Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting information

Visible-light-mediated decarboxylative (*E*)-alkenylation of aliphatic carboxylic acids with aryl styryl sulfones under metal-free-conditions

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Contents

General information:

Low-resolution mass spectrometry analyses were carried out using an AGILENT 6890N spectrometer joint to a gas spectrometer. The chromatographic conditions were as follows: Carrier gas helium (2mL/min), 270 ºC in the injection tower and detector, and 1.0 µL of the sample. The temperature program was: initial temperature 60 ºC, 3 min initial time, heating speed of 15 ºC/min and 270 ºC final temperature for 10 minutes; HP-1 column, 12 cm long, with the stationary phase being OV-101. For the electronic impact detection, 70 eV was used and the ions from the fragmentations were shown as a percentual relative intensity versus the base peak. High-resolution mass spectroscopy analyses were carried out in an AGILENT 7200 using the Electron Impact mode at 70 eV by GCQ-TOF.

Nuclear magnetic resonance spectra were registered at 300 MHz or 400 MHz for ^{1}H-NMR and 75 MHz or 101 MHz for ^{13}C-NMR. The relative chemical shifts (δ) were given in parts per million (ppm) with respect to TMS, and the coupling constants (J) were given in hertz (Hz). The multiplicity of the signals is assigned using the following abbreviations: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet).

Thin layer chromatographies (TLC) were performed using prefabricated chromatoplates on aluminum support with silica gel 60 [Merck silica gel 60 F254]. The spots were visualized using a UV lamp, irradiating at $\lambda = 254$ nm.

Column chromatographies (CC) were performed using glass columns, with a stationary phase of silica gel Merck 60, with a particle size of 0.060-0.200 nm.

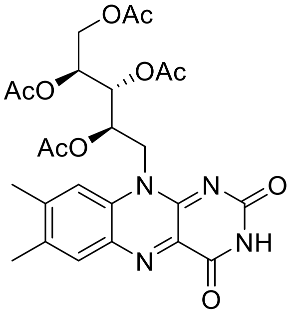
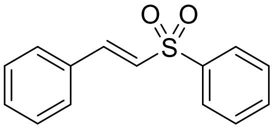
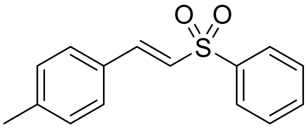
Photochemical reactions were run in a PhotoRedOx Box Duo (EvoluchemTM) reactor equipped with two LED CREE XPE 18W (450-455 nm) lamps (Light intensity = 15 ± 2 mW·cm^{-2}) and a fan to keep the reaction temperature at 30 ± 5 ºC.

For the scale-up reaction two blue LED bulbs of ABI 12W, 450 nm were used. Each bulb was placed at 8 cm from the reaction tube, so the light intensity was about 100 mW·cm^{-2}.

Quenching experiments were performed in a Horiba spectrofluorometer using a 0.1 s of integration time and 2.5 nm of entrance and exit slit for both, excitation, and emission monochromators.

Synthesis of starting materials:

The riboflavin tetraacetate (RFTA) photocatalyst and sulphones **1a-1i** and **1k-1l** were synthesized following the literature indicated, whilst sulphone **1j** was commercially available.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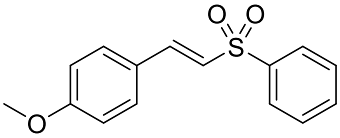	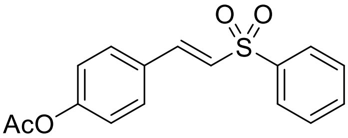	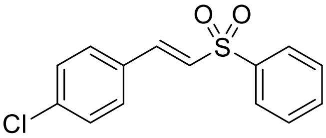
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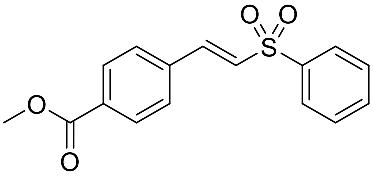	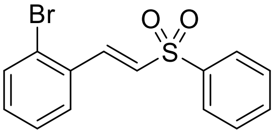	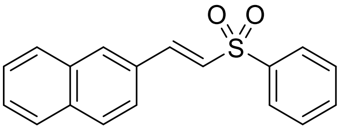
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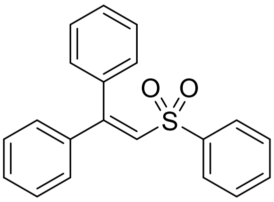	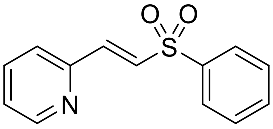	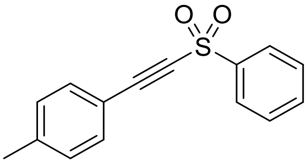
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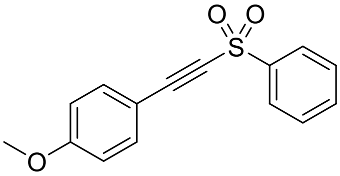
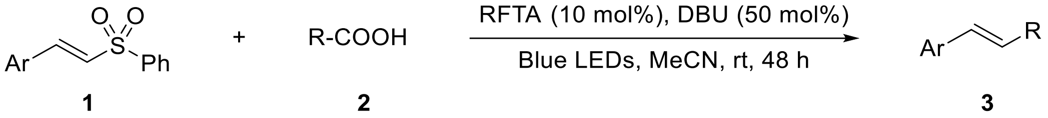
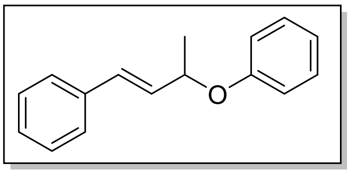
		
1m[5]		

General procedure for the decarboxylative alkenylation of carboxylic acids.

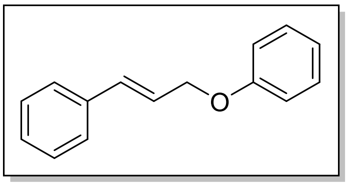


The corresponding sulphone (0.2 mmol), acid (0.3 mmol), DBU (0.1 mmol), and riboflavin tetraacetate (0.02 mmol) were placed in a 2-dram vial along with a stirring rod, and 1.5 mL of MeCN. The vial was capped with a septum, sealed, and submitted to 3 cycles of freeze-pump-thaw deoxygenation. The vial was placed in the PhotoRedOx Box Duo reactor and irradiated for 48 h. The solvent was evaporated, and the crude product was purified via flash column chromatography.

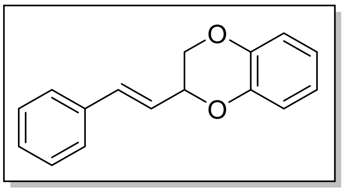
Characterization of the obtained products.



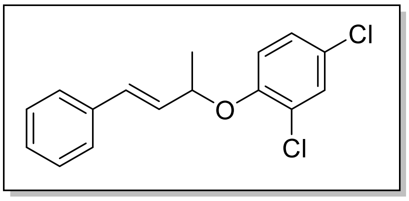
(*E*)-(3-phenoxybut-1-en-1-yl)benzene (3aa): Prepared from 2-phenoxypropanoic acid and sulphone **1a** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 98:2) gave the product (38.9 mg, 87% yield). $R_f = 0.74$ (Hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.32 – 7.21 (m, 5H), 6.97 – 6.88 (m, 3H), 6.65 – 6.56 (d, *J* = 15.5 Hz, 1H), 6.28 (dd, *J* = 16.1, 6.2 Hz, 1H), 4.96 (dquintet, *J* = 6.3, 1.2 Hz, 1H), 1. 52 (d, *J* = 6.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 158.1, 136.67, 130.8, 130.8, 129.5, 128.7, 127.8, 126.6, 120.9, 116.2, 74.6, 21.9 ppm; LRMS (EI, 70 eV): *m/z* (%) 224 (M^+, 0.6) 131 (100). Characterization data matched that reported in the literature.[6]



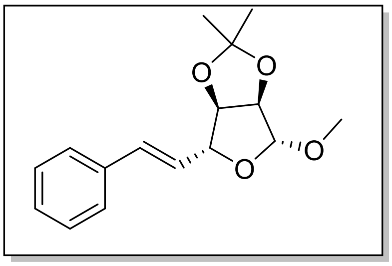
(*E*)-(Cinnamyloxy)benzene (3ab): Prepared from 2-phenoxyacetic acid and sulphone **1a** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 98:2) gave the product (13 mg, 31% yield). $R_f = 0.68$ (Hexane/EtOAc 9:1); ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.44 – 7.24 (m, 8H), 7.01 – 6.92 (m, 3H), 6.74 (dt, *J* = 16.0, 1.6 Hz, 1H), 6.42 (dt, *J* = 16.0, 5.8 Hz, 1H), 4.70 (dd, *J* = 5.8, 1.5 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 158.6, 136.5, 133.0, 129.5, 128.6, 127.9, 126.6, 124.5, 120.9, 114.8, 68.6 ppm; LRMS (EI, 70 eV): *m/z* (%) 210 (M^+, 2), 117 (100), 115 (33). Characterization data matched that reported in the literature.[7]



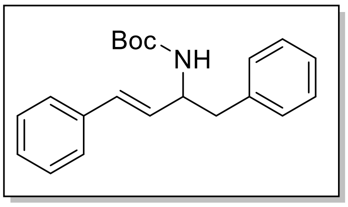
(*E*)-2-styryl-2,3-dihydrobenzo[b][1,4]dioxine (3ac): Prepared from 2,3-dihydrobenzo[b][1,4]dioxine-2-carboxylic acid and sulphone **1a** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 98:2) gave the product (37 mg, 78% yield). R_f = 0.63 (Hexane/EtOAc 9:1); ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.45 – 7.38 (m, 2H), 7.38 – 7.26 (m, 3H), 6.98 – 6.77 (m, 5H), 6.23 (dd, *J* = 16.0, 6.6 Hz, 1H), 4.79 (dddd, *J* = 7.9, 6.6, 2.4, 1.3 Hz, 1H), 4.32 (dd, *J* = 11.3, 2.4 Hz, 1H), 4.00 (dd, *J* = 11.3, 8.0 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 143.2, 143.1, 135.9, 134.3, 128.7, 128.3, 126.7, 123.1, 121.7, 121.5, 117.4, 117.1, 73.7, 67.9; LRMS (EI, 70 eV): *m/z* (%) 238 (M^+, 53), 130 (50), 129 (100), 128 (53). Characterization data matched that reported in the literature.[8]



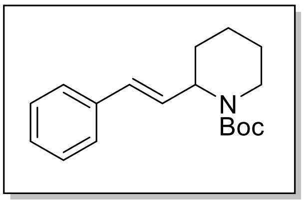
(*E*)-2,4-dichloro-1-((4-phenylbut-3-en-2-yl)oxy)benzene (3ad): Prepared from 2-(2,4-dichlorophenoxy)propanoic acid and sulphone **1a** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 95:5) gave the product (28 mg, 49% yield). R_f = 0.65 (Hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.32 – 7.15 (m, 6H), 7.03 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.49 (d, *J* = 16.1 Hz, 1H), 6.17 (dd, *J* = 16.1, 6.7 Hz, 1H), 4.83 (p, *J* = 6.4 Hz, 1H), 1.50 (d, *J* = 6.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 152.5, 136.2, 131.6, 130.0, 129.6, 128.6, 128.0, 127.4, 126.6, 126.2, 125.1, 117.6, 77.3, 21.7. HRMS (GCQ-TOF) *m*/*z* calcd. for $C_{16}H_{14}Cl_2O$ ($[M+H]^+$) 292.0422, found 292.0413.



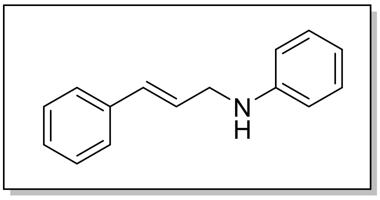
Methyl (E)-5,6-dideoxy-2,3-O-isopropylidene-6-phenyl-b-Dribo-hex-5-enofuranoside (3ae): Prepared from 2,3-O-Isopropylidene-1-O-methyl-D-ribosic acid and sulphone **1a** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 95:5) gave the product (16 mg, 28% yield). R_f = 0.49 (Hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.19 (m, 5H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.14 (dd, *J* = 15.9, 8.8 Hz, 1H), 4.96 (s, 1H), 4.73 (dt, *J* = 8.8, 1.1 Hz, 1H), 4.66 – 4.58 (m, 2H), 3.31 (s, 3H), 1.45 (s, 3H), 1.27 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 136.4, 132.9, 128.7, 128.6, 127.9, 126.6, 112.4, 109.3, 88.3, 85.7, 84.8, 54.6, 26.5, 25.0 ppm; MS (EI, 70 eV): *m/z* (%) 158 (68), 133 (30), 132 (34), 131 (100), 130 (38), 129 (50), 128 (32), 115 (43), 87 (30), 85 (57). Characterization data matched that reported in the literature.[9]



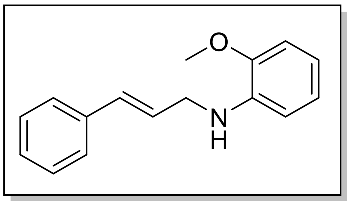
(*E*)-*N*-Boc-(1,4-diphenylbut-3-en-2-yl) (3af): Prepared from *N*-Boc-phenylalanine and sulphone **1a** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 95:5) gave the product (19 mg, 65% yield). R_f = 0.4 (Hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37 – 7.22 (m, 10H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.17 (dd, *J* = 15.9, 5.8 Hz, 1H), 4.61 (s, 2H), 2.96 (d, *J* = 6.3 Hz, 2H), 1.45 (s, 9H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 155.2, 137.4, 136.8, 130.2, 129.8, 129.6, 128.5, 128.4, 127.5, 126.5, 126.4, 79.5, 53.4, 41.9, 28.4 ppm; LRMS (EI, 70 eV): *m/z* (%) 163 (100), 119 (72), 118 (49), 57 (86). Characterization data matched that reported in the literature.[10]



(*E*)-*N*-Boc-2-styrylpiperidine (3ag): Prepared from *N*-Boc-piperidine-2-carboxylic acid and sulphone **1a** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 98:2) gave the product (25 mg, 44% yield). R_f = 0.76 (Hexane/EtOAc 9:1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.45 – 7.16 (m, 5H), 6.40 (dd, *J* = 16.1, 1.9 Hz, 1H), 6.19 (dd, *J* = 16.1, 4.7 Hz, 1H), 4.98 (s, 1H), 4.01 (d, *J* = 13.4 Hz, 1H), 2.92 (td, *J* = 12.9, 2.5 Hz, 1H), 1.90 – 1.58 (m, 6H), 1.49 (s, 9H) ppm; ^{13}C NMR (101 MHz, CDCl$_3$) δ 155.5, 137.2, 130.9, 128.9, 128.7, 127.5, 126.4, 79.6, 52.4, 40.0, 29.6, 28.6, 25.7, 19.8 ppm; LRMS (EI, 70 eV): *m/z* (%) 231 (48), 186 (100). Characterization data matched that reported in the literature.[11]

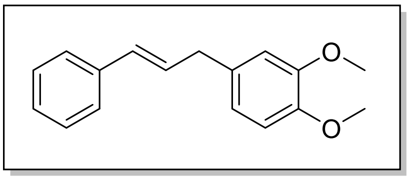


(*E*)-N-cinnamylaniline (3ah): Prepared from phenylglycine and sulphone **1a** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 98:2) gave the product (11 mg, 26% yield). R_f = 0.76 (Hexane/EtOAc 9:1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.43 – 7.29 (m, 5H), 7.28 – 7.18 (m, 2H), 6.83 – 6.74 (m, 3H), 6.70 – 6.60 (m, 1H), 6.37 (dt, *J* = 15.9, 5.9 Hz, 1H), 3.98 (dd, *J* = 5.8, 1.6 Hz, 2H) ppm; ^{13}C NMR (101 MHz, CDCl$_3$) δ 147.2, 136.8, 132.0, 129.3, 128.6, 127.6, 126.5, 126.4, 118.4, 113.7, 46.7 ppm; LRMS (EI, 70 eV): *m/z* (%) 209 (M$^+$, 68), 117 (100), 115 (46). Characterization data matched that reported in the literature.[12]

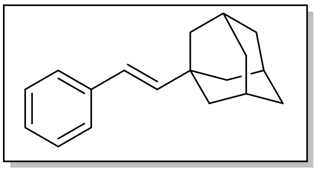


(*E*)-*N*-cinnamyl-2-methoxyaniline (3ai): Prepared from (2-methoxyphenyl)glycine and sulphone **1a** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 98:2) gave the product (15 mg, 32% yield). R_f = 0.78 (Hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.33 (m, 2H), 7.29 (ddd, *J* = 7.7, 6.7, 1.3 Hz, 2H), 7.24 – 7.18 (m, 1H), 6.86 (td, *J* = 7.6, 1.4 Hz, 1H), 6.78 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.71 – 6.65 (m, 2H), 6.62 (dt, *J* = 15.9, 1.6 Hz, 1H), 6.34 (dt, *J* = 15.9, 5.8 Hz, 1H), 3.94 (dd, *J* = 5.8, 1.6 Hz, 2H), 3.84 (s, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): ^{13}C NMR (101 MHz,

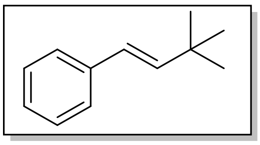
$CDCl_3$) δ 147.0, 138.0, 137.0, 131.4, 128.6, 127.5, 127.3, 126.4, 121.4, 116.7, 110.3, 109.5, 55.5, 46.0 ppm; LRMS (EI, 70 eV): *m/z* (%) , 239 (M^+, 81), 117 (100) 115 (42). Characterization data matched that reported in the literature.[13]



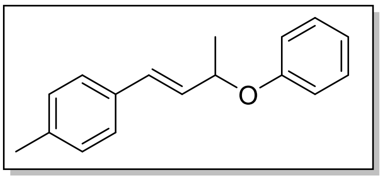
(*E*)-4-cinnamyl-1,2-dimethoxybenzene (3aj): Prepared from 2-(3,4-dimethoxyphenyl)acetic acid and sulphone **1a** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 95:5) gave the product (14 mg, 28% yield): R_f = 0.35 (Hexane/EtOAc 9:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.32 – 7.27(m, 2H), 7.24 – 7.18 (m, 1H), 6.86 – 6.74 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.34 (dt, *J* = 15.7, 6.4 Hz, 1H), 3.87 (s, 6H), 3.50 (d, *J* = 6.3 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 147.5, 137.5, 132.7, 130.9, 129.5, 128.5, 127.1, 126.1, 120.5, 112.0, 111.3, 56.0, 55.9, 38.9 ppm; LRMS (EI, 70 eV): *m/z* (%) 254 (M^+, 100), 223 (62). Characterization data matched that reported in the literature.**[14]**



1-((*E*)-styryl)adamantane (3ak): Prepared from 1-Adamantanoic acid and sulphone **1a** following the *general procedure*. Purification by silica gel column chromatography (hexanes) gave the product (25 mg, 53% yield). R_f = 0.89 (Hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.31 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.23 – 7.17 (m, 1H), 6.27 (d, *J* = 16.2 Hz, 1H), 6.13 (d, *J* = 16.3 Hz, 1H), 2.10 – 2.01 (m, 3H), 1.82 – 1.76 (m, 3H), 1.73 (dd, *J* = 7.4, 2.2 Hz, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 138.2, 128.5, 126.7, 126.0, 124.5, 42.3, 36.9, 35.2, 28.5 ppm; LRMS (EI, 70 eV): *m/z* (%) 238 (100), 181 (55). Characterization data matched that reported in the literature.**[15]**

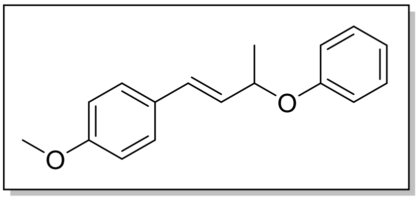


(*E*)-(3,3-dimethylbut-1-en-1-yl)benzene (3al): Prepared from 3,3-dimethyl-2-oxobutanoic acid and sulphone **1a** following the *general procedure*. Purification by silica gel column chromatography (hexane) gave the product (13 mg, 42% yield). R_f = 0.91 (Hexane/EtOAc 9:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.27 (m, 4H), 7.26 – 7.17 (m, 1H), 6.31 (s, 1H), 6.30 (s, 1H), 1.14 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 138.0, 128.5, 126.7, 126.0, 124.5, 33.4, 29.6 ppm; MS (EI, 70 eV): *m/z* (%) 160 (M^+, 30), 145 (100). Characterization data matched that reported in the literature.**[16]**

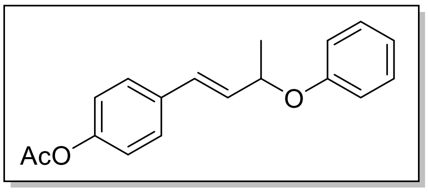


(*E*)-1-methyl-4-(3-phenoxybut-1-en-1-yl)benzene. (3ba) Prepared from 2-Phenoxybenzoic acid and sulphone **1b** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 98:2) gave the product (28 mg, 60% yield). R_f = 0.78 (Hexane/EtOAc 9:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 4H), 7.18 (d, *J* = 7.7 Hz, 2H), 7.05 – 6.96 (m, 3H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.30 (dd, *J* = 16.1, 6.3 Hz, 1H), 5.02 (quintet, *J* = 6.4 Hz, 1H), 2.39 (s, 3H), 1.59 (d, *J* = 6.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ

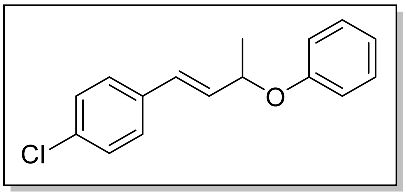
158.1, 137.6, 133.8, 130.6, 129.7, 129.4, 129.3, 126.4, 120.8, 116.2, 74.6, 21.8, 21.2 ppm; HRMS (GCQ-TOF) *m*/*z* calcd. for $C_{17}H_{18}O$ ([M+H]$^+$) 238.1358, found 238.1352.



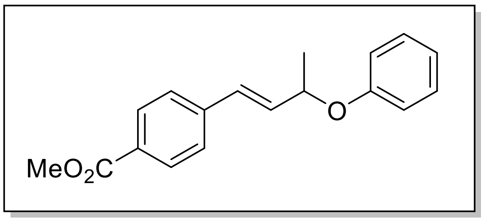
(*E*)-1-methoxy-4-(3-phenoxybut-1-en-1-yl)benzene (3ca): Prepared from 2-Phenoxybenzoic acid and sulphone **1c** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 95:5) gave the product (26 mg, 52% yield). $R_f = 0.67$ (Hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 5H), 7.00 – 6.93 (m, 3H), 6.90 – 6.86 (m, 2H), 6.58 (d, *J* = 16.1 Hz, 1H), 6.17 (dd, *J* = 16.1, 6.4 Hz, 1H), 4.98 (dquintet, *J* = 6.3, 1.2 Hz, 1H), 3.83 (s, 3H), 1.55 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 158.1, 130.2, 129.4, 129.3, 128.5, 127.7, 120.7, 116.2, 114.0, 74.7, 55.3, 21.8 ppm; HRMS (GCQ-TOF) *m*/*z* calcd. for $C_{17}H_{18}O_2$ ([M+H]$^+$) 254.1307, found 254.1304.



(*E*)-4-(3-phenoxybut-1-en-1-yl)phenyl acetate (3da): Prepared from 2-Phenoxybenzoic acid and sulphone **1d** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 95:5) gave the product (26 mg, 47% yield). $R_f = 0.35$ (Hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 2H), 7.33 – 7.25 (m, 2H), 7.09 – 7.02 (m, 2H), 7.02 – 6.90 (m, 3H), 6.61 (d, *J* = 16.1 Hz, 1H), 6.27 (dd, *J* = 16.1, 6.1 Hz, 1H), 4.99 (dquintet, *J* = 6.3, 1.2 Hz, 1H), 2.31 (s, 3H), 1.55 (d, *J* = 6.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 158.0, 150.1, 134.4, 131.0, 129.7, 129.4, 127.4, 121.7, 120.9, 116.1, 74.4, 21.7, 21.1 ppm; HRMS (GCQ-TOF) *m*/*z* calcd. for $C_{18}H_{18}O_3$ ([M+H]$^+$) 282.1256, found 282.1238.

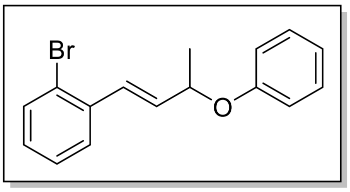


(*E*)-1-chloro-4-(3-phenoxybut-1-en-1-yl)benzene (3ea): Prepared from 2-Phenoxybenzoic acid and sulphone **1e** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 98:2) gave the product (27 mg, 52% yield). $R_f = 0.76$ (Hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 6H), 6.98 (dt, *J* = 7.7, 1.2 Hz, 3H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.29 (dd, *J* = 16.1, 6.0 Hz, 1H), 5.00 (quintet, *J* = 6.3 Hz, 1H), 1.55 (d, *J* = 6.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 135.1, 133.3, 131.4, 129.4, 129.4, 128.7, 127.7, 120.9, 116.1, 74.3, 21.6 ppm; HRMS (GCQ-TOF) *m*/*z* calcd. for $C_{16}H_{15}ClO$ ([M+H]$^+$) 258.0811, found 258.0813.

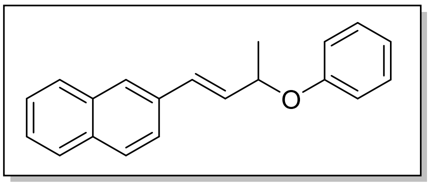


Methyl (*E*)-4-(3-phenoxybut-1-en-1-yl)benzoate (3fa): Prepared from 2-Phenoxybenzoic acid and sulphone **1f** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 98:2) gave the product (25 mg, 44% yield). $R_f = 0.50$ (Hexane/EtOAc 9:1);

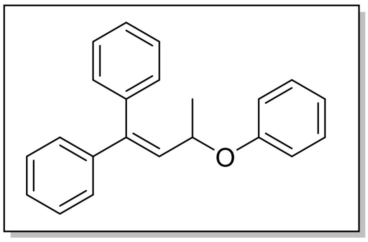
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.93 – 7.85 (m, 2H), 7.38 – 7.31 (m, 2H), 7.19 (m, 2H), 6.90 – 6.82 (m, 3H), 6.57 (d, J = 16.1 Hz, 1H), 6.33 (dd, J = 16.1, 5.9 Hz, 1H), 4.91 (pd, J = 6.4, 1.3 Hz, 1H), 3.83 (s, 3H), 1.45 (d, J = 6.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.0, 158.0, 141.2, 133.6, 130.0, 129.7, 129.6, 129.3, 126.5, 121.1, 116.1, 74.3, 52.2, 21.7 ppm; HRMS (GCQ-TOF) *m*/*z* calcd. for $C_{18}H_{18}O_3$ ([M+H]$^+$) 282.1256, found 282.1259.



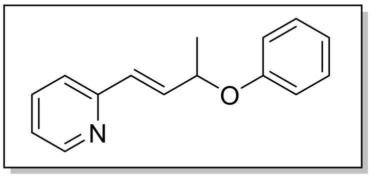
(*E*)-1-bromo-2-(3-phenoxybut-1-en-1-yl)benzene (3ga): Prepared from 2-Phenoxybenzoic acid and sulphone **1f** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 98:2) gave the product (41 mg, 67% yield). R$_f$ = 0.49 (Hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.54 (m, 2H), 7.36 – 7.27 (m, 3H), 7.12 (m, 1H), 7.06 – 6.94 (m, 4H), 6.24 (dd, J = 16.0, 6.4 Hz, 1H), 5.06 (dquintet, J = 6.4, 1.3 Hz, 1H), 1.59 (d, J = 6.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl$_3$) δ 157.9, 136.5, 133.9, 132.9, 129.9, 129.4, 129.0, 127.5, 127.2, 123.7, 120.9, 116.2, 74.3, 21.6; HRMS (GCQ-TOF) *m*/*z* calcd. for $C_{16}H_{15}BrO$ ([M+H]$^+$) 302.0306, found 302.0303.



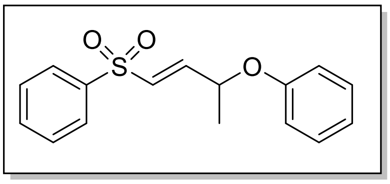
(*E*)-2-(3-phenoxybut-1-en-1-yl)naphthalene (3ha): Prepared from 2-Phenoxybenzoic acid and sulphone **1g** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 98:2) gave the product (31 mg, 57% yield). R$_f$ = 0.86 (Hexane/EtOAc 9:1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.81 – 7.73 (m, 3H), 7.71 (d, J = 1.7 Hz, 1H), 7.57 (dd, J = 8.6, 1.8 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.31 – 7.23 (m, 2H), 7.01 – 6.88 (m, 3H), 6.76 (d, J = 16.1 Hz, 1H), 6.40 (dd, J = 16.1, 6.1 Hz, 1H), 5.02 (dquintet, J = 6.3, 1.2 Hz, 1H), 1.56 (d, J = 6.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl$_3$) δ 158.2, 134.1, 133.7, 133.1, 131.2, 130.8, 129.6, 128.3, 128.1, 127.8, 126.7, 126.4, 126.0, 123.6, 120.9, 116.2, 74.6, 21.9 ppm; HRMS (GCQ-TOF) *m*/*z* calcd. for $C_{20}H_{18}O$ ([M+H]$^+$) 274.1358, found 274.1359.



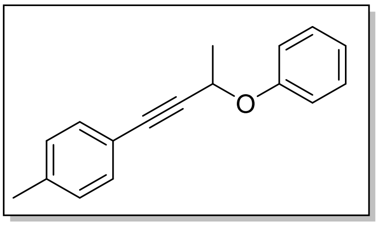
(3-phenoxybut-1-ene-1,1-diyl)dibenzene (3ia): Prepared from 2-Phenoxybenzoic acid and sulphone **1h** following the *general procedure*. Purification by silica gel column chromatography (hexane) gave the product (30 mg, 90% pure, 45% yield). R$_f$ = 0.84 (Hexane/EtOAc 9:1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.49 – 7.42 (m, 2H), 7.32 – 7.23 (m, 10H), 6.97 – 6.92 (m, 1H), 6.80 – 6.75 (m, 2H), 6.16 (d, J = 8.9 Hz, 1H), 4.89 (dq, J = 8.9, 6.2 Hz, 1H), 1.59 (d, J = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 157.7, 143.5, 141.5, 139.3, 130.3, 129.7, 129.3, 128.4, 128.2, 127.8, 127.7, 127.5, 120.7, 116.3, 71.7, 21.9 ppm; HRMS (GCQ-TOF) *m*/*z* calcd. for $C_{22}H_{20}O$ ([M+H]$^+$) 300.1514, found 300.1515.



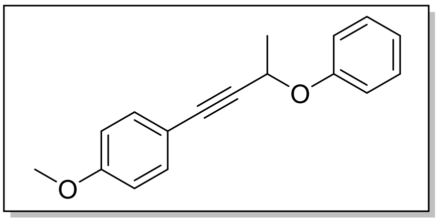
(*E*)-2-(3-phenoxybut-1-en-1-yl)pyridine (3ja): Prepared from 2-Phenoxybenzoic acid and sulphone **1i** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 8:2) gave the product (20 mg, 46% yield). R$_f$ = 0.57 (Hexane/EtOAc 7:3); ^{1}H NMR (300 MHz, CDCl$_3$) *δ* 8.62 – 8.51 (m, 1H), 7.70 (td, *J* = 7.7, 1.8 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.30 – 7.17 (m, 3H), 7.02 – 6.84 (m, 5H), 6.75 (dd, *J* = 16.0, 1.3 Hz, 1H), 5.18 – 4.93 (m, 1H), 1.54 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl$_3$) *δ* 157.8, 154.1, 148.0, 138.0, 137.3, 129.5, 122.6, 122.3, 120.9, 115.9, 73.7, 21.4 ppm; HRMS (GCQ-TOF) *m*/*z* calcd. for $C_{15}H_{15}NO$ ([M+H]$^+$) 225.1154, found 225.1153.



(*E*)-((3-phenoxybut-1-en-1-yl)sulfonyl)benzene (3ka): Prepared from 2-Phenoxybenzoic acid and sulphone **1j** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 95:5) gave the product (39 mg, 67% yield). R$_f$ = 0.54 (Hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 – 7.83 (m, 2H), 7.66 – 7.60 (m, 1H), 7.57 – 7.51 (m, 2H), 7.29 – 7.21 (m, 2H), 7.08 (dd, *J* = 15.1, 3.8 Hz, 1H), 6.97 (m, 1H), 6.87 – 6.82 (m, 2H), 6.61 (dd, *J* = 15.1, 1.6 Hz, 1H), 5.01 (m, 1H), 1.49 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl$_3$) δ 156.9, 145.9, 140.1, 133.5, 130.6, 129.6, 129.3, 127.6, 121.7, 115.8, 72.0, 20.1 ppm; HRMS (GCQ-TOF) *m*/*z* calcd. for $C_{16}H_{16}O_3S$ ([M+H]$^+$) 288.0820, found 288.0824.



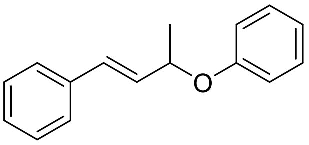
1-methyl-4-(3-phenoxybut-1-yn-1-yl)benzene (3la): Prepared from 2-Phenoxybenzoic acid and sulphone **1k** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 98:2) gave the product (21 mg, 45% yield). R$_f$ = 0.81 (Hexane/EtOAc 9:1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.37 – 7.29 (m, 4H), 7.10 (m, 4H), 7.04 – 6.97 (m, 1H), 5.11 (q, *J* = 6.6 Hz, 1H), 2.35 (s, 3H), 1.76 (d, *J* = 6.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 157.6, 138.6, 131.6, 129.4, 129.0, 121.2, 115.9, 87.6, 85.8, 64.3, 22.4, 21.5 ppm; HRMS (GCQ-TOF) *m*/*z* calcd. for $C_{17}H_{16}O$ ([M+H]$^+$) 236.1201, found 236.1195.



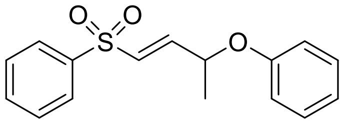
1-methoxy-4-(3-phenoxybut-1-yn-1-yl)benzene (3ma): Prepared from 2-Phenoxybenzoic acid and sulphone **1l** following the *general procedure*. Purification by silica gel column chromatography (hexane/EtOAc 98:2) gave the product (19 mg, 38% yield). R$_f$ = 0.59 (Hexane/EtOAc 9:1); ^{1}H NMR (300 MHz, CDCl$_3$) *δ* 7.40 – 7.29 (m, 4H), 7.13 – 7.07 (m, 2H), 7.05 – 6.95 (m, 1H), 6.86 – 6.80 (m, 2H), 5.11 (q, *J* = 6.6 Hz, 1H), 3.81 (s, 3H), 1.76 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) *δ* 159.7, 157.6, 133.2, 129.3, 121.2, 115.9, 114.5, 113.9, 87.0, 85.6, 64.4, 55.3, 22.4 ppm; HRMS (GCQ-TOF) *m*/*z* calcd. for $C_{17}H_{16}O_2$ ([M+H]$^+$) 252.1150, found 252.1143.

Scale-up of the reaction.

The corresponding sulphone (2 mmol, 1 equiv), Acid (3 mmol, 1.5 equiv, 498 mg), DBU (1 mmol, 0.5 equiv, 152 µL) and Riboflavin tetraacetate (0.2 mmol, 0.1 equiv, 109.6 mg) were placed in a schlenk flask (3 cm diameter) followed by 15 mL of MeCN and a stirring bar. The vessel was capped with a septum and deoxygenated by spurging Ar for 30 min. The flask was irradiated with 2 blue LED bulbs (450 nm) while stirring at room temperature under an Ar atmosphere for the time indicated below. When the reaction needed more than 24 h, the reaction mixture was spurged with Ar for 30 min to remove the CO_2 every 24 h. for the first 2 days. The solvent was evaporated, and the crude product was purified via column chromatography.



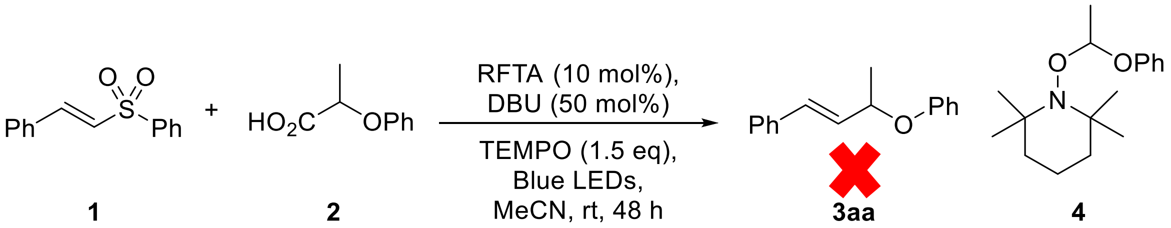
7 days, 291 mg, 65 %



24 h, 362 mg, 63 %

Mechanistic Studies.

Inhibition with TEMPO



Sulphone **1a** (0.2 mmol, 1 equiv, 48.8 mg), 2-Phenoxypropanoic acid (0.3 mmol, 1.5 equiv, 49.8 mg), DBU (0.1 mmol, 0.5 equiv, 15 µL) TEMPO (0.3 mmol, 1.5 equiv, 46.8 mg) and riboflavin tetraacetate (0.02 mmol, 10 mol%, 10.86 mg) were placed in a vial along with a stirring rod and 1.5 mL of MeCN. The vial was capped with a septum, sealed, and submitted to 3 cycles of freeze-pump-thaw deoxygenation. The vial was placed in the PhotoRedOx Box Duo reactor and irradiated for 48 h. Upon analysis, via GC-MS the absence of compound **3aa** was observed. After further analysis via LC-MS (ESI), the formation of **4** could be seen.

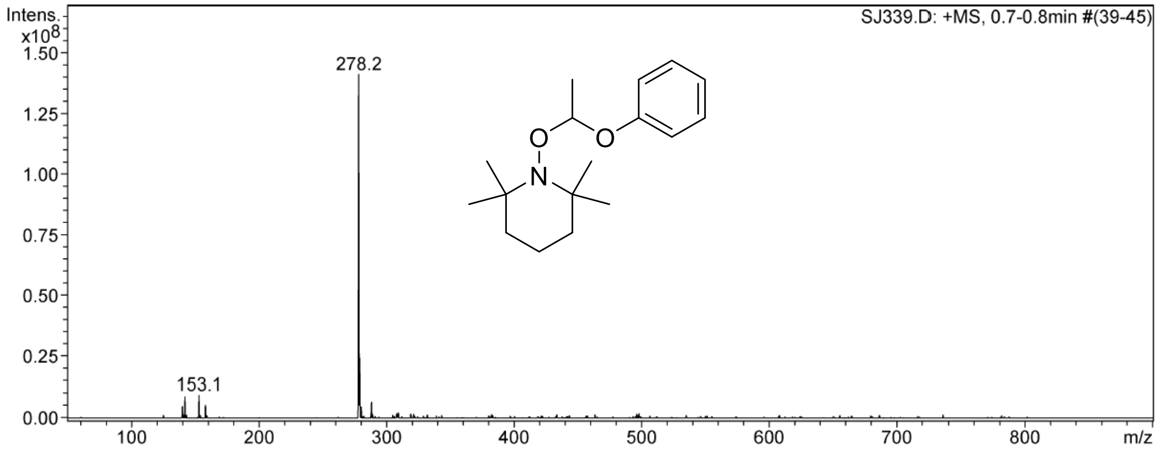
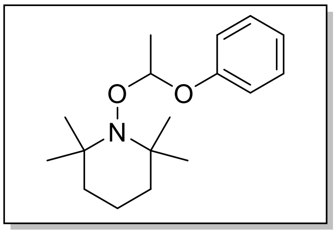


Figure 1. TEMPO Adduct in LC-MS (ESI)

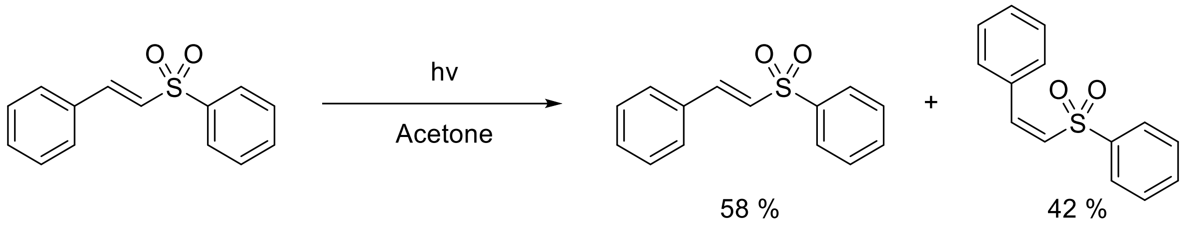


2,2,6,6-tetramethyl-1-(1-phenoxyethoxy)piperidine. **(4)** Purification by silica gel column chromatography (hexane/EtOAc 9:1) gave the product (37 mg, 67% yield): $R_f = 0.70$ (Hexane/EtOAc 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.7 Hz, 2H), 7.19 – 7.02 (m, 3H), 5.70 (d, *J* = 5.3 Hz, 1H), 1.59 (d, *J* = 5.3 Hz, 6H), 1.40 – 1.22 (m, 15H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6, 129.5, 121.2, 117.4, 105.4, 60.8, 59.5, 40.4, 40.1, 33.5, 29.8, 20.7, 20.3, 19.4, 17.3 ppm; LRMS (EI, 70 eV): *m/z* (%) 140.1 (100). Characterization data matched that reported in the literature.[17]

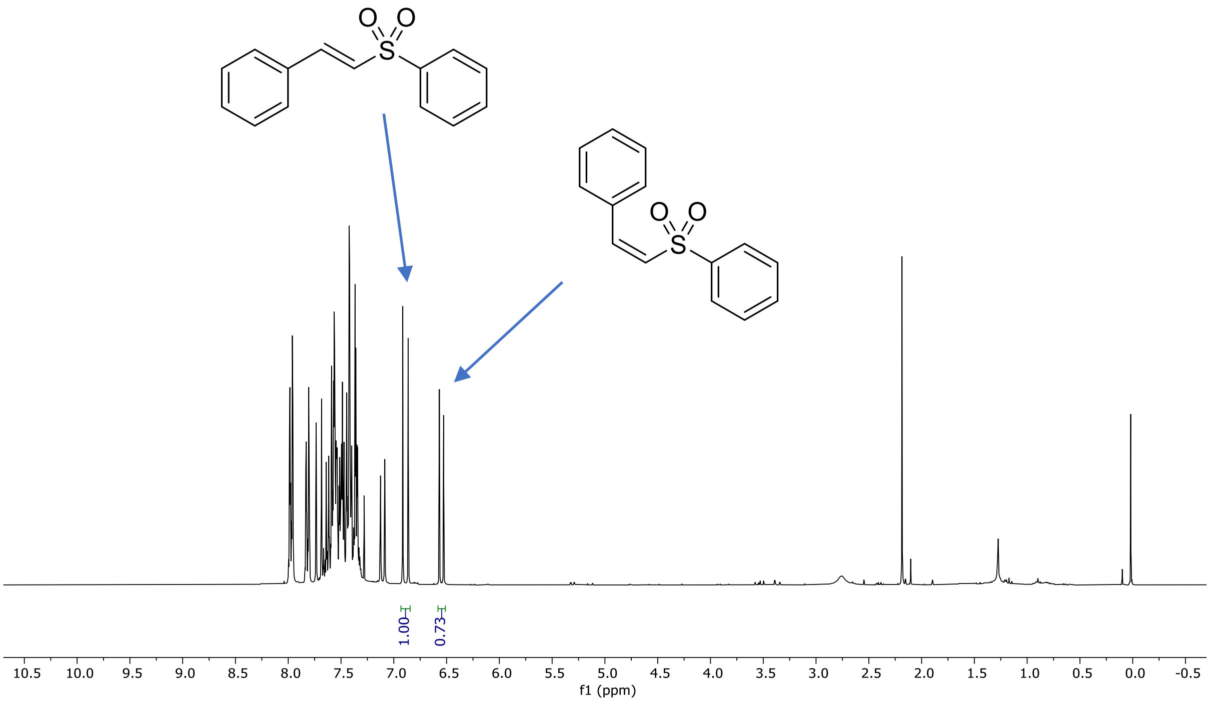
Reaction with diphenylethylene.

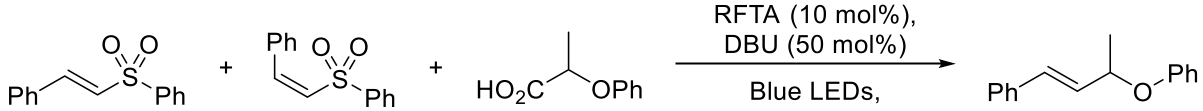
Diphenylathylene **1a** (0.2 mmol, 1 equiv, 36 mg), 2-Phenoxypropanoic acid (0.3 mmol, 1.5 equiv, 49.8 mg), DBU (0.1 mmol, 0.5 equiv, 15 µL) and riboflavin tetraacetate (0.02 mmol, 10 mol%, 10.86 mg) were placed in a vial along with a stirring rod and 1.5 mL of MeCN. The vial was capped with a septum, sealed, and submitted to 3 cycles of freeze-pump-thaw deoxygenation. The vial was placed in the PhotoRedOx Box Duo reactor and irradiated for 48 h. Upon analysis via GC-MS, compound **3ha** was observed as the minor product, with the major one being product **5** without the double bond (Ratio 5/95).

Isomerization of sulphone **1a**.



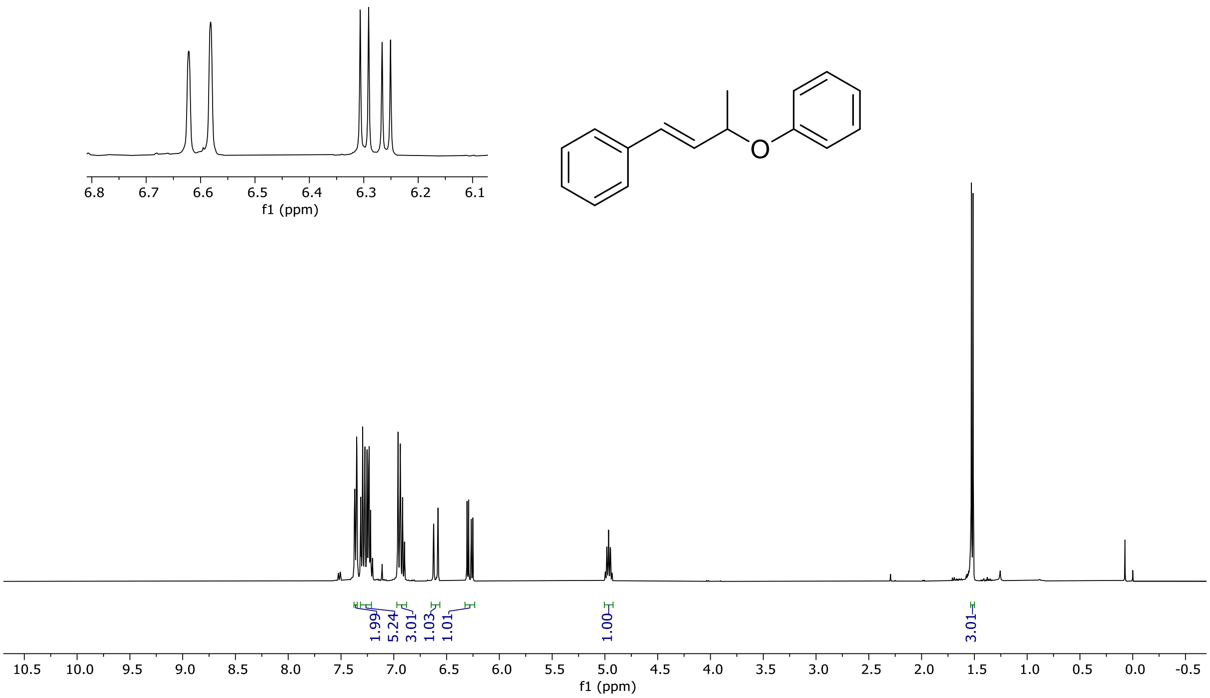
Sulphone **1a** (500 mg, 2 mmol) was added to a schlenk tube, dissolved in acetone (50 mL), and irradiated for 10 h using a 125-watt high-pressure mercury lamp (Osram). The acetone was evaporated under reduced pressure yielding the desired isomerized mixture (*E/Z*, 58/42, ^{1}H NMR 300 MHz, $CDCl_3$).





