Electronic Supplementary Information for

Unique Site-Selectivity Control in Asymmetric Michael Addition of Azlactone to Alkenyl Dienyl Ketones Enabled by *P*-Spiro Chiral Iminophosphorane Catalysis

Ken Yoshioka[1], Kohei Yamada[1], Daisuke Uraguchi[1] and Takashi Ooi[1,2]

[1]Institute of Transformative Bio-Molecules (WPI-ITbM) and Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

[2]CREST, Japan Science and Technology Agency (JST), Nagoya University, Nagoya 464-8603, Japan

Correspondence and requests for materials should be addressed to T.O. (email: tooi@apchem.nagoya-u.ac.jp)

Table of Contents

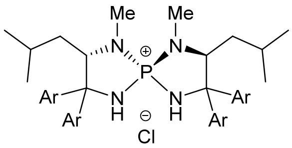
General Information: Infrared spectra were recorded on a Shimadzu IRAffinity-1 spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM-ECZ400S (400 MHz), JEOL JNM-ECA500II (500 MHz), or JEOL JNM-ECA600II (600 MHz). Chemical shifts are reported in ppm from the solvent resonance (CD_3OD; 3.31 ppm) or tetramethylsilane (0.0 ppm) resonance as the internal standard ($CDCl_3$). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL JNM-ECZ400S (101 MHz), JEOL JNM-ECA500II (126 MHz), or JEOL JNM-ECA600II (151 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard (CD_3OD; 49.0 ppm, $CDCl_3$; 77.16 ppm). ^{31}P NMR spectra were recorded on a JEOL JNM-ECZ400S (162 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from H_3PO_4 (0.0 ppm) resonance as the external standard. The high resolution mass spectra were conducted on Thermo Fisher Scientific Exactive. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm). Flash column chromatography was conducted on silica gel 60 (spherical, 40–50 μm; Kanto Chemical Co., Inc.), silica gel 60N (spherical, 40–50 μm; Kanto Chemical Co., Inc.), PSQ60AB (spherical, av. 55 μm; Fuji Silysia Chemical ltd.), and Silica gel 60 (Merck 1.09385.9929, 230–400 mesh). Recycling preparative HPLC was performed using YMC HPLC LC-forte/R equipped with a silica gel column (ϕ 20 mm x 250 mm, YMC-Pack SIL SL12S05-2520WT). Enantiomeric excesses were determined by HPLC analysis using chiral columns [ϕ 4.6 mm x 250 mm, DAICEL CHIRALPAK AZ-3 (AZ3), CHIRALCEL OD-3 (OD3), CHIRALCEL OZ-3 (OZ3), and CHIRALCEL OX-3 (OX3)] with hexane (H), 2-propanol (IPA), and ethanol (EtOH) as eluent.

Toluene, dichloromethane (CH_2Cl_2), 1,2-dichloroethane (DCE), diethyl ether (Et_2O), and tetrahydrofuran (THF) were supplied from Kanto Chemical Co., Inc. as "Dehydrated" and further purified by passing through neutral alumina under nitrogen atmosphere. Chiral tetraaminophosphonium salts **1**·HCl,[1] chiral triaminoimino-phosphoranes **1**,[1] azlactones **2**,[2] dienyl phenyl ketone **5**,[3] alkenyl phenyl ketone **6**[4] were prepared by following the literature procedure. Powdered molecular sieves 4A (MS4A) was supplied from Sigma-Aldrich. Other simple chemicals were purchased and used as such.

(1) D. Uraguchi, K. Yoshioka, Y. Ueki and T. Ooi, *J. Am. Chem. Soc.*, 2012, **134**, 19370–19373.
(2) J. C. Ruble and G. C. Fu, *J. Am. Chem. Soc.*, 1998, **120**, 11532–11533.
(3) X.-Y. Yang, W. W. Tay, Y. Li, S. A. Pullarkat and P.-H. Leung, *Organometallics*, 2015, **34**, 5196–5201.
(4) F. D. Therkelsen, A.-L. L. Hansen, E. B. Pedersen and C. Nielsen, *Org. Biomol. Chem.*, 2003, **1**, 2908–2918.

Experimental Section:

Characterization of Tetraaminophosphonium Salt 1f·HCl:

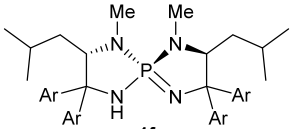


1f·HCl

(Ar = 4-FC_6H_4)

1f·HCl[1]**:** ^{1}H NMR (400 MHz, CD_3OD) δ 7.57 (4H, dd, $J_{H\text{-}H}$ = 8.7 Hz, $J_{F\text{-}H}$ = 5.0 Hz), 7.33 (4H, dd, $J_{H\text{-}H}$ = 8.7 Hz, $J_{F\text{-}H}$ = 5.5 Hz), 7.20 (4H, t, $J_{H\text{-}H}$ = $J_{F\text{-}H}$ = 8.7 Hz), 7.09 (4H, t, $J_{H\text{-}H}$ = $J_{F\text{-}H}$ = 8.7 Hz), 4.10 (2H, ddd, $J_{P\text{-}H}$ = 22.4 Hz, $J_{H\text{-}H}$ = 7.3, 4.6 Hz), 1.99 (6H, d, $J_{P\text{-}H}$ = 10.5 Hz), 1.42 (2H, ddd, J = 14.1, 7.3, 4.6 Hz), 1.26 (2H, ddd, J = 14.1, 7.3, 5.0 Hz), 0.81 (6H, d, J = 6.2 Hz), 0.64 (2H, m), 0.62 (6H, brs), N-H protons were not found due to deuterium exchange.

Characterization of Triaminoiminophosphorane 1f:

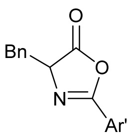


1f

(Ar = 4-FC_6H_4)

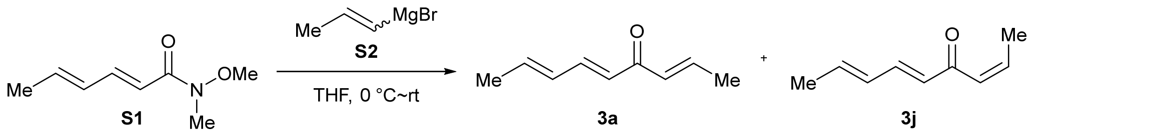
1f[1]**:** ^{1}H NMR (400 MHz, CD_3OD) δ 7.55 (4H, dd, $J_{H\text{-}H}$ = 8.8 Hz, $J_{F\text{-}H}$ = 5.0 Hz), 7.34 (4H, dd, $J_{H\text{-}H}$ = 8.8 Hz, $J_{F\text{-}H}$ = 5.5 Hz), 7.16 (4H, t, $J_{H\text{-}H}$ = $J_{F\text{-}H}$ = 8.8 Hz), 7.06 (4H, t, $J_{H\text{-}H}$ = $J_{F\text{-}H}$ = 8.8 Hz), 4.04 (2H, ddd, $J_{P\text{-}H}$ = 22.4 Hz, $J_{H\text{-}H}$ = 7.4, 4.9 Hz), 1.96 (6H, d, $J_{P\text{-}H}$ = 10.6 Hz), 1.39 (2H, ddd, J = 14.2, 7.4, 4.9 Hz), 1.24 (2H, ddd, J = 14.2, 7.4, 4.9 Hz), 0.80 (6H, d, J = 6.0 Hz), 0.63 (2H, m), 0.61 (6H, brs), N-H proton was not found due to deuterium exchange.

Characterization of Azlactone 2 (Ar' = 2,6-$(MeO)_2C_6H_3$):

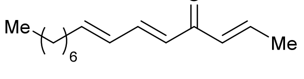


2[1]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (1H, t, J = 8.5 Hz), 7.32-7.21 (5H, m), 6.52 (2H, d, J = 8.5 Hz), 4.70 (1H, dd, J = 6.4, 5.1 Hz), 3.72 (6H, s), 3.39 (1H, dd, J = 14.2, 5.1 Hz), 3.24 (1H, dd, J = 14.2, 6.4 Hz).

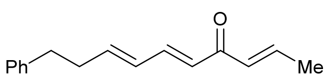
Preparation and Characterization of Alkenyl Dienyl Ketones 3:



The Weinreb amide **S1** was prepared by following the literature procedure.[5] To a solution of prop-1-en-1-ylmagnesium bromide (*cis*- and *trans*- mixture) **S2** in THF (1.0 M, 15.0 mL) was added a solution of **S1** (1.55 g, 10.0 mmol) in THF (3.0 mL) at 0 °C under argon (Ar) and this mixture was stirred at room temperature for 3 h. The reaction mixture was then poured into a saturated aqueous solution of NH_4Cl at 0 °C and extracted with ethyl acetate (EA) three times. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated. After preliminary purification of the crude material by column chromatography on silica gel (H/EA = 20:1~10:1 as eluent), futher purification by recycling preparative HPLC (H/EA = 10:1 as eluent) afforded **3a** in 20% yield (0.27 g, 2.0 mmol) and **3i** in 64% yield (0.87 g, 6.4 mmol), respectively. **3a:** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (1H, dd, J = 15.2, 9.6 Hz), 6.92 (1H, dq, J = 14.8, 7.1 Hz), 6.36 (1H, dq, J = 14.8, 1.3 Hz), 6.29 (1H, d, J = 15.2 Hz), 6.24 (1H, dd, J = 15.3, 9.6 Hz), 6.20 (1H, dq, J = 15.3, 6.2 Hz), 1.92 (3H, dd, J = 7.1, 1.3 Hz), 1.87 (3H, d, J = 6.2 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.7, 143.5, 142.7, 140.4, 130.9, 130.7, 126.4, 19.0, 18.5; IR (film): 3024, 2938, 2913, 2853, 1661, 1639, 1618, 1585, 1443, 1337, 1252, 1200, 1067, 997, 966 cm^{-1}; HRMS (ESI) Calcd for $C_9H_{12}O_5Na$ ($[M+Na]^+$) 159.0780. Found 159.0780.; **3j:** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (1H, dd, J = 15.4, 9.0 Hz), 6.33 (1H, dq, J = 11.9, 1.5 Hz), 6.25 (1H, dq, J = 11.9, 7.4 Hz), 6.23 (1H, dd, J = 15.1, 9.0 Hz), 6.18 (1H, dq, J = 15.1, 5.9 Hz), 6.13 (1H, d, J = 15.4 Hz), 2.11 (3H, dd, J = 7.4, 1.5 Hz), 1.87 (3H, d, J = 5.9 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.9, 143.4, 142.8, 140.3, 130.6, 129.5, 127.3, 19.0, 16.2; IR (film): 3026, 2913, 2849, 1655, 1638, 1616, 1589, 1441, 1327, 1209, 1069, 999 cm^{-1}; HRMS (ESI) Calcd for $C_9H_{13}O$ ($[M+H]^+$) 137.0961. Found 137.0962.



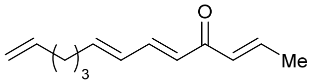
3b: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (1H, dd, J = 15.4, 9.4 Hz), 6.91 (1H, dq, J = 15.9, 6.9 Hz), 6.36 (1H, dq, J = 15.9, 1.8 Hz), 6.30 (1H, d, J = 15.4 Hz), 6.21 (1H, dd, J = 15.2, 9.4 Hz), 6.18 (1H, dt, J = 15.2, 7.0 Hz), 2.18 (2H, q, J = 7.0 Hz), 1.92 (3H, dd, J = 6.9, 1.8 Hz), 1.43 (2H, quin, J = 7.0 Hz), 1.35-1.21 (8H, m), 0.88 (3H, t, J = 6.6 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.7, 146.0, 143.7, 142.6, 130.8, 129.2, 126.5, 33.3, 31.9, 29.3, 29.2, 28.9, 22.8, 18.5, 14.2; IR (film): 3022, 2924, 2855, 1663, 1636, 1620, 1589, 1443, 1339, 1283, 1202, 1069, 999, 966 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{25}O$ ($[M+H]^+$) 221.1900. Found 221.1902.



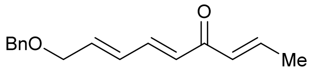
3c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (2H, t, J = 7.2 Hz), 7.25-7.14 (4H, m), 6.91 (1H, dq, J = 15.8, 6.9 Hz), 6.35 (1H, dq, J = 15.8, 1.7 Hz), 6.29 (1H, d, J = 15.2 Hz),

(5) (a) D. F. Netz and J. L. Seidel, *Tetrahedron Lett.*, 1992, **33**, 1957–1958; (b) C.-Y. Wu, T. Horibe, C. B. Jacobsen and F. D. Toste, *Nature*, 2015, **517**, 449–454.

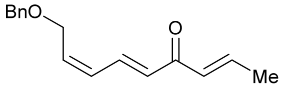
6.23 (1H, dd, J = 15.3, 9.0 Hz), 6.19 (1H, dt, J = 15.3, 6.1 Hz), 2.75 (2H, t, J = 7.6 Hz), 2.51 (2H, td, J = 7.6, 6.1 Hz), 1.91 (3H, dd, J = 6.9, 1.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.6, 144.2, 143.4, 142.8, 141.2, 130.9, 129.8, 128.6, 128.5, 127.0, 126.2, 35.2, 35.0, 18.5; IR (film): 3028, 2934, 2855, 1661, 1636, 1620, 1587, 1497, 1443, 1341, 1283, 1258, 1204, 1070, 1001, 968 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{18}ONa$ ([M+Na]$^+$) 249.1250. Found 249.1250.



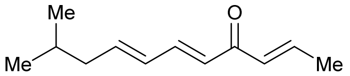
3d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (1H, dd, J = 15.2, 9.3 Hz), 6.91 (1H, dq, J = 15.5, 6.9 Hz), 6.36 (1H, dq, J = 15.5, 1.4 Hz), 6.30 (1H, d, J = 15.2 Hz), 6.22 (1H, dd, J = 15.2, 9.3 Hz), 6.17 (1H, dt, J = 15.2, 7.1 Hz), 5.79 (1H, ddt, J = 16.5, 10.6, 7.1 Hz), 5.01 (1H, dd, J = 16.5, 1.3 Hz), 4.97 (1H, dd, J = 10.6, 1.3 Hz), 2.20 (2H, q, J = 7.1 Hz), 2.08 (2H, q, J = 7.1 Hz), 1.92 (3H, dd, J = 6.9, 1.4 Hz), 1.54 (1H, quin, J = 7.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.5, 145.2, 143.5, 142.6, 138.3, 130.8, 129.4, 126.7, 115.0, 33.2, 32.5, 28.0, 18.4; IR (film): 3076, 2928, 2857, 1661, 1636, 1620, 1587, 1441, 1341, 1281, 1252, 1202, 1070, 997, 966, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{18}ONa$ ([M+Na]$^+$) 213.1250. Found 213.1248.



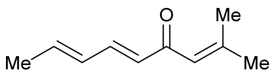
3e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.28 (5H, m), 7.25 (1H, dd, J = 16.3, 10.5 Hz), 6.93 (1H, dq, J = 15.6, 6.9 Hz), 6.46 (1H, dd, J = 15.2, 10.5 Hz), 6.40 (1H, d, J = 16.3 Hz), 6.36 (1H, dq, J = 15.6, 1.7 Hz), 6.23 (1H, dt, J = 15.2, 5.3 Hz), 4.55 (2H, s), 4.15 (2H, d, J = 5.3 Hz), 1.93 (3H, dd, J = 6.9, 1.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.5, 143.2, 142.2, 139.5, 138.1, 130.9, 130.0, 128.6, 128.5, 127.9_3, 127.8_9, 72.8, 69.9, 18.6; IR (film): 3032, 2911, 2851, 1661, 1641, 1622, 1591, 1443, 1335, 1312, 1238, 1198, 1113, 1072, 1001, 968 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{18}O_2Na$ ([M+Na]$^+$) 265.1199. Found 265.1197.



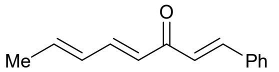
***Z*-3e:** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (1H, dd, J = 15.2, 11.5 Hz), 7.38-7.31 (4H, m), 7.29 (1H, tt, J = 8.7, 4.3 Hz), 6.93 (1H, dq, J = 15.3, 6.9 Hz), 6.41 (1H, d, J = 15.2 Hz), 6.32 (1H, dq, J = 15.3, 1.2 Hz), 6.27 (1H, t, J = 11.5 Hz), 6.01 (1H, dt, J = 11.5, 6.0 Hz), 4.53 (2H, s), 4.30 (2H, d, J = 6.0 Hz), 1.91 (3H, d, J = 6.9 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.2, 143.4, 137.9, 136.9, 136.8, 130.8, 129.7, 129.2, 128.5, 127.9, 127.8, 72.7, 66.1, 18.5; IR (film): 3028, 2909, 2855, 1661, 1634, 1614, 1585, 1441, 1335, 1283, 1196, 1072, 966 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{18}O_2Na$ ([M+Na]$^+$) 265.1199. Found 265.1195.



3f: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (1H, dd, J = 15.6, 9.6 Hz), 6.92 (1H, dq, J = 15.2, 7.3 Hz), 6.37 (1H, dq, J = 15.2, 1.5 Hz), 6.31 (1H, d, J = 15.6 Hz), 6.21 (1H, dd, J = 14.7, 9.6 Hz), 6.17 (1H, dt, J = 14.7, 6.6 Hz), 2.08 (2H, t, J = 6.6 Hz), 1.92 (3H, dd, J = 7.3, 1.5 Hz), 1.72 (1H, septet, J = 6.4 Hz), 0.91 (6H, d, J = 6.4 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.7, 144.7, 143.6, 142.7, 130.8, 130.3, 126.6, 42.6, 28.5, 22.5, 18.5; IR (film): 2955, 2870, 1663, 1636, 1618, 1589, 1443, 1358, 1331, 1277, 1200, 1070, 1001, 964 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{18}ONa$ ([M+Na]$^+$) 201.1250. Found 201.1247.

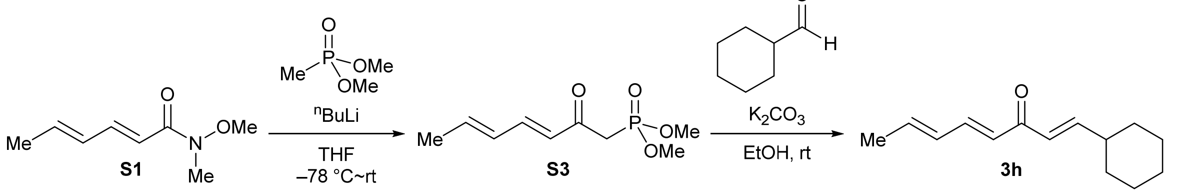


3k: (2-Methylprop-1-en-1-yl)magnesium bromide was used instead of **S2**; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 (1H, dd, J = 15.2, 9.8 Hz), 6.22 (1H, s), 6.21 (1H, dd, J = 15.1, 9.8 Hz), 6.16 (1H, dq, J = 15.1, 6.1 Hz), 6.11 (1H, d, J = 15.2 Hz), 2.17 (3H, s), 1.92 (3H, s), 1.86 (3H, d, J = 6.1 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.9, 155.4, 142.5, 139.6, 130.7, 129.9, 123.6, 27.9, 21.1, 18.9; IR (film): 3026, 2972, 2913, 1636, 1616, 1589, 1445, 1325, 1236, 1105, 1043, 999 cm^{-1}; HRMS (ESI) Calcd for $C_{10}H_{14}ONa$ ([M+Na]$^+$) 173.0937. Found 173.0937.



3i: Styrylmagnesium bromide was used instead of **S2**; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (1H, d, J = 16.5 Hz), 7.61-7.55 (2H, m), 7.43-7.36 (3H, m), 7.33 (1H, dd, J = 15.0, 9.3 Hz), 6.98 (1H, d, J = 16.5 Hz), 6.42 (1H, d, J = 15.0 Hz), 6.29 (1H, dd, J = 14.7, 9.3 Hz), 6.25 (1H, dq, J = 14.7, 6.0 Hz), 1.90 (3H, d, J = 6.0 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.5, 143.9, 142.8, 140.9, 135.1, 130.7, 130.5, 129.1, 128.4, 127.0, 125.6, 19.0; IR (film): 3026, 2911, 1653, 1632, 1611, 1585, 1449, 1341, 1198, 1098, 1072, 999 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{14}ONa$ ([M+Na]$^+$) 221.0937. Found 221.0937.

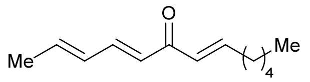
Preparation and Characterization of Alkenyl Dienyl Ketones 3f and 3g:



The synthesis of **3h** was performed by modifying the reported procedure.[6] To a solution of dimethyl methylphosphonate (1.66 mL, 15.4 mmol) in THF (28.0 mL) was added ^{n}BuLi (1.64 M in ^{n}hexane, 9.39 mL, 15.4

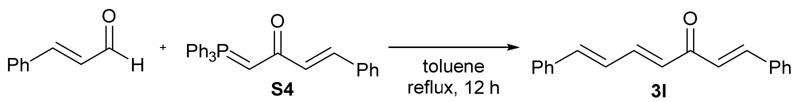
(6) A. C. Silvanus, B. J. Groombridge, B. I. Andrews, G. Kociok-Köhn and D. R. Carbery, *J. Org. Chem.*, 2010, **75**, 7491–7493.

mmol) dropwise at –78 °C. After being stirred for 1 h, a solution of **S1** (2.17 g, 14 mmol) in THF (5.0 mL) was introduced slowly into the flask, and the whole reaction mixture was warmed up to room temperature over 2 h. The reaction was quenched with a saturated aqueous solution of NH_4Cl and extracted with EA three times. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography on silica gel (100% EA as eluent) to afford **S3** as a pale yellow oil (2.27 g, 10.4 mmol, 74%). **S3:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (1H, dd, J = 15.9, 9.5 Hz), 6.29 (1H, dq, J = 15.1, 6.1 Hz), 6.23 (1H, dd, J = 15.1, 9.5 Hz), 6.20 (1H, d, J = 15.9 Hz), 3.78 (6H, d, $J_{P\text{-}H}$ = 11.6 Hz), 3.23 (2H, d, $J_{P\text{-}H}$ = 22.8 Hz), 1.89 (3H, d, J = 6.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9 (d, $J_{P\text{-}C}$ = 5.8 Hz), 145.3, 142.1, 130.0, 127.0, 52.9 (d, $J_{P\text{-}C}$ = 6.8 Hz), 39.3 (d, $J_{P\text{-}C}$ = 129.7 Hz), 18.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.8; IR (film): 3001, 2957, 2853, 1682, 1659, 1634, 1591, 1447, 1246, 1182, 1020 cm^{-1}; HRMS (ESI) Calcd for $C_9H_{15}O_4NaP$ ([M+Na]$^+$) 241.0600. Found 241.0598.; A solution of **S3** (0.96 g, 4.4 mmol) in EtOH (20 mL) was treated with K_2CO_3 (0.58 g, 4.2 mmol) at room temperature for 30 min. Cyclohexanecarboxaldehyde (0.48 mL, 4.0 mmol) was added dropwise to the suspension and the resulting mixture was stirred for a further 4 h. The reaction was quenched with a saturated aqueous solution of NH_4Cl and extracted with EA three times. The combined organic phases were washed with brine and dried over Na_2SO_4. After concentration, the crude residue was purified by column chromatography on silica gel (H/EA = 10:1 as eluent) to afford **3h** as a colorless solid (0.31 g, 1.52 mmol, 38%). **3h:** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (1H, dd, J = 15.2, 10.0 Hz), 6.84 (1H, dd, J = 16.0, 7.1 Hz), 6.31 (1H, d, J = 15.2 Hz), 6.27 (1H, d, J = 16.0 Hz), 6.24 (1H, dd, J = 14.8, 10.0 Hz), 6.19 (1H, dq, J = 14.8, 6.2 Hz), 2.17 (1H, tdt, J = 10.9, 7.1, 3.5 Hz), 1.87 (3H, d, J = 6.2 Hz), 1.82-1.73 (4H, m), 1.72-1.65 (1H, m), 1.36-1.26 (2H, m), 1.24-1.12 (3H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.2, 152.6, 143.4, 140.3, 130.7, 126.9, 126.5, 40.9, 32.0, 26.1, 25.9, 19.0; IR (film): 3026, 2924, 2851, 1659, 1638, 1618, 1587, 1449, 1339, 1252, 1063, 999 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{20}ONa$ ([M+Na]$^+$) 227.1406. Found 227.1408.

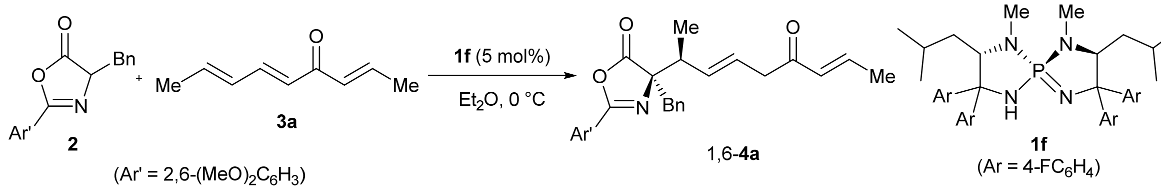


3g: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (1H, dd, J = 15.0, 9.3 Hz), 6.91 (1H, dt, J = 15.4, 7.1 Hz), 6.32 (1H, d, J = 15.4 Hz), 6.31 (1H, d, J = 15.0 Hz), 6.24 (1H, dd, J = 15.4, 9.3 Hz), 6.20 (1H, dq, J = 15.4, 6.0 Hz), 2.24 (2H, q, J = 7.1 Hz), 1.87 (3H, d, J = 6.0 Hz), 1.48 (2H, quin, J = 7.1 Hz), 1.39-1.25 (4H, m), 0.90 (3H, d, J = 6.9 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.9, 147.9, 143.5, 140.4, 130.7, 129.3, 126.5, 32.8, 31.5, 28.0, 22.6, 19.0, 14.1; IR (film): 3030, 2959, 2930, 2859, 1661, 1639, 1620, 1589, 1341, 1252, 1001 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{20}ONa$ ([M+Na]$^+$) 215.1406. Found 215.1405.

Preparation and Characterization of Alkenyl Dienyl Ketone 3k:



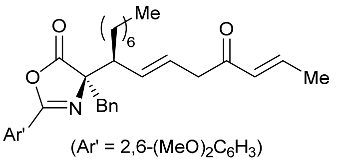
The Wittig reagent **S4** was prepared by using the literature procedure.7 To a suspension of **S4** (1.79 g, 4.4 mmol) in toluene (13.0 mL) was added *trans*-cinnamaldehyde (0.50 mL, 4.0 mmol) at room temperature and the reaction mixture was stirred for 12 h under reflux. The mixture was cooled to room temperature and concentrated. The crude residue was purified by silica gel chromatography (H/EA = 10/1 as eluent), and the product was futher purified by recrystallization from a H/EA solvent system to afford **3l** as a yellow solid in 50% yield (0.52 g, 2.0 mmol). **3l:** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (1H, d, J = 15.6 Hz), 7.64-7.57 (2H, m), 7.53 (1H, dd, J = 15.3, 9.6 Hz), 7.50 (2H, d, J = 9.0 Hz), 7.44-7.39 (3H, m), 7.38 (2H, t, J = 7.5 Hz), 7.33 (1H, t, J = 7.5 Hz), 7.02$_4$ (1H, d, J = 15.6 Hz), 7.01$_5$ (1H, d, J = 15.0 Hz), 6.97 (1H, dd, J = 15.0, 9.6 Hz), 6.64 (1H, d, J = 15.3 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.1, 143.5, 143.1, 141.8, 136.3, 135.0, 130.6, 129.4, 129.1, 129.0, 128.5, 127.4, 127.1, 125.6, one carbon atom was not found probably due to overlapping.; IR (film): 3057, 3026, 1647, 1612, 1578, 1449, 1352, 1188, 1084, 999 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{16}ONa$ ([M+Na]$^+$) 283.1093. Found 283.1092.



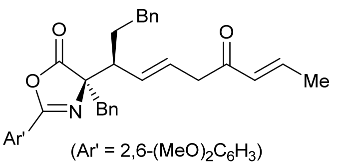
Representative Procedure for Asymmetric 1,6-Addition of Azlactone 2 to Alkenyl Dienyl Ketone 3 with Chiral Iminophosphorane 1f as a Catalyst: Azlactone **2** (31.1 mg, 0.10 mmol) and alkenyl dienyl ketone **3a** (15.0 mg, 0.11 mmol) was dissolved into Et_2O (1.0 mL) under Ar atmosphere. Chiral iminophosphorane **1f** (3.40 mg, 5.0 μmol) was added slowly as a solid at 0 °C and the resulting reaction mixture was stirred for 3 h. The reaction was

(7) (a) H. Kusama, Y. Karibe, R. Imai, Y. Onizawa, H. Yamabe and N. Iwasawa, *Chem. Eur. J.*, 2011, **17**, 4839–4848; (b) K. S. Babu, X.-C. Li, M. R. Jacob, Q. Zhang, S. I. Khan, D. Ferreira and A. M. Clark, *J. Med. Chem.*, 2006, **49**, 7877–7886.

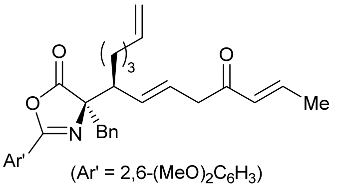
quenched by the addition of a solution of trifluoroacetic acid in toluene (0.5 M, 50.0 μL) and all volatiles were removed by evaporation to give the crude residue. The regio- and diastereomeric ratio of **4a** was determined by ^{1}H NMR analysis of it. Subsequent purification by column chromatography on silica gel (H/EA = 1:1 as eluent) gave the adducts in 86% yield as a mixture of isomers (38.5 mg, 0.086 mmol). The enantiomeric excess of 1,6-**4a** was determined by HPLC analysis on chiral stationary phase. 1,6-**4a:** HPLC AZ3, H/EtOH = 10:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 13.2 min (minor isomer of major diastereomer), 15.7 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer *δ* 7.30 (1H, t, *J* = 8.7 Hz), 7.26-7.16 (5H, m), 6.88 (1H, dq, *J* = 15.8, 6.8 Hz), 6.48 (2H, d, *J* = 8.7 Hz), 6.15 (1H, dq, *J* = 15.8, 1.8 Hz), 5.83 (1H, dt, *J* = 15.4, 6.0 Hz), 5.76 (1H, dd, *J* = 15.4, 8.2 Hz), 3.64 (6H, s), 3.36 (1H, dd, *J* = 15.7, 6.0 Hz), 3.31 (1H, dd, *J* = 15.7, 6.0 Hz), 3.29 (1H, d, *J* = 13.4 Hz), 3.06 (1H, d, *J* = 13.4 Hz), 2.82 (1H, dq, *J* = 8.2, 7.0 Hz), 1.87 (3H, dd, *J* = 6.8, 1.8 Hz), 1.12 (3H, d, *J* = 7.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer *δ* 197.9, 180.4, 159.2, 157.7, 143.4, 135.1, 134.3, 132.8, 131.4, 130.8, 128.0, 126.8, 125.9, 105.9, 103.7, 77.7, 55.9, 44.9, 44.1, 42.1, 18.4, 15.7; IR (film): 3030, 2967, 2938, 2841, 1805, 1670, 1595, 1476, 1456, 1433, 1302, 1258, 1113, 961 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{30}NO_5$ ([M+H]$^+$) 448.2118. Found 448.2109.



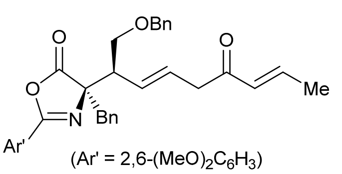
1,6-**4b:** HPLC OZ3, H/EtOH = 10:1, flow rate = 1.0 mL/min, rt, λ = 210 nm, 7.68 min (major isomer of major diastereomer), 8.19 min (minor isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer *δ* 7.29 (1H, t, *J* = 8.4 Hz), 7.26-7.14 (5H, m), 6.88 (1H, dq, *J* = 15.8, 6.8 Hz), 6.47 (2H, d, *J* = 8.4 Hz), 6.16 (1H, dq, *J* = 15.8, 1.5 Hz), 5.79 (1H, dt, *J* = 15.4. 6.7 Hz), 5.63 (1H, dd, *J* = 15.4, 10.0 Hz), 3.63 (6H, s), 3.38 (1H, ddd, *J* = 16.2, 6.7, 1.5 Hz), 3.33 (1H, ddd, *J* = 16.2, 6.7, 1.5 Hz), 3.30 (1H, d, *J* = 13.2 Hz), 3.02 (1H, d, *J* = 13.2 Hz), 2.59 (1H, td, *J* = 10.0, 2.2 Hz), 1.88 (3H, dd, *J* = 6.8, 1.5 Hz), 1.56-1.38 (1H, m), 1.38-1.08 (12H, m), 0.87 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer *δ* 197.8, 180.7, 159.2, 157.5, 143.3, 135.0, 133.0, 132.8, 131.3, 130.8, 128.0, 127.5, 126.7, 105.9, 103.6, 77.9, 55.8, 51.0, 44.3, 42.3, 32.0, 29.7, 29.3, 27.5, 22.8, 18.4, 14.2, one carbon atom was not found probably due to overlapping.; IR (film): 3032, 2926, 2855, 1805, 1672, 1595, 1476, 1456, 1433, 1300, 1258, 1113, 1032, 961, 910 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{42}NO_5$ ([M+H]$^+$) 532.3057. Found 532.3055.



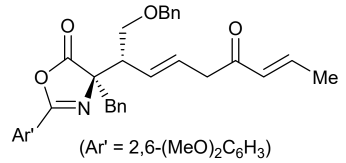
1,6-**4c:** HPLC AZ3, H/IPA = 10:1, flow rate = 1.0 mL/min, rt, λ = 254 nm, 29.5 min (minor isomer of major diastereomer), 35.0 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer *δ* 7.30-7.11 (11H, m), 6.91 (1H, dq, *J* = 15.7, 7.0 Hz), 6.42 (2H, t, *J* = 8.8 Hz), 6.19 (1H, dq, *J* = 15.7, 1.7 Hz), 5.85 (1H, dt, *J* = 15.6, 6.8 Hz), 5.71 (1H, dd, *J* = 15.6, 9.6 Hz), 3.44 (6H, s), 3.42 (1H, ddd, *J* = 16.4, 6.8, 1.6 Hz), 3.38 (1H, ddd, *J* = 16.4, 6.8, 1.6 Hz), 3.31 (1H, d, *J* = 13.6 Hz), 3.02 (1H, d, *J* = 13.6 Hz), 2.74-2.63 (2H, m), 2.49 (1H, ddd, *J* = 13.7, 10.7, 7.0 Hz), 1.89 (3H, dd, *J* = 7.0, 1.7 Hz), 1.77 (1H, dtd, *J* = 13.6, 7.0, 4.5 Hz), 1.63 (1H, dddd, *J* = 13.6, 10.7, 6.5, 3.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer *δ* 197.7, 180.6, 159.1, 157.8, 143.4, 142.2, 134.9, 132.7, 132.6, 131.4, 130.8, 128.6, 128.4, 128.3, 128.0, 126.8, 125.9, 105.8, 103.5, 77.8, 55.6, 50.8, 44.2, 42.3, 33.7. 32.1, 18.4; IR (film): 3028, 2938, 2839, 1805, 1672, 1595, 1476, 1454, 1433, 1298, 1258, 1113, 961, 910 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{36}NO_5$ ([M+H]$^+$) 538.2588. Found 538.2585.



