en−1−yl acetate
125 MHz, CDCl3



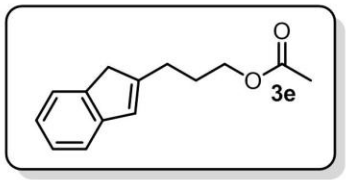


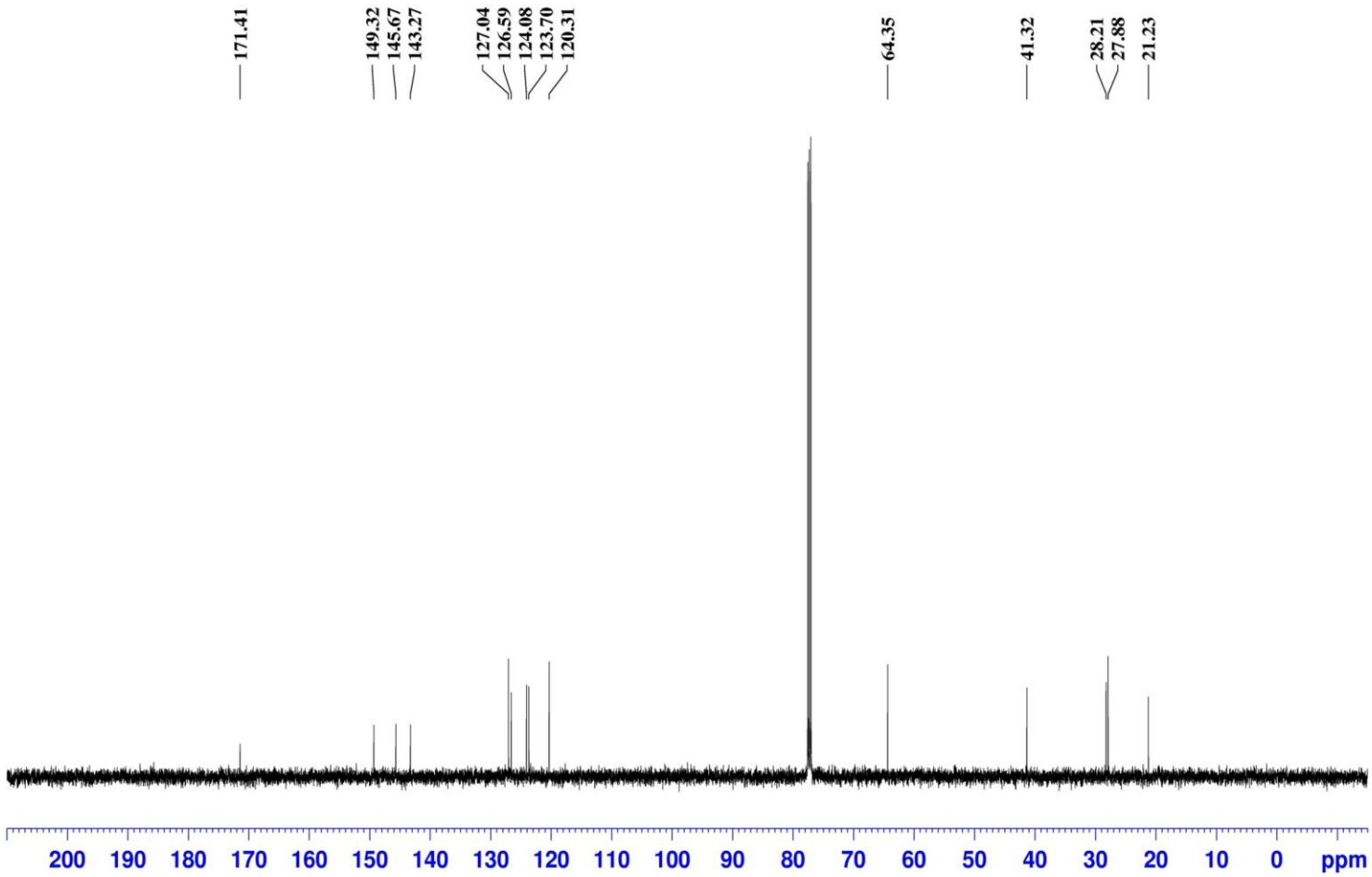
(E)−5−(4−chlorophenyl)pent−4−en−1−yl acetate
125 MHz, CDCl3



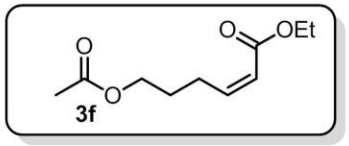


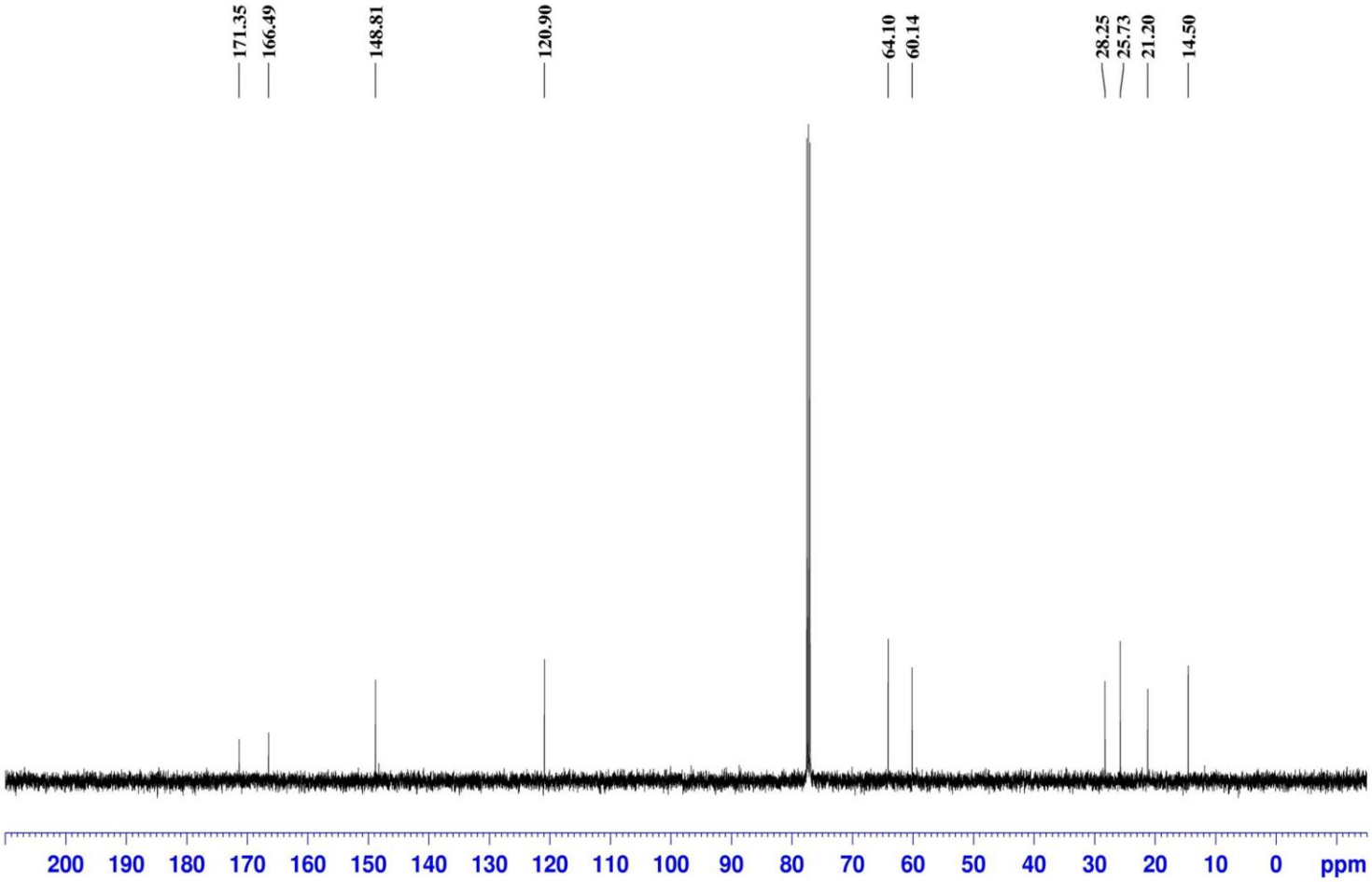
3–(1H–inden–2–yl)propyl acetate
125 MHz, CDCl3



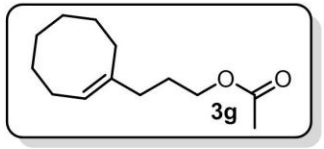


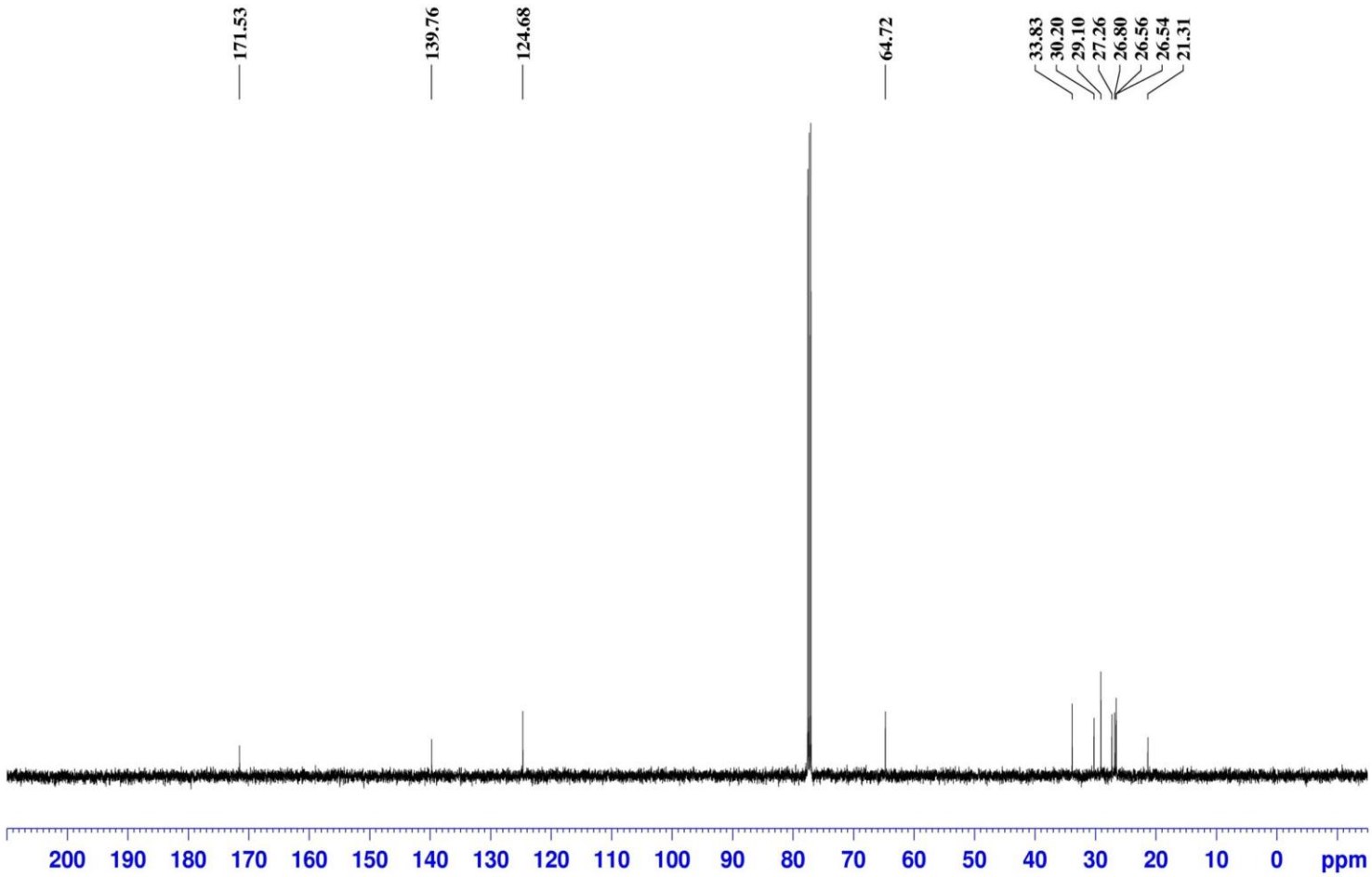
(Z)–ethyl 6–acetoxyhex–2–enoate
125 MHz, CDCl3



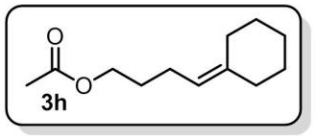


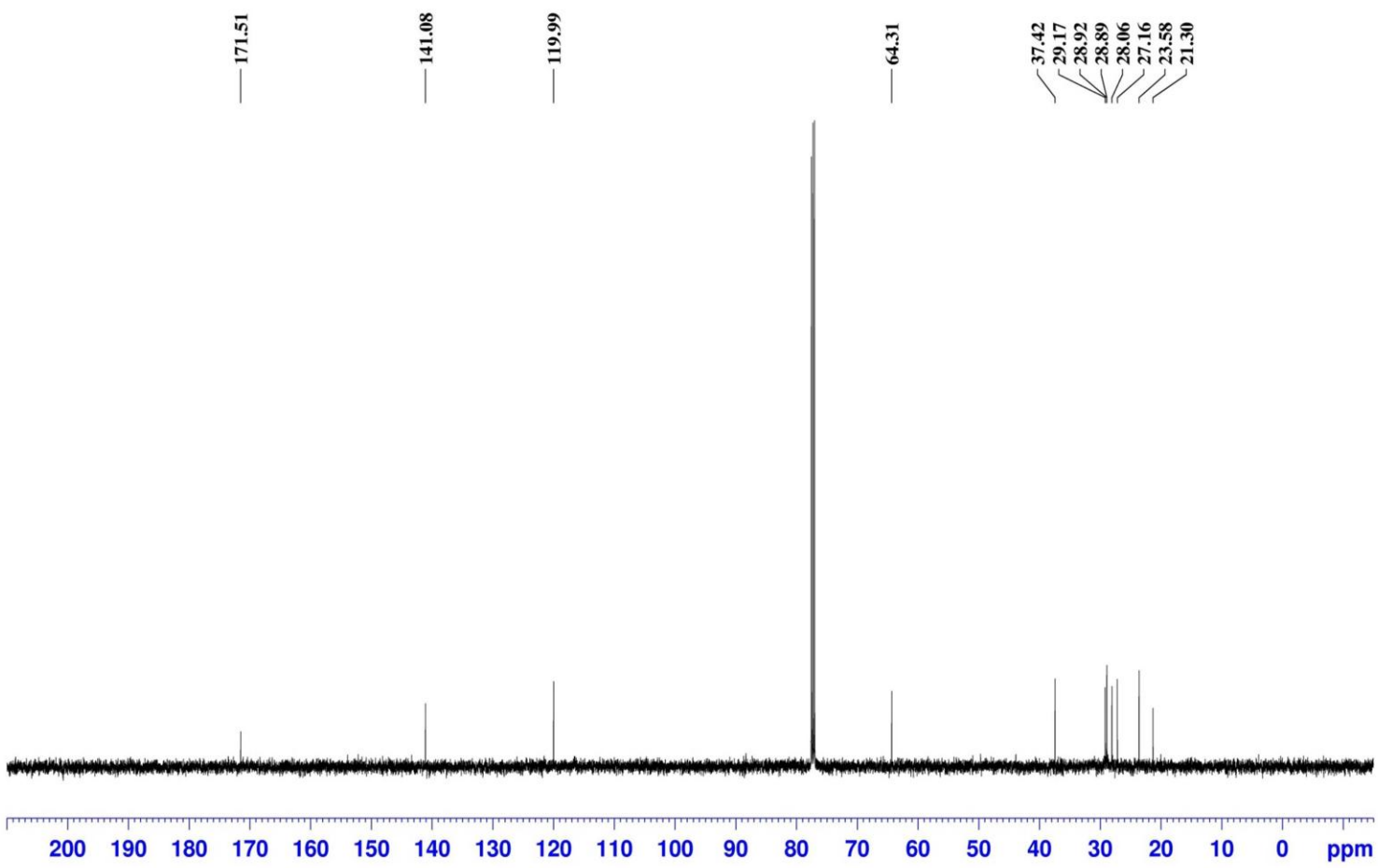
(E)–3–(cyclooct–1–en–1–yl)propyl acetate
125 MHz, CDCl3