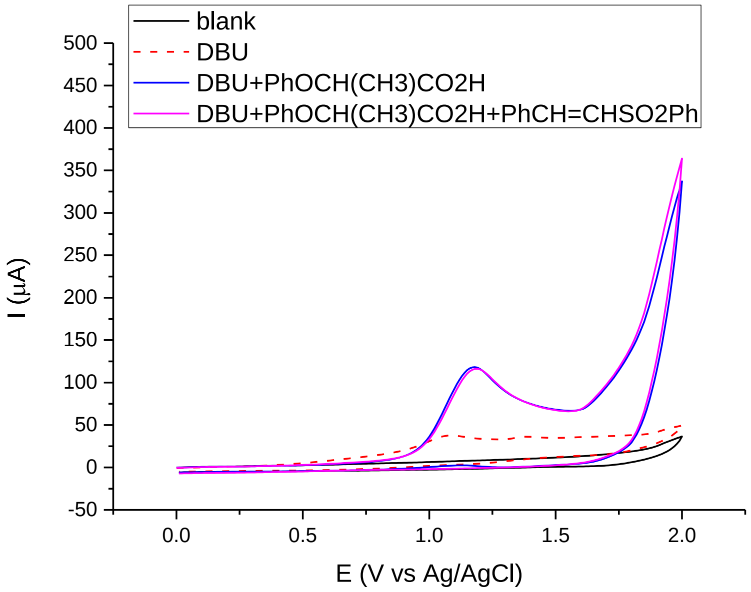
(*E*)-3aa

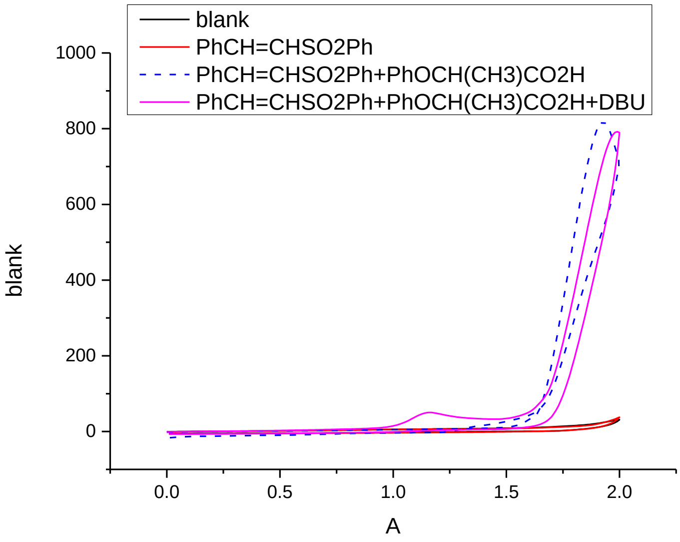
The isomerized mixture was submitted to the reaction described in general procedure A, obtaining solely the *E* isomer.



Cyclic voltammetry measurements.

Measurements were performed using EmStatblue+ potentiostat at a scan rate of 100 mV/s. A glassy carbon electrode of 3 mm diameter was used as a working electrode, a platinum wire as a counter electrode, and a Ag/AgCl (aq., 0.01 M KCl) as a reference electrode. Measurements were performed in 3 mL of blank solution (0.1 M Bu_4NPF_6 in MeCN, black line) with the corresponding compound (0.05 M, red line). Ferrocene was used as an internal standard.





UV-Vis spectra of reagents/RFTA and quenching experiments.

Stock solutions of RFTA ([RFTA] = 1.36·10^{-4} M) and quenchers ([Q] = 3·10^{-2} M, for **1a**, **2a**, DBU, **2a**+DBU (3:1 molar ratio) and DBU + 4 M HCl (1:1 molar ratio)) were prepared.

UV-Vis spectra of the stock solutions of RFTA**, 1a**, **2a**, DBU, **2a**+DBU (3:1 molar ratio) and DBU + 4 M HCl (1:1 molar ratio) were recorded from 350 nm to 750 nm (**Figure 2**). A maximum of absorbance for RFTA was detected at 440 nm.

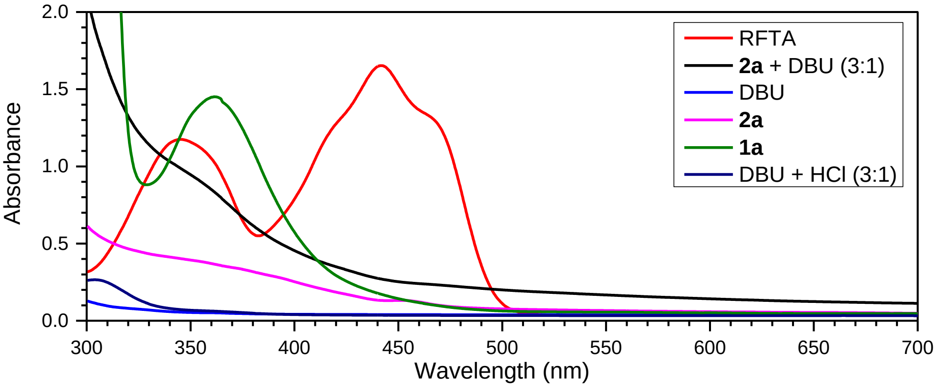


***Figure 2**: Absorption spectra for the RFTA photocatalyst, **1a**, **2a**, **2a**+DBU, DBU and DBU+HCl stock solutions.*

For the quenching studies, 15 µL of the stock solution of RFTA were mixed with the corresponding amount of stock solution of Q (0.3 mL to 1.5 mL) and diluted to a final volume of 3 mL ([Q]final = 0, 3, 6, 9, 12, and 15 mM). Samples were irradiated at 440 nm and the emission spectra were recorded from 450 nm to 750 nm, observing a maximum of emission at 505 nm (**Figures 3a** and **4a**). Stern-Volmer plots for RFTA* quenching were represented using the cps at 505 nm (**Figure 3b** and **4b**).

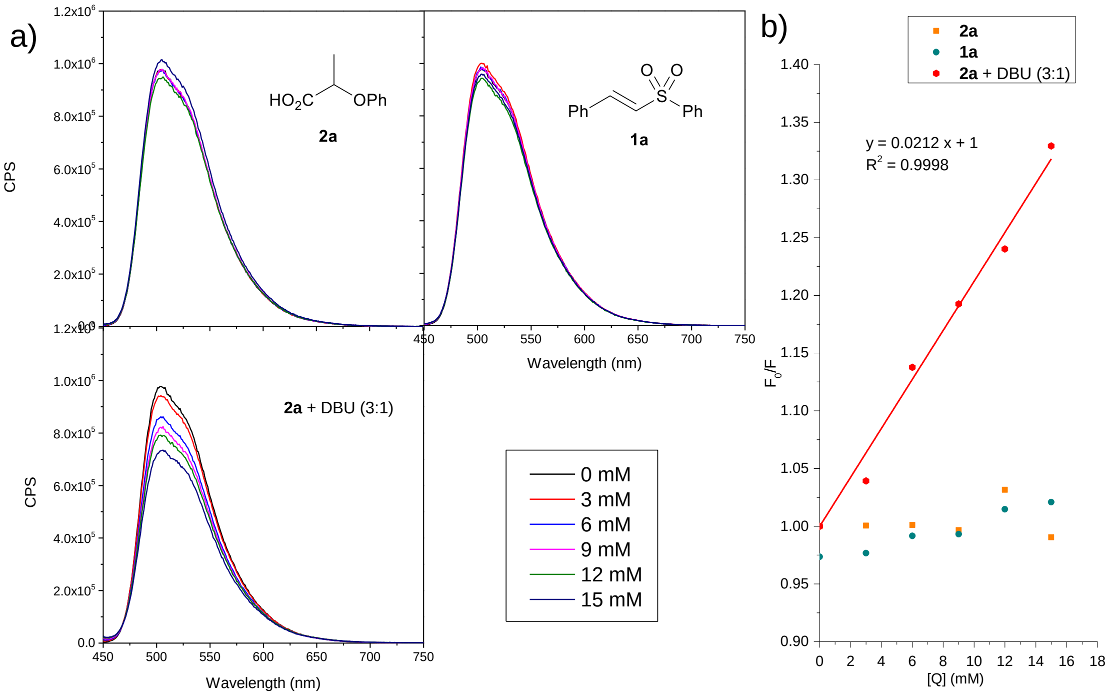


__Figure 3__: (a) Emission spectra for the RFTA photocatalyst in the presence of variable concentrations of __2a__, __1a__ and __2a__+DBU (3:1). (b) Stern-Volmer plot.*

$$\text{Stern-Volmer equation for } \mathbf{2a}\text{+DBU: } \frac{F_0}{F_{\mathbf{2a}+DBU}} = 0.0212\,[\mathbf{2a} + DBU] + 1$$

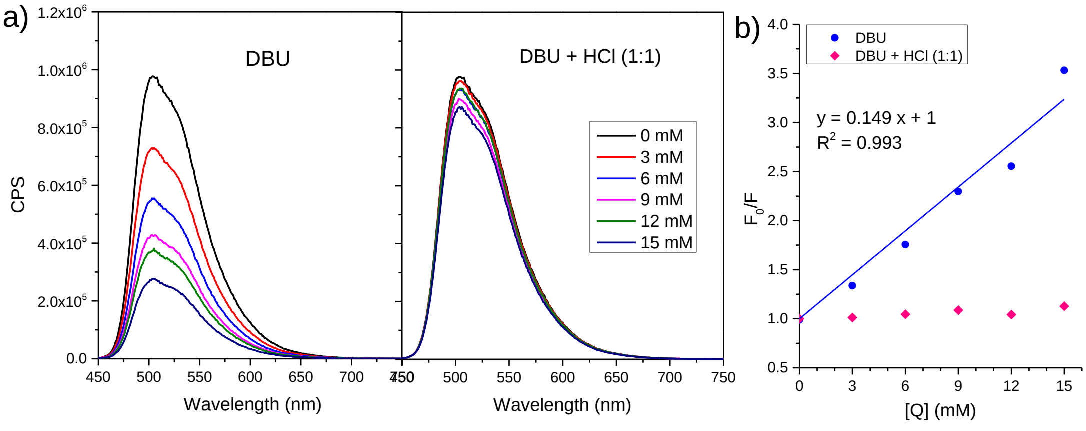
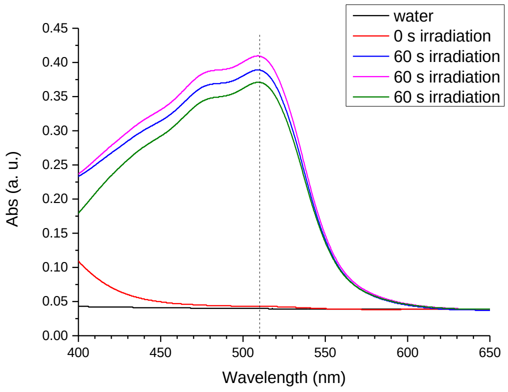


Figure 4: (a) Emission spectra for the RFTA* photocatalyst in the presence of variable concentrations of DBU and DBU+HCl (1:1). (b) Stern-Volmer plot.

Determination of the quantum yield using the ferrioxalate actinometry.

A 0.15 M solution of $K_2Fe(C_2O_4)_3$ was prepared by mixing 1 mL of a $FeCl_3$ solution (prepared by adding 0.811 g of $FeCl_3 \cdot 6H_2O$ to 1 mL of H_2SO_4 and diluting with water up to 10 mL) and 1 mL of an oxalic acid solution (prepared by mixing 1.49 g of oxalic acid and 1.86 g of KOH and diluting with water up to 10 mL). The mixture was placed in a reaction vial with a stir bar and irradiated for 60 s under blue LEDs. After this time, 50 µL of this irradiated mixture were quenched with 2 mL of the 1,10-phenanthroline solution (prepared by dissolving 20 mg of 1,10-phenanthroline and diluting up to 10 mL with water) and diluted up to 25 mL with water. To adjust the absorbance, 12 mL of this diluted solution were re-diluted with water up to 25 mL. The UV-Vis spectra of this solution was recorded. This procedure was repeated three times.

The same procedure, but in the dark, was repeated to obtain the UV-Vis spectra of the blank sample (0 s irradiation).



The amount of Fe^{2+} formed was measured by determining the absorbance of the Fe-phenanthroline complex at 510 nm:

$$mmol\ Fe^{2+} = \frac{\Delta Abs}{\varepsilon \cdot d} \cdot \frac{25\ mL}{12\ mL} \cdot \frac{25\ mL}{0.05\ mL} \cdot 2\ mL$$

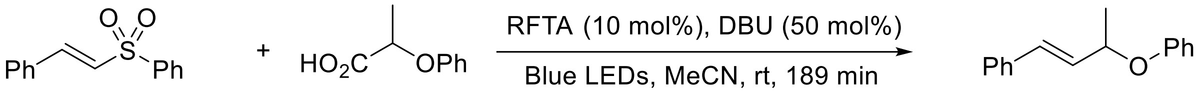
Where ΔAbs is the difference between the absorbance of the sample at 510 nm after 0 s and after 60 s (average of the three repetitions) of irradiation, ε is the extinction coefficient of the complex at 510 nm ($\varepsilon = 1.11 \cdot 10^4\ L \cdot mol^{-1} \cdot cm^{-1}$) and d is the light path length of the cuvette (d = 1 cm). The dilutions performed were considered to calculate the amount of ferrous ion formed.

Thus, the amount of ferrous ion formed was:

$$mmol\ Fe^{2+} = \frac{0.390}{1.11 \cdot 10^4\ L \cdot mol^{-1} \cdot cm^{-1} \cdot 1\ cm} \cdot \frac{25\ mL}{12\ mL} \cdot \frac{25\ mL}{0.05\ mL} 2\ mL = 0.07320\ mmol$$

Considering the irradiation time (t = 60 s), the quantum yield of the photolysis of $K_2Fe(C_2O_4)_3$ ($\phi_{450\ nm} = 1$), and the total light absorption ($f = 1$), the photon flux can be calculated as:

$$photon\,flux = \frac{mmol\,Fe^{2+}}{t \cdot \phi_{450\,nm} \cdot f} \cdot \frac{1\,mol}{10^3 mmol} = \frac{7.32 \cdot 10^{-5}\,mol}{60\,s \cdot 1 \cdot 1} = 1.22 \cdot 10^{-6} Einstein \cdot s^{-1}$$



The reaction was set up as described in the General Procedure, using 0.20 mmol of starting material and run for 189 min under blue LEDs. The reaction mixture was concentrated to dryness and dissolved into 0.5 mL of a solution of an internal standard (Stock solution of 38.8 mg of 1,2-dibromoethane in 2 mL of $CDCl_3$). An aliquot of this mixture was submitted to ^{1}H-NMR analysis and this procedure was performed in duplicate.

The analysis of the duplicated reaction mixtures revealed a 22% and a 23% yield of the product respectively, an average of 0.045 mmol of product formed after 189 min of irradiation.

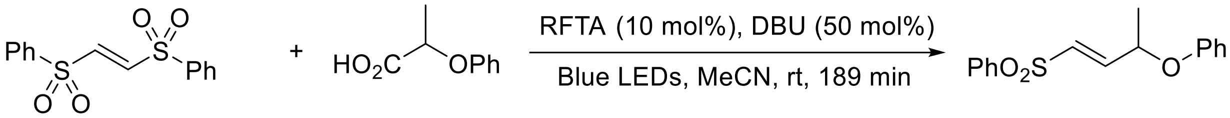
The quantum yield was calculated as:

$$\phi_{450\,nm} = \frac{mol\,product}{t \cdot photon\,flux} \cdot 100\%$$

Where *mol product* represents the amount of product generated and *t* the irradiation time in seconds. Thus:

$$\phi_{450\,nm} = \frac{0.045 \cdot 10^{-3} mol}{189 \cdot 60\,s \cdot 1.22 \cdot 10^{-6} Einstein \cdot s^{-1}} \cdot 100 = 0.32\%$$

This analysis was also carried out with disulphone as the starting material, following the same method:



The reaction was set up as described in the General Procedure, using 0.20 mmol of starting material and run for 189 min under blue LEDs. The reaction mixture was concentrated to dryness and dissolved into 0.5 mL of a solution of an internal standard (Stock solution of 20.7 mg of 1,2-dichloroethane in 2 mL of $CDCl_3$). An aliquot of this mixture was submitted to ^{1}H-NMR analysis and this procedure was performed in duplicate.

The analysis of the duplicated reaction mixtures revealed a 56% and a 57% yield of the product respectively, an average of 0.114 mmol of product formed after 209 min of irradiation.

The quantum yield was calculated as:

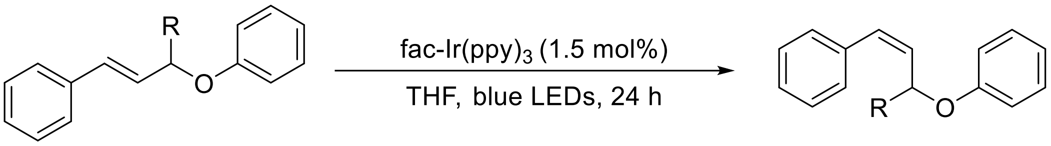
$$\phi_{450\ nm} = \frac{mol\ product}{t \cdot photon\ flux} \cdot 100\%$$

Where *mol product* represents the amount of product generated and *t* the irradiation time in seconds. Thus:

$$\phi_{450\ nm} = \frac{0.114 \cdot 10^{-3} mol}{209 \cdot 60\ s \cdot 1.22 \cdot 10^{-6} Einstein \cdot s^{-1}} \cdot 100 = 0.74\%$$

Synthetic applications.

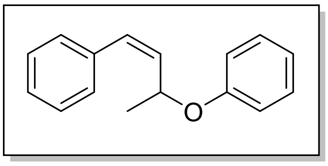
Photocatalytic *E*-to-*Z* isomerization of compound **3aa** and **3ab**.



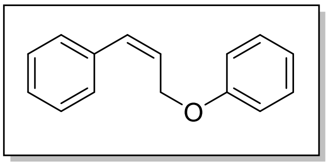
3aa (R = Me)
3ab (R = H)

6a (R = Me)
6b (R = H)

Compound **3** (0.2 mmol) and fac-Ir(ppy)$_3$ (1.5 mol%) were placed in a 2-dram vial along with a stirring rod and 1.5 mL of dry THF. The vial was capped with a septum, sealed, and submitted to 3 cycles of freeze-pump-thaw deoxygenation. The vial was placed in the PhotoRedOx Box Duo reactor and irradiated for 24 h. The solvent was evaporated, and the crude product was filtered through silica gel, eluting with EtOAc, yielding quantitative conversion.[18]

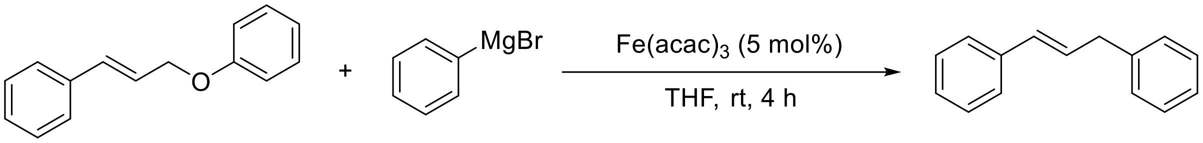


(*Z*)-(3-phenoxybut-1-en-1-yl)benzene (6a). *Z/E* (^{1}H NMR) = >99/1 (44 mg, 98% yield). R$_f$ = 0.71 (Hexane/EtOAc 9:1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.42 – 7.20 (m, 7H), 6.90 – 6.80 (m, 1H), 6.72 – 6.64 (m, 2H), 6.58 (d, J = 11.8 Hz, 1H), 5.69 (dd, J = 11.8, 9.0 Hz, 1H), 5.25 (m, 1H), 1.56 (d, J = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 157.7, 136.8, 133.9, 131.1, 129.4, 128.8, 128.6, 127.6, 120.7, 115.8, 69.8, 21.3 ppm. HRMS (GCQ-TOF) *m*/*z* calcd. for $C_{16}H_{16}O$ ([M+H]$^+$) 224.1201, found 224.1203.



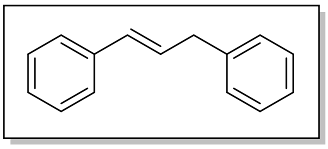
(*Z*)-(Cinnamyloxy)benzene (6b). *Z/E* (^{1}H NMR) = 85/15 (41 mg, 98% yield). R$_f$ = 0.67 (Hexane/EtOAc 9:1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.53 – 7.17 (m, 5H), 7.05 – 6.88 (m, 5H), 6.75 (dt, J = 11.7, 1.8 Hz, 1H), 6.02 (dt, J = 11.7, 6.3 Hz, 1H), 4.85 (dd, J = 6.3, 1.7 Hz, 2H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ 158.5, 136.4, 132.5, 129.5, 128.8, 128.5, 127.6, 127.5, 120.9, 114.8, 64.8 ppm Characterization data matched that reported in the literature.[18]

Iron-catalyzed cross-coupling.



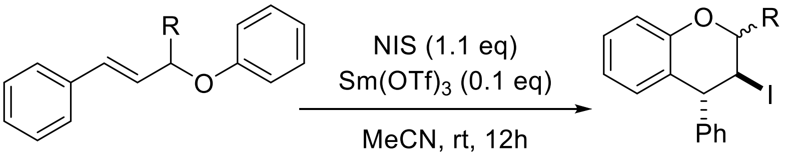
3ab **7**

To a solution of Fe(acac)$_3$ (0.025 mmol, 5 mol %, 9 mg) and **3ab** (0.5 mmol, 1 eq, 105 mg) in dry THF, the phenylmagnesium bromide (1 mmol, 2 eq, 1 mL) was added dropwise, followed by 4 h of stirring at room temperature. After completion of the reaction, it was quenched with a 1 M solution of HCl (10 mL) and extracted with DCM. The organic phase was washed with deionized water and brine, dried over $MgSO_{4,}$ and concentrated under reduced pressure obtaining compound **7**.[19]



(*E*)-Prop-1-ene-1,3-diyldibenzene (7). Purified by preparative TLC in pentane (65 mg, 62% yield). $R_f = 0.9$ (Pentane); ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.58 – 6.87 (m, 10H), 6.46 (d, *J* = 15.9 Hz, 1H), 6.35 (dt, *J* = 15.7, 6.4, 1H), 3.54 (d, *J* = 6.4 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.3, 137.6, 131.2, 129.4, 128.8, 128.6 (2), 127.2, 126.3, 126.2, 39.5 ppm. Characterization data matched that reported in the literature.[20]

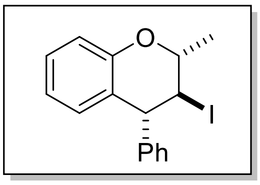
Samarium-catalyzed cyclization.



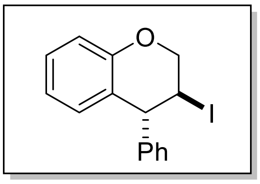
3aa (R = Me)
3ab (R = H)

8a (R = Me)
8b (R = H)

N-Iodosuccinimide (1.1 eq, 0.22 mmol, 50 mg), the corresponding ether (1 eq, 0.2 mmol, 50 mg) and samarium (III) triflate (0.1 eq, 0.02, 12 mg) were dissolved in dry MeCN and stirred at room temperature for 12 h. The crude solution was extracted with EtOAc, washed with water and brine, followed by drying over $MgSO_4$ and concentrated under reduced pressure.[21]

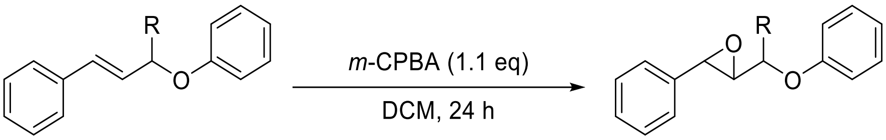


***trans-cis*-3-iodo-2-methyl-4-phenylchromane (8a).** Purified by preparative TLC (Hexane/EtOAc: 98/2) yielding a yellow/white solid (20 mg, 30% yield). $R_f = 0.75$ (Hexane/EtOAc: 7/3); ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.39 – 7.30 (m, 3H), 7.21 – 7.16 (m, 2H), 7.15 – 7-09 (m, 1H), 6.84 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.75 (ddd, *J* = 8.5, 7.2, 1.3 Hz, 1H), 6.61 – 6.56 (m, 1H), 4.55 (dd, *J* = 10.8, 1.1 Hz, 1H), 4.51 – 4.42 (m, 1H), 4.29 (t, *J* = 10.6 Hz, 1H), 1.77 (d, *J* = 6.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 143.3, 130.1, 129.2, 128.7, 128.2, 127.6, 124.9, 121.4, 116.7, 54.7, 40.5, 29.8, 23.5. ppm; HRMS (GCQ-TOF) *m*/*z* calcd. for $C_{16}H_{15}IO$ ($[M+H]^+$) 350.0168, found 350.0165.



***trans*-3-iodo-4-phenylchromane (8b).** Purified by preparative TLC in hexane (40 mg, 80% yield). R_f = 0.72 (Hexane:EtOAc 7:3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 3H), 7.23 – 7.12 (m, 3H), 6.90 (dd, J = 8.2, 1.2 Hz, 1H), 6.83 (td, J = 7.5, 1.3 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 4.58 (dt, J = 8.0, 3.1, 1H), 4.49 (d, J = 7.6 Hz, 1H), 4.44 (dd, J = 11.5, 3.1 Hz, 1H), 4.30 (ddd, J = 11.5, 8.1, 0.8 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 143.2, 130.6, 128.9, 128.7, 128.4, 127.5, 123.0, 121.3, 116.8, 70.2, 52.9, 28.9 ppm. Characterization data matched that reported in the literature.[22]

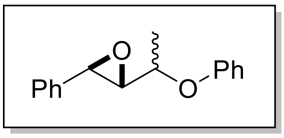
Epoxidation with *m*-CPBA.



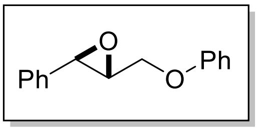
3aa (R = Me)
3ab (R = H)

9a (R = Me)
9b (R = H)

The corresponding ether, (1 eq, 0.5 mmol) and *m*-chloroperbenzoic acid (1.1 equiv., 0.55 mmol, 95 mg) were dissolved in dry DCM at 0 ºC, stirred at this temperature for 1 h, and then left to reach room temperature and stirred for a further 24 h. The resulting crude product was extracted with DCM, washed with $NaHCO_3$, and dried over $MgSO_4$, yielding the desired product.



***trans*-2-(1-phenoxyethyl)-3-phenyloxirane (9a).** Diastereomeric ratio = 71/29 (^{1}H NMR). Purified by column chromatography (Hexane:EtOAc 95:5) giving a white solid (70 mg, 58 % yield). R_f = 0.75 (Hexane:EtOAc 95:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ Major diastereoisomer: 7.32 – 7.13 (m, 8H), 6.98 – 6.87 (m, 2H), 4.42 – 4.25 (m, 1H), 3.78 (d, J = 2.1 Hz, 1H), 3.17 (dd, J = 5.2, 2.1 Hz, 1H), 1.41 (d, J = 6.5 Hz, 3H) ppm; Minor diastereoisomer: 7.32 – 7.13 (m, 8H), 6.98 – 6.87 (m, 2H), 4.42 – 4.25 (m, 1H), 3.79 (d, J = 2.1 Hz, 1H), 3.08 (dd, J = 4.7, 2.1 Hz, 1H), 1.41 (d, J = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ Major diastereoisomer 157.9, 136.7, 129.6, 128.6, 125.6, 121.3, 116.7, 116.0, 73.8, 64.8, 56.1, 17.1 ppm; Minor diastereoisomer: 157.9, 136.8, 129.5, 128.5, 128.2, 125.6, 121.6, 116.2, 73.7, 64.2, 57.0, 29.7 ppm. HRMS (GCQ-TOF) m/z calcd. for $C_{16}H_{16}O_2$ ($[M+H]^+$) 240.1150, found 240.1148.



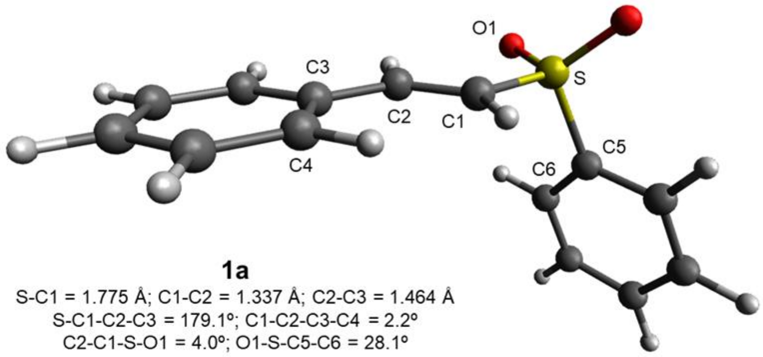
***trans*-2-(Phenoxymethyl)-3-phenyloxirane (9b).** Purified by column chromatography (Hexane:EtOAc 95:5) giving a white solid (90 mg, 80 % yield). R_f = 0.7 (Hexane:EtOAc 95:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 – 7.18 (m, 7H), 6.92 – 6.82 (m, 3H), 4.21 (dd, J = 11.2, 3.2 Hz, 1H), 4.02 (dd, J = 11.2, 5.2 Hz, 1H), 3.81 (d, J = 2.1 Hz, 1H), 3.30 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.5, 136.6, 129.6, 128.6, 128.5, 125.8, 121.4, 114.8, 67.9, 60.3, 56.4 ppm. Characterization data matched that reported in the literature.[23]

DFT calculations.

The optimications of the geometry were performed by DFT calculations with the program package Gaussian 16, revision C.01,[24] using the B3LYP function[25] with D3 dispersion correction[26] and the 6-311G(d,p) basis set.[27] The effect of the bulk solvent acetonitrile (ε = 37.5) was estimated by using the Solvation Model based on Density (SMD).[28] Vibrational frequency calculations were carried out at the same level of theory and they confirmed that the optimized structures were either minimum (no imaginary frequencies) or transition state (only one imaginary frequency) on the potential energy surfaces (PES). For each transition state structure, the intrinsic reaction coordinate (IRC) routes towards the corresponding minimum were calculated and, if the IRC calculations failed to reach the energy minimum, geometry optimizations were performed from the final point of the IRC analysis. Gibbs free energies at 298.15 K were obtained from the vibrational frequency calculations and a correction term of 1.89 kcal/mol was added to them to consider the change in the standard state from 1 atm to 1 M.

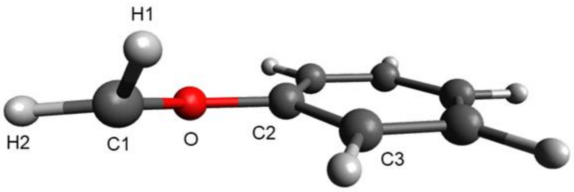
Optimized structures of the starting alkene **1a** and the radical $PhOCH_2\cdot$.

Figure S1 shows the optimized structures of the species used as reagent for the computational study.



1a

S-C1 = 1.775 Å; C1-C2 = 1.337 Å; C2-C3 = 1.464 Å
S-C1-C2-C3 = 179.1°; C1-C2-C3-C4 = 2.2°
C2-C1-S-O1 = 4.0°; O1-S-C5-C6 = 28.1°



$PhOCH_2\cdot$

O-C1 = 1.364 Å; O-C2 = 1.376 Å
H2-C1-O-C2 = 177.0°; H1-C1-O-C2 = 31.4°; C1-O-C2-C3 = 19.9°

Figure S1. Optimized structures of alkene **1a** and starting radical $PhOCH_2\cdot$ at the B3LYP-D3/6-311G(d,p) level in acetonitrile. (Color of atoms: C, grey; H, white; O, red; S, yellow).

Alkene **1a** has a bent conformation. The olefinic C=C bond and the phenyl group bonded to it are almost coplanar. That C=C bond and the S=O1 bond shows a *s-cis* conformation (dihedral angle 4.0 º). The phenyl group bonded to the S atom is not coplanar with any of the S=O bonds.

Concerning $PhOCH_2$, the radical carbon C1 has a pyramidal shape (dihedral angle H1-C1-O-C2 = 31.4º), suggesting that it has an sp^3 hybridization. The C1-O bond is not coplanar with the phenyl ring.

Regiochemistry of the addition of radical $PhOCH_2\cdot$ to alkene **1a**.

The reactions of radical $PhOCH_2\cdot$ with both carbon atoms of the C=C of **1a** were evaluated. The obtained energy profiles are shown in Figure S2. The two reaction pathways have almost identical barriers but the energy of the radical resulting from the reaction at atom C2 (**NBR**) is higher than the one of **Ic** [ΔG (**Ic**-**NBR**) = -12.7 kcal/mol].

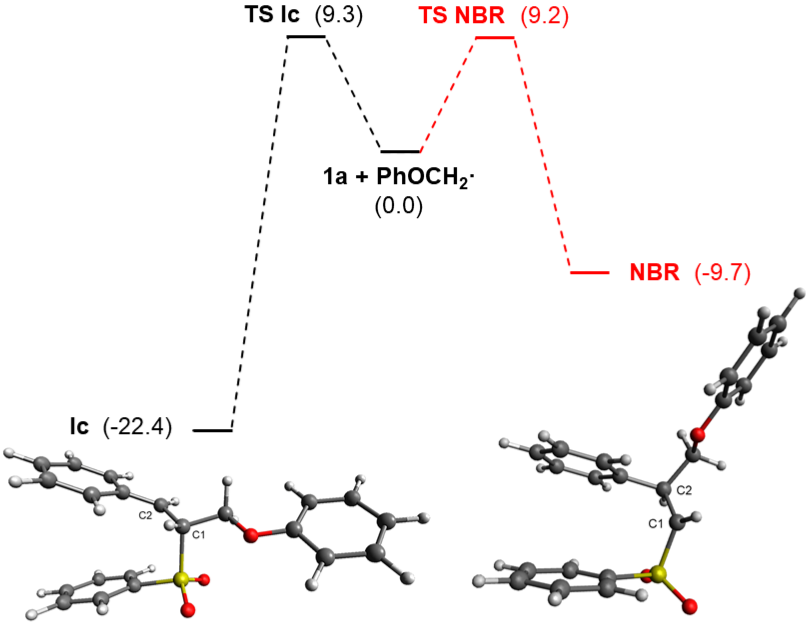
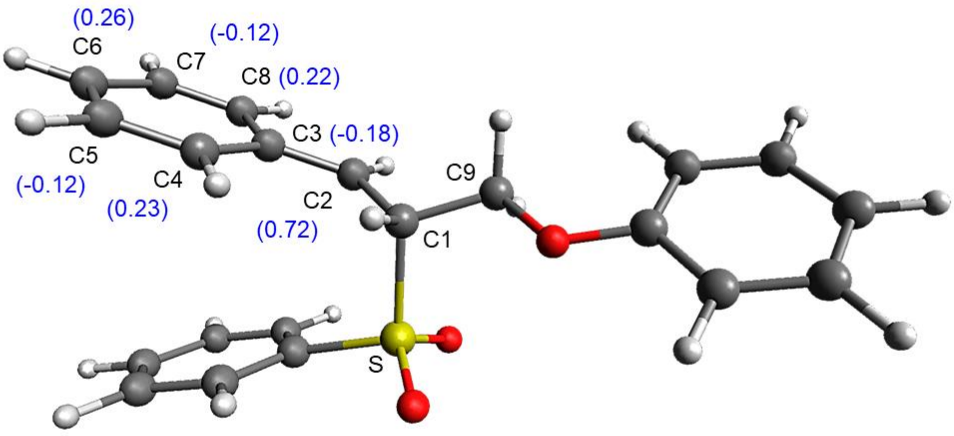


Figure S2. Energy profile for the addition of radical $PhOCH_2\cdot$ to both carbon atoms of the C=C bond of **1a**, obtained from DFT calculations [B3LYP-D3/6-311G(d,p) in acetonitrile]. Relative Gibbs free energy values are given in brackets (kcal/mol). Separated **1a** and $PhOCH_2\cdot$ were taken as zero-energy. (Color of atoms: C, grey; H, white; O, red; S, yellow).

Figure S3 shows the optimized structure obtained for radical **Ic**. Most of the spin density is located on the benzylic carbon C2, which is planar and coplanar with the neighboring phenyl ring. The spin density values on the aromatic ring atoms C4, C6, and C8 and the shortening of the C2-C3 bond distance from 1.464 Å in **1a** (see Figure S1) to 1.415 Å in **Ic** suggest that partial delocalization of the radical through the phenyl ring takes place, leading to its stabilization. The C1-S bond is almost perpendicular to the plane in which the benzylic carbon is contained, resulting in a conformation in which the β-elimination of the $PhSO_2\cdot$ group would be highly favored.



Ic

S-C1 = 1.907 Å; C1-C9 = 1.523 Å; C1-C2 = 1.478 Å; C2-C3 = 1.415 Å
S-C1-C2-C3 = 97.5º

Figure S3. Optimized structure of radical **Ic** at the B3LYP-D3/6-311G(d,p) level in acetonitrile. Relevant spin densities are given in brackets. (Color of atoms: C, grey; H, white; O, red; S, yellow).

The delocalization of the radical in **Ic** through the phenyl ring bonded to C2 (see Figure 1 of the main text) could contribute to the increase of its stability in comparison with the non-benzylic radical **NBR**. According to the calculated spin density distribution of the latter, the radical is almost completely localized on atom C1 (spin density 0.96).

Addition of radical $PhOCH_2\cdot$ to alkene **1a** and subsequent β-elimination of radical $PhSO_2\cdot$ to give product **3ab**.

Observing the preferred conformation of the starting alkene **1a**, it can be deduced that, for steric reasons, only one face of the olefinic carbon C1 bonded to the sulfur atom is available for the attack of the radical $PhOCH_2\cdot$ (the *Si* face in the case of Figure S1). There is another equivalent conformation (with the phenyl group pointing upwards) in which the *Re* face is the one that is free of steric hindrance, but the addition of $PhOCH_2\cdot$ to it would give a radical that is enantiomeric to the one formed by the addition to the *Si* face. Therefore, for the computational study, we only considered the addition to the *Si* face of the alkene.

Several conformations of the radical generated by the addition of $PhOCH_2\cdot$ to **1a** were calculated and the more relevant to understanding the kinetics and the thermodynamics of the overall conversion of **1a** to **3ab** are depicted in Figure S3. The three conformers have the C-S bond almost perpendicular to the plane containing the radical carbon C2 and the neighboring phenyl ring, which will facilitate the following *β*-elimination leading to alkene **3ab**.

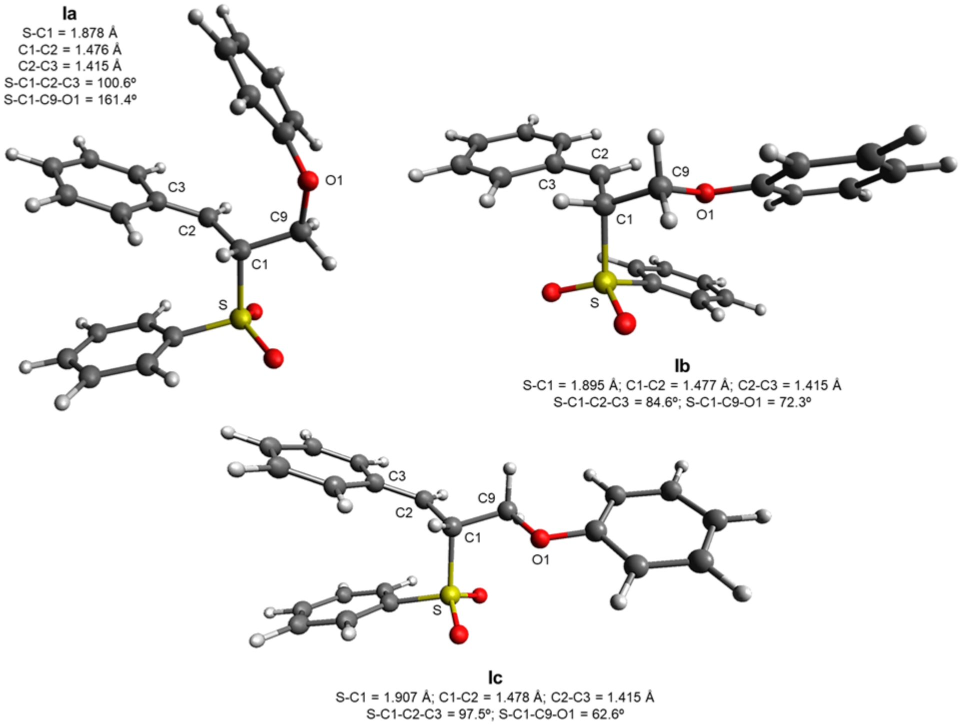


Figure S3. Optimized structures of intermediate radicals **Ia**, **Ib,** and **Ic** at the B3LYP-D3/6-311G(d,p) level in acetonitrile. (Color of atoms: C, grey; H, white; O, red; S, yellow).

The reaction pathway for the formation of the radical from the reagents and the subsequent elimination of $PhSO_2\cdot$ to afford alkene **3ab** was studied for each of the three radicals **Ia**, **Ib,** and **Ic,** and the corresponding energy profiles are represented in Figure S4. As it can be seen, the addition step is very exergonic in the three cases (the fall in energy from the corresponding transition state ranges from 27.5 kcal/mol for **Ia** to 32.7 kcal/mol for **Ib**) and we can assume that this first step could be irreversible. The formation of **Ia** has an activation barrier considerably lower than the other two routes and, therefore, this will probably be the preferred way for the addition of $PhOCH_2\cdot$ to the starting alkene **1a**. Once the radical **Ia** has been generated, it could directly undergo the elimination of $PhSO_2\cdot$ to give product **3ab** (activation barrier 5.1 kcal/mol). But the activation barriers for the elimination step for radicals **Ib** and **Ic** are lower (3.5 and 3.0 kcal/mol, respectively). If **Ia** could easily change its conformation to **Ib** or **Ic**, the elimination step from them would be much faster.

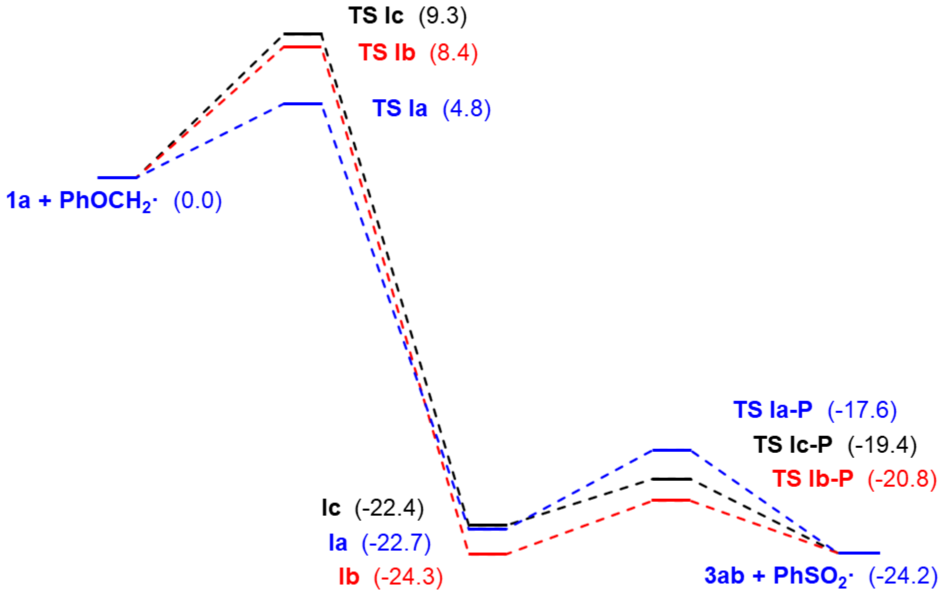
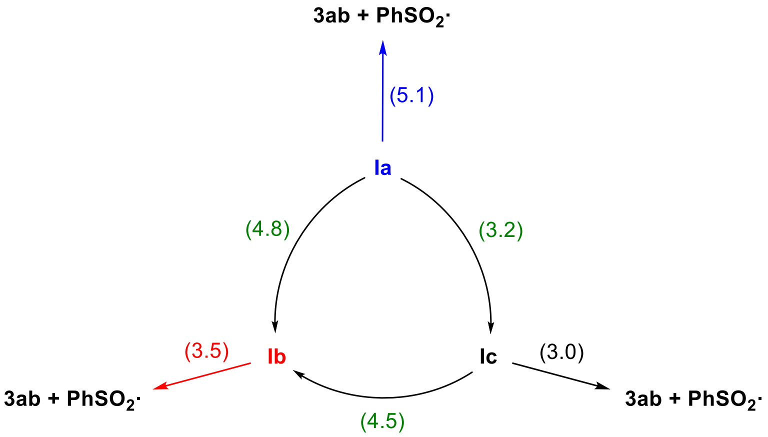


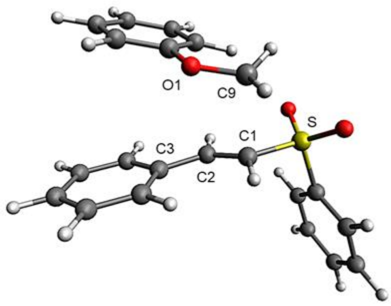
Figure S4. Energy profiles for three possible reaction pathways for the addition of radical $PhOCH_2$· to **1a** and the subsequent elimination of $PhSO_2$· to give **3ab**, obtained from DFT calculations [B3LYP-D3/6-311G(d,p) in acetonitrile]. Relative Gibbs free energy values are given in brackets (kcal/mol). Separated **1a** and $PhOCH_2$· were taken as zero-energy.

Thus, we decided to do a conformational analysis for the interconversion of the three radicals **Ia**, **Ib,** and **Ic,** and the results are shown in Scheme S1. Once radical **Ia** has been formed, its conversion to conformer **Ic** (which is almost isoenergetic with **Ia**) is kinetically favored (barrier of 3.2 in comparison with 4.8 and 5.1 kcal/mol for the other two possible routes). The activation barrier for the elimination of $PhSO_2$· from **Ic** is only 3.0 kcal/mol, lower than the highest barrier that must be overcome to change from **Ic** to the more stable conformer **Ib** (4.5 kcal/mol). According to this data, we consider that the most likely route to the elimination of products from the initially formed radical **Ia** would be via its conformer **Ic**. However, the formation of alkene **3ab** from radical **Ia**, to some extent, should not be directly ruled out, since its activation barrier is quite low (5.1 kcal/mol).



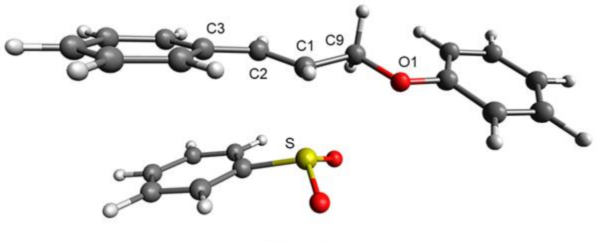
Scheme S1. Barriers (Gibbs free energy, kcal/mol) for the transformations indicated. For each interconversion between conformers **Ia**, **Ib,** and **Ic**, in green is the highest barrier that must be overcome. Other numbers are the activation barriers for the conversion of radical **Ia**, **Ib,** or **Ic** into the elimination products.

