

Supporting Information

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Supporting Information for

Palladium-Catalyzed Decarbonylative Dehydration of Fatty Acids for the Production of Linear Alpha Olefins

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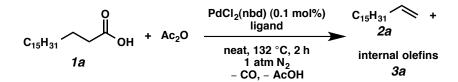
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Materials and Methods.

Unless otherwise stated, reactions were performed in flame-dried glassware under a nitrogen atmosphere or under vacuum without the use of solvents. Reaction progress was monitored by ¹H NMR analysis of the crude reaction mixture. Silicycle SiliaFlash® P60 Academic Silica gel (particle size 40–63 nm) was used for flash chromatography. ¹H NMR spectra were recorded on a Varian Inova 500 MHz spectrometer and are reported relative to residual CHCl₃ (δ 7.26 ppm) or DMSO (δ 2.50 ppm). ¹³C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer (125 MHz) and are reported relative to CHCl₃ (δ 77.16 ppm) or DMSO (δ 39.52 ppm). Data for ¹H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept =septuplet, m = multiplet, br s = broad singlet, br d = broad doublet, app = apparent. Data for ¹³C NMR are reported in terms of chemical shifts (δ ppm). IR spectra were obtained by use of a Perkin Elmer Spectrum BXII spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm⁻¹). High resolution mass spectra (HRMS) were provided by the California Institute of Technology Mass Spectrometry Facility using a JEOL JMS-600H High Resolution Mass Spectrometer by positive-ion FAB, or obtained with an Agilent 6200 Series TOF using Agilent G1978A Multimode source in negative electrospray ionization (ESI-), negative atmospheric pressure chemical ionization (APCI-), or negative mixed ionization mode (NMM: ESI-APCI-).

Reagents were purchased from Sigma-Aldrich, Acros Organics, Strem, or Alfa Aesar and used as received unless otherwise stated.





To a 20 x 150 mm Kimble glass tube equipped with a magnetic stir bar was added PdCl₂(nbd) (0.005 mmol, 0.1 mol%), ligand (monophosphine: 0.04 mmol, 0.8 mol%; diphosphine: 0.02 mmol, 0.4 mol%), and stearic acid **1a** (5 mmol, 1 equiv). The tube was sealed with a rubber septum, evacuated and refilled with N₂ (x 3), and acetic anhydride (10 mmol, 2 equiv) was added via syringe. The reaction tube placed in a preheated 132 °C oil bath (glass thermometer reading = 132 °C, IKA reading = 140 °C) and stirred for 2 h. The oil bath was removed, and methyl benzoate (internal standard, 5 mmol, 1 equiv) was added and the resulting mixture stirred for 1 min. An aliquot of the crude mixture was taken by pipette and analyzed by ¹H NMR. The results of additional ligand screen are listed below.

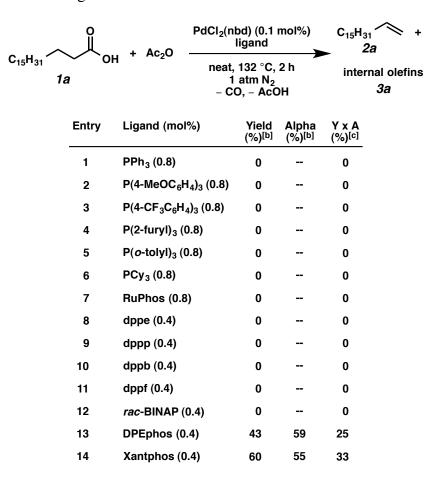
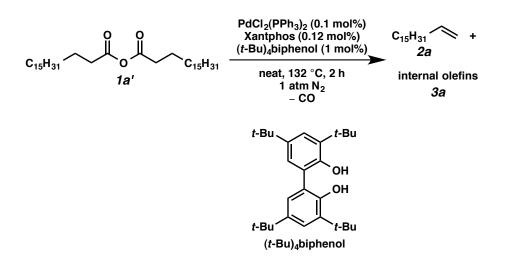


 Table S1. Additional ligand screen.^[a]

^[a] **1a** (5 mmol, 1 equiv), Ac₂O (2 equiv). ^[b] Determined by ¹H NMR with methyl benzoate as internal standard. ^[c] Y x A = Yield x Alpha.

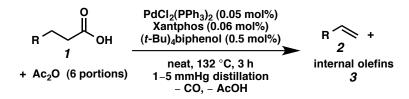


General Procedure for Optimization Reactions (Route B)

The procedure for the representative reaction (Table 1, entry 12) is shown as follows. To a 20 x 150 mm Kimble glass tube equipped with a magnetic stir bar was added $PdCl_2(PPh_3)_2$ (0.005 mmol, 0.1 mol%), Xantphos (0.006 mmol, 0.12 mol%), (*t*-Bu)_4biphenol (0.05 mmol, 1 mol%), and stearic anhydride **1a'** (5 mmol, 1 equiv). The tube was sealed with a rubber septum, evacuated and refilled with N₂ (x 3), and placed in a preheated 132 °C oil bath and stirred for 2 h. The oil bath was removed, and methyl benzoate (internal standard, 5 mmol, 1 equiv) was added and the resulting mixture stirred for 1 min. An aliquot of the crude mixture was taken by pipette and analyzed by ¹H NMR.

General Procedure for Preparative Pd-Catalyzed Decarbonylative

Dehydration



A 15 mL round-bottom flask was charged with PdCl₂(PPh₃)₂ (0.01 mmol, 0.05 mol%), Xantphos (0.012 mmol, 0.06 mol%), (*t*-Bu)₄biphenol (0.1 mmol, 0.5 mol%), and fatty acid substrate (20 mmol, 1 equiv). The flask was equipped with a distillation head and a 25 mL round-bottom receiving flask. The closed system was connected to a vacuum manifold, equipped with a needle valve and a digital vacuum gauge. The system was evacuated and refilled with N₂ (x 3), and the first portion of acetic anhydride (20 mmol, 1 equiv) was added via syringe through the septum that seals the top of the distillation head. The flask was lowered into a 20 °C oil bath and gradually heated to 132 °C in 23 min.[†] When oil bath temperature rose to 122 °C, the needle valve was closed, switched to vacuum, and the needle valve carefully and slowly opened to allow distillation of acetic acid into a receiving flask, which was cooled to -78 °C. When the oil bath temperature reached 130 °C, time was recorded as t = 0. After distillation ceased (about t = 3 min), the needle valve was opened fully and a vacuum of 1–5 mmHg was drawn. At t = 30 min, the system was refilled with N₂, and the second portion of acetic anhydride (2.8 mmol, 0.14 equiv) was

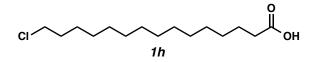
[†] When the reaction was performed at 100 mmol scale with high-melting substrates such as stearic acid, the reaction flask was first heated to 85 °C until all solid melted, and then to 132 °C. Overall heating time from 20 to 132 °C was approximately 40 min.

added via syringe. The system was then gradually (t = 35 min) resubjected to a vacuum of 1-5 mmHg. Acetic anhydride was added as follows (0.12, 0.10, 0.09. 0.08 equiv) in the same manner every 30 min. The reaction was stopped at t = 3 h and allowed to cool to ambient temperature. The residual reaction mixture was purified by flash chromatography. If it contained solids, it was suction-filtered first and the solids washed with hexanes, and the filtrate was concentrated and purified by chromatography. In cases where the product was distilled together with acetic acid, the distillate was added dropwise to a saturated NaHCO₃ solution, stirred for 30 min, and the resulting mixture was extracted with dichloromethane (30 mL x 3). The combined extracts were dried over Na₂SO₄, filtered and concentrated. The crude product was then subjected to flash chromatography or distillation to afford the olefin in pure form.

Spectroscopic Data for Acid Substrates

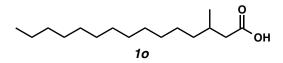
Saturated fatty acids **1a–1d** and **1m** are commercially available. Carboxylic acids **1e**,^[1] **1f**,^[2] **1g**,^[3] **1i**,^[4] **1j**,^[5] **1k**,^[6] **1l**,^[7] and **1n**^[8] are known compounds and prepared according to literature methods.

15-Chloropentadecanoic acid (1h)



¹H NMR (500 MHz, CDCl₃) δ 3.52 (t, *J* = 6.8 Hz, 2H), 2.34 (t, *J* = 7.5 Hz, 2H), 1.79–1.73 (m, 2H), 1.62 (p, *J* = 7.5 Hz, 2H), 1.46–1.20 (m, 20H); ¹³C NMR (126 MHz, CDCl₃) δ 180.6, 45.3, 34.2, 32.8, 29.7, 29.7, 29.7, 29.7, 29.6, 29.6, 29.4, 29.2, 29.0, 27.0, 24.8; IR (Neat Film) 2916, 2848, 1701, 1462, 1410, 1302, 943, 721 cm⁻¹; HRMS (NMM: ESI-APCI–) *m/z* calc'd for C₁₅H₂₈O₂Cl [M–H]⁻: 275.1783, found 275.1794.

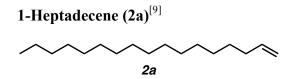
3-Methylpentadecanoic acid (10)



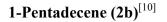
¹H NMR (500 MHz, CDCl₃) δ 2.35 (dd, J = 15.0, 5.9 Hz, 1H), 2.14 (dd, J = 15.0, 8.2 Hz, 1H), 2.01–1.90 (m, 1H), 1.38–1.15 (m, 22H), 0.96 (d, J = 6.7 Hz, 3H), 0.88 (t, J = 6.9 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 180.1, 41.8, 36.8, 32.1, 30.3, 29.9, 29.8, 29

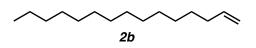
1300, 1151, 1123, 954, 715; HRMS (NMM: ESI-APCI–) *m/z* calc'd for C₁₆H₃₁O₂ [M–H]⁻: 255.2330, found 255.2328.

Spectroscopic Data for Olefin Products

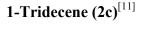


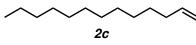
¹H NMR (500 MHz, CDCl₃) δ 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.07–4.86 (m, 2H), 2.11–1.98 (m, 2H), 1.49–1.08 (m, 26H), 0.88 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 139.4, 114.2, 34.0, 32.1, 29.9, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 29.5, 29.4, 29.3, 29.1, 22.9, 14.3.