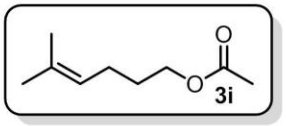


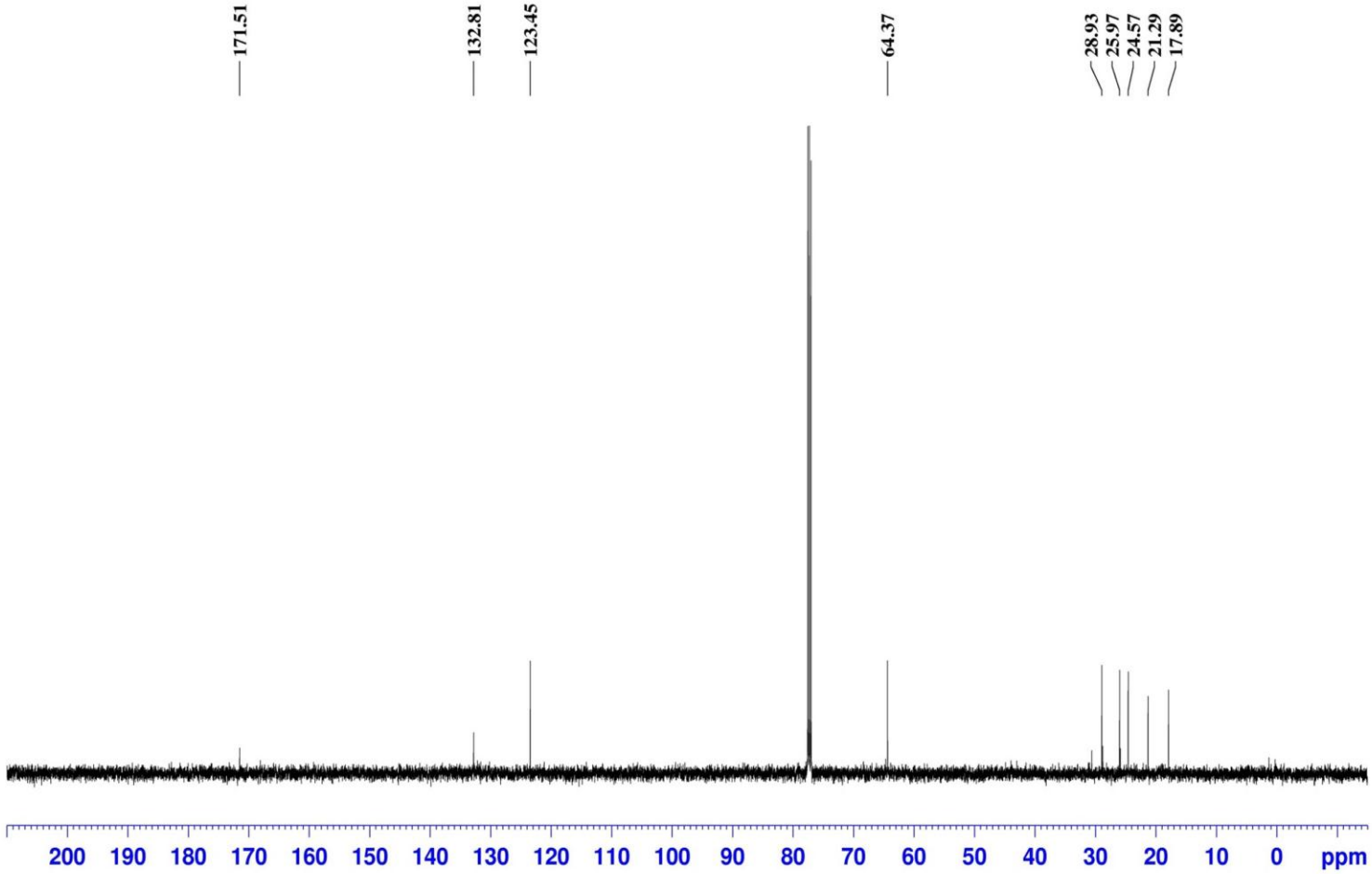
4–cyclohexylidenebutyl acetate
125 MHz, CDCl3



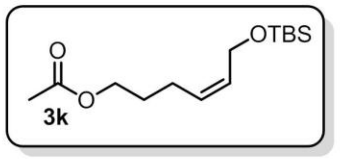


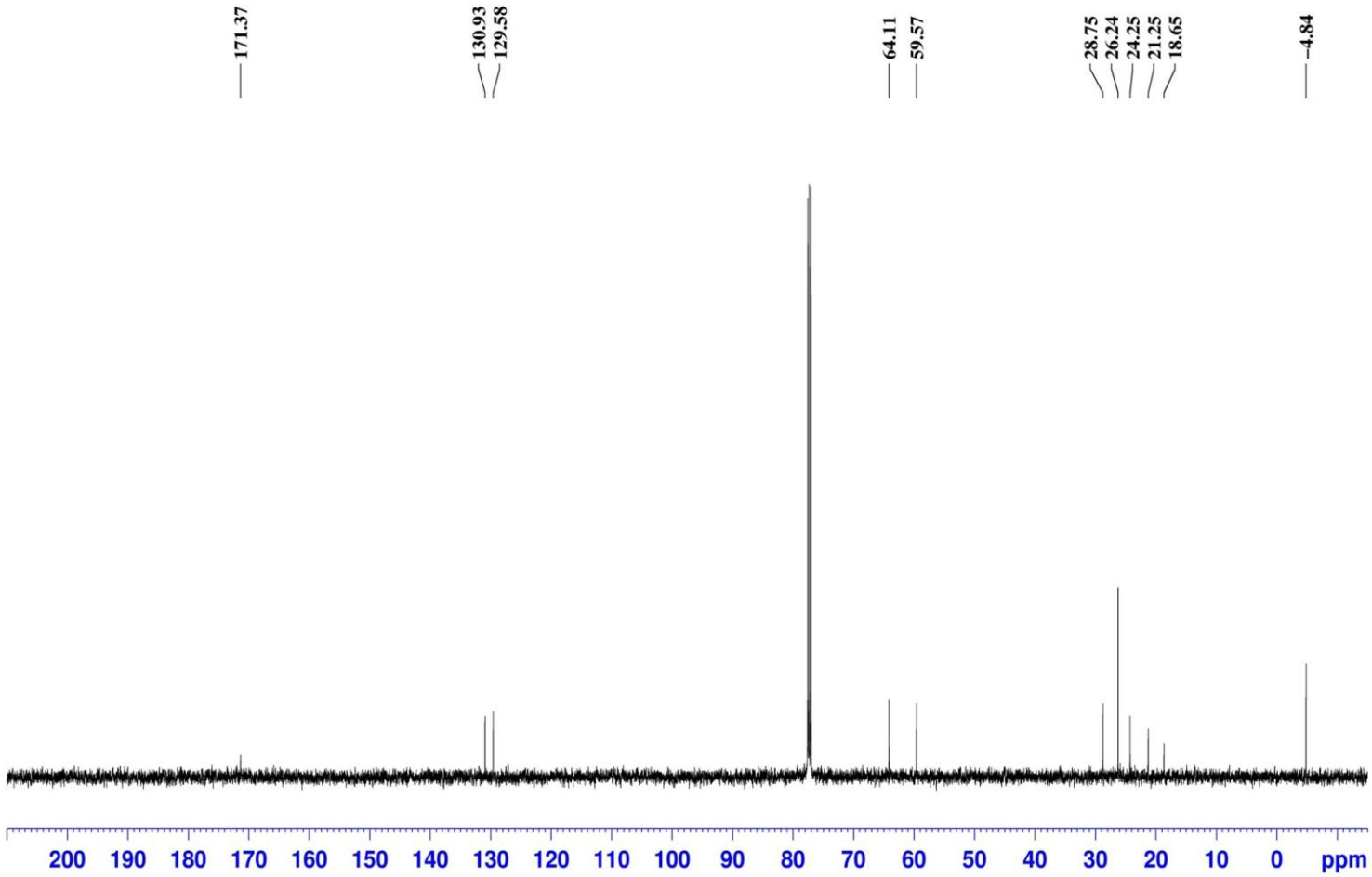
5–methylhex–4–en–1–yl acetate
125 MHz, CDCl3



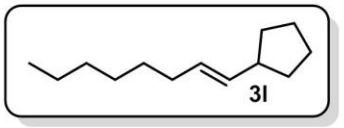


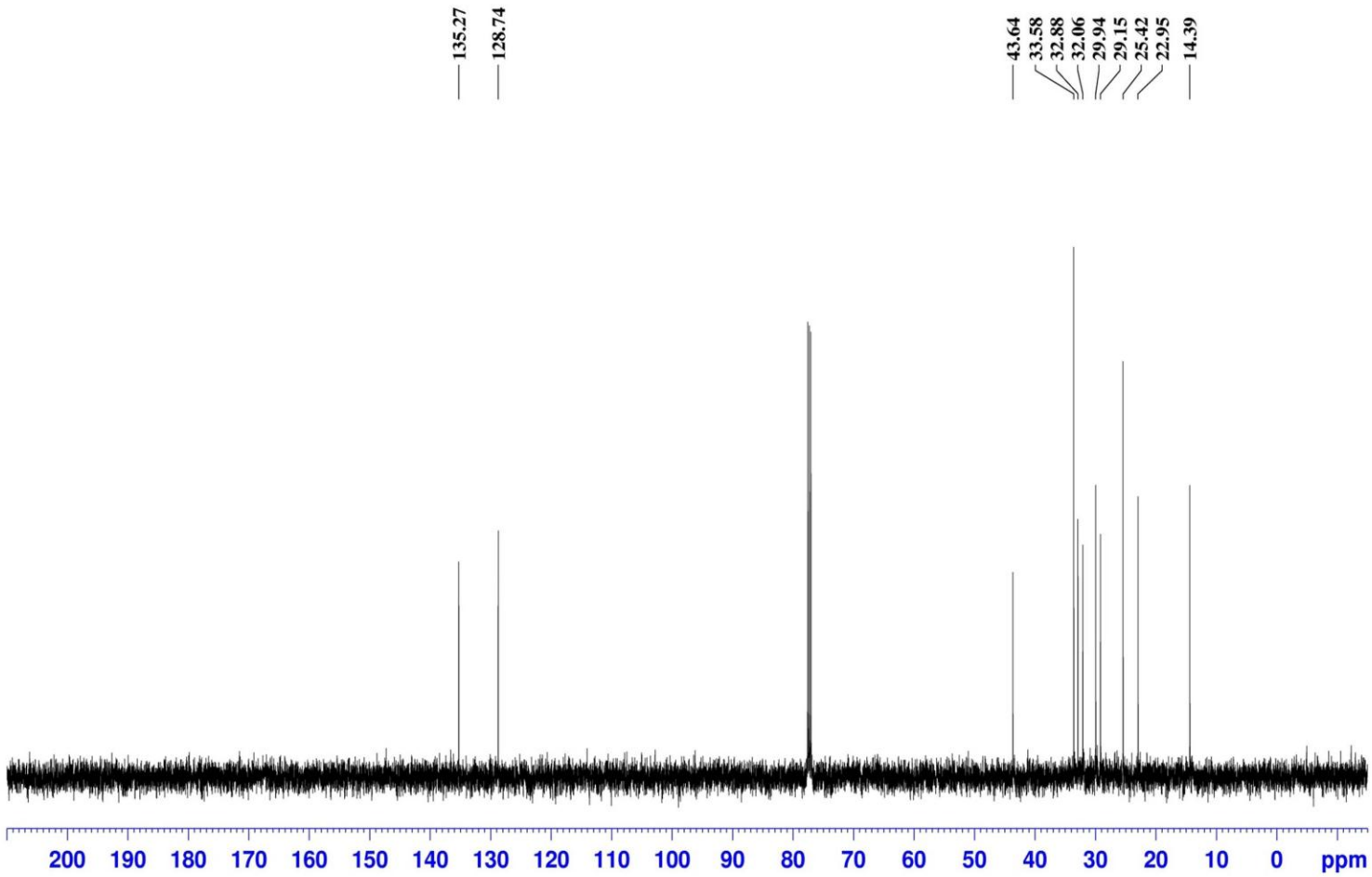
(Z)−6−((tert−butyldimethylsilyl)oxy)hex−4−en−1−yl acetate
125 MHz, CDCl3



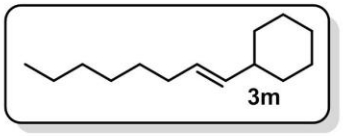


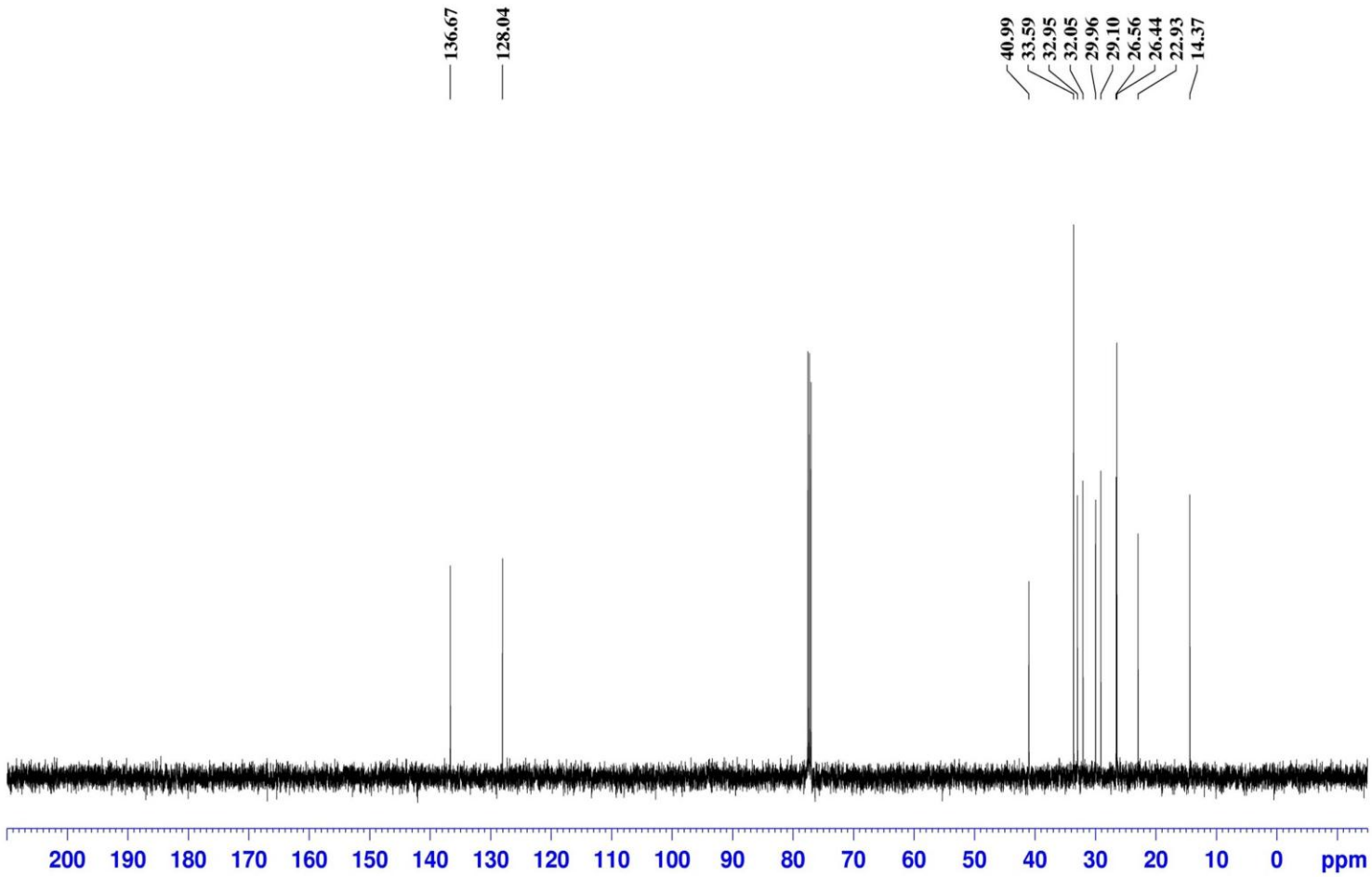
(E)–oct–1–en–1–ylcyclopentane
125 MHz, CDCl3