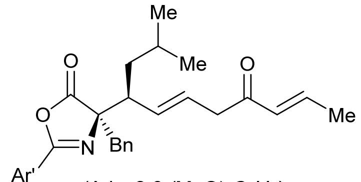
1,6-**4d:** HPLC OZ3, H/IPA = 10:1, flow rate = 1.0 mL/min, rt, λ = 254 nm, 13.1 min (minor isomer of major diastereomer), 15.9 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer *δ* 7.30 (1H, t, *J* = 8.7 Hz), 7.26-7.14 (5H, m), 6.89 (1H, dq, *J* = 15.3, 7.0 Hz), 6.47 (2H, d, *J* = 8.7 Hz), 6.16 (1H, dq, *J* = 15.3, 1.2 Hz), 5.80 (1H, dt, *J* = 15.4, 6.8 Hz), 5.78 (1H, ddt, *J* = 17.0, 10.2, 6.8 Hz), 5.63 (1H, dd, *J* = 15.4, 10.4 Hz), 5.00 (1H, d, *J* = 17.0 Hz), 4.93 (1H, d, *J* = 10.2 Hz), 3.63 (6H, s), 3.38 (1H, dd, *J* = 17.3, 6.8 Hz), 3.34 (1H, dd, *J* = 17.3, 6.8 Hz), 3.31 (1H, d, *J* = 13.6 Hz), 3.02 (1H, d, *J* = 13.6 Hz), 2.61 (1H, td, *J* = 10.2, 2.0 Hz), 2.08 (1H, dq, *J* = 14.2, 6.8 Hz), 1.98 (1H, dq, *J* = 14.2, 6.8 Hz), 1.88 (3H, dd, *J* = 7.0, 1.2 Hz), 1.59-1.39 (2H, m), 1.39-1.23 (2H, m); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer *δ* 197.7, 180.6, 159.2, 157.5, 143.3, 138.6, 134.9, 132.7_9, 132.7_6, 131.3, 130.8, 128.0, 127.7, 126.7, 114.6, 105.8, 103.6, 77.8, 55.8, 50.9, 44.2, 42.3, 33.7, 29.2, 26.9, 18.3; IR (film): 3030, 2936, 2839, 1805, 1672, 1595, 1476, 1456, 1433, 1298, 1258, 1113, 961, 887 cm^{-1}; HRMS (ESI) Calcd for $C_{31}H_{36}NO_5$ ([M+H]$^+$) 502.2588. Found 502.2583.



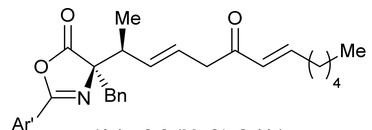
1,6-**4e:** The absolute configuration of 1,6-**4e** was determined by comparison of HPLC retention time to that of the configurationary identified 1,6-**4e** which synthesized by treating the previously reported 1,6-adduct of **2** to dienyl *N*-acyl pyrrole with **S2**.[1]; HPLC AZ3, H/EtOH = 10:1, flow rate = 1.0 mL/min, rt, λ = 190 nm, 54.4 min (minor isomer of major diastereomer), 66.1 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer *δ* 7.29 (1H, t, *J* = 8.4 Hz), 7.27-7.24 (4H, m), 7.24-7.15 (6H, m), 6.88 (1H, dq, *J* = 15.8, 6.8 Hz), 6.47 (2H, d, *J* = 8.4 Hz), 6.15 (1H, dq, *J* = 15.8, 1.5 Hz), 5.95 (1H, dt, *J* = 15.7, 6.9 Hz), 5.74 (1H, dd, *J* = 15.7, 9.6 Hz), 4.49 (1H, d, *J* = 11.8 Hz), 4.39 (1H, d, J = 11.8 Hz), 3.66 (1H, t, J = 9.6 Hz), 3.58 (6H, s), 3.46 (1H, dd, J = 9.6, 5.7 Hz), 3.39 (1H, ddd, J = 16.4, 6.9, 1.2 Hz), 3.33 (1H, ddd, J = 16.4, 6.9, 1.2 Hz), 3.30 (1H, d, J = 13.2 Hz), 3.23 (1H, td, J = 9.6, 5.7 Hz), 3.01 (1H, d, J = 13.2 Hz), 1.87 (3H, dd, J = 6.8, 1.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer δ 197.5, 179.9, 159.3, 158.3, 143.5, 138.2, 134.4, 132.8, 131.3, 131.1, 129.6, 128.8, 128.3, 127.9, 127.4, 127.3, 126.8, 105.9, 103.6, 74.3, 72.8, 70.3, 55.8, 50.6, 44.1, 42.4, 18.4; IR (film): 3030, 2938, 2839, 1809, 1667, 1595, 1476, 1454, 1433, 1298, 1256, 1111, 959, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{36}NO_6$ ([M+H]$^+$) 554.2537. Found 554.2525.


(Ar' = 2,6-$(MeO)_2C_6H_3$)

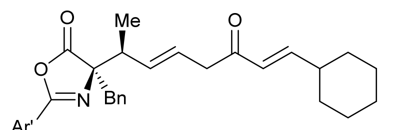
epi-1,6-**4e:** HPLC OZ3, H/EtOH = 19:1, flow rate = 1.0 mL/min, rt, λ = 230 nm, 37.4 min (minor isomer of major diastereomer), 41.0 min (major isomer of major diastereomer); ^{1}H NMR (600 MHz, $CDCl_3$) major diastereomer δ 7.40-7.16 (11H, m), 6.90 (1H, dq, J = 15.6, 6.8 Hz), 6.48 (2H, d, J = 7.8 Hz), 6.16 (1H, dq, J = 15.6, 1.6 Hz), 6.13 (1H, dd, J = 15.8, 9.9 Hz), 5.86 (1H, dt, J = 15.8, 6.8 Hz), 4.54 (1H, d, J = 11.7 Hz), 4.41 (1H, d, J = 11.7 Hz), 3.85 (1H, dd, J = 8.8, 4.0 Hz), 3.68 (1H, dd, J = 8.8, 4.0 Hz), 3.61 (6H, s), 3.42 (1H, ddd, J = 16.0, 6.8, 1.3 Hz), 3.34 (1H, ddd, J = 16.0, 6.8, 1.3 Hz), 3.28 (1H, d, J = 13.5 Hz), 3.20 (1H, d, J = 13.5 Hz), 2.96 (1H, dt, J = 9.9, 4.0 Hz), 1.85 (3H, dd, J = 6.8, 1.6 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) major diastereomer δ 198.0, 179.0, 159.3, 157.9, 143.7, 138.4, 134.7, 132.8, 131.3, 131.0, 130.4, 128.4, 128.0, 127.8, 127.4, 127.2, 126.8, 105.7, 103.6, 74.4, 73.1, 70.7, 55.9, 50.8, 44.4, 42.6, 18.4; IR (film): 3032, 2938, 2839, 1805, 1668, 1593, 1476, 1454, 1433, 1298, 1256, 1111, 959, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{36}NO_6$ ([M+H]$^+$) 554.2537. Found 554.2531.


(Ar' = 2,6-$(MeO)_2C_6H_3$)

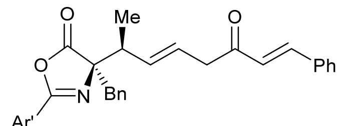
1,6-**4f:** HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, rt, λ = 210 nm, 9.50 min (minor isomer of major diastereomer), 26.7 min (major isomer of major diastereomer); ^{1}H NMR (500 MHz, $CDCl_3$) major diastereomer δ 7.30 (1H, t, J = 8.3 Hz), 7.25-7.20 (3H, m), 7.19-7.16 (2H, m), 6.89 (1H, dq, J = 16.1, 7.0 Hz), 6.47 (2H, d, J = 8.3 Hz), 6.16 (1H, dq, J = 16.1, 1.5 Hz), 5.81 (1H, dt, J = 15.4. 7.5 Hz), 5.61 (1H, dd, J = 15.4, 10.9 Hz), 3.63 (6H, s), 3.39 (1H, dd, J = 16.1, 7.5 Hz), 3.34 (1H, dd, J = 16.1, 7.5 Hz), 3.32 (1H, d, J = 14.0 Hz), 3.03 (1H, d, J = 14.0 Hz), 2.72 (1H, td, J = 10.9, 2.4 Hz), 1.88 (3H, dd, J = 7.0, 1.5 Hz), 1.61-1.53 (2H, m), 0.95 (1H, ddd, J = 13.8, 10.9, 2.4 Hz), 0.90 (3H, d, J = 6.5 Hz), 0.87 (3H, d, J = 6.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) major diastereomer δ 197.9, 180.6, 159.2, 157.6, 143.5, 135.0, 132.9, 132.8, 131.3, 130.8, 128.0, 127.4, 126.8, 105.8, 103.6, 77.9, 55.8, 48.8, 44.3, 42.3, 38.7, 25.0, 24.4, 20.7, 18.4; IR (film): 2955, 2934, 2841, 1805, 1672, 1595, 1476, 1433, 1298, 1260, 1115, 962 cm^{-1}; HRMS (ESI) Calcd for $C_{30}H_{36}NO_5$ ([M+H]$^+$) 490.2588. Found 490.2583.


(Ar' = 2,6-$(MeO)_2C_6H_3$)

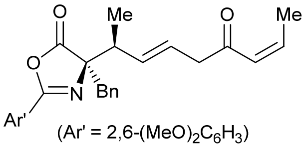
1,6-**4g:** HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, rt, λ = 254 nm, 16.7 min (minor isomer of major diastereomer), 23.9 min (major isomer of major diastereomer); ^{1}H NMR (600 MHz, $CDCl_3$) major diastereomer δ 7.30 (1H, t, J = 8.6 Hz), 7.25-7.16 (5H, m), 6.87 (1H, dt, J = 15.7, 7.1 Hz), 6.48 (2H, d, J = 8.6 Hz), 6.13 (1H, d, J = 15.7 Hz), 5.83 (1H, dt, J = 15.6, 6.5 Hz), 5.76 (1H, dd, J = 15.6, 9.0 Hz), 3.64 (6H, s), 3.36 (1H, dd, J = 16.5, 6.5 Hz), 3.32 (1H, dd, J = 16.5, 6.5 Hz), 3.29 (1H, d, J = 13.8 Hz), 3.06 (1H, d, J = 13.8 Hz), 2.82 (1H, dq, J = 9.0, 6.8 Hz), 2.19 (2H, q, J = 7.1 Hz), 1.44 (2H, quin, J = 7.1 Hz), 1.34-1.20 (4H, m), 1.11 (3H, d, J = 6.8 Hz), 0.87 (3H, t, J = 6.9 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) major diastereomer δ 198.2, 180.4, 159.2, 157.6, 148.5, 135.1, 134.3, 132.8, 130.8, 129.7, 128.0, 126.8, 125.9, 105.9, 103.6, 77.7, 55.9, 44.9, 44.2, 42.1, 32.6, 31.5, 27.9, 22.5, 15.8, 14.1; IR (film): 3013, 2930, 2874, 1805, 1674, 1626, 1595, 1477, 1456, 1433, 1304, 1258, 1115, 962 cm^{-1}; HRMS (ESI) Calcd for $C_{31}H_{38}NO_5$ ([M+H]$^+$) 504.2744. Found 504.2743.


(Ar' = 2,6-$(MeO)_2C_6H_3$)

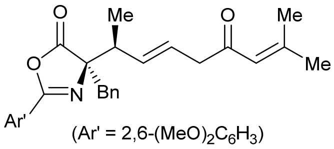
1,6-**4h:** HPLC AZ3, H/EtOH = 94:6, flow rate = 1.0 mL/min, rt, λ = 210 nm, 20.9 min (minor isomer of major diastereomer), 26.7 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 7.30 (1H, t, J = 8.7 Hz), 7.26-7.16 (5H, m), 6.80 (1H, dd, J = 15.8, 6.8 Hz), 6.48 (2H, d, J = 8.7 Hz), 6.08 (1H, dd, J = 15.8, 1.4 Hz), 5.83 (1H, dt, J = 15.7, 5.9 Hz), 5.76 (1H, dd, J = 15.7, 8.0 Hz), 3.63 (6H, s), 3.37 (1H, dd, J = 15.9, 5.9 Hz), 3.31 (1H, dd, J = 15.9, 5.9 Hz), 3.29 (1H, d, J = 13.8 Hz), 3.06 (1H, d, J = 13.8 Hz), 2.82 (1H, dq, J = 8.0, 6.8 Hz), 2.11 (1H, tdtd, J = 10.9, 6.8, 3.3, 1.4 Hz), 1.80-1.59 (5H, m), 1.34-1.05 (5H, m), 1.11 (3H, d, J = 6.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer δ 198.5, 180.4, 159.2, 157.6, 153.2, 135.0, 134.3, 132.8, 130.7, 128.0, 127.1, 126.7, 126.0, 105.9, 103.6, 77.7, 55.9, 44.9, 44.3, 42.1, 40.7, 31.8, 26.0, 25.8, 15.8; IR (film): 3032, 2924, 2851, 1805, 1672, 1595, 1476, 1454, 1433, 1302, 1258, 1113, 961 cm^{-1}; HRMS (ESI) Calcd for $C_{32}H_{38}NO_5$ ([M+H]$^+$) 516.2744. Found 516.2743.


(Ar' = 2,6-$(MeO)_2C_6H_3$)

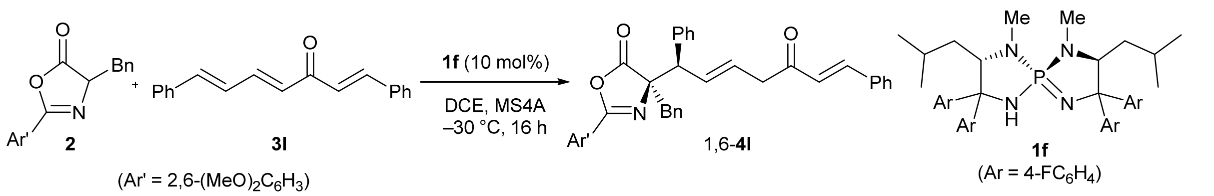
1,6-**4i:** HPLC OX3, H/EtOH = 10:1, flow rate = 1.0 mL/min, rt, λ = 254 nm, 32.8 min (minor isomer of major diastereomer), 35.7 min (major isomer of major diastereomer); ^{1}H NMR (500 MHz, $CDCl_3$) major diastereomer δ 7.58 (1H, d, J = 16.3 Hz), 7.52 (2H, d, J = 8.0 Hz), 7.41-7.31 (3H, m), 7.29 (1H, t, J = 8.3 Hz), 7.25-7.14 (5H, m), 6.79 (1H, d, J = 16.3 Hz), 6.47 (2H, d, J = 8.3 Hz), 5.89 (1H, dt, J = 15.6, 5.7 Hz), 5.84 (1H, dd, J = 15.6, 7.3 Hz), 3.63 (6H, s), 3.49 (1H, dd, J = 16.1, 5.7 Hz), 3.45 (1H, dd, J = 16.1, 5.7 Hz), 3.32 (1H, d, J = 13.3 Hz), 3.09 (1H, d, J = 13.3 Hz), 2.85 (1H, quin, J = 7.3 Hz), 1.14 (3H, d, J = 7.3 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) major diastereomer δ 197.9, 180.4, 159.2, 157.6, 143.2, 135.0, 134.7, 134.5, 132.8, 130.8, 130.6, 129.0, 128.5, 128.0, 126.8, 125.7, 125.4, 105.8, 103.6, 77.7, 55.9, 45.1, 44.8, 42.1, 15.7; IR (film): 3030, 2968, 2936, 2839, 1805, 1672, 1595, 1476, 1454, 1433, 1304, 1258, 1113, 961 cm^{-1}; HRMS (ESI) Calcd for $C_{32}H_{31}NO_5Na$ ([M+Na]$^+$) 532.2094. Found 532.2098.



1,6-**4j:** HPLC OZ3, H/IPA = 10:1, flow rate = 1.0 mL/min, rt, λ = 210 nm, 8.5 min (minor isomer of major diastereomer), 9.7 min (major isomer of major diastereomer); ^{1}H NMR (600 MHz, CDCl$_3$) major diastereomer δ 7.30 (1H, t, J = 8.6 Hz), 7.25-7.17 (5H, m), 6.48 (2H, d, J = 8.6 Hz), 6.22 (1H, dq, J = 10.5, 5.4 Hz), 6.20 (1H, d, J = 10.5 Hz), 5.81 (1H, dt, J = 15.6, 6.5 Hz), 5.76 (1H, dd, J = 15.6, 8.7 Hz), 3.62 (6H, s), 3.30 (1H, d, J = 13.2 Hz), 3.27 (1H, dd, J = 17.2, 6.5 Hz), 3.23 (1H, dd, J = 17.2, 6.5 Hz), 3.07 (1H, d, J = 13.2 Hz), 2.83 (1H, dq, J = 8.7, 6.6 Hz), 2.11 (3H, d, J = 5.4 Hz), 1.12 (3H, d, J = 6.6 Hz); ^{13}C NMR (151 MHz, CDCl$_3$) major diastereomer δ 199.3, 180.5, 159.3, 157.7, 144.0, 135.1, 134.6, 132.8, 130.8, 128.1, 127.1, 126.8, 125.7, 105.9, 103.6, 77.7, 55.9, 48.0, 45.0, 42.1, 16.1, 15.8; IR (film): 3028, 2968, 2936, 2841, 1805, 1676, 1595, 1477, 1456, 1433, 1304, 1258, 1113, 961 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{30}NO_5$ ([M+H]$^+$) 448.2118. Found 448.2130.

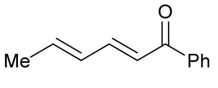


1,6-**4k:** HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 254 nm, rt, 15.7 min (minor isomer of major diastereomer), 23.1 min (major isomer of major diastereomer); ^{1}H NMR (600 MHz, CDCl$_3$) major diastereomer δ 7.30 (1H, t, J = 8.8 Hz), 7.25-7.16 (5H, m), 6.47 (2H, d, J = 8.8 Hz), 6.11 (1H, s), 5.82 (1H, dt, J = 15.6. 6.6 Hz), 5.74 (1H, dd, J = 15.6, 9.0 Hz), 3.63 (6H, s), 3.53 (1H, d, J = 13.8 Hz), 3.23 (1H, dd, J = 16.2, 6.6 Hz), 3.18 (1H, dd, J = 16.2, 6.6 Hz), 3.07 (1H, d, J = 13.8 Hz), 2.82 (1H, dq, J = 9.0, 6.7 Hz), 2.13 (3H, s), 1.86 (3H, s), 1.12 (3H, d, J = 6.7 Hz); ^{13}C NMR (151 MHz, CDCl$_3$) major diastereomer δ 198.5, 180.5, 159.2, 157.6, 156.3, 135.2, 134.2, 132.8, 130.8, 128.0, 126.8, 126.2, 123.2, 105.9, 103.6, 77.8, 55.9, 48.2, 44.9, 42.1, 27.8, 20.9, 15.8; IR (film): 3030, 2970, 2936, 2839, 1805, 1680, 1595, 1477, 1456, 1433, 1304, 1258, 1115, 961 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{32}NO_5$ ([M+H]$^+$) 462.2275. Found 462.2261.



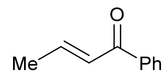
Procedure for Asymmetric 1,6-Addition of Azlactone 2 to Alkenyl Dienyl Ketone 3l with Chiral Iminophosphorane 1f as a Catalyst: A test tube was charged with a magnetic stirrer bar and molecular sieves 4Å (MS4A, 100.0 mg) under argon atmosphere. MS4A was then dried with a heat gun under reduced pressure for 5 min and the test tube was refilled with argon. Azlactone **2** (62.3 mg, 0.20 mmol) and alkenyl dienyl ketone **3l** (26.0 mg, 0.10 mmol) were added to the test tube, and dissolved in DCE (0.50 mL). After cooling to –30 °C, chiral iminophosphorane **1f** was added slowly as a solid and the reaction mixture was stirred for 16 h. A solution of trifluoroacetic acid in toluene (0.5 M, 50 μL) was then introduced to the reaction mixture to quench the reaction. The whole mixture was passed through a pad of Celite with the aid of toluene to remove MS4A and the filtrate was concentrated. The regio- and diastereomeric ratio of adducts were determined by ^{1}H NMR analysis (600 MHz). Subsequent purification by colomn chromatography on silica gel (H/EA = 1:1 as eluent) gave the adduct in 64% yield as a mixture of isomers. The enantiomeric excess of 1,6-**4l** was determined by HPLC analysis. 1,6-**4l:** HPLC OD3, H/EtOH = 10:1, flow rate = 1.0 mL/min, rt, λ = 300 nm, 34.9 min (major isomer of major diastereomer), 53.6 min (minor isomer of major diastereomer); ^{1}H NMR (600 MHz, CDCl$_3$) major diastereomer δ 7.54 (1H, d, J = 15.9 Hz), 7.46 (2H, d, J = 7.2 Hz), 7.40 (2H, d, J = 7.2 Hz), 7.38-7.29 (4H, m), 7.28-7.24 (4H, m), 7.24-7.15 (6H, m), 6.75 (1H, d, J = 15.9 Hz), 6.40 (2H, d, J = 9.0 Hz), 6.35 (1H, dd, J = 15.0, 9.8 Hz), 5.97 (1H, dt, J = 15.0, 6.8 Hz), 3.97 (1H, d, J = 9.8 Hz), 3.57 (6H, s), 3.51 (1H, dd, J = 17.0, 6.8 Hz), 3.45$_4$ (1H, dd, J = 17.0, 6.8 Hz), 3.44$_7$ (1H, d, J = 13.8 Hz), 3.17 (1H, d, J = 13.8 Hz); ^{13}C NMR (151 MHz, CDCl$_3$) major diastereomer δ 197.6, 179.1, 159.4, 158.0, 143.2, 138.4, 134.7, 134.5, 132.9, 132.2, 130.9, 130.6, 129.6, 129.0, 128.5, 128.3, 127.9, 127.4, 127.3, 126.9, 125.3, 105.1, 103.5, 78.2, 56.2, 55.9, 45.3, 42.9; IR (film): 3030, 2936, 2839, 1805, 1661, 1595, 1476, 1454, 1431, 1300, 1256, 1113, 964, 907 cm^{-1}; HRMS (ESI) Calcd for $C_{37}H_{34}NO_5$ ([M+H]$^+$) 572.2431. Found 572.2427.

Characterization of Dienyl Phenyl Ketone 5:

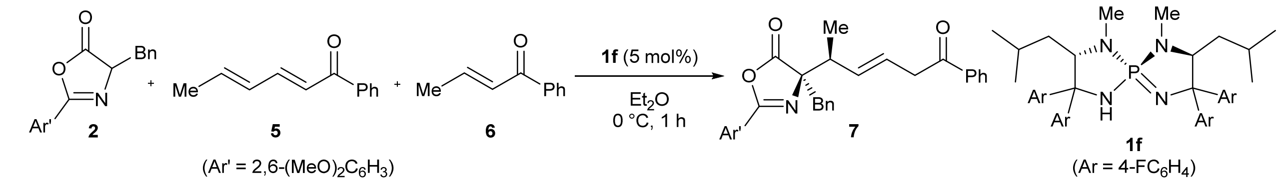


5: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.93 (2H, d, J = 7.3 Hz), 7.55 (1H, t, J = 7.3 Hz), 7.47 (2H, t, J = 7.3 Hz), 7.40 (1H, dd, J = 15.2, 10.6 Hz), 6.87 (1H, d, J = 15.2 Hz), 6.34 (1H, dd, J = 15.0, 10.6 Hz), 6.27 (1H, dq, J = 15.0, 6.5 Hz), 1.90 (3H, d, J = 6.5 Hz); ^{13}C NMR (151 MHz, CDCl$_3$) δ 191.1, 145.4, 141.2, 138.5, 132.6, 130.7, 128.7, 128.5, 123.5, 19.0; IR (film): 3024, 2911, 1661, 1630, 1587, 1447, 1341, 1256, 1015, 999 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{13}O$ ([M+H]$^+$) 173.0961. Found 173.0963.

Characterization of Alkenyl Phenyl Ketone 6:



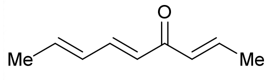
6[8]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (2H, d, J = 7.4 Hz), 7.55 (1H, t, J = 7.4 Hz), 7.46 (2H, t, J = 7.4 Hz), 7.07 (1H, dq, J = 15.4, 6.7 Hz), 6.91 (1H, dq, J = 15.4, 1.3 Hz), 2.00 (3H, dd, J = 6.7, 1.3 Hz).



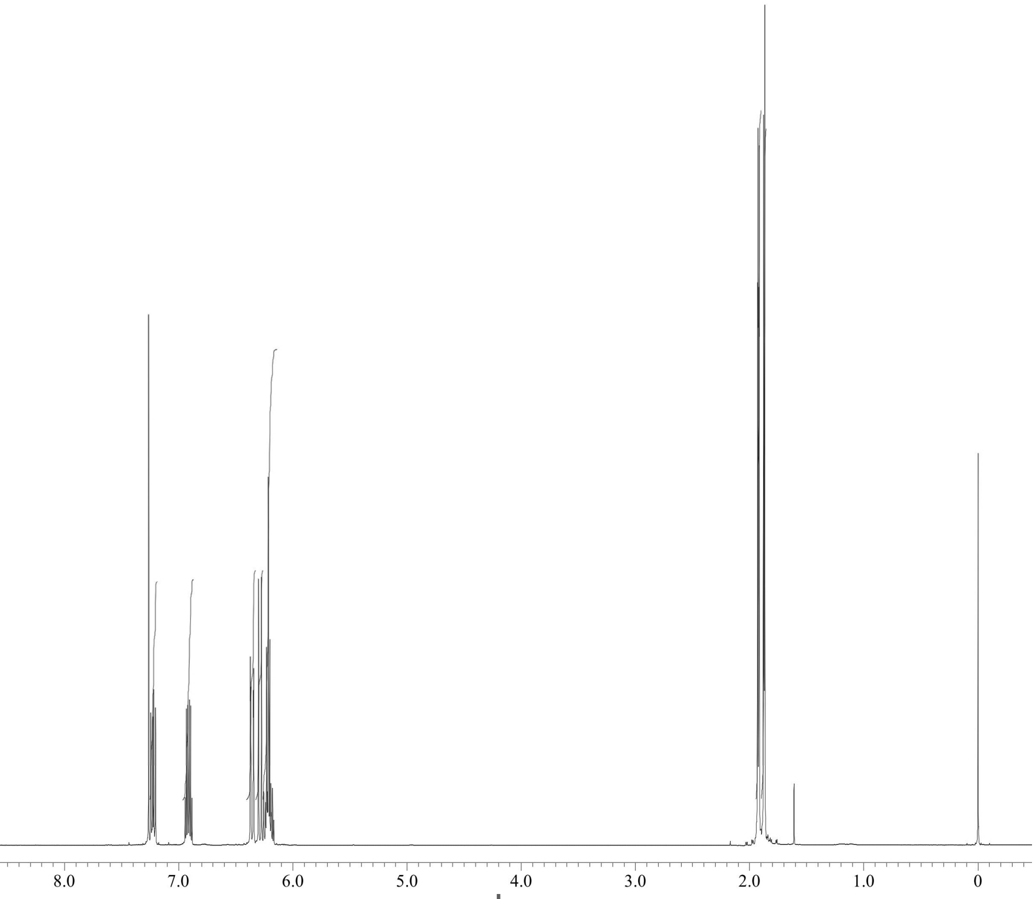
Procedure for Discriminative Asymmetric 1,6-Addition of Azlactone 2 to Dienyl Ketone 5 in the Presence of Enone 6 under the Catalysis of Chiral Iminophosphorane 1f: Azlactone **2** (31.1 mg, 0.10 mmol), 1-phenylhexa-2,4-dien-1-one **5** (19.0 mg, 0.11 mmol), and 1-phenylbut-2-en-1-one **6** (16.1 mg, 0.11 mmol) were dissolved into Et_2O (1.0 mL) under Ar atmosphere. Chiral iminophosphorane **1f** (3.40 mg, 5.0 μmol) was added slowly as a solid at 0 °C and the resulting reaction mixture was stirred for 1 h. The reaction was quenched by the addition of a solution of trifluoroacetic acid in toluene (0.5 M, 50.0 μL) and all volatiles were removed by evaporation to give the crude residue. The ratio of the adducts and the regio- and diastereomeric ratio of **7** were determined by ^{1}H NMR analysis (500 MHz) of it. Subsequent purification by column chromatography on silica gel (H/EA = 1:1 as eluent) gave the adduct in 93% yield as a mixture of isomers (45.0 mg, 0.093 mmol). The enantiomeric excess of **7** was determined by HPLC analysis. **7:** HPLC OX3, H/EtOH = 10:1, flow rate = 1.0 mL/min, rt, λ = 254 nm, 17.4 min (minor isomer of major diastereomer), 21.7 min (major isomer of major diastereomer); ^{1}H NMR (600 MHz, $CDCl_3$) major diastereomer δ 7.97 (2H, d, J = 7.8 Hz), 7.55 (1H, t, J = 7.8 Hz), 7.45 (2H, t, J = 7.8 Hz), 7.30 (1H, t, J = 8.2 Hz), 7.25-7.19 (3H, m), 7.18 (2H, d, J = 8.2 Hz), 6.47 (2H, d, J = 8.2 Hz), 5.96 (1H, dt, J = 15.4, 6.7 Hz), 5.84 (1H, dd, J = 15.4, 9.1 Hz), 3.82 (1H, dd, J = 16.9, 6.7 Hz), 3.78 (1H, dd, J = 16.9, 6.7 Hz), 3.63 (6H, s), 3.29 (1H, d, J = 13.8 Hz), 3.06 (2H, d, J = 13.8 Hz), 2.85 (1H, dq, J = 9.1, 6.8 Hz), 1.12 (3H, d, J = 6.8 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.2, 180.5, 159.2, 157.6, 136.7, 135.1, 134.4, 133.3, 132.8, 130.8, 128.7, 128.4, 128.0, 126.8, 125.9, 105.9, 103.6, 77.8, 55.9, 44.9, 42.5, 42.1, 15.8; IR (film): 3030, 2936, 2839, 1805, 1678, 1595, 1476, 1449, 1433, 1304, 1258, 1113, 961 cm^{-1}; HRMS (ESI) Calcd for $C_{30}H_{30}NO_5$ ($[M+H]^+$) 484.2118. Found 484.2112.

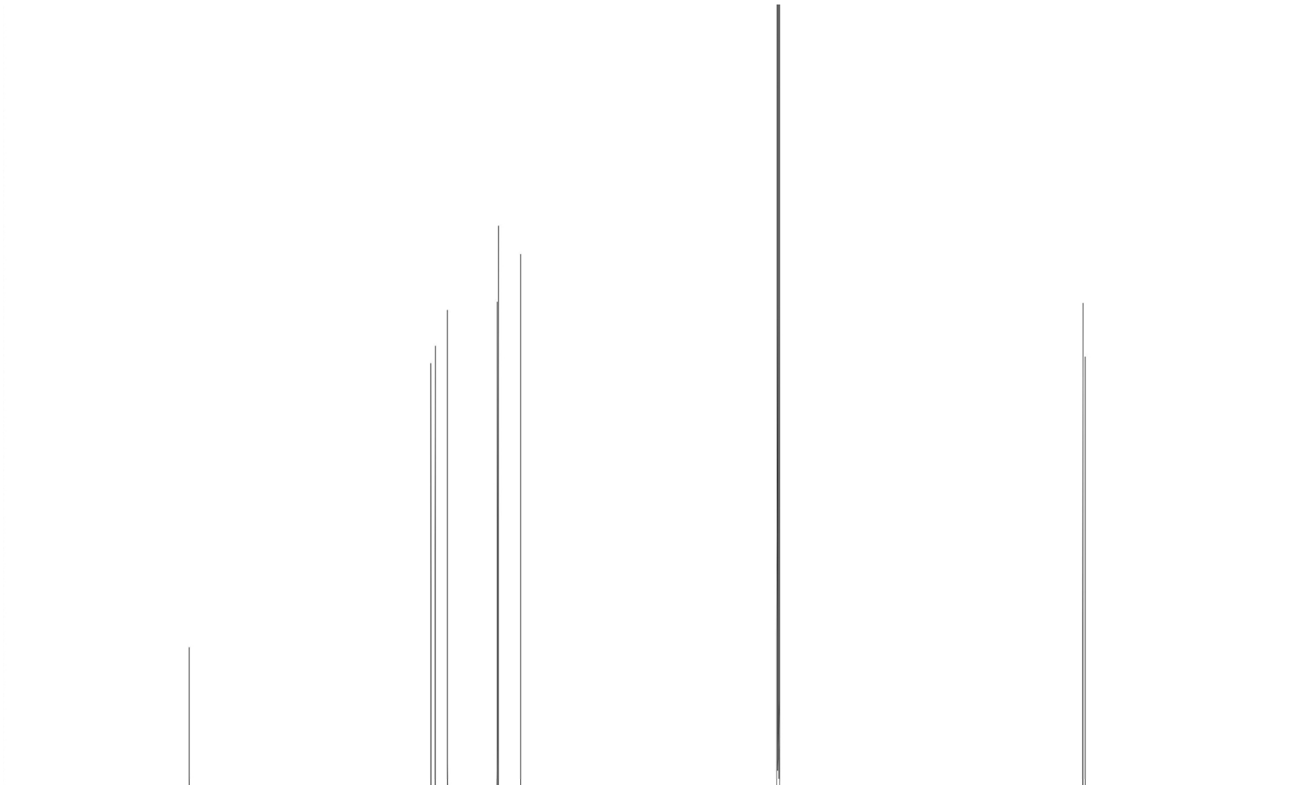
(8) M. Breugst, E. Detmar and D. von der Heiden, *ACS Catal.*, 2016, **6**, 3203–3212.