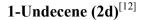


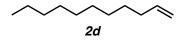
¹H NMR (500 MHz, CDCl₃) δ 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.07–4.85 (m, 2H), 2.11–1.97 (m, 2H), 1.46–1.08 (m, 22H), 0.88 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 139.4, 114.2, 34.0, 32.1, 29.9, 29.9, 29.8, 29.8, 29.8, 29.7, 29.6, 29.3, 29.1, 22.9, 14.3.





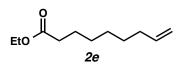
¹H NMR (500 MHz, CDCl₃) δ 5.82 (ddt, J = 17.0, 10.1, 6.7 Hz, 1H), 5.09–4.83 (m, 2H), 2.11–1.97 (m, 2H), 1.48–1.11 (m, 18H), 0.88 (t, J = 6.9 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 139.4, 114.2, 34.0, 32.1, 29.8, 29.8, 29.8, 29.7, 29.5, 29.3, 29.1, 22.9, 14.3.





¹H NMR (500 MHz, CDCl₃) δ 5.82 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.08–4.84 (m, 2H), 2.11–1.98 (m, 2H), 1.47–1.09 (m, 14H), 0.88 (t, J = 6.9 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 139.4, 114.2, 34.0, 32.1, 29.8, 29.7, 29.5, 29.3, 29.1, 22.8, 14.3.

Ethyl non-8-enoate (2e)^[13]

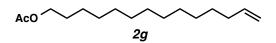


¹H NMR (500 MHz, CDCl₃) δ 5.80 (ddt, *J* = 16.6, 9.9, 6.8 Hz, 1H), 5.07–4.87 (m, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 2.28 (t, *J* = 7.5 Hz, 2H), 2.10–1.98 (m, 2H), 1.69–1.54 (m, 2H), 1.46–1.28 (m, 6H), 1.25 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 174.0, 139.1, 114.4, 60.3, 34.5, 33.8, 29.1, 28.8, 28.8, 25.0, 14.4.

Non-8-en-1-yl acetate (2f)^[14]

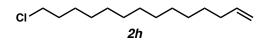
¹H NMR (500 MHz, CDCl₃) δ 5.80 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.07–4.87 (m, 2H), 4.05 (t, J = 6.8 Hz, 2H), 2.14–1.94 (m, 5H), 1.70–1.52 (m, 2H), 1.47–1.18 (m, 8H); ¹³C NMR (126 MHz, CDCl₃) δ 171.4, 139.2, 114.4, 64.8, 33.9, 29.2, 29.1, 29.0, 28.7, 26.0, 21.2.

Tetradec-13-en-1-yl acetate (2g)^[15]



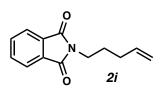
¹H NMR (500 MHz, CDCl₃) δ 5.81 (ddt, *J* = 16.8, 10.1, 6.8 Hz, 1H), 5.08–4.86 (m, 2H), 4.05 (t, *J* = 6.8 Hz, 2H), 2.11–1.98 (m, 5H), 1.69–1.53 (m, 2H), 1.45–1.09 (m, 18H); ¹³C NMR (126 MHz, CDCl₃) δ 171.4, 139.4, 114.2, 64.8, 34.0, 29.8, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 29.1, 28.7, 26.0, 21.2.

14-Chlorotetradec-1-ene (2h)



¹H NMR (500 MHz, CDCl₃) δ 5.81 (ddt, J = 17.0, 10.2, 6.7 Hz, 1H), 5.07–4.86 (m, 2H), 3.53 (t, J = 6.8 Hz, 2H), 2.11–1.98 (m, 2H), 1.77 (dt, J = 14.5, 6.9 Hz, 2H), 1.50–1.10 (m, 18H); ¹³C NMR (126 MHz, CDCl₃) δ 139.4, 114.2, 45.3, 34.0, 32.8, 29.8, 29.7, 29.7, 29.6, 29.6, 29.3, 29.1, 29.0, 27.0; IR (Neat Film, NaCl) 3076, 2925, 2854, 1641, 1465, 1309, 993, 966, 909, 723 cm⁻¹; HRMS (FAB+) *m/z* calc'd for C₁₄H₂₇³⁵Cl [M]⁺: 230.1801, found 230.1808.

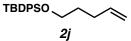
2-(Pent-4-en-1-yl)isoindoline-1,3-dione (2i)^[16]



¹H NMR (500 MHz, CDCl₃) δ 7.89–7.73 (m, 2H), 7.73–7.58 (m, 2H), 5.77 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.10–4.87 (m, 2H), 3.74–3.57 (m, 2H), 2.17–2.00 (m, 2H), 1.74 (p, *J* =

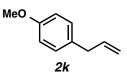
7.5 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 168.4, 137.3, 133.9, 132.2, 123.2, 115.3, 37.6, 31.0, 27.7.

tert-Butyl(pent-4-en-1-yloxy)diphenylsilane (2j)^[17]



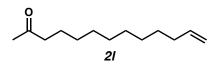
¹H NMR (500 MHz, CDCl₃) δ 7.67 (dt, J = 6.5, 1.5 Hz, 4H), 7.39 (dddd, J = 14.4, 8.3, 6.0, 2.1 Hz, 6H), 5.80 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.09–4.87 (m, 2H), 3.68 (t, J = 6.5 Hz, 2H), 2.15 (tdd, J = 8.1, 6.8, 1.4 Hz, 2H), 1.73–1.60 (m, 2H), 1.05 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 138.7, 135.7, 134.2, 129.7, 127.7, 114.7, 63.4, 32.0, 30.2, 27.0, 19.4.

1-Allyl-4-methoxybenzene (2k)^[18]



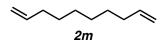
¹H NMR (500 MHz, CDCl₃) δ 7.17–7.06 (m, 2H), 6.91–6.78 (m, 2H), 5.96 (ddt, *J* = 16.8, 10.1, 6.7 Hz, 1H), 5.13–4.99 (m, 2H), 3.79 (s, 3H), 3.34 (d, *J* = 6.7 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 158.1, 138.0, 132.2, 129.6, 115.5, 113.9, 55.4, 39.5.

Tridec-12-en-2-one (21)^[19]



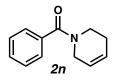
¹H NMR (500 MHz, CDCl₃) δ 5.81 (ddt, J = 16.9, 10.1, 6.7 Hz, 1H), 5.06–4.87 (m, 2H), 2.41 (t, J = 7.5 Hz, 2H), 2.13 (s, 3H), 2.09–1.97 (m, 2H), 1.62–1.49 (m, 2H), 1.46–1.11 (m, 12H); ¹³C NMR (126 MHz, CDCl₃) δ 209.5, 139.3, 114.2, 43.9, 33.9, 30.0, 29.5, 29.5, 29.5, 29.5, 29.5, 29.3, 29.2, 29.0, 24.0.

Deca-1,9-diene (2m)^[20]



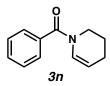
¹H NMR (500 MHz, CDCl₃) δ 5.81 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 2H), 5.08–4.86 (m, 4H), 2.11–1.98 (m, 4H), 1.48–1.21 (m, 8H); ¹³C NMR (126 MHz, CDCl₃) δ 139.3, 114.3, 33.9, 29.1, 29.0.

(3,6-Dihydropyridin-1(2*H*)-yl)(phenyl)methanone (2n)^[21]



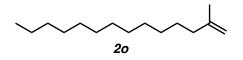
¹H NMR (500 MHz, DMSO-d₆, 130 °C) δ 7.41 (ddd, J = 24.3, 6.8, 3.4 Hz, 5H), 5.90–5.82 (m, 1H), 5.78–5.64 (m, 1H), 4.00 (p, J = 2.8 Hz, 2H), 3.56 (t, J = 5.8 Hz, 2H), 2.16 (dp, J = 8.7, 3.2 Hz, 2H); ¹³C NMR (126 MHz, DMSO-d₆, 130 °C) δ 168.8, 136.1, 128.5, 127.5, 125.9, 124.6, 123.7, 43.4, 41.1, 24.3.

(3,4-Dihydropyridin-1(2*H*)-yl)(phenyl)methanone (3n)^[22]

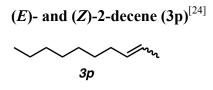


¹H NMR (500 MHz, DMSO-d₆, 130 °C) δ 7.45 (tdd, *J* = 6.0, 3.9, 2.4 Hz, 5H), 6.78–6.61 (m, 1H), 4.97 (dt, *J* = 8.2, 3.9 Hz, 1H), 3.72–3.60 (m, 2H), 2.09 (tdd, *J* = 6.2, 3.8, 2.0 Hz, 2H), 1.85 (p, *J* = 6.1 Hz, 2H); ¹³C NMR (126 MHz, DMSO-d₆, 130 °C) δ 167.2, 135.0, 129.0, 127.5, 126.6, 125.6, 107.1, 42.0, 20.9, 20.8.

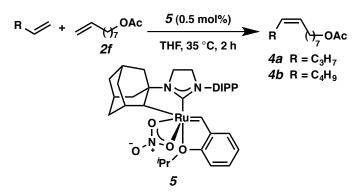
2-Methyltetradec-1-ene (20)^[23]



¹H NMR (500 MHz, CDCl₃) δ 4.72–4.63 (m, 2H), 2.00 (t, *J* = 7.7 Hz, 2H), 1.71 (s, 3H), 1.47–1.11 (m, 20H), 0.88 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 146.5, 109.6, 38.0, 32.1, 29.9, 29.9, 29.8, 29.8, 29.7, 29.5, 29.5, 27.8, 22.9, 22.6, 14.3.

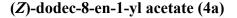


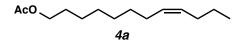
¹H NMR (500 MHz, CDCl₃) δ 5.48–5.35 (m, 2H), 2.07–1.93 (m, 2H), 1.64 (d, *J* = 4.2 Hz, 3H, *E*-olefin), 1.60 (d, *J* = 6.1 Hz, 3H, *Z*-olefin), 1.43–1.20 (m, 10H), 0.88 (t, *J* = 6.6 Hz, 3H).