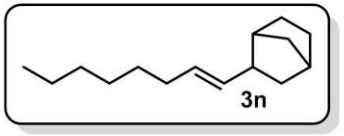


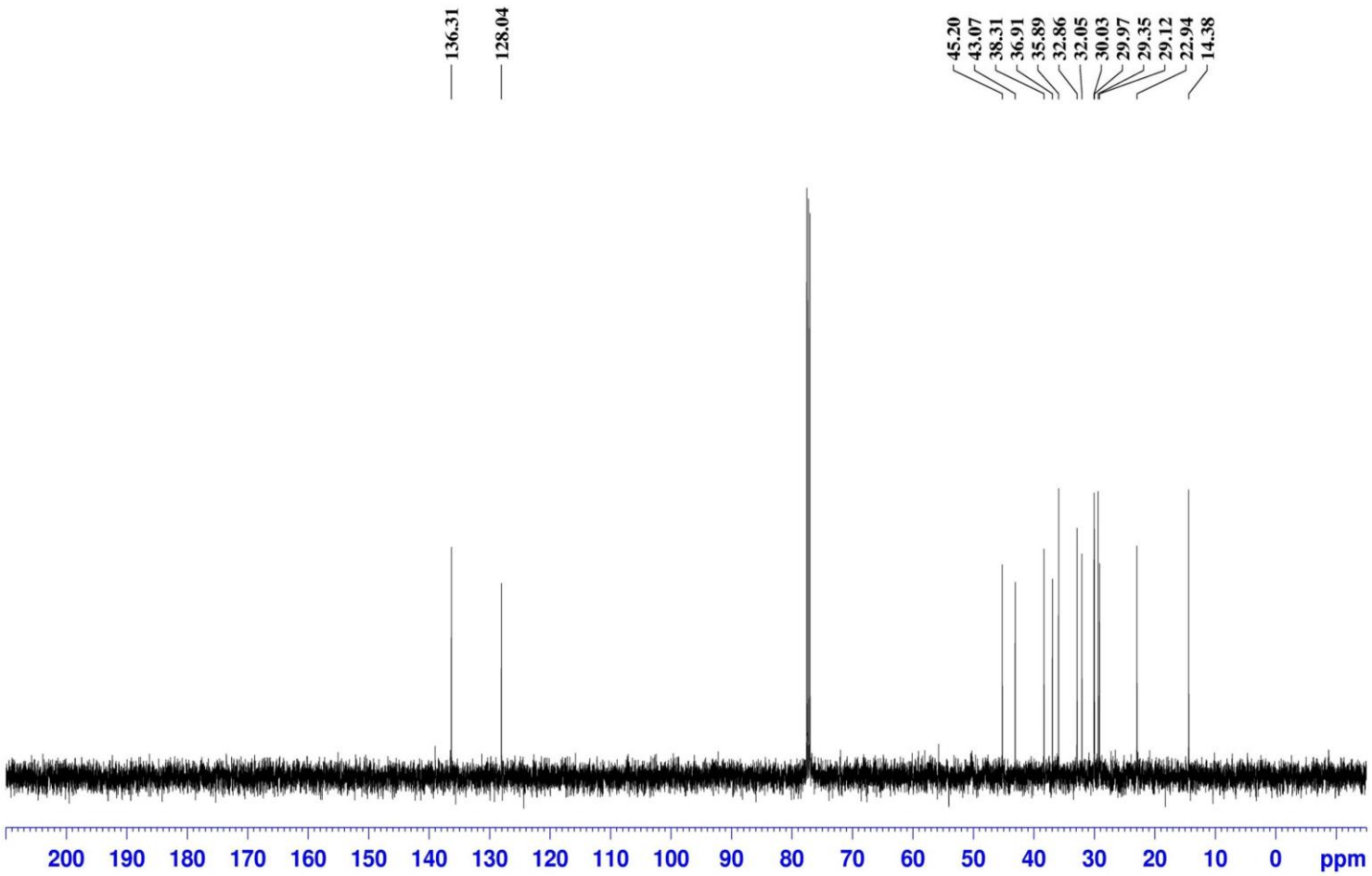
(E)–oct–1–en–1–ylcyclohexane
125 MHz, CDCl3



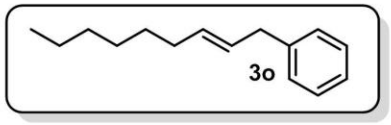


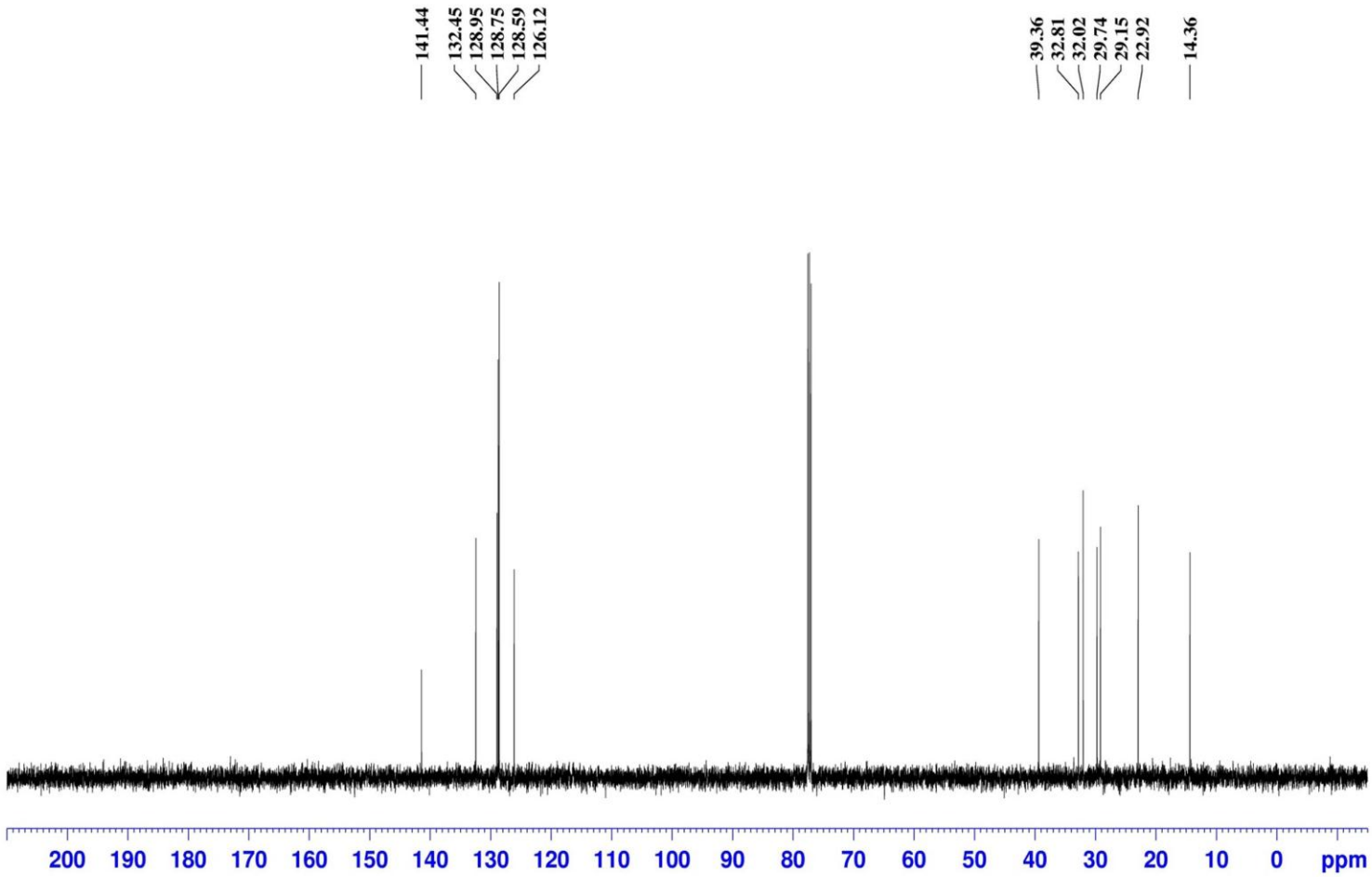
(E)−2−(oct−1−en−1−yl)bicyclo[2.2.1]heptane
125 MHz, CDCl3