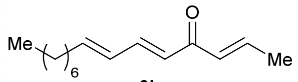
Copies of ^{1}H and ^{13}C NMR Spectra:



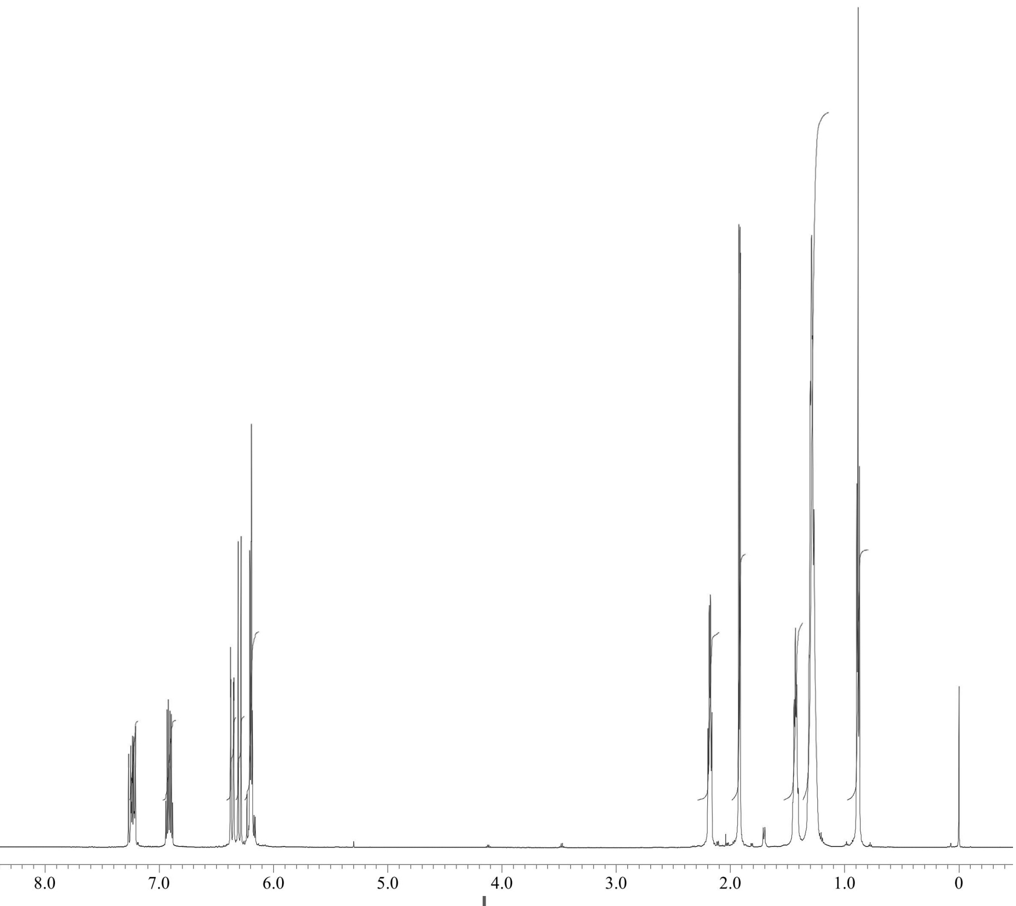
3a

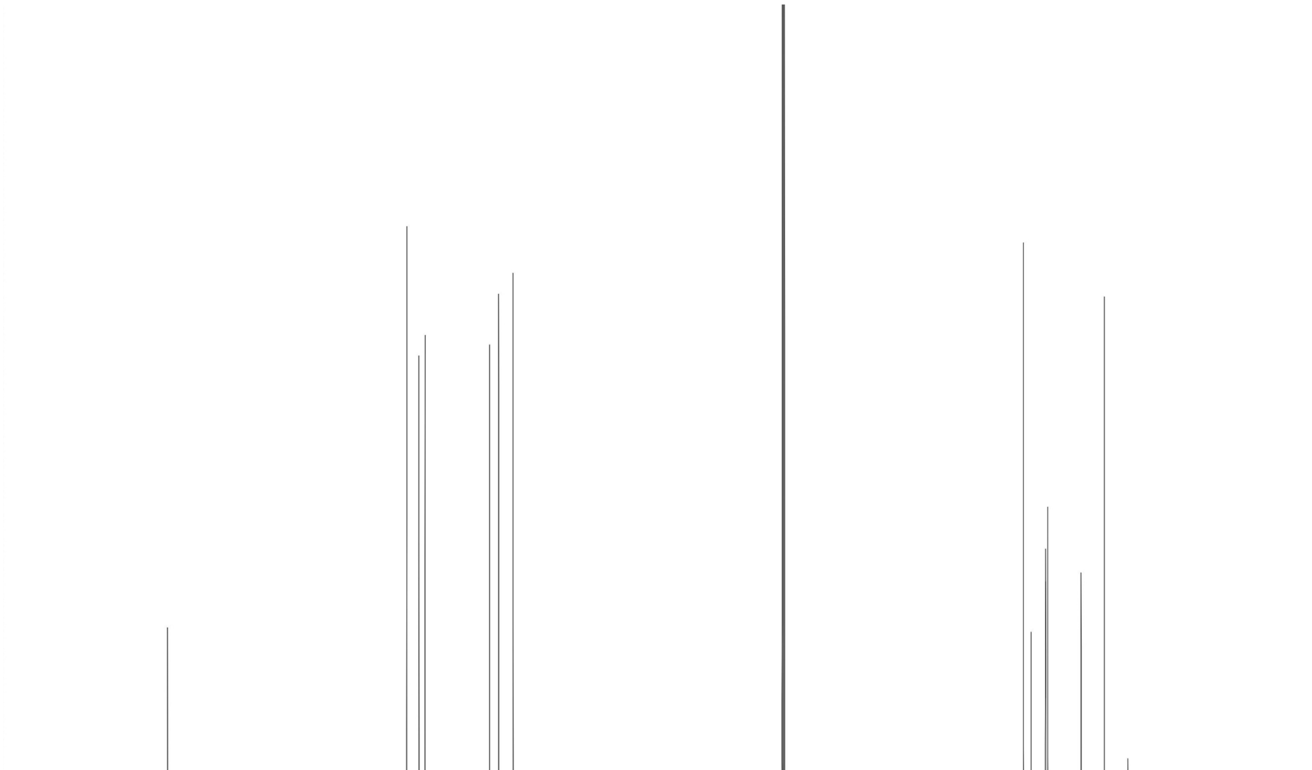


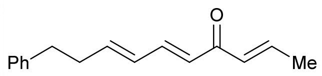



Me
6
O
Me

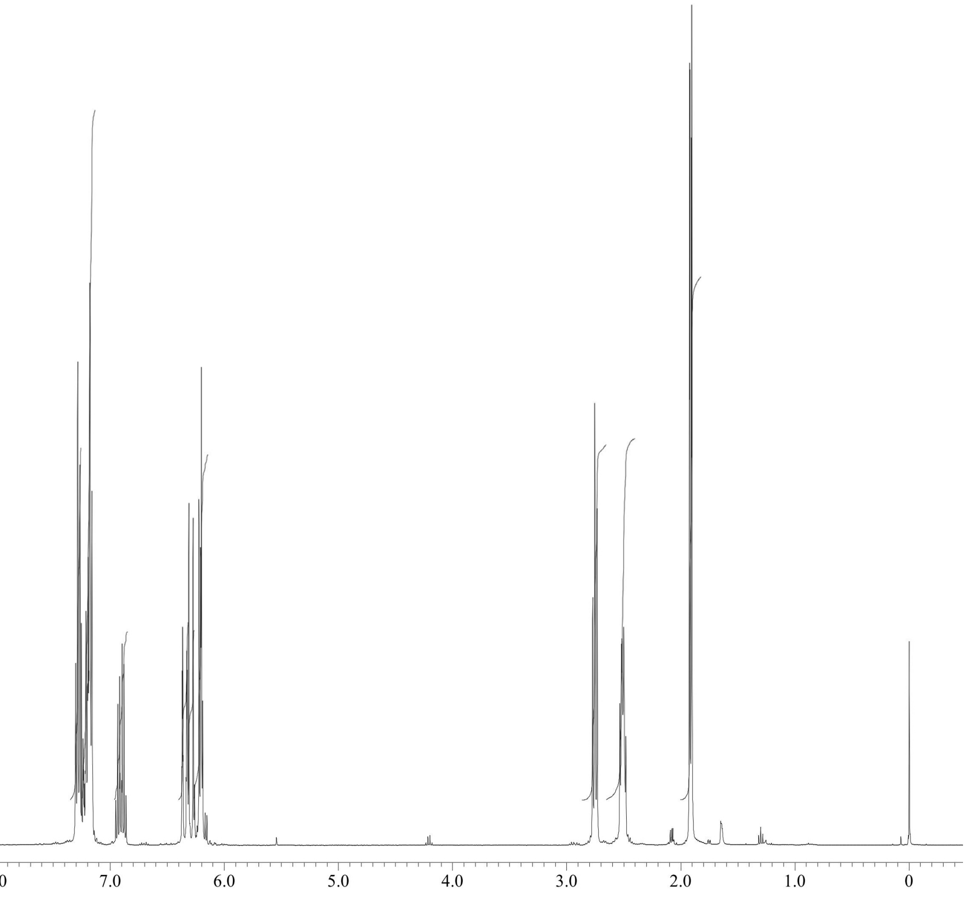
3b

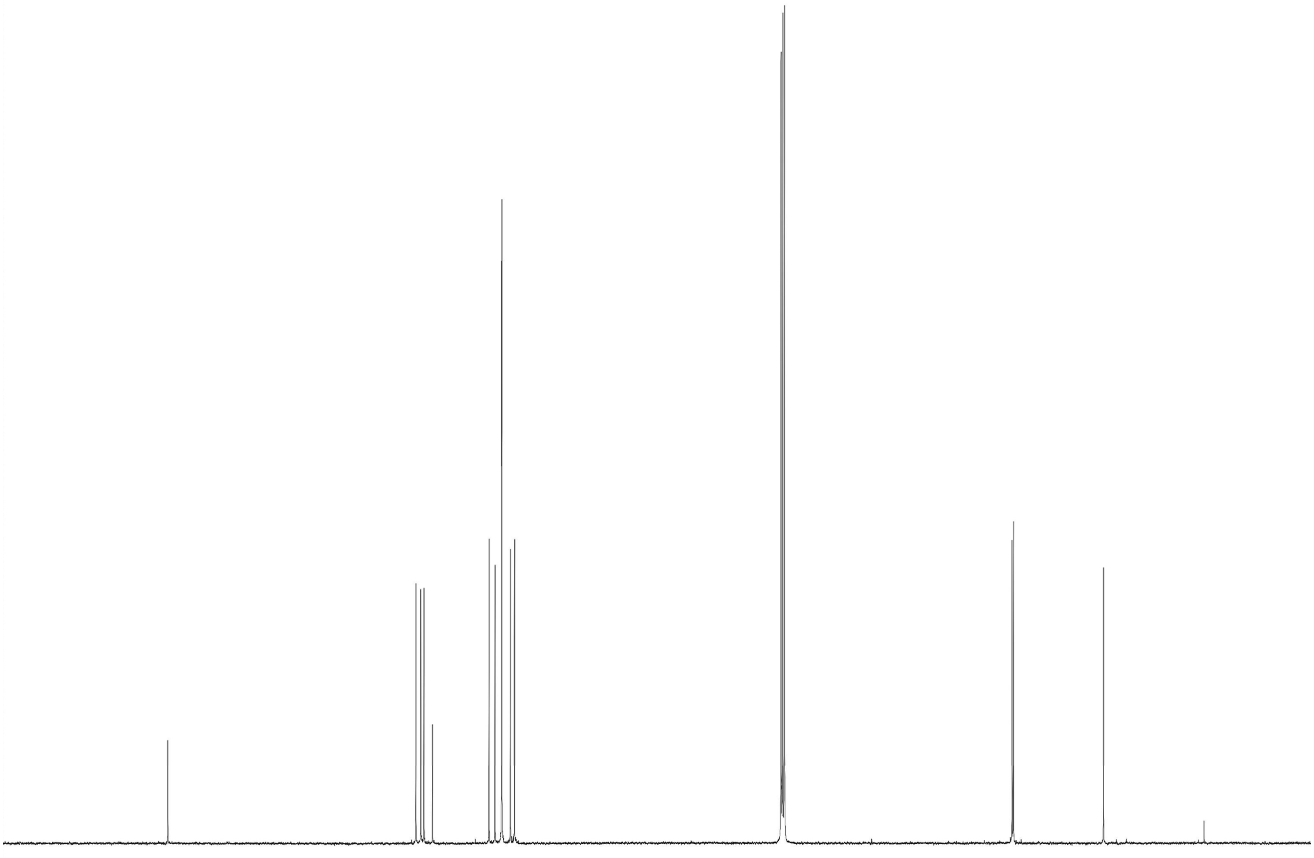

10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

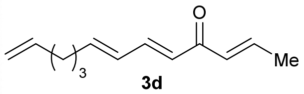

210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0-20.0


O
Ph
Me

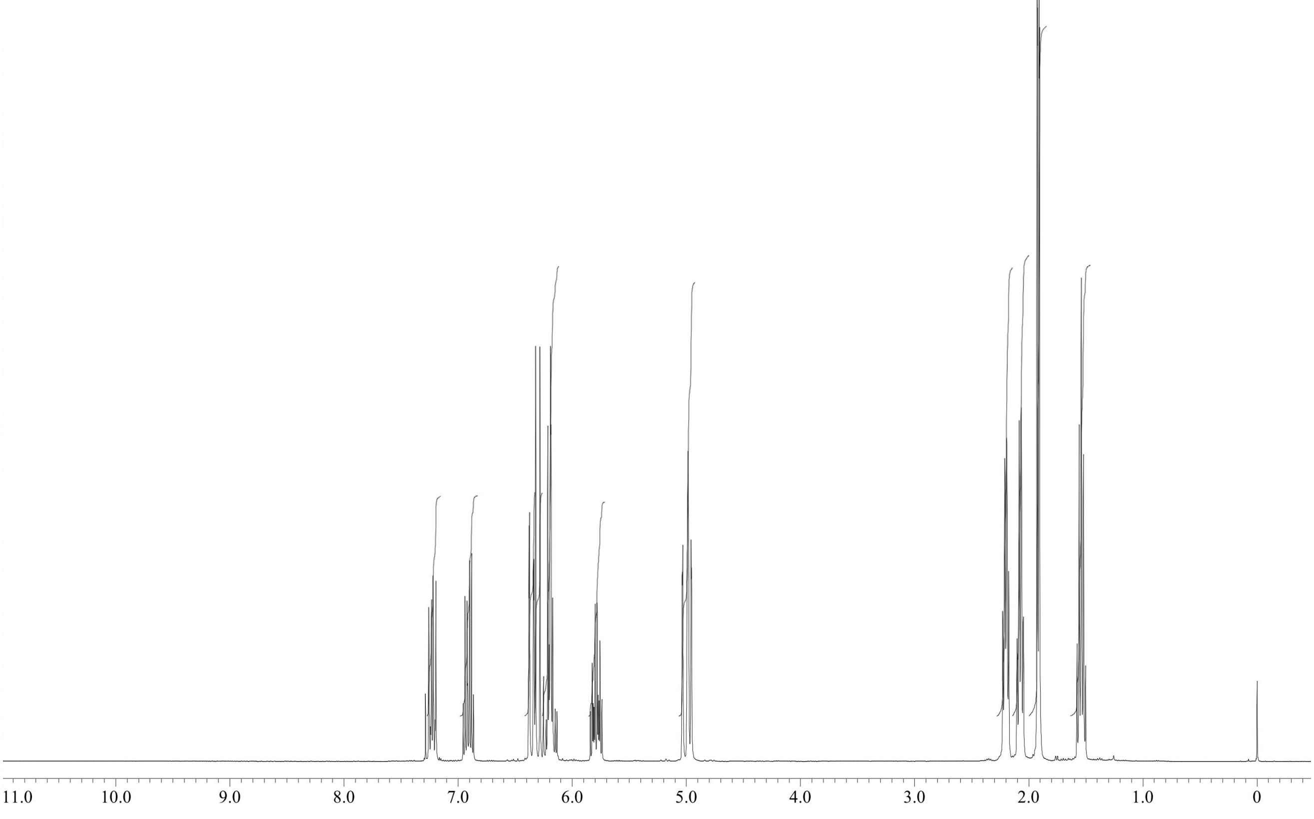
3c

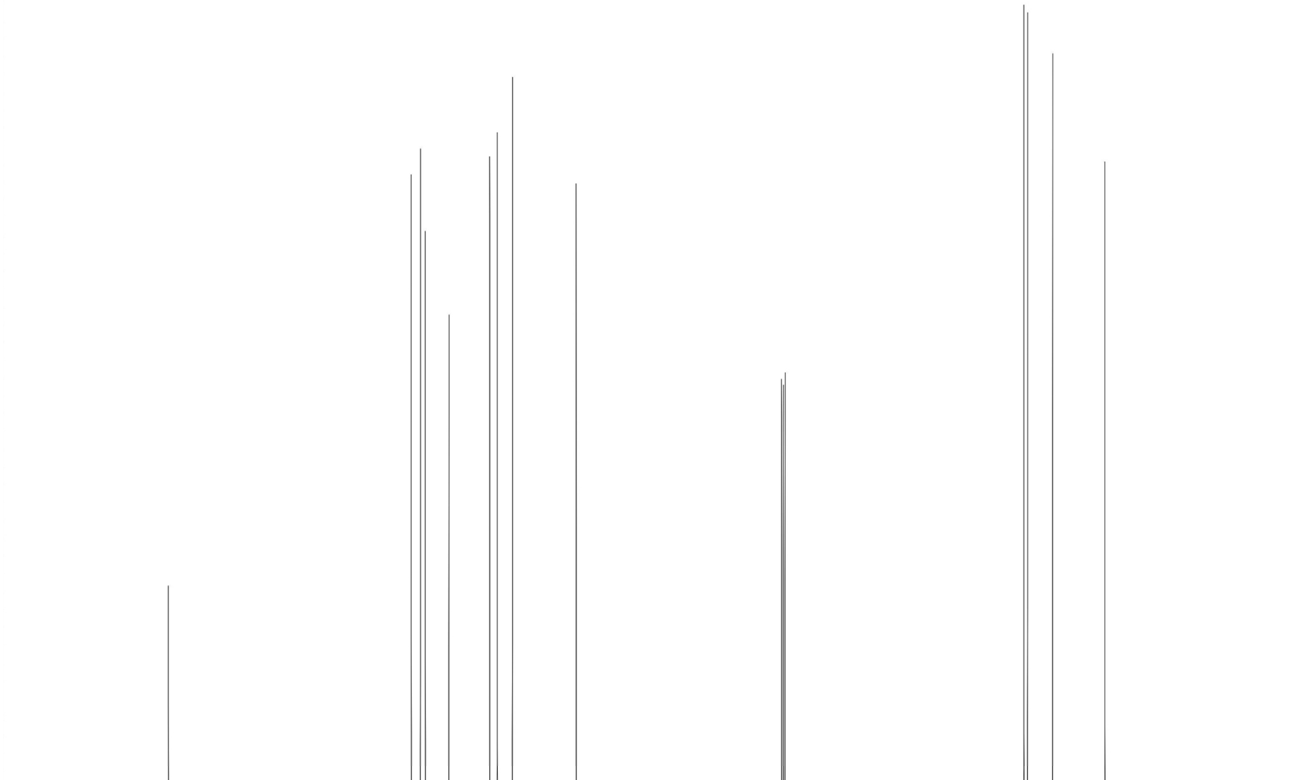

11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

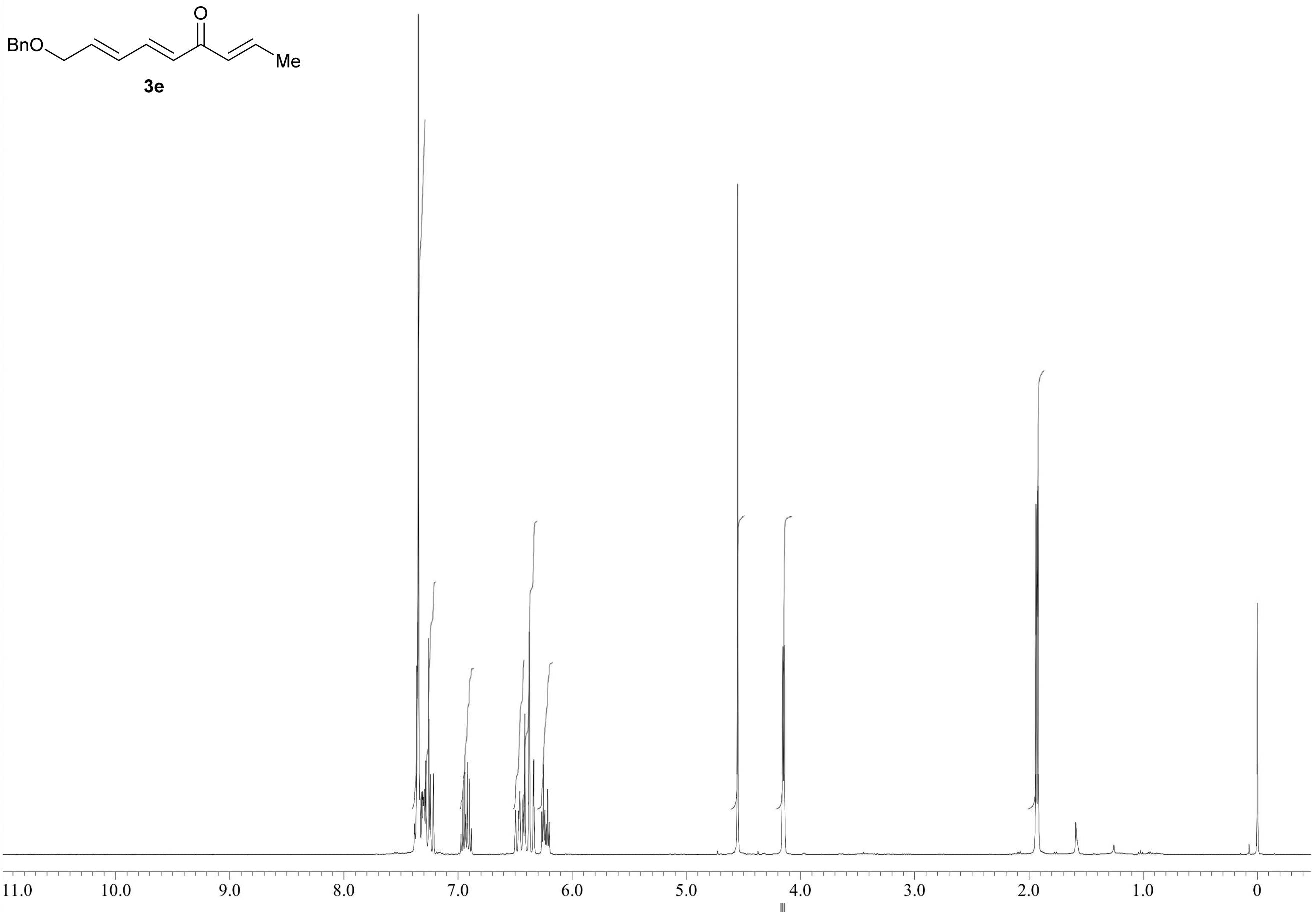

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0

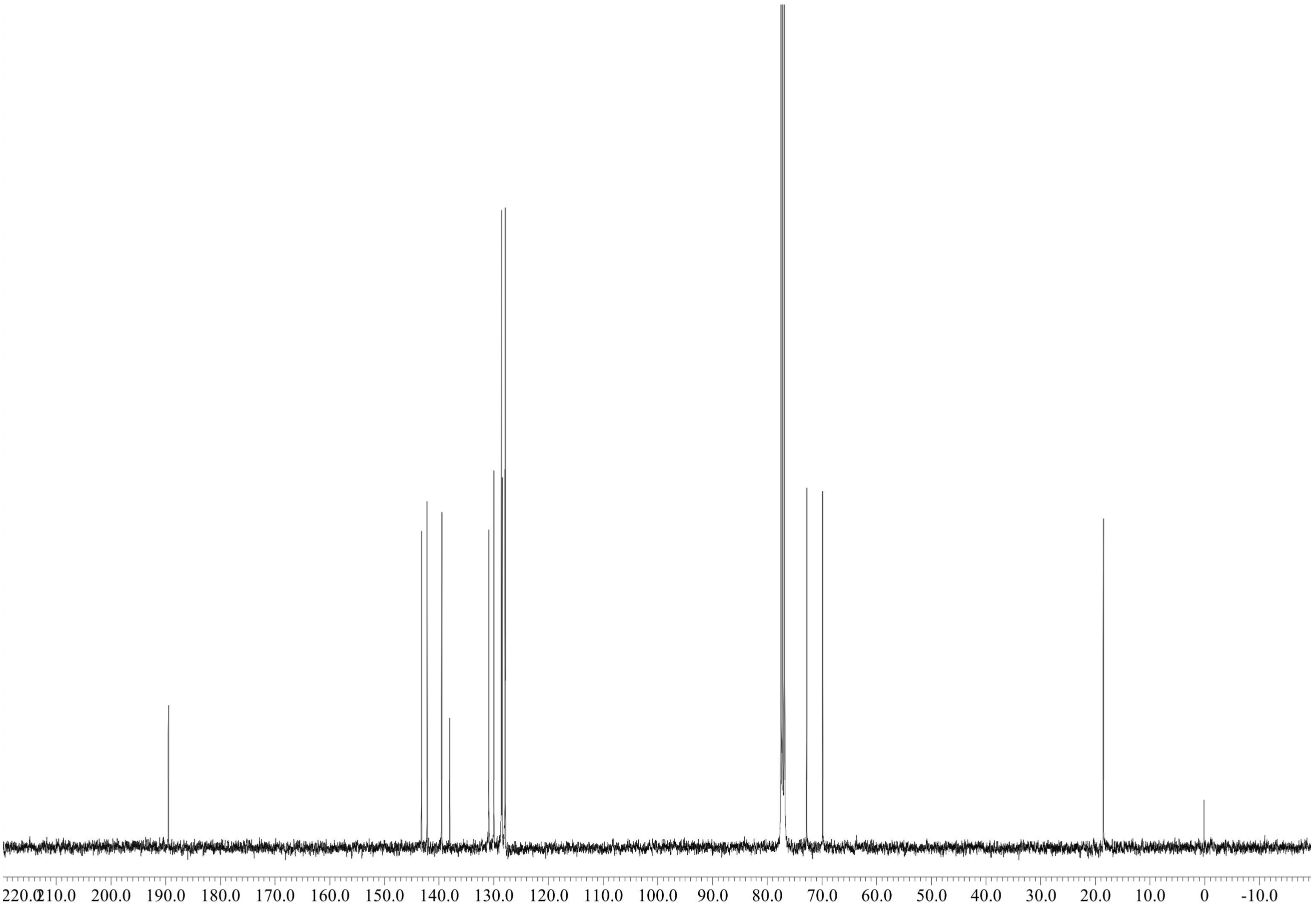

O
Me
3

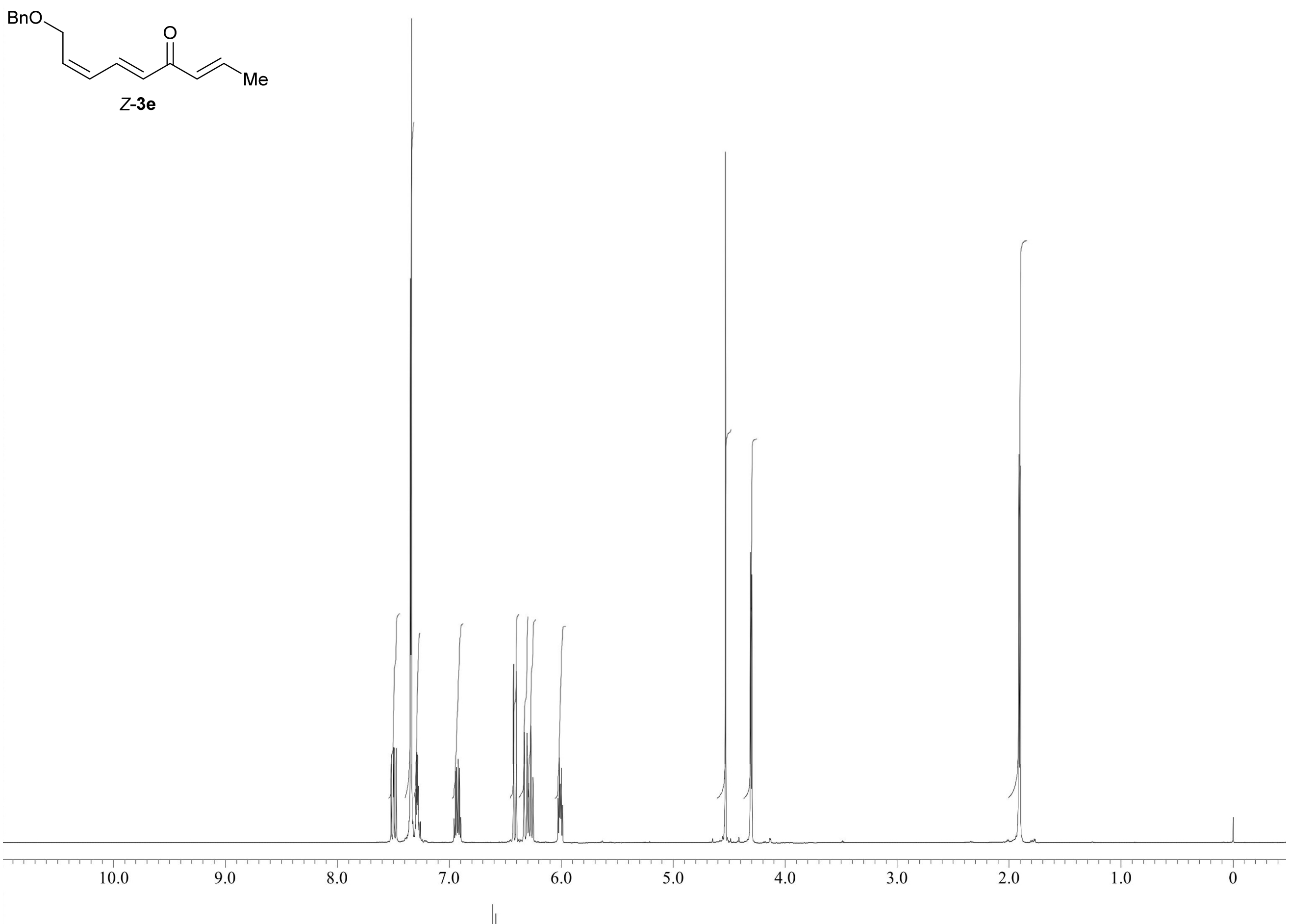
3d

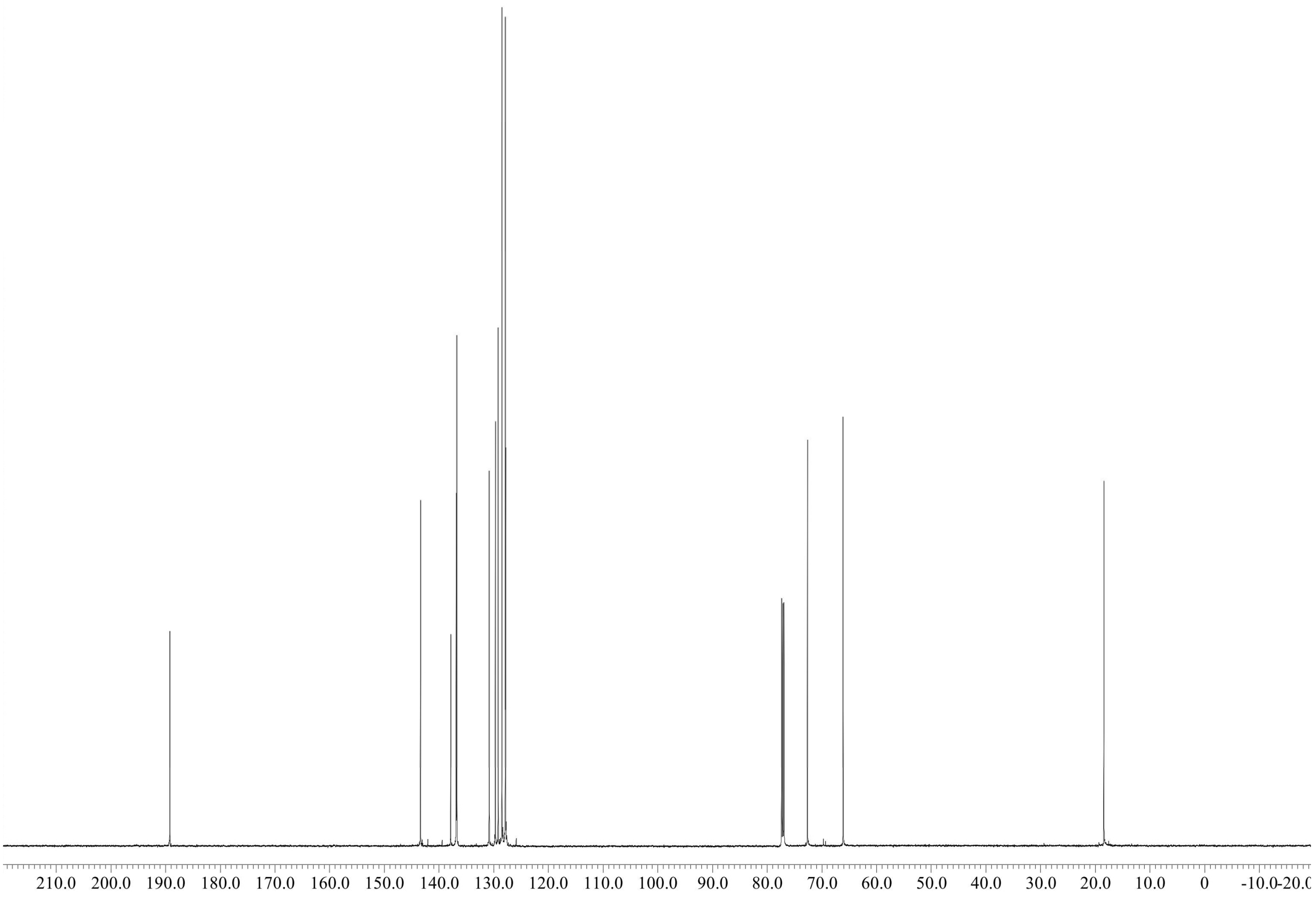

11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

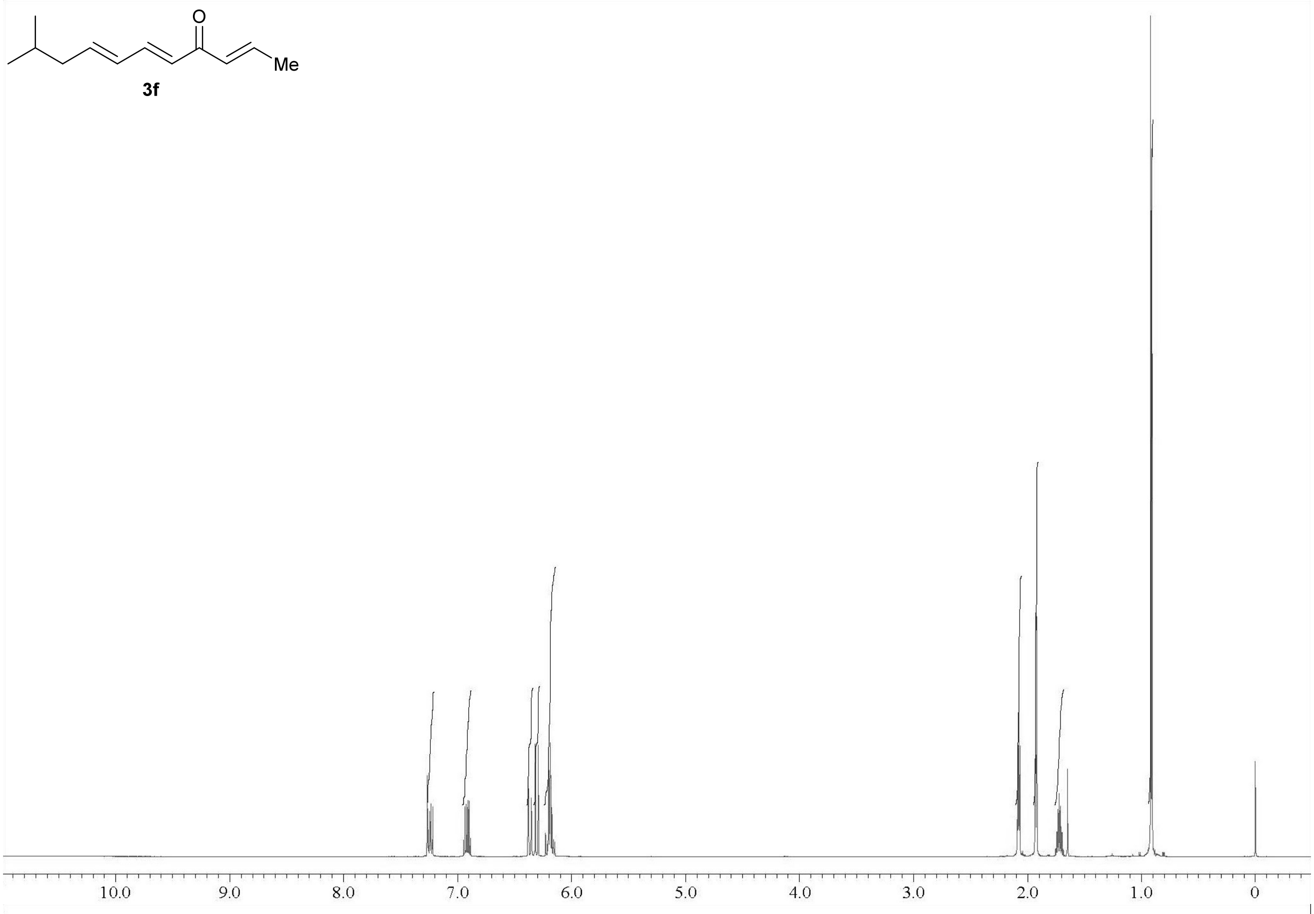

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0

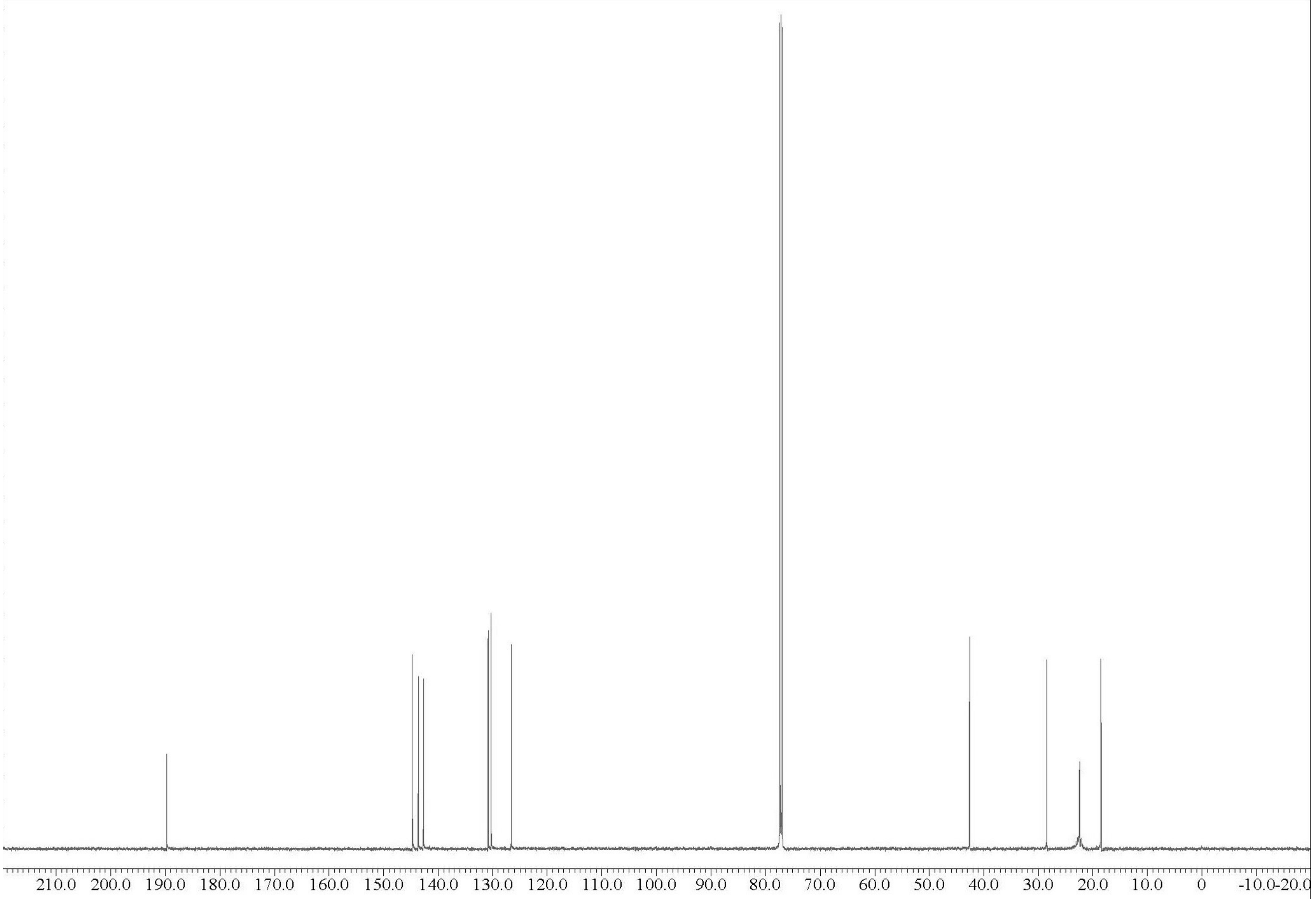

BnO
O
Me
3e
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

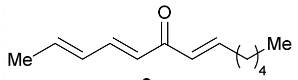