General Procedure for Pheromone Synthesis by Ru-Catalyzed Cross Metathesis^[25]

In a glovebox, a 20 mL vial was charged with 8-nonenyl acetate (2f,^{††} 1.0 mL, 4.8 mmol), 1-pentene or 1-hexene (48 mmol), and THF (2.6 mL). Ruthenium metathesis catalyst **5** (16 mg, 0.024 mmol, 0.5 mol%) was added and the reaction was stirred at 35 °C in an open vial for 2 hours. The vial was removed from the glovebox, quenched with ethyl vinyl ether (2.5 mL) and stirred for 30 minutes. The solvent was then removed *in vacuo*. The crude mixture was passed through a SiO₂ plug (hexane to 4% ethyl acetate in hexanes) to provide a mixture of unreacted 8-nonenyl acetate and pheromone **4**. Pheromone **4** was isolated by distillation using a Kugelrohr apparatus.



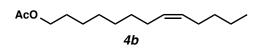


¹H NMR (500 MHz, CDCl₃) δ 5.35 (2H, m), 4.04 (2H, t, *J* = 6.8 Hz), 2.04 (3H, s), 2.01 (4H, m), 1.61 (2H, m), 1.27–1.39 (10H, m), 0.89 (3H, t, *J* = 7.4 Hz); ¹³C NMR (CDCl₃): δ

^{††} An inseparable mixture of olefin isomers **2f** and **3f** was used for this reaction. For **4a**, the mixture was 98% alpha (**2f**:**3f** = 98:2); for **4b**, the mixture was 96% alpha (**2f**:**3f** = 96:4).

171.4, 130.1, 129.9, 64.8, 29.8, 29.4, 29.3 (2C), 28.7, 27.3, 26.0, 23.0, 21.2, 14.0; HRMS (EI+) *m/z* calc'd for C₁₄H₂₇O₂ [M+H]⁺: 227.2011, found 227.2012.

(Z)-tridec-8-en-1-yl acetate (4b)



¹H NMR (500 MHz, CDCl₃) δ 5.34 (m, 2H), 4.05 (t, J = 6.8 Hz, 2H), 2.00–2.04 (m, 7H), 1.60–1.63 (m, 2H), 1.29–1.36 (m, 12H), 0.88–0.91 (m, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 171.4, 130.1, 129.9, 64.8, 32.1, 29.8, 29.3, 28.7, 27.3, 27.1, 26.0, 22.5, 21.2, 14.2; HRMS (EI+) m/z calc'd for C₁₅H₂₉O₂ [M+H]⁺: 241.2168, found 241.2167.

References

[1] J. Regourd, A. A. Ali, A. Thompson, J. Med. Chem. 2007, 50, 1528–1536.

- [2] R. Kazlauskas, P. T. Murphy, R. J. Wells, A. J. Blackman, Aust. J. Chem. 1982, 35, 113–120.
- [3] E. Melliou, I. Chinou, J. Agric. Food Chem. 2005, 53, 8987–8992.
- [4] E.; Guenin, M. Monteil, N. Bouchemal, T. Prange, M. Lecouvey, *Eur. J. Org. Chem.* **2007**, 3380–3391.
- [5] W. Oppolzer, R. N. Radinov, E. El-Sayed, J. Org. Chem. 2001, 66, 4766-4770.
- [6] T. Ohishi, L. Zhang, M. Nishiura, Z. Hou, Angew. Chem. Int. Ed. 2011, 50, 8114-8117.
- [7] R. Kaiser, D. Lamparsky, Helv. Chim. Acta 1978, 61, 2671–2680.
- [8] Z. Wang, L. Zhu, F. Yin, Z. Su, Z. Li, C. Li, J. Am. Chem. Soc. 2012, 134, 4258-4263.
- [9] D. H. R. Barton, J. Boivin, E. Crépon, J. Sarma, H. Togo, S. Z. Zard, *Tetrahedron* **1991**, *47*, 7091–7108.
- [10] D. H. Burns, J. D. Miller, H.-K. Chan, M. O. Delaney, J. Am. Chem. Soc. 1997, 119, 2125–2133.
- [11] G. Rojas, K. B. Wagener, J. Org. Chem. 2008, 73, 4962–4970.
- [12] T. Vijai Kumar Reddy, B. L. A. Prabhavathi Devi, R. B. N. Prasad, M. Poornima, C. Ganesh Kumar, *Bioorg. Med. Chem. Lett.* **2012**, *22*, 4678–4680.
- [13] V. R. Ravu, G. Y. C. Leung, C. S. Lim, S. Y. Ng, R. J. Sum, D. Y.-K. Chen, *Eur. J. Org. Chem.* **2011**, 463–468.
- [14] K. Mori, Tetrahedron 2009, 65, 3900–3909.
- [15] J. Lin, F. Liu, Y. Wang, M. Liu, Synth. Commun. 1995, 25, 3457–3461.
- [16] A. M. Whittaker, G. Lalic, Org. Lett. 2013, 15, 1112–1115.
- [17] D. A. Dias, M. A. Kerr, Org. Lett. 2009, 11, 3694–3697.
- [18] L. Ackermann, A. R. Kapdi, C. Schulzke, Org. Lett. 2010, 12, 2298–2301.

[19] D. Arbain, N. Dasman, S. Ibrahim, M. V. Sargent, Aust. J. Chem. 1990, 43, 1949–1952.

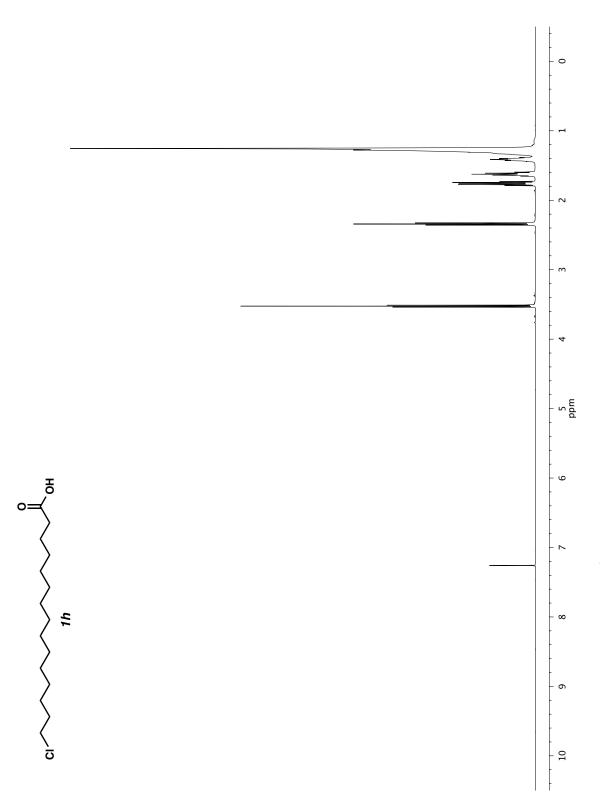
[20] R. F. Garwood, Naser-ud-Din, C. J. Scott, B. C. L. Weedon, J. Chem. Soc., Perkin Trans. 1 1973, 2714–2721.
[21] R. A. Olofson, D. E. Abbott, J. Org. Chem. 1984, 49, 2795–2799.

[22] N. Gigant, L. Chausset-Boissarie, B.-C. Belhomme, T. Poisson, X. Pannecoucke, G. Isabelle, *Org. Lett.* **2013**, *15*, 278–281.

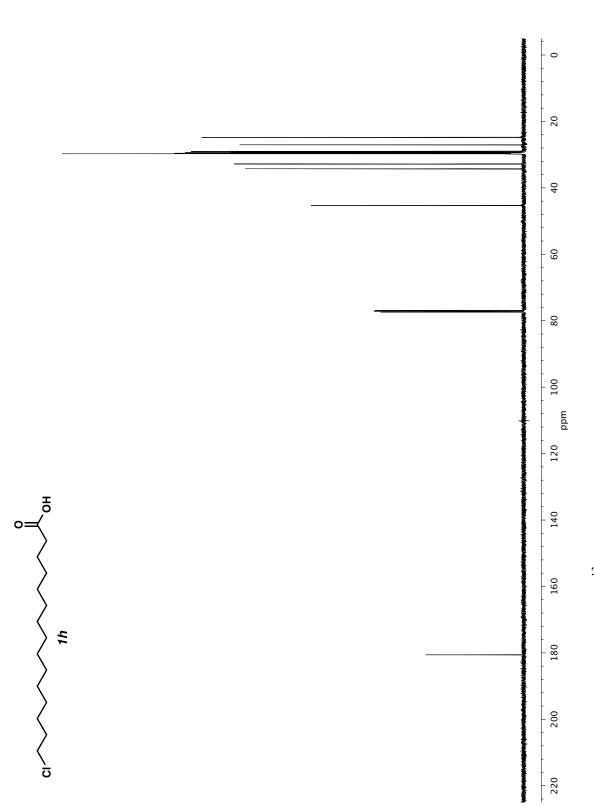
[23] B. A. Pearlman, S. R. Putt, J. A. Fleming, J. Org. Chem. 1985, 50, 3625-3626.

[24] A. Yanagisawa, S. Habaue, K. Yasue, H. Yamamoto, J. Am. Chem. Soc. 1994, 116, 6130-6141.