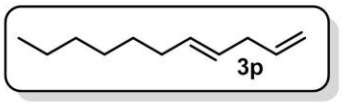


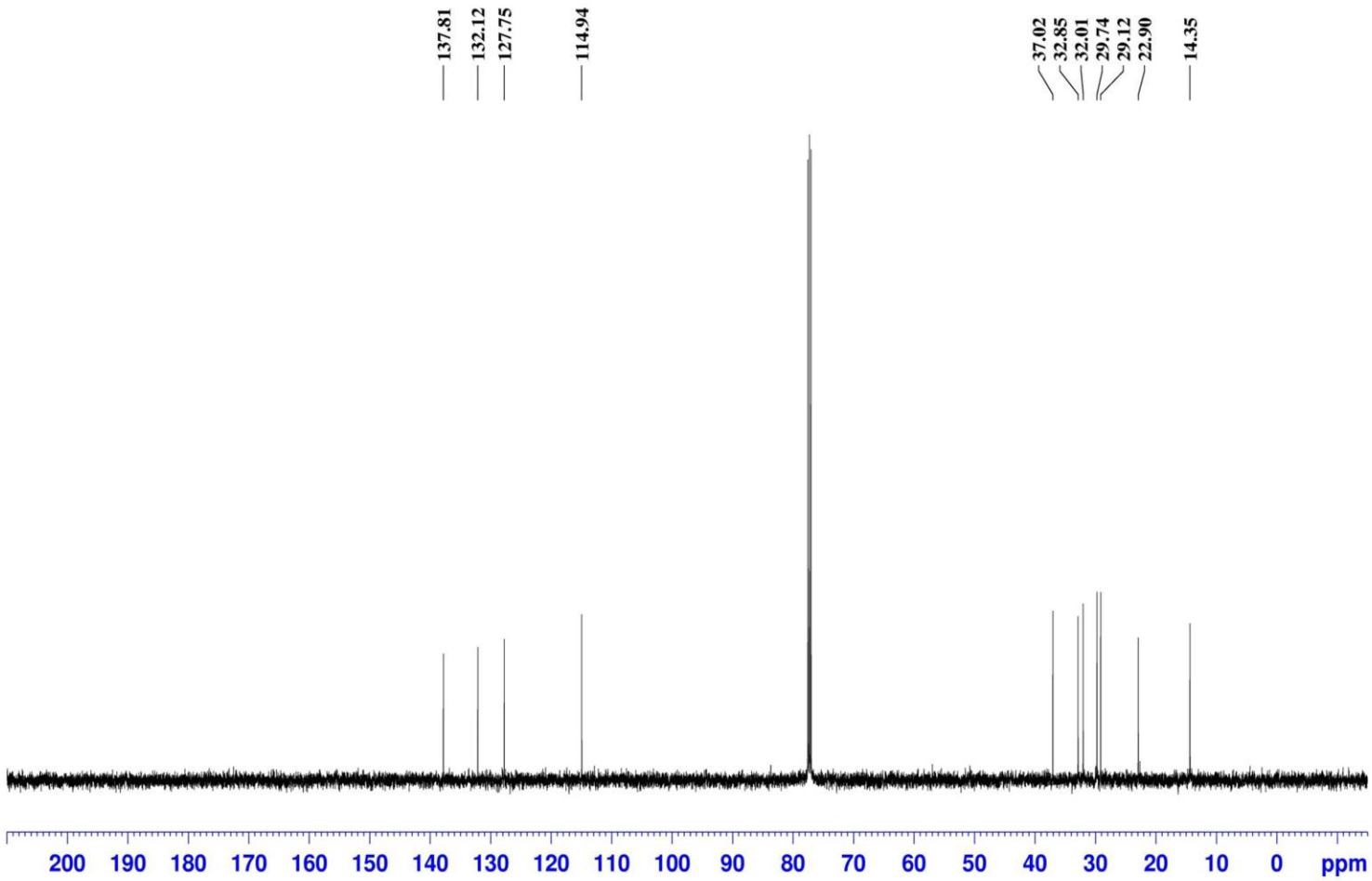
(E)–non–2–en–1–ylbenzene
125 MHz, CDCl3



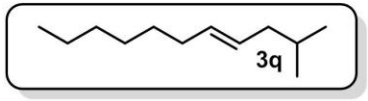


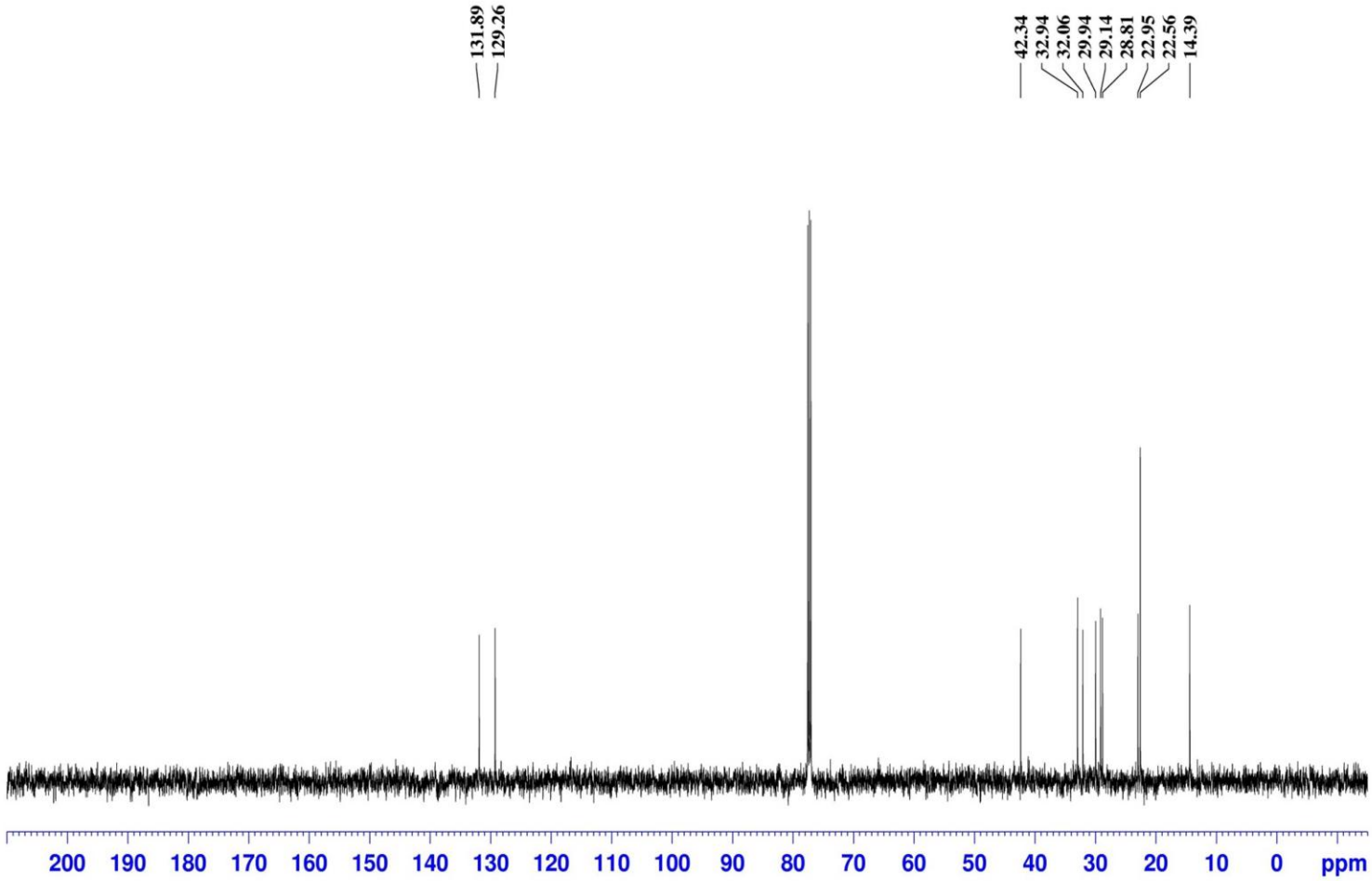
(E)−undeca−1,4−diene
125 MHz, CDCl3



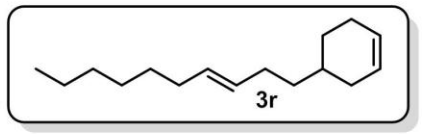


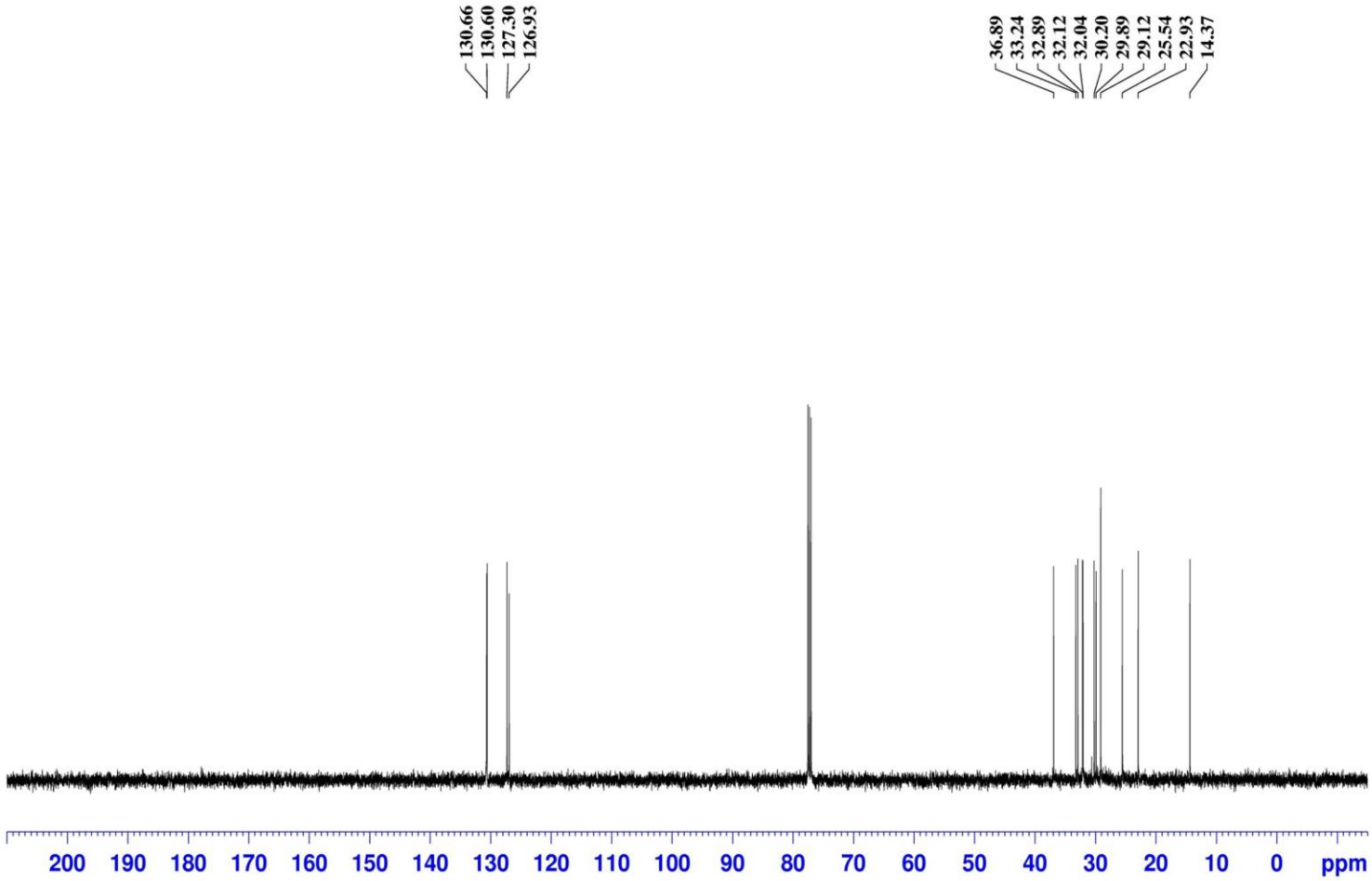
(E)−2−methylundec−4−ene
125 MHz, CDCl3



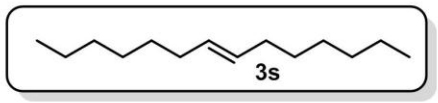


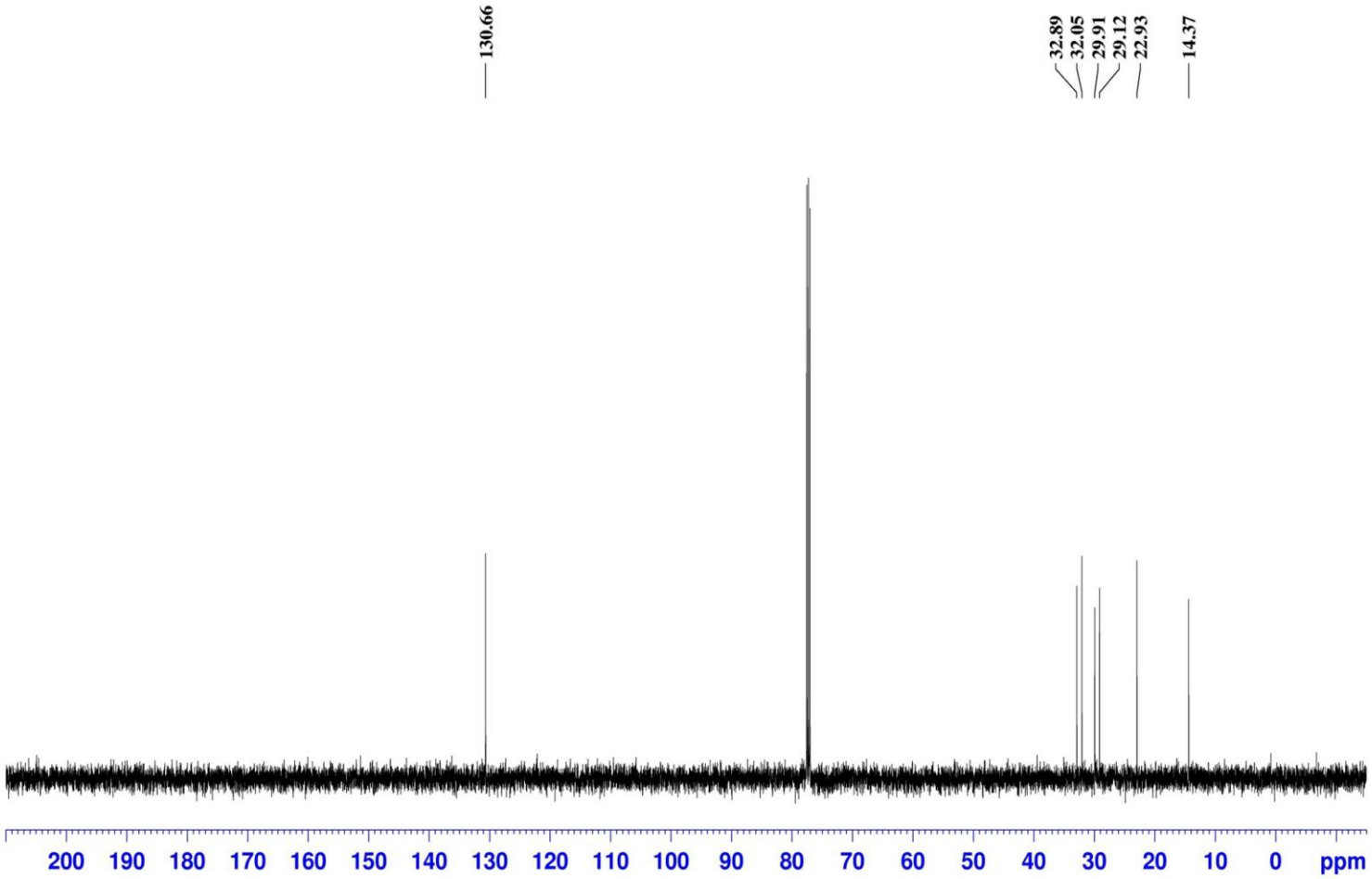
(E)−4−(dec−3−en−1−yl)cyclohex−1−ene
125 MHz, CDCl3