The optimized structures of the transition states involved in the most likely route, **TS Ia** and **TS Ic-P**, are shown in Figure S6. **TS Ia** is an early transition state with a C1-C9 distance of 2.489 Å and a dihedral angle between the S-C1 bond of the alkene and the C9-O1 bond of the approaching radical of 147.4º. In **TS Ic-P**, the distance between atom C1 and the S atom of the leaving sulfonyl radical is 2.379 Å and the S-C1 partial bond is almost perpendicular to the plane containing atom C2 and the phenyl ring attached to it (dihedral angle S-C1-C2-C3 = 85.7º), suggesting the plausible β-elimination.



TS Ia

S-C1 = 1.777 Å; C1-C9 = 2.489 Å; C1-C2 = 1.357 Å; C2-C3 = 1.452 Å
S-C1-C2-C3 = 175.0º; S-C1-C9-O1 = 147.4º



TS Ic-P

S-C1 = 2.379 Å; C1-C9 = 1.501 Å; C1-C2 = 1.391 Å; C2-C3 = 1.440 Å
S-C1-C2-C3 = 85.7º; S-C1-C9-O1 = 62.2º

Figure S6. Optimized structures of transition states **TS Ia** and **TS Ic-P** at the B3LYP-D3/6-311G(d,p) level in acetonitrile. (Color of atoms: C, grey; H, white; O, red; S, yellow).

Stereochemical outcome: exclusive formation of the *E*-alkene product.

As indicated above, radical **Ic** is a key intermediate in the transformation of starting alkene **1a** into the product **3ab**. The *β*-elimination process from **Ic** would lead to the *E* configuration in the olefinic product. However, if radical **Ic** could rotate through the C1-C2 bond, conformer **II** would be formed (Figure S7), which could yield the alkene product with the *Z* configuration after the elimination of $PhSO_2\cdot$. To study the feasibility of this change of conformation, the corresponding barrier was calculated, and we obtained a value of 10.8 kcal/mol, which is much higher than the activation barrier for the generation of the *E* alkene **3ab** from **Ic** (3.0 kcal/mol), indicating that the formation of **3ab** should be much faster than the change of conformation from **Ic** to **II**. Moreover, **II** is 2,7 kcal/mol less stable than **Ic**, making the transformation of **Ic** to **II** thermodynamically disfavoured. This agrees with the experimental results since a complete *E* selectivity was observed in almost all cases.

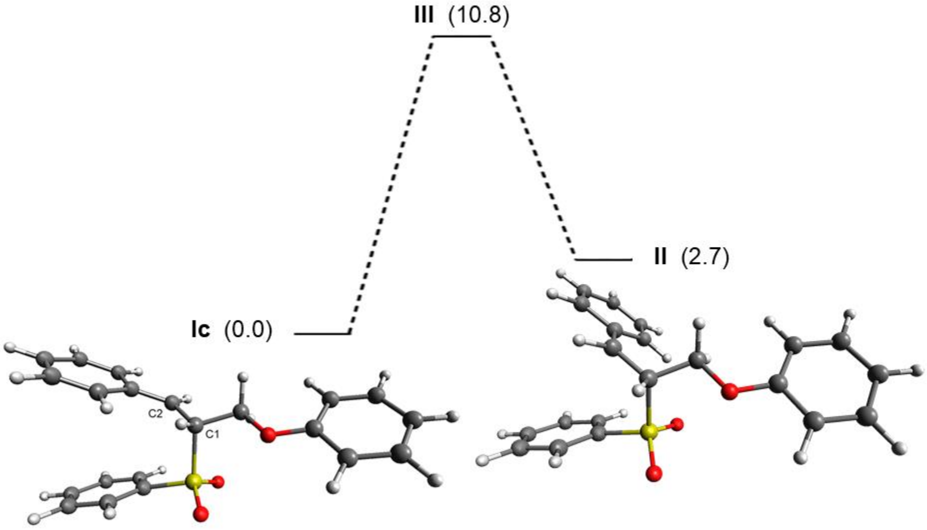


Figure S7. Energy profile for the conversion of radical **Ic** into its conformer **II**, obtained from DFT calculations [B3LYP-D3/6-311G(d,p) in acetonitrile]. Relative Gibbs free energy values are given in brackets (kcal/mol). **Ic** was taken as zero-energy. (Color of atoms: C, grey; H, white; O, red; S, yellow).

On the other hand, a diastereoconvergency was observed when the reaction was performed with an *E*/*Z* diastereomeric mixture of substrate **1a** (see Scheme 5, Eq. 3 of the main text), alkene **(*E*)-3ab** being the only product that was detected. To try to understand this behavior, we decided to do a computational study for the addition of $PhOCH_2\cdot$ to **(*Z*)-1a**, leading to radical **II**, and for the following elimination of $PhSO_2\cdot$ to afford the product **(*Z*)-3ab** and the results are shown in Figure S8. The activation barrier for the addition step (8.2 kcal/mol) is higher than the one that we obtained for the formation of radical **Ia** (4.8 kcal/mol; see Figure S4). The addition step is very exergonic, the energy falling 32.8 kcal/mol from **TS II** to **II**, probably due to the generation of the stabilized benzylic radical. Once radical **II** has been formed, the following elimination step should be fast, since its activation barrier is only 3.0 kcal/mol. This energy profile is similar to the one that we had obtained before for the reaction with alkene **(*E*)-1a** and, in principle, the transformation represented in Figure S8 could also be viable. There is a difference in energy between the starting materials [**(*Z*)-1a + PhOCH₂·** are 4.8 kcal/mol less stable than **1a + PhOCH₂·**] and the products [**(*Z*)-3ab + PhSO₂·** are 2.5 kcal/mol less stable than **3ab + PhSO₂·**]. Then, why is alkene **(*E*)-3ab** obtained exclusively when an *E*/*Z* mixture of **1a** was used as substrate?

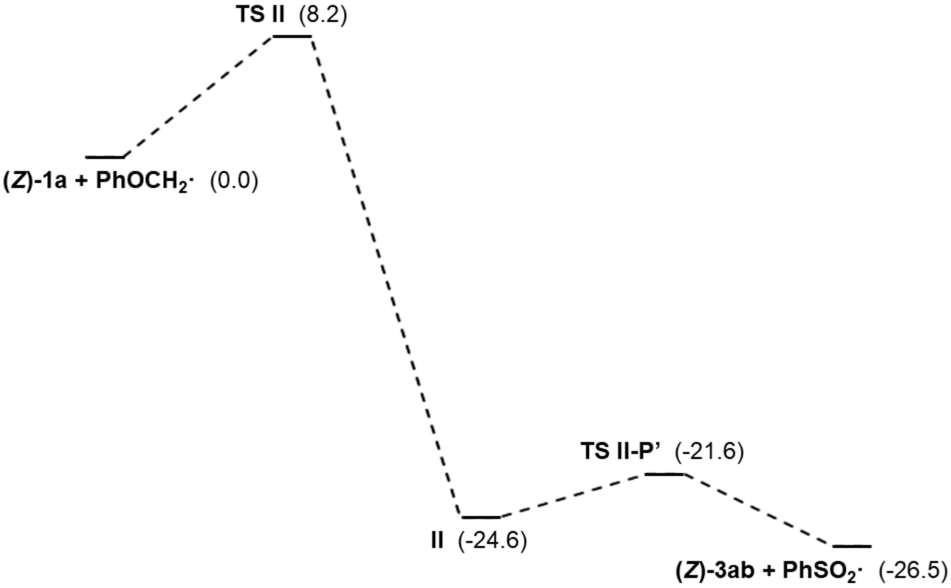


Figure S8. Energy profile for the addition of radical $PhOCH_2\cdot$ to **(*Z*)-1a** and the subsequent elimination of $PhSO_2\cdot$ to give **(*Z*)-3ab**, obtained from DFT calculations [B3LYP-D3/6-311G(d,p) in acetonitrile]. Relative Gibbs free energy values are given in brackets (kcal/mol). Separated **(*Z*)-1a** and $PhOCH_2\cdot$ were taken as zero-energy.

Data shown in Figure S9 can help to find a possible explanation for this result. The elimination of $PhSO_2\cdot$ from **II** to afford the product **(*Z*)-3ab** should be very fast since its activation barrier is 3.0 kcal/mol. However, in principle, the barriers for the reverse reaction (4.9 kcal/mol) and for the change of conformation of **II** to **Ic** (8.1 kcal/mol) could also be overcome at room temperature and this is an overall exergonic process. The formed radical **Ic** could then rapidly evolve to alkene **(*E*)-3ab**. This means that, finally, a thermodynamic control could be established and the ratio between the *E* and *Z* alkenes could be determined by the difference in their Gibbs free energies. As indicated above, the calculated value of ΔG between **3ab** and **(*Z*)-3ab** is -2.5 kcal/mol, which represents a theoretical diastereomeric ratio **3ab**:**(*Z*)-3ab** of *ca.* 99:1. This agrees with the fact that only the *E* alkene was obtained experimentally.

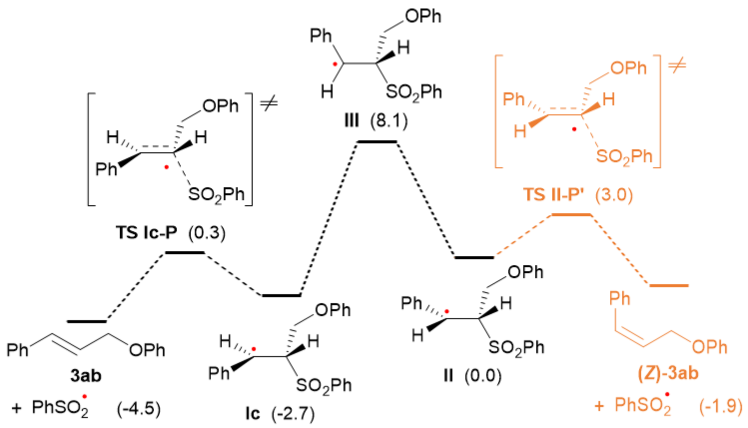
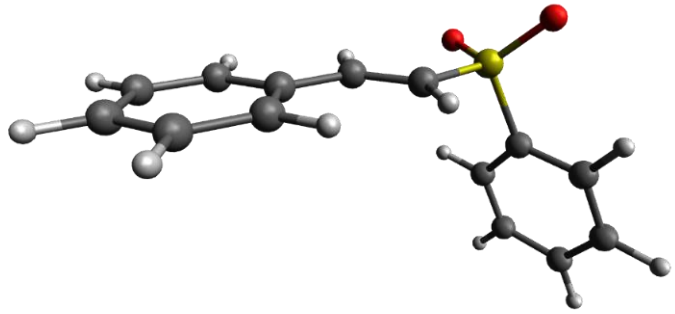


Figure S9. Relative Gibbs free energies (numbers in brackets, kcal/mol) for the transformation of radical **II** to either **3ab** (black profile) or **(*Z*)-3ab** (orange profile), obtained from DFT calculations [B3LYP-D3/6-311G(d,p) in acetonitrile]. Radical **II** was taken as zero-energy.

Cartesian coordinates and energies of the optimized geometries

Gibbs free energies at 298.15 K were obtained from the vibrational frequency calculations (Sum of electronic and thermal Free Energies) and a correction term of 0.003019831 a.u. (corresponding to 1.89 kcal/mol) was added to them in order to consider the change in the standard state from 1 atm to 1 M. All Gibbs free energy values are given in a.u.



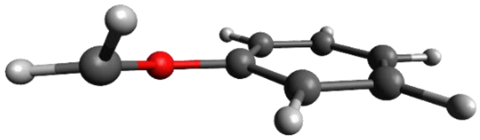
1a

Gibbs free energy = -1089,341357

Cartesian coordinates:

C	4.31367	-1.02213	-1.30116
C	5.22251	-1.02739	-0.23890
C	4.85041	-0.49508	0.99420
C	3.57600	0.03915	1.16471
C	2.65212	0.04745	0.10664
C	3.04137	-0.49099	-1.13325
C	1.32524	0.61576	0.35064
C	0.30748	0.67064	-0.51493
S	-1.23171	1.42283	-0.05102
C	-2.36757	0.03017	0.03407
O	-1.65812	2.28858	-1.16495
O	-1.10602	1.99466	1.30098

C	-3.08819	-0.32792	-1.10384
C	-3.94787	-1.42229	-1.03392
C	-4.07308	-2.13906	0.15615
C	-3.34195	-1.76693	1.28581
C	-2.47834	-0.67660	1.23124
H	4.60171	-1.43309	-2.26224
H	6.21459	-1.44293	-0.37572
H	5.55067	-0.49454	1.82187
H	3.28656	0.45415	2.12435
H	2.35080	-0.49143	-1.96846
H	1.16831	1.03207	1.34263
H	0.30218	0.29023	-1.52922
H	-2.98740	0.24358	-2.01786
H	-4.52006	-1.71116	-1.90777
H	-4.74371	-2.98940	0.20485
H	-3.44541	-2.32356	2.20987
H	-1.90871	-0.37372	2.10098

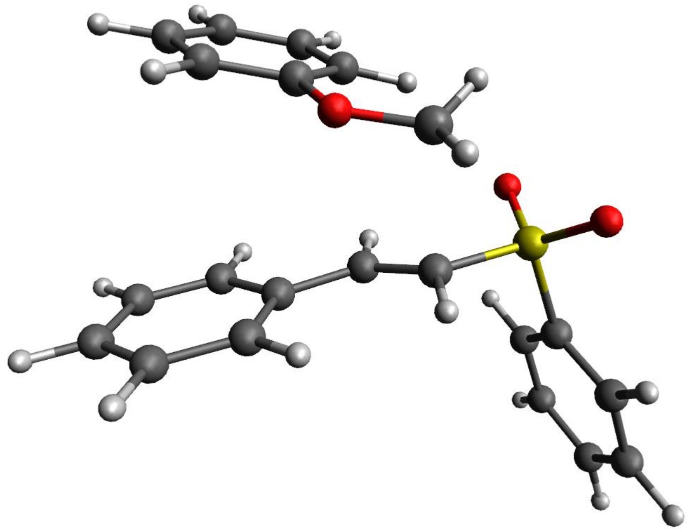


$PhOCH_2\cdot$

Gibbs free energy = -346,1235192

Cartesian coordinates:

C	-1.33091	1.33147	-0.03232
C	-2.23713	0.27637	0.05559
C	-1.76279	-1.03787	0.07021
C	-0.39740	-1.29409	0.00586
C	0.50141	-0.22745	-0.07395
C	0.04217	1.09105	-0.10126
O	1.83186	-0.57013	-0.15419
C	2.79839	0.34751	0.13607
H	-1.68869	2.35490	-0.05600
H	-3.30167	0.47347	0.10727
H	-2.45790	-1.86757	0.13506
H	-0.01037	-2.30619	0.02023
H	0.73867	1.91448	-0.19410
H	3.79596	-0.04029	-0.01778
H	2.58672	1.11040	0.87772



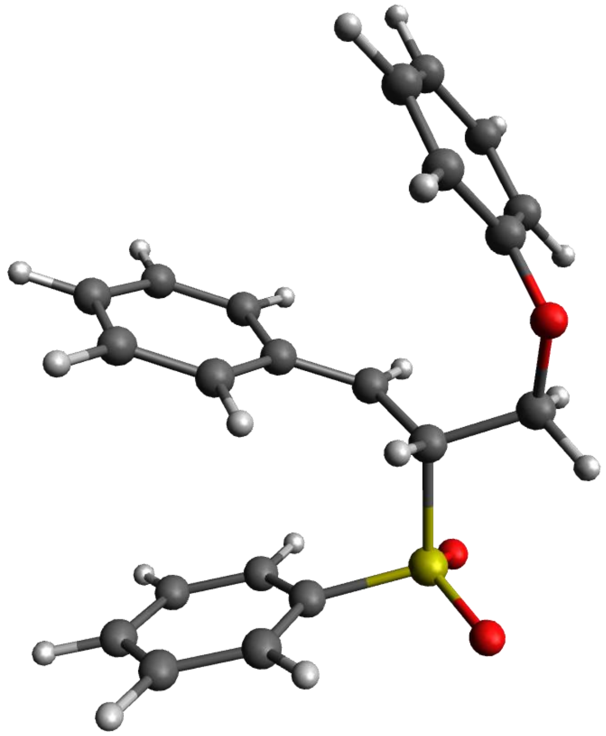
TS Ia

Gibbs free energy = -1435,457245

Cartesian coordinates:

C	-0.10670	0.52488	0.19488
C	0.67895	-0.00756	-0.77566
S	1.91296	-1.21201	-0.34672
C	3.33629	-0.22827	0.15701
O	1.45144	-1.96905	0.83251
O	2.28922	-1.93987	-1.57194
C	4.24457	0.19215	-0.81316
C	5.32654	0.97778	-0.42170
C	5.48639	1.33209	0.91818
C	4.56763	0.90131	1.87650
C	3.47997	0.11743	1.49981
C	-1.08137	1.58683	0.01772
C	-1.88769	1.94957	1.11440
C	-2.86820	2.92769	0.98975
C	-3.06755	3.56685	-0.23447
C	-2.27585	3.21718	-1.33292
C	-1.29591	2.24062	-1.21260
C	-0.76474	-1.62598	-1.99729
O	-1.98104	-1.09718	-1.72984
C	-2.62630	-1.34024	-0.53682
C	-3.91031	-0.79904	-0.44090
C	-4.64016	-0.96581	0.73000
C	-4.09565	-1.67101	1.80659
C	-2.81217	-2.20302	1.69784
C	-2.06466	-2.04401	0.53002
H	-0.08013	0.06529	1.17745
H	0.85594	0.43660	-1.74643
H	4.11396	-0.09722	-1.84837
H	6.04416	1.30959	-1.16296
H	6.33054	1.94302	1.21713
H	4.69775	1.17303	2.91758
H	2.76305	-0.22917	2.23332
H	-1.74531	1.44315	2.06316
H	-3.48119	3.18763	1.84566
H	-3.83381	4.32723	-0.33564

H	-2.42926	3.70784	-2.28789
H	-0.70219	1.97532	-2.07907
H	-0.50381	-2.58428	-1.56412
H	-4.30910	-0.24591	-1.28278
H	-5.63466	-0.54028	0.80330
H	-4.66407	-1.79764	2.72066
H	-2.37370	-2.74004	2.53171
H	-1.05295	-2.42242	0.48336
H	-0.41792	-1.36749	-2.98746



Ia

Gibbs free energy = -1435,501053

Cartesian coordinates:

C	-0.42913	-0.18726	0.64233
C	-0.06965	-1.32106	-0.23198
S	1.56954	-2.04980	0.32222
C	2.70752	-0.67843	0.10145
O	1.47726	-2.36114	1.76106
O	1.93549	-3.12443	-0.62093
C	3.26799	-0.47061	-1.15752
C	4.08700	0.63913	-1.34751
C	4.32538	1.52108	-0.29235
C	3.75722	1.29518	0.96159
C	2.93813	0.18790	1.16772
C	-0.26371	1.18401	0.33604
C	-0.66373	2.15970	1.29270
C	-0.51543	3.51301	1.04096
C	0.03575	3.95157	-0.16955

C	0.43378	3.01047	-1.12687
C	0.28761	1.65383	-0.88840
C	-1.10329	-2.46130	-0.24771
O	-2.22378	-2.08141	-1.05467
C	-3.06829	-1.10390	-0.57206
C	-3.39675	-0.06403	-1.44292
C	-4.27220	0.93658	-1.02784
C	-4.81806	0.90683	0.25605
C	-4.49452	-0.14314	1.11645
C	-3.62706	-1.15449	0.70775
H	-0.82876	-0.44548	1.61613
H	0.13856	-1.03006	-1.26248
H	3.07076	-1.16197	-1.96723
H	4.53538	0.81563	-2.31809
H	4.95740	2.38783	-0.44829
H	3.94591	1.98195	1.77817
H	2.48522	0.00036	2.13251
H	-1.09009	1.82365	2.23191
H	-0.82783	4.23611	1.78650
H	0.15433	5.01136	-0.36387
H	0.86403	3.34439	-2.06476
H	0.61228	0.94673	-1.64068
H	-1.40190	-2.72714	0.76876
H	-2.94854	-0.04766	-2.42935
H	-4.51652	1.74746	-1.70512
H	-5.49113	1.69150	0.58192
H	-4.92099	-0.18022	2.11285
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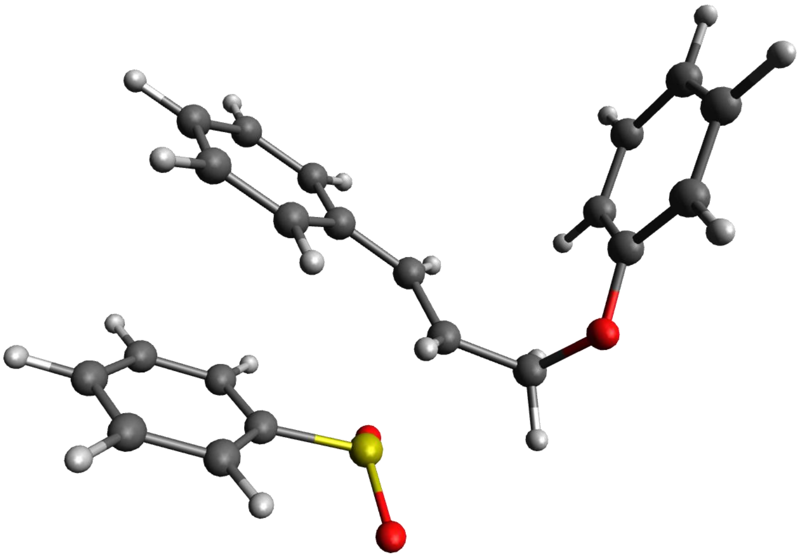
H	-0.69091	-3.34316	-0.73649



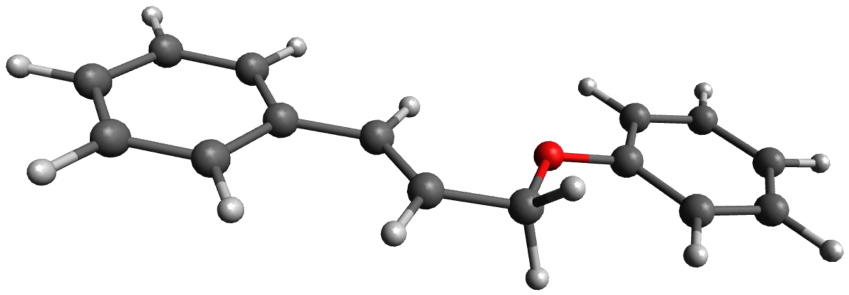
TS Ia-P

Gibbs free energy = -1435,492846

Cartesian coordinates:

C	0.48637	0.22006	-0.71225

C	0.58655	-0.91702	0.07725
S	-1.33562	-2.18113	-0.52406
C	-2.66680	-1.08759	0.01998
O	-1.40988	-2.27779	-2.00567
O	-1.41079	-3.43110	0.28264
C	-3.04996	-1.11705	1.35952
C	-4.01162	-0.21030	1.79746
C	-4.56011	0.71366	0.90635
C	-4.15734	0.73277	-0.42907
C	-3.19700	-0.16845	-0.88253
C	-0.23255	1.42534	-0.38514
C	-0.39953	2.41024	-1.38488
C	-1.11394	3.57308	-1.12978
C	-1.67451	3.78756	0.13148
C	-1.50818	2.82928	1.13745
C	-0.79709	1.66616	0.88860
C	1.63683	-1.97155	-0.18418
O	2.78010	-1.74306	0.66151
C	3.65665	-0.72783	0.38630
C	4.47606	-0.34056	1.45414
C	5.43234	0.65269	1.27676
C	5.58003	1.27999	0.03695
C	4.76205	0.89232	-1.02128
C	3.80065	-0.10768	-0.85886
H	0.90788	0.17085	-1.71123
H	0.28066	-0.86224	1.11880
H	-2.61358	-1.83792	2.03980
H	-4.32944	-0.22374	2.83344
H	-5.30112	1.42349	1.25567
H	-4.58210	1.45406	-1.11724
H	-2.86794	-0.16296	-1.91340
H	0.03087	2.24057	-2.36618
H	-1.23754	4.31345	-1.91219
H	-2.23531	4.69349	0.33170
H	-1.94242	2.99297	2.11717
H	-0.68543	0.93401	1.67788
H	1.91270	-2.01886	-1.24031
H	4.34634	-0.83281	2.41106
H	6.06049	0.94182	2.11233
H	6.32179	2.05846	-0.09925
H	4.86516	1.36790	-1.99061
H	3.18554	-0.39349	-1.70006
H	1.28437	-2.95597	0.12416

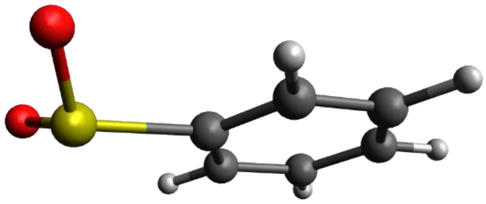


3ab

Gibbs free energy = -655,2255552

Cartesian coordinates:

C	1.37168	-0.10561	-0.00000
C	0.67978	-1.24967	-0.00002
C	2.83615	0.04161	0.00000
C	3.38199	1.33649	-0.00005
C	4.76063	1.53983	-0.00005
C	5.62837	0.44924	0.00000
C	5.10214	-0.84537	0.00006
C	3.72654	-1.04807	0.00006
C	-0.81080	-1.36161	-0.00003
O	-1.40171	-0.06196	0.00000
C	-2.76046	0.04701	0.00000
C	-3.26234	1.35609	0.00004
C	-4.63396	1.57631	0.00005
C	-5.52599	0.49955	0.00001
C	-5.02238	-0.79802	-0.00003
C	-3.64539	-1.03691	-0.00003
H	0.81582	0.82720	0.00001
H	1.18253	-2.21322	-0.00004
H	2.71287	2.19111	-0.00009
H	5.15526	2.55016	-0.00009
H	6.70177	0.60283	0.00000
H	5.76934	-1.70070	0.00010
H	3.34319	-2.06199	0.00011
H	-1.13787	-1.92763	0.88370
H	-2.56026	2.18203	0.00007
H	-5.00902	2.59402	0.00007
H	-6.59579	0.67363	0.00001
H	-5.70091	-1.64435	-0.00006
H	-3.28115	-2.05511	-0.00006
H	-1.13786	-1.92758	-0.88379



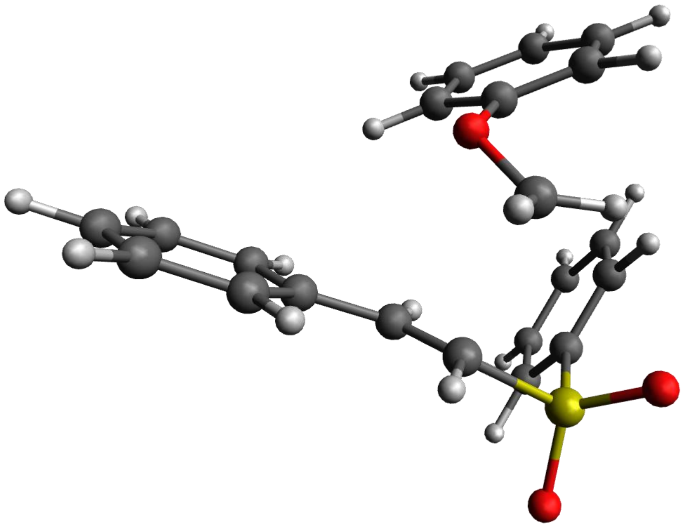
PhSO$_2$ ·

Gibbs free energy = -780,2779032

Cartesian coordinates:

S	-1.70214	0.00000	-0.25872
C	0.10539	0.00000	-0.08918
O	-2.21485	1.29111	0.27356
O	-2.21485	-1.29112	0.27354
C	0.77069	-1.22358	-0.06077
C	2.15983	-1.21204	0.03528
C	2.85029	-0.00000	0.08134

C	2.15984	1.21204	0.03528
C	0.77069	1.22358	-0.06078
H	0.21976	-2.15468	-0.09289
H	2.70006	-2.15048	0.07484
H	3.93186	-0.00000	0.15198
H	2.70006	2.15047	0.07483
H	0.21977	2.15468	-0.09291



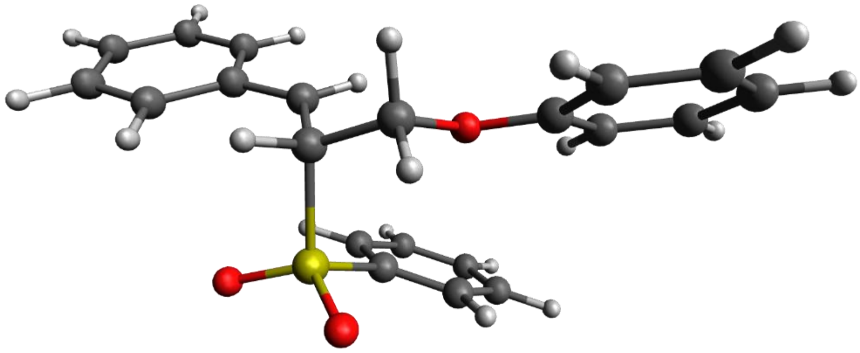
TS Ib

Gibbs free energy = -1435,451438

Cartesian coordinates:

C	1.19561	-0.95142	0.32863
C	0.71477	-1.62047	-0.75275
S	-0.88589	-2.40843	-0.72757
C	-1.88313	-1.44892	0.41946
O	-1.48556	-2.30136	-2.07208
O	-0.71868	-3.76267	-0.16211
C	-1.91776	-1.82322	1.76199
C	-2.67022	-1.05894	2.65070
C	-3.37035	0.05780	2.19301
C	-3.32907	0.41440	0.84479
C	-2.57964	-0.33924	-0.05465
C	2.55842	-0.47692	0.49318
C	2.89617	0.20845	1.67797
C	4.18172	0.69811	1.88173
C	5.16282	0.51894	0.90514
C	4.84322	-0.15596	-0.27662
C	3.56053	-0.64786	-0.48375
C	0.38821	0.15431	-2.43812
O	0.79987	1.25356	-1.76361
C	-0.13169	2.05110	-1.11966
C	0.19201	2.48617	0.16353
C	-0.68964	3.32515	0.84044
C	-1.88250	3.72886	0.23837
C	-2.18652	3.29414	-1.05166

C	-1.31362	2.45382	-1.74053
H	0.50567	-0.66266	1.11401
H	1.33869	-2.08901	-1.50491
H	-1.37013	-2.69385	2.09960
H	-2.70876	-1.33622	3.69760
H	-3.95219	0.65124	2.88907
H	-3.87293	1.28164	0.49206
H	-2.54058	-0.07161	-1.10137
H	2.13488	0.35382	2.43742
H	4.41876	1.22200	2.80130
H	6.16509	0.90230	1.06006
H	5.59971	-0.29436	-1.04147
H	3.33308	-1.15908	-1.41166
H	-0.66674	0.00372	-2.61925
H	1.11944	2.15537	0.61335
H	-0.44521	3.65734	1.84311
H	-2.56875	4.37815	0.76958
H	-3.10692	3.60993	-1.52981
H	-1.54135	2.12414	-2.74674
H	1.13152	-0.22398	-3.12562



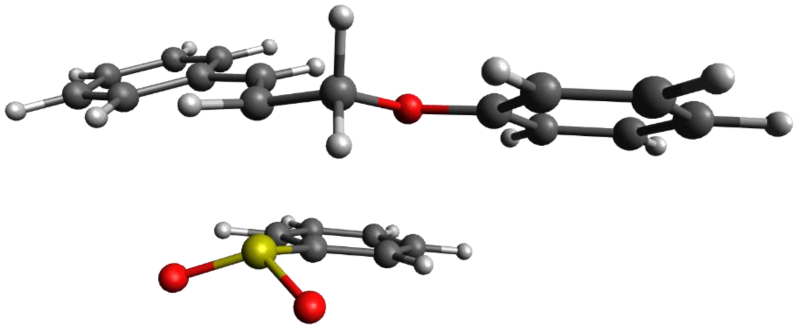
Ib

Gibbs free energy = -1435,503588

Cartesian coordinates:

C	1.37857	-0.96009	-0.38489
C	0.67805	-1.03873	0.91317
S	0.62368	0.65638	1.75771
C	-0.00961	1.81680	0.53909
O	-0.34120	0.58038	2.87373
O	2.02313	1.02275	2.04592
C	0.86777	2.33870	-0.41016
C	0.36607	3.21354	-1.37159
C	-0.98626	3.55697	-1.36734
C	-1.84669	3.03075	-0.40241
C	-1.36212	2.14691	0.55770
C	2.77725	-1.03681	-0.58331
C	3.28800	-0.95277	-1.91094
C	4.64697	-1.02843	-2.16291
C	5.55342	-1.18877	-1.10720
C	5.07594	-1.26771	0.20680
C	3.71841	-1.19227	0.47317

C	-0.72804	-1.61746	0.84274
O	-1.45612	-0.88007	-0.13801
C	-2.78544	-1.13456	-0.31455
C	-3.43804	-0.30980	-1.24004
C	-4.79385	-0.48468	-1.48783
C	-5.51456	-1.47994	-0.82071
C	-4.85782	-2.29707	0.09516
C	-3.49455	-2.13450	0.35679
H	0.75121	-0.80430	-1.25377
H	1.23707	-1.59993	1.66698
H	1.91729	2.07539	-0.39288
H	1.03276	3.62853	-2.11840
H	-1.37078	4.23960	-2.11665
H	-2.89600	3.30105	-0.40082
H	-2.01854	1.71932	1.30377
H	2.58827	-0.82756	-2.73061
H	5.01007	-0.96250	-3.18276
H	6.61752	-1.24769	-1.30543
H	5.77563	-1.38488	1.02730
H	3.37582	-1.23149	1.49853
H	-1.21299	-1.54693	1.81992
H	-2.86623	0.45985	-1.74428
H	-5.29090	0.16007	-2.20446
H	-6.57236	-1.61406	-1.01521
H	-5.40318	-3.07499	0.61843
H	-3.00563	-2.78339	1.07099
H	-0.65517	-2.67303	0.55855



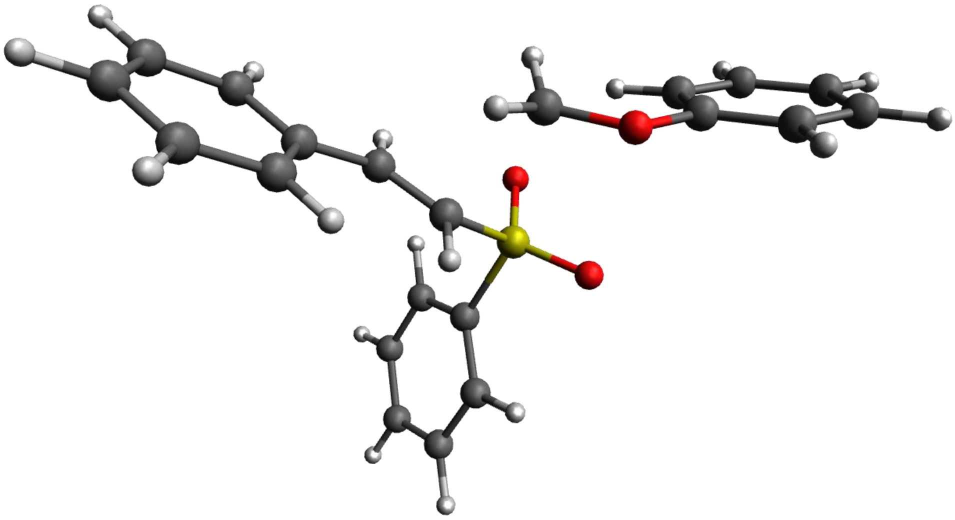
TS Ib-P

Gibbs free energy = -1435,498055

Cartesian coordinates:

C	1.05995	-1.20857	-0.79722
C	0.34786	-1.77228	0.25274
S	0.42676	-0.07378	1.94219
C	0.47918	1.46246	0.98926
O	-0.83945	-0.07109	2.73020
O	1.72134	-0.18746	2.66930
C	1.71408	1.94152	0.55784
C	1.74337	3.07318	-0.25521
C	0.55299	3.69725	-0.62909
C	-0.67509	3.19615	-0.19258

C	-0.72054	2.06295	0.61543
C	2.49381	-1.13018	-0.91052
C	3.04878	-0.46596	-2.02848
C	4.42264	-0.33076	-2.17088
C	5.28147	-0.85063	-1.19893
C	4.75100	-1.50808	-0.08418
C	3.37858	-1.64924	0.06270
C	-1.14160	-1.95415	0.18184
O	-1.69573	-0.83002	-0.50090
C	-3.05194	-0.71095	-0.59666
C	-3.51100	0.45829	-1.21754
C	-4.87553	0.67707	-1.36079
C	-5.79818	-0.26226	-0.89029
C	-5.33416	-1.42231	-0.27653
C	-3.96503	-1.65790	-0.12403
H	0.48942	-0.69240	-1.56158
H	0.84110	-2.47474	0.91794
H	2.62824	1.44448	0.85577
H	2.69534	3.46227	-0.59725
H	0.58110	4.57538	-1.26429
H	-1.59822	3.68372	-0.48400
H	-1.66427	1.65337	0.94975
H	2.38130	-0.05135	-2.77634
H	4.82809	0.18339	-3.03510
H	6.35484	-0.74219	-1.30625
H	5.41542	-1.90758	0.67395
H	2.98799	-2.14533	0.94175
H	-1.56068	-2.03610	1.18955
H	-2.78372	1.17742	-1.57500
H	-5.22084	1.58586	-1.84159
H	-6.86219	-0.08900	-1.00256
H	-6.03765	-2.16083	0.09240
H	-3.62852	-2.56724	0.35552
H	-1.36793	-2.88369	-0.35764

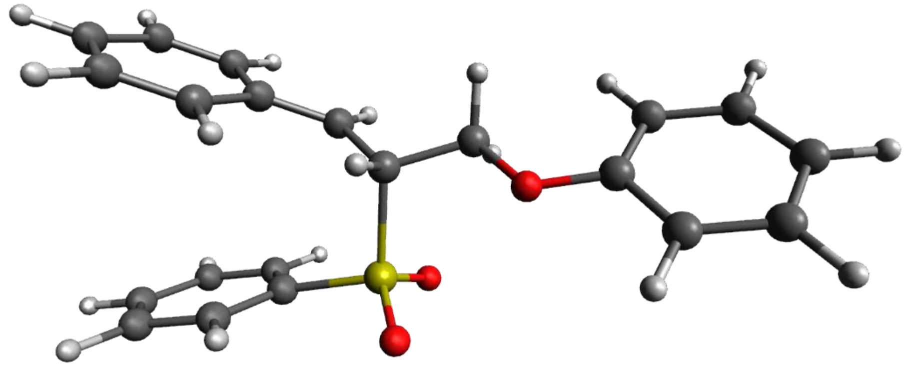


TS Ic

Gibbs free energy = -1435,450107

Cartesian coordinates:

C	-1.59190	-0.77789	0.58085
C	-0.68690	-0.25282	-0.29123
S	0.28002	1.15530	0.20046
C	-0.83691	2.55065	-0.04119
O	0.56561	1.06007	1.64488
O	1.38818	1.30989	-0.75555
C	-0.90424	3.14818	-1.29871
C	-1.78760	4.20835	-1.49036
C	-2.58619	4.65361	-0.43650
C	-2.50507	4.04418	0.81651
C	-1.62818	2.98189	1.02210
C	-2.57716	-1.79637	0.26791
C	-3.42863	-2.25699	1.29332
C	-4.38743	-3.23248	1.04402
C	-4.51857	-3.77660	-0.23473
C	-3.68007	-3.33400	-1.26209
C	-2.72199	-2.35820	-1.01878
C	1.06693	-1.96060	-0.30371
O	2.23306	-1.80289	-0.97051
C	3.36251	-1.29669	-0.36056
C	4.52982	-1.38373	-1.12104
C	5.72821	-0.90871	-0.59822
C	5.76541	-0.34682	0.67988
C	4.59003	-0.25993	1.42444
C	3.37976	-0.72925	0.91351
H	-1.53424	-0.46993	1.62072
H	-0.73586	-0.34993	-1.36808
H	-0.27181	2.79876	-2.10530
H	-1.84878	4.68675	-2.46091
H	-3.27161	5.47917	-0.59082
H	-3.12224	4.39632	1.63492
H	-1.54955	2.50385	1.99026
H	-3.32816	-1.83862	2.28942
H	-5.03258	-3.57072	1.84742
H	-5.26459	-4.53860	-0.43020
H	-3.77562	-3.75426	-2.25730
H	-2.08167	-2.03097	-1.82940
H	0.36506	-2.55306	-0.87417
H	4.47966	-1.82526	-2.10940
H	6.63361	-0.97917	-1.19061
H	6.69888	0.02421	1.08701
H	4.60429	0.18779	2.41206
H	2.47258	-0.61384	1.48923
H	1.09649	-2.06836	0.77467



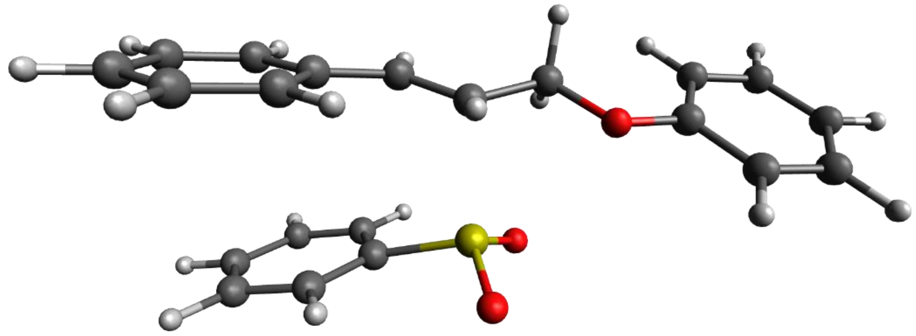
Ic

Gibbs free energy = -1435,500619

Cartesian coordinates:

C	-0.74490	1.19930	-0.64038
C	0.27831	0.45392	0.12151
S	0.07136	-1.41854	-0.17578
C	-1.71256	-1.66120	-0.18060
O	0.57332	-1.69944	-1.53584
O	0.61827	-2.17201	0.96735
C	-2.35980	-1.88276	1.03242
C	-3.74580	-2.02193	1.03518
C	-4.45968	-1.93177	-0.15979
C	-3.79375	-1.71312	-1.36674
C	-2.40825	-1.57510	-1.38448
C	-1.97296	1.68723	-0.13365
C	-2.87229	2.34384	-1.02215
C	-4.09333	2.82383	-0.58183
C	-4.47064	2.67326	0.75868
C	-3.60296	2.03440	1.65185
C	-2.37826	1.54824	1.22329
C	1.68367	0.84159	-0.32043
O	2.61832	0.14388	0.49827
C	3.95216	0.30708	0.25732
C	4.80817	-0.45198	1.06597
C	6.18434	-0.35404	0.90352
C	6.72593	0.49727	-0.06455
C	5.86949	1.24795	-0.86483
C	4.48275	1.16187	-0.71373
H	-0.53817	1.35058	-1.69514
H	0.18059	0.53975	1.20337
H	-1.79276	-1.94668	1.95238
H	-4.26592	-2.19518	1.96991
H	-5.53886	-2.03370	-0.15131
H	-4.35163	-1.64734	-2.29339
H	-1.87611	-1.40371	-2.31135
H	-2.58691	2.45692	-2.06263
H	-4.76156	3.31591	-1.28002
H	-5.42824	3.04754	1.10195
H	-3.89167	1.91274	2.69011
H	-1.73079	1.05033	1.93375
H	1.79191	1.92432	-0.19347
H	4.37258	-1.10837	1.81042
H	6.83789	-0.94671	1.53435

H	7.79992	0.57137	-0.19020
H	6.27450	1.91296	-1.61996
H	3.83828	1.75627	-1.34731
H	1.82816	0.59286	-1.37672



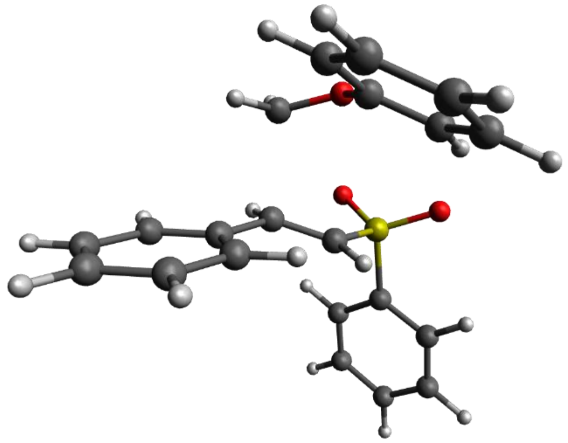
TS Ic-P

Gibbs free energy = -1435,49582

Cartesian coordinates:

C	0.82438	-1.34651	-0.77130
C	-0.29108	-1.10663	0.02438
S	-0.19371	1.21748	0.52144
C	1.50682	1.63962	0.06262
O	-1.08306	1.92516	-0.44003
O	-0.34174	1.49201	1.97717
C	2.51417	1.52313	1.01630
C	3.83297	1.74789	0.62771
C	4.12727	2.06783	-0.69798
C	3.10513	2.17267	-1.64216
C	1.78201	1.95015	-1.26704
C	2.15337	-1.63862	-0.30072
C	3.21628	-1.65983	-1.23241
C	4.52067	-1.90213	-0.82431
C	4.80137	-2.13620	0.52404
C	3.76198	-2.12777	1.46013
C	2.45739	-1.88251	1.05964
C	-1.66339	-1.12209	-0.58361
O	-2.57600	-0.71138	0.43534
C	-3.88926	-0.53244	0.11342
C	-4.70380	-0.05184	1.14721
C	-6.05886	0.15695	0.92380
C	-6.62052	-0.10711	-0.32923
C	-5.80541	-0.58366	-1.35198
C	-4.44057	-0.80029	-1.14342
H	0.71018	-1.21983	-1.84464
H	-0.26444	-1.37618	1.07539
H	2.27197	1.26243	2.03856
H	4.62904	1.66157	1.35793
H	5.15627	2.23192	-0.99687
H	3.33638	2.42291	-2.67107
H	0.97741	2.02602	-1.98743
H	3.00137	-1.46769	-2.27799

H	5.32243	-1.90450	-1.55418
H	5.82001	-2.32404	0.84389
H	3.97601	-2.31059	2.50722
H	1.66889	-1.87545	1.80234
H	-1.90534	-2.13862	-0.91885
H	-4.25340	0.15007	2.11225
H	-6.67972	0.53016	1.73102
H	-7.67779	0.05775	-0.50174
H	-6.22636	-0.79333	-2.32941
H	-3.82881	-1.17295	-1.95394
H	-1.71396	-0.44918	-1.44606



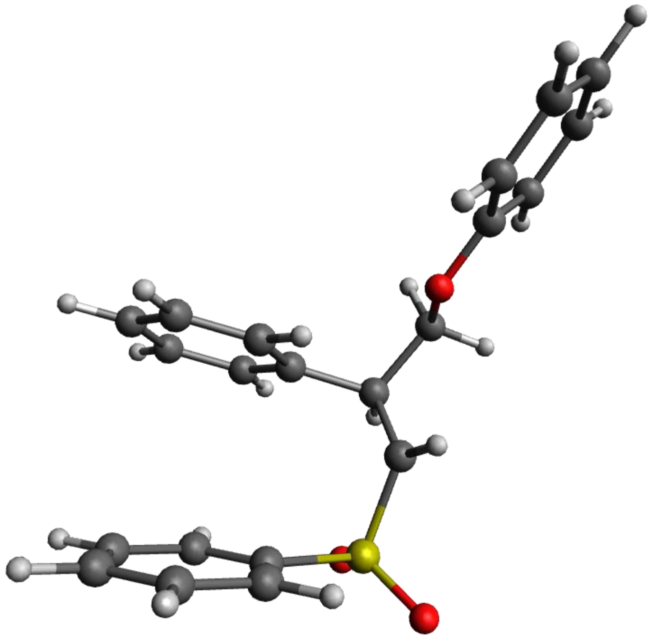
TS NBR

Gibbs free energy = -1435,450264

Cartesian coordinates:

C	-0.47548	0.03698	-0.05403
S	-1.78124	-0.86657	-0.78942
C	-3.25991	-0.26035	0.04641
O	-1.63886	-2.29117	-0.42371
O	-1.89062	-0.49467	-2.21404
C	-3.69247	-0.89539	1.20987
C	-4.81403	-0.39778	1.87005
C	-5.48367	0.71900	1.36921
C	-5.03761	1.34377	0.20315
C	-3.91711	0.85837	-0.46585
C	1.17327	1.92277	-0.11469
C	1.44980	3.16111	-0.71330
C	2.39320	4.02602	-0.16296
C	3.08414	3.66392	0.99283
C	2.82376	2.42933	1.59199
C	1.88007	1.56602	1.04524
O	1.57055	-1.33961	-1.73413
C	2.32967	-1.69358	-0.62650
C	1.73229	-2.57823	0.26855
C	2.44554	-2.99216	1.39113
C	3.74206	-2.52526	1.61484
C	4.32859	-1.64905	0.70146
C	3.62829	-1.22875	-0.42843

C	1.53787	-0.04983	-2.13854
C	0.17995	1.02916	-0.74886
H	-0.20815	-0.32284	0.92985
H	-3.16899	-1.76716	1.58183
H	-5.16509	-0.88484	2.77247
H	-6.35622	1.10188	1.88624
H	-5.56282	2.20793	-0.18698
H	-3.56446	1.33071	-1.37426
H	0.91832	3.44342	-1.61628
H	2.58924	4.98091	-0.63837
H	3.82196	4.33334	1.42082
H	3.36369	2.13525	2.48540
H	1.70956	0.60297	1.51147
H	0.71570	-2.90235	0.08226
H	1.98262	-3.67401	2.09566
H	4.29301	-2.84539	2.49172
H	5.33865	-1.28974	0.86287
H	4.08957	-0.55524	-1.13960
H	0.98528	0.06118	-3.06267
H	2.41775	0.56398	-1.98116
H	-0.31767	1.43221	-1.62497



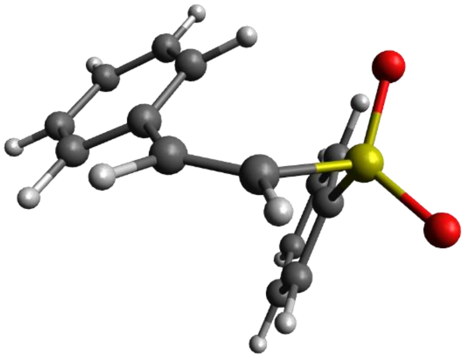
NBR

Gibbs free energy = -1435,480323

Cartesian coordinates:

C	-0.21062	-1.45271	-0.42212
S	-1.86813	-2.02413	-0.56386
C	-2.81181	-0.89504	0.46602
O	-1.92606	-3.36176	0.05227
O	-2.30705	-1.84415	-1.95945
C	-2.79076	-1.07385	1.84992

C	-3.46849	-0.16000	2.65170
C	-4.15063	0.91032	2.07035
C	-4.16309	1.07172	0.68437
C	-3.48558	0.16917	-0.13054
C	-0.25732	0.96549	-1.02422
C	-0.87195	1.71233	-2.03238
C	-1.42786	2.96035	-1.75150
C	-1.37999	3.47081	-0.45511
C	-0.77017	2.72845	0.55721
C	-0.21442	1.48300	0.27642
O	2.30754	-0.20001	-0.01504
C	3.64719	-0.13719	0.23500
C	4.00369	0.09889	1.56957
C	5.34377	0.18016	1.92688
C	6.34572	0.02823	0.96351
C	5.98475	-0.20594	-0.36030
C	4.64145	-0.29064	-0.73650
C	1.85768	-0.42881	-1.35312
C	0.32628	-0.41331	-1.34747
H	0.29919	-1.77125	0.47888
H	-2.26091	-1.91034	2.28850
H	-3.46496	-0.28462	3.72816
H	-4.67301	1.62145	2.70003
H	-4.69218	1.90439	0.23646
H	-3.47358	0.28765	-1.20551
H	-0.92361	1.31086	-3.03893
H	-1.90406	3.52789	-2.54352
H	-1.81977	4.43679	-0.23303
H	-0.73562	3.11579	1.56951
H	0.24731	0.90613	1.06698
H	3.21681	0.21484	2.30603
H	5.60781	0.36335	2.96278
H	7.39056	0.09201	1.24451
H	6.75034	-0.32612	-1.11923
H	4.38705	-0.47356	-1.77174
H	2.21790	-1.39974	-1.71034
H	2.22565	0.35658	-2.02103
H	0.01267	-0.66706	-2.36512

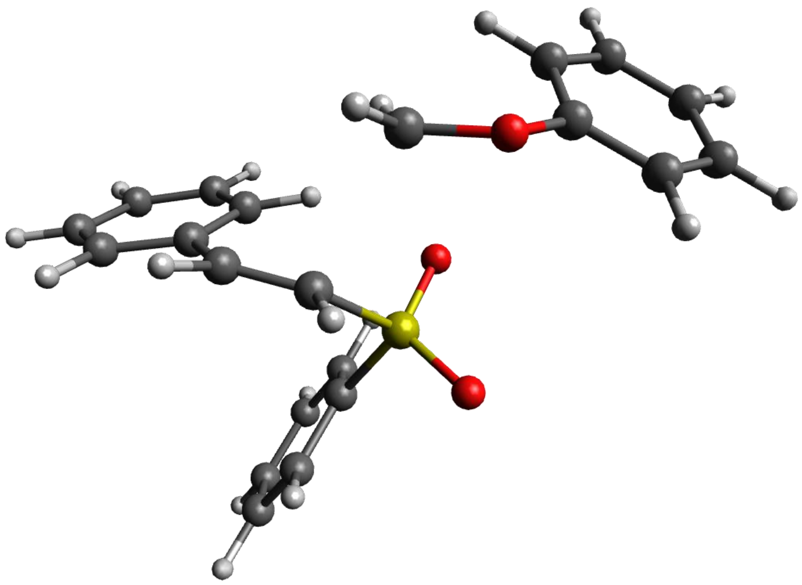


(*Z*)-1a

Gibbs free energy = -1089,33364

Cartesian coordinates:

C	-2.52040	-0.08416	1.47983
C	-3.60037	0.25200	0.66412
C	-3.63215	-0.18681	-0.66070
C	-2.58727	-0.95323	-1.16459
C	-1.47593	-1.26637	-0.36214
C	-1.46329	-0.83450	0.97357
C	-0.39842	-2.06090	-0.96081
C	0.92636	-2.04474	-0.76501
S	1.90469	-0.95505	0.26206
C	1.25454	0.70245	-0.00633
O	3.26093	-1.01257	-0.31451
O	1.74419	-1.28705	1.69108
C	1.16951	1.18802	-1.31074
C	0.69276	2.47954	-1.51228
C	0.32744	3.26984	-0.42040
C	0.43412	2.77264	0.87756
C	0.89726	1.47610	1.09357
H	-2.49929	0.23859	2.51454
H	-4.41886	0.84201	1.06107
H	-4.47464	0.06091	-1.29648
H	-2.61708	-1.30343	-2.19074
H	-0.64138	-1.10649	1.62176
H	-0.72765	-2.76469	-1.72308
H	1.58631	-2.71442	-1.30485
H	1.45150	0.56852	-2.15374
H	0.60835	2.86875	-2.52007
H	-0.04314	4.27535	-0.58390
H	0.14828	3.38687	1.72328
H	0.96666	1.06654	2.09287

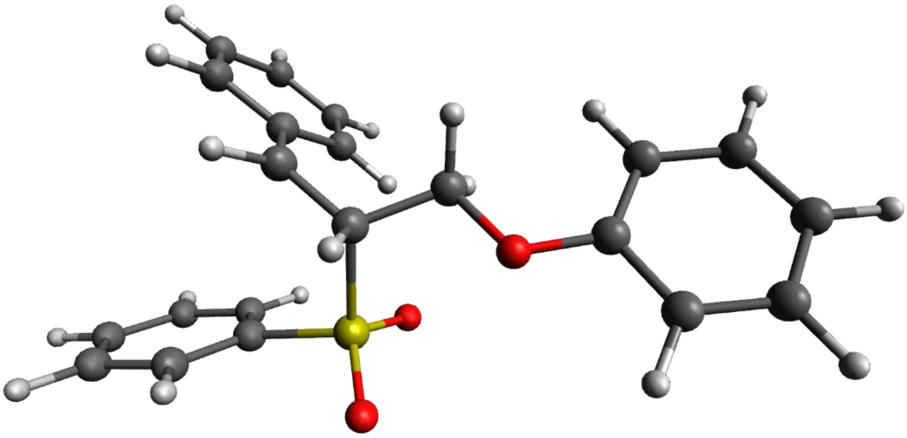


TS II

Gibbs free energy = -1435,444153

Cartesian coordinates:

C	1.29871	1.01424	-1.81971
C	0.26813	0.12353	-1.82721
S	-0.16131	-1.05245	-0.53499
C	1.42549	-1.65055	0.08530
O	-0.87063	-0.43329	0.59979
O	-0.82489	-2.16646	-1.24076
C	2.30243	-2.27261	-0.80317
C	3.52105	-2.74201	-0.32324
C	3.84499	-2.59605	1.02767
C	2.95247	-1.98107	1.90371
C	1.73119	-1.49911	1.43399
C	2.04237	1.60783	-0.71854
C	3.32574	2.12867	-0.98551
C	4.09173	2.69786	0.02408
C	3.58728	2.78294	1.32400
C	2.30745	2.29943	1.59804
C	1.54119	1.71704	0.59364
C	-1.82105	1.44433	-1.61824
O	-2.98144	0.74527	-1.61823
C	-3.68084	0.50064	-0.45116
C	-4.41416	-0.68446	-0.41846
C	-5.17638	-0.98680	0.70590
C	-5.20868	-0.11039	1.79247
C	-4.48086	1.07818	1.73876
C	-3.71578	1.39560	0.61733
H	1.59615	1.35728	-2.80796
H	-0.10658	-0.25482	-2.76978
H	2.04650	-2.37954	-1.85045
H	4.21650	-3.22147	-1.00216
H	4.79664	-2.96230	1.39567
H	3.20564	-1.86739	2.95129
H	1.03161	-1.00761	2.09679
H	3.71933	2.06930	-1.99484
H	5.08111	3.08036	-0.20146
H	4.18182	3.23190	2.11173
H	1.90132	2.37784	2.60059
H	0.54443	1.36663	0.82207
H	-1.60448	1.88970	-2.57901
H	-4.36635	-1.35565	-1.26756
H	-5.74099	-1.91204	0.73443
H	-5.79962	-0.34908	2.66921
H	-4.50960	1.77124	2.57233
H	-3.16667	2.32751	0.57695
H	-1.48502	1.90979	-0.70235



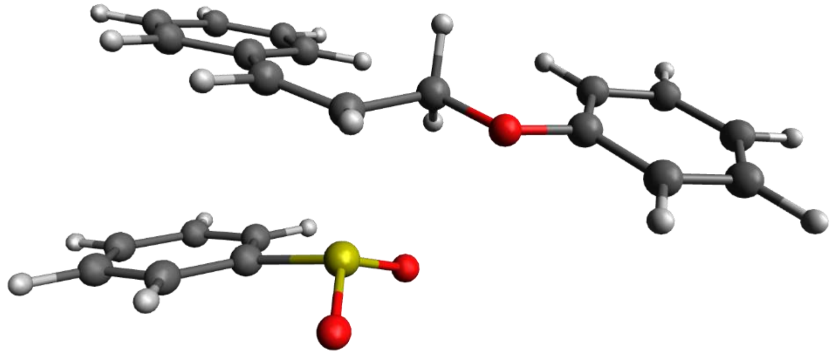
II

Gibbs free energy = -1435,49636

Cartesian coordinates:

C	-0.99603	0.56784	1.46923
C	0.16534	-0.27868	1.09139
S	-0.23269	-1.47950	-0.33746
C	-2.02954	-1.62027	-0.30348
O	0.14938	-0.83900	-1.61266
O	0.32628	-2.80277	-0.00492
C	-2.61768	-2.38975	0.69966
C	-4.00623	-2.47748	0.74618
C	-4.78170	-1.80922	-0.20315
C	-4.17481	-1.05306	-1.20569
C	-2.78632	-0.95051	-1.26044
C	-1.58458	1.63326	0.74432
C	-2.66609	2.34173	1.34470
C	-3.30176	3.37908	0.68551
C	-2.89477	3.75414	-0.60109
C	-1.84371	3.06677	-1.21783
C	-1.19818	2.02640	-0.56830
C	1.45021	0.46575	0.73986
O	2.49519	-0.50506	0.68761
C	3.74351	-0.10255	0.30613
C	4.69534	-1.12286	0.18303
C	5.99685	-0.81570	-0.19353
C	6.36694	0.50733	-0.45357
C	5.41596	1.51602	-0.32871
C	4.10279	1.22440	0.05063
H	-1.46153	0.30581	2.41198
H	0.38147	-0.97693	1.90033
H	-2.00614	-2.91035	1.42639
H	-4.48109	-3.06906	1.52007
H	-5.86259	-1.88094	-0.16190
H	-4.77938	-0.53848	-1.94330
H	-2.29913	-0.36023	-2.02495
H	-2.98929	2.05295	2.33914
H	-4.12072	3.90112	1.16808
H	-3.39436	4.56565	-1.11754
H	-1.53369	3.34219	-2.21996
H	-0.41634	1.49095	-1.08751
H	1.64310	1.20157	1.52761

H	4.39237	-2.14358	0.38587
H	6.72571	-1.61339	-0.28725
H	7.38259	0.74440	-0.74851
H	5.68799	2.54729	-0.52595
H	3.38364	2.02721	0.14372
H	1.37031	0.98447	-0.21648



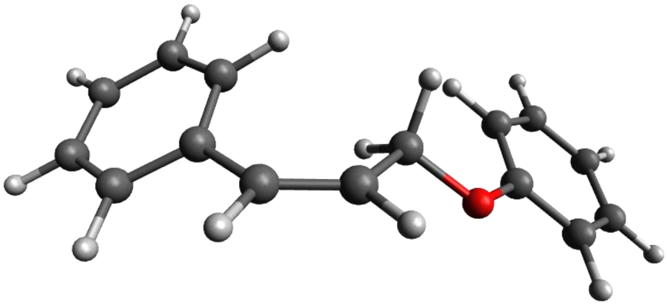
TS II-P’

Gibbs free energy = -1435,491591

Cartesian coordinates:

C	1.03362	0.46473	-1.66465
C	-0.25934	-0.03565	-1.46501
S	0.00967	-1.78930	0.07231
C	1.77402	-1.68235	0.46472
O	-0.73040	-1.47282	1.32529
O	-0.22940	-3.09781	-0.59295
C	2.68969	-2.29568	-0.38683
C	4.05019	-2.10968	-0.15108
C	4.47364	-1.30991	0.91145
C	3.54120	-0.69722	1.74889
C	2.17778	-0.87415	1.52446
C	1.77699	1.46339	-0.94508
C	3.14585	1.61968	-1.27822
C	3.95362	2.52383	-0.60593
C	3.42252	3.30806	0.42165
C	2.07331	3.17803	0.76223
C	1.25923	2.27439	0.09396
C	-1.39574	0.67271	-0.78109
O	-2.54938	-0.14754	-0.98490
C	-3.71206	0.19674	-0.35864
C	-4.76725	-0.71416	-0.49833
C	-5.99493	-0.45134	0.09640
C	-6.18874	0.71847	0.83741
C	-5.13664	1.61997	0.97096
C	-3.89584	1.37115	0.37798
H	1.60976	-0.07171	-2.41161
H	-0.60412	-0.71056	-2.24339
H	2.34686	-2.91040	-1.20996
H	4.77714	-2.58586	-0.79876
H	5.53329	-1.16065	1.08463
H	3.87240	-0.07226	2.56997

H	1.44136	-0.39534	2.15667
H	3.56567	1.00284	-2.06518
H	4.99969	2.61623	-0.87543
H	4.05243	4.01373	0.95117
H	1.65554	3.78515	1.55750
H	0.22324	2.19808	0.38852
H	-1.54318	1.66254	-1.23054
H	-4.60090	-1.61814	-1.07278
H	-6.80405	-1.16476	-0.01636
H	-7.14683	0.92047	1.30220
H	-5.27186	2.53262	1.54129
H	-3.09487	2.08891	0.49367
H	-1.21958	0.79709	0.29052



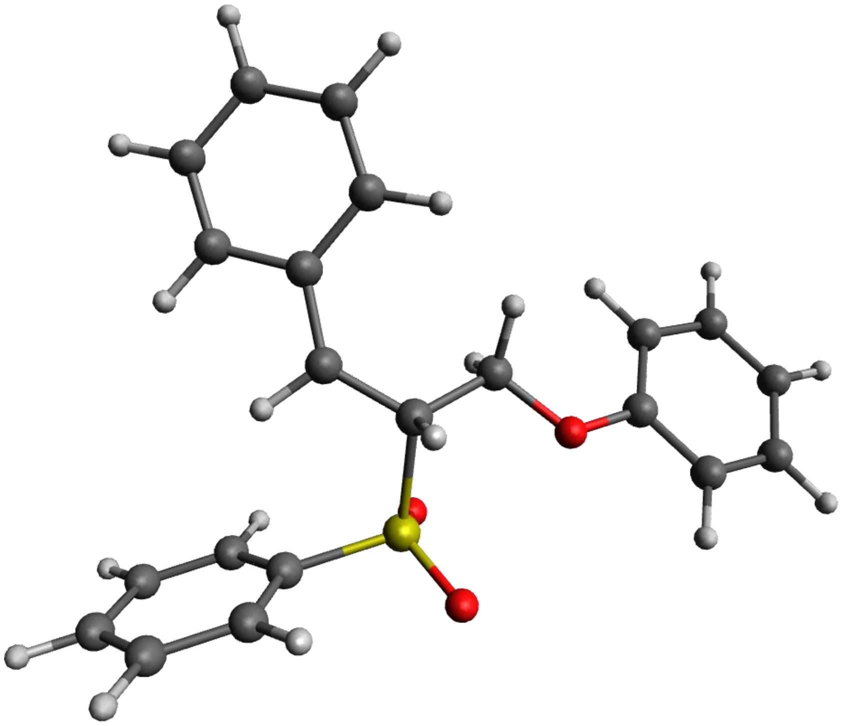
(*Z*)-3ab

Gibbs free energy = -655,2215182

Cartesian coordinates:

C	1.99292	-1.77161	-0.38672
C	0.66906	-1.82602	-0.58571
C	2.83654	-0.58924	-0.14184
C	3.97533	-0.73090	0.67173
C	4.79504	0.35689	0.95557
C	4.50674	1.61168	0.41586
C	3.39910	1.76283	-0.41755
C	2.57422	0.67504	-0.69774
C	-0.30302	-0.68879	-0.58949
O	-1.53865	-1.20397	-0.06252
C	-2.60926	-0.36673	0.02504
C	-3.78307	-0.93543	0.54093
C	-4.93186	-0.16591	0.67293
C	-4.93233	1.18022	0.29401
C	-3.76538	1.74050	-0.21748
C	-2.60071	0.98031	-0.35590
H	2.52577	-2.71948	-0.36910
H	0.21281	-2.79760	-0.75522
H	4.20740	-1.70460	1.09104
H	5.66175	0.22594	1.59430
H	5.14701	2.45959	0.63241
H	3.18046	2.72816	-0.86104
H	1.74457	0.80523	-1.38134
H	-0.46877	-0.31570	-1.60926
H	-3.76833	-1.97988	0.83068

H	-5.83216	-0.61896	1.07383
H	-5.82985	1.77897	0.39749
H	-3.74883	2.78332	-0.51564
H	-1.70810	1.44257	-0.75507
H	0.04567	0.14727	0.02531



III

Gibbs free energy = -1435,483468

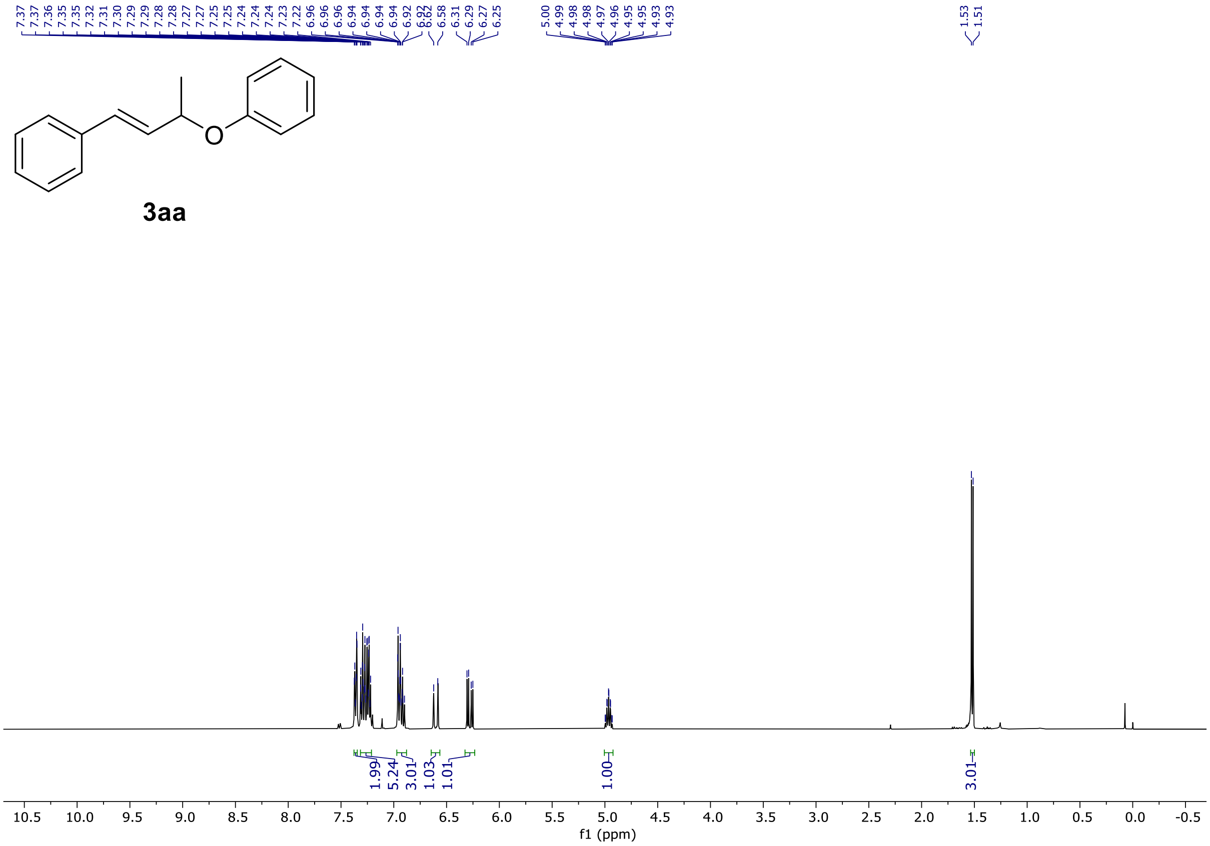
Cartesian coordinates:

C	1.26867	0.93853	-0.37528
C	0.13714	0.02398	-0.72013
S	0.42069	-1.67409	0.08820
C	2.20645	-1.92569	0.11643
O	-0.03753	-1.57799	1.48700
O	-0.13723	-2.71083	-0.79640
C	2.84329	-2.33801	-1.05299
C	4.22264	-2.52790	-1.03064
C	4.94040	-2.30940	0.14629
C	4.28539	-1.90077	1.30837
C	2.90689	-1.69964	1.29911
C	1.33371	2.35211	-0.25950
C	2.55638	2.89675	0.24250
C	2.73526	4.25887	0.40143
C	1.71315	5.15197	0.05623
C	0.51497	4.65054	-0.46127
C	0.32163	3.28644	-0.62079
C	-1.25008	0.47777	-0.27487
O	-2.17800	-0.55012	-0.61060
C	-3.47513	-0.41273	-0.20770

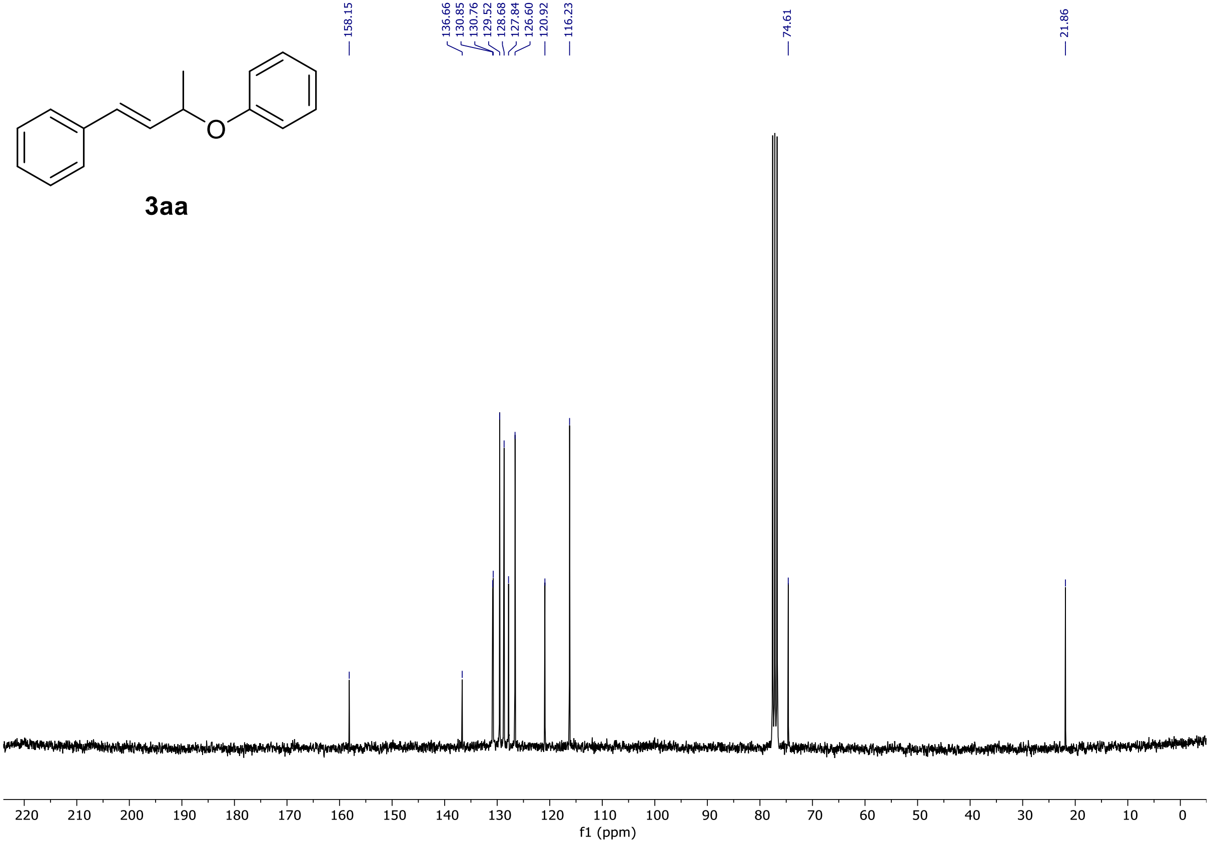
C	-4.30939	-1.50470	-0.47955
C	-5.65024	-1.45957	-0.11890
C	-6.17654	-0.33110	0.51733
C	-5.34125	0.74973	0.78502
C	-3.99040	0.72142	0.42765
H	2.22102	0.44470	-0.23276
H	0.12568	-0.23733	-1.78517
H	2.27476	-2.51347	-1.95782
H	4.73471	-2.84985	-1.92982
H	6.01372	-2.46101	0.15794
H	4.84536	-1.73612	2.22146
H	2.38180	-1.37725	2.18911
H	3.35438	2.21400	0.51455
H	3.67383	4.63431	0.79438
H	1.85263	6.21974	0.17957
H	-0.27508	5.33434	-0.75218
H	-0.60537	2.94787	-1.05803
H	-1.52107	1.39139	-0.80251
H	-3.88555	-2.37249	-0.97146
H	-6.28753	-2.31056	-0.33335
H	-7.22273	-0.29865	0.79865
H	-5.73512	1.63224	1.27745
H	-3.36220	1.57511	0.64458
H	-1.24988	0.66851	0.80187

Spectra.

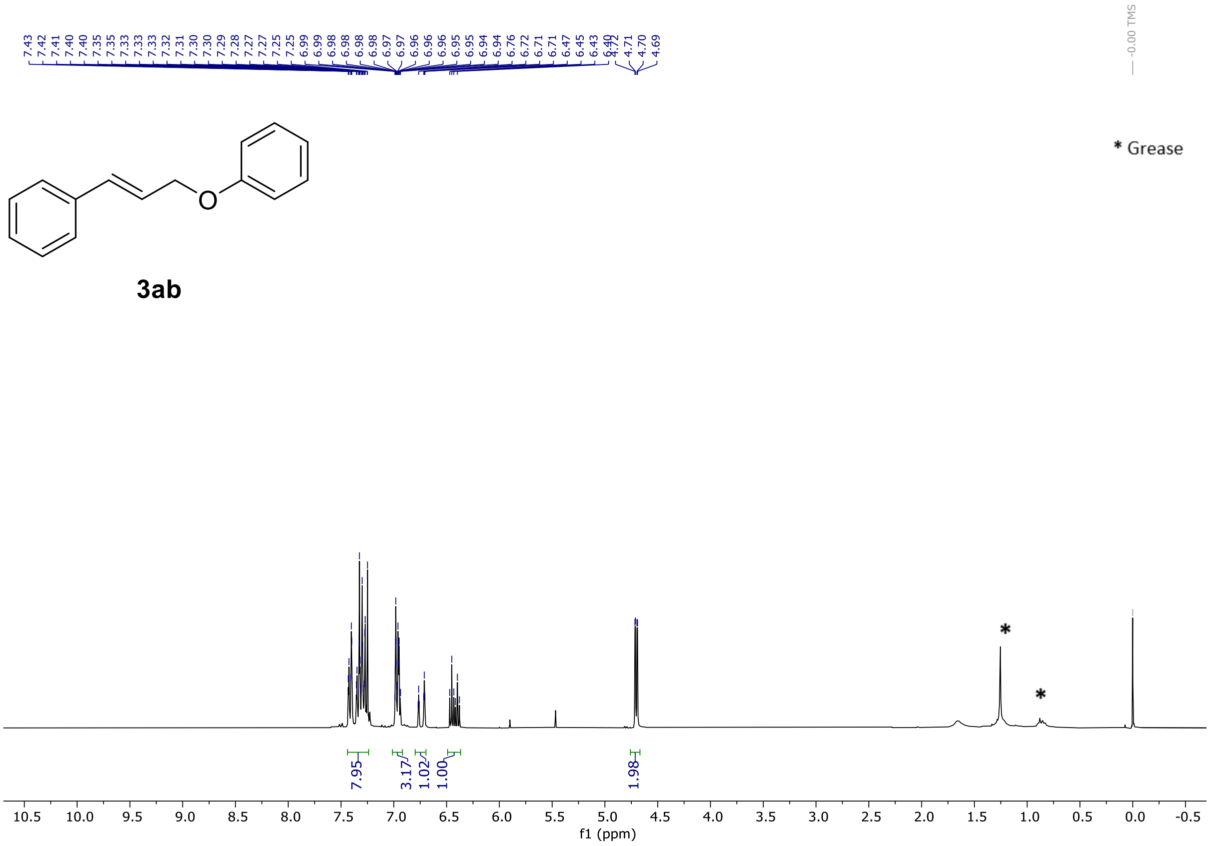
^{1}H NMR (400 MHz, $CDCl_3$)



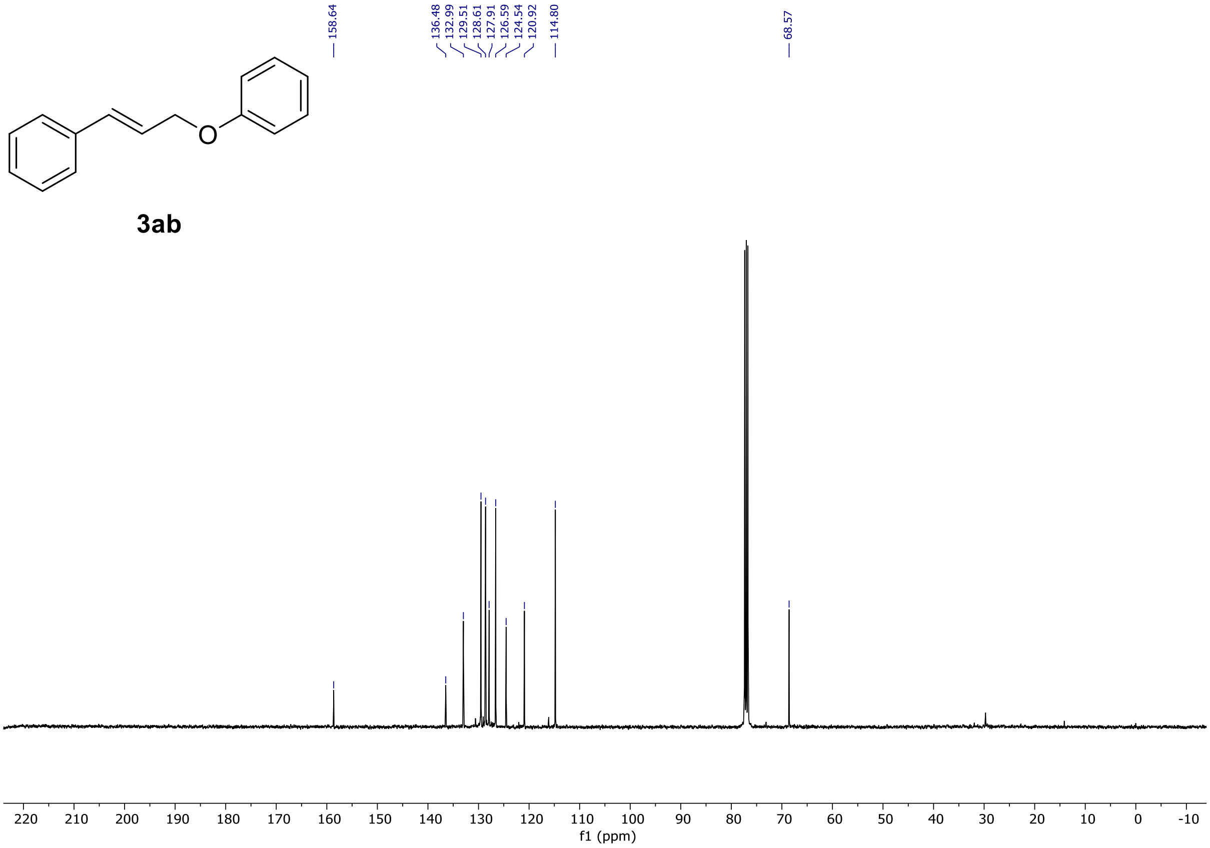
^{13}C NMR (75 MHz, $CDCl_3$)



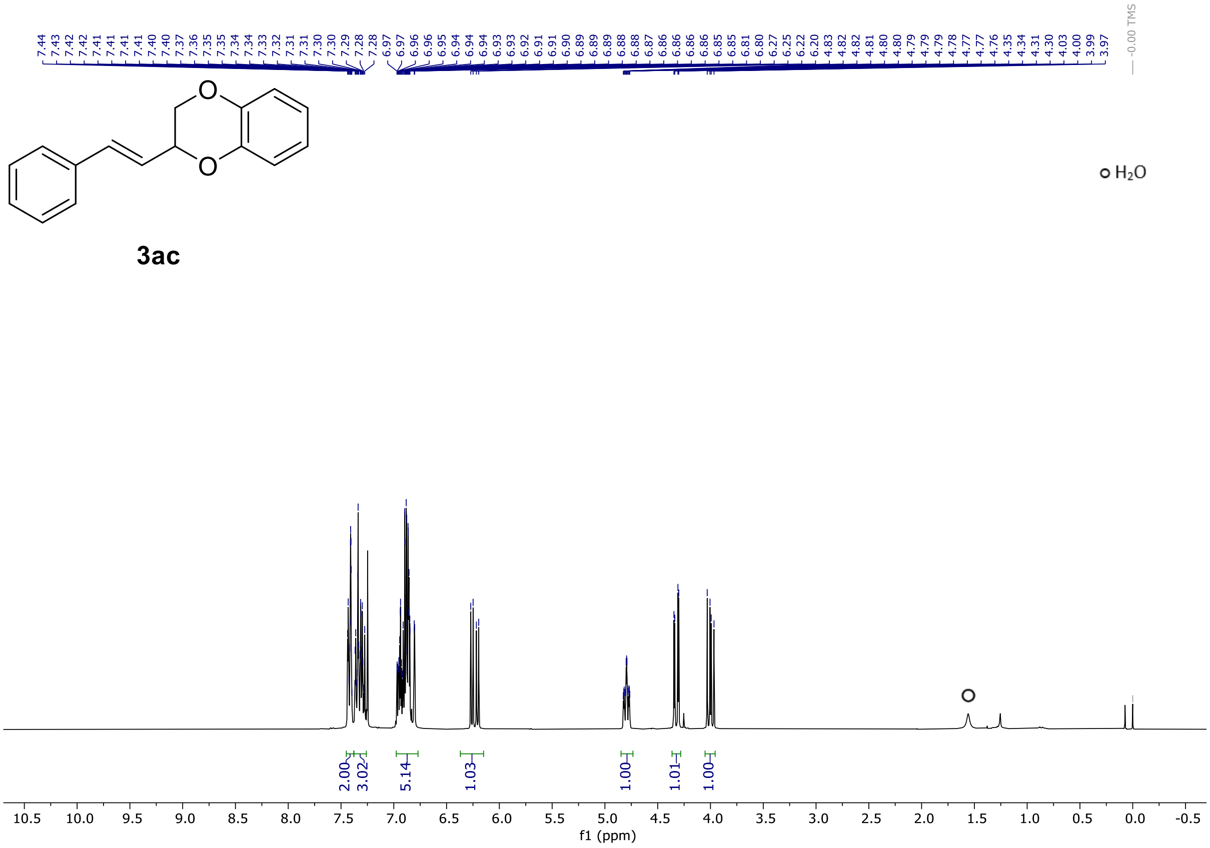
^{1}H NMR (400 MHz, CDCl$_3$)



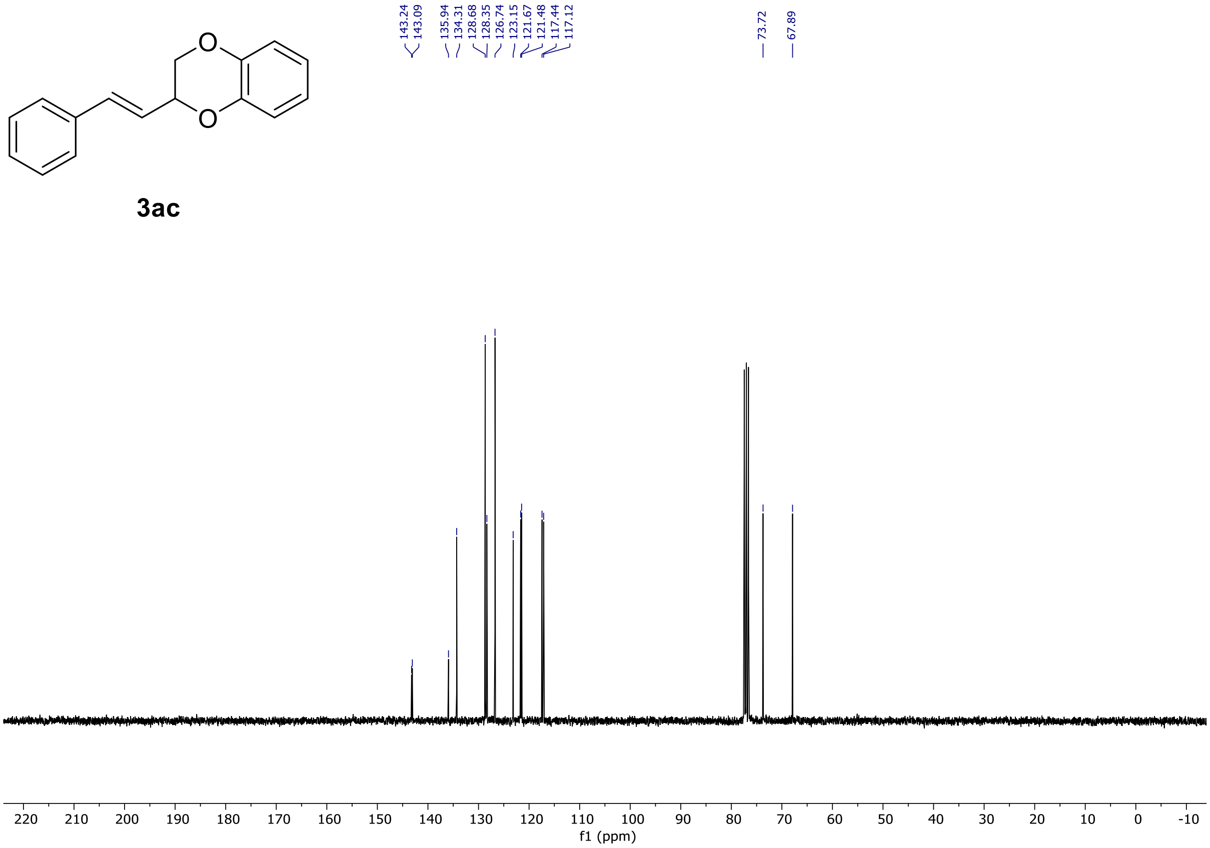
^{13}C NMR (101 MHz, CDCl$_3$)



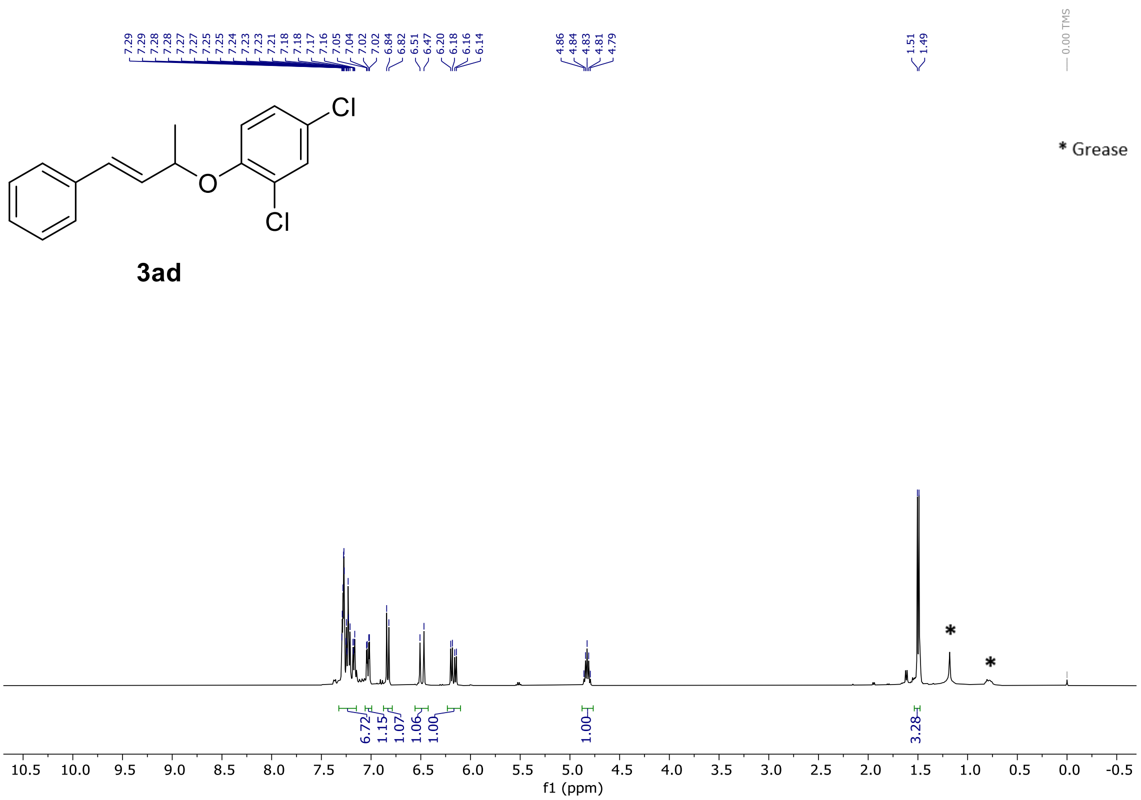
^{1}H NMR (300 MHz, $CDCl_3$)



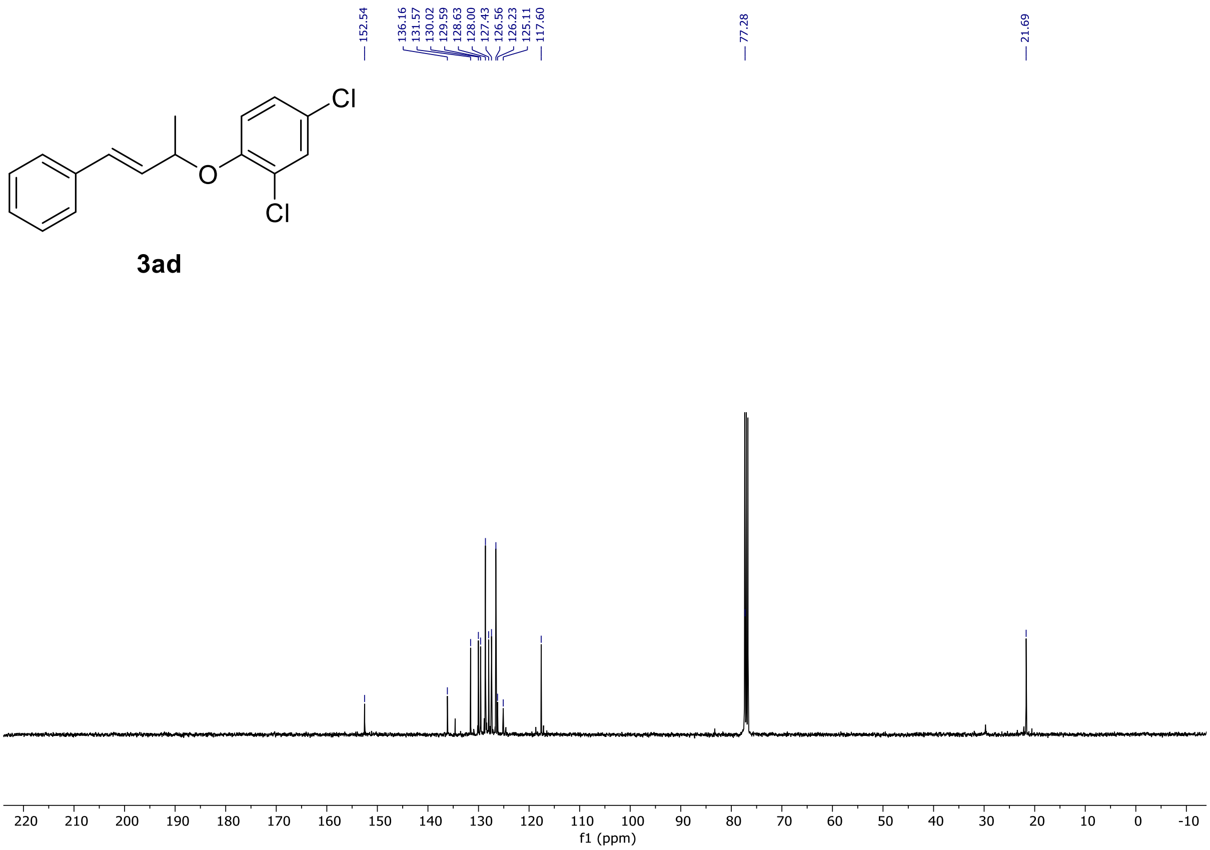
^{13}C NMR (75 MHz, $CDCl_3$)