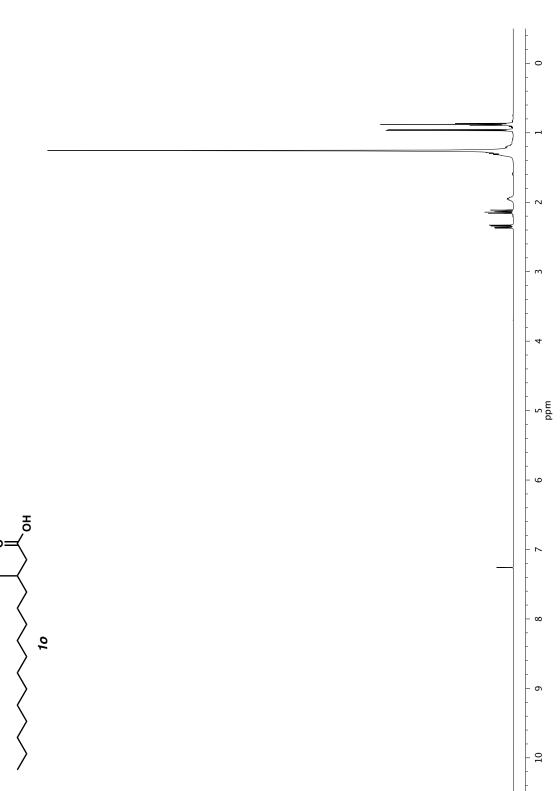
[25] L. E. Rosebrugh, M. B. Herbert, V. M. Marx, B. K. Keitz, R. H. Grubbs, J. Am. Chem Soc. 2013, 135, 1276–1279.



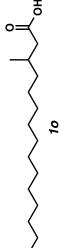


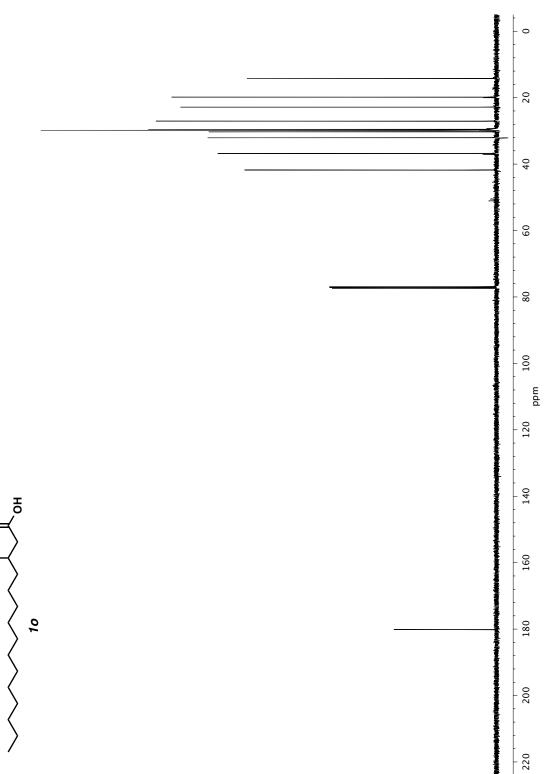


¹³C NMR (126 MHz, CDCl₃) of compound **1h**.

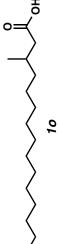


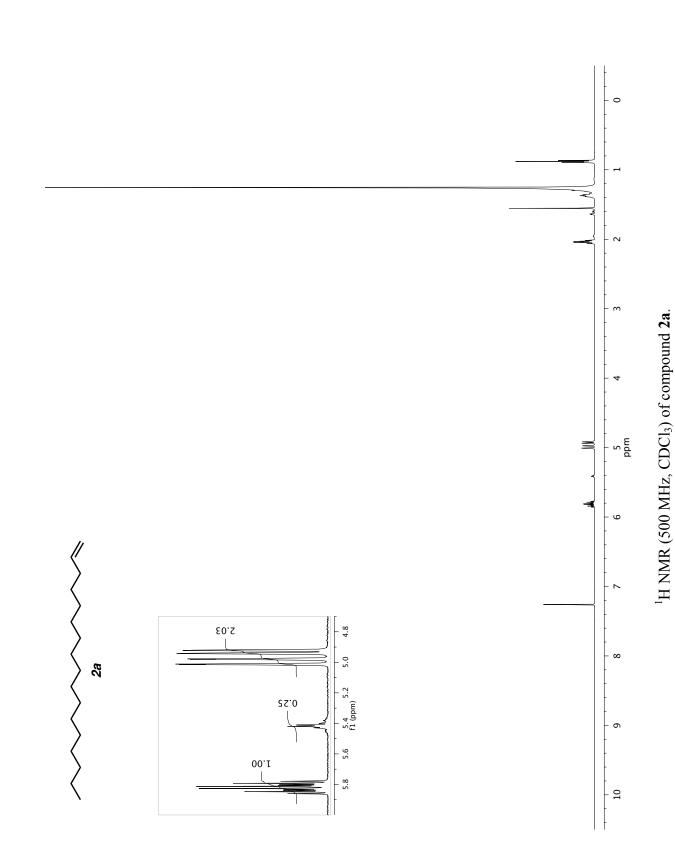
 $^1\mathrm{H}$ NMR (500 MHz, CDCl₃) of compound 10.

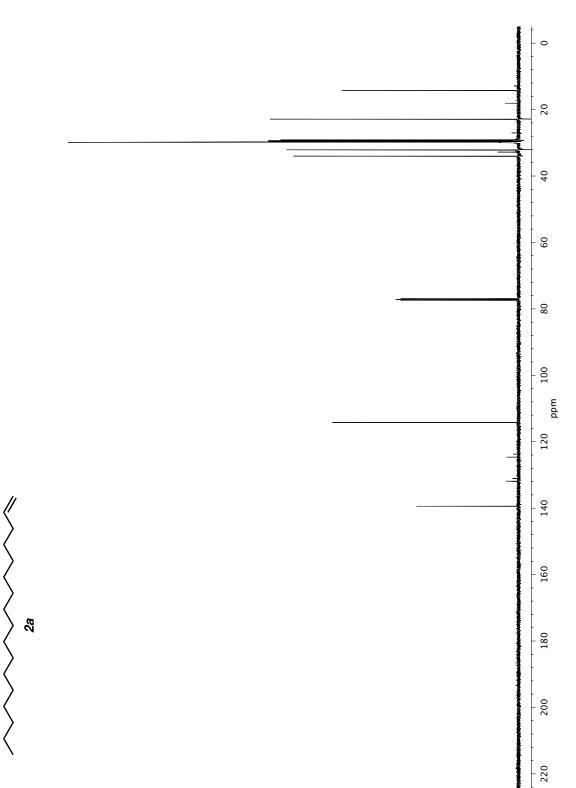




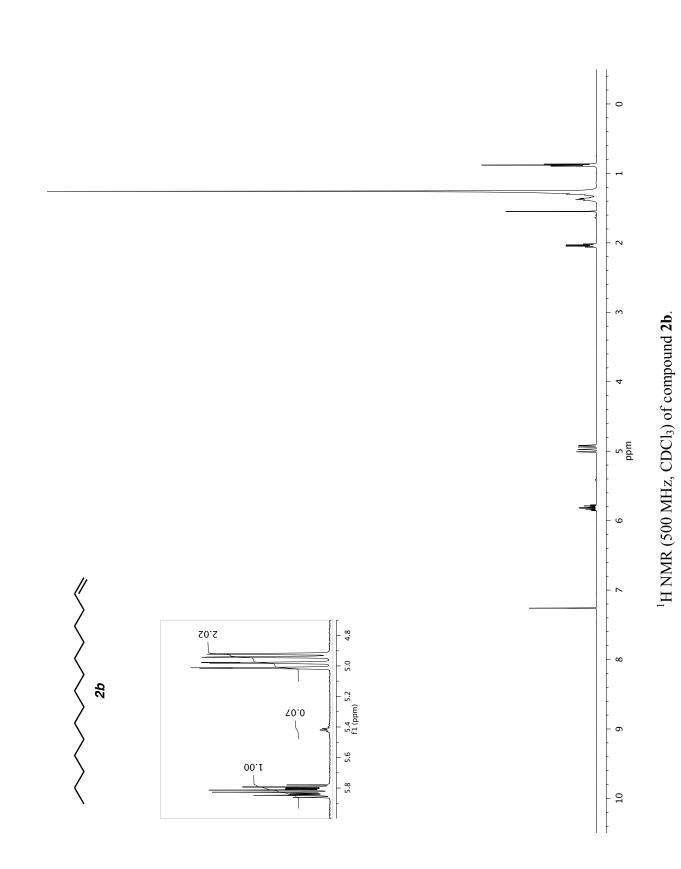
 ^{13}C NMR (126 MHz, CDCl₃) of compound 10.