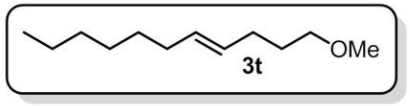


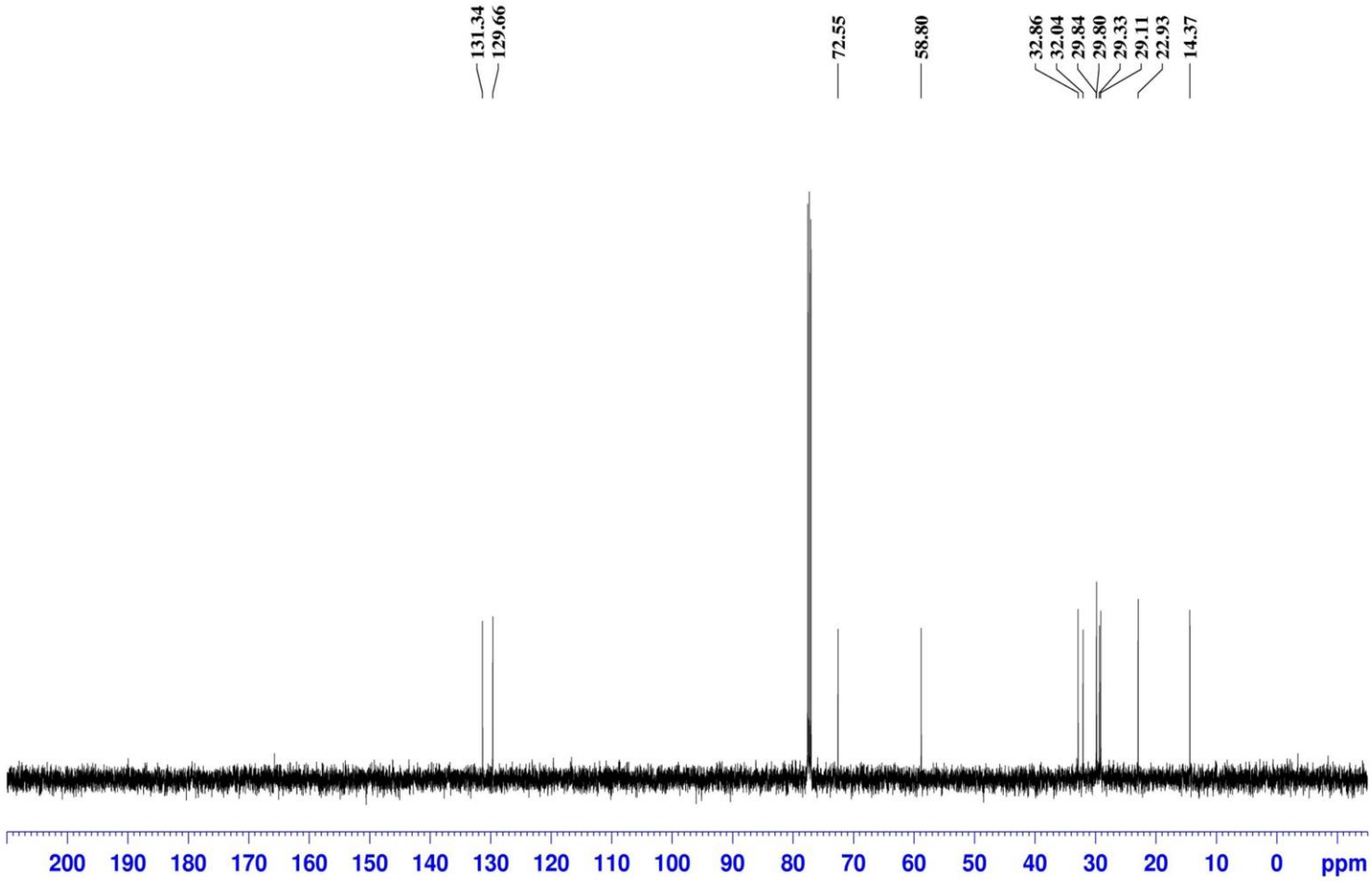
(E)−tetradec−7−ene
125 MHz, CDCl3



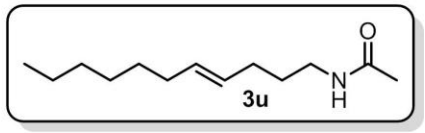


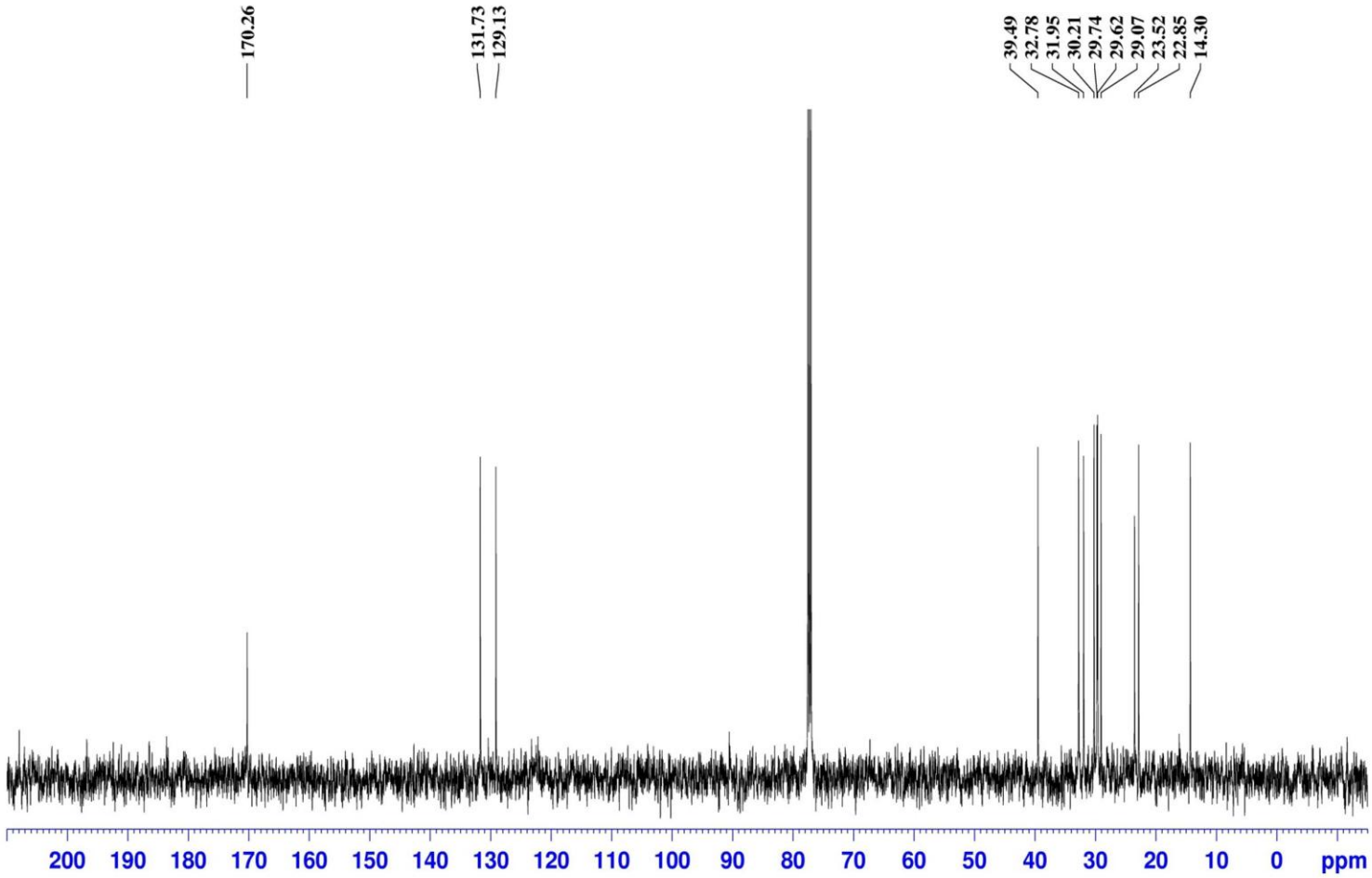
(E)−1−methoxyundec−4−ene
125 MHz, CDCl3



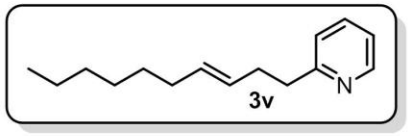


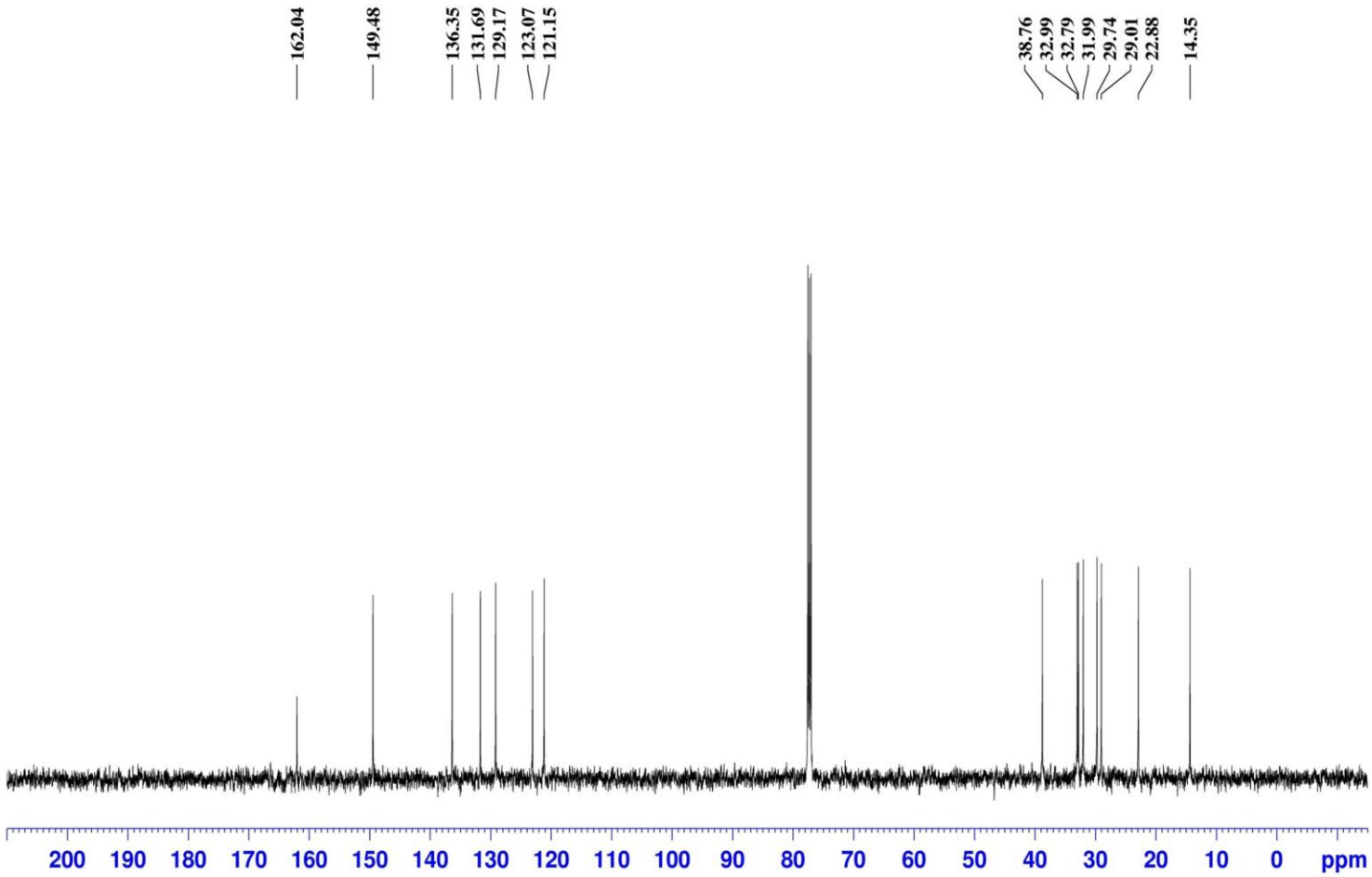
(E)–N–(undec–4–en–1–yl)acetamide
125 MHz, CDCl3



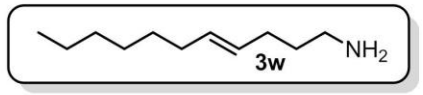


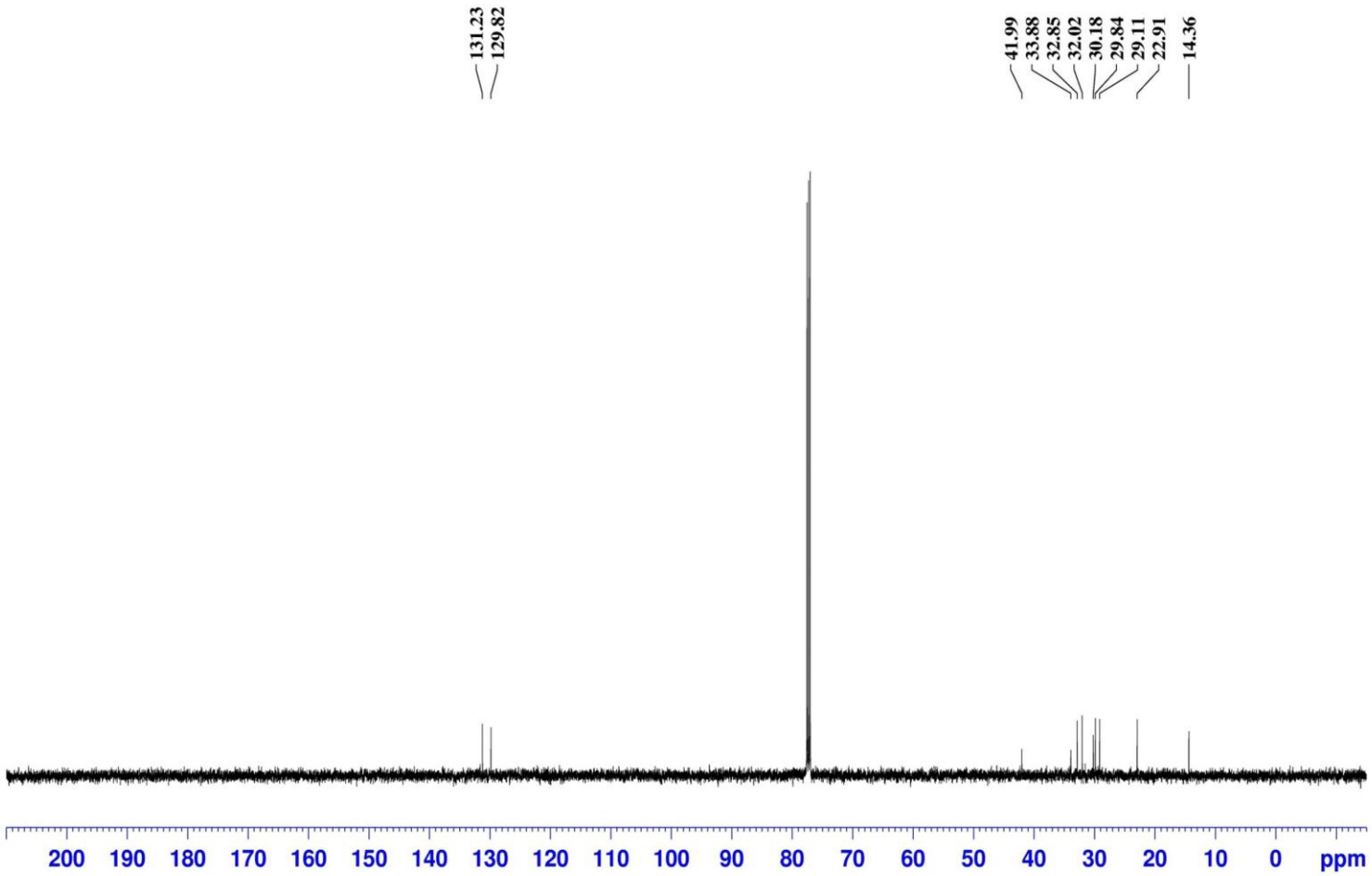
(E)−2−(dec−3−en−1−yl)pyridine
125 MHz, CDCl3



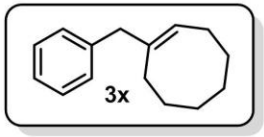


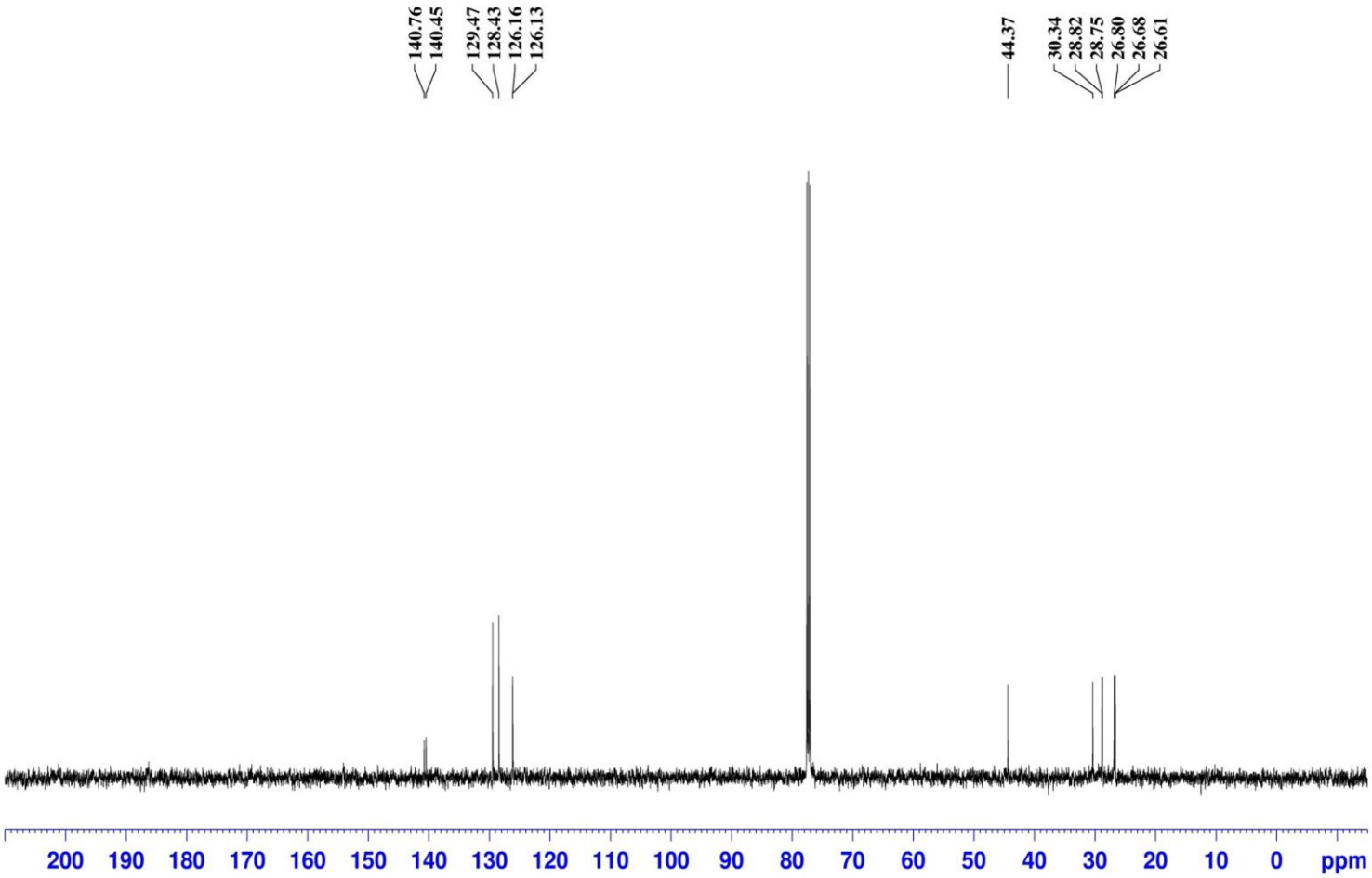
(E)–undec–4–en–1–amine
125 MHz, CDCl3



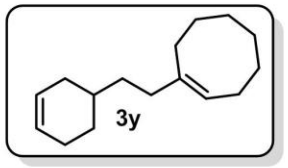


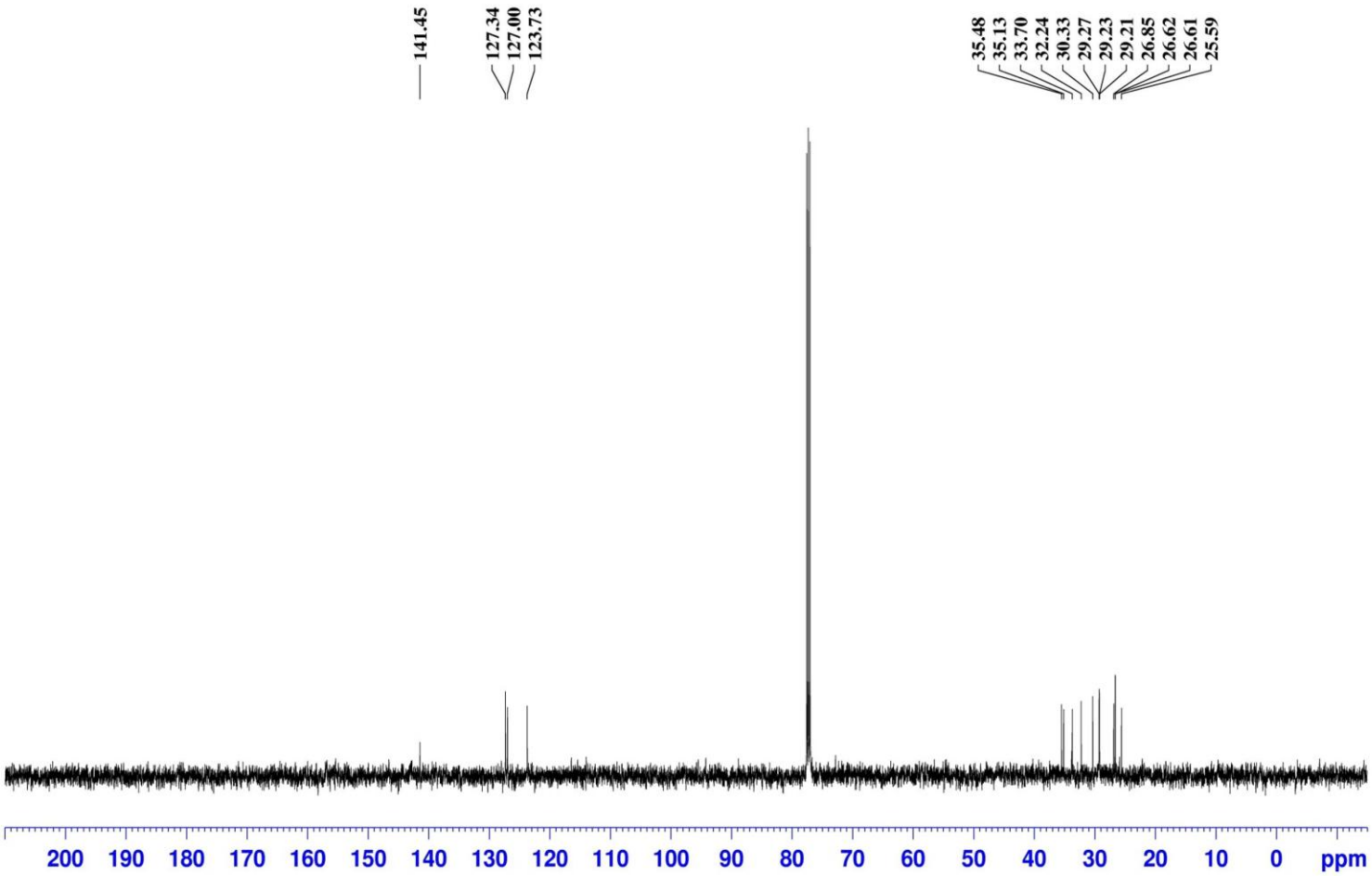
(E)−1−benzylcyclooct−1−ene
125 MHz, CDCl3