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0


BnO
O
Me
Z-3e
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

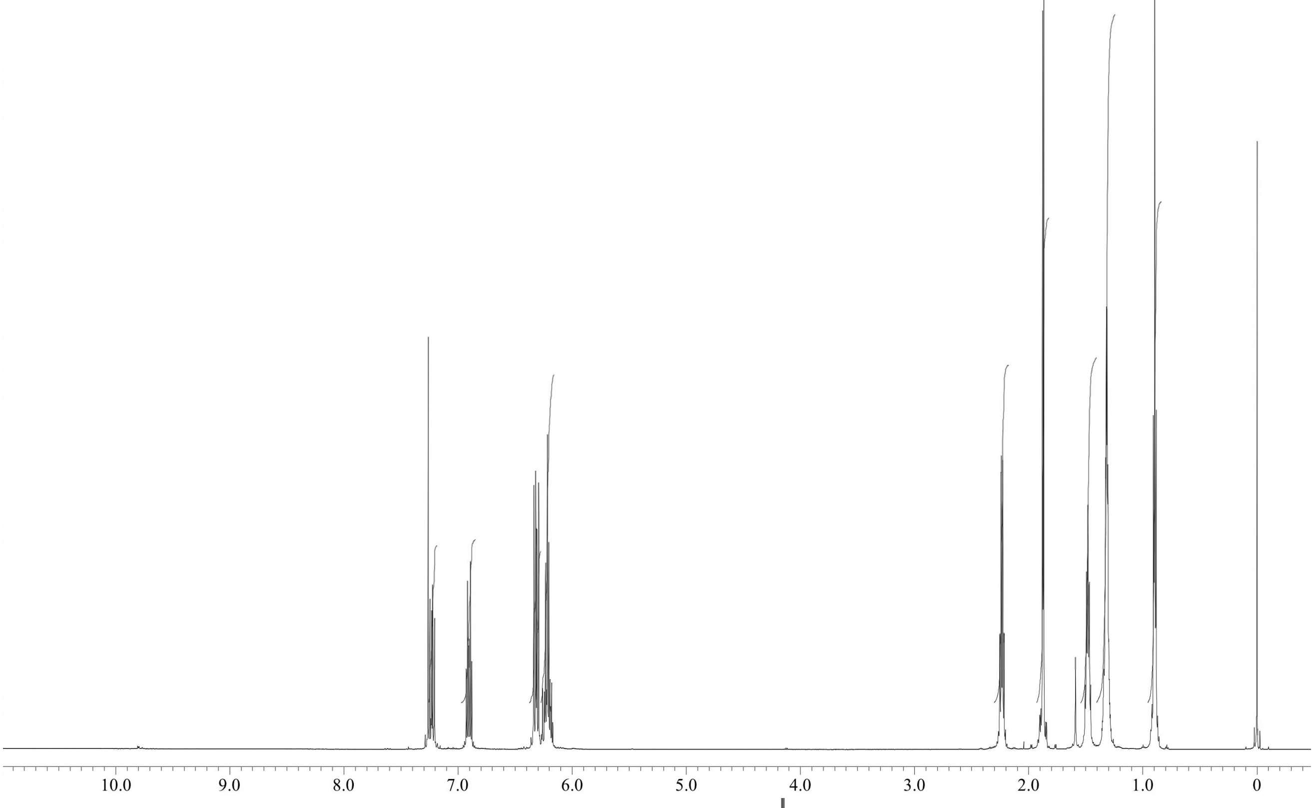

210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0-20.0

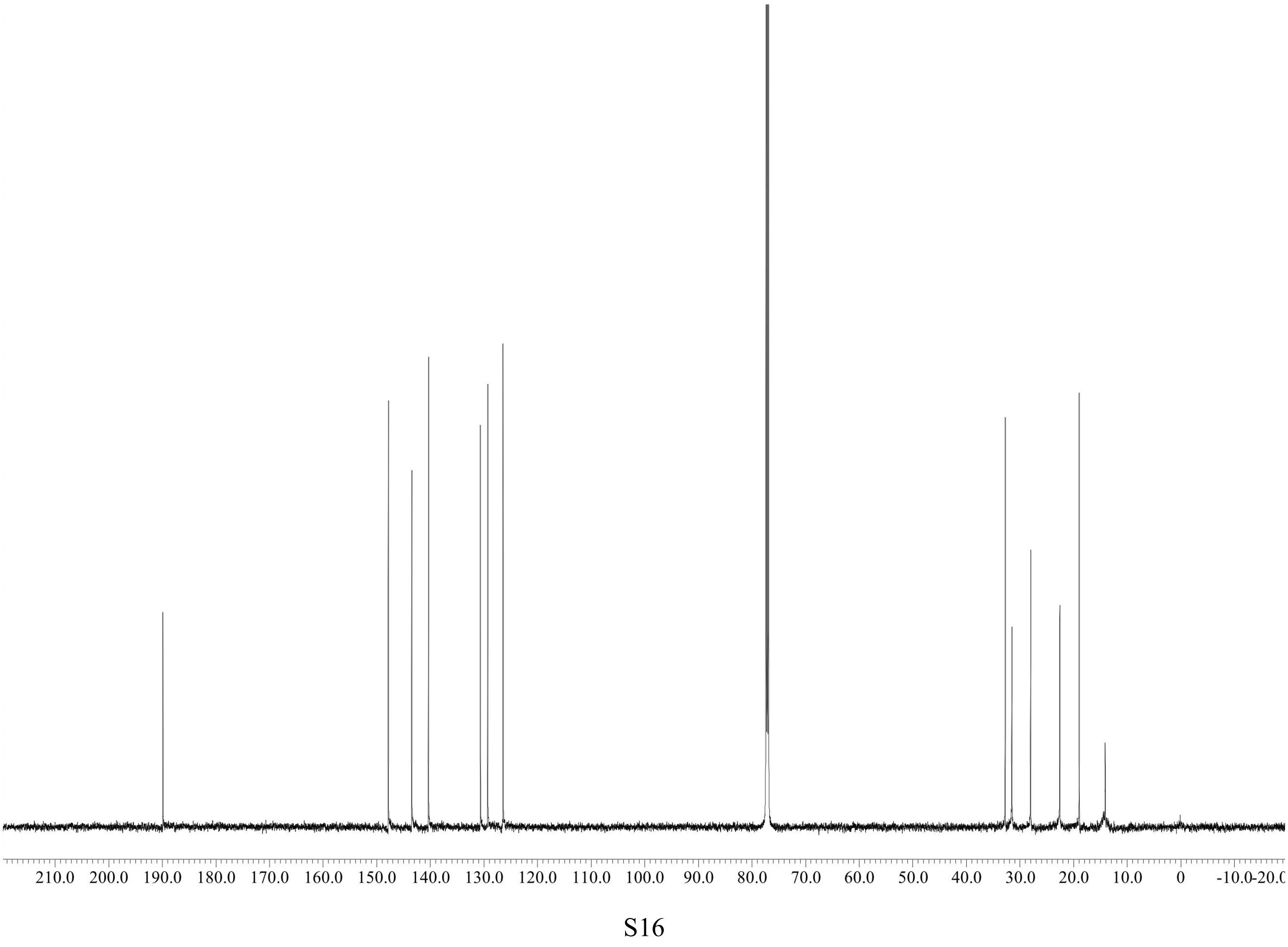

O
Me
3f
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

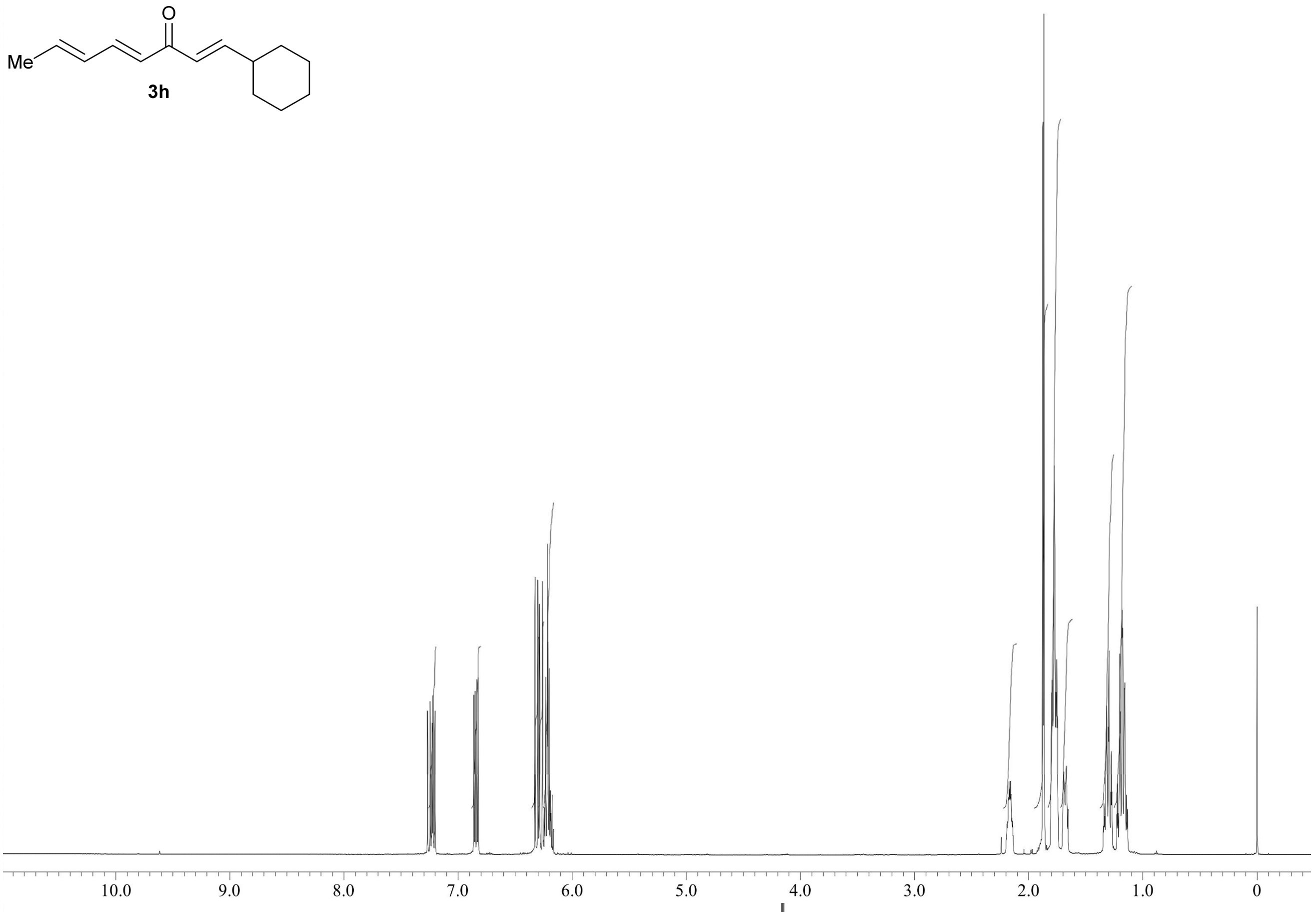

210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0-20.0

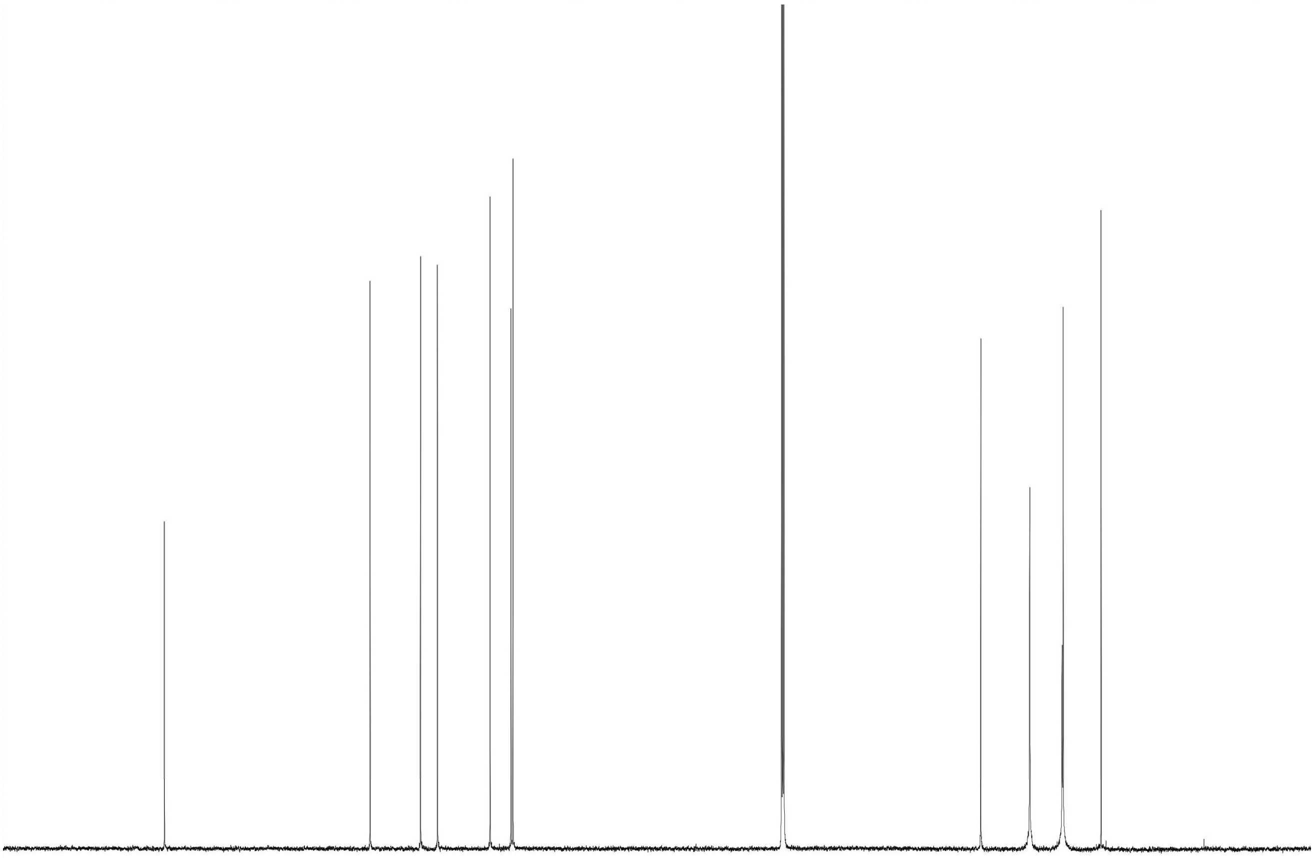

O
Me
Me
4

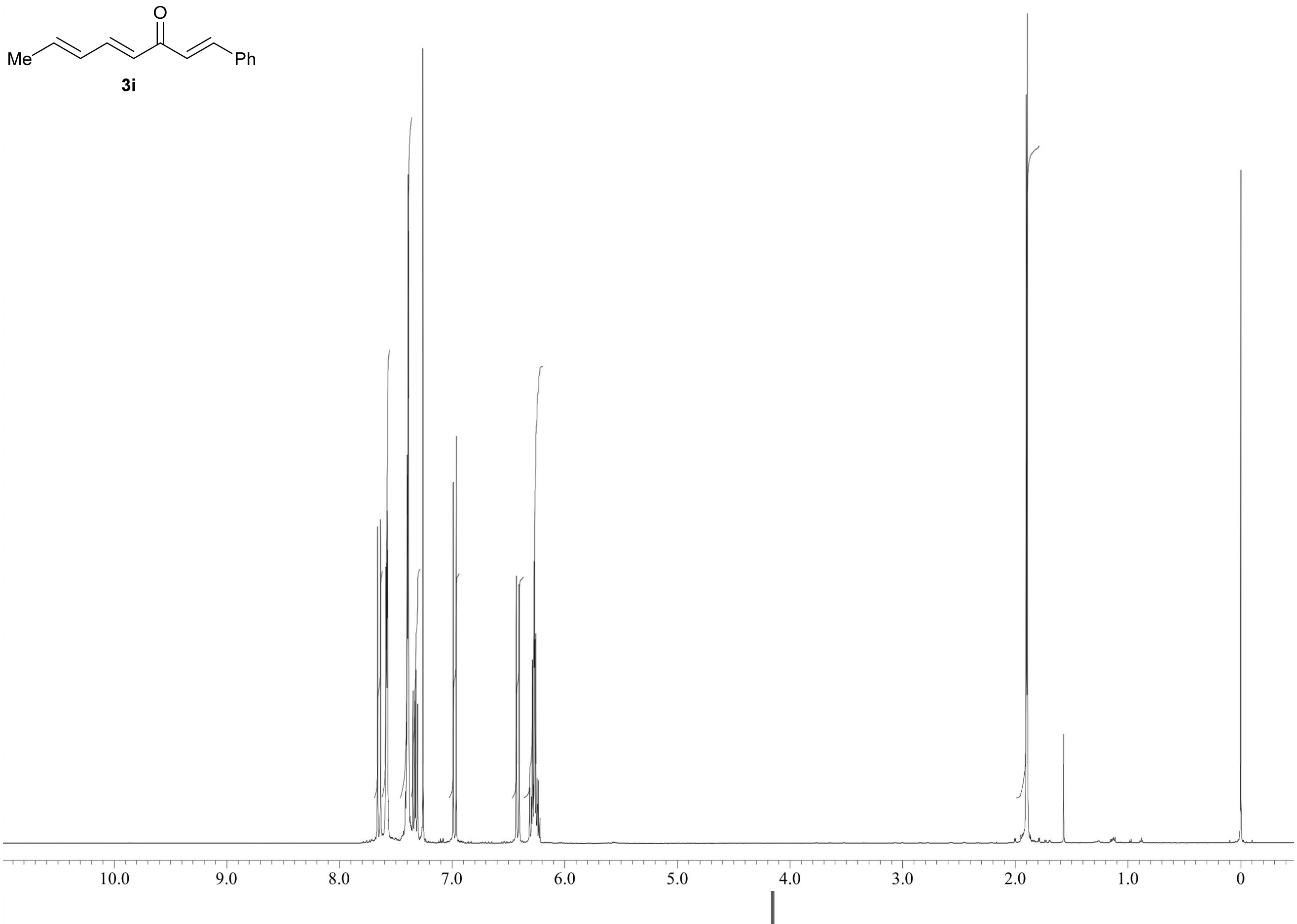
3g

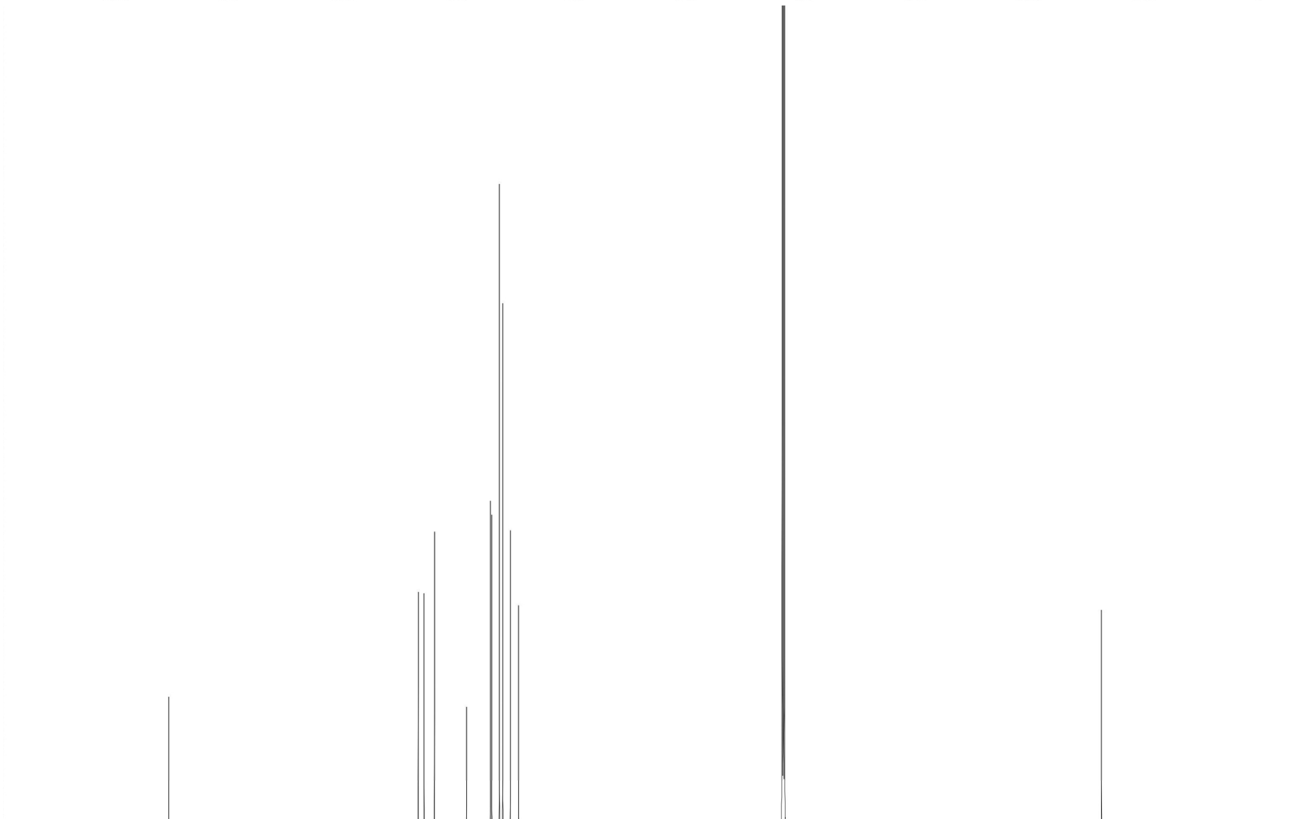

10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

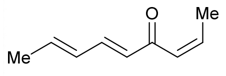

210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0


Me
O
3h
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

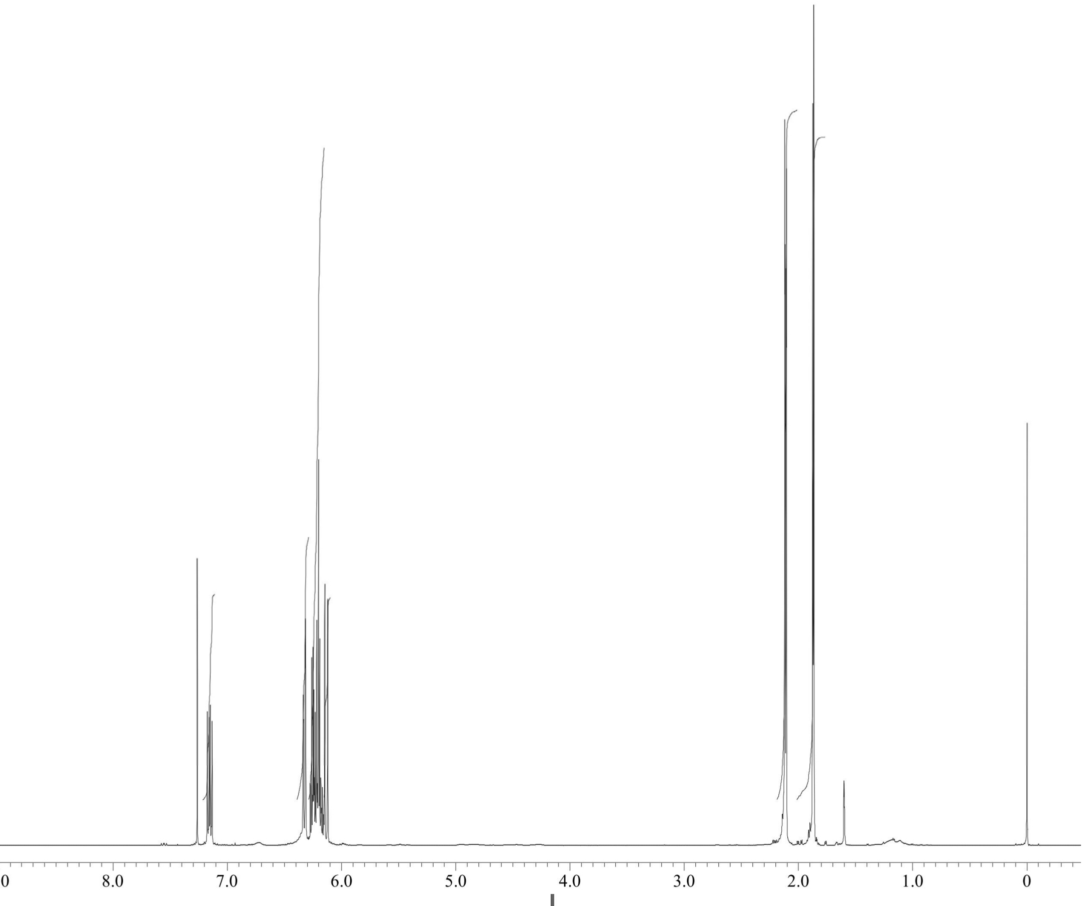

210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0-20.0

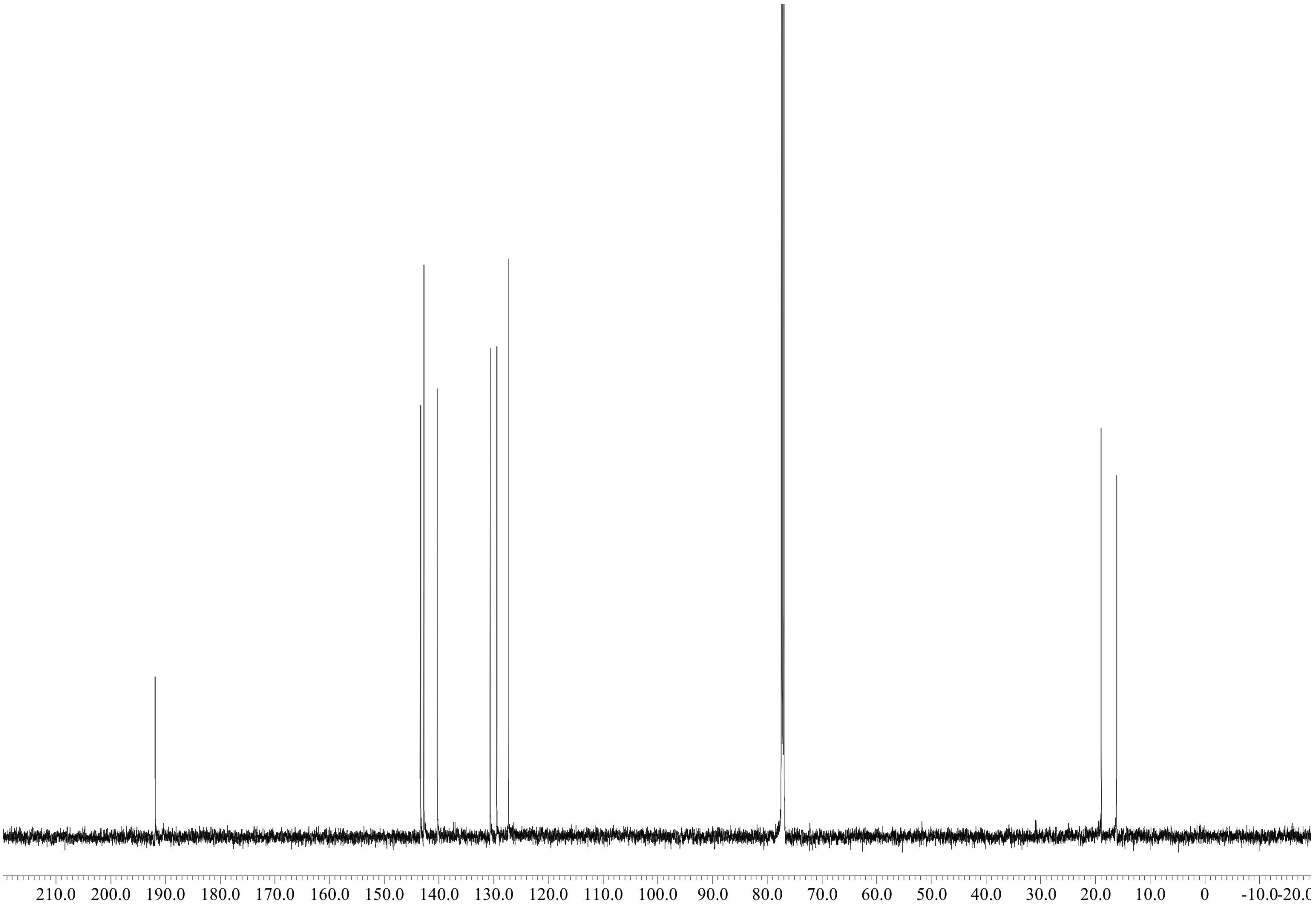

O
Me
Ph
3i
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

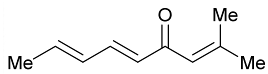

210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0-20.0


O
Me
Me

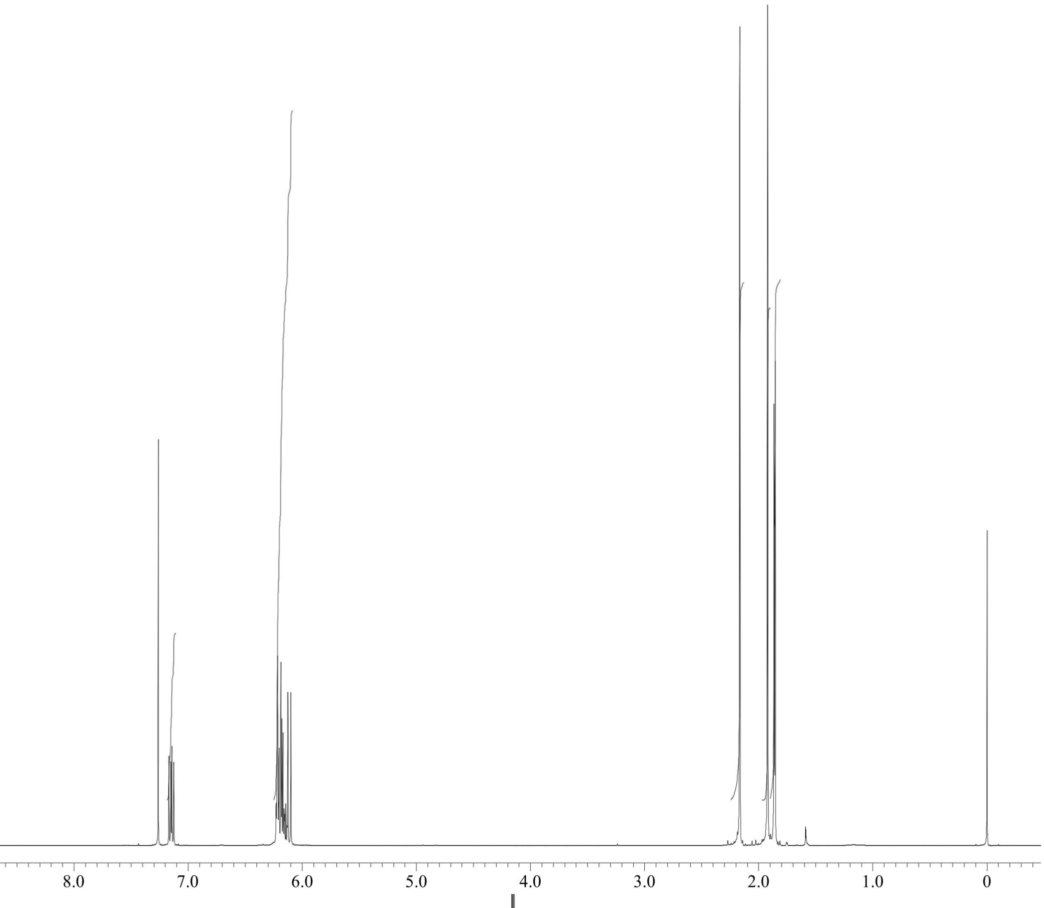