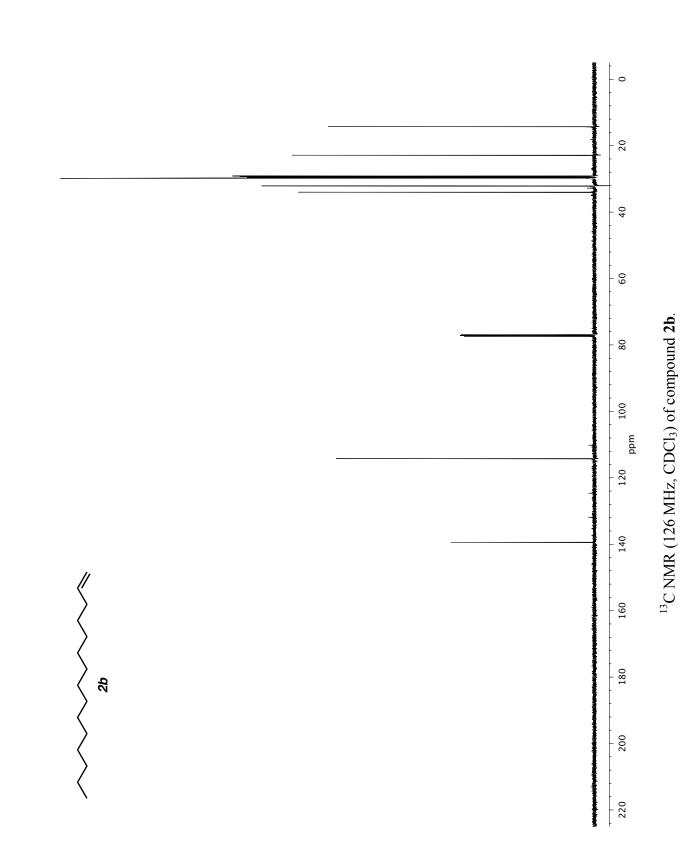


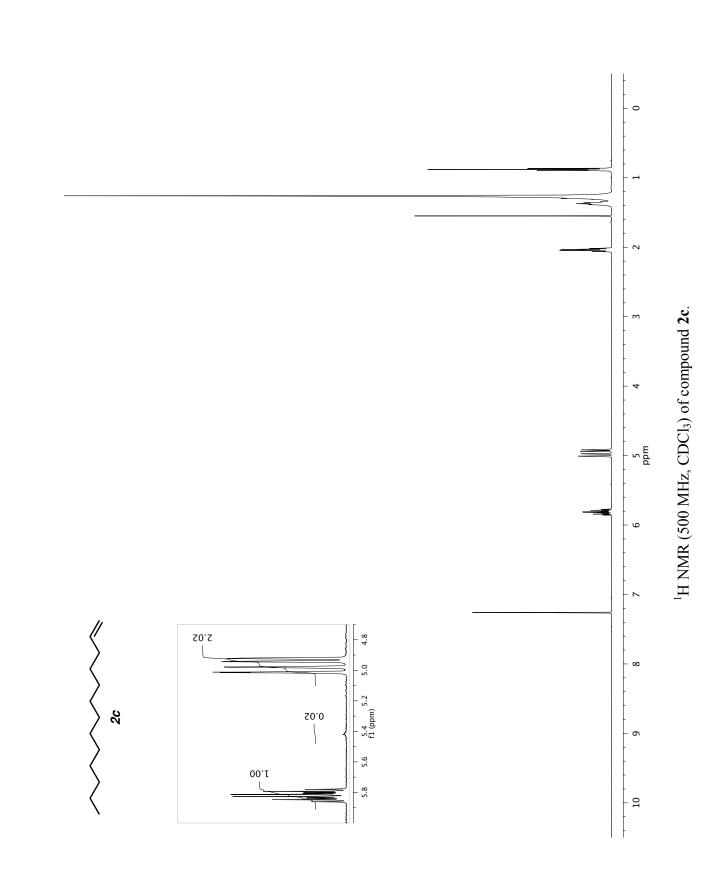


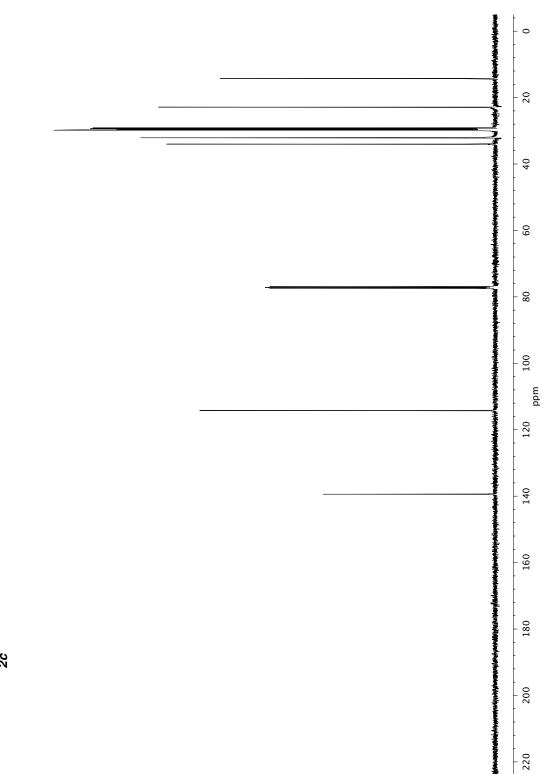


 ^{13}C NMR (126 MHz, CDCl₃) of compound **2a**.