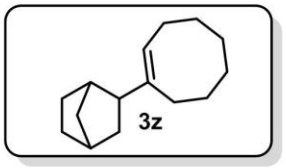


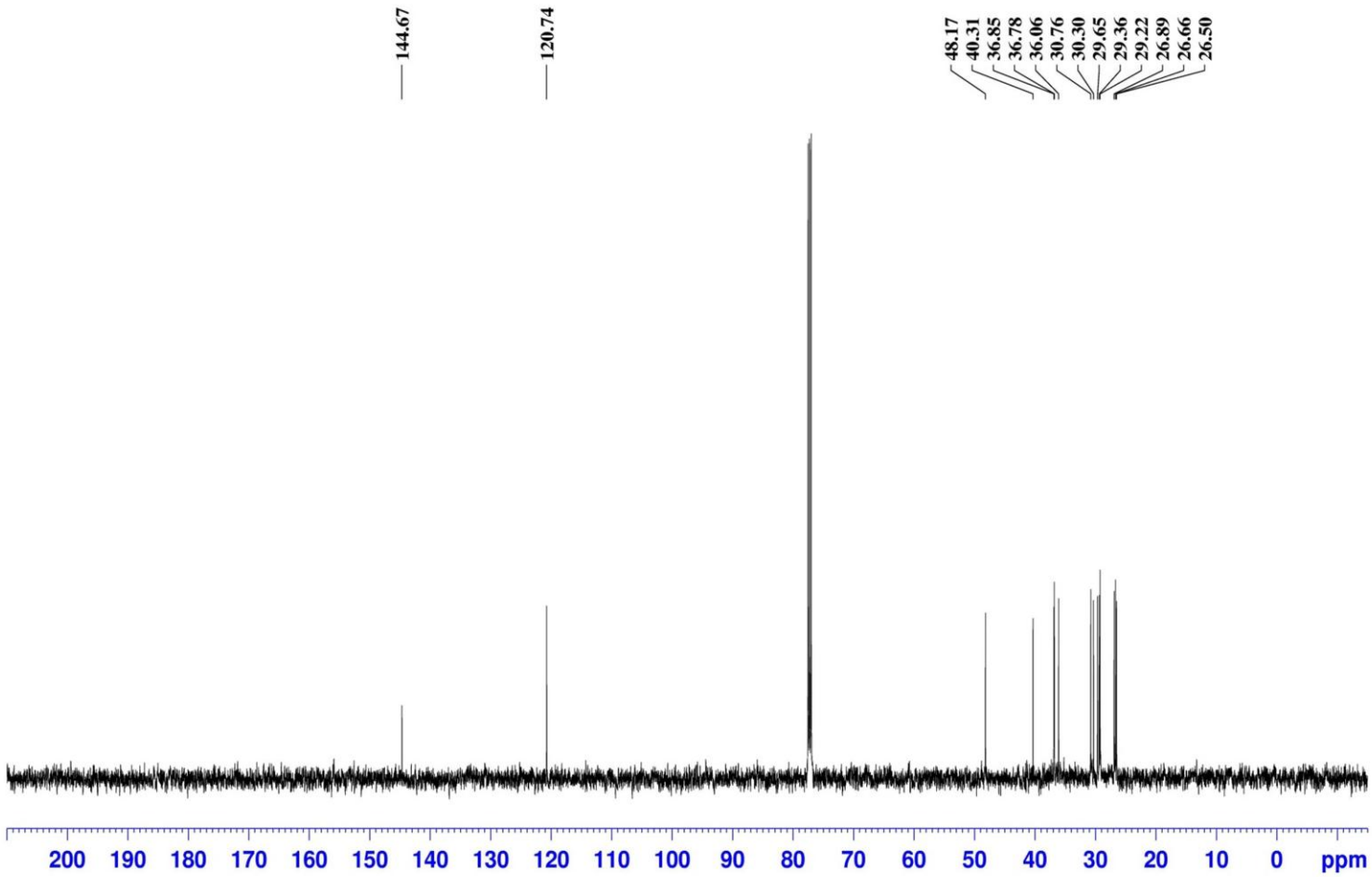
(E)−1−(2−(cyclohex−3−en−1−yl)ethyl)cyclooct−1−ene
125 MHz, CDCl3



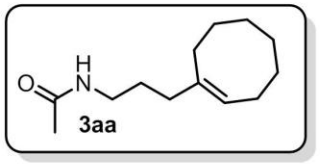


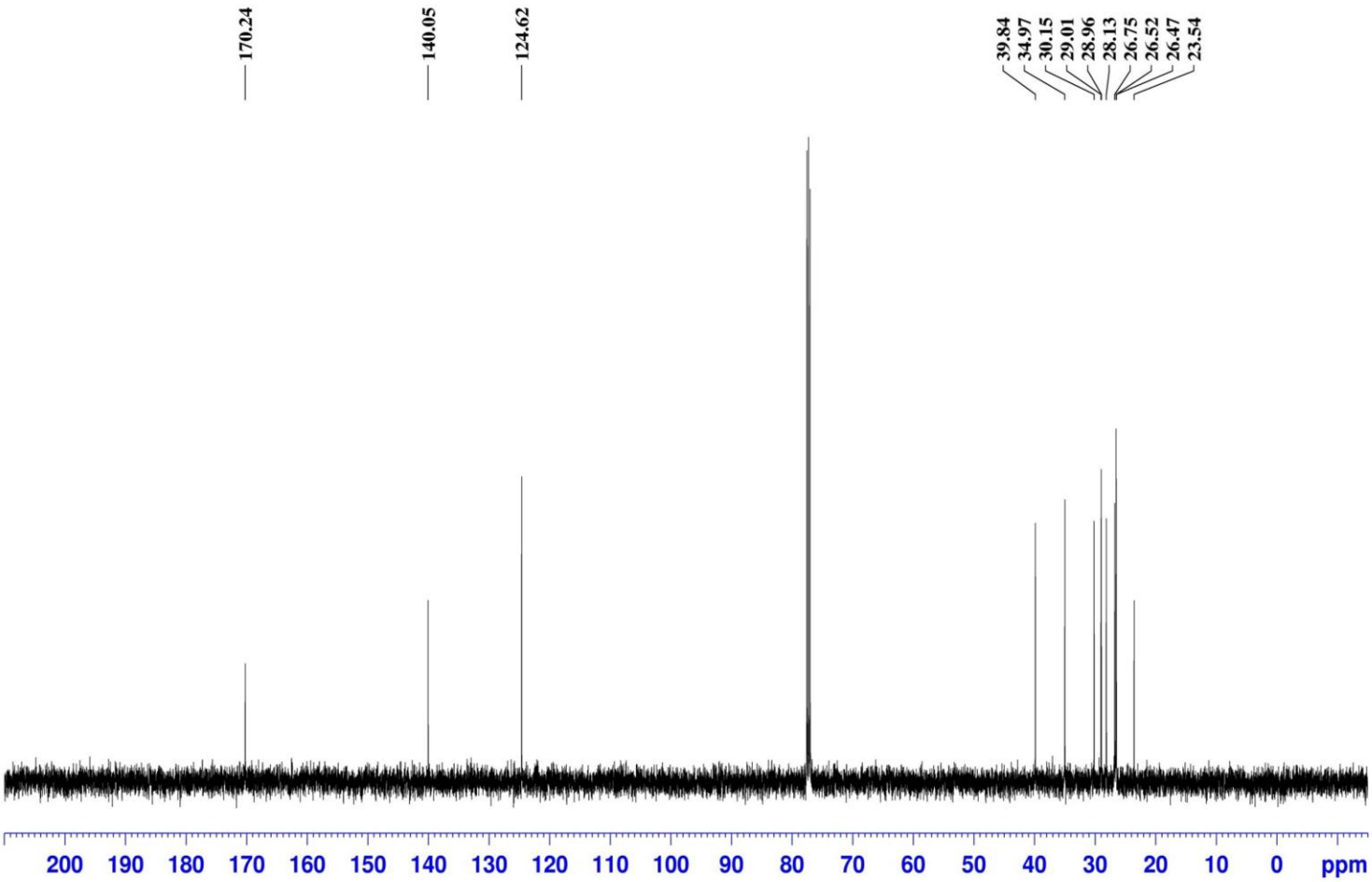
(E)−2−(cyclooct−1−en−1−yl)bicyclo[2.2.1]heptane
125 MHz, CDCl3



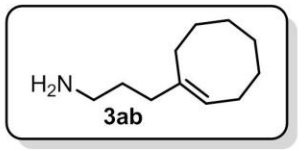


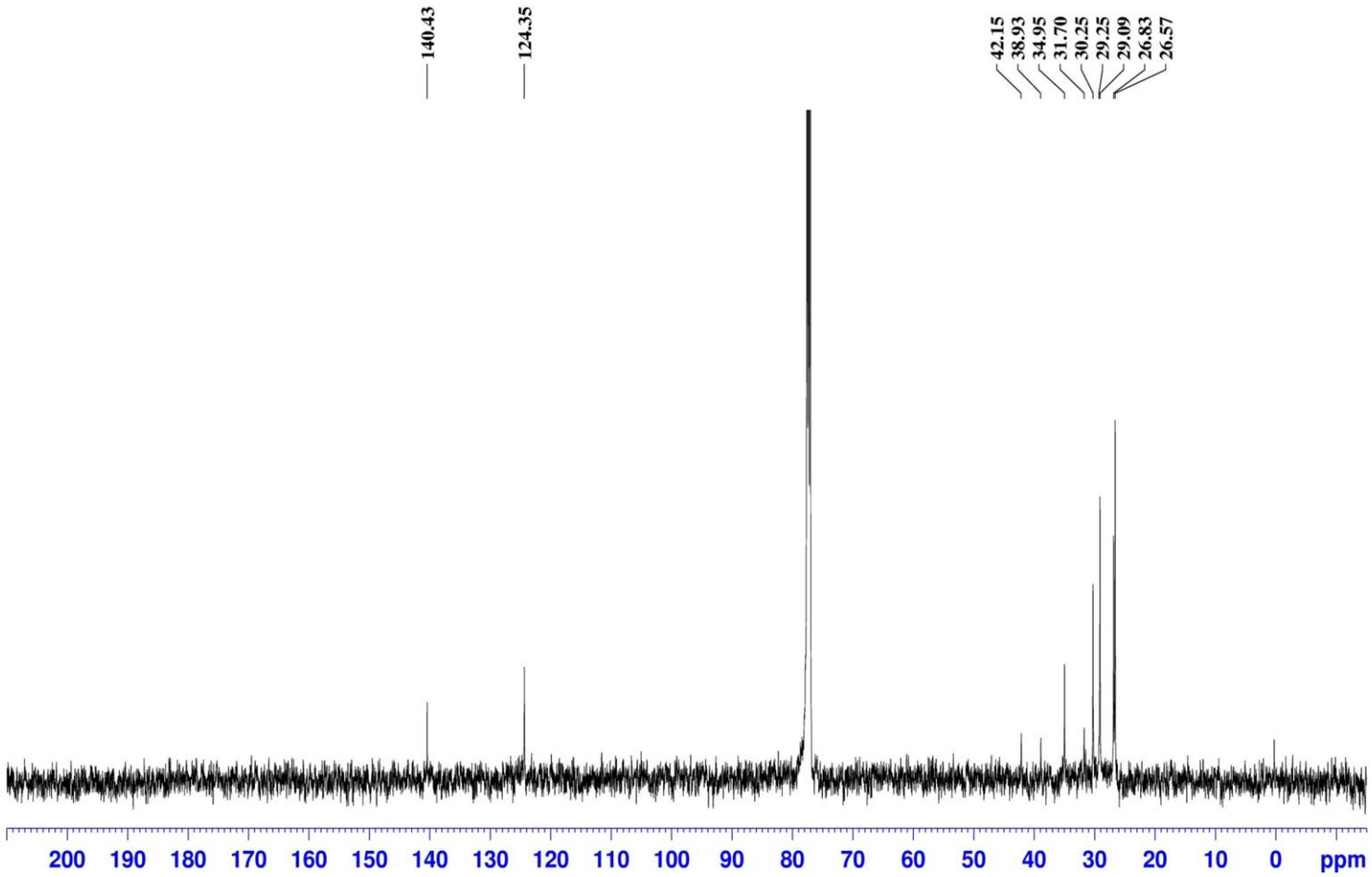
(E)–N–(3–(cyclooct–1–en–1–yl)propyl)acetamide
125 MHz, CDCl3