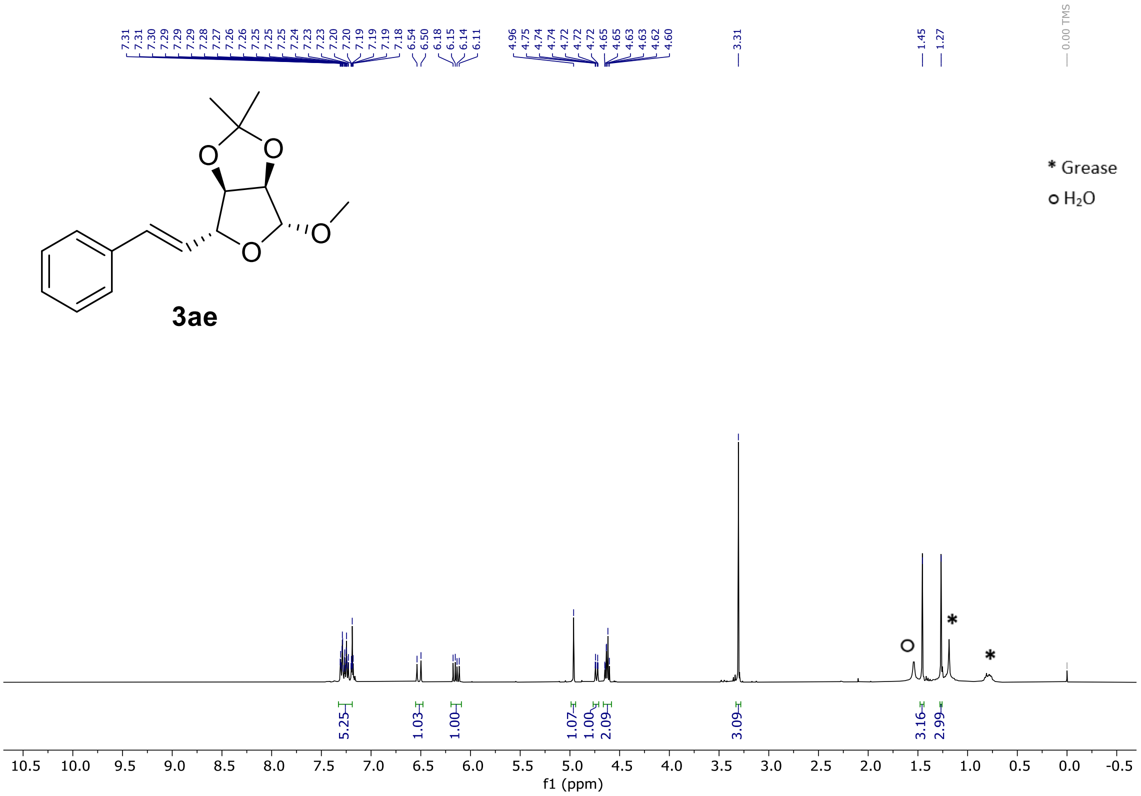
^{1}H NMR (400 MHz, $CDCl_3$)



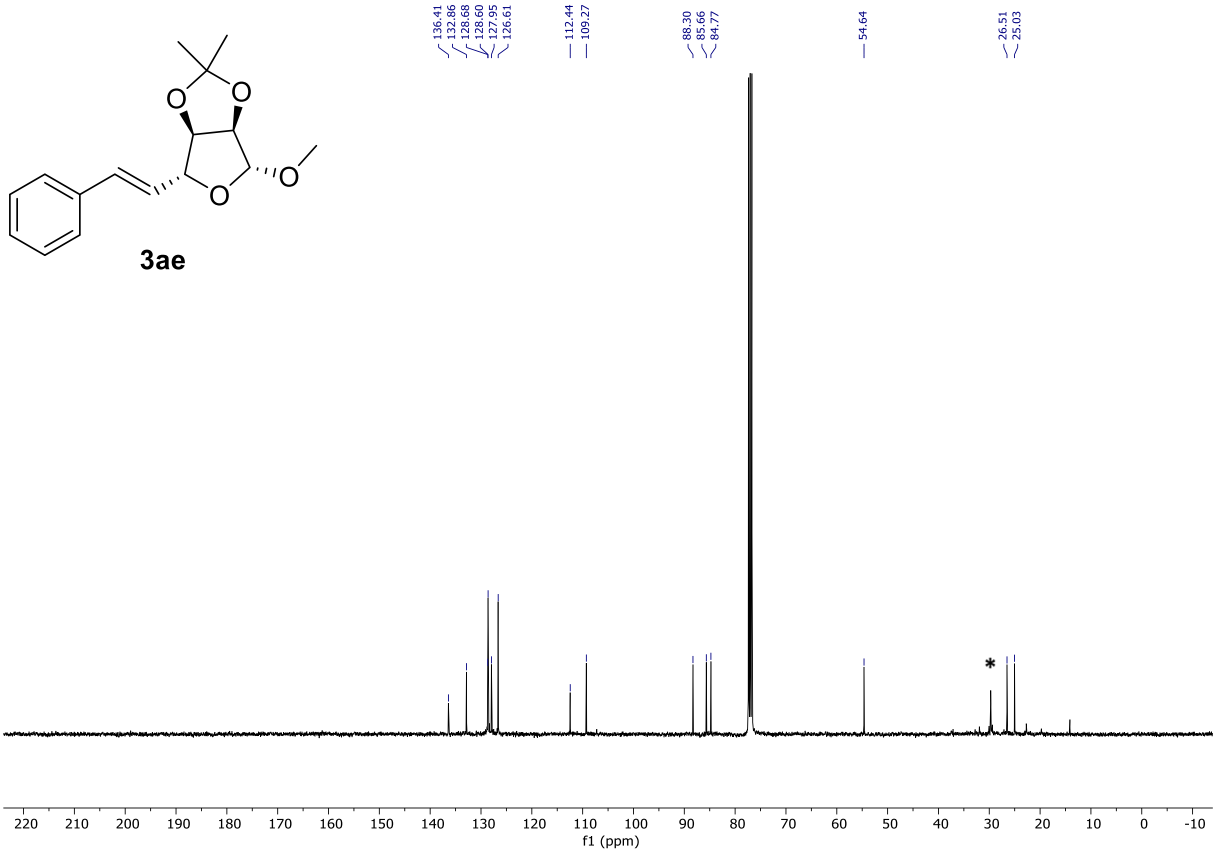
^{13}C NMR (101 MHz, $CDCl_3$)



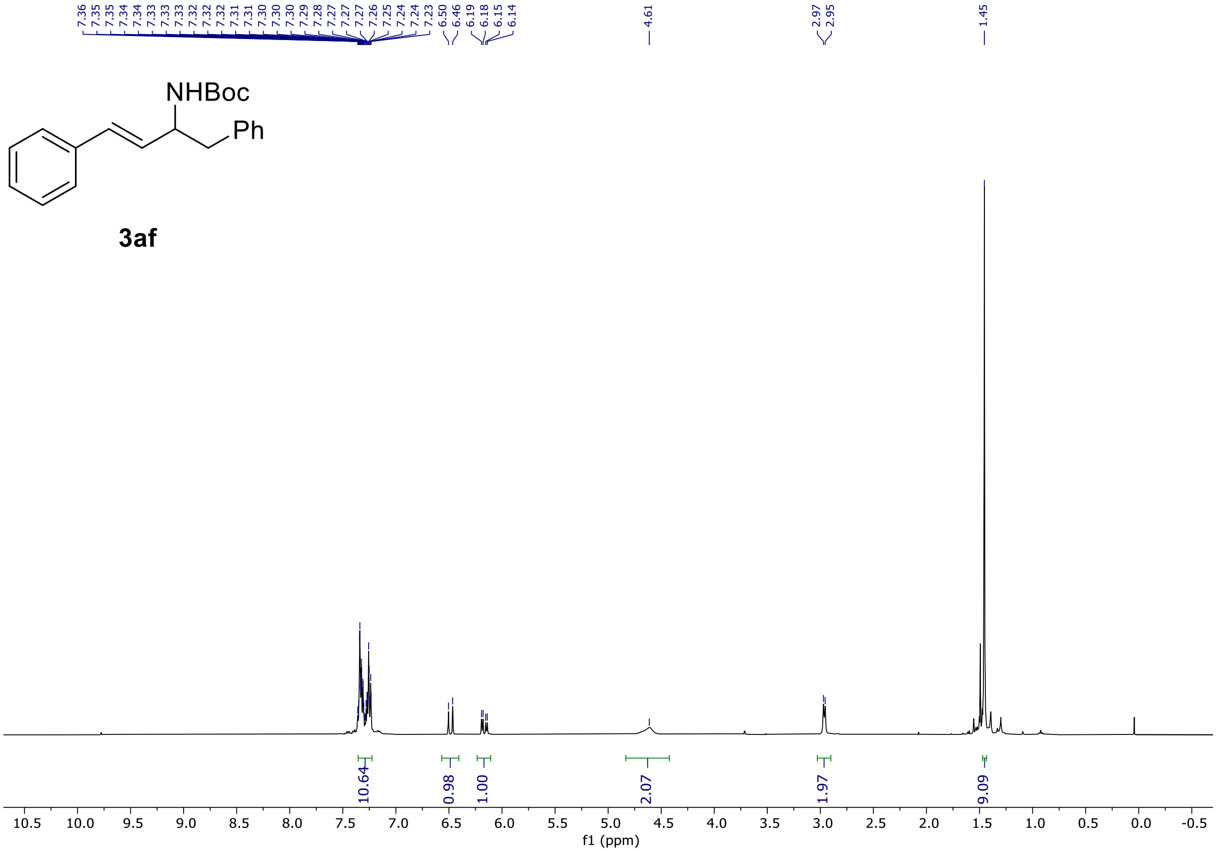
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, CDCl$_3$)



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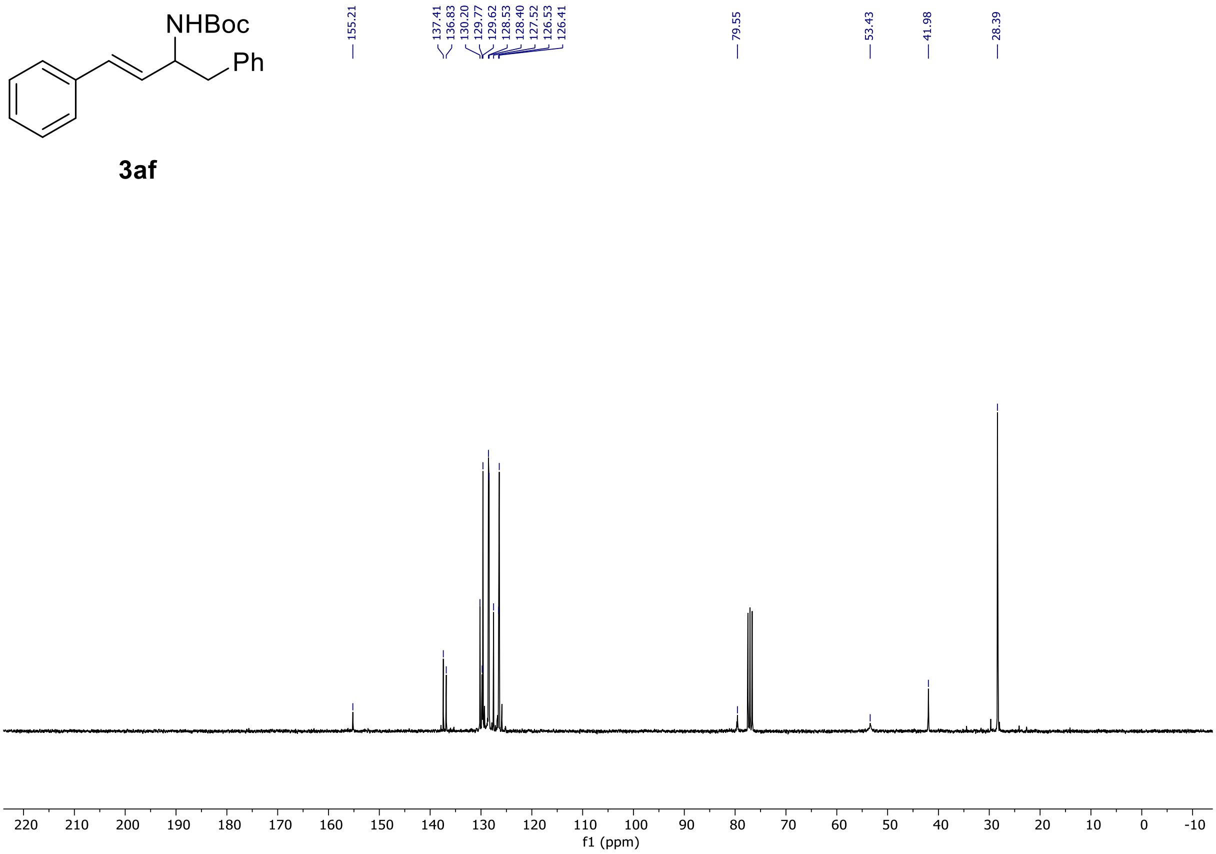

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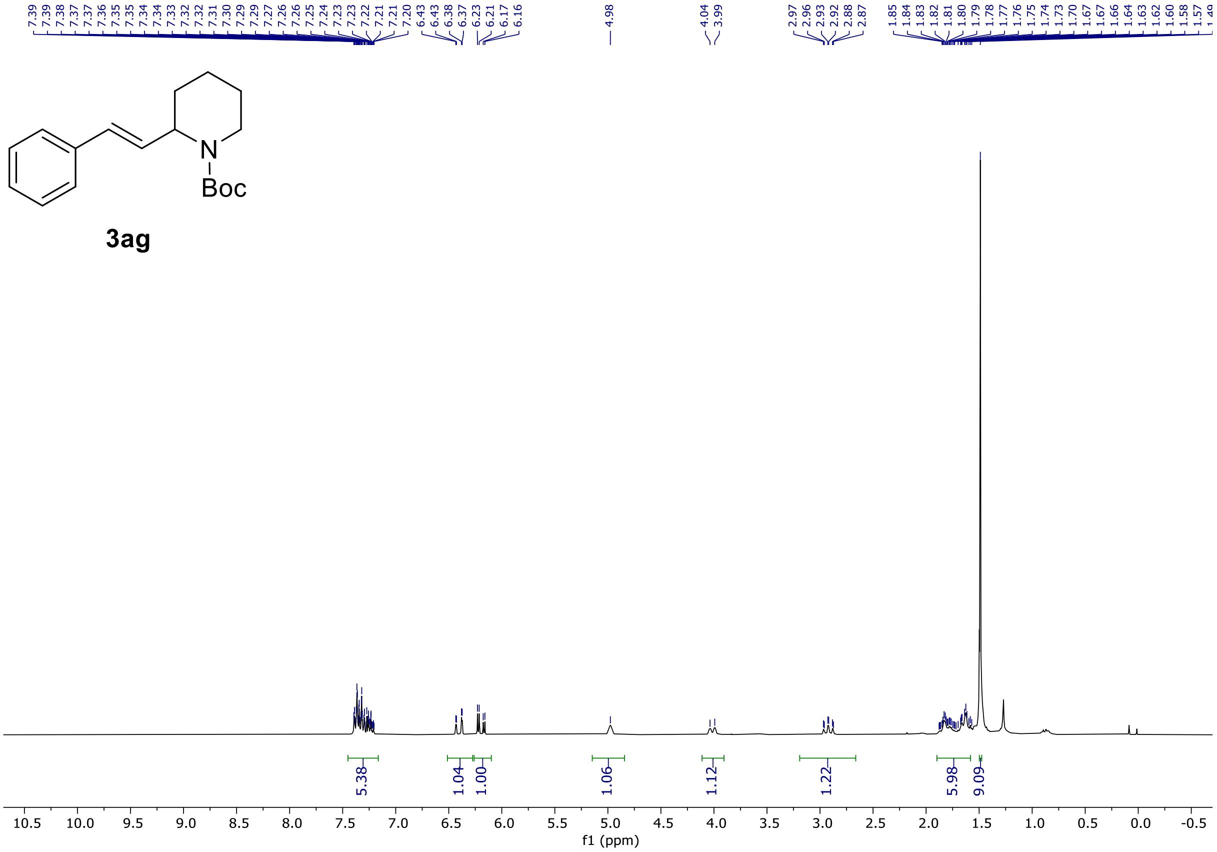
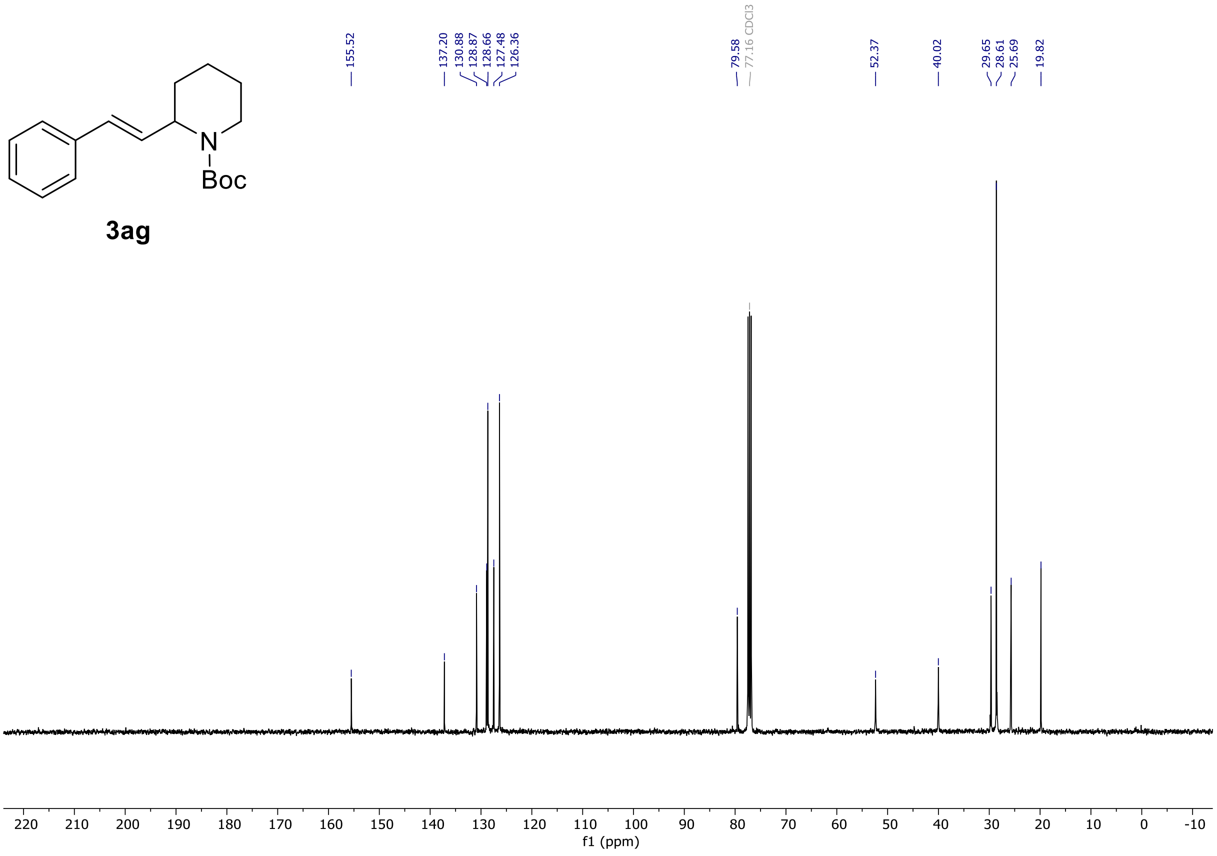


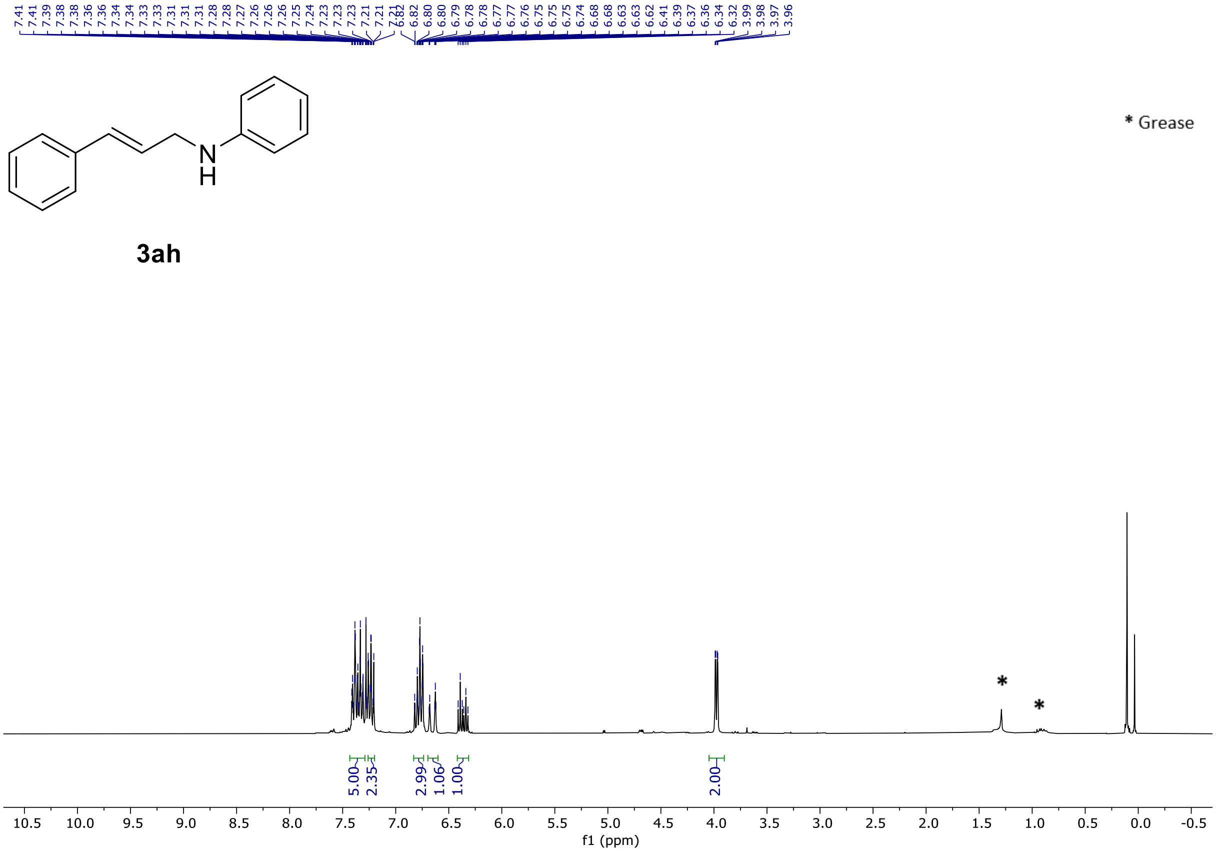
3ag

^{13}C NMR (101 MHz, CDCl$_3$)

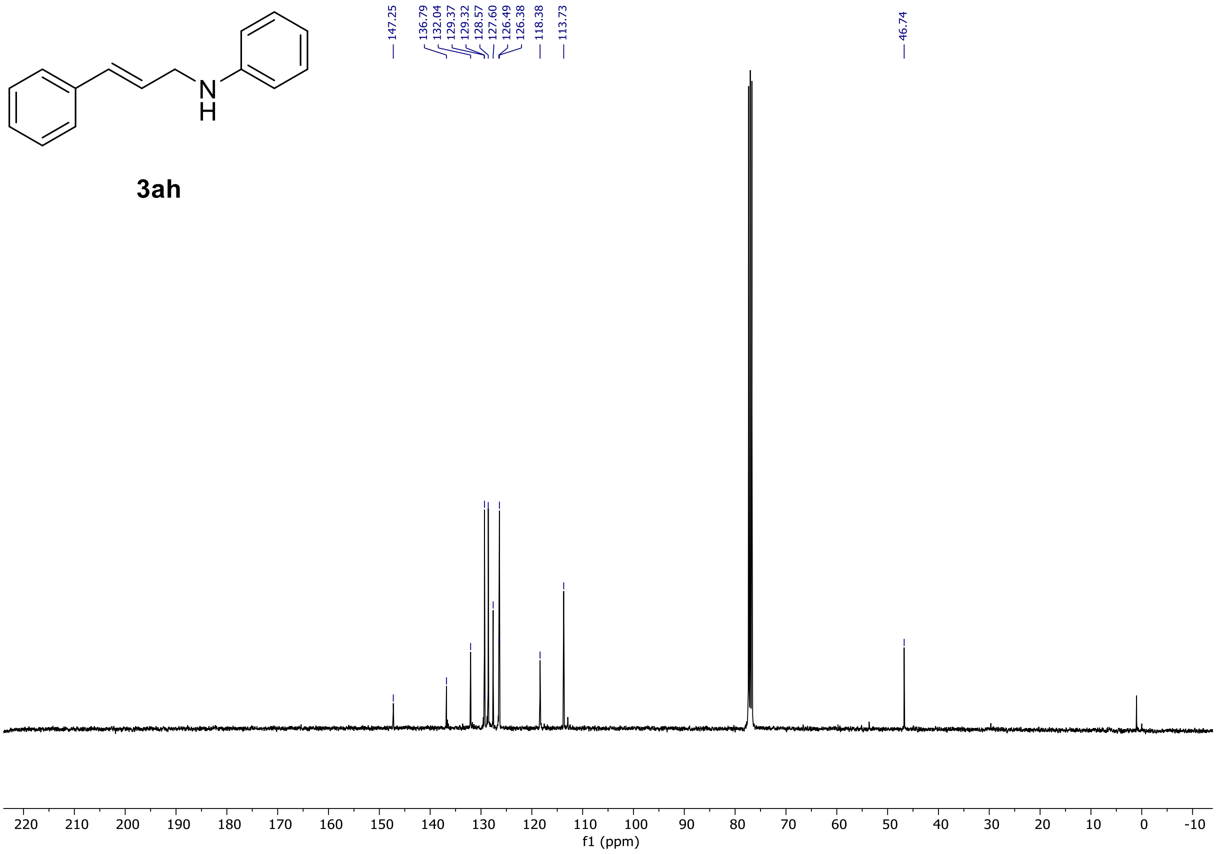


3ag

^1H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



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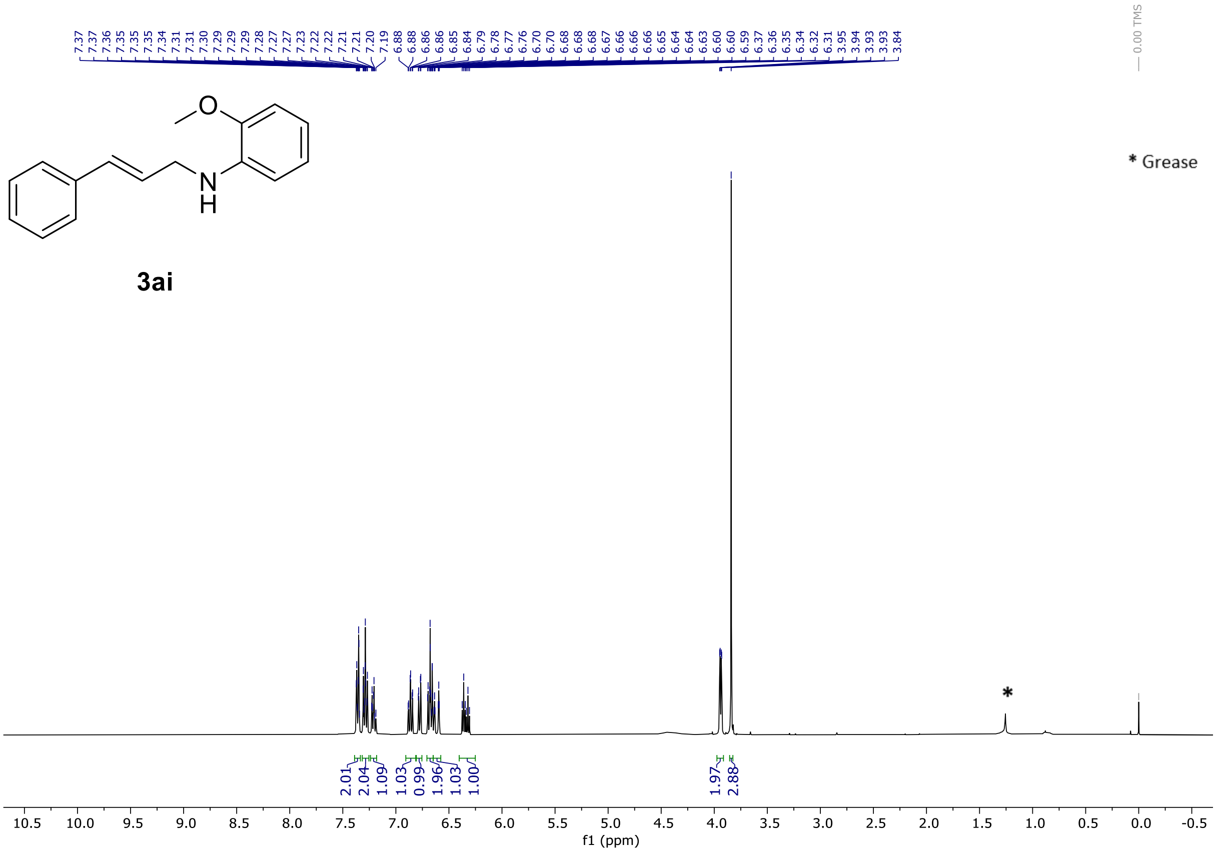

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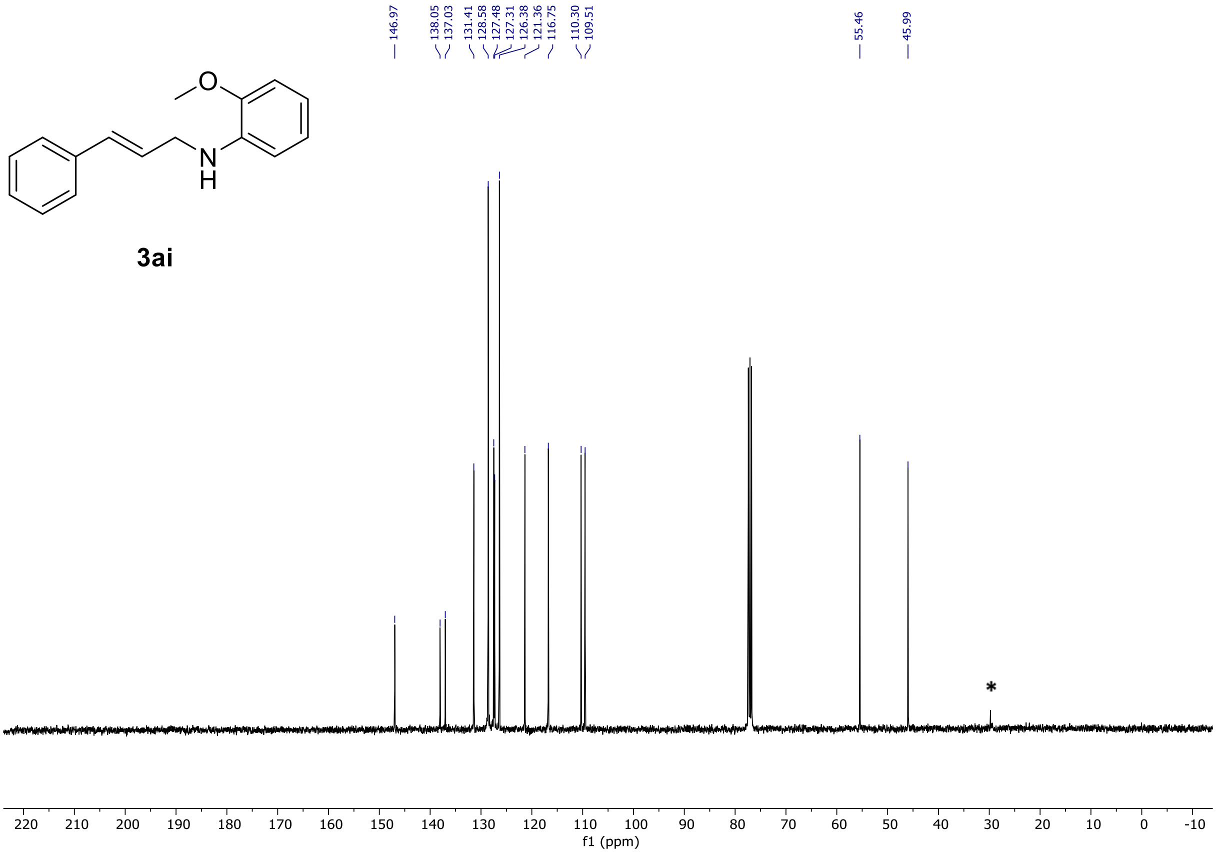

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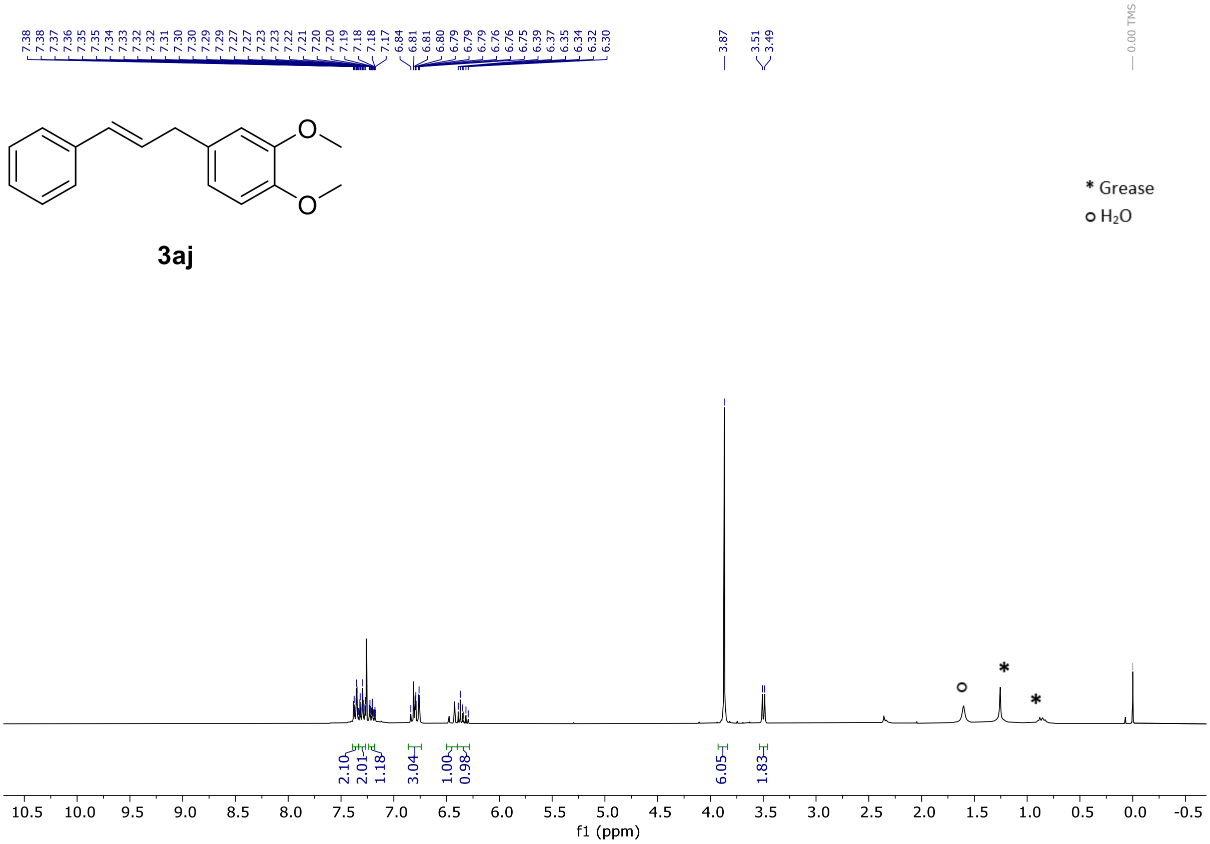

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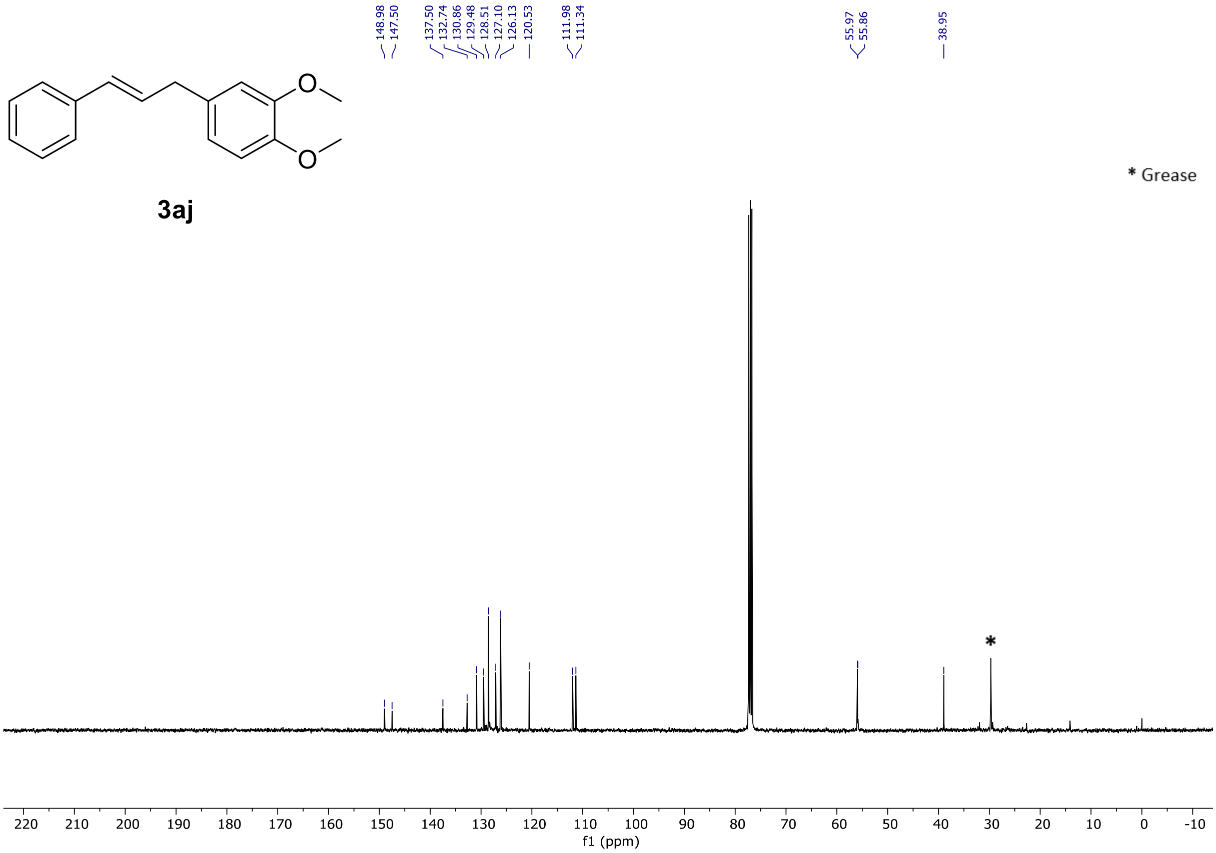

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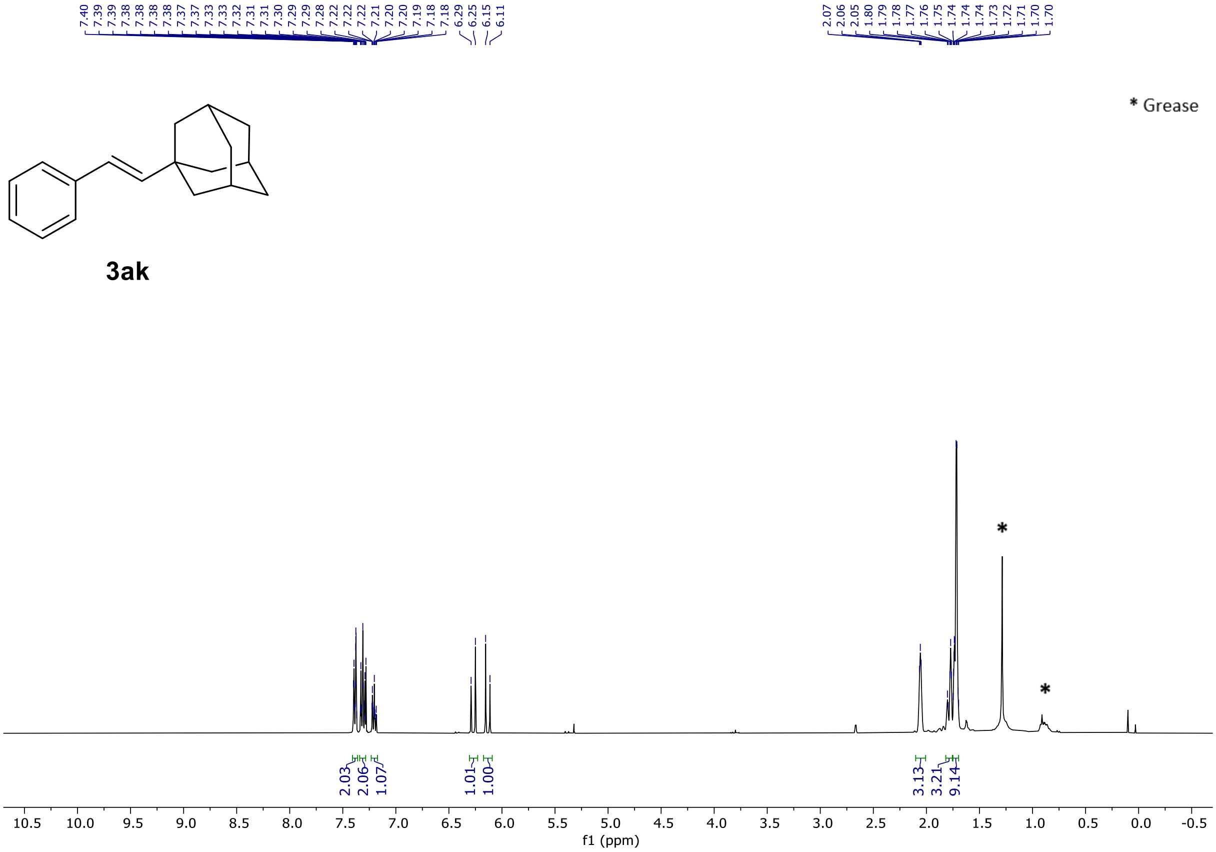

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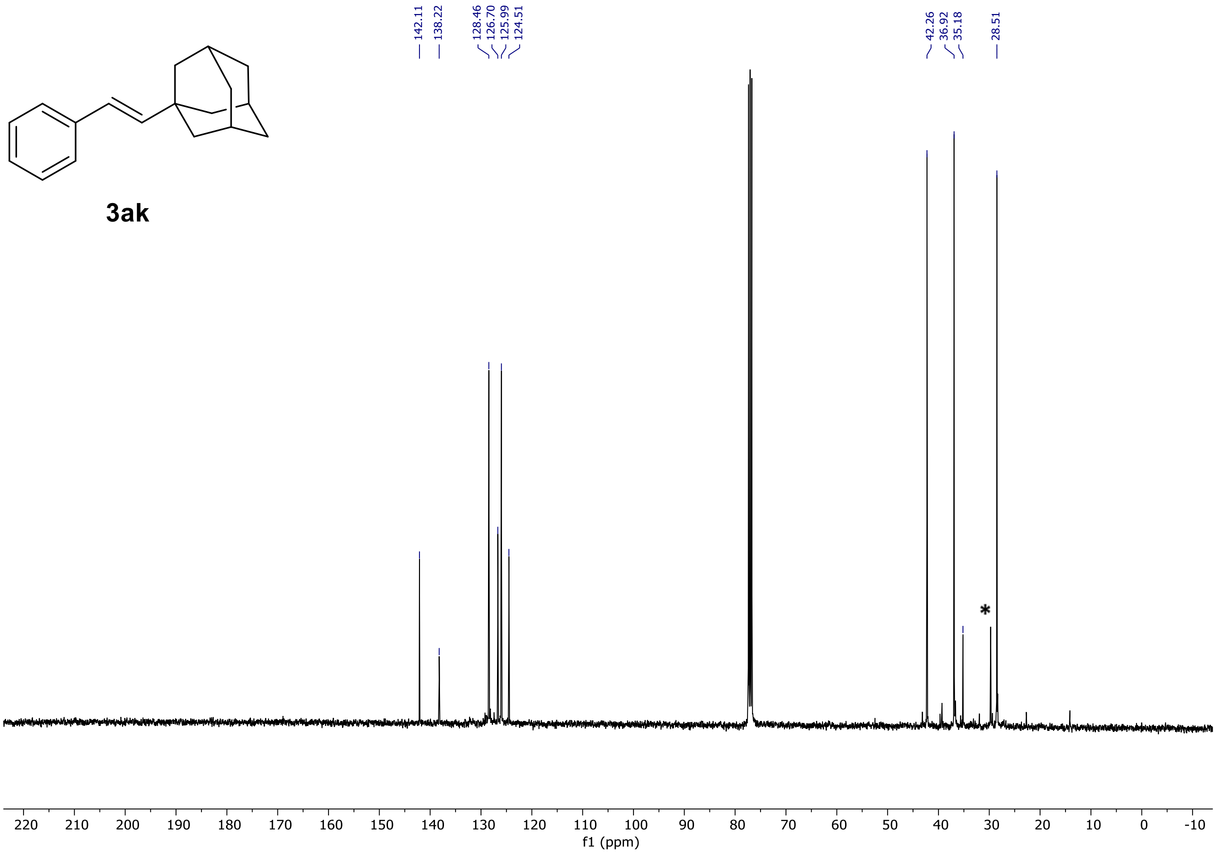