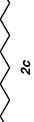


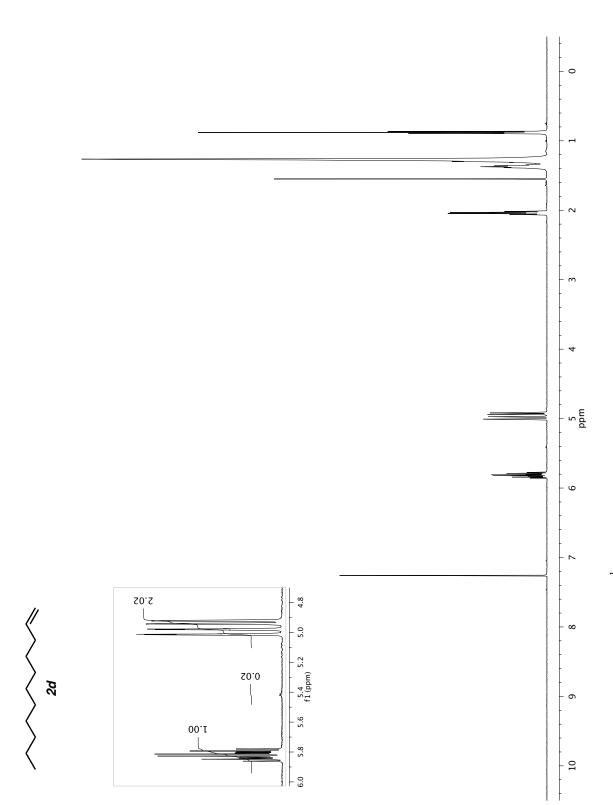


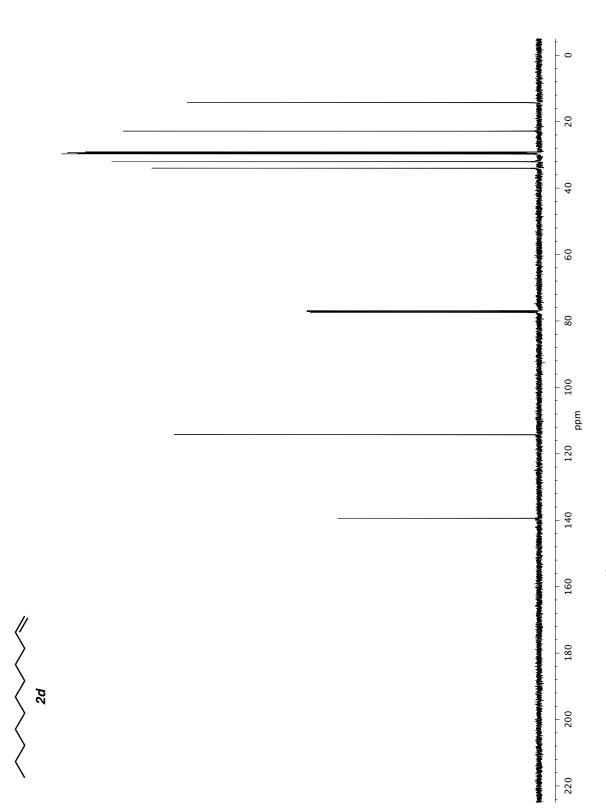




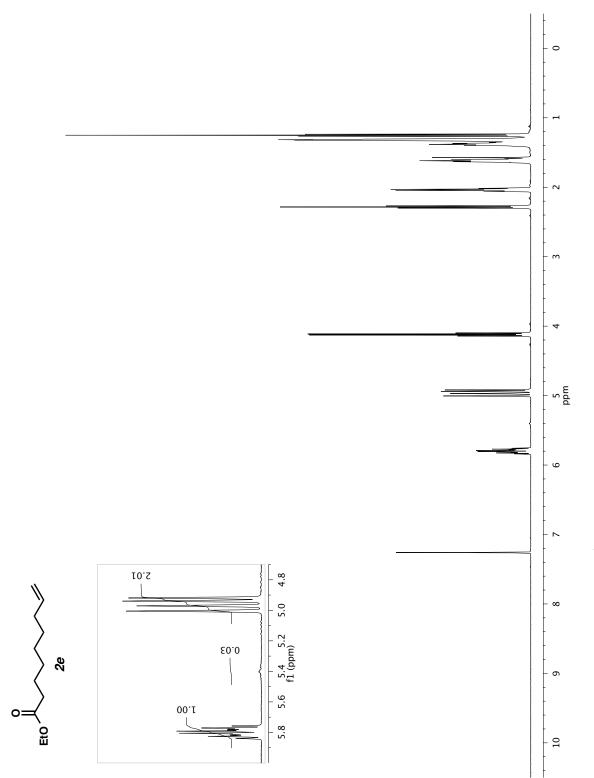


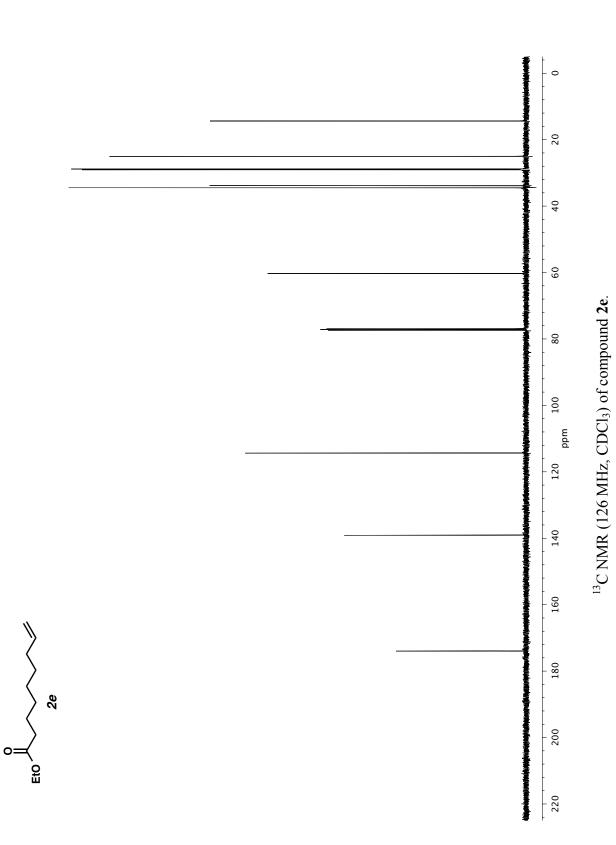


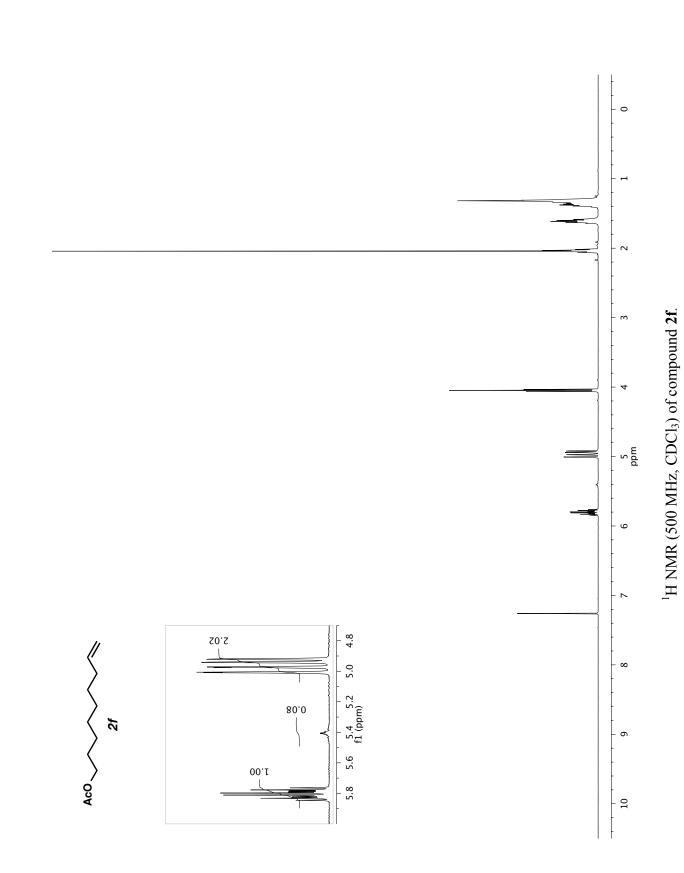


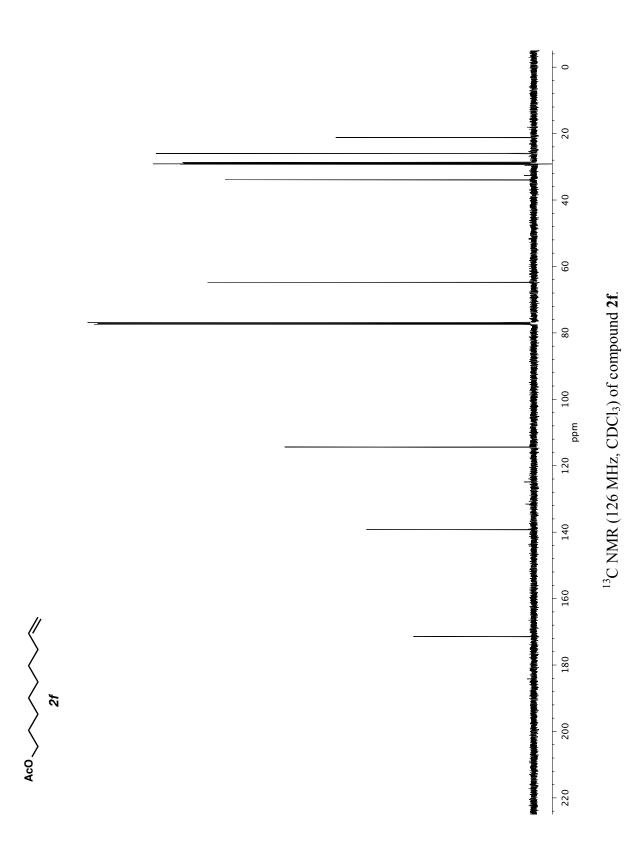




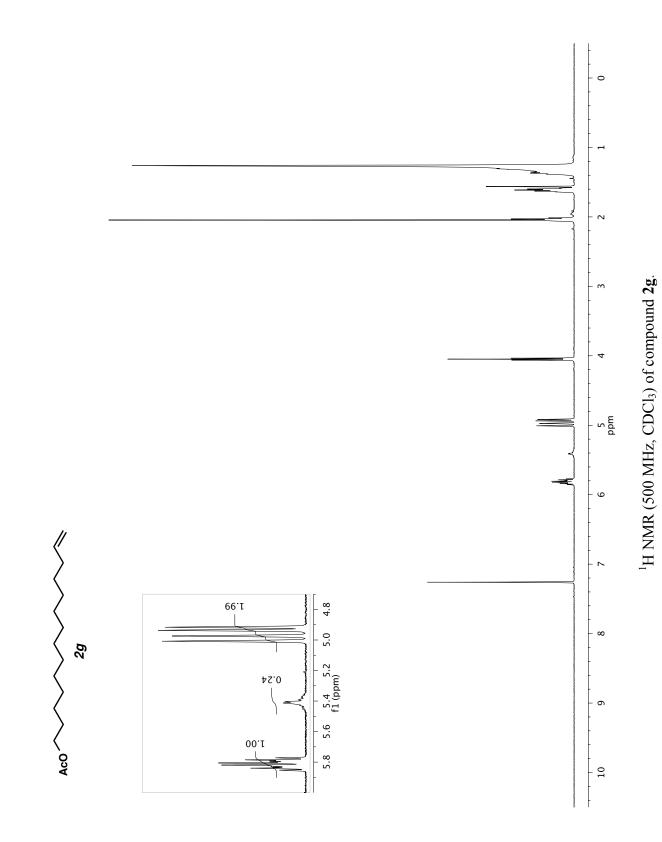


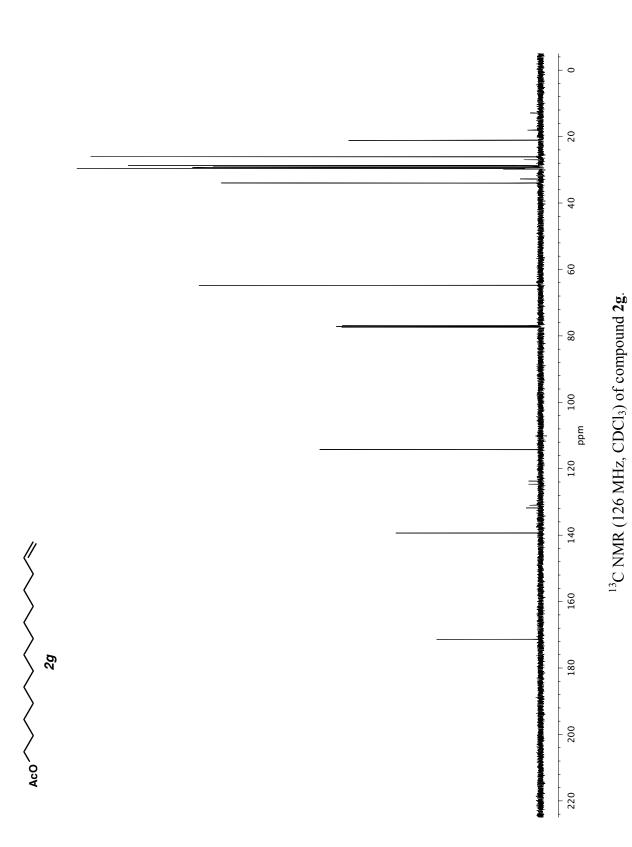


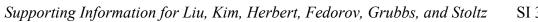




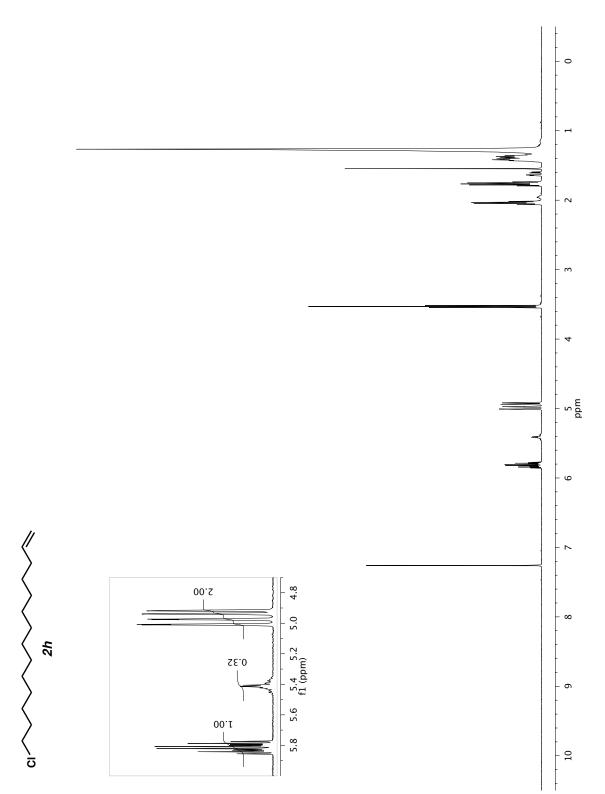
SI 35