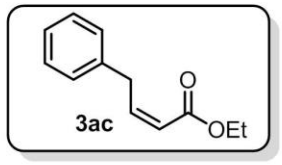


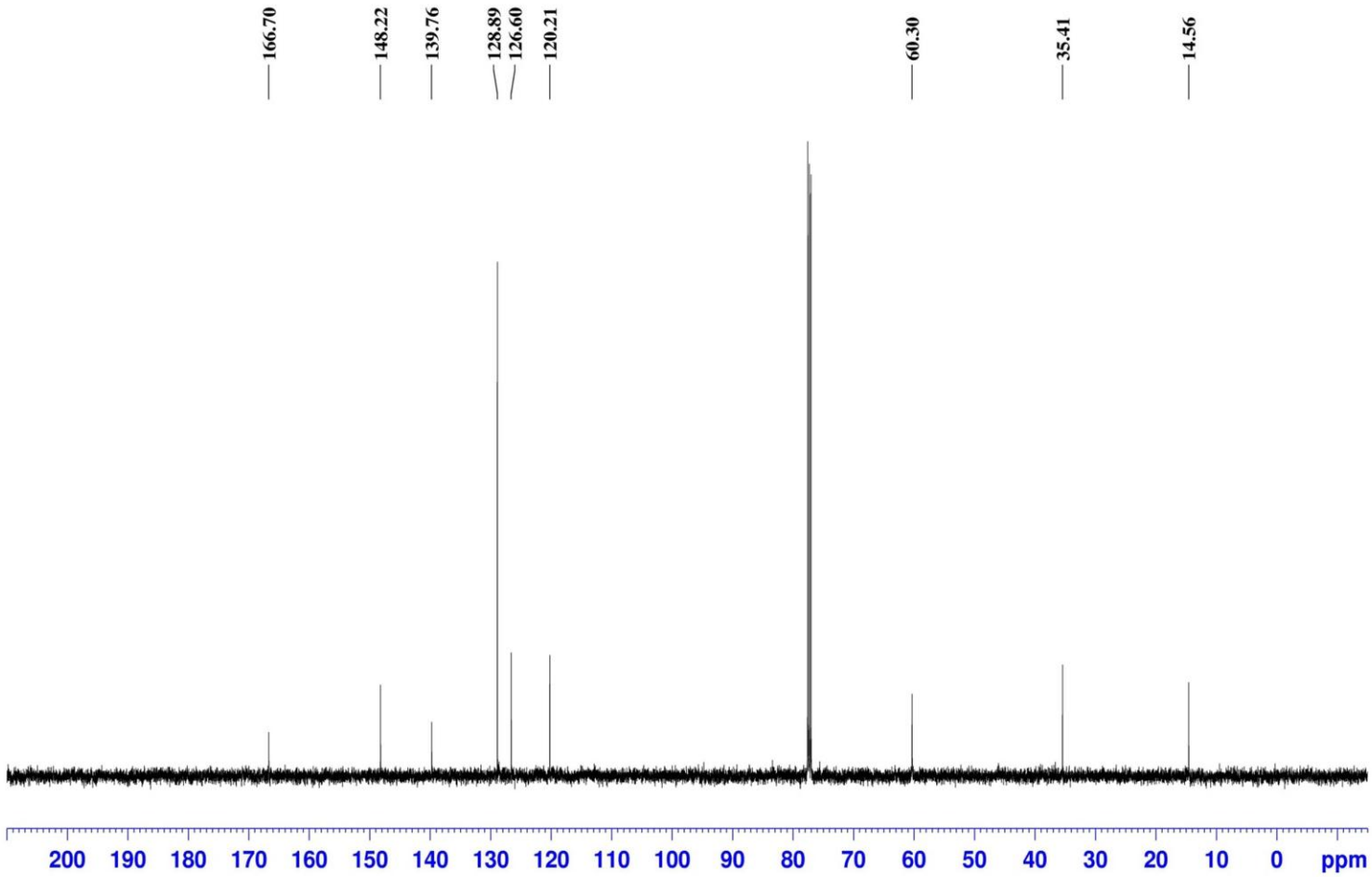
(E)–3–(cyclooct–1–en–1–yl)propan–1–amine
125 MHz, CDCl3



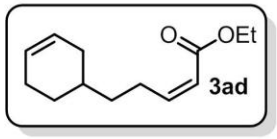


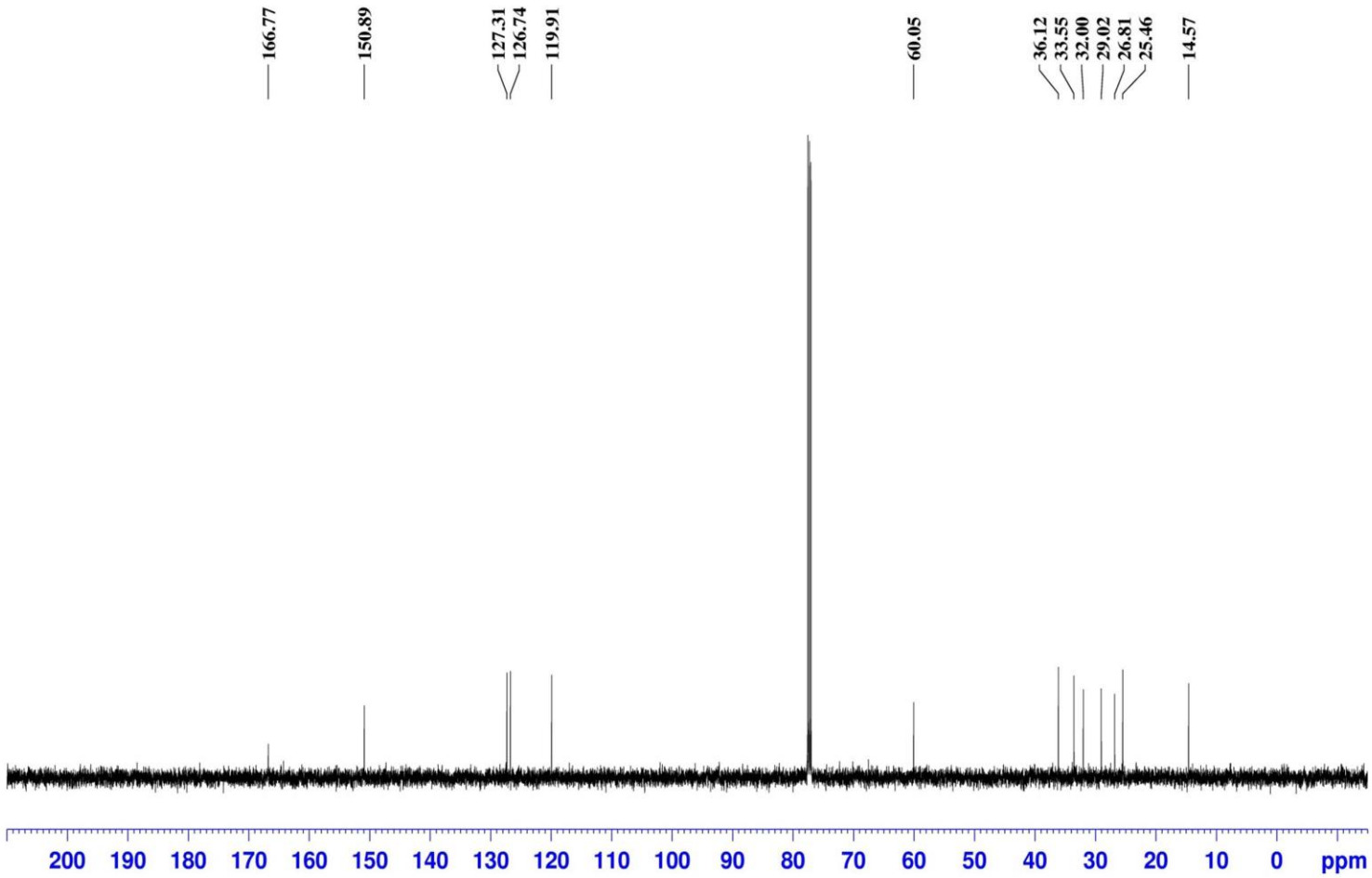
(Z)–ethyl 4–phenylbut–2–enoate
125 MHz, CDCl3



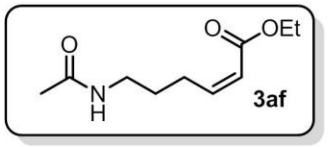


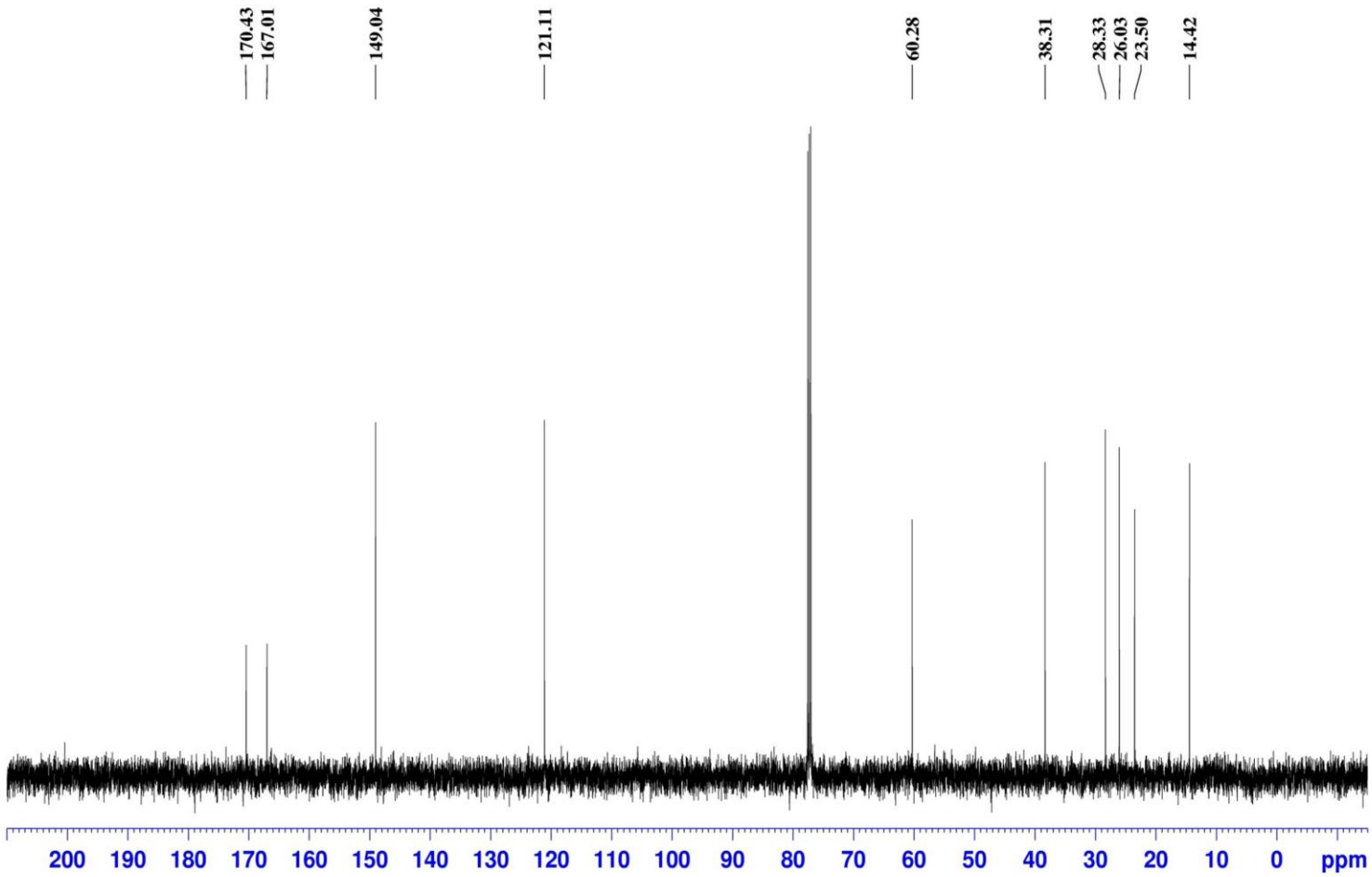
(Z)−ethyl 5−(cyclohex−3−en−1−yl)pent−2−enoate
125 MHz, CDCl3



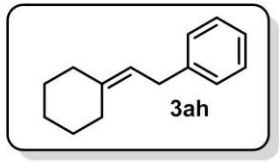


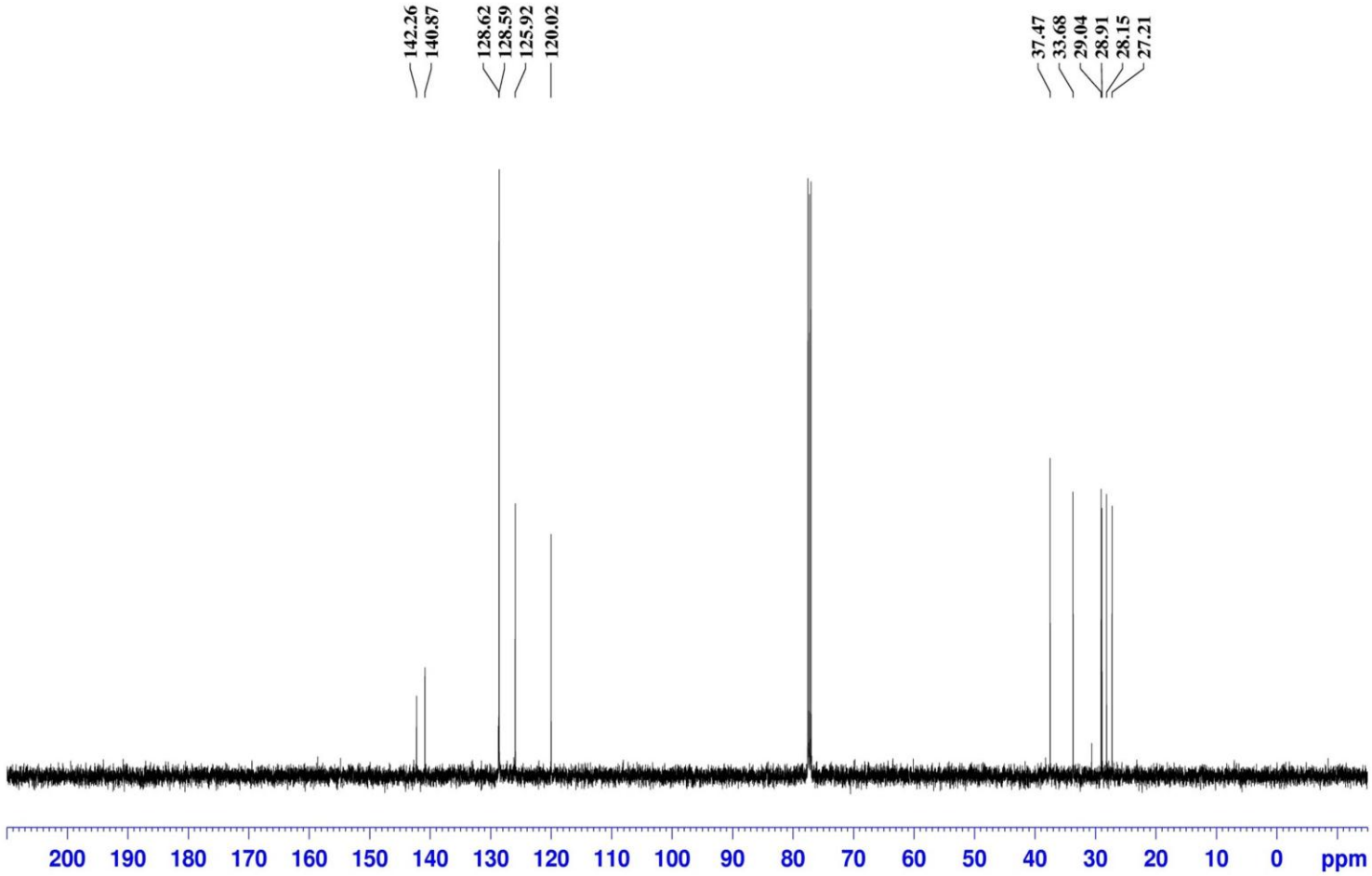
(Z)–ethyl 6–acetamidohex–2–enoate
125 MHz, CDCl3