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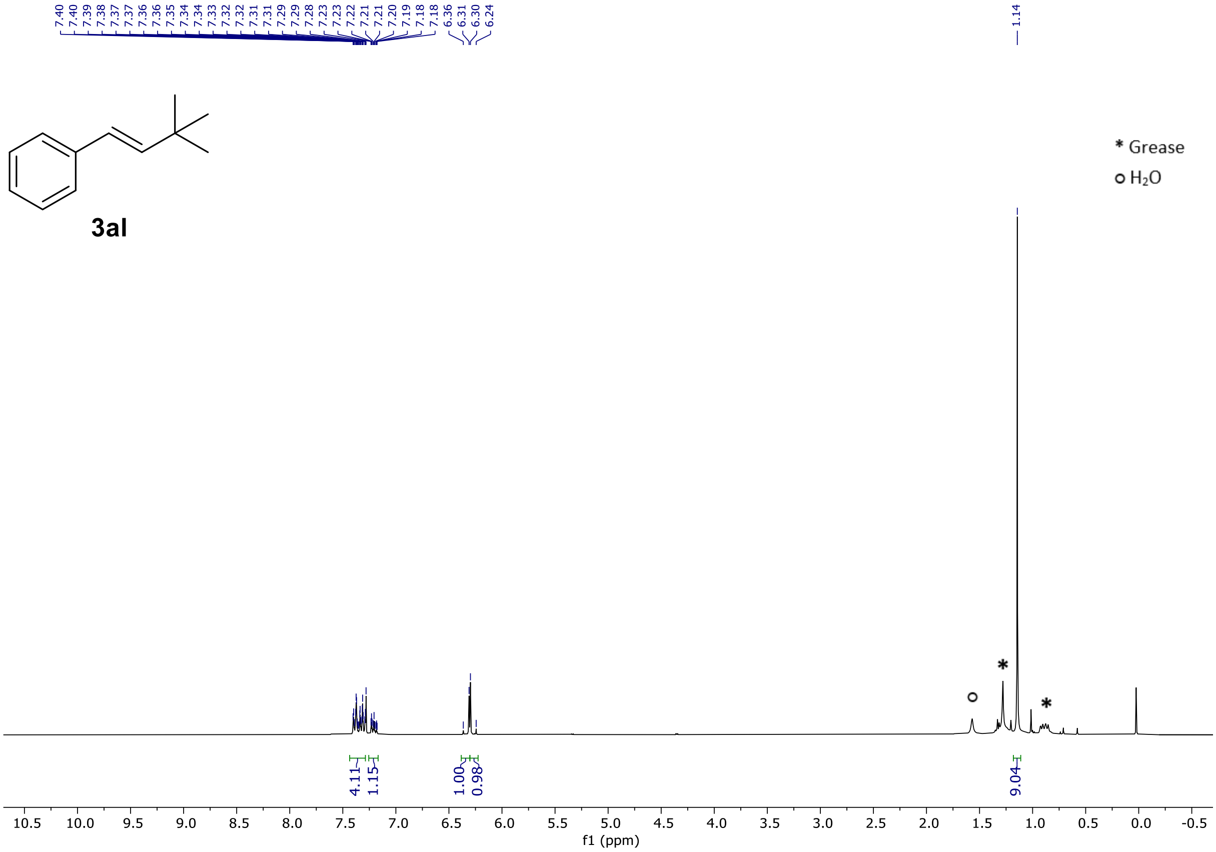

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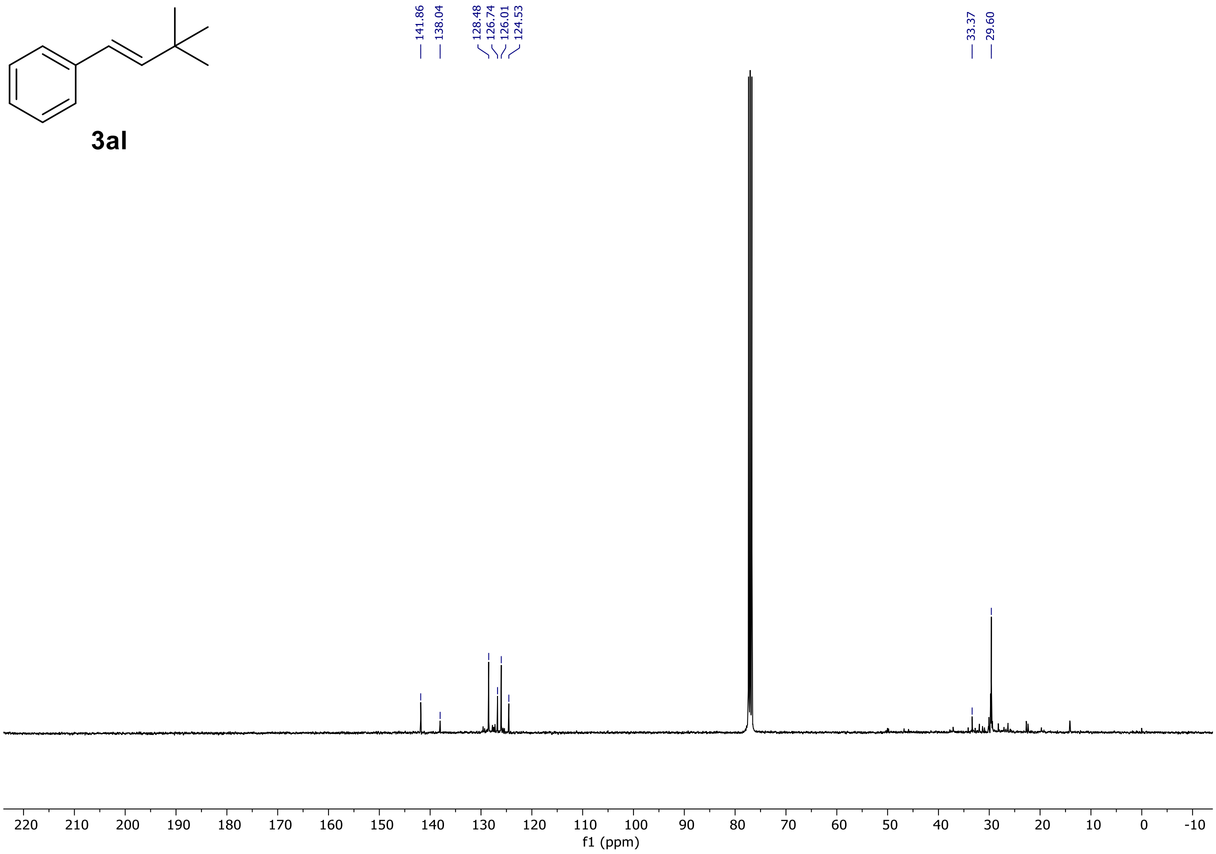

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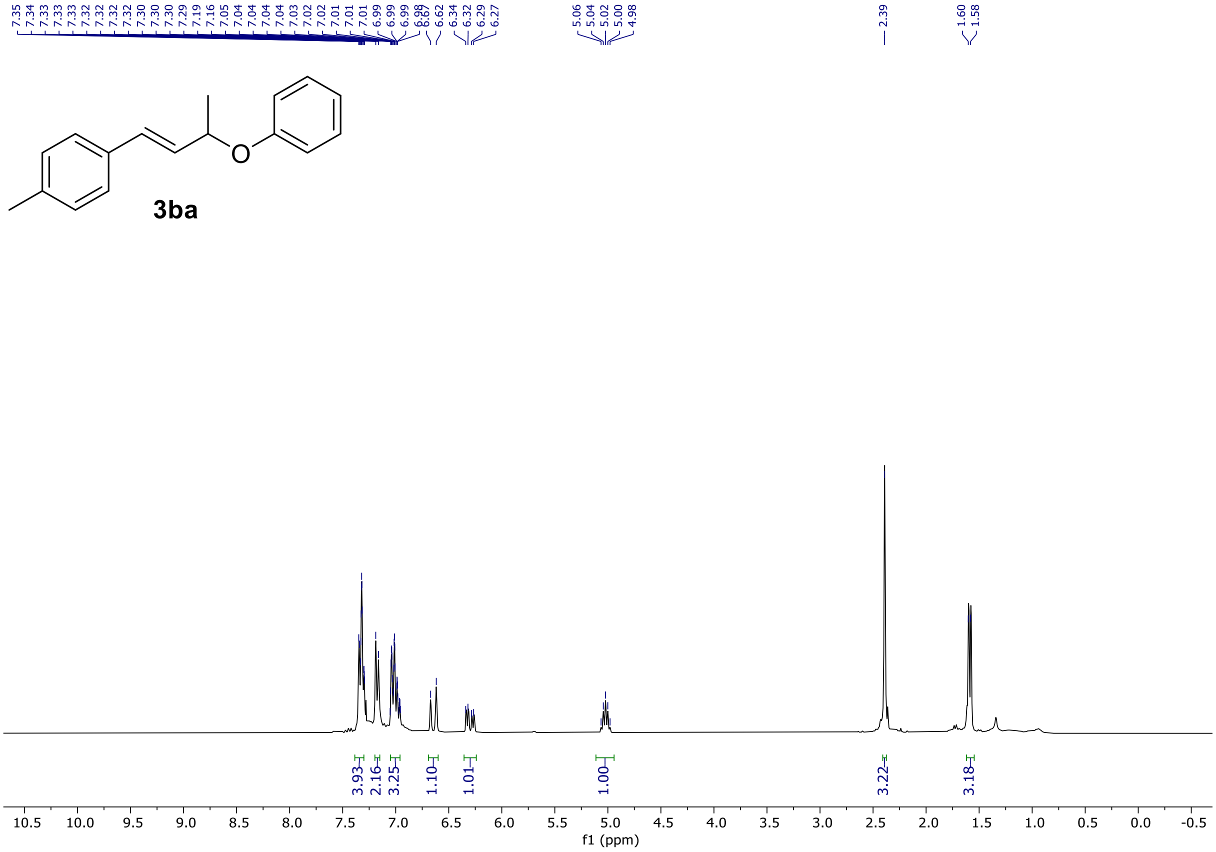

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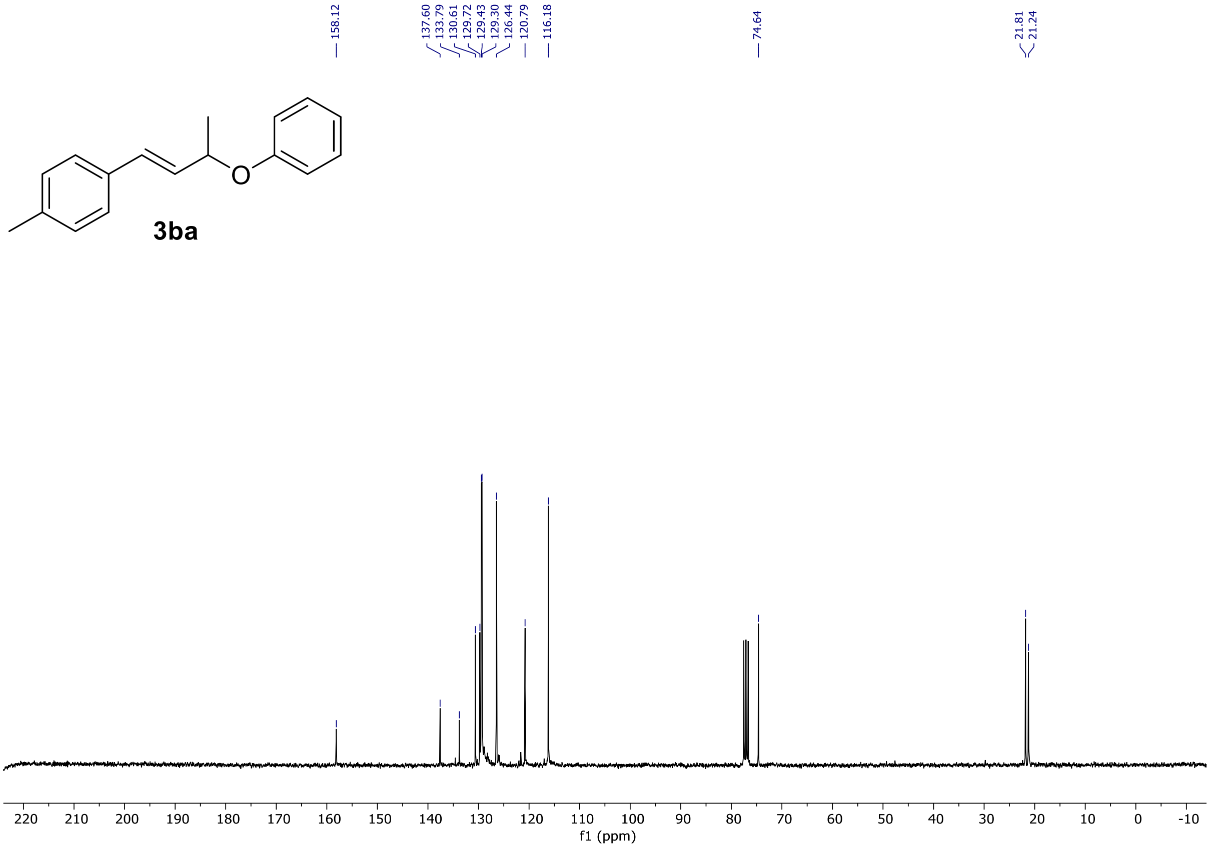

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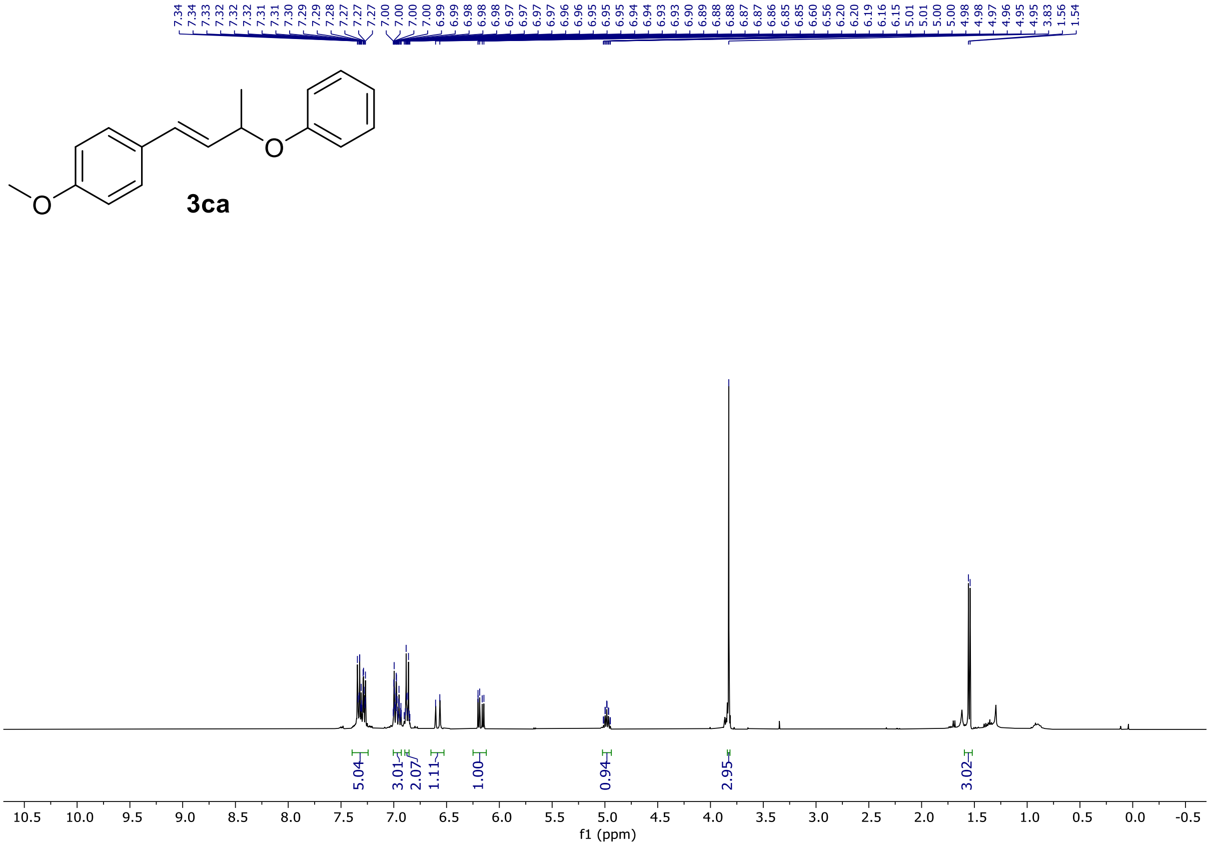

3ca

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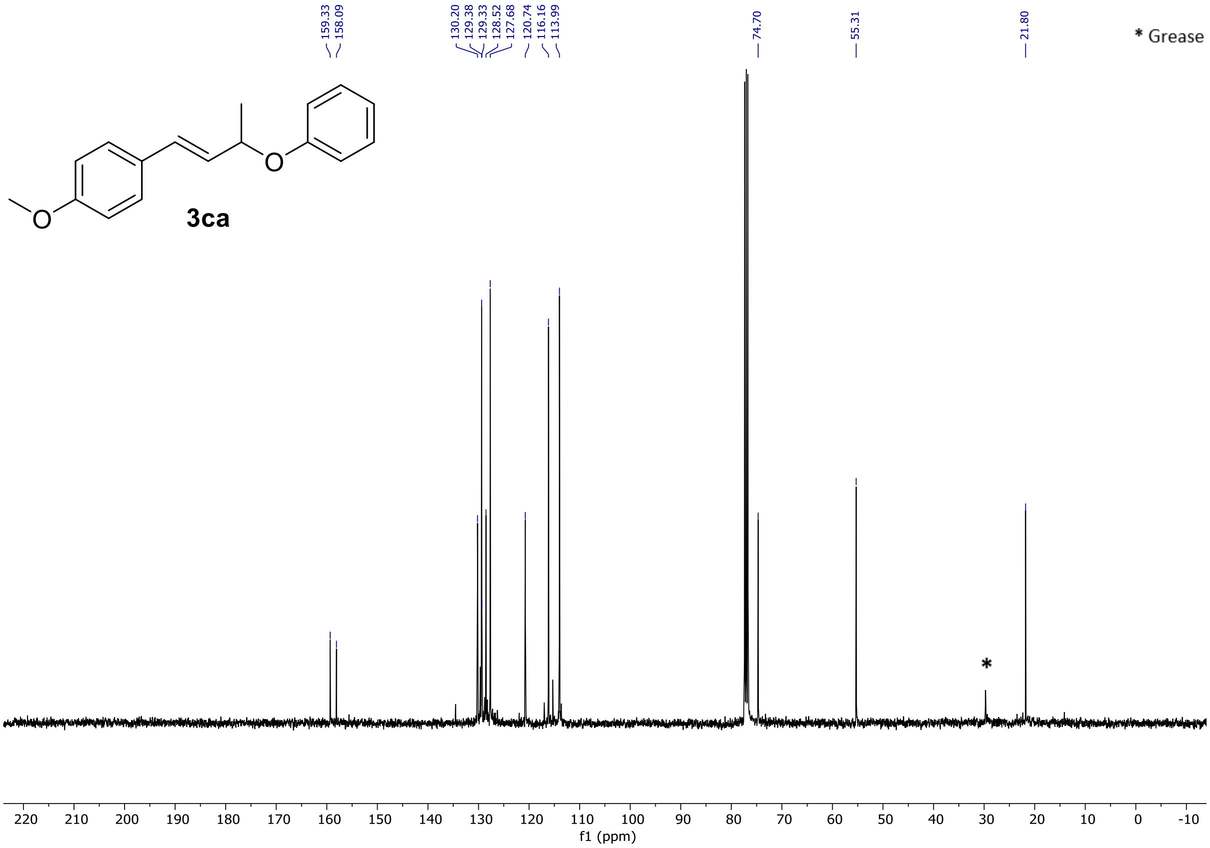

3ca

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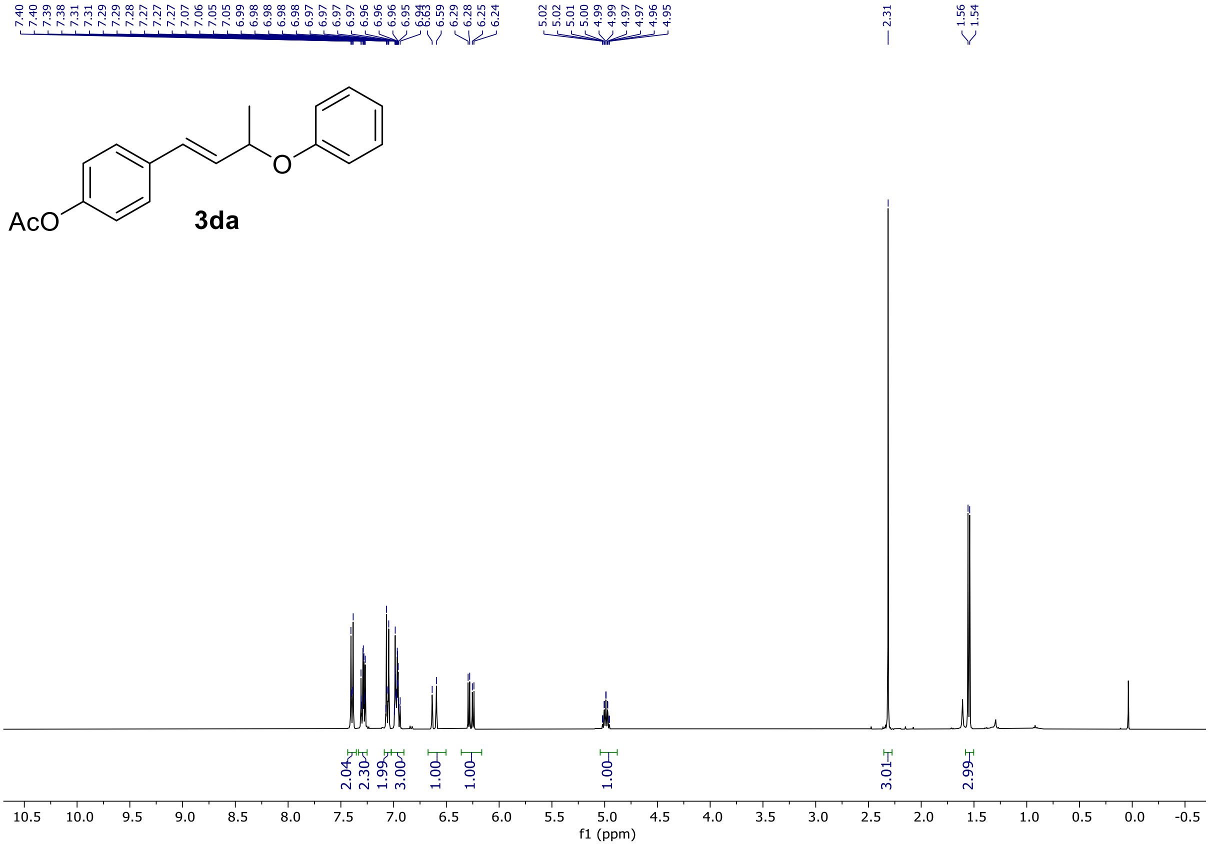

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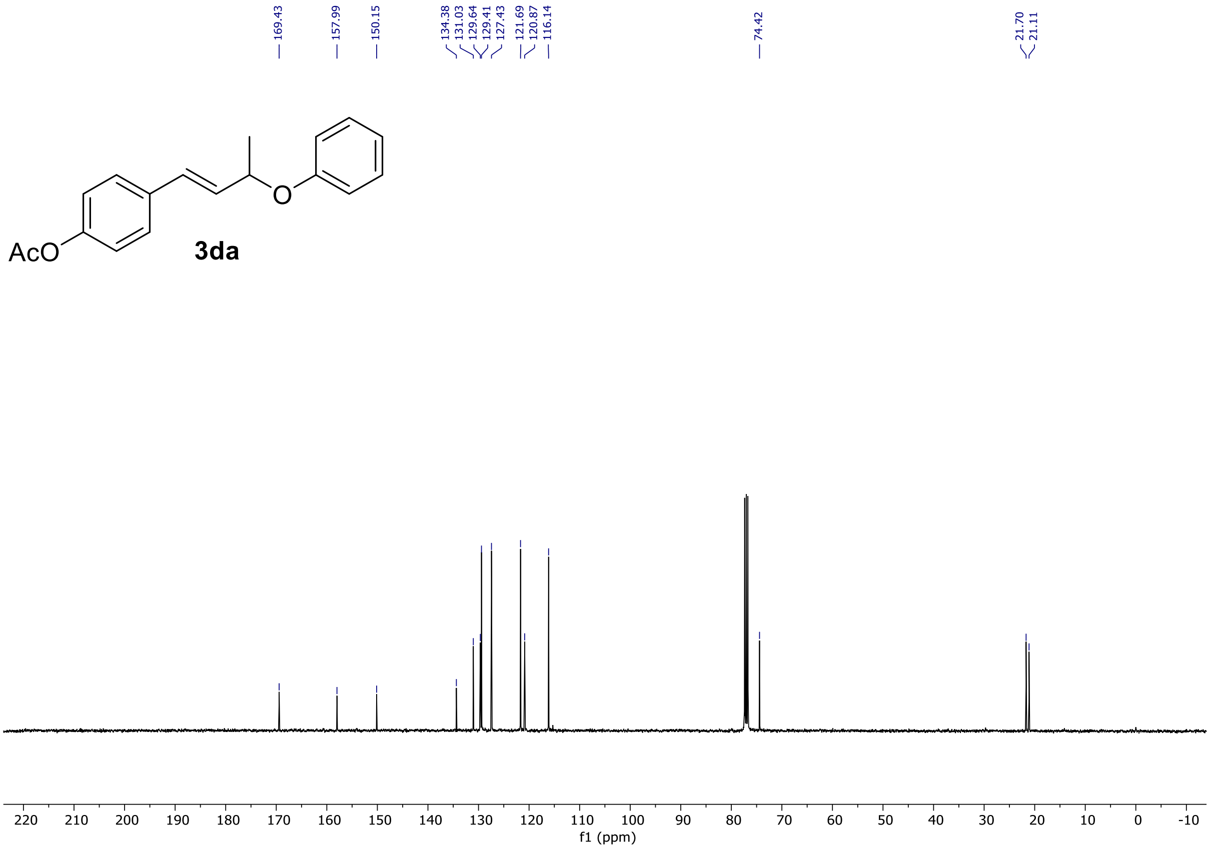

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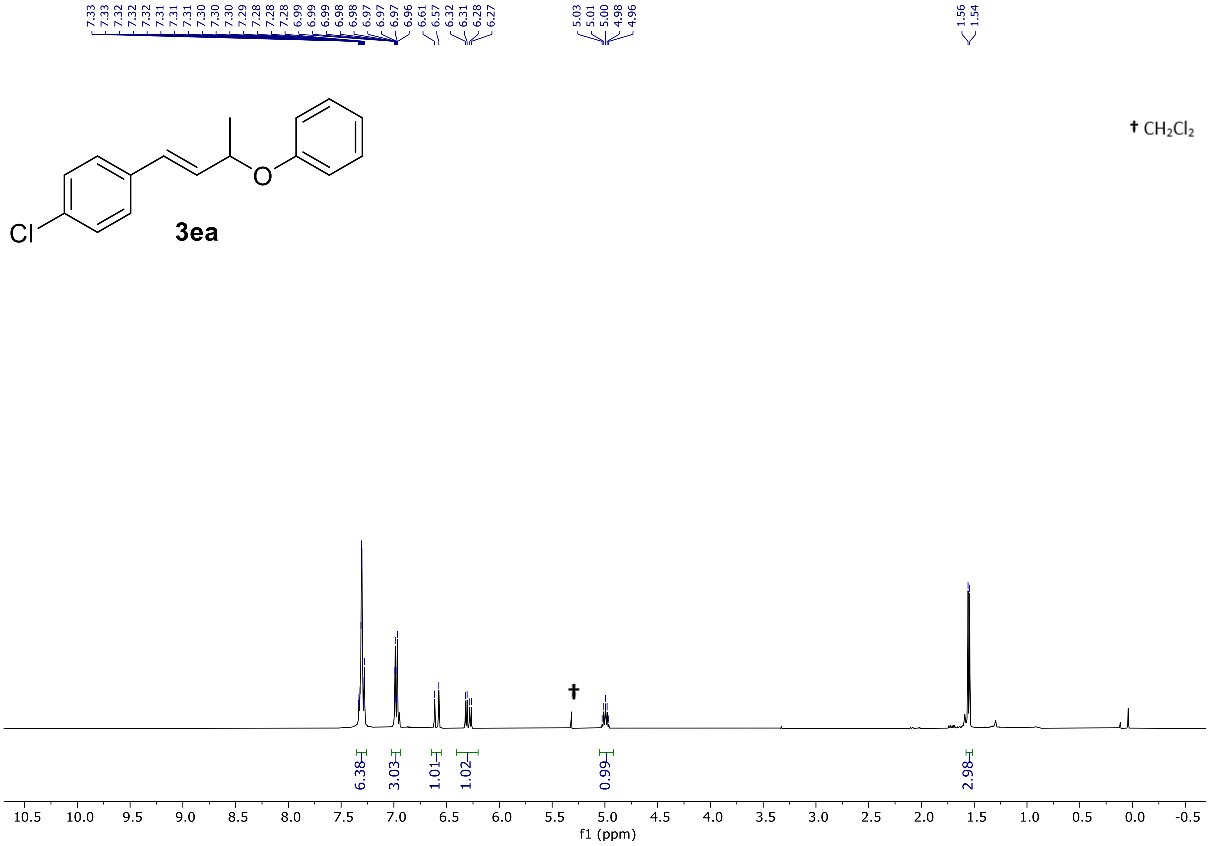

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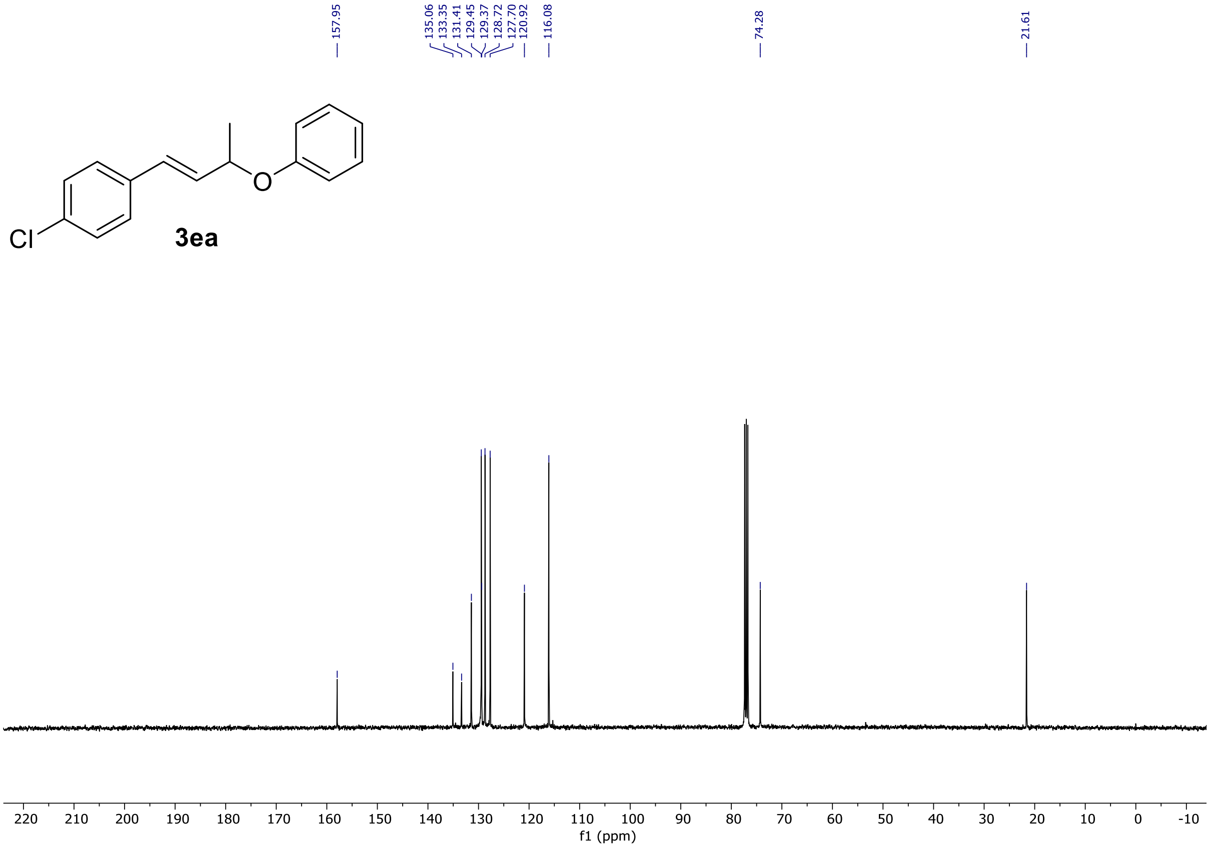

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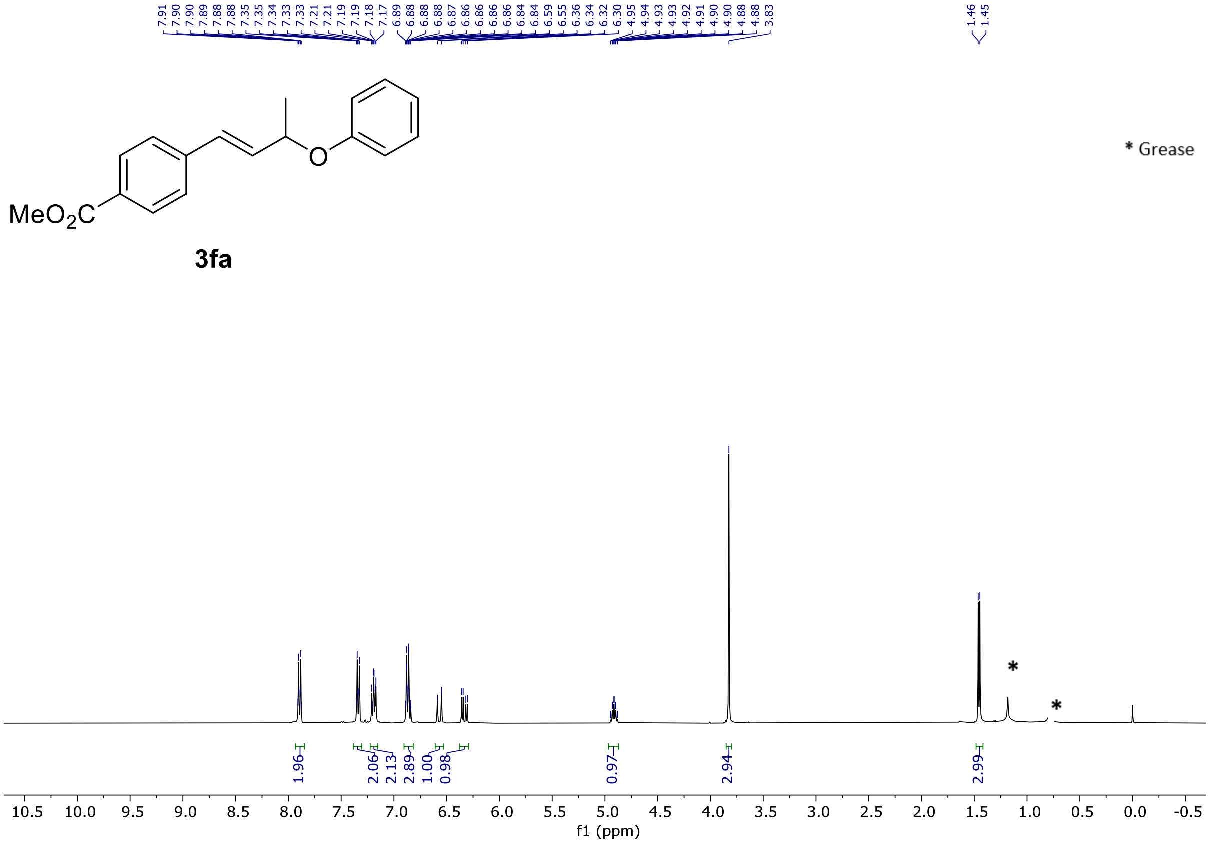

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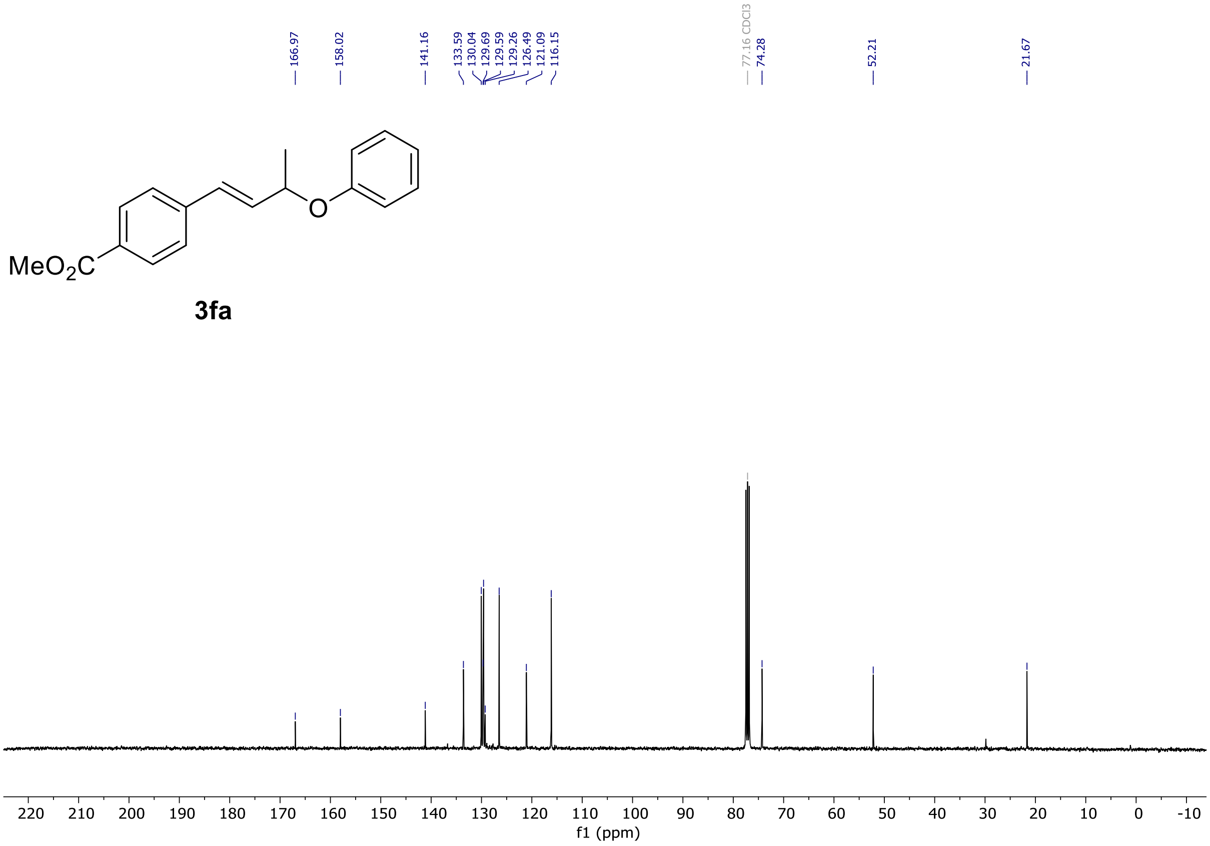

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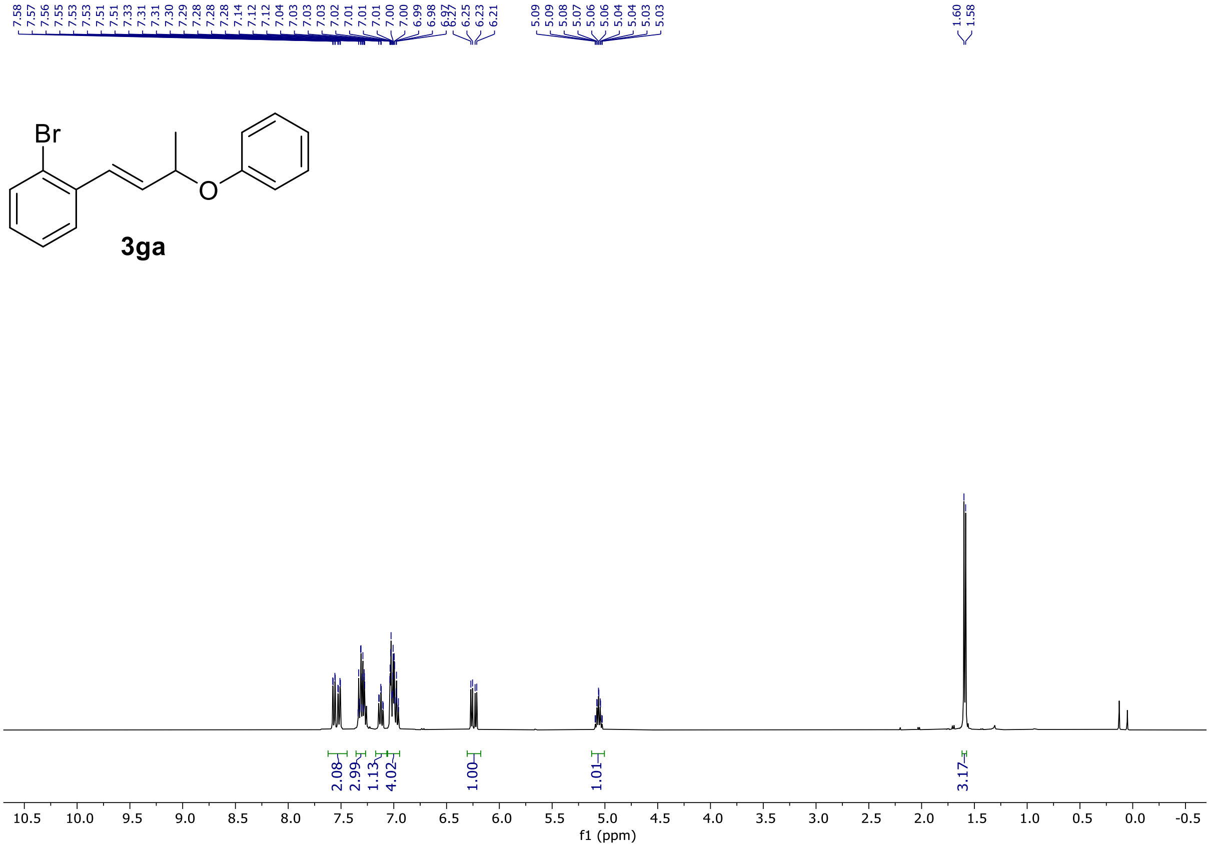

3ga

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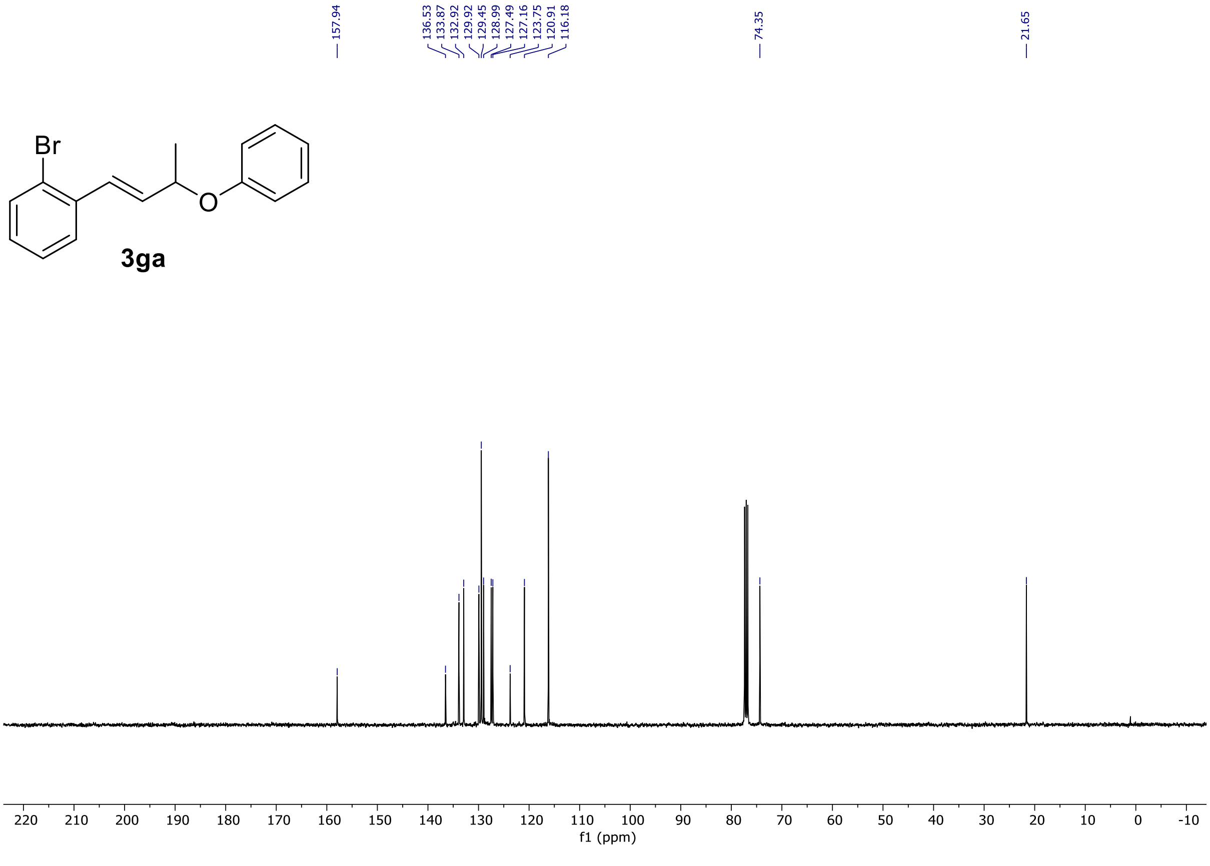

3ga

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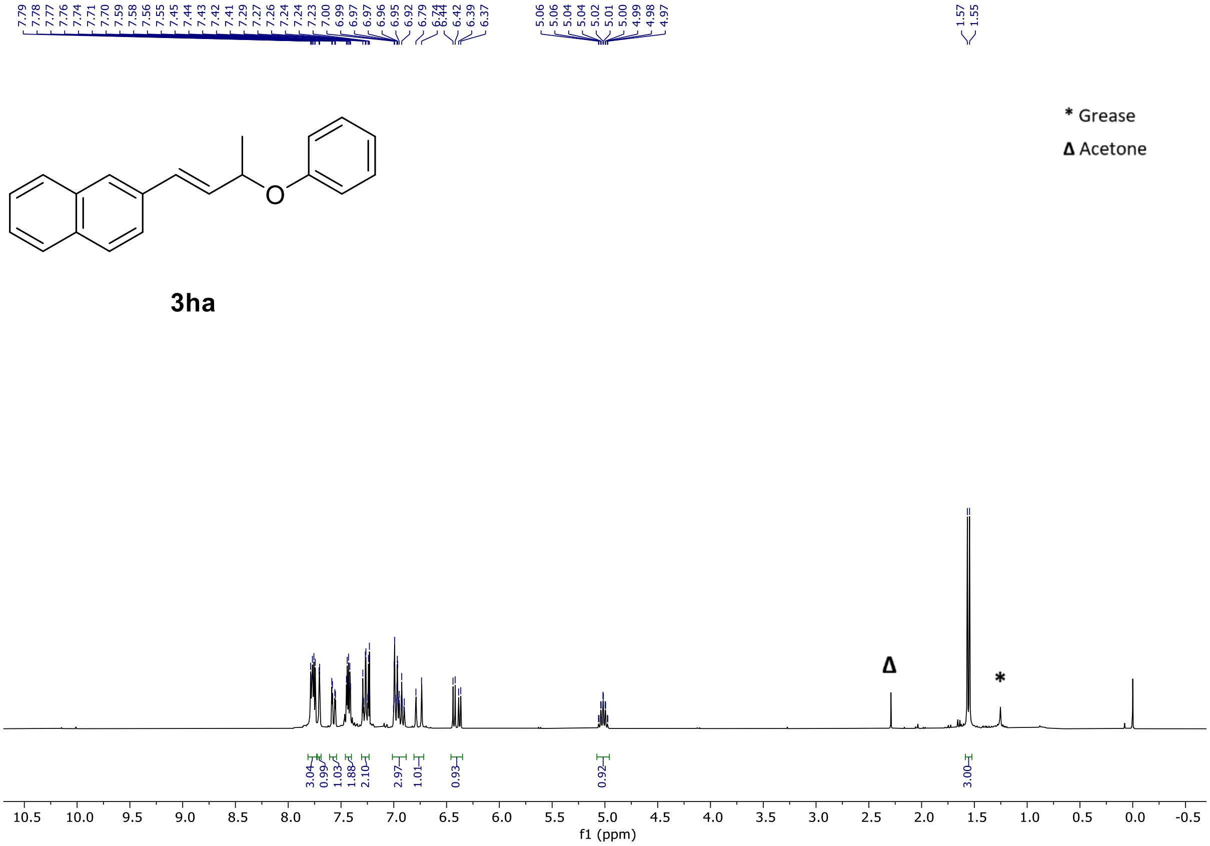