3j

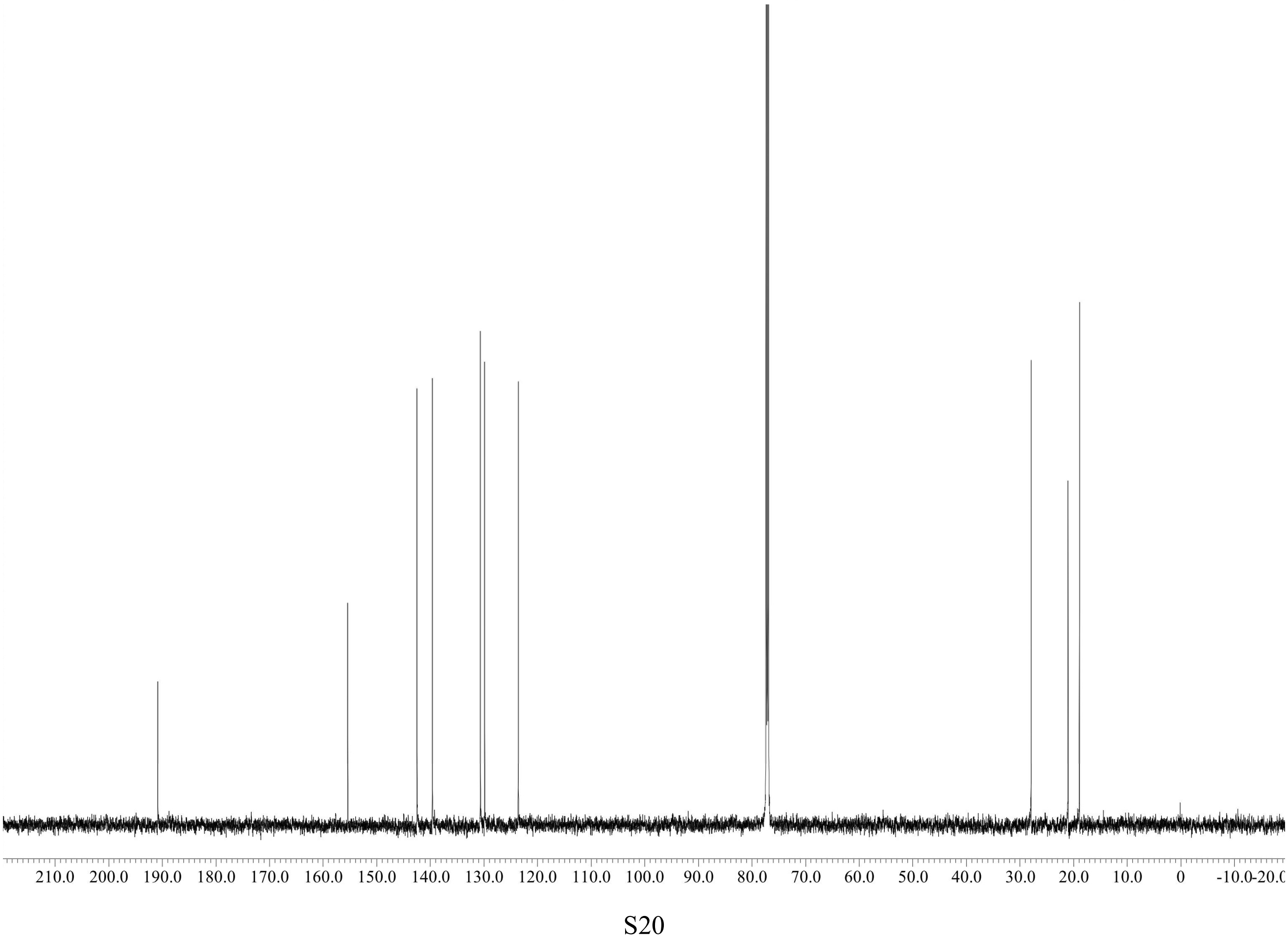

10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

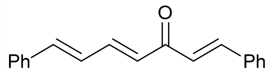

210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0-20.0


O
Me
Me
Me

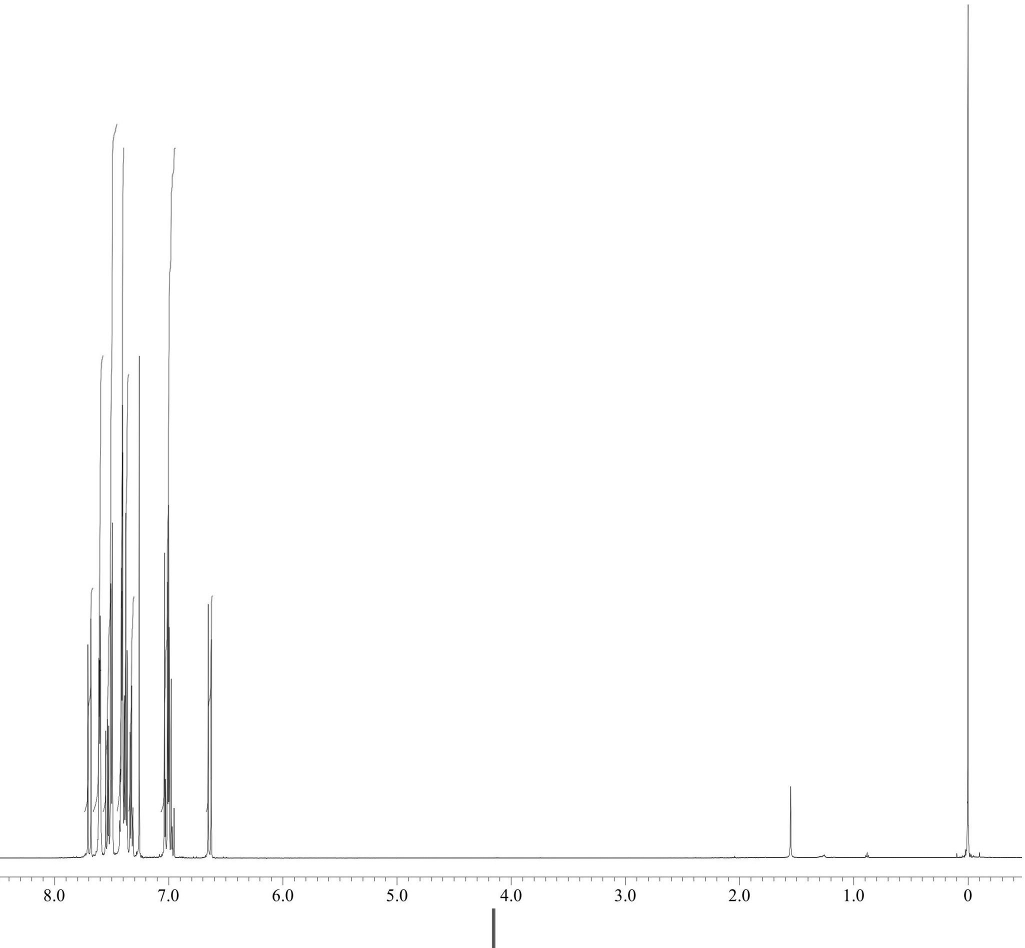
3k

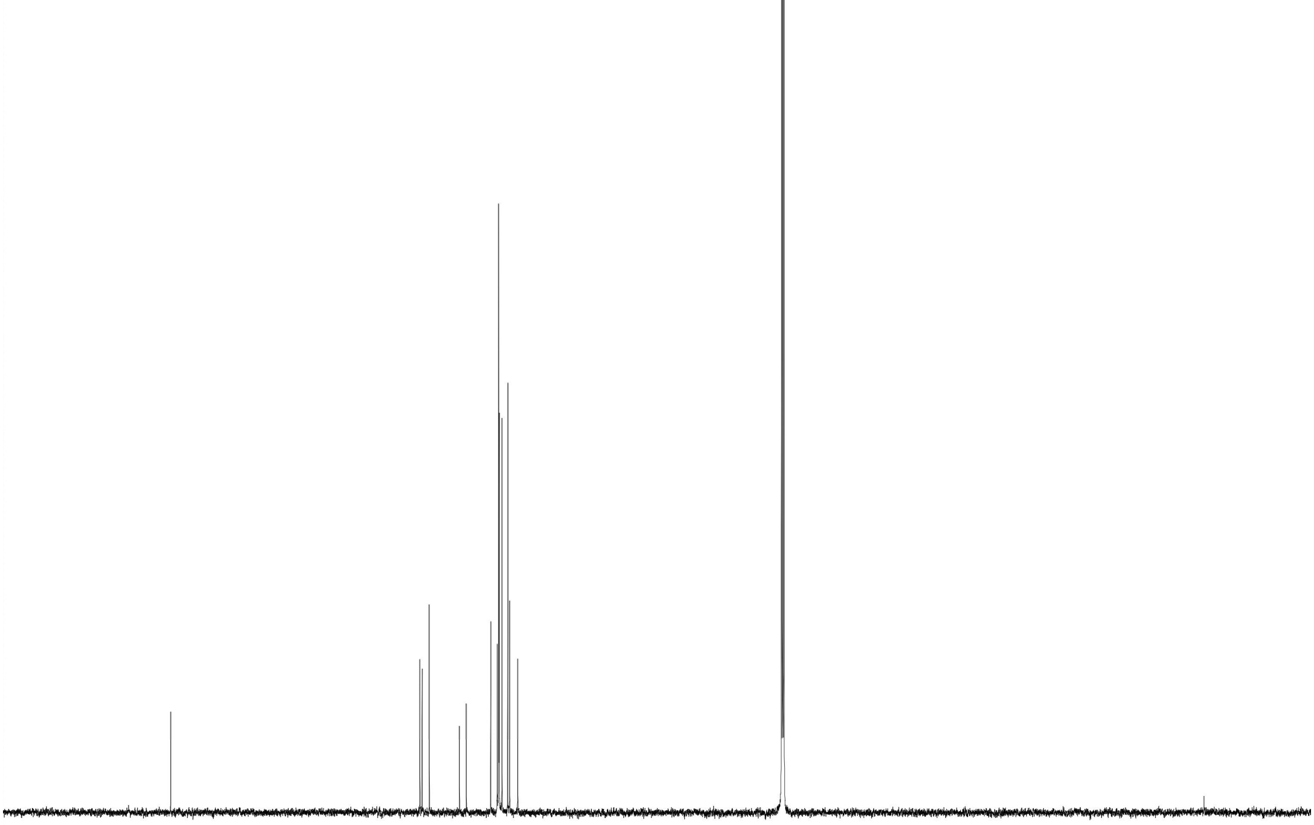

10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

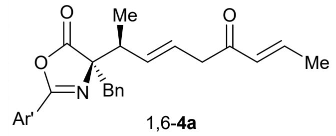

210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0-20.0


O
Ph
Ph

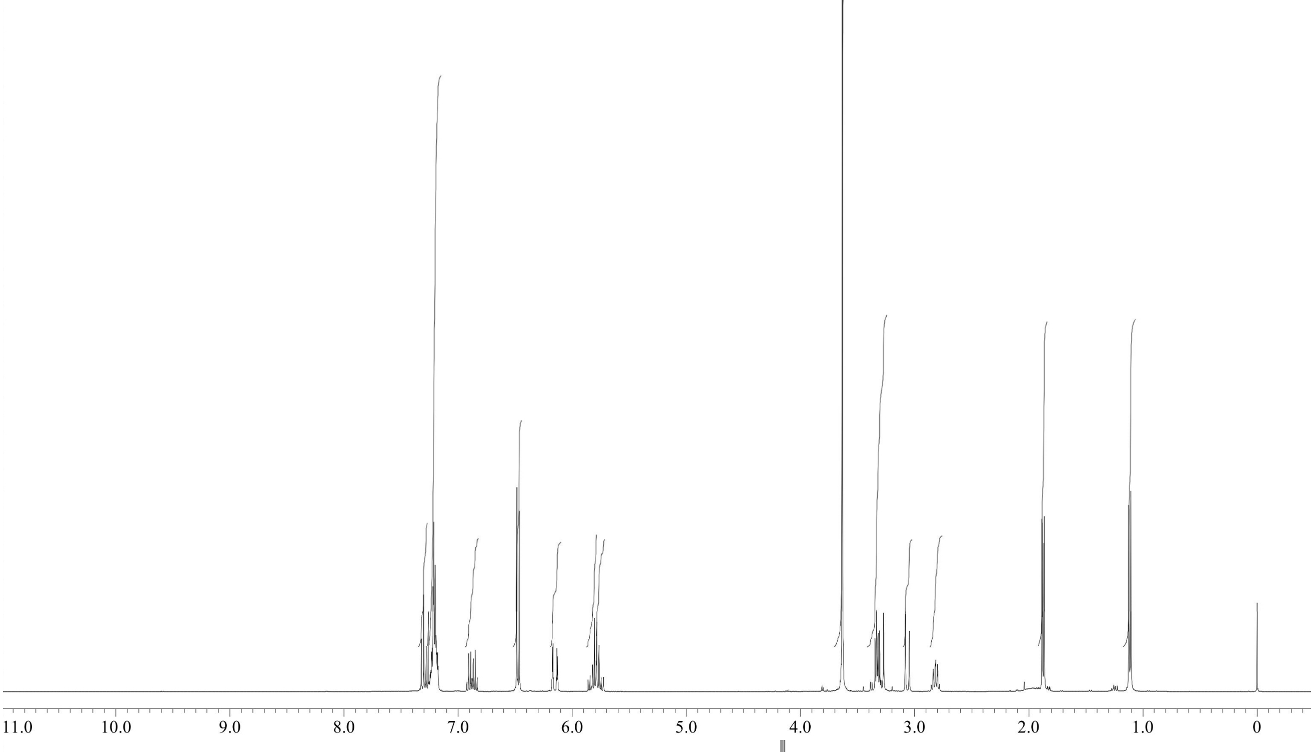
3l

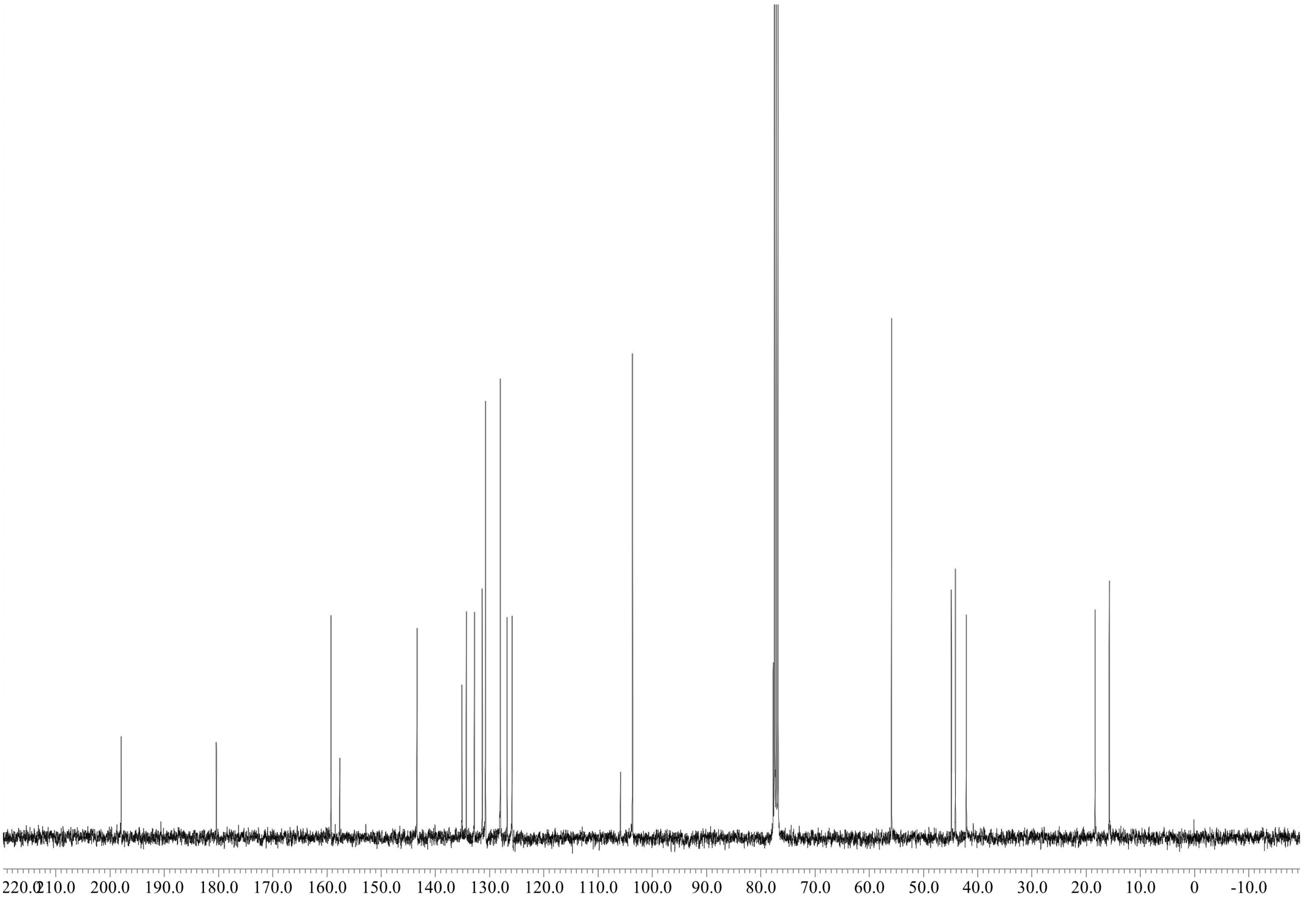

10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

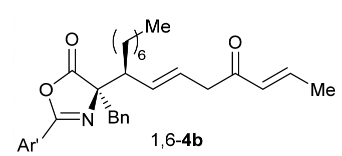

210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0-20.0



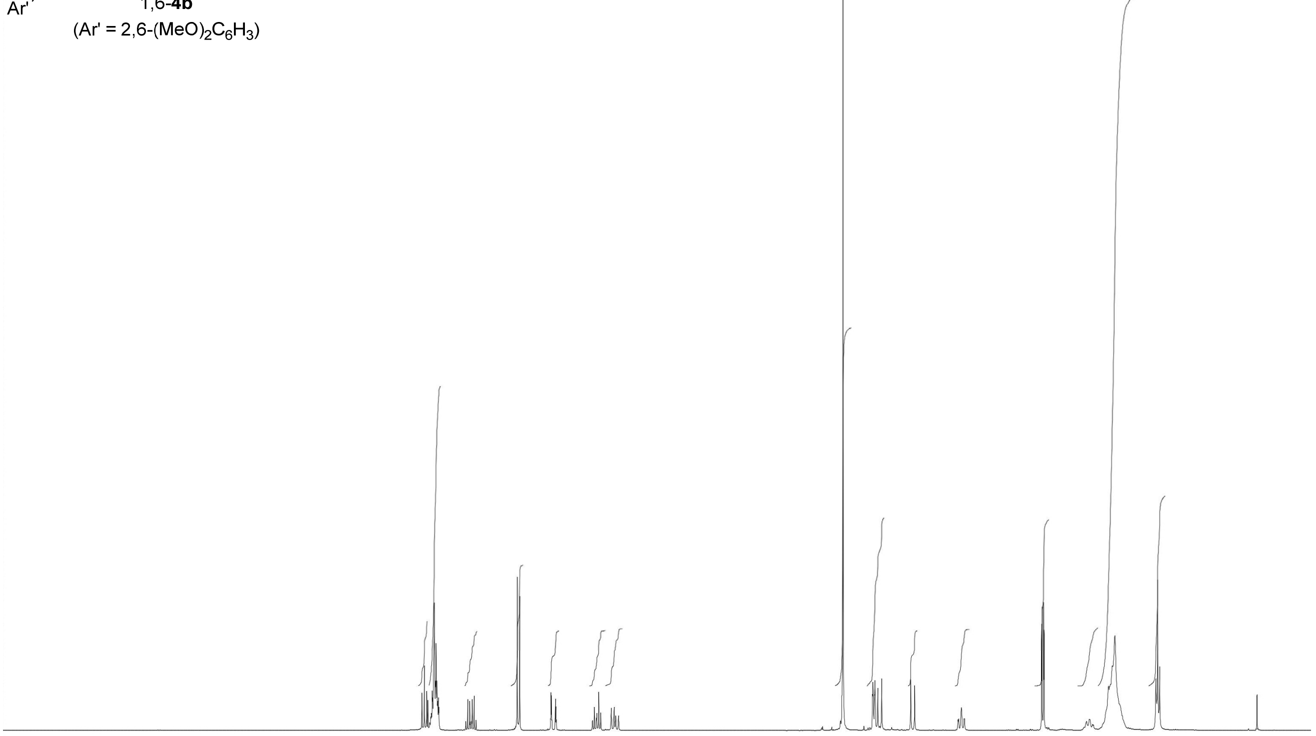
1,6-**4a**
(Ar' = 2,6-$(MeO)_2C_6H_3$)

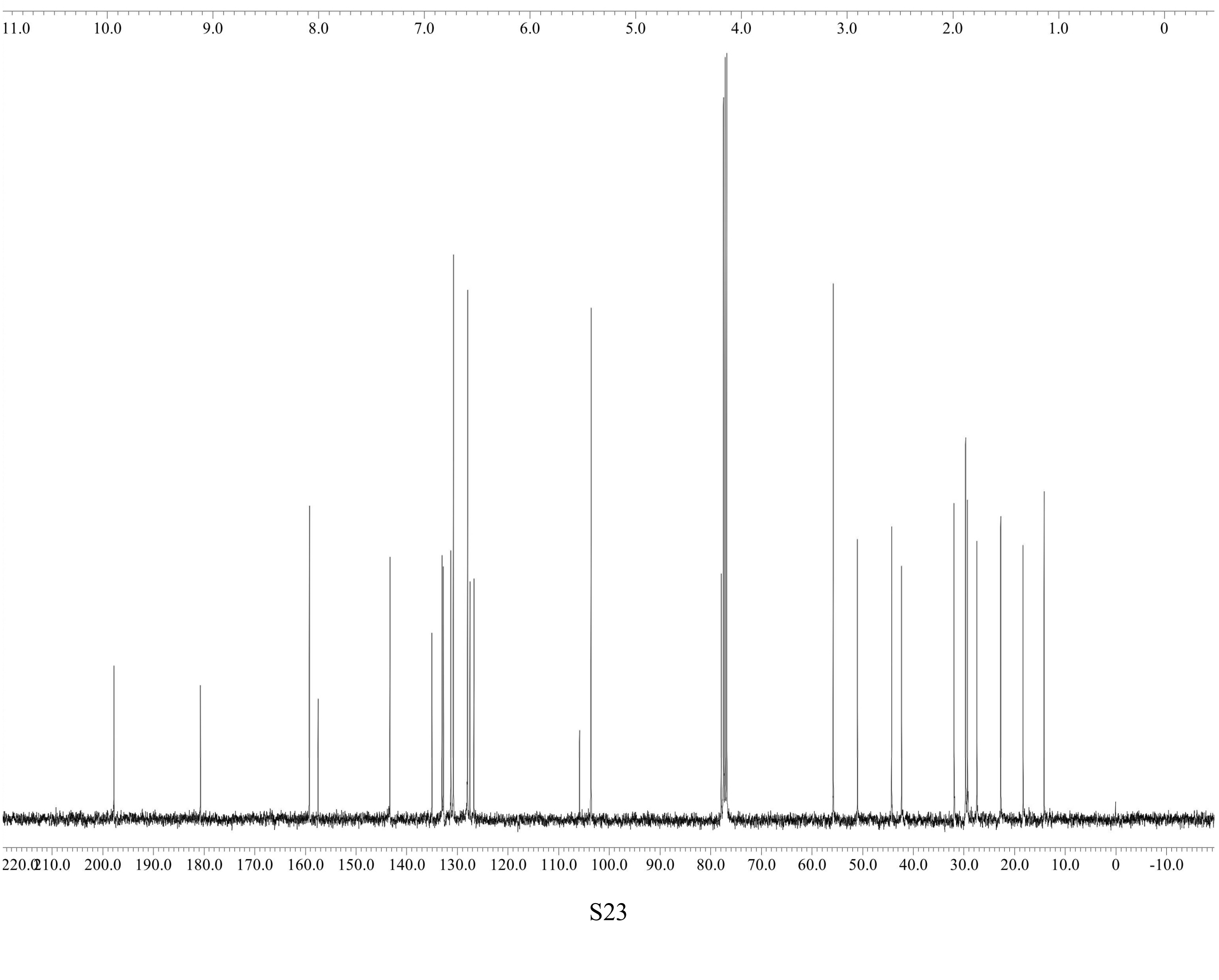


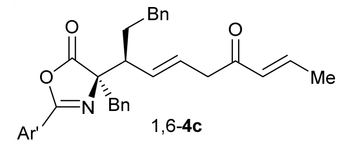




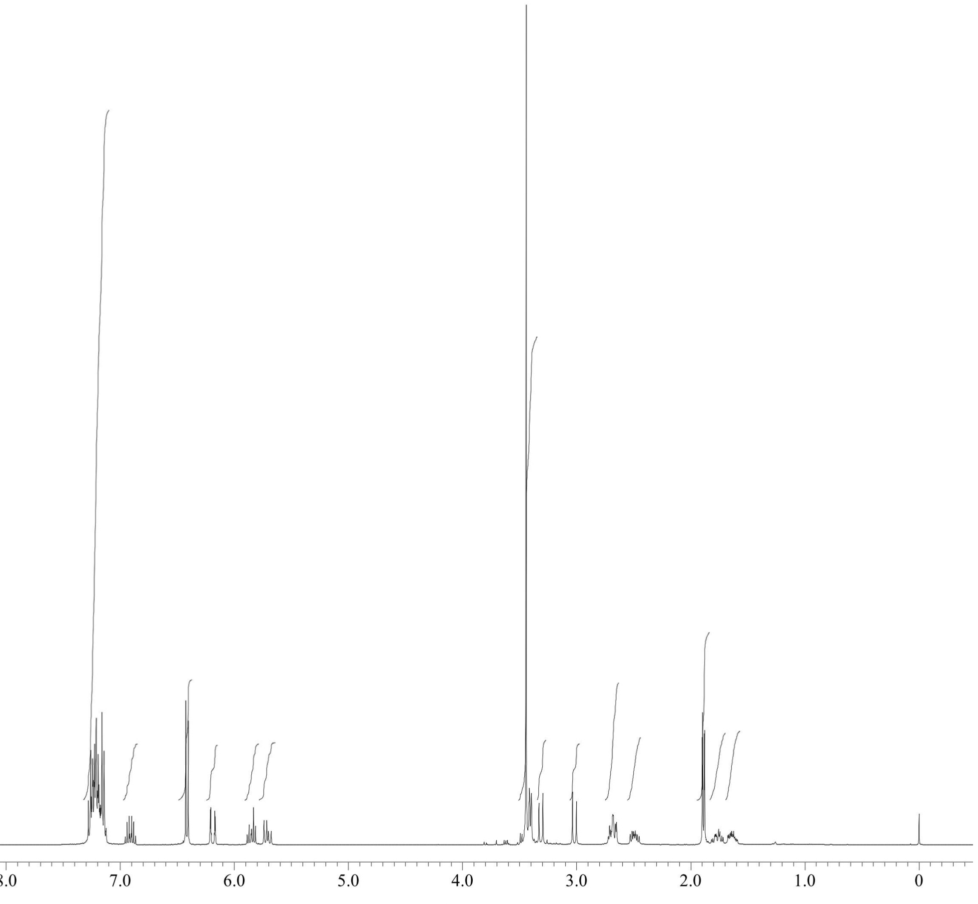
1,6-**4b**
(Ar' = 2,6-$(MeO)_2C_6H_3$)

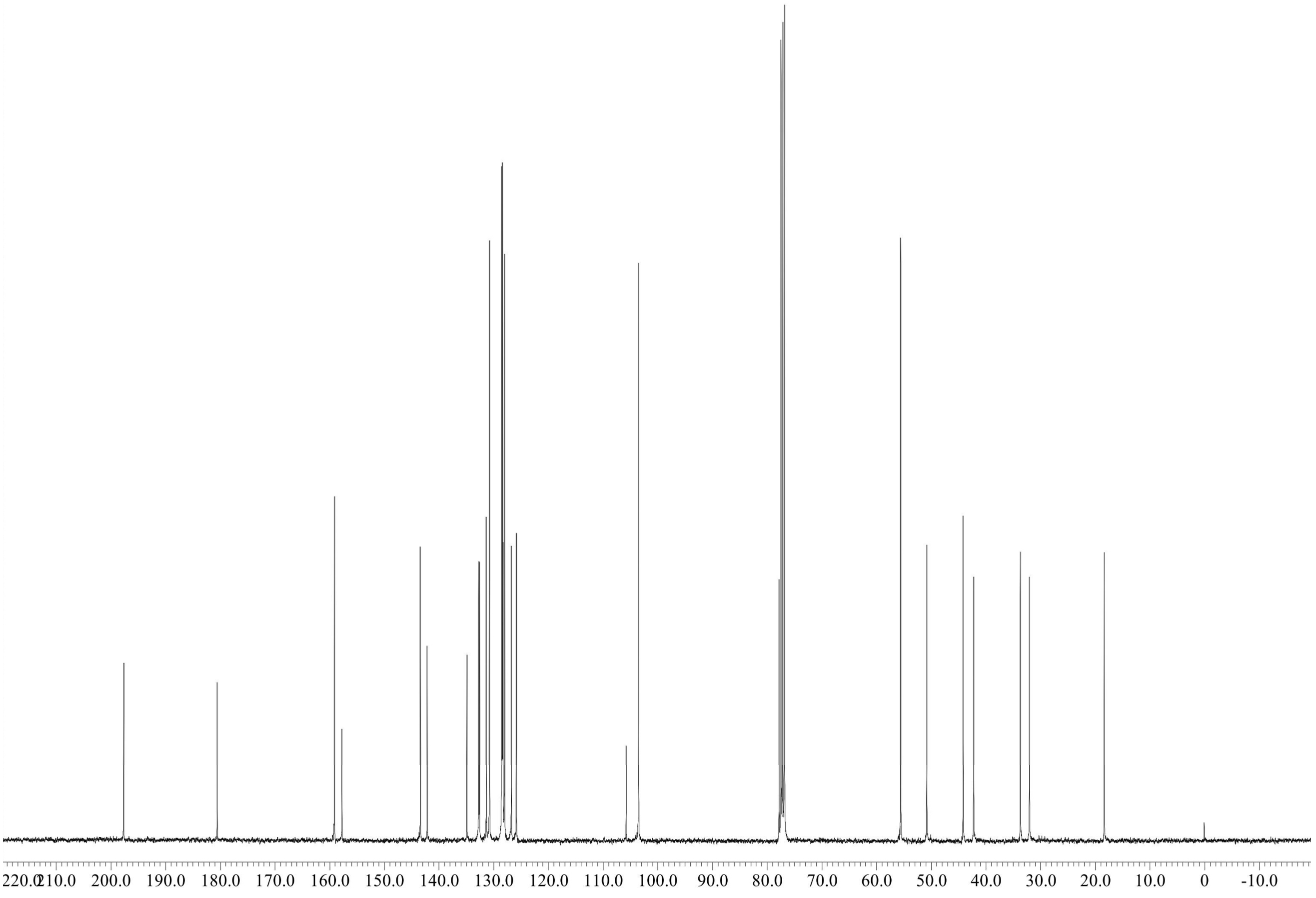


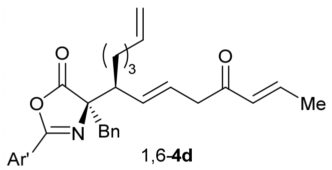




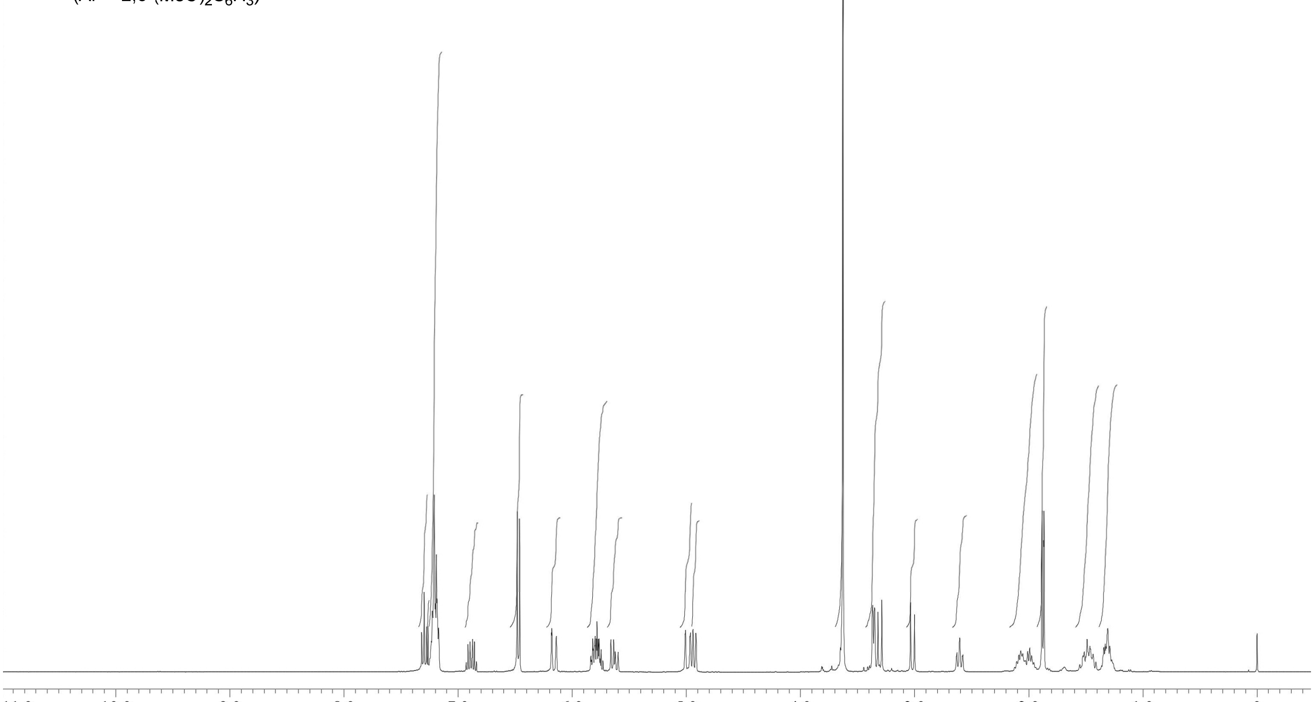
1,6-**4c**
(Ar' = 2,6-$(MeO)_2C_6H_3$)