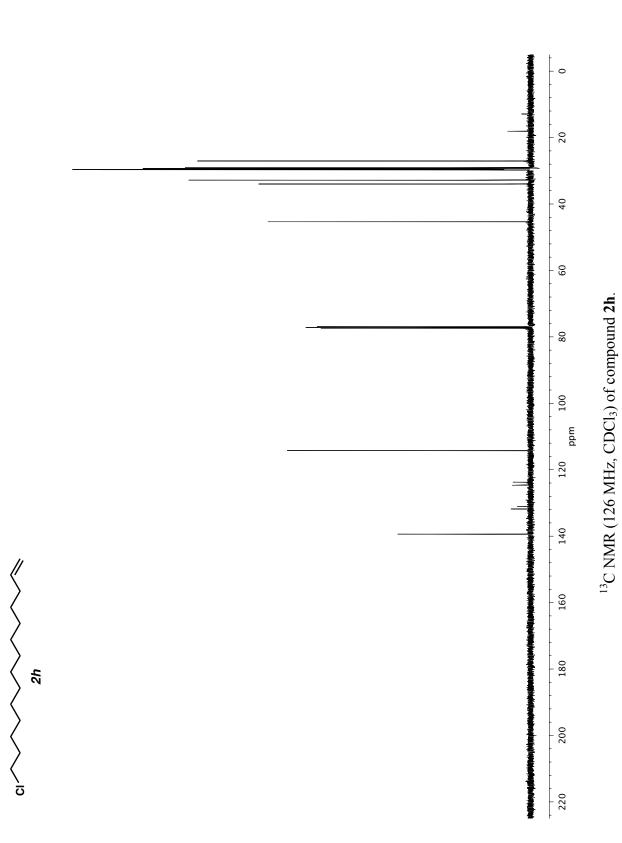


SI 37

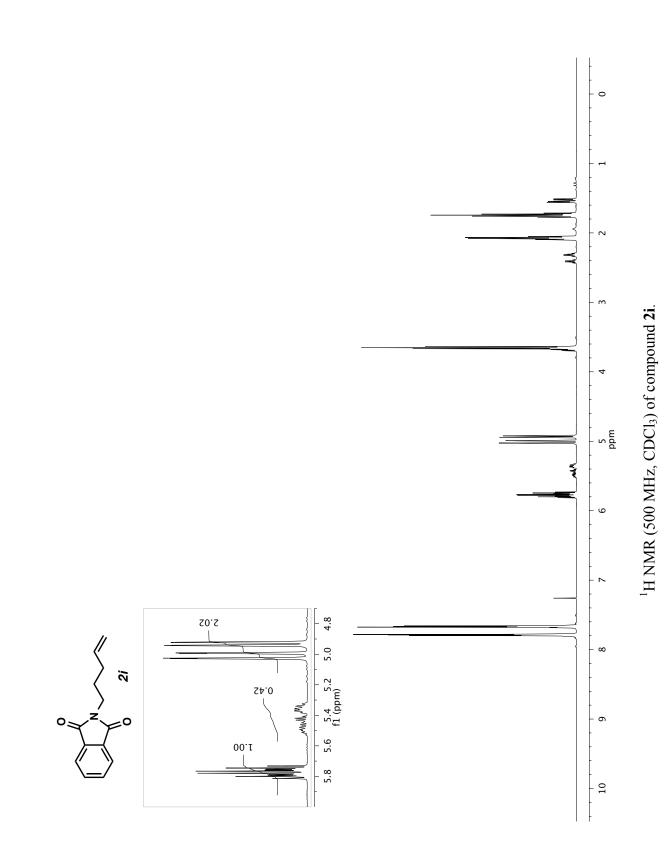


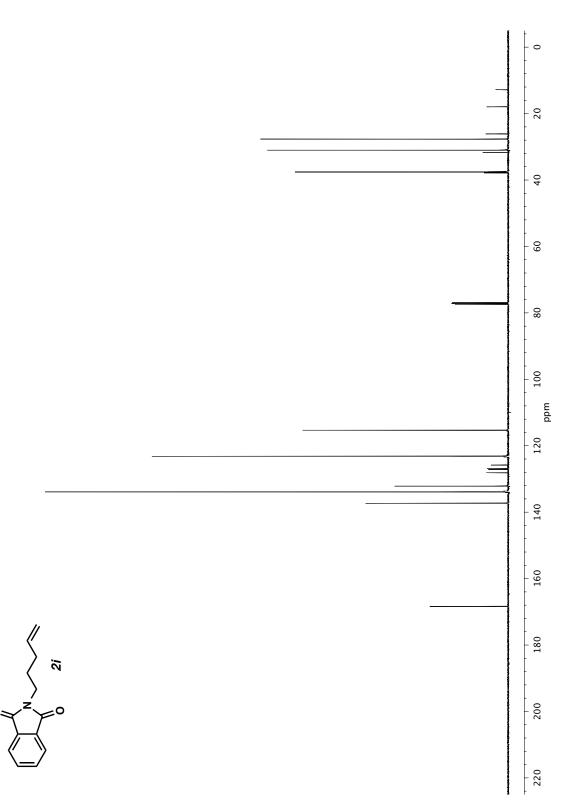


SI 38

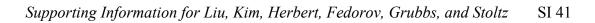


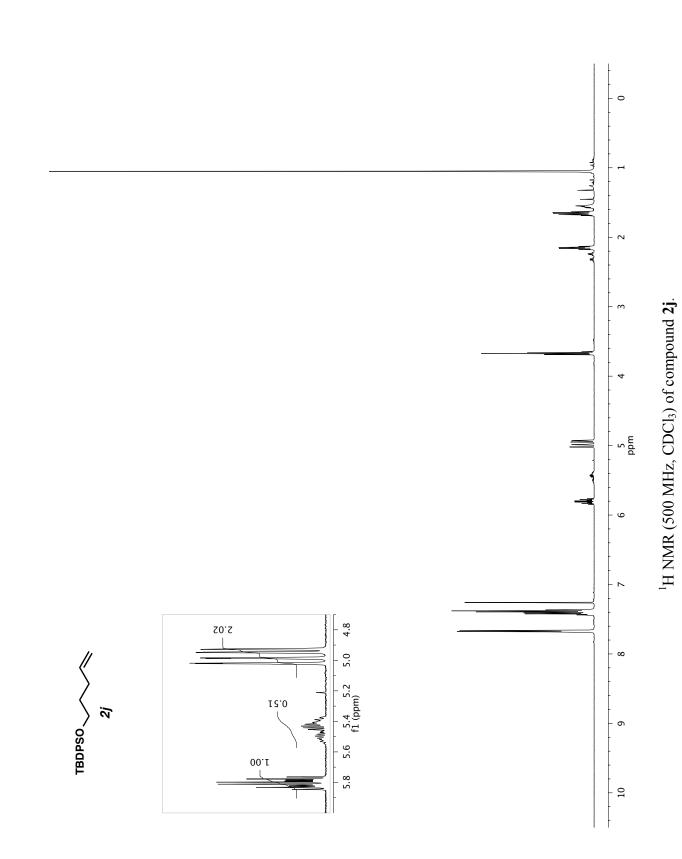
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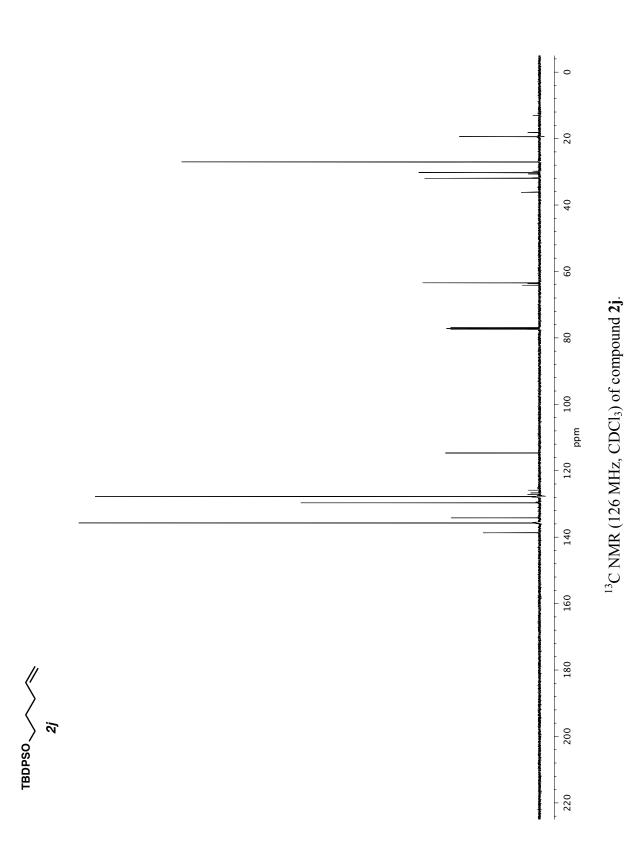


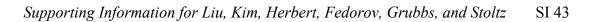


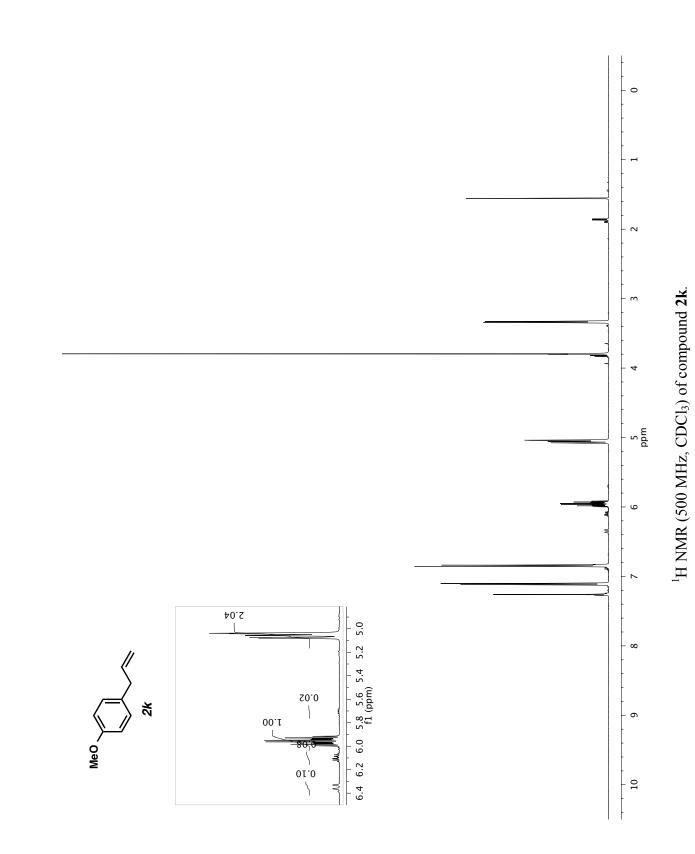
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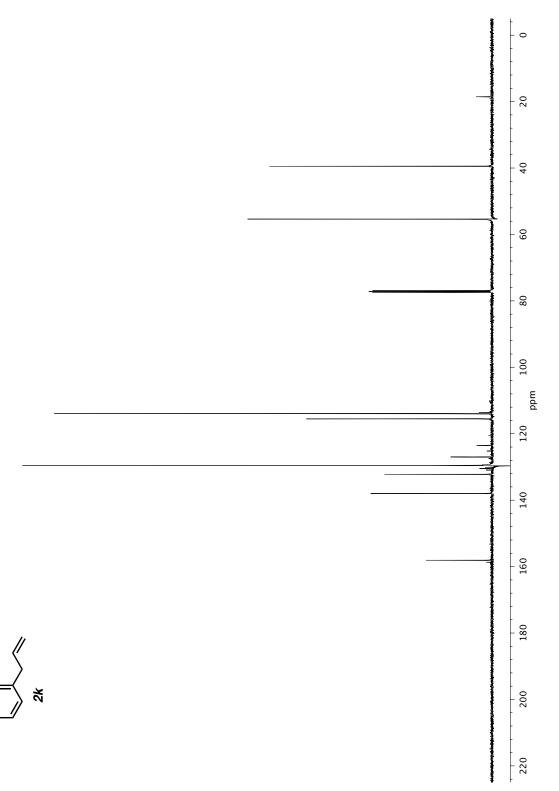