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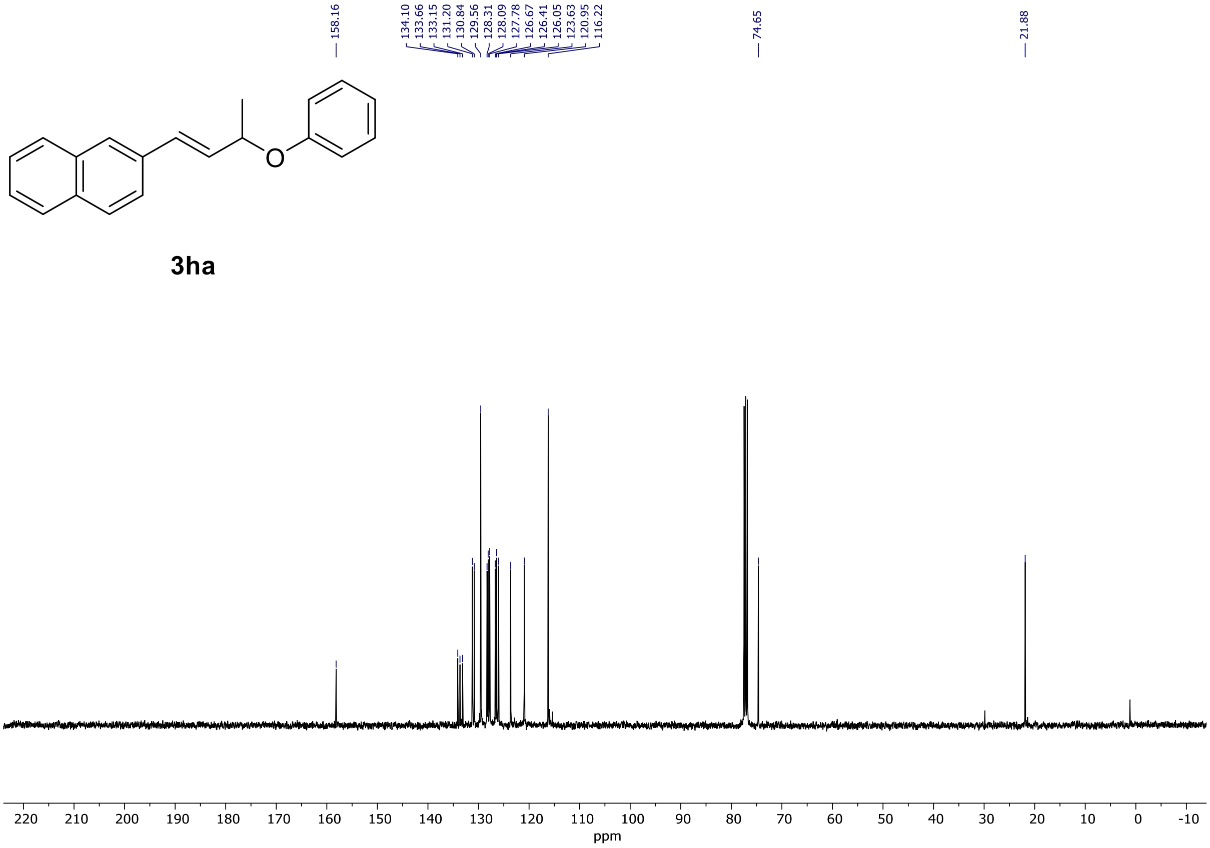

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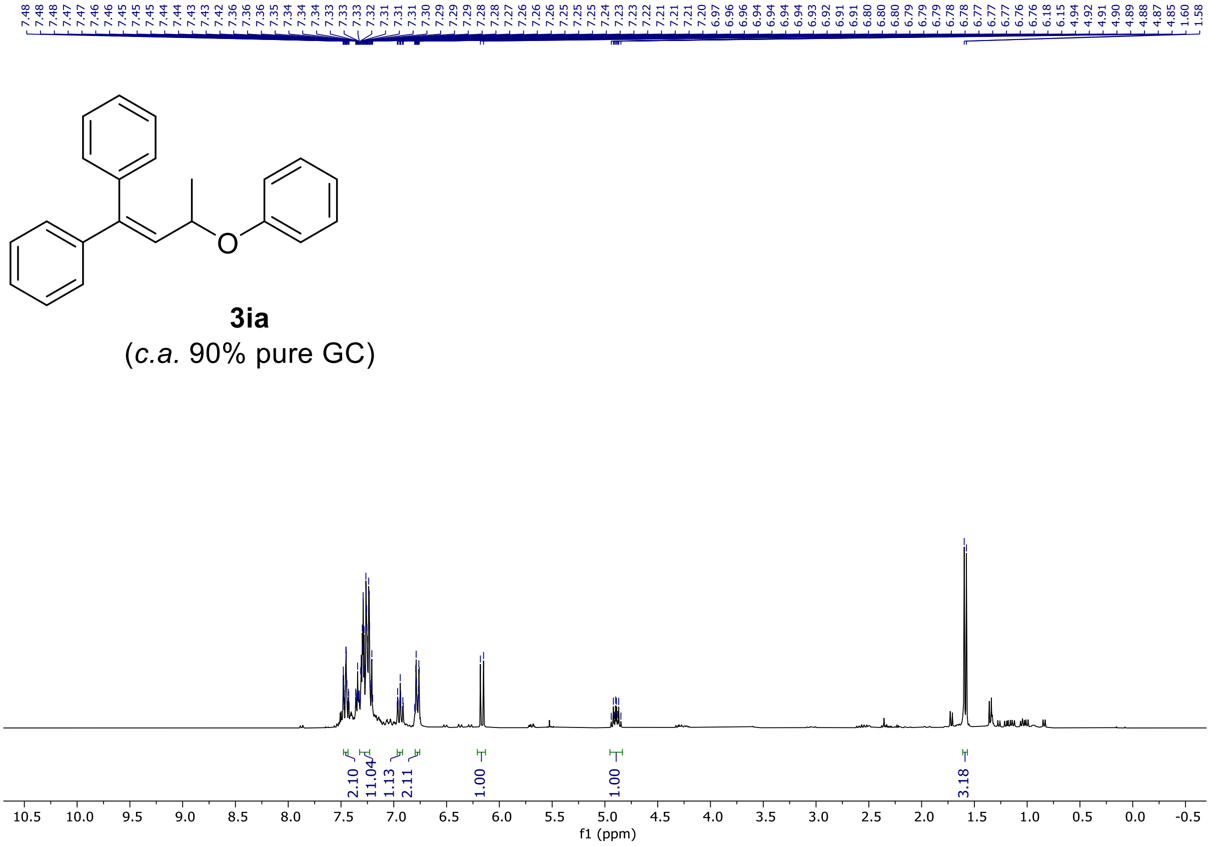
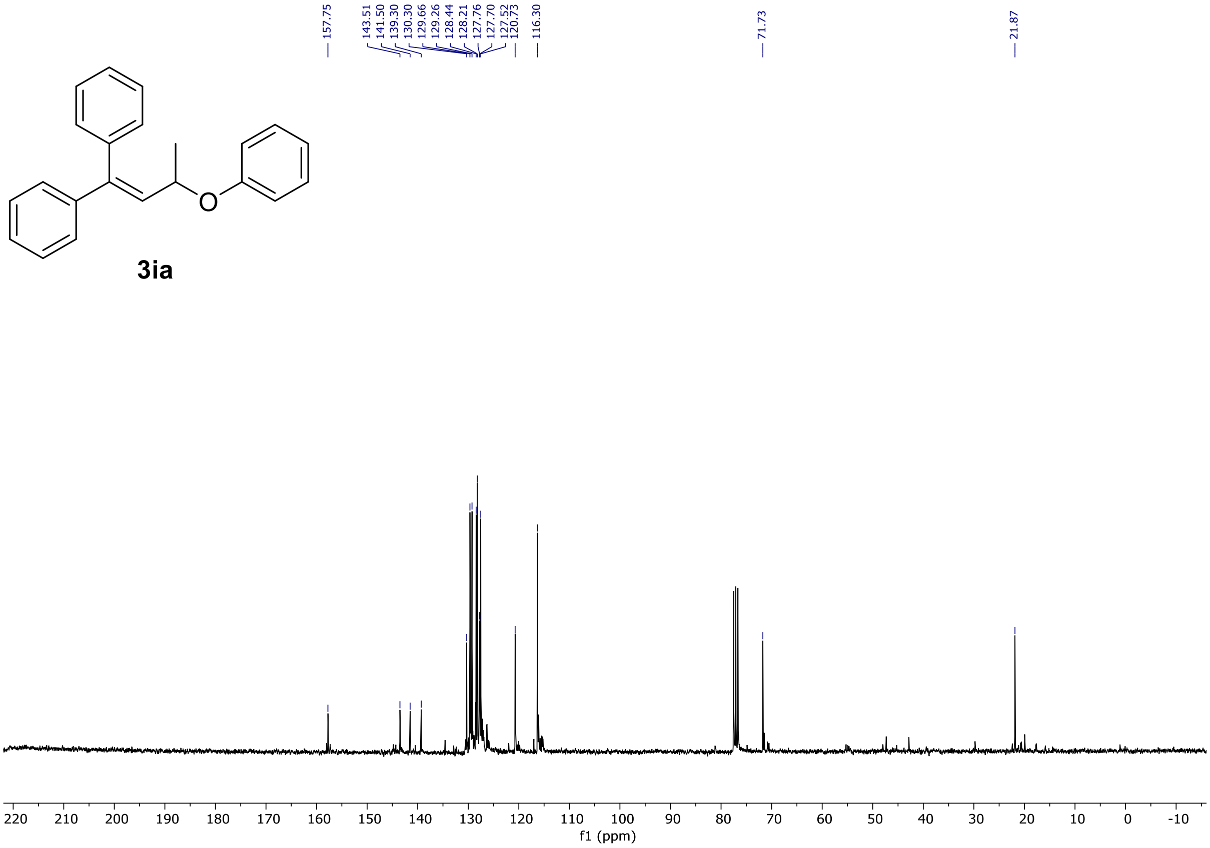


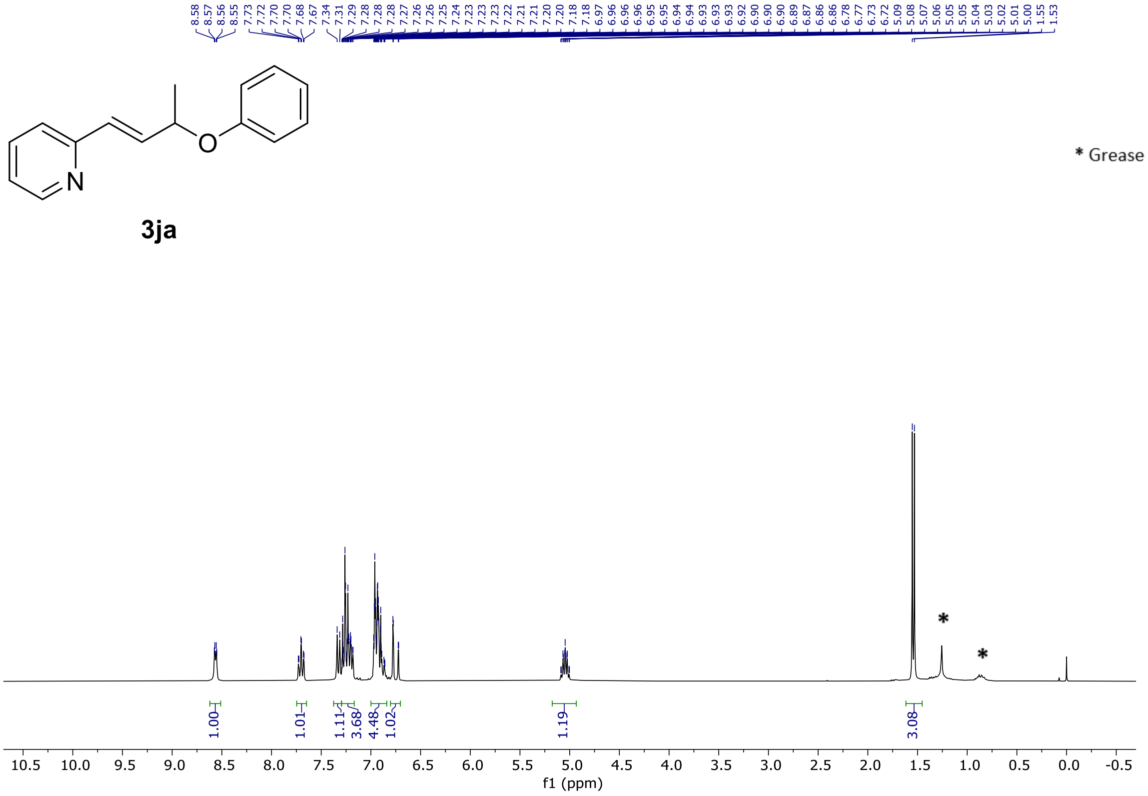
3ia
(*c.a.* 90% pure GC)

^{13}C NMR (75 MHz, CDCl$_3$)



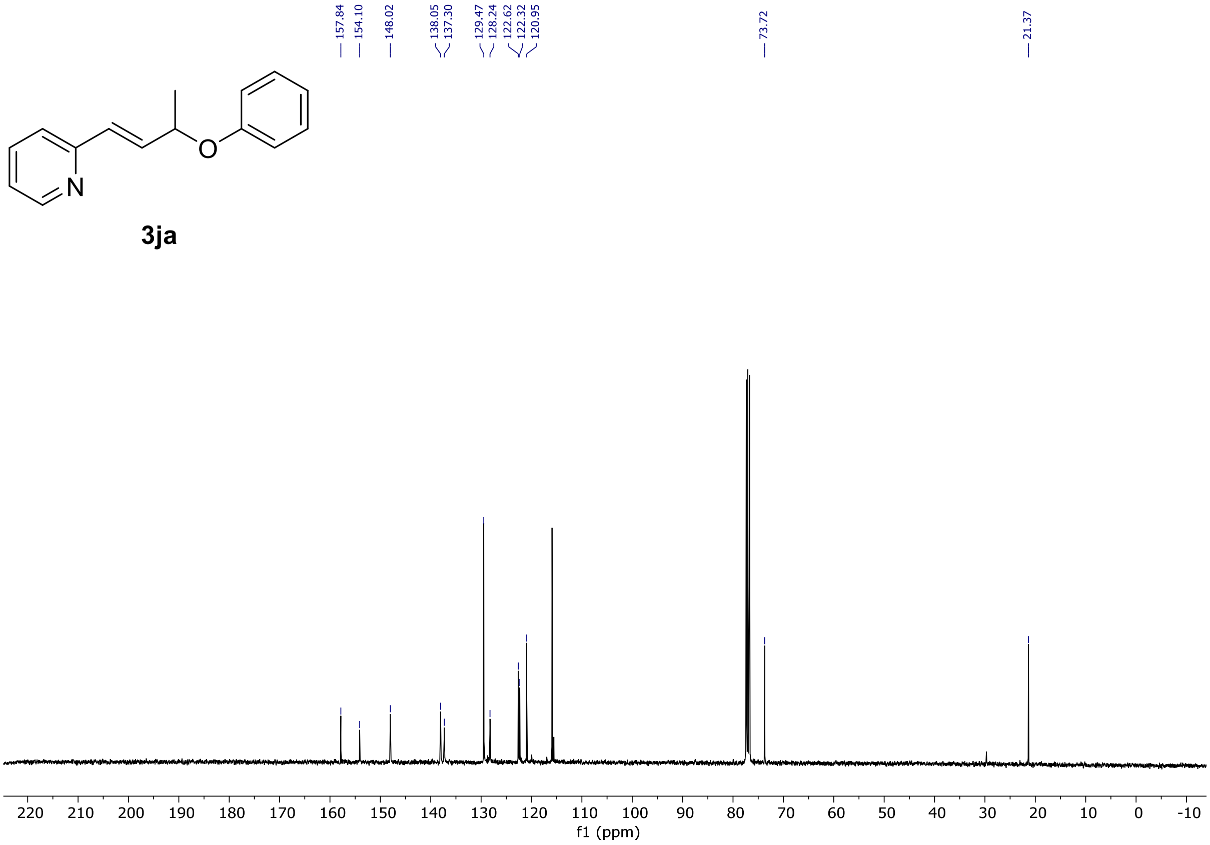
3ia

^{1}H NMR (300 MHz, CDCl$_3$)



3ja

^{13}C NMR (101 MHz, CDCl$_3$)



3ja

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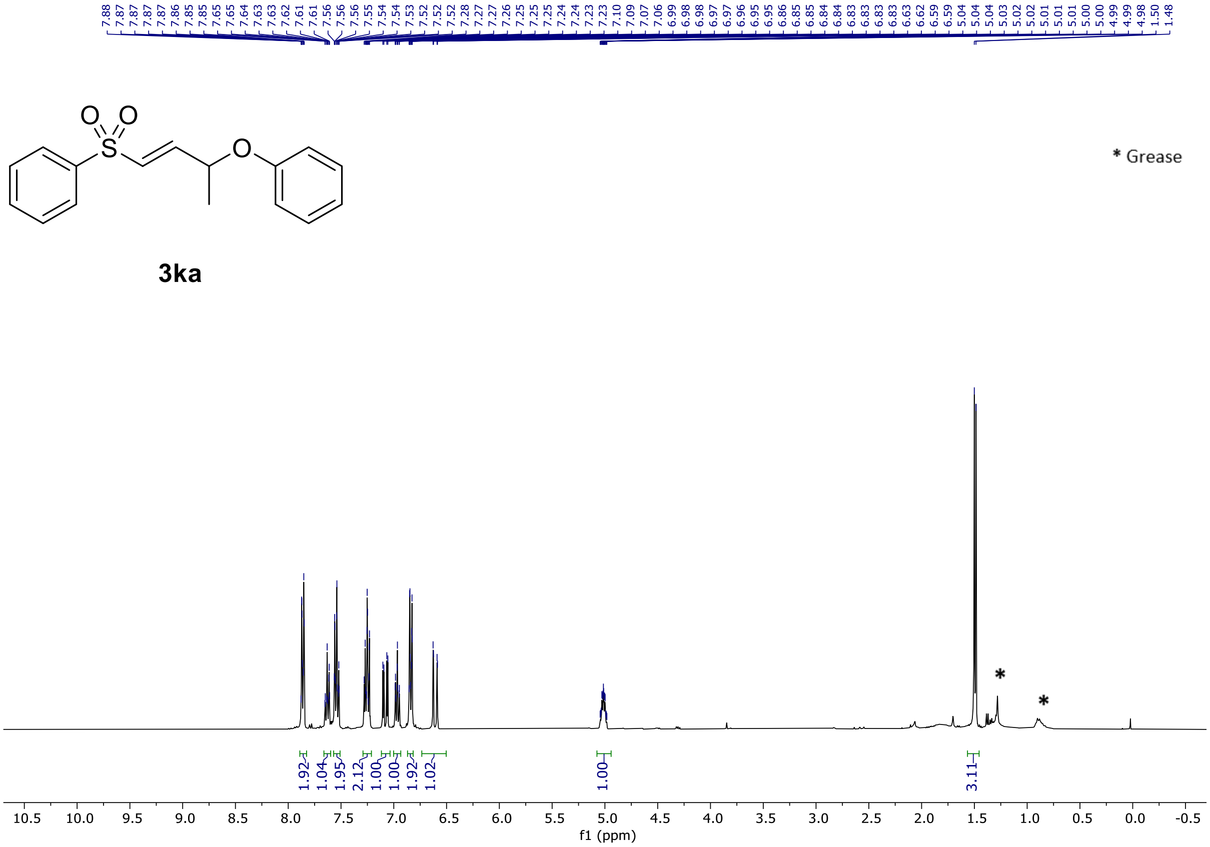

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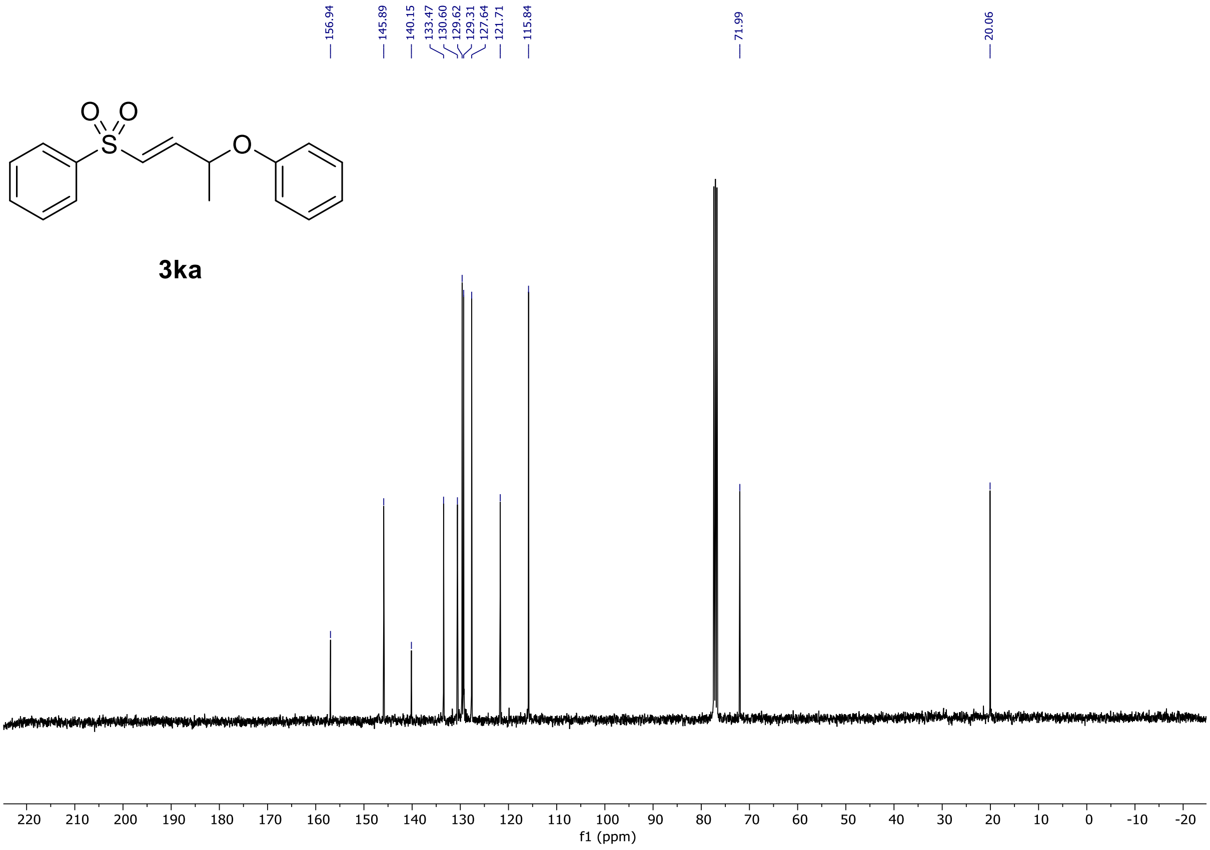

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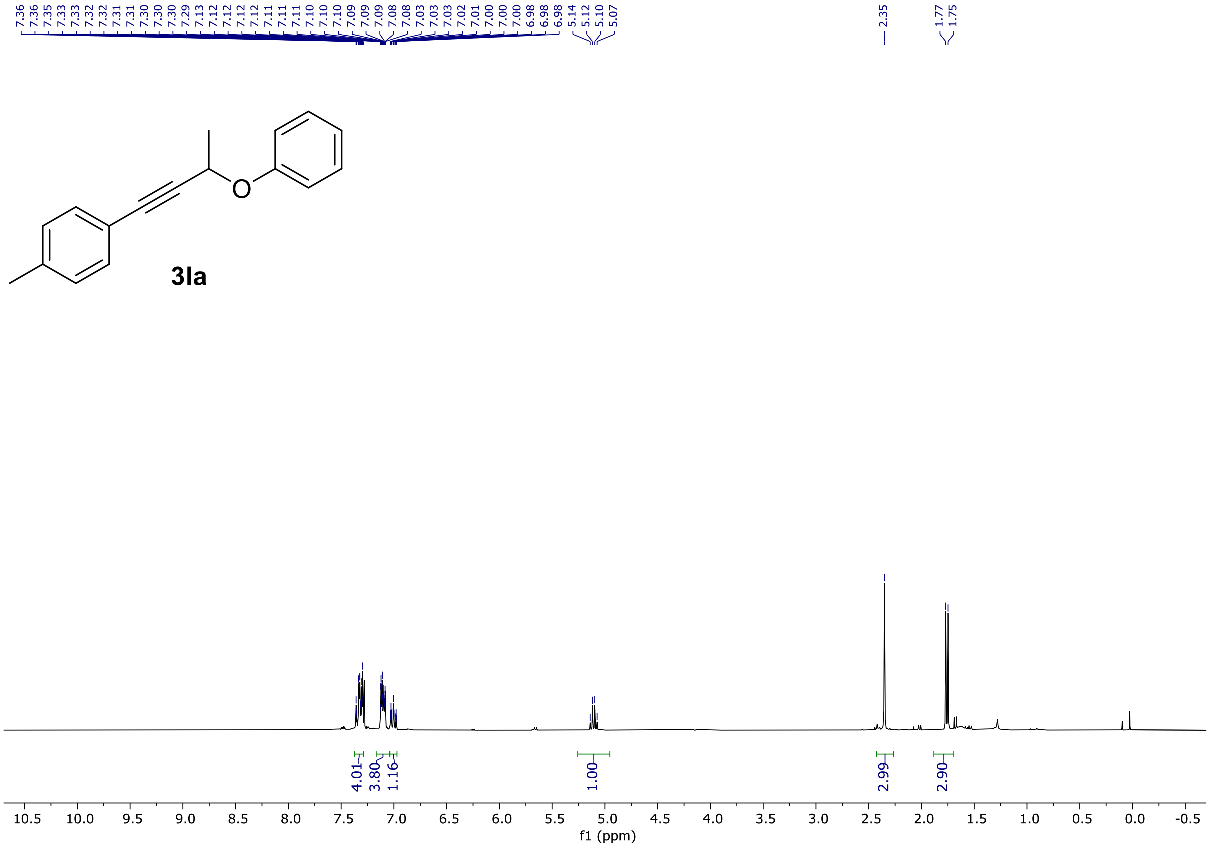

3la

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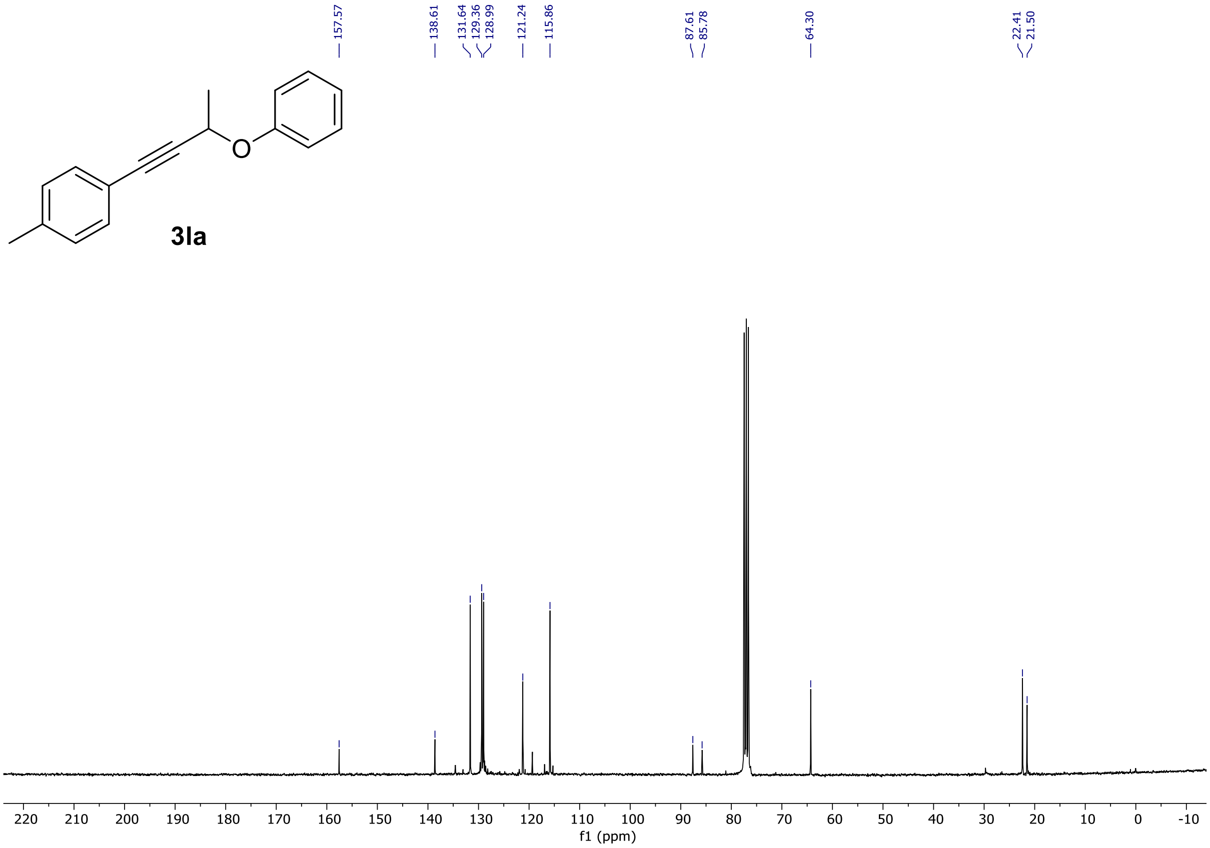

3la

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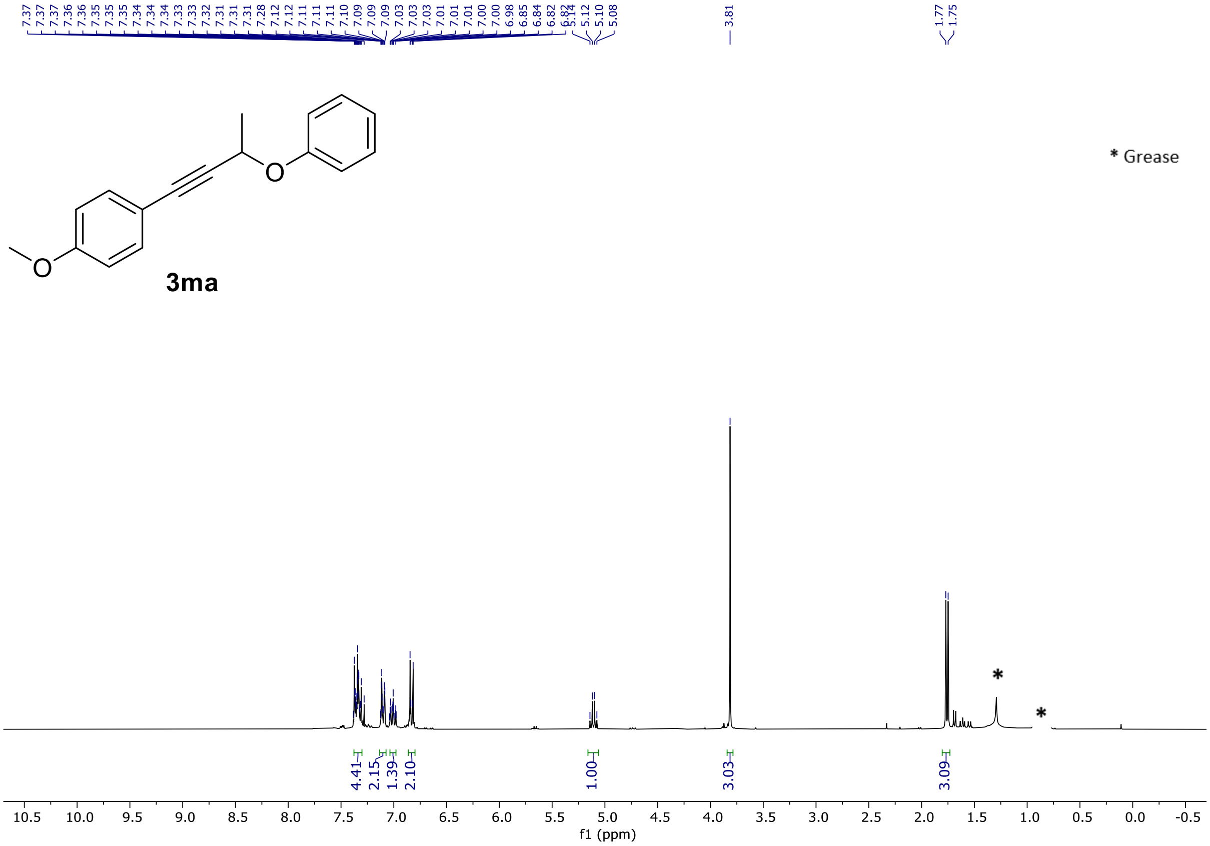
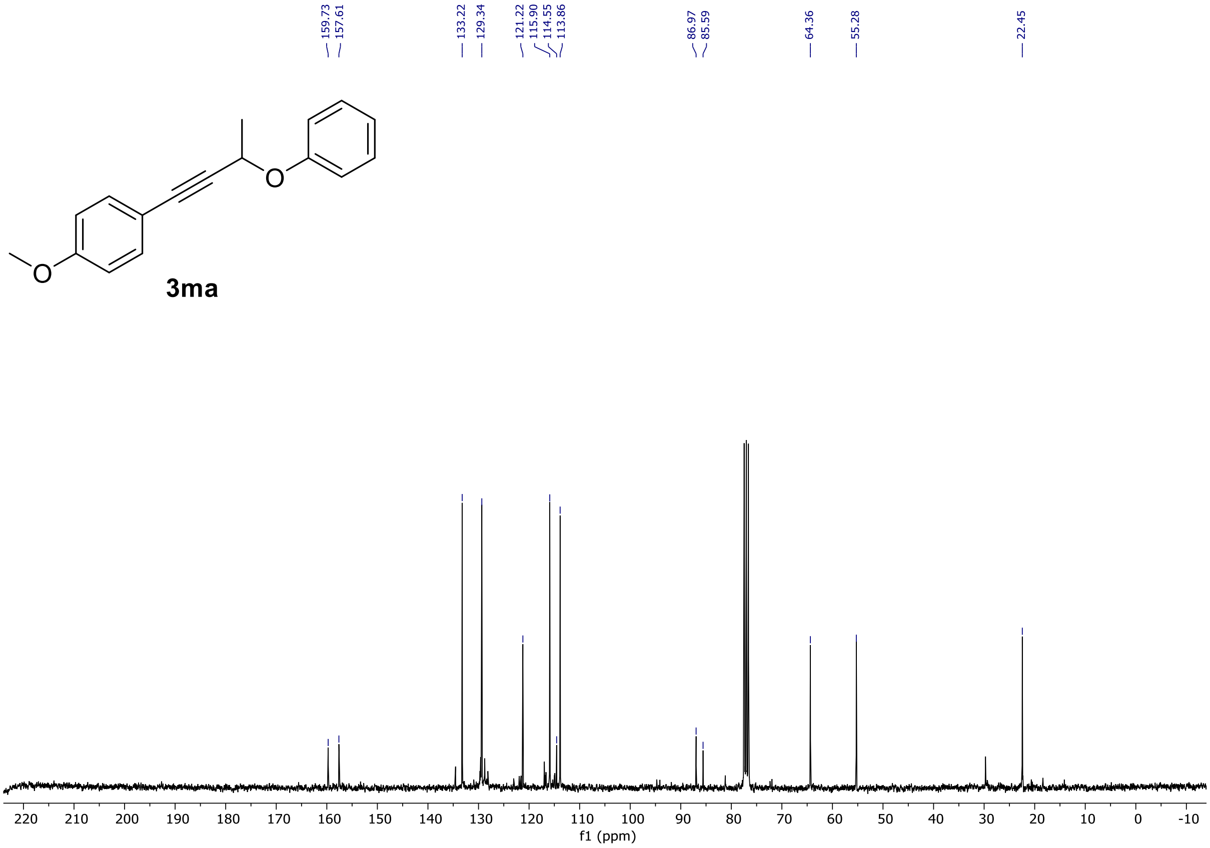


^{13}C NMR (75 MHz, $CDCl_3$)



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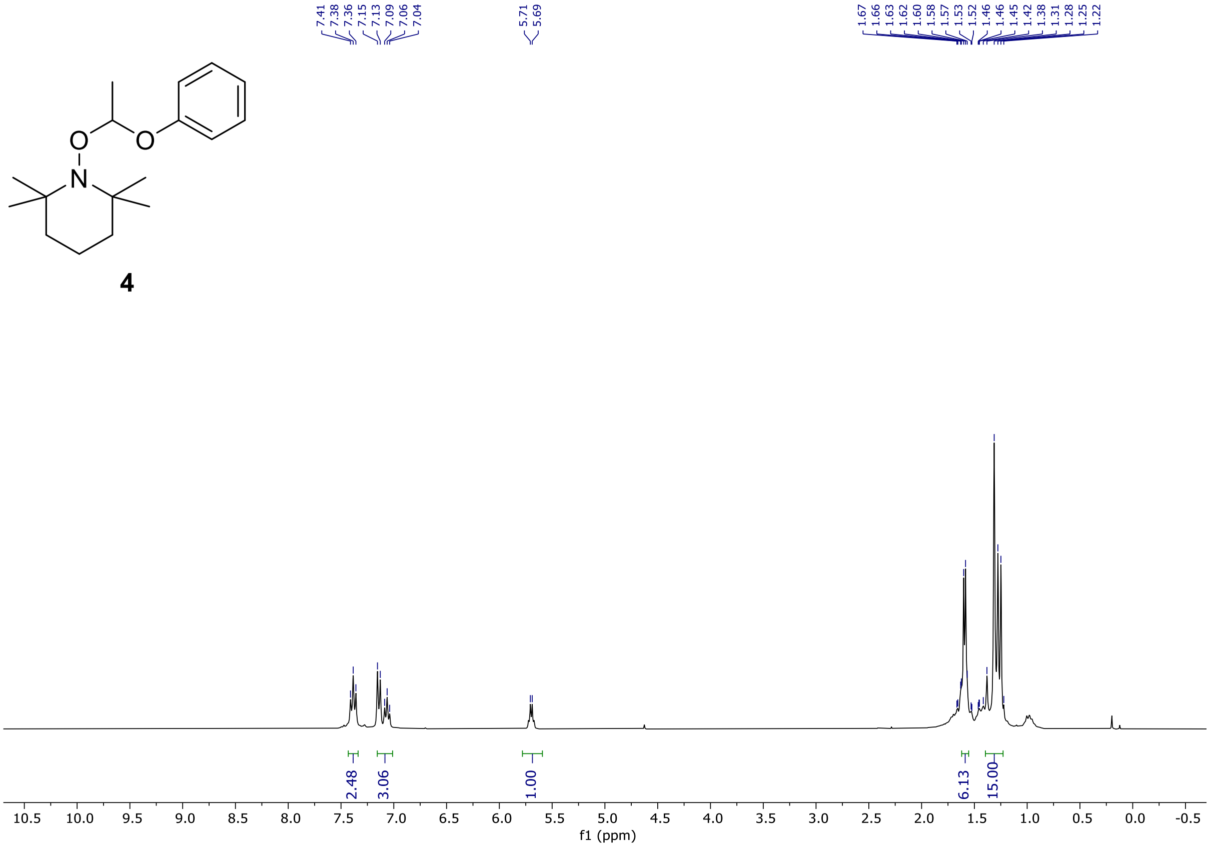

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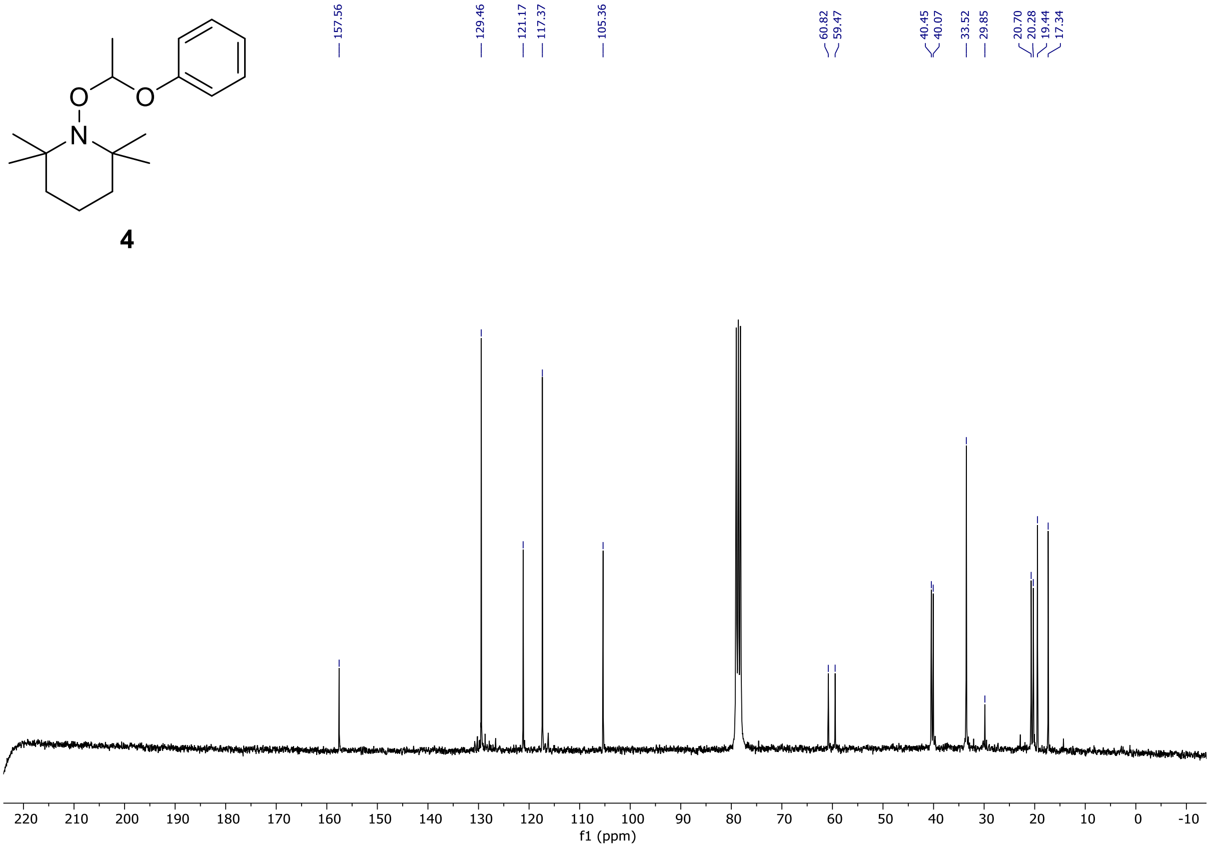

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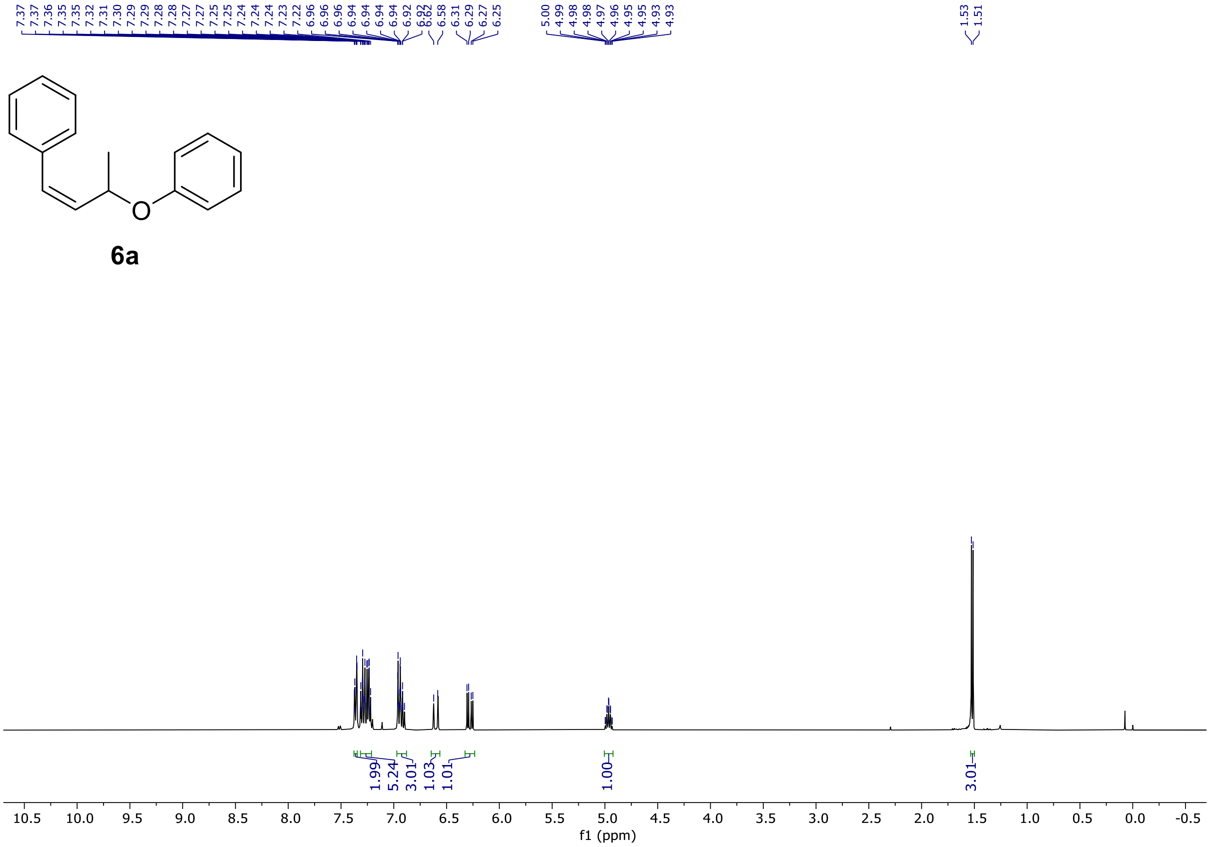

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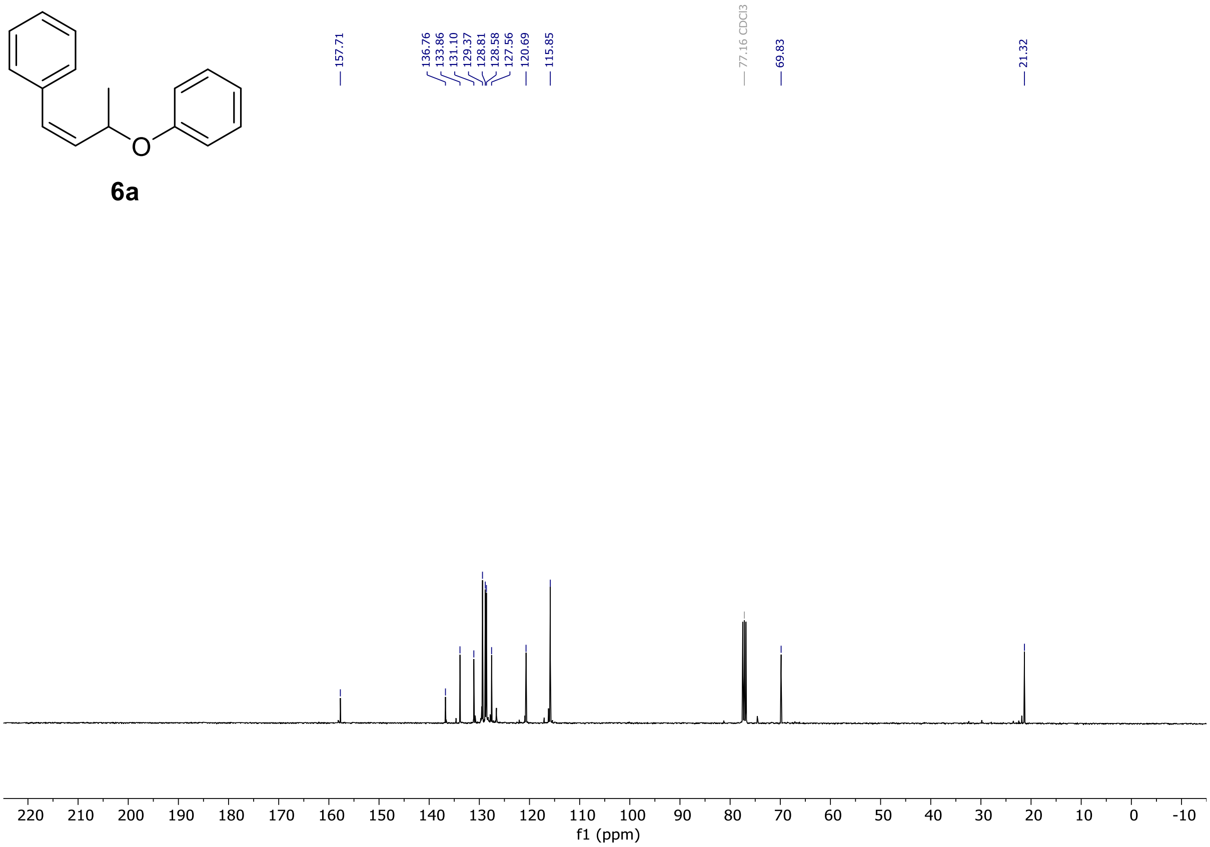