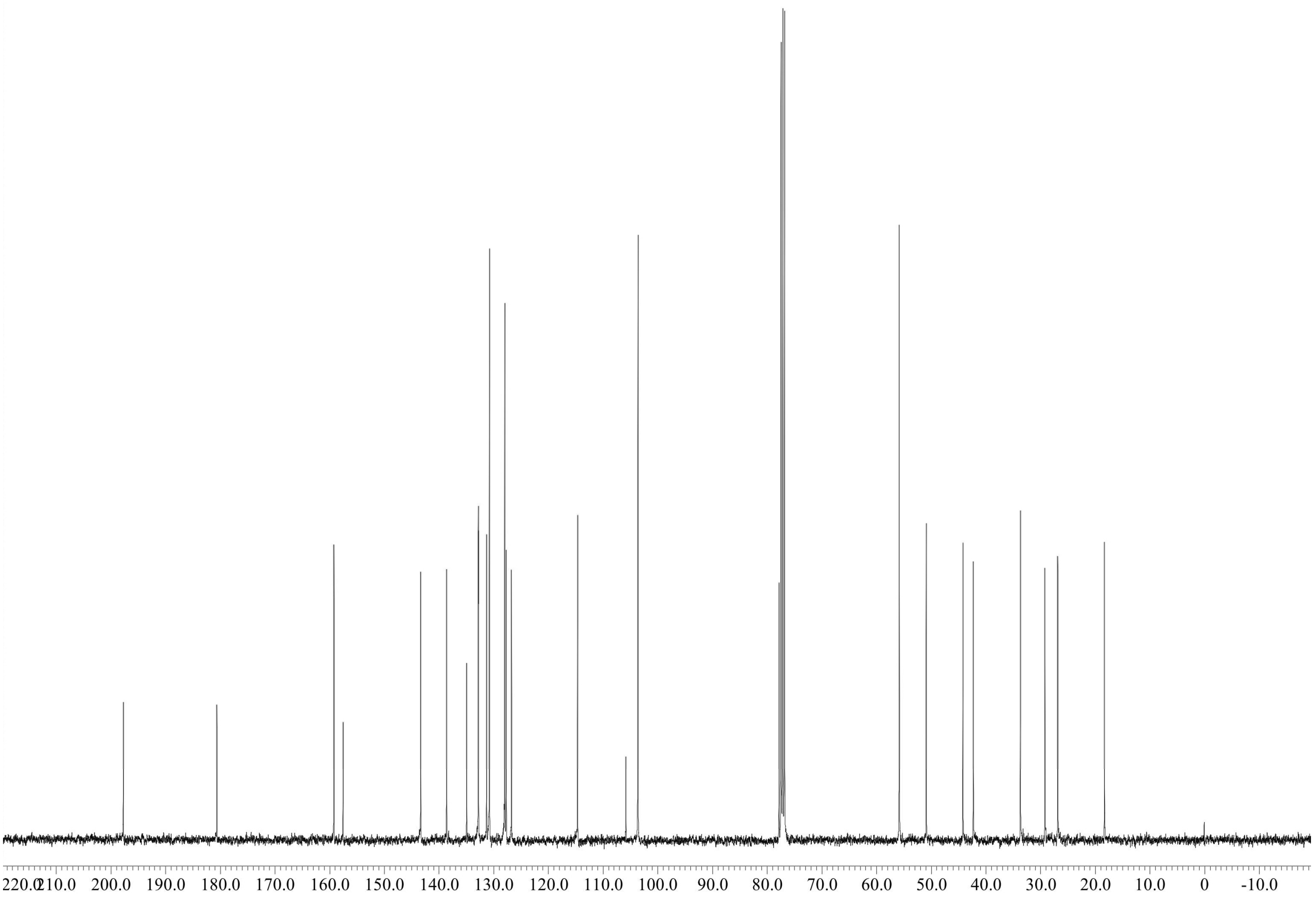


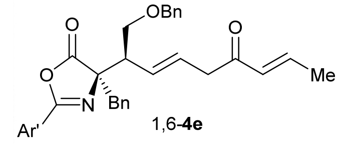




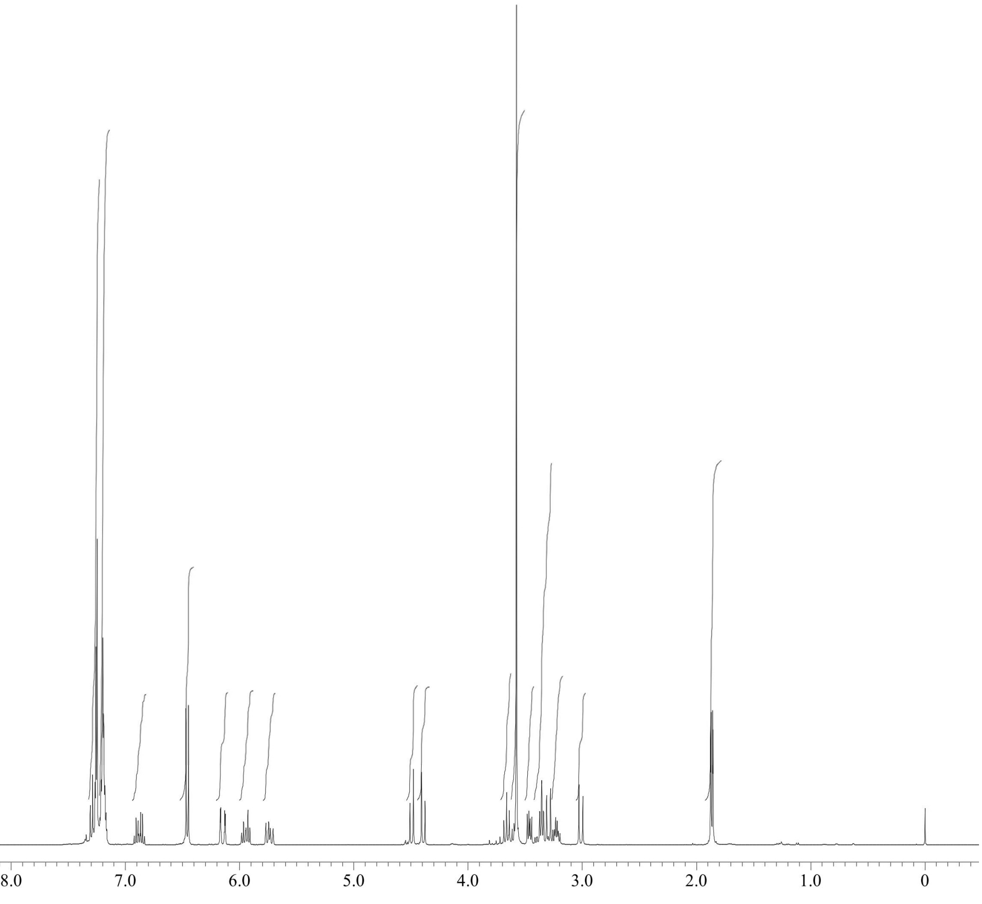
1,6-**4d**
(Ar' = 2,6-$(MeO)_2C_6H_3$)

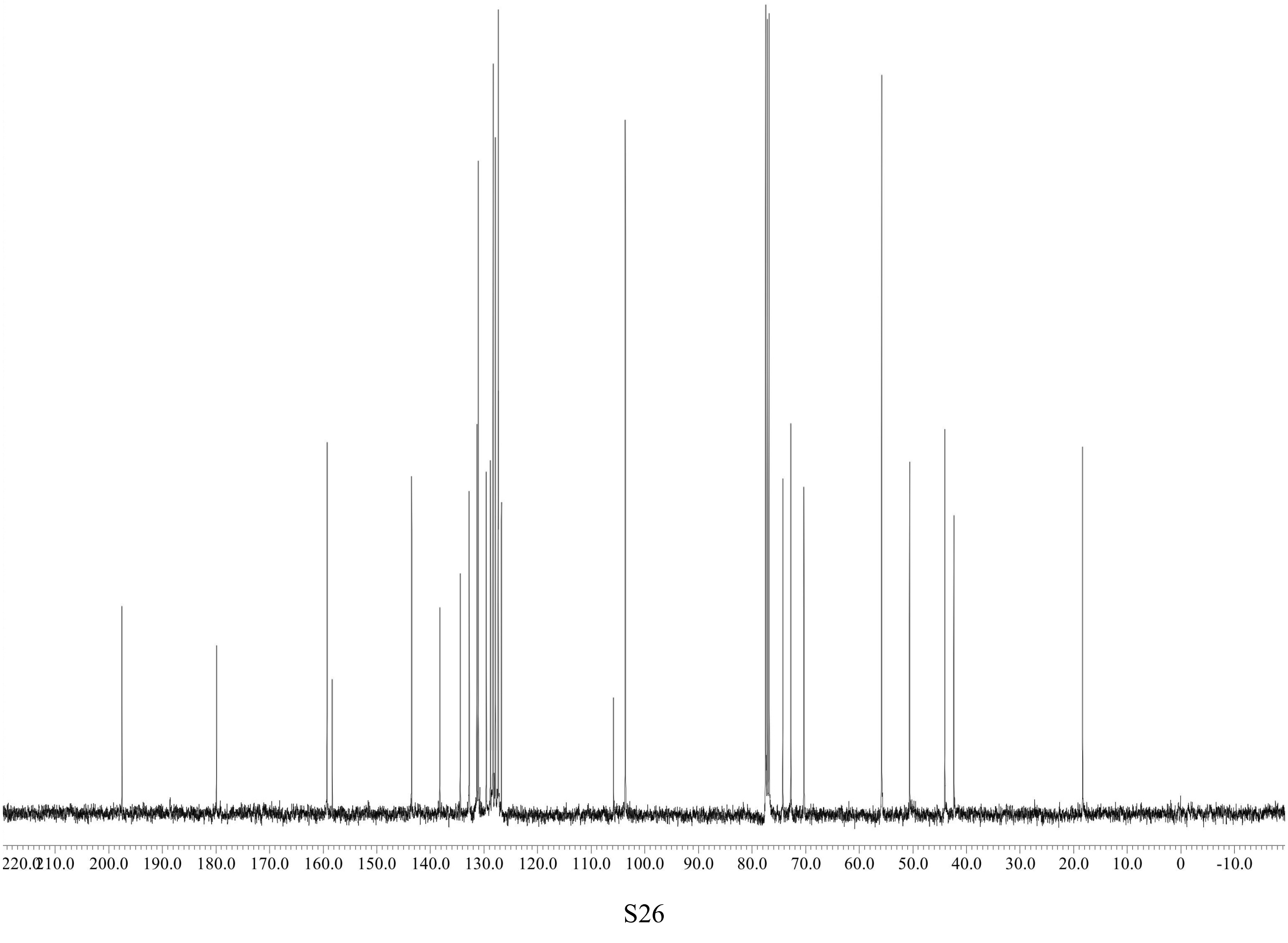


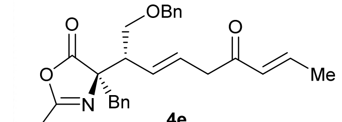




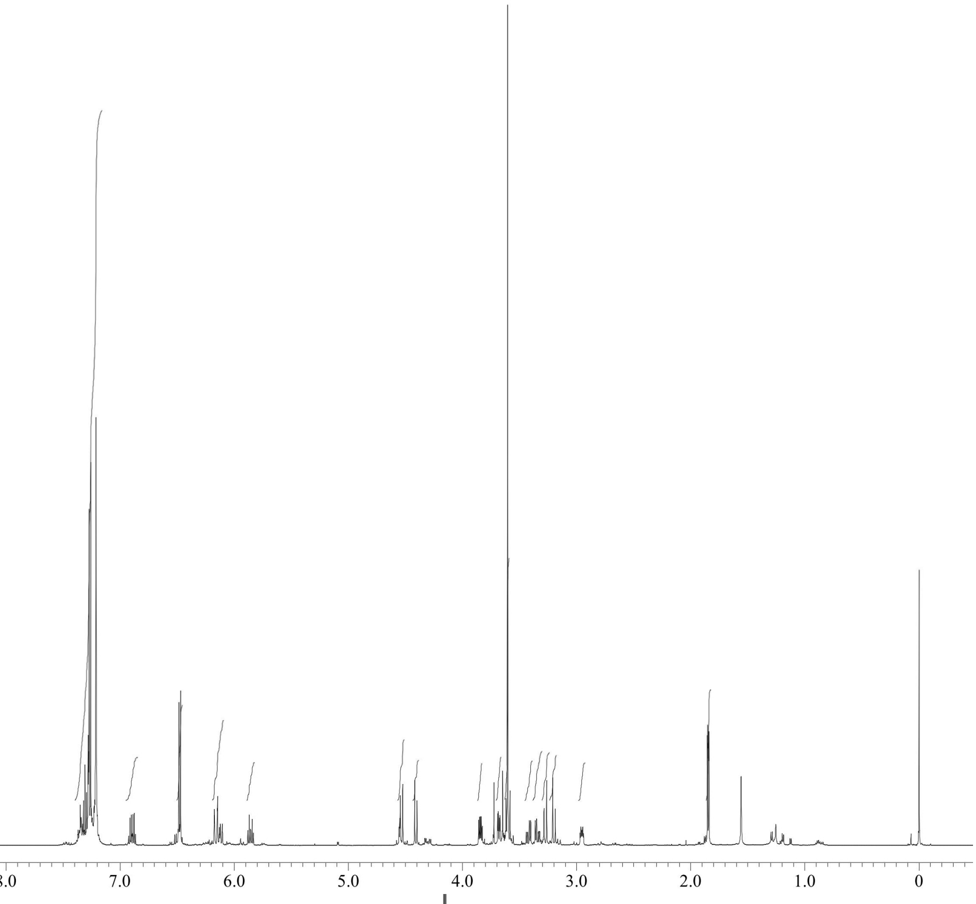
1,6-**4e**
(Ar' = 2,6-$(MeO)_2C_6H_3$)

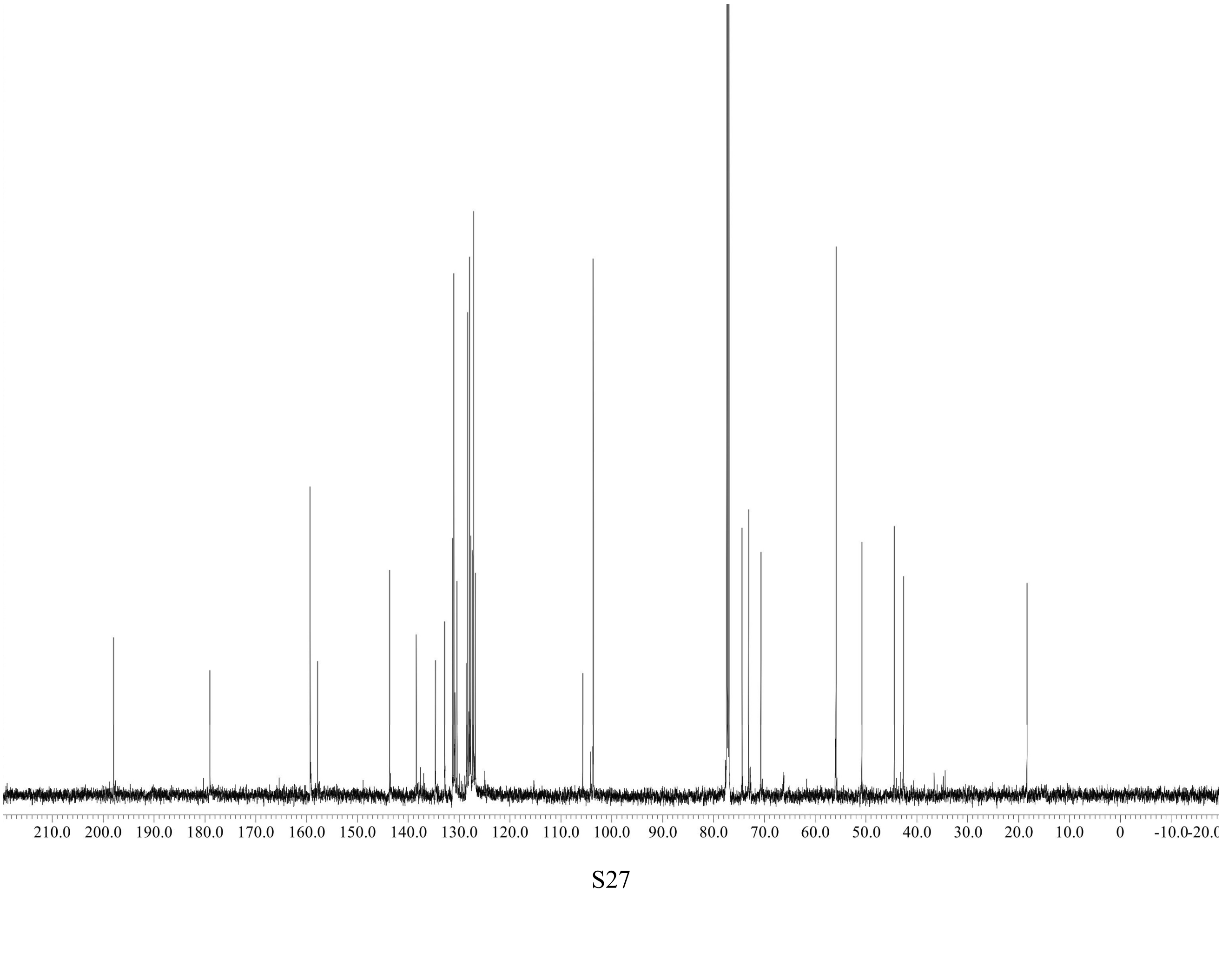


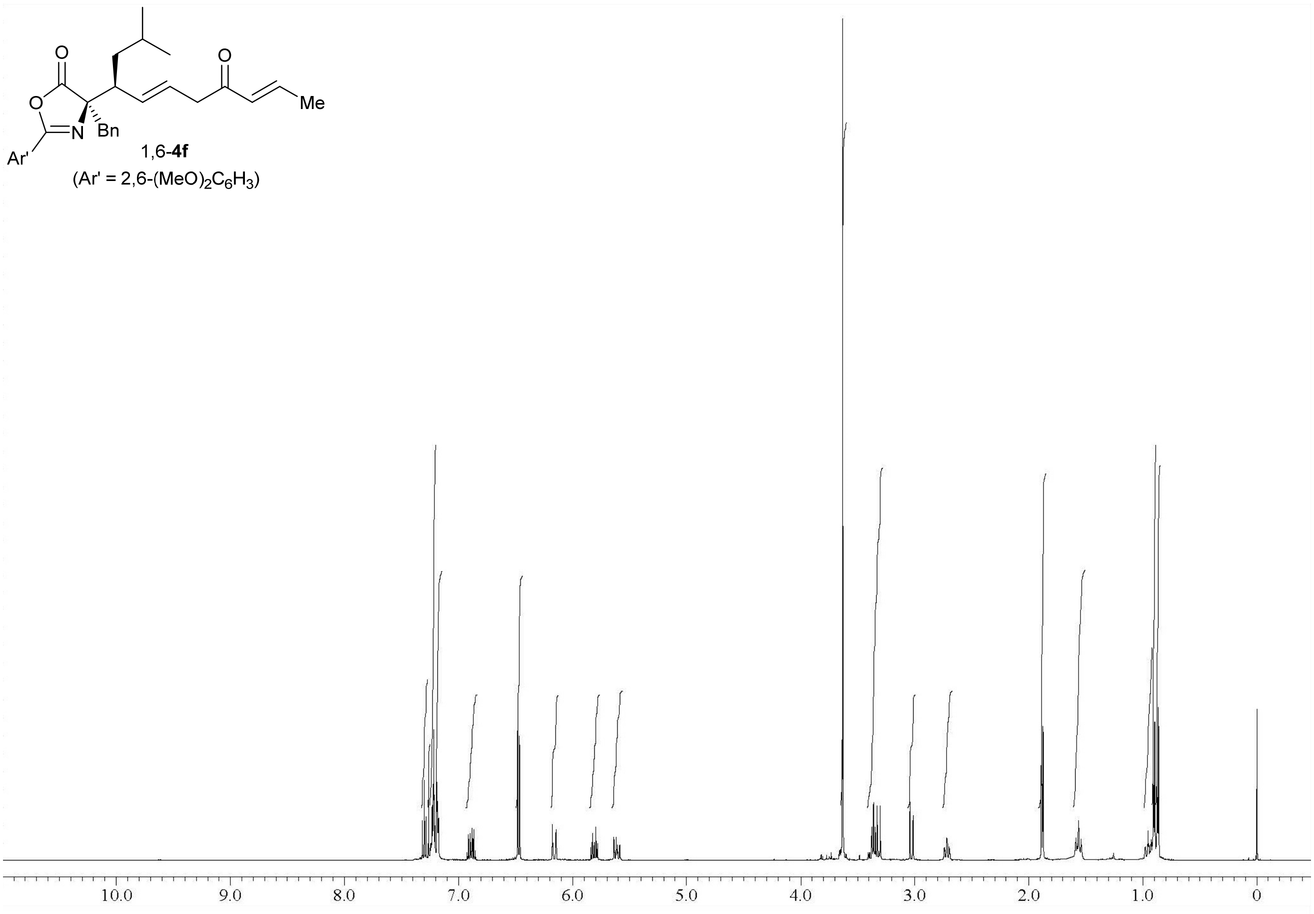




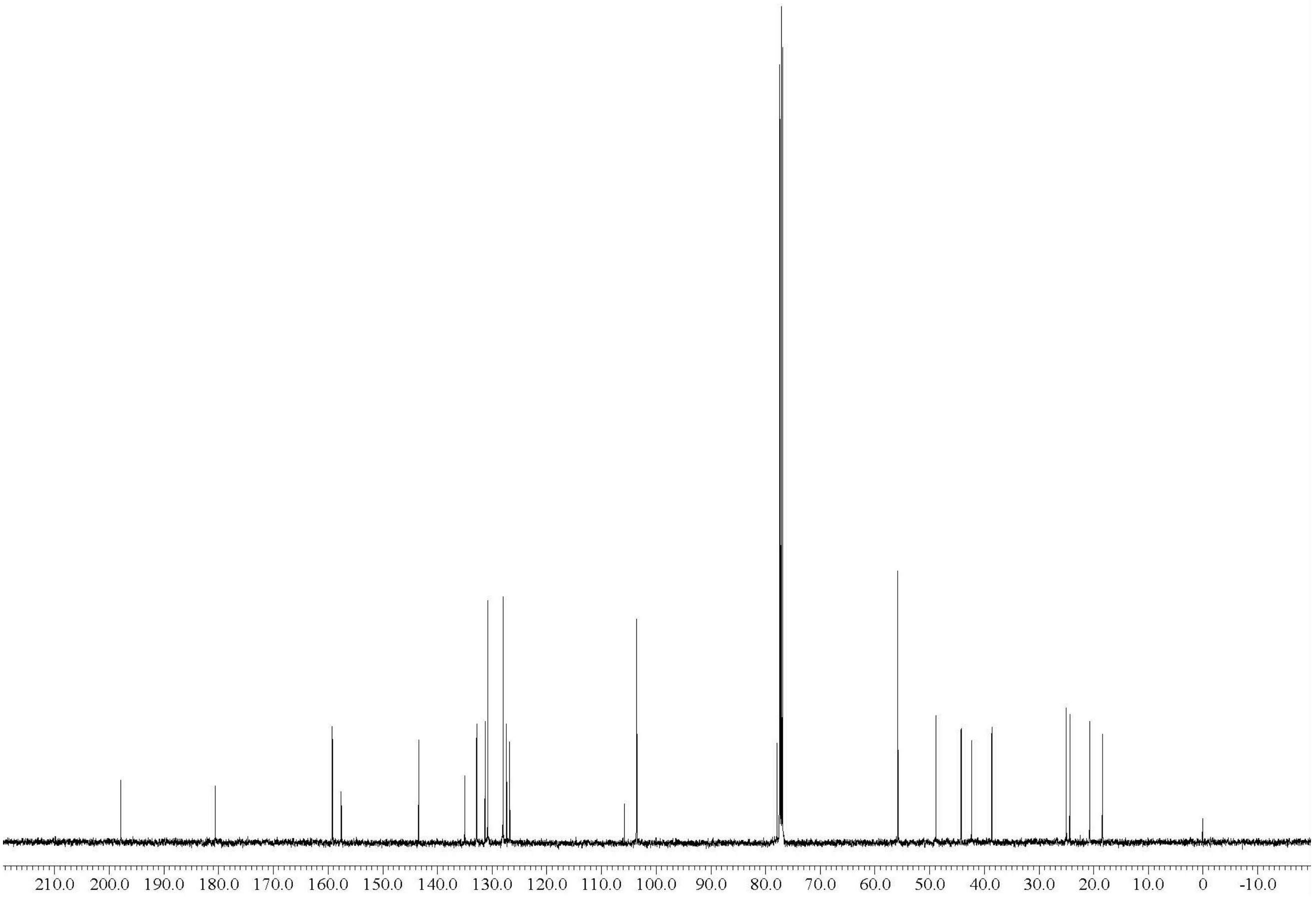
4e
(Ar' = 2,6-(MeO)$_2$C$_6$H$_3$)



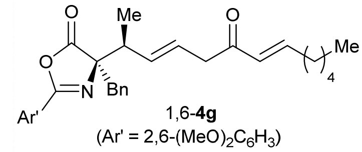




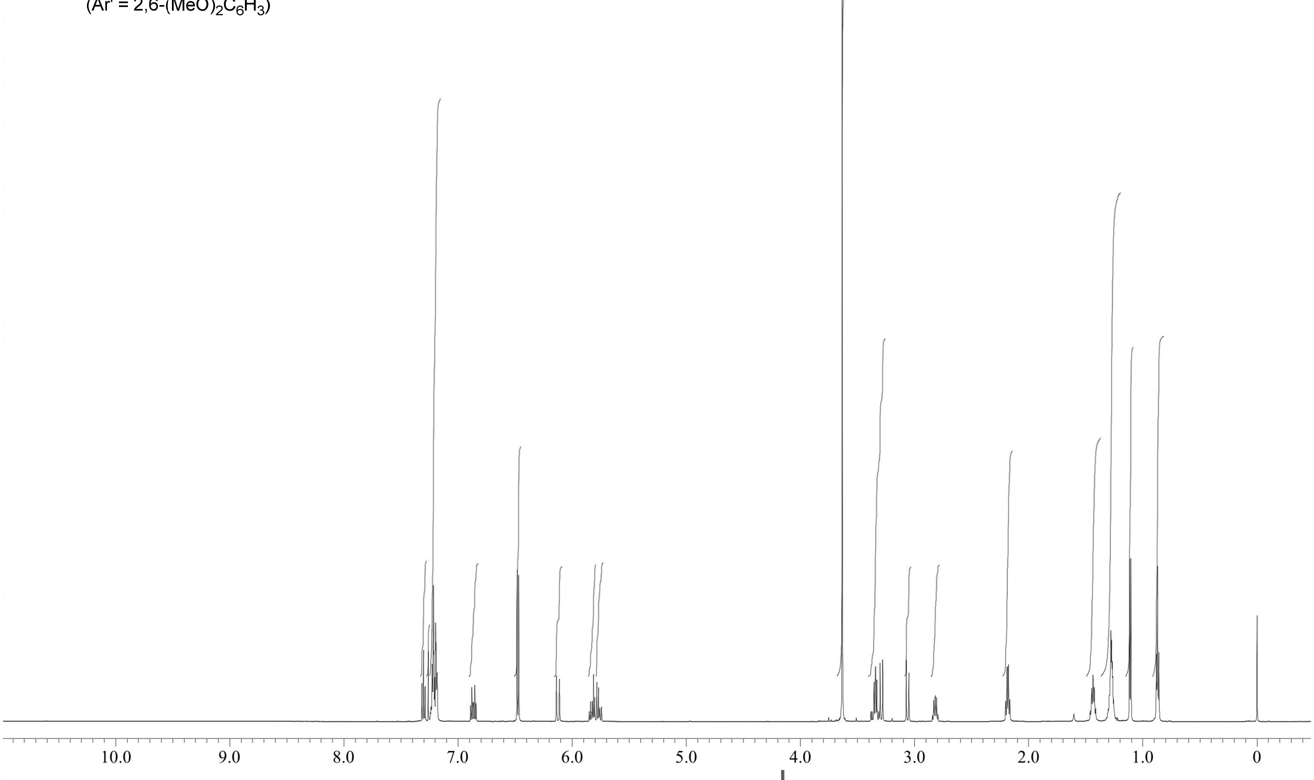
Me
Bn
Ar'
1,6-4f
(Ar' = 2,6-(MeO)2C6H3)
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

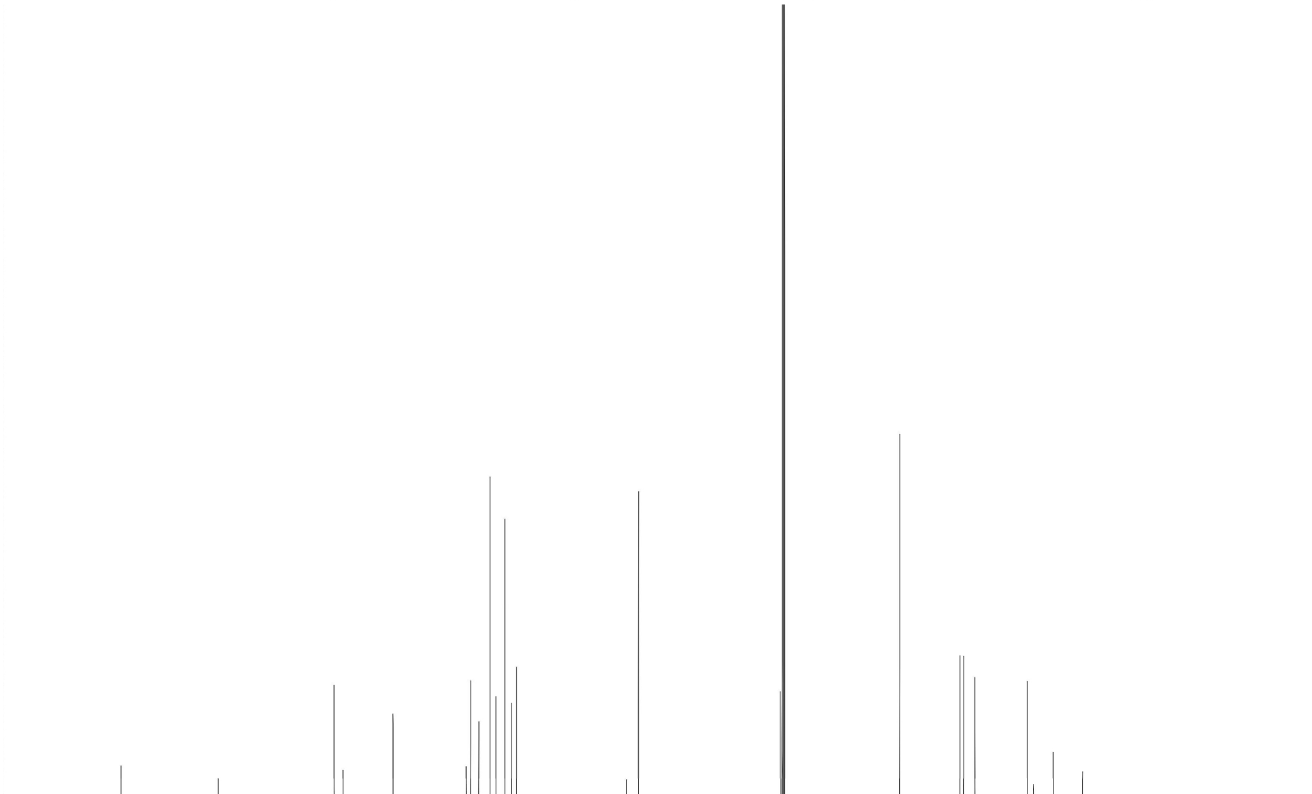


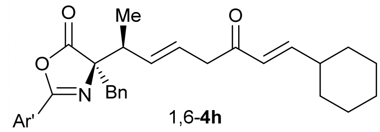
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0