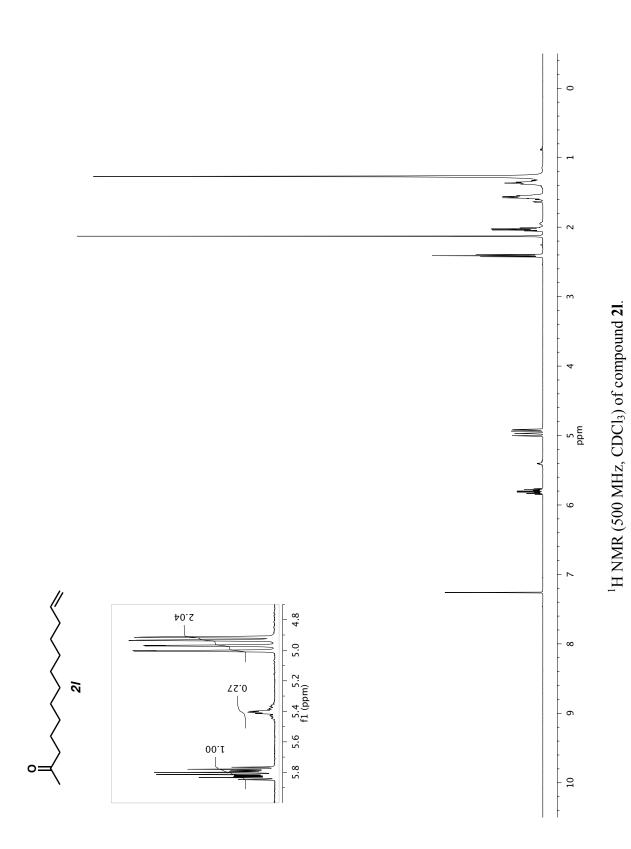


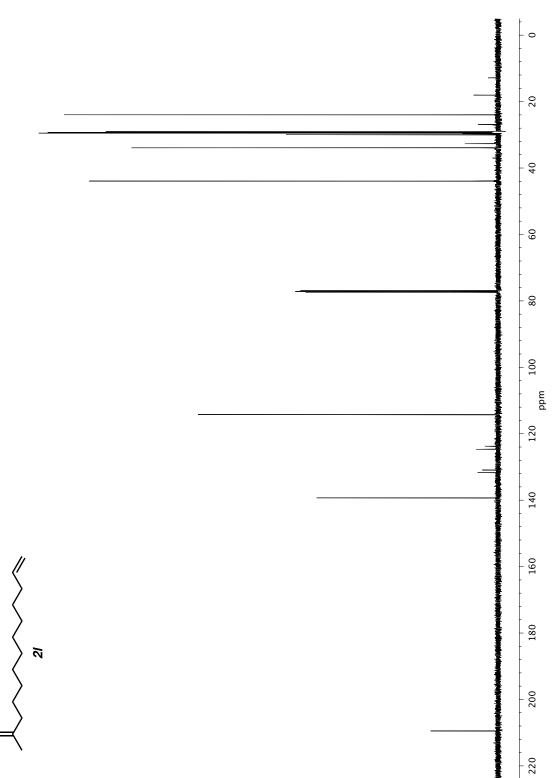




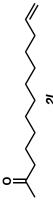
MeO,

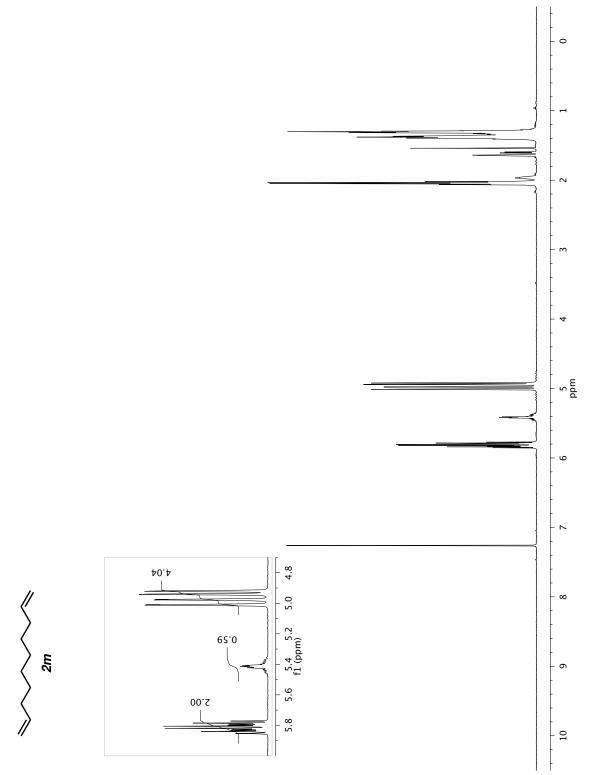




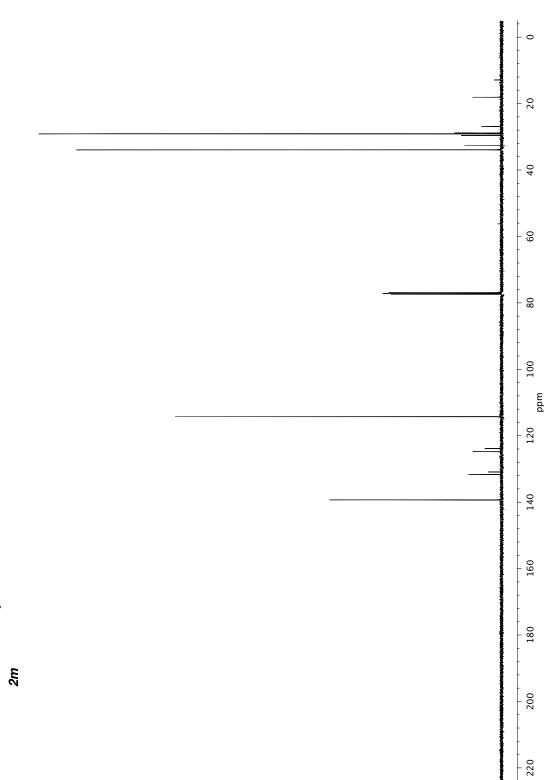


¹³C NMR (126 MHz, CDCl₃) of compound **21**.

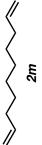


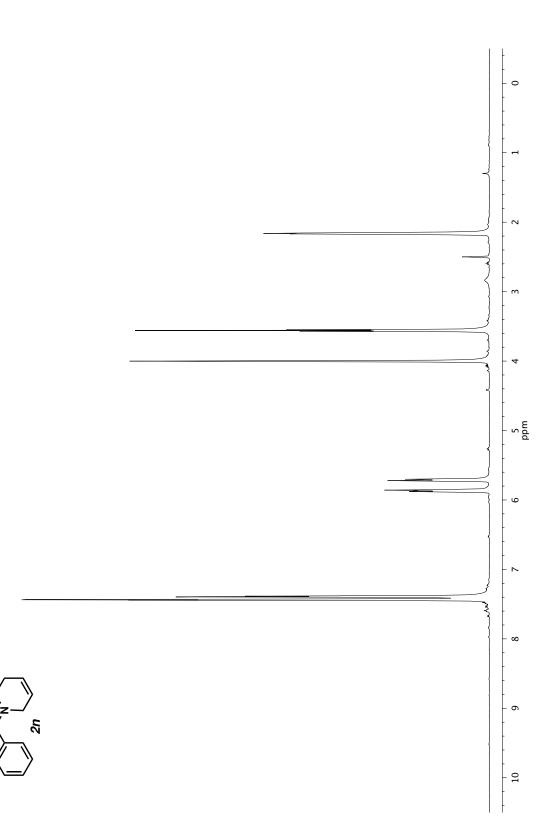






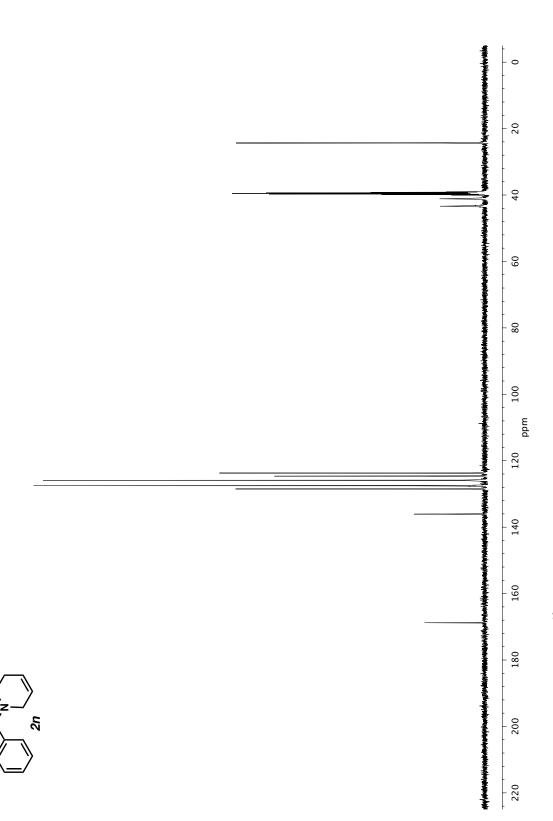
 ^{13}C NMR (126 MHz, CDCl₃) of compound **2m**.





0=

 1H NMR (500 MHz, DMSO-d₆, 130 °C) of compound 2n.



0=