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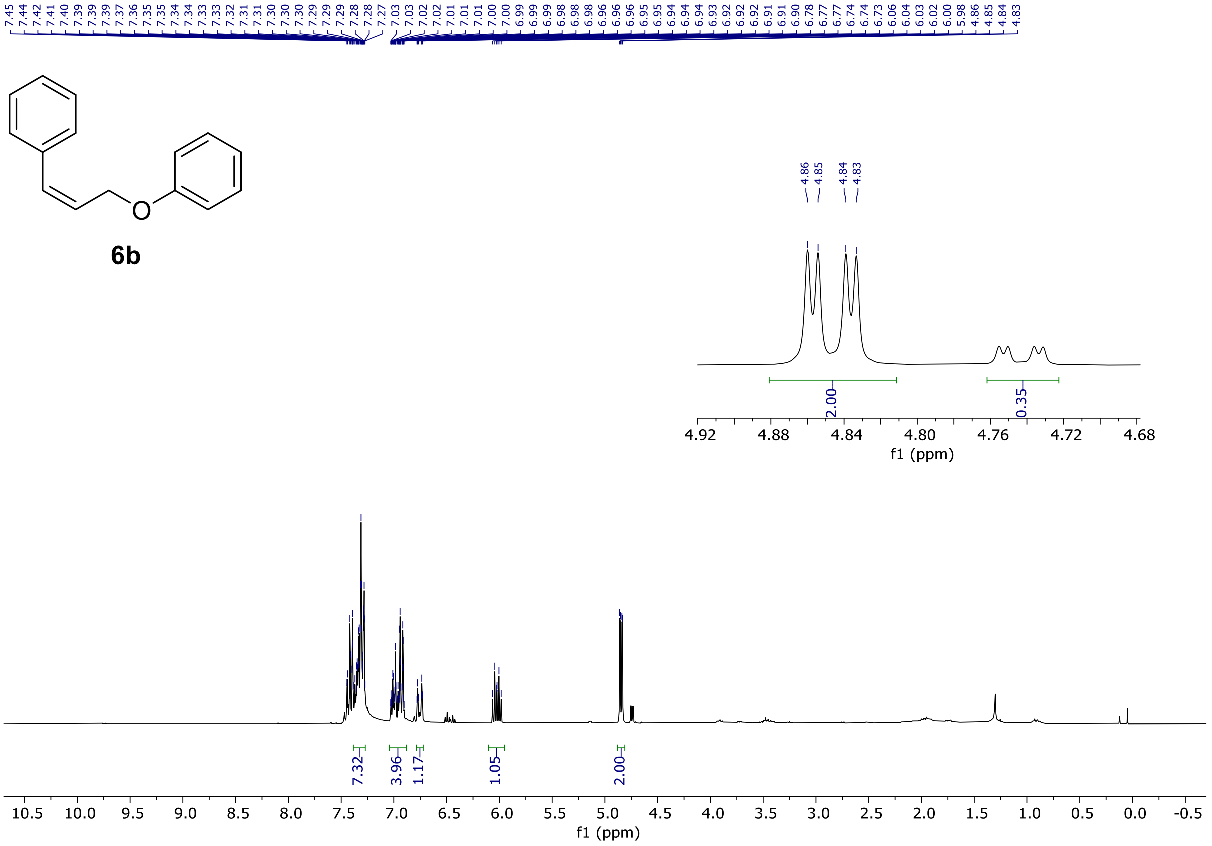

6b

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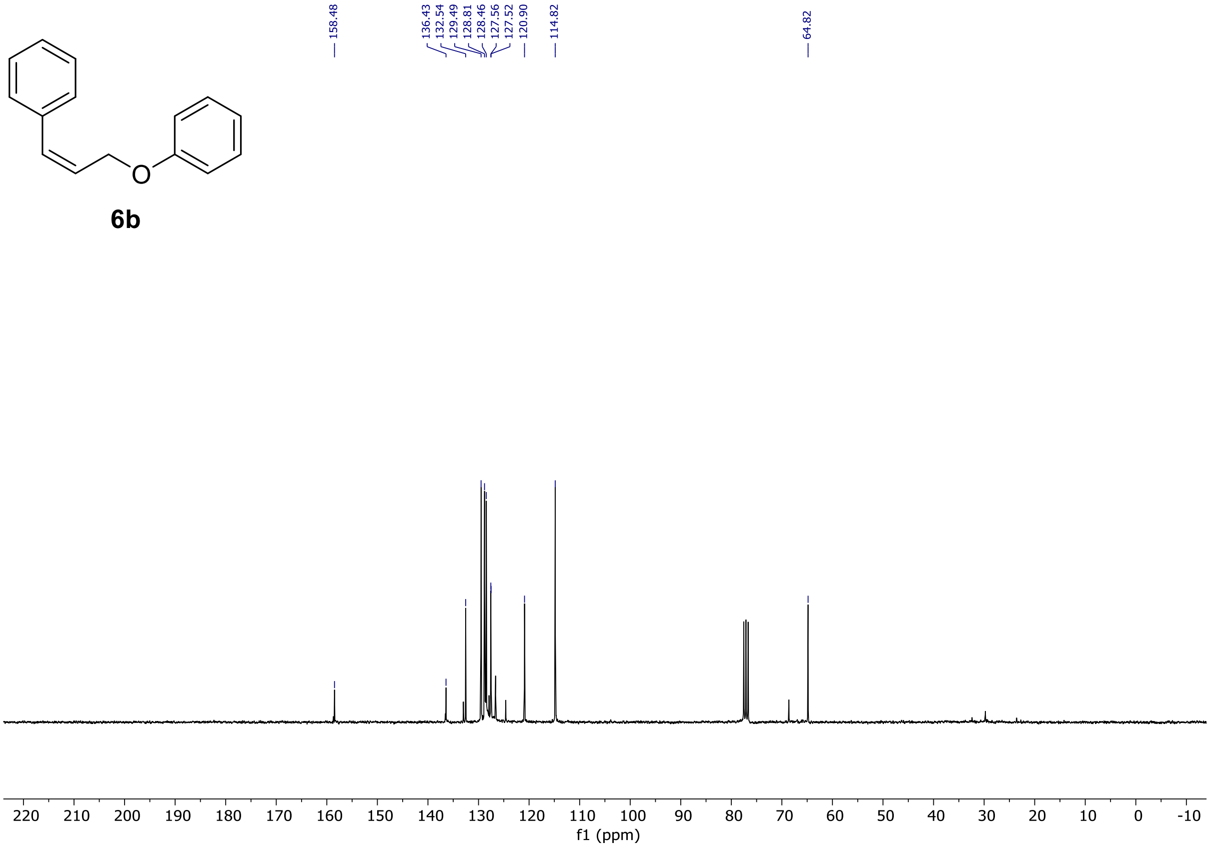

6b

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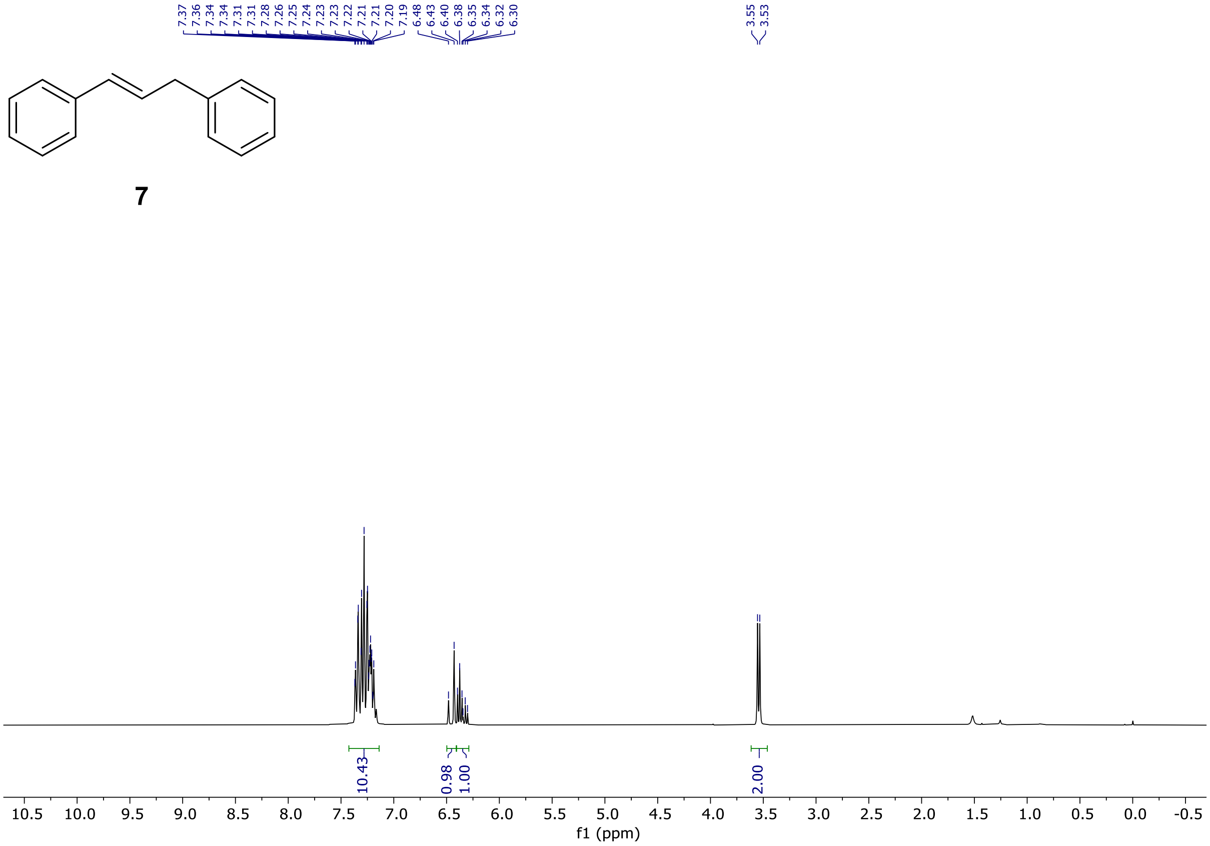

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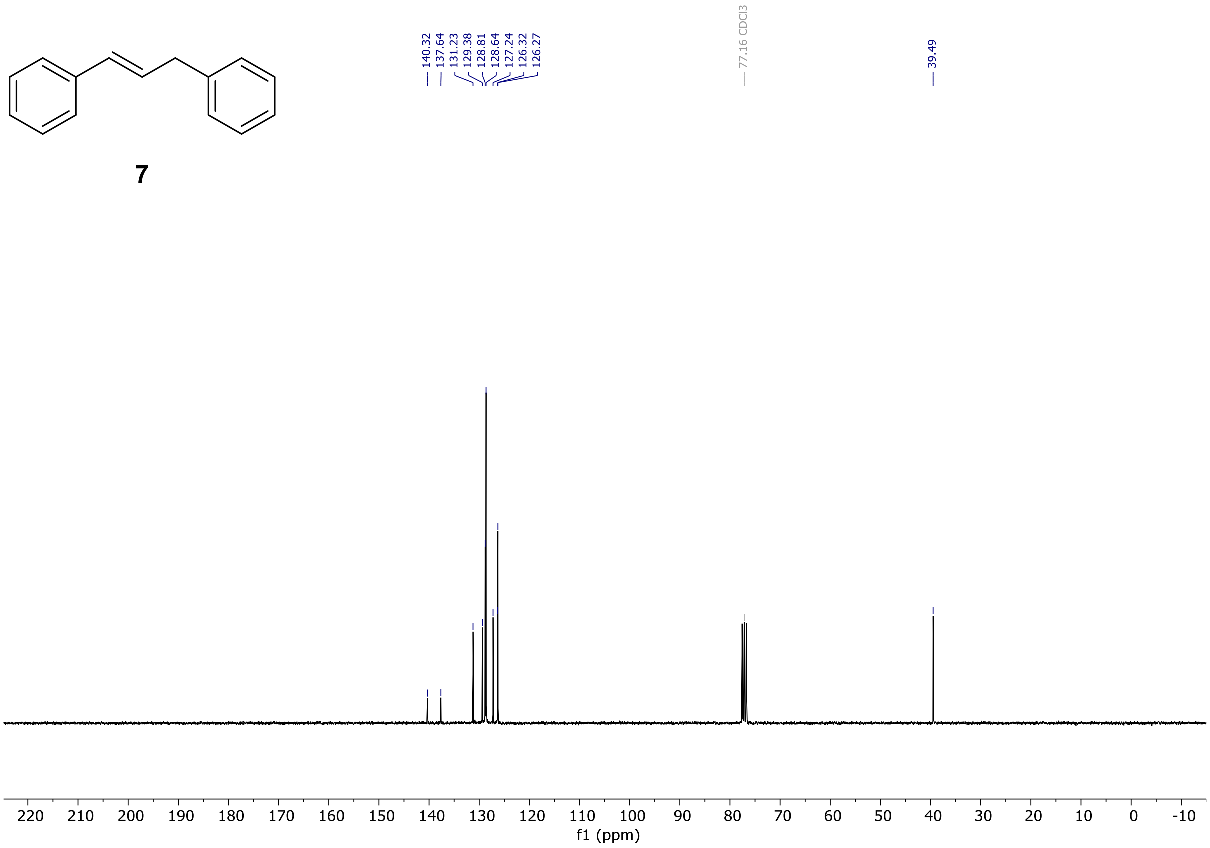

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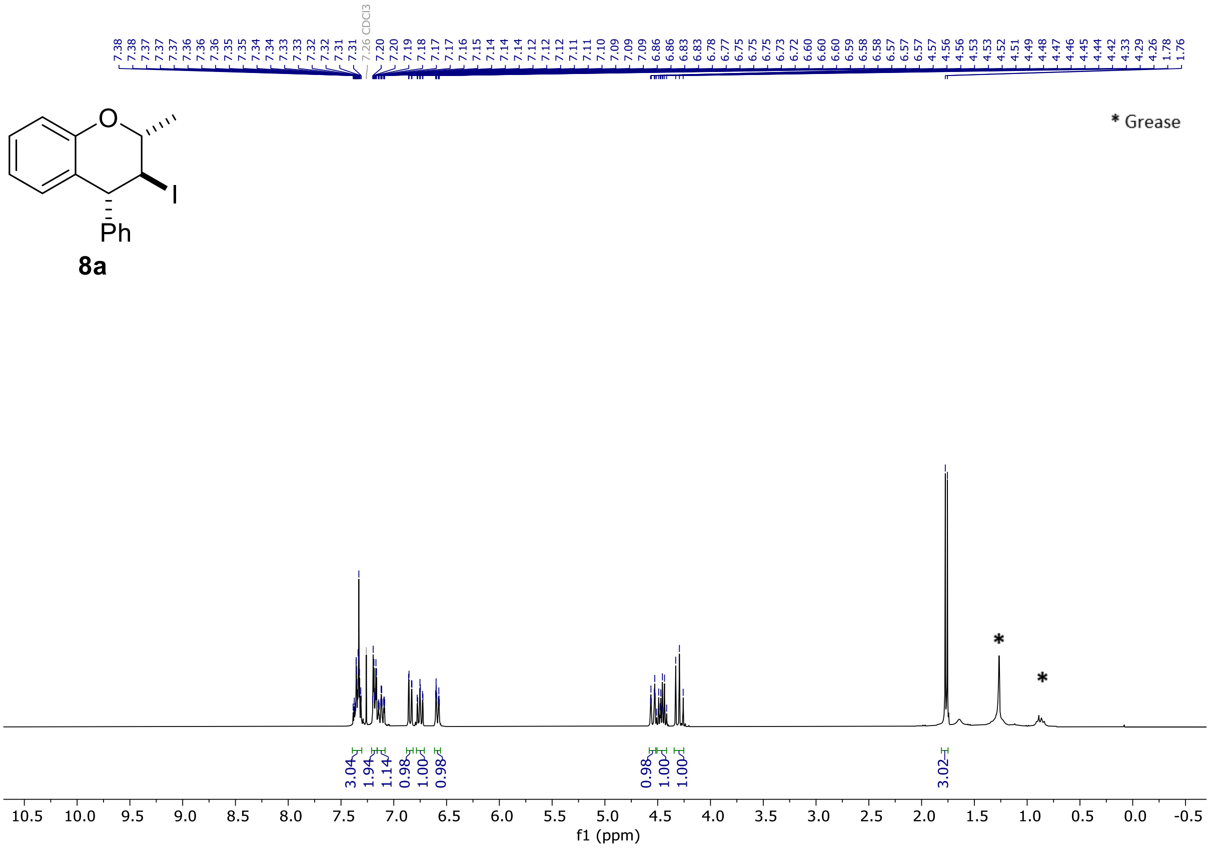
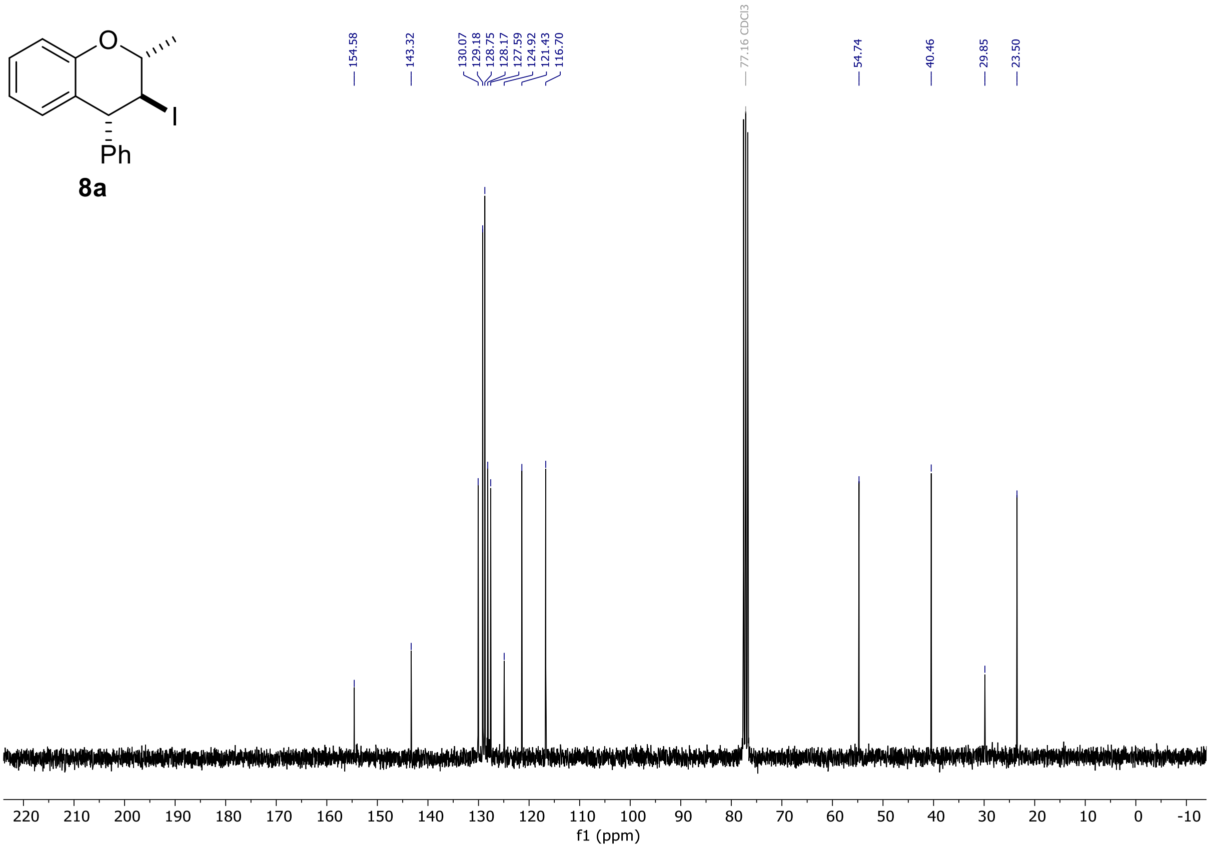
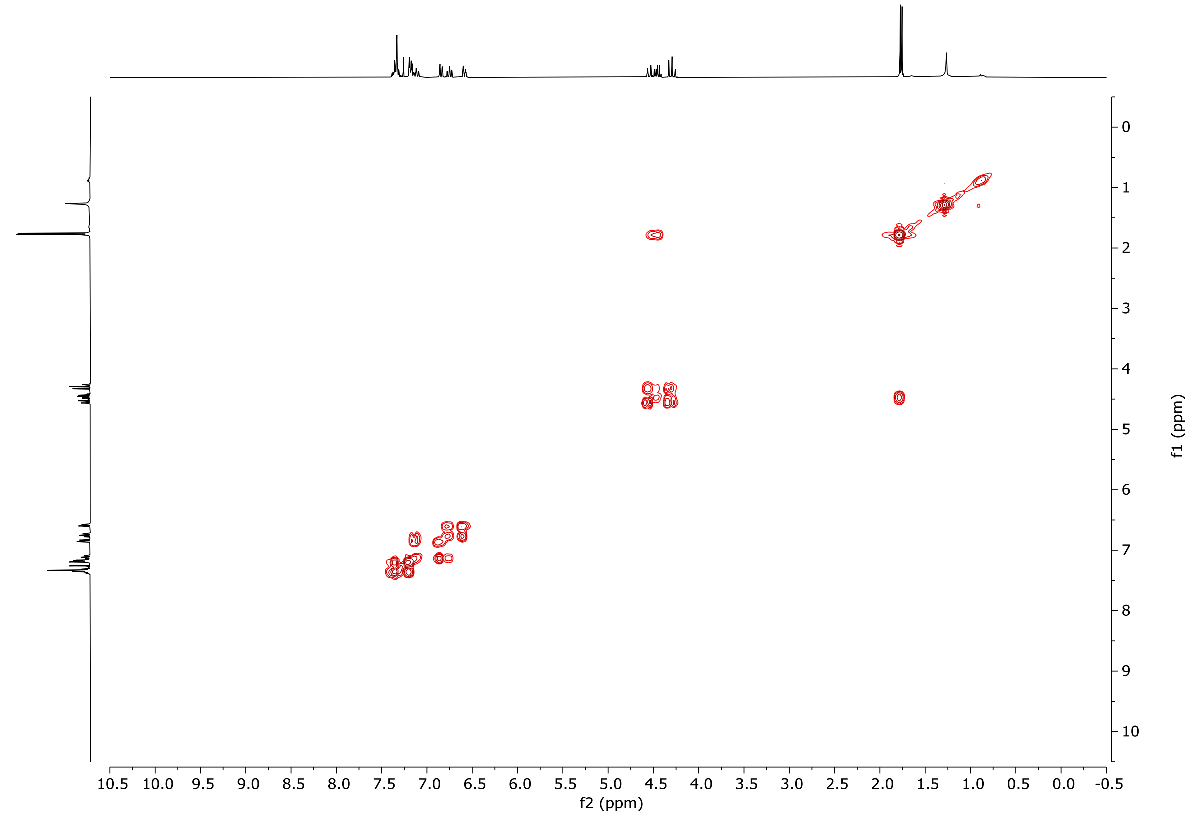


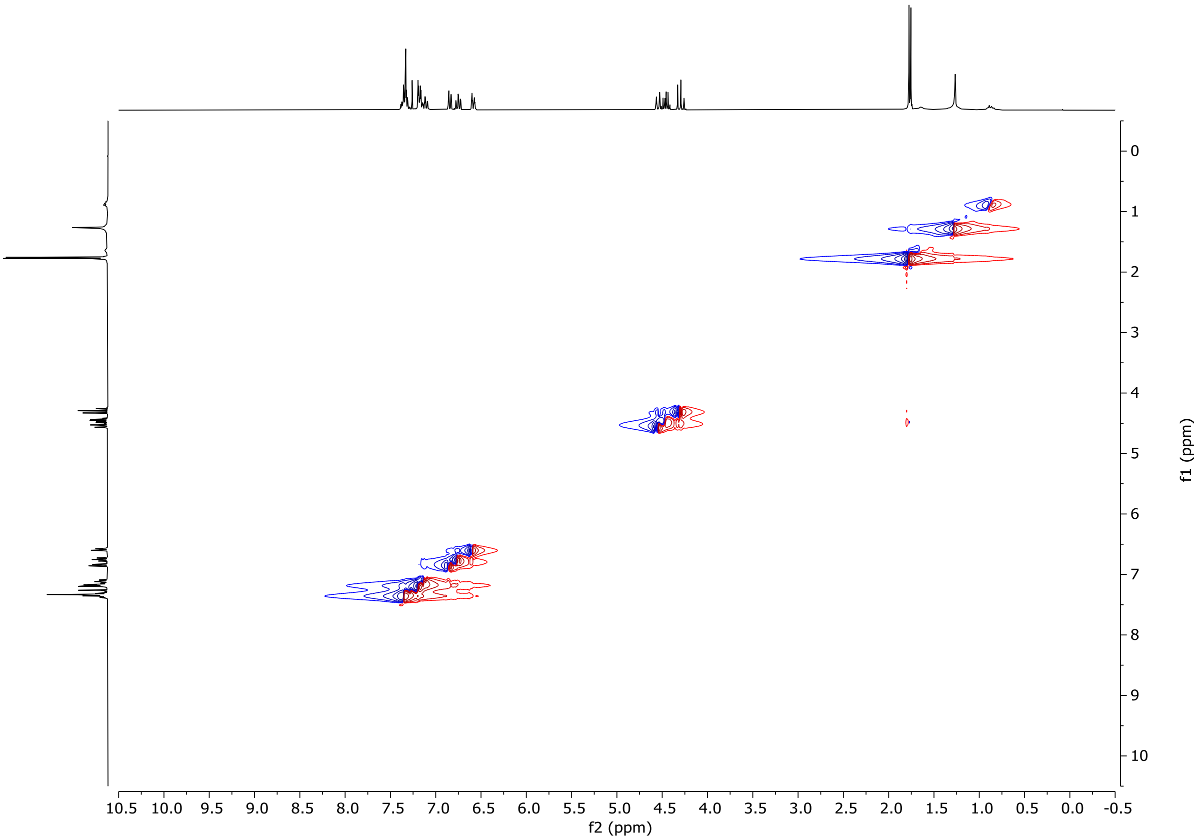
^{13}C NMR (75 MHz, $CDCl_3$)



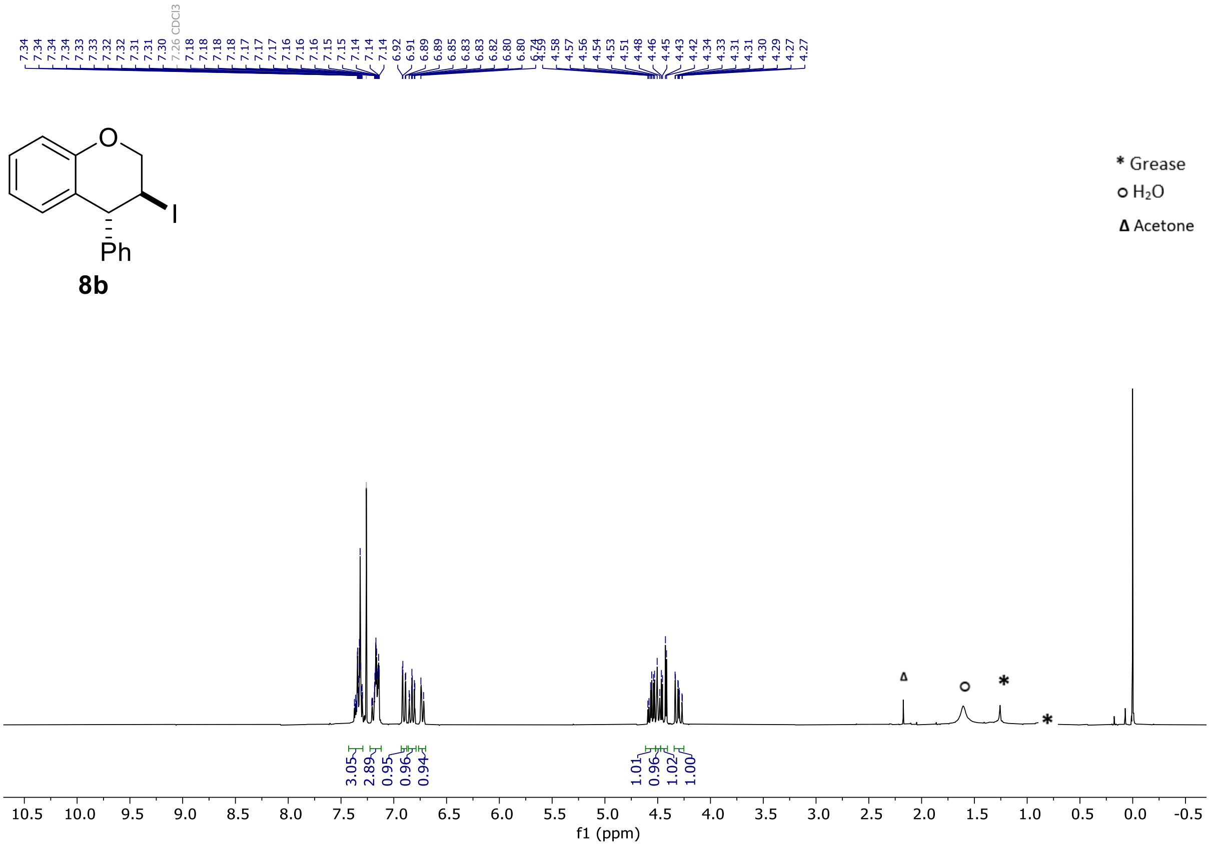
COSY (300 MHz, $CDCl_3$)



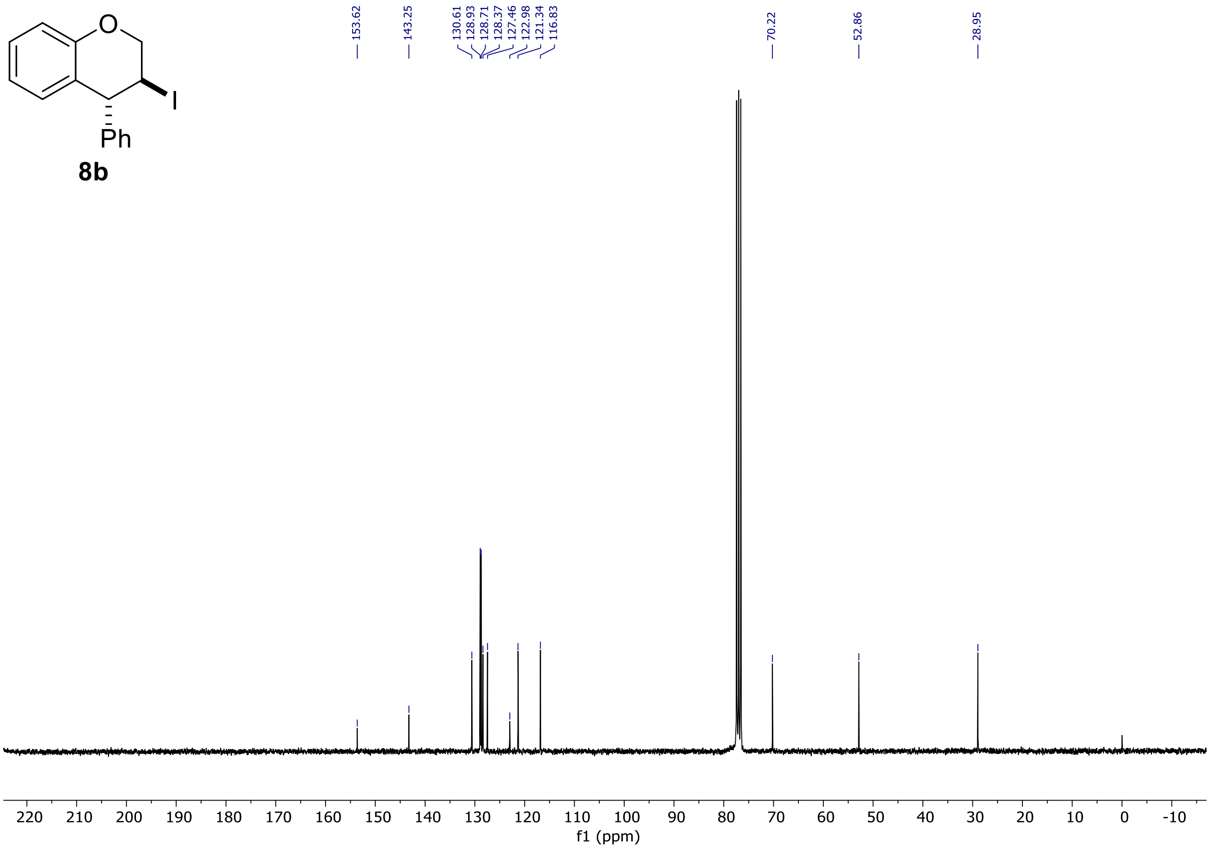
NOESY (300 MHz, $CDCl_3$)



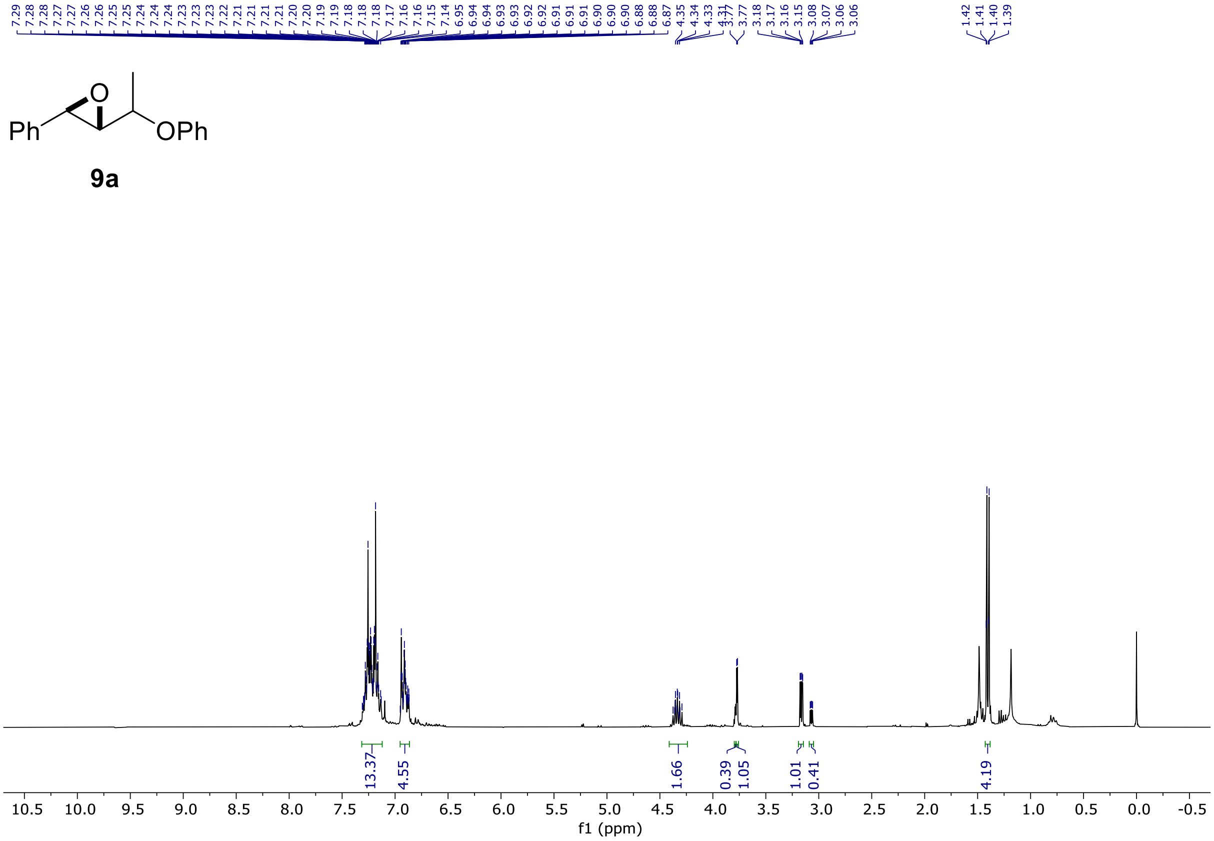
^{1}H NMR (300 MHz, $CDCl_3$)


8b

^{13}C NMR (75 MHz, $CDCl_3$)

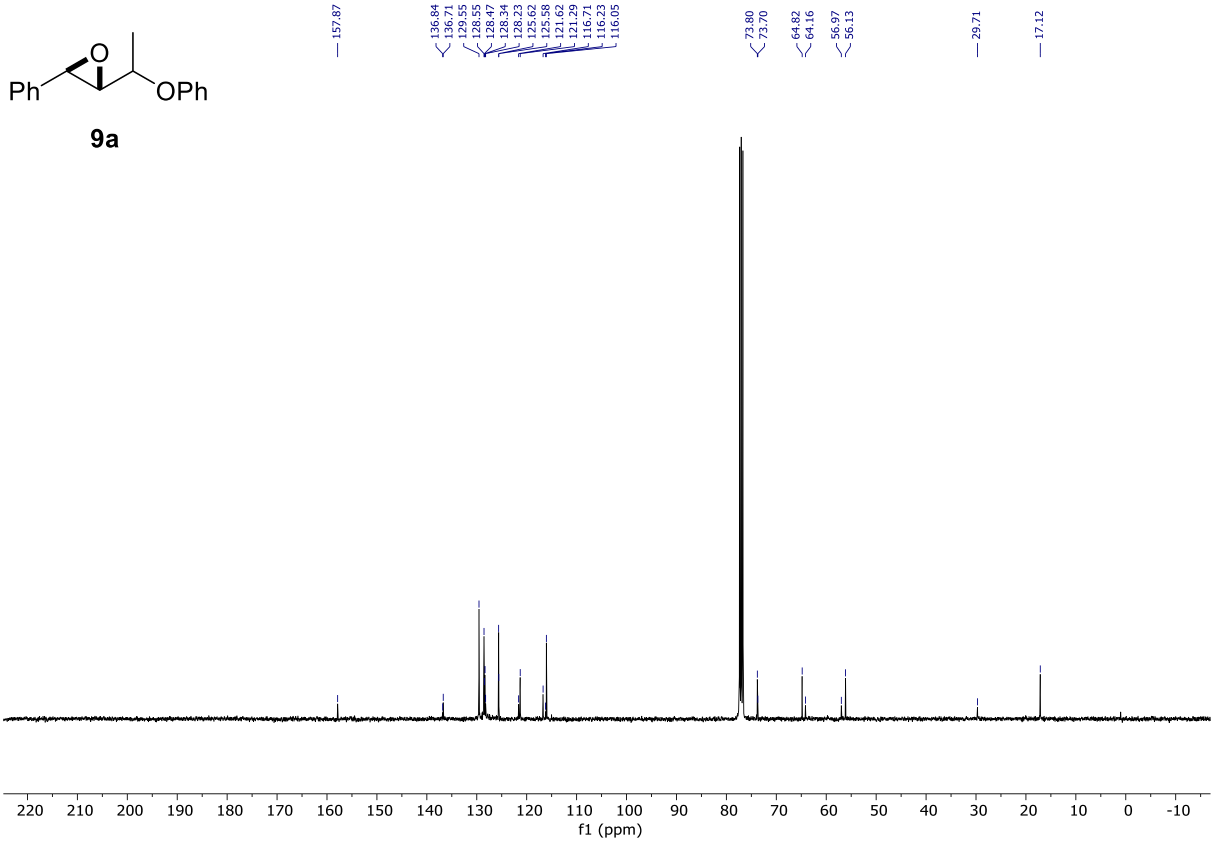

8b

^{1}H NMR (300 MHz, $CDCl_3$)



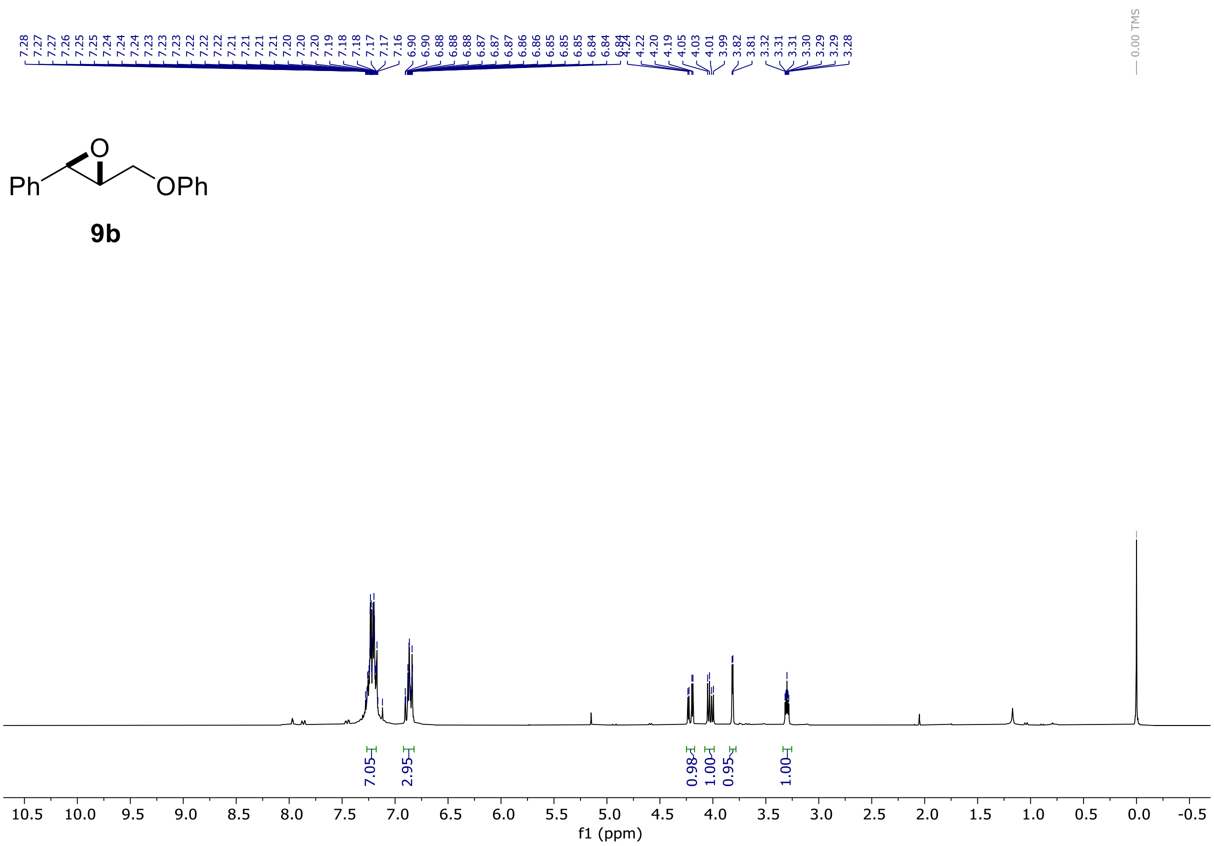
9a

^{13}C NMR (75 MHz, $CDCl_3$)



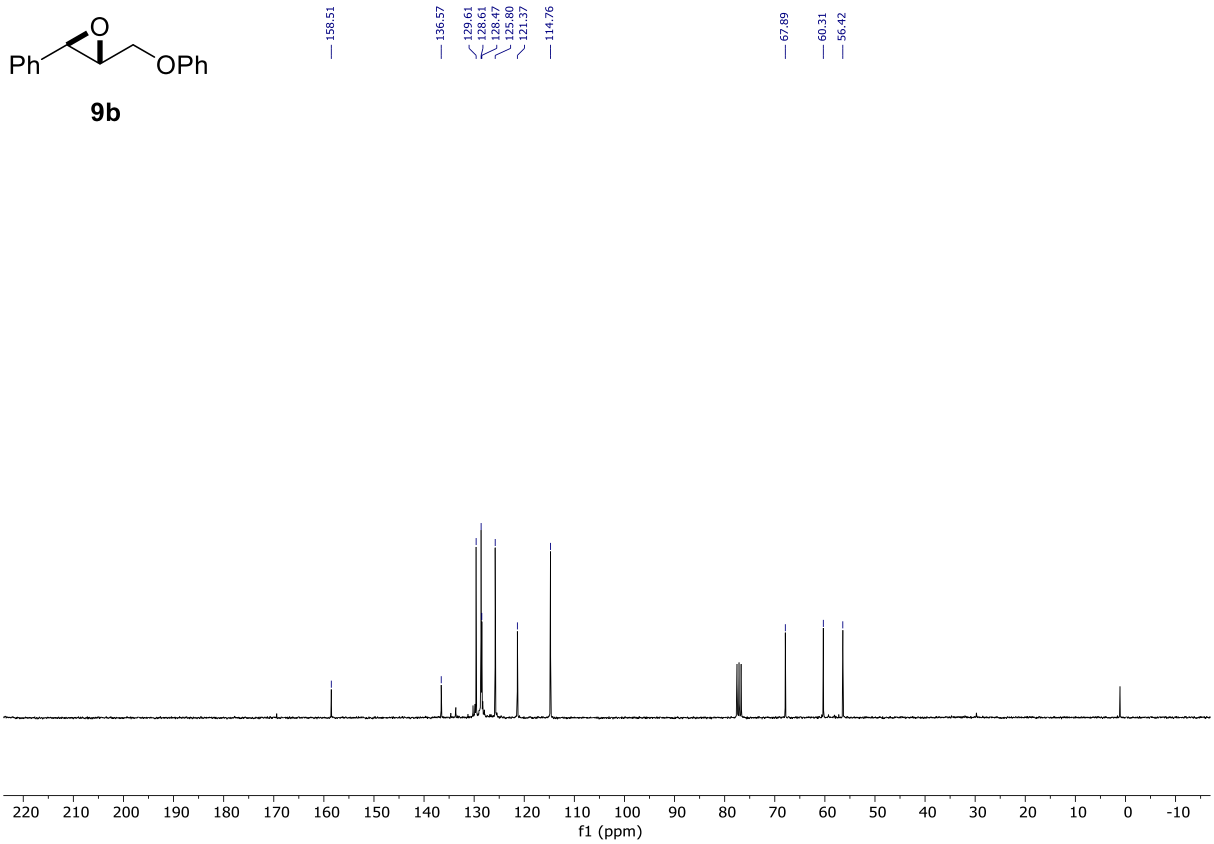
9a

^{1}H NMR (300 MHz, CDCl$_3$)



9b

^{13}C NMR (75 MHz, CDCl$_3$)



9b

1. Literature.

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