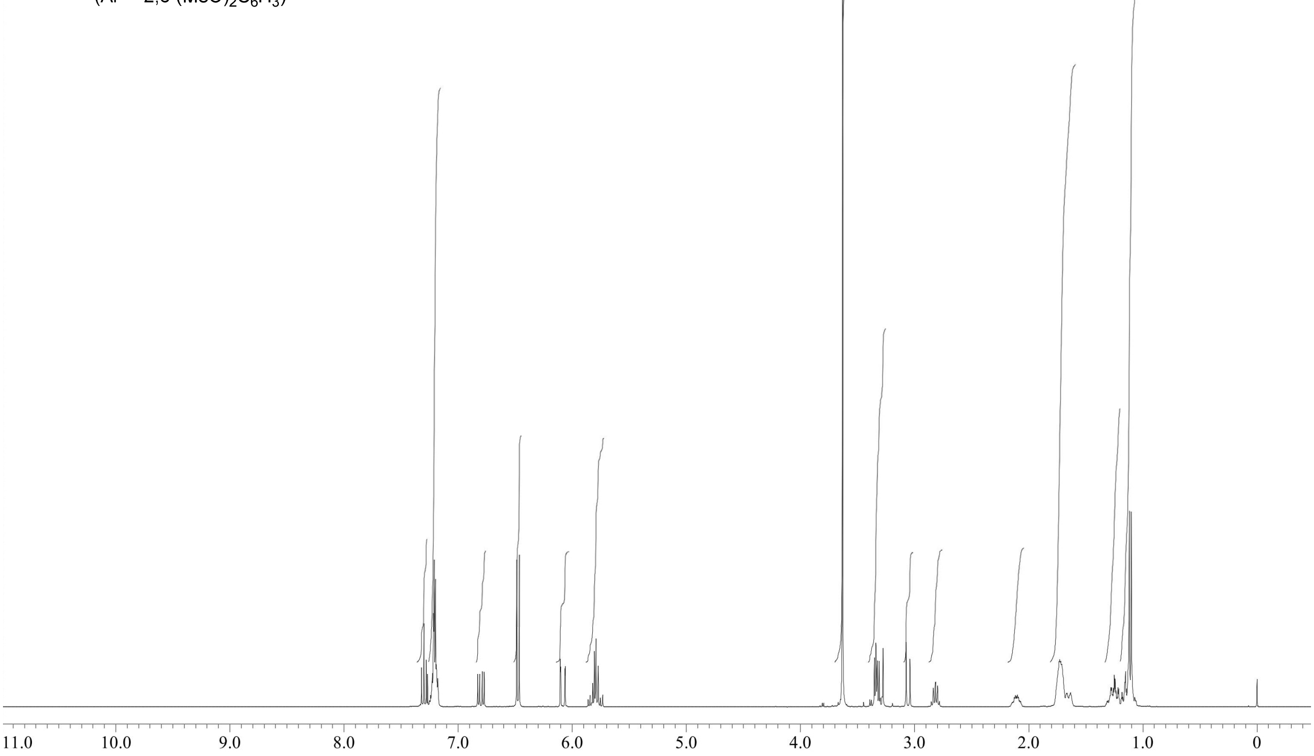
1,6-**4g**
(Ar' = 2,6-(MeO)$_2$C$_6$H$_3$)

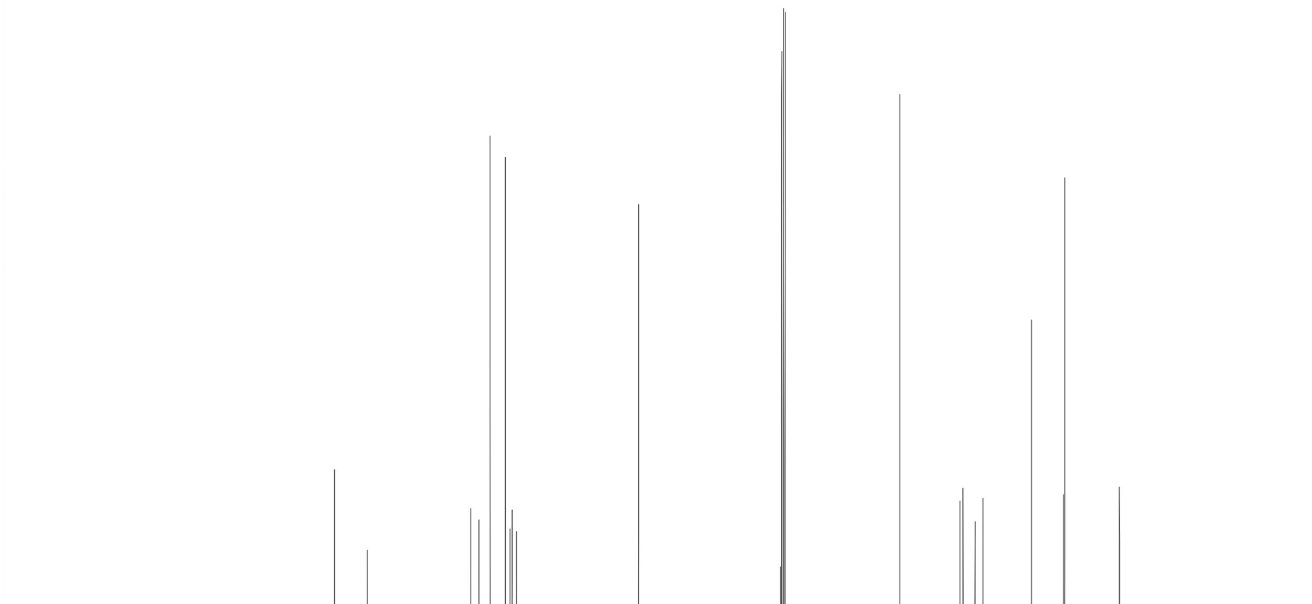


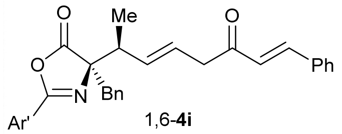




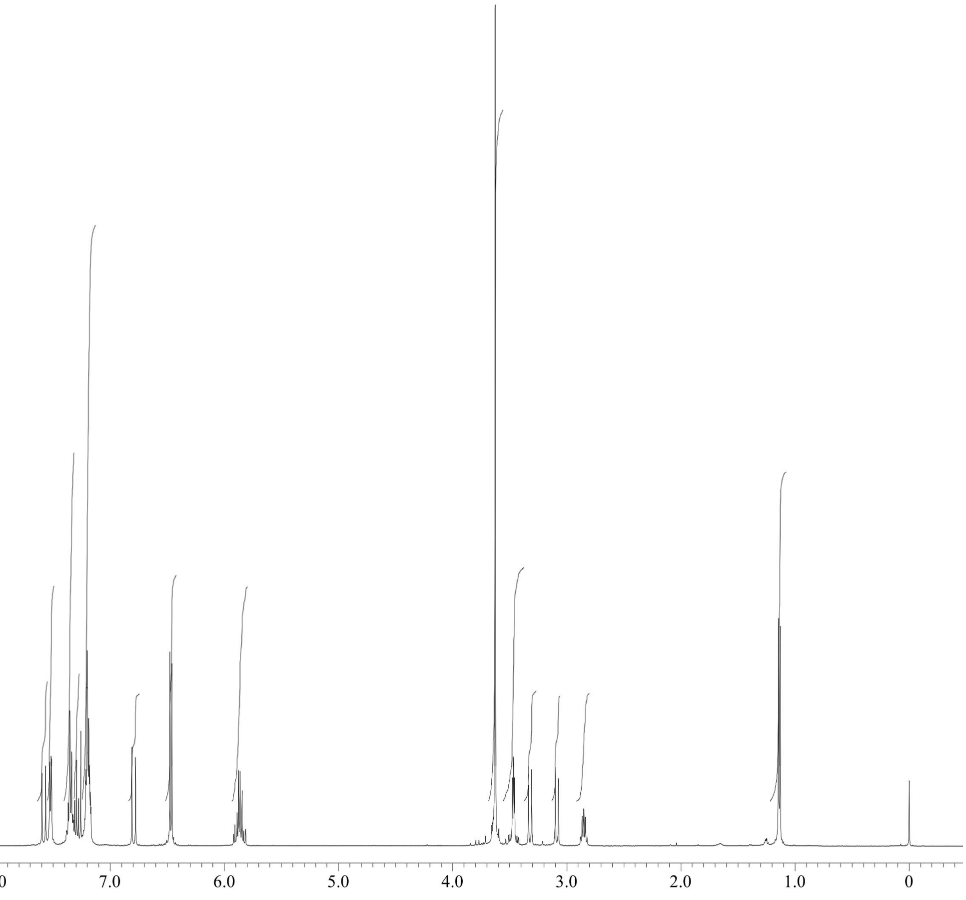
1,6-**4h**
(Ar' = 2,6-(MeO)$_2$C$_6$H$_3$)

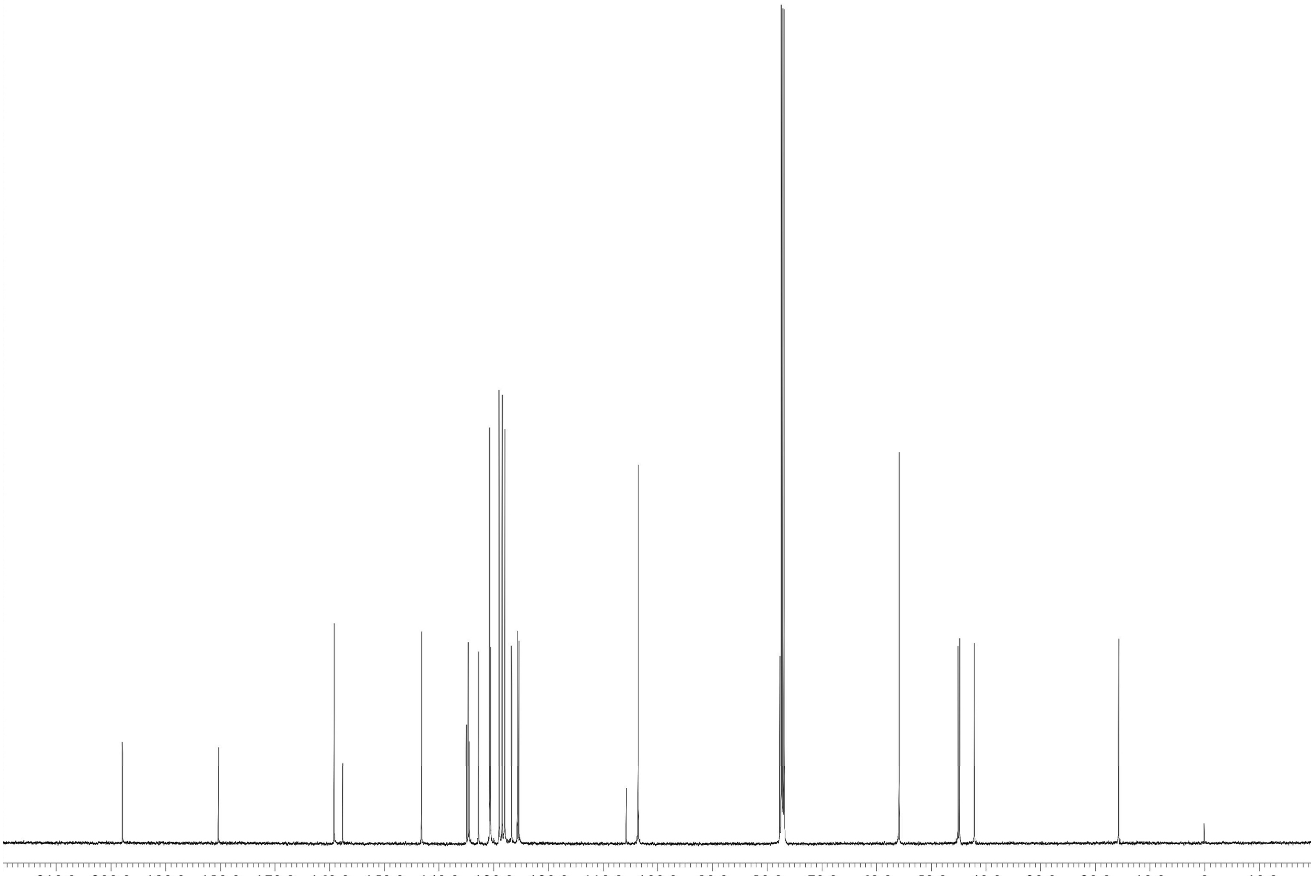


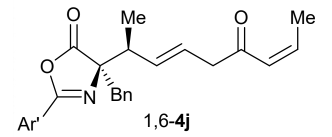




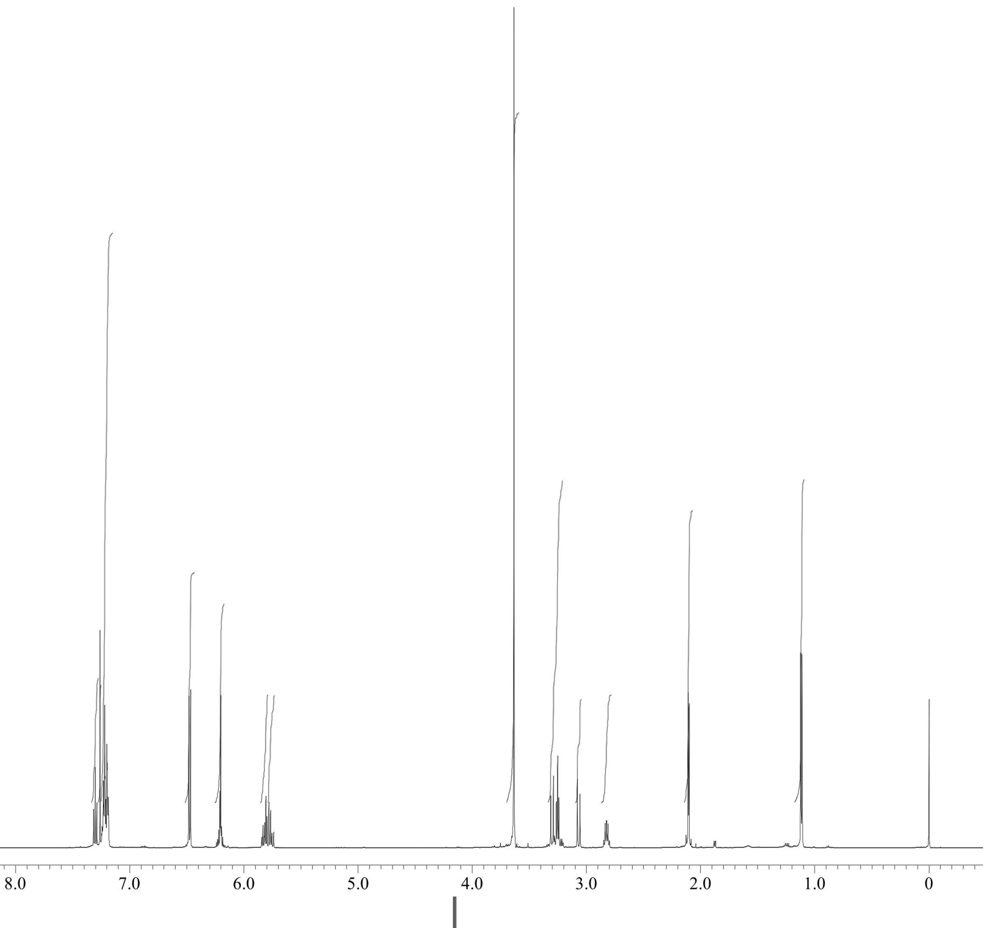
1,6-**4i**
(Ar' = 2,6-(MeO)$_2$C$_6$H$_3$)

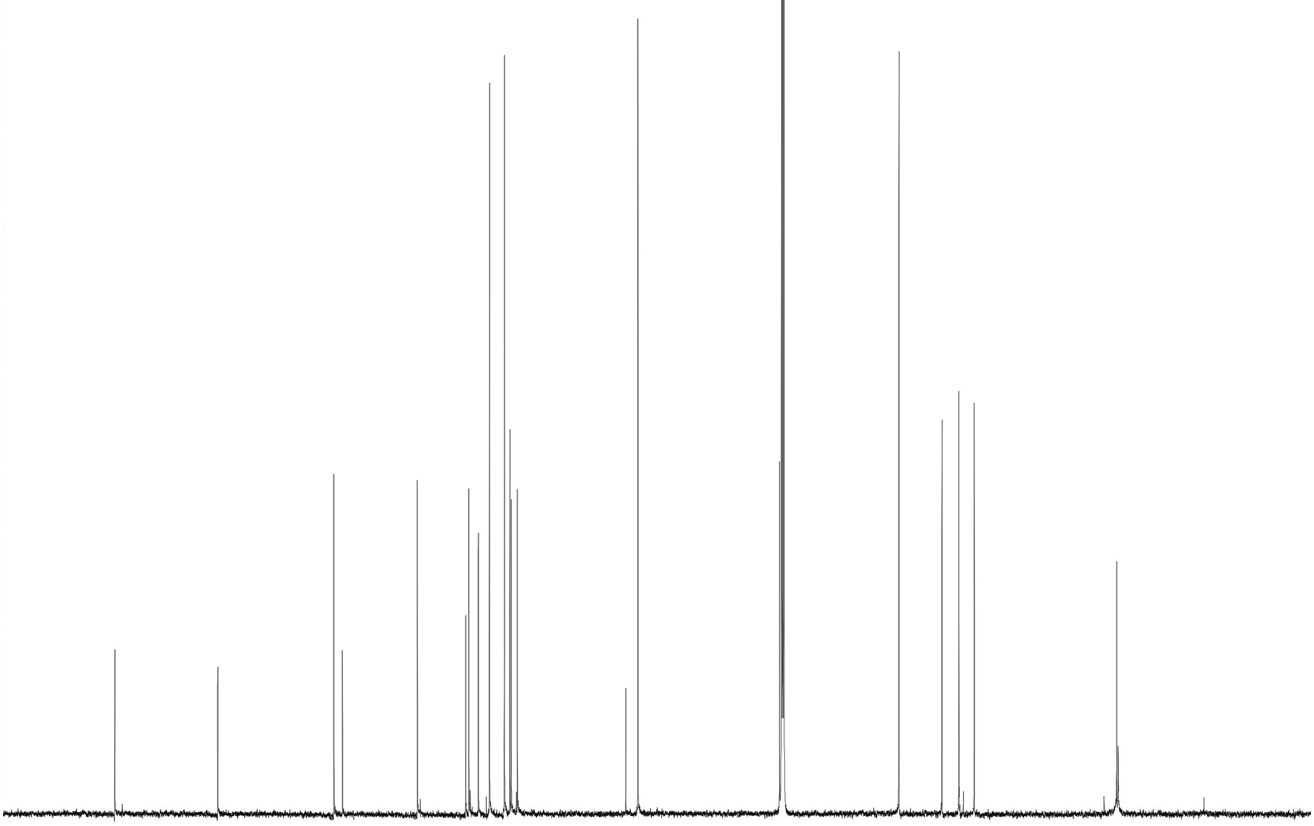


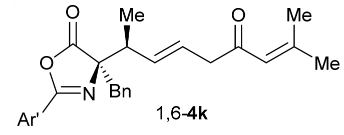




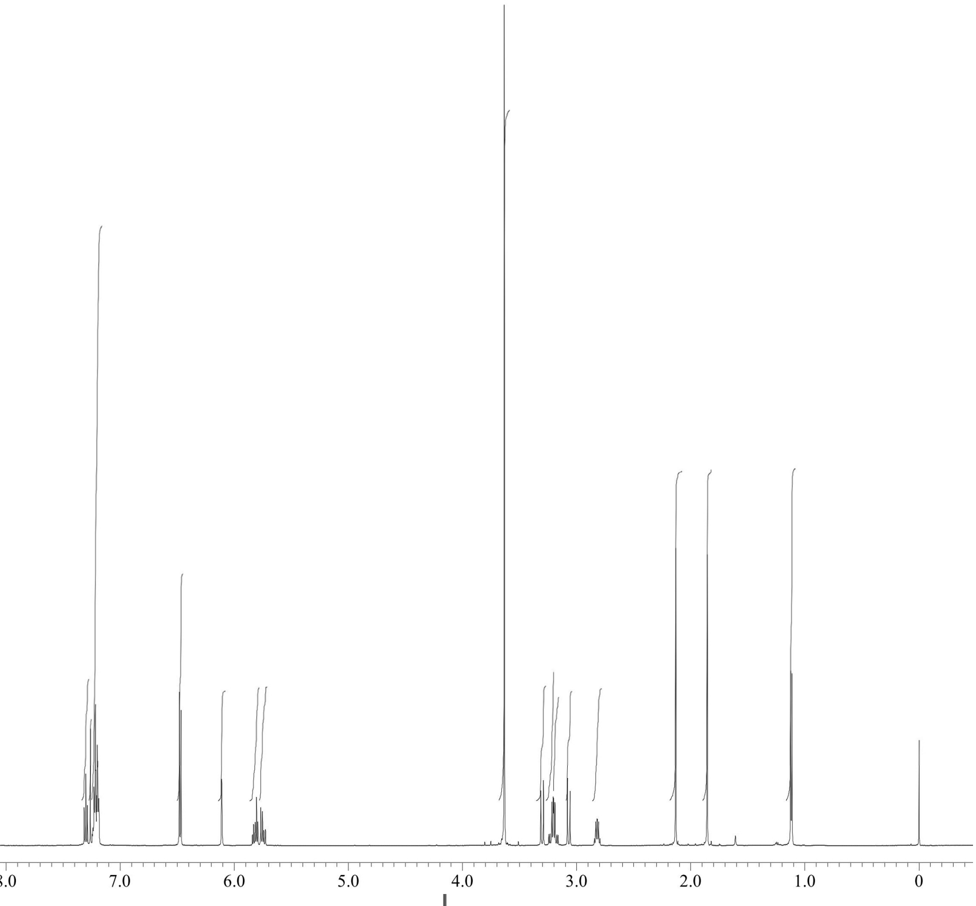
1,6-**4j**
(Ar' = 2,6-$(MeO)_2C_6H_3$)

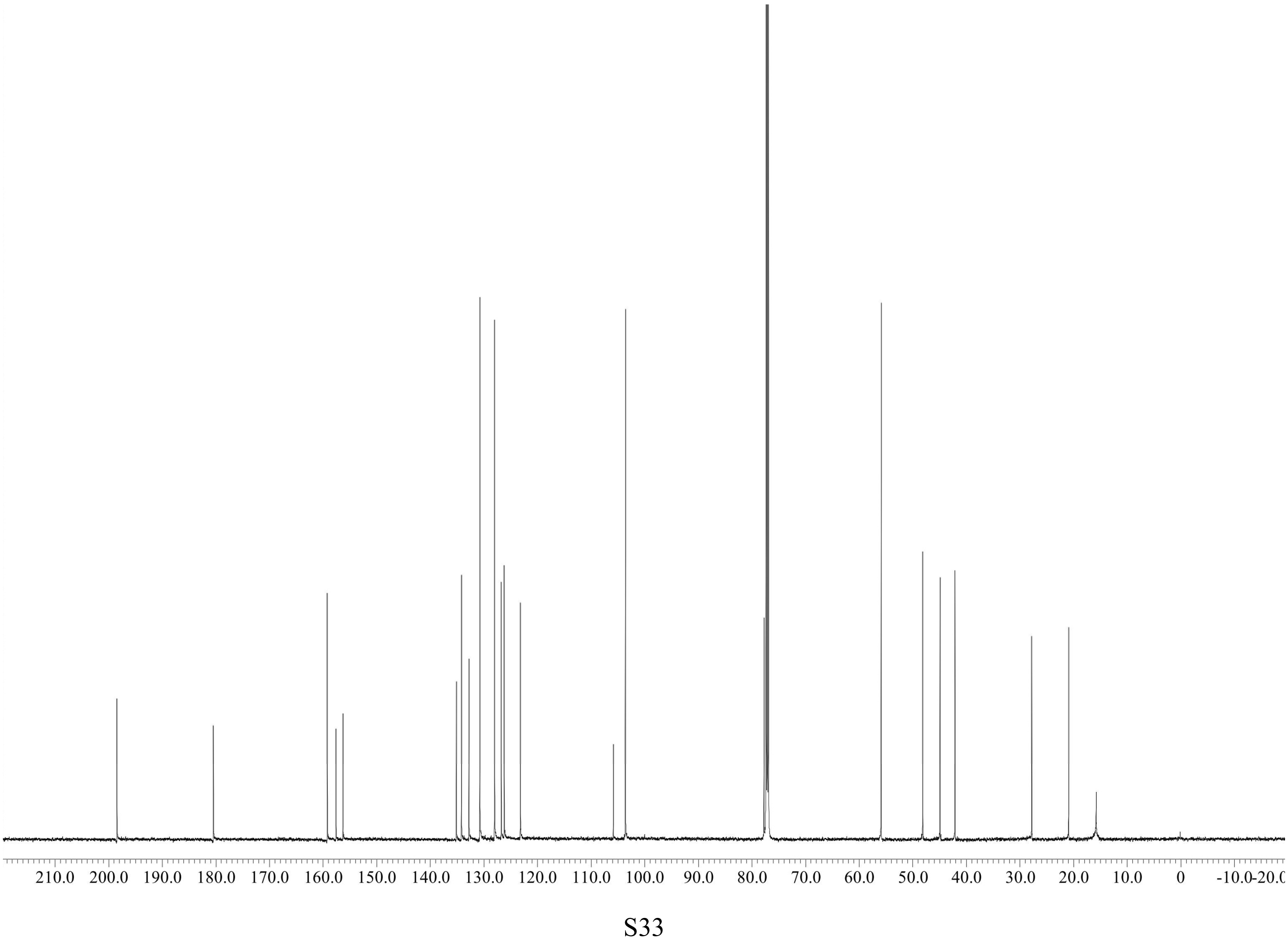


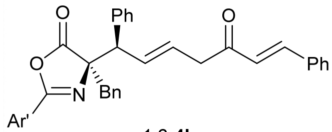




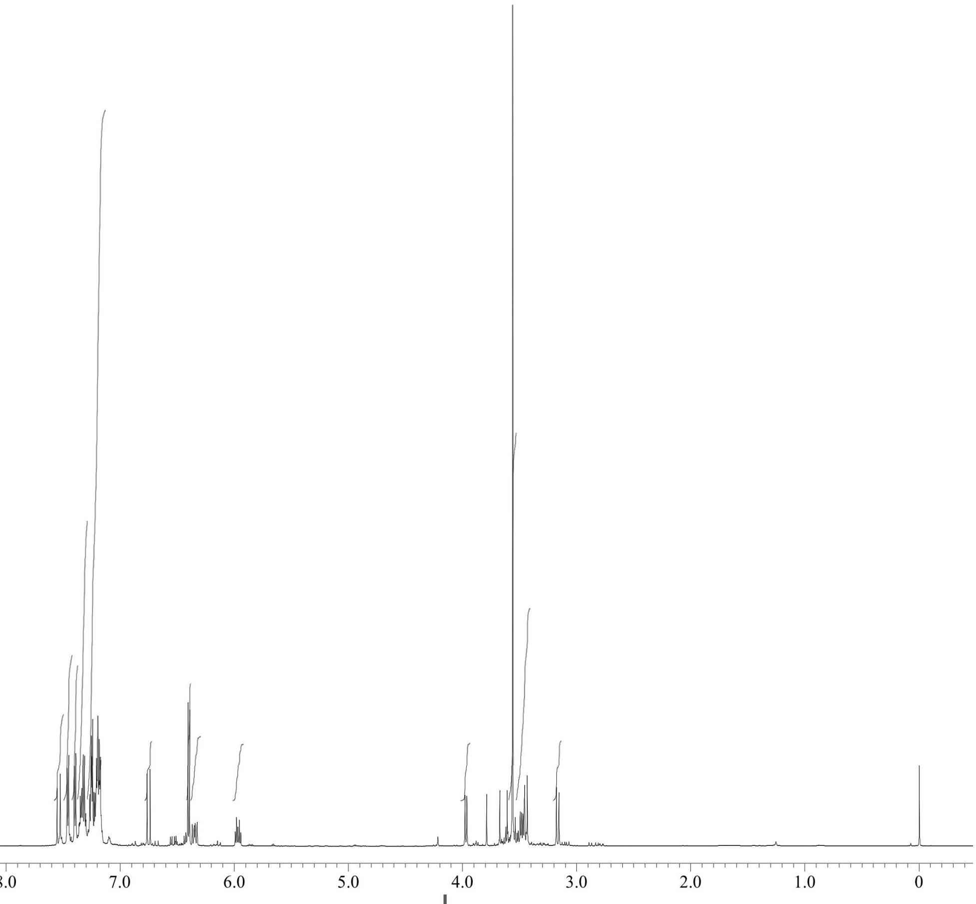
1,6-**4k**
(Ar' = 2,6-$(MeO)_2C_6H_3$)