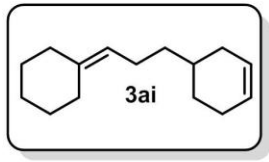


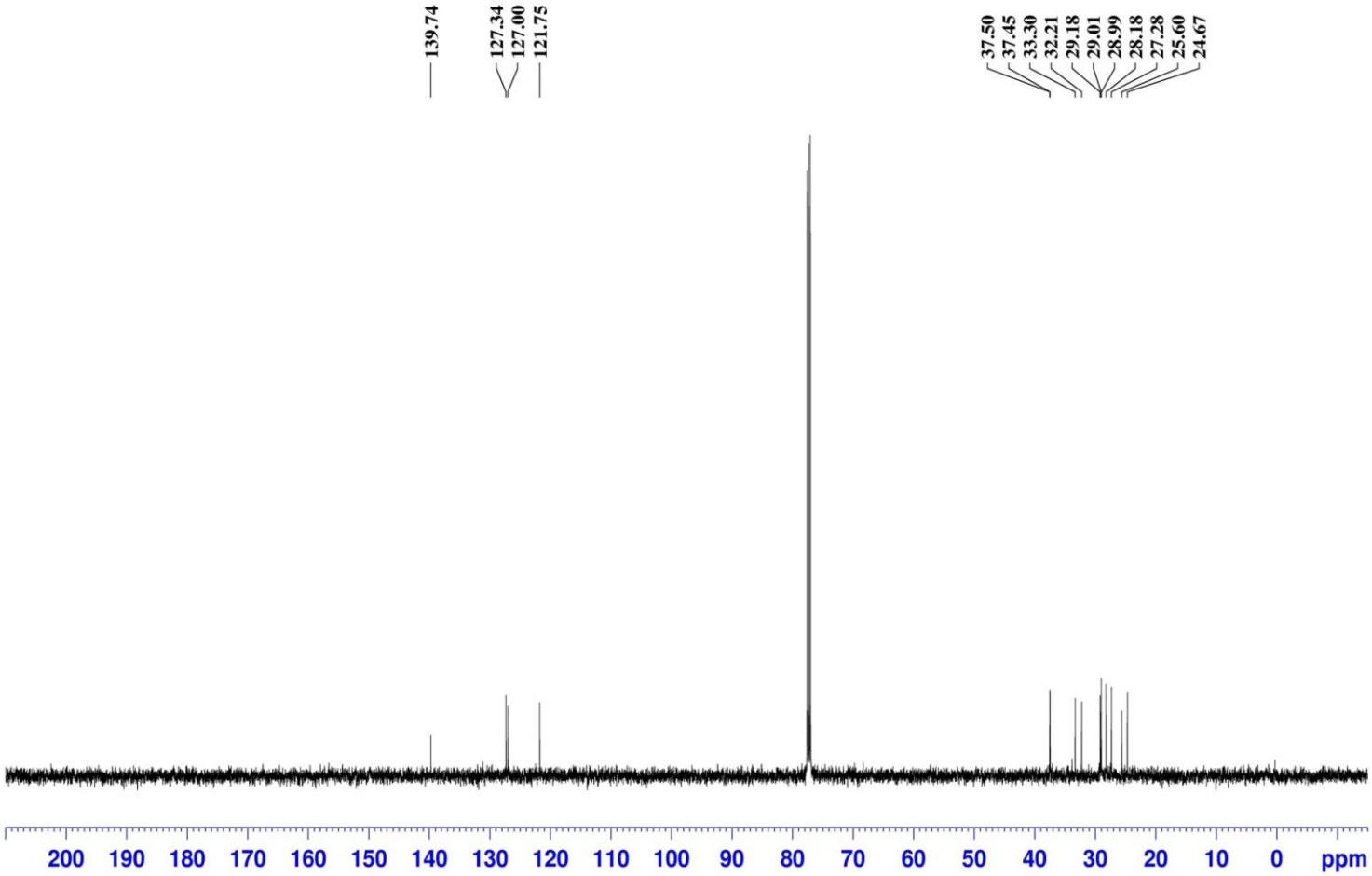
(2−cyclohexylideneethyl)benzene
125 MHz, CDCl3



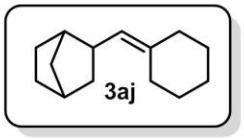


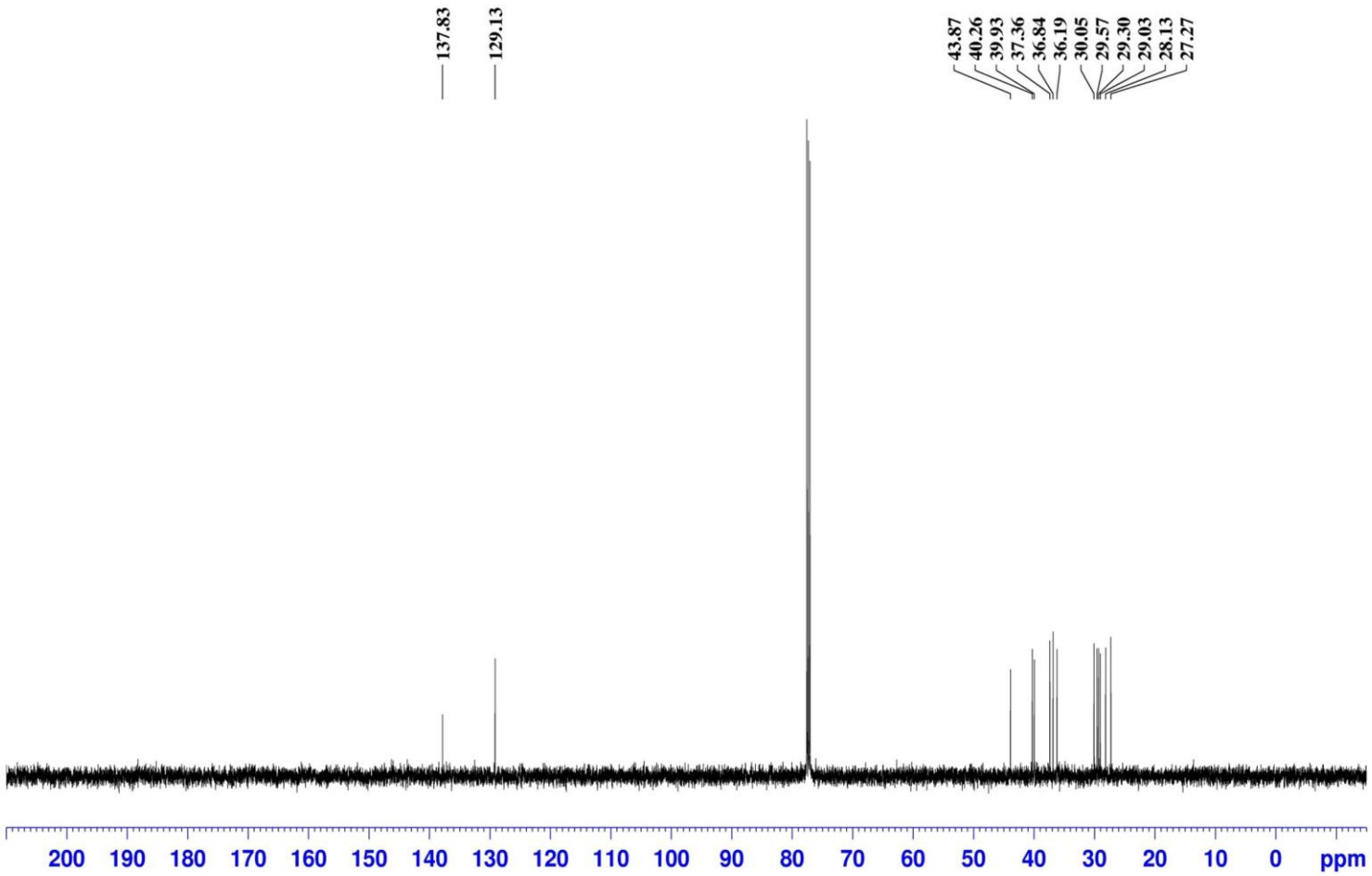
4–(3–cyclohexylidenepropyl)cyclohex–1–ene
125 MHz, CDCl3



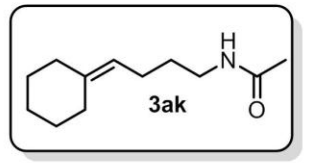


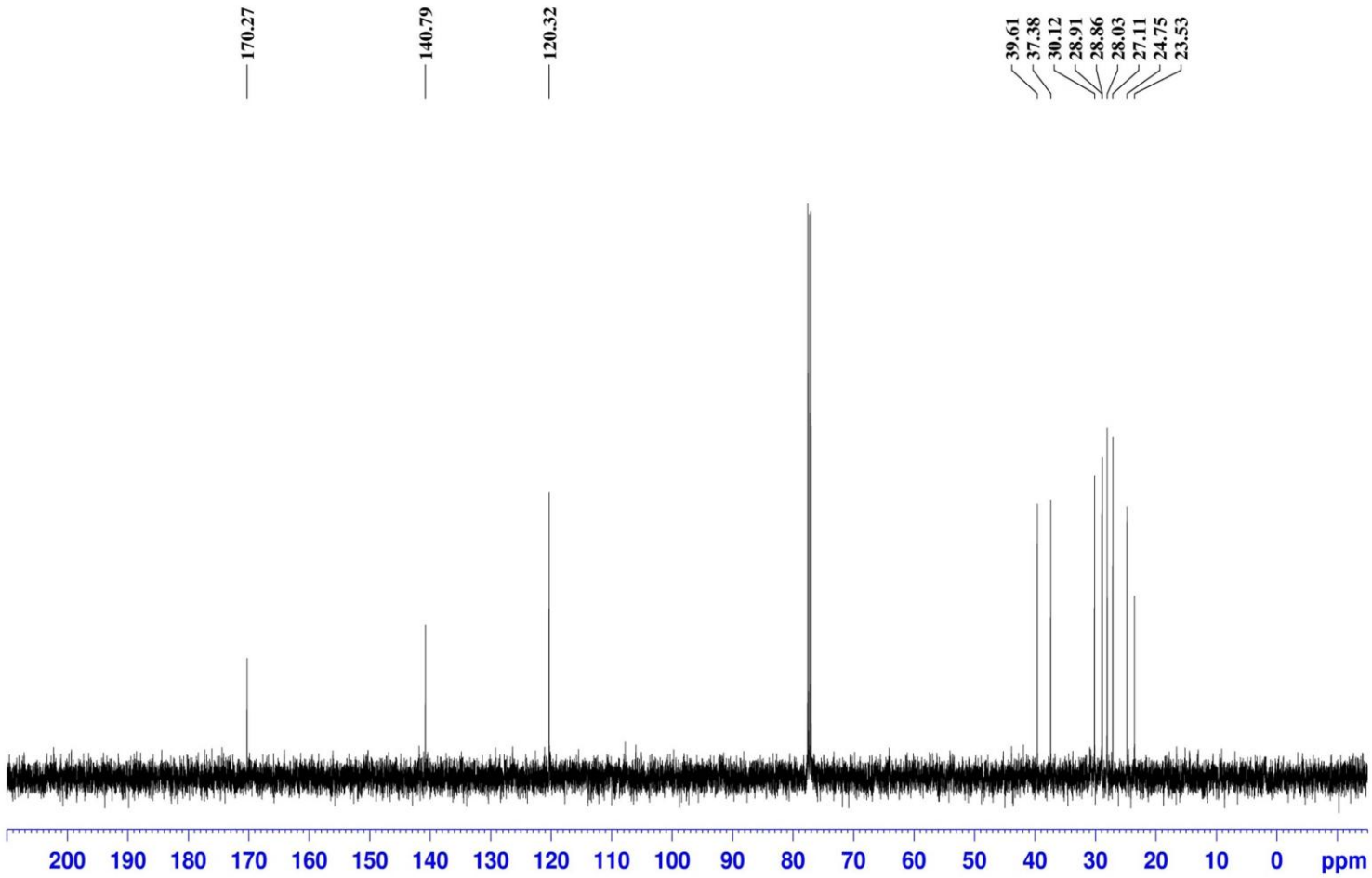
2–(cyclohexylidenemethyl)bicyclo[2.2.1]heptane
125 MHz, CDCl3



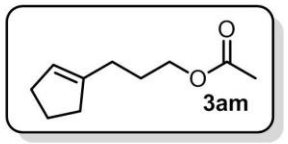


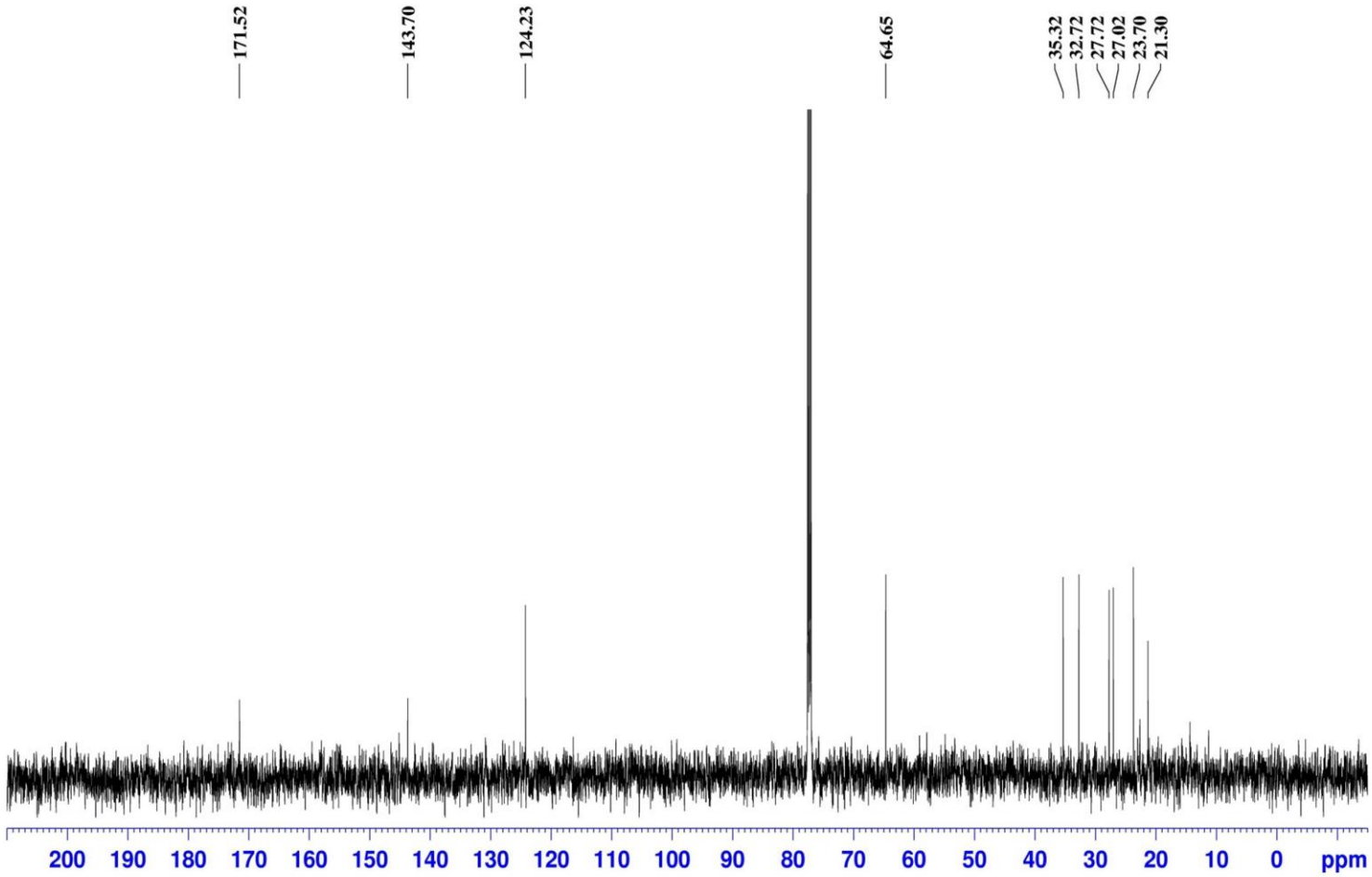
N–(4–cyclohexylidenebutyl)acetamide
125 MHz, CDCl3





3–(cyclopent–1–en–1–yl)propyl acetate
125 MHz, CDCl3





(E)−1−methoxy−4−(5−methoxypent−1−en−1−yl)benzene
125 MHz, CDCl3