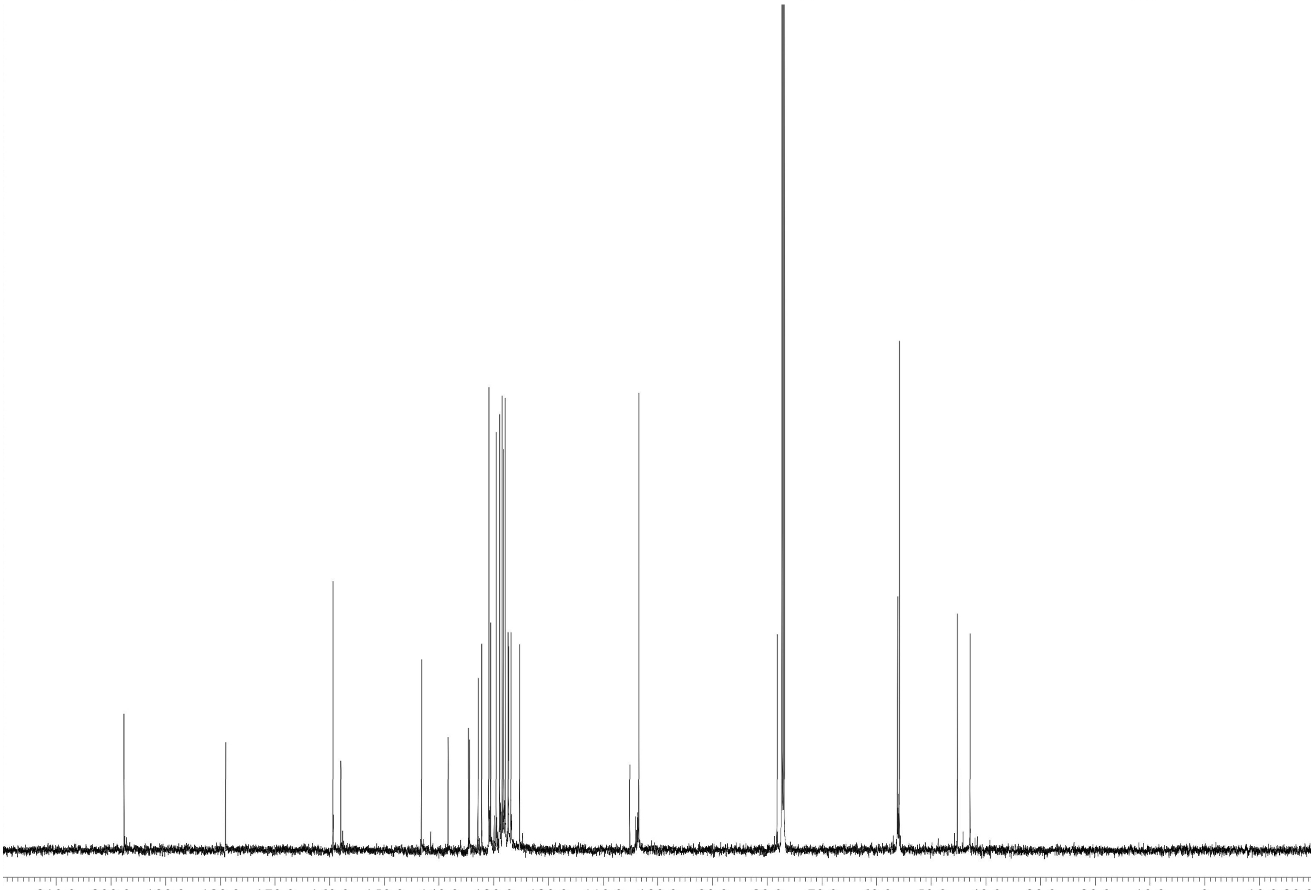


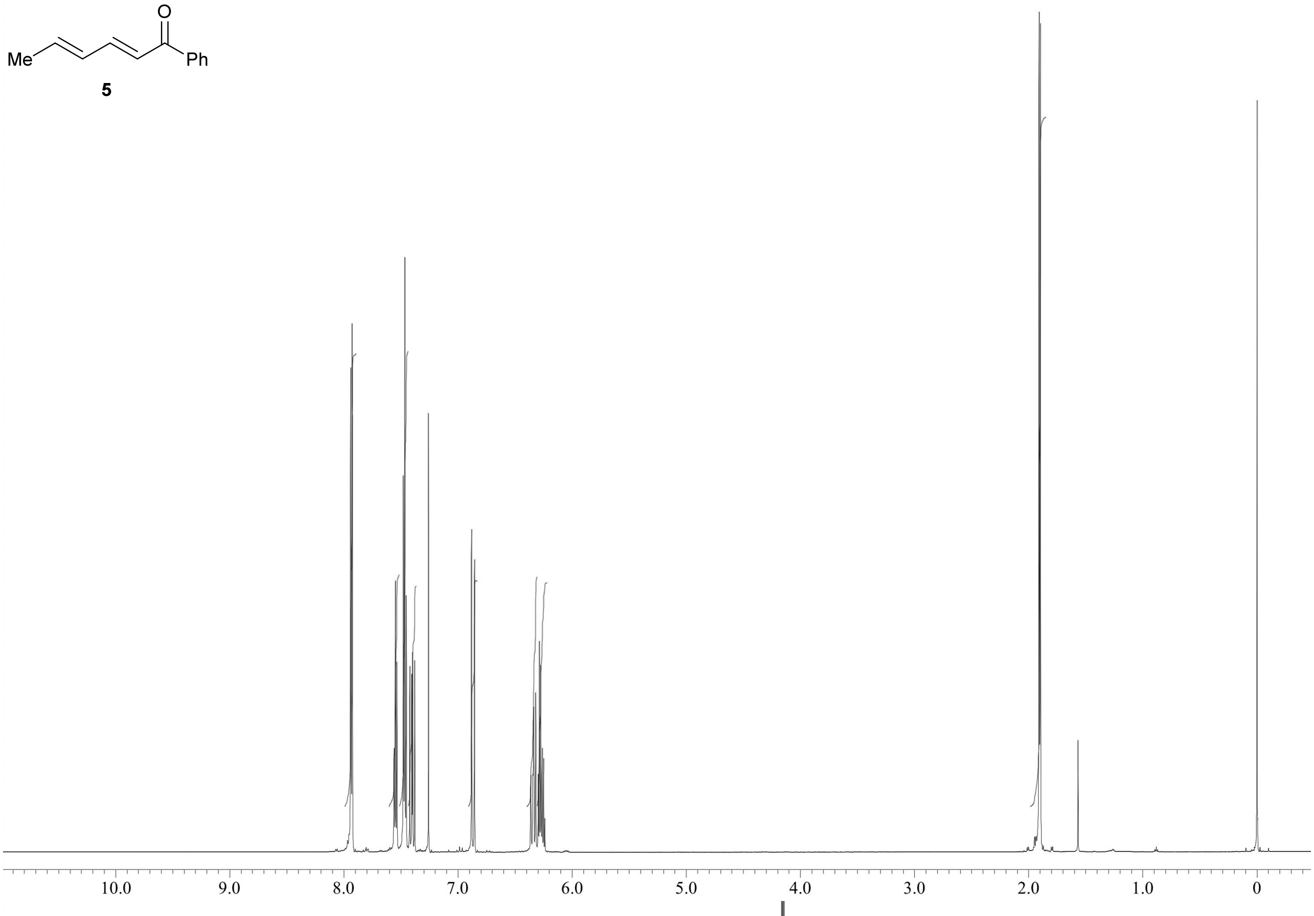


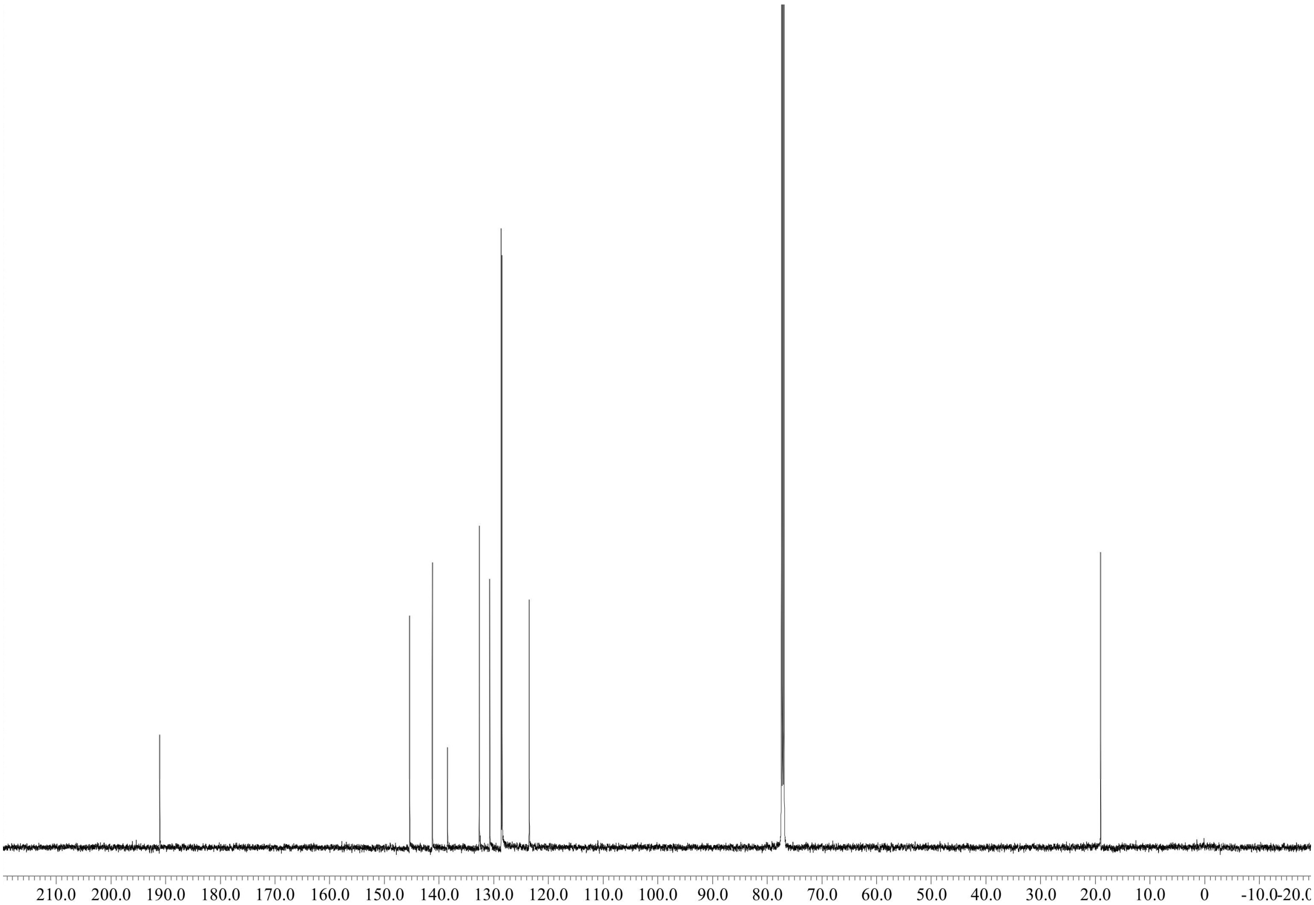


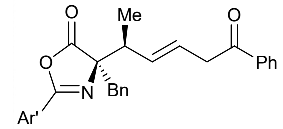
1,6-**4l**





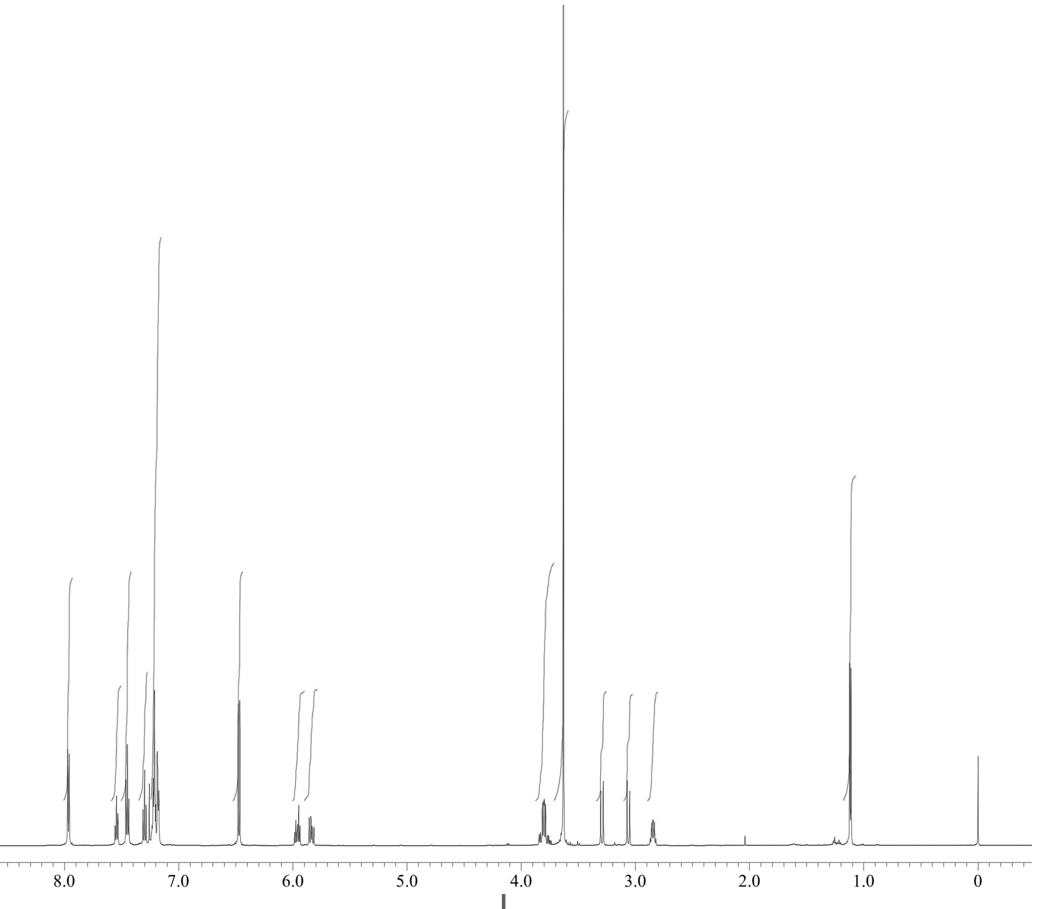

Me
O
Ph
5
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0


210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0-20.0

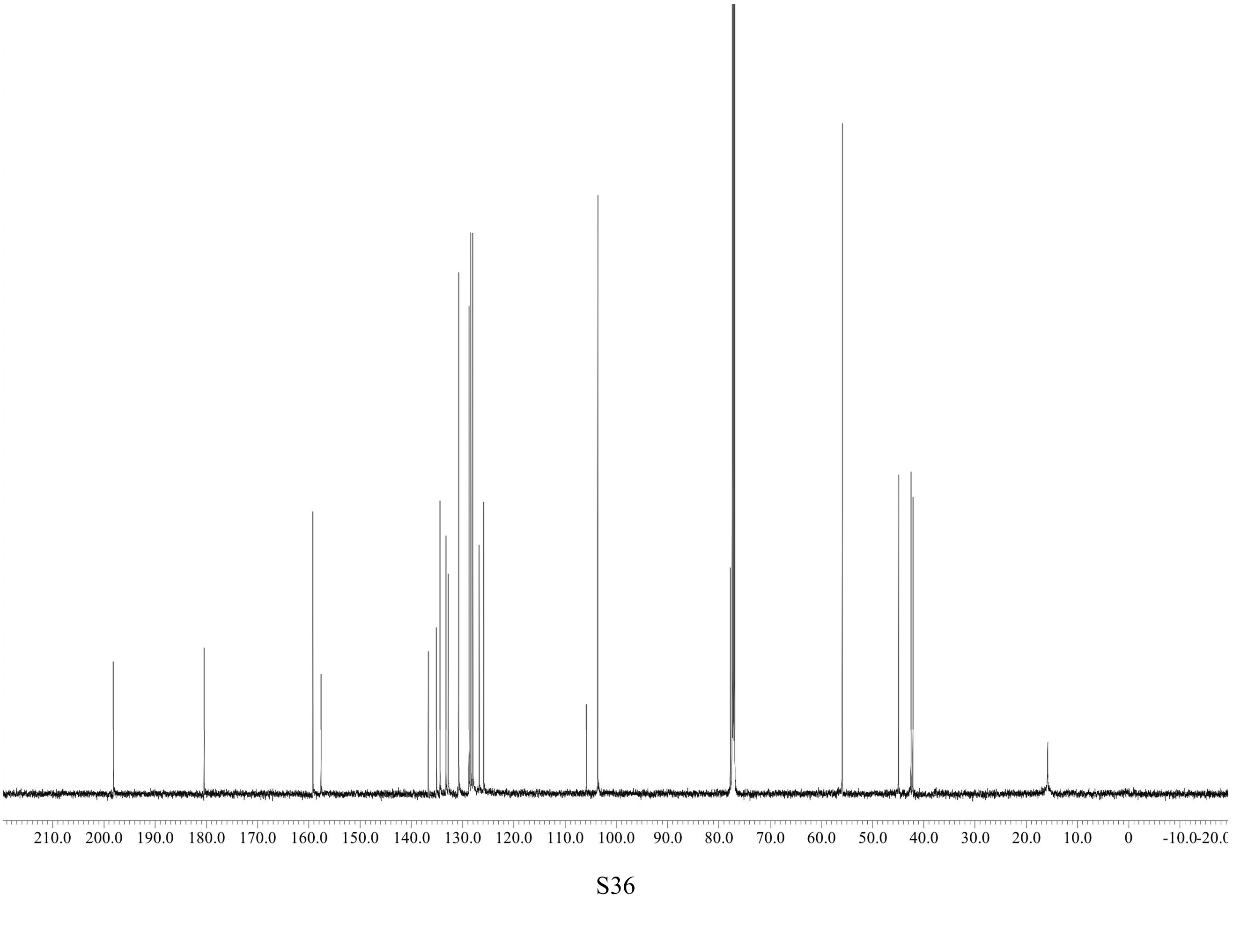


O
Me
O
O
Ph
N
Bn
Ar'

7



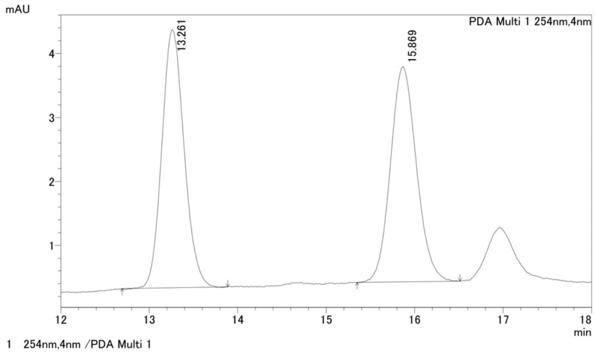
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

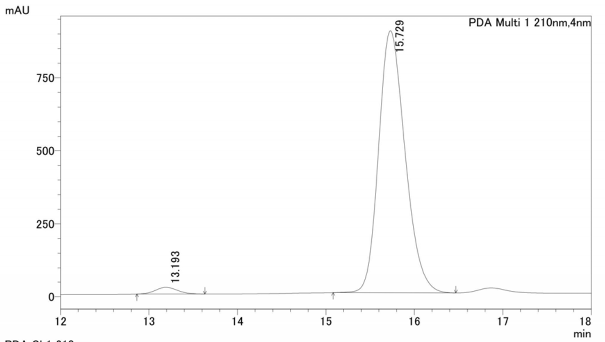


210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0-20.0

HPLC Traces:

1,6-**4a**

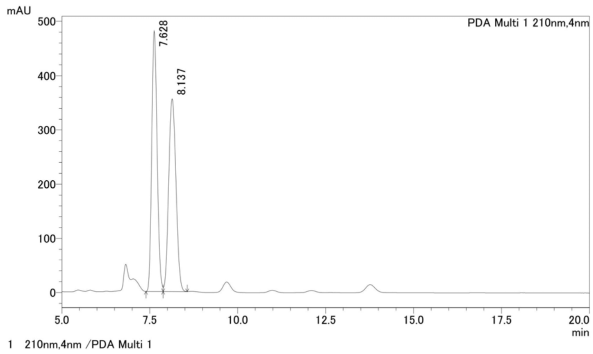


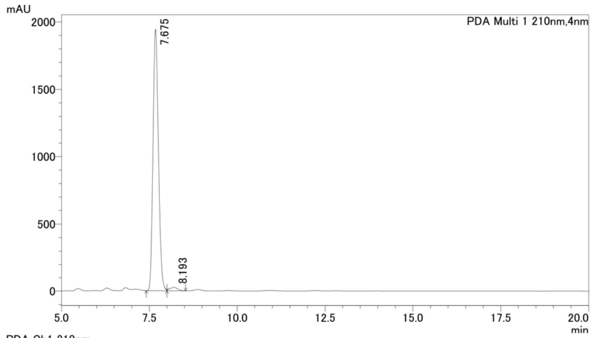


PDA Ch1 210nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	13.193	403272	23319	2.114	207/198/283
2	15.729	18676571	897098	97.886	206/284
合計		19079843	920417	100.000	

1,6-**4b**

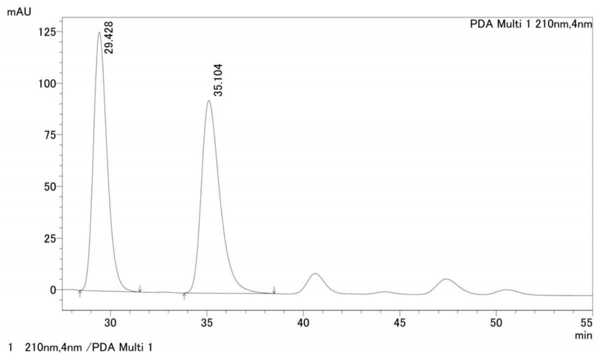


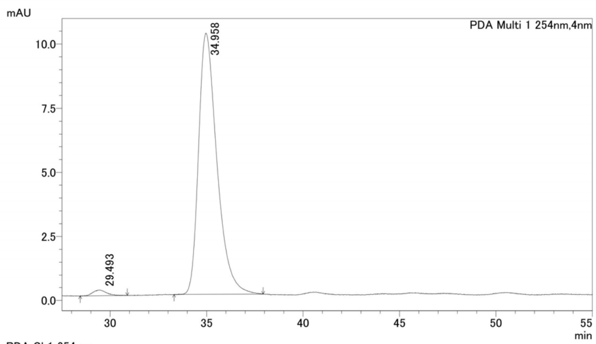


PDA Ch1 210nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	7.675	20821734	1941324	98.218	203/284
2	8.193	377874	25132	1.782	204/285
合計		21199609	1966455	100.000	

1,6-**4c**

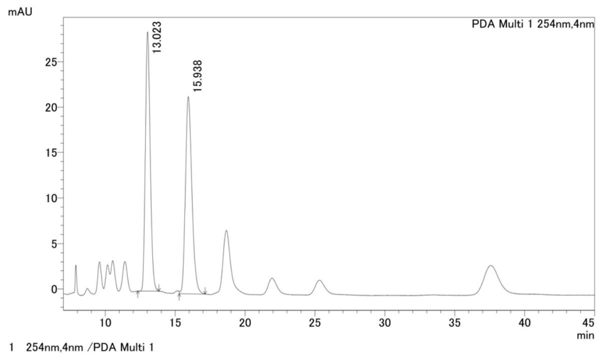


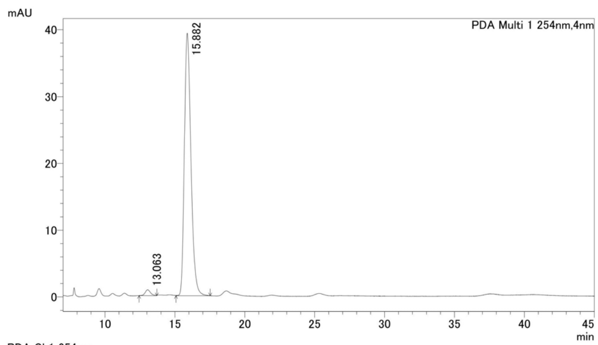


PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	29.493	11136	224	1.622	196
2	34.958	675284	10177	98.378	207/284
合計		686420	10401	100.000	

1,6-**4d**

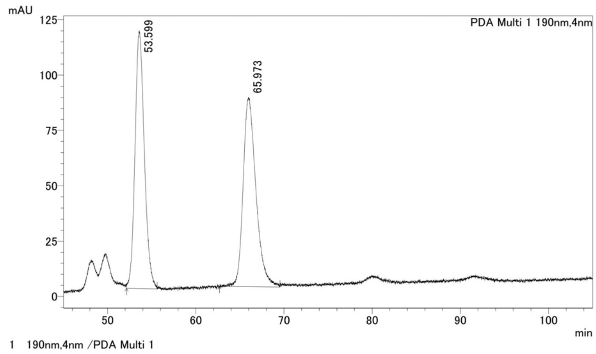


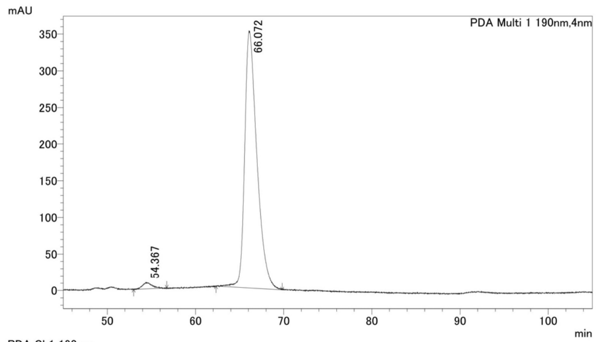


PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	13.063	23590	868	1.803	197/208/283
2	15.882	1285135	39281	98.197	207/284
合計		1308725	40150	100.000	

1,6-**4e**

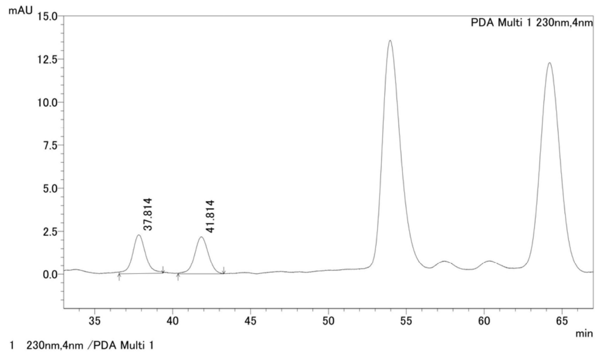


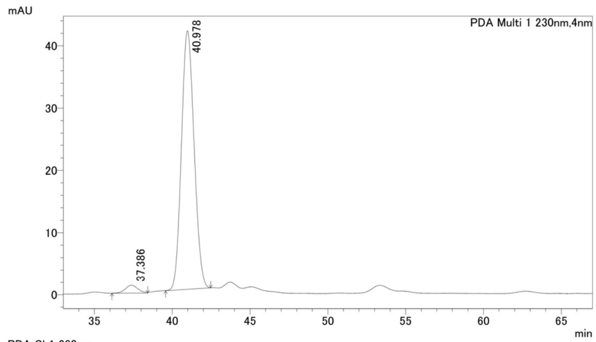


PDA Ch1 190nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	54.367	650738	9067	1.884	285
2	66.072	33885356	350957	98.116	205/285
合計		34536094	360024	100.000	

minor diastereomer of 1,6-**4e**

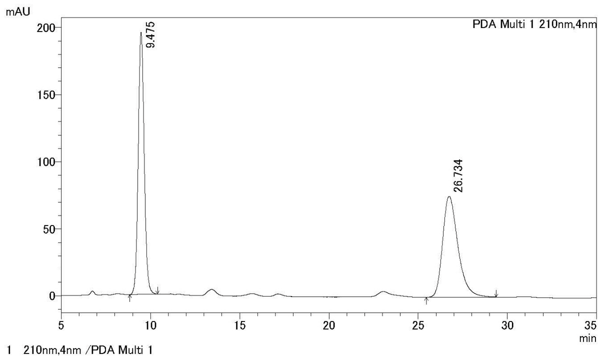


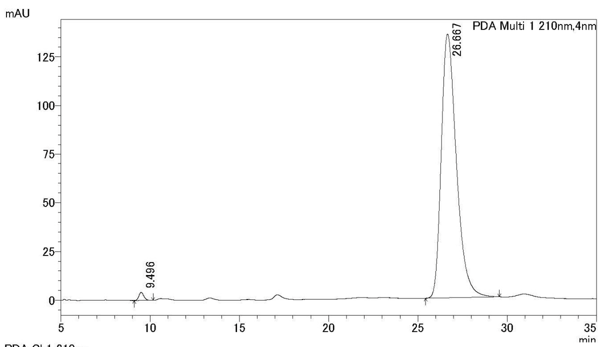


PDA Ch1 230nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	37.386	71464	1280	2.943	269
2	40.978	2357063	41517	97.057	206/284
合計		2428527	42797	100.000	

1,6-**4f**

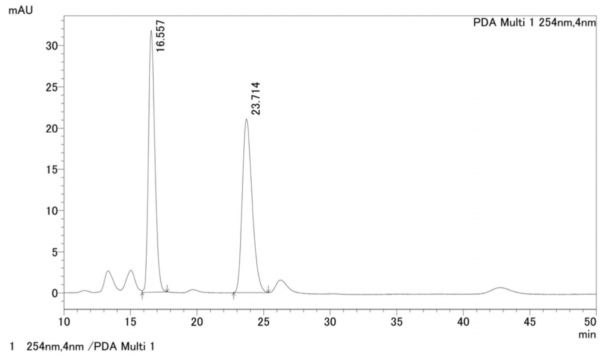


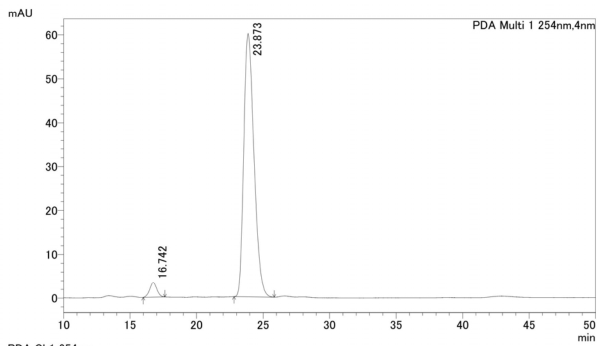


PDA Ch1 210nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	9.496	80924	4131	1.006	208
2	26.667	7964128	135434	98.994	206/284
合計		8045051	139564	100.000	

1,6-**4g**

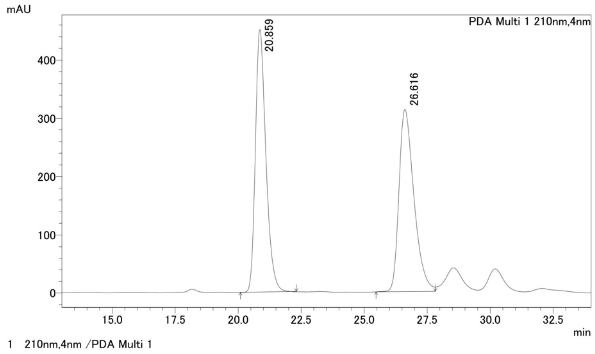


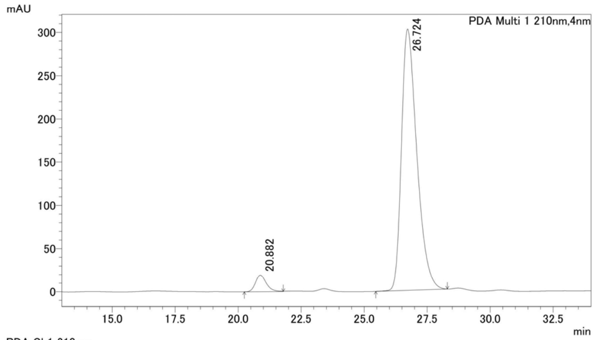


PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	16.742	125536	3363	3.764	207/283
2	23.873	3209958	60005	96.236	207/284
合計		3335494	63369	100.000	

1,6-**4h**

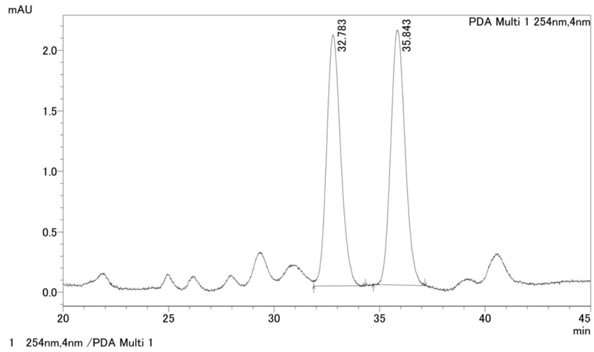


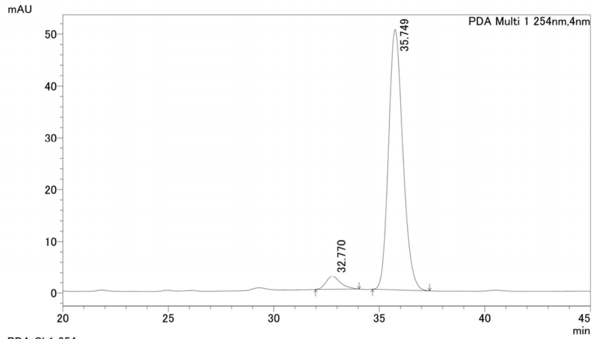


PDA Ch1 210nm

ピーク#	保持時間	面積	高さ	面積%	λmax
1	20.882	582586	19362	4.337	204/284
2	26.724	12851076	302323	95.663	204/284
合計		13433661	321685	100.000	

1,6-**4i**

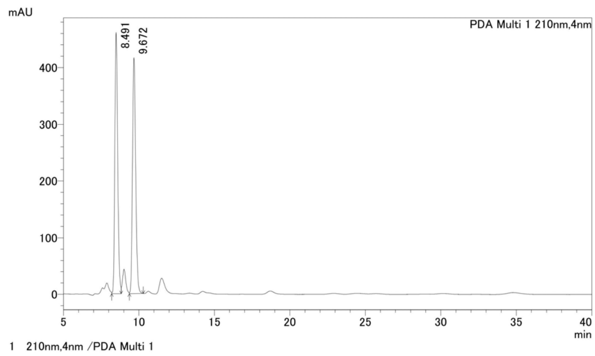


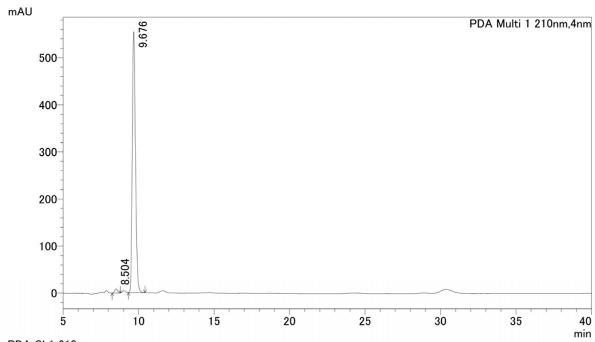


PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λmax
1	32.770	122492	2570	4.900	204/284
2	35.749	2377421	50287	95.100	205/285
合計		2499913	52858	100.000	

1,6-**4j**

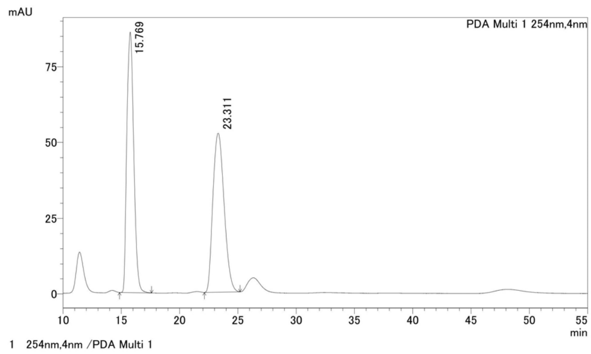


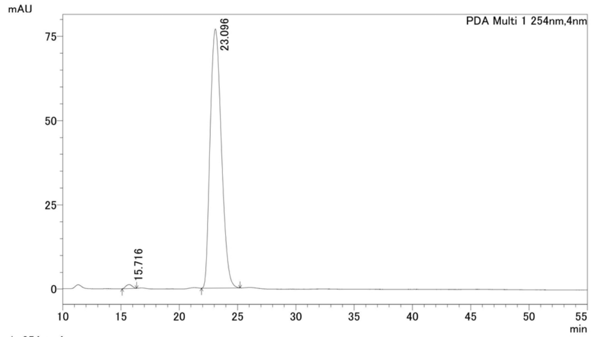


PDA Ch1 210nm

ピーク#	保持時間	面積	高さ	面積%	λmax
1	8.504	120915	8997	1.453	208
2	9.676	8202007	553888	98.547	207/284
合計		8322922	562885	100.000	

1,6-**4k**

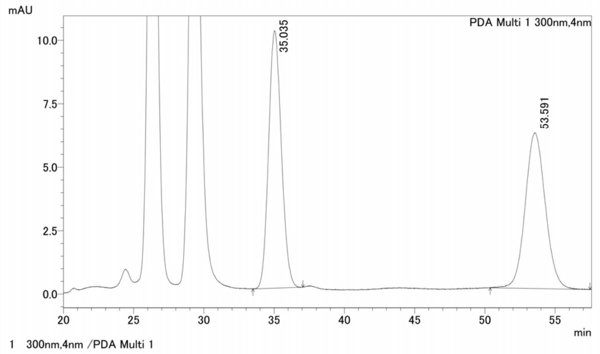


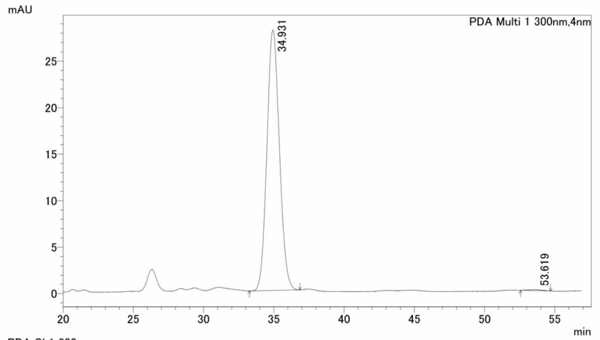


1 254nm,4nm
PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λmax
1	15.716	44029	1172	0.848	
2	23.096	5147502	76899	99.152	206/284
合計		5191532	78071	100.000	

1,6-**4l**

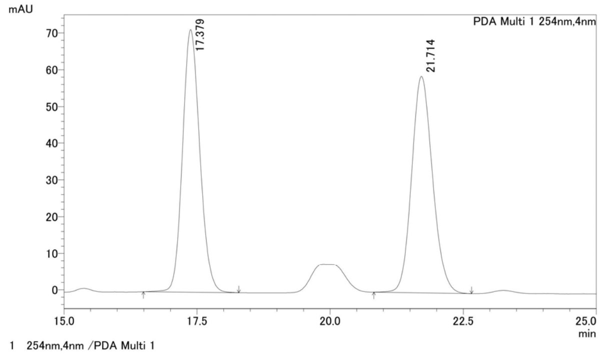


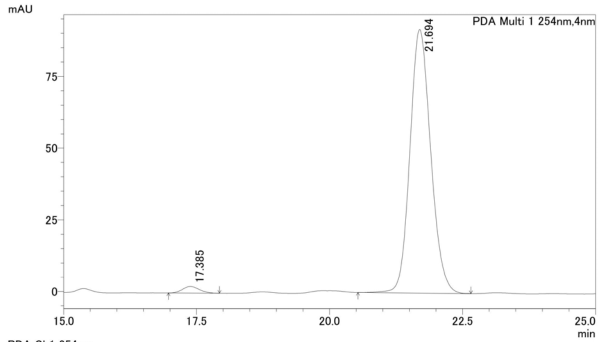


PDA Ch1 300nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	34.931	1731861	28022	99.643	205/287
2	53.619	6212	107	0.357	263/286/225
合計		1738073	28129	100.000	

7





PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	17.385	50159	2295	1.963	205/240/283
2	21.694	2505338	91910	98.037	206/240/282
合計		2555498	94205	100.000	